Supporting Information

C=N Bonds Formation via Palladium-Catalyzed Carbene Insertion into N=N Bonds: Inhibiting the General 1,2-Migration Process of Ylide Intermediates

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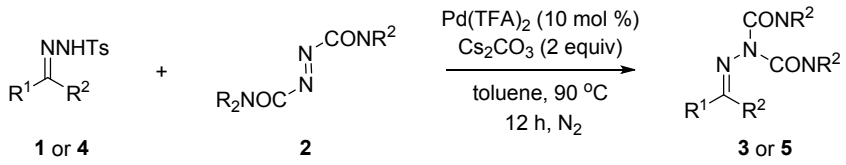
A. General Information

Melting points were measured using a melting point instrument and are uncorrected. Chemical shifts were reported in ppm from the solvent resonance as the internal standard ($CDCl_3$ δ_H = 7.26 ppm, δ_C = 77.16 ppm; D_2O δ_H = 4.79 ppm). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). Coupling constants were reported in Hertz (Hz). IR spectra were obtained with an infrared spectrometer on either potassium bromide pellets or liquid films between two potassium bromide pellets. GC−MS data were obtained using electron ionization. HRMS was carried out on a high-resolution mass spectrometer (LCMS-IT-TOF). TLC was performed using commercially available 100−400 mesh silica gel plates (GF_{254}). X-ray structural analyses were conducted on an X-ray analysis instrument.

Materials. Tetrahydrofuran (THF) and toluene were distilled from sodium/benzophenone; 1,2-dichloroethane (DCE) was distilled from calcium hydride; acetonitrile (CH_3CN) was distilled from phosphorus pentoxide. Other commercially available reagents were purchased and used without further purification. Analytical thin-layer chromatography was performed on 0.20 mm silica gel plates (GF_{254}) using UV light as a visualizing agent. Flash column chromatography was carried out using silica gel (200–300 mesh) with the indicated solvent system. All reactions were conducted in oven-dried Schlenk tubes. All the reaction temperatures reported are oil bath temperatures.

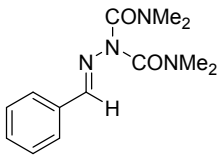
B. General Procedure for the Carbene Insertion of *N*-Tosylhydrazones with Azo Compounds



A 25 mL Schlenk tube placed with a magnetic stirring bar, *N*-tosylhydrazones (0.2 mmol), $Pd(TFA)_2$ (10 mmol %), Cs_2CO_3 (0.2 mmol), toluene (2 mL), and azo compound **2** (0.1 mmol) was vigorously stirred at 90 °C for 12 h under N_2 in an oil bath. Then the resulting solution was cooled to room temperature, added water (10 mL), extracted with EtOAc (3 × 10 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. Further purification by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate) provided the pure product **3** or **5**.

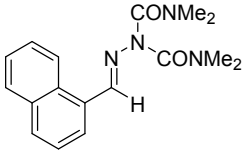
C. Analysis Data for the Products

(*E*)-2-Benzylidene-*N*,*N*,*N*',*N*'-Tetramethylhydrazine-1,1-Dicarboxamide (3a)



23.8 mg, 91% yield; viscous liquid; TLC (petroleum ether/ethyl acetate, 1:2 v/v): R_f = 0.40; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.63−7.66 (m, 2H), 7.36−7.38 (m, 3H), 3.06 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 145.7, 134.5, 129.9, 128.6, 127.1, 37.6; IR (KBr): 2930, 1688, 1487, 1380, 1261, 1160, 1061 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{13}H_{18}N_4O_2$+H, 263.1503; found, 263.1501.

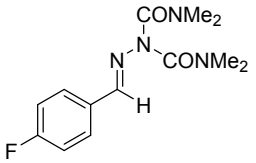
(*E*)-*N*,*N*,*N*',*N*'-Tetramethyl-2-(naphthalen-1-ylmethylene)hydrazine-1,1-Dicarboxamide (3b)



26.2 mg, 84% yield; viscous liquid; TLC (petroleum ether/ethyl acetate, 1:2 v/v): R_f = 0.42; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63−7.66 (m, 2H), 7.86−7.89 (m, 3H), 7.46−7.57 (m, 3H), 3.09 (s,

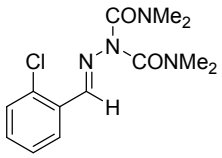
12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 146.1, 133.8, 131.0, 130.5, 130.1, 128.7, 127.0, 126.8, 126.1, 125.3, 124.0, 37.7; IR (KBr): 2929, 1687, 1488, 1380, 1262, 1161, 1063 cm^{-1}; HRMS (ESI, m/z): $[M+Na]^+$ Calcd. for $C_{17}H_{20}N_4O_2$+Na, 335.1478; found, 335.1479.

(*E*)-2-(4-Fluorobenzylidene)-*N*,*N*,*N*',*N*'-Tetramethylhydrazine-1,1-Dicarboxamide (3c)



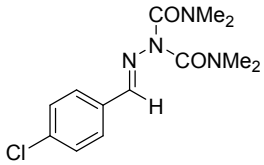
24.6 mg, 88% yield; viscous liquid; TLC (petroleum ether/ethyl acetate, 1:2 v/v): R_f = 0.41; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.62−7.66 (m, 2H), 7.07 (t, *J* = 8.8 Hz, 2H), 3.06 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7 (d, $^1J_{F\text{-}C}$ = 248.7 Hz), 156.2, 145.0, 130.7 (d, $^4J_{F\text{-}C}$ = 3.2 Hz), 128.9 (d, $^3J_{F\text{-}C}$ = 8.4 Hz), 115.7 (d, $^2J_{F\text{-}C}$ = 21.8 Hz), 37.6; IR (KBr): 2929, 1688, 1495, 1377, 1230, 1156, 1061 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{13}H_{17}FN_4O_2$+H, 281.1408; found, 281.1407.

(*E*)-2-(2-Chlorobenzylidene)-*N*,*N*,*N*',*N*'-Tetramethylhydrazine-1,1-Dicarboxamide (3d)



25.2 mg, 85% yield; viscous liquid; TLC (petroleum ether/ethyl acetate, 1:2 v/v): R_f = 0.41; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.94−7.96 (m, 1H), 7.35−7.37 (m, 1H), 7.27−7.30 (m, 2H), 3.06 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 142.2, 134.3, 132.0, 130.7, 129.8, 126.9, 126.8, 37.6; IR (KBr): 2931, 1686, 1498, 1381, 1262, 1158, 1054 cm^{-1}; HRMS (ESI, m/z): $[M+Na]^+$ Calcd. for $C_{13}H_{17}ClN_4O_2$+Na, 319.0932; found, 319.0935.

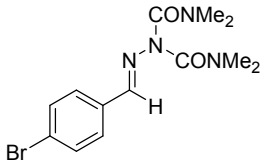
(*E*)-2-(4-Chlorobenzylidene)-*N*,*N*,*N*',*N*'-Tetramethylhydrazine-1,1-Dicarboxamide (3e)



26.0 mg, 88% yield; viscous liquid; TLC (petroleum ether/ethyl acetate, 1:2 v/v): R_f = 0.41; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 3.06 (s,

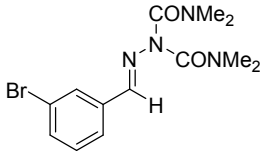
12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 144.6, 135.7, 133.1, 128.9, 128.2, 37.6; IR (KBr): 2928, 1687, 1487, 1377, 1261, 1159, 1087 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{13}H_{17}ClN_4O_2$+H, 297.1113; found, 297.1111.

(*E*)-2-(4-Bromobenzylidene)-*N*,*N*,*N*',*N*'-Tetramethylhydrazine-1,1-Dicarboxamide (3f)



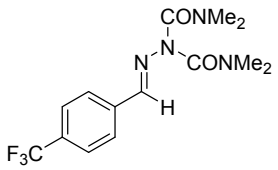
30.9 mg, 91% yield; viscous liquid; TLC (petroleum ether/ethyl acetate, 1:2 v/v): R_f = 0.40; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.44−7.58 (m, 4H), 3.06 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 144.6, 133.5, 131.8, 128.5, 124.0, 37.6; IR (KBr): 2929, 1688, 1486, 1378, 1261, 1159, 1063 cm^{-1}; HRMS (ESI, m/z): $[M+Na]^+$ Calcd. for $C_{13}H_{17}BrN_4O_2$+Na, 363.0427; found, 363.0423.

(*E*)-2-(3-Bromobenzylidene)-*N*,*N*,*N*',*N*'-Tetramethylhydrazine-1,1-Dicarboxamide (3g)



30.9 mg, 91% yield; viscous liquid; TLC (petroleum ether/ethyl acetate, 1:2 v/v): R_f = 0.42; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.75 (s, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.4 (d, *J* = 8.0 Hz, 1H), 7.25 (t, *J* = 8.0 Hz, 1H), 3.06 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 143.9, 136.6, 130.2, 129.5, 126.0, 122.9, 37.6; IR (KBr): 2929, 1688, 1483, 1381, 1261, 1158, 1060 cm^{-1}; HRMS (ESI, m/z): $[M+Na]^+$ Calcd. for $C_{13}H_{17}BrN_4O_2$+Na, 363.0427; found, 363.0429.

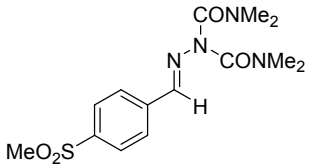
(*E*)-*N*,*N*,*N*',*N*'-Tetramethyl-2-(4-(Trifluoromethyl)benzylidene)hydrazine-1,1-Dicarboxamide (3h)



30.0 mg, 91% yield; viscous liquid; TLC (petroleum ether/ethyl acetate, 1:2 v/v): R_f = 0.43; ^{1}H

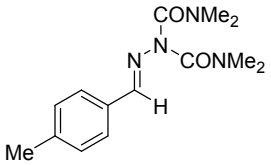
NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.75 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 8.4 Hz, 2H), 3.08 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 143.7, 138.0, 131.3 (q, $^2J_{F-C}$ = 33.4 Hz), 127.2, 125.6 (q, $^3J_{F-C}$ = 3.8 Hz), 121.2 (q, $^1J_{F-C}$ = 270.5 Hz), 37.6; IR (KBr): 2933, 1691, 1495, 1324, 1261, 1162, 1064 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{14}H_{17}F_3N_4O_2$+H, 331.1376; found, 331.1373.

(*E*)-*N*,*N*,*N*',*N*'-Tetramethyl-2-(4-(Methylsulfonyl)benzylidene)hydrazine-1,1-Dicarboxamide (3i)



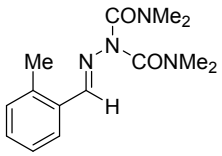
25.2 mg, 74% yield; viscous liquid; TLC (petroleum ether/ethyl acetate, 1:2 v/v): R_f = 0.17; ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.0 Hz, 2H), 7.89 (s, 1H), 7.82 (d, J = 8.0 Hz, 2H), 3.08 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 142.9, 141.0, 139.8, 127.8, 127.6, 44.5, 37.6; IR (KBr): 2926, 2857, 1687, 1486, 1394, 1305, 1145, 1065 cm^{-1}; HRMS (ESI, m/z): $[M+Na]^+$ Calcd. for $C_{14}H_{20}N_4O_4S$+Na, 363.1097; found, 363.1098.

(*E*)-*N*,*N*,*N*',*N*'-Tetramethyl-2-(4-Methylbenzylidene)hydrazine-1,1-Dicarboxamide (3j)



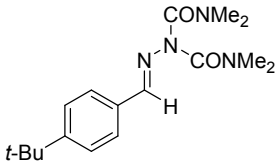
25.1 mg, 91% yield; viscous liquid; TLC (petroleum ether/ethyl acetate, 1:2 v/v): R_f = 0.42; ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.53 (s, 2H), 7.18 (s, 2H), 3.05−3.05 (m, 12H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 146.1, 140.2, 131.8, 129.4, 127.1, 37.6, 21.4; IR (KBr): 2927, 1688, 1488, 1374, 1261, 1159, 1059 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{14}H_{20}N_4O_2$+H, 277.1659; found, 277.1656.

(*E*)-*N*,*N*,*N*',*N*'-Tetramethyl-2-(2-Methylbenzylidene)hydrazine-1,1-Dicarboxamide (3k)



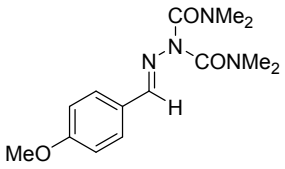
22.9 mg, 83% yield; viscous liquid; TLC (petroleum ether/ethyl acetate, 1:2 v/v): R_f = 0.42; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.16−7.28 (m, 3H), 3.06 (s, 12H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.4, 145.1, 137.0, 129.7, 126.2, 126.1, 37.6, 19.5; IR (KBr): 2929, 1687, 1487, 1376, 1262, 1158, 1060 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{14}H_{20}N_4O_2$+H, 277.1659; found, 277.1660.

(*E*)-2-(4-(*tert*-Butyl)benzylidene)-*N*,*N*,*N*',*N*'-Tetramethylhydrazine-1,1-Dicarboxamide (3l)



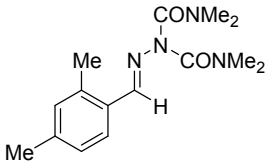
28.6 mg, 90% yield; viscous liquid; TLC (petroleum ether/ethyl acetate, 1:2 v/v): R_f = 0.41; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 3.06 (s, 12H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 153.3, 145.8, 131.8, 126.9, 125.6, 37.7, 34.8, 31.2; IR (KBr): 2955, 1686, 1486, 1374, 1262, 1159, 1060 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{17}H_{26}N_4O_2$+H, 319.2129; found, 319.2128.

(*E*)-2-(4-Methoxybenzylidene)-*N*,*N*,*N*',*N*'-Tetramethylhydrazine-1,1-Dicarboxamide (3m)



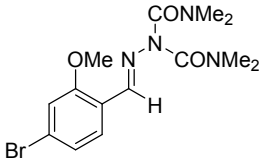
26.6 mg, 91% yield; viscous liquid; TLC (petroleum ether/ethyl acetate, 1:2 v/v): R_f = 0.40; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.59 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.4 Hz, 2H), 3.83 (s, 3H), 3.06 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1, 156.5, 146.2, 128.7, 127.3, 114.1, 55.3, 37.6; IR (KBr): 2925, 2854, 1682, 1606, 1497, 1377, 1252, 1161, 1029 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{14}H_{20}N_4O_3$+H, 293.1608; found, 293.1608.

(*E*)-2-(2,4-Dimethylbenzylidene)-*N*,*N*,*N*',*N*'-Tetramethylhydrazine-1,1-Dicarboxamide (3n)



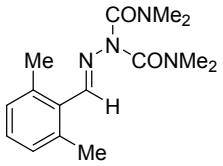
23.2 mg, 80% yield; yellow solid, mp: 135−136 °C; TLC (petroleum ether/ethyl acetate, 1:2 v/v): R_f = 0.42; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 1H), 6.98 (s, 1H), 3.05 (s, 12H), 2.40 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 145.5, 139.8, 136.9, 131.6, 129.8, 127.0, 126.3, 37.6, 21.3, 19.5; IR (KBr): 2930, 1680, 1497, 1376, 1262, 1158, 1059 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{15}H_{22}N_4O_2$+H, 291.1816; found, 291.1813.

(*E*)-2-(4-Bromo-2-Methoxybenzylidene)-*N*,*N*,*N*',*N*'-Tetramethylhydrazine-1,1-Dicarboxamide (3o)



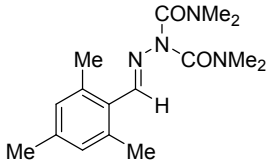
30.2 mg, 83% yield; yellow solid, mp: 99−100 °C; TLC (petroleum ether/ethyl acetate, 1:2 v/v): R_f = 0.41; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.98 (s, 1H), 7.41 (d, *J* = 8.8 Hz, 1H), 6.77 (d, *J* = 8.8 Hz, 1H), 3.81 (s, 3H), 3.05 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 156.2, 140.7, 133.5, 128.4, 124.9, 113.4, 112.9, 55.8, 37.6; IR (KBr): 2934, 1682, 1483, 1376, 1262, 1161, 1062 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{14}H_{19}BrN_4O_3$+H, 371.0713; found, 371.0711.

(*E*)-2-(2,6-Dimethylbenzylidene)-*N*,*N*,*N*',*N*'-Tetramethylhydrazine-1,1-Dicarboxamide (3p)



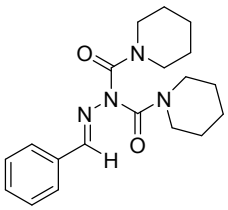
22.0 mg, 76% yield; yellow solid, mp: 110−111 °C; TLC (petroleum ether/ethyl acetate, 1:2 v/v): R_f = 0.41; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.12−7.16 (m, 1H), 7.03−7.05 (m, 2H), 3.05 (s, 12H), 2.43 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7, 148.4, 137.4, 131.7, 128.8, 128.4, 37.6, 21.0; IR (KBr): 2930, 1681, 1483, 1379, 1262, 1156, 1061 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{15}H_{22}N_4O_2$+H, 291.1816; found, 291.1817.

(*E*)-*N*,*N*,*N*',*N*'-Tetramethyl-2-(2,4,6-Trimethylbenzylidene)hydrazine-1,1-Dicarboxamide (3q)



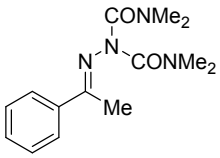
22.5 mg, 74% yield; yellow solid, mp: 151−152 °C; TLC (petroleum ether/ethyl acetate, 1:2 v/v): R_f = 0.43; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 6.88 (s, 2H), 3.05 (s, 12H), 2.41 (s, 6H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 148.4, 138.8, 137.5, 129.4, 128.7, 37.6, 21.0; IR (KBr): 2928, 1679, 1486, 1378, 1262, 1156, 1059 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{16}H_{24}N_4O_2$+H, 305.1972; found, 305.1974.

(*E*)-*N'*-Benzylidene-*N*-(Piperidine-1-Carbonyl)piperidine-1-Carbohydrazide (3r)



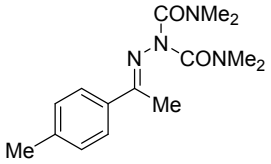
30.4 mg, 89% yield; yellow solid, mp: 127−128 °C; TLC (petroleum ether/ethyl acetate, 1:1 v/v): R_f = 0.37; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.63−7.65 (s, 2H), 7.37−7.38 (s, 3H), 3.54 (s, 9H), 1.65 (s, 13H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 144.8, 134.6, 129.8, 128.7, 127.1, 46.6, 25.8, 24.4; IR (KBr): 2934, 2857, 1680, 1426, 1259, 1145, 1017 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{19}H_{26}N_4O_2$+H, 343.2129; found, 343.2127.

(*E*)-*N*,*N*,*N*',*N*'-Tetramethyl-2-(1-Phenylethylidene)hydrazine-1,1-Dicarboxamide (5a)



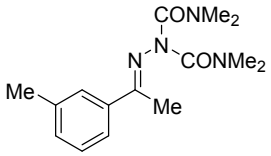
24.8 mg, 90% yield; white solid, mp: 161−162 °C; TLC (petroleum ether/ethyl acetate, 1:2 v/v): R_f = 0.23; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81−7.83 (m, 2H), 7.37−7.39 (m, 3H), 3.01 (s, 12H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 157.8, 137.6, 130.0, 128.3, 126.7, 37.3, 16.9; IR (KBr): 2929, 1677, 1488, 1378, 1265, 1177, 1067 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{14}H_{20}N_4O_2$+H, 277.1659; found, 277.1658.

(*E*)-*N*,*N*,*N*',*N*'-Tetramethyl-2-(1-(*p*-tolyl)ethylidene)hydrazine-1,1-Dicarboxamide (5b)



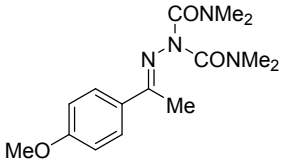
26.1 mg, 90% yield; viscous liquid; TLC (petroleum ether/ethyl acetate, 1:2 v/v): R_f = 0.23; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 3.00 (s, 12H), 2.37 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 157.9, 140.2, 134.8, 129.0, 126.7, 37.3, 21.3, 16.8; IR (KBr): 2929, 1677, 1489, 1377, 1265, 1178, 1066 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{15}H_{22}N_4O_2$+H, 291.1816; found, 291.1815.

(*E*)-*N*,*N*,*N*',*N*'-Tetramethyl-2-(1-(*m*-tolyl)ethylidene)hydrazine-1,1-Dicarboxamide (5c)



25.2 mg, 87% yield; white solid, mp: 104−105 °C; TLC (petroleum ether/ethyl acetate, 1:2 v/v): R_f = 0.23; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.21−7.27 (m, 2H), 3.00 (s, 12H), 2.38 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 157.8, 137.9, 137.6, 130.8, 128.2, 127.4, 123.9, 37.3, 21.4, 17.1; IR (KBr): 2929, 1676, 1488, 1377, 1264, 1173, 1063 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{15}H_{22}N_4O_2$+H, 291.1816; found, 291.1818.

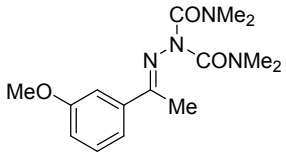
(*E*)-2-(1-(4-Methoxyphenyl)ethylidene)-*N*,*N*,*N*',*N*'-Tetramethylhydrazine-1,1-Dicarboxamide (5d)



27.8 mg, 91% yield; viscous liquid; TLC (petroleum ether/ethyl acetate, 1:2 v/v): R_f = 0.22; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 3.82 (s, 3H), 2.99 (s, 12H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 161.2, 158.0, 130.0, 128.3, 113.6, 55.3, 37.3, 16.6; IR (KBr): 2932, 2853, 1682, 1497, 1378, 1258, 1176, 1029 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{15}H_{22}N_4O_3$+H, 307.1765; found, 307.1766.

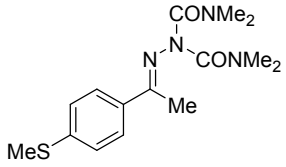
(*E*)-2-(1-(3-Methoxyphenyl)ethylidene)-*N*,*N*,*N*',*N*'-Tetramethylhydrazine-1,1-Dicarboxamide

(5e)



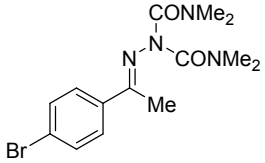
26.3 mg, 86% yield; white solid, mp: 112−113 °C; TLC (petroleum ether/ethyl acetate, 1:2 v/v): R_f = 0.22; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35−7.40 (m, 2H), 7.27−7.31 (m, 1H), 6.95 (dd, *J* = 0.8 Hz, *J* = 0.8 Hz, 1H), 3.83 (s, 3H), 3.00 (s, 12H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 159.5, 157.8, 138.9, 129.2, 119.3, 115.8, 112.1, 55.4, 37.3, 17.1; IR (KBr): 2933, 1683, 1483, 1380, 1269, 1173, 1050 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{15}H_{22}N_4O_3$+H, 307.1765; found, 307.1767.

(*E*)-2-(1-(4-Methoxyphenyl)ethylidene)-*N*,*N*,*N*',*N*'-Tetramethylhydrazine-1,1-Dicarboxamide (5f)



25.8 mg, 80% yield; yellow solid, mp: 170−171 °C; TLC (petroleum ether/ethyl acetate, 1:2 v/v): R_f = 0.21; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 3.00 (s, 12H), 2.49 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 157.8, 141.2, 134.1, 127.1, 125.6, 37.3, 16.6, 15.3; IR (KBr): 2927, 1681, 1488, 1378, 1264, 1177, 1067 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{15}H_{22}N_4O_2S$+H, 323.1536; found, 323.1232.

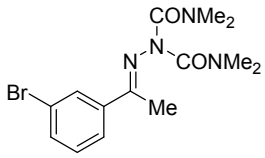
(*E*)-2-(1-(4-Bromophenyl)ethylidene)-*N*,*N*,*N*',*N*'-Tetramethylhydrazine-1,1-Dicarboxamide (5g)



30.8 mg, 87% yield; white solid, mp: 173−174 °C; TLC (petroleum ether/ethyl acetate, 1:2 v/v): R_f = 0.23; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67−7.70 (m, 2H), 7.48−7.50 (m, 2H), 2.99 (s, 12H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 157.6, 136.5, 131.4, 128.3, 124.4, 37.3, 16.7; IR (KBr): 2927, 1681, 1488, 1378, 1264, 1177, 1067 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for

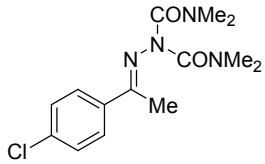
$C_{14}H_{19}BrN_4O_2$+H, 355.0764; found, 355.0767.

(*E*)-2-(1-(3-Bromophenyl)ethylidene)-*N*,*N*,*N*',*N*'-Tetramethylhydrazine-1,1-Dicarboxamide (5h)



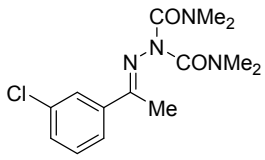
32.4 mg, 91% yield; white solid, mp: 171−172 °C; TLC (petroleum ether/ethyl acetate, 1:2 v/v): R_f = 0.23; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.72 (d, *J* = 7.6 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.26 (d, *J* = 8.4 Hz, 1H), 3.01 (s, 12H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6, 157.5, 139.6, 132.8, 129.7, 125.4, 122.6, 37.3, 16.9; IR (KBr): 2931, 1680, 1487, 1377, 1264, 1173, 1065 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{14}H_{19}BrN_4O_2$+H, 355.0764; found, 355.0765.

(*E*)-2-(1-(4-Chlorophenyl)ethylidene)-*N*,*N*,*N*',*N*'-Tetramethylhydrazine-1,1-Dicarboxamide (5i)



27.9 mg, 90% yield; white solid, mp: 167−168 °C; TLC (petroleum ether/ethyl acetate, 1:2 v/v): R_f = 0.23; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 3.00 (s, 12H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 157.6, 136.0, 136.0, 128.5, 128.0, 37.3, 16.7; IR (KBr): 2932, 1683, 1488, 1378, 1264, 1176, 1089 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{14}H_{19}ClN_4O_2$+H, 311.1269; found, 311.1268.

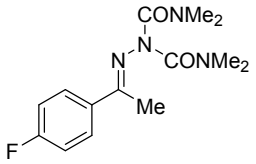
(*E*)-2-(1-(3-Chlorophenyl)ethylidene)-*N*,*N*,*N*',*N*'-Tetramethylhydrazine-1,1-Dicarboxamide (5j)



28.2 mg, 91% yield; white solid, mp: 156−157 °C; TLC (petroleum ether/ethyl acetate, 1:2 v/v): R_f

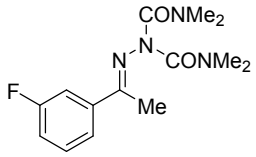
= 0.23; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82−7.83 (m, 1H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.31 (t, *J* = 8.0 Hz, 1H), 3.01 (s, 12H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6, 157.5, 139.4, 134.4, 129.9, 129.5, 126.8, 124.9, 37.3, 16.9; IR (KBr): 2929, 1681, 1487, 1377, 1264, 1174, 1066 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{14}H_{19}ClN_4O_2$+H, 311.1269; found, 311.1267.

(*E*)-2-(1-(4-Fluorophenyl)ethylidene)-*N*,*N*,*N*',*N*'-Tetramethylhydrazine-1,1-Dicarboxamide (5k)



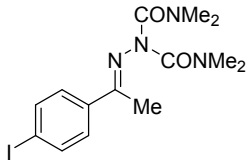
25.6 mg, 87% yield; white solid, mp: 137−138 °C; TLC (petroleum ether/ethyl acetate, 1:2 v/v): R_f = 0.23; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80−7.84 (m, 2H), 7.05 (t, *J* = 8.8 Hz, 2H), 3.00 (s, 12H), 2.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9 (d, $^1J_{F\text{-}C}$ = 248.3 Hz), 162.3, 157.7, 133.7 (d, $^4J_{F\text{-}C}$ = 3.3 Hz), 128.7 (d, $^3J_{F\text{-}C}$ = 8.4 Hz), 115.2 (d, $^2J_{F\text{-}C}$ = 21.7 Hz), 37.6, 16.8; IR (KBr): 2929, 1680, 1495, 1378, 1264, 1165, 1070 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{14}H_{19}FN_4O_2$+H, 295.1565; found, 295.1562.

(*E*)-2-(1-(3-Fluorophenyl)ethylidene)-*N*,*N*,*N*',*N*'-Tetramethylhydrazine-1,1-Dicarboxamide (5l)



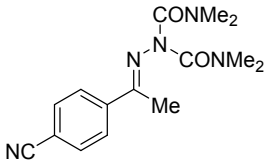
24.4 mg, 83% yield; yellow solid, mp: 139−140 °C; TLC (petroleum ether/ethyl acetate, 1:2 v/v): R_f = 0.24; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.4 Hz, 2H), 7.34 (q, *J* = 7.2 Hz, 1H), 7.09 (t, *J* = 8.0 Hz, 1H), 3.00 (s, 12H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7 (d, $^1J_{F\text{-}C}$ = 243.9 Hz), 161.6 (d, $^7J_{F\text{-}C}$ = 2.3 Hz), 157.6, 139.9 (d, $^3J_{F\text{-}C}$ = 7.5 Hz), 129.8 (d, $^3J_{F\text{-}C}$ = 8.1 Hz), 122.5 (d, $^4J_{F\text{-}C}$ = 2.8 Hz), 116.7 (d, $^4J_{F\text{-}C}$ = 2.3 Hz), 113.5 (d, $^2J_{F\text{-}C}$ = 22.9 Hz), 37.3, 16.9; IR (KBr): 2931, 1680, 1487, 1378, 1264, 1170, 1068 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{14}H_{19}FN_4O_2$+H, 295.1565; found, 295.1566.

(*E*)-2-(1-(4-Iodophenyl)ethylidene)-*N*,*N*,*N*',*N*'-Tetramethylhydrazine-1,1-Dicarboxamide (5m)



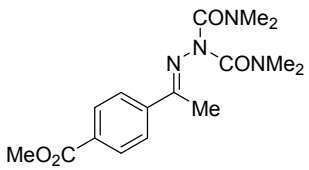
32.6 mg, 81% yield; white solid, mp: 184−185 °C; TLC (petroleum ether/ethyl acetate, 1:2 v/v): R_f = 0.23; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 3.00 (s, 12H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 157.6, 137.4, 137.1, 128.4, 96.5, 37.3, 16.6; IR (KBr): 2928, 1680, 1486, 1380, 1264, 1174, 1071 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{14}H_{19}IN_4O_2$+H, 403.0626; found, 403.0631.

(*E*)-2-(1-(4-Cyanophenyl)ethylidene)-*N*,*N*,*N*',*N*'-Tetramethylhydrazine-1,1-Dicarboxamide (5n)



24.4 mg, 81% yield; white solid, mp: 193−194 °C; TLC (petroleum ether/ethyl acetate, 1:2 v/v): R_f = 0.23; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.6 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 2H), 3.01 (s, 12H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 157.3, 141.7, 132.1, 127.2, 118.6, 113.2, 37.3, 18.6; IR (KBr): 2928, 1681, 1489, 1379, 1264, 1174, 1073 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{15}H_{19}N_5O_2$+H, 302.1612; found, 302.1609.

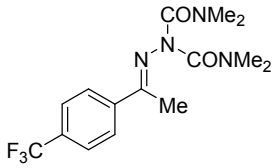
Methyl (*E*)-4-(1-(2,2-Bis(dimethylcarbamoyl)hydrazono)ethyl)benzoate (5o)



30.1 mg, 90% yield; yellow solid, mp: 162−163 °C; TLC (petroleum ether/ethyl acetate, 1:2 v/v): R_f = 0.20; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.4 Hz, 2H), 7.88 (d, *J* = 8.0 Hz, 2H), 3.93 (s, 3H), 3.02 (s, 12H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 161.8, 157.5, 141.7, 131.1,

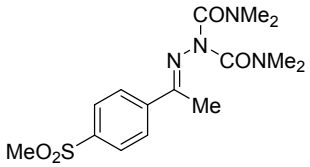
129.5, 126.6, 52.2, 37.3, 17.0; IR (KBr): 2933, 1683, 1490, 1379, 1277, 1180, 1110 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{16}H_{22}N_4O_4$+H, 335.1714; found, 335.1714.

(*E*)-*N*,*N*,*N*',*N*'-Tetramethyl-2-(1-(4-(Trifluoromethyl)phenyl)ethylidene)hydrazine-1,1-Dicarboxamide (5p)



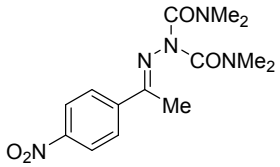
29.9 mg, 87% yield; yellow solid, mp: 176−177 °C; TLC (petroleum ether/ethyl acetate, 1:2 v/v): R_f = 0.24; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 3.01 (s, 12H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 157.5, 141.0, 131.5 (q, $^2J_{F\text{-}C}$ = 31.4 Hz), 127.0, 125.2 (q, $^3J_{F\text{-}C}$ = 3.7 Hz), 124.0 (q, $^1J_{F\text{-}C}$ = 270.4 Hz), 37.3, 16.9; IR (KBr): 2937, 1681, 1485, 1390, 1265, 1166, 1116, 1068 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{15}H_{19}F_3N_4O_2$+H, 345.1533; found, 345.1536.

(*E*)-*N*,*N*,*N*',*N*'-Tetramethyl-2-(1-(4-(Methylsulfonyl)phenyl)ethylidene)hydrazine-1,1-Dicarboxamide (5q)



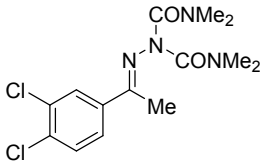
20.2 mg, 57% yield; white solid, mp: 197−198 °C; TLC (petroleum ether/ethyl acetate, 1:2 v/v): R_f = 0.15; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93−8.01 (m, 4H), 3.05 (s, 3H), 3.02 (s, 12H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 157.3, 142.7, 141.3, 127.6, 127.4, 44.5, 37.3, 17.0; IR (KBr): 2930, 1680, 1489, 1383, 1307, 1155, 1082 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{15}H_{22}N_4O_4S$+H, 355.1435; found, 355.1434.

(*E*)-*N*,*N*,*N*',*N*'-Tetramethyl-2-(1-(4-Nitrophenyl)ethylidene)hydrazine-1,1-Dicarboxamide (5r)



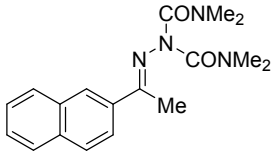
19.6 mg, 61% yield; yellow solid, mp: 197−198 °C; TLC (petroleum ether/ethyl acetate, 1:2 v/v): R_f = 0.20; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 7.2 Hz, 2H), 7.99 (d, *J* = 7.2 Hz, 2H), 3.03 (s, 12H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 157.3, 148.5, 143.5, 127.5, 123.5, 37.3, 17.0; IR (KBr): 2933, 1670, 1503, 1384, 1264, 1172, 1070 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{14}H_{19}N_5O_4$+H, 322.1510; found, 322.1511.

(*E*)-2-(1-(3,4-Dichlorophenyl)ethylidene)-*N*,*N*,*N*',*N*'-Tetramethylhydrazine-1,1-Dicarboxamide (5s)



31.3 mg, 91% yield; white solid, mp: 199−200 °C; TLC (petroleum ether/ethyl acetate, 1:2 v/v): R_f = 0.23; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 3.00 (s, 12H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 157.4, 137.5, 134.0, 132.6, 130.2, 128.6, 125.9, 37.3, 16.7; IR (KBr): 2927, 1678, 1452, 1377, 1261, 1177, 1067 cm^{-1}; HRMS (ESI, m/z): $[M+Na]^+$ Calcd. for $C_{14}H_{18}Cl_2N_4O_2$+Na, 367.0699; found, 367.0696.

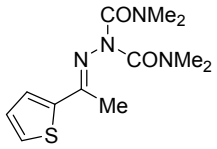
(*E*)-*N*,*N*,*N*',*N*'-Tetramethyl-2-(1-(Naphthalen-2-yl)ethylidene)hydrazine-1,1-Dicarboxamide (5t)



29.3 mg, 90% yield; white solid, mp: 179−180 °C; TLC (petroleum ether/ethyl acetate, 1:2 v/v): R_f = 0.23; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 8.07 (d, *J* = 8.8 Hz, 1H), 7.79−7.87 (m, 3H), 7.47−7.48 (m, 2H), 3.01 (s, 12H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 157.8, 135.1, 134.1, 132.9, 128.7, 127.8, 127.6, 127.0, 127.0, 126.3, 123.9, 37.4, 16.8; IR (KBr): 2930, 1681, 1488, 1377, 1264, 1175, 1067 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{18}H_{22}N_4O_2$+H,

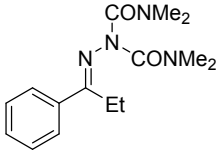
327.1816; found, 327.1814.

(*E*)-*N*,*N*,*N*',*N*'-Tetramethyl-2-(1-(Thiophen-2-yl)ethylidene)hydrazine-1,1-Dicarboxamide (5u)



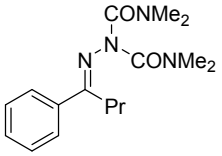
14.9 mg, 53% yield; viscous liquid; TLC (petroleum ether/ethyl acetate, 1:2 v/v): R_f = 0.17; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34−7.36 (m, 2H), 7.03 (t, *J* = 4.4 Hz, 1H), 3.00 (s, 12H), 1.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 157.5, 142.7, 128.7, 127.7, 127.1, 37.4, 16.7; IR (KBr): 2925, 1681, 1488, 1373, 1264, 1172, 1062 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{12}H_{18}N_4O_2S$+H, 283.1223; found, 283.1226.

(*E*)-*N*,*N*,*N*',*N*'-Tetramethyl-2-(1-Phenylpropylidene)hydrazine-1,1-Dicarboxamide (5v)



22.1 mg, 76% yield; viscous liquid; TLC (petroleum ether/ethyl acetate, 1:2 v/v): R_f = 0.23; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71−7.74 (m, 2H), 7.38−7.40 (m, 3H), 3.00 (s, 12H), 2.60 (q, *J* = 7.6 Hz, 2H), 1.05 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 158.3, 136.3, 129.8, 128.3, 127.3, 37.3, 23.3, 10.1; IR (KBr): 2930, 1678, 1488, 1378, 1265, 1183, 1060 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{15}H_{22}N_4O_2$+H, 291.1816; found, 291.1816.

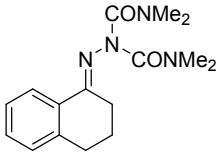
(*E*)-*N*,*N*,*N*',*N*'-Tetramethyl-2-(1-Phenylbutylidene)hydrazine-1,1-Dicarboxamide (5w)



24.3 mg, 80% yield; viscous liquid; TLC (petroleum ether/ethyl acetate, 1:2 v/v): R_f = 0.31; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69−7.71 (m, 2H), 7.34−7.39 (m, 3H), 3.01 (s, 12H), 2.54 (t, *J* = 7.6 Hz, 2H), 1.45−1.52 (m, 2H), 0.90 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 158.3, 136.8, 129.7, 128.33, 127.2, 37.3, 32.5, 19.1, 14.5; IR (KBr): 2934, 1680, 1488, 1379, 1268, 1188,

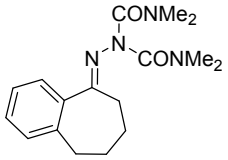
1061 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{16}H_{24}N_4O_2$+H, 305.1972; found, 305.1973.

(*E*)-2-(3,4-Dihydronaphthalen-1(2*H*)-ylidene)-*N*,*N*,*N*',*N*'-Tetramethylhydrazine-1,1-Dicarboxamide (5x)



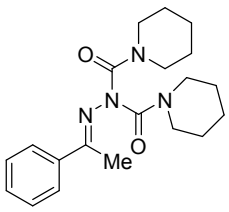
22.3 mg, 74% yield; white solid, mp: 165−166 °C; TLC (petroleum ether/ethyl acetate, 1:2 v/v): R_f = 0.23; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.0 Hz, 1H), 7.29 (t, *J* = 8.0 Hz, 1H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.13 (d, *J* = 7.6 Hz, 1H), 2.99 (s, 12H), 2.83 (t, *J* = 6.0 Hz, 2H), 2.25 (t, *J* = 6.4 Hz, 2H), 1.90 (quint, *J* = 6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 157.9, 140.3, 131.9, 130.1, 128.6, 126.3, 125.9, 37.4, 29.6, 28.4, 22.3; IR (KBr): 2934, 1680, 1488, 1377, 1264, 1180, 1061 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{16}H_{22}N_4O_2$+H, 303.1816; found, 303.1814.

(*E*)-*N*,*N*,*N*',*N*'-Tetramethyl-2-(6,7,8,9-Tetrahydro-5*H*-Benzo[7]annulen-5-ylidene)hydrazine-1,1-Dicarboxamide (5y)



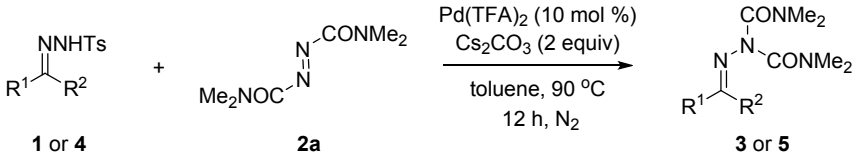
16.1 mg, 51% yield; viscous liquid; TLC (petroleum ether/ethyl acetate, 1:3 v/v): R_f = 0.17; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.6 Hz, 1H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.24 (t, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 7.6 Hz, 1H), 2.99 (s, 12H), 2.76 (t, *J* = 6.4 Hz, 2H), 2.45 (t, *J* = 5.6 Hz, 2H), 1.74−1.79 (m, 2H), 1.61 (quint, *J* = 6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 157.9, 139.1, 137.6, 129.8, 128.6, 127.8, 126.5, 37.3, 30.2, 25.9, 21.3; IR (KBr): 2930, 2861, 1677, 1486, 1376, 1264, 1172, 1062 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{17}H_{24}N_4O_2$+H, 317.1971; found, 317.1971.

(*E*)-*N'*-(1-Phenylethylidene)-*N*-(Piperidine-1-Carbonyl)piperidine-1-Carbohydrazide (5z)



31.7 mg, 89% yield; viscous liquid; TLC (petroleum ether/ethyl acetate, 1:1 v/v): R_f = 0.41; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81−7.84 (m, 2H), 7.37−7.33 (m, 3H),3.47 (brs, 9H), 2.18 (s, 3H), 1.61 (brs, 13H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 156.9, 137.8, 129.8, 128.2, 126.7, 46.1, 25.8, 24.5, 16.8; IR (KBr): 2934, 2856, 1679, 1425, 1225, 1145, 1022 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{20}H_{28}N_4O_2$+H, 357.2285; found, 357.2283.

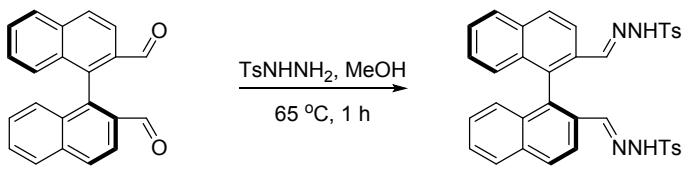
D. Procedure for the Gram-Scale Synthesis of 3a, 5a and 5g



1 or **4** **2a** **3** or **5**

A 250 mL round bottom flask placed with a magnetic stirring bar, *N*-tosylhydrazones (10 mmol), $Pd(TFA)_2$ (10 mol %), Cs_2CO_3 (10 mmol), toluene (100 mL), and azo compound **2a** (5 mmol) was vigorously stirred at 90 °C for 12 h under N_2 in an oil bath. Then the resulting solution was cooled to room temperature, added water (100 mL), extracted with EtOAc (3 × 100 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. Further purification by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate) provided the pure product **3a** (87%, 1.14 g), **5a** (85%, 1.17 g), and **5g** (89%, 1.58 g).

E. Procedure for the Synthesis of Chiral Hydrozones

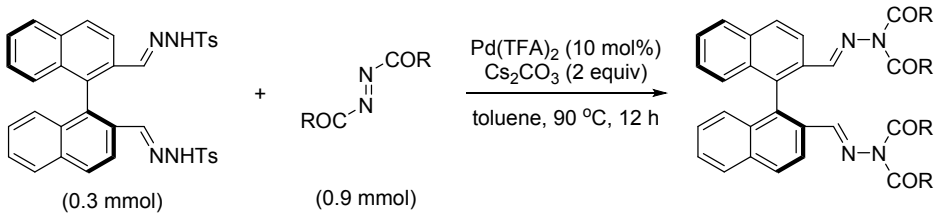


(S)-I **(S)-6a**

A 50 mL round bottom flask placed with a magnetic stirring bar, aldehyde (*S*)-**I**[1] (1.55 g, 5 mmol), $TsNHNH_2$ (2.23 g, 12 mmol), and MeOH (10 mL) was vigorously stirred at 65 °C for 1 h in an oil bath. Then the resulting solution was cooled to room temperature, concentrated *in vacuo*. Further

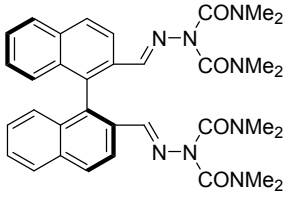
purification by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate) provided the pure product (*S*)-**6a**.

3.17 g, 98% yield; yellow solid, mp > 180 °C (decomposed); $[\alpha]_D^{20}$ = 4.9 (*c* 0.143, CH_2Cl_2); TLC (petroleum ether/ethyl acetate, 3:1 v/v): R_f = 0.40; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.8 Hz, 2H), 7.89 (d, *J* = 8.8 Hz, 2H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.24−7.26 (m, 4H), 7.08−7.12 (m, 4H), 6.89 (d, *J* = 8.4 Hz, 2H), 2.38 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 144.2, 135.2, 134.8, 134.1, 132.9, 130.8, 129.7, 129.1, 127.9, 127.2, 126.6, 122.5, 21.6; IR (KBr): 3034, 2949, 2871, 1678, 1600, 1443, 1358, 1319, 1163, 1071 cm^{-1}; HRMS (ESI, m/z): $[M+Na]^+$ Calcd. for $C_{36}H_{30}N_4O_4S_2$+Na, 669.1601; found, 669.1601.



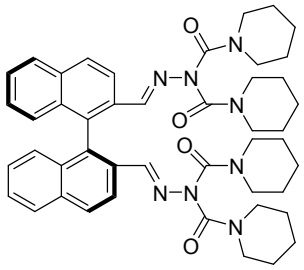
A 25 mL Schlenk tube placed with a magnetic stirring bar, *N*-tosylhydrazone (*S*)-**6a** (0.3 mmol), $Pd(TFA)_2$ (10 mmol %), Cs_2CO_3 (0.6 mmol), toluene (6 mL), and azo compound **2** (0.9 mmol) was vigorously stirred at 90 °C for 12 h under N_2 in an oil bath. Then the resulting solution was cooled to room temperature, added water (10 mL), extracted with EtOAc (3 × 10 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. Further purification by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate) provided the pure product **7**.

2,2'-(((*S*)-[1,1'-Binaphthalene]-2,2'-diyl)bis(methanylylidene))bis(*N*,*N*,*N'*,*N'*-Tetramethylhydrazine-1,1-Dicarboxamide) (7a)



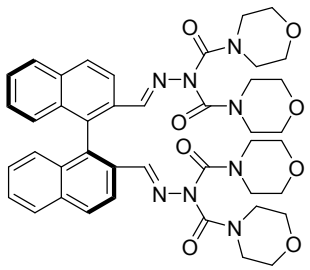
125.0 mg, 67% yield; yellow solid, mp: 141−142 °C; $[\alpha]_D^{20}$ = −7.3 (*c* 0.963, CH_2Cl_2); TLC (ethyl acetate): R_f = 0.30; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.8 Hz, 2H), 7.99 (d, *J* = 8.8 Hz, 2H), 7.94 (d, *J* = 8.4 Hz, 2H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.27−7.31 (m, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 6.94 (s, 2H), 2.72 (s, 24H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 140.2, 134.9, 133.9, 133.2, 131.7, 128.9, 128.3, 127.3, 126.6, 122.1, 37.4; IR (KBr): 2931, 2861, 1693, 1483, 1452, 1374, 1262, 1155, 1057 cm^{-1}; HRMS (ESI, m/z): $[M+Na]^+$ Calcd. for $C_{34}H_{38}N_8O_4$+Na, 645.2908; found, 645.2913.

N′,N‴-(((*S*)-[1,1'-Binaphthalene]-2,2'-diyl)bis(methanylylidene))bis(*N*-(Piperidine-1-Carbonyl)piperidine-1-Carbohydrazide) (7b)



150.0 mg, 64% yield; yellow solid, mp: 127−128 °C; $[\alpha]_D^{20}$ = 34.4 (*c* 0.929, CH_2Cl_2); TLC (ethyl acetate): R_f = 0.30; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.8 Hz, 2H), 7.98 (d, *J* = 8.8 Hz, 2H), 7.93 (d, *J* = 8.0 Hz, 2H), 7.49 (t, *J* = 7.2 Hz, 2H), 7.25−7.29 (m, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 6.98 (s, 2H), 3.15−3.19 (m, 16H), 1.40−1.48 (m, 24H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.0, 139.3, 134.8, 133.6, 133.2, 131.9, 128.9, 128.2, 127.3, 127.2, 126.7, 122.0, 46.4, 25.7, 24.3; IR (KBr): 2937, 2858, 1691, 1420, 1273, 1149, 1023 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{46}H_{54}N_8O_4$+H, 783.4341; found, 783.4337.

N′,N‴-(((*S*)-[1,1'-Binaphthalene]-2,2'-diyl)bis(methanylylidene))bis(*N*-(Morpholine-4-Carbonyl)morpholine-4-Carbohydrazide) (7c)



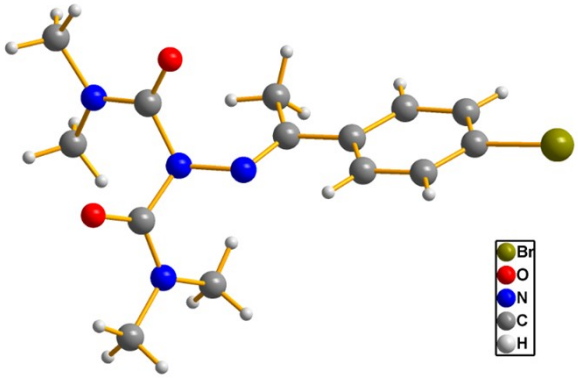
154.1 mg, 65% yield; yellow solid, mp: 147−148 °C; $[\alpha]_D^{20}$ = 41.7 (*c* 0.885, CH_2Cl_2); TLC (ethyl acetate): R_f = 0.30; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.8 Hz, 2H), 8.02 (d, *J* = 8.8 Hz, 2H), 7.97 (d, *J* = 8.0 Hz, 2H), 7.55 (t, *J* = 7.2 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 7.02 (s, 2H), 3.44−3.52 (m, 16H), 3.27−3.36 (m, 16H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8, 140.8, 135.1, 134.0, 133.1, 131.3, 129.2, 128.4, 127.7, 127.6, 126.6, 121.6, 66.4, 45.8; IR (KBr): 2965, 2858, 1694, 1452, 1420, 1269, 1222, 1114, 1006 cm^{-1}; HRMS (ESI, m/z): $[M+Na]^+$ Calcd. for $C_{42}H_{46}N_8O_8$+Na, 813.3331; found, 813.3339.

Reference:

(1) Shen, H.; Tang, J.; Chang, H.; Yang, C.; Liu, R. *J. Org. Chem.* **2005**, *70*, 10113.

F. X-ray Crystallographic Data

The X-ray crystallographic structure for **5g**. ORTEP representation with 50% probability thermal ellipsoids. Solvent and hydrogen are omitted for clarity. Crystal data have been deposited to CCDC, number 1486805.

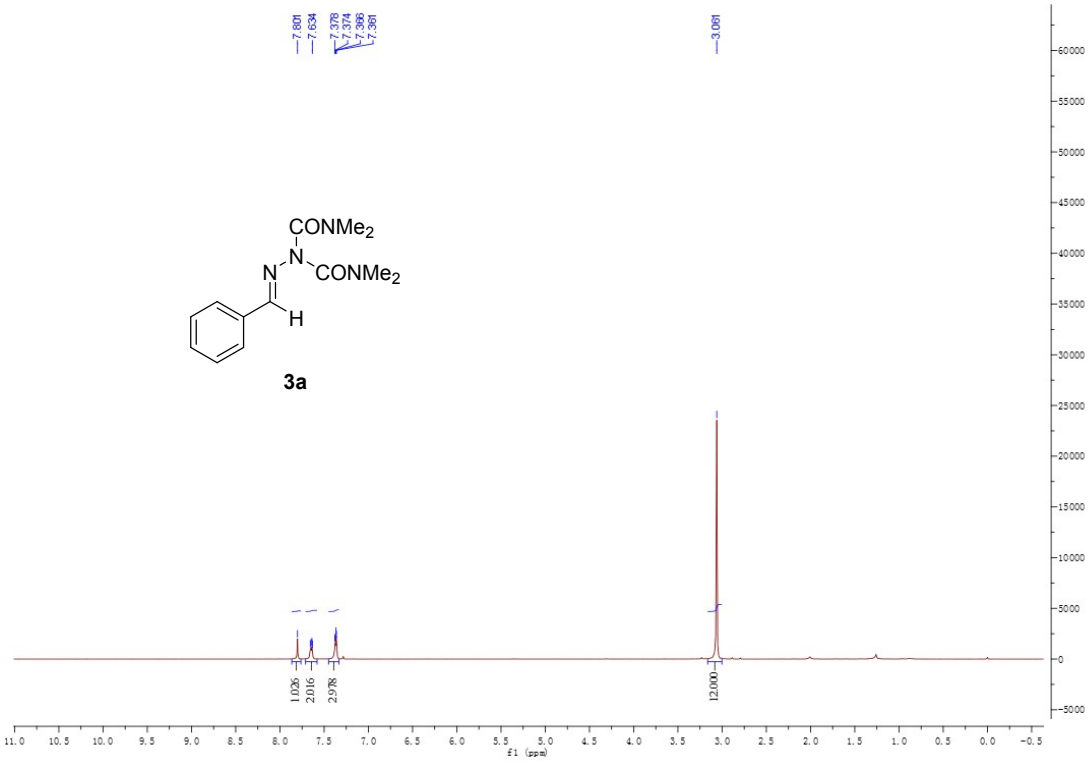


Empirical formula	$C_{14}H_{19}BrN_4O_2$
Formula weight	355.24
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	ORTHORHOMBIC, P2(1)2(1)2(1)

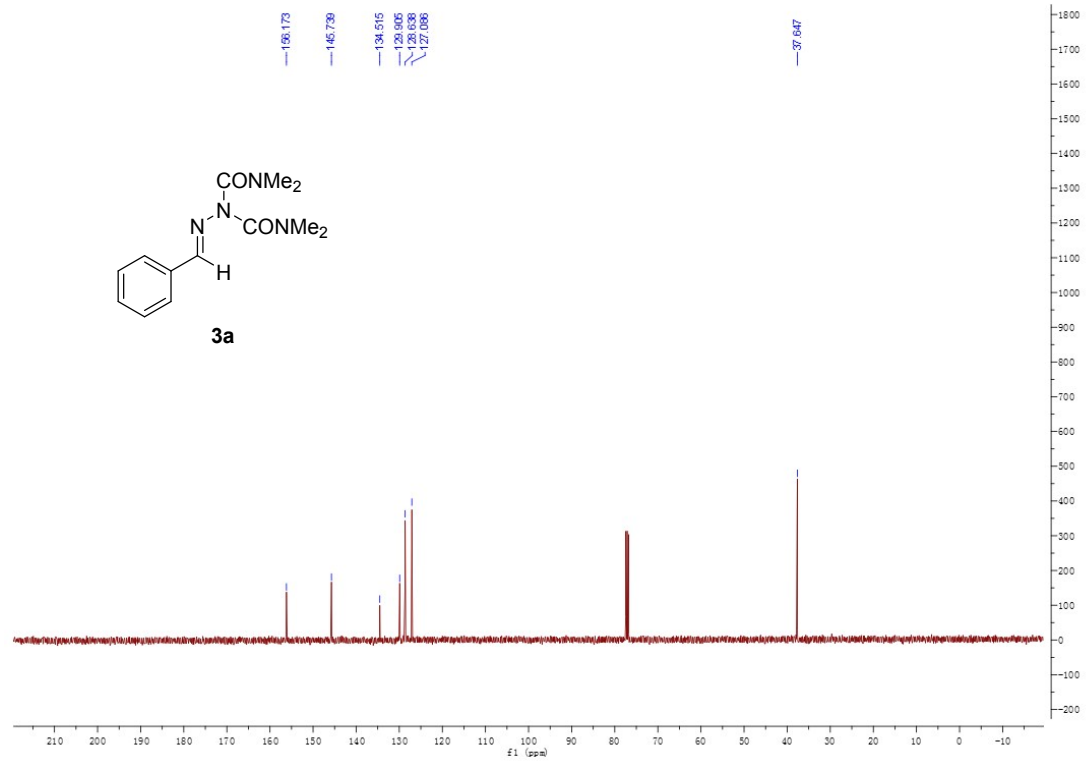
Unit cell dimensions	a = 5.1666(10) Å alpha = 90 deg. b = 12.446(3) Å beta = 90 deg. c = 25.390(5) Å gamma = 90 deg.
Volume	1632.6(6) $Å^3$
Z, Calculated density	4, 1.445 Mg/m^3
Absorption coefficient	2.528 mm^{-1}
F(000)	728
Crystal size	0.10×0.10×0.10 mm
Theta range for data collection	3.21 to 27.46 deg.
Limiting indices	$-6 \leq h \leq 5$, $-16 \leq k \leq 16$, $-32 \leq l \leq 32$
Reflections collected / unique	14756 / 3690 [R(int) = 0.1165]
Completeness to theta = 27.46	99.5%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3690 / 0 / 191
Goodness-of-fit on F^2	0.914
Final R indices [I>2sigma(I)]	R1 = 0.0440, wR2 = 0.0585
R indices (all data)	R1 = 0.1714, wR2 = 0.0743
Extinction coefficient	0.000(4)
Largest diff. peak and hole	0.218 and -0.211 e. $Å^{-3}$

G. NMR Spectra of New Compounds

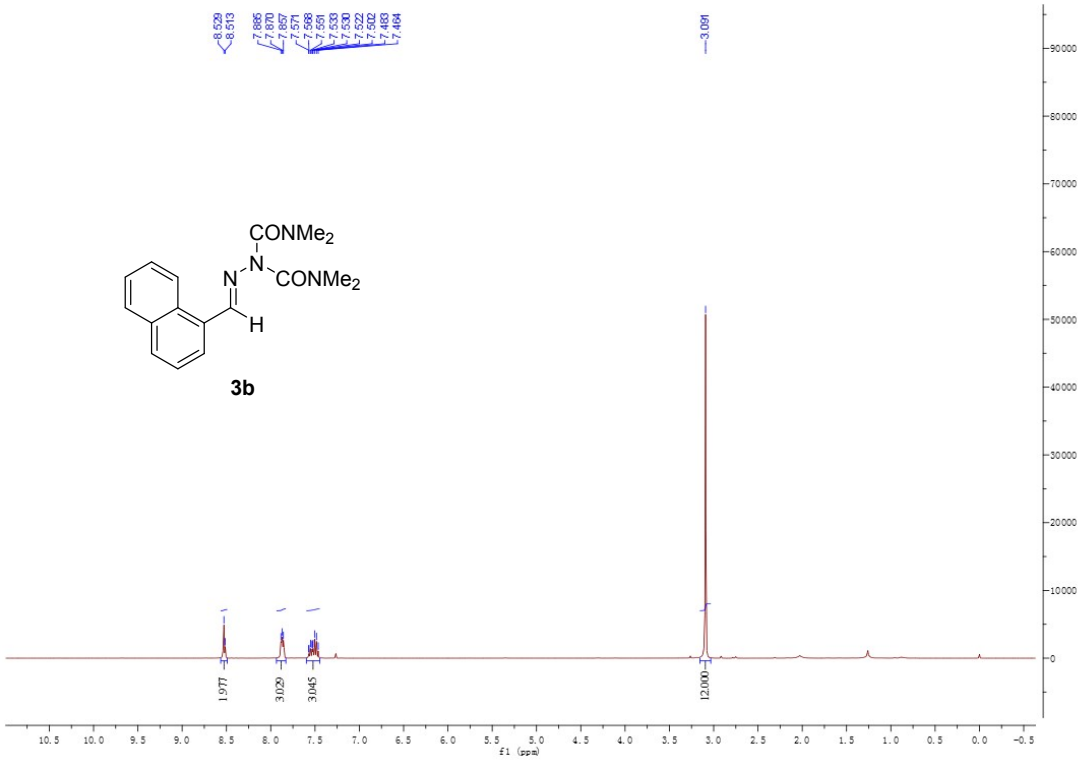
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3a



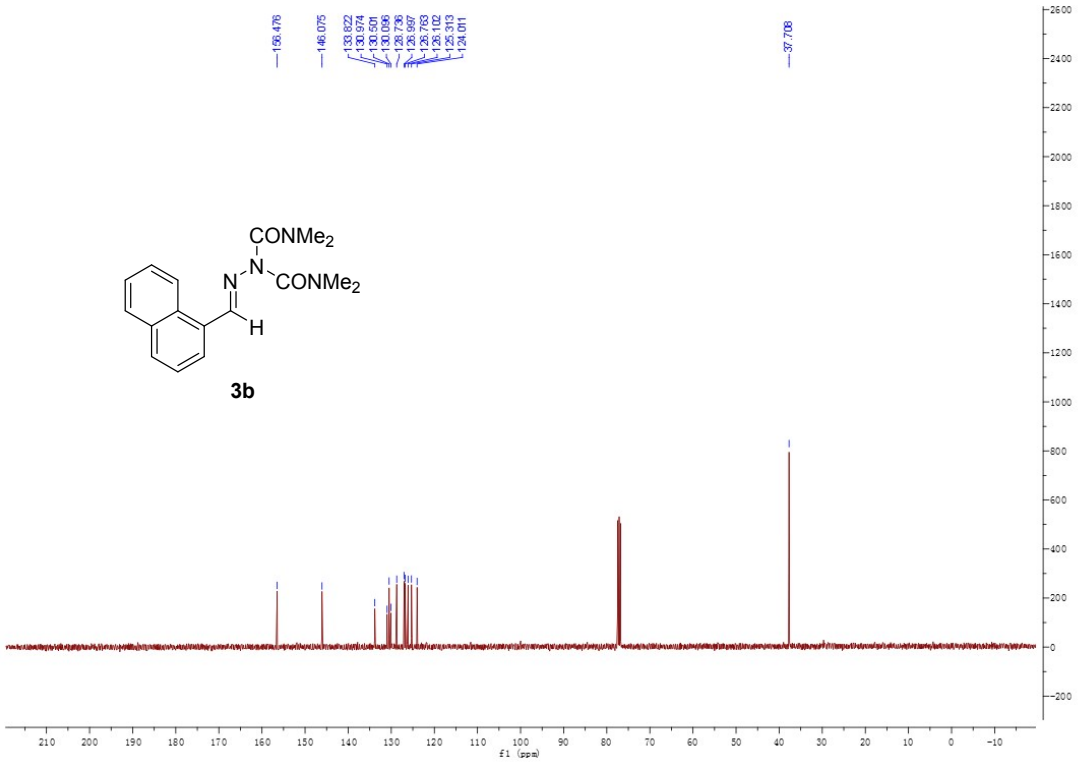
^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 3a



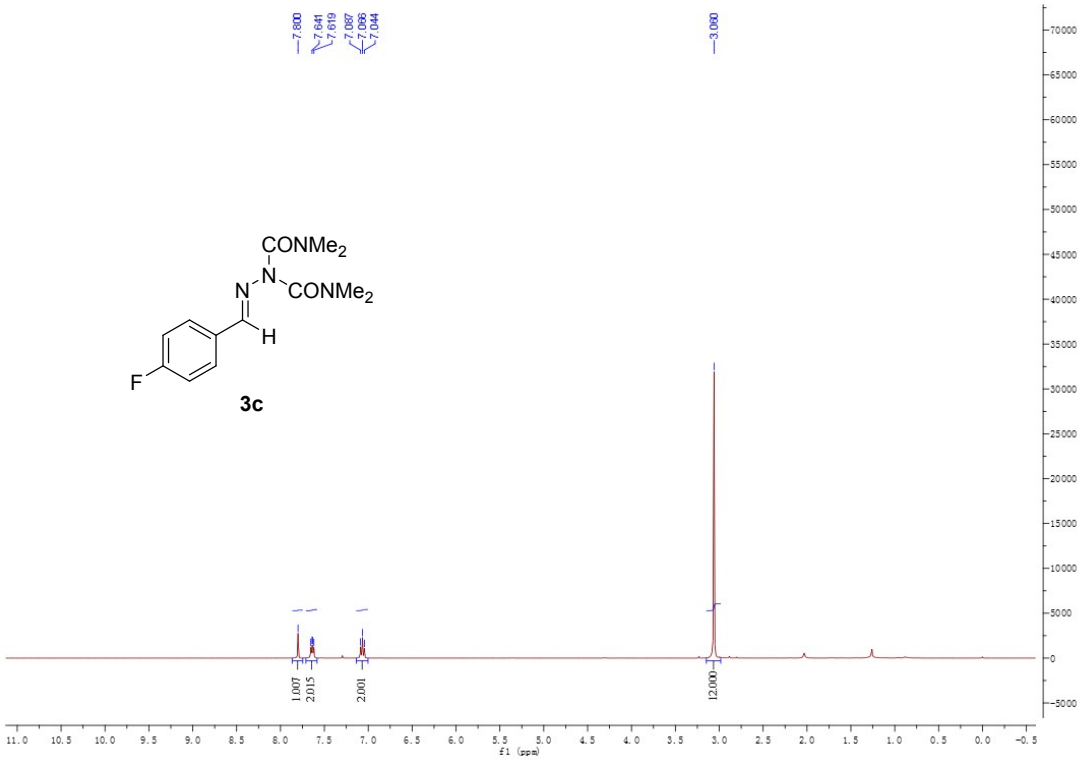
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3b



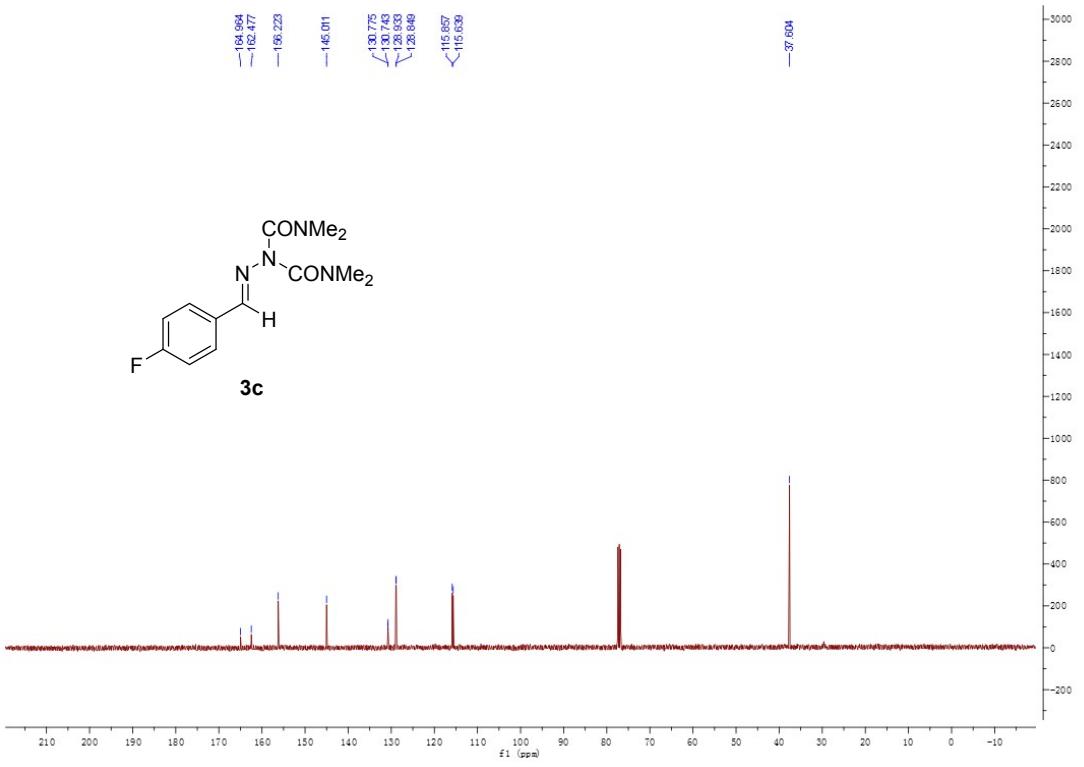
^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 3b



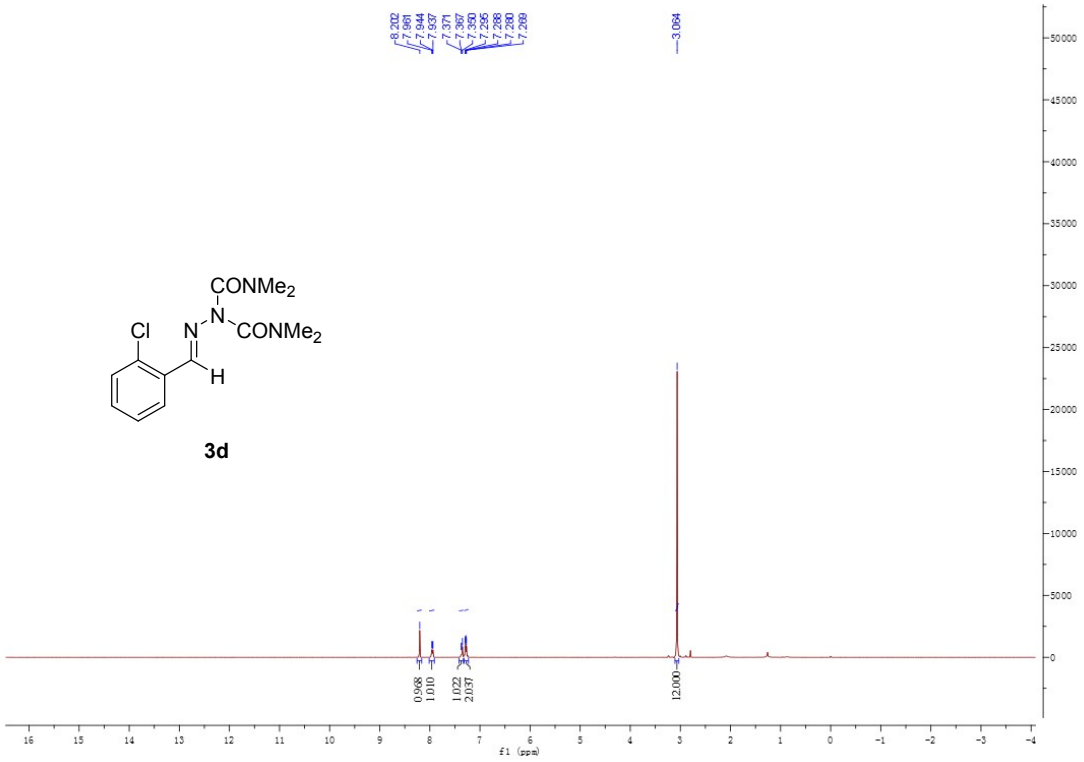
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3c



^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 3c

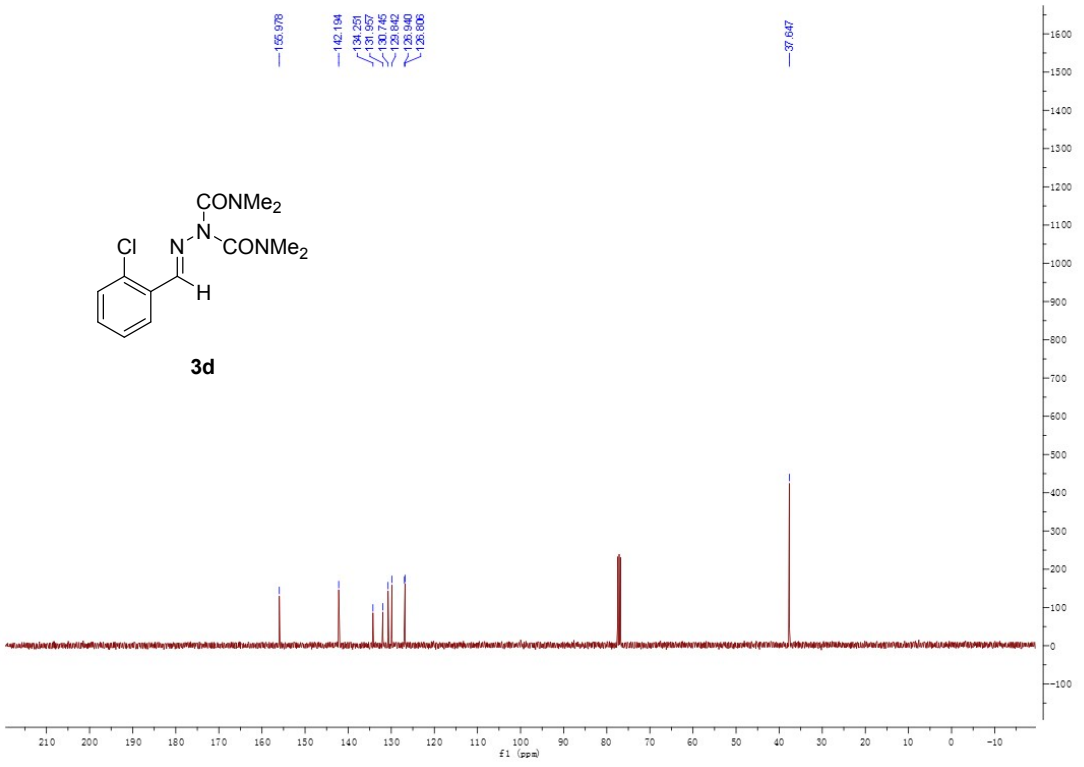


^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3d



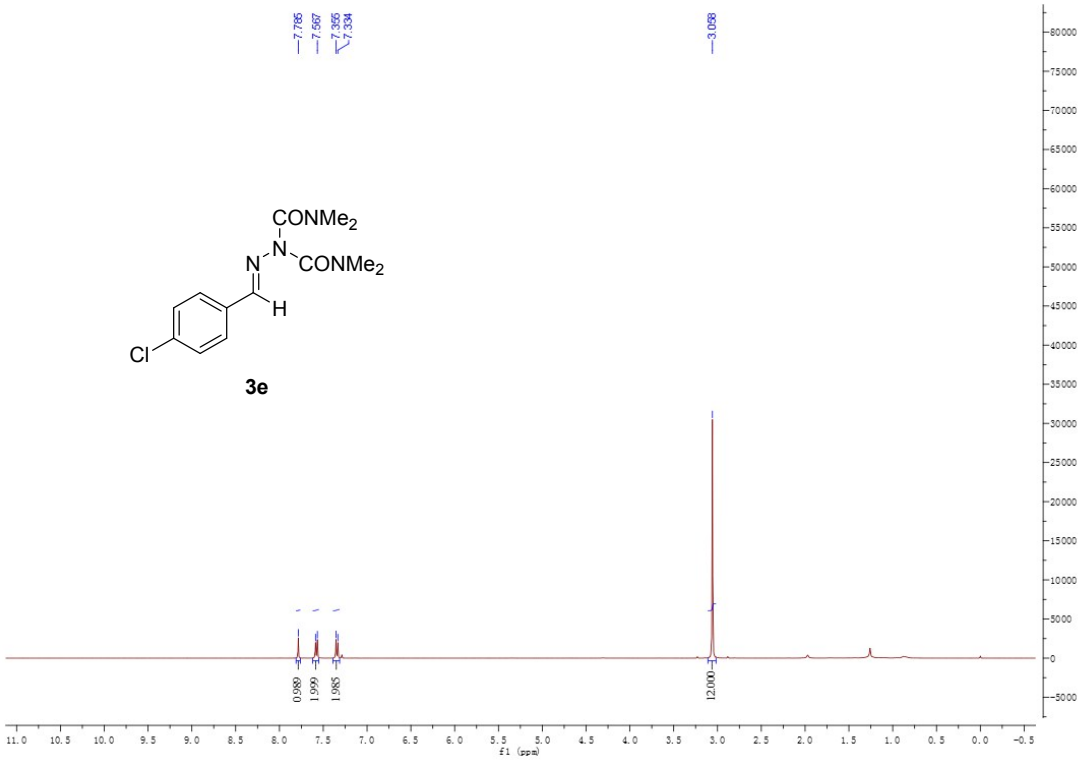
3d

^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 3d



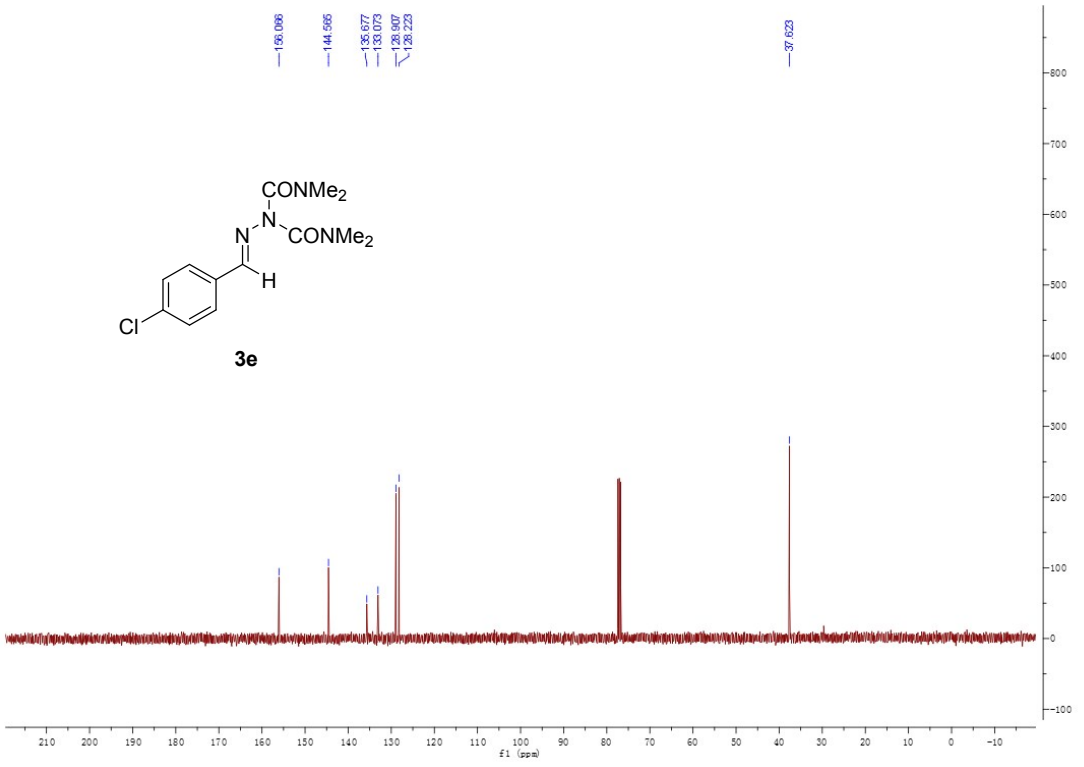
3d

^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3e



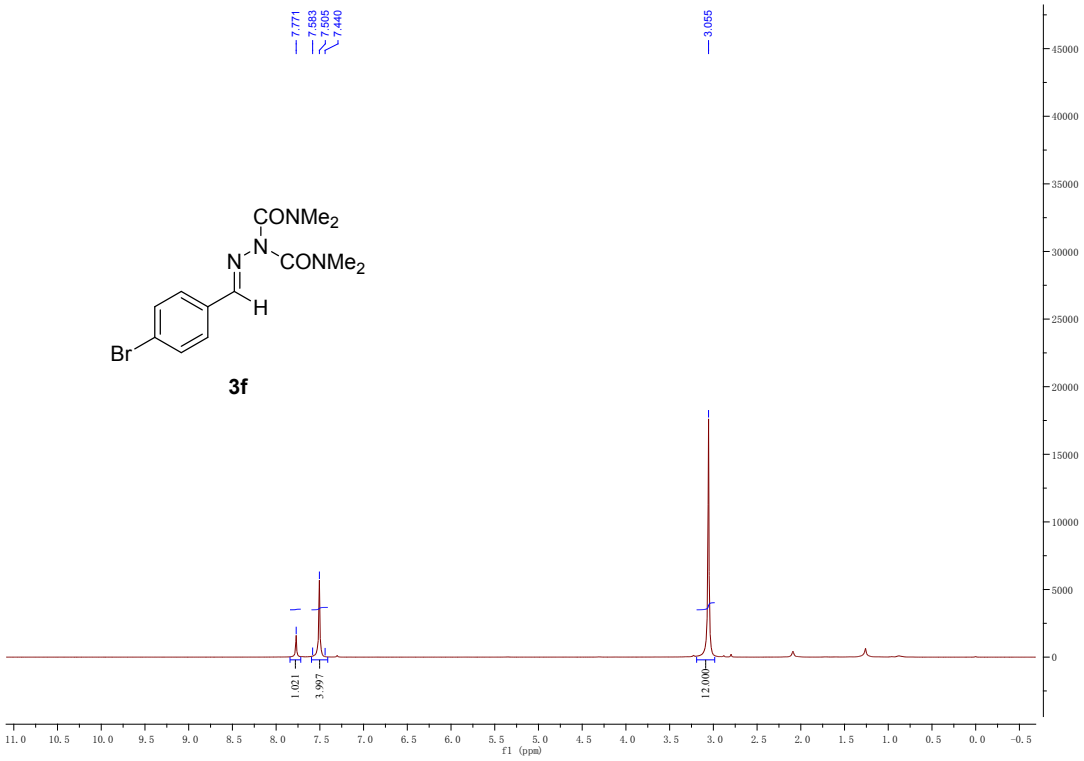
3e

^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 3e

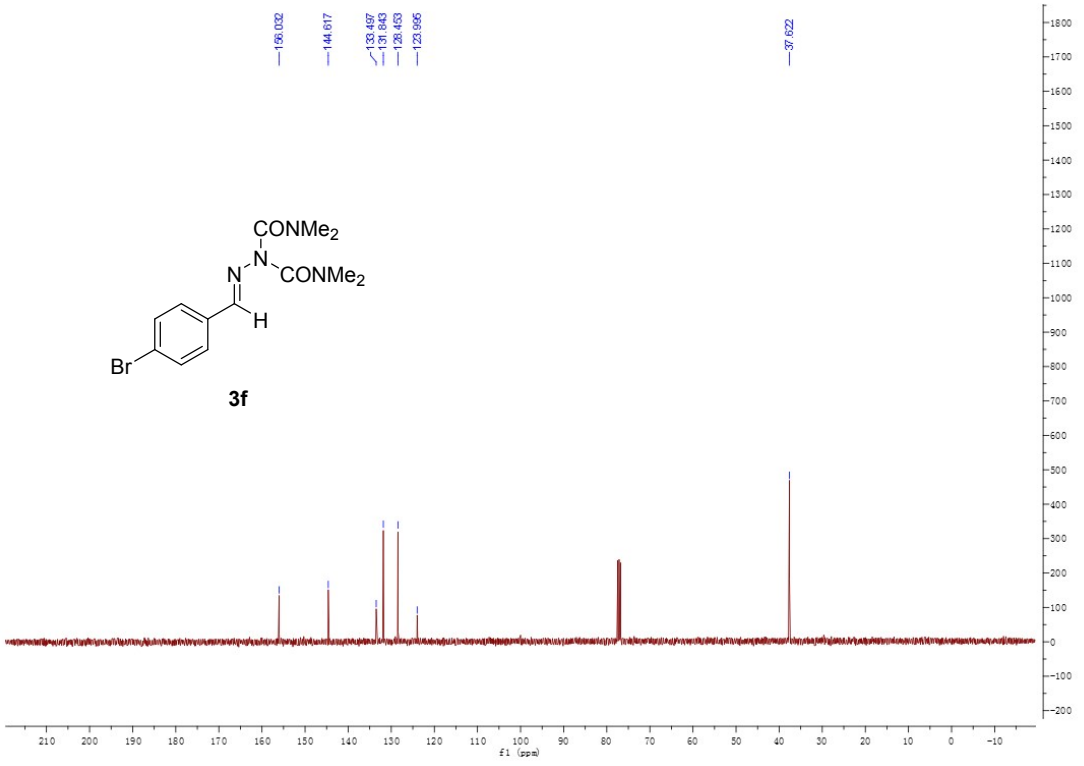


3e

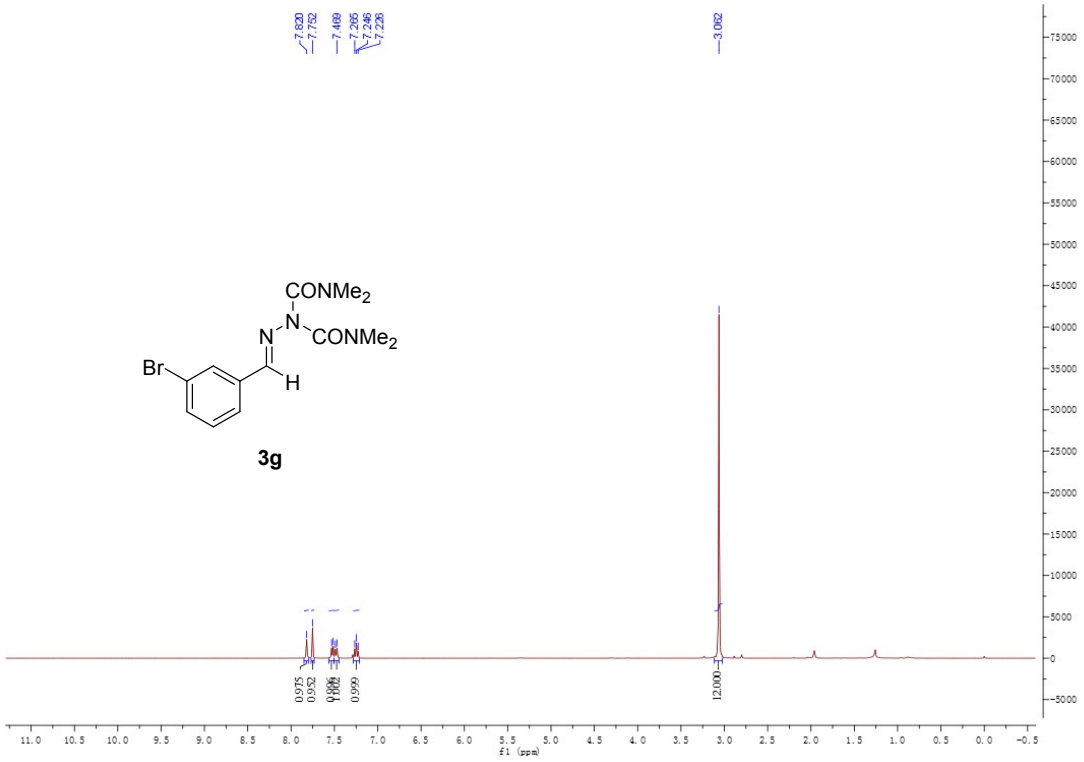
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3f



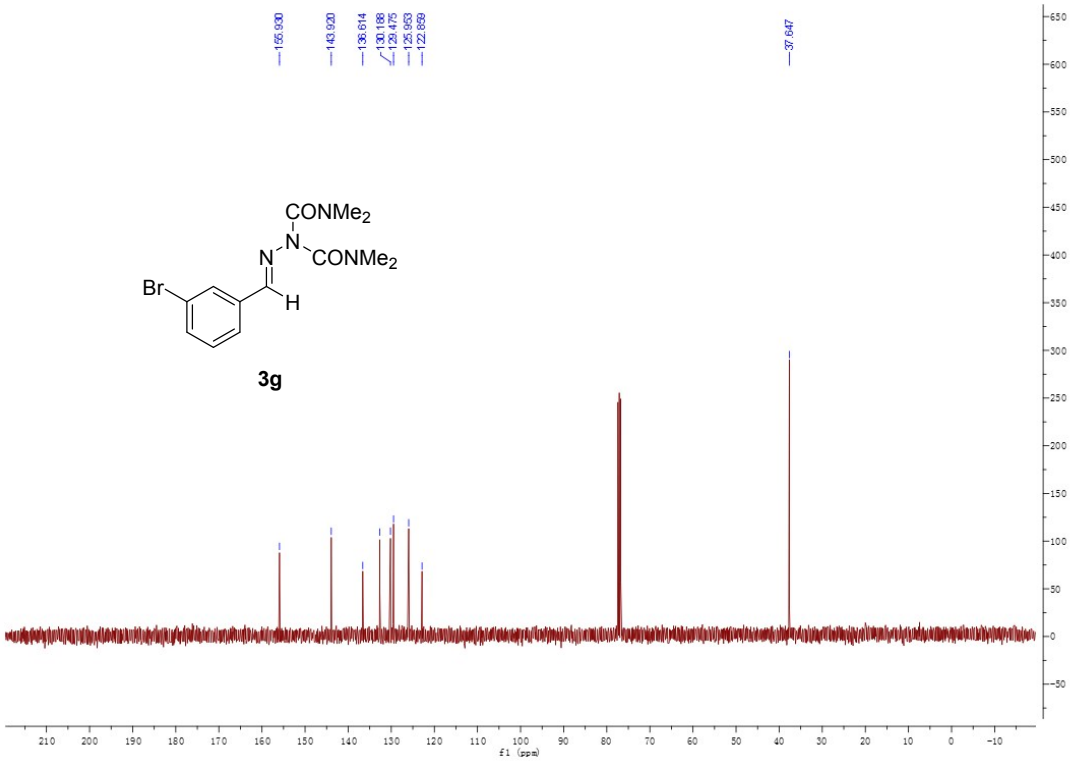
^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 3f



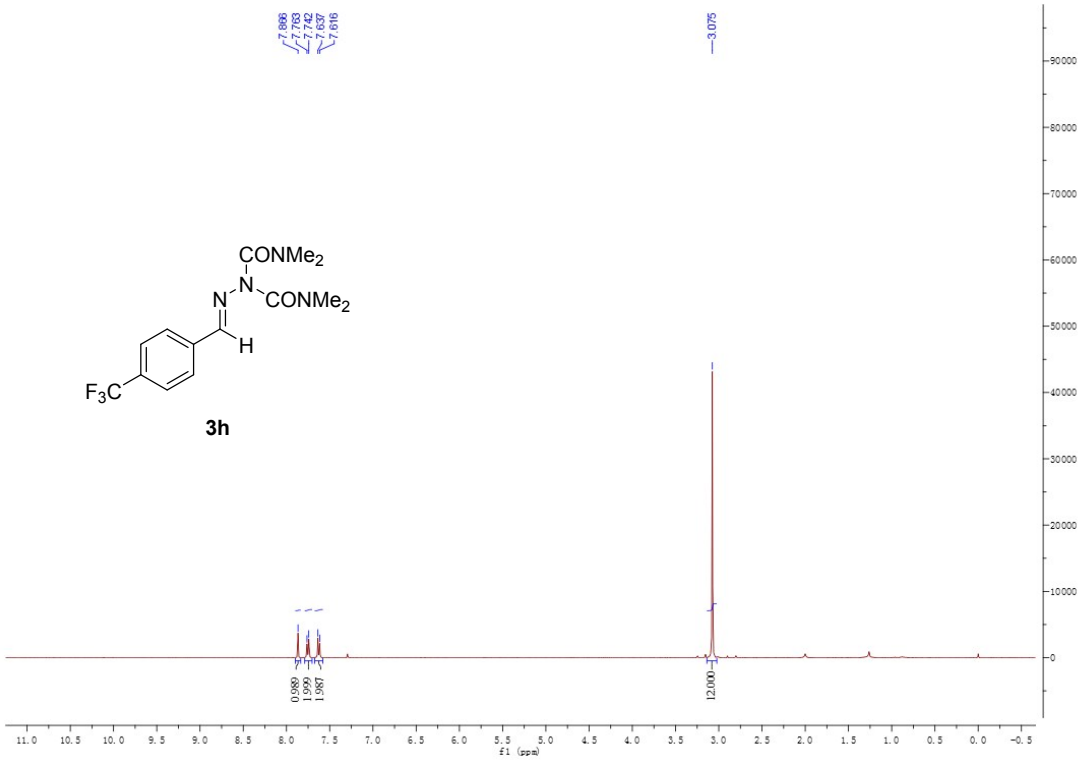
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3g



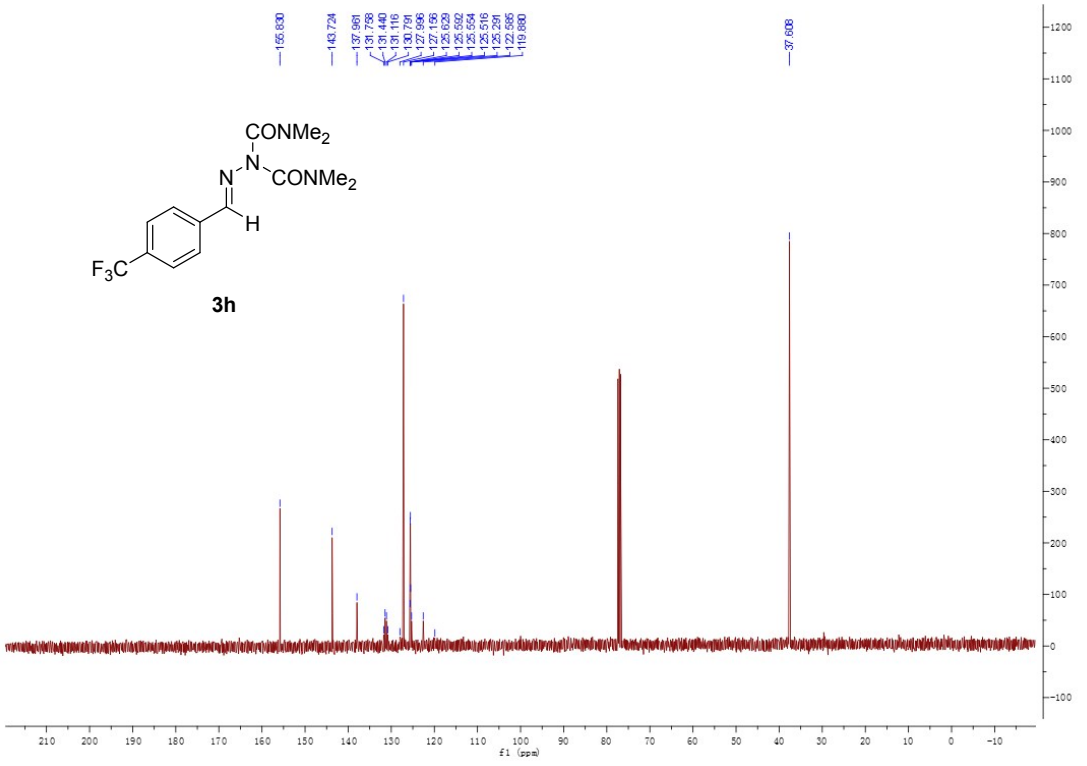
^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 3g



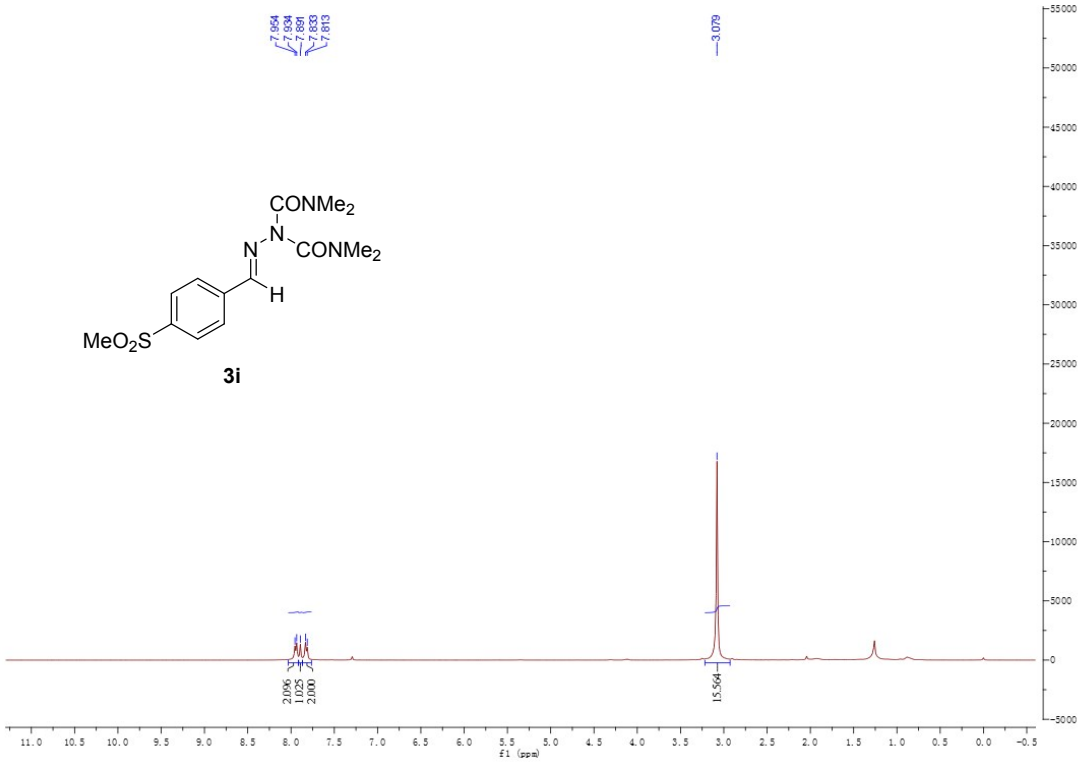
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3h



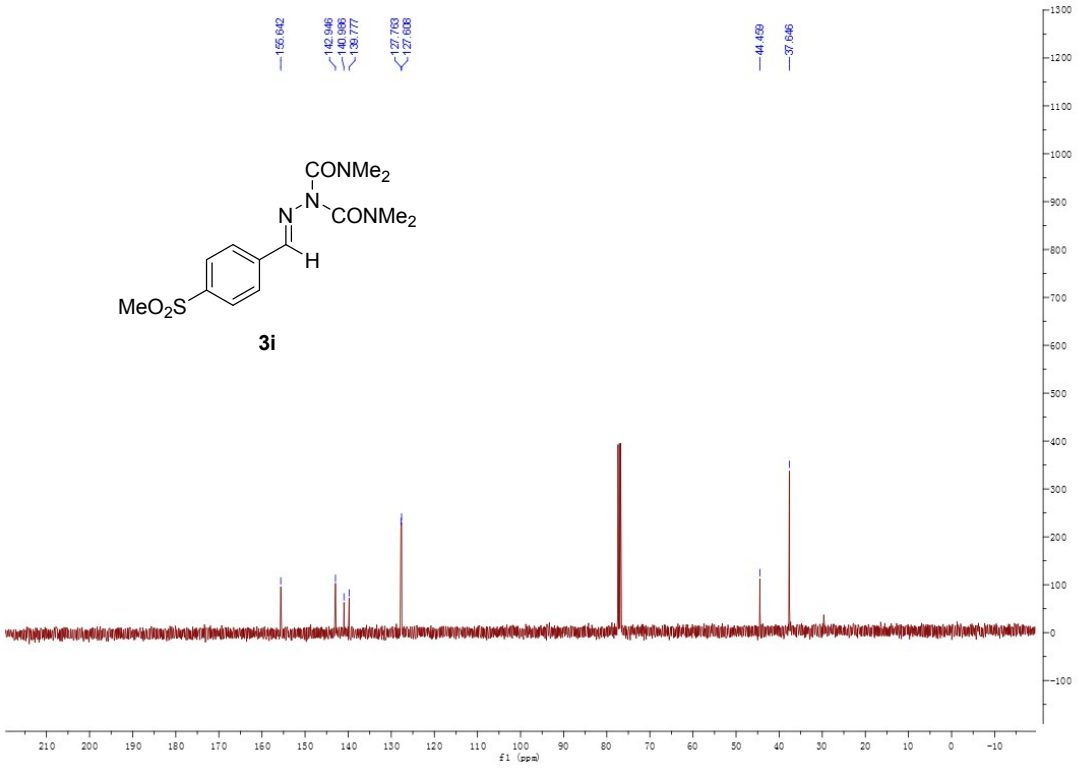
^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 3h



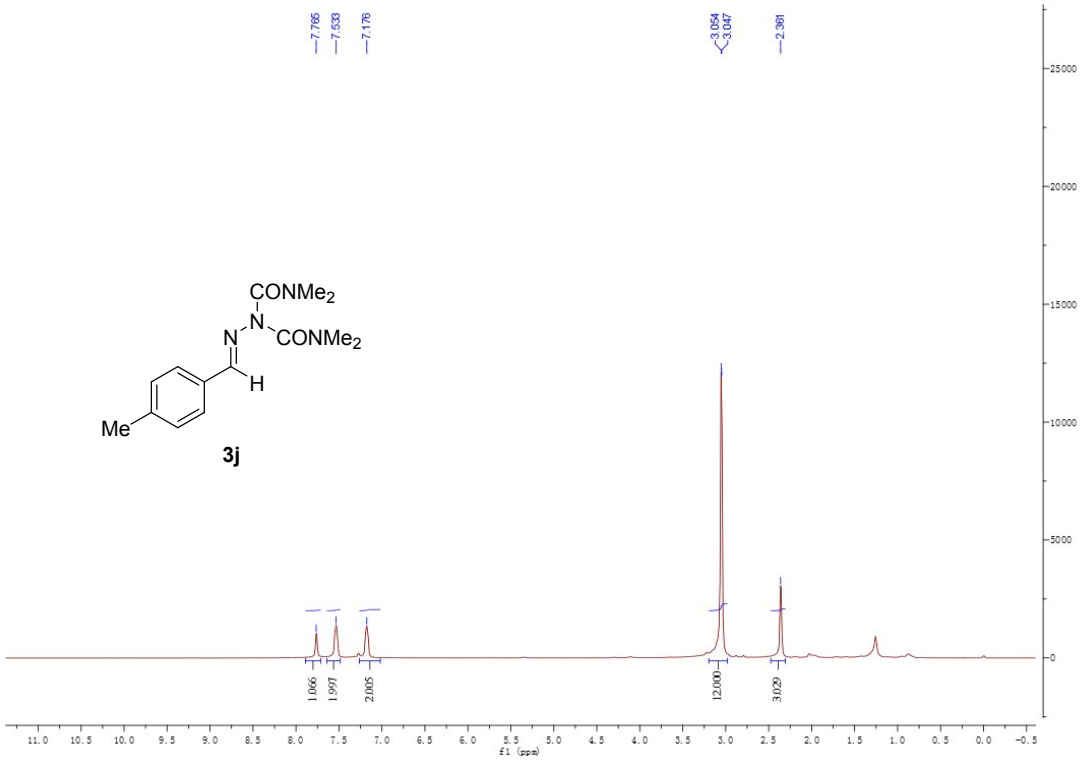
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3i



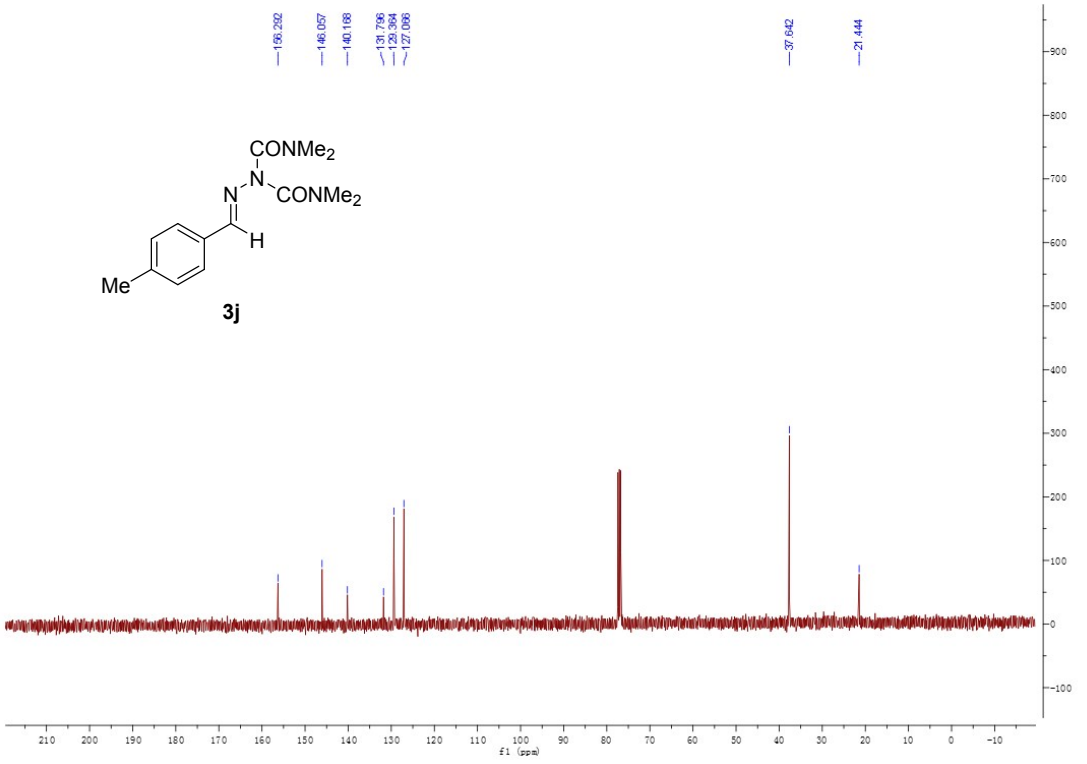
^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 3i



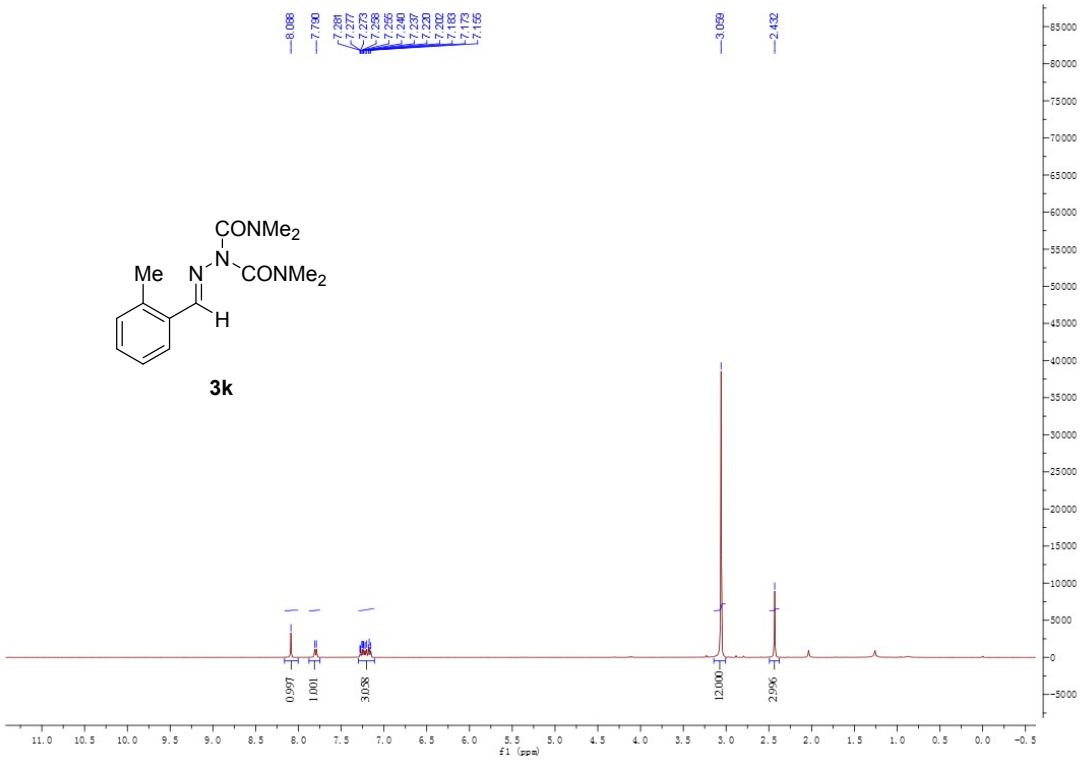
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3j



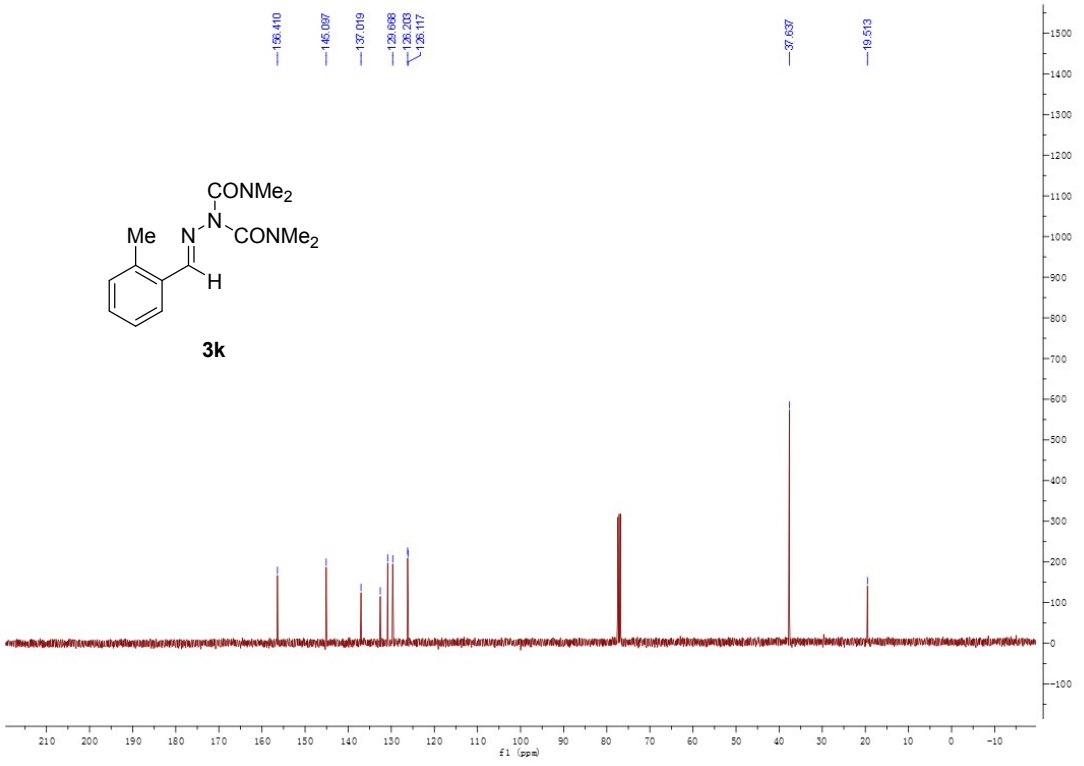
^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 3j



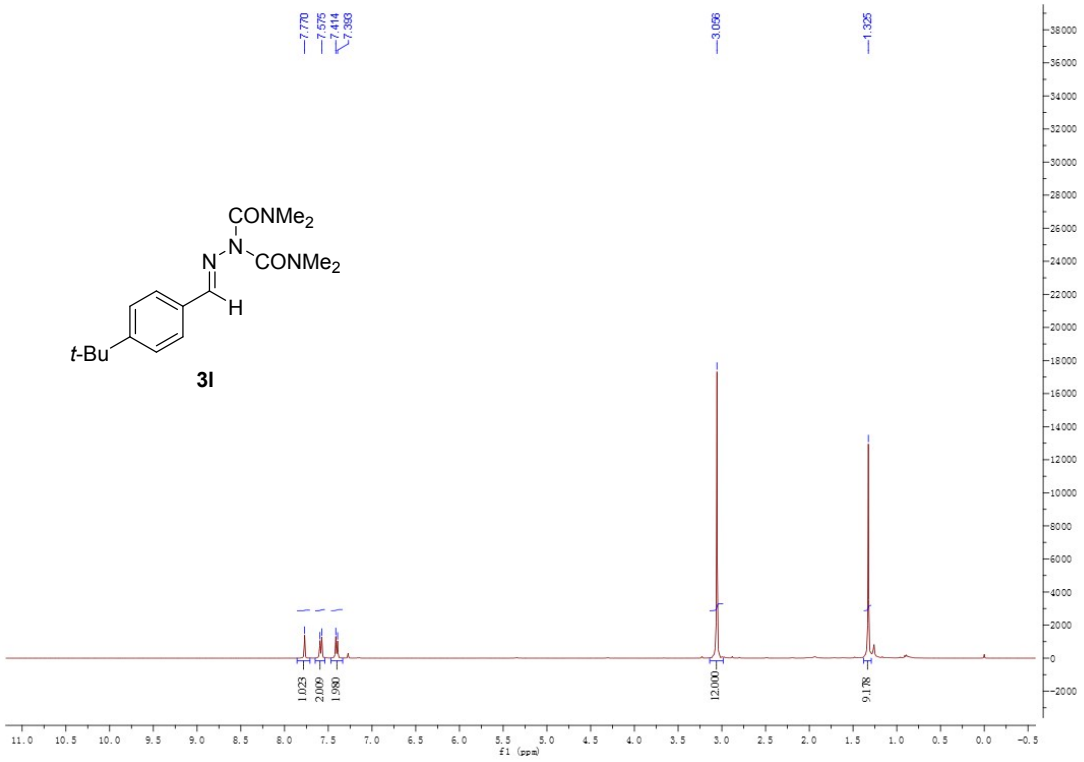
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3k



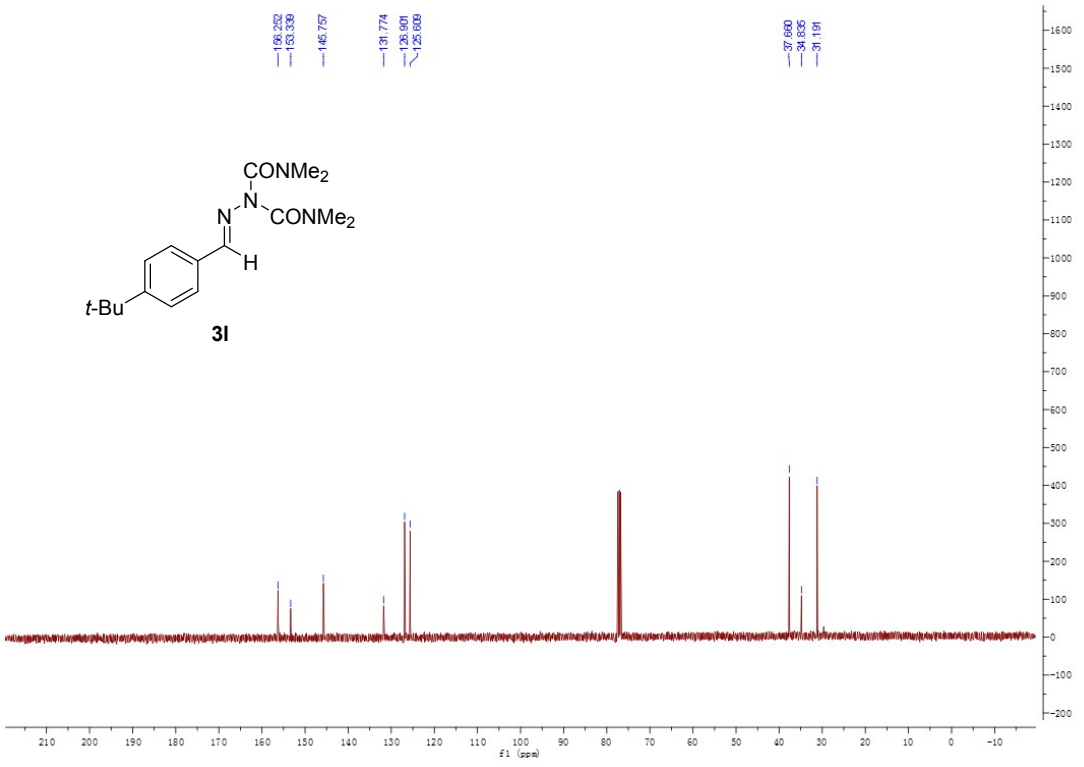
^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 3k



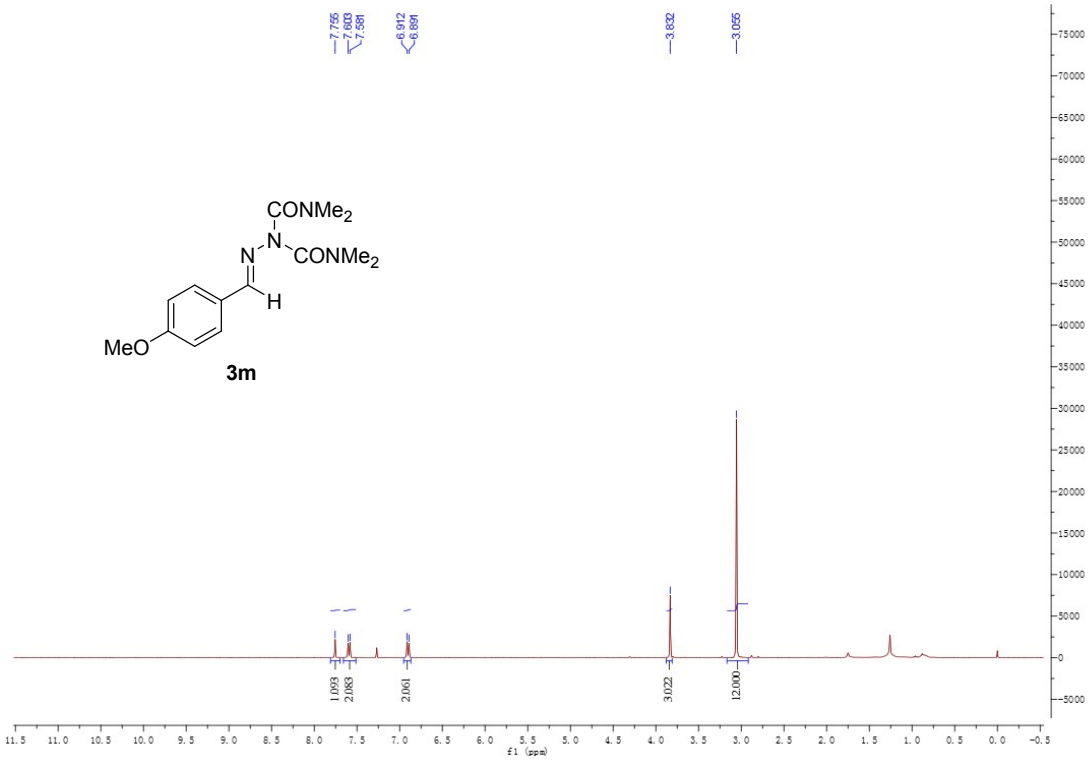
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3l



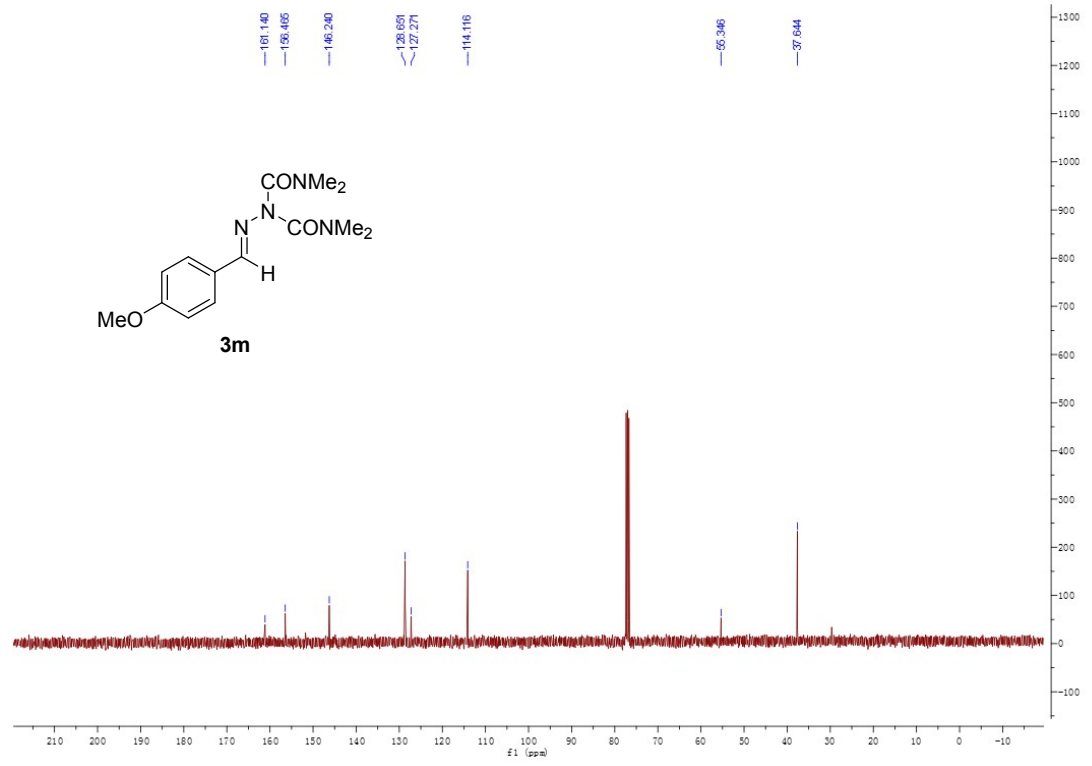
^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 3l



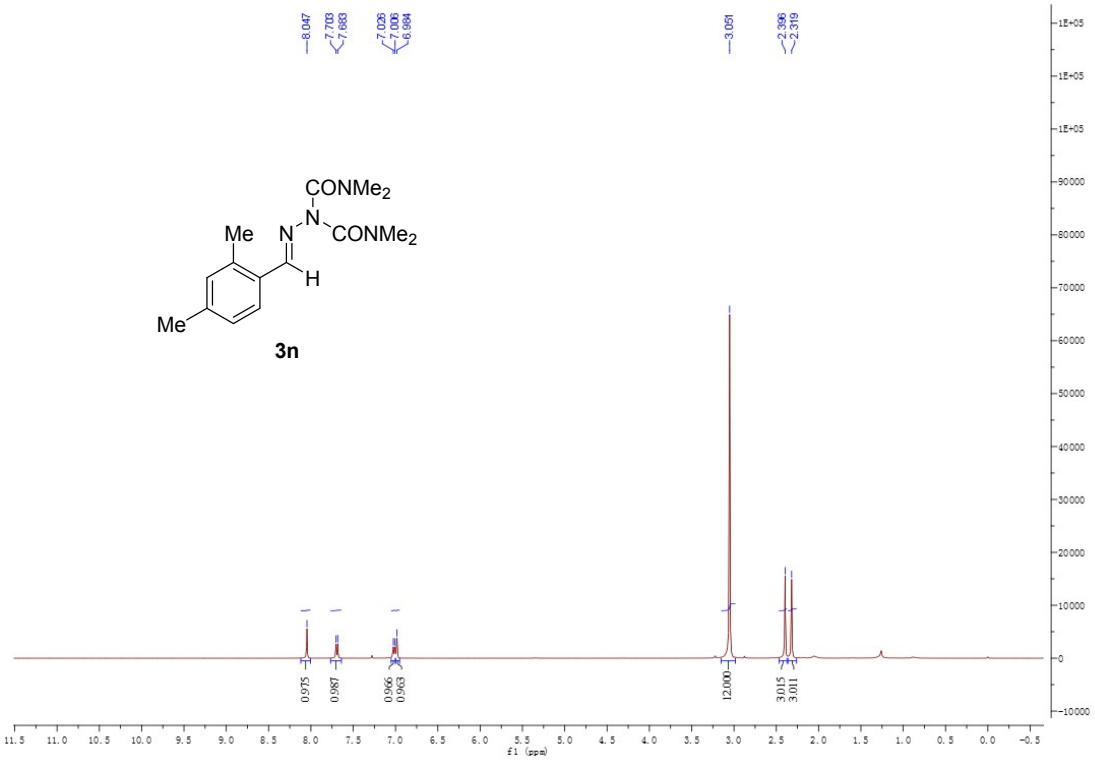
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3m



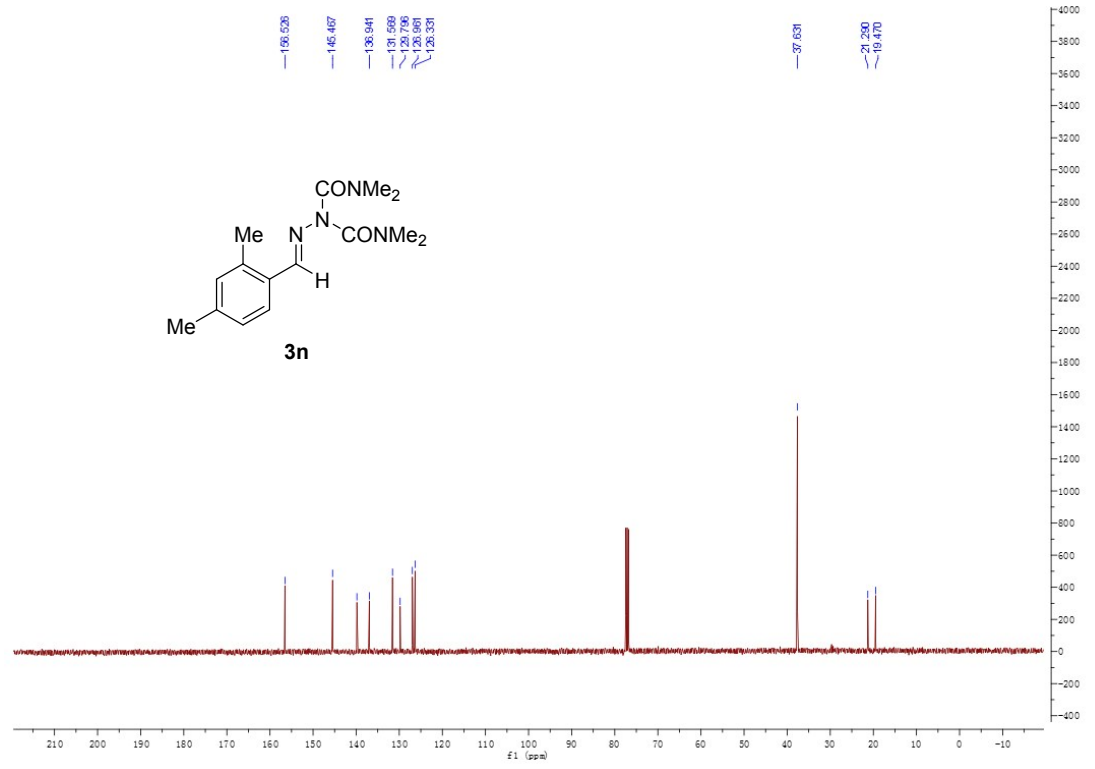
^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 3m



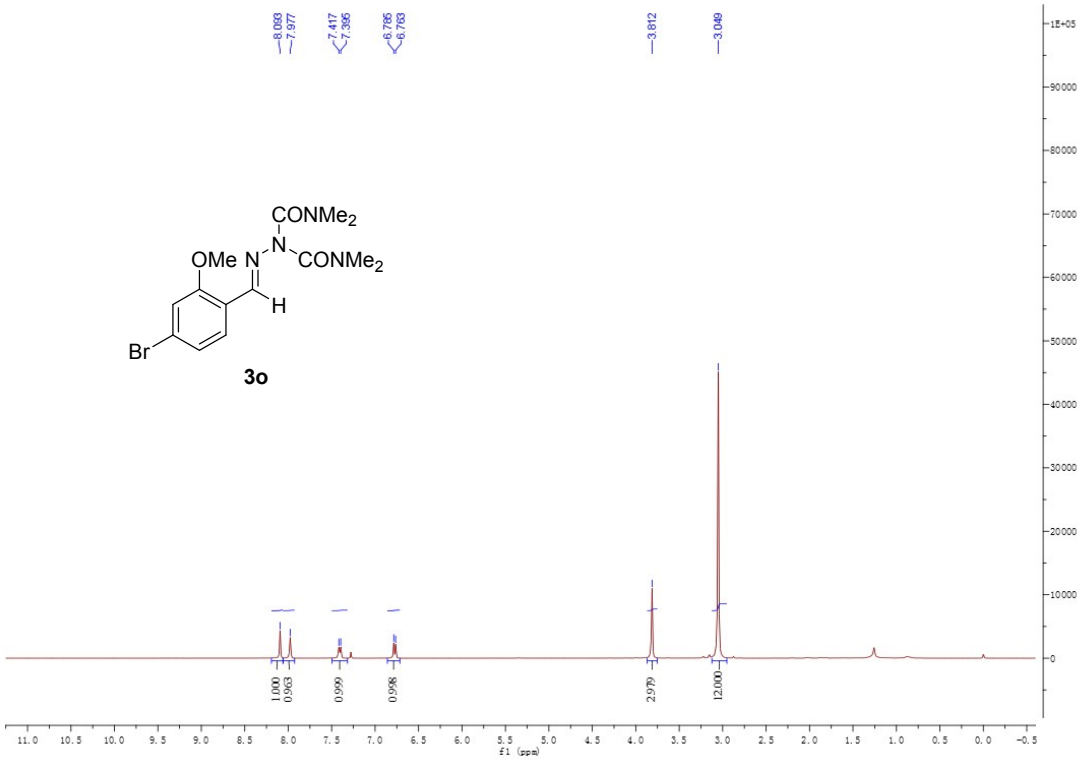
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3n



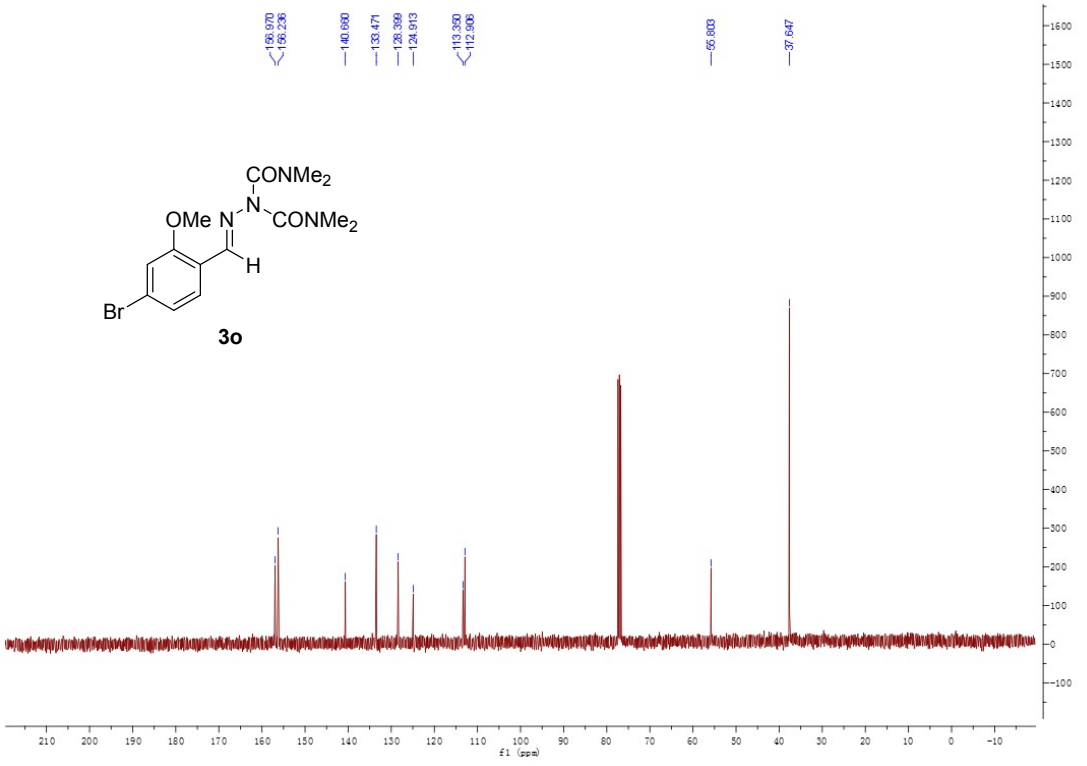
^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 3n



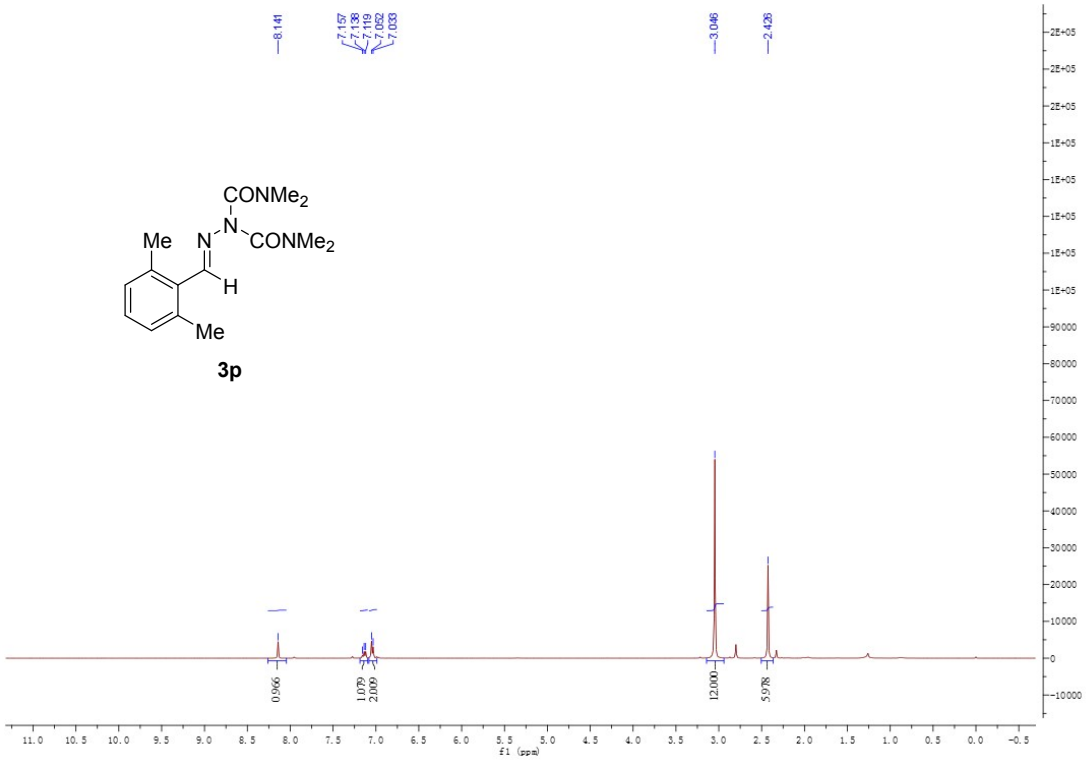
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3o



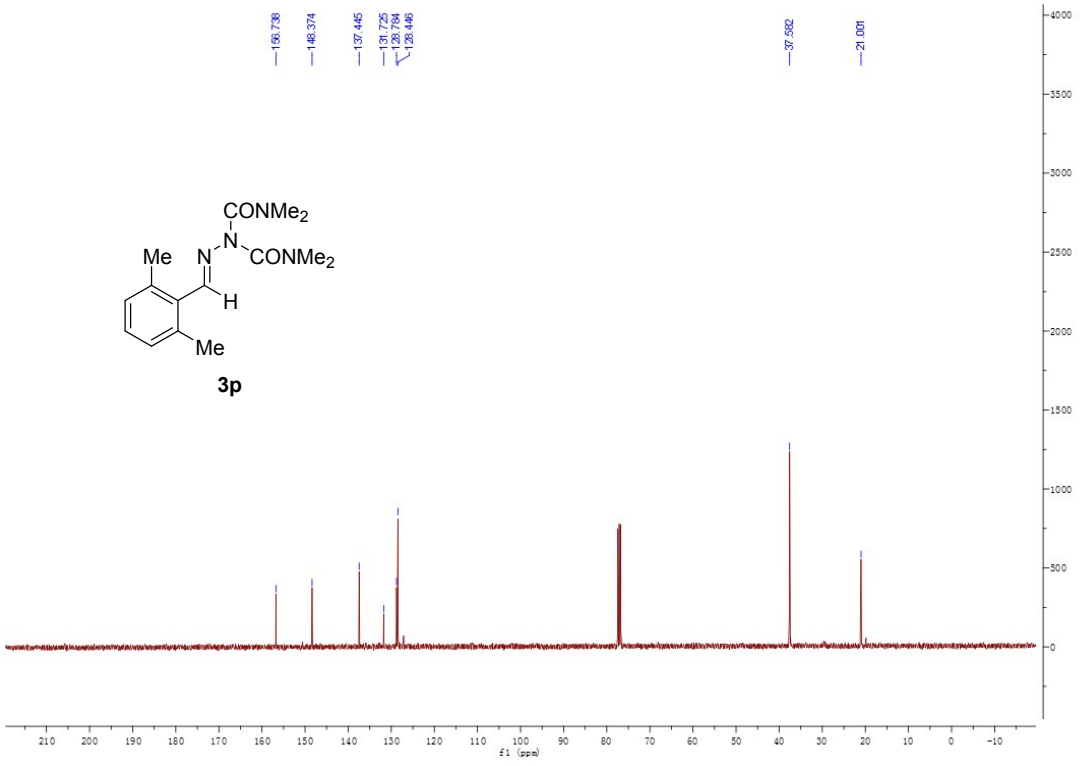
^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 3o



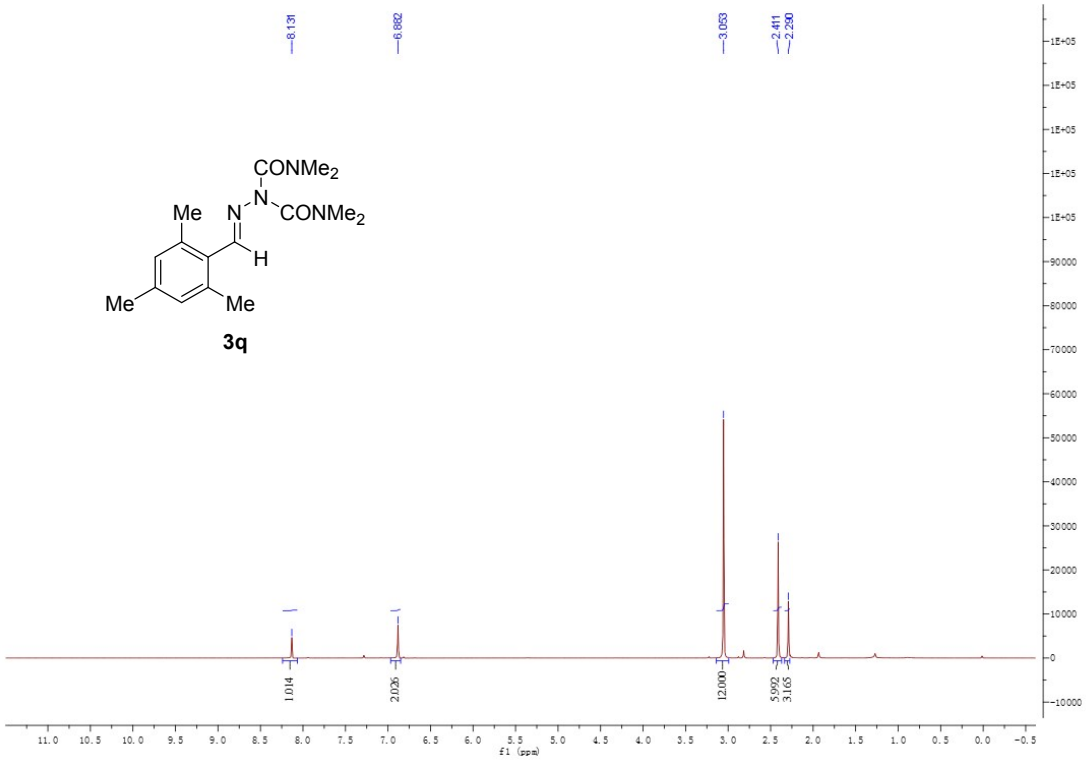
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3p



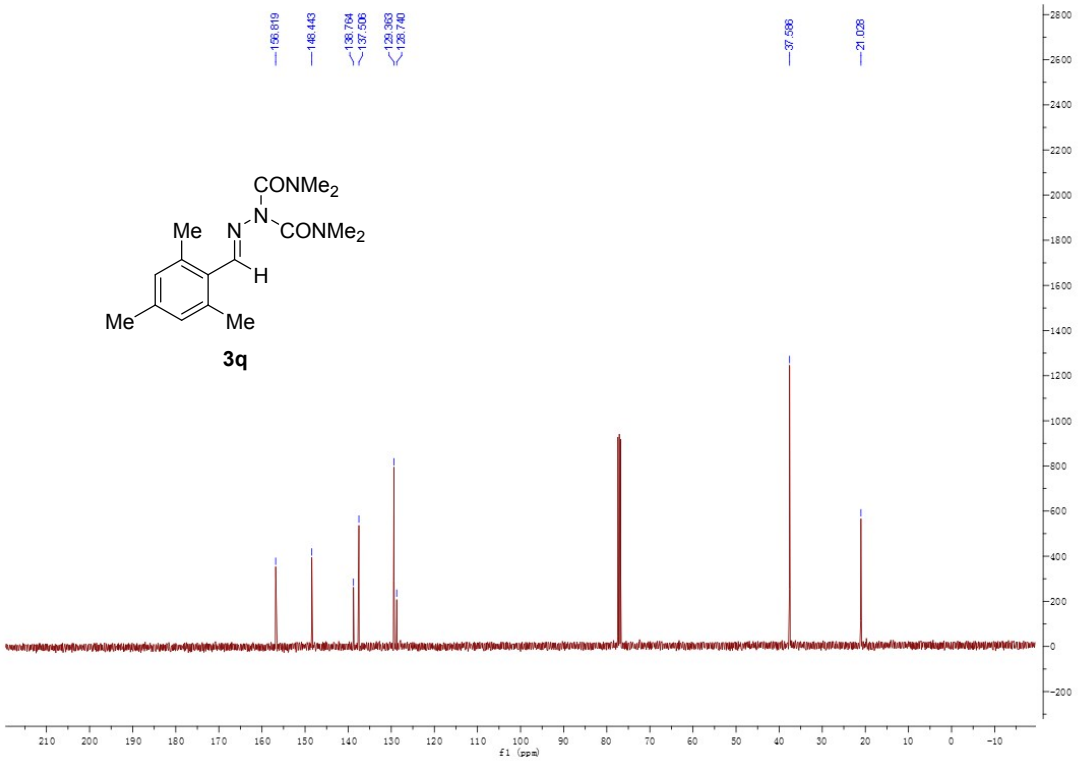
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 3p



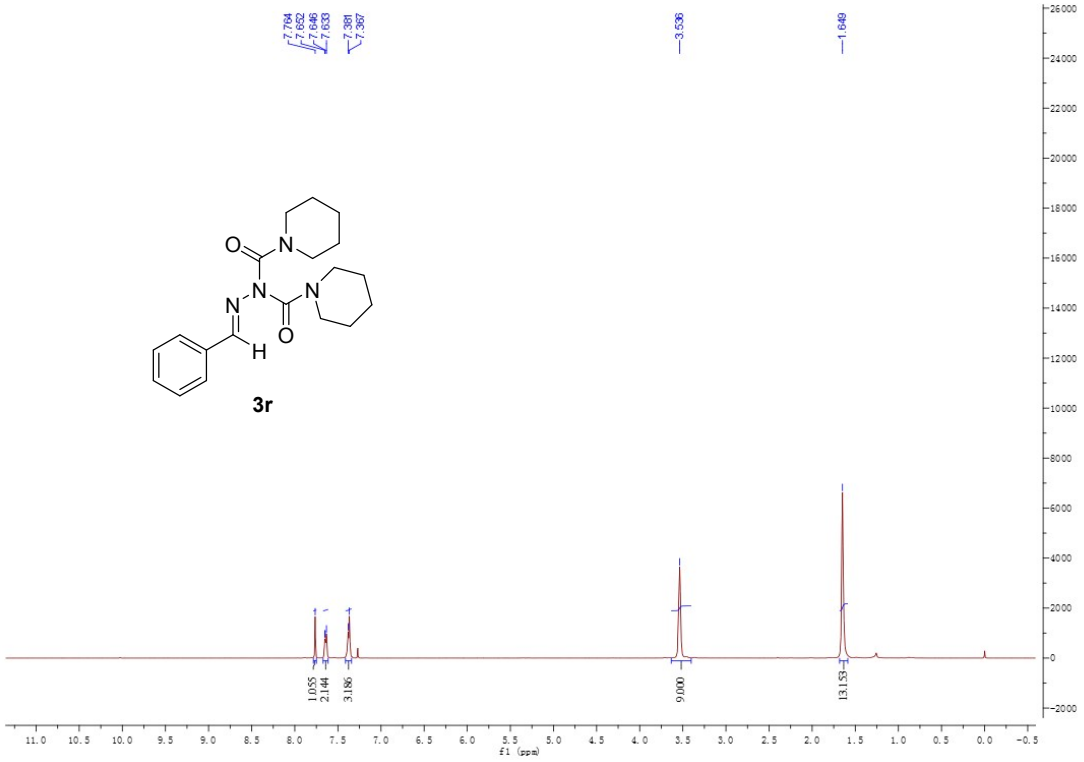
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3q



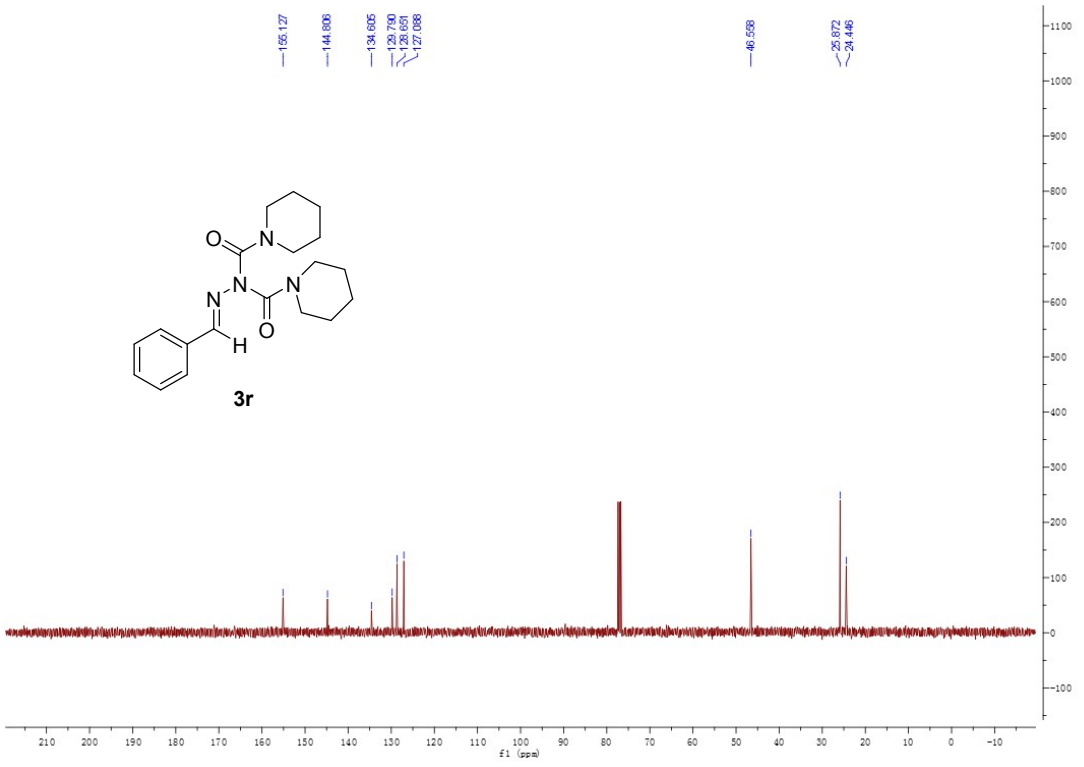
^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 3q



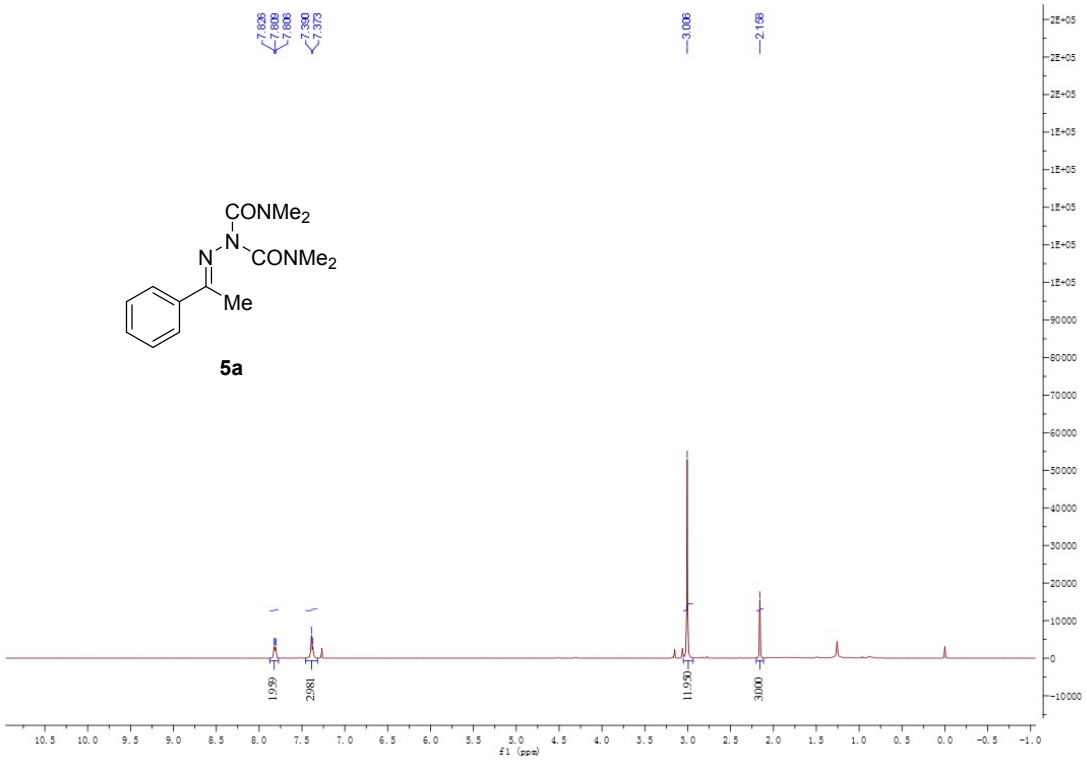
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3r



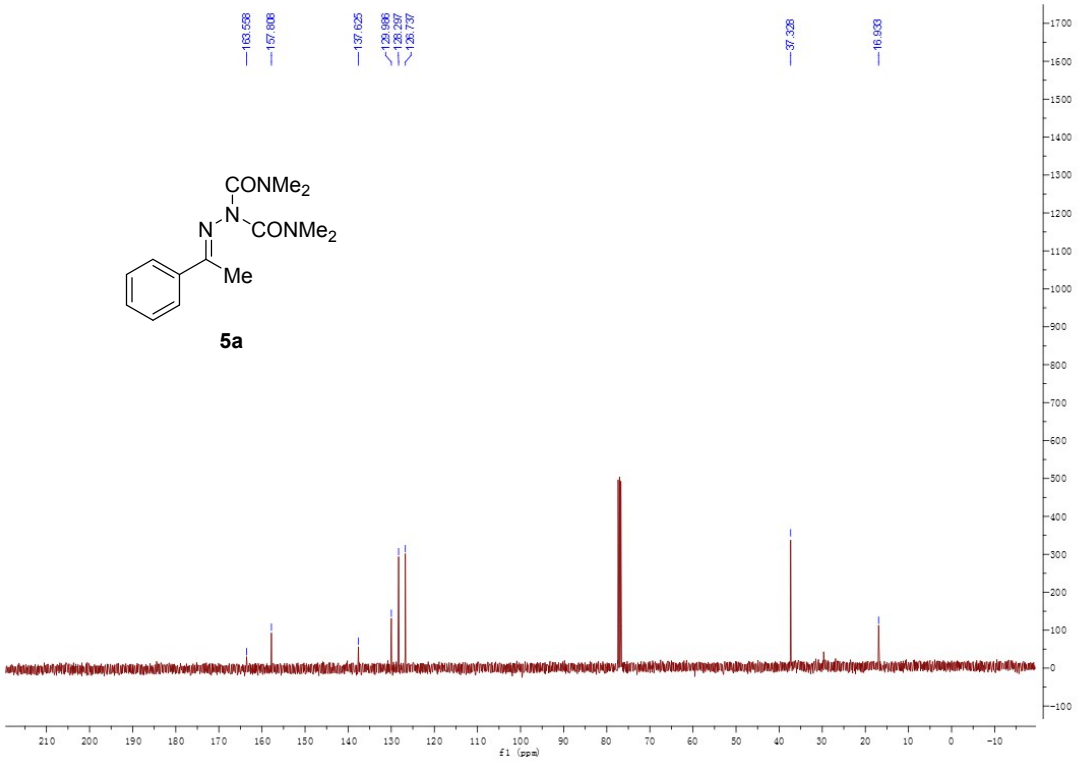
^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 3r



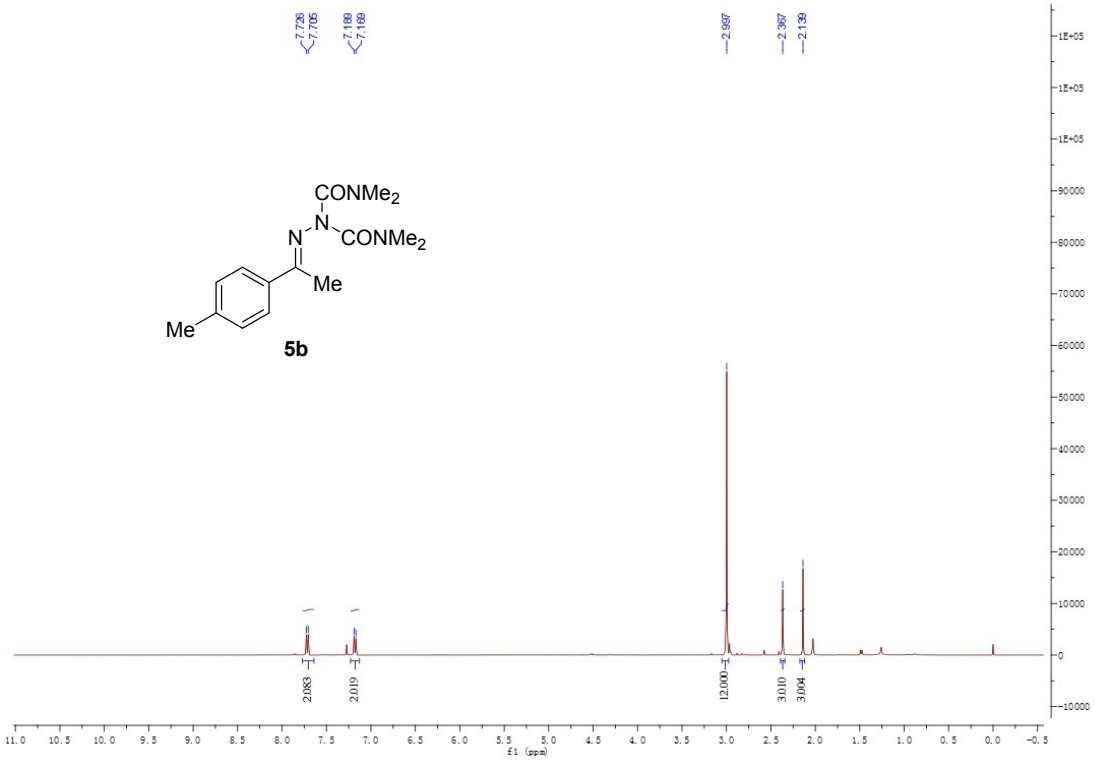
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 5a



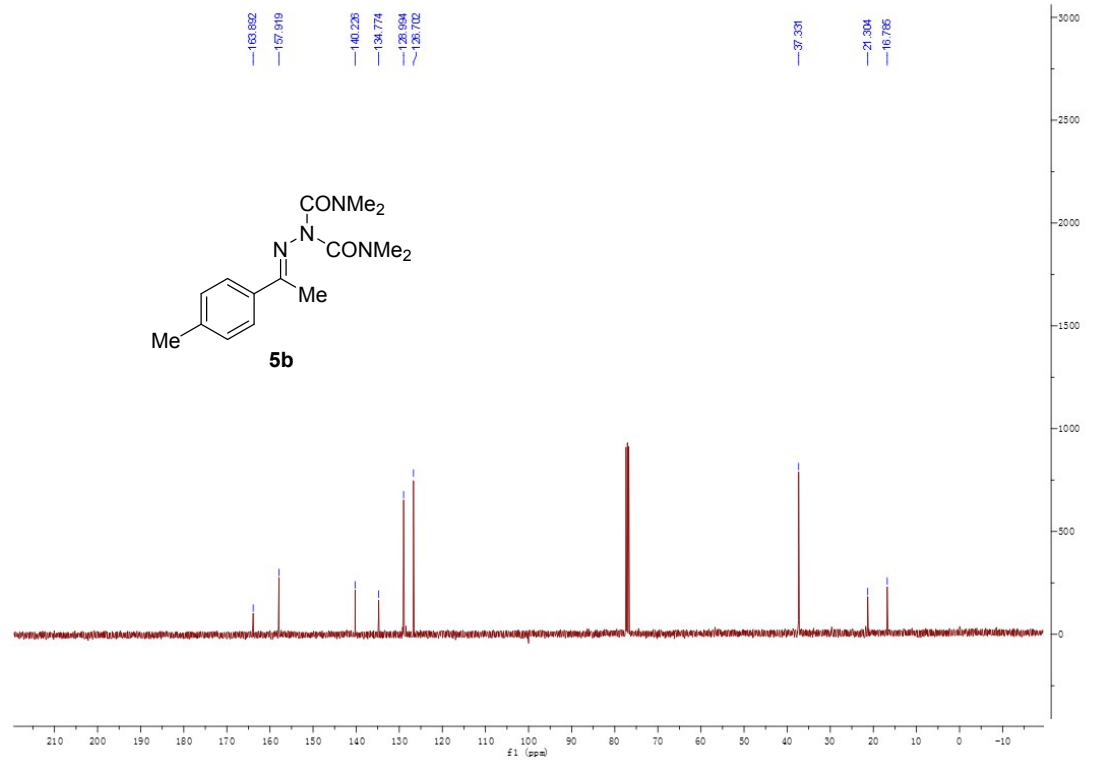
^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 5a



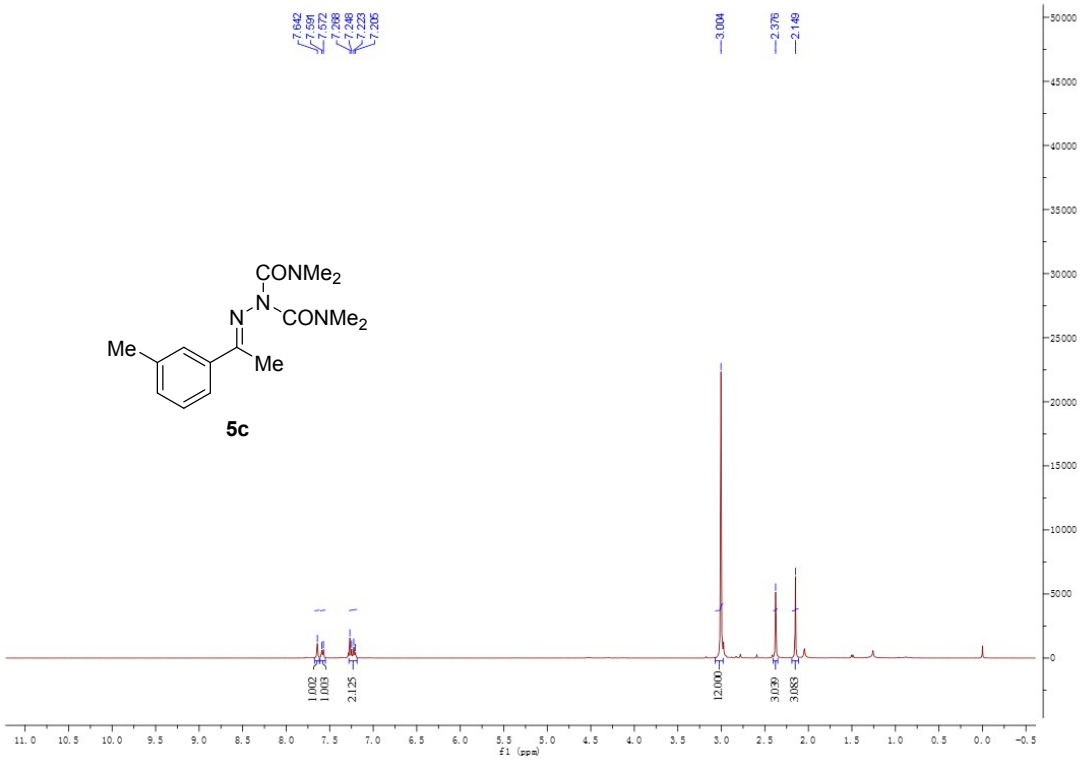
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 5b



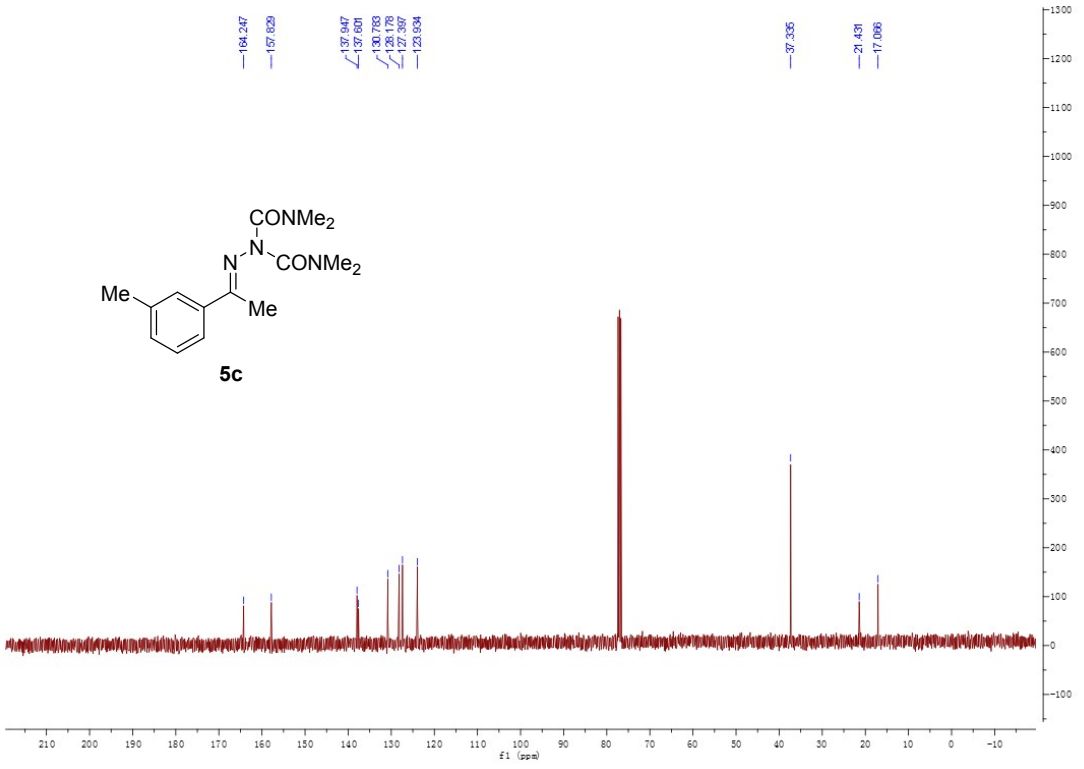
^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 5b



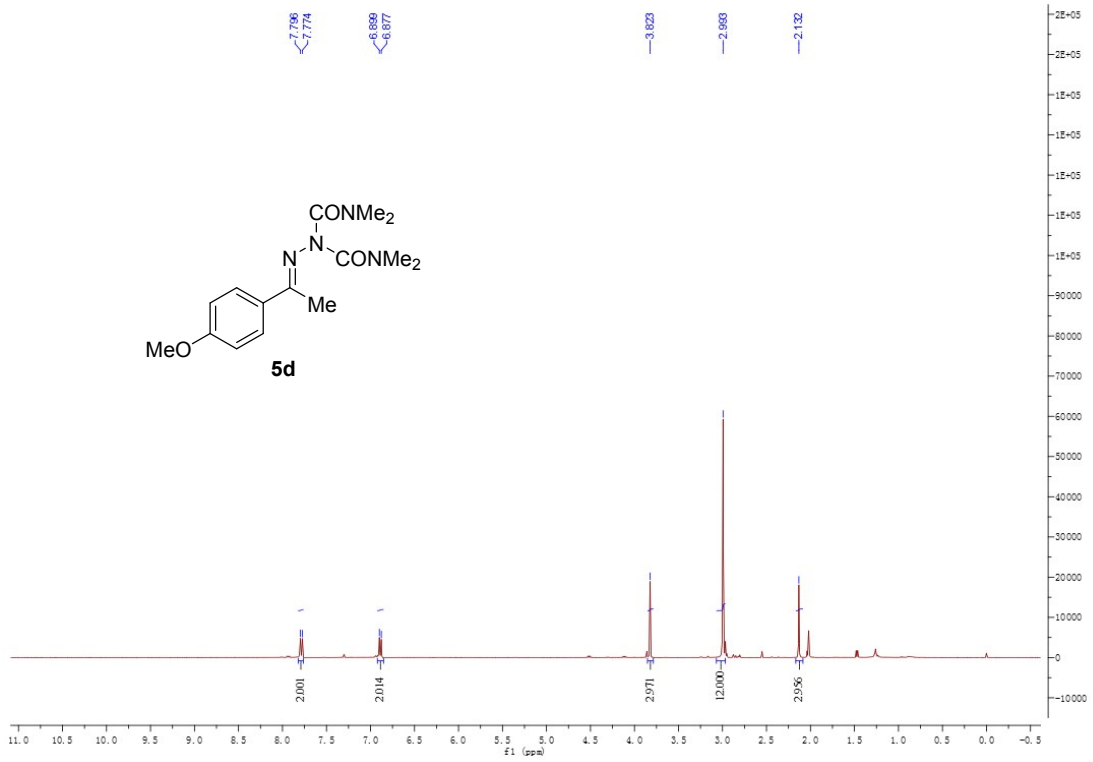
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 5c



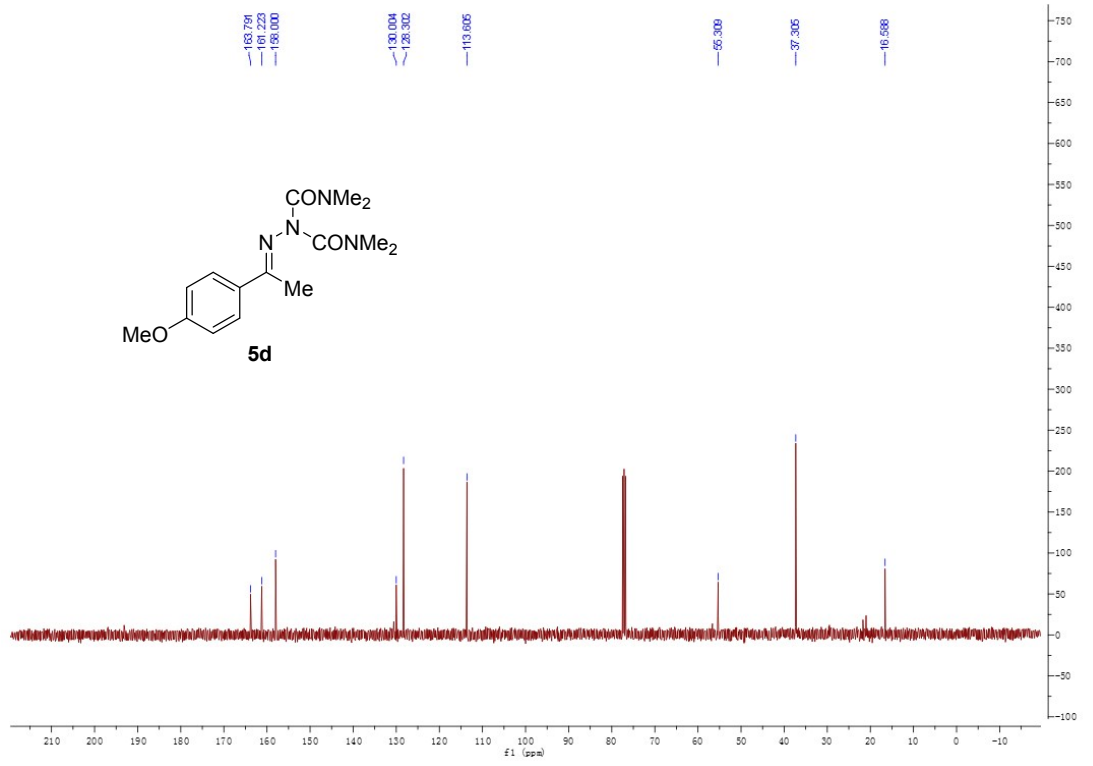
^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 5c



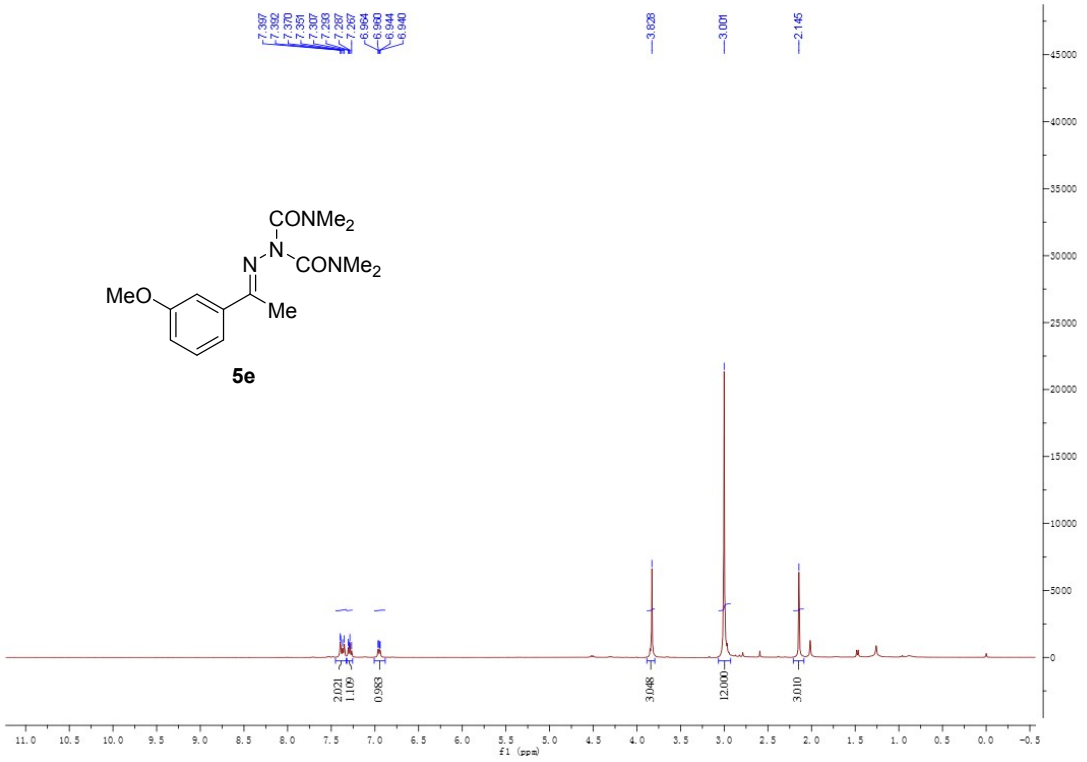
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 5d



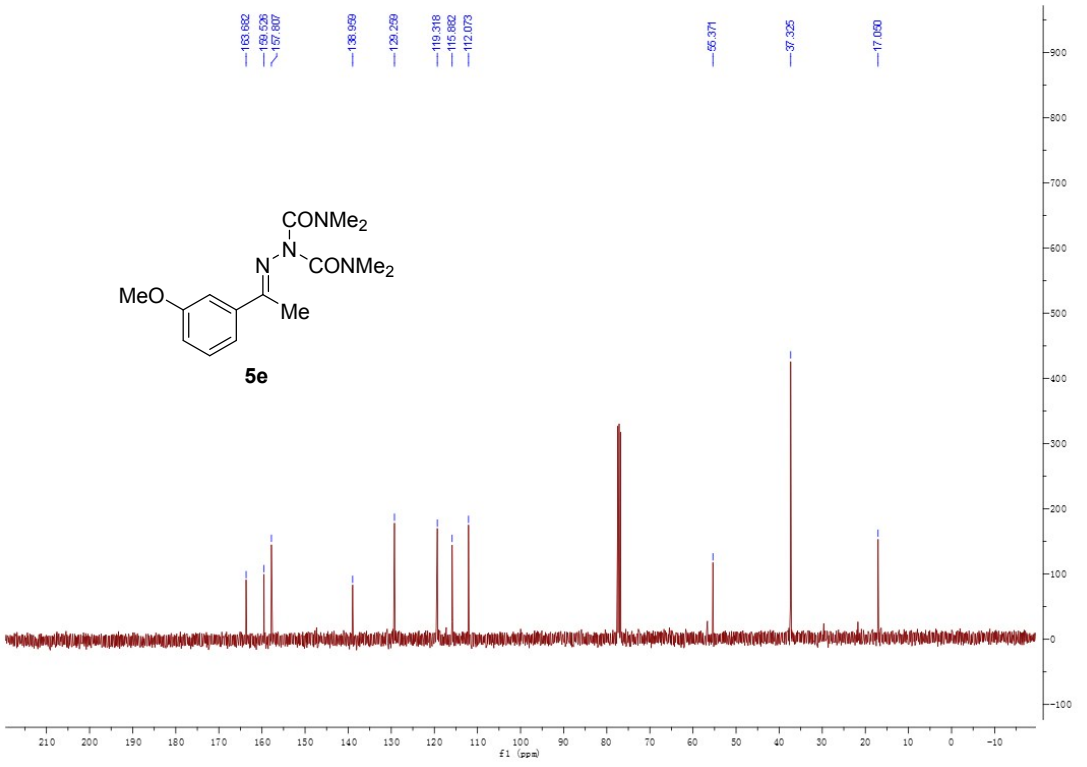
^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 5d



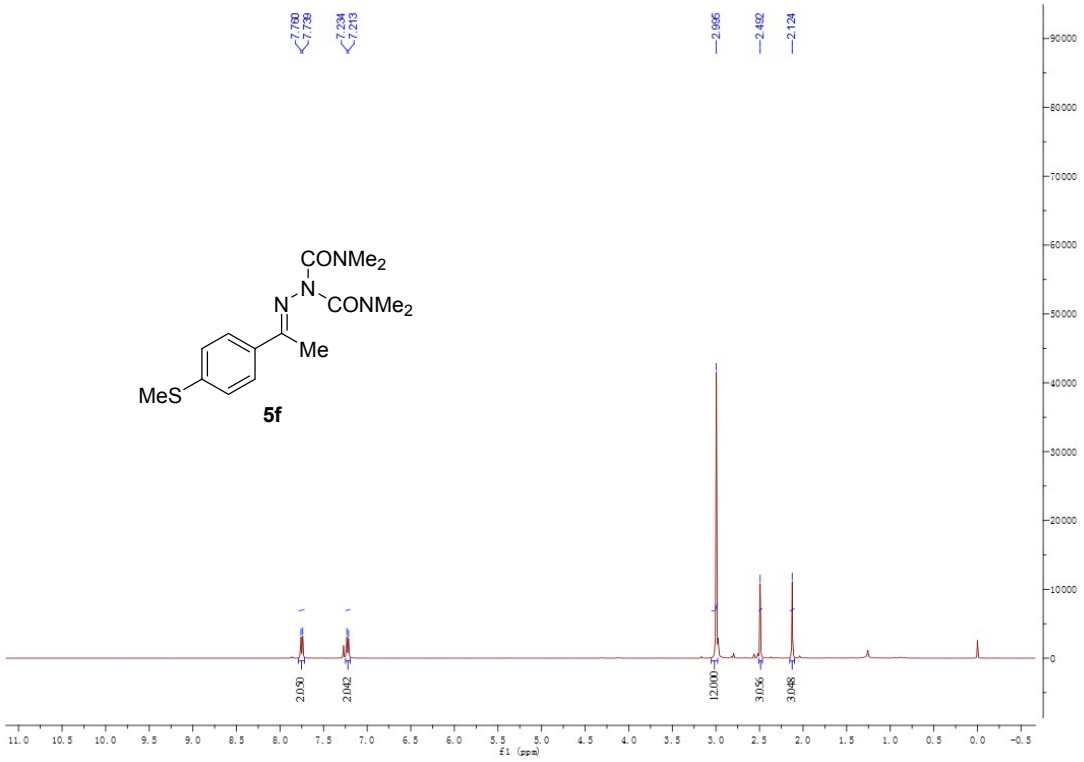
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 5e



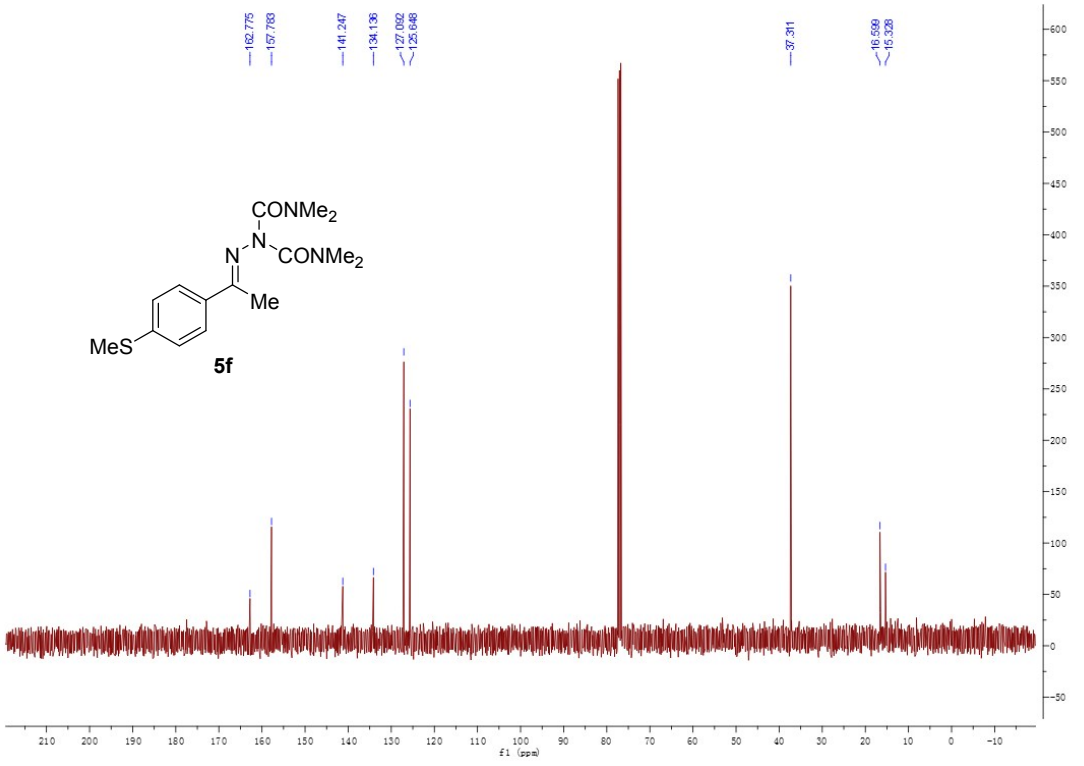
^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 5e



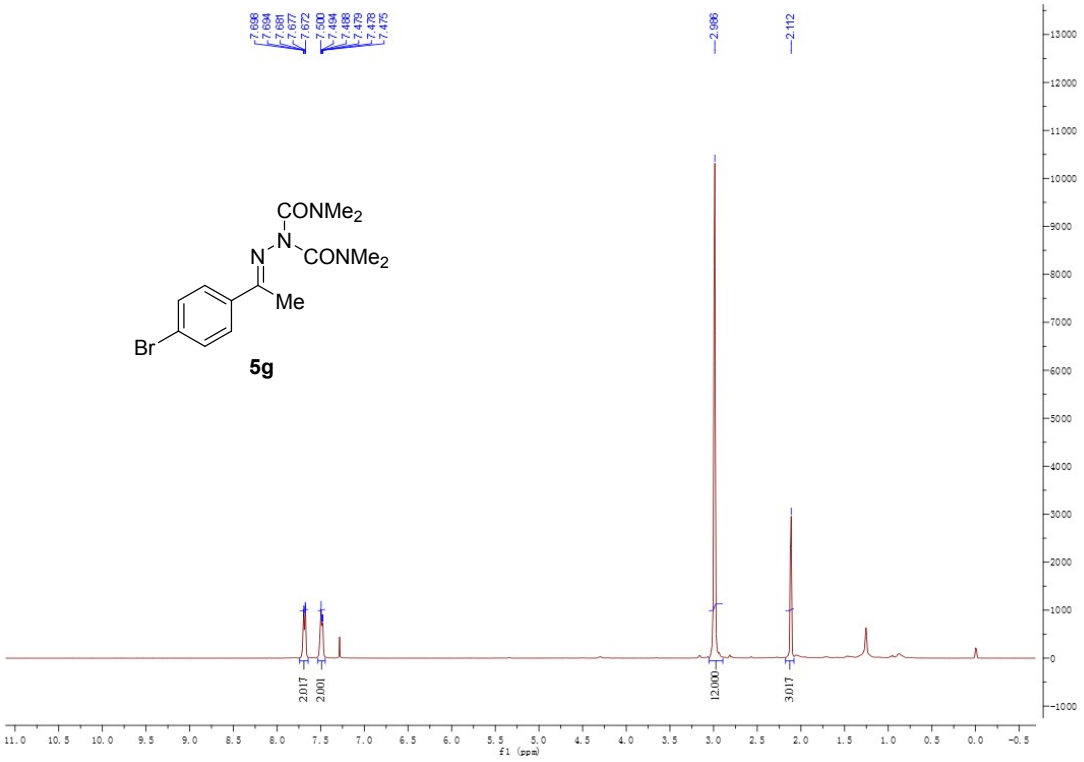
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 5f



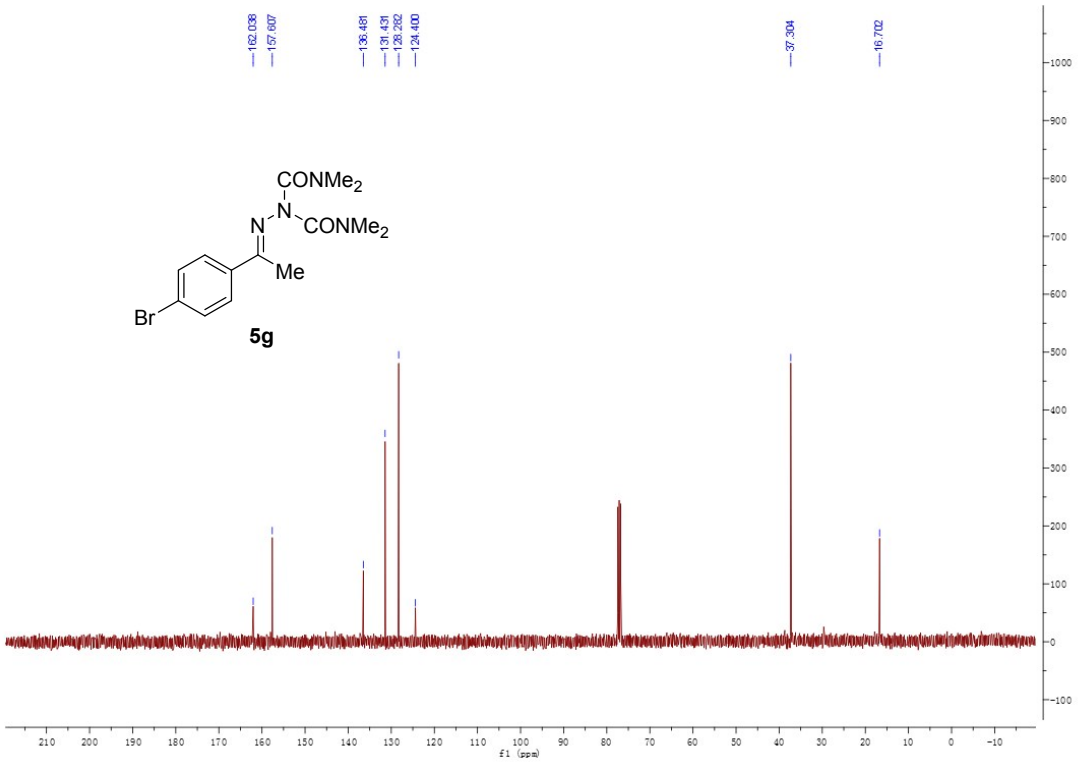
^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 5f



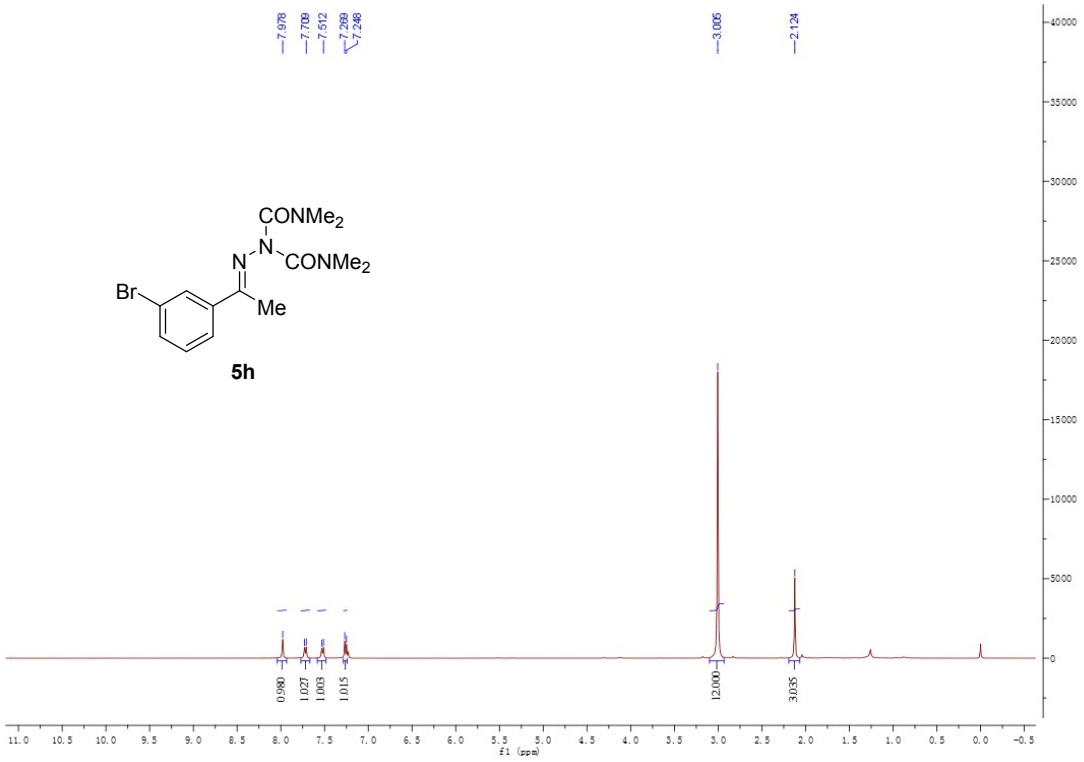
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 5g



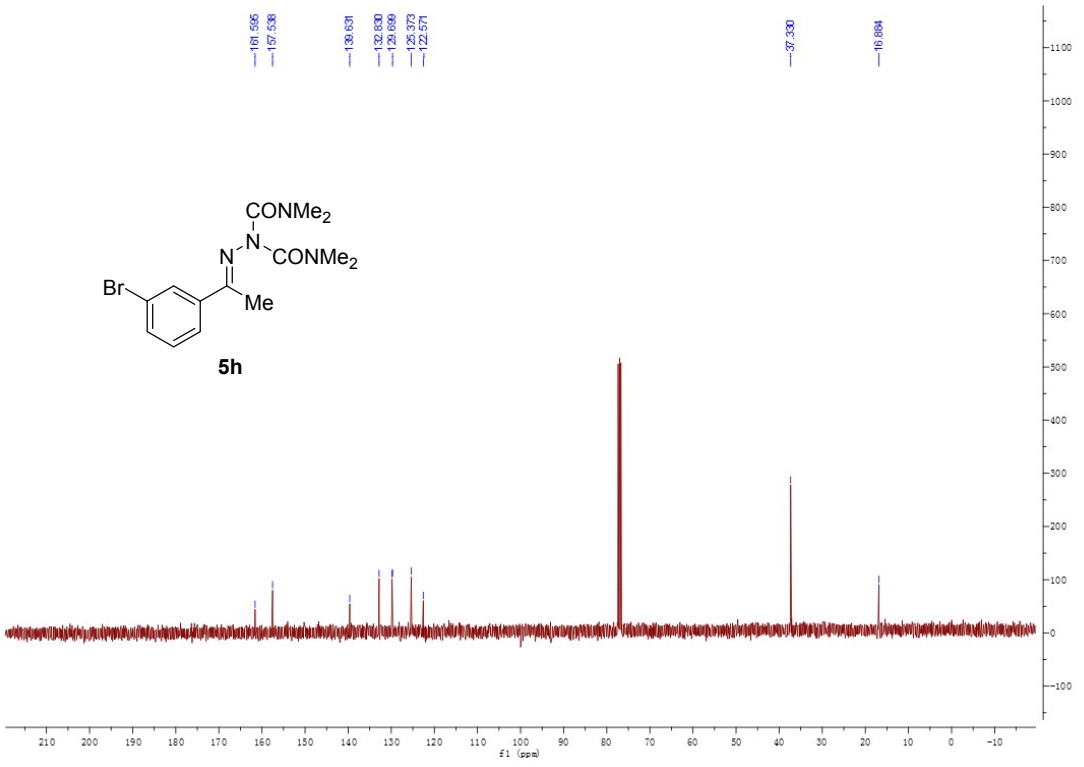
^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 5g



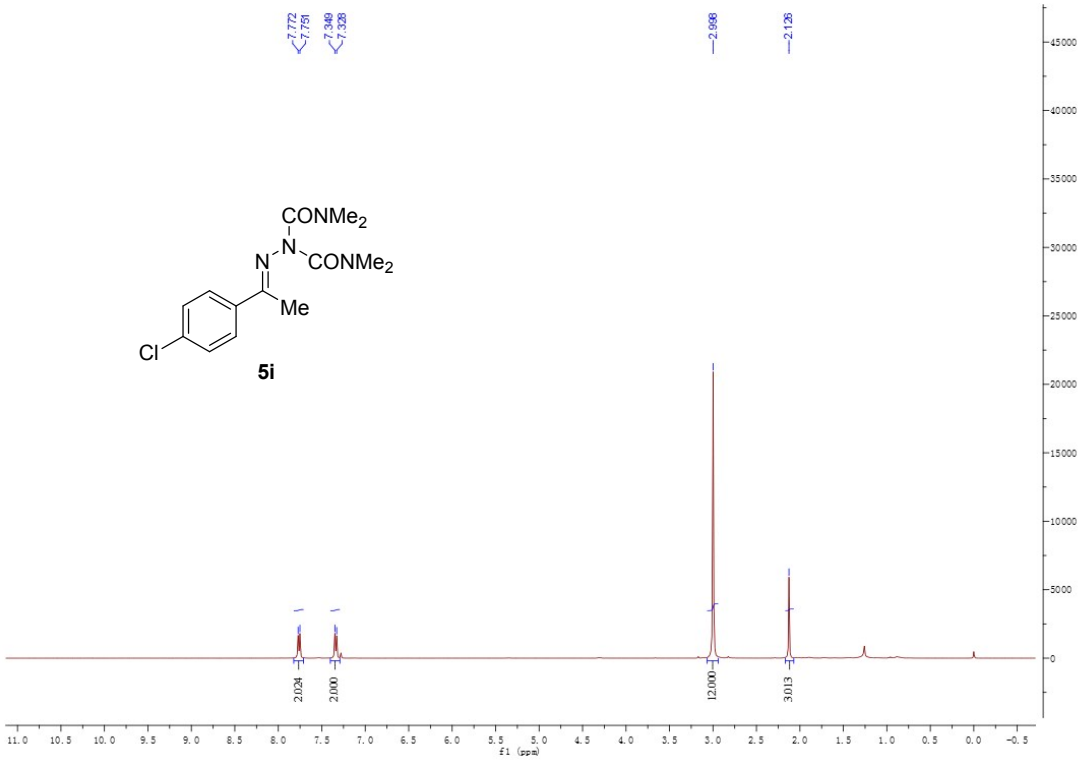
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 5h



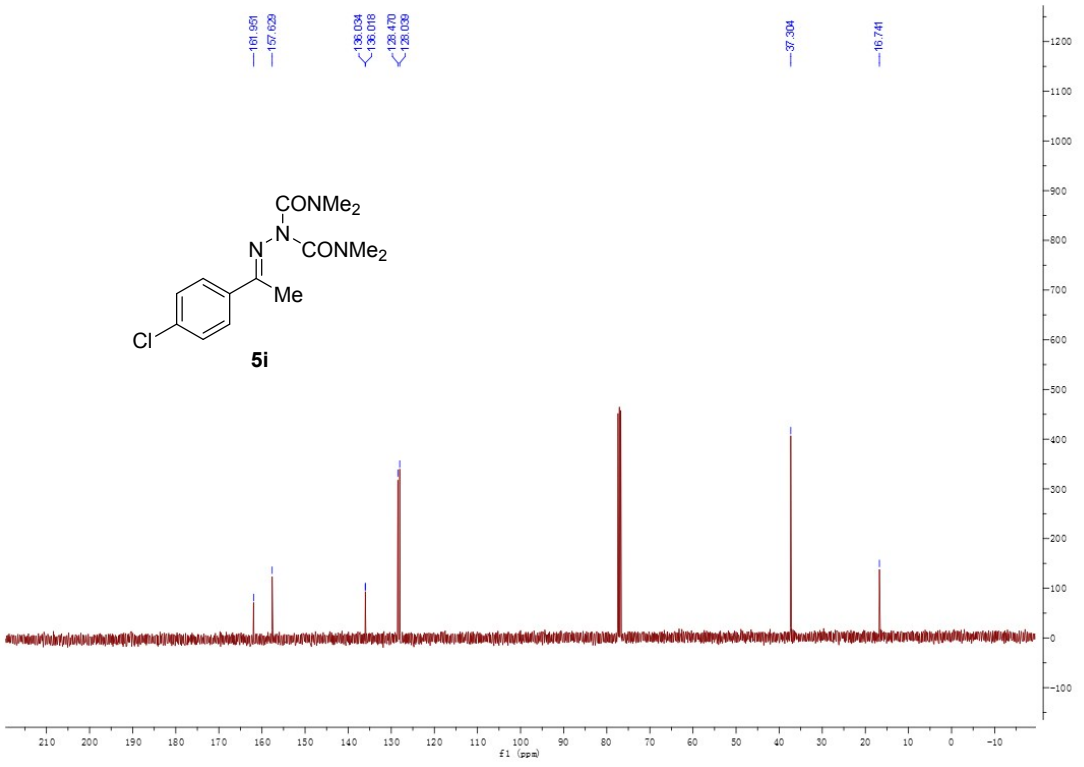
^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 5h



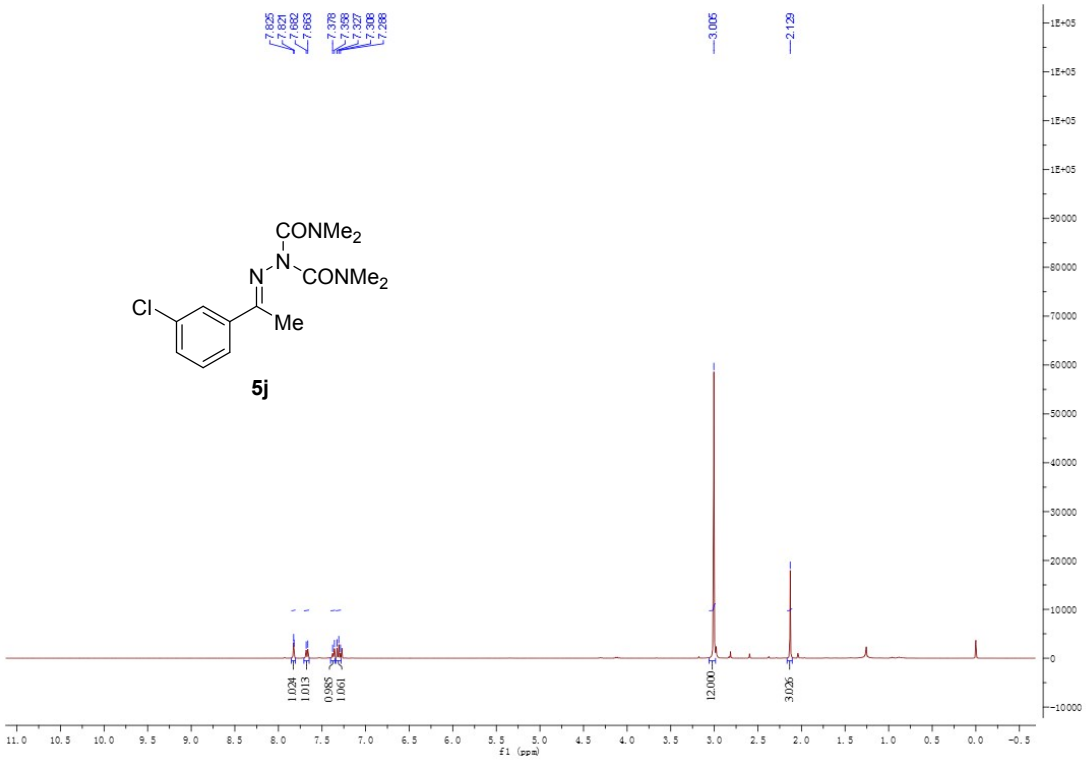
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 5i



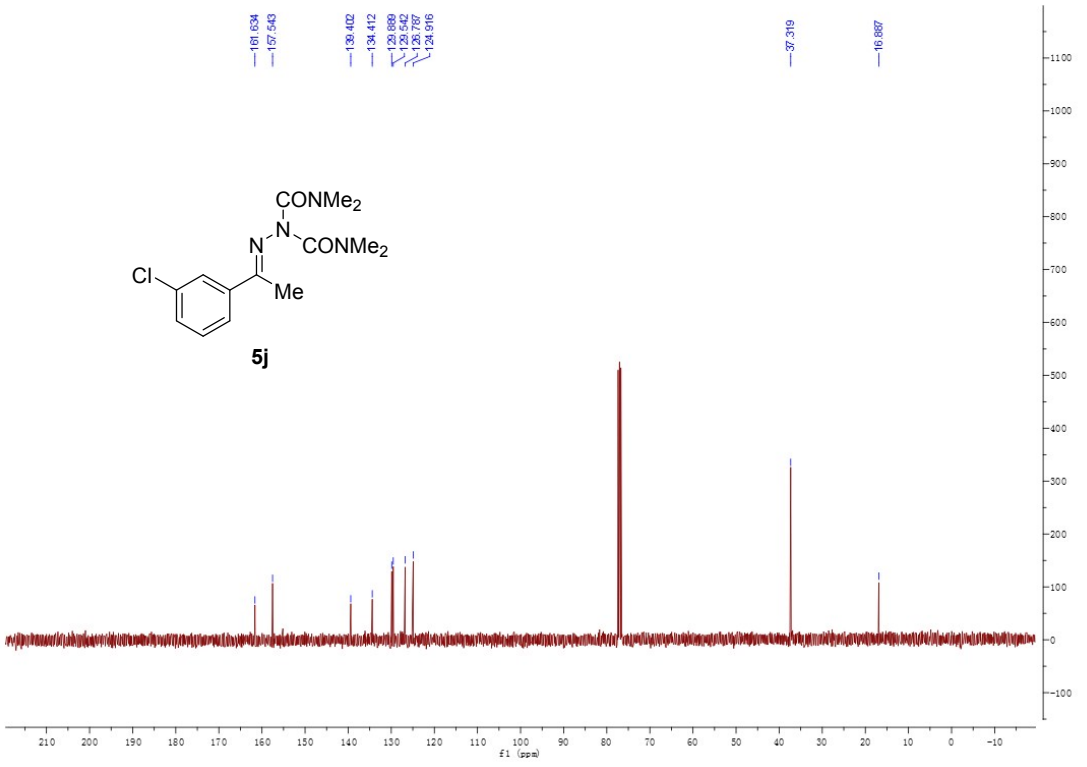
^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 5i



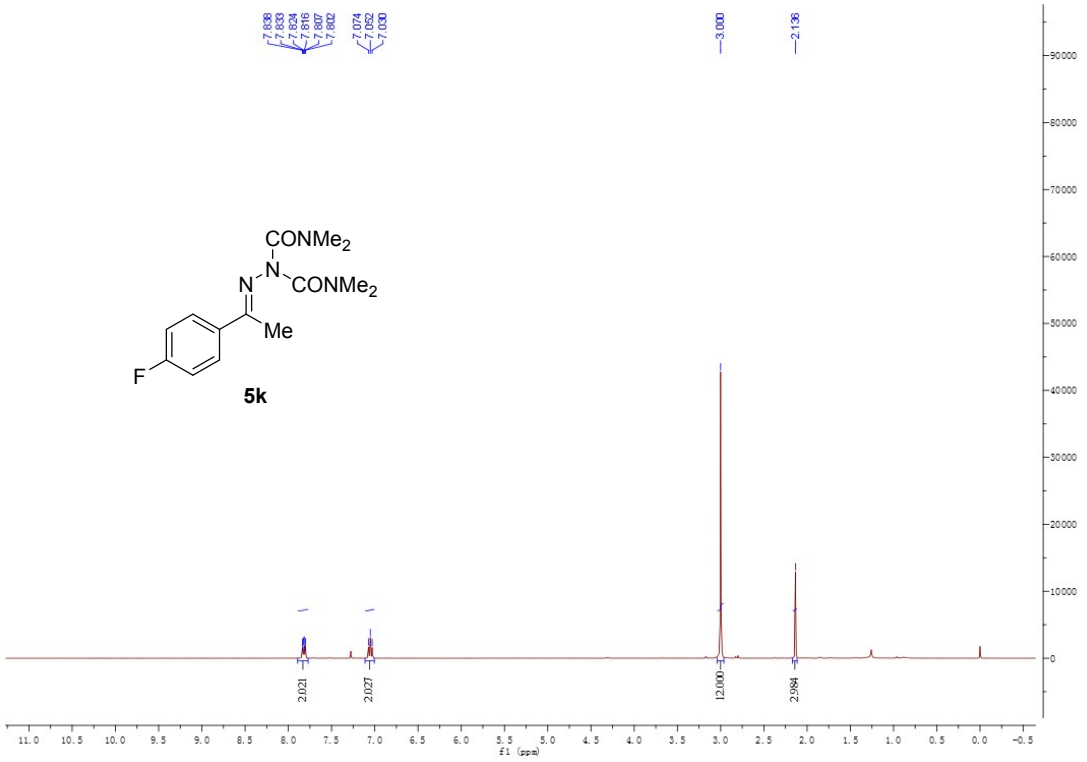
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 5j



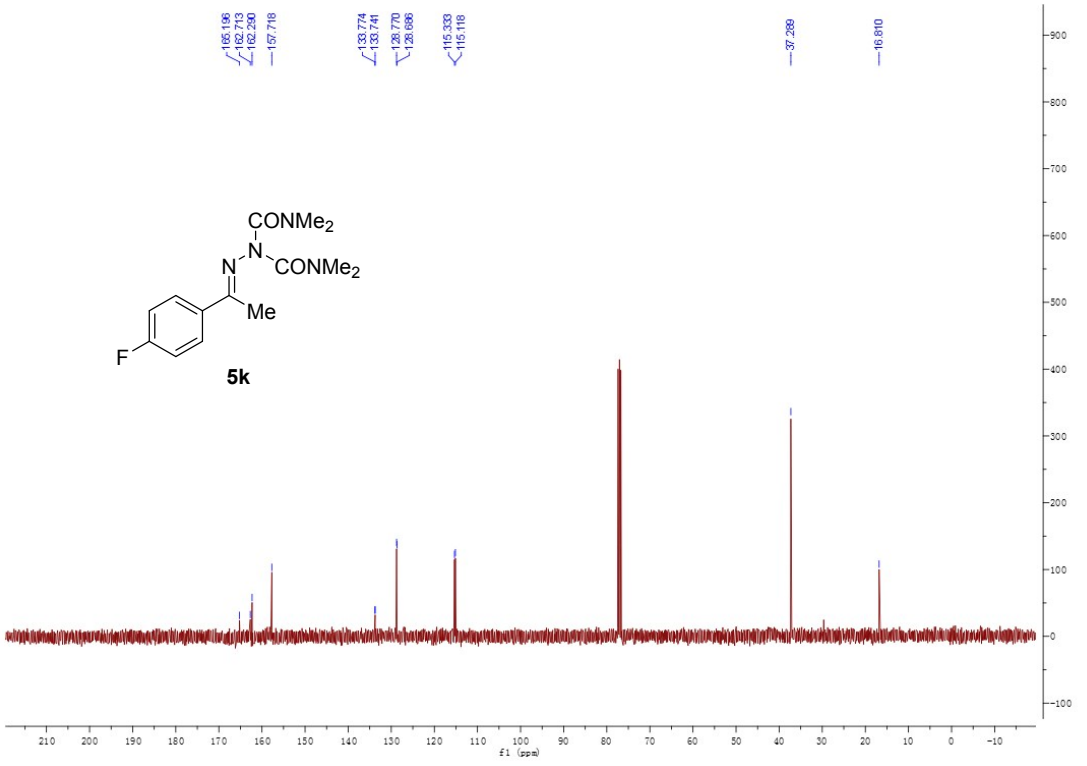
^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 5j



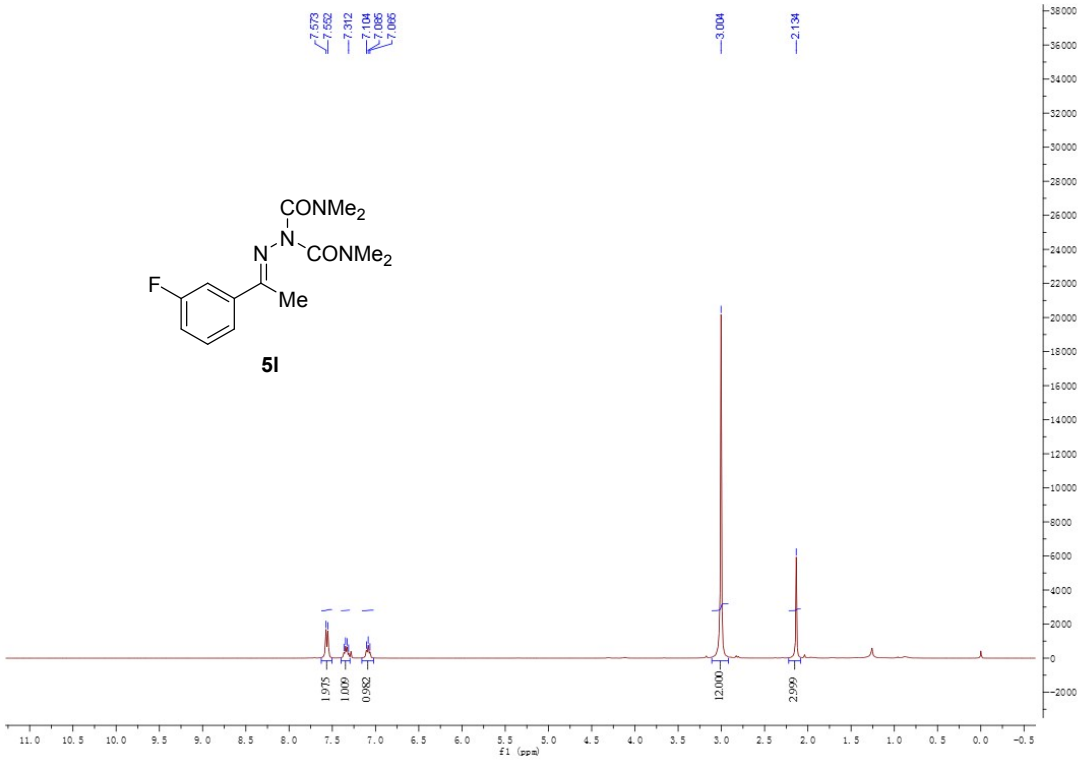
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 5k



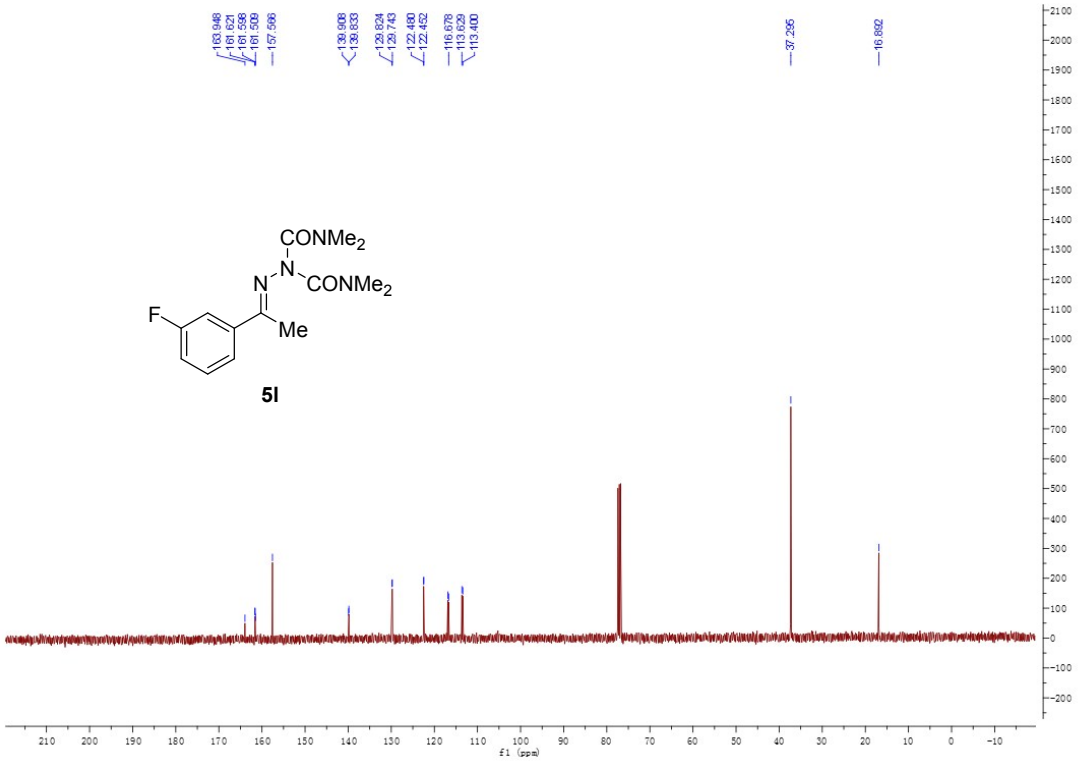
^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 5k



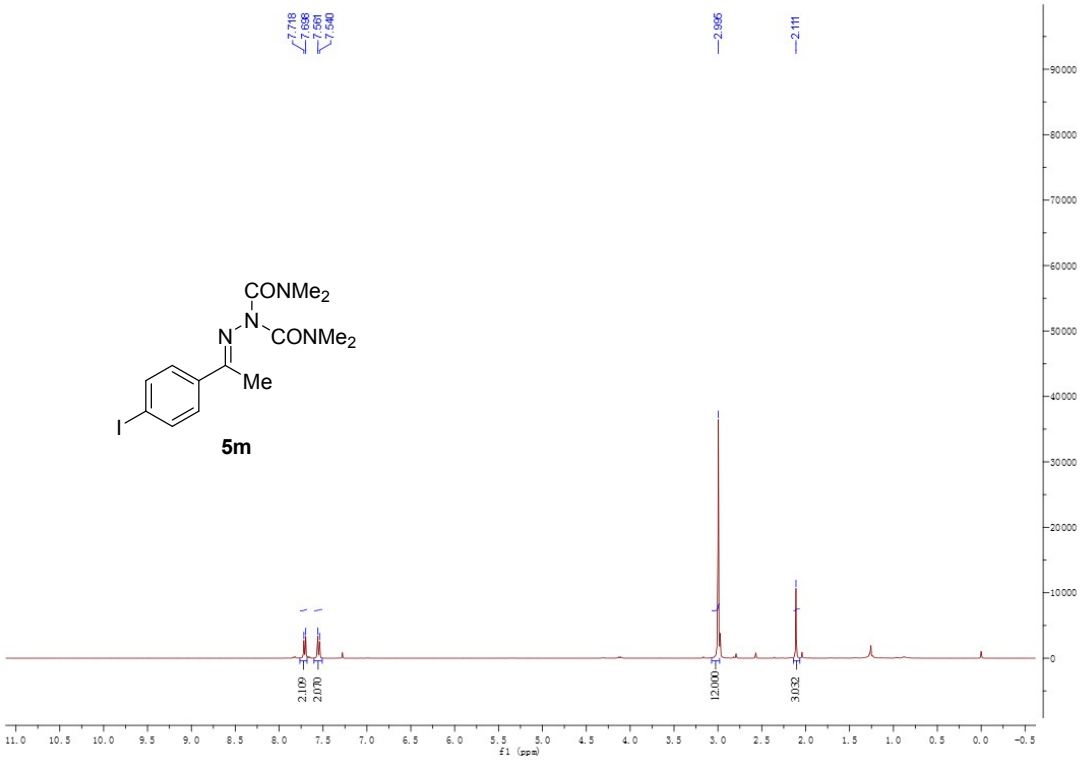
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 5l



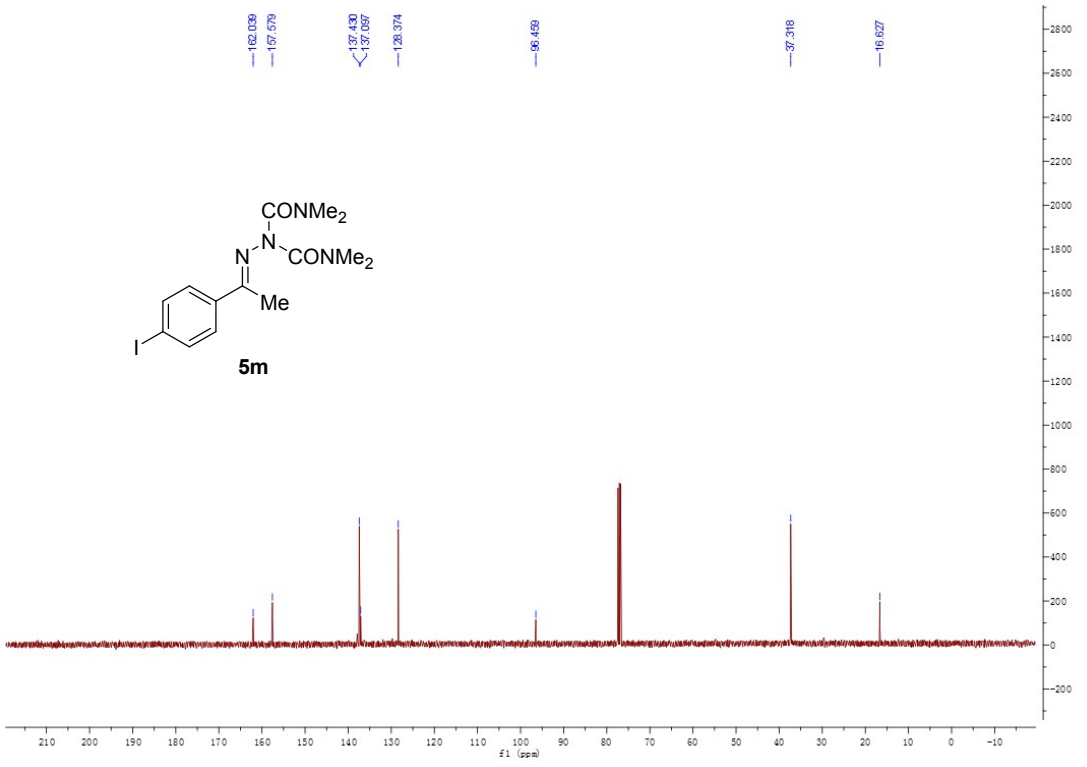
^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 5l



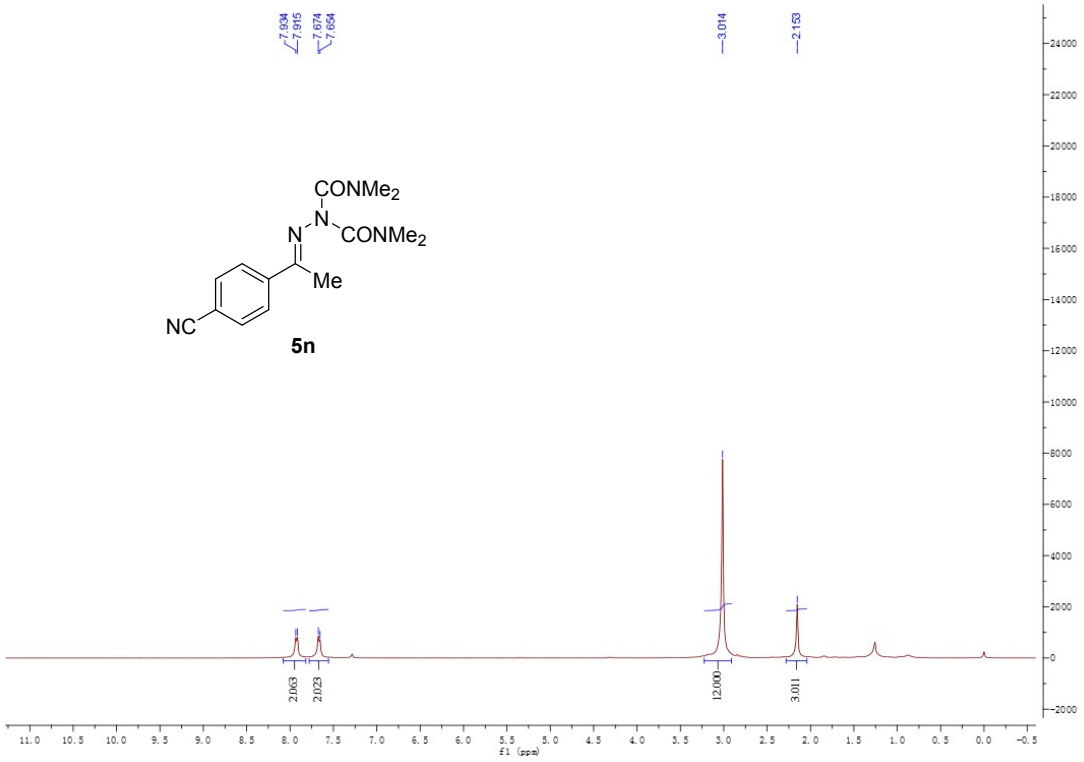
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 5m



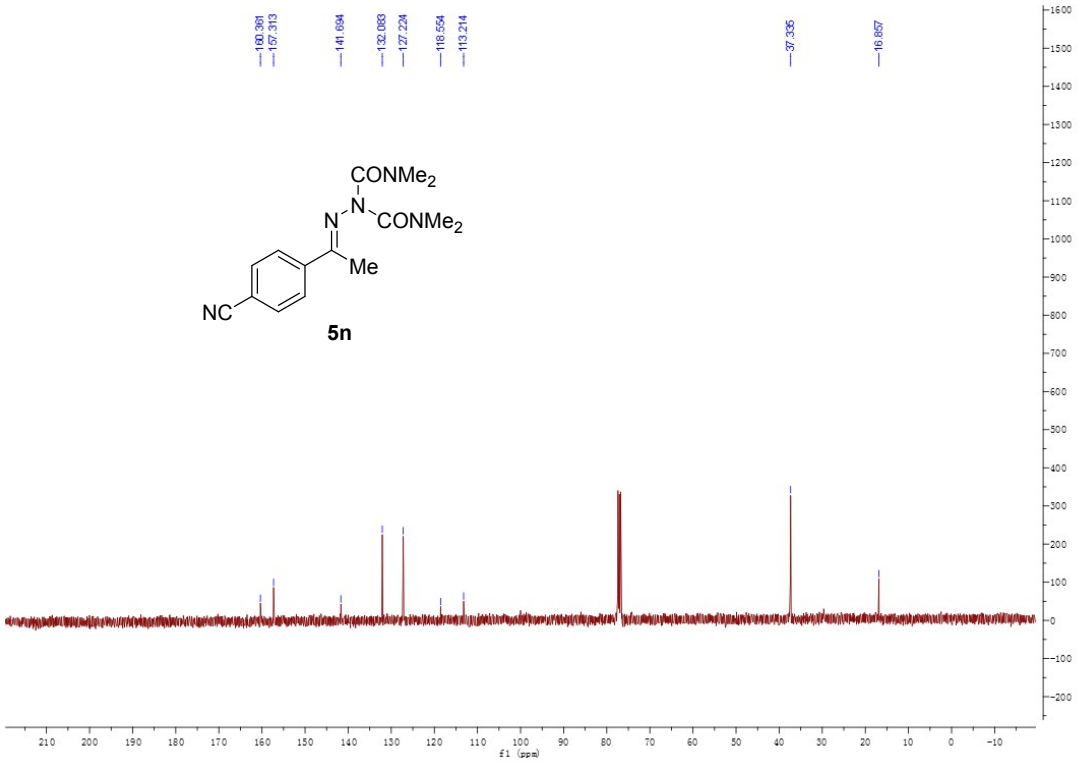
^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 5m



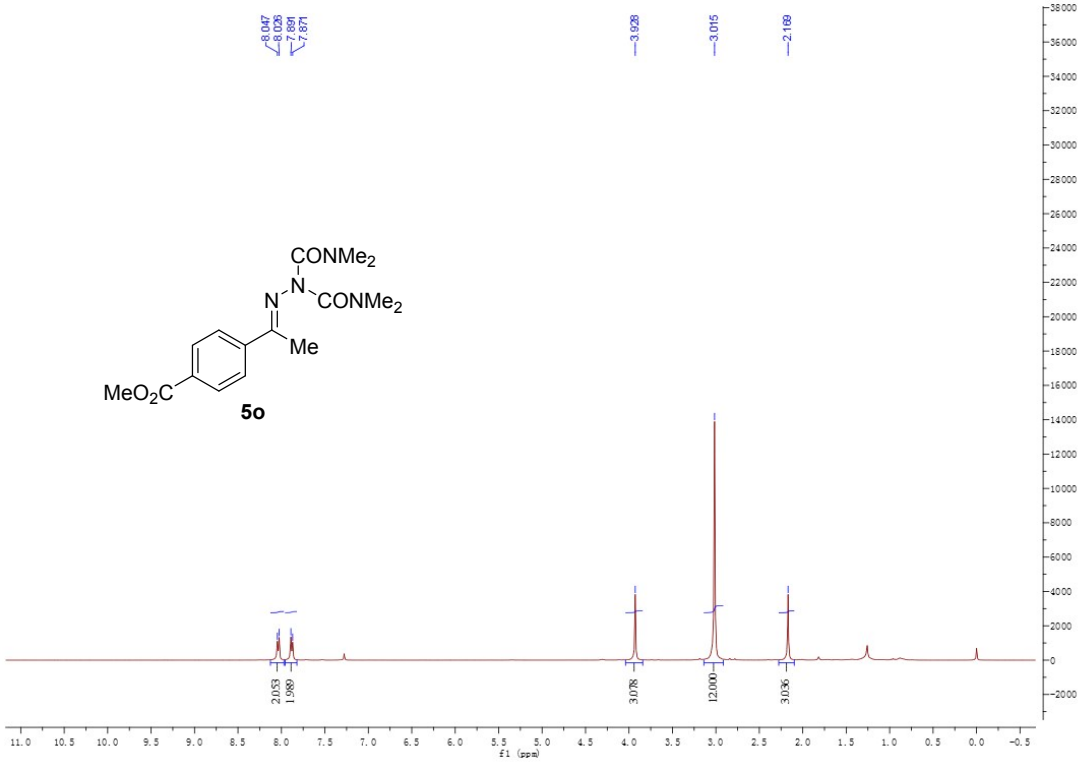
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 5n



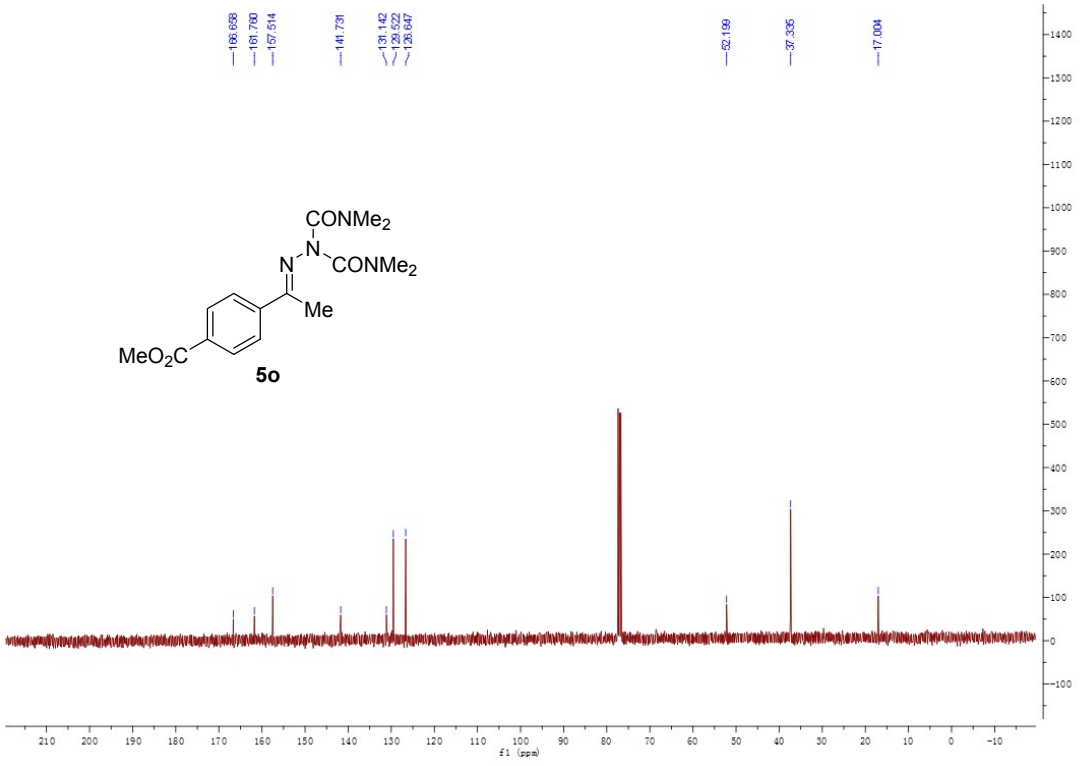
^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 5n



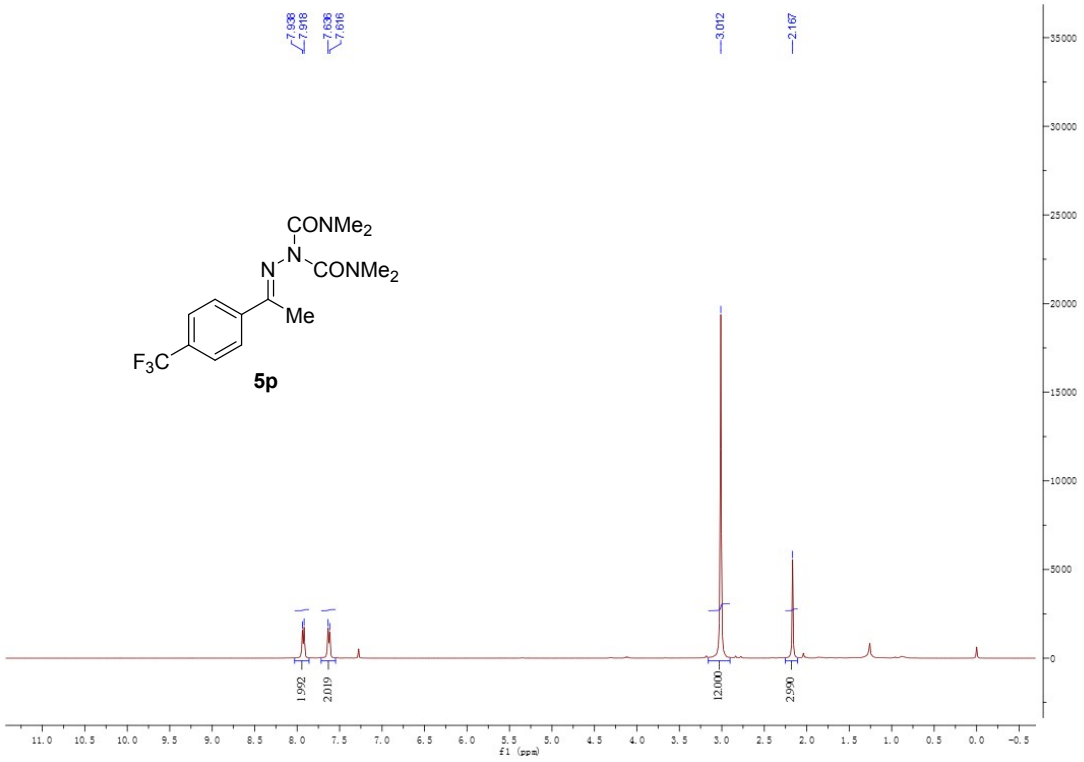
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 5o



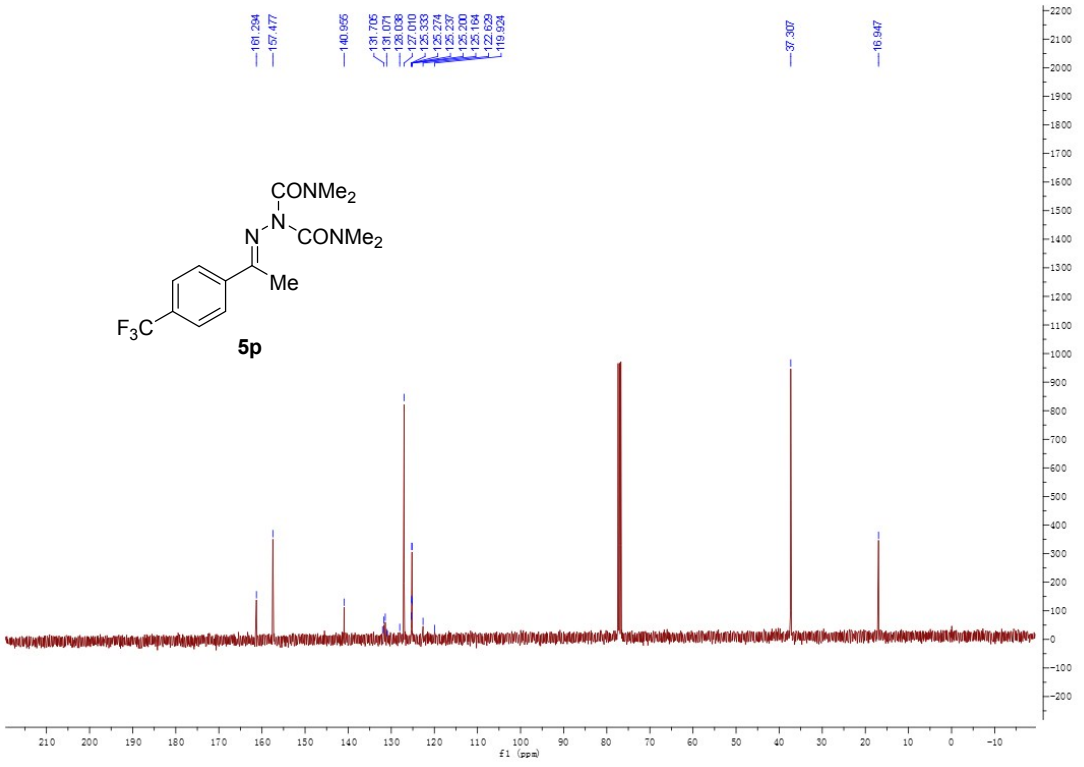
^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 5o



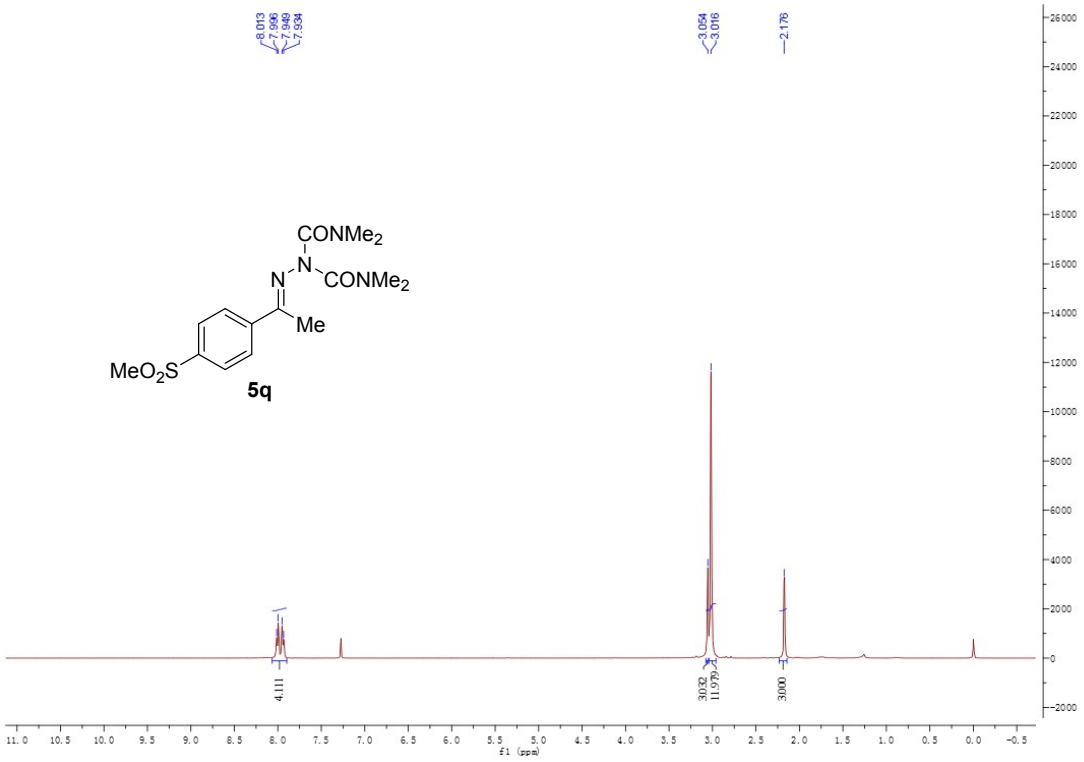
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 5p



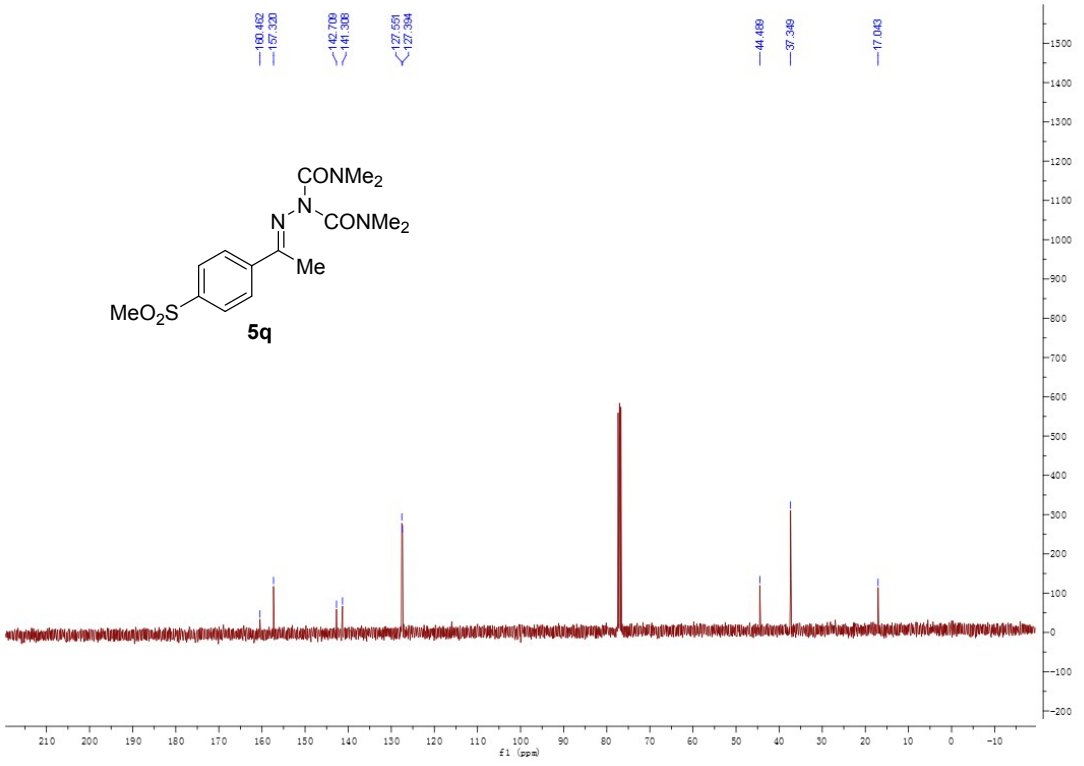
^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 5p



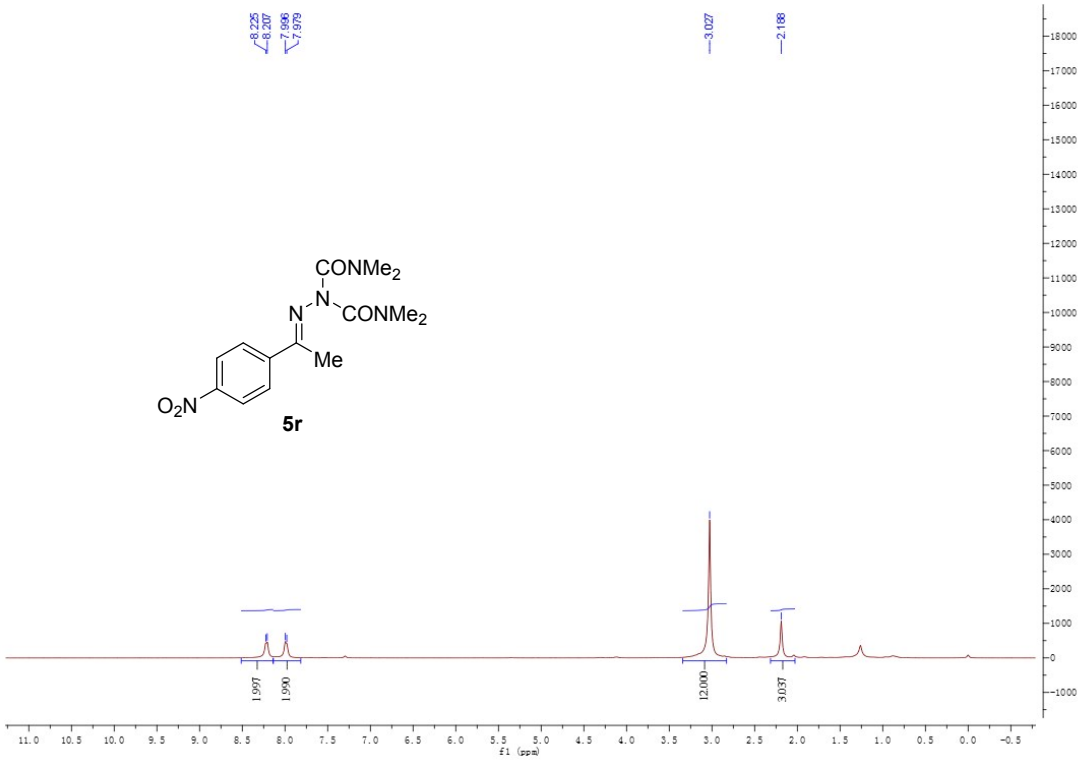
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 5q



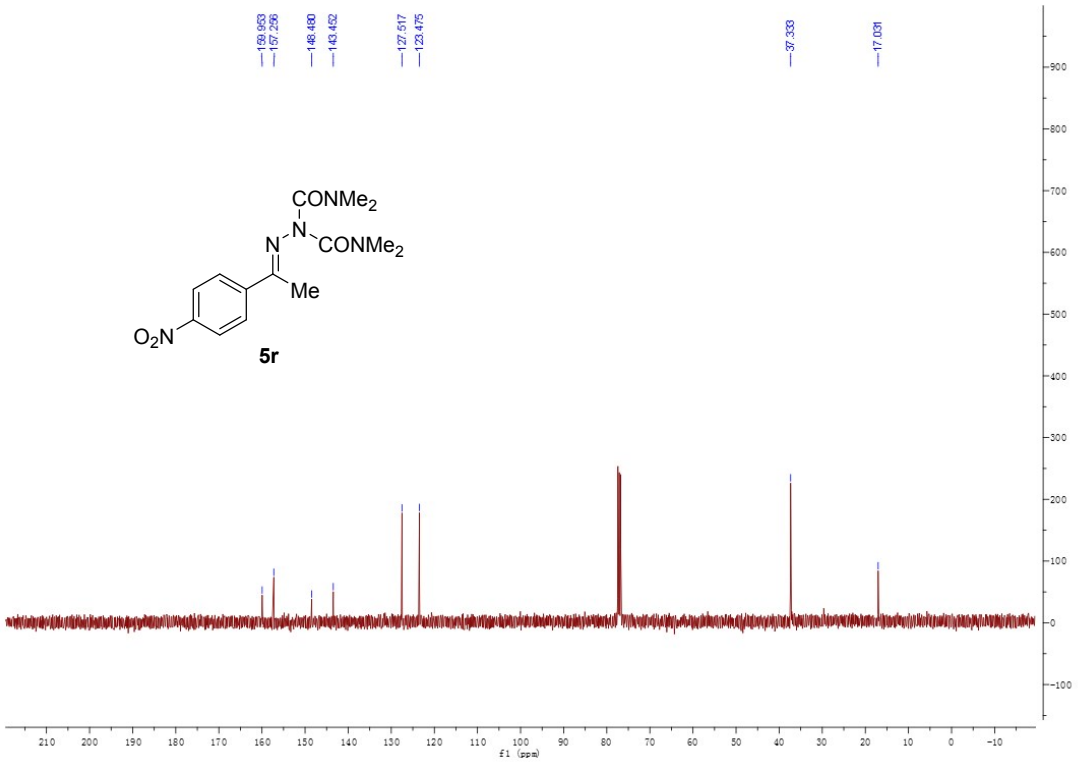
^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 5q



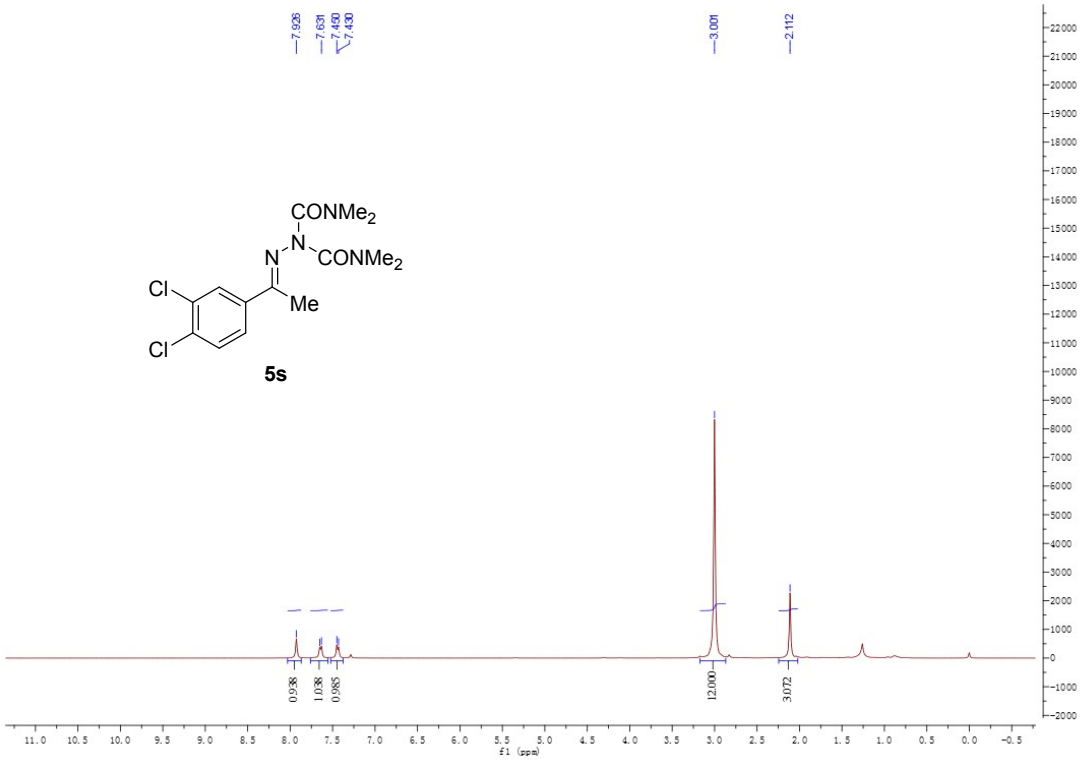
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 5r



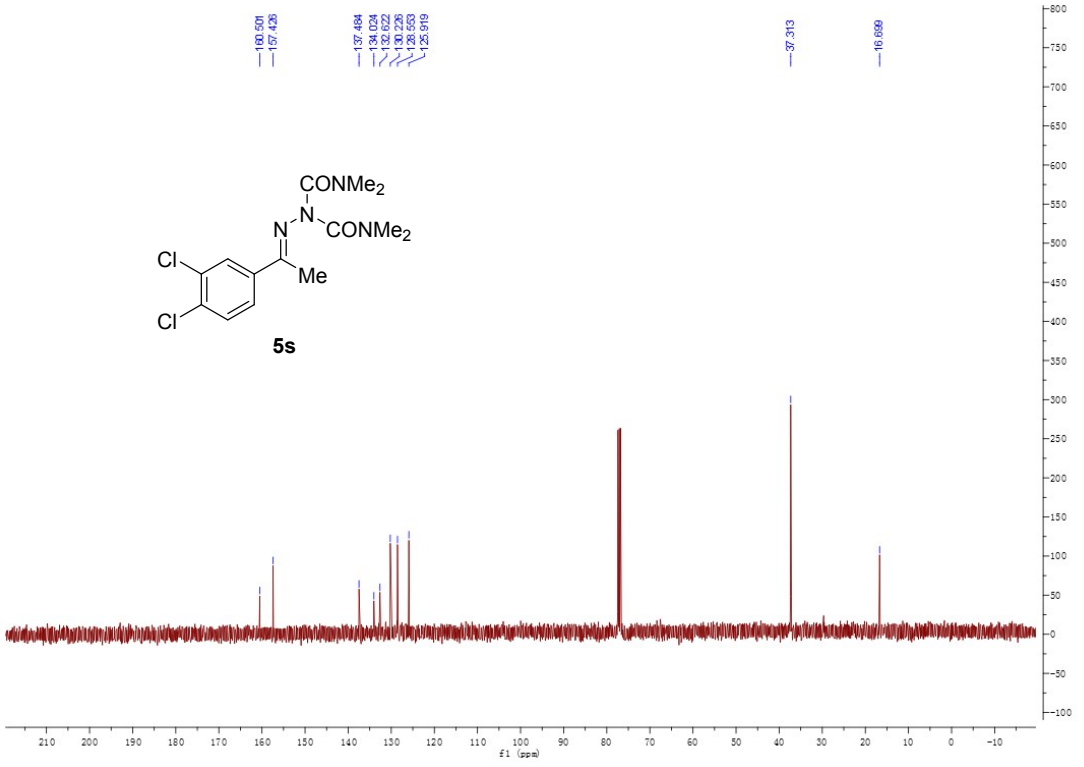
^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 5r



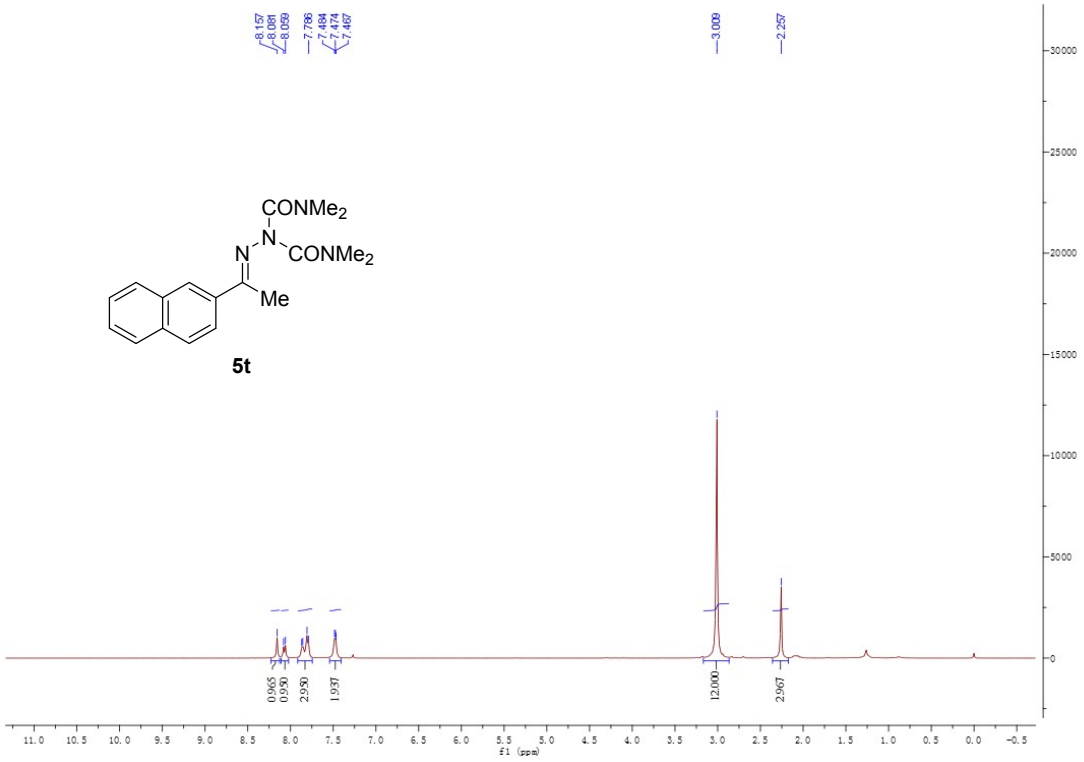
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 5s



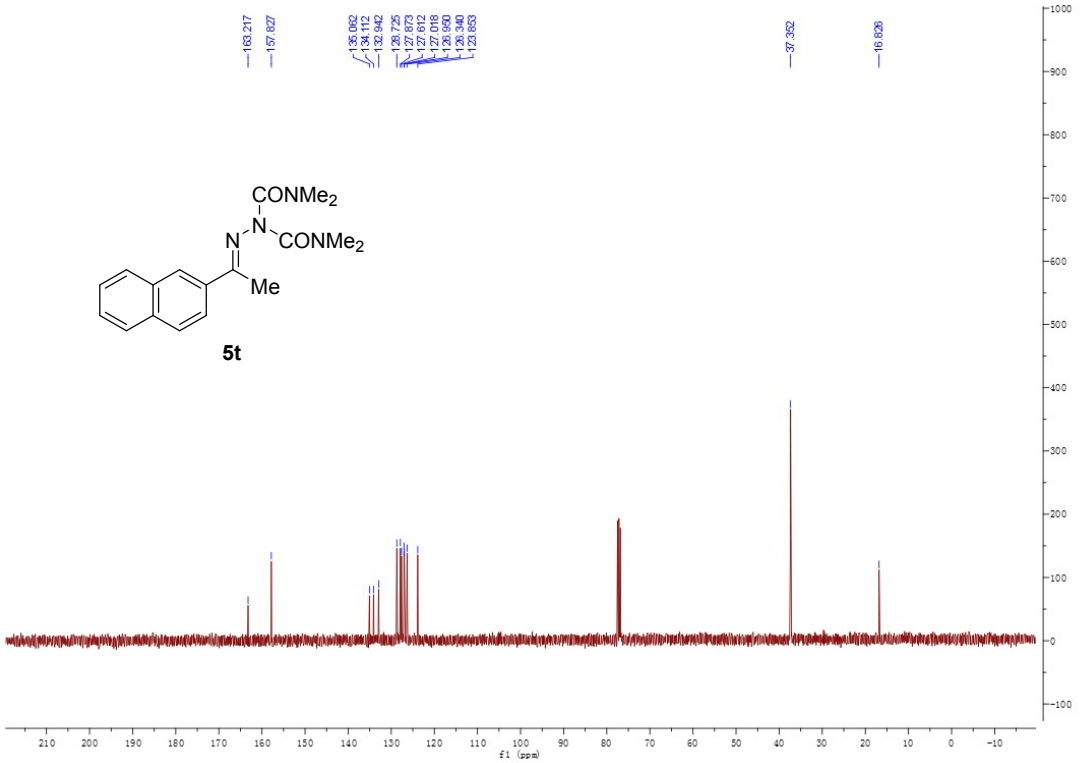
^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 5s



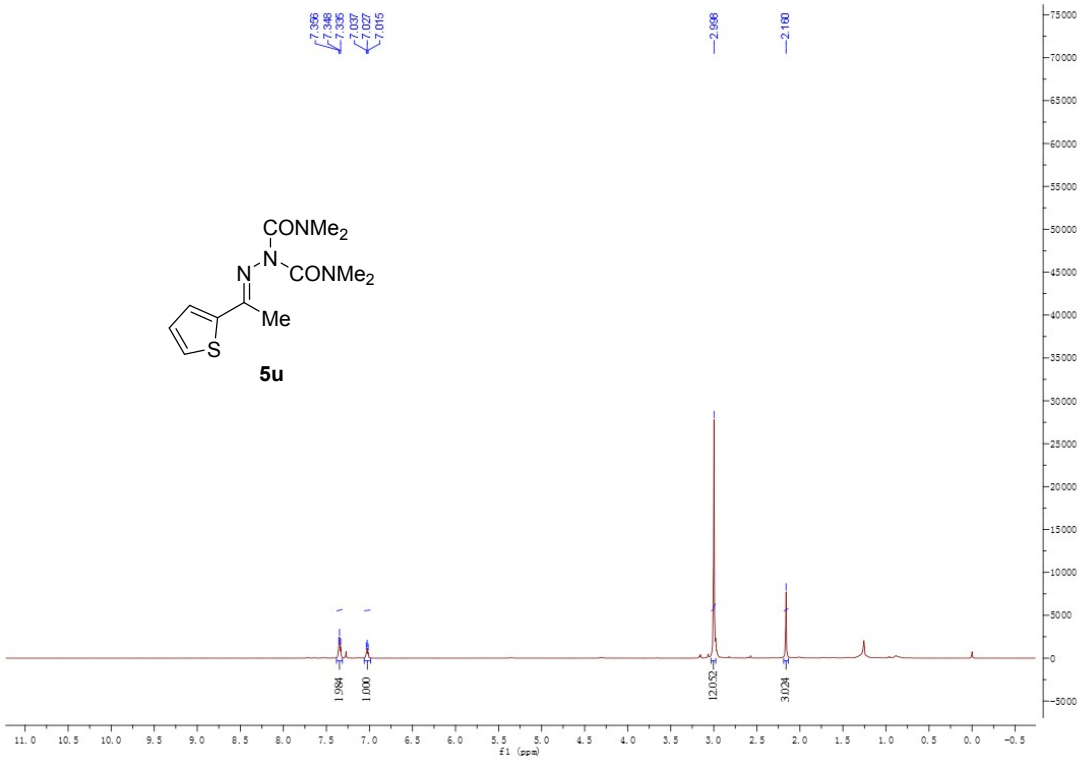
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 5t



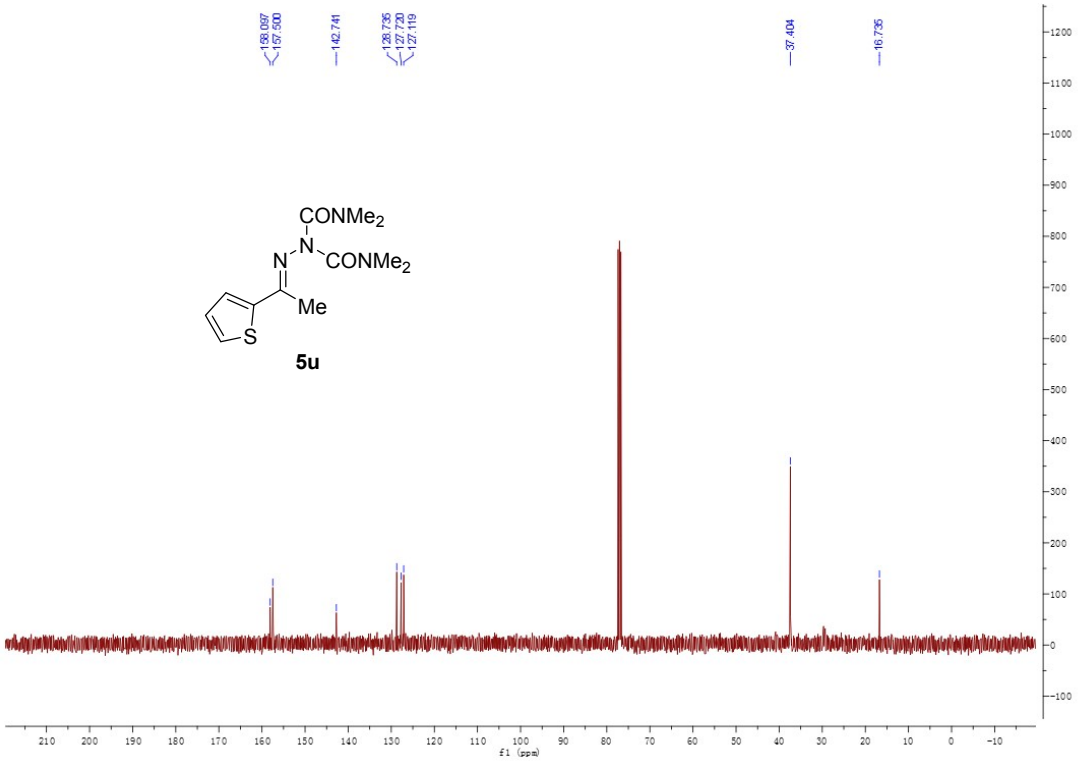
^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 5t



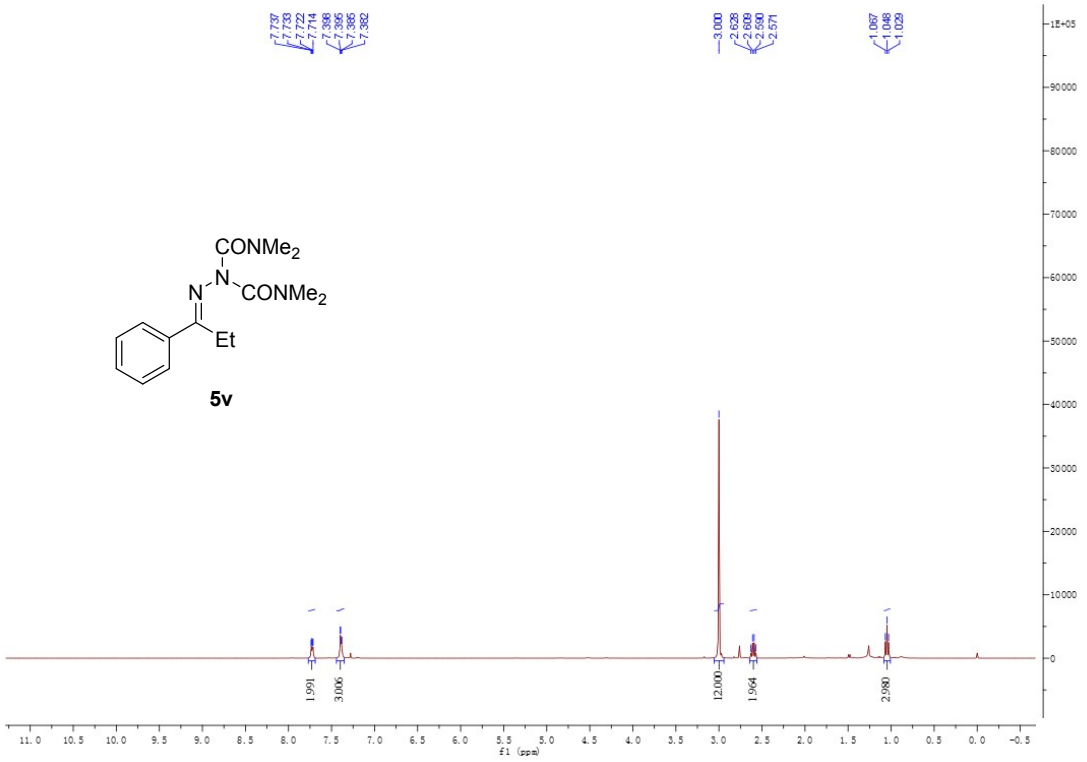
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 5u



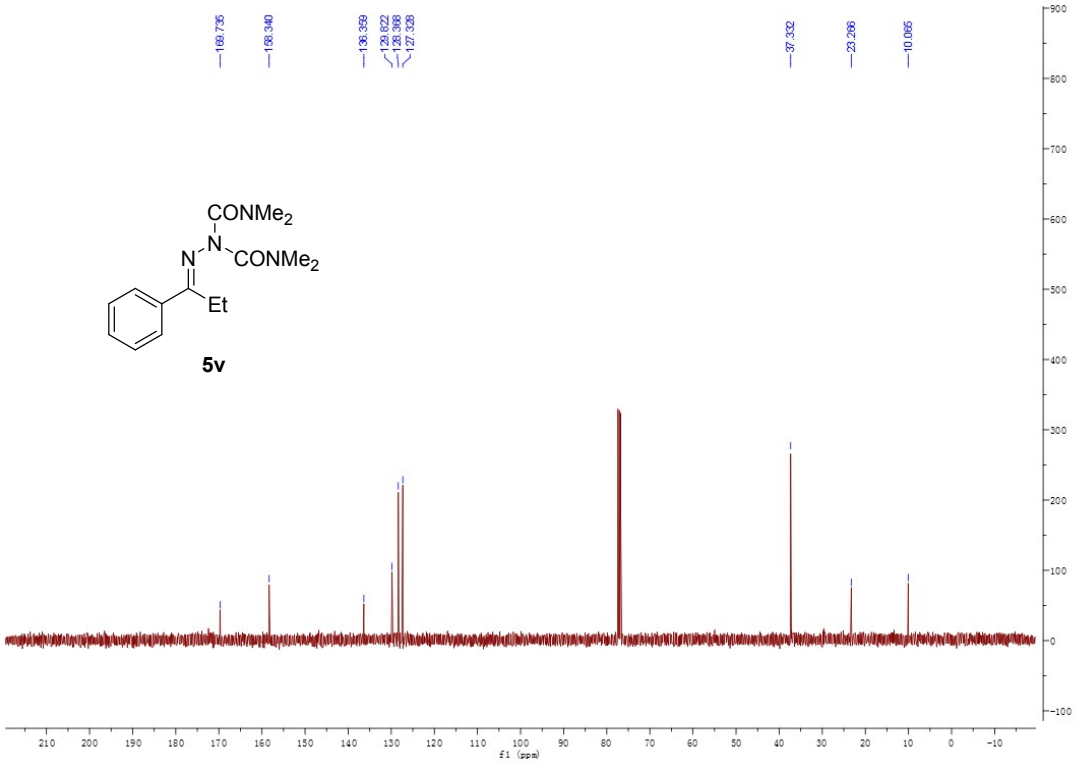
^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 5u



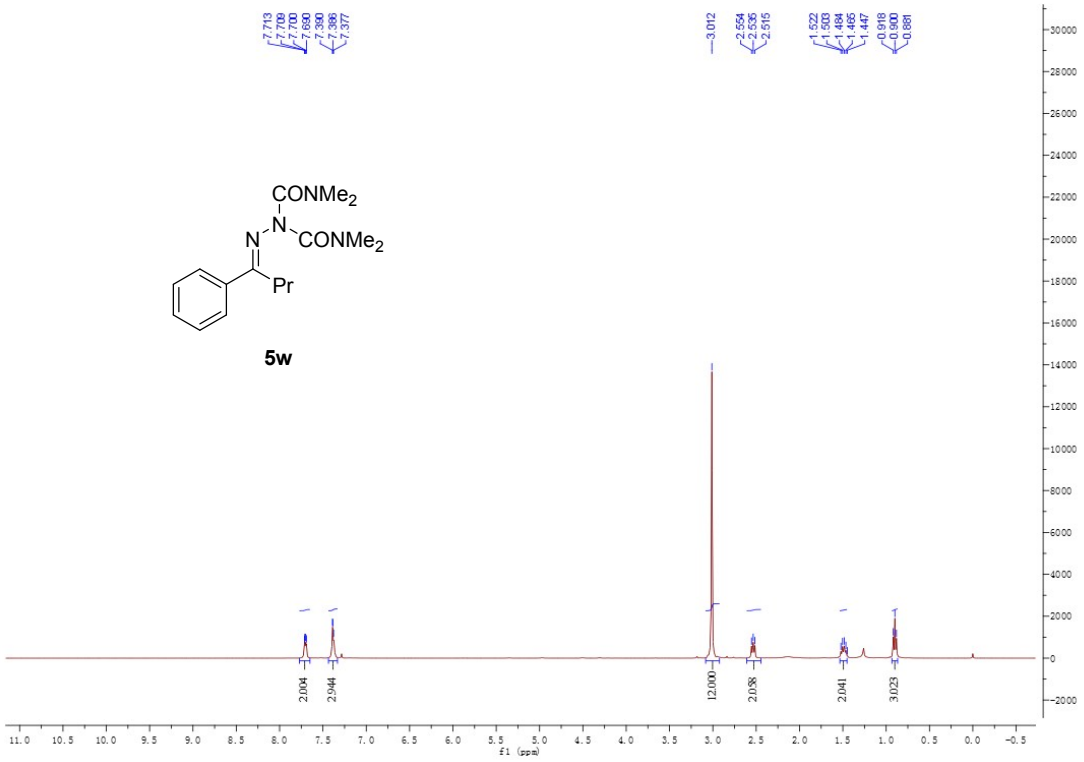
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 5v



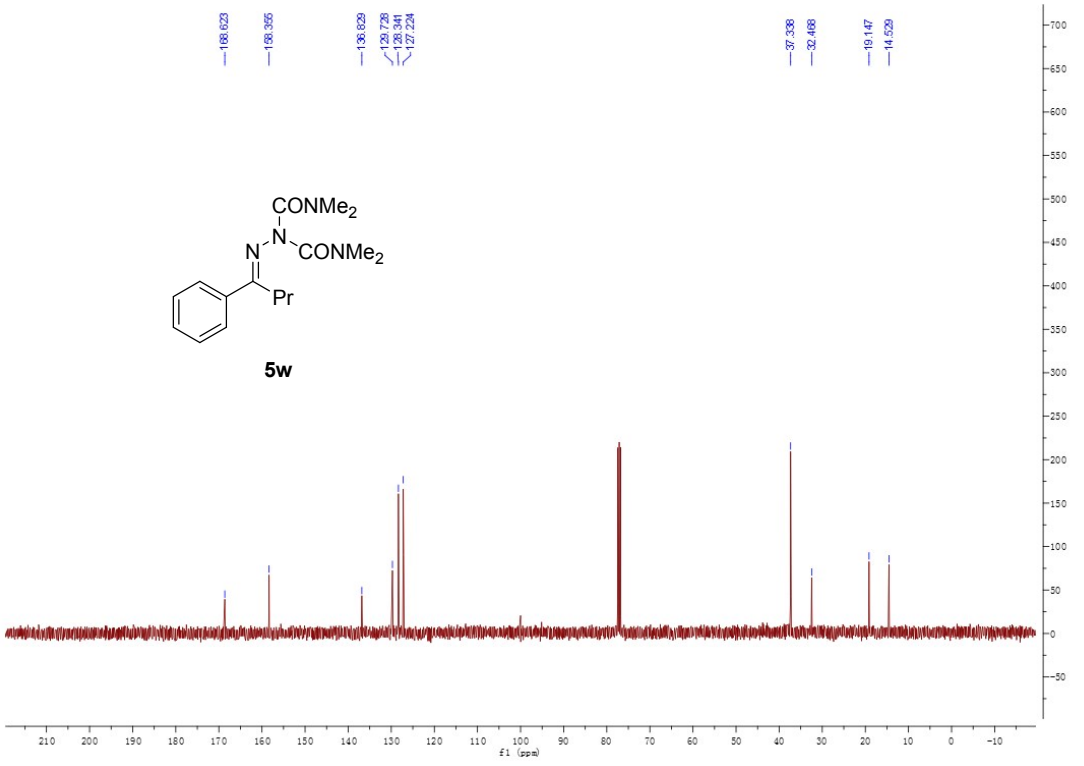
^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 5v



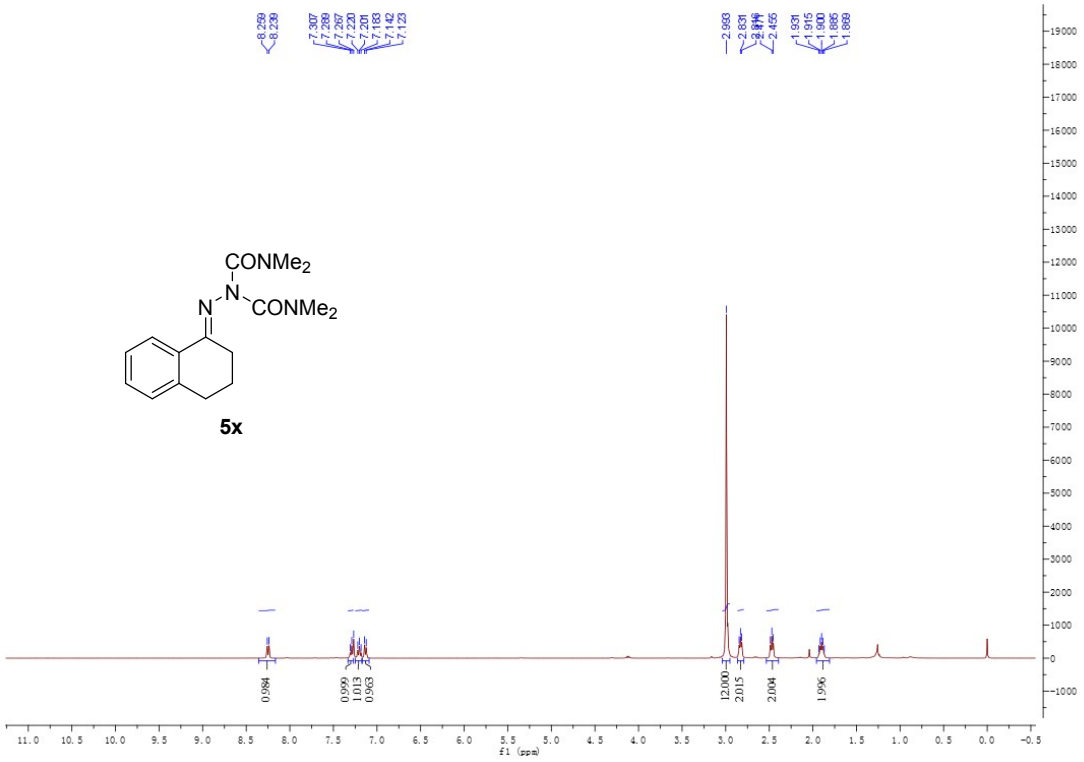
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 5w



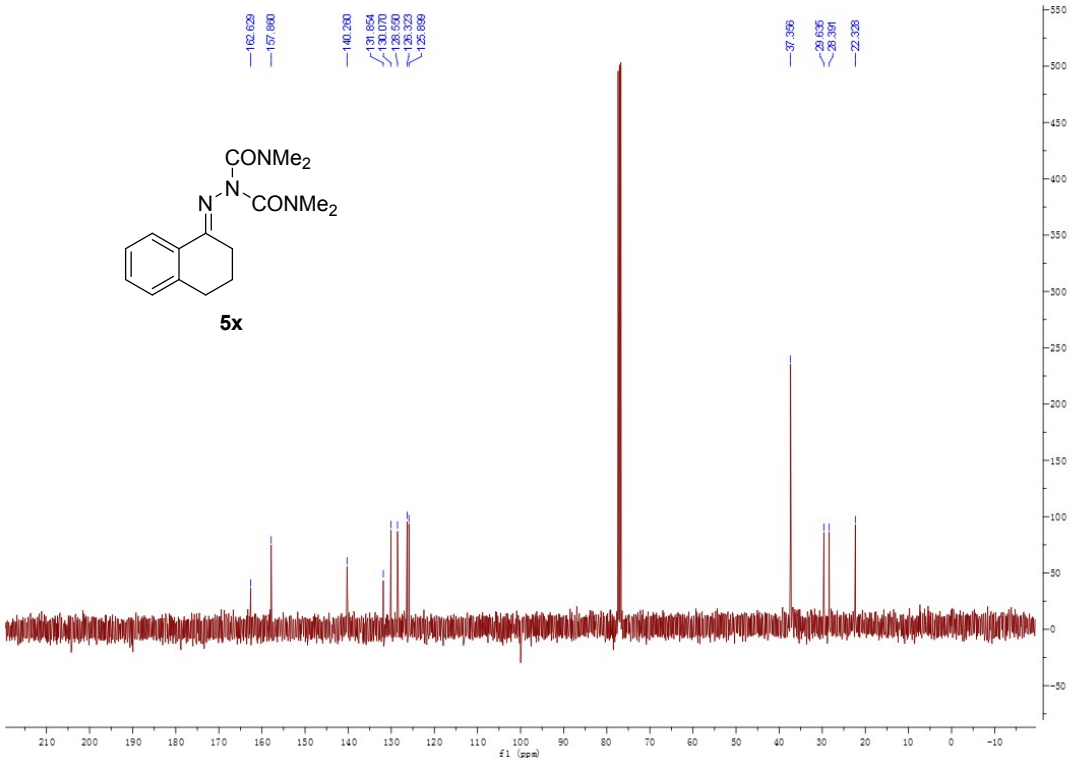
^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 5w



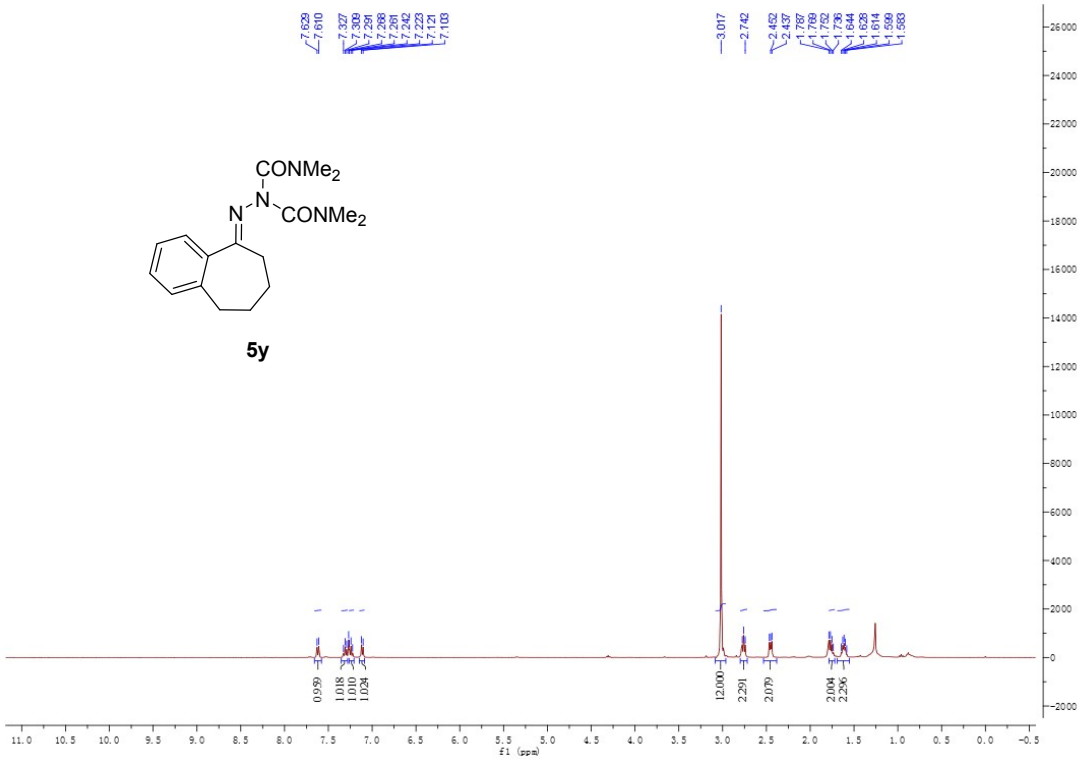
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 5x



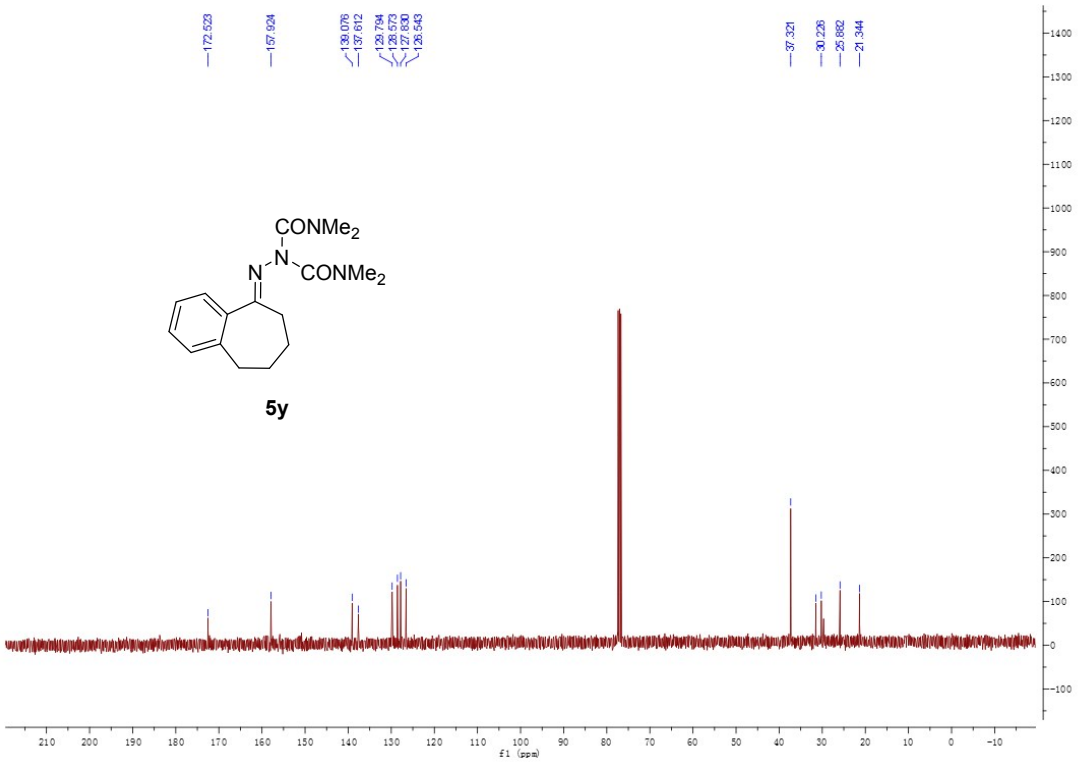
^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 5x



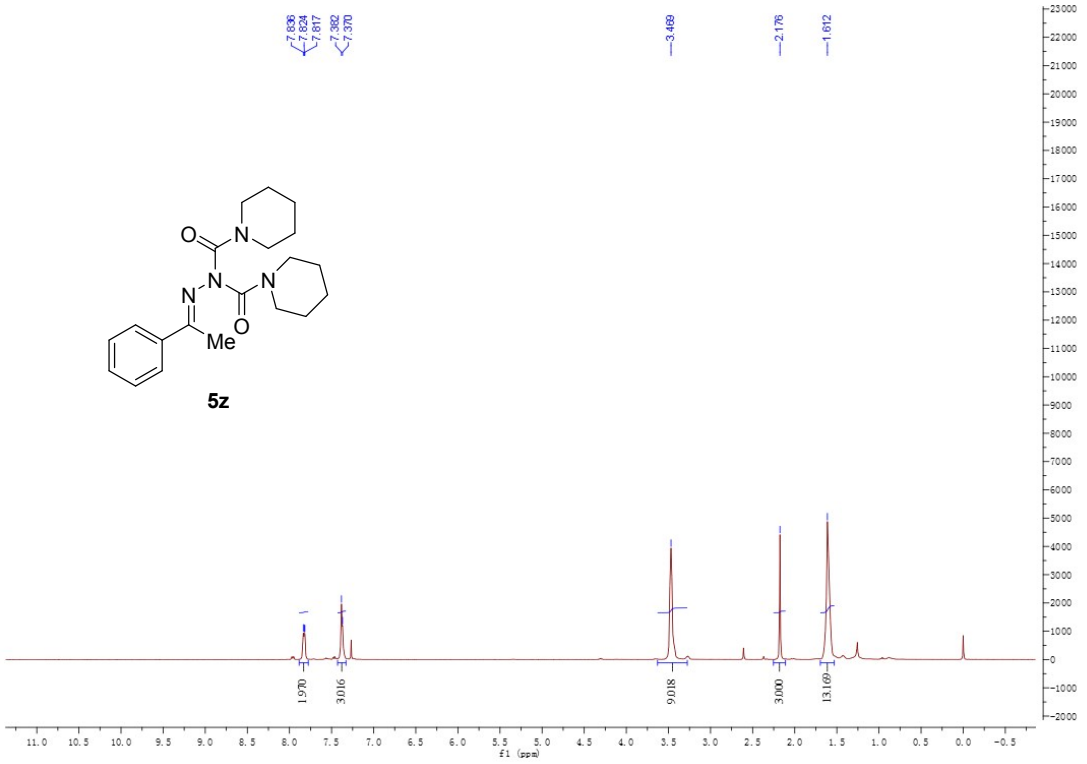
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 5y



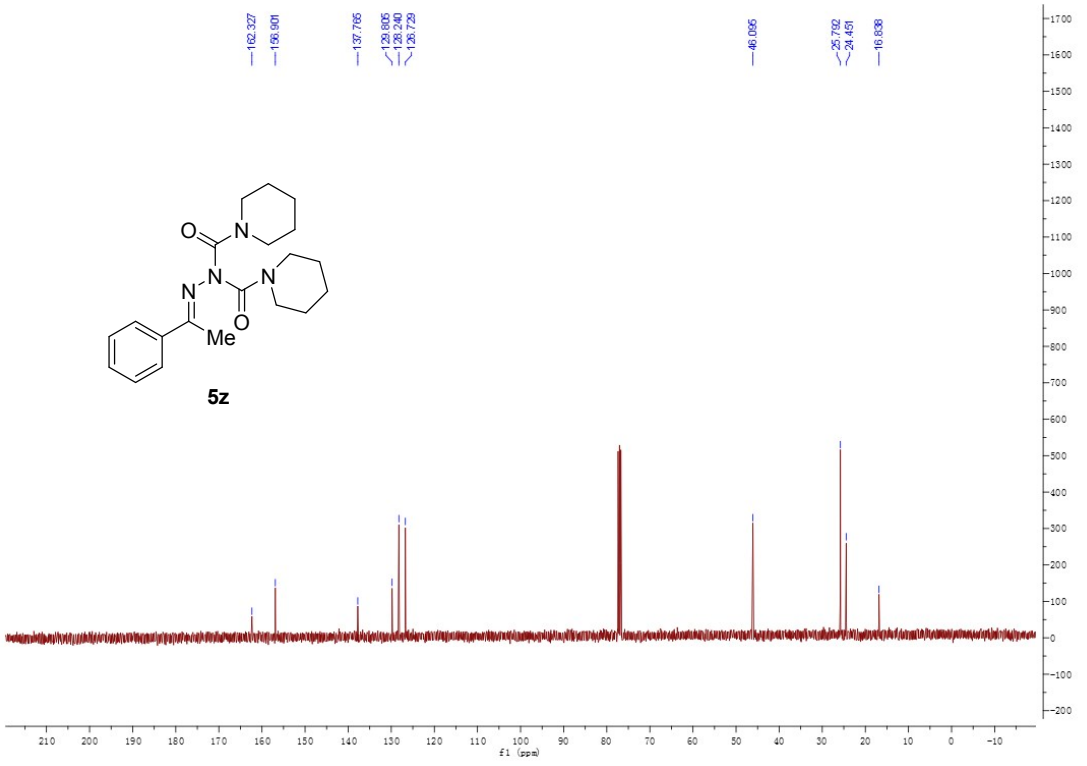
^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 5y



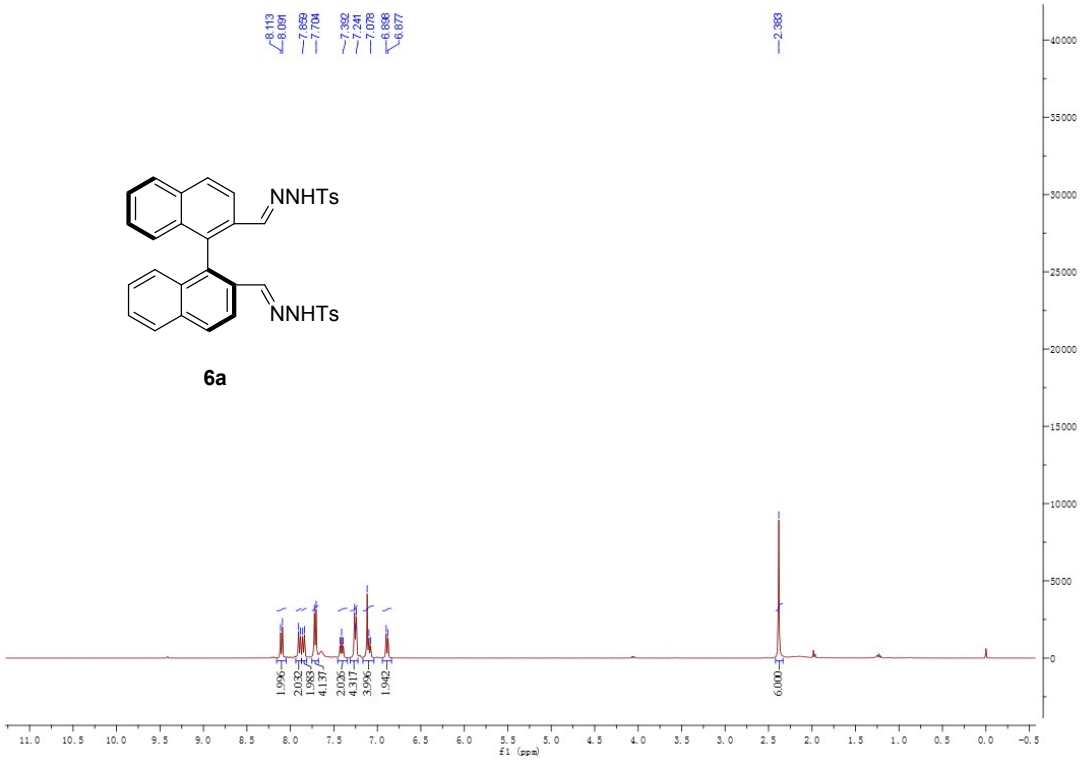
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 5z



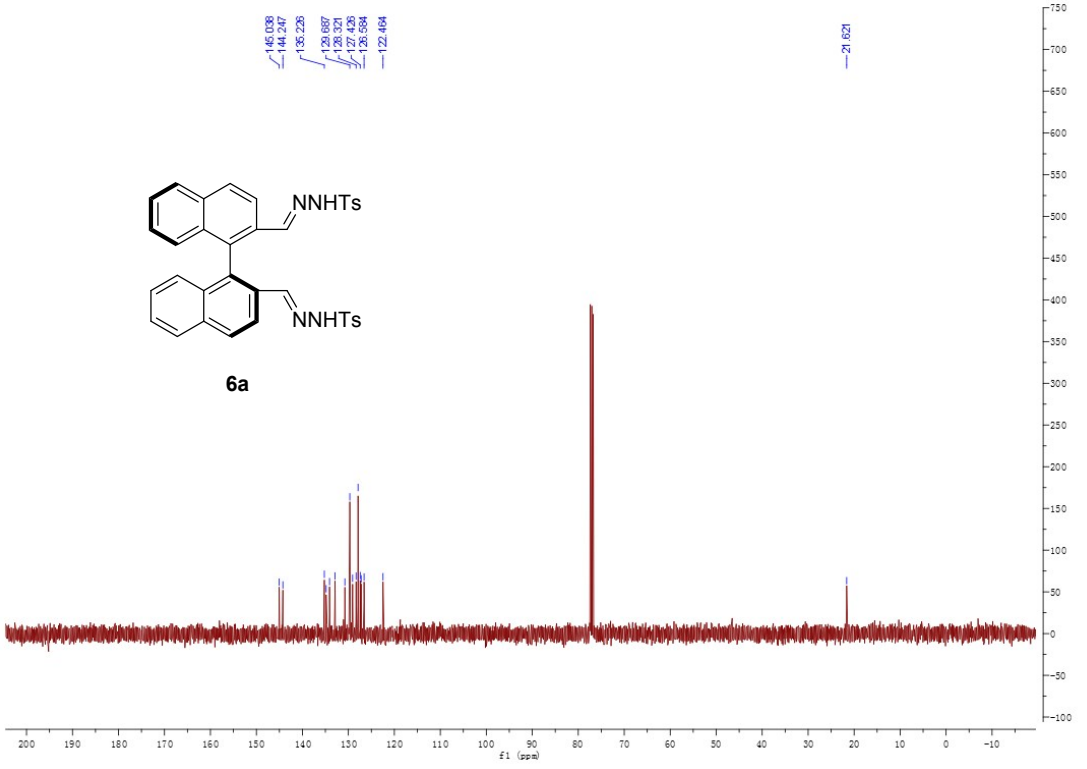
^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 5z



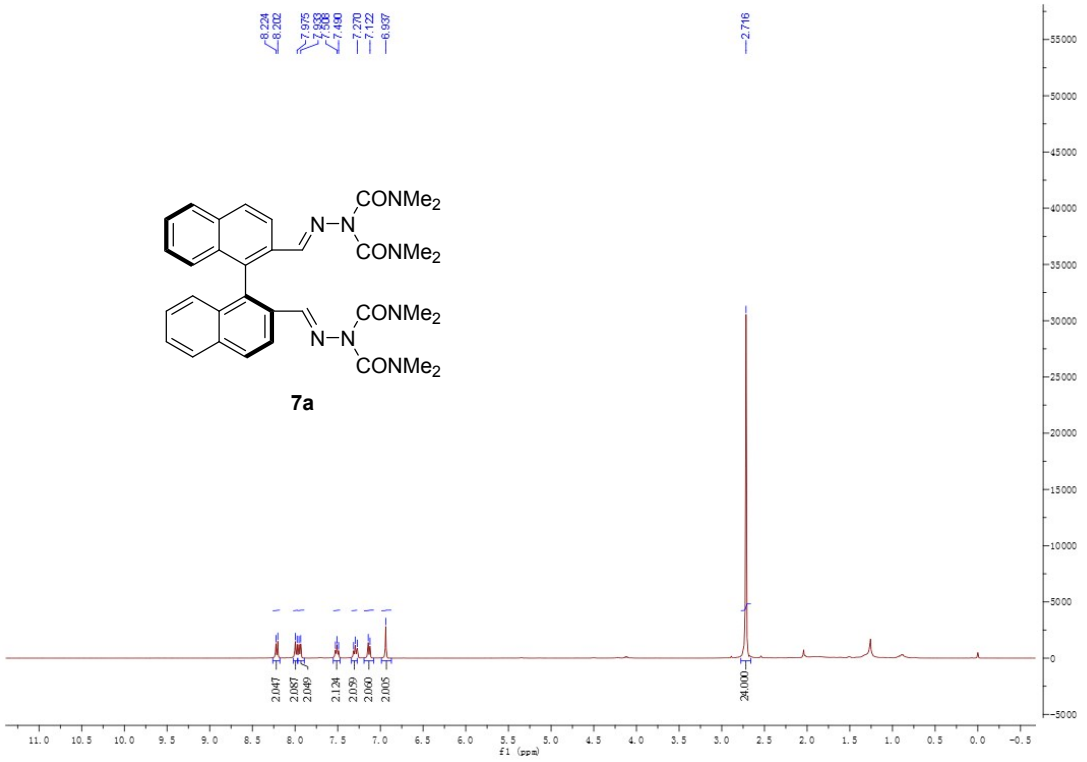
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 6a



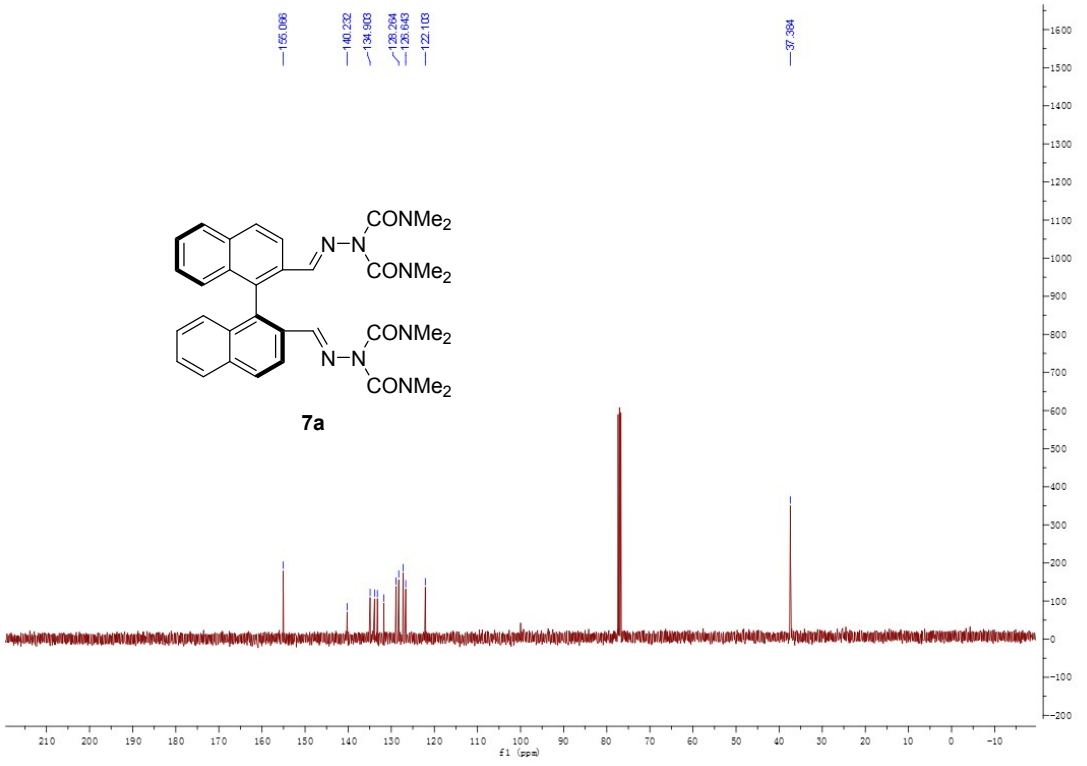
^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 6a



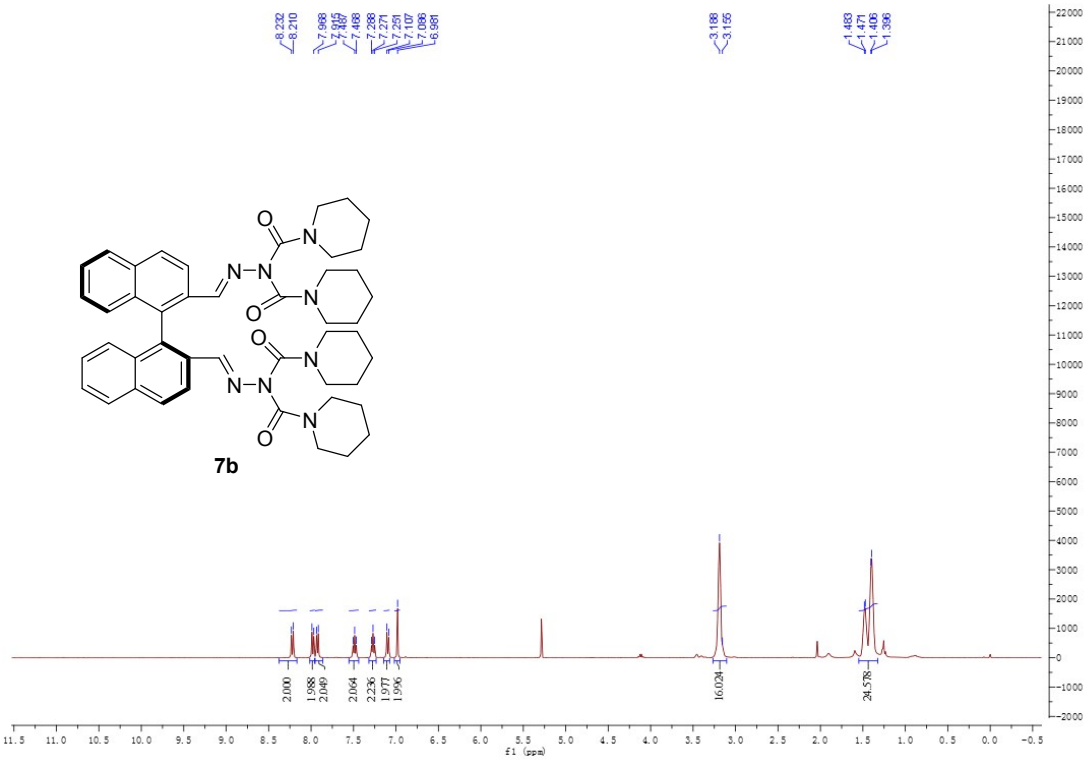
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 7a



^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 7a

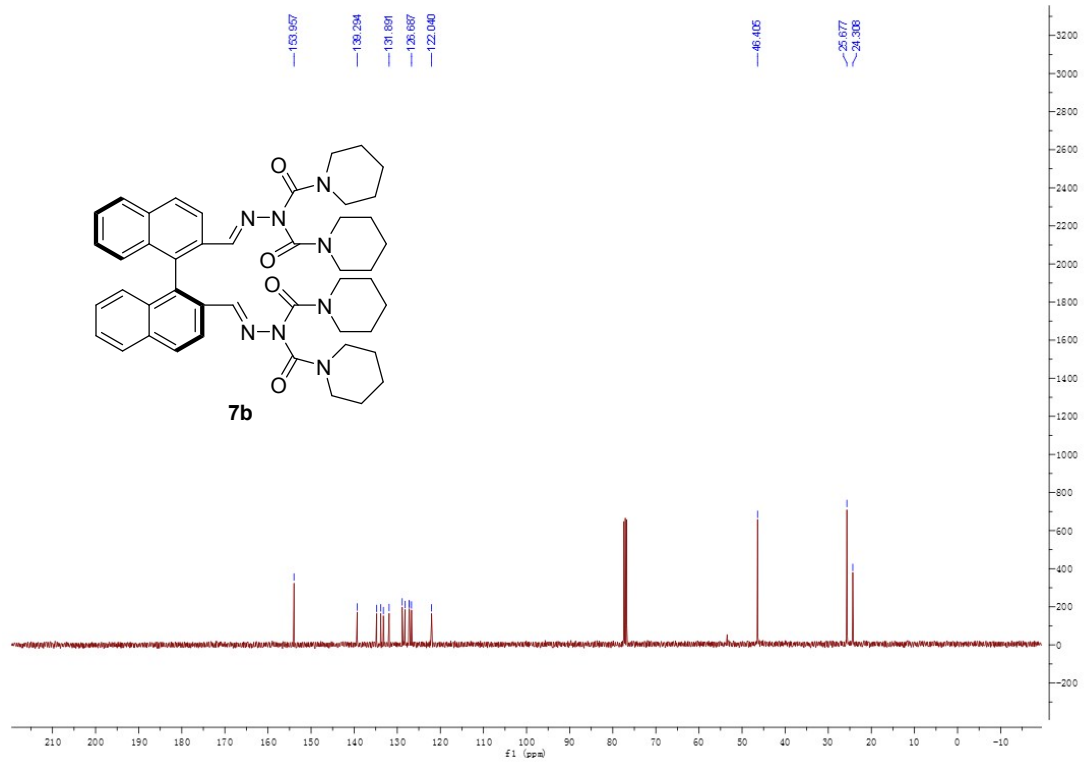


^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 7b



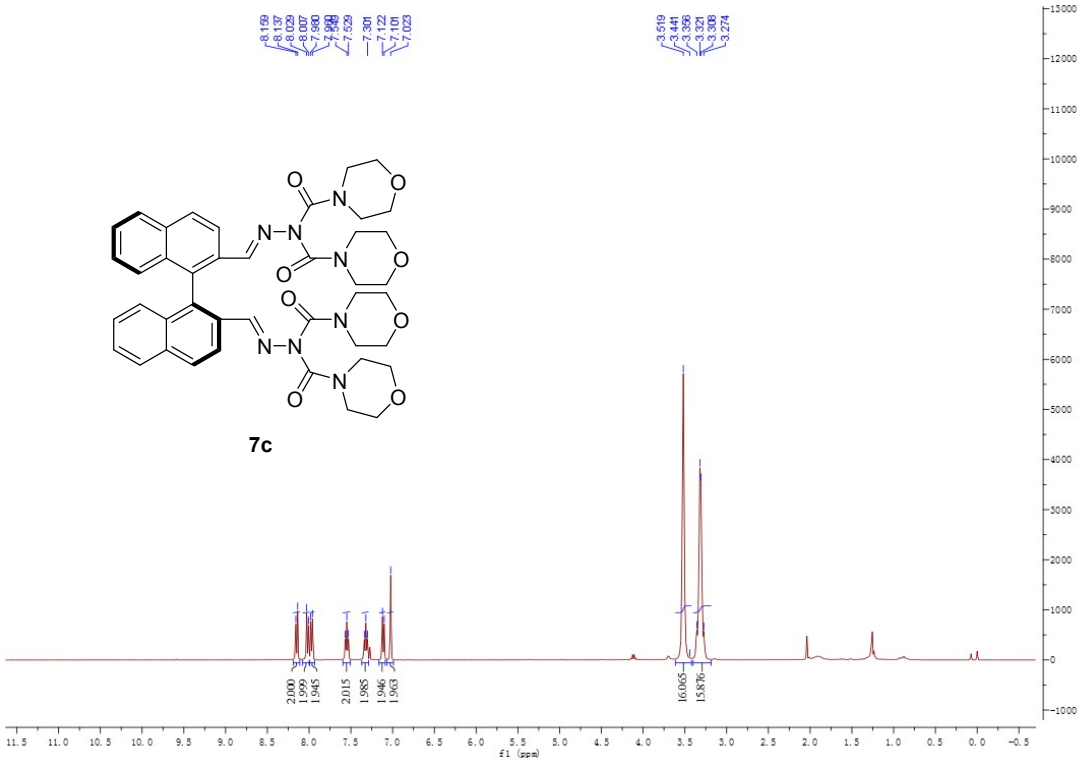
7b

^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 7b



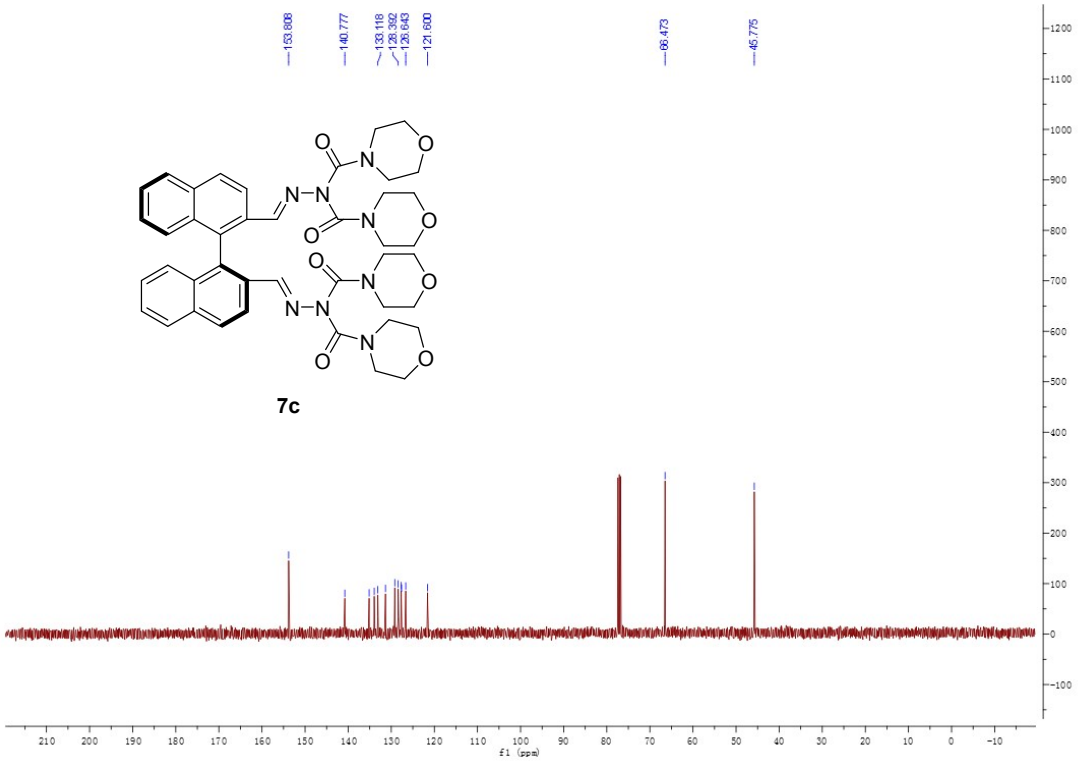
7b

^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 7c



7c

^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 7c



7c