*Electronic Supplementary Information*（ESI）*for*

# Efficient and Scalable Pd-Catalyzed Double Aminocarbonylations under Atmospheric Pressure at Low Catalyst Loadings

Shuangliang Liu,[a,b] Qinyue Deng,[a] Weiwei Fang,[a] Jun-Fang Gong,*[b] Mao-Ping Song,*[b] Mizhi Xu[a] and Tao Tu*[a]

[a] Department of Chemistry, Fudan University, 220 Handan Road, 200433, Shanghai, China,

Fax: (+86) 21-65102412, E-mail: taotu@fudan.edu.cn

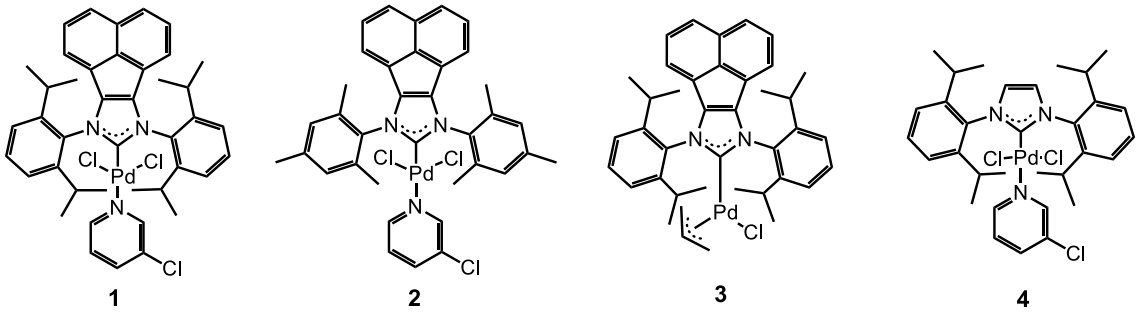
[b] College of Chemistry and Molecular Engineering, Zhengzhou University,

100 Science Avenue, 450001, Zhengzhou, China,

## Contents

# 1. Experimental sections

## 1.1 Synthesis of the Pd-NHC complexes.




**Scheme S1.** Pd-NHC complexes.

**Pd-NHC complex 1** was prepared according to literature procedure.[S1] Yield: 361 mg, 90%. $^{1}$H NMR (400 MHz, $CDCl_3$, 298 K): δ = 8.68 (d, *J* = 2.0 Hz, 1H), 8.61 (dd, *J* = 5.2 Hz, 0.8 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.64 (t, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 4H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.10 (dd, *J* = 8.0 Hz, 5.6 Hz, 1H), 6.80 (d, *J* = 7.32 Hz, 2H), 3.45-3.35 (m, 4H), 1.46 (d, *J* = 6.4 Hz, 12H), 0.92 (d, *J* = 6.4 Hz, 12H); $^{13}$C NMR (100 MHz, $CDCl_3$, 298 K): δ = 159.07, 150.49, 149.48, 147.21, 140.39, 137.37, 133.79, 131.78, 130.65, 129.51, 129.05, 128.06, 127.21, 126.02, 124.71, 124.24, 122.13, 28.86, 25.76, 24.24; HR-MS (ESI): *m/z* 617.2226 ([M-Cl-Py-2Cl], calcd.); 617.2163 (found, $[M\text{-}Cl\text{-}Py\text{-}2Cl]^+$).

**Pd-NHC complex 2** was prepared according to literature procedure.[S2] Yield: 339 mg, 86 %. $^{1}$H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.69 (d, *J* = 8.4 Hz, 2H), 7.54 (t, *J* = 8.0 Hz, 2H), 7.39-7.32 (m, 6H), 6.84 (d, *J* = 6.8 Hz, 2H), 4.97-4.89 (m, 1H), 3.98 (d, *J* = 7.2 Hz, 1H), 3.37-3.27 (m, 3H), 3.16-3.10 (m, 2H), 2.90 (d, *J* = 13.2 Hz, 1H), 1.86 (d, *J* = 11.6 Hz, 1H), 1.37 (d, *J* = 6.0 Hz, 12H), 0.96 (m,12H); $^{13}$C NMR (100 MHz, $CDCl_3$, 298 K): δ = 192.89, 146.33, 146.16, 140.31, 134.56, 130.18, 129.83, 129.59, 127.74, 127.28, 126.21, 124.40, 124.14, 121.57, 114.44, 73.54, 50.25, 28.67, 28.63, 25.59, 25.31, 23.78, 23.26; HR-MS (ESI): *m/z* 659.2618 (calcd, $[M\text{-}Cl]^+$); 659.2633 (found, $[M\text{-}Cl]^+$).

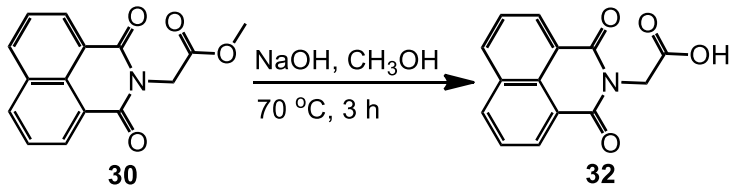
**Pd-NHC complex 3** was prepared according to literature procedure.[S3] Yield: 603 mg, 80%. $^{1}$H NMR (400 MHz, $CDCl_3$, 298 K): δ=8.65 (s, 1H), 8.56 (d, *J* = 5.2 Hz,1H), 7.74 (d, *J* = 8 Hz, 2H), 7.56 (d, *J* = 8 Hz,1H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.14 (s, 4H),

7.11-7.06 (m, 1H), 6.95 (d, $J$ = 6.8 Hz,2H), 2.44 (s, 24H); $^{13}$C NMR (100 MHz, $CDCl_3$, 298 K): δ= 156.14, 150.57, 149.66, 139.49, 138.76, 137.62, 136.24, 133.72, 132.04, 129.65, 129.26, 128.19, 127.70, 125.74, 124.40, 120.87, 21.46, 19.26; HR-MS (ESI): *m/z* 683.1086 (Calcd. $[M\text{-}Cl]^+$); 684.1036 (Found, $[M\text{-}Cl]^+$).

According to literature, [S4] the Pd-NHC **4** is also readily accessed.

**1.2 Synthesis of compounds 32-33.**

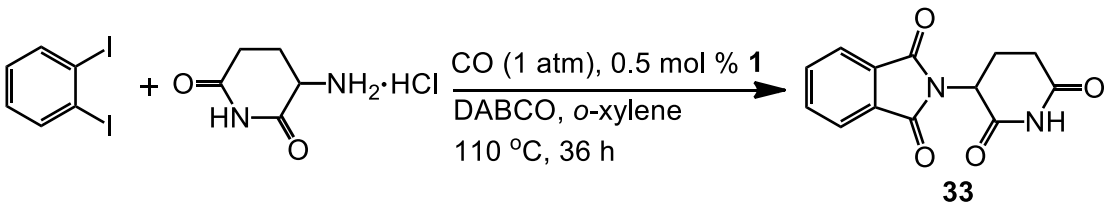
**Synthesis of alrestatin 32**




**Scheme S2.** Synthesis of Alrestatin **32**.

To a 50 mL round bottom flask containing complex **30** (175 mg, 0.65 mmol) and NaOH (100 mg, 2.5 mmol) was added methanol (2.5 mL) followed by $H_2O$ (2.0 mL). The resulting mixture was then heated at 70 $^o$C for 3 hours. After cooling to the room temperature, the reaction mixture was acidified with 2.0 M HCl to pH = 2. The crude solid formed was filtered off and washed with DCM and dried in vacuo to afford alrestatin **32** as an analytically pure white powder. Yield: 166 mg, >99%. $^1$H NMR (400 MHz, DMSO-$d_6$, 298 K): δ = 13.08 (s, 1H), 8.57-8.45 (m, 4H), 7.90 (t, $J$ = 7.8 Hz, 2H), 4.73 (s, 2H); $^{13}$C NMR (100 MHz, DMSO-$d_6$, 298 K): δ = 169.8, 163.5, 135.2, 131.7, 131.5, 127.7, 121.8, 41.6.

**Synthesis of thalidomide 33**

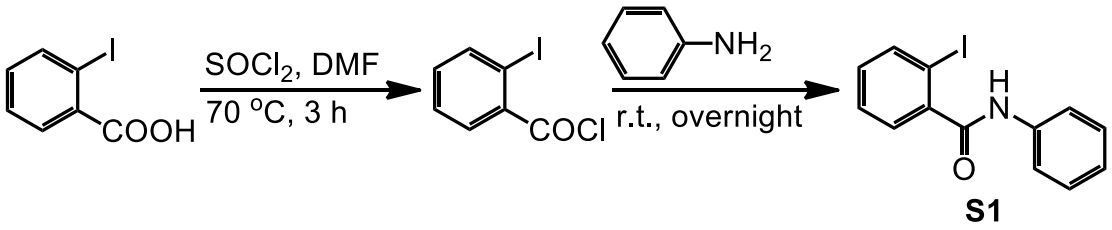



**Scheme S3.** Synthesis of thalidomide **33**.

To a 50 mL schlenk tube containing 3-aminopiperidine-2,6-dione hydrochloride (165 mg, 1.0 mmol), DABCO (281 mg, 2.5 mmol), complex **1** (2.0 mg, 0.5 mol %) purged twice with $N_2$ and then filled with CO. The *o*-diiodobenzene (0.5 mmol) was added subsequently. After 7 mL *o*-xylene was injected via a syringe, the reaction mixture was purged with CO for additional 30 seconds and stirred for 30 min at room temperature. The resulting mixture was then heated at 110 $^{o}$C for 36 h during which an atmosphere of CO was maintained by using a balloon. After cooling to the room temperature, a small amount of silica gel was added and the solvent was removed *in vacuo*. The mixture was ready for purification by flash chromatography to yield the products. Yield: 105 mg, 81%. $^{1}$H NMR (400 MHz, DMSO-$d_6$, 298 K): δ = 11.13 (s, 1H), 7.99-7.80 (m, 4H), 5.15 (dd, *J* = 12.8 Hz, 5.6 Hz, 1H), 2.97-2.78 (m, 1H), 2.65-2.49 (m, 2H), 2.12-1.97 (m, 1H); $^{13}$C NMR (100 MHz, DMSO-$d_6$, 298 K): δ = 173.3, 170.4, 167.7, 135.4, 131.7, 123.9, 49.5, 31.4, 22.5.

### 1.3 Control reactions and Mercury tests

In assistance with GC-MS analysis, the aminocarbonylation process was monitored and the key intermediate **S1** was detected (GC-MS: *m/z* = 323.4 [$M^+$]). Compound **S1** was then synthesized (**Scheme S4)**. By using compound **S1** as staring material under the standard reaction conditions, the aminocarbonylation product **5** was isolated in a 98 % yield.

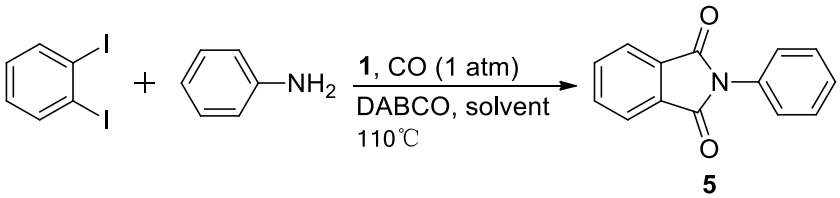



**Scheme S4.** Synthesis of intermediate **S1**.

Synthesis of intermediate **S1**: Intermediate **S1** was prepared according to literature procedure.[S5] Yield: 2.4 g, 74 %. $^{1}$H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.86 (d, *J* = 7.6 Hz, 1H), 7.76 (s, 1H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 7.2 Hz, 1H), 7.42-7.30 (m, 3H), 7.21-7.06 (d, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$, 298 K): δ = 167.4, 142.1, 140.0, 137.6, 131.5, 129.1, 128.5, 128.3, 124.9, 120.2, 92.5. GC-MS: *m/z* = 323.4 [$M]^+$, 231.4, 203.3.

In addition, a set of mercury tests was performed under the optimal conditions.[S6] With 0.5 mol % catalyst loading, one drop of Hg was added onto the reaction system after 0, 2, and 4 hours, resulted in 33 %, 54 %, and 82 % yields after 24 h reactions, respectively. These results indicated that Hg may influence on the catalytic process, but the molecular catalyst played the "real role" in the reaction.

**Table S1.** Mercury tests.

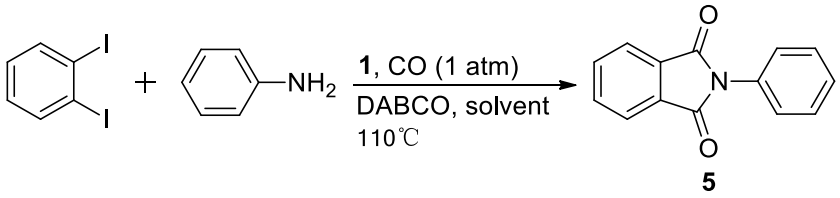



**5**

| Entry | Catalyst (mol %) | Additive or Note | Time (h) | Yield (%) |
|---|---|---|---|---|
| 1 | 0.5 mol % | Hg (1 drop after 0 h) | 24 | 33 |
| 2 | 0.5 mol % | Hg (1 drop after 2 h) | 24 | 54 |
| 3 | 0.5 mol % | Hg (1 drop after 4 h) | 24 | 82 |

## 2. Optimization of reaction conditions.

**Table S2.** Optimization of reaction conditions.[a]



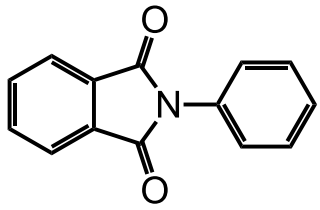

**5**

| Entry | $V_{solvent}$ (mL) | Cat. (mol%) | Solvent | Base | Yield (%)[b] |
|---|---|---|---|---|---|
| 1 | 7 | **1**(1.0) | toluene | DABCO | 70[c,d] |
| 2 | 7 | **1**(1.0) | toluene | DABCO | 74[c,e] |
| 3 | 2 | **1**(1.0) | toluene | DABCO | 63[c,e] |
| 4 | 7 | **1**(1.0) | toluene | DABCO | 89[e] |
| 5 | 7 | **1**(1.0) | toluene | DABCO | 94 |
| 6 | 5 | **1**(1.0) | toluene | DABCO | 79 |
| 7 | 7 | **1**(1.0) | toluene | DBU | 9 |
| 8 | 7 | **1**(1.0) | toluene | DMAP | 18 |

| | | | | | |
|---|---|---|---|---|---|
| 9 | 7 | **1**(1.0) | toluene | $Et_3N$ | 77 |
| 10 | 7 | **1**(1.0) | toluene | DIPEA | 79 |
| 11 | 7 | **1**(1.0) | toluene | $K_3CO_3$ | 70 |
| 12 | 7 | **1**(1.0) | toluene | $Cs_2CO_3$ | 32 |
| 13 | 7 | **1**(1.0) | NMP | DABCO | 57 |
| 14 | 7 | **1**(1.0) | DMSO | DABCO | 90 |
| 15 | 7 | **1**(1.0) | DMF | DABCO | 87 |
| 16 | 7 | **1**(1.0) | ACN | DABCO | 70[f] |
| 17 | 7 | **1**(1.0) | THF | DABCO | 41[g] |
| 18 | 7 | **1**(1.0) | dioxane | DABCO | 77[h] |
| 19 | 7 | **1**(1.0) | *o*-xylene | DABCO | >99 |
| 20 | 7 | **1**(1.0) | *m*-xylene | DABCO | 96 |
| 21 | 7 | **1**(1.0) | *p*-xylene | DABCO | >99 |
| 22 | 7 | **1**(1.0) | mesitylene | DABCO | >99 |
| 23 | 7 | **1**(0.5) | *o*-xylene | DABCO | >99 |
| 24 | 7 | **1**(0.5) | *p*-xylene | DABCO | >99 |
| 25 | 7 | **1**(0.5) | mesitylene | DABCO | >99 |
| 26 | 7 | **1**(0.05) | *o*-xylene | DABCO | 71 |
| 27 | 7 | **1**(0.05) | *p*-xylene | DABCO | 65 |
| 28 | 7 | **1**(0.05) | mesitylene | DABCO | 39 |
| 29 | 7 | **1**(0.5) | *o*-xylene | DABCO | >99[e] |
| 30 | 7 | **1**(0.5) | *p*-xylene | DABCO | 83[e] |
| 31 | 7 | **1**(0.5) | mesitylene | DABCO | 93[e] |
| 32 | 7 | **2**(0.5) | *o*-xylene | DABCO | 91[e] |
| 33 | 7 | **3**(0.5) | *o*-xylene | DABCO | >99[e] |
| 34 | 7 | **4**(0.5) | *o*-xylene | DABCO | 96[e] |
| 35 | 7 | **$Pd(OAc)_2$/$PPh_3$**(0.5) | *o*-xylene | DABCO | 47[e] |

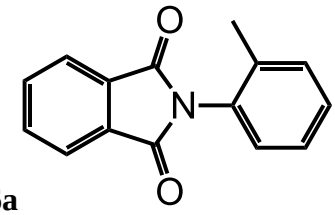
[a] Reactions were carried out on a 0.5 mmol scale *o*-iodobenzene with 1.0 mmol aniline, 1.5 mmol base in 7 mL solvent at 110 °C for 30 h with Pd-NHC complex **1**. [b] Isolated yield. [c] 0.7 mmol aniline was used. [d] After 12 h. [e] After 24 h. [f] T = 66 °C. [g] T = 80 °C. [h] T = 100 °C.

**3. Analytical data of the products.**



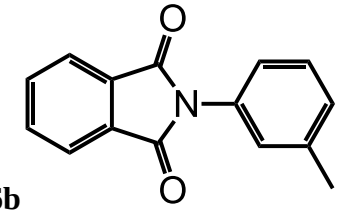
**5**

$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K): δ = 8.03-7.91 (m, 2H), 7.86-7.75 (m, 2H), 7.57-7.48 (m, 2H), 7.48-7.37 (m, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, 298 K): δ = 167.3, 134.4, 131.8, 131.7, 129.2, 128.1, 126.6, 123.8.



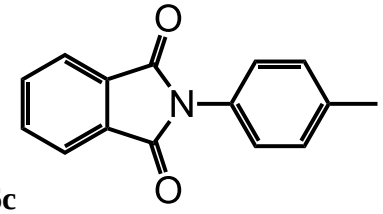
**6a**

$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K): δ = 8.00-7.93 (m, 2H), 7.84-7.77 (m, 2H), 7.41-7.30 (m, 3H), 7.21 (d, *J* = 7.6 Hz, 1H), 2.22 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, 298 K): δ = 167.4, 136.6, 134.4, 132.1, 131.2, 130.6, 129.5, 128.8, 126.9, 123.8,18.1.



**6b**

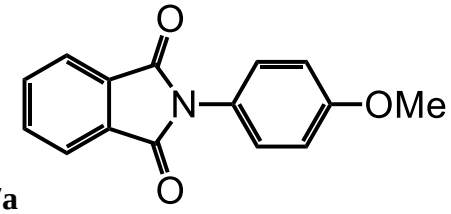
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K): δ = 8.00-7.92 (m, 2H), 7.84-7.75 (m, 2H), 7.43-7.37 (m, 1H), 7.25-7.19 (m, 3H) 2.43 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, 298 K): δ = 167.4, 139.2, 134.4, 131.8, 131.5, 129.1, 129.0, 127.3, 123.8, 123.7, 21.4.



**6c**

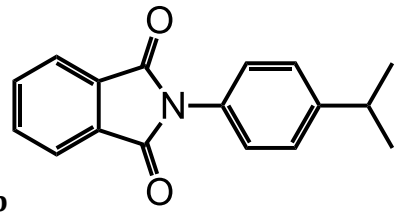
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.99-7.92 (m, 2H), 7.82-7.75 (m, 2H), 7.31 (s, 4H), 2.41 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, 298 K): δ = 167.5, 138.2, 134.4,

131.9, 129.8, 129.0, 126.5, 123.7, 21.3.



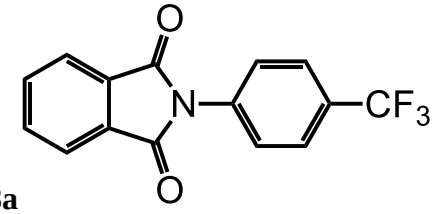

**7a**

$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K): δ = 8.00-7.90 (m, 2H), 7.84-7.74 (m, 2H), 7.34 (d, *J* = 9.2 Hz, 2H), 7.03 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, 298 K): δ = 167.6, 159.3, 134.3, 131.8, 128.0, 124.3, 123.7, 114.5, 55.5.



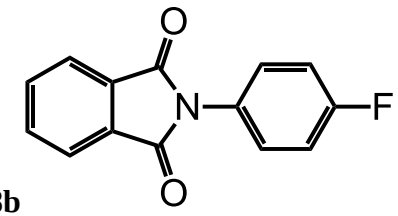

**7b**

$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K): δ = 8.04-7.91 (m, 2H), 7.85-7.75 (m, 2H), 7.38 (d, *J* = 1.2 Hz, 4H), 3.07-2.91 (m, 1H), 1.31 (d, *J* = 7.2 Hz, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$, 298 K): δ = 167.5, 148.9, 134.4, 131.9, 129.2, 127.3, 126.5, 123.7, 34.0, 24.0.



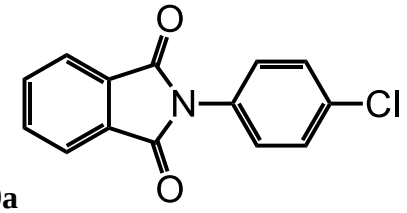

**8a**

$^{1}$H NMR (400 MHz, DMSO-$d_6$, 298 K): δ = 8.04-7.83 (m, 6H), 7.72 (d, *J* = 8.4 Hz, 2H); $^{13}$C NMR (100 MHz, DMSO-$d_6$, 298 K): δ = 167.1, 136.1, 135.4, 132.0, 128.8, 128.4, 128.3, 126.4, 126.4, 125.9, 124.1; $^{19}$F NMR (400 MHz, DMSO-$d_6$, 298 K): δ = - 61.4.



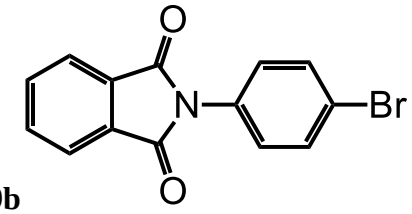

**8b**

$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.96 (dd, *J* = 5.4 Hz, 3.0 Hz, 2H), 7.81 (dd, *J* = 5.4 Hz, 3.0 Hz, 2H), 7.48-7.37 (m, 2H), 7.20 (t, *J* = 8.6 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$, 298 K): δ = 167.2, 163.2, 160.7, 134.5, 131.7, 128.4, 128.4, 127.6, 123.8, 116.3, 116.0; $^{19}$F NMR (400 MHz, $CDCl_3$, 298 K): δ = - 113.5.



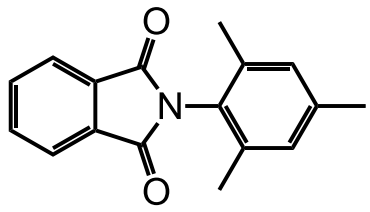

**9a**

$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K): δ = 8.02-7.89 (m, 2H), 7.86-7.75 (m, 2H), 7.48 (d, *J* = 8.8 Hz, 2H), 7.41 (d, *J* = 8.8 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$, 298 K): δ = 167.0, 134.6, 133.8, 131.6, 130.2, 129.3, 127.7, 123.9.



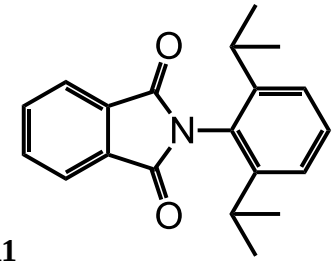

**9b**

$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.95 (dd, *J* = 5.6 Hz, 3.2 Hz, 2H), 7.80 (dd, *J* = 5.6 Hz, 3.0 Hz, 2H), 7.63 (d, *J* = 8.8 Hz, 2H), 7.36 (d, *J* = 8.8 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$, 298 K): δ = 166.9, 134.6, 132.3, 131.6, 130.8, 128.0, 123.9, 121.8.



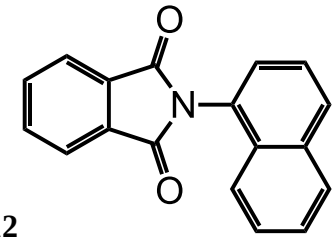

**10**

$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K): δ = 8.00-7.93 (m, 2H), 7.84-7.77 (m, 2H), 7.02 (s, 2H), 2.34 (s, 3H), 2.13 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$, 298 K): δ = 167.5, 139.4, 136.5, 134.3, 132.1, 129.3, 127.1, 123.8, 21.2, 18.0.



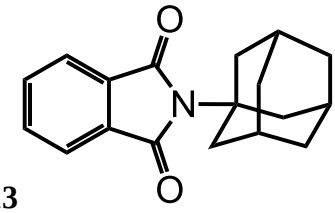
**11**

$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K): δ = 8.02-7.94 (m, 2H), 7.87-7.78 (m, 2H), 7.47 (t, *J* = 8.0 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 2.78-2.66 (m, 2H), 1.17 (d, *J* = 6.8 Hz, 12H); $^{13}$C NMR (100 MHz, $CDCl_3$, 298 K): δ = 168.3, 147.3, 134.4, 132.0, 130.2, 126.9, 124.0, 123.9, 29.4, 24.0.



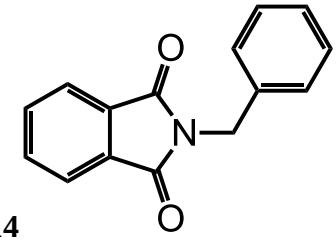
**12**

$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K): δ = 8.09-7.90 (m, 4H), 7.87-7.77 (m, 2H), 7.68-7.58 (m, 2H), 7.58-7.45 (m, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, 298 K): δ = 167.8, 134.5, 132.1, 130.3, 130.0, 128.7, 128.3, 127.2, 127.1, 126.6, 125.5, 124.0, 122.5.



**13**

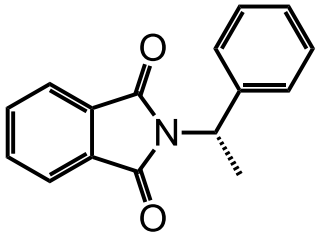
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.79-7.71 (m, 2H), 7.70-7.62 (m, 2H), 2.51 (d, *J* = 2.8 Hz, 6H), 2.17 (s, 3H), 1.84-1.66 (m, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$, 298 K): δ = 169.8, 133.6, 132.0, 122.5, 60.4, 40.2, 36.2, 29.8.



**14**

$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.89-7.80 (m, 2H), 7.75-7.66 (m, 2H), 7.46-7.41 (m, 2H), 7.36-7.23 (m, 3H), 4.86 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$, 298

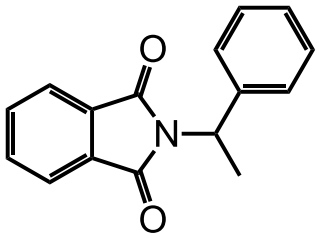
K): δ = 168.0, 136.4, 134.0, 132.1, 128.7, 128.6, 127.9, 123.4, 41.6.



(*S*)-**15**

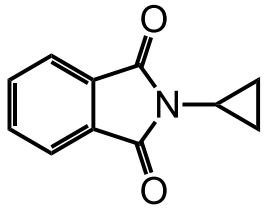
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.81-7.79 (m, 2H), 7.69-7.67 (m, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.33 (t, *J* = 8.0 Hz, 2H), 7.26 (t, *J* = 8.0 Hz, 1H), 5.58 (q, *J* = 7.2 Hz, 1H), 1.93 (d, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, 298 K): δ = 168.2, 140.3, 133.9, 132.0, 128.5, 127.7, 127.5, 123.2, 49.6, 17.6.

The enantiomeric excess of **15** was determined by HPLC (OJ-3 column, Hex/IPA = 70:30, 1.0 mL/min, 254 nm), > 99% *ee*, $t_{major}$ = 9.64 min, $t_{minor}$ = 19.96 min.



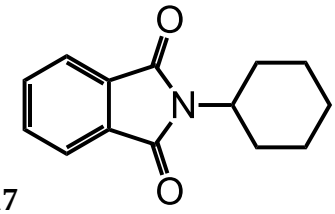
**15** (*rac*)

$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.83-7.77 (m, 2H), 7.72-7.66 (m, 2H), 7.51 (d, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 2H), 7.29-7.23 (m, 1H), 5.57 (q, *J* = 7.2 Hz, 1H), 1.93 (d, *J* = 7.6 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, 298 K): δ = 168.2, 140.4, 133.9, 132.0, 128.5, 127.7, 127.5, 123.2, 49.7, 17.6.



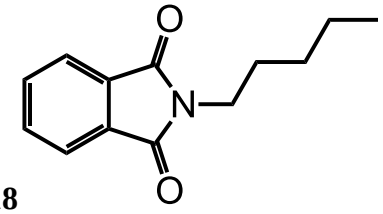
**16**

$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.85-7.77 (m, 2H), 7.73-7.65 (m, 2H), 2.77-2.63 (m, 1H), 1.05-0.98 (m, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$, 298 K): δ = 168.8, 134.0, 131.8, 123.1, 20.9, 5.2.



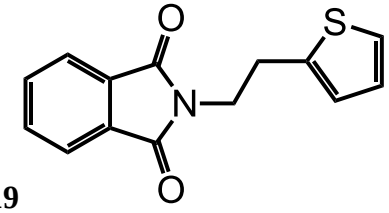
**17**

$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.85-7.77 (m, 2H), 7.73-7.65 (m, 2H), 4.17-4.04 (m, 1H), 2.28-2.12 (m, 2H), 1.93-1.80 (m, 2H), 1.77-1.65 (m, 3H), 1.44-1.27 (m, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, 298 K): δ = 168.4, 133.7, 132.1, 123.0, 50.9, 29.9, 26.0, 25.1.



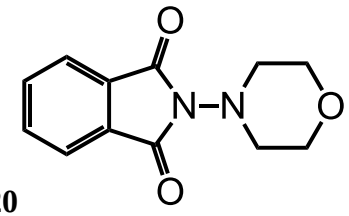
**18**

$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.85-7.76 (m, 2H), 7.72-7.63 (m, 2H), 3.64 (t, *J* = 7.2 Hz, 2H), 1.64 (t, *J* = 7.2 Hz, 2H), 1.38-1.23 (m, 4H), 0.86 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, 298 K): δ = 168.5, 133.8, 132.2, 123.1, 38.0, 29.0, 28.3, 22.3, 13.9.



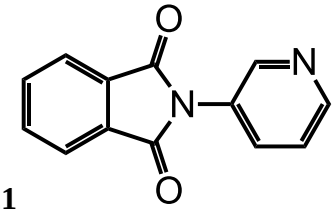
**19**

$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.89-7.79 (m, 2H), 7.76-7.66 (m, 2H), 7.18-7.10 (m, 1H), 6.94-6.89 (m, 1H), 6.87 (d, *J* = 2.8 Hz, 1H), 3.97 (t, *J* = 7.2 Hz, 2H), 3.23 (t, *J* = 7.2 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$, 298 K): δ = 168.1, 140.0, 134.0, 132.0, 127.0, 125.6, 124.2, 123.3, 39.4, 28.6.



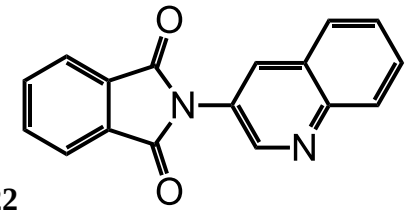
**20**

$^{1}$H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 7.84-7.77 (m, 2H), 7.75-7.69 (m, 2H), 3.85 (t, *J* = 4.0 Hz, 4H), 3.43-3.34 (m, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$, 298 K): δ = 166.8, 134.4, 130.1, 123.3, 67.0, 52.5; HR-MS(ESI): *m/z* = 255.0740 (calcd, $[M+Na]^+$); 255.0747 (found, $[M+Na]^+$); IR (KBr): *v* = 3445, 2965, 2913, 2861, 1723, 1461, 1369, 1272, 1191, 1109, 984, 864, 714 $cm^{-1}$.



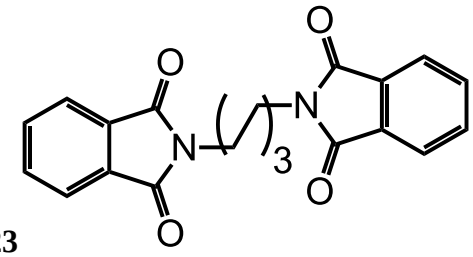
**21**

$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K): δ = 8.77 (s, 1H), 8.66-8.58 (m, 1H), 8.00-7.91 (m, 2H), 7.85-7.78 (m, 3H), 7.48-7.39 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$, 298 K): δ = 166.8, 148.8, 147.3, 134.8, 133.6, 131.5, 128.8, 124.0, 123.7.



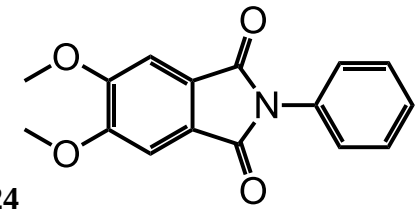
**22**

$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K): δ = 9.04 (d, *J* = 2.0 Hz, 1H), 8.29 (d, *J* = 1.6 Hz, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 8.03-7.92 (m, 2H), 7.90-7.72 (m, 4H), 7.59 (d, *J* = 7.6 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$, 298 K): δ = 167.0, 148.0, 147.0, 134.8, 132.6, 131.6, 130.1, 129.4, 128.1,127.6, 127.4, 125.6, 124.0.



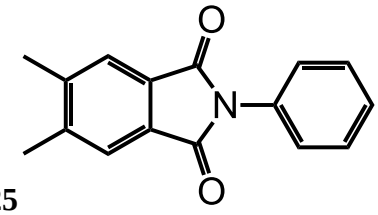
**23**

$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.87-7.74 (m, 2H), 7.73-7.63 (m, 5H), 3.75-3.55 (m, 4H); 1.75-1.56 (m, 4H), 1.45-1.27 (m, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$, 298 K): δ = 168.4, 133.8, 132.2, 123.2, 37.9, 28.5, 26.4.



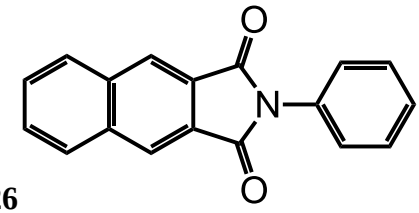
**24**

$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.54-7.47 (m, 2H), 7.46-7.34 (m, 5H), 4.03 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$, 298 K): δ = 167.4, 154.2, 132.0, 129.1, 127.8, 126.5, 125.2, 105.6, 56.7.



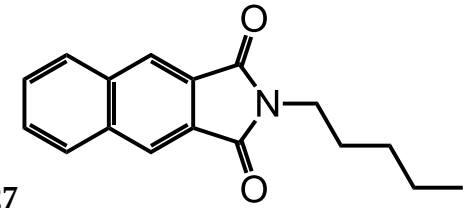
**25**

$^{1}$H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 7.71 (s, 2H), 7.50 (t, *J* = 8.0 Hz, 2H), 7.46-7.35 (m, 3H), 2.44 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$, 298 K): δ = 167.6, 144.2, 132.0, 129.8, 129.0, 127.9, 126.6, 124.7, 20.7.



**26**

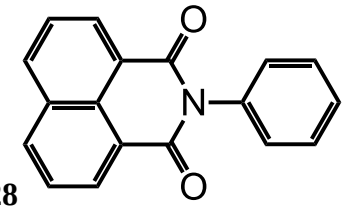
$^{1}$H NMR (400 MHz, DMSO-$d_6$, 298 K): δ = 8.59 (s, 2H), 8.34-8.21 (m, 2H), 7.84-7.71 (m, 2H), 7.61-7.33 (m, 5H); $^{13}$C NMR (100 MHz, DMSO-$d_6$, 298 K): δ = 167.1, 135.7, 132.6, 130.8, 129.8, 129.3, 129.1, 128.6, 127.8, 125.3.



**27**

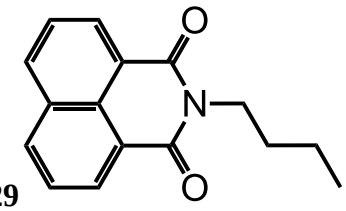
$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K): δ = 8.27 (s, 2H), 8.07-7.94 (m, 2H), 7.71-7.59 (m, 2H), 3.72 (t, *J* = 7.4 Hz, 2H), 1.78-1.63 (m, 2H), 1.42-1.27 (m, 4H), 0.94-0.83 (t, *J* = 6.8 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, 298 K): δ = 168.1, 135.4, 130.2, 129.0,

127.9, 124.4, 38.3, 29.0, 28.2, 22.3, 14.0.



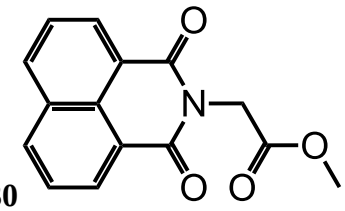
**28**

$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K): δ = 8.64 (d, *J* = 7.6 Hz, 2H), 8.26 (d, *J* = 8.0 Hz, 2H), 7.78 (t, *J* = 7.8 Hz, 2H), 7.61-7.53 (m, 2H), 7.53-7.46 (m, 1H), 7.40-7.28 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$, 298 K): δ = 164.4, 135.5, 134.3, 131.8, 131.6, 129.4, 128.7, 128.7, 127.1, 122.8.



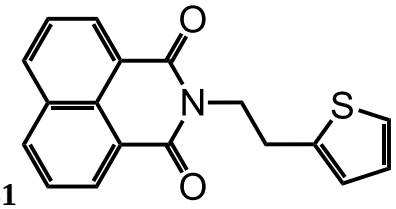
**29**

$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K): δ = 8.56 (m, 2H), 8.17 (d, *J* = 8.0 Hz, 2H), 7.72 (t, *J* = 7.6 Hz, 2H), 4.16 (t, *J* = 7.6 Hz, 2H), 1.77-1.65 (m, 2H), 1.50-1.38 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, 298 K): δ = 164.2, 133.8, 131.5, 131.1, 128.1, 126.9, 122.7, 40.2, 30.2, 20.4, 13.9.



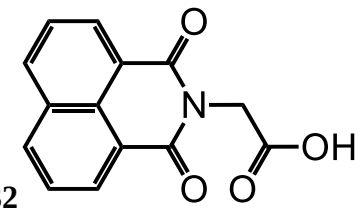
**30**

$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K): δ = 8.58-8.46 (m, 2H), 8.24-8.10 (m, 2H), 7.76-7.63 (m, 2H), 4.94 (s, 2H), 3.78 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, 298 K): δ = 168.6, 163.8, 134.4, 131.5, 128.8, 128.2, 126.9, 122.1, 52.5, 41.2.



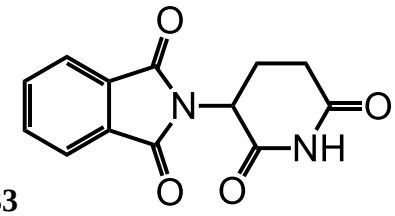
**31**

$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K): δ = 8.59 (d, *J* = 7.2 Hz, 2H), 8.20 (d, *J* = 7.6 Hz, 2H), 7.74 (t, *J* = 7.6 Hz, 2H), 7.16 (dd, *J* = 4.4 Hz, 1.6 Hz, 1H), 7.02-6.87 (m, 2H), 4.46 (t, *J* = 8.0 Hz, 2H), 3.28 (t, *J* = 7.8 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$, 298 K): δ = 164.0, 140.8, 134.0, 131.6, 131.2, 128.1, 127.0, 125.5, 123.9, 122.5, 41.7, 28.2; HR-MS(ESI): *m/z* = 330.0559 (calcd, $[M+Na]^+$); 330.0557 (found, $[M+Na]^+$); IR (KBr): *v* = 3428, 3067, 2920, 2356, 1655, 1439, 1347, 1229, 1165, 1021, 778, 727 $cm^{-1}$.




**32**

$^{1}$H NMR (400 MHz, DMSO-$d_6$, 298 K): δ = 13.08 (s, 1H), 8.57-8.45 (m, 4H), 7.90 (t, *J* = 7.8 Hz, 2H), 4.73 (s, 2H); $^{13}$C NMR (100 MHz, DMSO-$d_6$, 298 K): δ = 169.8, 163.5, 135.2, 131.7, 131.5, 127.7, 121.8.




**33**

$^{1}$H NMR (400 MHz, *DMSO-$d_6$*, 298 K): δ = 11.13 (s, 1H), 7.99-7.80 (m, 4H), 5.15 (dd, *J* = 12.8 Hz, 5.6 Hz, 1H), 2.97-2.78 (m, 1H), 2.65-2.49 (m, 2H), 2.12-1.97(m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$, 298 K): δ = 173.3, 170.4, 167.7, 135.4, 131.7, 123.9, 49.5, 31.4, 22.5.

## 4. NMR and IR spectra of the products.

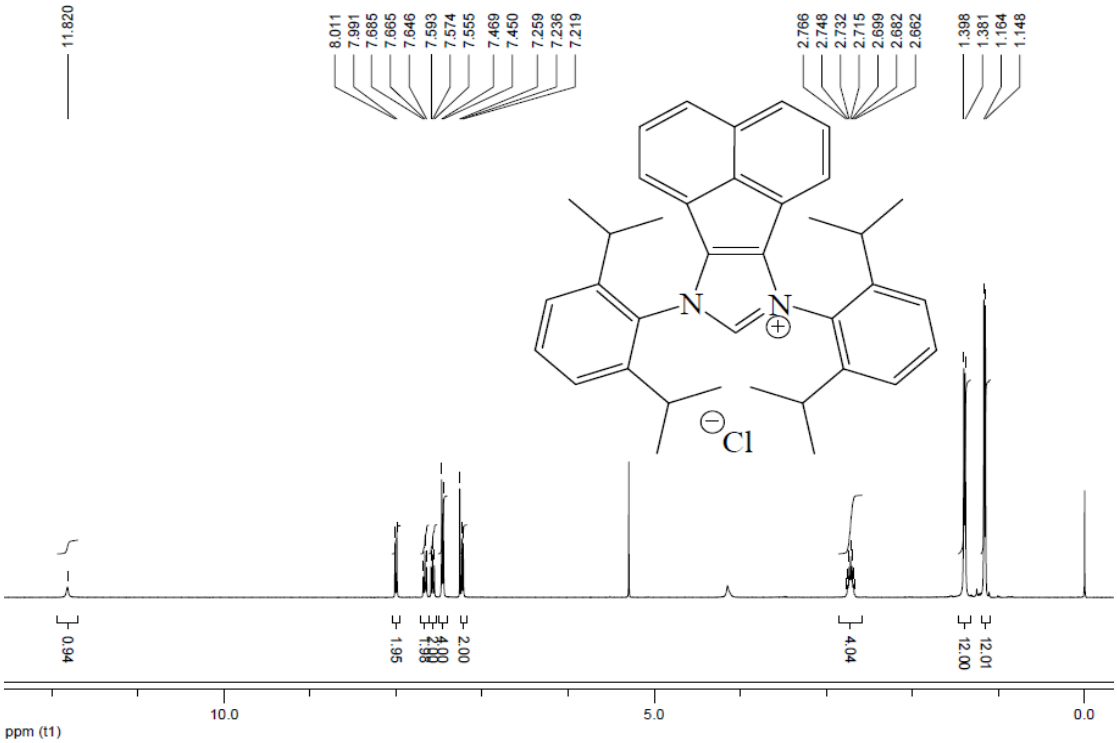



***Figure S1.*** [1]H NMR spectrum of acenaphthoimidazolium chloride.

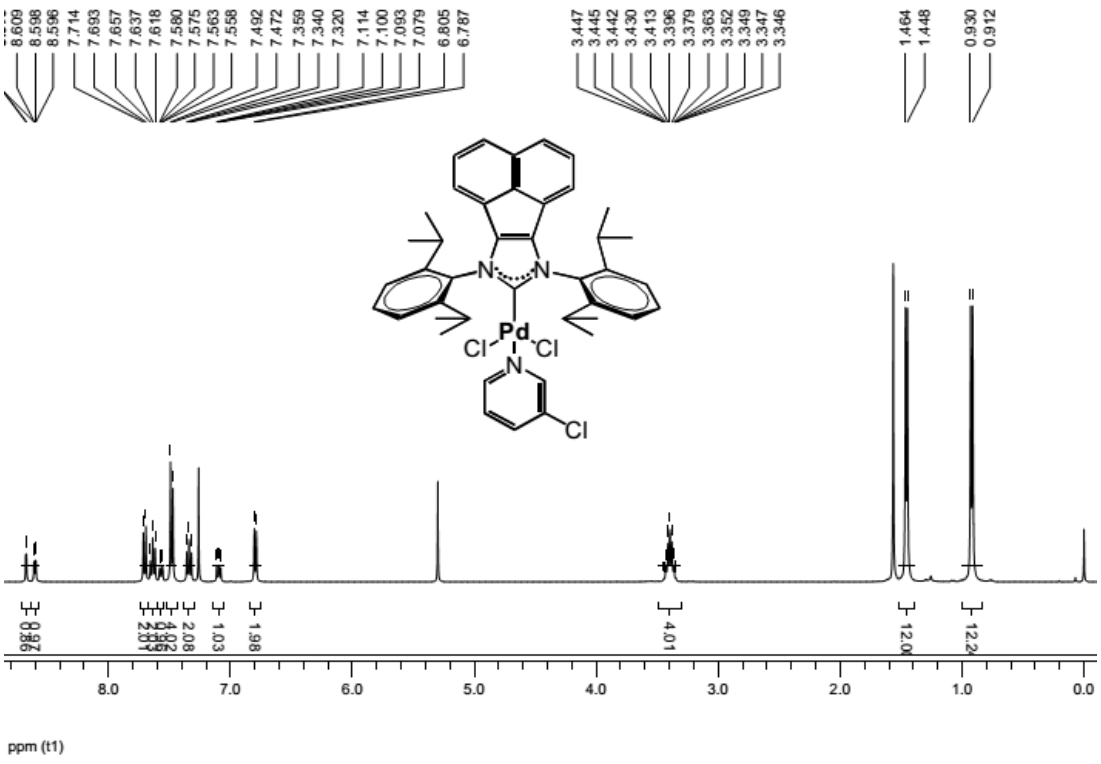



***Figure S2.*** [1]HNMR spectrum of compound **1**.

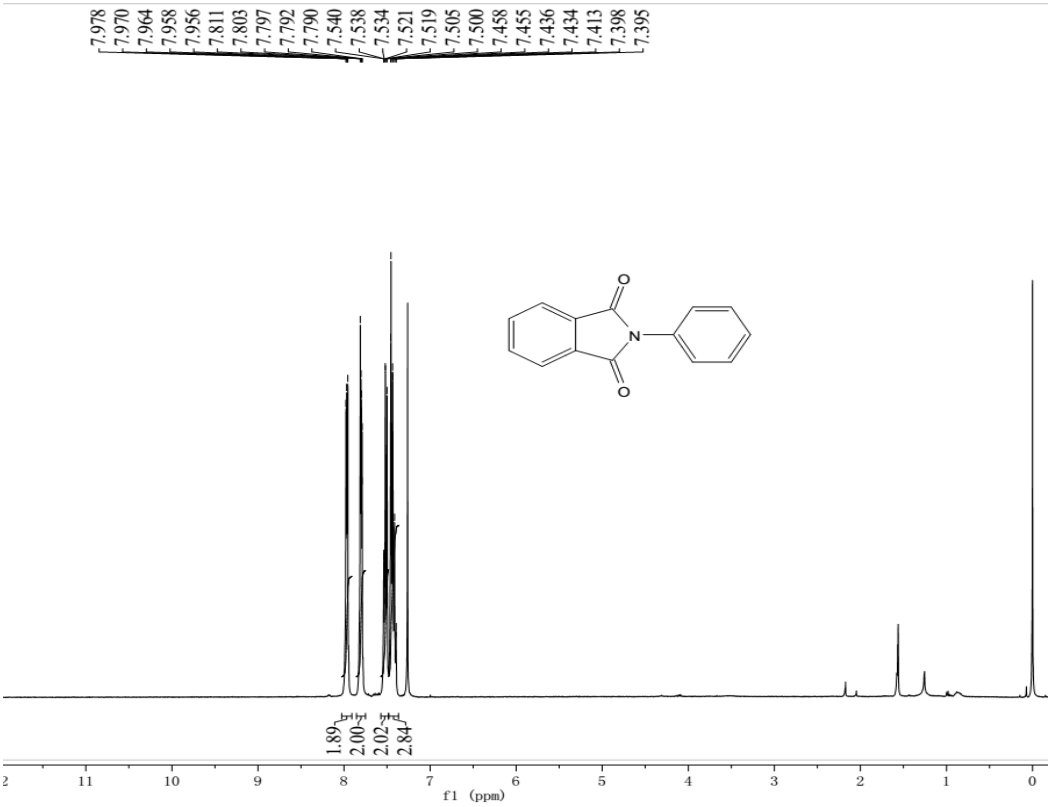



***Figure S3.*** $^{1}$H NMR spectrum of compound **5**.

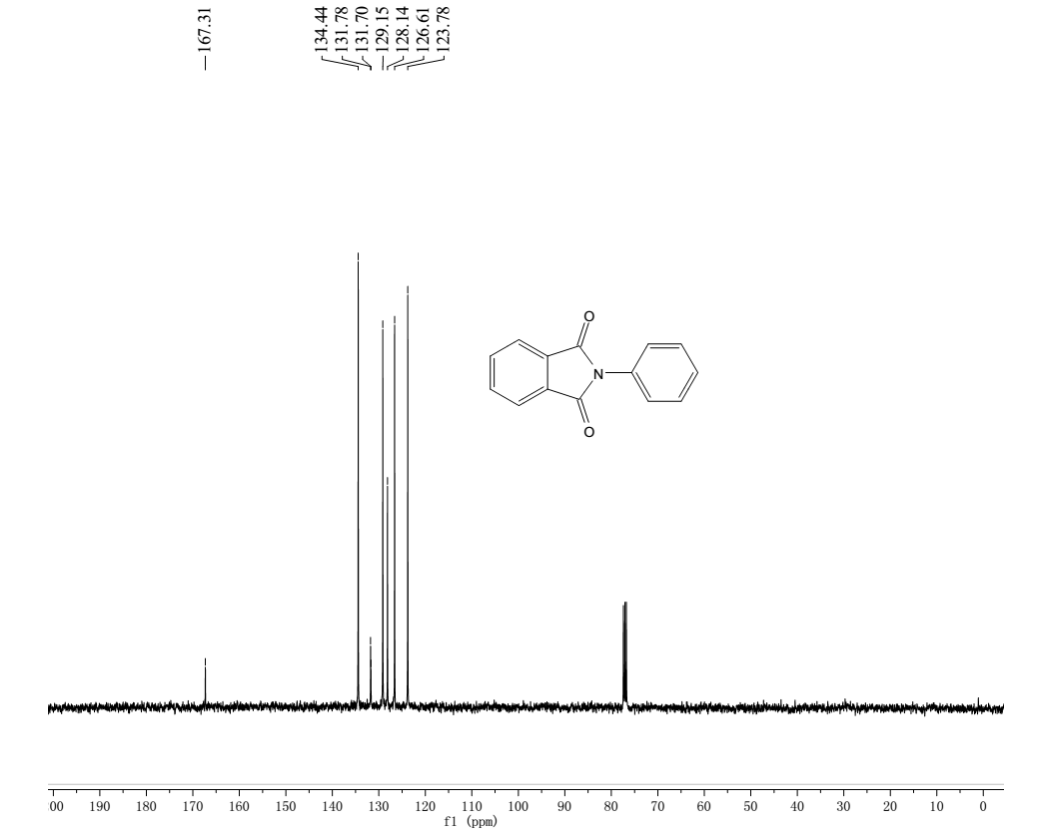



***Figure S4.*** $^{13}$C NMR spectrum of compound **5**.

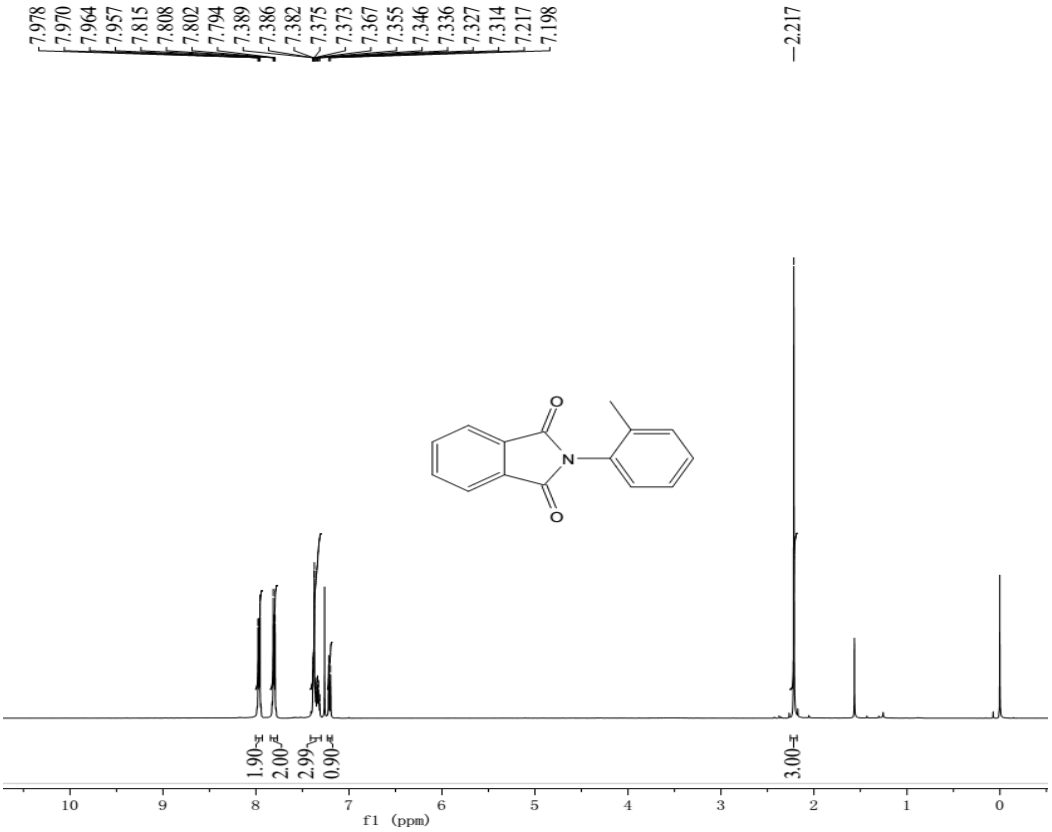



***Figure S5.*** $^{1}$H NMR spectrum of compound **6a**.

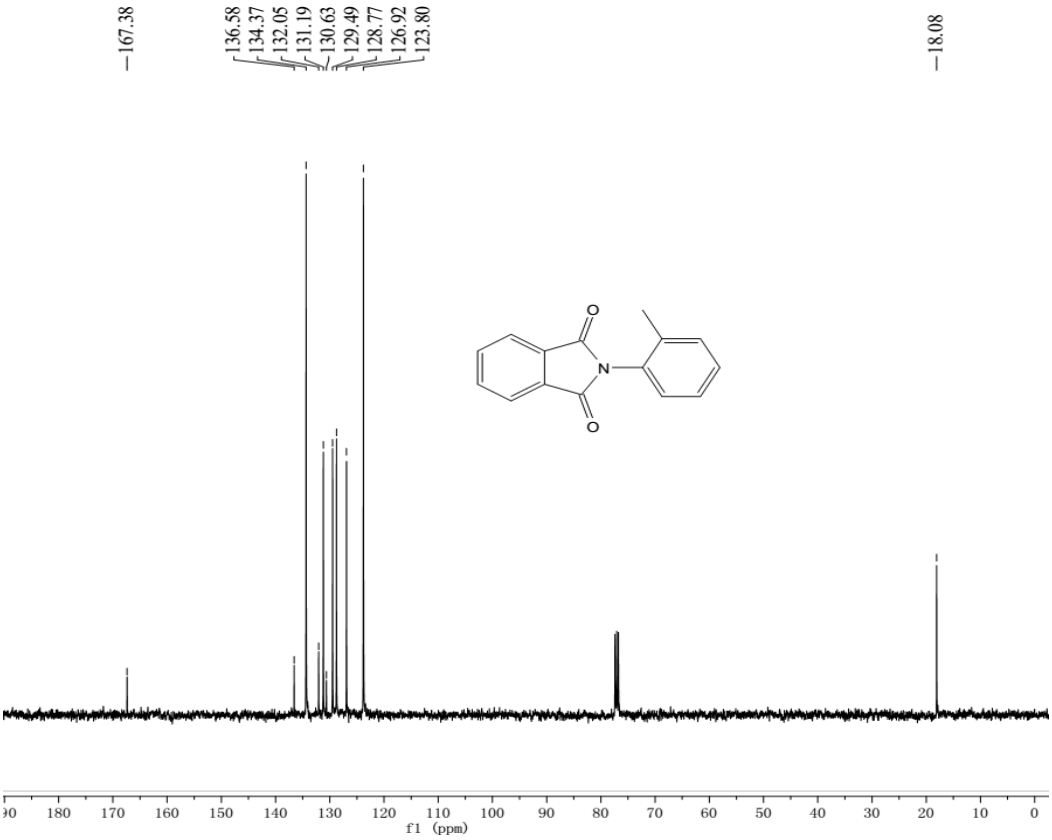



***Figure S6.*** $^{13}$C NMR spectrum of compound **6a**.

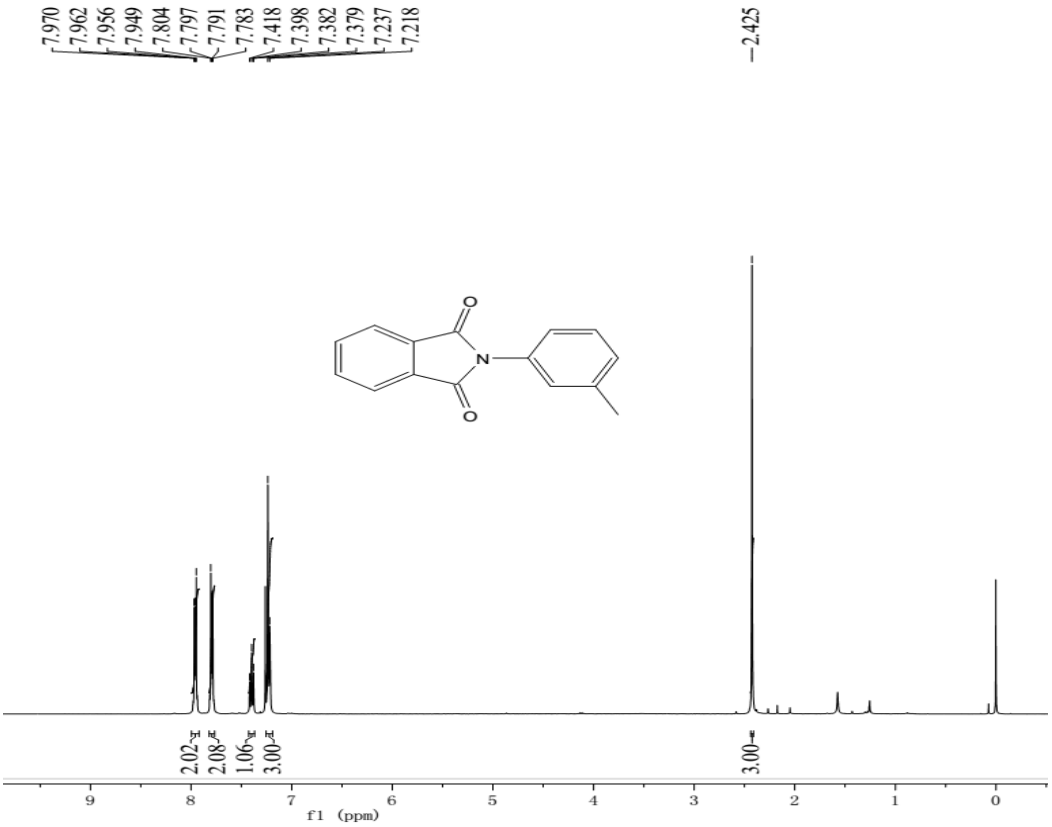



***Figure S7.*** $^{1}$H NMR spectrum of compound **6b**.

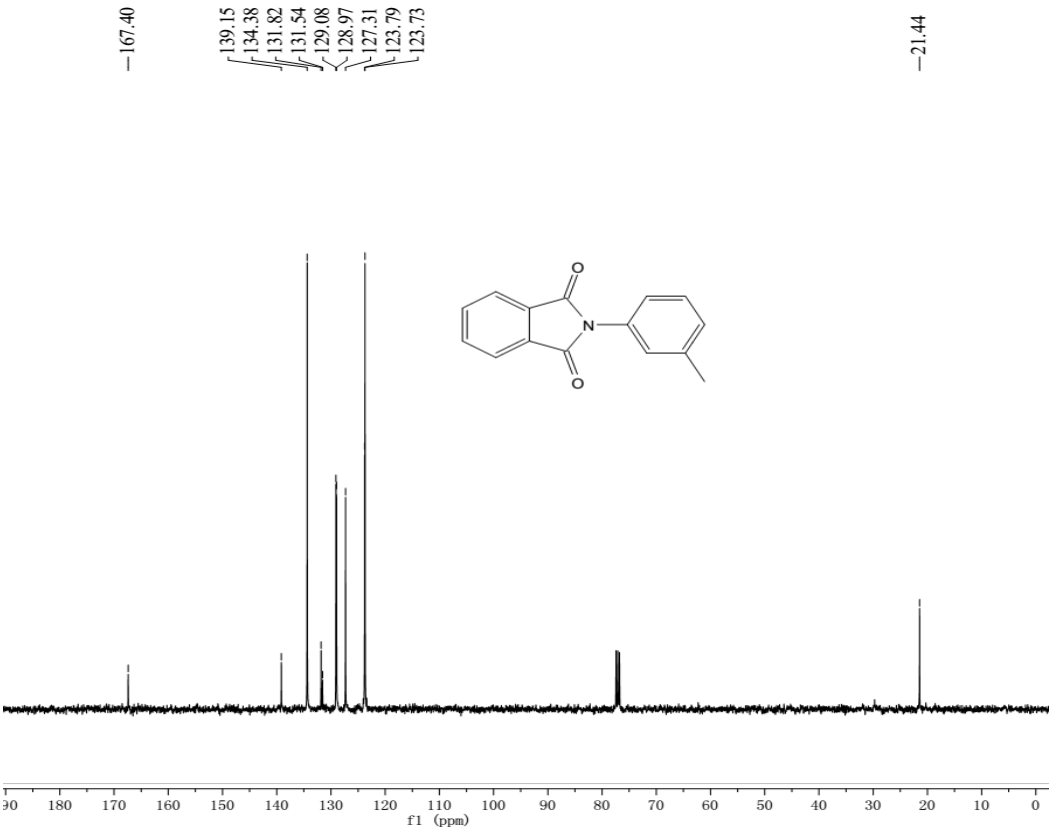



***Figure S8.*** $^{13}$C NMR spectrum of compound **6b**.

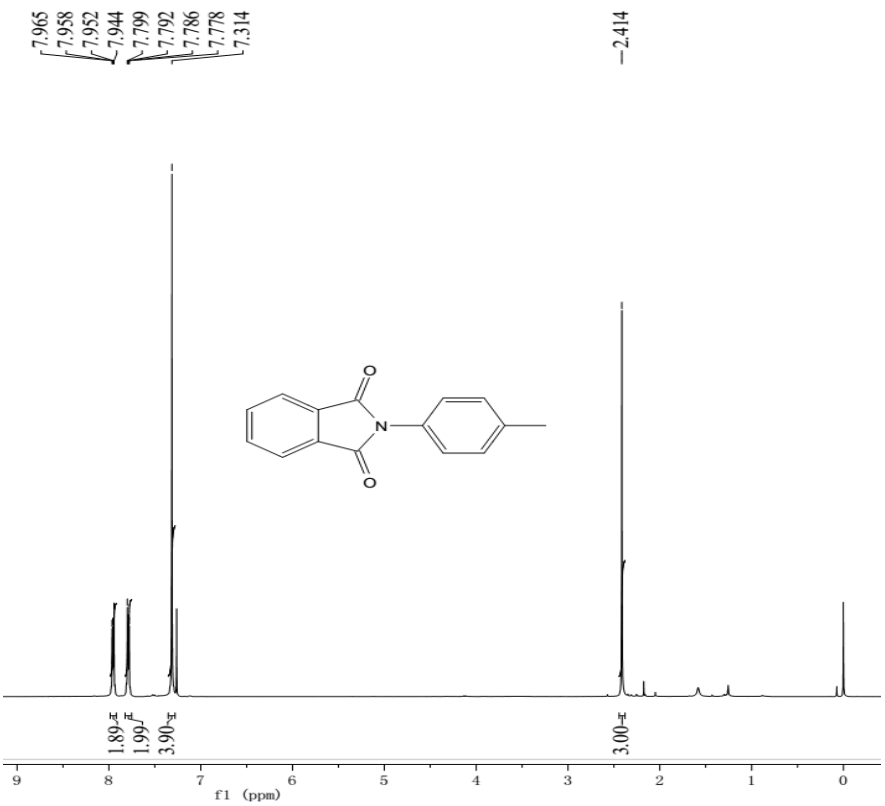



***Figure S9.*** $^{1}$H NMR spectrum of compound **6c**.

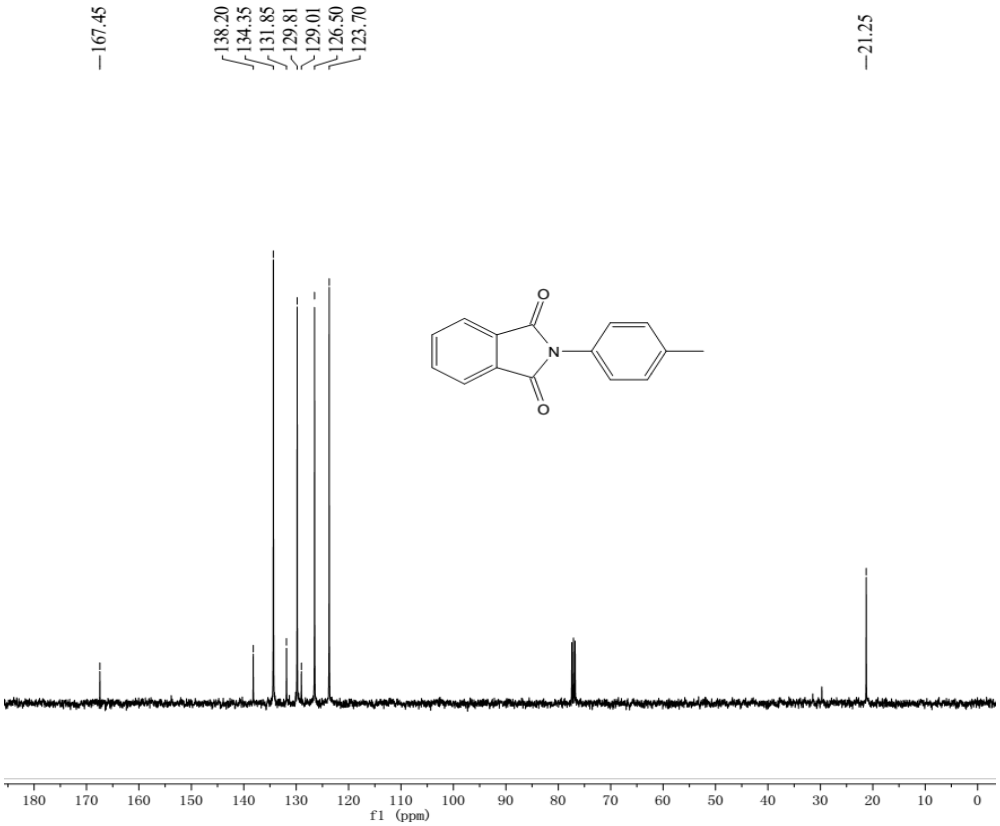



***Figure S10.*** $^{13}$C NMR spectrum of compound **6c**.

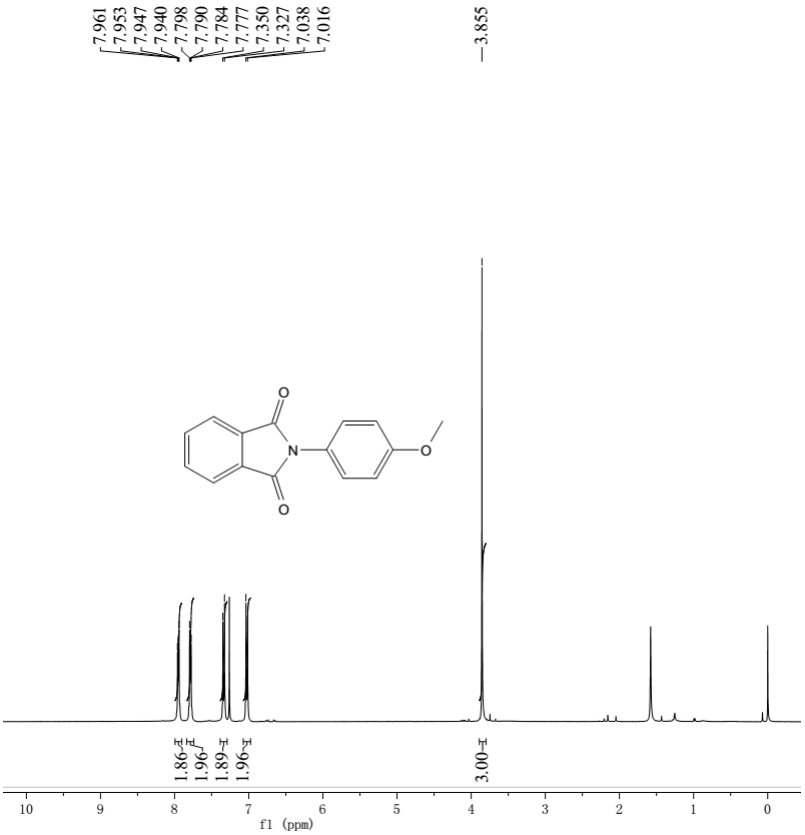



***Figure S11.*** $^{1}$H NMR spectrum of compound **7a**.

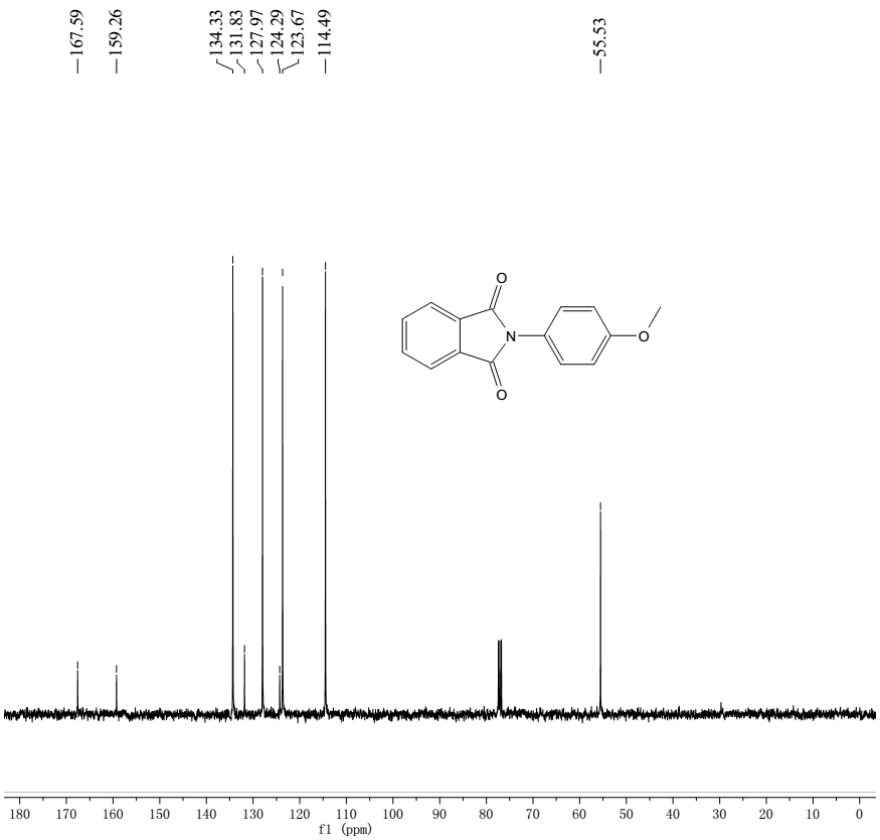



***Figure S12.*** $^{13}$C NMR spectrum of compound **7a**.

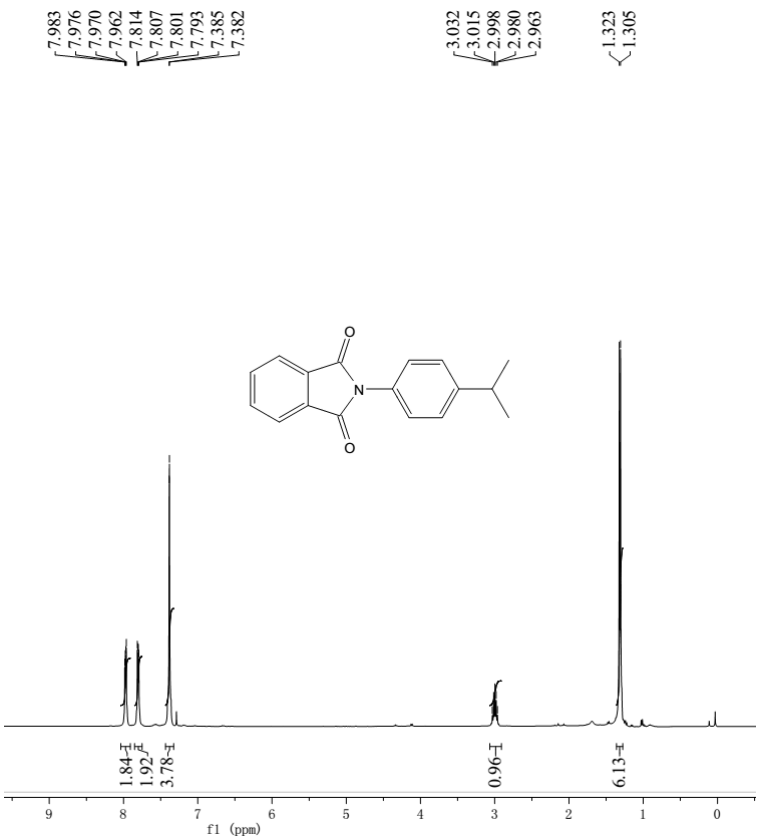



***Figure S13.*** $^{1}$H NMR spectrum of compound **7b**.

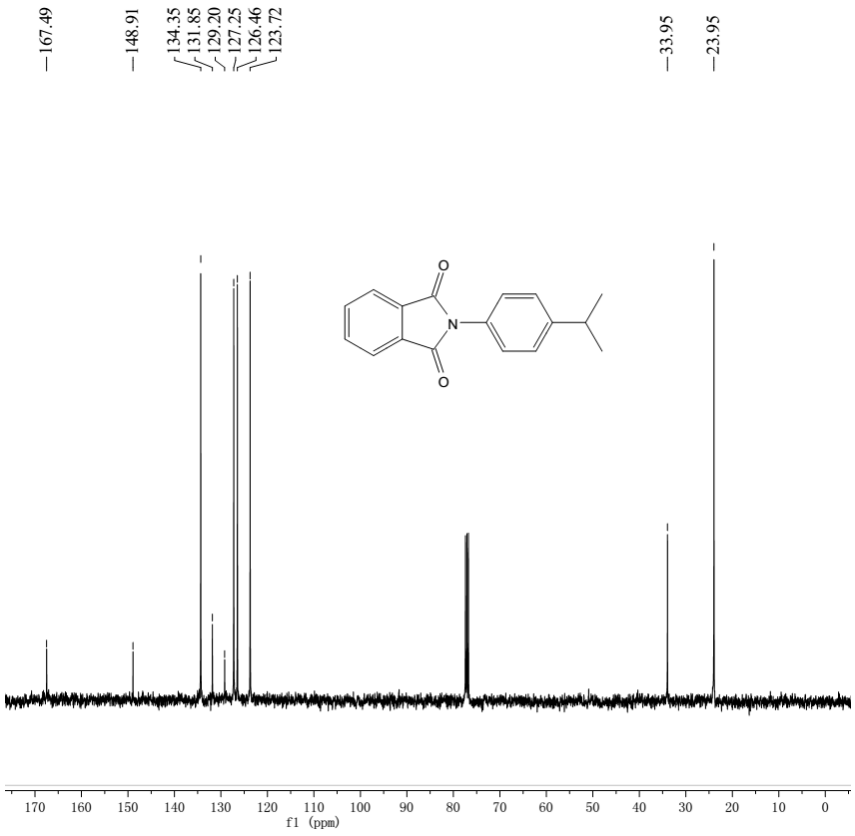



***Figure S14.*** $^{13}$C NMR spectrum of compound **7b**.

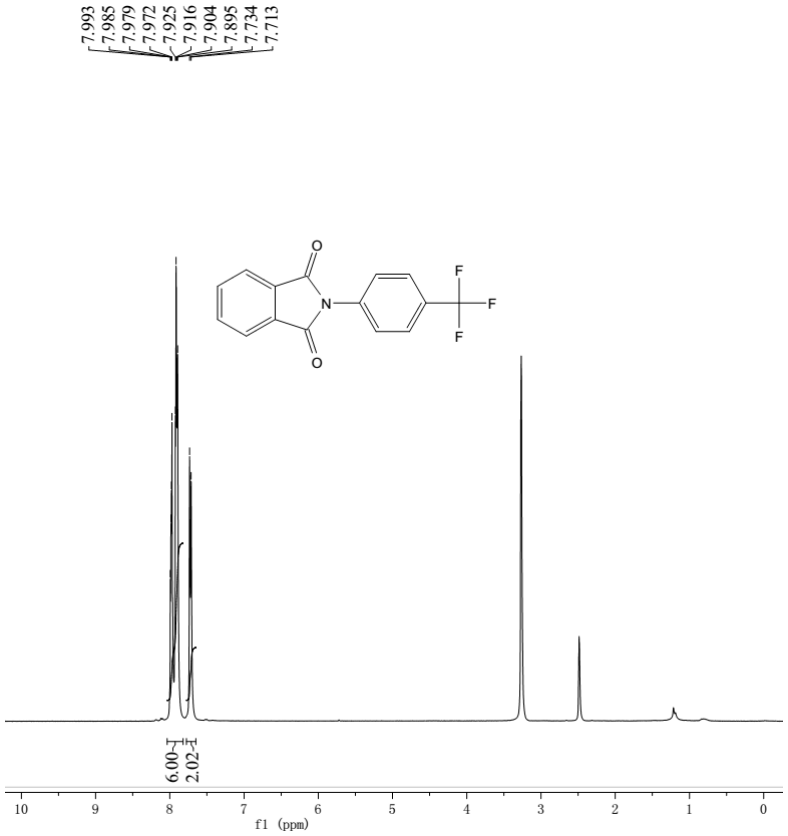



***Figure S15.*** $^{1}$H NMR spectrum of compound **8a**.

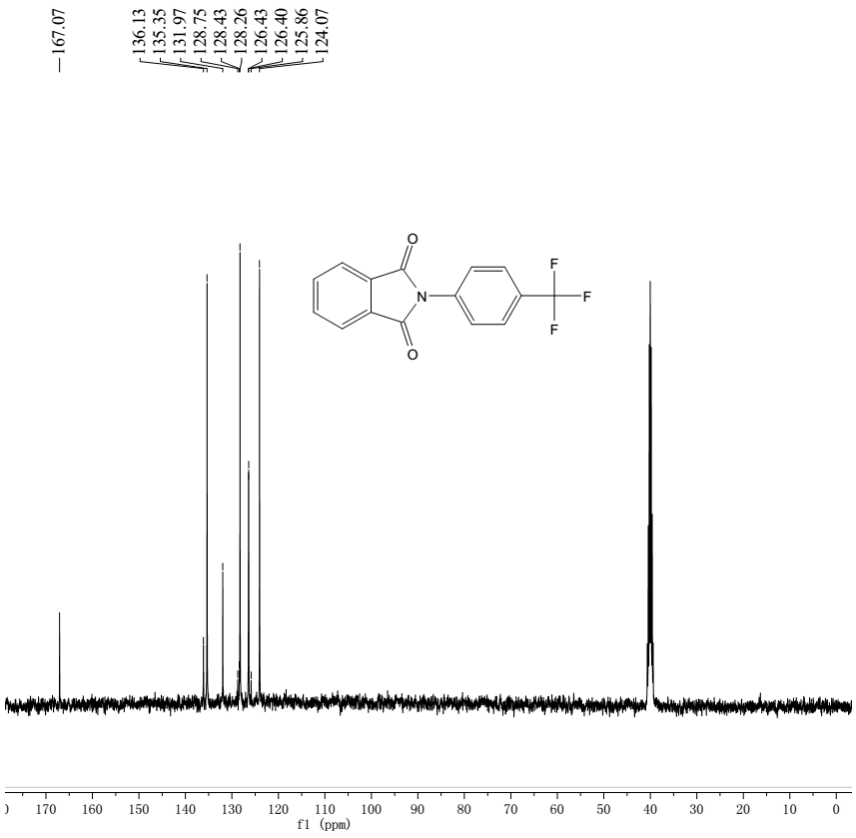



***Figure S16.*** $^{13}$C NMR spectrum of compound **8a**.

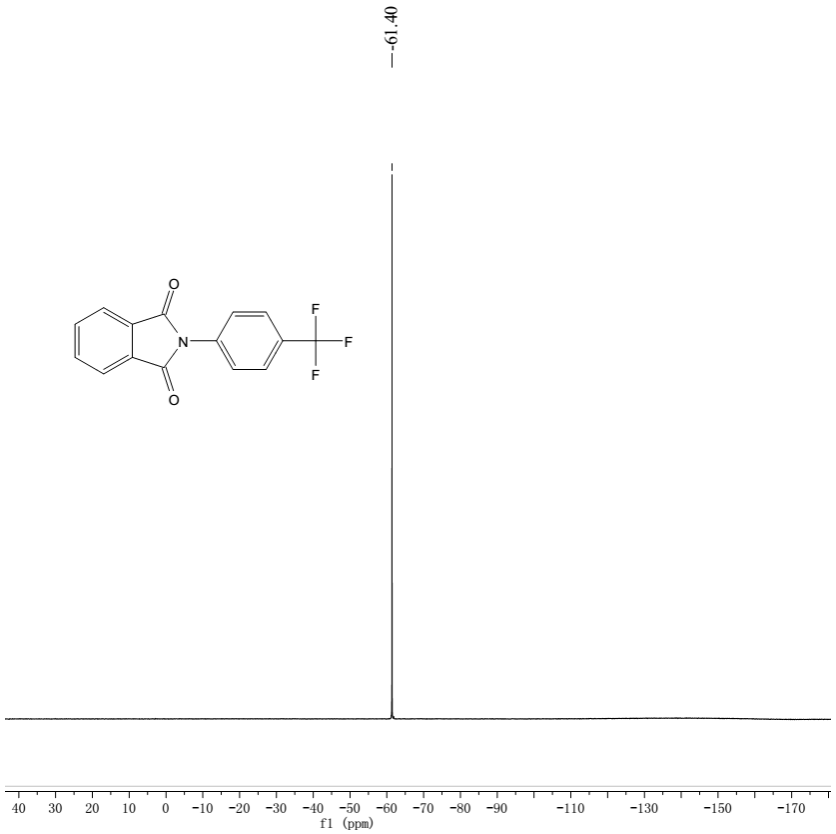



***Figure S17.*** $^{19}$F NMR spectrum of compound **8a**.

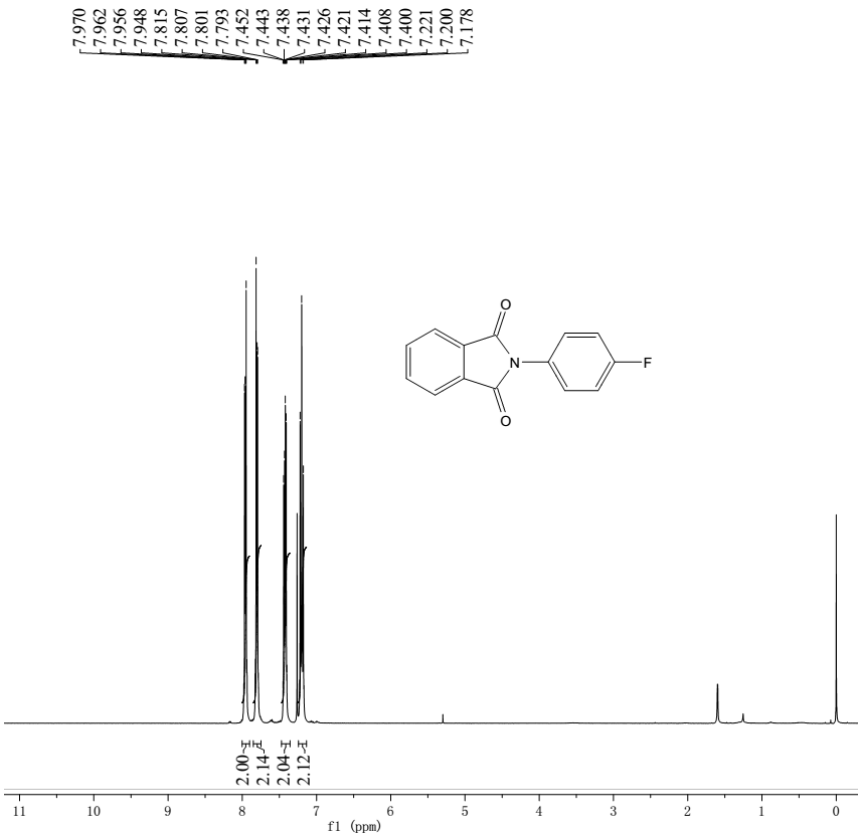



***Figure S18.*** $^{1}$H NMR spectrum of compound **8b**.

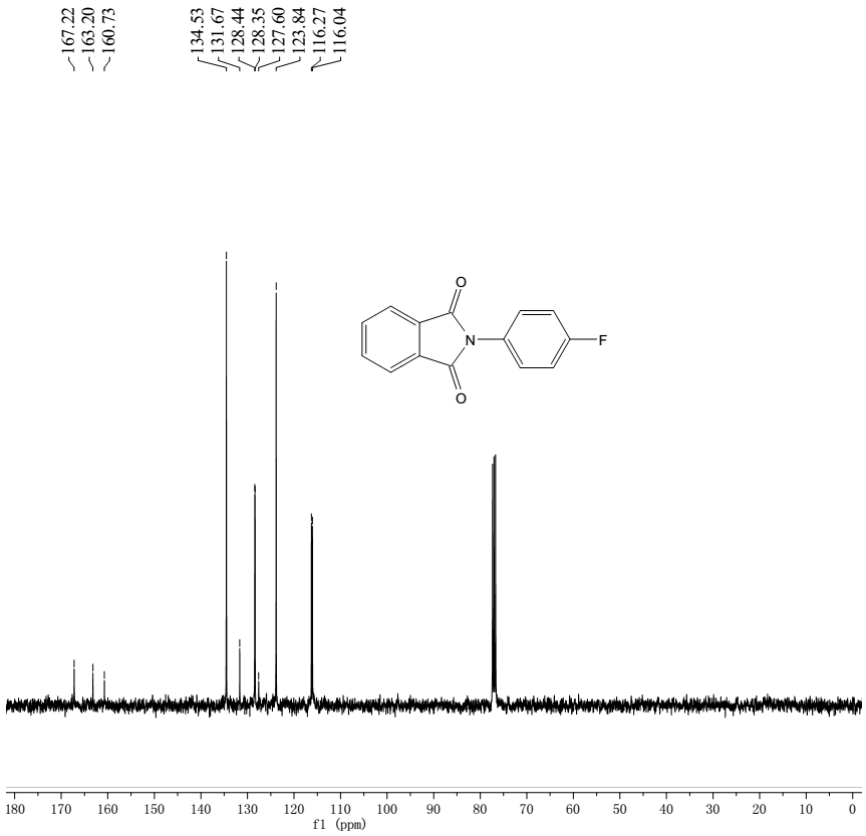



***Figure S19.*** $^{13}$C NMR spectrum of compound **8b**.

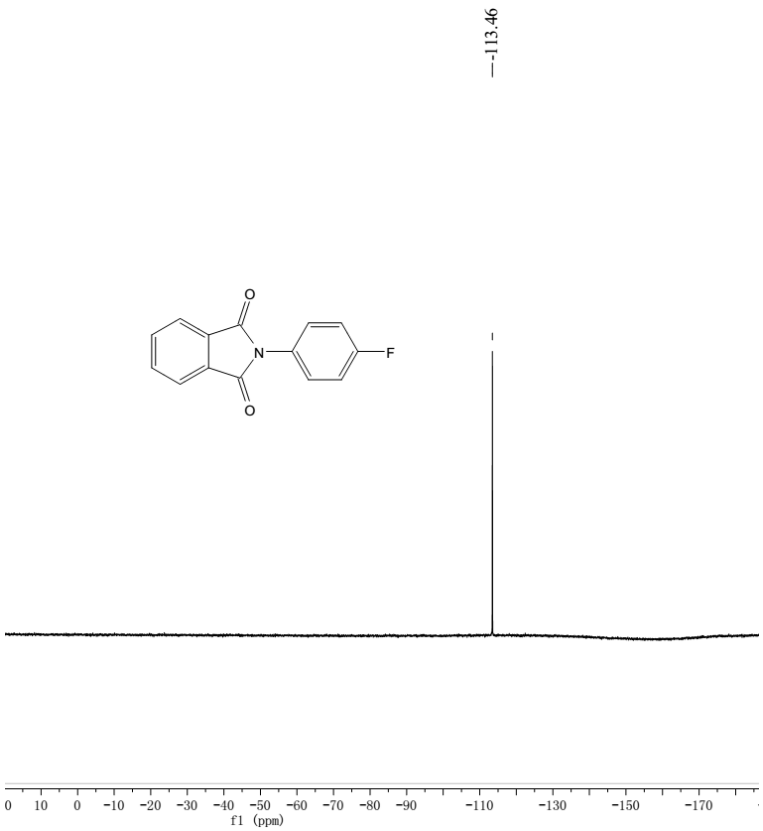



***Figure S20.*** $^{19}$F NMR spectrum of compound **8b**.

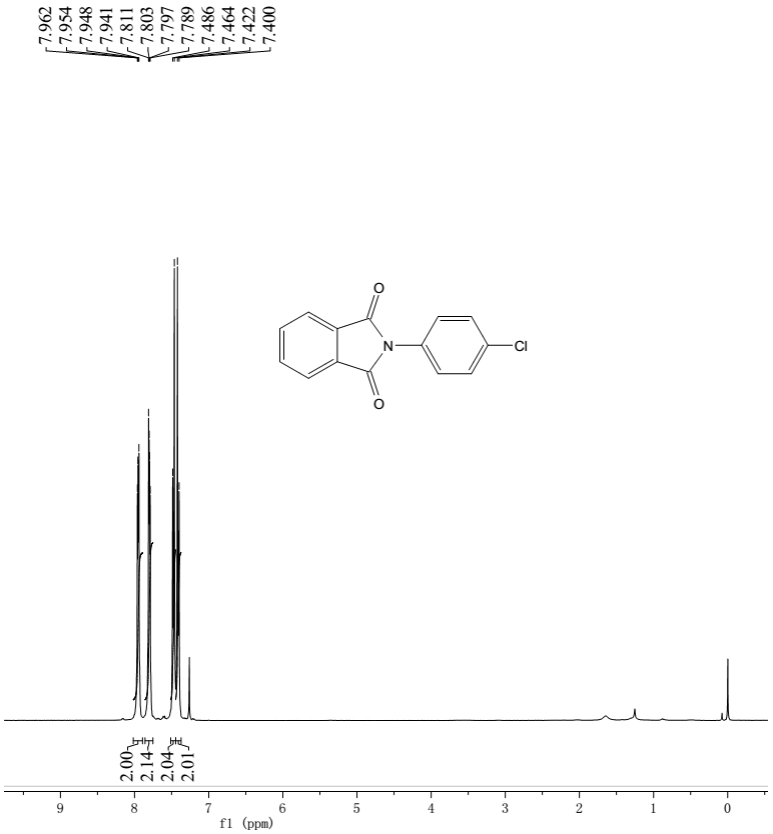



***Figure S21.*** $^{1}$H NMR spectrum of compound **9a**.

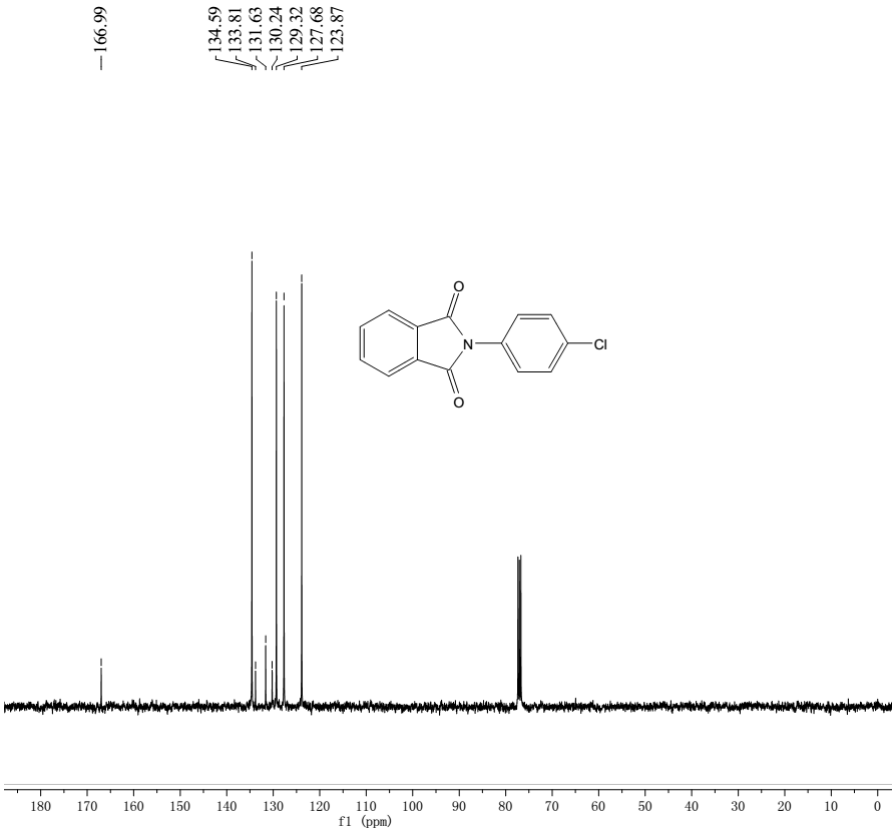



***Figure S22.*** $^{13}$C NMR spectrum of compound **9a**.

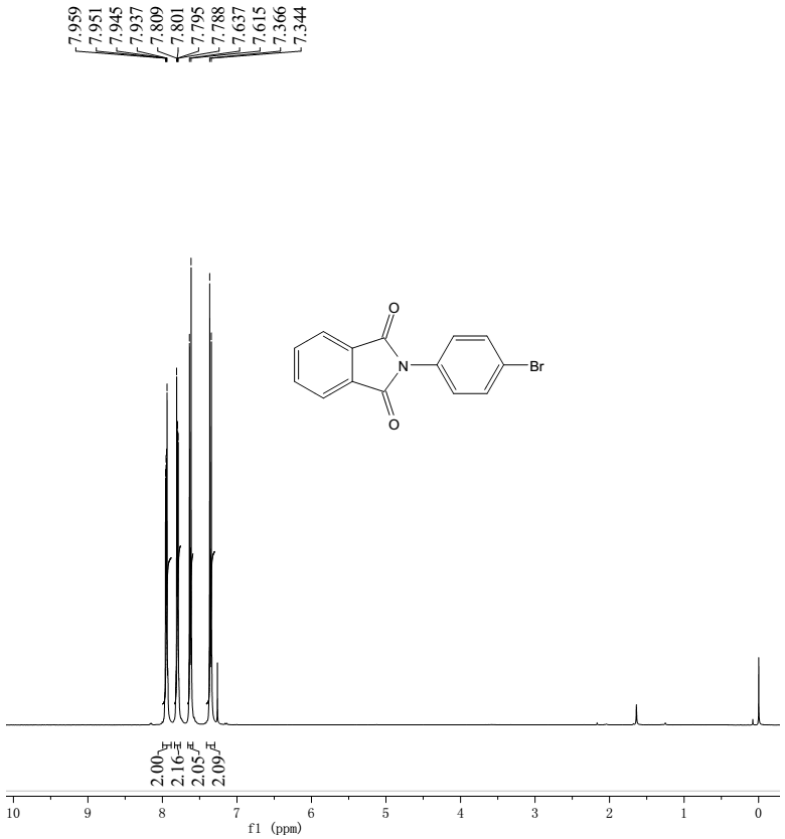



***Figure S23.*** $^{1}$H NMR spectrum of compound **9b**.

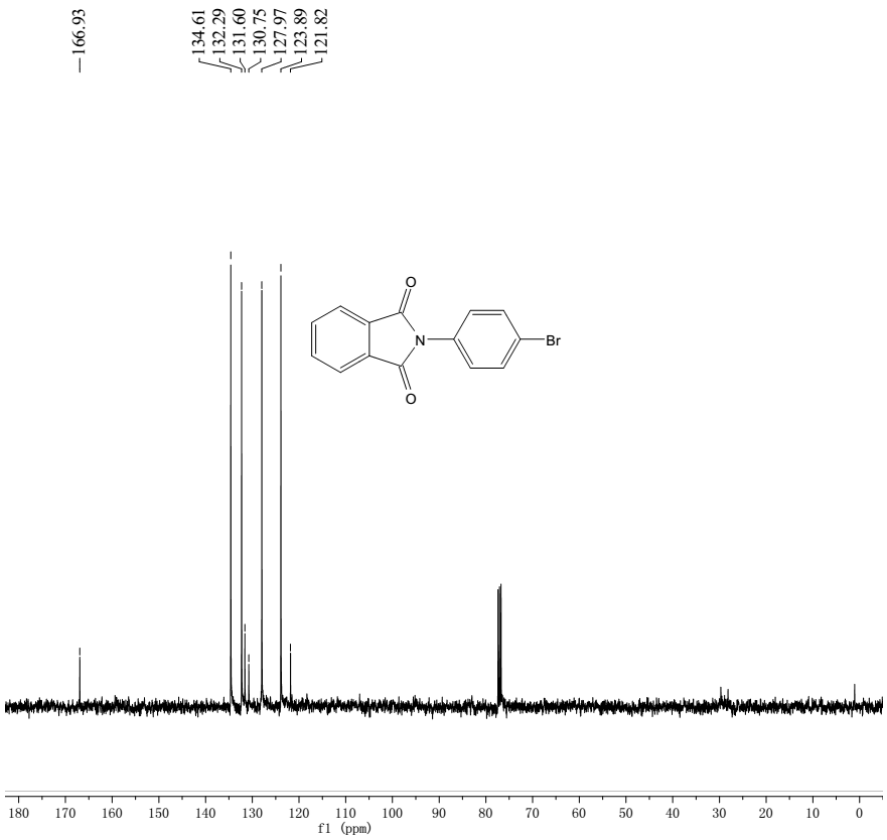



***Figure S24.*** $^{13}$C NMR spectrum of compound **9b**.

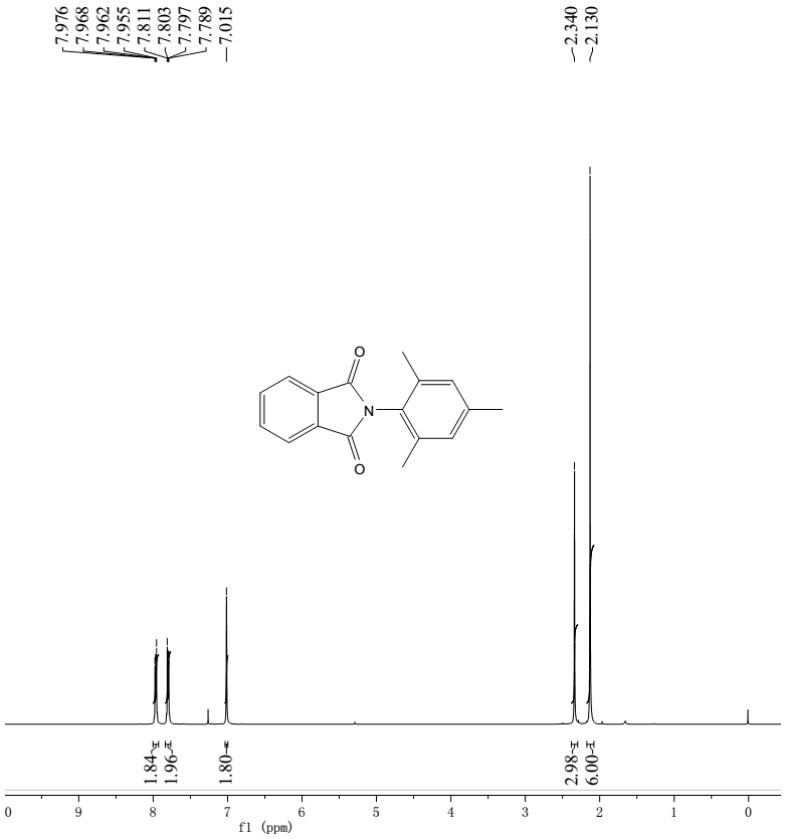



***Figure S25.*** $^{1}$H NMR spectrum of compound **10**.

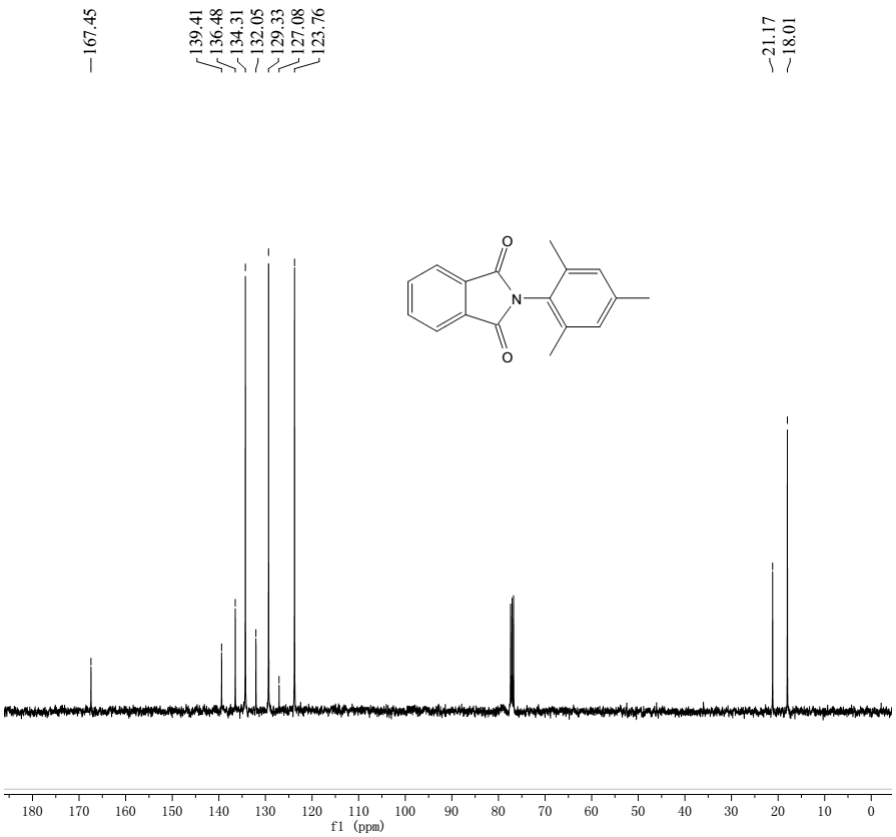



***Figure S26.*** $^{13}$C NMR spectrum of compound **10**.

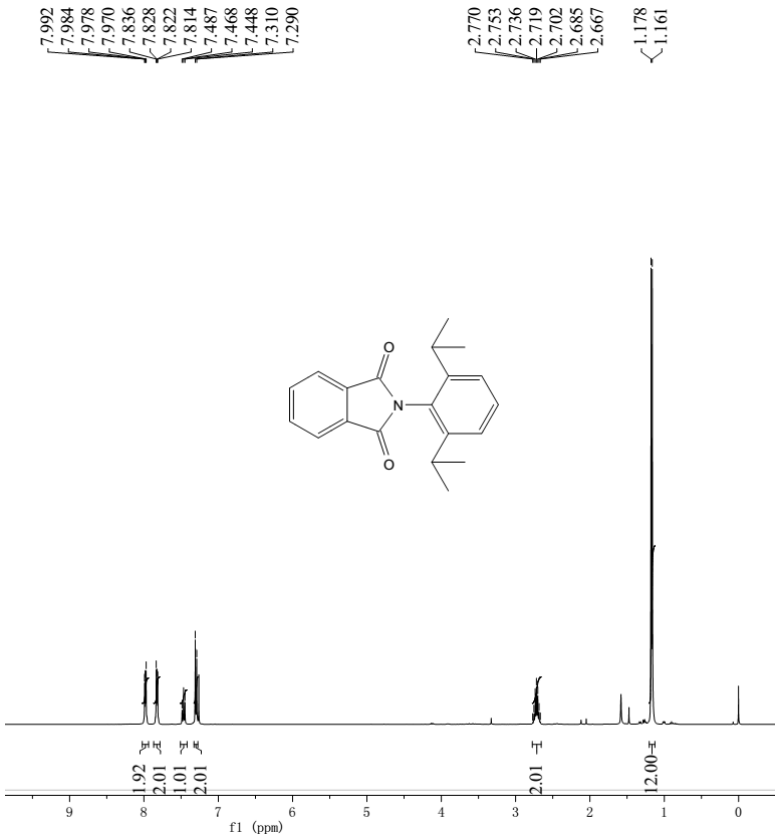



***Figure S27.*** $^{1}$H NMR spectrum of compound **11**.

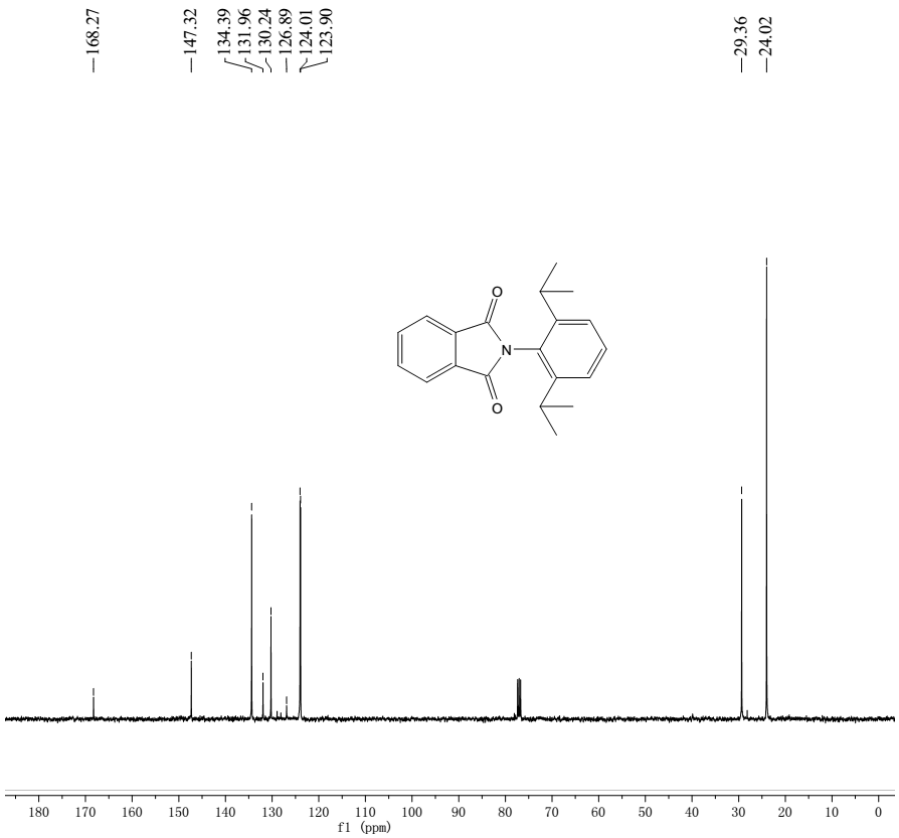



***Figure S28.*** $^{13}$C NMR spectrum of compound **11**.

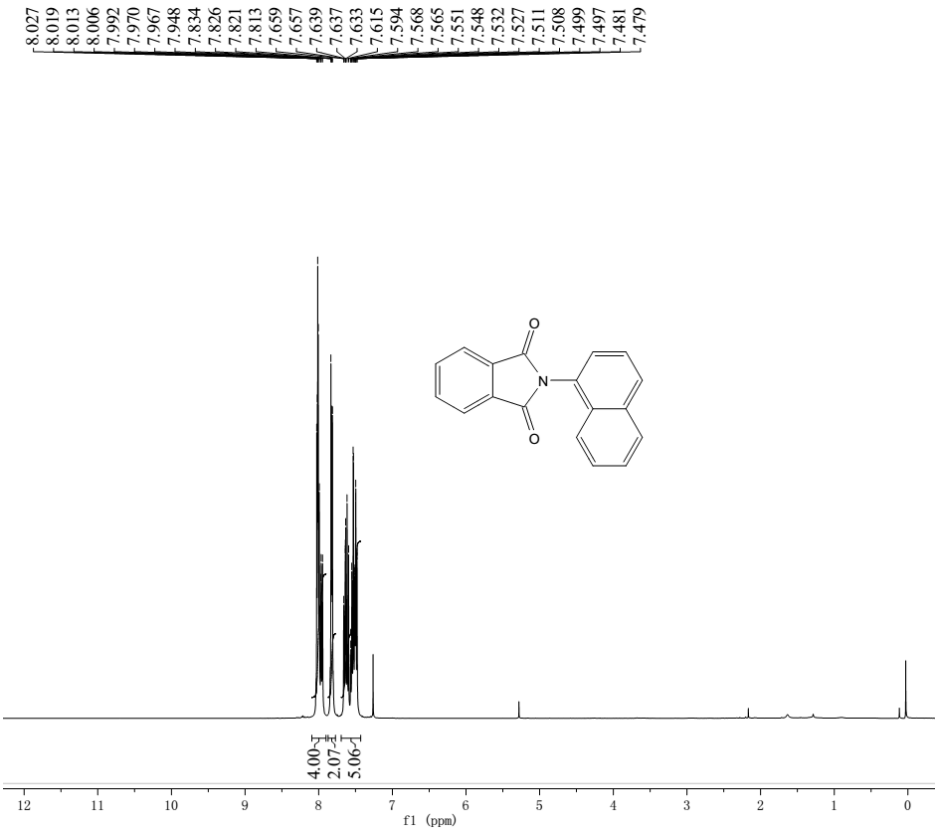



***Figure S29.*** $^{1}$H NMR spectrum of compound **12**.

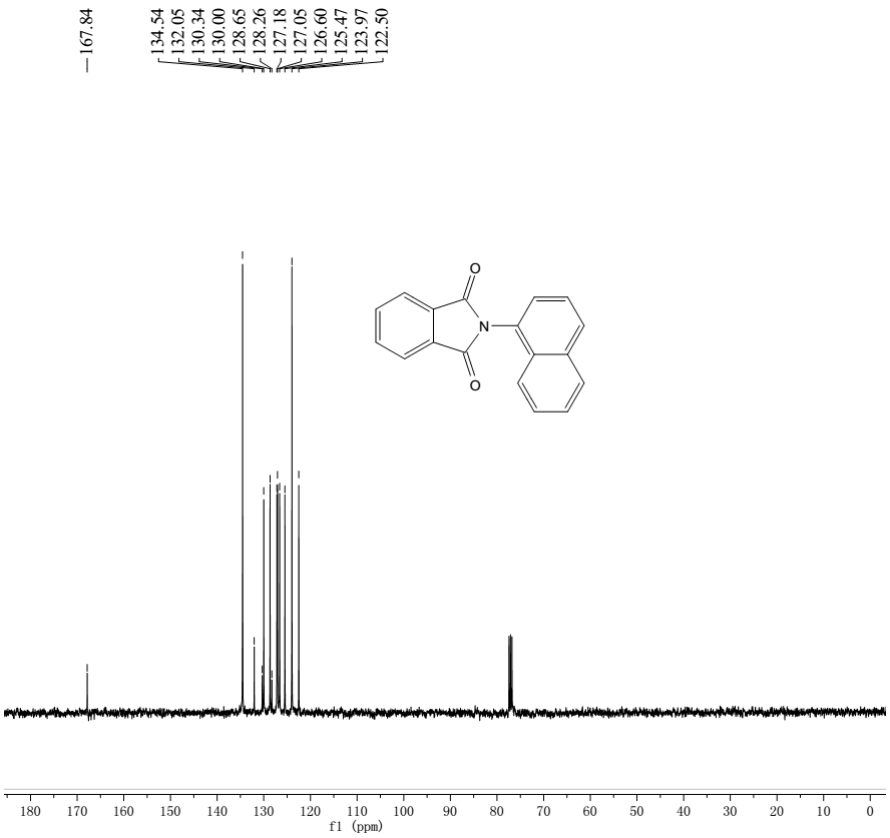



***Figure S30.*** $^{13}$C NMR spectrum of compound **12**.

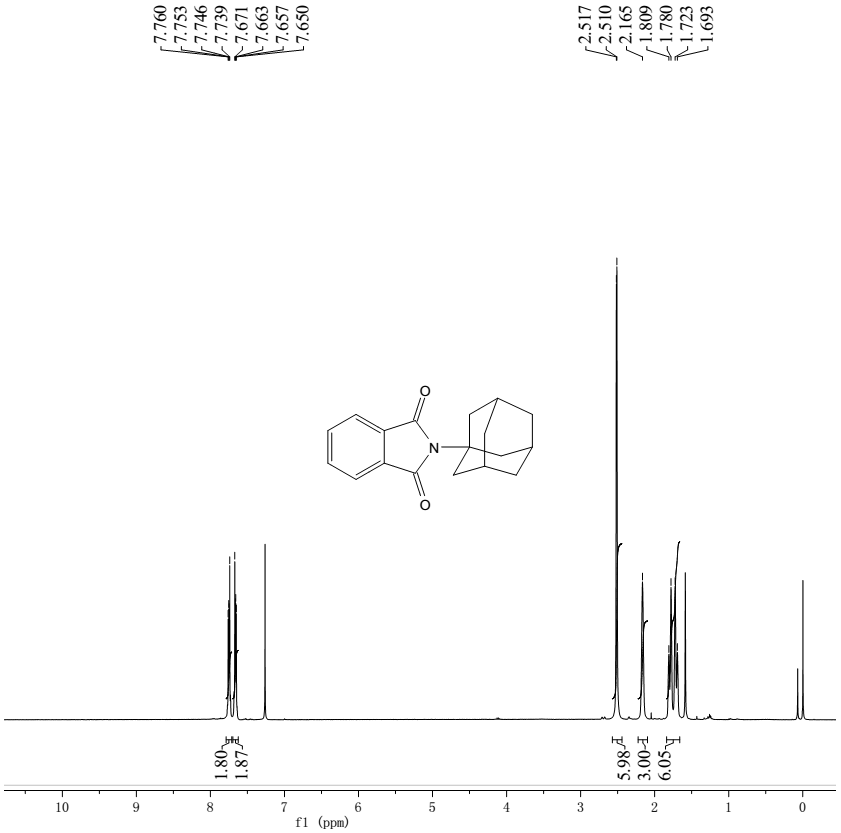



***Figure S31.*** $^{1}$H NMR spectrum of compound **13**.

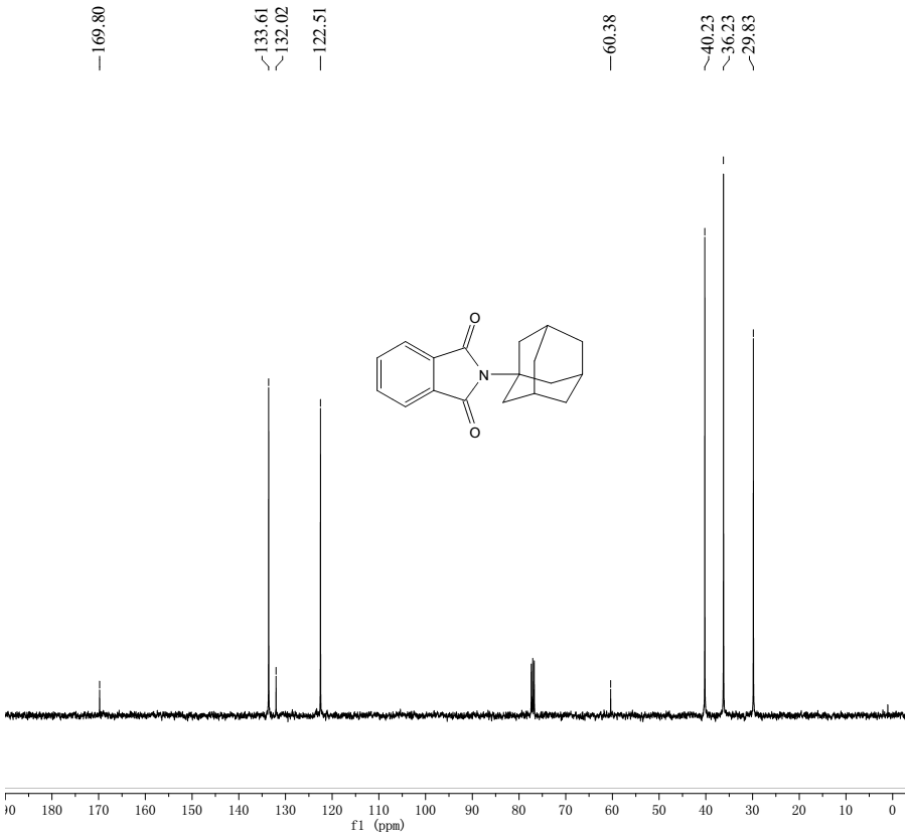



***Figure S32.*** $^{13}$C NMR spectrum of compound **13**.

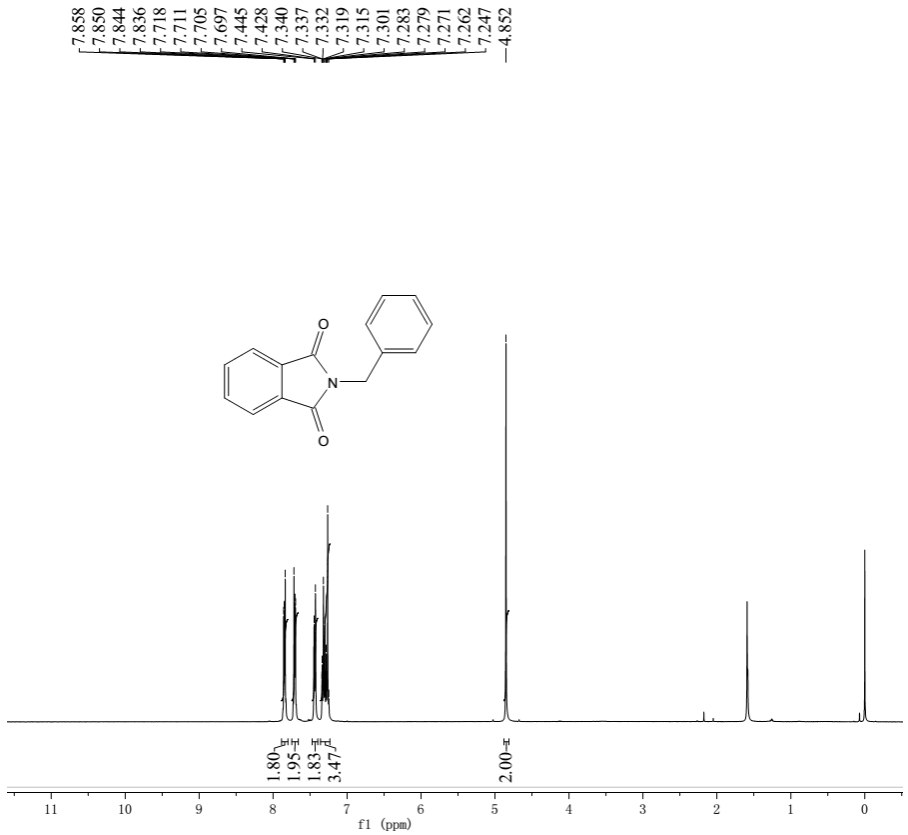



***Figure S33.*** $^{1}$H NMR spectrum of compound **14**.

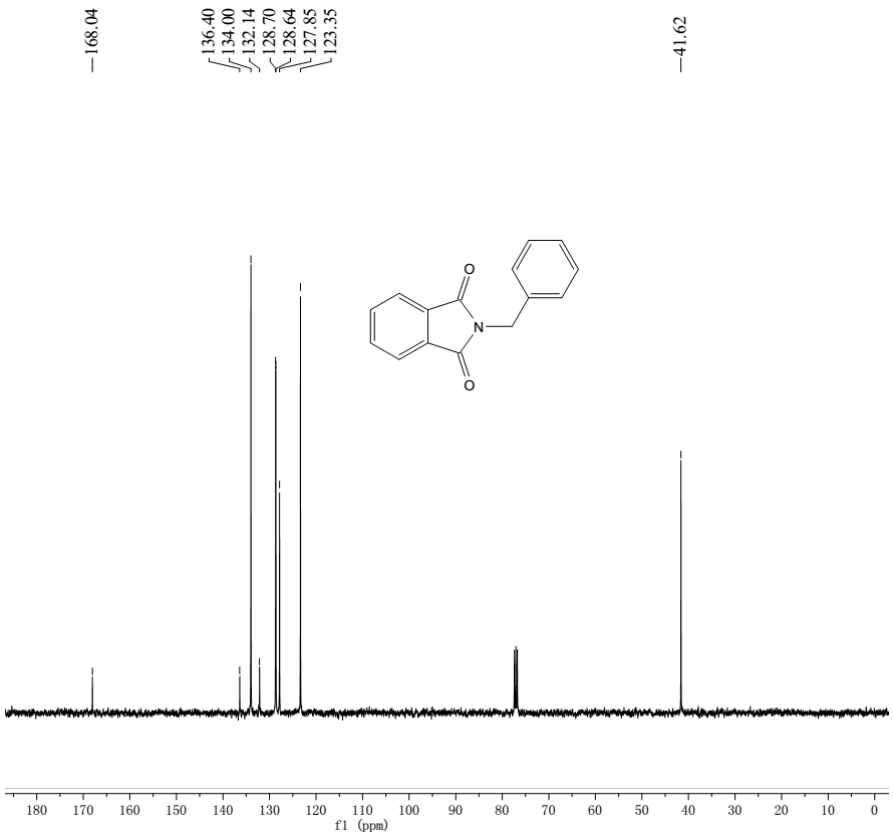



***Figure S34.*** $^{13}$C NMR spectrum of compound **14**.

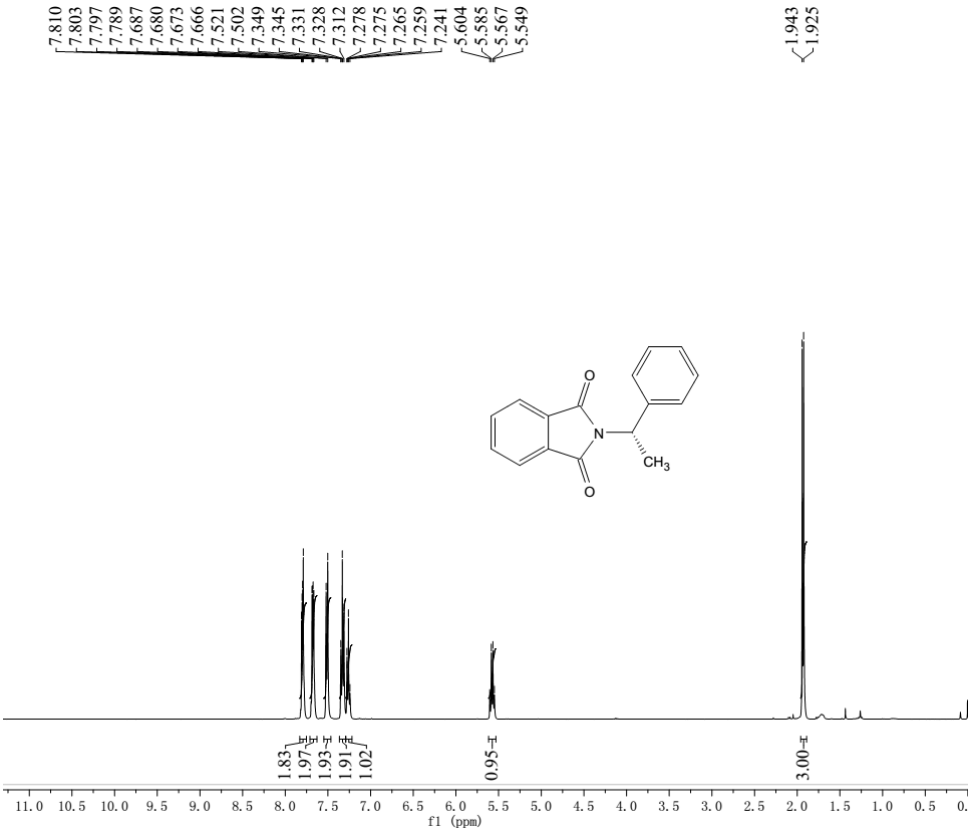



***Figure S35.*** $^{1}$H NMR spectrum of compound **15** (*s*).

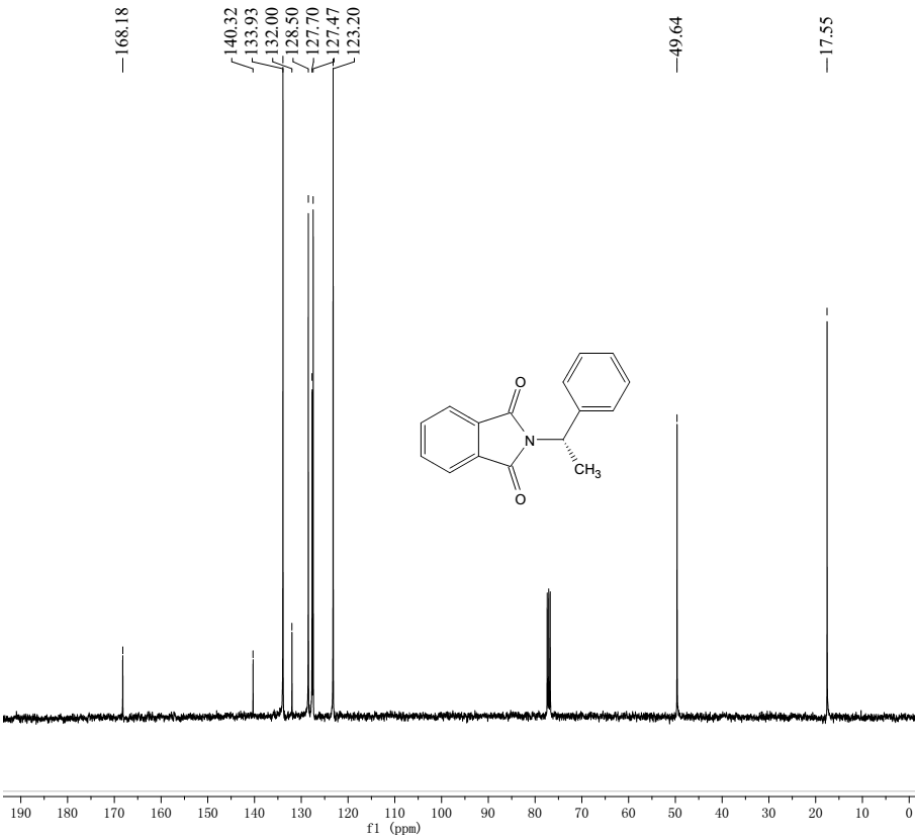



***Figure S36.*** $^{13}$C NMR spectrum of compound **15** (*s*).

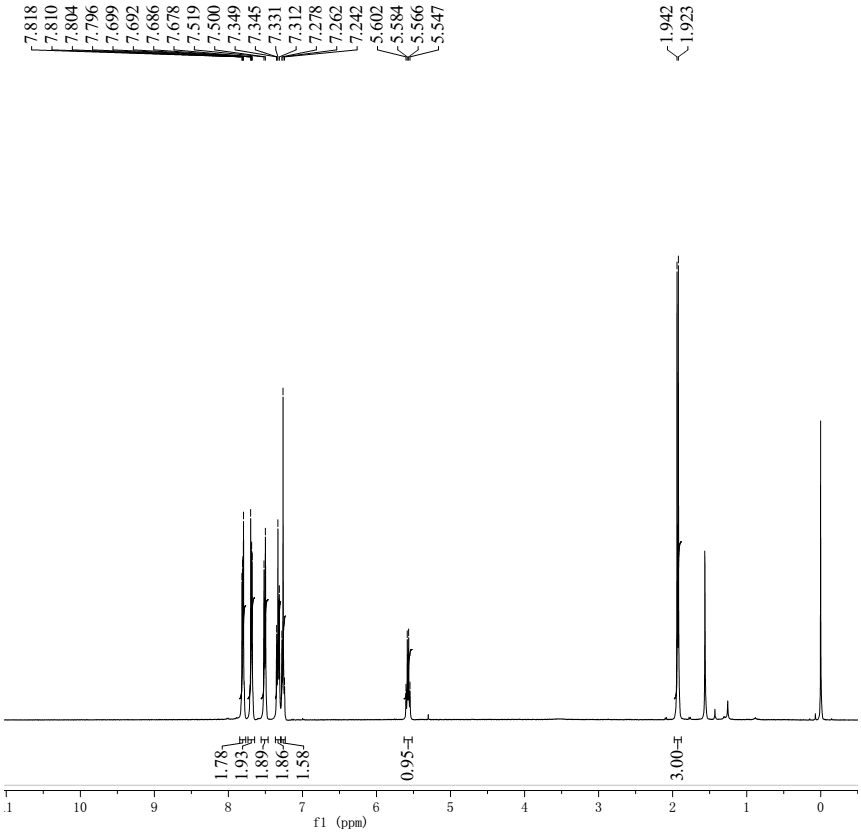



***Figure S37.*** $^{1}$H NMR spectrum of compound **15** (*rac*).

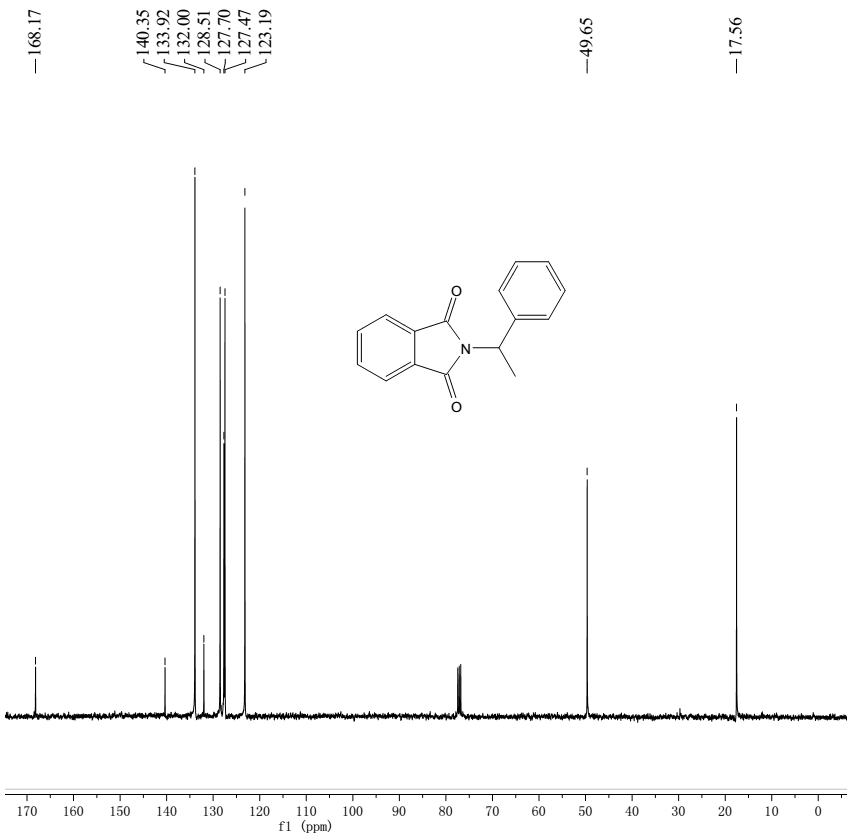



***Figure S38.*** $^{13}$C NMR spectrum of compound **15** (*rac*).

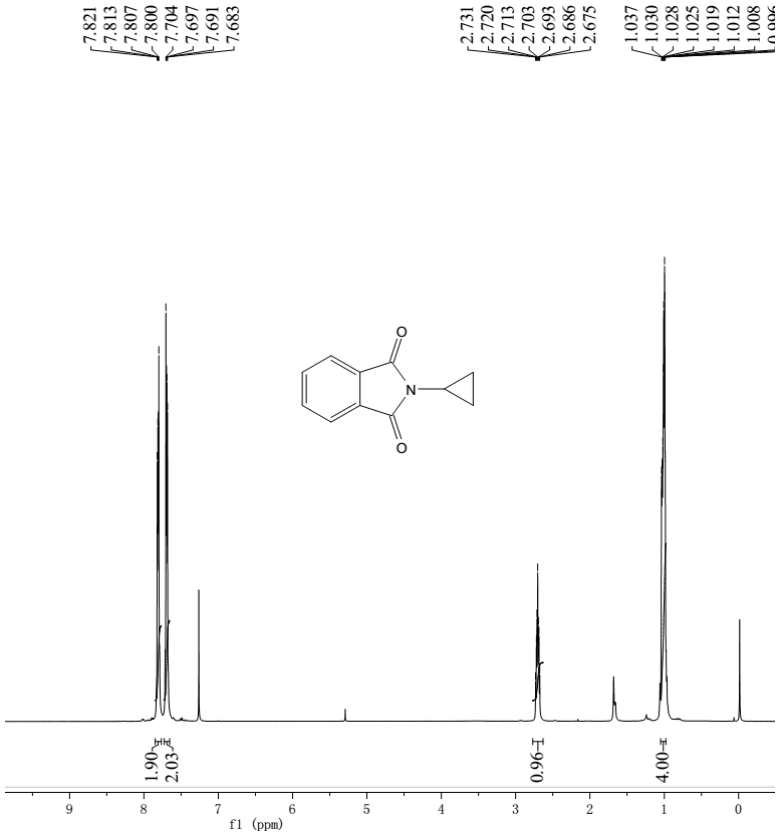



***Figure S39.*** $^{1}$H NMR spectrum of compound **16**.

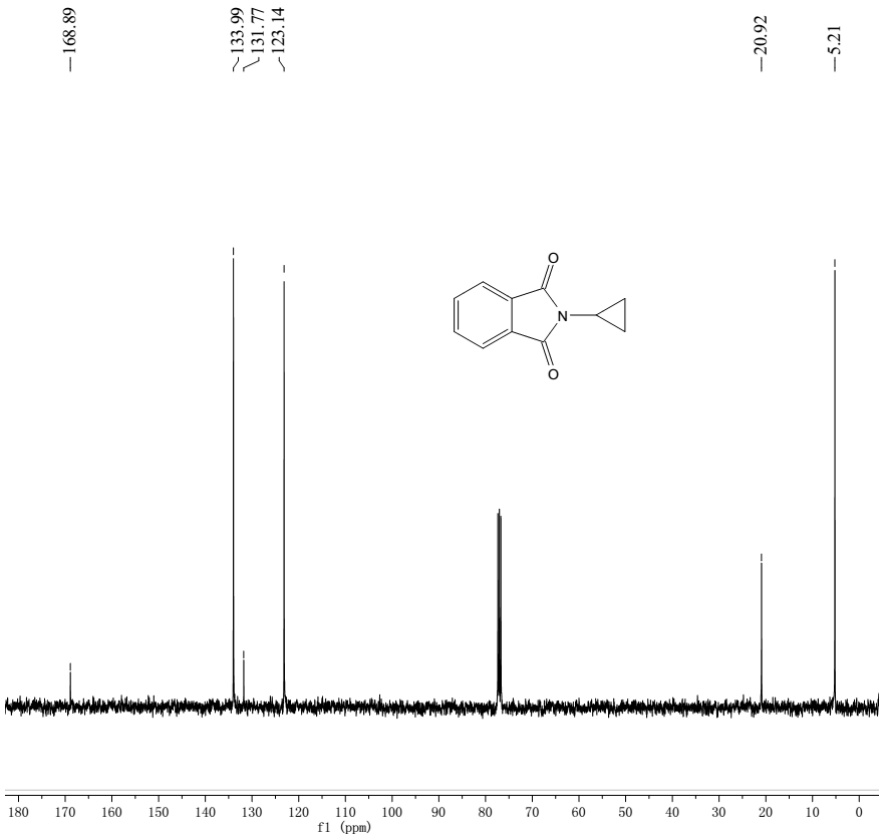



***Figure S40.*** $^{13}$C NMR spectrum of compound **16**.

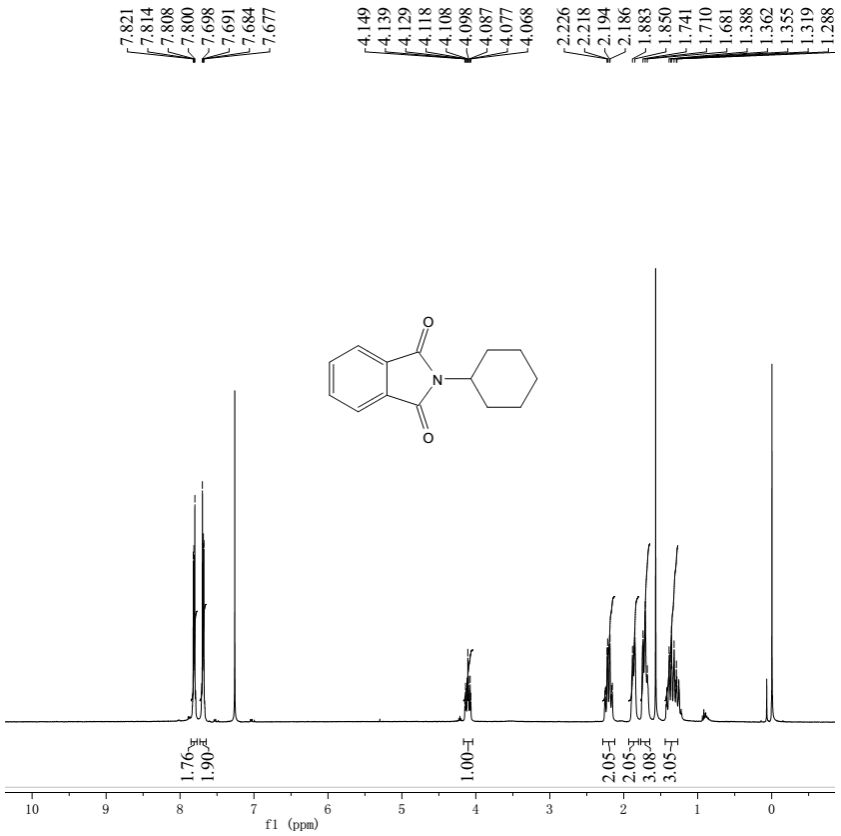



***Figure S41.*** $^{1}$H NMR spectrum of compound **17**.

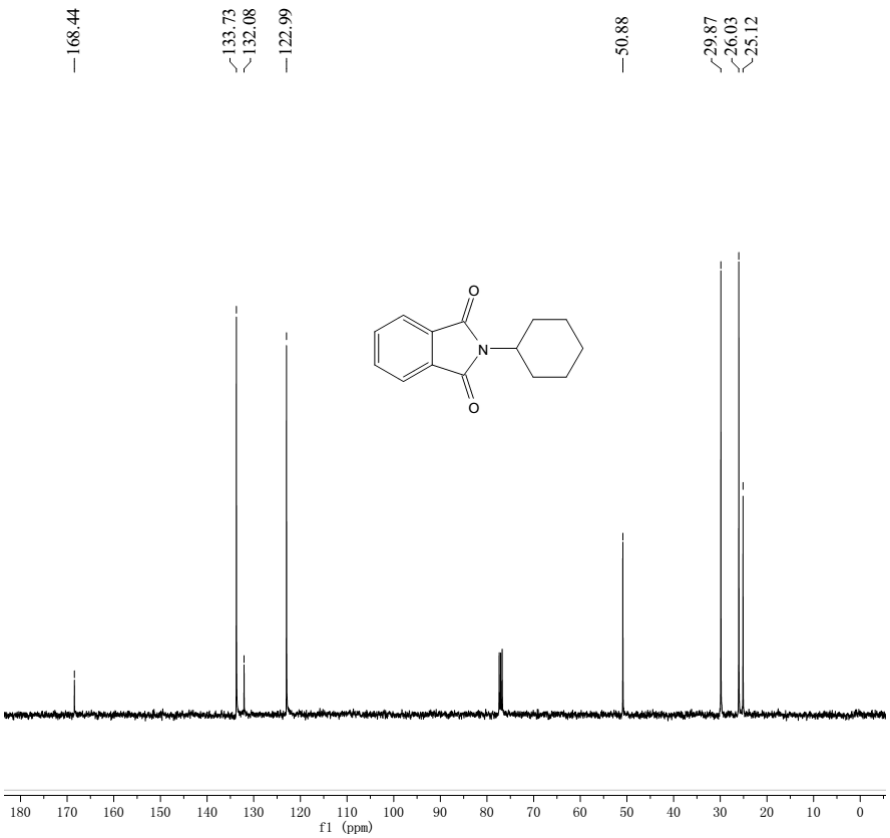



***Figure S42.*** $^{13}$C NMR spectrum of compound **17**.

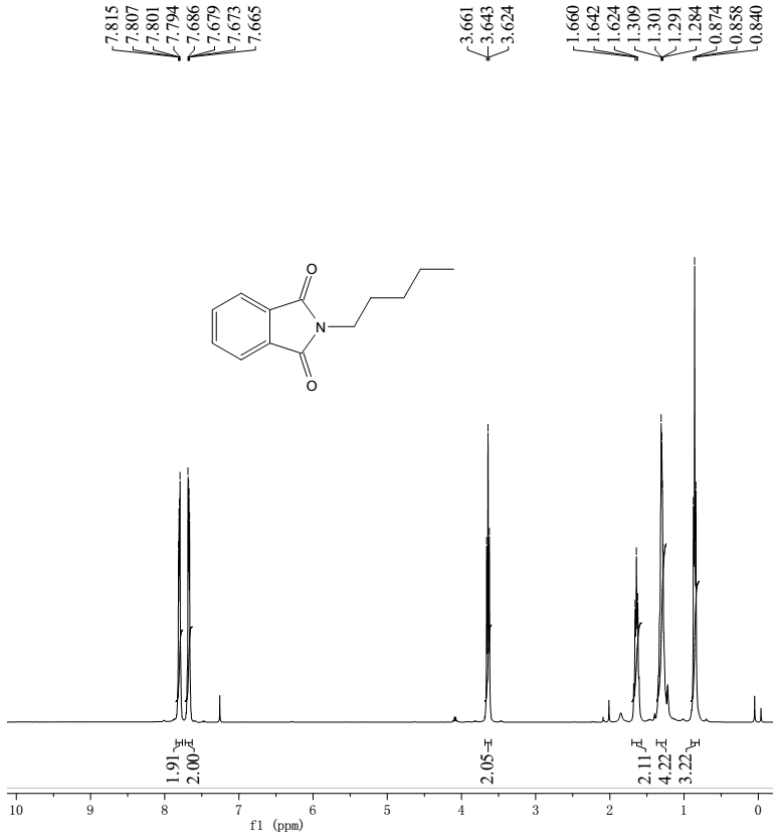



***Figure S43.*** $^{1}$H NMR spectrum of compound **18**.

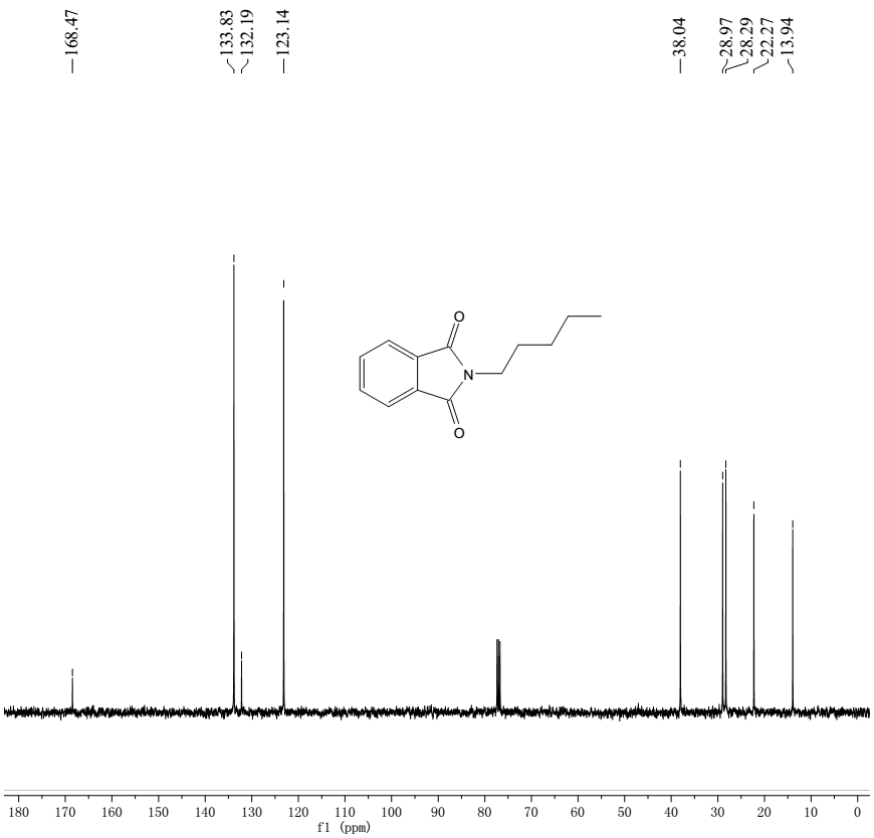



***Figure S44.*** $^{13}$C NMR spectrum of compound **18**.

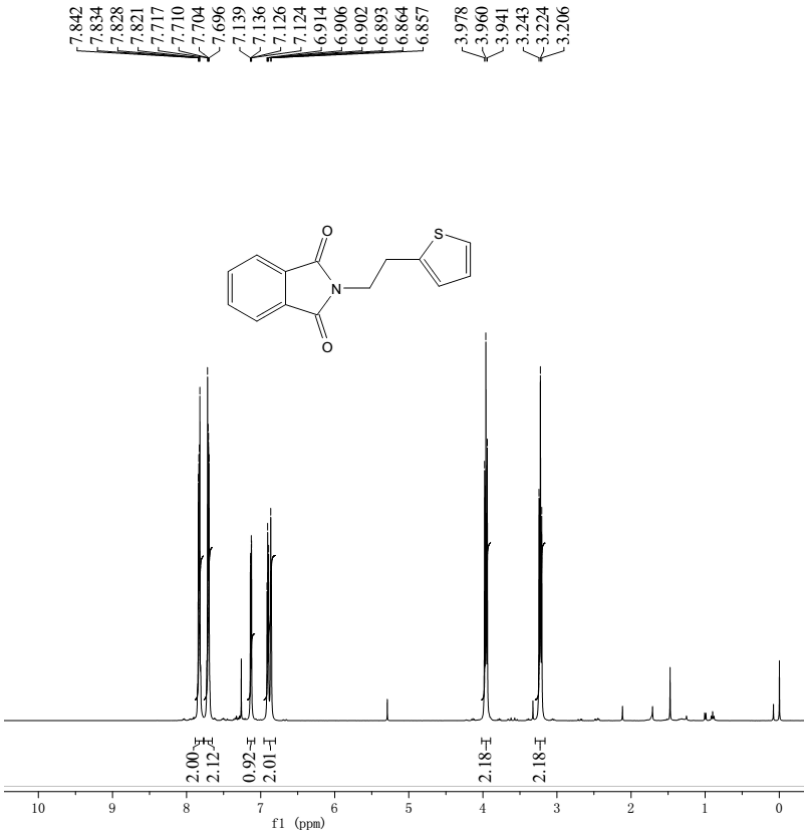



***Figure S45.*** $^{1}$H NMR spectrum of compound **19**.

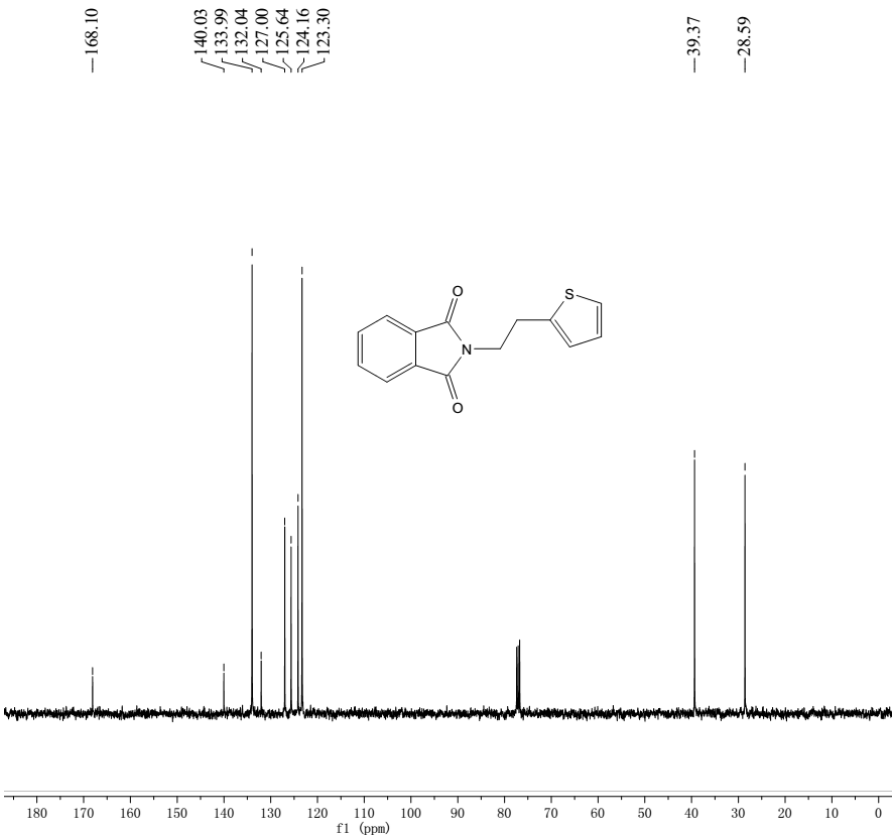



***Figure S46.*** $^{13}$C NMR spectrum of compound **19**.

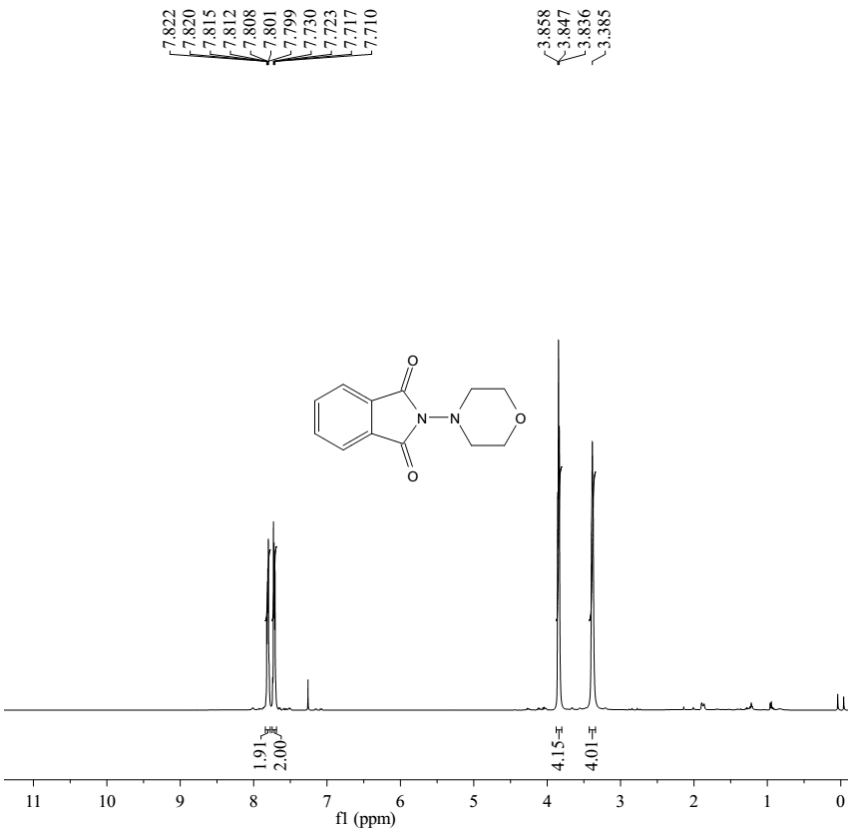



***Figure S47.*** $^{1}$H NMR spectrum of compound **20**.

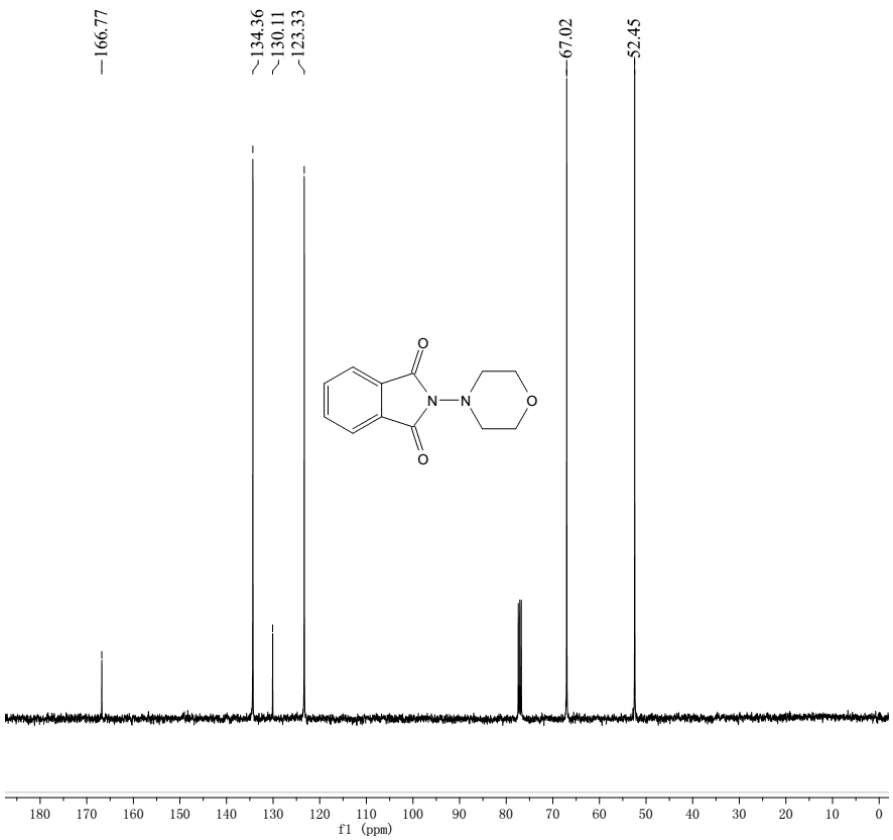



***Figure S48.*** $^{13}$C NMR spectrum of compound **20**.

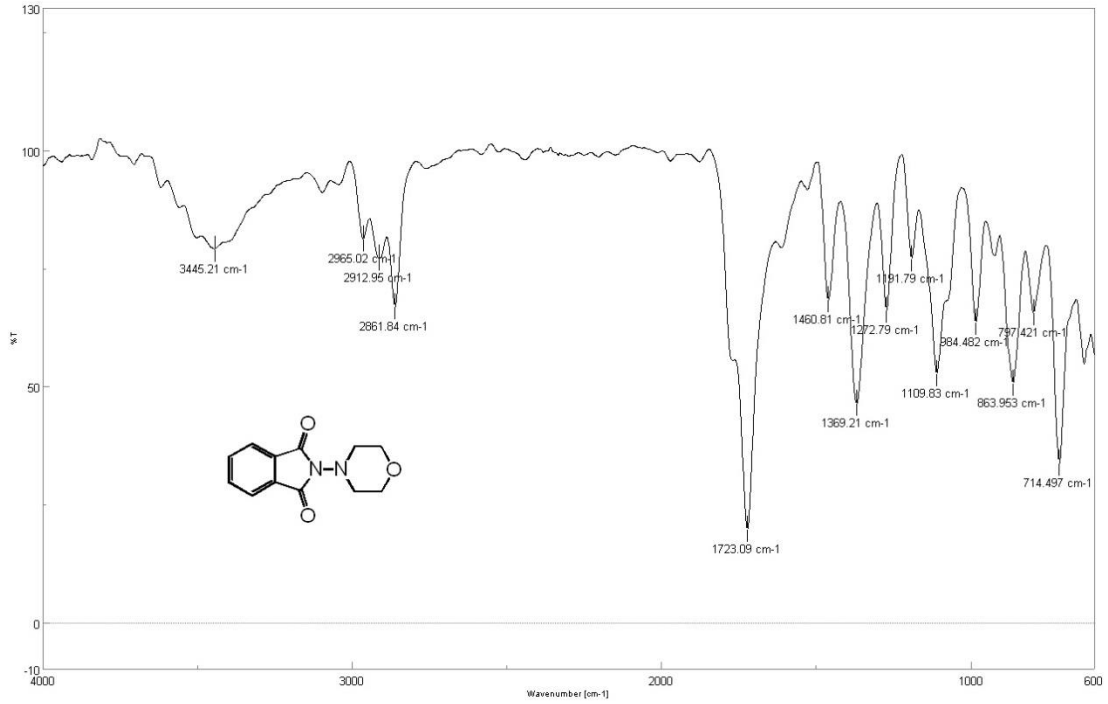



***Figure S49.*** IR spectrum of compound **20**.

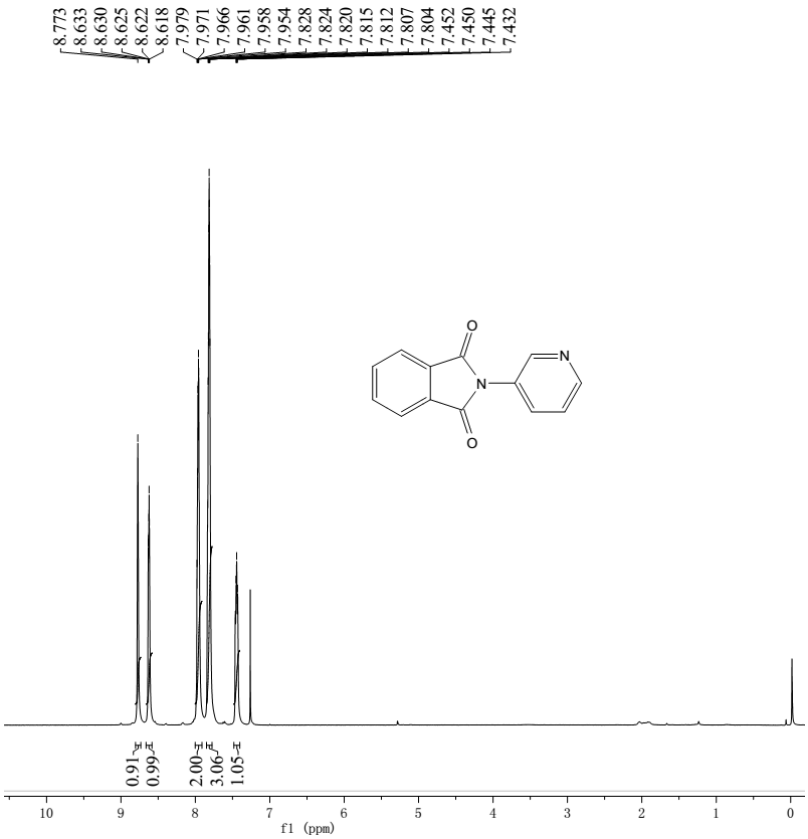



***Figure S50.*** $^{1}$H NMR spectrum of compound **21**

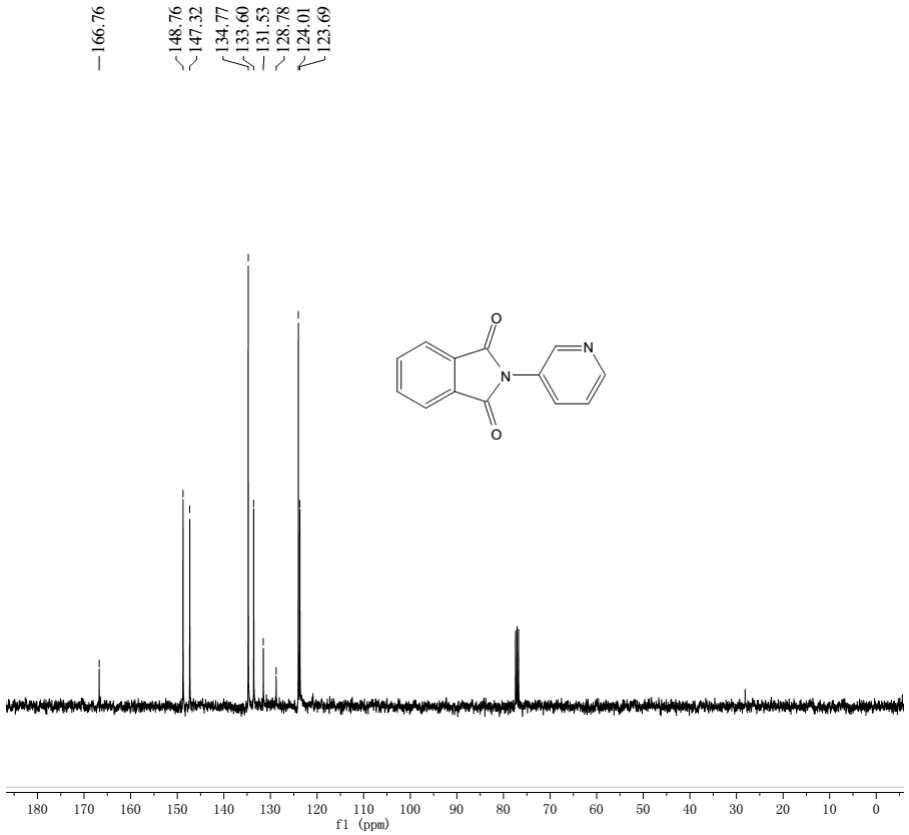



***Figure S51.*** $^{13}$C NMR spectrum of compound **21**

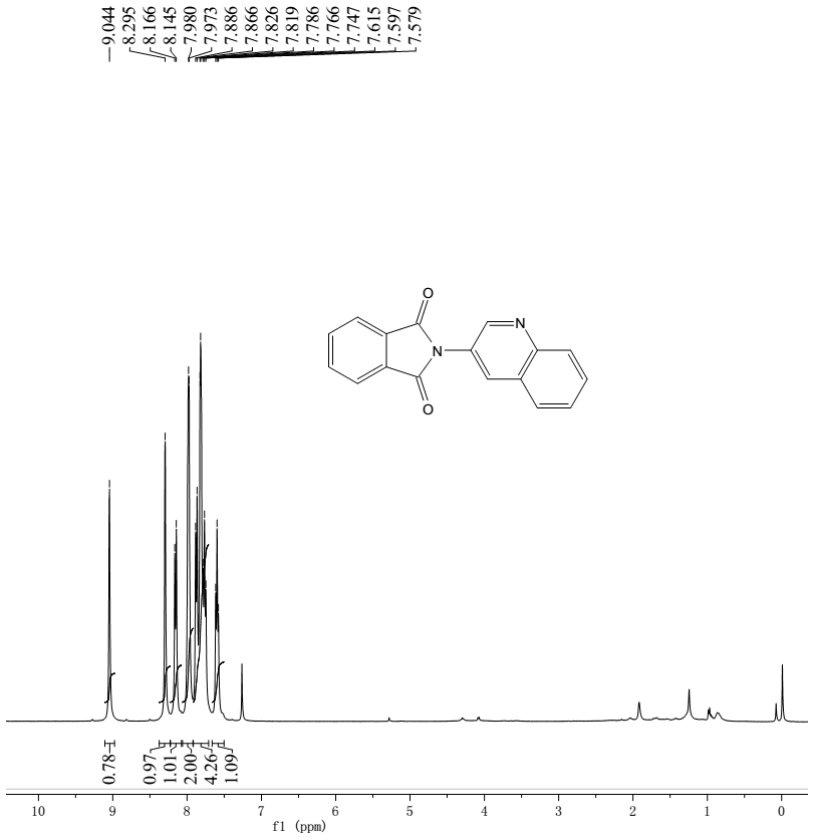



***Figure S52.*** $^{1}$H NMR spectrum of compound **22**.

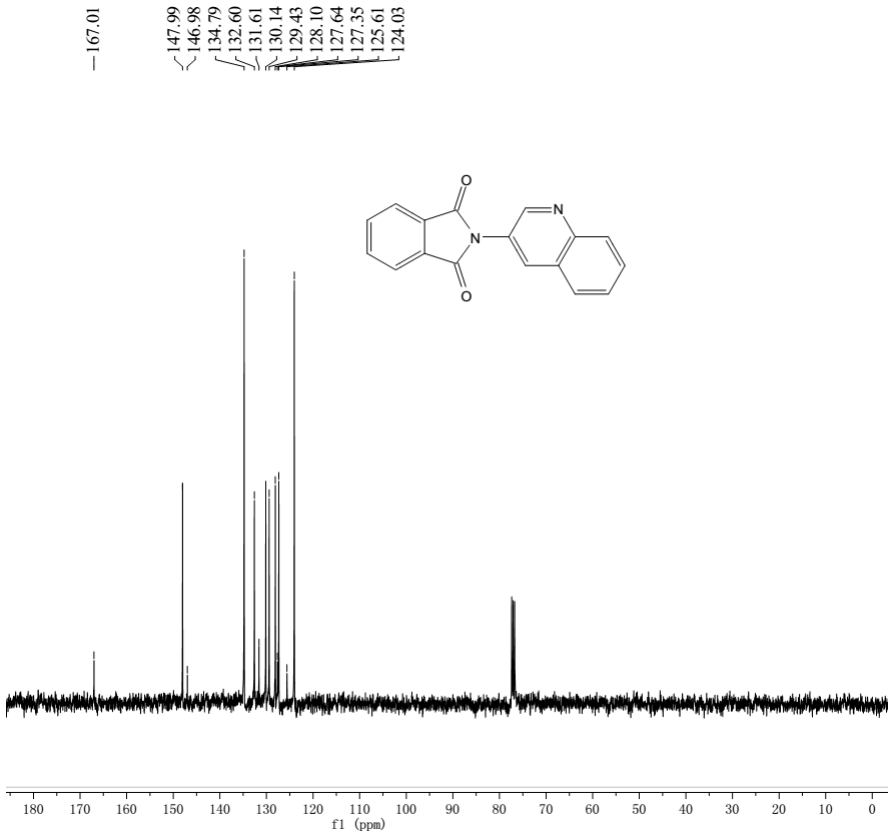



***Figure S53.*** $^{13}$C NMR spectrum of compound **22**.

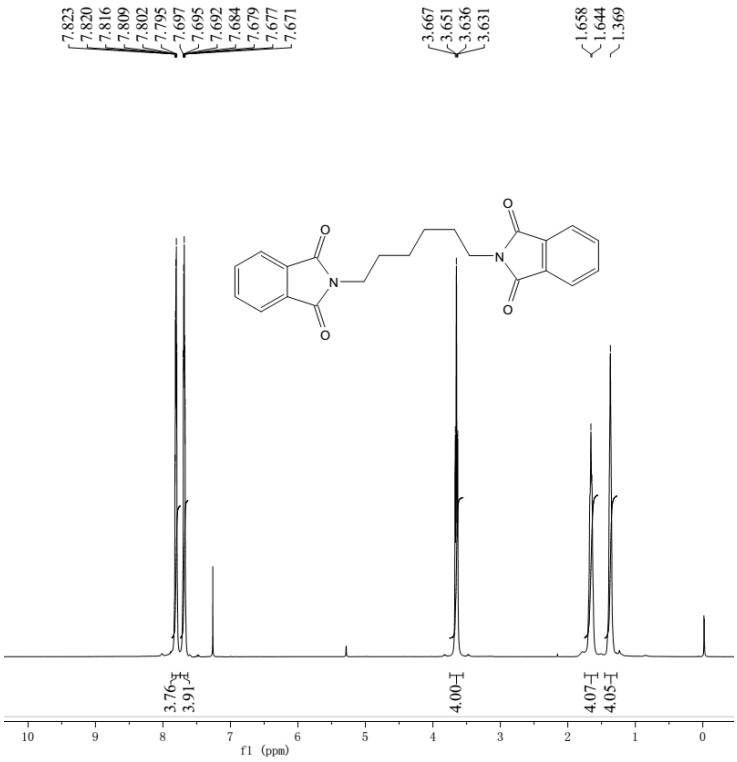



***Figure S54.*** $^{1}$H NMR spectrum of compound **23**.

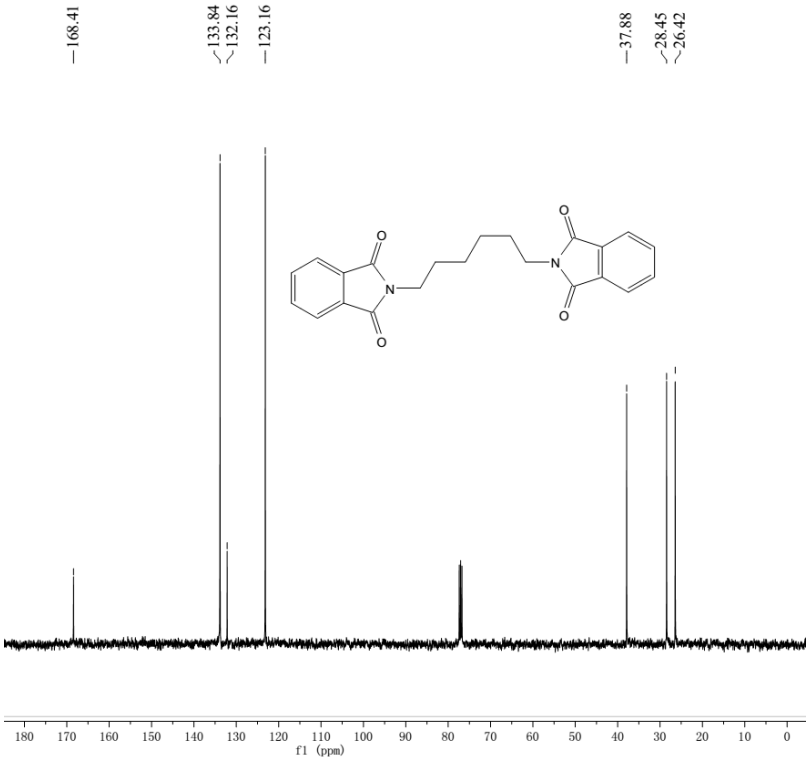



***Figure S55.*** $^{13}$C NMR spectrum of compound **23**.

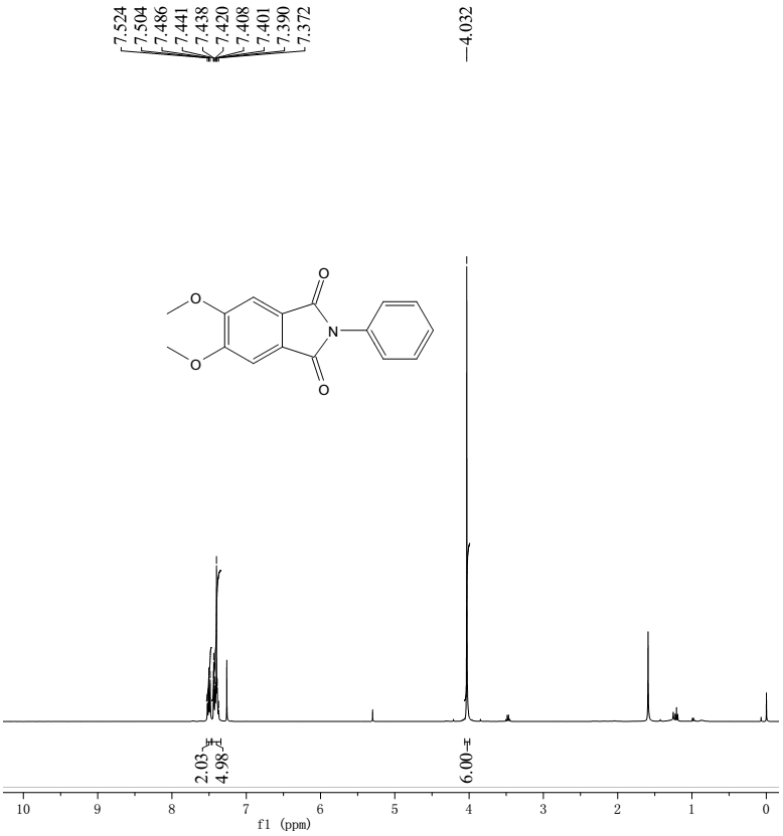



***Figure S56.*** $^{1}$H NMR spectrum of compound **24**.

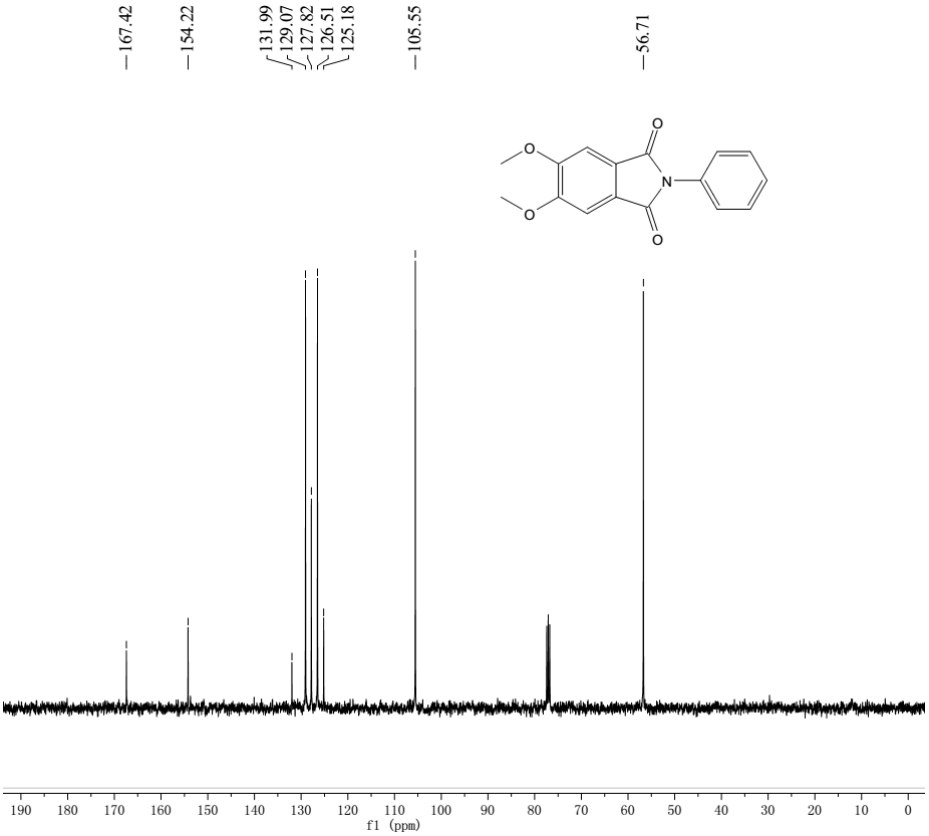



***Figure S57.*** $^{13}$C NMR spectrum of compound **24**.

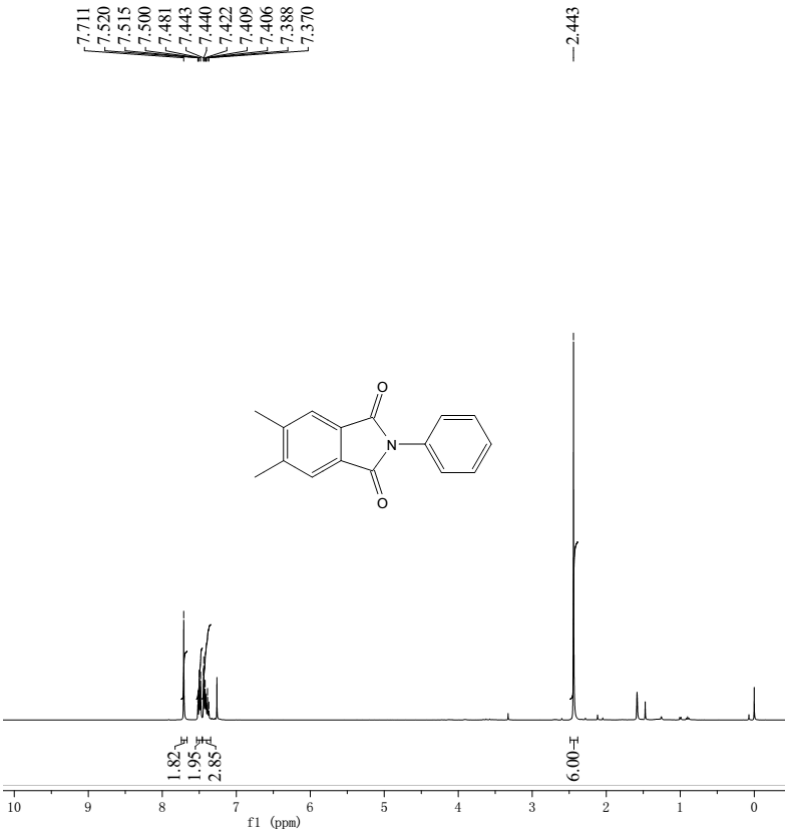



***Figure S58.*** $^{1}$H NMR spectrum of compound **25**.

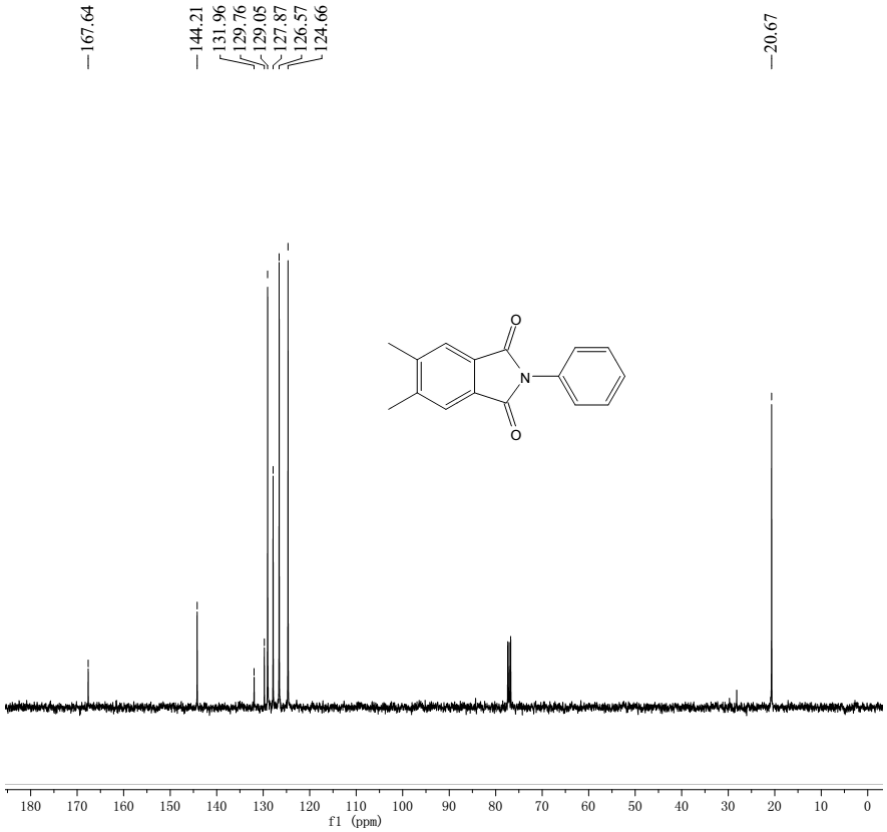



***Figure S59.*** $^{13}$C NMR spectrum of compound **25**.

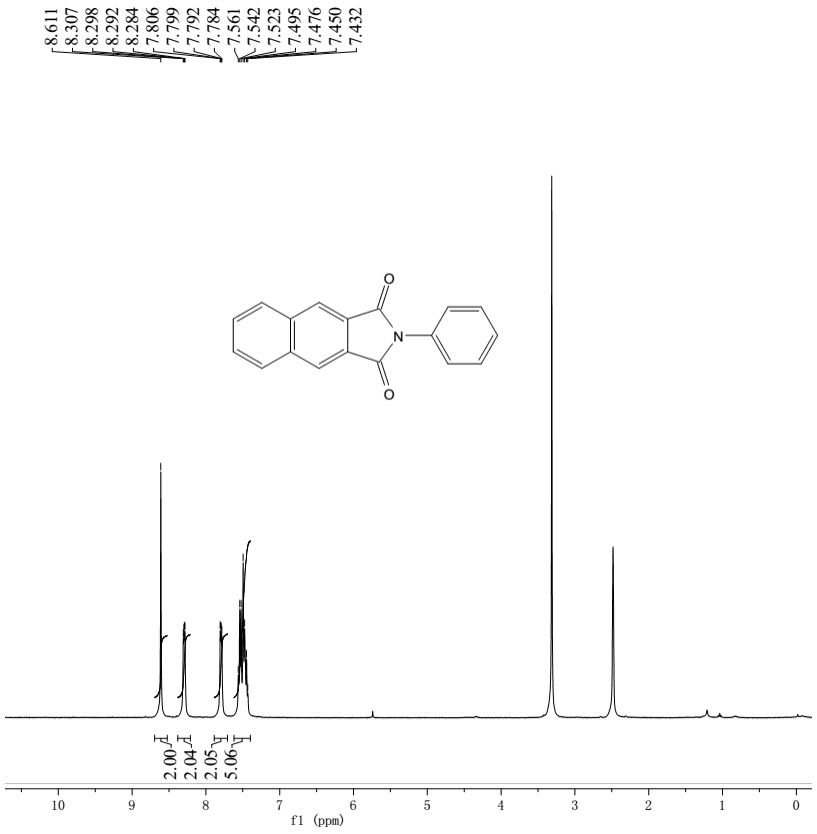



***Figure S60.*** $^{1}$H NMR spectrum of compound **26**.

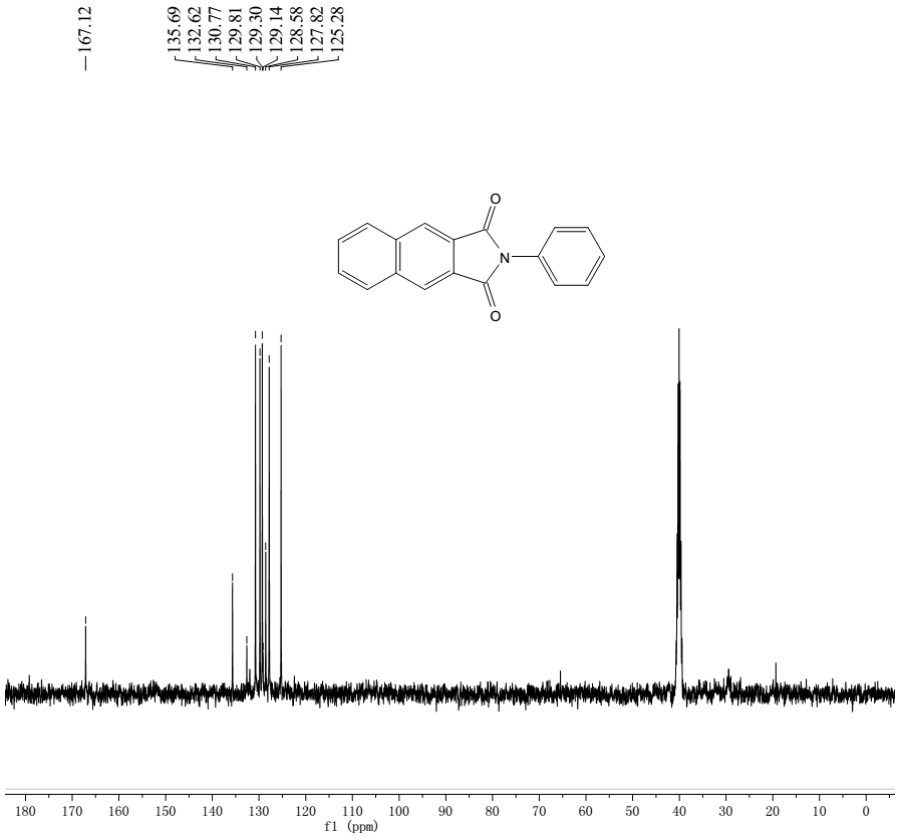



***Figure S61.*** $^{13}$C NMR spectrum of compound **26**.

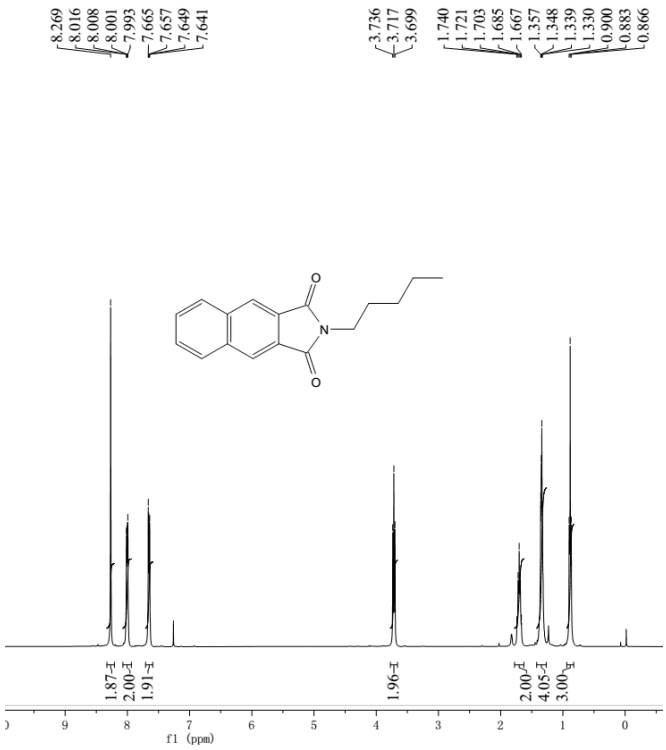



***Figure S62.*** $^{1}$H NMR spectrum of compound **27**.

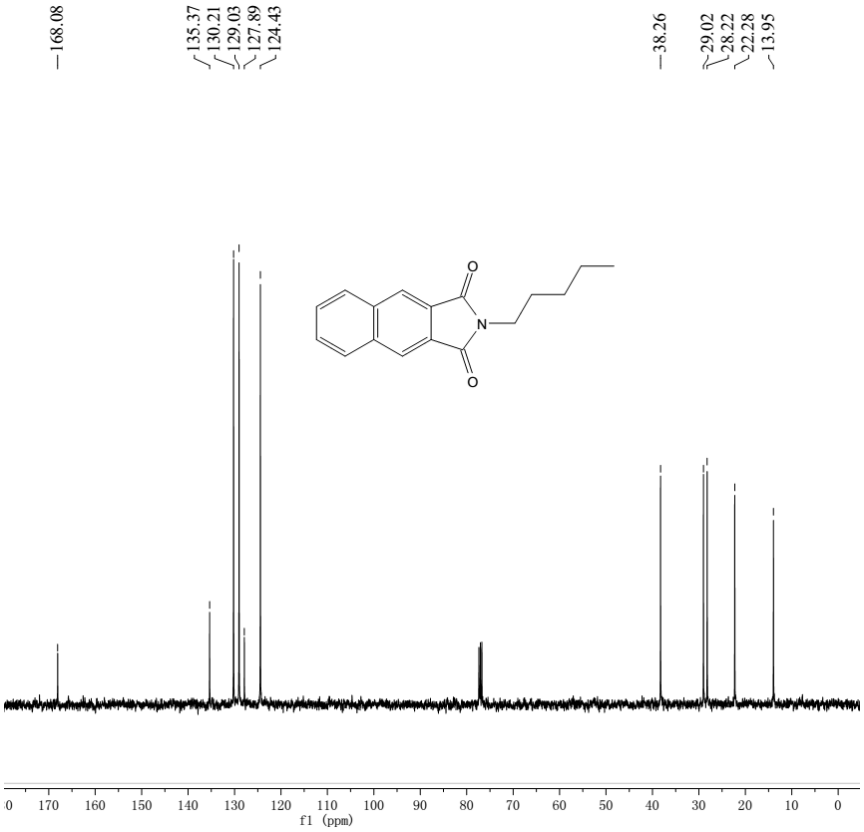



***Figure S63.*** $^{13}$C NMR spectrum of compound **27**.

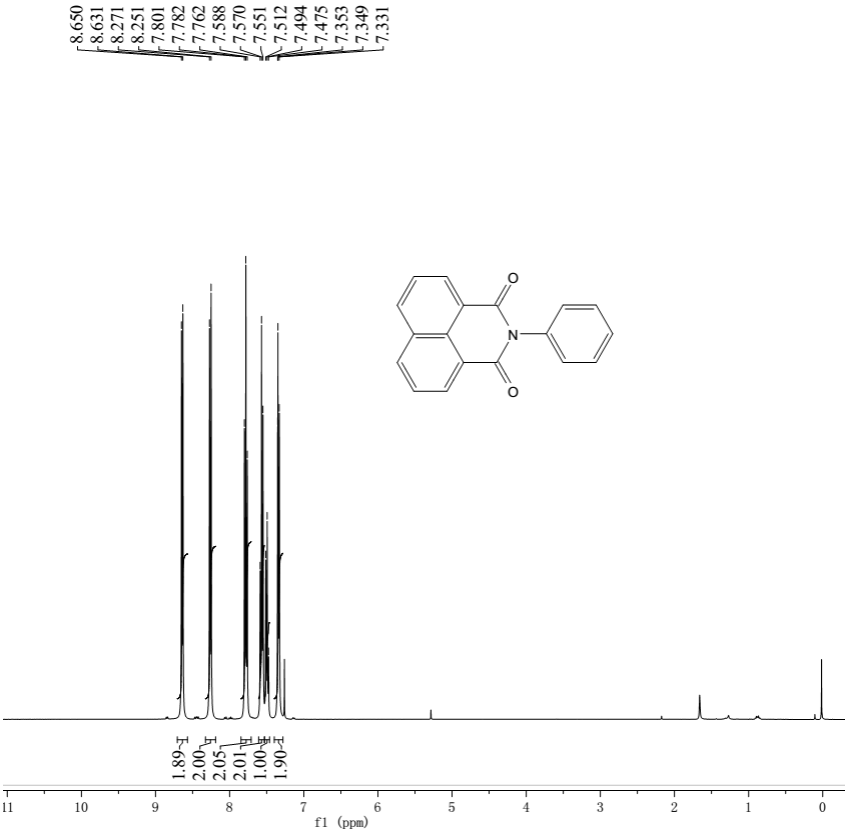



***Figure S64.*** $^{1}$H NMR spectrum of compound **28**.

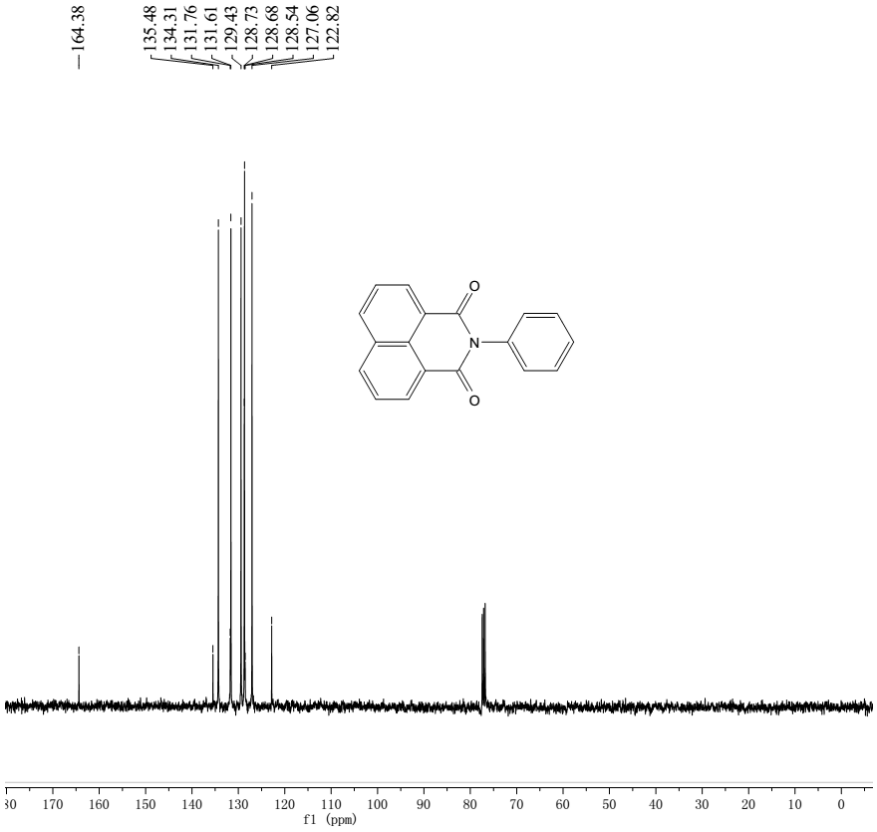



***Figure S65.*** $^{13}$C NMR spectrum of compound **28**.

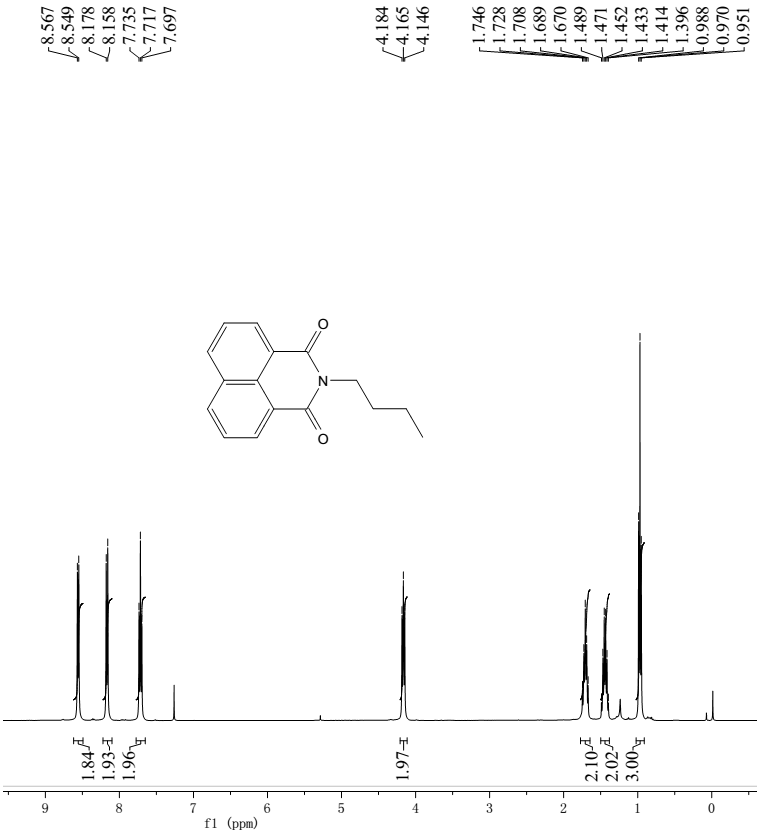



***Figure S66.*** $^{1}$H NMR spectrum of compound **29**.

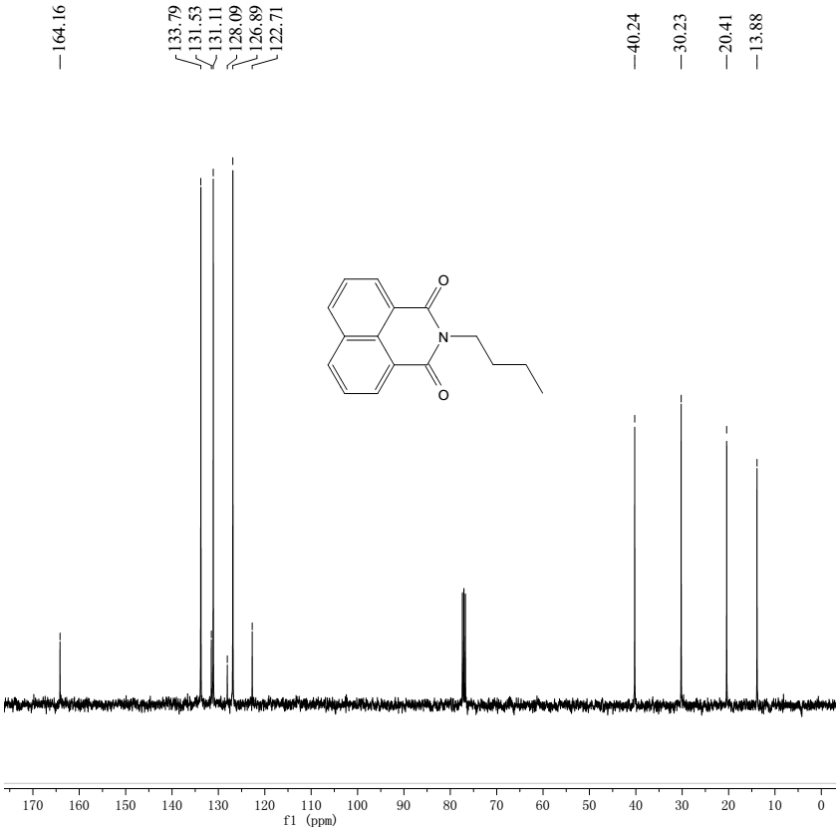



***Figure S67.*** $^{13}$C NMR spectrum of compound **29**.

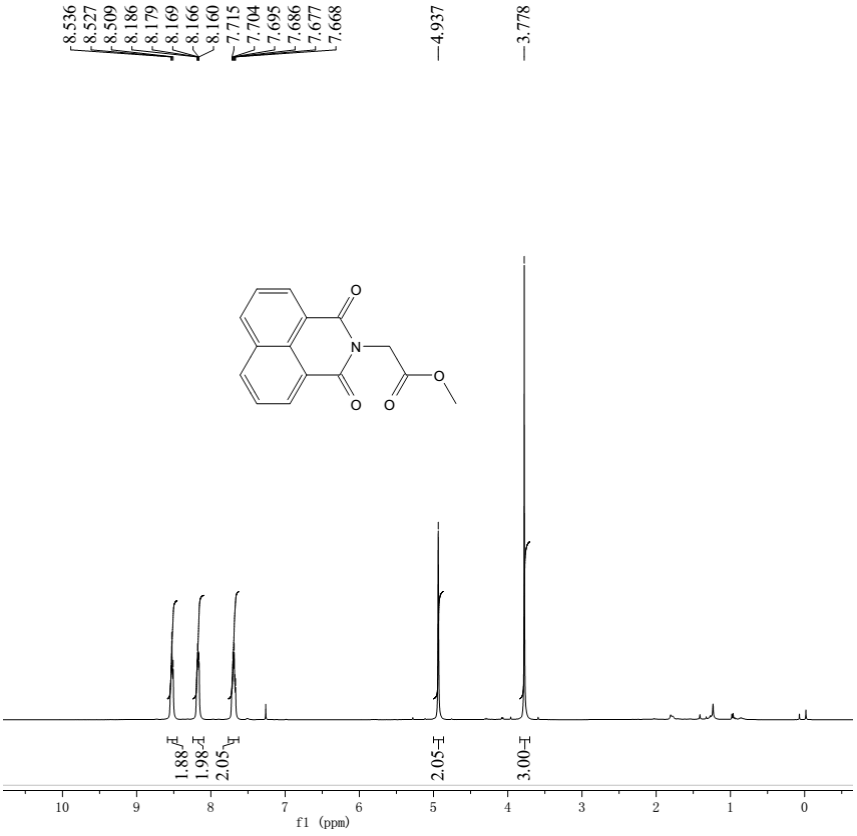



***Figure S68.*** $^{1}$H NMR spectrum of compound **30**.

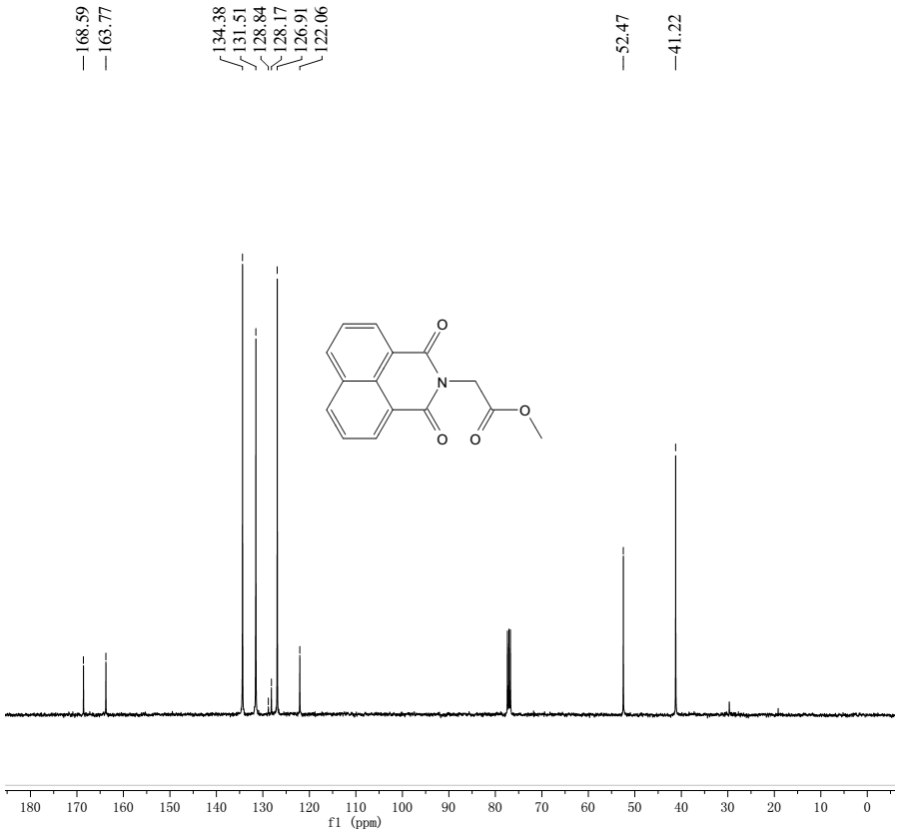



***Figure S69.*** $^{13}$C NMR spectrum of compound **30**.

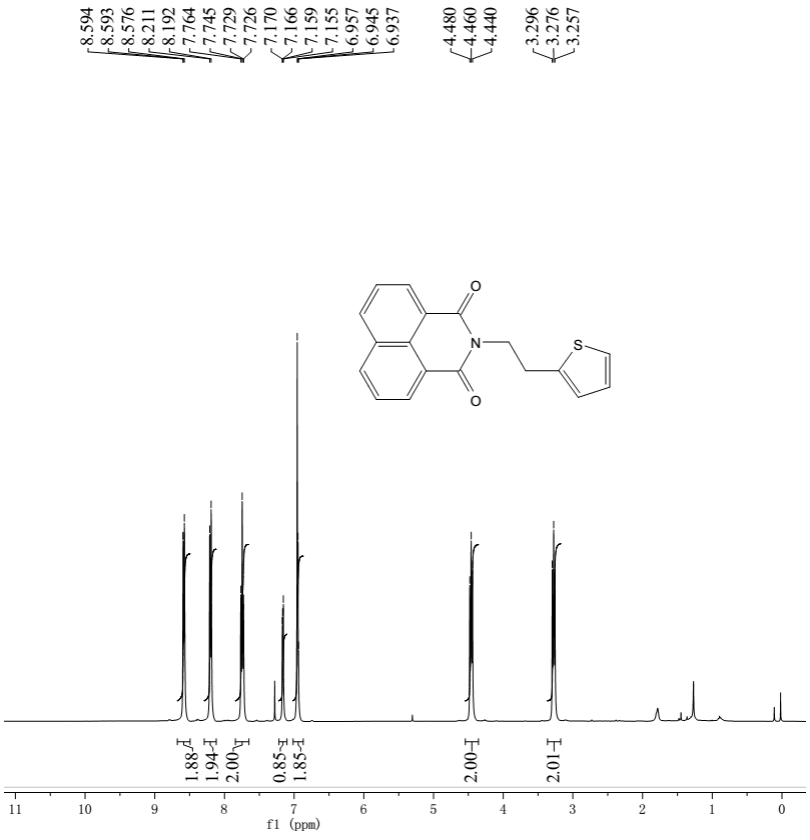



***Figure S70.*** $^{1}$H NMR spectrum of compound **31**.

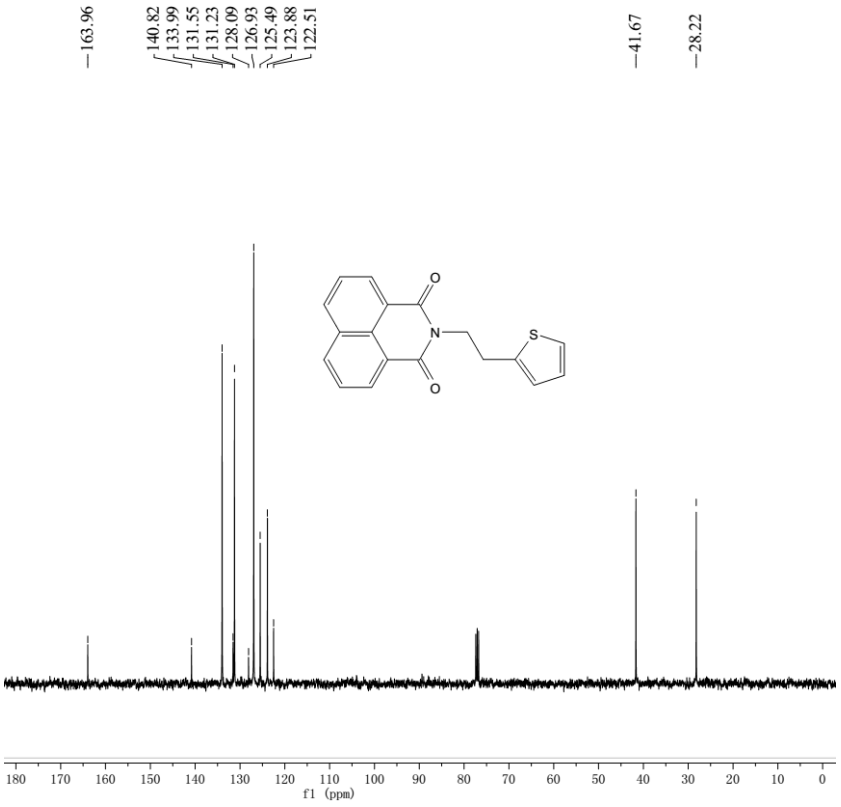



***Figure S71.*** $^{13}$C NMR spectrum of compound **31**.

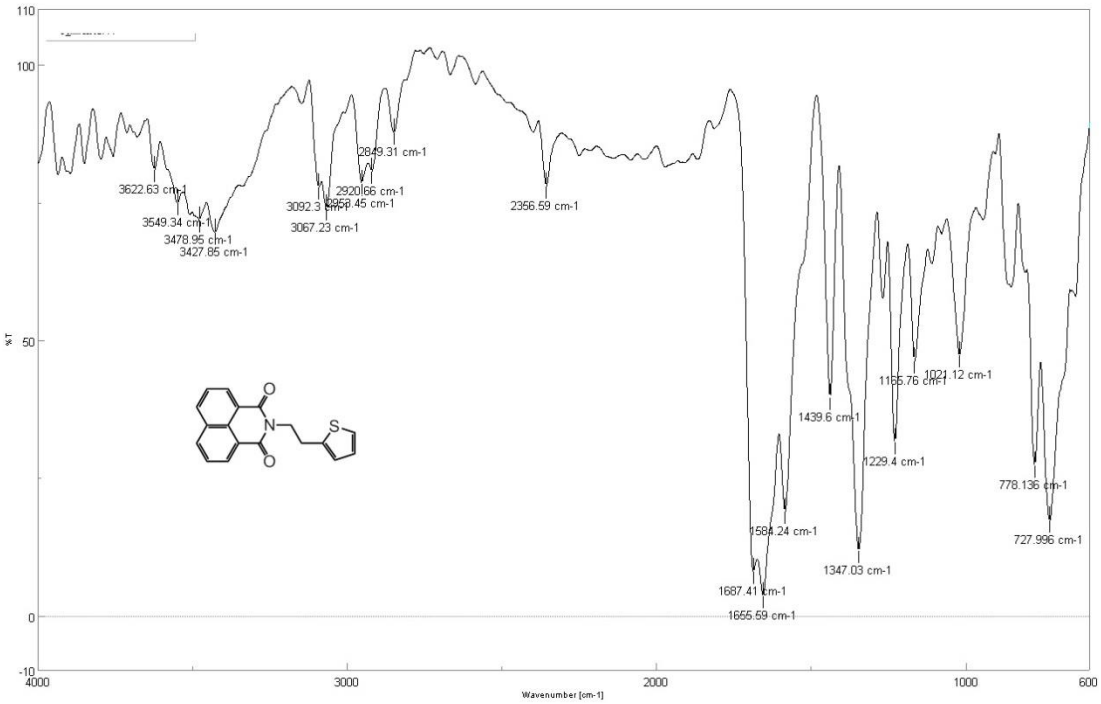



***Figure S72.*** IR spectrum of compound **31**.

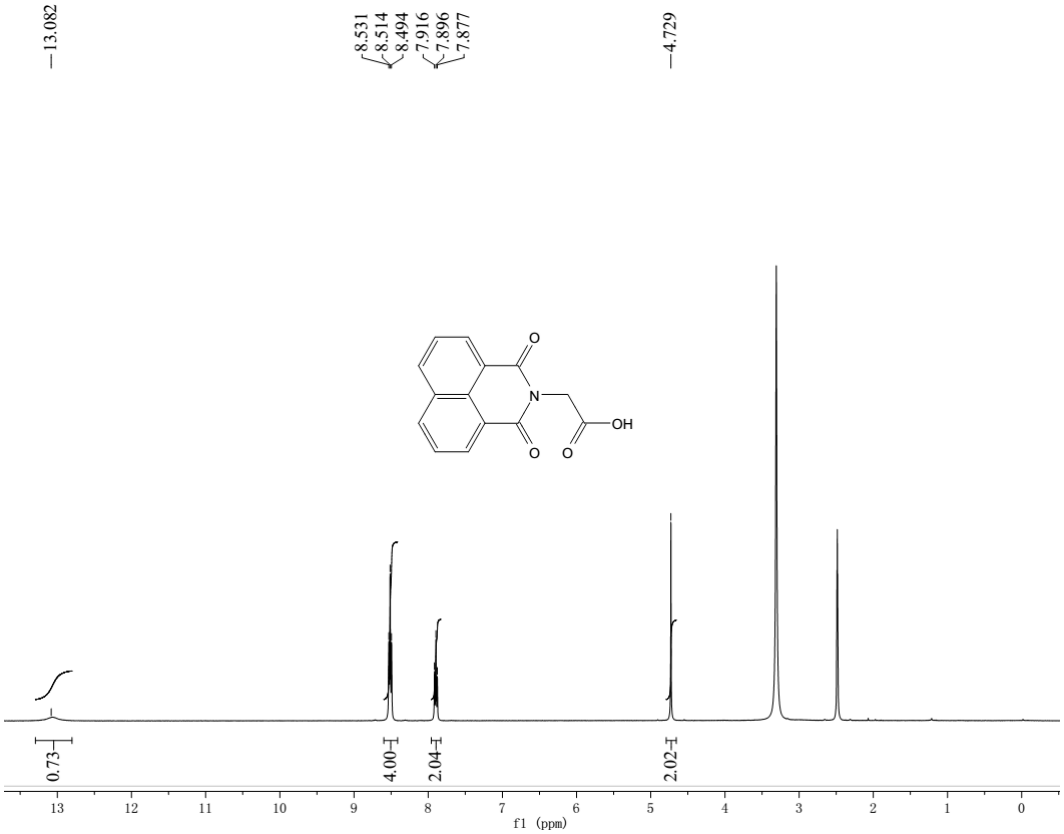



***Figure S73.*** $^{1}$H NMR spectrum of compound **32**.

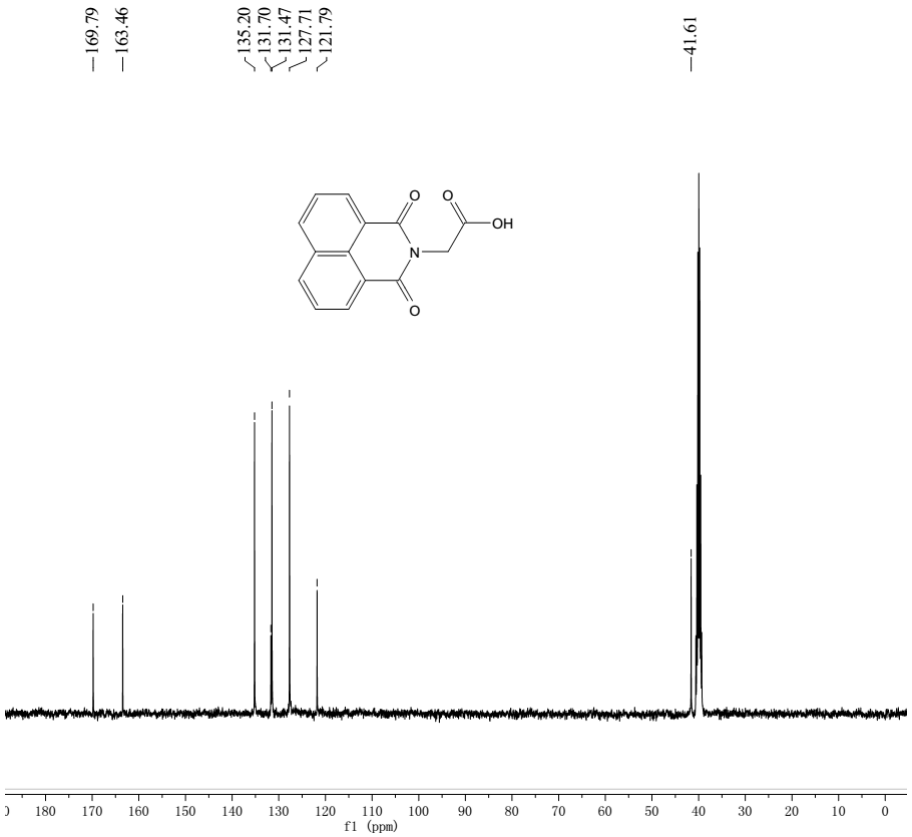



***Figure S74.*** $^{13}$C NMR spectrum of compound **32**.

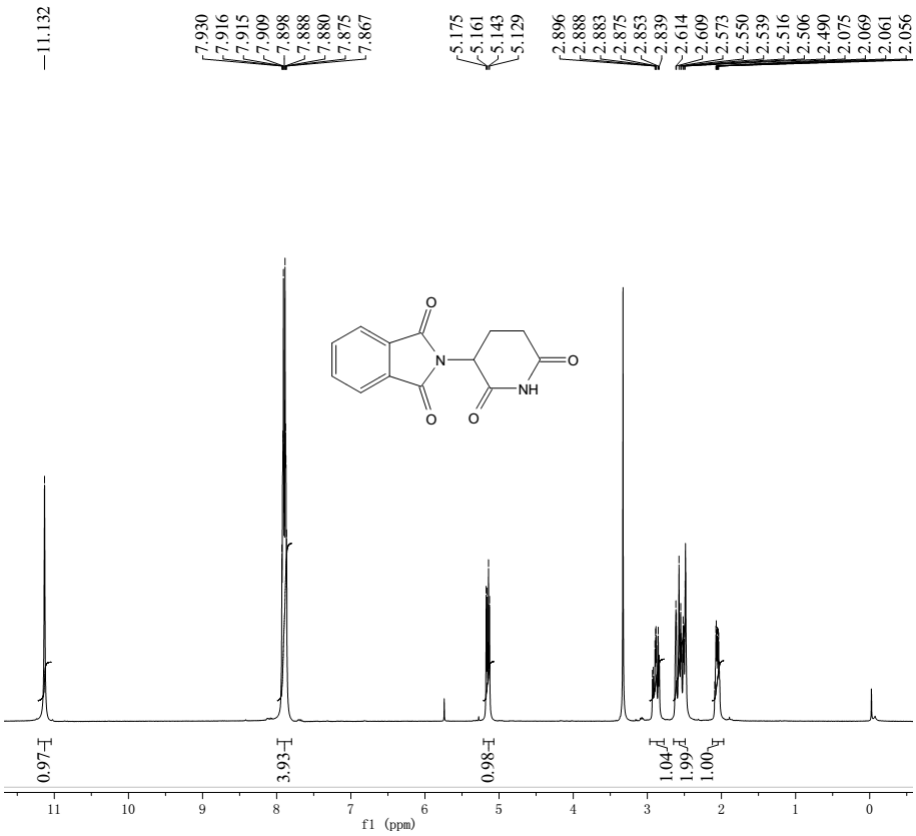



***Figure S75.*** $^{1}$H NMR spectrum of compound **33**.

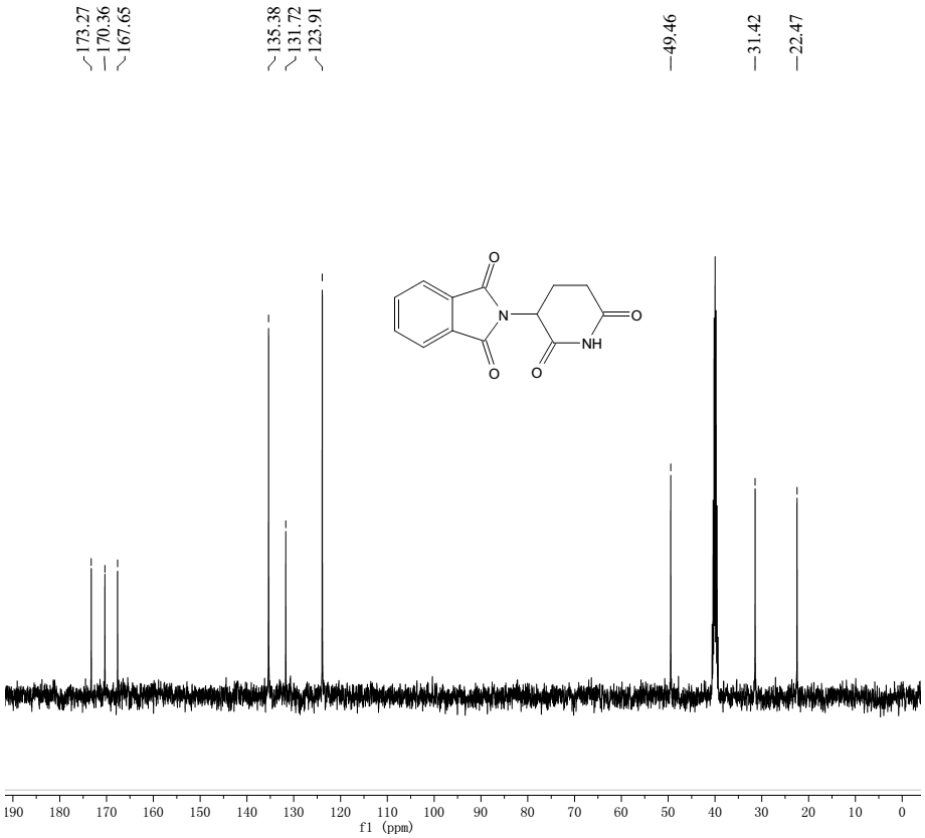



***Figure S76.*** $^{13}$C NMR spectrum of compound **33**.

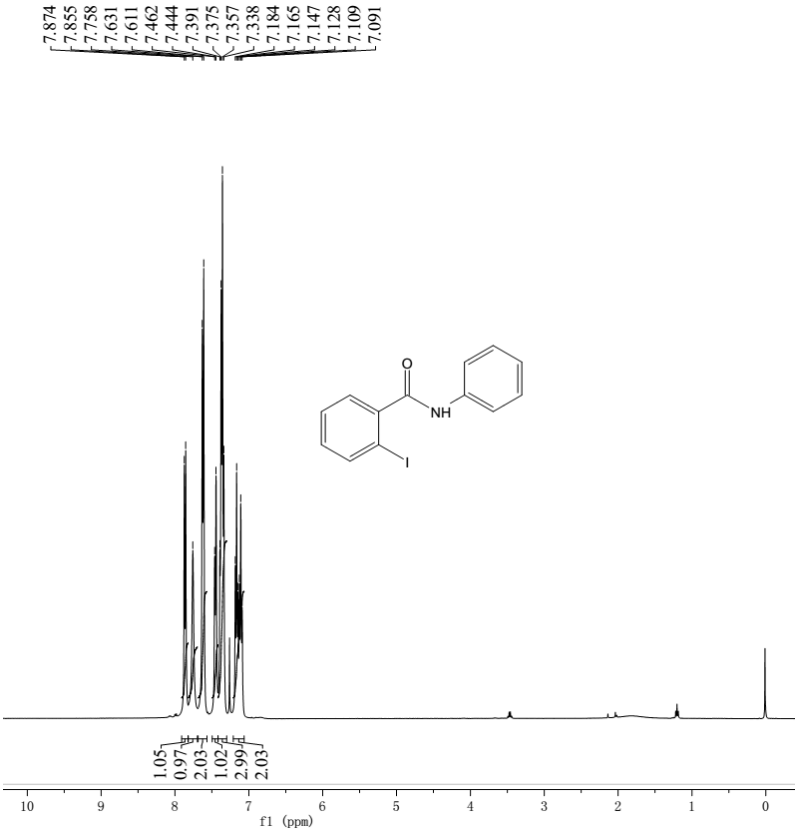



***Figure S77.*** $^{1}$H NMR spectrum of compound **S1**.

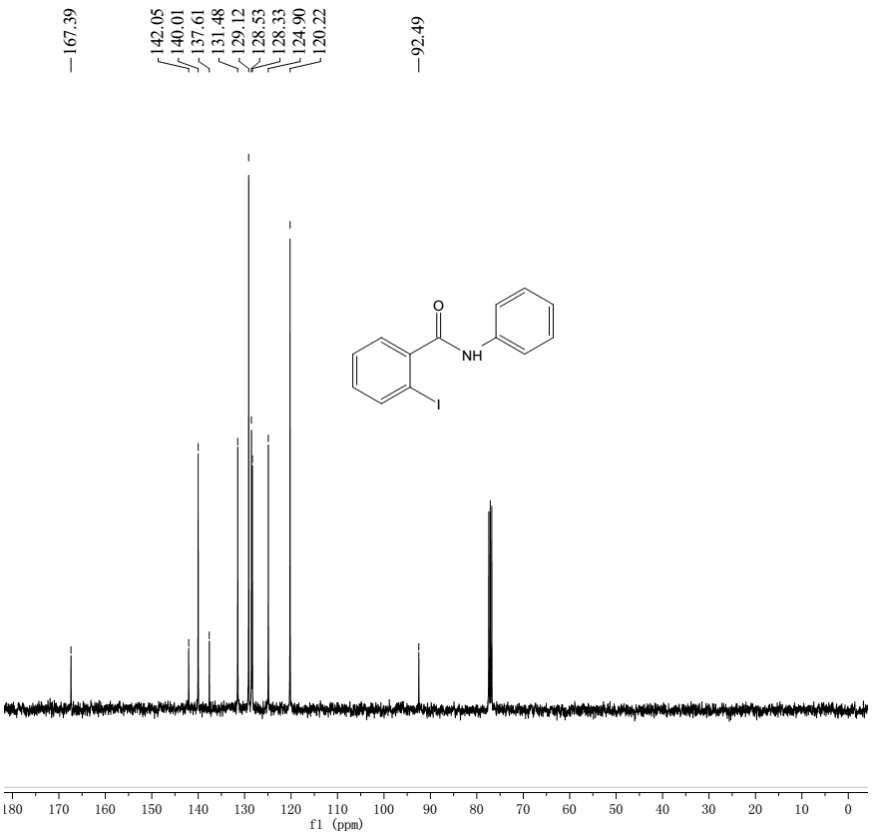



***Figure S78.*** $^{13}$C NMR spectrum of compound **S1**.

## 5. References


S1 T. Tu, W. Fang and J. Jiang, *Chem. Commun.*, 2011, **47**, 12358.

S2 W. Fang, Q. Deng, M. Xu and Tu. T, *Org. Lett.*, 2013, **15**, 3678.

S3 W. Fang, Q. Deng, M. Xu and T. Tu, *Org. Lett.*, 2013, **15**, 3678.

S4 C. J. O'Brien, E. A. B. Kantchev, C. Valente, N. Hadei, G. A. Chass, A. Lough, A. C. Hopkinson and M. G. Organ. *Chem. Eur. J.*, 2006, **12**, 4743.

S5 R. J. Perry and S. R. Turner, *J. Org. Chem.*, 1991, **56**, 6573.

S6 T. Tu, X. Feng, Z. Wang and X. Liu, *Dalton Trans.*, 2010, **39**, 10598.