Supporting Information For

Porous cross-linked polymer copper and iridium catalyzed the synthesis of quinoxalines and functionalized ketones under solvent-free conditions †

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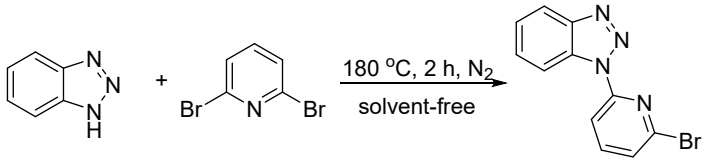
Contents

1. General methods and materials

Unless the special instructions, all the reagents were provided from commercial suppliers and used without further purifications (J&K, Energy Chemical, Acros, TCI, etc.). All the obtained products were characterized by ^{1}H-NMR, ^{13}C-NMR and referenced to DMSO-d_6 (2.50 ppm for ^{1}H, and 39.5 ppm for ^{13}C) or $CDCl_3$ (7.26 ppm for ^{1}H, and 77.1 ppm for ^{13}C) with tetramethylsilane as internal standard (0 ppm). ^{1}H-NMR and ^{13}C-NMR spectra were obtained on Varian 400 or 101 MHz respectively on Bruker Advance III HD 400 MHz spectrometer. Analytical thin layer chromatography (TLC) was performed using commercially prepared 100-400 mesh silica gel plates (SGF254). Flash column chromatography was performed on 230-430 mesh silica gel. High resolution mass spectra (HRMS) were recorded on LTQ-FTUHRA mass spectrometer. GC-MS recorded on GCMS-QP2010Ultra.

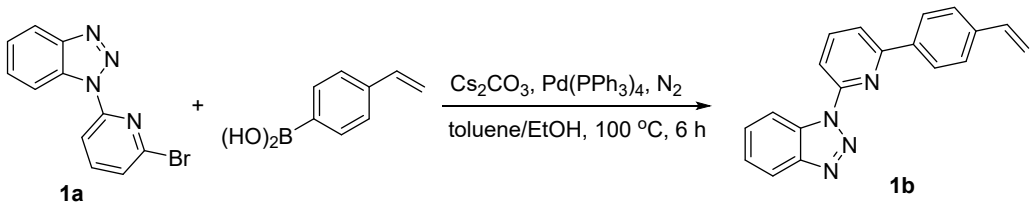
2. Synthesis of PCP-BTA-Cu and PCP-BTA-Ir

2.1 Procedure for synthesis of 1-(6-bromo-2-pyridinyl)-1H-benzotriazole (**1a**)



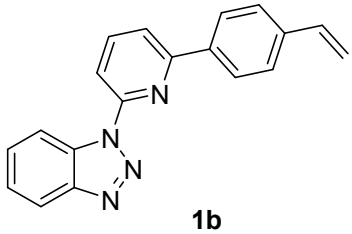
1-(6-Bromo-2-pyridinyl)-1H-benzotriazole (**1a**) was synthesized according to literature[1]. A mixture of benzotriazole (3.570 g, 30.0 mmol) and 2,6-dibromopyridine (4.740 g, 20.0 mmol) was heated to 180 °C under N_2 and allowed to stir for 2 h. After the reaction mixture was cooled to room temperature, the reaction mixture was added water and extracted with dichloromethane three times. The organic phases were dried over anhydrous Na_2SO_4 and concentrated by removing the solvent under vacuum to give a crude product. Finally, the residue was subjected to purification by silica gel column chromatography with eluent petroleum ether/ethyl acetate to afford the desired product (**1a**, 70% yield, 3.861 g, Mp.80.1−82.6 °C).

2.2. Procedure for synthesis of 1-(6-(4-vinylphenyl)pyridin-2-yl)-1H-benzo[d][1,2,3]triazole (**1b**).



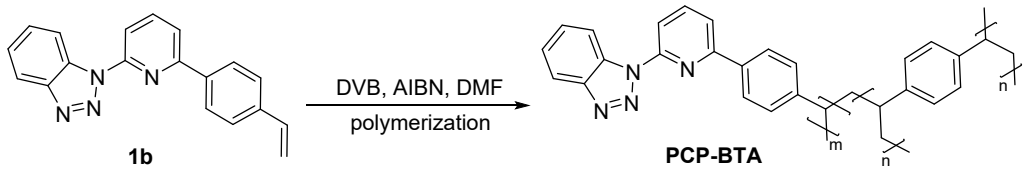
1-(6-(4-vinylphenyl) pyridin-2-yl)-1*H*-benzo[d] [1,2,3] triazole (**1b**) was synthesized according to literature.[2] A mixture of triazole intermediate (**1a**, 1.38 g, 5 mmol), 4-vinylbenzyl boronic acid (1.030 g, 7 mmol) and Cs_2CO_3 (2.600 g, 8 mmol) were dissolved in solvent mixture of toluene/EtOH (10:1 mixture, 40 mL) and $Pd(PPh_3)_4$ (0.290 g, 0.25 mmol) was added subsequently. The resulting mixture was stirred at 100 °C for 6 hours under N_2 atmosphere. After the reaction mixture was cooled to room temperature, the reaction mixture was added water and extracted with ethyl acetate three times. The organic phases were dried over anhydrous $MgSO_4$ and concentrated by removing the solvent under vacuum to give a crude product. The crude product was purified by column chromatography, eluting with petroleum ether/ethyl acetate to afford the desired product (**1b**, 80% yield, 1.190 g, Mp.166.5-168.3 °C).

1-(6-(4-vinylphenyl) pyridin-2-yl)-1*H*-benzo[d] [1,2,3] triazole (1b)



White solid, Mp.166.5-168.3 °C, 80% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, *J* = 8.4 Hz, 1H), 8.25 (d, *J* = 8.1 Hz, 1H), 8.17 (d, *J* = 8.3 Hz, 1H), 8.10 (d, *J* = 8.3 Hz, 2H), 8.00 (t, *J* = 7.9 Hz, 1H), 7.77 (d, *J* = 7.7 Hz, 1H), 7.64 (dd, *J* = 15.5, 8.0 Hz, 3H), 7.50 (t, *J* = 7.5 Hz, 1H), 6.83 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.90 (d, *J* = 17.6 Hz, 1H), 5.38 (d, *J* = 10.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.09, 151.54, 146.81, 139.70, 138.83, 137.65, 136.22, 131.53, 128.89, 127.14, 126.85, 124.94, 119.92, 118.58, 115.08, 114.80, 112.71. HRMS Calculated for $C_{19}H_{15}N_4$ $[M+H]^+$ 299.1297, found 299.1293.

2.3 Procedure for synthesis of **PCP-BTA**



The polymer monomer **1b** (0.500 g) and Divinylbenzene (DVB, 2.000 g) were dissolved in DMF (20 mL), followed by the addition of 2,2'-azobis (2-methylpropionitrile) (AIBN, 0.050 g). After stirring for 2 h at room temperature, the solution was transferred into an autoclave for 24 h at 100 °C. Subsequently, the mixture solution was cooled to room temperature and the obtained solid was washed three times with anhydrous ethanol, a white solid product was obtained, which was **PCP-BTA**.

2.4.1 Procedure for synthesis of **PCP-BTA-Cu**

Under N_2 atmosphere, **PCP-BTA** (1.000 g), $Cu(CH_3COOH)_2 \cdot H_2O$ (200 mg) and dry DMF (20 mL) was added to 50 mL Schlenk tube. Then, the resulting mixture was stirred at 70 °C for 12 h. After cooling down to room temperature centrifugation, washing with water three times, and drying at 80°C, the dark green solid was obtained, which was denoted as **PCP-BTA-Cu.**

2.4.2 Procedure for synthesis of **PCP-BTA-Ir**

Under N_2 atmosphere, **PCP-BTA** (1.000 g), $[Cp^*IrCl_2]_2$ (200 mg) and dry methanol (20 mL) was added to 50 mL Schlenk tube. Then, the resulting mixture was stirred at 60°C for 12 h. After cooling down to room temperature centrifugation, washing with methanol three times, and drying at 75 °C, the yellow solid was obtained, which was denoted as **PCP-BTA-Ir.**

3. Characterization of PCP-BTA-Cu and PCP-BTA-Ir

Fig.S1 showed SEM and TEM images of PCP-BTA-Cu, PCP-BTA-Ir after five runs.

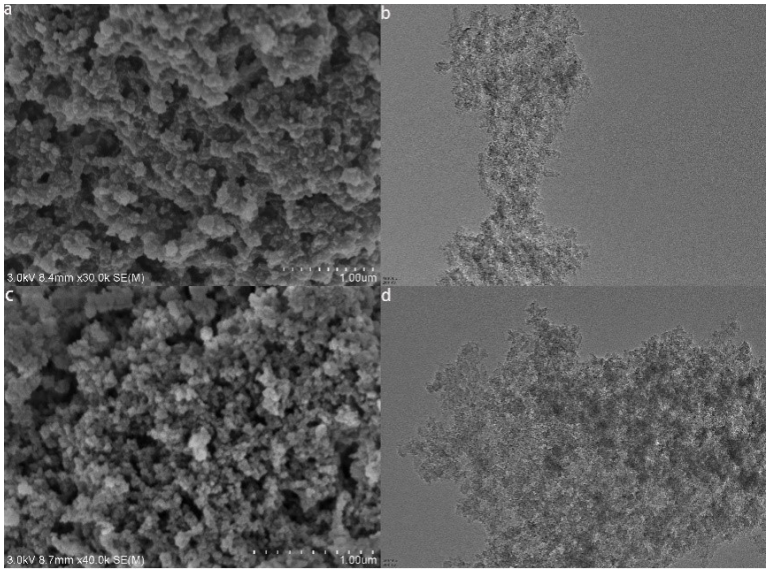


Fig.S1. (a) SEM images of PCP-BTA-Cu after five runs, (b) TEM images of PCP-BTA-Cu after five runs, (c) SEM images of PCP-BTA-Ir after five runs, (d) TEM images of PCP-BTA-Ir after five runs.

Fig.S2 showed SEM EDS image of PCP-BTA-Cu (a), (b), and corresponding elemental mapping images of (c) C, (d) N, (e) Cu, (f) O, which revealed cooper complex was supported on PCP-BTA successfully.

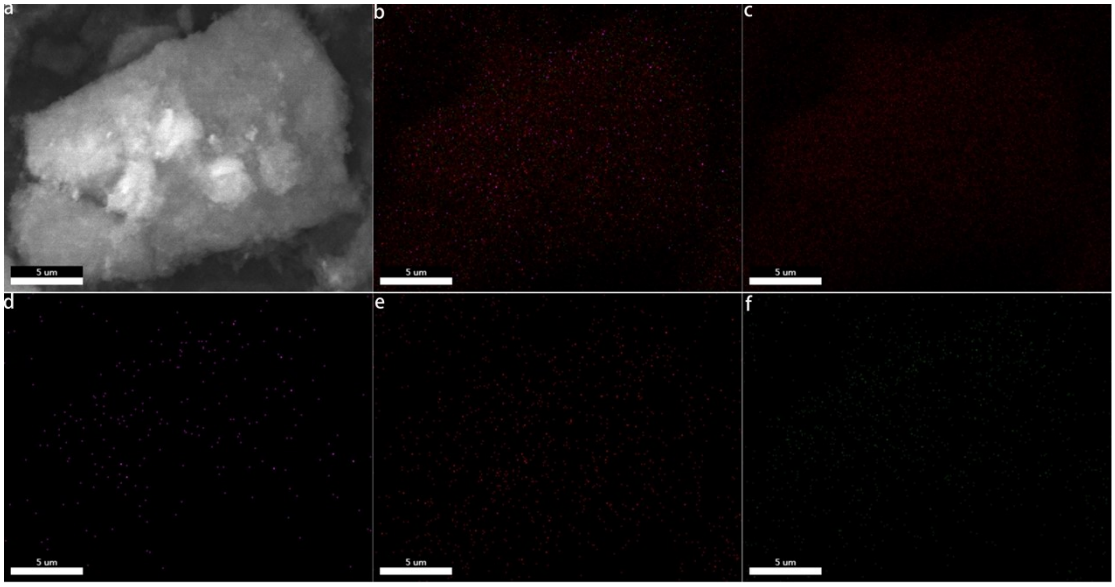


Fig.S2. SEM EDS image of PCP-BTA-Cu (a), (b), and corresponding elemental mapping images of (c) C, (d) N, (e) Cu, (f) O.

Fig.S3 showed SEM EDS image of PCP-BTA-Ir (a), (b), and corresponding elemental mapping images of (c) C, (d) N, (e) Ir, (f) Cl, which revealed iridium complex was supported on PCP-BTA successfully.

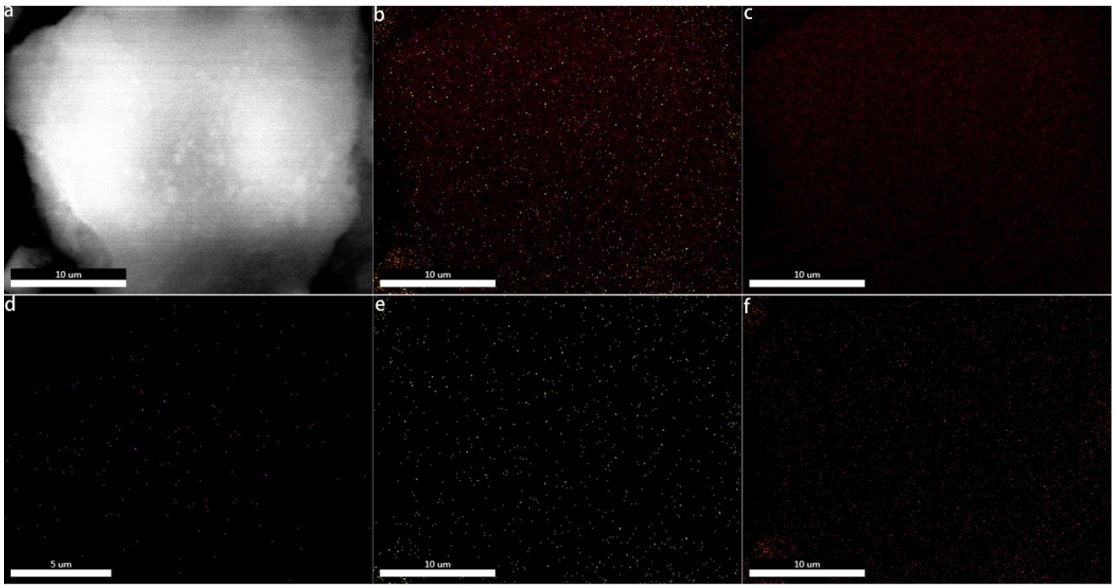


Fig.S3. SEM EDS image of PCP-BTA-Ir (a), (b), and corresponding elemental mapping images of (c) C, (d) N, (e) Ir, (f) Cl.

Table.S1. Quantitative elemental composition of C, O, N and Cu from the PCP-BTA-Cu XPS data.

Name	Start (BE)	Peak (BE)	End (BE)	Height (CPS)	FWHM (eV)	Area (P) CPS. (eV)	Area (N) TPP-2M	Atomic (%)
N 1s	408	398.39	394	1365.59	1.62	3463.98	31.27	2.08
Cu 2p	967.63	932.78	929	2486.65	3.34	20790.11	19.54	1.3
O 1s	540	531.44	526	2152.85	2.86	8187.33	47.48	3.16
C 1s	296	283.99	281	54853.37	1.56	100163.22	1403.8	93.46

Table.S2. Quantitative elemental composition of C, Ir, N and Cl from the PCP-BTA-Ir XPS data.

Name	Start (BE)	Peak (BE)	End (BE)	Height (CPS)	FWHM (eV)	Area (P) CPS.(eV)	Area (N) TPP-2M	Atomic (%)
Ir 4f	72.58	62.65	56.78	1627.32	1.78	5656.54	0.01	0.55
Cl 2p	210.58	198.89	190.78	822.88	3.02	3032.98	0.02	1.54
C 1s	296.58	284.77	279.78	35275.94	1.63	66563.14	1.52	94.19
N 1s	410.58	399.15	392.78	965.46	1.53	4286.15	0.06	3.72

4. General procedure for 4 from diamines

To 25 mL pressure tube was added 1,2-diamine (1.0 mmol), vicinal diol (2.5 mmol), PCP-BTA-Cu (15 mg), $CsOH·H_2O$ (0.75 equiv.). Then, the pressure tube was placed in oil bath (150 ^oC) for 12 h. After the reaction mixture was cooled to room temperature, the reaction mixture was added water and extracted with ethyl acetate three times. The organic phases were dried over anhydrous $MgSO_4$ and concentrated by removing the solvent under vacuum to give a crude product. The crude product was purified by column chromatography, eluting with petroleum ether/ethyl acetate to afford the desired product **4**.

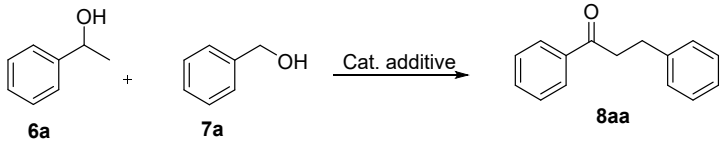
5. General procedure for 4 from nitroanilines

To 25 mL pressure tube was added 2-nitroaniline (1.0 mmol), vicinal diol (3.0 mmol), PCP-BTA-Cu (15 mg), $CsOH·H_2O$ (0.75 equiv.). Then, the pressure tube was placed in oil bath (150 ^oC) for 12 h. After the reaction mixture was cooled to room temperature, the reaction mixture was added water and extracted with ethyl acetate three times. The organic phases were dried over anhydrous $MgSO_4$ and concentrated by removing the solvent under vacuum to give a crude product. The crude product was purified by column chromatography, eluting with petroleum ether/ethyl acetate to afford the desired product **4**.

6. General procedure for 8

To 25 mL reaction tube was added secondary alcohol (1.0 mmol), primary alcohol (3.0 mmol), PCP-BTA-Ir (15 mg), KOH (0.5 equiv.). Then, the mixture was heated at 100 °C for 12 h. After the reaction mixture was cooled to room temperature, the reaction mixture was added water and extracted with ethyl acetate three times. The organic phases were dried over anhydrous $MgSO_4$ and concentrated by removing the solvent under vacuum to give a crude product. The crude product was purified by column chromatography, eluting with petroleum ether/ethyl acetate to afford the desired product **8**. Please see Table S3 for the optimization of reaction conditions.

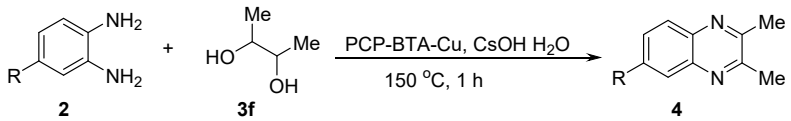
Table S3. Optimization of reaction conditions. [a]



Entry	Catalyst	Base	Time [h]	Solvent	Temperature [°C]	Yield [%][b]
1	—	KOH	12	toluene	100	15
2	PCP-BTA-Ir	KOH	12	toluene	100	88
3	**PCP-BTA-Ir**	**KOH**	**12**	**-**	**100**	**92**
4	PCP-BTA-Ir	K_2CO_3	12	toluene	100	25
5	PCP-BTA-Ir	NaOH	12	toluene	100	80
6	PCP-BTA-Ir	KO*t*Bu	12	toluene	100	45
7	PCP-BTA-Ir	$CsOH·H_2O$	12	toluene	100	81
8	PCP-BTA-Ir	KOH	12	H_2O	100	10
9	PCP-BTA-Ir	KOH	12	1,4-dioxane	100	75
10	PCP-BTA-Ir	KOH	12	-	130	91
11	PCP-BTA-Ir	KOH	12	-	90	87
12	PCP-BTA-Ir	KOH	8	-	100	84
13	PCP-BTA-Ir	KOH	16	-	100	92

[a] Reagents and conditions: **6a** (1.0 mmol), **7a** (3.0 mmol), KOH (0.5 mmol), PCP-BTA-Ir (15 mg), 100 °C, 12 h. [b] Yields of isolated product.

7. Hammett plot equation



Experimental procedure: To 25 mL pressure tube was added 1,2-diamine (1.0 mmol), 2,3-butanediol (**3f**, 2.5 mmol), PCP-BTA-Cu (15 mg), $CsOH·H_2O$ (0.75 equiv.). Then, the pressure

tube was heated at 150 °C for 1 h. After centrifugation and recycle the catalyst, the water mixture was extracted with ethyl acetate three times. Next, the yield of product **4** was determined by GC.

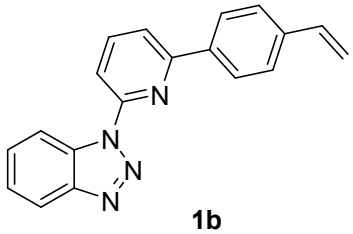
R	OMe	Me	H	F	Cl
Yield	22%	18%	14%	8%	6%

8. Reusability of the catalyst

To 25 mL pressure tube was added *o*-phenylenediamine (1.0 mmol), 1,2-propanediol (2.5 mmol), PCP-BTA-Cu (15 mg), $CsOH·H_2O$ (0.75 equiv.) and NaOAc (0.2 equiv.). Then, the pressure tube was placed in oil bath (150 °C) for 12 h. After the reaction mixture was cooled to room temperature, the catalyst was separated by centrifugation with ethyl acetate, washed with methanol and ethanol, dried in a vacuum, and reused for the next time.

9. Analytical data of the obtained compounds

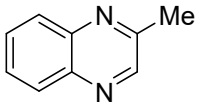
1-(6-(4-vinylphenyl) pyridin-2-yl)-1*H*-benzo[d] [1,2,3] triazole (1b)



1b

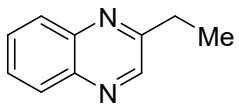
White solid, Mp.166.5-168.3 °C, 80% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, *J* = 8.4 Hz, 1H), 8.25 (d, *J* = 8.1 Hz, 1H), 8.17 (d, *J* = 8.3 Hz, 1H), 8.10 (d, *J* = 8.3 Hz, 2H), 8.00 (t, *J* = 7.9 Hz, 1H), 7.77 (d, *J* = 7.7 Hz, 1H), 7.64 (dd, *J* = 15.5, 8.0 Hz, 3H), 7.50 (t, *J* = 7.5 Hz, 1H), 6.83 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.90 (d, *J* = 17.6 Hz, 1H), 5.38 (d, *J* = 10.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.09, 151.54, 146.81, 139.70, 138.83, 137.65, 136.22, 131.53, 128.89, 127.14, 126.85, 124.94, 119.92, 118.58, 115.08, 114.80, 112.71. HRMS Calculated for $C_{19}H_{15}N_4$ $[M+H]^+$ 299.1297, found 299.1293.

(1) 2-methylquinoxaline (4aa) [3]**.**



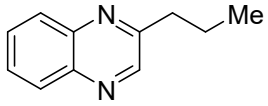
Yellow liquid, 90% from diamine, 91% from nitroaniline; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (s, 1H), 8.05 (d, *J* = 7.7 Hz, 1H), 8.00 (d, *J* = 8.1 Hz, 1H), 7.74 – 7.65 (m, 2H), 2.75 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.76, 145.99, 142.04, 140.94, 130.00, 129.15, 128.91, 128.64, 22.57.

(2) 2-ethylquinoxaline (4ab) [3]**.**



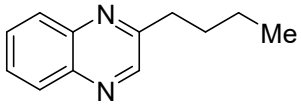
Yellow liquid, 88% from diamine, 89% from nitroaniline; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (s, 1H), 7.97 – 7.91 (m, 2H), 7.59 (ddd, *J* = 9.6, 7.8, 1.6 Hz, 2H), 2.93 (q, *J* = 7.6 Hz, 2H), 1.32 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.38, 145.51, 142.08, 141.16, 129.84, 129.11, 128.83, 128.80, 29.56, 13.35.

(3) 2-propylquinoxaline (4ac) [4]**.**



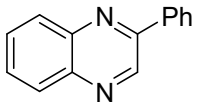
Yellow liquid, 80% from diamine, 83% from nitroaniline; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (s, 1H), 8.12 – 8.04 (m, 2H), 7.79 – 7.68 (m, 2H), 3.05 – 2.98 (m, 2H), 1.91 (h, *J* = 7.4 Hz, 2H), 1.06 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.48, 145.85, 142.19, 141.23, 129.94, 129.17, 128.94, 128.85, 38.42, 22.85, 13.93.

(4) 2-butylquinoxaline (4ad) [3]**.**



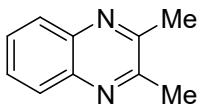
Yellow dense liquid, 77% from diamine, 79% from nitroaniline; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (s, 1H), 8.14 – 8.04 (m, 2H), 7.81 – 7.68 (m, 2H), 3.09 – 3.00 (m, 2H), 1.86 (t, *J* = 7.7 Hz, 2H), 1.49 (q, *J* = 7.5 Hz, 2H), 1.00 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.70, 145.84, 142.14, 141.20, 129.98, 129.16, 128.96, 128.81, 36.24, 31.66, 22.59, 13.90.

(5) 2-phenylquinoxaline (4ae) [3]**.**



Yellow dense liquid, 86% from diamine, 82% from nitroaniline; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.36 (s, 1H), 8.30 – 8.10 (m, 4H), 7.86 – 7.74 (m, 2H), 7.63 – 7.51 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.89, 143.36, 142.33, 141.57, 136.79, 130.33, 130.22, 129.65, 129.59, 129.19, 129.13, 127.58.

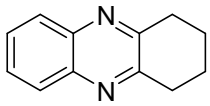
(6) 2,3-dimethylquinoxaline (4af) [3]**.**



Yellow solid, Mp.104.2-106.8 °C, 85% from diamine, 92% from nitroaniline; ^{1}H NMR (400 MHz,

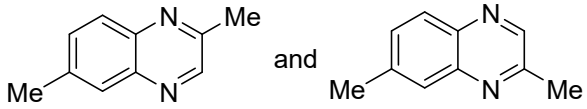
$CDCl_3$) δ 7.99 (dd, *J* = 6.3, 3.5 Hz, 2H), 7.67 (dd, *J* = 6.4, 3.4 Hz, 2H), 2.74 (s, 6H). ^{3}C NMR (101 MHz, $CDCl_3$) δ 153.41, 141.04, 128.78, 128.28, 23.14.

(7) 1,2,3,4-tetrahydrophenazine (4ag) [5]**.**



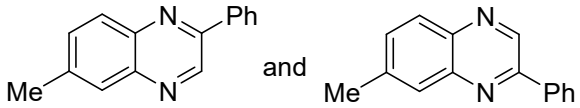
Yellow solid, Mp.91.9-93.3 °C, 92% from diamine, 80% from nitroaniline; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 6.3, 3.5 Hz, 2H), 7.67 (dd, *J* = 6.4, 3.4 Hz, 2H), 3.22 – 3.13 (m, 4H), 2.05 (p, *J* = 3.3 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.14, 141.19, 128.93, 128.32, 33.19, 22.79.

(8) 2,6-dimethylquinoxaline and 2,7-dimethylquinoxaline (4ah) [3]**.**



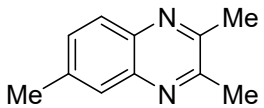
Yellow solid, the two regio-isomers were inseparable in column chromatography. 83% isolated yield from diamine; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 10.3 Hz, 1H), 7.96 – 7.88 (m, 1H), 7.84 – 7.75 (m, 1H), 7.54 (ddd, *J* = 15.4, 8.6, 2.0 Hz, 1H), 2.75 (s, 3H), 2.57 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.61, 152.76, 145.87, 145.08, 142.07, 141.00, 140.55, 140.47, 139.43, 139.33, 132.28, 131.20, 128.65, 128.13, 128.02, 127.52, 22.52, 22.42, 21.84, 21.68.

(9) 6-methyl-2-phenylquinoxaline and 7-methyl-2-phenylquinoxaline (4ai) [3]**.**



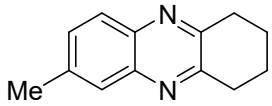
Yellow solid, the two regio-isomers were inseparable in column chromatography. 83% isolated yield from diamine; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.29 (d, *J* = 9.8 Hz, 1H), 8.20 (dd, *J* = 7.3, 1.7 Hz, 2H), 8.04 (dd, *J* = 16.2, 8.6 Hz, 1H), 7.97 – 7.89 (m, 1H), 7.66 – 7.50 (m, 4H), 2.63 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.81, 151.10, 143.26, 142.48, 142.40, 141.64, 140.87, 140.79, 140.17, 136.97, 132.65, 131.91, 130.08, 129.99, 129.14, 128.62, 128.48, 127.97, 127.53, 127.44, 21.89, 21.86.

(10) 2,3,6-trimethylquinoxaline (4aj) [3]**.**



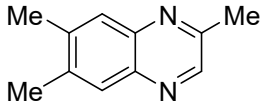
Yellow solid, Mp.92.3-94.9 °C, 86% from diamine, 87% from nitroaniline; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.5 Hz, 1H), 7.75 (s, 1H), 7.49 (dd, *J* = 8.5, 1.9 Hz, 1H), 2.71 (s, 6H), 2.55 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.28, 152.42, 141.09, 139.45, 139.14, 131.03, 127.79, 127.26, 23.14, 23.04, 21.73.

(11) 7-methyl-1,2,3,4-tetrahydrophenazine (4ak) [5]**.**



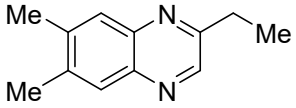
Yellow solid, Mp.80.5.3-82.1 °C, 78% from diamine, 73% from nitroaniline; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.5 Hz, 1H), 7.72 (s, 1H), 7.48 (dd, *J* = 8.5, 2.0 Hz, 1H), 3.12 (d, *J* = 6.0 Hz, 4H), 2.55 (s, 3H), 2.02 (p, *J* = 3.4 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.91, 153.06, 143.44, 139.63, 138.75, 130.17, 127.81, 126.57, 33.16, 33.06, 22.84, 22.82, 21.75.

(12) 2,6,7-trimethylquinoxaline (4al) [3]**.**



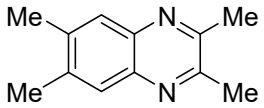
Yellow solid, Mp.115.9-117.2 °C, 86% from diamine, 86% from nitroaniline; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 7.69 (s, 1H), 7.64 (s, 1H), 2.64 (s, 3H), 2.36 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.56, 144.91, 140.87, 140.30, 139.80, 139.10, 128.10, 127.65, 22.36, 20.27, 20.11.

(13) 2-ethyl-6,7-dimethylquinoxaline (4am) [5]**.**



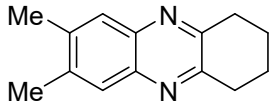
Yellow solid, Mp.115.2-116.8 °C, 74% from diamine, 77% from nitroaniline; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 7.80 (d, *J* = 6.9 Hz, 2H), 3.02 (q, *J* = 7.6 Hz, 2H), 2.49 (s, 6H), 1.43 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.46, 144.53, 141.05, 140.37, 140.16, 139.24, 128.18, 127.93, 29.52, 20.34, 20.21, 13.53.

(14) 2,3,6,7-tetramethylquinoxaline (4an) [5]**.**



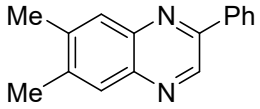
Yellow solid, Mp.181.1-183.7 °C, 88% from diamine, 88% from nitroaniline; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 2H), 2.70 (s, 6H), 2.46 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.32, 139.95, 139.05, 127.46, 23.05, 20.25.

(15) 7,8-dimethyl-1,2,3,4-tetrahydrophenazine (4ao) [6]**.**



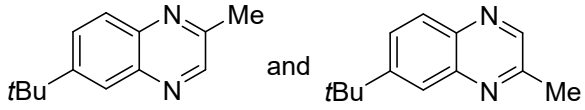
Yellow solid, Mp.147.2-148.2 °C, 80% from diamine, 70% from nitroaniline; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 2H), 3.16 – 3.09 (m, 4H), 2.45 (s, 6H), 2.02 (p, J = 3.2 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.93, 140.12, 139.22, 127.39, 33.06, 22.88, 20.28.

(16) 6,7-dimethyl-2-phenylquinoxaline (4ap) [3]**.**



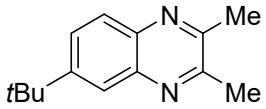
Yellow solid, Mp.121.3-123.1 °C, 85% from diamine, 80% from nitroaniline; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (s, 1H), 8.13 – 8.06 (m, 2H), 7.84 (s, 1H), 7.78 (s, 1H), 7.51 – 7.43 (m, 3H), 2.44 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.06, 142.39, 141.26, 140.91, 140.50, 140.24, 137.12, 129.89, 129.12, 128.66, 128.11, 127.42, 20.44, 20.40.

(17) 6-(tert-butyl)-2-methylquinoxaline and 7-(tert-butyl)-2-methylquinoxaline (4aq) [5]**.**



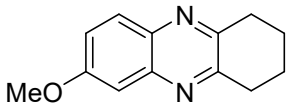
Yellow solid, the two regio-isomers were inseparable in column chromatography, 65% isolated yield from diamine; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, J = 8.0 Hz, 1H), 8.03 – 7.94 (m, 2H), 7.86 – 7.78 (m, 1H), 2.76 (d, J = 2.1 Hz, 3H), 1.44 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.57, 153.55, 153.02, 152.36, 145.81, 145.30, 144.87, 144.32, 141.92, 140.86, 140.40, 139.36, 128.98, 128.44, 127.93, 127.89, 124.36, 123.91, 35.24, 35.11, 31.11, 22.52, 22.44.

(18) 6-(tert-butyl)-2,3-dimethylquinoxaline (4ar) [5]**.**



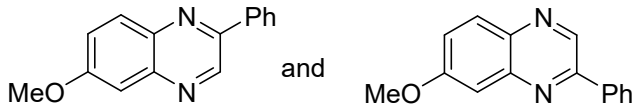
Yellow solid, Mp.52.4-53.8 °C, 70% from diamine; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 2.2 Hz, 1H), 7.91 (d, *J* = 8.8 Hz, 1H), 7.76 (dd, *J* = 8.8, 2.2 Hz, 1H), 2.71 (d, *J* = 1.9 Hz, 6H), 1.43 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.20, 152.67, 152.23, 140.89, 139.38, 127.68, 127.60, 123.63, 35.11, 31.18, 23.14, 23.07.

(19) 7-methoxy-1,2,3,4-tetrahydrophenazine (4as) [5]**.**



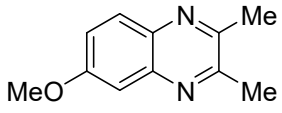
Yellow solid, Mp.114.9-115.3 °C, 86% from diamine; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 9.0 Hz, 1H), 7.29 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.24 (d, *J* = 2.8 Hz, 1H), 3.92 (s, 3H), 3.11 (d, *J* = 4.6 Hz, 4H), 2.03 – 1.98 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.89, 153.77, 151.12, 142.46, 137.13, 129.17, 121.96, 105.75, 55.56, 33.02, 32.72, 22.82, 22.75.

(20) 6-methoxy-2-phenylquinoxaline and 7-methoxy-2-phenylquinoxaline (4at) [3]**.**



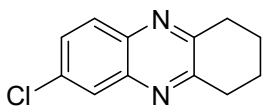
Yellow solid, the two regio-isomers were inseparable in column chromatography, 77% isolated yield from diamine; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.12 (s, 1H), 8.17 – 8.11 (m, 2H), 7.96 (d, *J* = 9.2 Hz, 1H), 7.57 – 7.49 (m, 3H), 7.40 (dd, *J* = 14.6, 2.8 Hz, 2H), 3.96 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.08, 151.95, 143.98, 140.74, 137.75, 136.98, 130.02, 129.15, 128.46, 127.54, 122.95, 106.87, 55.86.

(21) 6-methoxy-2,3-dimethylquinoxaline (4au) [3]**.**



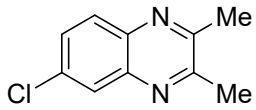
Yellow solid, Mp.99.3-100.9 °C, 89% from diamine; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.8 Hz, 1H), 7.35 – 7.27 (m, 2H), 3.95 (s, 3H), 2.72 (s, 3H), 2.70 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.97, 153.36, 150.64, 142.43, 136.99, 129.24, 121.70, 106.15, 55.69, 23.10, 22.80.

(22) 7-chloro-1,2,3,4-tetrahydrophenazine (4av) [6]**.**



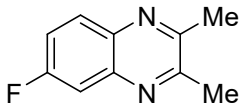
Yellow dense liquid, 78% from diamine, 82% from nitroaniline; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 2.3 Hz, 1H), 7.84 (d, *J* = 8.9 Hz, 1H), 7.54 (dd, *J* = 8.9, 2.3 Hz, 1H), 3.09 (td, *J* = 4.7, 2.3 Hz, 4H), 2.00 – 1.95 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.26, 154.46, 141.44, 139.63, 134.64, 130.00, 129.55, 127.30, 33.17, 33.11, 22.67, 22.65.

(23) 6-chloro-2,3-dimethylquinoxaline (4aw) [5]**.**



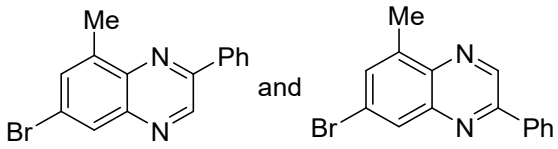
Yellow solid, Mp.91.0-92.5 °C, 78% from diamine, 75% from nitroaniline; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 2.3 Hz, 1H), 7.78 (d, *J* = 8.9 Hz, 1H), 7.49 (dd, *J* = 8.9, 2.3 Hz, 1H), 2.61 (s, 3H), 2.61 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.48, 152.68, 140.26, 138.44, 133.29, 128.67, 128.49, 126.27, 22.15, 22.09.

(24) 6-fluoro-2,3-dimethylquinoxaline (4ax) [6]**.**



Yellow solid, Mp.108.2-110.3 °C, 70% from diamine, 74% from nitroaniline; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 9.2, 5.7 Hz, 1H), 7.59 (dd, *J* = 9.3, 2.8 Hz, 1H), 7.46 – 7.39 (m, 1H), 2.71 (d, *J* = 3.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.07 (d, *J* = 249.8 Hz), 154.41, 152.73 (d, *J* = 3.0 Hz), 141.71 (d, *J* = 12.9 Hz), 138.17, 130.23 (d, *J* = 10.1 Hz), 118.84 (d, *J* = 25.6 Hz), 111.99 (d, *J* = 21.5 Hz), 23.13, 22.97. ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.26.

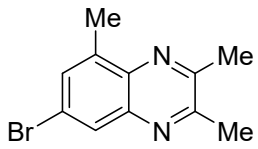
(25) 6-bromo-8-methyl-2-phenylquinoxaline and 7-bromo-5-methyl-2-phenylquinoxaline (4ba) [5]**.**



Yellow solid, the two regio-isomers were inseparable in column chromatography, 85% from nitroaniline; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.28 (s, 1H), 8.27 – 7.96 (m, 3H), 7.66 (d, *J* = 17.6 Hz, 1H), 7.59 – 7.48 (m, 3H), 2.79 (d, *J* = 18.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.03, 150.36, 143.39,

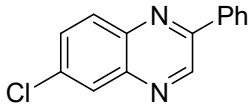
143.02, 142.11, 139.87, 139.56, 139.25, 136.59, 136.39, 133.49, 132.45, 130.43, 130.33, 129.67, 129.20, 129.16, 129.13, 127.55, 127.42, 124.05, 123.20, 17.36, 17.09.

(26) 7-bromo-2,3,5-trimethylquinoxaline (4bb) [3]**.**



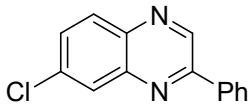
Yellow solid, Mp.66.1-68.6 °C,79% from nitroaniline; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.57 (s, 1H), 2.72 (s, 3H), 2.70 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.90, 152.58, 141.65, 139.05, 138.68, 132.01, 128.40, 122.08, 23.35, 23.08, 16.91.

(27) 6-chloro-2-phenylquinoxaline (4bc) [3]**.**



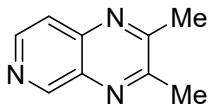
White solid, Mp.125.3-127.1 °C,two regio-isomers were separated by column chromatography, 80% from nitroaniline, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.29 (s, 1H), 8.39 – 8.14 (m, 2H), 8.13 – 7.97 (m, 2H), 7.69 (dd, *J* = 8.9, 2.3 Hz, 1H), 7.55 (qd, *J* = 7.8, 6.8, 3.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.71, 143.47, 141.80, 140.82, 135.98, 135.24, 131.31, 130.84, 130.45, 129.23, 128.08, 127.51.

(28) 7-chloro-2-phenylquinoxaline (4bc') [3]**.**



White solid, Mp.146.3-148.2 °C, two regio-isomers were separated by column chromatography, 80% from nitroaniline, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.32 (s, 1H), 8.26 – 8.11 (m, 3H), 8.06 (d, *J* = 6.1 Hz, 1H), 7.69 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.63 – 7.49 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.51, 143.46, 142.64, 140.11, 136.32, 136.14, 130.60, 130.57, 130.38, 129.26, 128.52, 127.64.

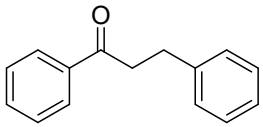
(29) 2,3-dimethylpyrido[3,4-b] pyrazine (4bd) [6]**.**



Gray solid; Mp.109.8-111.4 °C, 65% from nitroaniline; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.34 (s, 1H),

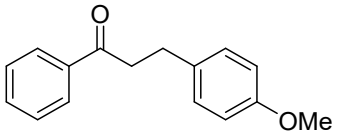
8.67 (d, *J* = 5.7 Hz, 1H), 7.75 (d, *J* = 5.7 Hz, 1H), 2.72 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.82, 155.73, 153.36, 146.60, 143.76, 136.50, 120.91, 23.70, 23.33.

(30) 1,3-diphenylpropan-1-one (8aa) [7]**.**



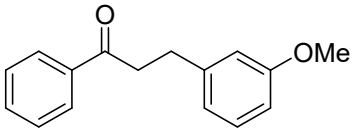
White solid, Mp.72.3-73.9 °C, 92% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.00 (m, 2H), 7.60 (d, *J* = 7.4 Hz, 1H), 7.51 (dd, *J* = 8.5, 7.0 Hz, 2H), 7.39 – 7.31 (m, 4H), 7.29 (d, *J* = 6.9 Hz, 1H), 3.36 (dd, *J* = 8.5, 6.9 Hz, 2H), 3.15 (dd, *J* = 8.5, 6.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.23, 141.32, 136.92, 133.07, 128.63, 128.55, 128.45, 128.07, 126.16, 40.46, 30.17.

(31) 3-(4-methoxyphenyl)-1-phenylpropan-1-one (8ab) [7]**.**



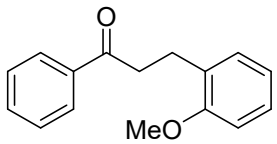
White solid, Mp.59.1-61.2 °C, 86% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.95 (m, 2H), 7.57 (d, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.23 – 7.17 (m, 2H), 6.91 – 6.85 (m, 2H), 3.82 (s, 3H), 3.30 (dd, *J* = 8.4, 6.9 Hz, 2H), 3.05 (t, *J* = 7.7 Hz, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 197.81, 163.48, 141.50, 130.32, 130.04, 128.52, 128.44, 126.09, 113.76, 55.46, 40.11, 30.37.

(32) 3-(3-methoxyphenyl)-1-phenylpropan-1-one (8ac) [7]**.**



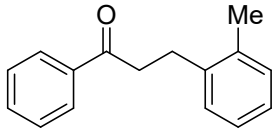
White solid, Mp.66.7-68.2 °C, 84% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.51 (m, 2H), 7.38 (t, *J* = 7.9 Hz, 1H), 7.36 – 7.31 (m, 2H), 7.31 – 7.27 (m, 2H), 7.26 – 7.23 (m, 1H), 7.13 (ddd, *J* = 8.2, 2.7, 1.0 Hz, 1H), 3.88 (s, 3H), 3.32 (dd, *J* = 8.5, 7.0 Hz, 2H), 3.10 (dd, *J* = 8.5, 6.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.95, 157.57, 137.06, 132.86, 130.16, 129.59, 128.52, 128.12, 127.51, 120.56, 110.31, 55.21, 38.96, 25.75.

(33) 3-(2-methoxyphenyl)-1-phenylpropan-1-one (8ad) [7]**.**



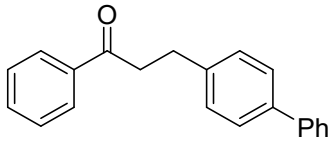
Colorless liquid, 81% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.97 (m, 2H), 7.61 – 7.54 (m, 1H), 7.51 – 7.45 (m, 2H), 7.24 (ddd, *J* = 7.2, 4.4, 2.6 Hz, 2H), 6.96 – 6.87 (m, 2H), 3.86 (s, 3H), 3.30 (dd, *J* = 8.9, 6.9 Hz, 2H), 3.09 (dd, *J* = 8.7, 6.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.02, 159.91, 141.30, 138.32, 129.59, 128.54, 128.44, 126.15, 120.68, 119.57, 112.35, 55.45, 40.55, 30.23.

(34) 1-phenyl-3-(*o*-tolyl) propan-1-one (8ae) [8]**.**



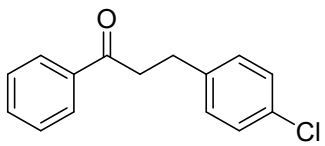
Colorless liquid, 88% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 7.97 (m, 2H), 7.65 – 7.56 (m, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.16 (m, 4H), 3.34 – 3.26 (m, 2H), 3.14 – 3.07 (m, 2H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.38, 139.42, 136.91, 136.02, 133.11, 130.38, 128.77, 128.66, 128.08, 126.36, 126.21, 39.14, 27.56, 19.38.

(35) 3-([1,1'-biphenyl]-4-yl)-1-phenylpropan-1-one (8af) [8]**.**



White solid, Mp.68.3-70.2 °C,83% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 7.2 Hz, 2H), 7.60 (dd, *J* = 7.8, 3.6 Hz, 3H), 7.49 (dt, *J* = 10.1, 7.8 Hz, 4H), 7.42 – 7.35 (m, 3H), 3.39 (t, *J* = 7.6 Hz, 2H), 3.17 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.21, 141.03, 140.47, 139.18, 136.92, 133.15, 128.93, 128.80, 128.68, 128.11, 127.32, 127.17, 127.06, 40.41, 29.79.

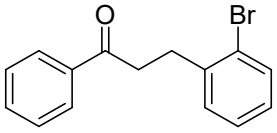
(36) 3-(4-chlorophenyl)-1-phenylpropan-1-one (8ag) [7]**.**



White solid, Mp.58.2-59.9 °C,82% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.94 (m, 2H), 7.62 – 7.56 (m, 1H), 7.52 – 7.45 (m, 2H), 7.28 (dt, *J* = 6.8, 2.2 Hz, 2H), 7.23 – 7.19 (m, 2H), 3.31 (t, *J* = 7.5 Hz, 2H), 3.07 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.82, 139.74, 136.79, 133.15,

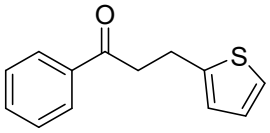
131.89, 129.82, 128.64, 128.60, 128.01, 40.13, 29.40.

(37) 3-(2-bromophenyl)-1-phenylpropan-1-one (8ah) [7]**.**



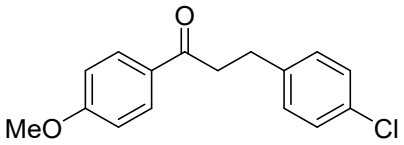
Colorless liquid, 80% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.97 (m, 2H), 7.58 (dd, *J* = 7.9, 1.4 Hz, 2H), 7.48 (dd, *J* = 8.4, 7.0 Hz, 2H), 7.35 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.27 (td, *J* = 7.5, 1.3 Hz, 1H), 7.11 (td, *J* = 7.6, 1.8 Hz, 1H), 3.35 (dd, *J* = 8.3, 6.3 Hz, 2H), 3.22 (t, *J* = 7.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.91, 140.60, 136.81, 133.14, 132.92, 130.83, 128.64, 128.10, 128.01, 127.67, 124.40, 38.63, 30.83.

(38) 1-phenyl-3-(thiophen-2-yl) propan-1-one (8ai) [7]**.**



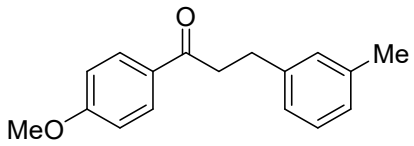
Yellow liquid, 88% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.64 – 7.56 (m, 1H), 7.49 (dd, *J* = 8.3, 6.9 Hz, 2H), 7.16 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.96 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.90 (dd, *J* = 3.4, 1.1 Hz, 1H), 3.40 (ddd, *J* = 7.5, 6.2, 1.8 Hz, 2H), 3.36 – 3.30 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.59, 143.91, 136.79, 133.18, 128.66, 128.06, 126.88, 124.70, 123.40, 40.46, 24.17.

(39) 3-(4-chlorophenyl)-1-(4-methoxyphenyl) propan-1-one (8aj) [9]**.**



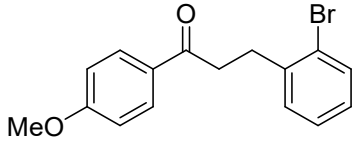
Colorless liquid, 77% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.91 (m, 2H), 7.30 – 7.25 (m, 2H), 7.21 – 7.18 (m, 2H), 6.97 – 6.91 (m, 2H), 3.87 (s, 3H), 3.24 (t, *J* = 7.7 Hz, 2H), 3.04 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.41, 163.61, 139.96, 137.93, 131.80, 130.31, 129.86, 128.58, 113.79, 55.49, 39.78, 29.58.

(40) 1-(4-methoxyphenyl)-3-(m-tolyl) propan-1-one (8ak) [9]**.**



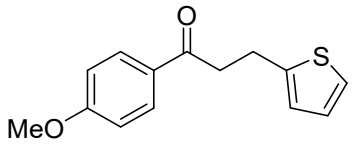
Colorless liquid, 78% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.9 Hz, 2H), 7.25 (t, *J* = 7.5 Hz, 1H), 7.15 – 7.06 (m, 3H), 7.00 – 6.95 (m, 2H), 3.89 (s, 3H), 3.31 – 3.25 (m, 2H), 3.11 – 3.04 (m, 2H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.83, 163.50, 141.48, 138.07, 130.35, 130.08, 129.29, 128.47, 126.88, 125.46, 113.78, 55.45, 40.19, 30.33, 21.44.

(41) 3-(2-bromophenyl)-1-(4-methoxyphenyl) propan-1-one (8al) [10]**.**



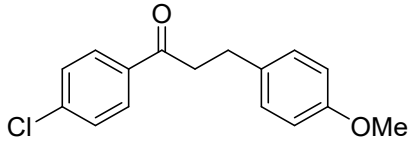
Yellow oil, 73% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.90 (m, 2H), 7.43 (s, 1H), 7.35 (dt, *J* = 7.3, 1.9 Hz, 1H), 7.22 – 7.13 (m, 2H), 6.99 – 6.91 (m, 2H), 3.87 (s, 3H), 3.25 (t, *J* = 7.6 Hz, 2H), 3.04 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.17, 163.56, 143.91, 132.02, 131.51, 130.30, 130.07, 129.22, 127.22, 122.52, 113.80, 55.48, 39.64, 29.84.

(42) 1-(4-methoxyphenyl)-3-(thiophen-2-yl) propan-1-one (8am) [10]**.**



Yellow oil, 75% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.96 (m, 2H), 7.15 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.98 – 6.93 (m, 3H), 6.88 (dd, *J* = 3.4, 1.1 Hz, 1H), 3.88 (s, 3H), 3.32 (d, *J* = 2.0 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.13, 163.56, 144.12, 130.33, 129.90, 126.86, 124.64, 123.34, 113.79, 55.48, 40.19, 24.41.

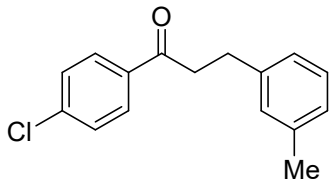
(43) 1-(4-chlorophenyl)-3-(4-methoxyphenyl) propan-1-one (8an) [11]**.**



Yellow oil, 78% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.88 (m, 2H), 7.47 – 7.42 (m, 2H), 7.20 – 7.16 (m, 2H), 6.90 – 6.84 (m, 2H), 3.81 (s, 3H), 3.26 (t, *J* = 7.4 Hz, 2H), 3.03 (t, *J* = 7.6 Hz, 2H). ^{13}C

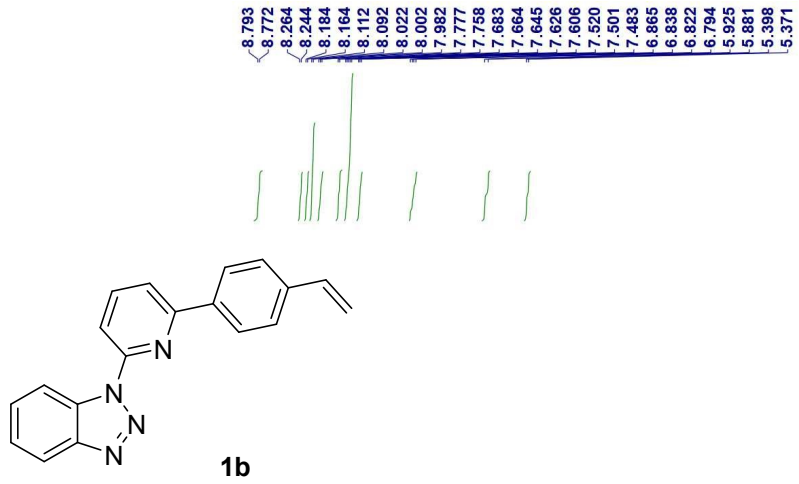
NMR (101 MHz, $CDCl_3$) δ 198.15, 158.08, 139.47, 135.24, 133.09, 129.48, 129.36, 128.92, 114.00, 55.29, 40.69, 29.23.

(44) 1-(4-chlorophenyl)-3-(*m*-tolyl) propan-1-one (8ao) [11]**.**



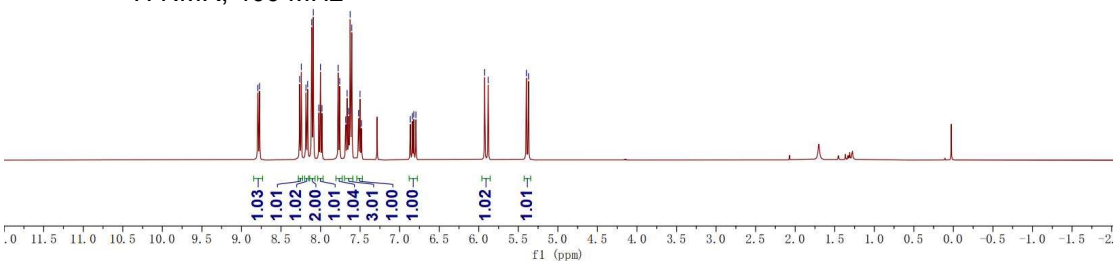
Yellow oil, 82% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.90 (m, 2H), 7.48 – 7.43 (m, 2H), 7.25 (t, *J* = 7.5 Hz, 1H), 7.16 – 7.08 (m, 3H), 3.30 (dd, *J* = 8.5, 6.9 Hz, 2H), 3.09 (d, *J* = 8.0 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.99, 141.08, 139.47, 138.17, 135.26, 129.52, 129.29, 128.94, 128.54, 127.03, 125.46, 40.52, 30.04, 21.47.

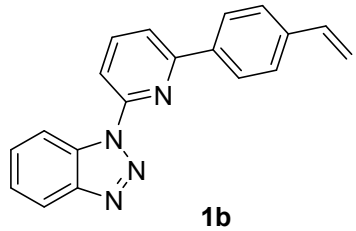
10. NMR spectra of obtained compounds



1b

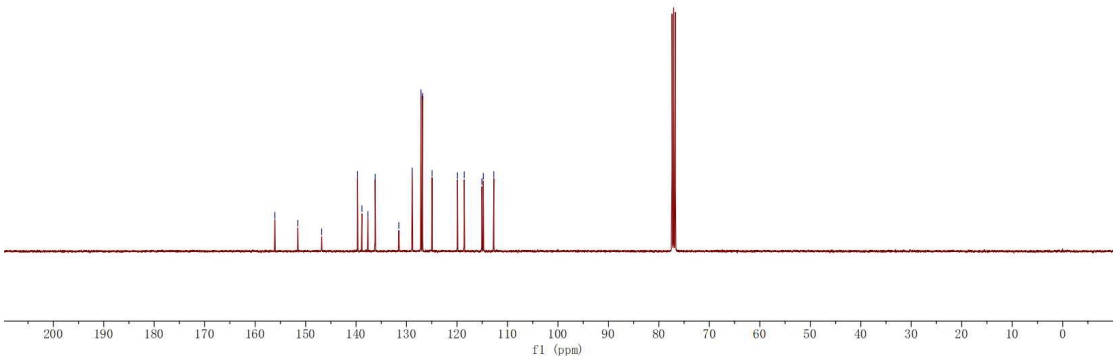
^{1}H NMR, 400 MHz

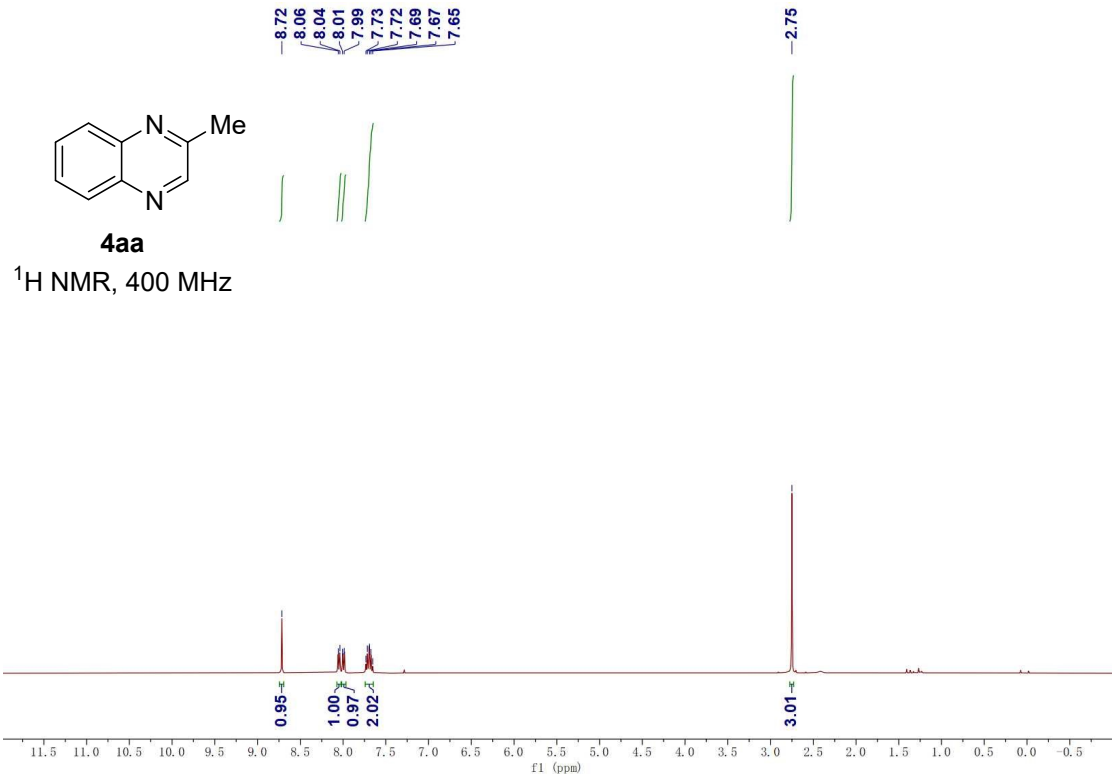




1b

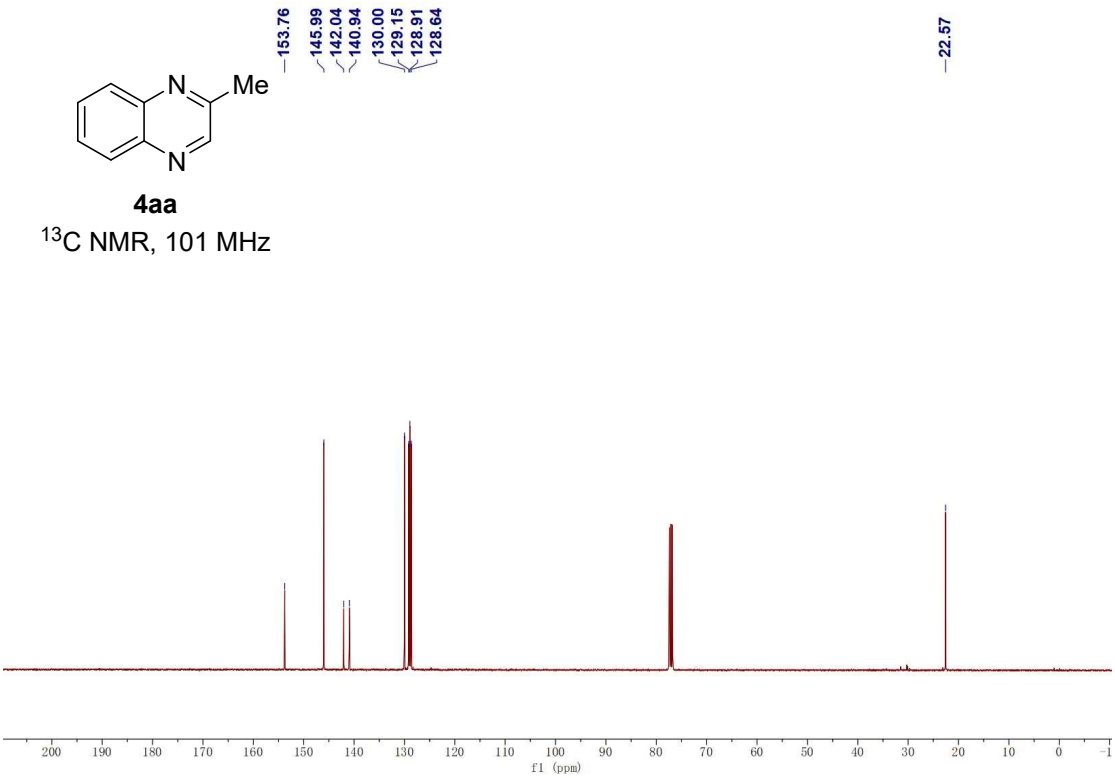
^{13}C NMR, 101 MHz





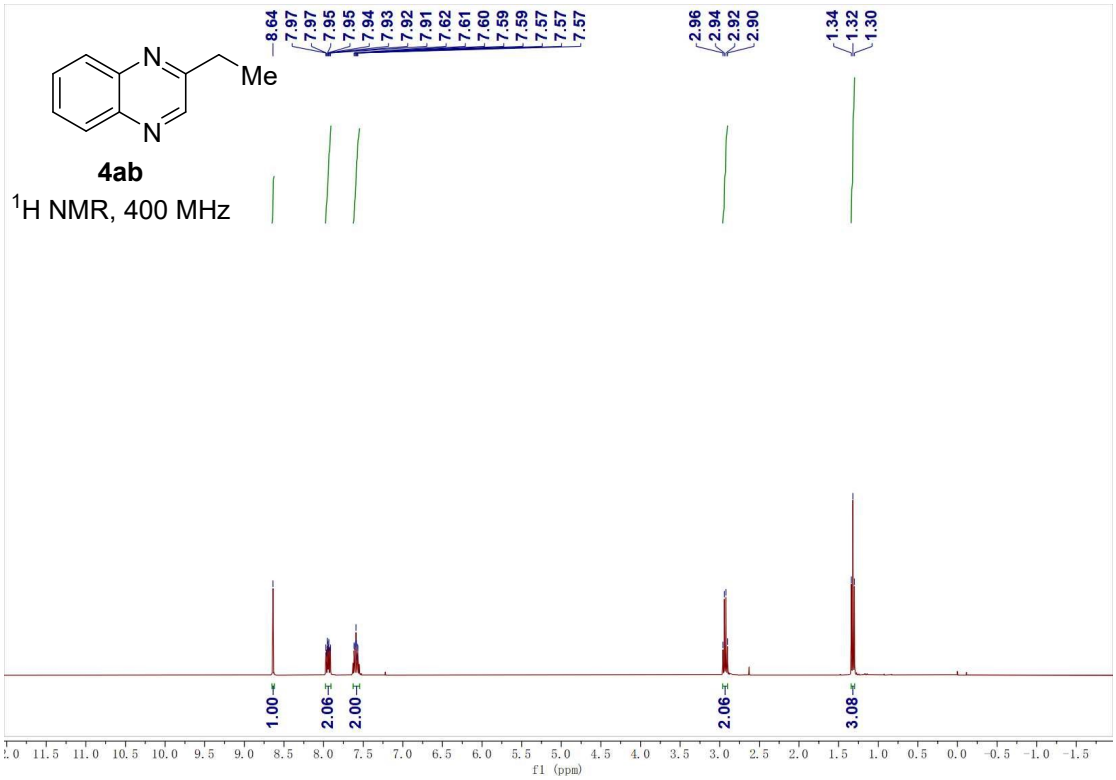
4aa

^{1}H NMR, 400 MHz



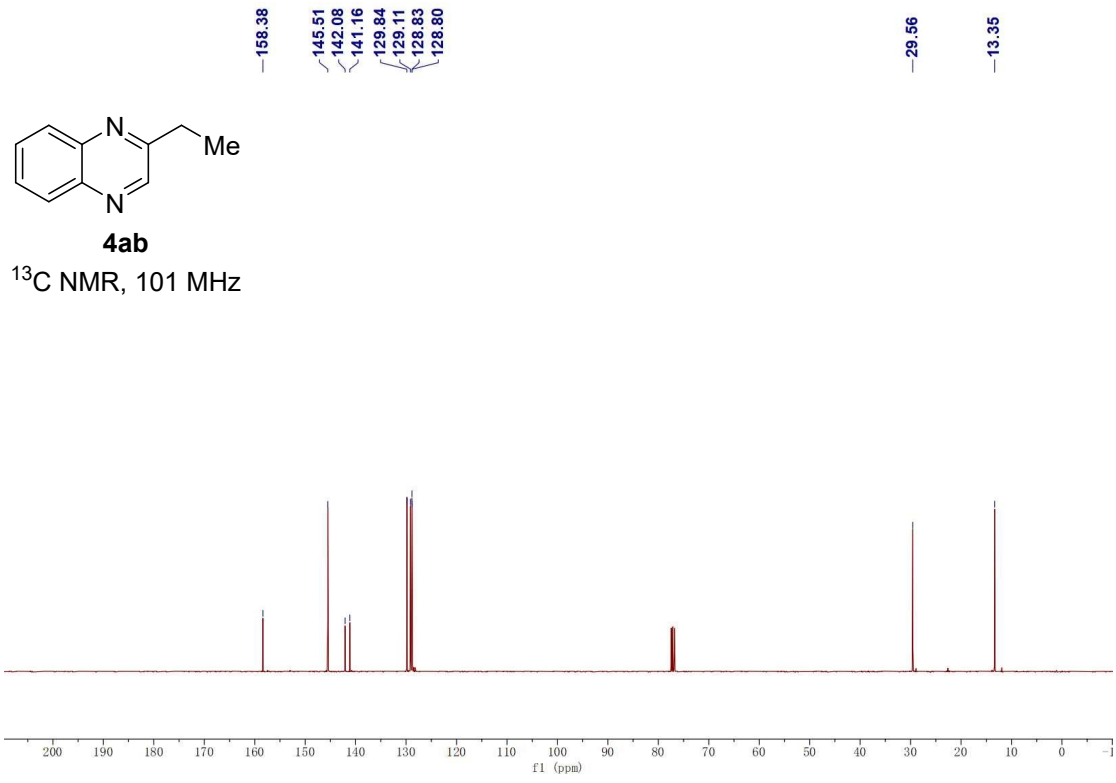
4aa

^{13}C NMR, 101 MHz



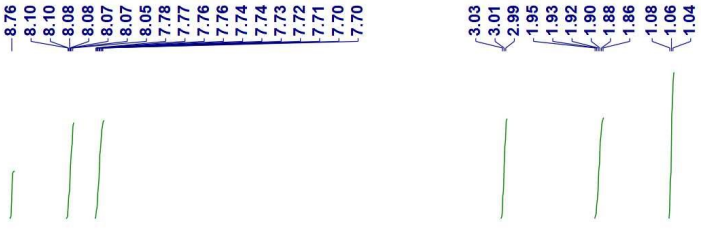
4ab

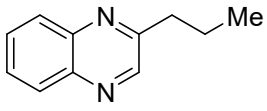
^{1}H NMR, 400 MHz



4ab

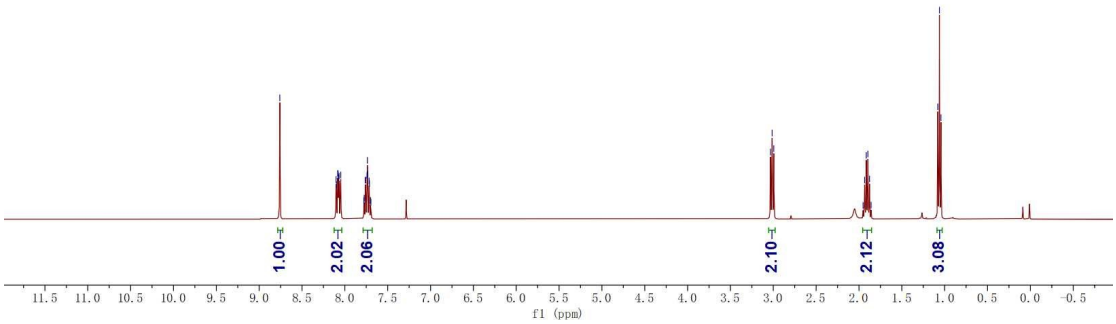
^{13}C NMR, 101 MHz

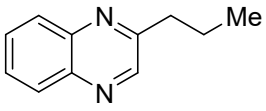




4ac

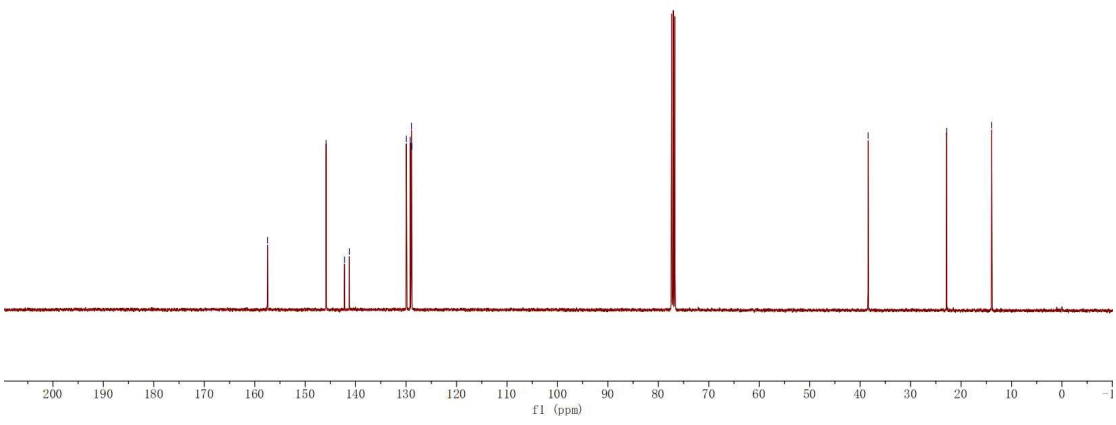
^{1}H NMR, 400 MHz

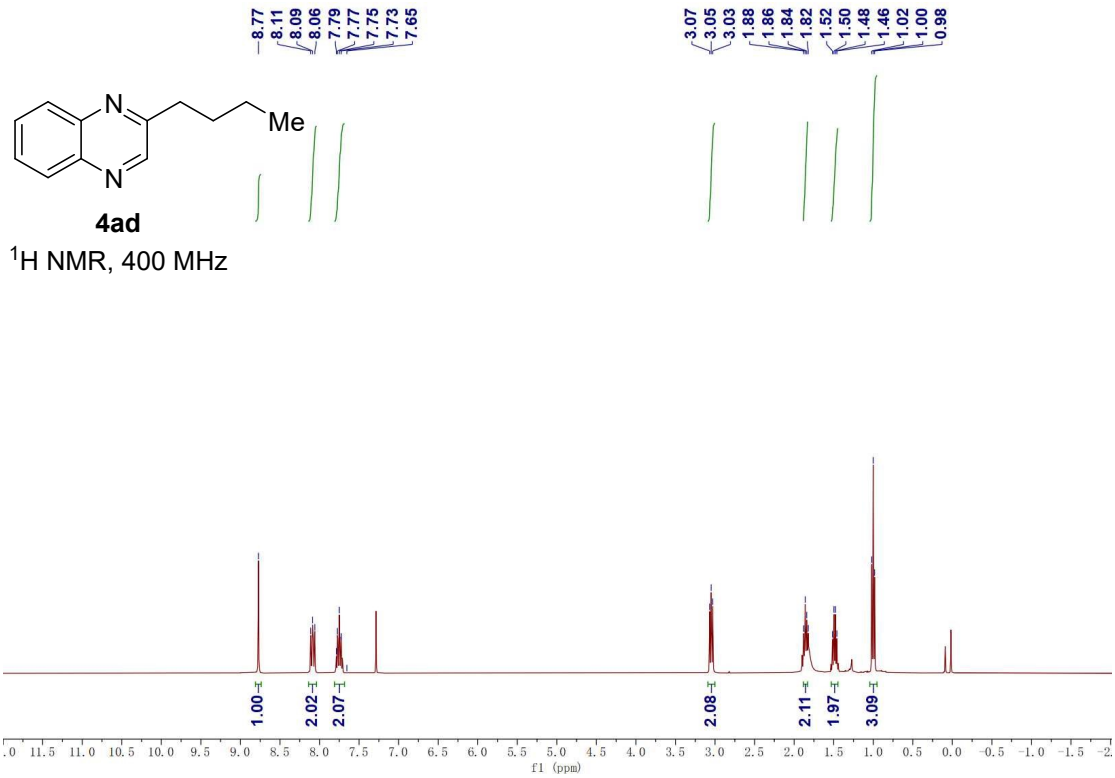




4ac

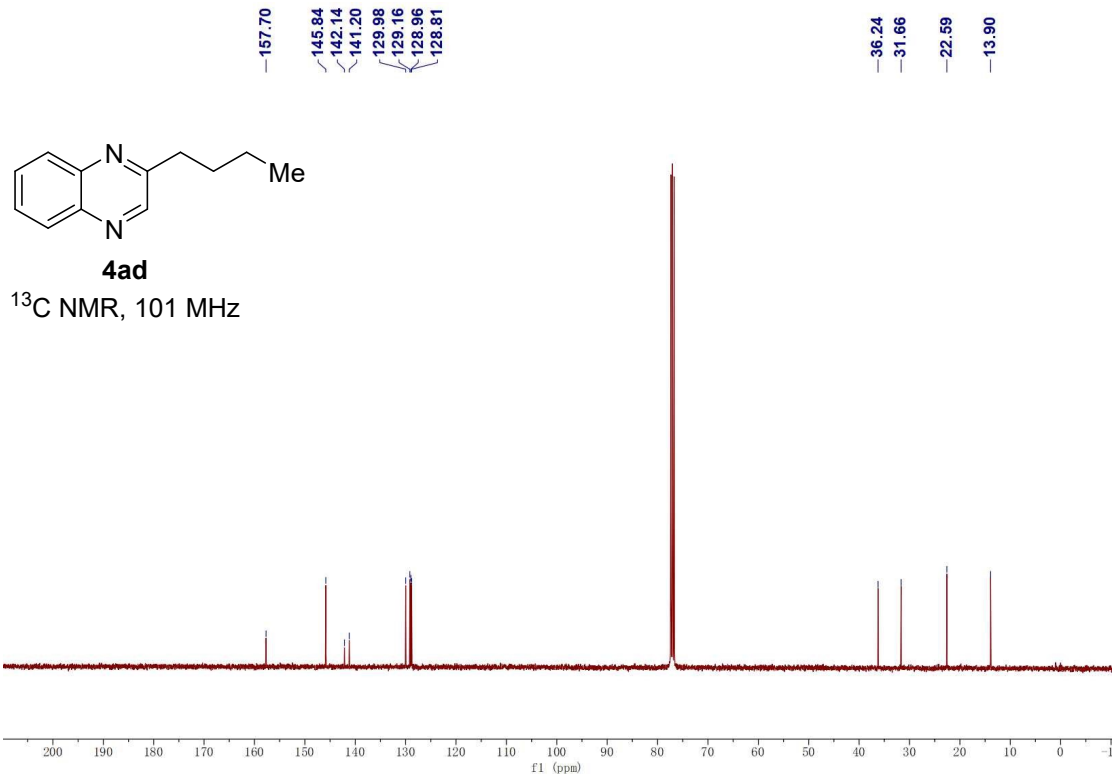
^{13}C NMR, 101 MHz





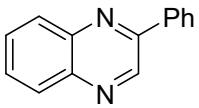
4ad

^{1}H NMR, 400 MHz



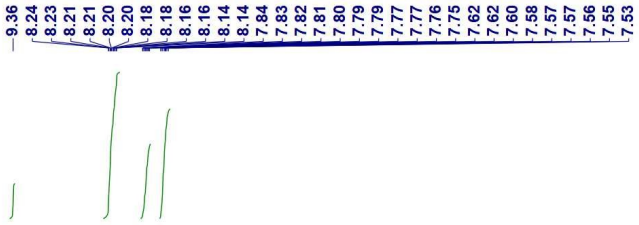
4ad

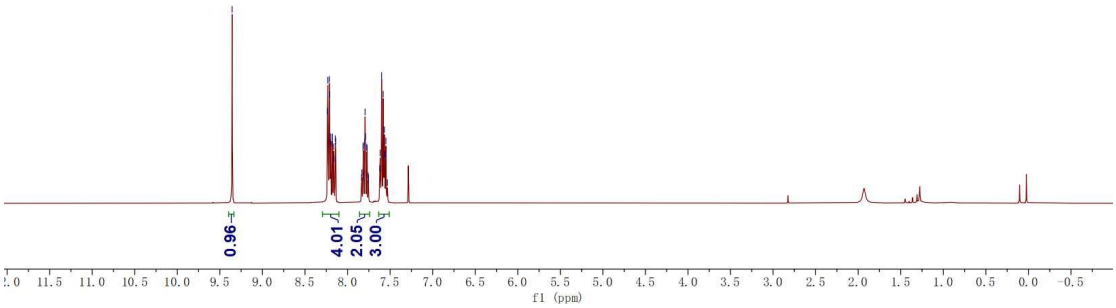
^{13}C NMR, 101 MHz

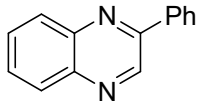


4ae

^{1}H NMR, 400 MHz

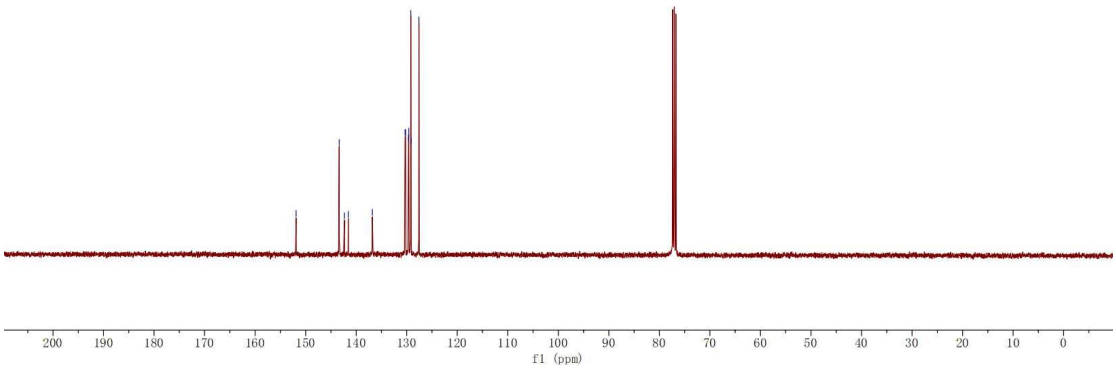


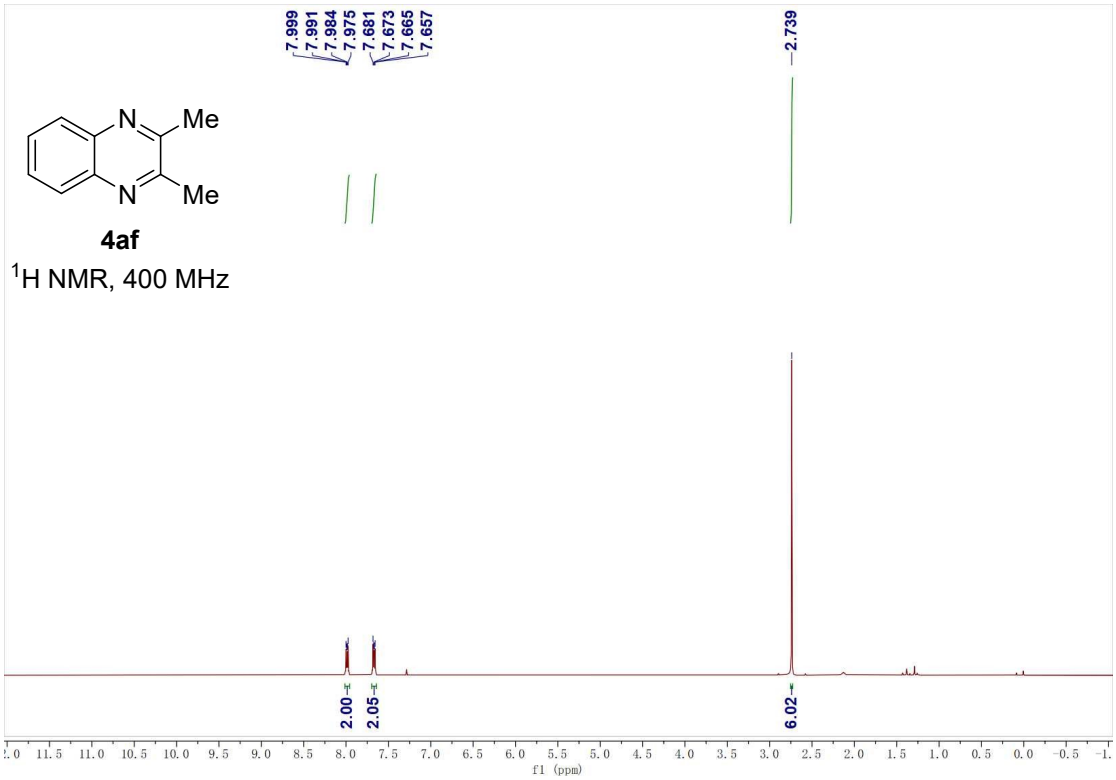




4ae

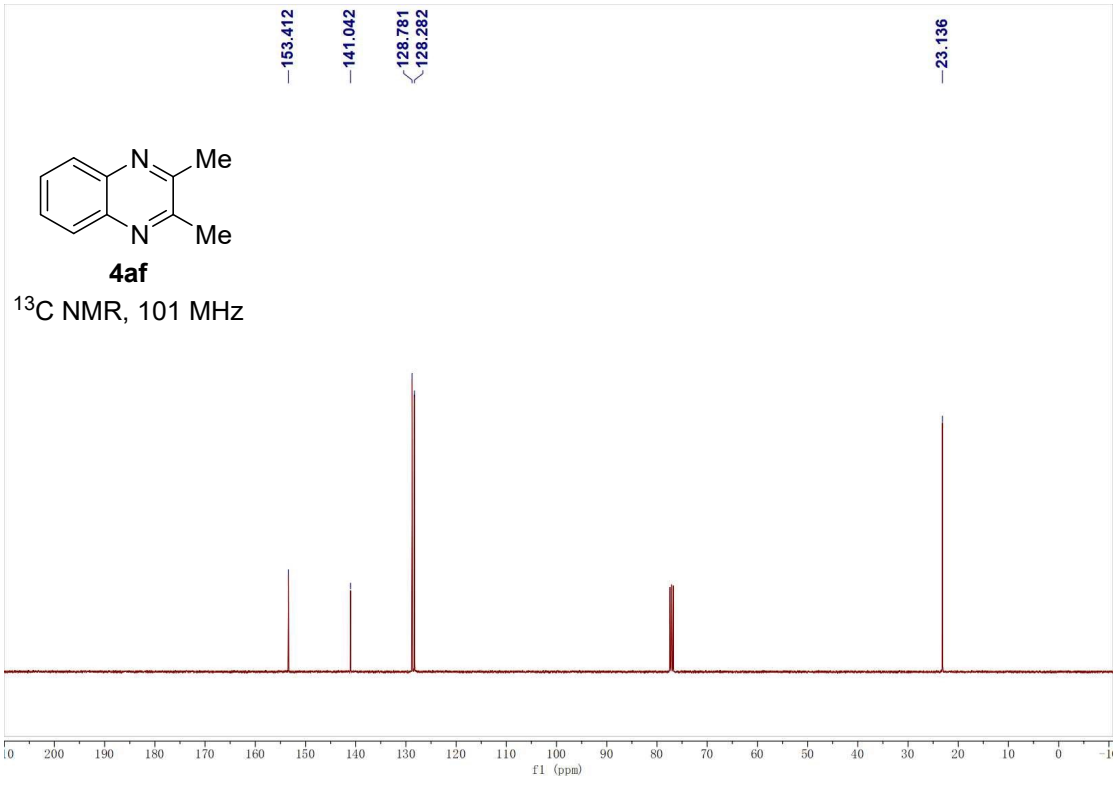
^{13}C NMR, 101 MHz





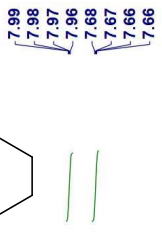
4af

^{1}H NMR, 400 MHz



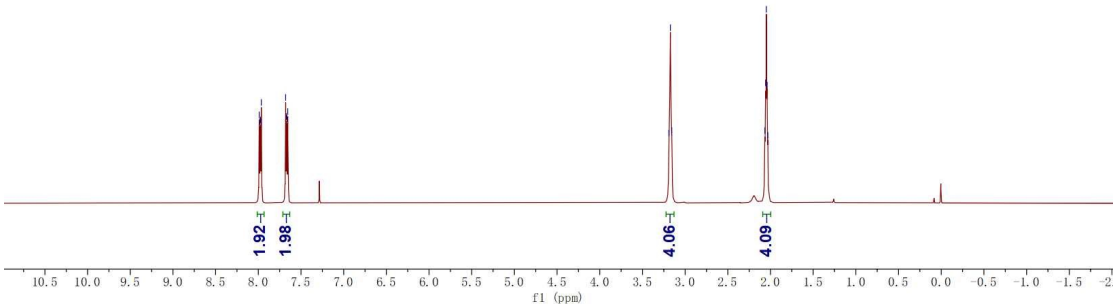
4af

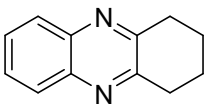
^{13}C NMR, 101 MHz



4ag

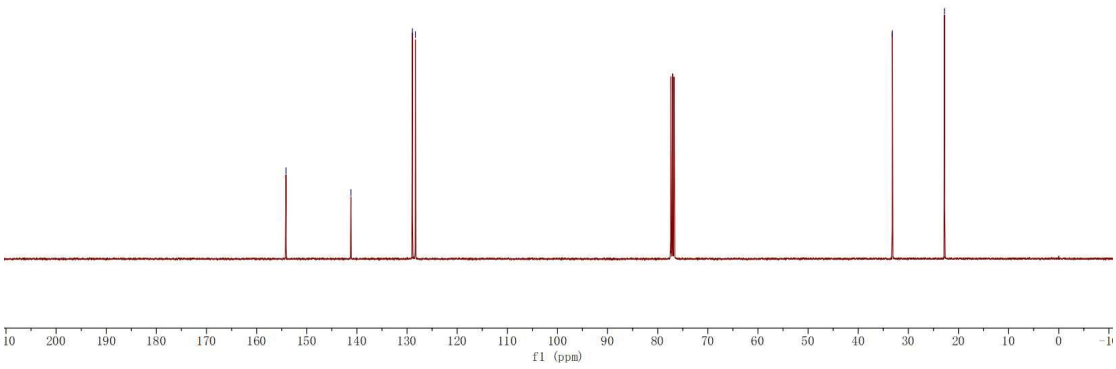
^{1}H NMR, 400 MHz

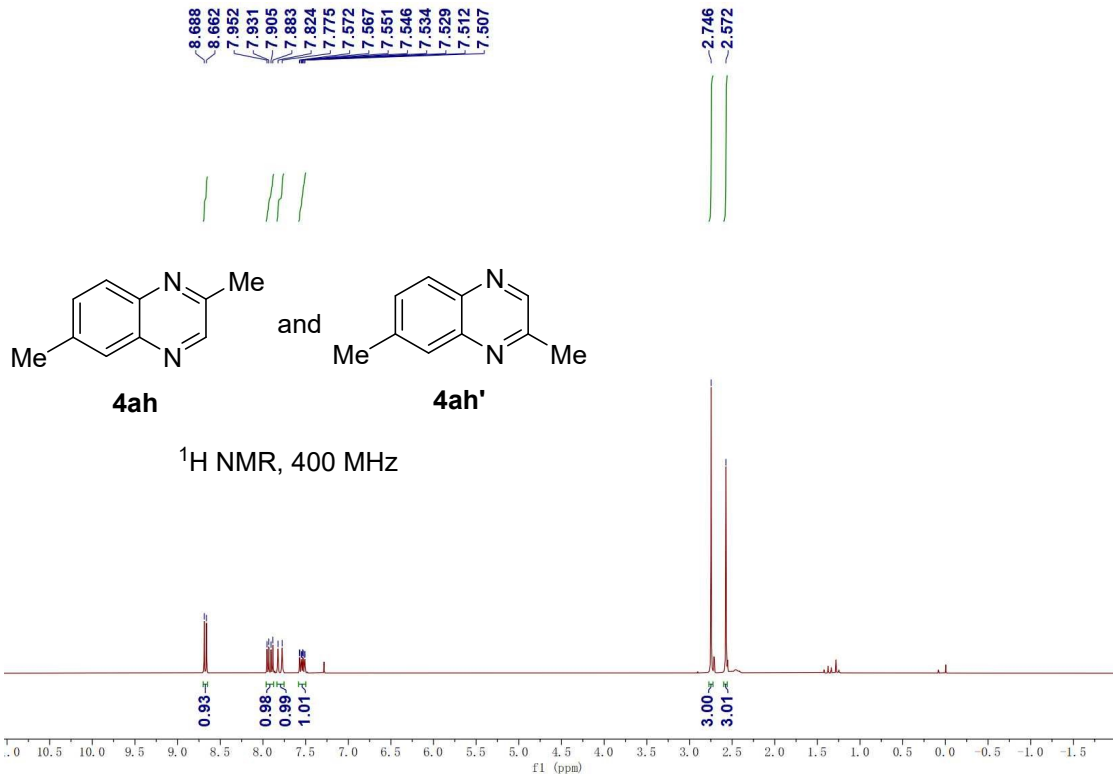




4ag

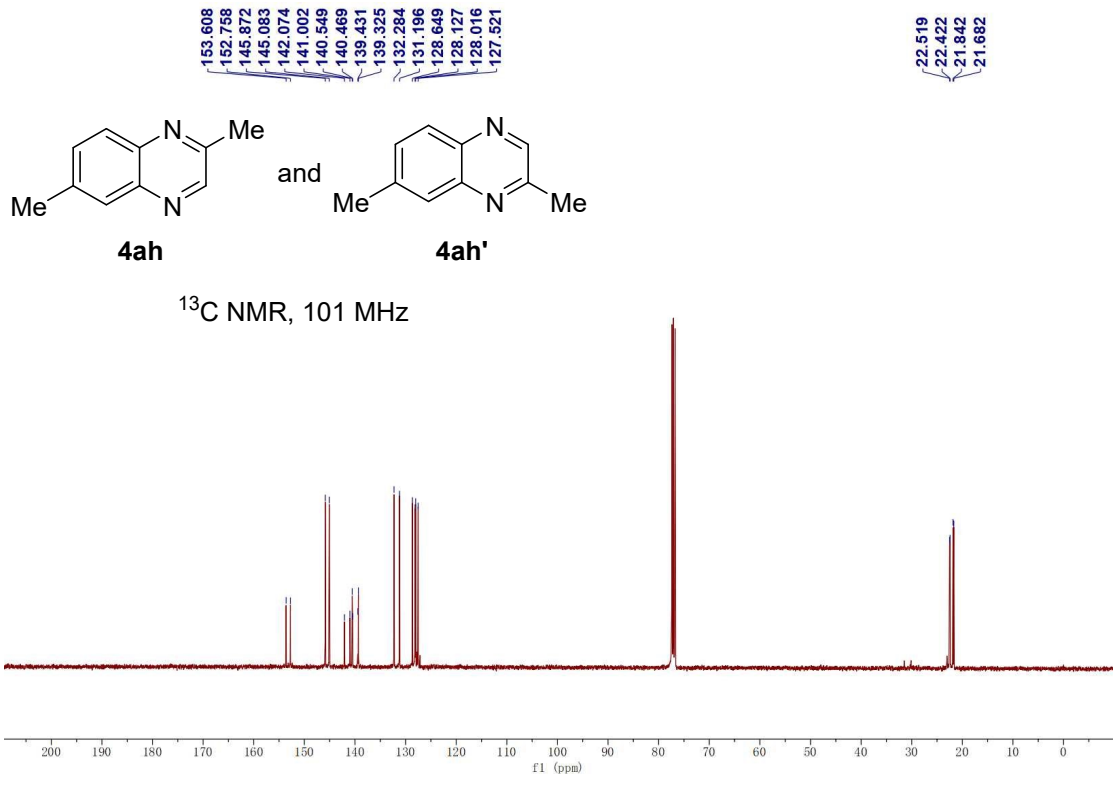
^{13}C NMR, 101 MHz





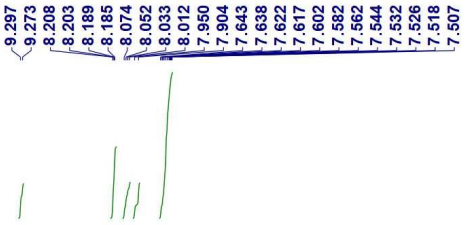
4ah and **4ah'**

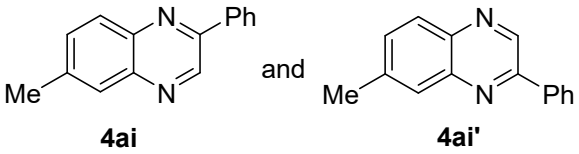
^{1}H NMR, 400 MHz



4ah and **4ah'**

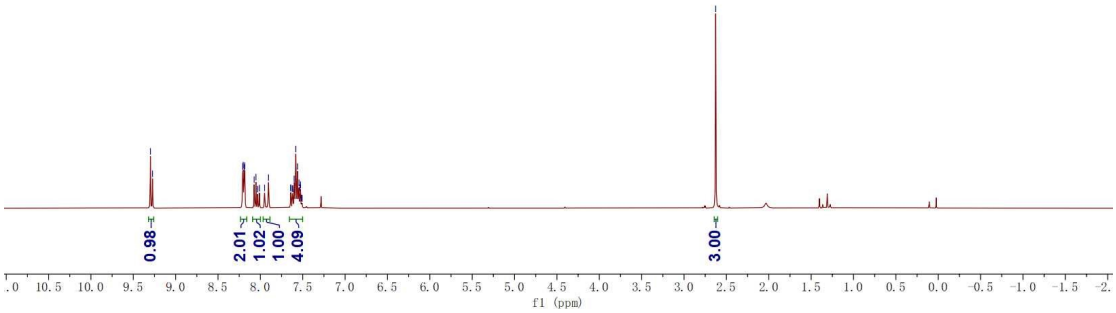
^{13}C NMR, 101 MHz

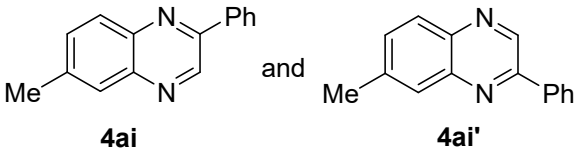




4ai **4ai'**

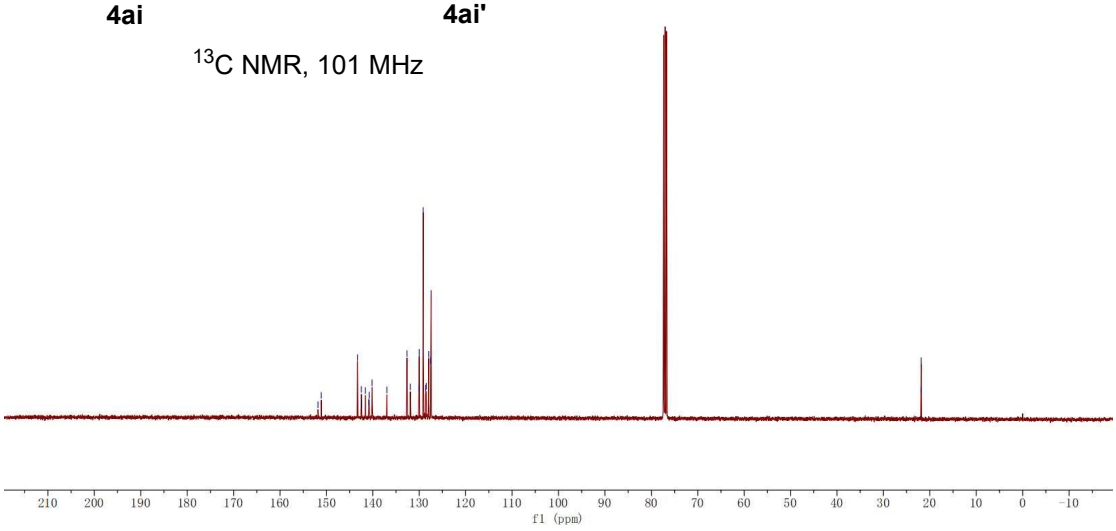
^{1}H NMR, 400 MHz

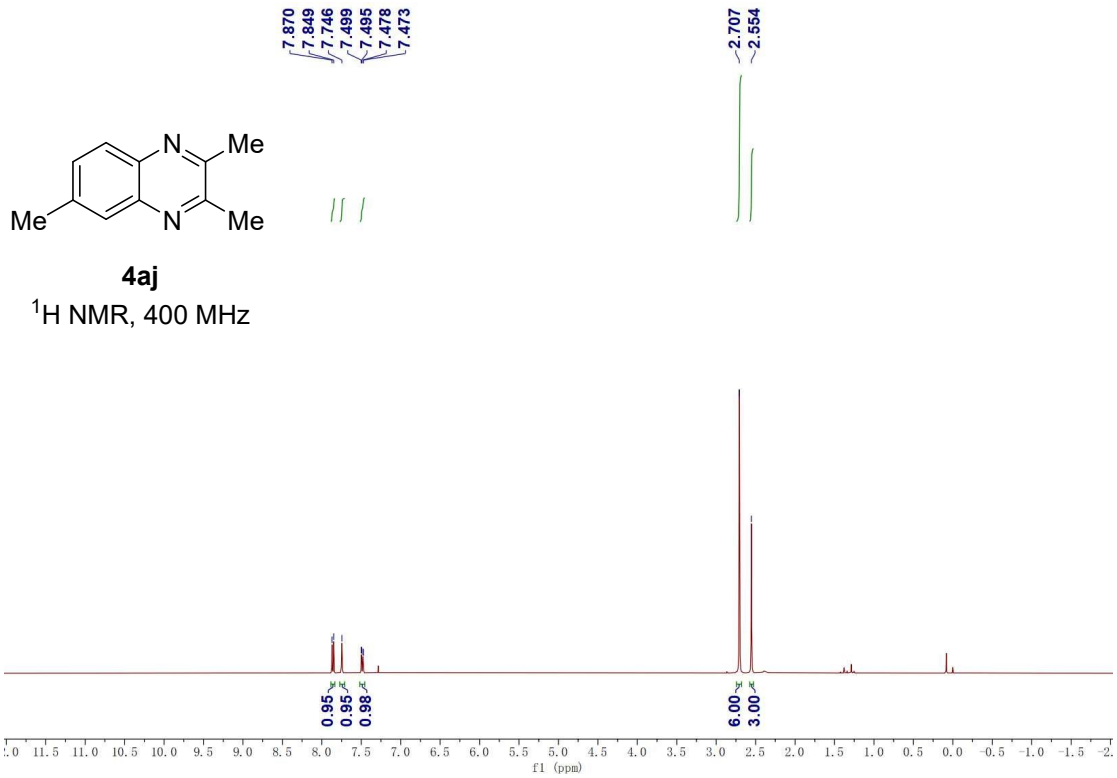




4ai **4ai'**

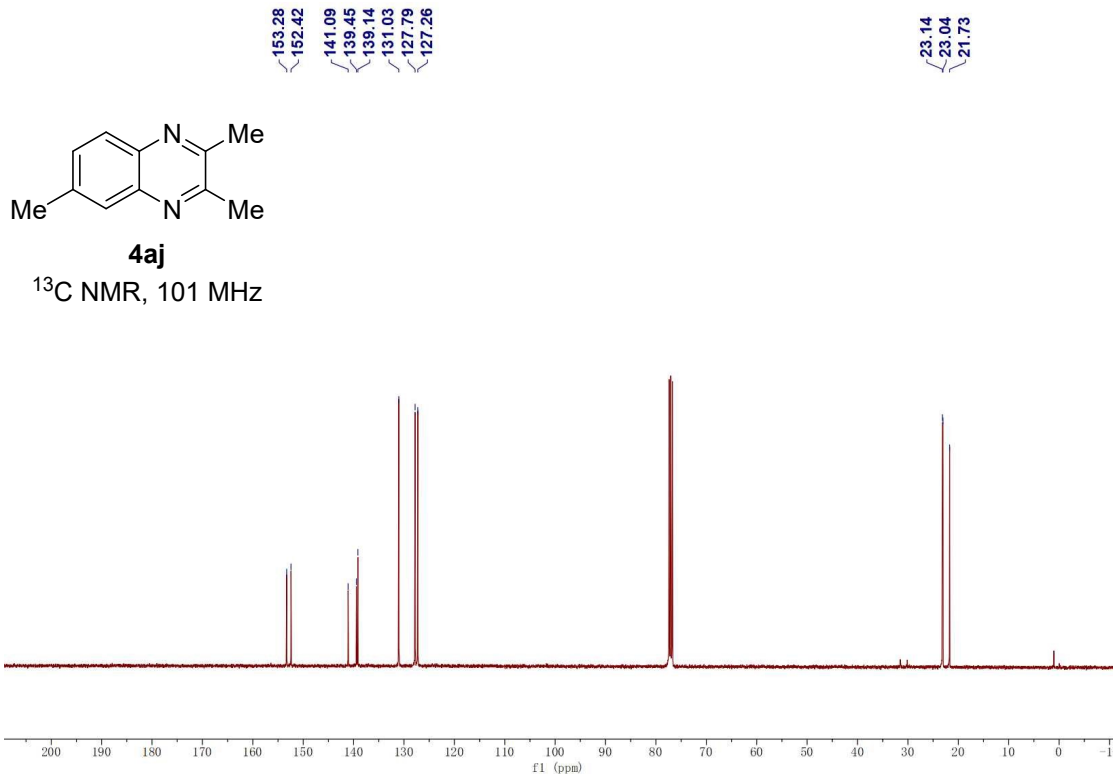
^{13}C NMR, 101 MHz





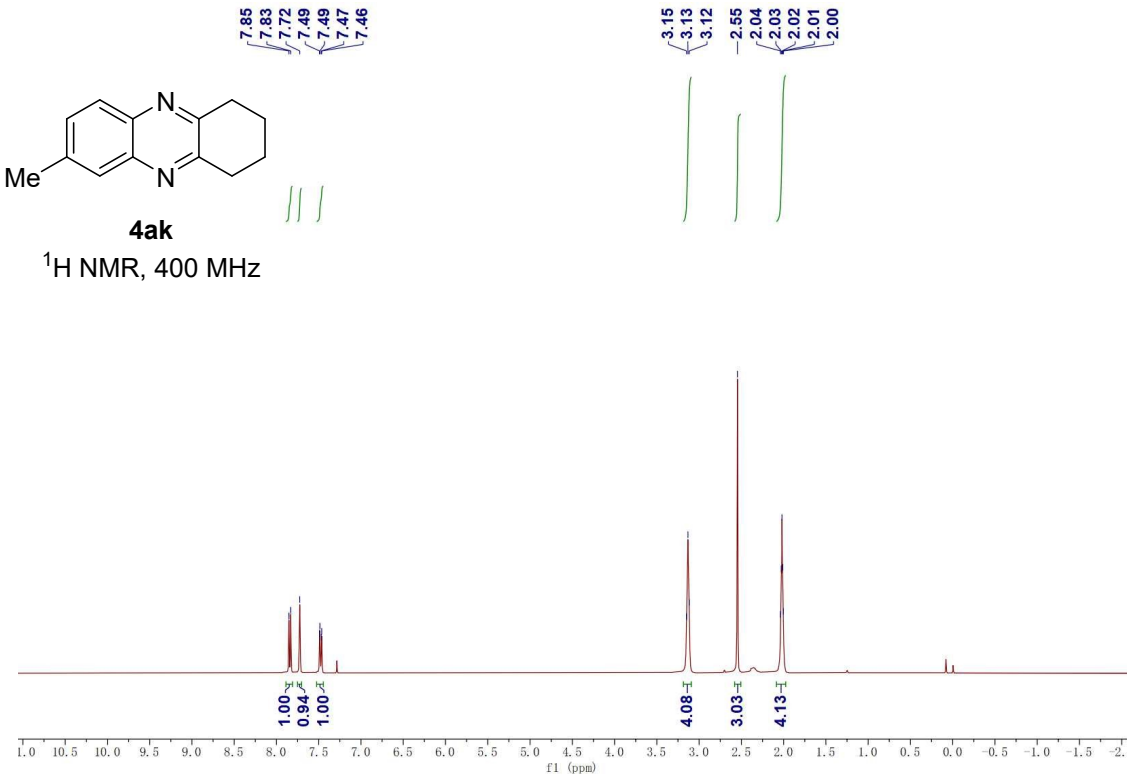
4aj

^{1}H NMR, 400 MHz



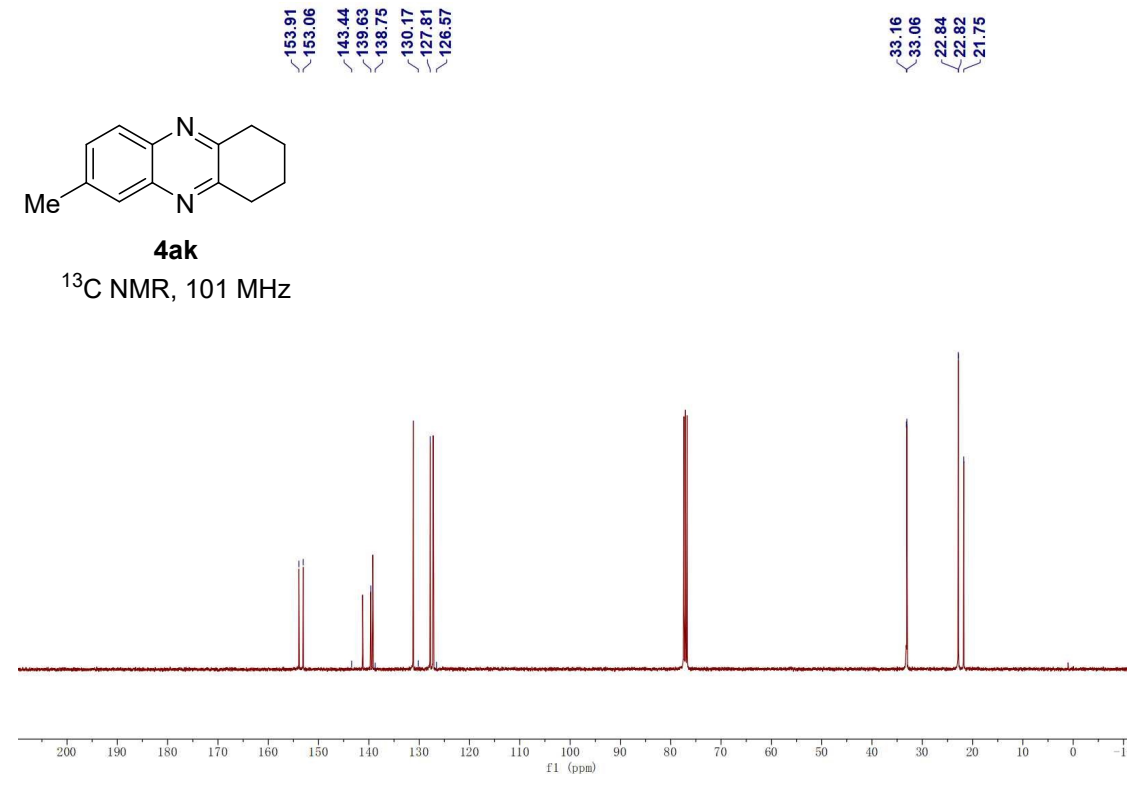
4aj

^{13}C NMR, 101 MHz



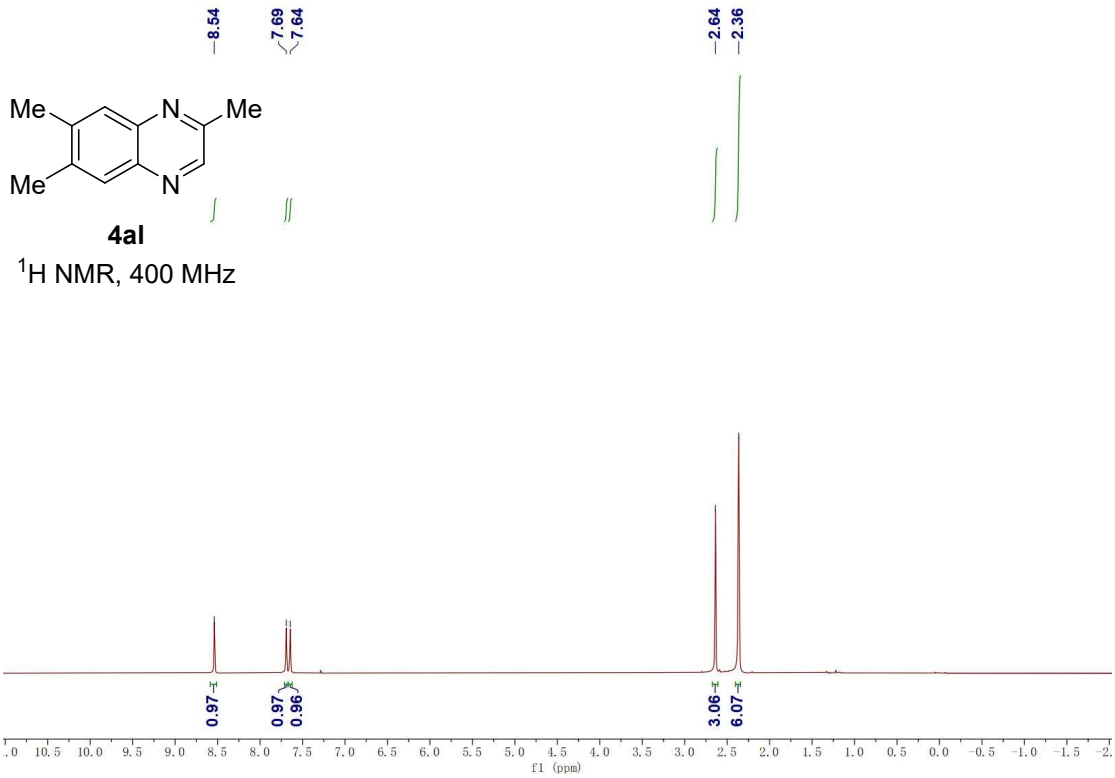
4ak

^{1}H NMR, 400 MHz



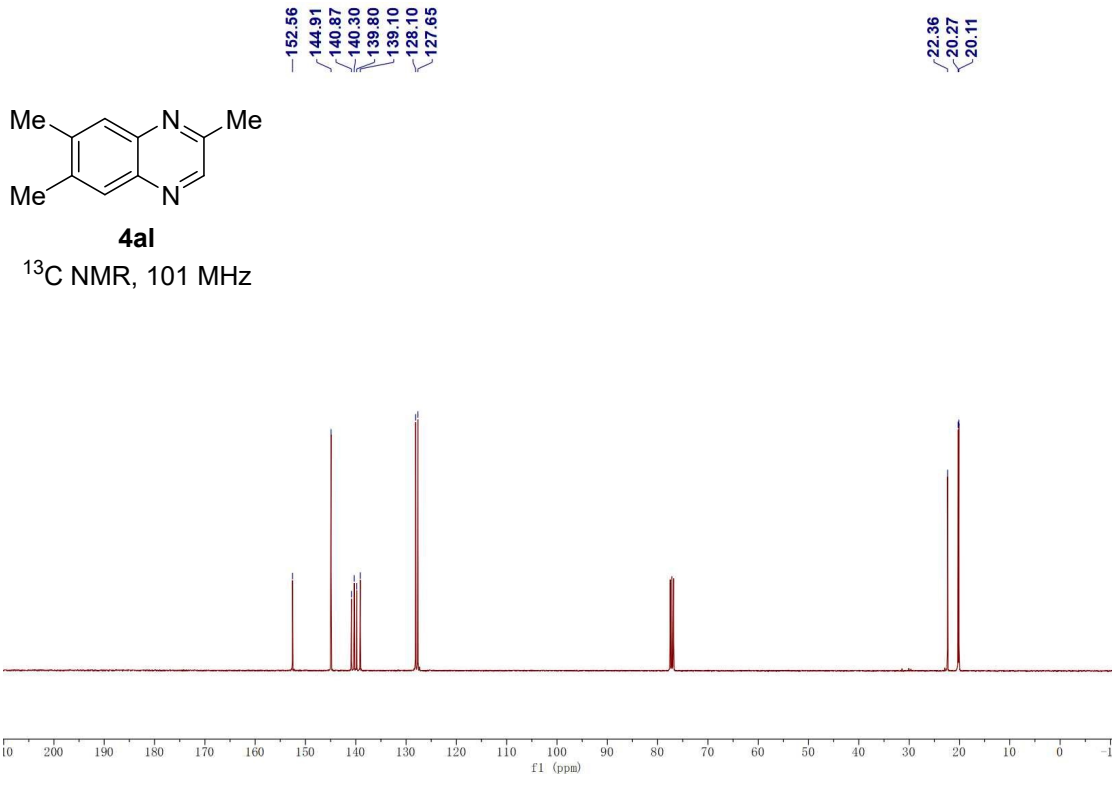
4ak

^{13}C NMR, 101 MHz



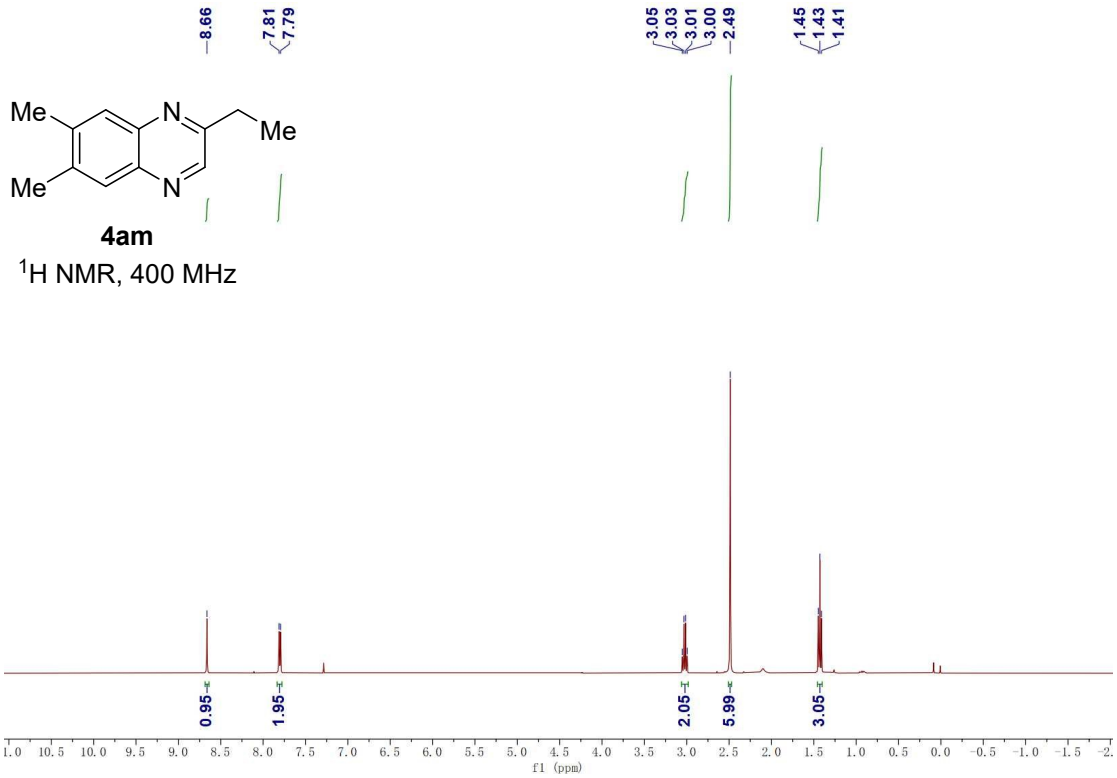
4al

^{1}H NMR, 400 MHz



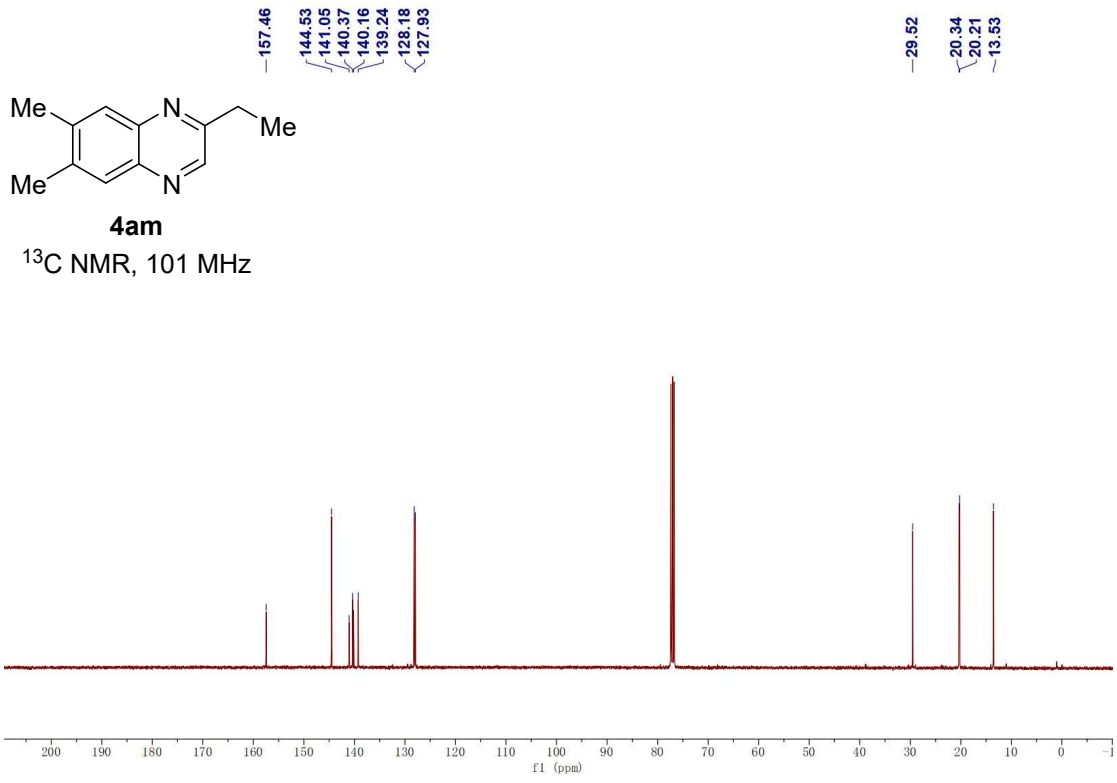
4al

^{13}C NMR, 101 MHz



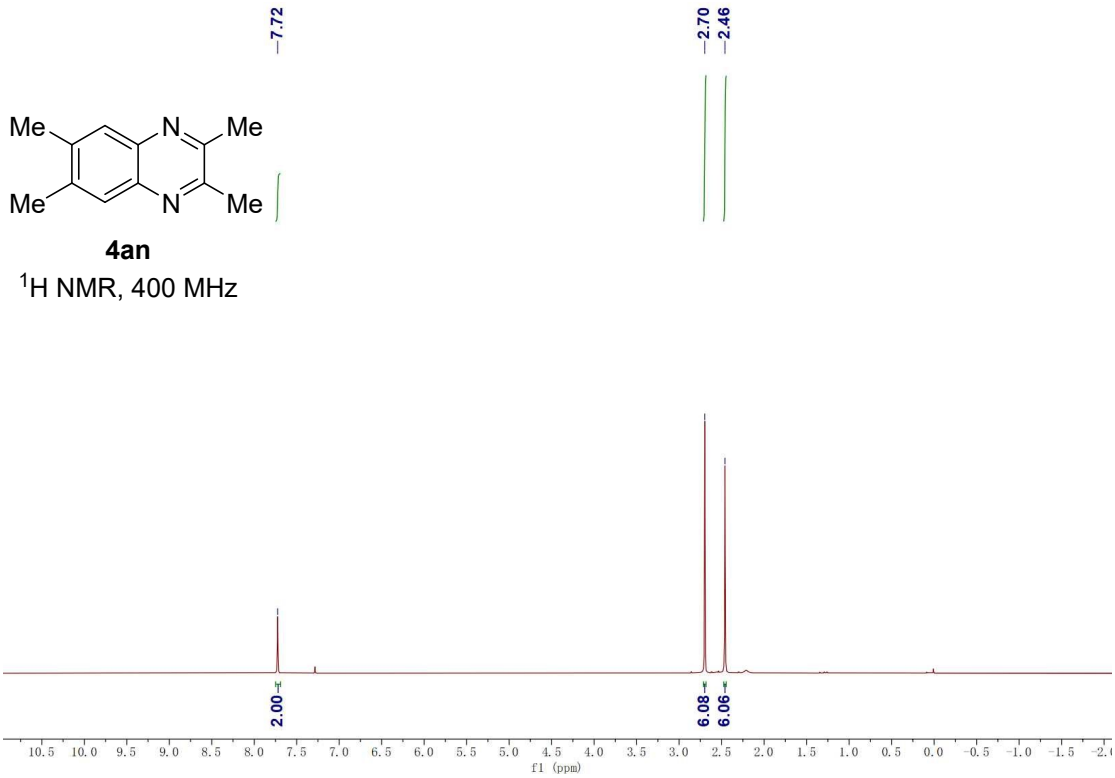
4am

^{1}H NMR, 400 MHz



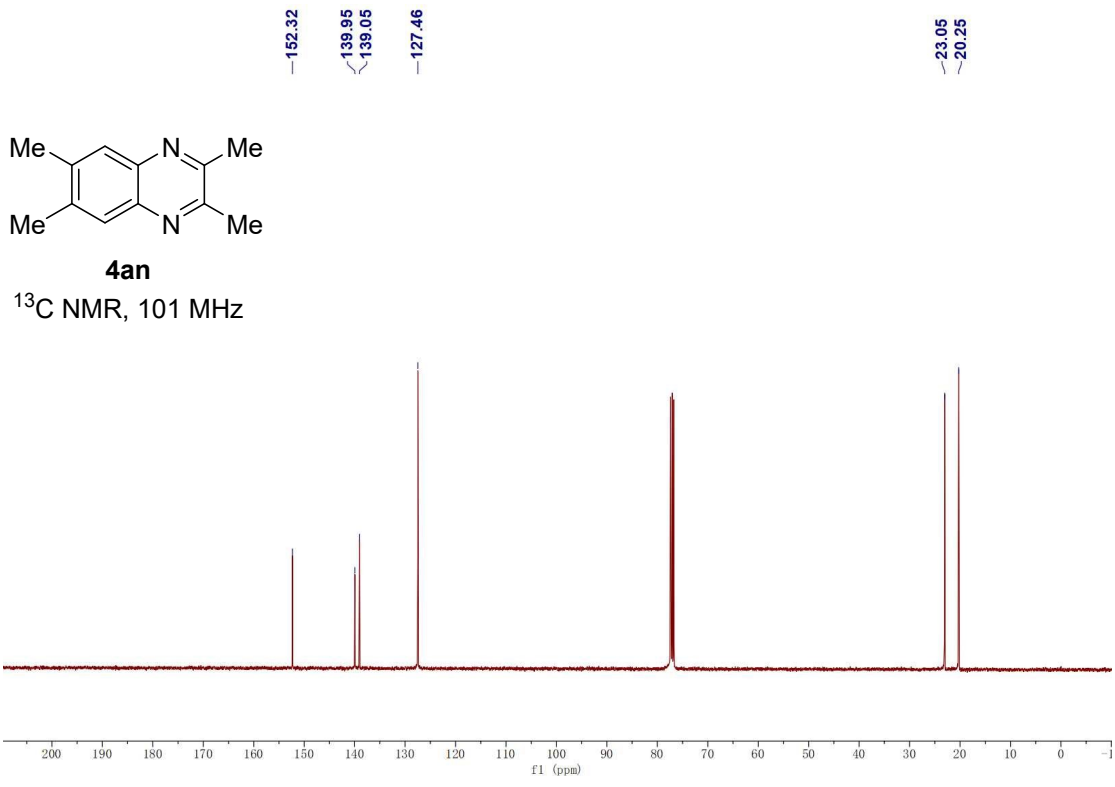
4am

^{13}C NMR, 101 MHz



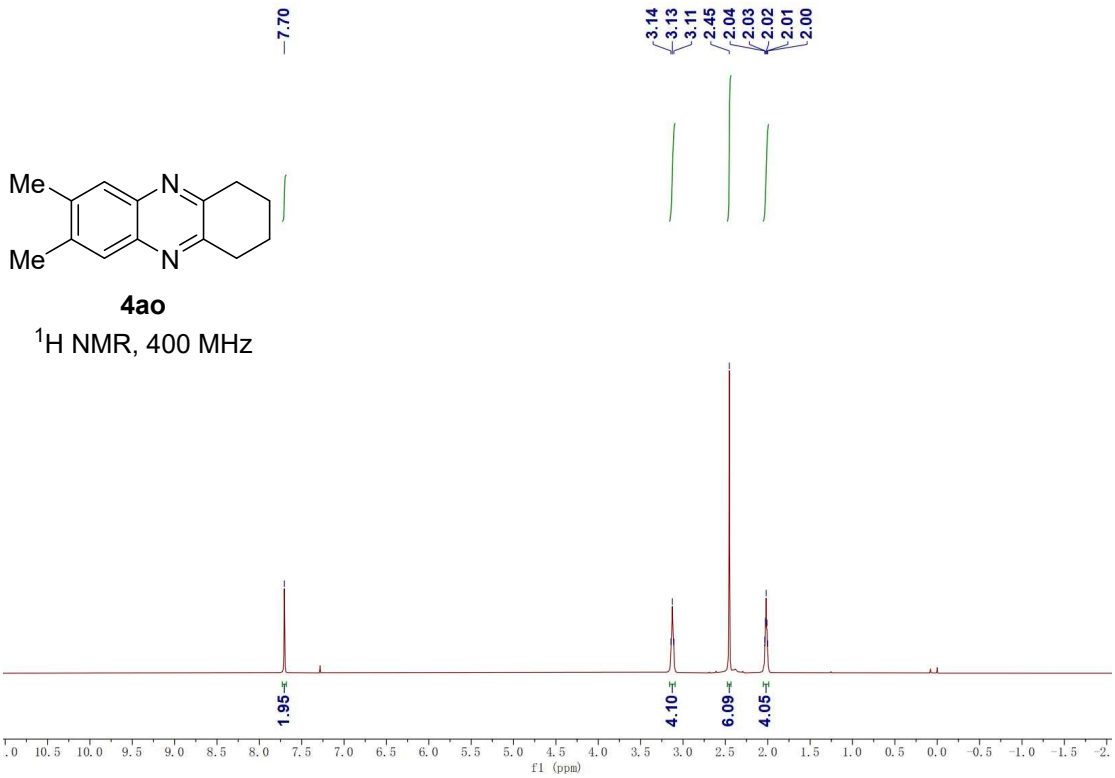
4an

^{1}H NMR, 400 MHz



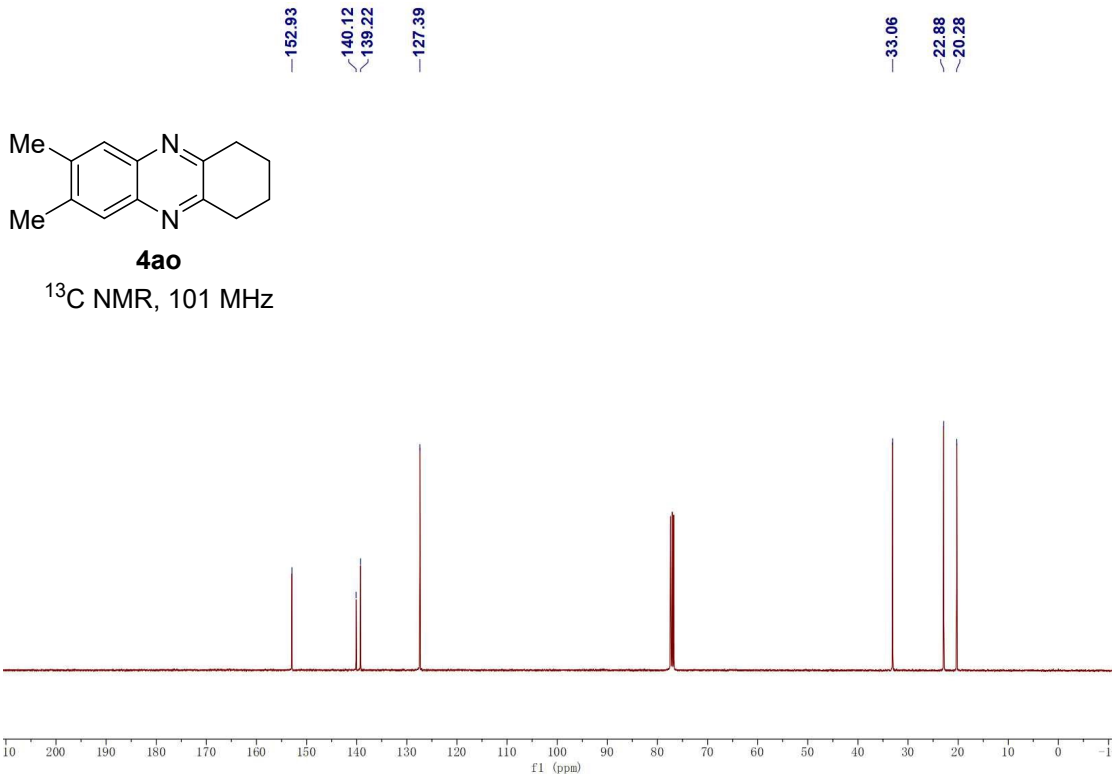
4an

^{13}C NMR, 101 MHz



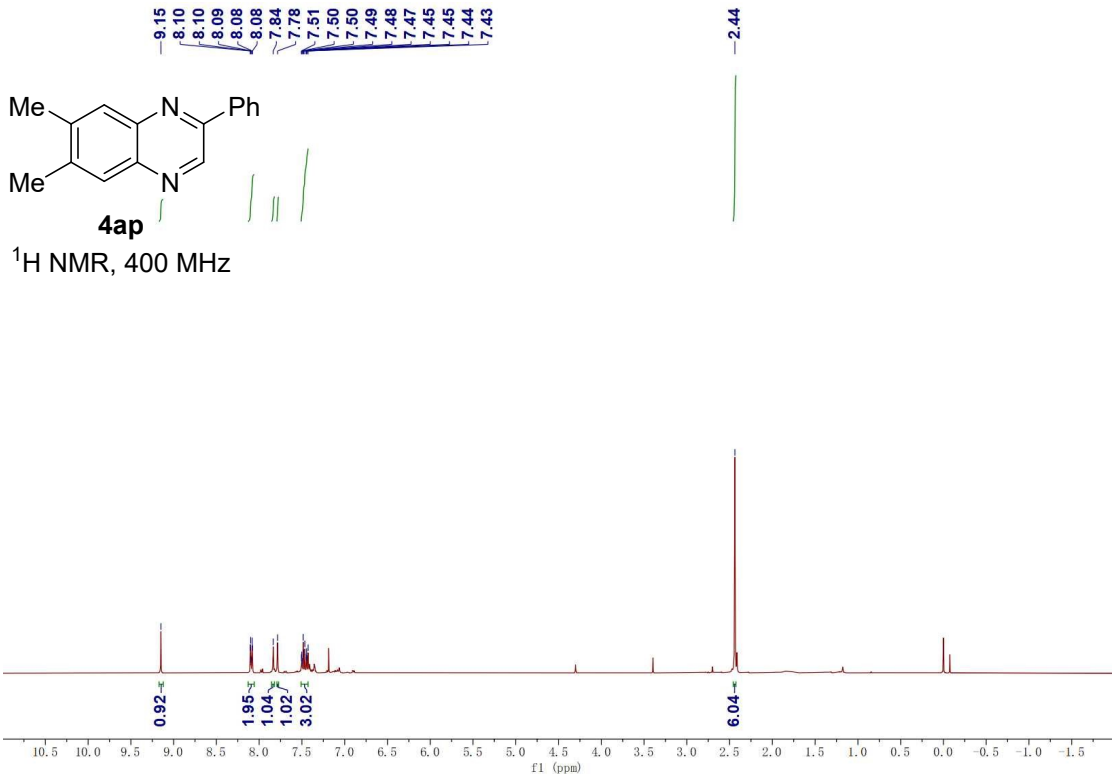
4ao

^{1}H NMR, 400 MHz



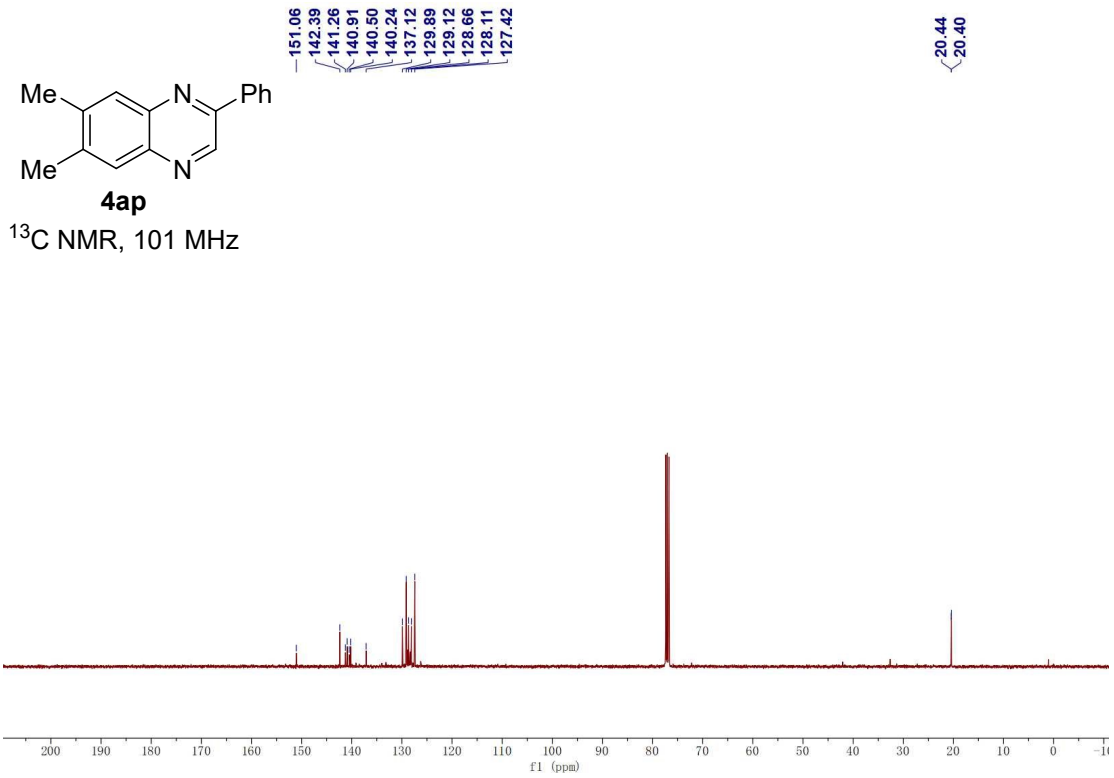
4ao

^{13}C NMR, 101 MHz



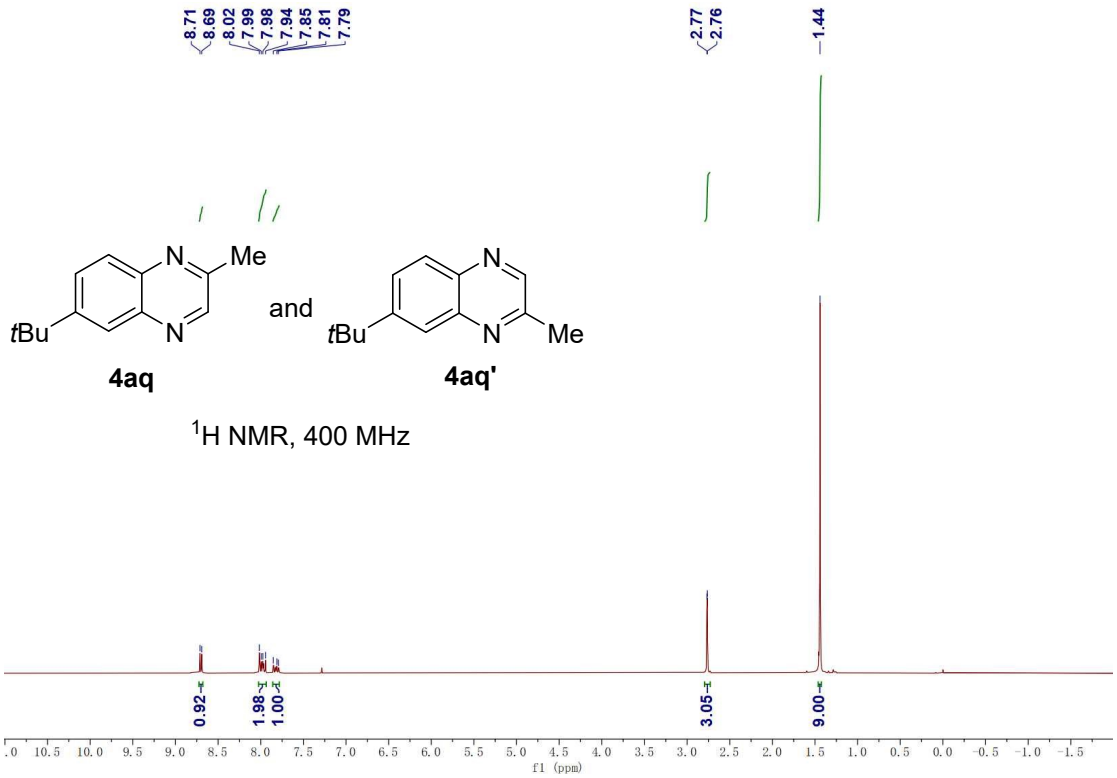
4ap

^{1}H NMR, 400 MHz



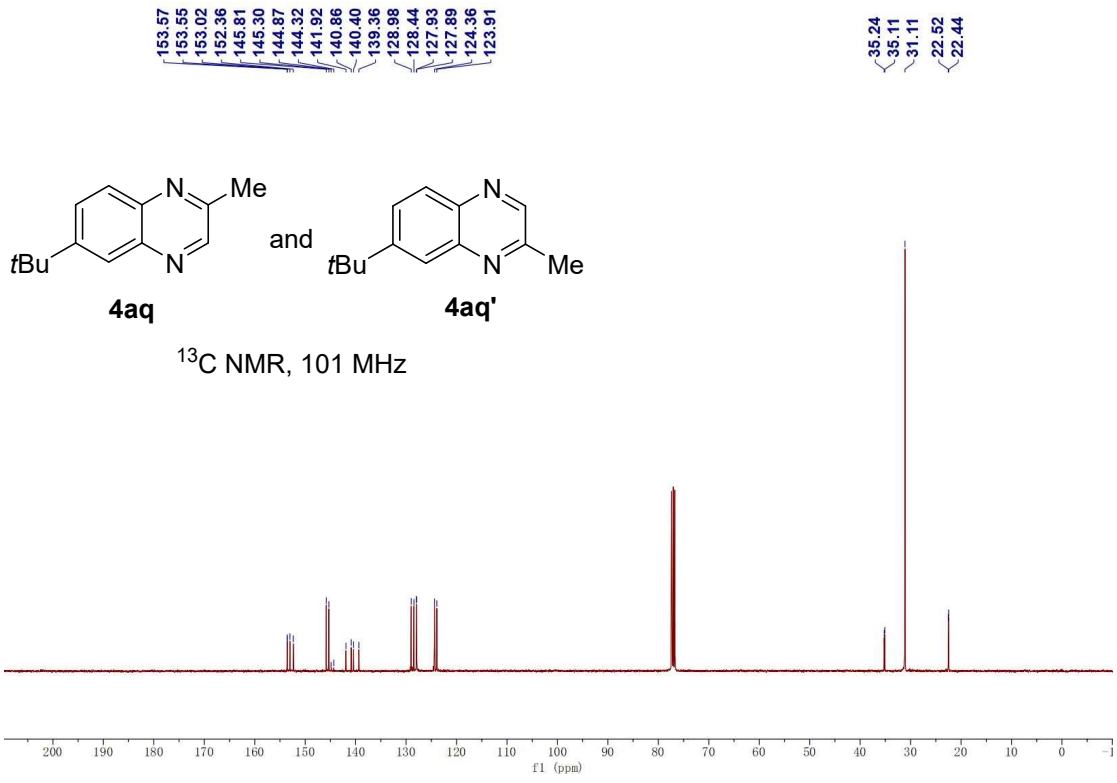
4ap

^{13}C NMR, 101 MHz



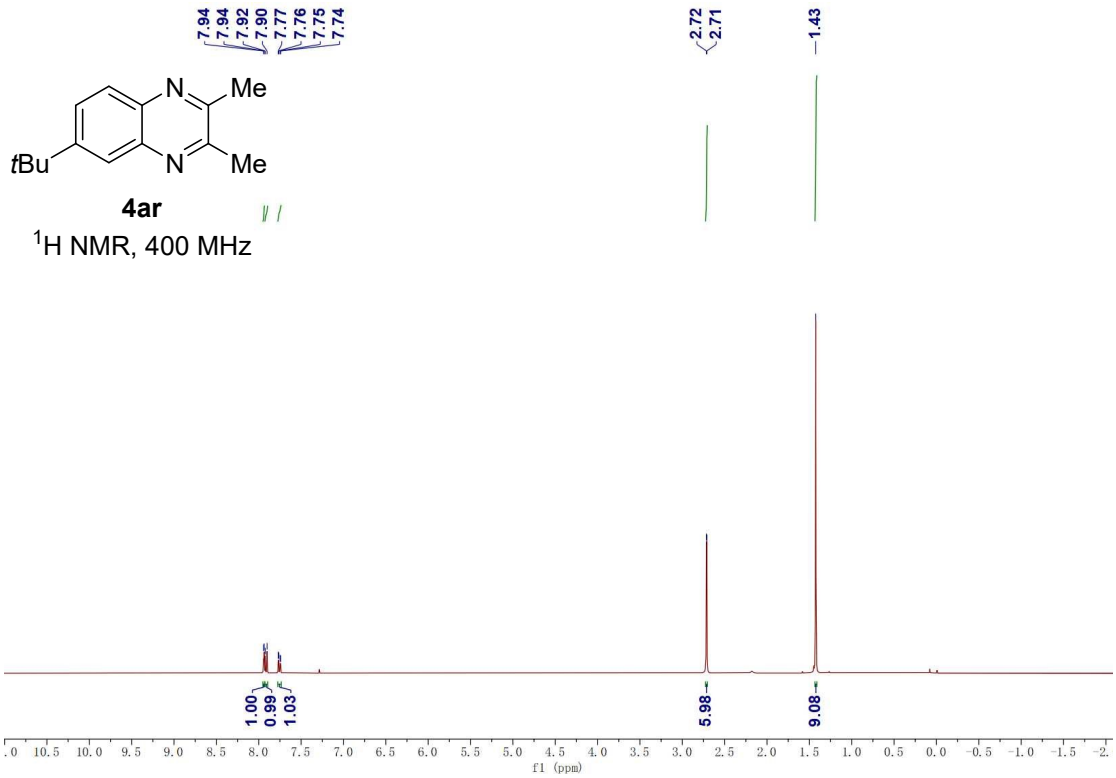
4aq **4aq'**

^{1}H NMR, 400 MHz



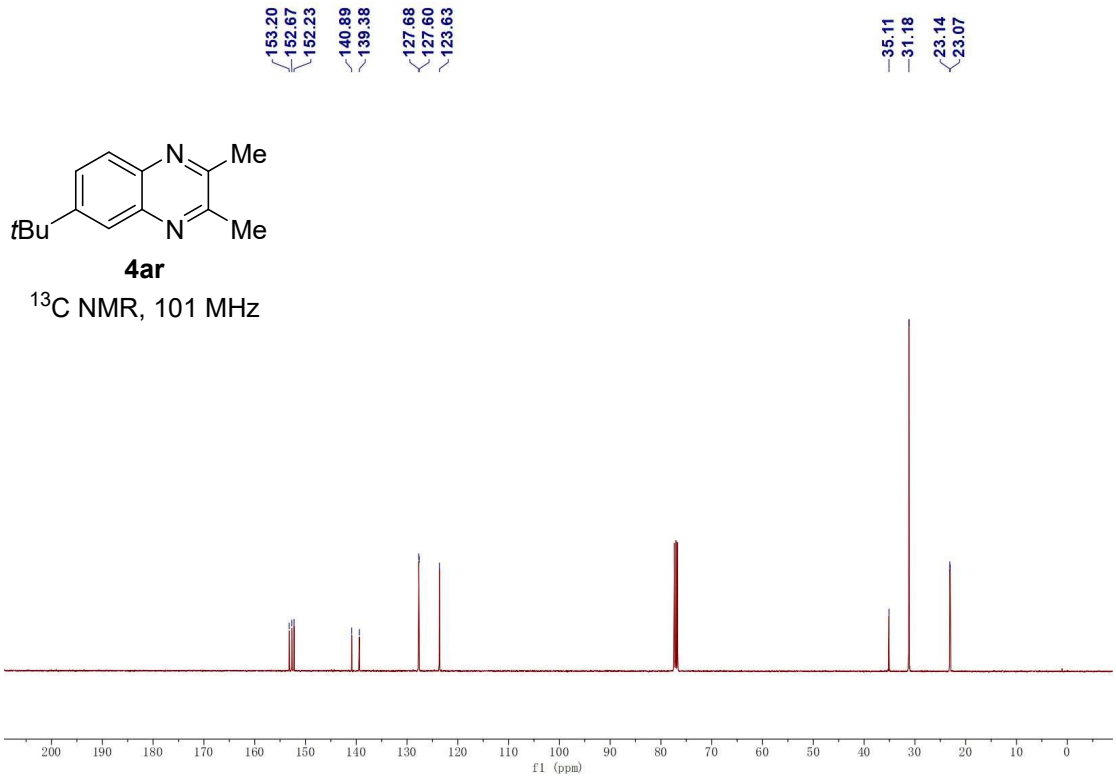
4aq **4aq'**

^{13}C NMR, 101 MHz



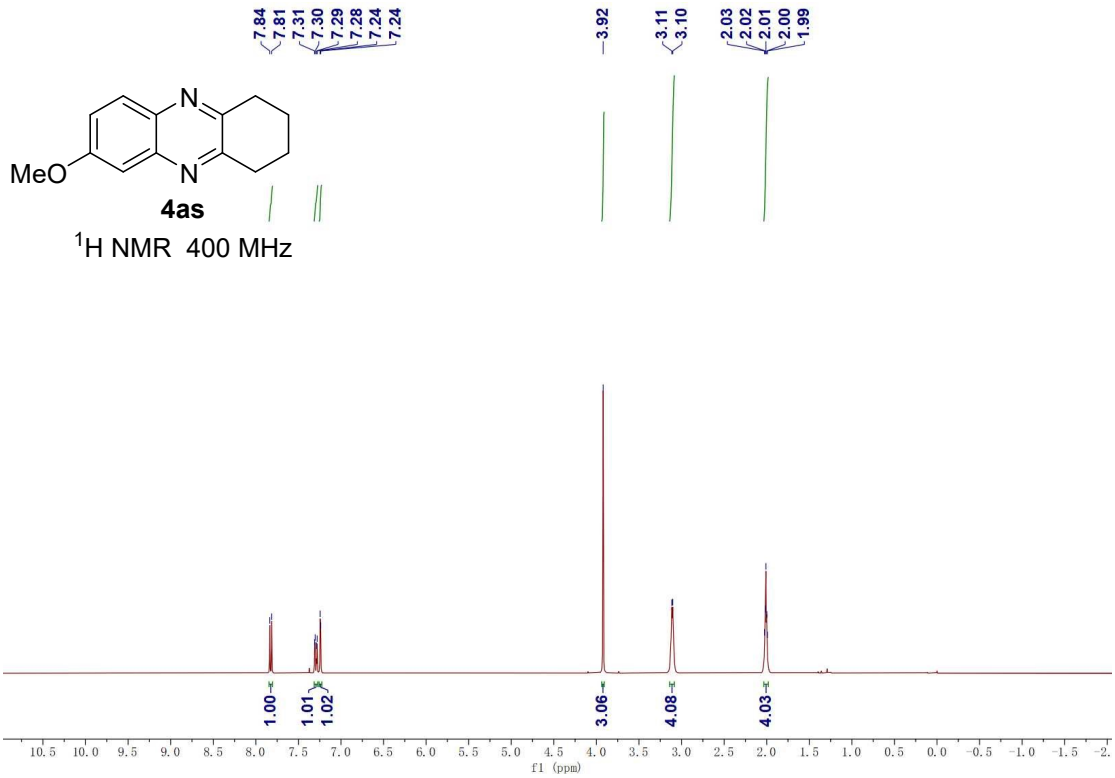
4ar

^{1}H NMR, 400 MHz



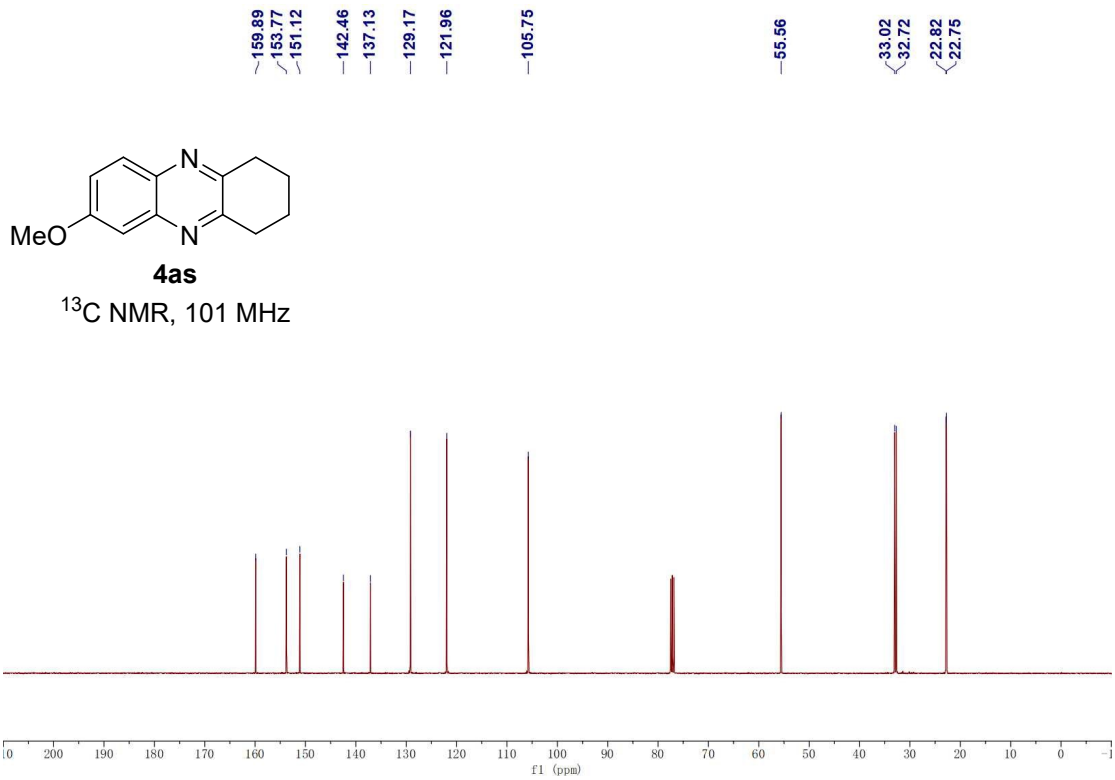
4ar

^{13}C NMR, 101 MHz



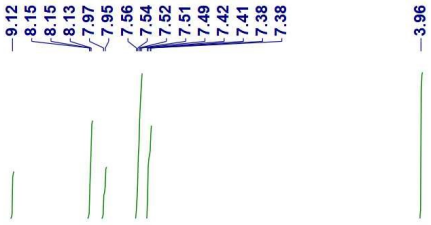
4as

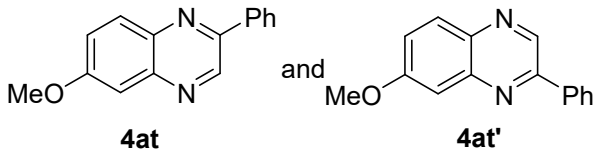
^{1}H NMR 400 MHz



4as

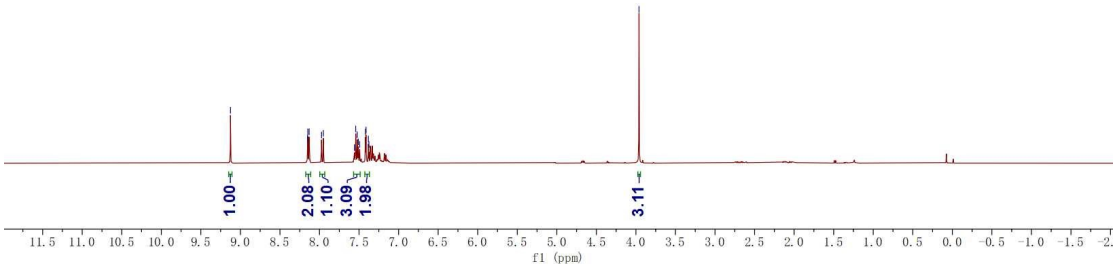
^{13}C NMR, 101 MHz

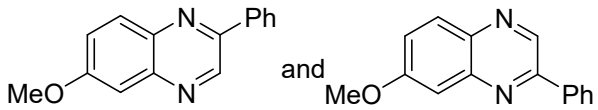




4at **4at'**

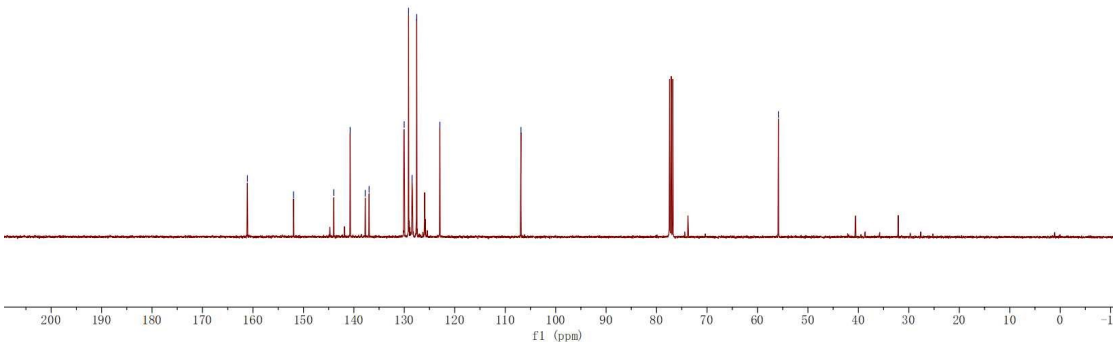
^{1}H NMR, 400 MHz

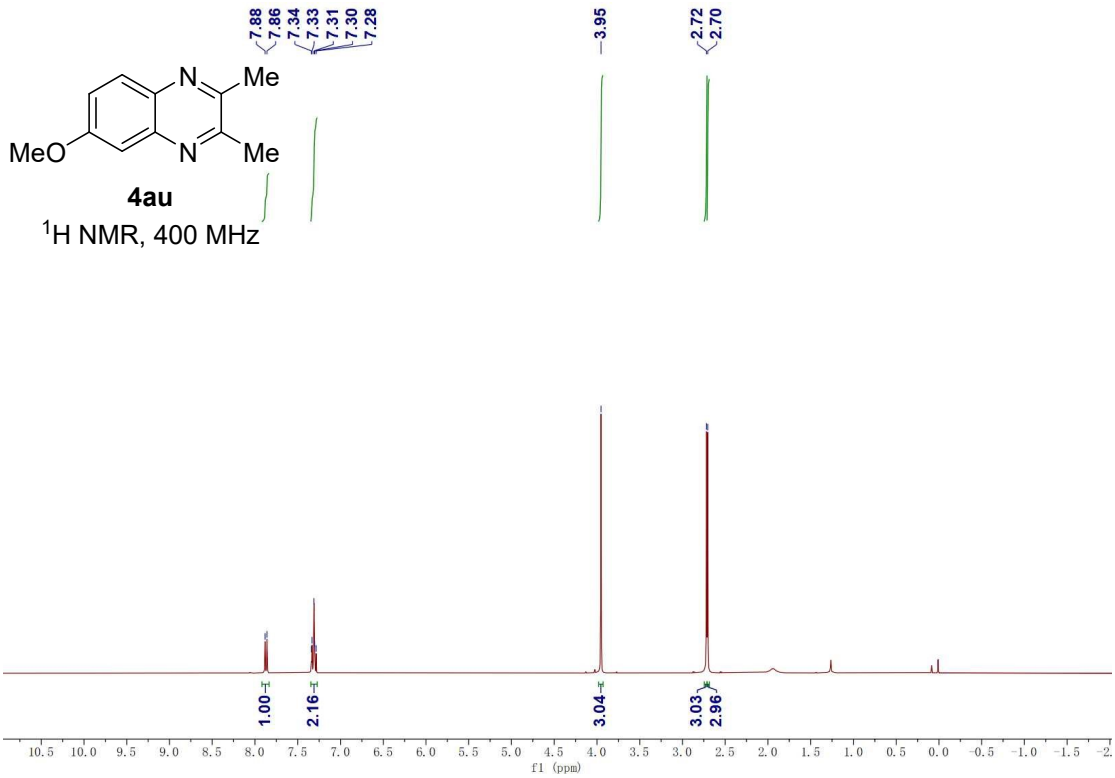




4at **4at'**

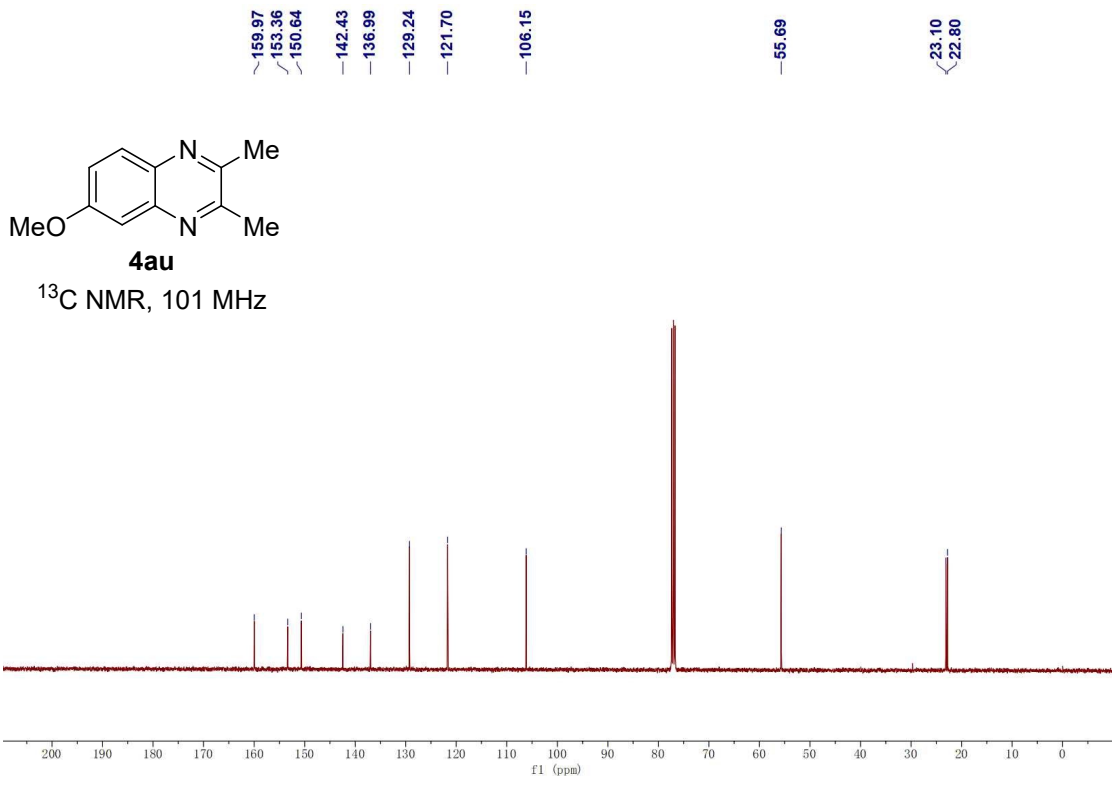
^{13}C NMR, 101 MHz





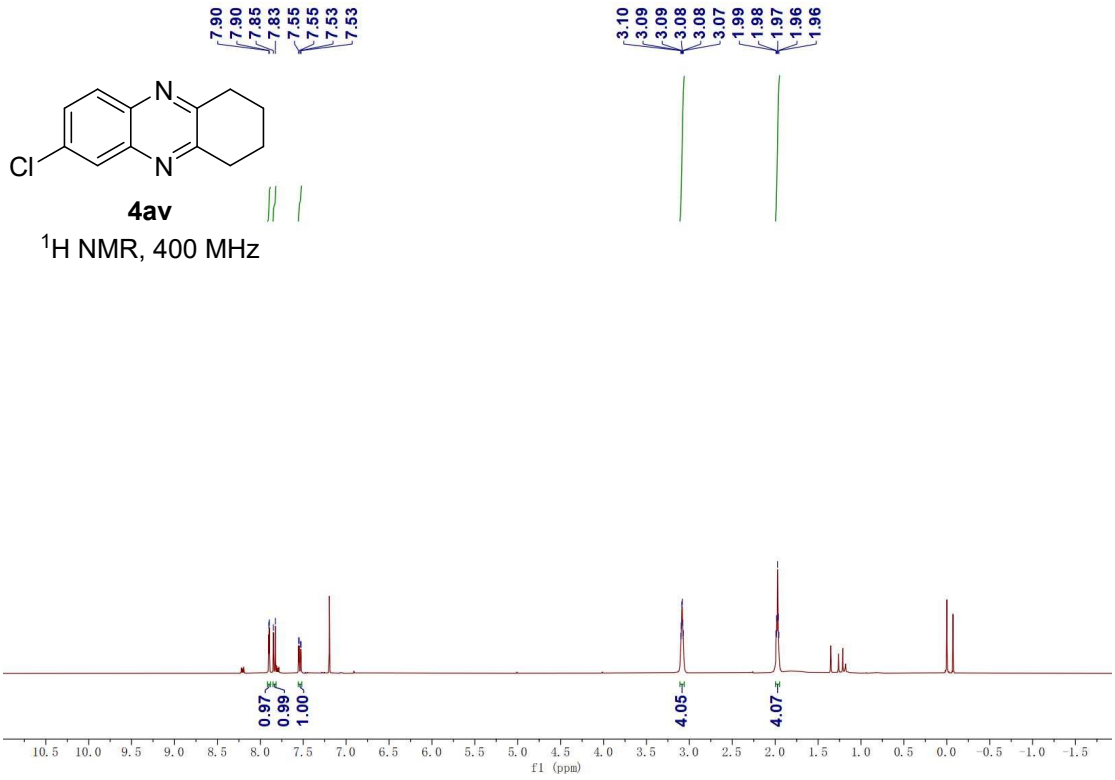
4au

^{1}H NMR, 400 MHz



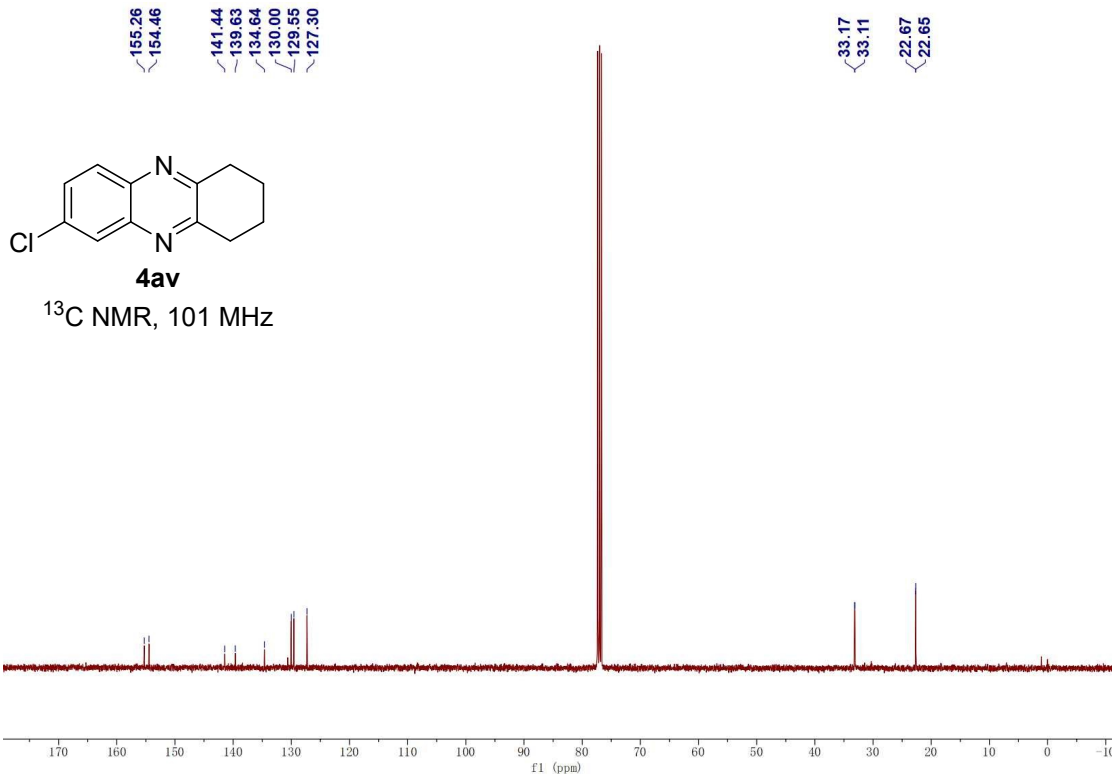
4au

^{13}C NMR, 101 MHz



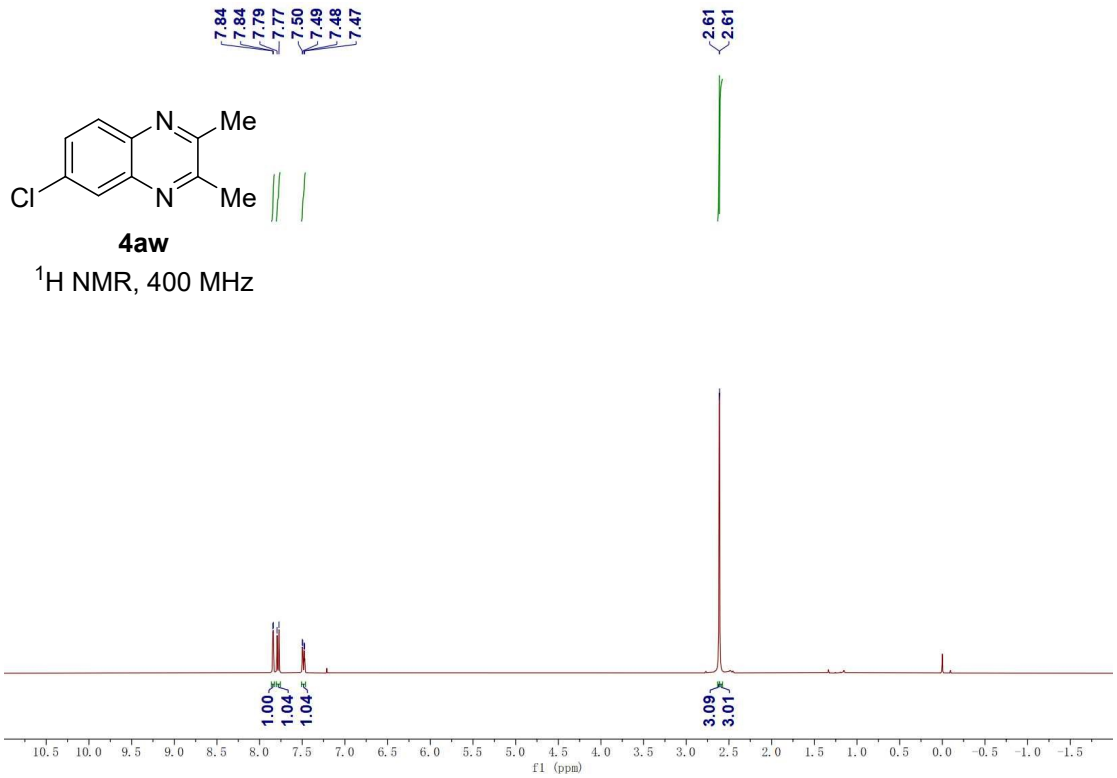
4av

^{1}H NMR, 400 MHz



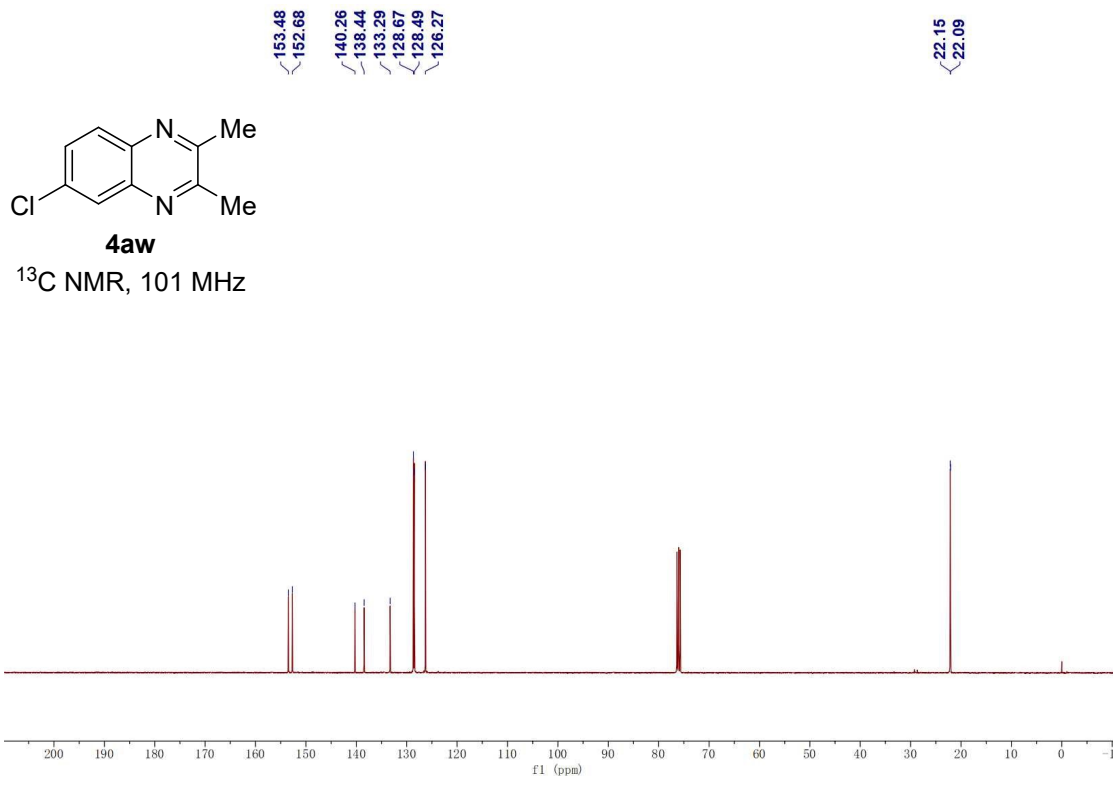
4av

^{13}C NMR, 101 MHz



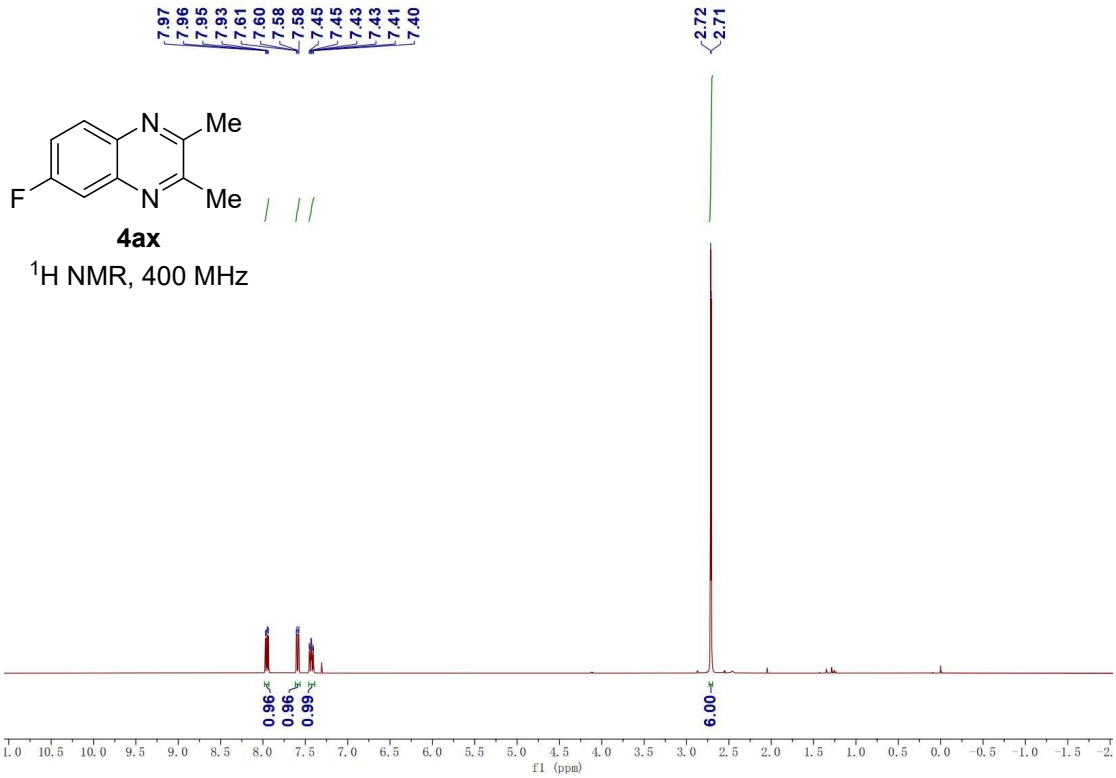
4aw

^{1}H NMR, 400 MHz



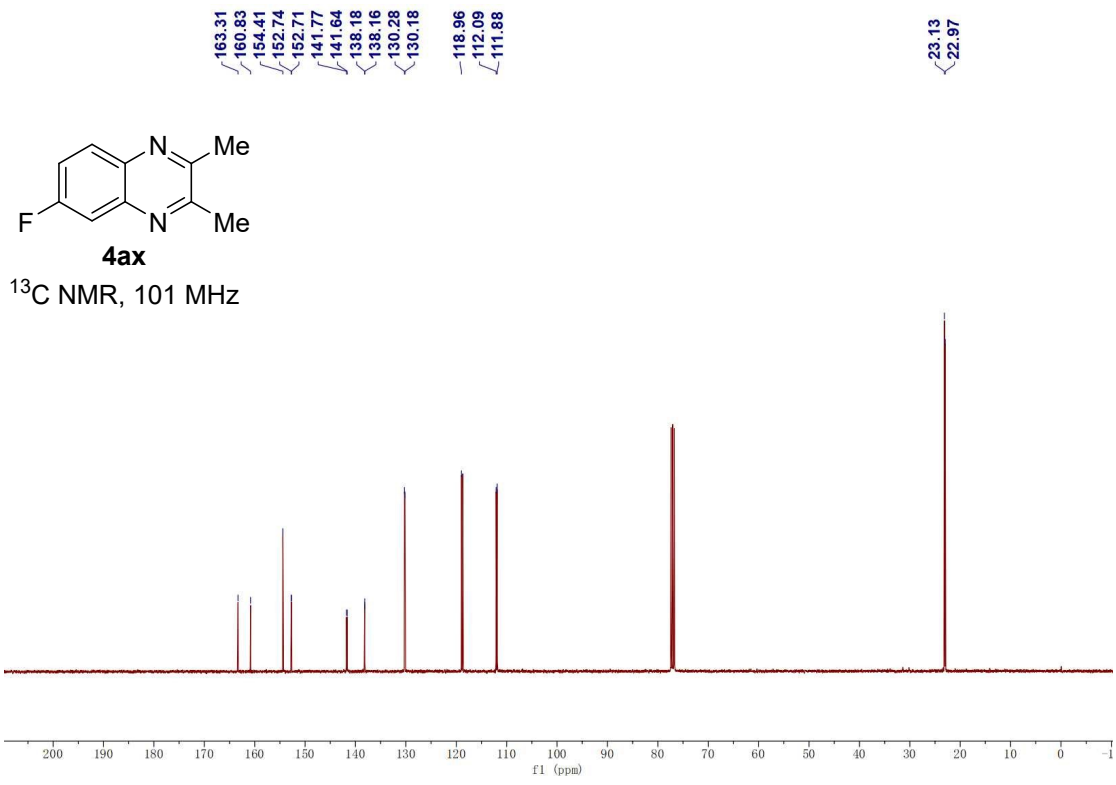
4aw

^{13}C NMR, 101 MHz



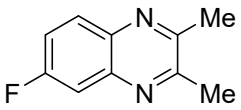
4ax

^{1}H NMR, 400 MHz



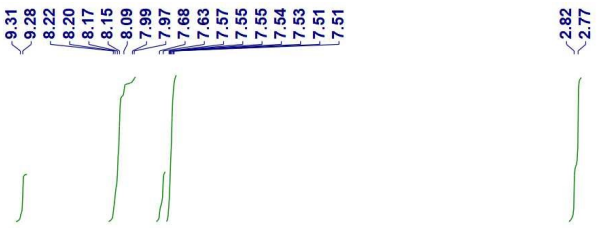
4ax

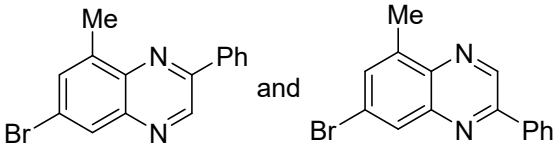
^{13}C NMR, 101 MHz



4ax

^{19}F NMR, 376 MHz

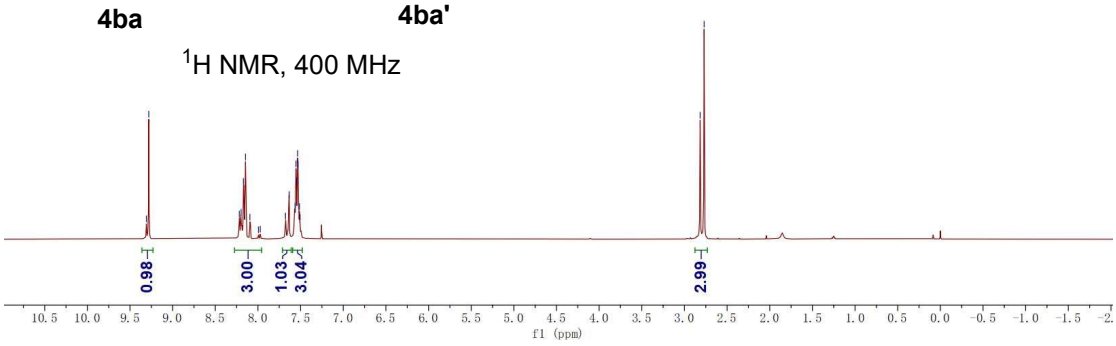


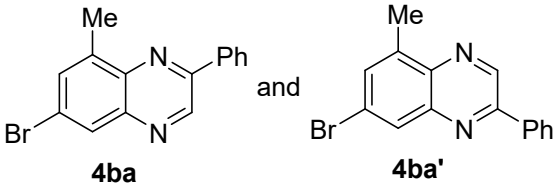


and

4ba **4ba'**

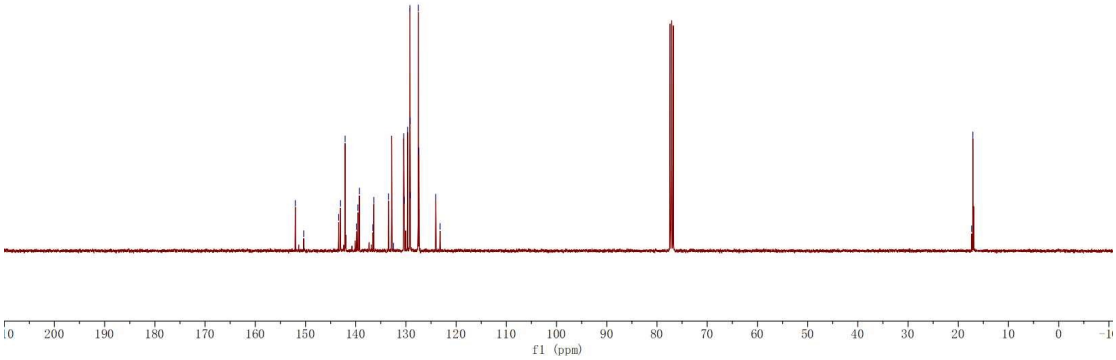
^{1}H NMR, 400 MHz

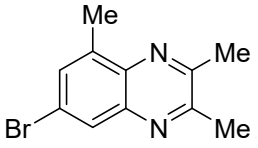




4ba **4ba'**

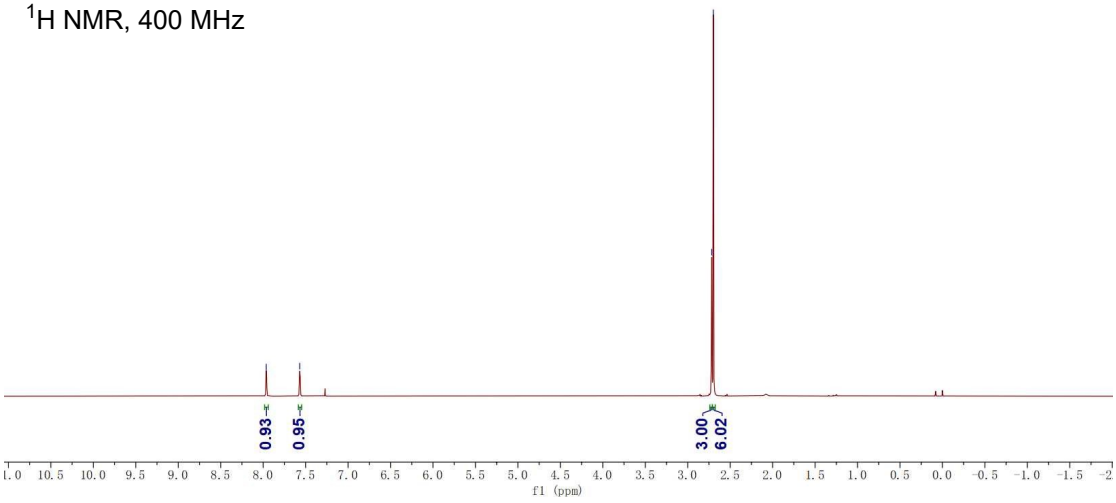
^{13}C NMR, 101 MHz

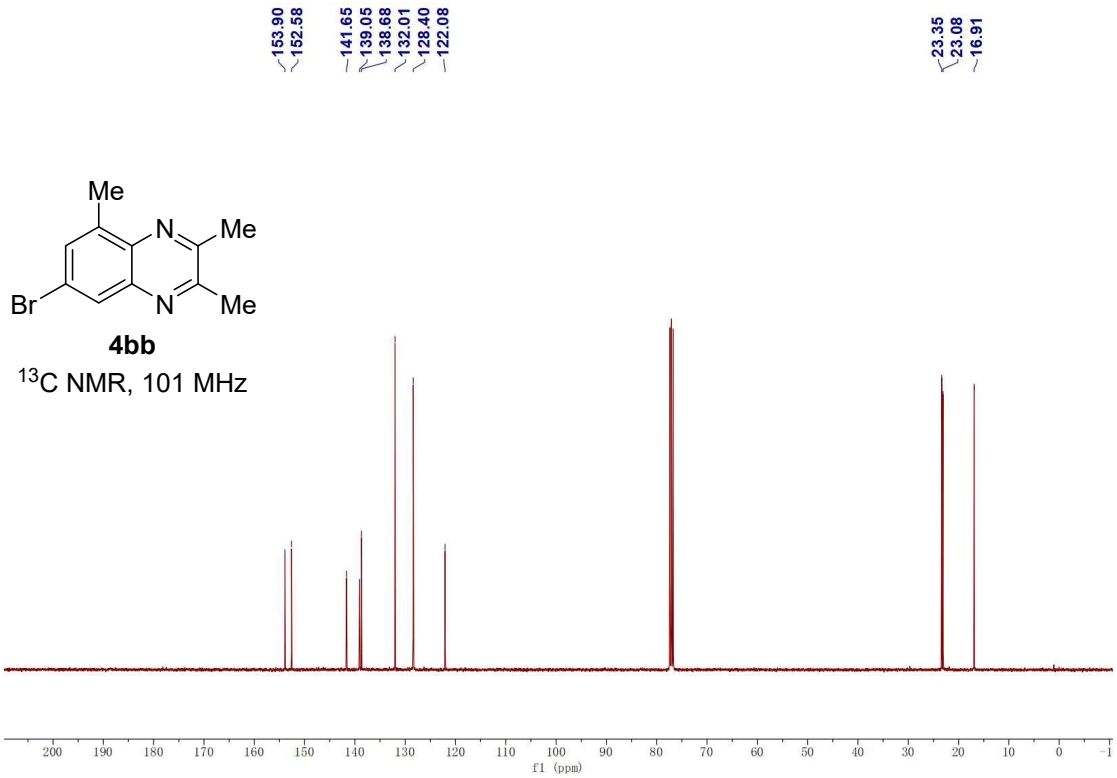




4bb

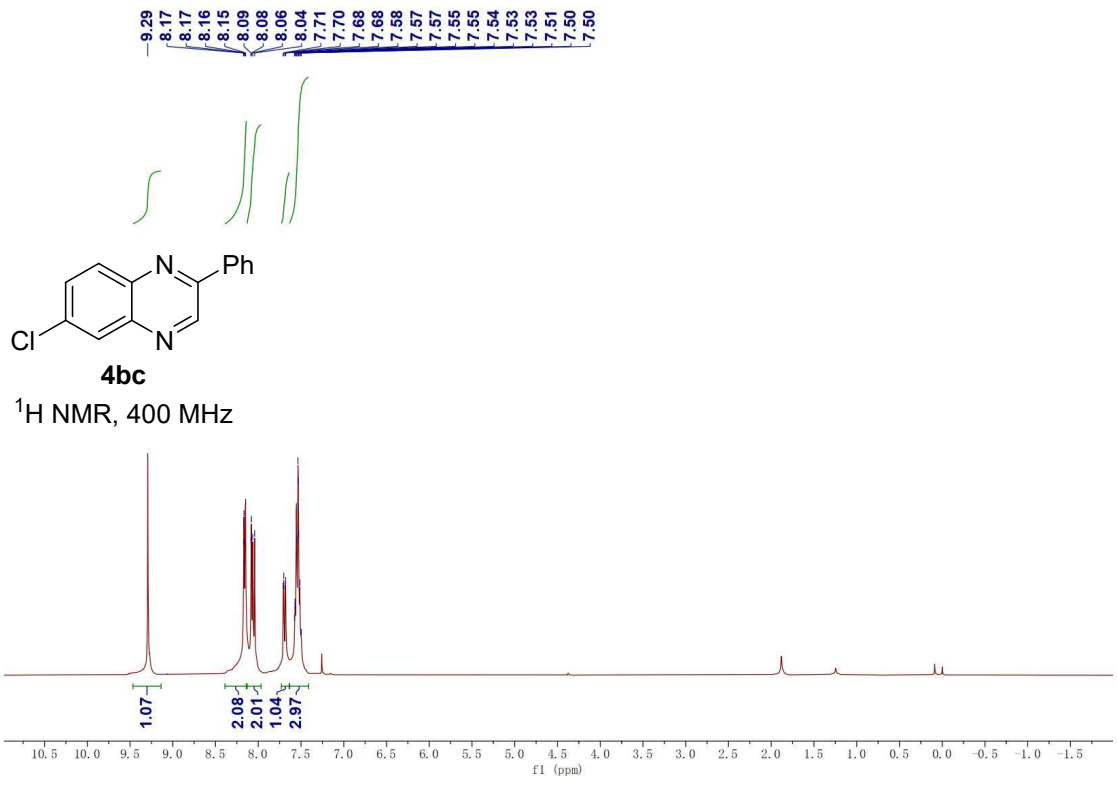
^{1}H NMR, 400 MHz





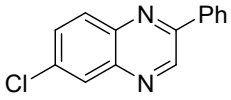
4bb

^{13}C NMR, 101 MHz



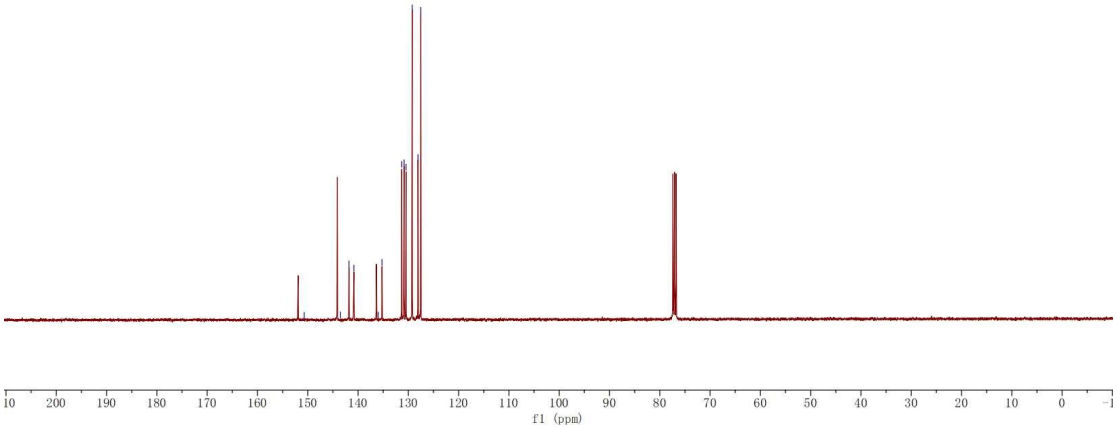
4bc

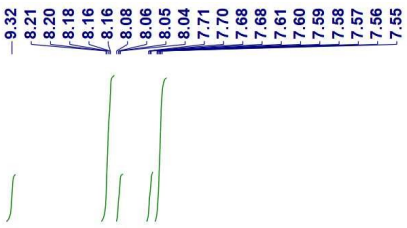
^{1}H NMR, 400 MHz

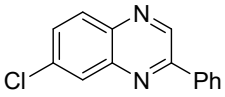


4bc

^{13}C NMR, 101 MHz

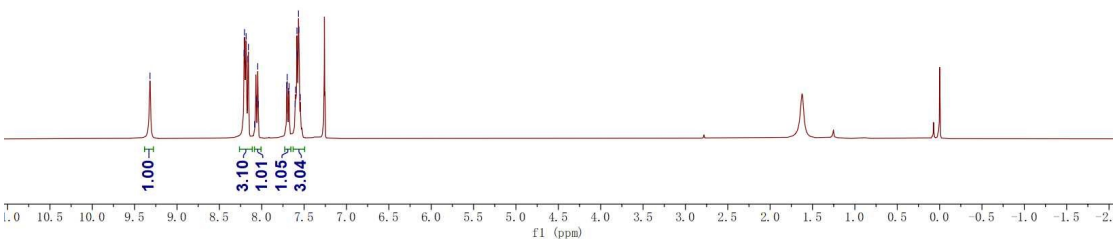


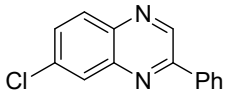




4bc'

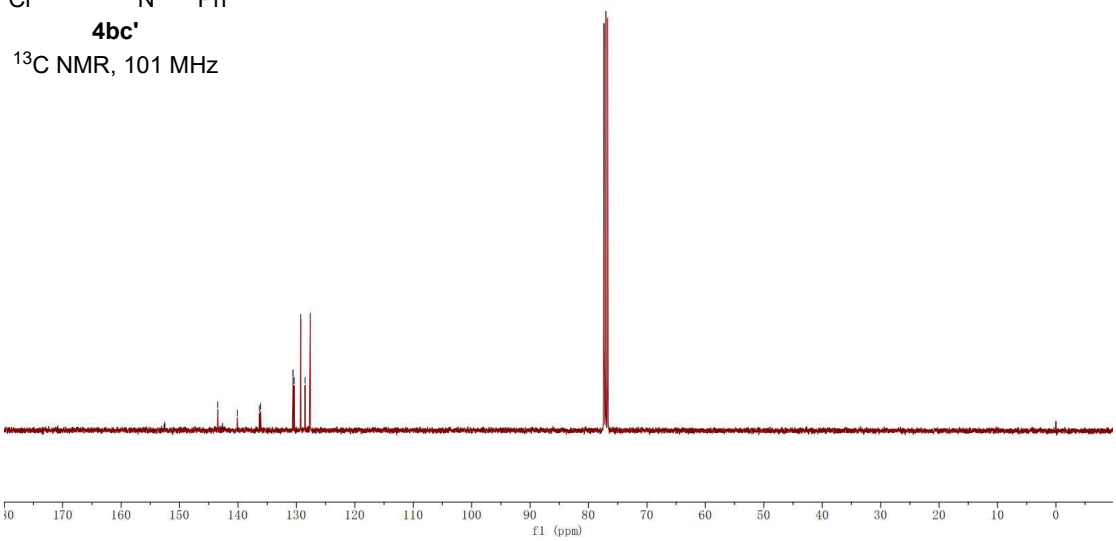
^{1}H NMR, 400 MHz

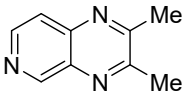




4bc'

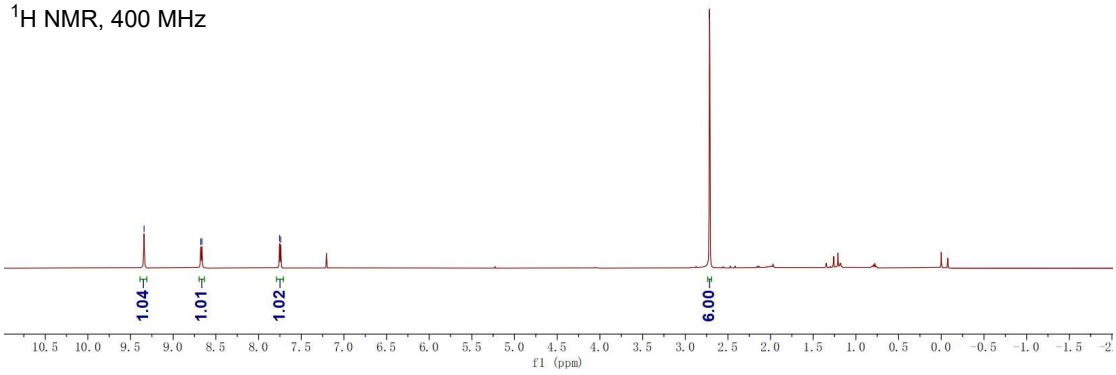
^{13}C NMR, 101 MHz

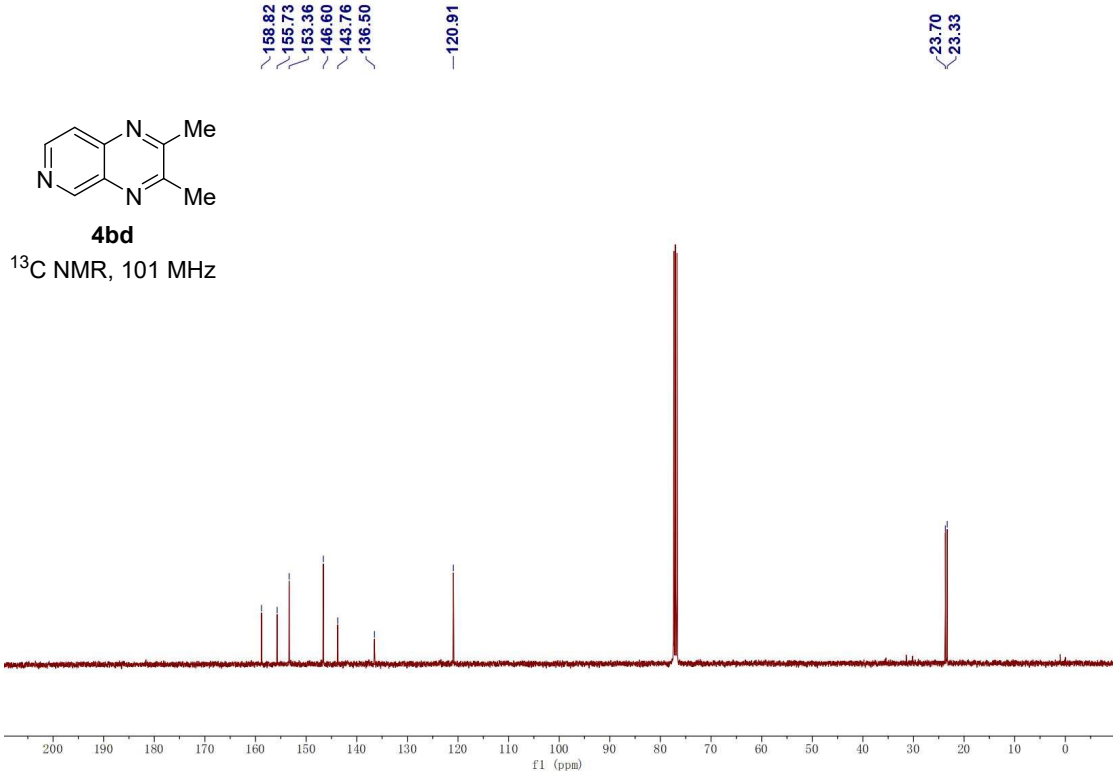




4bd

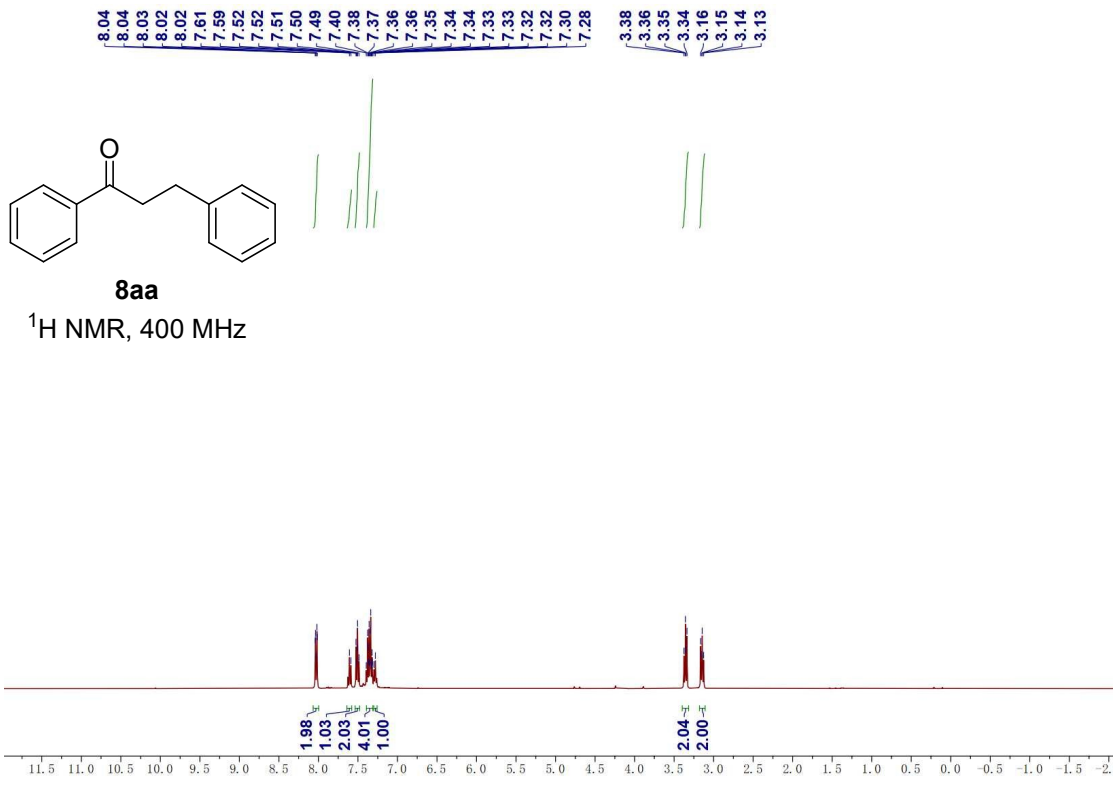
^{1}H NMR, 400 MHz





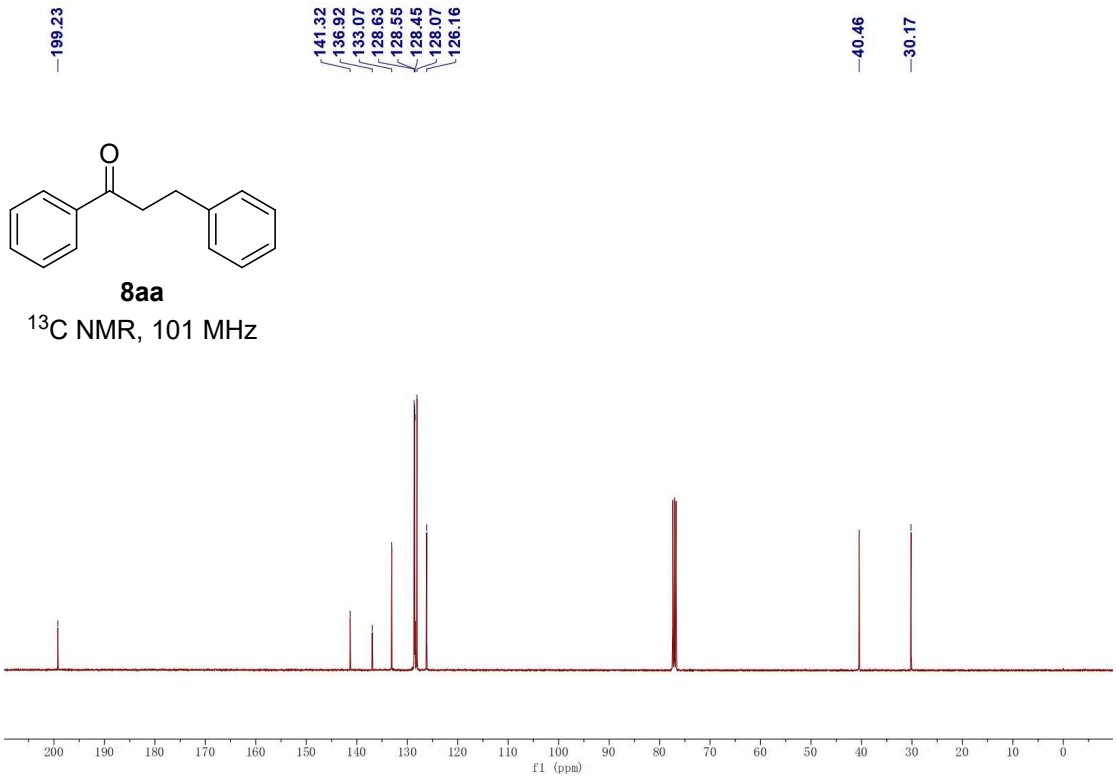
4bd

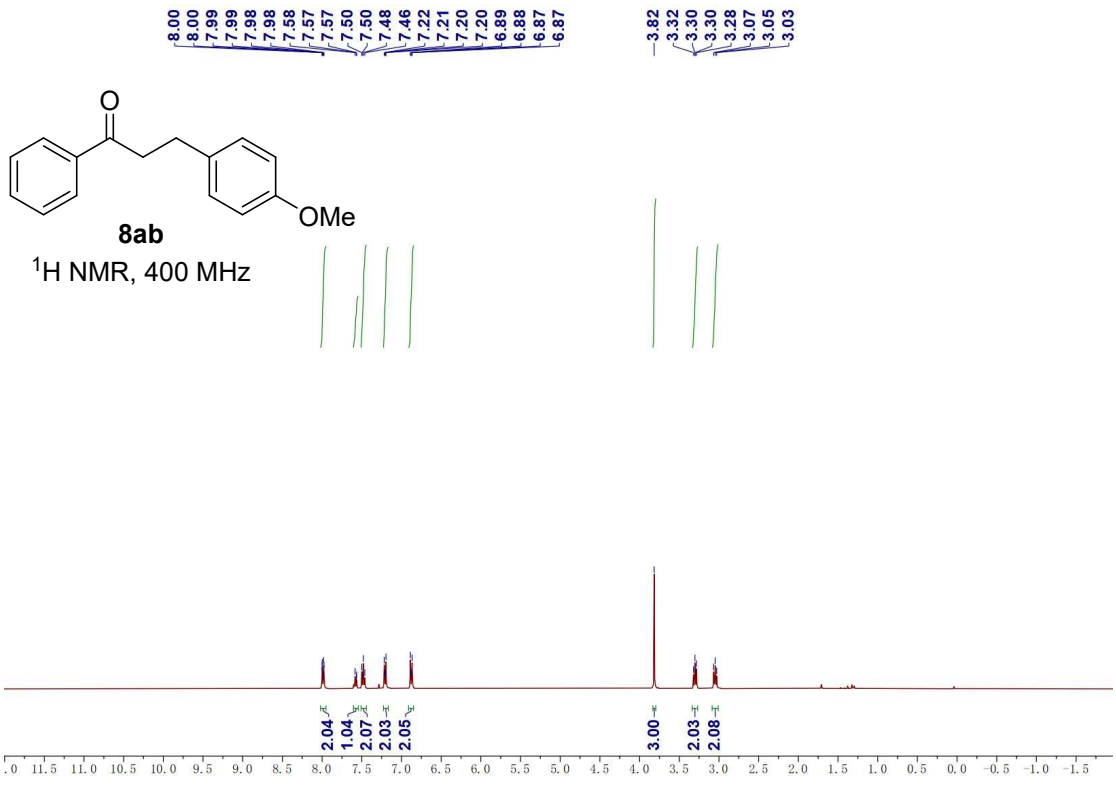
^{13}C NMR, 101 MHz

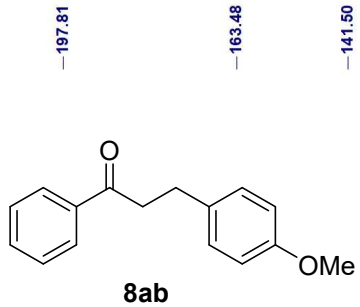


8aa

^{1}H NMR, 400 MHz

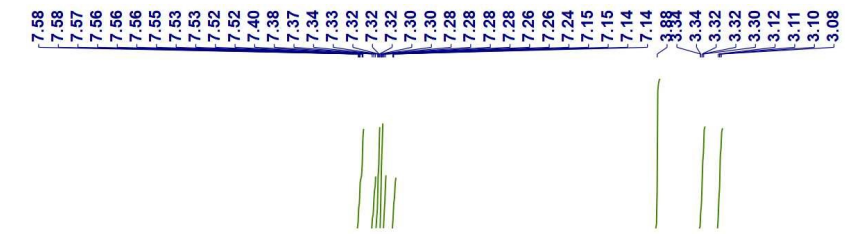

199.23
141.32
136.92
133.07
128.63
128.55
128.45
128.07
126.16
40.46
30.17
O
8aa
13C NMR, 101 MHz
f1 (ppm)

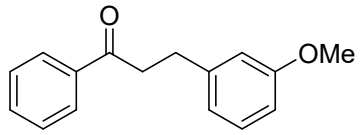

8.00
8.00
7.99
7.99
7.98
7.98
7.58
7.57
7.57
7.50
7.50
7.48
7.46
7.22
7.21
7.20
7.20
6.89
6.88
6.87
6.87
3.82
3.32
3.30
3.30
3.28
3.07
3.05
3.03
O
OMe
8ab
1H NMR, 400 MHz
2.04
1.04
2.07
2.03
2.05
3.00
2.03
2.08



8ab

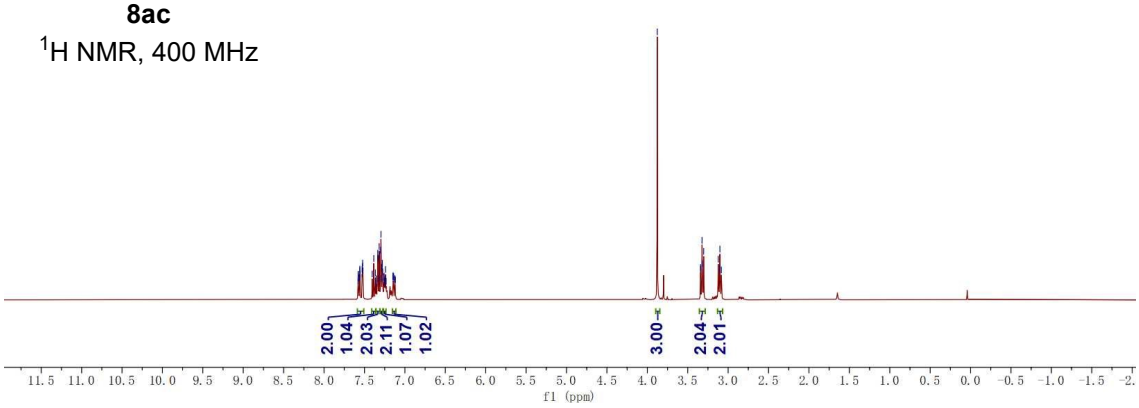
^{13}C NMR, 101 MHz

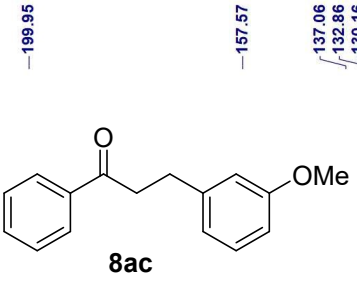




8ac

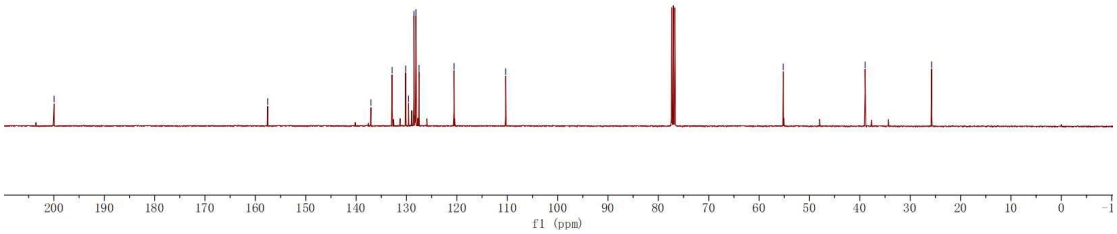
^{1}H NMR, 400 MHz

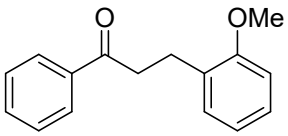




8ac

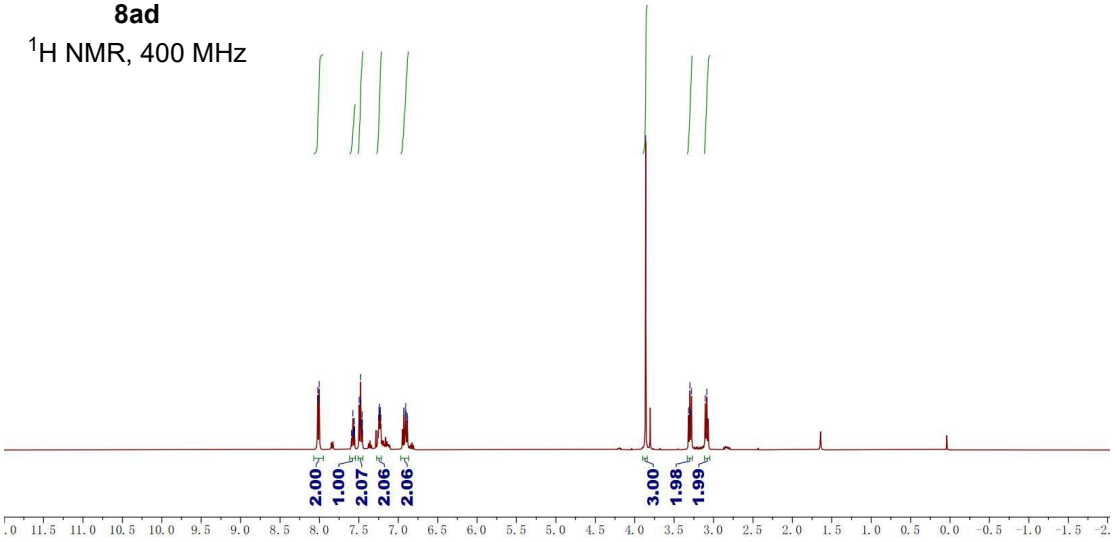
^{13}C NMR, 101 MHz

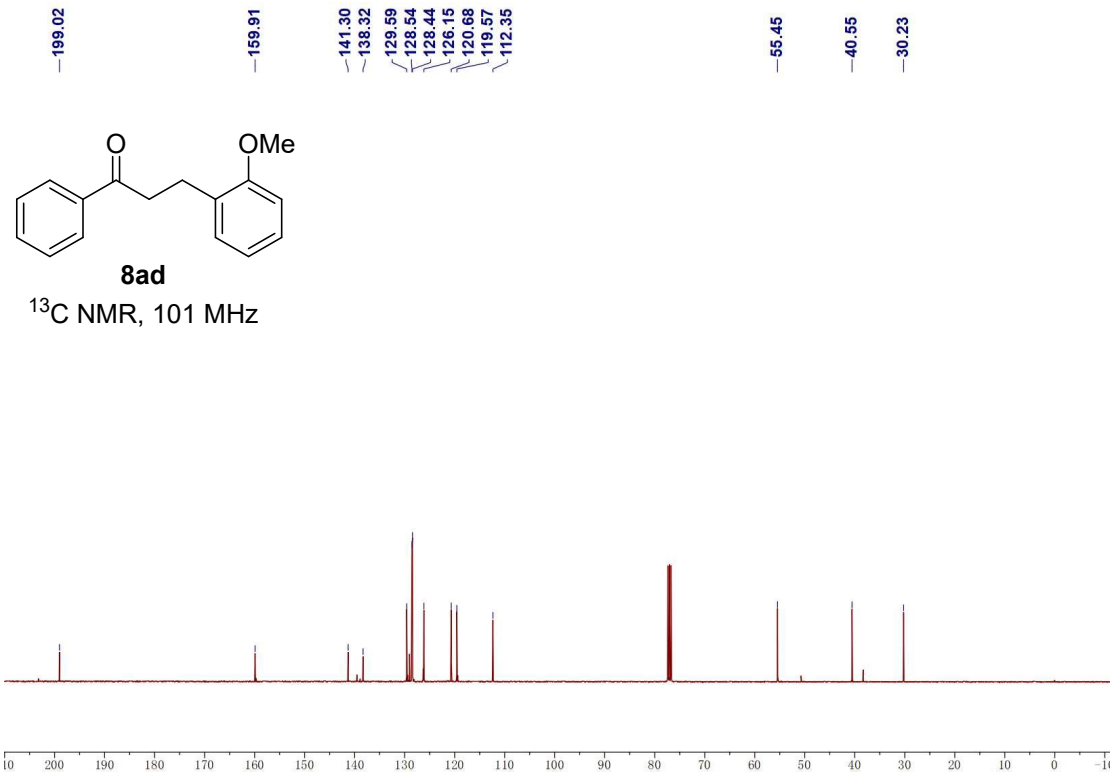




8ad

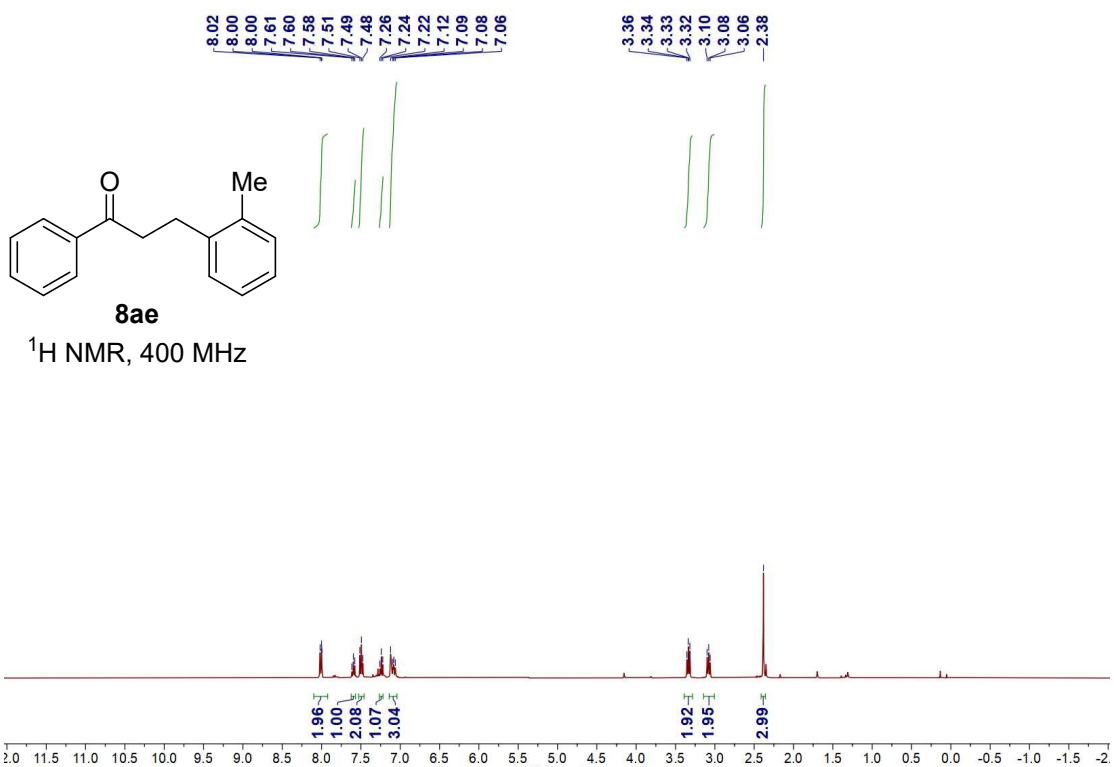
^{1}H NMR, 400 MHz





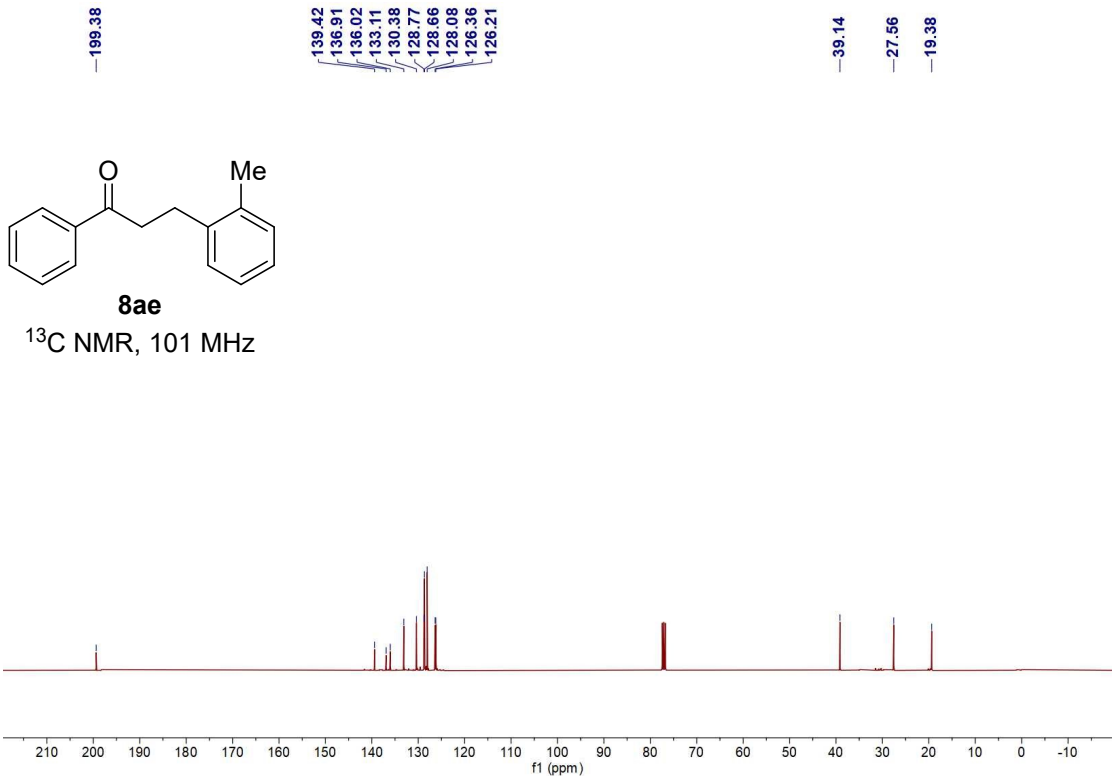
8ad

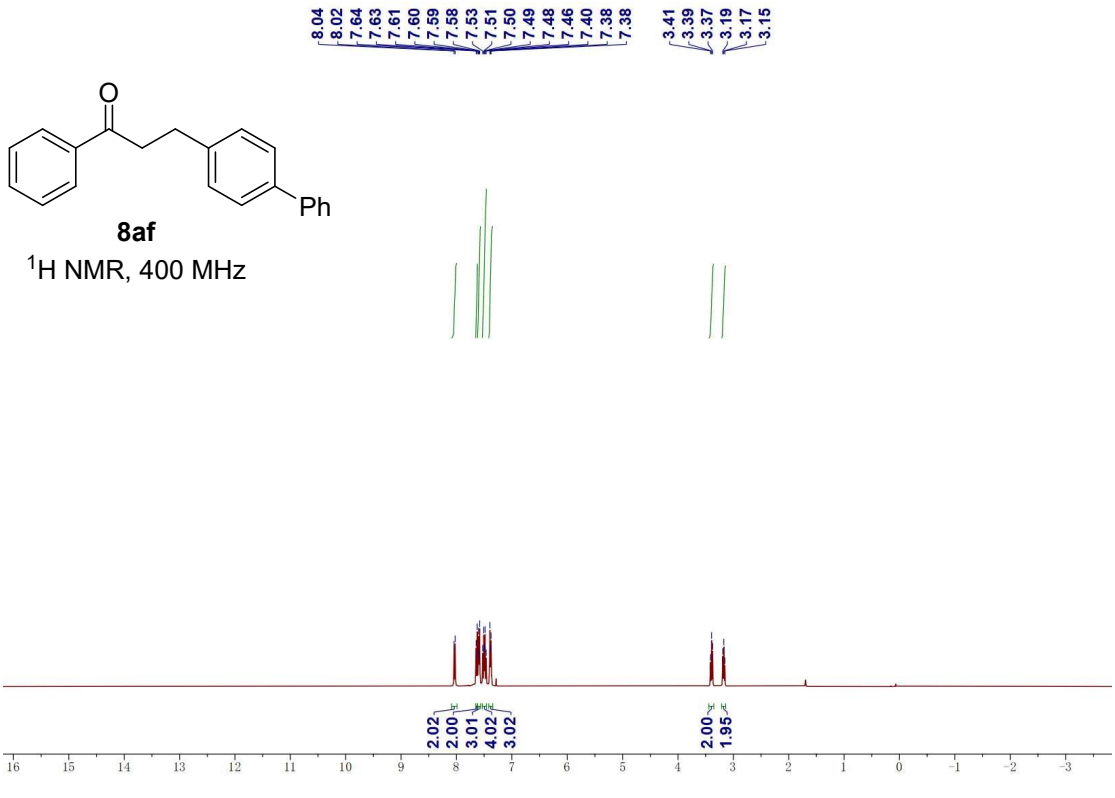
^{13}C NMR, 101 MHz



8ae

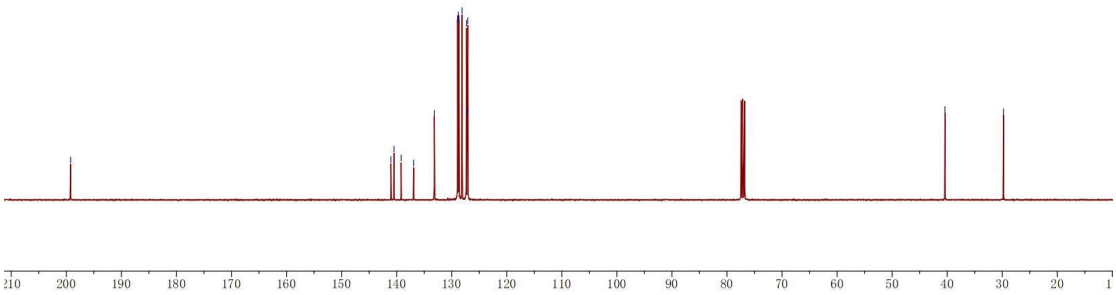
^{1}H NMR, 400 MHz

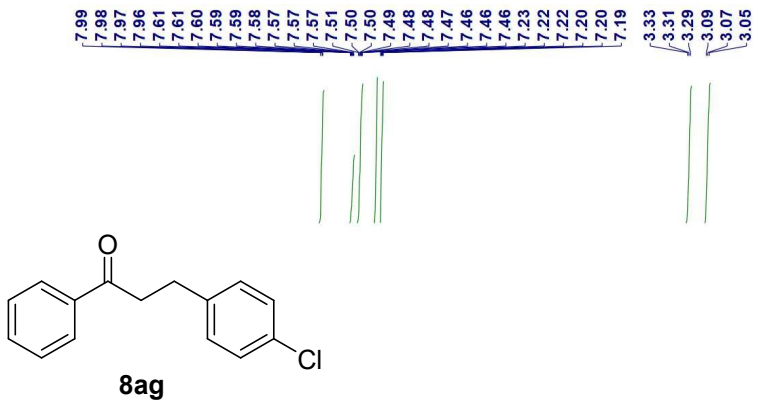

199.38
139.42
136.91
136.02
133.11
130.38
128.77
128.66
128.08
126.36
126.21
39.14
27.56
19.38
O
Me
8ae
13C NMR, 101 MHz
f1 (ppm)


8.04
8.02
7.64
7.63
7.61
7.60
7.59
7.58
7.53
7.51
7.50
7.49
7.48
7.46
7.40
7.38
3.41
3.39
3.37
3.19
3.17
3.15
O
Ph
8af
1H NMR, 400 MHz
2.02
2.00
3.01
4.02
3.02
2.00
1.95

8af

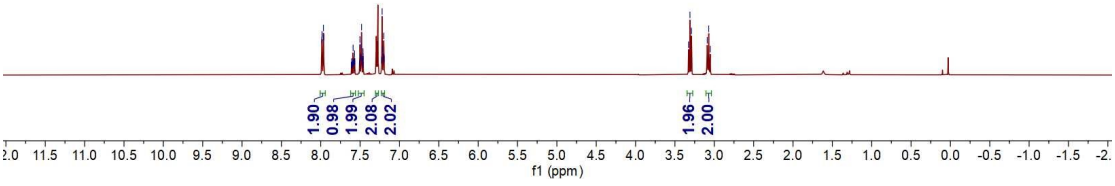
^{13}C NMR, 101 MHz

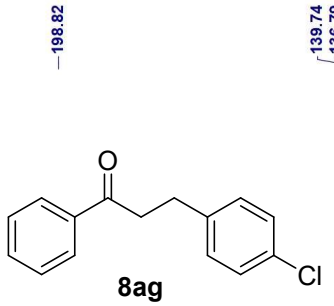




8ag

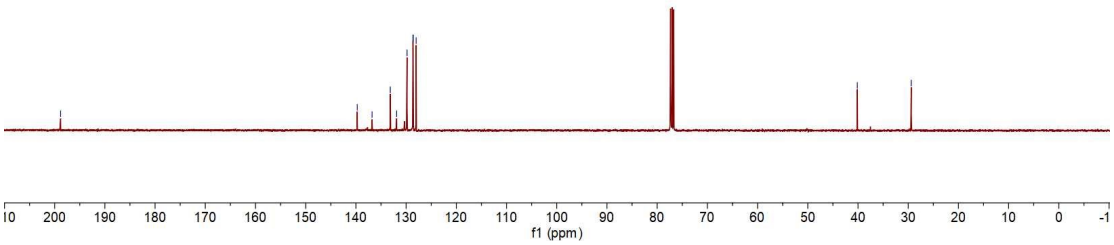
^{1}H NMR, 400 MHz

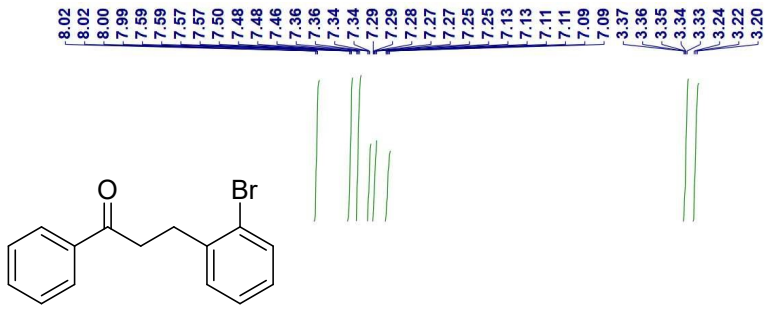




8ag

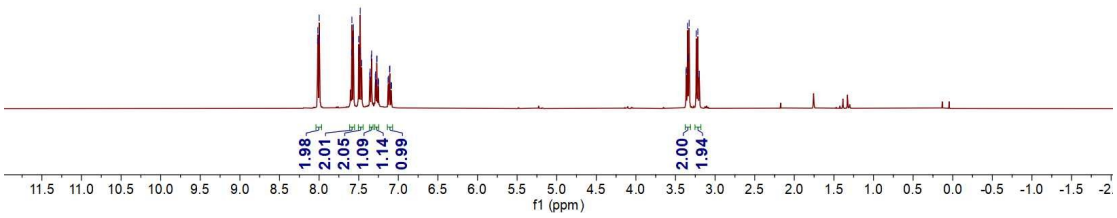
^{13}C NMR, 101 MHz

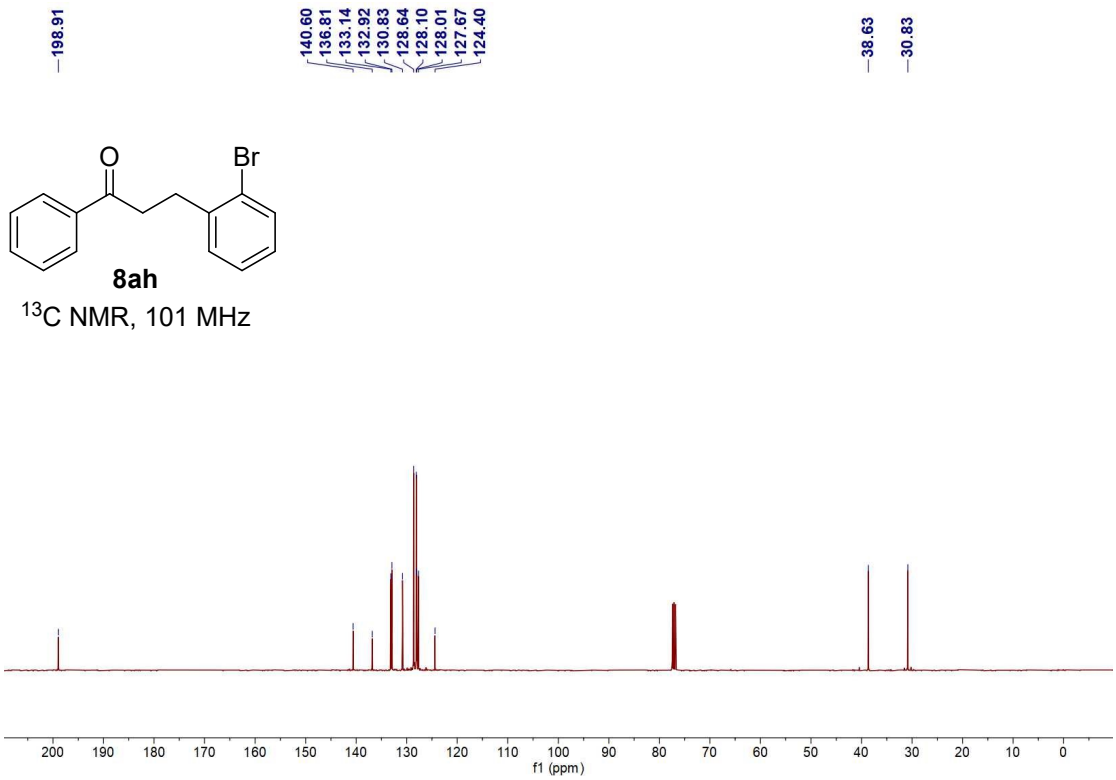




8ah

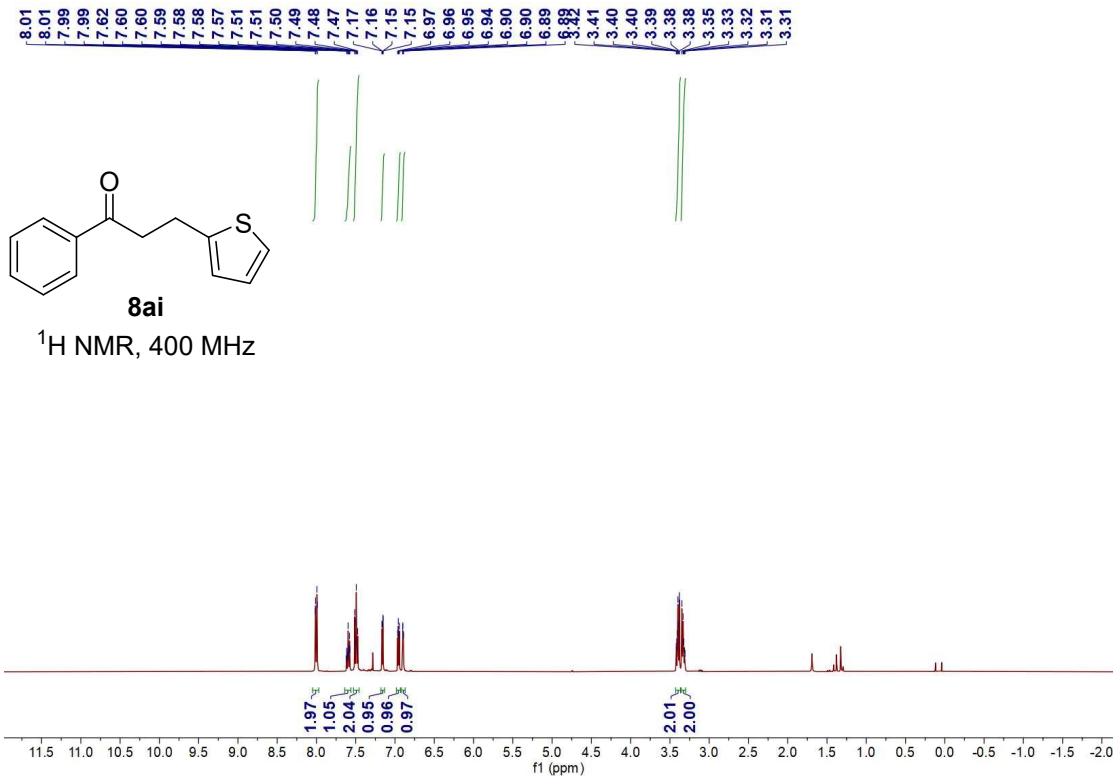
^{1}H NMR, 400 MHz





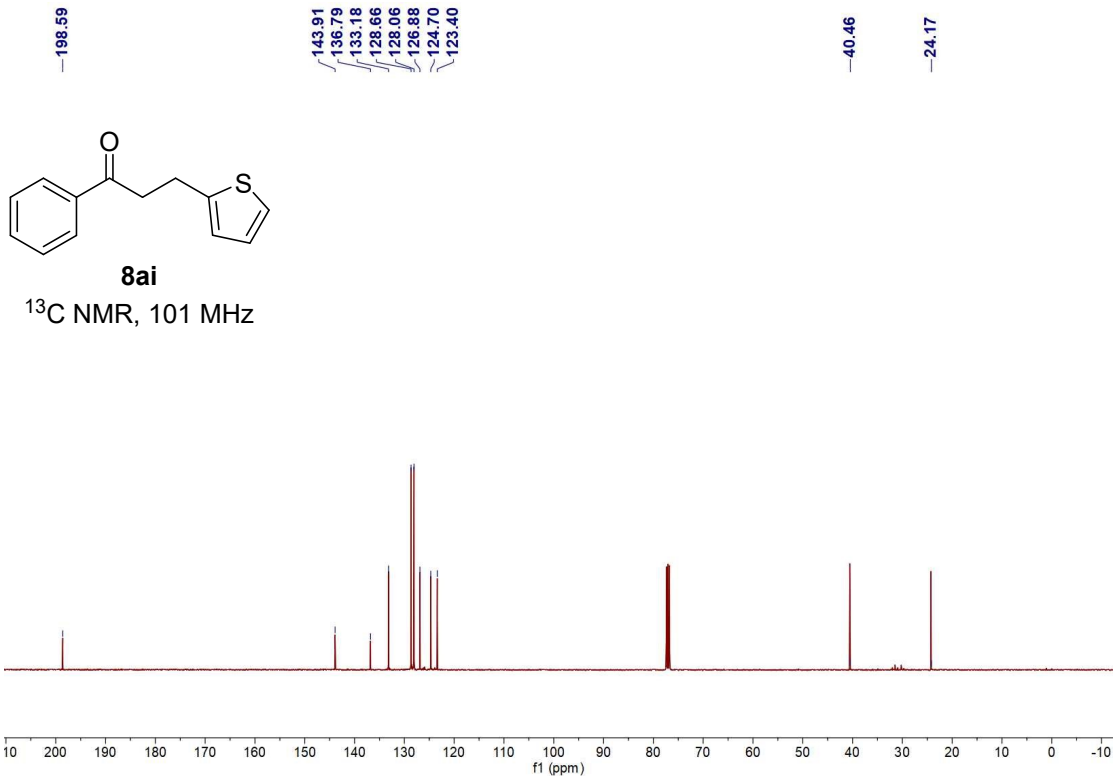
8ah

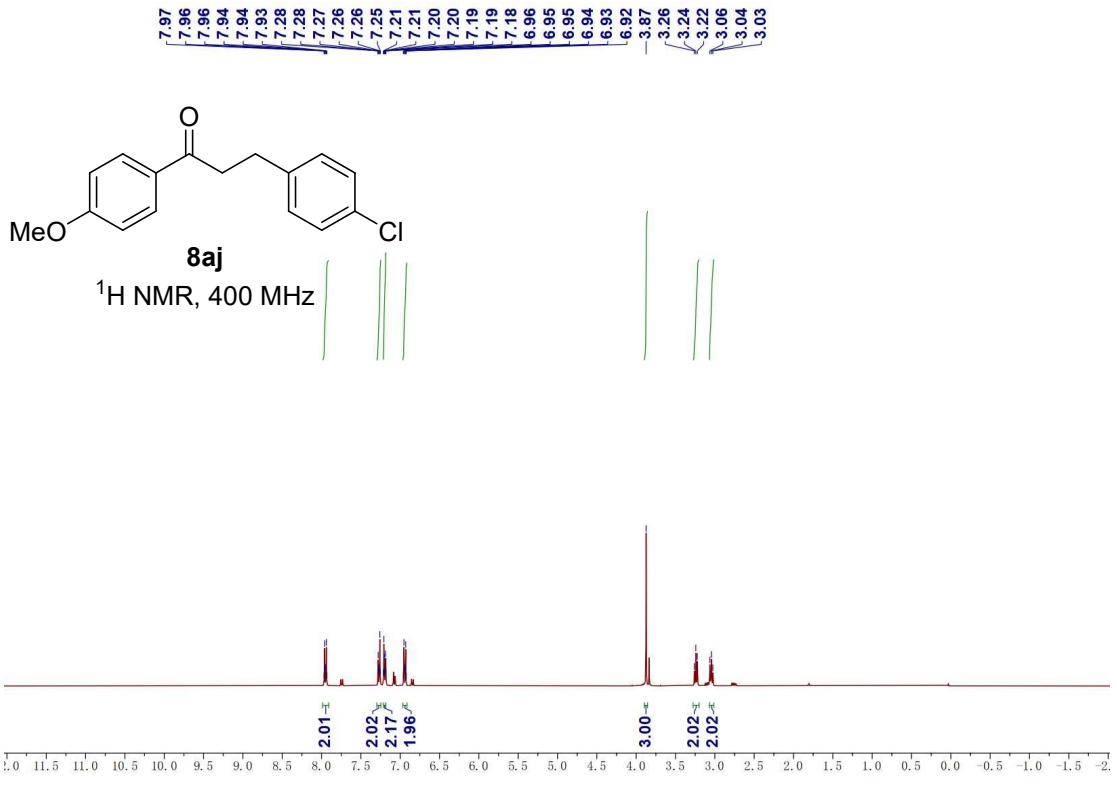
^{13}C NMR, 101 MHz

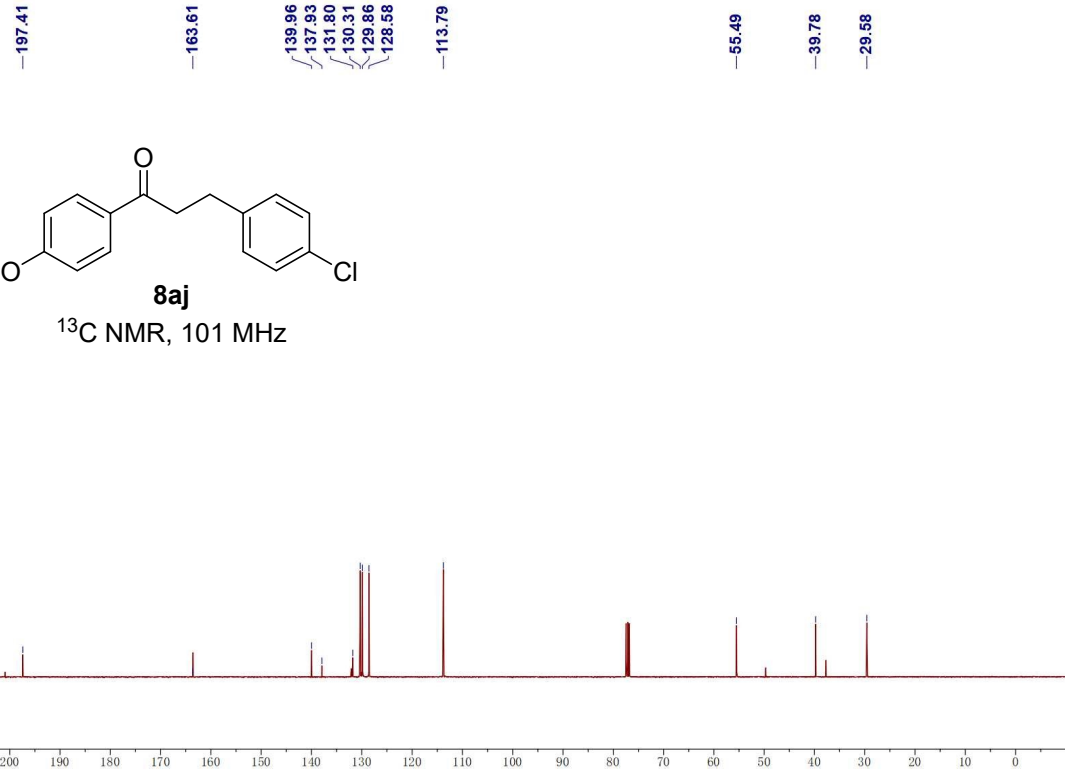


8ai

^{1}H NMR, 400 MHz

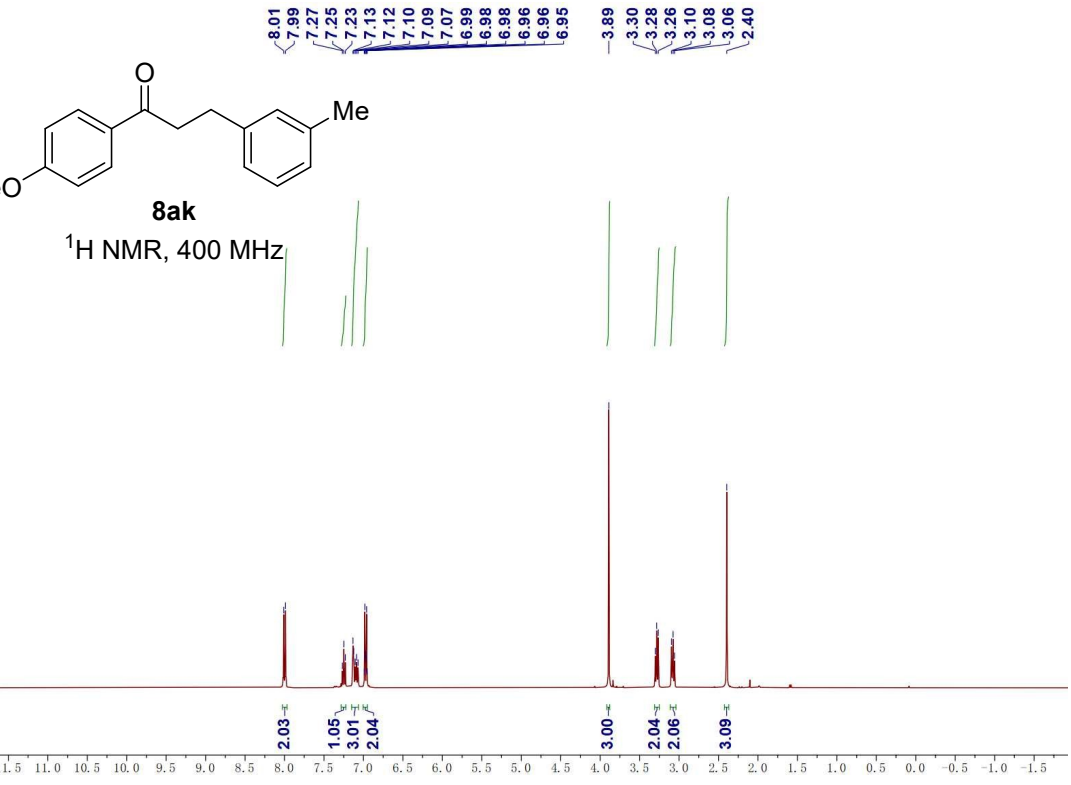

198.59
143.91
136.79
133.18
128.66
128.06
126.88
124.70
123.40
40.46
24.17
O
S
8ai
13C NMR, 101 MHz
f1 (ppm)


7.97
7.96
7.96
7.94
7.94
7.93
7.28
7.28
7.27
7.26
7.26
7.25
7.21
7.21
7.20
7.20
7.19
7.19
7.18
6.96
6.95
6.95
6.94
6.93
6.92
3.87
3.26
3.24
3.22
3.06
3.04
3.03
O
MeO
Cl
8aj
1H NMR, 400 MHz
2.01
2.02
2.17
1.96
3.00
2.02
2.02



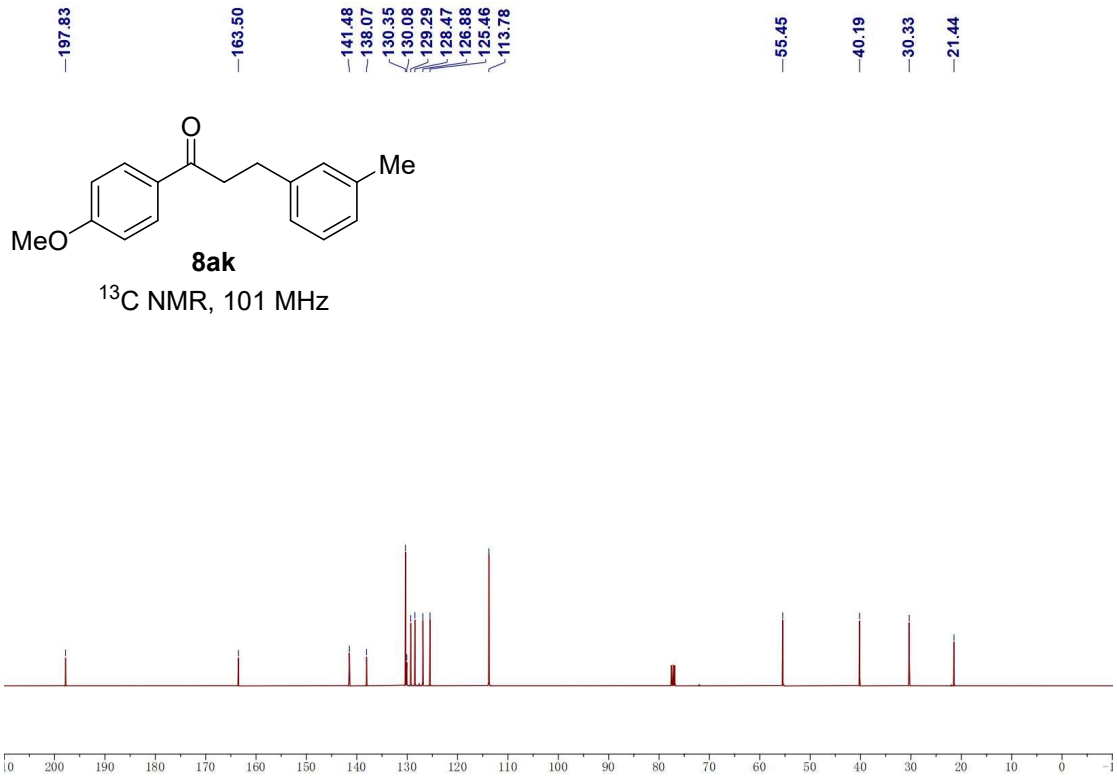
8aj

^{13}C NMR, 101 MHz



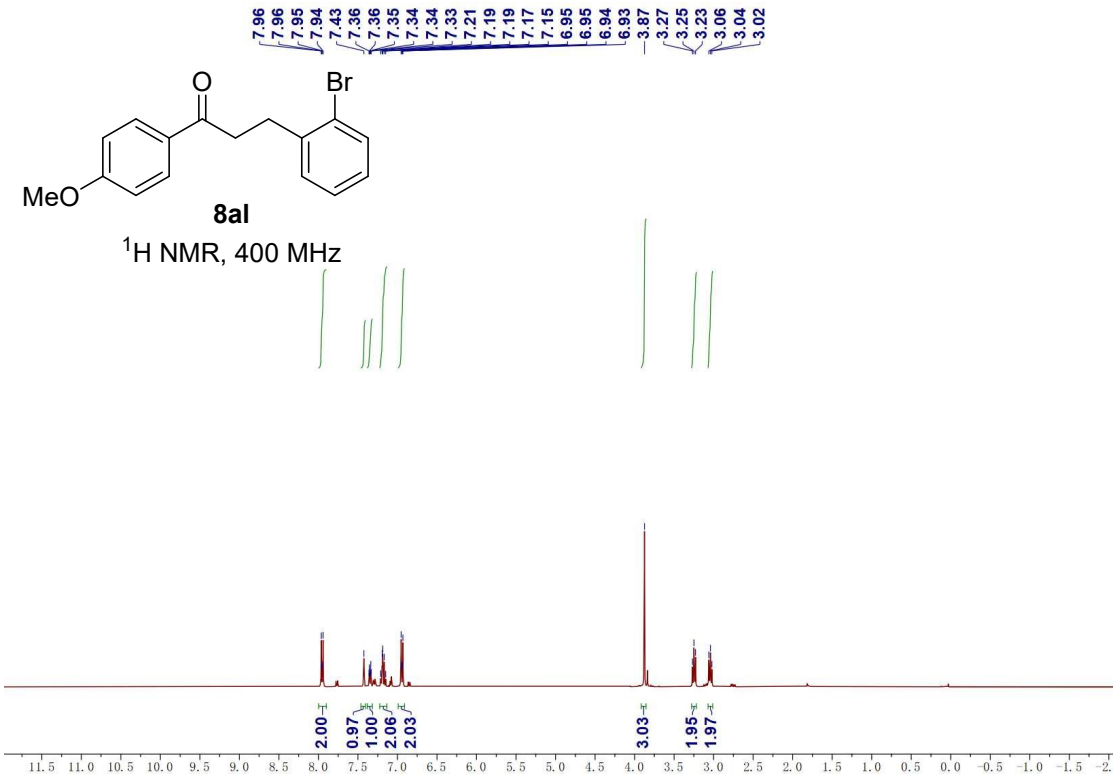
8ak

^{1}H NMR, 400 MHz



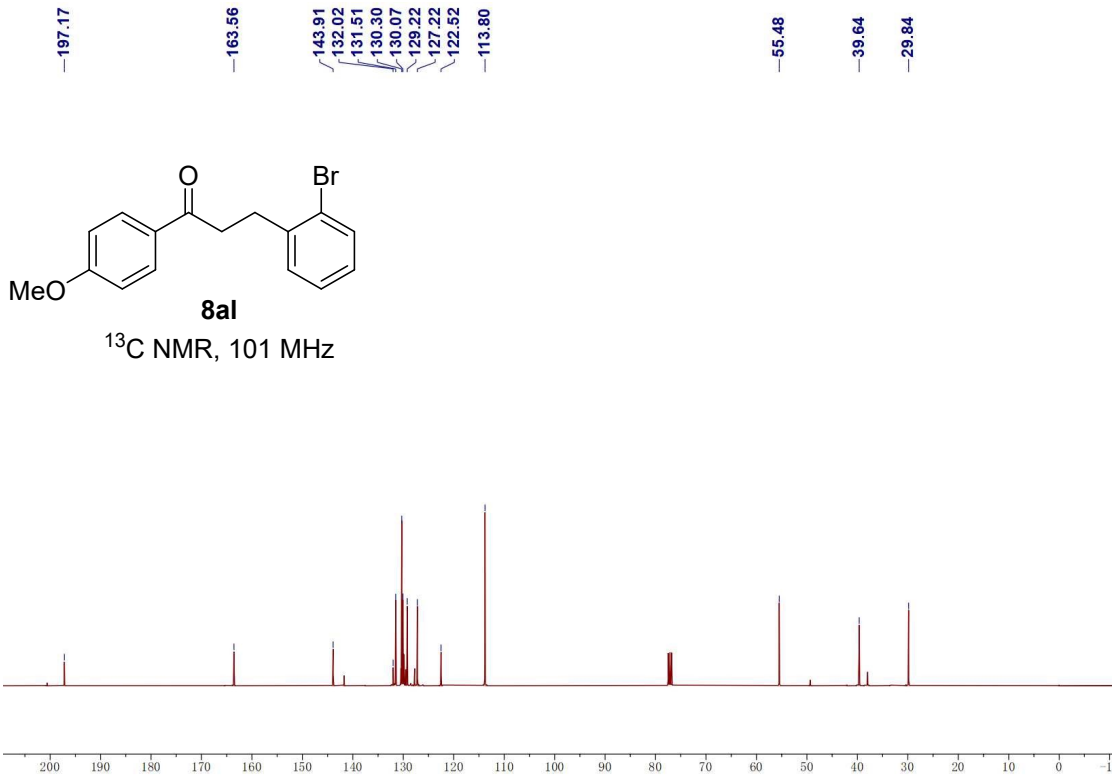
8ak

^{13}C NMR, 101 MHz



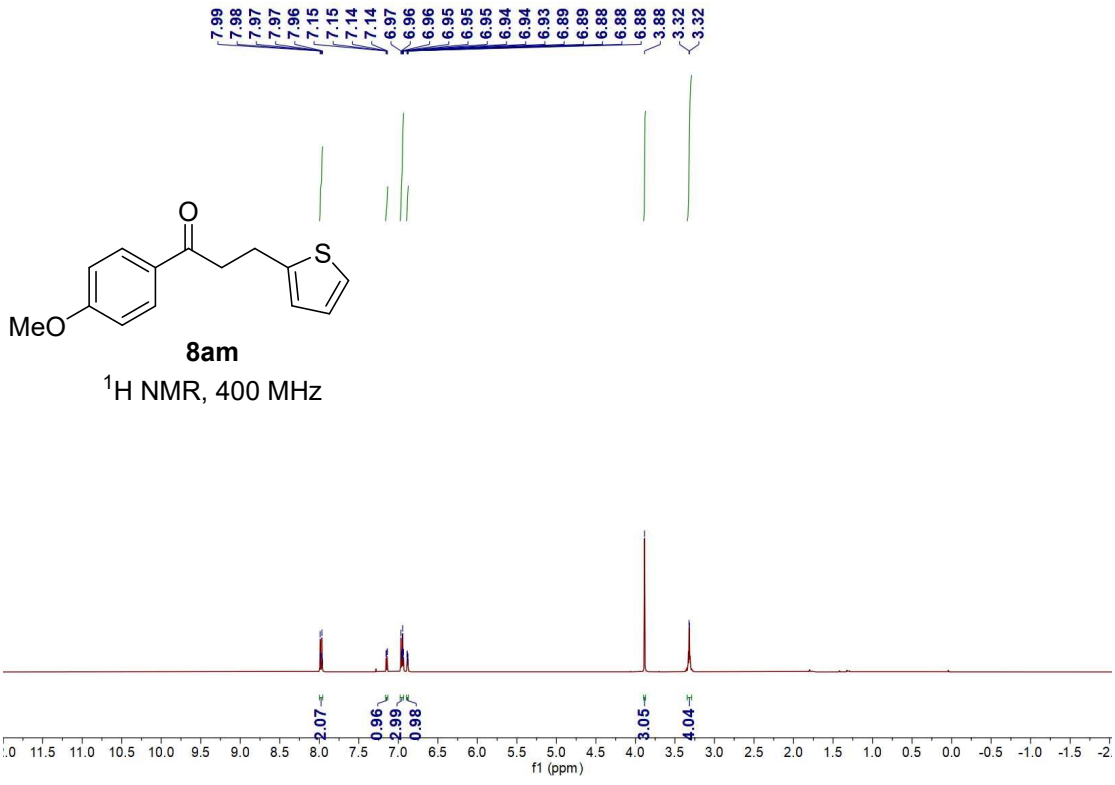
8al

^{1}H NMR, 400 MHz



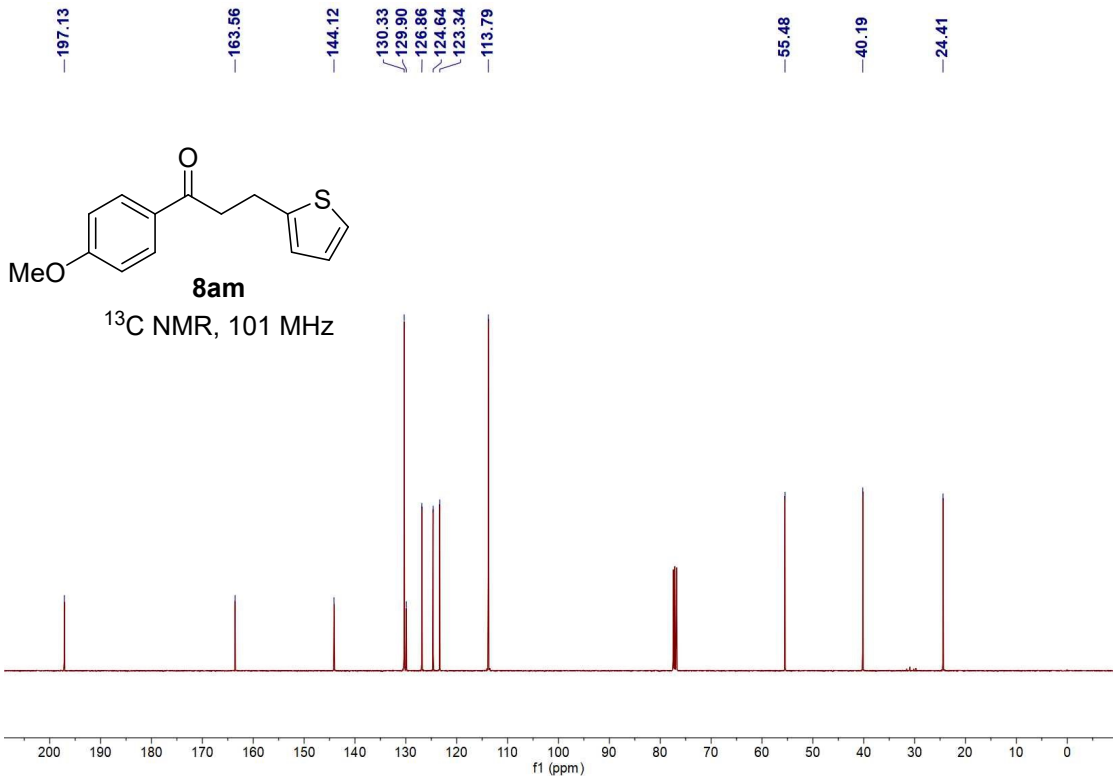
8al

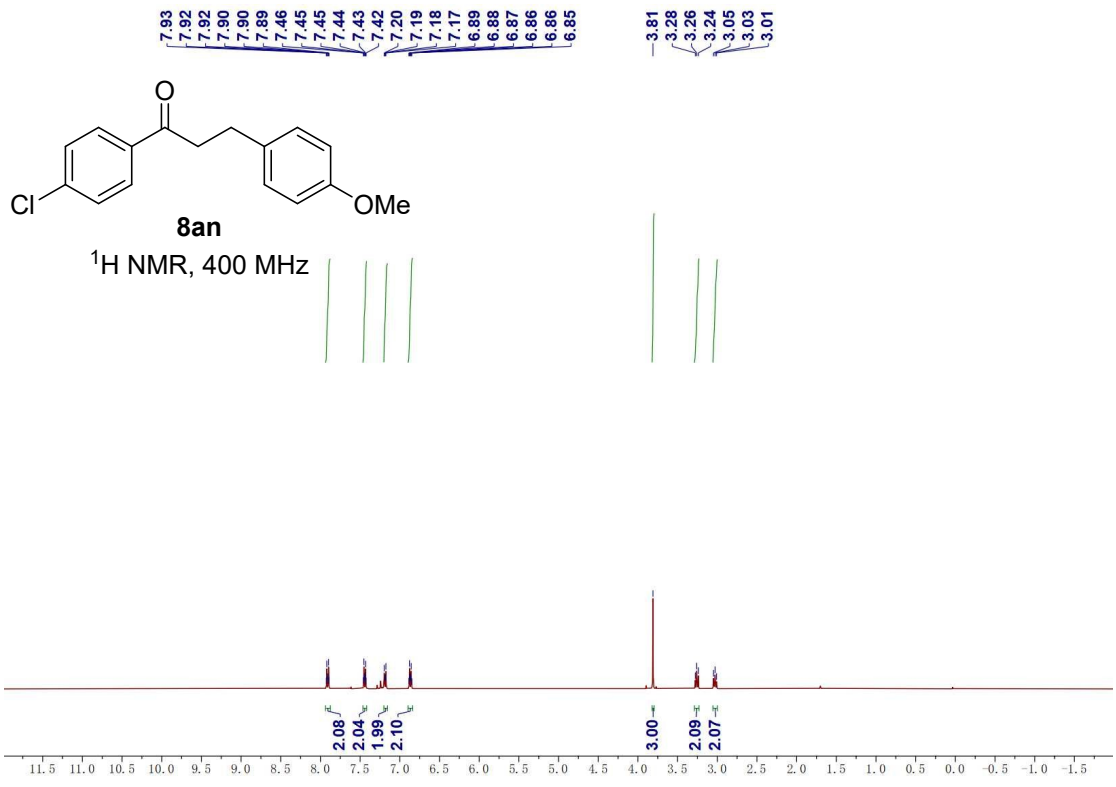
^{13}C NMR, 101 MHz

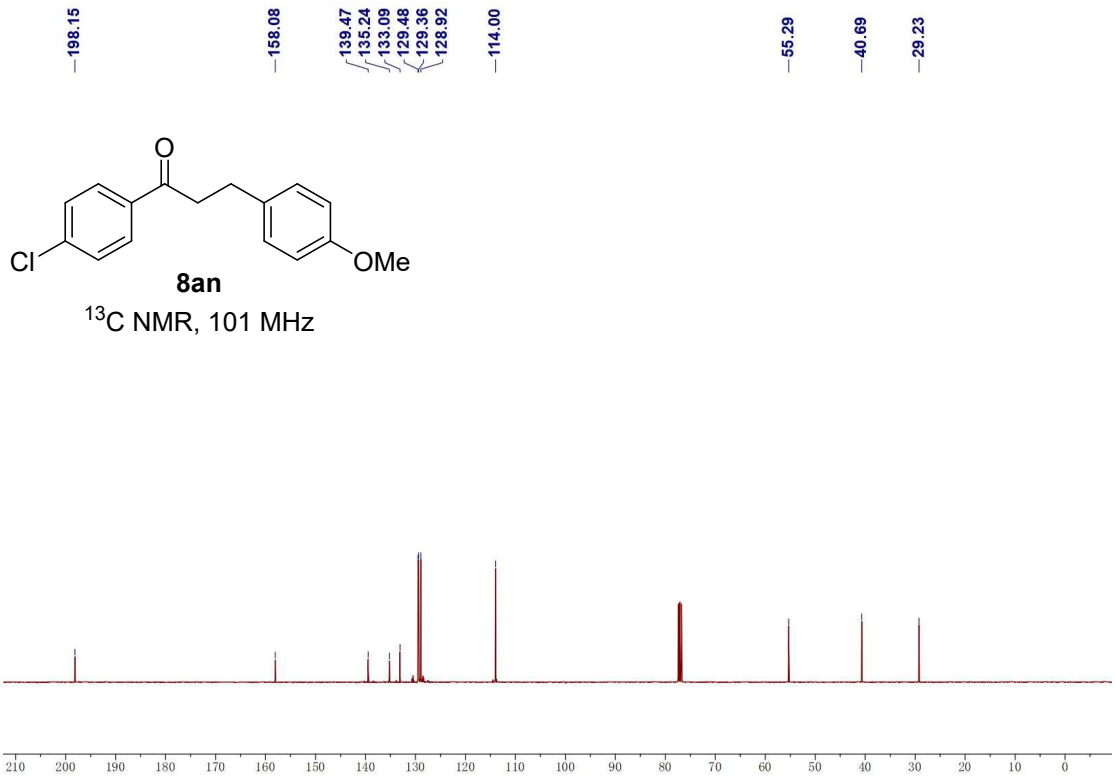


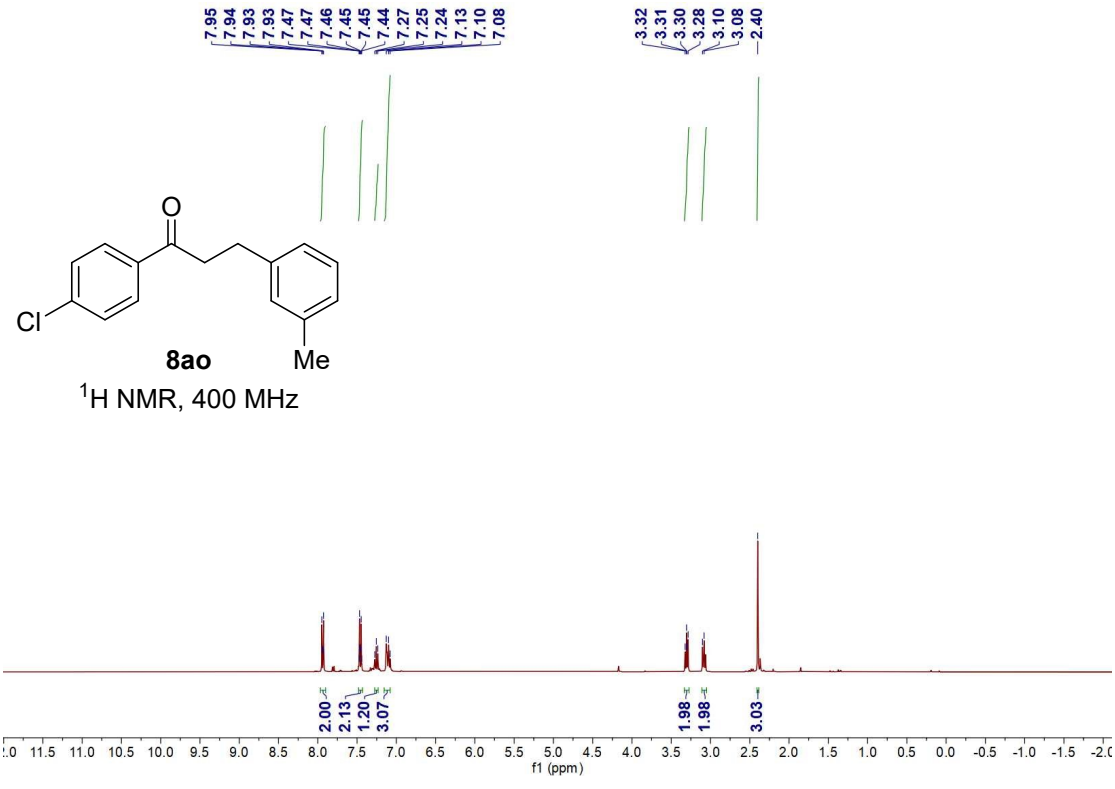
8am

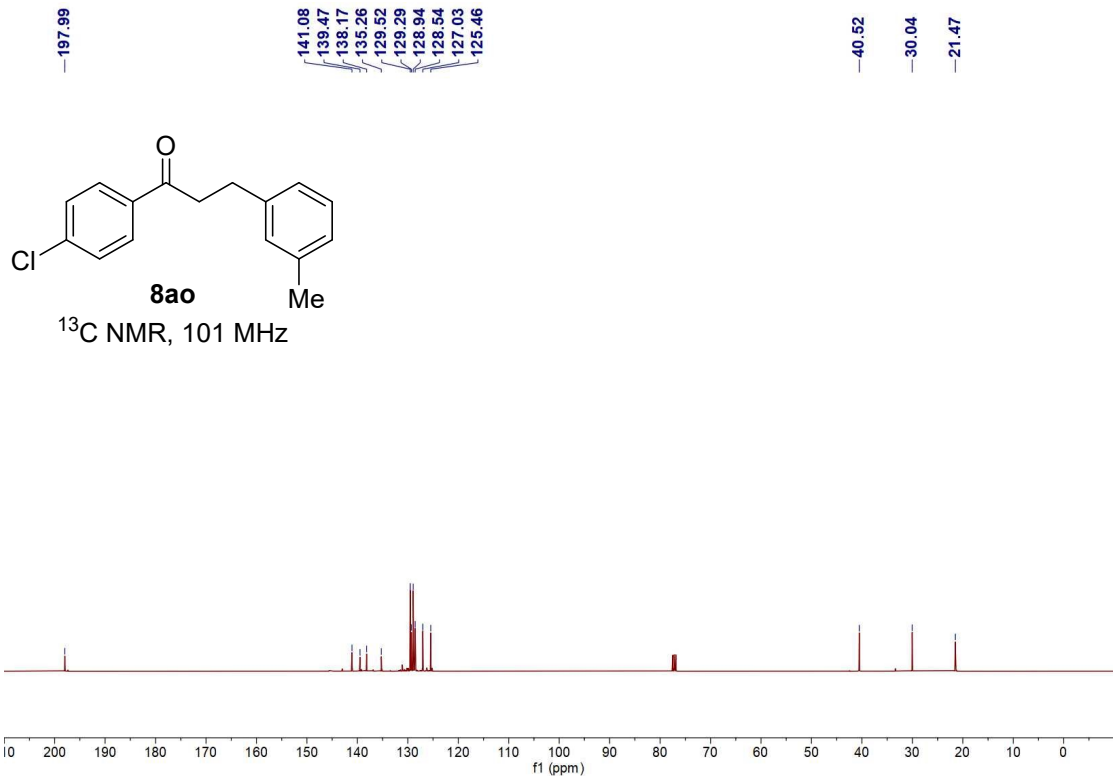
^{1}H NMR, 400 MHz


197.13
163.56
144.12
130.33
129.90
126.86
124.64
123.34
113.79
55.48
40.19
24.41
O
S
MeO
8am
13C NMR, 101 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.93
7.92
7.92
7.90
7.90
7.89
7.46
7.45
7.45
7.44
7.43
7.42
7.20
7.19
7.18
7.17
6.89
6.88
6.87
6.86
6.86
6.85
3.81
3.28
3.26
3.24
3.05
3.03
3.01
O
Cl
OMe
8an
1H NMR, 400 MHz
2.08
2.04
1.99
2.10
3.00
2.09
2.07
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 -1.5


198.15
158.08
139.47
135.24
133.09
129.48
129.36
128.92
114.00
55.29
40.69
29.23
O
Cl
OMe
8an
13C NMR, 101 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


7.95
7.94
7.93
7.93
7.47
7.47
7.46
7.45
7.45
7.44
7.27
7.25
7.24
7.13
7.10
7.08
3.32
3.31
3.30
3.28
3.10
3.08
2.40
O
Cl
8ao
Me
1H NMR, 400 MHz
2.00
2.13
1.20
3.07
1.98
1.98
3.03
f1 (ppm)


197.99
141.08
139.47
138.17
135.26
129.52
129.29
128.94
128.54
127.03
125.46
40.52
30.04
21.47
O
Cl
Me
8ao
13C NMR, 101 MHz
f1 (ppm)

10. References

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