

Supporting Information

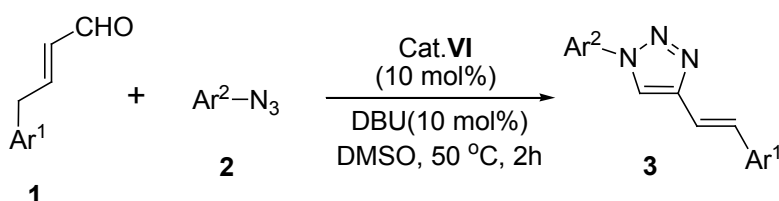
A: General Information and Starting Materials	2
B: General Procedure for Dienamine-Catalyzed [3+2] Cycloaddition Reactions	2
C: Characterization Data of Triazole Derivatives.....	2
D: Dienamine-Catalyzed [3+2] Cycloaddition Reaction of Trans-2-octenal with Azide	7
E: Trienamine-Catalyzed [3+2] Cycloaddition Reaction of α,β -Unsaturated Aldehyde with Azide	9
F: Reduction of Triazole Derivative	11
G: NMR Study for the Formation of Dienamine	13
H: NMR Analysis of Triazole Derivatives	14
I: Reference	31

A: General Information and Starting Materials

General Information. Proton nuclear magnetic resonance (^1H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker ACF300 spectrometer (500 MHz and 125 MHz). Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent (CDCl_3 : δ 7.26). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent (CDCl_3 : δ 77.16). Data are represented as follows: chemical shift, integration, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz). All high resolution mass spectra were obtained on a Finnigan/MAT 95XL-T mass spectrometer. For thin layer chromatography (TLC), Merck pre-coated TLC plates (Merck 60 F254) were used, and compounds were visualized with a UV light at 254 nm. Flash chromatography separations were performed on Merck 60 (0.040-0.063 mm) mesh silica gel.

Starting Materials. All solvents and inorganic reagents were from commercial sources and used without purification unless otherwise noted. α,β -unsaturated aldehydes **1** were prepared following the literature procedures.¹

B: General Procedure for Dienamine-Catalyzed [3+2] Cycloaddition Reactions



To a solution of DMSO (0.3 mL) were added α,β -unsaturated aldehydes **1** (0.15 mmol), azides **2** (0.10 mmol), catalyst **VI** (0.01 mmol) and DBU (0.01 mmol). The reaction mixture was stirred at 50 °C for 2h. Then 1.0 mL of H_2O was added to the reaction mixture and the aqueous phase was extracted with DCM (3*2 mL). The organic solvent was dried with Na_2SO_4 and removed under vacuum to give a residue, which was purified by silica gel chromatography to yield the desired product.

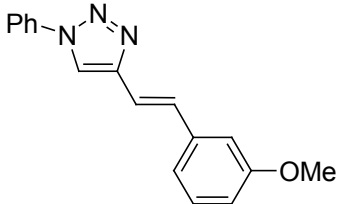
C: Characterization Data of Triazole Derivatives

(E)-1-phenyl-4-styryl-1H-1,2,3-triazole (3aa)

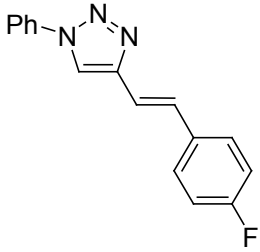
Yellow solid, 21.0 mg, 85% yield; mp = 88-89 °C; IR ν 3451, 2924, 2854, 1732, 1499, 1463 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz): δ (ppm) 8.04 (s, 1H), 7.79 (d, J = 8.0 HMz, 2H), 7.58-7.55 (m, 4H), 7.49-7.47 (m, 2H), 7.43-7.39 (m, 3H), 7.33-7.32 (m, 1H), 7.19 (d, J = 16.5 HMz, 1H). ^{13}C NMR (CDCl_3 , 125 MHz): δ (ppm) 146.8, 136.6, 131.3, 129.8, 128.7, 128.1, 126.6, 120.4, 118.2, 116.3. HRMS (EI): exact mass calculated for

M (C₁₆H₁₃N₃) requires m/z 247.1109, found m/z 247.1116.

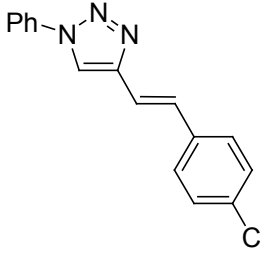
(E)-4-(3-methoxystyryl)-1-phenyl-1H-1,2,3-triazole (3ba)

 Yellow solid, 24.3 mg, 88% yield; mp = 97-98^oC; IR ν 3445, 3141, 2924, 2853, 1593, 1494, 1462 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz): δ (ppm) 8.04 (s, 1H), 7.79 (d, *J* = 8.0 HMz, 2H), 7.58-7.55 (m, 2H), 7.49-7.46 (m, 1H), 7.43-7.40 (m, 1H), 7.33-7.30 (m, 1H), 7.19-7.18 (m, 2H), 7.15-7.10 (m, 1H), 6.89-6.87 (m, 1H), 3.88 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz): δ (ppm) 159.9, 146.8, 138.1, 137.0, 131.2, 129.8, 129.7, 128.7, 120.4, 119.3, 118.2, 116.7, 113.8, 111.8, 55.2. HRMS (EI): exact mass calculated for M (C₁₇H₁₅N₃O) requires m/z 277.1215, found m/z 277.1214.

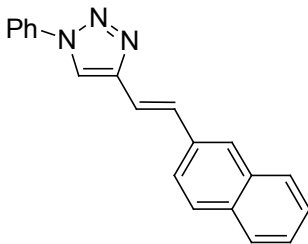
(E)-4-(4-fluorostyryl)-1-phenyl-1H-1,2,3-triazole (3ca)

 Yellow solid, 21.9 mg, 83% yield; mp = 95-96^oC; IR ν 3444, 2923, 2852, 1599, 1506, 1455 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz): δ (ppm) 8.03 (s, 1H), 7.70-7.68 (m, 1H), 7.63-7.61 (m, 1H), 7.54-7.48 (m, 4H), 7.45 (d, *J* = 16.0 HMz, 1H), 7.11-7.08 (m, 4H). ¹³C NMR (CDCl₃, 125 MHz): δ (ppm) 145.7, 134.7, 132.8, 130.8, 130.7, 130.1, 128.0 (t, *J* = 5.0 HMz), 127.6, 122.2, 115.9, 115.8, 115.7, 115.5. HRMS (EI): exact mass calculated for M (C₁₆H₁₂N₃F) requires m/z 265.1015, found m/z 265.1028.

(E)-4-(4-chlorostyryl)-1-phenyl-1H-1,2,3-triazole (3da)

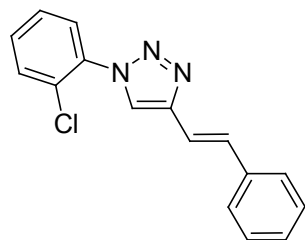
 Yellow solid, 23.0 mg, 82% yield; mp = 99-100^oC; IR ν 3450, 2929, 2856, 1590, 1497, 1446 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz): δ (ppm) 8.03 (s, 1H), 7.79 (d, *J* = 8.0 HMz, 2H), 7.59-7.56 (m, 2H), 7.50-7.47 (m, 3H), 7.43-7.40 (m, 1H), 7.38-7.36 (m, 2H), 7.15 (d, *J* = 16.5 HMz, 1H). ¹³C NMR (CDCl₃, 125 MHz): δ (ppm) 146.4, 136.8, 135.1, 133.6, 129.9, 129.7, 128.8, 128.7, 127.7, 120.4, 118.4, 116.8. HRMS (EI): exact mass calculated for M (C₁₆H₁₂N₃Cl) requires m/z 281.0720, found m/z 281.0724.

(E)-4-(2-(naphthalen-2-yl)vinyl)-1-phenyl-1H-1,2,3-triazole (3ea)

 Yellow solid, 24.3 mg, 82% yield; mp = 90-92^oC; IR ν 3449, 3124, 3033, 2925, 2853, 1592, 1432 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz): δ (ppm) 8.07 (s, 1H), 7.91 (s, 1H), 7.88-7.84 (m, 3H), 7.82-7.76 (m, 3H), 7.64-7.57 (m, 3H), 7.52-7.49 (m, 3H), 7.31 (d, *J* = 16.5 HMz, 1H). ¹³C NMR (CDCl₃, 125 MHz): δ (ppm) 134.1, 133.6, 133.2, 131.4,

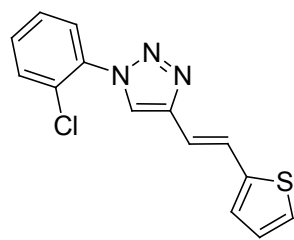
129.8, 128.7, 128.4, 128.1, 127.7, 127.0, 126.4, 126.1, 123.2, 120.5, 118.3, 116.6. HRMS (EI): exact mass calculated for M (C₂₀H₁₅N₃) requires m/z 297.1266, found m/z 297.1266.

(E)-1-(2-chlorophenyl)-4-styryl-1H-1,2,3-triazole (3ab)



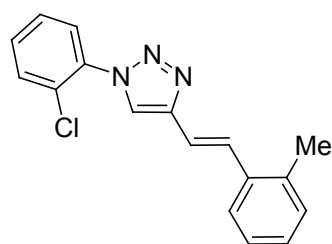
Yellow solid, 26.7 mg, 95% yield; mp = 94-96⁰C; IR ν 3451, 3135, 2924, 2853, 1598, 1495, 1444 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz): δ (ppm) 8.05 (s, 1H), 7.69-7.67 (m, 1H), 7.62-7.60 (m, 1H), 7.57-7.55 (m, 2H), 7.49-7.46 (m, 3H), 7.42-7.38 (m, 2H), 7.33-7.31 (m, 1H), 7.19 (d, J = 16.5 HMz, 1H). ¹³C NMR (CDCl₃, 125 MHz): δ (ppm) 146.0, 136.7, 134.8, 131.4, 130.8, 130.7, 128.7, 128.5, 128.1, 128.0, 127.7, 126.6, 122.3, 116.2. HRMS (EI): exact mass calculated for M (C₁₆H₁₂N₃Cl) requires m/z 281.0720, found m/z 281.0713.

(E)-1-(2-chlorophenyl)-4-(2-(thiophen-2-yl)vinyl)-1H-1,2,3-triazole (3fb)



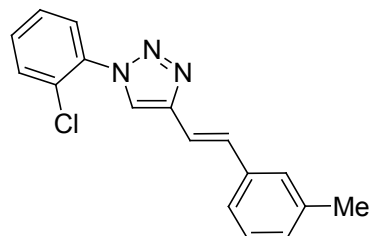
Yellow oil, 24.1 mg, 84% yield; IR ν 3449, 2931, 2853, 1641, 1586, 1487, 1454 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz): δ (ppm) 7.99 (s, 1H), 7.68-7.65 (m, 1H), 7.63-7.60 (m, 2H), 7.49-7.47 (m, 3H), 7.26-7.25 (m, 1H), 7.15-7.14 (m, 1H), 7.05-7.03 (m, 1H), 6.99 (d, J = 16.5 HMz, 1H). ¹³C NMR (CDCl₃, 125 MHz): δ (ppm) 145.5, 142.0, 134.8, 130.8, 130.7, 128.5, 128.0, 127.7, 126.8, 124.9, 124.4, 122.3, 117.6, 115.5. HRMS (EI): exact mass calculated for M (C₁₄H₁₀N₃ClS) requires m/z 287.0284, found m/z 287.0275.

(E)-4-(2-methylstyryl)-1-(2-chlorophenyl)-1H-1,2,3-triazole (3gb)



Yellow oil, 26.5 mg, 90% yield; IR ν 3446, 2922, 2852, 1583, 1494, 1455 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz): δ (ppm) 8.04 (s, 1H), 7.75-7.72 (m, 1H), 7.69-7.67 (m, 1H), 7.64-7.61 (m, 2H), 7.50-7.48 (m, 2H), 7.25-7.23 (m, 3H), 7.08 (d, J = 16.5 HMz, 1H), 2.49 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz): δ (ppm) 146.2, 136.1, 135.7, 134.9, 130.8, 130.7, 130.5, 129.1, 128.6, 128.0, 127.7, 126.2, 125.3, 122.4, 117.3, 20.0. HRMS (EI): exact mass calculated for M (C₁₇H₁₄N₃Cl) requires m/z 295.0876, found m/z 295.0877.

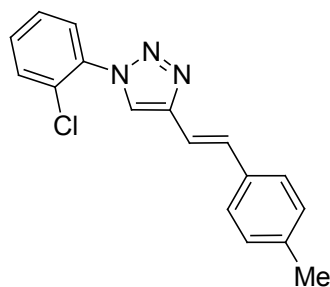
(E)-4-(3-methylstyryl)-1-(2-chlorophenyl)-1H-1,2,3-triazole (3hb)



Yellow solid, 25.0 mg, 85% yield; mp = 112-113⁰C; IR ν 3445, 3125, 2923, 1600, 1494, 1442 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz): δ (ppm) 8.04 (s, 1H), 7.69-7.67 (m, 1H), 7.63-7.61 (m, 1H), 7.49-7.48 (m, 2H), 7.46-7.43

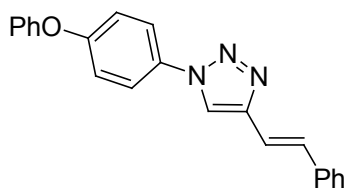
(m, 1H), 7.38-7.36 (m, 2H), 7.31-7.28 (m, 1H), 7.19-7.13 (m, 2H), 2.41 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz): δ (ppm) 146.1, 138.3, 136.6, 134.9, 131.4, 130.8, 130.7, 128.9, 128.6, 128.5, 127.9, 127.7, 127.3, 123.7, 122.2, 116.0, 21.4. HRMS (EI): exact mass calculated for M (C₁₇H₁₄N₃Cl) requires m/z 295.0876, found m/z 295.0873.

(E)-4-(4-methylstyryl)-1-(2-chlorophenyl)-1H-1,2,3-triazole (3ib)



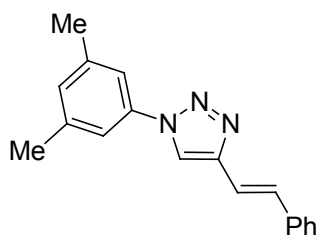
Yellow solid, 25.9 mg, 88% yield; mp = 124-125°C; IR ν 3435, 3132, 2923, 2853, 1595, 1491, 1450 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz): δ (ppm) 8.03 (s, 1H), 7.69-7.67 (m, 1H), 7.63-7.61 (m, 1H), 7.50-7.42 (m, 5H), 7.22-7.20 (m, 2H), 7.14 (d, *J* = 16.5 HMz, 1H), 2.39 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz): δ (ppm) 146.2, 138.0, 134.9, 134.0, 131.4, 130.8, 130.7, 129.5, 128.6, 127.9, 127.7, 126.5, 122.1, 115.2, 21.3. HRMS (EI): exact mass calculated for M (C₁₇H₁₄N₃Cl) requires m/z 295.0876, found m/z 295.0875.

(E)-1-(4-phenoxyphenyl)-4-styryl-1H-1,2,3-triazole (3ac)



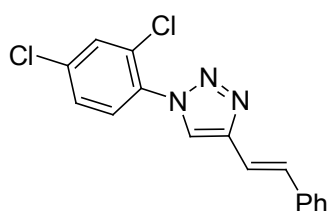
Yellow solid, 28.1 mg, 83% yield; mp = 94-95°C; IR ν 3445, 3126, 2922, 2852, 1651, 1586, 1509 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz): δ (ppm) 7.98 (s, 1H), 7.73 (d, *J* = 8.0 HMz, 2H), 7.56 (d, *J* = 8.0 HMz, 2H), 7.46-7.39 (m, 5H), 7.32-7.28 (m, 2H), 7.21-7.16 (m, 4H), 7.11-7.09 (m, 1H). ¹³C NMR (CDCl₃, 125 MHz): δ (ppm) 136.7, 131.3, 130.0, 128.7, 128.1, 126.6, 124.2, 122.2, 119.5, 119.4, 118.3, 116.3. HRMS (EI): exact mass calculated for M (C₂₂H₁₇N₃O) requires m/z 339.1372, found m/z 339.1385.

(E)-1-(3,5-dimethylphenyl)-4-styryl-1H-1,2,3-triazole (3ad)



Yellow oil, 23.9 mg, 87% yield; IR ν 3441, 3134, 2928, 2854, 1659, 1499, 1456 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz): δ (ppm) 8.01 (s, 1H), 7.56-7.55 (m, 2H), 7.44-7.39 (m, 5H), 7.33-7.31 (m, 1H), 7.18 (d, *J* = 16.5 HMz, 1H), 7.10 (s, 1H), 2.44 (s, 6H). ¹³C NMR (CDCl₃, 125 MHz): δ (ppm) 139.7, 136.7, 131.1, 130.4, 128.7, 128.0, 126.6, 118.4, 118.2, 116.5, 21.3. HRMS (EI): exact mass calculated for M (C₁₈H₁₇N₃) requires m/z 275.1422, found m/z 275.1425.

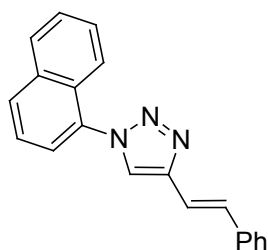
(E)-1-(2,4-dichlorophenyl)-4-styryl-1H-1,2,3-triazole (3ae)



Yellow solid, 29.3 mg, 93% yield; mp = 125-126°C; IR ν 3447, 3125, 2923, 2853, 1633, 1592, 1494 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz): δ (ppm) 8.03 (s, 1H), 7.64-7.63 (m, 2H), 7.56-7.55 (m, 2H), 7.49-7.46 (m, 2H), 7.42-7.39 (m,

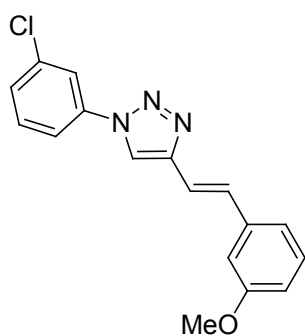
2H), 7.33-7.29 (m, 1H), 7.18 (d, $J = 16.5$ Hz, 1H). ^{13}C NMR (CDCl_3 , 125 MHz): δ (ppm) 146.2, 136.6, 136.2, 133.5, 131.6, 130.6, 129.2, 128.7, 128.4, 128.3, 128.2, 126.6, 122.1, 115.9. HRMS (EI): exact mass calculated for $\text{M}(\text{C}_{16}\text{H}_{11}\text{N}_3\text{Cl}_2)$ requires m/z 315.0330, found m/z 315.0337.

(E)-1-(naphthalen-1-yl)-4-styryl-1H-1,2,3-triazole (3af)



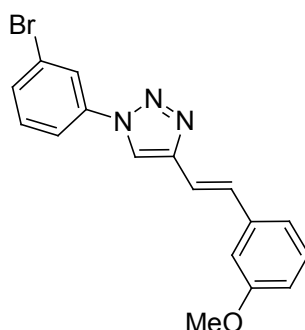
Yellow oil, 27.3 mg, 92% yield; IR ν 3445, 3134, 3055, 2923, 1596, 1429 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz): δ (ppm) 8.07-8.06 (m, 1H), 8.01-7.99 (m, 2H), 7.72-7.70 (m, 1H), 7.65-7.58 (m, 6H), 7.51 (d, $J = 16.5$ Hz, 1H), 7.43-7.40 (m, 2H), 7.34-7.31 (m, 1H), 7.26 (d, $J = 16.5$ Hz, 1H). ^{13}C NMR (CDCl_3 , 125 MHz): δ (ppm) 146.2, 136.7, 134.2, 131.3, 130.5, 128.8, 128.5, 128.3, 128.1, 128.0, 127.1, 126.6, 125.0, 123.5, 123.0, 122.4, 116.4. HRMS (EI): exact mass calculated for $\text{M}(\text{C}_{20}\text{H}_{15}\text{N}_3)$ requires m/z 297.1266, found m/z 297.1273.

(E)-4-(3-methoxystyryl)-1-(3-chlorophenyl)-1H-1,2,3-triazole (3jg)



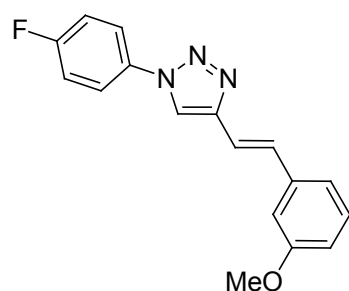
Yellow solid, 29.5 mg, 95% yield; mp = 102-104 $^{\circ}\text{C}$; IR ν 3450, 3116, 2925, 2840, 1592, 1486, 1436 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz): δ (ppm) 8.03 (s, 1H), 7.83 (s, 1H), 7.70-7.68 (m, 1H), 7.51-7.48 (m, 1H), 7.45-7.40 (m, 2H), 7.33-7.30 (m, 1H), 7.17-7.13 (m, 2H), 7.08 (s, 1H), 6.89-6.87 (m, 1H), 3.87 (s, 3H). ^{13}C NMR (CDCl_3 , 125 MHz): δ (ppm) 159.9, 147.0, 137.9, 135.6, 131.6, 130.8, 129.7, 128.7, 120.7, 119.3, 118.3, 118.0, 116.3, 113.9, 111.9, 55.3. HRMS (EI): exact mass calculated for $\text{M}(\text{C}_{17}\text{H}_{14}\text{N}_3\text{ClO})$ requires m/z 311.0825, found m/z 311.0824.

(E)-4-(3-methoxystyryl)-1-(3-bromophenyl)-1H-1,2,3-triazole (3jh)



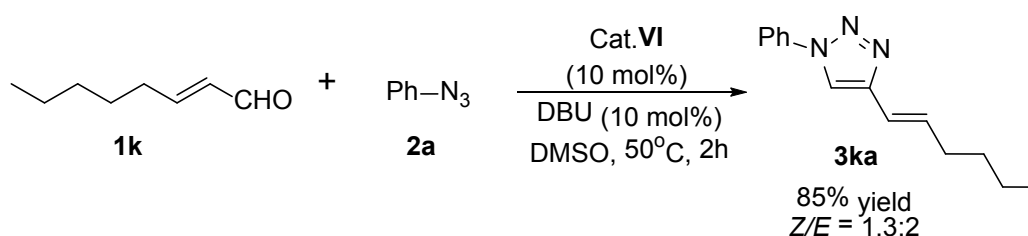
Yellow solid, 32.3 mg, 91% yield; mp = 110-111 $^{\circ}\text{C}$; IR ν 3123, 2923, 2836, 1584, 1485, 1455 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz): δ (ppm) 8.01-7.97 (m, 2H), 7.74-7.73 (m, 1H), 7.60-7.58 (m, 1H), 7.44-7.39 (m, 2H), 7.32-7.29 (m, 1H), 7.16-7.12 (m, 2H), 7.08 (s, 1H), 6.89-6.87 (m, 1H), 3.87 (s, 3H). ^{13}C NMR (CDCl_3 , 125 MHz): δ (ppm) 159.9, 147.0, 137.9, 137.8, 131.7, 131.6, 131.1, 129.7, 123.4, 123.3, 119.3, 118.8, 118.0, 116.3, 113.9, 111.9, 55.3. HRMS (EI): exact mass calculated for $\text{M}(\text{C}_{17}\text{H}_{14}\text{N}_3\text{BrO})$ requires m/z 355.0320, found m/z 355.0324.

(E)-4-(3-methoxystyryl)-1-(4-fluorophenyl)-1H-1,2,3-triazole (3ji)



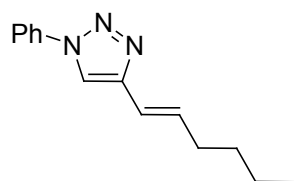
Yellow solid, 25.6 mg, 87% yield; mp = 117-118^oC; IR ν 3450, 3125, 2923, 2852, 1602, 1577, 1513, 1432 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz): δ (ppm) 7.98 (s, 1H), 7.77-7.75 (m, 2H), 7.41 (d, J = 16.5 HMz, 1H), 7.33-7.29 (m, 1H), 7.26-7.24 (m, 2H), 7.18-7.14 (m, 2H), 7.09 (s, 1H), 6.89-6.87 (m, 1H), 3.88 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz): δ (ppm) 159.9, 147.0, 137.9, 137.8, 131.7, 131.6, 131.1, 129.7, 123.4, 123.3, 119.3, 118.8, 118.0, 116.3, 113.9, 111.9, 55.3. HRMS (EI): exact mass calculated for M (C₁₇H₁₄N₃FO) requires m/z 295.1121, found m/z 295.1117.

D: Dienamine-Catalyzed [3+2] Cycloaddition Reaction of Trans-2-octenal with Azide



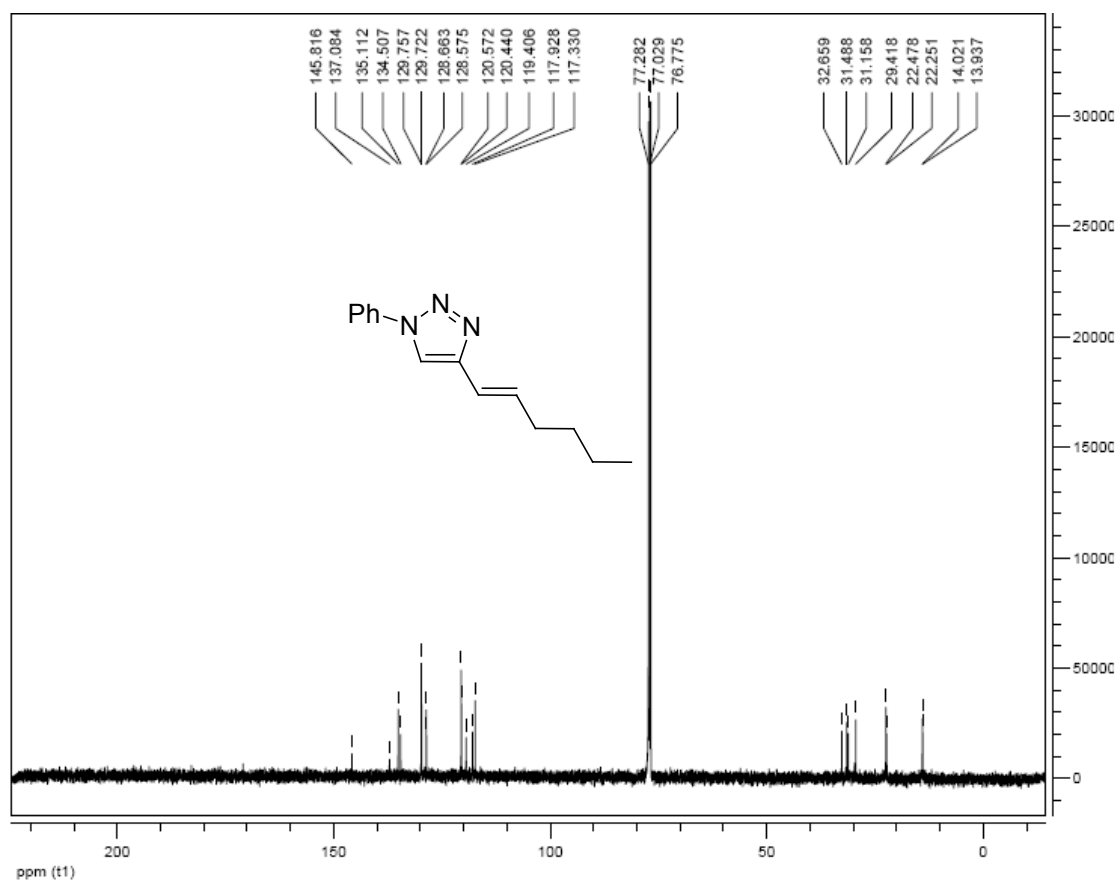
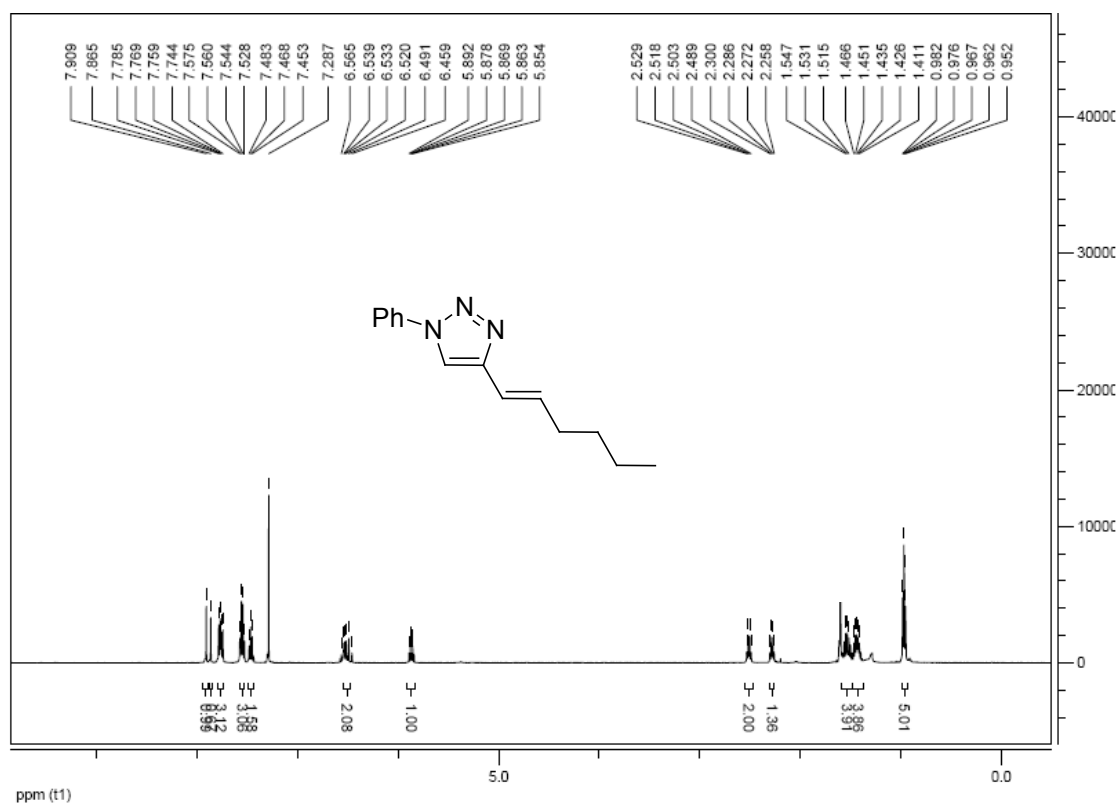
To a solution of DMSO (0.3 mL) were added trans-2-octenal **1k** (0.15 mmol), azide **2a** (0.10 mmol), catalyst **VI** (0.01 mmol) and DBU (0.01 mmol). The reaction mixture was stirred at 50 ^oC for 2h. Then 1.0 mL of H₂O was added to the reaction mixture and the aqueous phase was extracted with DCM (3*2 mL). The organic solvent was dried with Na₂SO₄ and removed under vacuum to give a residue, which was purified by silica gel chromatography to yield the desired product **3ka**.

(E)-4-(hex-1-enyl)-1-phenyl-1H-1,2,3-triazole (3ka)

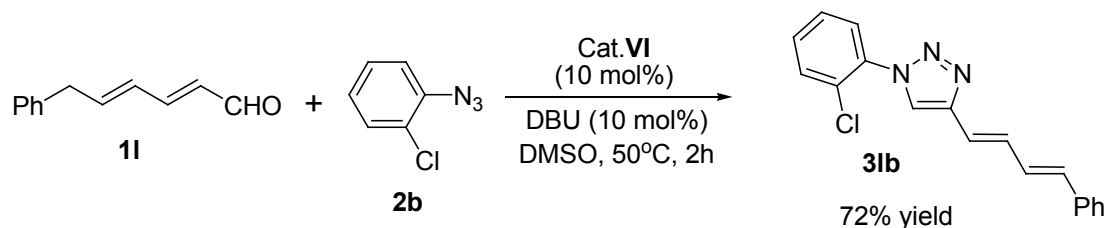


Yellow oil, 19.3 mg, 85% yield; IR ν 3445, 3122, 2925, 2853, 1587, 1498, 1412 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz): δ (ppm) 7.91 (s, 1H), 7.86 (s, 0.65H), 7.78-7.74 (m, 3H), 7.57-7.52 (m, 3H), 7.48-7.45 (m, 1.6H), 6.56-6.46 (m, 2H), 5.89-5.84 (m, 1H), 2.52-2.49 (m, 2H), 2.30-2.25 (m, 1.3H), 1.55-1.49 (m, 4H), 1.47-1.41 (m, 4H), 0.98-0.95 (m, 5H). ¹³C NMR (CDCl₃, 125 MHz): δ (ppm) 145.8, 137.1, 135.1, 134.5, 129.8, 129.7, 128.7, 128.6, 120.6, 120.4, 119.4, 117.9, 117.3, 32.6, 31.4, 31.1, 29.4, 22.5, 22.2, 14.0, 13.9. HRMS (EI): exact mass calculated for M (C₁₄H₁₇N₃) requires m/z 227.1422, found m/z 227.1420.

(E)-4-(hex-1-enyl)-1-phenyl-1H-1,2,3-triazole (3ka)

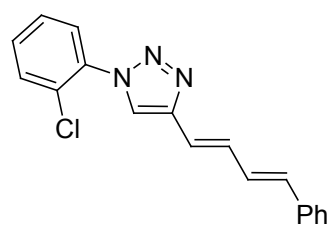


E: Trienamine-Catalyzed [3+2] Cycloaddition Reaction of α,β -Unsaturated Aldehyde with Azide



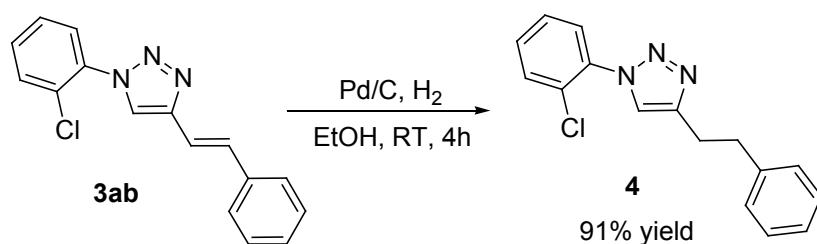
To a solution of DMSO (0.3 mL) were added α,β -unsaturated aldehyde **1I** (0.15 mmol), azide **2b** (0.10 mmol), catalyst **VI** (0.01 mmol) and DBU (0.01 mmol). The reaction mixture was stirred at 50 °C for 2h. Then 1.0 mL of H₂O was added to the reaction mixture and the aqueous phase was extracted with DCM (3*2 mL). The organic solvent was dried with Na₂SO₄ and removed under vacuum to give a residue, which was purified by silica gel chromatography to yield the desired product **3Ib**.

1-(2-chlorophenyl)-4-((1E,3E)-4-phenylbuta-1,3-dienyl)-1H-1,2,3-triazole (**3Ib**)



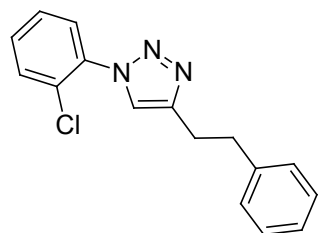
Yellow solid, 21.4 mg, 72% yield; mp = 106-108°C; IR ν 3446, 3138, 2924, 1675, 1591, 1492, 1449 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz): δ (ppm) 7.98 (s, 1H), 7.68-7.66 (m, 1H), 7.62-7.60 (m, 1H), 7.57-7.55 (m, 1H), 7.49-7.46 (m, 4H), 7.40-7.35 (m, 2H), 7.27-7.17 (m, 1H), 7.01-6.96 (dd, J = 15.5 HMz, 1H), 6.75 (d, J = 15.5 HMz, 2H). ¹³C NMR (CDCl₃, 125 MHz): δ (ppm) 146.0, 137.1, 134.8, 134.0, 131.9, 131.4, 130.8, 130.7, 128.8, 128.7, 128.5, 128.1, 127.9, 127.8, 127.7, 126.6, 126.5, 122.3, 122.2, 119.8, 116.2. HRMS (EI): exact mass calculated for M(C₁₈H₁₄N₃Cl) requires m/z 307.0876, found m/z 307.0878.

F: Reduction of Triazole Derivative



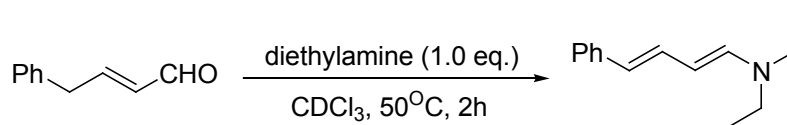
To a solution of EtOH (2.0 mL) were added **3ab** (0.10 mmol) and 10% Pd/C (30.0 mg). The reaction mixture was stirred at room temperature for 4h under H₂. Then Pd/C was removed by filtration and the residue was purified by silica gel chromatography to yield the desired product **4**.

1-(2-chlorophenyl)-4-phenethyl-1H-1,2,3-triazole (**4**)

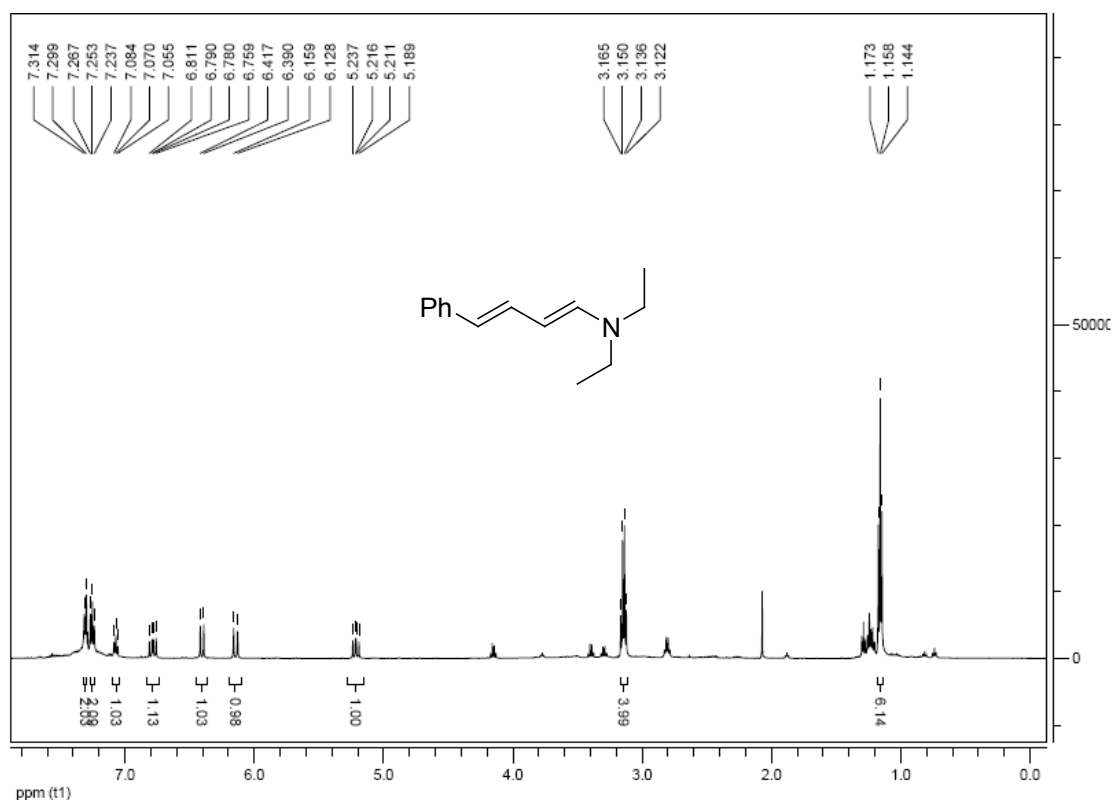


Yellow solid, 25.8 mg, 91% yield; mp = 106-107^oC; IR ν 3459, 3128, 2924, 1597, 1499, 1453 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz): δ (ppm) 7.71-7.69 (m, 2H), 7.58 (s, 1H), 7.54-7.51 (m, 2H), 7.45-7.42 (m, 1H), 7.34-7.31 (m, 2H), 7.26-7.23 (m, 2H), 3.16 (t, J = 7.5 HMz, 2H), 3.10 (t, J = 7.5 HMz, 2H). ¹³C NMR (CDCl₃, 125 MHz): δ (ppm) 147.9, 141.1, 137.2, 129.7, 128.6, 128.5, 128.4, 126.2, 120.4, 119.2, 35.5, 27.5.

G: NMR Study for the Formation of Dienamine

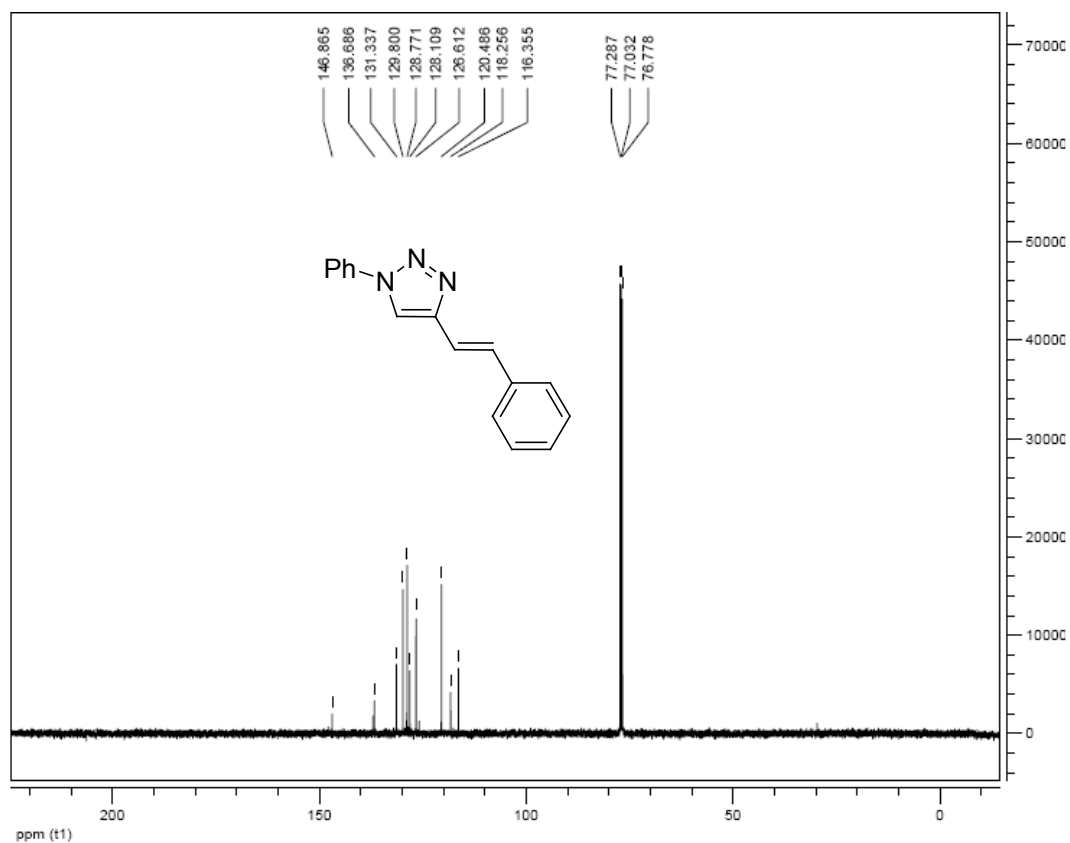
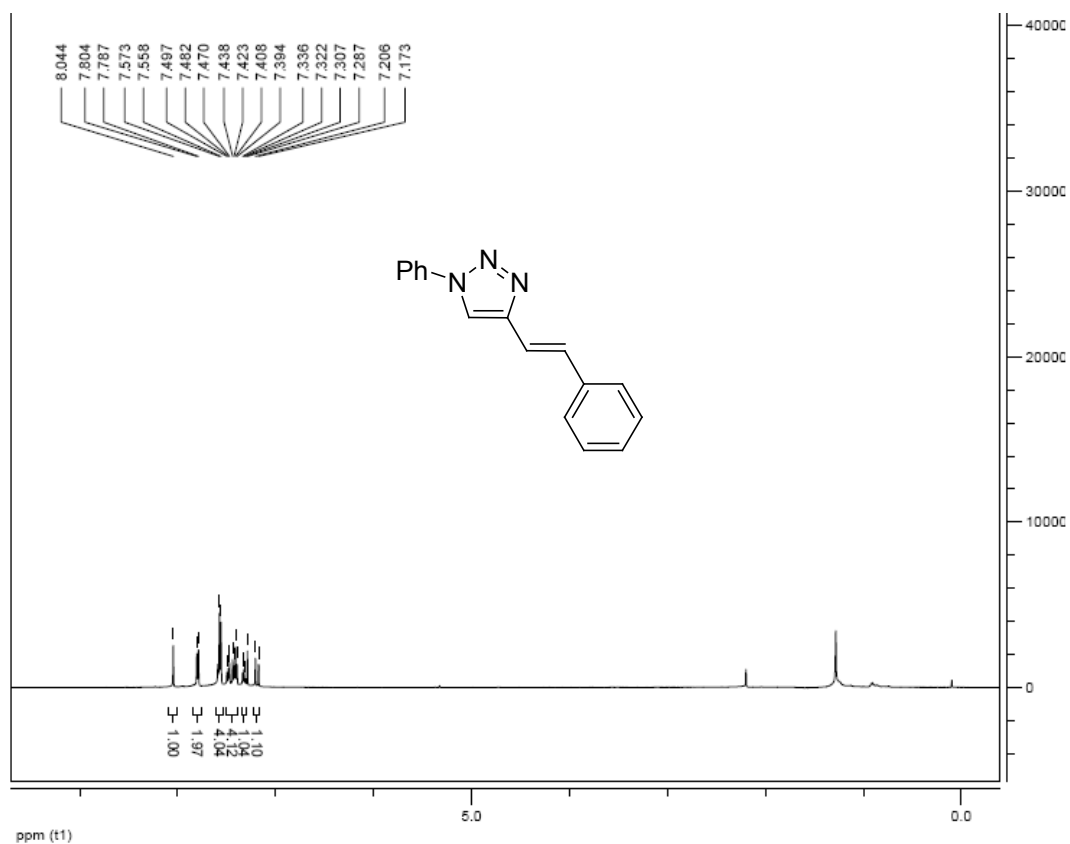


To a solution of CDCl_3 (0.6 mL) were added α,β -unsaturated aldehyde (0.10 mmol) and diethylamine (0.10 mmol). The reaction mixture was stirred at 50°C for 2h. Then the reaction mixture was conducted to run the crude NMR, which indicated the formation of dienamine intermediate. ^1H NMR (CDCl_3 , 500 MHz): δ (ppm) 7.31-7.28 (m, 2H), 7.26-7.23 (m, 2H), 7.08-7.05 (m, 1H), 6.85 (dd, $J = 15.5$ HMz, 1H), 6.40 (d, $J = 13.5$ HMz, 1H), 6.15 (d, $J = 15.5$ HMz, 1H), 5.21 (dd, $J = 13.5$ HMz, 1H), 3.14 (q, $J = 7.5$ HMz, 4H), 3.14 (t, $J = 7.5$ HMz, 6H).

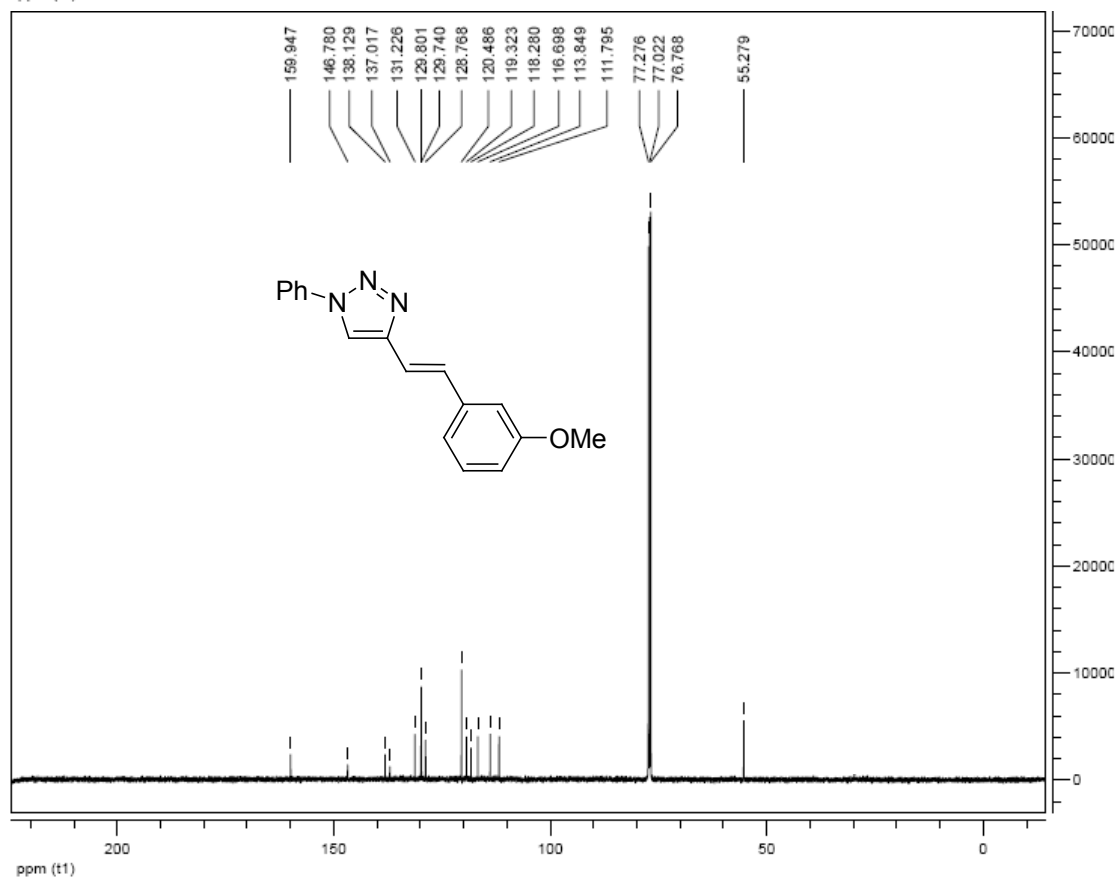
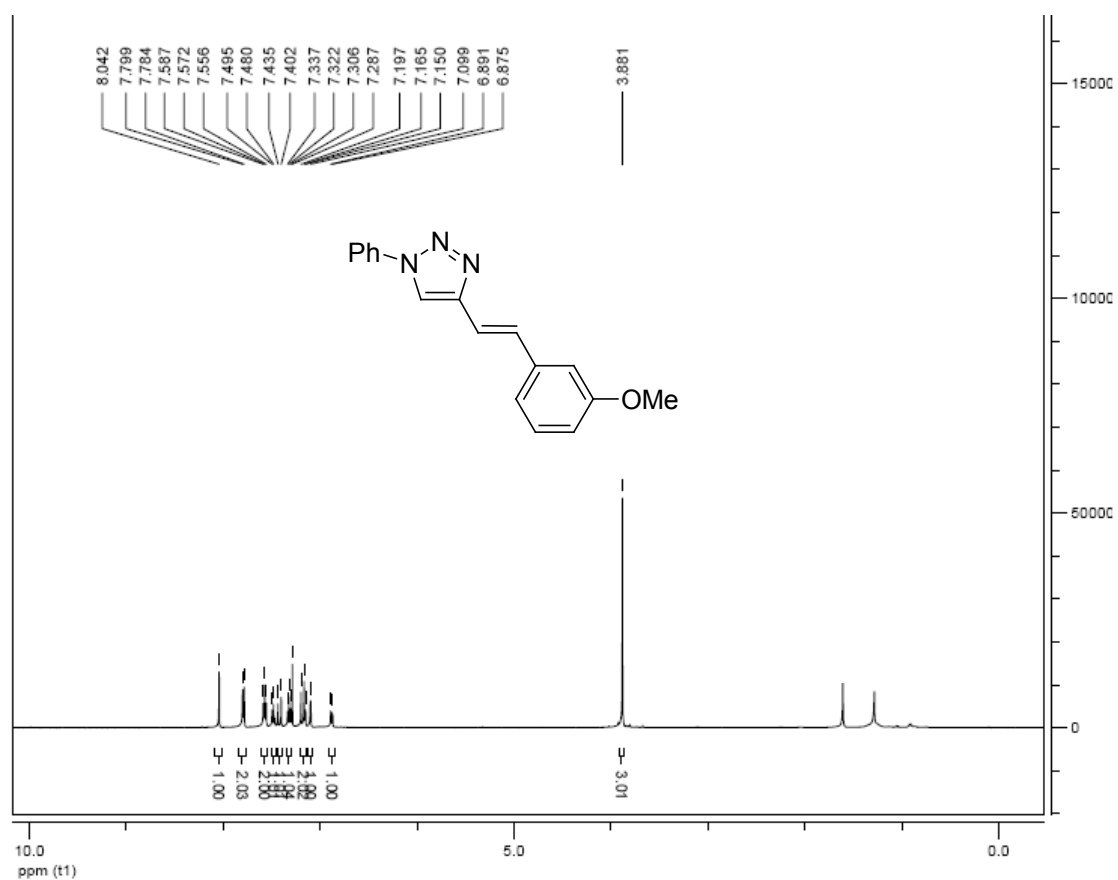


H: NMR Analysis of Triazole Derivatives

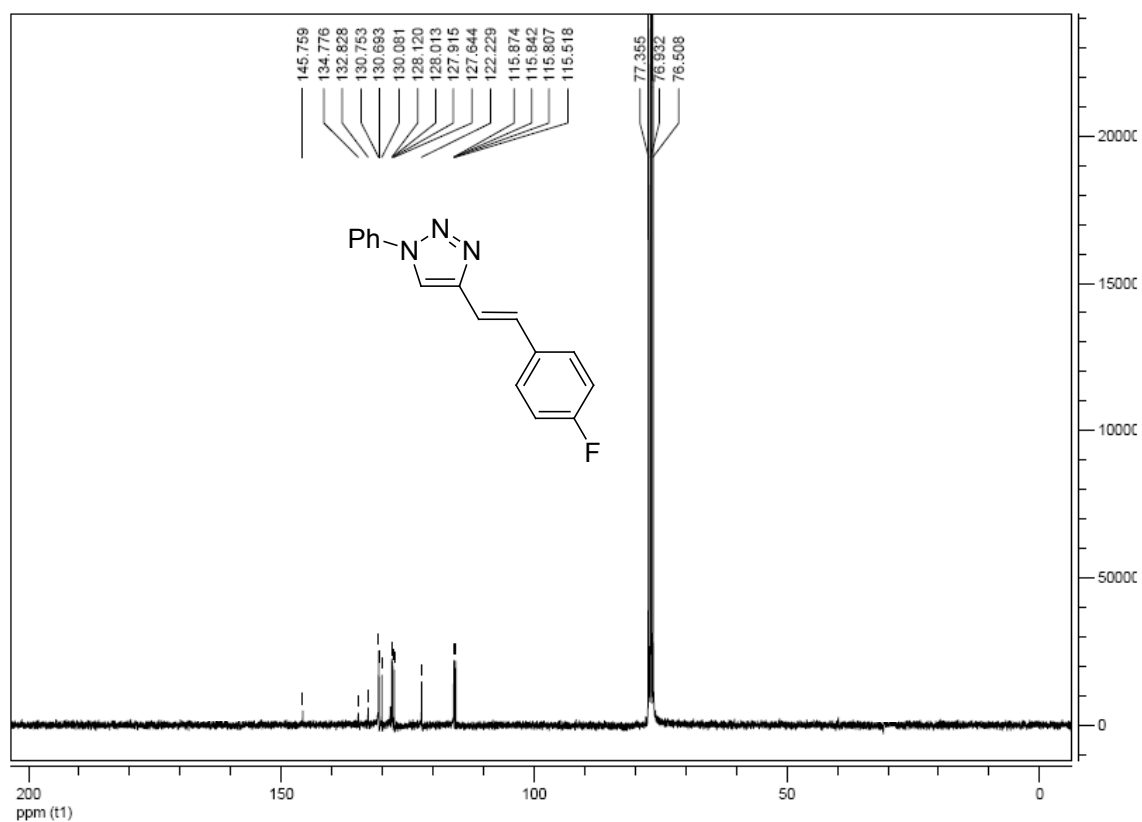
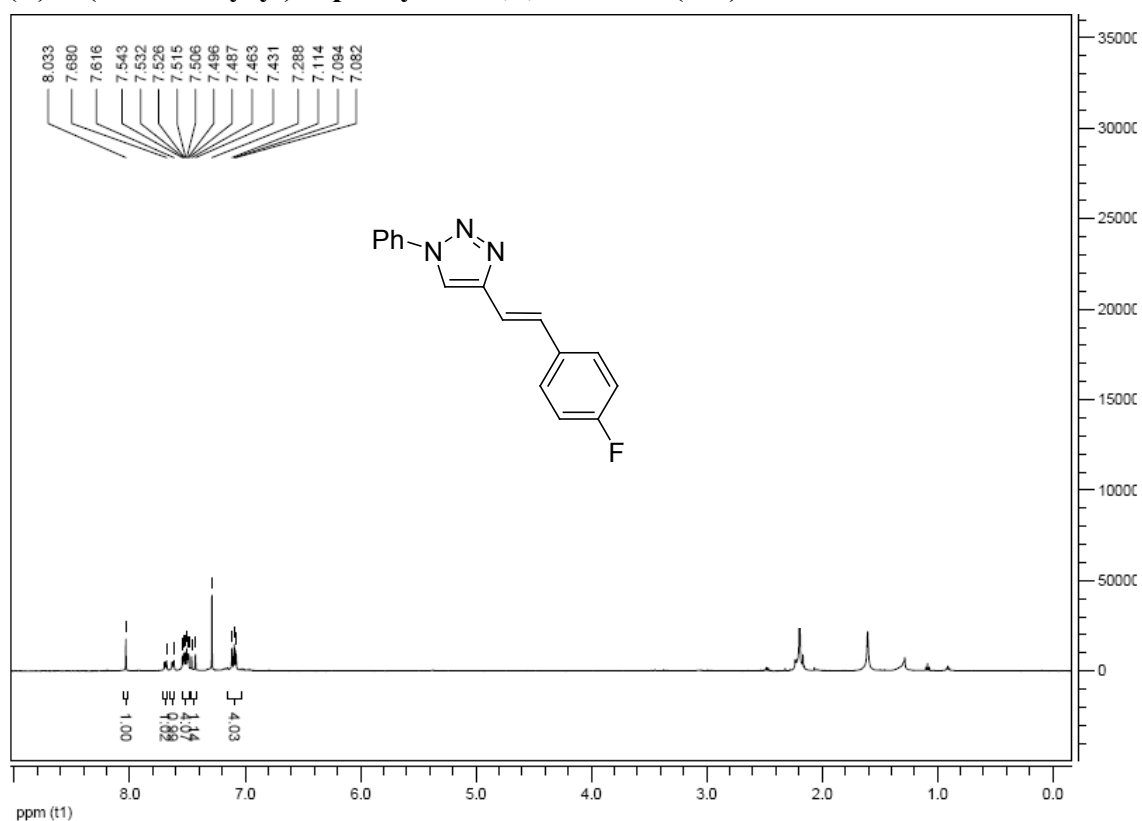
(E)-1-phenyl-4-styryl-1H-1,2,3-triazole (3aa)



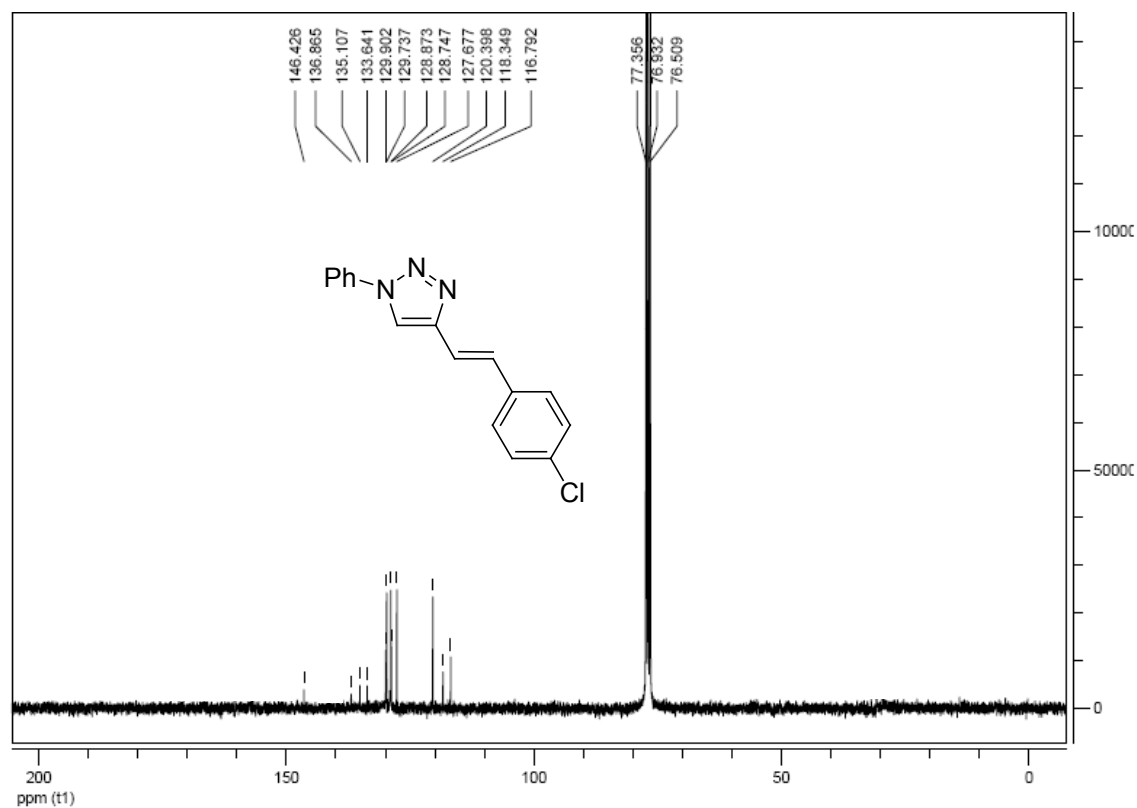
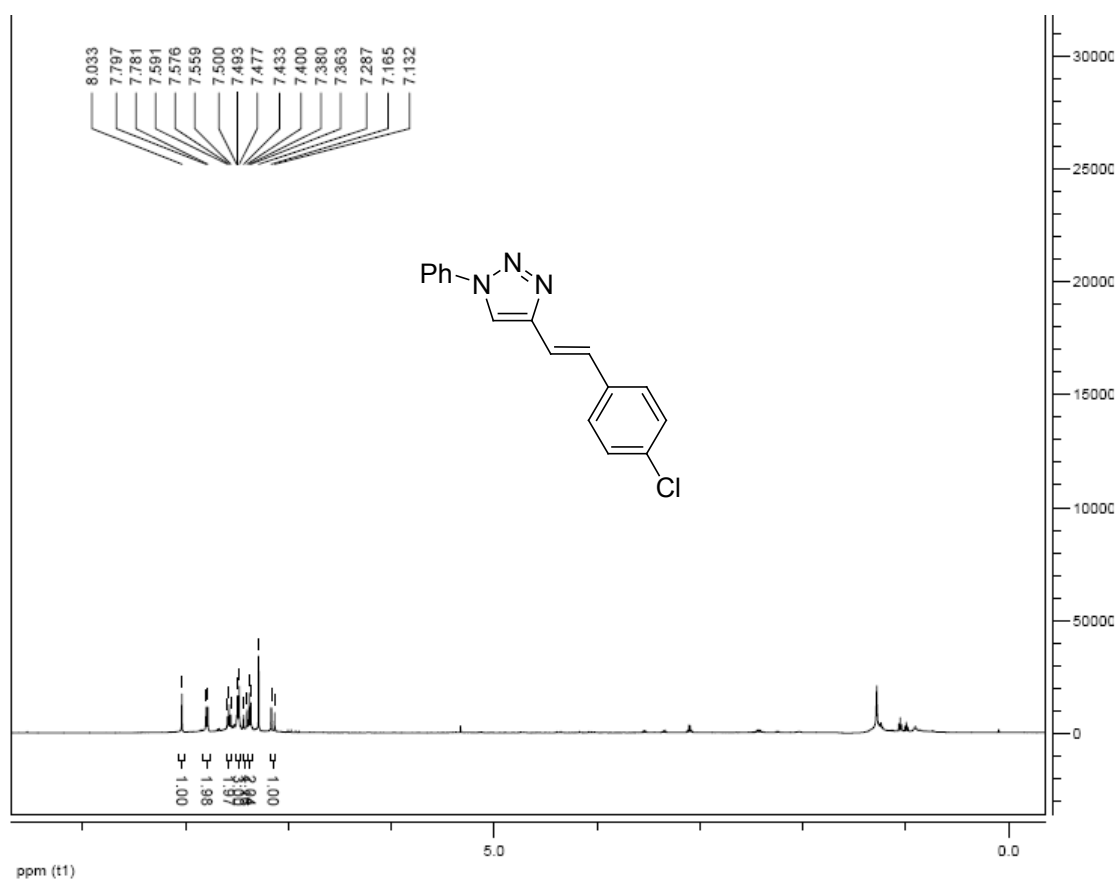
(E)-4-(3-methoxystyryl)-1-phenyl-1H-1,2,3-triazole (3ba)



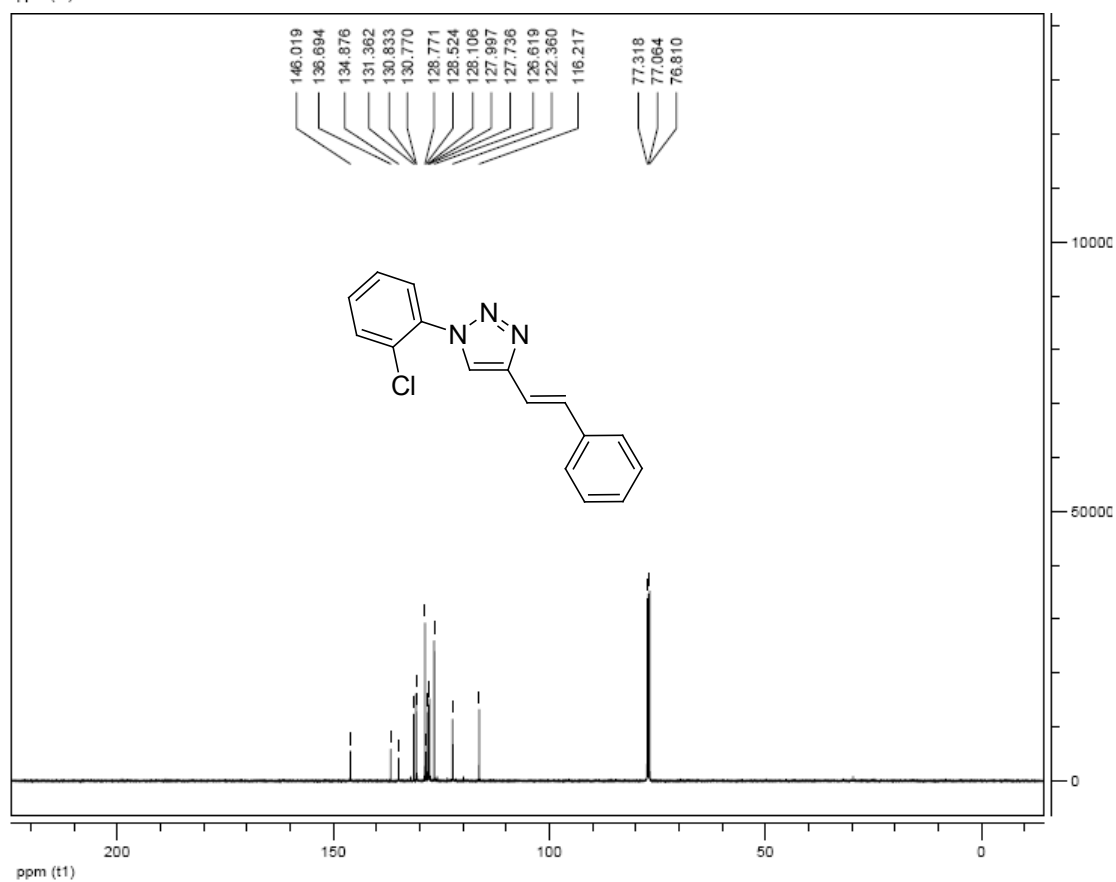
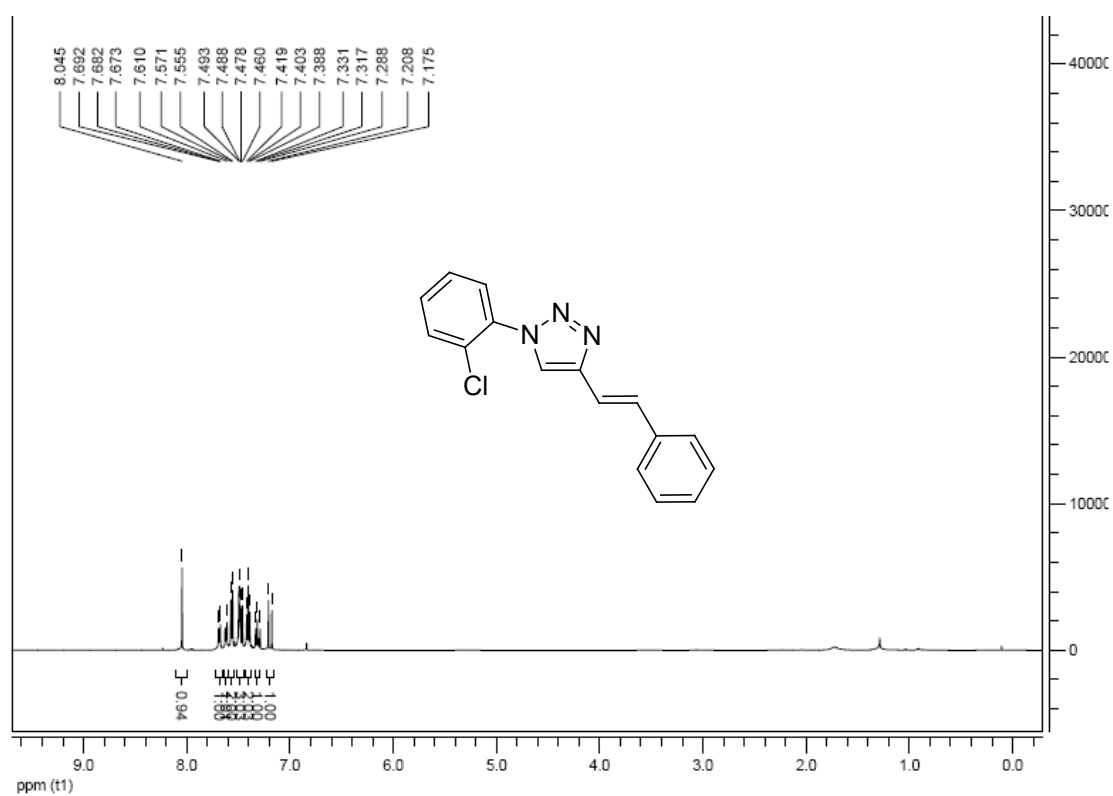
(E)-4-(4-fluorostyryl)-1-phenyl-1H-1,2,3-triazole (3ca)



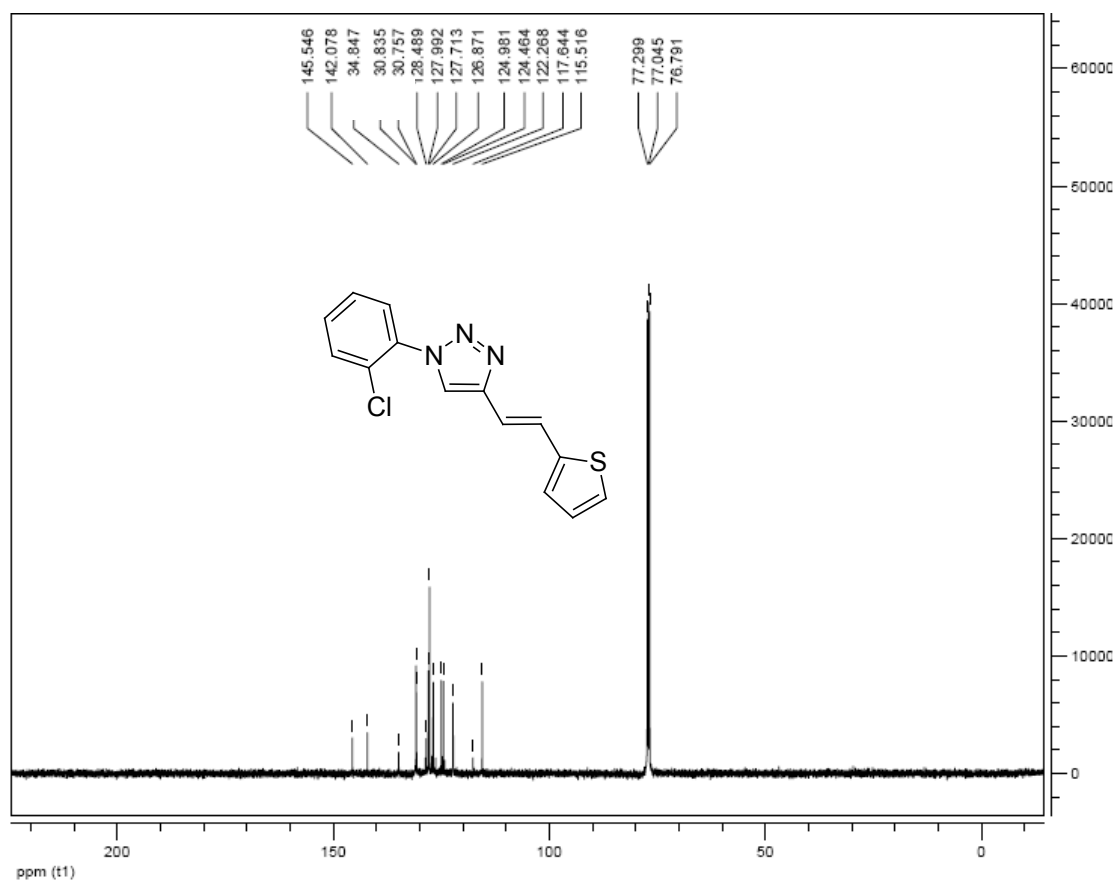
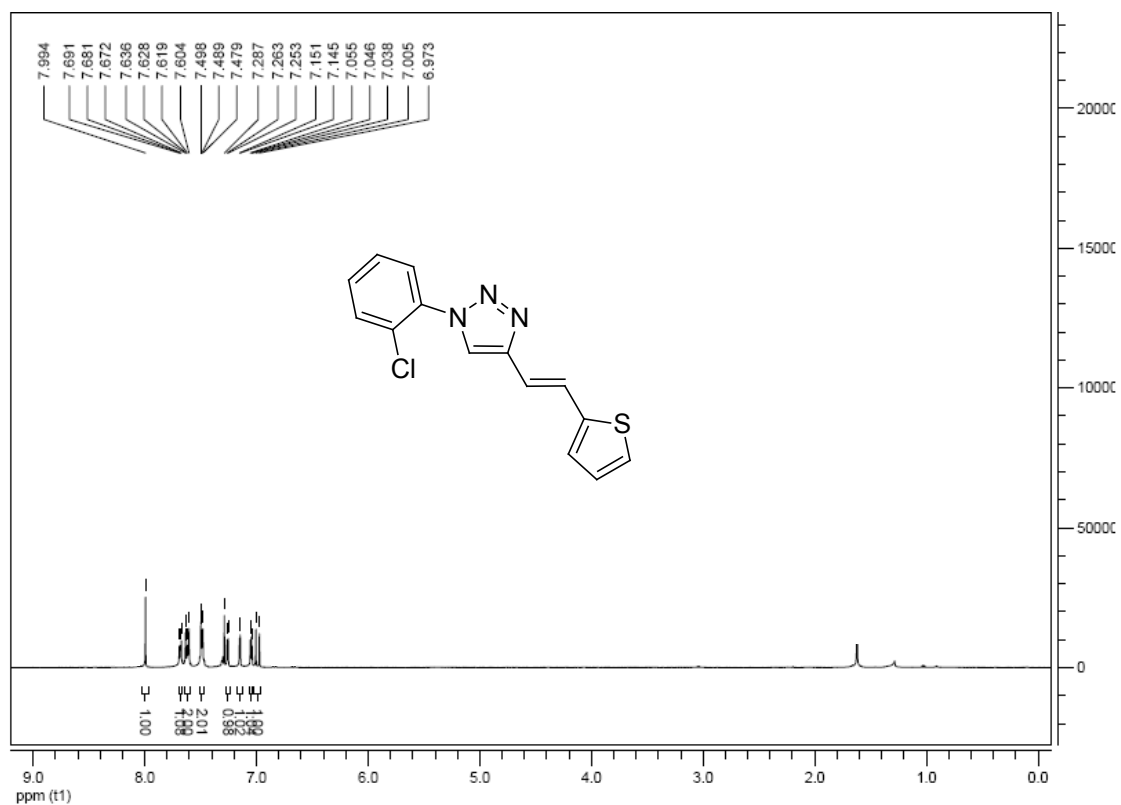
(E)-4-(4-chlorostyryl)-1-phenyl-1H-1,2,3-triazole (3da)



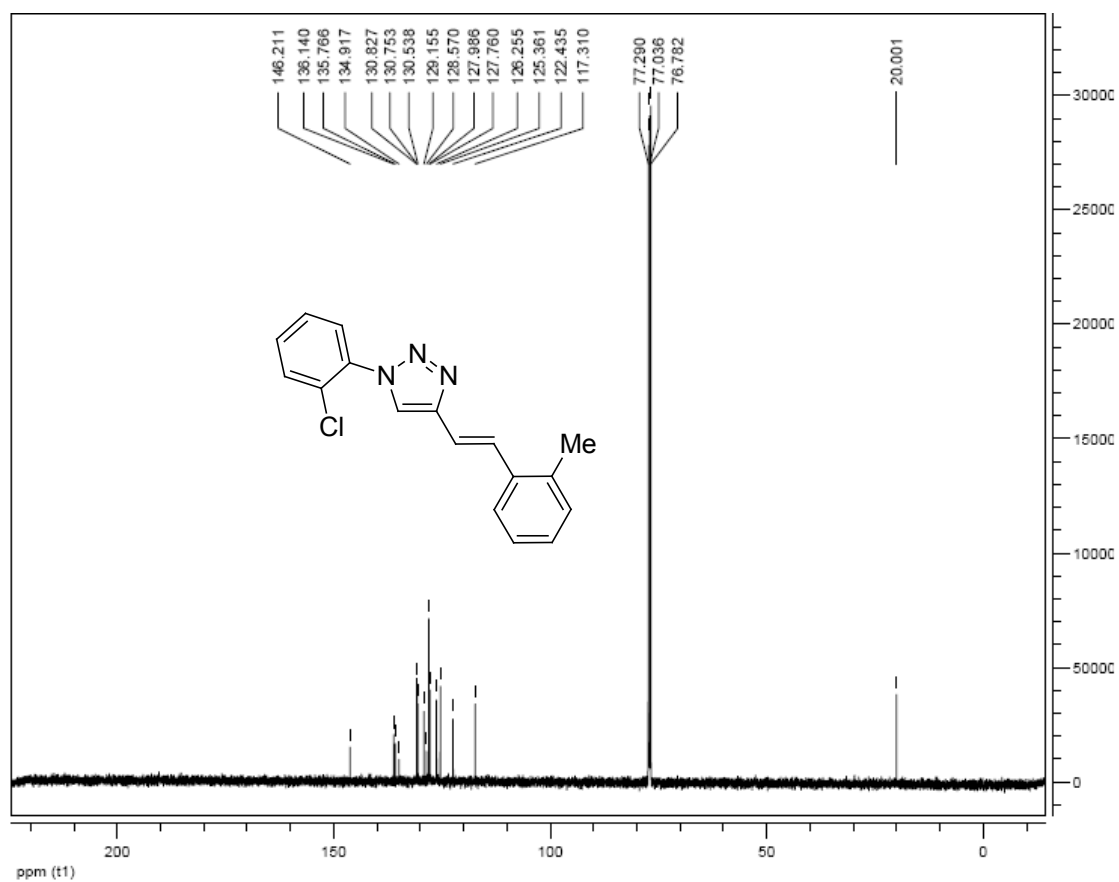
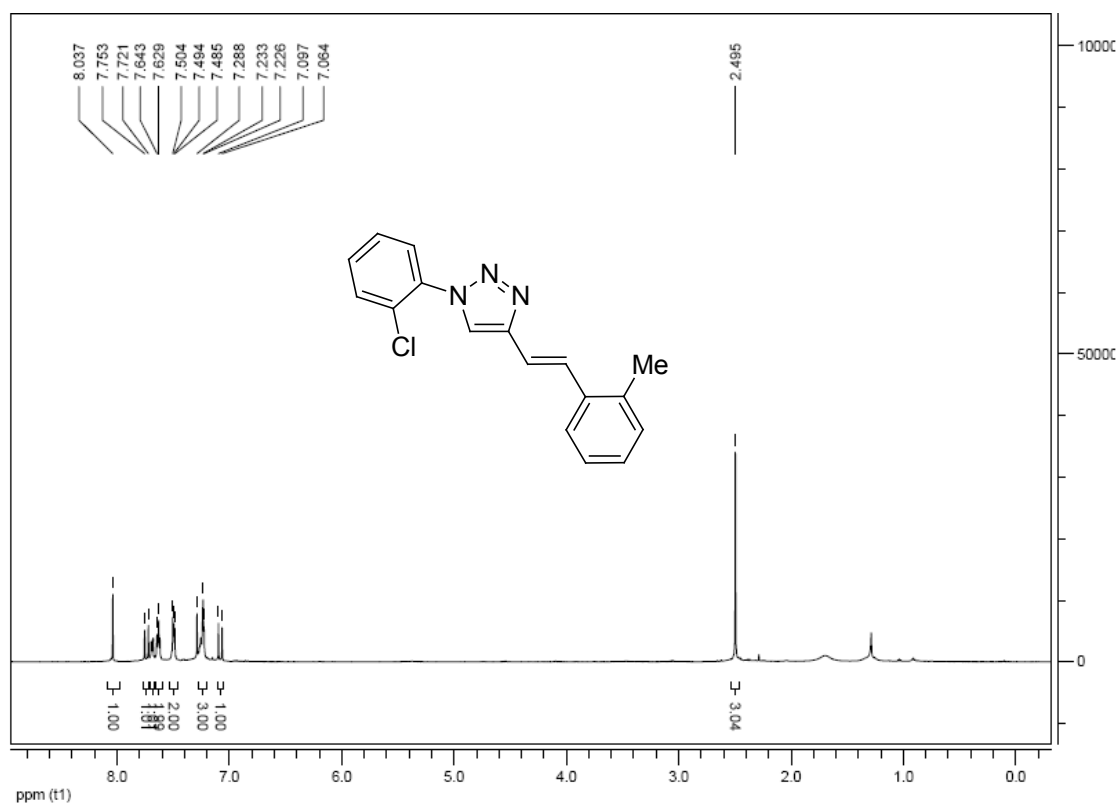
(E)-1-(2-chlorophenyl)-4-styryl-1H-1,2,3-triazole (3ab)



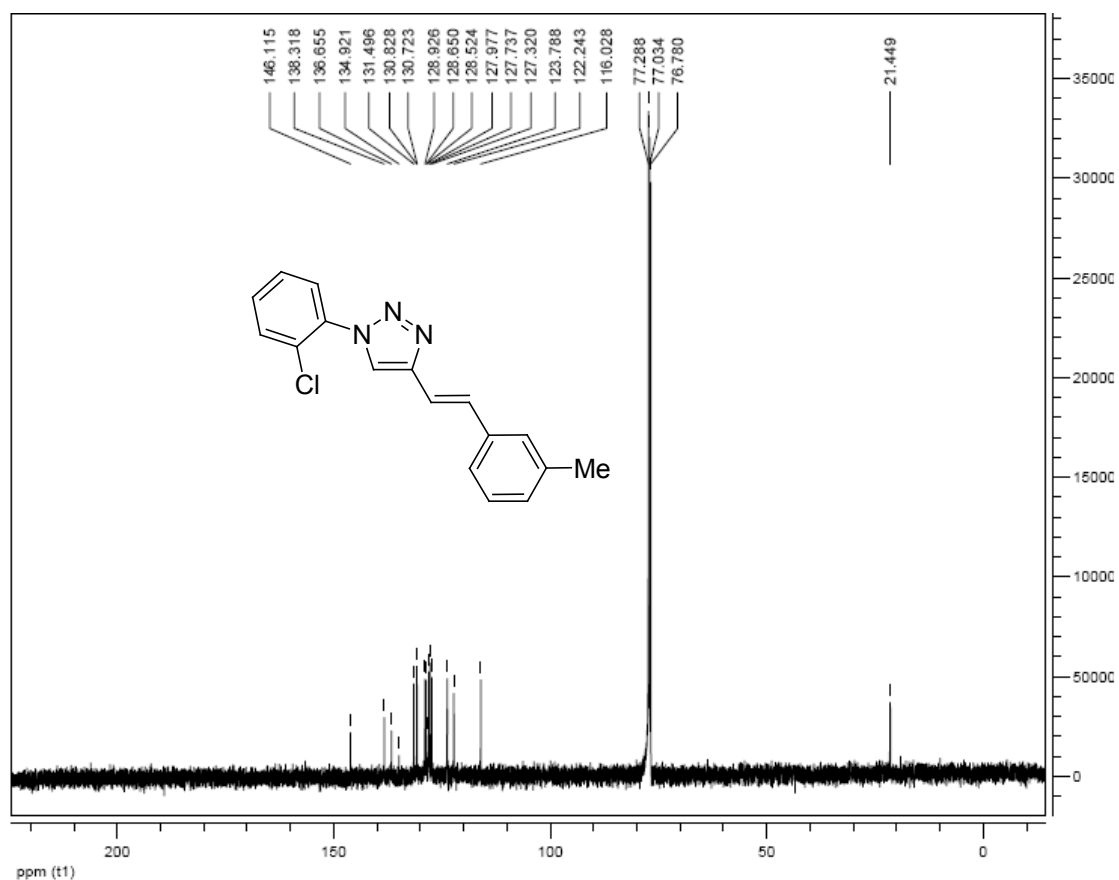
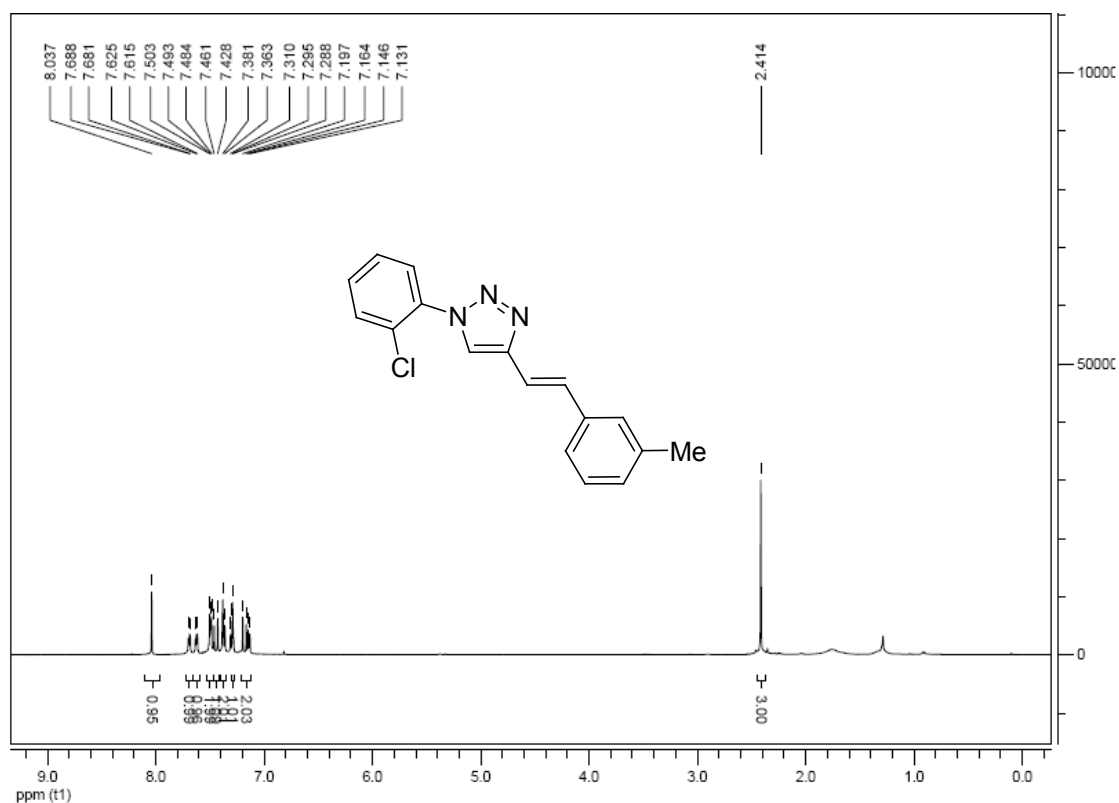
(E)-1-(2-chlorophenyl)-4-(2-(thiophen-2-yl)vinyl)-1H-1,2,3-triazole (3fb)



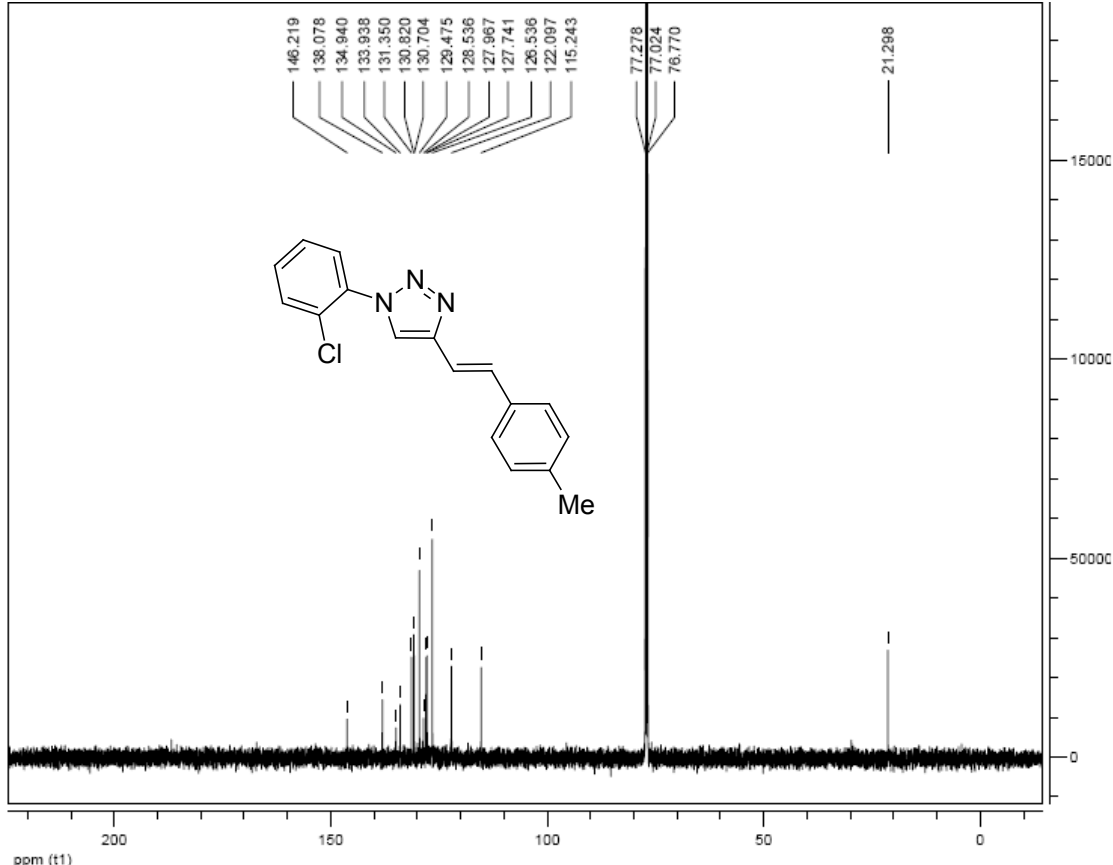
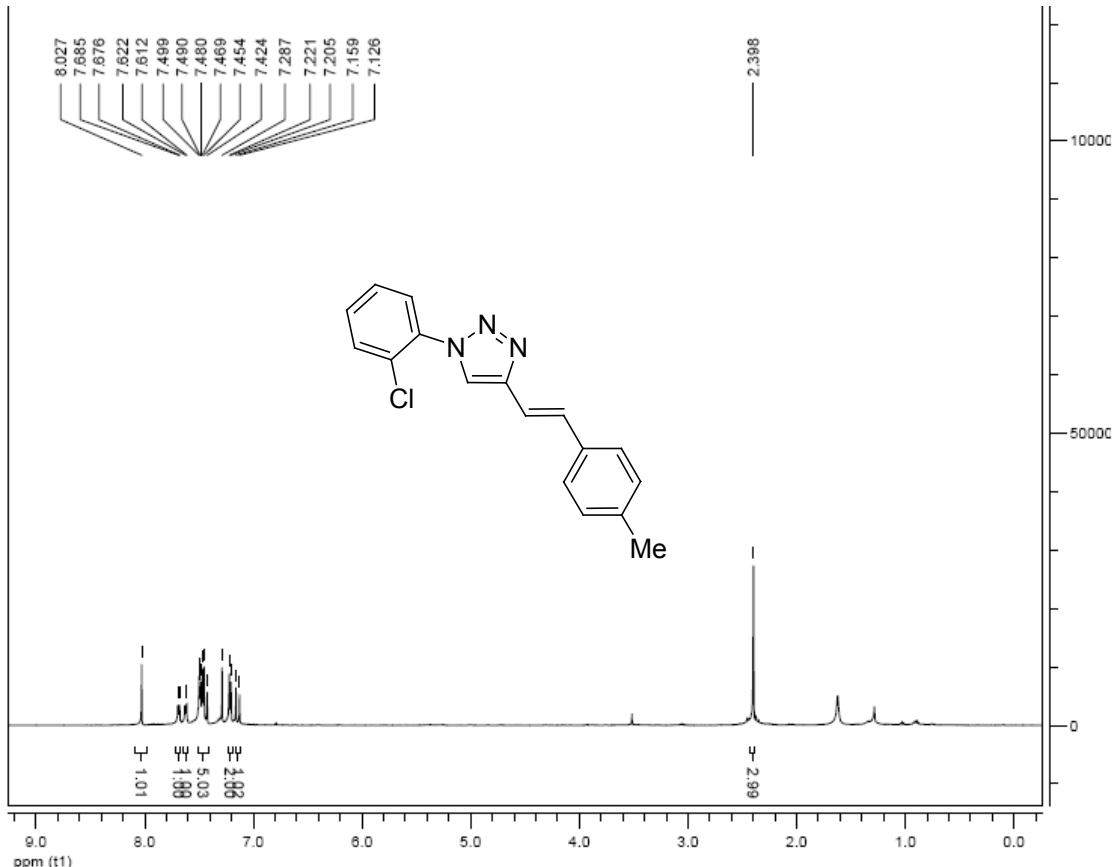
(E)-4-(2-methylstyryl)-1-(2-chlorophenyl)-1H-1,2,3-triazole (3gb)



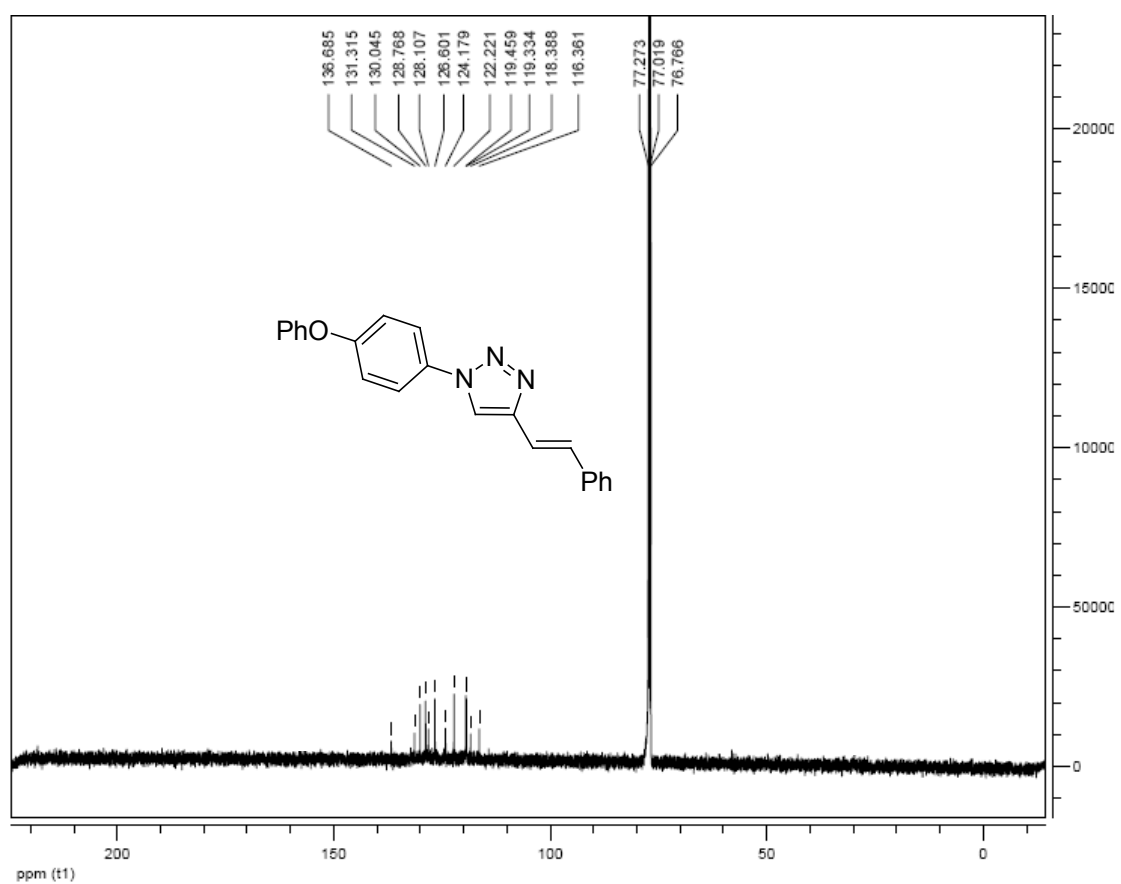
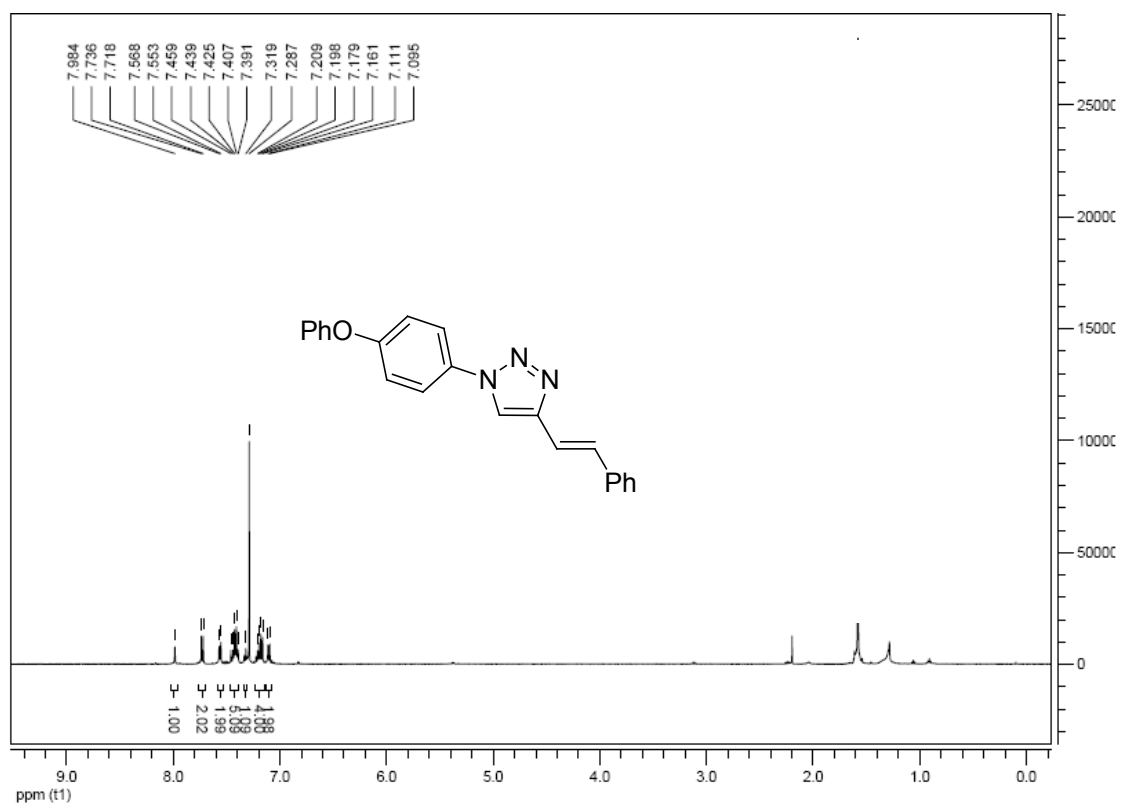
(E)-4-(3-methylstyryl)-1-(2-chlorophenyl)-1H-1,2,3-triazole (3hb)



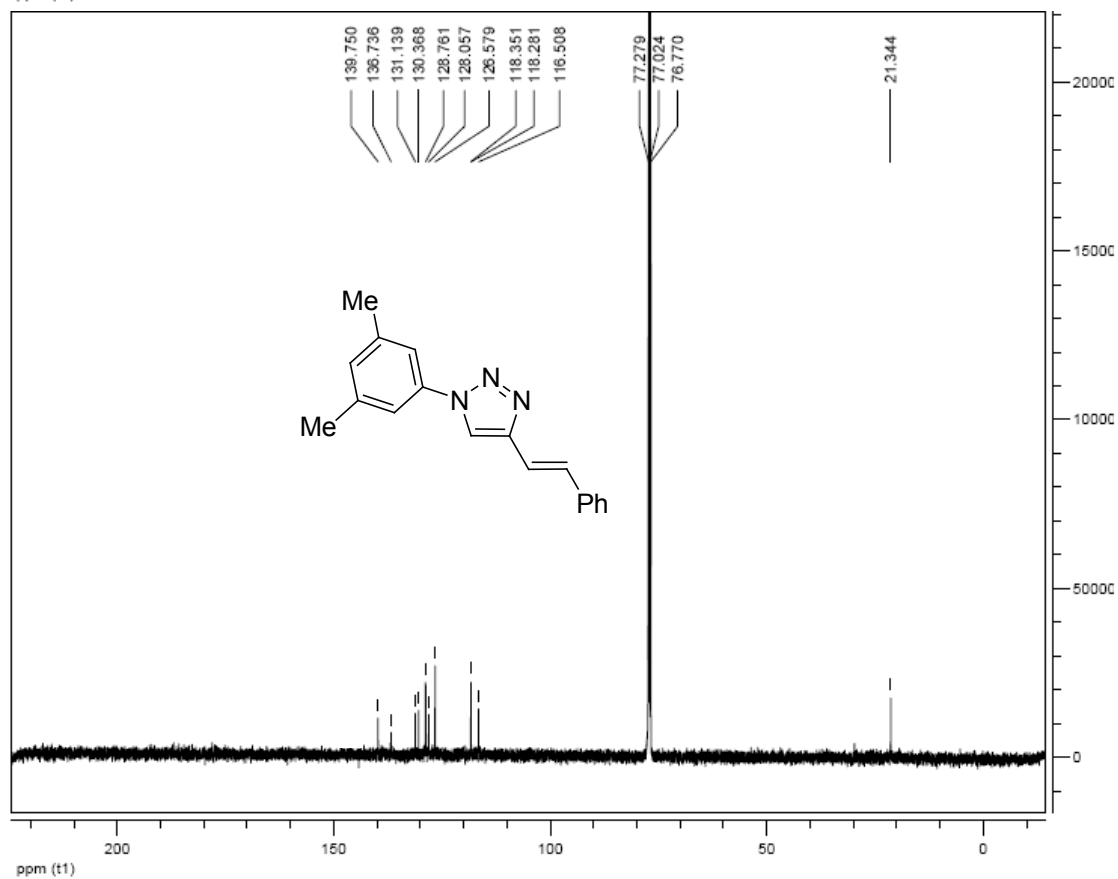
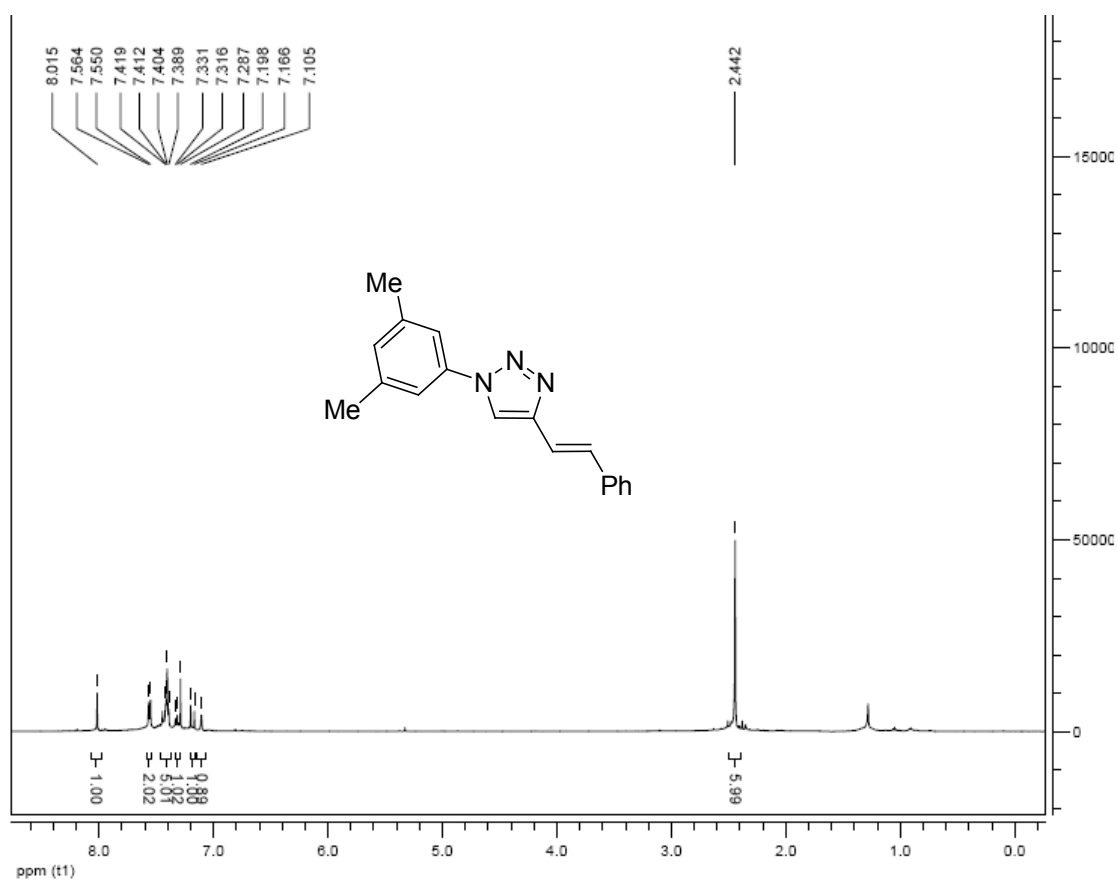
(E)-4-(4-methylstyryl)-1-(2-chlorophenyl)-1H-1,2,3-triazole (3ib)



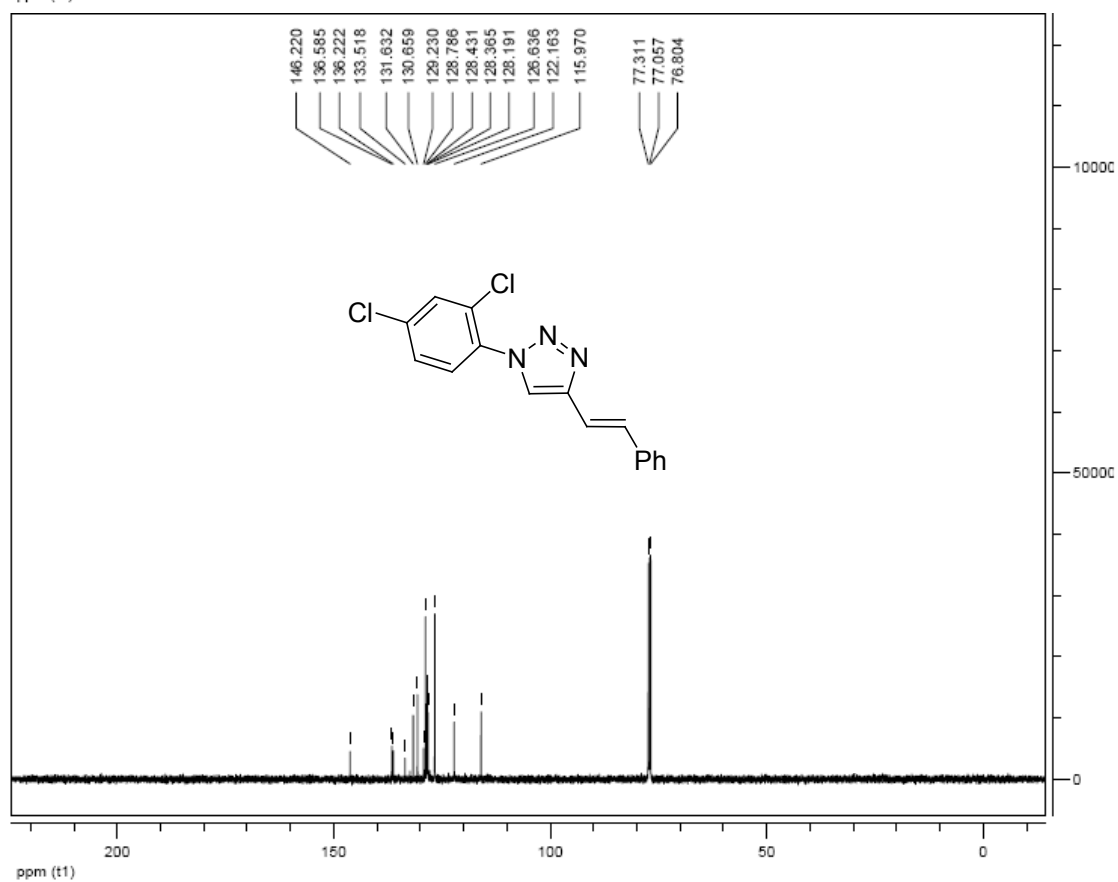
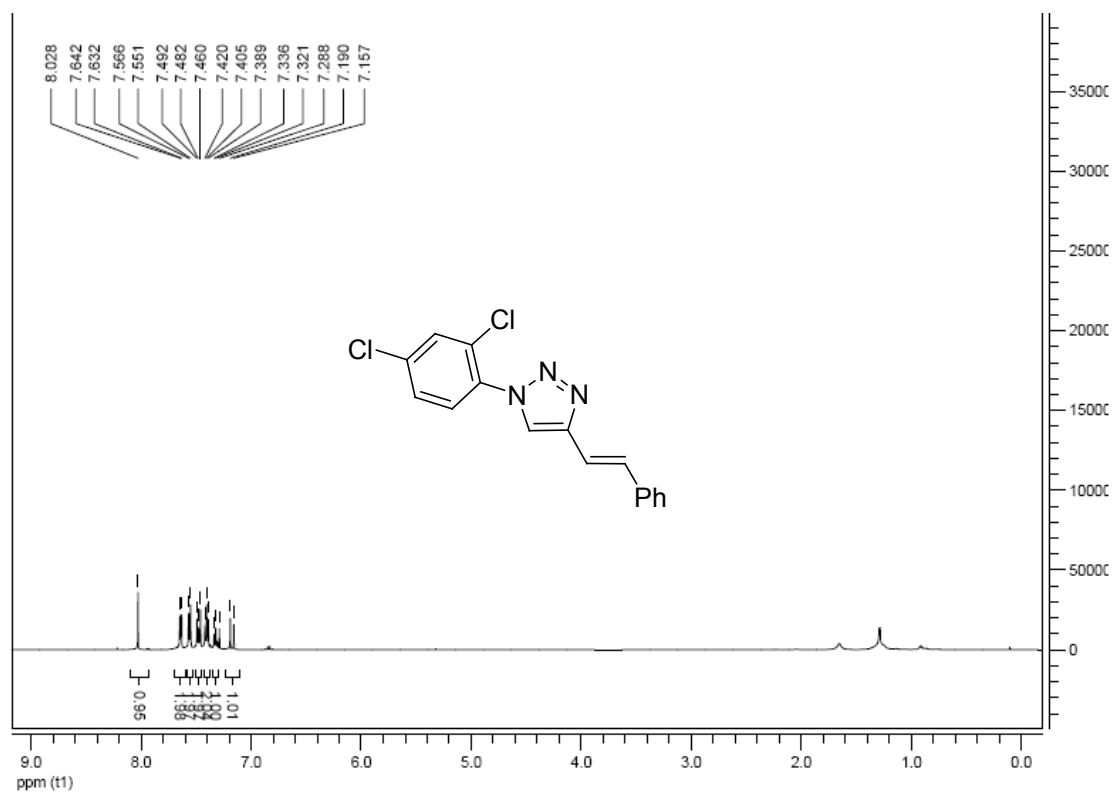
(E)-1-(4-phenoxyphenyl)-4-styryl-1H-1,2,3-triazole (3ac)



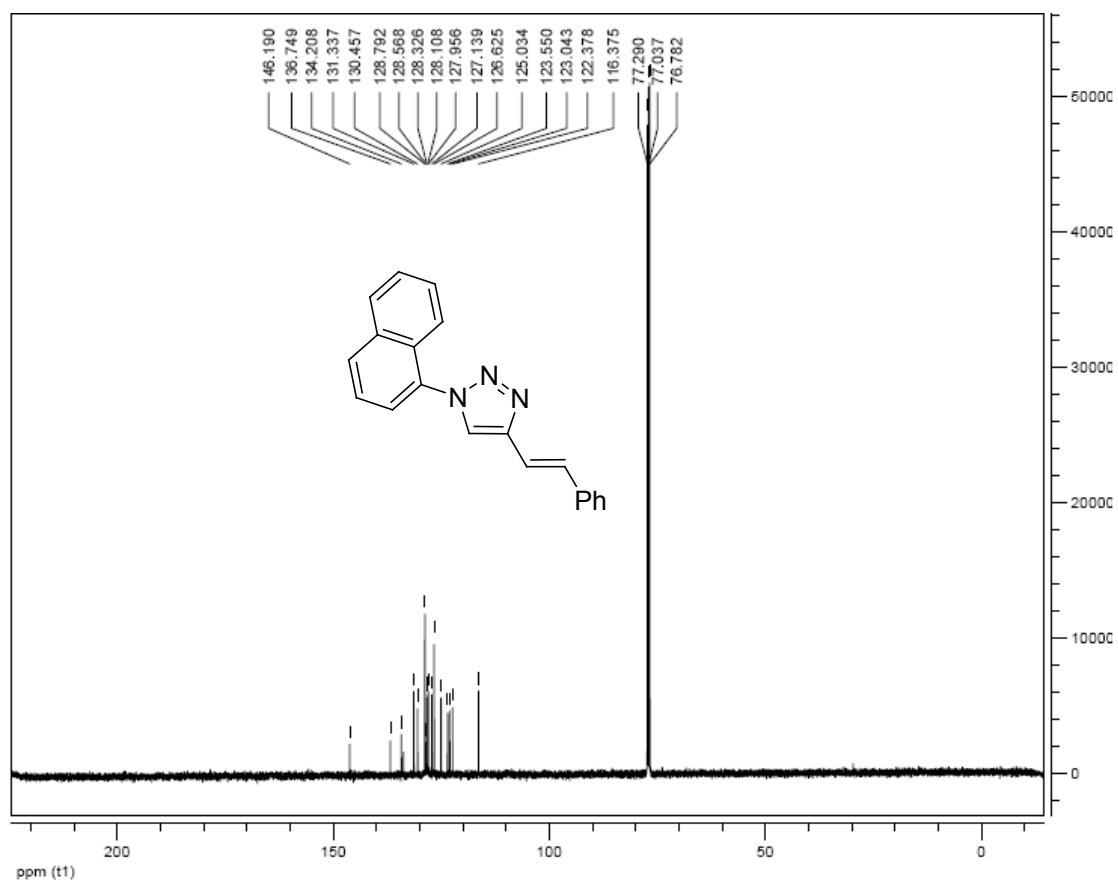
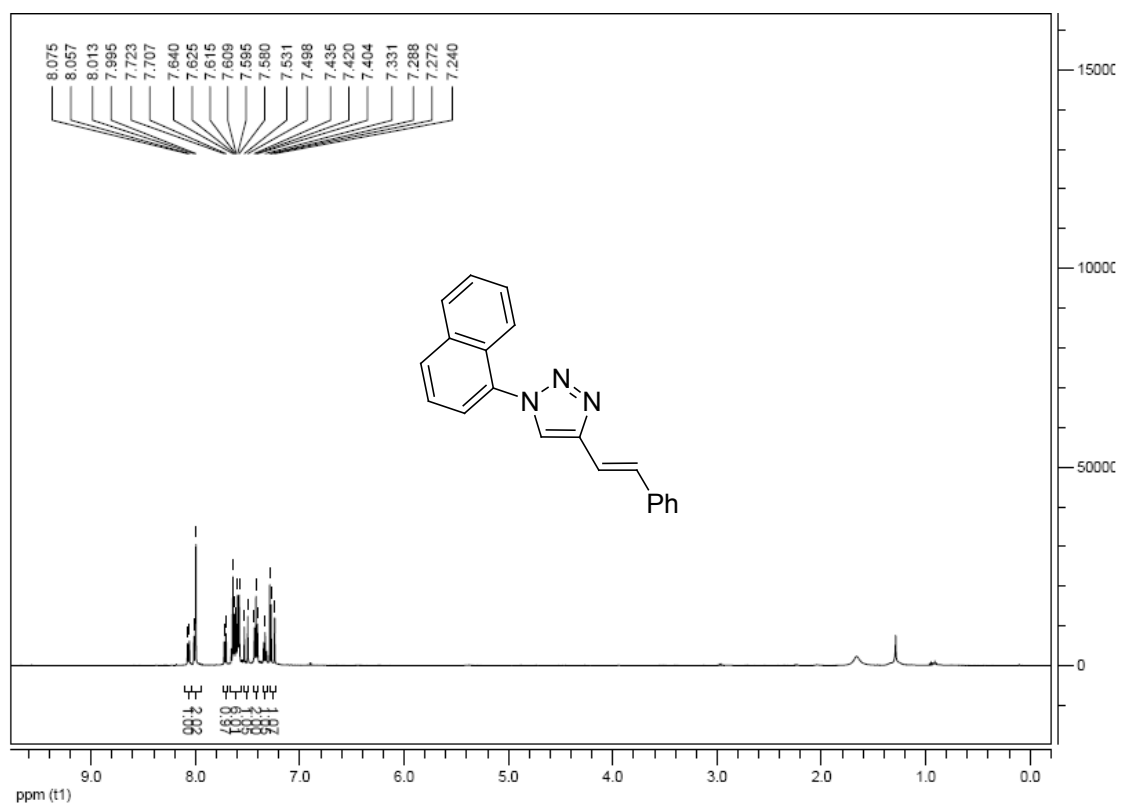
(E)-1-(3,5-dimethylphenyl)-4-styryl-1H-1,2,3-triazole (3ad)



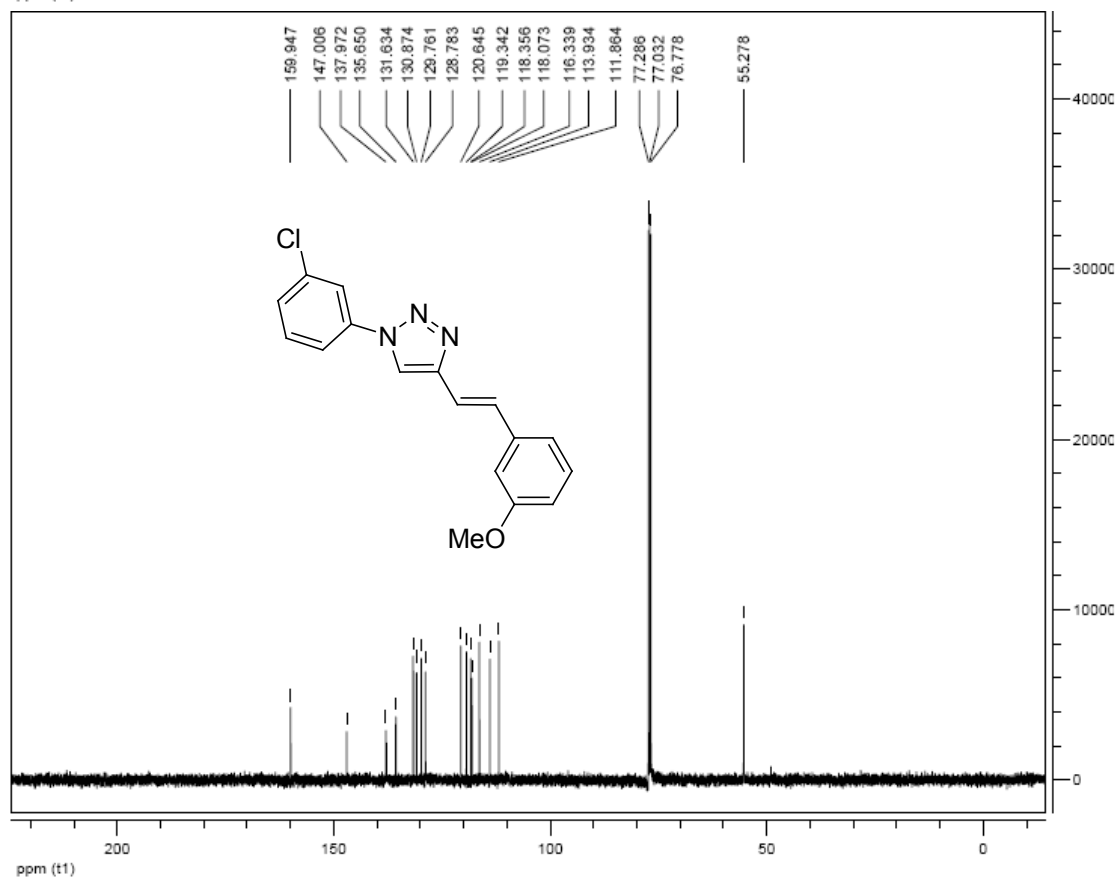
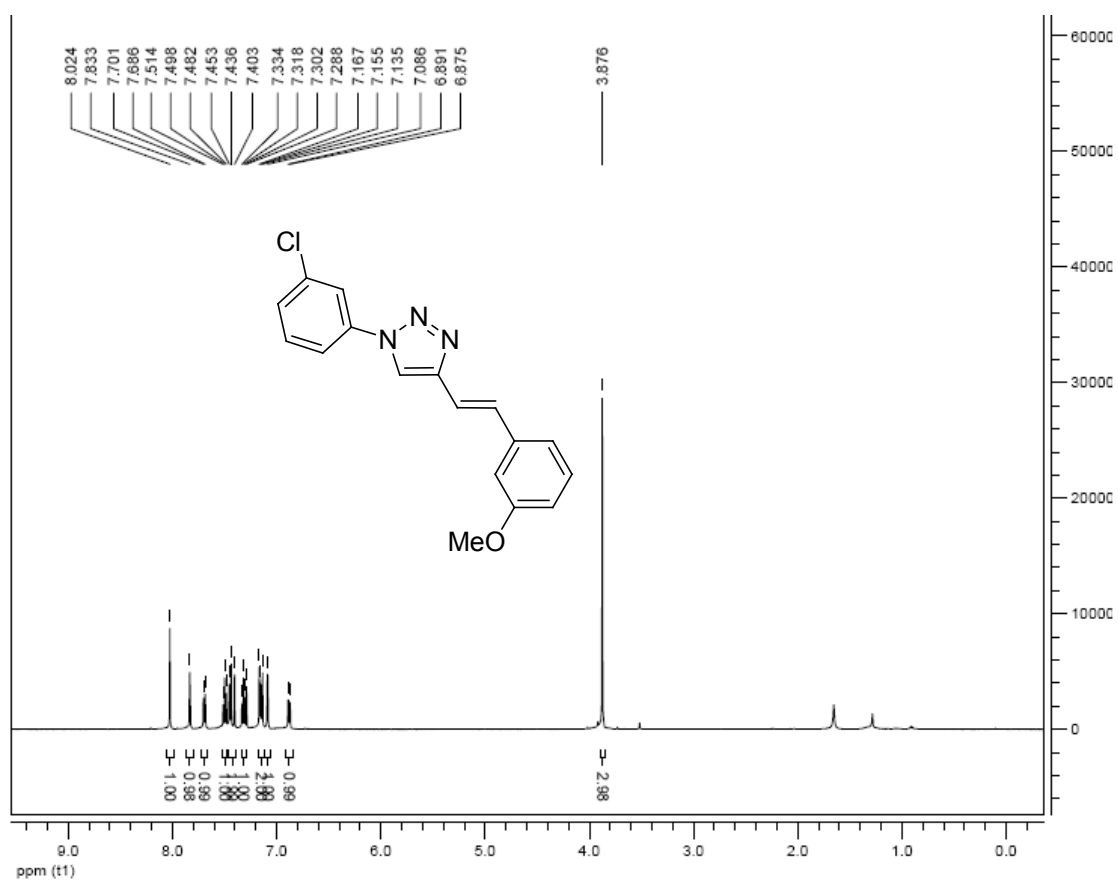
(E)-1-(2,4-dichlorophenyl)-4-styryl-1H-1,2,3-triazole (3ae)



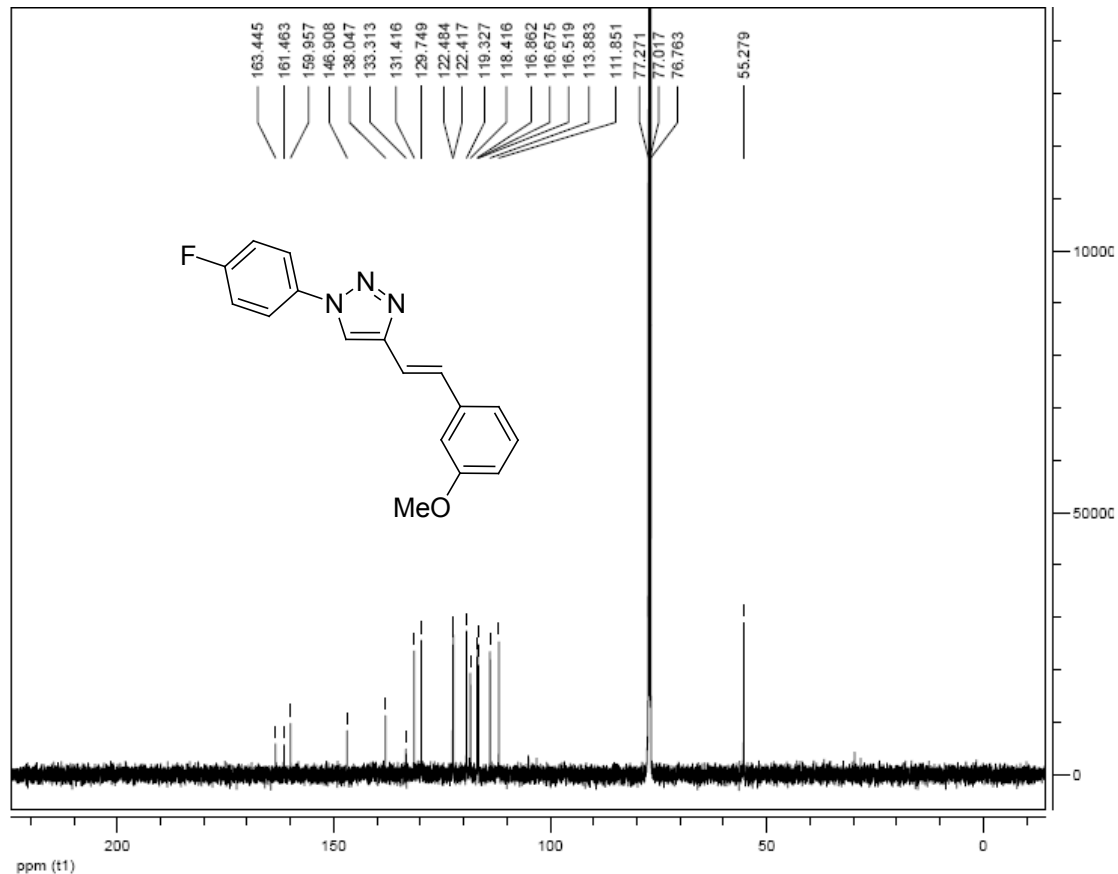
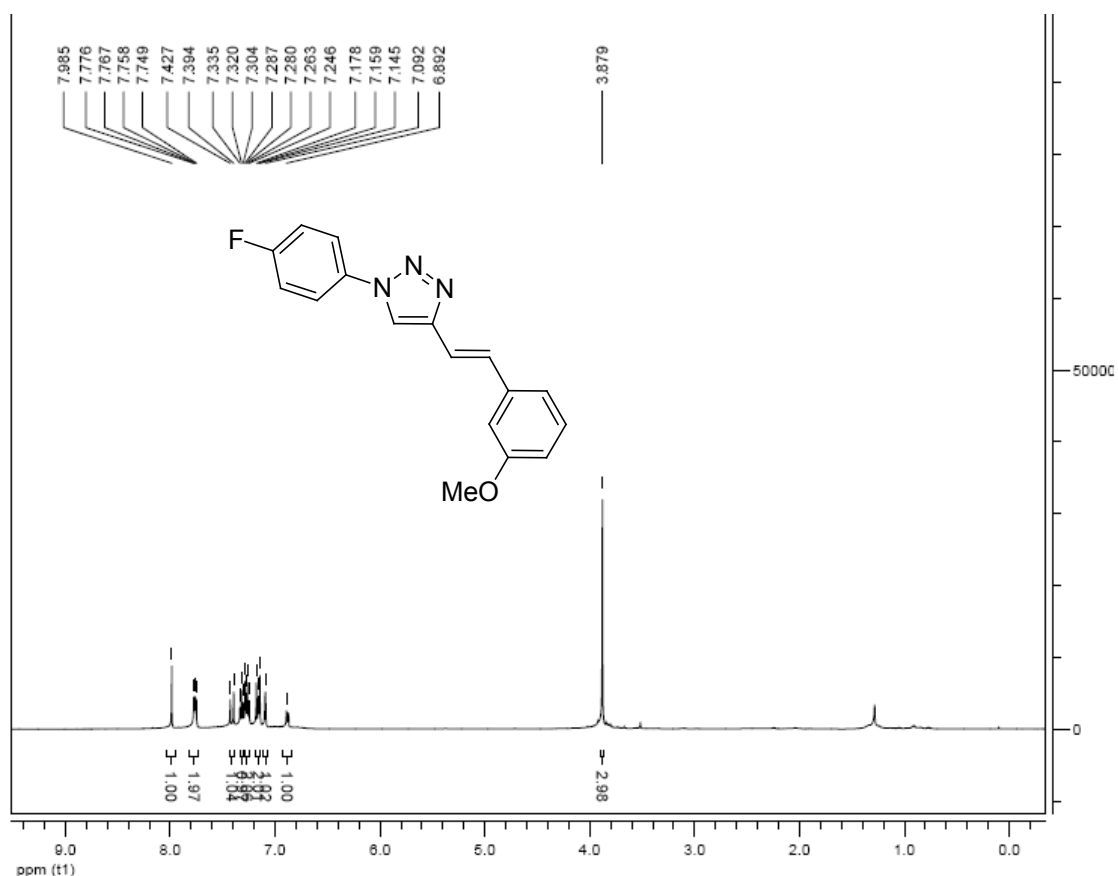
(E)-1-(naphthalen-1-yl)-4-styryl-1H-1,2,3-triazole (3af)



(E)-4-(3-methoxystyryl)-1-(3-chlorophenyl)-1H-1,2,3-triazole (3jg)



(E)-4-(3-methoxystyryl)-1-(4-fluorophenyl)-1H-1,2,3-triazole (3ji)



I: Reference

1. L. Albrecht, G. Dickmeiss, C. F. Weise, C. Rodríguez-Escrich, K. A. Jørgensen, *Angew. Chem. Int. Ed.* 2012, **51**, 13109-13113.