Supporting Information

C-H acylation of Aniline derivatives with α-Oxocarboxylic Acids under Ruthenium Catalyst

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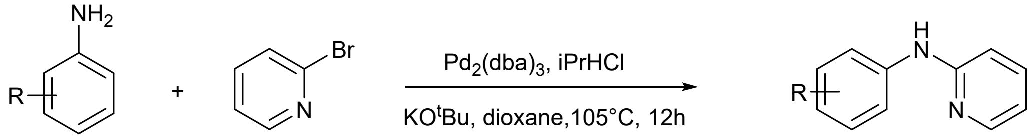
1. General information

Chemicals and reagents were purchased from commercial suppliers and used without special instructions. [1]H NMR and [13]C NMR spectra were obtained on a Bruker 400 MHz instrument in $CDCl_3$ using TMS as internal standard, operating at 400 MHz and 101 MHz, respectively. Infrared spectra (IR) were recorded on a Brucker TENSOR 27 FTIR spectrophotometer and are reported as wavelength numbers (cm^{-1}). Infrared spectra were recorded by preparing a KBr pellet containing the title compound. Chemical shifts (d) are expressed in ppm and coupling constants J are given in Hz. Abbreviations are as follows: s (singlet), d (doublet), t (triplet), m (multiplet). High resolution mass spectra (HRMS) were obtained on Agilent 6520 LC/MS with ESI source. Unless otherwise noted, the purification was performed using column chromatography on silica gel.

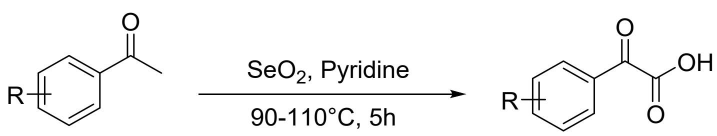
2. General Procedure for Synthesis of Products

General Procedure for the Synthesis of N-(2-pyridyl)-anilines 1a−1m [1]



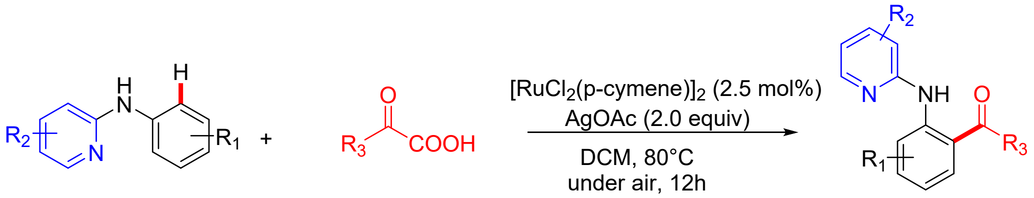
N-(2-pyridyl)-anilines were synthesized by following literature report.[1] 1,4-Dioxane (10 mL), KO^tBu (505 mg, 4.5 mmol), 2-bromo-pyridine (3.0 mmol), and arylamine (3.6 mmol) were added in turn to a round bottom flask charged with $Pd_2(dba)_3$ (54mg, 0.06 mmol), 1,3-bis(2,6-diisopropylphenyl) imidazolium chloride (iPr·HCl) (48 mg, 4 mol%), and a magnetic stirring bar. The flask tube was placed in a 105 °C oil bath and was stirred for 12 h. The mixture was then allowed to cool to room temperature. The mixture was diluted with water then extracted with diethyl ether. The extracts were combined, washed with brine, and then dried over Na_2SO_4. The solvent was removed under vacuum and the residue was purified by flash chromatography (petroleum ether/ethyl acetate (10:1)).

Synthesis of α-Oxocarboxylic Acids [2]



Methyl ketones (5.0 mmol), SeO_2 (6.0 mmol), 20 mL of pyridine were added in a 50 mL round bottom flask. The reaction mixture was stirred at 110 °C for 1 h in an oil bath, then reduce the temperature to 90 °C for 4 h. The desired products were isolated by flash chromatography on silica gel using petroleum ether/ethyl acetate = 20:1 to give α-oxocarboxylic acids **2**.

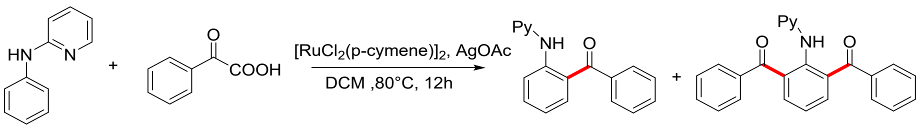
General Procedure for the Ruthenium(II)-Catalyzed Decarboxylative *Ortho* Acylation of N-(2-pyridyl)-anilines with α-Oxocarboxylic Acids



1 2 3

A mixture of (0.2 mmol) N-(2-pyridyl)-anilines, $[Ru(p\text{-cymene})Cl_2]_2$ (0.005 mmol, 2.5 mol %) and AgOAc (0.4 mmol, 2.0 equiv) was taken in a 25 mL pressure tube. To this reaction mixture, DCM (2.0 mL) and the corresponding α-oxocarboxylic acid (0.3 mmol) were added, and the closed reaction mixture was allowed to stirred at 80 °C for 12 h. After completion, as indicated by TLC, only C-H acylated products and incompletely converted starting materials were monitored, and no obviously by-products were produced. After dilution with dichloromethane and then filtered through Celite and silica gel. The solvent was removed under reduced pressure and the crude product was purified by column chromatography on a silica gel using petroleum ether/ethyl acetate as the eluent to afford the desired compound **3**.

The Double-Acylation Product Experiment

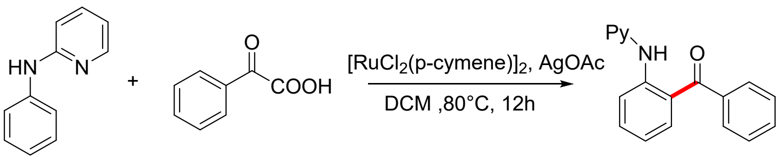


1a 2a 3aa 3aa′

Entry	2a (mmol)	[Ru] (mol%)	3aa (Isolated yield)	3aa’
1	0.6	2.5	80%	nd
2	0.3	5	83%	nd

Conditions: **1a** (0.2 mmol), AgOAc (2.0 equiv), DCM (2 mL) at 80 °C under air for 12 h.

The AgOAc amount Experiments



1a 2a 3aa

Entry	AgOAc (equiv.)	Isolated yield of 3aa
1	0.5	53%
2	1.0	75%
3	2.0	83%
4	3.0	45%

Standard conditions: **1a**(0.2 mmol), **2a** (0.3 mmol) $[RuCl_2(p\text{-cymene})]_2$ (2.5 mol%), DCM (2 mL) at 80 °C under air for 12 h.

3. Experimental characterization data for compounds

Phenyl(2-(pyridin-2-ylamino)phenyl)methanone (3aa). Yield 83%; white solid; M.p: 141-143 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (dd, J = 5.0, 1.9 Hz, 1H), 7.69 (td, J = 7.7, 2.0 Hz, 1H), 7.53 – 7.49 (m, 2H), 7.34 (td, J = 7.5, 5.0 Hz, 3H), 7.28 – 7.22 (m, 4H), 7.22 – 7.18 (m, 2H), 7.14 (ddd, J = 7.4, 4.9, 1.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.03, 156.26, 148.83, 142.67, 138.04, 135.97, 130.48, 129.28, 129.11, 127.95, 127.80, 126.84, 121.90, 121.34. HR-MS (ESI): m/z calcd for $C_{18}H_{14}N_2O$ $[M+H]^+$ 275.1179, found: 275.1182. IR (KBr): 3052.96, 2998.51, 1658.72, 1578.65, 1341.64, 704.27 cm^{-1}.

(5-Methyl-2-(pyridin-2-ylamino)phenyl)(phenyl)methanone (3ba). Yield 78%; white solid; M.p: 144-145 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (dd, J = 5.3, 1.9 Hz, 1H), 7.64 (td, J = 7.8, 2.0 Hz, 1H), 7.51 – 7.45 (m, 2H), 7.30 (t, J = 7.4 Hz, 1H), 7.25 – 7.19 (m, 3H), 7.14 – 7.03 (m, 5H), 2.31 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 171.04, 156.39, 148.82, 140.07, 137.89, 136.70, 136.10, 130.36, 129.96, 129.08, 127.91, 127.62, 121.74, 121.17, 21.06. HR-MS (ESI): m/z calcd for $C_{19}H_{16}N_2O$ $[M+H]^+$ 289.1335, found: 289.1346. IR (KBr): 3077.58, 2997.51, 1661.92, 1581.85, 1332.03, 710.68 cm^{-1}.

(5-Methoxy-2-(pyridin-2-ylamino) phenyl) (phenyl)methanone (3ca). Yield 80%; white solid; M.p: 101-102 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (dd, J = 4.9, 1.9 Hz, 1H), 7.66 (td, J = 7.7, 1.9 Hz, 1H), 7.48 (d, J = 7.1 Hz, 2H), 7.30 (t, J = 7.4 Hz, 1H), 7.26 – 7.19 (m, 3H), 7.11 (d, J = 8.8 Hz, 3H), 6.84 (d, J = 8.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.06, 158.21, 156.49, 149.00, 137.77, 136.67, 136.15, 135.50, 130.37, 130.31, 129.97, 129.08, 129.05, 127.95, 127.62, 114.59, 55.41.HR-MS (ESI): m/z calcd for $C_{19}H_{16}N_2O2$ $[M+H]^+$ 305.1285, found: 305.1281. IR (KBr): 3051.96, 1655.52, 1572.24, 1332.42, 1042.56, 701.07 cm^{-1}.

(5-(Tert-butyl)-2-(pyridin-2-ylamino) phenyl) (phenyl) methanone (3da). Yield 79%; white solid; M.p: 130-132 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, J = 3.1 Hz, 1H), 7.64 (td, J = 7.7, 1.8 Hz, 1H), 7.48 (d, J = 8.0 Hz, 2H), 7.35 – 7.28 (m, 3H), 7.24 – 7.17 (m, 3H), 7.10 (d, J = 8.4 Hz, 3H), 1.29 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.03, 156.51, 149.65, 148.98, 139.88, 137.91, 136.16, 130.36, 129.09, 127.90, 127.00, 126.24, 122.02, 121.28, 34.54, 31.32. HR-MS (ESI): m/z calcd for $C_{22}H_{22}N_2O$ $[M+H]^+$ 331.1805, found: 331.1801. IR (KBr): 3055.16, 2962.28, 1655.52, 1469.75, 1332.03, 707.47 cm^{-1}.

(5-Fluoro-2-(pyridin-2-ylamino)phenyl)(phenyl)methanone (3ea). Yield 76%; white solid; M.p: 157-158 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (dd, J = 5.1, 1.9 Hz, 1H), 7.64 (td, J = 7.8, 2.0 Hz, 1H), 7.49 – 7.43 (m, 2H), 7.34 – 7.29 (m, 1H), 7.23 (dd, J = 9.3, 7.8 Hz, 3H), 7.19 – 7.13 (m, 2H), 7.09 (ddd, J = 7.5, 4.9, 1.0 Hz, 1H), 7.02 (t, J = 8.6 Hz, 2H). ^{13}C NMR (101 MHz, CDCl3) δ 171.02, 162.34, 159.89, 156.20, 149.09, 138.62(d, J_{C-F} = 3.3 Hz), 137.91, 135.81, 130.57, 129.48(d, J_{C-F} = 8.6 Hz), 129.01, 128.06, 121.76, 121.42, 116.33, 116.10. HR-MS (ESI): m/z calcd for $C_{18}H_{13}FN_2O$ $[M+H]^+$ 293.1085, found: 293.1081. IR (KBr): 3058.36, 3010.32, 1658.72, 1581.58, 1335.23, 1149.47, 697.86 cm^{-1}.

(5-Chloro-2-(pyridin-2-ylamino)phenyl)(phenyl)methanone (3fa). Yield 68%; white solid; M.p: 142-143 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (dd, J = 5.1, 2.0 Hz, 1H), 7.65

(td, J = 7.8, 1.9 Hz, 1H), 7.49 – 7.44 (m, 2H), 7.35 – 7.28 (m, 3H), 7.26 – 7.19 (m, 3H), 7.11 (dt, J = 8.5, 2.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.93, 155.97, 149.05, 141.20, 138.10, 135.62, 132.47, 130.74, 129.46, 129.07, 128.94, 128.12, 121.95, 121.59. HR-MS (ESI): m/z calcd for $C_{18}H_{13}ClN_2O$ [M+H]$^+$ 309.0789, found: 309.0785. IR (KBr): 3064.77, 2997.51, 1661.92, 1578.65, 1335.23, 1085.41, 701.07 cm^{-1}.

(5-bromo-2-(pyridin-2-ylamino)phenyl)(phenyl)methanone (3ga). Yield 71%; white solid; M.p: 57-58 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (dd, J = 4.9, 1.7 Hz, 1H), 7.64 (td, J = 7.7, 1.9 Hz, 1H), 7.50 – 7.40 (m, 4H), 7.33 (t, J = 7.4 Hz, 1H), 7.26 – 7.18 (m, 3H), 7.11 (ddd, J = 7.5, 4.9, 1.0 Hz, 1H), 7.05 (d, J = 8.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.85, 155.90, 149.03, 141.70, 138.06, 135.56, 132.39, 130.73, 129.22, 129.04, 128.09, 121.93, 121.57, 120.41. HR-MS (ESI): m/z calcd for $C_{18}H_{13}BrN_2O$ [M+H]$^+$ 354.0284, found: 354.0286. IR (KBr): 3064.77, 3000.71, 1658.72, 1585.05, 1332.03, 1062.99, 701.07 cm^{-1}.

Phenyl(2-(pyridin-2-ylamino)-4-(trifluoromethyl)phenyl)methanone (3ha). Yield 59%; white solid; M.p: 127-129 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (dd, J = 5.0, 1.9 Hz, 1H), 7.68 (td, J = 7.7, 2.0 Hz, 1H), 7.61 (d, J = 8.3 Hz, 2H), 7.52 – 7.48 (m, 2H), 7.40 – 7.34 (m, 1H), 7.32 – 7.26 (m, 4H), 7.23 – 7.13 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.94, 155.96, 149.35, 145.84, 138.06, 135.49, 130.92, 129.09, 128.60, 128.28, 128.16, 127.48, 126.33 (q, J = 3.8 Hz), 125.23, 122.53, 122.22, 121.80.HR-MS (ESI): m/z calcd for $C_{19}H_{13}F_3N_2O$ [M+H]$^+$ 343.1053, found: 343.1059. IR (KBr): 3055.16, 2997.05, 1658.72, 1585.05, 1322.42, 1139.86, 694.66 cm^{-1}.

Methyl-2-(pyridin-2-ylamino)phenyl)(phenyl)methanone (3ia). Yield 62%; white solid; M.p: 110-111 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (dd, J = 5.3, 1.5 Hz, 1H), 7.64 (td, J = 7.7, 2.0 Hz, 1H), 7.50 – 7.46 (m, 2H), 7.31 (t, J = 7.4 Hz, 1H), 7.25 – 7.18 (m, 4H), 7.09 (ddd, J = 7.4, 4.9, 1.0 Hz, 1H), 7.05 – 6.99 (m, 2H), 6.96 (d, J = 9.2 Hz, 1H), 2.28 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 171.05, 156.43, 148.93, 142.55, 139.21, 137.88, 136.11, 130.41, 129.06, 129.03, 128.37, 127.91, 127.73, 124.82, 121.87, 121.24, 21.32.HR-MS (ESI): m/z calcd for $C_{19}H_{16}N_2O$ [M+H]$^+$ 289.1335, found: 289.1327. IR (KBr): 3080.78, 2000.91, 1658.72, 1585.05, 1562.63, 1328.83, 694.66 cm^{-1}.

(2-Methyl-6-(pyridin-2-ylamino)phenyl)(phenyl)methanone (3ja). Yield 74%; white solid; M.p: 118-119°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (dd, J = 4.9, 2.9 Hz, 1H), 7.61 (td, J = 8.1, 1.9 Hz, 1H), 7.51 – 7.45 (m, 2H), 7.34 – 7.27 (m, 1H), 7.25 – 7.08 (m, 7H), 7.03 (ddd, J = 7.3, 4.9, 0.8 Hz, 1H), 2.25 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.80, 156.08, 148.71, 141.30, 137.54, 136.17, 135.95, 131.31, 130.45, 129.35, 128.79, 127.92, 127.90, 126.96, 120.72, 120.66, 18.30. HR-MS (ESI): m/z calcd for $C_{19}H_{16}N_2O$ [M+H]$^+$ 289.1335, found: 289.1349. IR (KBr): 3055.61, 3013.52, 1661.92, 1581.85, 1562.63 1332.42, 704.27 cm^{-1}.

(2-((5-Methylpyridin-2-yl)amino)phenyl)(phenyl)methanone (3ka). Yield 70%; white solid; M.p: 136-137 °C. ^{1}H NMR (400 MHz, CDCl3) δ 8.38 (d, J = 4.9 Hz, 1H), 7.64 (t, J = 7.8 Hz, 1H), 7.48 (d, J = 7.7 Hz, 2H), 7.30 (t, J = 7.7 Hz, 1H), 7.22 (t, J = 8.6 Hz, 3H), 7.14 – 7.03 (m, 5H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 171.21, 156.48, 149.03, 142.79, 137.82, 137.80, 135.93, 131.23, 129.84, 129.21, 127.75, 127.68, 126.72, 126.13, 121.91, 121.27, 21.21. HR-MS (ESI): m/z calcd for $C_{19}H_{16}N_2O$ [M+H]$^+$ 289.1336, found: 289.1339. IR (KBr): 3061.57, 3007.12, 1665.12, 1585.05, 1565.84, 1325.62, 701.07 cm^{-1}.

(2-((5-Fluoropyridin-2-yl)amino)phenyl)(phenyl)methanone (3la). Yield 61%; white solid; M.p: 114-115°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 2.9 Hz, 1H), 7.48 – 7.44 (m, 2H), 7.39 (td, J = 8.1, 7.4, 3.0 Hz, 1H), 7.34 – 7.27 (m, 4H), 7.25 – 7.19 (m, 3H), 7.14 (d, J = 7.1 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.96, 158.66, 156.12, 152.20 (d, J_{C-F} = 3.0 Hz), 142.57, 136.89, 136.64, 135.68, 130.55, 129.30, 129.03, 128.01, 127.72, 126.91, 125.04, 124.84, 122.80 (d, J_{C-F} = 4.8 Hz). HR-MS (ESI): m/z calcd for $C_{18}H_{13}FN_2O$

$[M+H]^+$ 293.1085, found: 293.1083. IR (KBr): 3058.36, 3023.13, 1674.73, 1575.44, 1328.83, 1224.23, 691.46 cm^{-1}.

(4,5-Dimethyl-2-(pyridin-2-ylamino)phenyl)(phenyl)methanone (3ma). Yield 66%; white solid; M.p: 173-174 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.38 (dd, *J* = 4.9, 1.2 Hz, 1H), 7.63 (td, *J* = 7.8, 2.0 Hz, 1H), 7.51 – 7.46 (m, 2H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.25 – 7.17 (m, 3H), 7.10 – 7.05 (m, 2H), 6.97 (d, *J* = 2.3 Hz, 1H), 6.89 (dd, *J* = 8.0, 2.3 Hz, 1H), 2.21 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.12, 156.49, 148.87, 140.21, 137.90, 137.75, 136.13, 135.53, 130.44, 130.37, 129.09, 128.75, 127.92, 125.10, 121.81, 121.14, 19.89, 19.44.HR-MS (ESI): m/z calcd for $C_{20}H_{18}N_2O$ $[M+H]^+$ 303.1492, found: 303.1498. IR (KBr): 3061.57, 2975.09, 1655.52, 1575.44, 1485.77, 1332.03, 694.66 cm^{-1}.

(2-(Pyridin-2-ylamino)phenyl)(p-tolyl)methanone (3ab). Yield 77%; white solid; M.p: 122-123 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.40 (dd, *J* = 5.1, 2.1 Hz, 1H), 7.66 (td, *J* = 7.7, 1.9 Hz, 1H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.32 (t, *J* = 7.7 Hz, 2H), 7.22 (d, *J* = 7.5 Hz, 2H), 7.18 – 7.14 (m, 2H), 7.11 (ddd, *J* = 7.4, 4.9, 1.0 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 2H), 2.29 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 171.05, 156.41, 148.74, 142.87, 140.96, 138.07, 132.94, 129.32, 129.26, 128.64, 127.77, 126.72, 121.95, 121.22, 21.44. HR-MS (ESI): m/z calcd for $C_{19}H_{16}N_2O$ $[M+H]^+$ 289.1335, found: 289.1338. IR (KBr): 3064.77, 3000.71, 1658.72, 1585.05, 1332.03, 1062.99, 701.07 cm^{-1}.

(4-Fluorophenyl)(2-(pyridin-2-ylamino)phenyl)methanone (3ac). Yield 75%; white solid. M.p: 125-126 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.39 (dd, *J* = 4.9, 1.9 Hz, 1H), 7.66 (td, *J* = 7.7, 1.9 Hz, 1H), 7.49 (dd, *J* = 8.8, 5.3 Hz, 2H), 7.33 (t, *J* = 7.7 Hz, 2H), 7.23 (t, *J* = 8.2 Hz, 2H), 7.16 (d, *J* = 7.2 Hz, 2H), 7.11 (dd, *J* = 7.4, 4.9 Hz, 1H), 6.93 – 6.87 (m, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 169.95, 165.02, 162.52, 156.30, 149.04 (d, $J_{C\text{-}F}$ = 1.8 Hz), 142.66, 138.01 (d, $J_{C\text{-}F}$ = 1.7 Hz), 132.09 (dd, $J_{C\text{-}F}$ = 2.9, 1.8 Hz), 131.54, 131.45, 129.36, 127.71, 126.93, 121.72, 121.43, 115.21, 114.99. HR-MS (ESI): m/z calcd for $C_{18}H_{13}FN_2O$ $[M+H]^+$ 293.1085, found: 293.1089.IR (KBr): 3051.96, 1658.72, 1575.44, 1335.23, 1274.38, 701.47 cm^{-1}.

(4-Chlorophenyl)(2-(pyridin-2-ylamino)phenyl)methanone (3ad). Yield 66%; white solid; M.p: 139-140 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.39 (dd, *J* = 5.0, 1.9 Hz, 1H), 7.68 (td, *J* = 7.8, 1.9 Hz, 1H), 7.42 (d, *J* = 8.6 Hz, 2H), 7.33 (t, *J* = 7.7 Hz, 2H), 7.25 – 7.20 (m, 3H), 7.20 – 7.14 (m, 3H), 7.13 (ddd, *J* = 7.5, 4.9, 1.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.92, 156.03, 148.95, 142.41, 138.17, 136.60, 134.39, 130.52, 129.40, 128.26, 127.70, 127.05, 121.69, 121.55. HR-MS (ESI): m/z calcd for $C_{18}H_{13}ClN_2O$ $[M+H]^+$ 309.0789, found: 309.0784. IR (KBr): 3039.15, 1652.31, 1585.05, 1328.83, 1088.61, 704.27 cm^{-1}.

(4-Bromophenyl)(2-(pyridin-2-ylamino)phenyl)methanone (3ae). Yield 72%; white solid; M.p: 128-129 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.42 (dd, *J* = 5.0, 1.9 Hz, 1H), 7.70 (td, *J* = 7.8, 1.9 Hz, 1H), 7.52 (dd, *J* = 8.7, 5.5 Hz, 2H), 7.36 (t, *J* = 7.7 Hz, 2H), 7.25 (d, *J* = 8.6 Hz, 2H), 7.20 – 7.13 (m, 3H), 6.93 (t, *J* = 8.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.01, 156.10, 149.08, 142.44, 138.11, 134.94, 131.25, 130.70, 129.42, 127.71, 127.07, 125.08, 121.68, 121.57. HR-MS (ESI): m/z calcd for $C_{18}H_{13}BrN_2O$ $[M+H]^+$ 353.0284, found: 353.0287. IR (KBr): 3064.77, 1665.12, 1581.85, 1332.03, 1062.99, 701.07 cm^{-1}.

(2-**(Pyridin-2-ylamino)phenyl)(4(trifluoromethyl)phenyl)methanone (3af).** Yield 69%; white solid; M.p: 130-132 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.37 (dd, *J* = 5.2, 1.9 Hz, 1H), 7.68 (td, *J* = 7.7, 2.0 Hz, 1H), 7.58 (d, *J* = 8.1 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.28 (s, 1H), 7.24 (s, 1H), 7.19 (d, *J* = 7.1 Hz, 2H), 7.13 (ddd, *J* = 7.5, 4.9, 1.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.61, 155.86, 149.14, 142.12, 139.69, 138.10, 131.94(q, $J_{C–F}$ = 32.6 Hz), 129.46, 129.24, 127.74, 127.27, 125.00 (q, $J_{C–F}$ = 3.8 Hz) 121.73, 121.55. HR-MS (ESI): m/z calcd for $C_{19}H_{13}F_3N_2O$ $[M+H]^+$ 343.1053, found: 343.1057. IR (KBr): 3058.36, 1665.12, 1575.44, 1338.43, 1322.42, 694.66 cm^{-1}.

[1,1'-Biphenyl]-4-yl(2-(pyridin-2-ylamino)phenyl)methanone (3ag). Yield 59%; white solid; M.p: 164-166 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (dd, *J* = 4.9, 1.9 Hz, 1H), 7.67 (td, *J* = 7.7, 1.9 Hz, 1H), 7.55 (t, *J* = 7.1 Hz, 4H), 7.48 – 7.39 (m, 4H), 7.34 (t, *J* = 7.8 Hz, 3H), 7.27 (s, 1H), 7.21 (t, *J* = 8.9 Hz, 3H), 7.11 (dd, *J* = 7.4, 4.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 170.78, 156.41, 149.03, 143.16, 142.77, 139.97, 138.01, 134.67, 129.76, 129.35, 128.86, 127.92, 127.78, 127.13, 126.86, 126.59, 121.90, 121.37. HR-MS (ESI): m/z calcd for $C_{24}H_{18}N_2O$ $[M+H]^+$ 351.1492, found: 351.1494. IR (KBr): 3083.99, 1652.81, 1581.85, 1431.32, 1328.83, 710.68 cm^{-1}.

Naphthalen-1-yl(2-(pyridin-2-ylamino)phenyl)methanone (3ah). Yield 52%; white solid; M.p: 155-157 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 – 8.28 (m, 2H), 7.82 – 7.71 (m, 2H), 7.63 – 7.54 (m, 2H), 7.51 – 7.43 (m, 2H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.24 (d, *J* = 4.3 Hz, 4H), 7.16 (h, *J* = 4.2 Hz, 1H), 7.06 (dd, *J* = 7.4, 4.8 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) *δ* 170.72, 155.48, 148.80, 141.92, 138.05, 133.98, 133.38, 130.50, 129.91, 129.11, 128.28, 127.65, 127.07, 127.02, 126.51, 126.23, 125.39, 124.37, 121.80, 121.56. HR-MS (ESI): m/z calcd for $C_{22}H_{16}N_2O$ $[M+H]^+$ 325.1336, found: 325.1338. IR (KBr): 3042.35, 1652.31, 1578.65, 1328.83, 781.14, 707.47 cm^{-1}.

(2-(Pyridin-2-ylamino)phenyl)(o-tolyl)methanone (3ai). Yield 62%; white solid; M.p: 114-116 °C. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.39 (dd, *J* = 5.1, 1.9 Hz, 1H), 7.64 (td, *J* = 7.8, 2.0 Hz, 1H), 7.51 – 7.45 (m, 2H), 7.34 – 7.28 (m, 1H), 7.25 – 7.18 (m, 4H), 7.10 (ddd, *J* = 7.4, 4.9, 1.0 Hz, 1H), 7.06 – 7.00 (m, 2H), 6.96 (d, *J* = 8.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 171.10, 156.38, 148.95, 142.51, 139.27, 137.98, 136.02, 130.48, 129.09, 128.35, 127.96, 127.78, 124.82, 121.94, 121.31, 21.37. HR-MS (ESI): m/z calcd for $C_{19}H_{16}N_2O$ $[M+H]^+$ 289.1335, found: 289.1339. IR (KBr): 3055.16, 1661.92, 1581.85, 1565.84, 1341.64, 704.27 cm^{-1}.

(2-Bromophenyl)(2-(pyridin-2-ylamino) phenyl)methanone (3aj). Yield 73%; white solid; M.p: 147-149 °C. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.39 (dd, *J* = 5.3, 1.3 Hz, 1H), 7.65 (td, *J* = 7.8, 2.0 Hz, 1H), 7.51 – 7.46 (m, 2H), 7.34 – 7.28 (m, 3H), 7.25 – 7.15 (m, 5H), 7.10 (ddd, *J* = 7.5, 4.9, 1.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 171.05, 156.30, 148.95, 142.68, 137.99, 135.97, 130.50, 129.29, 129.11, 127.97, 127.79, 126.84, 121.92, 121.38. HR-MS (ESI): m/z calcd for $C_{18}H_{13}BrN_2O$ $[M+H]^+$ 353.0284, found: 353.0276. IR (KBr): 3055.16, 1652.31, 1575.44, 1341.64, 1117.44, 697.86 cm^{-1}.

(3-Methoxyphenyl)(2-(pyridin-2-ylamino)phenyl)methanone (3ak). Yield 80%; white solid; M.p: 177-178 °C. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.41 (dd, *J* = 5.0, 1.9 Hz, 1H), 7.67 (td, *J* = 7.7, 1.9 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.16 (m, 4H), 7.15 – 7.08 (m, 2H), 7.06 – 7.02 (m, 2H), 6.85 (dd, *J* = 8.2, 1.6 Hz, 1H), 3.68 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 170.77, 159.13, 156.27, 148.94, 142.66, 138.06, 137.15, 129.29, 129.00, 127.70, 126.86, 121.96, 121.60, 121.44, 117.11, 113.87, 55.28. HR-MS (ESI): m/z calcd for $C_{19}H_{16}N_2O_2$ $[M+H]^+$ 305.1285, found: 305.1279. IR (KBr): 3055.16, 1652.31, 1575.44, 1341.64, 1117.44, 697.86 cm^{-1}.

(2-(Pyridin-2-ylamino)phenyl)(m-tolyl)methanone (3al). Yield 63%; white solid; M.p: 118-120 °C. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.22 (d, *J* = 2.4 Hz, 1H), 7.51 – 7.42 (m, 3H), 7.34 – 7.27 (m, 3H), 7.25 – 7.09 (m, 6H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 170.92, 154.04, 149.22, 142.83, 138.60, 136.13, 131.20, 130.34, 129.19, 129.08, 127.92, 127.55, 126.62, 121.55, 17.93. HR-MS (ESI): m/z calcd for $C_{19}H_{16}N_2O$ $[M+H]^+$ 289.1335, found: 289.1322. IR (KBr): 3083.99, 3000.71, 1655.52, 1578.65, 1504.98, 1332.03, 701.07 cm^{-1}.

(3-Chlorophenyl)(2-(pyridin-2-ylamino)phenyl)methanone (3am). Yield 81%; white solid; M.p: 142-143 °C. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.41 (dd, *J* = 5.0, 1.9 Hz, 1H), 7.70 (td, *J* = 7.8, 1.9 Hz, 1H), 7.51 (t, *J* = 1.9 Hz, 1H), 7.40 – 7.28 (m, 4H), 7.26 – 7.11 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 169.52, 155.92, 149.02, 142.24, 138.10, 137.83, 134.08, 130.49, 129.39, 129.18, 127.71, 127.14, 127.02, 121.62. HR-MS (ESI): m/z calcd for

$C_{18}H_{13}ClN_2O$ [M+H]$^+$ 309.0789, found: 309.0780. IR (KBr): 3042.35, 1652.31, 1581.85, 1335.23, 1085.41, 701.07 cm^{-1}.

(Pyridin-2-ylamino)phenyl)(thiophen-2-yl)methanone (3an). Yield 45%; brown solid. M.p: 129-130 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 – 8.43 (m, 1H), 7.73 (td, J = 7.8, 1.9 Hz, 1H), 7.48 – 7.32 (m, 7H), 7.19 – 7.14 (m, 1H), 6.95 (dd, J = 3.8, 1.1 Hz, 1H), 6.86 (dd, J = 4.9, 3.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.44, 155.88, 149.05, 142.18, 138.62, 137.91, 133.00, 131.52, 129.48, 128.71, 127.74, 126.89, 121.88, 121.63. HR-MS (ESI): m/z calcd for $C_{16}H_{12}N_2OS$ [M+H]$^+$ 351.1492, found: 351.1497. IR (KBr): 3128.83, 3109.61, 1658.72, 1588.26, 1335.23, 1130.23, 697.86 cm^{-1}.

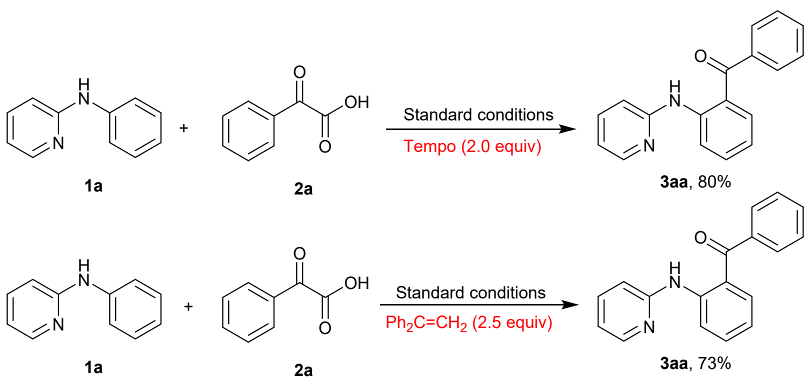
Furan-2-yl(2-(pyridin-2-ylamino)phenyl)methanone (3ao). Yield 64%; white solid; M.p: 147-148 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (dd, J = 4.9, 1.9 Hz, 1H), 7.72 (td, J = 7.8, 2.0 Hz, 1H), 7.39 (d, J = 7.9 Hz, 3H), 7.33 (d, J = 7.3 Hz, 2H), 7.27 (d, J = 5.4 Hz, 2H), 7.15 (dd, J = 7.4, 4.9 Hz, 1H), 6.33 – 6.24 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.78, 155.59, 148.87, 147.55, 144.87, 141.88, 137.99, 129.41, 128.15, 127.53, 121.48, 121.33, 117.78, 111.41. HR-MS (ESI): m/z calcd for $C_{16}H_{12}N_2O_2$ [M+H]$^+$ 265.0972, found: 265.0976. IR (KBr): 3125.26, 3106.41, 1652.31, 1585.05, 1335.23, 694.66 cm^{-1}.

Benzo[d][1,3]dioxol-5-yl(2-(phenylamino) phenyl)methanone (3ap). Yield 35%; white solid; M.p: 165-166 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (dd, J = 4.9, 1.2 Hz, 1H), 7.65 (td, J = 7.7, 2.0 Hz, 1H), 7.33 (t, J = 7.7 Hz, 2H), 7.25 – 7.18 (m, 2H), 7.15 (d, J = 7.2 Hz, 2H), 7.10 (ddd, J = 7.4, 4.9, 1.0 Hz, 1H), 7.02 (d, J = 7.3 Hz, 2H), 6.62 (d, J = 8.7 Hz, 1H), 5.94 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.38, 156.70, 149.56, 149.14, 147.32, 143.01, 137.85, 129.77, 129.31, 127.58, 126.69, 124.66, 121.72, 121.22, 109.69, 107.68, 101.50. HR-MS (ESI): m/z calcd for $C_{20}H_{15}NO_3$ [M+H]$^+$ 319.1077, found: 319.1071. IR (KBr): 3067.97, 2914.23, 1658.72, 1578.65, 1354.45, 1021.32, 691.46 cm^{-1}.

(3,4-Dimethylphenyl)(2-(pyridin-2-ylamino)phenyl)methanone (3aq). Yield 71%; white solid; M.p: 132-133 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (dd, J = 4.9, 1.9 Hz, 1H), 7.62 (td, J = 7.8, 1.9 Hz, 1H), 7.35 – 7.28 (m, 3H), 7.22 – 7.11 (m, 5H), 7.07 (dd, J = 7.4, 4.9 Hz, 1H), 6.92 (d, J = 7.8 Hz, 1H), 2.18 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.17, 156.70, 149.03, 143.03, 139.64, 137.76, 136.40, 133.31, 130.60, 129.21, 129.00, 127.72, 126.76, 126.60, 121.95, 121.12, 19.81, 19.61. HR-MS (ESI): m/z calcd for $C_{20}H_{18}N_2O$ [M+H]$^+$ 303.1492, found: 303.1494. IR (KBr): 3067.97, 1658.72, 1575.44, 1466.55, 1332.03, 691.46 cm^{-1}.

4. Mechanistic Investigation

Radical inhibition/capture experiments



A solution of N-phenylpyridin-2-amine (0.2 mmol), α-oxocarboxylic acid (0.3 mmol), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 2.5 mol%), AgOAc (66.8 mg, 0.4 mmol) and TEMPO (64 mg, 0.4 mmol) or 1,1-diphenylethylene (90 mg, 0.15 mmol) in DCM (2 mL) was stirred in a sealed tube under an atmosphere of air at 80 °C for 12 h. Subsequently, the reaction mixture was cooled to room temperature, and the solid residue is filtered through a short silica gel column to give product **3aa**.

H/D Exchange of N-(2-pyridyl)-aniline (1a)

A mixture of N-(2-pyridyl)-aniline **1a** (34.0 mg, 0.2 mmol), D_2O (40.0 mg, 2.0 mmol, 10.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 0.005 mmol, 2.5 mol%), AgOAc (66.8 mg, 0.4 mmol, 2.0 equiv) in DCE (2.0 mL) was allowed to stir at 80 °C for 12 h. After completion, the mixture was cooled to room temperature and then purified by column chromatography on silica gel (petroleum ether/ethyl acetate=15:1) to afford the desired products **[D]-1a** as white solid. The ratio of H/D exchange (H/D = 50%) was determined by ^{1}H-NMR analysis (Figure S-1).

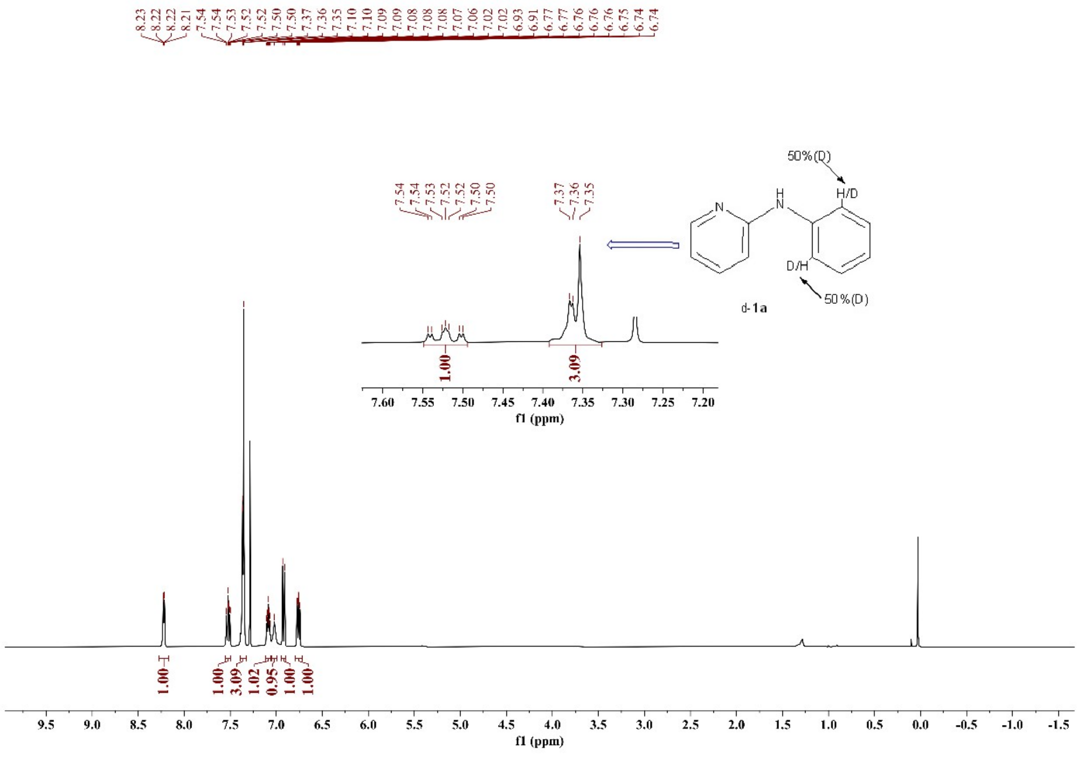
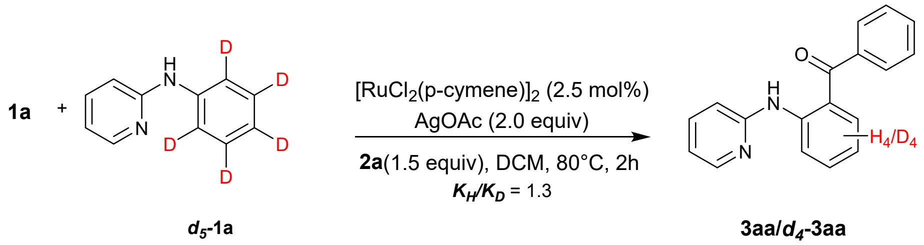


Figure S-1 The ^{1}H NMR spectra of **[D]-1a** (400 MHz, $CDCl_3$).

Kinetic isotope effect of the transformation about 1a/d5-1a



A mixture of N-(2-pyridyl)-aniline **1a** (34 mg, 0.2 mmol), ***d5*-1a** (37 mg, 0.2 mmol), α-oxocarboxylic (45.0 mg, 0.3 mmol), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 0.005 mmol, 2.5 mol%) and AgOAc (66.8mg, 0.4 mmol, 2.0 equiv), in DCM (1.5 mL) was allowed to stir at 80 °C for 2 h. After completion, the mixture was cooled to room temperature and then purified by column chromatography on silica gel (PE/EtOAc = 10:1) to afford the desired products **3aa** and ***d₄*-3aa** as white solid. The deuterium incorporation was determined to be k_H/k_D = 1.3 by ^{1}H NMR.

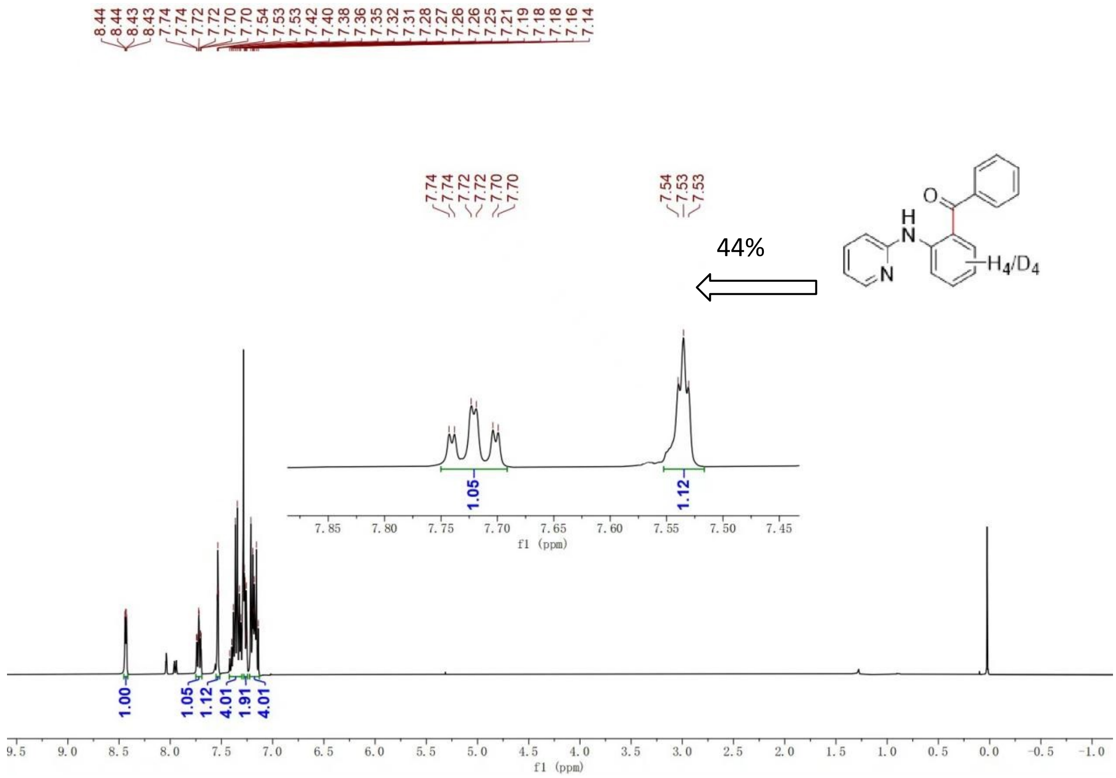
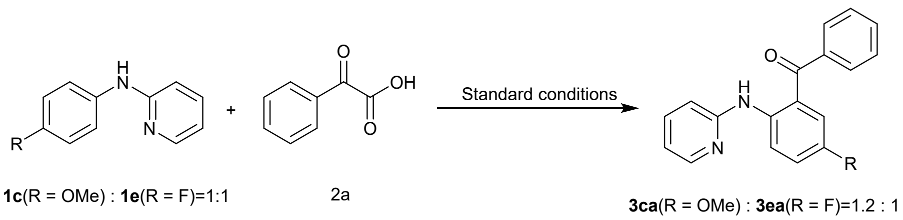


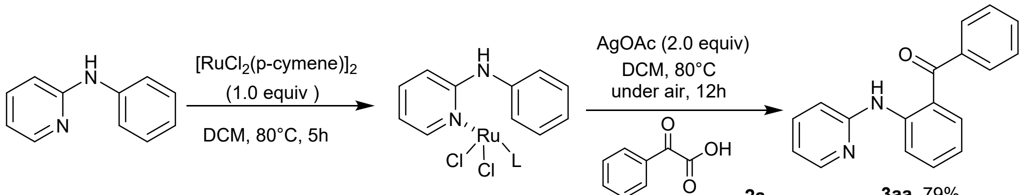
Figure S-2 The ^{1}H NMR spectra of ***d₄*-3aa** (400 MHz, $CDCl_3$).

Intermolecular competition experiments



A mixture of N-(4-methoxyphenyl) pyridin-2-amine **1c** (37.6 mg, 0.2 mmol), N-(4-fluorphenyl) pyridin-2-amine **1e** (40.0 mg, 0.2 mmol), ɑ-oxocarboxylic (45.0 mg, 0.3 mmol), [RuCl$_2$(p-cymene)]$_2$ (3.1 mg, 0.005 mmol, 2.5 mol%) and AgOAc (66.8mg, 0.4 mmol, 2.0 equiv), in DCM (1.5 mL) was allowed to stir at 80 °C for 12 h. After completion, the mixture was cooled to room temperature and then purified by column chromatography on silica gel (petroleum ether/ethyl acetate=10:1) to afford the desired products **3ca** (24.3mg, 0.08mmol)/**3ea**(19.9mg，0.07mmol) = 1.2.

Procedure for the Preparation of Ruthenium Complex A[3]



1a **A**, 77% **2a** **3aa**, 79%

A 15 mL pressure tube was filled with [RuCl$_2$(p-cymene)]$_2$ (89 mg), N-phenylpyridine-2-amine **1a** (50 mg) and DCM (2.0 mL). The reaction mixture was stirred at 80°C for 5 h, then filtered with a sintered crucible and washed with DCM solvent (10.0 mL) to obtain pure complex **A** (77% yield). The pure complex **A** was then mixed with ɑ-oxocarboxylic **2a**, 2.0 equiv AgOAc in DCM (2.0 ml) and stir at 80 °C for 12 h. After that, the reaction tube is cooled to room temperature and then purified by column chromatography on silica gel (petroleum ether/ethyl acetate=20:1) to afford the desired products **3aa** (79% yield). ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.99 (s, 1H), 8.14 (dd, *J* = 5.4, 2.4 Hz, 1H), 7.67 (d, *J* = 7.5 Hz, 2H), 7.58 – 7.52 (m, 1H), 7.24 (d, *J* = 8.6 Hz, 2H), 6.88 (t, *J* = 7.3 Hz, 1H), 6.83 (d, *J* = 8.4 Hz, 1H), 6.73 (ddd, *J* = 7.1, 5.0, 0.9 Hz, 1H), 5.85 – 5.74 (m, 4H), 2.84 (p, *J* = 6.9 Hz, 1H), 2.09 (s, 3H), 1.20 (d, *J* = 6.9 Hz, 6H).^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 156.37, 147.68, 142.19, 137.65, 129.03, 120.78, 118.43, 114.67, 111.12, 106.87, 100.57, 86.83, 85.98, 30.45, 21.97, 18.34. HR-MS (ESI): m/z calcd for $C_{21}H_{24}Cl_2N_2Ru$ $[M+H]^+$ 447.0438, found: 447.0450.

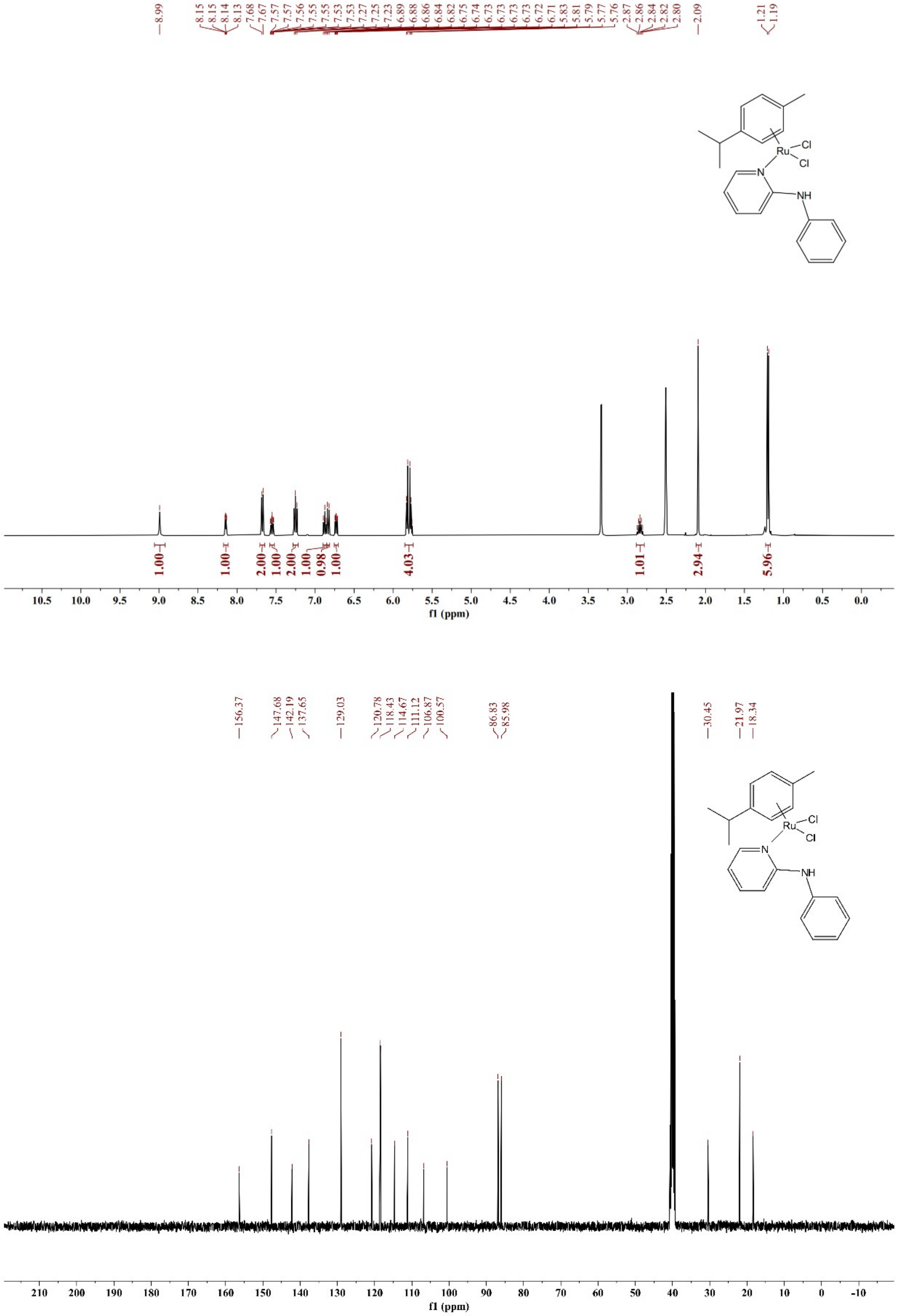
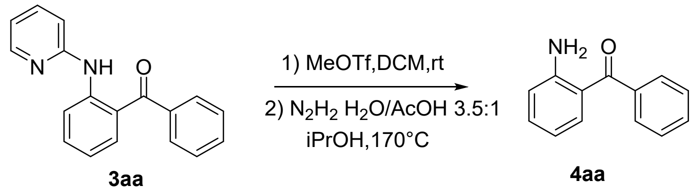


Figure S-3 The ^{1}H NMR and ^{13}C NMR spectra of Complex **A**. (400 MHz, DMSO-d_6).

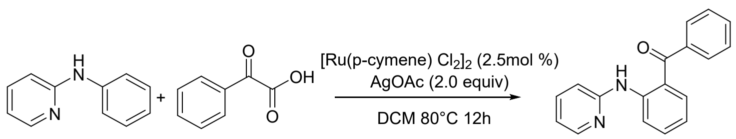
5. Scale-up Reactions and Remove of Directing Group

Remove of Directing Group[4]



To a solution of **3aa** (0.14 g, 0.50 mmol, 1.0 equiv) in DCM (2.0 mL) was added MeOTf (113 μL, 1.0 mmol, 2.0 equiv) dropwise. And the mixture was stirred for 1h at room temp. Solvent was removed under reduced pressure. The residue was then dissolved in iPrOH (2.0 mL). A mixed solution of hydrazine/acetic acid (5.2 mL/1.5 mL) was added. The resulting solution was heated to 170 °C and stirred for 2 days. After the mixture was cooled to rt, we analyzed the crude mixture, besides desired product, it mainly includes the unconverted starting material 3aa, and no by-products were produced. The mixture quenched with water (20 mL) and extracted with EtOAc (3x15 mL). The combined organic layers were washed with brine (15 mL), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (CH_2Cl_2/MeOH = 200:1) to afford **4aa** (77.9 mg, 79 %) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.64 (m, 2H), 7.58 – 7.52 (m, 1H), 7.51 – 7.45 (m, 3H), 7.32 (ddd, J = 8.5, 7.1, 1.6 Hz, 1H), 6.77 (dd, J = 8.3, 1.1 Hz, 1H), 6.64 (ddd, J = 8.1, 7.1, 1.2 Hz, 1H), 6.01 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.10, 150.79, 140.10, 134.61, 134.27, 131.09, 129.15, 128.11, 118.28, 117.12, 115.65. HR-MS (ESI): m/z calcd for $C_{13}H_{11}NO$ $[M+H]^+$ 198.0914, found: 198.0917.

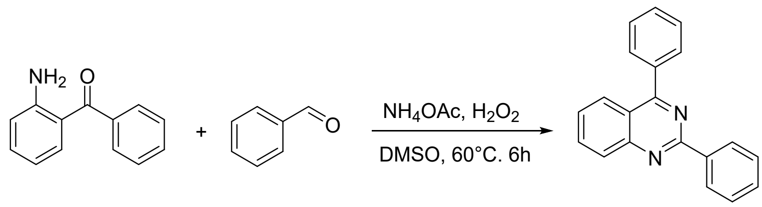
Scale-up Reactions



1a, 4 mmol **2a,** 6 mmol **3aa**, 0.80 g, 73%

N-phenylpyridin-2-amine **1a** (4.0 mmol), ɑ-oxocarboxylic acid **2a** (6.0 mmol), $[RuCl_2(p\text{-}cymene)]_2$ (2.5 mol %), AgOAc (2.0 equiv) and DCM (10 mL) were added to a test tube. The reaction mixture was stirred at 80°C under air for 12 h. Upon completion, the solvent was removed under reduced pressure and the crude product was purified by column chromatography on a silica gel using petroleum ether/ethyl acetate as the eluent to afford the product **3aa** in 73% yield.

6. Further Synthetic Application[5]



4aa **5aa,** 81%

To a solution of 2-aminobenzoketone **1** (0.1 mmol) in 1.0 mL DMSO was added NH_4OAc (0.3 mmol) and aldehydes (0.2 mmol), followed by adding H_2O_2 (0.4 mmol). The reaction mixture was stirred in a pressure tube at 60 °C for 6 hours. After the reaction finished, the reaction mixture was cooled to room temperature and then directly purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 5:1) to afford the desired product **5aa** in 81% yield. ^{1}H NMR(400 MHz, $CDCl_3$) δ 8.73 (dd, J = 8.0, 1.8 Hz, 2H), 8.23 – 8.14 (m, 2H), 7.95 – 7.89 (m, 3H), 7.63 (dd, J = 5.0, 2.0 Hz, 3H), 7.60 – 7.53 (m, 4H).

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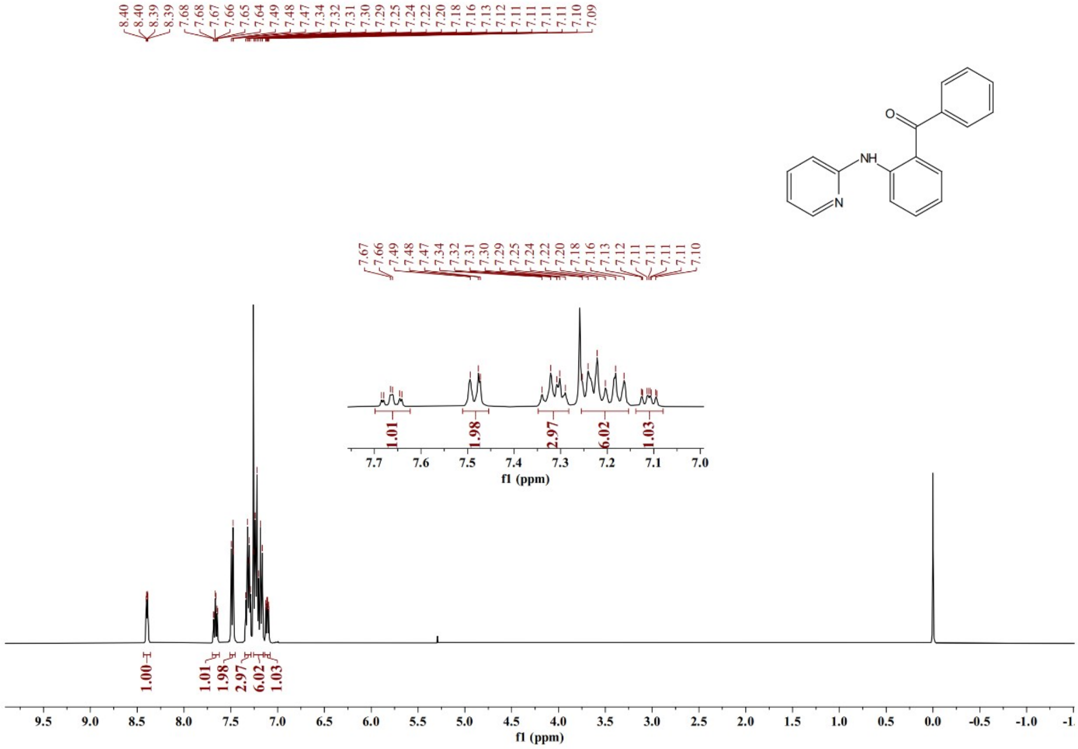
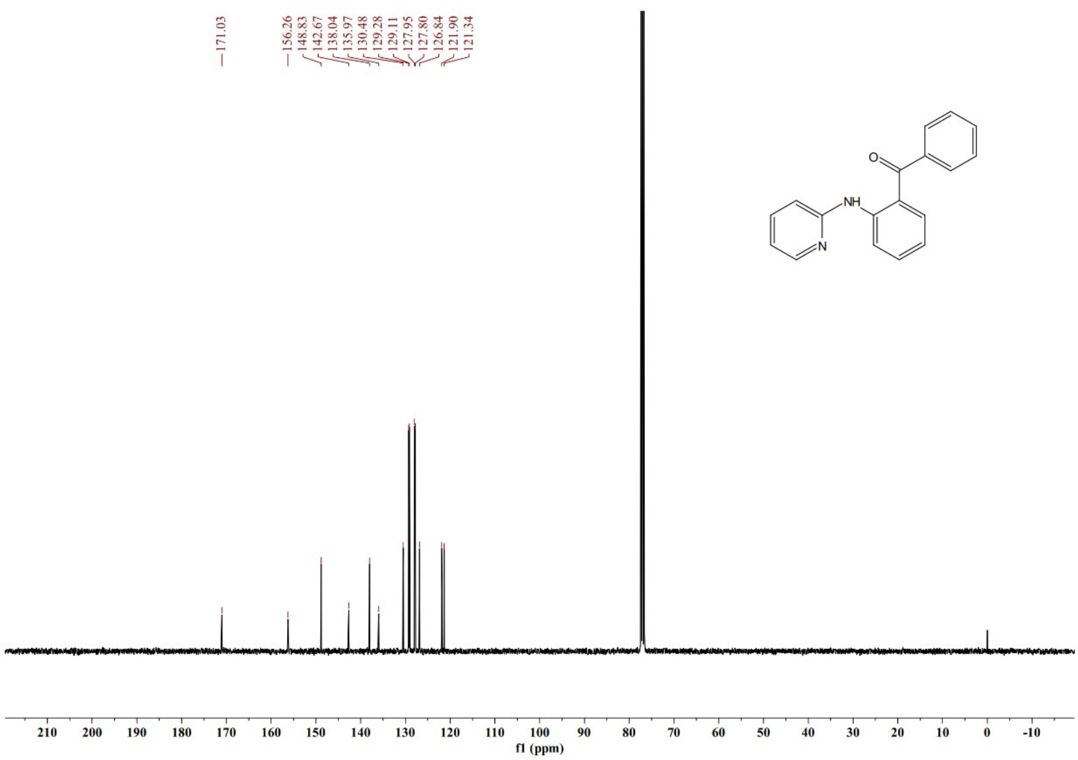
^{1}H- and ^{13}C-NMR Spectra

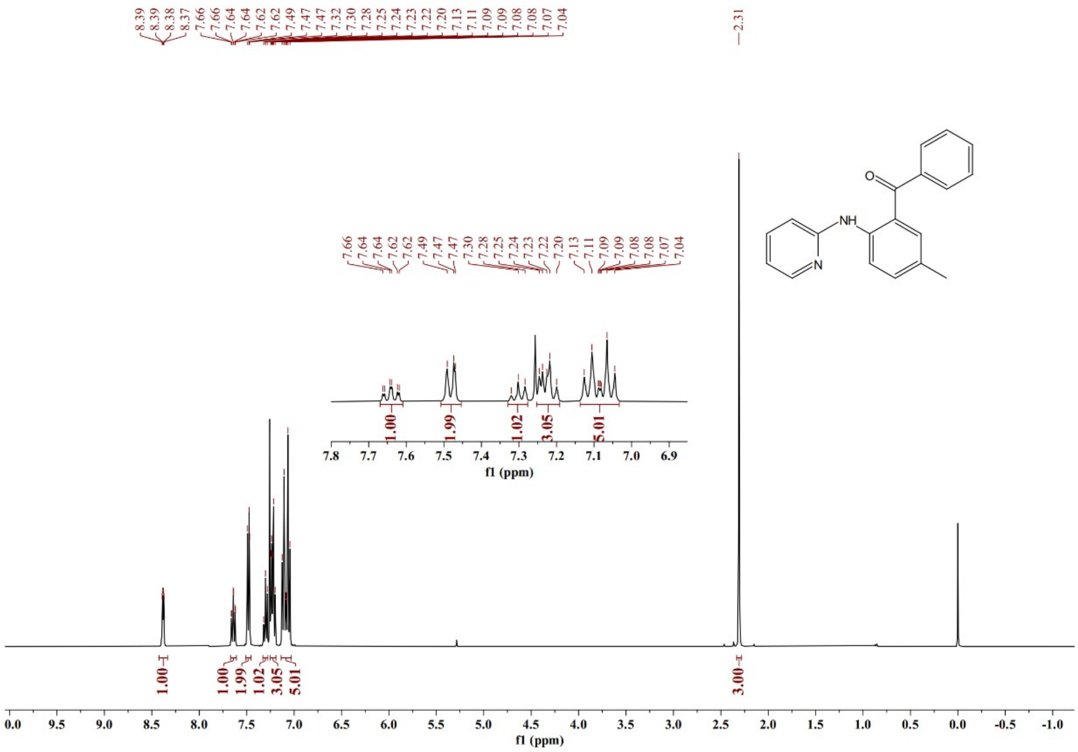
^{1}H NMR (400 MHz, $CDCl_3$) of 3aa



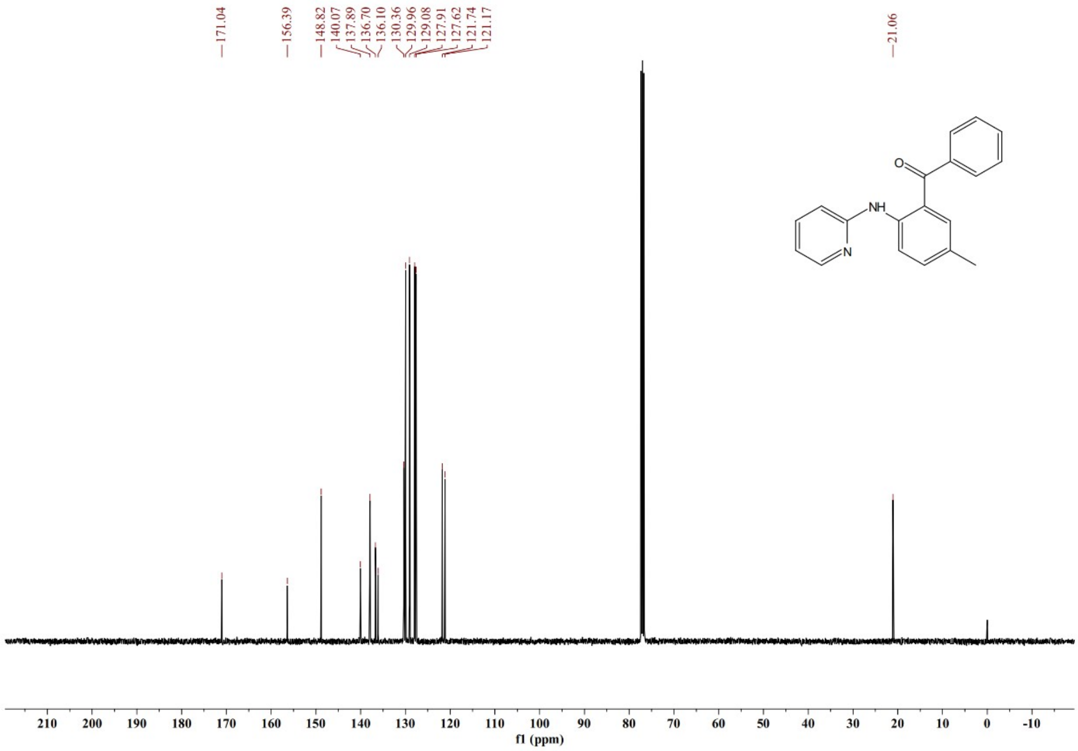
^{13}C NMR (101 MHz, $CDCl_3$) of 3aa



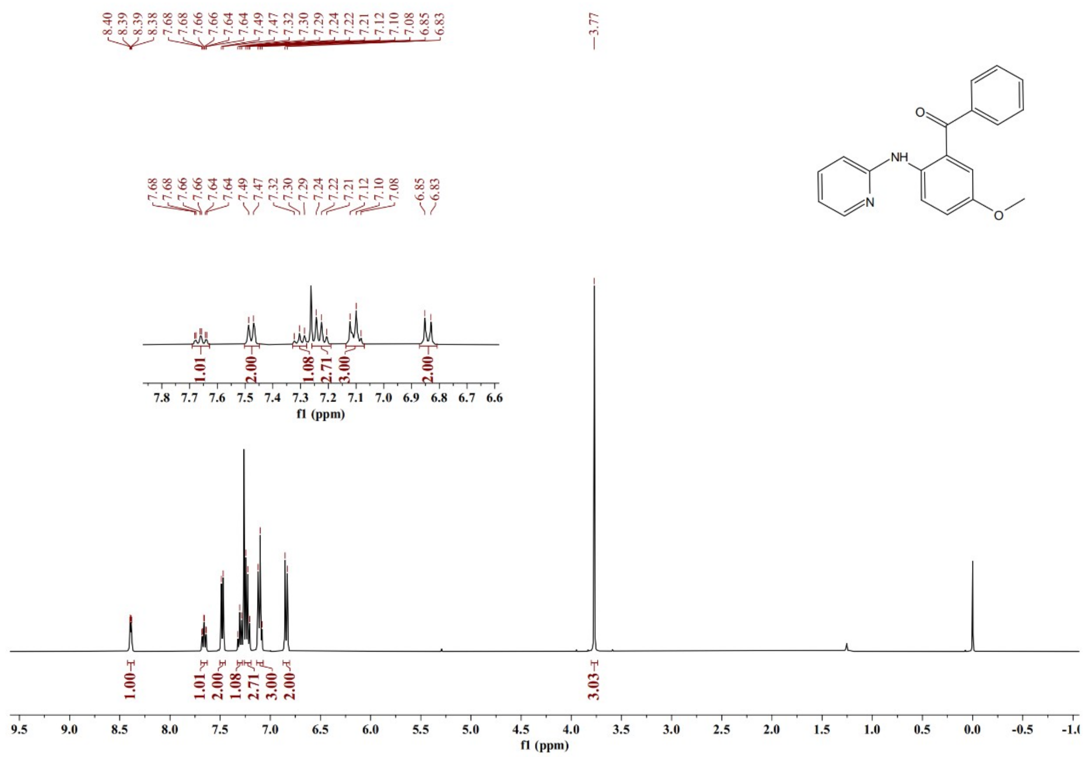
^{1}H NMR (400 MHz, $CDCl_3$) of 3ba



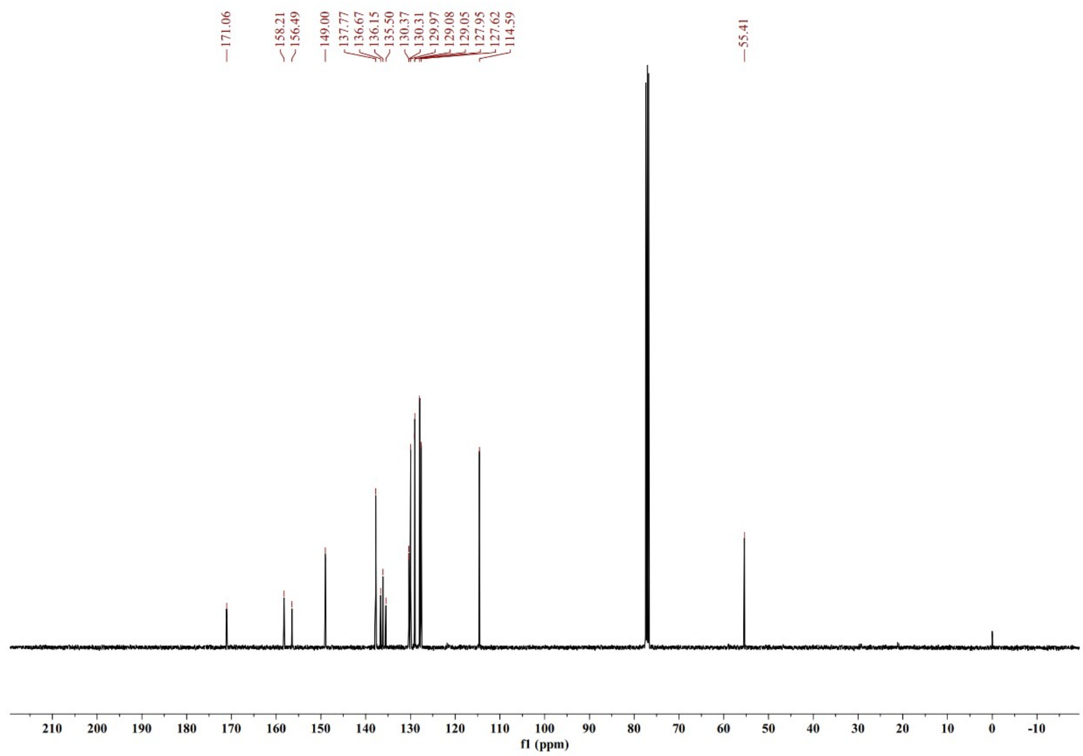
^{13}C NMR (101 MHz, $CDCl_3$) of 3ba



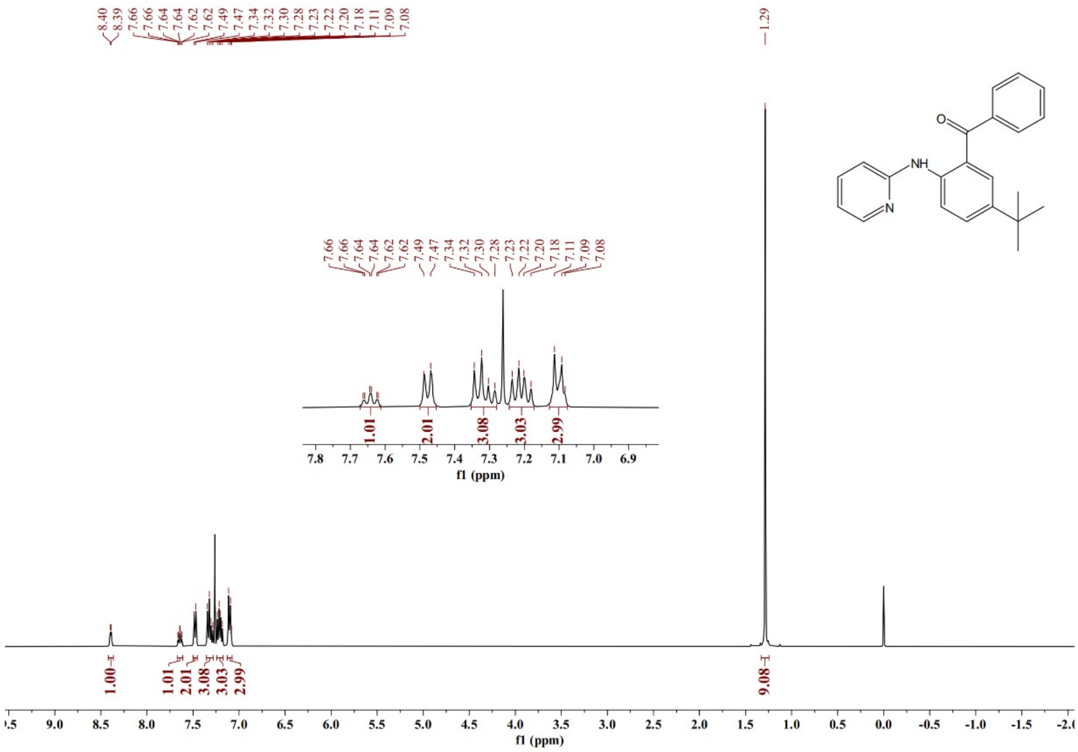
^{1}H NMR (400 MHz, $CDCl_3$) of 3ca



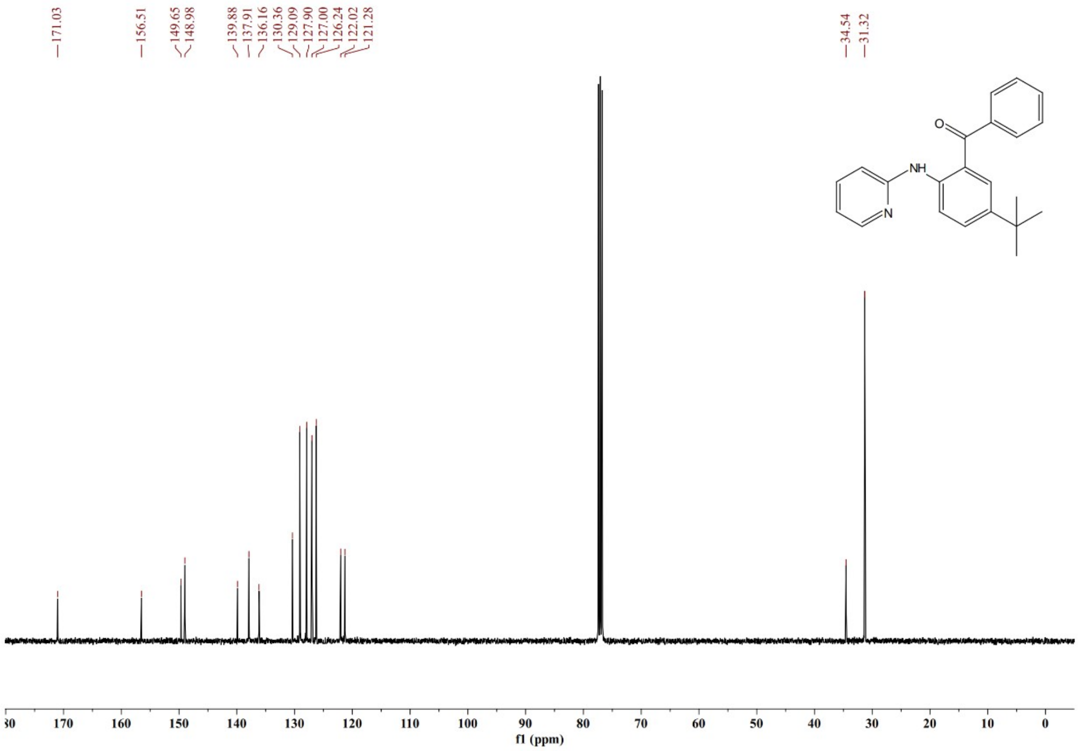
^{13}C NMR (101 MHz, $CDCl_3$) of 3ca



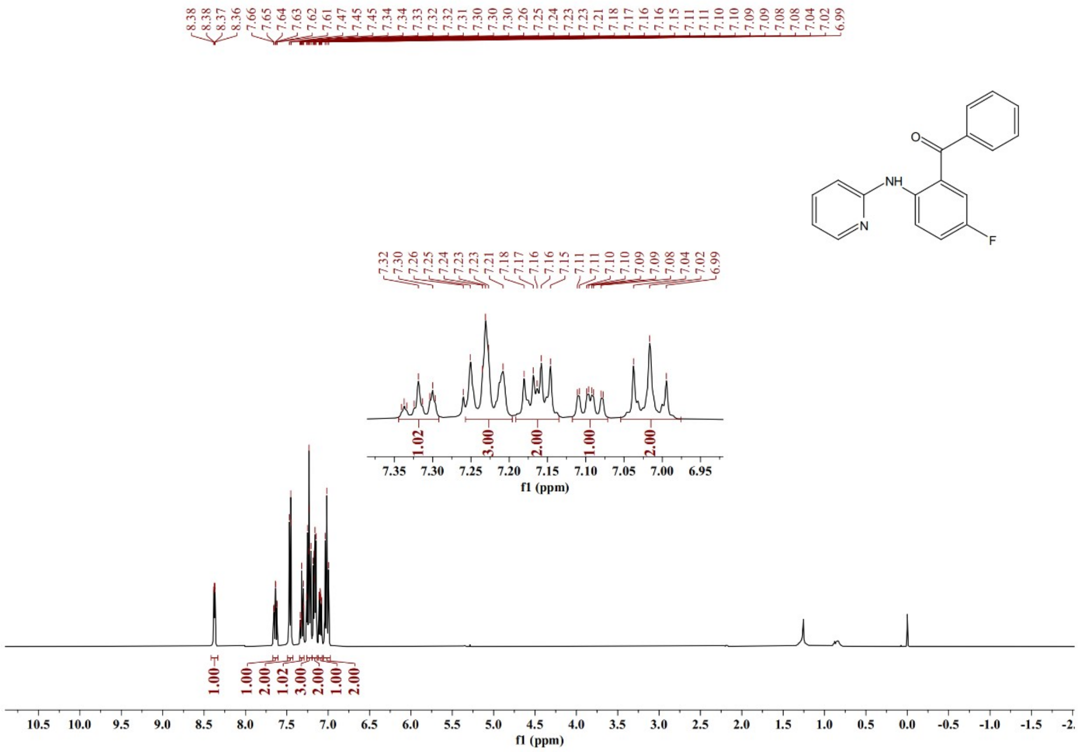
^1H NMR (400 MHz, $CDCl_3$) of 3da



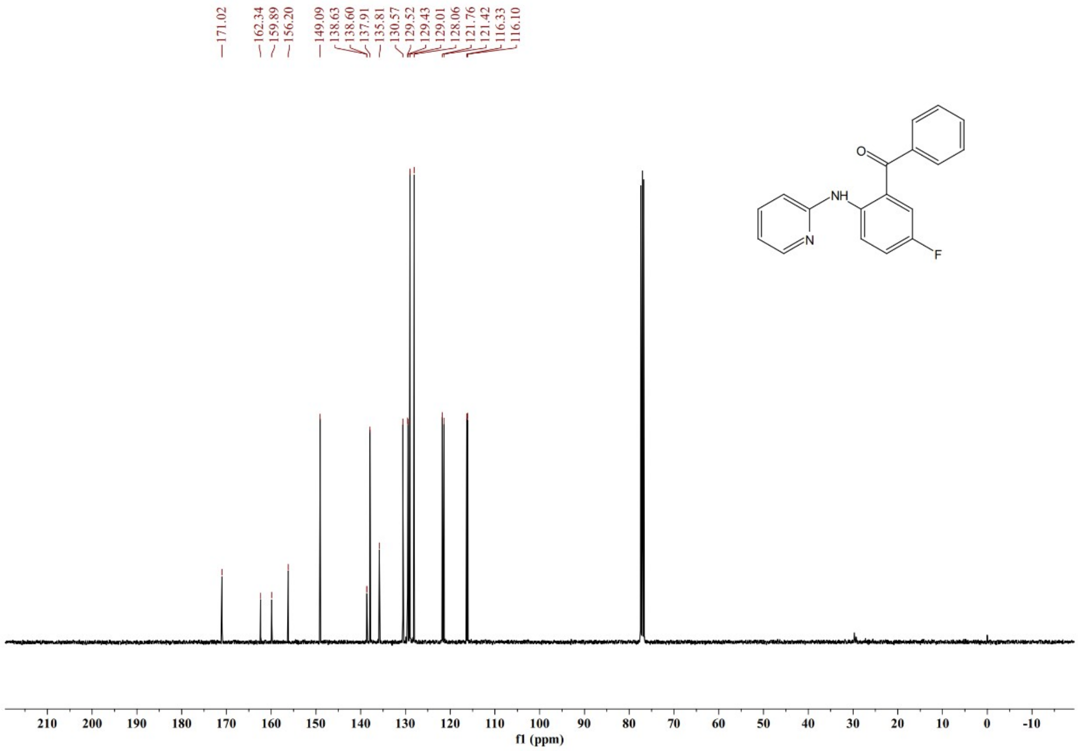
^{13}C NMR (101 MHz, $CDCl_3$) of 3da



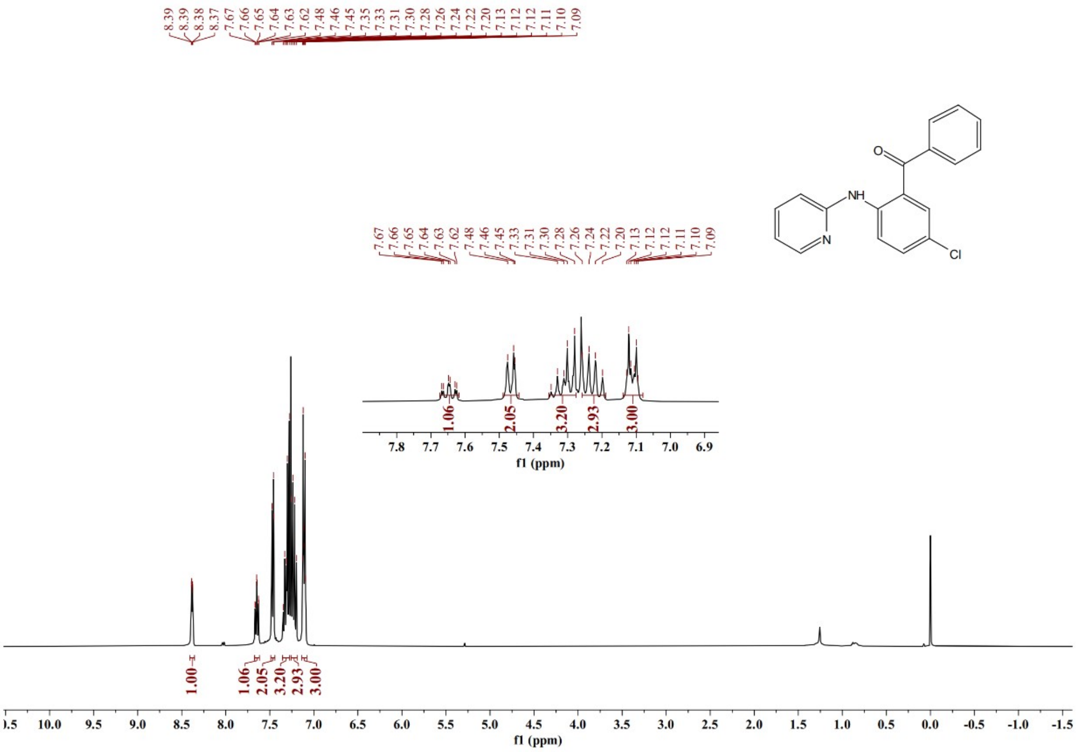
^{1}H NMR (400 MHz, $CDCl_3$) of 3ea



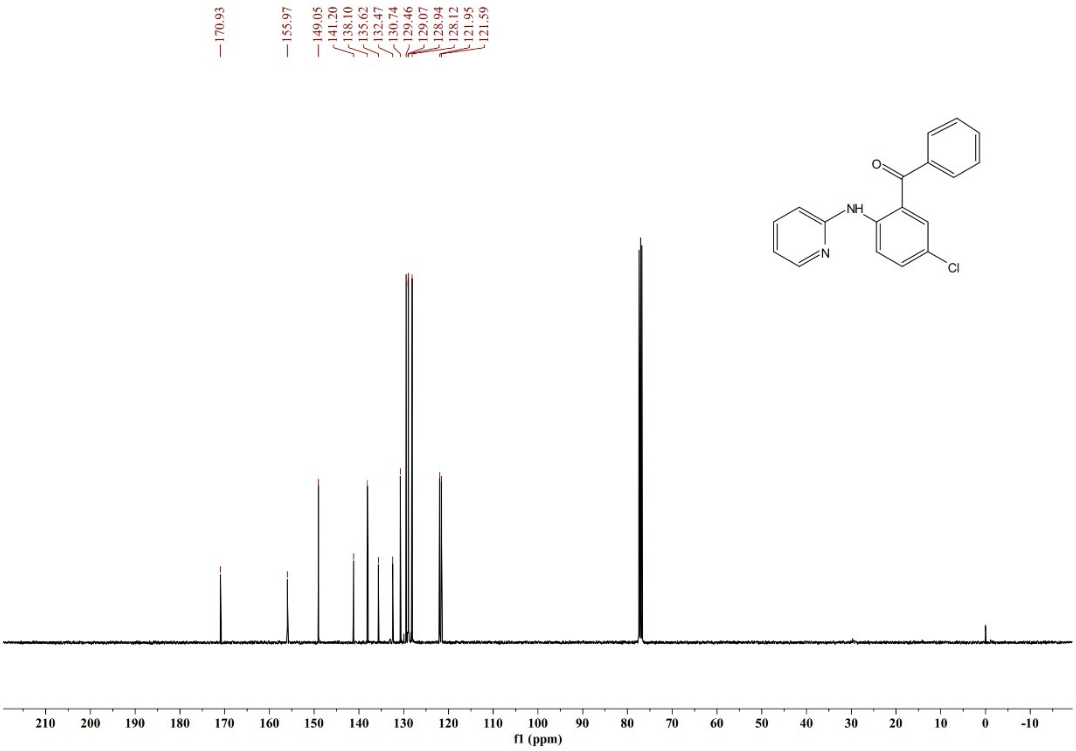
^{13}C NMR (101 MHz, $CDCl_3$) of 3ea



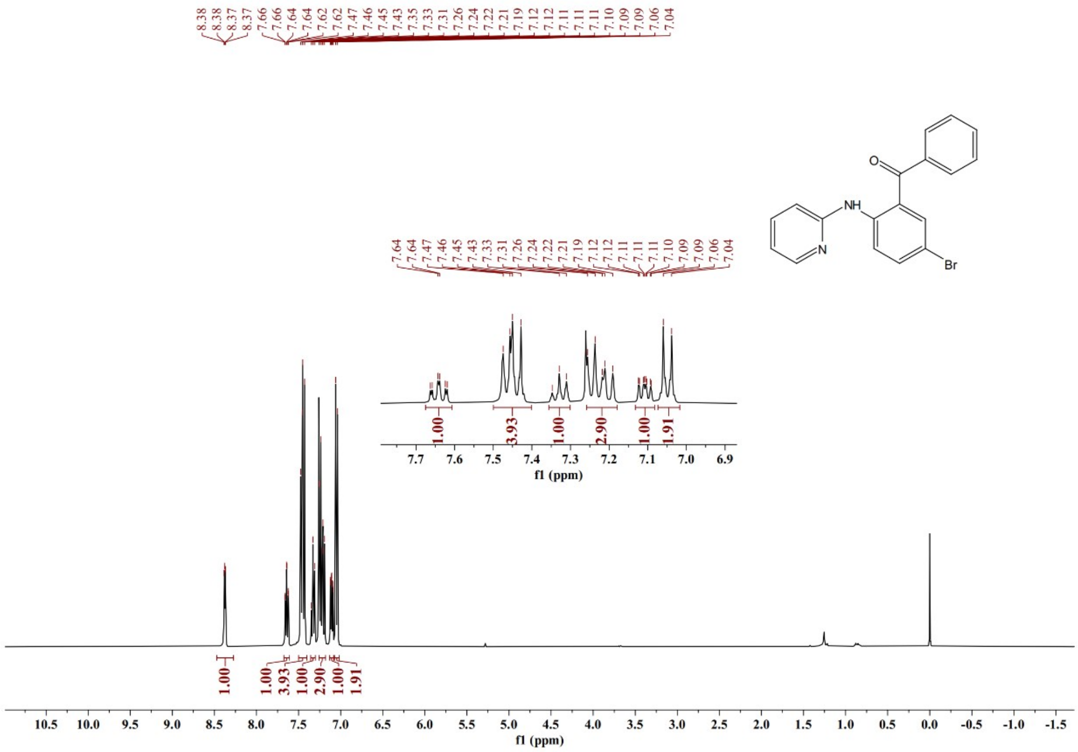
^{1}H NMR (400 MHz, $CDCl_3$) of 3fa



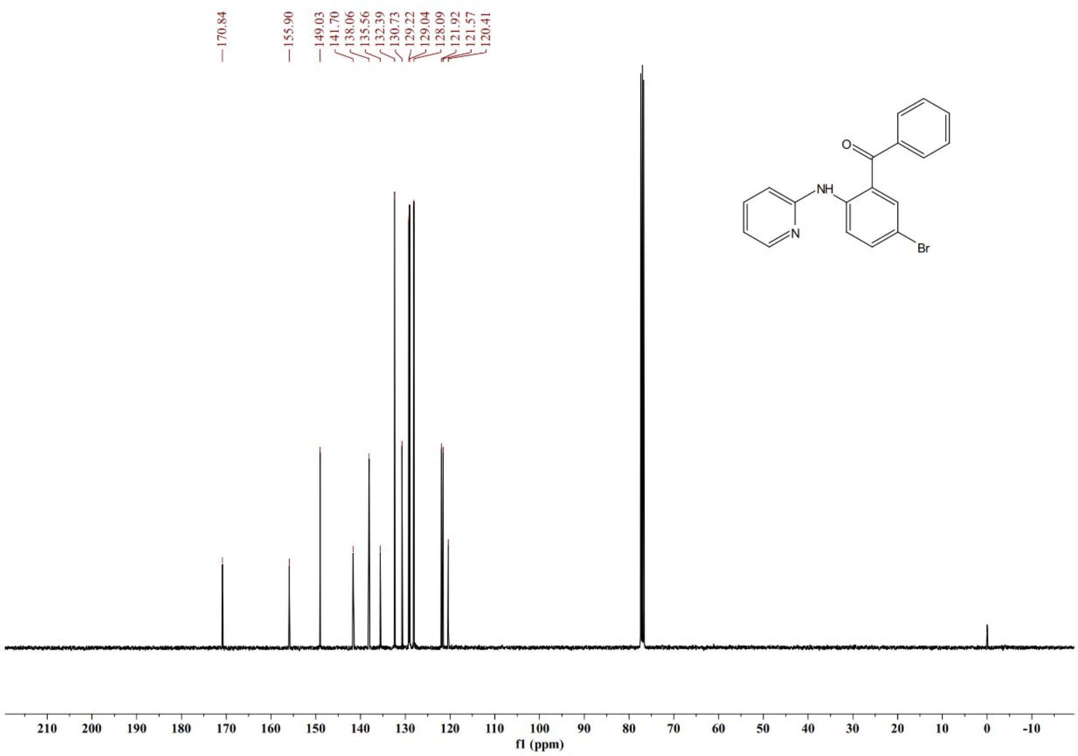
^{13}C NMR (101 MHz, $CDCl_3$) of 3fa



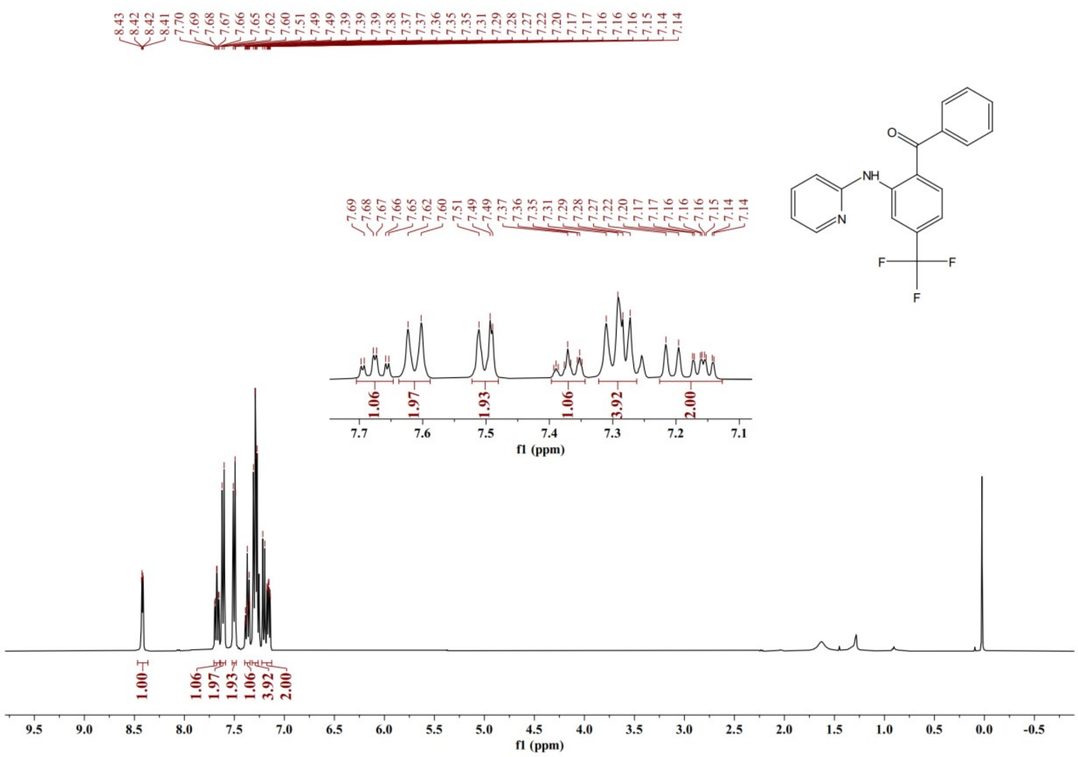
^{1}H NMR (400 MHz, $CDCl_3$) of 3ga



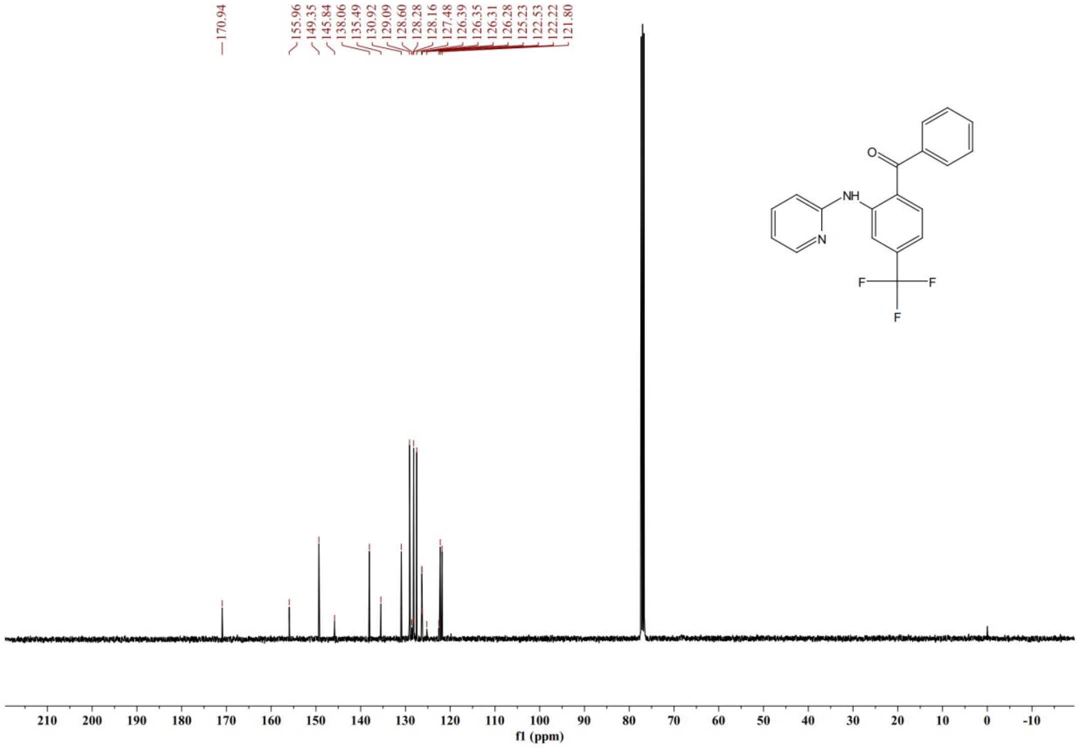
^{13}C NMR (101 MHz, $CDCl_3$) of 3ga



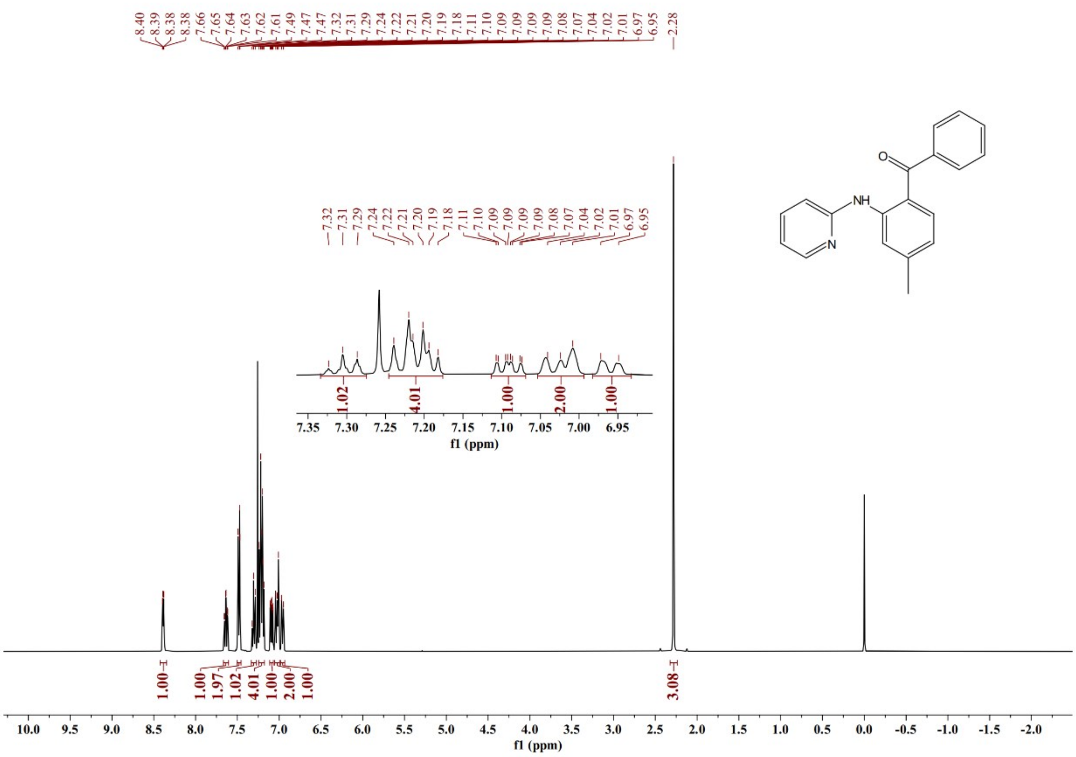
^{1}H NMR (400 MHz, $CDCl_3$) of 3ha



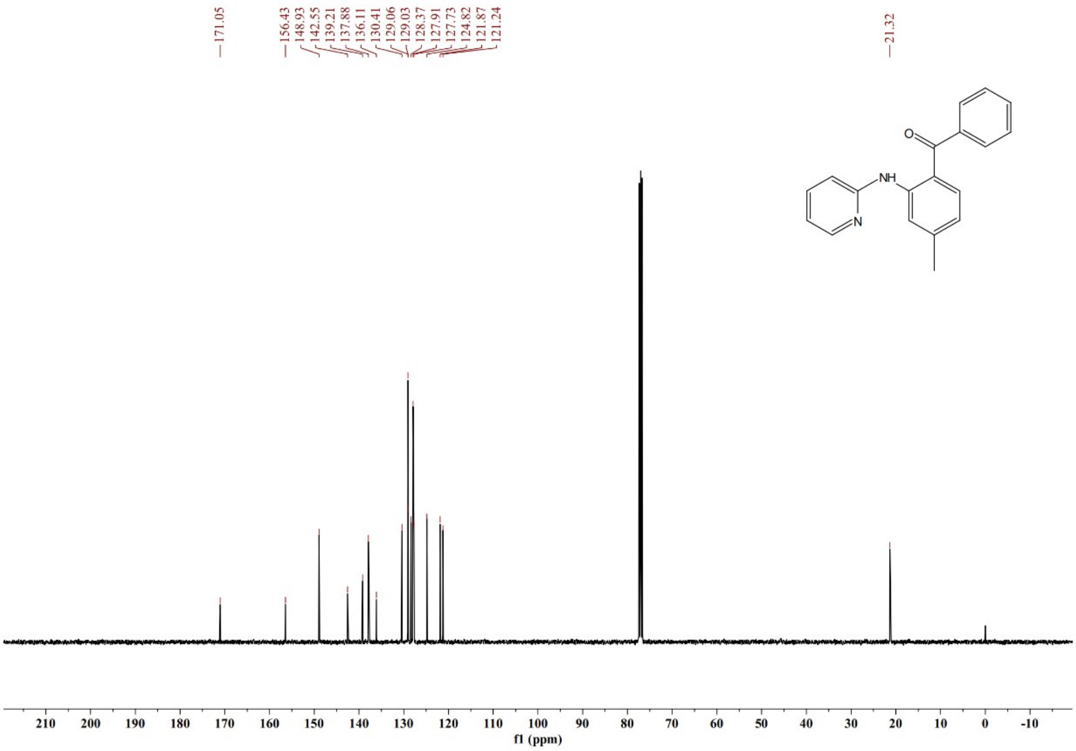
^{13}C NMR (101 MHz, $CDCl_3$) of 3ha



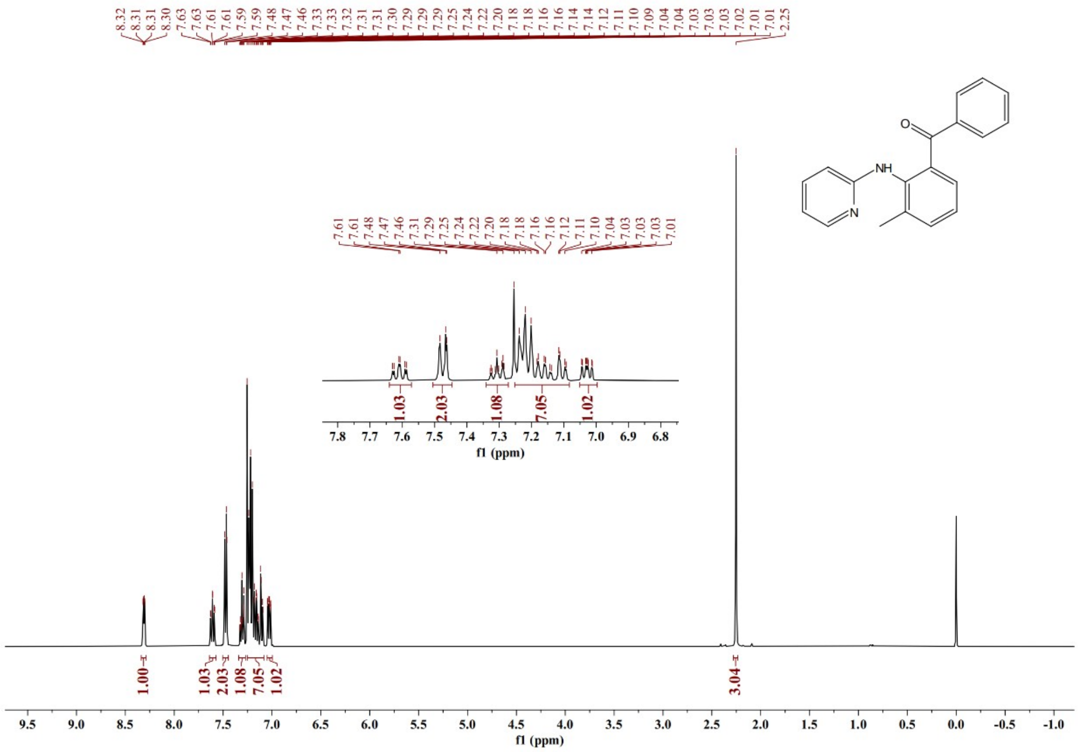
^{1}H NMR (400 MHz, $CDCl_3$) of 3ia



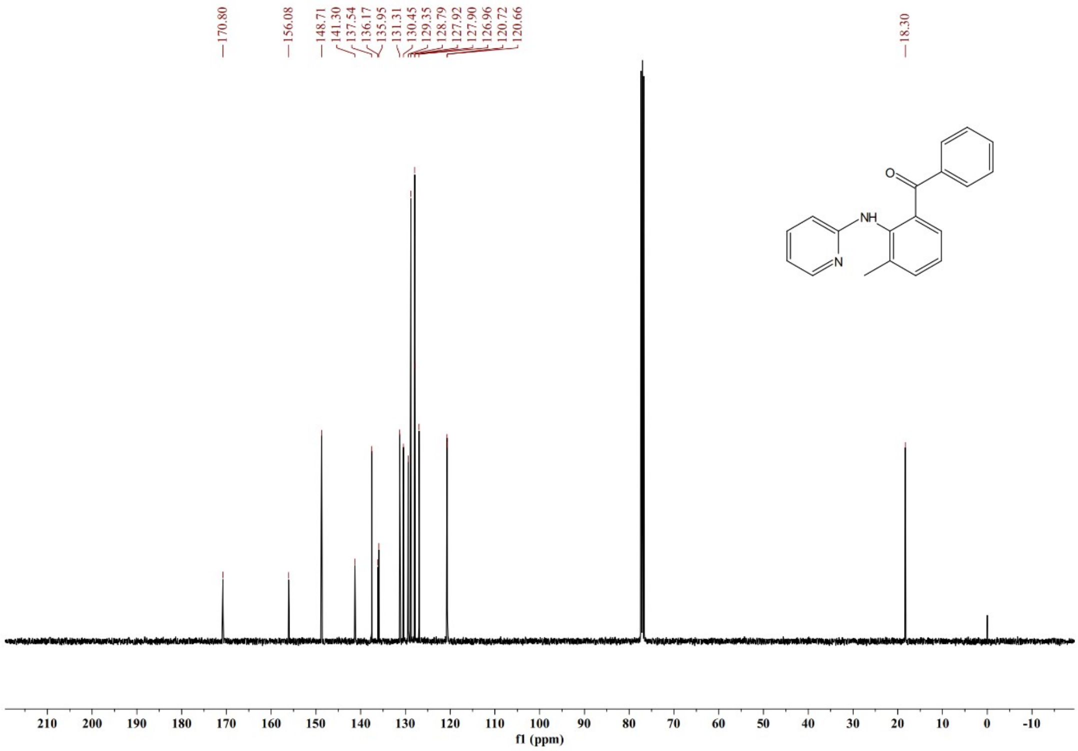
^{13}C NMR (101 MHz, $CDCl_3$) of 3ia



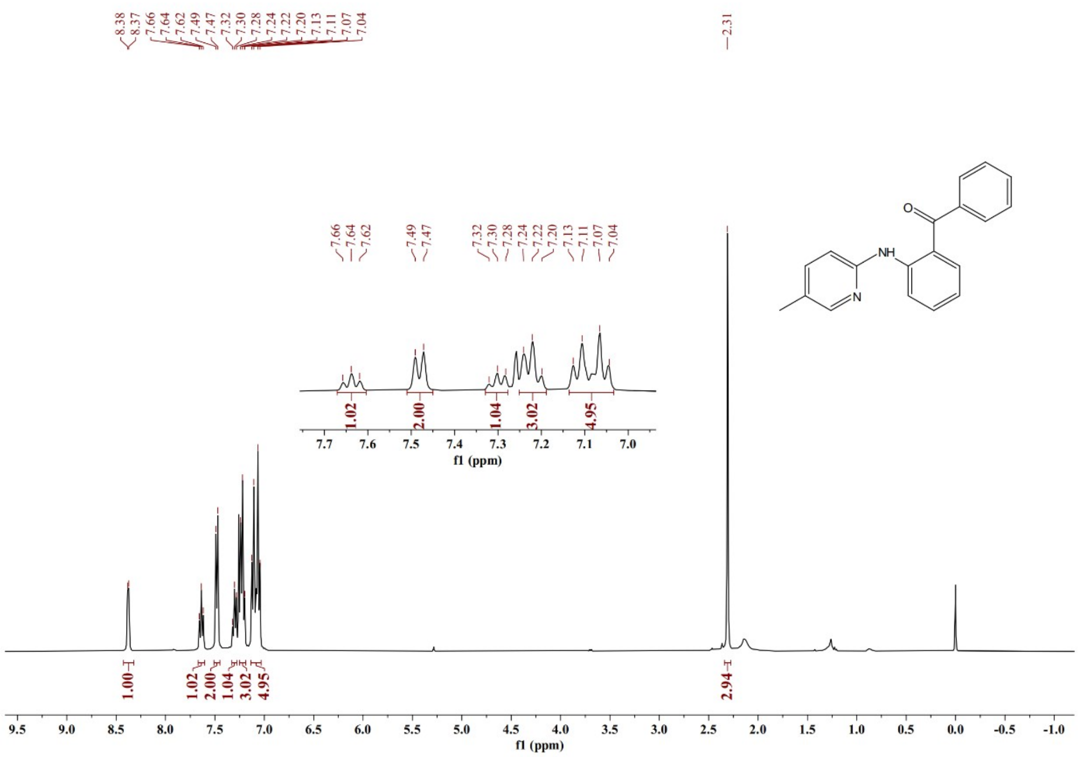
[1]H NMR (400 MHz, $CDCl_3$) of 3ja



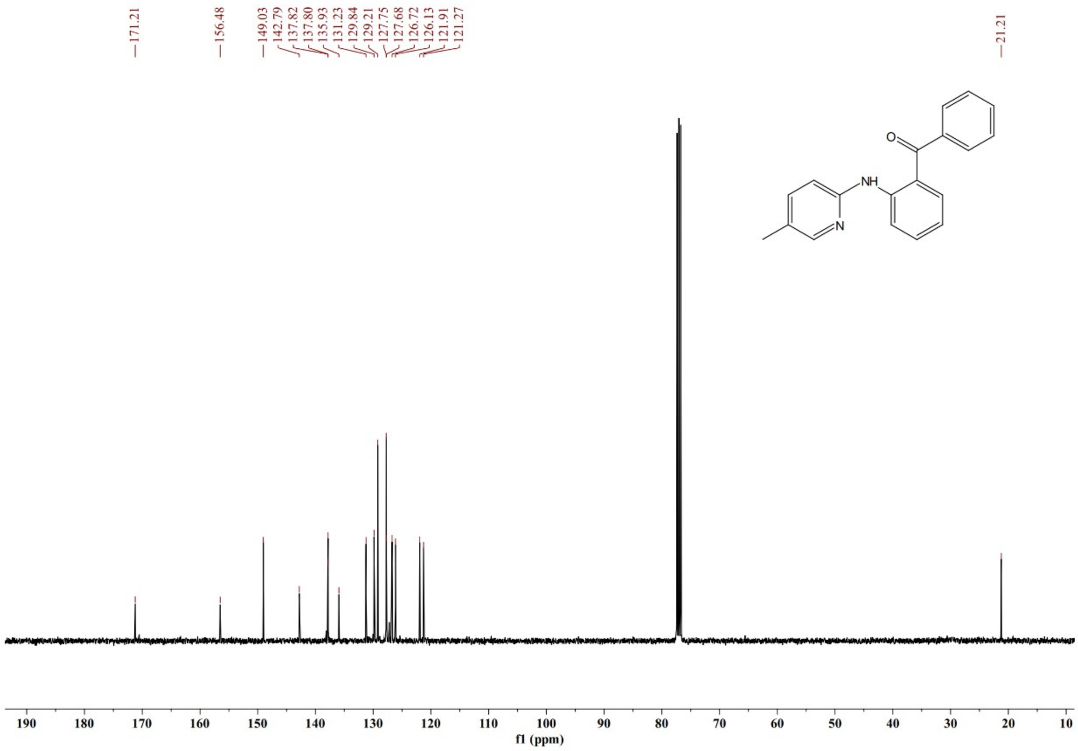
[13]C NMR (101 MHz, $CDCl_3$) of 3ja



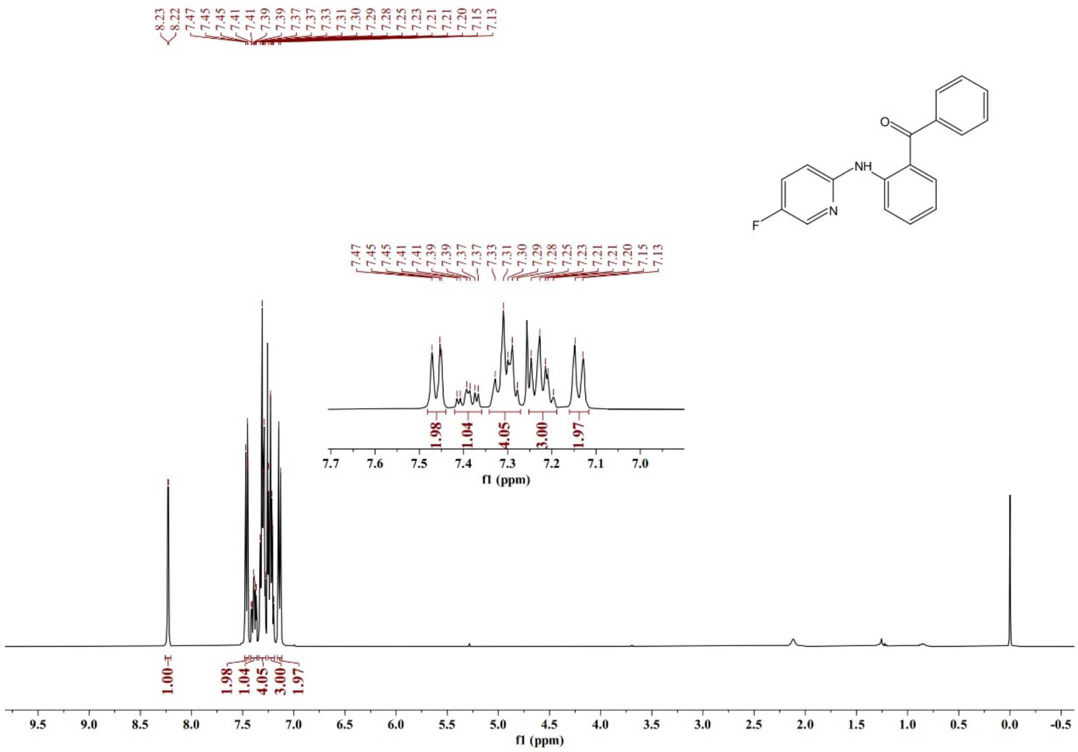
^{1}H NMR (400 MHz, $CDCl_3$) of 3ka



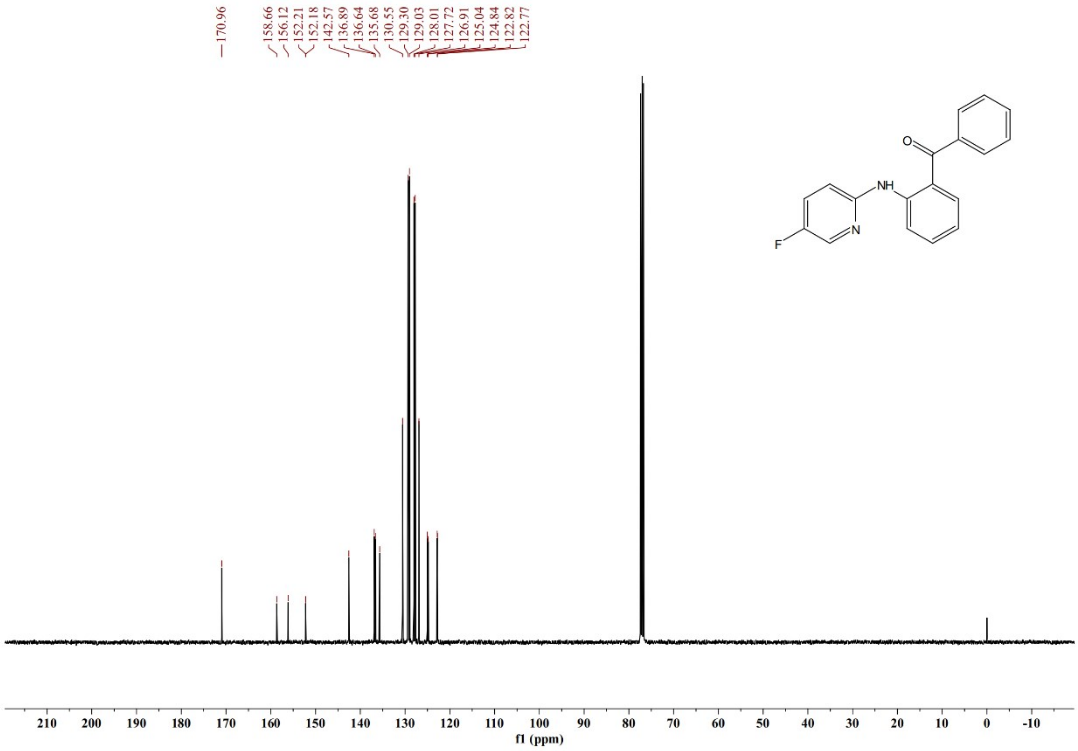
^{13}C NMR (101 MHz, $CDCl_3$) of 3ka



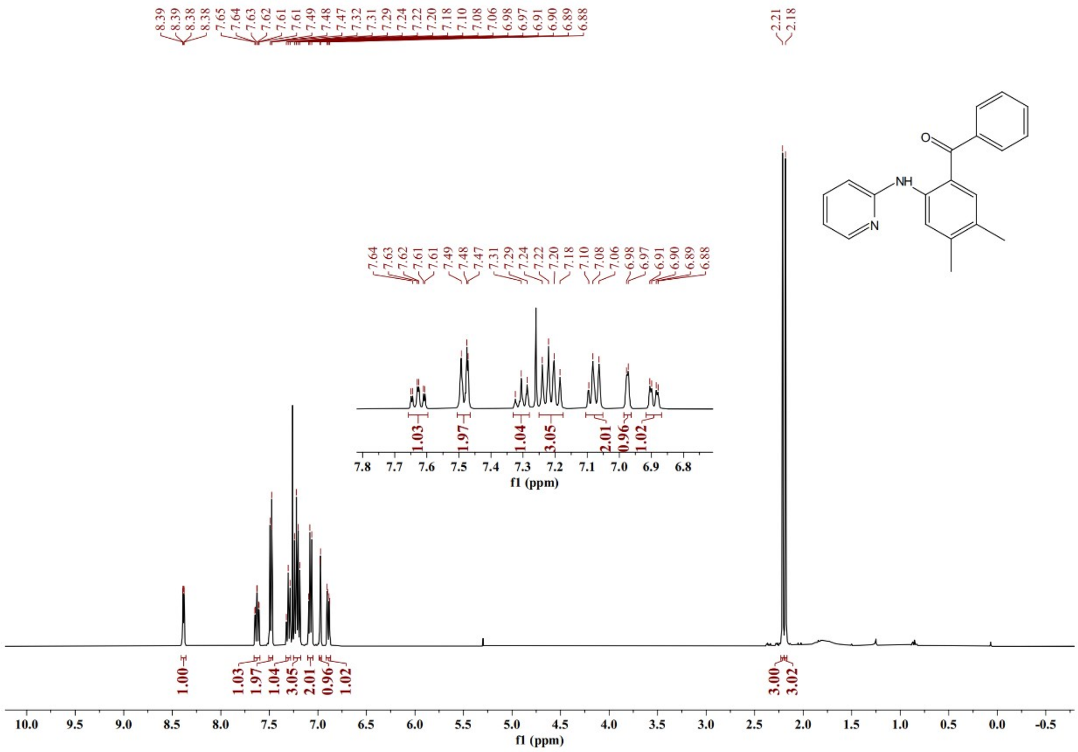
^{1}H NMR (400 MHz, $CDCl_3$) of 3la



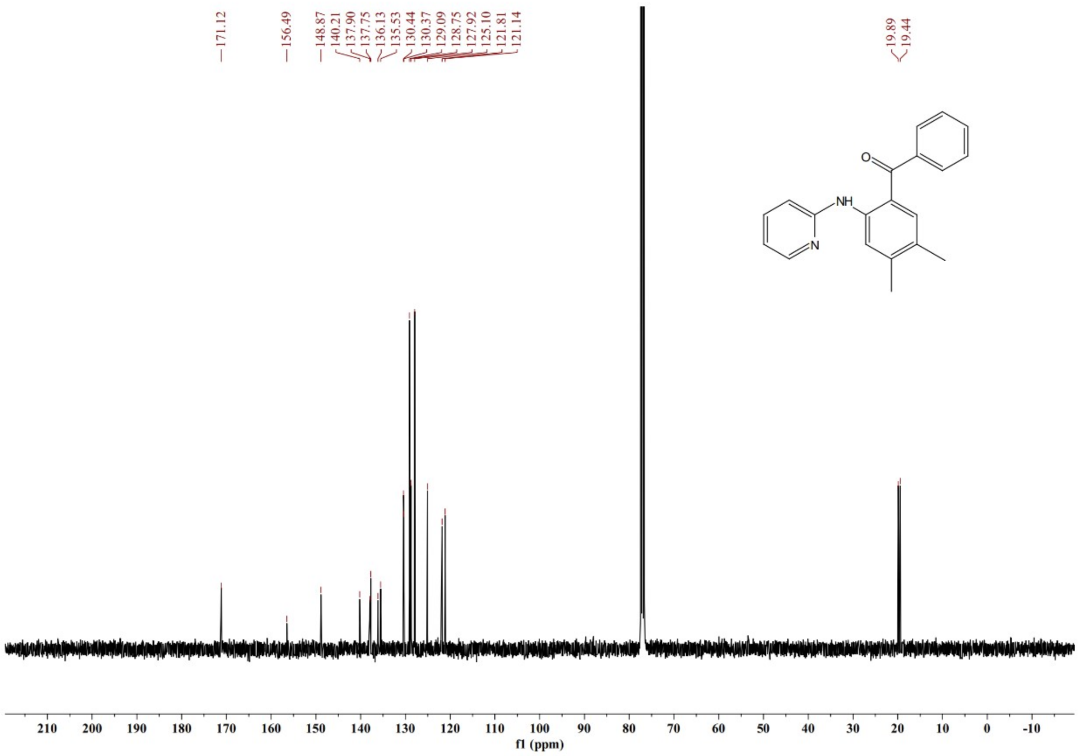
^{13}C NMR (101 MHz, $CDCl_3$) of 3la



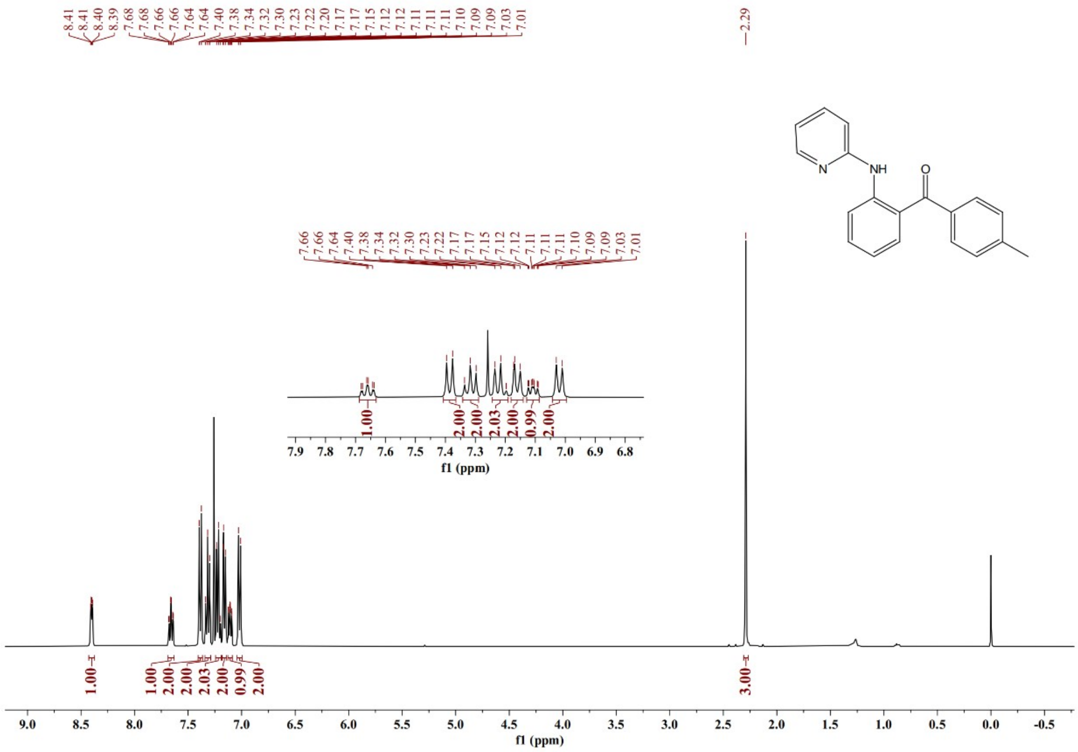
^{1}H NMR (400 MHz, $CDCl_3$) of 3ma



^{13}C NMR (101 MHz, $CDCl_3$) of 3ma



^{1}H NMR (400 MHz, $CDCl_3$) of 3ab



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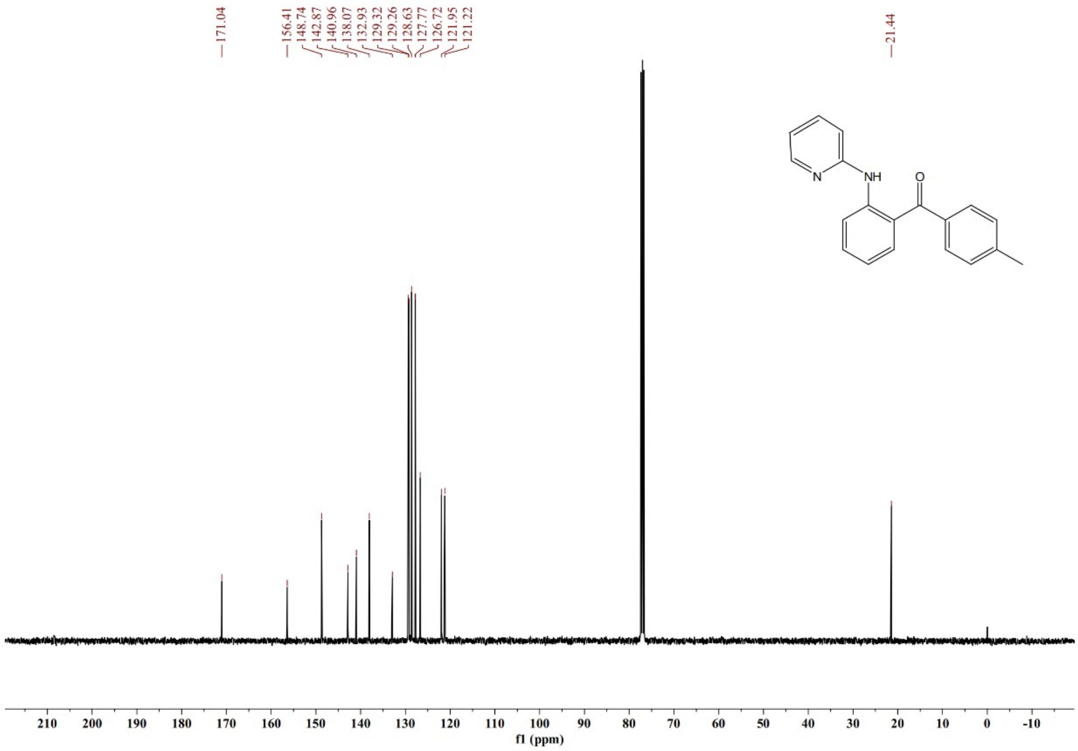
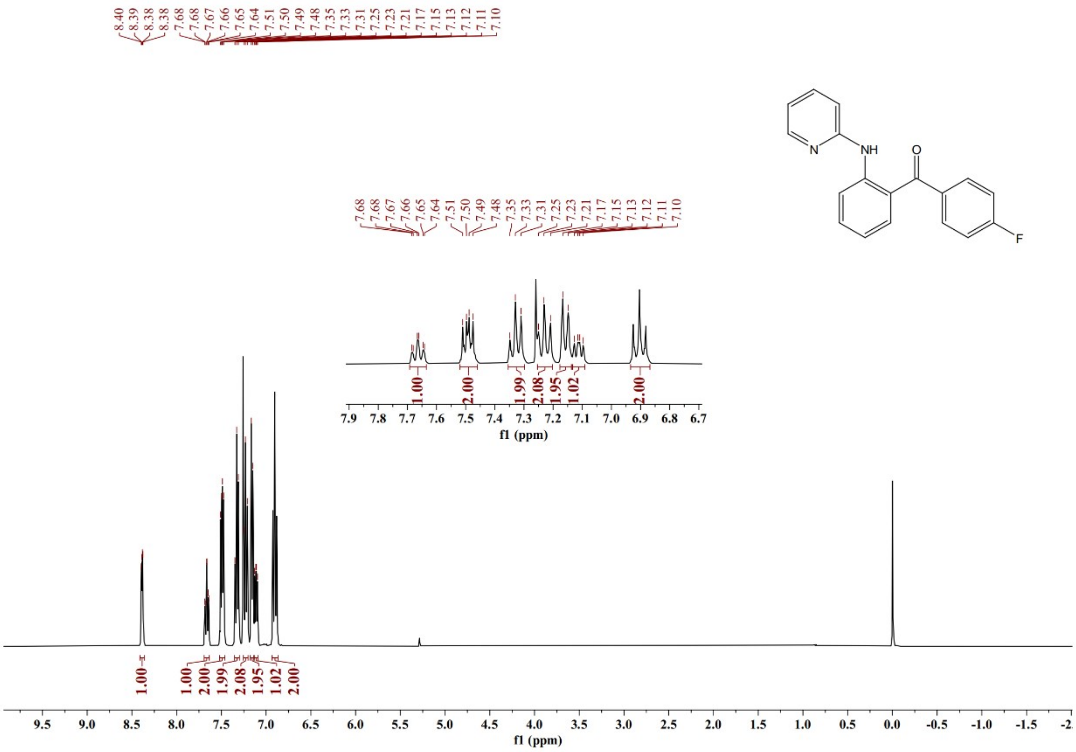
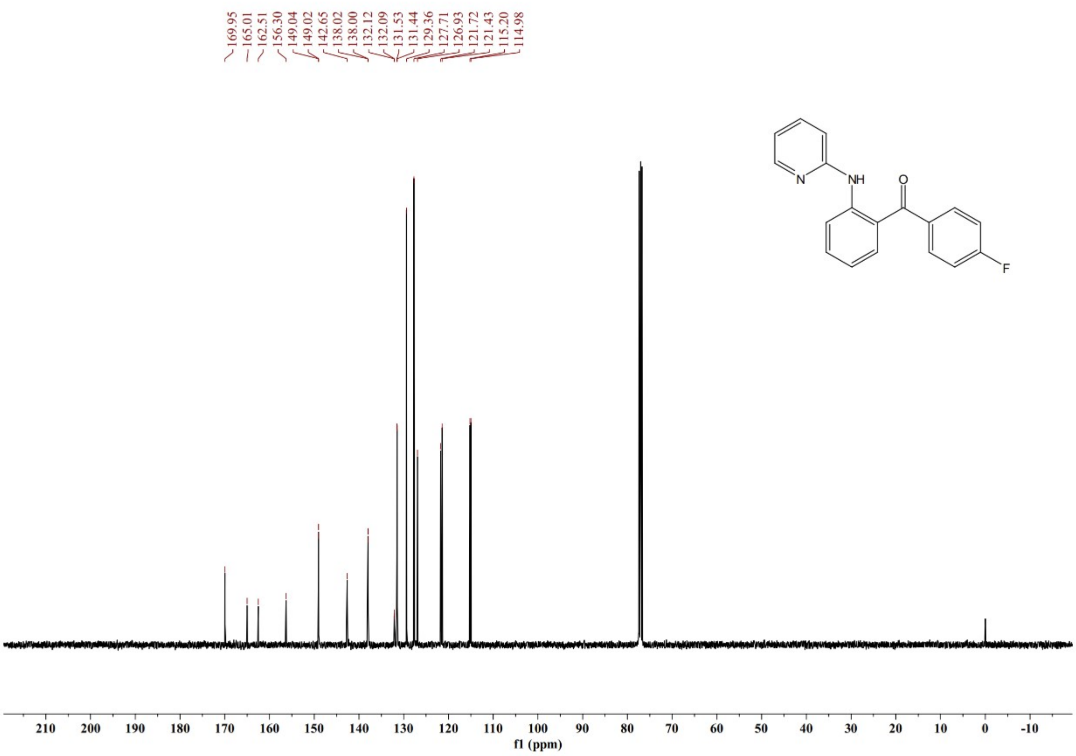


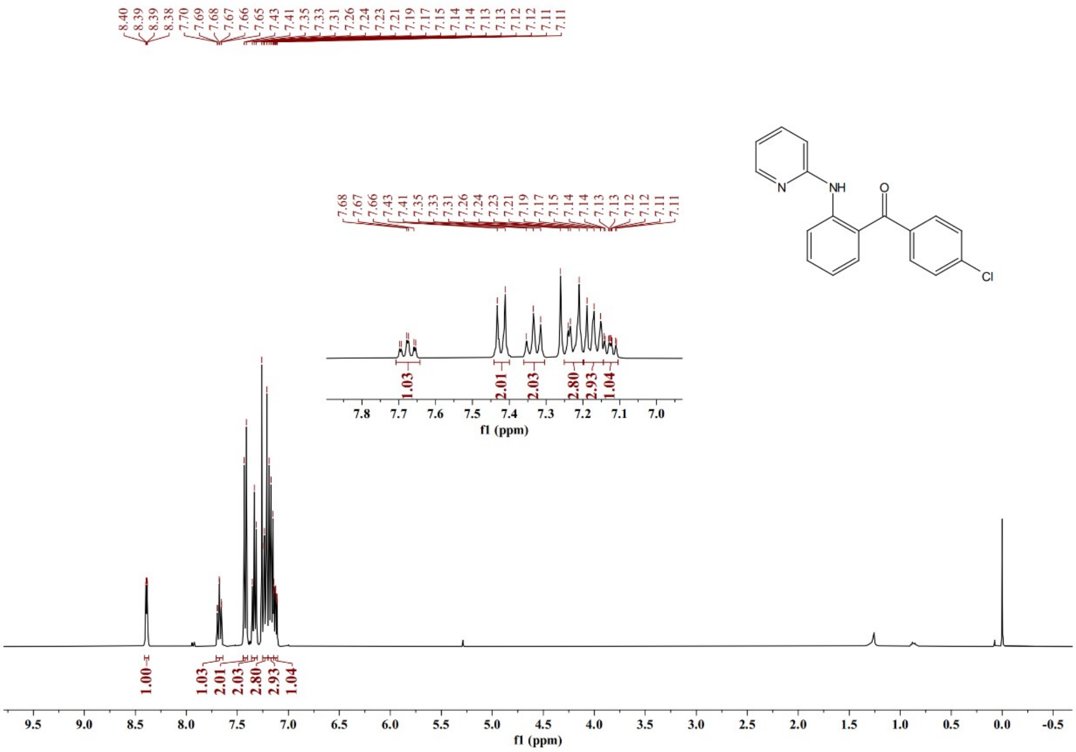
^{1}H NMR (400 MHz, CDCl$_3$) of 3ac



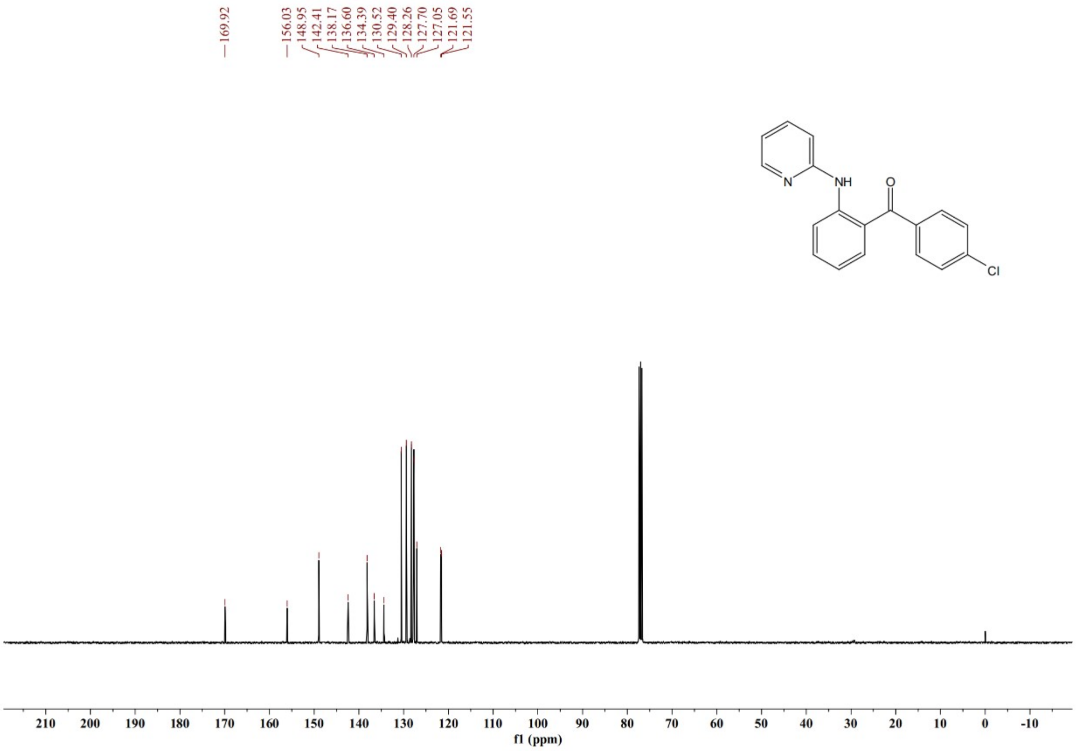
^{13}C NMR (101 MHz, CDCl$_3$) of 3ac



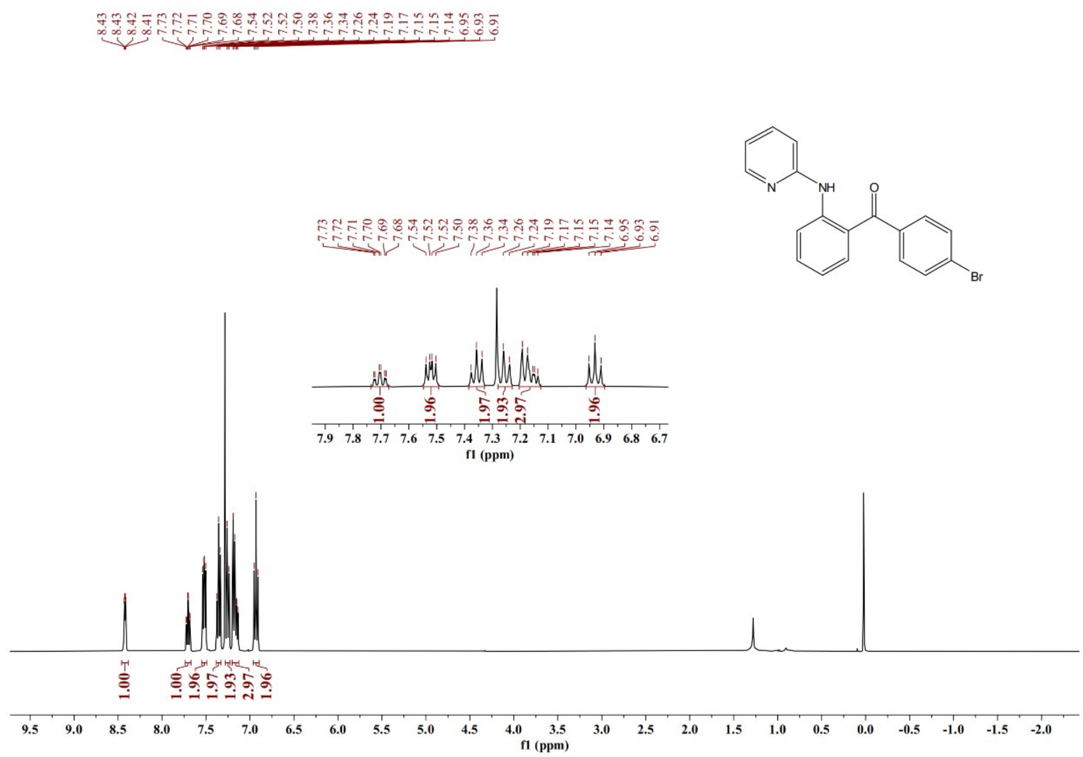
^{1}H NMR (400 MHz, $CDCl_3$) of 3ad



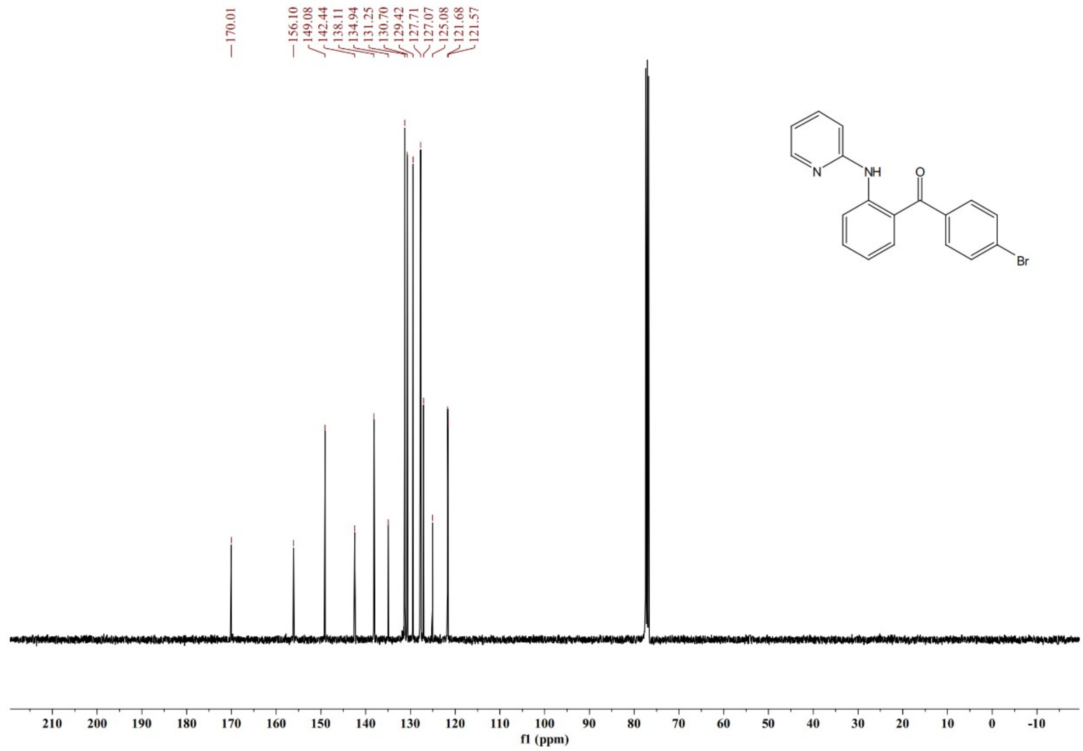
^{13}C NMR (101 MHz, $CDCl_3$) of 3ad



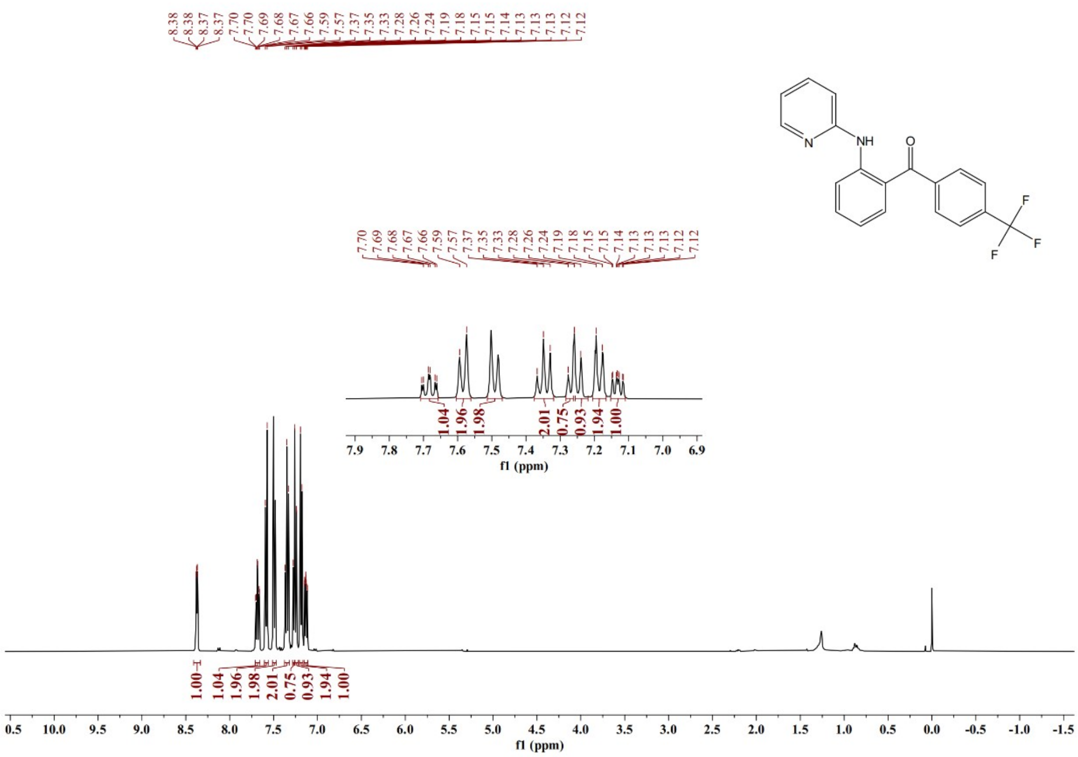
^{1}H NMR (400 MHz, $CDCl_3$) of 3ae



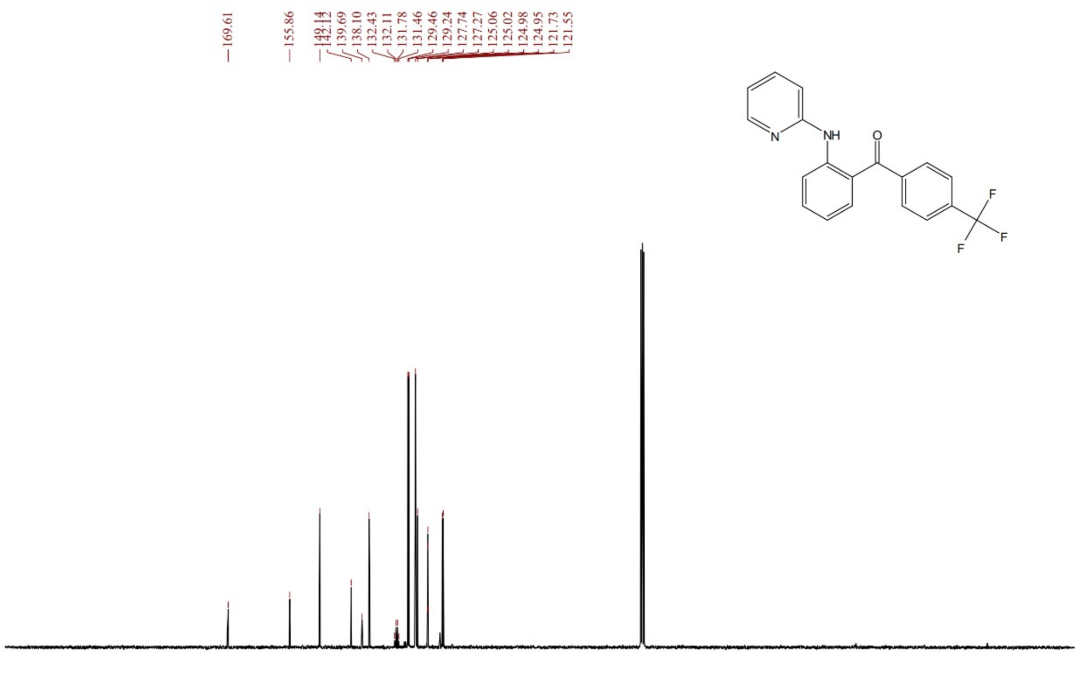
^{13}C NMR (101 MHz, $CDCl_3$) of 3ae



^{1}H NMR (400 MHz, $CDCl_3$) of 3af



^{13}C NMR (101 MHz, $CDCl_3$) of 3af



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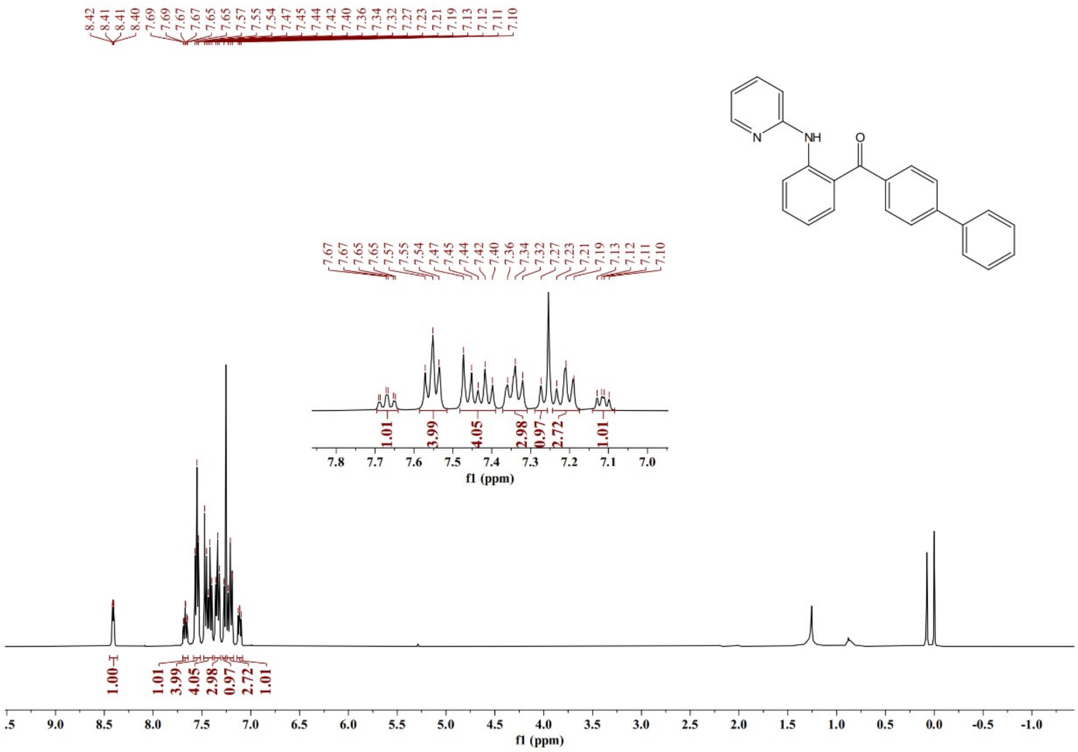
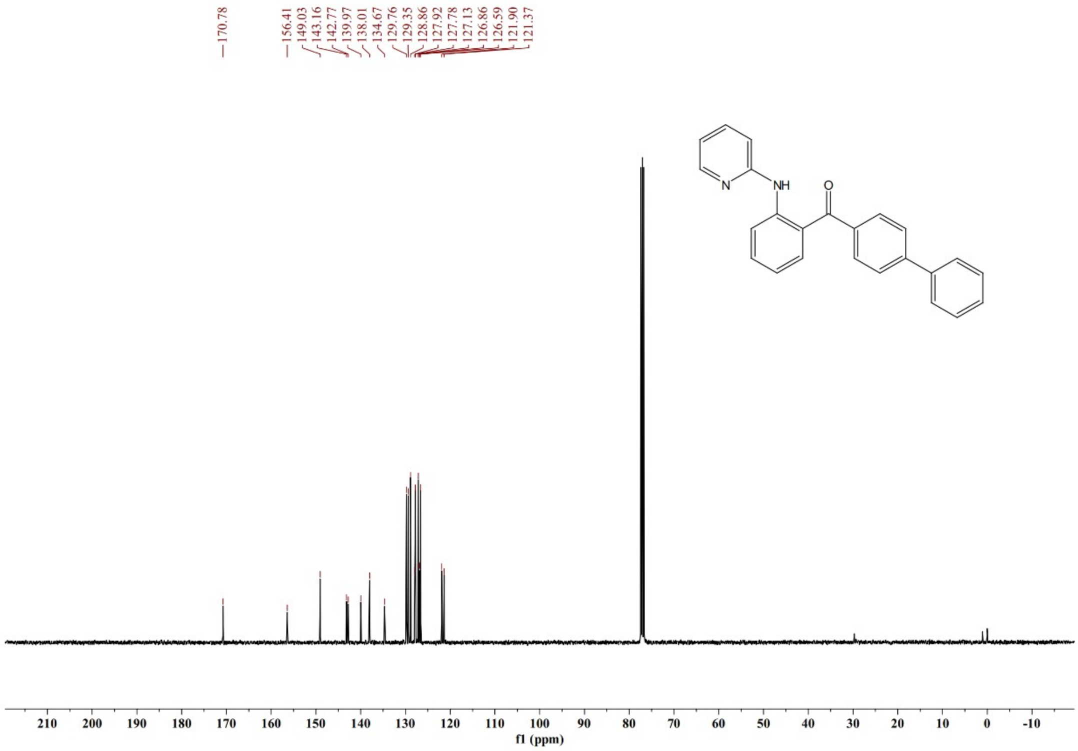
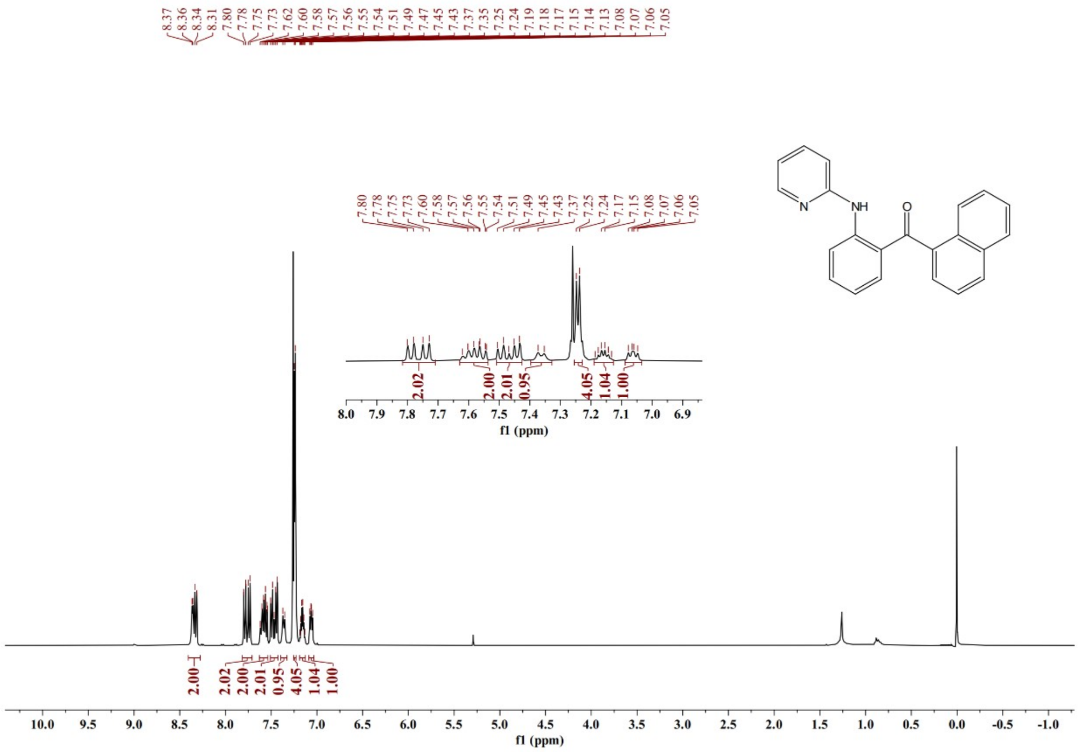


^{13}C NMR (101 MHz, $CDCl_3$) of 3ag



^{1}H NMR (400 MHz, $CDCl_3$) of 3ah



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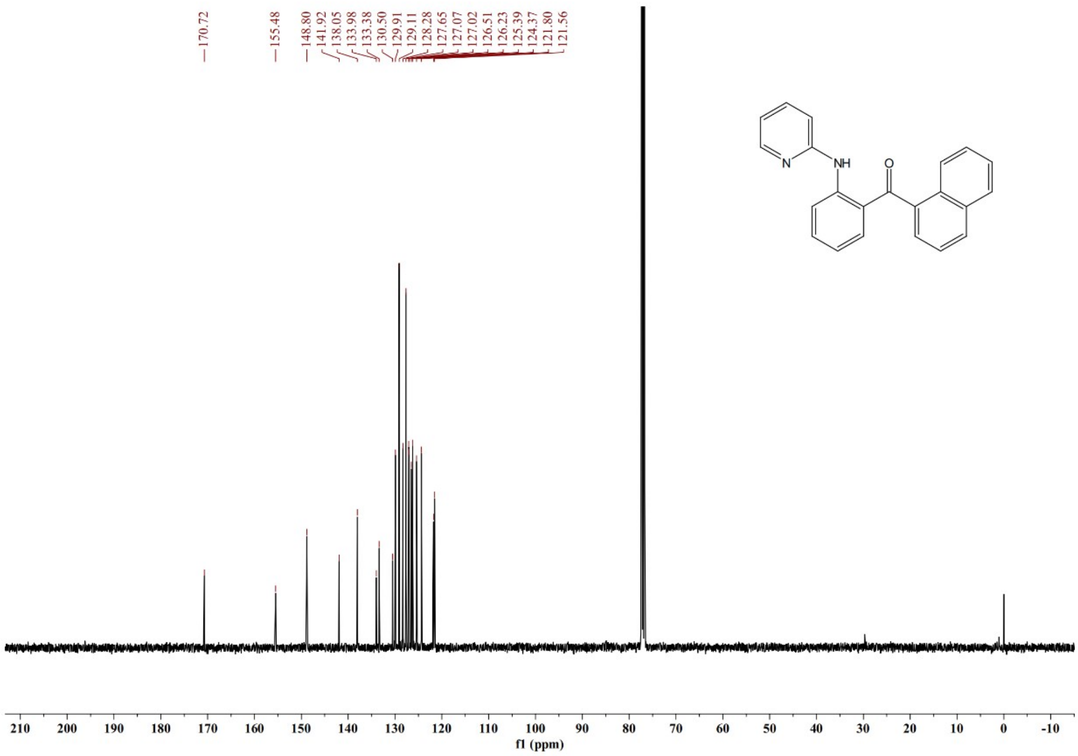
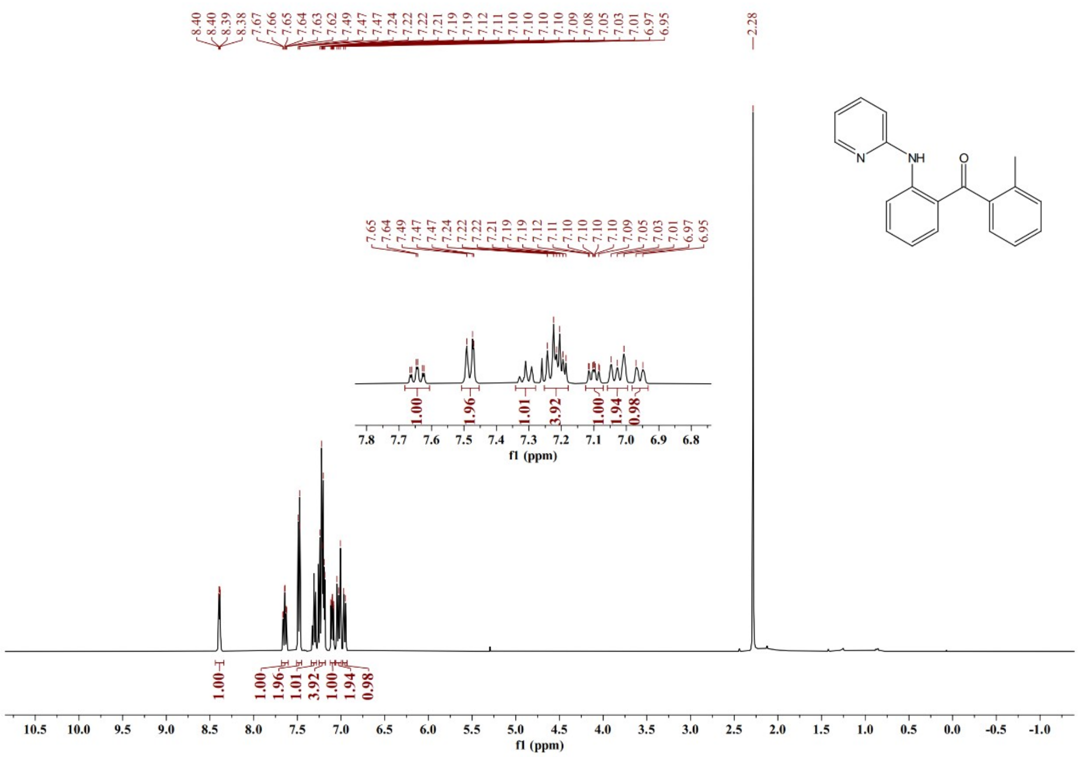
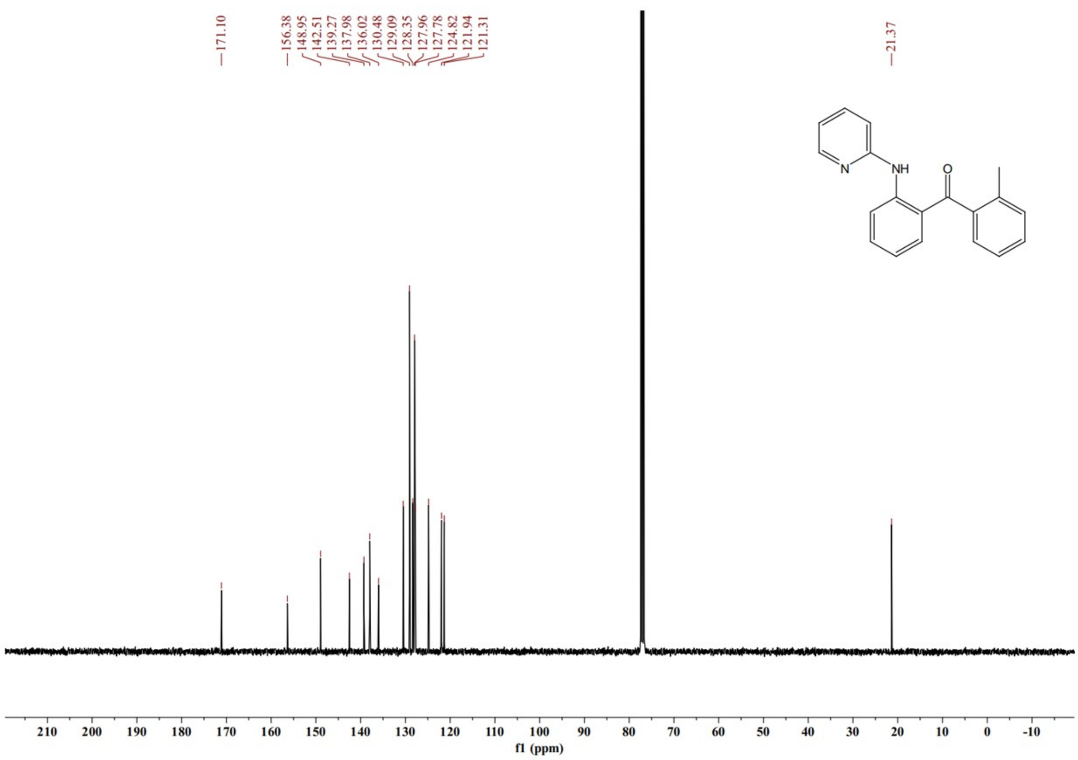


^{1}H NMR (400 MHz, $CDCl_3$) of 3ai



^{13}C NMR (101 MHz, $CDCl_3$) of 3ai



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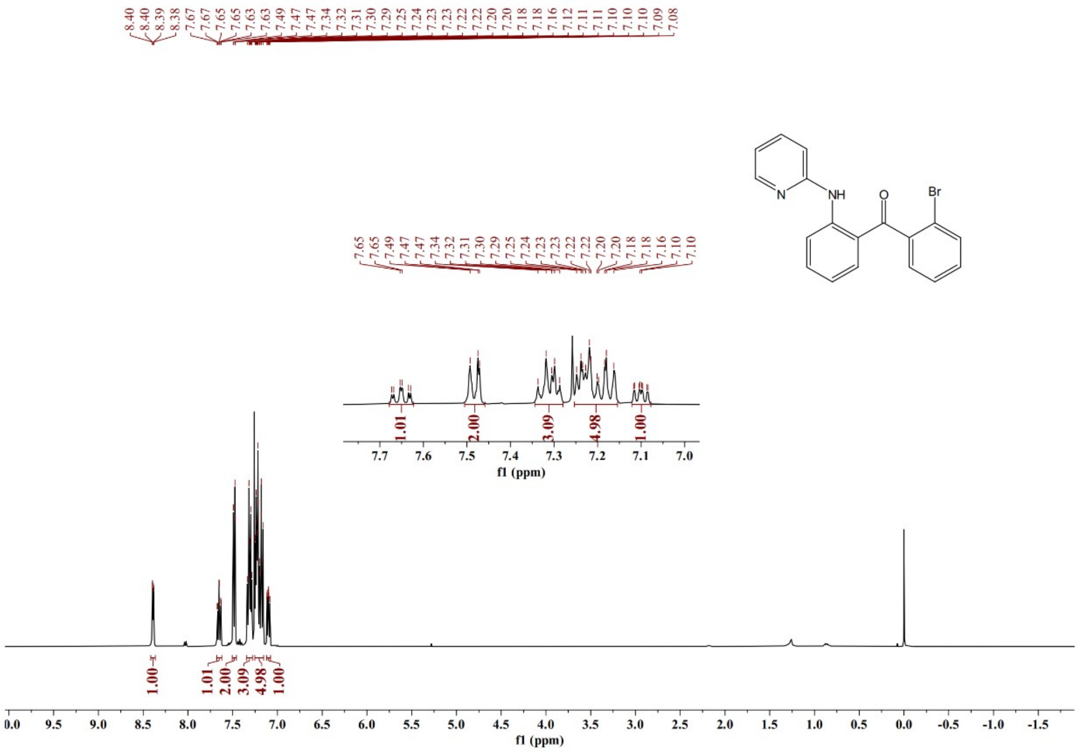
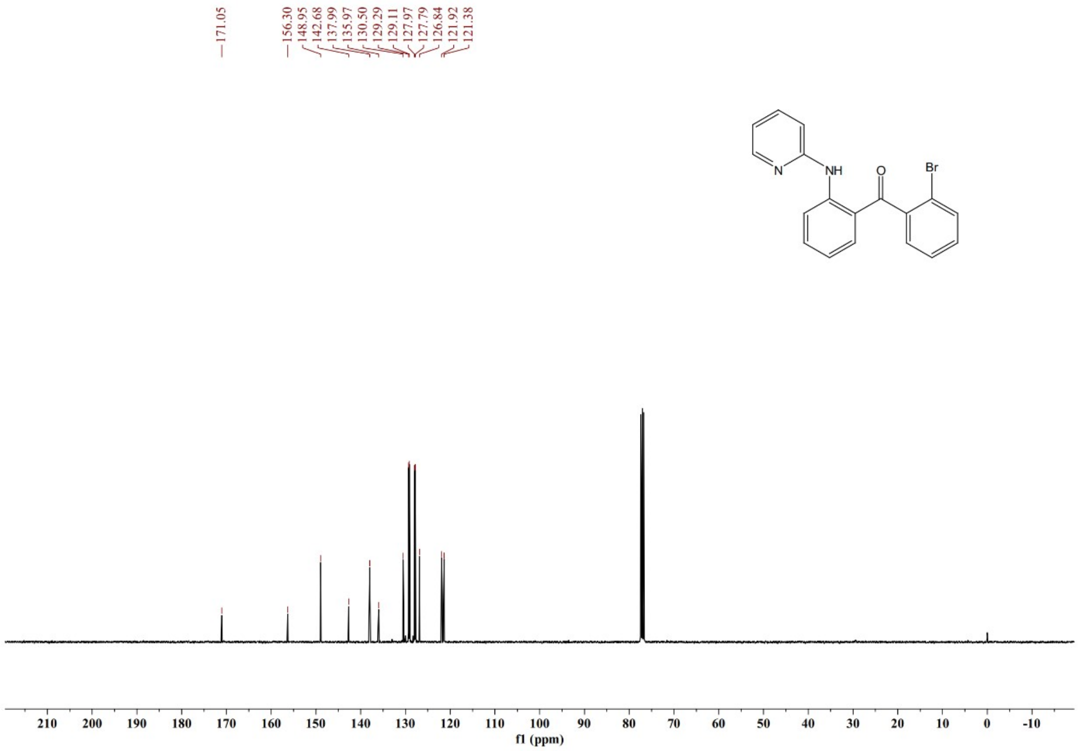
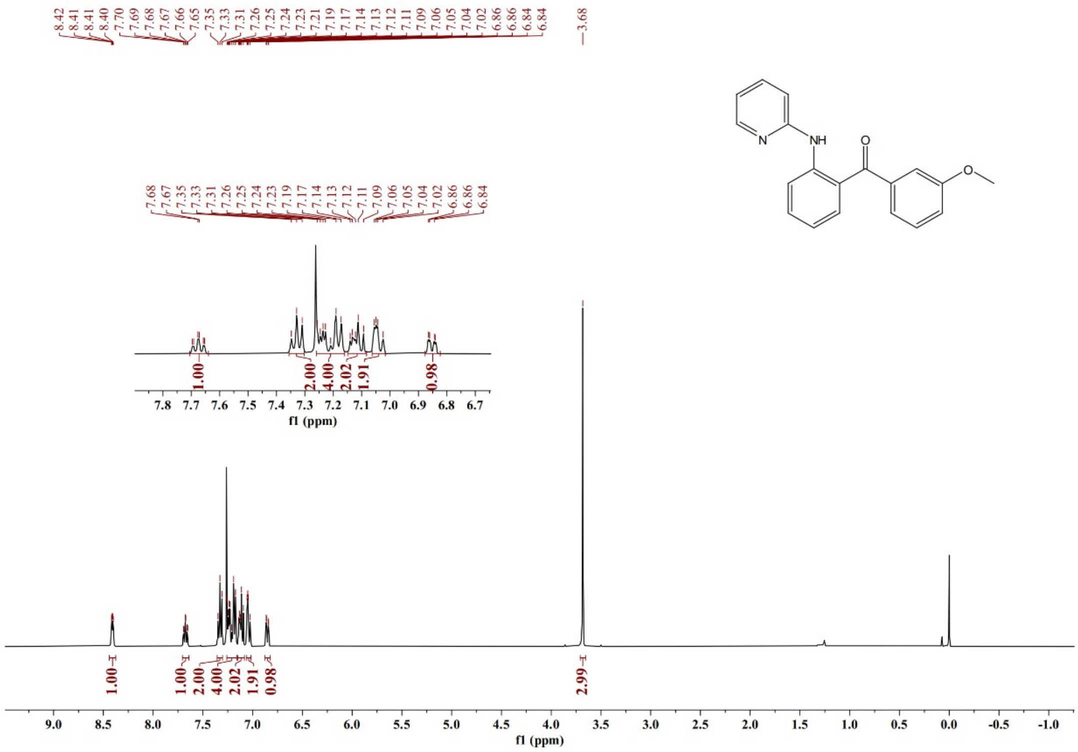


^{13}C NMR (101 MHz, $CDCl_3$) of 3aj



^{1}H NMR (400 MHz, $CDCl_3$) of 3ak



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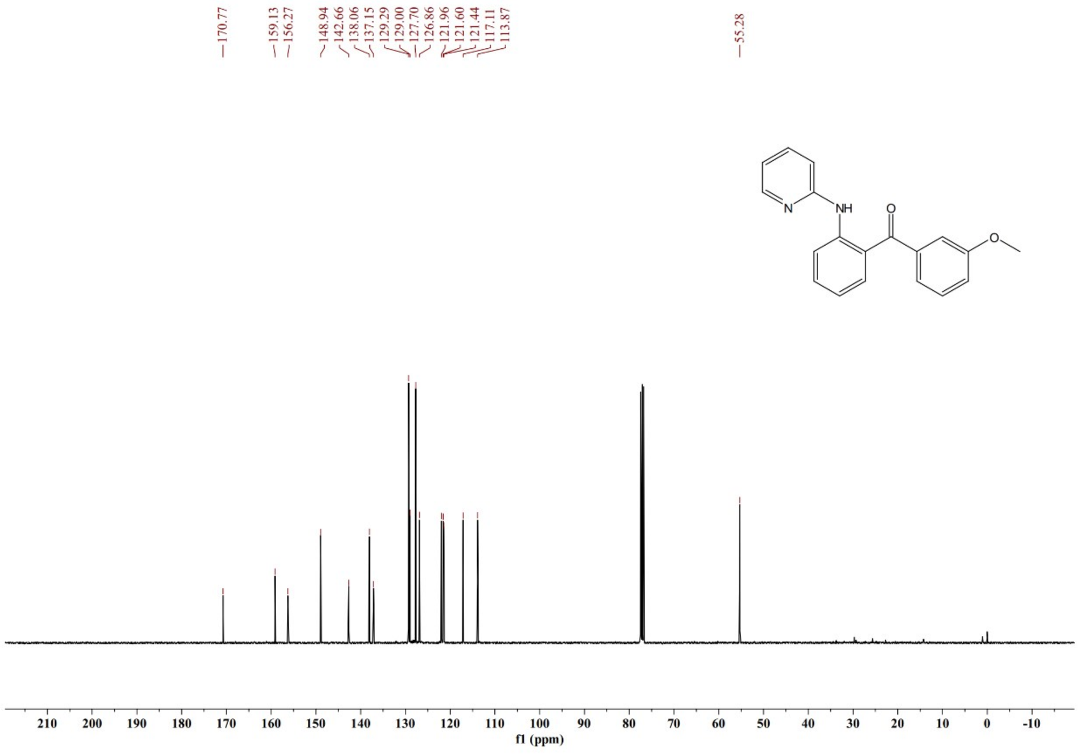
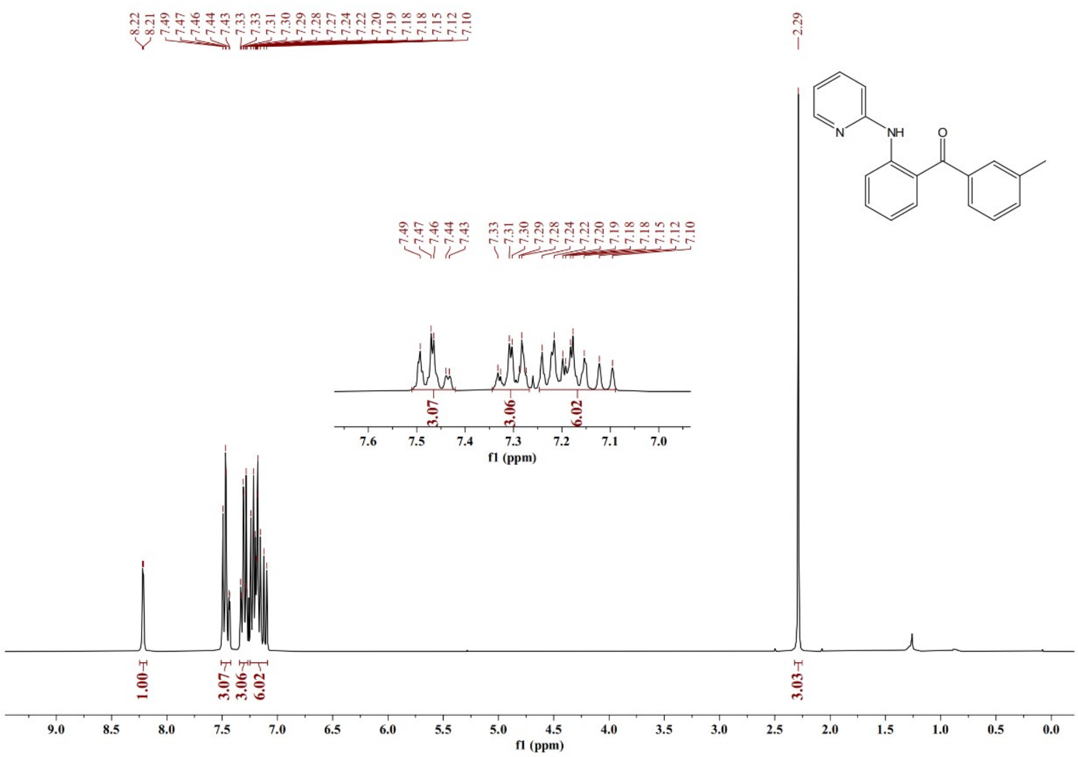
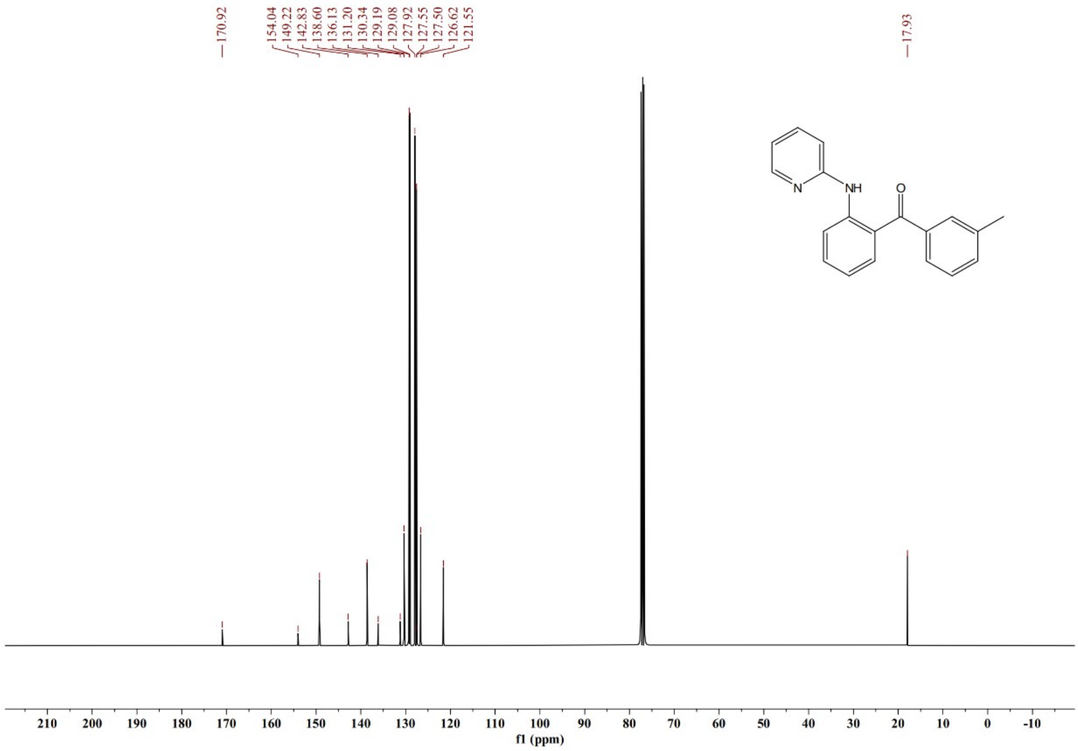


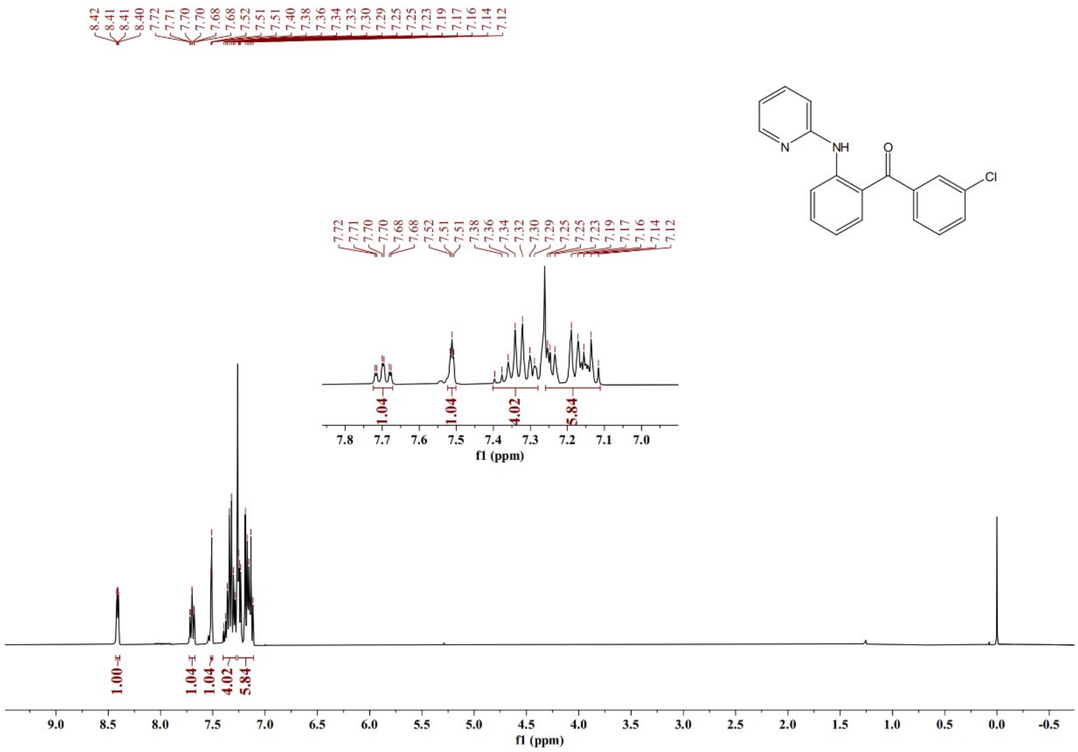
^{1}H NMR (400 MHz, $CDCl_3$) of 3al



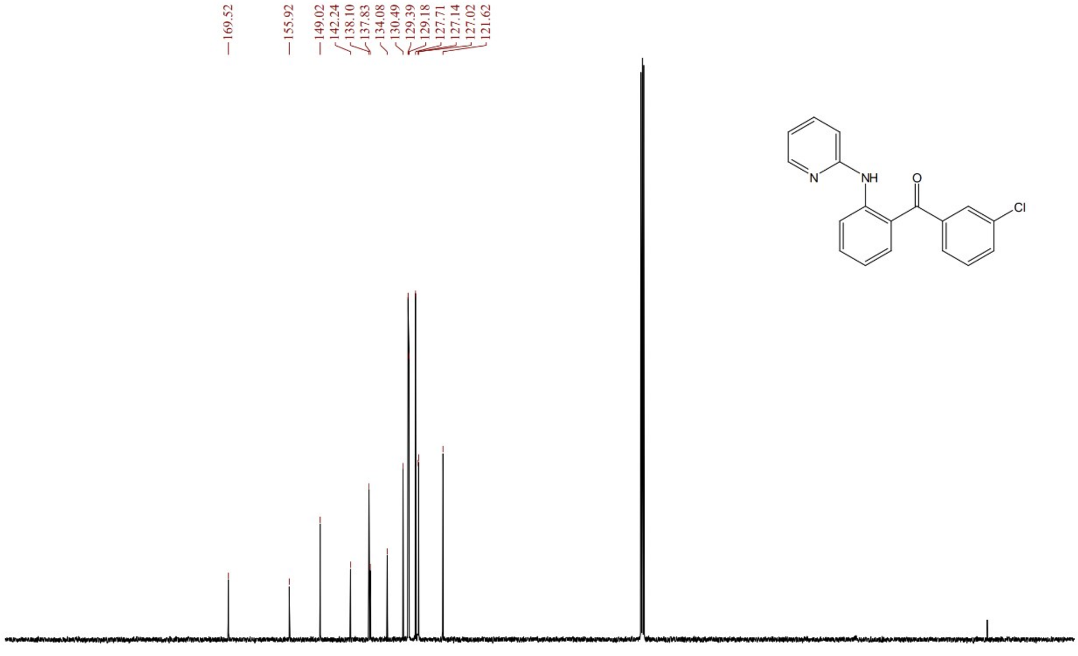
^{13}C NMR (101 MHz, $CDCl_3$) of 3al



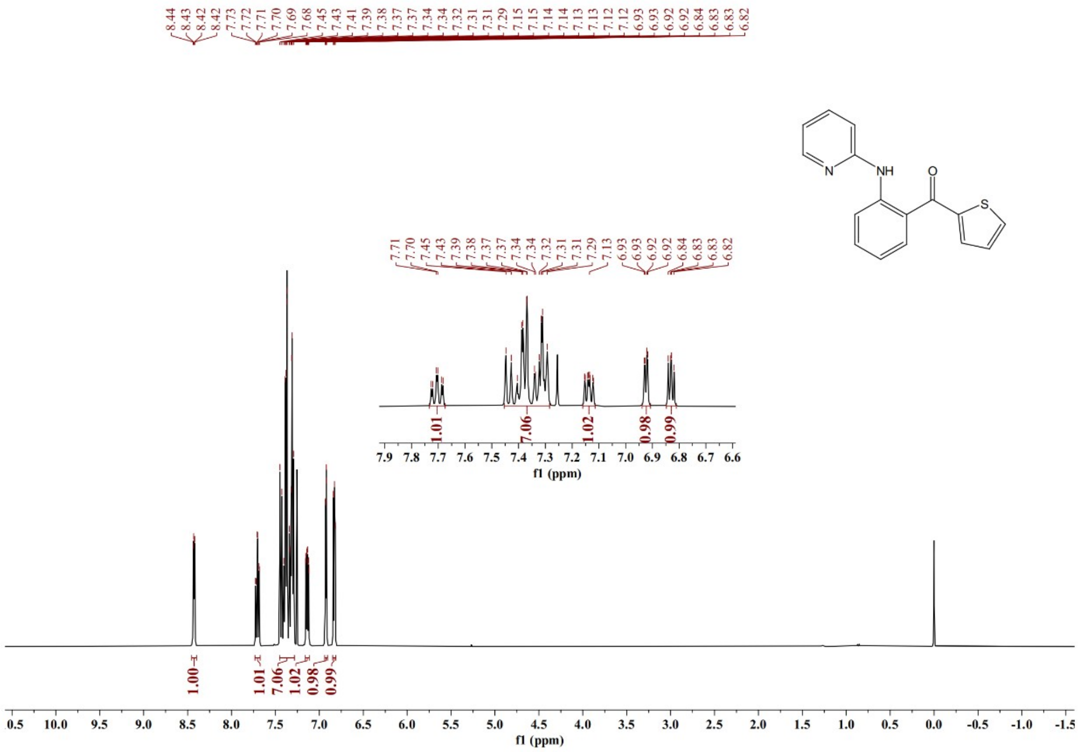
^{1}H NMR (400 MHz, $CDCl_3$) of 3am



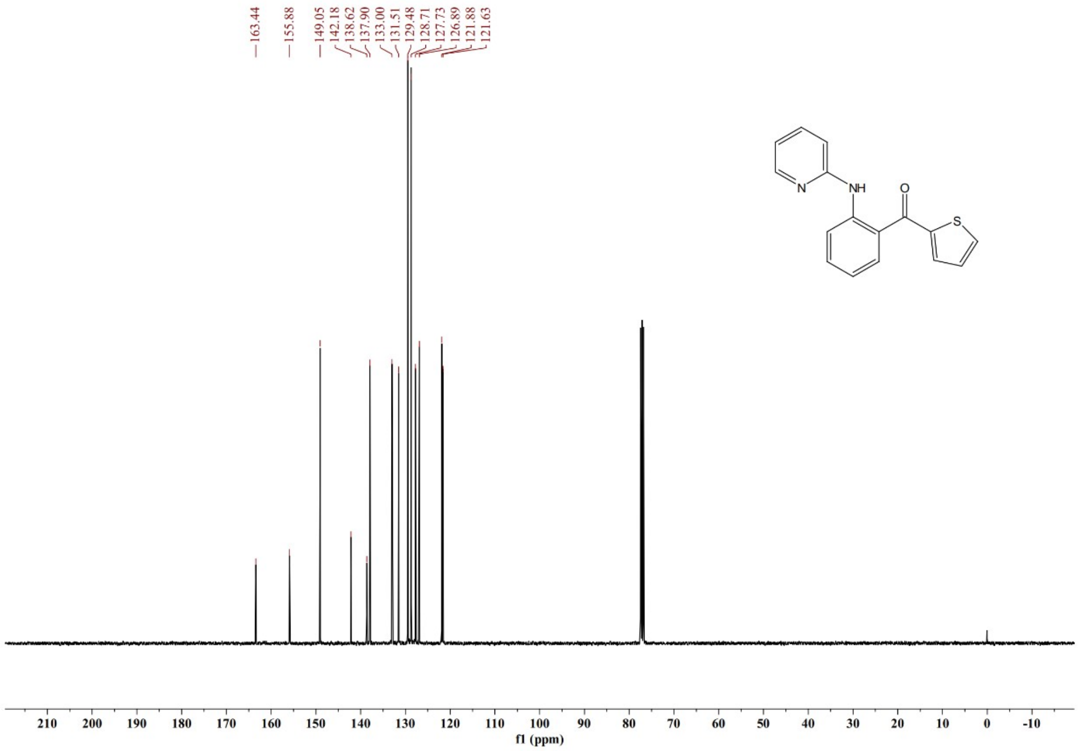
^{13}C NMR (101 MHz, $CDCl_3$) of 3am



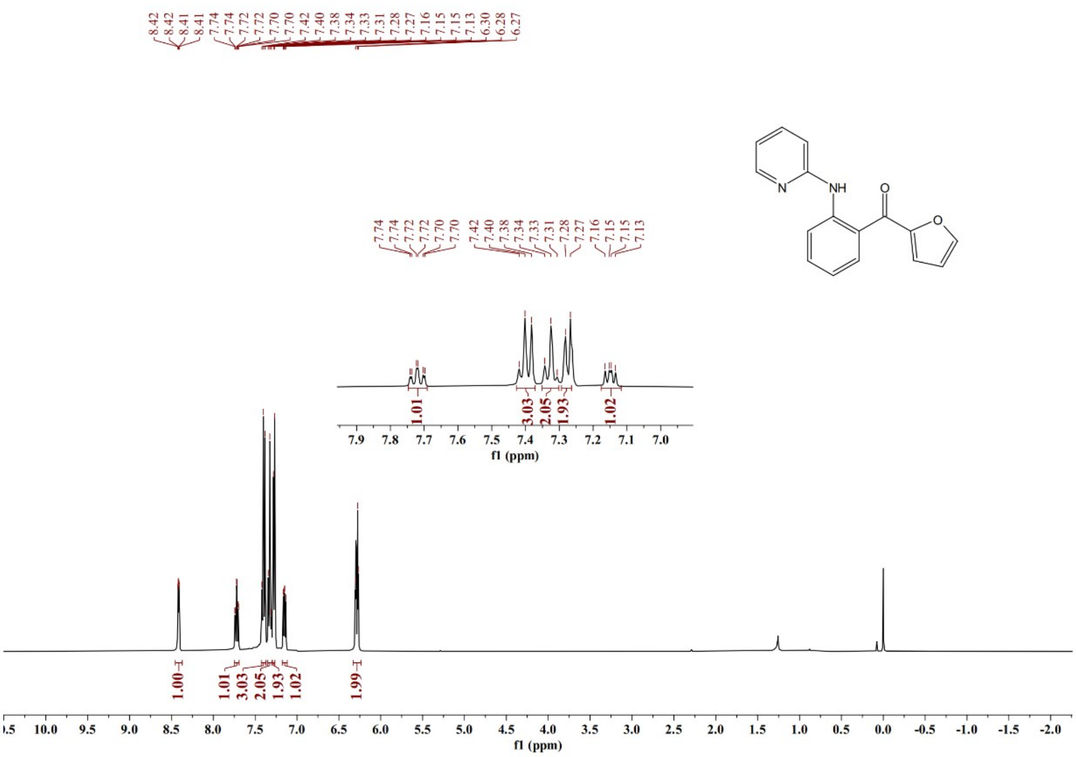
^{1}H NMR (400 MHz, $CDCl_3$) of 3an



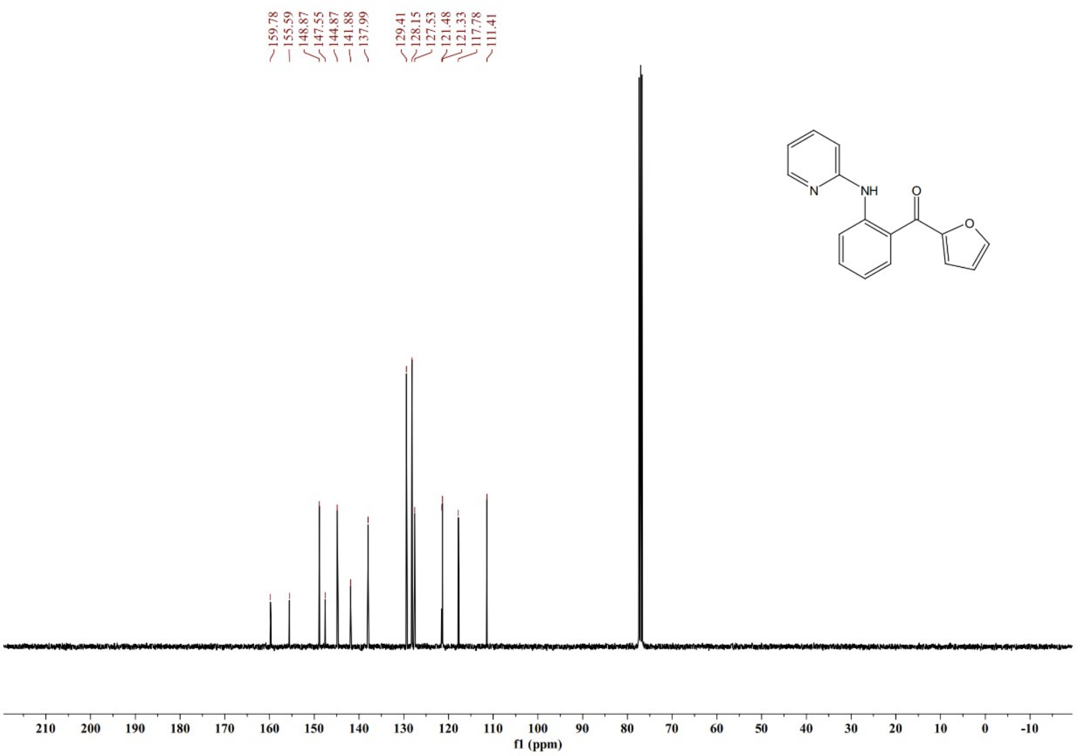
^{13}C NMR (101 MHz, $CDCl_3$) of 3an



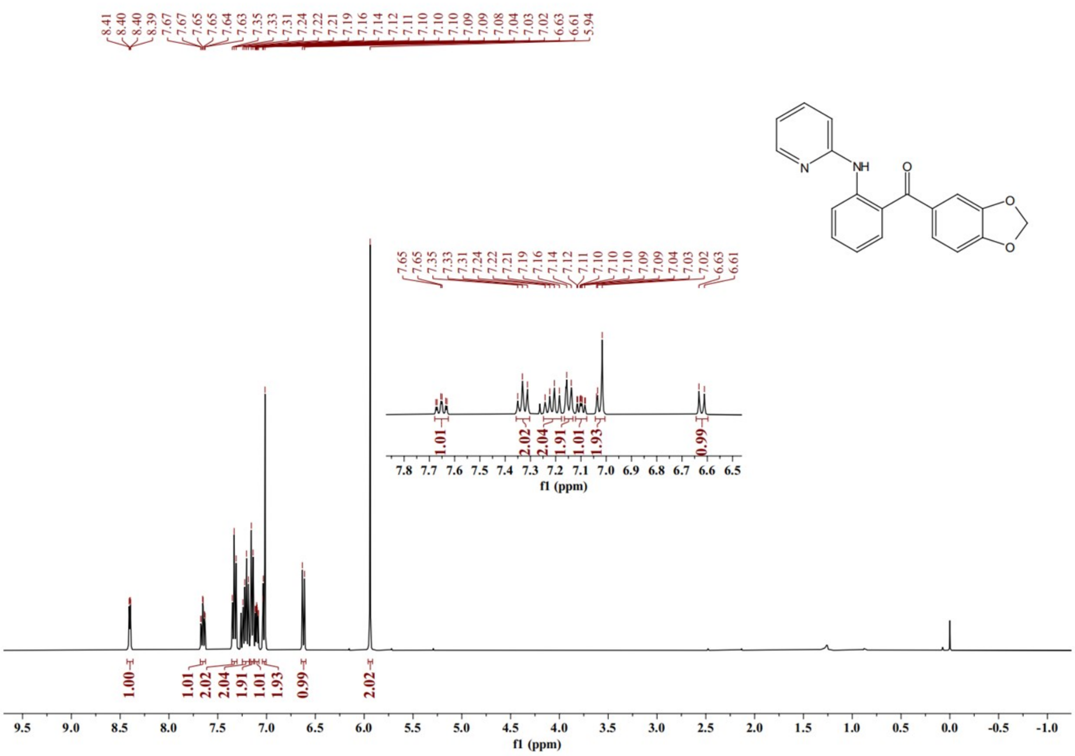
^{1}H NMR (400 MHz, $CDCl_3$) of 3ao



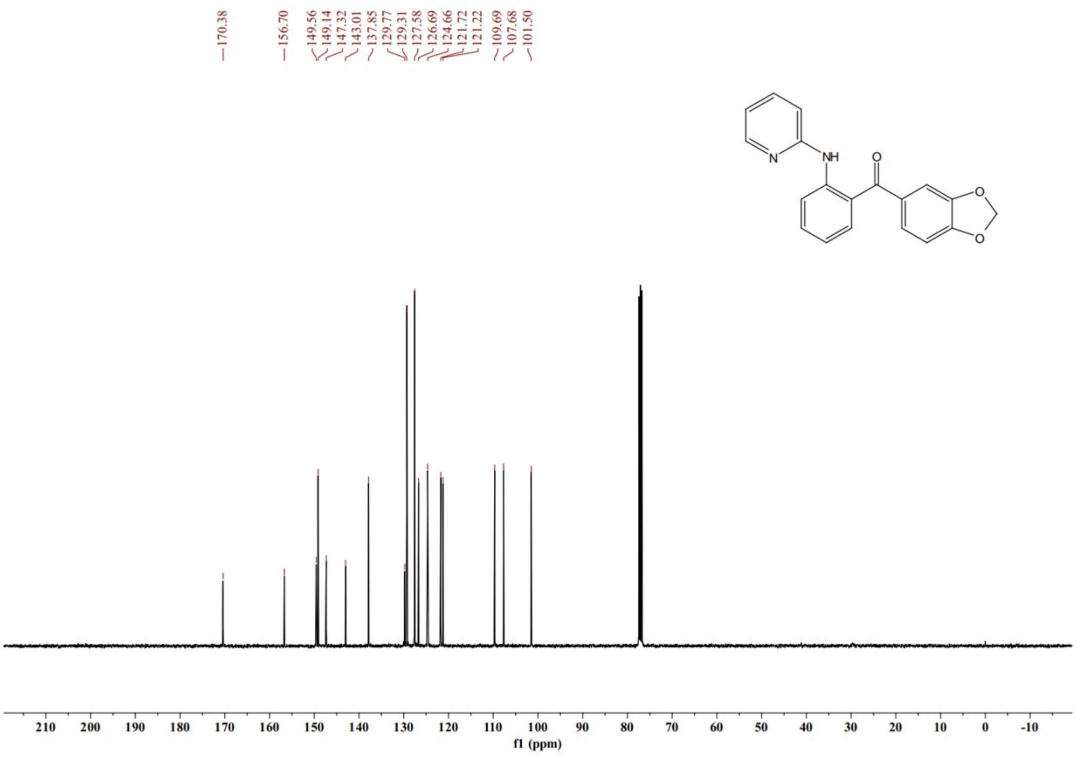
^{13}C NMR (101 MHz, $CDCl_3$) of 3ao



^{1}H NMR (400 MHz, $CDCl_3$) of 3ap



^{13}C NMR (101 MHz, $CDCl_3$) of 3ap



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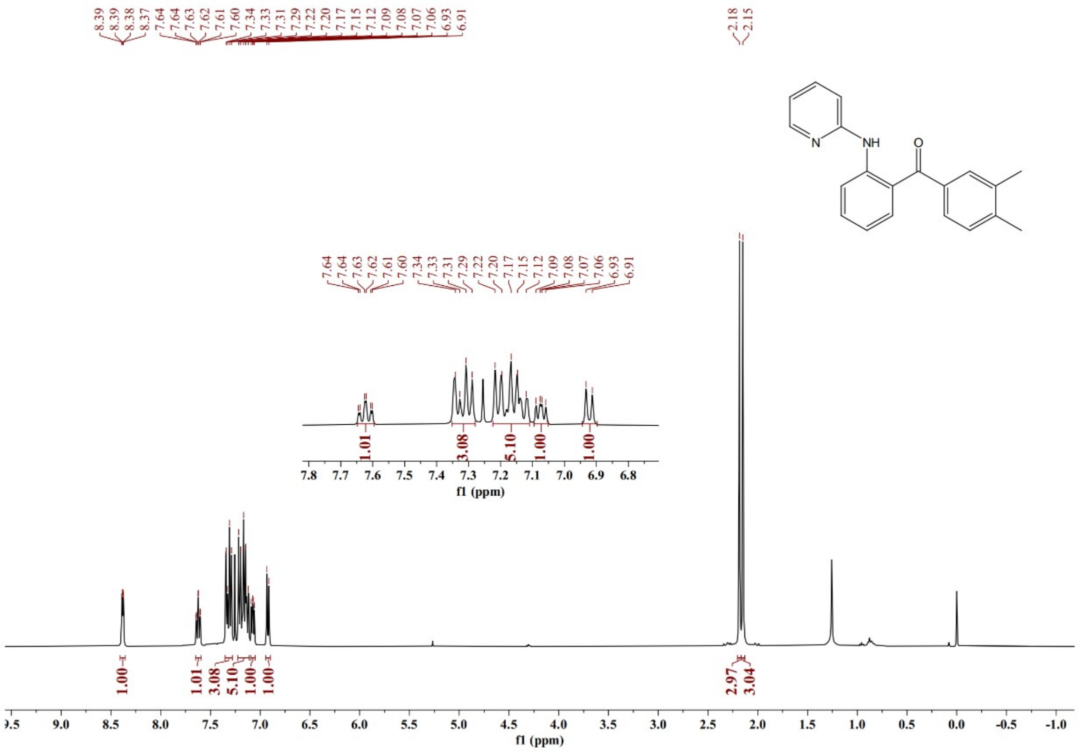
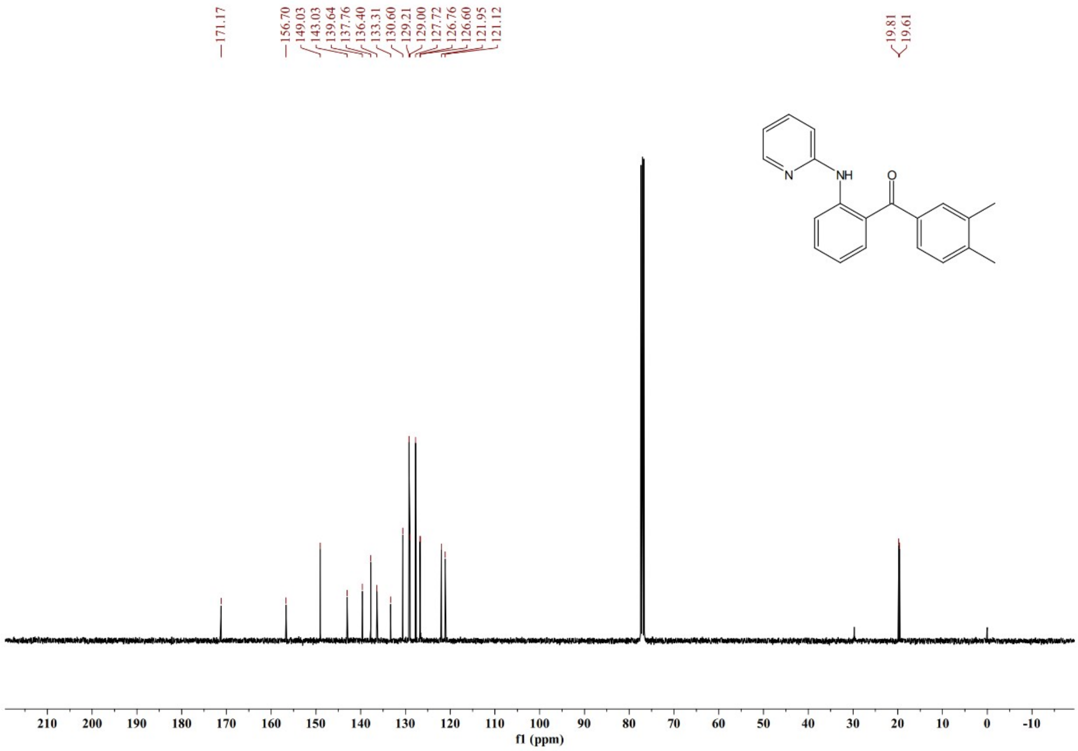
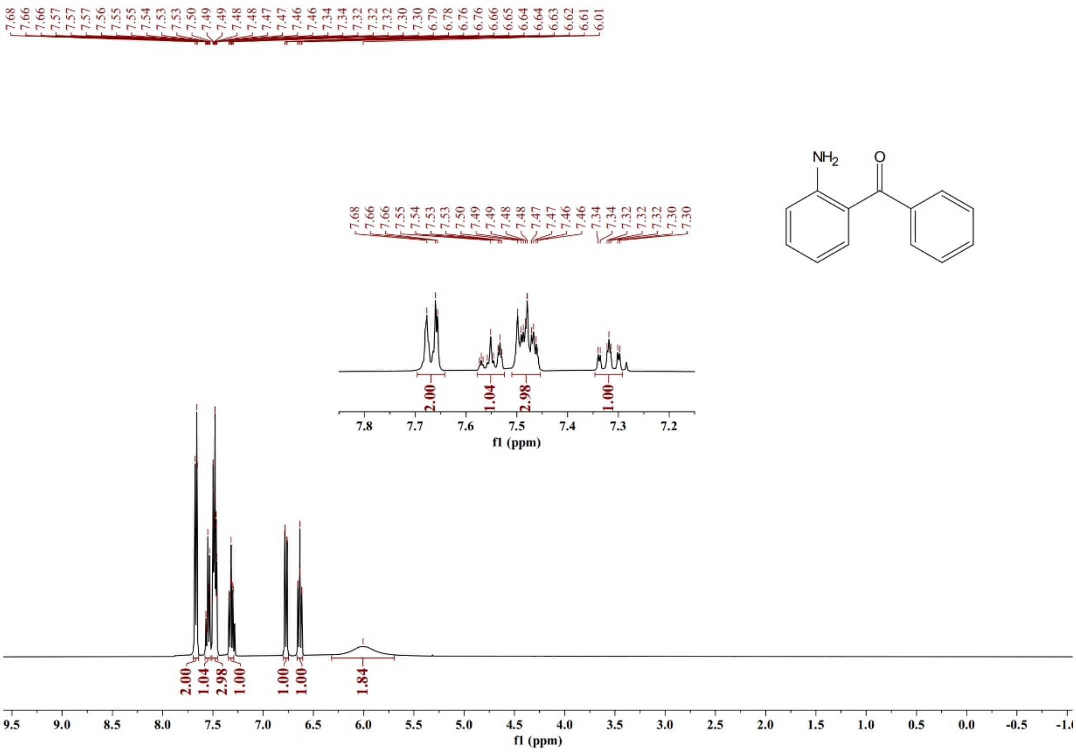


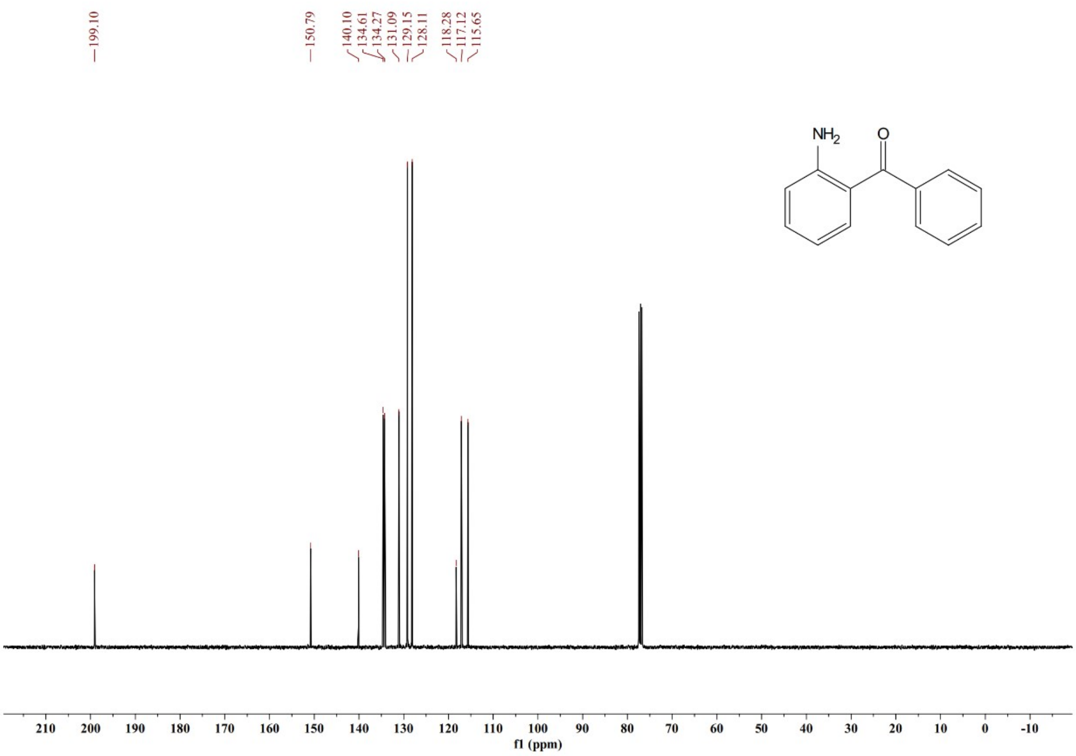
[13]C NMR (101 MHz, $CDCl_3$) of 3aq



^{1}H NMR (400 MHz, $CDCl_3$) of 4aa



^{13}C NMR (101 MHz, $CDCl_3$) of 4aa



¹H NMR (400 MHz, $CDCl_3$) of 5aa