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Visible-light photocatalytic N-radical cascade of hydrazones for the synthesis of dihydropyrazole-fused benzosultams

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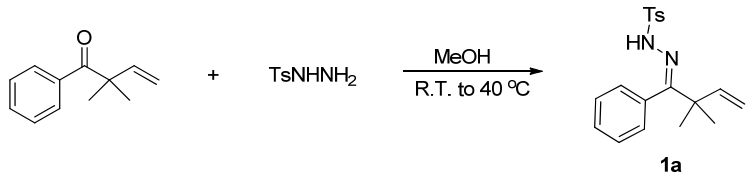
1. General Information

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. All the solvents were treated according to general methods. Flash column chromatography was performed using 200-300 mesh silica gel. ^{1}H NMR spectra were recorded on 400/600 MHz spectrophotometers. Chemical shifts are reported in delta (δ) units in parts per million (ppm) relative to the singlet (0 ppm) for tetramethylsilane (TMS). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR spectra were recorded on Varian Mercury 400 (100 MHz) with complete proton decoupling spectrophotometers ($CDCl_3$: 77.0 ppm). HRMS was recorded on Bruker ultrafleXtreme MALDITOF/TOF mass spectrometer.

2. Preparation and Spectral Data of Substrates

2.1 General procedure for preparation of β,γ-unsaturated hydrazones 1a-q, 1r-v.



1a

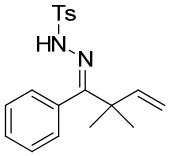
To a stirred solution of β,γ-unsaturated ketone (20 mmol, 1.0 eq.) in MeOH (30 mL), *p*-toluenesulfonyl hydrazide (22 mmol, 1.1 eq.) was added at room temperature. Then, the mixture was stirred at 40 ^{o}C until the reaction was completed, as monitored by TLC. Then, the solvent was removed and the residue was purified by flash column chromatography to give compound **1a** as a white solid (3.4 g, 50% yield). Other β,γ-unsaturated hydrazones **1b-q, 1r-v** were prepared according to the above procedure. [1-2]

References: [1] X.-Q. Hu, J.-R. Chen, Q. Wei, F.-L. Liu, Q.-H. Deng, A. M. Beauchemin and W.-J. Xiao, *Angew. Chem. Int. Ed.*, 2014, **53**, 12163-12167.

[2] X.-Q. Hu, X. Qi, J.-R. Chen, Q.-Q. Zhao, Q. Wei, Y. Lan and W.-J. Xiao, *Nat. Commun.*, 2016, **7**: 11188.

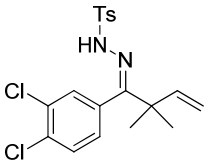
2.2 Spectral data of the substrates 1a-f, 1h-p, 1r-1v, 3c

Substrate 1a



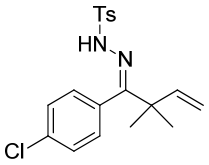
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.75 (d, *J* = 8.2 Hz, 2H), 7.36 (t, *J* = 6.3 Hz 3H), 7.31 (d, *J* = 8.0 Hz, 2H), 6.92 (s, 1H), 6.80 – 6.78 (m, 2H), 5.71 (dd, *J* = 17.3, 10.6 Hz, 1H), 4.94 (d, *J* = 10.5 Hz, 1H), 4.82 (d, *J* = 17.3 Hz, 1H), 2.46 (s, 3H), 1.15 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.7, 143.6, 143.6, 135.0, 131.2, 129.1, 129.1, 128.9, 127.6, 127.4, 112.9, 44.4, 25.2, 21.7. M.P.: 112.5 – 113.5. IR (in KBr): 1630, 1387, 1334, 1157, 1093, 545 cm^{-1}. HRMS (EI): m/z [M + H]$^+$ calcd for $C_{19}H_{23}N_2O_2S$: 343.1474; found: 343.1475.

Substrate 1b



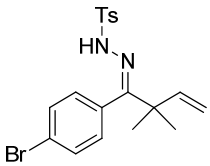
^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.78 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.1 Hz, 1H), 7.34 (d, *J* = 7.8 Hz, 2H), 6.93 (s, 2H), 6.73 (d, *J* = 8.0 Hz, 1H), 5.71 – 5.66 (dd, *J* = 17.4, 10.6 Hz, 1H), 5.01 (d, *J* = 10.6 Hz, 1H), 4.85 (d, *J* = 17.4 Hz, 1H), 2.47 (s, 3H), 1.16 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.8, 143.9, 143.2, 134.8, 133.7, 133.4, 131.1, 131.0, 129.4, 129.3, 127.7, 127.1, 113.8, 44.5, 25.2, 21.7. M.P.: 173.3 – 173.9 °C. IR (in KBr): 1629, 1390, 1333, 1156, 1096, 549 cm^{-1}. HRMS (EI): m/z [M + H]$^+$ calcd for $C_{19}H_{21}Cl_2N_2O_2S$: 411.0695; found: 411.0691.

Substrate 1c



^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.78 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 6.91 (s, 1H), 6.79 (d, *J* = 8.4 Hz, 2H), 5.70 (dd, *J* = 17.4, 10.6 Hz, 1H), 4.98 (d, *J* = 10.5 Hz, 1H), 4.84 (d, *J* = 17.4 Hz, 1H), 2.46 (s, 3H), 1.15 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.3, 143.8, 143.4, 135.4, 135.0, 129.6, 129.3, 129.2, 129.0, 127.7, 113.4, 44.5, 25.2, 21.7. M.P.: 143.2 – 143.5 °C. IR (in KBr): 1630, 1391, 1334, 1155, 1091, 547 cm^{-1}. HRMS (EI): m/z [M + H]$^+$ calcd for $C_{19}H_{22}ClN_2O_2S$: 377.1095; found: 377.1085.

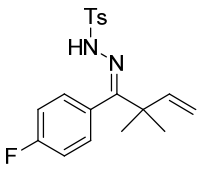
Substrate 1d



^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.78 (d, *J* = 8.2 Hz, 2H), 7.53 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 6.90 (s, 1H), 6.72 (d, *J* = 8.3 Hz, 2H), 5.69 (dd, *J* = 17.4, 10.6 Hz, 1H), 4.98 (d, *J* = 10.6 Hz, 1H), 4.84 (d, *J* = 17.4 Hz, 1H), 2.46 (s, 3H), 1.15 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.5, 144.0, 143.6, 135.1, 132.4, 129.4, 129.4, 127.9, 123.8, 113.6, 44.4,

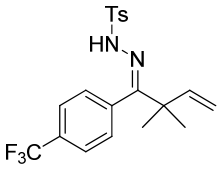
25.1, 21.6. M.P.: 142.0 – 143.2 °C. IR (in KBr): 1629, 1389, 1335, 1159, 1095, 547 cm^{-1}. HRMS (EI): m/z $[M + H]^+$ calcd for $C_{19}H_{22}N_2O_2SBr$: 421.0586; found: 421.0580.

Substrate 1e



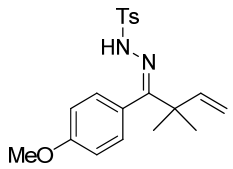
^1H NMR (600 MHz, $CDCl_3$) δ = 7.78 (d, *J* = 7.7 Hz, 2H), 7.33 (d, *J* = 7.7 Hz, 2H), 7.09 (t, *J* = 8.2 Hz, 2H), 6.93 (s, 1H), 6.84 (d, *J* = 5.3 Hz, 2H), 5.70 (dd, *J* = 17.3, 10.6 Hz, 1H), 4.97 (d, *J* = 10.5 Hz, 1H), 4.83 (d, *J* = 17.4 Hz, 1H), 2.46 (s, 3H), 1.15 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.7 (d, *J* = 248.0 Hz), 161.6, 143.8, 143.6, 135.1, 129.7 (d, *J* = 8.1 Hz), 129.2, 127.7, 127.1 (d, *J* = 3.4 Hz), 116.2 (d, *J* = 21.4 Hz) 113.3, 44.6, 25.4, 25.1, 21.7. M.P.: 142.0 – 142.7 °C. IR (in KBr): 1630, 1386, 1335, 1083, 547 cm^{-1}. HRMS (EI): m/z $[M + H]^+$ calcd for $C_{19}H_{22}FN_2O_2S$: 361.1381; found: 361.1386.

Substrate 1f



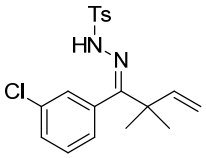
^1H NMR (600 MHz, $CDCl_3$) δ = 7.79 (d, *J* = 8.1 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.00 (d, *J* = 7.9 Hz, 2H), 6.84 (s, 1H), 5.71 (dd, *J* = 17.4, 10.6 Hz, 1H), 5.00 (d, *J* = 10.6 Hz, 1H), 4.85 (d, *J* = 17.4 Hz, 1H), 2.47 (s, 3H), 1.17 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.1, 144.2, 143.4, 135.3, 135.1, 131.6 (q, *J* = 32.8 Hz), 129.5, 128.4, 127.9, 126.1 (q, *J* = 3.7 Hz), 123.5 (q, *J* = 271.0 Hz), 113.8, 44.5, 25.1, 21.6. M.P.: 153.0 – 154.5 °C. IR (in KBr): 1630, 1409, 1332, 1161, 1102, 545 cm^{-1}. HRMS (EI): m/z $[M + H]^+$ calcd for $C_{20}H_{22}F_3N_2O_2S$: 411.1349; found: 411.1347.

Substrate 1h



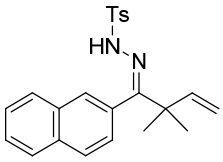
^1H NMR (400 MHz, $CDCl_3$) δ = 7.74 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.00 (s, 1H), 6.86 (d, *J* = 8.7 Hz, 2H), 6.72 (d, *J* = 8.6 Hz, 2H), 5.70 (dd, *J* = 17.3, 10.5 Hz, 1H), 4.93 (d, *J* = 10.5 Hz, 1H), 4.81 (d, *J* = 17.3 Hz, 1H), 3.79 (s, 3H), 2.44 (s, 3H), 1.14 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.7, 159.8, 143.8, 143.6, 135.1, 129.1, 128.9, 127.7, 123.0, 114.4, 112.8, 55.3, 44.6, 25.3, 21.7. M.P.: 105.9 – 106.9 °C. IR (in KBr): 1608, 1510, 1343, 1173, 1026, 551 cm^{-1}. HRMS (EI): m/z $[M + H]^+$ calcd for $C_{20}H_{25}N_2O_3S$: 373.1570; found: 373.1580.

Substrate 1i



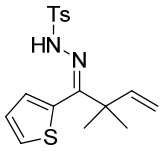
^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.79 (d, *J* = 8.1 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.35 – 7.33 (m, 3H), 6.93 (s, 1H), 6.80 (s, 1H), 6.75 (d, *J* = 7.3 Hz, 1H), 5.70 (dd, *J* = 17.5, 10.6 Hz, 1H), 4.99 (d, *J* = 10.6 Hz, 1H), 4.85 (d, *J* = 17.4 Hz, 1H), 2.47 (s, 3H), 1.16 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 161.1, 144.0, 143.4, 135.0, 134.9, 133.1, 130.4, 129.5, 129.4, 127.8, 127.5, 125.9, 113.6, 44.3, 25.0, 21.5. M.P.: 106.7 – 107.2 °C. IR (in KBr): 1630, 1595, 1565, 1409, 1385, 1333, 1159, 1095, 508 cm^{-1}. HRMS (EI): m/z $[M + H]^+$ calcd for $C_{19}H_{22}ClN_2O_2S$: 377.1081; found: 377.1085.

Substrate 1j



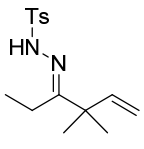
^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.86 (d, J = 8.2 Hz, 2H), 7.78 (t, *J* = 7.4 Hz, 3H), 7.58 – 7.53 (m, 2H), 7.35 (d, *J* = 7.9 Hz, 2H), 7.30 (s, 1H), 6.98 (s, 1H), 6.90 (d, *J* = 8.3 Hz, 1H), 5.81 (dd, *J* = 17.4, 10.6 Hz, 1H), 4.99 (d, *J* = 10.6 Hz, 1H), 4.87 (d, *J* = 17.4 Hz, 1H), 2.48 (s, 3H), 1.22 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.7, 143.7, 135.1, 132.9, 132.6, 129.2, 129.0, 128.7, 128.0, 127.8, 127.6, 127.1, 127.1, 127.0, 126.7, 124.6, 113.1, 44.7, 25.4, 21.8. M.P.: 148.9 – 149.8 °C. IR (in KBr): 1631, 1388, 1333, 1157, 1092, 548 cm^{-1}. HRMS (EI): m/z $[M + H]^+$ calcd for $C_{23}H_{25}N_2O_2S$: 393.1631; found: 393.1620.

Substrate 1k



^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.75 (d, *J* = 8.2 Hz, 2H), 7.48 (s, 1H), 7.41 – 7.39 (m, 1H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.06 – 7.03 (m, 1H), 6.79 – 6.78 (m, 1H), 5.70 (dd, *J* = 17.4, 10.5 Hz, 1H), 4.97 (d, *J* = 10.5 Hz, 1H), 4.81 (d, *J* = 17.4 Hz, 1H), 2.43 (s, 3H), 1.17 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 155.4, 143.8, 143.4, 134.8, 129.2, 128.9, 128.6, 128.1, 127.7, 127.2, 113.9, 44.9, 25.5, 21.7. M.P.: 62.9 – 63.4 °C. IR (in KBr): 1630, 1386, 1335, 1082, 548 cm^{-1}. HRMS (EI): m/z $[M + H]^+$ calcd for $C_{17}H_{21}N_2O_2S_2$: 349.1039; found: 349.1039.

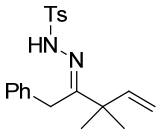
Substrate 1l



^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.01 (s, 1H), 7.83 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 5.62 (dd, *J* = 17.4, 10.6 Hz, 1H), 4.92 (dd, *J* = 22.7, 10.6 Hz, 2H), 2.42 (s, 3H), 2.10 (q, *J* = 7.6 Hz, 2H), 1.12 (s, 6H), 0.96 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =

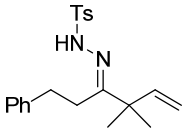
164.5, 143.8, 143.5, 134.8, 129.0, 127.7, 112.8, 45.3, 24.6, 21.6, 19.9, 10.1. M.P.: 100.3 – 101.3 °C. IR (in KBr): 1629, 1385, 1340, 1167, 1094, 884, 557 cm^{-1}. HRMS (EI): m/z $[M + Na]^+$ calcd for $C_{15}H_{22}N_2O_2S$: 317.1287; found: 317.1294.

Substrate 1m



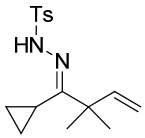
^1H NMR (600 MHz, $CDCl_3$) δ = 7.66 (d, *J* = 7.8 Hz, 2H), 7.31 (d, *J* = 7.7 Hz, 2H), 7.21 (t, *J* = 7.0 Hz, 1H), 7.16 (t, *J* = 7.4 Hz, 2H), 7.13 (s, 1H), 6.74 (d, *J* = 7.3 Hz, 2H), 5.75 (dd, *J* = 17.5, 10.5 Hz, 1H), 5.05 (s, 1H), 5.03 (d, *J* = 4.4 Hz, 1H), 3.53 (s, 2H), 2.47 (s, 3H), 1.19 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.1, 143.7, 143.4, 134.6, 132.9, 129.0, 128.9, 127.9, 127.2, 126.9, 113.6, 45.5, 33.0, 24.6, 21.8. M.P.: 92.8 – 93.9 °C. IR (in KBr): 1630, 1408, 1332, 1161, 1101, 545 cm^{-1}. HRMS (EI): m/z $[M + H]^+$ calcd for $C_{20}H_{25}N_2O_2S$: 357.1640; found: 357.1631.

Substrate 1n



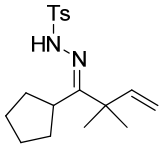
^1H NMR (400 MHz, $CDCl_3$) δ = 7.75 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 7.21 – 7.16 (m, 3H), 7.08 – 7.06 (m, 2H), 7.04 (s, 1H), 5.68 (dd, *J* = 17.3, 10.5 Hz, 1H), 4.99 (dd, *J* = 18.7, 14.0 Hz, 2H), 2.69 – 2.65 (m, 2H), 2.42 (s, 3H), 2.39 – 2.35 (m, 2H), 1.16 (m, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 163.2, 144.1, 143.7, 140.3, 134.8, 129.1, 128.6, 128.1, 128.0, 126.4, 113.2, 45.4, 31.0, 28.9, 24.7, 21.5. M.P.: 112.8 – 113.3 °C. IR (in KBr): 1628, 1404, 1338, 1156, 1098, 683, 581, 550 cm^{-1}. HRMS (EI): m/z $[M + H]^+$ calcd for $C_{21}H_{27}N_2O_2S$: 371.1789; found: 371.1788.

Substrate 1o



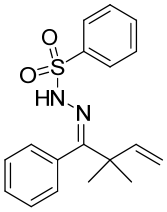
^1H NMR (400 MHz, $CDCl_3$) δ = 7.94 (s, 1H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 5.67 (dd, *J* = 17.4, 10.5 Hz, 1H), 4.78 (d, *J* = 10.5 Hz, 1H), 4.63 (d, *J* = 17.4 Hz, 1H), 2.41 (s, 3H), 1.20 (s, 6H), 0.99 – 0.97 (m, 1H), 0.84 – 0.81 (m, 2H), 0.60 – 0.57 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.0, 145.4, 143.7, 135.3, 129.2, 127.8, 112.2, 44.9, 26.1, 21.4, 8.6, 4.9. M.P.: 76.0 – 77.2 °C. IR (in KBr): 1633, 1411, 1159, 1087, 552 cm^{-1}. HRMS (EI): m/z $[M + H]^+$ calcd for $C_{16}H_{23}N_2O_2S$: 307.1475; found: 307.1475.

Substrate 1p



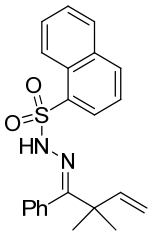
^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.82 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.17 (s, 1H), 5.66 (dd, *J* = 17.5, 10.6 Hz, 1H), 5.01 (d, *J* = 10.6 Hz, 1H), 4.92 (d, *J* = 17.5 Hz, 1H), 2.43 (s, 3H), 1.81 (s, 2H), 1.67 – 1.60 (m, 7H), 1.11 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.9, 143.9, 143.6, 134.7, 129.0, 127.8, 113.2, 46.1, 38.7, 28.4, 27.0, 24.9, 21.6. M.P.: 83.0 – 83.9 °C. IR (in KBr): 1630, 1600, 1384, 1364, 1337, 1171, 1091, 586, 582, 545 cm^{-1}. HRMS (EI): m/z $[M + H]^+$ calcd for $C_{18}H_{27}N_2O_2S$: 335.1781; found: 335.1788.

Substrate 1r



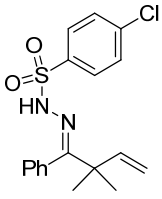
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.90 – 7.84 (m, 2H), 7.60 (t, *J* = 7.3 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 3.1 Hz 3H), 6.95 (s, 1H), 6.79 – 6.76 (m, 2H), 5.69 (dd, *J* = 17.3, 10.5 Hz, 1H), 4.94 (d, *J* = 10.5 Hz, 1H), 4.82 (d, *J* = 17.3 Hz, 1H), 1.15 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.3, 143.8, 138.2, 133.1, 131.4, 129.6, 129.2, 128.8, 127.9, 127.6, 113.3, 44.5, 25.2. M.P.: 115.2 – 115.8 °C. IR (in KBr): 1631, 1386, 1340, 1167, 1093, 560 cm^{-1}. HRMS (EI): m/z $[M + Na]^+$ calcd for $C_{18}H_{20}N_2O_2S$: 351.1134; found: 351.1138.

Substrate 1s



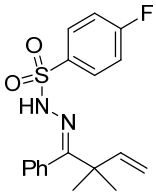
^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.56 (d, *J* = 8.2 Hz, 1H), 8.37 (d, *J* = 7.5 Hz, 1H), 8.12 (d, *J* = 8.3 Hz, 1H), 7.98 (d, *J* = 7.8 Hz, 1H), 7.65 – 7.51(m, 3H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.21 (s, 1H), 6.57 (d, *J* = 7.1 Hz, 2H), 5.46 (dd, *J* = 17.4, 10.6 Hz, 1H), 4.80 (d, *J* = 10.7 Hz, 1H), 4.63 (d, *J* = 17.4 Hz, 1H), 0.97 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.8, 143.6, 134.6, 134.0, 133.5, 131.1, 129.3, 129.0, 128.3, 128.1, 127.7, 126.8, 124.7, 124.2, 113.0, 44.3, 25.0. M.P.: 76.5 – 77.0 °C. IR (in KBr): 1629, 1412, 1337, 1108, 627 cm^{-1}. HRMS (EI): m/z $[M + H]^+$ calcd for $C_{22}H_{23}N_2O_2S$: 349.1475; found: 349.1477.

Substrate 1t



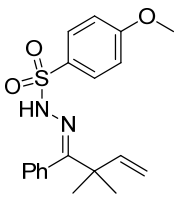
^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.85 (d, *J* = 8.2 Hz, 2H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.44 – 7.40 (m, 3H), 6.99 (s, 1H), 6.85 (dd, *J* = 6.6, 3.2 Hz, 2H), 5.75 (dd, *J* = 17.4, 10.6 Hz, 1H), 4.99 (d, *J* = 10.5 Hz, 1H), 4.87 (d, *J* = 17.4 Hz, 1H), 1.17 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.5, 143.7, 139.6, 136.8, 131.3, 129.5, 129.4, 129.2, 129.1, 127.6, 113.3, 44.5, 25.2. M.P.: 132.2 – 132.9 °C. IR (in KBr): 1629, 1385, 1338, 1163, 1085, 581 cm^{-1}. HRMS (EI): m/z $[M + H]^+$ calcd for $C_{18}H_{20}ClN_2O_2S$: 363.0929; found: 363.0931.

Substrate 1u



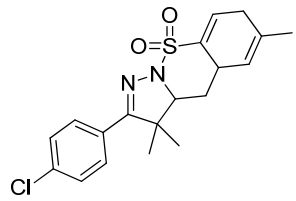
^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.93 (dd, *J* = 8.5, 5.2 Hz, 2H), 7.41 – 7.40 (m, 3H), 7.22 (t, *J* = 8.4 Hz, 2H), 6.97 (s, 1H), 6.85 – 6.83 (m, 2H), 5.74 (dd, *J* = 17.4, 10.6 Hz, 1H), 4.99 (d, *J* = 10.6 Hz, 1H), 4.87 (d, *J* = 17.5 Hz, 1H), 1.17 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 165.4 (*J* = 256.6 Hz), 163.4, 143.75, 134.3 (*J* = 3.4 Hz), 131.3, 130.7 (*J* = 9.4 Hz) 129.5, 129.2, 127.6, 116.0 (*J* = 22.7 Hz), 113.3, 44.5, 25.2. M.P.: 123.2 – 123.9 ^{o}C. IR (in KBr): 1629, 1411, 1385, 1336, 1152, 1092, 545 cm^{-1}. HRMS (EI): m/z $[M + H]^+$ calcd for $C_{18}H_{20}FN_2O_2S$: 347.1224; found: 347.1220.

Substrate 1v



^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.80 (d, *J* = 8.8 Hz, 2H), 7.36 – 7.34 (m, 3H), 6.97 (d, *J* = 8.7 Hz, 2H), 6.92 (s, 1H), 6.79 – 6.78 (m, 2H), 5.72 (dd, *J* = 17.3, 10.5 Hz, 1H), 4.95 (d, *J* = 10.5 Hz, 1H), 4.83 (d, *J* = 17.3 Hz, 1H), 3.88 (s, 3H), 1.16 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.1, 162.8, 137.3, 130.2, 123.0, 128.4, 128.3, 127.9, 127.7, 114.4, 112.5, 72.0, 55.6, 51.3, 28.1, 26.8, 20.5. M.P.: 90.0 – 90.9 ^{o}C. IR (in KBr): 1632, 1597, 1344, 1162, 1095, 1024, 555 cm^{-1}. HRMS (EI): m/z $[M - H]^+$ calcd for $C_{19}H_{21}N_2O_3S$: 357.1268; found: 357.1278.

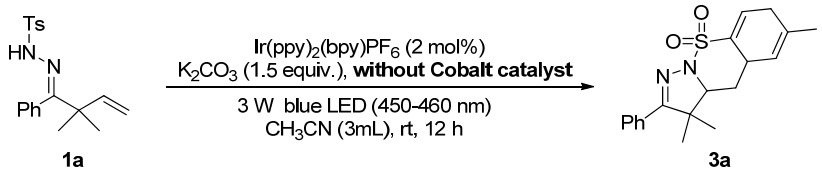
Substrate 3c



^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.64 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 6.90 (m, 1H), 5.37 (s, 1H), 3.93 (dd, *J* = 12.3, 2.9 Hz, 1H), 3.48 (s, 1H), 2.90 – 2.78 (m, 2H), 1.84 (m, 1H), 1.73 (s, 3H), 1.65 (q, *J* = 12.6 Hz, 1H), 1.41 (s, 3H), 1.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.8, 136.3, 136.0, 131.7, 130.6, 129.1, 128.8, 128.7, 120.8, 72.5, 51.0, 35.4, 32.5, 31.2, 23.5, 22.6, 18.5. M.P.: 130.2 – 130.9 ^{o}C. IR (in KBr): 1631, 1402, 1385, 1158, 1091, 543 cm^{-1}. HRMS (EI): m/z $[M + H]^+$ calcd for $C_{19}H_{22}N_2O_2S$: 377.1085; found: 377.1087.

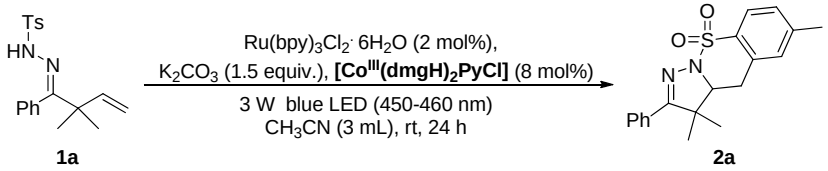
3. General Procedure and Spectral Data of the Products

3.1 General procedure for the synthesis of 3a



1a (68.5 mg, 0.2 mmol), $Ir(ppy)_2(bpy)PF_6$ (3.2 mg, 0.004 mmol), K_2CO_3 (41.5 mg, 0.3 mmol), were dissolved in CH_3CN (3.0 mL). Then, the resulting mixture was degassed via 'freeze-pump-thaw' procedure (3 times) under argon atmosphere. After that, the solution was stirred at a distance of ~5 cm from a 3W blue LEDs (450-460 nm) at room temperature about 12 h until the reaction was completed, as monitored by TLC analysis. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 10:1~3:1) directly to give the desired product **3a** in 85% isolated yield as a white solid.

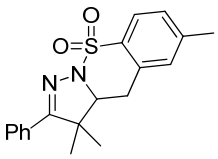
3.2 General procedure for the synthesis of benzosultam 2



1a (68.5 mg, 0.2 mmol), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (3.0 mg. 0.004 mmol), K_2CO_3 (41.5 mg, 0.3 mmol) , $[Co^{III}(dmgH)_2PyCl]$ (6.5 mg, 0.016 mmol) were dissolved in CH_3CN (3.0 mL). Then, the resulting mixture was degassed via 'freeze-pump-thaw' procedure (3 times) under argon atmosphere. After that, the solution was stirred at a distance of ~5 cm from a 3 W blue LEDs (450-460 nm) at room temperature about 24 h until the reaction was completed, as monitored by TLC analysis. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 10:1~3:1) directly to give the desired product **2a** in 73% isolated yield as a white solid.

3.3 Spectral data of the desired products 2a-2v, 3a and 4

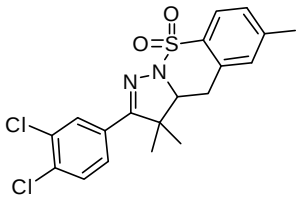
Product 2a



Yield of **2a** : 73% as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.84 (d, *J* = 7.9 Hz, 1H), 7.41 (d, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.26 (s,

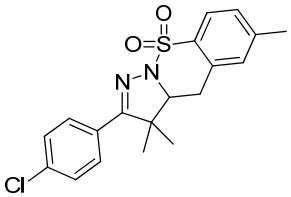
1H), 7.08 (s, 1H), 4.38 – 4.36 (m, 1H), 3.22 (dd, *J* = 15.9, 7.2 Hz, 1H), 3.03 (dd, *J* = 15.9, 4.3 Hz, 1H), 2.38 (s, 3H), 1.55 (s, 3H), 1.36 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ = 165.9, 143.4, 134.9, 132.8, 130.0, 129.8, 129.2, 128.1, 127.5, 125.4, 72.0, 51.3, 27.8, 26.8, 21.7, 20.5. M.P.: 169.2 – 170.6 °C. IR (in KBr): 1631, 1411, 1340, 1081, 984, 546 cm^{-1}. HRMS (EI): m/z $[M + H]^+$ calcd for $C_{19}H_{21}N_2O_2S$: 341.1318; found: 341.1317.

Product 2b



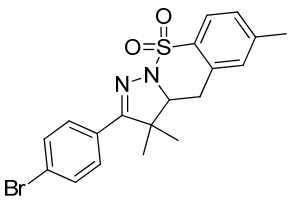
Yield of **2b** : 46% as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.81 (d, *J* = 8.0 Hz, 1H), 7.49 (s, 1H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.29 – 7.25 (m, 2H), 7.05 (s, 1H), 4.37 – 4.34 (m, 1H), 3.21 (dd, *J* = 16.0, 7.0 Hz, 1H), 3.02 (dd, *J* = 15.8, 4.9 Hz, 1H), 2.38 (s, 3H), 1.53 (s, 3H), 1.36 (s, 3H). 13C NMR (100 MHz, $CDCl_3$) δ = 163.6, 143.7, 134.6, 134.2, 132.7, 132.5, 130.2, 129.8, 129.3, 129.2, 128.4, 126.6, 125.5, 72.1, 51.1, 27.8, 26.6, 21.7, 20.5. M.P.: 189.3 – 190.1 °C. IR (in KBr): 1632, 1465, 1318, 1081, 678, 570 cm^{-1}. HRMS (EI): m/z $[M + Na]^+$ calcd for $C_{19}H_{18}N_2O_2SCl_2$: 431.0361; found: 431.0358.

Product 2c



Yield of **2c** : 77% as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.79 (d, *J* = 7.9 Hz, 1H), 7.35 (d, *J* = 8.5 Hz, 2H), 7.24 (d, *J* = 6.9 Hz, 3H), 7.05 (s, 1H), 4.34 (dd, *J* = 6.7, 5.2 Hz, 1H), 3.20 (dd, *J* = 15.9, 7.0 Hz, 1H), 3.02 (dd, *J* = 15.9, 5.0 Hz, 1H), 2.36 (s, 3H), 1.52 (s, 3H), 1.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.7, 143.5, 135.9, 134.7, 132.7, 129.2, 128.8, 128.4, 128.4, 128.2, 125.4, 72.0, 51.2, 27.8, 26.7, 21.7, 20.5. M.P.: 157.2 – 158.0 °C. IR (in KBr): 1631, 1413, 1345, 1187, 1077, 983, 576 cm^{-1}. HRMS (EI): m/z $[M + H]^+$ calcd for: $C_{19}H_{20}N_2O_2SCl$: 375.0938; found: 375.0929.

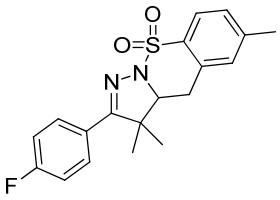
Product 2d



Yield of **2d** : 51% as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.80 (d, *J* = 8.0 Hz, 1H), 7.42 – 7.40 (m, 2H), 7.29 – 7.27 (m, 2H), 7.22 (s, 1H), 7.05 (s, 1H), 4.34 (dd, *J* = 7.1, 5.0 Hz, 1H), 3.20 (dd, *J* = 15.9, 7.1 Hz, 1H), 3.02 (dd, *J* = 15.9, 5.0 Hz, 1H), 2.37 (s, 3H), 1.52 (s, 3H), 1.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$)

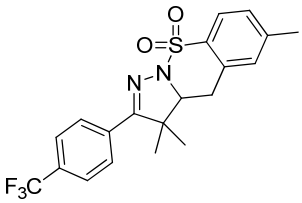
δ = 165.0, 143.7, 134.9, 133.0, 131.6, 129.4, 129.2, 129.0, 128.5, 125.7, 124.6, 72.1, 51.1, 27.7, 26.6, 21.6, 20.4. M.P.: 137.1 – 138.4 °C. IR (in KBr): 1632, 1415, 1317, 1078, 988, 687, 575 cm^{-1}. HRMS (EI): m/z $[M + H]^+$ calcd for: $C_{19}H_{19}N_2O_2SBr$: 419.0435; found: 419.0423.

Product 2e



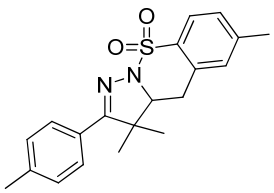
Yield of **2e** : 54% as a white solid. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.81 (d, *J* = 7.9 Hz, 1H), 7.40 (dd, *J* = 8.5, 5.4 Hz, 2H), 7.24 (d, *J* = 7.6 Hz 1H), 7.06 (s, 1H), 6.97 (t, *J* = 8.5 Hz, 2H), 4.34 (dd, *J* = 6.8, 5.2 Hz, 1H), 3.20 (dd, *J* = 15.9, 7.0 Hz, 1H), 3.02 (dd, *J* = 15.9, 5.1 Hz, 1H), 2.37 (s, 3H), 1.53 (s, 3H), 1.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 165.1, 163.7 (d, *J* = 249.6 Hz), 143.7, 134.9, 133.0, 129.7 (d, *J* = 8.5 Hz), 129.3, 128.4, 126.3 (d, *J* = 3.4 Hz), 125.7, 115.6, 115.4, 71.9, 51.2, 27.7, 26.6, 21.6, 20.4. M.P.: 199.5 – 200.2 °C. IR (in KBr): 1631, 1387, 1336, 1161, 1075, 673, 547 cm^{-1}. HRMS (EI): m/z $[M + H]^+$ calcd for: $C_{19}H_{20}N_2O_2FS$: 359.1221; found: 359.1224.

Product 2f



Yield of **2f** : 34% as a white solid. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.81 (d, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 1.1 Hz, 4H), 7.26 (s, 1H), 7.06 (s, 1H), 4.39 (dd, *J* = 7.2, 4.8 Hz, 1H), 3.23 (dd, *J* = 16.0, 7.2 Hz, 1H), 3.03 (dd, *J* = 15.9, 4.7 Hz, 1H), 2.38 (s, 3H), 1.56 (s, 3H), 1.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.7, 143.9, 134.8, 133.7, 133.0, 131.7 (q, *J* = 32.6 Hz), 129.4, 128.5, 128.0, 127.2, 125.7, 125.3 (q, *J* = 3.7 Hz), 123.7 (q, *J* = 271.0 Hz), 72.2, 51.2, 27.7, 26.6, 21.6, 20.3. M.P.: 176.9 – 177.5 °C. IR (in KBr): 1630, 1411, 1387, 1332, 1074, 984, 576 cm^{-1}. HRMS (EI): m/z $[M + H]^+$ calcd for: $C_{20}H_{20}N_2O_2F_3S$: 409.1194; found: 409.1192.

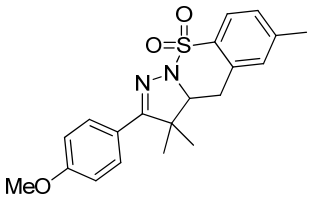
Product 2g



Yield of **2g** : 56% as a white solid. ^1H NMR (600 MHz, $CDCl_3$) δ = 7.83 (d, *J* = 7.9 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.6 Hz, 1H), 7.10 (d, *J* = 7.8 Hz, 2H), 7.06 (s, 1H), 4.35– 4.33 (m, 1H), 3.20 (dd, *J* = 15.9, 7.1 Hz, 1H), 3.02 (dd, *J* = 15.9, 4.8 Hz, 1H), 2.37 (s, 3H), 2.33 (s, 3H), 1.54 (s, 3H), 1.36 (s, 3H). ^{13}C NMR

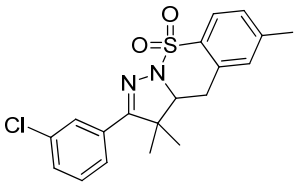
(100 MHz, $CDCl_3$) δ = 166.0, 143.6, 140.3, 135.1, 133.0, 129.3, 129.0, 128.3, 127.6, 127.3, 125.7, 71.9, 51.2, 27.7, 26.7, 21.6, 21.3, 20.4. M.P.: 185.1 – 185.9 °C.IR (in KBr): 1632, 1463, 1314, 1147, 1079, 987, 613 cm^{-1}. HRMS (EI): m/z $[M + H]^+$ calcd for: $C_{20}H_{23}N_2O_2S$: 355.1472; found: 355.1475.

Product 2h



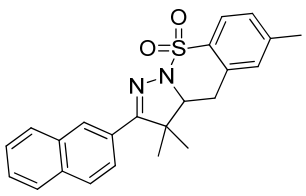
Yield of **2h** : 46% as a white solid. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.81 (d, *J* = 7.9 Hz, 1H), 7.40 (d, *J* = 8.8 Hz, 2H), 7.21 (s, 1H), 7.04 (s, 1H), 6.79 (d, *J* = 8.9 Hz, 2H), 4.31 (dd, *J* = 6.9, 5.3 Hz, 1H), 3.78 (s, 3H), 3.18 (dd, *J* = 15.9, 6.9 Hz, 1H), 3.02 (dd, *J* = 15.9, 5.2 Hz, 1H), 2.36 (s, 3H), 1.54 (s, 3H), 1.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 165.6, 161.0, 143.5, 135.0, 133.1, 129.4, 129.2, 128.3, 125.7, 122.5, 113.7, 71.8, 55.3, 51.1, 27.7, 26.6, 21.5, 20.5. M.P.: 180.1 – 181.7 °C. IR (in KBr): 2973, 1632, 1141, 1081, 988, 568 cm^{-1}. HRMS (EI): m/z $[M + H]^+$ calcd for: $C_{20}H_{23}N_2O_3S$: 371.1422; found: 371.1424.

Product 2i



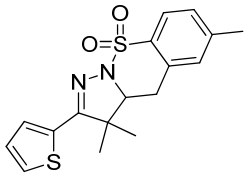
Yield of **2i** : 58% as a white solid. ^1H NMR (600 MHz, $CDCl_3$) δ = 7.84 (d, *J* = 7.9 Hz, 1H), 7.38 (s, 1H), 7.33 (dd, *J* = 11.7, 8.6 Hz, 2H), 7.28 (s, 1H), 7.24 (d, *J* = 7.8 Hz, 1H), 7.08 (s, 1H), 4.39 – 4.35 (m, 1H), 3.22 (dd, *J* = 15.8, 7.0 Hz, 1H), 3.03 (dd, *J* = 16.0, 4.4 Hz, 1H), 2.39 (s, 3H), 1.54 (s, 3H), 1.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.6, 143.6, 134.7, 134.1, 132.7, 131.7, 129.9, 129.5, 129.3, 128.3, 127.6, 125.5, 72.1, 51.3, 27.8, 26.7, 21.7, 20.5. M.P.: 148.3 – 148.9 °C. IR (in KBr): 1631, 1412, 1342, 1079, 984, 576 cm^{-1}. HRMS (EI): m/z $[M + H]^+$ calcd for $C_{19}H_{20}N_2O_2SCl$: 375.0933; found: 375.0929.

Product 2j



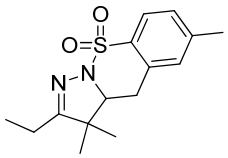
Yield of **2j** : 56% as a white solid. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.89 (s, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 9.3 Hz, 2H), 7.73 (d, *J* = 8.6 Hz, 1H), 7.57 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.48 – 7.45 (m, 2H), 7.26 – 7.24 (m, 1H), 7.06 (s, 1H), 4.39 (dd, *J* = 6.9, 5.3 Hz, 1H), 3.23 (dd, *J* = 15.9, 7.0 Hz, 1H), 3.07 (dd, *J* = 15.9, 5.2 Hz, 1H), 2.37 (s, 3H), 1.64 (s, 3H), 1.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 165.8, 143.6, 135.0, 133.7, 133.1, 132.5, 129.4, 128.4, 128.3, 128.1, 127.6, 127.3, 127.1, 126.5, 125.6, 124.9, 72.0, 51.2, 27.7, 26.7, 21.5, 20.5. M.P.: 217.7 – 218.8 °C. IR (in KBr): 1632, 1415, 1317, 1078, 988, 575 cm^{-1}. HRMS (EI): m/z $[M + H]^+$ calcd for $C_{23}H_{23}N_2O_2S$: 391.1484; found: 391.1475.

Product 2k



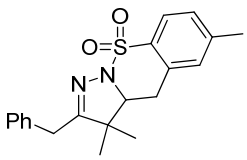
Yield of **2k** : 34% as a yellow solid. ^{1}H NMR (400 MHz, cdcl$_3$) δ = 7.79 (d, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 3.6 Hz, 1H), 7.32 (d, *J* = 5.0 Hz, 1H), 7.20 (d, *J* = 7.8 Hz, 1H), 7.05 (s, 1H), 7.00 – 6.97 (m, 1H), 4.32 (t, *J* = 6.2 Hz, 1H), 3.19 (dd, *J* = 15.9, 6.7 Hz, 1H), 3.06 (dd, *J* = 15.9, 5.7 Hz, 1H), 2.36 (s, 3H), 1.54 (s, 3H), 1.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.9, 143.6, 134.7, 133.3, 132.6, 129.4, 128.6, 128.5, 128.0, 127.3, 125.6, 71.4, 51.4, 27.9, 26.5, 21.6, 20.6. M.P.: 239.4 – 240.2 °C. IR (in KBr): 1631, 1412, 1344, 1078, 985, 550 cm^{-1}. HRMS (EI): m/z $[M + H]^+$ calcd for: $C_{17}H_{19}N_2O_2S_2$: 347.0882; found: 347.0882.

Product 2l



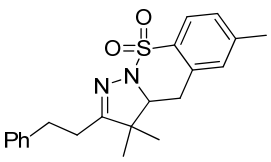
Yield of **2l** : 45% as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.79 (d, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 7.9 Hz, 1H), 7.07 (s, 1H), 4.21 – 4.16 (m, 1H), 3.16 (dd, *J* = 15.9, 7.1 Hz, 1H), 2.93 (dd, *J* = 15.9, 4.8 Hz, 1H), 2.38 (s, 3H), 2.23 – 2.17 (m, 1H), 2.12 – 2.06 (m, 1H), 1.27 (s, 3H), 1.17 (s, 3H), 1.00 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.0, 143.4, 135.1, 133.1, 129.2, 128.3, 125.8, 70.2, 51.5, 27.9, 25.8, 21.6, 19.6, 19.6, 10.8. M.P.: 99.3 – 100.8 °C. IR (in KBr): 1630, 1413, 1386, 1340, 1187, 1077, 564 cm^{-1}. HRMS (EI): m/z $[M + H]^+$ calcd for: $C_{15}H_{21}N_2O_2S$: 293.1315; found: 293.1318.

Product 2m



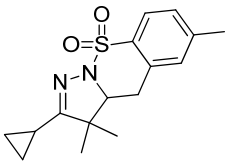
Yield of **2m** : 53% as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.81 (d, *J* = 7.9 Hz, 1H), 7.28 (d, *J* = 7.7 Hz, 1H), 7.10 (t, *J* = 7.2 Hz, 1H), 7.02 (t, *J* = 7.4 Hz, 2H), 6.87 (s, 1H), 6.64 (d, *J* = 7.4 Hz, 2H), 4.29 (dd, *J* = 8.3, 2.1 Hz, 1H), 3.60 (d, *J* = 14.5 Hz, 1H), 3.34 (d, *J* = 14.5 Hz, 1H), 3.18 (dd, *J* = 15.8, 8.3 Hz, 1H), 2.71 (dd, *J* = 15.8, 2.0 Hz, 1H), 2.38 (s, 3H), 1.21 (s, 3H), 0.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.5, 143.7, 135.4, 135.3, 132.1, 129.4, 128.2, 128.2, 126.4, 126.1, 71.0, 51.8, 32.7, 27.2, 27.0, 21.6, 20.2. M.P.: 130.5 – 131.8 °C. IR (in KBr): 1631, 1386, 1344, 1075, 724, 549 cm^{-1}. HRMS (EI): m/z $[M + H]^+$ calcd for: $C_{20}H_{23}N_2O_2S$: 355.1483; found: 355.1475.

Product 2n



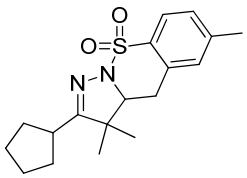
Yield of **2n** : 61% as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.77 (d, *J* = 7.9 Hz, 1H), 7.21 – 7.17 (m, 3H), 7.14 (d, *J* = 7.0 Hz, 1H), 7.05 (d, *J* = 8.2 Hz, 3H), 4.18 (dd, *J* = 6.8, 5.1 Hz, 1H), 3.15 (dd, *J* = 15.8, 7.1 Hz, 1H), 2.91 (dd, *J* = 15.9, 4.9 Hz, 1H), 2.80 – 2.71 (m, 2H), 2.50 – 2.42 (m, 2H), 2.38 (s, 3H), 1.22 (s, 3H), 1.13 (s, 3H). ^{13}C NMR (100 MHz, CDCl3) δ = 169.1, 143.4, 141.0, 135.0, 132.9, 129.2, 128.3, 128.3, 128.1, 126.0, 125.6, 70.0, 51.6, 32.1, 28.0, 27.8, 25.5, 21.5, 19.4. M.P.: 138.6 – 139.0 °C. IR (in KBr): 1631, 1412, 1387, 1080, 984, 546 cm^{-1}. HRMS (EI): m/z $[M + H]^+$ calcd for: $C_{21}H_{25}N_2O_2S$: 369.1623; found: 369.1631.

Product 2o



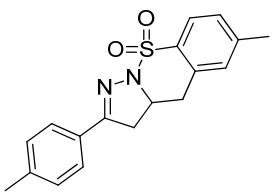
Yield of **2o** : 42% as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.72 (d, *J* = 7.9 Hz, 1H), 7.19 (d, *J* = 7.9 Hz, 1H), 7.05 (s, 1H), 4.18 (dd, *J* = 7.0, 4.9 Hz, 1H), 3.15 (dd, *J* = 15.8, 7.1 Hz, 1H), 2.91 (dd, *J* = 15.8, 4.8 Hz, 1H), 2.38 (s, 3H), 1.33 (s, 3H), 1.24 (s, 3H), 0.97 – 0.93 (m, 1H), 0.81 – 0.66 (m, 3H), 0.35 – 0.29 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 172.2, 143.3, 135.2, 133.1, 129.2, 128.2, 125.8, 70.5, 51.7, 27.9, 26.0, 21.6, 19.8, 9.1, 7.5, 6.8. M.P.: 147.0 – 147.9 °C. IR (in KBr): 1629, 1604, 1412, 1386, 1080, 983, 578, 546 cm^{-1}. HRMS (EI): m/z $[M + H]^+$ calcd for: $C_{16}H_{21}N_2O_2S$: 305.1303; found: 305.1318.

Product 2p



Yield of **2p** : 31% as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.77 (d, *J* = 7.9 Hz, 1H), 7.22 (d, *J* = 7.8 Hz, 1H), 7.07 (s, 1H), 4.20 (dd, *J* = 7.0, 4.3 Hz, 1H), 3.17 (dd, *J* = 15.7, 7.3 Hz, 1H), 2.90 (dd, *J* = 15.8, 4.0 Hz, 1H), 2.48 – 2.43 (m, 1H), 2.38 (s, 3H), 1.81 – 1.59 (m, 6H), 1.47 – 1.43 (m, 2H), 1.26 (s, 3H), 1.19 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 173.3, 143.3, 135.3, 133.0, 129.1, 128.1, 125.9, 70.6, 51.6, 37.1, 32.4, 31.9, 27.7, 26.1, 25.3, 25.1, 21.5, 19.8. M.P.: 156.9 – 157.5 °C. IR (in KBr): 1631, 1416, 1311, 1140, 1074, 981, 681, 576 cm^{-1}. HRMS (EI): m/z $[M + H]^+$ calcd for: $C_{18}H_{25}N_2O_2S$: 333.1616; found: 333.1631.

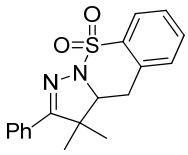
Product 2q



Yield of **2q** : 34% as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.79 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 7.9 Hz, 2H), 7.27 (s, 1H), 7.17 (d, *J* = 7.7 Hz, 2H), 3.89 – 3.84 (m, 1H), 3.15 (dd, *J* = 16.8, 10.6 Hz, 1H), 2.74 (dd, *J* = 16.8, 9.8 Hz, 1H),

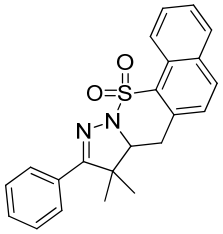
2.37 (d, *J* = 6.7 Hz, 6H), 1.62 (d, *J* = 6.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.6, 143.8, 141.1, 134.6, 132.5, 129.8, 129.1, 128.5, 127.6, 127.0, 126.0, 60.1, 41.9, 34.0, 21.6, 21.4. M.P.: 150.4 – 152.0 °C. IR (in KBr): 1632, 1412, 1385, 1083, 811, 573, 547 cm^{-1}. HRMS (EI): m/z [M + H] $^+$ calcd for: $C_{18}H_{21}N_2O_2S$: 329.1310; found: 329.1318.

Product 2r



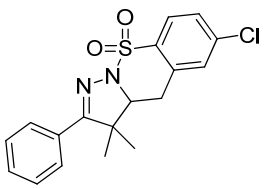
Yield of **2r** : 48% as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.97 (d, *J* = 7.2 Hz, 1H), 7.52 – 7.46 (m, 2H), 7.36 – 7.35 (m, 3H), 7.29 (t, *J* = 6.7 Hz, 3H), 4.41 (dd, *J* = 7.2, 4.3 Hz, 1H), 3.28 (dd, *J* = 15.8, 7.4 Hz, 1H), 3.07 (dd, *J* = 15.9, 4.2 Hz, 1H), 1.56 (s, 3H), 1.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.4, 135.7, 135.2, 132.9, 130.0, 123.0, 128.8, 128.3, 127.7, 127.6, 125.8, 72.1, 51.3, 27.6, 26.9, 20.4. M.P.: 163.9 – 164.8 °C. IR (in KBr): 1630, 1388, 1343, 1179, 1074, 982, 719, 576 cm^{-1}. HRMS (EI): m/z [M + H] $^+$ calcd for: $C_{18}H_{19}N_2O_2S$: 327.1167; found: 327.1162.

Product 2s



Yield of **2s** : 35% as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.94 (d, *J* = 8.7 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.70 – 7.68 (m, 1H), 7.59 – 7.56 (m, 3H), 7.38 (t, *J* = 7.3 Hz, 1H), 7.34 – 7.30 (m, 3H), 4.36 (dd, *J* = 8.3, 5.6 Hz, 1H), 3.39 (dd, *J* = 16.3, 8.3 Hz, 1H), 3.21 (dd, *J* = 16.3, 5.6 Hz, 1H), 1.58 (s, 3H), 1.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 165.9, 134.6, 133.1, 132.7, 131.8, 130.1, 128.5, 128.3, 128.3, 127.6, 126.7, 126.0, 124.9, 69.8, 51.8, 29.5, 25.5, 20.1. M.P.: 212.0 – 212.9 °C. IR (in KBr): 1628, 1413, 1336, 1112, 987, 624 cm^{-1}. HRMS (EI): m/z [M + H]$^+$ calcd for $C_{22}H_{21}N_2O_2S$: 377.1318; found: 377.1316.

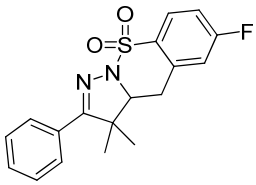
Product 2t



Yield of **2t** : 47% as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.90 (d, *J* = 8.3 Hz, 1H), 7.45 (d, *J* = 8.4 Hz, 1H), 7.38 (d, *J* = 7.7 Hz, 3H), 7.31 (dd, *J* = 14.0, 6.4 Hz, 3H), 4.42 (dd, *J* = 7.7, 4.0 Hz, 1H), 3.26 (dd, *J* = 16.1, 7.7 Hz, 1H), 3.03 (dd, *J* = 16.1, 4.1 Hz, 1H), 1.56 (s, 3H), 1.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =

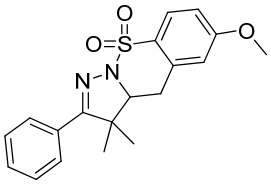
166.4, 139.0, 137.1, 134.2, 130.2, 129.9, 128.8, 128.4, 128.1, 127.7, 127.4, 72.1, 51.4, 27.5, 26.9, 20.6. M.P.: 197.0 – 197.9 °C. IR (in KBr): 1629, 1411, 1351, 1095, 620 cm^{-1}. HRMS (EI): m/z $[M + H]^+$ calcd for $C_{18}H_{18}ClN_2O_2S$: 361.0772; found: 361.0775.

Product 2u



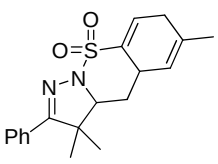
Yield of **2u** : 57% as a white solid. ^1H NMR (600 MHz, $CDCl_3$) δ = 7.98 (dd, *J* = 8.7, 5.4 Hz, 1H), 7.39 – 7.36 (m, 3H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.16 (t, *J* = 8.1 Hz, 1H), 7.00 (dd, *J* = 8.7, 2.4 Hz, 1H), 4.43 (dd, *J* = 7.7, 4.0 Hz, 1H), 3.28 (dd, *J* = 16.1, 7.7 Hz, 1H), 3.05 (dd, *J* = 16.0, 4.0 Hz, 1H), 1.56 (s, 3H), 1.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.4, 164.8 (*J* = 256.2), 138.4 (*J* = 8.8 Hz), 131.9 (*J* = 3.3 Hz), 130.2, 129.9, 128.7 (*J* = 9.6 Hz), 128.4, 127.7, 115.9 (*J* = 22.8 Hz), 115.1 (*J* = 22.7 Hz), 72.1, 51.4, 27.8, 26.9, 20.5. M.P.: 187.0 – 187.9 °C. IR (in KBr): 1628, 1412, 1387, 1114, 987, 624 cm^{-1}. HRMS (EI): m/z $[M + H]^+$ calcd for $C_{18}H_{18}FN_2O_2S$: 345.1068; found: 345.1068.

Product 2v



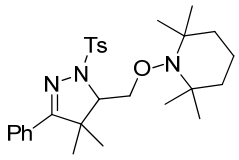
Yield of **2v** : 57% as a white solid. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.86 (d, *J* = 8.6 Hz, 1H), 7.40 – 7.29 (m, 4H), 7.24 (d, *J* = 7.6 Hz, 1H), 6.90 (d, *J* = 8.5 Hz, 1H), 6.74 (s, 1H), 4.37 – 4.34 (m, 1H), 3.82 (s, 3H), 3.23 (dd, *J* = 15.8, 7.2 Hz, 1H), 3.01 (dd, *J* = 15.8, 4.5 Hz, 1H), 1.54 (s, 3H), 1.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.1, 162.8, 137.3, 130.2, 130.0, 128.4, 128.3, 127.9, 127.7, 114.4, 112.5, 72.0, 55.6, 51.3, 28.1, 26.8, 20.5. M.P.: 172.0 – 173 °C. IR (in KBr): 1631, 1387, 1342, 1076, 561 cm^{-1}. HRMS (EI): m/z $[M + H]^+$ calcd for $C_{19}H_{21}N_2O_3S$: 357.1269; found: 357.1267.

Product 3a



Yield of **3a** : 85% as a white solid. ^1H NMR (600 MHz, $CDCl_3$) δ = 7.68 (d, *J* = 7.2 Hz, 2H), 7.41 – 7.36 (m, 3H), 6.90 (s, 1H), 5.37 (s, 1H), 3.95 (d, *J* = 12.1 Hz, 1H), 3.48 (s, 1H), 2.90 – 2.78 (m, 2H), 1.83 (d, *J* = 12.8 Hz, 1H), 1.72 (s, 3H), 1.70 – 1.63 (m, 1H), 1.43 (s, 3H), 1.25 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 164.9, 136.3, 131.5, 130.6, 130.5, 129.9, 128.3, 127.5, 120.8, 72.4, 51.1, 35.3, 32.5, 31.1, 23.5, 22.6, 18.5. M.P.: 175.0 – 176.5 °C. IR (in KBr): 1633, 1411, 1323, 1079, 983, 543 cm^{-1}. HRMS (EI): m/z $[M + H]^+$ calcd for $C_{19}H_{23}N_2O_2S$: 343.1482; found: 343.1475.

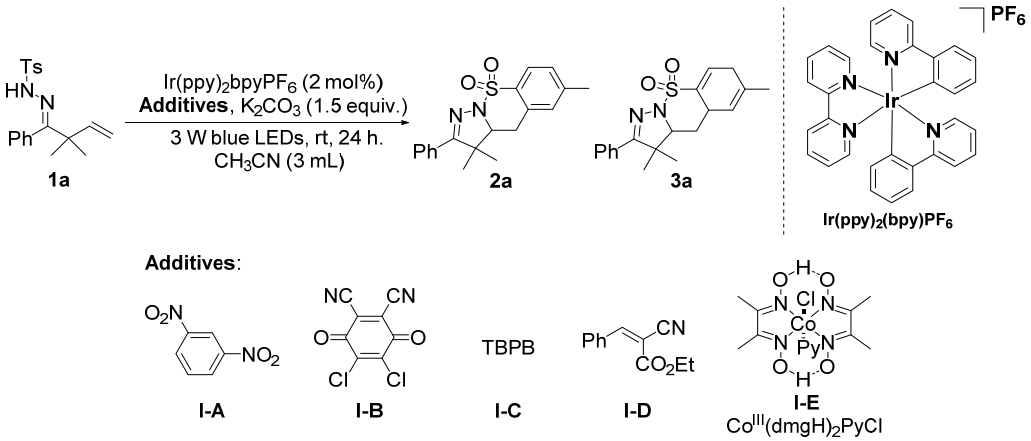
Product 4



Yield of **4** : 75% as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.77 (d, *J* = 8.2 Hz, 2H), 7.58 – 7.55 (m, 2H), 7.36 – 7.28 (m, 5H), 4.59 (dd, *J* = 10.2, 4.6 Hz, 1H), 4.28 (t, *J* = 10.1 Hz, 1H), 3.34 (dd, *J* = 9.9, 4.6 Hz, 1H), 2.41 (s, 3H), 1.52 – 1.47 (m, 5H), 1.45 (s, 3H), 1.28 – 1.23 (m, 7H), 1.21 (s, 3H), 1.08 (d, *J* = 11.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.8, 144.0, 130.6, 130.2, 129.5, 129.0, 128.7, 128.1, 127.4, 75.3, 69.9, 59.7, 51.8, 39.8, 39.5, 33.5, 32.5, 26.1, 21.6, 20.3, 20.2, 20.0, 17.1. M.P.: 138.2 – 139.6 °C. IR (in KBr): 1630, 1413, 1340, 1076, 605 cm^{-1}. HRMS (EI): m/z $[M + H]^+$ calcd for $C_{28}H_{40}N_3O_3S$: 498.2795; found: 498.2785.

4. Optimization of the Reaction Conditions

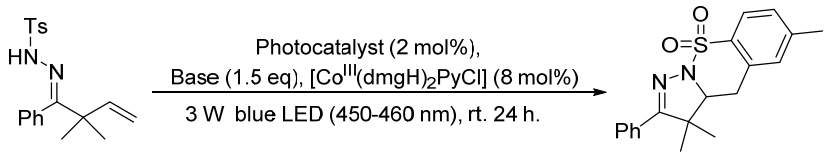
4.1The effect of additives[a]



Entry	PC	Solvent	Additive	3a/2a Yield[b]
1	$Ir(ppy)_2bpy\ PF_6$	CH_3CN	---	85%/0%
2	$Ir(ppy)_2bpy\ PF_6$	CH_3CN	I-A	trace/49%
3	$Ir(ppy)_2bpy\ PF_6$	CH_3CN	I-B	0
4	$Ir(ppy)_2bpy\ PF_6$	CH_3CN	I-C	Trace/31%
5	$Ir(ppy)_2bpy\ PF_6$	CH_3CN	I-D	Trace/35%
6	**$Ir(ppy)_2bpy\ PF_6$**	**CH_3CN**	**I-E**	**Trace/58**
7[c]	$Ir(ppy)_2bpy\ PF_6$	CH_3CN	---	0
8[d]	---	CH_3CN	---	0
9[e]	$Ir(ppy)_2bpy\ PF_6$	CH_3CN	---	0

[a] Reaction conditions: **1a** (0.2 mmol), $Ir(ppy)_2bpyPF_6$ (2 mol%), K_2CO_3 (0.3 mmol), additive (1.5 equiv) for **I-A**, **I-B**, **I-C**, **I-D** or (8 mol%) for **I-E**, 3.0 mL solvent, under argon atmosphere, 3 W blue LEDs and room temperature. [b] Isolated yields. [c] Without visible light irradiation. [d] Without photocatalyst. [e] Without base.

4.2 The effect of photocatalysts and bases[a]

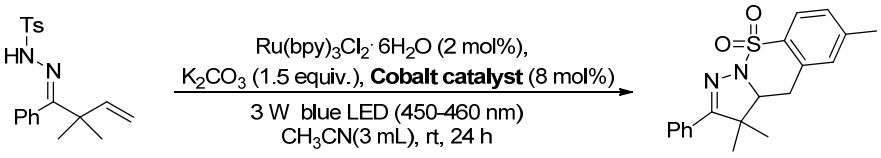


1a **2a**

Entry	Photocatalyst	Solvent	Base	Yield (%)[b]
1	$Ir(ppy)_2bpyPF_6$	CH_3CN	K_2CO_3	58
2	$Ir(ppy)_2(dtbbpy)PF_6$	CH_3CN	K_2CO_3	Trace
3	$Ru(bpz)_3(PF_6)_2$	CH_3CN	K_2CO_3	Trace
4	$Ru(bpm)_3(BArF)_2$	CH_3CN	K_2CO_3	25
5	$[Ru(phen)_3]Cl_2$	CH_3CN	K_2CO_3	37
6	$Ru(bpy)_3(PF_6)_2$	CH_3CN	K_2CO_3	65
7	**$Ru(bpy)_3Cl_2{\cdot}6H_2O$**	**CH_3CN**	**K_2CO_3**	**73**
8	$Ru(bpy)_3Cl_2.6H_2O$	DMF	K_2CO_3	26
9	$Ru(bpy)_3Cl_2.6H_2O$	$CHCl_3$	K_2CO_3	nd
10	$Ru(bpy)_3Cl_2.6H_2O$	THF	K_2CO_3	nd
11	$Ru(bpy)_3Cl_2.6H_2O$	DMSO	K_2CO_3	nd
12	$Ru(bpy)_3Cl_2.6H_2O$	CH_3CN	Li_2CO_3	Trace
13	$Ru(bpy)_3Cl_2.6H_2O$	CH_3CN	KH_2PO_4	Trace
14	$Ru(bpy)_3Cl_2.6H_2O$	CH_3CN	$NaHCO_3$	69
15	$Ru(bpy)_3Cl_2.6H_2O$	CH_3CN	Cs_2CO_3	57
16	$Ru(bpy)_3Cl_2.6H_2O$	CH_3CN	KO-^{t}Bu	Trace
17 [c]	$Ru(bpy)_3Cl_2.6H_2O$	CH_3CN	K_2CO_3	Trace
18	_	CH_3CN	K_2CO_3	Trace
19	$Ru(bpy)_3Cl_2.6H_2O$	CH_3CN	_	Trace

[a] Reaction conditions: **1a** (0.2 mmol), photocatalyst (2 mol%), base (1.5 equiv.), solvent (3 mL), under argon atmosphere, 3 W blue LEDs and room temperature. [b] Isolated yields. [c] Without visible light irradiation. nd = not detected; DMF = N,N-dimethylformamide.

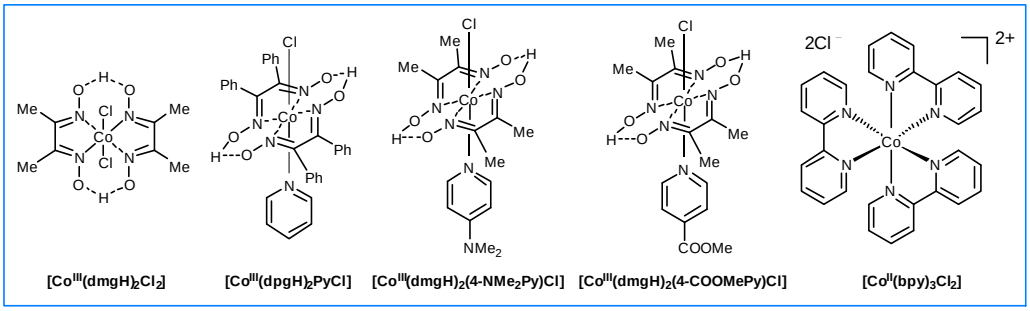
4.3 The effect of cobalt catalysts[a]



1a **2a**

Entry	Cobalt catalyst	Yield (%)[b]
1	$[Co^{III}(dmgH)_2Cl_2]$	60
2	$[Co^{III}(dpgH)_2Cl_2]$	41
3	$[Co^{III}(dmgH)_2(4\text{-}NMe_2Py)Cl]$	33
4	$[Co^{III}(dmgH)_2(4\text{-}COOMePy)Cl]$	40
5	$[Co^{II}(bpy)_3Cl_2]$	Trace

[a] Reaction conditions: **1a** (0.2 mmol), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (2 mol%), K_2CO_3 (1.5 equiv.), CH_3CN (3 mL), under argon atmosphere, 3 W blue LEDs and room temperature. [b] Isolated yields.



5. Mechanistic Studies

5.1 Luminescence quenching experiments

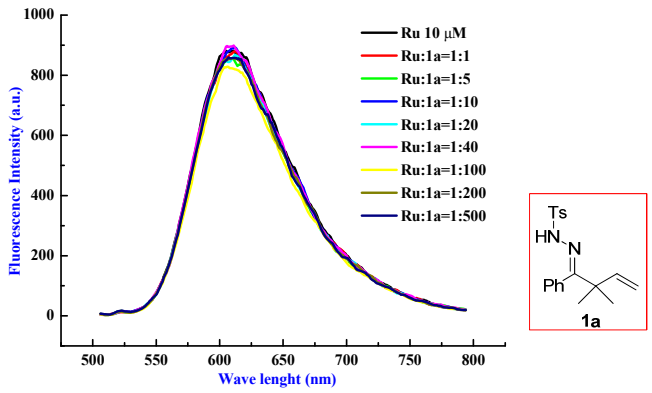


Figure S1

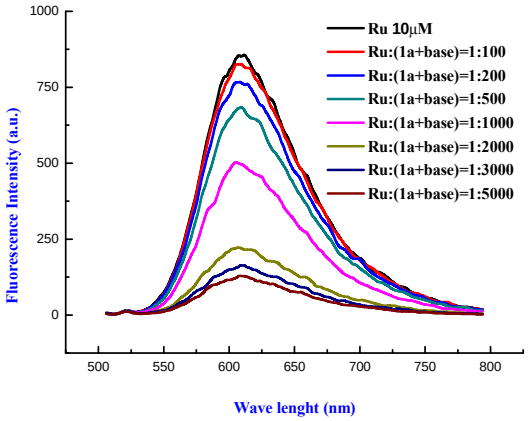


Figure S2

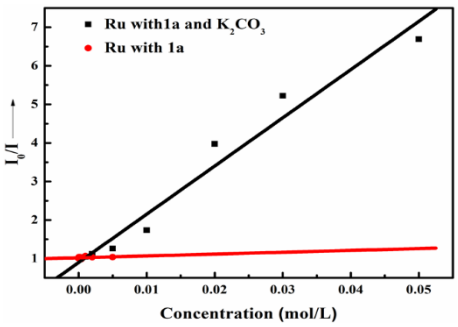
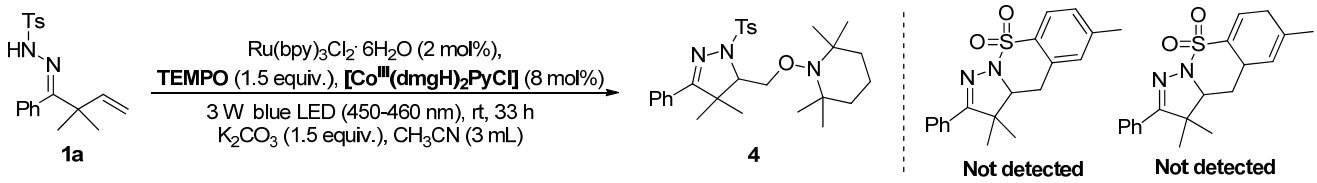


Fig. 2 $Ru(bpy)_3Cl_2 \cdot 6H_2O$ emission quenching with hydrazone 1a in the presence and absence of K_2CO_3. I_0 and I represent the intensities of the emission in the absence and presence of the quencher.

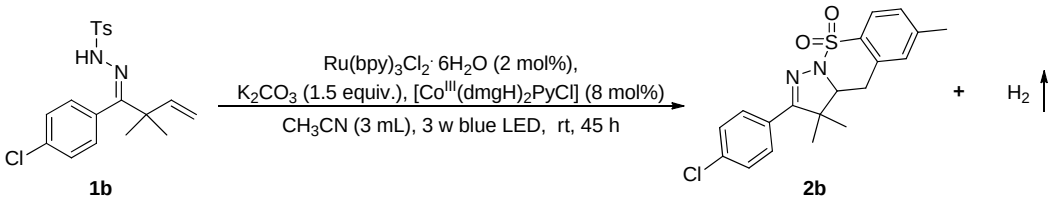
Fluorescence spectra were collected on Cary Eclipse Fluorescence Spectrophotometer. All the $Ru(bpy)_3Cl_2 \cdot 6H_2O$ solutions were excited at 452 nm and the emission intensity at 616 nm was observed.In a typical experiment, the emission spectrum of a 1×10^{-5} M solution of $Ru(bpy)_3Cl_2 \cdot 6H_2O$ in CH_3CN was collected. The decrease of $Ru(bpy)3^{2+}$ luminescence couldn't be observed in the presence of substrate **1a** (Figure S1). Under basic condition, a significant decrease of $Ru(bpy)3^{2+}$ luminescence was successfully observed in the presence of **1a** using K_2CO_3 as base (Figure S2). ***These results suggested that it was the nitrogen anion of ß,γ-unsaturated hydrazone instead of C=C double bond that quenched the excited photocatalyst *Ru(bpy)$_3^{2+}$.***

5.2 Trapping of the C-radical intermediate

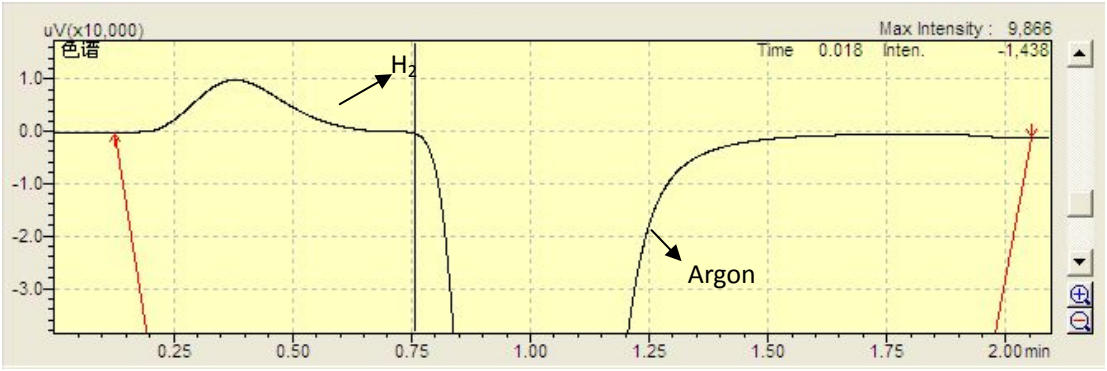


1a (68.5 mg, 0.2 mmol), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (3.0 mg, 0.004 mmol), K_2CO_3 (41.5 mg, 0.3 mmol), $[Co^{III}(dmgH)_2PyCl]$ (6.5 mg, 0.016 mmol) and TEMPO (46.9 mg, 0.3 mmol) were dissolved in CH_3CN (3.0 mL). Then, the resulting mixture was degassed via 'freeze-pump-thaw' procedure (3 times) under argon atmosphere. After that, the solution was stirred at a distance of ~5 cm from a 3 W blue LEDs (450-460 nm) at room temperature about 33 h until the reaction was completed, as monitored by TLC analysis. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 30:1~10:1) directly to give the desired product **4** in 75% isolated yield as a white solid. ***The result showed that terminal C-centred radical does work as the intermediate in the reaction system***

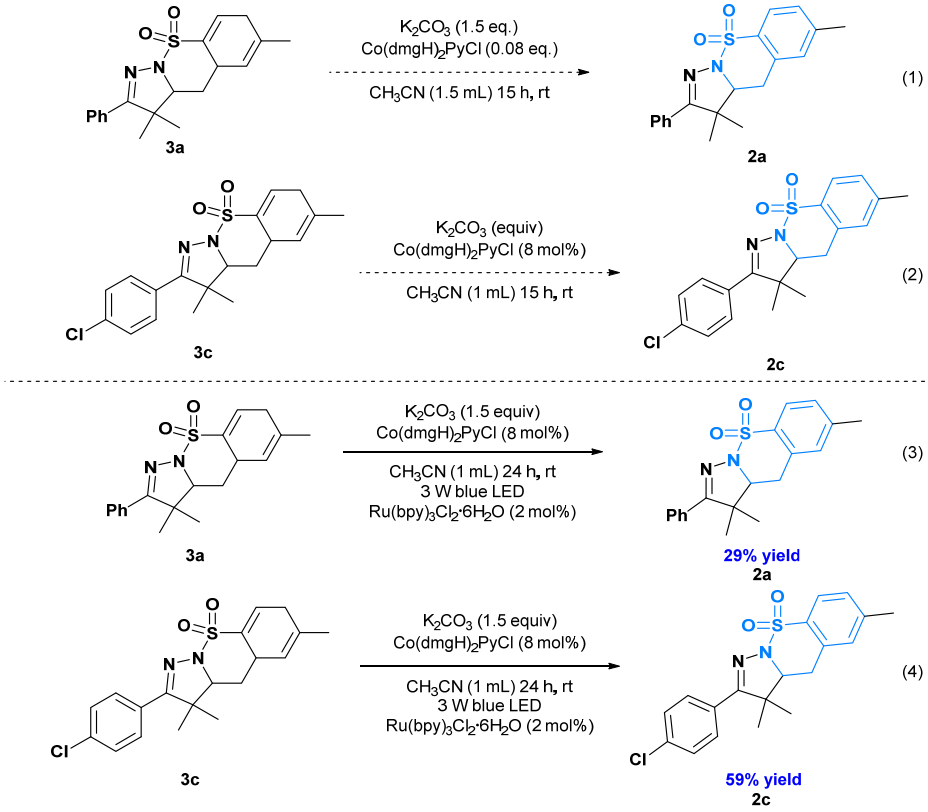
5.3 Detecting the byproduct H_2



1b (75.4 mg, 0.2 mmol), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (3.0 mg, 0.004 mmol), K_2CO_3 (41.5 mg, 0.3 mmol), $[Co^{III}(dmgH)_2PyCl]$ (6.5 mg, 0.016 mmol) were dissolved in CH_3CN (3.0 mL). Then, the resulting mixture was degassed via 'freeze-pump-thaw' procedure (3 times) under argon atmosphere. After that, the solution was stirred at a distance of ~5 cm from a 3W blue LEDs (450-460 nm) at room temperature for 45 h. Then, H_2 was detected by SHIMADZU GC-2014. Packed column: Part Nbr: 19808; Serial Nbr: C36880-14; Shincarbon ST 100/120; 2m 1mmID 1/16 OD Silco. The peak of H_2 appeared, as follows. ***The result suggested that H_2 was produced in the reaction system, which supported the mechanism we proposed.***

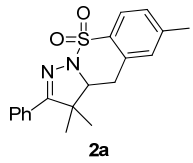


5.4 Control experiments



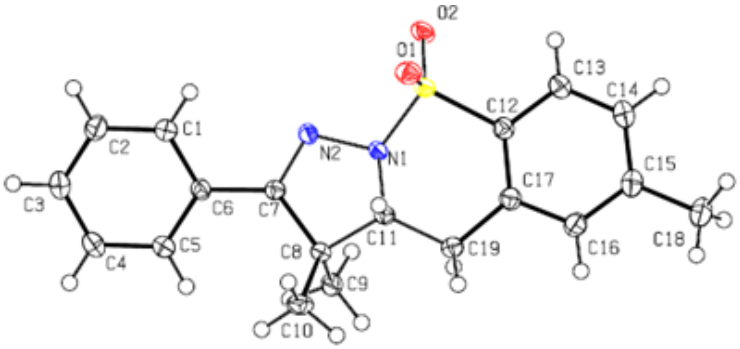
The control experiments revealed that that cyclised products 3a and 3c cannot be transformed into the final aromatization products 2a and 2c when using the cobalt complex alone. In contrast, subjection of them to the standard condition resulted in 2a and 2c in moderate yield, implying that 3a and 3c might also be involved as the possible intermediates. These results are in accordance with the optimization studies and highlight the uniquely enabling impact of photoredox cobalt catalysis.

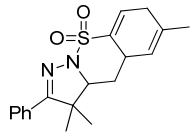
6. X-Ray Structures of 2a and 3a



2a

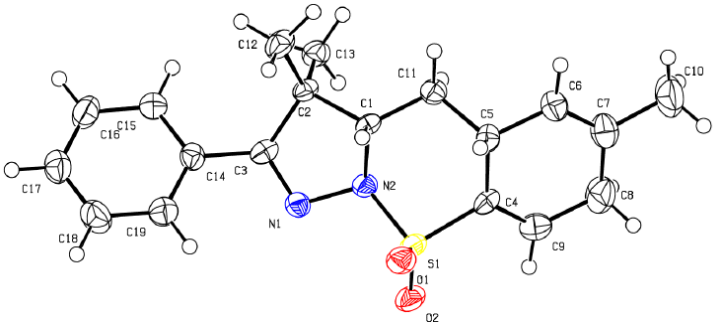
≡





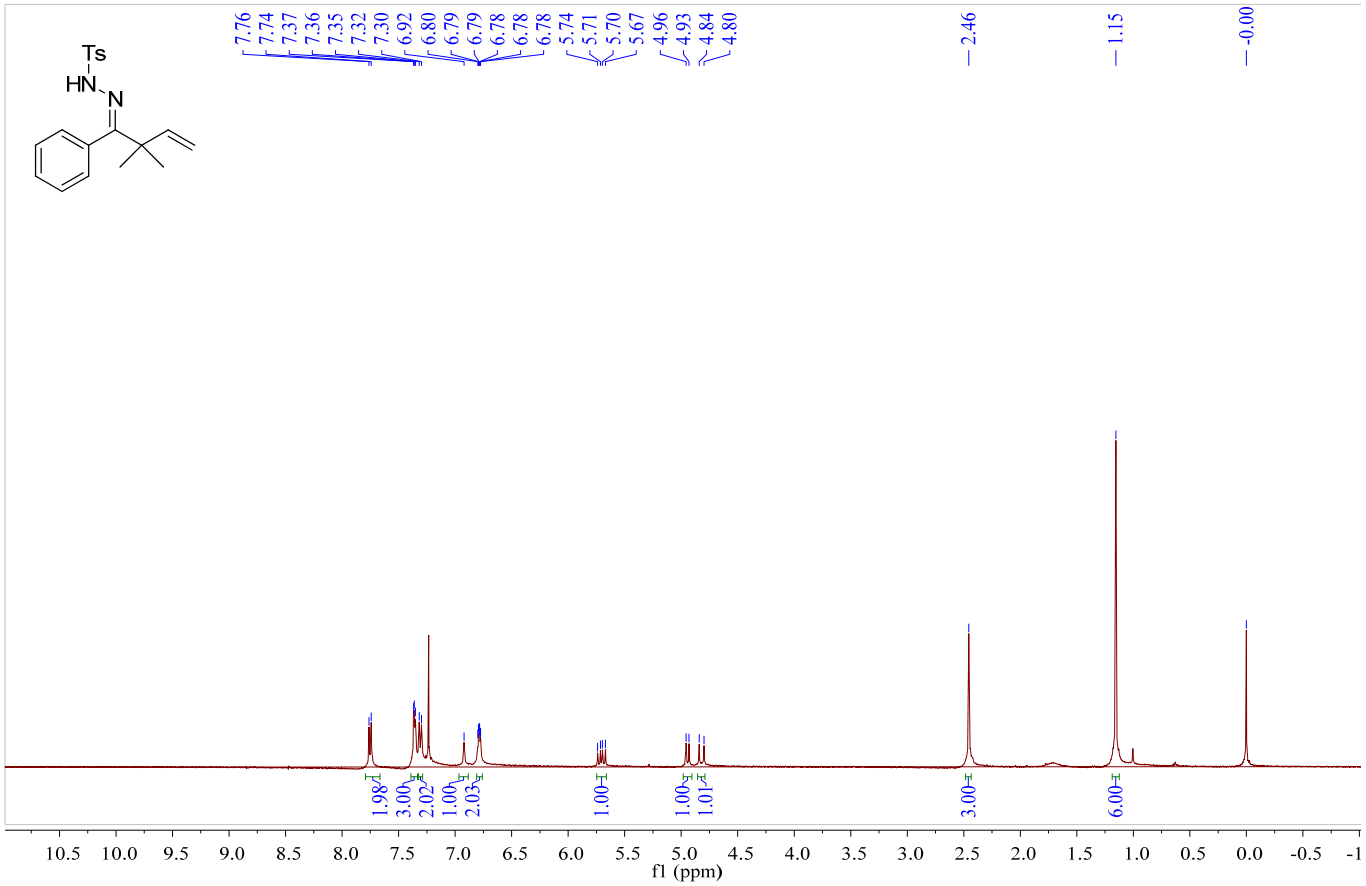
3a

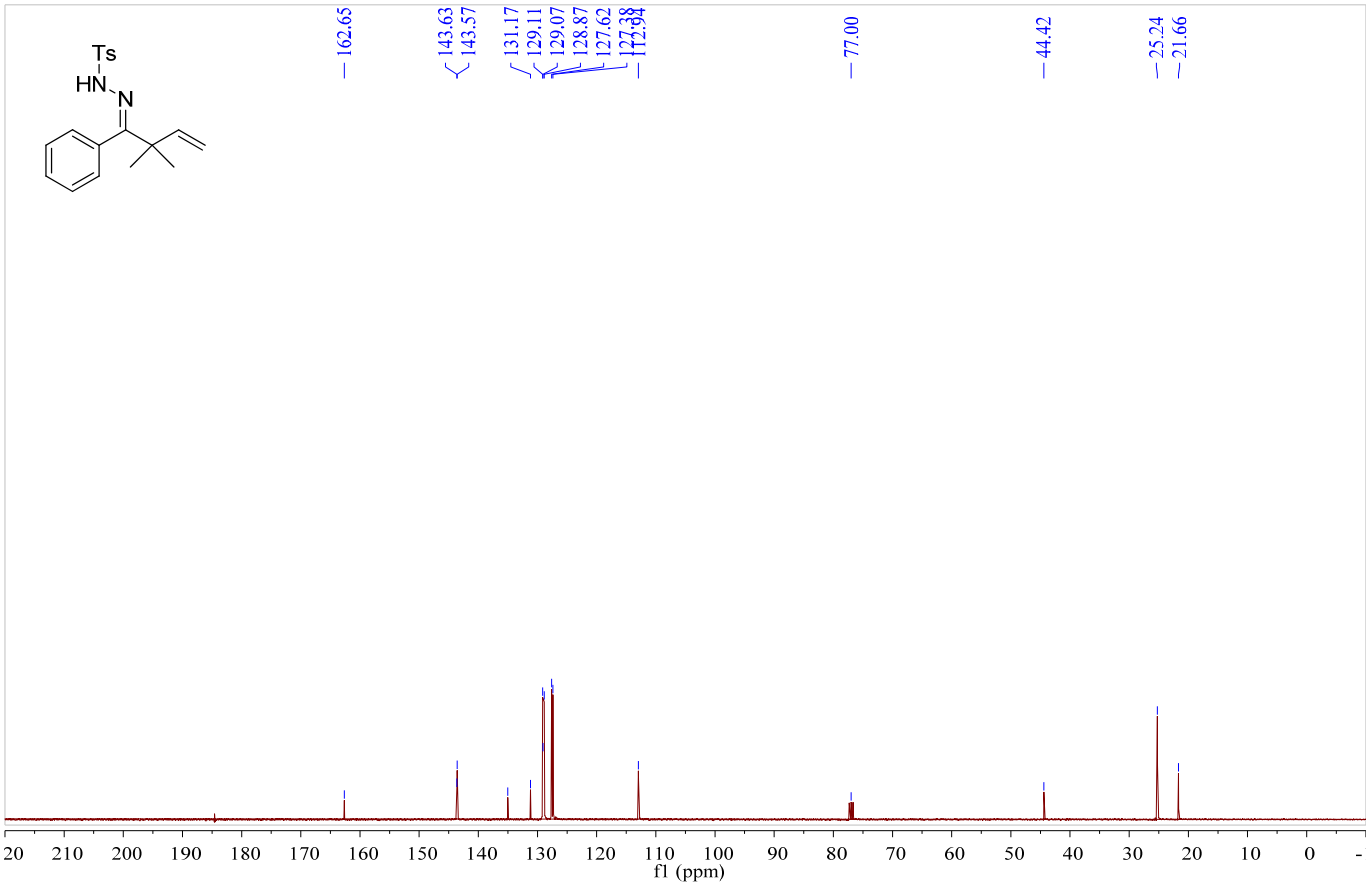
≡



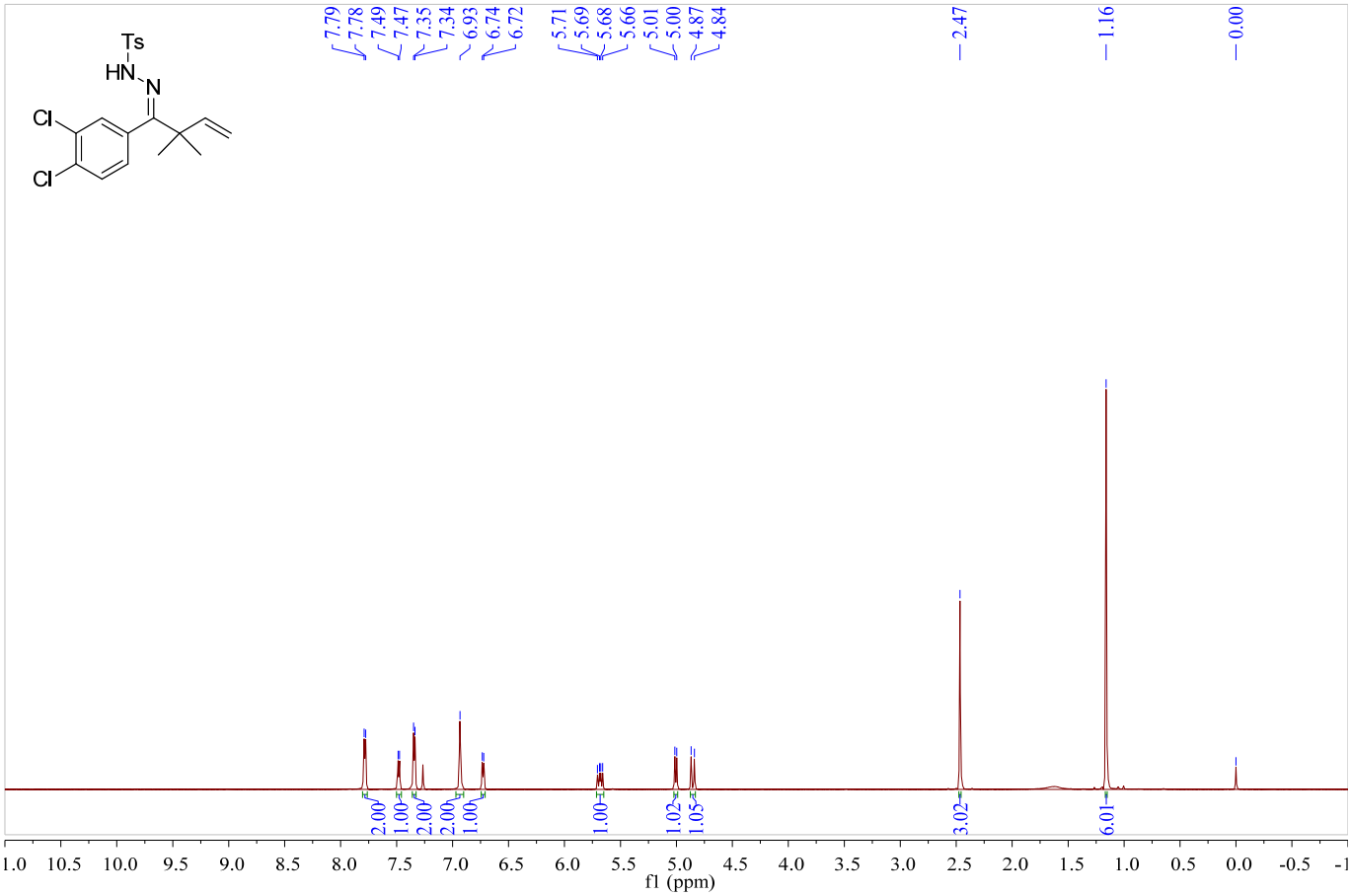
7. NMR Spectra of the Substrates 1a-f, 1h-p, 1r-v, 3c and Products 2a-v, 3a and 4a

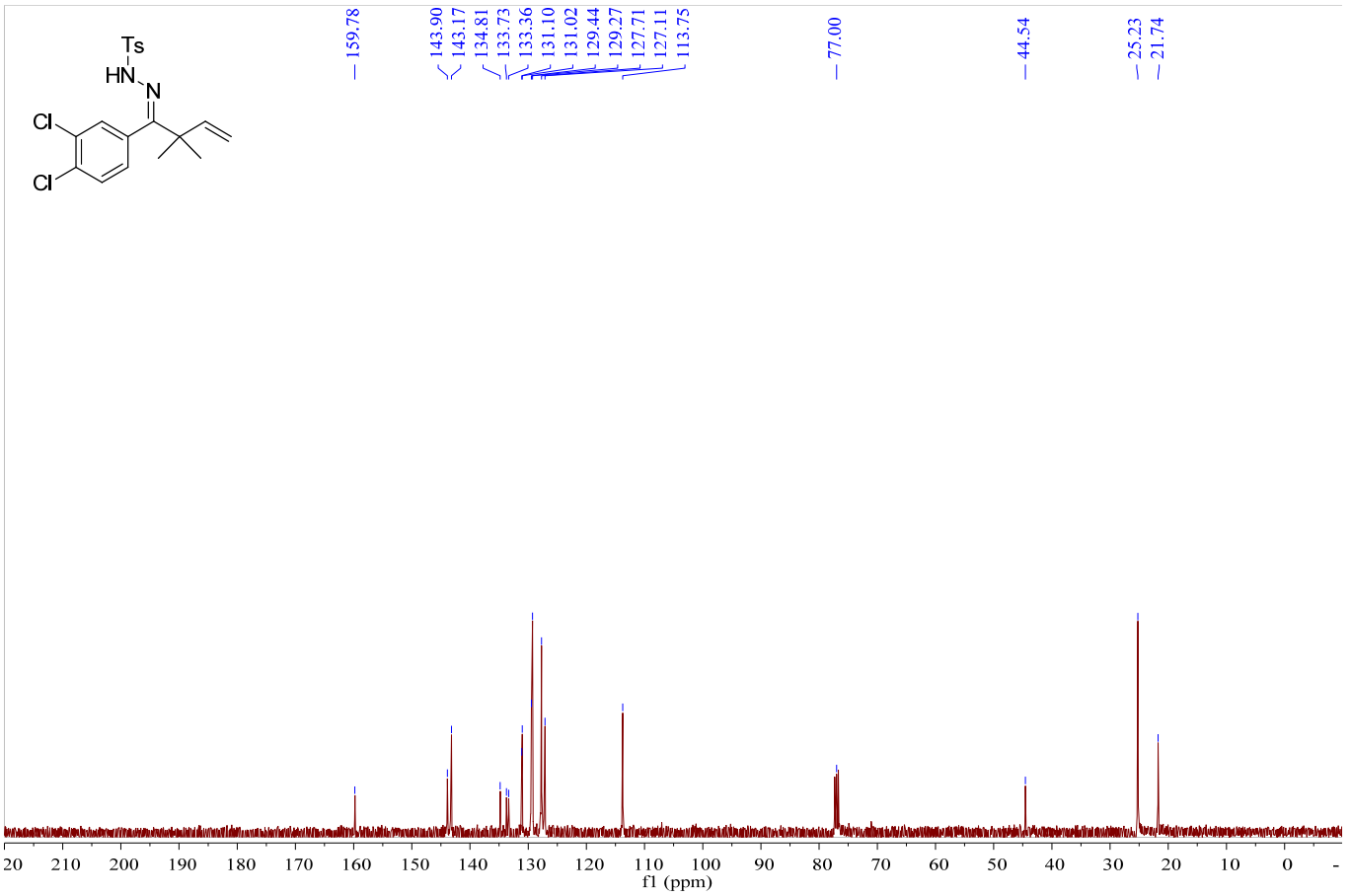
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of substrates 1a



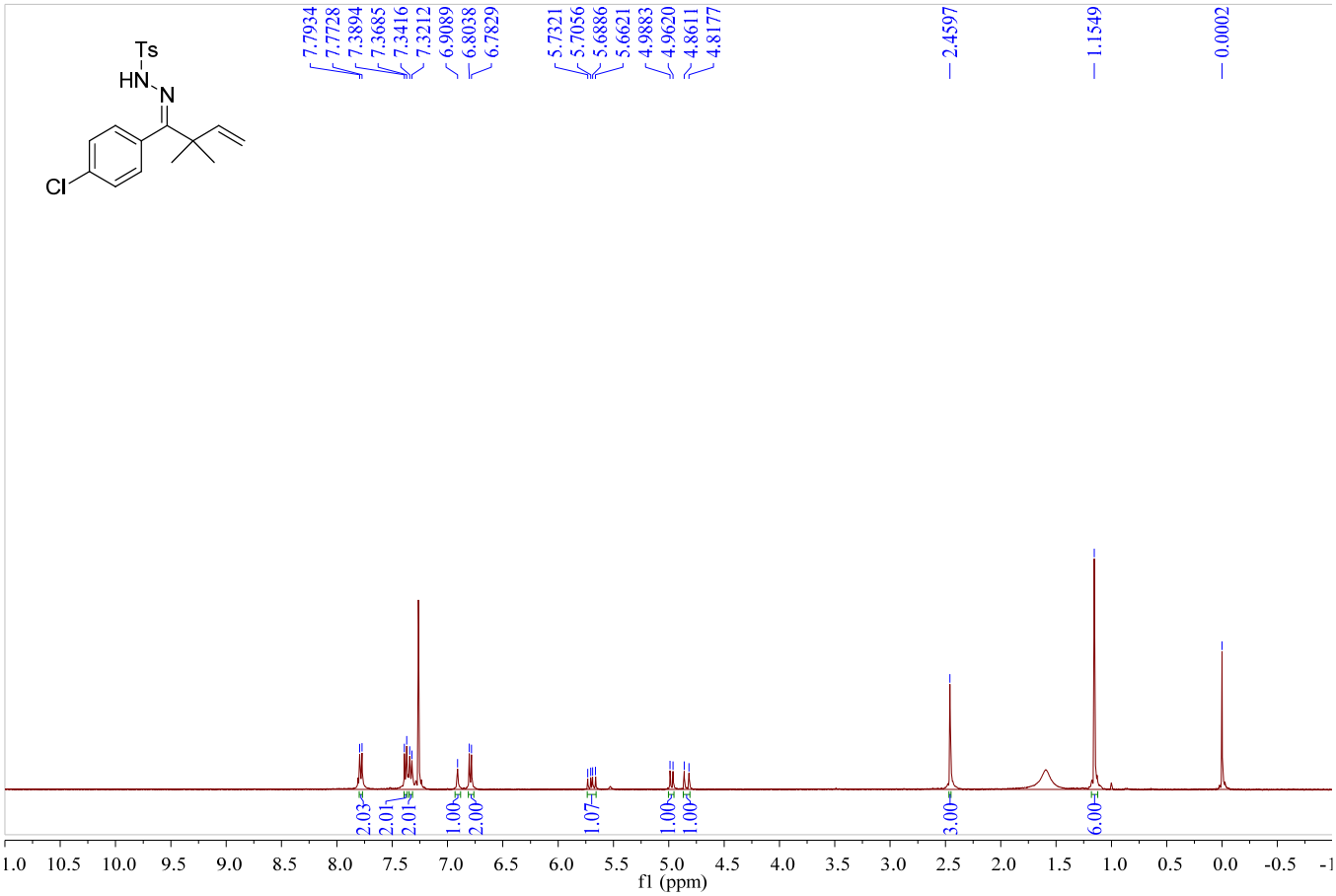


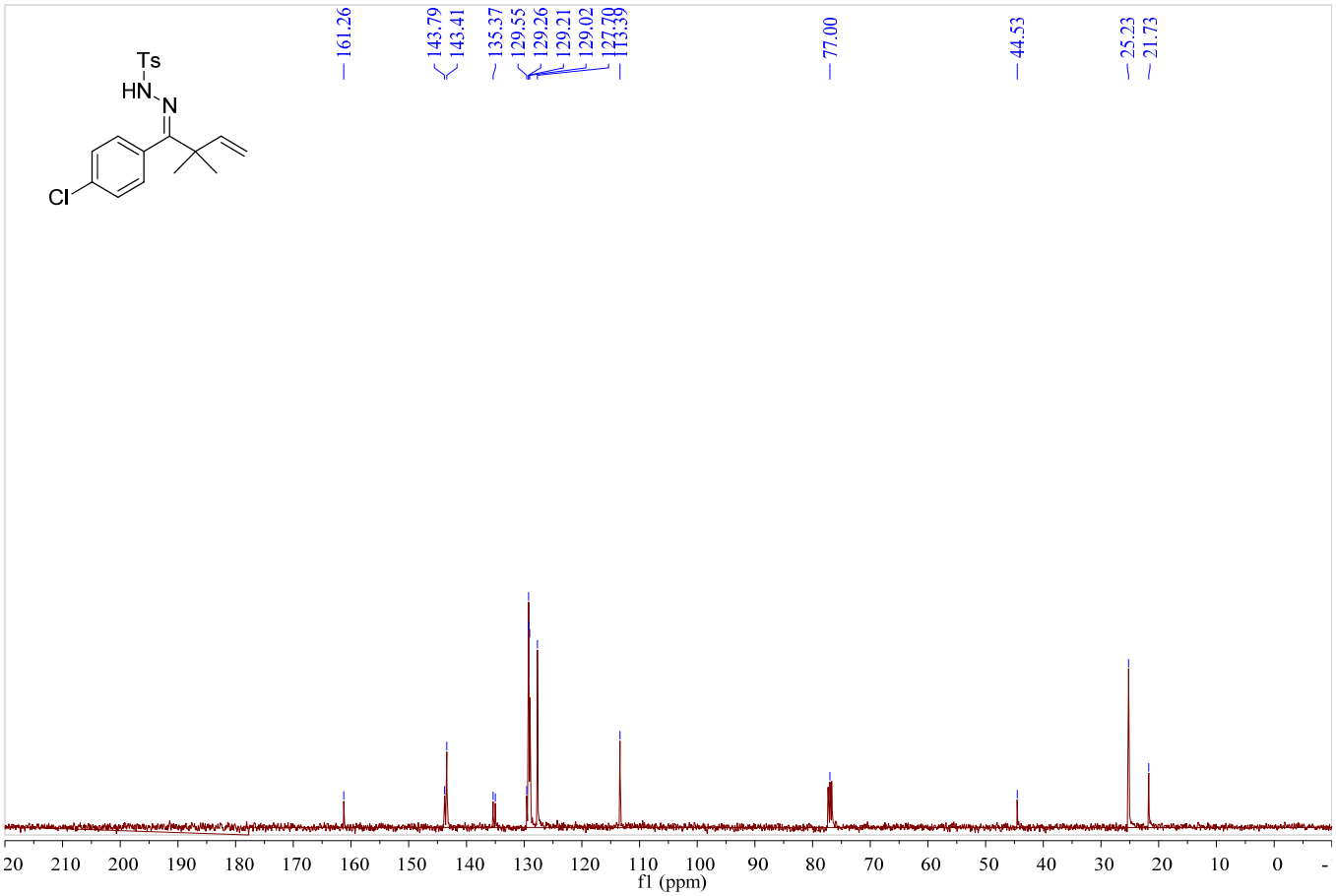
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of substrate 1b



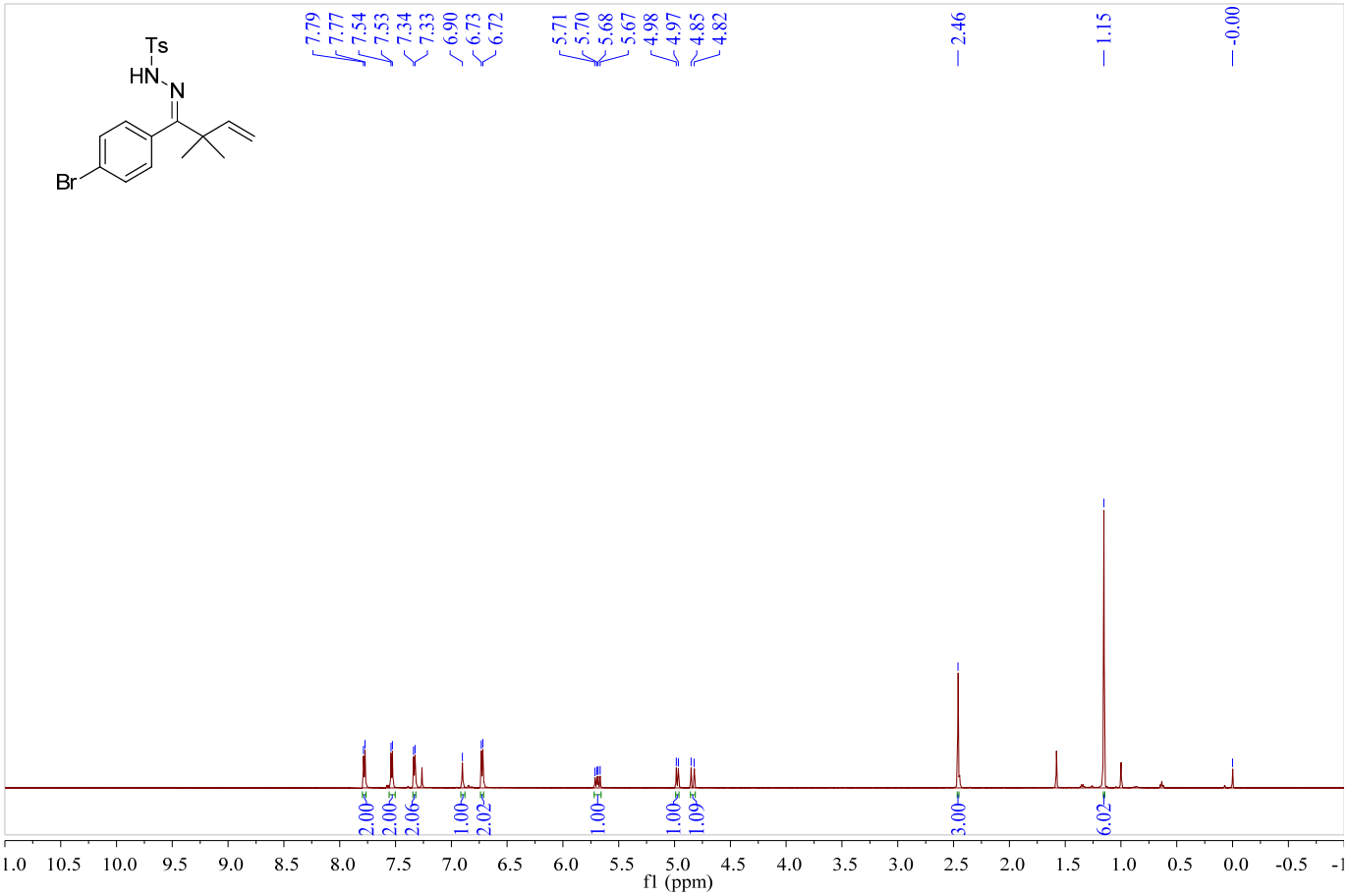


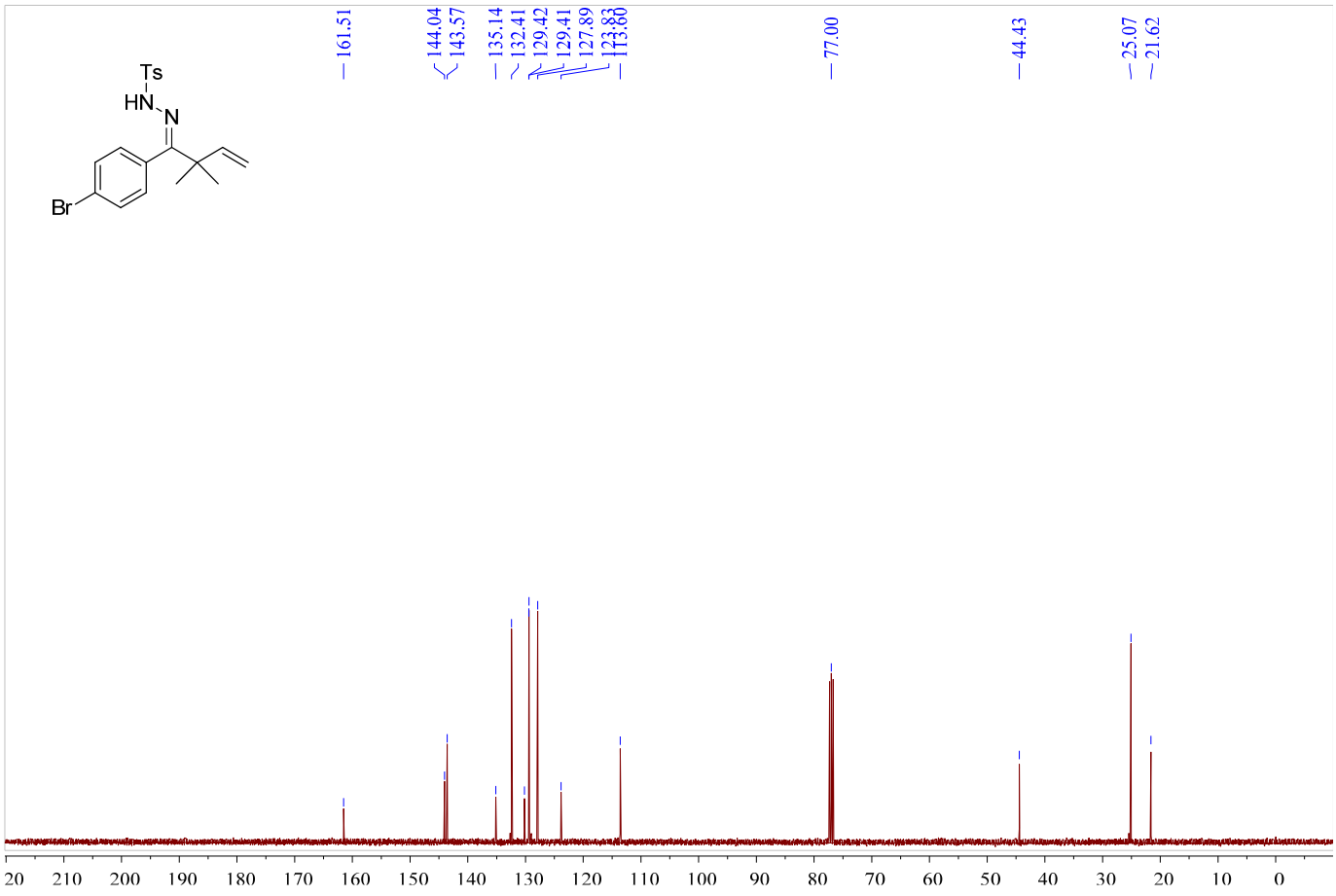
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of substrate 1c



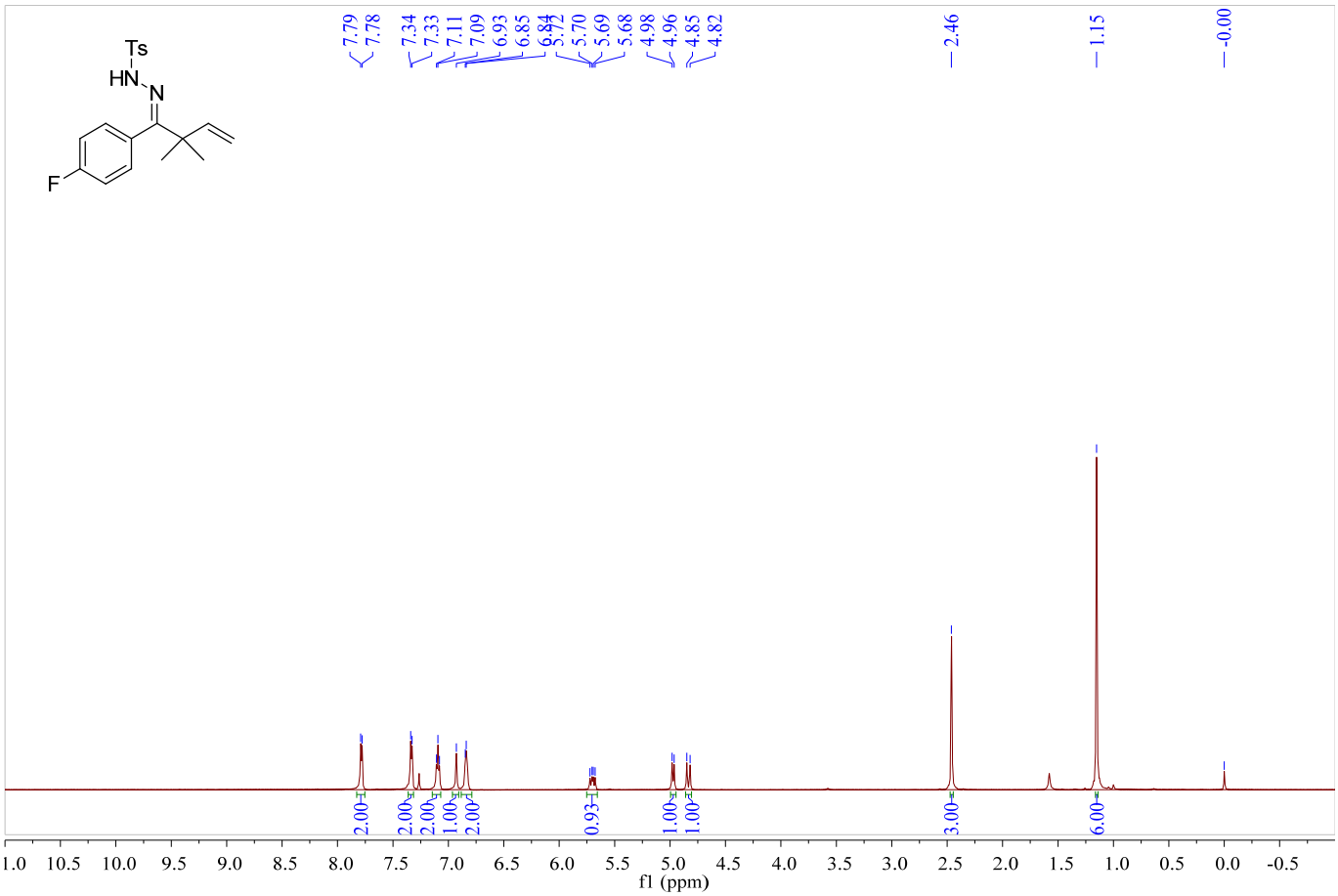


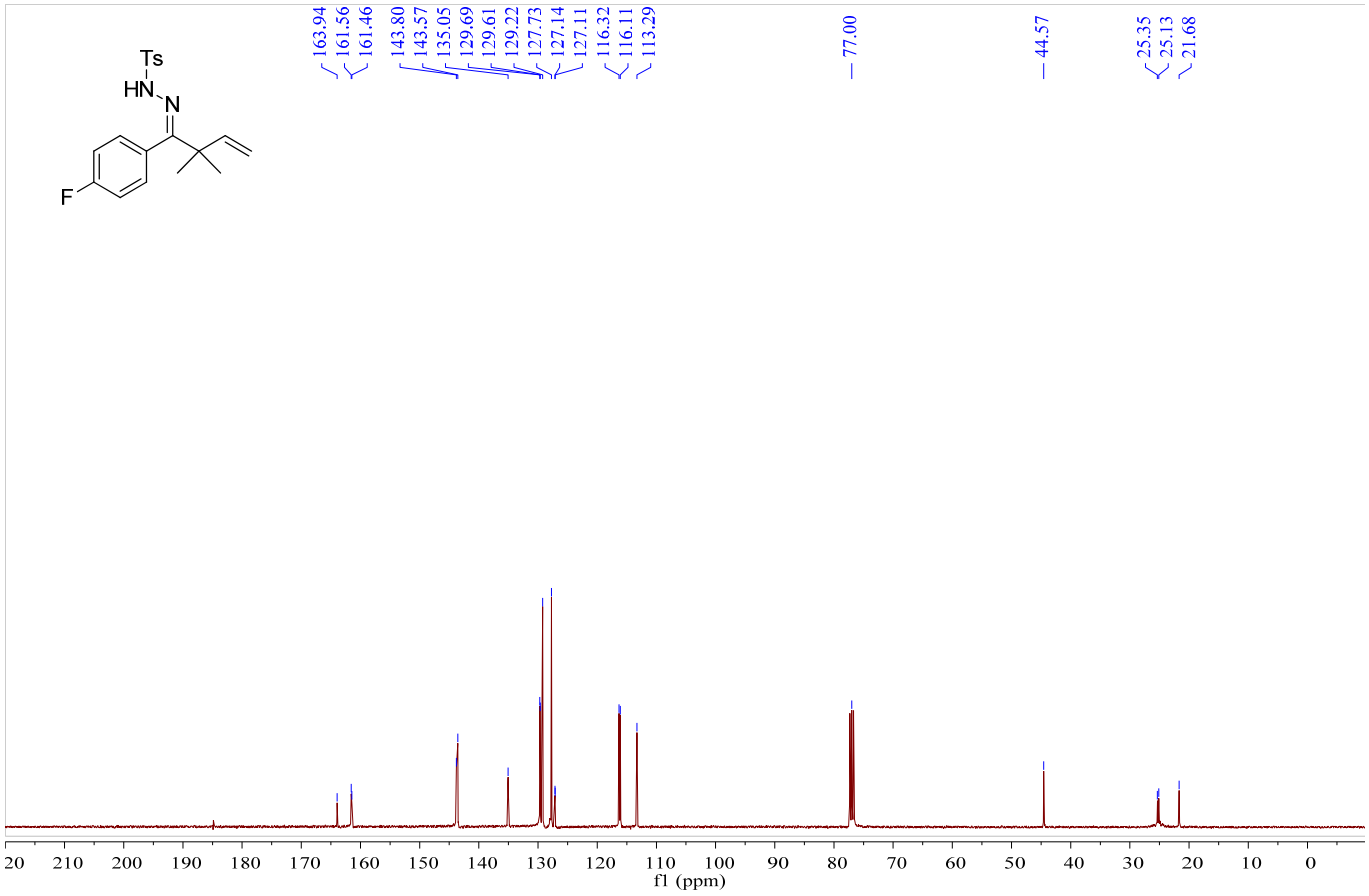
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of substrate 1d



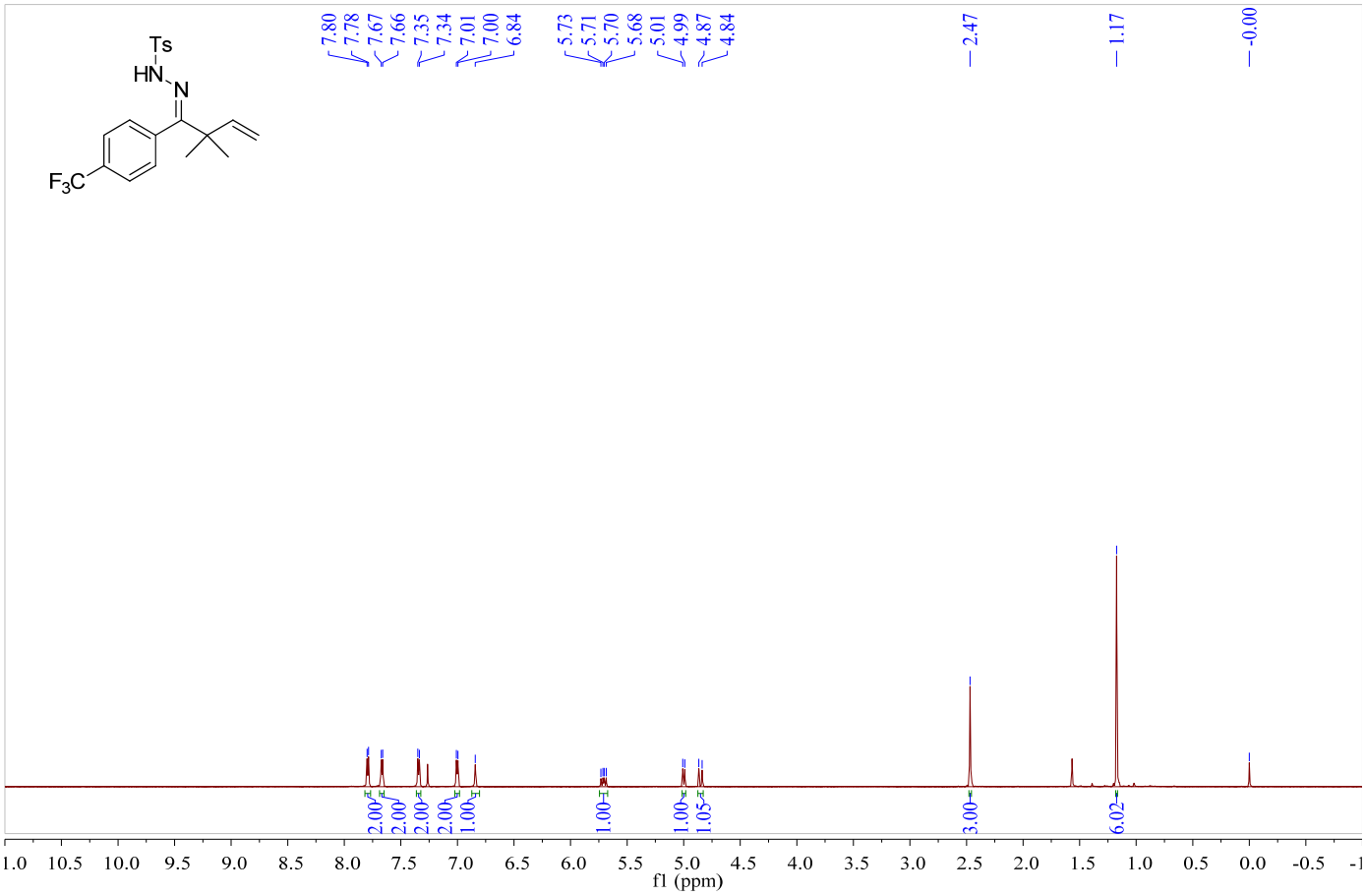


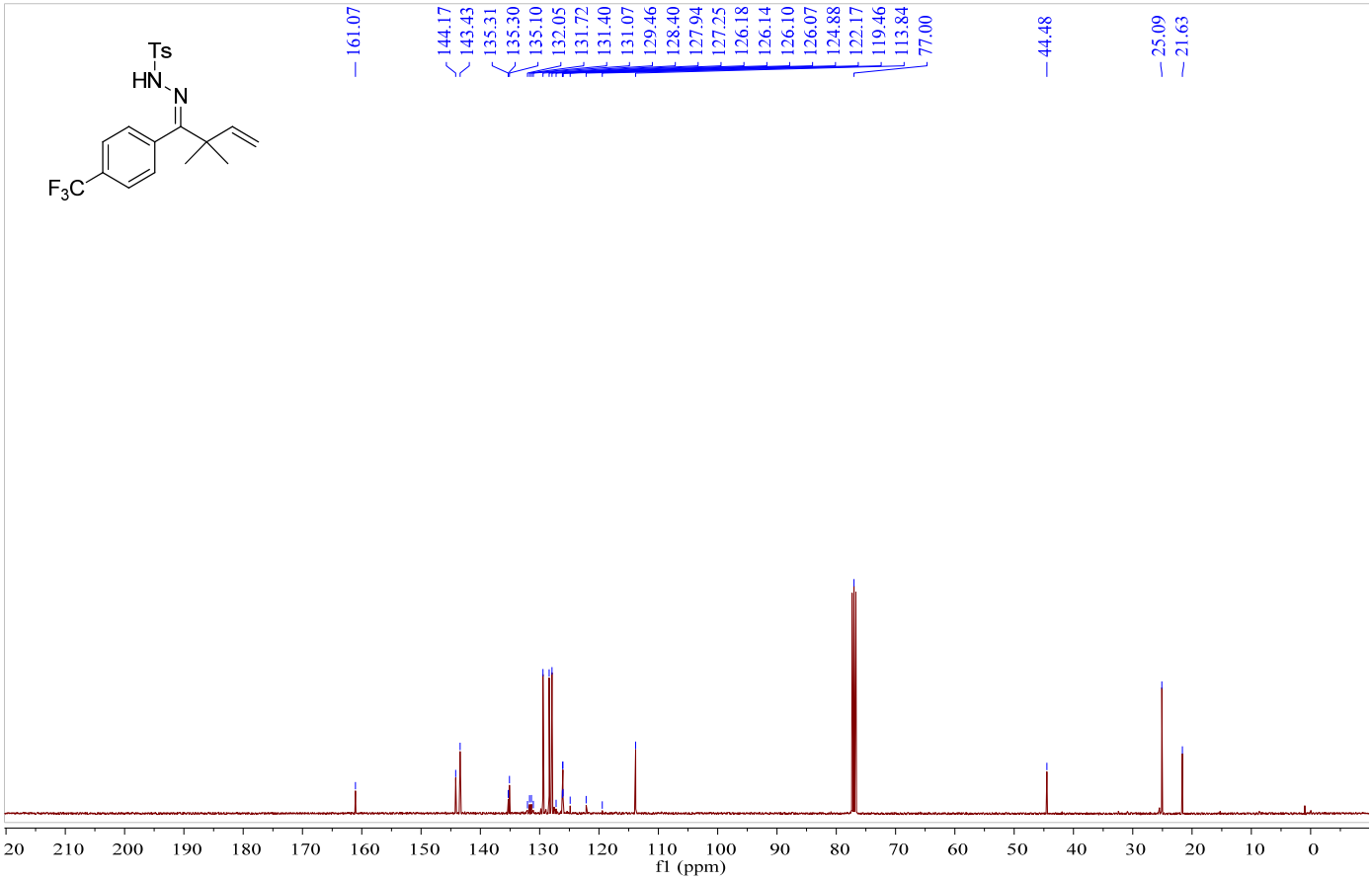
^{1}H NMR (600 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of substrate 1e



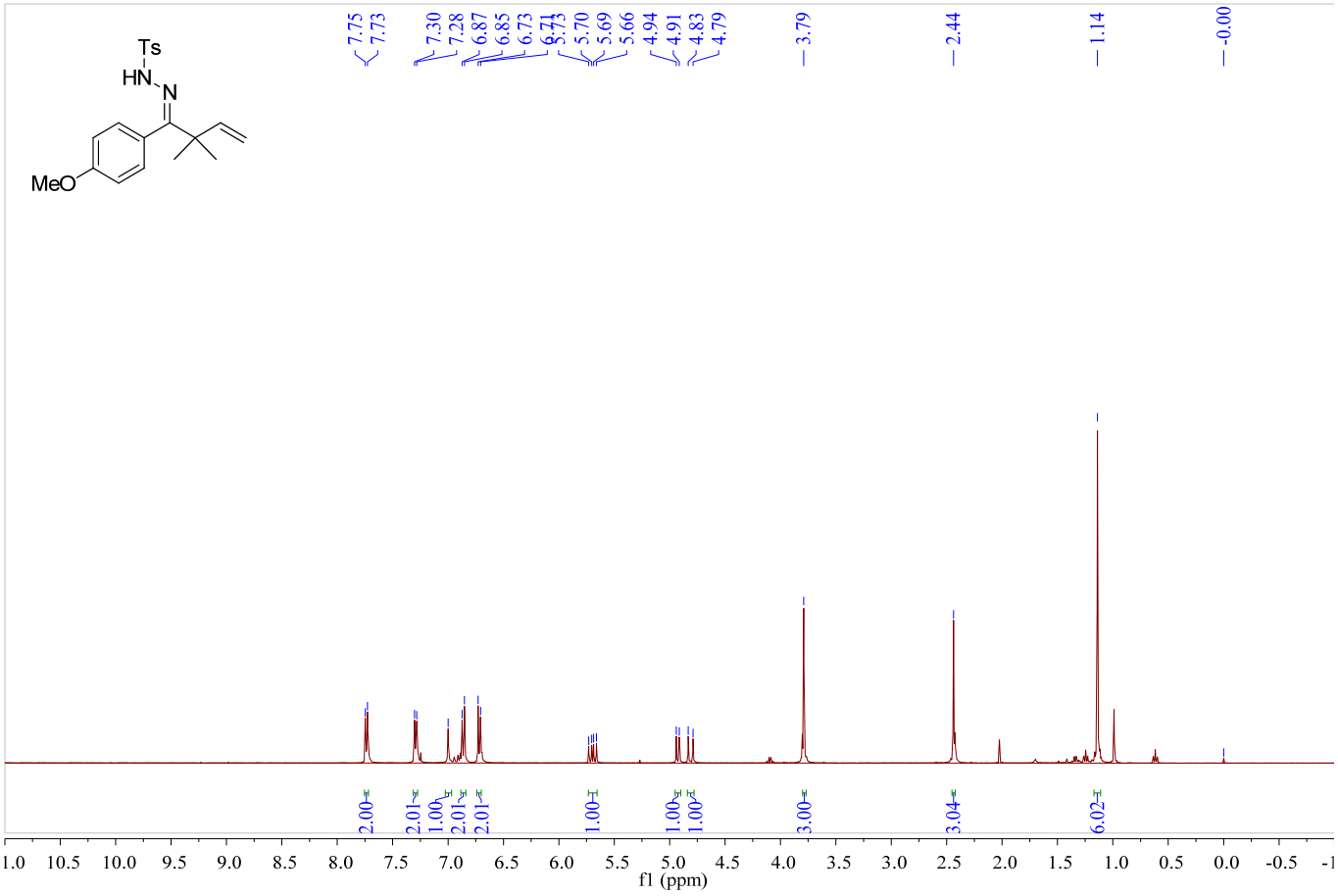


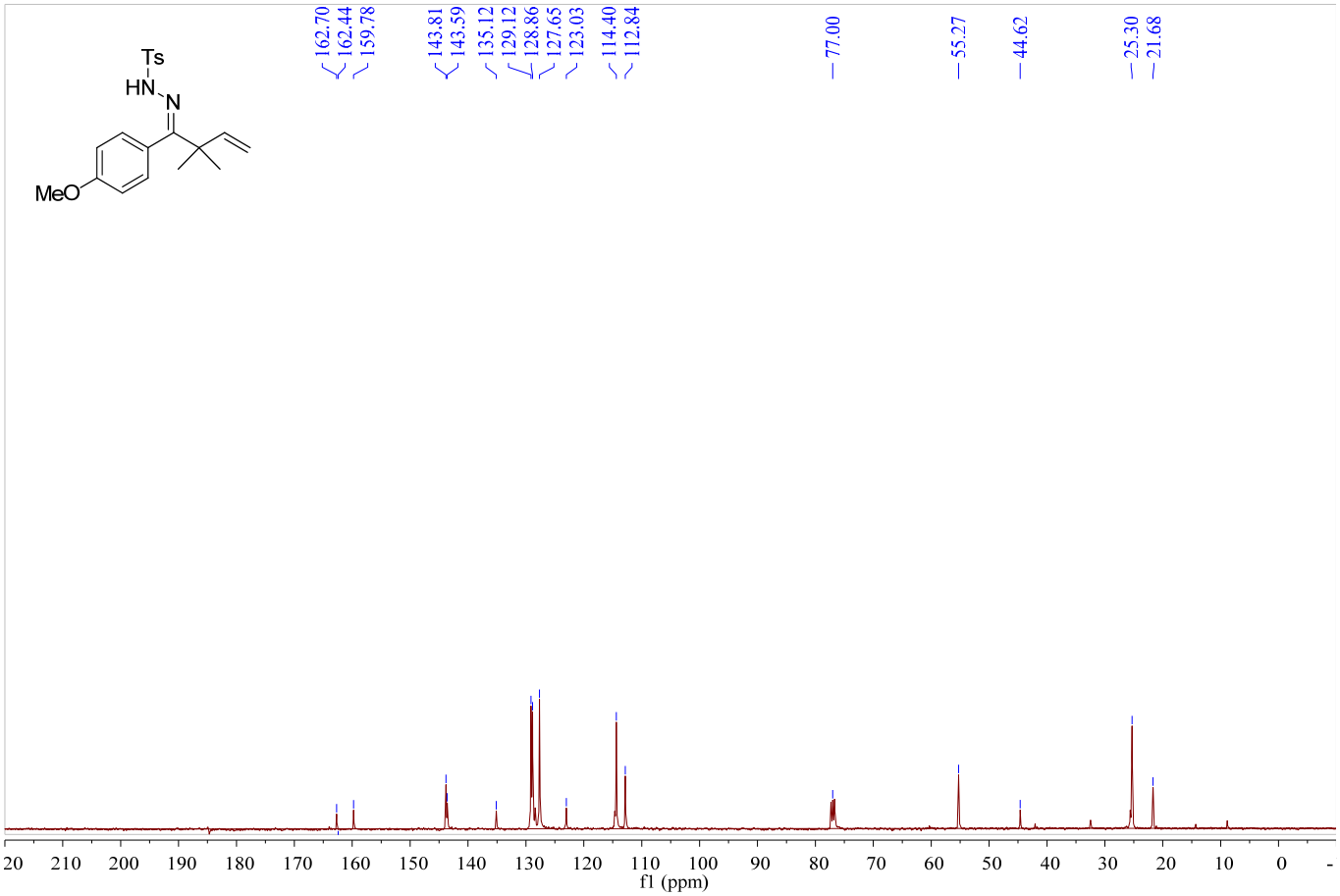
^{1}H NMR (600 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of substrate 1f



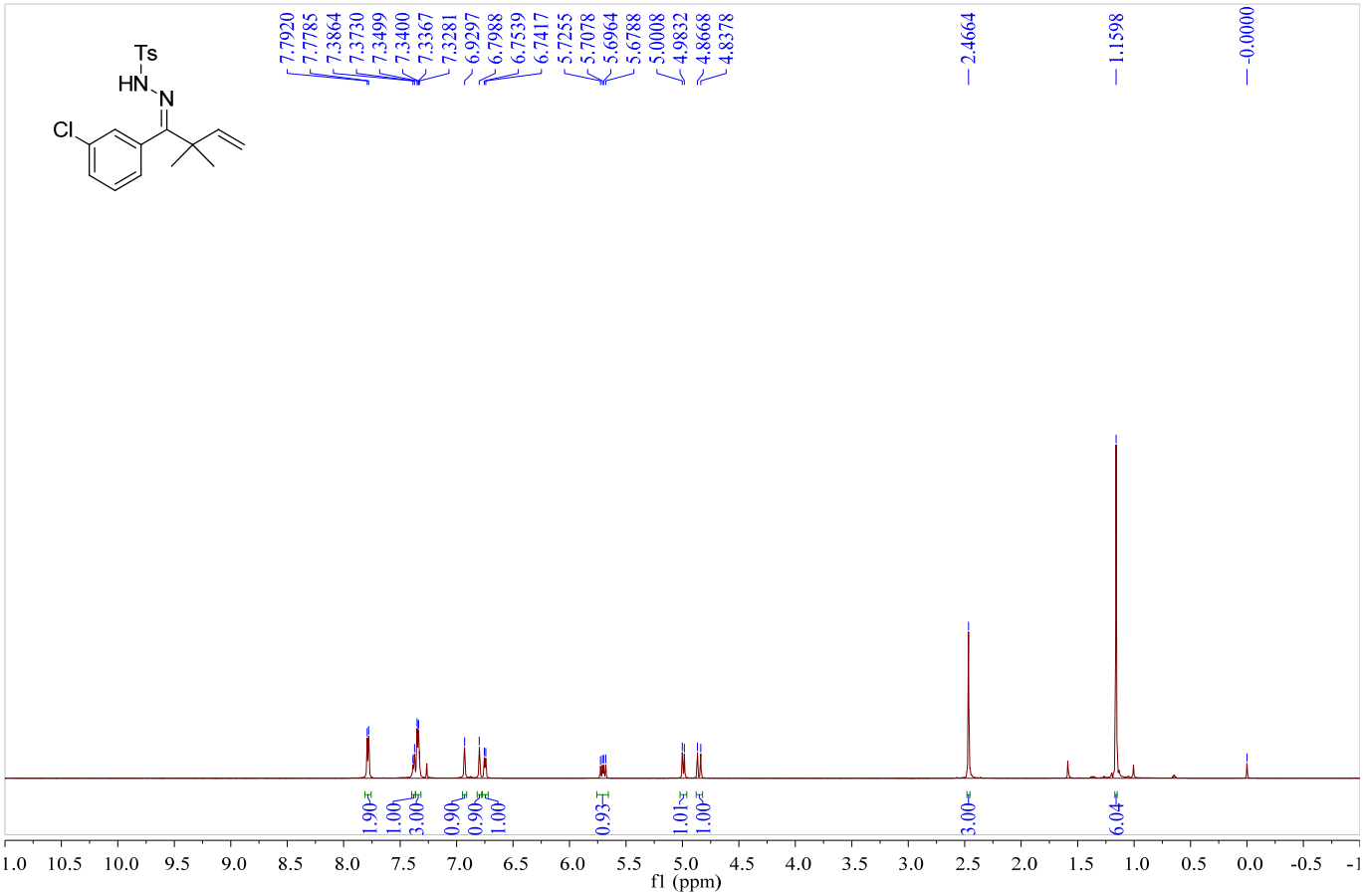


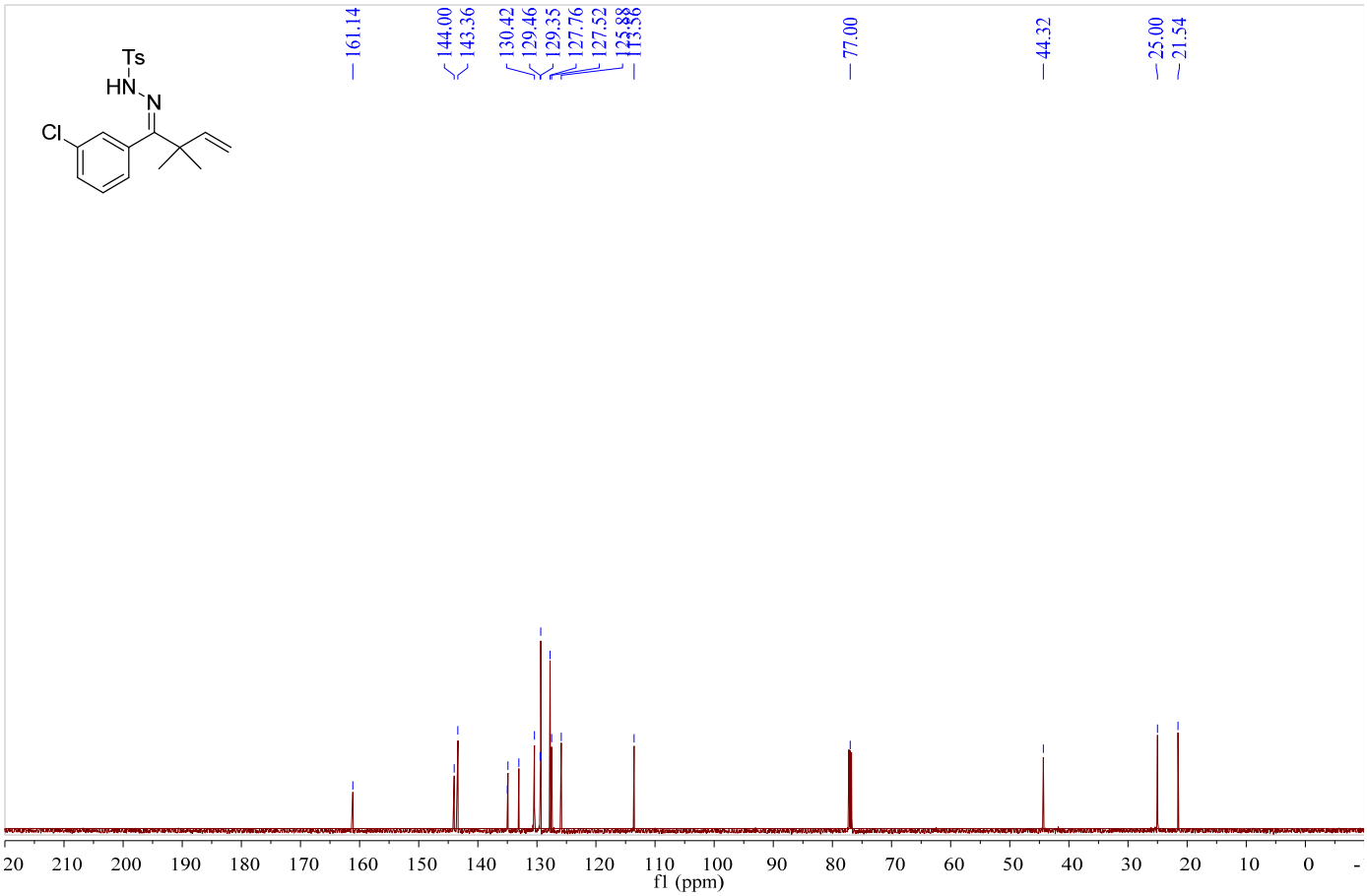
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of substrate 1h



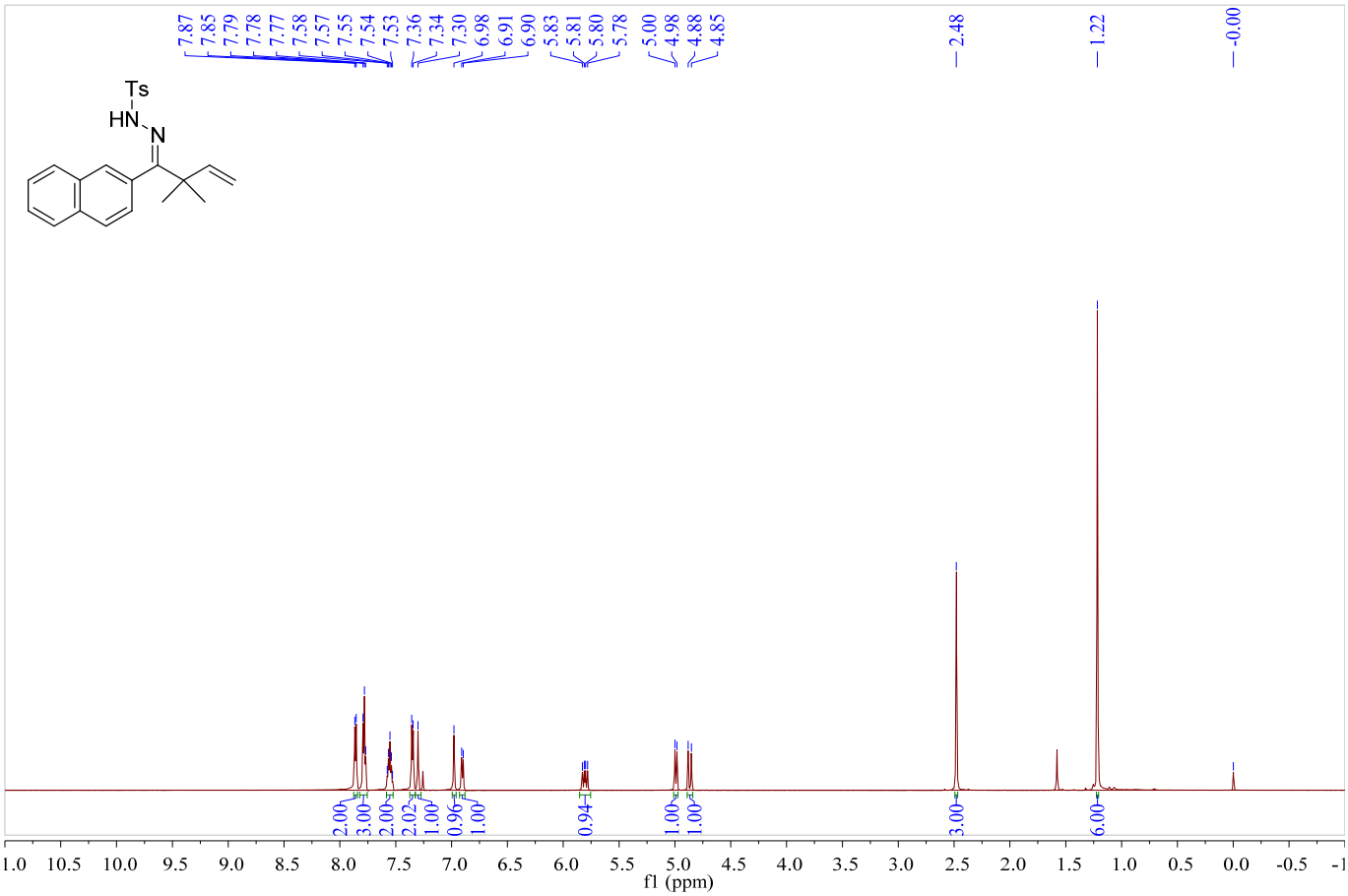


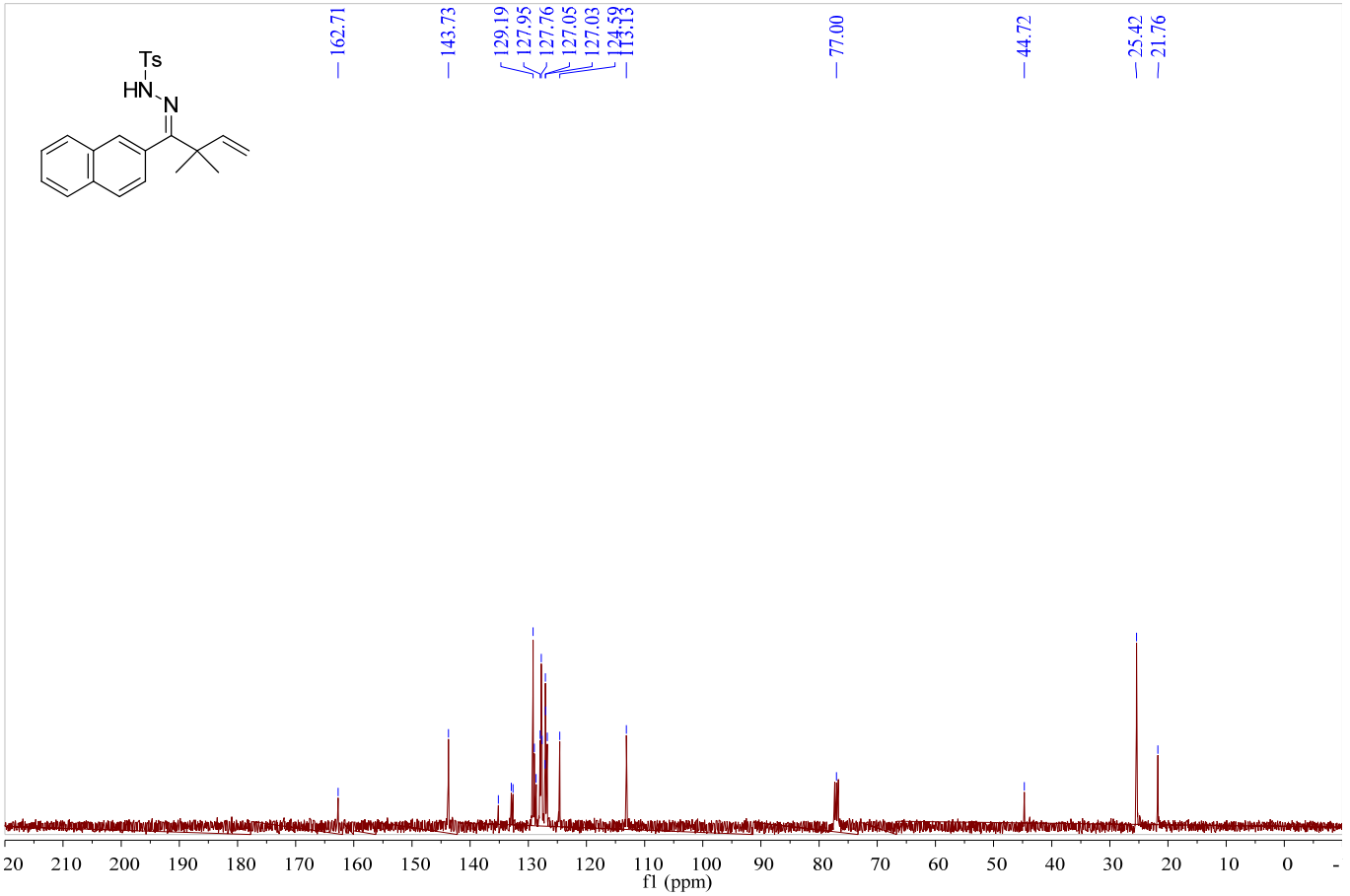
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of substrate 1i



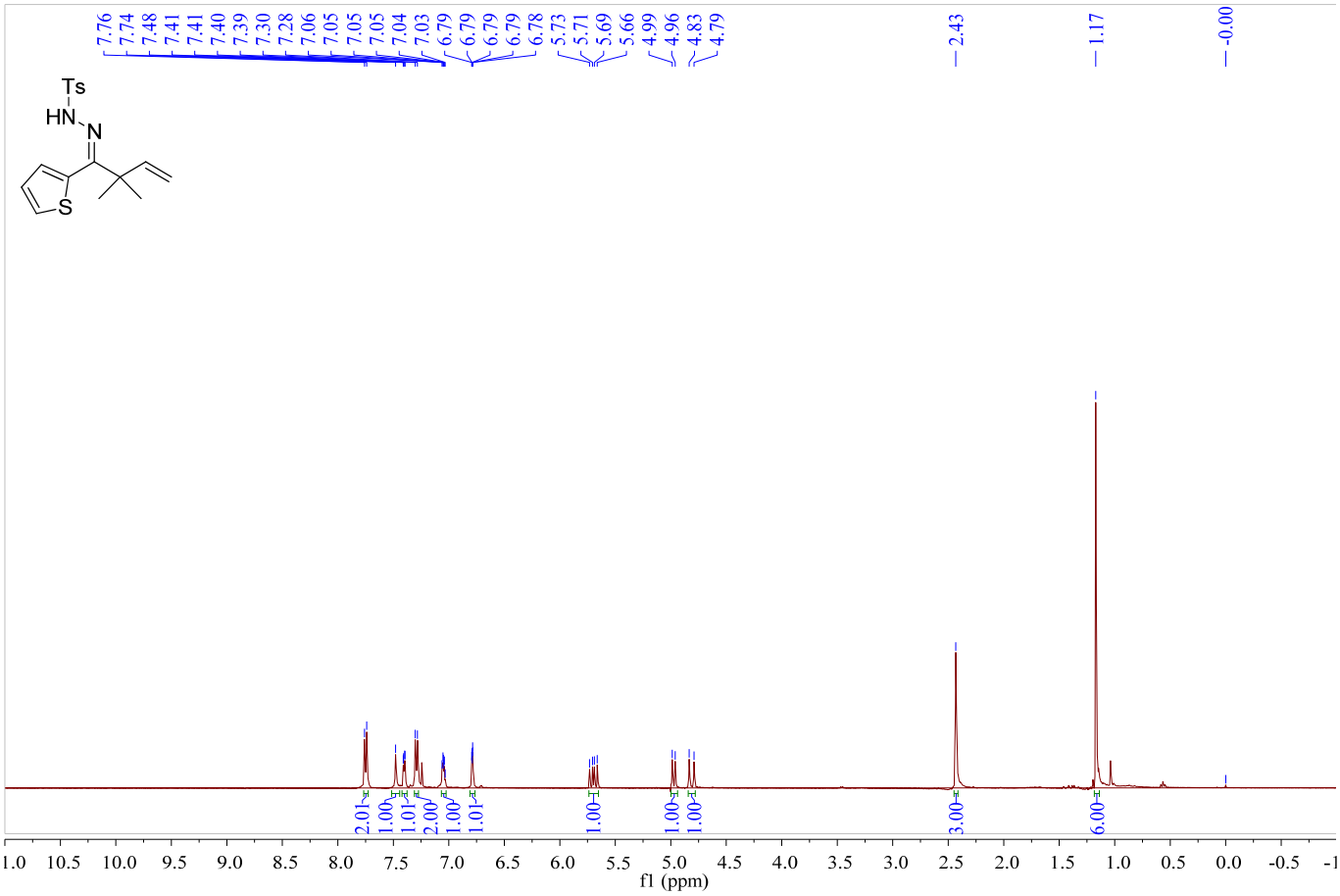


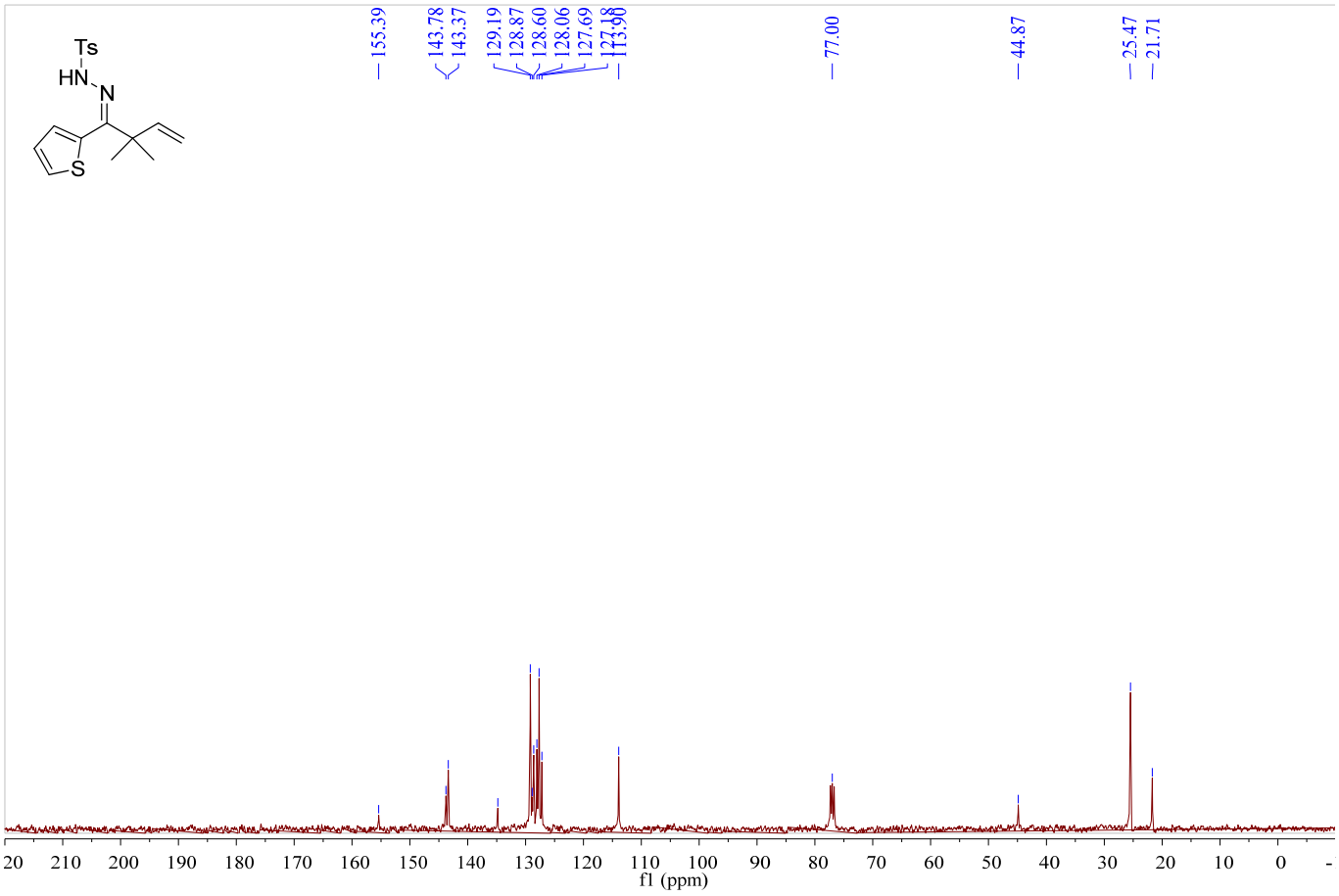
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of substrate 1j



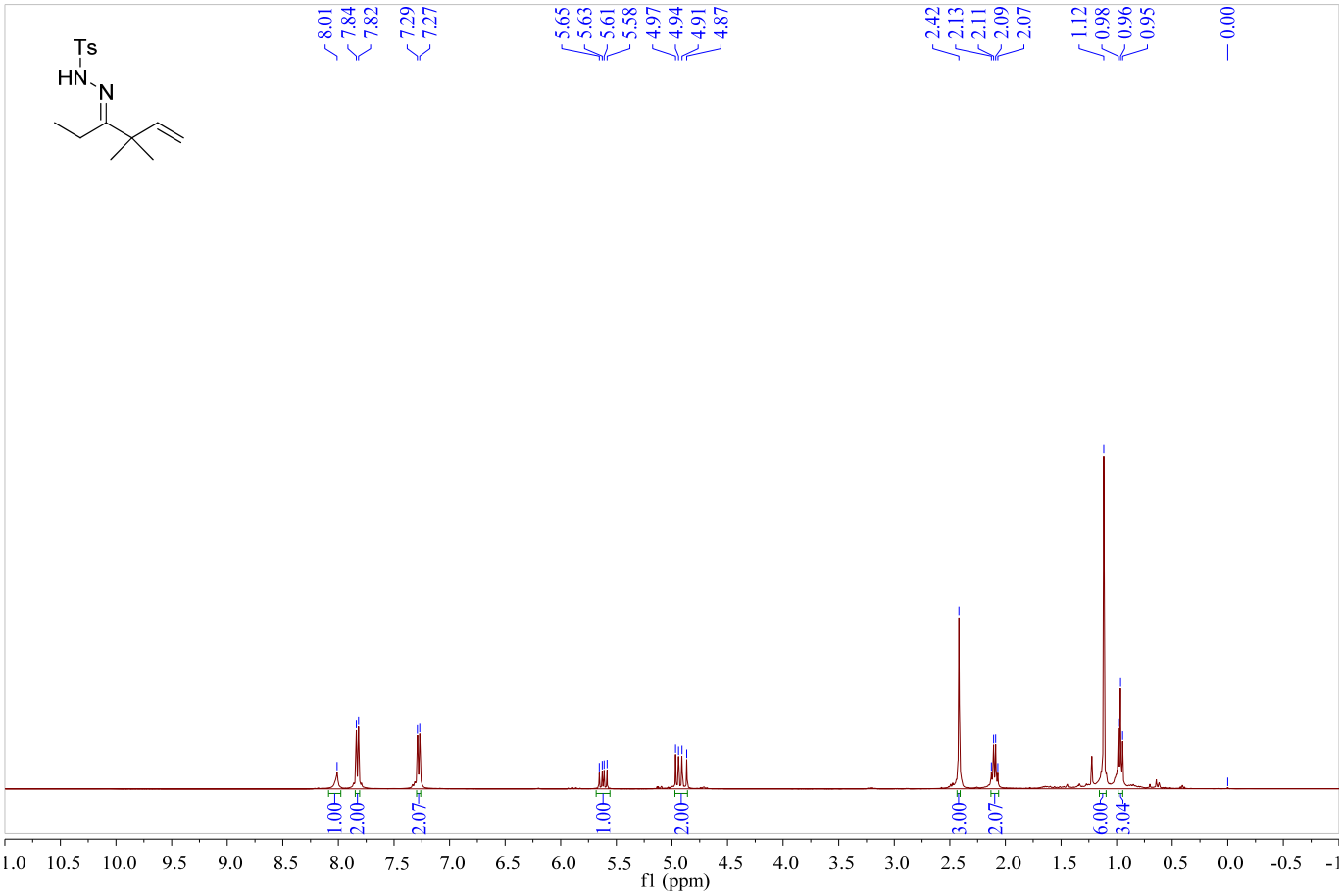


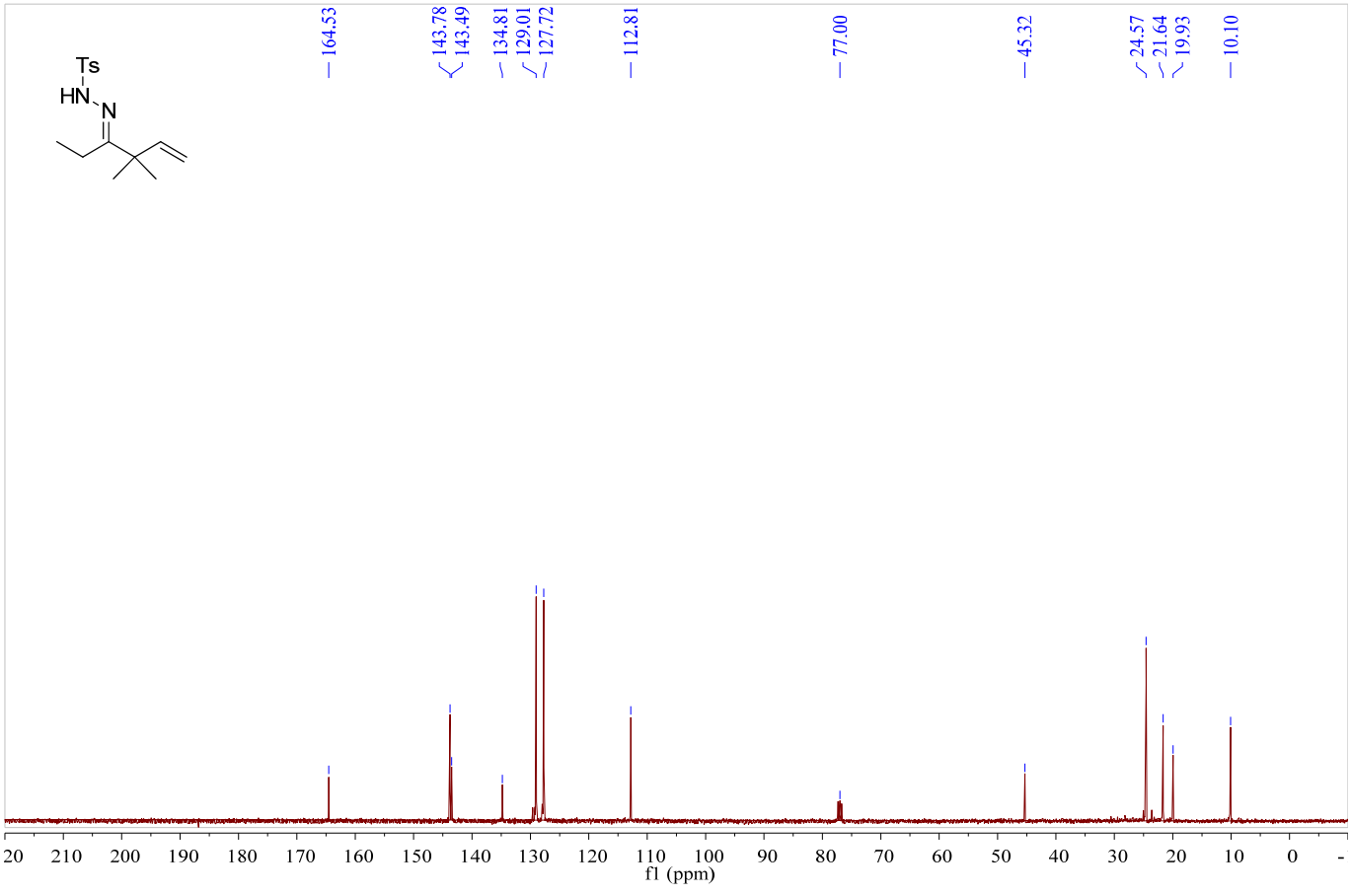
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of substrate 1k



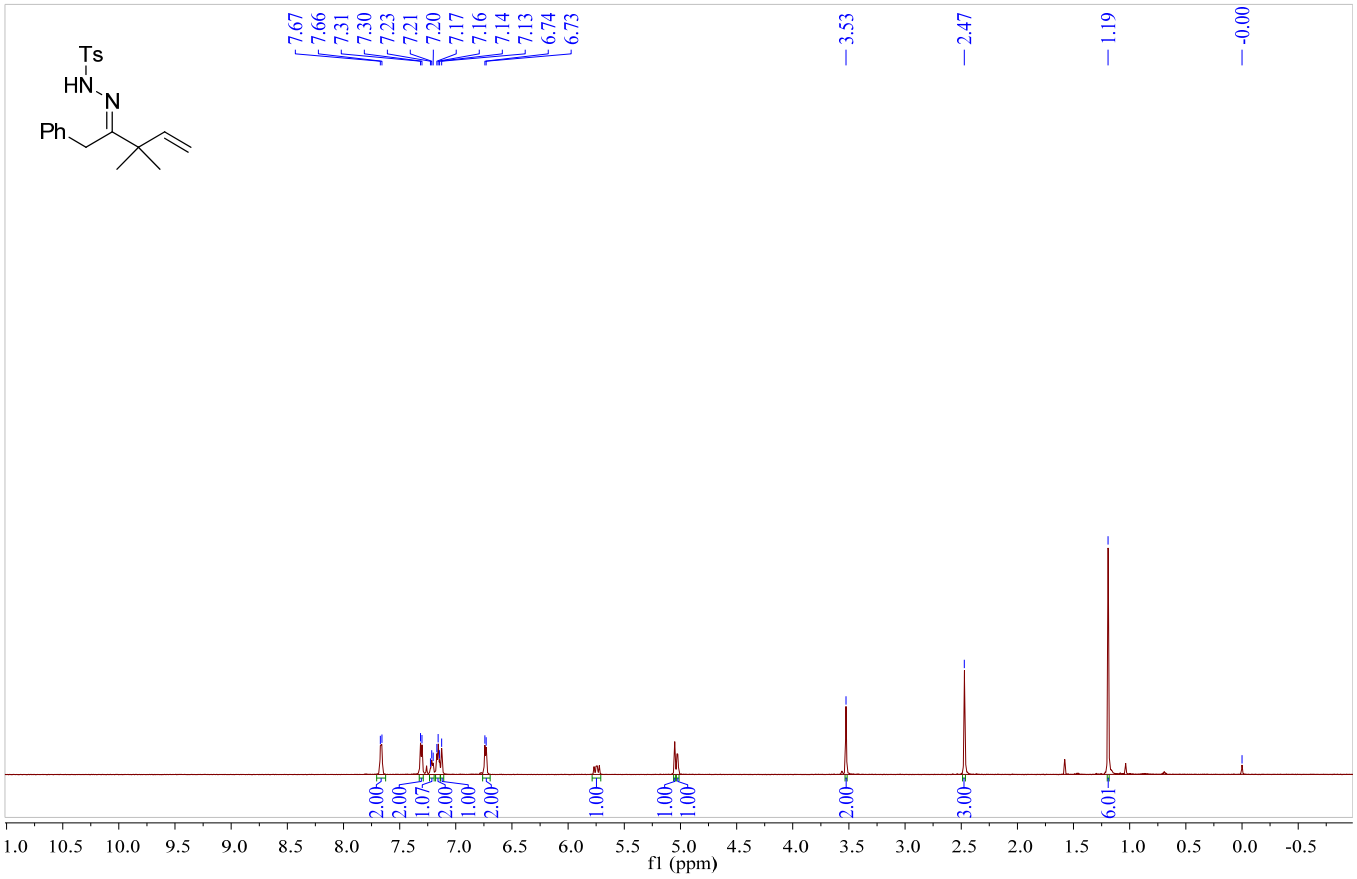


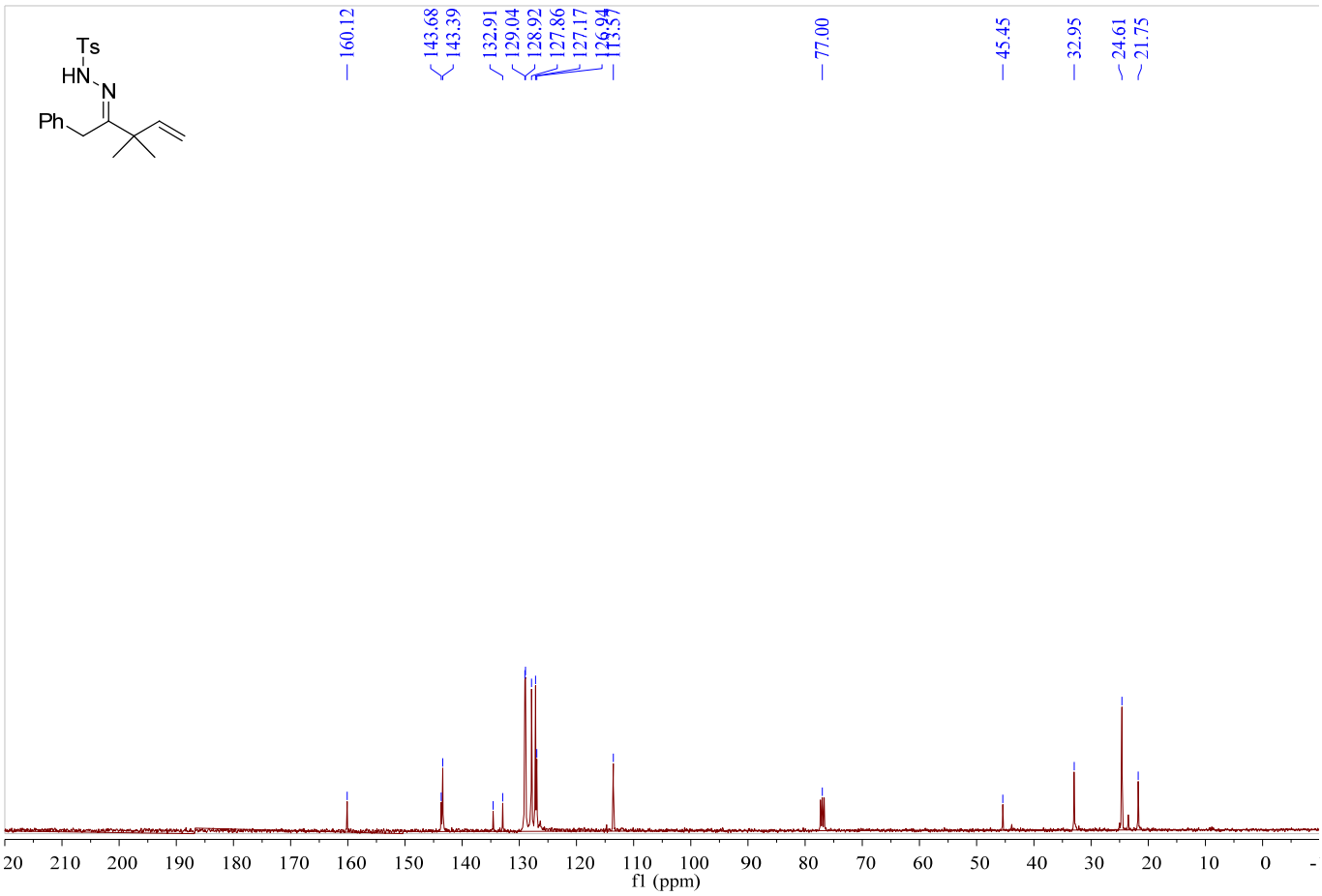
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of substrate 1l



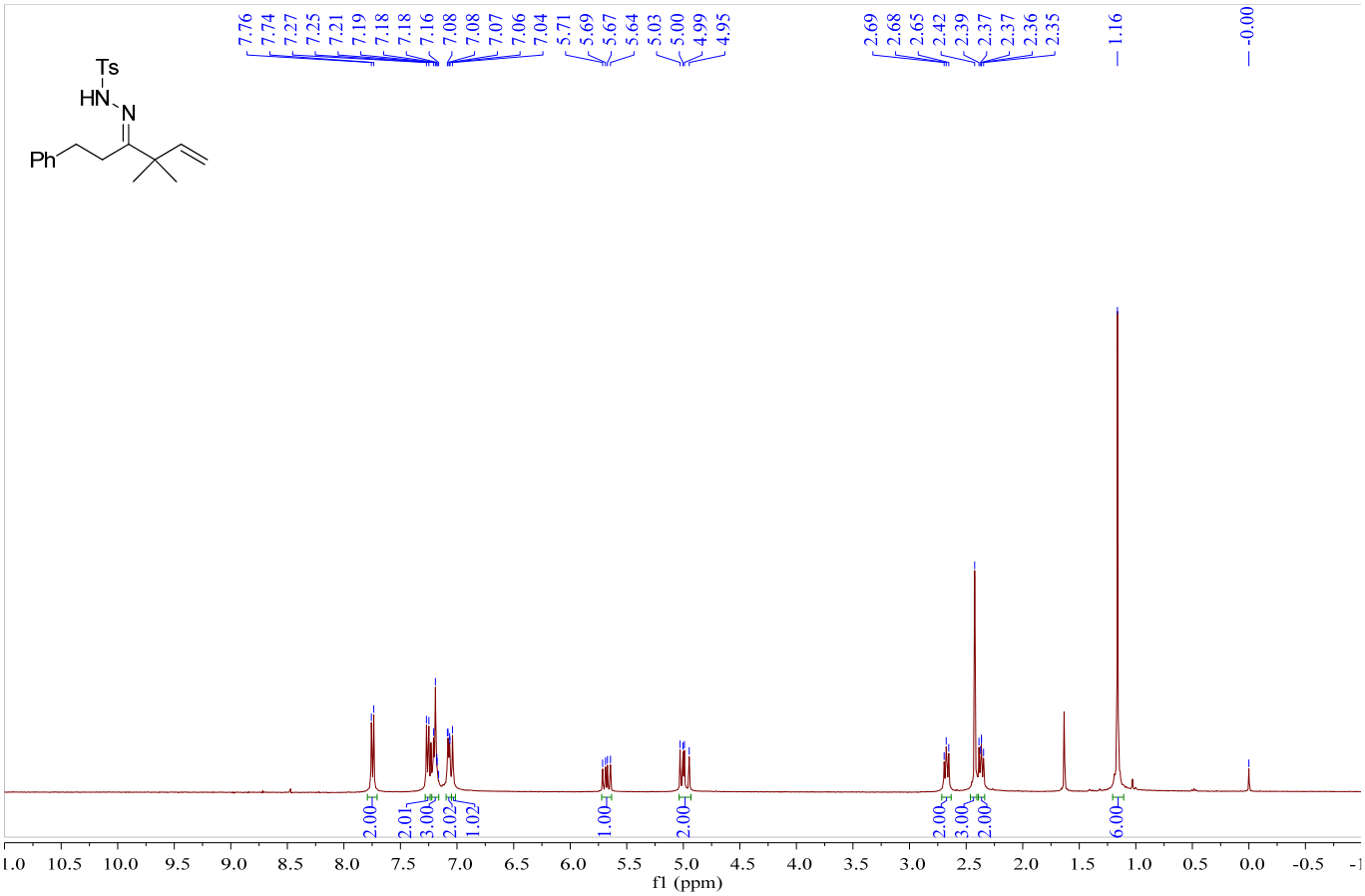


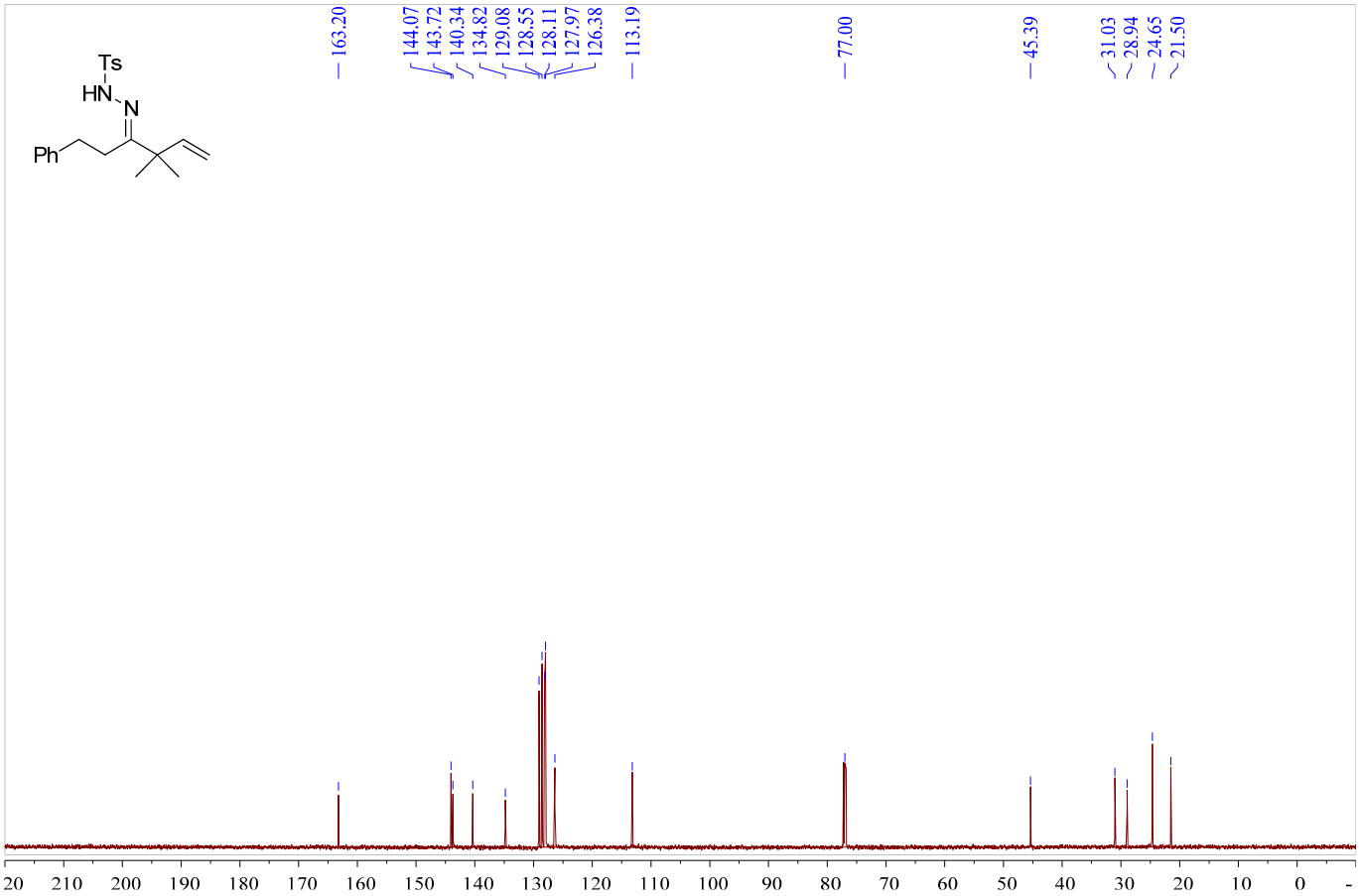
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of substrate 1m



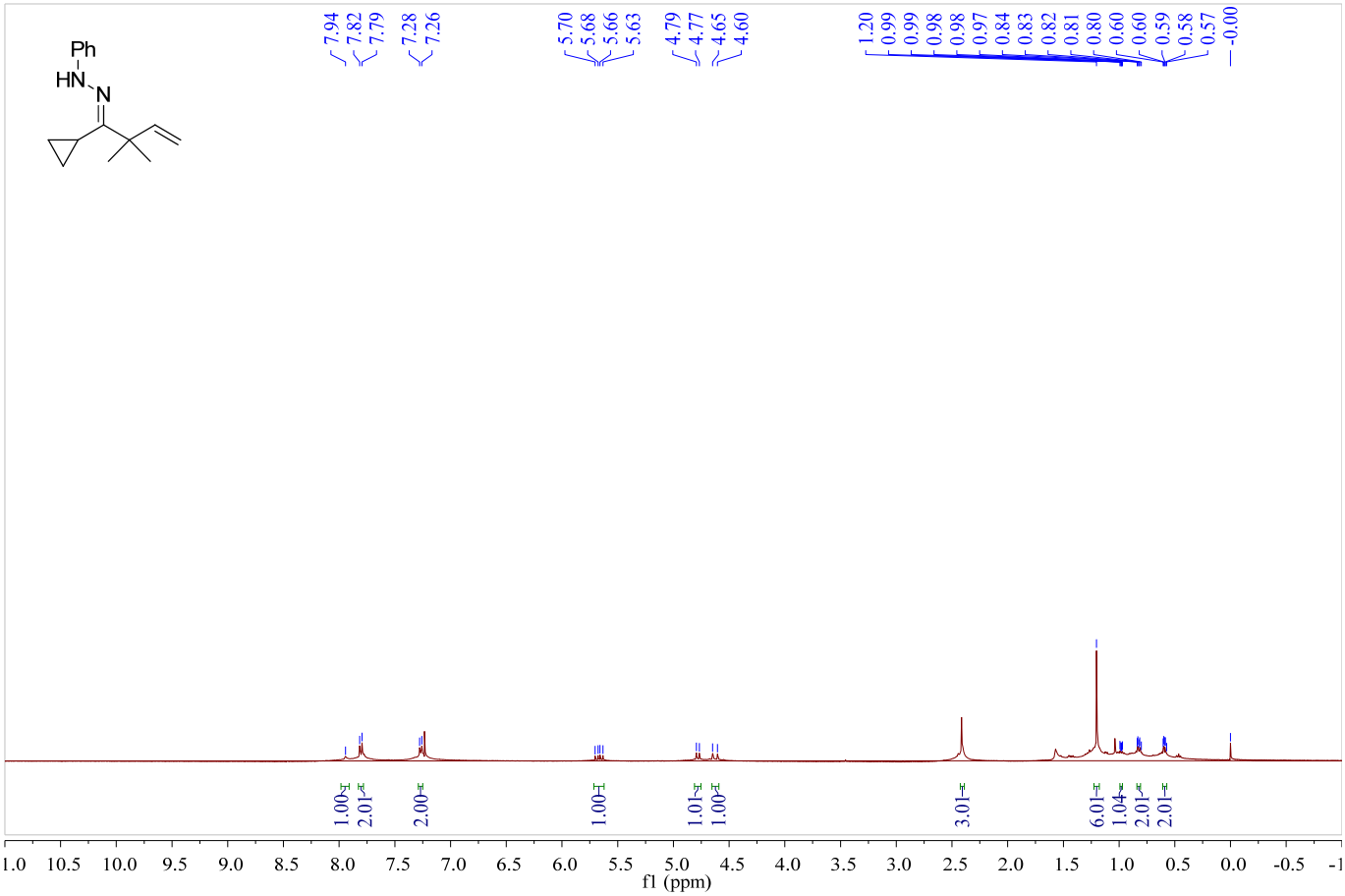


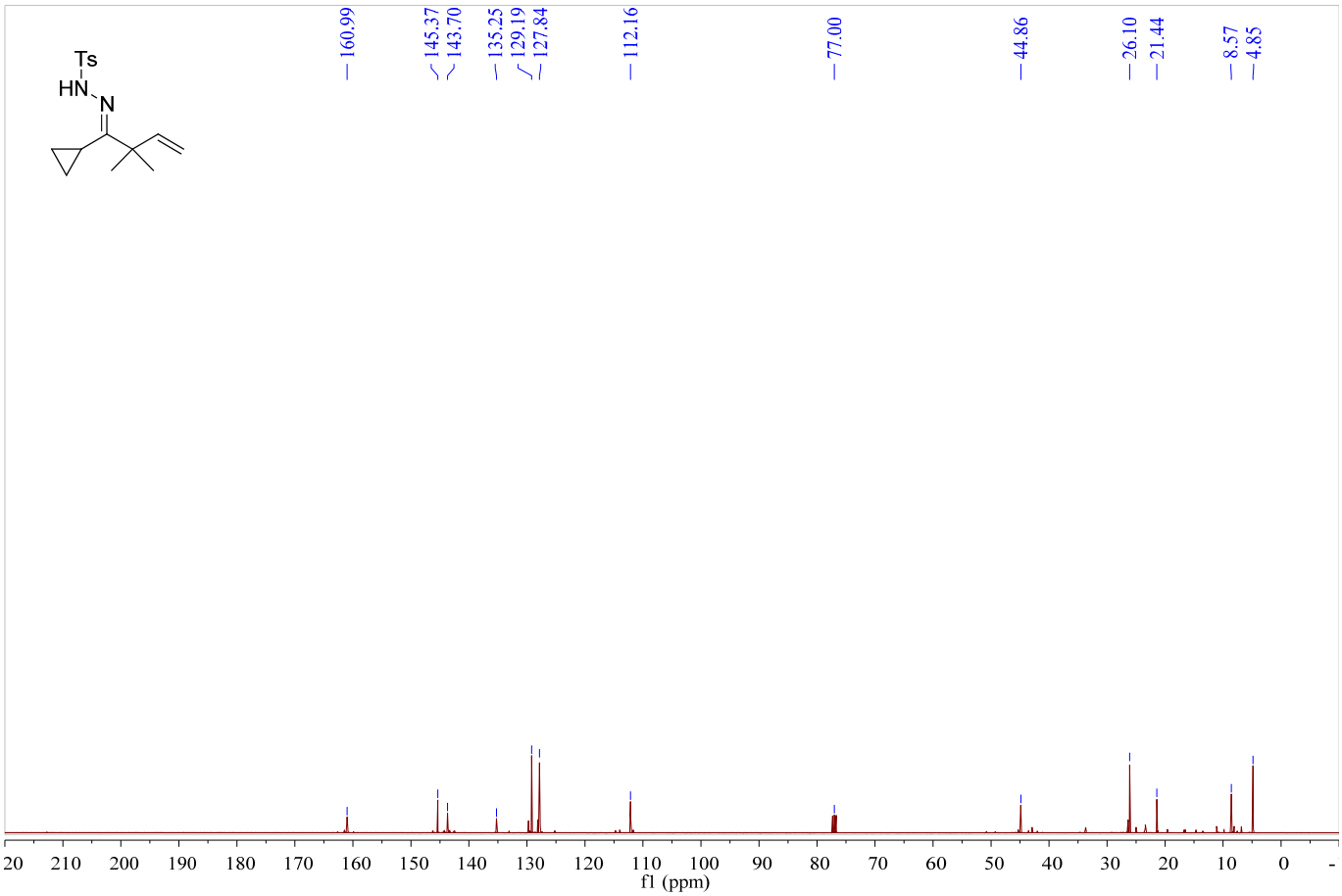
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of substrate 1n



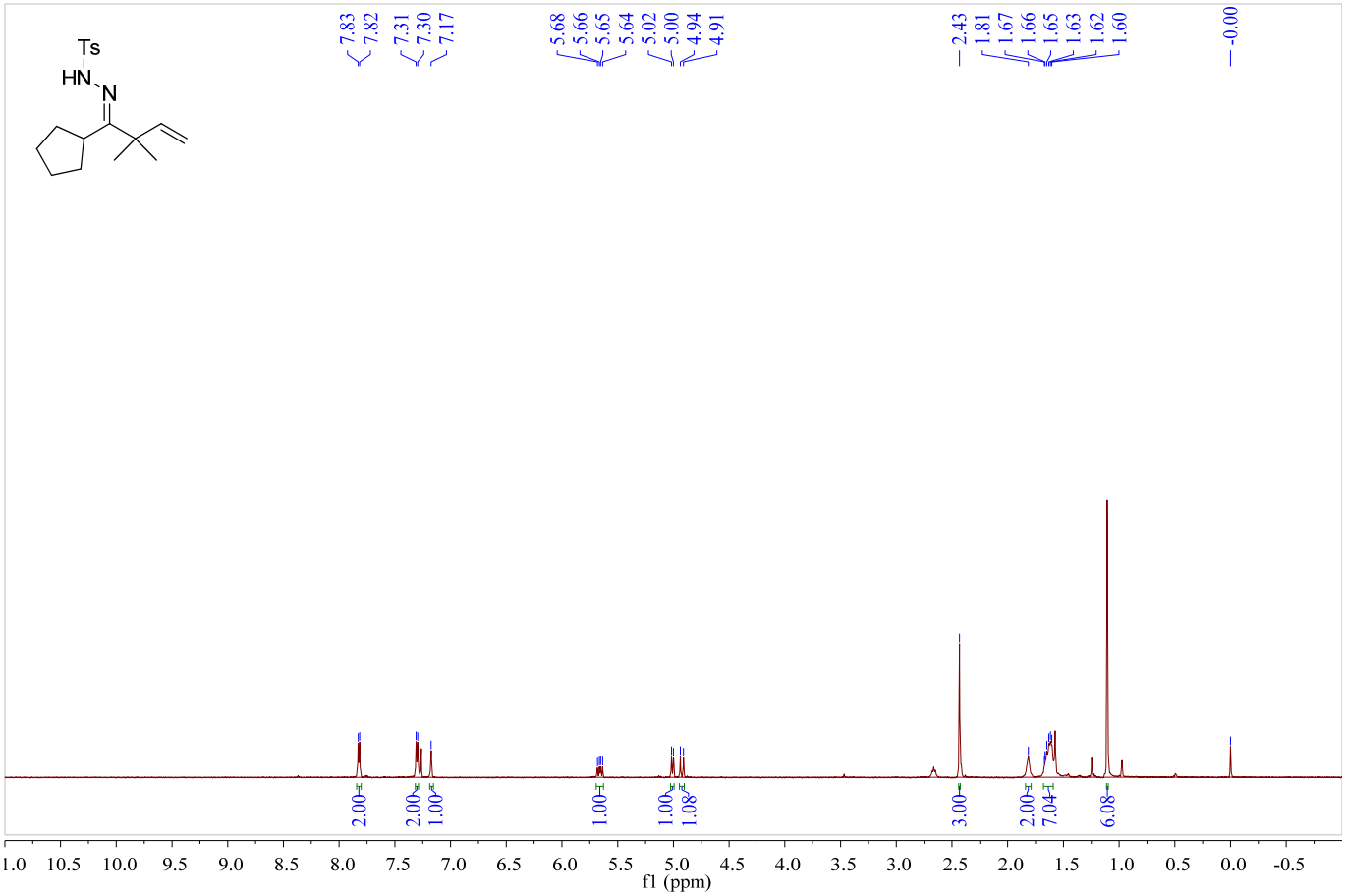


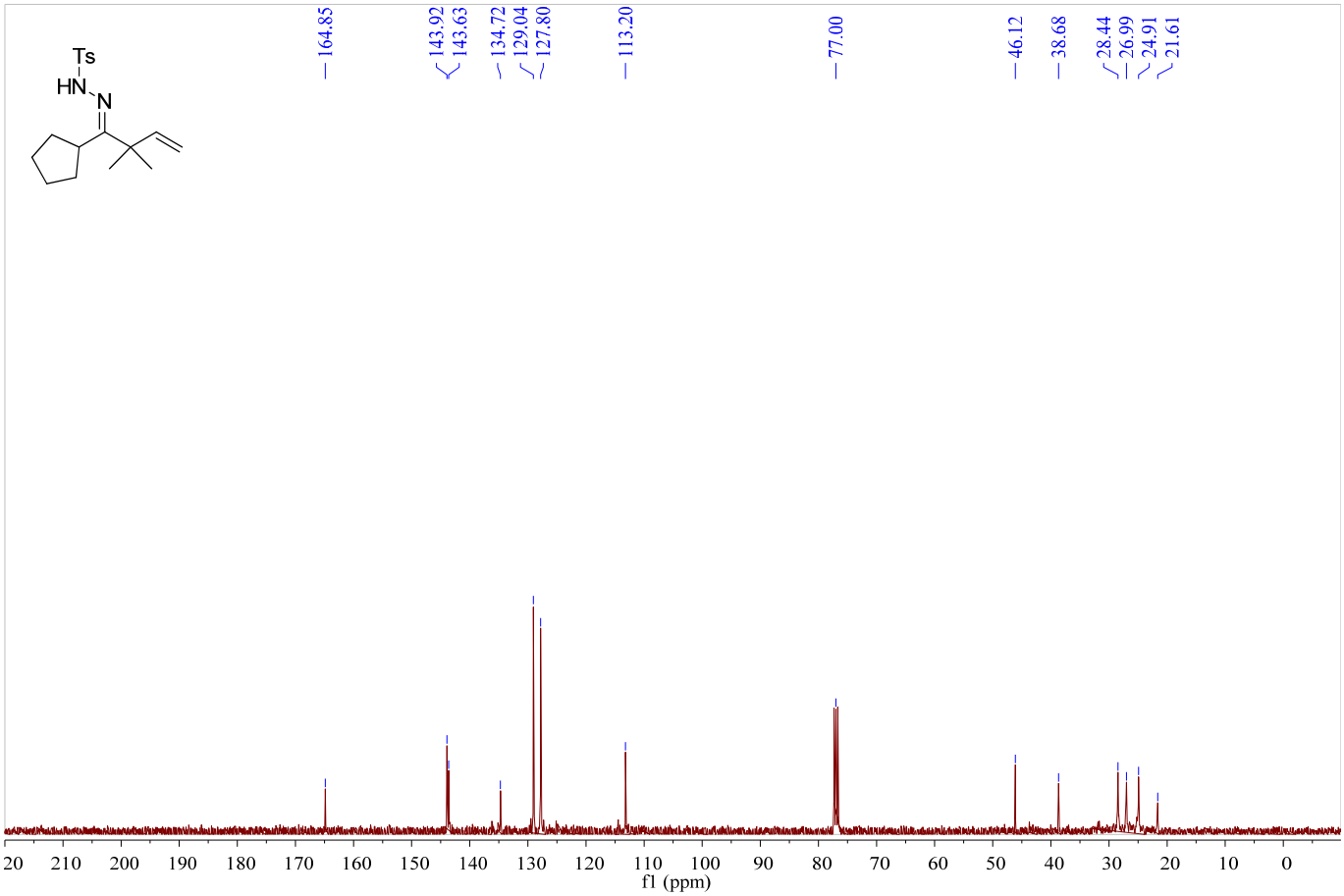
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of substrate 1o



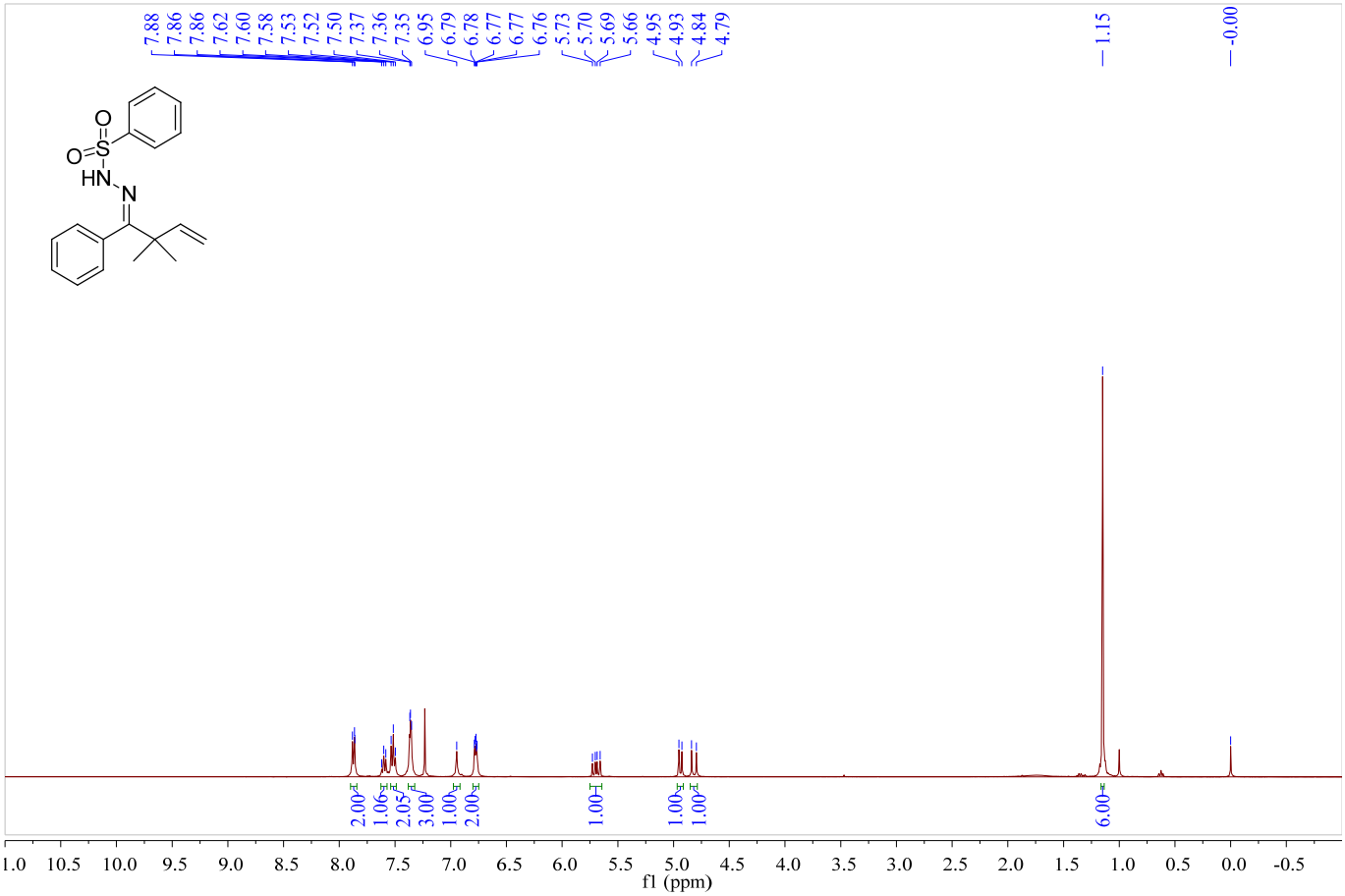


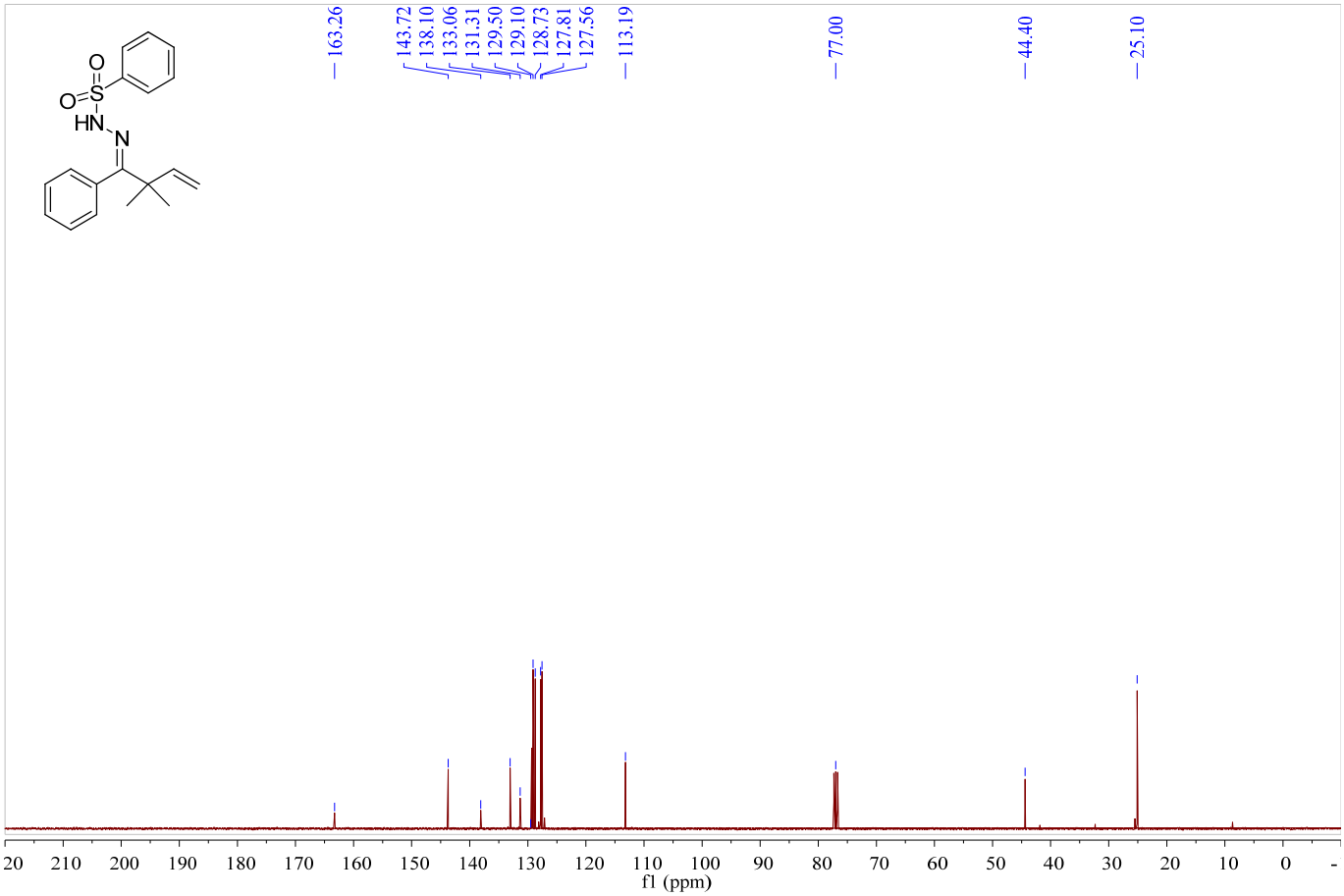
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of substrate 1p



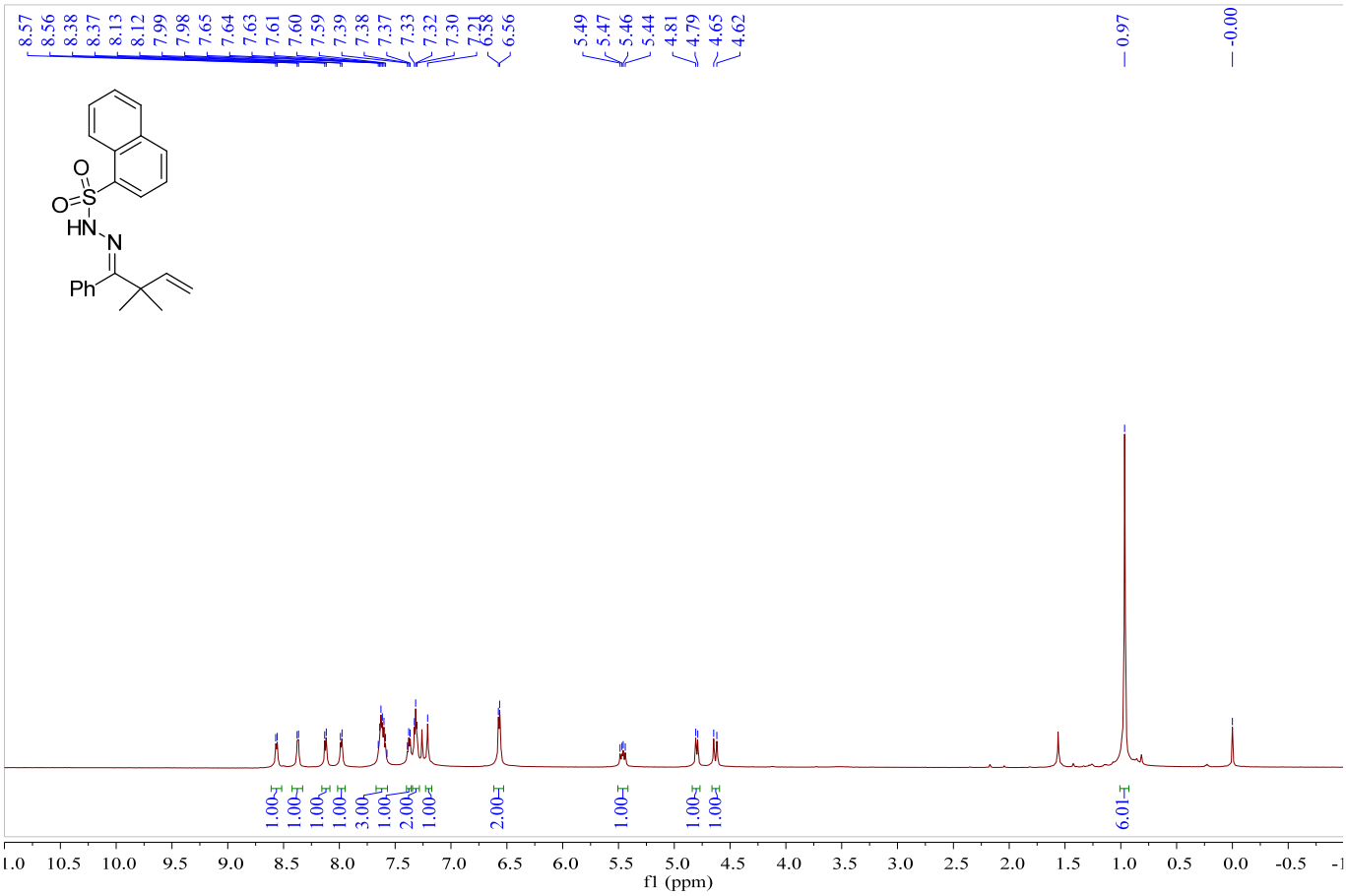


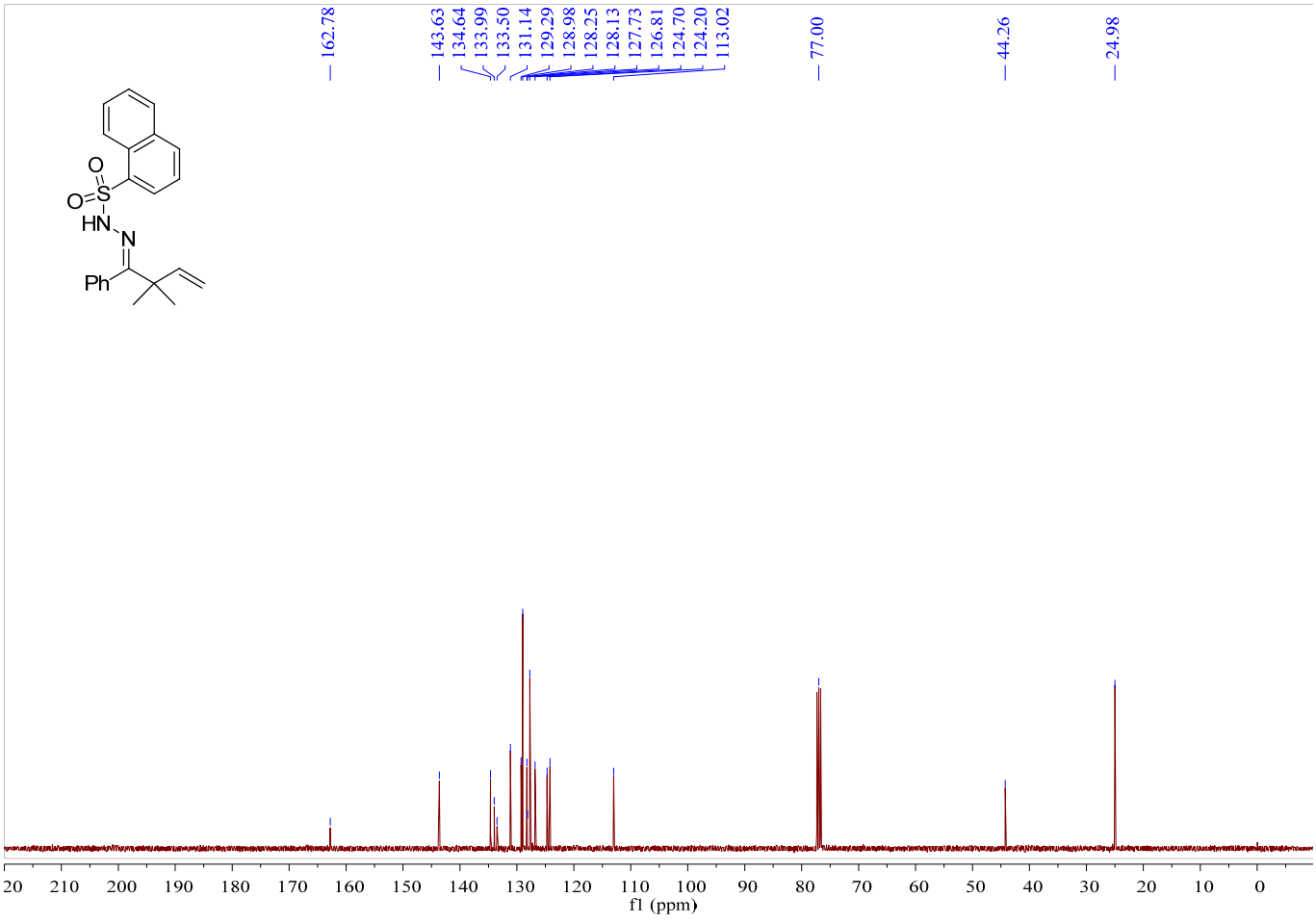
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of substrate 1r



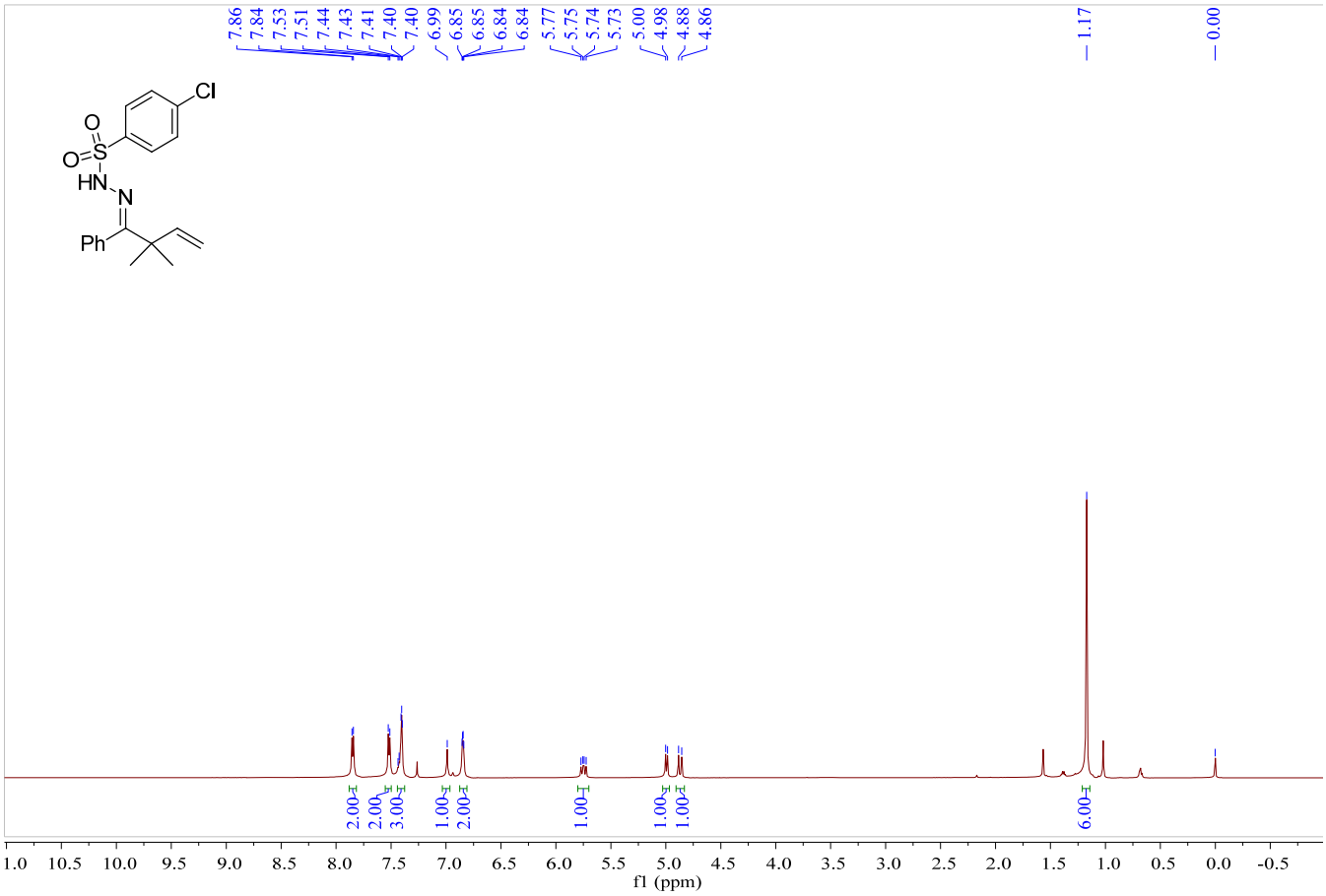


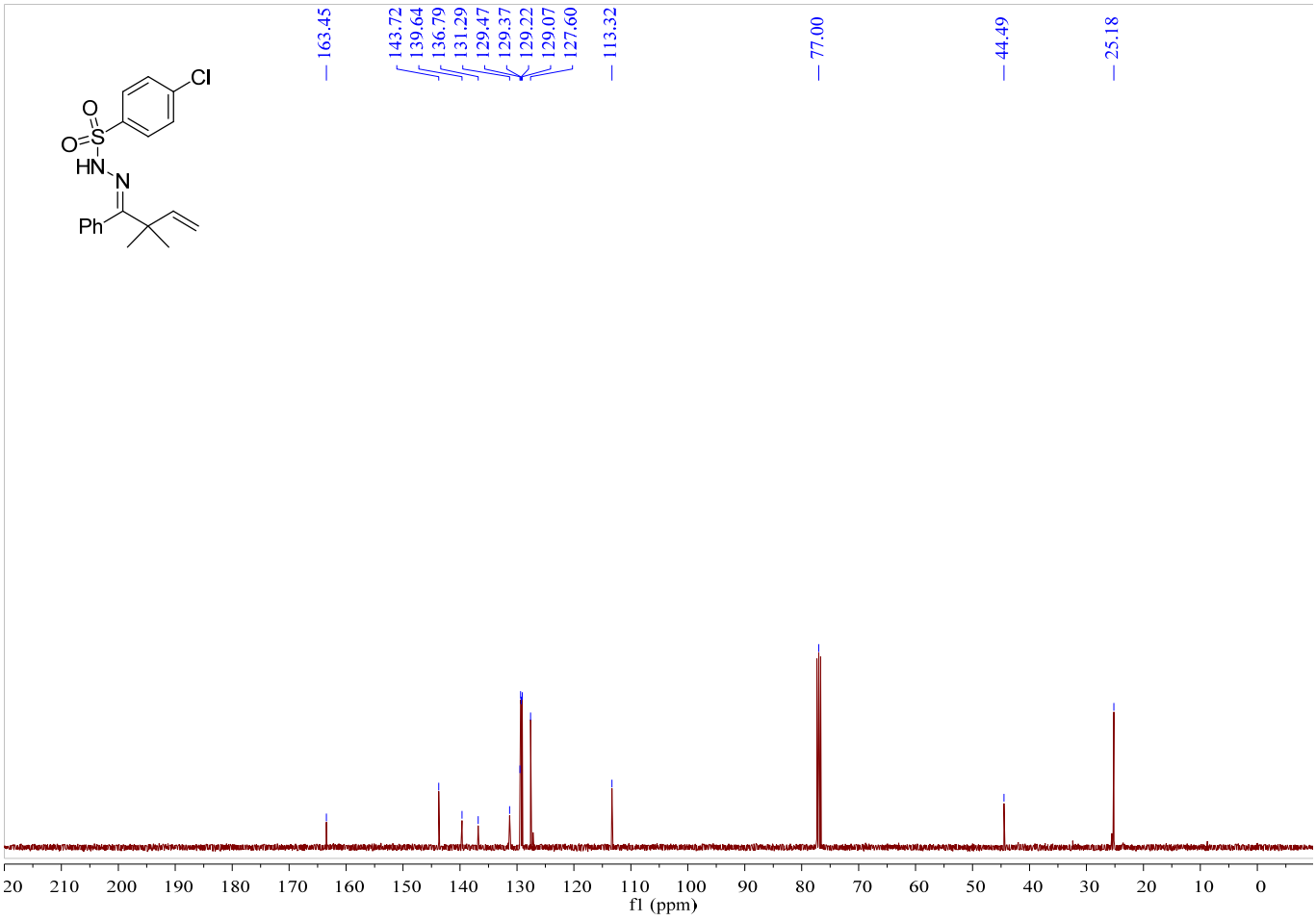
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of substrate 1s



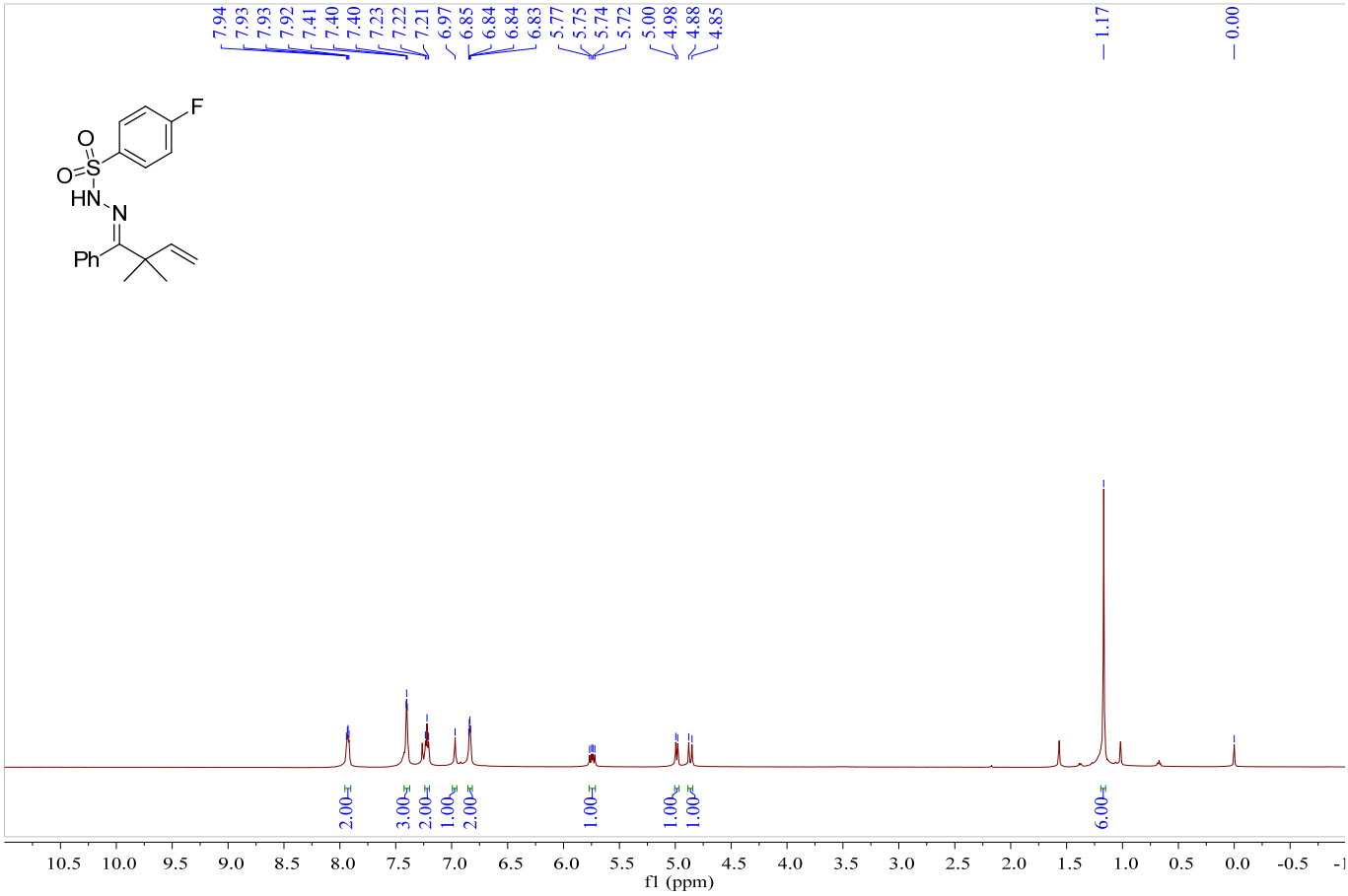


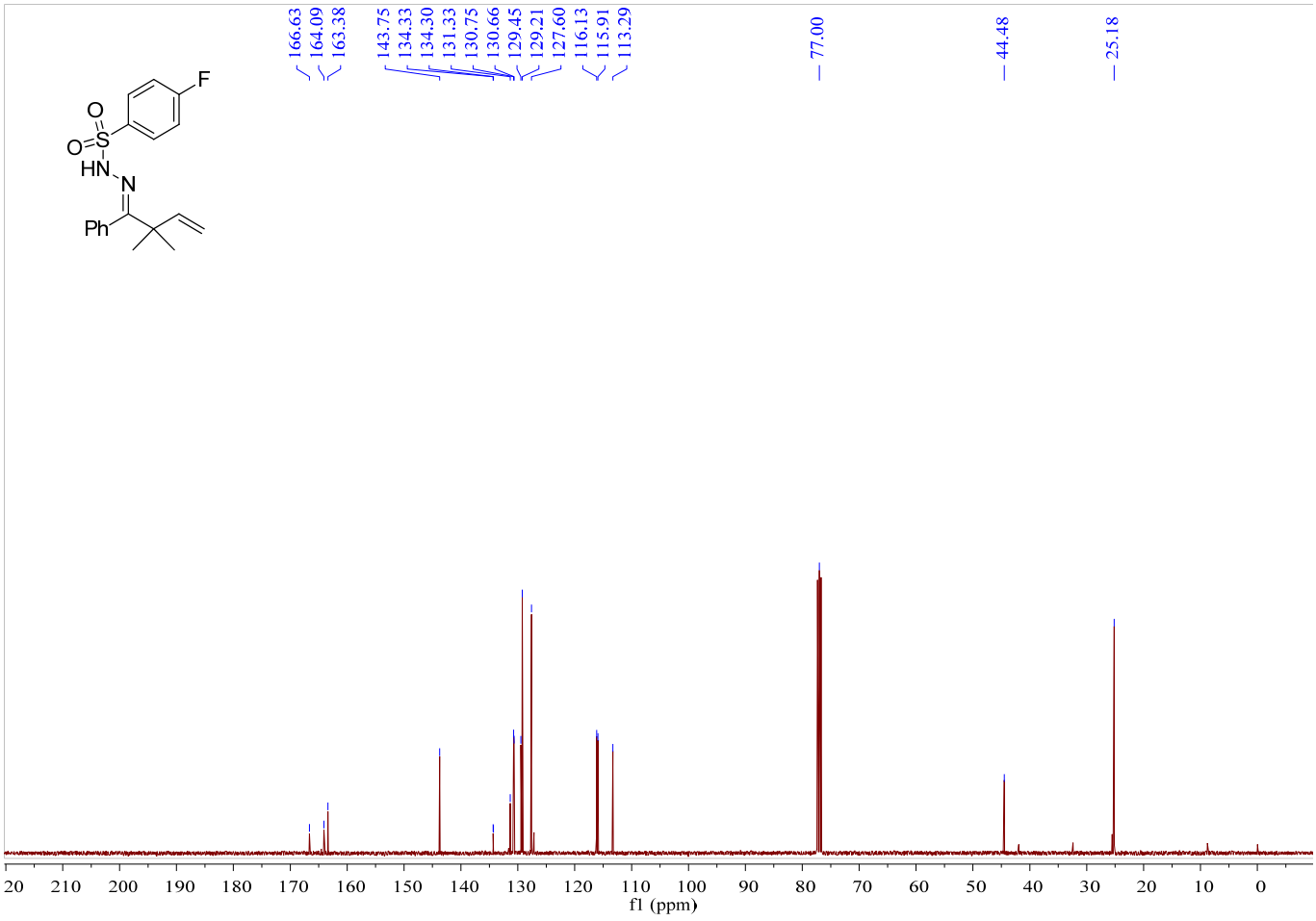
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of substrate 1t



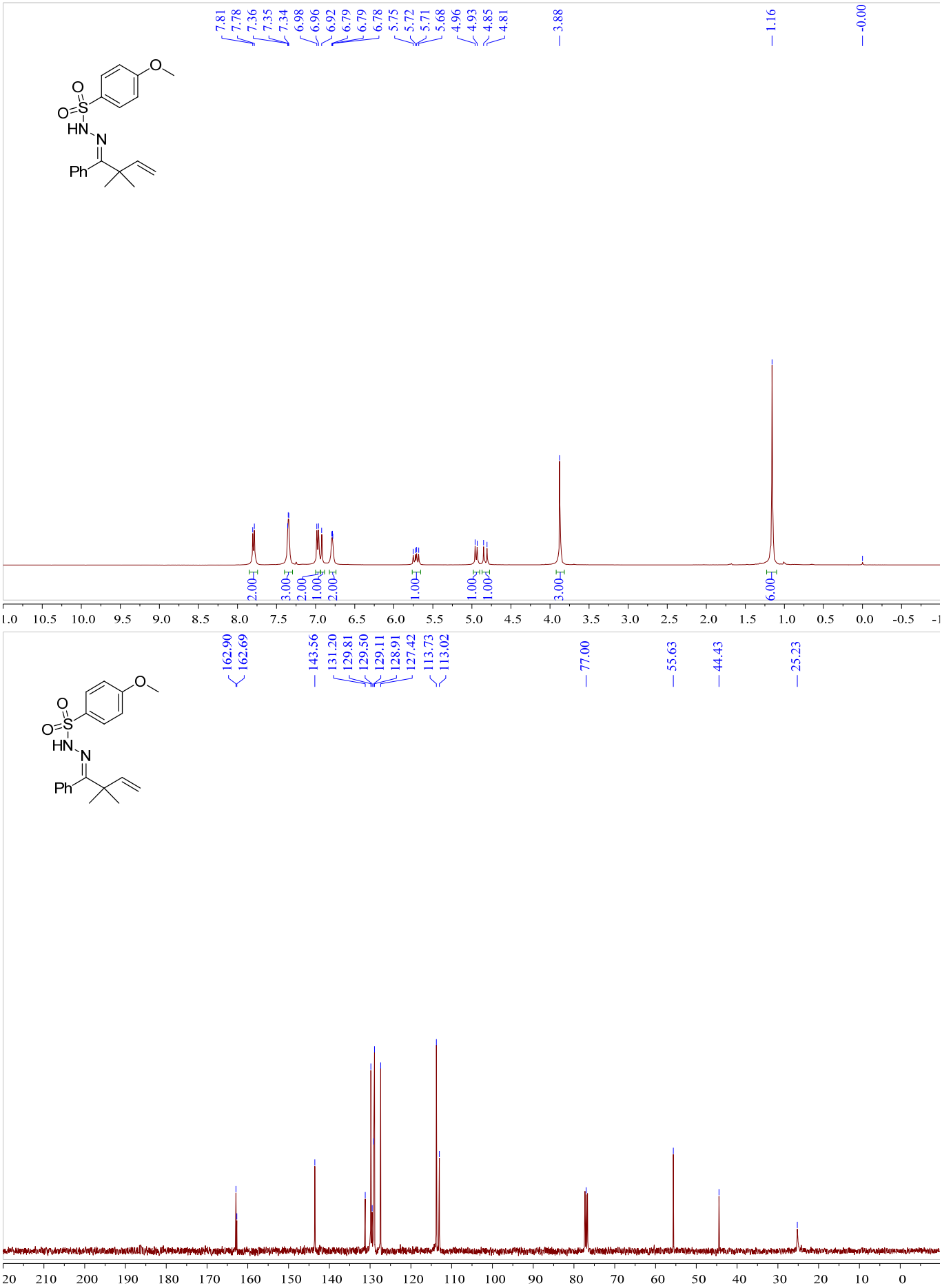


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of substrate 1u

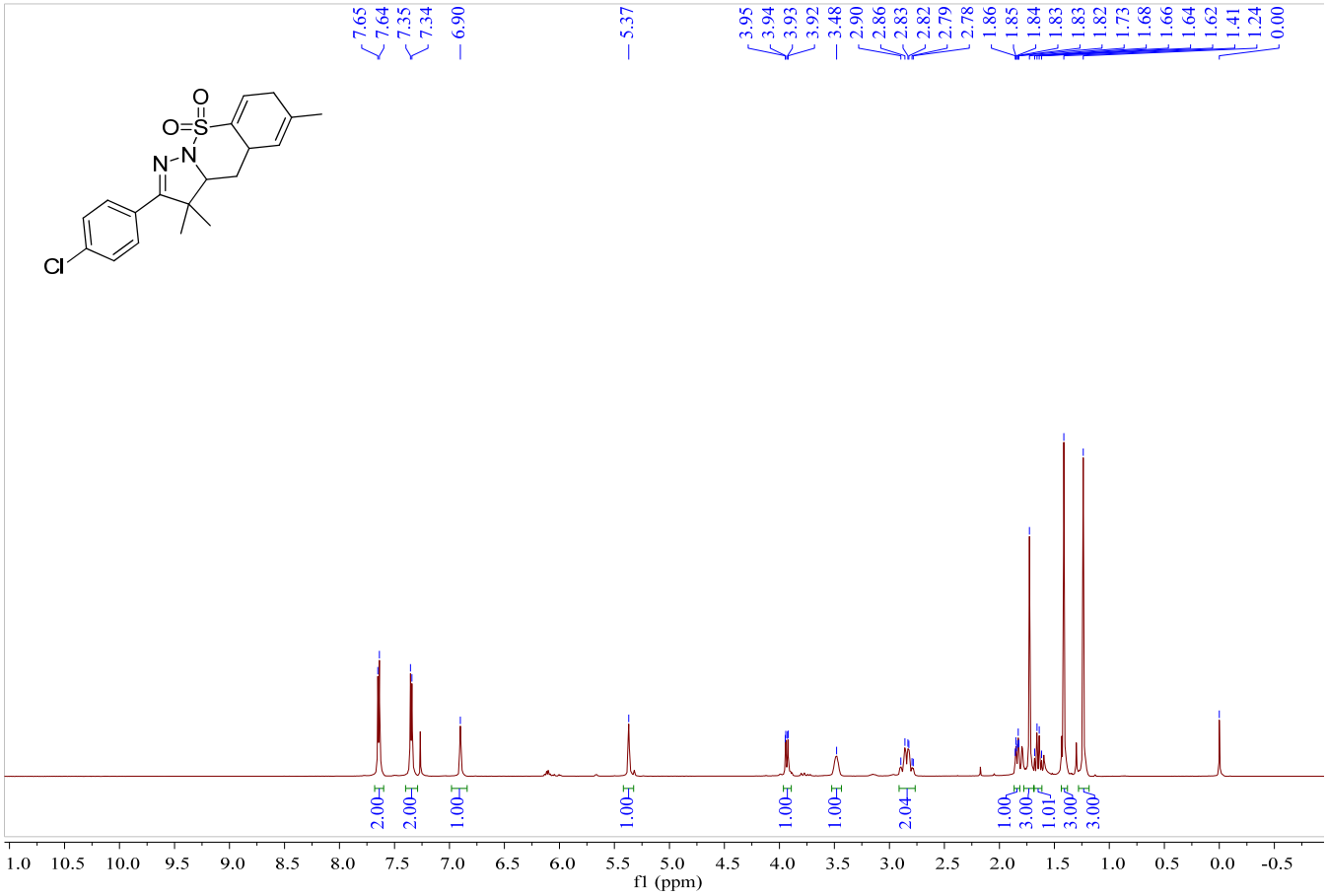


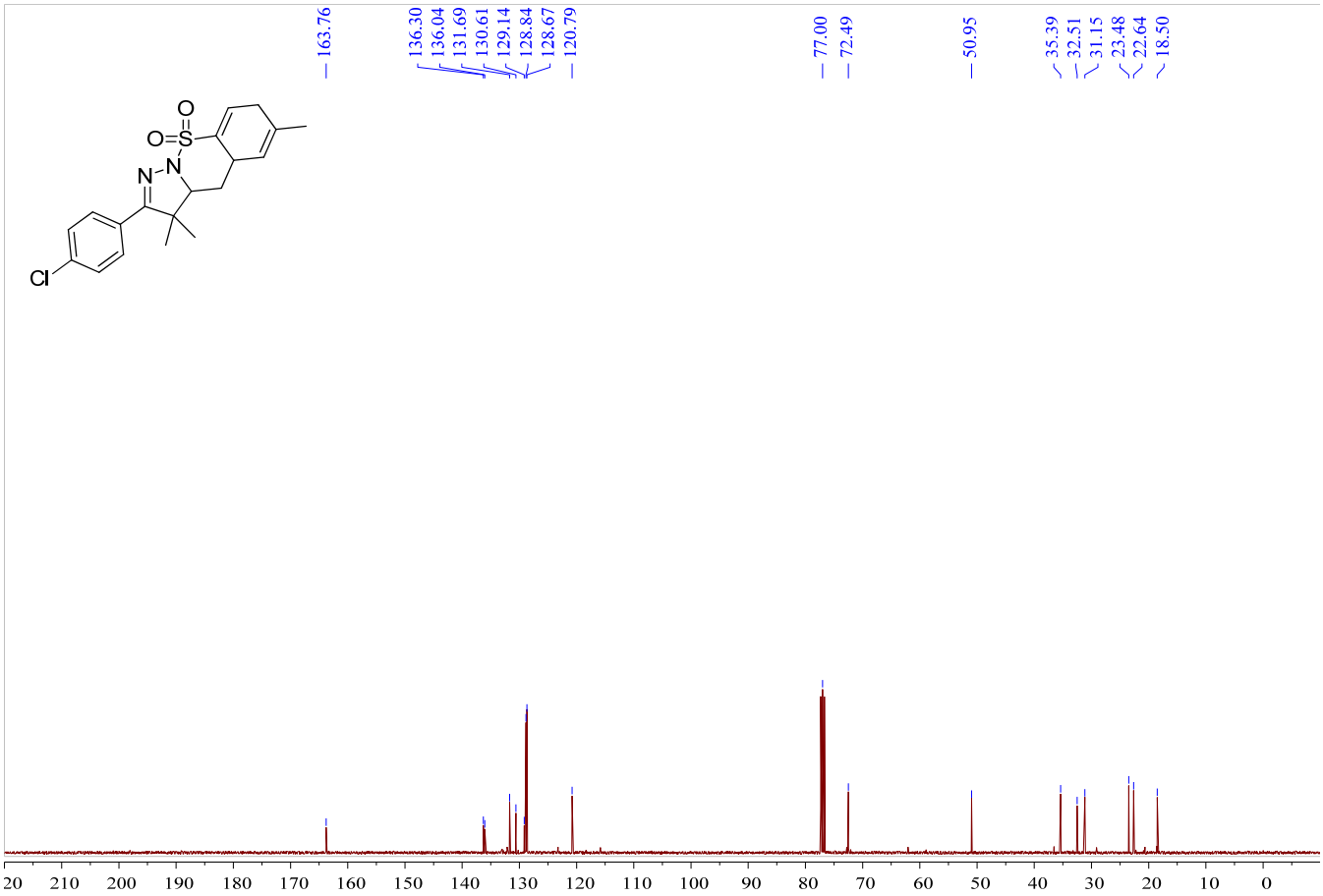


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of substrate 1v



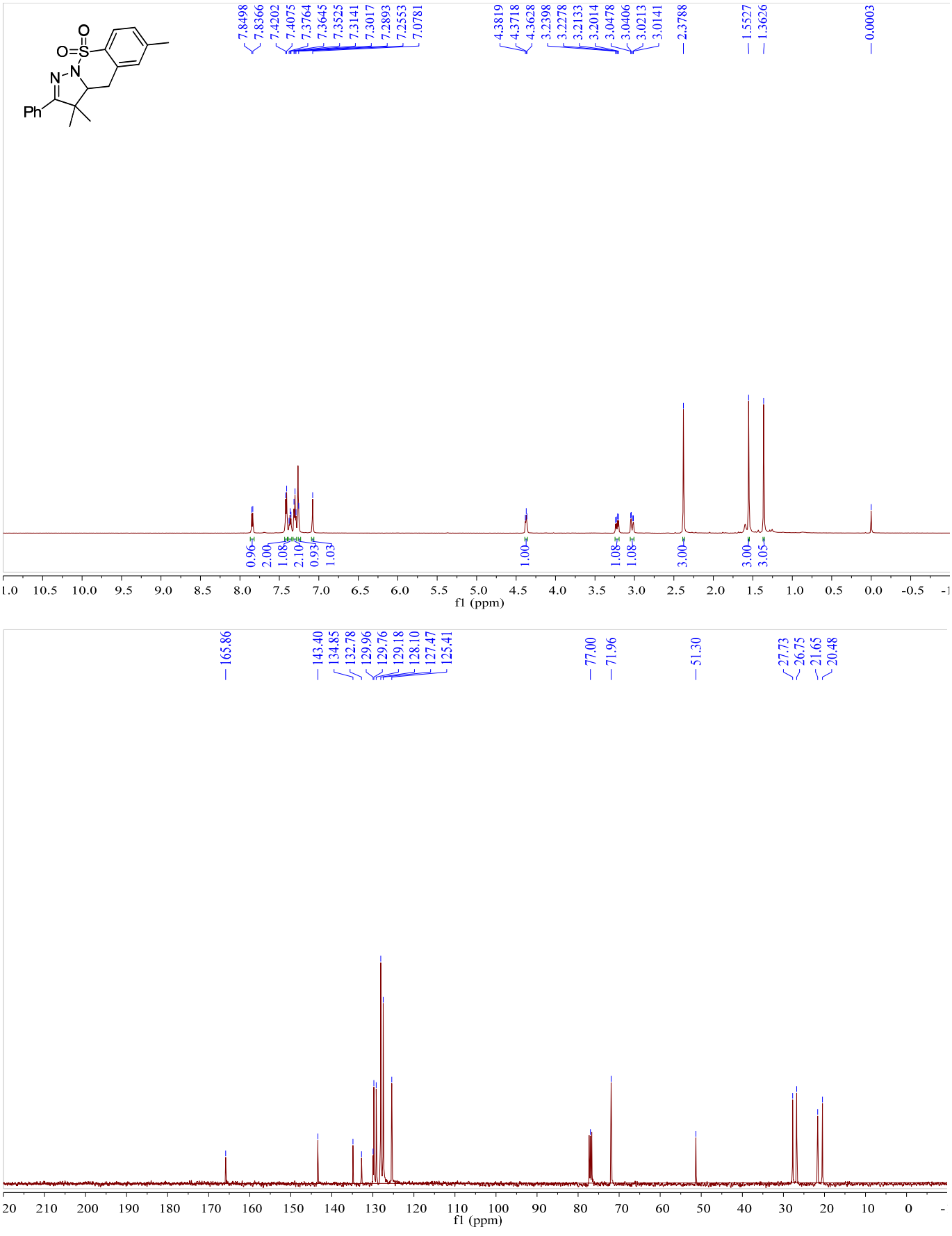
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of product 3c



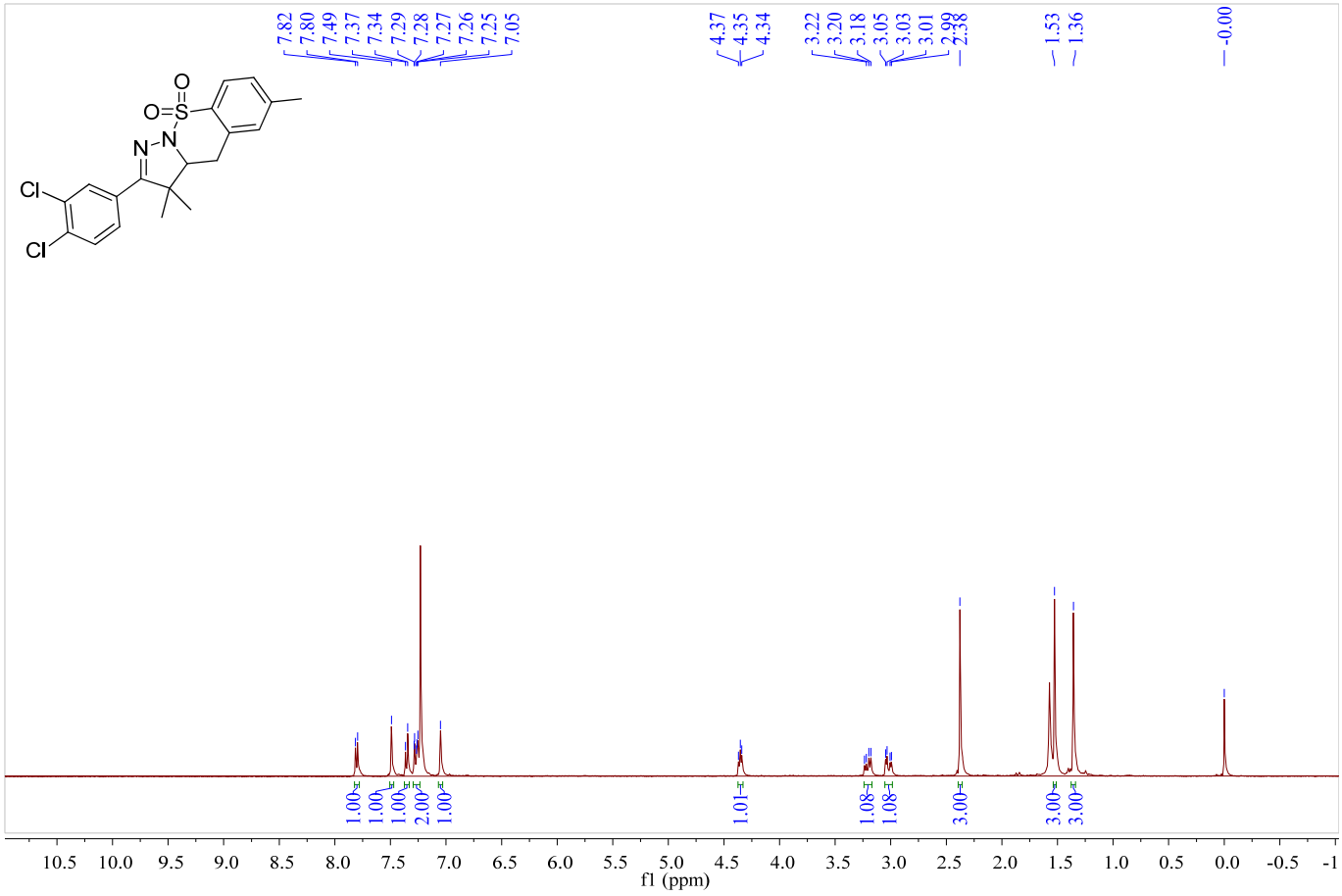


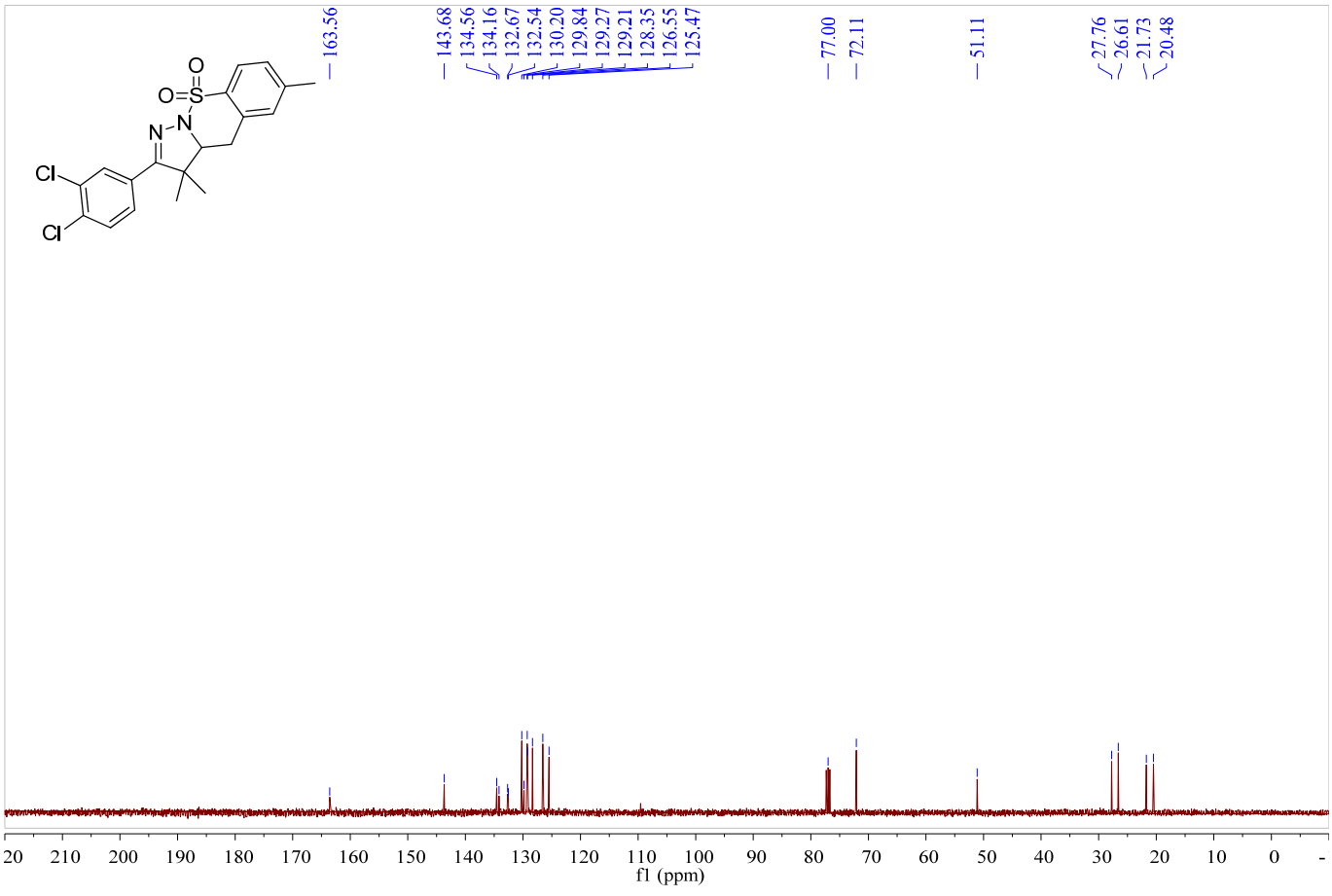
NMR Spectra of the Products 2a-v, 3a and 4

^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 2a

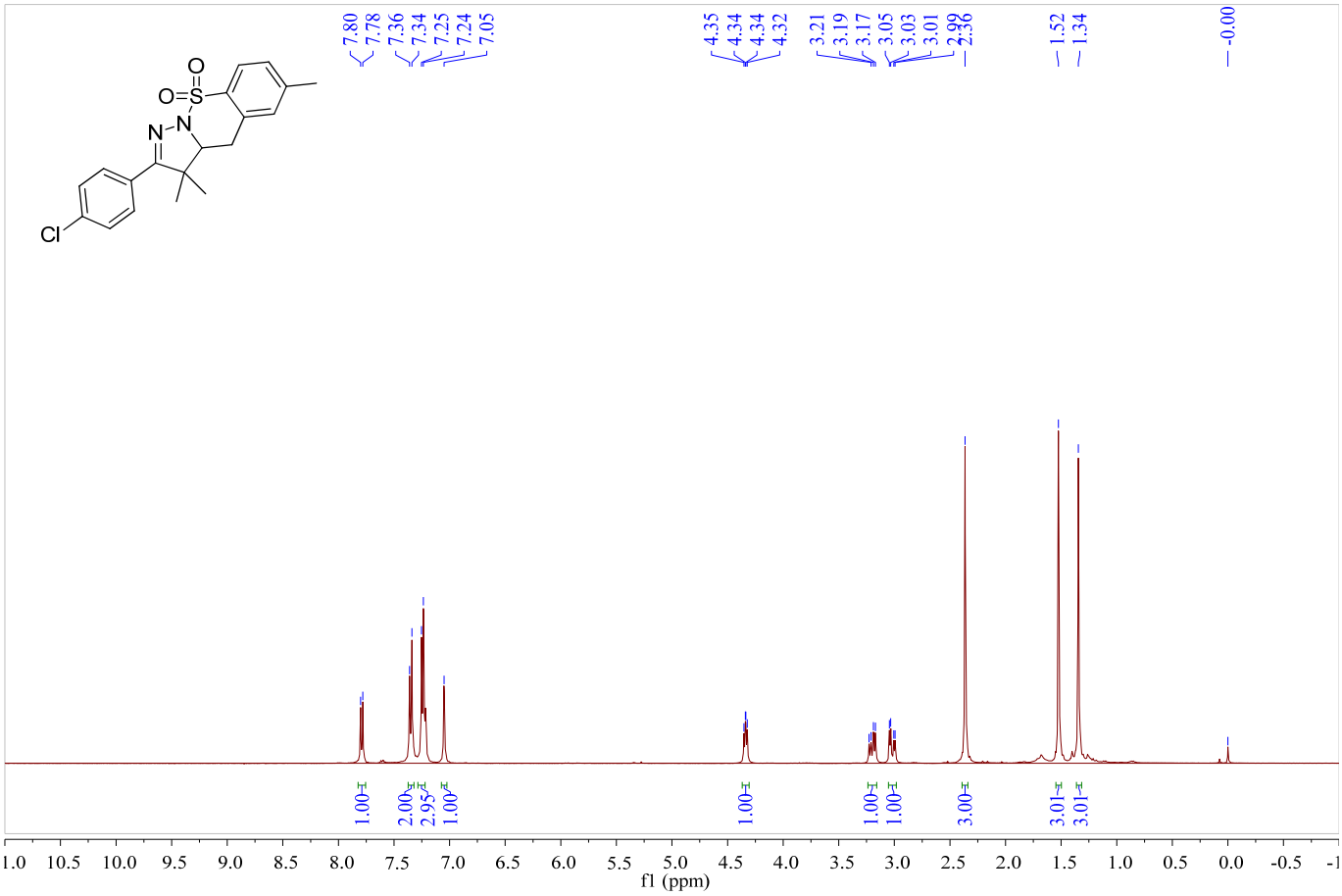


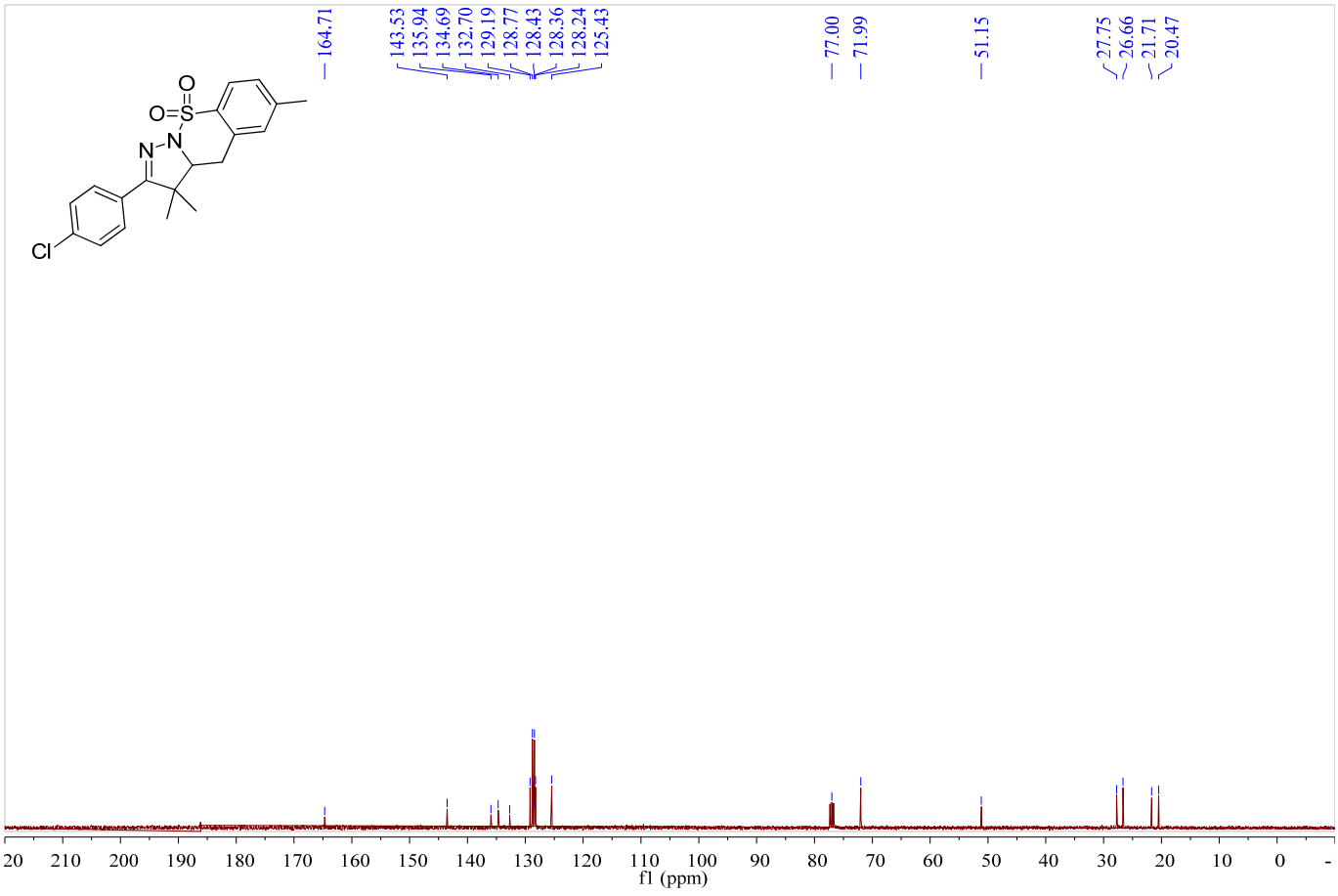
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 2b



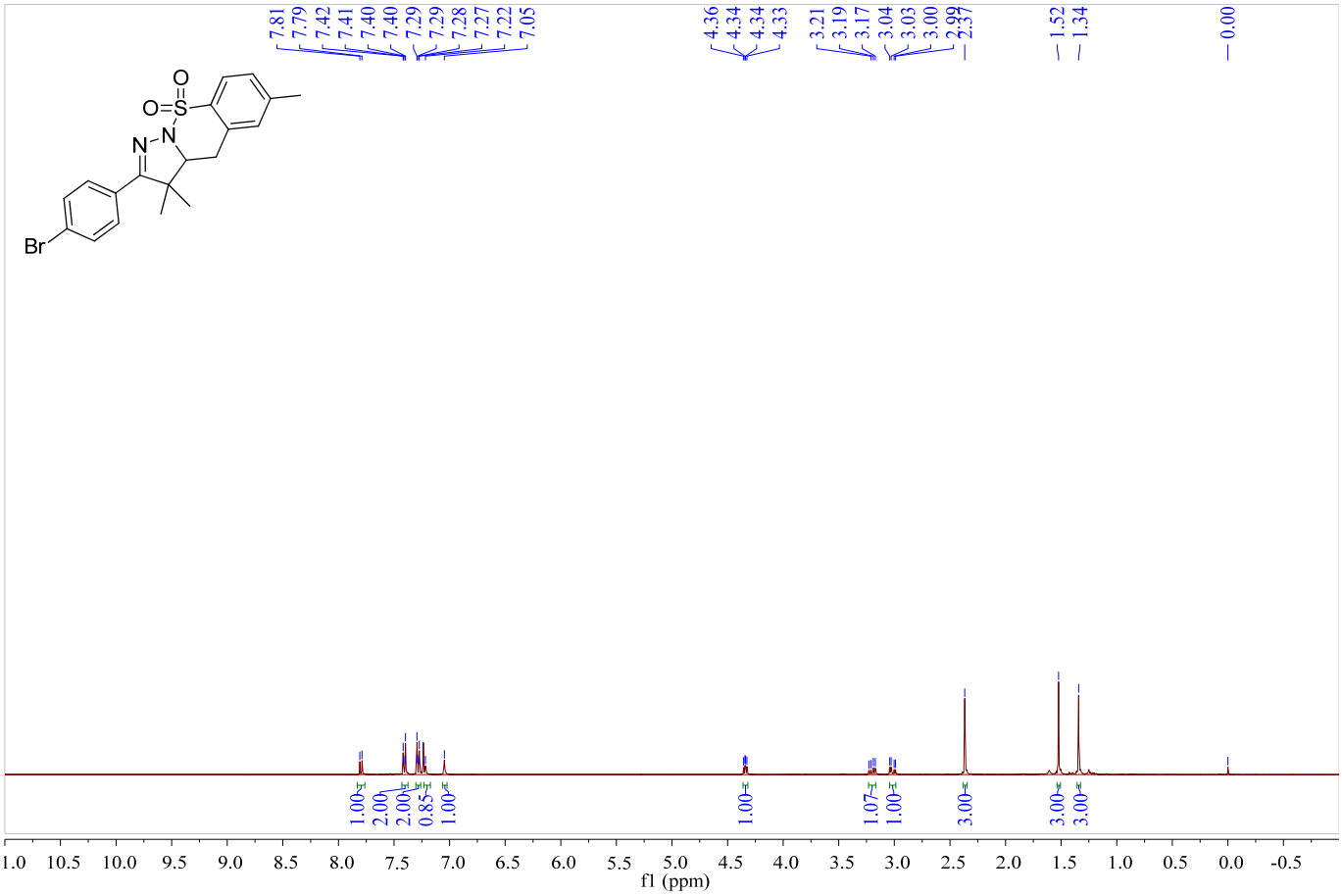


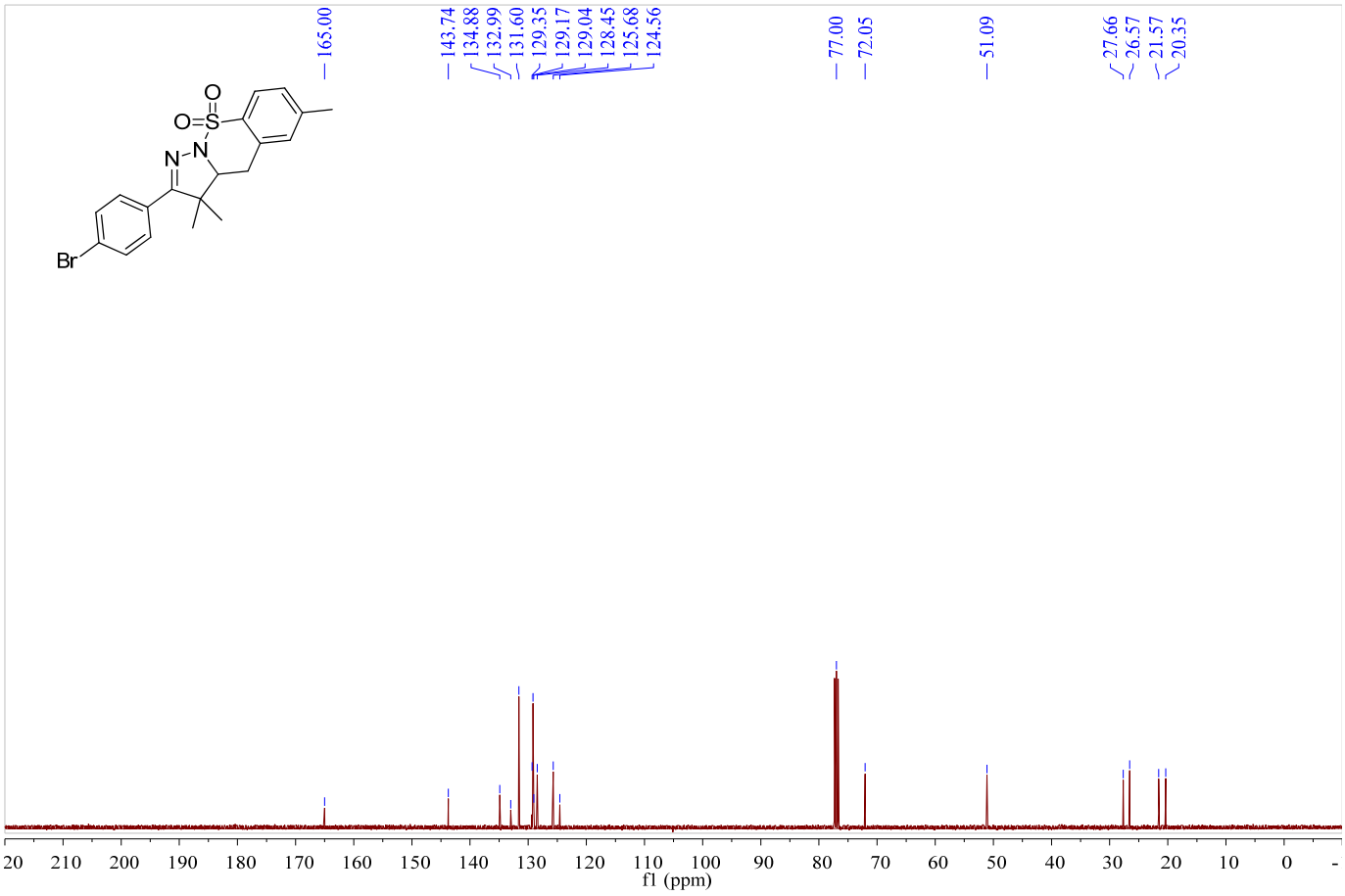
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 2c



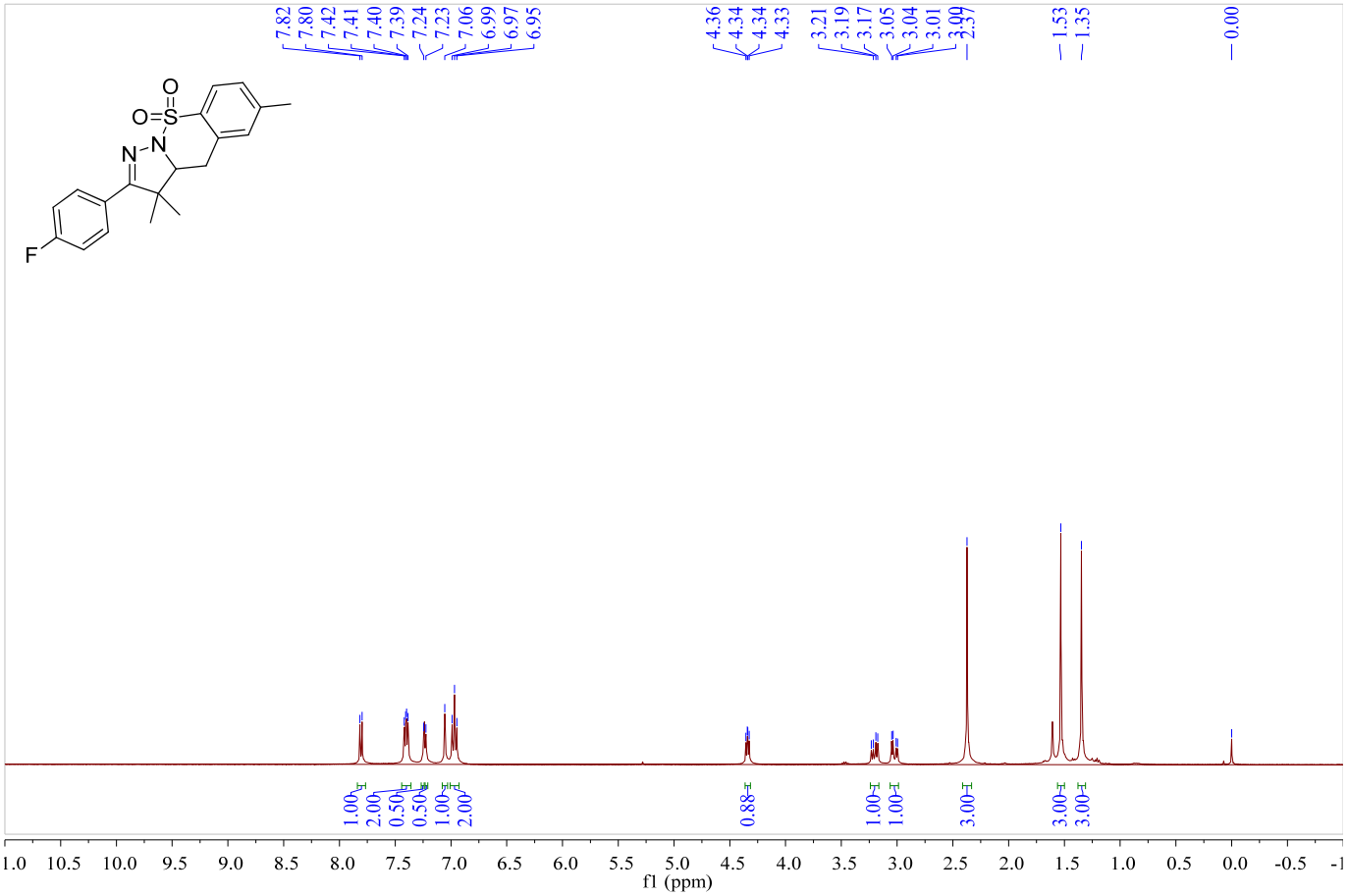


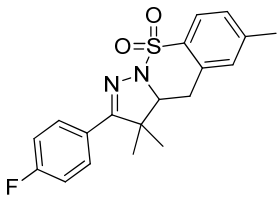
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 2d

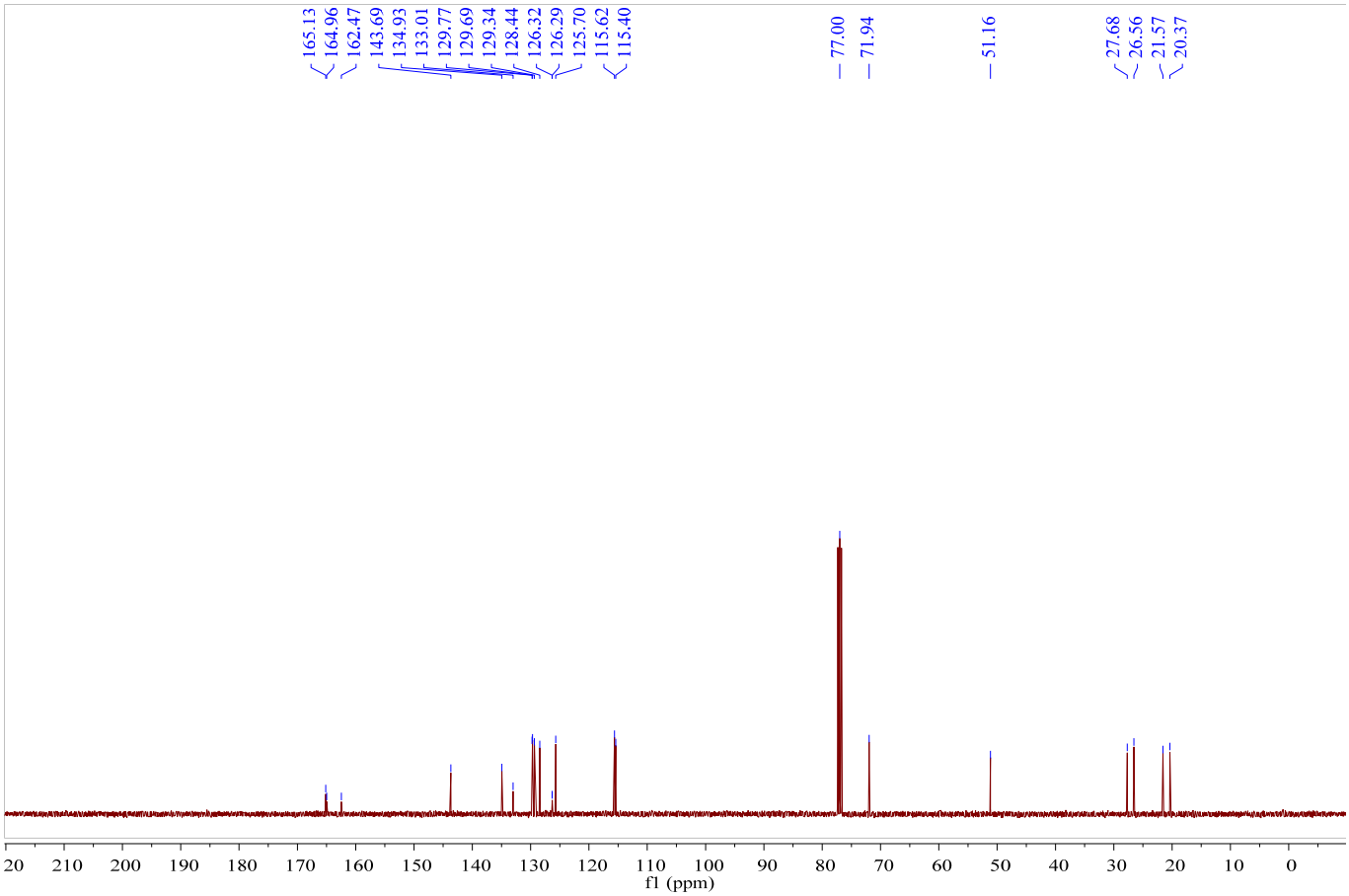




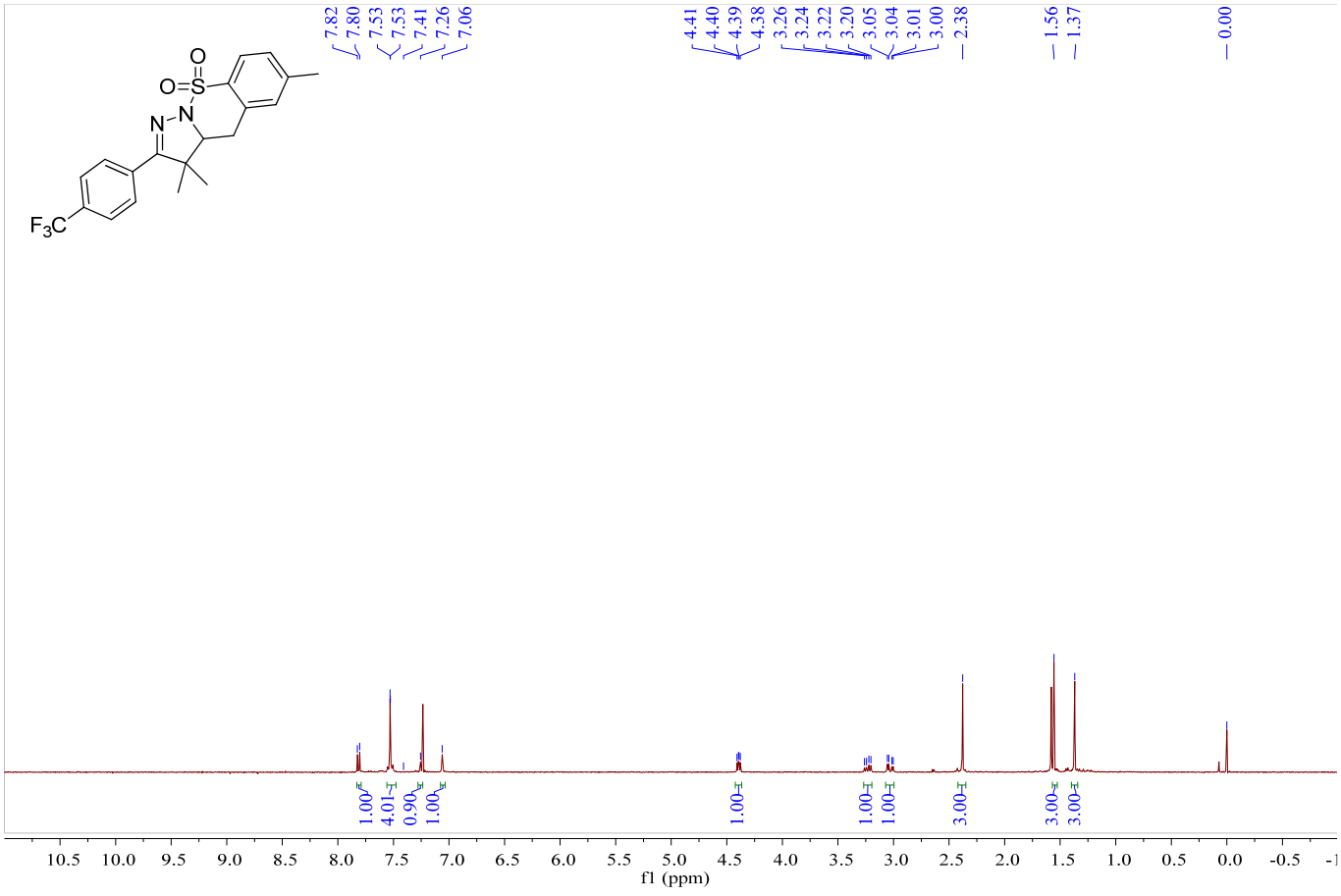
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 2e

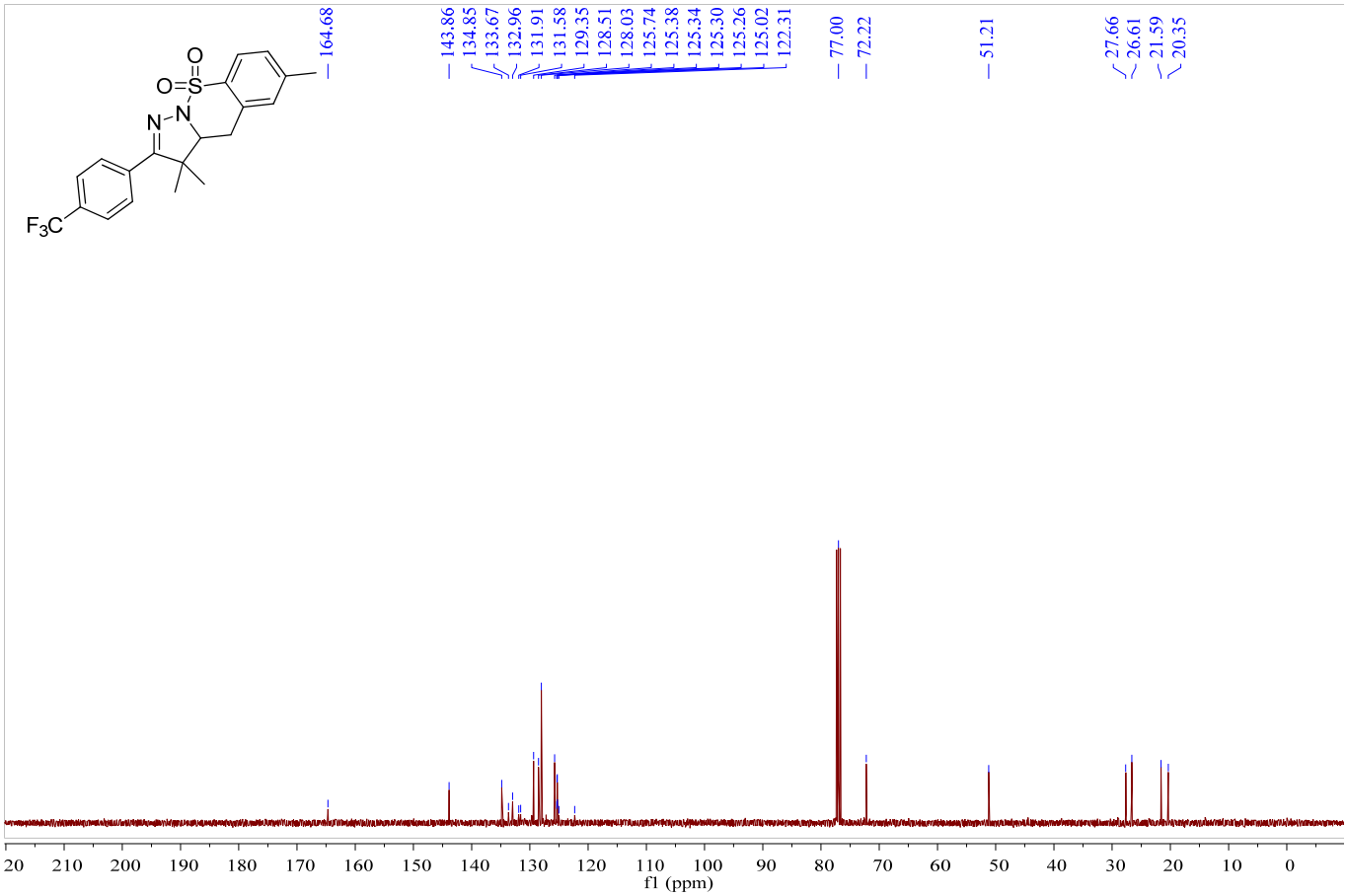




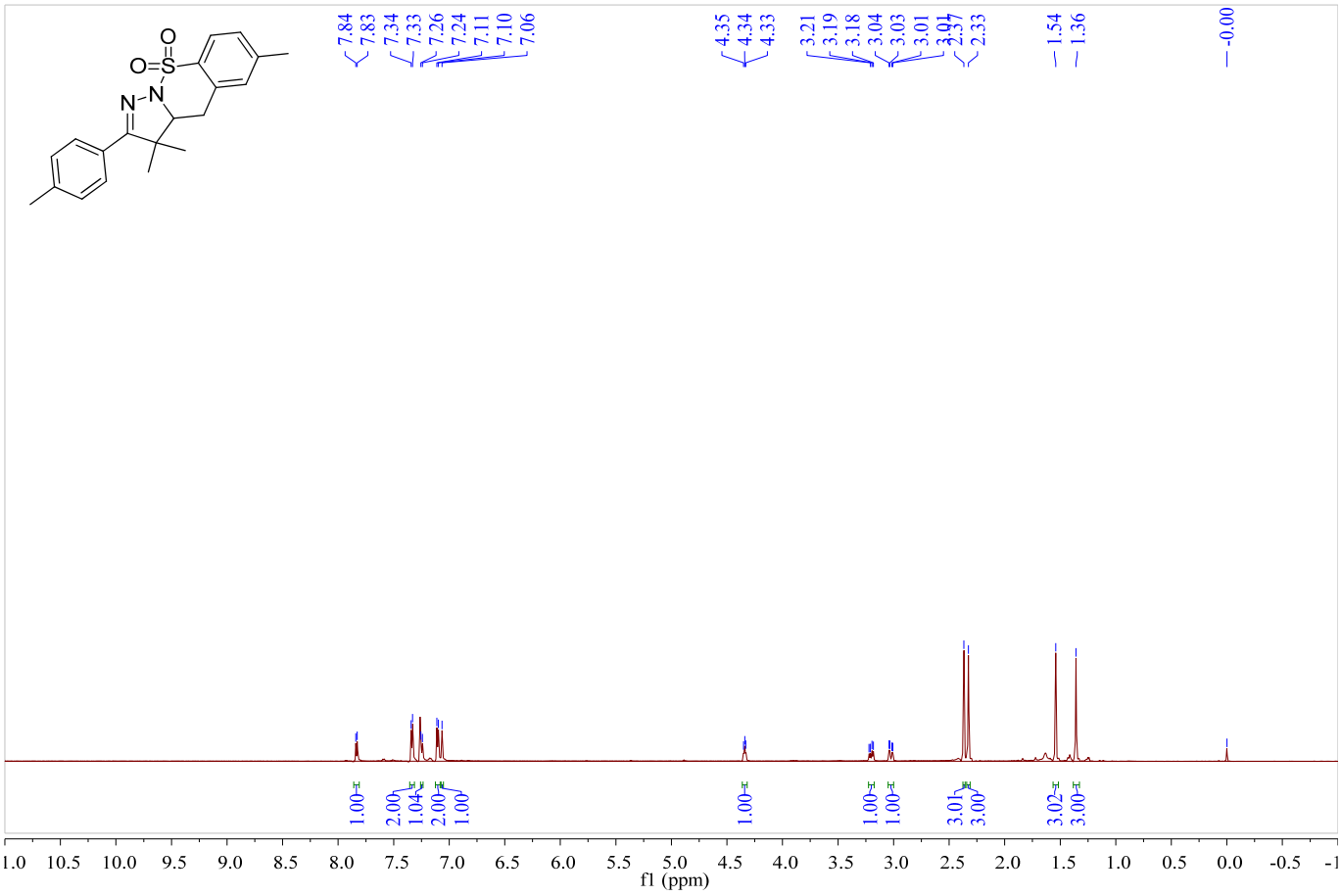


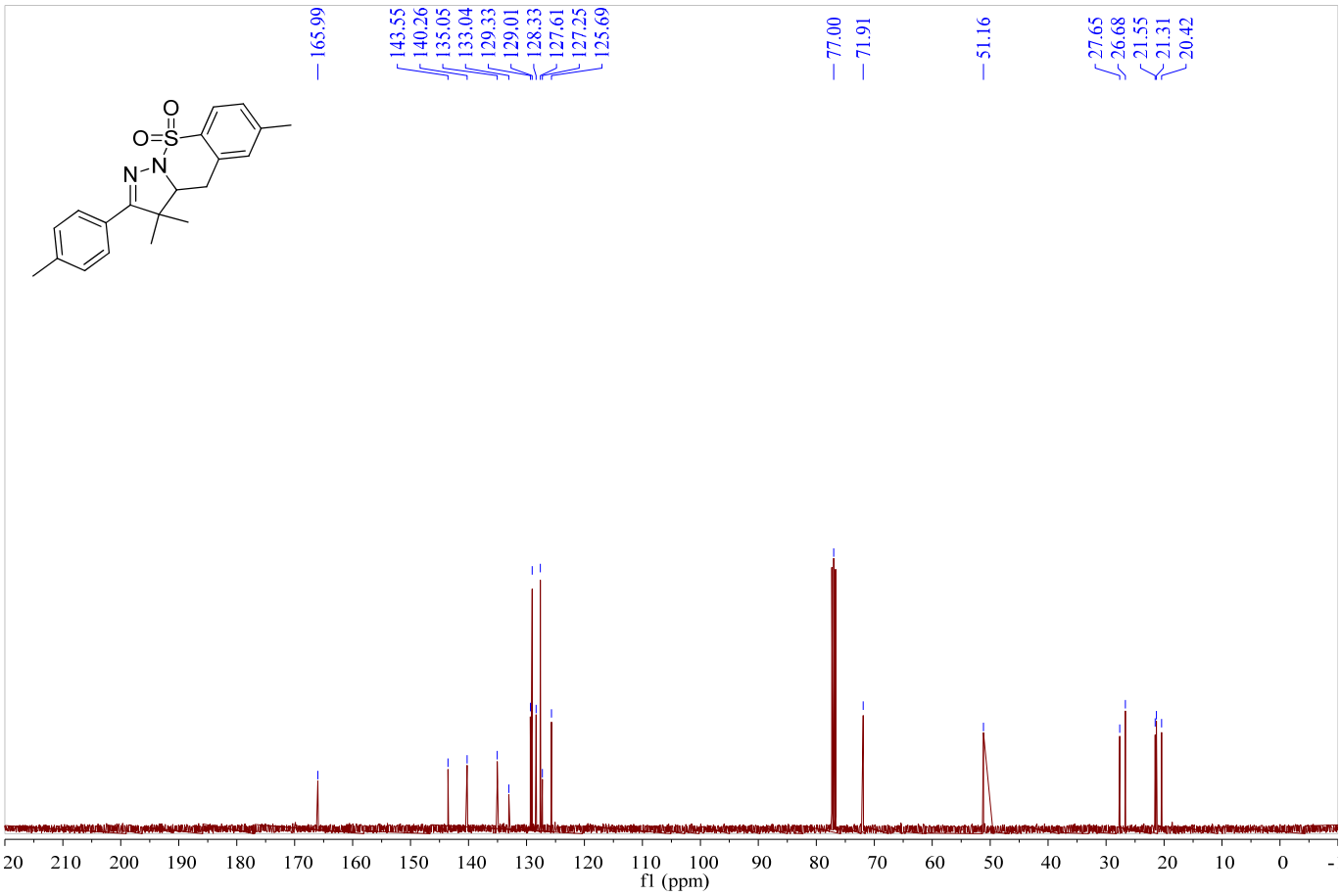
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 2f



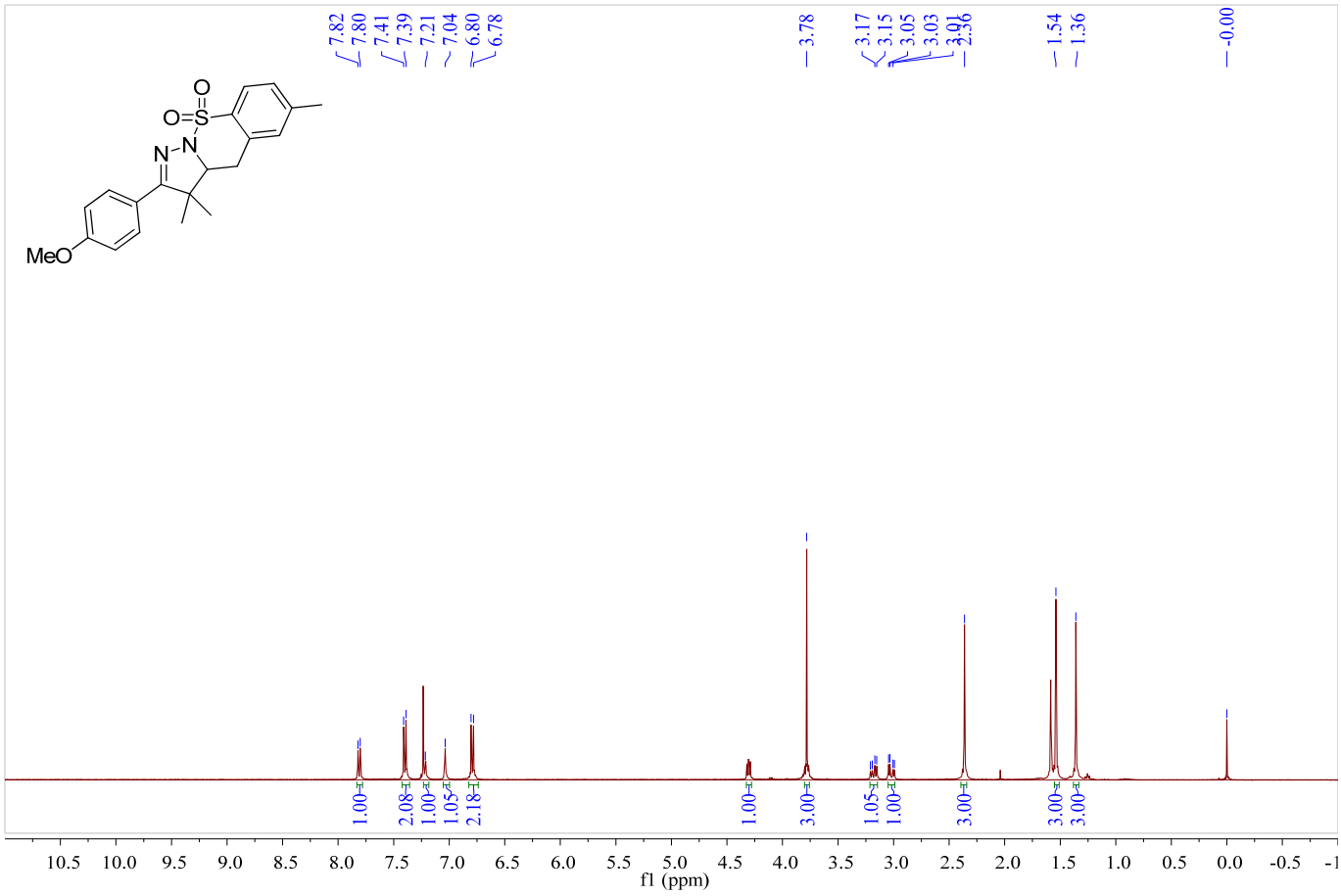


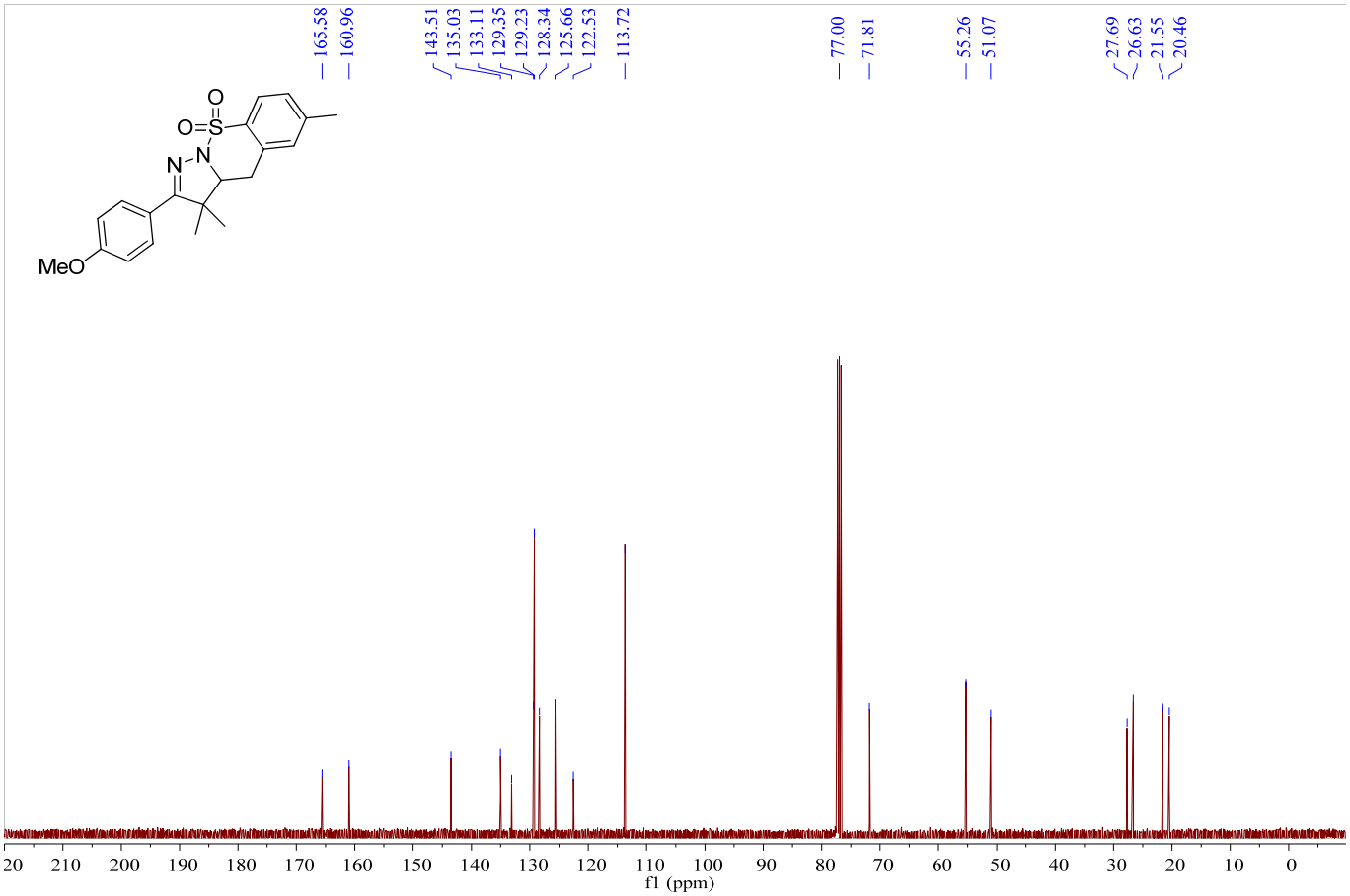
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 2g



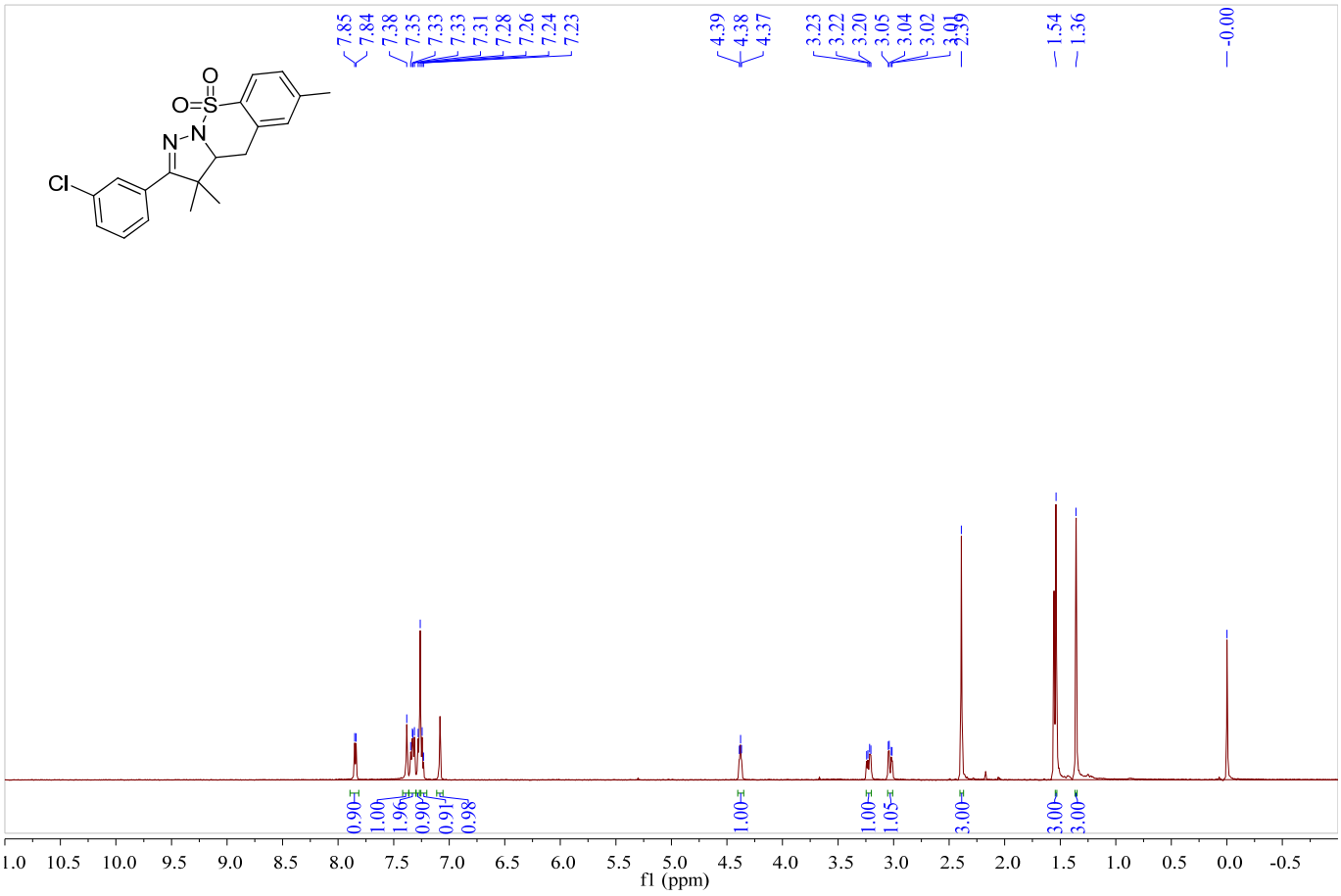


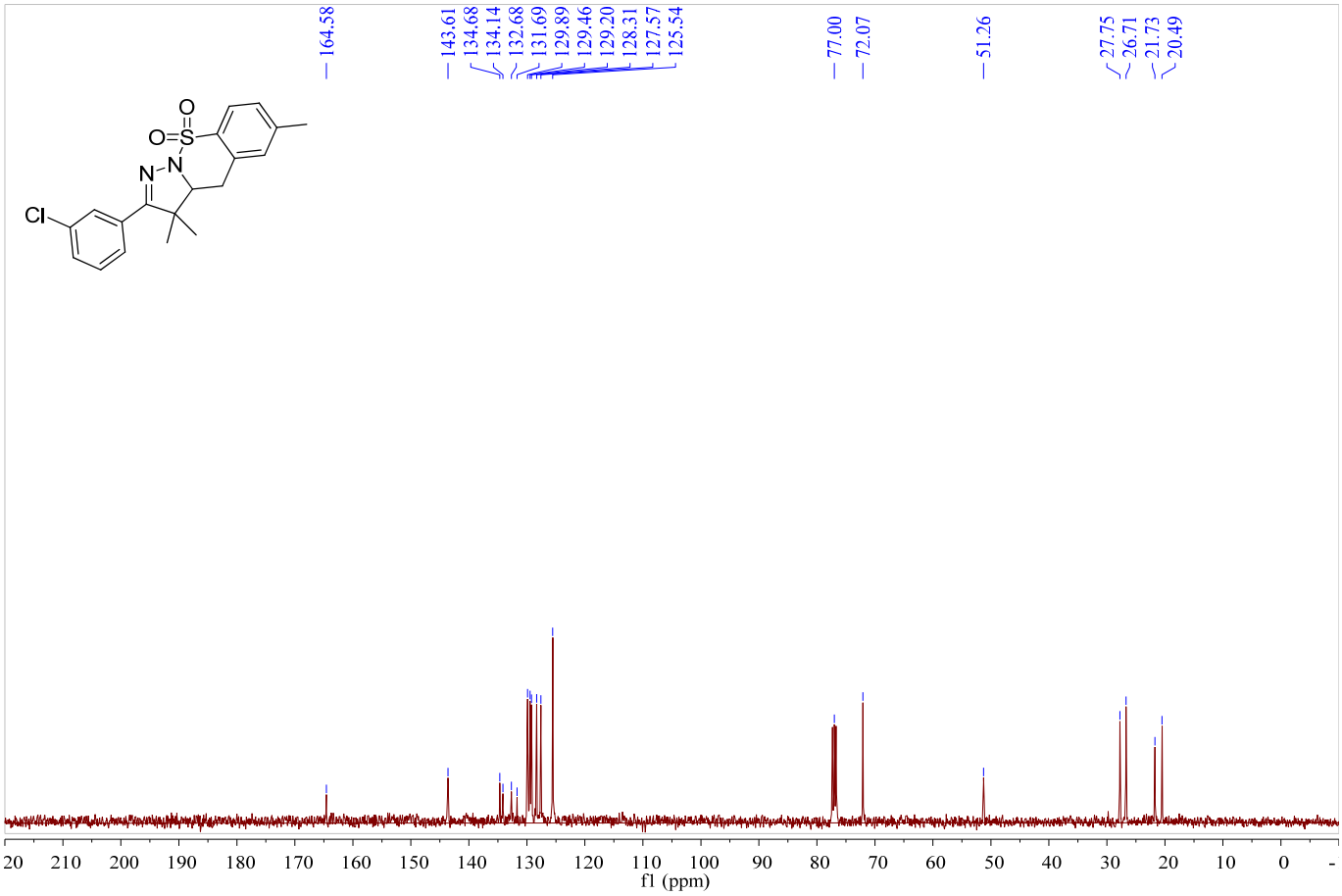
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 2h



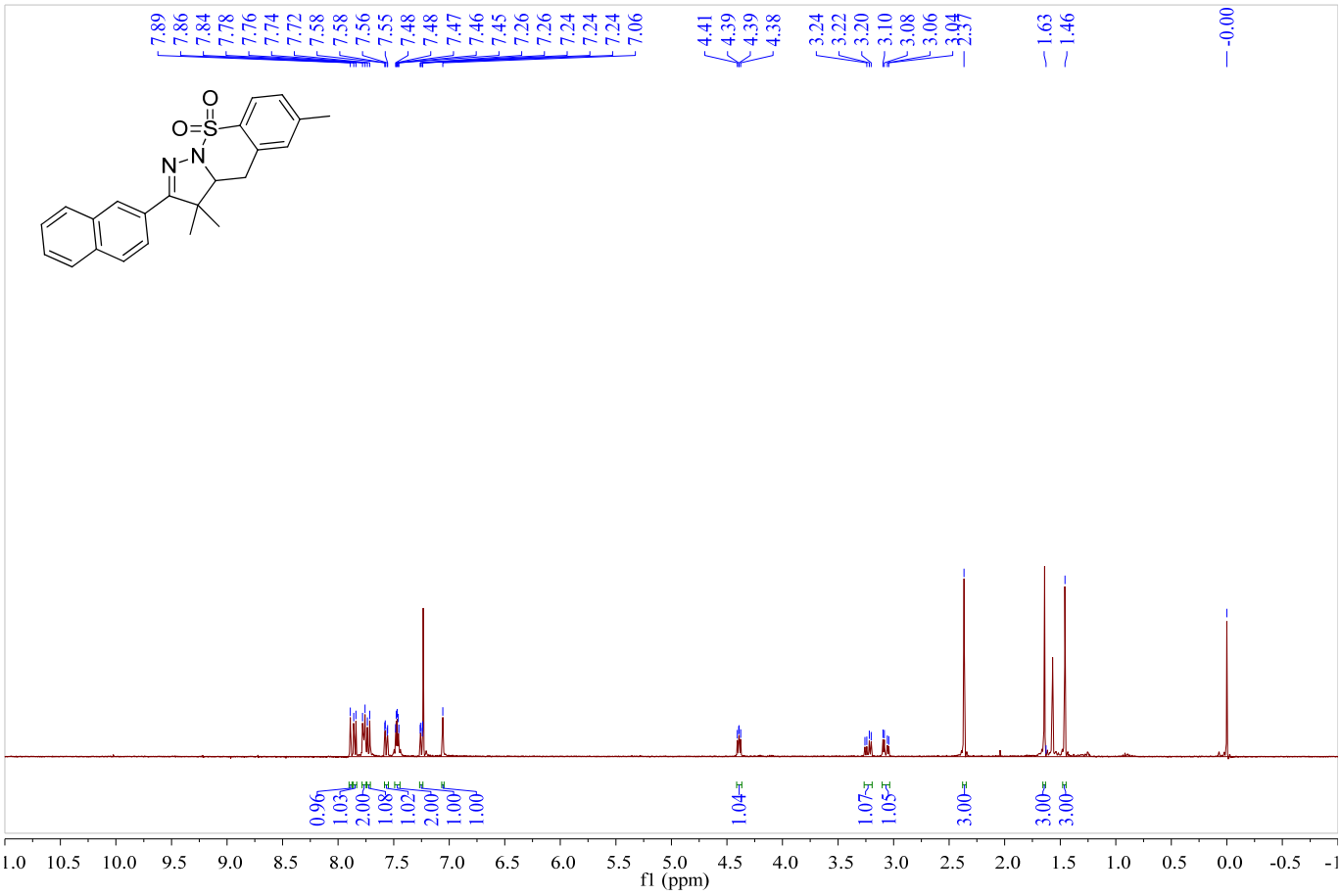


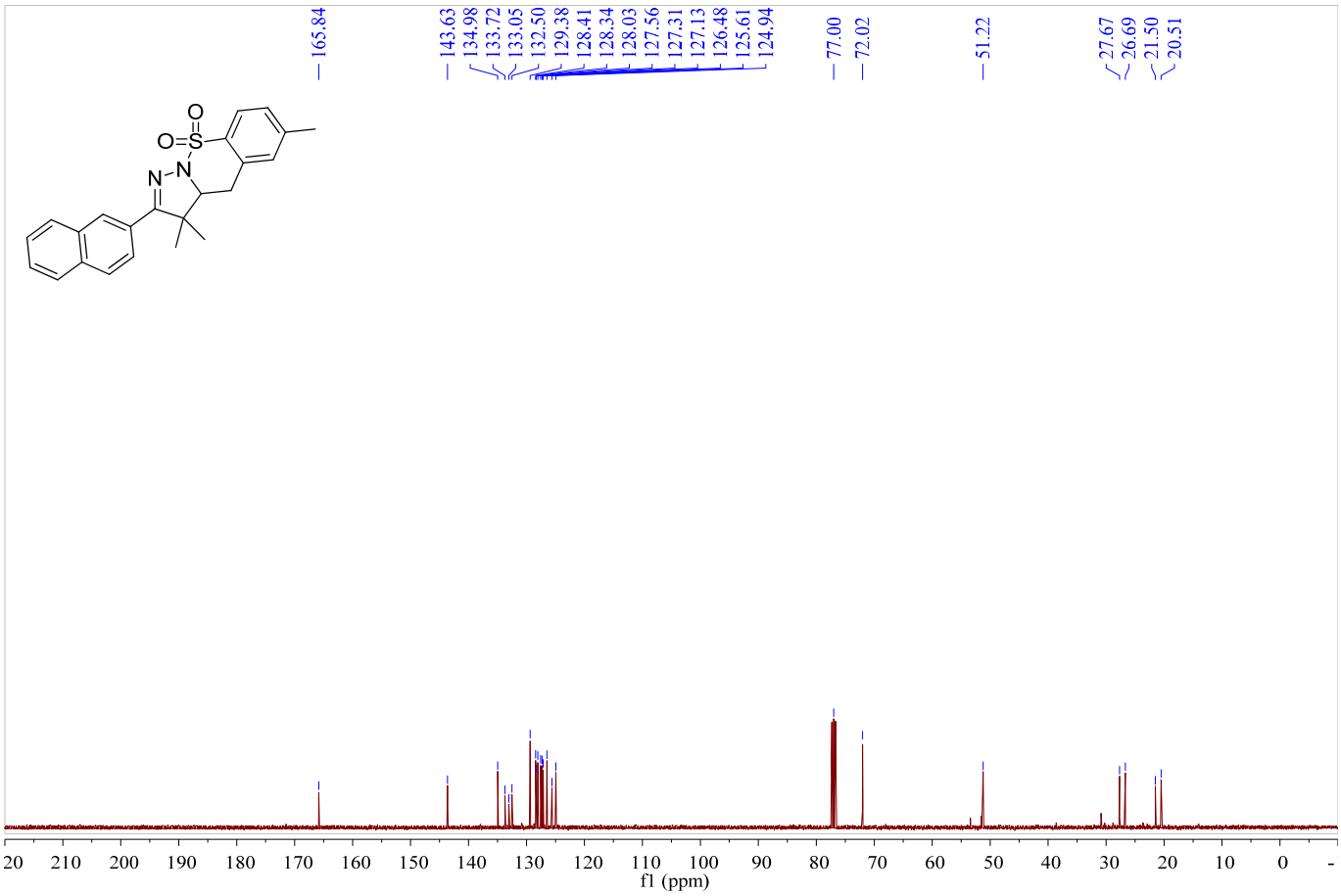
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of product 2i



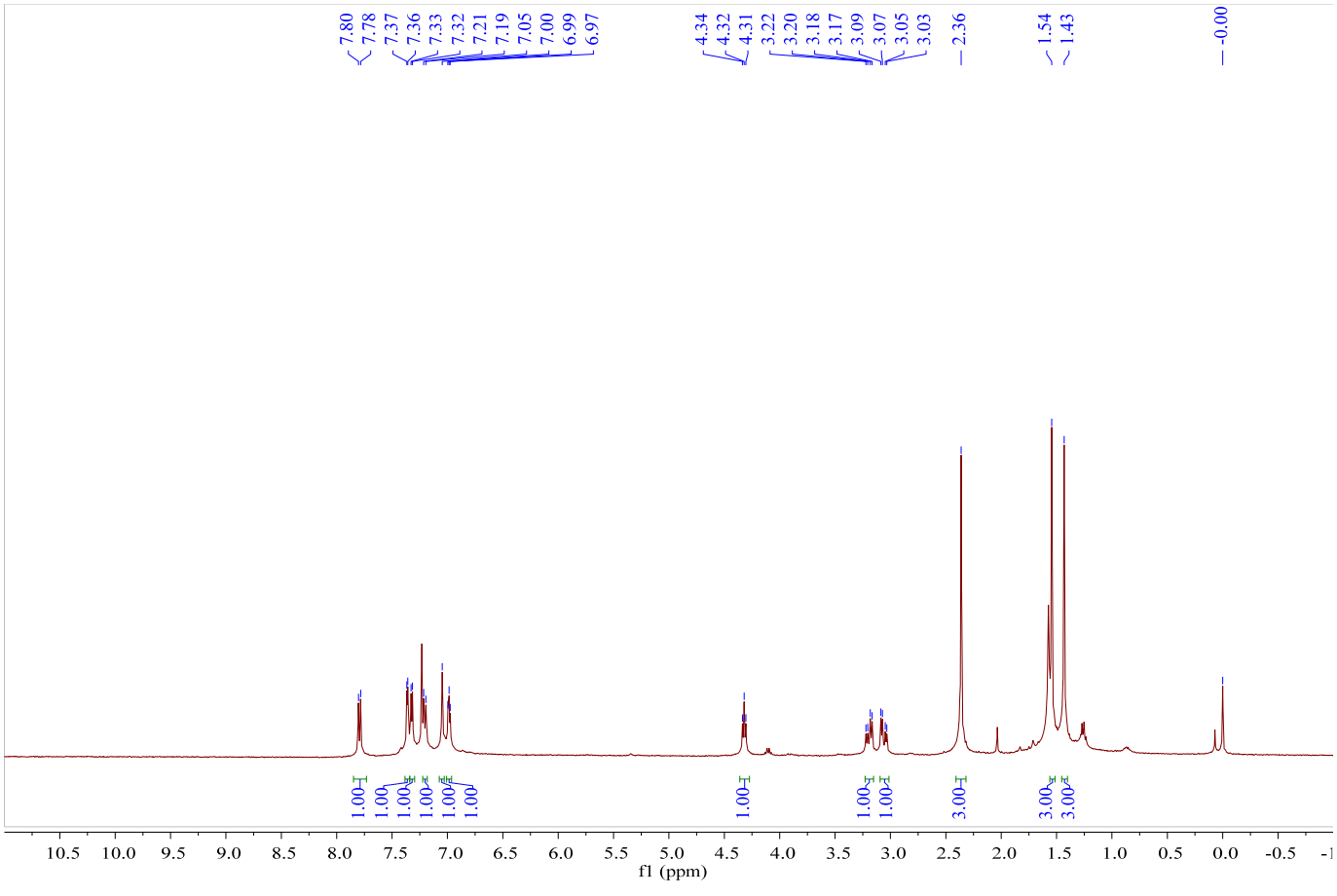


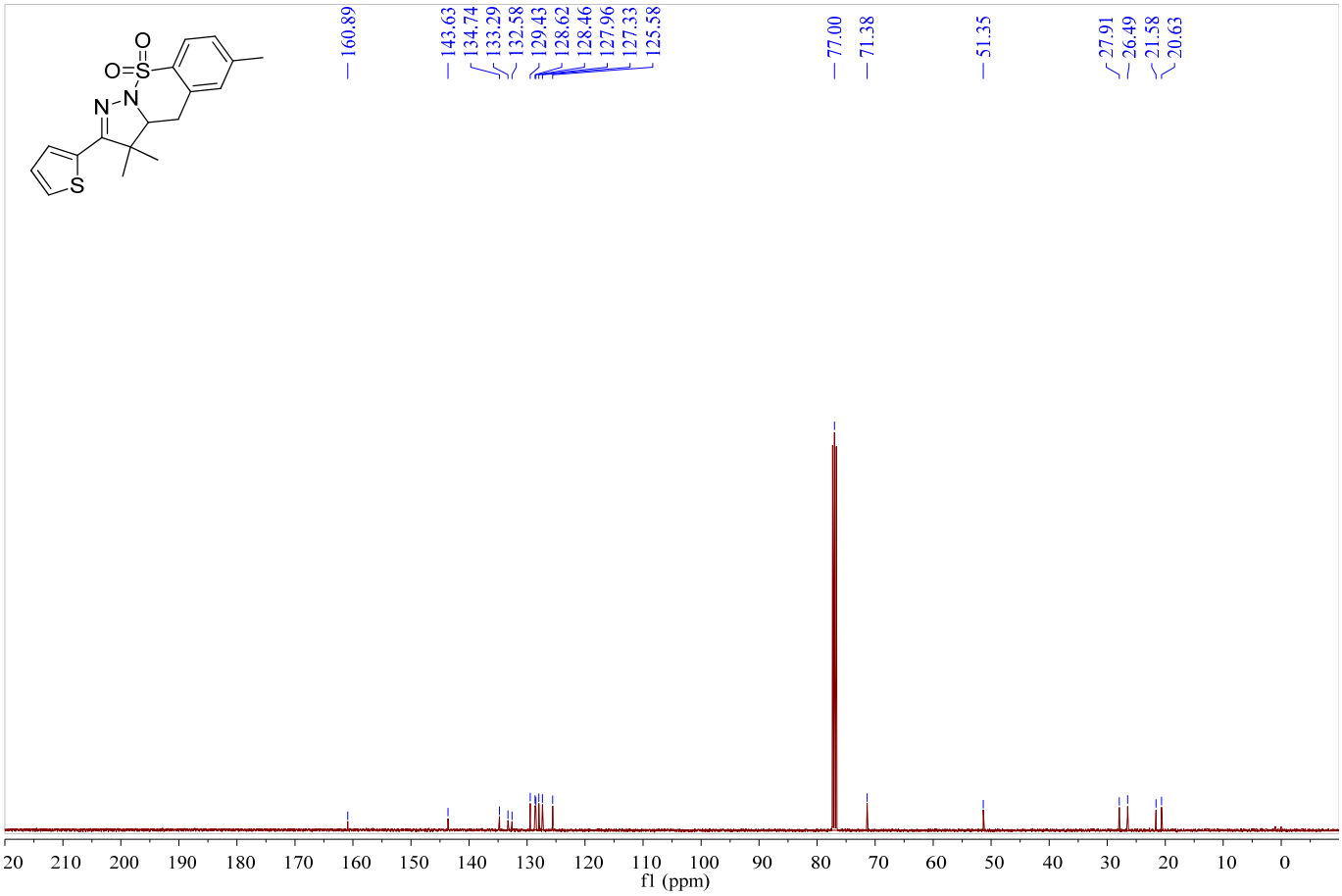
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of product 2j



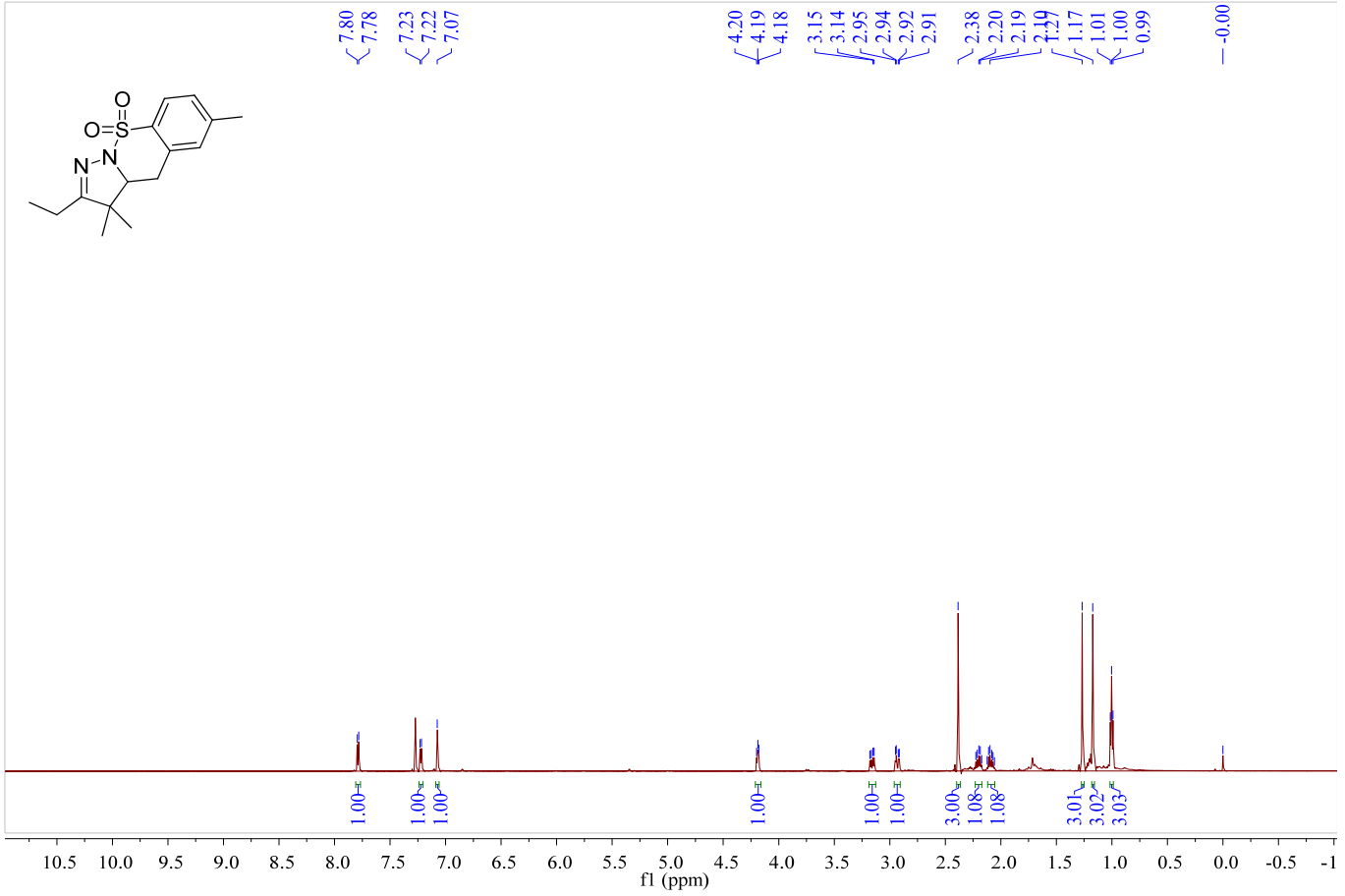


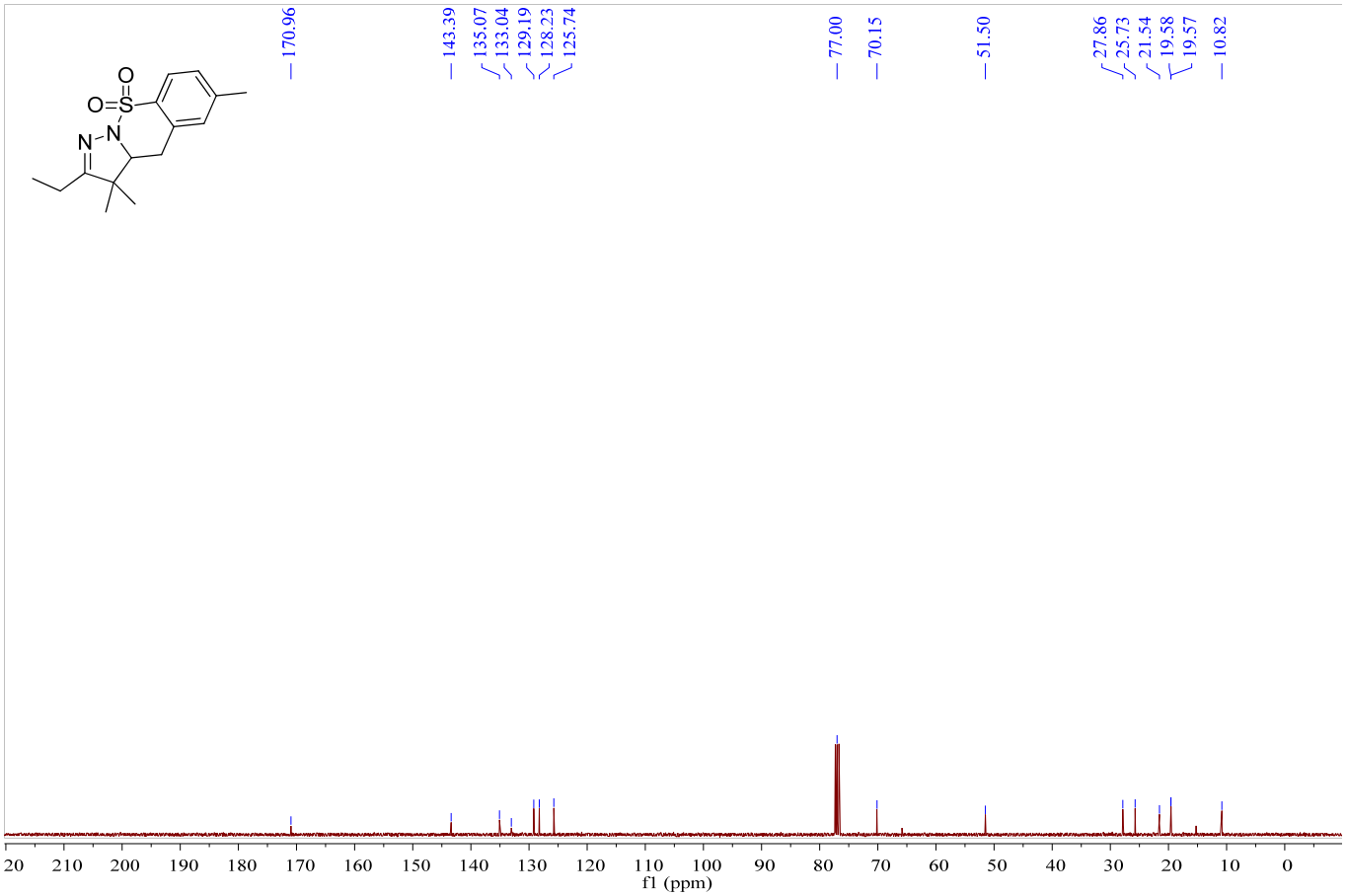
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 2k



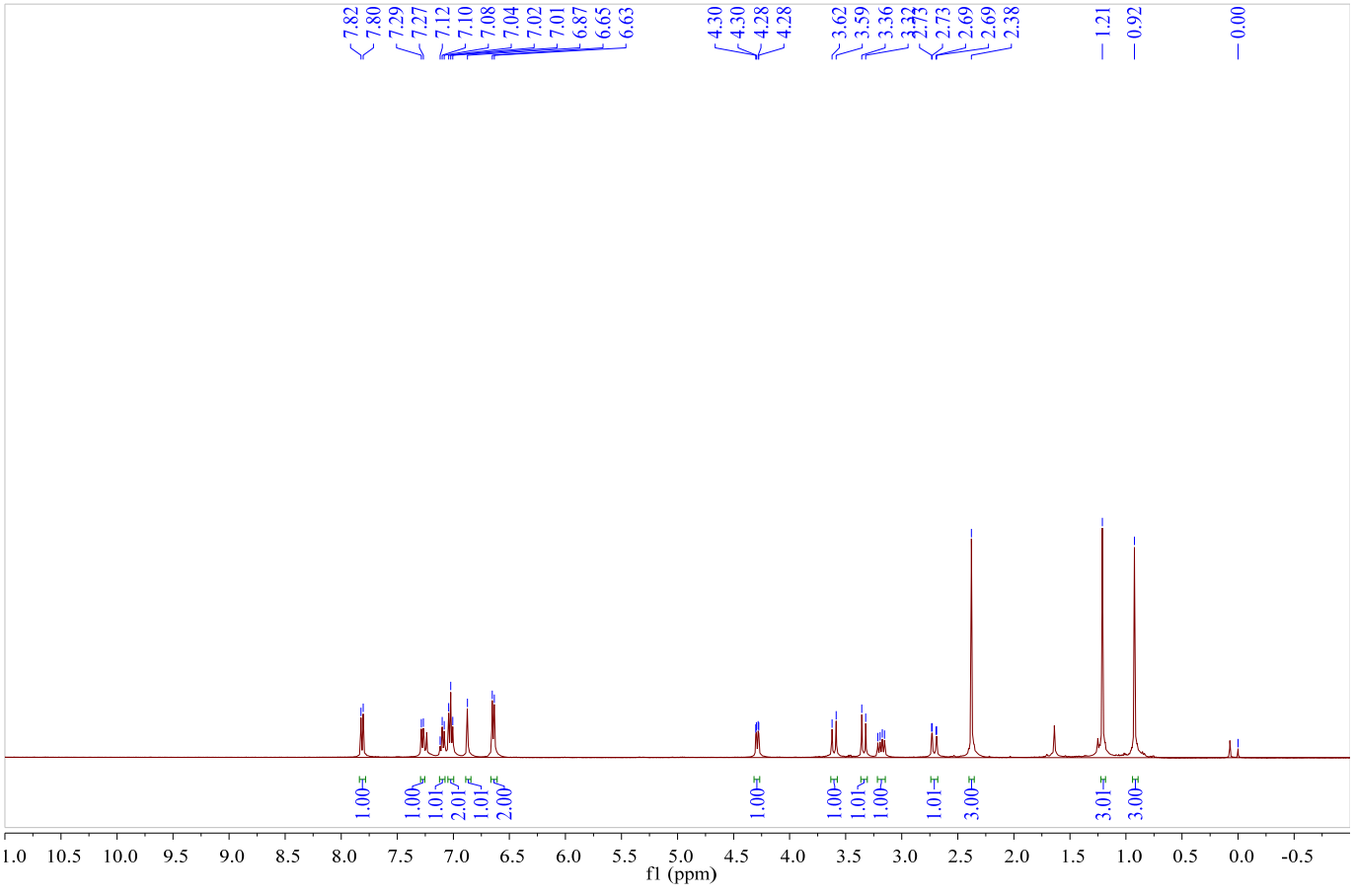


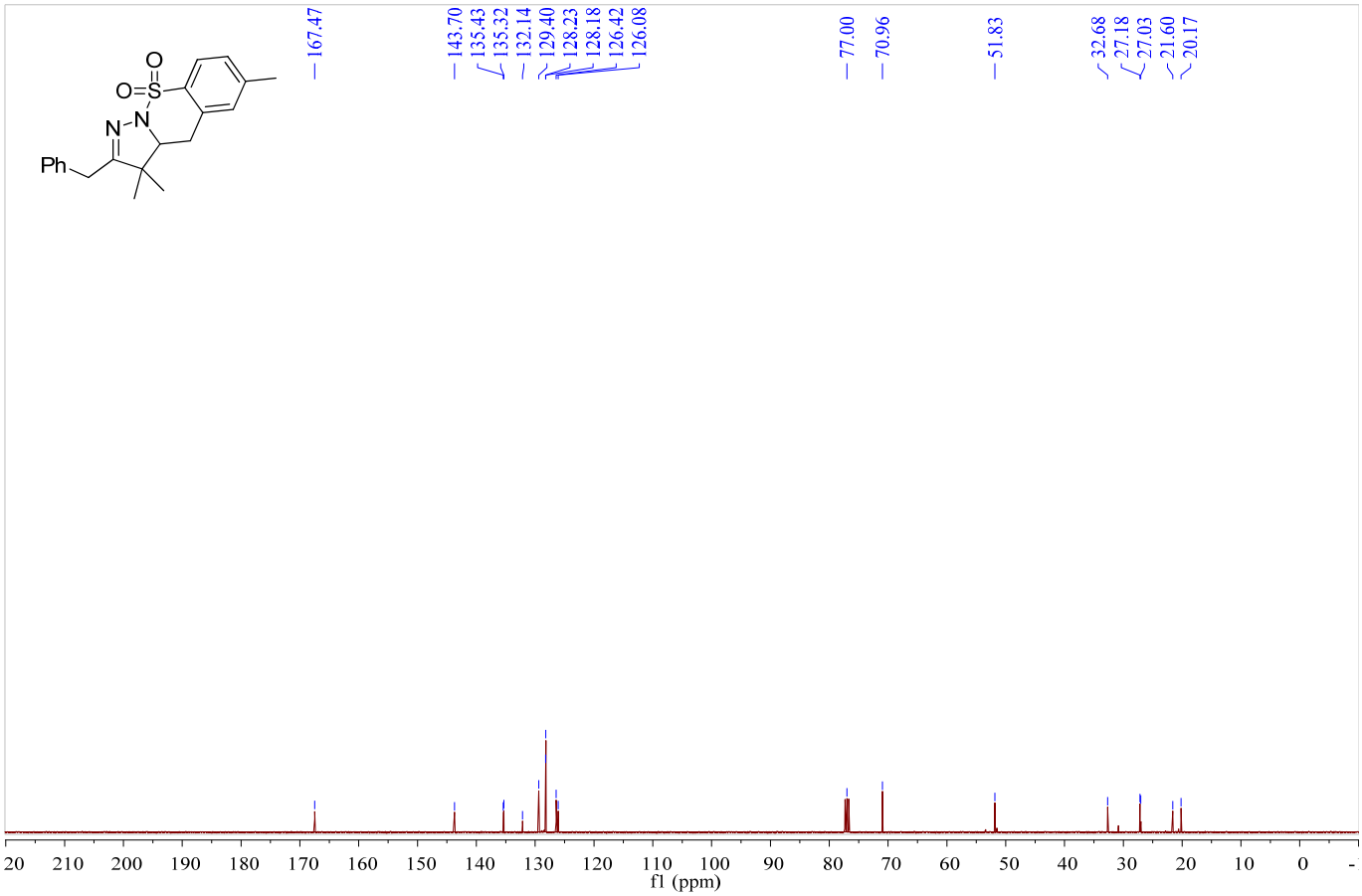
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 2l



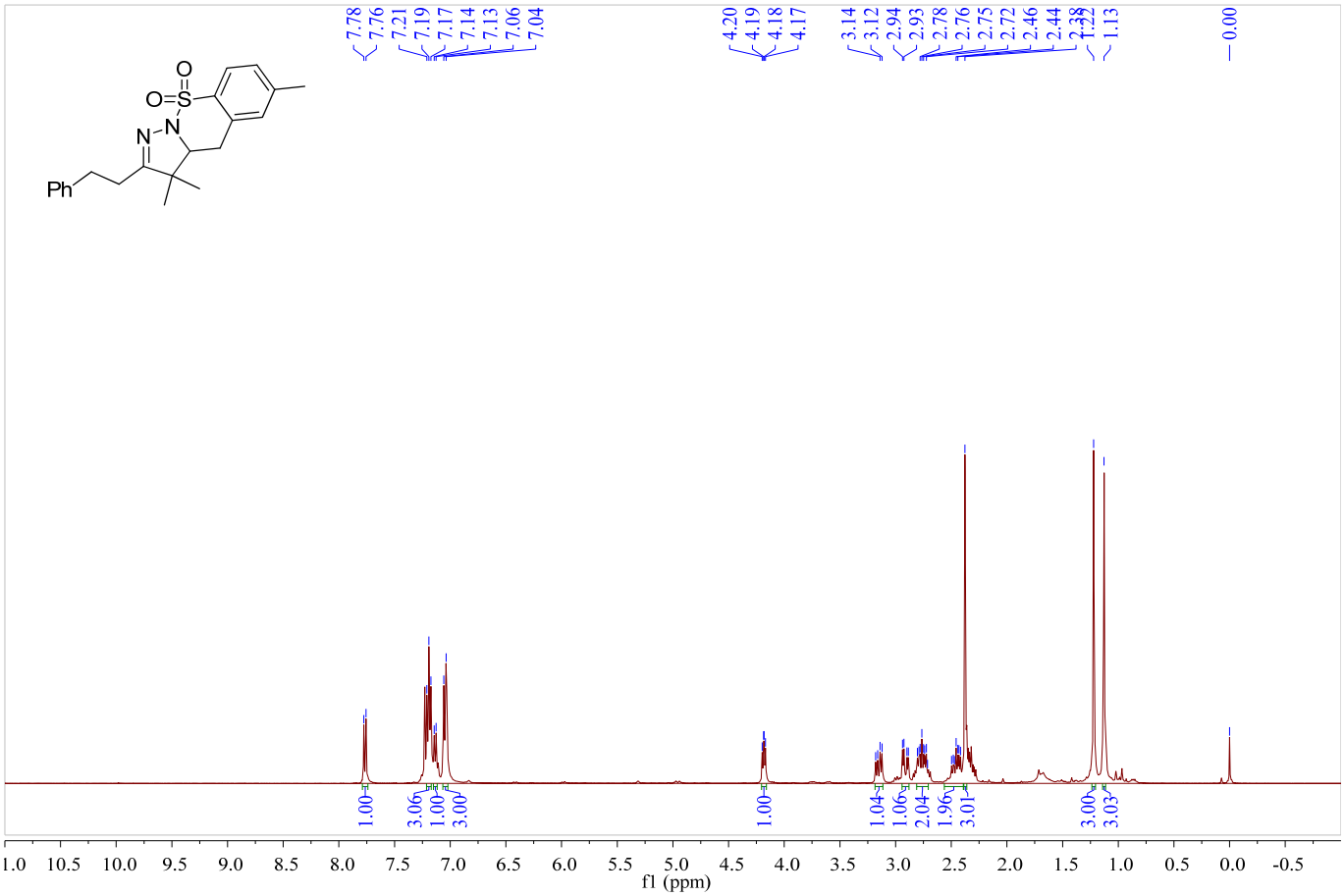


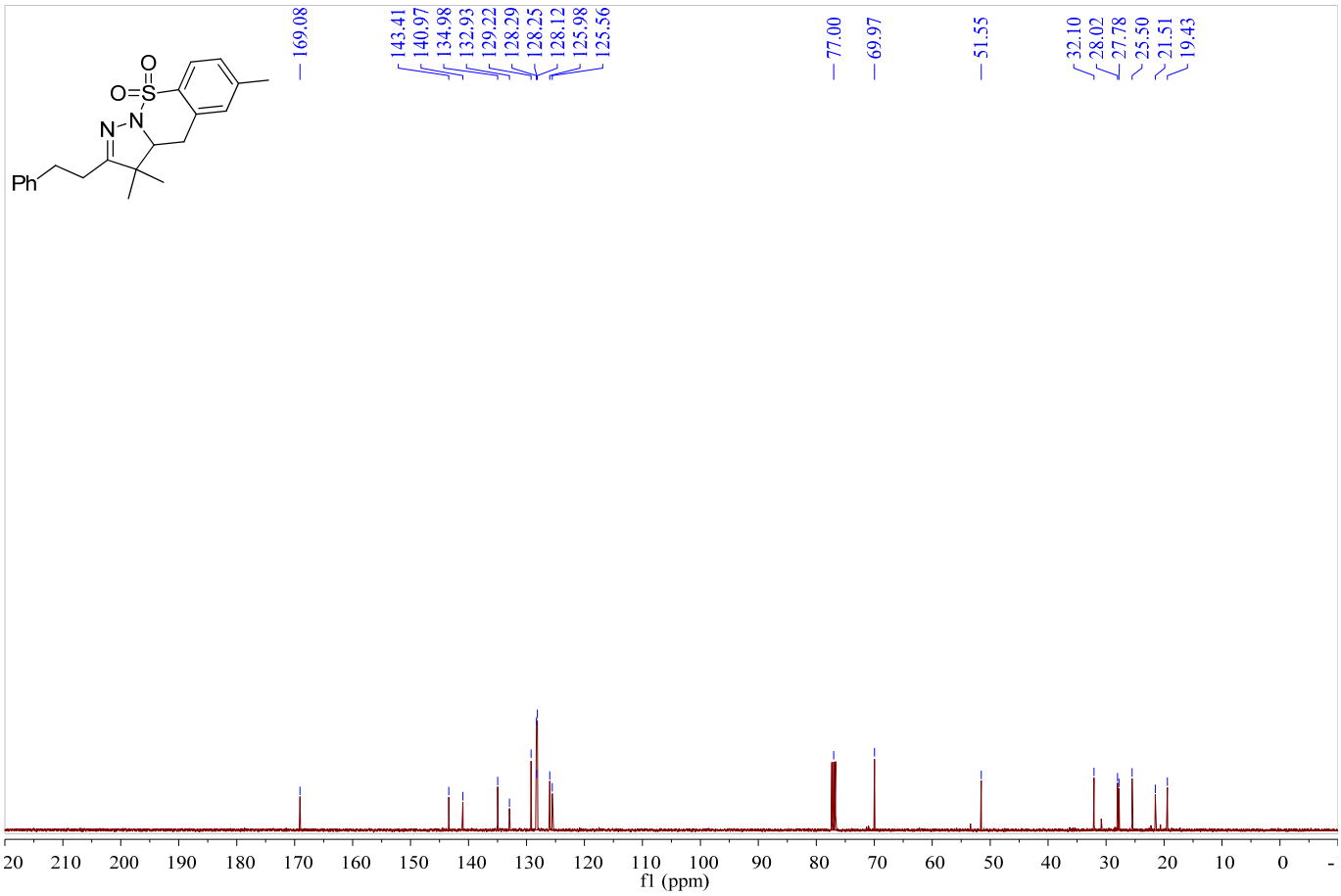
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 2m



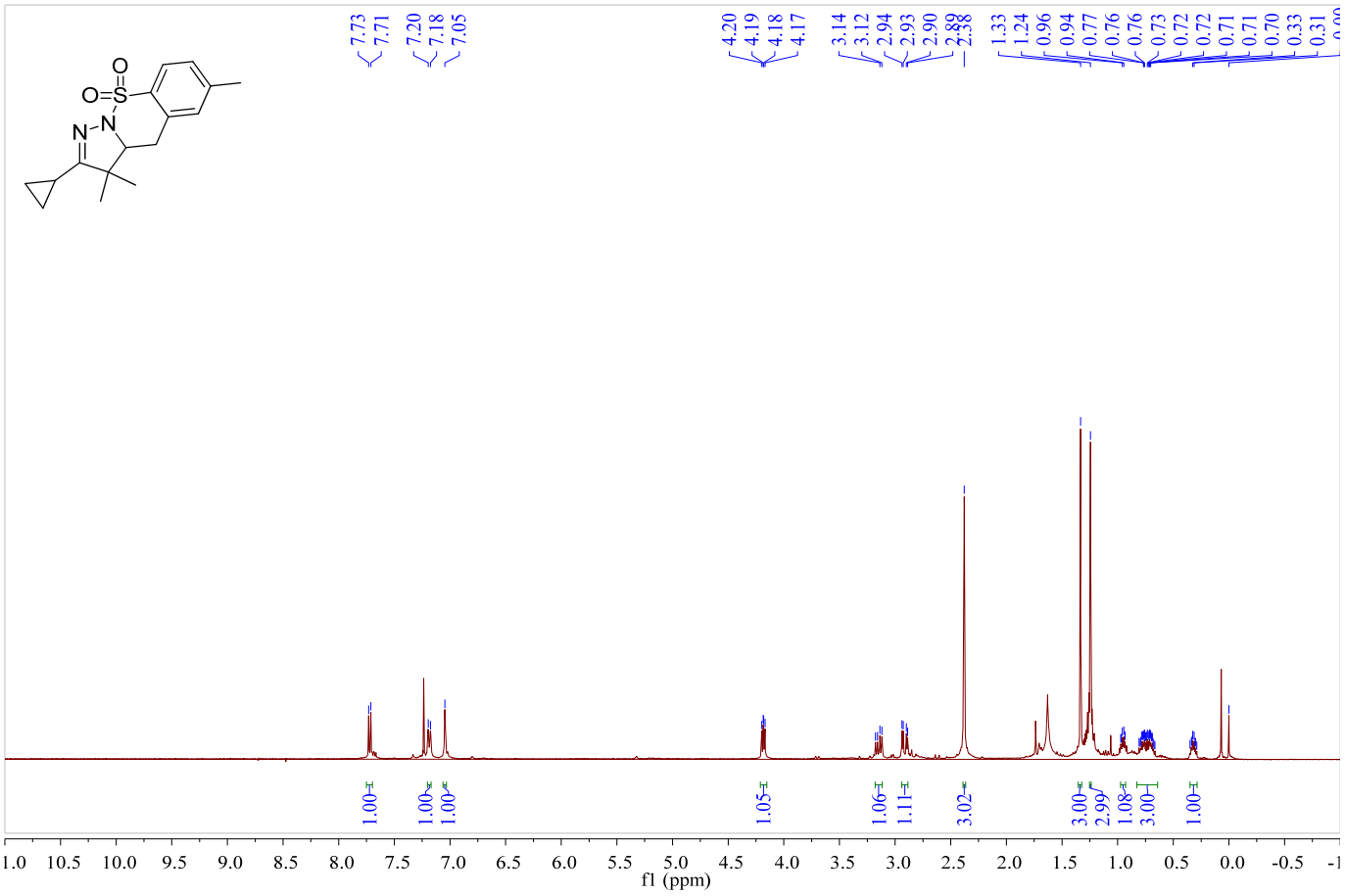


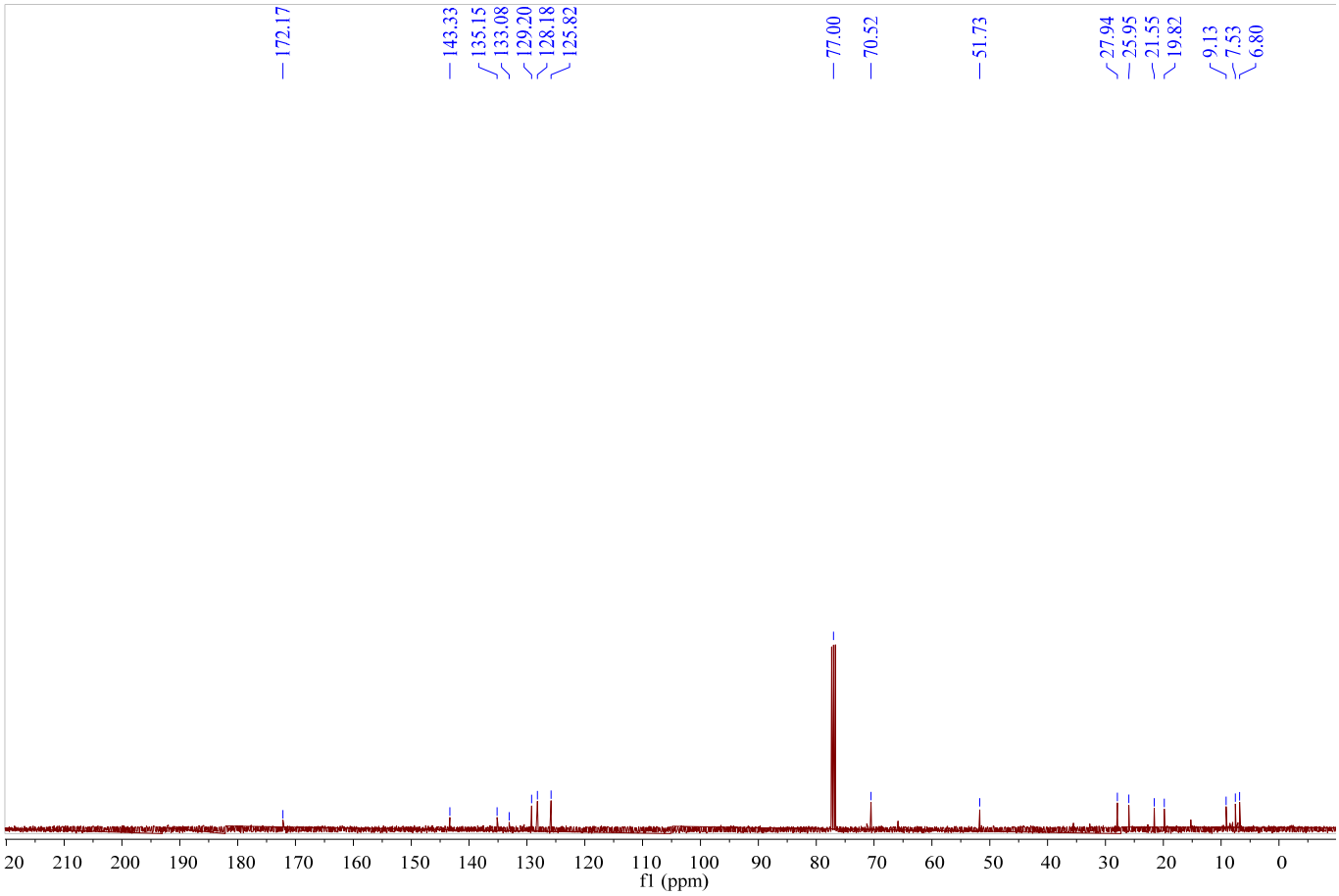
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 2n



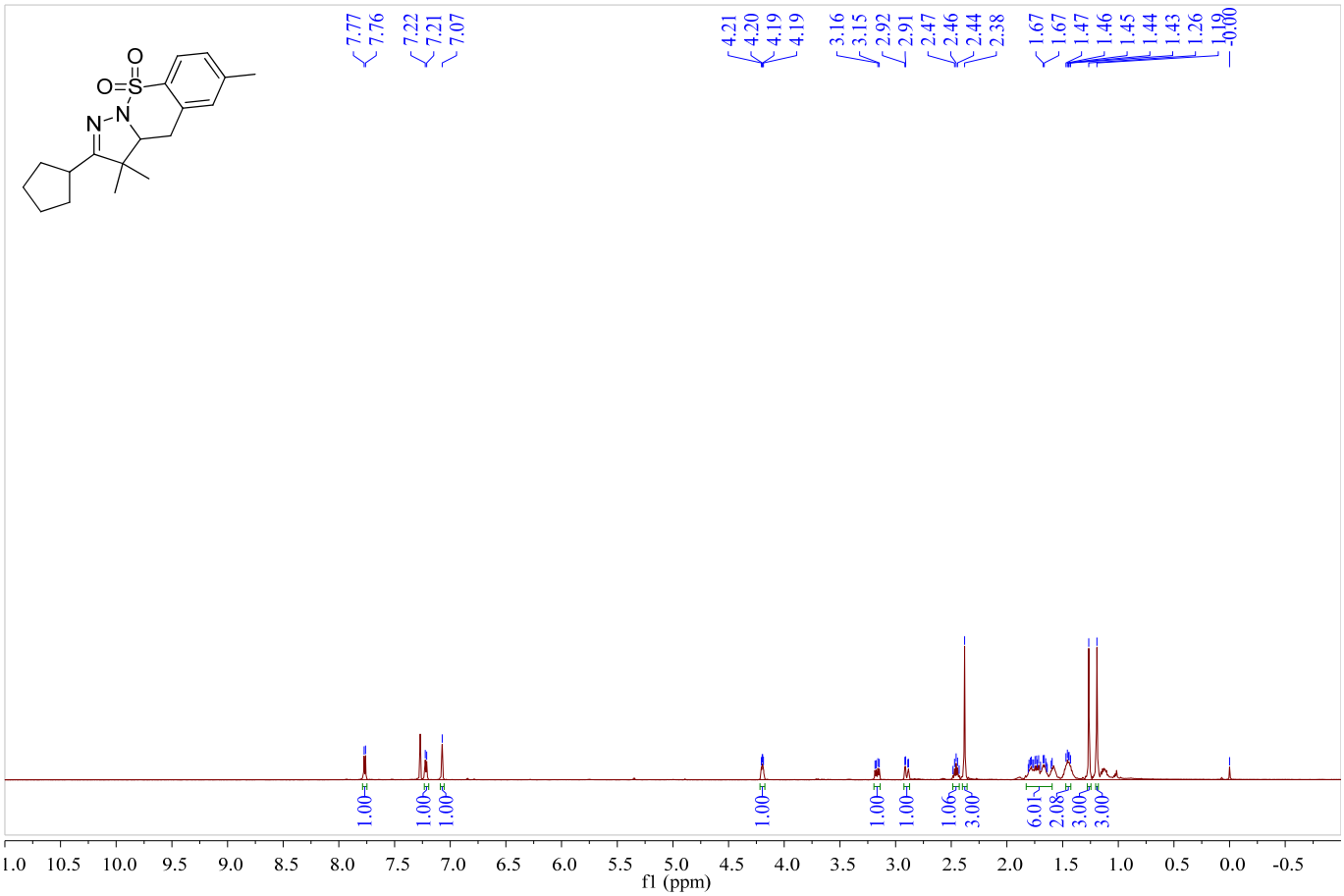


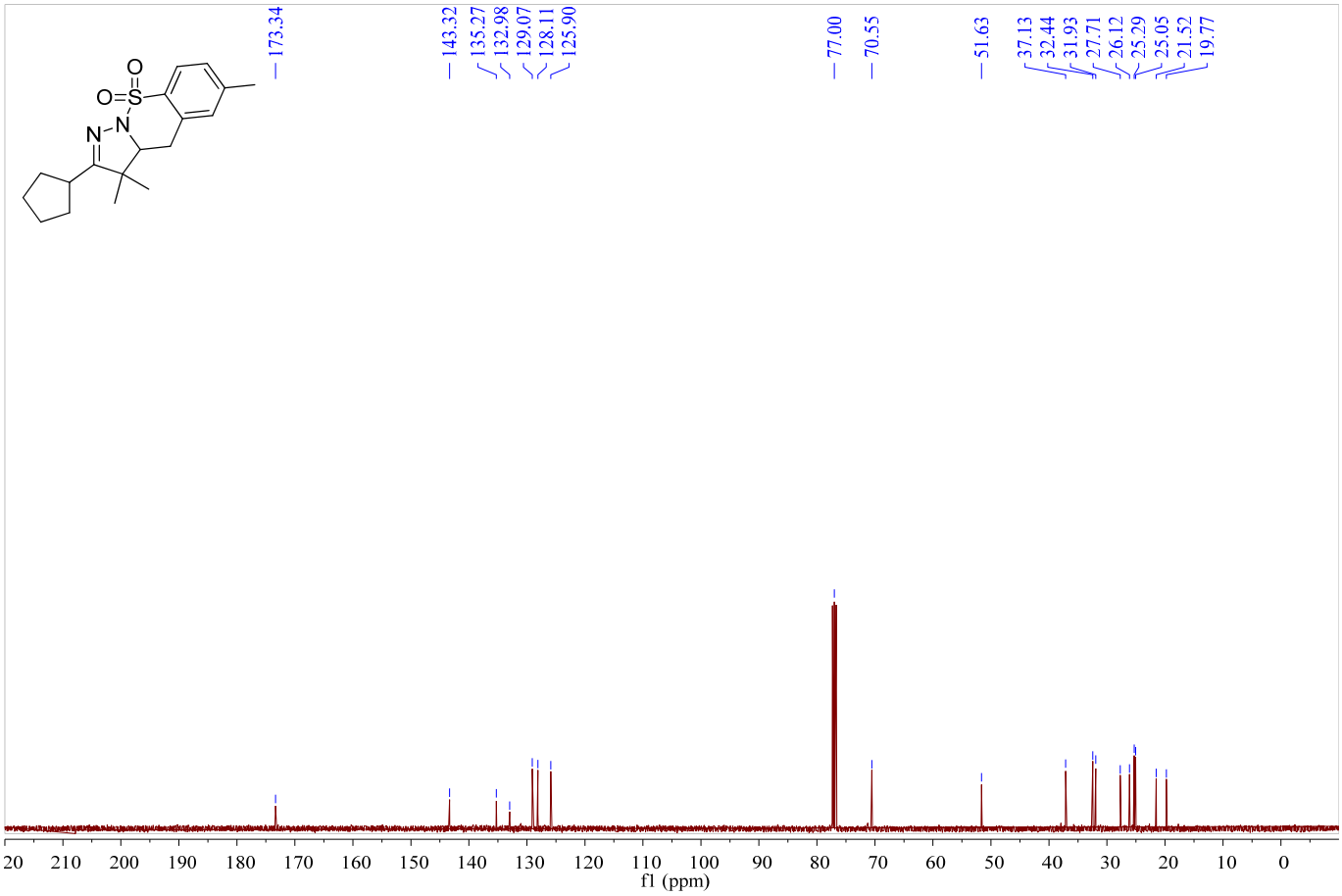
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 2o



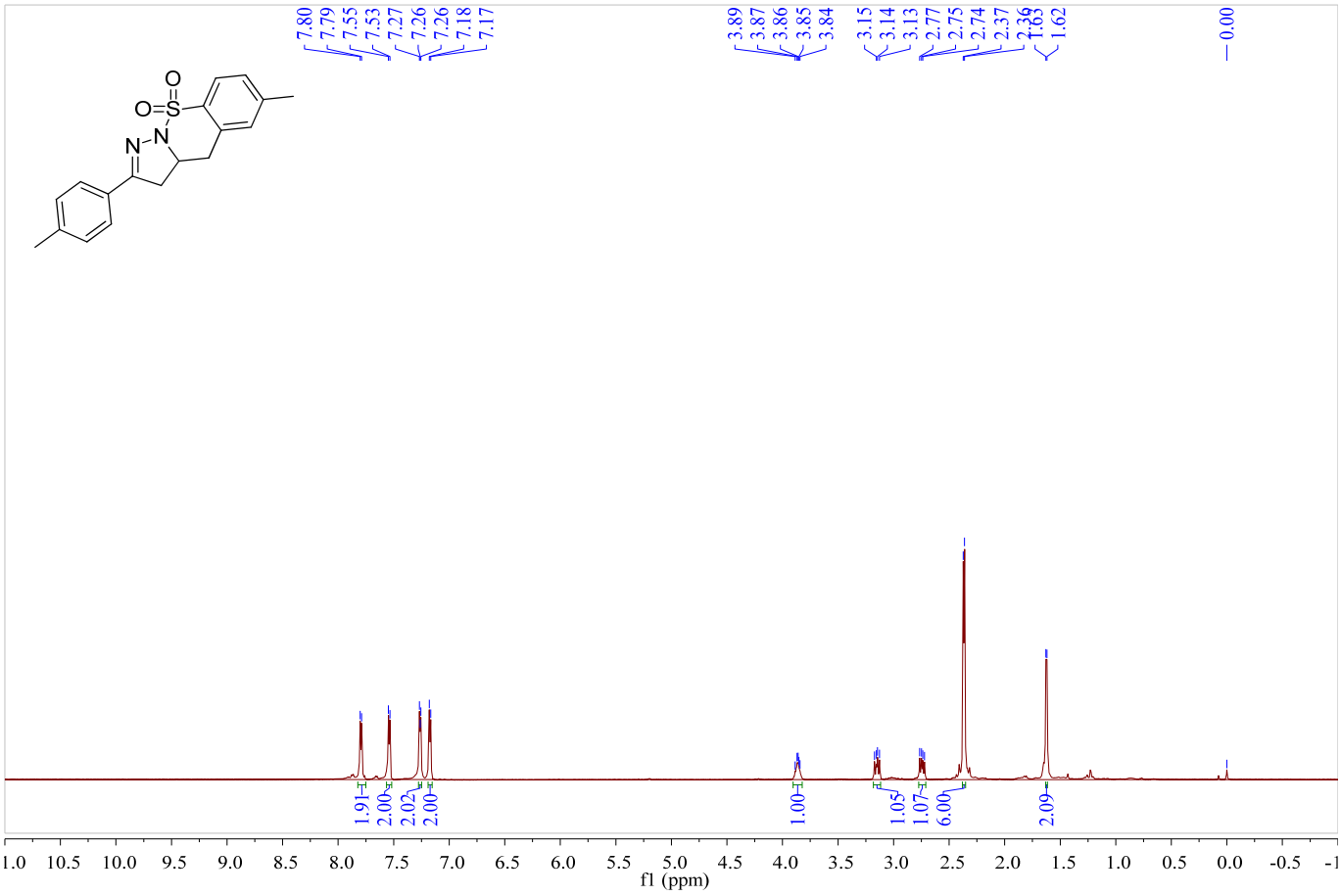


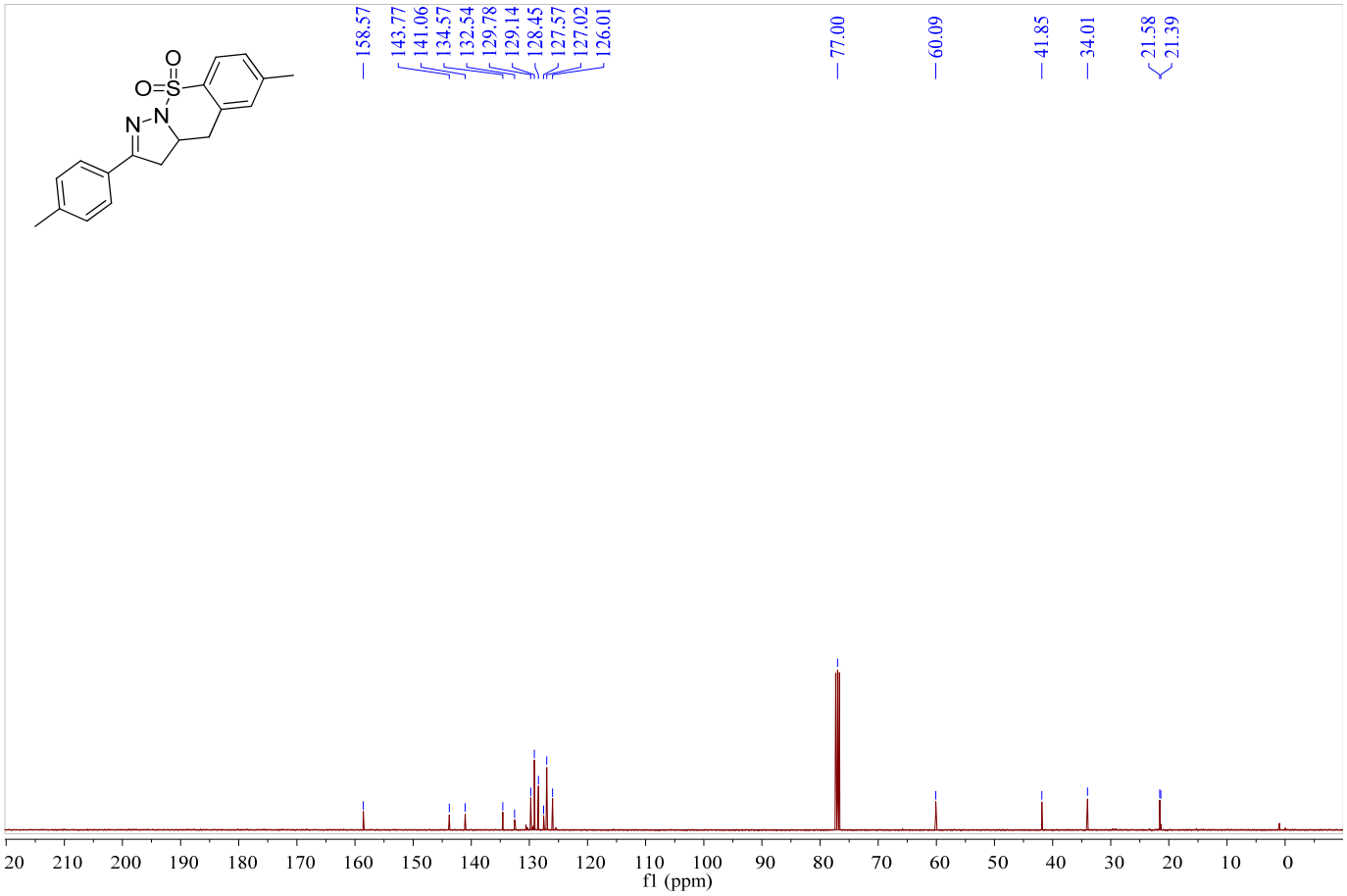
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 2p



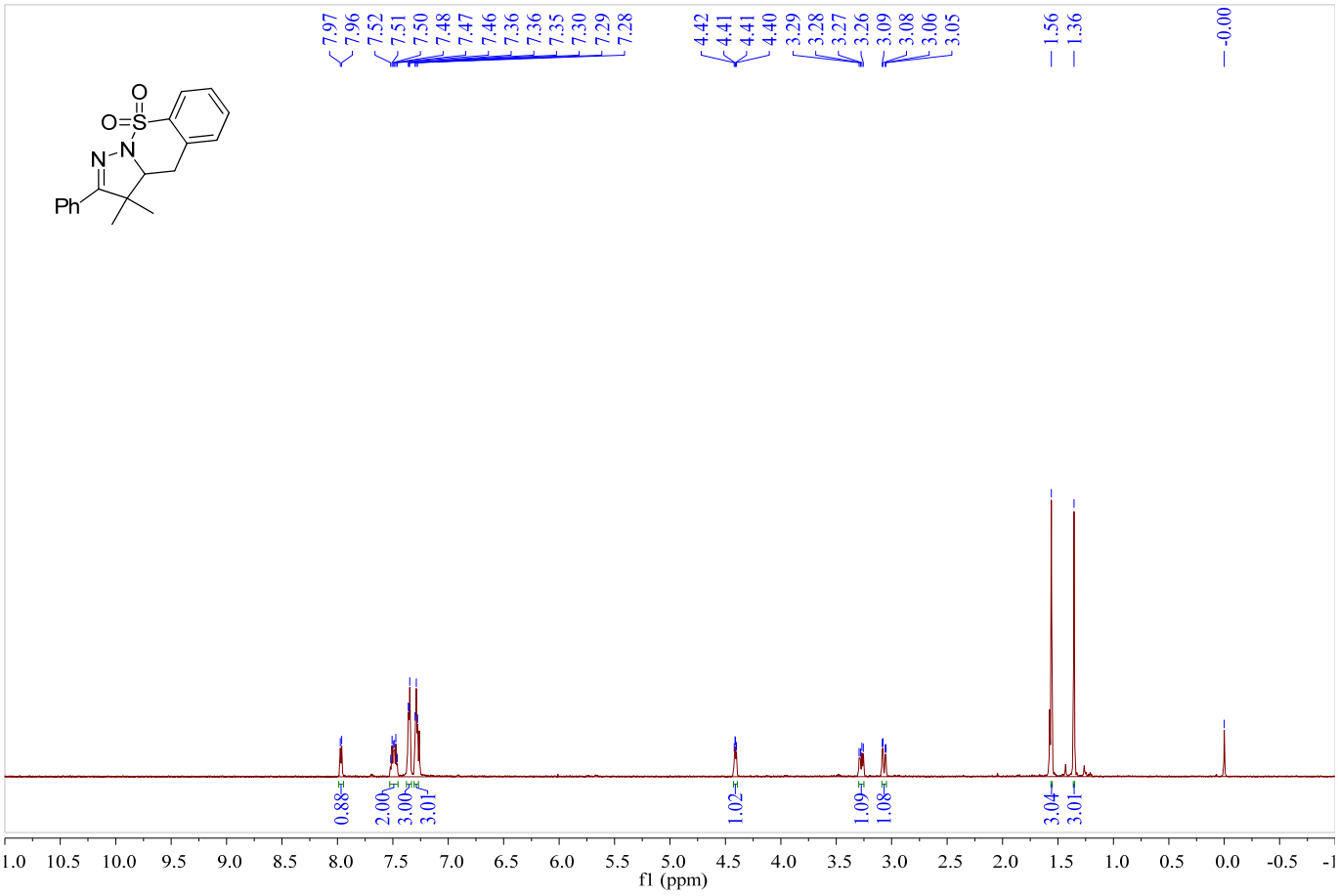


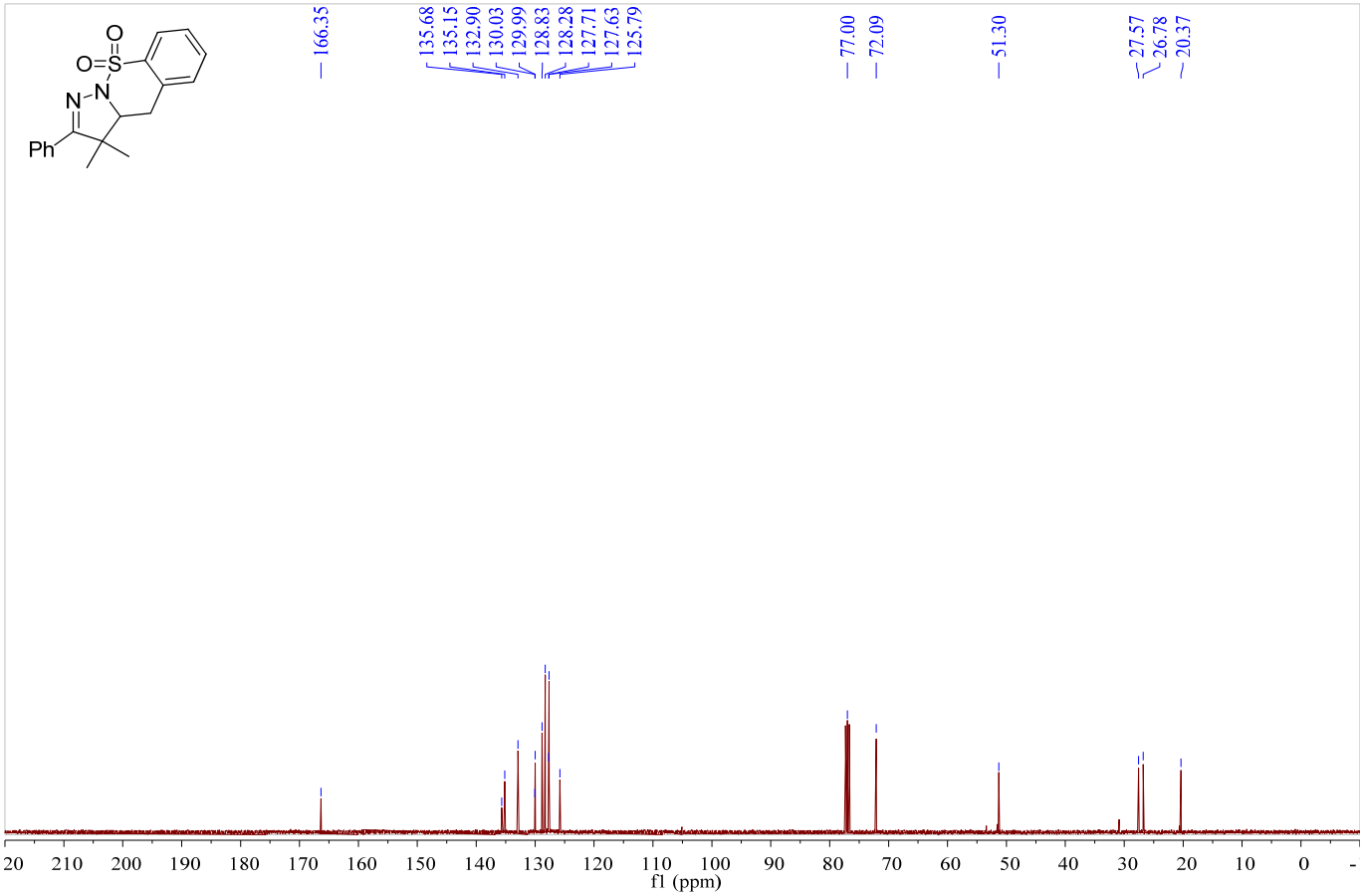
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 2q



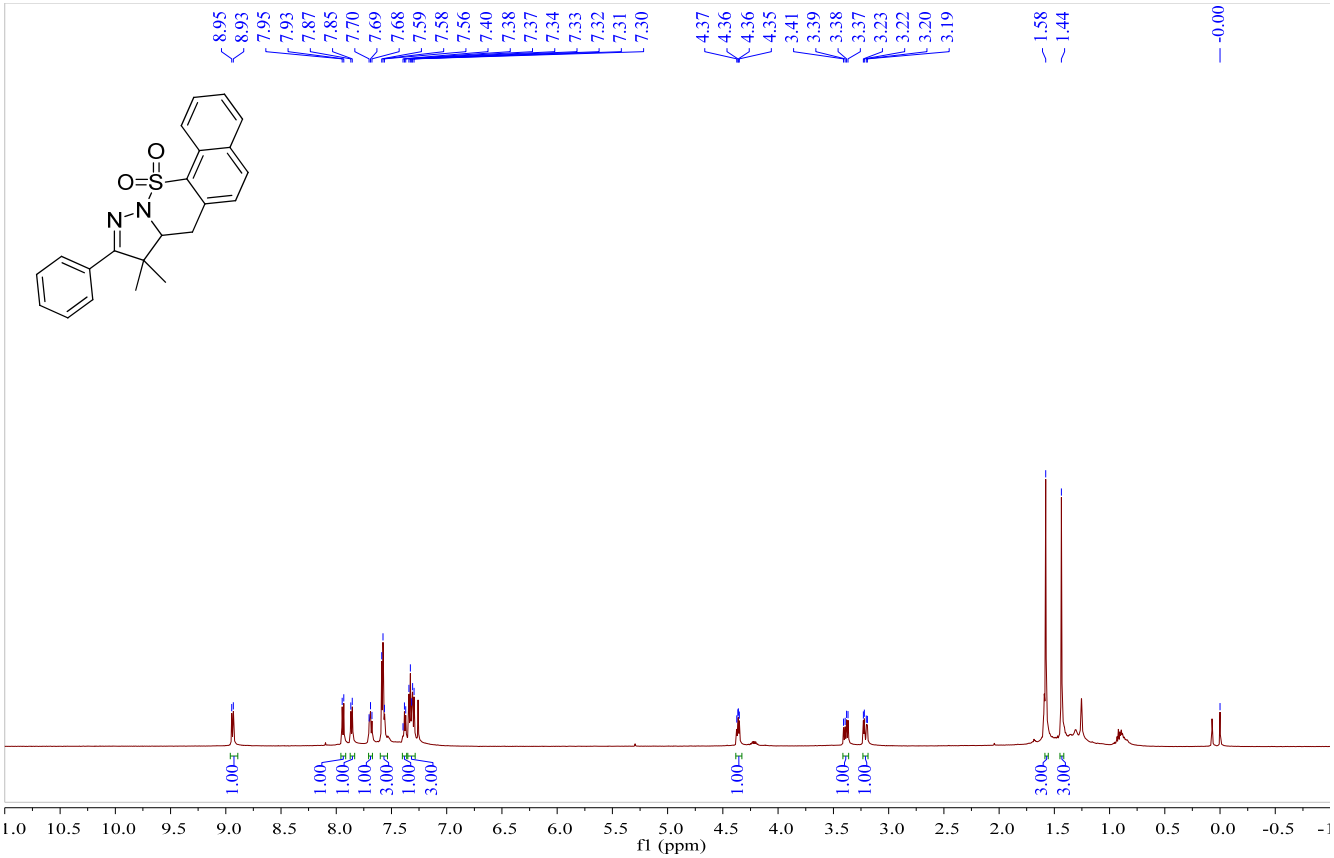


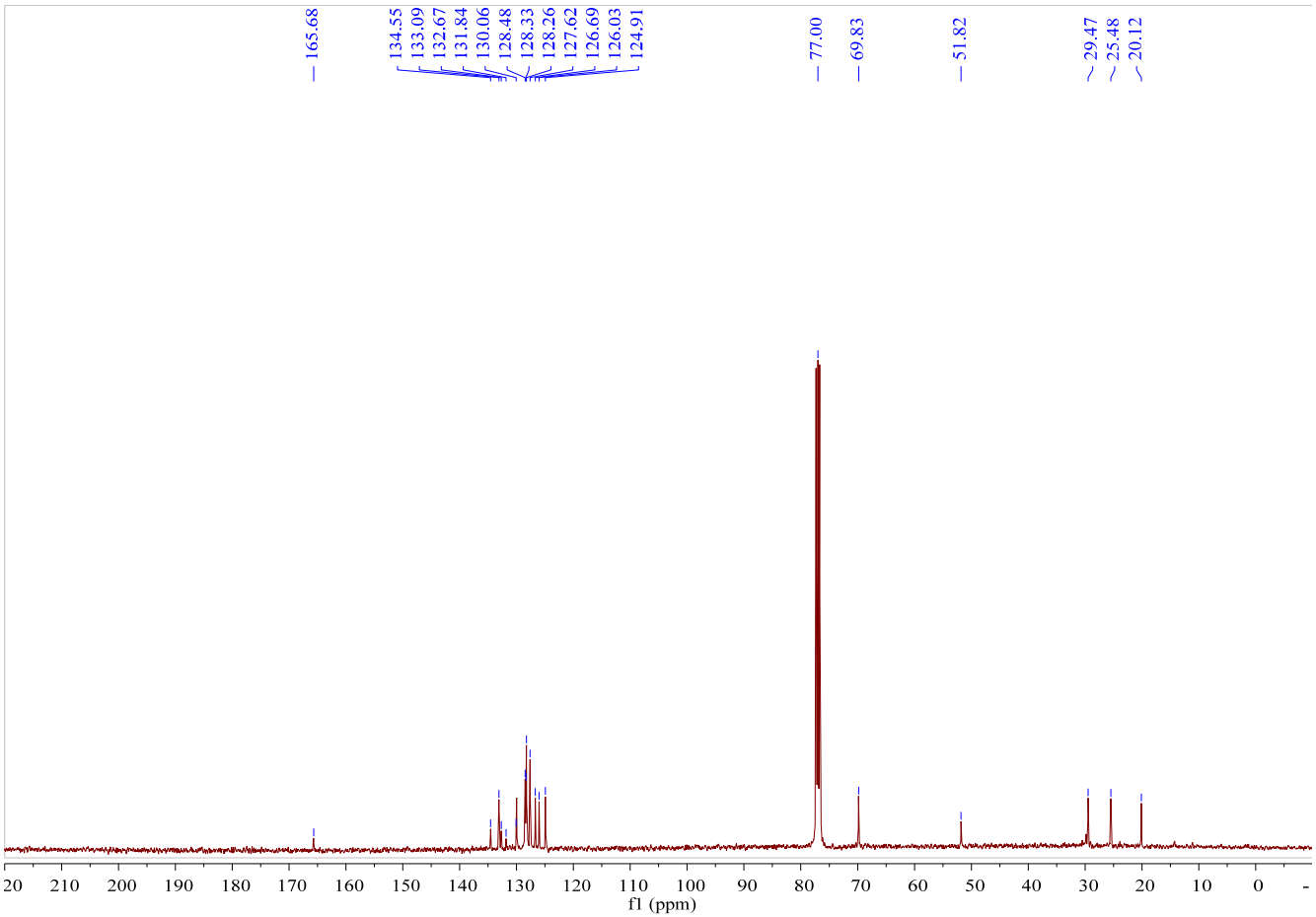
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 2r



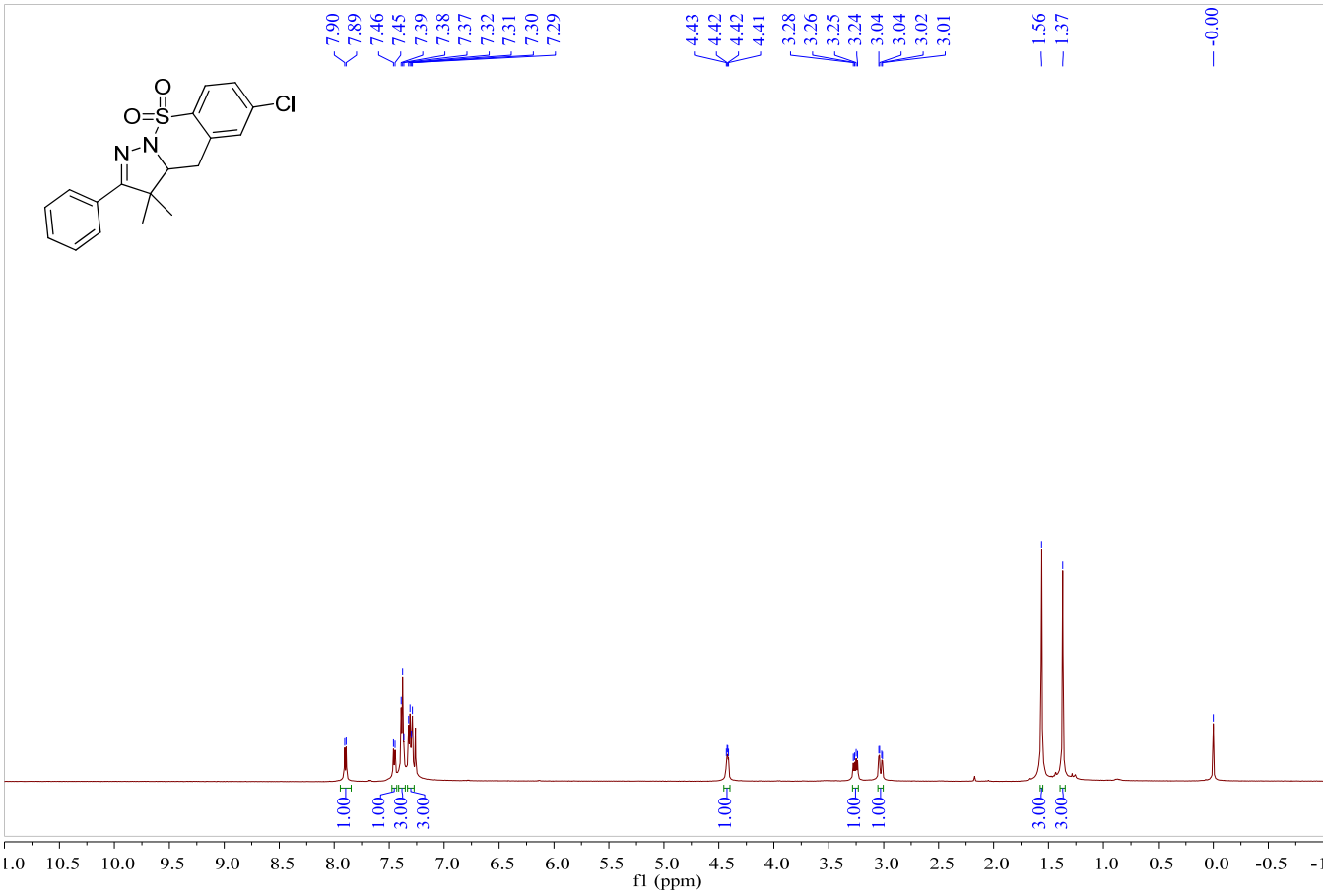


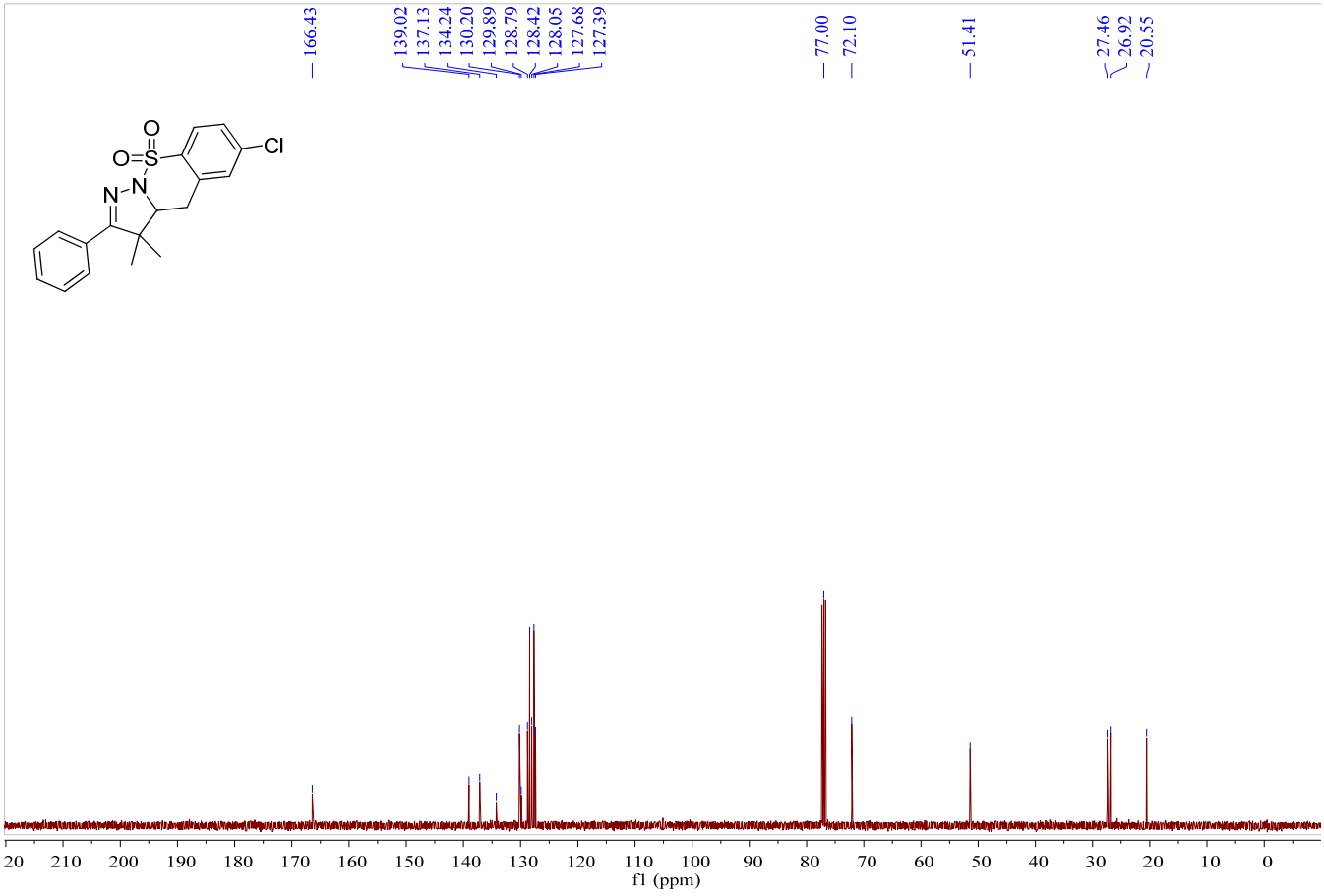
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 2s



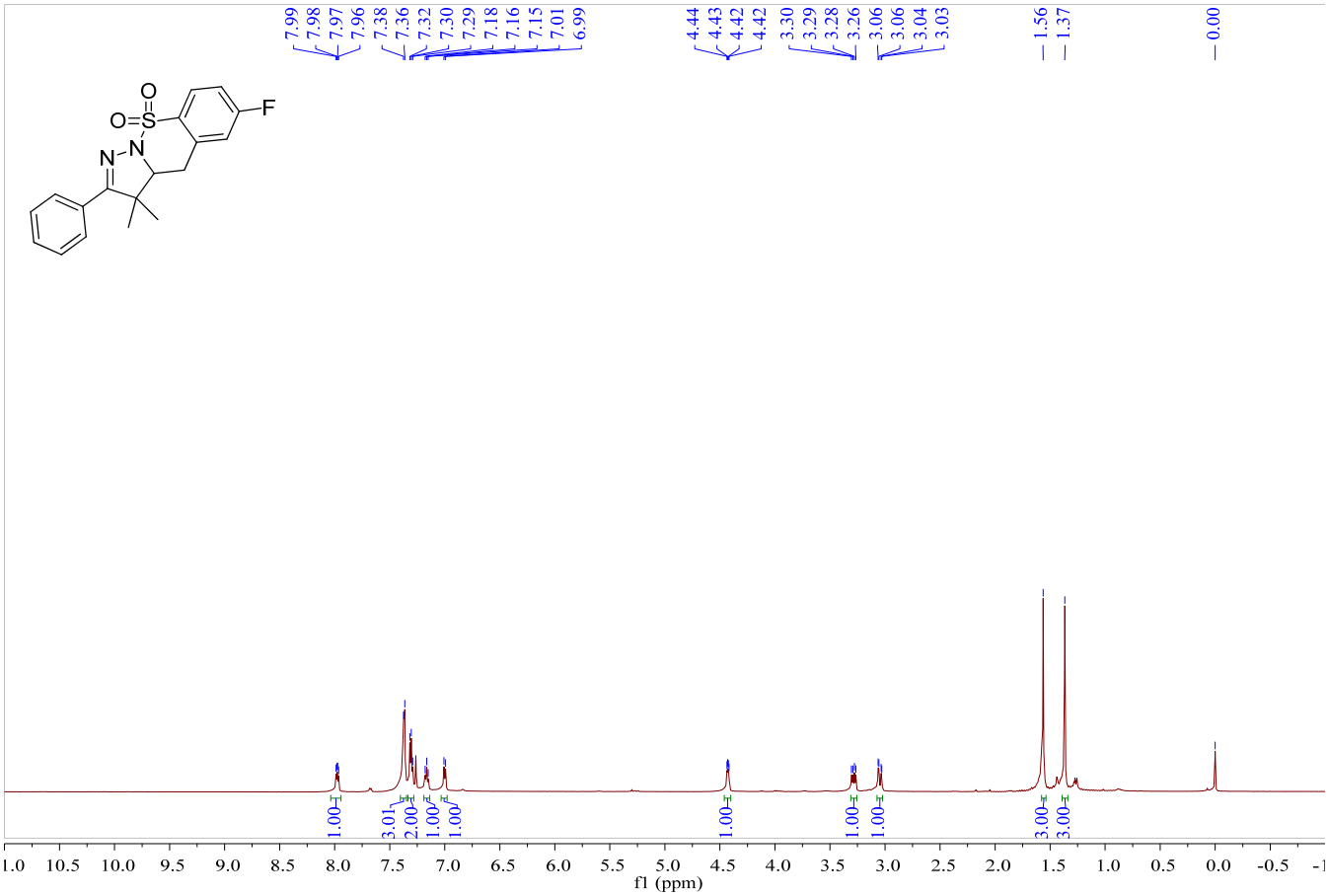


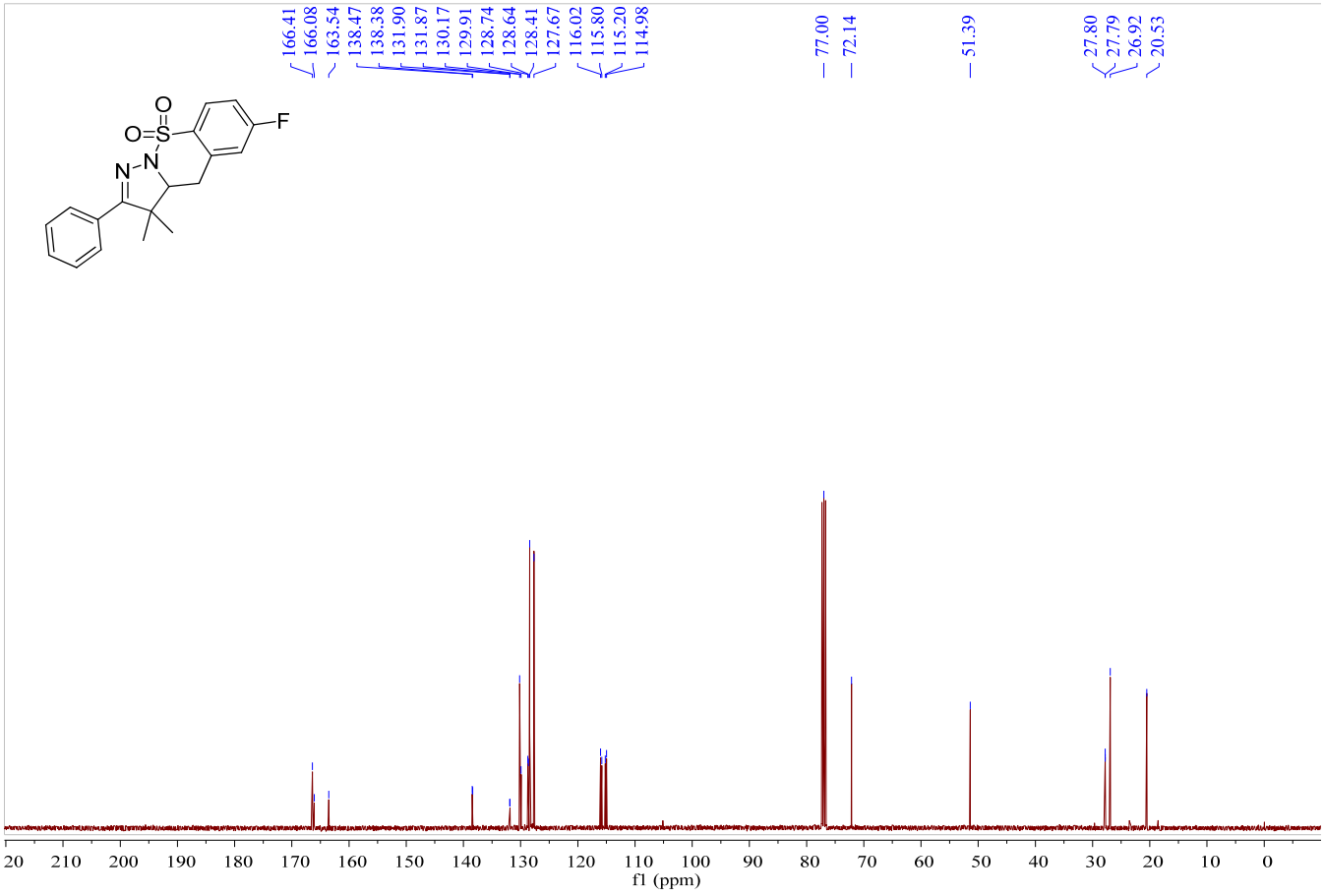
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 2t



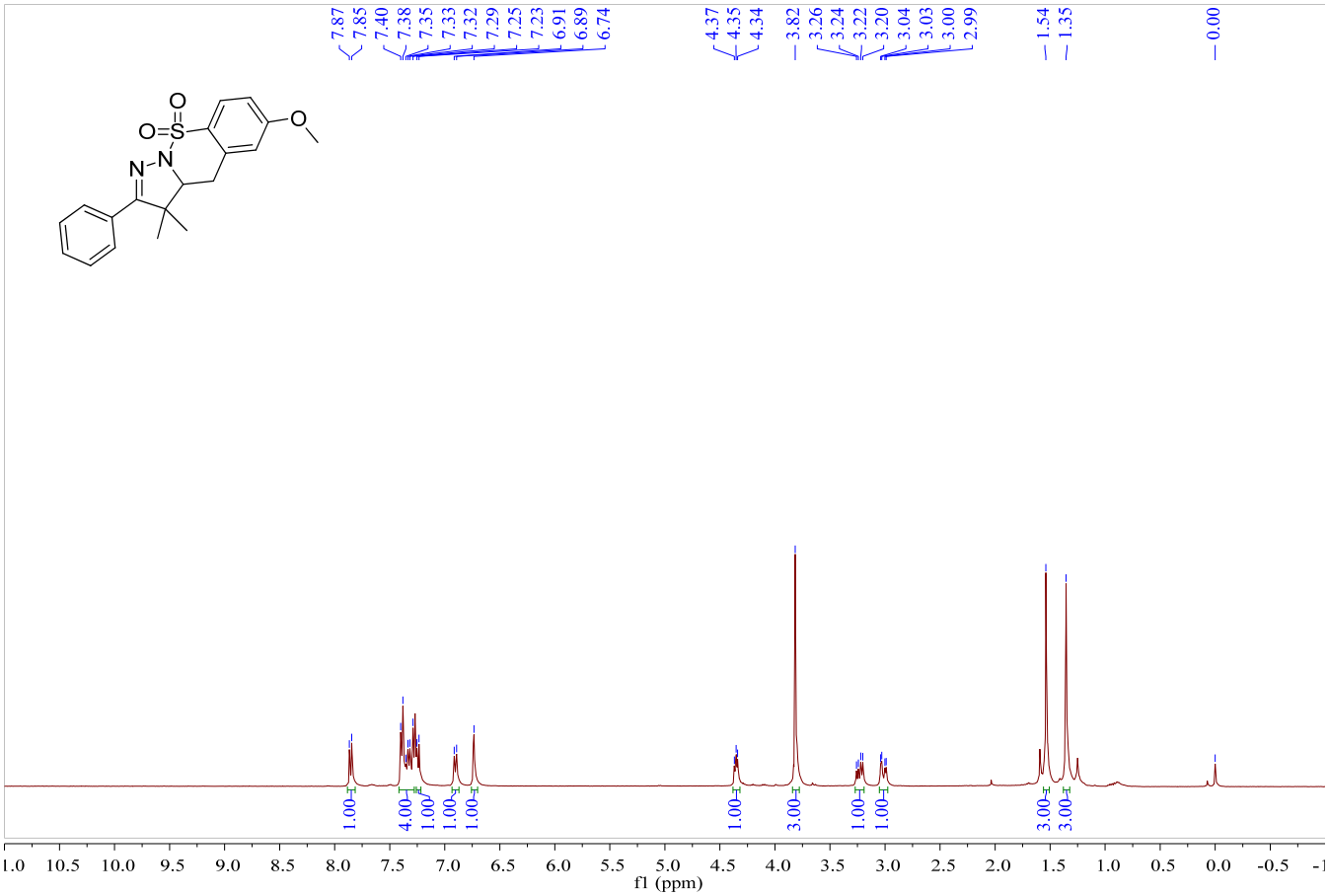


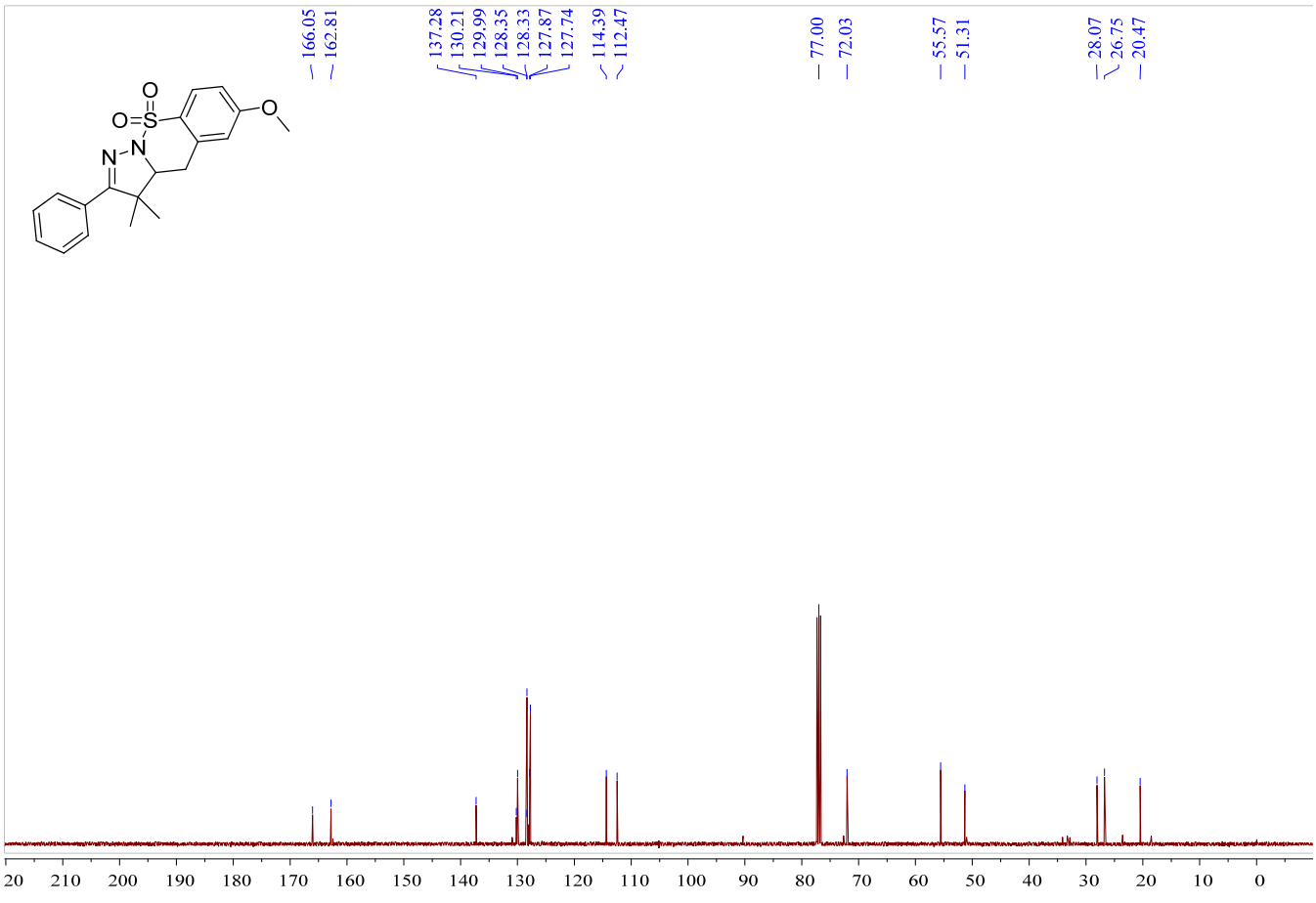
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 2u



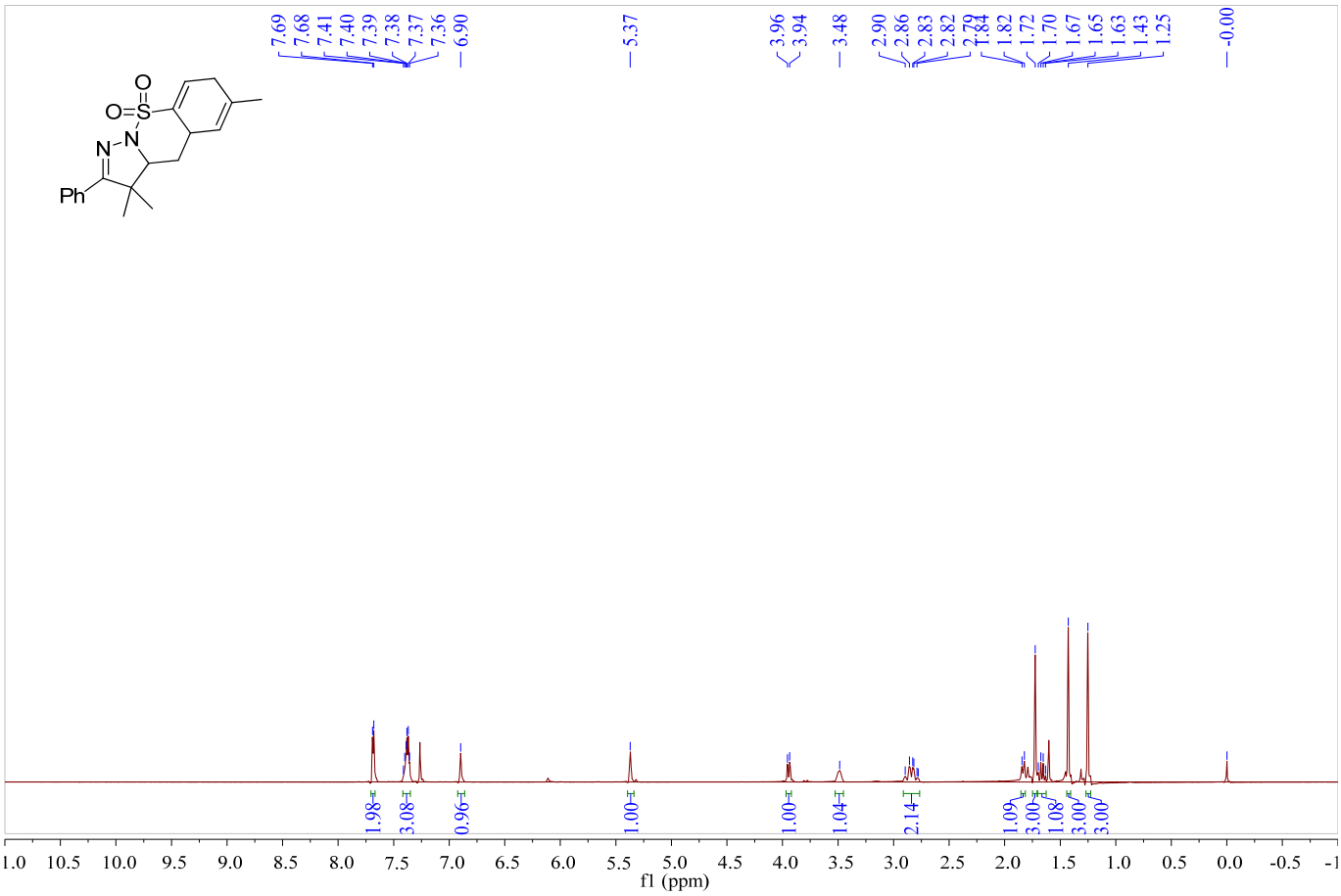


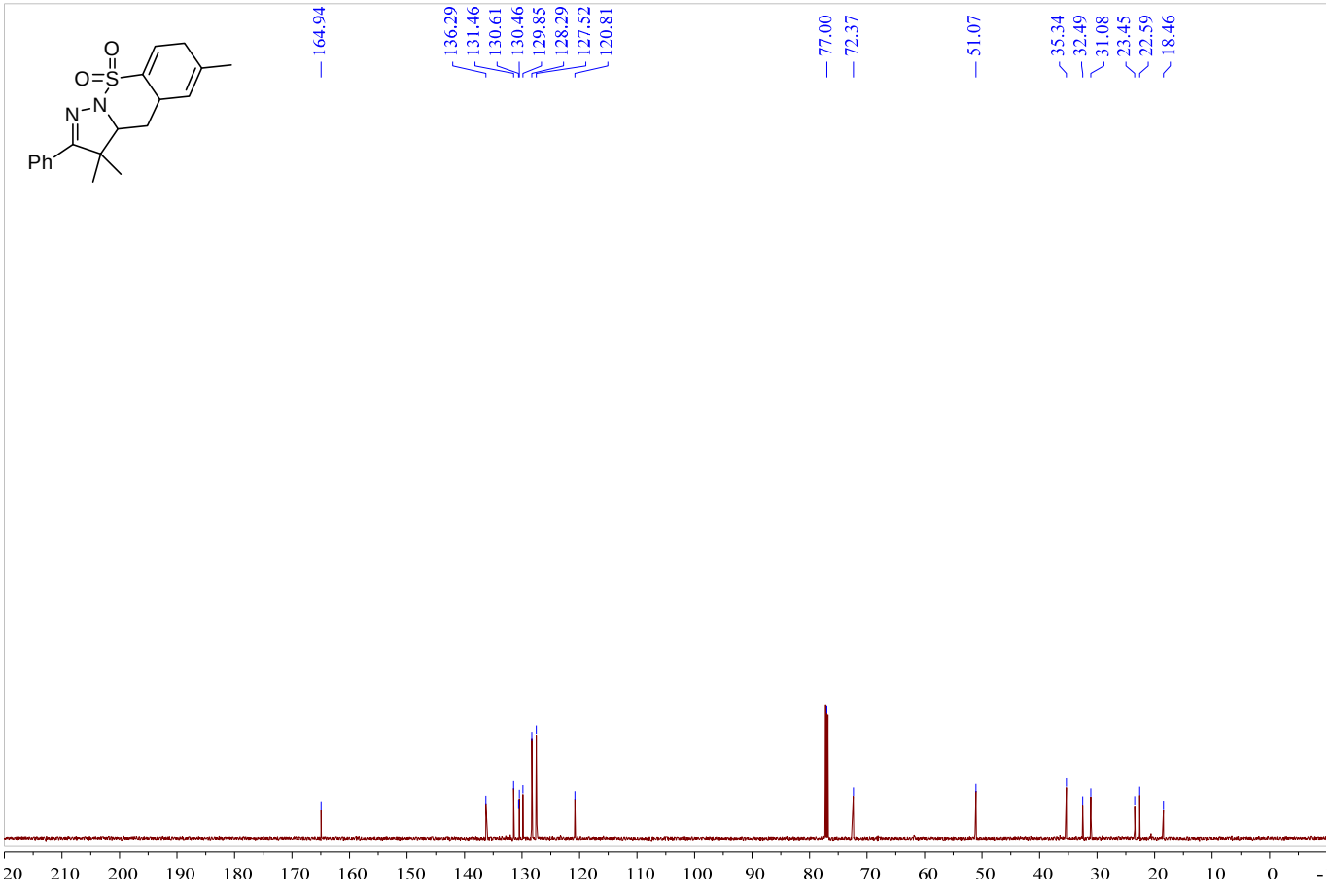
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 2v



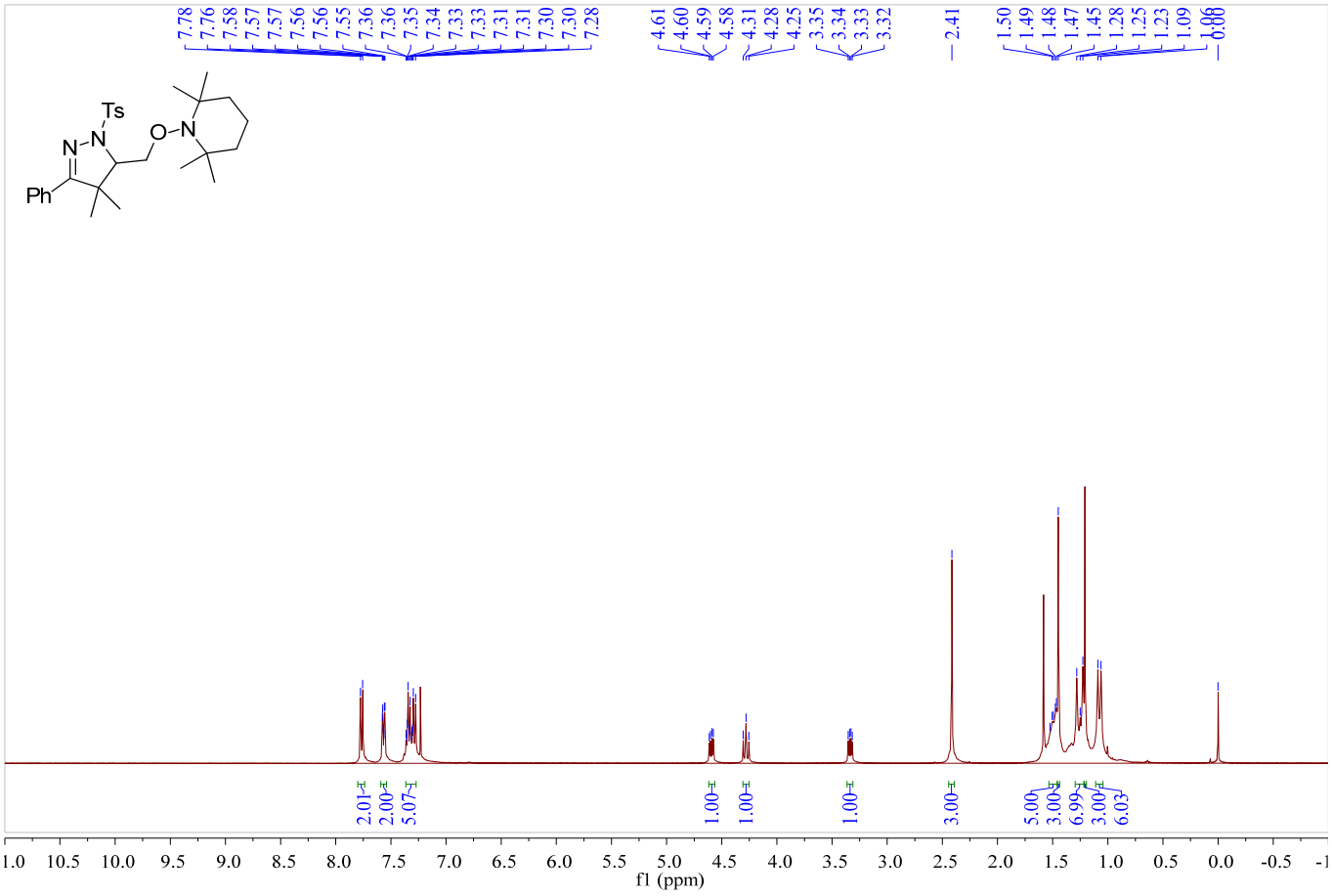


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of product 3a





^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 4


7.78 7.76 7.58 7.57 7.57 7.56 7.56 7.55 7.36 7.35 7.34 7.33 7.33 7.31 7.31 7.30 7.30 7.28
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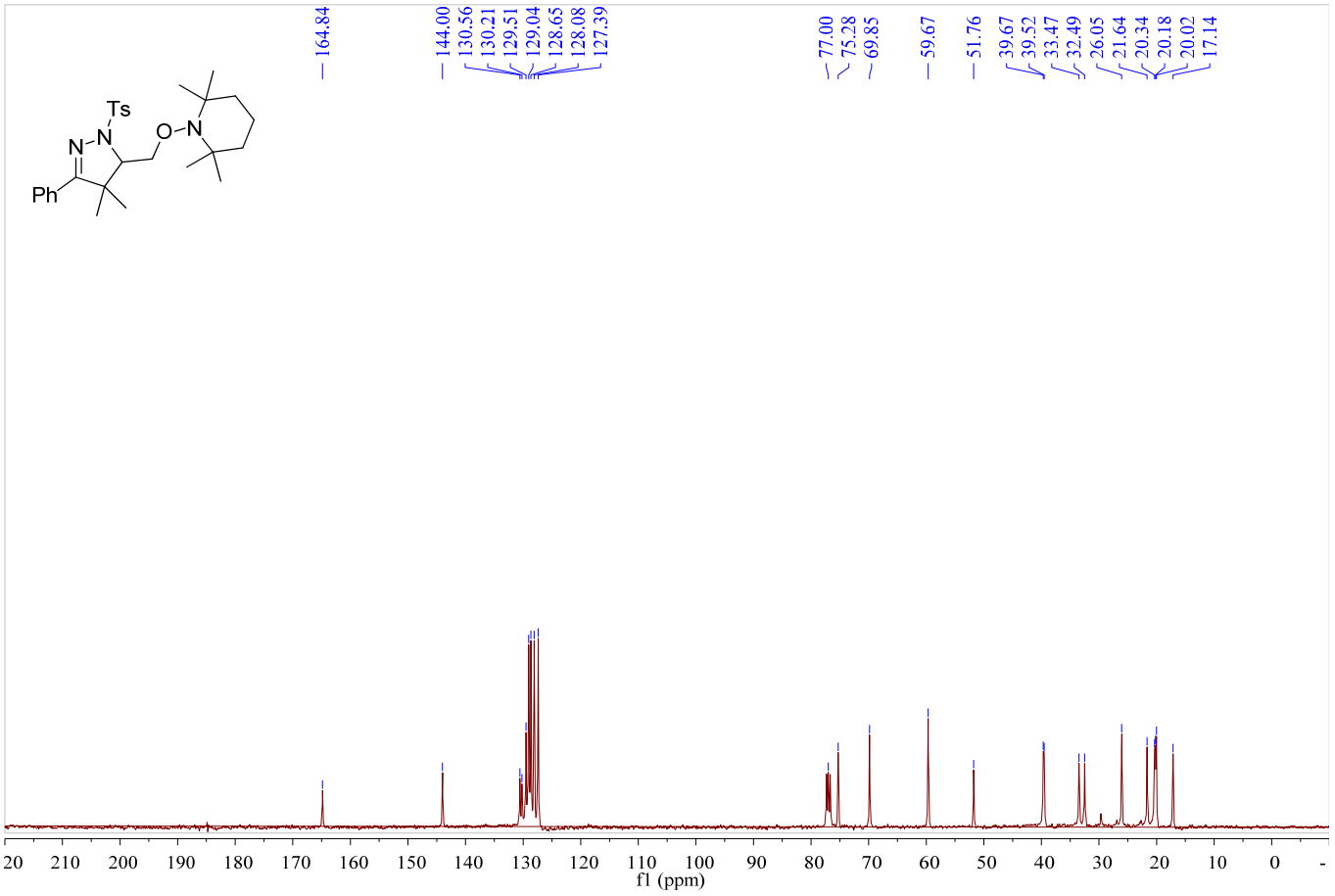
2.41
1.50 1.49 1.48 1.47 1.45 1.28 1.25 1.23 1.09 1.06 0.00
Ts
N
N
O
N
Ph
2.01 2.00 5.07 1.00 1.00 1.00 3.00 5.00 3.00 6.99 3.00 6.03
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


164.84
144.00 130.56 130.21 129.51 129.04 128.65 128.08 127.39
77.00 75.28 69.85
59.67
51.76
39.67 39.52 33.47 32.49 26.05 21.64 20.34 20.18 20.02 17.14
Ts
N
N
O
N
Ph
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)