

Supplementary Information

Three rare-earth incorporating 6-peroxotantalo-4-selenate and catalytic activities for imidation reaction

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Table S1. Crystal Data and Structure Refinement of Compounds **STD-Eu**, **STD-Gd** and **STD-Lu**.

	STD-Eu	STD-Gd	STD-Lu
Empirical formula	CsKEuSe ₄ Ta ₆ O ₅₃ H ₄	CsKGdSe ₄ Ta ₆ O ₅₃ H ₄	CsKLuSe ₄ Ta ₆ O ₅₁ H ₃
	3	3	9
Formula weight	2616.80	2622.09	2603.78
Temperature/K	296.15	296.15	296.15
Crystal system	monoclinic	monoclinic	monoclinic
Space group	<i>P2₁/c</i>	<i>P2₁/c</i>	<i>P2₁/c</i>
$\lambda / \text{\AA}$	0.71073	0.71073	0.71073
$a / \text{\AA}$	12.3382(7)	12.3307(5)	12.2537(9)
$b / \text{\AA}$	27.3560(15)	27.2604(11)	27.308(2)
$c / \text{\AA}$	14.0173(8)	14.0160(6)	13.9677(11)
$\alpha / ^\circ$	90	90	90
$\beta / ^\circ$	113.7870(10)	113.8540(10)	114.1800(10)
$\gamma / ^\circ$	90	90	90
Volume / \AA^3	4329.3(4)	4308.9(3)	4263.9(6)
Z	4	4	4
$D_c / \text{g cm}^{-3}$	3.875	3.901	3.970
μ / mm^{-1}	20.945	21.128	22.111
F(000)	4444.0	4448.0	4476.0
Crystal size / mm^3	0.14 × 0.12 × 0.11	0.34 × 0.17 × 0.13	0.21 × 0.16 × 0.13
2 θ range for data collection / $^\circ$	3.508 to 50.198	3.51 to 50.198	2.982 to 50.196
	-14 ≤ h ≤ 6	-14 ≤ h ≤ 14	-14 ≤ h ≤ 14
Limiting indices	-32 ≤ k ≤ 32	-21 ≤ k ≤ 32	-32 ≤ k ≤ 25
	-16 ≤ l ≤ 16	-16 ≤ l ≤ 16	-14 ≤ l ≤ 16
Reflections collected	22421	22215	22026
Independent reflections	$R_{int} = 0.0529,$ $R_{sigma} = 0.0610$	$R_{int} = 0.0422,$ $R_{sigma} = 0.0478$	$R_{int} = 0.0578,$ $R_{sigma} = 0.0658$
Data/restraints/parameters	7699/0/318	7652/0/318	7569/0/318

GOF on F^2	1.023	1.023	1.017
${}^a R_1, {}^b wR_2$ [$ I \geq 2\sigma(I)$]	$R_1 = 0.0421,$ $wR_2 = 0.0920$	$R_1 = 0.0388,$ $wR_2 = 0.0910$	$R_1 = 0.0437,$ $wR_2 = 0.0968$
${}^a R_1, {}^b wR_2$ [all data]	$R_1 = 0.0606,$ $wR_2 = 0.1007$	$R_1 = 0.0493,$ $wR_2 = 0.0963$	$R_1 = 0.0633,$ $wR_2 = 0.1059$
${}^a R_1 = \sum F_o - F_c / \sum F_o . \quad {}^b wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}.$			

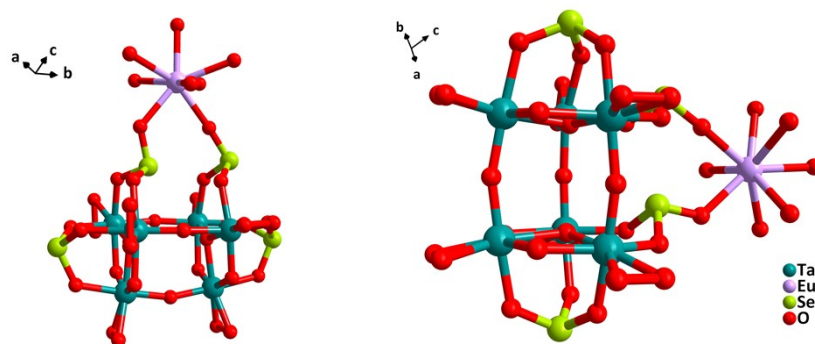


Figure S1. Composition of compounds **STD-Eu**, **STD-Gd** and **STD-Lu**.

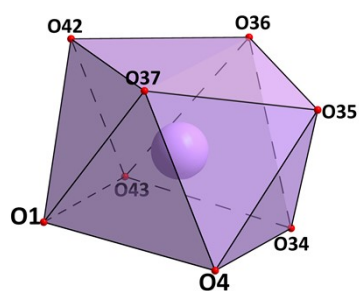


Figure S2. Representation of Ln coordination environment. Ln, lavender; O, red.

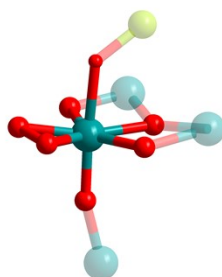


Figure S3. Connection mode of Ta atoms. Ta, teal; Se, lime; O, red; peroxo bond, red.

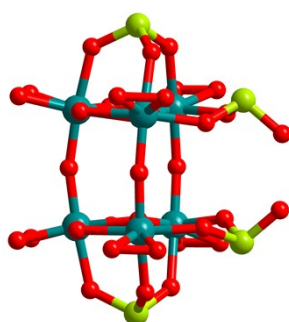


Figure S4. Ball-and-stick representation of polyanion $cis\text{-}\{\text{Se}_4(\text{TaO}_2)_6\}'$. Ta, teal; Se, lime; O, red; peroxo bond, red.

Table S2. $O_{\text{axial}}\text{-Ta-}O_{\text{axial}}$ angles in polyanions **STD-Eu**, **STD-Gd** and **STD-Lu**.

Polyanion	STD-Eu	STD-Gd	STD-Lu
O22-Ta1-O25	170.45°	170.10°	170.60°
O26-Ta2-O27	169.27°	168.72°	168.66°
O19-Ta3-O20	174.48°	173.88°	172.90°
O13-Ta4-O22	174.72°	174.54°	174.14°
O23-Ta5-O26	161.14°	160.47°	159.81°
O19-Ta6-O21	176.96°	176.62°	177.09°

Table S3. Bond lengths in **STD-Eu**, **STD-Gd** and **STD-Lu**.

Bond	Length			Bond	Length		
	STD-Eu	STD-Gd	STD-Lu		STD-Eu	STD-Gd	STD-Lu
Ta1-O22	1.894	1.898	1.889	Ta5-O23	2.161	2.167	2.169
Ta1-O16	1.982	1.977	1.969	Ta6-O19	1.897	1.895	1.906
Ta1-O18	1.985	1.999	1.991	Ta6-O7	1.974	1.968	1.961
Ta1-O33	2.054	2.057	2.054	Ta6-O3	1.978	1.979	1.992
Ta1-O24	2.077	2.061	2.063	Ta6-O28	1.995	2.008	2.012
Ta1-O25	2.063	2.067	2.052	Ta6-O31	2.072	2.080	2.082
Ta1-O30	2.069	2.086	2.067	Ta6-O29	2.074	2.084	2.088
Ta2-O26	1.847	1.842	1.842	Ta6-O21	2.149	2.135	2.136
Ta2-O6	1.986	1.995	1.985	Ln-O4	2.309	2.296	2.224
Ta2-O5	1.966	1.973	1.971	Ln-O43	2.384	2.355	2.292
Ta2-O9	2.051	2.054	2.058	Ln-O37	2.405	2.387	2.293
Ta2-O33	2.102	2.099	2.100	Ln-O1	2.406	2.401	2.317
Ta2-O32	2.094	2.105	2.092	Ln-O36	2.427	2.419	2.324
Ta2-O27	2.143	2.143	2.139	Ln-O34	2.448	2.421	2.346
Ta3-O19	1.897	1.891	1.883	Ln-O42	2.465	2.457	2.373
Ta3-O8	1.978	1.967	1.953	Ln-O35	2.503	2.504	2.431
Ta3-O12	1.979	1.984	1.975	Se1-O27	1.693	1.687	1.694
Ta3-O30	2.030	2.033	2.041	Se1-O20	1.706	1.714	1.708
Ta3-O32	2.048	2.045	2.052	Se1-O25	1.709	1.715	1.729
Ta3-O20	2.099	2.088	2.084	Se2-O13	1.693	1.696	1.683
Ta3-O33	2.091	2.097	2.095	Se2-O23	1.706	1.700	1.699

Ta4-O22	1.921	1.915	1.921	Se2-O21	1.694	1.700	1.694
Ta4-O14	1.976	1.988	1.979	Se3-O4	1.632	1.642	1.647
Ta4-O10	1.993	1.999	1.985	Se3-O15	1.710	1.716	1.704
Ta4-O31	2.040	2.037	2.031	Se3-O17	1.724	1.723	1.719
Ta4-O15	2.052	2.049	2.059	Se4-O1	1.661	1.653	1.667
Ta4-O29	2.086	2.072	2.073	Se4-O24	1.702	1.715	1.714
Ta4-O13	2.092	2.089	2.090	Se4-O9	1.708	1.723	1.713
Ta5-O28	1.920	1.924	1.912	O3-O7	1.504	1.509	1.537
Ta5-O11	1.956	1.964	1.931	O8-O12	1.509	1.539	1.486
Ta5-O2	1.992	1.965	1.980	O2-O11	1.439	1.478	1.451
Ta5-O26	2.001	2.006	2.006	O5-O6	1.484	1.485	1.478
Ta5-O17	2.049	2.041	2.035	O14-O10	1.488	1.494	1.501
Ta5-O31	2.114	2.112	2.116	O16-O18	1.508	1.494	1.494

Table S4. $O_{\text{peroxo}}\text{-Ta-}O_{\text{peroxo}}$, $O_{\text{apical}}\text{-Ta-}O_{\text{apical}}$ and $\text{Ta-}O_{\text{apical}}\text{-Ta}$ angle in polyanions **STD-Eu**, **STD-Gd**, **STD-Lu** and **Se₄Ta₆**.

Polyanion	STD-Eu	STD-Gd	STD-Lu	Polyanion	Se₄Ta₆
$O_{\text{peroxo}}\text{-Ta-}O_{\text{peroxo}}$ angle (°)					
O16-Ta1-O18	44.69	44.15	44.31	O4-Ta1-O5	44.23
O5-Ta2-O6	44.12	43.96	43.87	O7-Ta2-O8	44.91
O8-Ta3-O12	44.84	45.86	44.45	O10-Ta3-O11	45.02
O10-Ta4-O14	44.04	44.01	44.50	O30-Ta4-O31	45.64
O2-Ta5-O11	42.75	44.20	43.55	O21-Ta5-O22	45.06
O3-Ta6-O7	44.74	44.94	45.76	O25-Ta6-O26	44.74
Average value:	44.19	44.52	44.41	Average value:	45.02
$O_{\text{apical}}\text{-Ta-}O_{\text{apical}}$ angle (°)					
O22-Ta1-O25	170.45	170.10	170.60	O1-Ta1-O18	172.40
O26-Ta2-O27	169.27	168.72	168.66	O2-Ta2-O19	176.52
O19-Ta3-O20	174.48	173.88	172.90	O3-Ta3-O17	169.41
O13-Ta4-O22	174.72	174.54	174.13	O18-Ta4-O33	173.77
O23-Ta5-O26	161.14	160.47	159.81	O19-Ta5-O34	176.35
O19-Ta6-O21	176.95	176.62	177.09	O17-Ta6-O35	173.42
Average value:	171.16	170.72	170.53	Average value:	173.65
$\text{Ta-}O_{\text{apical}}\text{-Ta}$ angle (°)					
Ta1-O22-Ta4	163.56	164.49	164.05	Ta1-O18-Ta4	156.66
Ta2-O26-Ta5	166.73	167.73	167.51	Ta2-O19-Ta5	160.15
Ta3-O19-Ta6	162.41	164.11	162.85	Ta3-O17-Ta6	162.90
Average value:	164.23	165.44	164.80	Average value:	159.90

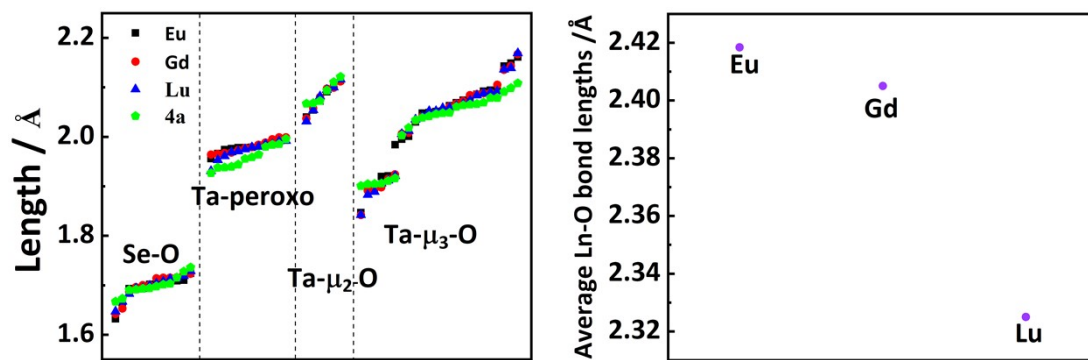


Figure S5. Se–O, Ta–O (left) bond lengths and the average Ln–O (right) bond length in **STD-Eu**, **STD-Gd** and **STD-Lu**.

Table S5. BVS calculation results.

Polyanion	STD-Eu	STD-Gd	STD-Lu	Polyanion	STD-Eu	STD-Gd	STD-Lu
Ta1	5.45	5.41	5.52	O15	2.01	1.99	2.02
Ta2	5.42	5.38	5.43	O16 [#]	0.84	0.85	0.87
Ta3	5.47	5.51	5.56	O17	1.97	1.99	2.01
Ta4	5.36	5.38	5.40	O18 [#]	0.84	0.81	0.82
Ta5	5.34	5.38	5.46	O19	2.12	2.15	2.14
Ta6	5.46	5.43	5.37	O20	1.94	1.94	1.96
Se1	4.02	3.99	3.94	O21	1.91	1.91	1.93
Se2	4.08	4.06	4.13	O22	2.07	2.07	2.08
Se3	4.19	4.14	4.17	O23	1.84	1.86	1.86
Se4	4.16	4.09	4.07	O24	1.99	1.98	1.98
Ln	3.20	3.23	3.11	O25	1.99	1.96	1.94
O1	1.91	1.93	1.87	O26	2.02	2.02	2.02
O2 [#]	0.82	0.88	0.85	O27	1.92	1.94	2.39
O3 [#]	0.85	0.85	0.82	O28	1.81	1.78	1.80
O4	2.15	2.11	2.06	O29 ^ψ	1.29	1.30	1.29
O5 [#]	0.88	0.87	0.87	O30 ^ψ	1.41	1.37	1.39
O6 [#]	0.83	0.82	0.83	O31	1.98	1.97	1.97
O7 [#]	0.86	0.88	0.89	O32 ^ψ	1.33	1.32	1.33
O8 [#]	0.85	0.88	0.91	O33	1.94	1.92	1.93
O9	2.02	1.96	1.99	O34 [‡]	0.37	0.38	0.36
O10 [#]	0.82	0.81	0.84	O35 [‡]	0.31	0.31	0.29
O11 [#]	0.90	0.89	0.97	O36 [‡]	0.39	0.38	0.38
O12 [#]	0.85	0.84	0.86	O37 [‡]	0.41	0.42	0.42
O13	1.99	1.99	2.04	O42 [‡]	0.35	0.35	0.34
O14 [#]	0.86	0.83	0.85	O43 [‡]	0.43	0.45	0.42

[#], [‡] and ^ψ represent peroxo oxygen atoms, H₂O and OH ligands.

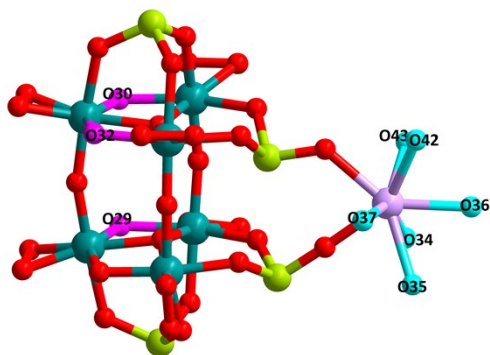


Figure S6. Ball-and-stick representation of polyanion **STD-Eu**, highlighting the protonated oxygen atoms. Ta, teal; Se, lime; Eu, lavender; H₂O, turquoise; OH, pink; O, red; peroxo bond, red.

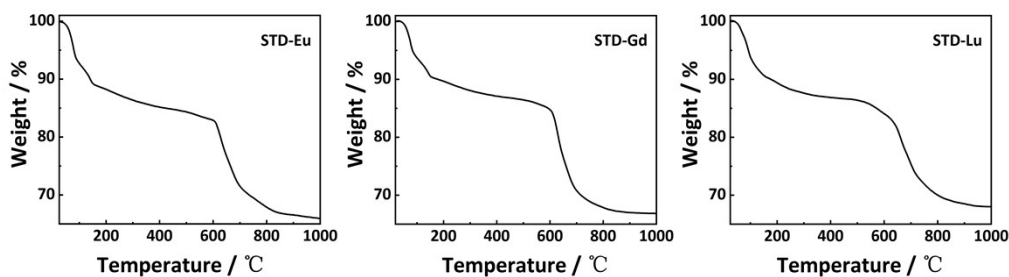


Figure S7. TG curves of compounds **STD-Eu**, **STD-Gd** and **STD-Lu**.

The TG curves of compounds **STD-Eu**, **STD-Gd** and **STD-Lu** show similar two-step weight loss behaviors in the temperature range of 25-1000 °C. The total weight loss of 32.62% (calcd 32.79%) for **STD-Eu** and 32.67% (calcd 32.73%) for **STD-Gd** can be attributed to 14 lattice water molecules, 9 coordinated water molecules and four SeO₂ molecules. However, the slightly smaller total weight loss of 31.86% (calcd 31.57%) for **STD-Lu** corresponds to 12 lattice water molecules, 9 coordinated water molecules and four SeO₂ molecules.

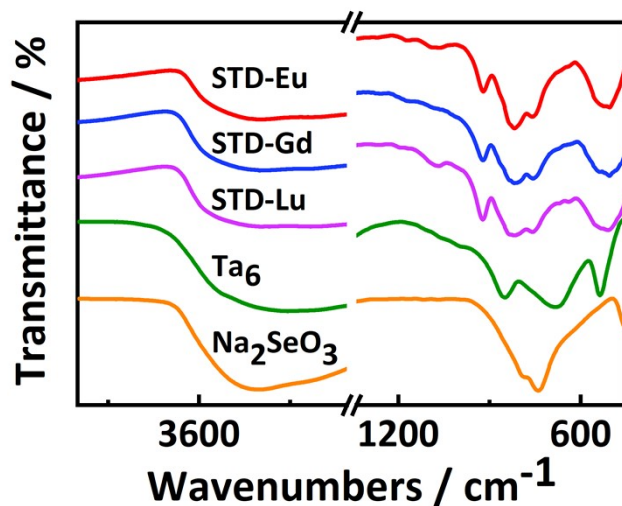


Figure S8. IR spectra for STD-Eu, STD-Gd, STD-Lu, Na₂SeO₃ and Ta₆ in the region from 4000 to 450 cm⁻¹.

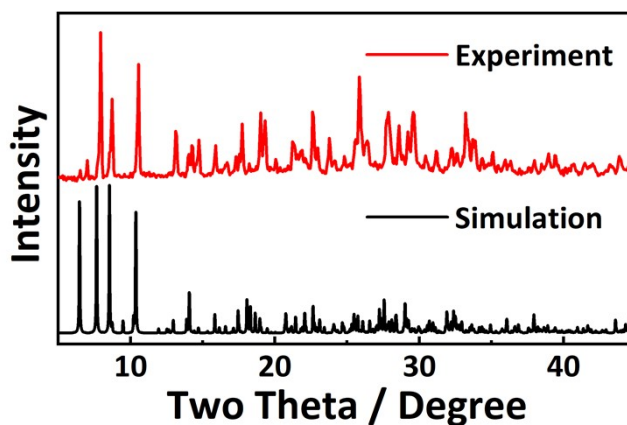


Figure S9. PXRD patterns (black) and simulated (red) of STD-Eu.

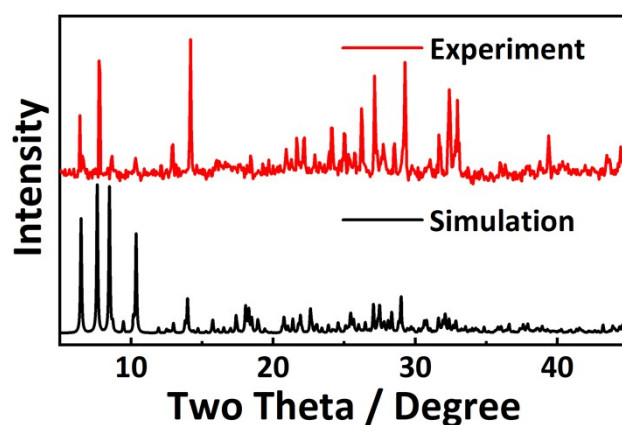


Figure S10. PXRD patterns (black) and simulated (red) of STD-Gd.

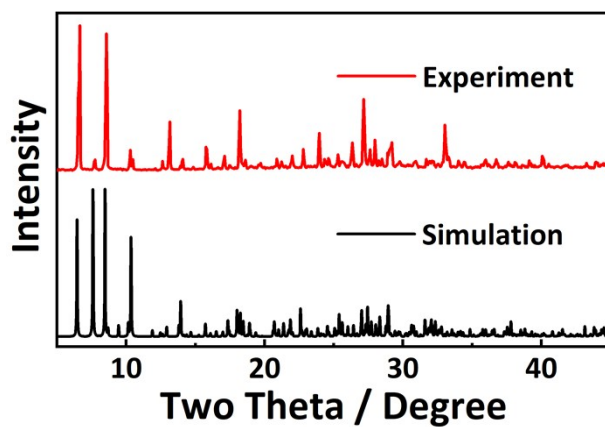


Figure S11. PXRD patterns (black) and simulated (red) of **STD-Lu**.

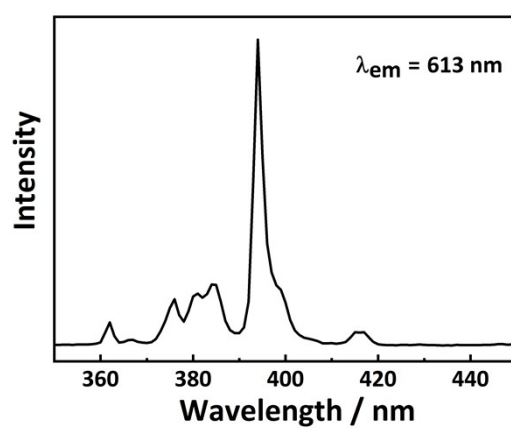


Figure S12. Excitation spectrum for **STD-Eu** ($\lambda_{em} = 613 \text{ nm}$).

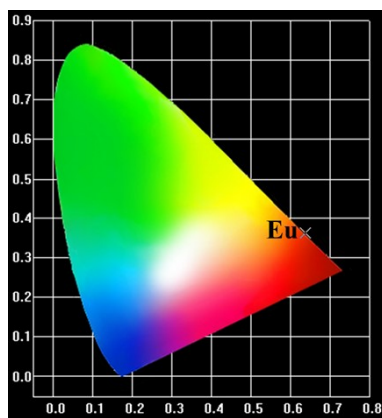
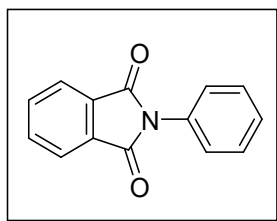


Figure S13. Corresponding color coordinates of **STD-Eu**.

Experimental section

Catalysis. The products were isolated by column chromatography on silica gel (200-300 mesh) using petroleum ether (60-90 °C) and ethyl acetate. All compounds were characterized by ^1H NMR, ^{13}C NMR and mass spectrometry, which were consistent with those reported in related literatures. NMR spectra were determined on Bruker ADVANCE III spectrometer at 500 MHz and 126 MHz. ^1H NMR peaks were labeled as singlet (s), doublet (d), triplet (t), and multiplet (m). The coupling constants, J , are reported in Hertz (Hz). GC analysis was performed on Agilent 7890B equipped with a capillary column (HP-5, 30 m \times 0.25 μm) using a flame ionization detector.

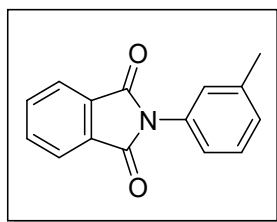
Characterization of substrates and products



2-phenylisoindoline-1,3-dione (3a)^{S1}

^1H NMR (500 MHz, CDCl_3) δ 7.94 (dt, J = 6.7, 3.4 Hz, 2H), 7.78 (dd, J = 5.3, 3.1 Hz, 2H), 7.51 (t, J = 7.7 Hz, 2H), 7.47-7.37 (m, 3H);

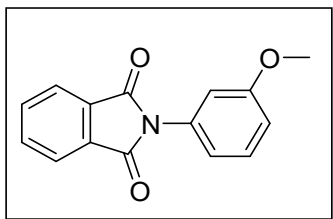
^{13}C NMR (126 MHz, CDCl_3) δ 167.34, 134.47, 131.76, 129.18, 128.17, 126.63, 123.80, 100.00.



2-(m-tolyl)isoindoline-1,3-dione (3b)^{S1}

^1H NMR (500 MHz, CDCl_3) δ 166.85, 134.67, 134.59, 132.82, 131.51, 130.08, 128.21, 126.66, 124.62, 123.92;

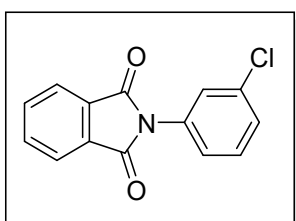
^{13}C NMR (126 MHz, CDCl_3) δ 176.50, 139.29, 131.86, 129.57, 129.06, 127.17, 123.65, 28.44, 21.38.



2-(3-methoxyphenyl)isoindoline-1,3-dione (3c)^{S2}

¹H NMR (500 MHz, CDCl₃) δ 7.92 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.78-7.74 (m, 2H), 7.39 (t, *J* = 7.7 Hz, 1H), 7.25-7.19 (m, 3H), 2.41 (s, 3H);

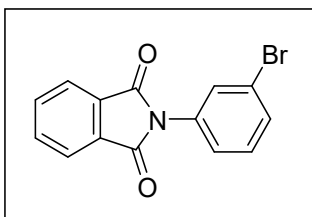
¹³C NMR (126 MHz, CDCl₃) δ 167.42, 139.16, 134.42, 131.78, 131.53, 129.09, 128.99, 127.32, 123.81, 123.74, 21.47.



2-(3-chlorophenyl)isoindoline-1,3-dione (3d)^{S2}

¹H NMR (500 MHz, CDCl₃) δ 7.95 (dd, *J* = 5.3, 3.0 Hz, 2H), 7.79 (dd, *J* = 5.3, 3.0 Hz, 2H), 7.41 (t, *J* = 8.1 Hz, 1H), 7.03 (d, *J* = 7.9 Hz, 1H), 7.00-6.93 (m, 2H), 3.84 (s, 3H);

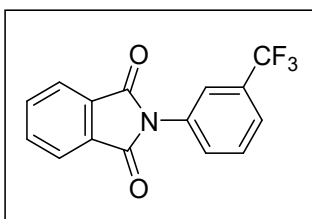
¹³C NMR (126 MHz, CDCl₃) δ 167.27, 160.05, 134.46, 132.65, 131.73, 129.85, 123.79, 118.91, 114.14, 112.37, 55.46.



2-(3-bromophenyl)isoindoline-1,3-dione (3e)^{S2}

¹H NMR (500 MHz, CDCl₃) δ 7.93 (dd, *J* = 4.9, 3.3 Hz, 2H), 7.79 (dd, *J* = 5.1, 3.1 Hz, 2H), 7.64 (s, 1H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.42 (d, *J* = 7.9 Hz, 1H), 7.37 (t, *J* = 7.9 Hz, 1H);

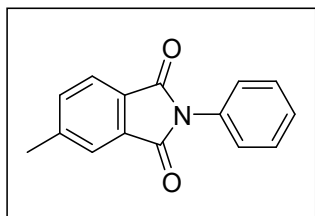
¹³C NMR (126 MHz, CDCl₃) δ 166.84, 134.68, 132.94, 131.49, 131.12, 130.35, 129.48, 125.12, 123.93, 122.41.



2-(3-(trifluoromethyl)phenyl)isoindoline-1,3-dione (3f)^{S2}

¹H NMR (500 MHz, CDCl₃) δ 7.92 (dd, *J* = 5.3, 3.1 Hz, 2H), 7.78 (dd, *J* = 5.5, 2.8 Hz, 3H), 7.68 (d, *J* = 7.2 Hz, 1H), 7.66-7.60 (m, 2H);

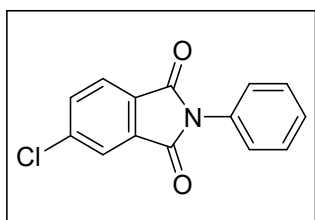
¹³C NMR (126 MHz, CDCl₃) δ 166.80 (s), 134.73 (s), 132.36 (s), 131.65-131.19 (m), 129.70 (s), 129.66 (s), 124.75 (s), 124.62 (d, *J* = 3.7 Hz), 123.91 (s), 123.33 (q, *J* = 3.8 Hz), 122.58 (s).



5-methyl-2-phenylisoindoline-1,3-dione (3g)^{S2}

¹H NMR (500 MHz, (CD₃)₂SO) δ 7.85 (d, *J* = 7.6 Hz, 1H), 7.79 (s, 1H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.55-7.50 (m, 2H), 7.47-7.41 (m, 3H), 2.52 (s, 3H);

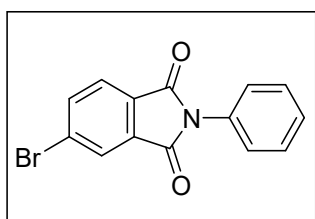
¹³C NMR (126 MHz, (CD₃)₂SO) δ 167.55, 167.45, 146.18, 135.55, 132.41, 132.33, 129.36, 129.31, 128.45, 127.81, 124.29, 123.83, 21.88.



5-chloro-2-phenylisoindoline-1,3-dione (3h)^{S2}

¹H NMR (500 MHz, (CD₃)₂SO) δ 8.05 (s, 1H), 8.00-7.94 (m, 2H), 7.56-7.52 (m, 2H), 7.46 (t, *J* = 7.1 Hz, 3H);

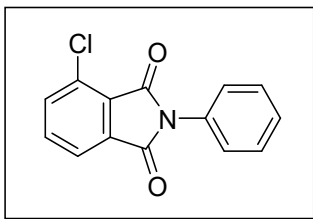
¹³C NMR (126 MHz, (CD₃)₂SO) δ 166.64, 166.28, 139.91, 134.92, 134.09, 132.19, 130.63, 129.37, 128.68, 127.80, 125.64, 123.96.



5-bromo-2-phenylisoindoline-1,3-dione (3i)^{S2}

¹H NMR (500 MHz, (CD₃)₂SO) δ 8.18 (d, *J* = 1.2 Hz, 1H), 8.11 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.90 (d, *J* = 7.9 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 2H), 7.45 (t, *J* = 7.4 Hz, 3H);

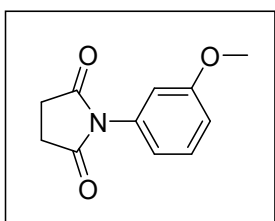
¹³C NMR (126 MHz, (CD₃)₂SO) δ 166.83, 166.25, 137.85, 134.08, 132.18, 131.03, 129.37, 128.69, 128.66, 127.81, 126.76, 125.75.



4-chloro-2-phenylisoindoline-1,3-dione (3j)^{S2}

¹H NMR (500 MHz, (CD₃)₂SO) δ 7.89 (dt, *J* = 22.3, 7.4 Hz, 3H), 7.58-7.51 (m, 2H), 7.46 (dd, *J* = 7.3, 4.8 Hz, 3H);

¹³C NMR (126 MHz, (CD₃)₂SO) δ 166.17, 165.18, 136.53, 136.30, 134.43, 132.14, 130.25, 129.36, 128.74, 127.99, 127.76, 122.78.

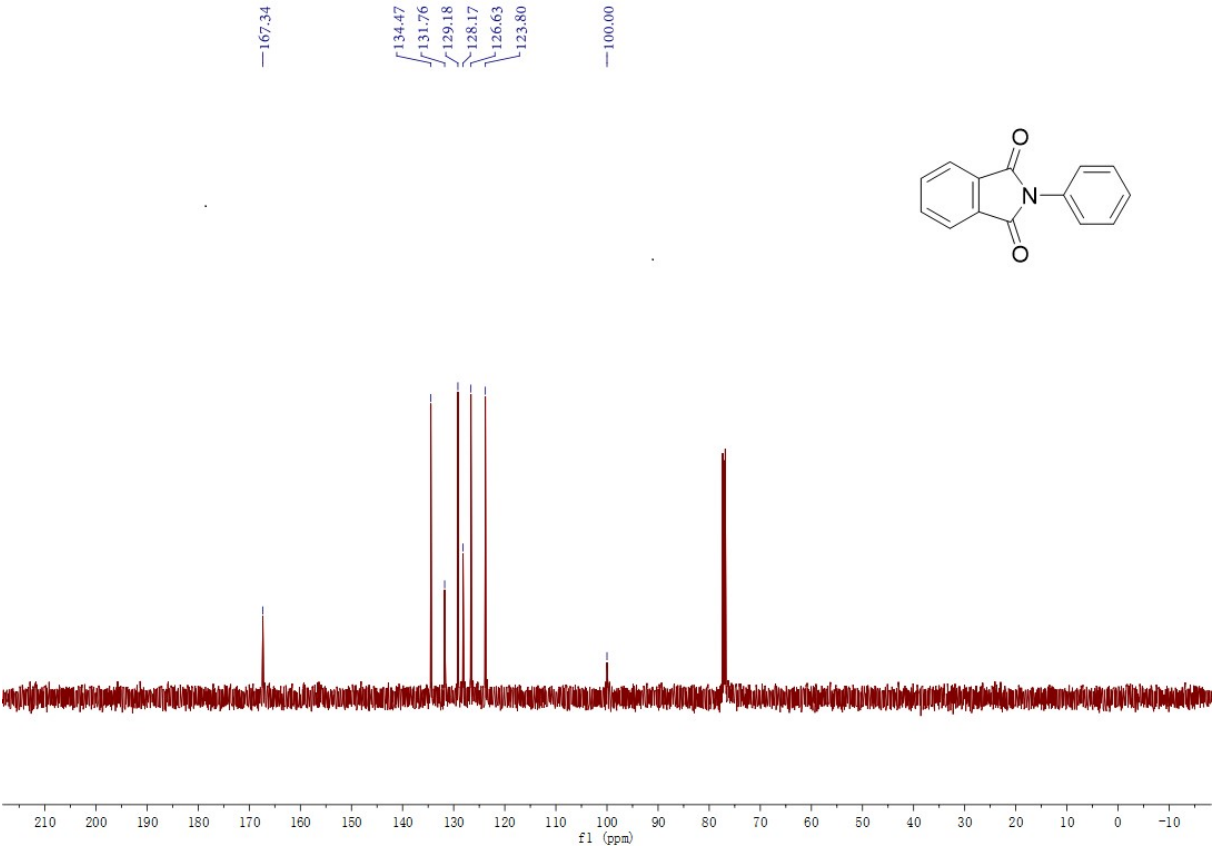
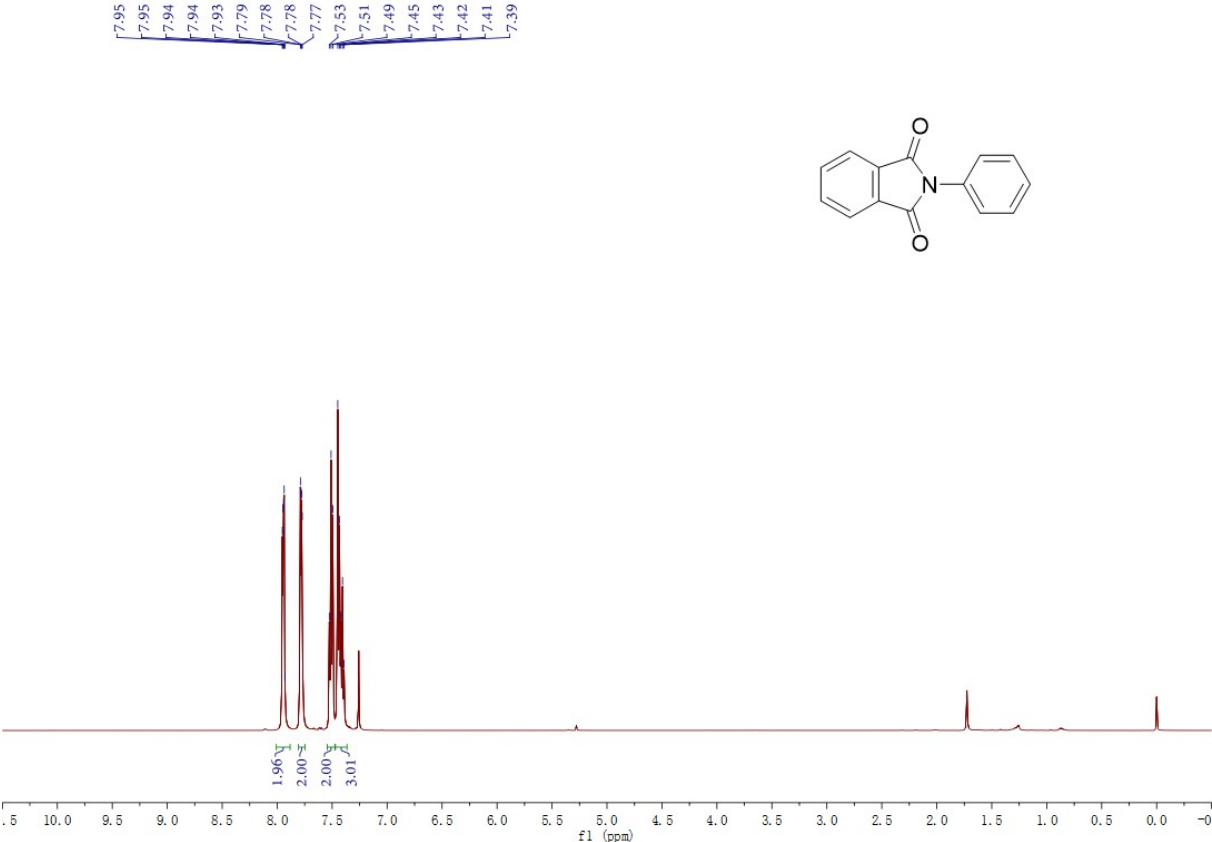


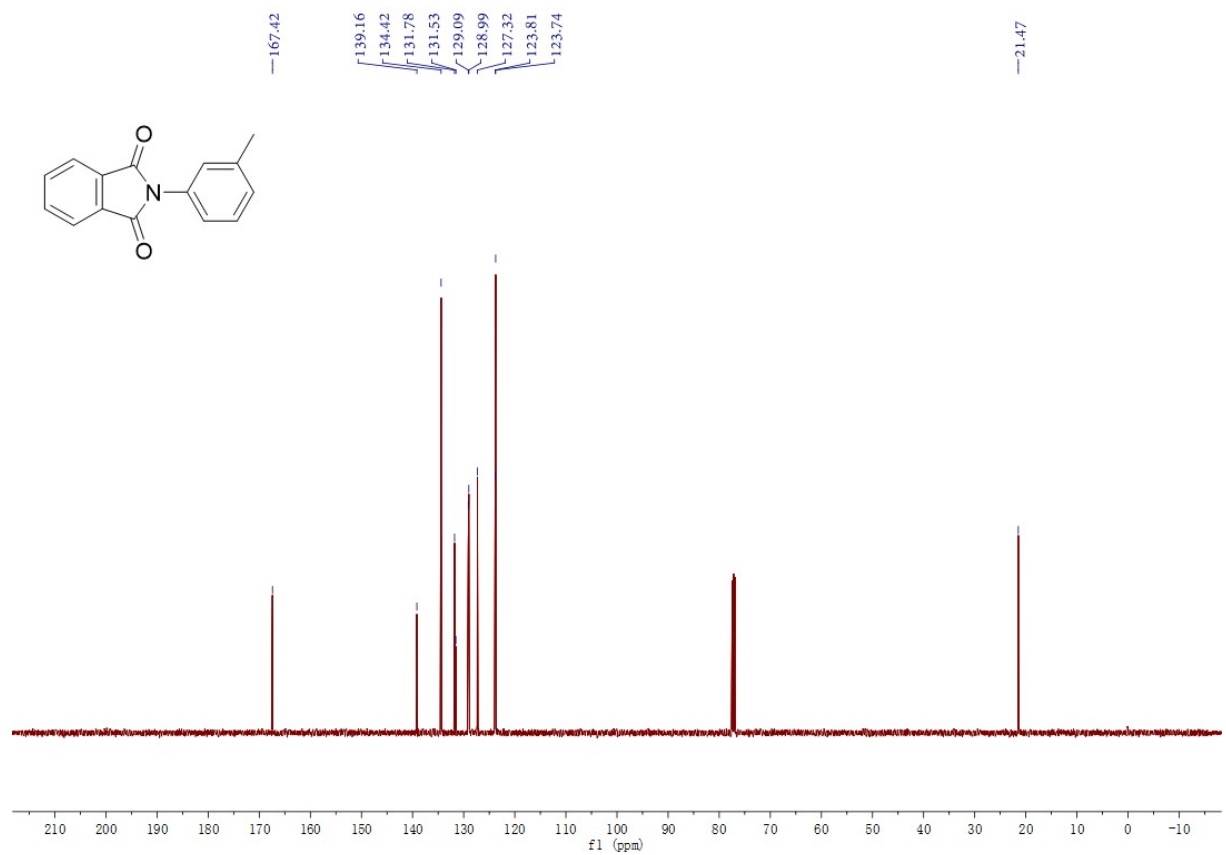
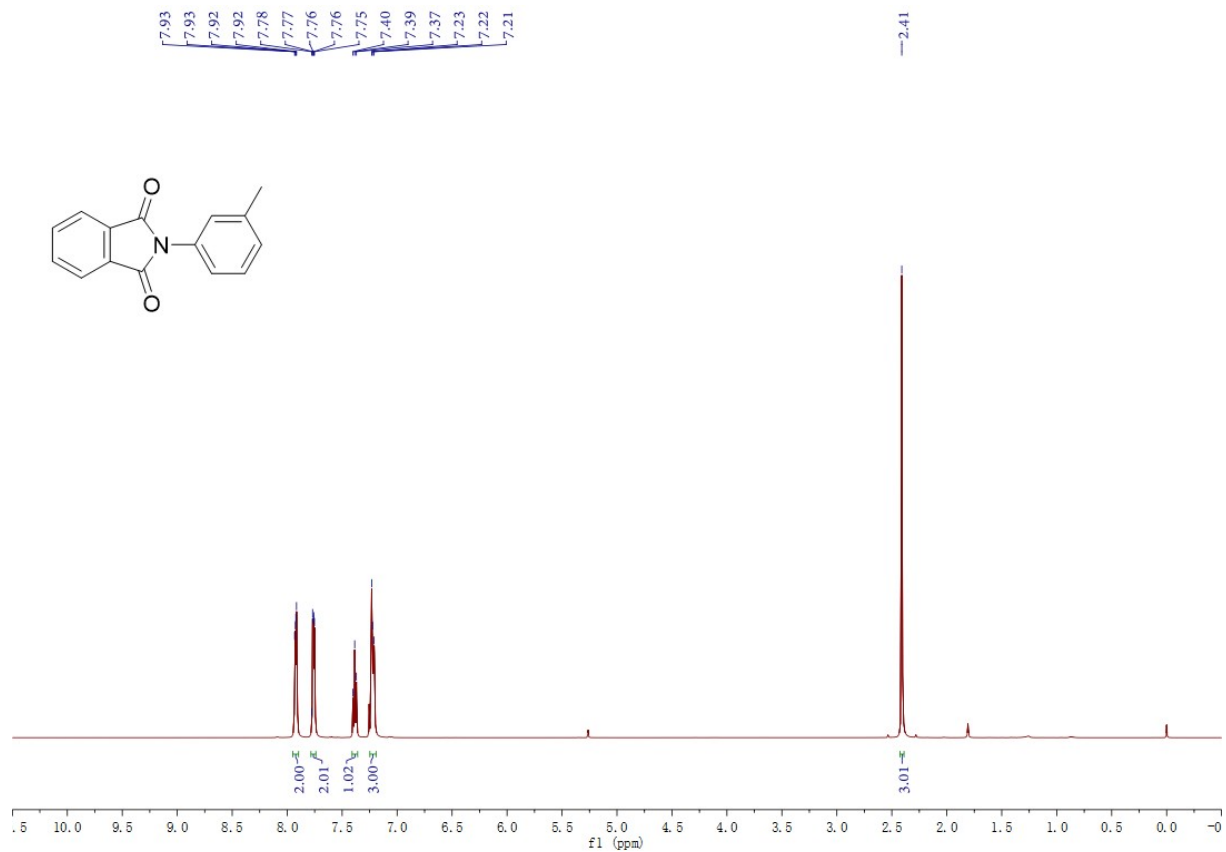
1-(3-methoxyphenyl)pyrrolidine-2,5-dione (3k)^{S3}

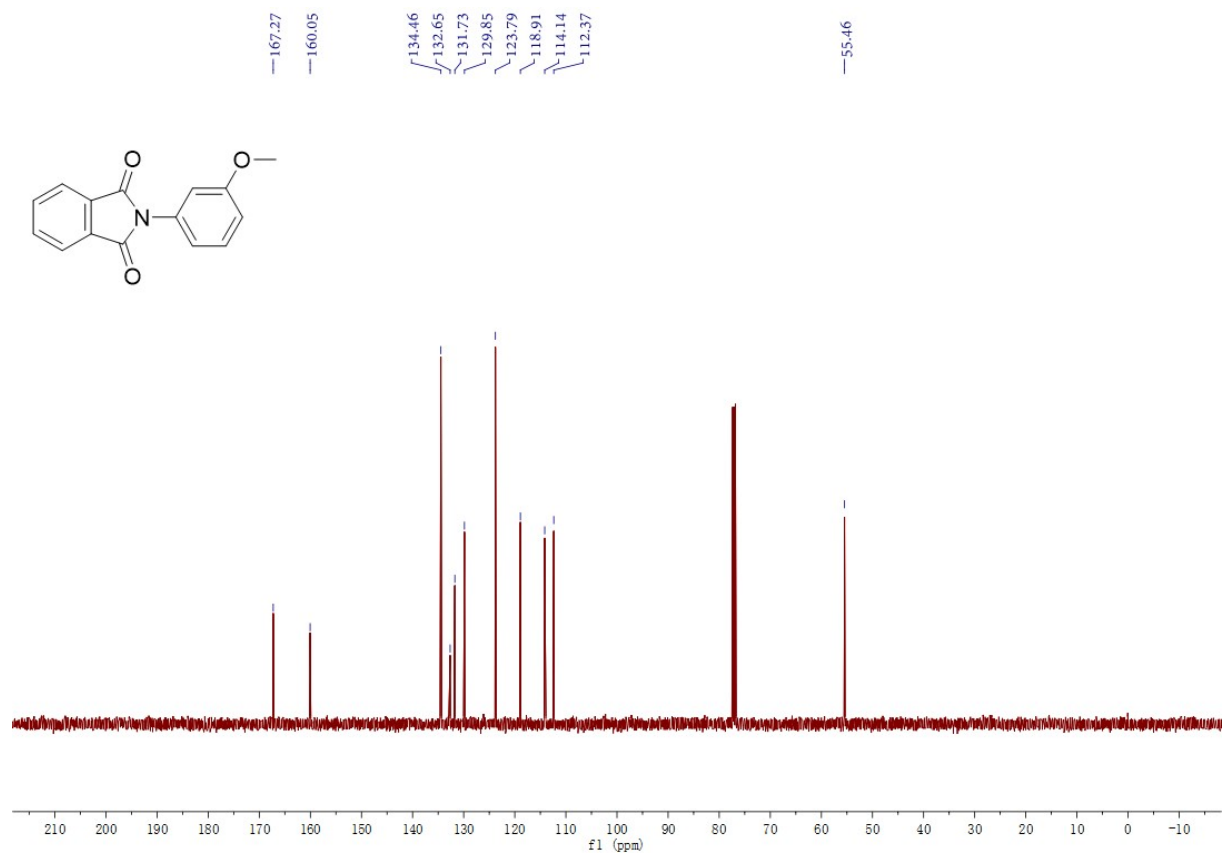
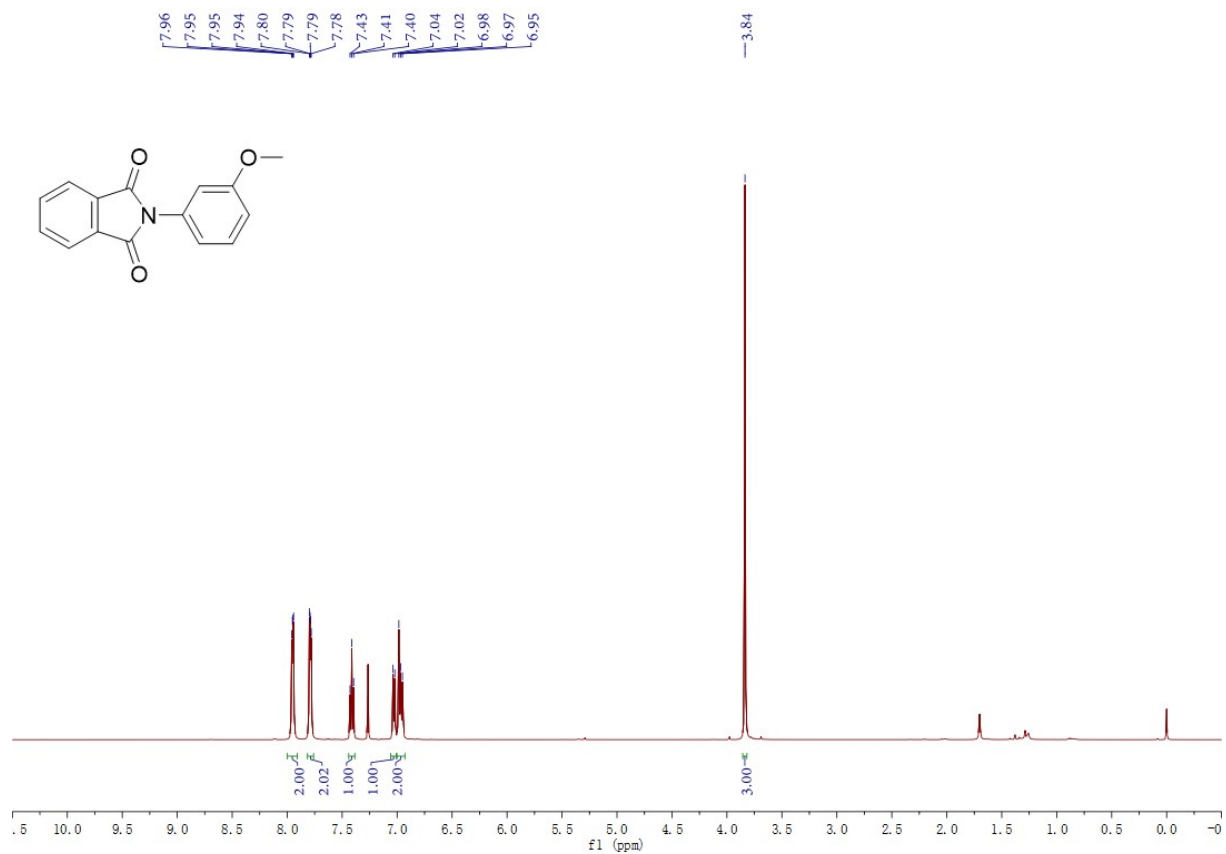
¹H NMR (500 MHz, (CD₃)₂SO) δ 7.39 (t, *J* = 8.3 Hz, 1H), 7.03-6.95 (m, 1H), 6.83 (d, *J* = 7.3 Hz, 2H), 3.75 (s, 3H), 2.76 (s, 4H);

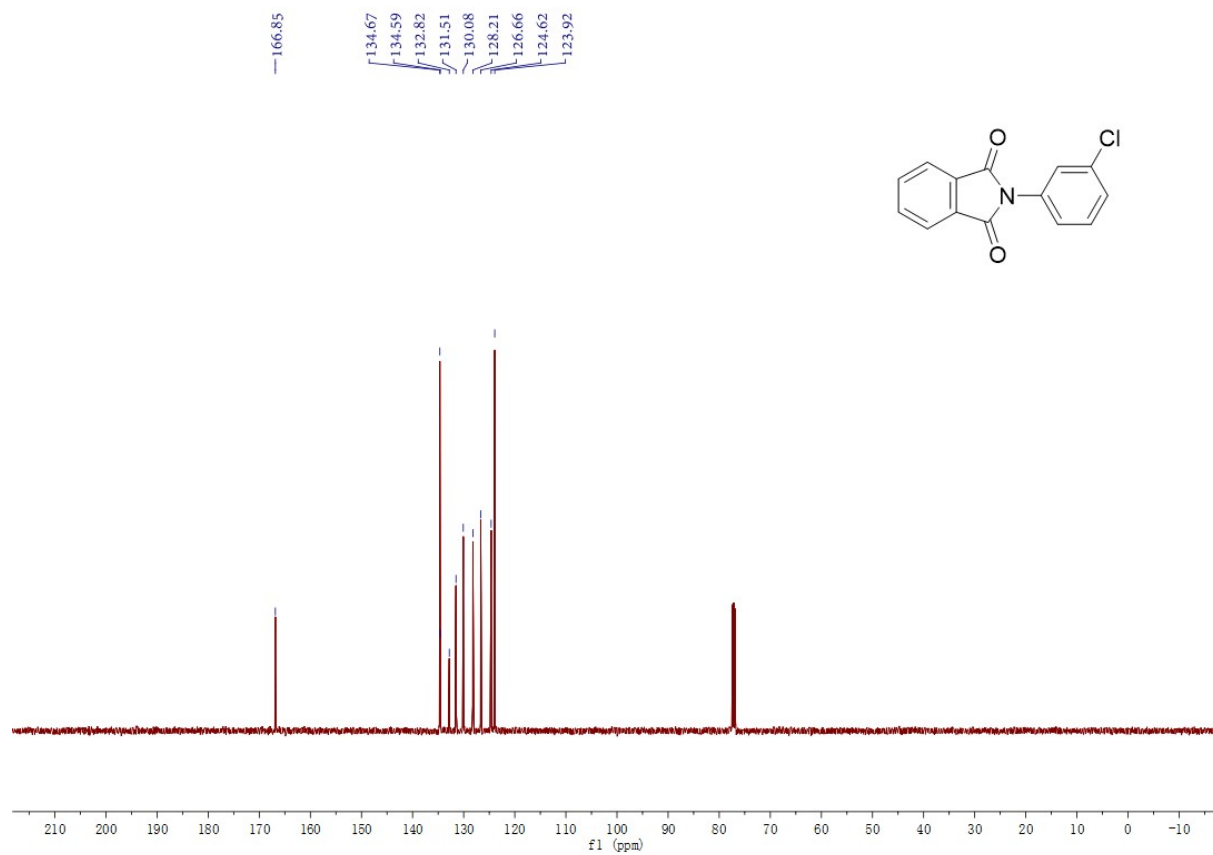
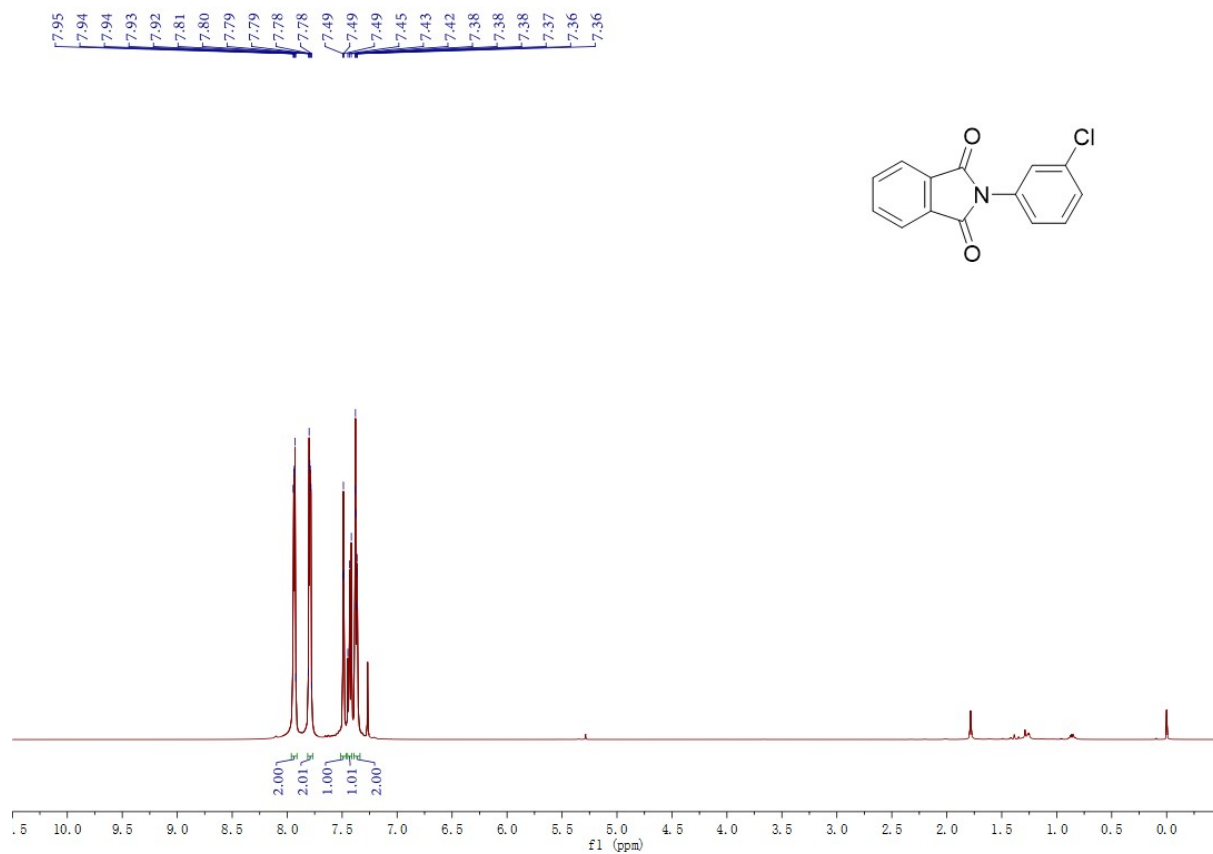
¹³C NMR (126 MHz, (CD₃)₂SO) δ 177.34, 159.90, 134.32, 130.06, 119.84, 114.19, 113.49, 55.76, 28.93.

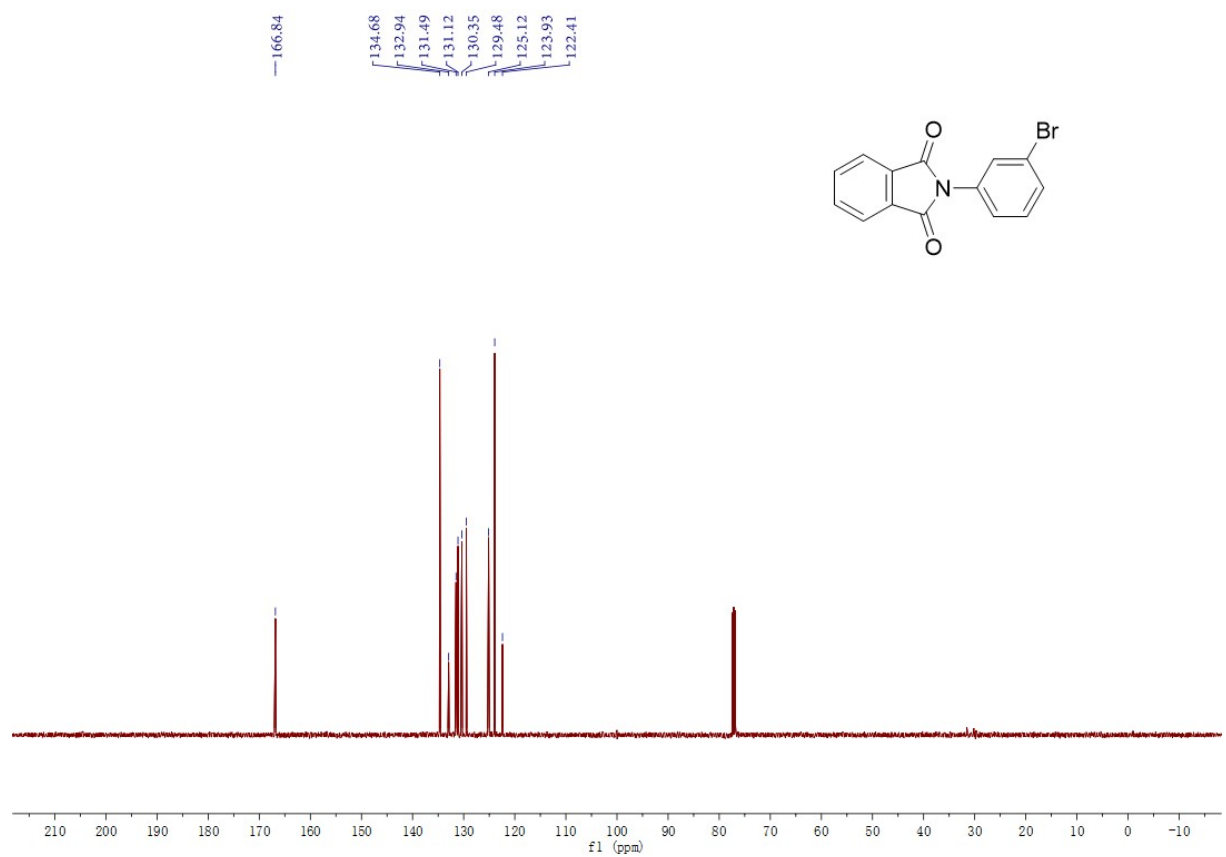
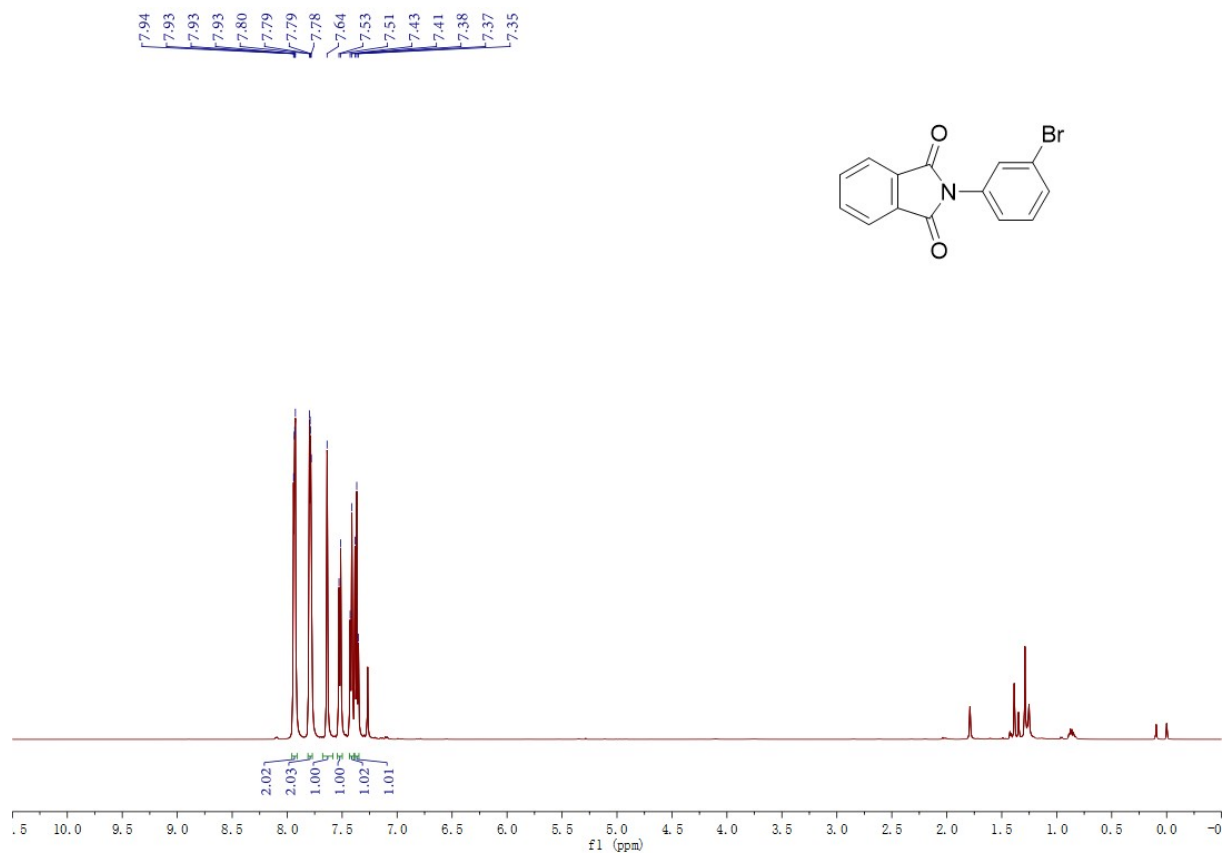
NMR Spectra

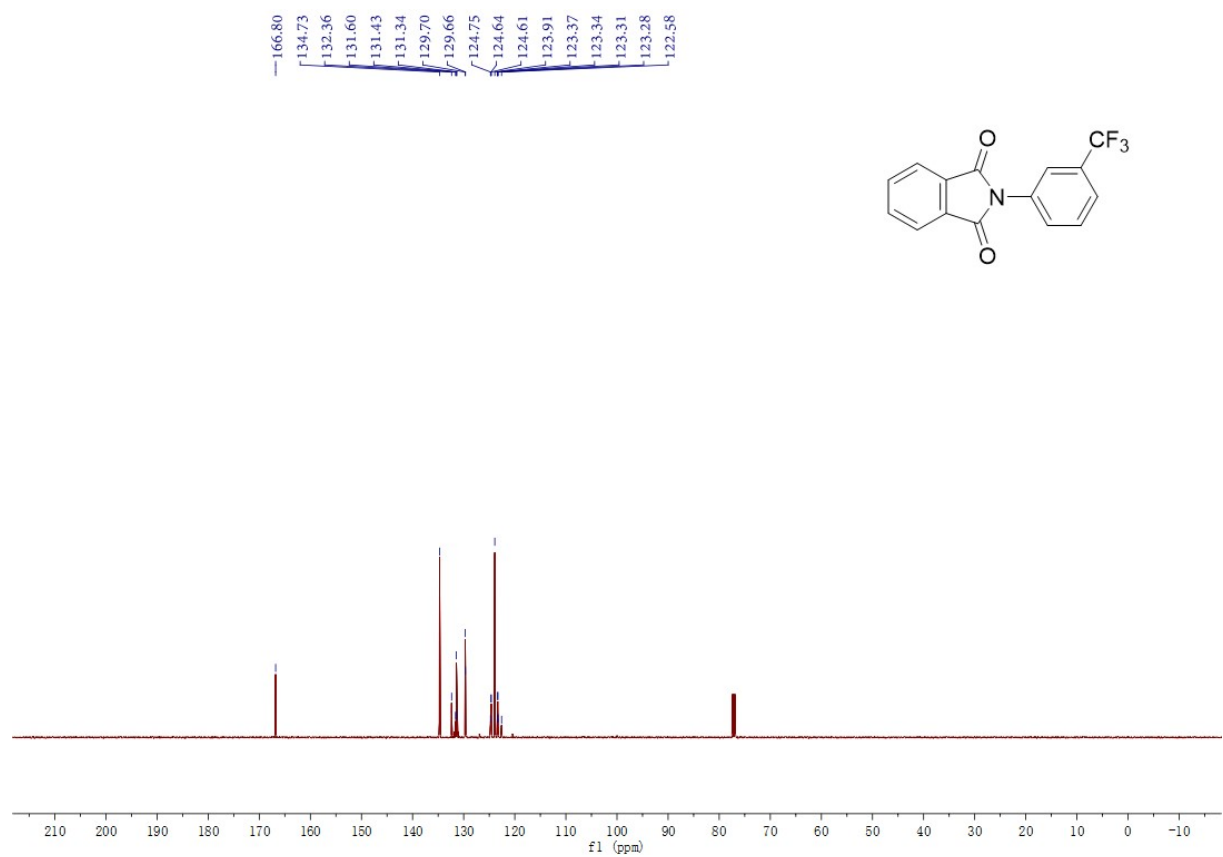
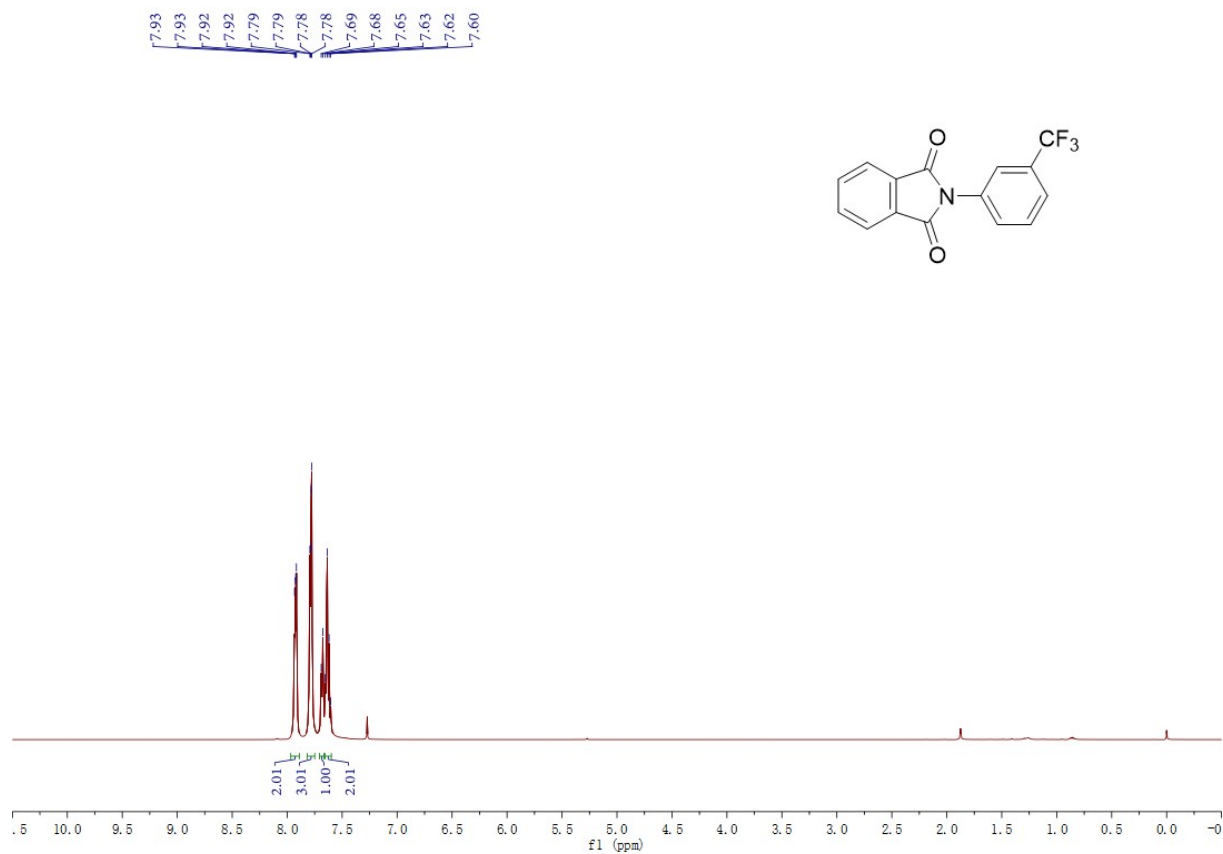


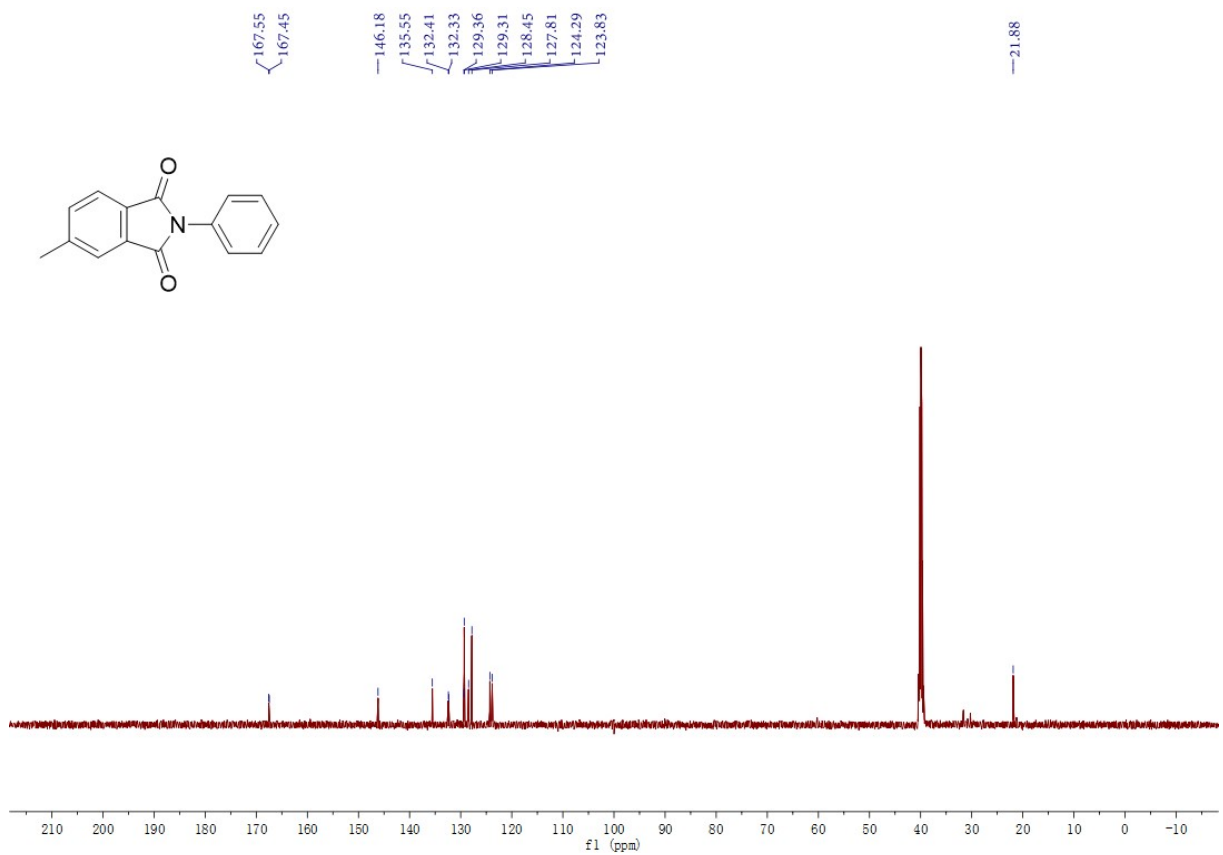
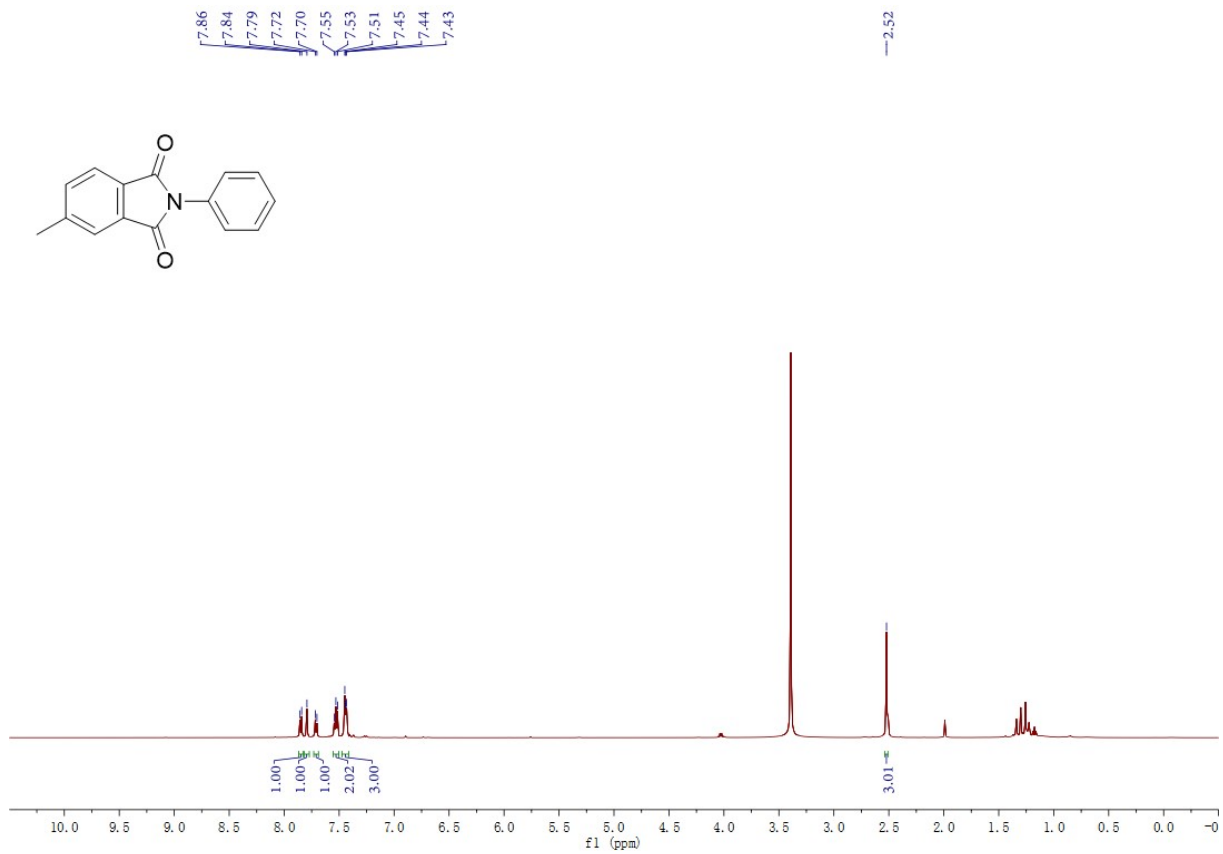


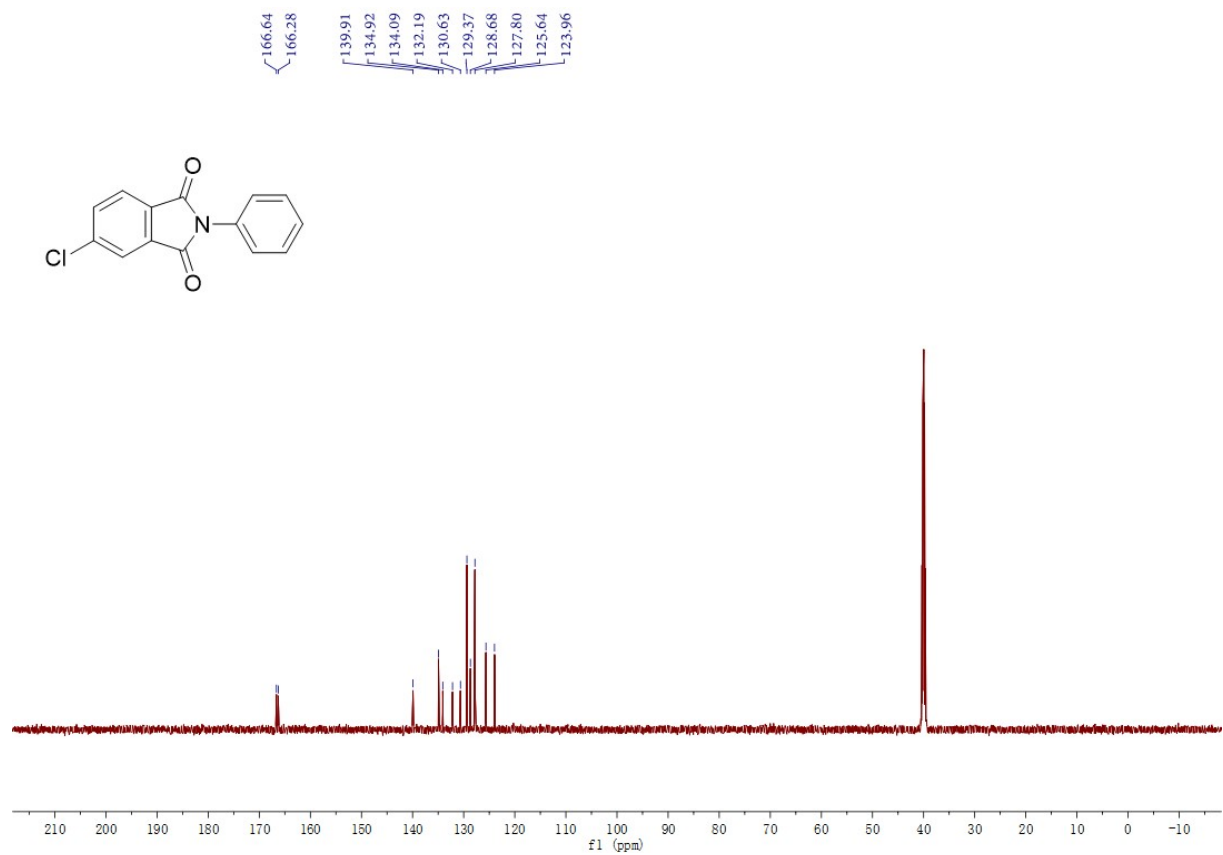
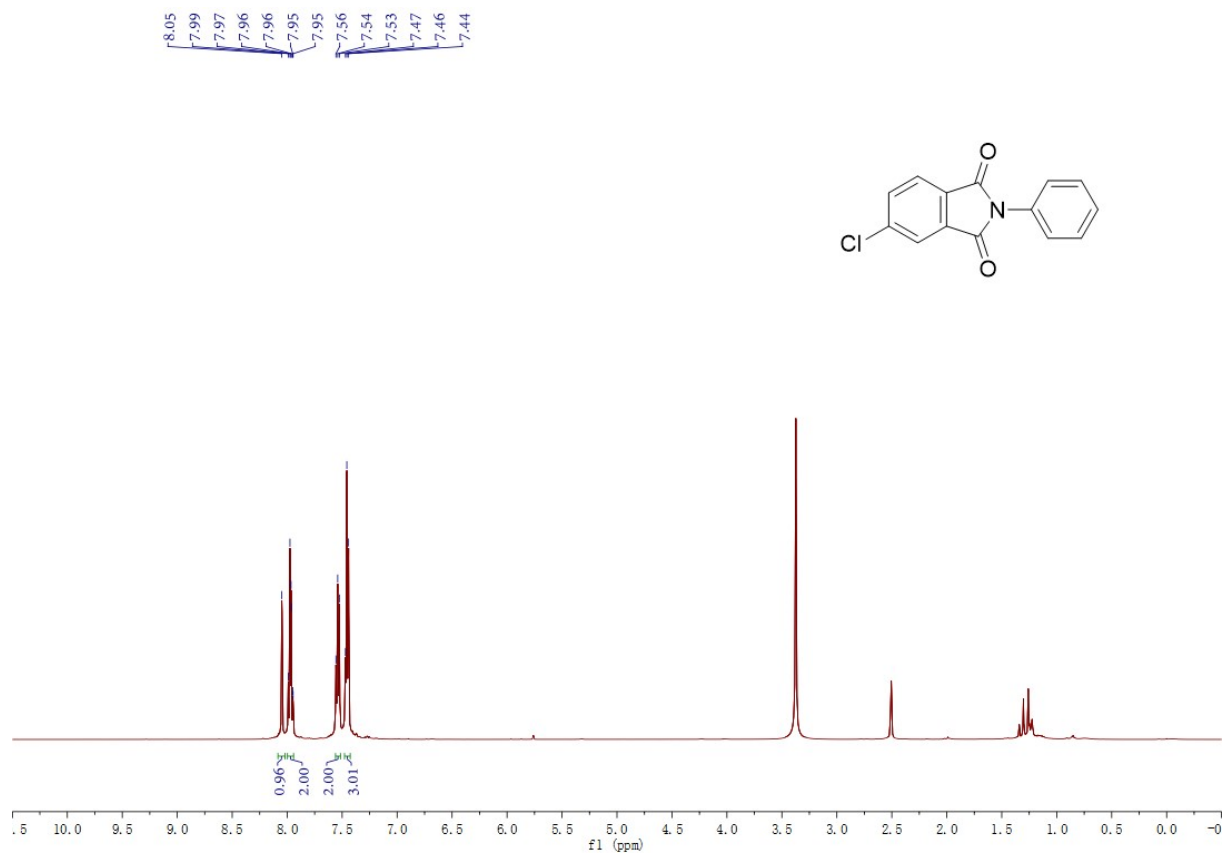


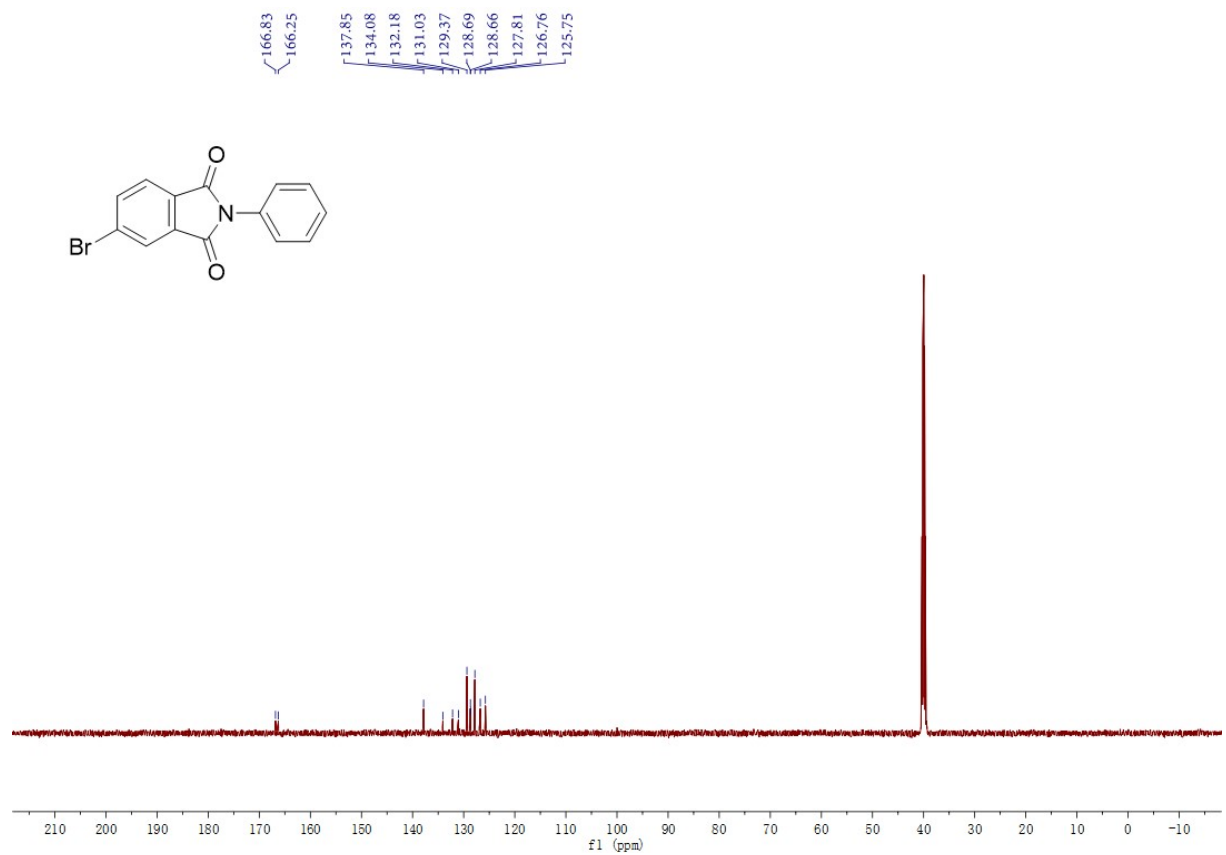
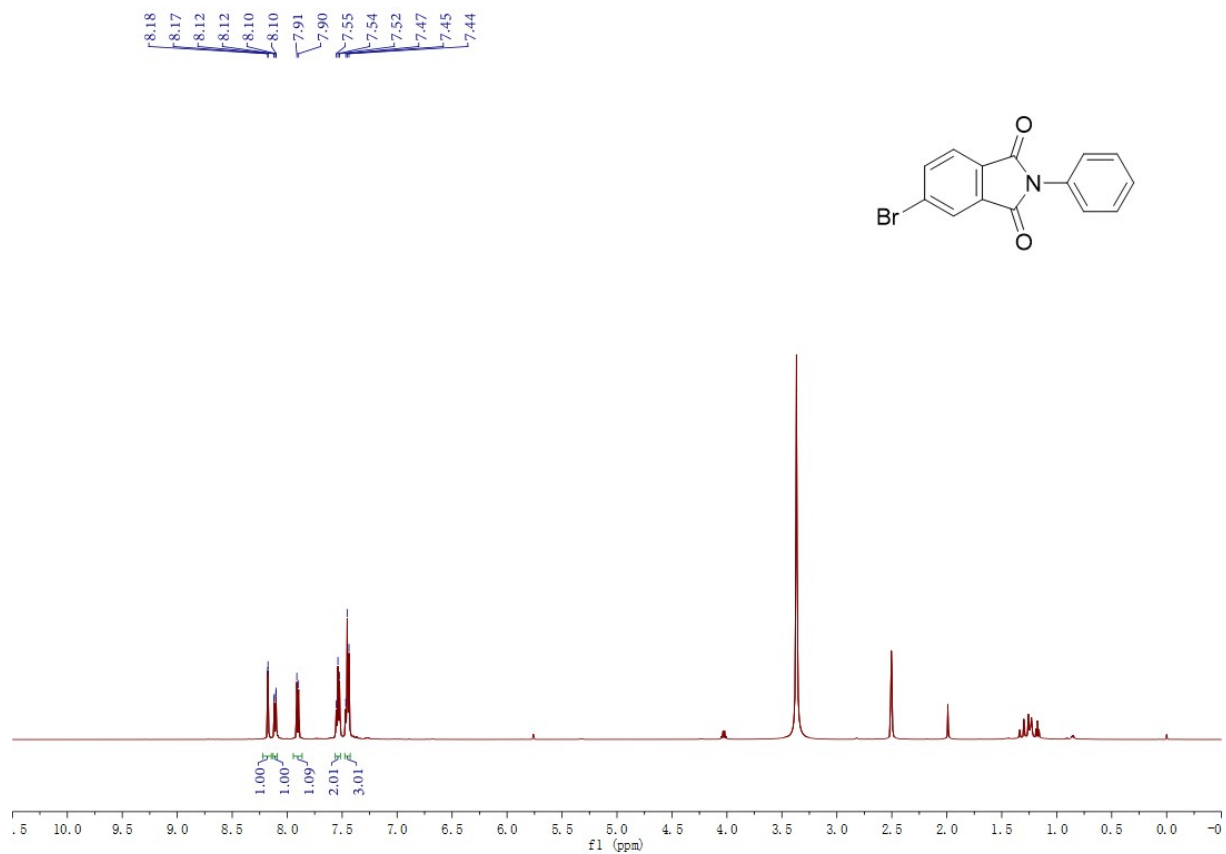




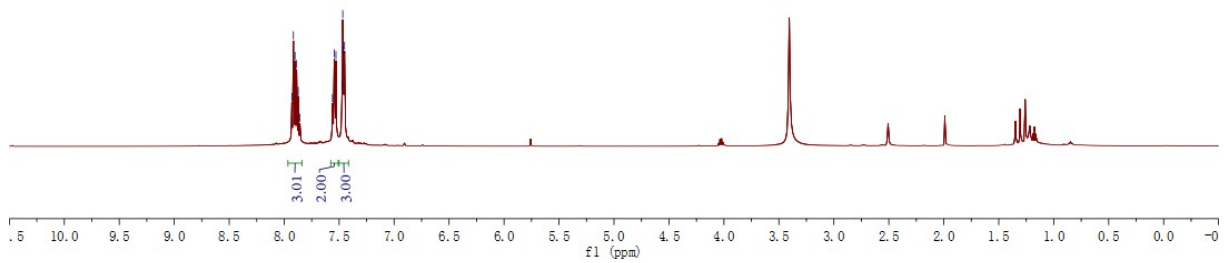
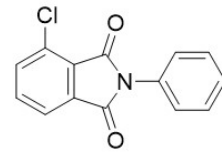




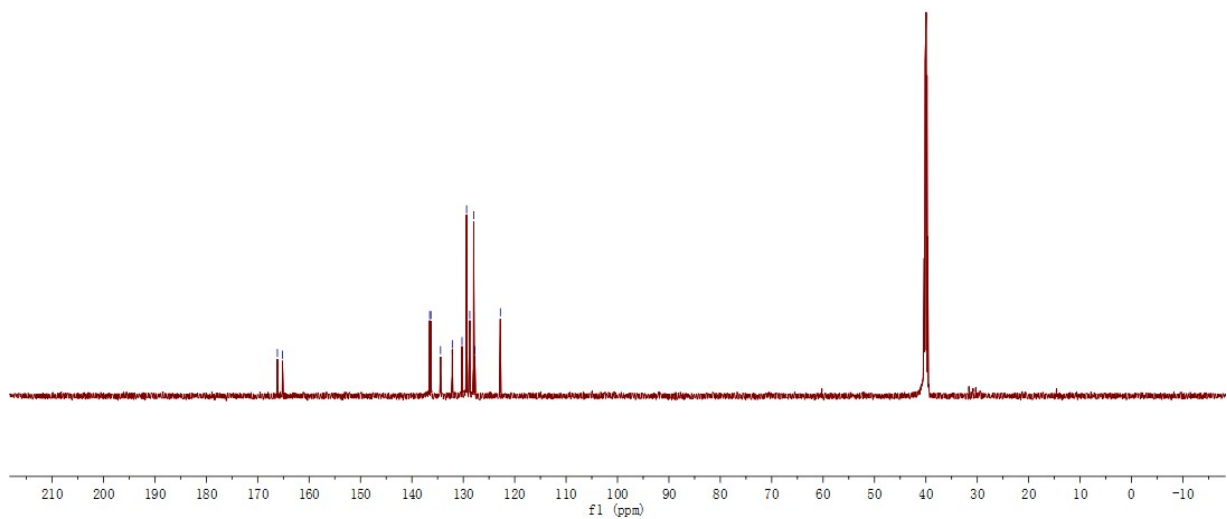
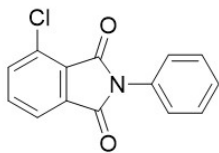


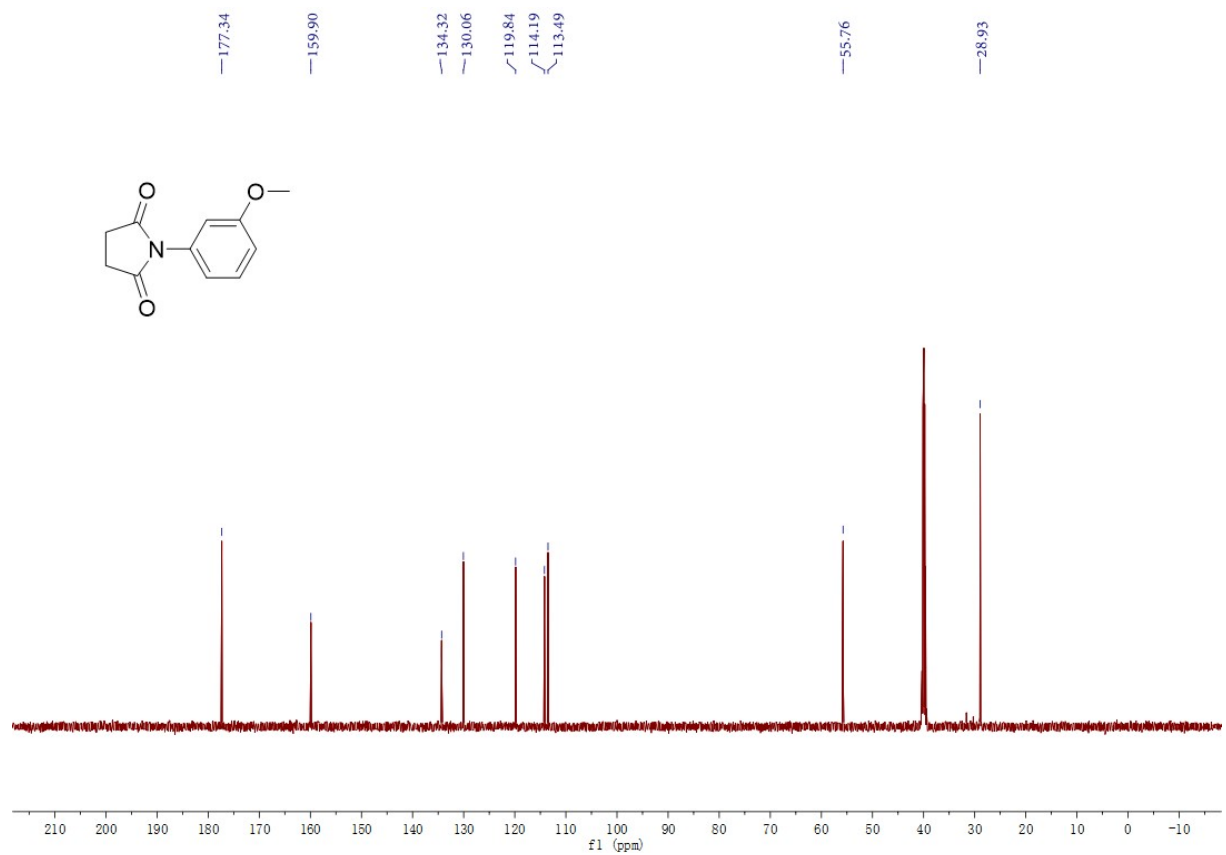
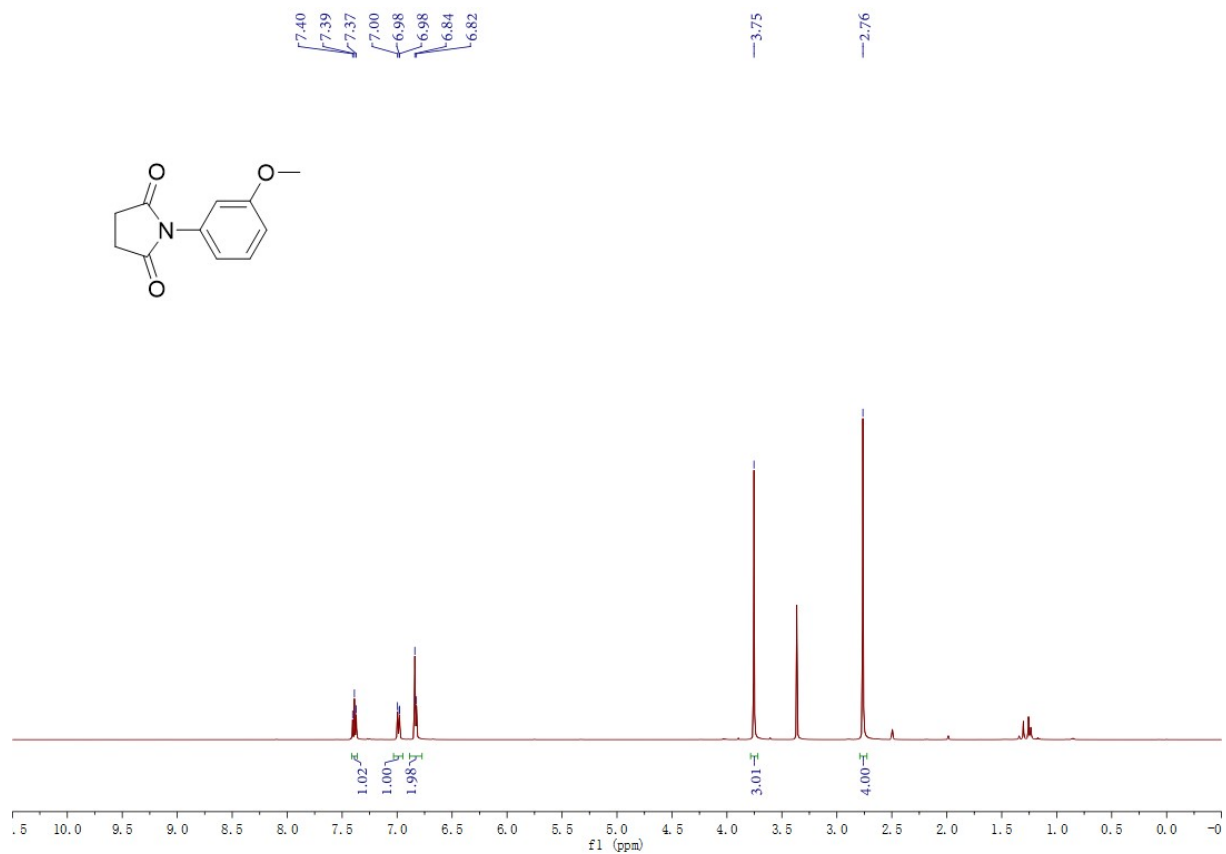


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References

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- (S3) F. P. L. Lim, L. Y. Tan, E. R. T. Tiekinkb, A. V. Dolzhenko. *RSC Adv.*, 2018, **8**, 22351-22360.