

Supporting Information

Visible Light-Induced Cyclization Reactions for the Synthesis of 1,2,4-Triazolines and 1,2,4-Triazoles

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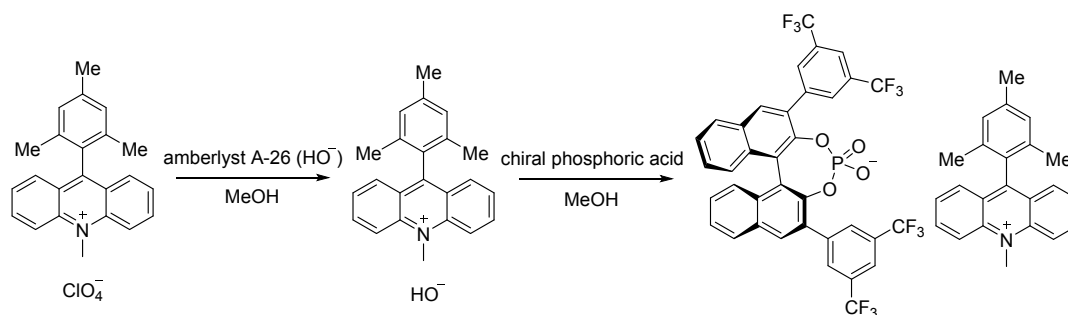
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General information

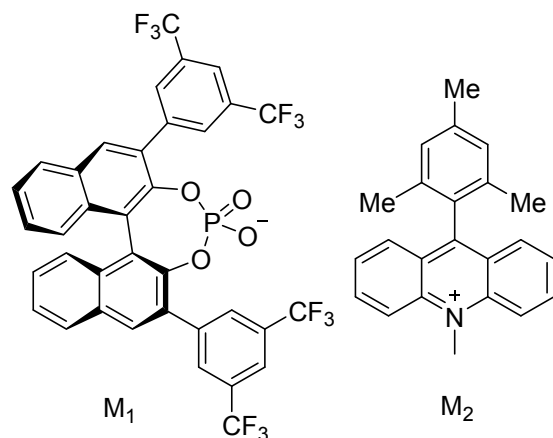
The commercial materials were purchased from Shanghai Energy or Tianjin Heowns. Solvents were treated by the standard methods. Reactions were powered by magnetic stirrers. Flash column chromatography was carried out on silica gel (300–400 mesh) using a forced flow of eluent. For TLC, silica gel plates were used and visualized by fluorescence quenching under UV light. All the NMR spectra were recorded on Bruker NMR spectrometers. Chemical shifts (δ) for ^1H NMR (400 Hz), ^{13}C NMR (100 Hz) were given in ppm. Data were reported as follows: chemical shift, integration, multiplicity (s = single, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet) and coupling constants (Hz). High resolution mass spectra (HRMS) were recorded on a Bruker DaltonicsmaXisUHR-TOF MS. Melting points were determined on a SGW X-4 microscope melting point apparatus and were uncorrected. X-ray crystallography analysis was performed on a Bruker X8 APEX X-ray diffraction meter. The blue light source (465nm) was provided by WATTECS WP-TEC-1020 parallel reactor.

The Chiral Photoredox Catalyst



A solution of 9-mesityl-10-methylacridinium perchlorate (0.5 mmol) in methanol passed ion-exchange resin (amberlyst A-26, OH⁻ form) for a long time, and the resin was washed by methanol three times. The resulting solution was treated with chiral phosphoric acid (0.5 mmol) at room temperature. The obtained phase was stirred for 5 minutes, and then was removed at reduced pressure to yield the chiral photosensitizer 9.

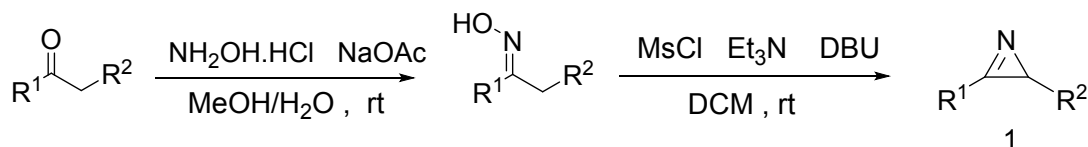
(R) - 9-mesityl-10-methylacridin-10-ium dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-olate 4-oxide (9)



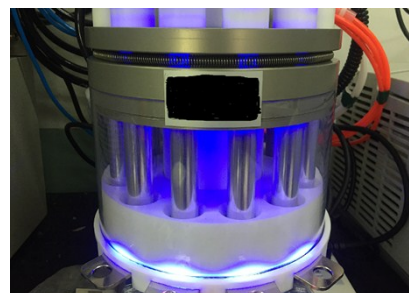
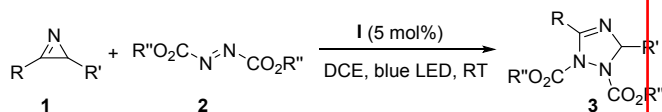
Yield: 99%, Brown solid; m.p.: 175-177 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.88-8.86 (d, $J = 8$ Hz, 2H), 8.58 (s, 4H), 8.19-8.15 (m, 2H), 7.99 (s, 2H), 7.95-7.93 (d, $J = 8$ Hz, 2H), 7.79-7.76 (m, 2H), 7.68-7.64 (m, 4H), 7.46-7.37 (m, 4H), 7.30-7.27 (m, 2H), 7.15 (s, 2H), 4.93 (s, 3H), 2.48 (s, 3H), 1.69 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.11, 147.28, 147.19, 141.39, 141.11, 140.33, 139.26, 135.73, 133.21, 132.16, 132.13, 130.93, 130.85, 130.69, 130.60, 129.40, 129.08, 128.44, 128.36, 128.27, 127.06, 126.55, 125.68, 125.18, 124.99, 123.86, 123.84, 122.27, 120.47, 120.43, 120.40, 119.83, 39.61, 21.26, 19.83; ^{31}P NMR (400 MHz, CDCl_3) δ 4.82; ^{19}F NMR (376 MHz, CDCl_3) δ -62.39; HRMS (ESI) m/z calcd for $\text{C}_{36}\text{H}_{16}\text{F}_{12}\text{O}_4\text{P}^- [\text{M}_1^-]$: 771.0600; found: 771.0671; m/z calcd for $\text{C}_{23}\text{H}_{22}\text{N}^+ [\text{M}_2^+]$: 312.1747; found: 312.1717.

The preparation of the substrates 1.

The substrates **1** used in this paper are synthesized according to the previous literatures.¹⁻³



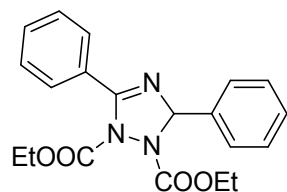
The preparation of the compounds 3.



The substrates **1** (0.5 mmol) was added into a DCE (2 mL) solution, then

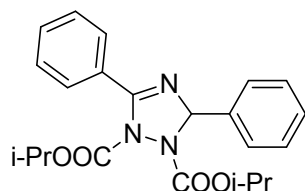
azodicarboxylates **2** (0.75 mmol) and catalyst **I** (5 mol%, 0.025 mmol) was added into the mixture. The mixture was stirred at room temperature under blue LED until finished (determined by TLC analysis). The crude product was purified by flash chromatography on silica gel (eluent: PE/EtOAc from 10:1 to 5:1) affording to corresponding **3**.

Diethyl 3,5-diphenyl-1H-1,2,4-triazole-1,2(3H)-dicarboxylate (3a)



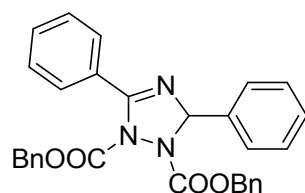
Colourless oil; 81% yield, 130 mg; ^1H NMR (400 MHz, CDCl_3) δ 7.84-7.82 (d, J = 8 Hz, 2H), 7.49-7.47 (d, J = 8 Hz, 2H), 7.42-7.34 (m, 6H), 6.89 (s, 1H), 4.42-4.30 (m, 2H), 4.20-4.08 (m, 2H), 1.39-1.35 (t, J = 8 Hz, 3H), 1.39-1.35 (t, J = 8 Hz, 3H), 1.12-1.08 (t, J = 8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 157.66, 156.80, 153.19, 137.97, 137.27, 131.09, 128.72, 128.64, 128.32, 127.50, 126.01, 85.41, 63.62, 63.38, 14.51, 14.00; HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{22}\text{N}_3\text{O}_4^+$ [(M+H) $^+$]: 368.1605; found: 368.1605.

Diisopropyl 3,5-diphenyl-1H-1,2,4-triazole-1,2(3H)-dicarboxylate (3b)



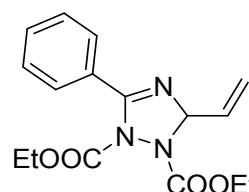
Yellow oil; 62% yield, 122 mg; ^1H NMR (400 MHz, CDCl_3) δ 7.88-7.86 (d, J = 8 Hz, 2H), 7.51-7.49 (d, J = 8 Hz, 3H), 7.45-7.33 (m, 5H), 6.88 (s, 1H), 5.16-5.10 (m, 1H), 4.90-4.84 (m, 1H), 1.37-1.34 (dd, J = 6 Hz, J = 4 Hz, 6H), 1.14-1.12 (d, J = 8 Hz, 3H), 1.06-1.04 (d, J = 8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 157.91, 152.74, 137.63, 131.63, 129.69, 129.26, 128.60, 128.55, 128.48, 127.96, 126.08, 85.09, 71.58, 71.18, 22.06, 22.04, 21.54, 21.44; HRMS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{26}\text{N}_3\text{O}_4^+$ [(M+H) $^+$]: 396.1918; found: 396.1919.

Dibenzyl 3,5-diphenyl-1H-1,2,4-triazole-1,2(3H)-dicarboxylate (3c)



Yellow oil; 60% yield, 147 mg; ^1H NMR (400 MHz, CDCl_3) δ 7.79-7.77 (m, 2H), 7.44-7.40 (m, 1H), 7.36-7.26 (m, 8H), 7.23-7.11 (m, 7H), 6.91-6.89 (d, J = 8 Hz, 2H), 6.85 (s, 1H), 5.30-5.18 (q, J = 12 Hz, 2H), 5.10-4.89 (q, J = 12 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 157.59, 153.12, 137.14, 135.46, 134.73, 131.83, 129.74, 128.85, 128.73, 128.67, 128.60, 128.47, 128.28, 128.12, 127.94, 127.74, 126.09, 85.44, 68.84, 68.75; HRMS (ESI) m/z calcd for $\text{C}_{30}\text{H}_{26}\text{N}_3\text{O}_4^+$ [(M+H) $^+$]: 492.1918; found: 492.1917.

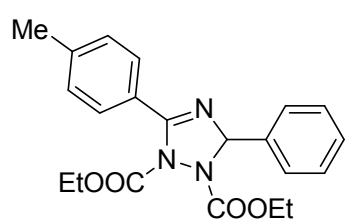
Diethyl 5-phenyl-3-vinyl-1H-1,2,4-triazole-1,2(3H)-dicarboxylate (3d)



Yellow oil; 47% yield, 75 mg; ^1H NMR (400 MHz, CDCl_3) δ 7.85-7.82 (m, 2H), 7.52-7.40 (m, 3H), 6.31-6.30 (m, 1H), 5.95-5.87 (m, 1H), 5.54-5.50 (d, J = 16 Hz, 1H), 5.26-5.24 (d, J = 8 Hz, 1H), 4.37-4.27 (m, 2H), 4.21-4.11 (m, 2H), 1.37-1.33 (t, J = 8 Hz, 3H), 1.15-1.01 (t, J = 8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 157.73, 157.67, 153.22, 132.60, 131.69, 129.61, 129.12, 127.97, 116.96,

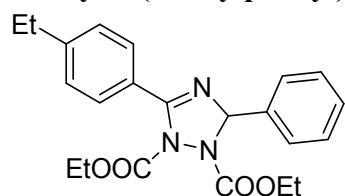
84.31, 63.44, 63.21, 29.72, 14.47, 13.97; HRMS (ESI) m/z calcd for $C_{16}H_{20}N_3O_4^+$ [(M+H)⁺]: 318.1448; found: 318.1448.

Diethyl 3-phenyl-5-(p-tolyl)-1H-1,2,4-triazole-1,2(3H)-dicarboxylate (3e)



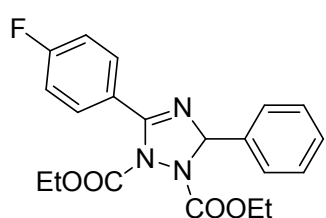
Colourless oil; 58% yield, 110 mg; ¹H NMR (400 MHz, CDCl₃) δ 7.80-7.78 (d, J = 8 Hz, 2H), 7.51-7.49 (d, J = 8 Hz, 2H), 7.40-7.34 (m, 3H), 7.25-7.23 (d, J = 8 Hz, 2H), 6.88 (s, 1H), 4.42-4.31 (m, 2H), 4.19-4.07 (m, 2H), 2.41 (s, 3H), 1.39-1.35 (t, J = 8 Hz, 3H), 1.11-1.07 (t, J = 8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 157.79, 153.27, 142.28, 137.58, 129.74, 128.70, 128.65, 128.51, 126.14, 126.10, 85.18, 63.39, 63.25, 29.72, 21.68, 14.53, 13.99; HRMS (ESI) m/z calcd for $C_{21}H_{24}N_3O_4^+$ [(M+H)⁺]: 382.1761; found: 382.1742.

Diethyl 5-(4-ethylphenyl)-3-phenyl-1H-1,2,4-triazole-1,2(3H)-dicarboxylate (3f)



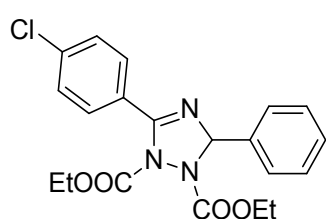
Colourless oil; 92% Yield, 181 mg; ¹H NMR (400 MHz, CDCl₃) δ 7.82-7.80 (d, J = 8 Hz, 2H), 7.51-7.49 (d, J = 8 Hz, 2H), 7.40-7.32 (m, 4H), 7.28-7.27 (br, 2H), 6.86 (s, 1H), 4.41-4.31 (m, 2H), 4.20-4.17 (m, 2H), 2.74-2.68 (q, J = 8 Hz, 2H), 1.39-1.35 (t, J = 8 Hz, 3H), 1.28-1.24 (t, J = 8 Hz, 3H), 1.11-1.07 (t, J = 8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 157.86, 153.25, 148.63, 137.51, 129.89, 128.67, 128.55, 127.54, 126.16, 126.10, 85.06, 63.44, 63.30, 28.99, 15.31, 14.56, 13.99; HRMS (ESI) m/z calcd for $C_{22}H_{24}N_3O_4^+$ [(M+H)⁺]: 396.1918; found: 396.1973.

Diethyl 5-(4-fluorophenyl)-3-phenyl-1H-1,2,4-triazole-1,2(3H)-dicarboxylate (3g)



Colourless oil; 75% yield, 144 mg; ¹H NMR (400 MHz, CDCl₃) δ 7.92-7.88 (m, 2H), 7.49-7.47 (m, 2H), 7.40-7.34 (m, 3H), 7.14-7.10 (m, 2H), 6.88 (s, 1H), 4.42-4.30 (m, 2H), 4.20-4.08 (m, 2H), 1.39-1.35 (t, J = 8 Hz, 3H), 1.12-1.08 (t, J = 8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.13, 156.73, 153.18, 137.36, 132.13, 132.04, 128.70, 128.61, 126.02, 125.19, 115.33, 115.11, 85.28, 63.57, 63.36, 14.51, 13.98; ¹⁹F NMR (376 MHz, CDCl₃) δ -107.29; HRMS (ESI) m/z calcd for $C_{20}H_{21}FN_3O_4^+$ [(M+H)⁺]: 386.1511; found: 386.1509.

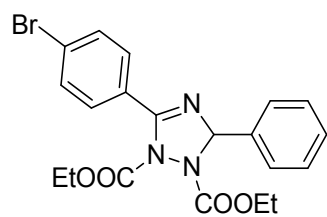
Diethyl 5-(4-chlorophenyl)-3-phenyl-1H-1,2,4-triazole-1,2(3H)-dicarboxylate (3h)



Colourless oil; 87% yield, 174 mg; ¹H NMR (400 MHz, CDCl₃) δ 7.84-7.82 (d, J = 8 Hz, 2H), 7.49-7.47 (m, 2H), 7.42-7.34 (m, 5H), 6.89 (s, 1H), 4.42-4.30 (m, 2H), 4.20-4.08 (m, 2H), 1.39-1.35 (t, J = 8 Hz, 3H), 1.12-1.08 (t, J = 8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 157.66, 156.79, 153.16, 137.97, 137.27, 131.09, 128.72, 128.64, 128.32,

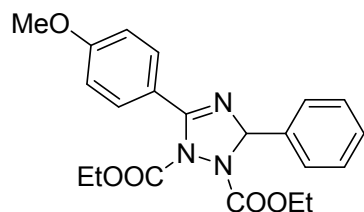
127.49, 126.01, 85.41, 63.62, 63.37, 14.52, 14.00; HRMS (ESI) m/z calcd for $C_{20}H_{21}ClN_3O_4^+ [(M+H)^+]$: 402.1215; found: 402.1216.

Diethyl 5-(4-bromophenyl)-3-phenyl-1H-1,2,4-triazole-1,2(3H)-dicarboxylate (3i)



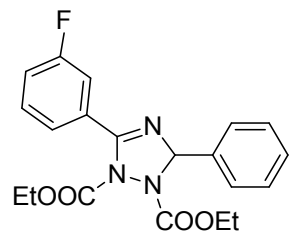
Colourless oil; 71% yield, 158 mg; 1H NMR (400 MHz, $CDCl_3$) δ 7.76-7.74 (d, J = 8 Hz, 2H), 7.58-7.56 (d, J = 8 Hz, 2H), 7.48-7.46 (m, 2H), 7.40-7.34 (m, 3H), 6.88 (s, 1H), 4.42-4.30 (m, 2H), 4.20-4.08 (m, 2H), 1.38-1.34 (t, J = 8 Hz, 3H), 1.12-1.08 (t, J = 8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.65, 156.91, 153.16, 137.24, 131.28, 131.25, 128.72, 128.64, 127.96, 126.47, 126.00, 85.45, 63.63, 63.38, 29.73, 14.52, 14.00; HRMS (ESI) m/z calcd for $C_{20}H_{21}BrN_3O_4^+ [(M+H)^+]$: 446.0710; found: 446.0710.

Diethyl 5-(4-methoxyphenyl)-3-phenyl-1H-1,2,4-triazole-1,2(3H)-dicarboxylate (3j)



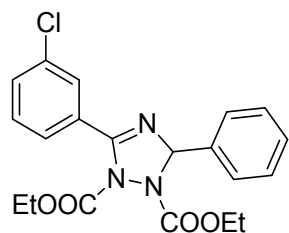
Yellow oil; 36% yield, 71 mg; 1H NMR (400 MHz, $CDCl_3$) δ 7.86-7.84 (d, J = 8 Hz, 2H), 7.50-7.48 (d, J = 8 Hz, 2H), 7.42-7.34 (m, 3H), 6.94-6.92 (d, J = 8 Hz, 2H), 6.86 (s, 1H), 4.38-4.32 (m, 2H), 4.20-4.07 (m, 2H), 3.86 (s, 3H), 1.38-1.34 (t, J = 8 Hz, 3H), 1.12-1.08 (t, J = 8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.47, 157.40, 153.35, 137.61, 131.71, 128.66, 128.52, 126.08, 121.14, 113.38, 84.95, 63.45, 63.27, 14.55, 14.06; HRMS (ESI) m/z calcd for $C_{21}H_{24}N_3O_5^+ [(M+H)^+]$: 398.1710; found: 398.1698.

Diethyl 5-(3-fluorophenyl)-3-phenyl-1H-1,2,4-triazole-1,2(3H)-dicarboxylate (3k)



Colourless oil; 60% yield, 116 mg; 1H NMR (400 MHz, $CDCl_3$) δ 7.68-7.66 (d, J = 8 Hz, 1H), 7.60-7.57 (m, 1H), 7.49-7.47 (d, J = 8 Hz, 2H), 7.43-7.34 (m, 4H), 7.24-7.19 (m, 1H), 6.90 (s, 1H), 4.42-4.31 (m, 2H), 4.20-4.07 (m, 2H), 1.39-1.35 (t, J = 8 Hz, 3H), 1.11-1.07 (t, J = 8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.38, 160.93, 157.70, 156.70, 153.09, 137.19, 131.11, 131.04, 129.65, 129.57, 128.73, 128.65, 126.01, 125.54, 125.52, 118.80, 118.59, 116.84, 116.59, 85.44, 63.62, 63.40, 29.72, 14.52, 13.93; ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.95; HRMS (ESI) m/z calcd for $C_{20}H_{21}FN_3O_4^+ [(M+H)^+]$: 386.1511; found: 386.1511.

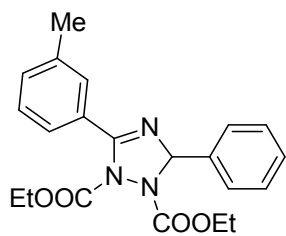
Diethyl 5-(3-chlorophenyl)-3-phenyl-1H-1,2,4-triazole-1,2(3H)-dicarboxylate (3l)



Colourless oil; 65% yield, 130 mg; 1H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.78-7.76 (d, J = 8 Hz, 1H), 7.50-7.49 (br, 3H), 7.42-7.33 (m, 3H), 6.91 (s, 1H), 4.44-4.30 (m, 2H), 4.24-4.06 (m, 2H), 1.39-1.35 (t, J = 8 Hz, 3H), 1.12-1.08 (t, J

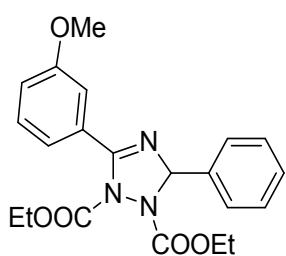
= 8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 157.67, 156.53, 153.03, 137.18, 134.05, 131.72, 130.74, 129.68, 129.28, 128.78, 128.69, 127.96, 126.00, 85.74, 63.69, 63.45, 12.56, 13.98; HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{21}\text{ClN}_3\text{O}_4^+$ [(M+H) $^+$]: 402.1215; found: 402.1278.

Diethyl 3-phenyl-5-(m-tolyl)-1H-1,2,4-triazole-1,2(3H)-dicarboxylate (3m)



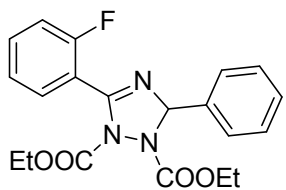
Colourless oil; 45% yield, 86 mg; ^1H NMR (400 MHz, CDCl_3) δ 7.69-7.65 (m, 2H), 7.5-7.49 (m, 2H), 7.40-7.32 (m, 5H), 6.88 (s, 1H), 4.39-4.33 (q, J = 8 Hz, 2H), 4.19-4.05 (m, 2H), 2.39 (s, 3H), 1.39-1.35 (t, J = 8 Hz, 3H), 1.09-1.05 (t, J = 8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 157.97, 153.16, 137.78, 137.48, 132.58, 130.06, 128.86, 128.68, 128.54, 127.85, 127.02, 126.07, 85.23, 63.42, 63.31, 21.29, 14.53, 13.96; HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{24}\text{N}_3\text{O}_4^+$ [(M+H) $^+$]: 382.1761; found: 382.1747.

Diethyl 5-(3-methoxyphenyl)-3-phenyl-1H-1,2,4-triazole-1,2(3H)-dicarboxylate (3n)



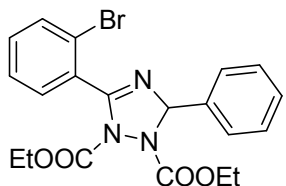
Yellow oil; 37% yield, 73 mg; ^1H NMR (400 MHz, CDCl_3) δ 7.51-7.49 (d, J = 8 Hz, 2H), 7.47-7.45 (d, J = 8 Hz, 2H), 7.40-7.32 (m, 5H), 7.07-7.05 (d, J = 8 Hz, 2H), 6.89 (s, 1H), 4.39-4.33 (m, 2H), 4.20-4.06 (m, 2H), 3.85 (s, 3H), 1.39-1.35 (t, J = 8 Hz, 3H), 1.12-1.08 (t, J = 8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.15, 157.74, 153.19, 137.34, 130.17, 129.07, 128.72, 128.61, 126.08, 122.40, 118.00, 114.36, 85.30, 63.50, 63.34, 55.50, 14.56, 14.00; HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{24}\text{N}_3\text{O}_5^+$ [(M+H) $^+$]: 398.1710; found: 398.1699.

Diethyl 5-(2-fluorophenyl)-3-phenyl-1H-1,2,4-triazole-1,2(3H)-dicarboxylate (3o)



Colourless oil; 92% yield, 177 mg; ^1H NMR (400 MHz, CDCl_3) δ 7.77-7.73 (t, J = 8 Hz, 1H), 7.52-7.50 (m, 3H), 7.40-7.34 (m, 3H), 7.23-7.19 (t, J = 8 Hz, 1H), 7.17-7.13 (t, J = 8 Hz, 1H), 6.91 (s, 1H), 4.39-4.35 (m, 2H), 4.16-4.09 (m, 2H), 1.39-1.35 (t, J = 8 Hz, 3H), 1.08-1.04 (t, J = 8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.19, 159.65, 158.09, 152.82, 152.04, 137.41, 133.38, 131.32, 128.73, 128.63, 126.04, 123.95, 116.02, 115.81, 85.25, 63.46, 63.41, 14.47, 13.88; ^{19}F NMR (376 MHz, CDCl_3) δ -111.12; HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{21}\text{FN}_3\text{O}_4^+$ [(M+H) $^+$]: 386.1511; found: 386.1563.

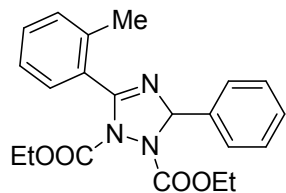
Diethyl 5-(2-bromophenyl)-3-phenyl-1H-1,2,4-triazole-1,2(3H)-dicarboxylate (3p)



Colourless oil; 56% yield, 125 mg; ^1H NMR (400 MHz, CDCl_3) δ 7.64-7.62 (d, J = 8 Hz, 1H), 7.56-7.54 (m, 3H), 7.42-7.33 (m, 5H), 6.93 (s, 1H), 4.40-4.34 (q, J = 8 Hz, 2H), 4.10-4.08 (m, 2H), 1.34-1.38 (t, J = 8 Hz, 3H), 1.03-0.99 (t, J

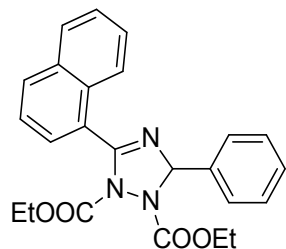
= 8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.06, 155.00, 151.27, 137.56, 133.08, 131.80, 131.45, 131.40, 128.70, 128.59, 127.06, 126.10, 122.48, 85.92, 63.45, 63.32, 14.52, 13.79; HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{21}\text{BrN}_3\text{O}_4^+$ [(M+H) $^+$]: 446.0710; found: 446.0729.

Diethyl 3-phenyl-5-(o-tolyl)-1H-1,2,4-triazole-1,2(3H)-dicarboxylate (3q)



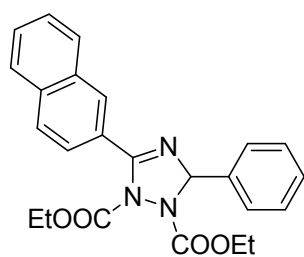
Colourless oil; 75% yield, 142 mg; ^1H NMR (400 MHz, CDCl_3) δ 7.48-7.46 (d, J = 8 Hz, 3H), 7.18-7.16 (d, J = 8 Hz, 2H), 6.83 (s, 1H), 4.33-4.27 (q, J = 8 Hz, 2H), 4.04-3.96 (m, 2H), 2.39, (s, 3H), 1.31-1.28 (t, J = 8 Hz, 3H), 0.95-0.91 (t, J = 8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 156.64, 151.92, 137.81, 130.79, 130.48, 129.11, 128.71, 128.53, 125.98, 125.52, 85.62, 63.44, 63.21, 19.93, 14.51, 13.84; HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{24}\text{N}_3\text{O}_4^+$ [(M+H) $^+$]: 382.1761; found: 382.1761.

Diethyl 5-(naphthalen-1-yl)-3-phenyl-1H-1,2,4-triazole-1,2(3H)-dicarboxylate (3r)



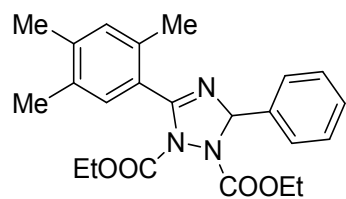
Colourless oil; 62% yield, 128 mg; ^1H NMR (400 MHz, CDCl_3) δ 8.45-8.43 (d, J = 8 Hz, 1H), 8.00-7.98 (d, J = 8 Hz, 1H), 7.90-7.86 (t, J = 8 Hz, 2H), 7.63-7.61 (d, J = 8 Hz, 2H), 7.57-7.50 (m, 3H), 7.47-7.43 (t, J = 8 Hz, 2H), 7.41-7.39 (d, J = 8 Hz, 1H), 6.99 (s, 1H), 4.47-4.44 (m, 2H), 3.99-3.87 (m, 2H), 2.39, (s, 3H), 1.46-1.42 (t, J = 8 Hz, 3H), 0.74-0.70 (t, J = 8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.36, 156.32, 151.81, 137.72, 133.28, 131.81, 131.39, 129.18, 128.85, 128.64, 128.50, 127.35, 126.76, 126.28, 126.04, 124.79, 124.71, 85.81, 63.60, 63.19, 14.59, 13.53; HRMS (ESI) m/z calcd for $\text{C}_{24}\text{H}_{24}\text{N}_3\text{O}_4^+$ [(M+H) $^+$]: 418.1761; found: 418.1758.

Diethyl 5-(naphthalen-2-yl)-3-phenyl-1H-1,2,4-triazole-1,2(3H)-dicarboxylate (3s)



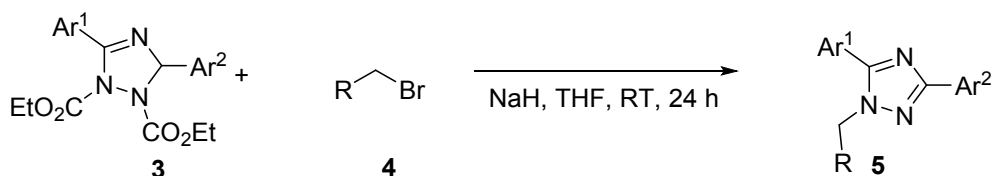
Colourless oil; 65% yield, 135 mg; ^1H NMR (400 MHz, CDCl_3) δ 8.44 (s, 1H), 7.94 (s, 2H), 7.90-7.87 (m, 2H), 7.57-7.52 (m, 4H), 7.44-7.40 (t, J = 8 Hz, 2H), 7.38-7.36 (d, J = 8 Hz, 1H), 6.96 (s, 1H), 4.45-4.35 (m, 2H), 4.23-4.04 (m, 2H), 1.42-1.38 (t, J = 8 Hz, 3H), 1.07-1.03 (t, J = 8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 157.90, 153.29, 137.49, 134.90, 132.42, 130.57, 129.02, 128.77, 128.64, 127.83, 127.64, 126.68, 126.32, 126.13, 126.00, 85.43, 63.54, 63.38, 14.60, 14.02; HRMS (ESI) m/z calcd for $\text{C}_{24}\text{H}_{24}\text{N}_3\text{O}_4^+$ [(M+H) $^+$]: 418.1761; found: 418.1785.

Diethyl 3-phenyl-5-(2,4,5-trimethylphenyl)-1H-1,2,4-triazole-1,2(3H)-dicarboxylate (3t)



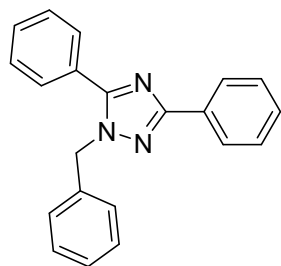
Colourless oil; 78% yield, 159 mg; ^1H NMR (400 MHz, CDCl_3) δ 7.54-7.52 (d, $J = 8$ Hz, 2H), 7.42-7.38 (t, $J = 8$ Hz, 2H), 7.36-7.34 (d, $J = 8$ Hz, 1H), 7.32 (s, 1H), 7.01 (s, 1H), 6.87 (s, 1H), 4.40-4.34 (q, $J = 8$ Hz, 2H), 4.14-4.06 (m, 2H), 2.40 (s, 3H), 2.25 (s, 3H), 2.23 (s, 3H), 1.39-1.35 (t, $J = 8$ Hz, 3H), 1.08-1.04 (t, $J = 8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.20, 157.00, 152.14, 139.73, 137.94, 135.09, 133.69, 131.97, 131.02, 128.69, 128.48, 126.28, 126.03, 85.45, 63.35, 63.13, 19.79, 19.36, 19.12, 14.52, 13.99; HRMS (ESI) m/z calcd for $\text{C}_{23}\text{H}_{28}\text{N}_3\text{O}_4^+$ [(M+H) $^+$]: 410.2074; found: 410.2085.

The preparation of the compounds 5.



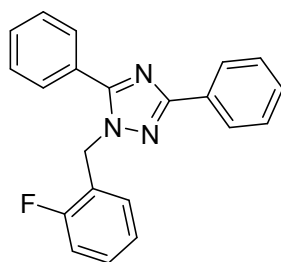
The compounds **3** (0.05 mmol) was added into a dry THF (2 mL) solution, then **4** (0.1 mmol) and NaH (0.5 mmol) was added into the system. The mixture was stirred at room temperature for 24 h. Until the reaction was finished (determined by TLC analysis), the crude product was purified by flash chromatography on silica gel (eluent: PE/EtOAc from 10:1) affording to the derivatives **5**.

1-benzyl-3,5-diphenyl-1H-1,2,4-triazole (**5a**)



White solid; 90% yield, 14.0 mg; m.p.: 82-84 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 8.21-8.19 (d, $J = 8$ Hz, 2H), 7.64-7.62 (d, $J = 8$ Hz, 2H), 7.48-7.41 (m, 6H), 7.37-7.31 (m, 3H), 7.23-7.21 (d, $J = 8$ Hz, 2H), 5.47 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 161.58, 156.16, 136.07, 130.98, 130.27, 129.25, 128.93, 128.89, 128.87, 128.57, 128.01, 126.87, 126.03, 52.80; HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{18}\text{N}_3^+$ [(M+H) $^+$]: 312.1495; found: 312.1465.

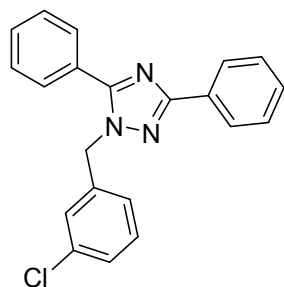
1-(2-fluorobenzyl)-3,5-diphenyl-1H-1,2,4-triazole (**5b**)



White solid; 75% yield, 12.3 mg; m.p.: 88-90 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 8.20-8.18 (d, $J = 8$ Hz, 2H), 7.64-7.63 (m, 2H), 7.49-7.41 (m, 6H), 7.31-7.29 (m, 1H), 7.15-7.09 (m, 3H), 5.53 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 161.91, 156.45, 130.93, 130.32, 129.84, 129.76, 129.31, 128.95, 128.86, 128.83, 128.73, 128.57, 127.85, 126.52, 124.67, 124.63, 123.40, 123.25, 115.58, 115.37, 46.78; ^{19}F NMR (376 MHz, CDCl_3) δ -118.34; HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{17}\text{FN}_3^+$ [(M+H) $^+$]: 330.1401;

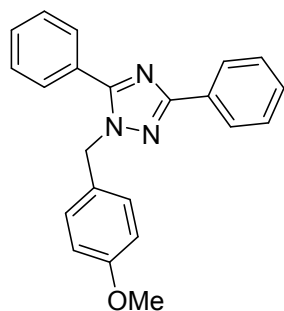
found: 330.1496.

1-(3-chlorobenzyl)-3,5-diphenyl-1H-1,2,4-triazole (5c)



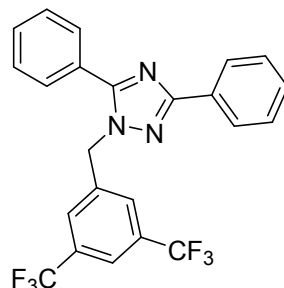
White solid; 78% yield, 13.4 mg; m.p.: 92-94 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.25-8.23 (d, J = 8 Hz, 2H), 7.66-7.64 (m, 2H), 7.54-7.46 (m, 6H), 7.33-7.30 (m, 3H), 7.13-7.12 (m, 1H), 5.47(s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 161.73, 156.25, 137.94, 134.91, 130.92, 130.76, 130.47, 130.25, 129.41, 129.01, 128.82, 128.61, 128.33, 127.72, 127.12, 126.56, 125.03, 52.22; HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{17}\text{ClN}_3^+[(\text{M}+\text{H})^+]$: 346.1106; found: 346.1065.

1-(4-methoxybenzyl)-3,5-diphenyl-1H-1,2,4-triazole (5d)



White solid; 65% yield, 11.1 mg; m.p.: 84-86 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.20-8.18 (d, J = 8 Hz, 2H), 7.64-7.62 (d, J = 8 Hz, 2H), 7.49-7.40 (m, 6H), 7.17-7.15 (d, J = 8 Hz, 2H), 6.85-6.87 (d, J = 8 Hz, 2H), 5.39 (s, 2H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 161.48, 159.35, 155.95, 131.05, 130.21, 129.20, 128.92, 128.87, 128.54, 128.37, 128.12, 126.50, 114.26, 55.31, 52.35; HRMS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{20}\text{N}_3\text{O}^+[(\text{M}+\text{H})^+]$: 342.1601; found: 342.1595.

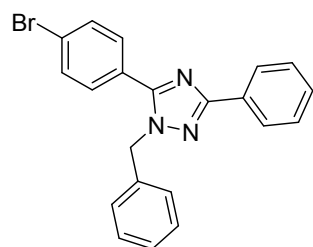
1-(3,5-bis(trifluoromethyl)benzyl)-3,5-diphenyl-1H-1,2,4-triazole (5e)



Colourless oil; 45% yield, 10.0 mg; ^1H NMR (400 MHz, CDCl_3) δ 8.18-8.16 (d, J = 8 Hz, 2H), 7.84 (s, 1H), 7.67 (s, 2H), 7.58-7.53 (m, 5H), 7.46-7.44 (m, 3H), 5.54 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.24, 156.49, 138.26, 132.54, 132.21, 130.72, 130.56, 129.57, 129.18, 128.75, 128.66, 127.58, 126.56, 124.33, 122.34, 122.30, 122.26, 121.62, 51.93; ^{19}F NMR (376 MHz, CDCl_3) δ -62.95; HRMS (ESI) m/z calcd for $\text{C}_{23}\text{H}_{16}\text{F}_6\text{N}_3^+[(\text{M}+\text{H})^+]$: 448.1243; found:

448.1186.

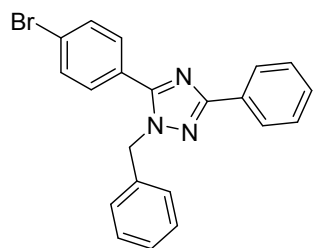
1-benzyl-5-(4-bromophenyl)-3-phenyl-1H-1,2,4-triazole (5f)



White solid, 70% yield, 13.6 mg; isomer ratio = 1:1.25; m.p.: 80-82 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.19-8.17 (d, J = 8 Hz, 2H), 8.07-8.05 (d, J = 8 Hz, 2.5H), 7.61-7.56 (m, 6.75H), 7.50-7.43(m, 9H), 7.35-7.33 (m, 6.75H), 7.21-7.20 (m, 4.5H), 5.45 (s, 4.5H); ^{13}C NMR (100 MHz, CDCl_3) δ 161.76, 160.77, 156.34, 155.12, 135.91, 135.85, 132.15, 131.72, 130.87, 130.35, 130.33, 130.06, 129.34, 129.03, 128.96, 128.93, 128.82, 128.60, 128.42, 128.15, 128.09, 127.90, 127.80, 126.97, 126.89, 126.75, 126.49, 124.83, 123.42, 52.94, 52.86; HRMS (ESI) m/z calcd for

$\text{C}_{21}\text{H}_{17}\text{BrN}_3^+ [(\text{M}+\text{H})^+]$: 390.0600; found: 390.0540.

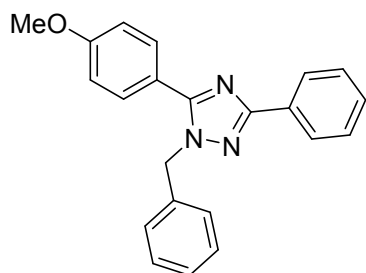
1-benzyl-5-(4-bromophenyl)-3-phenyl-1H-1,2,4-triazole (5f)



^1H NMR (400 MHz, CDCl_3) δ 8.08-8.06 (d, J = 8 Hz, 2H), 7.62-7.56 (m, 4H), 7.49 (s, 3H), 7.35-7.33 (m, 3H), 7.21-7.20 (m, 2H), 5.45 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.75, 156.33, 135.91, 132.15, 131.73, 130.36, 130.03, 129.03, 128.95, 128.93, 128.83, 128.60, 128.14, 128.09, 127.88, 126.89, 126.75, 126.50, 123.44, 52.87; HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{17}\text{BrN}_3^+ [(\text{M}+\text{H})^+]$: 390.0600; found:

390.0540.

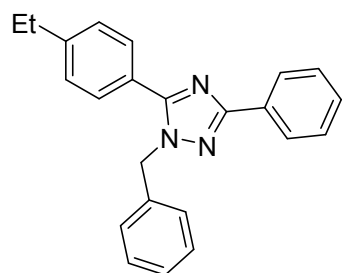
1-benzyl-5-(4-methoxyphenyl)-3-phenyl-1H-1,2,4-triazole (5g)



White solid, 62% yield, 10.6 mg; isomer ratio = 1:1; m.p.: 73-75 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.19-8.18 (d, J = 4 Hz, 2H), 8.13-8.11 (d, J = 8 Hz, 2H), 7.62-7.61 (d, J = 4 Hz, 2H), 7.57-7.55 (d, J = 8 Hz, 2H), 7.47-7.40 (m, 6H), 7.35-7.33 (m, 6H), 7.22 (m, 4H), 6.98-6.96 (d, J = 8 Hz, 4H), 5.45 (s, 4H), 3.86 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 161.53, 161.49, 161.08,

160.53, 156.09, 156.04, 136.24, 136.20, 131.17, 130.28, 130.16, 129.14, 128.92, 128.90, 128.85, 128.83, 128.53, 128.18, 127.93, 126.85, 126.79, 126.49, 123.85, 120.38, 114.30, 113.94, 55.41, 55.34, 52.74, 52.70; HRMS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{20}\text{N}_3\text{O}^+ [(\text{M}+\text{H})^+]$: 342.1601; found: 342.1591.

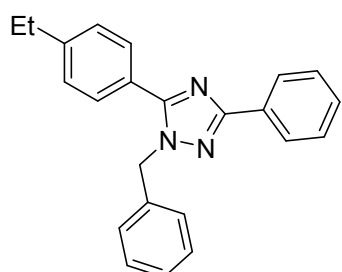
1-benzyl-5-(4-ethylphenyl)-3-phenyl-1H-1,2,4-triazole (5h)



Clourless oil, 85% yield, 14.4 mg; isomer ratio = 1:1; ^1H NMR (400 MHz, CDCl_3) δ 8.20-8.18 (d, J = 8 Hz, 2H), 8.12-8.10 (d, J = 8 Hz, 2H), 7.63-7.61 (d, J = 8 Hz, 2H), 7.56-7.54 (d, J = 8 Hz, 2H), 7.47-7.43 (m, 6H), 7.34-7.28 (m, 10H), 7.23-7.21 (m, 4H), 5.46 (s, 4H), 2.73-2.67 (m, 4H), 1.26 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 161.68, 161.49, 156.30, 156.04, 146.73, 145.54, 136.21,

136.17, 131.09, 130.18, 129.17, 128.89, 128.86, 128.83, 128.51, 128.47, 128.38, 128.12, 128.06, 127.95, 126.85, 126.54, 125.29, 52.76, 28.82, 28.80, 15.49, 15.34; HRMS (ESI) m/z calcd for $\text{C}_{23}\text{H}_{22}\text{N}_3^+ [(\text{M}+\text{H})^+]$: 340.1808; found: 340.1801.

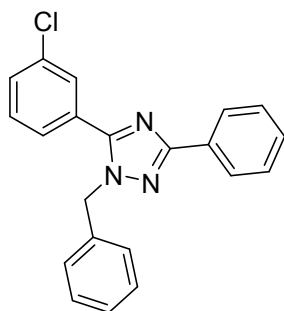
1-benzyl-5-(4-ethylphenyl)-3-phenyl-1H-1,2,4-triazole (5h)



^1H NMR (400 MHz, CDCl_3) δ 8.11-8.19 (d, J = 8 Hz,

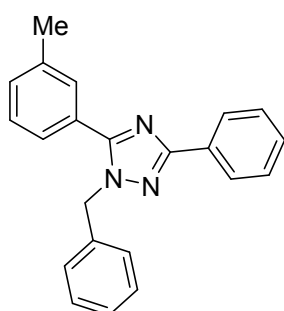
2H), 7.62-7.61 (m, 2H), 7.46 (m, 3H), 7.33-7.31 (d, $J = 8$ Hz, 2H), 7.28 (m, 1H), 7.25 (m, 2H), 7.20-7.18 (m, 2H), 5.44 (s, 2H), 2.71-2.65 (q, $J = 8$ Hz, 2H), 1.25-1.24 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 161.49, 155.95, 145.70, 136.07, 130.30, 128.91, 128.56, 128.09, 127.99, 126.58, 52.79, 28.83, 15.50; HRMS (ESI) m/z calcd for $\text{C}_{23}\text{H}_{22}\text{N}_3^+ [(M+H)^+]$: 340.1808; found: 340.1801.

1-benzyl-5-(3-chlorophenyl)-3-phenyl-1H-1,2,4-triazole (5i)



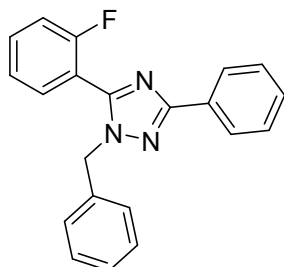
Clourless oil, 55% yield, 9.5 mg; isomer ratio = 1:2; ^1H NMR (400 MHz, CDCl_3) δ 8.20-8.18 (d, $J = 8$ Hz, 4H), 8.09-8.07 (m, 2H), 7.67 (s, 1H), 7.63-7.61 (m, 4H), 7.49-7.44 (m, 11H), 7.37-7.34 (m, 14H), 7.22 (s, 6H), 5.46 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 161.74, 160.48, 156.37, 154.72, 135.89, 135.77, 134.97, 134.63, 132.85, 130.85, 130.37, 130.13, 129.84, 129.76, 129.36, 129.20, 129.12, 129.02, 128.97, 128.94, 128.83, 128.61, 128.19, 128.10, 127.87, 126.90, 126.78, 126.59, 126.50, 124.57, 53.01, 52.89; HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{17}\text{ClN}_3^+ [(M+H)^+]$: 346.1106; found: 346.1062.

1-benzyl-3-phenyl-5-(m-tolyl)-1H-1,2,4-triazole (5j)



Clourless oil, 80% yield, 12.9 mg; isomer ratio = 1:1; ^1H NMR (400 MHz, CDCl_3) δ 8.20-8.18 (d, $J = 8$ Hz, 2H), 8.03-7.98 (m, 2H), 7.63-7.61 (m, 2H), 7.47-7.43 (m, 6H), 7.33-7.31 (m, 12H), 7.23-7.21 (m, 4H), 5.46 (s, 4H), 2.42 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 161.75, 161.54, 156.35, 156.15, 138.77, 138.24, 136.21, 136.13, 131.09, 130.99, 130.89, 130.22, 130.02, 129.69, 129.18, 128.92, 128.86, 128.70, 128.54, 128.49, 128.42, 128.08, 127.98, 127.93, 127.80, 127.64, 127.09, 126.95, 126.82, 126.52, 125.71, 123.66, 52.81, 52.77, 21.39, 21.37; HRMS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{20}\text{N}_3^+ [(M+H)^+]$: 326.1652; found: 326.1643.

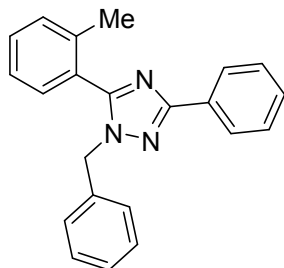
1-benzyl-5-(2-fluorophenyl)-3-phenyl-1H-1,2,4-triazole (5k)



Clourless oil, 80% yield, 13.1 mg; isomer ratio = 1:1; ^1H NMR (400 MHz, CDCl_3) δ 8.17-8.15 (d, $J = 8$ Hz, 3H), 7.63-7.61 (d, $J = 8$ Hz, 2H), 7.48-7.32 (m, 12H), 7.25-7.22 (m, 9H), 7.12 (s, 2H), 5.50 (s, 2H), 5.34 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.07, 161.67, 161.05, 159.15, 158.56, 155.84, 151.17, 135.99, 135.50, 132.53, 132.46, 131.89, 131.88, 130.92, 130.71, 130.61, 130.39, 130.35, 130.30, 129.25, 128.92, 128.87, 128.66, 128.54, 128.01, 127.47, 126.92, 126.47, 124.76, 124.73, 124.13, 124.09, 116.62, 116.40, 116.33, 116.12, 53.05, 53.01, 52.92; ^{19}F NMR (376 MHz, CDCl_3) δ -112.34, -112.55; HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{17}\text{FN}_3^+ [(M+H)^+]$: 330.1401; found: 330.1392.

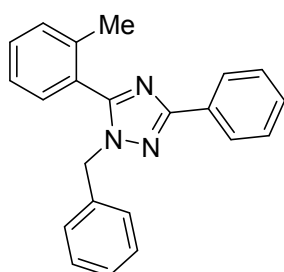
1-benzyl-3-phenyl-5-(o-tolyl)-1H-1,2,4-triazole (5l)

White solid, 95% yield, 15.4 mg; isomer ratio = 1:1.25; m.p.: 78-80 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.15-8.13 (d, *J* = 8 Hz, 2.5H), 7.99-7.98 (m, 1H), 7.60-7.59(m, 2H), 7.43-7.21 (m, 11H), 7.24-7.21 (m, 12.5H), 7.05-7.04 (m, 2H), 5.43 (s, 2H), 5.16

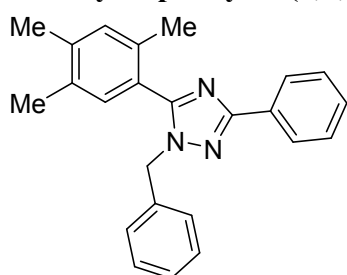


(s, 2.5H), 2.64 (s, 3H), 2.08 (s, 3.75H); ¹³C NMR (100 MHz, CDCl₃) δ 162.23, 161.40, 155.56, 155.26, 138.25, 137.21, 136.24, 135.64, 131.17, 131.10, 130.67, 130.32, 130.28, 130.14, 129.75, 129.54, 129.15, 128.89, 128.84, 128.78, 128.66, 128.54, 128.18, 128.04, 127.98, 127.90, 127.60, 126.98, 126.44, 125.87, 125.73, 52.81, 52.53, 21.86, 19.61; HRMS (ESI) *m/z* calcd for C₂₂H₂₀N₃⁺ [(M+H)⁺]: 326.1652;

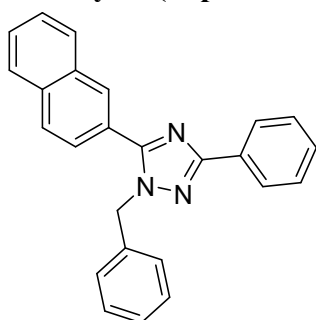
found: 326.1644.

1-benzyl-3-phenyl-5-(o-tolyl)-1H-1,2,4-triazole (5l)

¹H NMR (400 MHz, CDCl₃) δ 8.15-8.13 (d, *J* = 8 Hz, 2H), 7.43-7.35 (m, 4H), 7.21 (s, 6H), 7.05-7.04 (m, 2H), 5.16 (s, 2H), 2.08 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 161.33, 155.53, 138.26, 135.60, 131.11, 130.68, 130.35, 129.75, 129.18, 128.90, 128.84, 128.67, 128.56, 128.05, 127.60, 126.98, 126.46, 125.88, 52.55, 19.61; HRMS (ESI) *m/z* calcd for C₂₂H₂₀N₃⁺ [(M+H)⁺]: 326.1652; found: 326.1644.

1-benzyl-3-phenyl-5-(2,4,5-trimethylphenyl)-1H-1,2,4-triazole (5m)

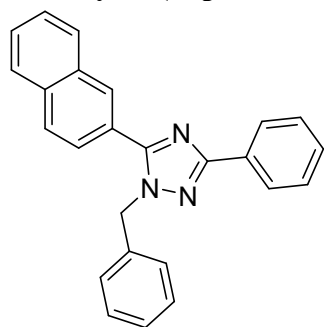
White solid, 72% yield, 12.7 mg; isomer ratio = 1:1.5; m.p.: 88-90 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.21-8.19 (d, *J* = 8 Hz, 3H), 7.85 (s, 1H), 7.66-7.64 (m, 2H), 7.49-7.35 (m, 10H), 7.28(m, 6H), 7.16-7.14 (m, 3H), 7.09 (s, 2.5H), 7.00 (s, 1.5H), 5.48 (s, 2H), 5.22 (s, 3H), 2.64 (s, 3H), 2.30 (s, 11.5H), 2.22 (s, 4.5H), 2.11 (s, 4.5H); ¹³C NMR (100 MHz, CDCl₃) δ 162.43, 161.34, 155.91, 155.12, 138.86, 137.20, 136.35, 135.88, 135.16, 134.31, 134.01, 133.77, 132.55, 131.91, 131.30, 130.92, 130.81, 130.47, 130.06, 129.05, 128.90, 128.85, 128.81, 128.61, 128.50, 128.42, 128.29, 127.95, 127.91, 127.81, 127.65, 127.55, 126.96, 126.44, 125.10, 52.72, 52.44, 21.29, 19.67, 19.50, 19.22, 19.10, 19.03; HRMS (ESI) *m/z* calcd for C₂₄H₂₄N₃⁺ [(M+H)⁺]: 354.1965; found: 354.1950.

1-benzyl-5-(naphthalen-2-yl)-3-phenyl-1H-1,2,4-triazole (5n)

White solid, 80% yield, 14.4 mg; isomer ratio = 1:1.2; m.p.: 104-106 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.69 (s, 1.2H), 8.29-8.27 (d, *J* = 8 Hz, 1.2H), 8.22-8.20 (d, *J* = 8 Hz, 2H),

8.06 (s, 1H), 7.92-7.83 (m, 5.6H), 7.80-7.78 (d, $J = 8$ Hz, 1H), 7.73-7.71 (d, $J = 8$ Hz, 1H), 7.64-7.63 (m, 2.4H), 7.53-7.41 (m, 11H), 7.34-7.32 (m, 6H), 7.23-7.22 (m, 5H), 5.51 (s, 2H), 5.48 (s, 2.4H); ^{13}C NMR (100 MHz, CDCl_3) δ 161.73, 161.70, 156.36, 156.21, 136.21, 136.08, 133.88, 133.82, 133.44, 132.85, 131.10, 130.91, 130.30, 129.25, 128.96, 128.92, 128.89, 128.77, 128.62, 128.59, 128.55, 128.43, 128.24, 128.08, 128.04, 127.85, 127.77, 127.45, 126.97, 126.90, 126.56, 126.39, 126.25, 125.83, 125.64, 125.34, 124.18, 53.03, 52.86; HRMS (ESI) m/z calcd for $\text{C}_{25}\text{H}_{20}\text{N}_3^+$ [(M+H) $^+$]: 362.1652; found: 362.1586.

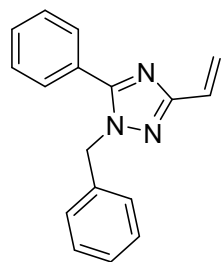
1-benzyl-5-(naphthalen-2-yl)-3-phenyl-1H-1,2,4-triazole (5n)



^1H NMR (400 MHz, CDCl_3) δ 8.73 (s, 1H), 8.33-8.31 (d, $J = 8$ Hz, 1H), 7.97-7.93 (m, 2H), 7.89-7.87 (m, 1H), 7.69-7.67 (m, 2H), 7.52 (s, 5H), 7.38-7.34 (m, 3H), 7.28 (s, 2H), 5.52 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 161.70, 156.37, 136.09, 133.89, 133.44, 130.29, 128.96, 128.92, 128.89, 128.62, 128.58, 128.43, 128.23, 128.09, 128.03, 127.77, 126.90, 126.40, 126.25, 125.82, 124.19, 52.86; HRMS (ESI) m/z calcd for $\text{C}_{25}\text{H}_{20}\text{N}_3^+$ [(M+H) $^+$]: 362.1652;

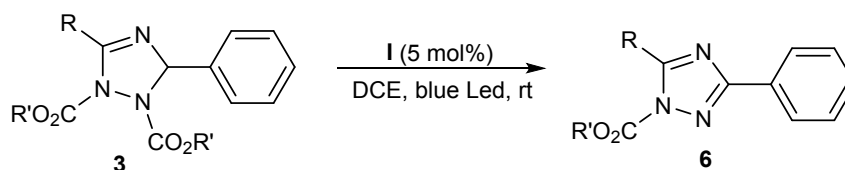
found: 362.1586.

1-benzyl-5-phenyl-3-vinyl-1H-1,2,4-triazole (5o)



Clourless oil, 70% yield, 9.1 mg; isomer ratio = 1:3; ^1H NMR (400 MHz, CDCl_3) δ 8.15-8.13 (d, $J = 8$ Hz, 6H), 7.59-7.57 (d, $J = 8$ Hz, 2H), 7.47-7.39 (m, 12H), 7.36-7.32 (m, 12H), 7.22-7.20 (d, $J = 8$ Hz, 6H), 7.17-7.15 (d, $J = 8$ Hz, 2H), 6.81-6.73 (m, 1H), 6.66-6.59 (m, 3H), 6.47-6.43 (d, $J = 16$ Hz, 3H), 6.35-6.31 (d, $J = 16$ Hz, 1H), 5.68-5.65 (d, $J = 12$ Hz, 3H), 5.56-5.53 (d, $J = 12$ Hz, 1H), 5.43 (s, 6H), 5.39 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 161.30, 160.86, 153.09, 135.89, 135.50, 130.89, 130.30, 129.23, 128.97, 128.93, 128.86, 128.83, 128.52, 128.20, 128.05, 126.93, 126.85, 126.64, 126.49, 123.86, 120.72, 119.73, 52.70, 52.24; HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{16}\text{N}_3^+$ [(M+H) $^+$]: 262.1339; found: 262.1313.

The preparation of the aromatization compounds 6.



The substrates **3** (0.05 mmol) was added into a DCE (0.5 mL) solution, then catalyst **I** (5 mol%, 0.0025 mmol) was added into the mixture. The mixture was

stirred at room temperature under blue LED until finished (determined by TLC analysis). The crude product was purified by flash chromatography on silica gel (eluent: PE/EtOAc from 10:1 to 5:1) affording to the aromatization compounds **6**.

Table 1. Optimization of Reaction Conditions.^a

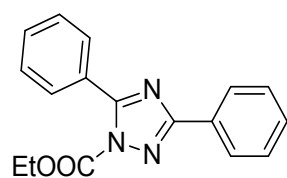
3a **6a**

Entry	Change from the "standard conditions"	Yield (%)
1	none	1 h, 99%
2	no light	1 h, trace
3	no photocatalyst	1 h, trace
4	in Ar	1 h, 35%
5	Ru(ppy) ₃ ·6H ₂ O, instead of I	1 h, NR
6	[Ir(ppy) ₂ (dtbbpy)]PF ₆ , instead of I	1 h, NR
7	EY, instead of I	1 h, NR
8	in toluene	24 h, 75%
9	in CH ₂ Cl ₂	1.5 h, 94%
10	in DMF	NR
11	in CHCl ₃	1 h, 60%
12	in CH ₃ CN	1 h, 95%
13	in acetone	1h, 94%

I

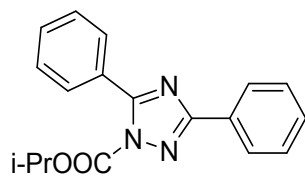
^aUnless otherwise noted, all the reactions were carried out with **3a** (0.05 mmol) in solvent (1 mL) catalyzed by the photosensitizer under visible light at 25 °C.

Ethyl 3,5-diphenyl-1H-1,2,4-triazole-1-carboxylate (**6a**)



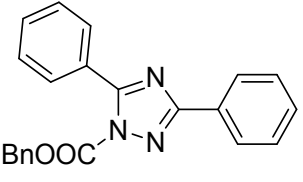
White solid; 99% yield, 14.5 mg; m.p.: 112-114 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.25-8.23 (m, 2H), 7.71-7.69 (m, 2H), 7.54-7.46 (m, 6H), 4.50-4.44 (q, *J* = 8 Hz, 2H), 1.38-1.34 (t, *J* = 8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 162.20, 159.43, 148.69, 130.64, 130.35, 129.53, 129.48, 128.94, 128.78, 128.64, 128.07, 127.27, 126.79, 65.31, 29.72, 13.95; HRMS (ESI) *m/z* calcd for C₁₇H₁₆N₃O₂⁺ [(M+H)⁺]: 294.1237; found: 294.1235.

Isopropyl 3,5-diphenyl-1H-1,2,4-triazole-1-carboxylate (**6b**)

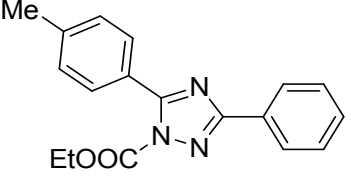


Yellow solid; 75% yield, 11.5 mg; m.p.: 86-88 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.27-8.24 (m, 2H), 7.68-7.66 (m, 2H), 7.54-7.46 (m, 6H), 5.22-5.16 (m, 1H), 1.32-1.30 (d, *J* = 8 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 162.06, 159.05, 130.47, 130.25, 129.59, 129.47, 129.15, 128.60, 128.03, 127.25, 74.19, 21.43; HRMS (ESI) *m/z* calcd for C₁₈H₁₈N₃O₂⁺ [(M+H)⁺]: 308.1394; found: 308.1396.

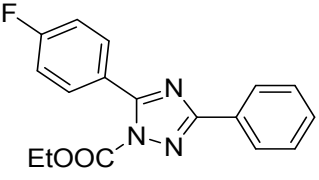
Benzyl 3,5-diphenyl-1H-1,2,4-triazole-1-carboxylate (**6c**)


 White solid; 81% yield, 14.3 mg; m.p.: 85-87 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.24-8.22 (m, 2H), 7.66-7.64 (m, 2H), 7.50-7.43 (m, 6H), 7.37-7.32 (m, 5H), 5.41 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 162.25, 159.45, 148.65, 133.75, 130.62, 130.36, 129.52, 129.45, 129.04, 128.93, 128.83, 128.72, 128.63, 128.10, 127.28, 126.88, 126.77, 126.56, 70.46; HRMS (ESI) *m/z* calcd for C₂₂H₁₈N₃O₂⁺ [(M+H)⁺]: 356.1394; found: 356.1388.

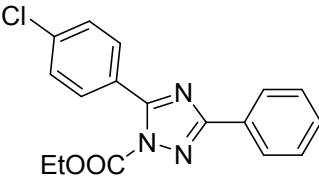
Ethyl 3-phenyl-5-(p-tolyl)-1H-1,2,4-triazole-1-carboxylate (6d)


 White solid; 65% yield, 10 mg; isomer ratio = 1.3:1; m.p.: 80-82 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.24-8.22 (m, 2.3H), 8.14-8.13 (d, *J* = 4 Hz, 1H), 8.12-8.11 (d, *J* = 4 Hz, 1.3H), 7.71-7.70 (m, 1H), 7.69-7.68 (m, 1.3H), 7.62-7.61 (d, *J* = 4 Hz, 1H), 7.60-7.59 (d, *J* = 4 Hz, 1.3H), 7.51-7.45 (m, 6.9H), 7.30 (s, 1.3H), 7.28 (s, 2H), 7.26 (s, 1.3H), 4.50-4.42 (m, 4.6H), 2.43 (s, 3.9H), 2.40 (s, 3H), 1.40-1.36 (t, *J* = 8 Hz, 3.9H), 1.37-1.33 (t, *J* = 8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 162.27, 162.12, 159.66, 159.34, 148.83, 148.72, 140.99, 140.51, 130.59, 130.28, 129.52, 129.49, 129.36, 128.77, 128.61, 128.04, 127.26, 127.20, 125.76, 65.26, 65.23, 21.58, 21.54, 14.02, 13.96; HRMS (ESI) *m/z* calcd for C₁₈H₁₈N₃O₂⁺ [(M+H)⁺]: 308.1394; found: 308.1392.

Ethyl 5-(4-fluorophenyl)-3-phenyl-1H-1,2,4-triazole-1-carboxylate (6e)

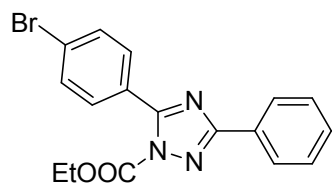

 White solid; 86% yield, 13.3 mg; isomer ratio = 1.3:1; m.p.: 117-119 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.25-8.21 (m, 4.6H), 7.75-7.68 (m, 4.6H), 7.54-7.46 (m, 6.9H), 7.20-7.16 (t, *J* = 8 Hz, 2H), 7.26-7.12 (t, *J* = 8 Hz, 2.6H), 4.51-4.43 (m, 4.6H), 1.41-1.37 (t, *J* = 8 Hz, 3H), 1.37-1.33 (t, *J* = 8 Hz, 3.9H); ¹³C NMR (100 MHz, CDCl₃) δ 165.45, 162.96, 162.17, 161.37, 159.50, 158.56, 148.72, 148.61, 131.94, 131.85, 130.71, 130.41, 129.50, 129.35, 129.27, 128.67, 128.09, 127.24, 125.77, 125.74, 124.80, 124.77, 115.83, 115.61, 115.41, 115.19, 65.42, 65.34, 14.02, 13.94; ¹⁹F NMR (376 MHz, CDCl₃) δ -110.23, -108.96; HRMS (ESI) *m/z* calcd for C₁₇H₁₅FN₃O₂⁺ [(M+H)⁺]: 312.1143; found: 312.1144.

Ethyl 5-(4-chlorophenyl)-3-phenyl-1H-1,2,4-triazole-1-carboxylate (6f)


 White solid; 91% yield, 14.9 mg; isomer ratio = 1.2:1; m.p.: 70-72 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.23-8.17 (m, 4.4H), 7.71-7.70 (m, 1.2H), 7.69-7.68 (m, 2H), 7.67-7.66 (m, 1.2H), 7.54-7.43 (m, 11H), 4.52-4.44 (m, 4.4H), 1.43-1.39 (t, *J* = 8 Hz, 3H), 1.38-1.34 (t, *J* = 8 Hz, 3.6H); ¹³C NMR (100 MHz, CDCl₃) δ 162.27, 161.29, 159.55, 158.45, 148.68, 148.57, 137.01, 136.41, 131.04, 130.76, 130.46, 129.49, 128.94, 128.68, 128.57, 128.40, 128.11, 127.24, 65.50, 65.42, 14.05, 13.96; HRMS (ESI) *m/z* calcd for

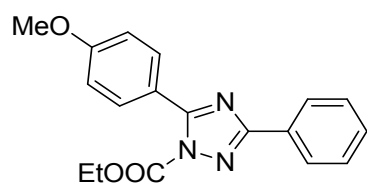
$C_{17}H_{15}ClN_3O_2^+ [(M+H)^+]$: 328.0847; found: 328.0867.

Ethyl 5-(4-bromophenyl)-3-phenyl-1H-1,2,4-triazole-1-carboxylate(6g)



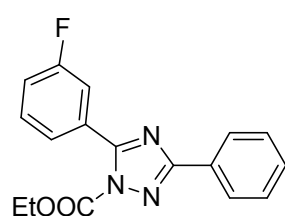
White solid; 88% yield, 16.3 mg; isomer ratio = 1.5:1; m.p.: 94-96 °C; 1H NMR (400 MHz, $CDCl_3$) δ 8.22-8.20 (m, 2H), 8.12-8.10 (m, 3H), 7.70-7.67 (m, 3H), 7.62 (m, 1.5H), 7.61-7.60 (m, 3H), 7.59-7.58 (m, 1.5H), 7.53-7.46 (m, 8.5H), 4.51-4.43 (m, 5H), 1.42-1.38 (t, J = 8 Hz, 3H), 1.37-1.33 (t, J = 8 Hz, 4.5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.29, 161.34, 159.56, 158.51, 148.67, 148.57, 131.90, 131.36, 131.23, 130.78, 130.48, 129.50, 128.79, 128.68, 128.12, 127.24, 125.39, 124.83, 65.53, 65.45, 14.07, 13.97; HRMS (ESI) m/z calcd for $C_{17}H_{15}BrN_3O_2^+ [(M+H)^+]$: 372.0342; found: 372.0374.

Ethyl 5-(4-methoxyphenyl)-3-phenyl-1H-1,2,4-triazole-1-carboxylate (6h)



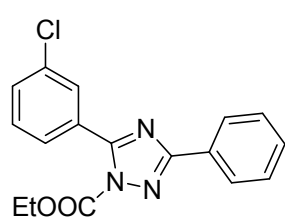
White solid; 34% yield, 5.5 mg; isomer ratio > 20:1; m.p.: 83-85 °C; 1H NMR (400 MHz, $CDCl_3$) δ 8.24-8.22 (m, 2H), 7.71-7.69 (d, J = 8 Hz, 2H), 7.47-7.45 (m, 3H), 7.01-6.99 (d, J = 8 Hz, 2H), 4.52-4.46 (q, J = 8 Hz, 2H), 3.88 (s, 3H), 1.43-1.39 (t, J = 8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.06, 161.53, 159.50, 148.98, 131.34, 130.28, 129.59, 128.60, 127.25, 120.75, 113.50, 65.27, 55.44, 14.09; HRMS (ESI) m/z calcd for $C_{18}H_{18}N_3O_3^+ [(M+H)^+]$: 324.1343; found: 324.1342.

Ethyl 5-(3-fluorophenyl)-3-phenyl-1H-1,2,4-triazole-1-carboxylate (6i)



White solid; 60% yield, 9.3 mg; isomer ratio = 1.5:1; m.p.: 64-66 °C; 1H NMR (400 MHz, $CDCl_3$) δ 8.24-8.21 (m, 2H), 8.04-8.02 (d, J = 8 Hz, 1.5H), 7.97-7.93 (dd, J = 8 Hz, J = 4 Hz, 1.5H), 7.72-7.71 (m, 1.5H), 7.69-7.68 (m, 1.5H), 7.55-7.43 (m, 12H), 7.27-7.22 (dt, J = 8 Hz, J = 4 Hz, 1H), 7.18-7.13 (dt, J = 8 Hz, J = 4 Hz, 1.5H), 4.52-4.45 (m, 5H), 1.41-1.35 (m, 7.5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.44, 165.40, 162.96, 162.18, 161.37, 159.51, 158.57, 148.73, 148.62, 131.94, 131.86, 130.73, 130.44, 129.50, 129.35, 129.26, 128.67, 128.10, 127.24, 115.85, 115.63, 115.43, 115.21, 65.45, 65.37, 29.73, 14.04, 13.97; ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.72, 112.9; HRMS (ESI) m/z calcd for $C_{17}H_{15}FN_3O_2^+ [(M+H)^+]$: 312.1143; found: 312.1144.

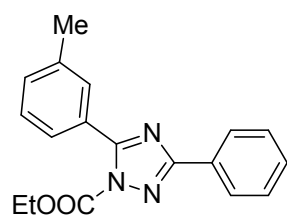
Ethyl 5-(3-chlorophenyl)-3-phenyl-1H-1,2,4-triazole-1-carboxylate (6j)



White solid; 93% yield, 15.2 mg; isomer ratio = 1.5:1; m.p.: 112-114 °C; 1H NMR (400 MHz, $CDCl_3$) δ 8.26-8.25 (m, 1.5H), 8.24-8.22 (m, 2H), 8.14-8.11 (m, 1.5H), 7.73-7.69 (m, 4H), 7.61-7.59 (m, 1H), 7.53-7.40 (m, 12.5H), 4.51-4.45 (m, 5H), 1.41-1.35 (m, 7.5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.01, 159.59, 148.54, 134.78, 134.10, 130.39, 130.81,

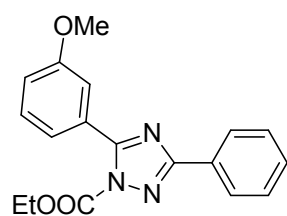
129.97, 129.52, 128.70, 128.14, 127.31, 127.25, 125.33, 65.56, 65.50, 13.99; HRMS (ESI) m/z calcd for $C_{17}H_{15}ClN_3O_2^+ [(M+H)^+]$: 328.0847; found: 328.0896.

Ethyl 3-phenyl-5-(m-tolyl)-1H-1,2,4-triazole-1-carboxylate (6k)



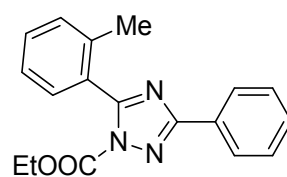
Yellow solid; 88% yield, 13.5 mg; isomer ratio = 1.3:1; m.p.: 58-60 °C; 1H NMR (400 MHz, $CDCl_3$) δ 8.25-8.24 (m, 1.3H), 8.23-8.22 (m, 1H), 8.07 (m, 1.3H), 8.05-8.03 (m, 1H), 7.71-7.70 (m, 1.3H), 7.69-7.68 (m, 1H), 7.52-7.45 (m, 9.2H), 7.39-7.28 (m, 4.6H), 4.50-4.44 (q, J = 8 Hz, 4.6H), 2.43 (s, 3.9H), 2.42 (s, 3H), 1.38-1.34 (m, 6.9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.14, 159.60, 148.70, 138.38, 137.91, 131.41, 130.31, 129.98, 129.52, 128.62, 128.08, 127.27, 126.64, 124.41, 65.30, 65.26, 21.35, 13.97; HRMS (ESI) m/z calcd for $C_{18}H_{18}N_3O_2^+ [(M+H)^+]$: 308.1394; found: 308.1392

Ethyl 5-(3-methoxyphenyl)-3-phenyl-1H-1,2,4-triazole-1-carboxylate (6l)



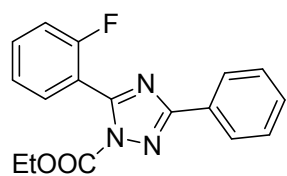
Yellow solid; 35% yield, 5.6 mg; isomer ratio = 1.2:1; m.p.: 64-66 °C; 1H NMR (400 MHz, $CDCl_3$) δ 8.25-8.22 (m, 2.2H), 7.85-7.83 (m, 1.2H), 7.77-7.76 (m, 1H), 7.71-7.70 (m, 1H), 7.69-7.68 (m, 1.2H), 7.53-7.35 (m, 8.8H), 7.27-7.26 (m, 1H), 7.25-7.23 (m, 1.2H), 7.08-7.05 (m, 1.2H), 7.03-7.00 (m, 1H), 4.50-4.44 (m, 4.4H), 3.89 (s, 3H), 3.86 (s, 3.6H), 1.38-1.34 (m, 6.6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.14, 159.85, 159.19, 148.63, 130.67, 130.36, 129.87, 129.73, 129.54, 129.20, 128.64, 128.09, 127.27, 121.91, 119.82, 117.09, 116.53, 114.89, 111.64, 65.34, 55.53, 13.99; HRMS (ESI) m/z calcd for $C_{18}H_{18}N_3O_3^+ [(M+H)^+]$: 324.1343; found: 324.1348.

Ethyl 3-phenyl-5-(o-tolyl)-1H-1,2,4-triazole-1-carboxylate (6m)



White solid; 95% yield, 14.5 mg; isomer ratio > 20:1; m.p.: 57-59 °C; 1H NMR (400 MHz, $CDCl_3$) δ 8.27-8.25 (m, 2H), 7.48-7.46 (m, 3H), 7.44-7.40 (m, 1H), 7.36-7.28 (m, 3H), 4.41-4.35 (q, J = 8 Hz, 2H), 2.24 (s, 3H), 1.27-1.23 (t, J = 8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.33, 158.76, 148.19, 137.07, 130.40, 130.28, 130.05, 129.46, 129.38, 129.03, 128.67, 127.27, 125.61, 65.16, 19.67, 13.81; HRMS (ESI) m/z calcd for $C_{18}H_{18}N_3O_2^+ [(M+H)^+]$: 308.1394; found: 308.1398.

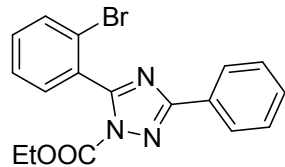
Ethyl 5-(2-fluorophenyl)-3-phenyl-1H-1,2,4-triazole-1-carboxylate (6n)



White solid; 55% yield, 8.5 mg; isomer ratio > 20:1; m.p.: 34-36 °C; 1H NMR (400 MHz, $CDCl_3$) δ 8.25-8.23 (m, 2H), 7.68-7.64 (dt, J = 8 Hz, J = 4 Hz, 1H), 7.57-7.51 (m, 1H), 7.48-7.46 (m, 3H), 7.33-7.29 (dt, J = 8 Hz, J = 4 Hz, 1H), 7.21-7.17 (m, 1H), 4.50-4.44 (q, J = 8 Hz, 2H), 1.36-1.32 (t, J = 8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.58, 153.89, 148.22, 132.74, 132.65,

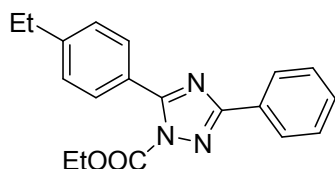
130.88, 130.43, 129.34, 128.68, 127.23, 124.38, 124.34, 115.69, 115.48, 65.44, 13.88; ^{19}F NMR (376 MHz, CDCl_3) δ 112.28; HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{15}\text{FN}_3\text{O}_2^+$ [(M+H) $^+$]: 312.1143; found: 312.1186.

Ethyl 5-(2-bromophenyl)-3-phenyl-1H-1,2,4-triazole-1-carboxylate (6o)



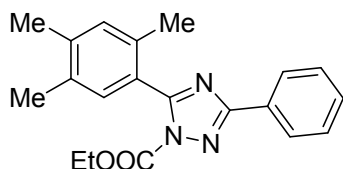
White solid; 98% yield, 18.2 mg; isomer ratio = 4:1; m.p.: 32-34 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.26-8.25 (m, 10H), 7.75-7.67 (m, 5H), 7.50-7.46 (m, 25H), 7.42-7.38 (m, 5H), 4.52-4.46 (q, J = 8 Hz, 2H), 4.44-4.38 (q, J = 8 Hz, 8H), 1.40-1.36 (t, J = 8 Hz, 3H), 1.27-1.23 (t, J = 8 Hz, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.40, 157.12, 147.89, 132.55, 131.61, 130.65, 130.46, 129.73, 129.31, 128.68, 128.07, 127.39, 127.28, 123.08, 65.35, 13.77; HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{15}\text{BrN}_3\text{O}_2^+$ [(M+H) $^+$]: 372.0342; found: 372.0365.

Ethyl 5-(4-ethylphenyl)-3-phenyl-1H-1,2,4-triazole-1-carboxylate (6p)



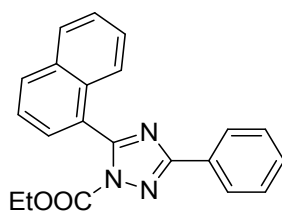
White solid; 72% yield, 11.5 mg; isomer ratio > 20:1; m.p.: 34-36 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.25-8.23 (m, 2H), 7.65-7.63 (d, J = 8 Hz, 2H), 7.47-7.45 (m, 3H), 7.33-7.31 (d, J = 8 Hz, 2H), 4.51-4.45 (q, J = 8 Hz, 2H), 2.76-2.70 (q, J = 8 Hz, 2H), 1.40-1.36 (t, J = 8 Hz, 3H), 1.30-1.26 (t, J = 8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.10, 159.69, 148.84, 147.28, 130.32, 129.58, 129.51, 128.63, 127.63, 127.27, 125.89, 65.62, 65.30, 29.75, 28.92, 15.29, 13.85; HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{20}\text{N}_3\text{O}_2^+$ [(M+H) $^+$]: 322.1550; found: 322.1596.

Ethyl 3-phenyl-5-(2,4,5-trimethylphenyl)-1H-1,2,4-triazole-1-carboxylate (6q)



White solid; 41% yield, 6.8 mg; isomer ratio > 20:1; m.p.: 39-41 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.26-8.24 (d, J = 8 Hz, 2H), 7.47-7.46 (d, J = 4 Hz, 3H), 7.13 (s, 1H), 7.07 (s, 1H), 4.45-4.39 (q, J = 8 Hz, 2H), 2.29 (s, 3H), 2.26 (s, 3H), 2.16 (s, 3H), 1.33-1.29 (t, J = 8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.23, 159.24, 148.35, 138.93, 134.19, 133.81, 131.41, 130.32, 129.97, 129.56, 128.63, 127.27, 126.51, 65.11, 19.77, 19.22, 19.08, 13.92; HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{22}\text{N}_3\text{O}_2^+$ [(M+H) $^+$]: 336.1707; found: 336.1725.

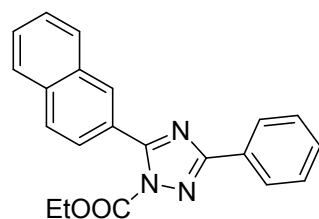
Ethyl 5-(naphthalen-1-yl)-3-phenyl-1H-1,2,4-triazole-1-carboxylate (6r)



White solid; 78% yield, 13.3 mg; isomer ratio > 20:1; m.p.: 35-37 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.32-8.29 (m, 2H), 8.03-8.01 (d, J = 8 Hz, 1H), 7.94-7.92 (d, J = 8 Hz, 1H), 7.65-7.63 (m, 1H), 7.60-7.48 (m, 7H), 4.22-4.16 (q, J = 8 Hz, 2H), 0.93-0.89 (t, J = 8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.62, 157.86, 147.99, 133.21, 131.67, 130.68, 130.44, 129.48, 128.69, 128.52, 128.09, 127.71, 127.34, 127.24, 127.17, 126.40, 124.84,

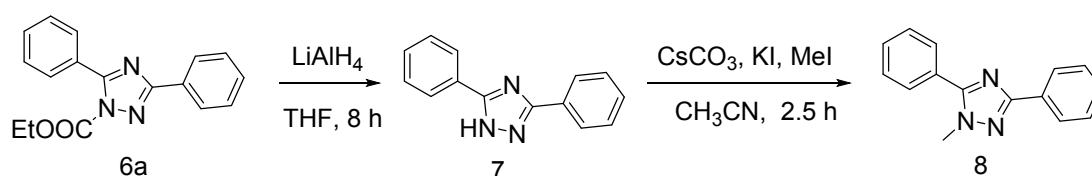
124.56, 65.03, 13.37; HRMS (ESI) m/z calcd for $C_{21}H_{18}N_3O_2^+$ [(M+H) $^+$]: 344.1394; found: 344.1399.

Ethyl 5-(naphthalen-2-yl)-3-phenyl-1H-1,2,4-triazole-1-carboxylate (6s)



White solid; 80% yield, 13.7 mg; isomer ratio = 2:1; m.p.: 38-40 °C; 1H NMR (400 MHz, $CDCl_3$) δ 8.28-8.26 (m, 6H), 7.95-7.90 (m, 9H), 7.75-7.73 (m, 4H), 7.59-7.47 (m, 17H), 4.52-4.45 (m, 6H), 1.40-1.33 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.30, 159.55, 148.76, 134.11, 132.52, 130.38, 129.90, 128.75, 128.67, 128.13, 127.84, 127.61, 127.34, 127.31, 126.75, 126.18, 124.21, 65.60, 65.37, 14.01; HRMS (ESI) m/z calcd for $C_{21}H_{18}N_3O_2^+$ [(M+H) $^+$]: 344.1394; found: 344.1399.

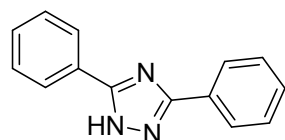
The preparation of the compound 7 and 8.



The $LiAlH_4$ (2 mmol) was added into a dry THF solution (5 mL). The system was stirred at ice bath for 10 min, then dry THF (1 mL) solution dissolving **6a** (0.5 mmol) was added into the mixture. The solution was stirred for another 15 min at ice bath, then refluxed overnight. After the system had cooled to room temperature, deionized water was added. After stirred at ice bath for 30 min, the residue was diluted by DCM and washed with water and brine sequentially, dried over Na_2SO_4 , filtered, and concentrated. The crude product was purified by flash chromatography on silica gel (eluent: PE/EtOAc from 5:1 to 2:1) to afford the product **7**.

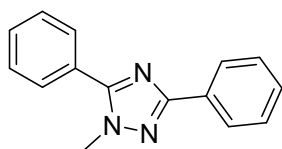
The product **7** (0.2 mmol), Cs_2CO_3 (0.3 mmol), KI (0.04 mmol) were dissolved in 5 mL CH_3CN , and then the MeI (0.22 mmol) was added to the mixture. The system was stirred at room temperature for 2 h. After finished (determined by TLC), the mixture was concentrated and washed by water and brine, dried over Na_2SO_4 , filtered, and concentrated to obtain the product **8**.

3,5-diphenyl-1H-1,2,4-triazole (7)



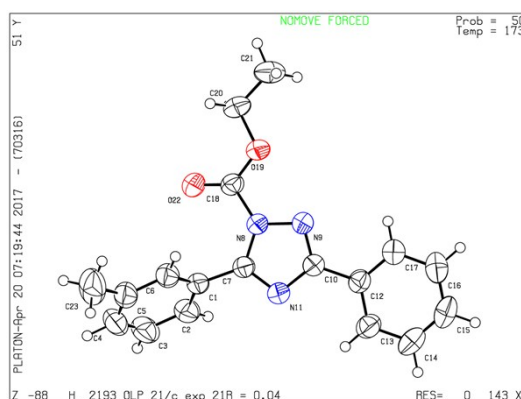
White solid; 75% yield, 82.9 mg; m.p.: 168-170 °C; 1H NMR (400 MHz, DMSO) δ 14.53 (s, 1H), 8.10-8.08 (d, J = 8 Hz, 4H), 7.53 (m, 6H); ^{13}C NMR (100 MHz, DMSO) δ 134.16, 131.24; HRMS (ESI) m/z calcd for $C_{14}H_{12}N_3^+$ [(M+H) $^+$]: 222.1026; found: 222.1048.

1-methyl-3,5-diphenyl-1H-1,2,4-triazole (8)



White solid; 78% yield, 55 mg; m.p.: 60-62 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.17-8.15 (d, J = 8 Hz, 2H), 7.75-7.73 (d, J = 8 Hz, 2H), 7.53 (m, 3H), 7.47-7.40 (m, 3H), 4.03 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 161.07, 155.61, 130.84, 130.22, 129.24, 128.93, 128.84, 128.62, 127.88, 126.38, 37.03; HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{14}\text{N}_3^+$ [(M+H) $^+$]: 236.1182; found: 236.1178.

Crystal data and structure refinement for 6k



Identification code	exp_2193
Empirical formula	$\text{C}_{18}\text{H}_{17}\text{N}_3\text{O}_2$
Formula weight	307.35
Temperature/K	298.7(2)
Crystal system	monoclinic
Space group	$\text{P2}_1/\text{c}$
$a/\text{\AA}$	10.5368(3)
$b/\text{\AA}$	10.0023(2)
$c/\text{\AA}$	15.9591(5)
$\alpha/^\circ$	90.00
$\beta/^\circ$	103.660(3)
$\gamma/^\circ$	90.00
Volume/ $\text{\AA}^3$	1634.40(7)
Z	4
$\rho_{\text{calc}}/\text{mg}/\text{mm}^3$	1.249
m/mm^{-1}	0.675
$F(000)$	648.0
Crystal size/ mm^3	$0.21 \times 0.13 \times 0.1$
2θ range for data collection	8.64 to 141.92°
Index ranges	$-12 \leq h \leq 11$, $-9 \leq k \leq 12$,

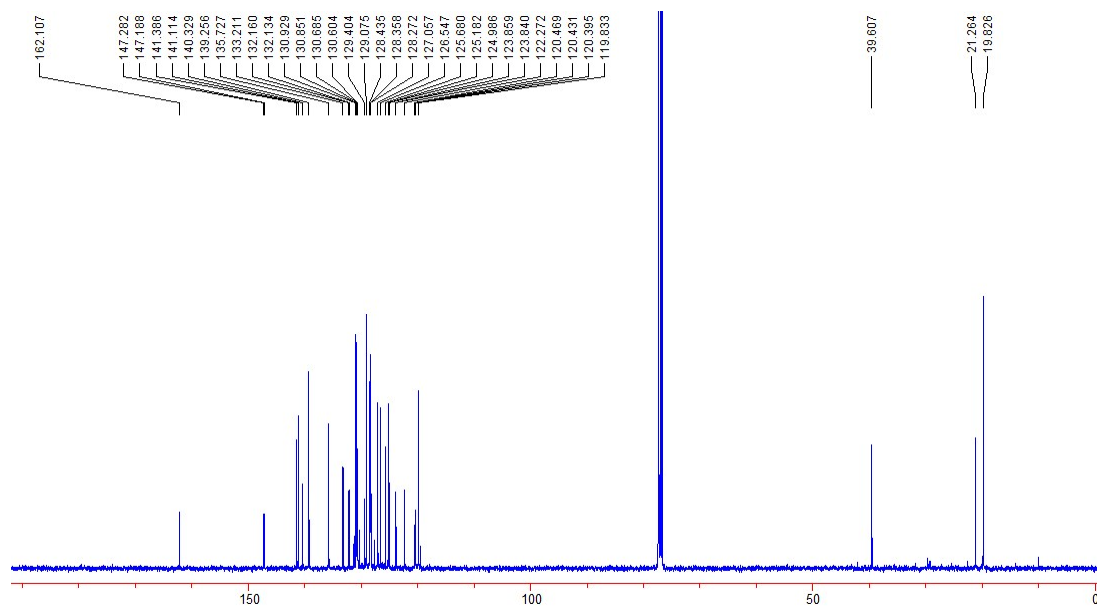
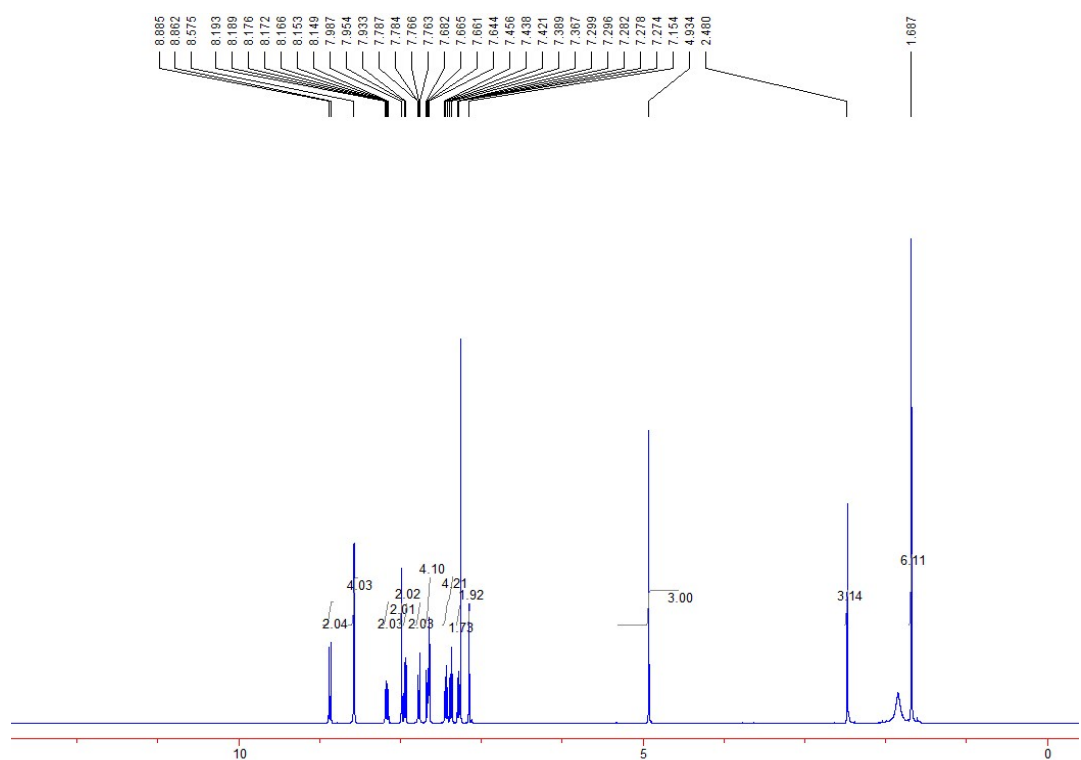
$-19 \leq h \leq 19$
 Reflections collected 6259
 Independent reflections 3095 [R(int) = 0.0129]
 Data/restraints/parameters 3095/0/211
 Goodness-of-fit on F² 1.048
 Final R indexes [I > 2σ(I)] R₁ = 0.0395, wR₂ = 0.1081
 Final R indexes [all data] R₁ = 0.0465, wR₂ = 0.1155
 Largest diff. peak/hole / e Å⁻³ 0.16/-0.14

References

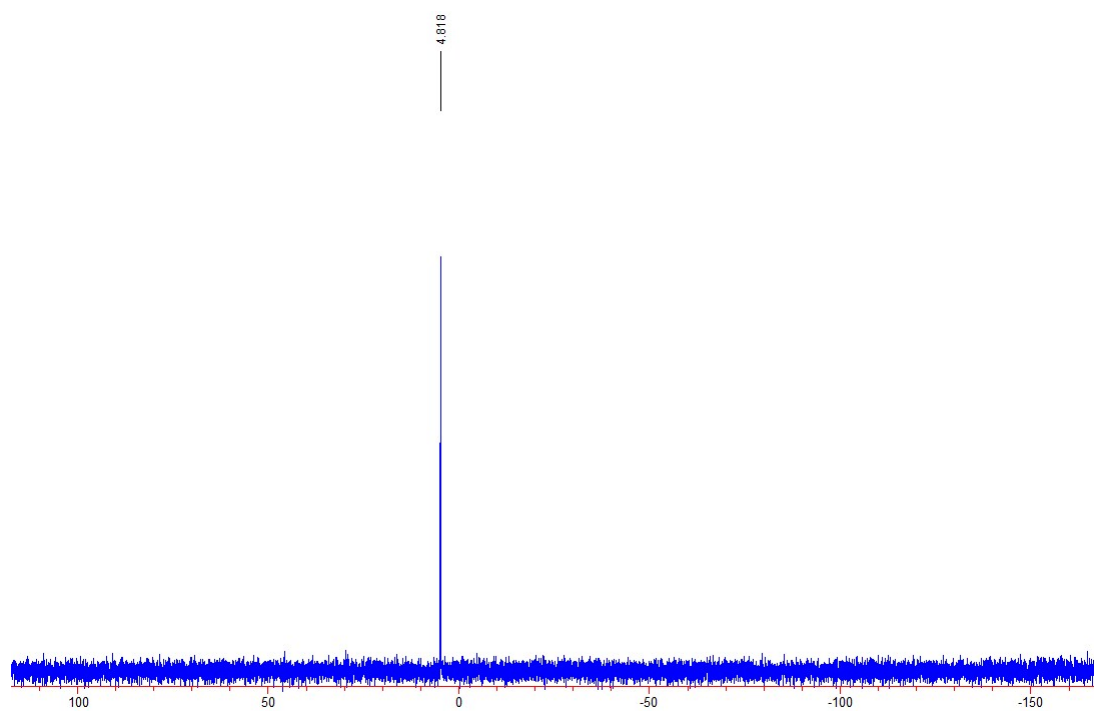
1. N. S. Y. Loy, A. Singh, X. Xu and C.-M. Park, *Angew. Chem. Int. Ed.* 2013, **52**, 2212–2216.
2. Y. Jiang, W. C. Chan and C.-M. Park, *J. Am. Chem. Soc.* 2012, **134**, 4104–4107.
3. S. Jana, M. D. Clements, B. K. Sharp and N. Zheng, *Org. Lett.* 2010, **12**, 3736–3739.

NMR spectra of the chiral photoredox catalyst **9**

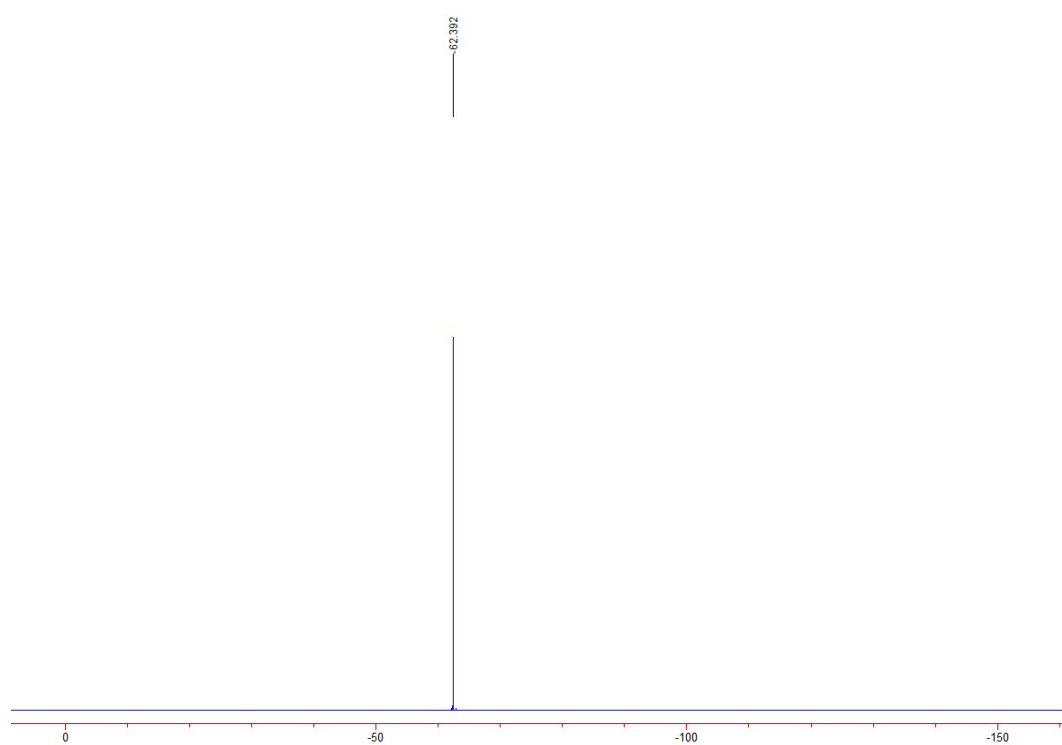
¹H-NMR and ¹³C-NMR spectra of the chiral photoredox catalyst **9**



³¹P-NMR spectra of the chiral photoredox catalyst **9**

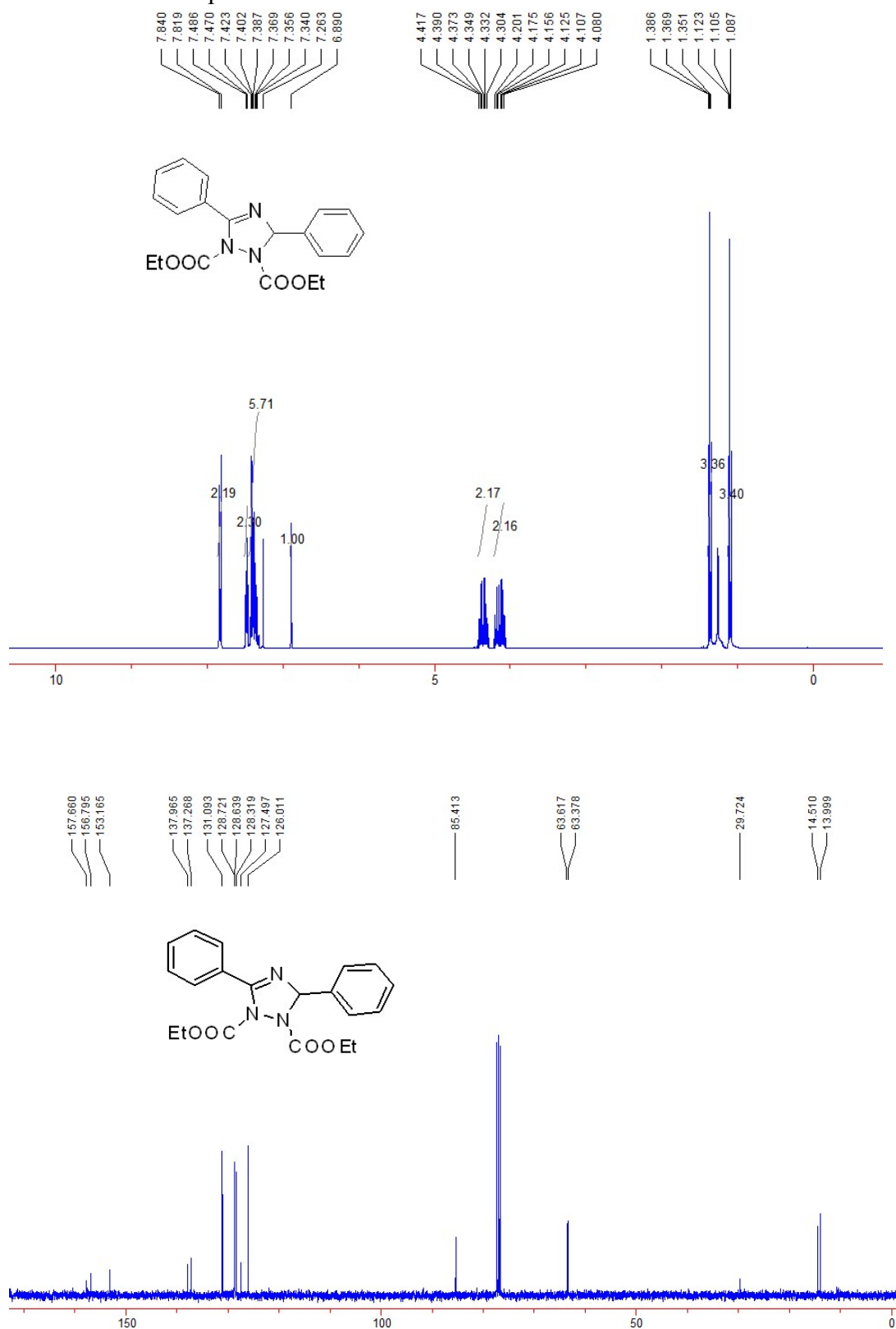


^{19}F -NMR spectra of the chiral photoredox catalyst **9**

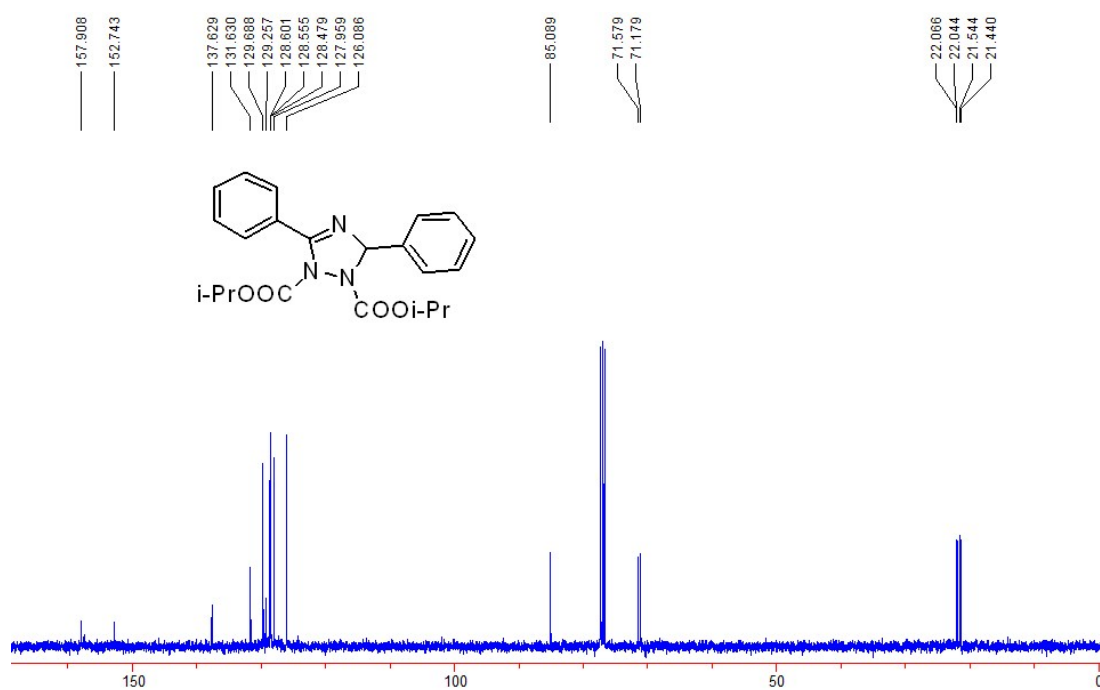
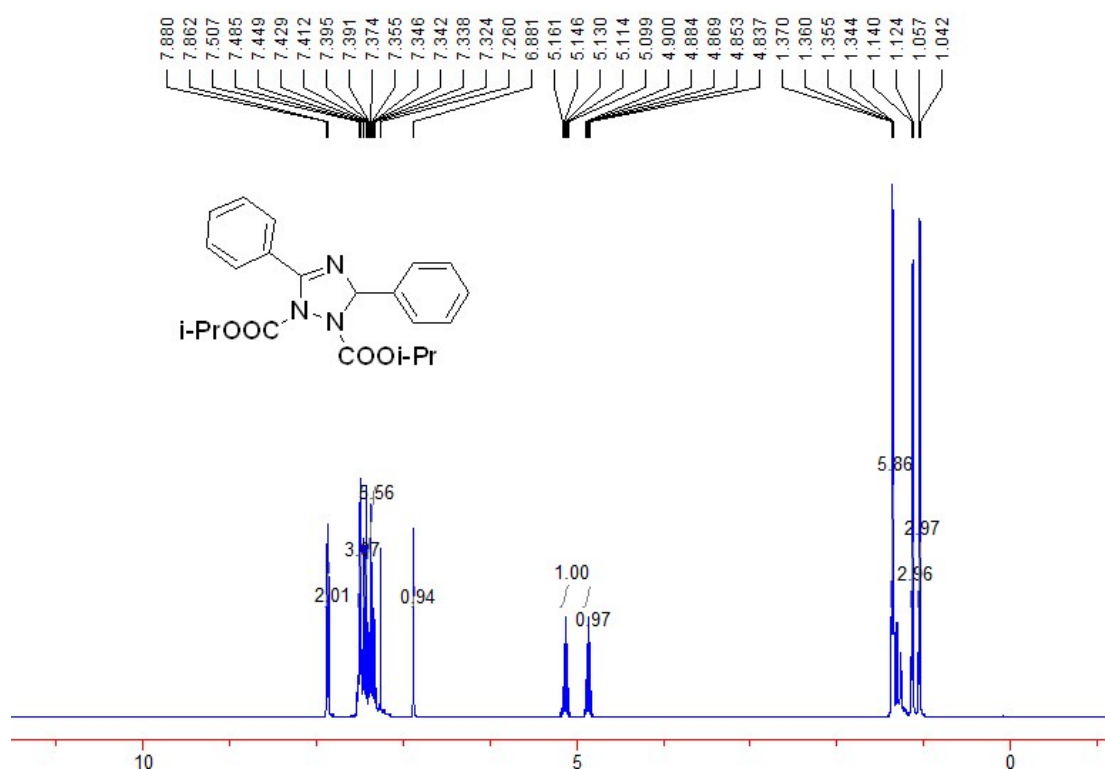


^1H -NMR and ^{13}C -NMR spectra of the compounds 3, 5, 6, 7 and 8

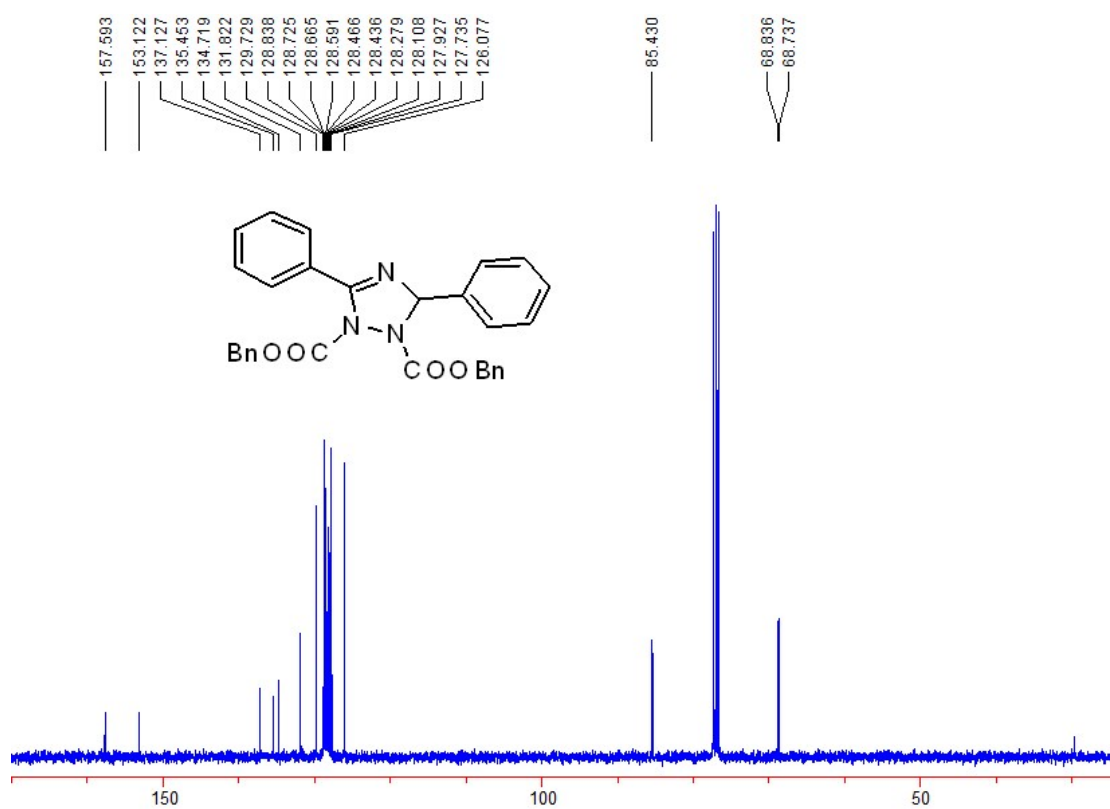
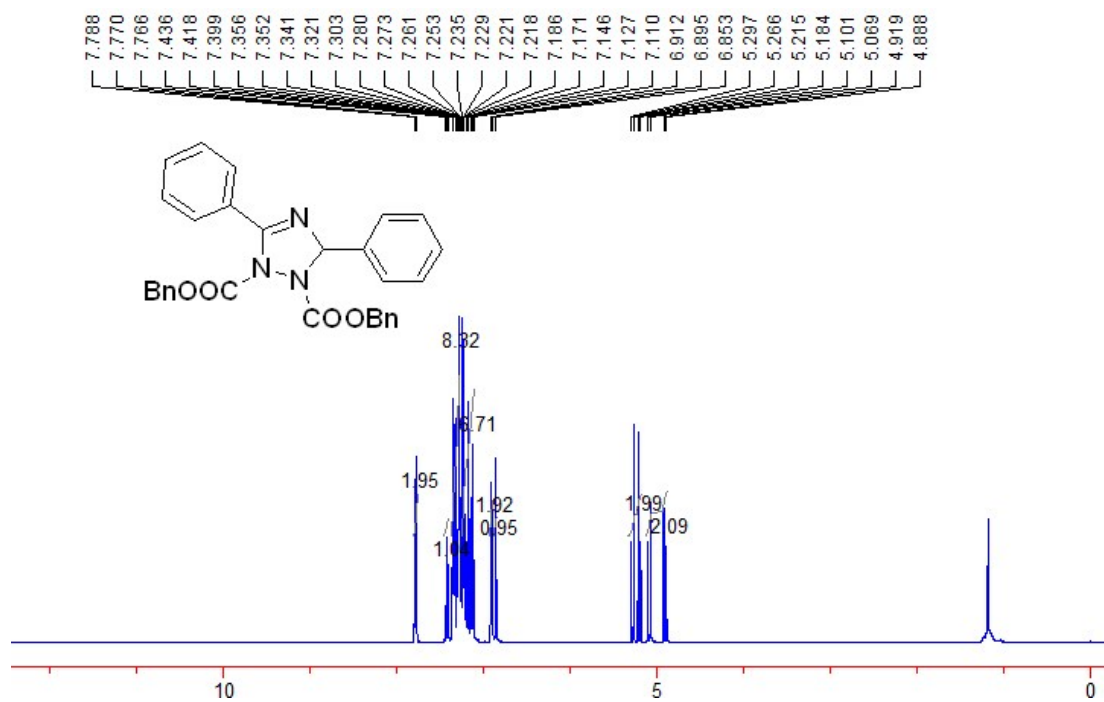
^1H and ^{13}C -NMR spectra of **3a**.



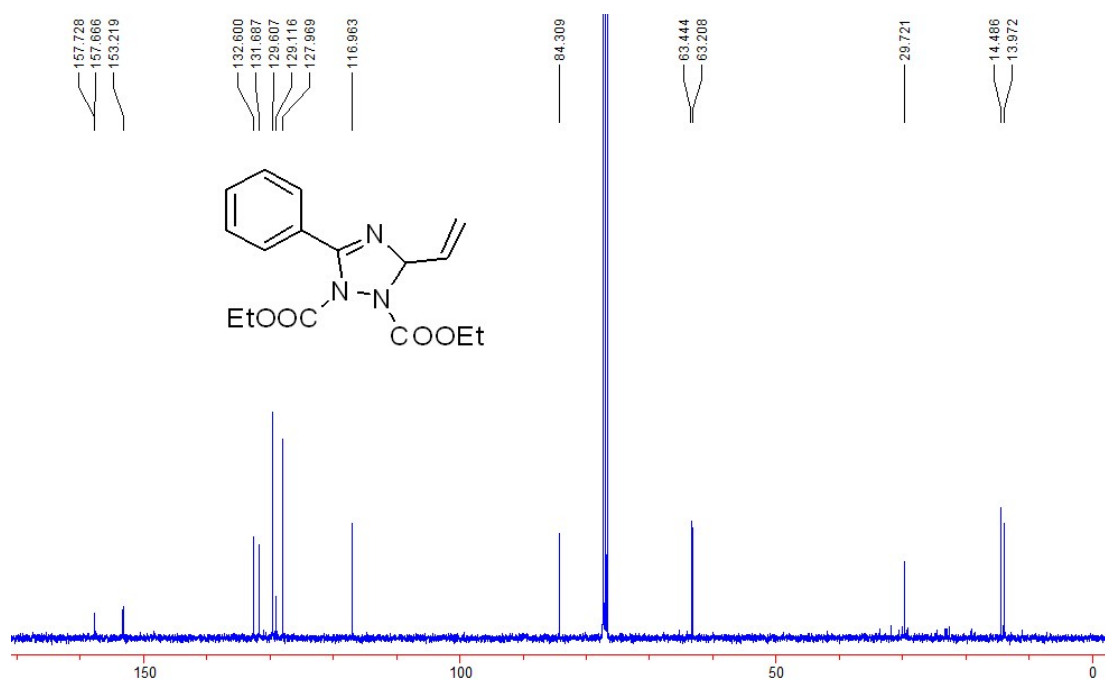
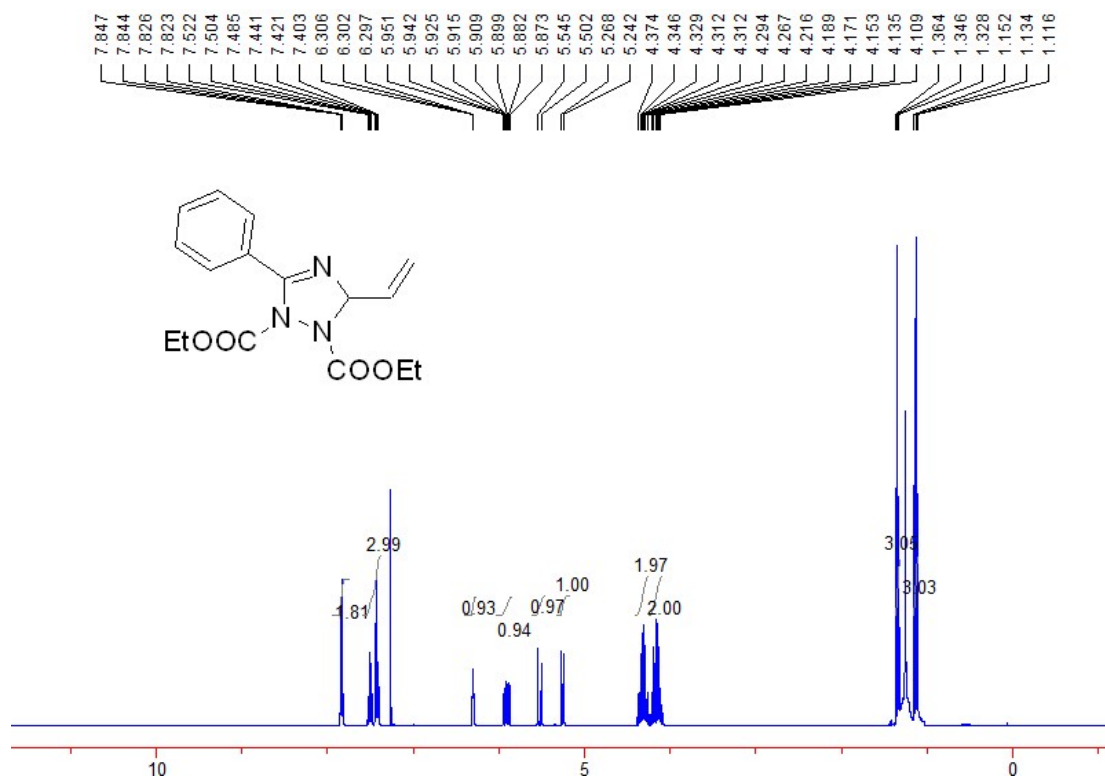
^1H and ^{13}C -NMR spectra of **3b**.



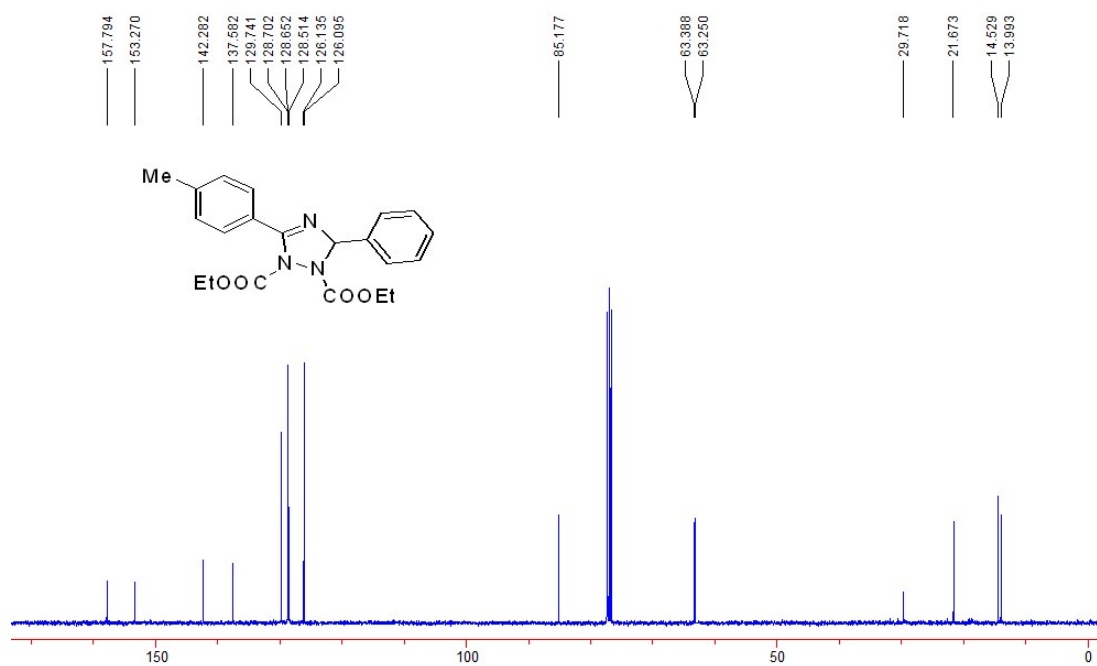
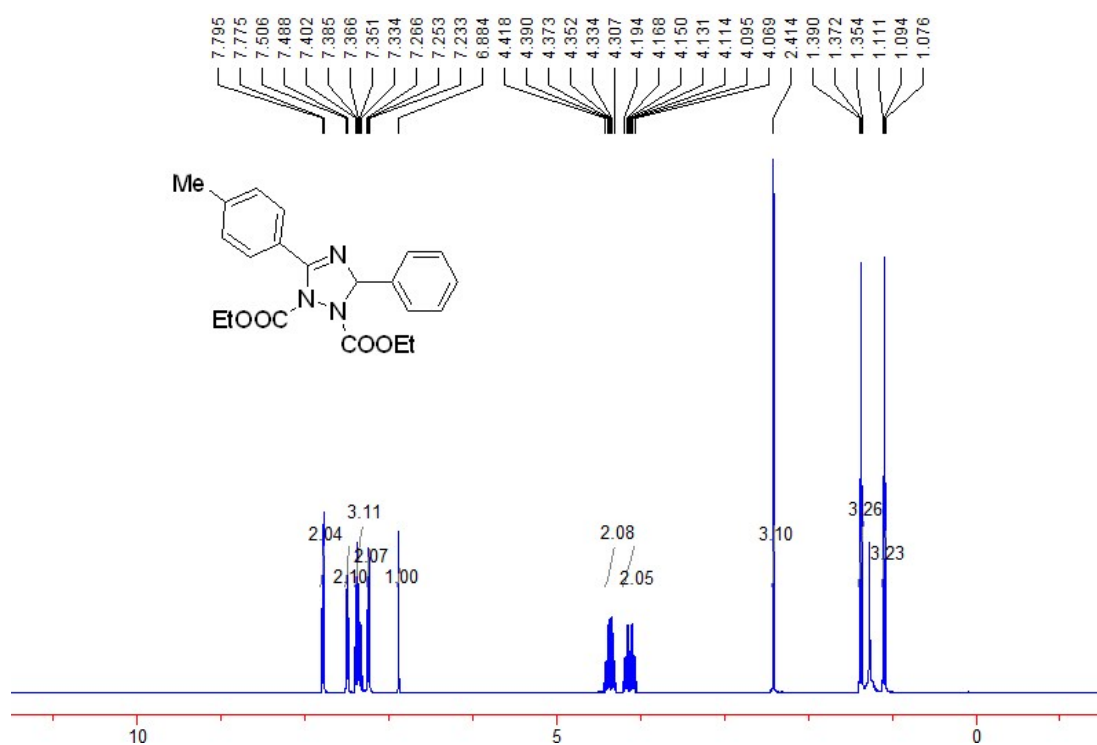
^1H and ^{13}C -NMR spectra of **3c**.



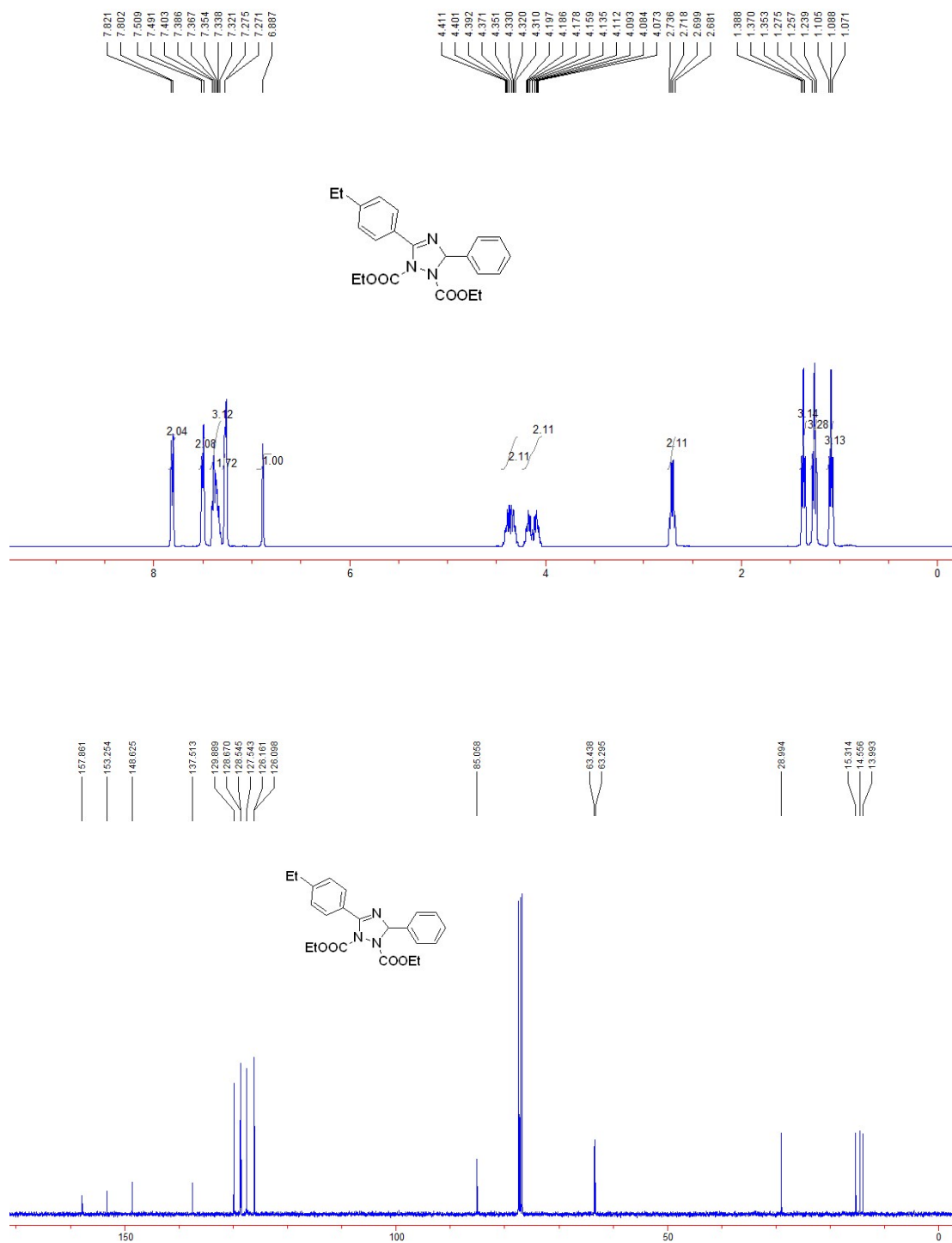
^1H and ^{13}C -NMR spectra of **3d**.



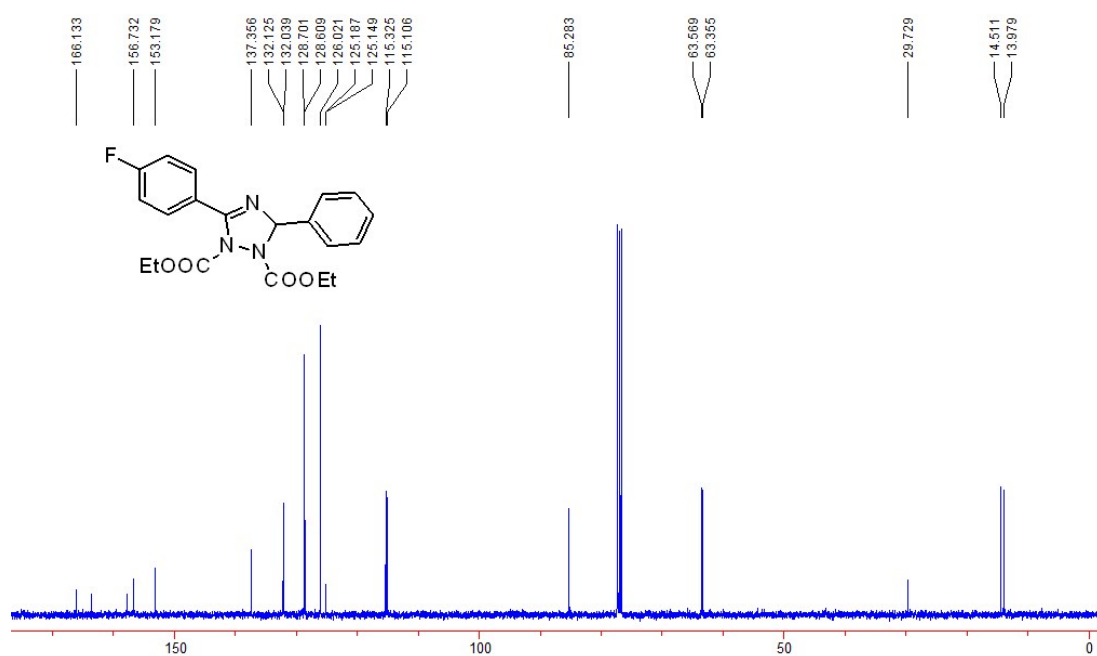
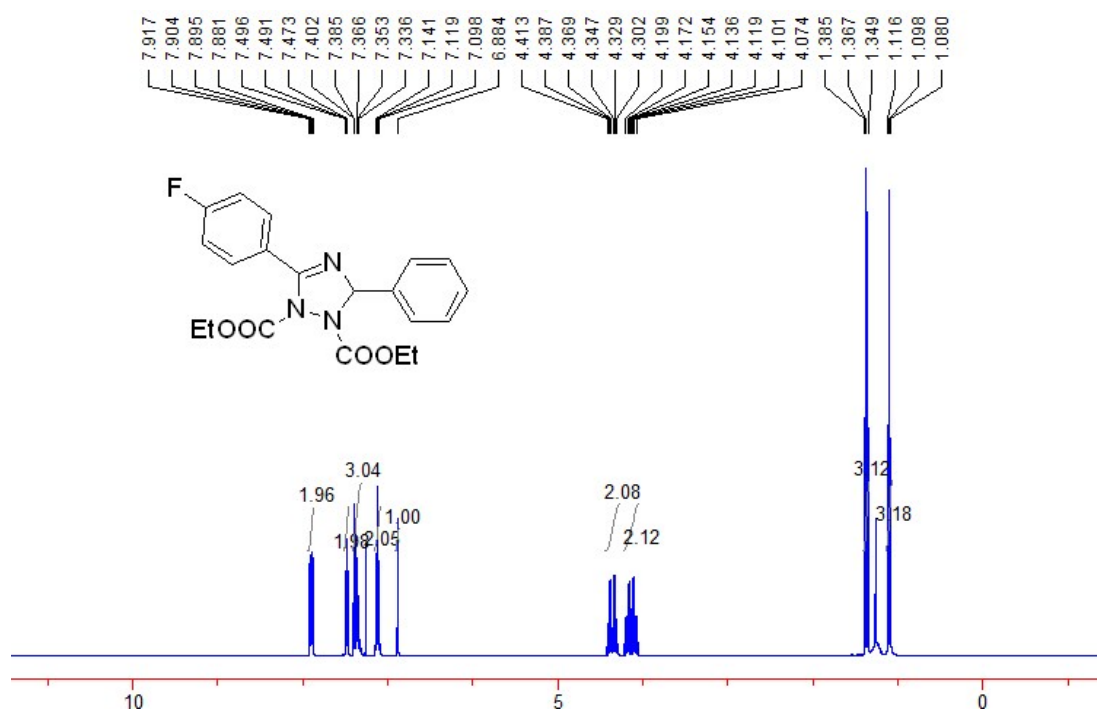
^1H and ^{13}C -NMR spectra of **3e**.



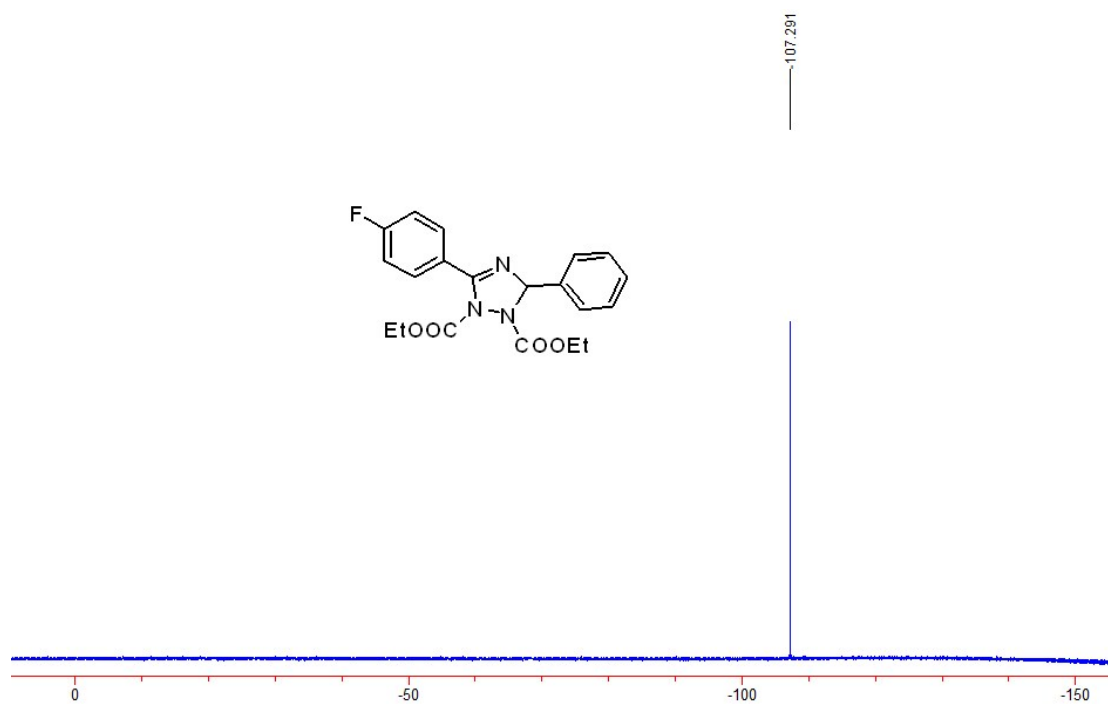
^1H and ^{13}C -NMR spectra of **3f**.



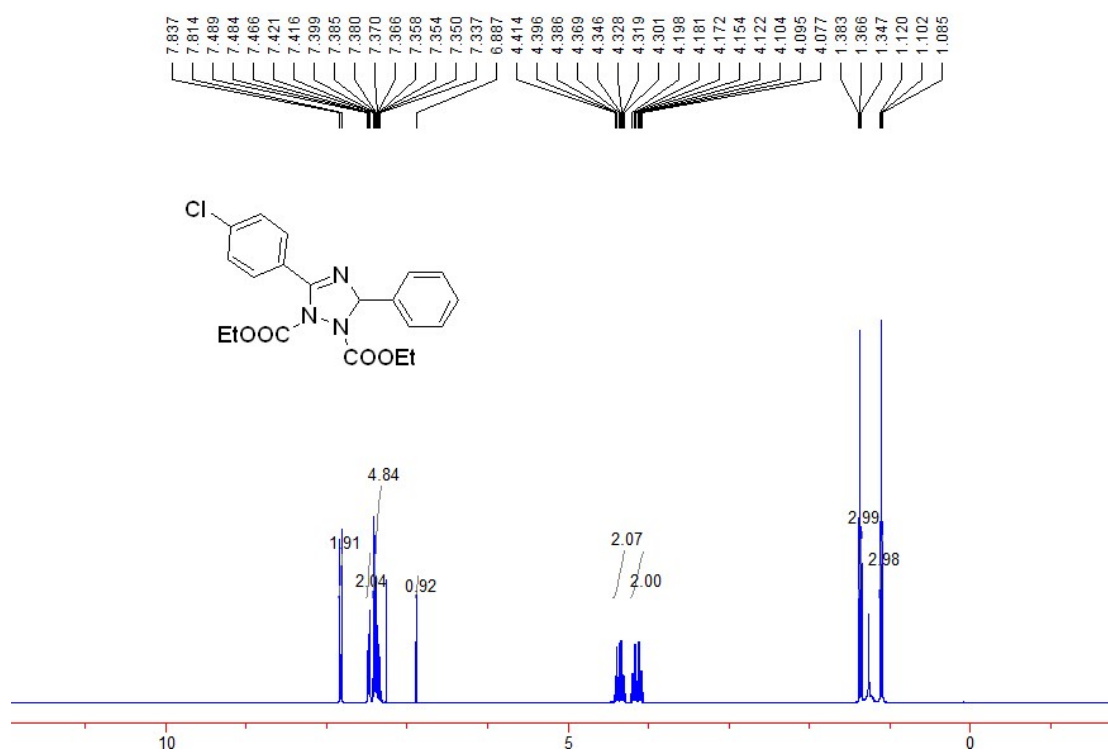
^1H and ^{13}C -NMR spectra of **3g**.

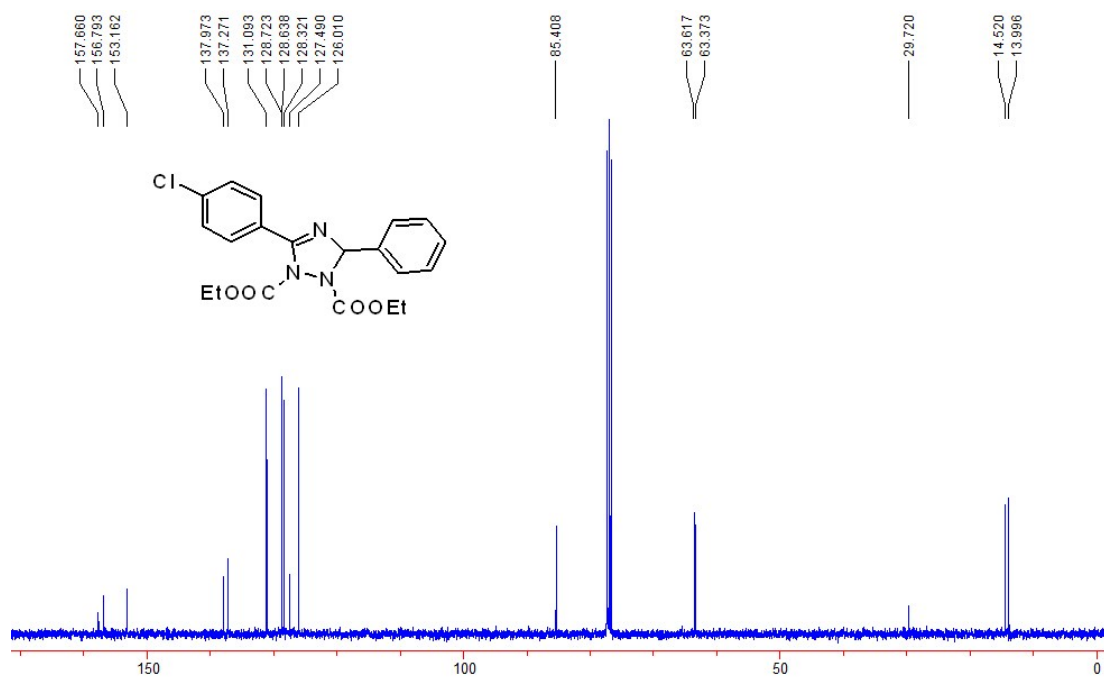


^{19}F -NMR spectra of **3g**

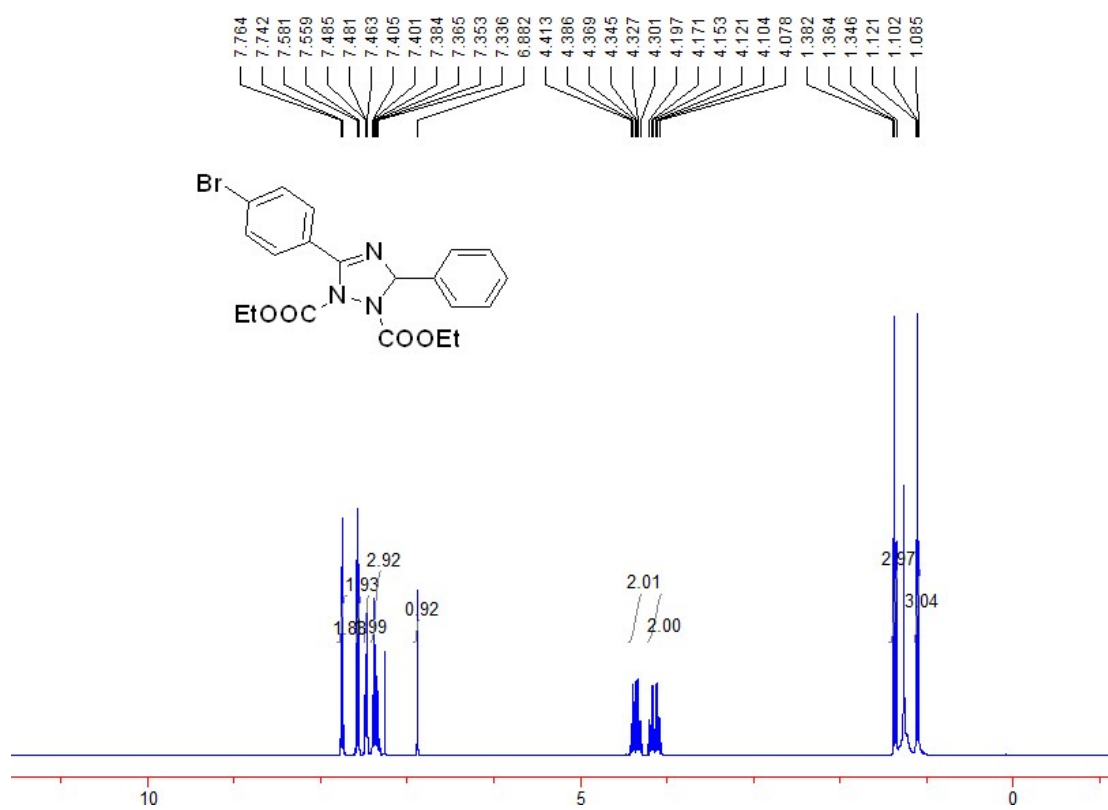


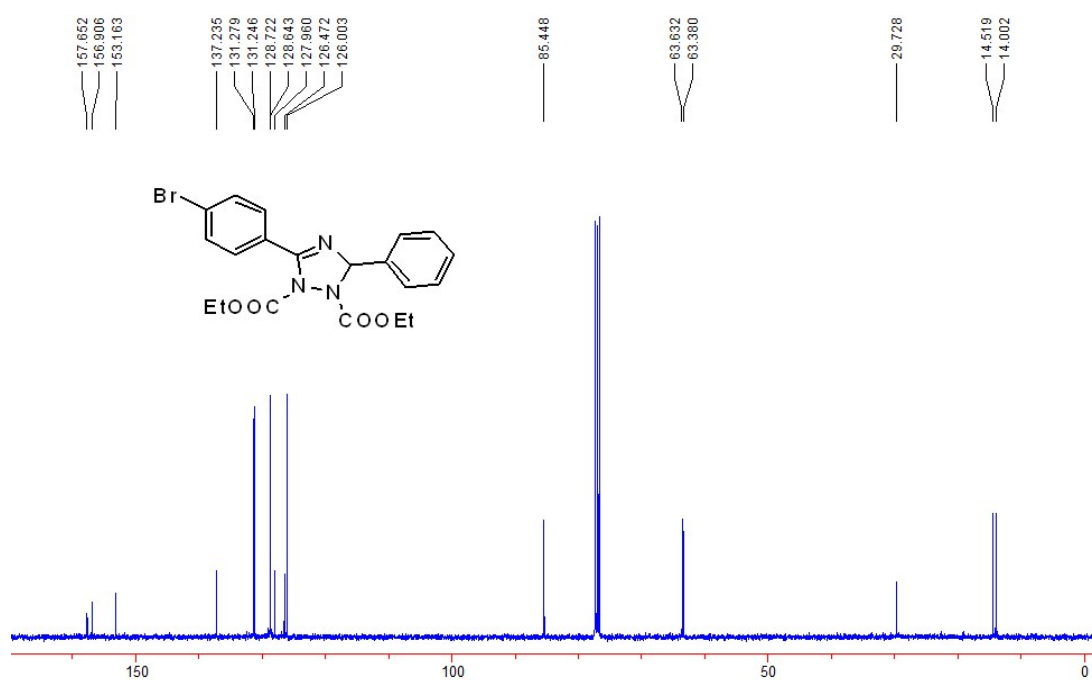
^1H and ^{13}C -NMR spectra of **3h**.



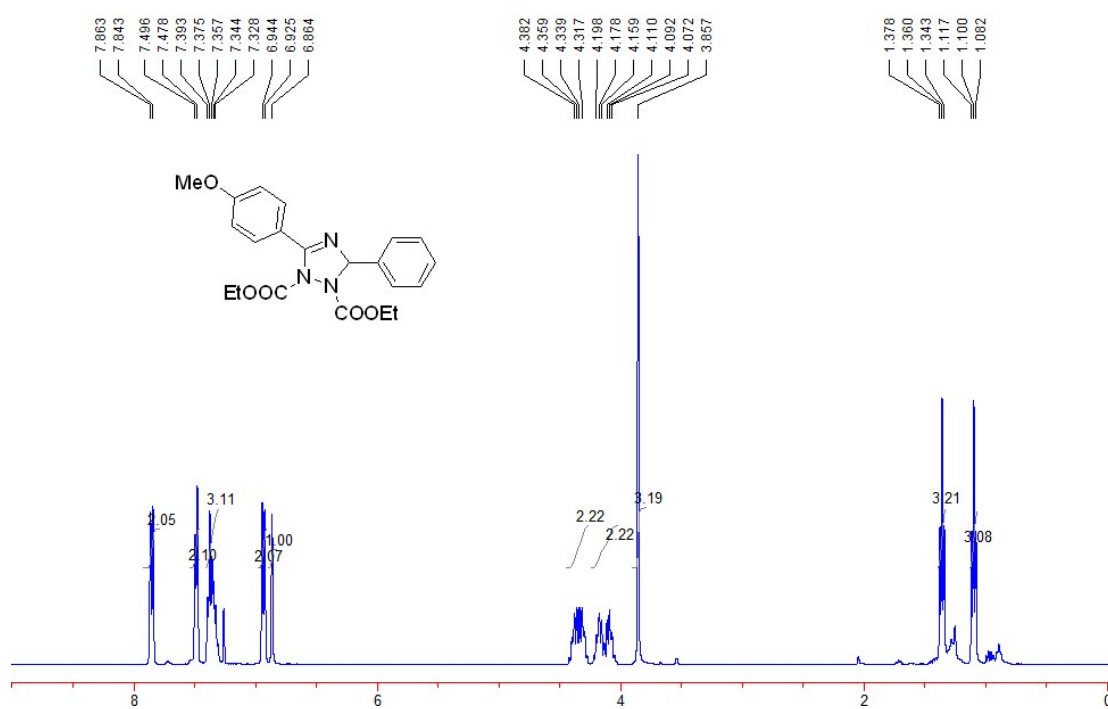


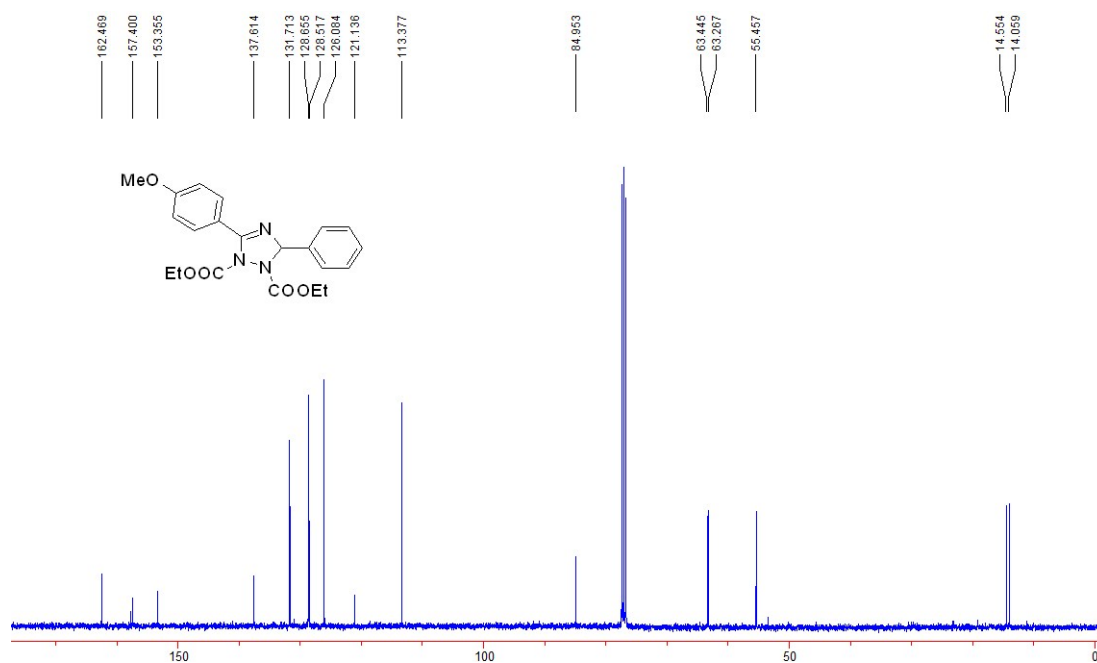
¹H and ¹³C-NMR spectra of **3i**.



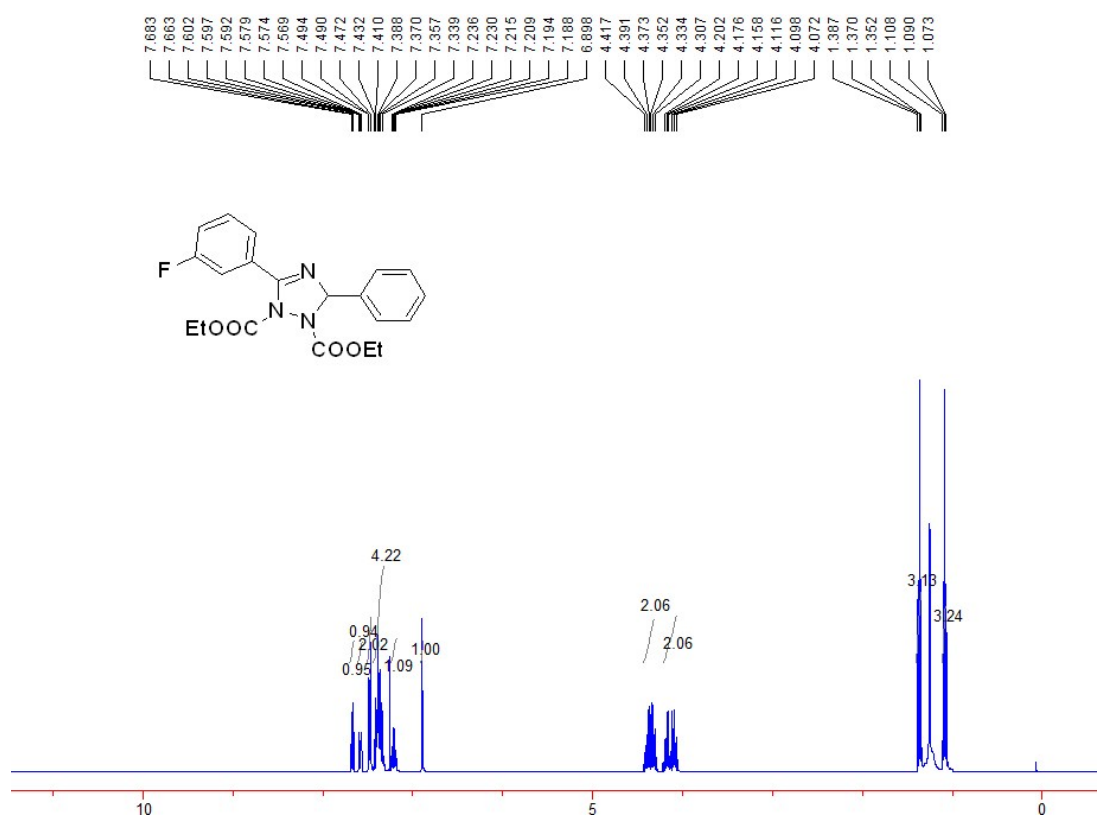


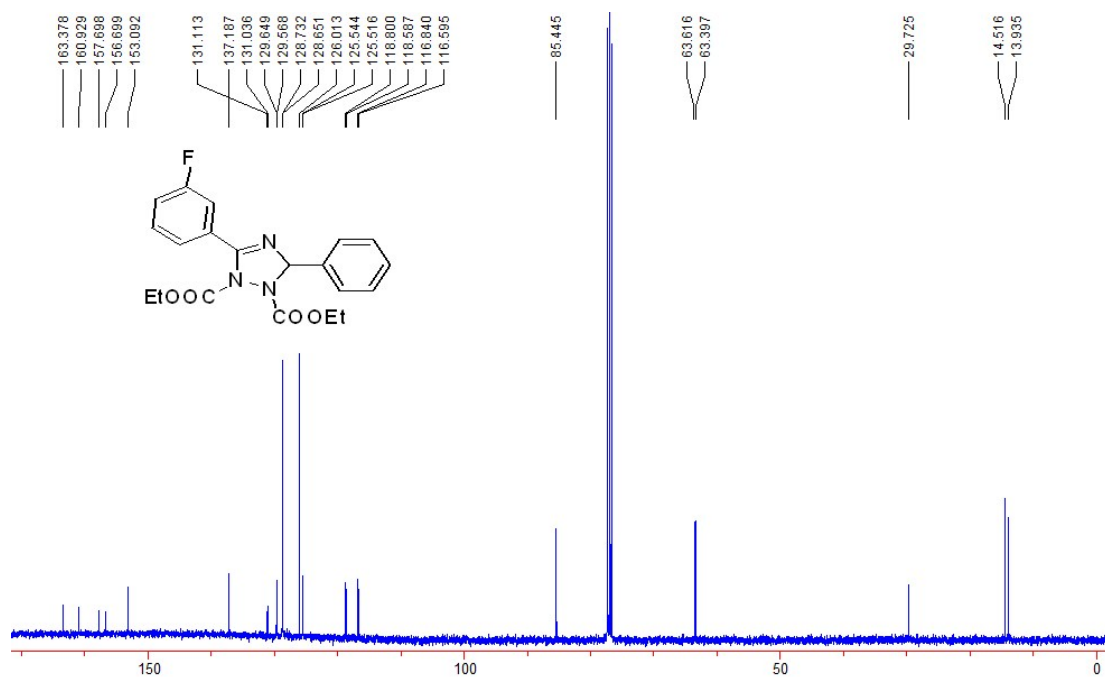
¹H and ¹³C-NMR spectra of **3j**.



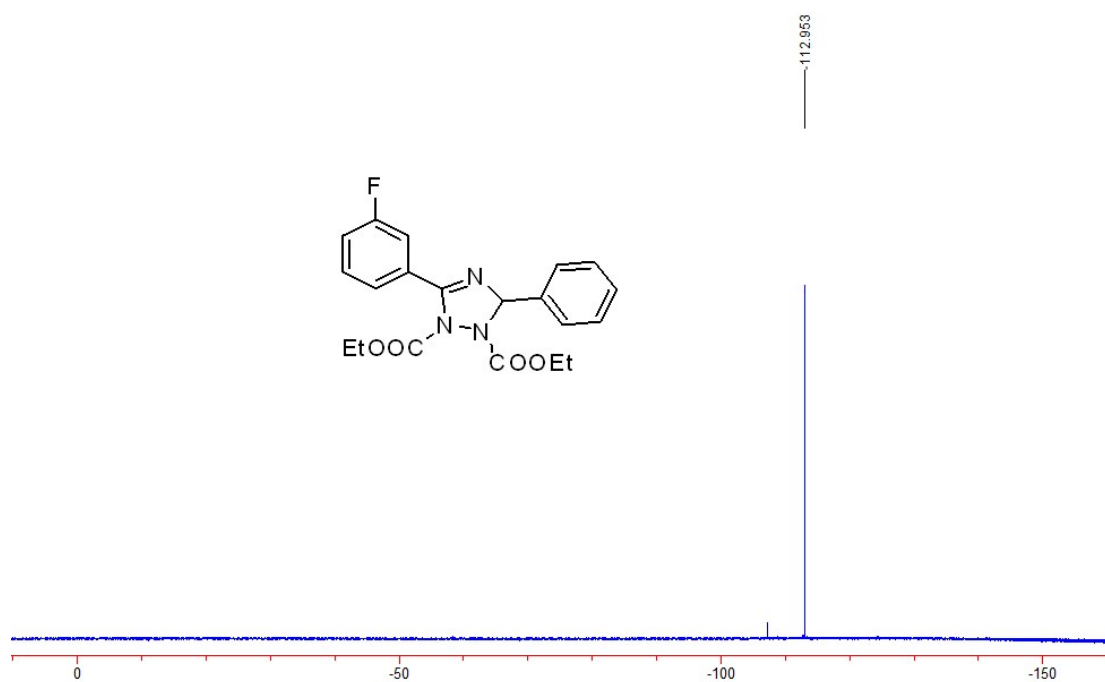


¹H and ¹³C-NMR spectra of **3k**.

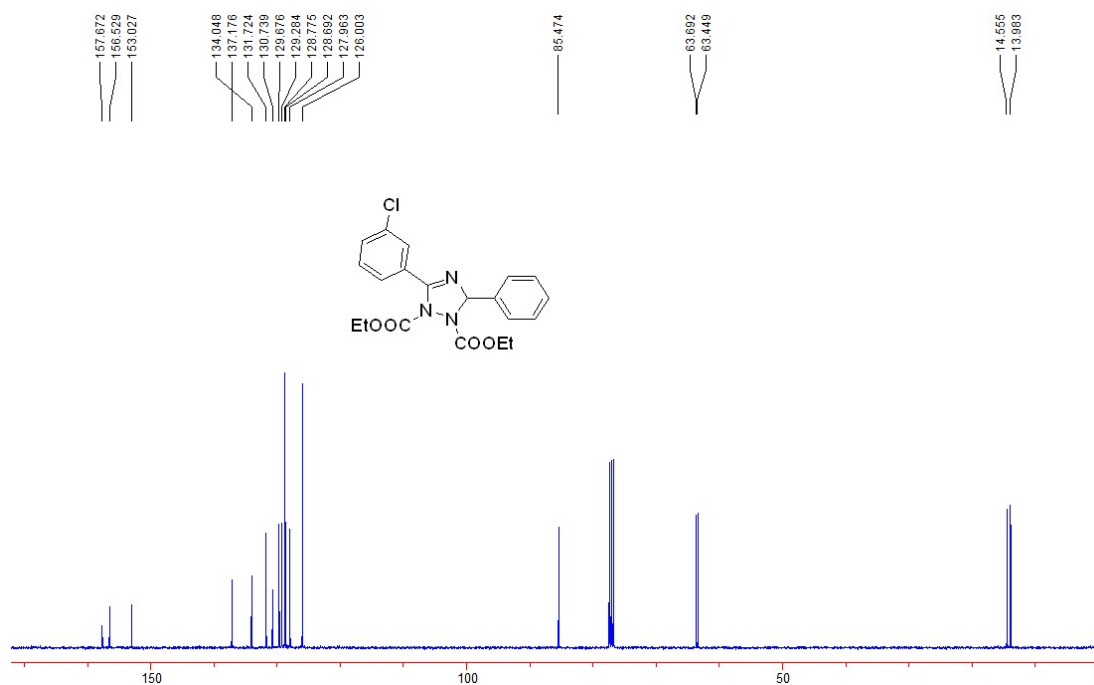
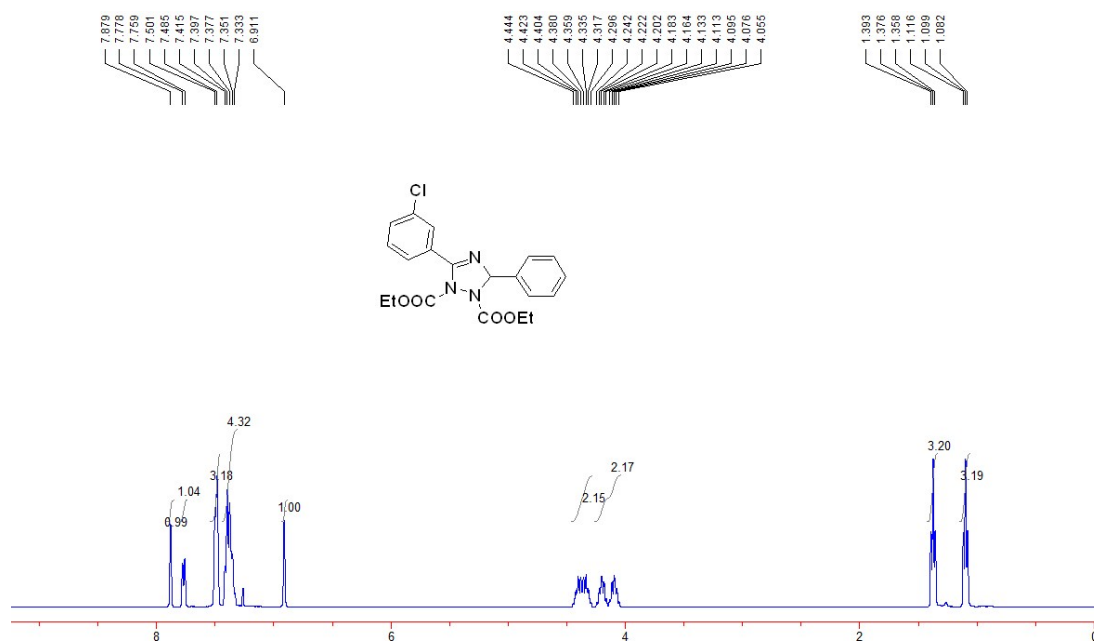




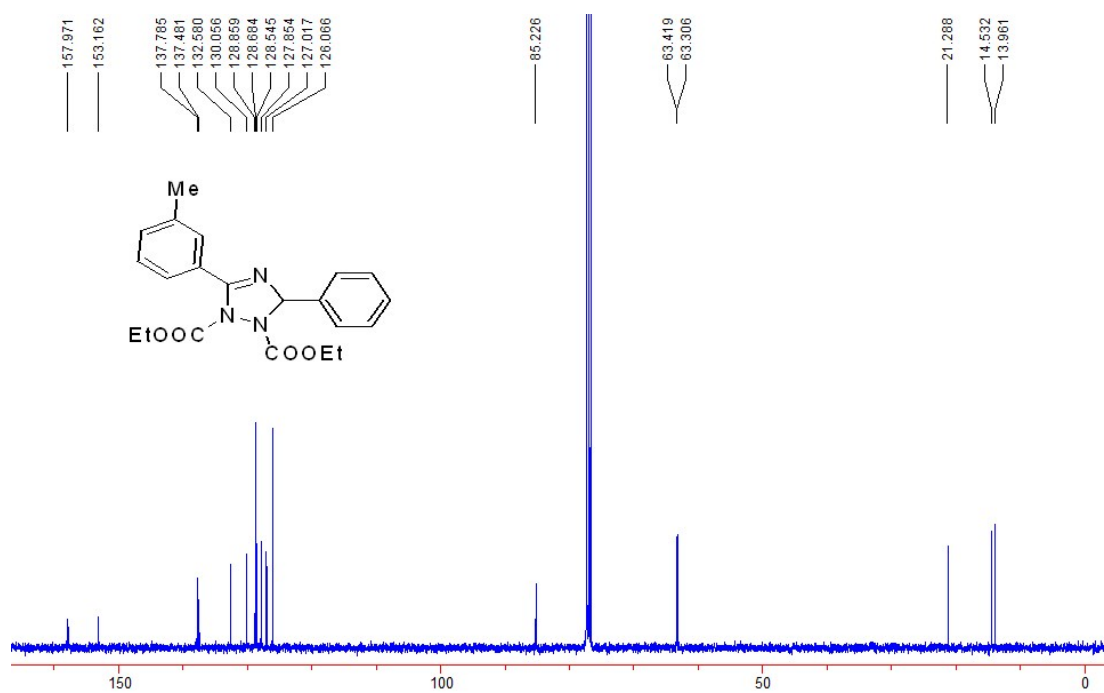
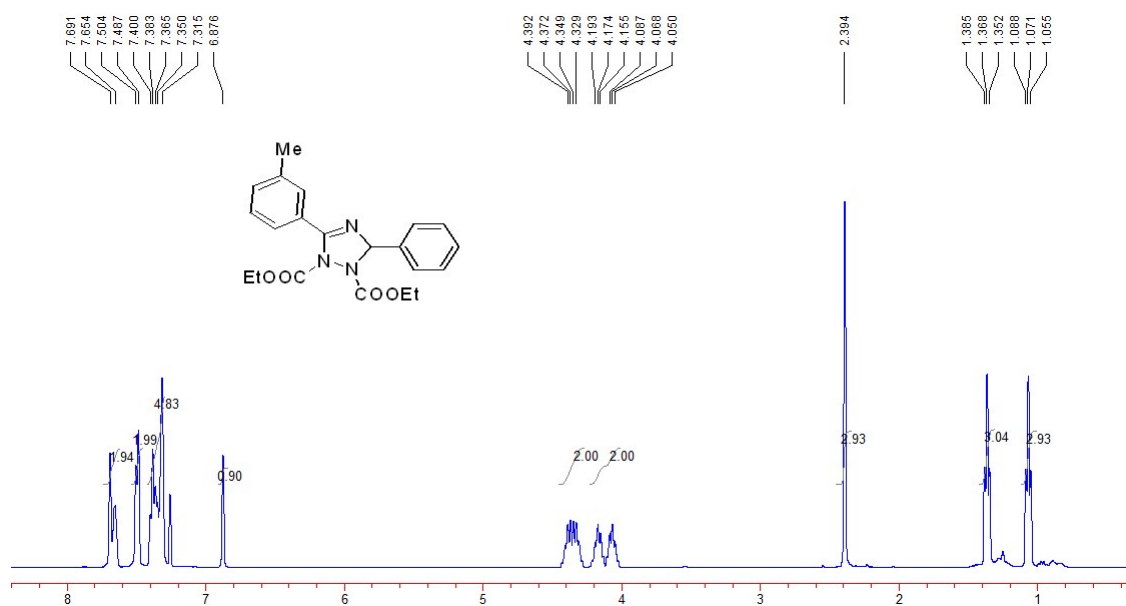
¹⁹F-NMR spectra of **3k**.



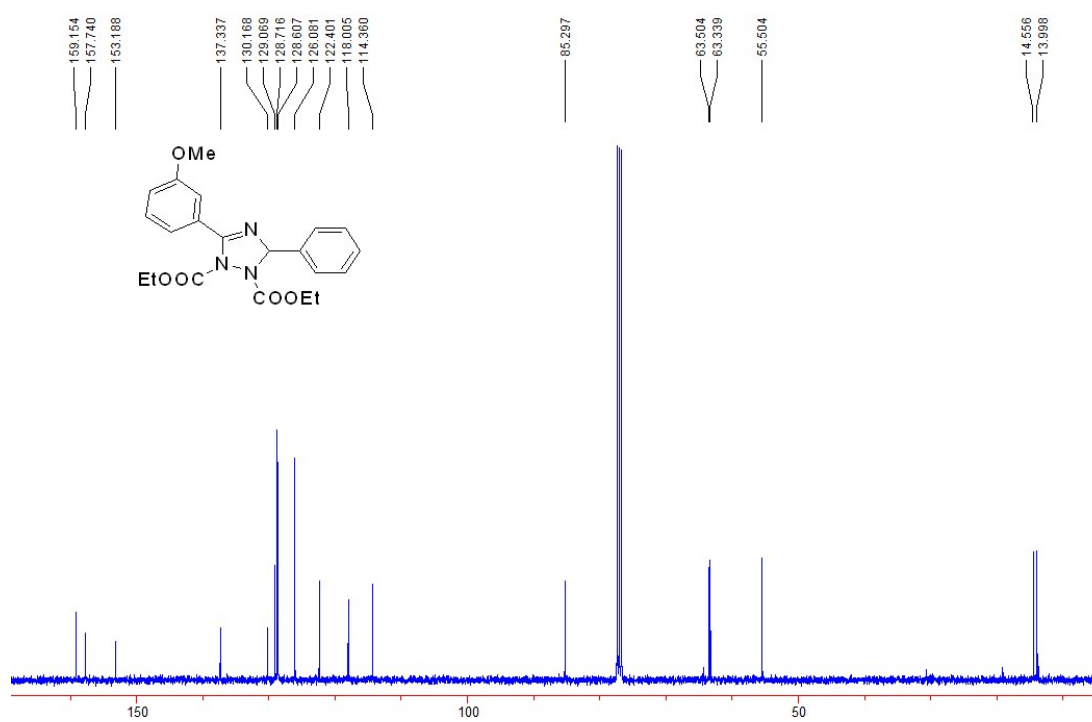
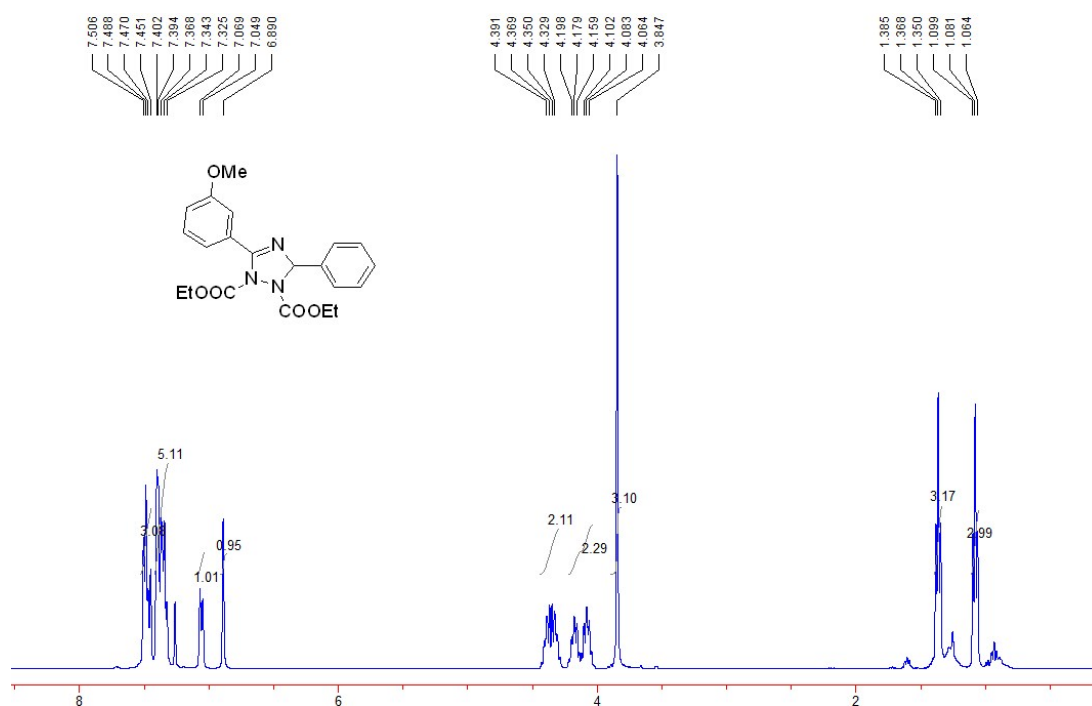
^1H and ^{13}C -NMR spectra of **3l**.



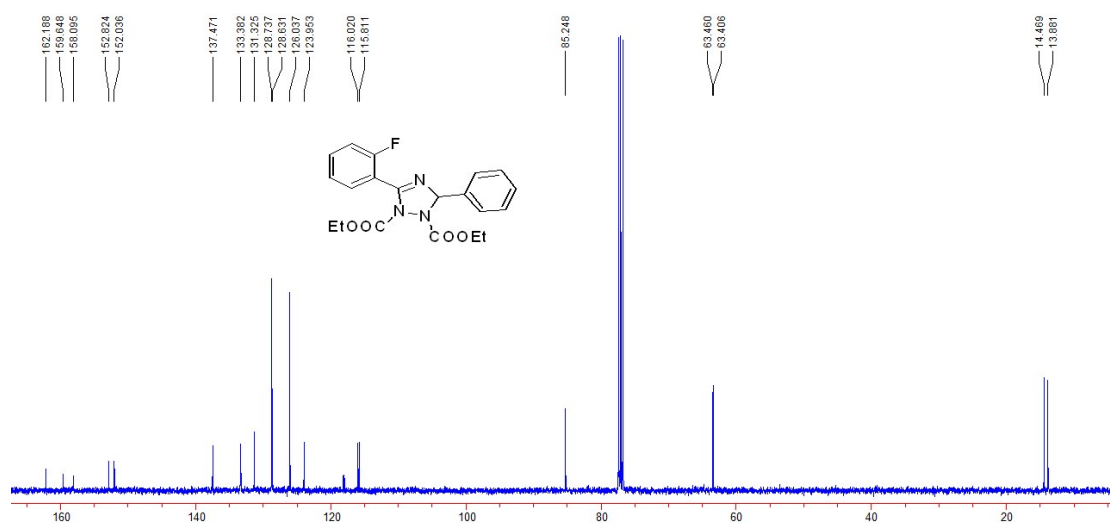
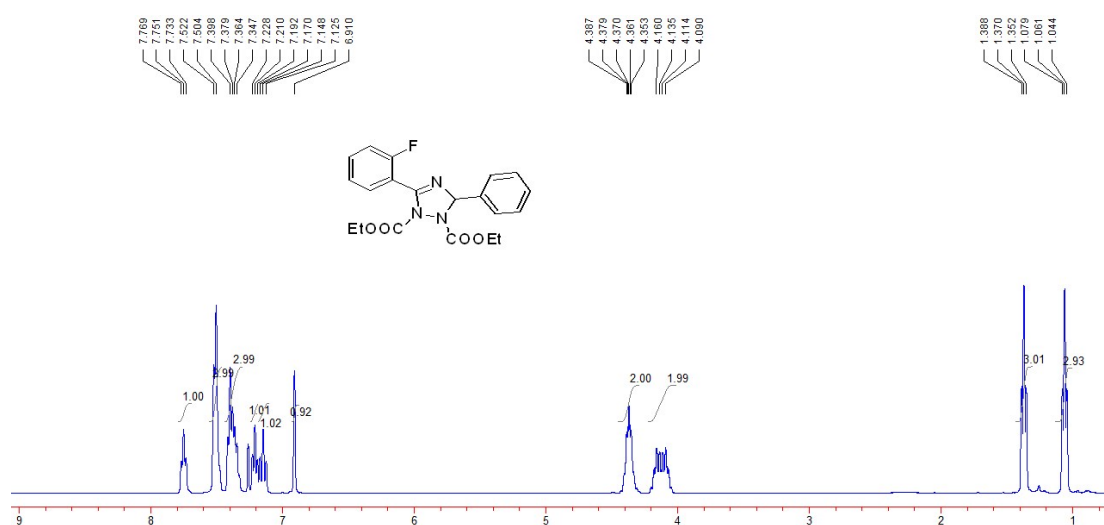
^1H and ^{13}C -NMR spectra of **3m**.



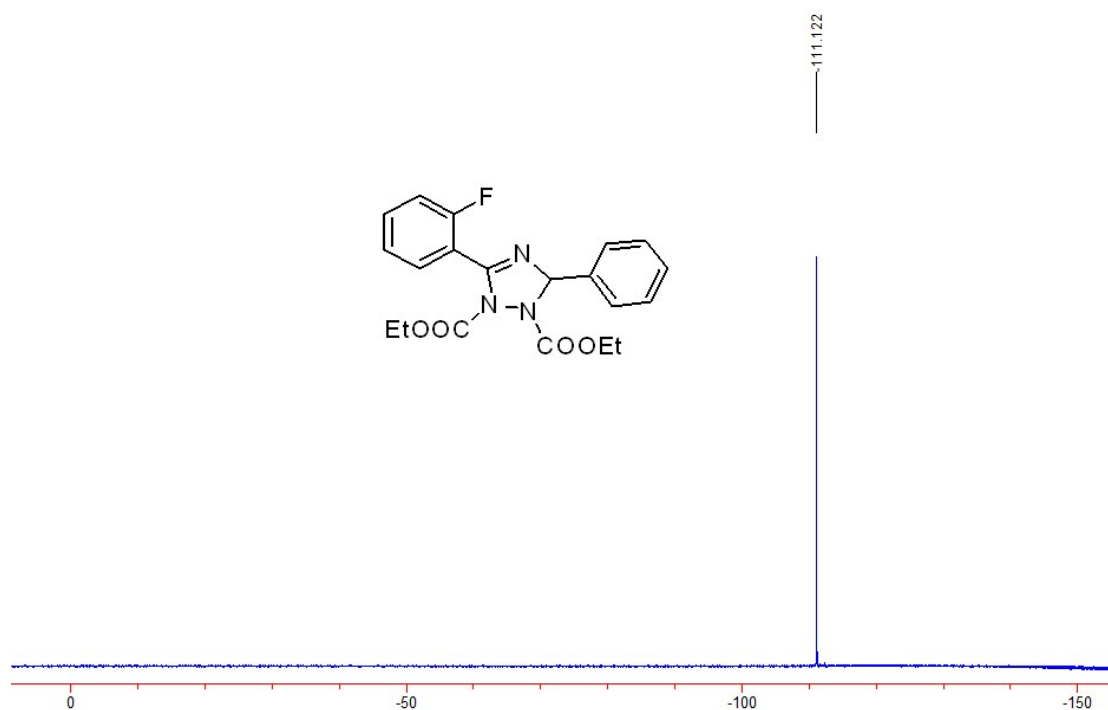
^1H and ^{13}C -NMR spectra of **3n**.



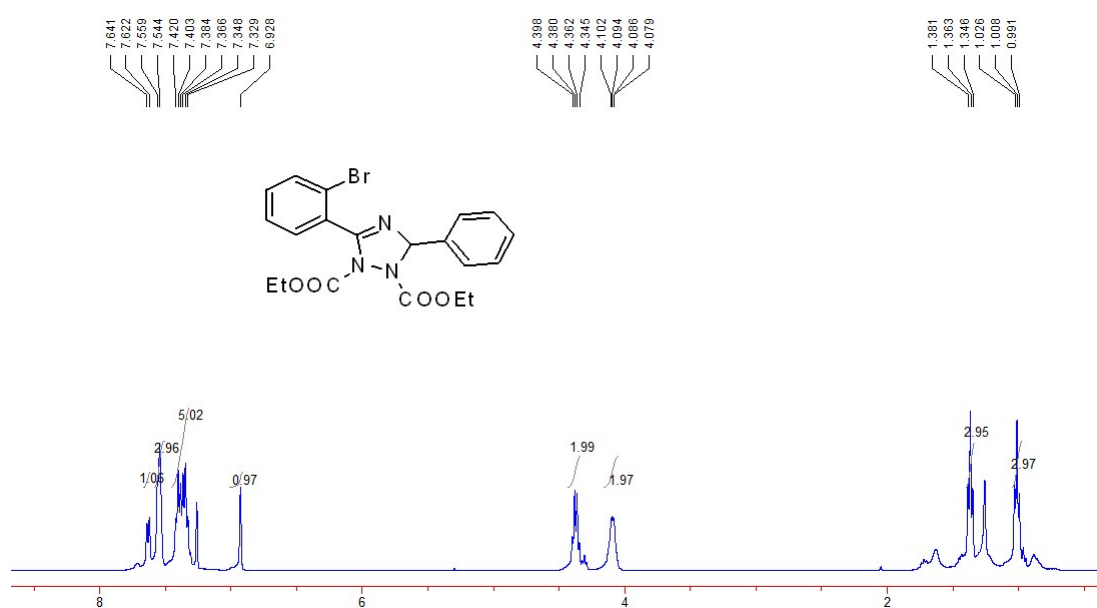
^1H and ^{13}C -NMR spectra of **3o**.

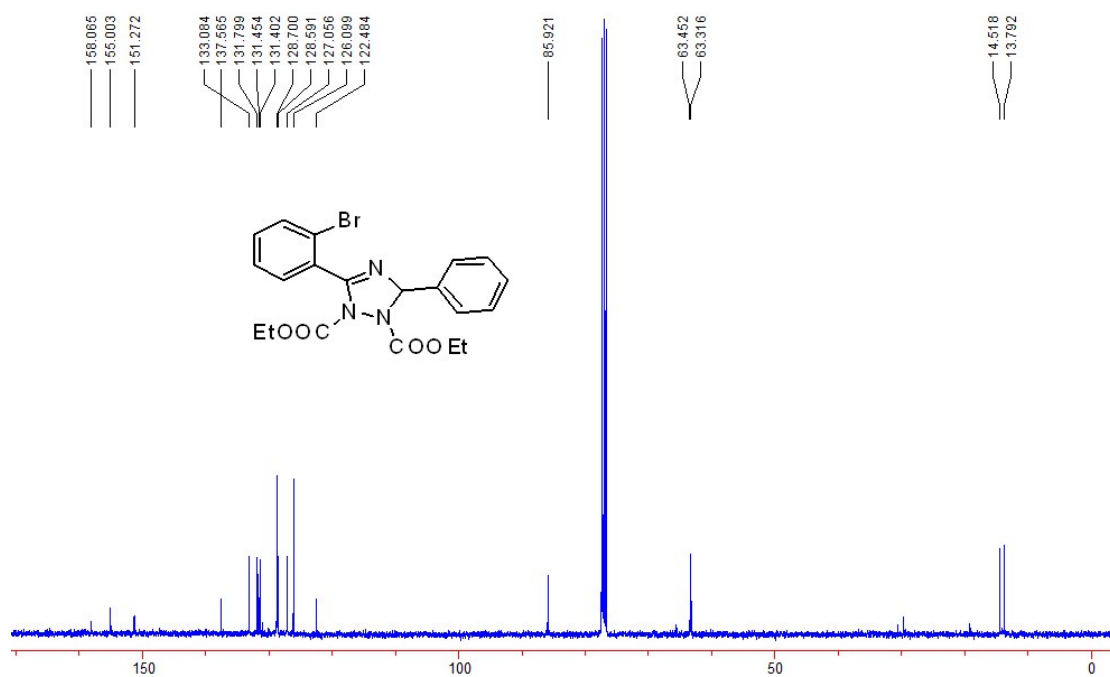


^{19}F -NMR spectra of **3o**.

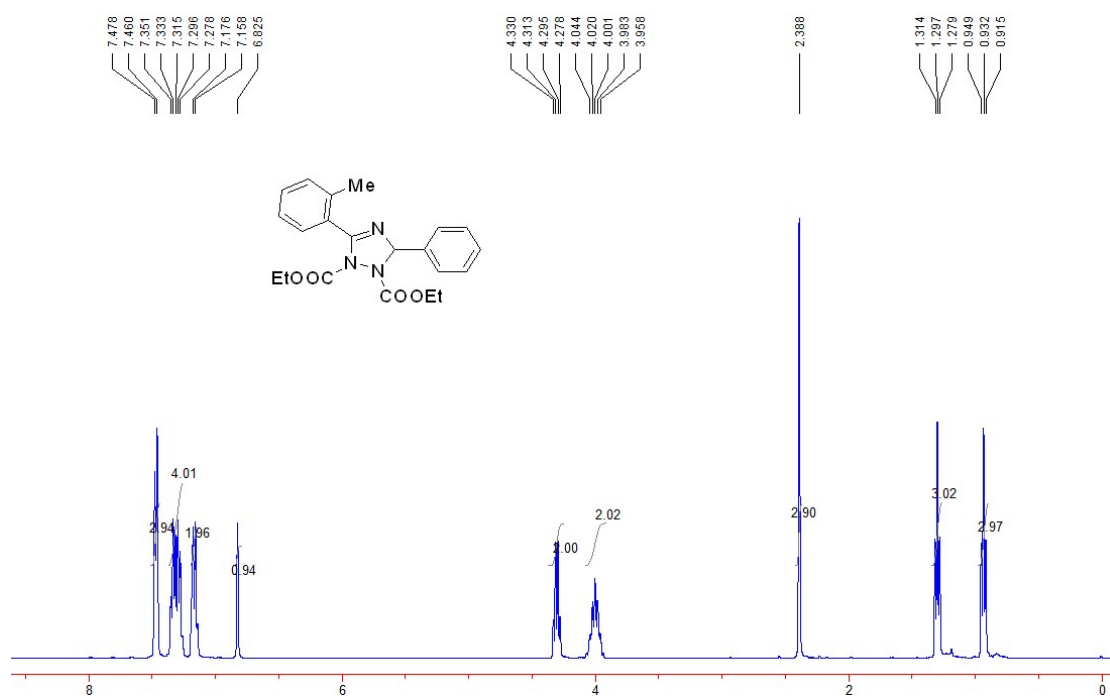


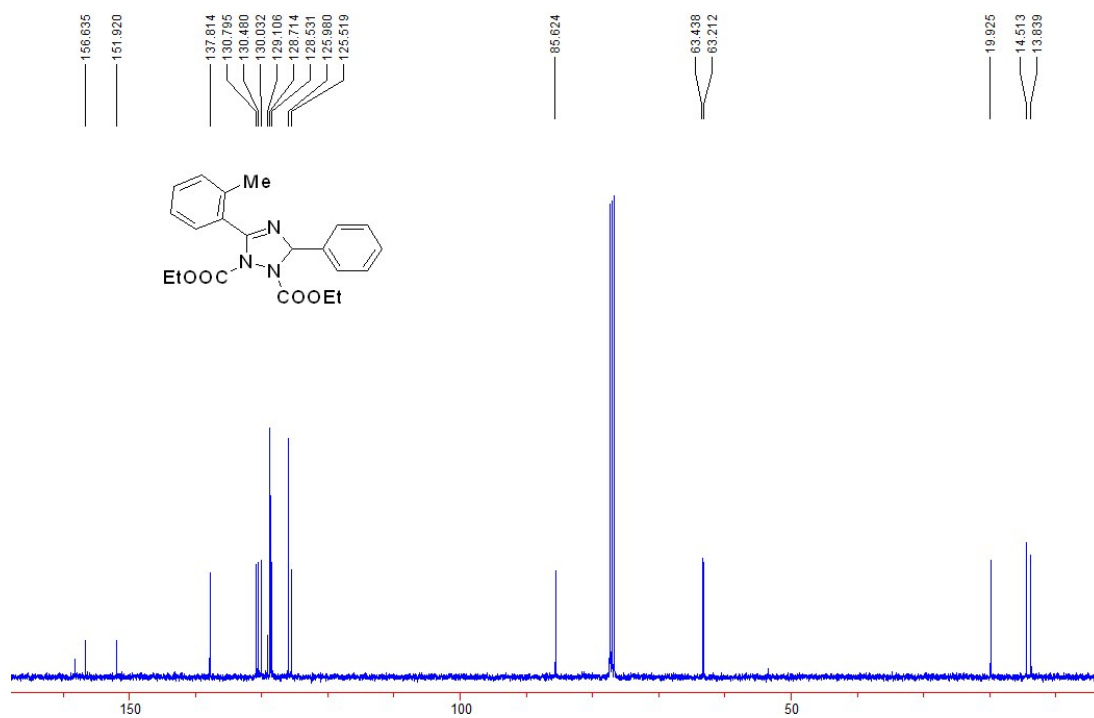
^1H and ^{13}C -NMR spectra of **3p**.



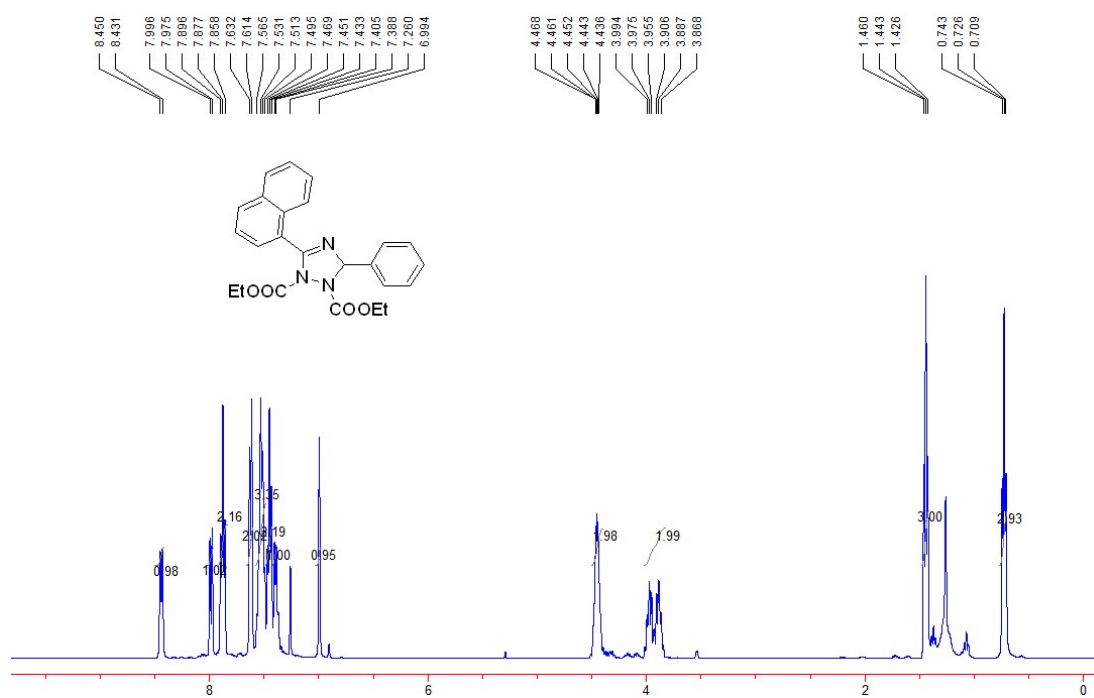


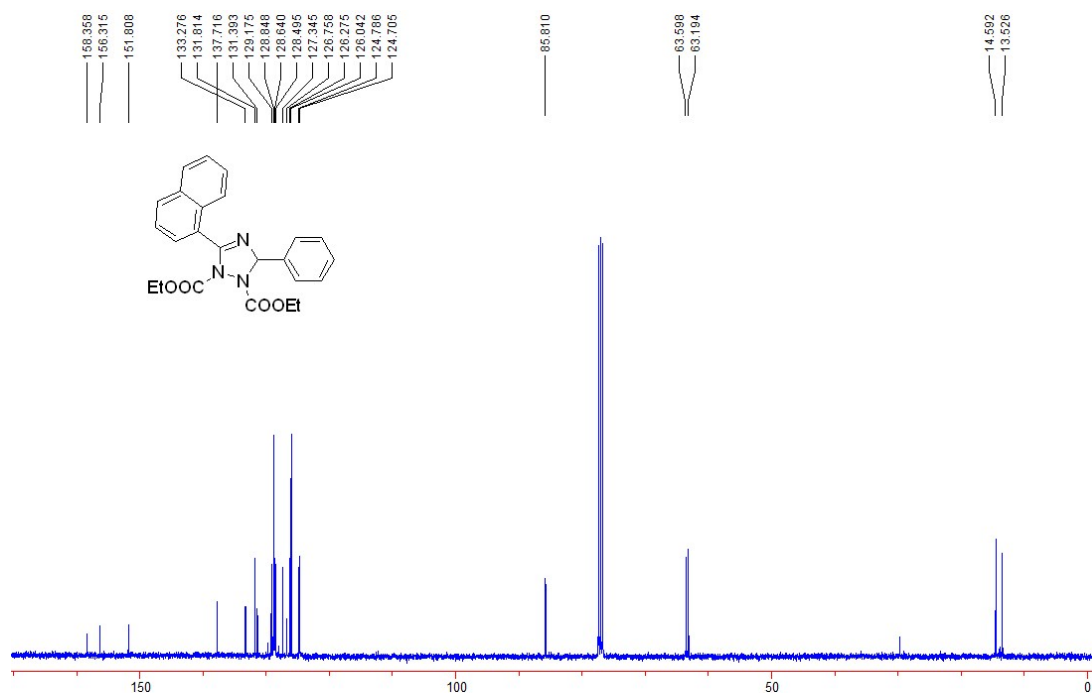
¹H and ¹³C-NMR spectra of **3q**.



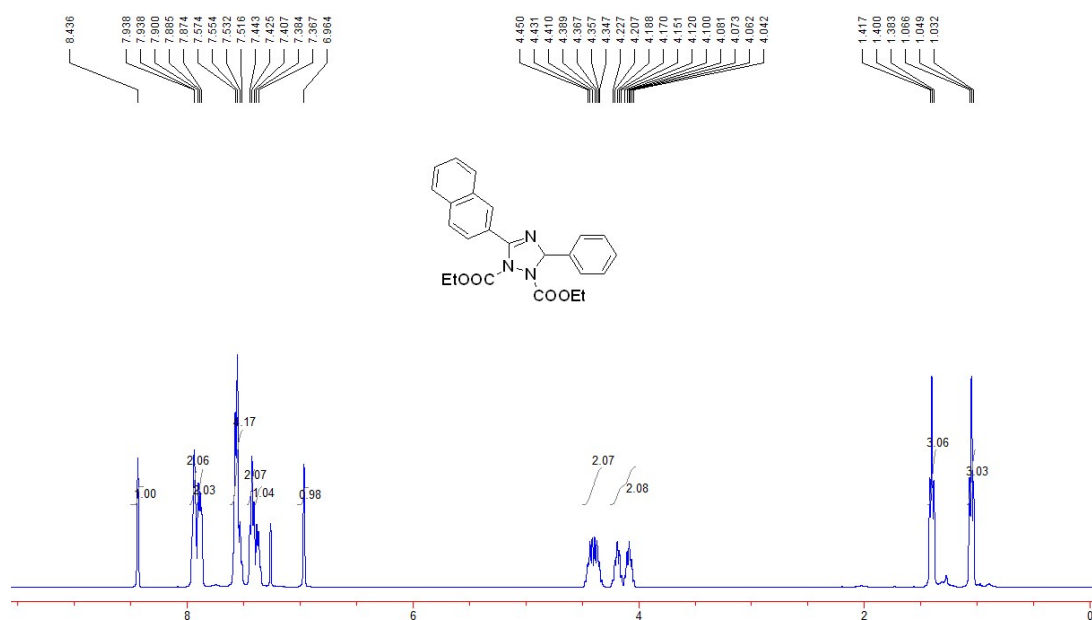


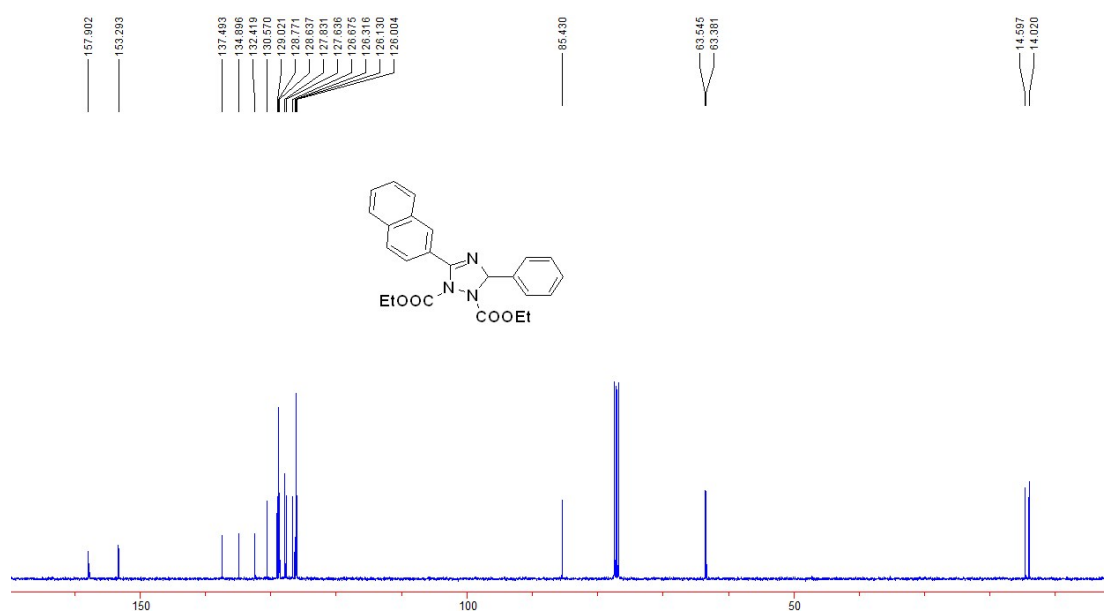
¹H and ¹³C-NMR spectra of **3r**.



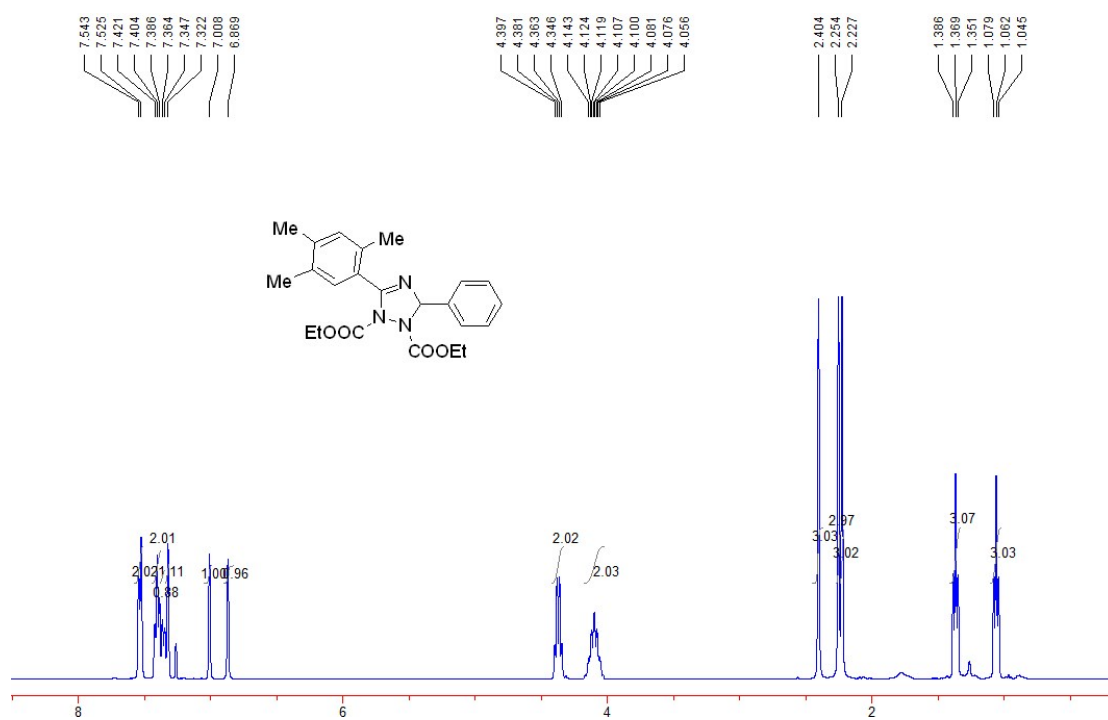


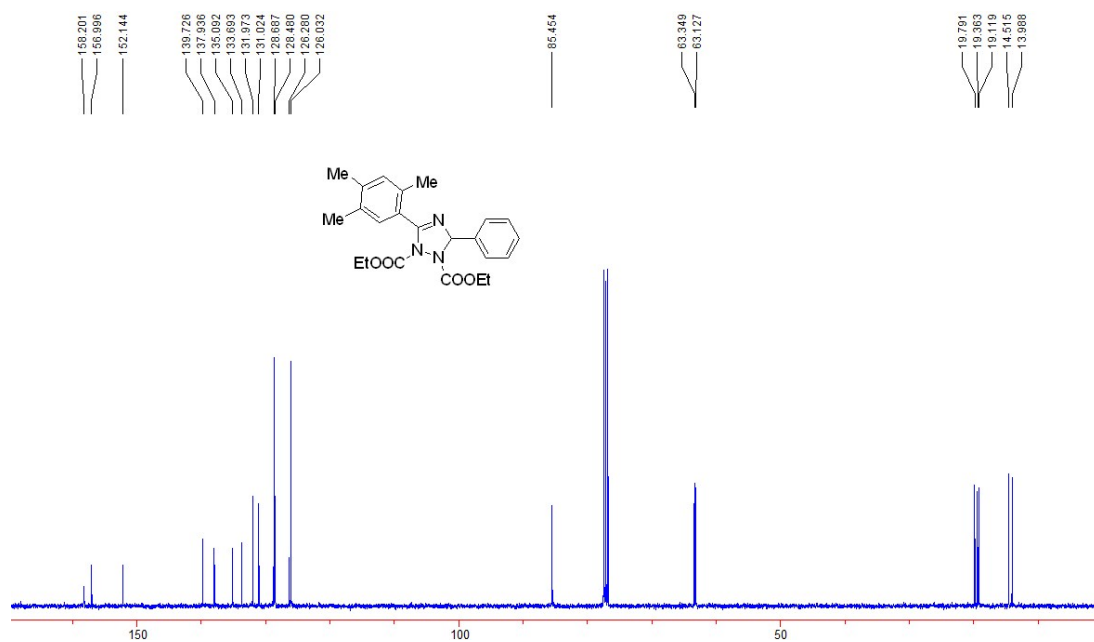
¹H and ¹³C-NMR spectra of **3s**.



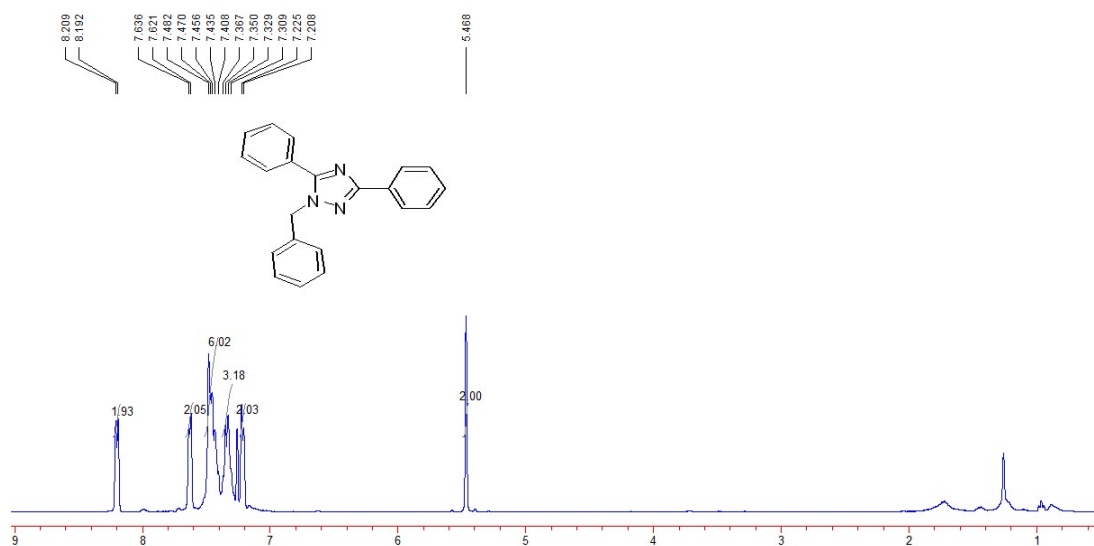


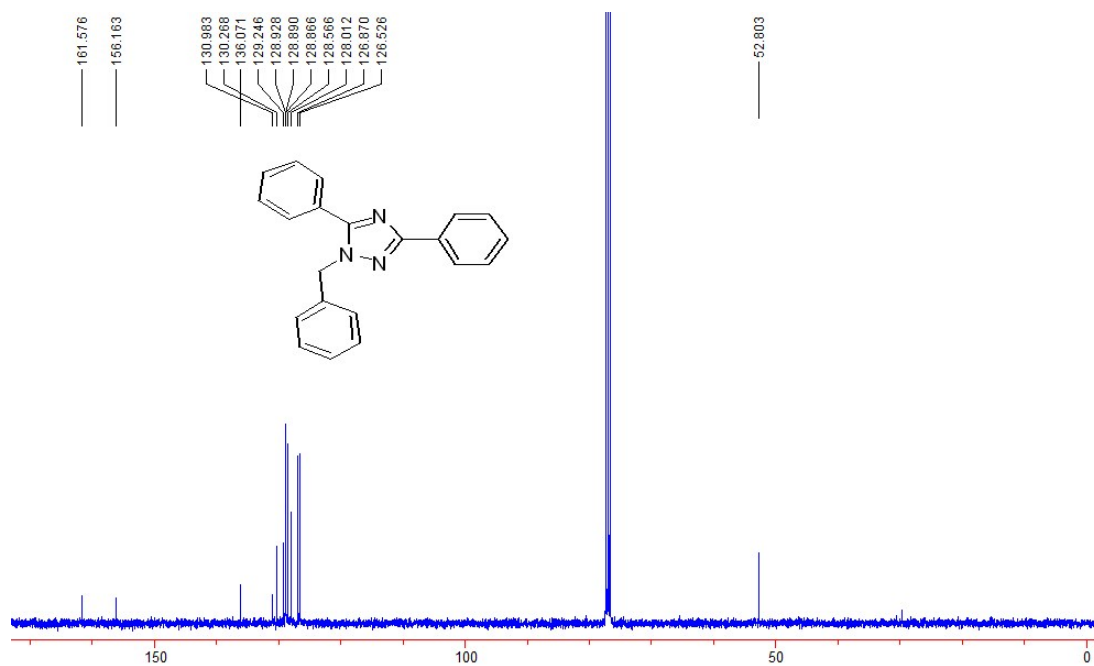
¹H and ¹³C-NMR spectra of **3t**.



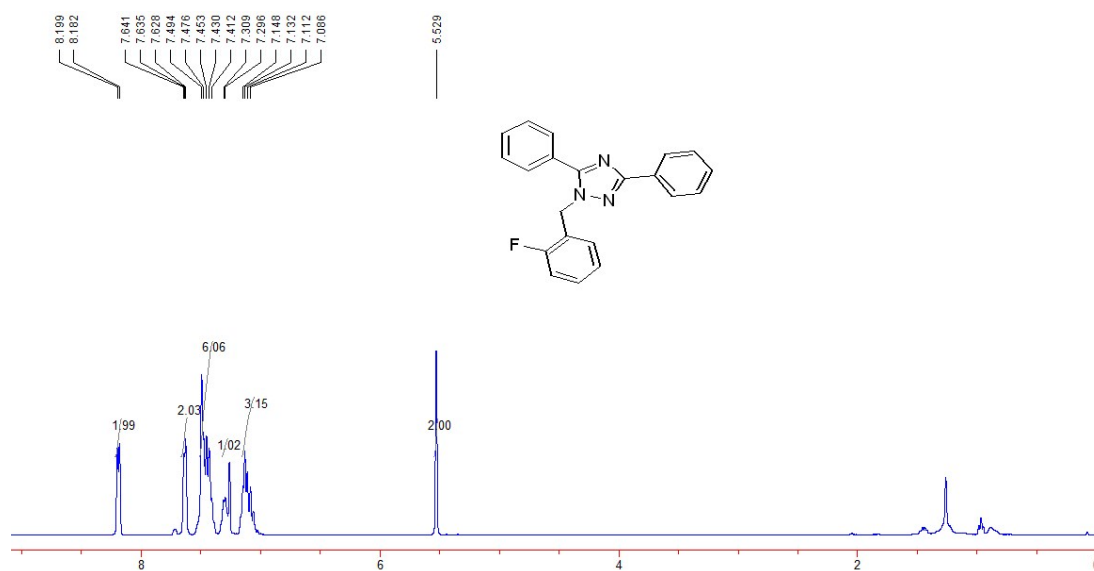


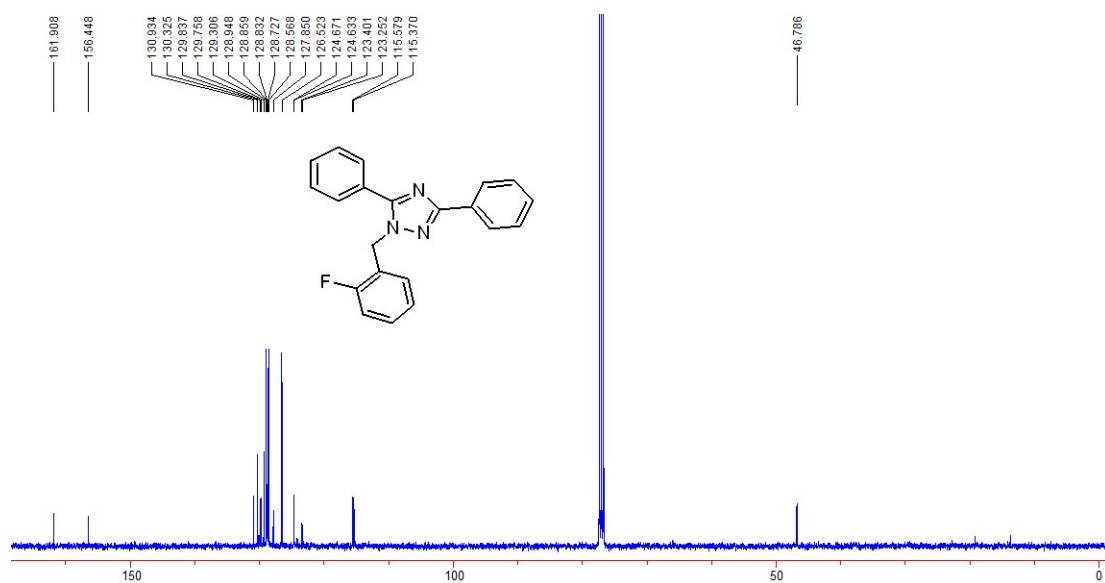
¹H and ¹³C-NMR spectra of **5a**.



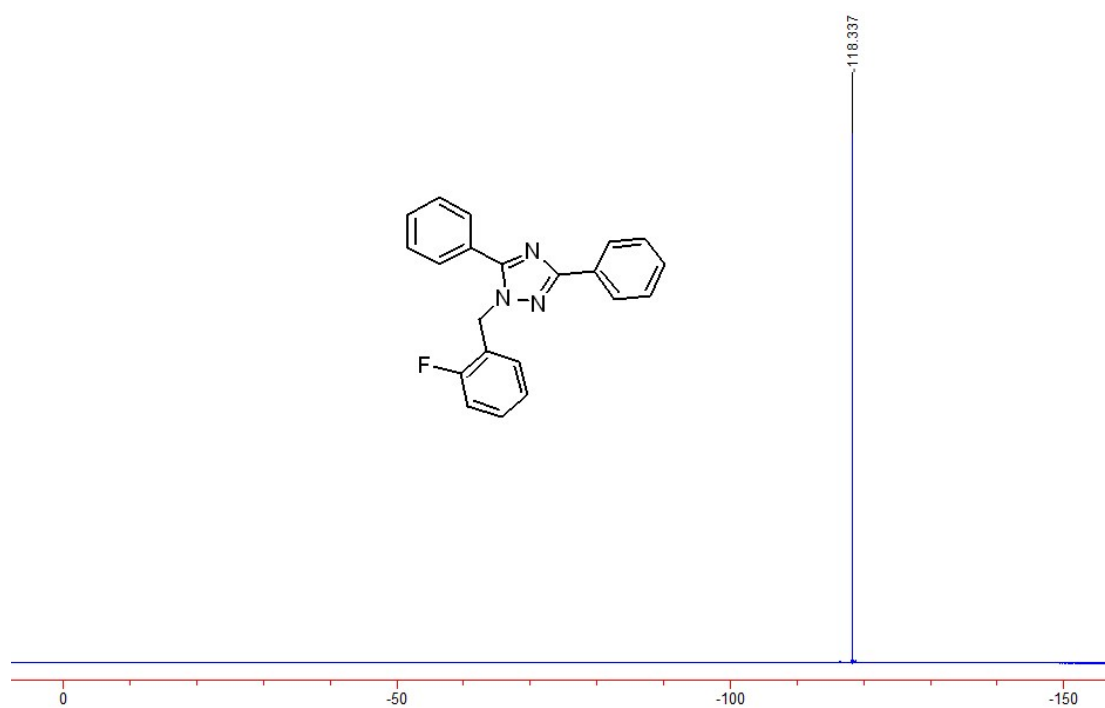


¹H and ¹³C-NMR spectra of **5b**.

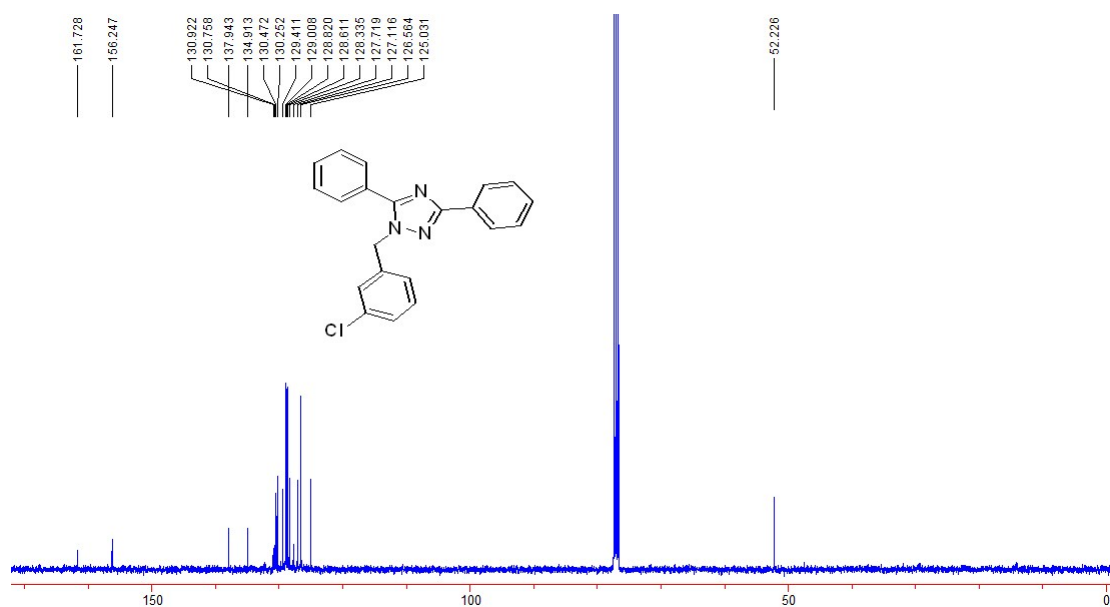
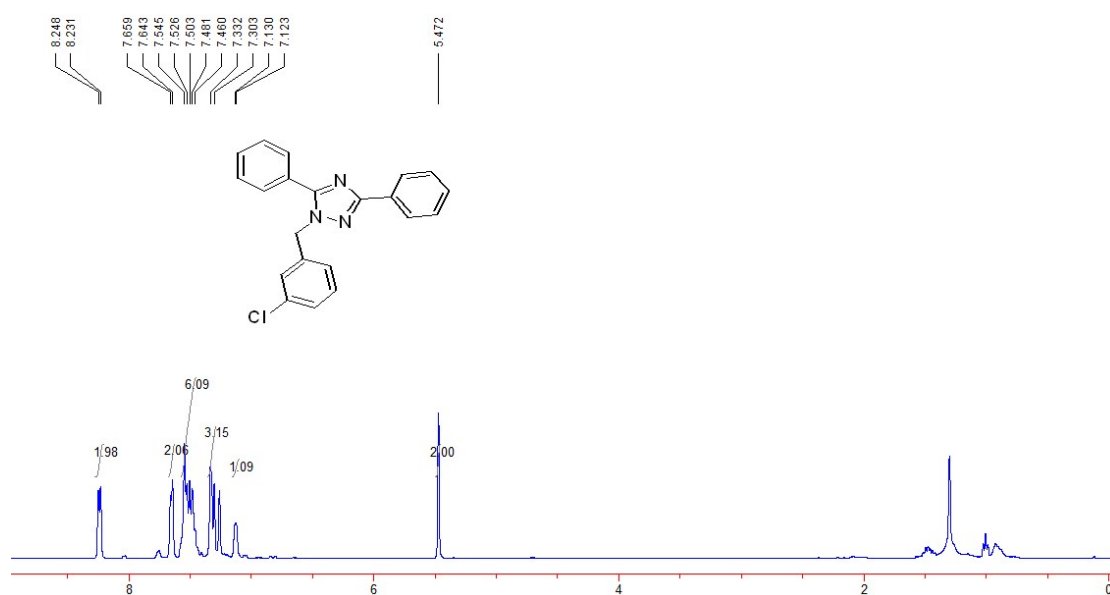




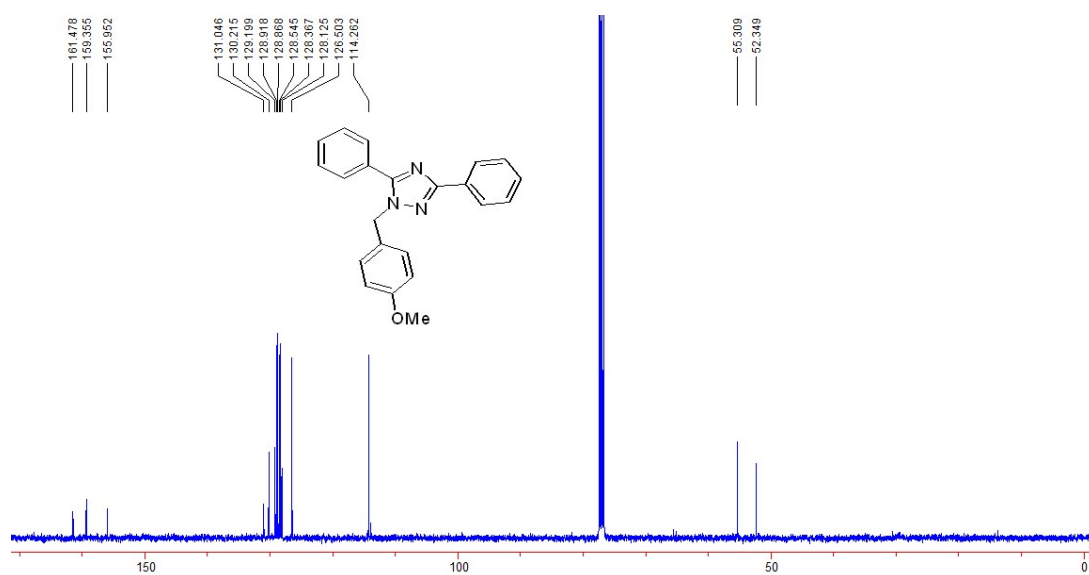
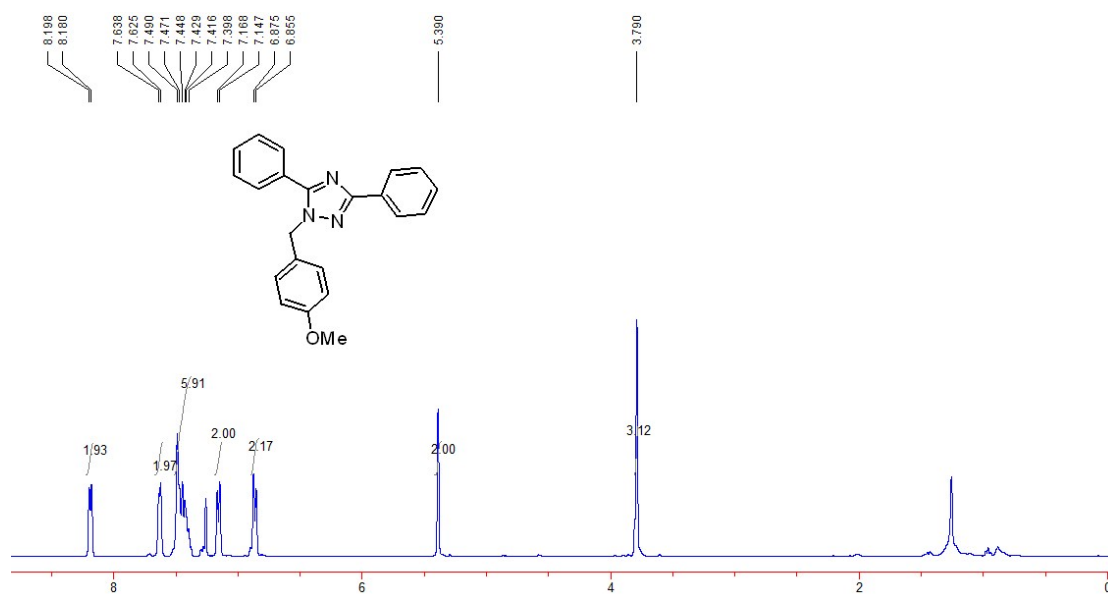
¹⁹F-NMR spectra of **5b**.



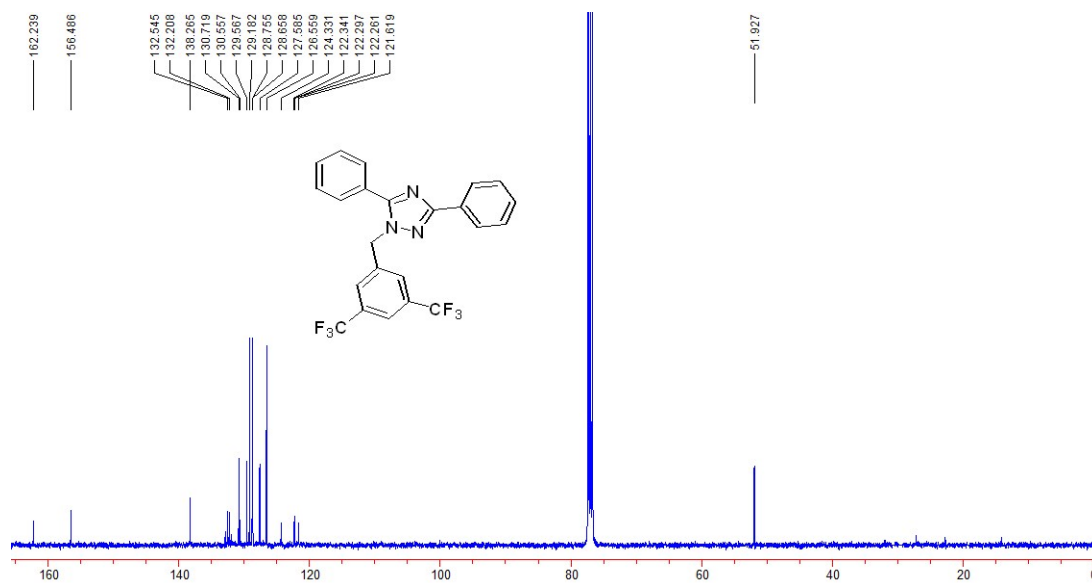
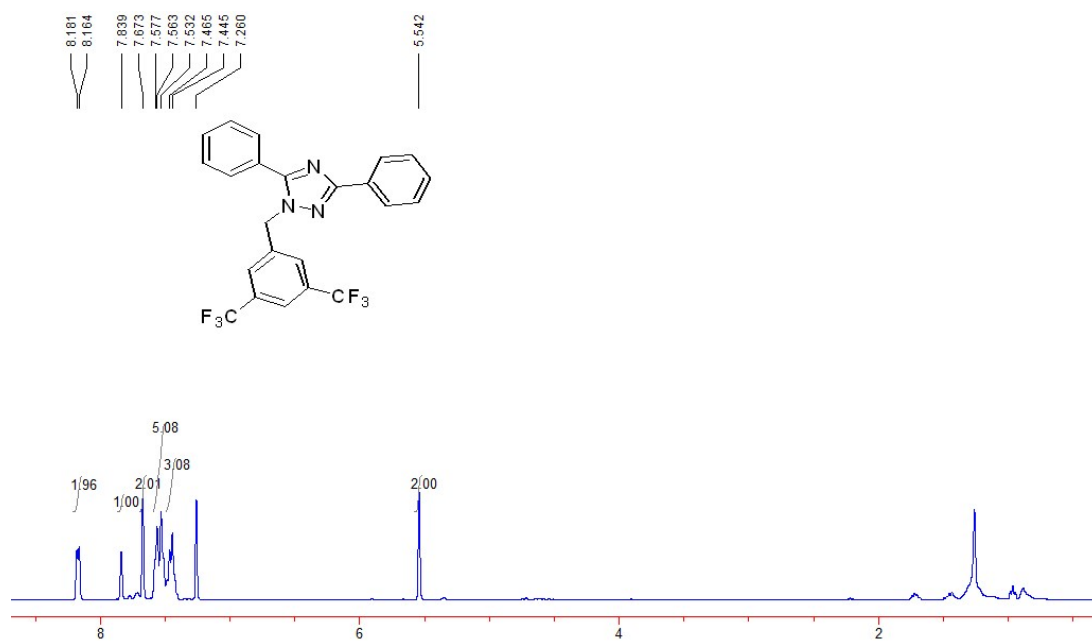
^1H and ^{13}C -NMR spectra of **5c**.



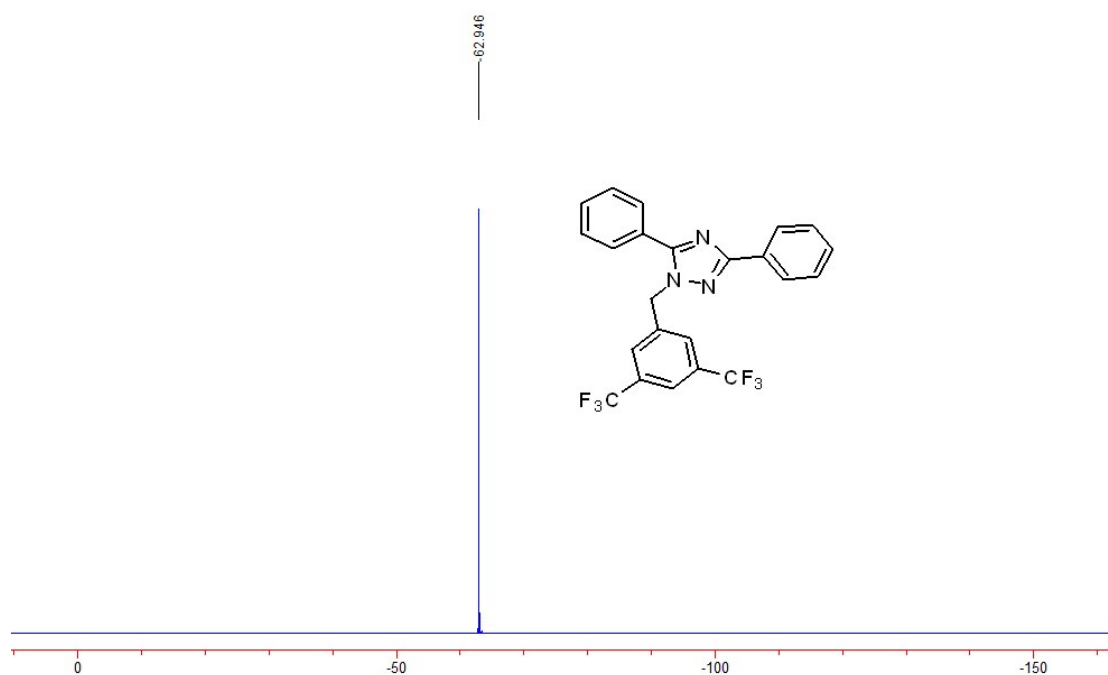
^1H and ^{13}C -NMR spectra of **5d**.



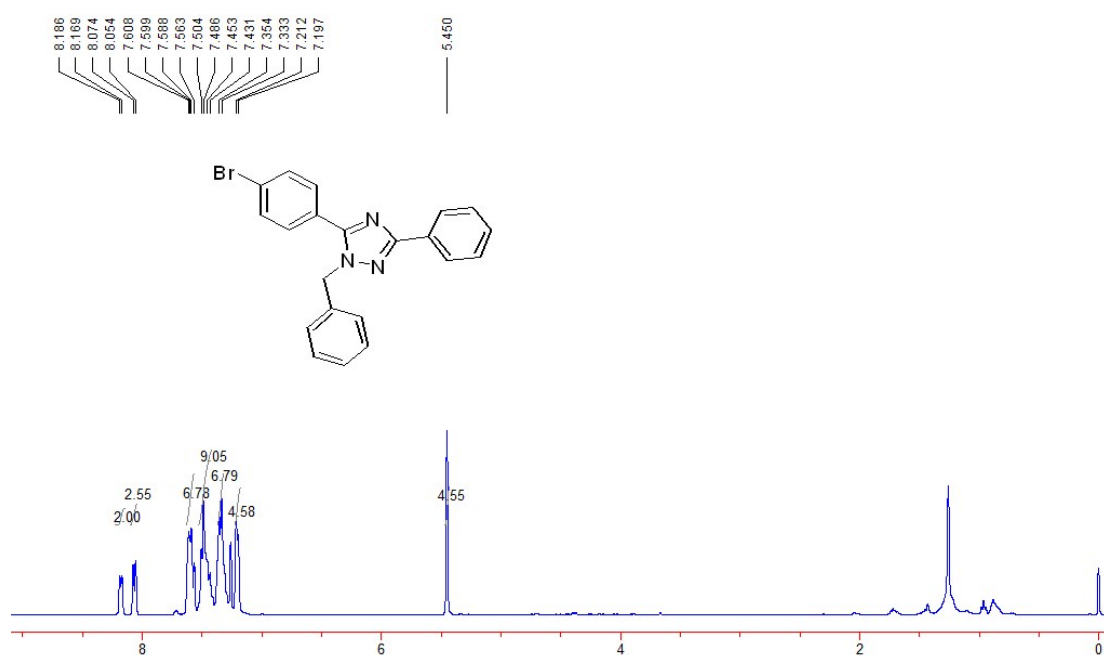
^1H and ^{13}C -NMR spectra of **5e**.

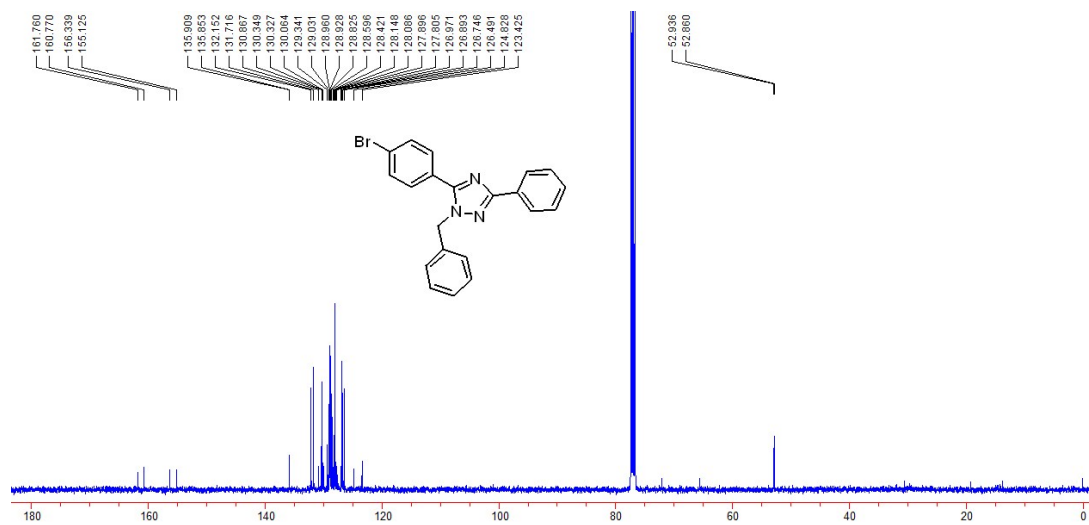


^{19}F -NMR spectra of **5e**.

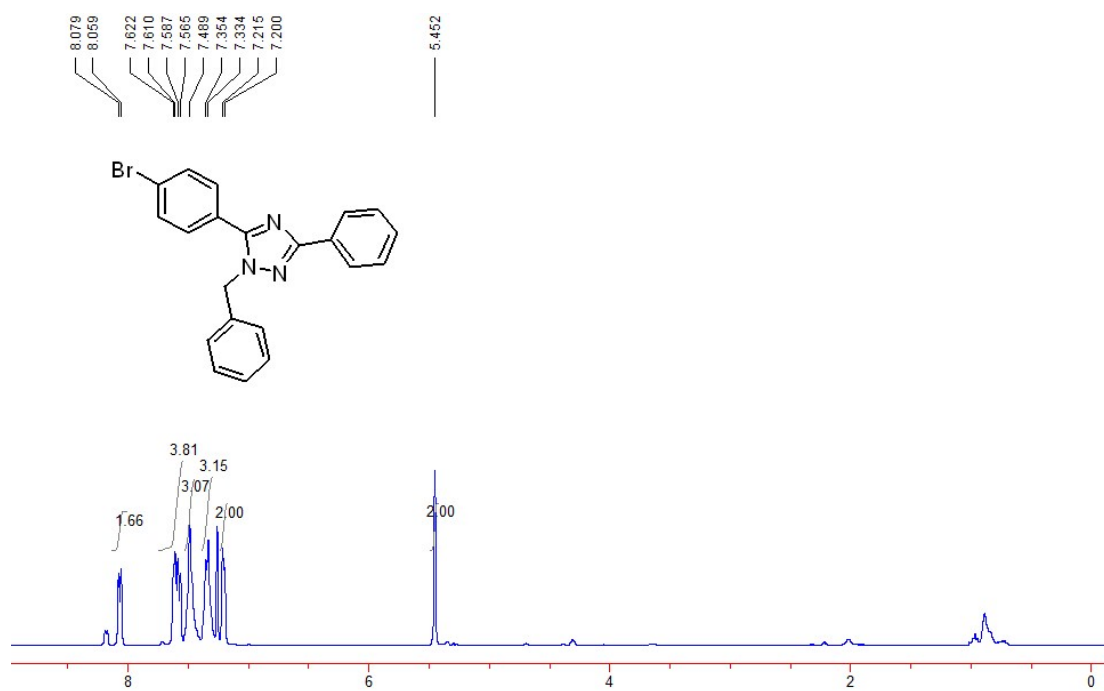


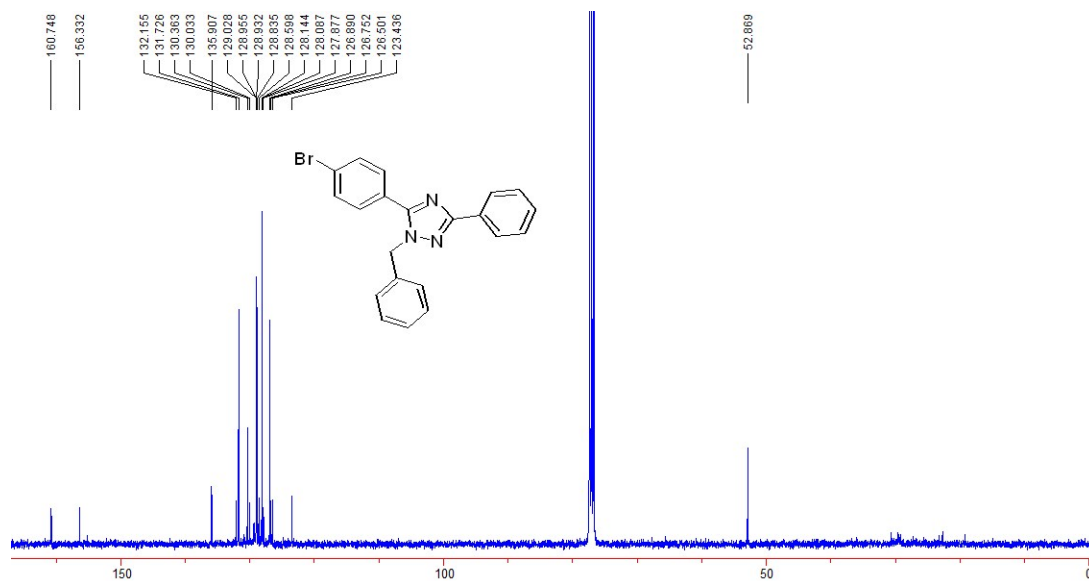
^1H and ^{13}C -NMR spectra of **5f**.



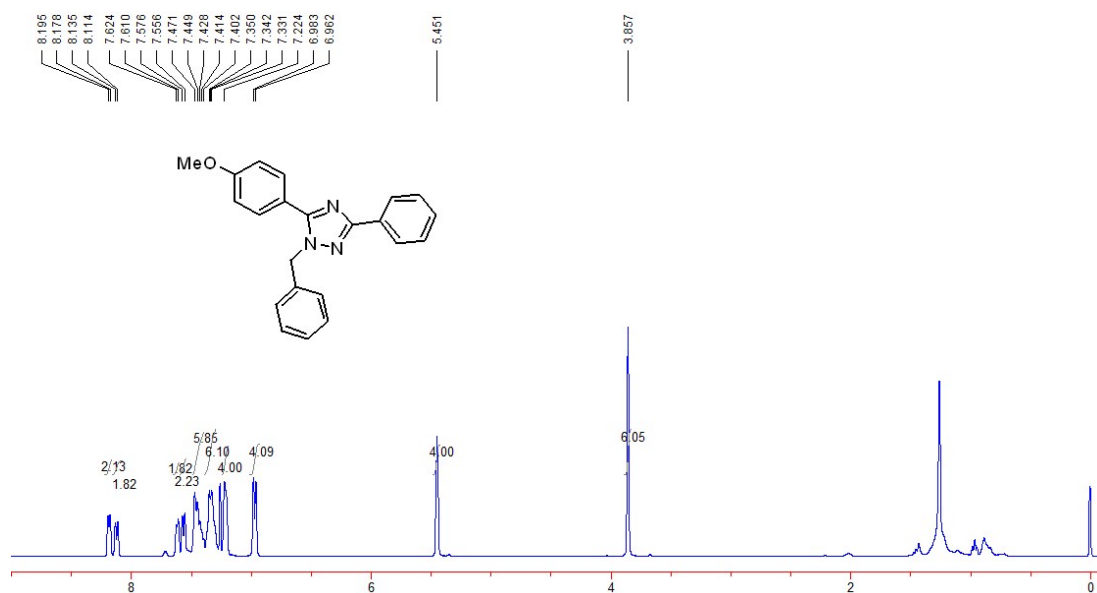


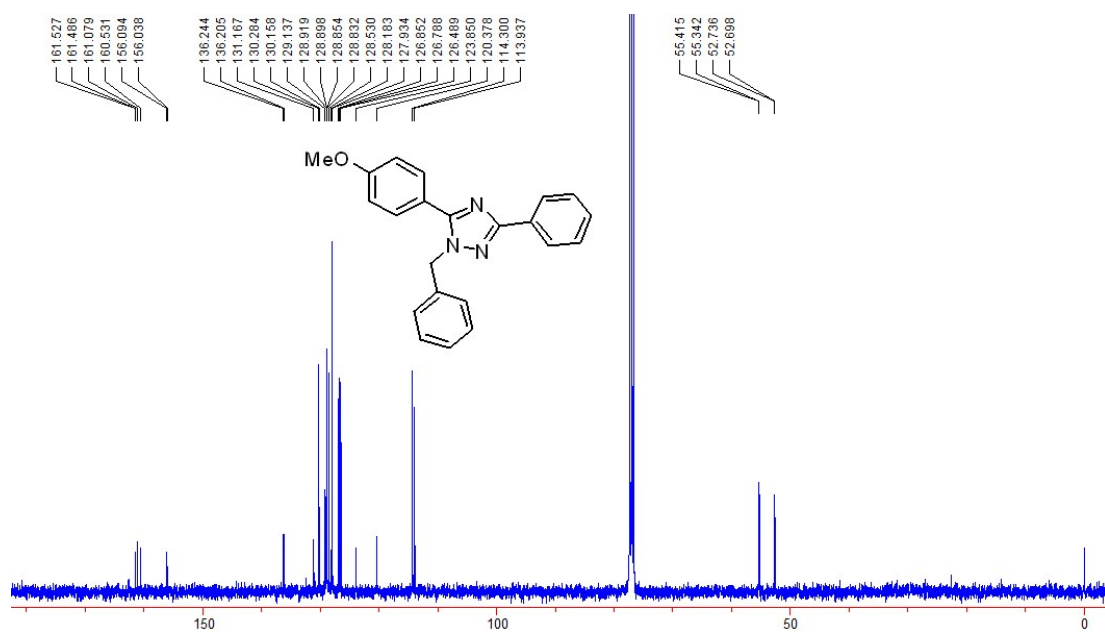
¹H and ¹³C-NMR spectra of **5f**.



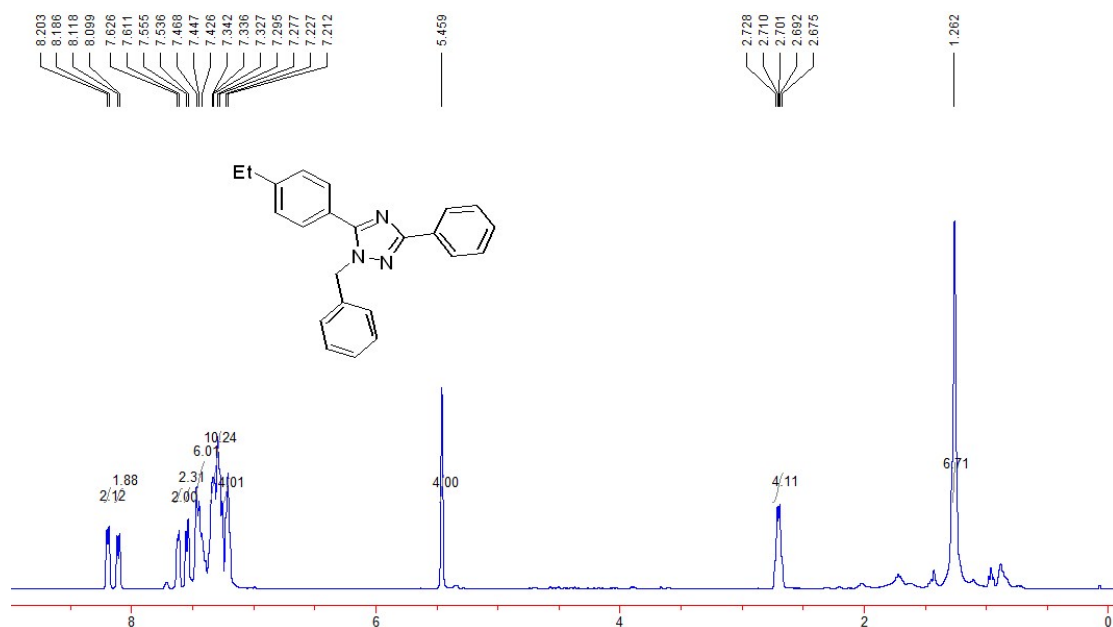


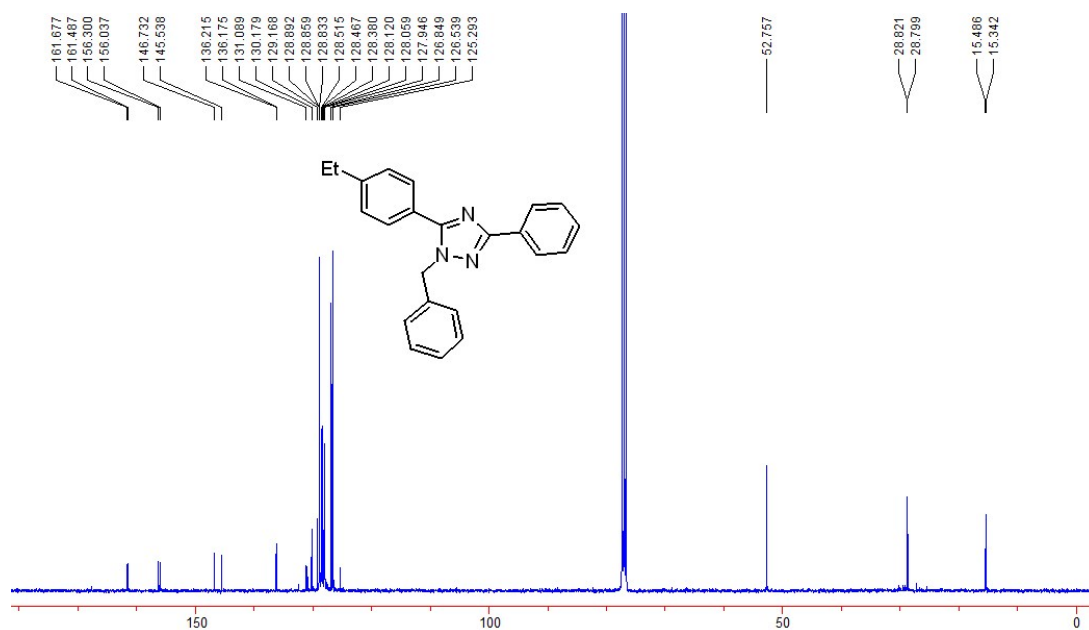
¹H and ¹³C-NMR spectra of **5g**.



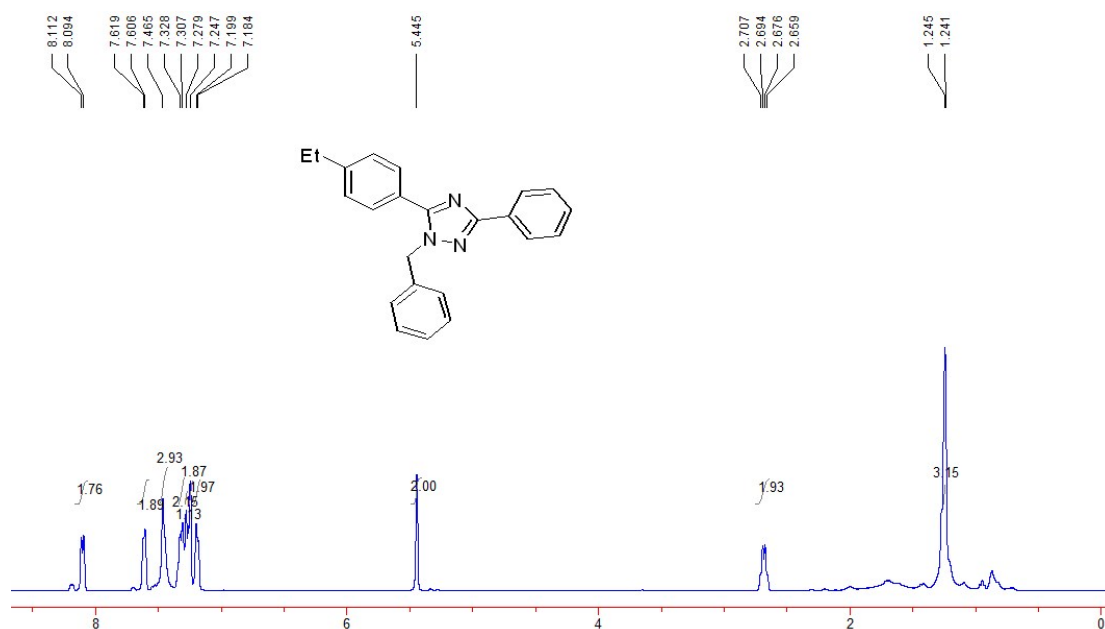


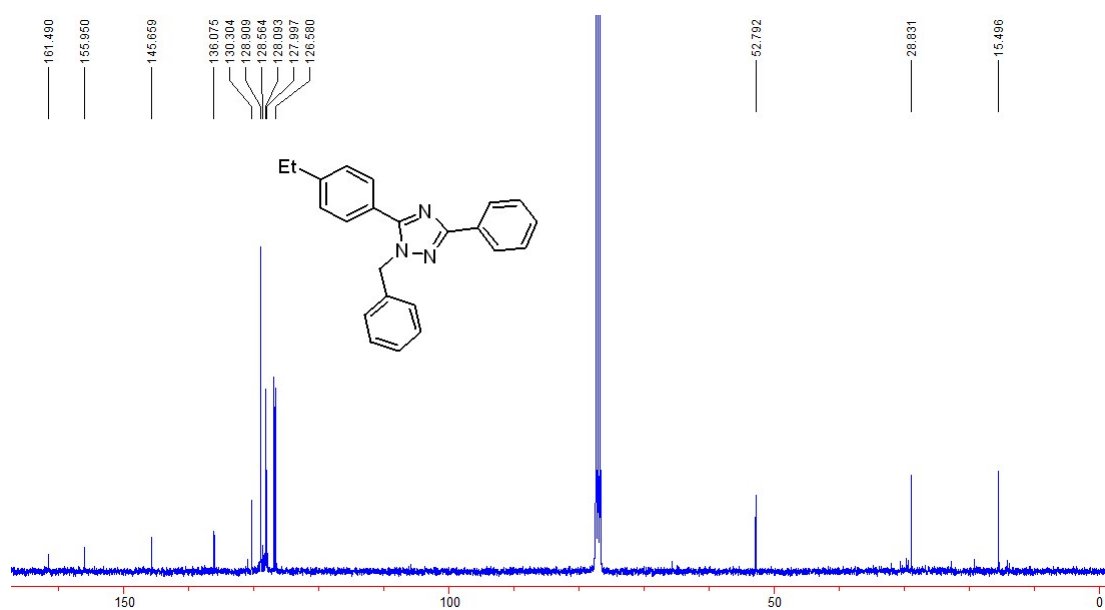
¹H and ¹³C-NMR spectra of **5h**.



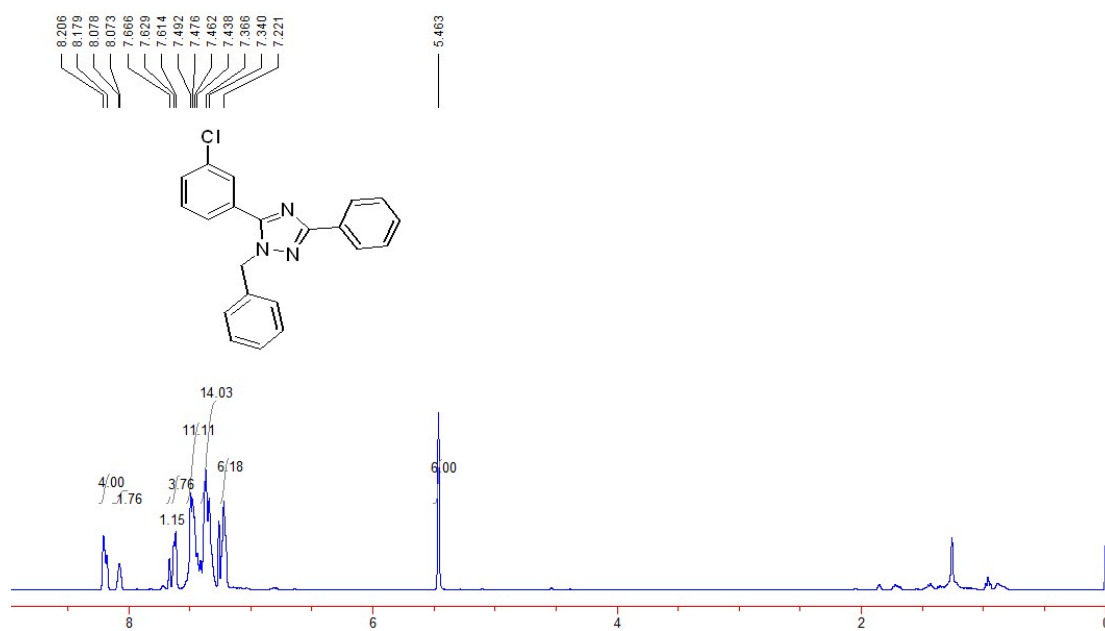


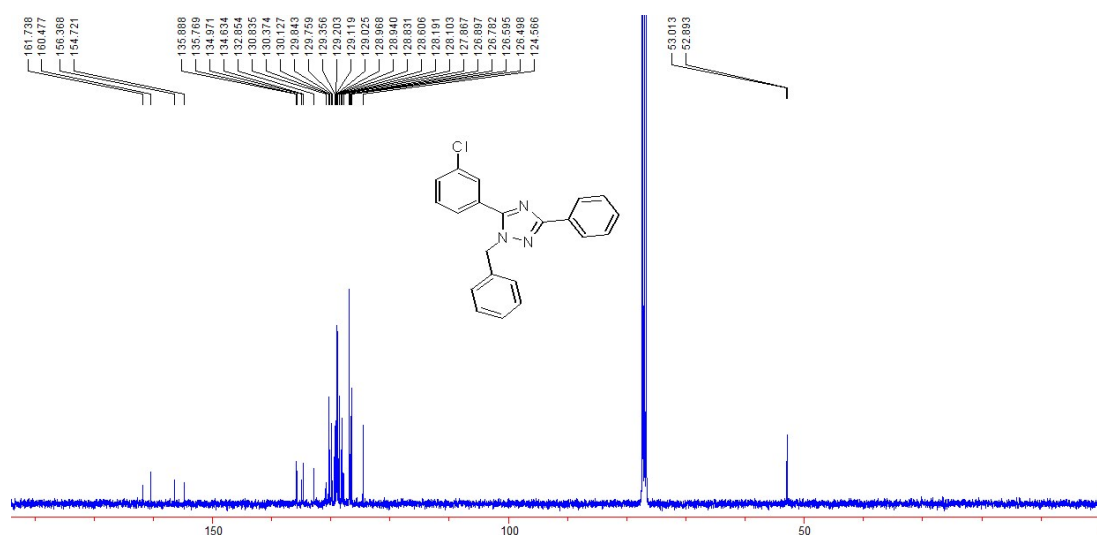
¹H and ¹³C-NMR spectra of **5h**.



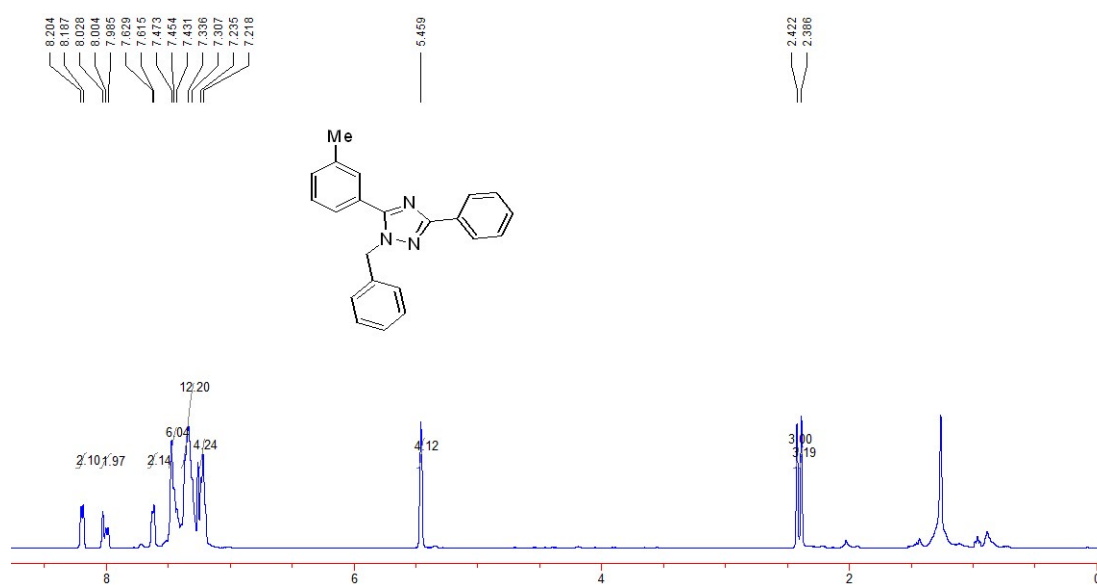


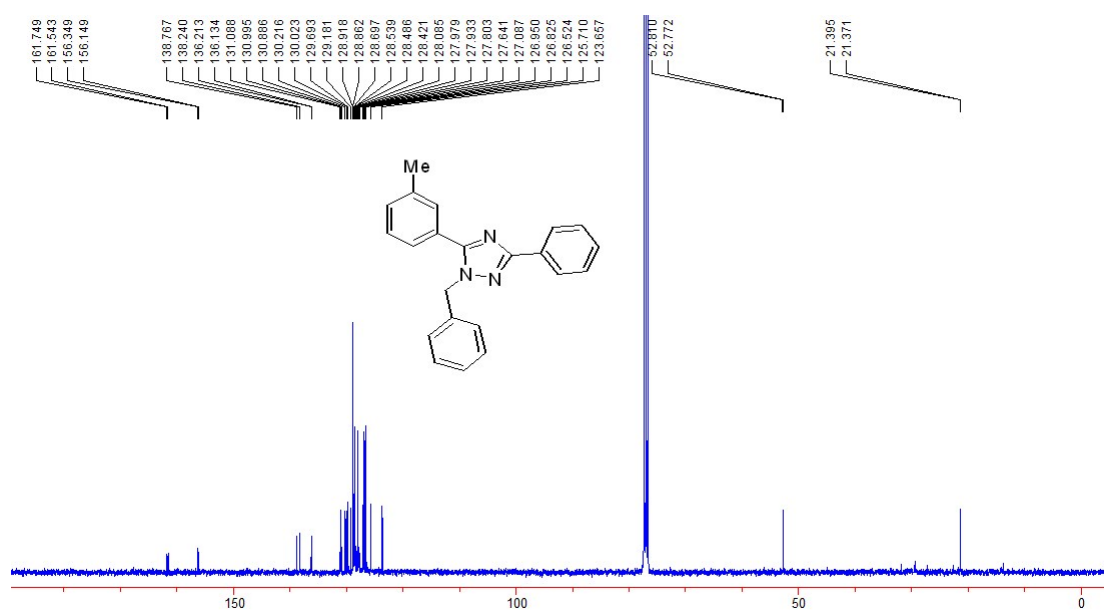
¹H and ¹³C-NMR spectra of **5i**.



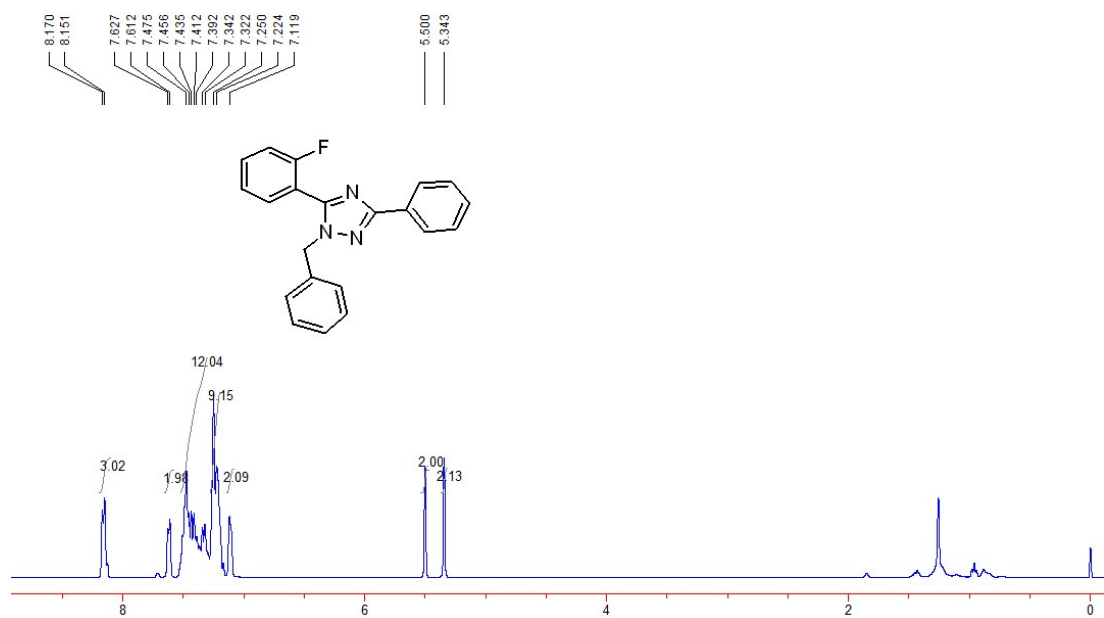


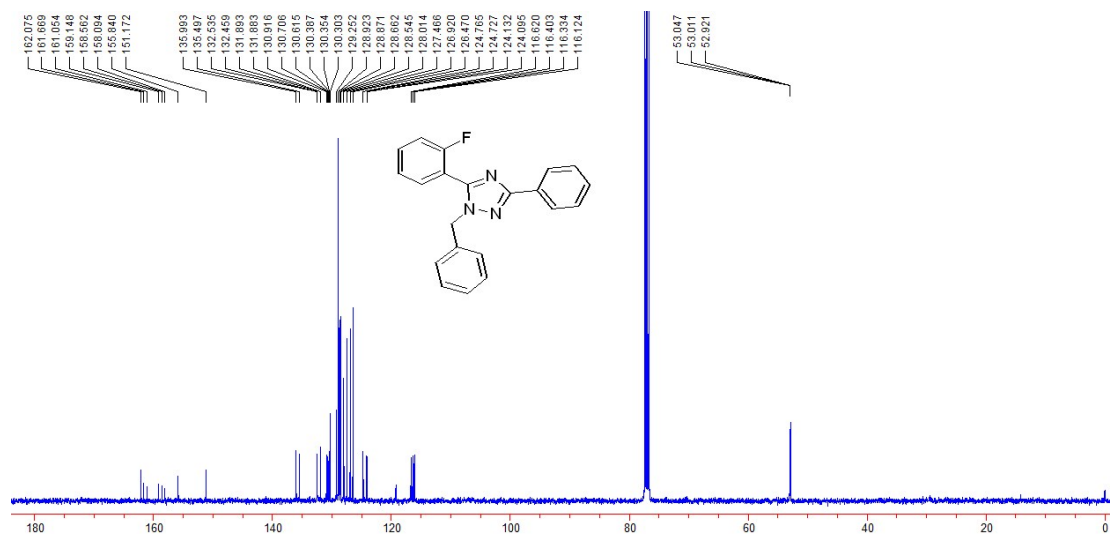
¹H and ¹³C-NMR spectra of **5j**.



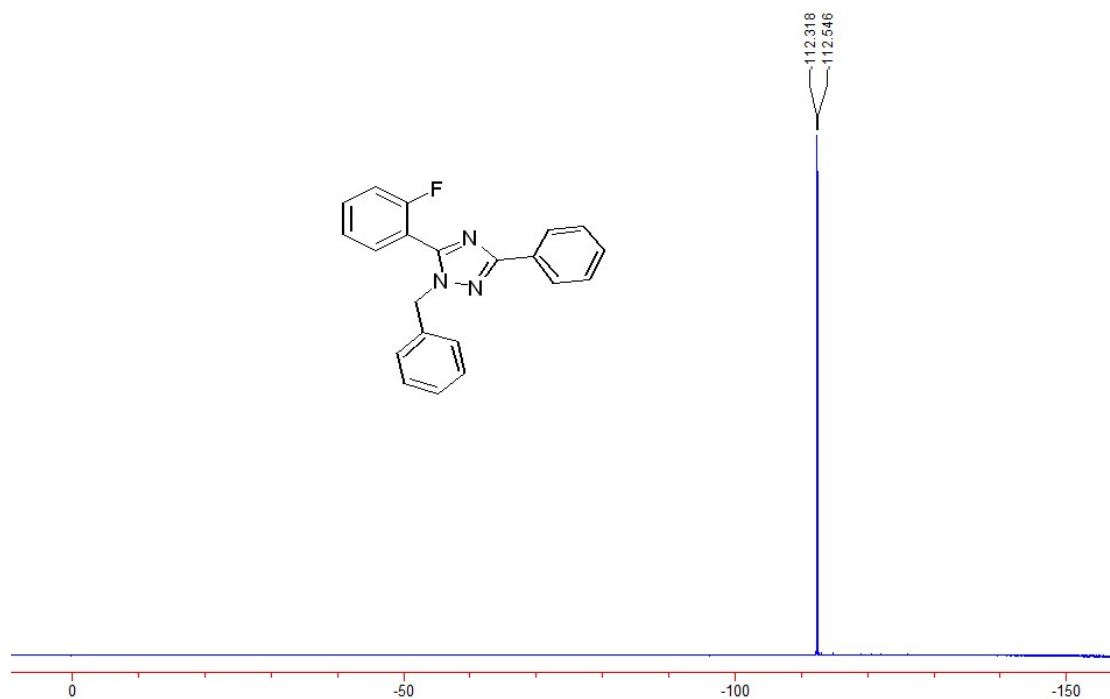


¹H and ¹³C-NMR spectra of **5k**.

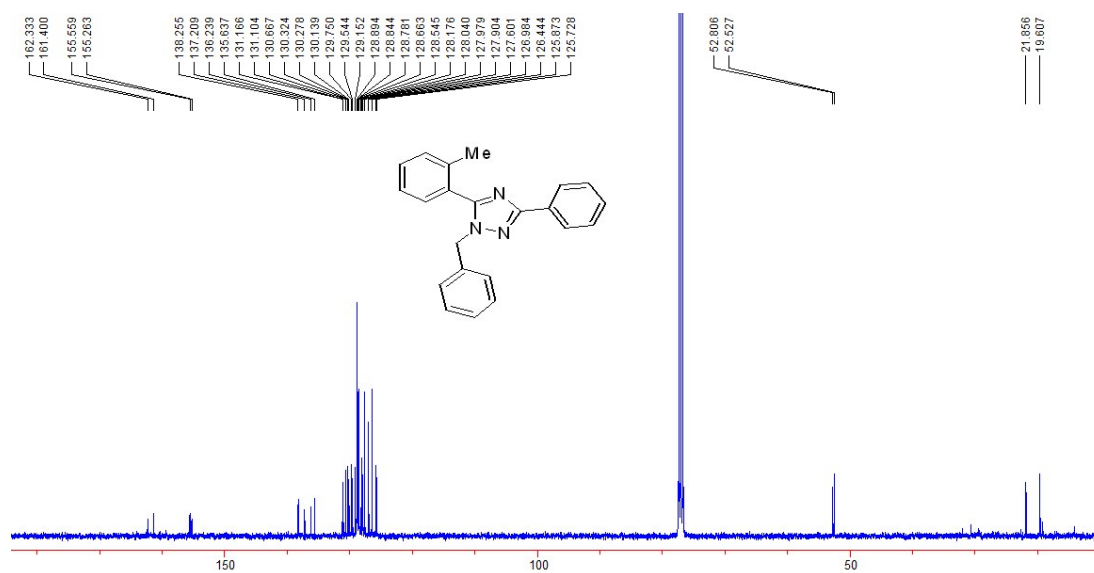
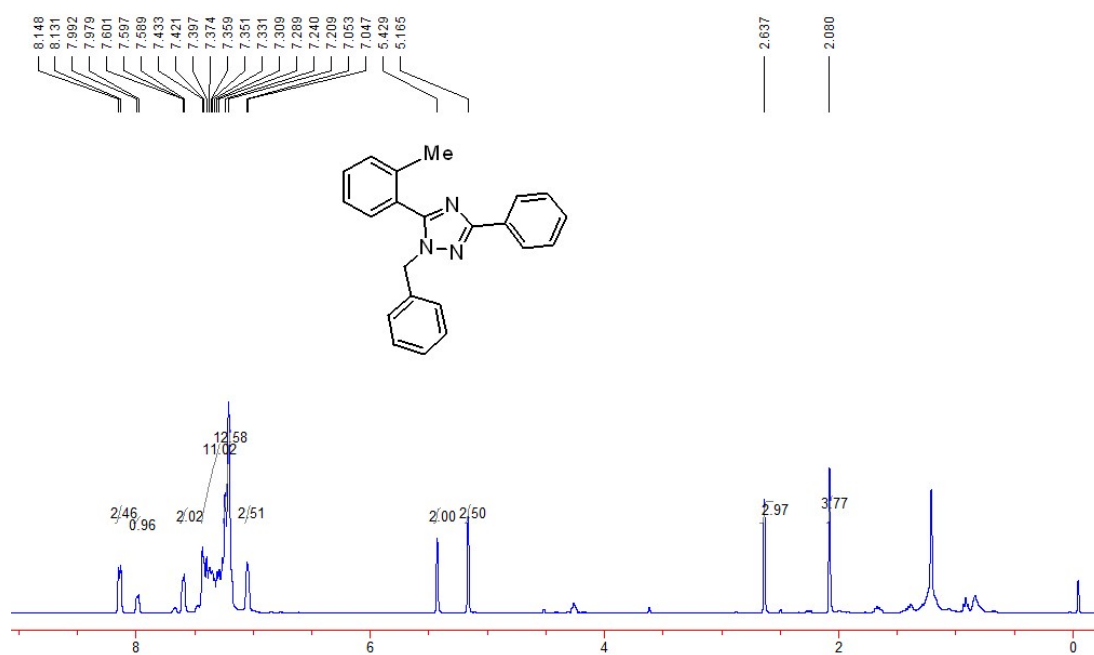




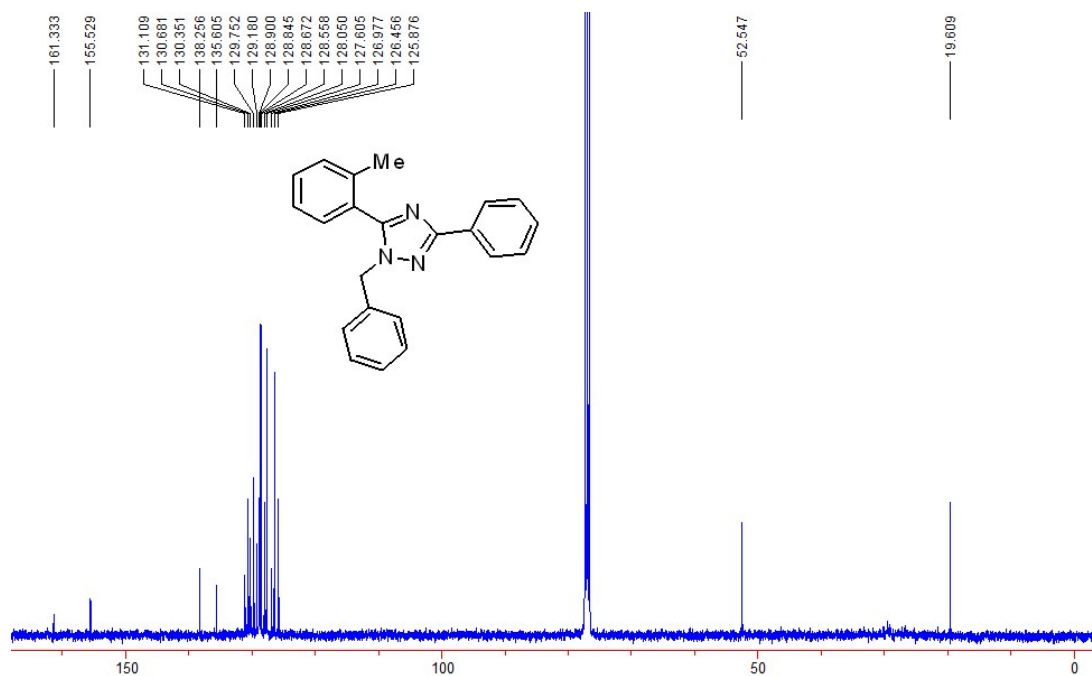
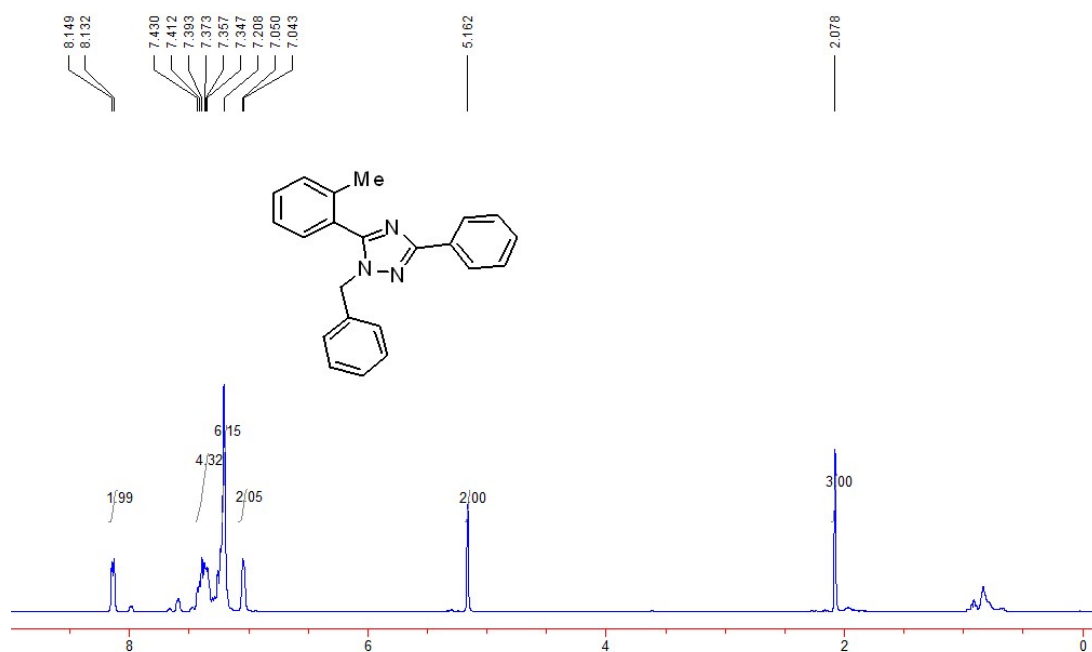
¹⁹F-NMR spectra of **5k**.



^1H and ^{13}C -NMR spectra of **5l**.



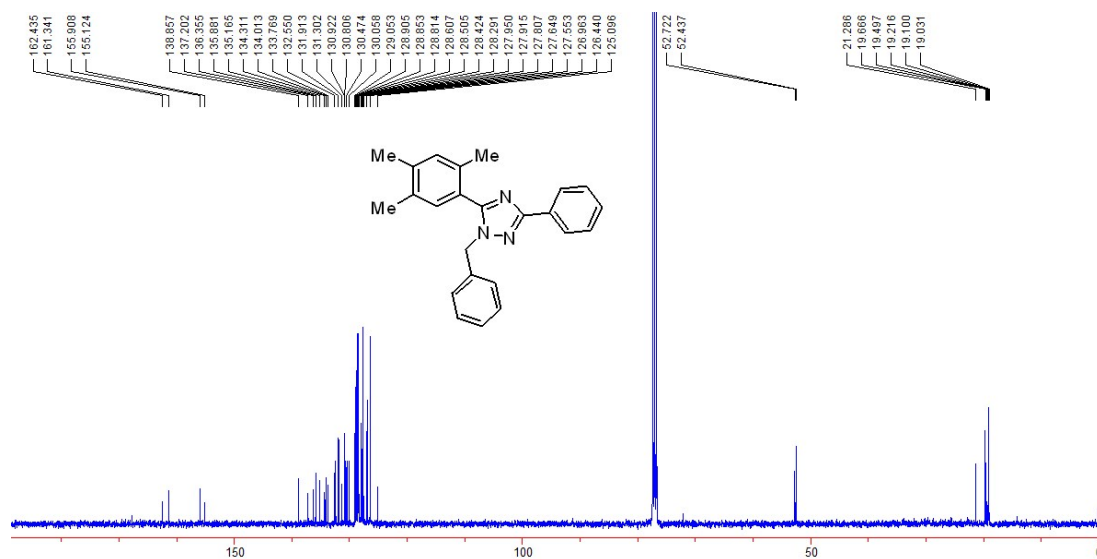
^1H and ^{13}C -NMR spectra of **5l**.



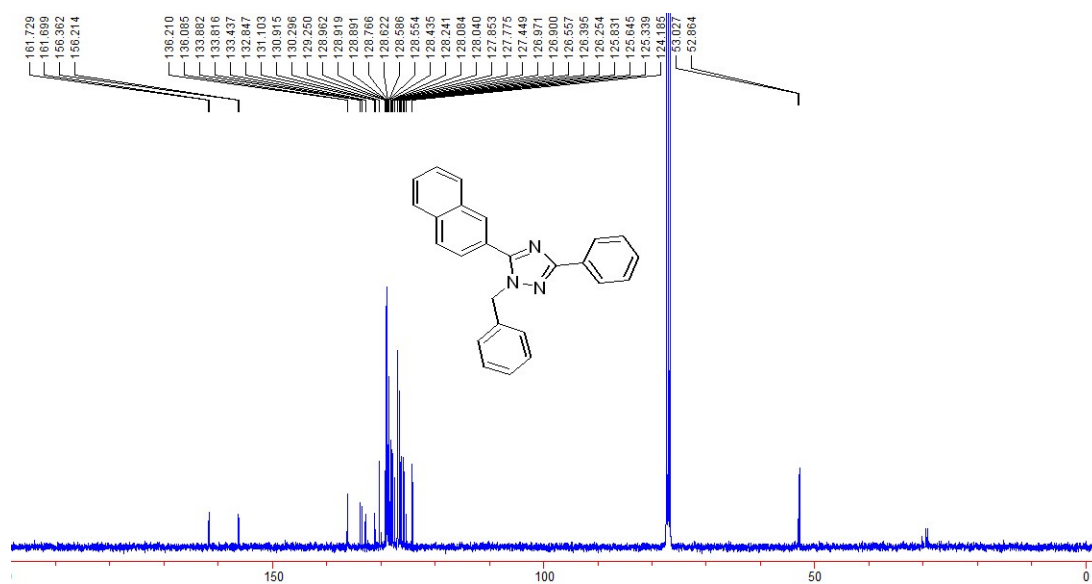
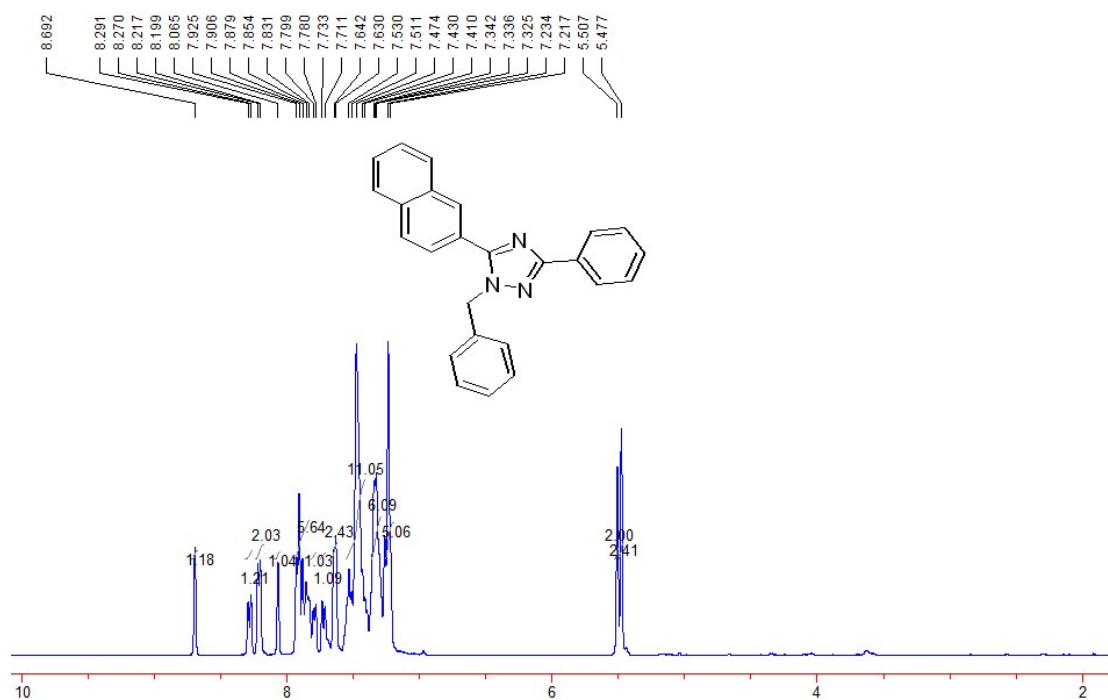
Chemical Structure: 1,3,5-trimethyl-2-((benzylideneamino)benzyl)-1H-1,2,4-triazole

¹H NMR Data (CDCl₃):

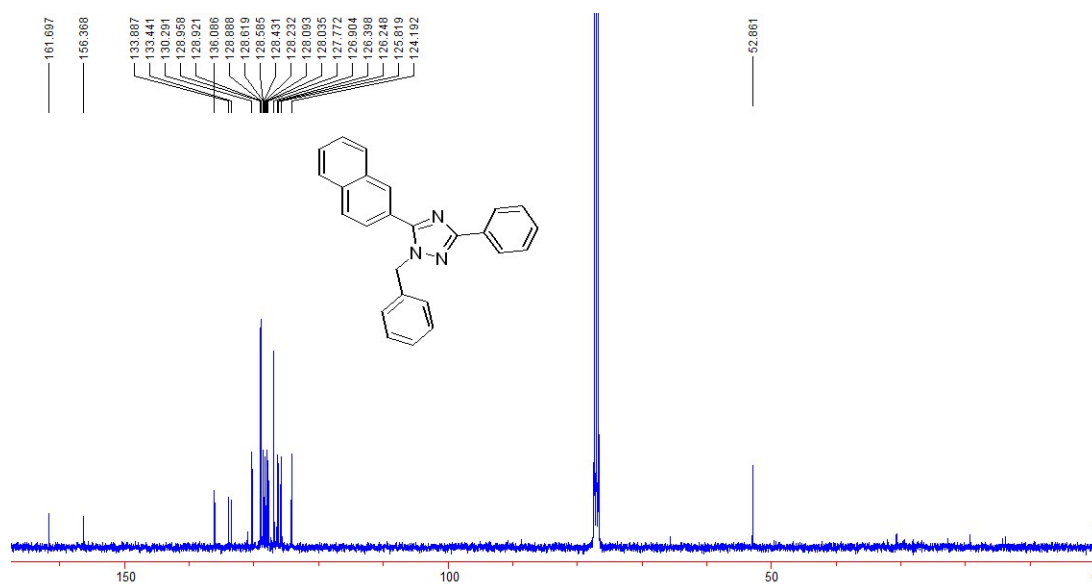
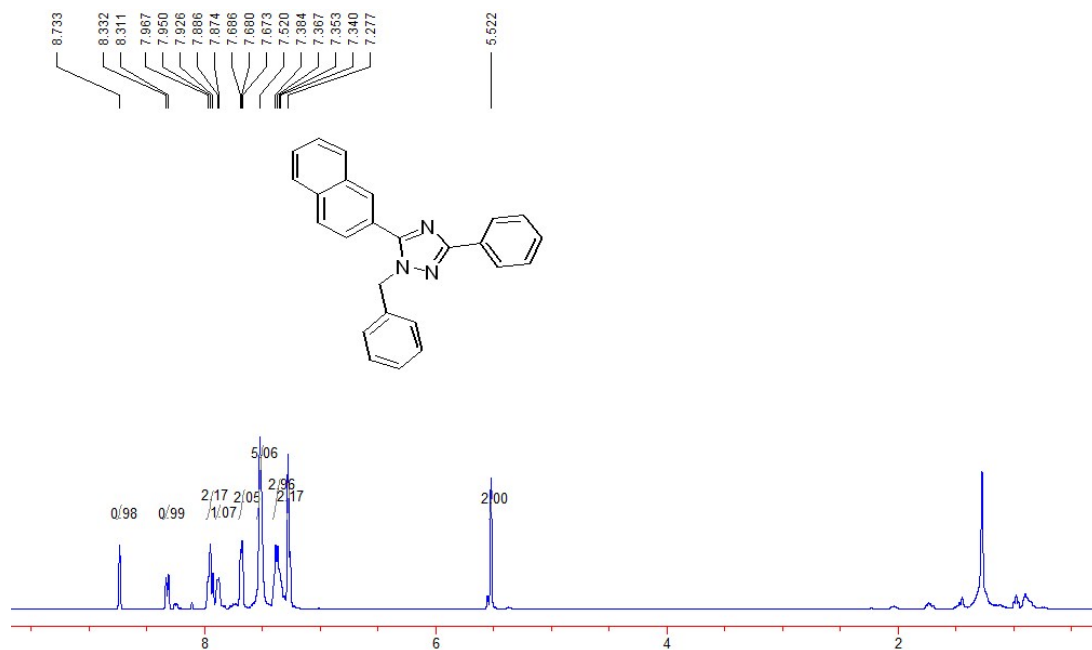
Chemical Shift (ppm)	Integration
8.214, 8.197	2.83
7.659	0.97
7.654	2.02
7.647	10.23
7.491	6.15
7.478	2.92
7.456	2.47
7.436	1.42
7.388	2.00
7.370	2.91
7.350	
7.284	
7.166	
7.148	
7.088	
7.005	
5.480	
5.224	
2.642	2.96
2.302	10.42
2.222	4.45
2.106	4.44



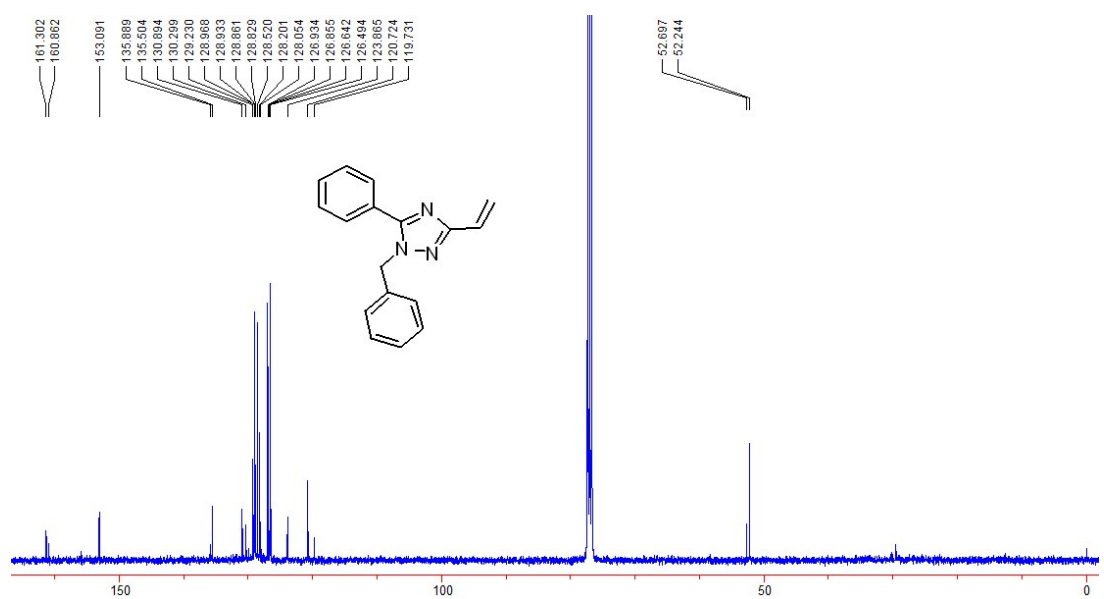
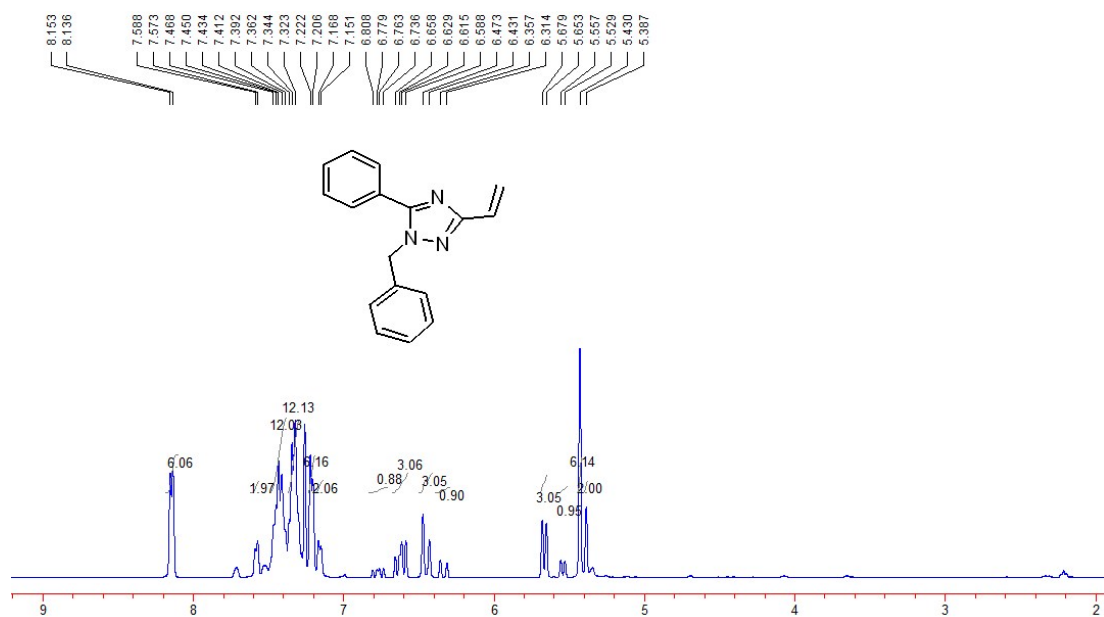
^1H and ^{13}C -NMR spectra of **5n**.



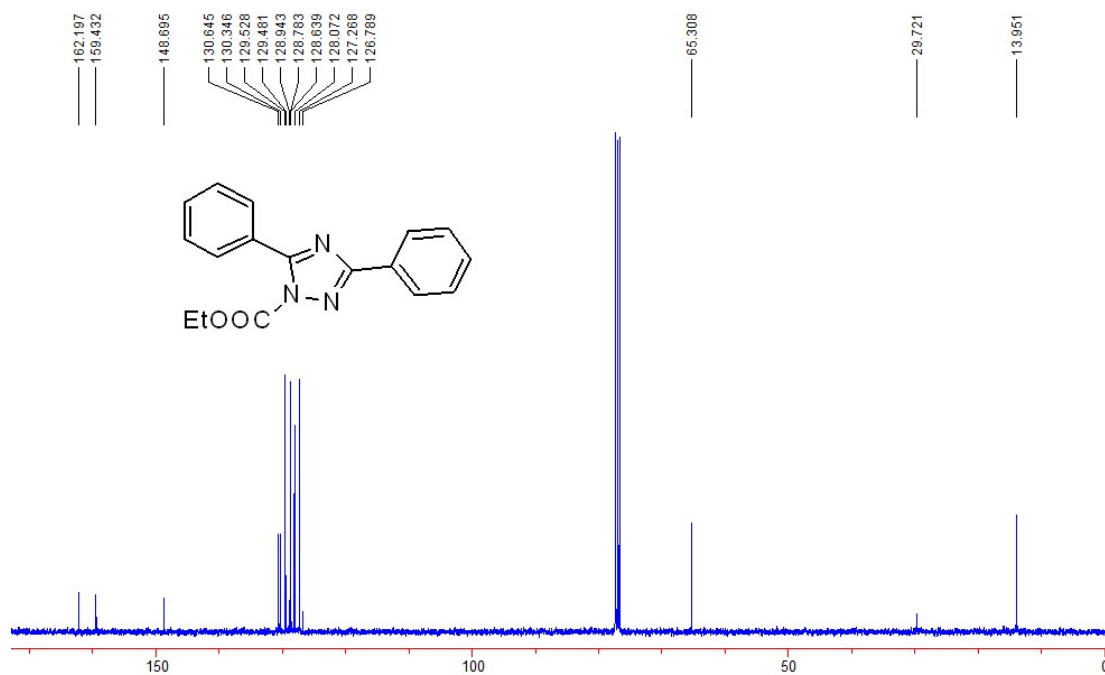
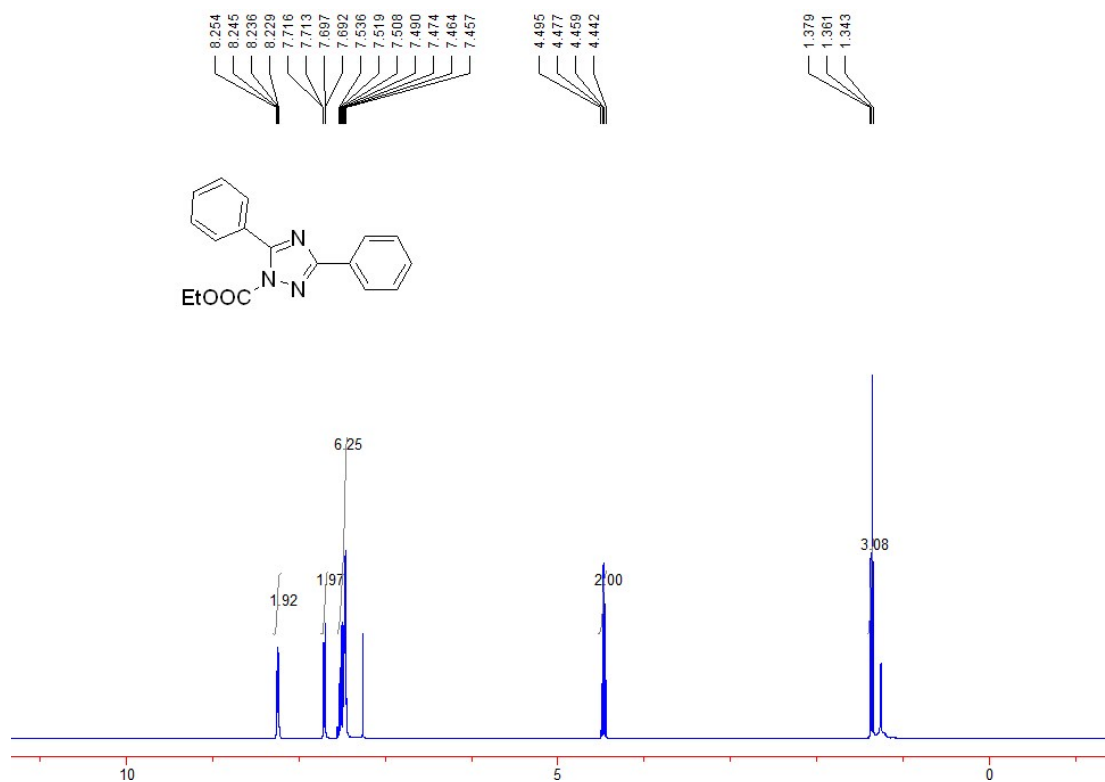
^1H and ^{13}C -NMR spectra of **5n**.



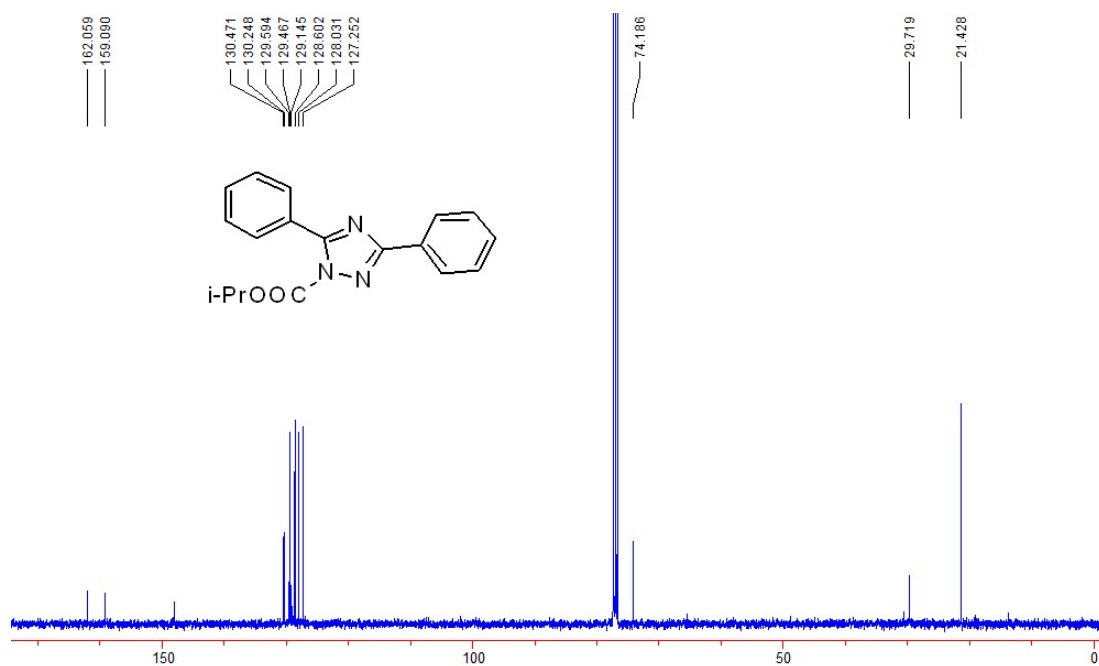
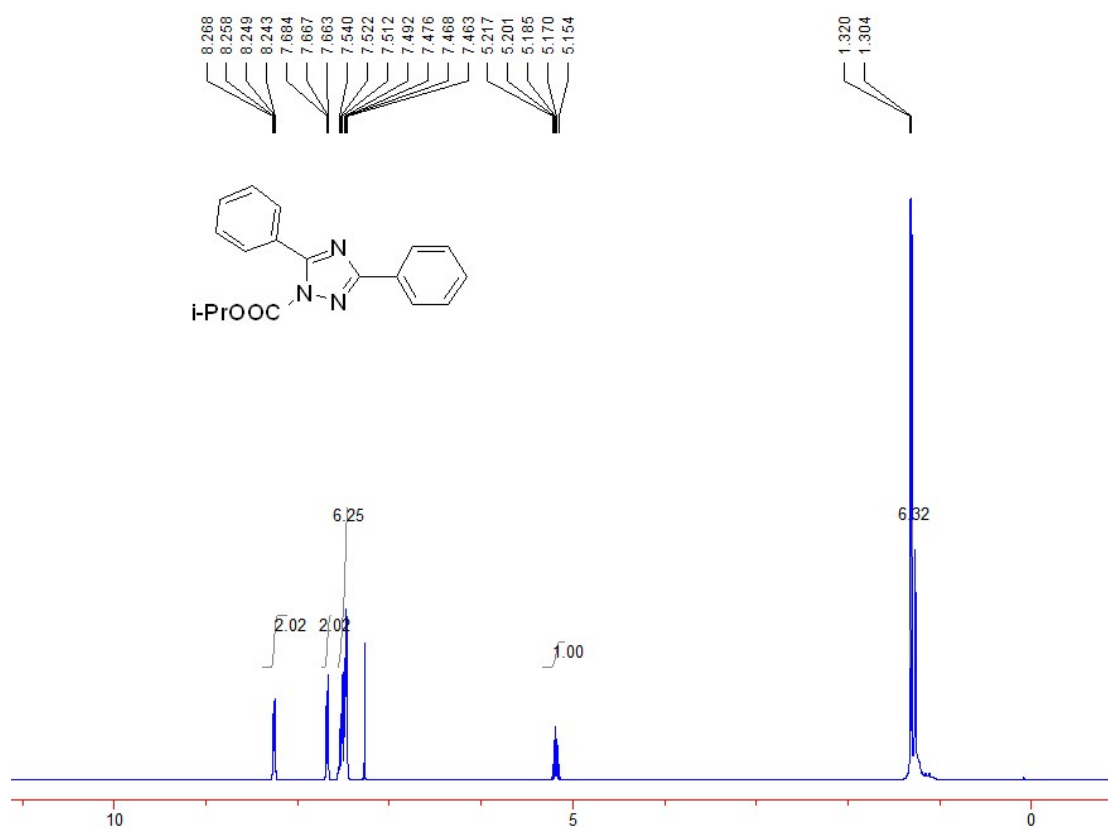
^1H and ^{13}C -NMR spectra of **5o**.



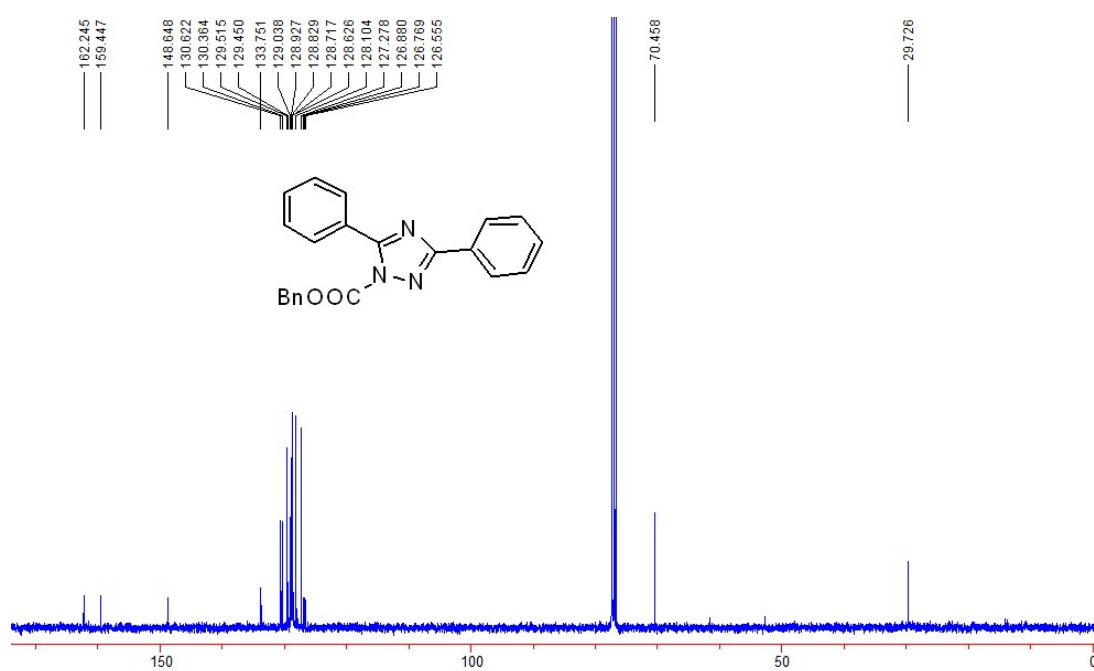
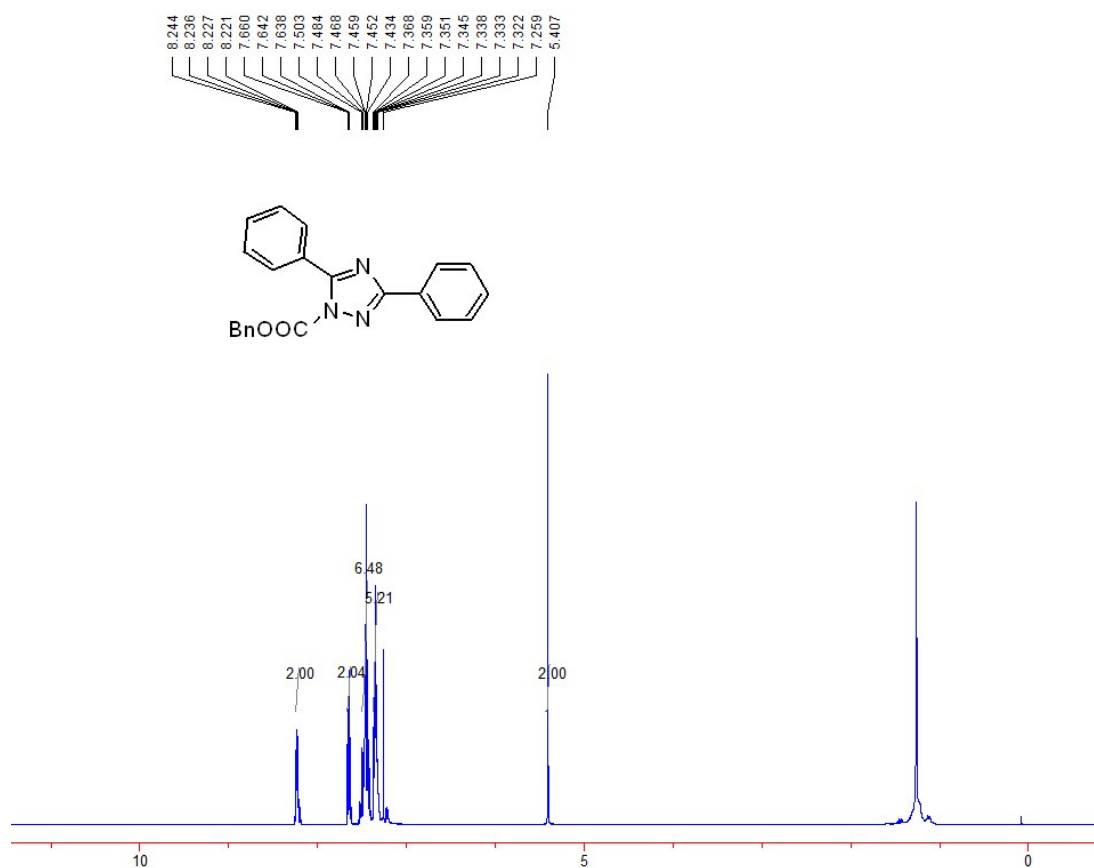
^1H and ^{13}C -NMR spectra of **6a**.



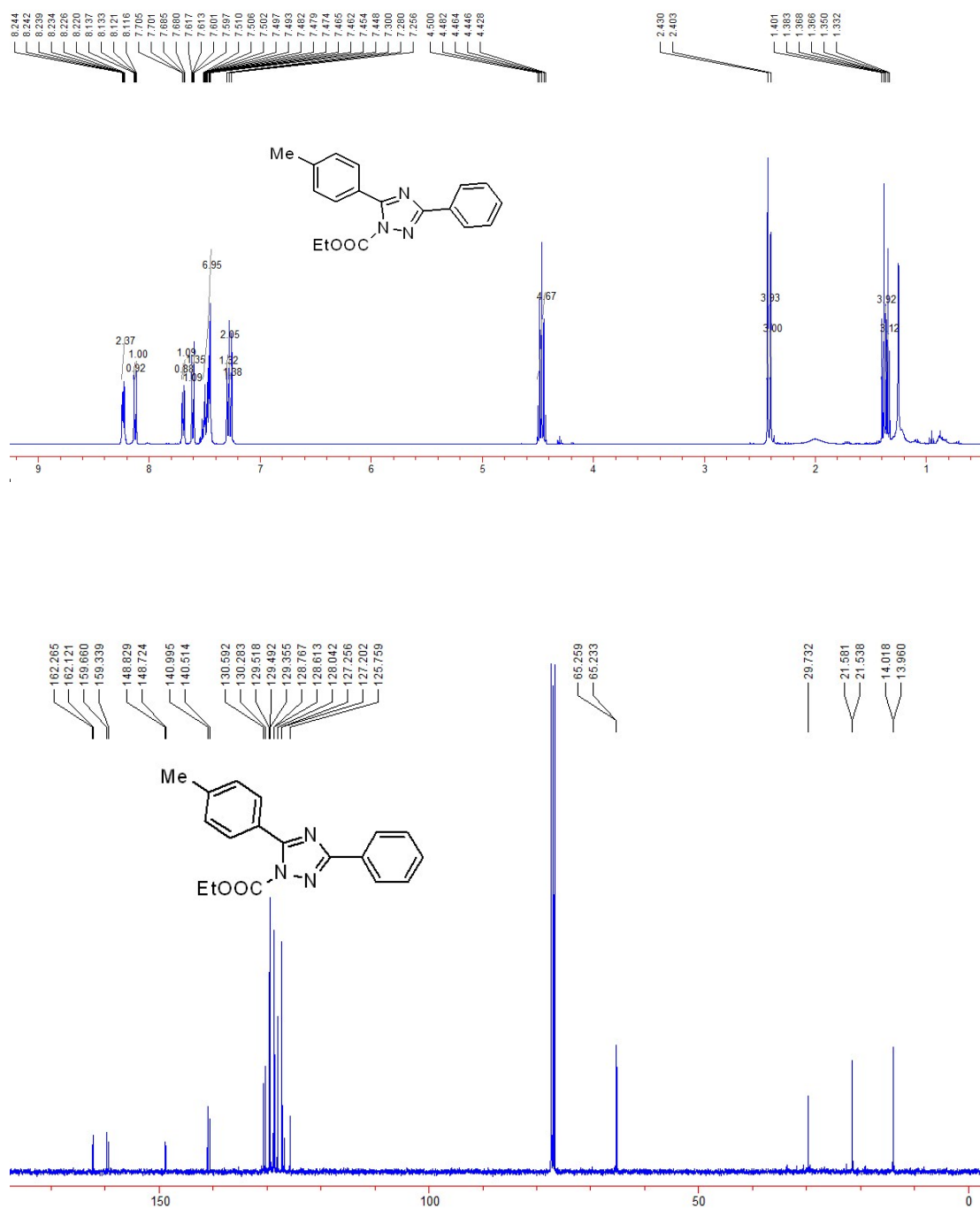
^1H and ^{13}C -NMR spectra of **6b**.



^1H and ^{13}C -NMR spectra of **6c**.

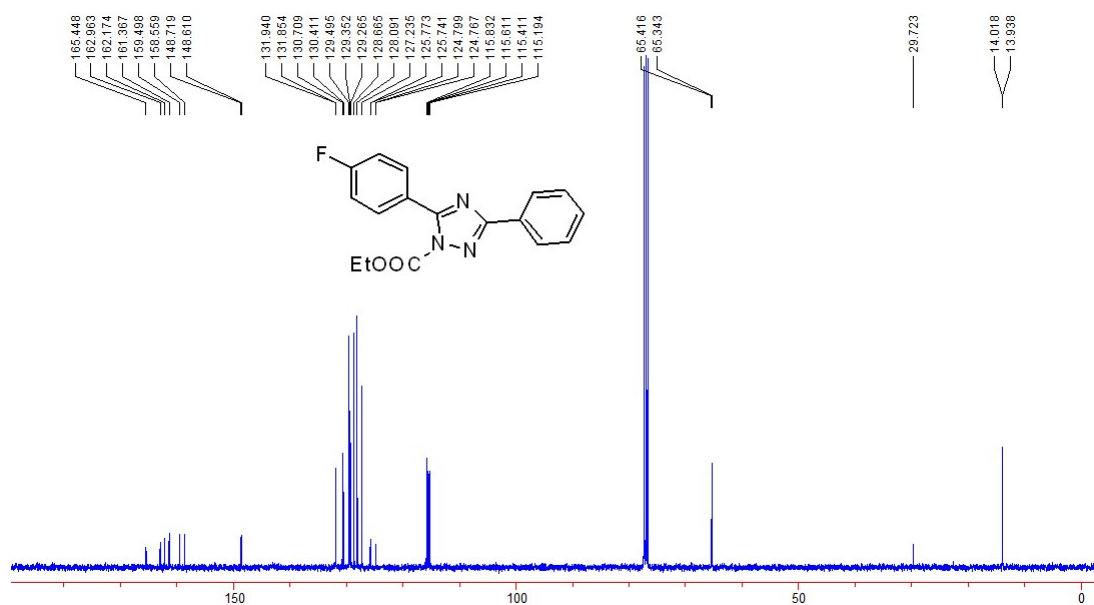


^1H and ^{13}C -NMR spectra of **6d**.

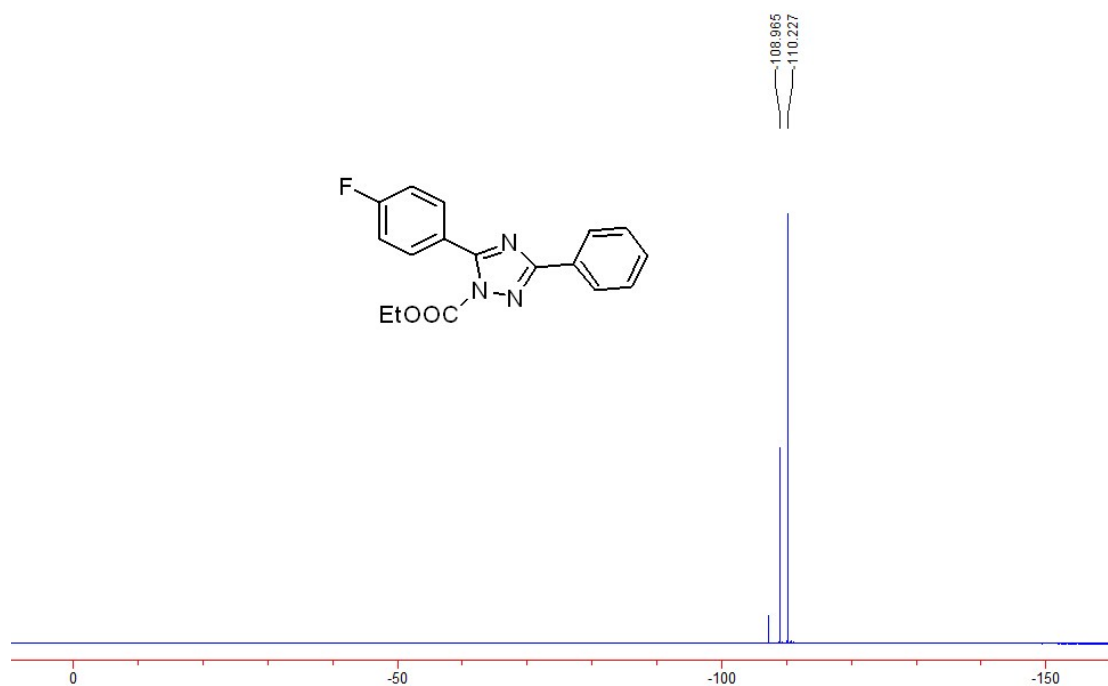


Chemical structure: CCOC(=O)c1nn(C2=CC=CC=C2)c(C3=CC=C(C=C3)F)n1

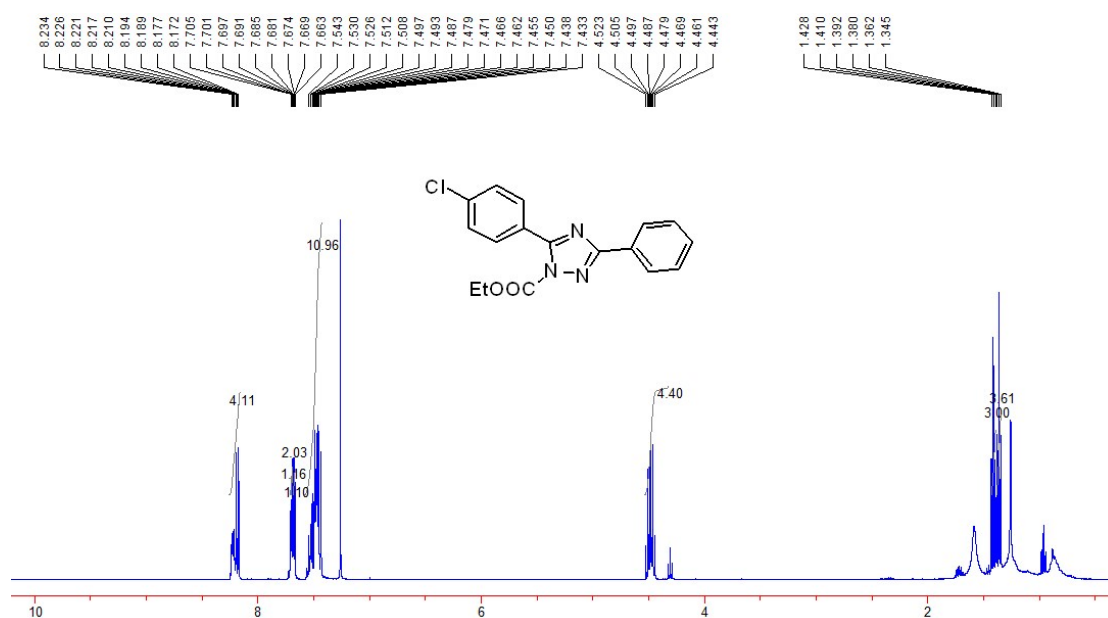
¹H NMR spectrum (CDCl₃) showing peaks at 8.249, 8.244, 8.236, 8.227, 8.218, 8.213, 7.752, 7.739, 7.735, 7.730, 7.717, 7.701, 7.684, 7.680, 7.536, 7.522, 7.519, 7.515, 7.507, 7.488, 7.482, 7.474, 7.465, 7.458, 7.204, 7.192, 7.169, 7.161, 7.148, 7.126, 4.512, 4.494, 4.488, 4.476, 4.470, 4.456, 4.452, 4.434, 1.414, 1.397, 1.379, 1.372, 1.354, and 1.336 ppm.

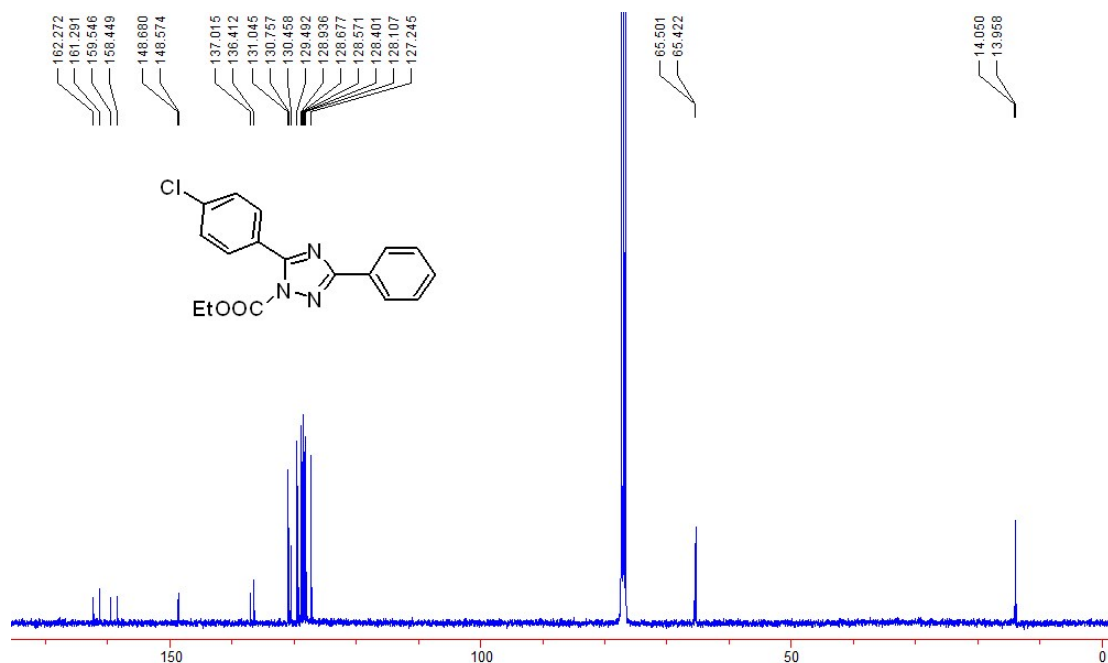


^{19}F -NMR spectra of **6e**.

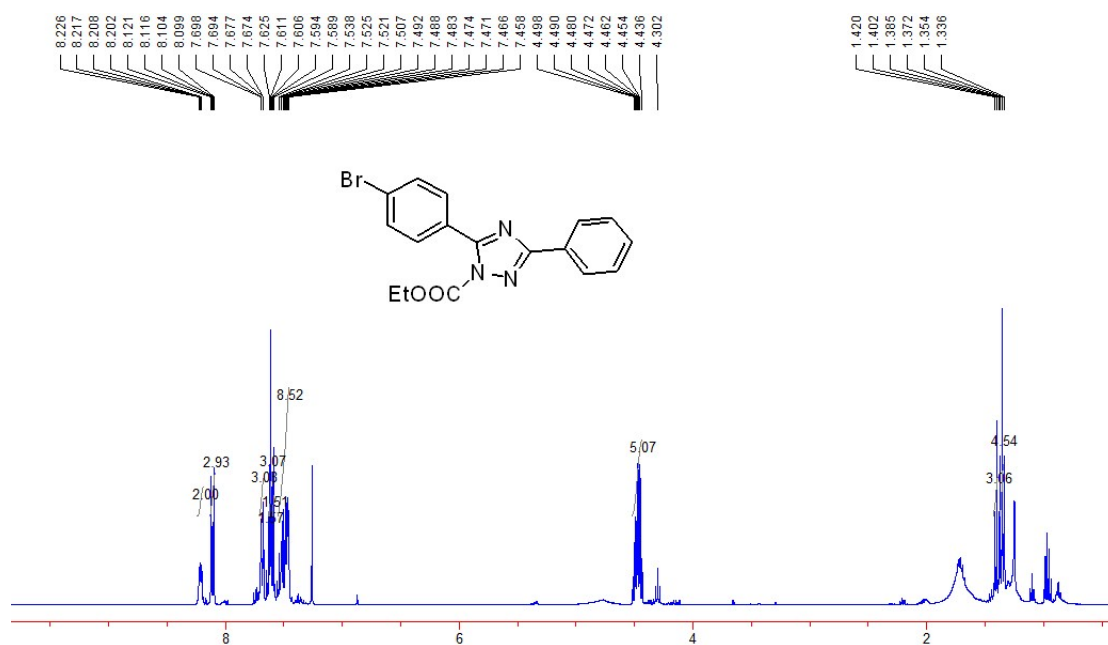


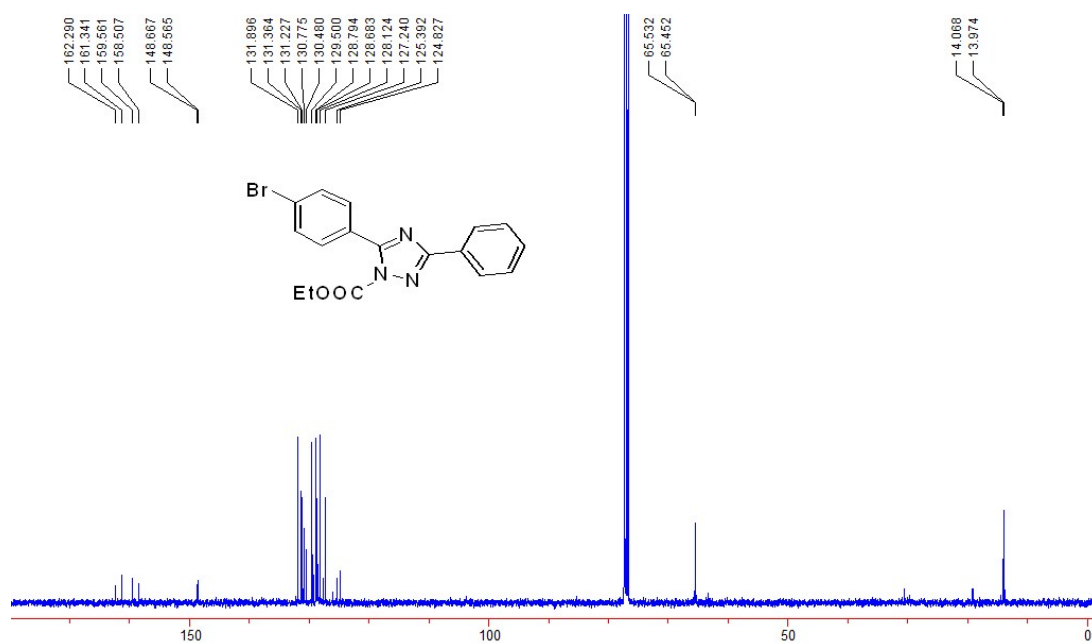
^1H and ^{13}C -NMR spectra of **6f**.



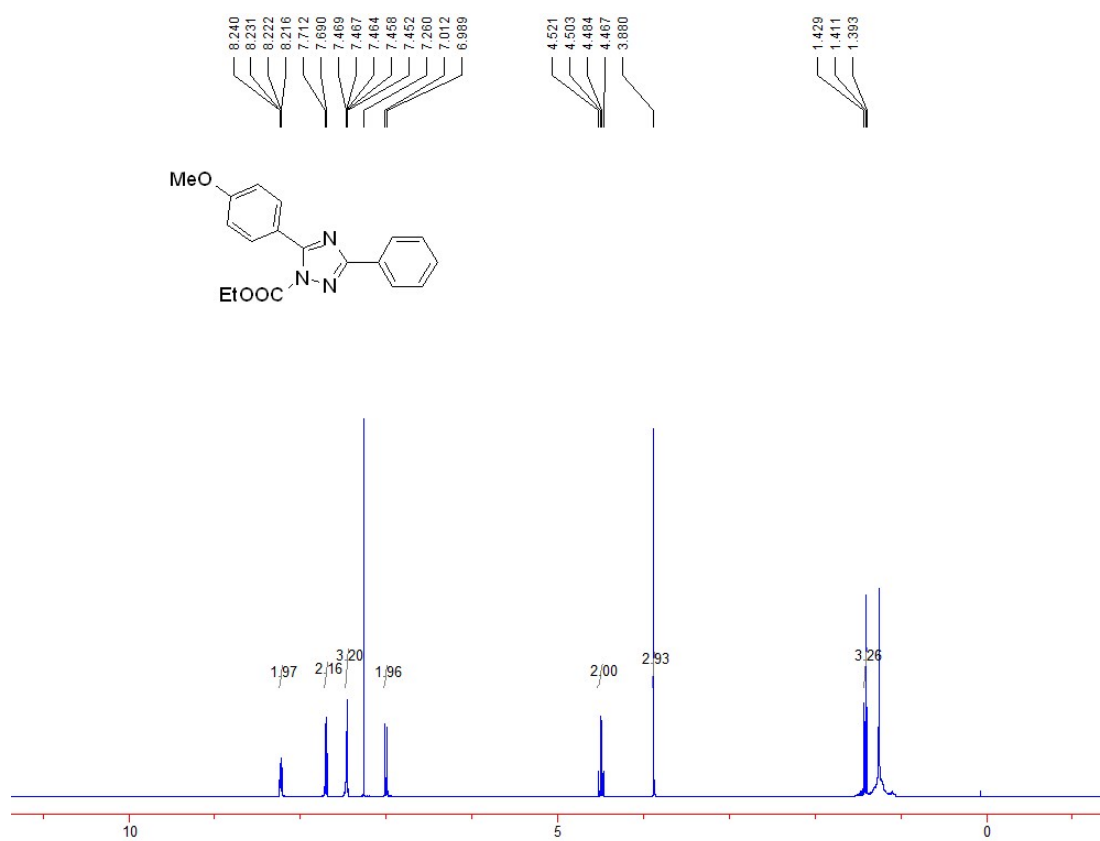


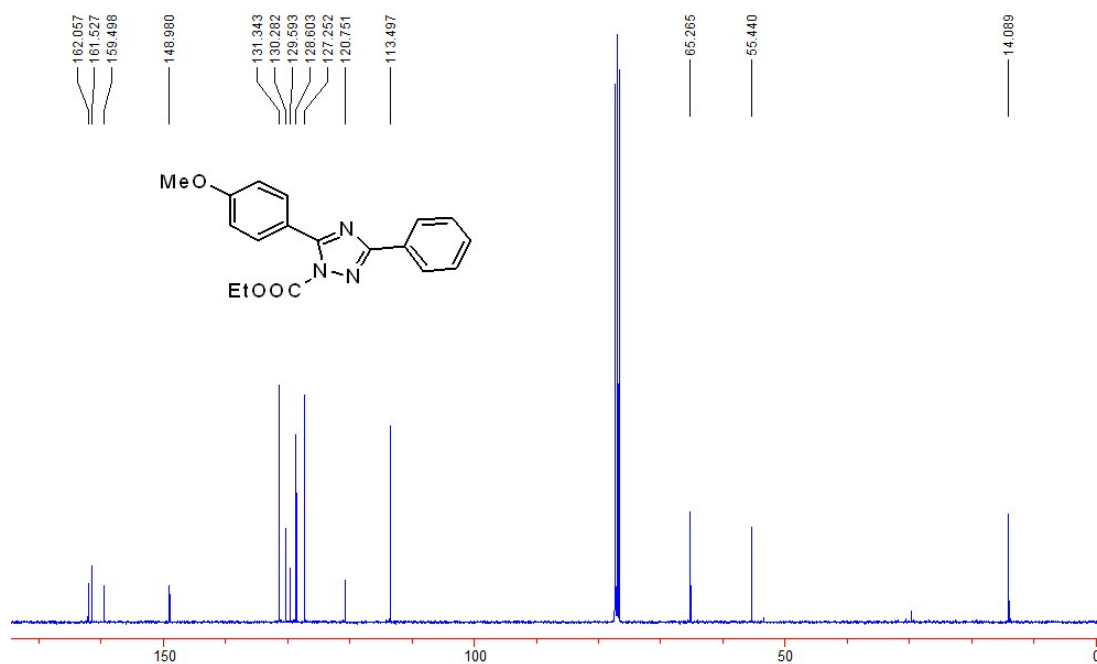
¹H and ¹³C-NMR spectra of **6g**.



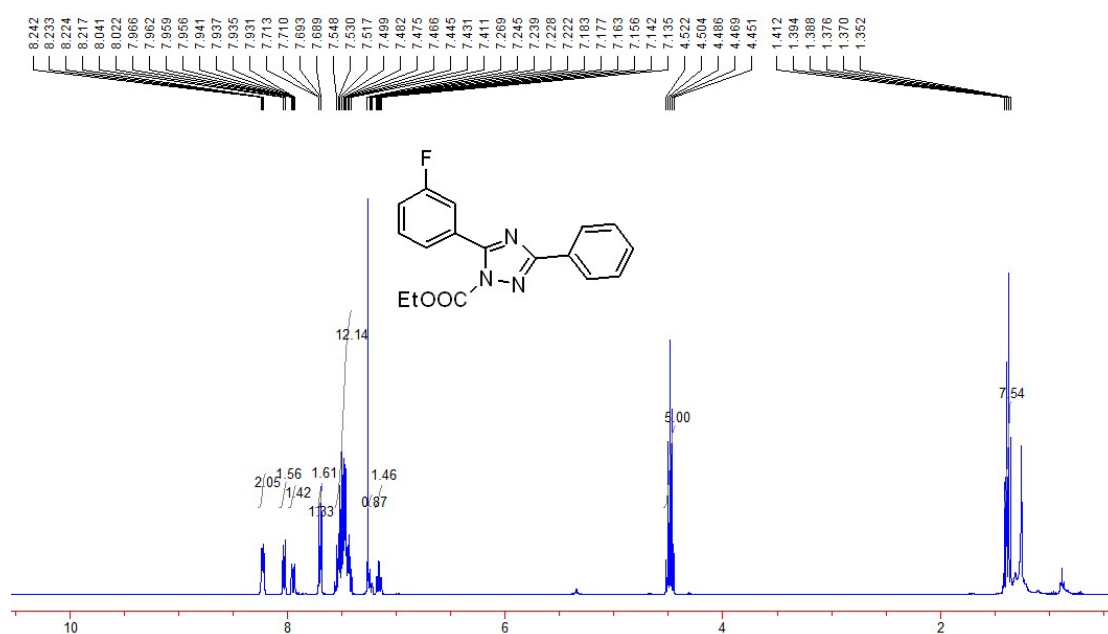


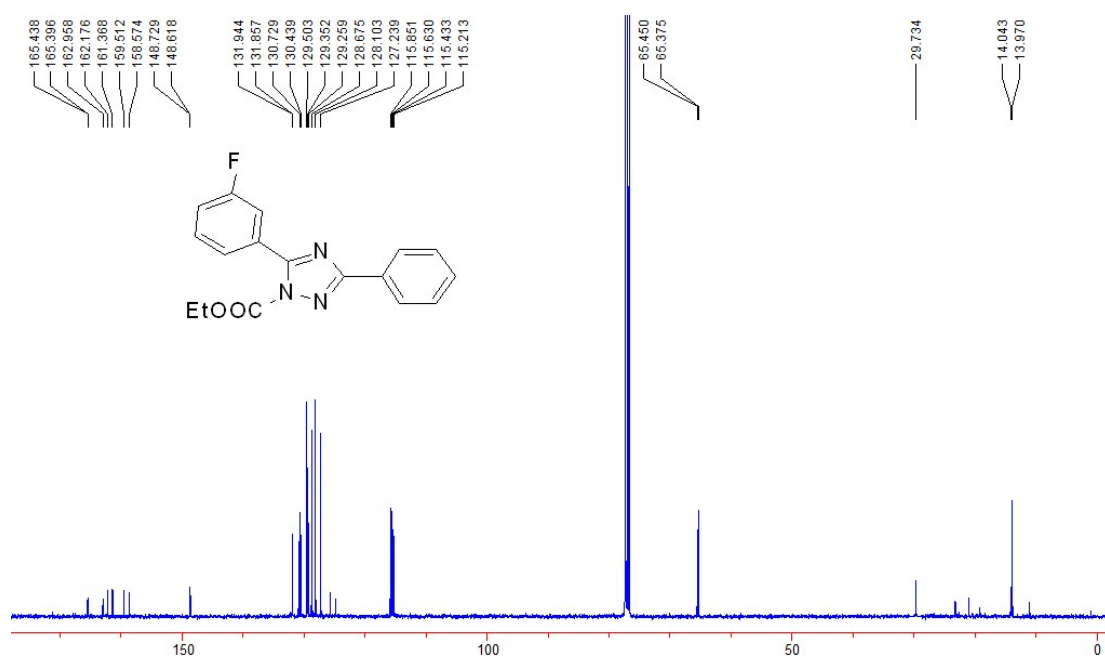
¹H and ¹³C-NMR spectra of **6h**.



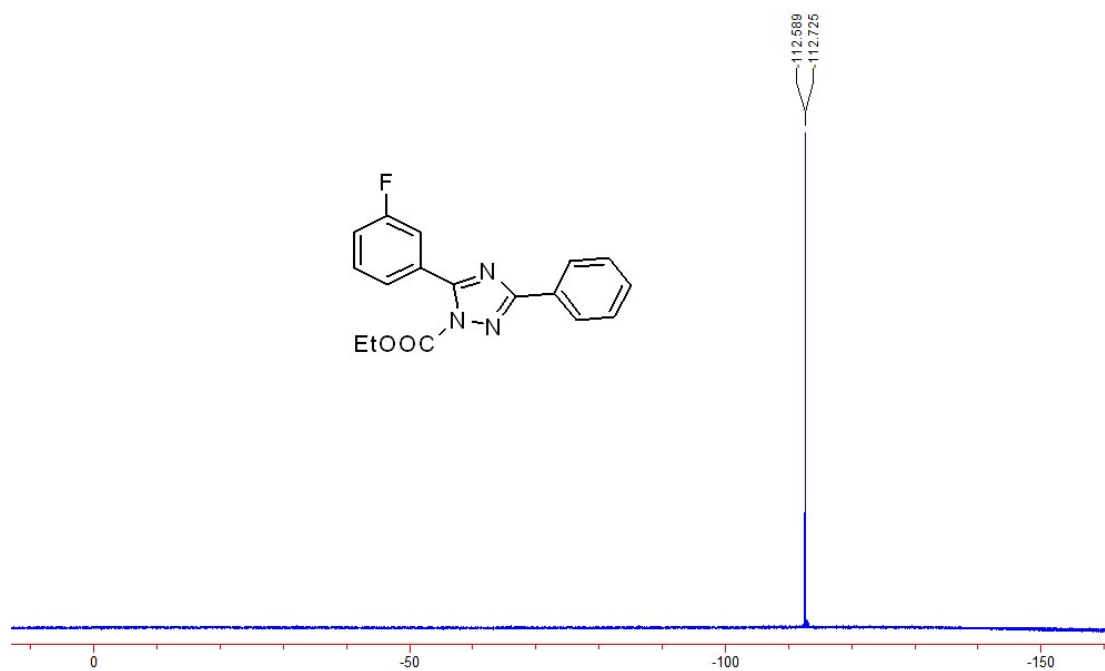


¹H and ¹³C-NMR spectra of **6i**.

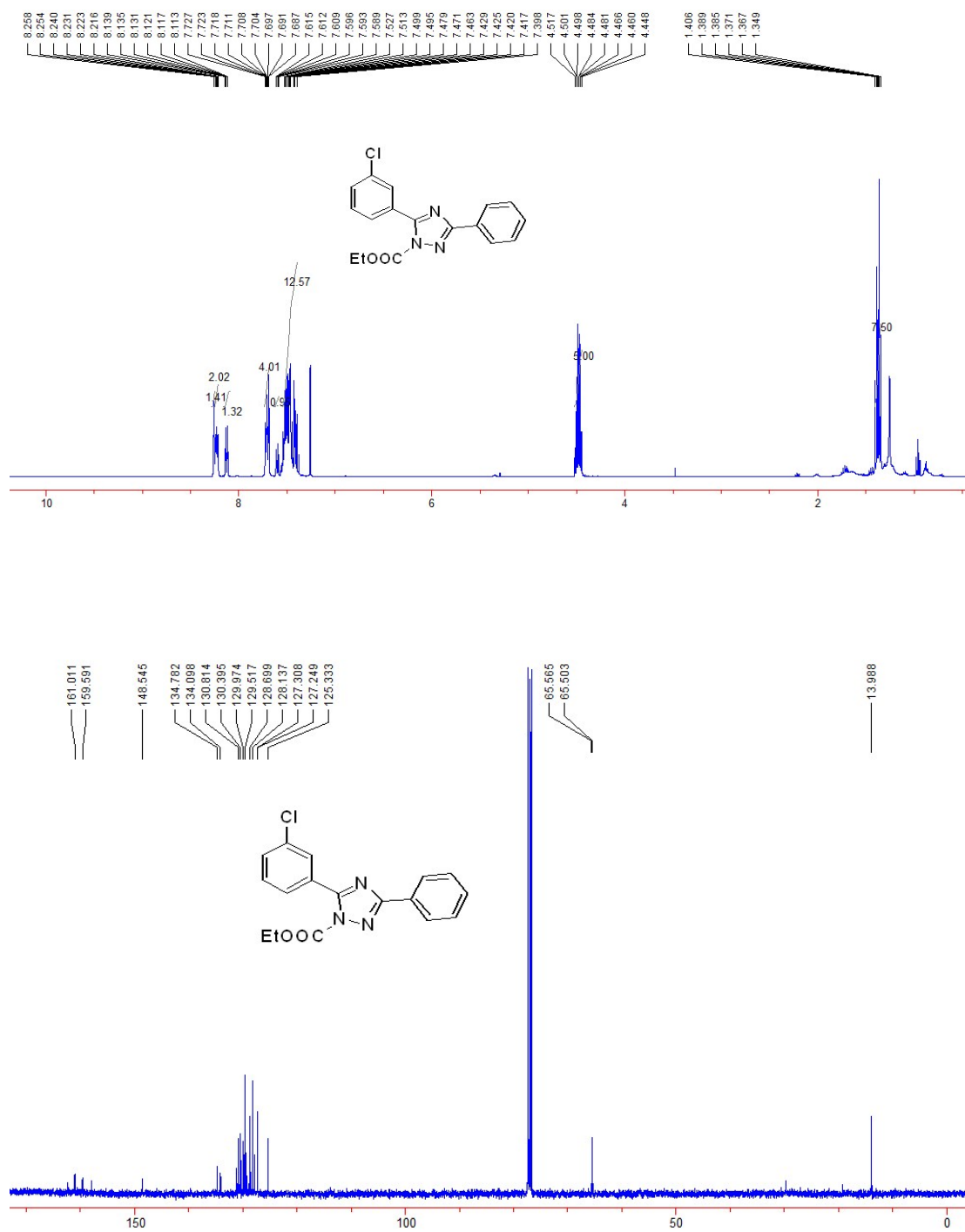




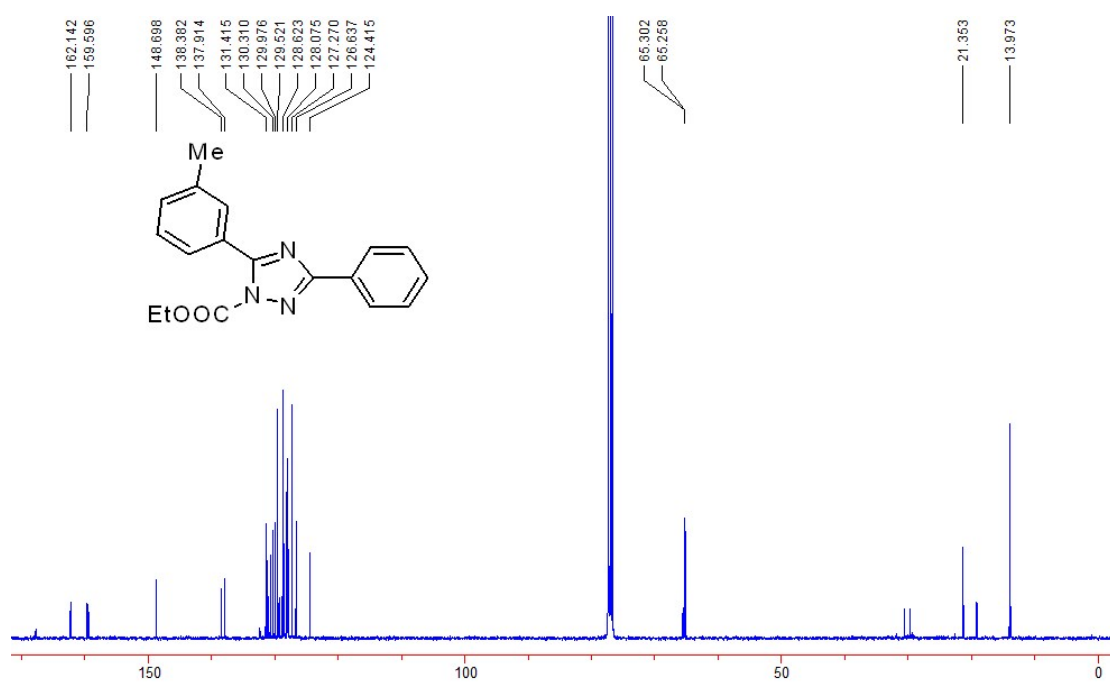
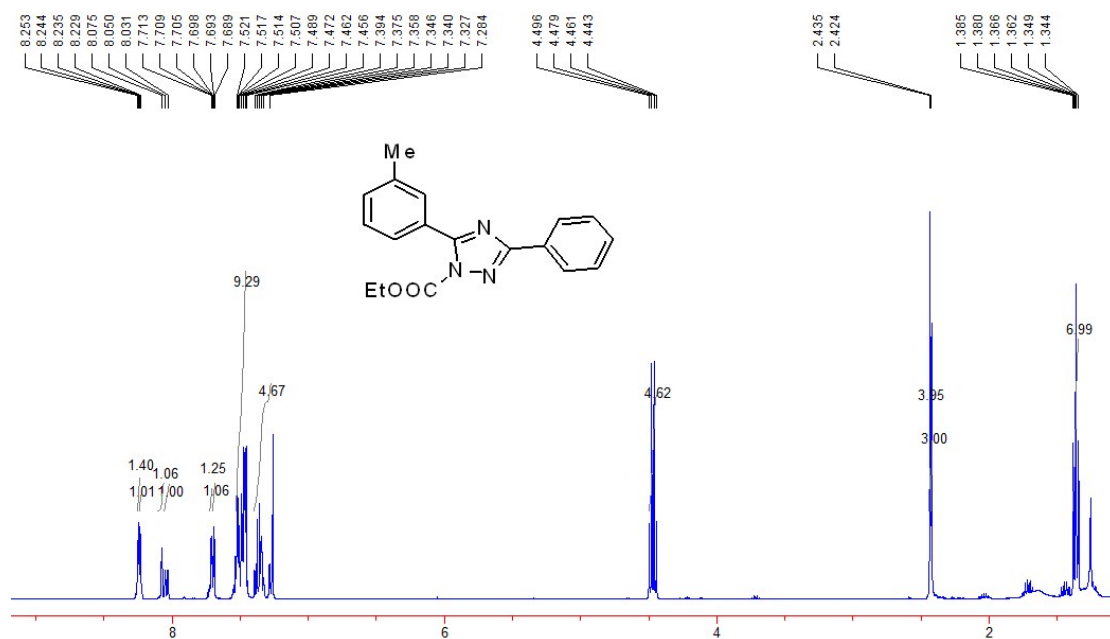
¹⁹F-NMR spectra of **6i**.



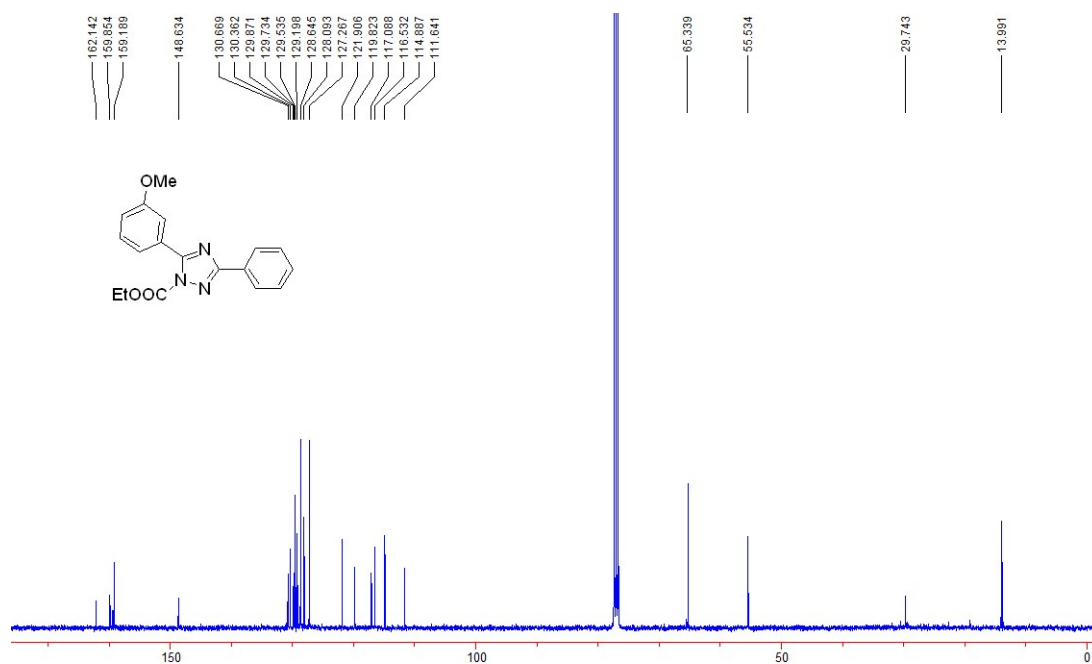
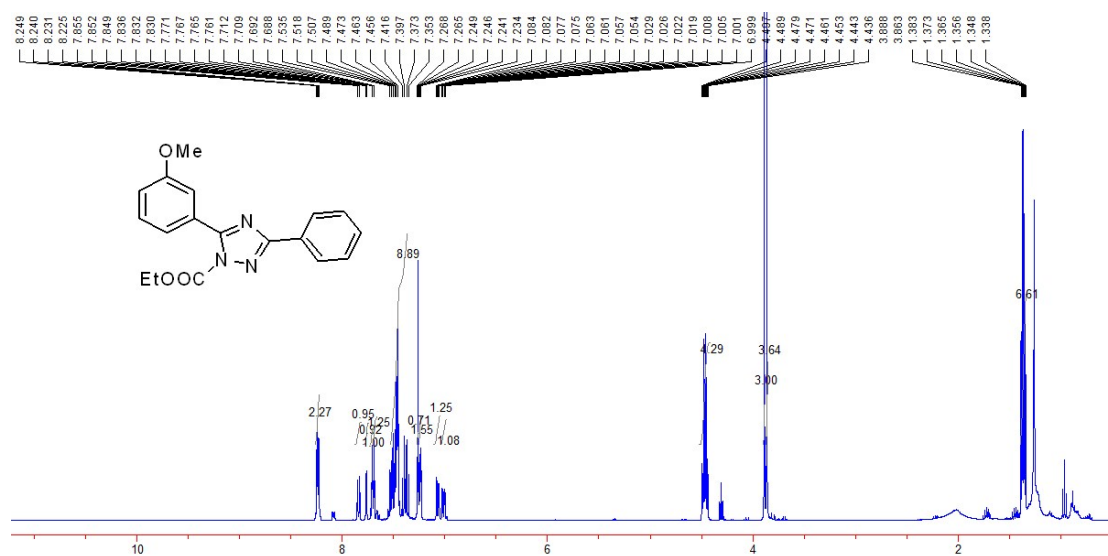
^1H and ^{13}C -NMR spectra of **6j**.



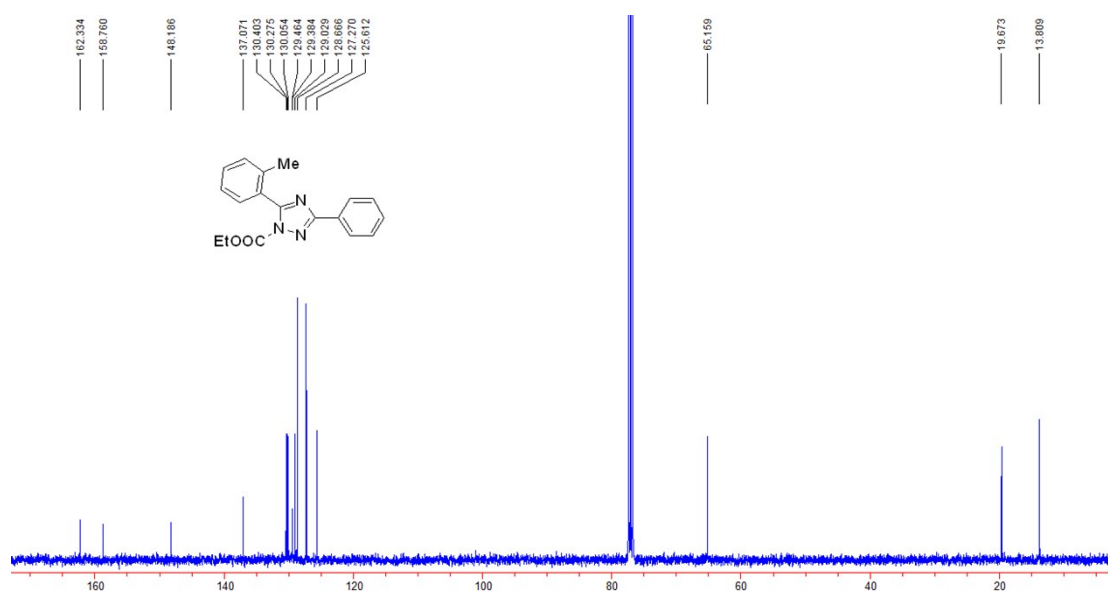
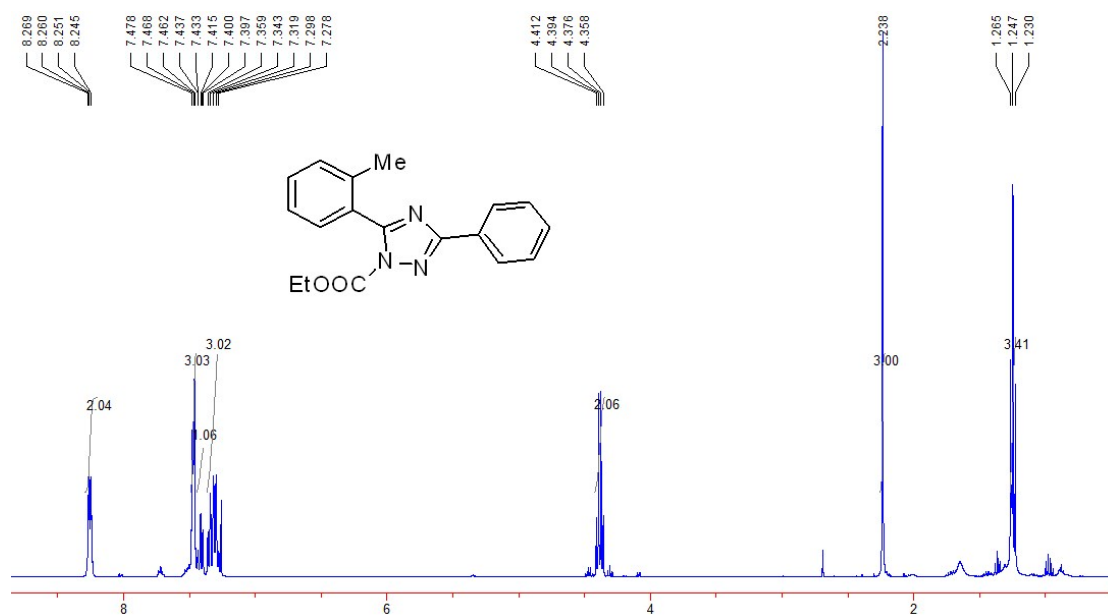
^1H and ^{13}C -NMR spectra of **6k**.



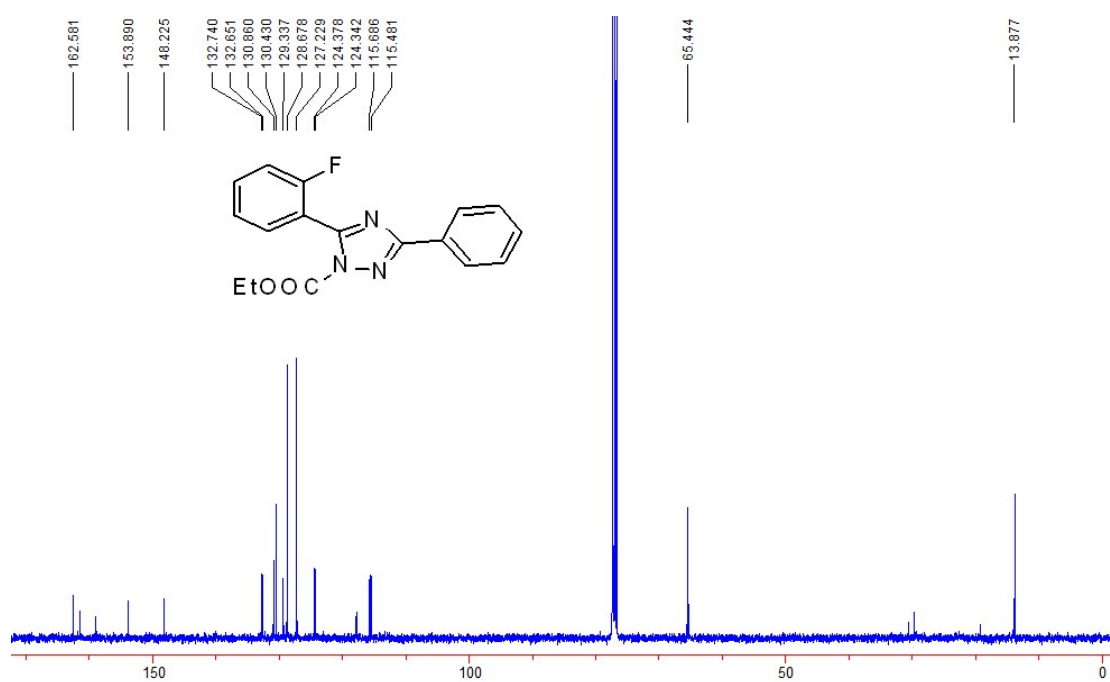
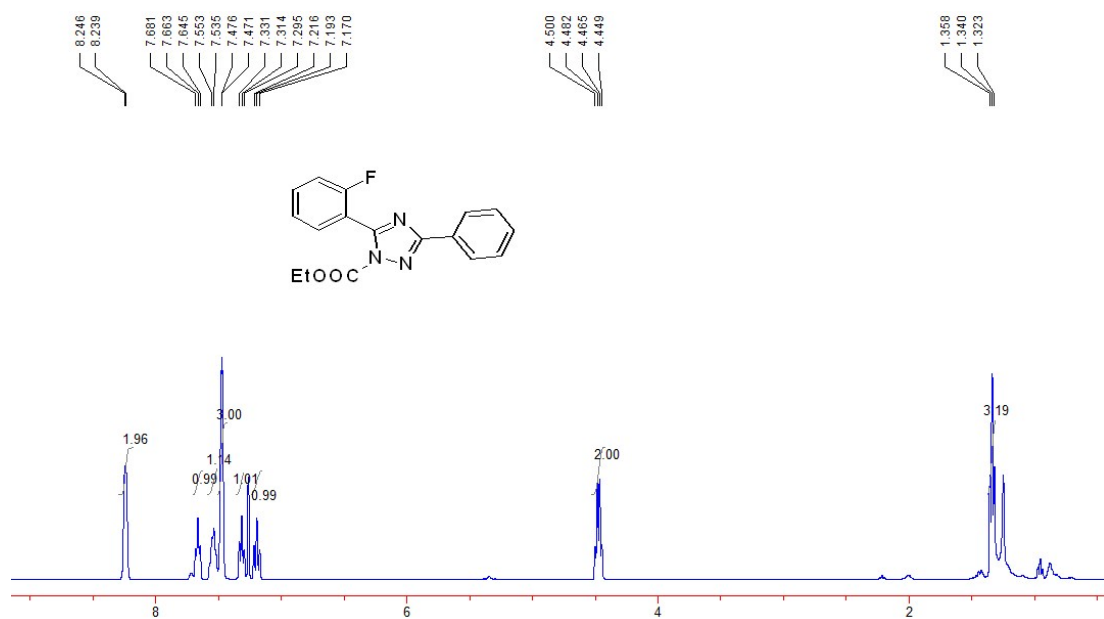
^1H and ^{13}C -NMR spectra of **6l**.



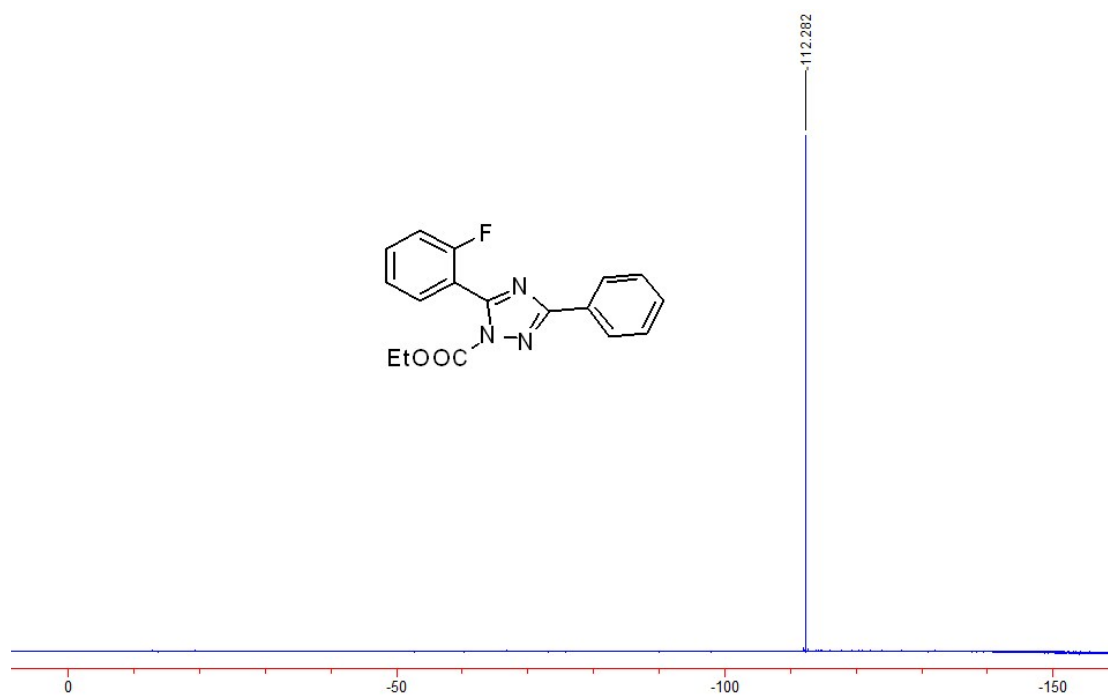
^1H and ^{13}C -NMR spectra of **6m**.



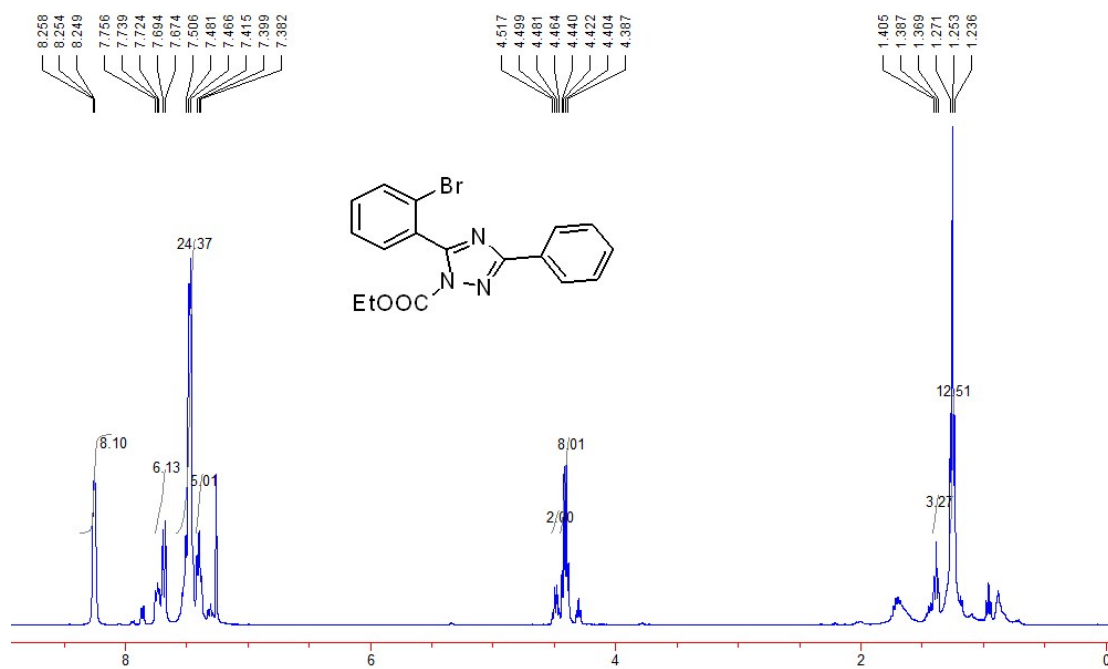
^1H and ^{13}C -NMR spectra of **6n**.

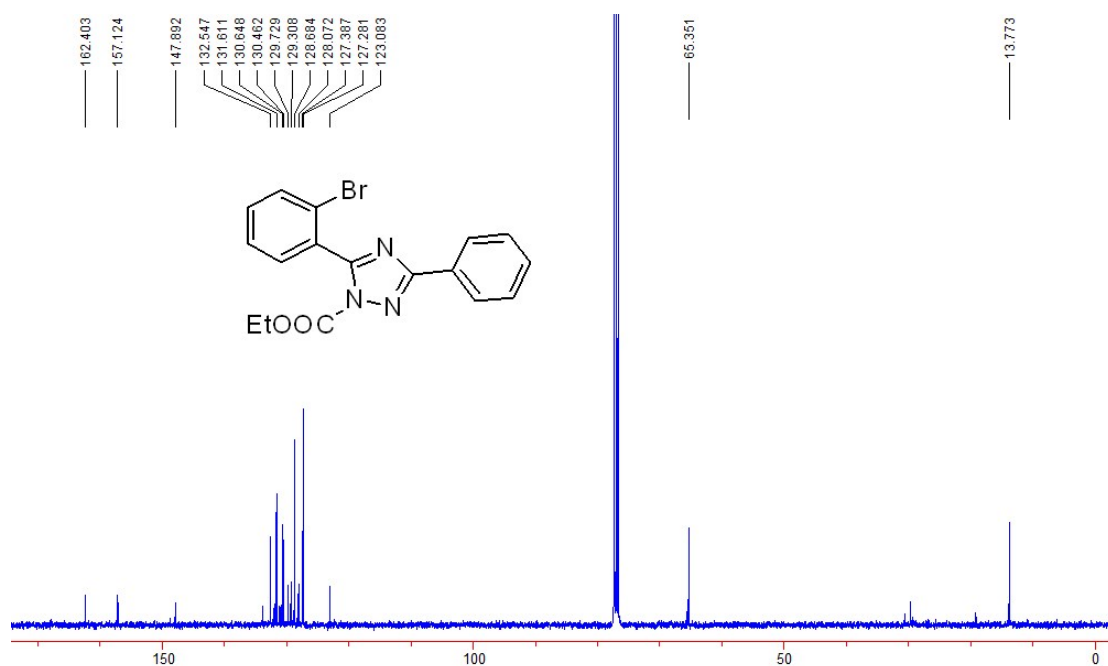


^{19}F -NMR spectra of **6n**.

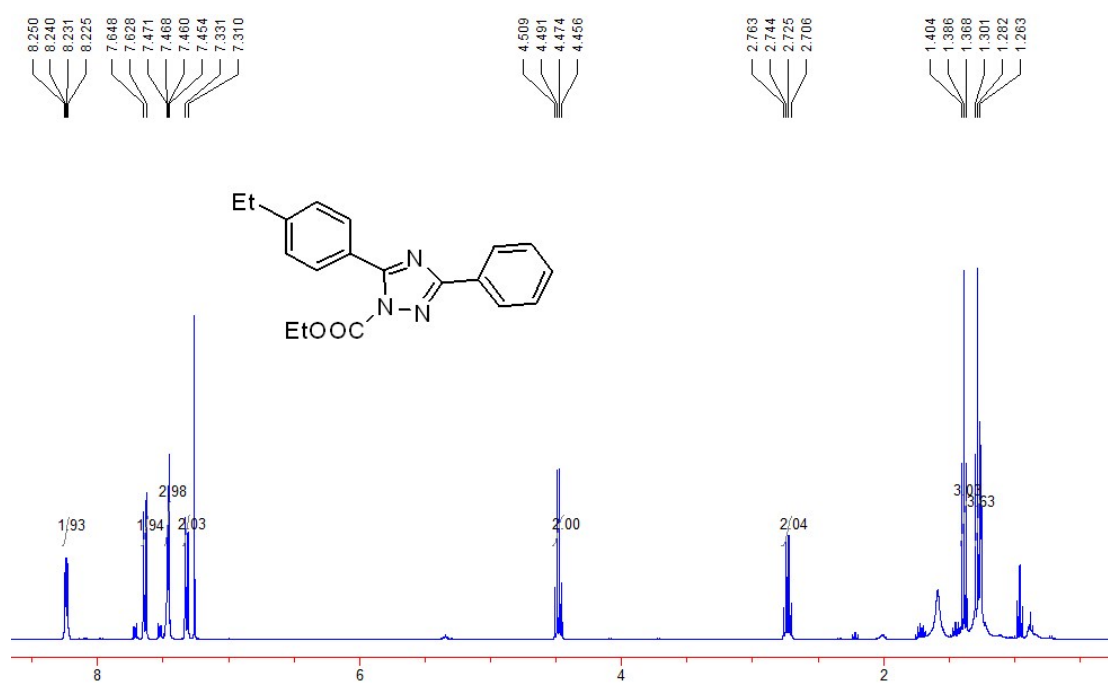


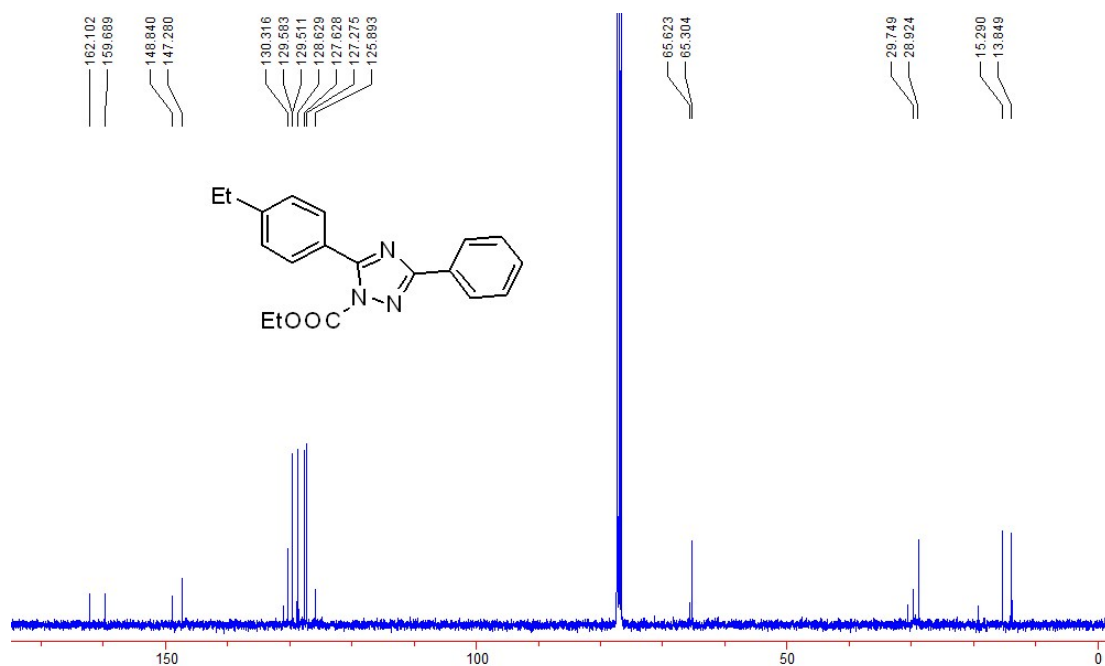
^1H and ^{13}C -NMR spectra of **6o**.



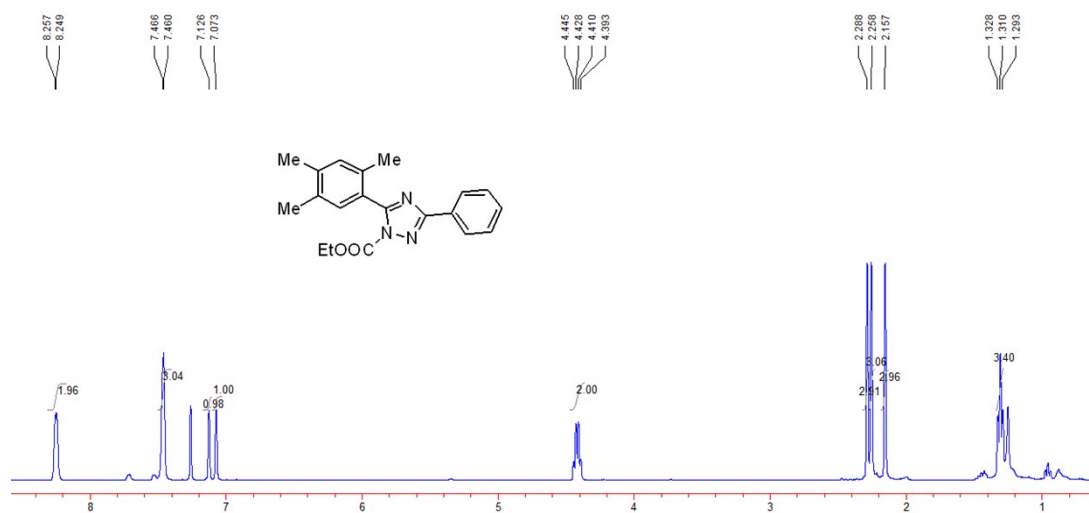


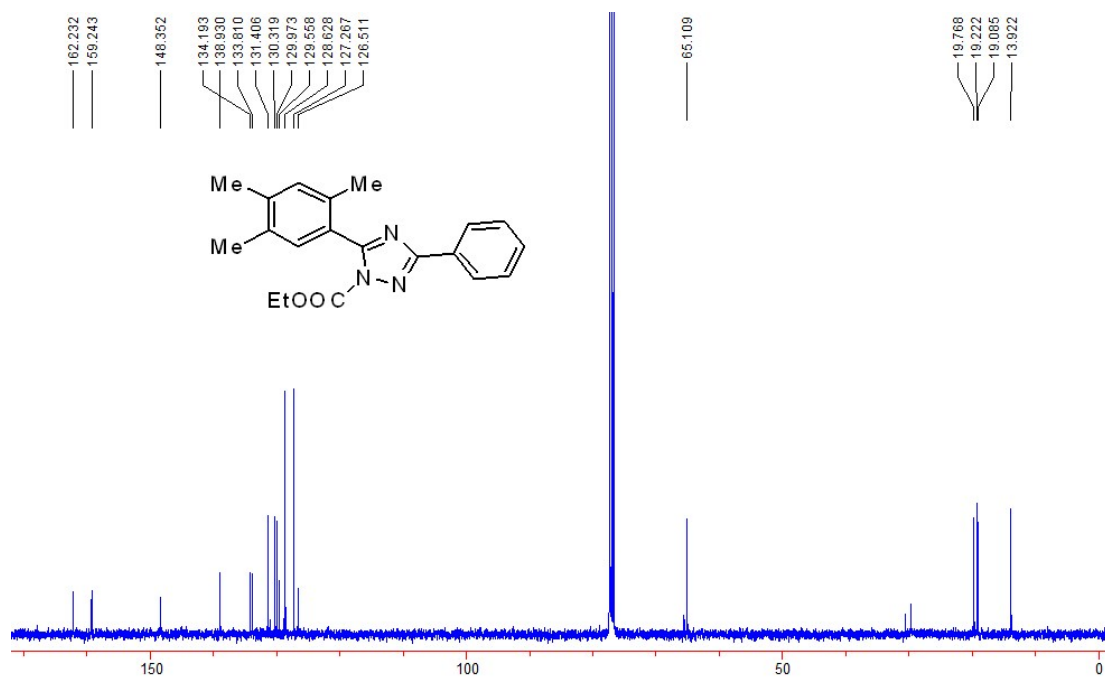
¹H and ¹³C-NMR spectra of **6p**.



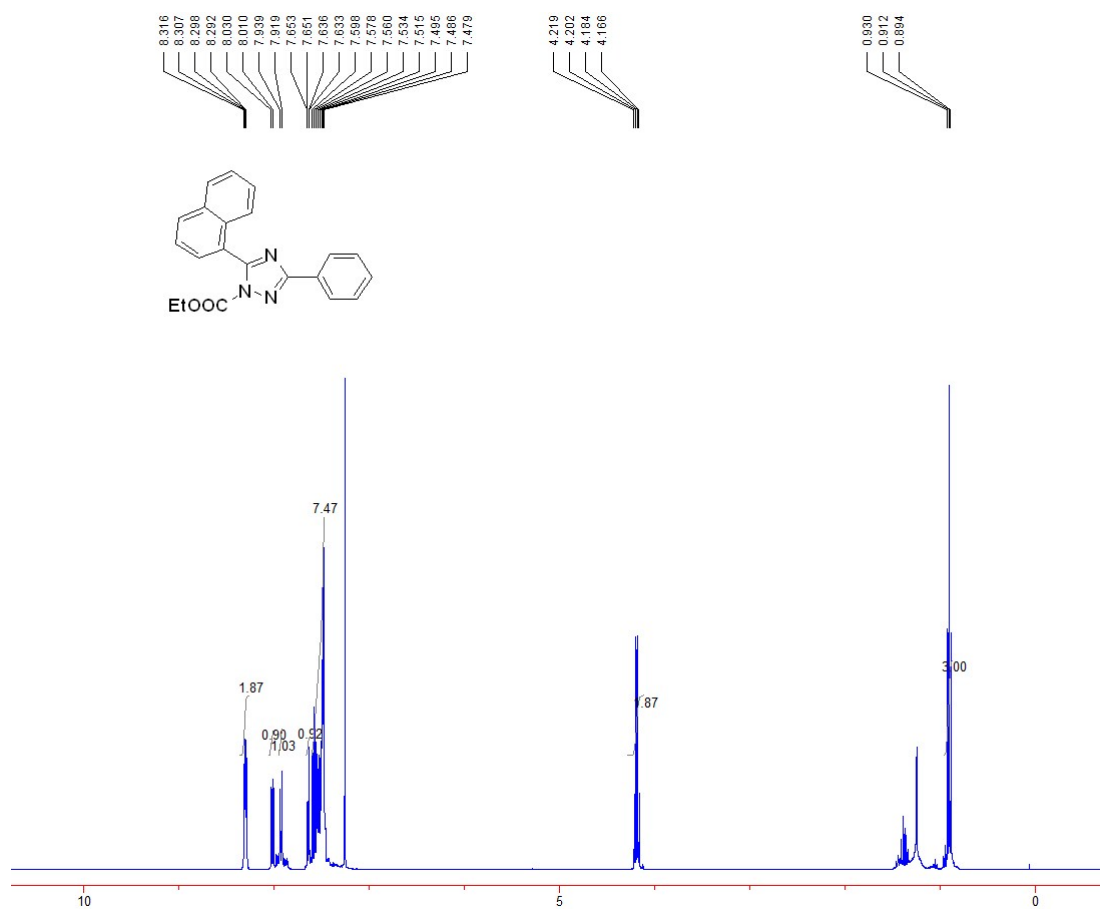


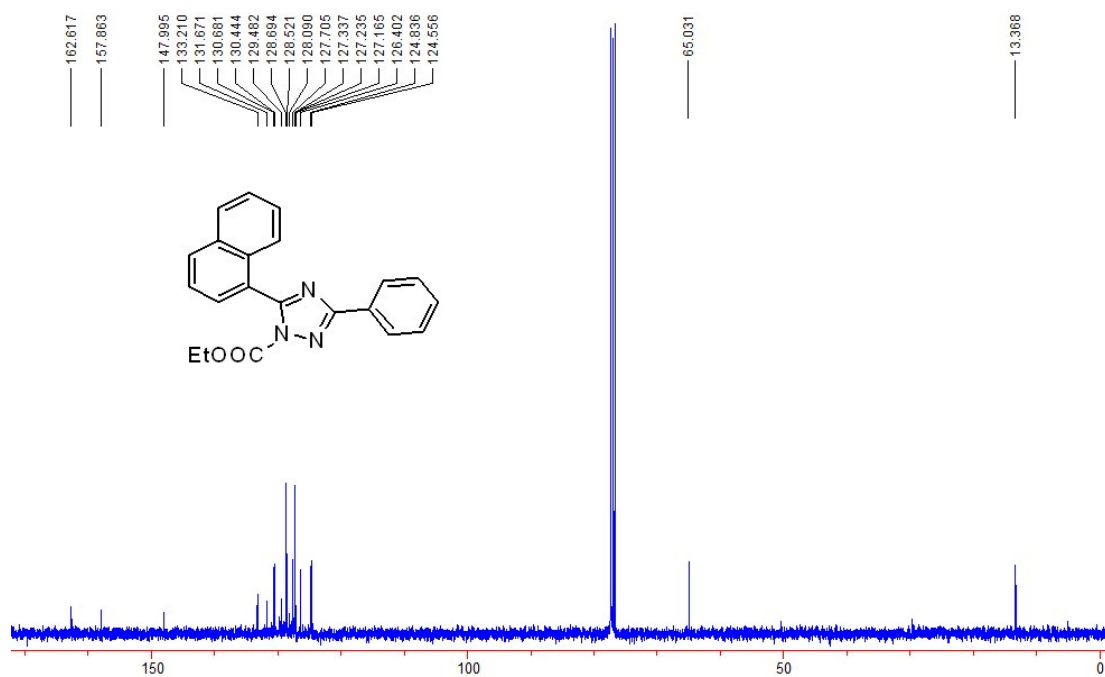
¹H and ¹³C-NMR spectra of **6q**.



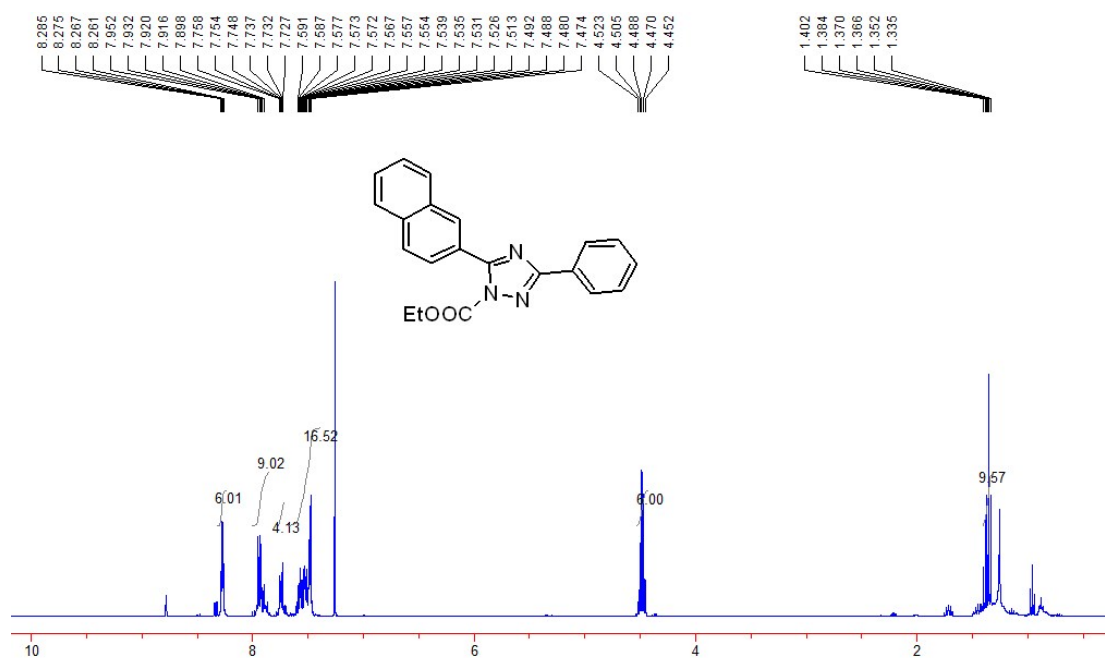


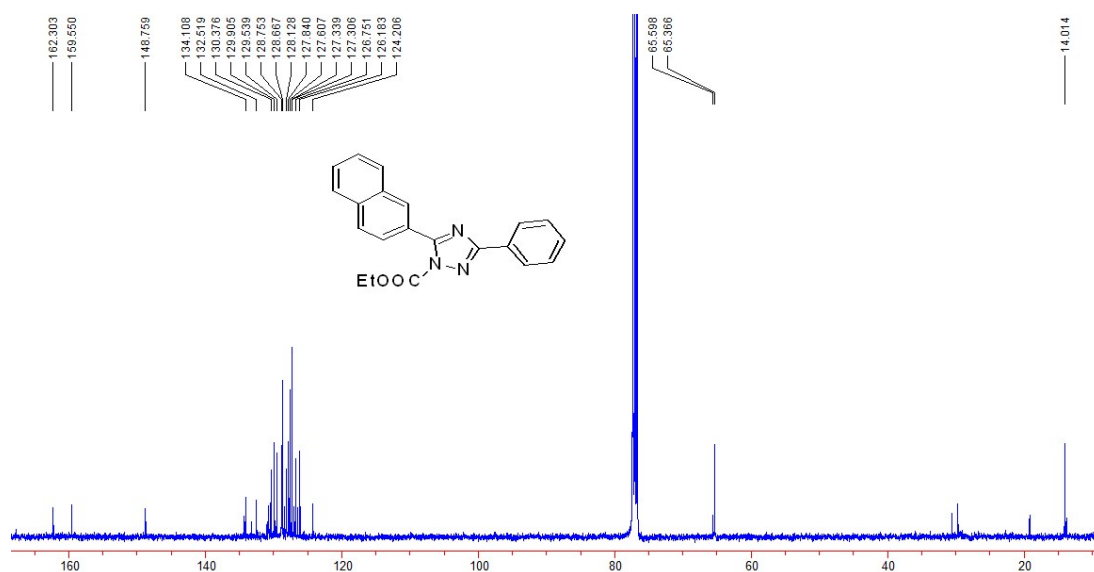
¹H and ¹³C-NMR spectra of **6r**.



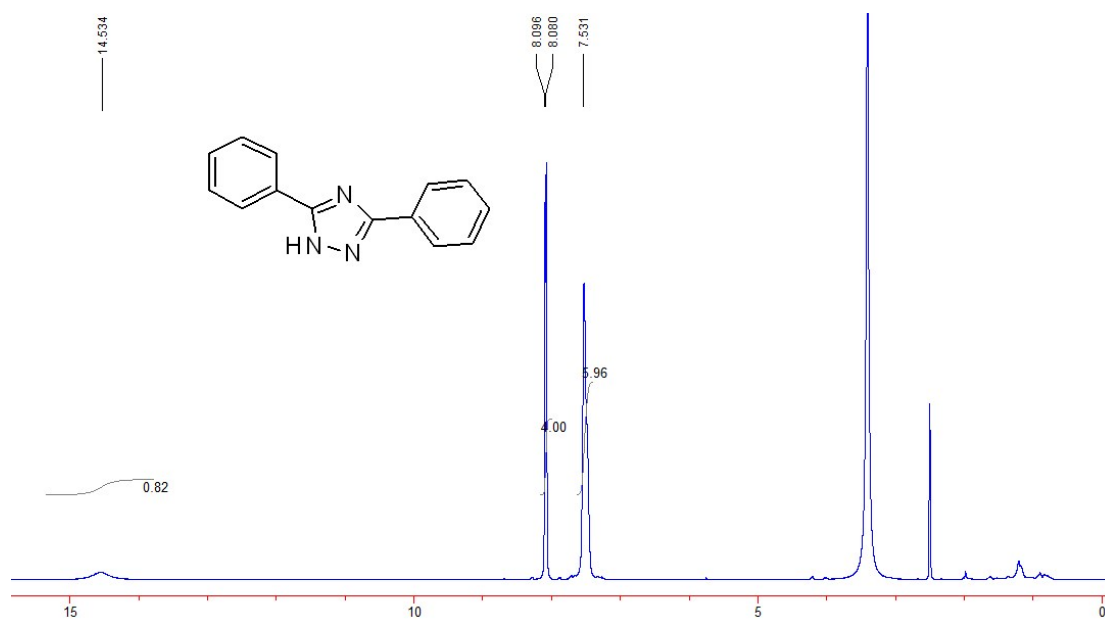


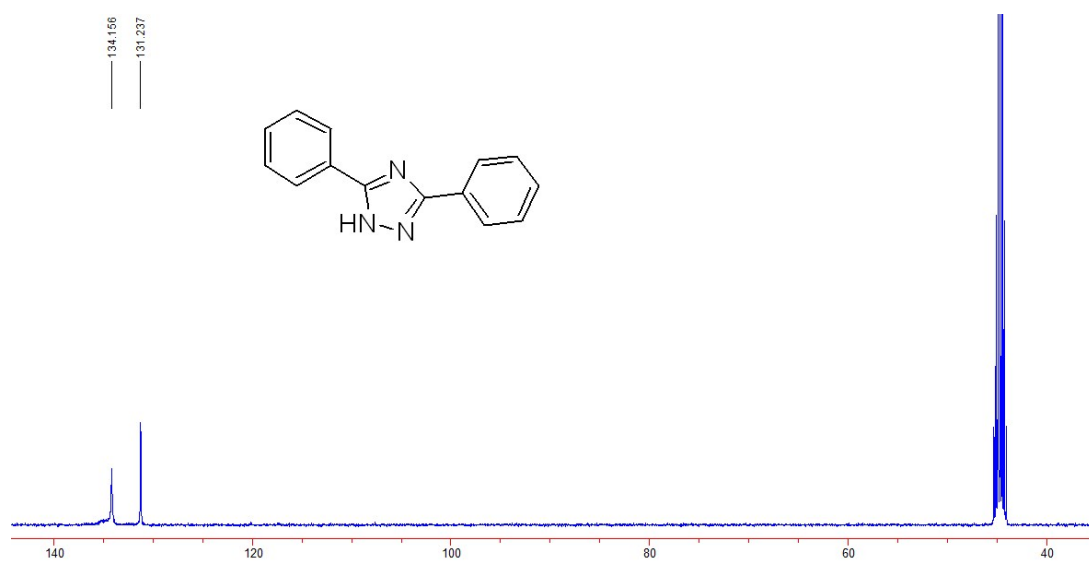
¹H and ¹³C-NMR spectra of 6s.





¹H and ¹³C-NMR spectra of 7.





¹H and ¹³C-NMR spectra of **8**.

