Ruthenium-Catalyzed C-H Amination of Aroylsilanes

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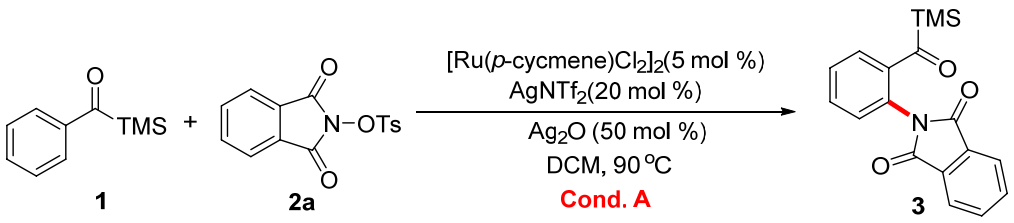
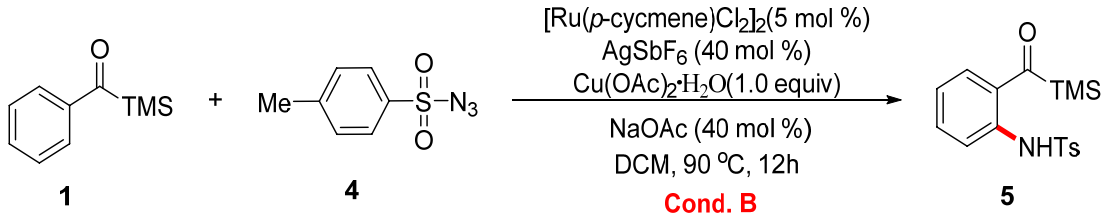
General Methods

Analytical thin layer chromatography (TLC) was performed using Merck 60 F254 precoated silica gel plate (0.2 mm thickness). Subsequent to elution, plates were visualized using UV radiation (254 nm) on Spectroline Model ENF-24061/F254 nm. Further visualization was possible by staining with basic solution of potassium permanganate or acidic solution of ceric molybdate. Flash column chromatography was performed using Merck aluminium oxide 90 active neutral with freshly distilled solvents. Columns were typically packed as slurry and equilibrated with the appropriate solvent system prior to use. Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on Bruker AMX400 and 500 MHz spectrophotometer ($CDCl_3$ as solvent). Chemical shifts for ^{1}H NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-*d* (δ 7.26, singlet). Multiplicities were given as: s (singlet), d (doublet), t (triplet), dd (doublets of doublet) or m (multiplets). The number of protons (n) for a given resonance is indicated by nH. Coupling constants are reported as a *J* value in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-*d* (δ 77.0, triplet). Mass spectrometry was performed by Waters Q-Tof Premier Micromass instrument, using Electro Spray Ionization (ESI) mode. IR spectra were recorded as thin films on KBr or NaCl plates on a Bio-Rad FTS 165 FTIR spectrometer and are reported in frequency of absorption (cm^{-1}). Other reagents, unless otherwise noted below, are commercially available from Alfa Aesar (China) Chemical Co., Ltd. and used without further purification. Acylsilanes were prepared by reported methods.[1-2]

General Procedure for Ru-Catalyzed C-H Amination

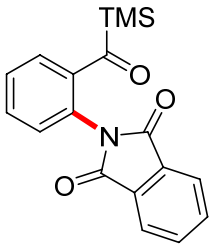


An oven-dried vial was charged with $[Ru(p\text{-cymene})Cl_2]_2$ (5 mol %, 0.005 mmol), $AgNTf_2$ (20 mol %, 0.02 mmol), Ag_2O (50 mol %, 0.05 mmol), **2a** (0.2 mmol, 63.4 mg) and DCM (0.7 mL). Then, acylsilane **1** (0.1 mmol, 17.8 mg) was added into the solution. The vial was sealed under argon and heated to 90 ℃ with stirring for 18 hours. After cooling down, the mixture was directly applied to a flash column chromatography (ethyl acetate/petroleum ether mixtures) on silica gel to afford **3**.



An oven-dried vial was charged with $[Ru(p\text{-cymene})Cl_2]_2$ (5 mol %, 0.005 mmol), $AgSbF_6$ (40 mol %, 0.04 mmol), $Cu(OAc)_2 \cdot H_2O$ (1.0 eq, 0.1 mmol), NaOAc (40 mol %, 0.04 mmol) and DCM (0.7 mL). Then, acylsilane **1** (0.1 mmol, 17.8 mg) and **4** (0.2 mmol, 39.4 mg) were added into the solution. The vial was sealed under argon and heated to 90 ℃ with stirring for 12 hours. After cooling down, the mixture was directly applied to a flash column chromatography (ethyl acetate/petroleum ether mixtures) on silica gel to afford **5.**

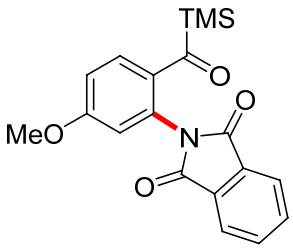
Characterization Data



(3aa)

2-(2-((trimethylsilyl)carbonyl)phenyl)isoindoline-1,3-dione

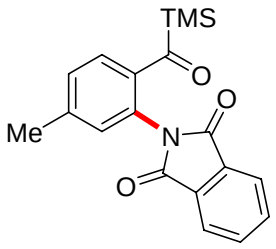
Following the general experiment procedure, **3aa** was obtained as a yellow solid (77%, 25.0 mg), m.p:155.3℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 11.53 (s, 1H), δ = 7.80 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.70 (d, *J* = 8.5Hz, 2H), 7.65 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.41 (td, *J* = 10.5, 1.5 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.13 (td, *J* = 7.5, 1 Hz, 1H), 2.35 (s, 3H), 0.31 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 240.21, 169.32, 141.48, 136.16, 133.96, 133.51, 131.86, 131.02, 130.34, 128.60, 125.58, 2.91. **HR-MS** (ESI): m/z calculated for $C_{20}H_{27}NO_3SSi$: $[M+H]^+$: 324.1051, found: 324.1054. **FTIR** (KBr, cm^{-1}): 3384.70, 2945.79, 2828.04, 1647.66, 1534.23, 1403.74, 1028.83.



(3ab)

2-(5-methoxy-2-((trimethylsilyl)carbonyl)phenyl)isoindoline-1,3-dione

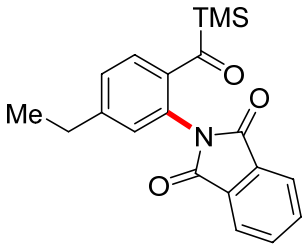
Following the general experiment procedure, **3ab** was obtained as a yellow solid (60%, 21.2 mg), m.p:137.9℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.92 (dd, *J* = 5.0, 3.0 Hz, 2H), 7.84 (d, *J* = 8.5 Hz, 1H), 7.77 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.06 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.88 (d, *J* = 2.5 Hz, 1H), 3.89 (s, 3H), 0.31 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 236.86, 169.10, 163.75, 135.81, 134.33, 133.83, 133.62, 130.62, 125.34, 118.07, 115.36, 57.32, 2.62. **HR-MS** (ESI): m/z calculated for $C_{19}H_{19}NO_4Si$: $[M+H]^+$: 354.1156, found:354.1156. **FTIR** (KBr, cm^{-1}): 3383.49, 2973.83, 2938.60, 2839.25, 1476.64, 1392.52, 1032.68, 1016.82.



(3ac)

2-(5-methyl-2-((trimethylsilyl)carbonyl)phenyl)isoindoline-1,3-dione

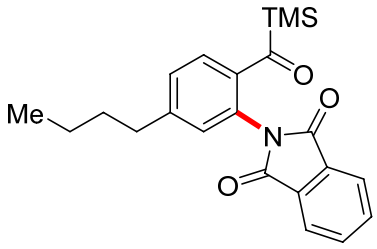
Following the general experiment procedure, **3ac** was obtained as a yellow solid (62%, 21 mg), m.p:133.2℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.92-7.89 (m, 2H), 7.78-7.74 (m, 2H), 7.71 (d, *J* = 7.5 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.18 (s, 1H), 2.45 (s, 3H), 0.31 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 239.15, 169.38, 144.53, 138.47, 135.96, 133.95, 132.71, 131.85, 131.04, 128.58, 125.45, 23.23, 2.79. **HR-MS** (ESI): m/z calculated for $C_{19}H_{19}NO_3Si$: $[M+H]^+$: 338.1207, found: 338.121. **FTIR** (KBr, cm^{-1}): 3731.69, 3627.12, 3383.79, 2922.90, 1734.58, 1557.44, 1403.00, 1026.47.



(3ad)

2-(5-ethyl-2-((trimethylsilyl)carbonyl)phenyl)isoindoline-1,3-dione

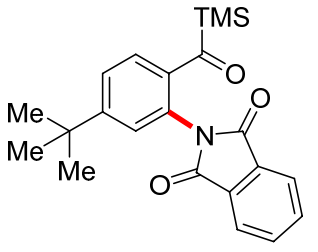
Following the general experiment procedure, **3ad** was obtained as a yellow solid (70%, 24.5 mg), m.p: 155.0℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.92 - 7.89 (m, 2H), 7.78-7.73 (m, 3H), 7.39 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.20 (d, *J* = 1Hz, 1H), 2.76 (q, *J* = 7.5 Hz, 2H), 1.39 (t, *J* = 7.5 Hz, 3H), 0.32 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 239.11, 169.37, 150.54, 138.59, 135.94, 133.95, 131.95, 131.56, 129.76, 128.64, 125.41, 30.39, 16.53, 2.77. **HR-MS** (ESI): m/z calculated for $C_{20}H_{21}NO_3Si$: $[M+H]^+$: 352.1363, found: 352.1364. **FTIR** (KBr, cm^{-1}): 3850.87, 3748.24, 3667.61, 3564.65, 2357.70, 1731.78, 1557.18, 1028.04.



(3ae)

2-(5-butyl-2-((trimethylsilyl)carbonyl)phenyl)isoindoline-1,3-dione

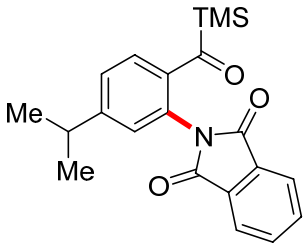
Following the general experiment procedure, **3ae** was obtained as a yellow solid (65%, 23.8 mg), m.p:165.4℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.90 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.77-7.72 (m, 3H), 7.37 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.19 (d, *J* = 1.5 Hz, 1H), 2.70 (t, J = 7.0 Hz, 2H), 1.69-1.63 (ddd, *J* = 9.5, 5.0, 2.0 Hz, 2H), 1.40 (dd, *J* = 15.0, 7.5 Hz, 2H), 0.94 (t, *J* = 7.5 Hz, 3H), 0.32 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 239.10, 169.34, 149.37, 138.54, 135.93, 133.94, 132.00, 131.84, 130.25, 128.57, 125.39, 37.17, 34.68, 24.12, 15.64, 2.77. **HR-MS** (ESI): m/z calculated for $C_{22}H_{25}F_3NO_3Si$: $[M+H]^+$: 380.1676, found: 380.1673. **FTIR** (KBr, cm^{-1}): 3850.96, 3708.81, 3646.24, 3422.68, 2357.60, 1651.54, 1557.31, 1021.07.



(3af)

2-(5-(tert-butyl)-2-((trimethylsilyl)carbonyl)phenyl)isoindoline-1,3-dione

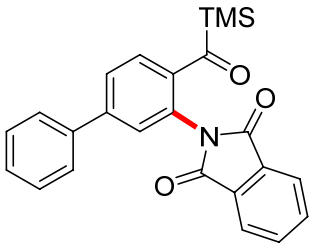
Following the general experiment procedure, **3af** was obtained as a yellow solid (80%, 30 mg), m.p: 196.0℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.91 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.78- 7.75 (m, 3H), 7.57 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.35 (d, *J* = 2.0 Hz, 1H), 1.37 (s, 9H), 0.32 (s, 9H).**^{13}C NMR** (125 MHz, $CDCl_3$) : δ = 238.97, 169.39, 157.48, 138.17, 135.89, 133.99, 131.80, 129.30, 128.45, 127.31, 125.38, 36.89, 32.77, 32.69, 2.75. **HR-MS** (ESI): m/z calculated for $C_{22}H_{25}NO_3Si$: $[M+H]^+$: 380.1676, found: 380.1673. **FTIR** (KBr, cm^{-1}): 3851.23, 3673.83, 3565.06, 3417.06, 2957.39, 1651.67, 1457.01, 1032.54.



(3ag)

2-(5-isopropyl-2-((trimethylsilyl)carbonyl)phenyl)isoindoline-1,3-dione

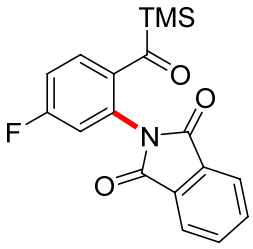
Following the general experiment procedure, **3ag** was obtained as a yellow solid (69%, 25 mg), m.p:143.8℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.91 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.77-7.75 (m, 3H), 7.42 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.22 (d, *J* = 1.5 Hz, 1H), 3.00 (dt, *J* = 14, 7.0 Hz, 1H), 1.31 (d, *J* = 6.9 Hz, 6H), 0.32 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 239.01, 169.36, 155.10, 138.61, 135.91, 133.94, 132.02, 130.34, 128.65, 128.33, 125.39, 35.77, 25.29, 2.76. **HR-MS** (ESI): m/z calculated for $C_{21}H_{23}NO_3Si$: $[M+H]^+$: 366.1520, found: 366.1522. **FTIR** (KBr, cm^{-1}): 3851.60, 3742.79, 3673.89, 3444.21, 1682.51, 1557.45, 1403.03, 1016.82.



(3ah)

2-(4-((trimethylsilyl)carbonyl)-[1,1'-biphenyl]-3-yl)isoindoline-1,3-dione

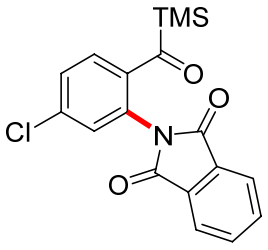
Following the general experiment procedure, **3ah** was obtained as a yellow solid (65%, 26 mg), m.p:159.0℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.93 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.79-7.76 (m, 3H), 7.65 -7.63 (m, 2H), 7.60 (d, *J* = 1.5 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.3 Hz, 1H), 0.36 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 239.37, 169.28, 146.63, 140.83, 139.51, 136.07, 133.93, 131.99, 130.78, 130.72, 130.21, 129.16, 129.12, 128.75, 125.52, 2.80. **HR-MS** (ESI): m/z calculated for $C_{24}H_{21}NO_3Si$: $[M+H]^+$: 400.1363, found: 400.1361. **FTIR** (KBr, cm^{-1}): 3868.36, 3742.97, 3471.24, 2359.32, 1681.31, 1557.66, 1398.11, 668.09.



(3ai)

2-(5-fluoro-2-((trimethylsilyl)carbonyl)phenyl)isoindoline-1,3-dione

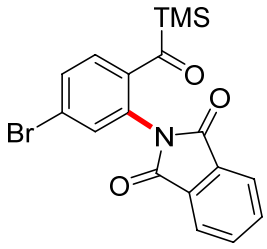
Following the general experiment procedure, **3ai** was obtained as a yellow solid (65%, 22.2 mg), m.p:133.9℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.92 (q, *J* = 3.0 Hz, 2H), 7.80 -7.75 (m, 3H), 7.26 -7.23 (m, 1H), 7.15 (dd, *J* = 9.0, 2.5 Hz, 1H), 0.33 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 238.54, 168.89, 165.47 (d, J_{C-F} = 252.6 Hz), 137.88 (d, J_{C-F} = 3.6 Hz), 136.34, 133.80, 133.02 (d, J_{C-F} = 9.7 Hz), 130.87 (d, J_{C-F} = 10.9 Hz), 125.74, 119.69 (d, J_{C-F} = 23.5 Hz), 117.23 (d, J_{C-F} = 21.1 Hz), 2.90. **HR-MS** (ESI): m/z calculated for $C_{18}H_{16}NO_3Si$: $[M+H]^+$: 342.0956, found: 342.0950. **FTIR** (KBr, cm^{-1}): 3667.90, 3564.88, 3472.93, 3383.78, 2358.15, 1731.78, 1684.11, 1403.01, 1028.04.



(3aj)

2-(5-chloro-2-((trimethylsilyl)carbonyl)phenyl)isoindoline-1,3-dione

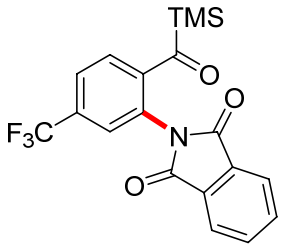
Following the general experiment procedure, **3aj** was obtained as a yellow solid (49%, 17.5 mg), m.p: 130.9℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.92 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.78 (dd, *J* = 5.5, 3.5 Hz, 2H), 7.68 (d, *J* = 8.5 Hz, 1H), 7.53 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.42 (d, *J* = 2.0 Hz, 1H), 0.32 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 239.11, 168.95, 139.82, 139.15, 136.41, 133.83, 132.21, 131.96, 130.51, 130.00, 125.79, 2.96. **HR-MS** (ESI): m/z calculated for $C_{18}H_{16}ClNO_3Si$: $[M+H]^+$: 358.0661, found:358.0655. **FTIR** (KBr, cm^{-1}): 3851.10, 3742.44, 3646.24, 3184.11, 1651.56, 1557.28, 1504.96, 1402.83, 1036.45.



(3ak)

2-(5-bromo-2-((trimethylsilyl)carbonyl)phenyl)isoindoline-1,3-dione

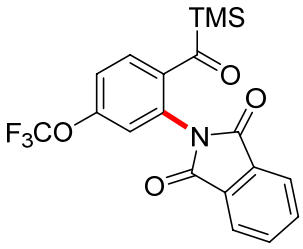
Following the general experiment procedure, **3ak** was obtained as a yellow solid (42%, 17 mg), m.p:75.9℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.91 (dd, *J* = 5.0, 3.0 Hz, 2H), 7.78 (dd, *J* = 5.5, 3.5 Hz, 2H), 7.69 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 1.5 Hz, 1H), 0.32 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 239.29, 168.95, 140.27, 136.43, 135.02, 133.83, 133.48, 132.01, 129.94, 127.20, 125.80, 2.96. **HR-MS** (ESI): m/z calculated for $C_{18}H_{16}BrNO_3Si$: $[M+H]^+$: 402.0156, found:402.0150. **FTIR** (KBr, cm^{-1}): 3686.55, 3654.57, 3417.41, 3209.36, 2958.12, 1731.78, 1650.47, 1555.14, 1025.23, 500.24.



(3al)

2-(5-(trifluoromethyl)-2-((trimethylsilyl)carbonyl)phenyl)isoindoline-1,3-dione

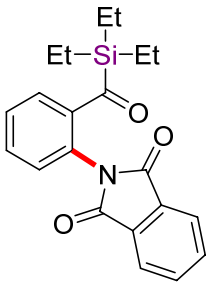
Following the general experiment procedure, **3al** was obtained as a yellow solid (43%, 16.5 mg), m.p:163.8℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.92 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.81 -7.77 (m, 4H), 7.70 (s, 1H), 0.34 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 168.77, 144.55, 136.48, 135.0 (d, $J_{C\text{-}F}$ = 33.2 Hz), 133.66, 130.31, 129.21, 128.68 (q, $J_{C\text{-}F}$ = 3.7 Hz), 127.06 (q, $J_{C\text{-}F}$ = 3.7 Hz), 125.78, 122.84 (q, $J_{C\text{-}F}$ = 271.2 Hz), 31.58, 2.90. **HR-MS** (ESI): m/z calculated for $C_{19}H_{16}F_3NO_3Si$: $[M+H]^+$: 392.0924, found: 392.0921. **FTIR** (KBr, cm^{-1}): 3673.76, 3417.35, 3209.57, 2923.90, 1731.92, 1402.97, 1137.38, 854.21, 716.82.



(3am)

2-(5-(trifluoromethoxy)-2-((trimethylsilyl)carbonyl)phenyl)isoindoline-1,3-dione

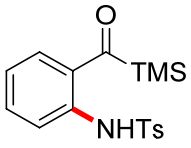
Following the general experiment procedure, **3am** was obtained as a yellow solid (52%, 20.7 mg), m.p:163.8℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.92 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.80 -7.76 (m, 3H), 7.39 (ddd, *J* = 8.5, 2.5, 1.5 Hz, 1H), 7.29 (d, *J* = 1.5 Hz, 1H), 0.34 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 168.84, 152.53, 152.52, 139.79, 136.49, 133.79, 132.19, 130.56, 125.84, 124.15, 121.74, 2.97. **HR-MS** (ESI): m/z calculated for $C_{19}H_{16}F_3NO_4Si$: $[M+H]^+$: 408.0873, found: 408.0866. **FTIR** (KBr, cm^{-1}): 3851.39, 3673.79, 3564.97, 3417.87, 1737.38, 1455.50, 1398.00, 1028.04.



(3an)

2-(2-((triethylsilyl)carbonyl)phenyl)isoindoline-1,3-dione

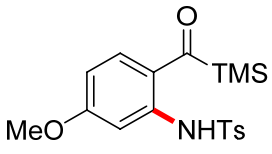
Following the general experiment procedure, **3an** was obtained as a yellow solid (50%, 18.5 mg), m.p:123.0℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.91 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.79-7.75 (m, 3H), 7.62-7.55 (m, 2H), 7.37 (dd, *J* = 7.5, 1.5 Hz, 1H), 0.97 (t, *J* = 8.0 Hz, 9H), 0.88-0.83 (m, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 237.30, 166.71, 139.46, 133.42, 131.35, 130.94, 129.50, 128.58, 127.88, 125.85, 122.87, 6.48, 2.69. **HR-MS** (ESI): m/z calculated for $C_{21}H_{23}NO_3Si$: $[M+H]^+$: 366.1520, found: 366.1521. **FTIR** (KBr, cm^{-1}): 3667.53, 3626.59, 3585.11, 3564.58, 1682.33, 1633.72, 1402.94, 1028.04.



(5aa)

4-methyl-N-(2-((trimethylsilyl)carbonyl)phenyl)benzenesulfonamide

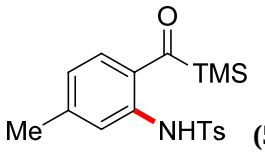
Following the general experiment procedure, **5aa** was obtained as a yellow liquid (79%, 27 mg). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 11.53 (s, 1H), 7.80 (dd, *J* = 7.5, 1.54 Hz, 1H), 7.70 (d, *J* = 8.5 Hz, 2H), 7.65 (dd, *J* = 8.0, 0.5 Hz, 1H), 7.43-7.40 (m, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.13 (td, *J* = 7.5, 1.0 Hz, 1H), 2.35 (s, 3H), 0.31 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 241.44, 145.23, 138.99, 138.12, 135.53, 135.36, 131.01, 128.68, 128.54, 124.08, 120.98, 22.93. **HR-MS** (ESI): m/z calculated for $C_{17}H_{21}NO_3SSi$: $[M+H]^+$: 348.1084, found: 348.1080. **FTIR** (KBr, cm^{-1}): 3852.36, 3626.72, 3383.51, 1651.53, 1538.26, 1403.03, 1026.73, 963.73.



(5ab)

N-(5-methoxy-2-((trimethylsilyl)carbonyl)phenyl)-4-methylbenzenesulfonamide

Following the general experiment procedure, **5ab** was obtained as a yellow liquid (65%, 25 mg). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 12.10 (s, 1H), 7.73 (dd, *J* = 14.5, 8.5 Hz, 3H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 2.5 Hz, 1H), 6.58 (dd, *J* = 9.0, 2.5 Hz, 1H), 3.82 (s, 3H), 2.36 (s, 3H), 0.31 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 165.12, 145.12, 142.00, 138.06, 137.51, 130.91, 128.62, 122.51, 110.01, 104.41, 56.92, 22.82, 2.34. **HR-MS** (ESI): m/z calculated for $C_{18}H_{23}NO_4SSi$: $[M+H]^+$: 378.1190, found: 378.1189. **FTIR** (KBr, cm^{-1}): 3626.63, 3585.09, 3417.52, 2920.56, 1684.11, 1651.55, 1455.18, 1162.62, 1032.53.

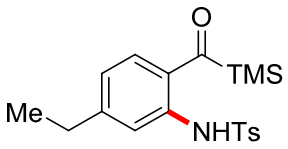


(5ac)

4-methyl-N-(5-methyl-2-((trimethylsilyl)carbonyl)phenyl)benzenesulfonamide

Following the general experiment procedure, **5ac** was obtained as a yellow liquid (58%, 21 mg). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 11.62 (s, 1H), 7.61 (dd, *J* = 20.0, 7.0 Hz, 3H), 7.46 (s, 1H), 7.21

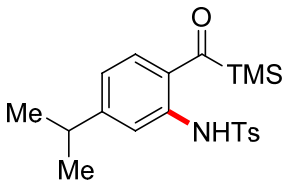
(d, *J* = 7.5 Hz, 2H), 6.92 (d, *J* = 8.0 Hz, 1H), 2.35 (d, *J* = 9.0 Hz, 6H), 0.30 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 240.17, 146.88, 145.06, 139.23, 138.25, 135.39, 130.93, 128.65, 126.53, 124.90, 121.20, 23.52, 22.89, 2.43. **HR-MS** (ESI): m/z calculated for $C_{18}H_{23}NO_3SSi$: $[M+H]^+$: 362.1241, found: 362.1232. **FTIR** (KBr, cm^{-1}): 3851.29, 3742.57, 3646.43, 2358.46, 1651.56, 1455.31, 1028.04, 667.77.



(5ad)

N-(5-ethyl-2-((trimethylsilyl)carbonyl)phenyl)-4-methylbenzenesulfonamide

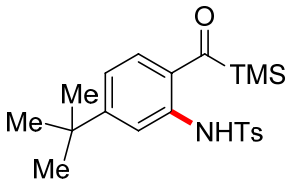
Following the general experiment procedure, **5ad** was obtained as a yellow liquid (60%, 23 mg). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 11.64 (s, 1H), 7.71 (dd, *J* = 8.0, 2.5 Hz, 3H), 7.49 (d, *J* = 1.0 Hz, 1H), 7.20 (d, *J* = 8.5 Hz, 2H), 6.94 (dd, *J* = 8.0, 1.0 Hz, 1H), 2.63 (q, *J* = 7.5 Hz, 2H), 2.35 (s, 3H), 1.20 (t, *J* = 7.5 Hz, 3H), 0.30 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 240.15, 152.90, 145.05, 139.31, 138.18, 135.52, 130.87, 128.72, 126.62, 123.61, 120.00, 30.63, 22.87, 16.18, 2.41. **HR-MS** (ESI): m/z calculated for $C_{19}H_{25}NO_3SSi$: $[M+H]^+$: 376.1397, found: 376.1393. **FTIR** (KBr, cm^{-1}): 3851.26, 3646.51, 3444.39, 2358.27, 1651.69, 1557.48, 1402.83, 1022.43.



(5ae)

N-(5-isopropyl-2-((trimethylsilyl)carbonyl)phenyl)-4-methylbenzenesulfonamide

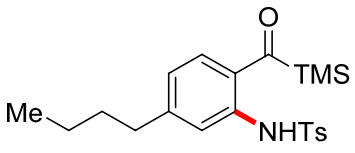
Following the general experiment procedure, **5ae** was obtained as a yellow liquid (60%, 23 mg). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 11.63 (s, 1H), 7.71 (dd, *J* = 8.0, 3.0 Hz, 3H), 7.51 (d, *J* = 1.5 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.96 (dd, *J* = 8.0, 1.5 Hz, 1H), 2.91-2.86 (m, 1H), 2.35 (s, 3H), 1.21 (d, *J* = 7.0 Hz, 6H), 0.30 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 240.15, 157.38, 145.08, 139.31, 138.06, 135.60, 130.84, 128.77, 126.64, 122.17, 118.61, 35.87, 24.71, 22.87, 2.41. **HR-MS** (ESI): m/z calculated for $C_{20}H_{27}NO_3SSi$: $[M+H]^+$: 390.1550, found: 390.1544. **FTIR** (KBr, cm^{-1}): 3686.48, 3444.48, 3170.89, 1651.56, 1557.22, 1402.85, 1025.15, 449.20.



(5af)

N-(5-(tert-butyl)-2-((trimethylsilyl)carbonyl)phenyl)-4-methylbenzenesulfonamide

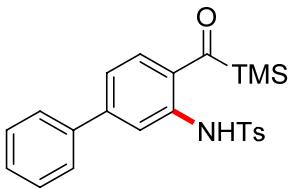
Following the general experiment procedure, **5af** was obtained as a yellow liquid (53%, 21 mg). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 11.62 (s, 1H), 7.72 (dd, *J* = 8.5, 2.5 Hz, 3H), 7.65 (d, *J* = 2.0 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.11 (dd, *J* = 8.5, 1.5 Hz, 1H), 2.35 (s, 3H), 1.28 (s, 9H), 0.31 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 240.10, 159.59, 145.06, 139.07, 138.17, 135.25, 130.84, 128.86, 126.19, 120.94, 117.81, 36.88, 32.18, 22.86, 2.41. **HR-MS** (ESI): m/z calculated for $C_{21}H_{29}NO_3SSi$: $[M+H]^+$: 404.1710, found: 404.1702. **FTIR** (KBr, cm^{-1}): 3851.09, 3417.32, 3209.05, 2957.01, 1651.51, 1557.22, 1402.95, 1028.04.



(5ag)

N-(5-butyl-2-((trimethylsilyl)carbonyl)phenyl)-4-methylbenzenesulfonamide

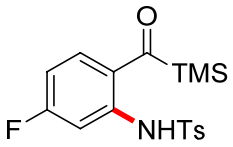
Following the general experiment procedure, **5ag** was obtained as a yellow liquid (62%, 25 mg). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 11.63 (s, 1H), 7.71-7.67 (m, 3H), 7.46 (d, *J* = 1.0 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.91 (dd, *J* = 8.0, 1.5 Hz, 1H), 2.59 (t, *J* = 7.5 Hz, 2H), 2.35 (s, 3H), 1.58-1.52 (m, 2H), 1.30-1.26 (m, 4H), 0.91 (t, *J* = 7.5 Hz, 3H), 0.30 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 240.14, 151.66, 145.02, 139.20, 138.13, 135.42, 130.85, 128.73, 126.60, 124.19, 120.53, 37.32, 34.18, 23.54, 22.85, 15.26, 2.40. **HR-MS** (ESI): m/z calculated for $C_{21}H_{29}NO_3SSi$: $[M+H]^+$: 404.1710, found: 404.1713. **FTIR** (KBr, cm^{-1}): 3850.83, 3673.41, 3606.00, 3444.07, 1684.11, 1557.15, 1402.95, 1171.03, 1028.04.



(5ah)

4-methyl-N-(4-((trimethylsilyl)carbonyl)-[1,1'-biphenyl]-3-yl)benzenesulfonamide

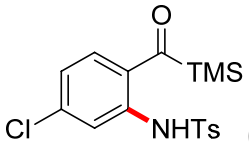
Following the general experiment procedure, **5ah** was obtained as a yellow liquid (60%, 25 mg). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 11.65 (s, 1H), 7.91 (d, *J* = 1.5 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.58-7.56 (m, 2H), 7.48-7.41 (m, 3H), 7.34 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 2.35 (s, 3H), 0.33 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 240.56, 148.01, 145.20, 140.58, 139.61, 138.21, 135.78, 131.00, 130.43, 130.16, 128.73, 128.69, 127.17, 122.53, 119.24, 22.89, 2.42. **HR-MS** (ESI): m/z calculated for $C_{23}H_{25}NO_3SSi$: $[M+H]^+$: 424.1397, found: 424.1395. **FTIR** (KBr, cm^{-1}): 3626.65, 3585.10, 1737.38, 1684.11, 1651.44, 1504.91, 1402.95, 1028.04.



(5ai)

N-(5-fluoro-2-((trimethylsilyl)carbonyl)phenyl)-4-methylbenzenesulfonamide

Following the general experiment procedure, **5ai** was obtained as a yellow liquid (64%, 24 mg). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 11.96 (s, 1H), 7.82 (dd, *J* = 8.5, 6.0 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.37 (dd, *J* = 11.0, 2.0 Hz, 1H), 7.26 (d, *J* = 8.5 Hz, 2H), 6.77 (ddd, *J* = 8.5, 8.0, 2.5 Hz, 1H), 2.38 (s, 3H), 0.33 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 239.44, 167.89, 165.85, 145.57, 142.25 (d, $J_{C\text{-}F}$ = 12.5 Hz), 137.95, 131.19, 128.72, 124.93 **(**d, $J_{C\text{-}F}$ = 2.5 Hz**)**, 110.97 (d, $J_{C\text{-}F}$ = 22.4 Hz), 107.34 (d, $J_{C\text{-}F}$ = 26.8 Hz), 22.96, 2.45. **HR-MS** (ESI): m/z calculated for $C_{17}H_{20}FNO_3SSi$: $[M+H]^+$: 366.0990, found: 366.0992. **FTIR** (KBr, cm^{-1}): 3867.95, 3731.10, 3686.54, 2358.07, 1682.41, 1557.32, 1402.90, 1025.85.

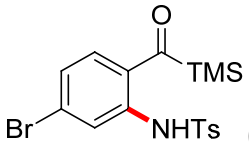


(5aj)

(2-amino-4-chlorophenyl)(trimethylsilyl)methanone

Following the general experiment procedure, **5aj** was obtained as a yellow liquid (73%, 28 mg). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 11.71 (s, 1H), 7.73 (t, *J* = 8.0 Hz, 3H), 7.68 (d, *J* = 2.0 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.07 (dd, *J* = 8.5, 2.0 Hz, 1H), 2.38 (s, 3H), 0.31 (s, 9H). **^{13}C NMR** (125

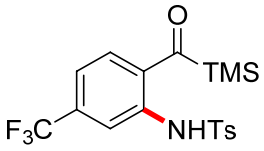
MHz, $CDCl_3$): δ = 240.36, 145.64, 141.92, 140.49, 137.89, 136.47, 131.24, 128.75, 126.44, 124.16, 120.50, 23.02, 2.52. HR-MS (ESI): m/z calculated for $C_{17}H_{20}ClNO_3SSi$: $[M+H]^+$: 382.0694, found: 382.0690. FTIR (KBr, cm^{-1}): 3813.78, 3673.59, 3417.25, 2957.01, 1651.54, 1557.26, 1402.91, 1022.43.



(5ak)

N-(5-bromo-2-((trimethylsilyl)carbonyl)phenyl)-4-methylbenzenesulfonamide

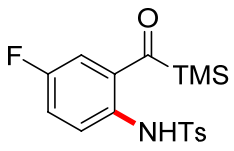
Following the general experiment procedure, **5ak** was obtained as a yellow liquid (65%, 28 mg). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 11.64 (s, 1H), 7.85 (d, *J* = 2.0 Hz, 1H), 7.73 (d, *J* = 8.5 Hz, 2H), 7.63 (d, *J* = 8.5 Hz, 1H), 7.24 (td, *J* = 8.0, 1.5 Hz, 3H), 2.38 (s, 3H), 0.31 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 240.60, 145.63, 140.32, 137.93, 136.41, 131.24, 130.62, 128.78, 127.15, 126.79, 123.60, 23.03, 2.52. **HR-MS** (ESI): m/z calculated for $C_{17}H_{20}BrNO_3SSi$: $[M+H]^+$: 426.0189, found: 426.0185. **FTIR** (KBr, cm^{-1}): 3852.36, 3627.65, 2358.90, 1682.44, 1651.59, 1505.11, 1455.34, 1393.47.



(5al)

4-methyl-N-(5-(trifluoromethyl)-2-((trimethylsilyl)carbonyl)phenyl)benzenesulfonamide

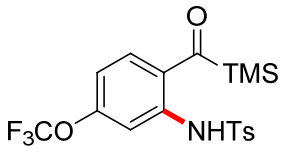
Following the general experiment procedure, **5ai** was obtained as a yellow liquid (72%, 29 mg). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 11.50 (s, 1H), 7.96 (d, *J* = 1.0 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.36 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 2.37 (s, 3H), 0.33 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 241.80, 145.89, 139.63, 137.84, 136.61 (q, J_{C-F} = 32.9 Hz), 135.72, 131.36, 128.92, 124.60 (q, J_{C-F} = 271.4 Hz), 120.52 (q, J_{C-F} = 3.7 Hz), 117.99 (q, J_{C-F} = 3.9 Hz), 23.10, 2.61. **HR-MS** (ESI): m/z calculated for $C_{18}H_{20}F_3NO_3SSi$: $[M+H]^+$: 416.0958, found: 416.0955. **FTIR** (KBr, cm^{-1}): 3851.56, 3654.62, 3555.22, 3384.07, 1682.56, 1402.94, 1025.23, 814.95, 667.84.



(5am)

N-(4-fluoro-2-((trimethylsilyl)carbonyl)phenyl)-4-methylbenzenesulfonamide

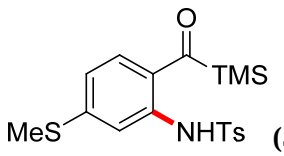
Following the general experiment procedure, **5am** was obtained as a yellow liquid (75%, 27 mg). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 10.11 (s, 1H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.55-7.52 (m, 1H), 7.26-7.22 (m, 4H), 2.39 (s, 3H), 0.27 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 241.04, 158.05 (d, $J_{C\text{-}F}$ = 252.9 Hz), 145.24, 138.76 (d, $J_{C\text{-}F}$ = 1.8 Hz), 135.26, 130.97, 129.48 (d, $J_{C\text{-}F}$ = 3.2 Hz), 129.04 (d, $J_{C\text{-}F}$ = 0.88 Hz), 127.25 (d, $J_{C\text{-}F}$ = 7.6 Hz), 126.27 (d, $J_{C\text{-}F}$ = 12.1 Hz), 122.58 (d, $J_{C\text{-}F}$ = 20.9 Hz), 23.20, 2.70. **HR-MS** (ESI): m/z calculated for $C_{17}H_{20}FNO_3SSi$: $[M+H]^+$: 366.0990, found: 366.0993. **FTIR** (KBr, cm^{-1}): 3853.37, 3675.46, 3422.43, 2360.84, 1560.75, 1454.21, 1397.85, 1025.23.



(5an)

4-methyl-N-(5-(trifluoromethoxy)-2-((trimethylsilyl)carbonyl)phenyl)benzenesulfonamide

Following the general experiment procedure, **5an** was obtained as a yellow liquid (62%, 27 mg). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 11.81 (s, 1H), 7.84 (d, *J* = 8.5 Hz, 1H), 7.76-7.74 (m, 2H), 7.53 (d, *J* = 1.5 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 2H), 6.92-6.89 (m, 1H), 2.37 (s, 3H), 0.33 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 240.08, 154.14 (d, $J_{C\text{-}F}$ = 1.5 Hz), 145.74, 141.55, 137.78, 137.32, 131.23, 128.84, 125.99, 121.67 (q, $J_{C\text{-}F}$ = 258.3 Hz), 114.79, 111.68, 23.01, 2.51. **HR-MS** (ESI): m/z calculated for $C_{18}H_{20}F_3NO_4SSi$: $[M+H]^+$: 432.0907, found: 432.0903. **FTIR** (KBr, cm^{-1}): 3851.17, 3585.34, 3195.50, 1651.55, 1557.26, 1455.23, 1402.95, 1032.09.

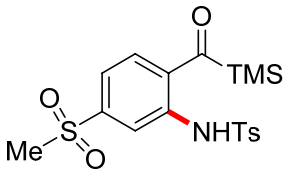


(5ao)

4-methyl-N-(5-(methylthio)-2-((trimethylsilyl)carbonyl)phenyl)benzenesulfonamide

Following the general experiment procedure, **5ao** was obtained as a yellow liquid (36%, 14 mg).

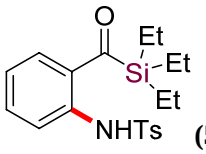
^{1}H NMR (500 MHz, $CDCl_3$): δ = 11.86 (s, 1H), 7.73 (d, *J* = 8.5 Hz, 2H), 7.65 (d, *J* = 8.5 Hz, 1H), 7.42 (d, *J* = 1.5 Hz, 1H), 7.23 (d, *J* = 8.5 Hz, 2H), 6.89 (dd, *J* = 8.5, 2.0 Hz, 1H), 2.47 (s, 3H), 2.37 (s, 3H), 0.30 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 239.06, 149.46, 145.26, 139.78, 138.10, 135.29, 131.00, 128.70, 124.86, 120.28, 115.32, 22.90, 15.91, 2.40. **HR-MS** (ESI): m/z calculated for $C_{18}H_{23}NO_3S_2Si$: $[M+H]^+$: 394.0961, found: 394.0954. **FTIR** (KBr, cm^{-1}): 3731.00, 3646.31, 3417.26, 2358.30, 1651.58, 1557.32, 1455.31, 1027.42.



(5ap)

4-methyl-N-(5-(methylsulfonyl)-2-((trimethylsilyl)carbonyl)phenyl)benzenesulfonamide

Following the general experiment procedure, **5ap** was obtained as a yellow liquid (60%, 29 mg). **^{1}H NMR** (500 MHz, CDCl3): δ = 11.55 (s, 1H), 8.21 (d, *J* = 2.0 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.5 Hz, 2H), 7.66 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.28-7.26 (m, 2H), 3.07 (s, 3H), 2.37 (s, 3H), 0.35 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 242.02, 146.26, 140.02, 137.51, 136.19, 131.50, 129.96, 129.07, 128.03, 121.84, 119.32, 45.59, 23.14, 2.60. **HR-MS** (ESI): m/z calculated for $C_{18}H_{23}NO_5S_2Si$: $[M+H]^+$: 426.0860, found: 426.0857. **FTIR** (KBr, cm^{-1}): 3718.51, 3686.30, 3585.10, 1682.36, 1651.50, 1455.23, 1402.97, 1030.84.



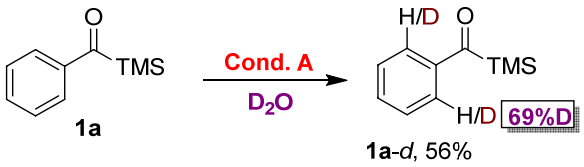
(5aq)

4-methyl-N-(2-((triethylsilyl)carbonyl)phenyl)benzenesulfonamide

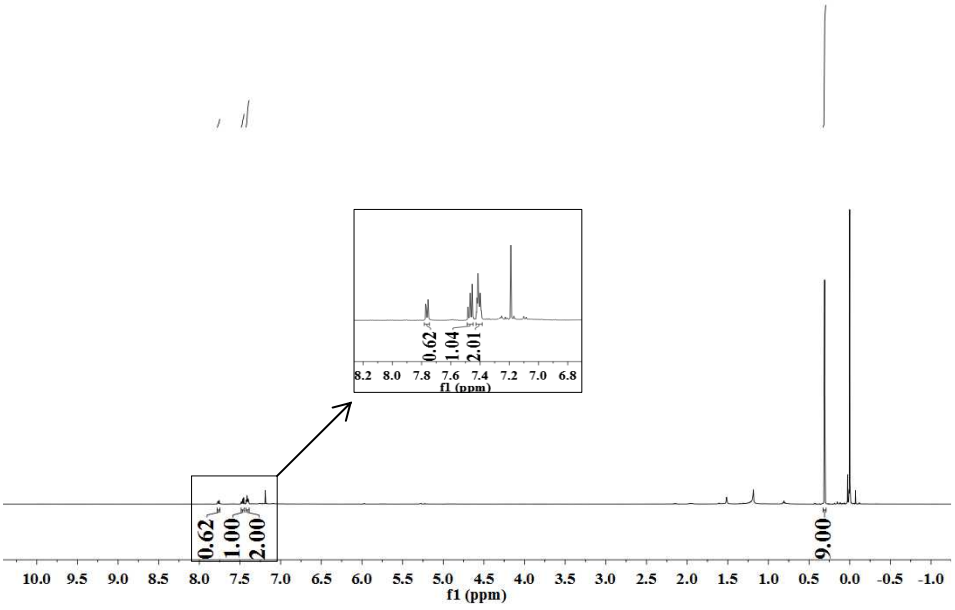
Following the general experiment procedure, **5aq** was obtained as a yellow liquid (60%, 23.5 mg). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 11.58 (s, 1H), 7.78 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.68 (dd, *J* = 8.0, 1.5 Hz, 3H), 7.43-7.40 (m, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.13 (td, *J* = 7.5, 1.0 Hz, 1H), 2.33 (s, 3H), 0.93-0.90 (m, 9H), 0.85-0.80 (m, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 239.25, 142.70, 136.25, 135.70, 133.03, 132.61, 128.53, 127.03, 126.15, 121.75, 118.57, 20.44, 6.31, 2.87.

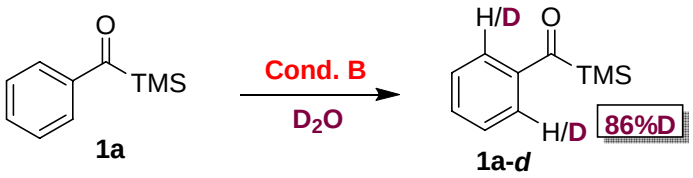
HR-MS (ESI): m/z calculated for $C_{20}H_{27}NO_3SSi$: $[M+H]^+$: 390.1554, found: 390.1553. **FTIR** (KBr, cm^{-1}): 3384.70, 2945.79, 2828.04, 1647.66, 1403.74, 1028.83.

Deuterium-Labeled Experiments

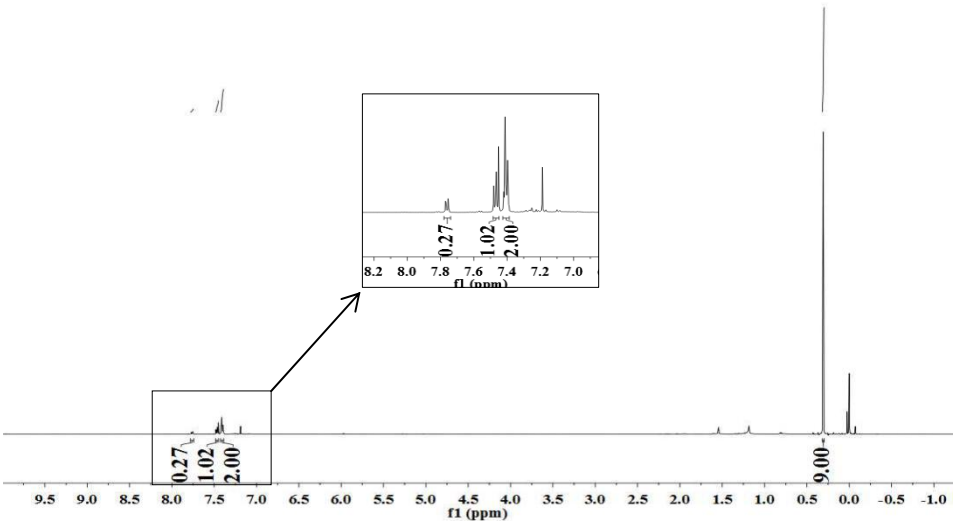


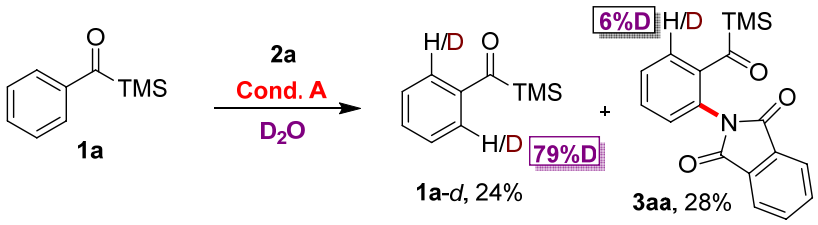
An oven-dried vial was charged with $[Ru(p\text{-cymene})Cl_2]_2$ (5 mol %, 0.005 mmol, 3.1 mg), $AgNTf_2$ (20 mol %, 0.02 mmol, 15.6 mg), Ag_2O (50 mol %, 0.05 mmol, 23.2 mg), **1a** (0.1 mmol, 17.8 mg) and DCM (0.7 mL). Then, D_2O (10.0 eq, 1.0 mmol, 20.3 mg) was added into the solution. The vial was sealed under argon and heated to 90 ℃ with stirring for 6 hours. After cooling down, the mixture was directly applied to a flash column chromatography (ethyl acetate/petroleum ether mixtures), providing deuterium labeled **1a-*d*** as a yellow oil (10 mg, 56% recovered). The D% was estimated by ^1H NMR.



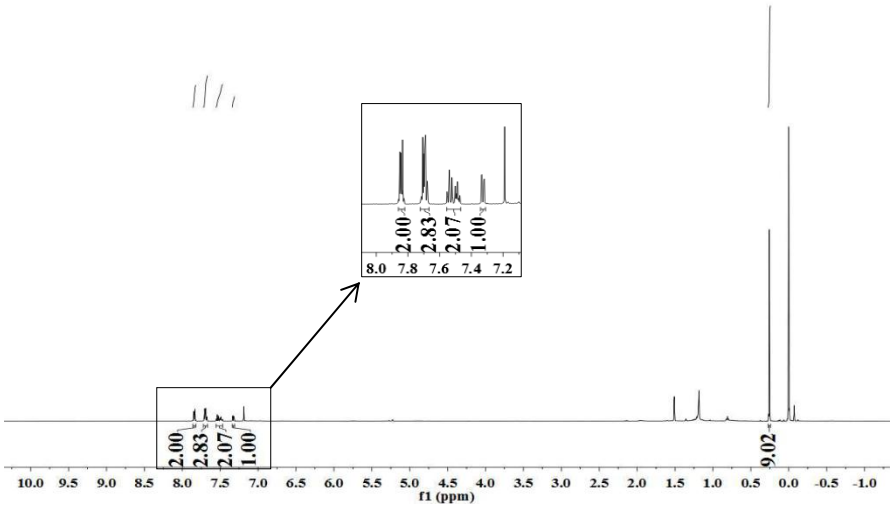


An oven-dried vial was charged with $[Ru(p\text{-cymene})Cl_2]_2$ (5 mol %, 0.005 mmol, 3.1 mg), $AgSbF_6$ (40 mol %, 0.04 mmol, 13.6 mg), $Cu(OAc)_2 \cdot H_2O$ (1.0 eq, 0.1 mmol, 20.0 mg), NaOAc (40 mol %, 0.04 mmol, 3.3 mg), **1a** (0.1 mmol, 17.8 mg) and DCM (0.7 mL). Then, D_2O (10.0 eq, 1.0 mmol, 20.3 mg) was added into the solution. The vial was sealed under argon and heated to 90 ℃ with stirring for 6 hours. After cooling down, the mixture was directly applied to a flash column chromatography (ethyl acetate/petroleum ether mixtures), providing deuterium labeled **1a-*d*** as a yellow oil (12 mg, 68% recovered). The D% of **1a-*d*** was estimated by ^1H NMR.

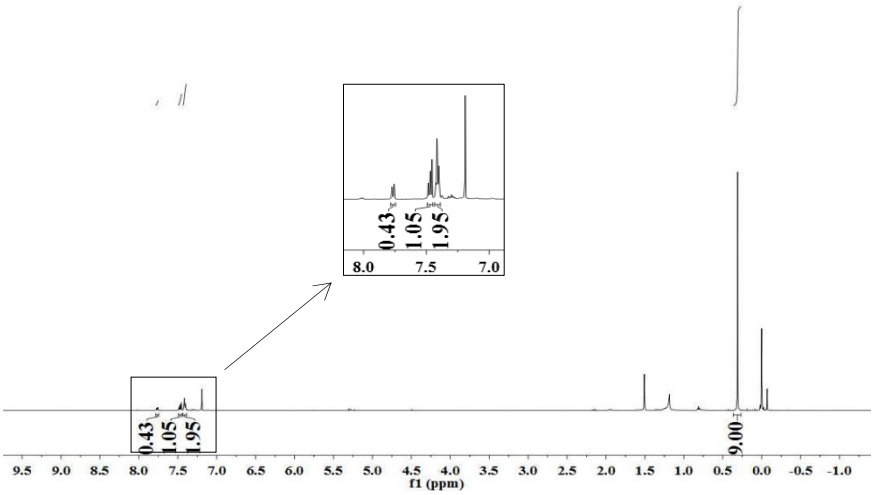




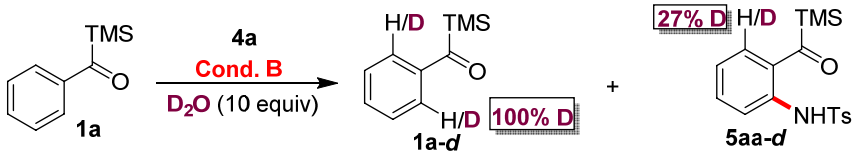
An oven-dried vial was charged with $[Ru(p\text{-cymene})Cl_2]_2$ (5 mol %, 0.005 mmol, 3.1 mg), $AgNTf_2$ (20 mol %, 0.02 mmol, 15.6 mg), Ag_2O (50 mol %, 0.05 mmol, 23.2 mg), **1a** (0.1 mmol, 17.8 mg), **2a** (0.2 mmol, 63.4 mg) and DCM (0.7 mL). Then, D_2O (10.0 eq, 1.0 mmol, 20.3 mg) was added into the solution. The vial was sealed under argon and heated to 90 ℃ with stirring for 12 hours. After cooling down, the mixture was directly applied to a flash column chromatography (ethyl acetate/petroleum ether mixtures) on silica gel to afford **3aa** (9.0 mg, 28% yield) and **1a-*d*** (4.3 mg, 24% recovered). The D% of **1a-*d*** and **3aa** were estimated by ^{1}H NMR.



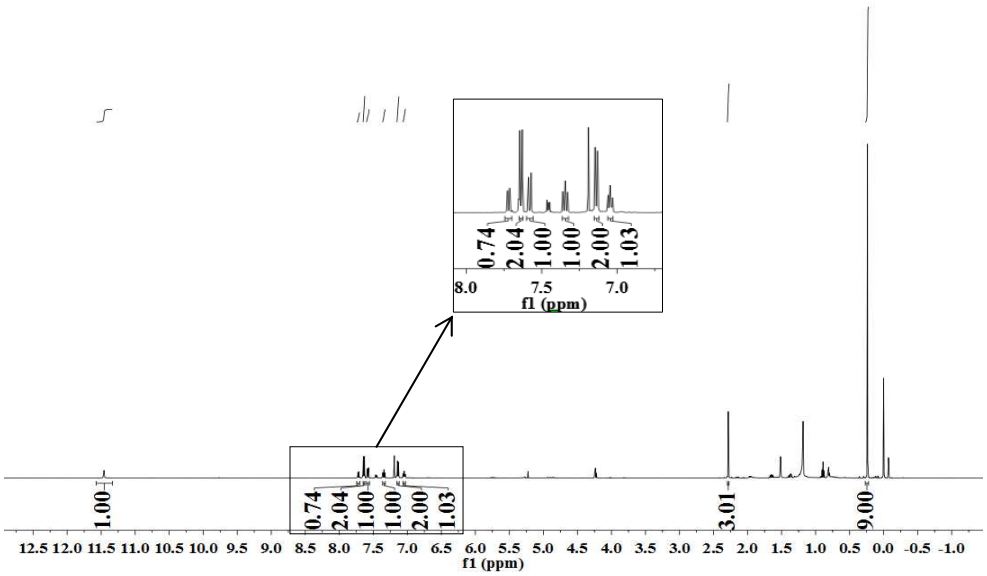
3aa



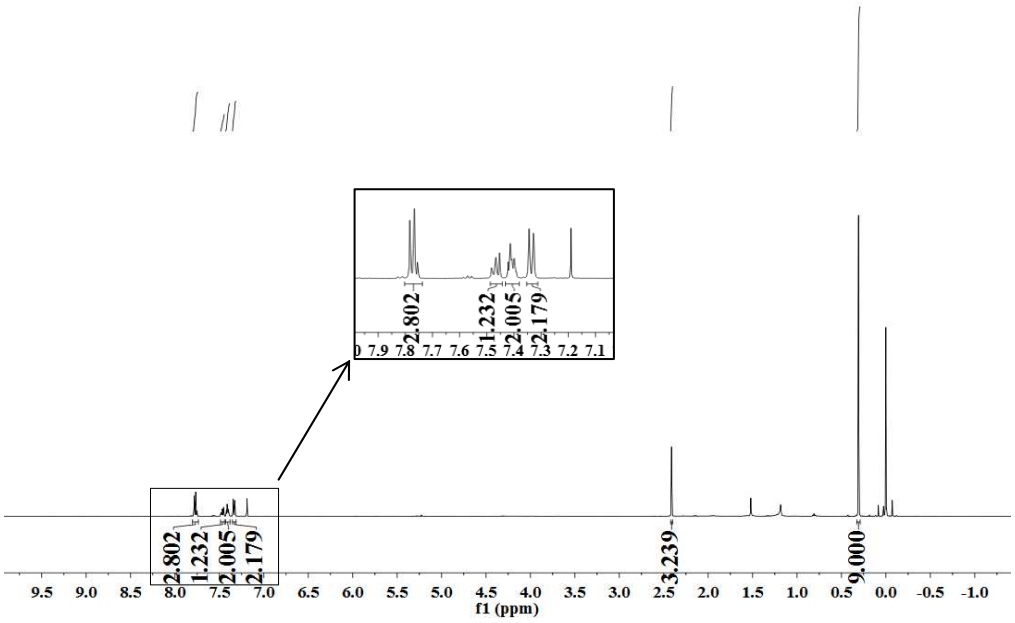
1a-*d*



An oven-dried vial was charged with $[Ru(p\text{-cymene})Cl_2]_2$ (5 mol %, 0.005 mmol, 3.1 mg), $AgSbF_6$ (40 mol %, 0.04 mmol, 13.6 mg), $Cu(OAc)_2 \cdot H_2O$ (1.0 eq, 0.1 mmol, 20.0 mg), NaOAc (40 mol %, 0.04 mmol, 3.3 mg), **1a** (0.1 mmol, 17.8 mg), **4a** (0.2 mmol, 39.4 mg) and DCM (0.7 mL). Then, D_2O (10.0 eq, 1.0 mmol, 20.3 mg) was added into the solution. The vial was sealed under argon and heated to 90 ℃ with stirring for 12 hours. After cooling down, the mixture was directly applied to a flash column chromatography (ethyl acetate/petroleum ether mixtures) on silica gel to afford **5aa-*d*** (11.6 mg, 33% yield) and **1a-*d*** (7.3 mg, 41% recovered). The D% of **1a-*d*** and **5aa-*d*** were estimated by ^1H NMR.

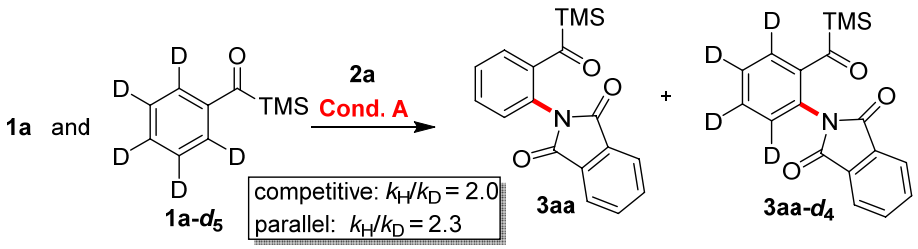

0.74
2.04
1.00
1.00
2.00
1.03
8.0
7.5
7.0
f1 (ppm)
1.00
0.74
2.04
1.00
1.00
2.00
1.03
3.01
9.00
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

5aa-*d*


2.802
1.232
2.005
2.179
7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1
2.802
1.232
2.005
2.179
3.239
9.000
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 -1.0
f1 (ppm)

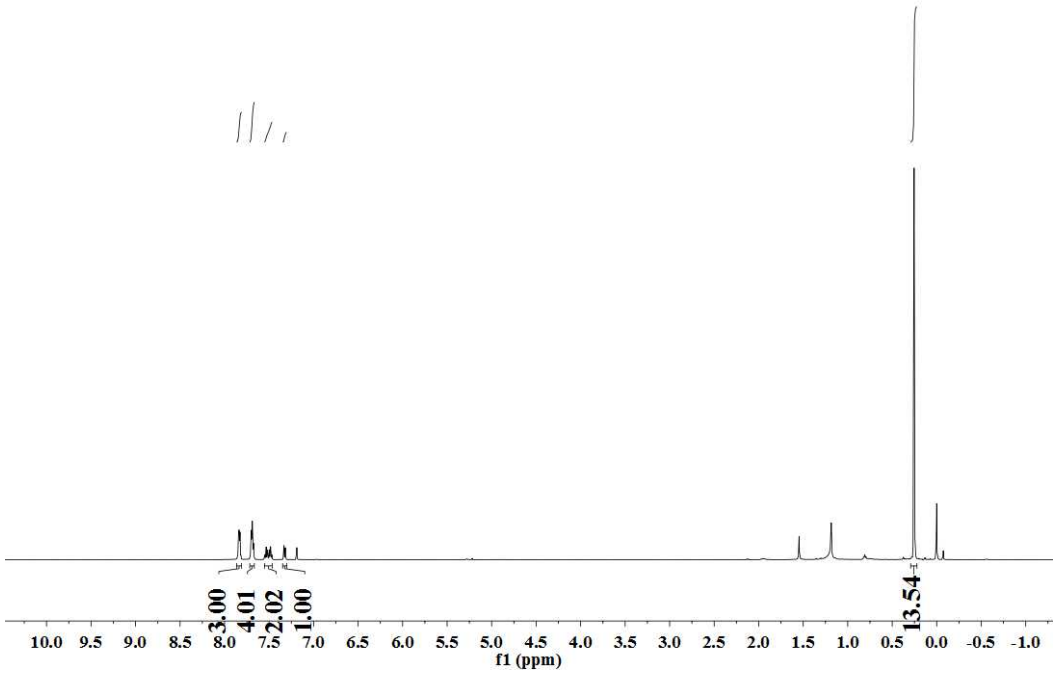
1a-*d*

Deuterium Experiments



Competitive KIE Experiments

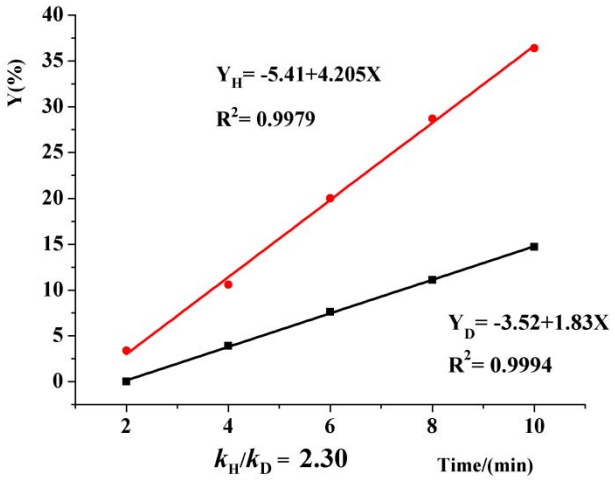
An oven-dried vial was charged with $[Ru(p\text{-cymene})Cl_2]_2$ (5 mol %, 0.005 mmol, 3.1 mg), $AgNTf_2$ (20 mol %, 0.02 mmol, 15.6 mg), Ag_2O (50 mol %, 0.05 mmol, 23.2 mg), **2a** (0.3 mmol, 95.2 mg) and DCM (0.7 mL). Then, **1a** (0.1 mmol, 17.8 mg) and **1a-*d*$_5$** (0.1 mmol, 18.3 mg) were added into the solution. The vial was sealed under argon and heated to 90 ℃ with stirring for 30 min. After cooling down, the mixture was directly applied to column chromatography for separation. The ratio of **3aa**/**3aa-*d*$_4$** (17.5 mg, 27% yield) was determined by ^{1}H NMR to be 2.0.

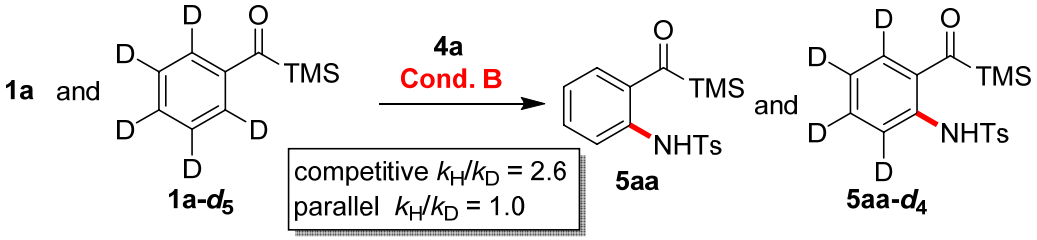


Parallel KIE Experiments

Parallel independent reactions of **1a** or **1a-d_5** with **2a** were performed to determine the corresponding KIE value. Each 10 mL vial was charged with [Ru(*p*-cymene)Cl_2]$_2$ (5 mol %, 0.005 mmol, 3.1 mg), $AgNTf_2$ (20 mol %, 0.02 mmol, 15.6 mg), Ag_2O (50 mol %, 0.05 mmol, 23.2 mg), **2a** (0.2 mmol, 63.4 mg) and DCM (0.7 mL). Then, **1a** (0.1 mmol, 17.8 mg) and **1a-d_5** (0.1 mmol, 18.3 mg) were added into the solution in sequence. The vials were sealed under Ar and heated to 90°C with stirring for 2, 4, 6, 8 or 10 minutes. After cooling down, the mixture was concentrated in vacuo and purified by column chromatography to determine the product yields. A KIE value was determined to be 2.30.

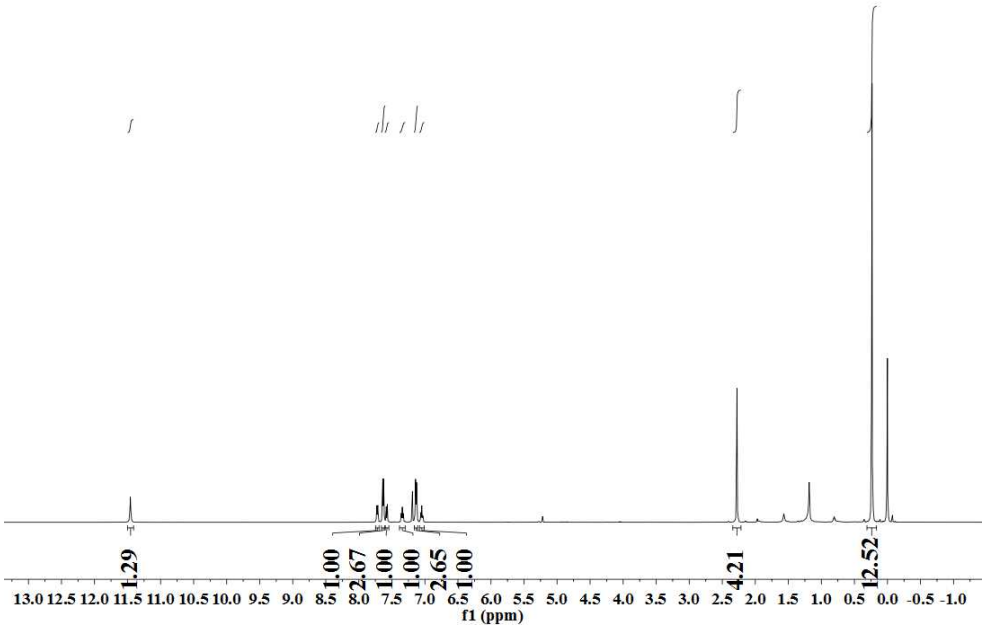
yield	2	4	6	8	10
ba	3.4%	10.6%	20%	28.7%	36.4%
ba-d_2	0 %	3.9%	7.6%	11.1%	14.7%





Competitive KIE Experiments

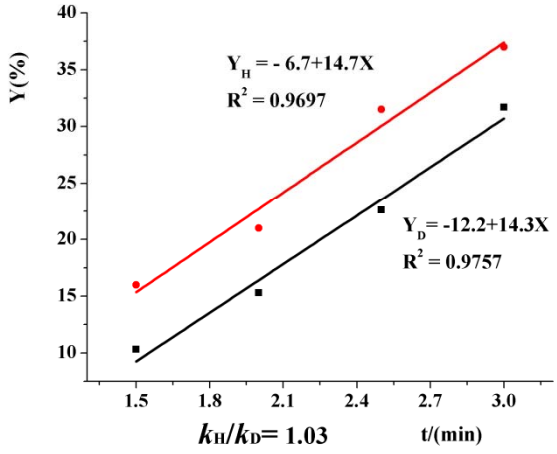
An oven-dried vial was charged with $[Ru(p\text{-cymene})Cl_2]_2$ (5 mol %, 0.005 mmol, 3.1 mg), $AgSbF_6$ (40 mol %, 0.04 mmol, 13.6 mg), $Cu(OAc)_2 \cdot H_2O$ (1.0 eq, 0.1 mmol, 20.0 mg), NaOAc (40 mol %, 0.04 mmol, 3.3 mg) and DCM (0.7 mL). Then, **1a** (0.1 mmol, 17.8 mg), **1a-*d*$_5$** (0.1 mmol, 18.3 mg) and **4a** (0.4 mmol, 79.0 mg) were added into the solution. The vial was sealed under argon and heated to 90℃ with stirring for 30 min. After cooling down, the mixture was directly applied to column chromatography for separation. The ratio of **5aa**/**5aa-*d*$_4$** (34.5 mg, 50% yield) was determined by ^{1}H NMR to be 2.6.



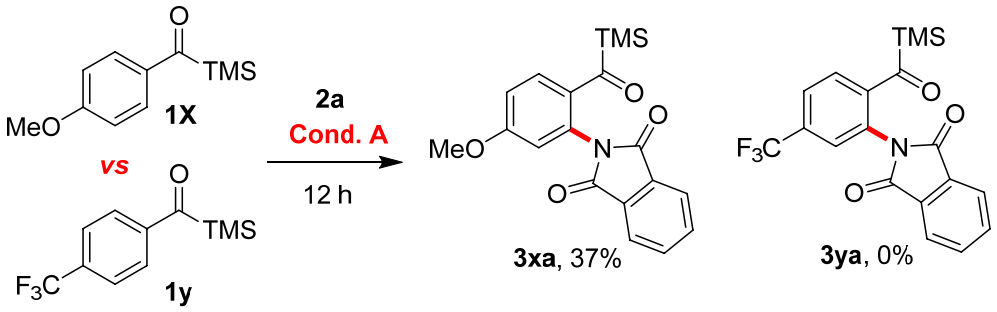
Parallel KIE Experiments

Parallel independent reactions of **1a** or **1a-d_5** with **4a** were performed to determine the corresponding KIE value. Each 10 mL vial was charged with [Ru(*p*-cymene)Cl_2]$_2$ (5 mol %, 0.005 mmol, 3.1 mg), $AgSbF_6$ (40 mol %, 0.04 mmol, 13.6 mg), $Cu(OAc)_2$•H_2O (1.0 eq, 0.1 mmol, 20.0 mg), NaOAc (40 mol %, 0.04 mmol, 3.3 mg) and DCM (0.7 mL). Then, **1a** (0.1 mmol, 17.8 mg), **1a-d_5** (0.1 mmol, 18.3 mg) and **4a** (0.2 mmol, 39.4 mg) were added into the solution. The vials were sealed under Ar and heated to 90°C with stirring for 1.5, 2, 2.5 or 3.0 minutes. After cooling down, the mixture was concentrated in vacuo and purified by column chromatography to determine the product yields. A KIE value was determined to be 1.0.

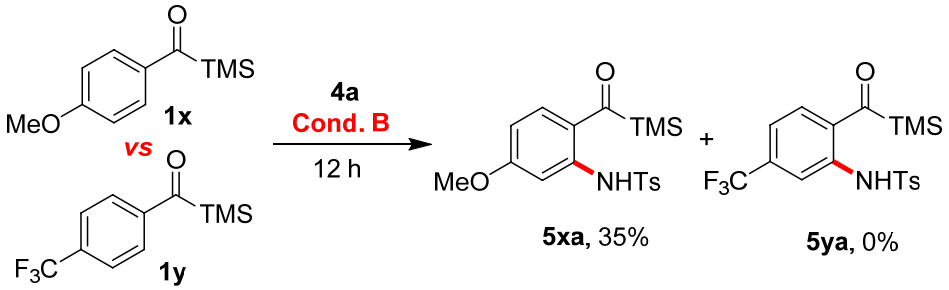
yield	1.5	2	2.5	3
ba	16%	21%	31.5%	37%
ba-d_2	10.3 %	15.3%	22.6%	31.7%



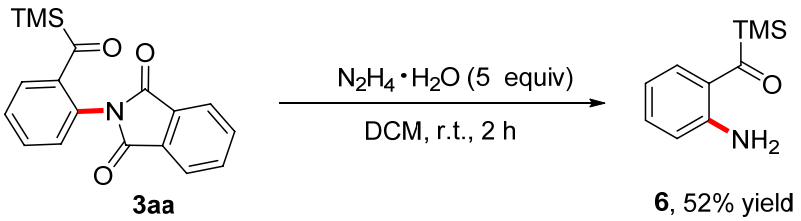
Competitive Reaction



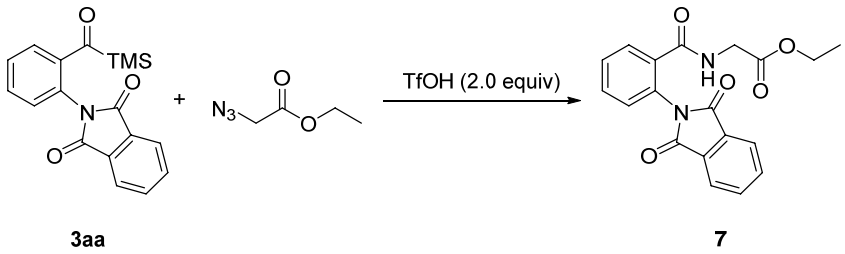
An oven-dried vial was charged with [Ru(*p*-cymene)Cl_2]$_2$ (5 mol%, 0.005 mmol, 3.1 mg), $AgNTf_2$ (20 mol%, 0.02 mmol, 15.6 mg), Ag_2O (50 mol%, 0.05 mmol, 23.2 mg), **2a** (0.2 mmol, 63.4 mg) and DCM (0.7 mL). Then, **1x** (0.1 mmol, 20.8 mg) and **1y** (0.1 mmol, 23.4 mg) were added into the solution. The vial was sealed under argon and heated to 90 ℃ with stirring for 12 hours. After cooling down, the mixture was concentrated in vacuo and purified by column chromatography to afford the product **3xa** (26 mg, 37%).



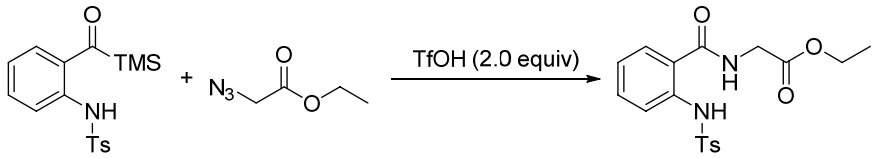
An oven-dried vial was charged with [Ru(*p*-cymene)Cl_2]$_2$ (5 mol %, 0.005 mmol, 3.1 mg), $AgSbF_6$ (40 mol %, 0.04 mmol, 13.6 mg), $Cu(OAc)_2$•H_2O (1.0 eq, 0.1 mmol, 20.0 mg), NaOAc (40 mol%, 0.04 mmol, 3.3 mg) and DCM (0.7 mL). Then, **1x** (0.1 mmol, 17.8 mg), **1y** (0.2 mmol, 39.4 mg) and **4a** was added into the solution. The vial was sealed under argon and heated to 90 ℃ with stirring for 12 hours. After cooling down, the mixture was concentrated in vacuo and purified by column chromatography to afford the product **5ax** (27 mg, 35%).



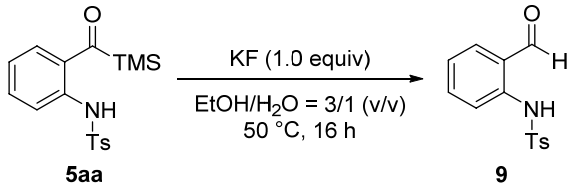
A suspension of **3aa** (32.3 mg, 0.1 mmol) and hydrazine (5.0 eq), was stirred at ambient temperature for 4 h. At ambient temperature, the reaction mixture was diluted with CH_2Cl_2 and passed through celite with CH_2Cl_2. The organic layer was dried over Na_2SO_4. After evaporation of the solvent in vacuo, the crude product was purified by column chromatography on silica gel to yield **6** (10.0 mg, 52 %) as a yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.06 (td, *J* = 8.0, 1.5 Hz, 1H), 6.77 (dd, *J* = 7.5, 1.5 Hz, 1H), 6.71 (t, *J* = 7.4 Hz, 1H), 6.65 (d, *J* = 8.0 Hz, 1H), 5.68 (s, 2H), 0.08 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 160.80, 144.61, 130.93, 129.73, 123.10, 120.45, 117.57, 2.93. **HR-MS** (ESI): m/z calculated for $C_{10}H_{15}NOSi$: $[M+H]^+$: 194.0996, found:194.0994. **FTIR** (KBr, cm^{-1}): 3851.10, 3646.24, 1651.56, 1557.20, 1504.96, 1404.83.



To a stirred mixture of **3aa** (0.2 mmol, 64.7 mg) and azide (0.36 mmol, 46.5 mg) in CH_2Cl_2 (1 mL) was slowly added TfOH (2.0 equiv, 0.4 mmol). The reaction mixture was kept for 30 min at room temperature, then it was quenched with aqueous KOH (10%, 5 mL), extracted with CH_2Cl_2 (15 mL*3), washed with brine (15 mL), dried over Mg_2SO_4 and concentrated. The residue was purified by flash chromatography (MeOH/DCM mixture) to give **7** as a white sticky liquid (56.3 mg, 80% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.95 – 7.89 (m, 2H), 7.79 – 7.74 (m, 2H), 7.74 – 7.71 (m, 1H), 7.64 – 7.59 (m, 1H), 7.54 – 7.48 (m, 1H), 7.43 – 7.36 (m, 1H), 6.67 (t, *J* = 5.1 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 4.05 (d, *J* = 5.1 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 168.53, 166.48, 165.80, 133.26, 132.42, 131.07, 130.59, 129.03, 128.15, 127.29, 122.82, 60.53, 40.82, 13.08. **HR-MS** (ESI): m/z calculated for $C_{19}H_{16}N_2O_5$: $[M+H]^+$: 353.1132, found: 353.1130. **FTIR** (KBr, cm^{-1}): 3415.24, 3233.65, 1714.95, 1636.92, 1616.43, 1381.31, 1196.26, 619.44.

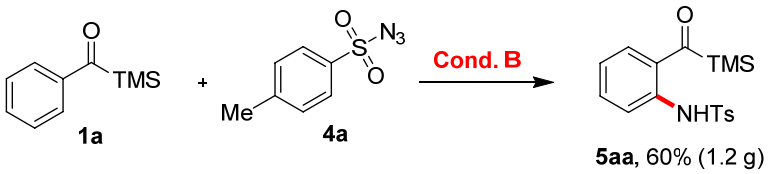


To a stirred mixture of **5aa** (0.2 mmol, 69.5 mg) and azide (0.36 mmol, 46.5 mg) in CH_2Cl_2 (1 mL) was slowly added TfOH (2.0 equiv, 0.4 mmol). The reaction mixture was kept for 30 min at room temperature, then it was quenched with aqueous KOH (10%, 5 mL), extracted with CH_2Cl_2 (15 mL*3), washed with brine (15 mL), dried over Mg_2SO_4 and concentrated. The residue was purified by flash chromatography (MeOH/DCM mixture) to give **8** as a light yellow solid (52.6 mg, 70% yield), m. p:128.2 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 10.69 (s, 1H), 7.68 – 7.63 (m, 3H), 7.45 – 7.44 (m, 1H), 7.39 – 7.35 (m, 1H), 7.18 (d, *J* = 8.1 Hz, 2H), 7.05 – 7.00 (m, 1H), 6.74 (t, *J* = 5.1 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 4.07 (d, *J* = 5.1 Hz, 2H), 2.33 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 169.53, 168.35, 143.73, 138.88, 136.37, 132.90, 129.53, 127.25, 127.10, 123.55, 121.00, 120.61, 61.86, 41.67, 21.49, 14.16. **HR-MS** (ESI): m/z calculated for $C_{18}H_{20}N_2O_5S$: $[M+H]^+$: 377.1166, found: 377.1165. **FTIR** (KBr, cm^{-1}): 2914.95, 1748.60, 1616.82, 1543.93, 1412.15, 1207.48, 1154.21, 1084.11.



A screw-cap vial was charged with KF (1.0 equiv, 0.2 mmol), EtOH/H_2O = 3/1 (1.5 mL/ 0.5 mL). Then **5aa** (0.2 mmol, 69.5 mg) were added into the solution in sequence. The vial was sealed under argon and heated to 50 ℃ with stirring for 16 h. After cooling down, the mixture was directly applied to a flash column chromatography (ethyl acetate/petroleum ether mixtures) to afford **9** as a white solid (43.4 mg, 79% yield). m. p:146.1 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 10.80 (s, 1H), 9.90 – 9.76 (m, 1H), 7.80 – 7.74 (m, 2H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.59 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.50 (ddd, *J* = 8.7, 7.4, 1.7 Hz, 1H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.16 (td, *J* = 7.5, 1.0 Hz, 1H), 2.36 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 195.08, 144.24, 139.89, 136.33, 136.17, 135.83, 129.78, 127.26, 123.01, 121.87, 117.71, 21.55. **HR-MS** (ESI): m/z calculated for $C_{14}H_{13}NO_3S$: $[M+H]^+$: 276.0689, found: 276.0682. **FTIR** (KBr, cm^{-1}): 3181.31, 1614.02, 1499.07, 1406.54, 1344.86, 1159.81, 1086.92, 927.10.

Gram-Scaled Synthesis



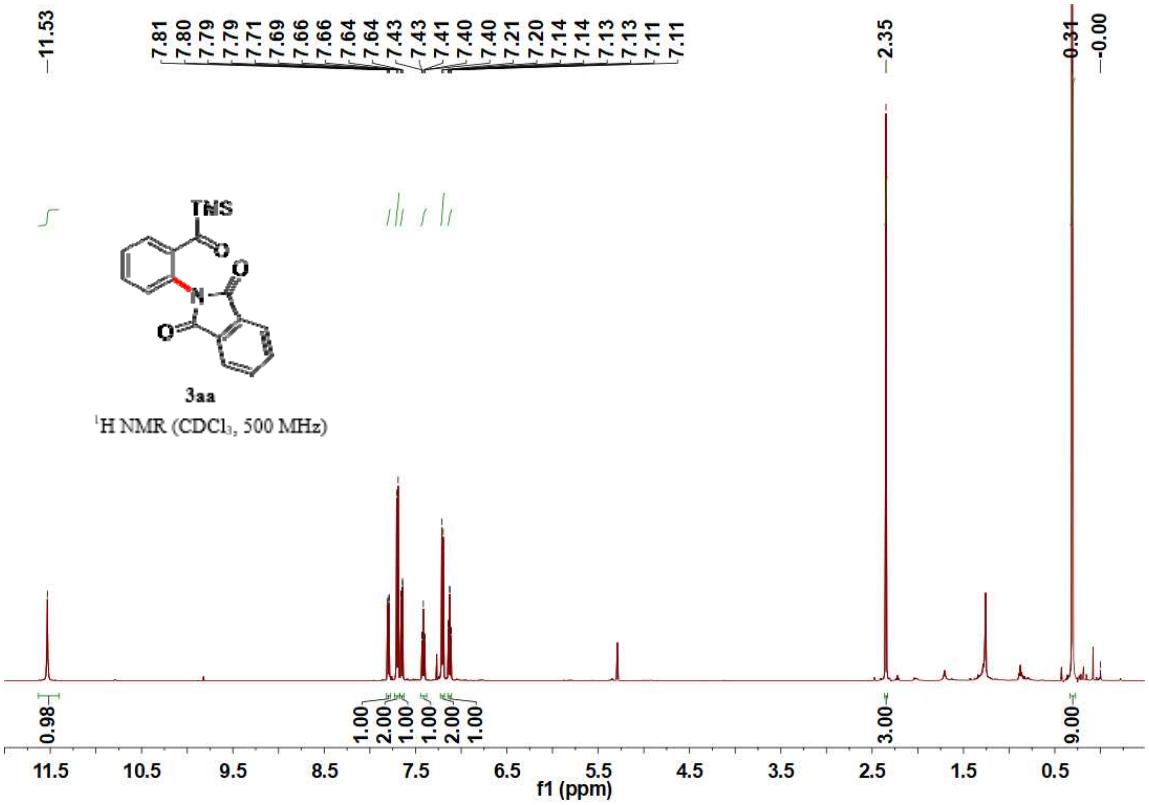
An oven-dried vial was charged with $[Ru(p\text{-cymene})Cl_2]_2$ (5 mol %, 170 mg), $AgSbF_6$ (40 mol %, 769 mg), $Cu(OAc)_2 \cdot H_2O$ (1.0 eq, 1.14 g), NaOAc (40 mol %, 184 mg) and DCM (40 mL). Then, **1a** (1.0 eq, 1.02 g) and **4a** (2.0 eq, 2.76 g) was added into the solution. The vial was sealed under argon and heated to 90 ℃ with stirring for 12 hours. After cooling down, the mixture was concentrated in vacuo and purified by column chromatography to afford the product **5aa** (1.2 g, 60%).

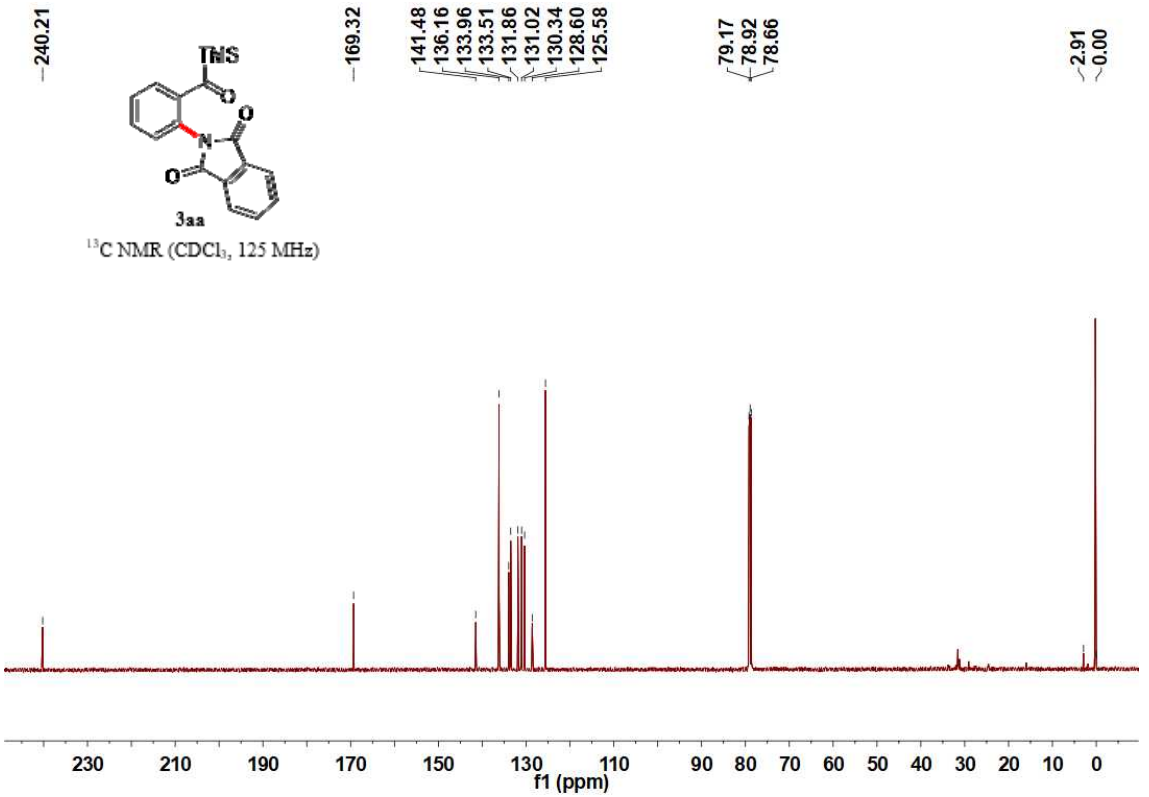
References:

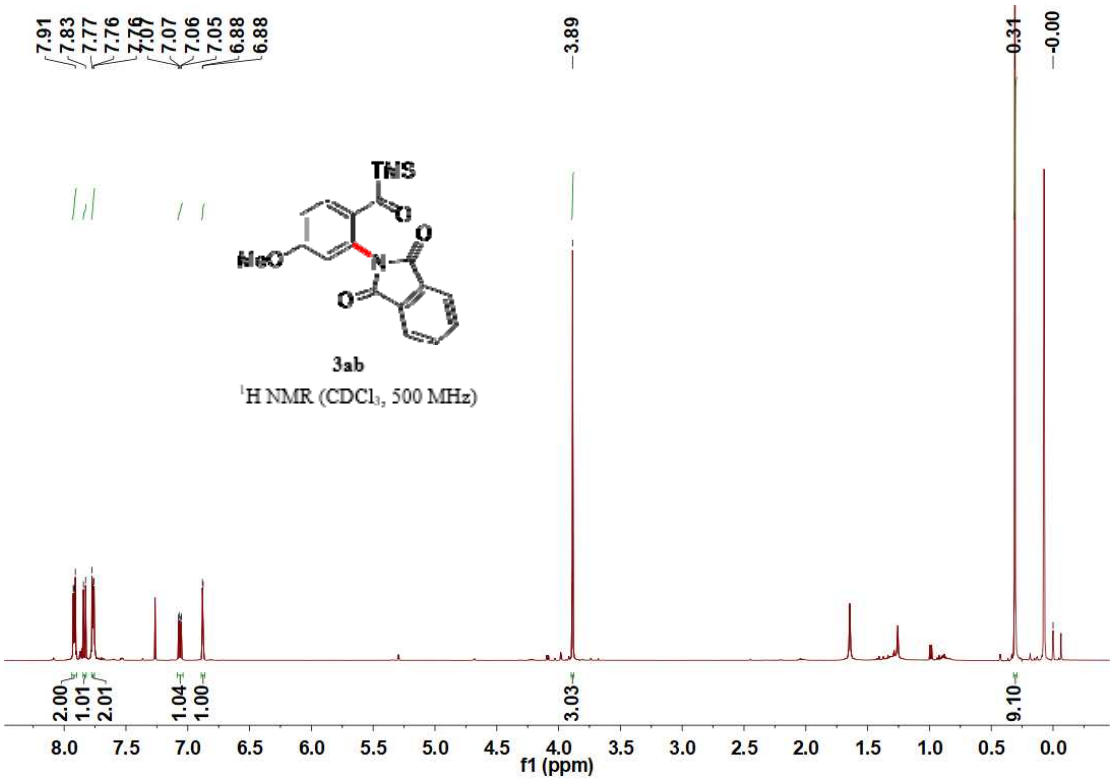
1. H.-J. Zhang, D. L. Priebbenow, C. Bolm, *Chem. Soc. Rev*. **2013**, *42*, 8540−8571.

2. P. Becker, R. Pirwerdjan, C. Bolm, *Angew. Chem. Int. Ed*. **2015**, *54*, 15493–15496.

NMR Spectra

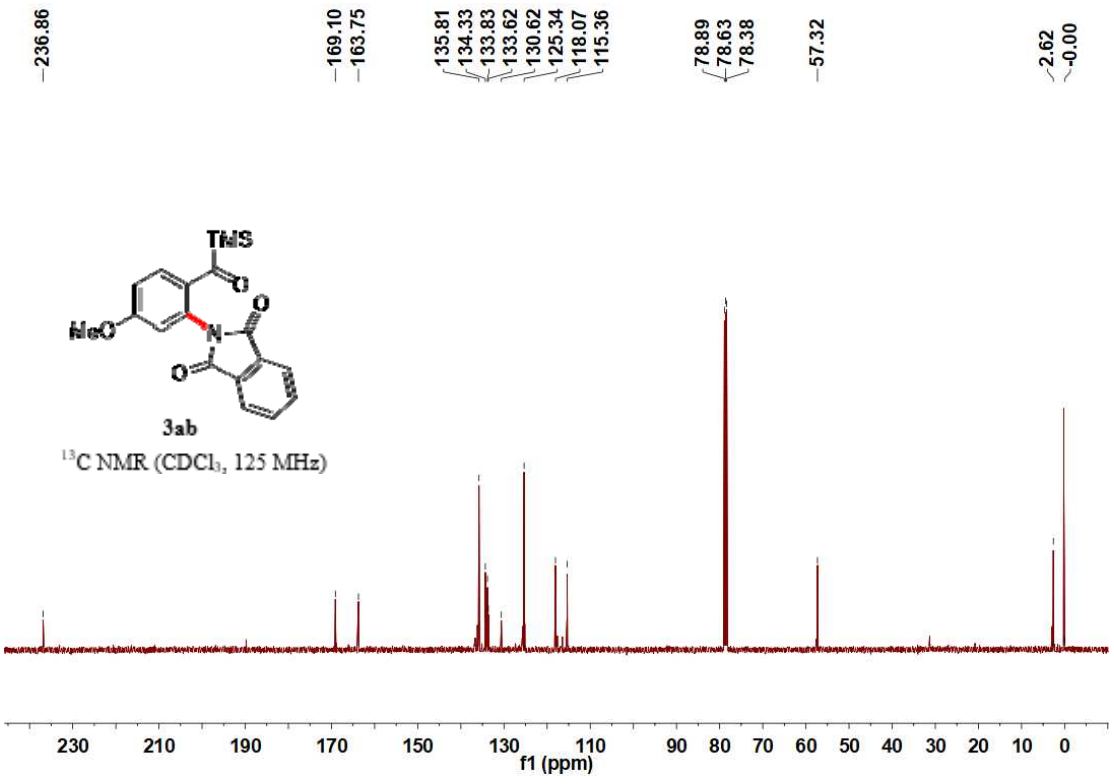

11.53
7.81
7.80
7.79
7.79
7.71
7.69
7.66
7.66
7.64
7.64
7.43
7.43
7.41
7.40
7.40
7.21
7.20
7.14
7.14
7.13
7.13
7.11
7.11
2.35
0.31
0.00
TNS
O
O
N
O
3aa
¹H NMR (CDCl₃, 500 MHz)
0.98
1.00
2.00
1.00
1.00
2.00
1.00
3.00
9.00
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)


240.21
169.32
141.48
136.16
133.96
133.51
131.86
131.02
130.34
128.60
125.58
79.17
78.92
78.66
2.91
0.00
TNS
O
O
N
O
3aa
¹³C NMR (CDCl₃, 125 MHz)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



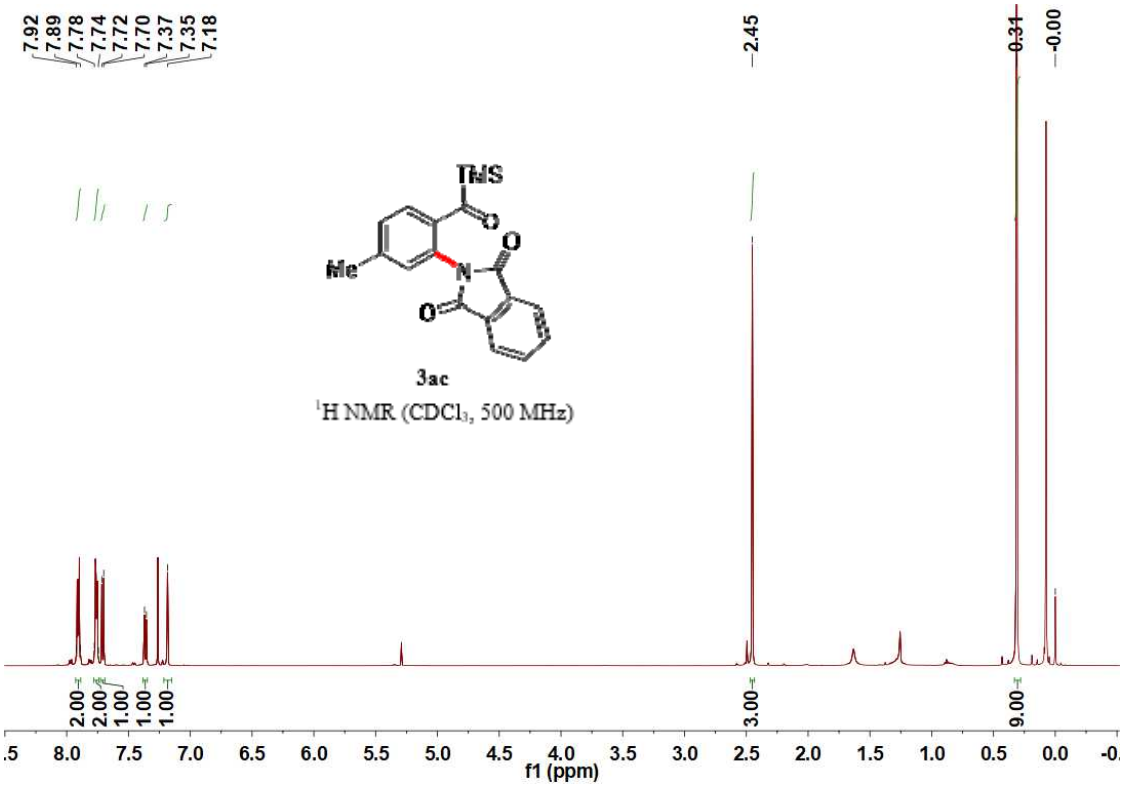
3ab

^{1}H NMR ($CDCl_3$, 500 MHz)



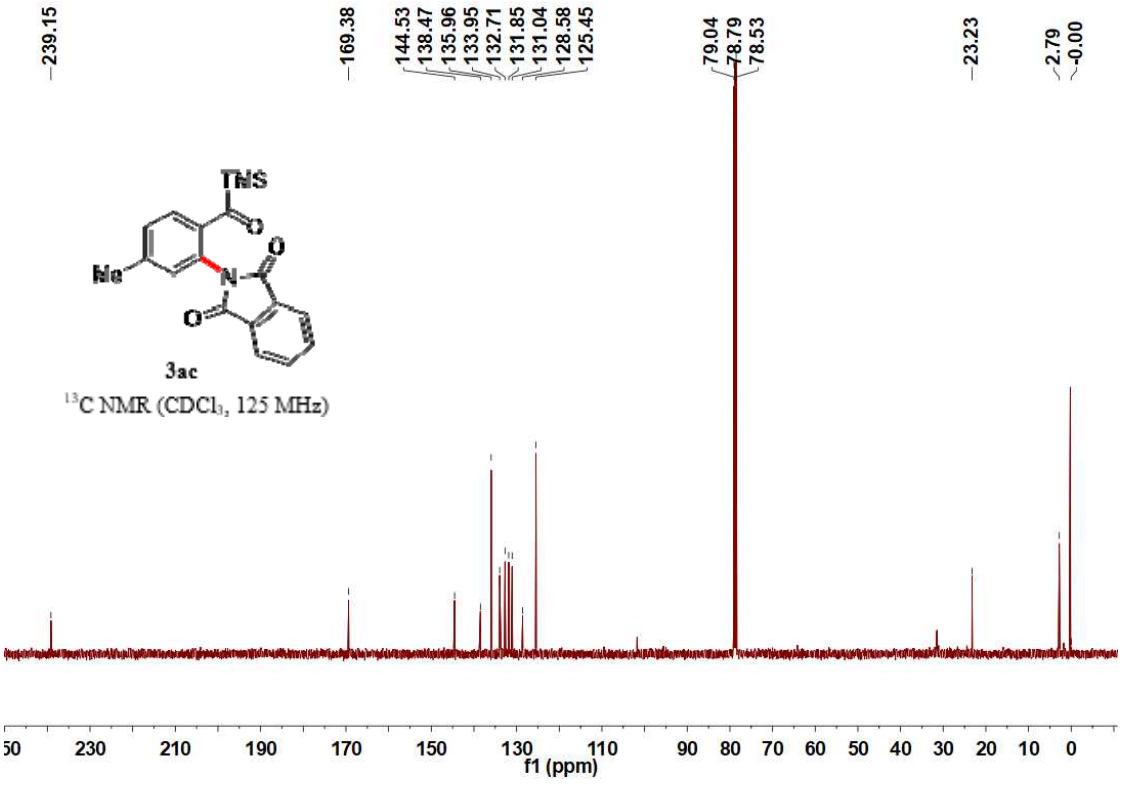
3ab

^{13}C NMR ($CDCl_3$, 125 MHz)



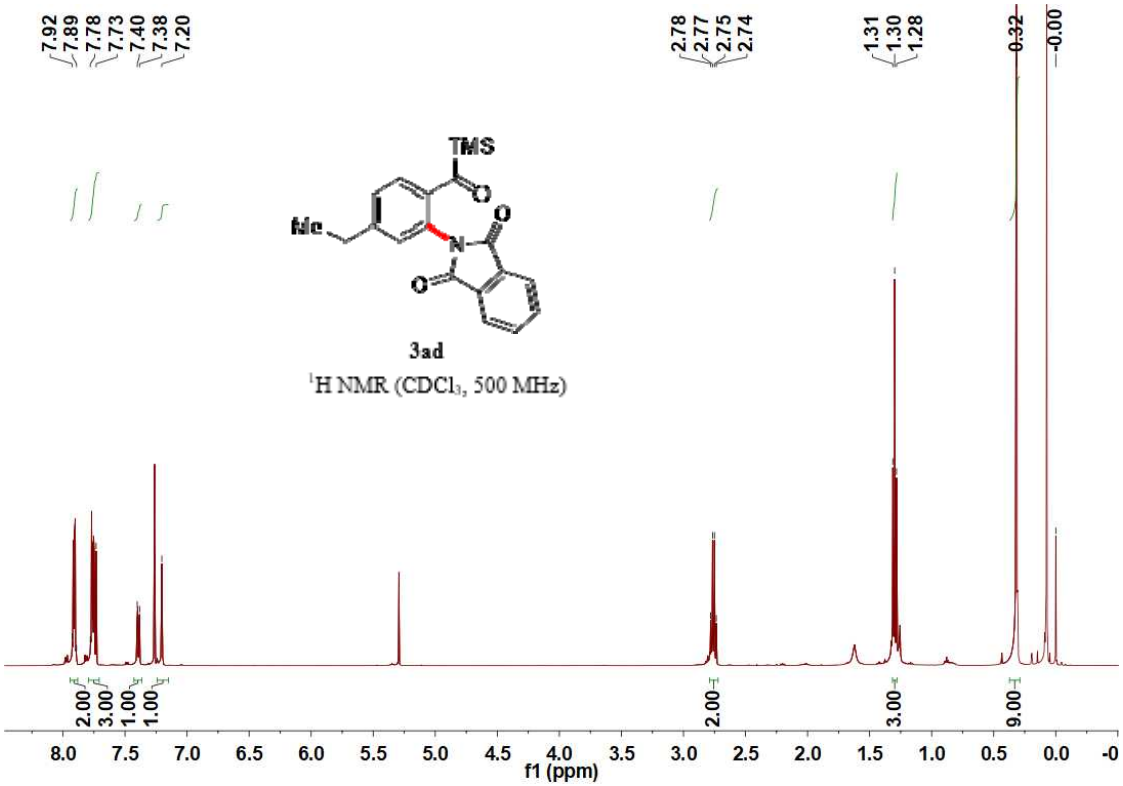
3ac

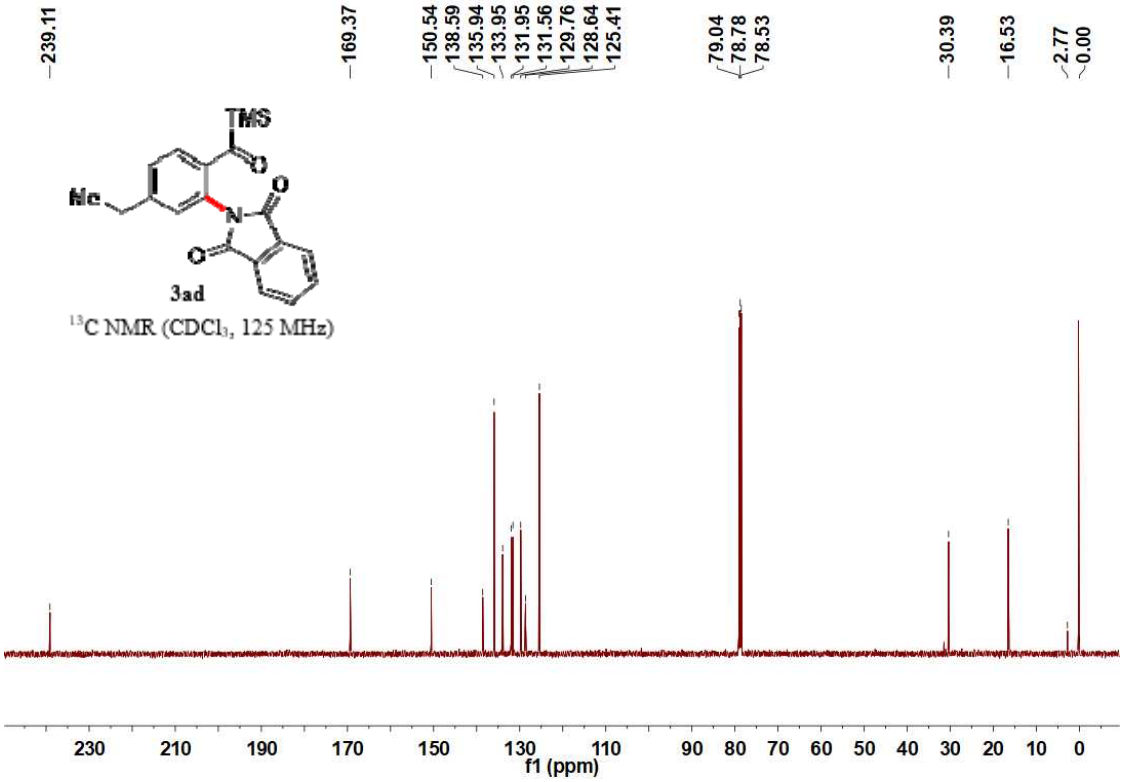
^{1}H NMR ($CDCl_3$, 500 MHz)

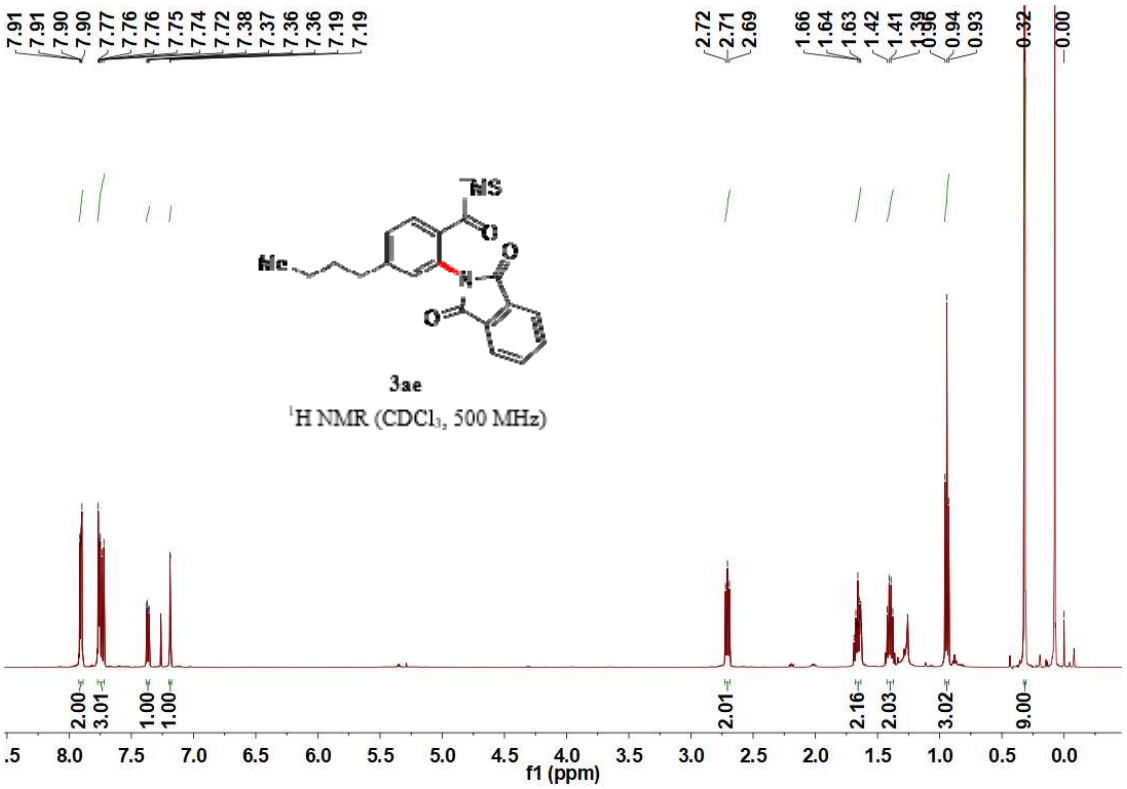


3ac

^{13}C NMR ($CDCl_3$, 125 MHz)

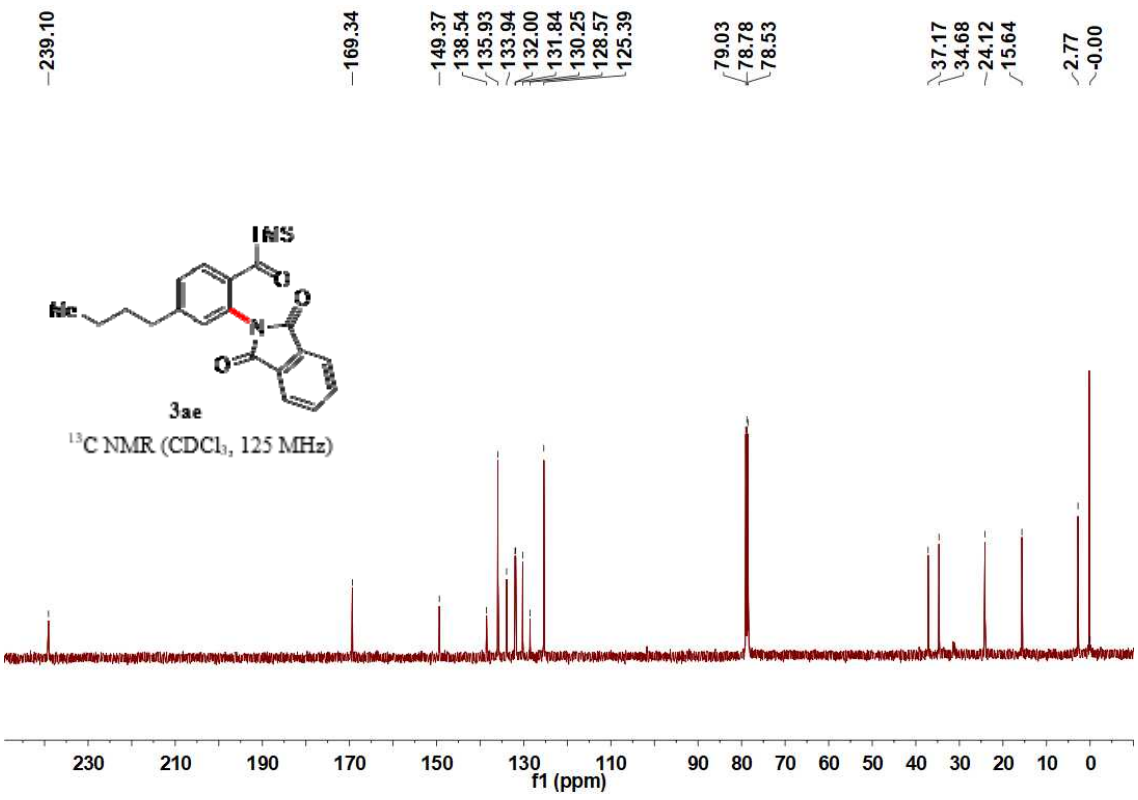

7.92
7.89
7.78
7.73
7.40
7.38
7.20
2.78
2.77
2.75
2.74
1.31
1.30
1.28
0.32
-0.00
TMS
Me
3ad
^{1}H NMR ($CDCl_3$, 500 MHz)
2.00
3.00
1.00
1.00
2.00
3.00
9.00
f1 (ppm)


239.11
169.37
150.54
138.59
135.94
133.95
131.95
131.56
129.76
128.64
125.41
79.04
78.78
78.53
30.39
16.53
2.77
0.00
TMS
Me
3ad
^{13}C NMR ($CDCl_3$, 125 MHz)
f1 (ppm)



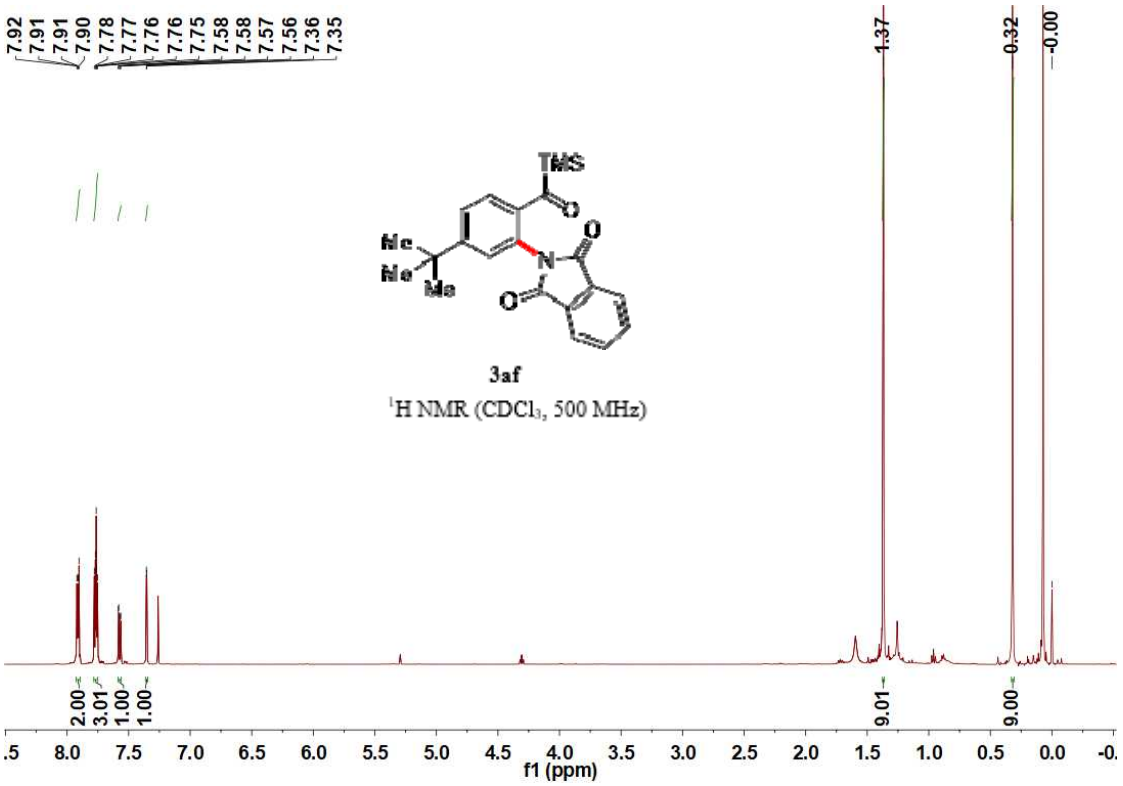
3ae

^{1}H NMR ($CDCl_3$, 500 MHz)



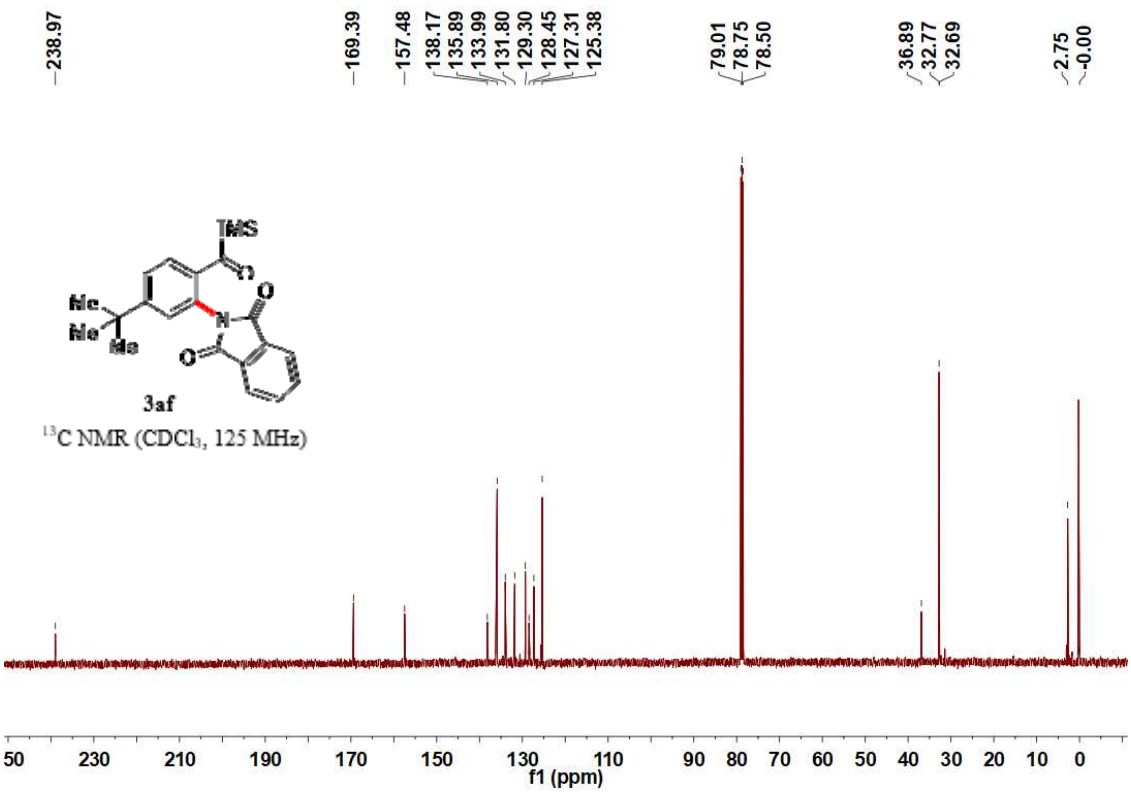
3ae

^{13}C NMR ($CDCl_3$, 125 MHz)



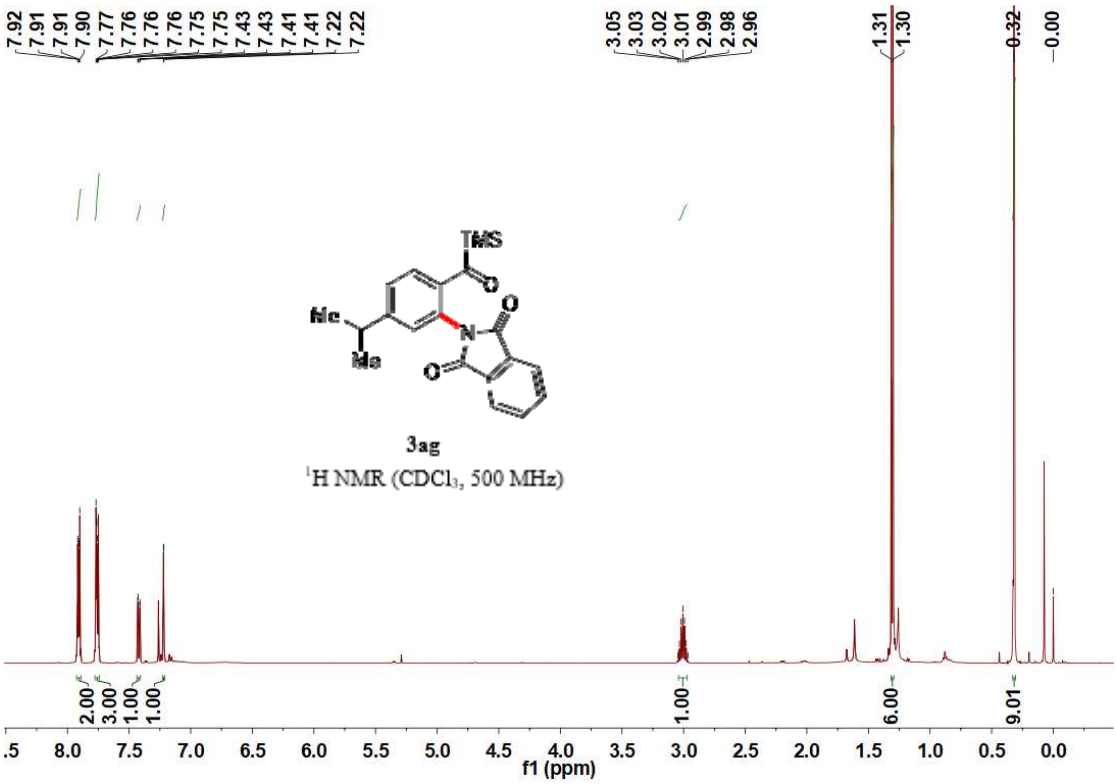
3af

^{1}H NMR ($CDCl_3$, 500 MHz)



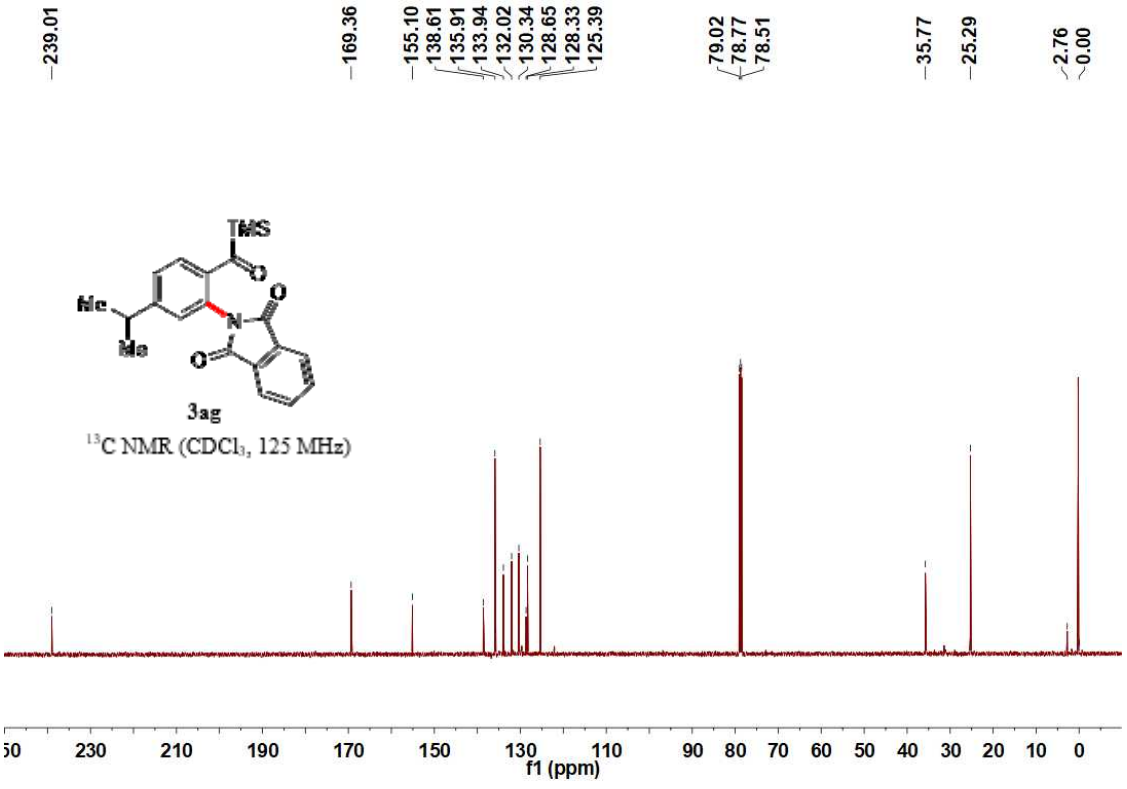
3af

^{13}C NMR ($CDCl_3$, 125 MHz)



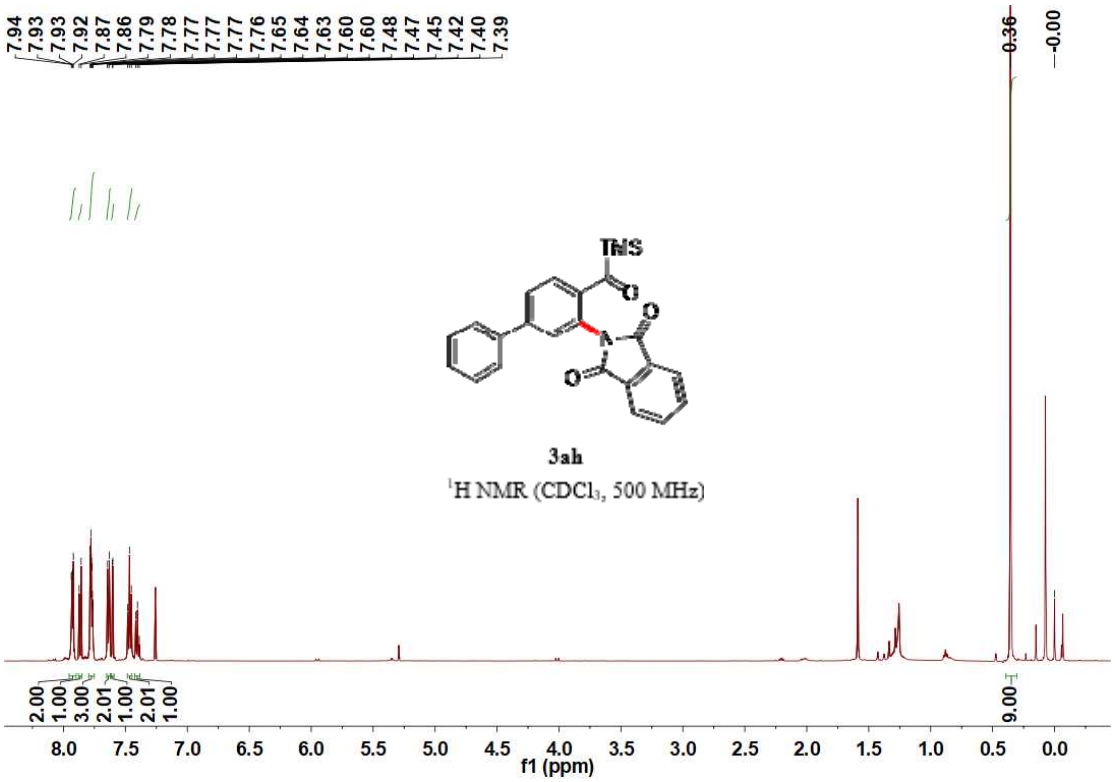
3ag

^{1}H NMR ($CDCl_3$, 500 MHz)



3ag

^{13}C NMR ($CDCl_3$, 125 MHz)



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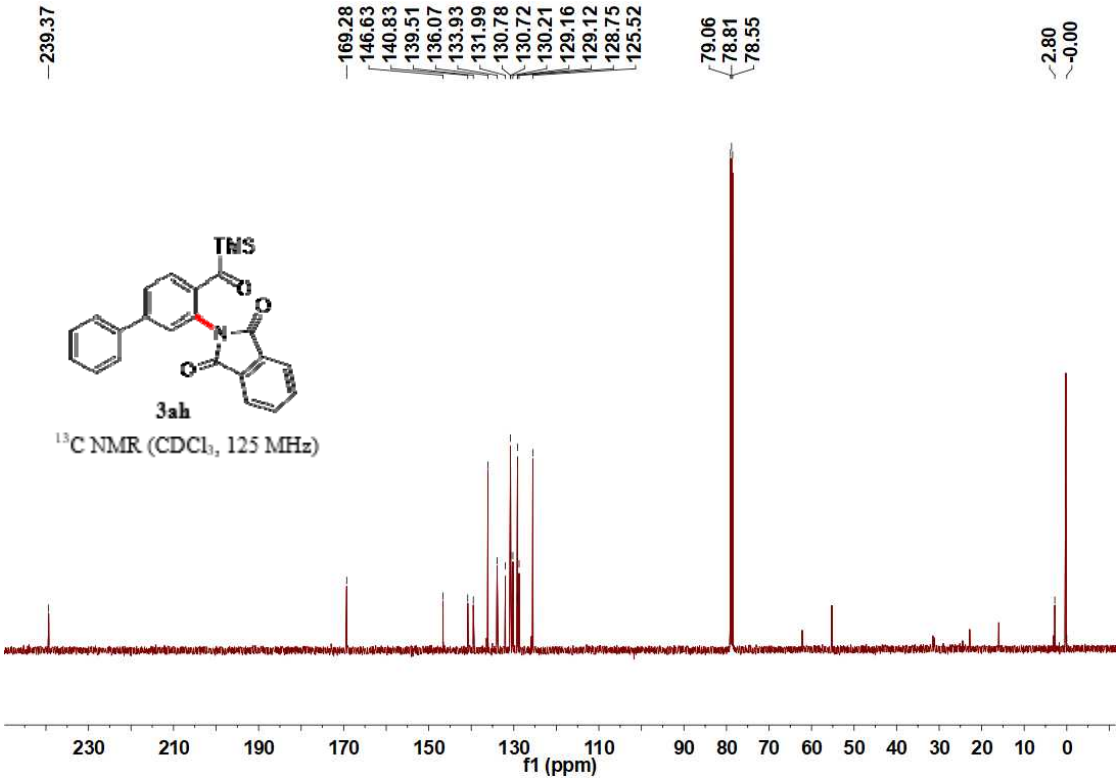
^{1}H NMR ($CDCl_3$, 500 MHz)



3ah

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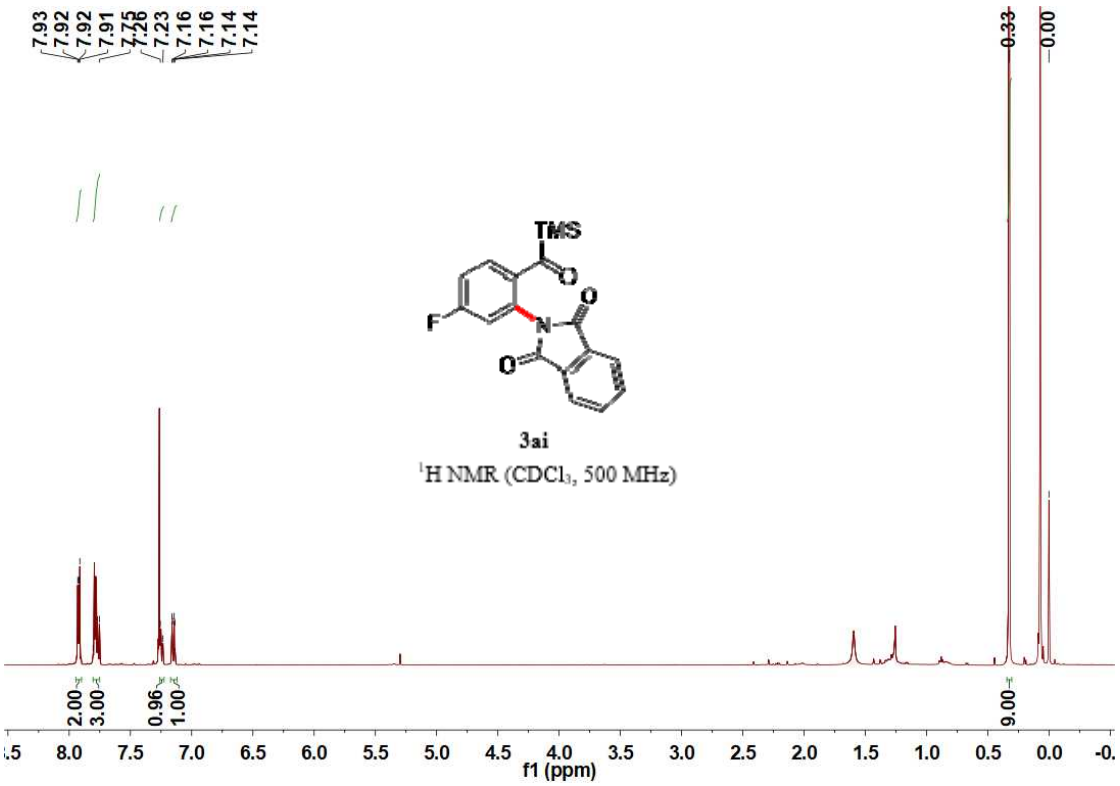
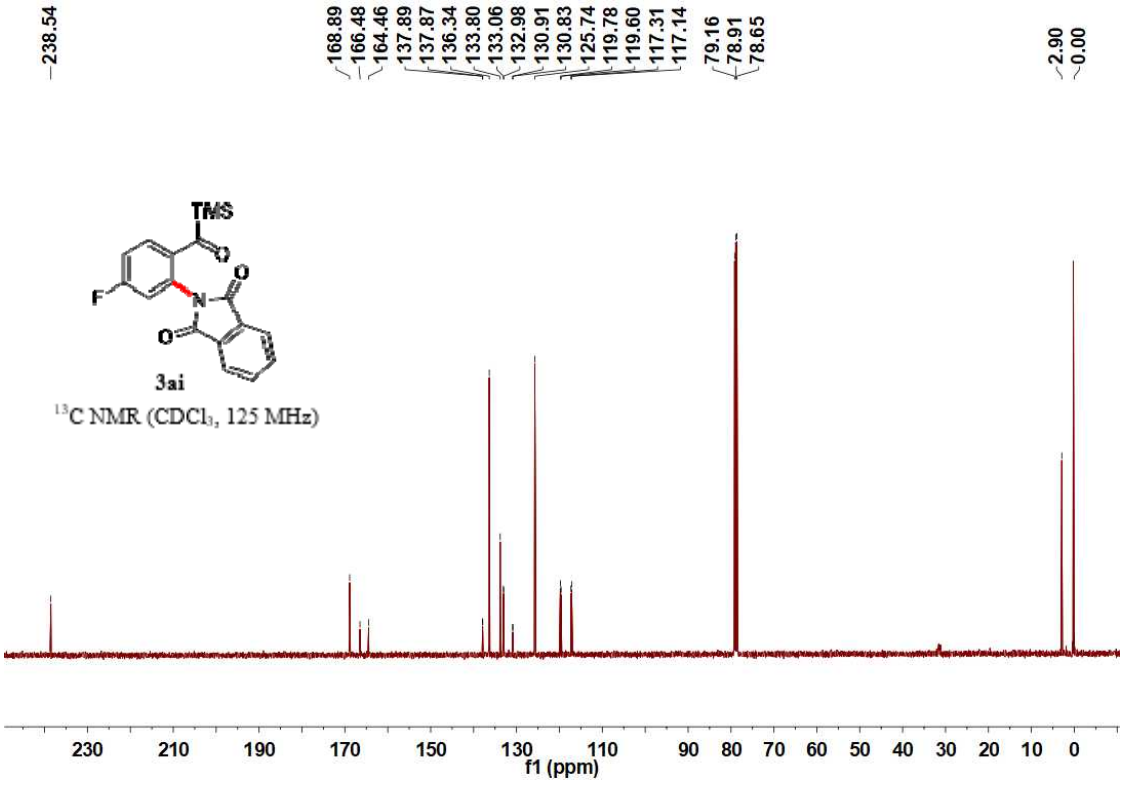


3ai

^{1}H NMR ($CDCl_3$, 500 MHz)



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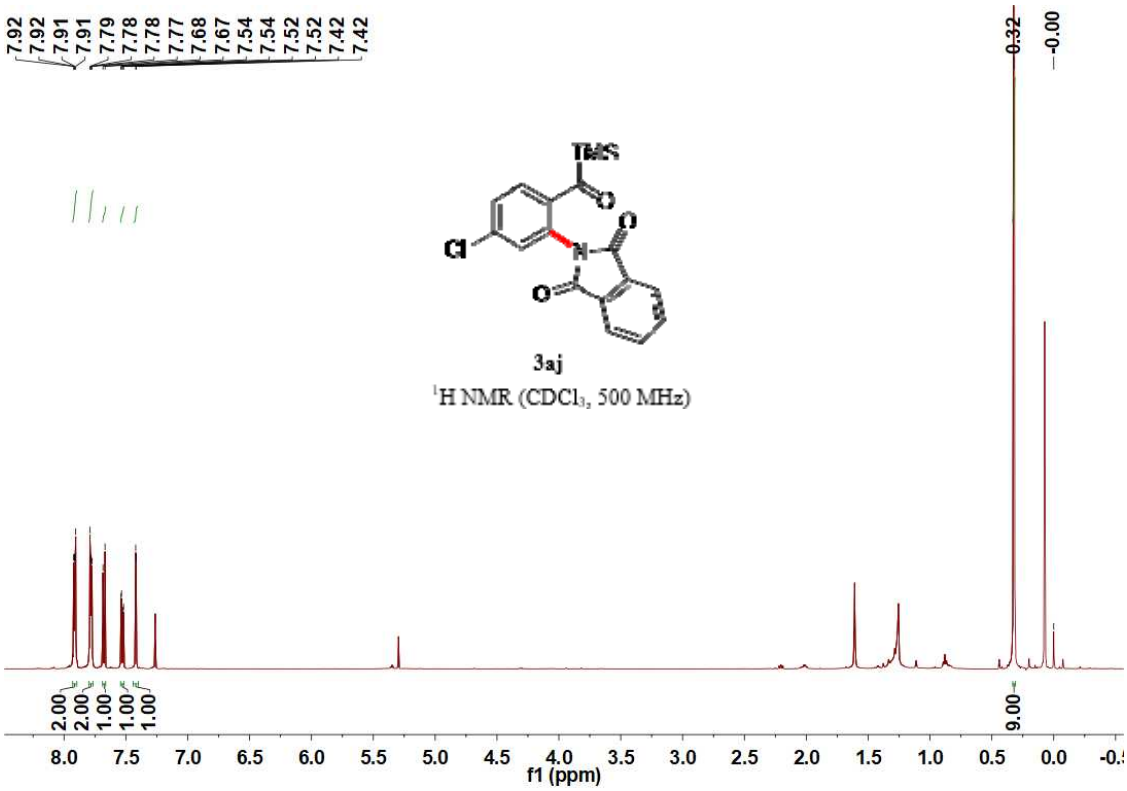
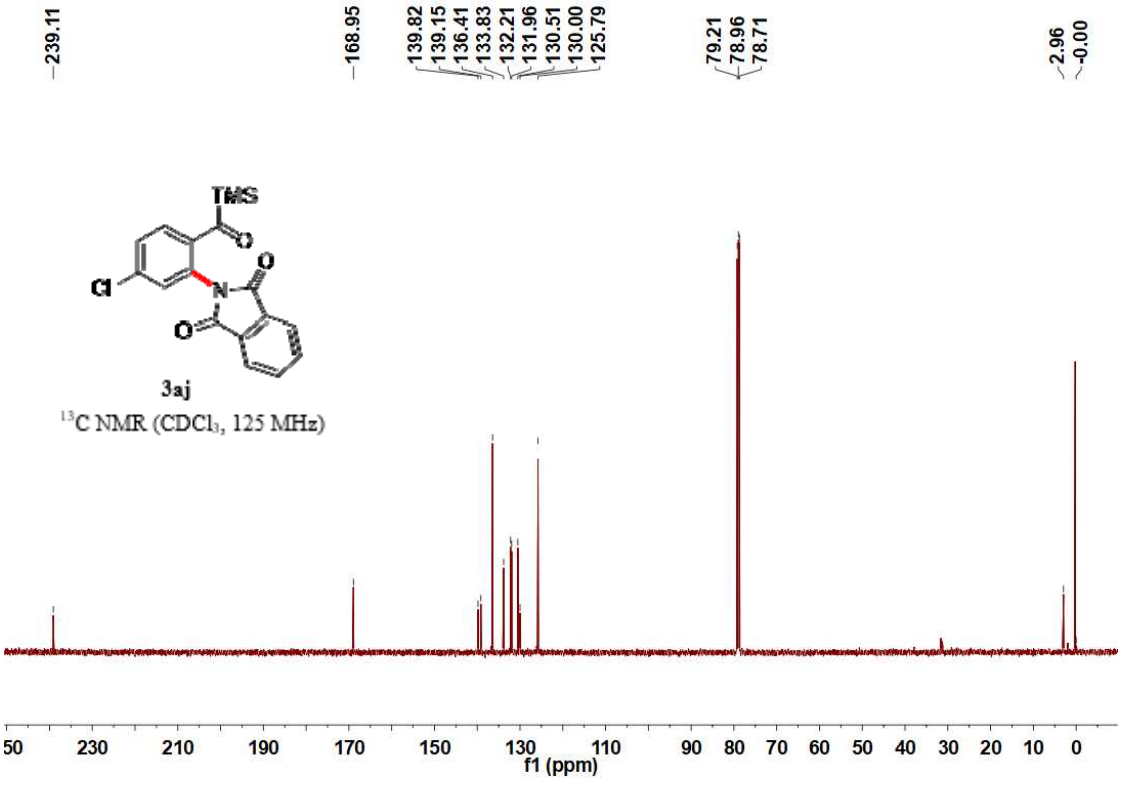
^{13}C NMR ($CDCl_3$, 125 MHz)



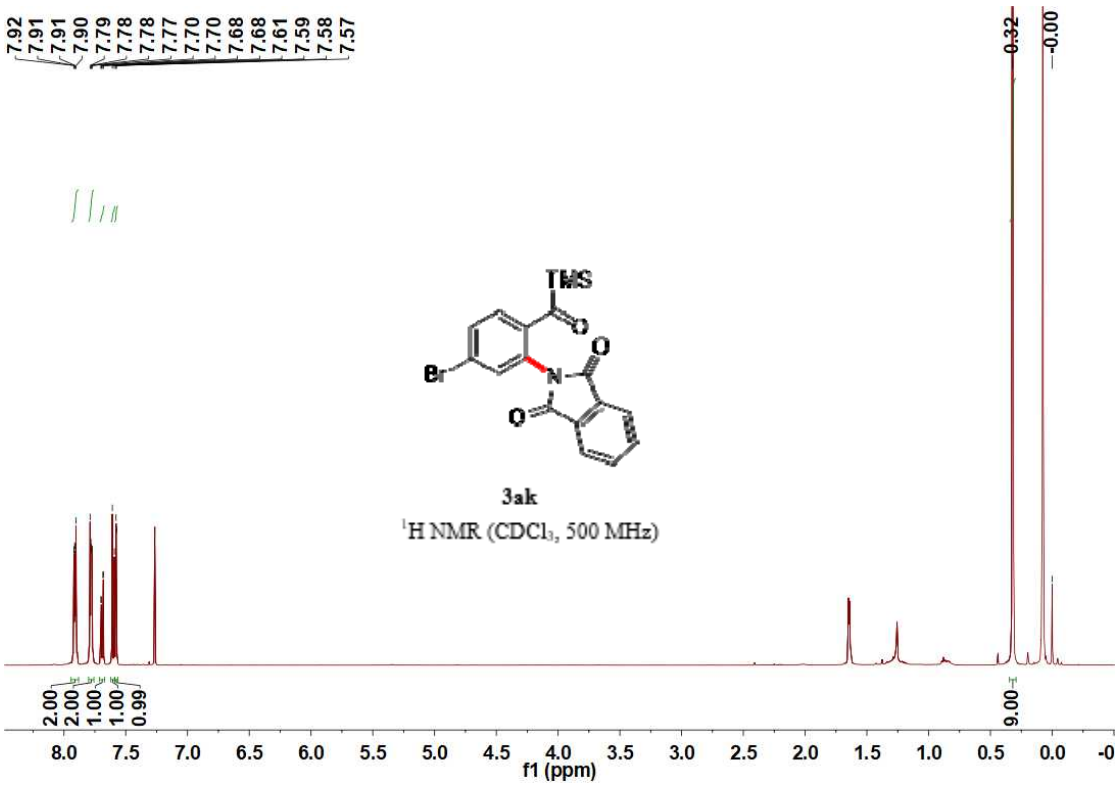
3aj

^{1}H NMR ($CDCl_3$, 500 MHz)



3aj

^{13}C NMR ($CDCl_3$, 125 MHz)



3ak

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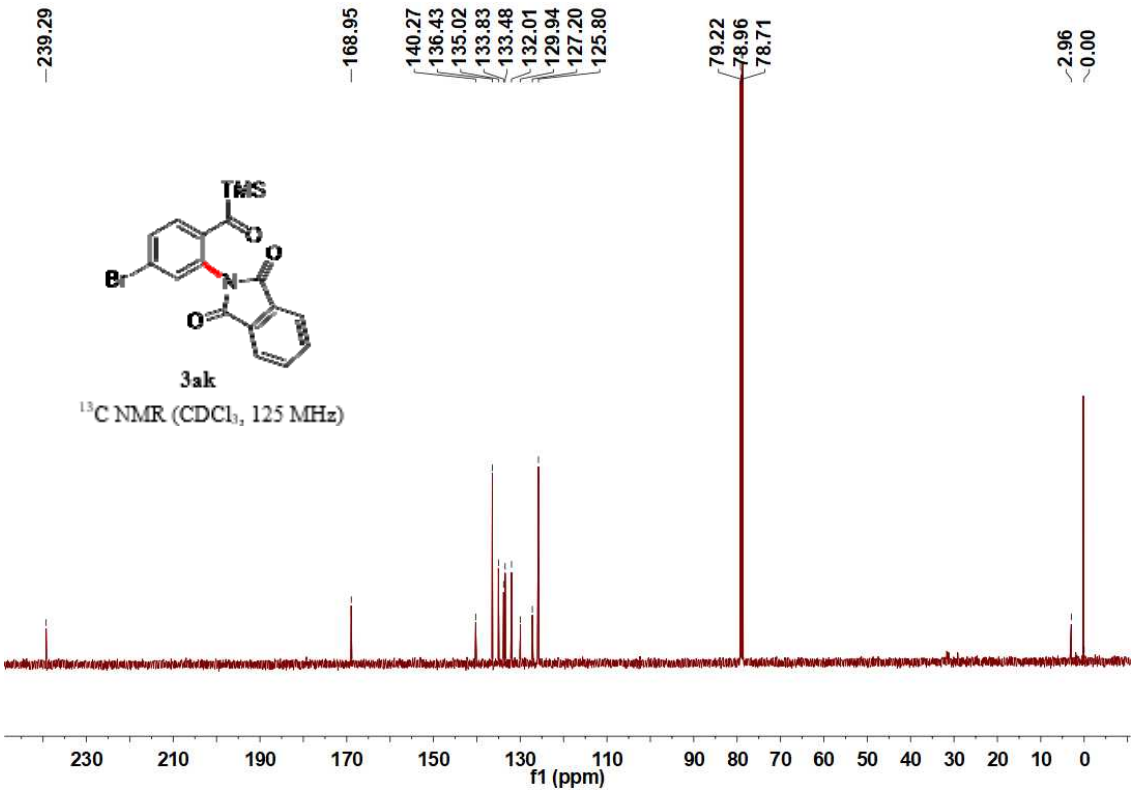
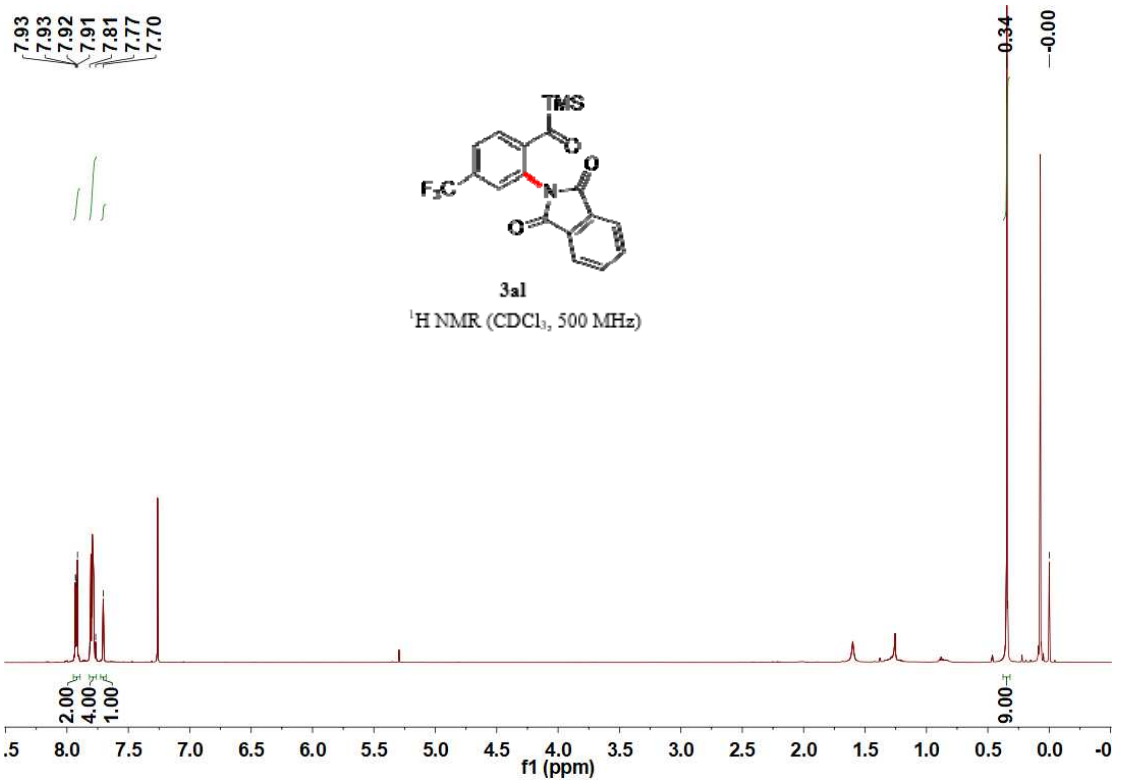


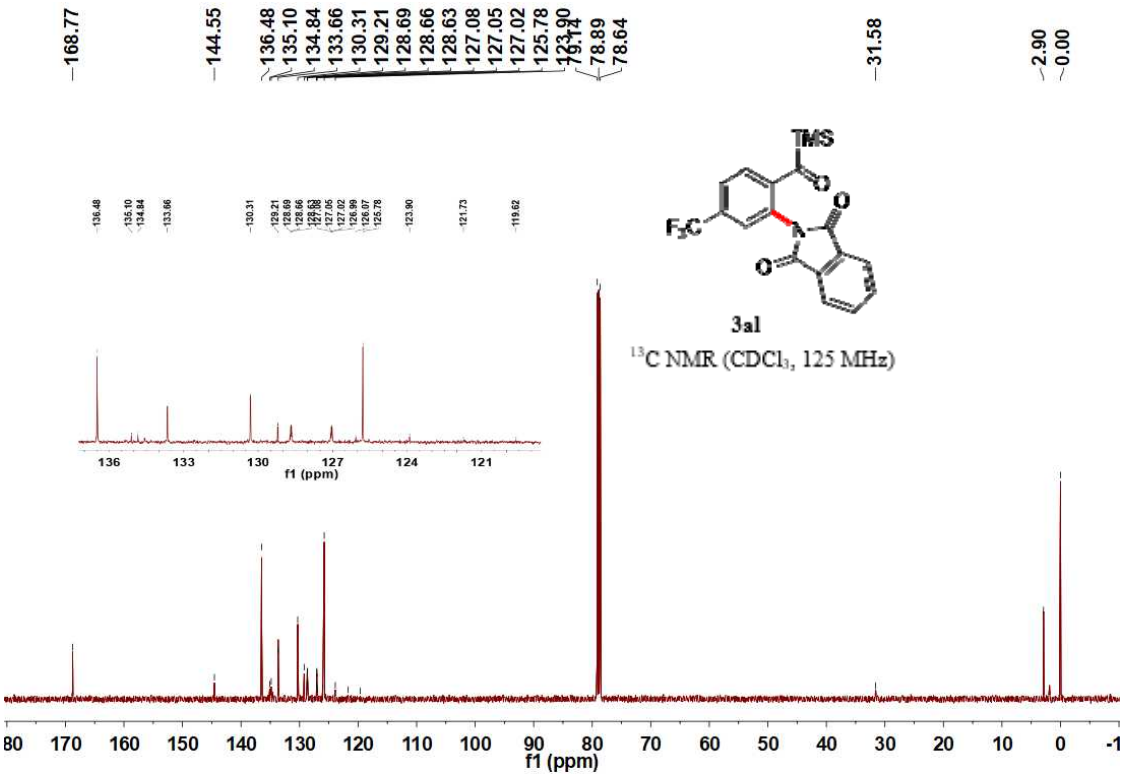
3ak

^{13}C NMR ($CDCl_3$, 125 MHz)



3al

^{1}H NMR ($CDCl_3$, 500 MHz)



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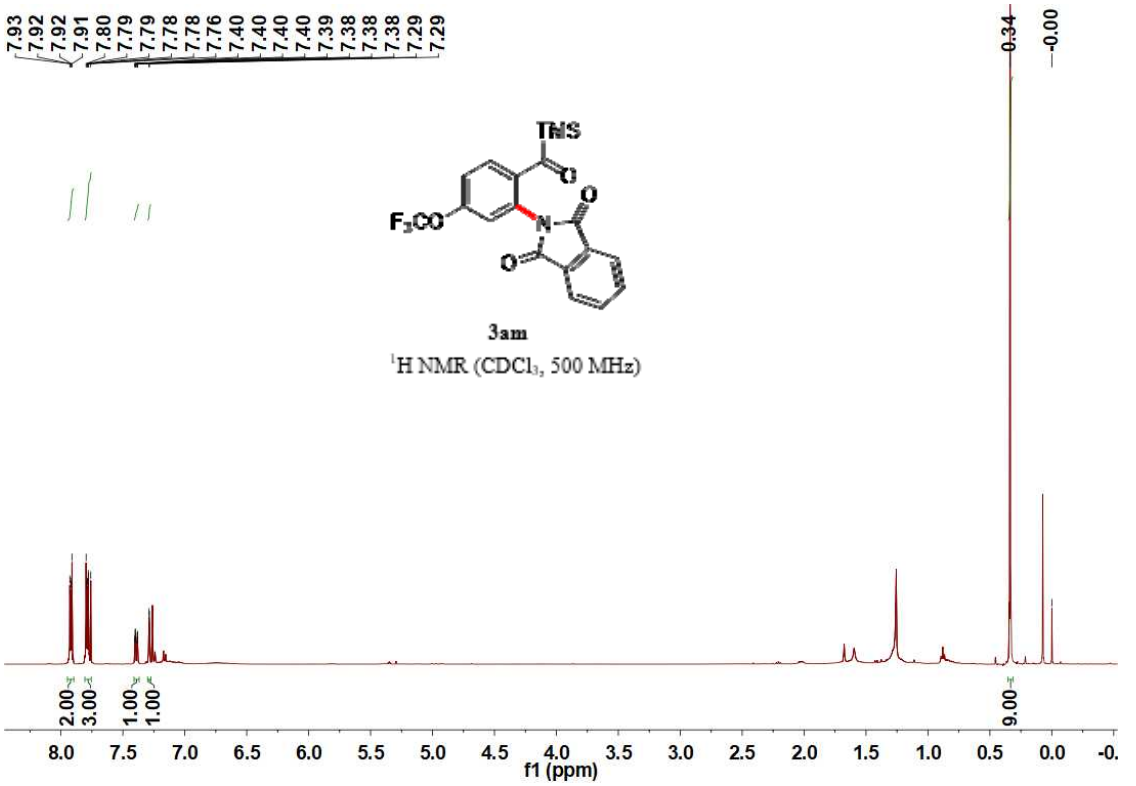
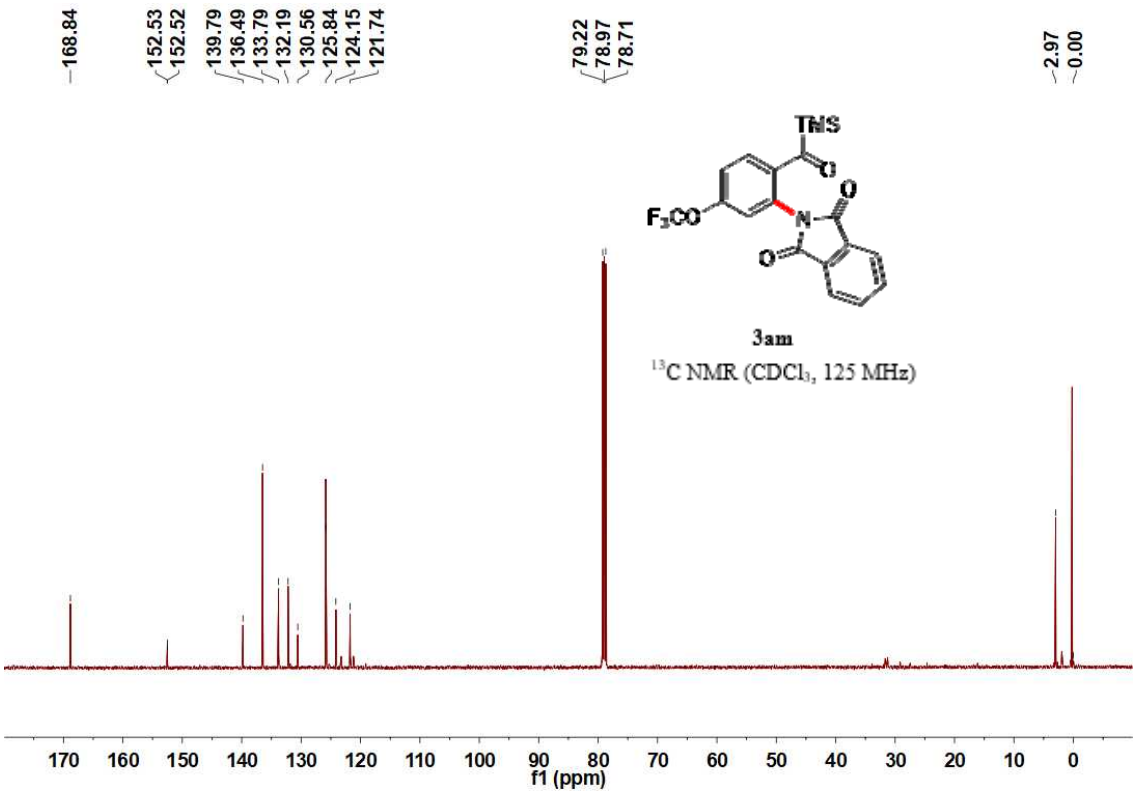
^{13}C NMR ($CDCl_3$, 125 MHz)



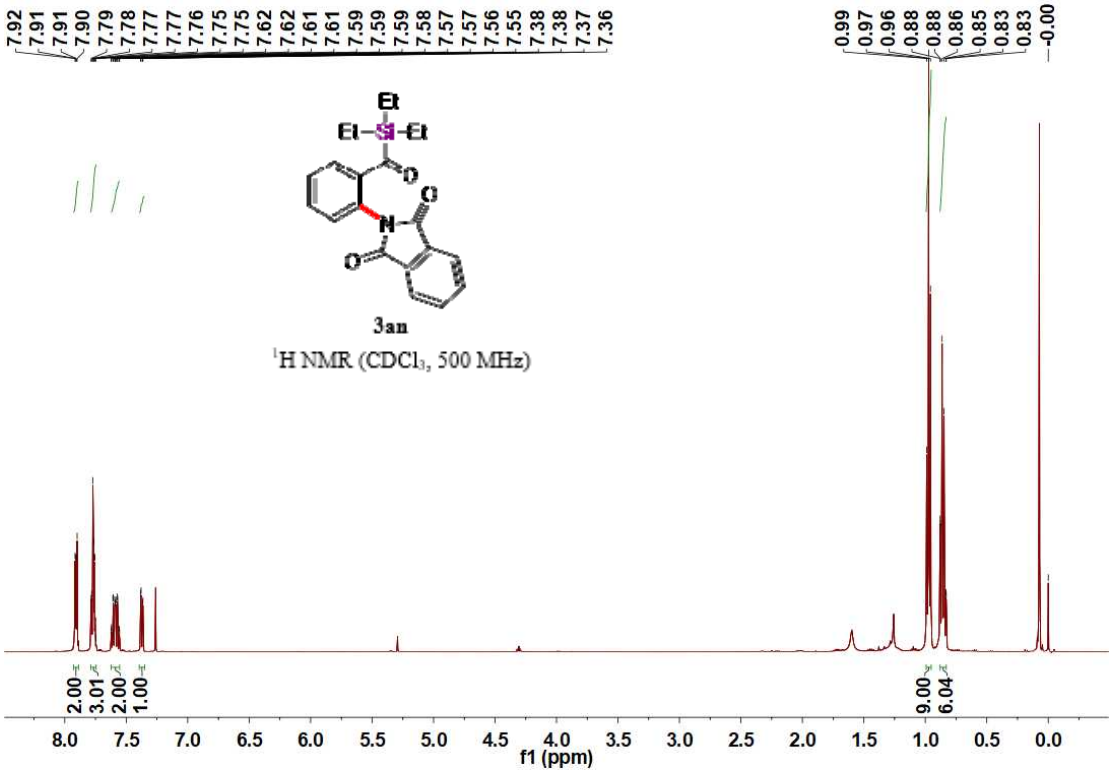
3am

^{1}H NMR ($CDCl_3$, 500 MHz)



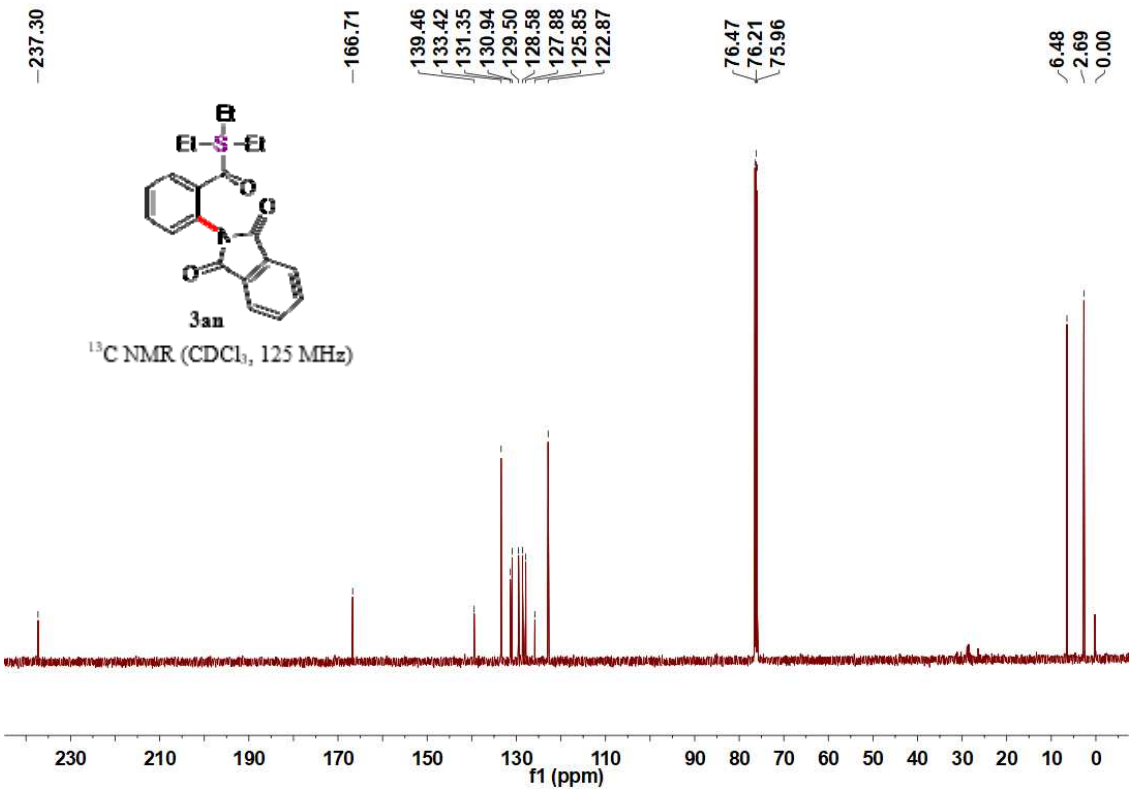
3am

^{13}C NMR ($CDCl_3$, 125 MHz)



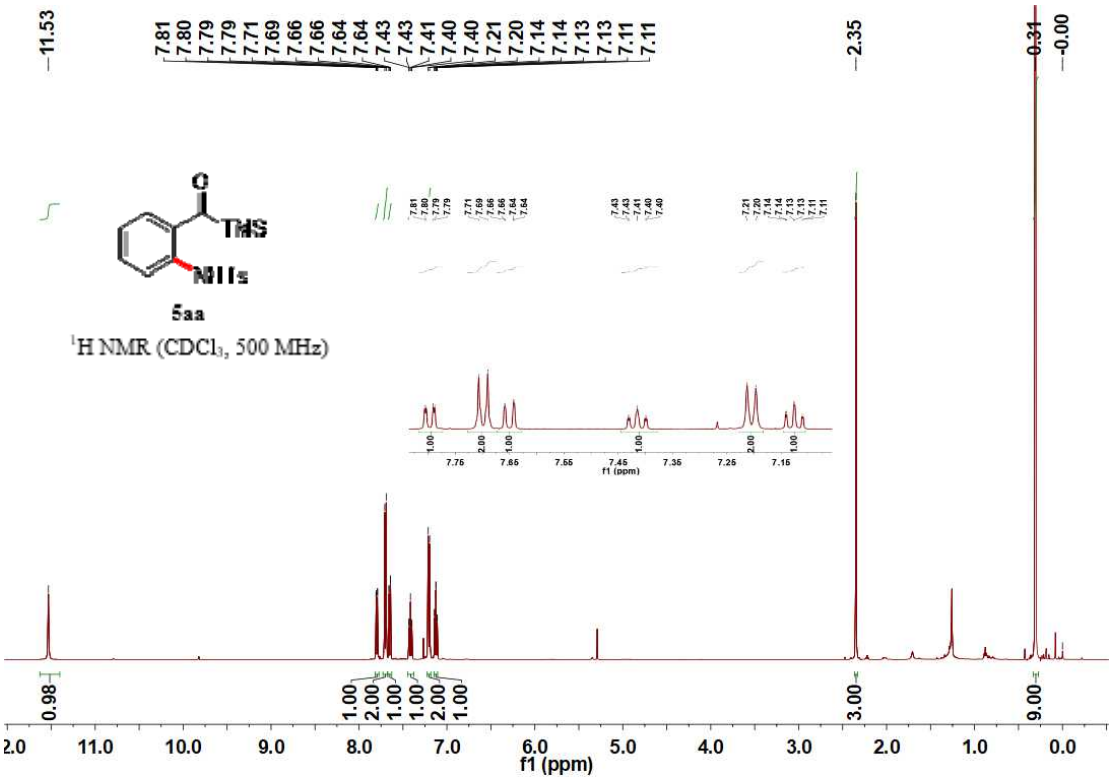
3an

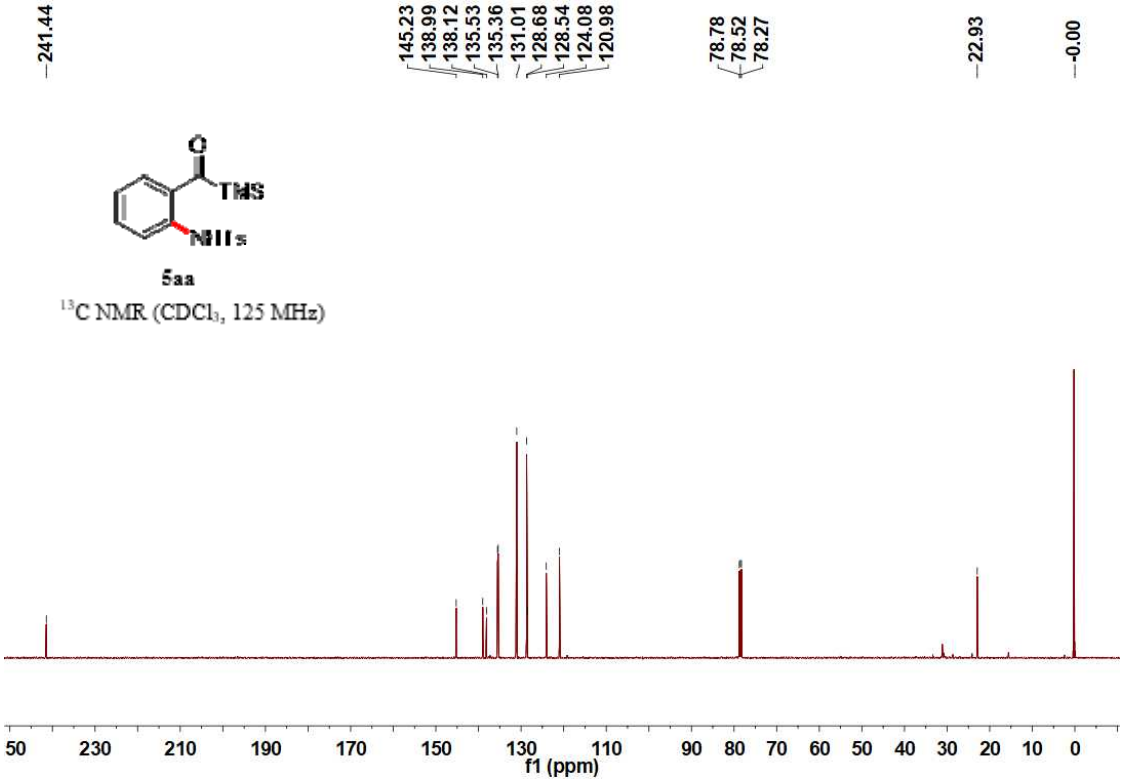
^{1}H NMR ($CDCl_3$, 500 MHz)

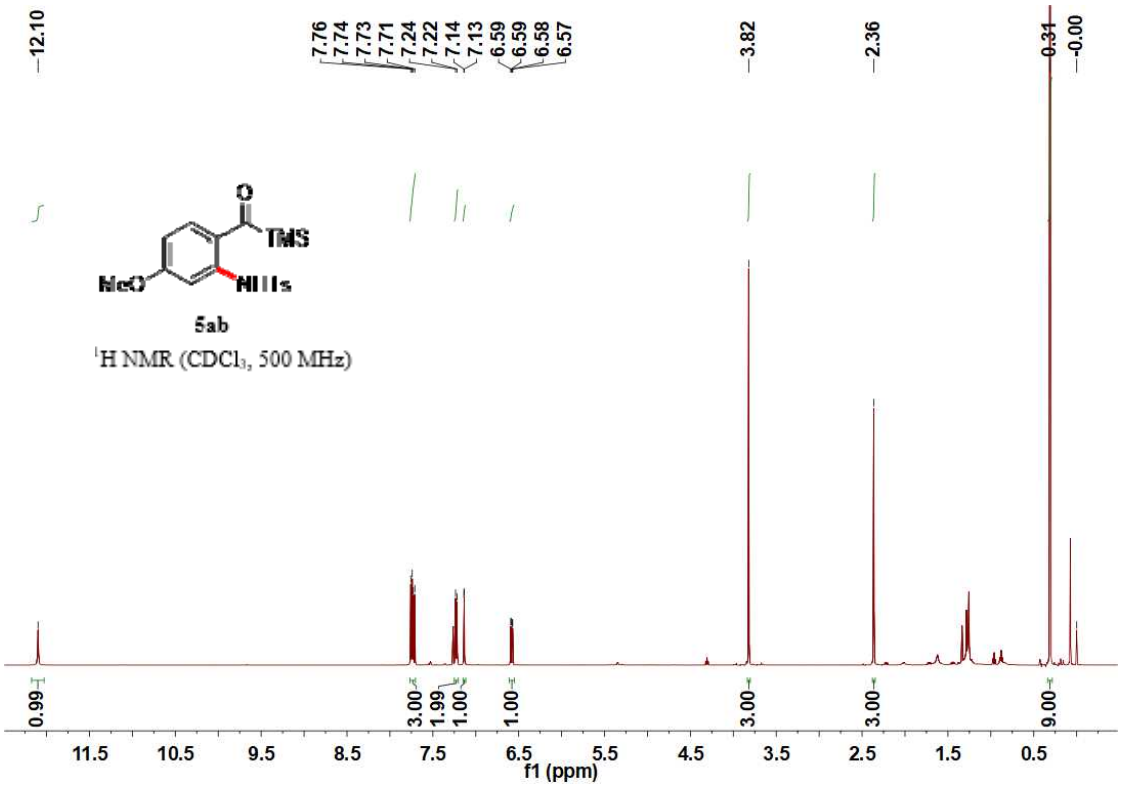


3an

^{13}C NMR ($CDCl_3$, 125 MHz)

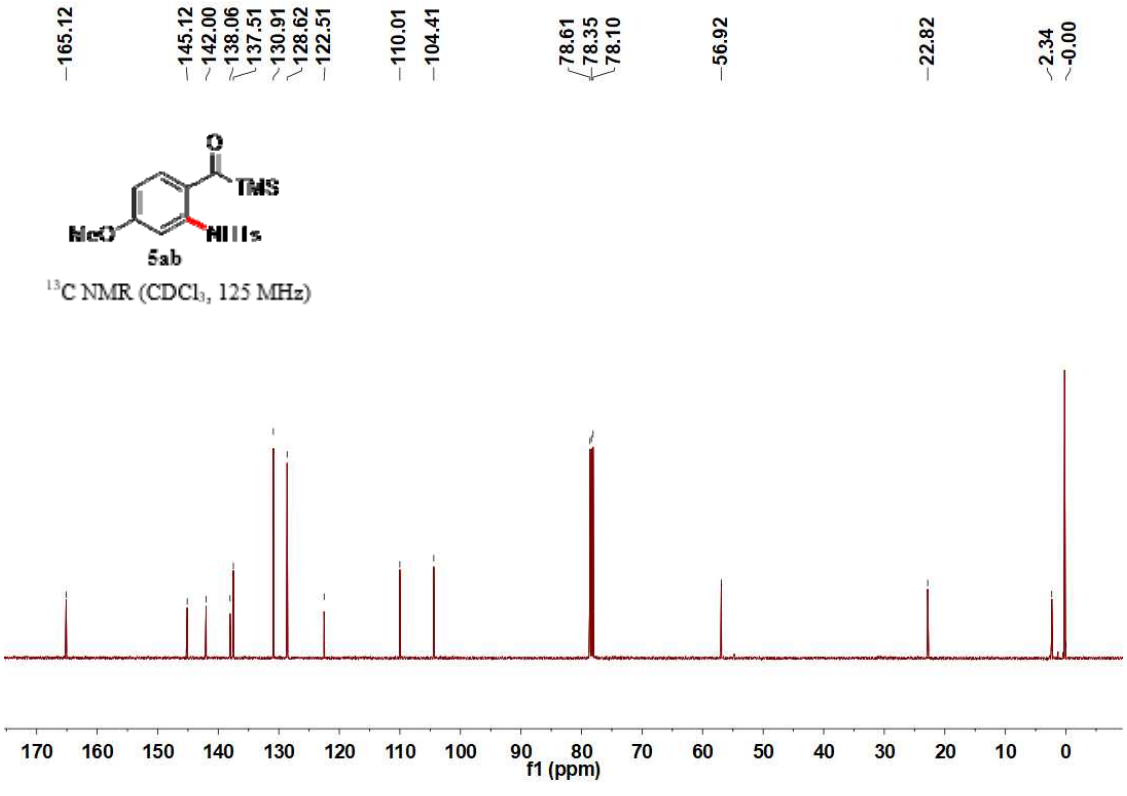

11.53
7.81
7.80
7.79
7.79
7.71
7.69
7.66
7.66
7.64
7.64
7.43
7.43
7.41
7.40
7.40
7.21
7.20
7.14
7.14
7.13
7.13
7.11
7.11
2.35
0.31
0.00
TMS
NHTs
5aa
1H NMR (CDCl3, 500 MHz)
0.98
1.00
2.00
1.00
1.00
2.00
1.00
3.00
9.00
f1 (ppm)


241.44
145.23
138.99
138.12
135.53
135.36
131.01
128.68
128.54
124.08
120.98
78.78
78.52
78.27
22.93
0.00
TMS
NHTs
5aa
13C NMR (CDCl3, 125 MHz)
f1 (ppm)



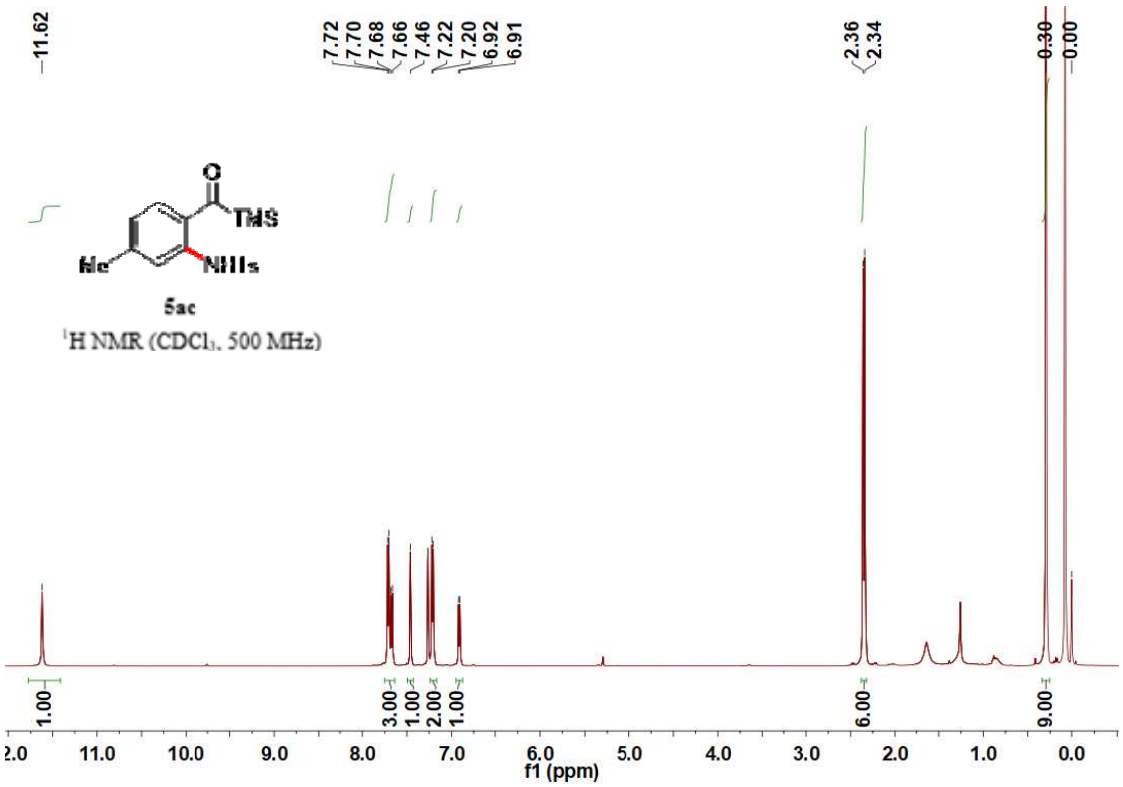
5ab

^{1}H NMR ($CDCl_3$, 500 MHz)



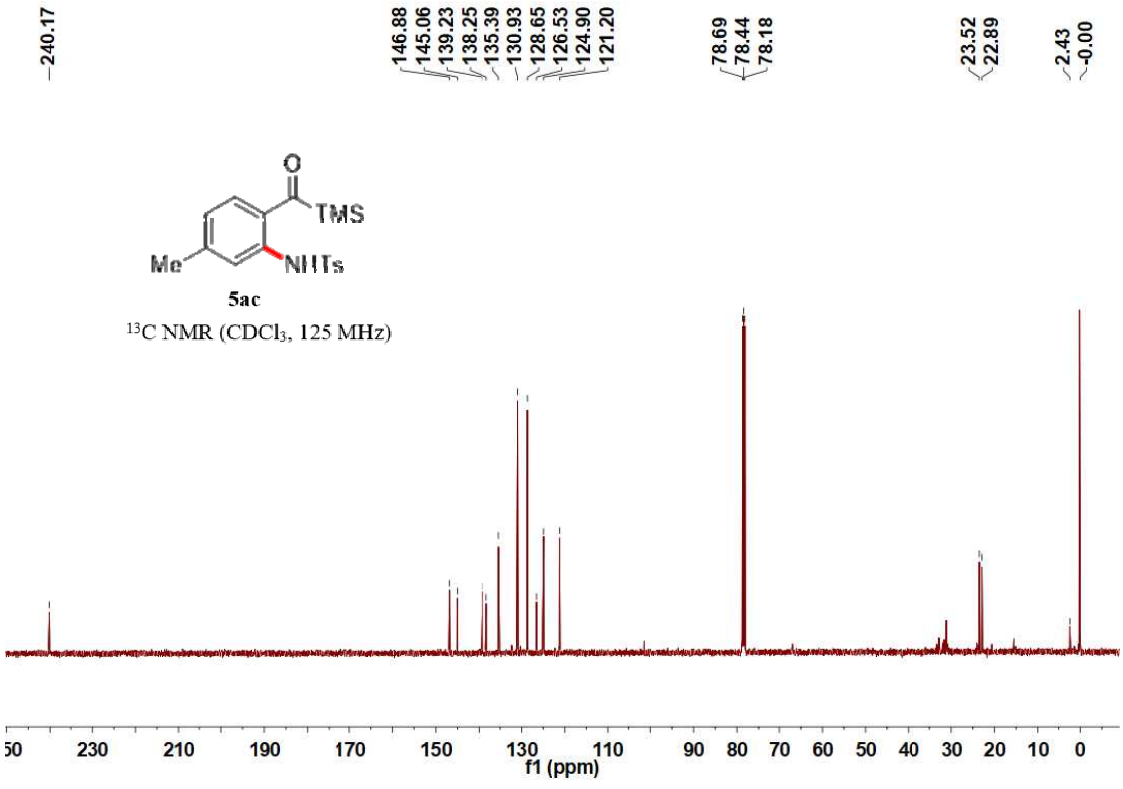
5ab

^{13}C NMR ($CDCl_3$, 125 MHz)



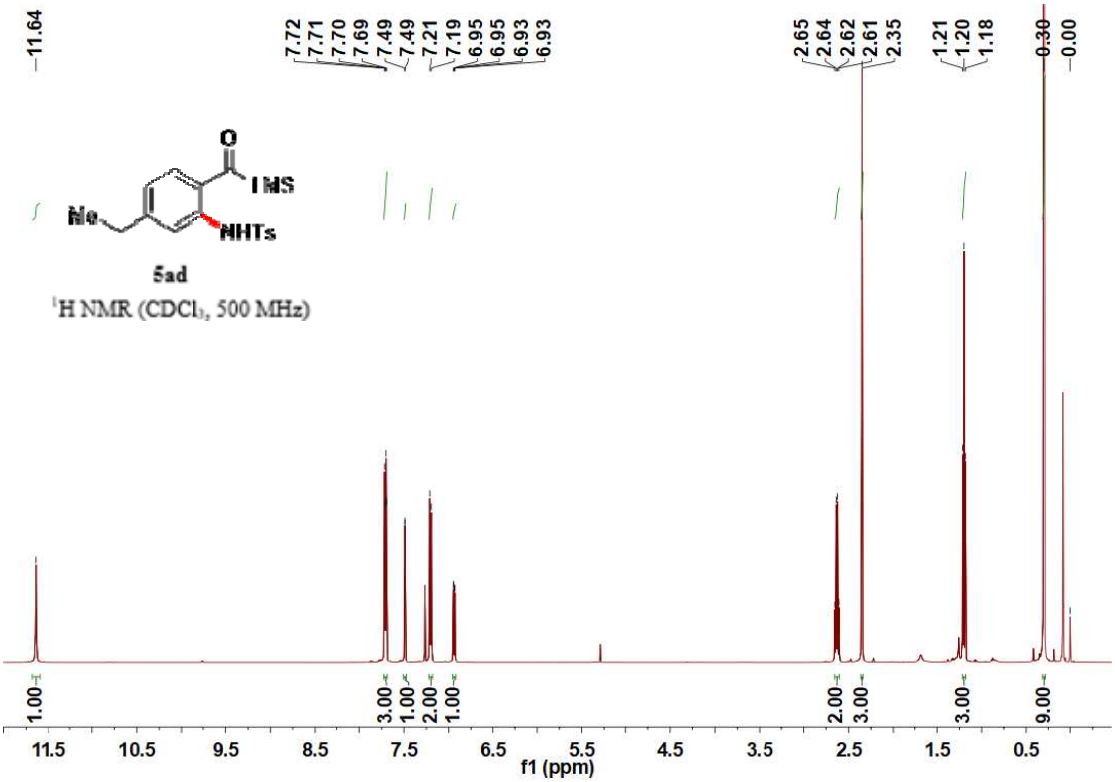
5ac

^{1}H NMR ($CDCl_3$, 500 MHz)



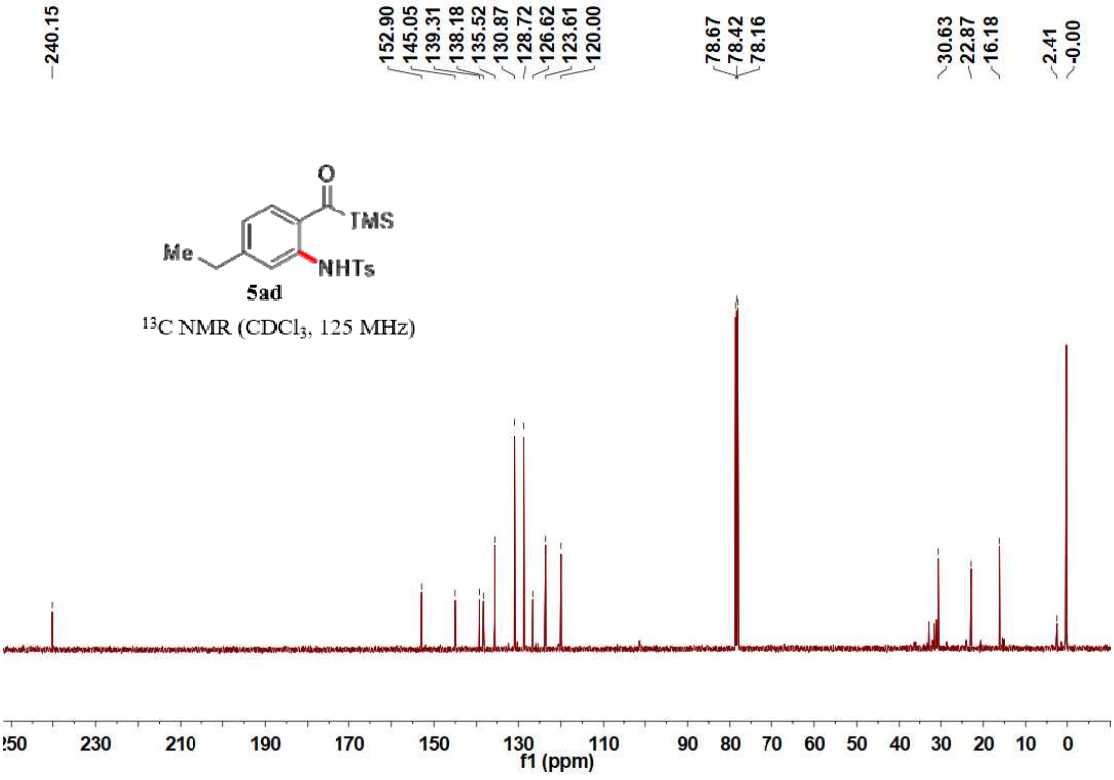
5ac

^{13}C NMR ($CDCl_3$, 125 MHz)



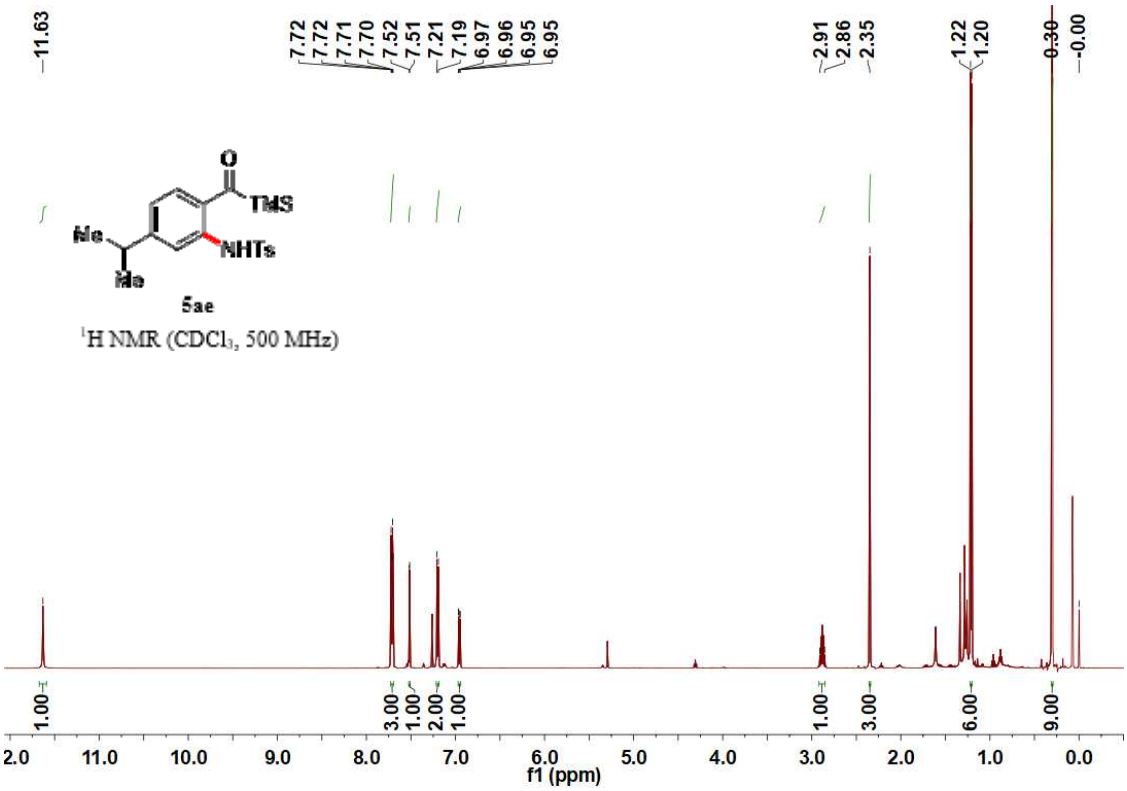
5ad

^{1}H NMR ($CDCl_3$, 500 MHz)



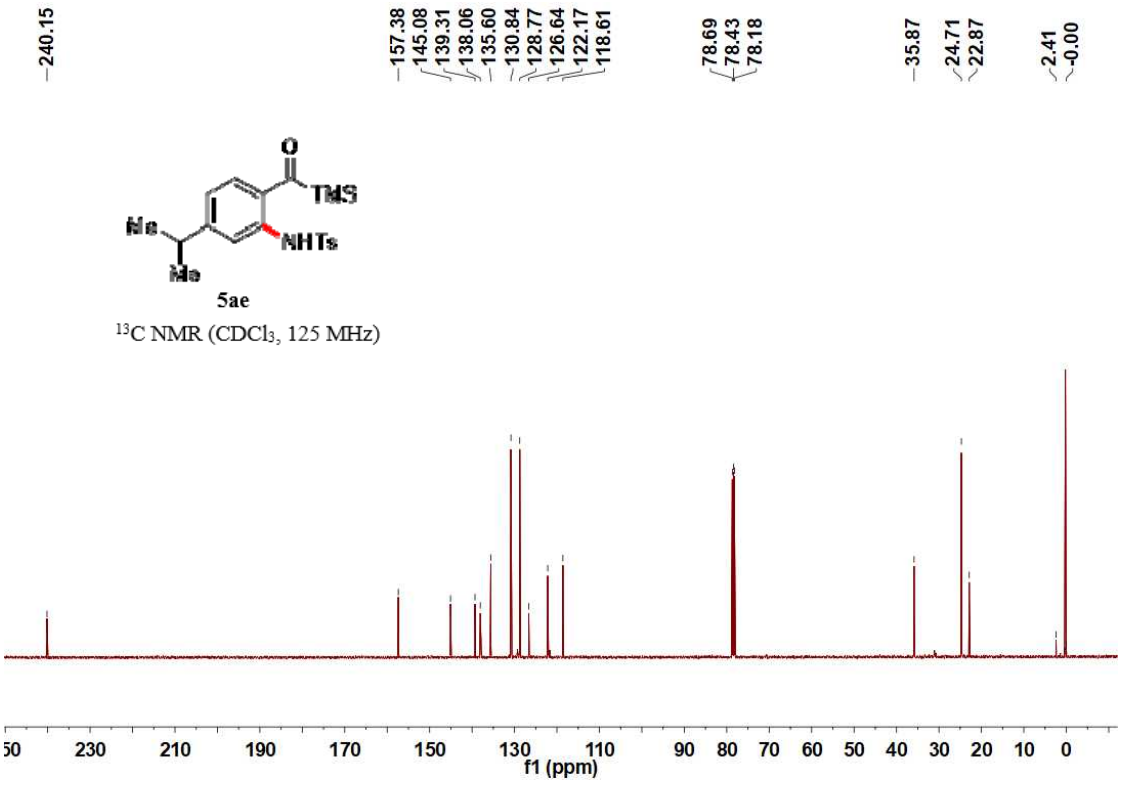
5ad

^{13}C NMR ($CDCl_3$, 125 MHz)



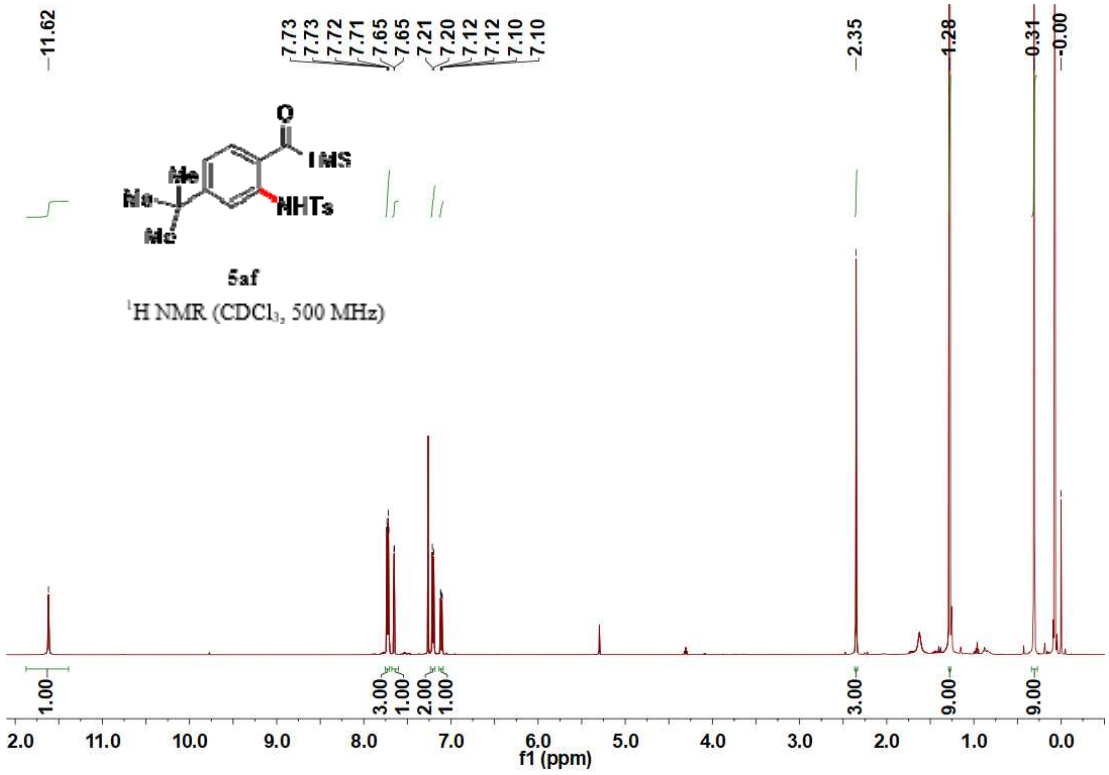
5ae

^{1}H NMR ($CDCl_3$, 500 MHz)



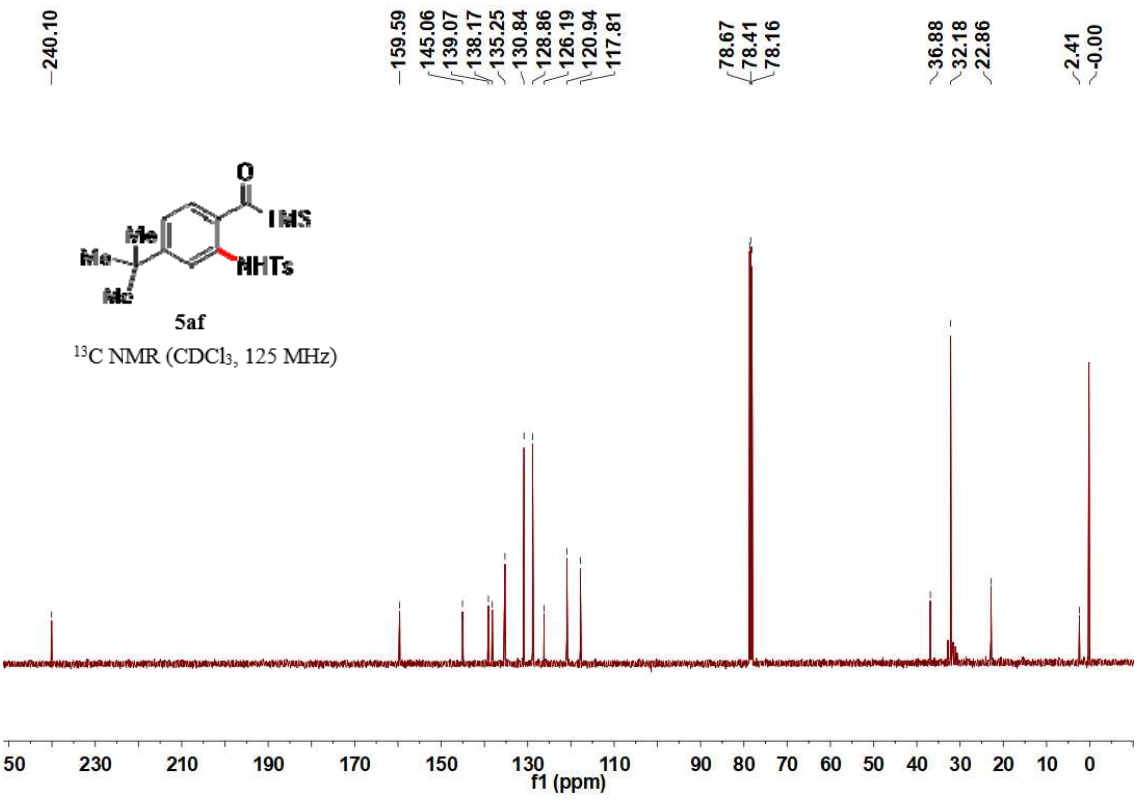
5ae

^{13}C NMR ($CDCl_3$, 125 MHz)



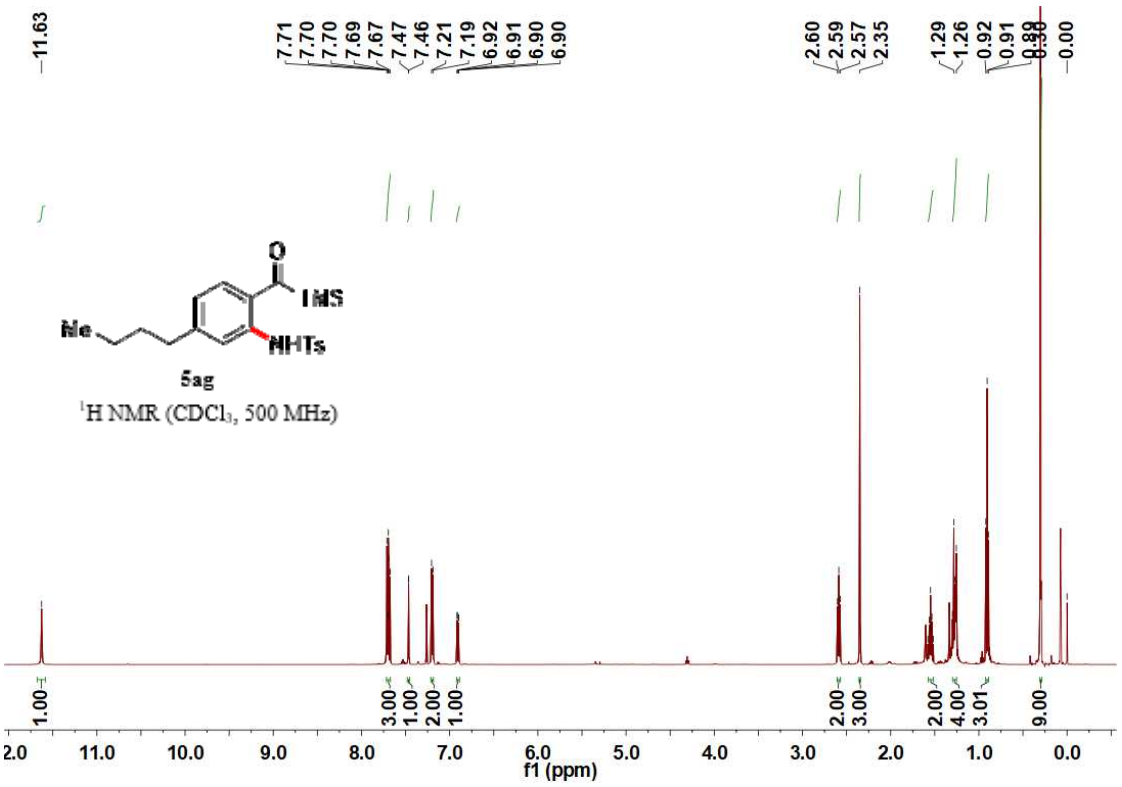
5af

^{1}H NMR ($CDCl_3$, 500 MHz)



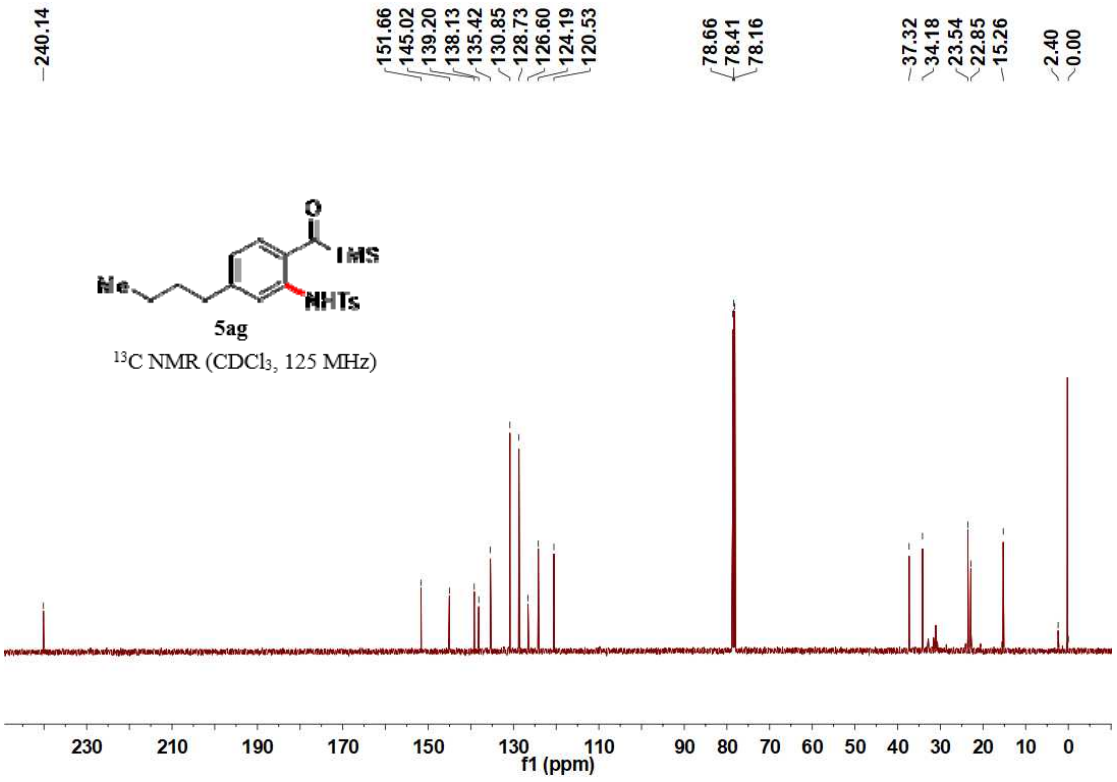
5af

^{13}C NMR ($CDCl_3$, 125 MHz)



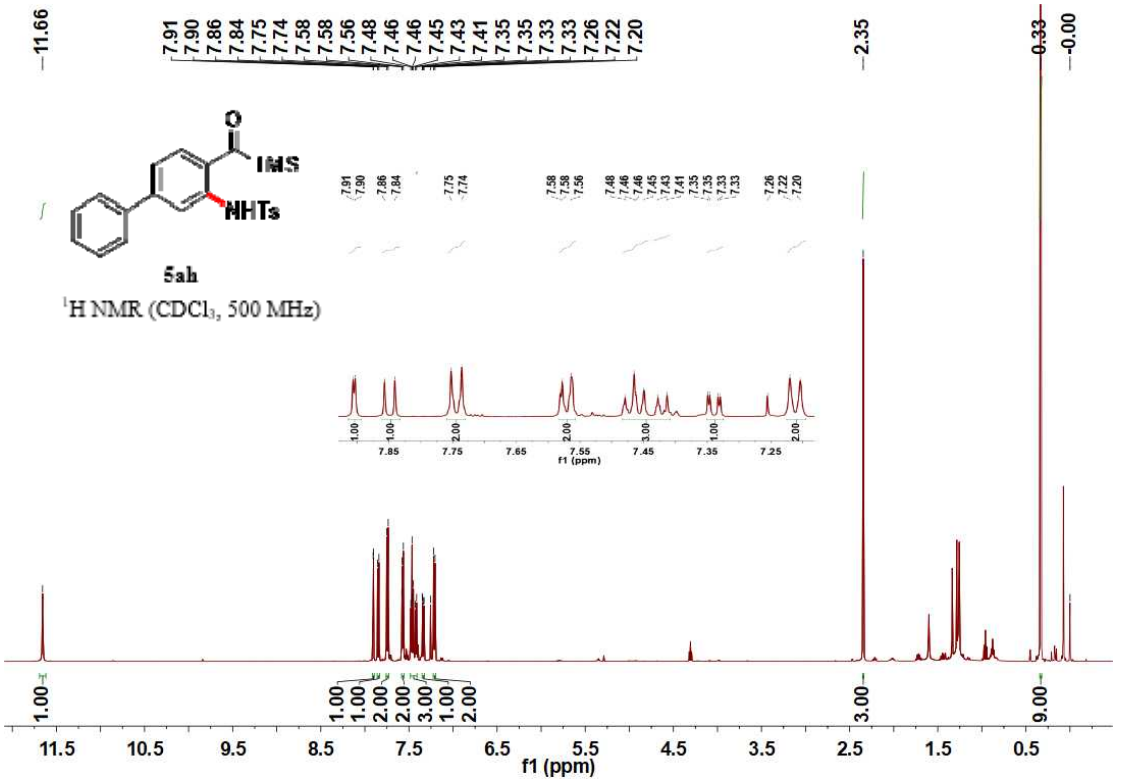
5ag

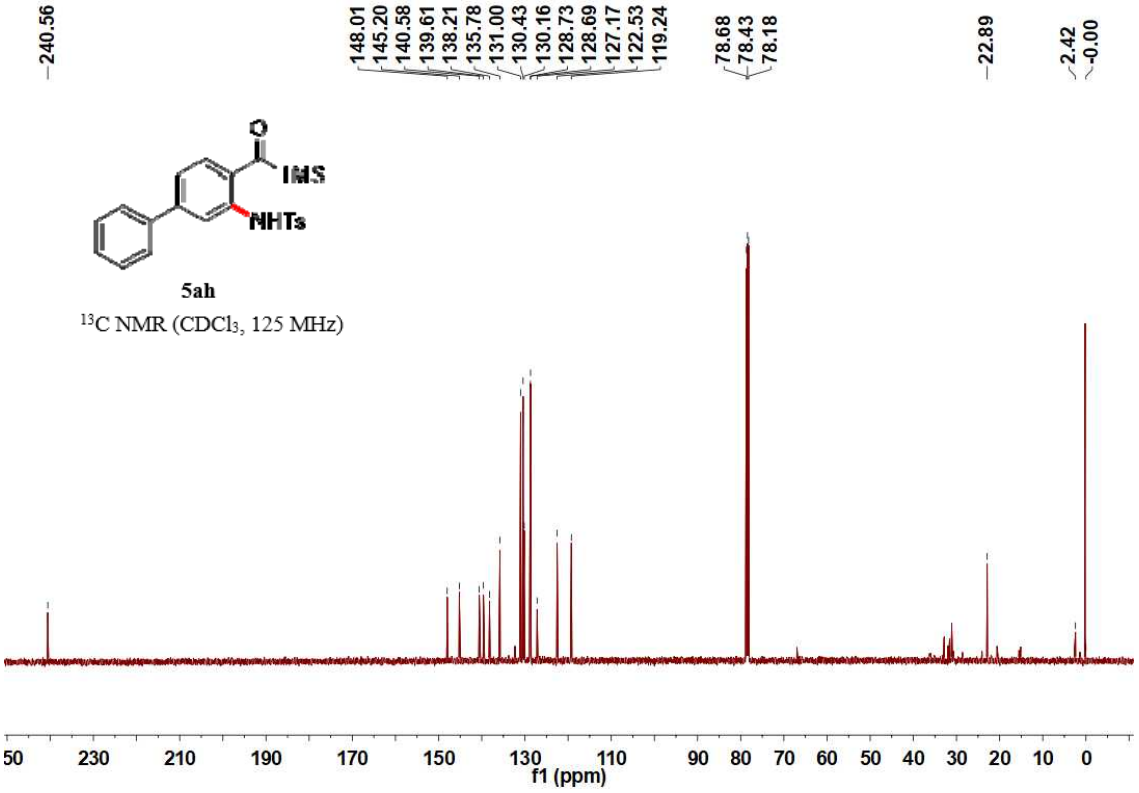
^{1}H NMR ($CDCl_3$, 500 MHz)

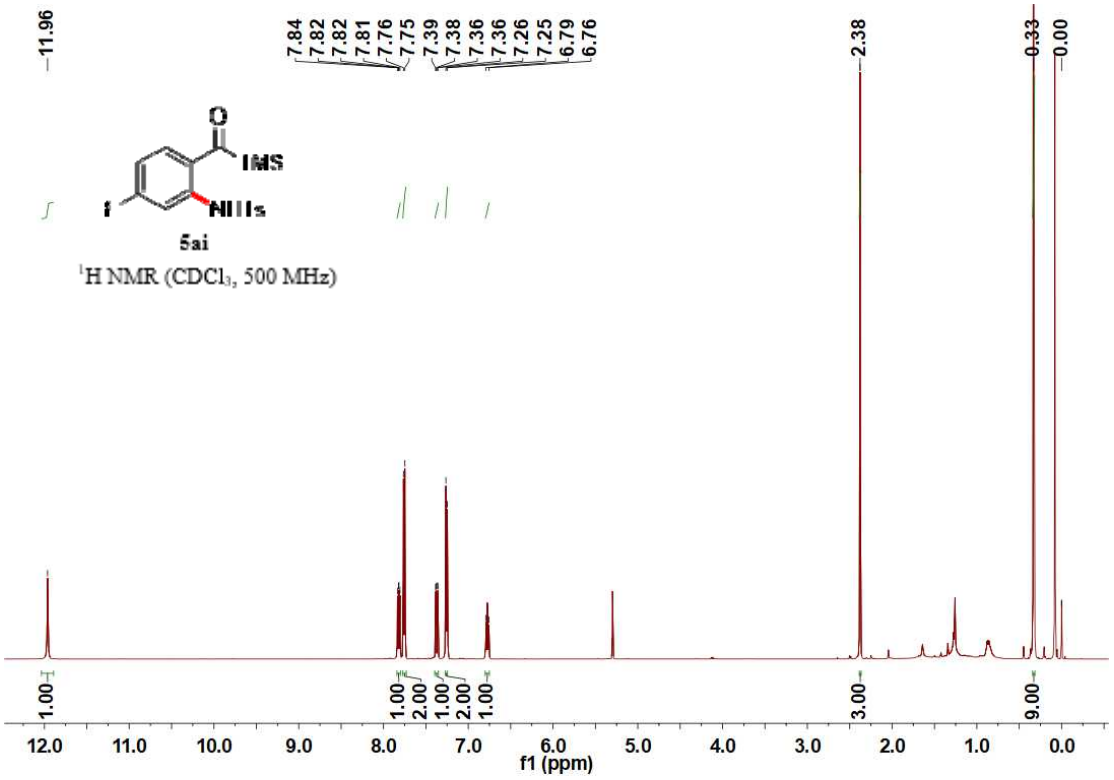


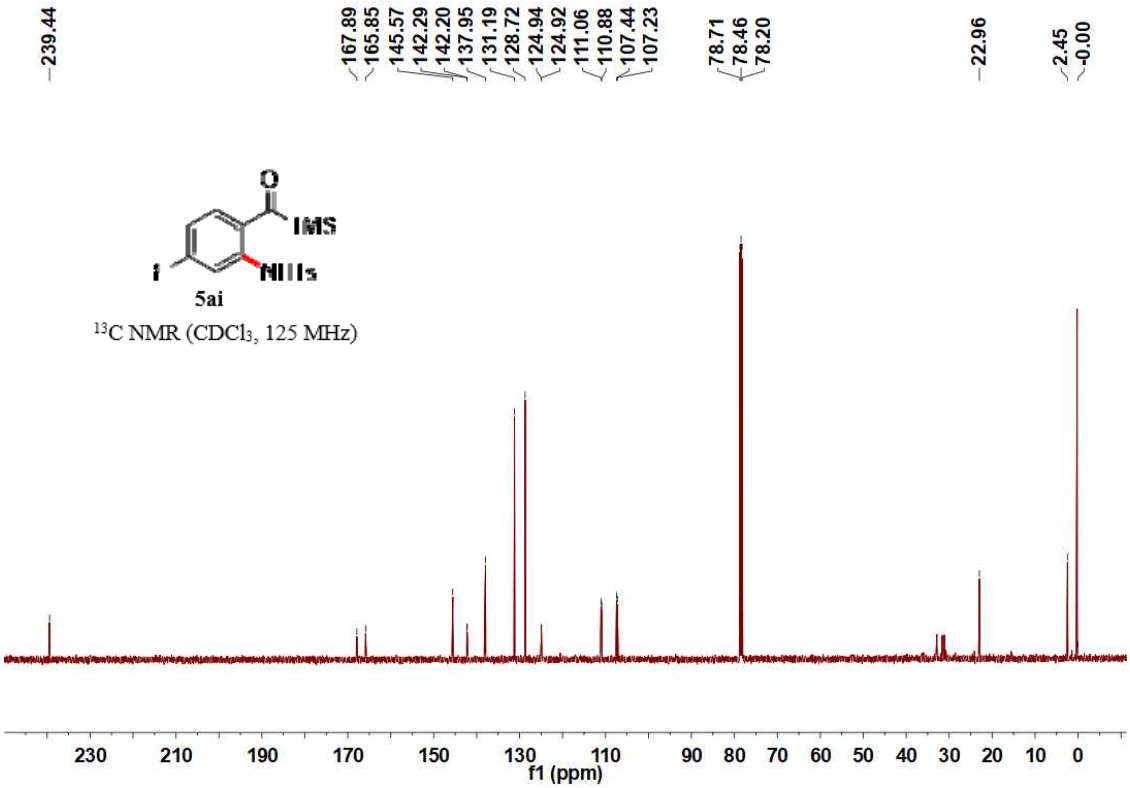
5ag

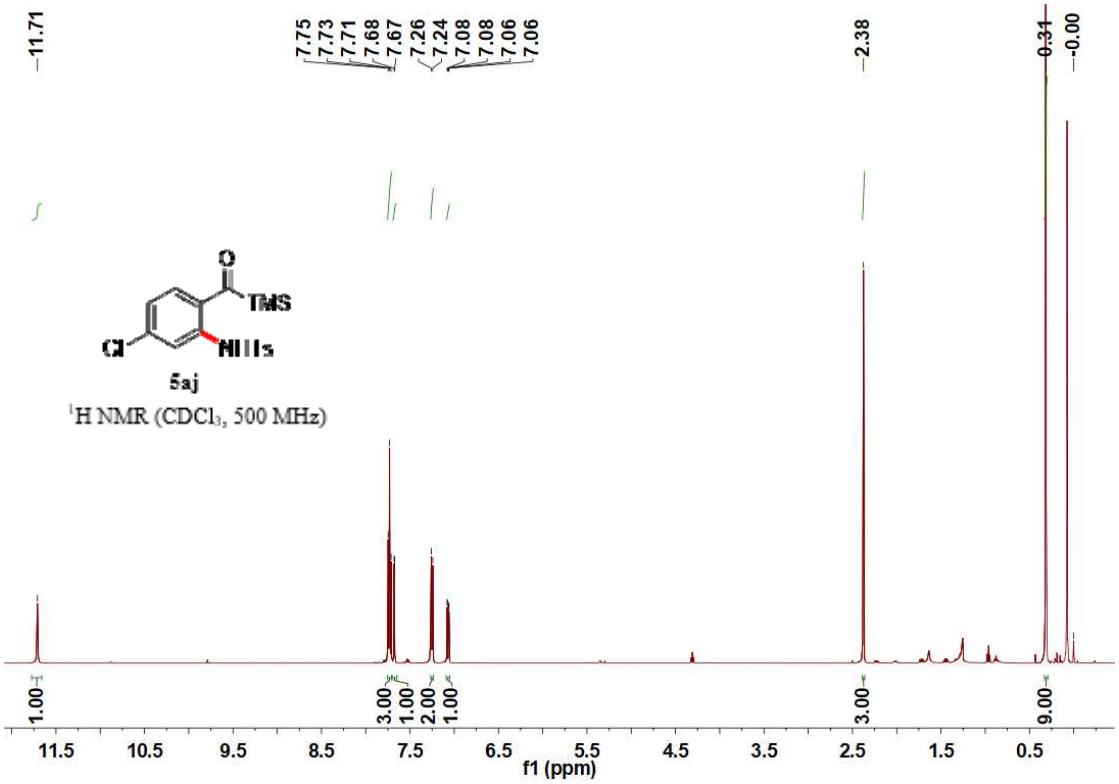
^{13}C NMR ($CDCl_3$, 125 MHz)


11.66
7.91
7.90
7.86
7.84
7.75
7.74
7.58
7.58
7.56
7.48
7.46
7.46
7.45
7.43
7.41
7.35
7.35
7.33
7.33
7.26
7.22
7.20
2.35
0.33
0.00
IMS
NHTs
5ah
1H NMR (CDCl3, 500 MHz)
1.00
1.00
2.00
2.00
3.00
1.00
2.00
3.00
9.00
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)


240.56
148.01
145.20
140.58
139.61
138.21
135.78
131.00
130.43
130.16
128.73
128.69
127.17
122.53
119.24
78.68
78.43
78.18
22.89
2.42
0.00
IMS
NHTs
5ah
13C NMR (CDCl3, 125 MHz)
50
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

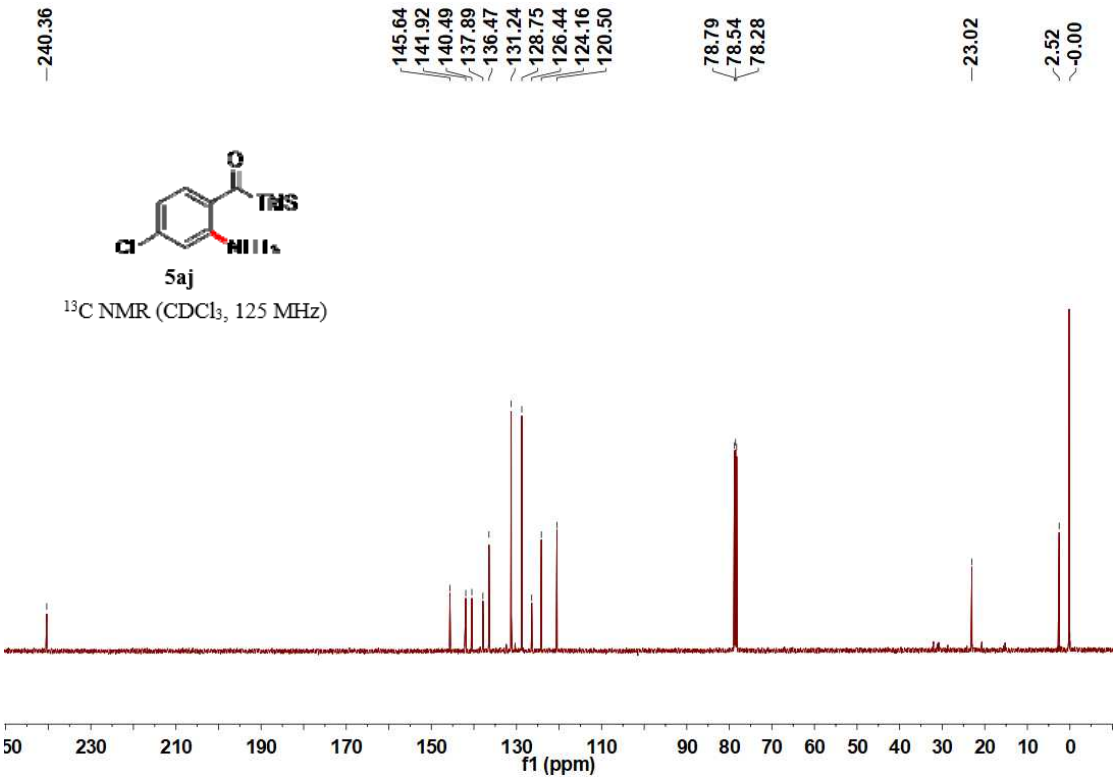

11.96
7.84
7.82
7.82
7.81
7.76
7.75
7.39
7.38
7.36
7.36
7.26
7.25
6.79
6.76
2.38
0.33
0.00
O
IMS
NIIIs
5ai
1H NMR (CDCl3, 500 MHz)
1.00
1.00
2.00
1.00
2.00
1.00
3.00
9.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


239.44
167.89
165.85
145.57
142.29
142.20
137.95
131.19
128.72
124.94
124.92
111.06
110.88
107.44
107.23
78.71
78.46
78.20
22.96
2.45
-0.00
O
IMS
NIIIs
5ai
13C NMR (CDCl3, 125 MHz)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



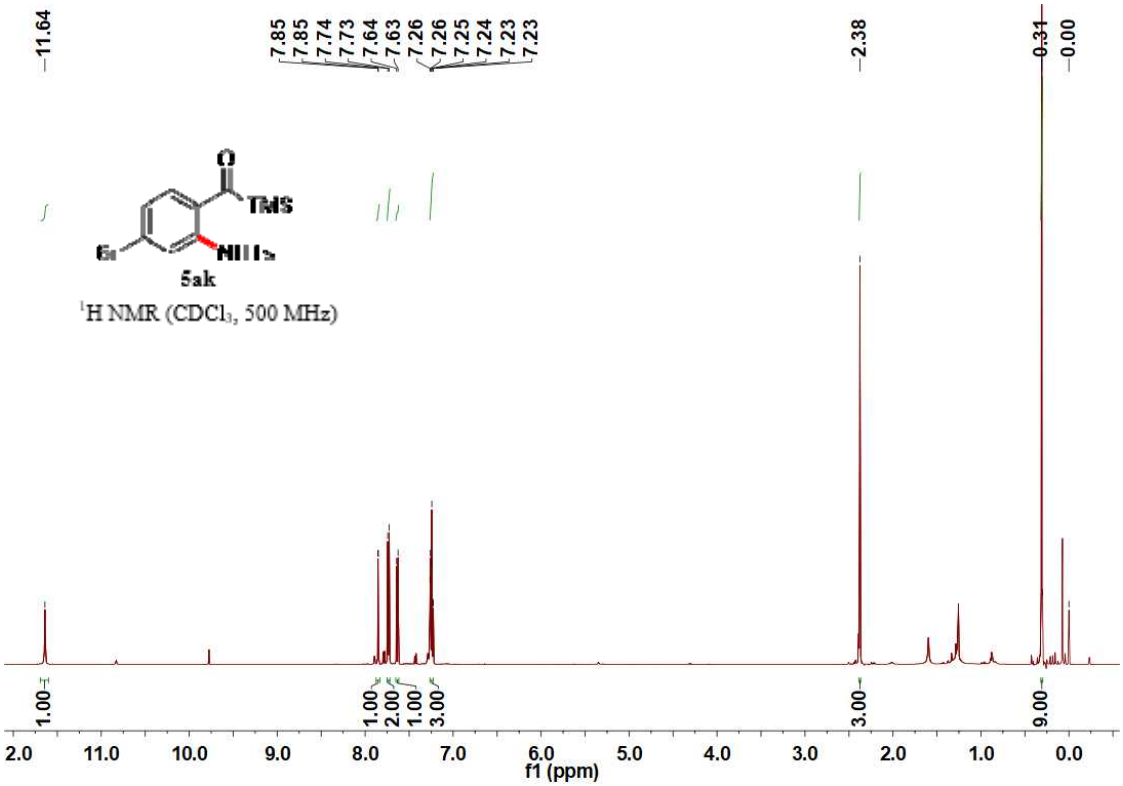
5aj

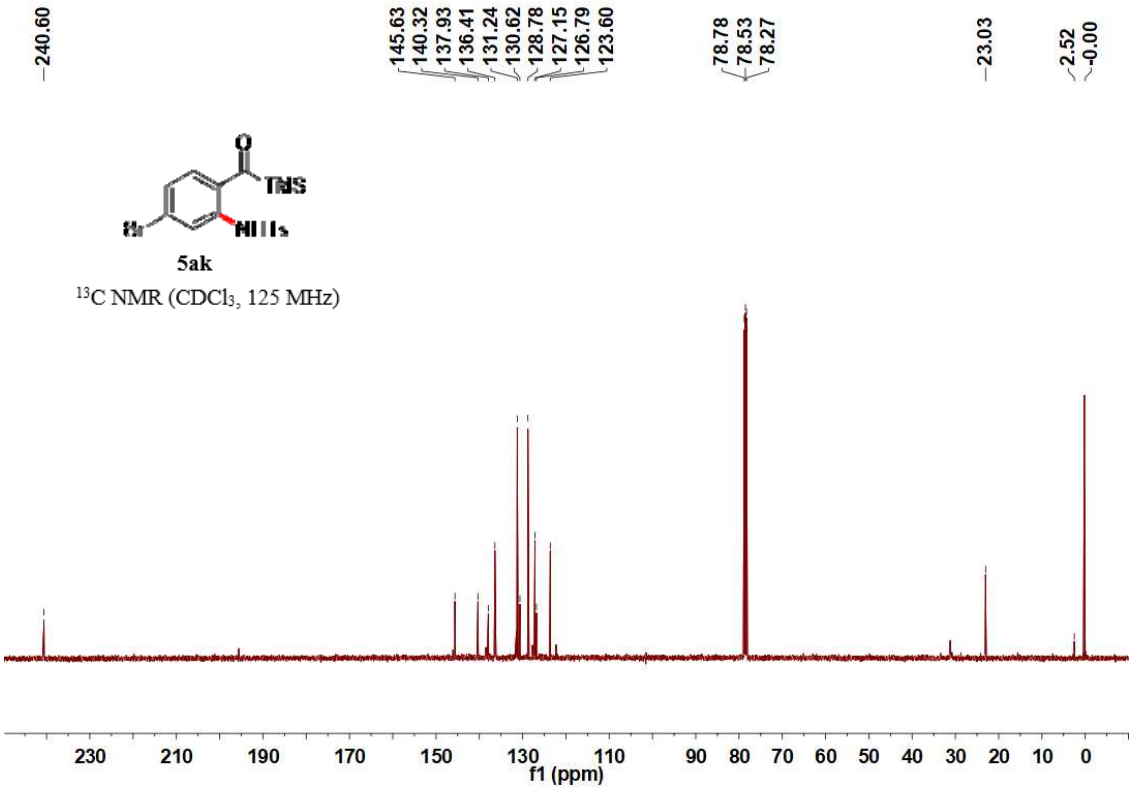
^{1}H NMR ($CDCl_3$, 500 MHz)

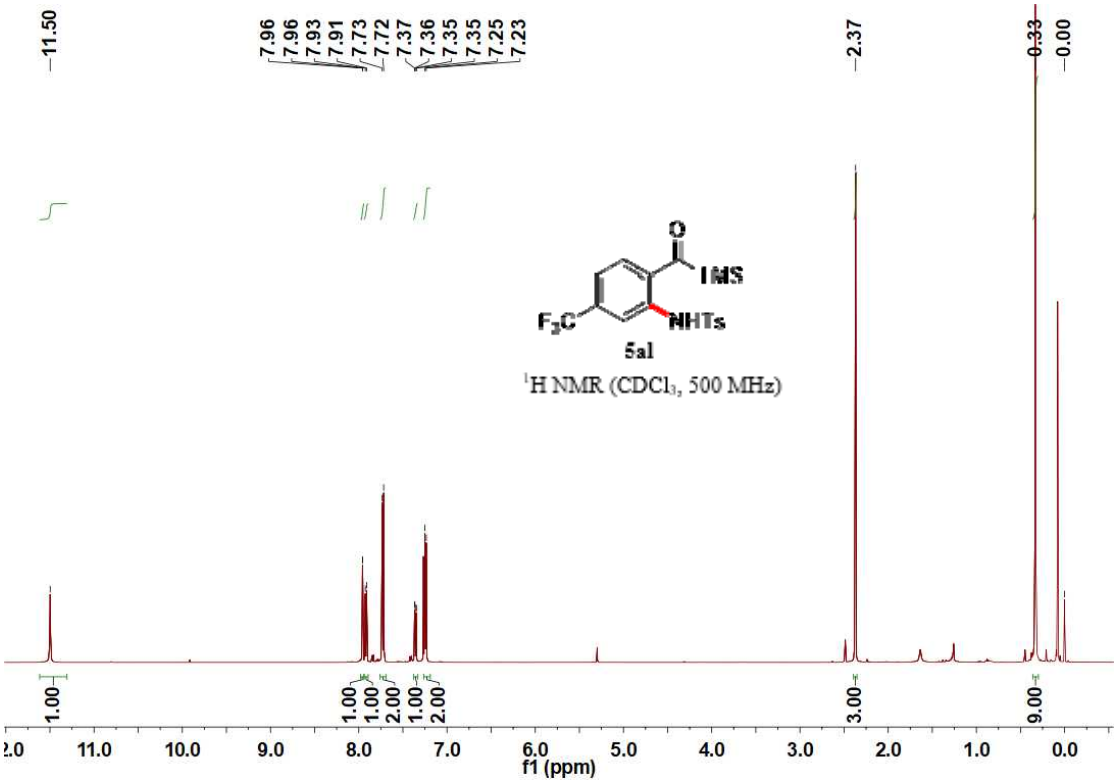


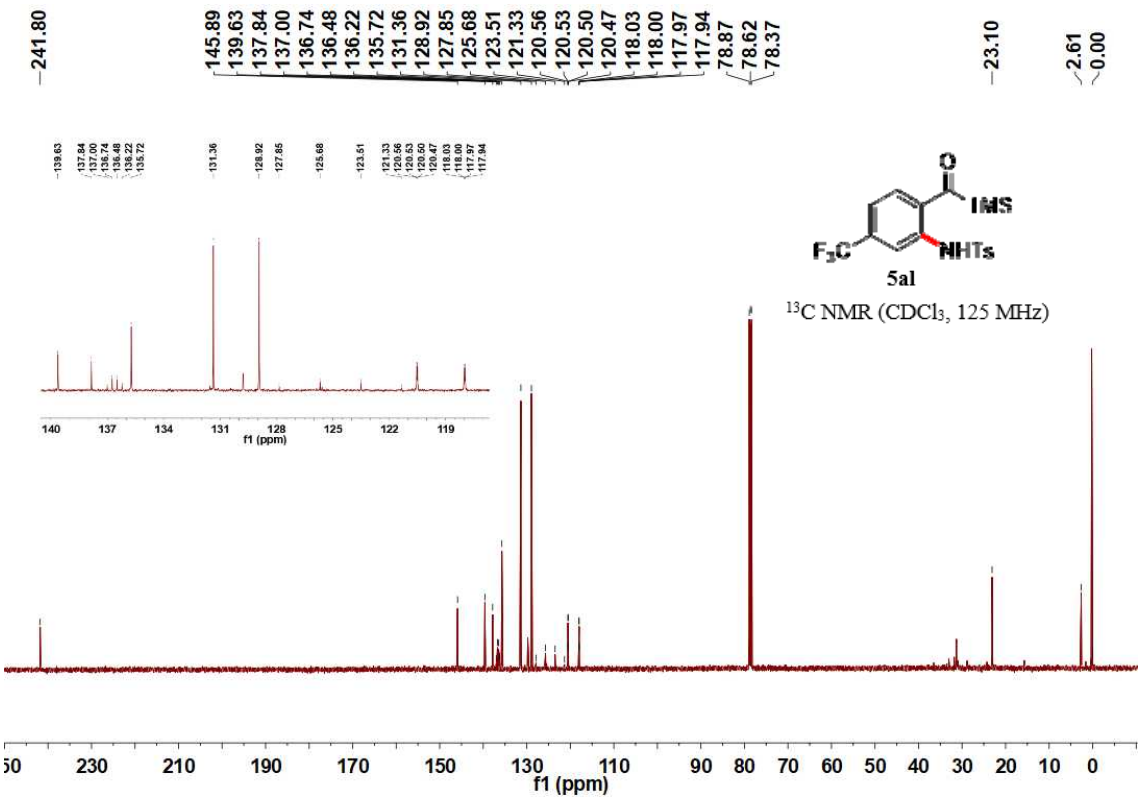
5aj

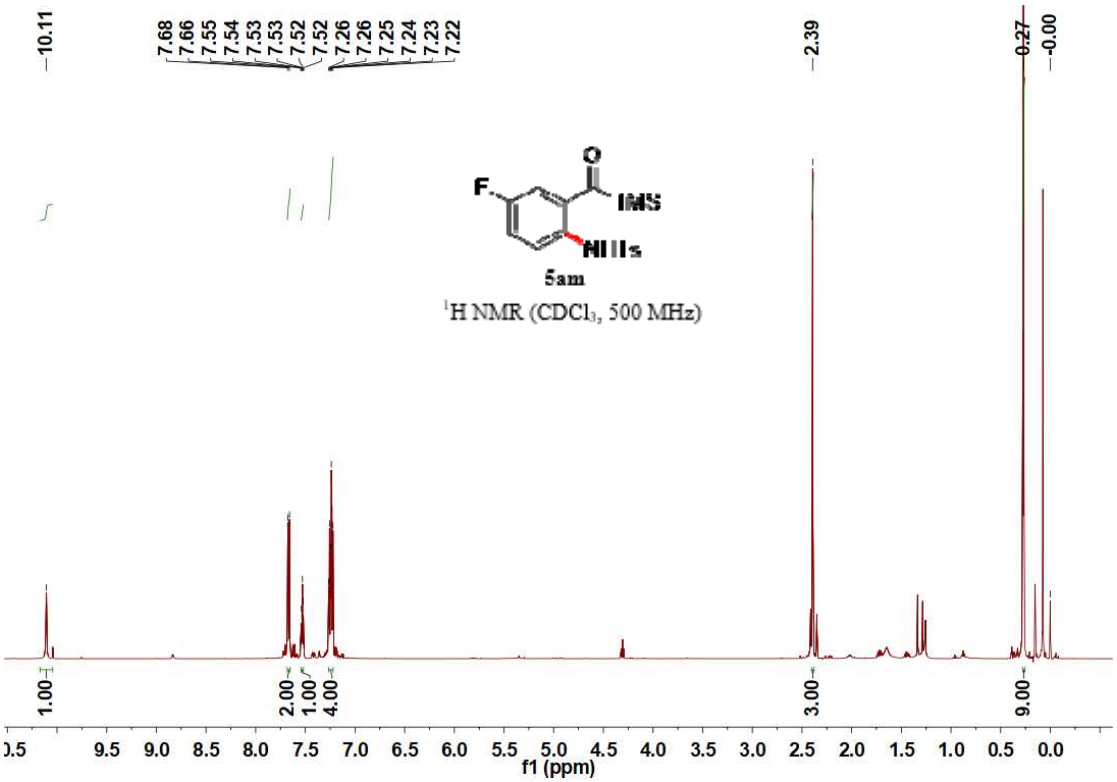
^{13}C NMR ($CDCl_3$, 125 MHz)


11.64
7.85
7.85
7.74
7.73
7.64
7.63
7.26
7.26
7.25
7.24
7.23
7.23
2.38
0.31
0.00
TMS
NHTs
5ak
1H NMR (CDCl3, 500 MHz)
1.00
1.00
2.00
1.00
3.00
3.00
9.00
f1 (ppm)


240.60
145.63
140.32
137.93
136.41
131.24
130.62
128.78
127.15
126.79
123.60
78.78
78.53
78.27
23.03
2.52
0.00
TMS
NHTs
5ak
13C NMR (CDCl3, 125 MHz)
f1 (ppm)

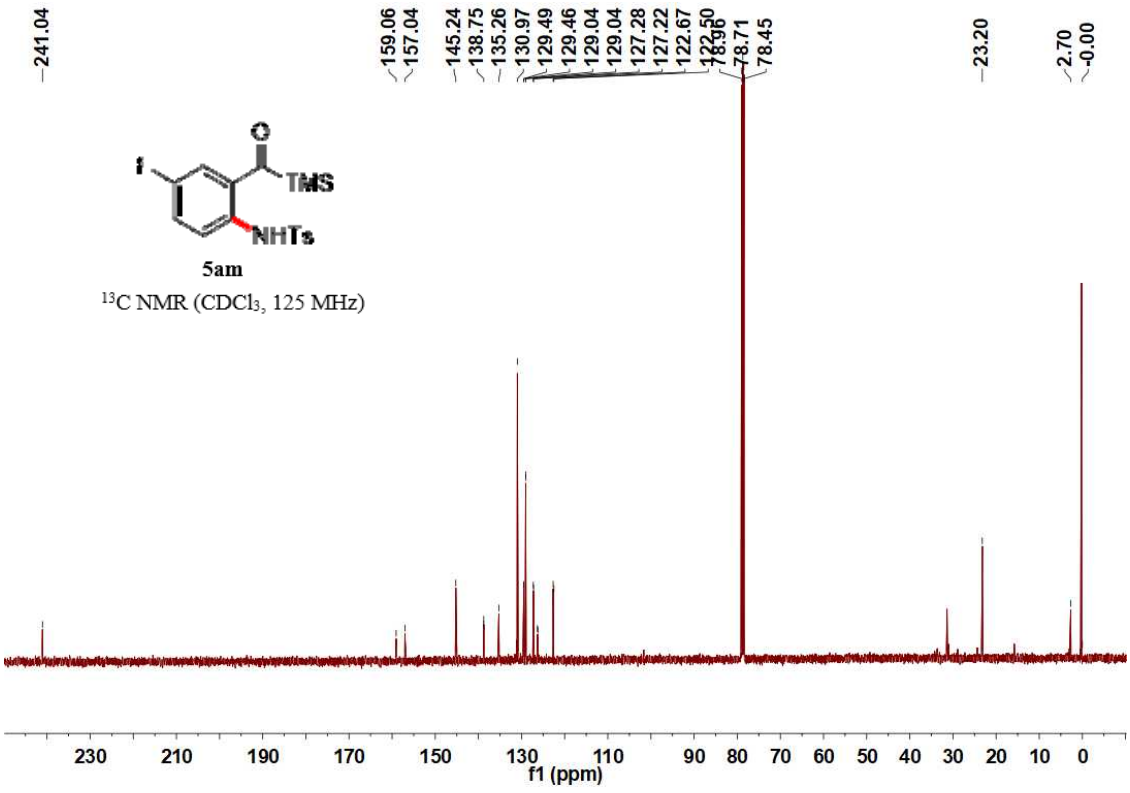

11.50
7.96
7.96
7.93
7.91
7.73
7.72
7.37
7.36
7.35
7.35
7.25
7.23
2.37
0.33
0.00
O
IMS
F3C
NHTs
5al
1H NMR (CDCl3, 500 MHz)
1.00
1.00
1.00
2.00
1.00
2.00
3.00
9.00
f1 (ppm)


241.80
145.89
139.63
137.84
137.00
136.74
136.48
136.22
135.72
131.36
128.92
127.85
125.68
123.51
121.33
120.56
120.53
120.50
120.47
118.03
118.00
117.97
117.94
78.87
78.62
78.37
23.10
2.61
0.00
O
IMS
F3C
NHTs
5al
13C NMR (CDCl3, 125 MHz)
f1 (ppm)



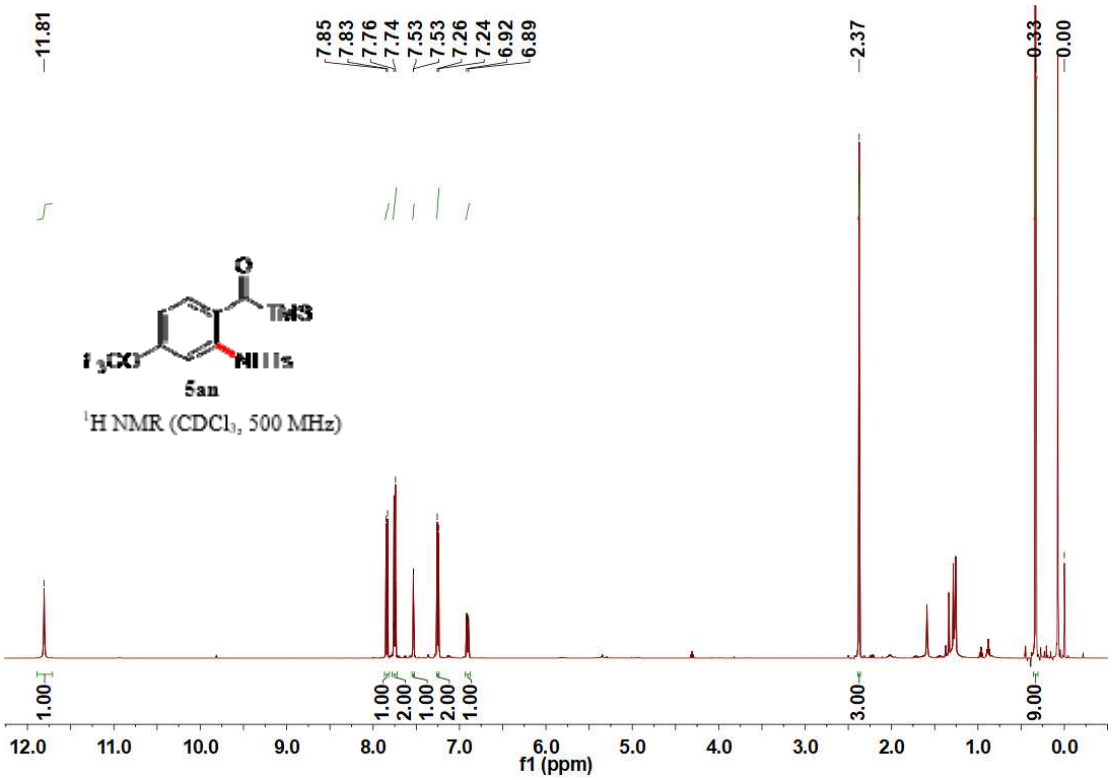
5am

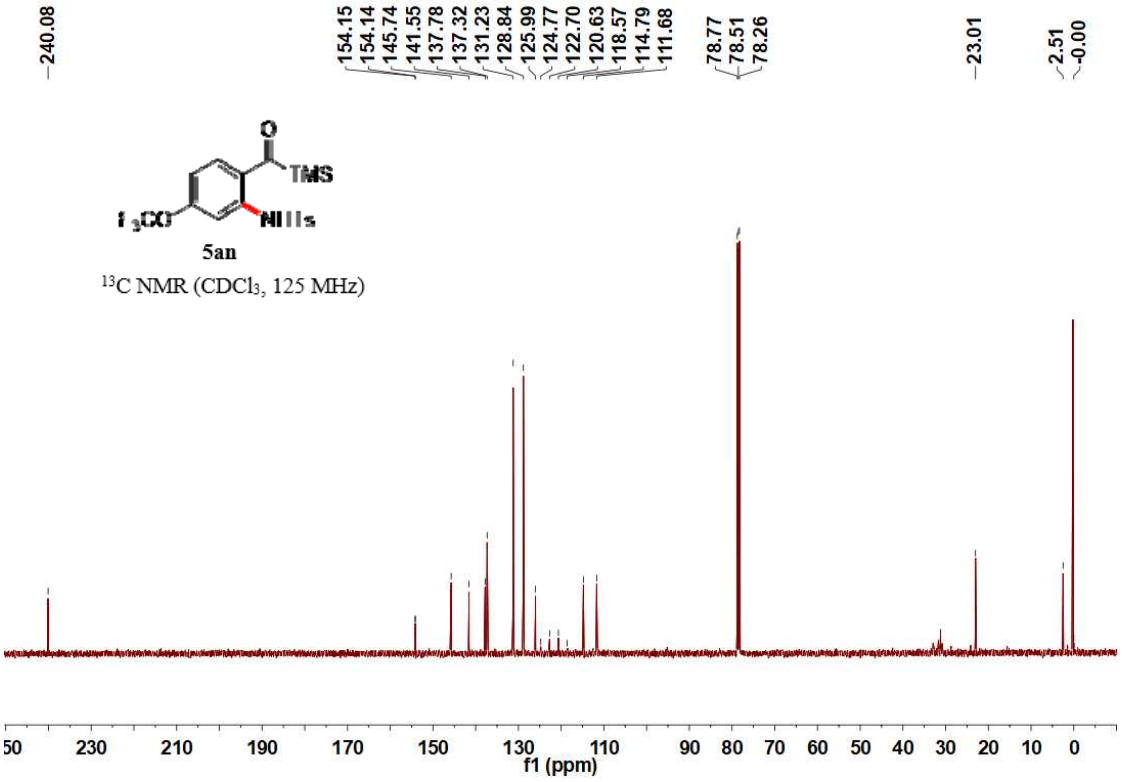
^{1}H NMR ($CDCl_3$, 500 MHz)

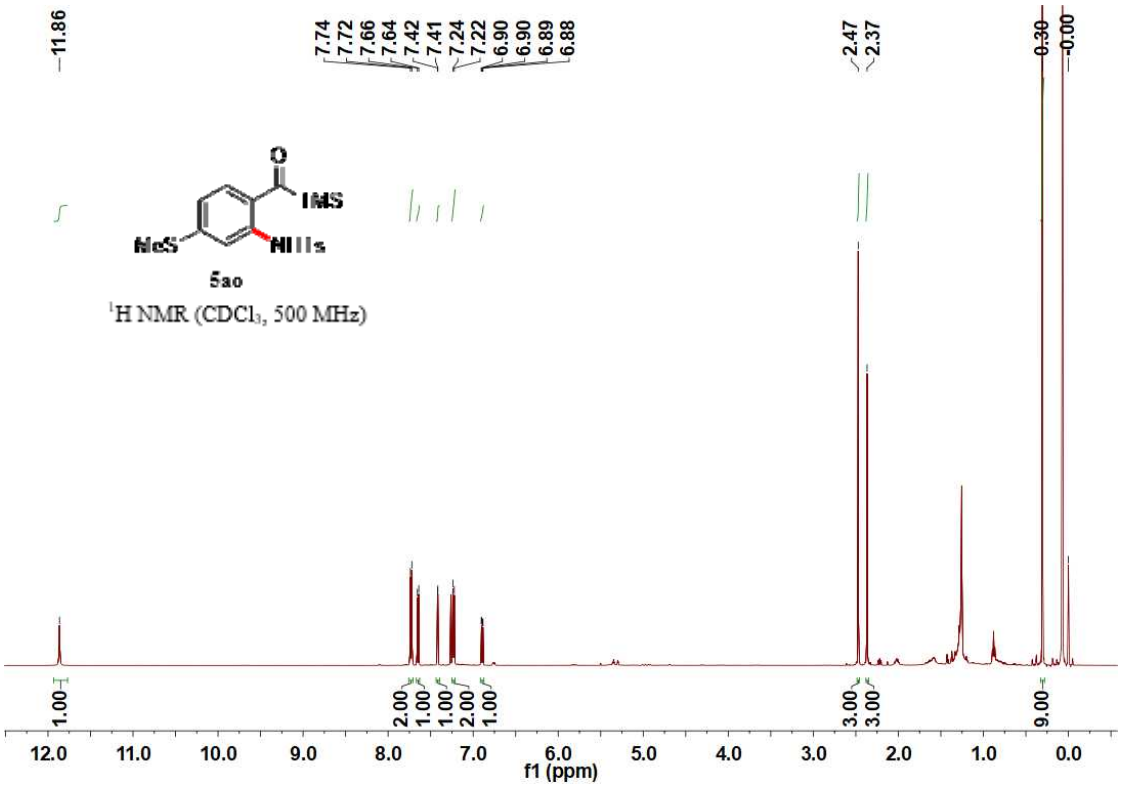


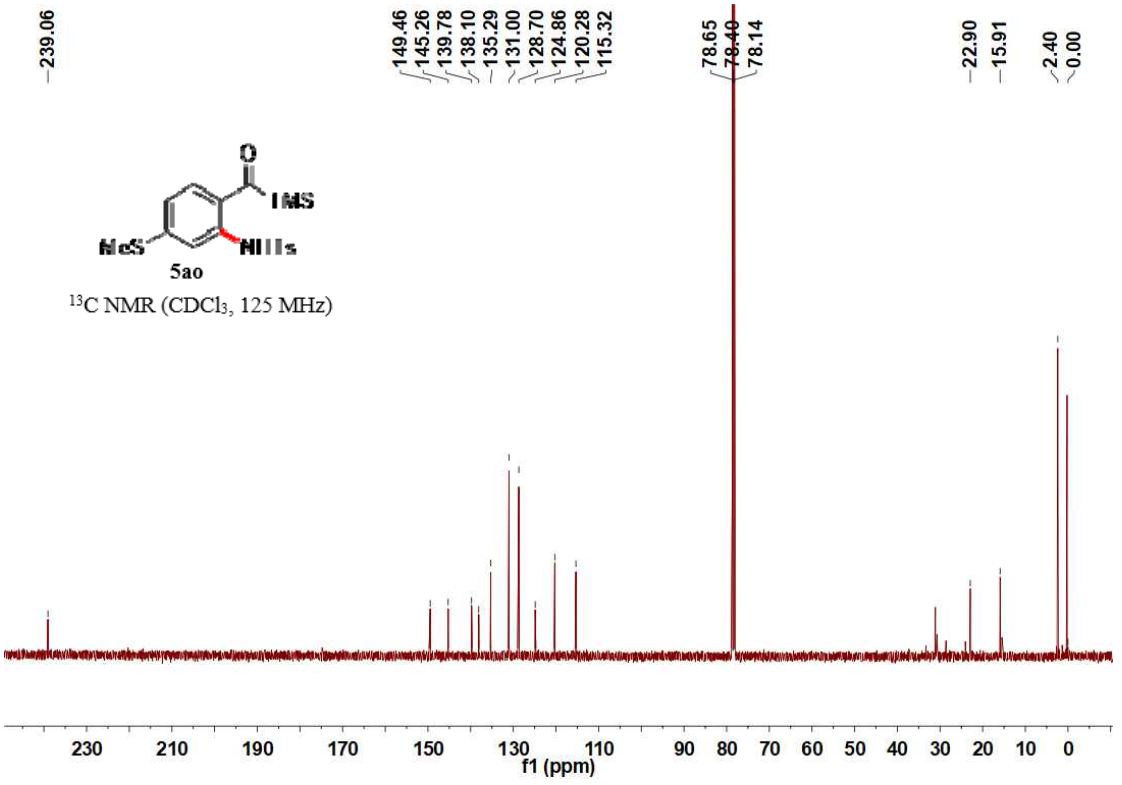
5am

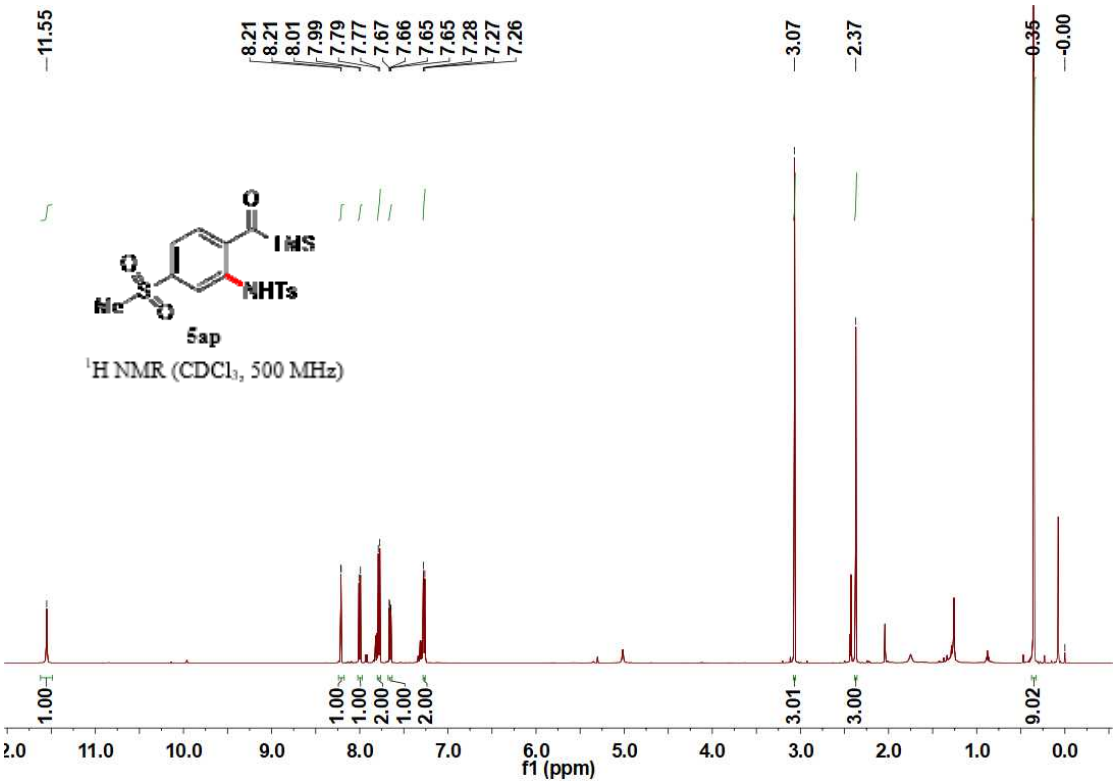
^{13}C NMR ($CDCl_3$, 125 MHz)


11.81
7.85
7.83
7.76
7.74
7.53
7.53
7.26
7.24
6.92
6.89
2.37
0.33
0.00
TMS
F3CO
NHTs
5an
1H NMR (CDCl3, 500 MHz)
1.00
1.00
2.00
1.00
2.00
1.00
3.00
9.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

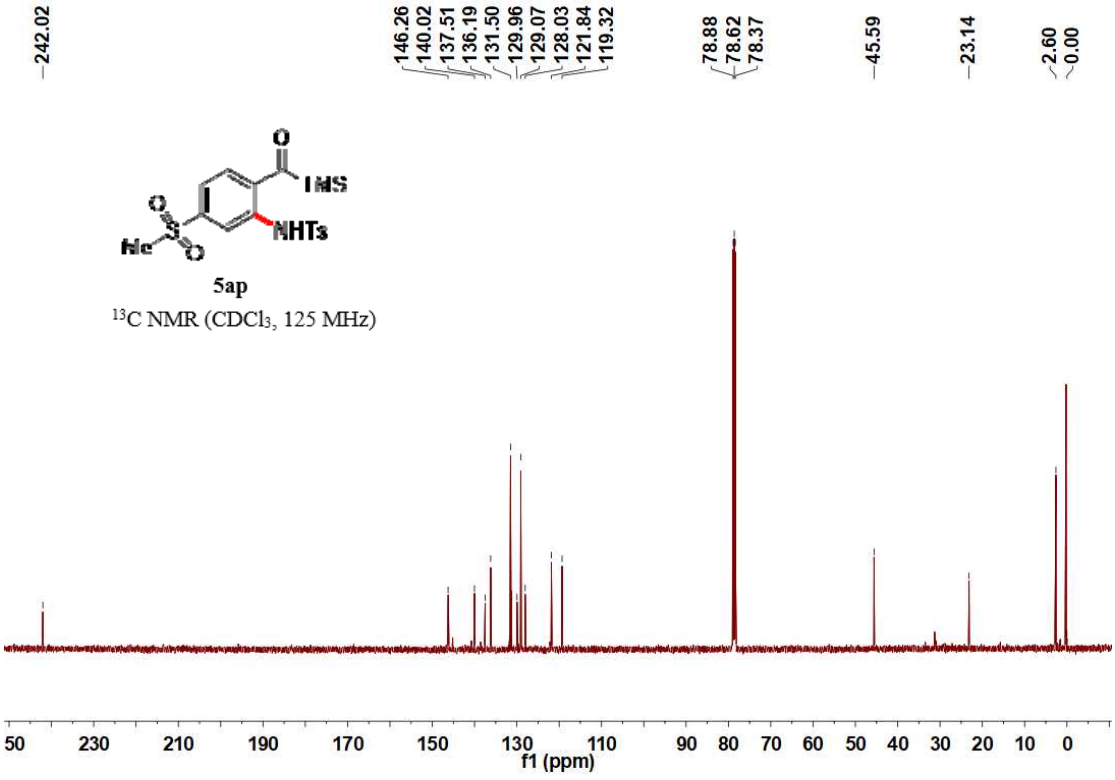

240.08
154.15
154.14
145.74
141.55
137.78
137.32
131.23
128.84
125.99
124.77
122.70
120.63
118.57
114.79
111.68
78.77
78.51
78.26
23.01
2.51
0.00
TMS
F3CO
NHTs
5an
13C NMR (CDCl3, 125 MHz)
50
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


11.86
7.74
7.72
7.66
7.64
7.42
7.41
7.24
7.22
6.90
6.89
6.88
2.47
2.37
0.30
0.00
IMS
NHTs
MeS
5ao
1H NMR (CDCl3, 500 MHz)
1.00
2.00
1.00
1.00
2.00
1.00
3.00
3.00
9.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

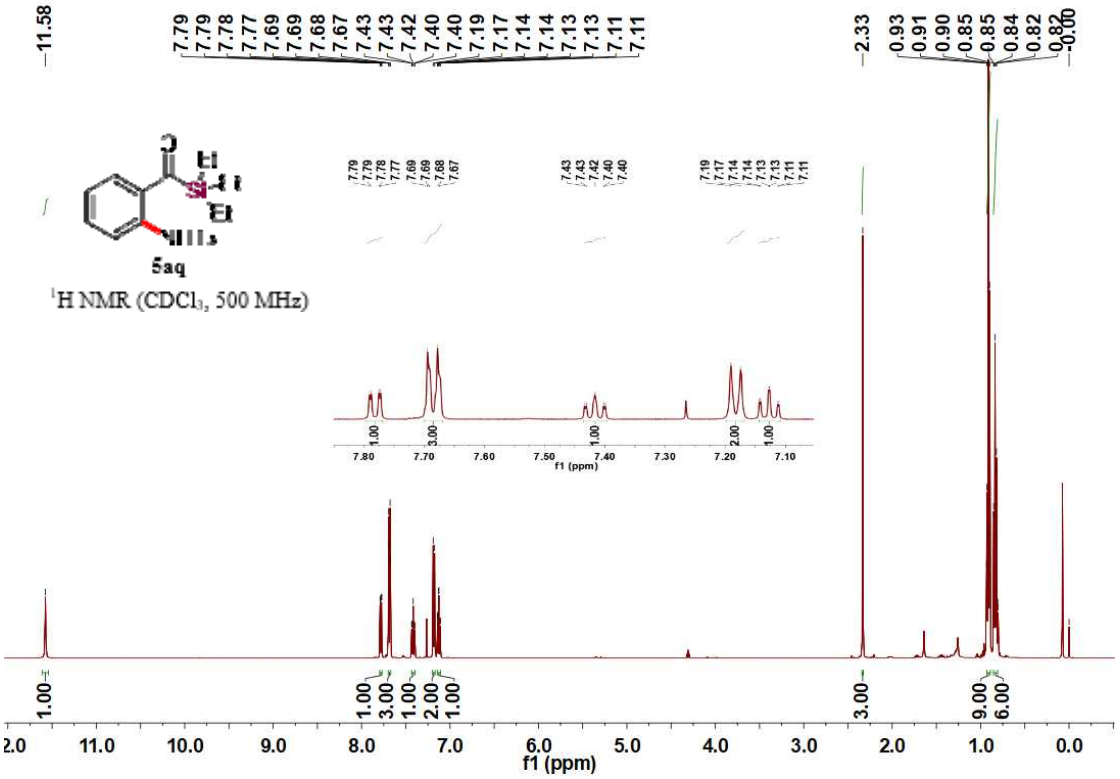

239.06
149.46
145.26
139.78
138.10
135.29
131.00
128.70
124.86
120.28
115.32
78.65
78.40
78.14
22.90
15.91
2.40
0.00
IMS
NHTs
MeS
5ao
13C NMR (CDCl3, 125 MHz)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

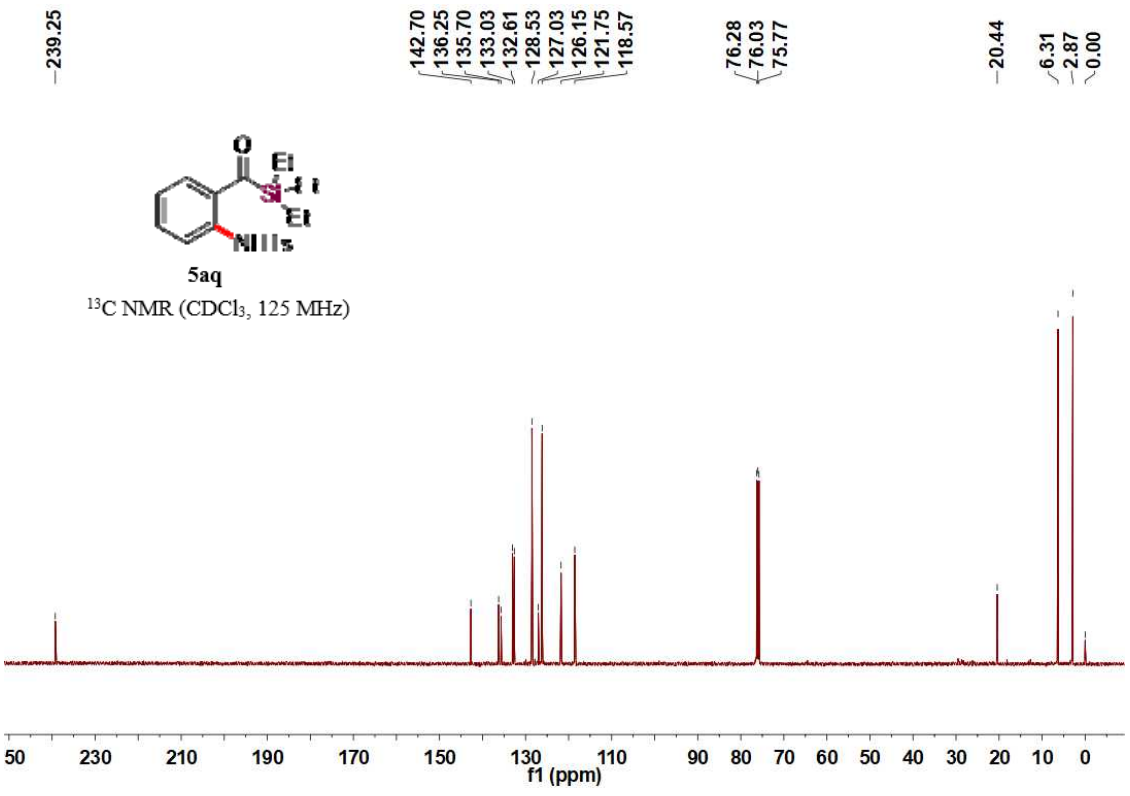


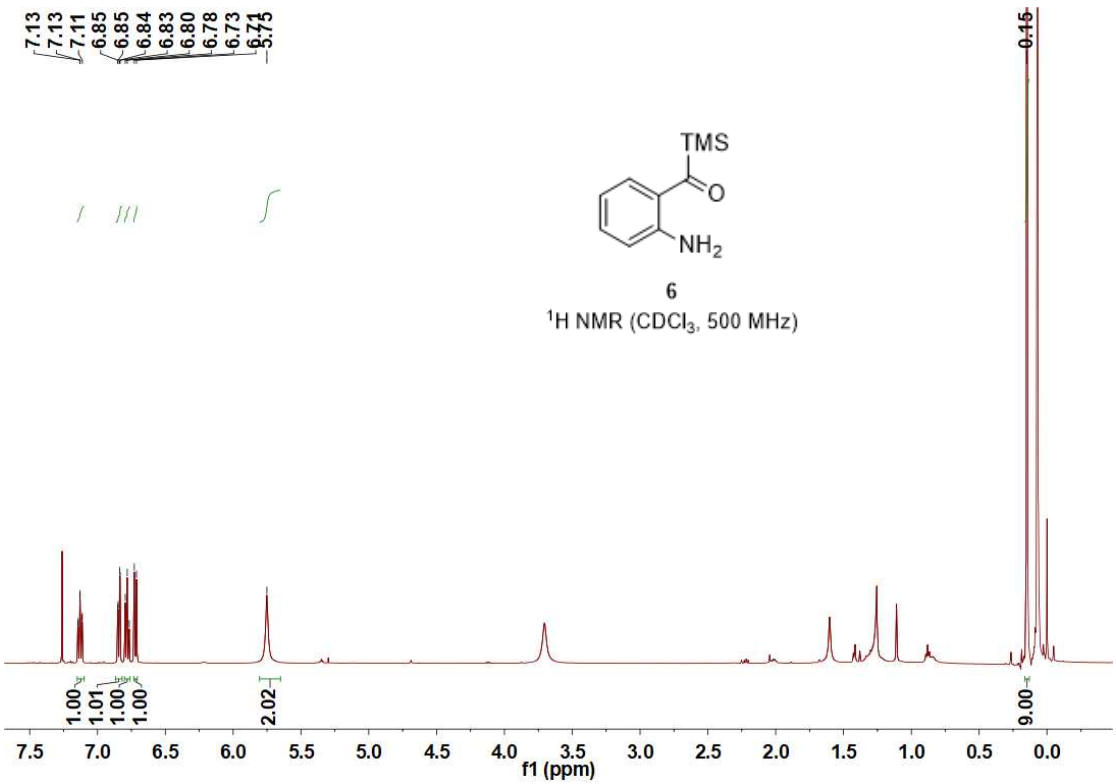
^{1}H NMR ($CDCl_3$, 500 MHz)

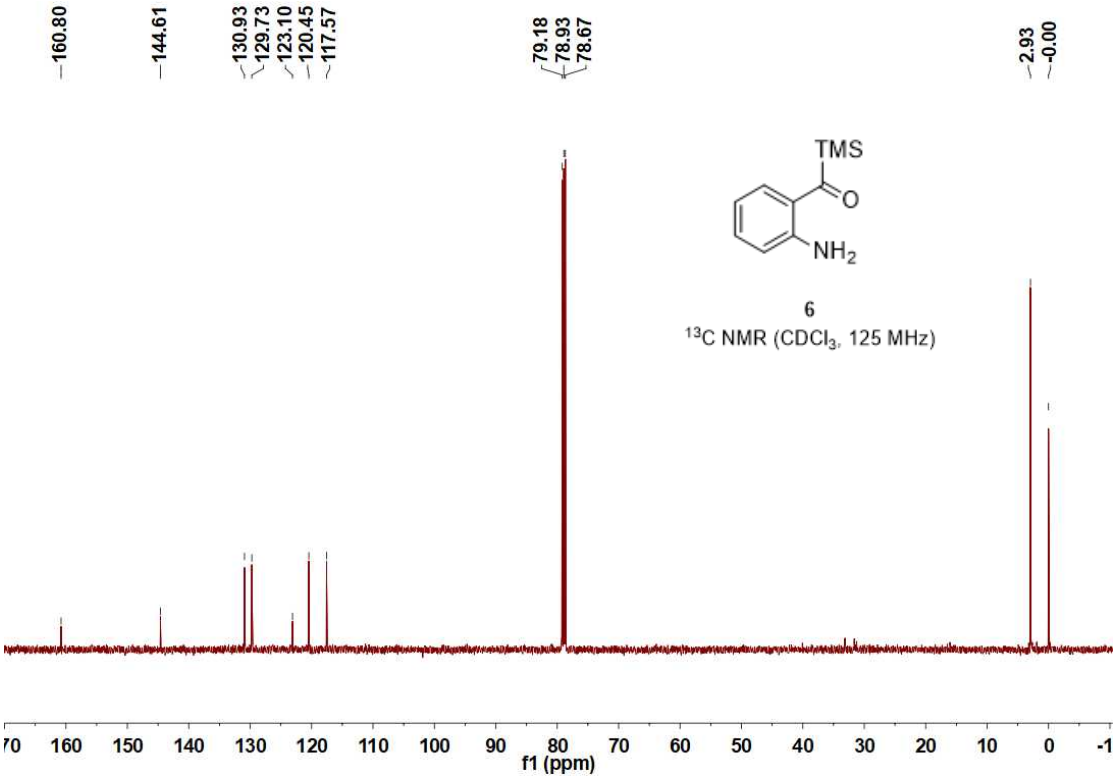


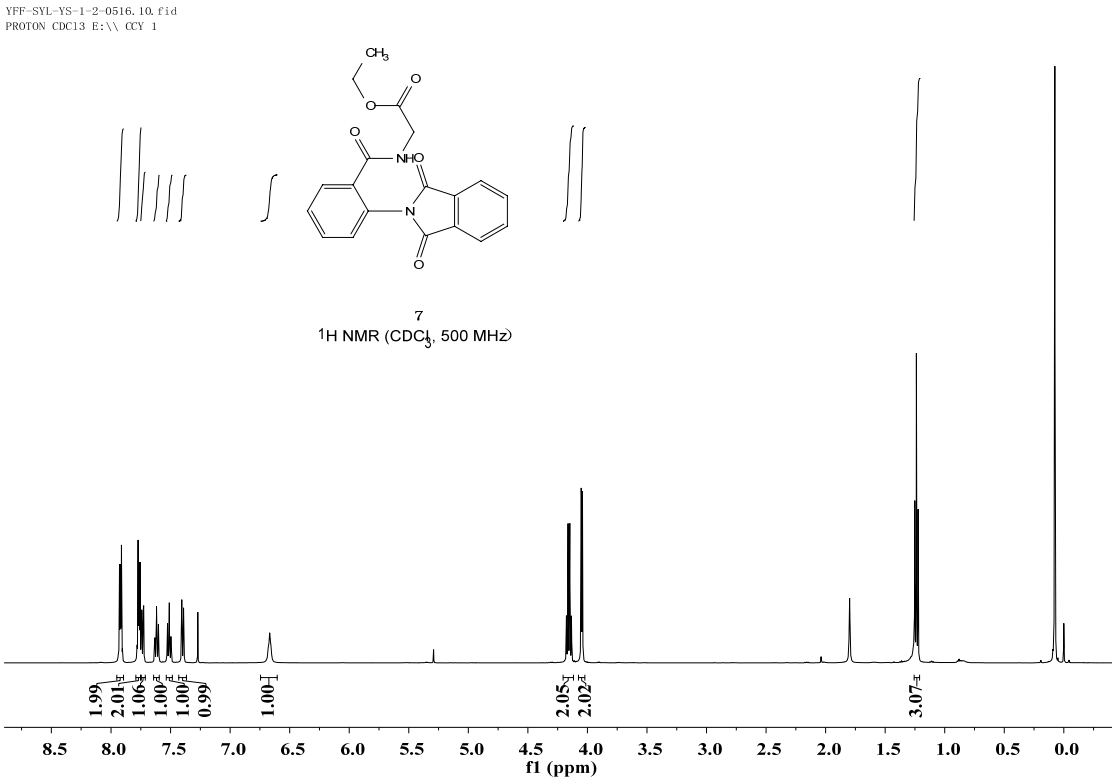
^{13}C NMR ($CDCl_3$, 125 MHz)

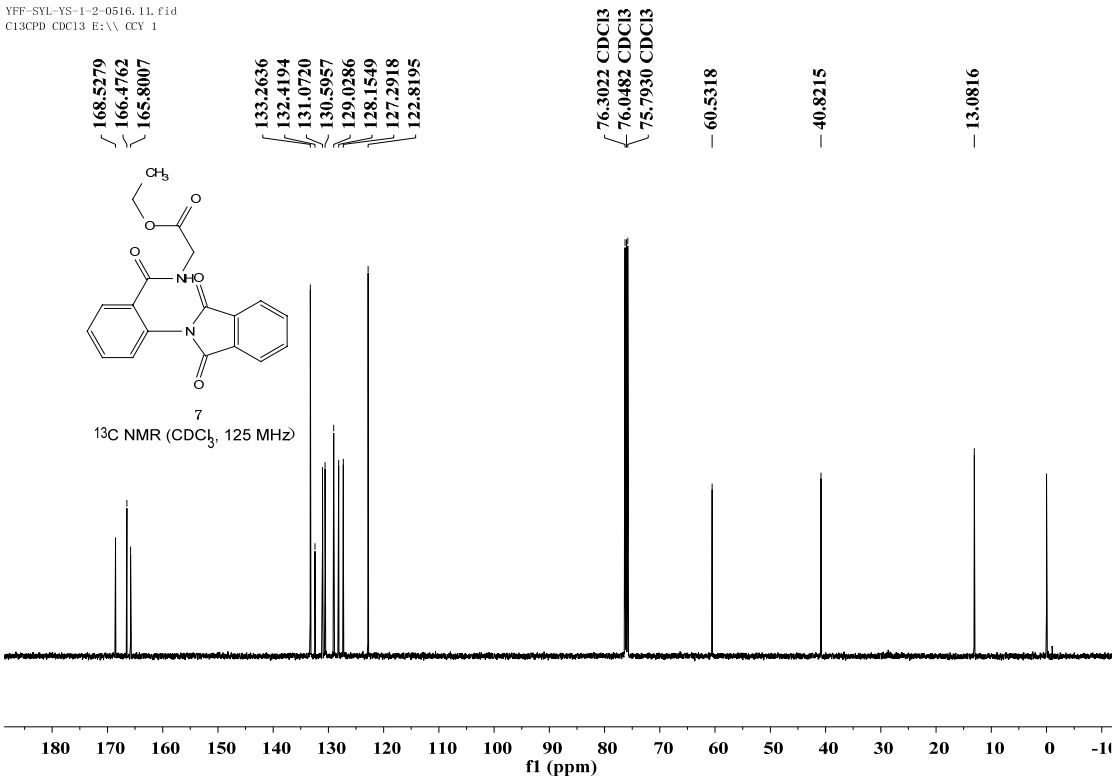

5aq
^{1}H NMR ($CDCl_3$, 500 MHz)
f1 (ppm)

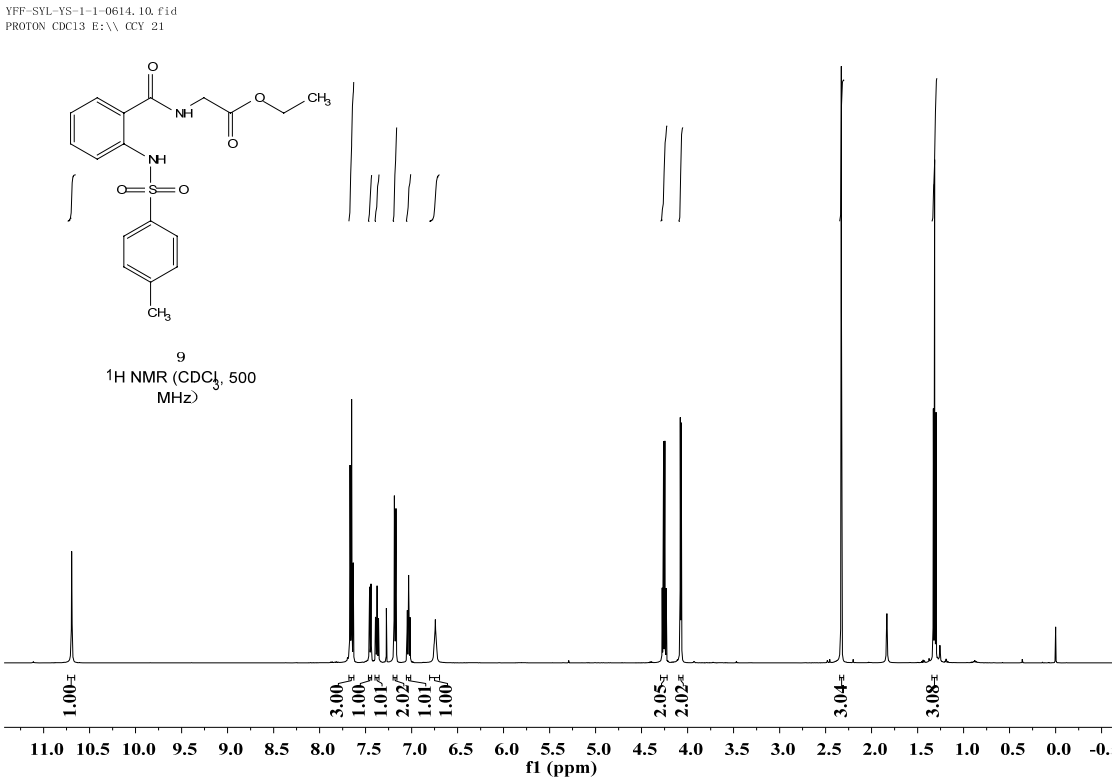

5aq
^{13}C NMR ($CDCl_3$, 125 MHz)
f1 (ppm)

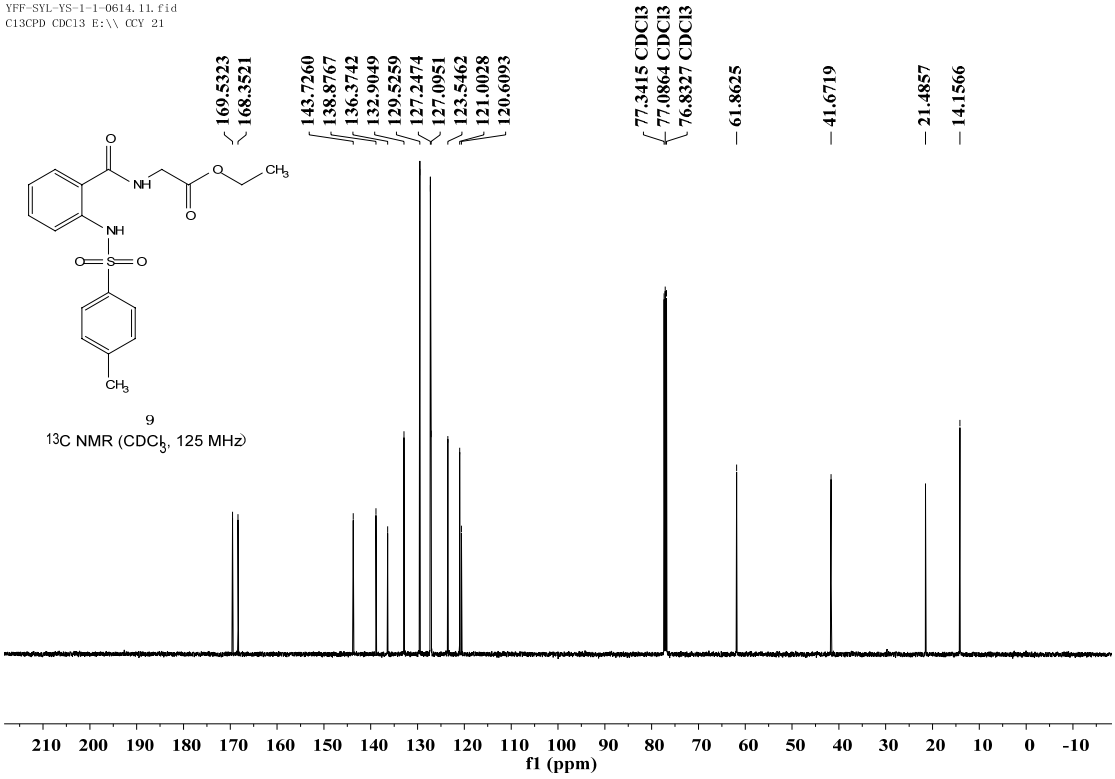

7.13
7.13
7.11
6.85
6.85
6.84
6.83
6.80
6.78
6.73
6.71
3.75
0.15
TMS
O
NH2
6
1H NMR (CDCl3, 500 MHz)
1.00
1.01
1.00
1.00
2.02
9.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

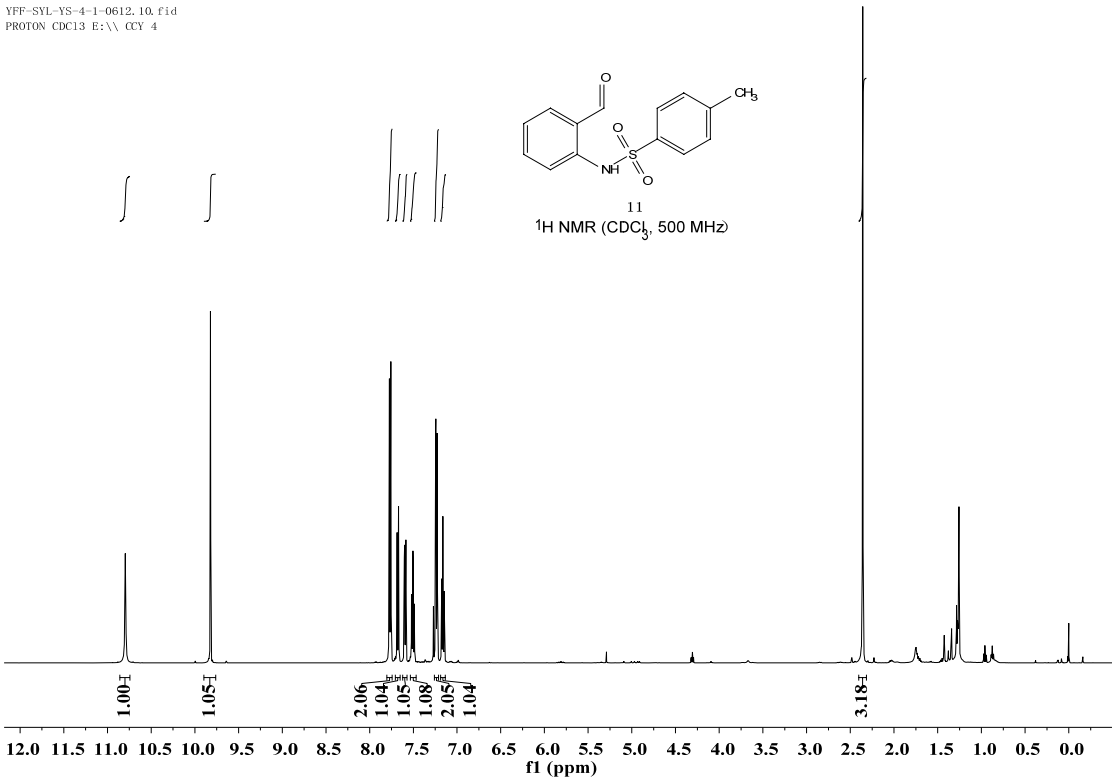

160.80
144.61
130.93
129.73
123.10
120.45
117.57
79.18
78.93
78.67
2.93
-0.00
TMS
O
NH2
6
13C NMR (CDCl3, 125 MHz)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

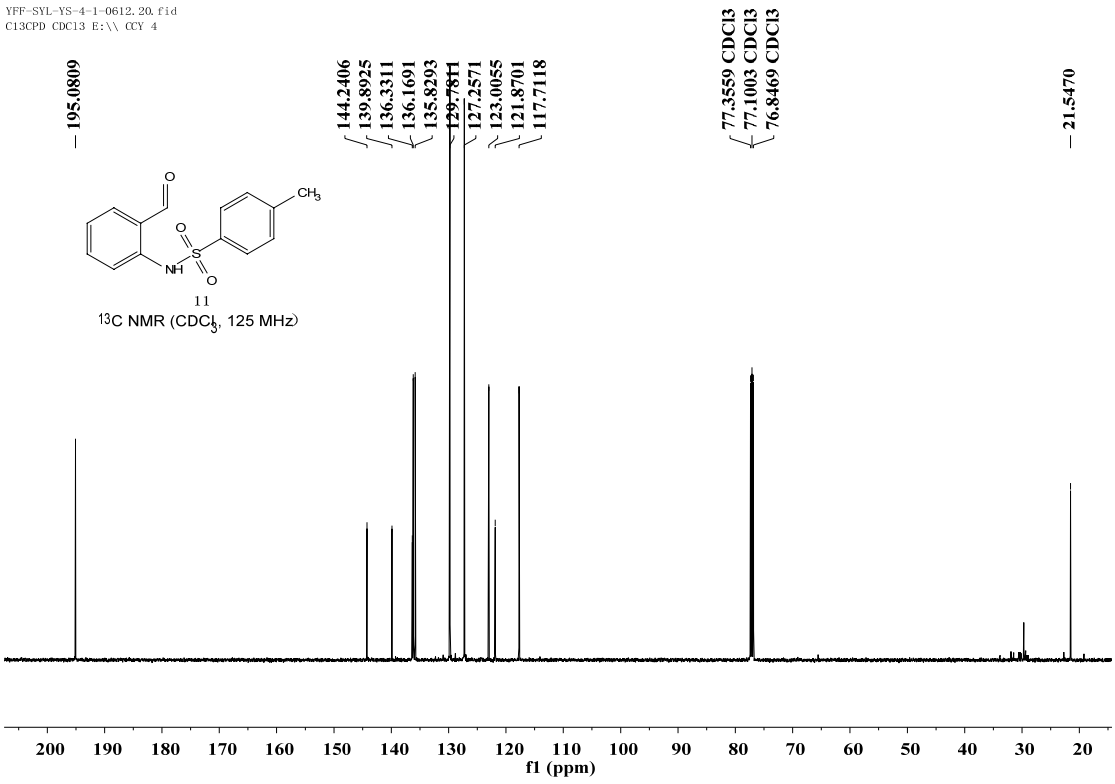

YFF-SYL-YS-1-2-0516.10.fid
PROTON CDCl3 E:\\ CCY 1
7
1H NMR (CDCl3, 500 MHz)
1.99
2.01
1.06
1.00
1.00
0.99
1.00
2.05
2.02
3.07
f1 (ppm)


YFF-SYL-YS-1-2-0516.11.fid
C13CPD CDCl3 E:\\ CCY 1
168.5279
166.4762
165.8007
133.2636
132.4194
131.0720
130.5957
129.0286
128.1549
127.2918
122.8195
76.3022 CDCl3
76.0482 CDCl3
75.7930 CDCl3
60.5318
40.8215
13.0816
7
13C NMR (CDCl3, 125 MHz)
f1 (ppm)


YFF-SYL-YS-1-1-0614.10.fid
PROTON CDCl3 E:\\ CCY 21
9
1H NMR (CDCl3, 500 MHz)
1.00
3.00
1.00
1.01
2.02
1.01
1.00
2.05
2.02
3.04
3.08
11.0 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.
f1 (ppm)


YFF-SYL-YS-1-1-0614.11.fid
C13CPD CDCl3 E:\\ CCY 21
169.5323
168.3521
143.7260
138.8767
136.3742
132.9049
129.5259
127.2474
127.0951
123.5462
121.0028
120.6093
77.3415 CDCl3
77.0864 CDCl3
76.8327 CDCl3
61.8625
41.6719
21.4857
14.1566
9
13C NMR (CDCl3, 125 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


YFF-SYL-YS-4-1-0612.10.fid
PROTON CDCl3 E:\\ CCY 4
11
1H NMR (CDCl3, 500 MHz)
1.00
1.05
2.06
1.04
1.05
1.08
2.05
1.04
3.18
12.0 11.5 11.0 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
f1 (ppm)


YFF-SYL-YS-4-1-0612.20.fid
C13CPD CDCl3 E:\\ CCY 4
195.0809
144.2406
139.8925
136.3311
136.1691
135.8293
129.7811
127.2571
123.0055
121.8701
117.7118
77.3559 CDCl3
77.1003 CDCl3
76.8469 CDCl3
21.5470
11
13C NMR (CDCl3, 125 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)