Supplementary Information (SI) for for Organic & Biomolecular Chemistry

Supporting Information

A Novel Acenaphthoimidazolyidene Oxazolinic Palladium Complex and its Efficient Catalysis in Suzuki Cross-Coupling Reactions of N-Acyl-Glutarimides via N-C Cleavage

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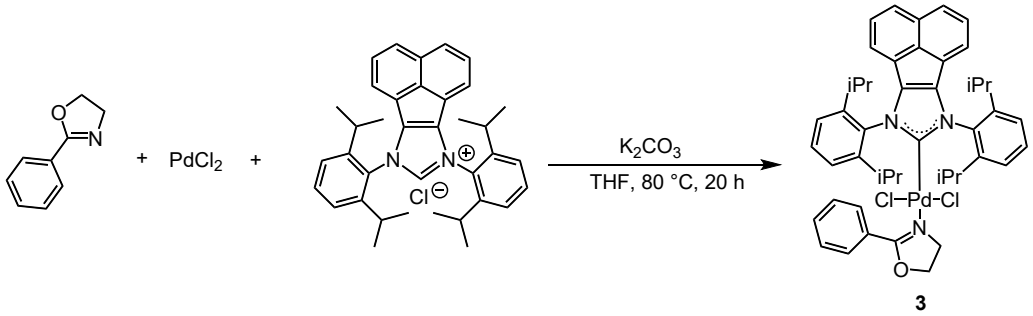
General Information

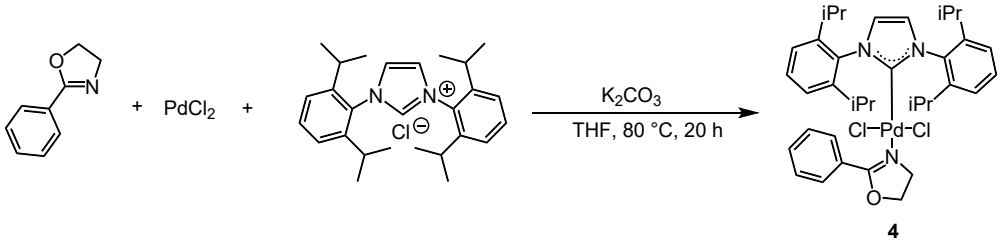
All commercial reagents were used directly without further purification, unless otherwise stated. Dry dimethyl sulfoxide (DMSO) was purchased from Alfa Aesar, stored over 4 Å molecular sieves, and handled under N_2. 1,4-dioxane, acetonitrile and 2-Propanol (^{i}PrOH) were distilled from anhydrous calcium chloride prior to use. Toluene, and tetrahydrofuran (THF) were distilled from sodium/benzophenone prior to use. *t*-BuOK was purchased from Acros. All reaction vials (50 mL) were purchased from Beijing Synthware Glass. $CDCl_3$ was purchased from Cambridge Isotope Laboratories. ^{1}H, ^{13}C NMR were recorded on Jeol ECA-400 and Bruker 400 DRX spectrometers. The chemical shifts (δ) for ^{1}H are given in parts per million (ppm) referenced to the residual proton signal of the deuterated solvent ($CHCl_3$ at δ 7.26 ppm); coupling constants are expressed in hertz (Hz). ^{13}C NMR spectra were referenced to the carbon signal of $CDCl_3$ (77.0 ppm). The following abbreviations are used to describe NMR signals: s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublets, q = quartet. ESI-MS spectra were recorded on an Aglient 7250& JEOL-JMS-T100LP AccuTOF instrument.

2.Synthetic procedures

2.1 Synthesis of the catalysts.



Scheme S1. Synthesis of Pd-NHC complex **3**.



Scheme S2. Synthesis of Pd-NHC complex **4**.

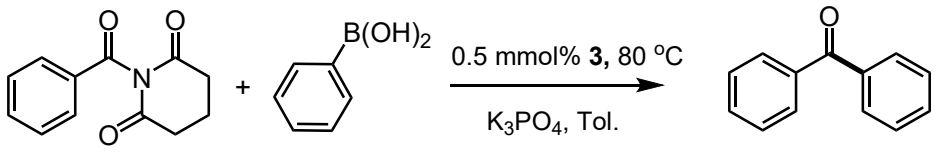
Acenaphthoimidazolylidene palladacycle complex 3 was prepared according to literature procedure[S1]. Under an N_2 atmosphere, a mixture of acenaphthoimidazolium (or imidazolium) chlorides[S2] (0.55 mmol), $PdCl_2$ (0.5 mmol), K_2CO_3 (2.0 mmol), 2-phenyl-2-oxazoline (0.75 mmol) was stirred in anhydrous THF (2.0 mL) under reflux for 20 h. After cooling down, the mixture was diluted with CH_2Cl_2, filtered. The product was loaded directly on a silica gel column and purified by flash chromatography to give a yellow solid.

3 (65%): To our delight, yellow crystals of palladacycle **1a**, which are suitable for single crystal diffraction analysis, were obtained by slow diffusion of petroleum ether into a dichloromethane solution of complex **1a** for 3d. The data can be obtained from The Cambridge Crystallographic Data Centre (2101485). ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 8.45 (d, J = 7.4 Hz, 2H), 7.70 (t, J = 8.1 Hz, 4H), 7.54 (d, J = 7.7 Hz, 4H), 7.40 – 7.31 (m, 3H), 7.04 (t, J = 7.7 Hz, 2H), 6.81 (d, J = 7.0 Hz, 2H), 4.35 (t, J = 9.8 Hz, 2H), 4.00 (t, J = 9.8 Hz, 2H), 3.48 – 3.34 (m, 4H), 1.38 (d, J = 6.5 Hz, 12H), 0.92 (d, J = 6.8 Hz, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 165.86, 163.09, 147.58, 140.32, 134.00, 131.78, 130.48, 129.80, 129.53, 129.17, 127.90, 127.23, 126.12, 125.10, 124.67, 122.00, 67.55, 53.94, 28.86, 25.75, 24.14. HR-MS (ESI): *m/z* 800.2594 (calcd, $[M\text{-}Cl]^+$); 800.2599 (found, $[M\text{-}Cl]^+$).

4 (67%): ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 8.33 (d, J = 7.8 Hz, 2H), 7.60 (t, J = 7.8 Hz, 2H), 7.40 (dd, J = 18.5, 7.7 Hz, 5H), 7.11 (d, J = 4.6 Hz, 4H), 4.30 (t, J = 9.8 Hz, 2H), 3.94 (t, J = 9.8 Hz, 2H), 3.22 – 3.07 (m, 4H), 1.38 (s, 12H), 1.10 (d, J = 6.8 Hz, 12H). ^{13}C NMR ($CDCl_3$,101 MHz, 298 K): δ 165.76, 156.92, 147.08, 135.18, 131.79, 130.11, 129.75, 127.97, 124.92, 123.94, 67.40, 54.14, 28.71, 26.38, 22.90.

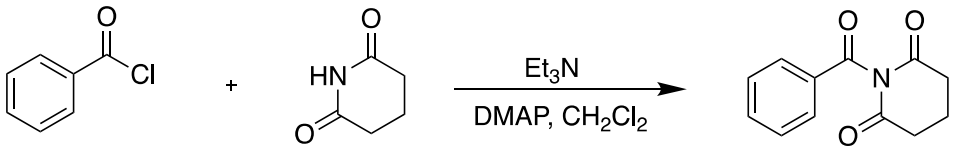
2.2 General procedure for Pd-catalyzed Suzuki−Miyaura Cross-coupling reactions of Amides.

To a 50 mL schlenk tube containing base (0.6 mmol), catalyst **3** (0.5 mol%) and boronic acids (0.6 mmol) purged with N_2 (3 times) and Toluene (2 mL) was injected via a syringe. The amides (0.4 mmol) were added subsequently. (Note: if amides were solid, it was introduced before adding Toluene). The result mixture was then heated at 80 ^{o}C for 5 h. After cooling to room temperature, a small amount of silica gel was added, and the solvent was removed in vacuo. The product was loaded directly on a silica gel column and purified by flash chromatography to provide the desired product.



Scheme S3. General procedure for Pd-catalyzed Suzuki−Miyaura Cross-coupling

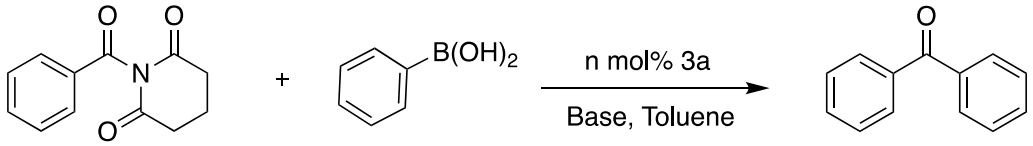
2.3 General procedure for the N-acyl-glutarimides synthesis.



Scheme S4. General procedure for the N-acyl-glutarimide synthesis

An oven-dried round-bottomed flask (100 mL) equipped with a stir bar was charged with amine (8.84 mmol, 1.0 equiv.), triethylamine(typically, 2.0 equiv.), DMAP(typically, 0.25 equiv.), and dichloromethane (typically, 50 mL), placed under a positive pressure of nitrogen, and subjected to three evacuation/backfill--ing cycles under high vacuum.87 Acyl chloride (typically, 1.1 equiv.) was added dropwise to the reaction mixture with vigorous stirring at 0 °C, and the reaction mixture was stirred overnight at room temperature. After the indicated time, the reaction mixture was diluted with Et_2O (20 mL) and filtered. The organic layer was washed with HCl (1.0 N, 30 mL) and brine (30 mL), dried, and concentrated. Unless stated otherwise, the crude product was purified by recrystallization (toluene) to give analytically pure product. [S3]

3.Optimization of Suzuki-Miyaura cross-coupling of N-acyl-glutarimides.

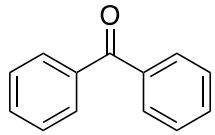


Entry	[Cat.]/mol%	Base	Solvent	T/°C	Yield/%
1	2	K_2CO_3	THF	80	85
2	2	K_3PO_4	THF	80	95
3	2	Na_2CO_3	THF	80	58

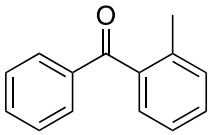
4	2	KOAc	THF	80	71
5	2	KOH	THF	80	45
6	2	TEA	THF	80	2
7	2	DBU	THF	80	ND
8	2	^{t}BuOK	THF	80	33
9	2	K_3PO_4	CH_3CN	80	5
10	2	K_3PO_4	Dioxane	80	98
11	2	K_3PO_4	^{i}PrOH	80	1
12	2	K_3PO_4	DMSO	80	ND
13	2	K_3PO_4	Toluene	80	99
14	2	K_3PO_4	Toluene	75	95
15	2	K_3PO_4	Toluene	65	83
16	2	K_3PO_4	Toluene	45	ND
17	2	K_3PO_4	Toluene	25	ND
18	1	K_3PO_4	Toluene	80	92
19	0.5	K_3PO_4	Toluene	80	92
20	0.3	K_3PO_4	Toluene	80	90
21	0.2	K_3PO_4	Toluene	80	89
22	0.1	K_3PO_4	Toluene	80	82
23	0.05	K_3PO_4	Toluene	80	57
24[c]	2	K_3PO_4	Toluene	80	95
25[d]	2	K_3PO_4	Toluene	80	98
26[d]	0.5	K_3PO_4	Toluene	80	98
27[e]	0.5	K_3PO_4	Toluene	80	92
28[f]	0.5	K_3PO_4	Toluene	80	82
29[g]	0.5	K_3PO_4	Toluene	80	66
30[h]	0.5	K_3PO_4	Toluene	80	61
31[i]	0.5	K_3PO_4	Toluene	80	72

[a] Conditions: N-acyl-glutarimide (0.4 mmol, 1.0 equiv.), phenylboronic acid (0.6 mmol, 1.5 equiv.), Base (0.6 mmol, 1.5 equiv.) were stirred in 2 mL solvent under N_2 atmosphere for 15 h. [b] Isolated yield.[c] 10 h.[d] 5 h. [e] 4 h. [f] 3 h. [g] 2 h. [h] 1 h. [i] 5 h in air.

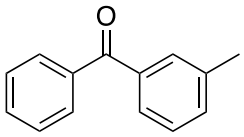
4. Isolated compounds data

7[S4]**:** 

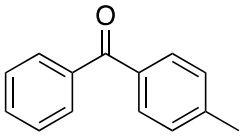
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.82 (d, J = 32.0 Hz, 4H), 7.56 (t, J = 8.0 Hz, 2H), 7.46 (t, J = 8.0 Hz, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 196.95, 137.79, 132.63, 130.26, 128.49.

8a[S4]**:** 

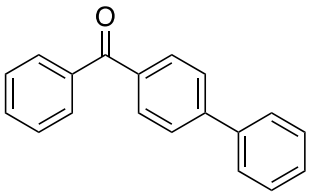
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.90 -7.79 (m, 2H), 7.63 -7.57 (m, 1H), 7.51-7.38 (m, 3H), 7.37-7.23 (m, 3H), 2.36 (s, 3H).^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 198.64, 133.14, 131.01, 130.25, 130.14, 128.53, 128.48, 125.21, 19.98.

8b[S4]**:** 

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.87 – 7.77 (m, 2H), 7.68 – 7.56 (m, 3H), 7.54 – 7.47 (m, 2H), 7.45 – 7.36 (m, 2H), 2.45 (s, 3H).^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 196.95, 138.13, 137.74, 137.61, 133.17, 132.31, 130.43, 130.02, 128.21, 128.06, 127.34, 21.34.

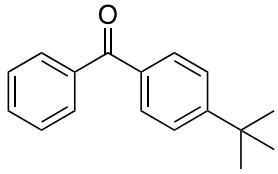
8c[S4]**:** 

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.83 – 7.76 (m, 2H), 7.75 – 7.70 (m, 2H), 7.62 – 7.54 (m, 1H), 7.51 – 7.44 (m, 2H), 7.30 – 7.26 (m, 2H), 2.45 (s, 3H).^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 196.54, 143.25, 137.99, 134.92, 132.16, 130.32, 129.94, 128.99, 128.22, 21.66.

9a[S4]**:** 

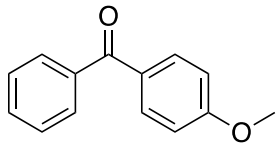
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K):δ 7.91 (d, J = 8.3 Hz, 2H), 7.85 (dd, J = 8.1, 1.4 Hz, 2H), 7.72 (d, J = 8.3 Hz, 2H), 7.66 (dd, J = 7.4, 1.8 Hz, 2H), 7.64 – 7.58 (m, 1H), 7.50 (dt, J = 9.9, 7.8 Hz, 4H), 7.45 – 7.39 (m, 1H)..^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 196.37, 145.26, 140.01, 137.80, 136.27, 132.39, 130.74, 130.02, 128.99, 128.33, 128.20, 127.32, 126.99.

9b[S4]**:**



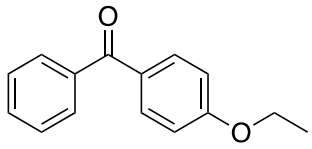
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.83 – 7.75 (m, 4H), 7.61 – 7.55 (m, 1H), 7.53 – 7.45 (m, 4H), 1.37 (s, 9H).^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 196.46, 156.19, 137.97, 134.85, 132.17, 130.15, 129.98, 128.21, 125.25, 35.12, 31.16.

10a[S4]**:**



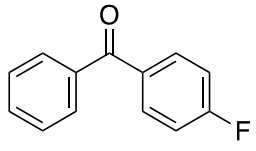
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.86 – 7.79 (m, 2H), 7.75 (dq, J = 9.1, 2.1 Hz, 2H), 7.59 – 7.52 (m, 1H), 7.49 – 7.42 (m, 2H), 6.99 – 6.92 (m, 2H), 3.87 (s, 3H).^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 195.52, 163.21, 138.25, 132.53, 131.87, 130.11, 129.69, 128.16, 113.53, 55.46.

10b[S5]**:**

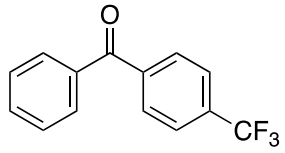


^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.87 – 7.80 (m, 2H), 7.77 (dt, J = 7.0, 1.4 Hz, 2H), 7.61 – 7.55 (m, 1H), 7.52 – 7.45 (m, 2H), 7.00 – 6.93 (m, 2H), 4.14 (q, J = 7.0 Hz, 2H), 1.47 (t, J = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 195.58, 162.69, 138.37, 132.58, 131.84, 129.97, 129.72, 128.18, 114.01, 63.79, 14.70.

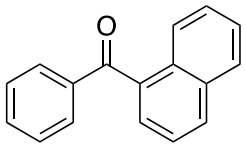
11a[S4]**:**



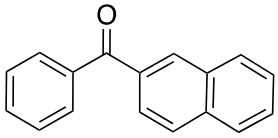
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.92 – 7.84 (m, 2H), 7.83 – 7.75 (m, 2H), 7.66 – 7.58 (m, 1H), 7.51 (dd, J = 8.3, 6.9 Hz, 2H), 7.23 – 7.14 (m, 2H).^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 195.26, 166.63, 137.47, 132.69, 132.60, 132.44, 129.85, 128.33, 115.54, 115.32.^{19}F NMR ($CDCl_3$, 376 MHz, 298 K): δ -105.97 (ddd, J = 13.6, 8.4, 5.4 Hz).

11b[S4]**:** 

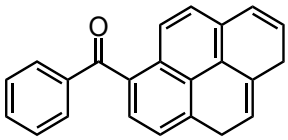
^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ 7.90 (d, J = 8.0 Hz, 2H), 7.83 – 7.78 (m, 2H), 7.76 (d, J = 8.1 Hz, 2H), 7.66 – 7.60 (m, 1H), 7.51 (t, J = 7.8 Hz, 2H).^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 195.53, 140.76, 136.76, 133.58, 133.09, 130.14, 130.11, 128.54, 125.41, 125.38, 125.34.^{19}F NMR ($CDCl_3$, 376 MHz, 298 K): δ -63.01.

12[S4]**:** 

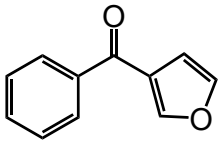
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 8.10 (dq, J = 7.8, 0.8 Hz, 1H), 8.01 (dt, J = 8.2, 1.2 Hz, 1H), 7.95 – 7.91 (m, 1H), 7.90 – 7.84 (m, 2H), 7.63 – 7.56 (m, 2H), 7.55 – 7.44 (m, 5H).^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 198.00, 138.29, 136.33, 133.20, 131.24, 130.38, 128.42, 128.38, 127.74, 127.23, 126.43, 125.67, 124.31.

13[S4]**:** 

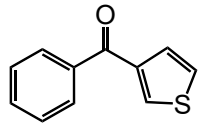
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 8.28 (t, J = 1.2 Hz, 1H), 7.97 – 7.85 (m, 6H), 7.64 – 7.49 (m, 5H).^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 196.74, 137.88, 135.25, 134.80, 132.36, 131.85, 130.08, 129.39, 128.32, 128.30, 128.28, 127.80, 126.78, 125.76.

14[S4]**:** 

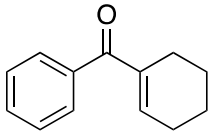
^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ 8.37 (d, J = 9.3 Hz, 1H), 8.26 – 8.16 (m, 4H), 8.18 – 8.02 (m, 4H), 7.91 (dd, J = 7.8, 1.7 Hz, 2H), 7.65 – 7.59 (m, 1H), 7.48 (t, J = 7.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 198.44, 138.75, 133.15, 131.16, 130.66, 130.59, 129.73, 129.12, 128.86, 128.45, 127.19, 126.94, 126.39, 126.05, 125.91, 124.79, 124.72, 124.41, 123.75.

15[S6]**:** 

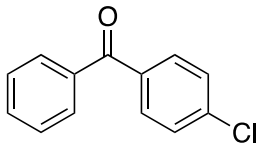
^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ 7.92 (s, 1H), 7.86 (d, J = 7.6 Hz, 2H), 7.59 (t, J = 7.4 Hz, 1H), 7.50 (d, J = 8.1 Hz, 3H), 6.91 (s, 1H)..^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 189.45, 148.57, 143.96, 138.84, 132.48, 128.83, 128.55, 126.54, 110.22.

16[S6]**:** 

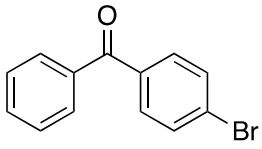
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.94 (dd, J = 3.0, 1.2 Hz, 1H), 7.91 – 7.82 (m, 2H), 7.64 – 7.56 (m, 2H), 7.50 (t, J = 7.6 Hz, 2H), 7.39 (dd, J = 5.1, 2.9 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 189.96, 141.26, 138.59, 133.92, 132.29, 129.34, 128.58, 128.36, 126.21.

17[S4]**:** 

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.68 – 7.60 (m, 2H), 7.54 – 7.46 (m, 1H), 7.42 (dd, J = 8.2, 6.7 Hz, 2H), 6.59 (tt, J = 3.7, 1.7 Hz, 1H), 2.44 (tq, J = 6.3, 2.2 Hz, 2H), 2.31 – 2.24 (m, 2H), 1.78 – 1.65 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 198.20, 144.03, 138.69, 131.20, 129.09, 127.96, 26.08, 23.91, 21.98, 21.62.

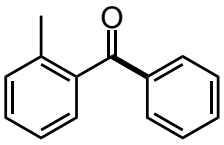
18a[S6]**:** 

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.81 – 7.74 (m, 4H), 7.63 – 7.58 (m, 1H), 7.52 – 7.44 (m, 4H).^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 195.49, 138.91, 137.28, 135.90, 132.64, 131.47, 130.21, 129.93, 129.56, 128.65, 128.41.

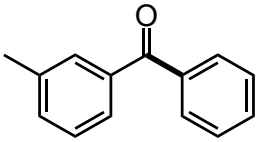
18b[S7]**:** 

^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ 7.81 – 7.75 (m, 2H), 7.68 (d, J = 8.6 Hz, 2H), 7.65 – 7.57 (m, 3H), 7.49 (dd, J = 8.3, 7.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 195.78, 137.30, 136.43, 132.82, 131.75, 131.70, 130.08,

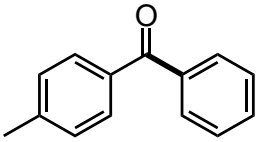
128.55, 127.65.

19a[S4]**:** 

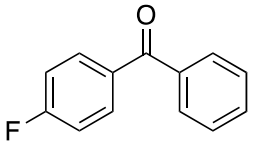
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.90 -7.79 (m, 2H), 7.63 -7.57 (m, 1H), 7.51-7.38 (m, 3H), 7.37-7.23 (m, 3H), 2.36 (s, 3H).^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 198.64, 133.14, 131.01, 130.25, 130.14, 128.53, 128.48, 125.21, 19.98.

19b[S4]**:** 

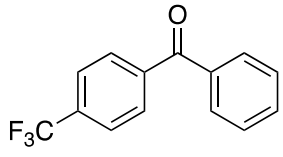
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.87 – 7.77 (m, 2H), 7.68 – 7.56 (m, 3H), 7.54 – 7.47 (m, 2H), 7.45 – 7.36 (m, 2H), 2.45 (s, 3H).^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 196.95, 138.13, 137.74, 137.61, 133.17, 132.31, 130.43, 130.02, 128.21, 128.06, 127.34, 21.34.

19c[S4]**:** 

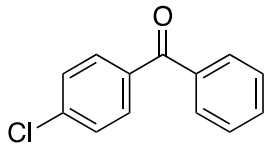
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.83 – 7.76 (m, 2H), 7.75 – 7.70 (m, 2H), 7.62 – 7.54 (m, 1H), 7.51 – 7.44 (m, 2H), 7.30 – 7.26 (m, 2H), 2.45 (s, 3H).^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 196.54, 143.25, 137.99, 134.92, 132.16, 130.32, 129.94, 128.99, 128.22, 21.66.

20a[S4]**:** 

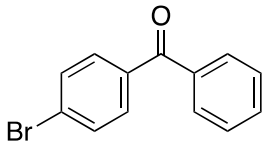
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.92 – 7.84 (m, 2H), 7.83 – 7.75 (m, 2H), 7.66 – 7.59 (m, 1H), 7.52 (dd, J = 8.4, 7.0 Hz, 2H), 7.23 – 7.14 (m, 2H).^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 195.27, 166.67, 164.15, 137.54, 132.72, 132.63, 132.47, 129.88, 128.37, 115.57, 115.35. ^{19}F NMR ($CDCl_3$, 100 MHz, 298 K): δ -105.98 (tt, J = 8.2, 5.5 Hz).

20b[S4]**:** 

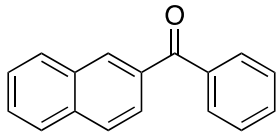
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.93 – 7.87 (m, 2H), 7.83 – 7.78 (m, 2H), 7.78 – 7.74 (m, 2H), 7.67 – 7.61 (m, 1H), 7.54 – 7.48 (m, 2H).^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 195.52, 140.70, 136.70, 133.06, 130.11, 130.08, 128.50, 125.38, 125.34, 125.30, 125.26.

21a[S6]**:** 

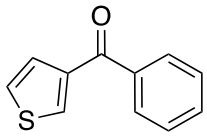
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.92 – 7.89 (m, 1H), 7.87 – 7.83 (m, 1H), 7.80 – 7.74 (m, 1H), 7.73 – 7.70 (m, 1H), 7.68 – 7.64 (m, 1H), 7.55 – 7.39 (m, 4H).^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 196.34, 145.26, 140.01, 137.81, 136.28, 132.65, 132.39, 131.48, 130.75, 130.02, 129.94, 128.99, 128.66, 128.43, 128.33, 128.21, 127.32, 126.99.

21b[S7]**:** 

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.95 – 7.82 (m, 3H), 7.72 (d, J = 8.2 Hz, 1H), 7.68 – 7.59 (m, 2H), 7.53 – 7.40 (m, 3H).^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 196.32, 145.21, 139.96, 137.75, 136.22, 132.37, 130.73, 129.99, 128.97, 128.31, 128.19, 127.29, 126.96.

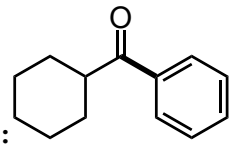
22[S4]**:** 

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 8.28 (t, J = 1.2 Hz, 1H), 7.97 – 7.85 (m, 6H), 7.64 – 7.49 (m, 5H).^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 196.74, 137.88, 135.25, 134.80, 132.36, 131.85, 130.08, 129.39, 128.32, 128.30, 128.28, 127.80, 126.78, 125.76.

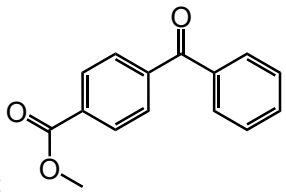
23[S6]**:** 

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.87 (dq, J = 7.7, 2.4, 1.8 Hz, 2H), 7.72 (dd, J = 4.9, 1.2 Hz, 1H), 7.65 (dd, J =

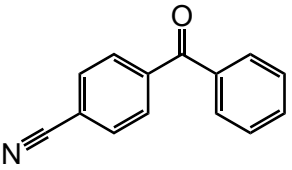
3.8, 1.2 Hz, 1H), 7.63 – 7.56 (m, 1H), 7.53 – 7.46 (m, 2H), 7.18 – 7.14 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 188.23, 143.66, 138.18, 134.84, 134.21, 132.28, 129.18, 128.43, 127.97.

24[S8]**:** 

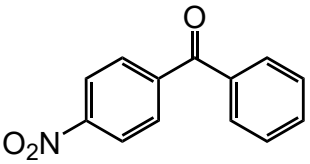
^{1}H NMR($CDCl_3$, 400 MHz, 298 K): δ 8.14-7.97 (m, 2H), 7.54 (t, J = 7.4 Hz, 1H), 7.43 (t, J = 7.6 Hz, 2H), 5.03 (ddd, J = 12.6, 8.6, 3.8 Hz, 1H), 2.06-1.88 (m, 2H), 1.87-1.71 (m, 2H), 1.58 (ddd, J = 9.4, 7.7, 3.2 Hz, 3H), 1.51-1.30 (m, 3H).^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 166.25, 132.92, 131.28, 129.78, 128.51, 73.28, 31.90, 25.75, 23.92.

25[S8]**:** 

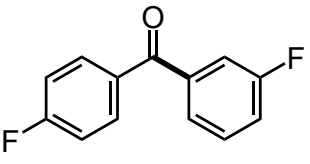
^{1}H NMR (CDCl3, 500 MHz, 298 K) δ 8.14 (d, J = 8.2 Hz, 2H), 7.84 (d, J = 8.3 Hz, 2H), 7.80 (dd, J = 8.2, 1.4 Hz, 2H), 7.64 – 7.59 (m, 1H), 7.49 (t, J = 7.7 Hz, 2H), 3.96 (s, 3H).^{13}C NMR ($CDCl_3$, 100 MHz, 298 K) δ 196.37, 166.65, 141.66, 137.28, 133.57, 133.33, 130.48, 130.15, 129.87, 128.84, 52.85.

26a[S6]**:** 

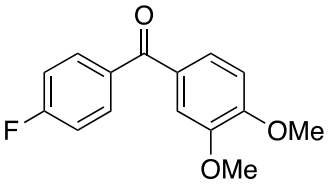
^{1}H NMR (CDCl3, 500 MHz, 298 K) δ 7.91 – 7.84 (m, 2H), 7.79 (dd, J = 7.8, 3.9 Hz, 4H), 7.67 – 7.61 (m, 1H), 7.51 (t, J = 7.8 Hz, 2H).^{13}C NMR ($CDCl_3$, 100 MHz, 298 K) δ 195.41, 141.56, 136.66, 133.71, 132.55, 130.61, 130.44, 129.01, 118.40, 115.99.

26b[S6]**:** 

^{1}H NMR (CDCl3, 500 MHz, 298 K) δ 8.34 (d, J = 8.7 Hz, 2H), 7.93 (d, J = 8.7 Hz, 2H), 7.83 – 7.77 (m, 2H), 7.65 (t, J = 7.5 Hz, 1H), 7.52 (t, J = 7.7 Hz, 2H).^{13}C NMR ($CDCl_3$, 100 MHz, 298 K) δ 194.57, 149.55, 142.62, 136.02, 133.25, 130.47, 129.87, 128.45, 123.31.

27[S9]**:** 

^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ 7.88 – 7.81 (m, 2H), 7.54 (dd, J = 7.7, 1.3 Hz, 1H), 7.47 (td, J = 8.1, 7.1, 4.6 Hz, 2H), 7.29 (td, J = 8.4, 2.7 Hz, 1H), 7.17 (t, J = 8.5 Hz, 2H)... ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K) δ 193.94, 166.73, 164.71, 163.63, 161.65, 139.71, 133.40, 133.38, 132.84, 132.77, 130.24, 130.18, 125.77, 125.74, 119.71, 119.54, 116.84, 116.66, 115.87, 115.70. ^{19}F NMR ($CDCl_3$, 100 MHz, 298 K) δ -105.18, -111.72.

28[S10]**:** 

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.86 – 7.79 (m, 2H), 7.48 (d, J = 2.0 Hz, 1H), 7.37 (dd, J = 8.3, 2.0 Hz, 1H), 7.22 – 7.13 (m, 2H), 6.92 (d, J = 8.3 Hz, 1H), 3.98 (d, J = 8.2 Hz, 6H).^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 194.12, 166.29, 163.78, 153.04, 149.06, 134.40 (d, J = 3.2 Hz), 132.28, 132.20, 130.07, 125.20, 115.40, 115.18, 112.04, 109.73, 56.08, 56.03. ^{19}F NMR ($CDCl_3$, 100 MHz, 298 K): δ -106.90 (ddd, J = 13.9, 8.3, 5.5 Hz).

5 Crystal structure information for Pd-NHC complex 3a

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) a

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: a

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Bond precision:  C-C = 0.0036 A          Wavelength=1.34139

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                alpha=90         beta=102.288(4)     gamma=90
Temperature:    193 K

                Calculated                Reported
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Hall group      -P 2yn                    -P 2yn
Moiety formula  C46 H49 Cl2 N3 O Pd       C46 H49 Cl2 N3 O Pd
Sum formula     C46 H49 Cl2 N3 O Pd       C46 H49 Cl2 N3 O Pd
Mr              837.18                    837.18
Dx,g cm-3       1.309                     1.309
Z               4                         4
Mu (mm-1)       3.339                     3.339
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F000'           1741.62
h,k,lmax        15,36,16                  15,36,16
Nref            9679                      9384
Tmin,Tmax       0.703,0.716               0.603,0.752
Tmin'           0.638

Correction method= # Reported T Limits: Tmin=0.603 Tmax=0.752
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R(reflections)= 0.0341( 8245)     wR2(reflections)= 0.0899( 9384)

S = 1.044                  Npar= 486
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Click on the hyperlinks for more details of the test.
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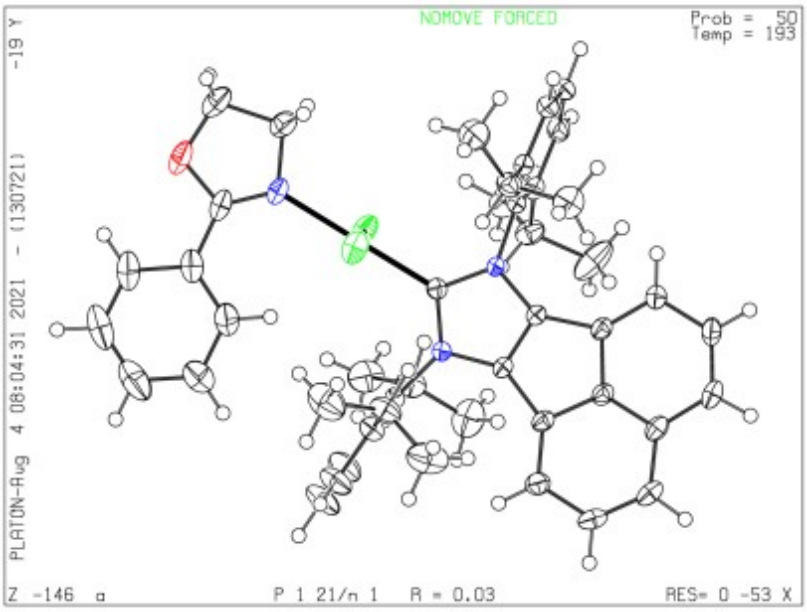


6 ^{1}H NMR, ^{13}C NMR and ESI-MS spectra for important compounds

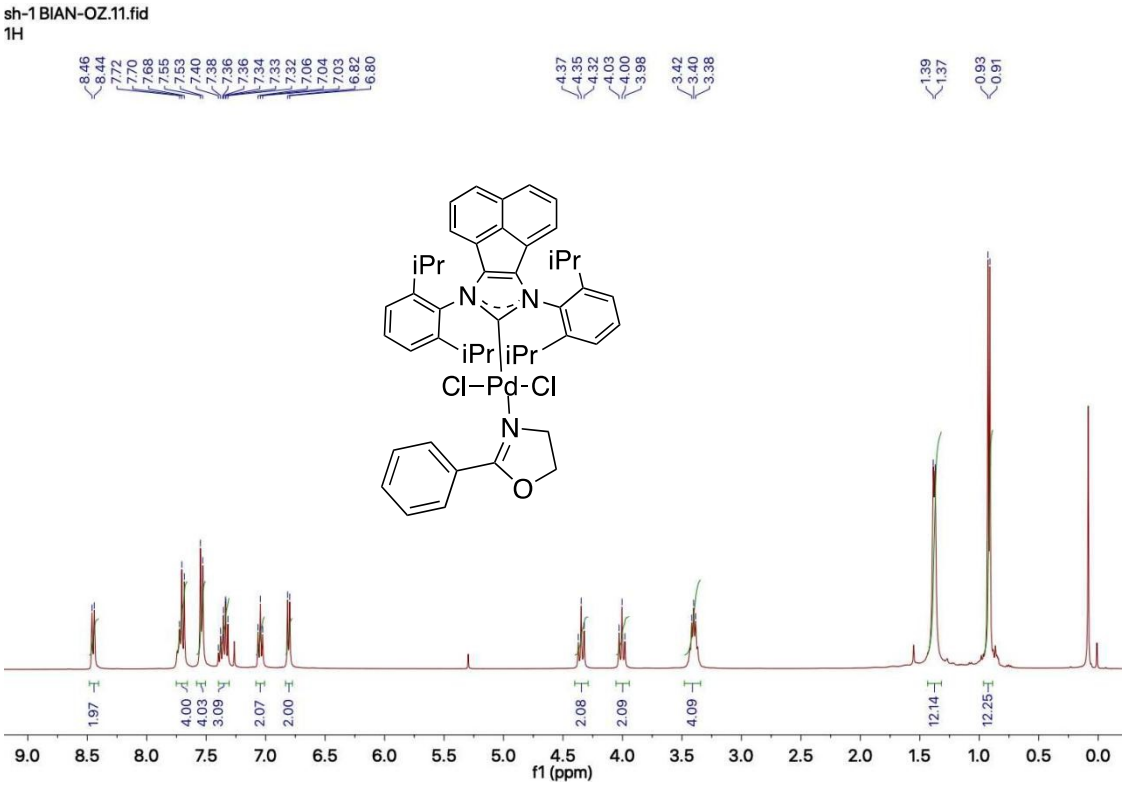


Figure S1. ^{1}H NMR spectrum of Pd-NHC complex **3**.

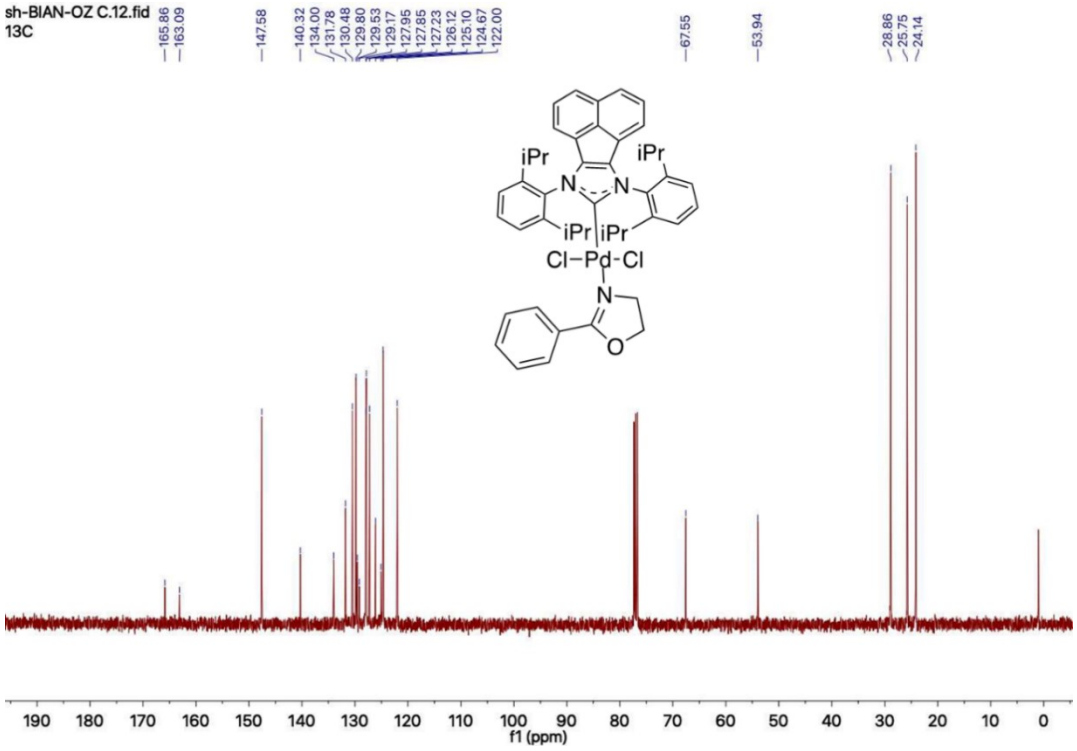
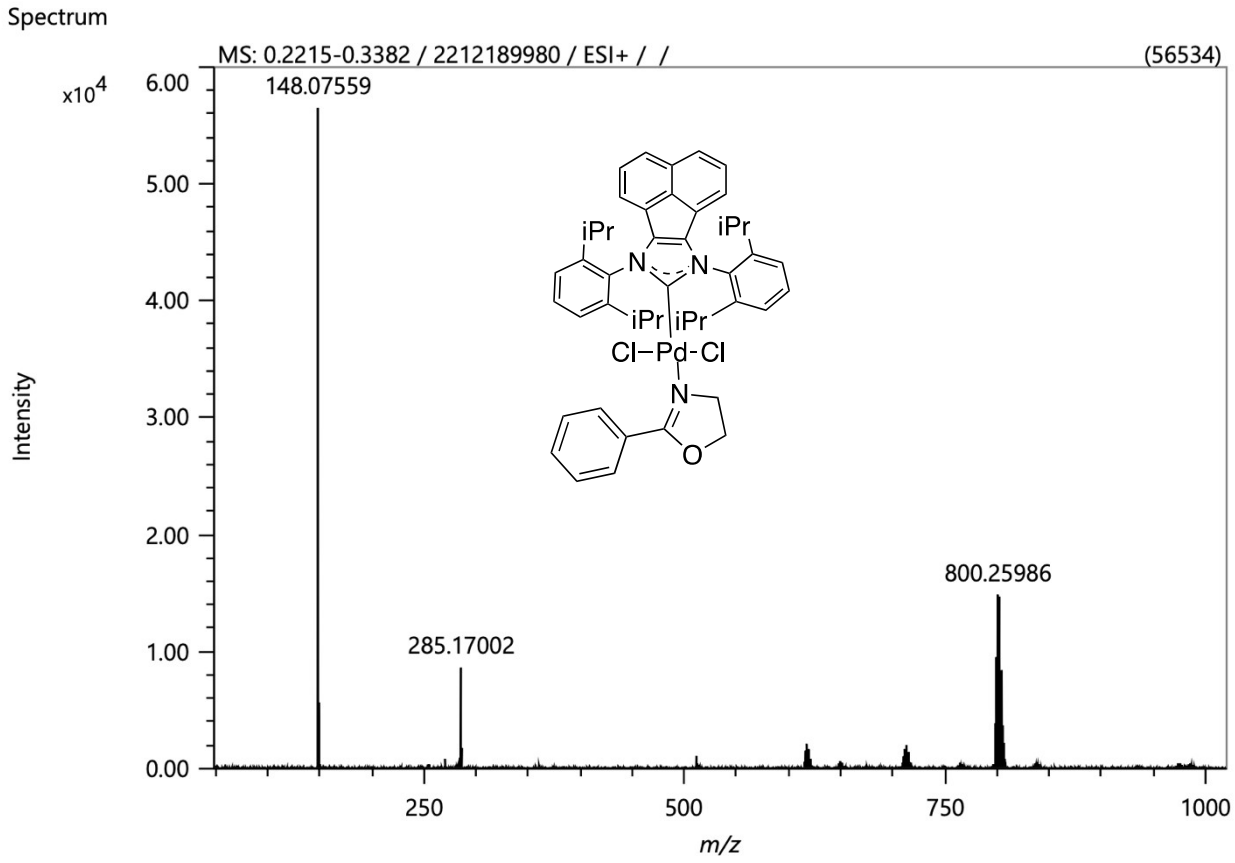


Figure S2. ^{13}C NMR spectrum of Pd-NHC complex **3**.



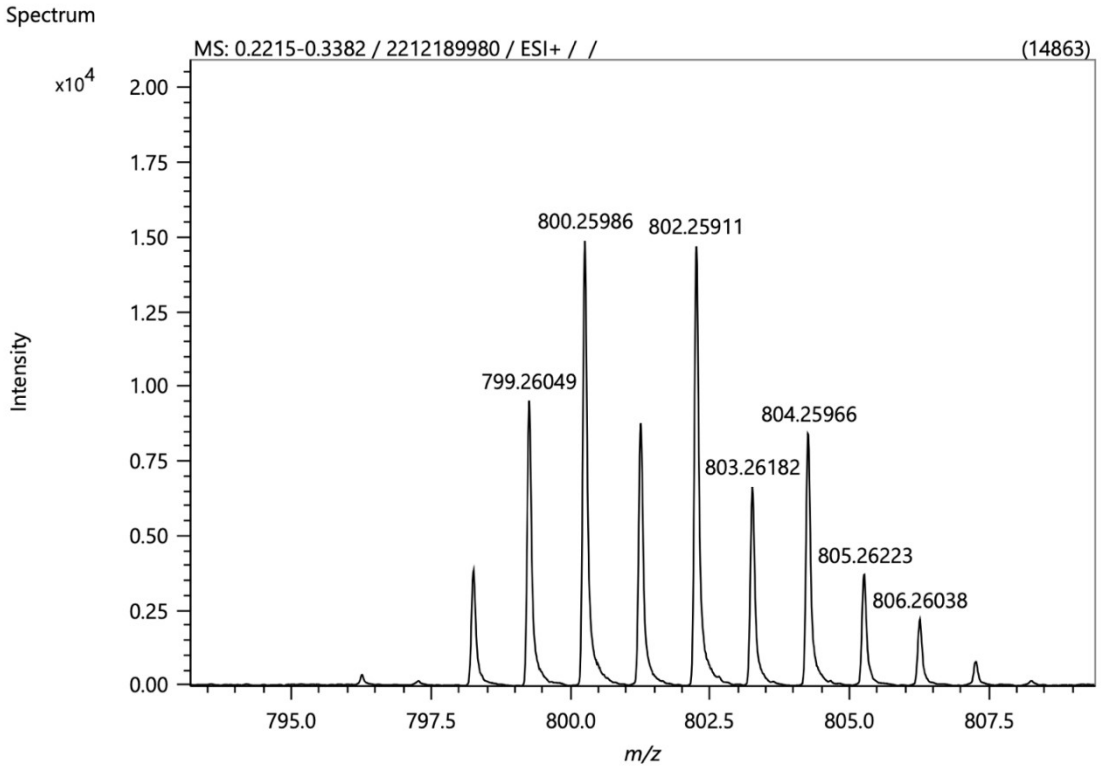


Figure S3. ESI-MS spectrum of Pd-NHC complex **3**.

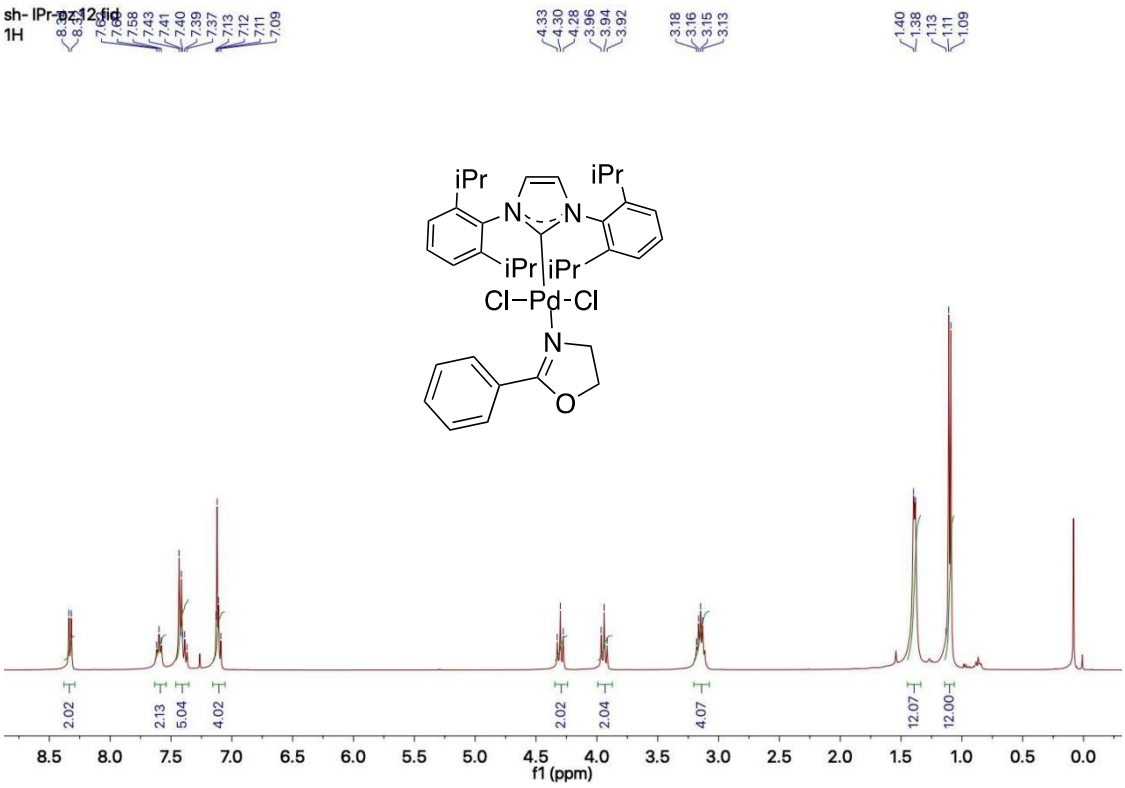


Figure S4. ^{1}H NMR spectrum of complex **4**.

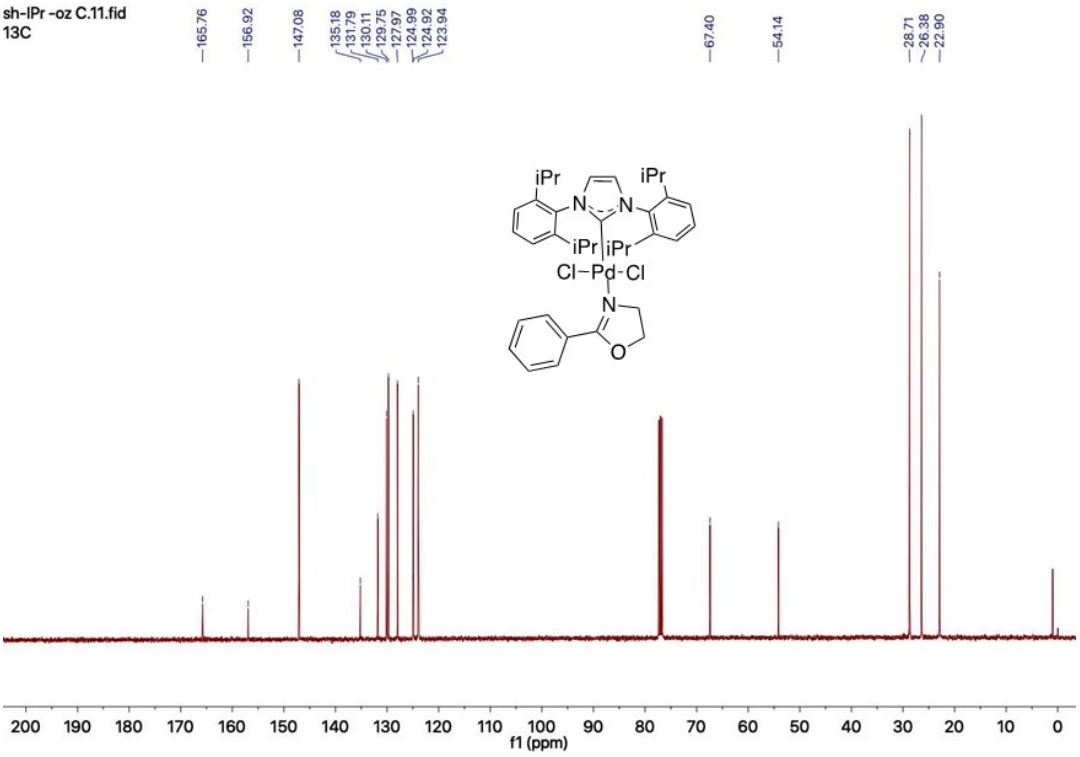


Figure S5. ^{13}C NMR spectrum of complex **4**.

Figure S6. ^{1}H NMR spectrum of compound **7**.

Figure S7.^{13}C NMR spectrum of compound **7**.

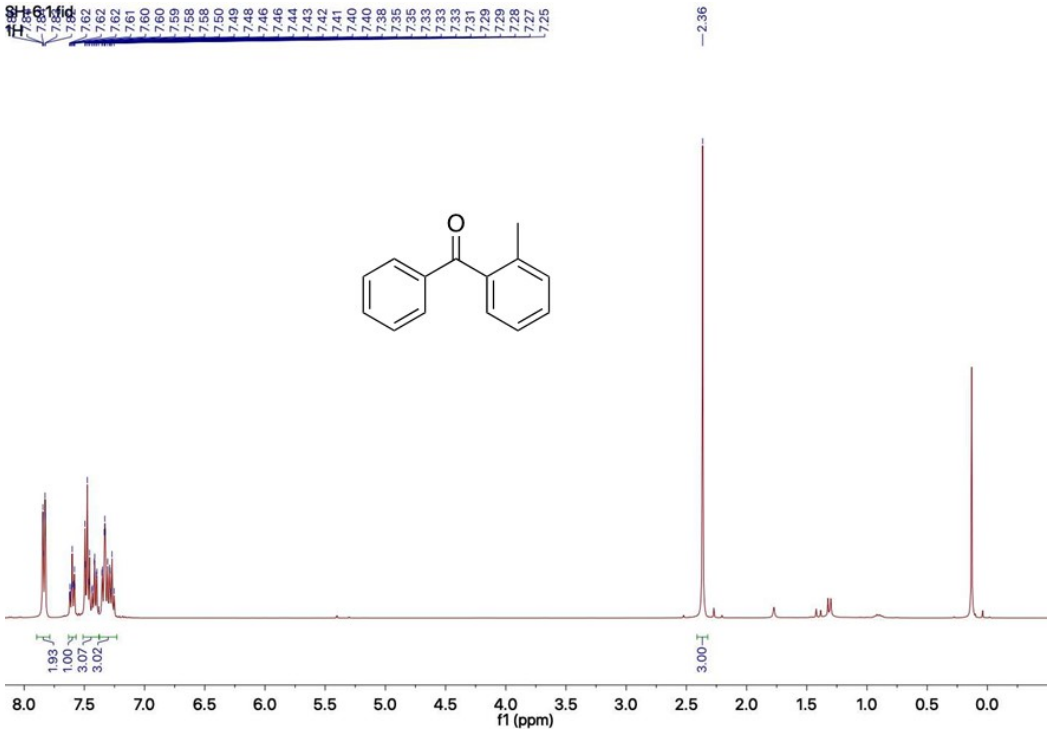


Figure S8. ^{1}H NMR spectrum of compound **8a**.

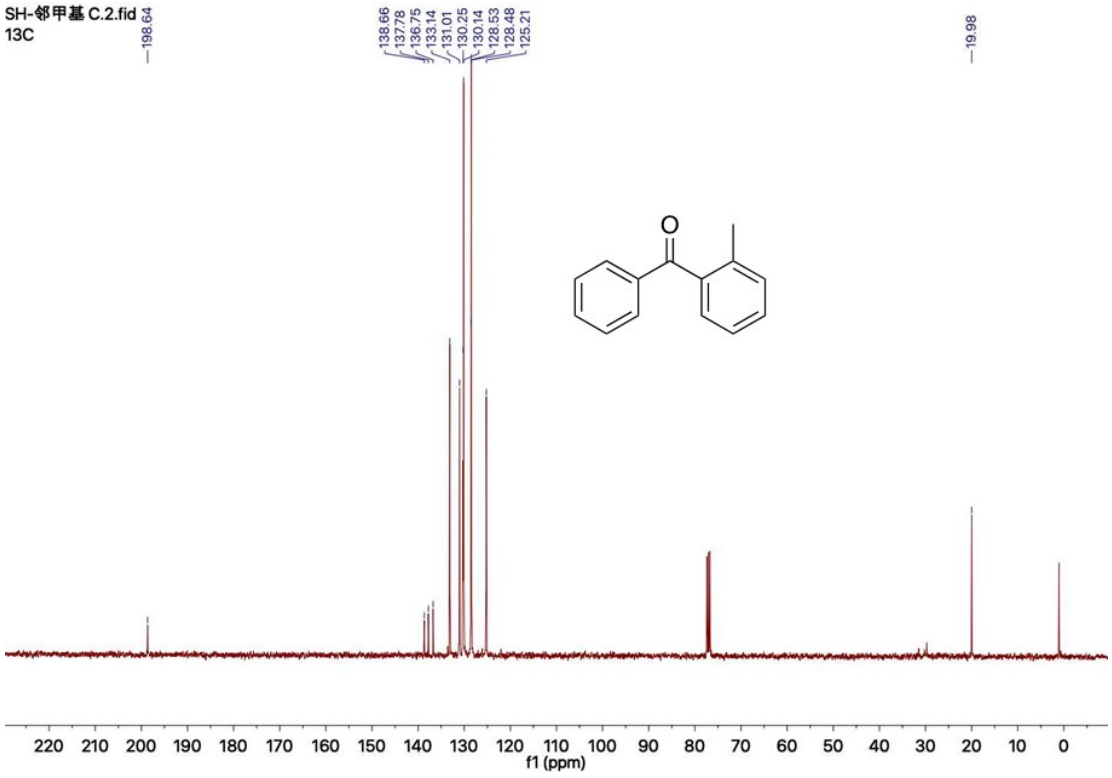


Figure S9. ^{13}C NMR spectrum of compound **8a**.

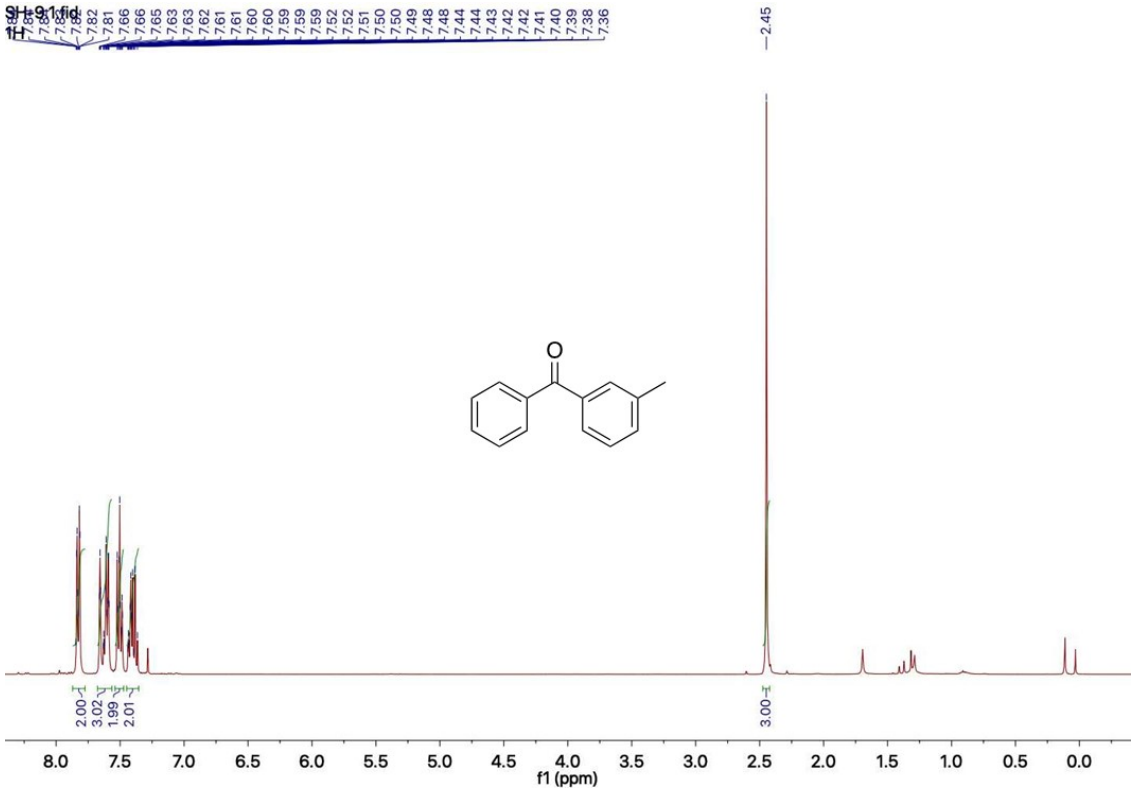


Figure S10. ^{1}H NMR spectrum of compound **8b**.

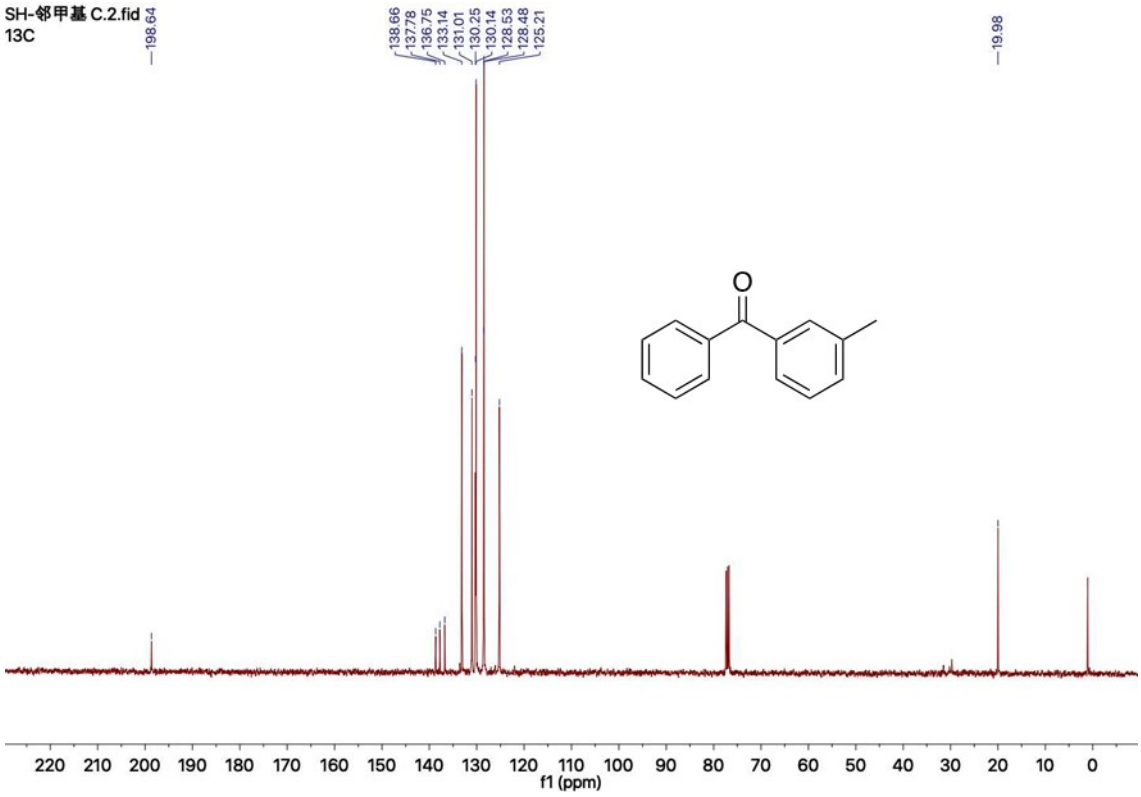


Figure S11. ^{13}C NMR spectrum of compound **8b**.

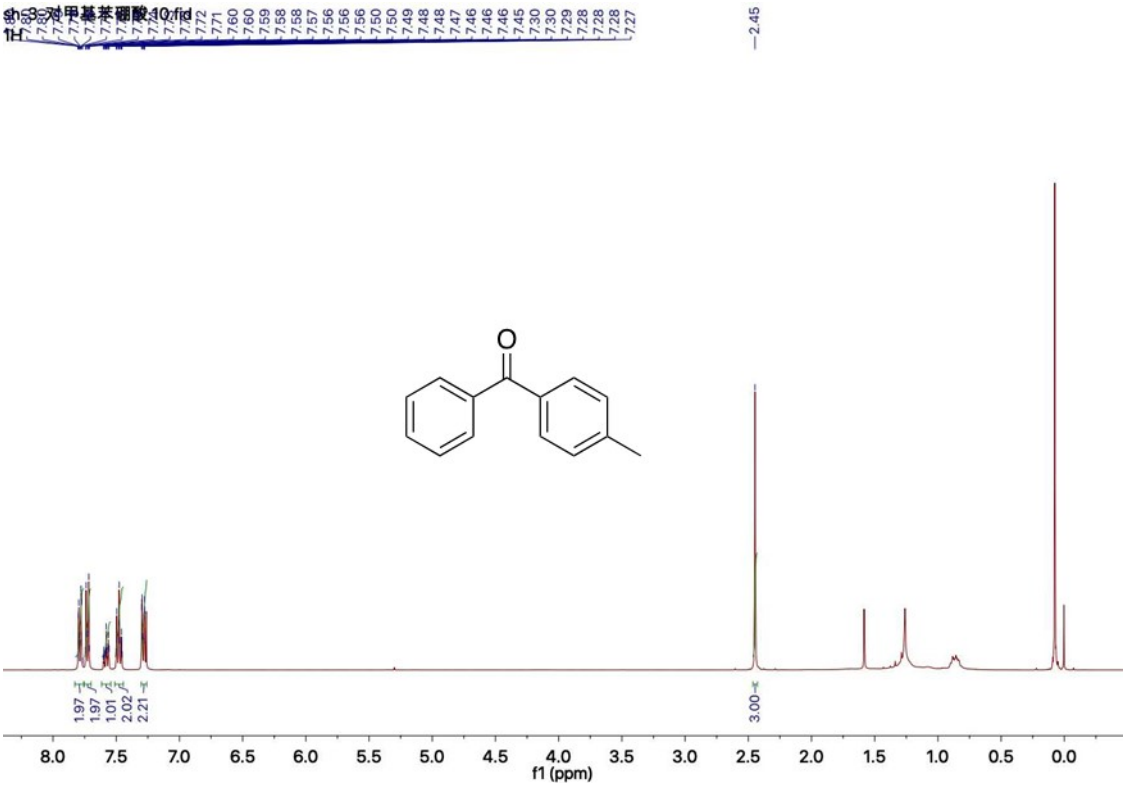


Figure S12. ^{1}H NMR spectrum of compound **8c**.

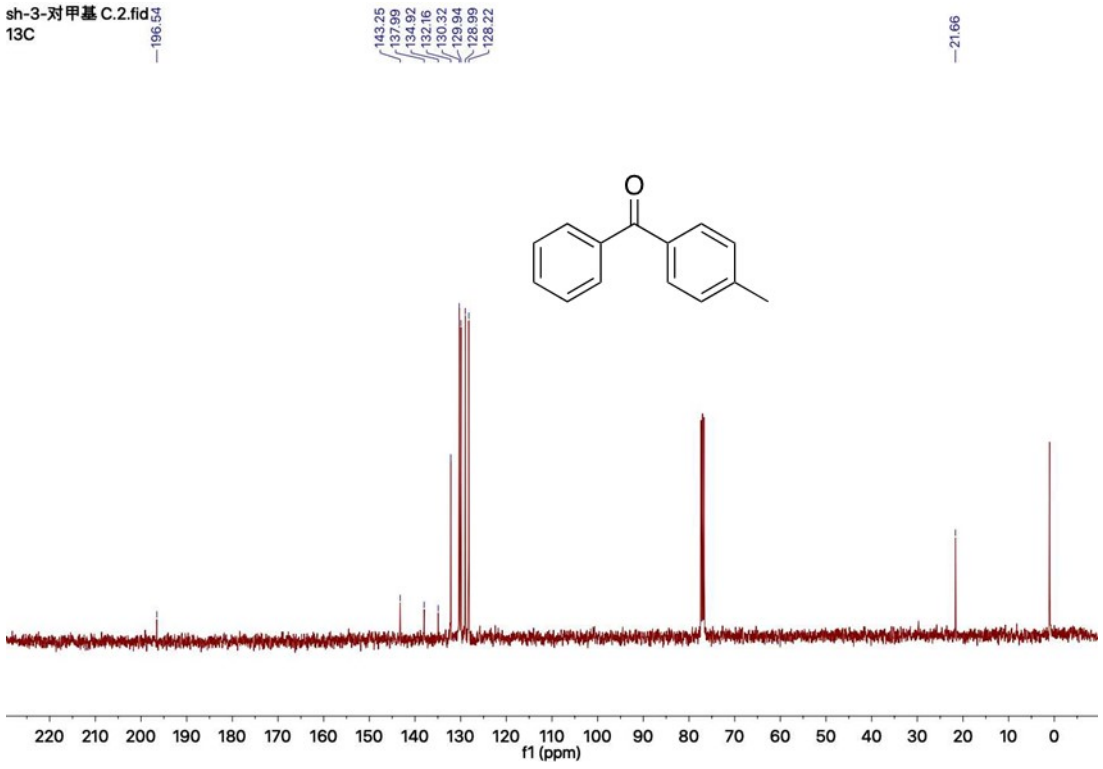


Figure S13. ^{13}C NMR spectrum of complex **8c**.

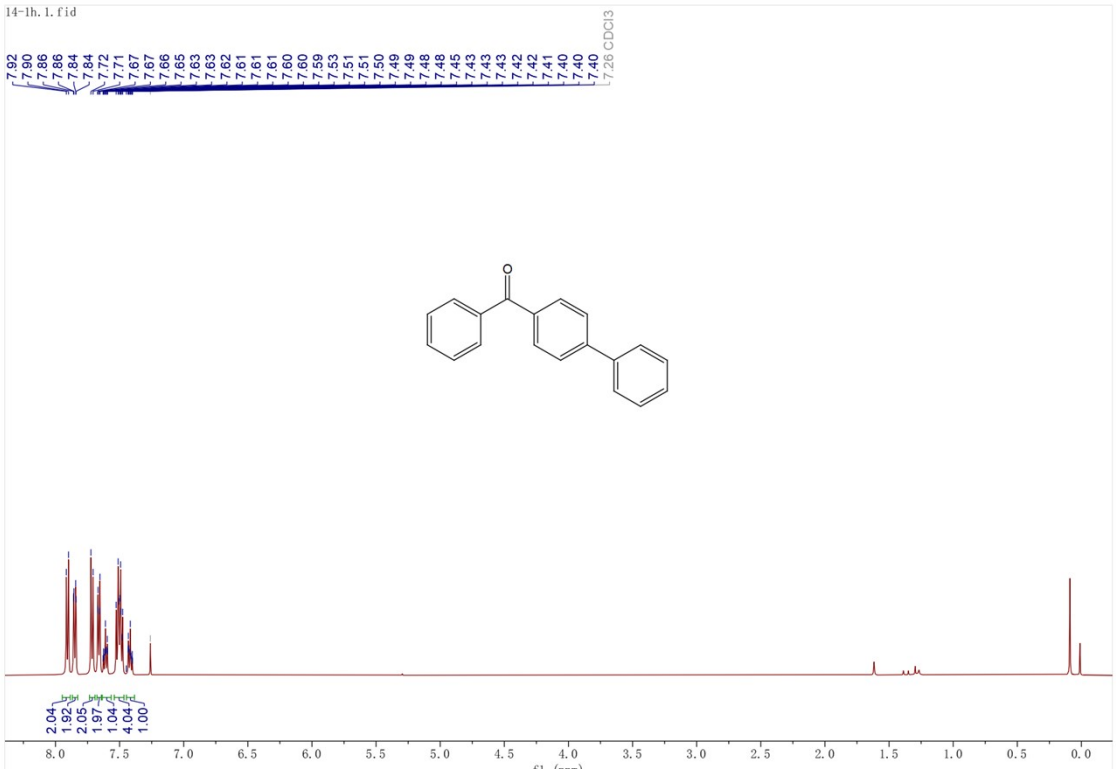


Figure S14. ^{1}H NMR spectrum of complex **9**.

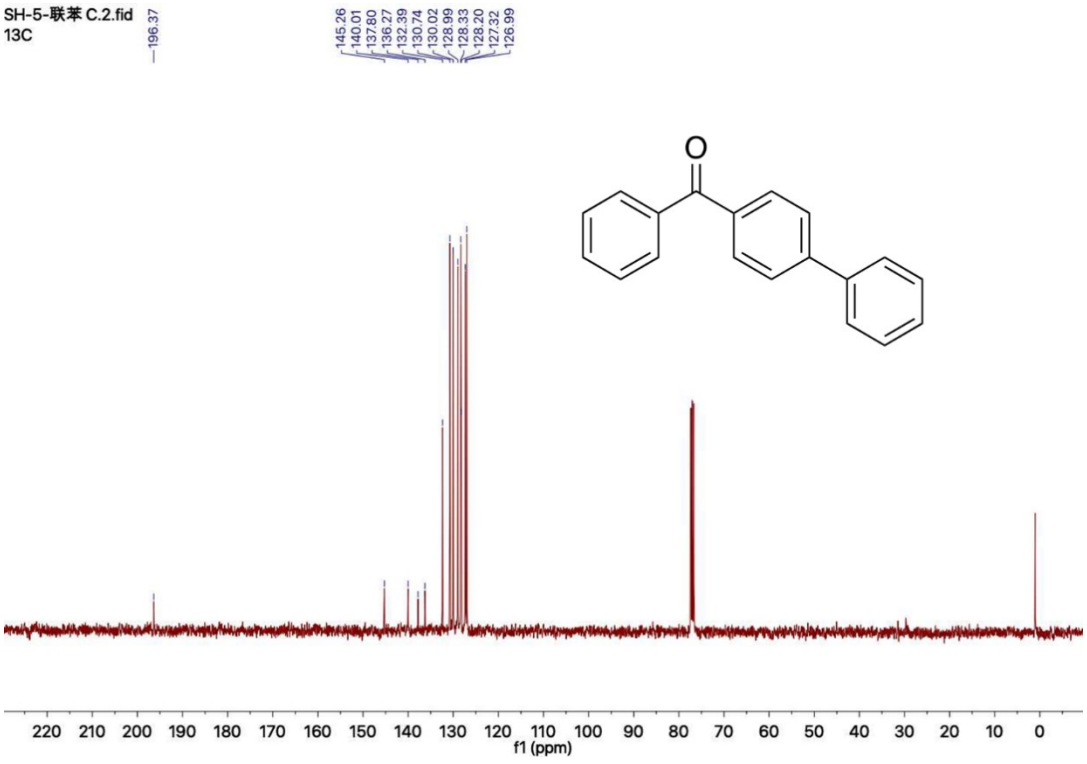


Figure S15. ^{13}C NMR spectrum of complex **9a**.

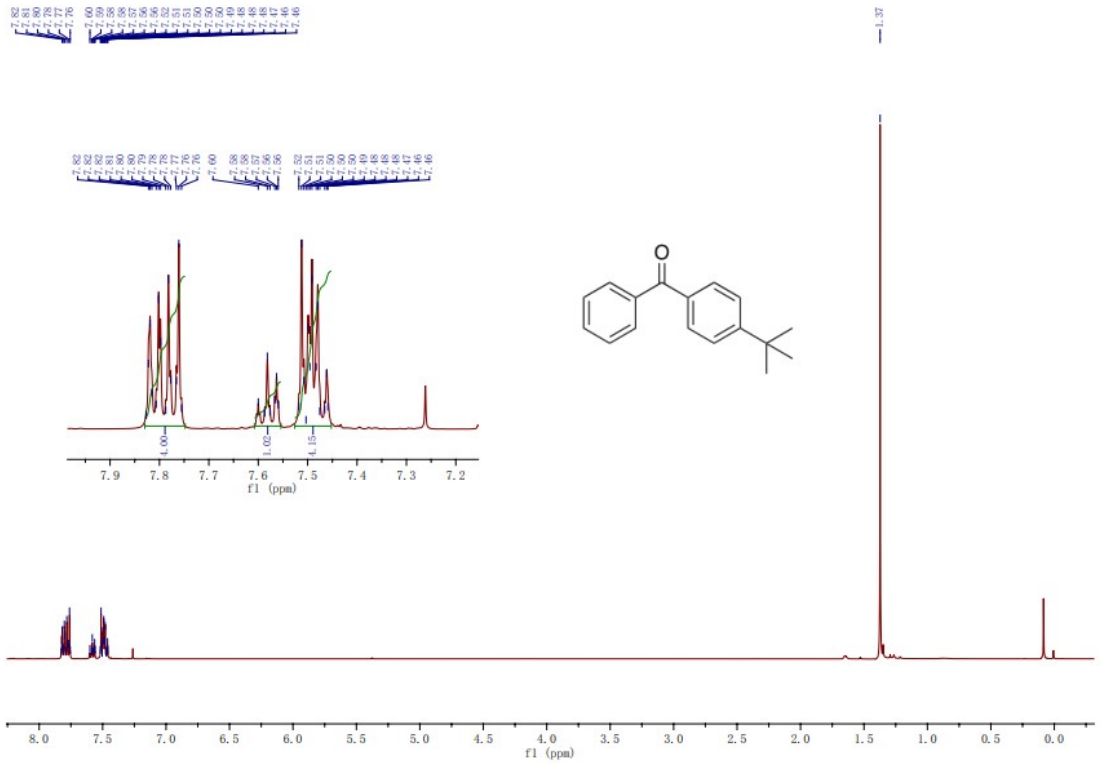


Figure S16. ^{1}H NMR spectrum of complex **9b**.

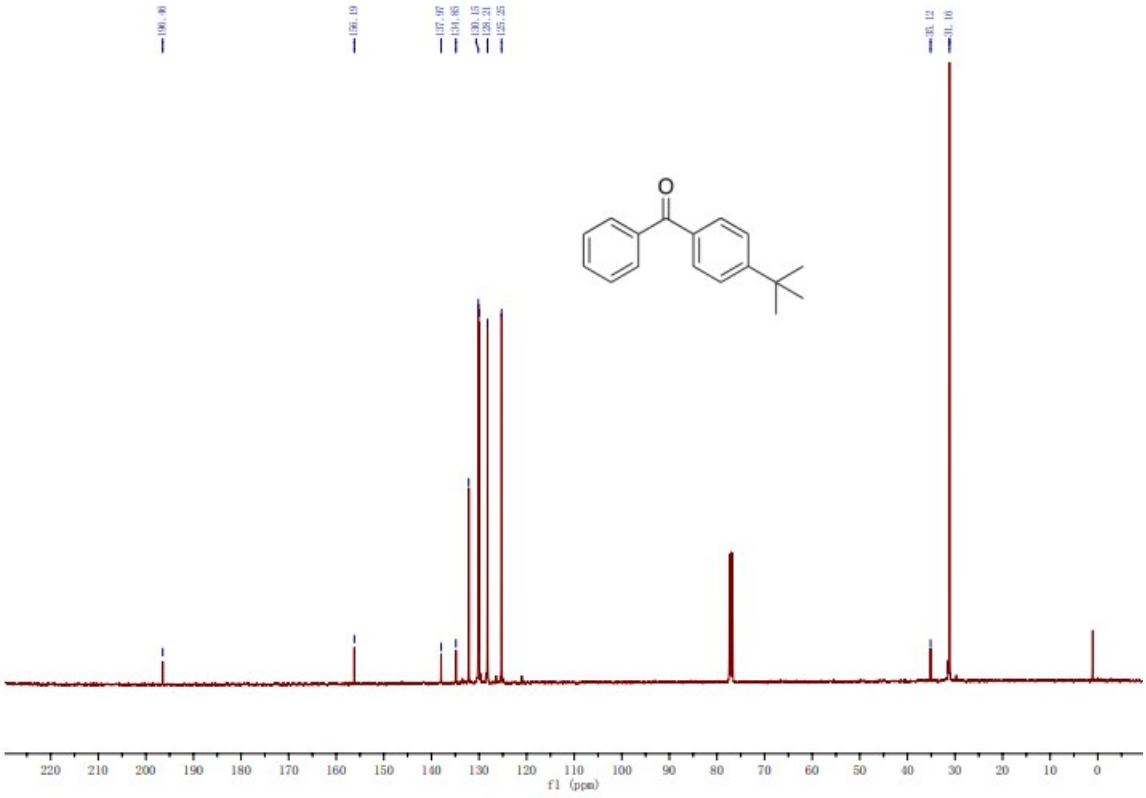


Figure S17. ^{13}C NMR spectrum of complex **9b**.

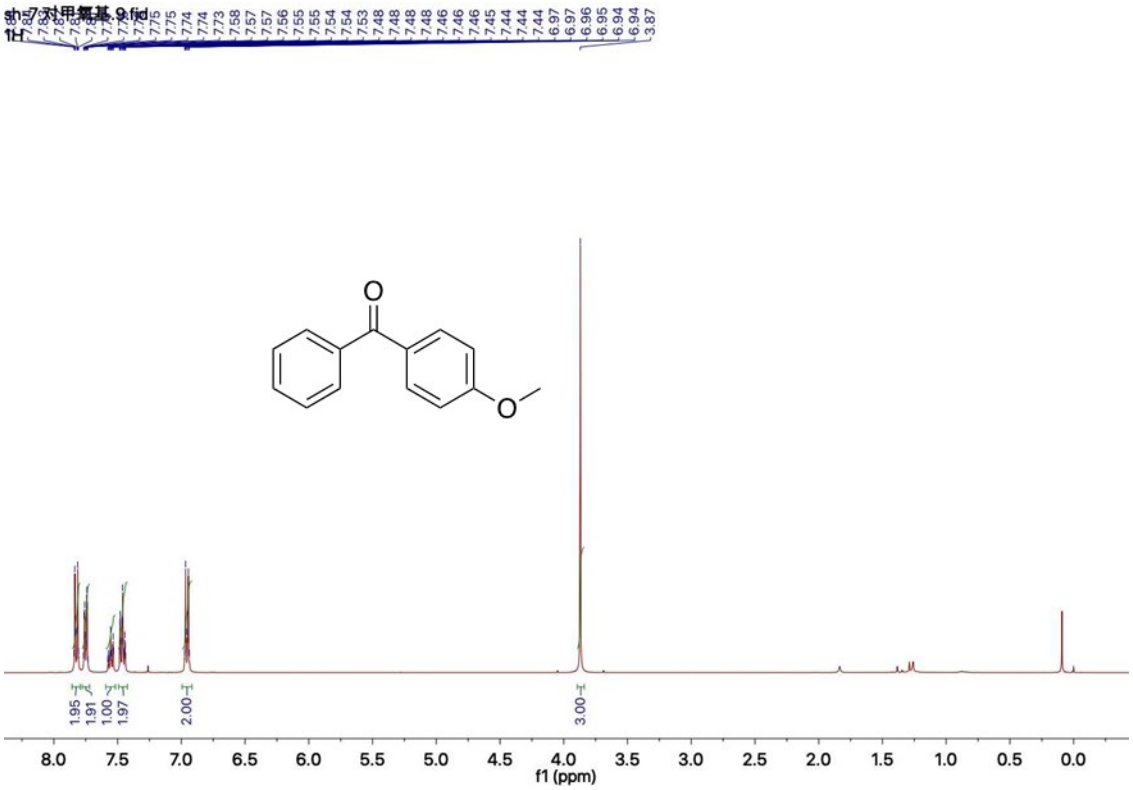


Figure S18. ^{1}H NMR spectrum of complex **10a**.

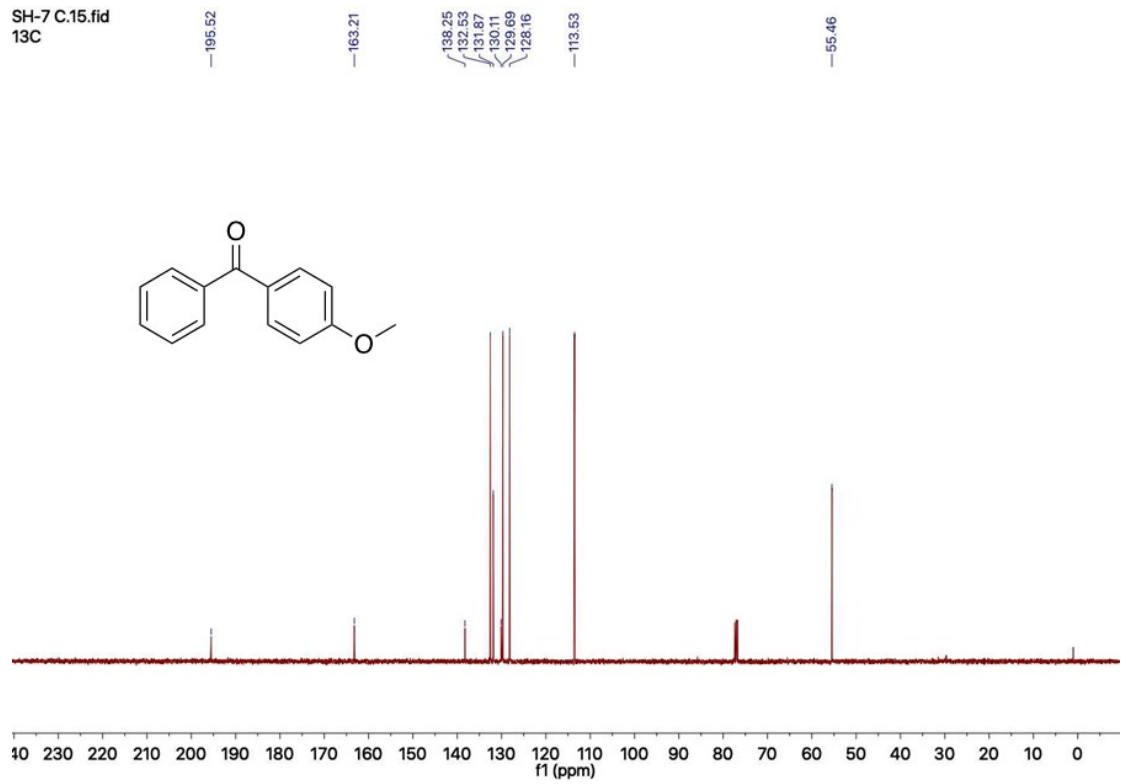


Figure S19. ^{13}C NMR spectrum of complex **10a**.

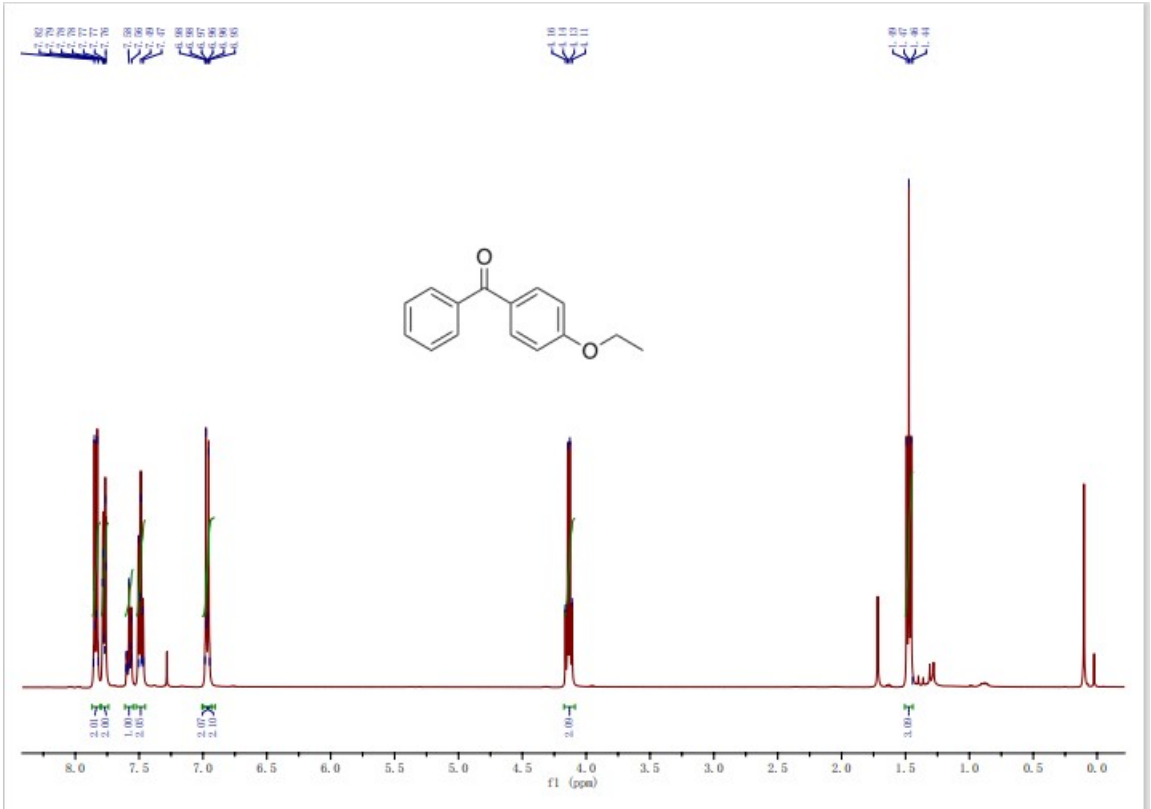


Figure S20. ^{1}H NMR spectrum of complex **10b**.

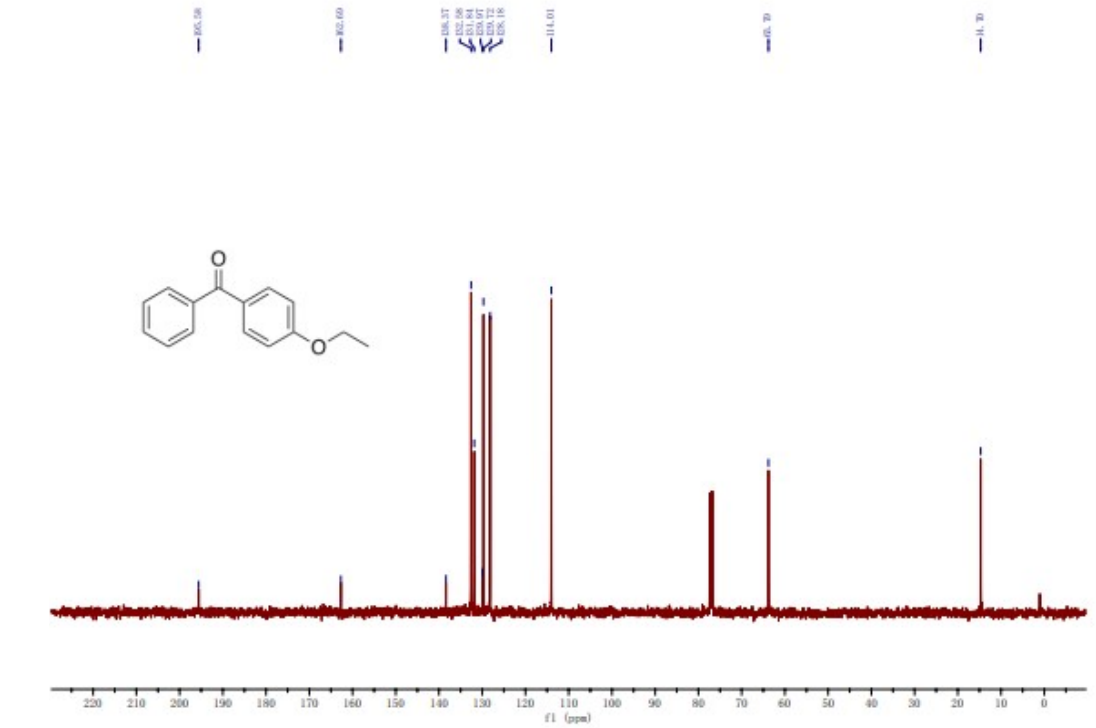


Figure S21. ^{13}C NMR spectrum of complex **10b**.

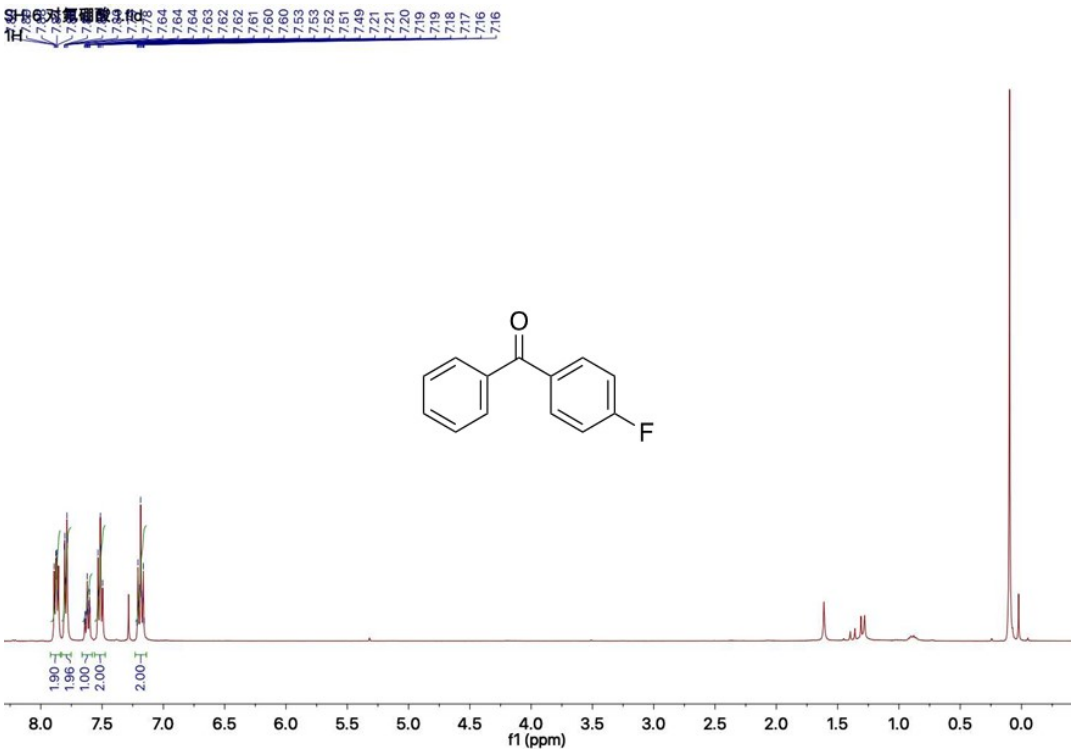


Figure S22. ^{1}H NMR spectrum of complex **11a**.

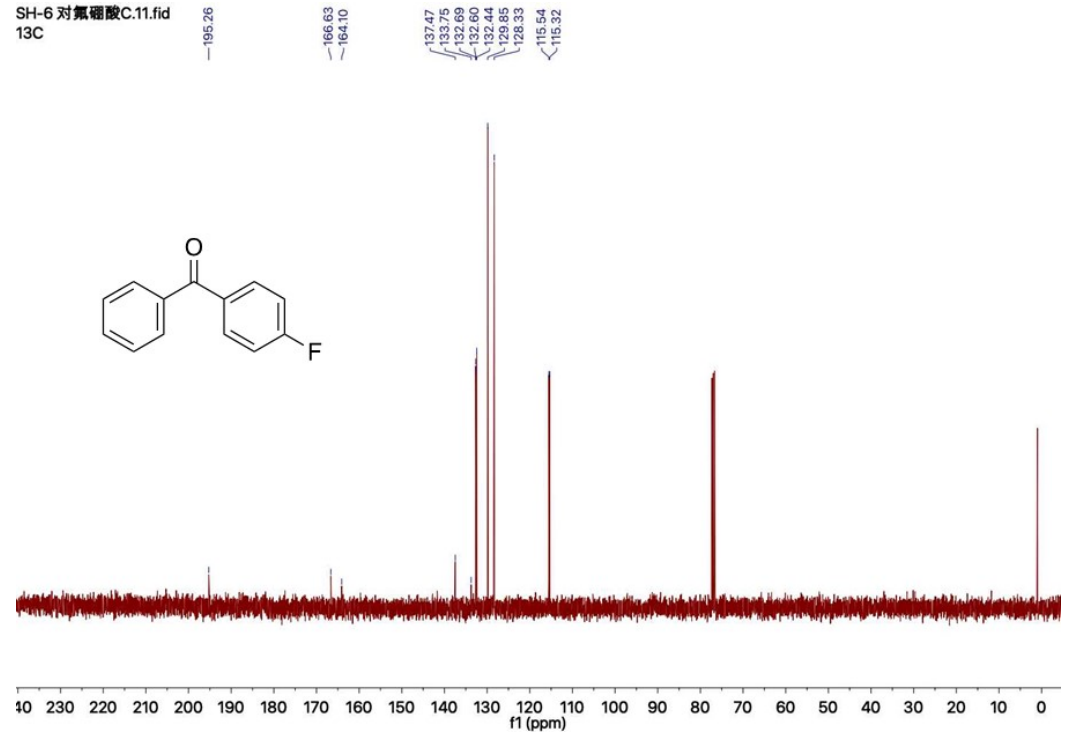


Figure S23. ^{13}C NMR spectrum of complex **11a**.

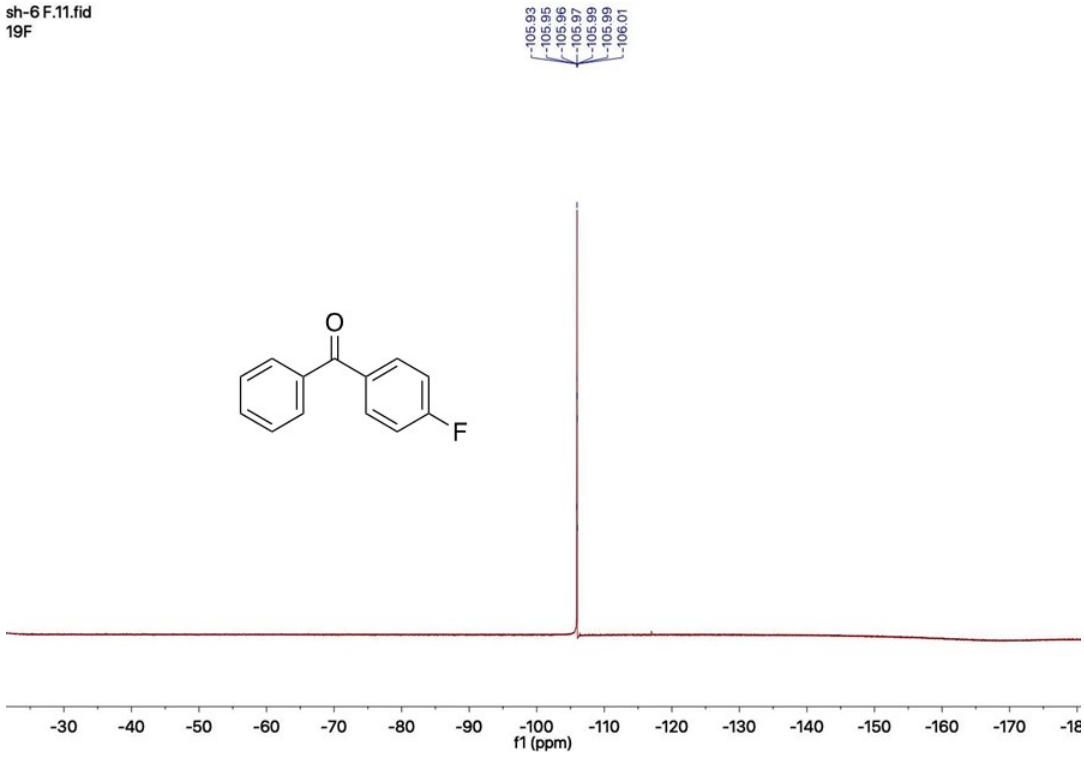


Figure S24. ^{19}F NMR spectrum of complex **11a**.

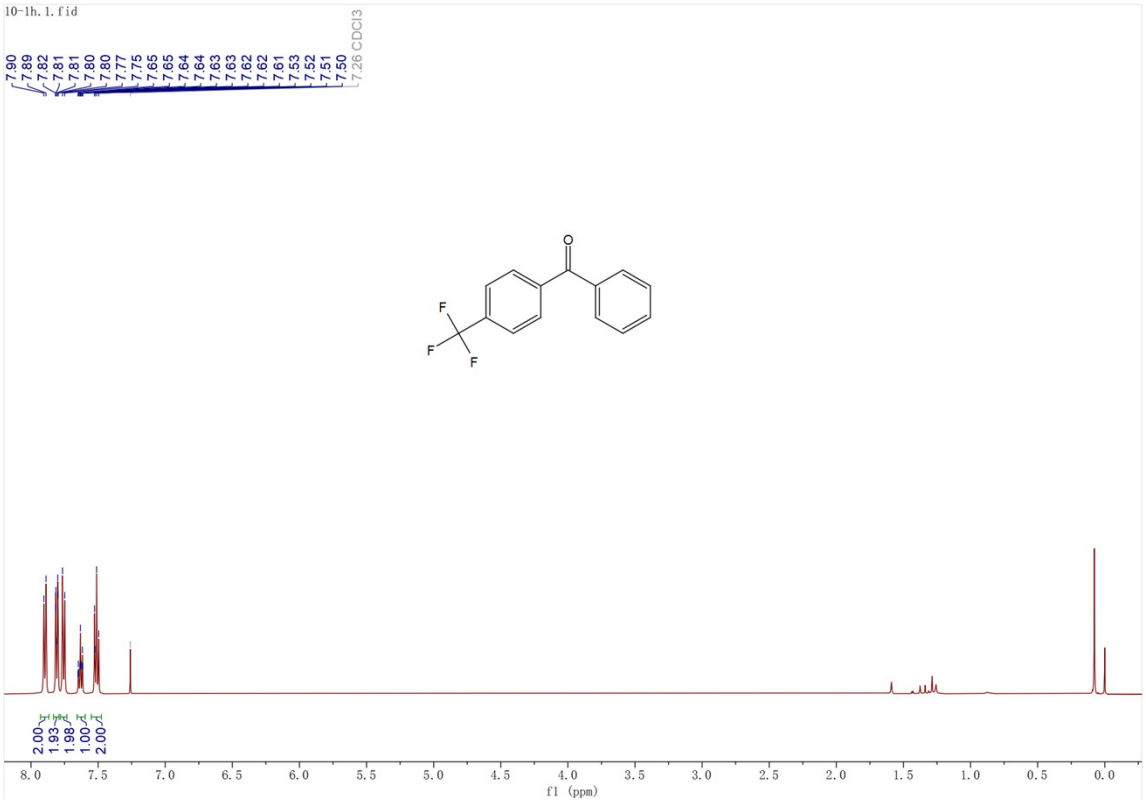


Figure S25. ^{1}H NMR spectrum of complex **11b**.

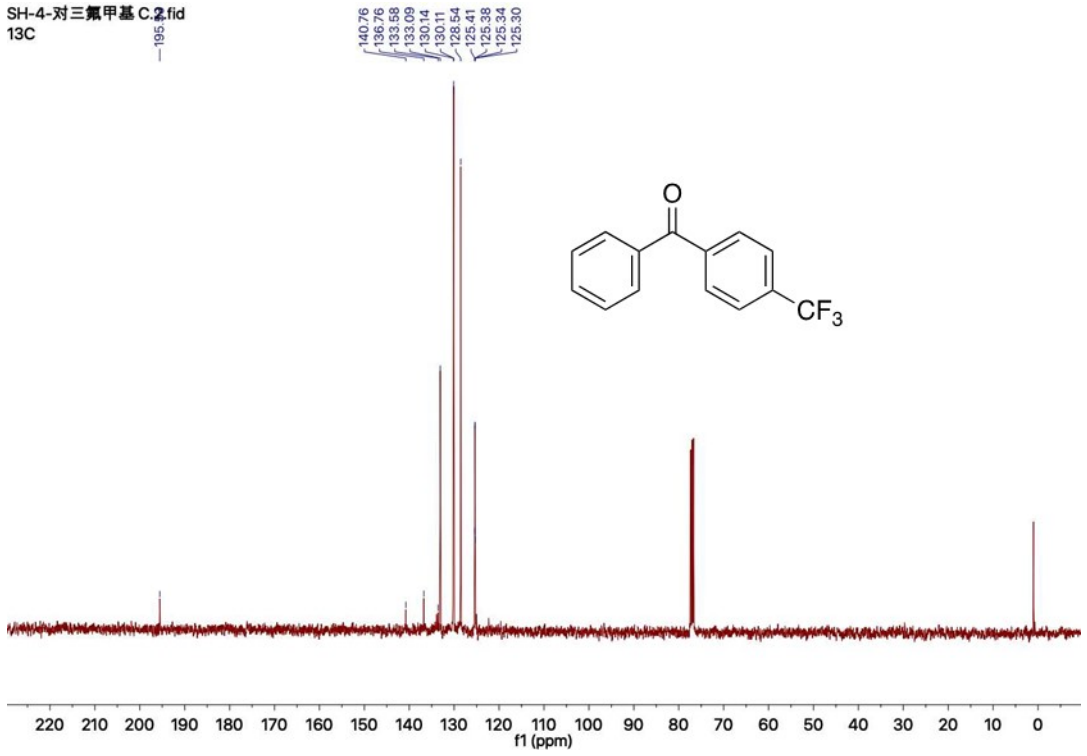


Figure S26. ^{13}C NMR spectrum of complex **11b**.

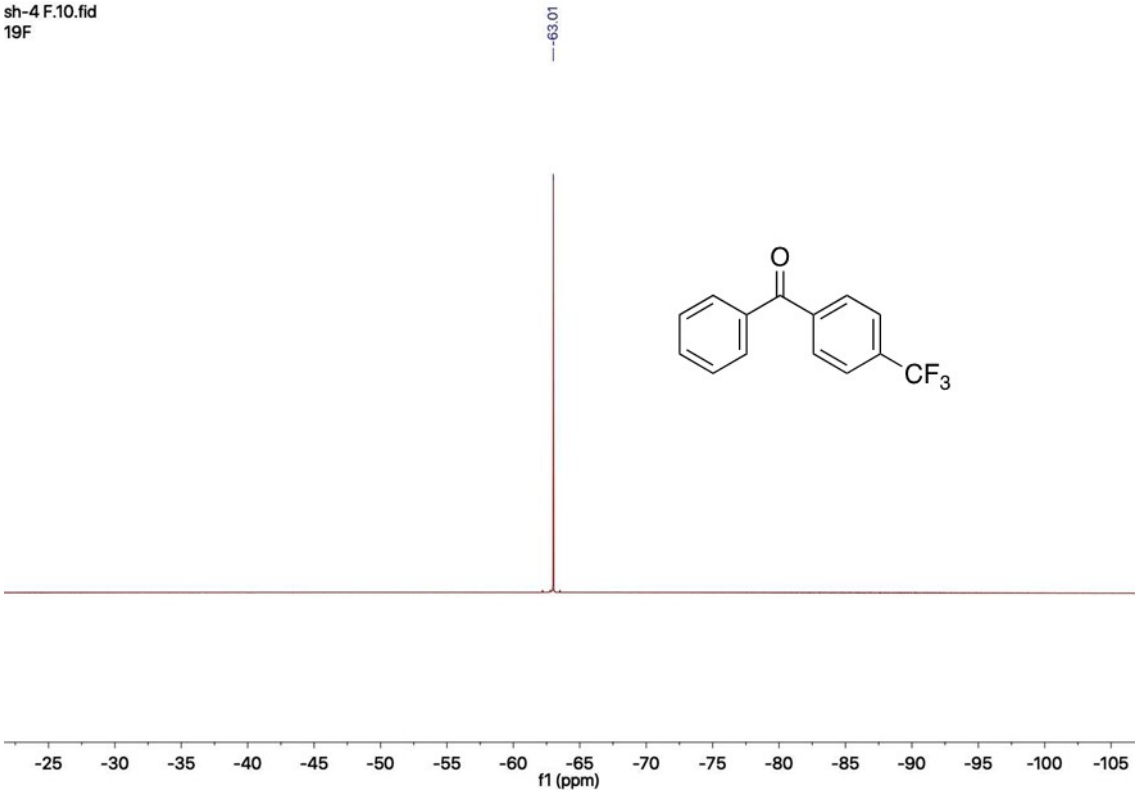


Figure S27. ^{19}F NMR spectrum of complex **11b**.

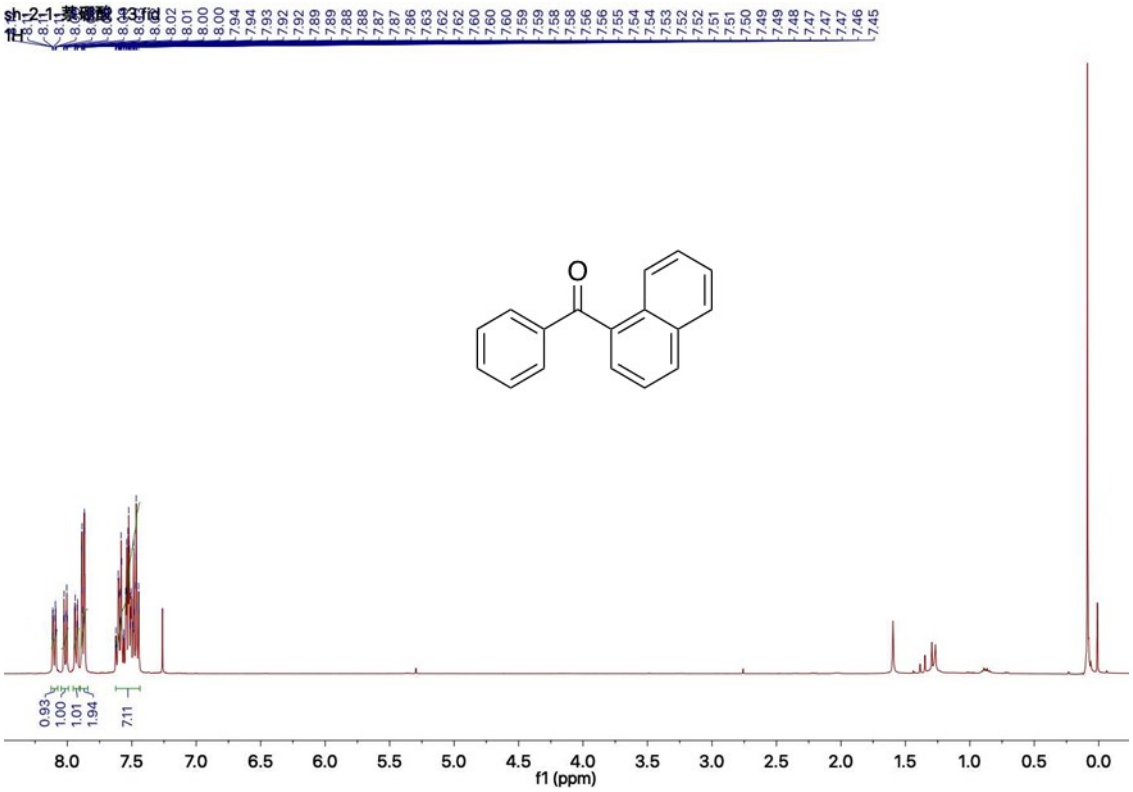


Figure S28. ^{1}H NMR spectrum of compound **12**.

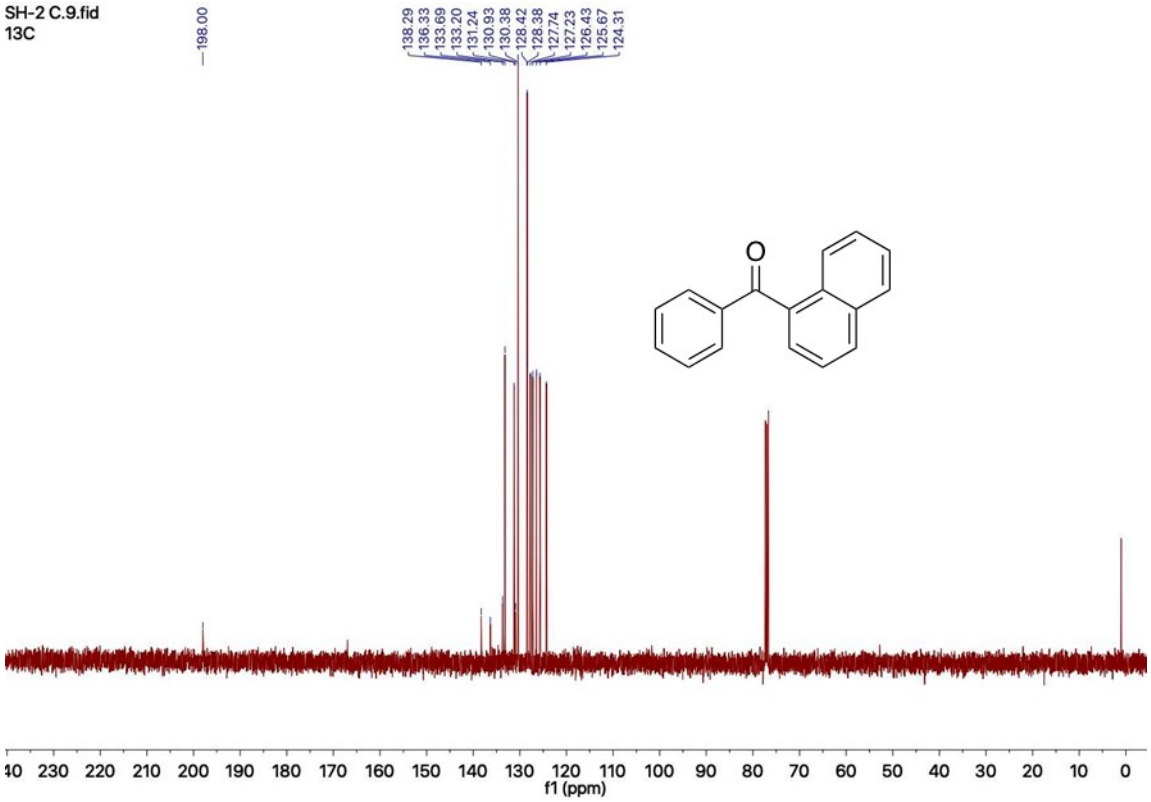


Figure S29. ^{13}C NMR spectrum of compound **12**.

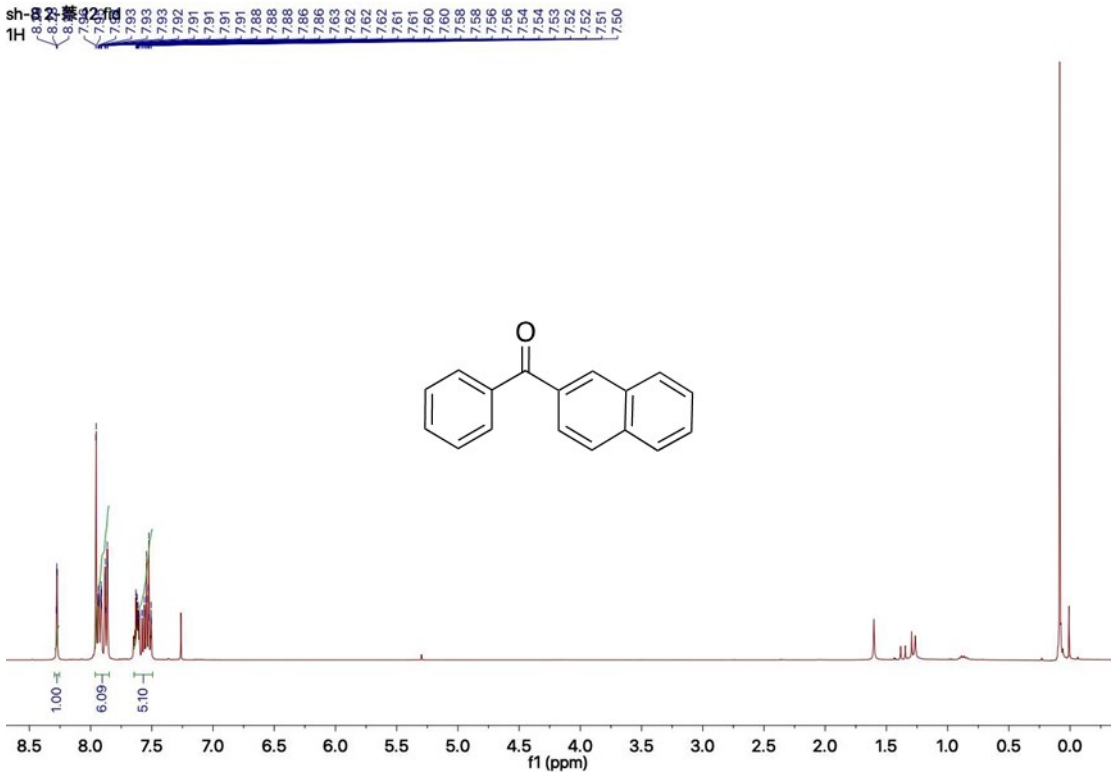


Figure S30. ^{1}H NMR spectrum of compound **13**.

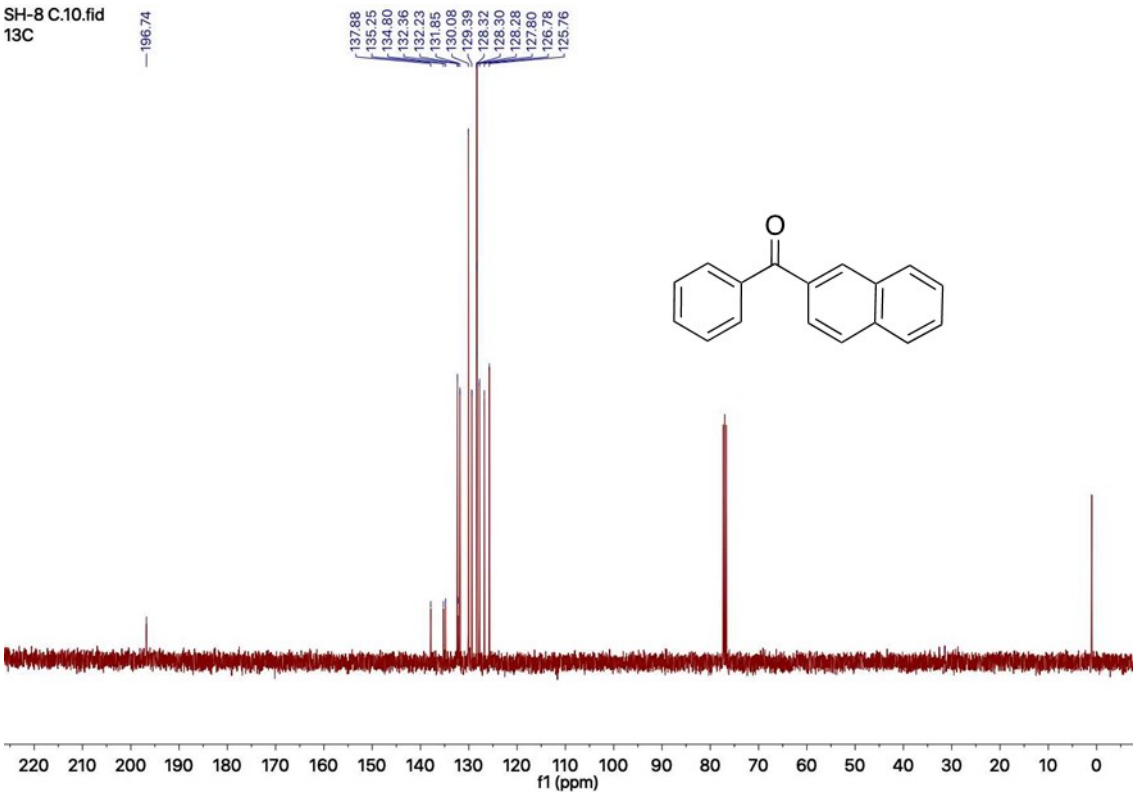


Figure S31. ^{13}C NMR spectrum of compound **13**.

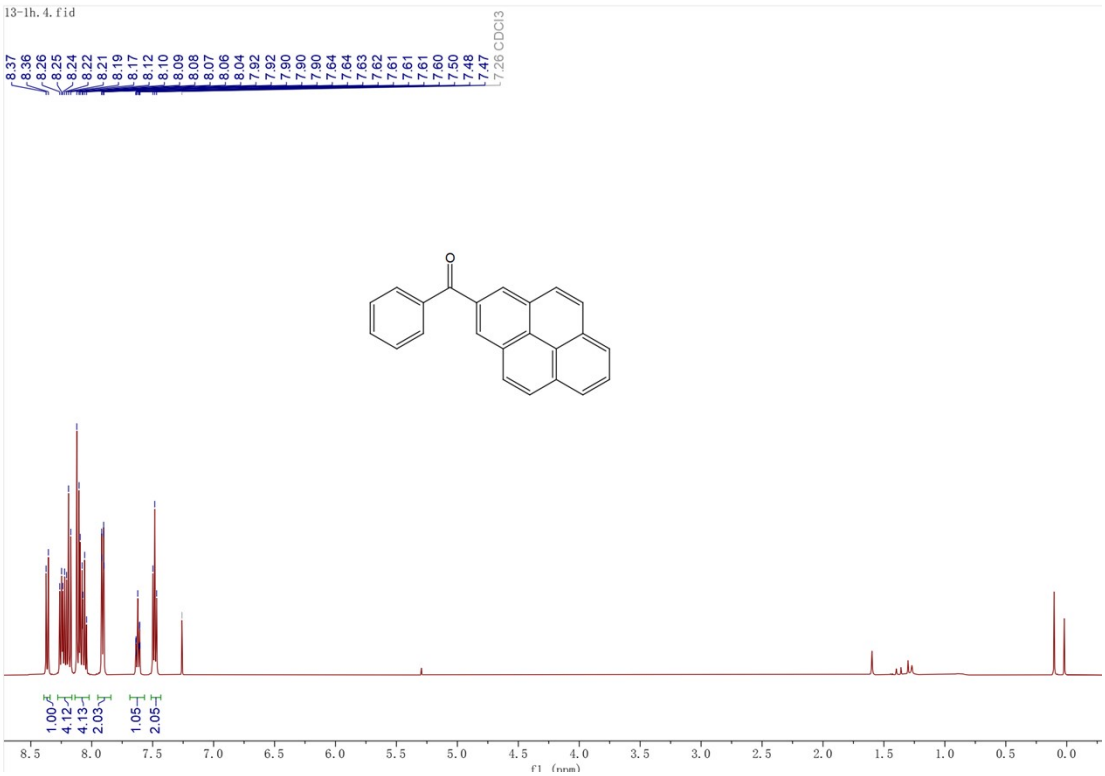


Figure S32. ^{1}H NMR spectrum of compound **14**.

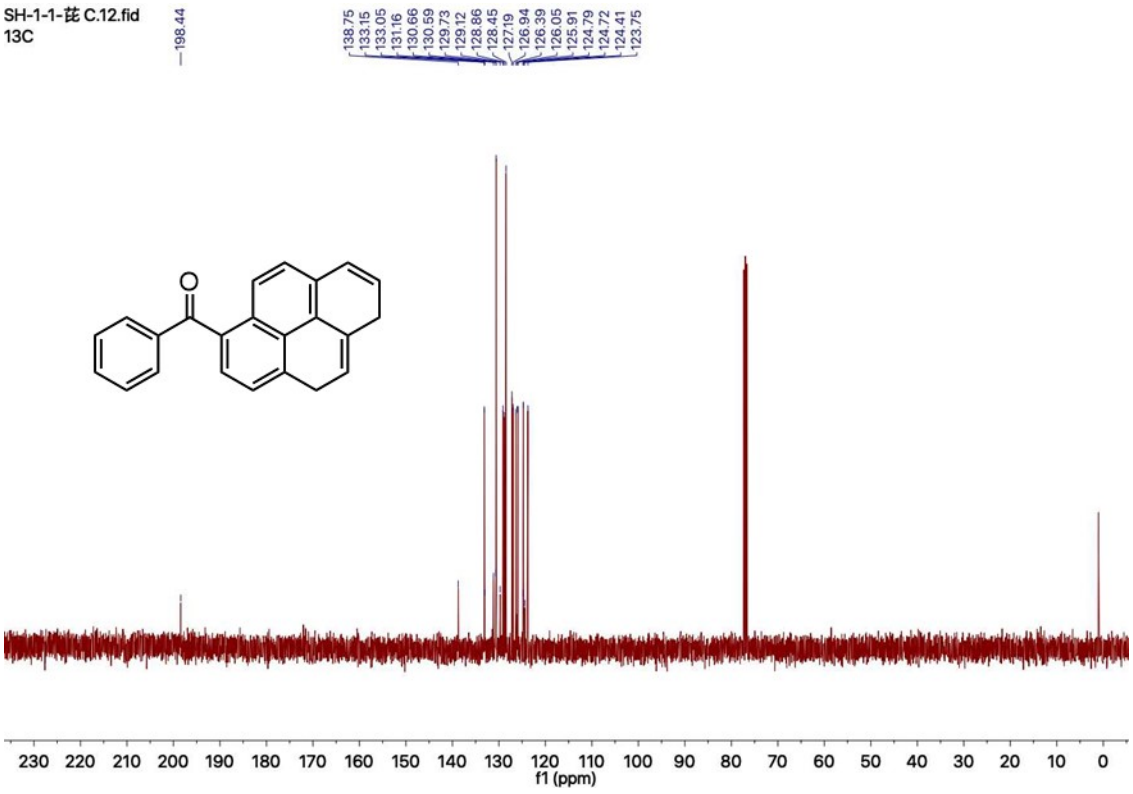


Figure S33. ^{13}C NMR spectrum of compound **14**.

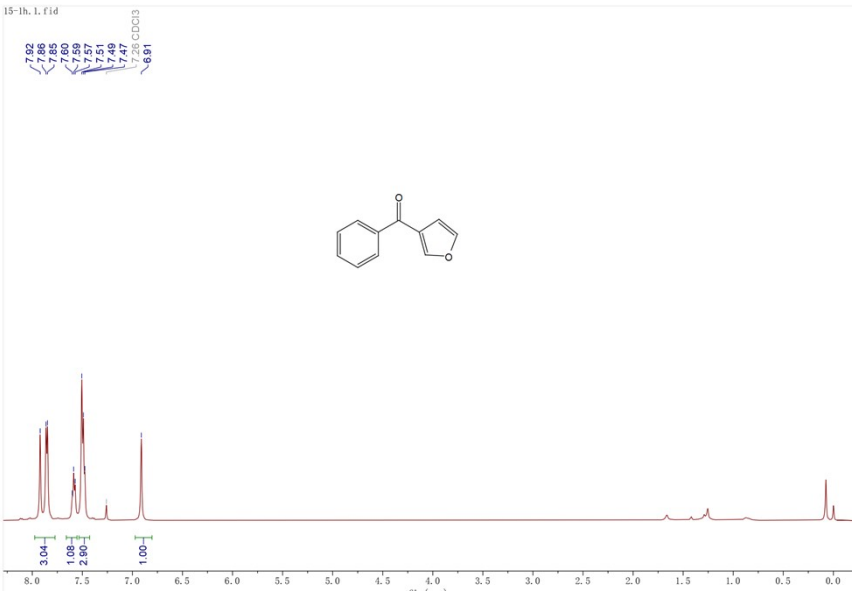


Figure S34. ^{1}H NMR spectrum of compound **15**.

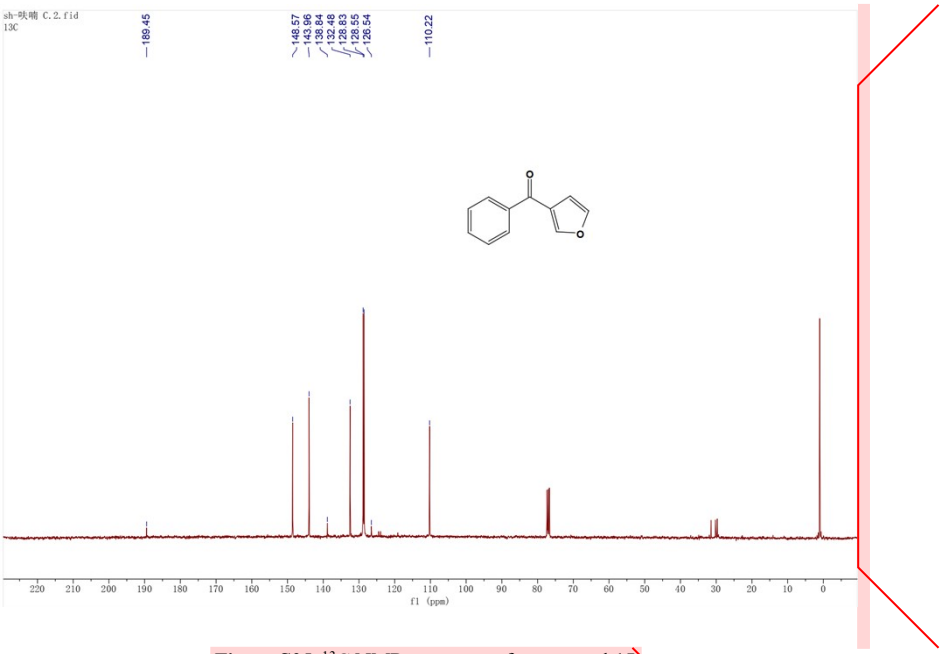


Figure S35. ^{13}C NMR spectrum of compound **15**.

Comment []: 结构式

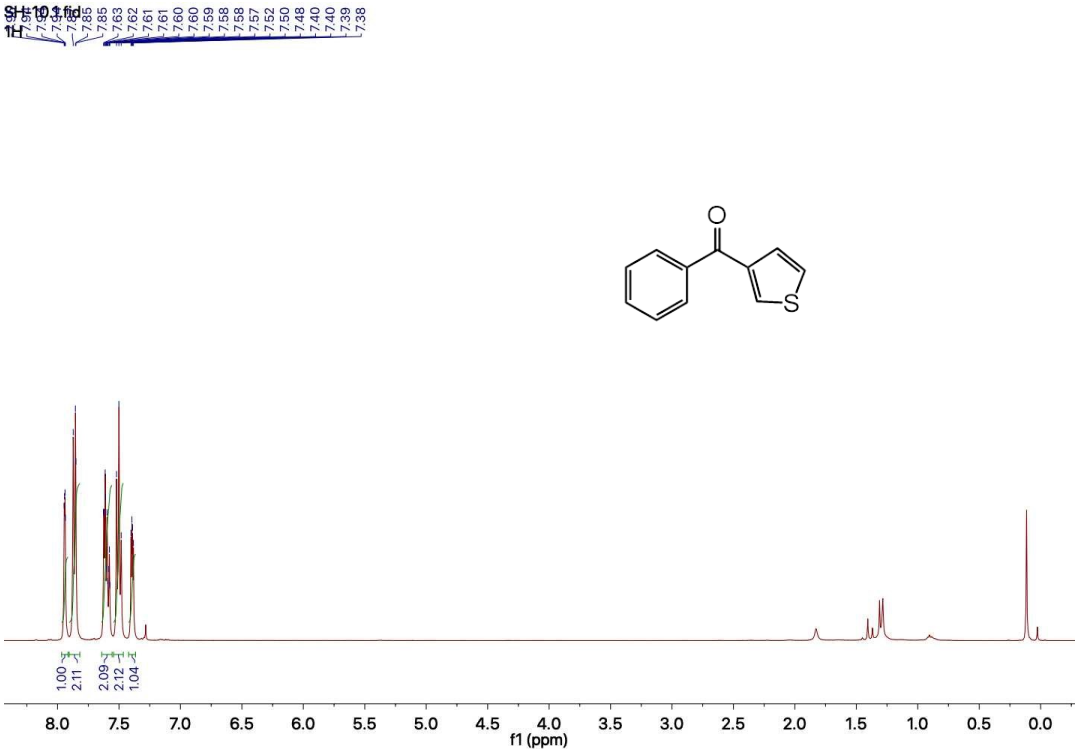


Figure S36. ^{1}H NMR spectrum of compound **16**.

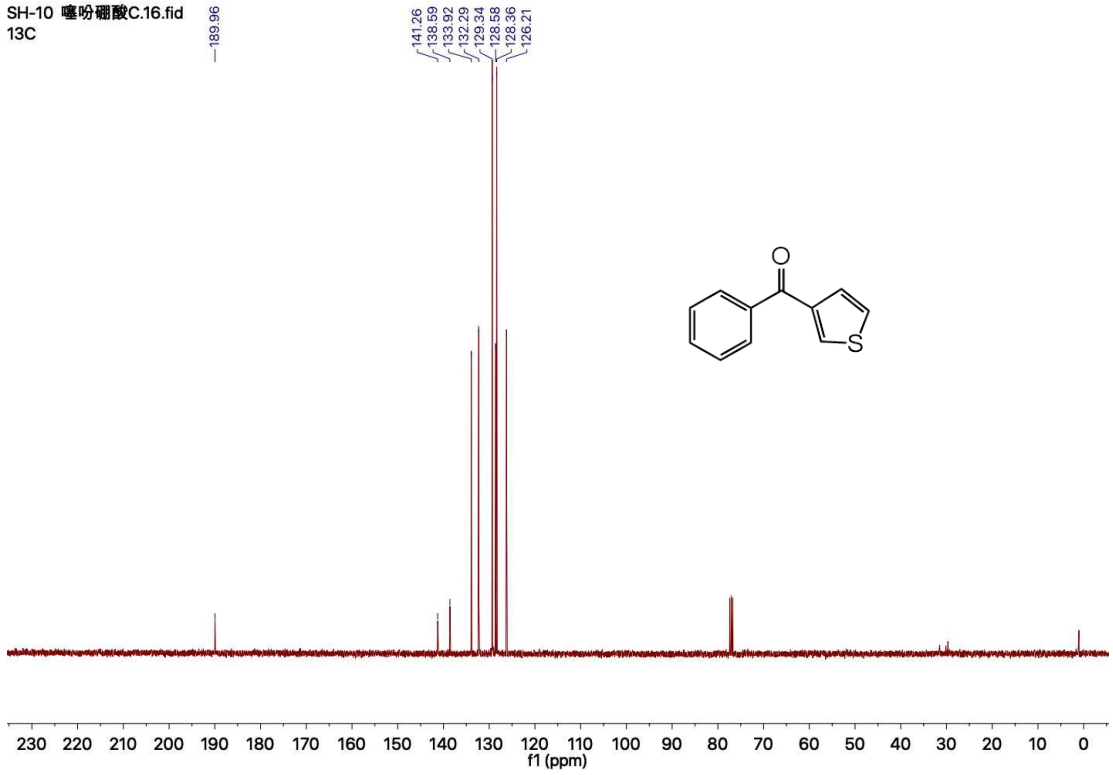


Figure S37. ^{13}C NMR spectrum of compound **16**.

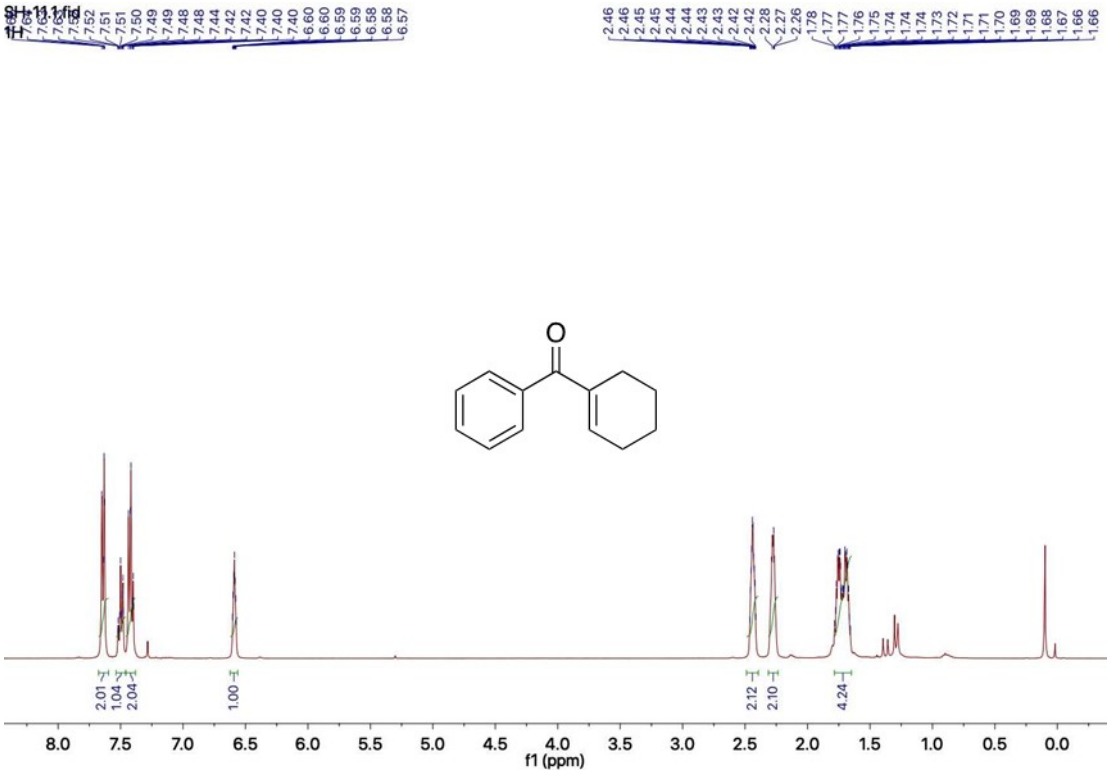


Figure S38. ^{1}H NMR spectrum of compound **17**.

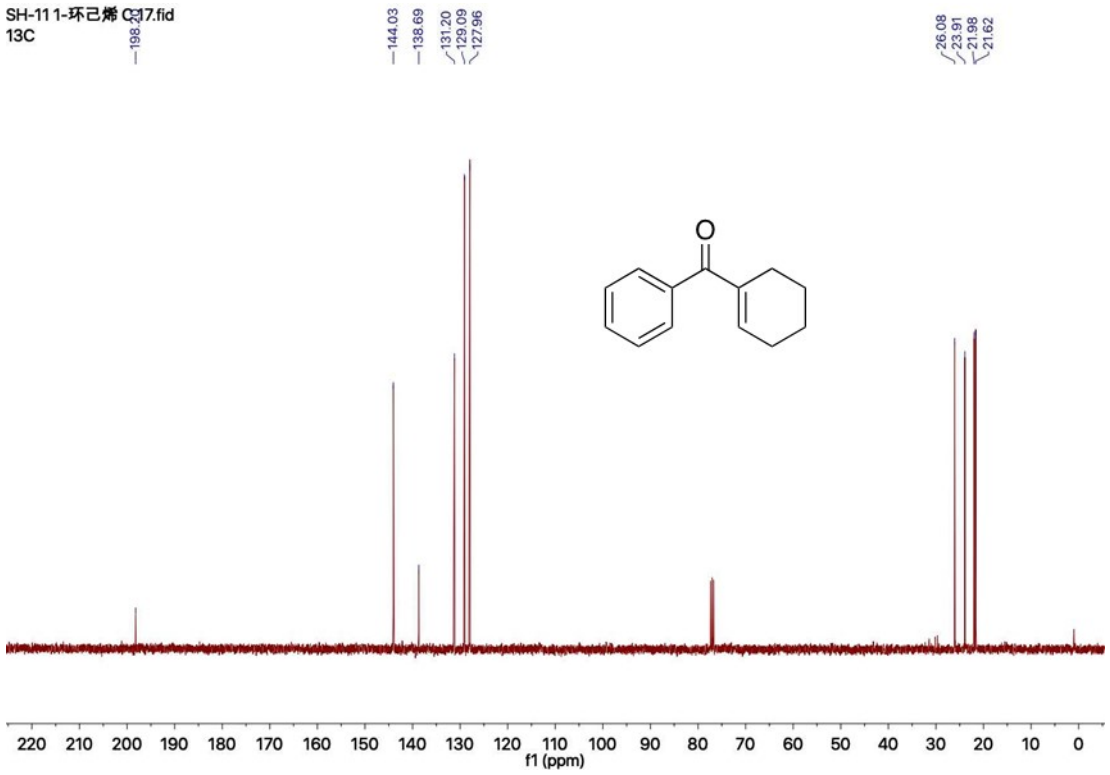


Figure S39. ^{13}C NMR spectrum of compound **17**.

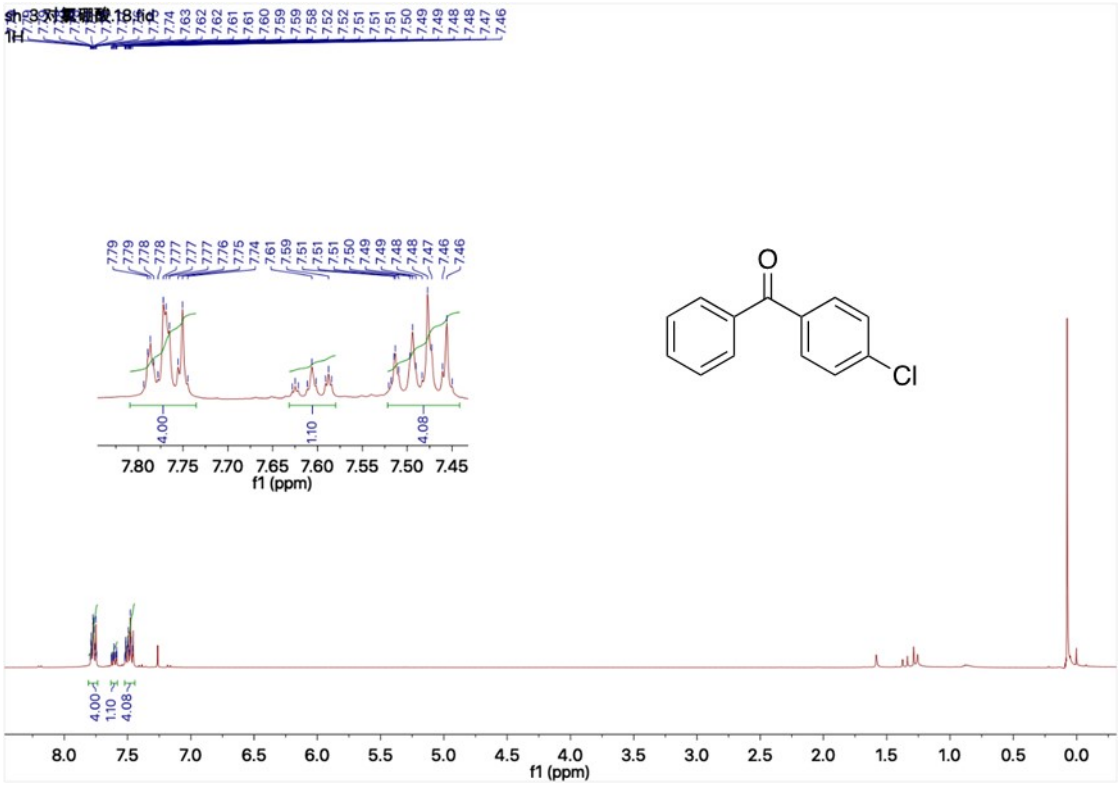


Figure S40. [1]H NMR spectrum of compound **18a**.

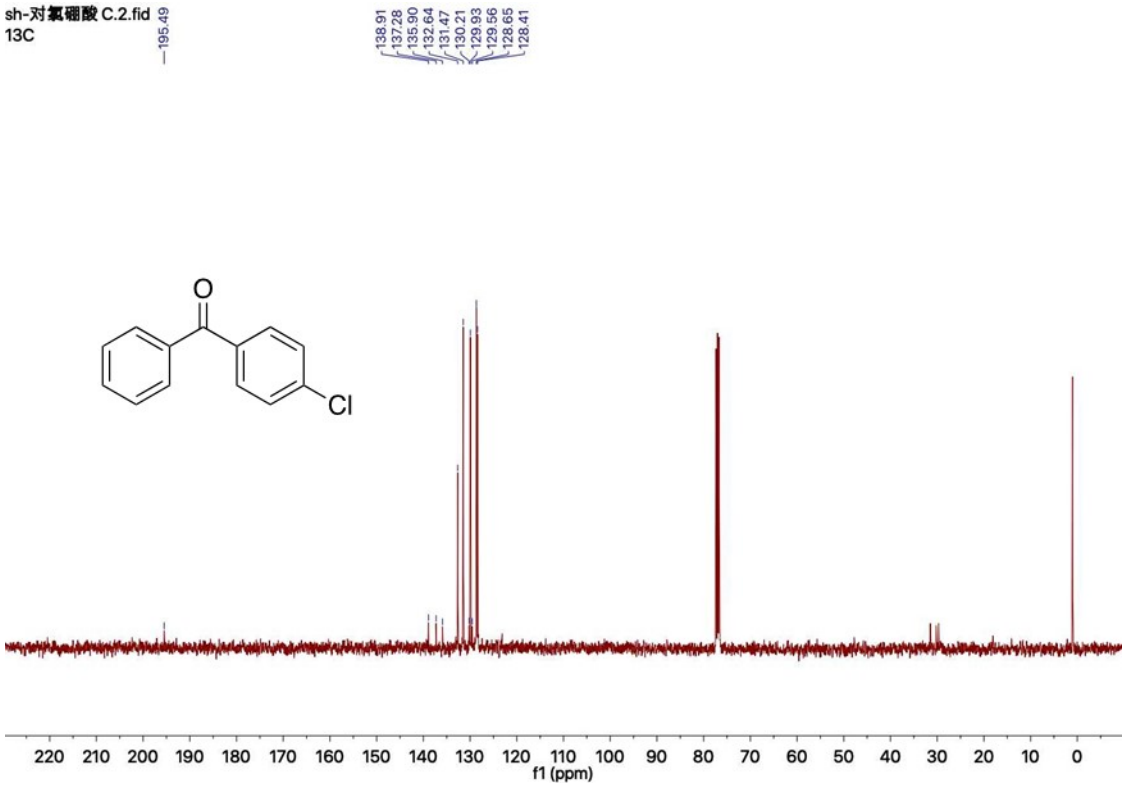


Figure S41. [13]C NMR spectrum of compound **18a**.

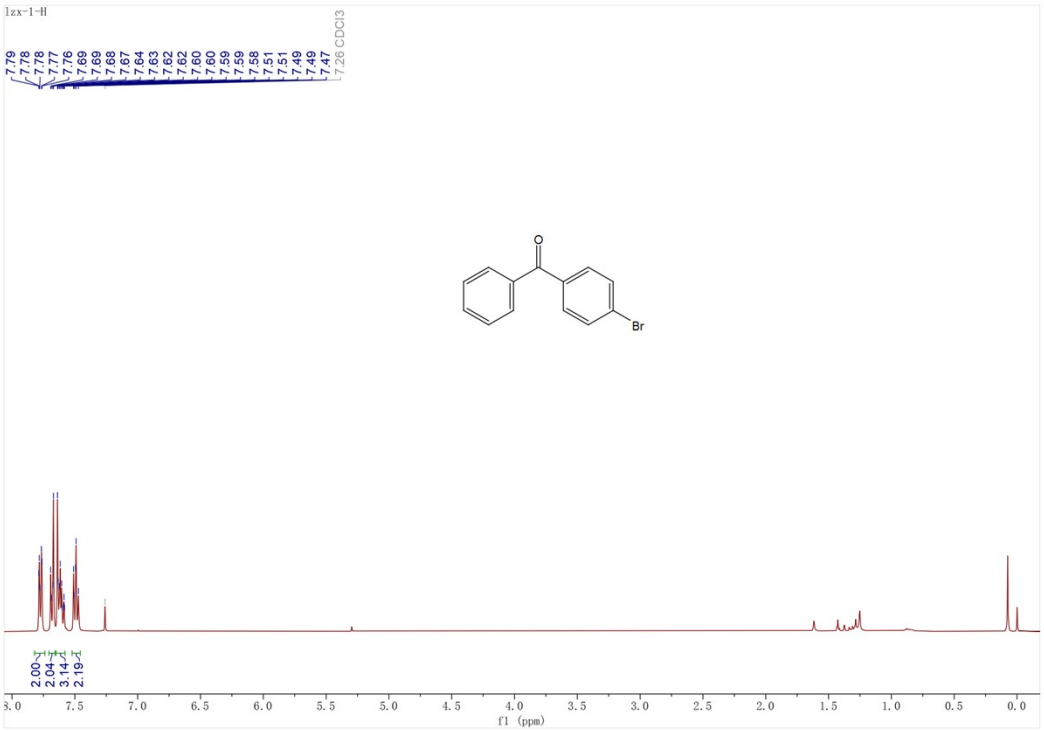


Figure S42. ^{1}H NMR spectrum of compound **18b**.

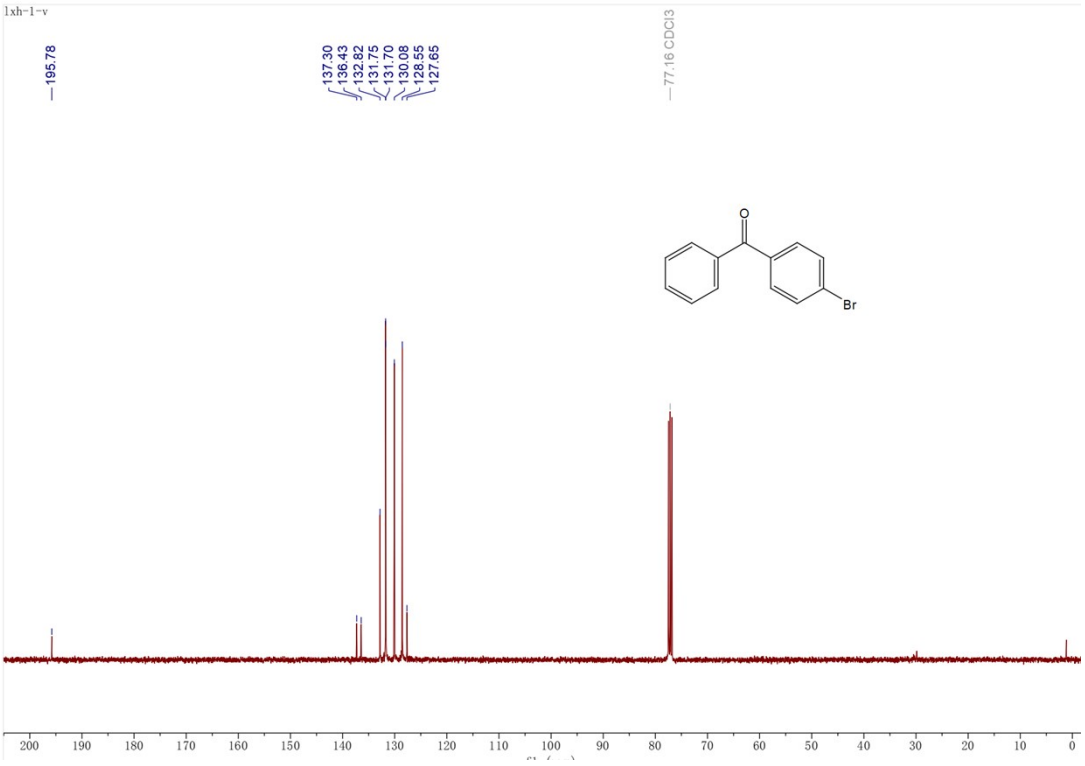


Figure S43. ^{13}C NMR spectrum of compound **18b**.

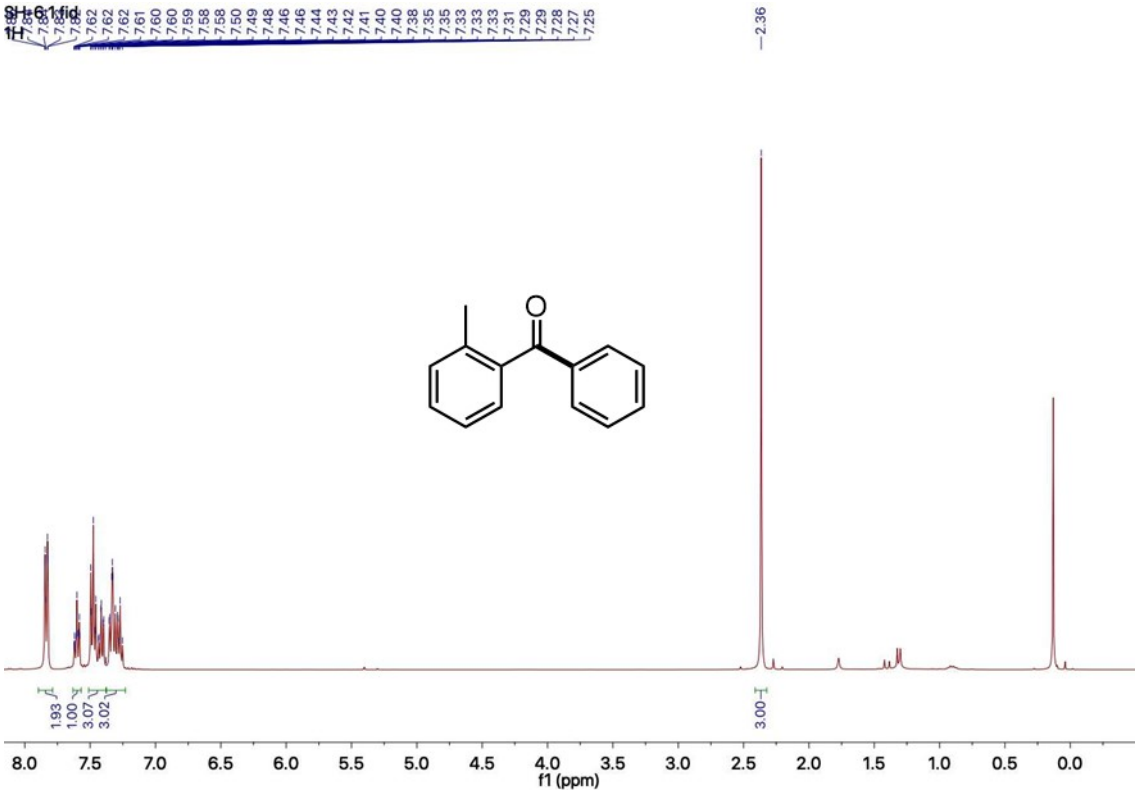


Figure S44. ^{1}H NMR spectrum of compound **19a**.

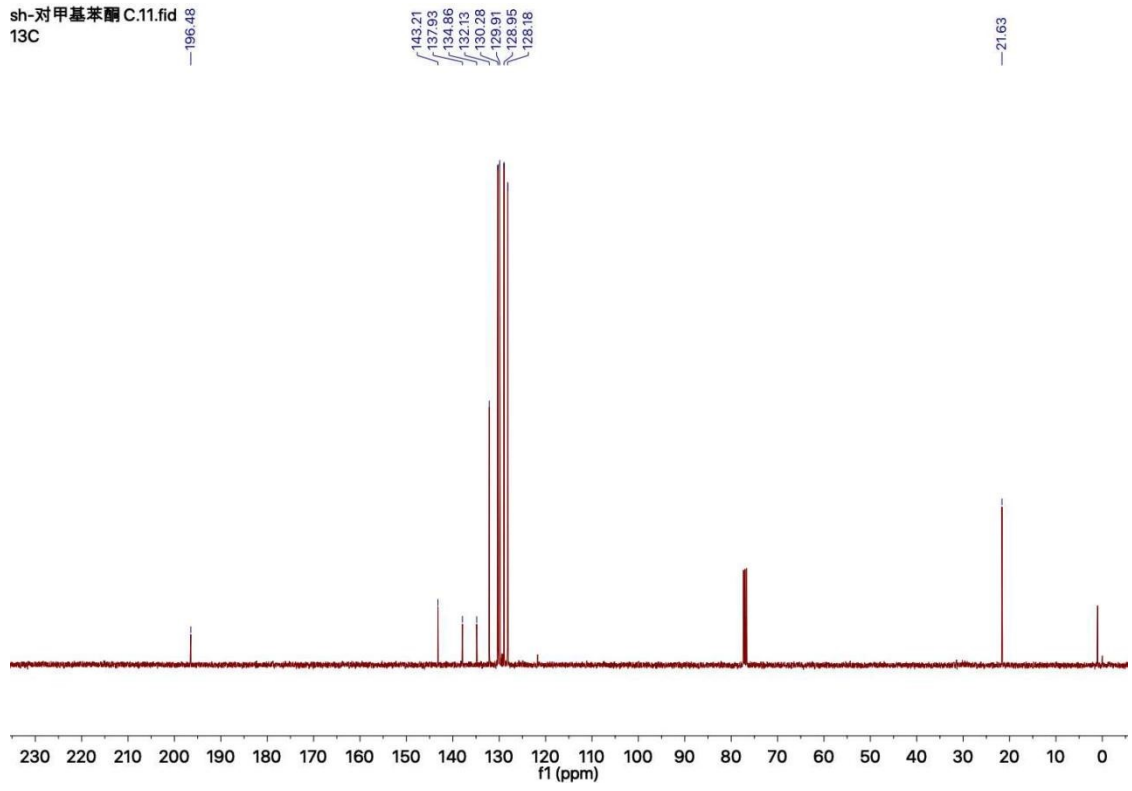


Figure S45. ^{13}C NMR spectrum of compound **19a**.

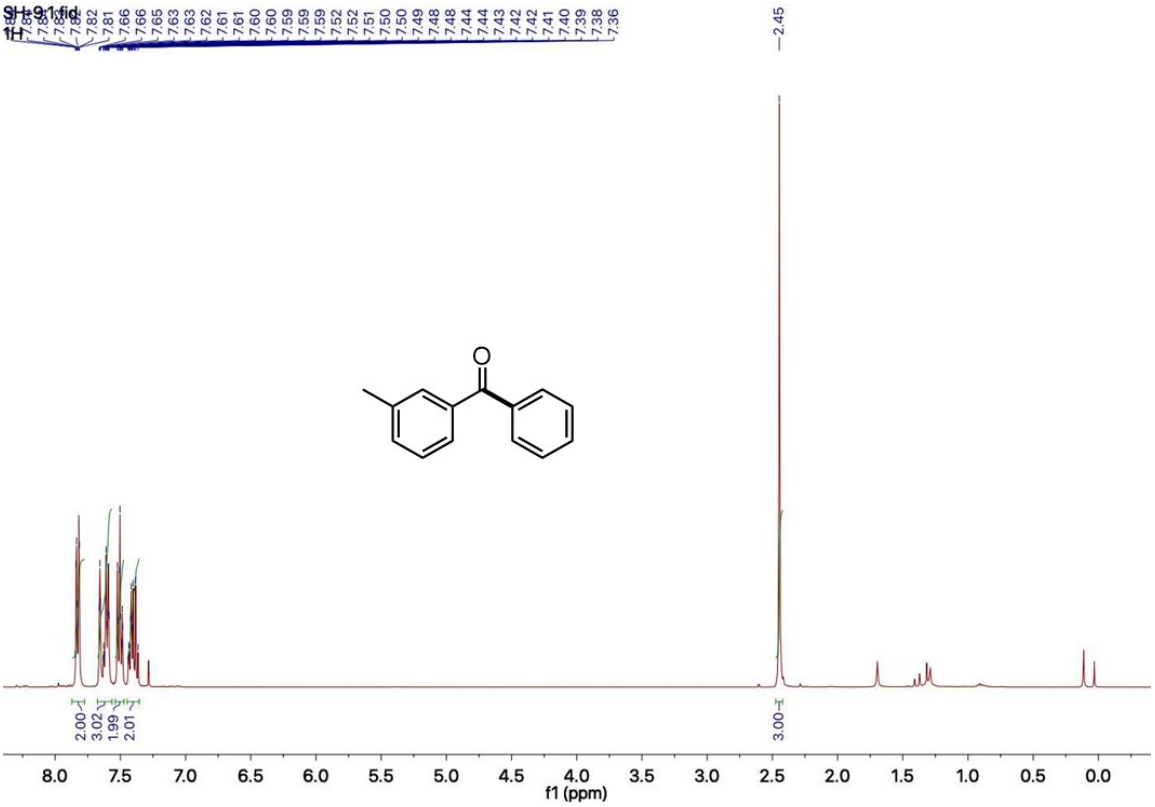


Figure S46. ^{1}H NMR spectrum of compound **19b**.

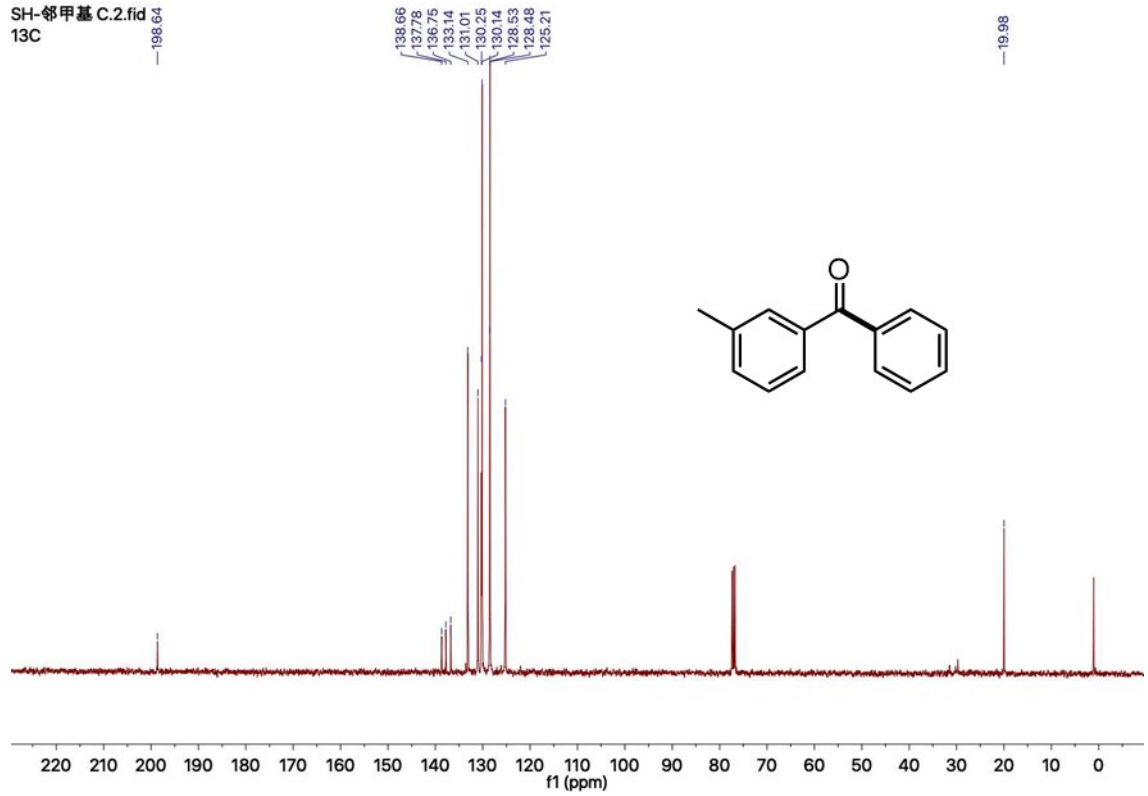


Figure S47. ^{13}C NMR spectrum of compound **19b**.

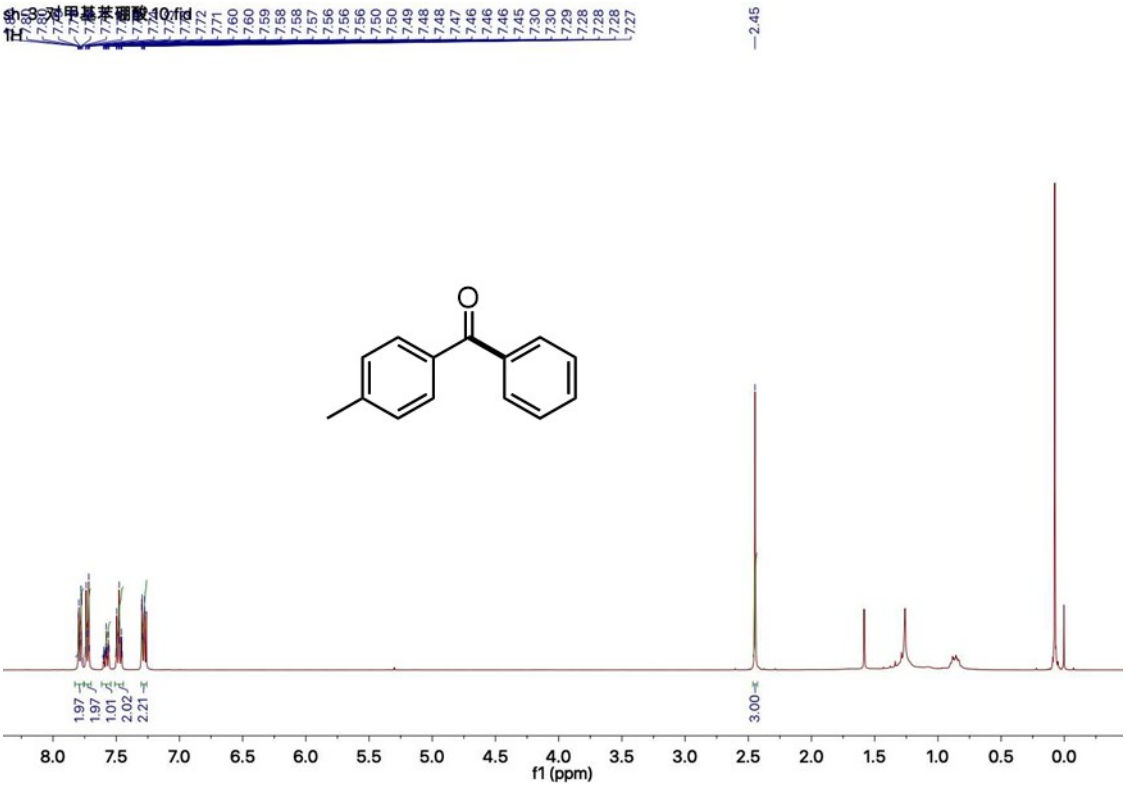


Figure S48. [1]H NMR spectrum of compound **19c**.

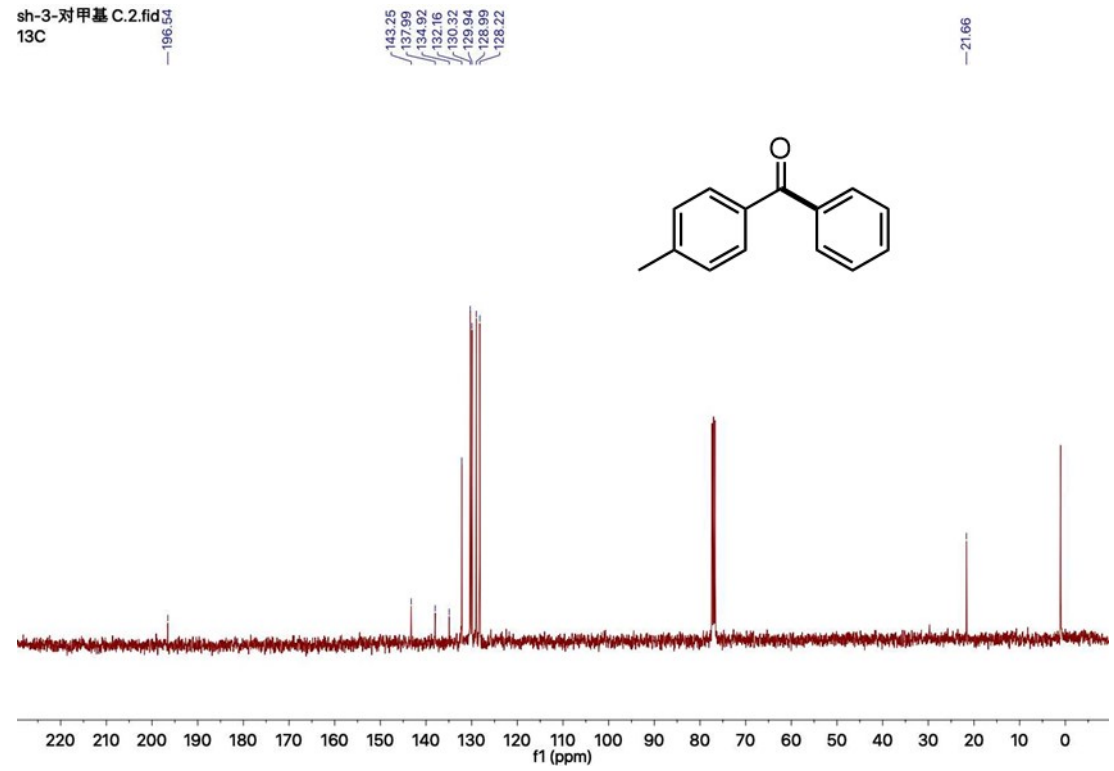


Figure S49. [13]C NMR spectrum of compound **19c**.

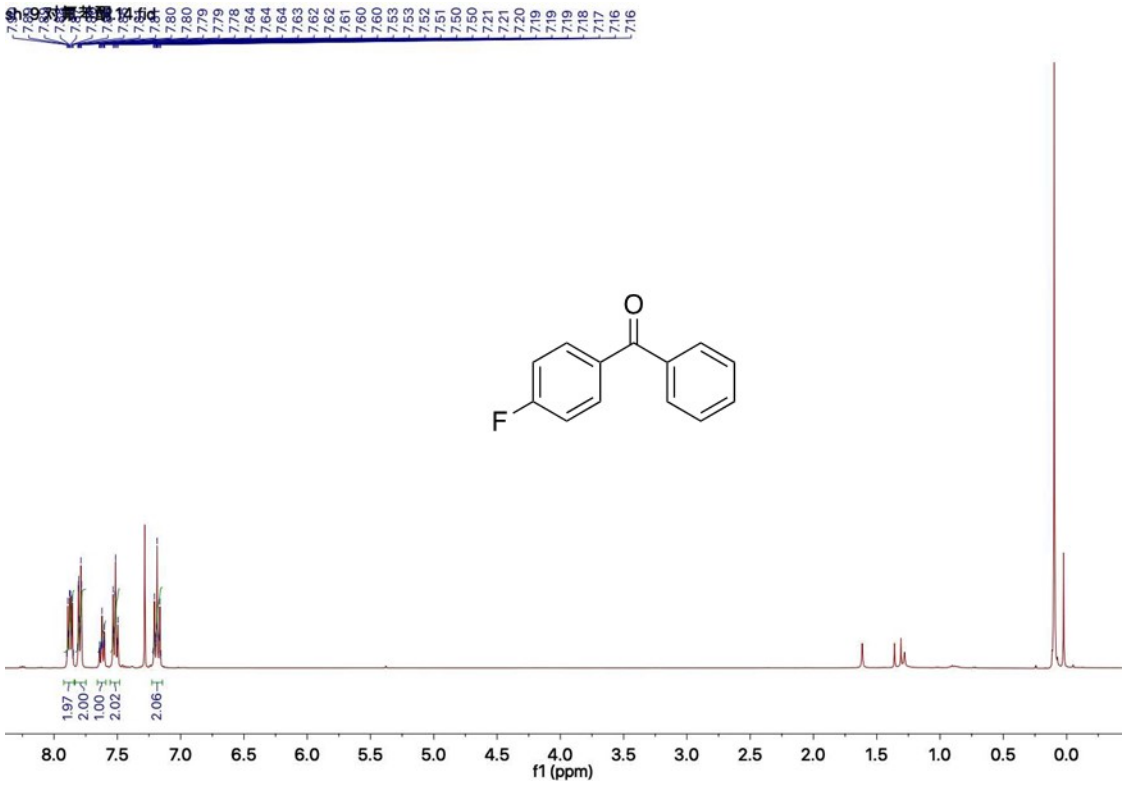


Figure S50. ^{1}H NMR spectrum of compound **20a**.

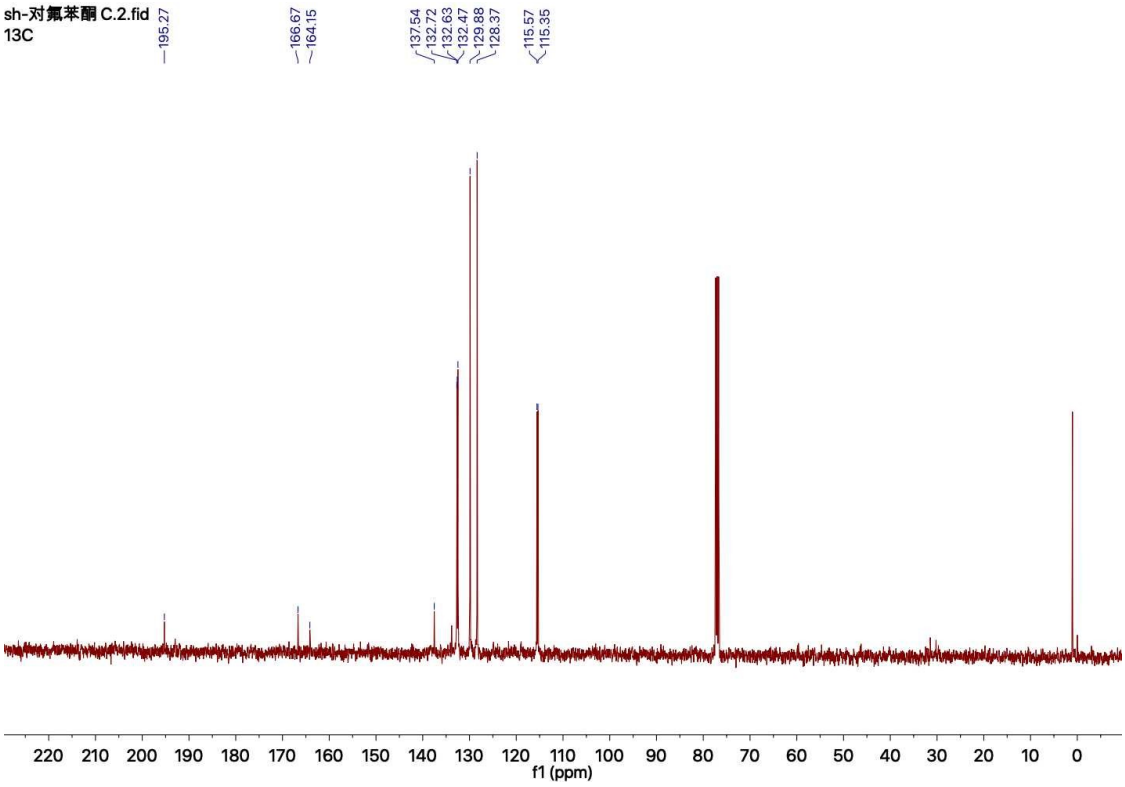


Figure S51. ^{13}C NMR spectrum of compound **20a**.

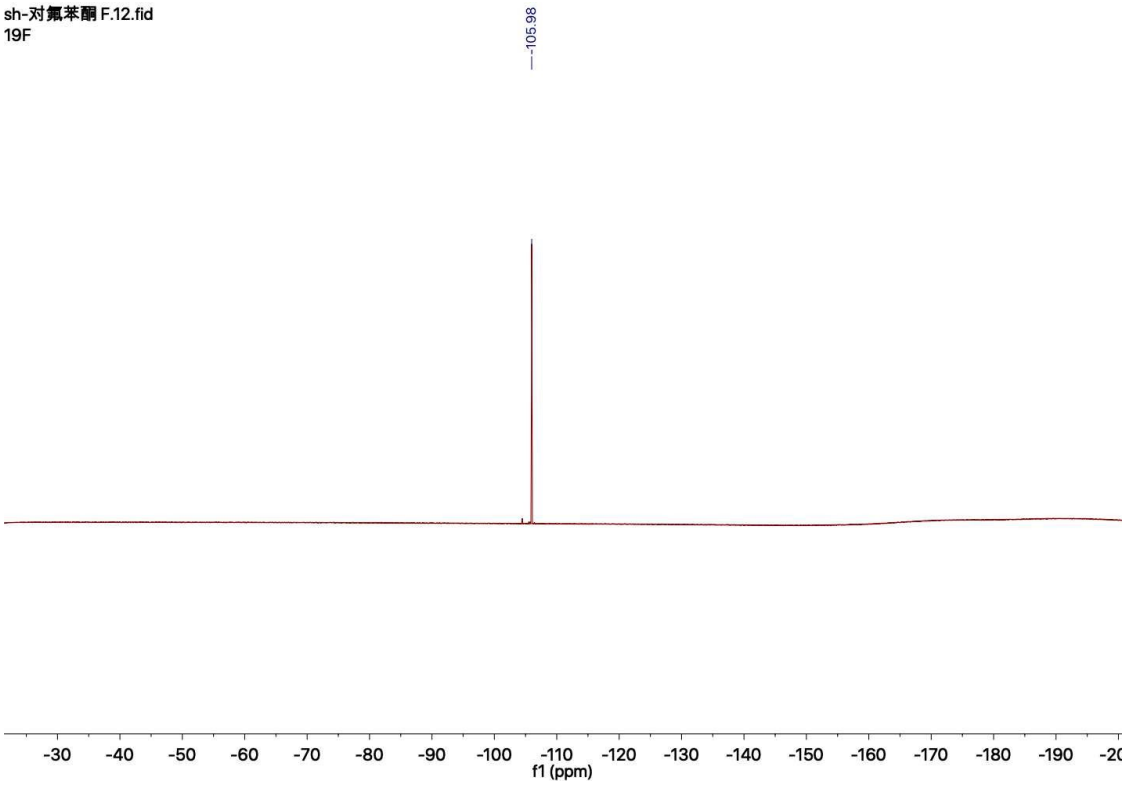


Figure S52. ^{19}F NMR spectrum of complex **20a**.

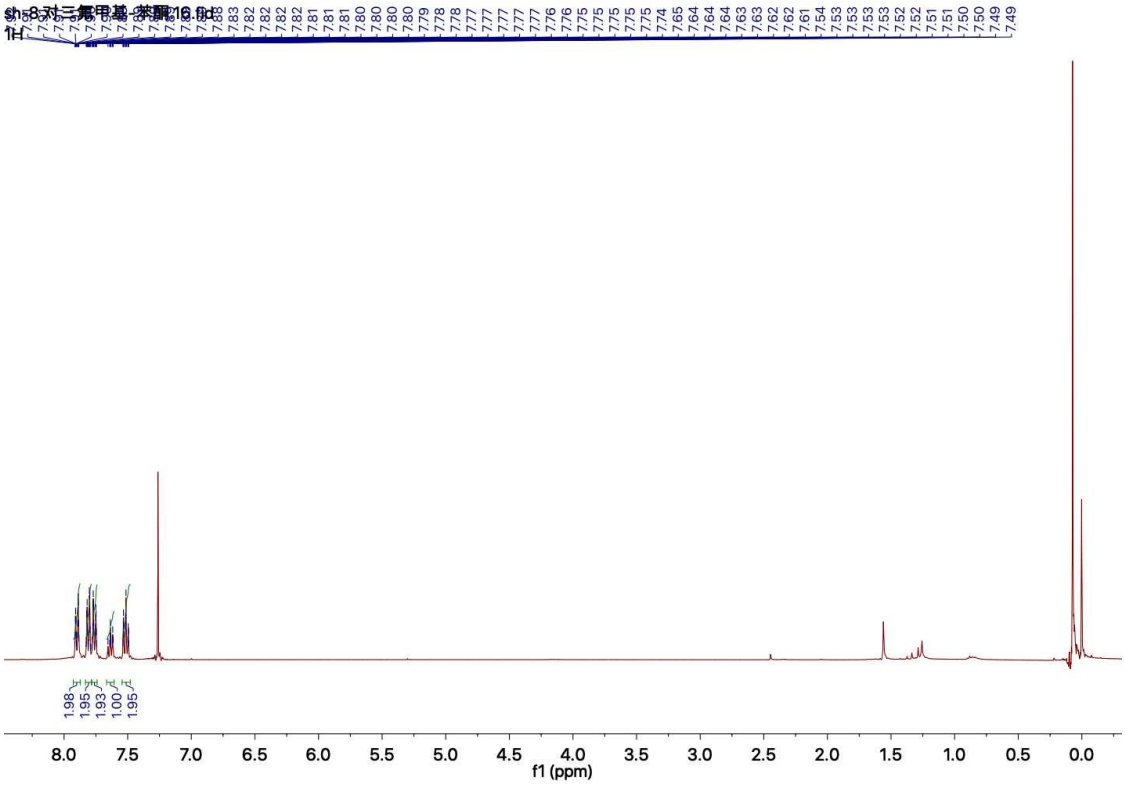


Figure S53. ^{1}H NMR spectrum of compound **20b**.

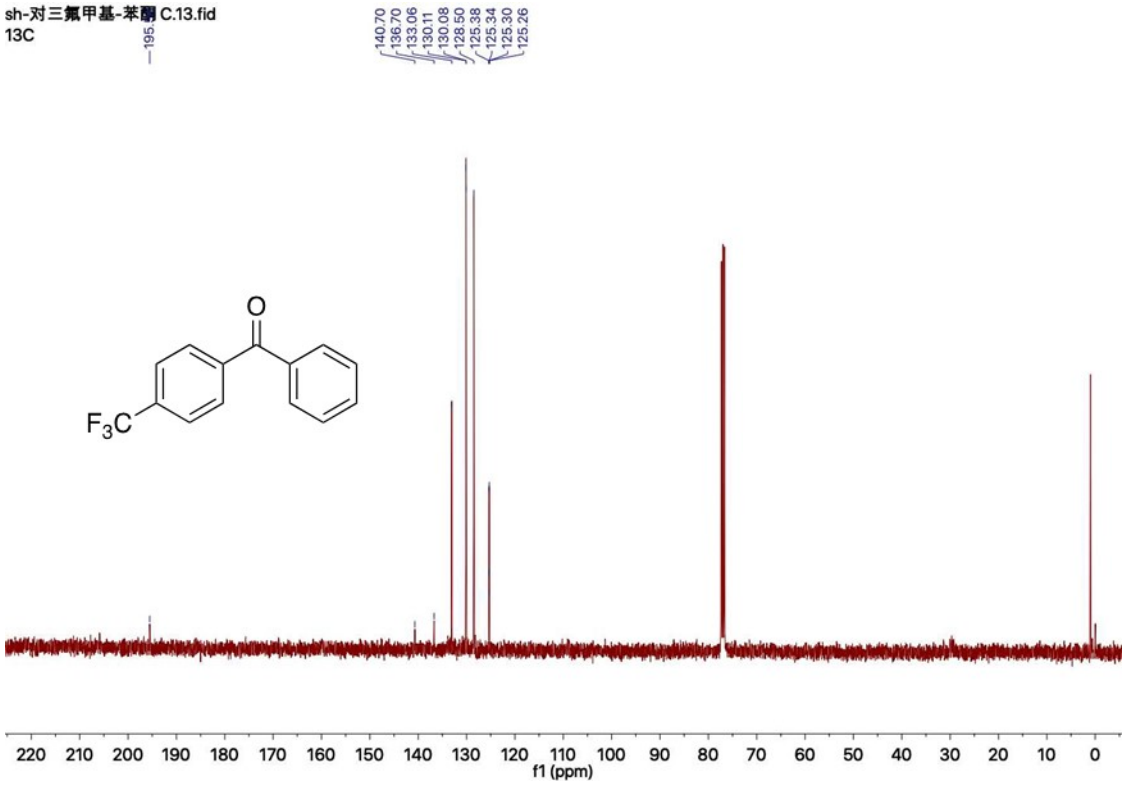


Figure S54. ^{13}C NMR spectrum of compound **20b**.

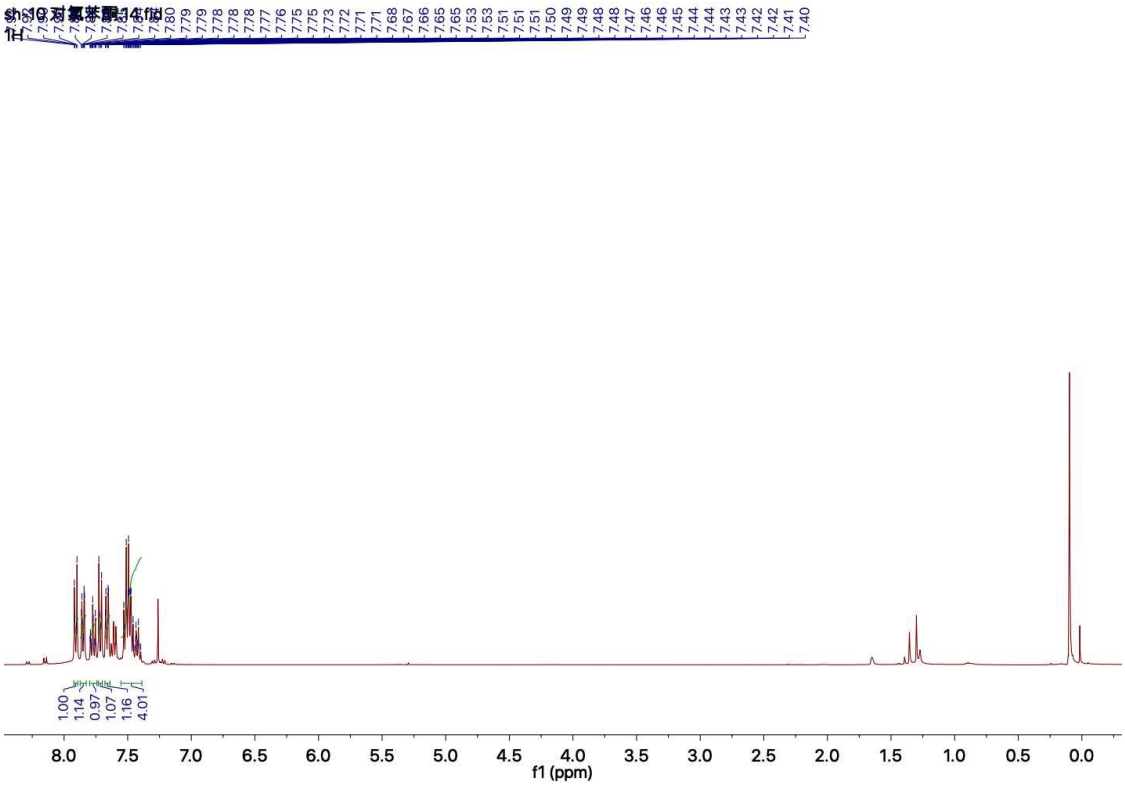


Figure S55. ^{1}H NMR spectrum of compound **21a**.

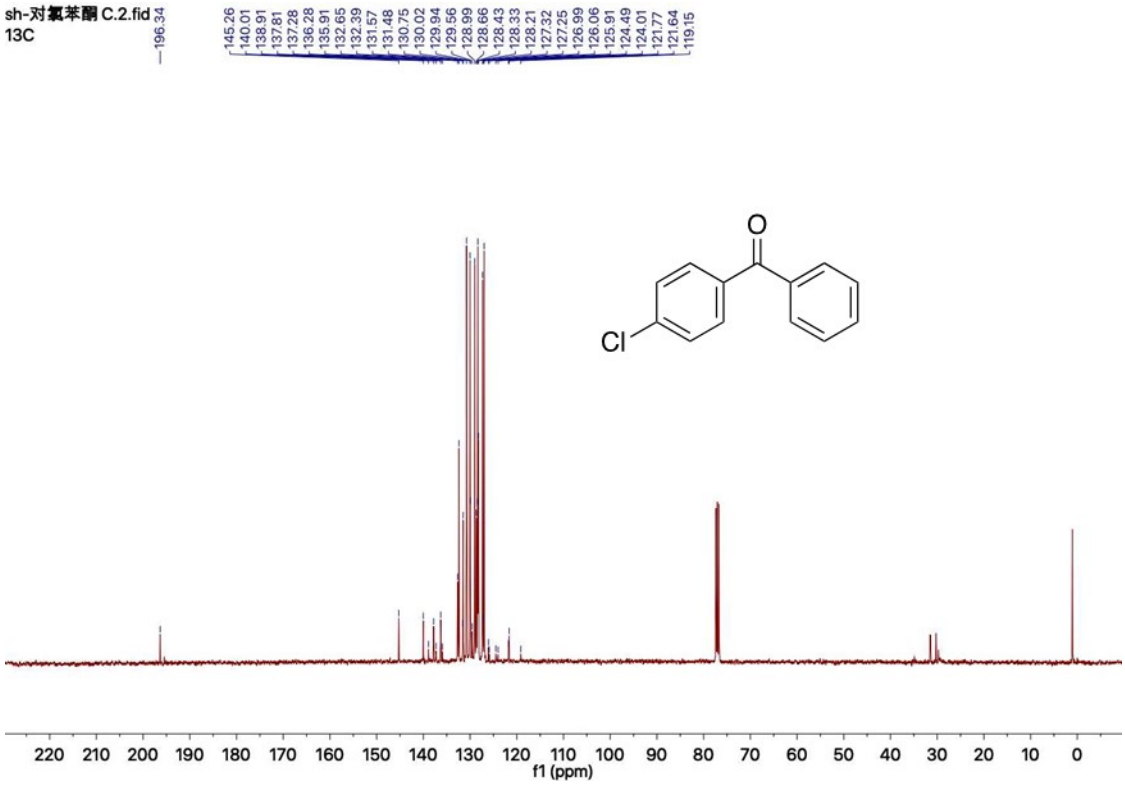


Figure S56. ^{13}C NMR spectrum of compound **21a**.

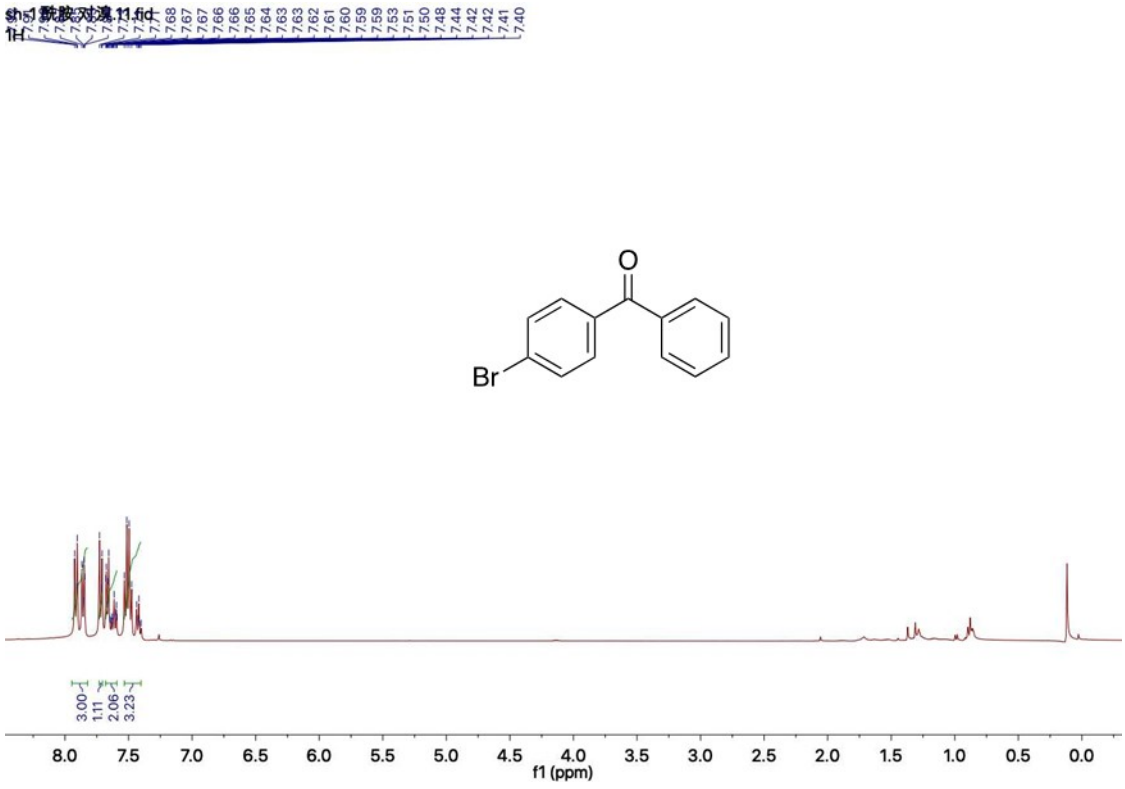


Figure S57. ^{1}H NMR spectrum of compound **21b**.

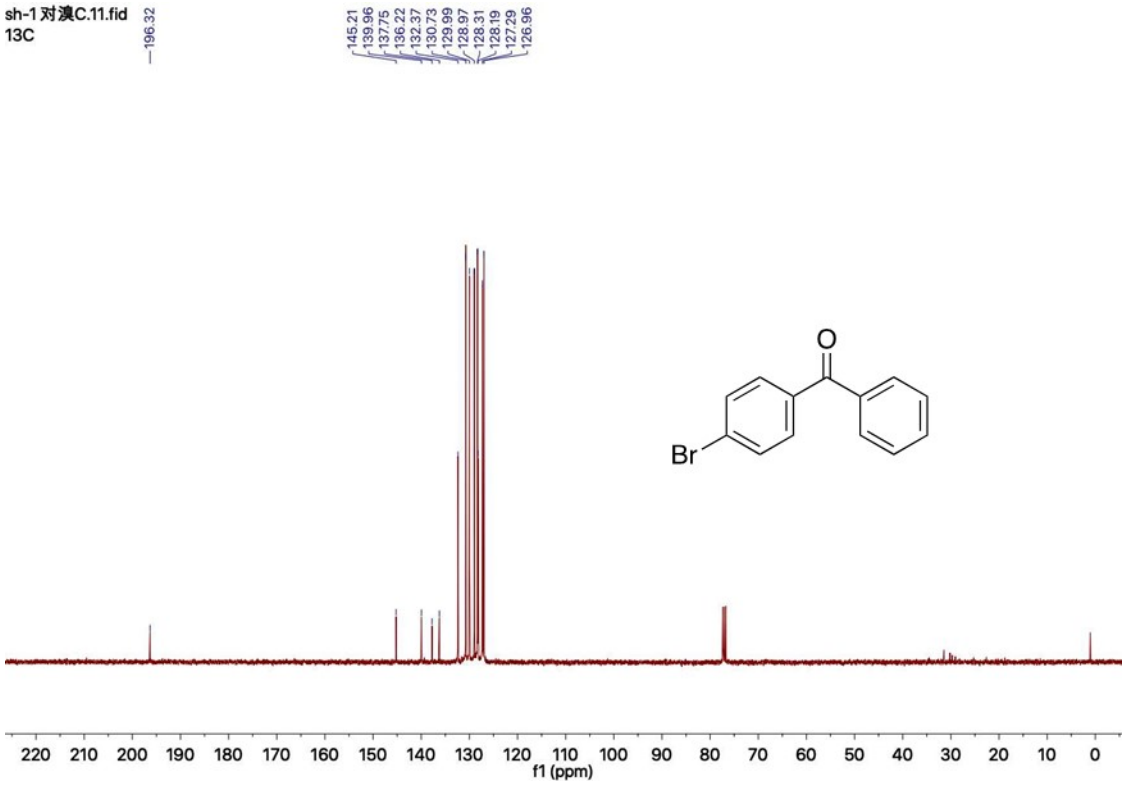


Figure S58. ^{13}C NMR spectrum of compound **21b**.

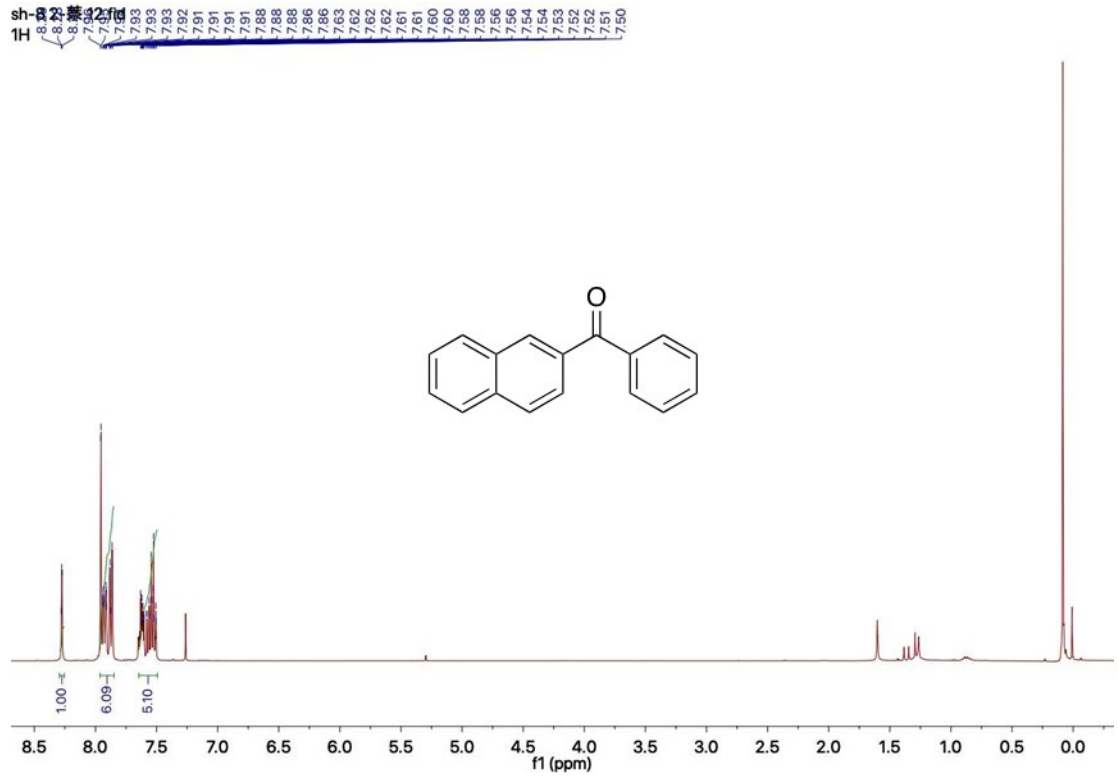


Figure S59. ^{1}H NMR spectrum of compound **22**.

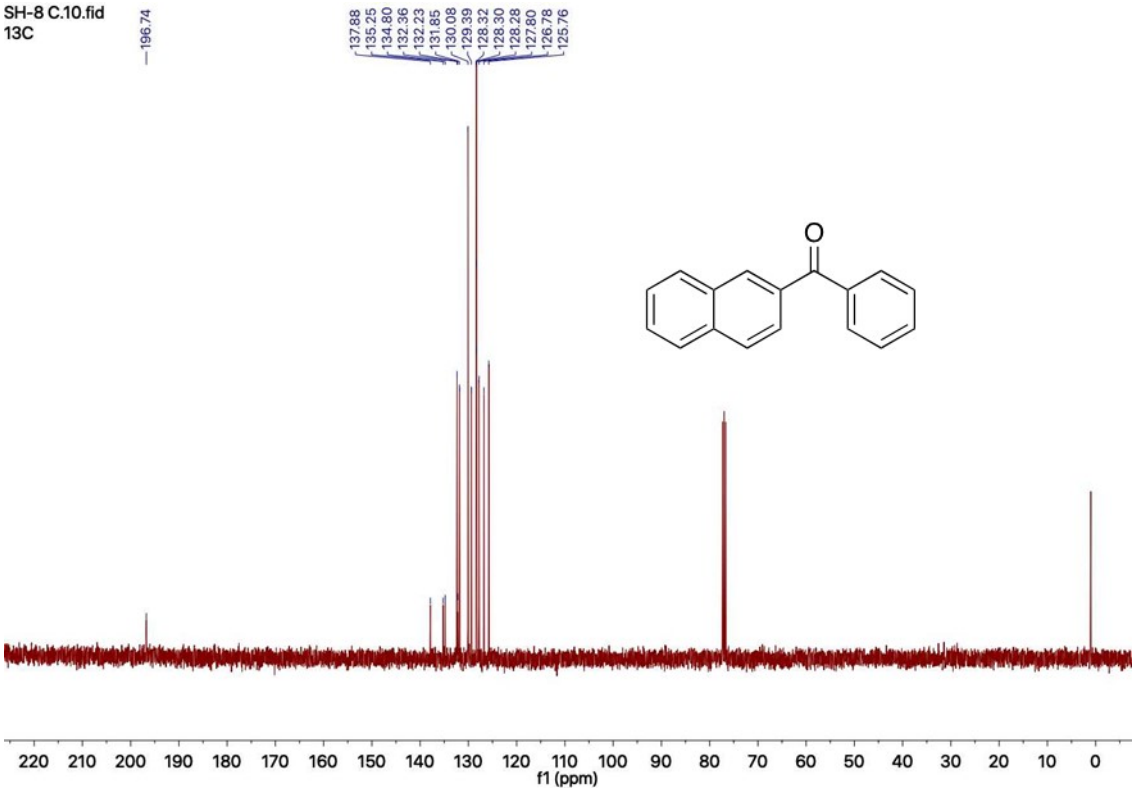


Figure S60. ^{13}C NMR spectrum of compound **22**.

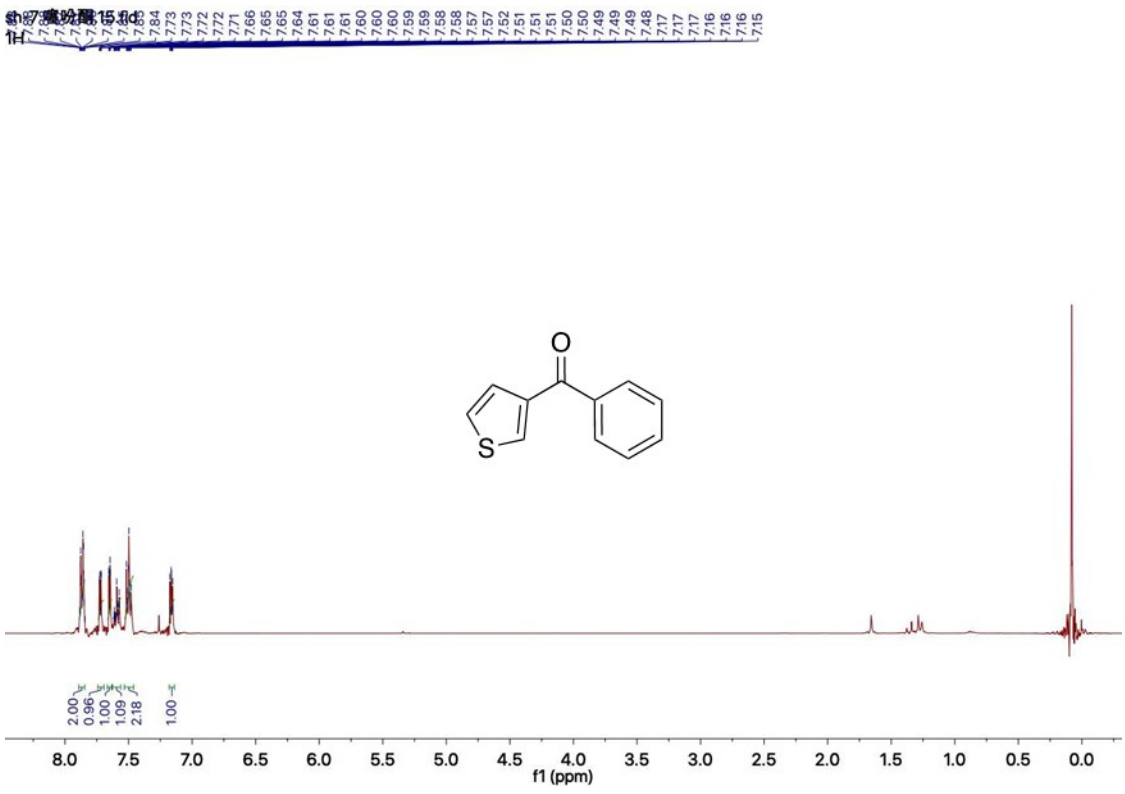


Figure S61. ^{1}H NMR spectrum of compound **23**.

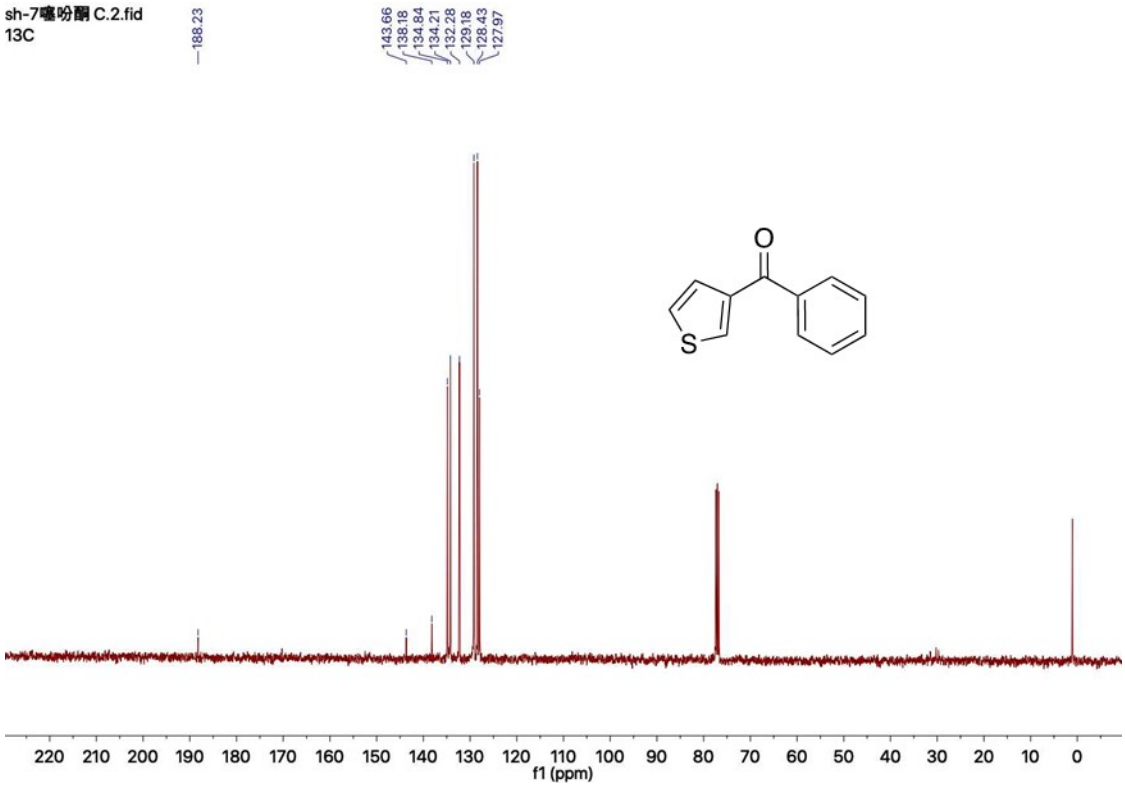


Figure S62. ^{13}C NMR spectrum of compound **23**.

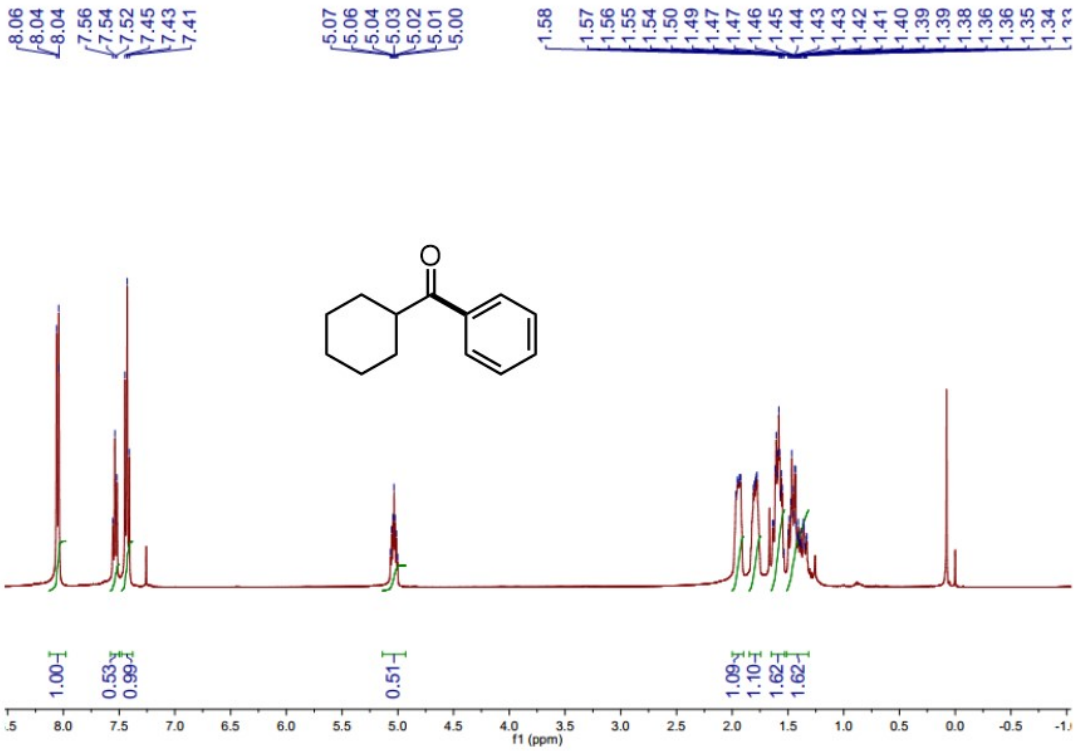


Figure S63. ^{1}H NMR spectrum of compound **24**.

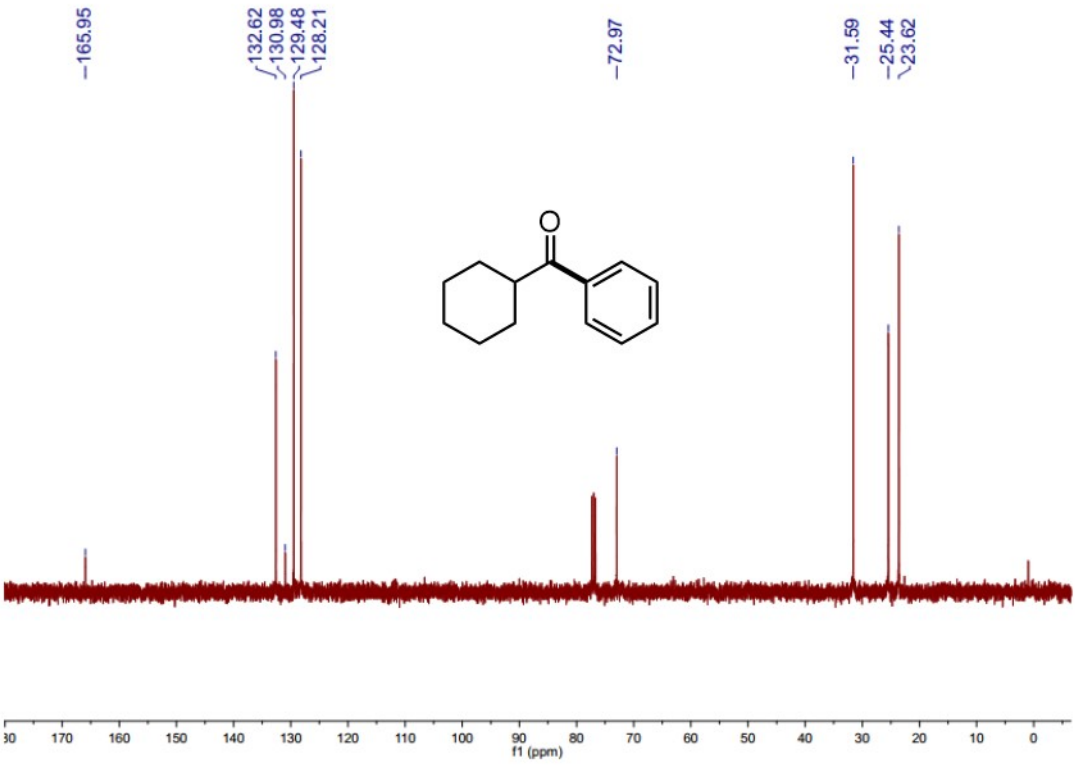


Figure S64. ^{13}C NMR spectrum of compound **24**.

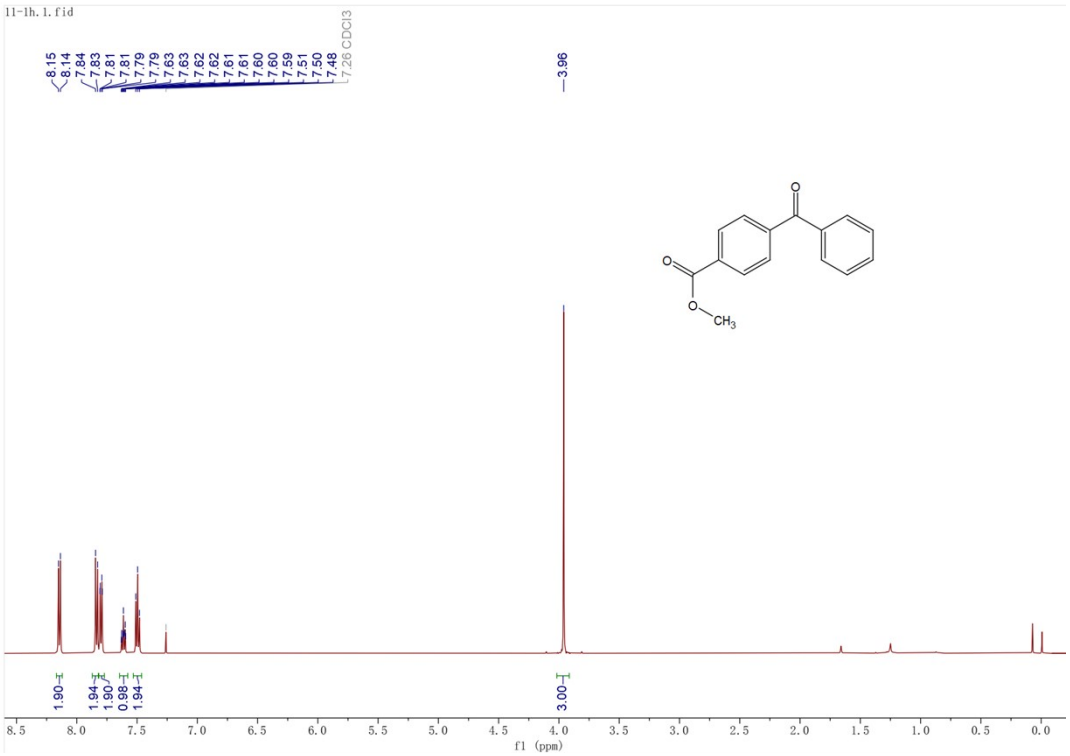


Figure S65. ^{1}H NMR spectrum of compound **25**.

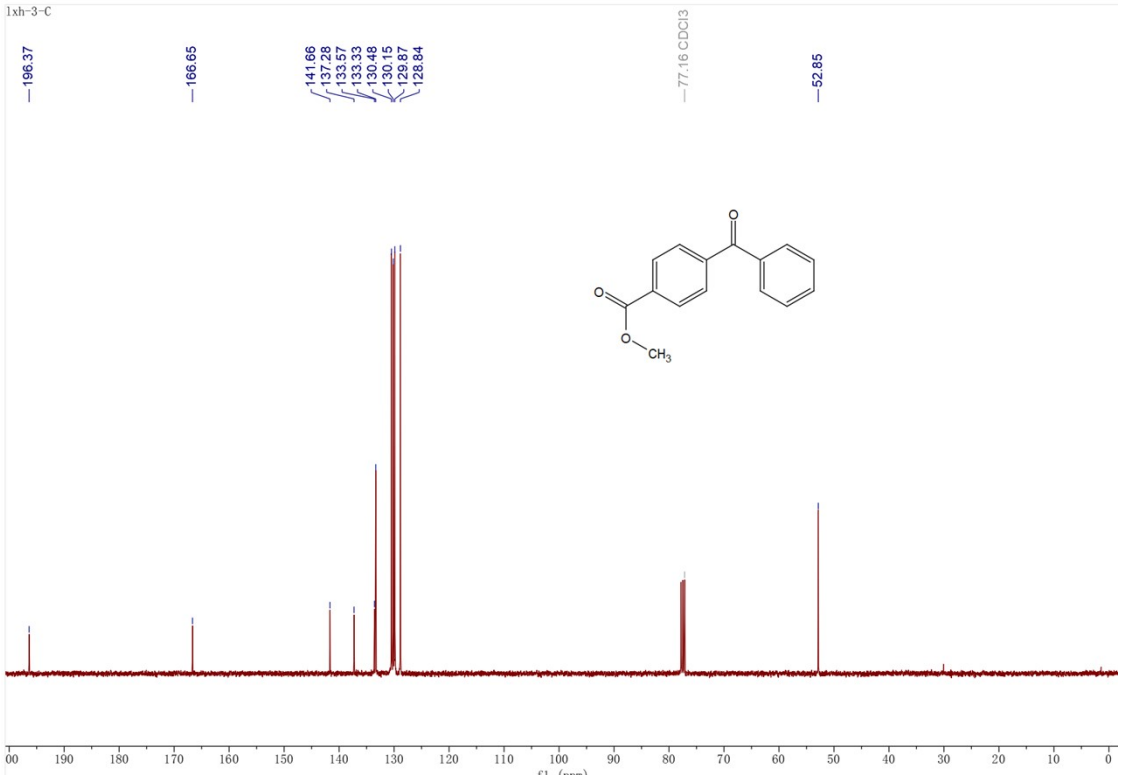


Figure S65. ^{13}C NMR spectrum of compound **25**.

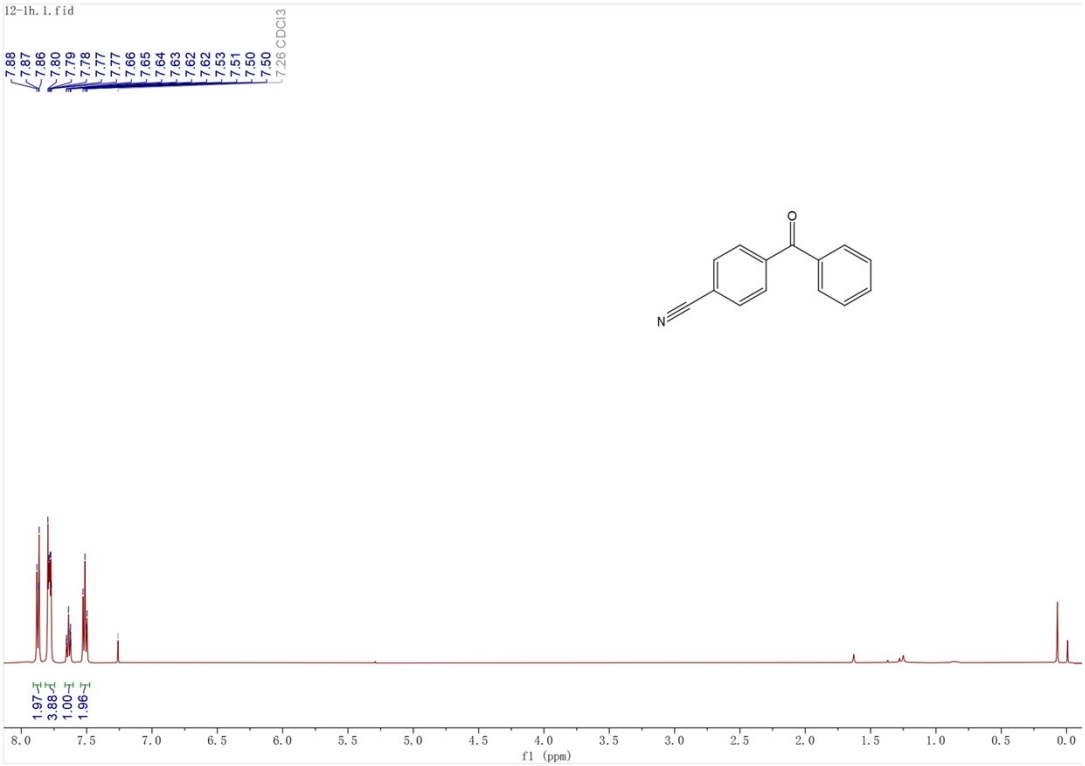


Figure S66. ^{1}H NMR spectrum of compound **26a**.

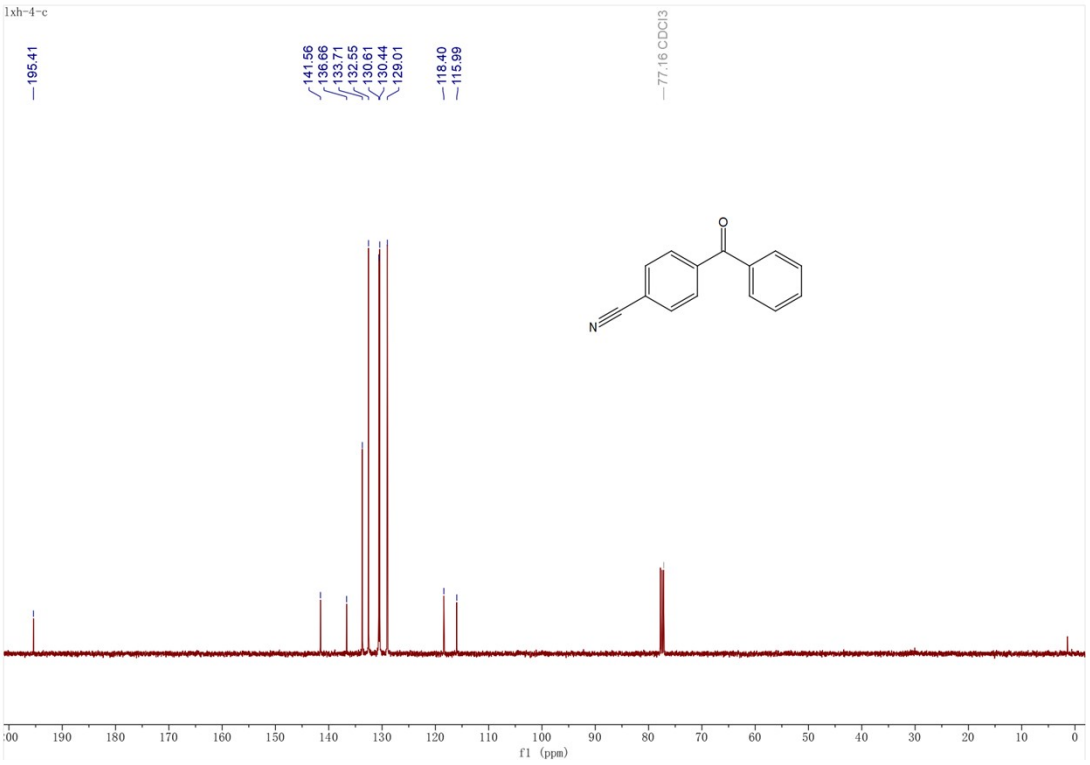


Figure S66. ^{13}C NMR spectrum of compound **26a**.

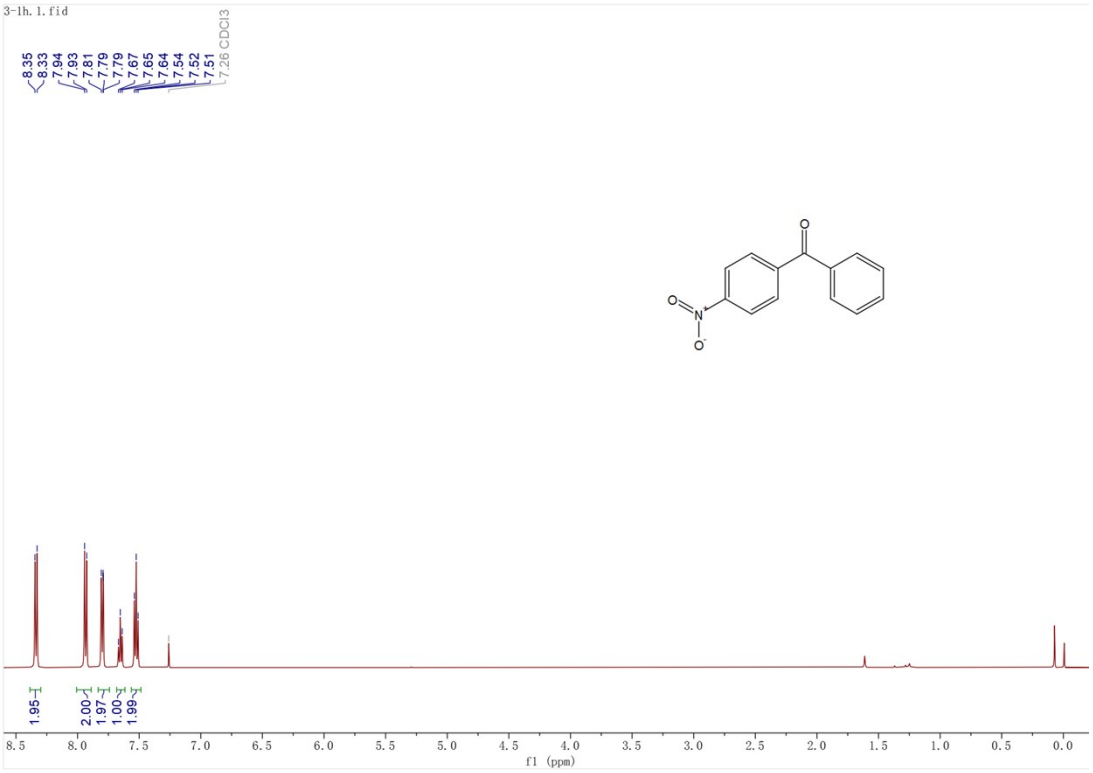


Figure S67. ^{1}H NMR spectrum of compound **26b**.

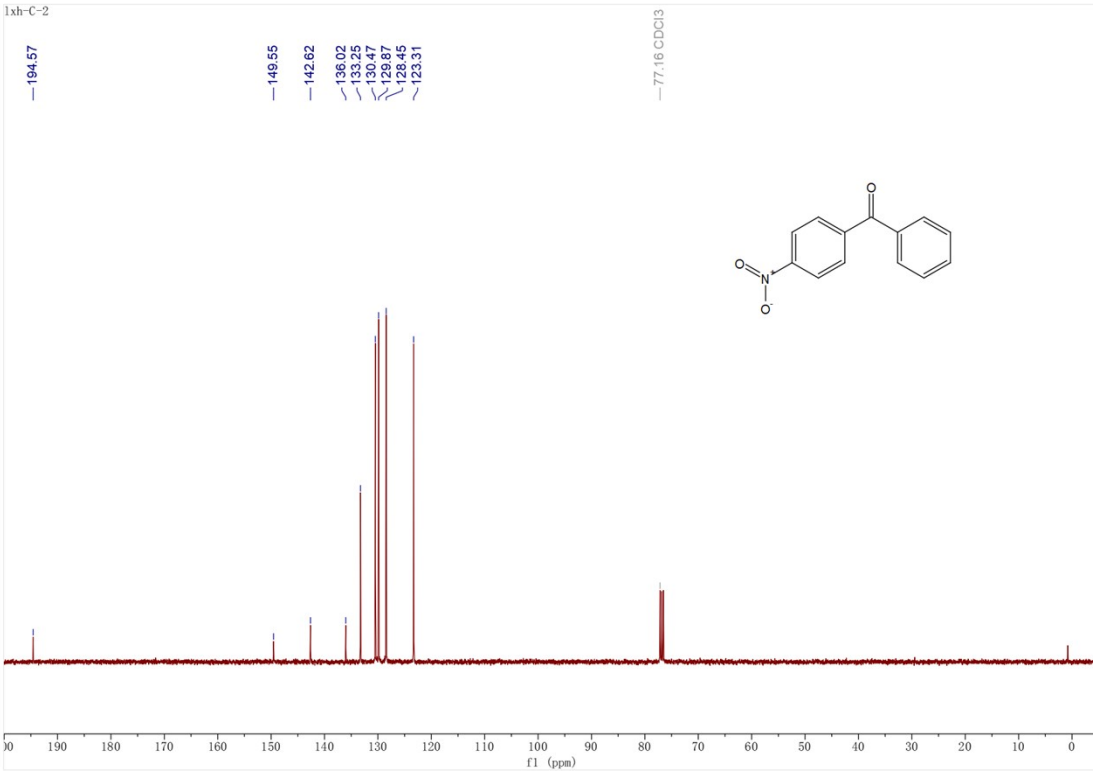


Figure S67. ^{13}C NMR spectrum of compound **26b**.

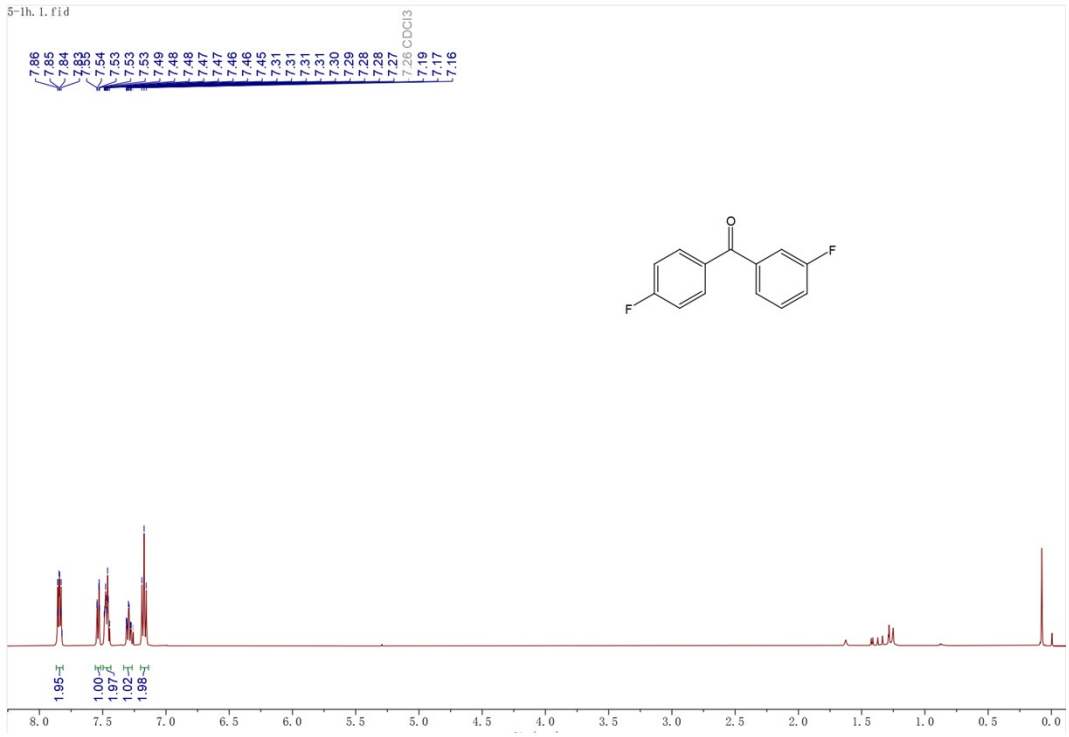


Figure S65. ^{1}H NMR spectrum of compound **27**.

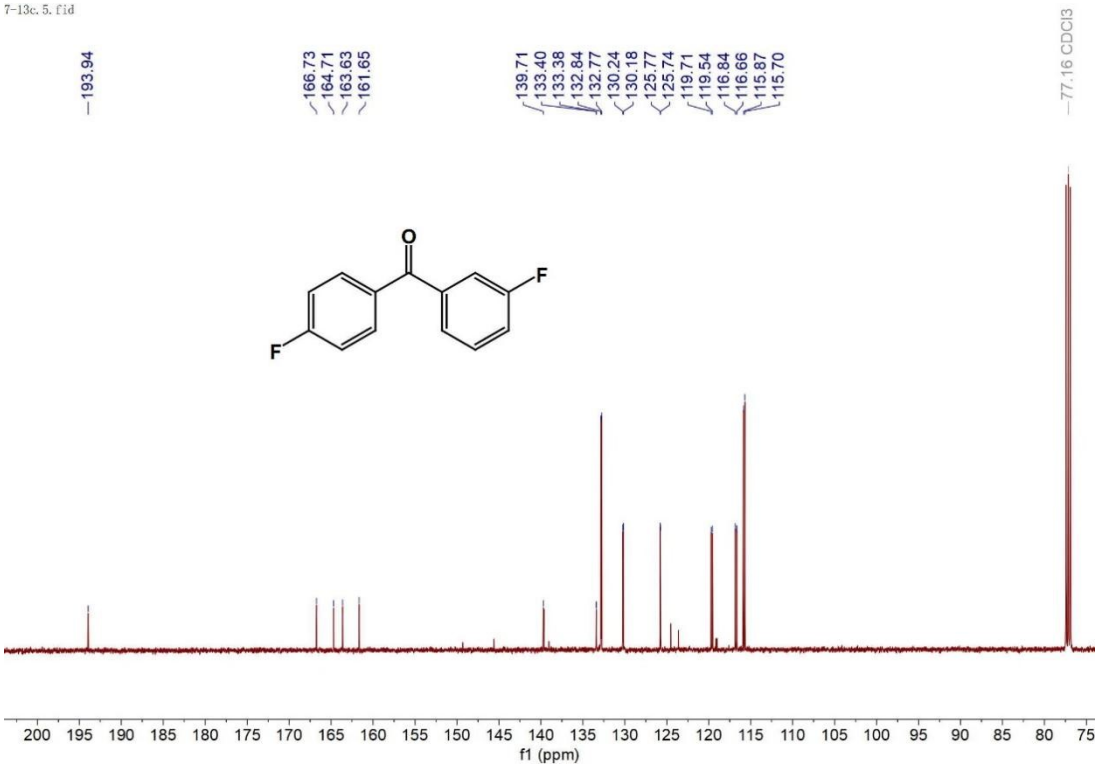


Figure S66. ^{13}C NMR spectrum of compound **27**.

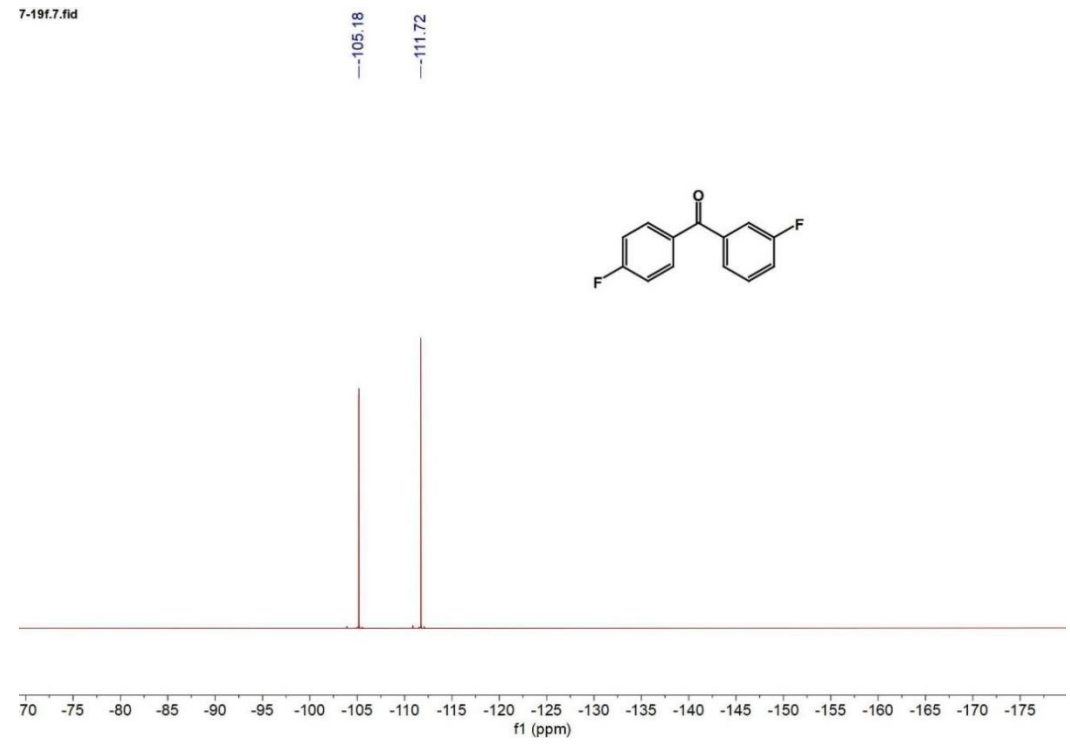


Figure S67. ^{19}F NMR spectrum of complex **27**.

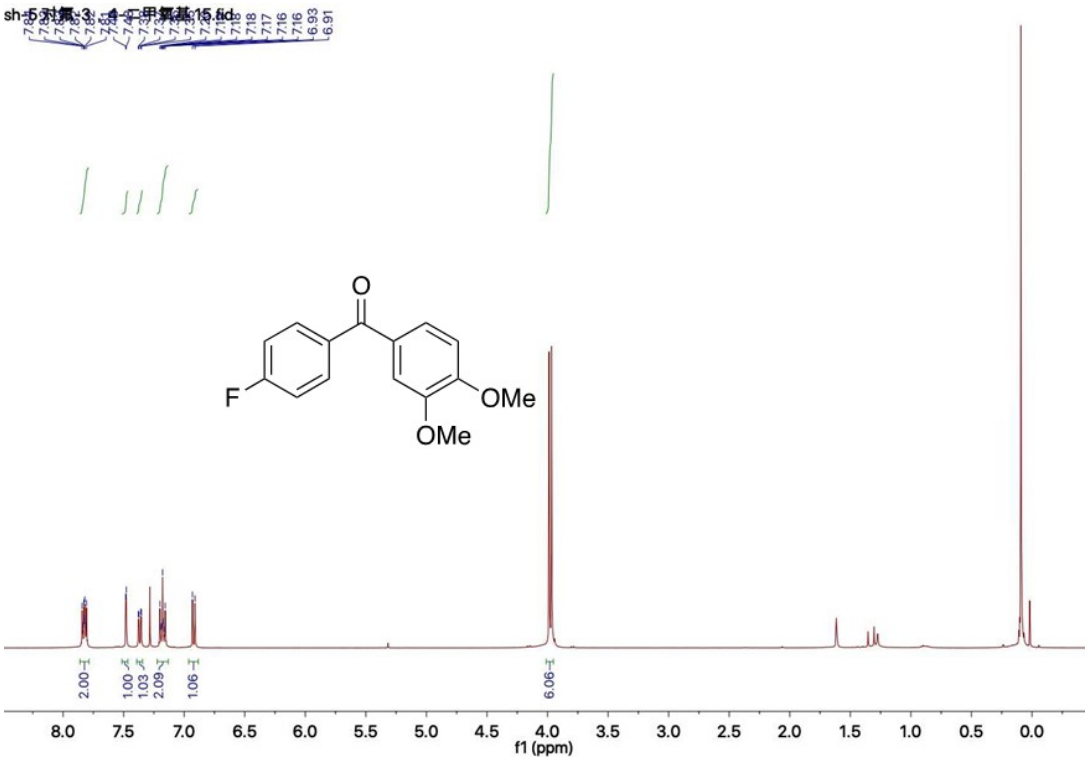


Figure S68. ^{1}H NMR spectrum of compound **28**.

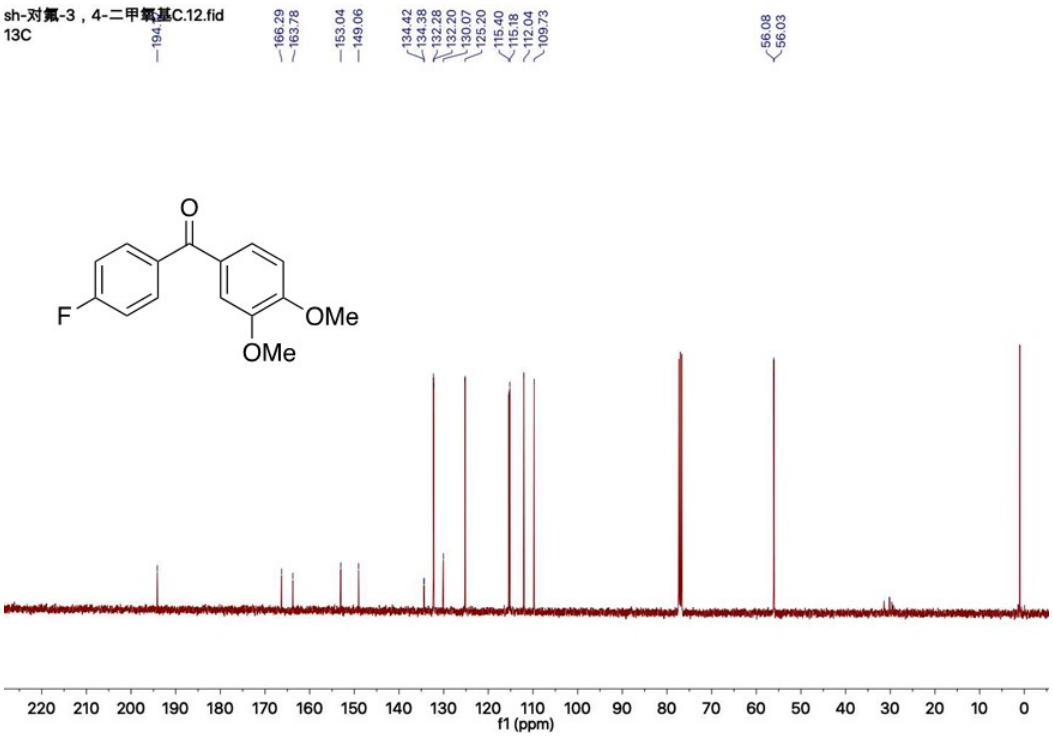


Figure S69. ^{13}C NMR spectrum of compound **28**.

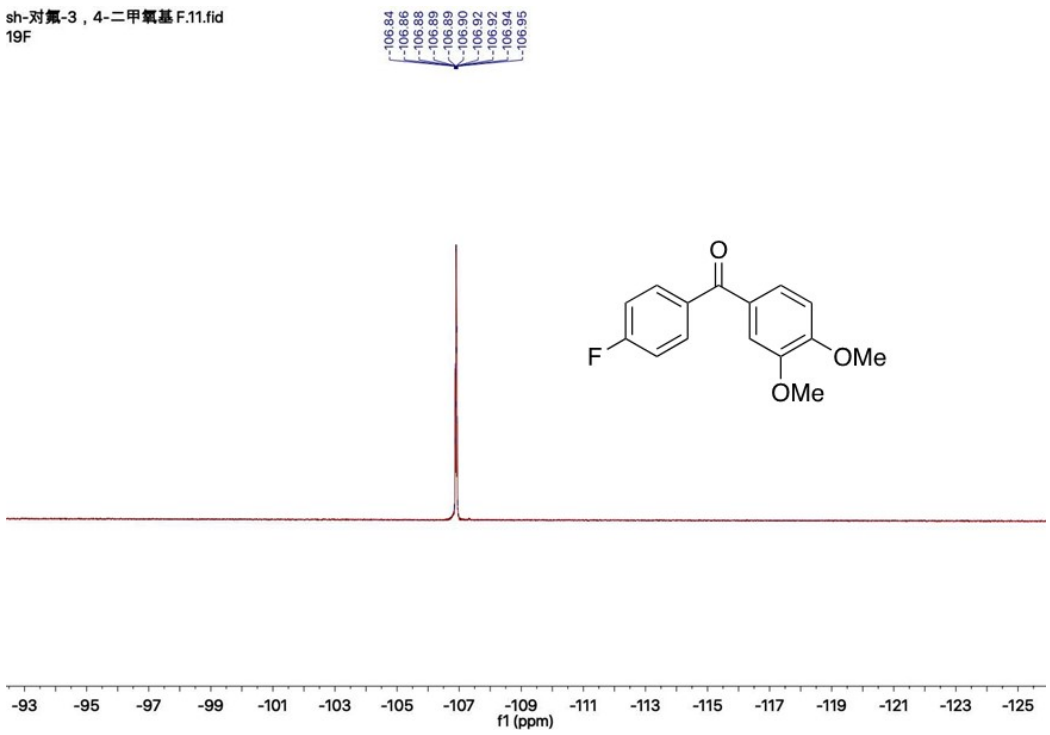


Figure S70. ^{19}F NMR spectrum of complex **28**.

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