Metal-Free Intermolecular Aminochlorination of Unactivated Alkenes

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Experimental Part

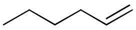
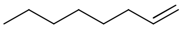
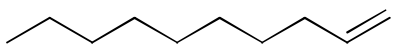
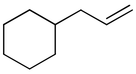
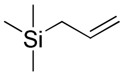
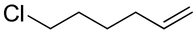
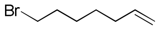
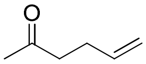
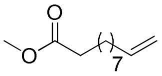
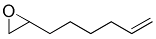
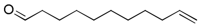
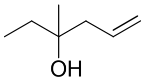
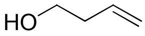
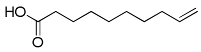
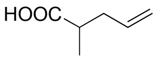
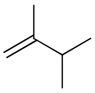
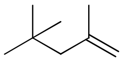
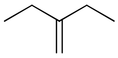
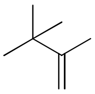
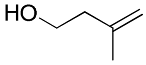
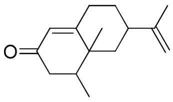
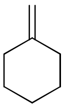
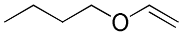
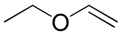
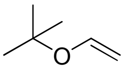
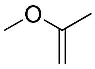
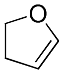
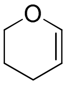
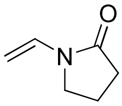
Experimental Part

Materials and Methods

All reactions were carried out under an atmosphere of nitrogen in flame-dried glassware with magnetic stirring unless otherwise indicated. Commercially obtained reagents were used as received. Solvents were dried by Innovative Technology Solvent Purification System. Liquids and solutions were transferred via syringe. All reactions were monitored by thin-layer chromatography. GC and GC-MS data were recorded on Thermo Trace 1300 and Thermo ISQ QD, respectively. ^{1}H and ^{13}C NMR spectra were recorded on Bruker-BioSpin AVANCE III HD. Data for ^{1}H NMR spectra are reported relative to chloroform (7.26 ppm) as an internal standard and are reported as follows: chemical shift (ppm), multiplicity, coupling constant (Hz) and integration. Data for ^{13}C NMR spectra are reported relative to chloroform (77.23 ppm) as an internal standard and are reported in terms of chemical shift (ppm). HRMS data were recorded on Bruker Impact II UHR-TOF. Melting Point were obtained from Shanghai Shengguang SGW X-4.

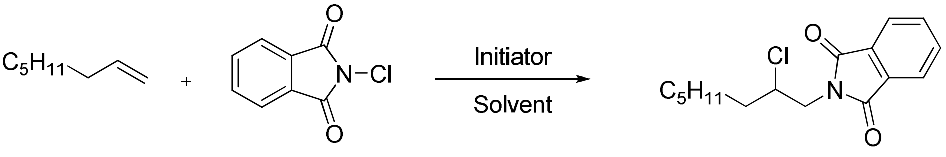
Synthesis of Alkenes

Alkenes were purchased from the following companies:

Alkene	Company	Alkene	Company	Alkene	Company
	TCI		J&K		Energy
	TCI		Aladdin		Energy
	Ark		Aladdin		Energy
	Alfa		Tansoole		Alfa
	Energy		Energy		TCI
	Adamas		Energy		Energy
	TCI		Energy		TCI
	Adamas		Energy		Ou he
	Heowns		Energy		Energy
	Energy		Energy		

General Procedure for the Chloroamination of Alkenes

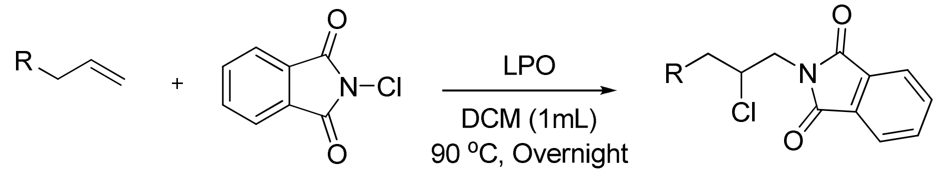
General Procedure for Reaction Condition Optimizations:



1a, 0.5 mmol NCP **2a**

1-octene **1a** (56 mg, 0.5 mmol, 1 equiv.), NCP, initiator, and solvent were added into a flame-dried Schlenk tube with a stirring bar under a nitrogen atmosphere. The reaction mixture was heated overnight. Then, the reaction mixture was cooled to ambient temperature. The reaction solution was diluted with 10 mL of CH_2Cl_2 and concentrated by rotary evaporator under reduced pressure and the residue was purified by column chromatography on silica gel (EA/PE=0/100-30/100) to yield **2a**.

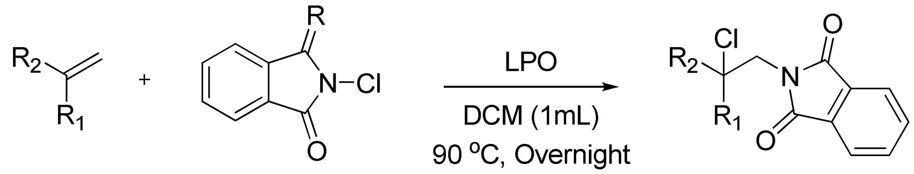
General Procedure for Monosubstituted Unactivated Alkenes:



1, 0.5 mmol NCP **2**

Alkene **1** (0.5 mmol, 1 equiv.), NCP (115 mg, 0.625 mmol, 1.25 equiv.), LPO (50 mg, 0.125 mmol, 0.25 equiv.), and DCM (1 mL) were added into a flame-dried Schlenk tube with a stirring bar under a nitrogen atmosphere. The reaction mixture was heated to 90 °C overnight. Then, the reaction mixture was cooled to ambient temperature. The reaction solution was diluted with 10 mL of CH_2Cl_2 and concentrated by rotary evaporator under reduced pressure and the residue was purified by column chromatography on silica gel (EA/PE=0/100-60/100) to yield **2**.

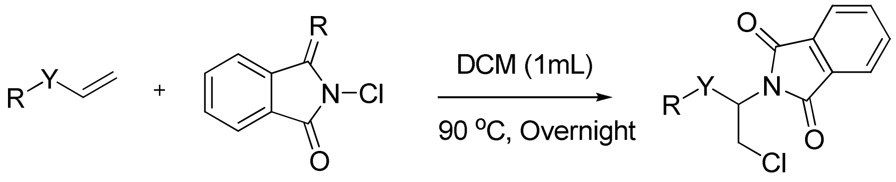
General Procedure for 1,1-Disubstituted Unactivated Alkenes:



3, 0.5 mmol NCP **4**

Alkene **3** (0.5 mmol, 1 equiv.), NCP (115 mg, 0.625 mmol, 1.25 equiv.), LPO (50 mg, 0.125 mmol, 0.25 equiv.), and DCM (1 mL) were added into a flame-dried Schlenk tube with a stirring bar under a nitrogen atmosphere. The reaction mixture was heated to 90 °C overnight. Then, the reaction mixture was cooled to ambient temperature. The reaction solution was diluted with 10 mL of CH_2Cl_2 and concentrated by rotary evaporator under reduced pressure and the residue was purified by column chromatography on silica gel (EA/PE=0/100-60/100) to yield **4**.

General Procedure for Heteroatom Substituted Alkenes:



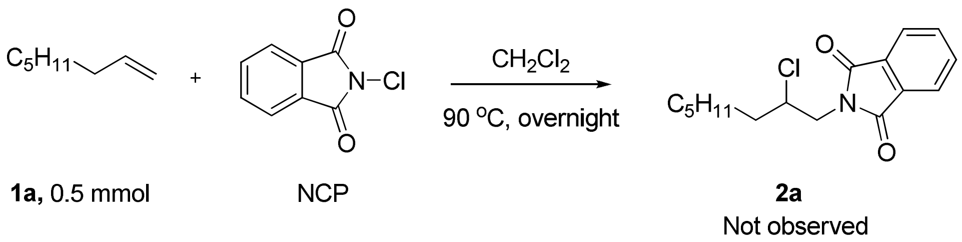
5, 0.5 mmol NCP **6**

Alkene **5** (0.5 mmol, 1 equiv.), NCP (115 mg, 0.625 mmol, 1.25 equiv.), and DCM (1 mL) were added into a flame-dried Schlenk tube with a stirring bar under a nitrogen atmosphere. The reaction mixture was heated to 90 °C overnight. Then, the reaction mixture was cooled to ambient temperature. The reaction solution was diluted with 10 mL of CH_2Cl_2 and concentrated by rotary evaporator under reduced pressure and the residue was purified by column chromatography on silica gel (EA/PE=0/100-40/100) to yield **6**.

General Procedure for Experimental Mechanistic Studies:

For alkene chloroamination without LPO:

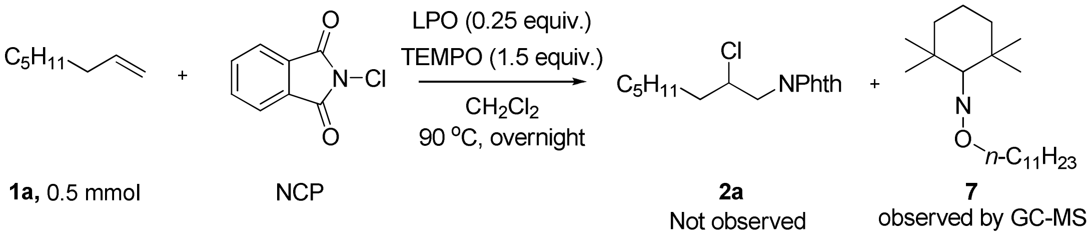
Without LPO



Alkene **1a** (0.5 mmol, 1 equiv.), NCP (115 mg, 0.625 mmol, 1.25 equiv.), and DCM (1 mL) were added into a flame-dried Schlenk tube with a stirring bar under a nitrogen atmosphere. The reaction mixture was heated to 90 °C overnight. Then, the reaction mixture was cooled to ambient temperature. The reaction solution was diluted with 10 mL of CH_2Cl_2 and passed through a short pad of celite. The filtrate was detected by TLC and GC-MS and compound **2a** was not observed.

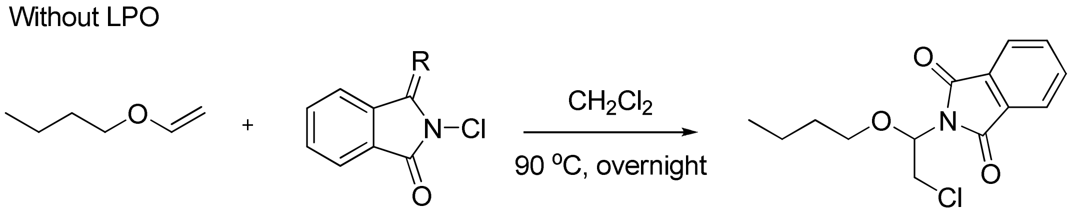
For alkene chloroamination with TEMPO:

With TEMPO



Alkene **1a** (0.5 mmol, 1 equiv.), NCP (115 mg, 0.625 mmol, 1.25 equiv.), LPO (50 mg, 0.125 mmol, 0.25 equiv.), TEMPO (117 mg, 0.75mmol, 1.5 equiv.), and DCM (1 mL) were added into a flame-dried Schlenk tube with a stirring bar under a nitrogen atmosphere. The reaction mixture was heated to 90 °C overnight. Then, the reaction mixture was cooled to ambient temperature. The reaction solution was diluted with 10 mL of CH_2Cl_2 and passed through a short pad of celite. The filtrate was detected by TLC and GC-MS. Compound **7** was observed, while **2a** was not observed.

For chloroamination of heteroatom-substituted alkene without LPO:

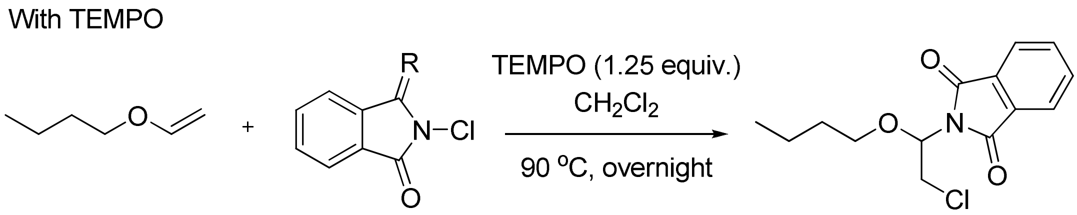


5a, 0.5mmol NCP, 1.25 equiv.

6a
83%, single regio

Alkene **5a** (0.5 mmol, 1 equiv.), NCP (115 mg, 0.625 mmol, 1.25 equiv.), and DCM (1 mL) were added into a flame-dried Schlenk tube with a stirring bar under a nitrogen atmosphere. The reaction mixture was heated to 90 ^oC overnight. Then, the reaction mixture was cooled to ambient temperature. The reaction solution was diluted with 10 mL of CH_2Cl_2 and concentrated by rotary evaporator under reduced pressure and the residue was purified by column chromatography on silica gel (EA/PE=0/100-20/100) to yield **6a**.

For chloroamination of heteroatom-substituted alkene with TEMPO:

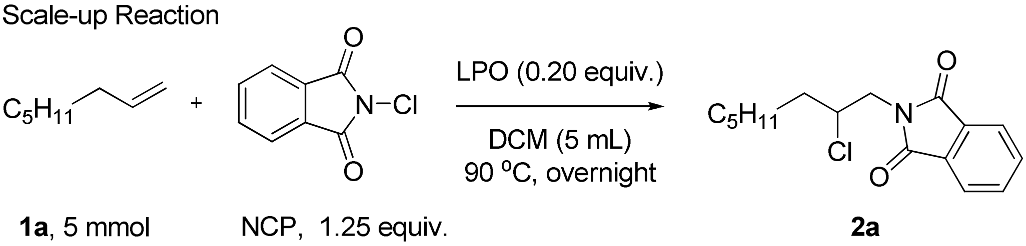


5a, 0.5 mmol NCP, 1.25 equiv.

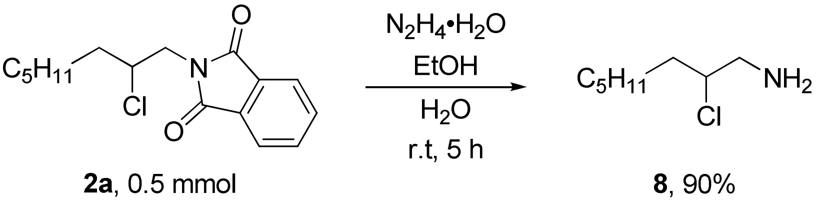
6a
81%, single regio

Alkene **5a** (0.5 mmol, 1 equiv.), NCP (115 mg, 0.625 mmol, 1.25 equiv.), TEMPO (97.5mg, 0.625 mmol, 1.25 equiv.), and DCM (1 mL) were added into a flame-dried Schlenk tube with a stirring bar under a nitrogen atmosphere. The reaction mixture was heated to 90 ^oC overnight. Then, the reaction mixture was cooled to ambient temperature. The reaction solution was diluted with 10 mL of CH_2Cl_2 and concentrated by rotary evaporator under reduced pressure and the residue was purified by column chromatography on silica gel (EA/PE=0/100-20/100) to yield **6a**.

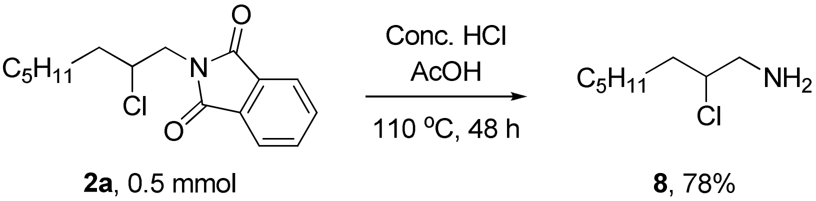
General Procedure for Synthetic Applications:



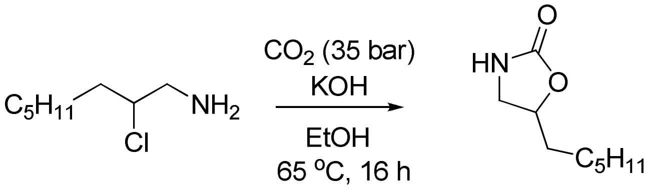
Alkene **1a** (5 mmol, 1 equiv.), NCP (1150 mg, 6.25 mmol, 1.25 equiv.), LPO (400 mg, 1.0 mmol, 0.20 equiv.), and DCM (5 mL) were added into a flame-dried Schlenk tube with a stirring bar under a nitrogen atmosphere. The reaction mixture was heated to 90 °C overnight. Then, the reaction mixture was cooled to ambient temperature. The reaction solution was diluted with 30 mL of CH_2Cl_2 and concentrated by rotary evaporator under reduced pressure and the residue was purified by column chromatography on silica gel (EA/PE=0/100-30/100) to yield **2a**.



2a (0.5 mmol, 1 equiv.), $N_2H_4{\cdot}H_2O$ (5 mmol, 10 equiv.), EtOH (6 mL), and H_2O (27 mg, 3 equiv.) were added into a flame-dried Schlenk tube with a stirring bar under a nitrogen atmosphere. The reaction mixture was stirred at room temperature for 5 hours. The reaction solution was clarified by filtration. 30 mL of petroleum ether was added to the filtrate. The solution was clarified by filtration and concentrated by rotary evaporator under reduced pressure. The reaction solution was washed by water and extraction with (20 mL × 3) CH_2Cl_2. The organic layer was dried over magnesium sulfate, filtered, and concentrated by rotary evaporator under reduced pressure to yield compound **8**.

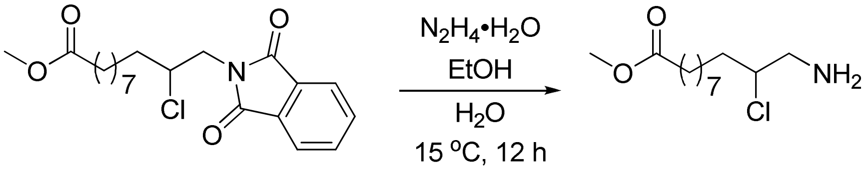


2a (0.5 mmol, 1 equiv.), Conc. HCl (3 mL), and AcOH (2 mL) were added into a flame-dried Schlenk tube with a stirring bar under nitrogen. The reaction mixture was heated to 110 °C for 48 hours. Then, the reaction mixture was cooled to ambient temperature. The reaction solution was clarified by filtration. 30 mL of petroleum ether was added to the filtrate. The solution was clarified by filtration and concentrated by rotary evaporator under reduced pressure. The residue was washed by sodium hydroxide solution and the pH was adjusted to 9-10. The solution was extracted with (20 mL × 3) CH_2Cl_2. The organic layer was dried over magnesium sulfate, filtered and concentrated by rotary evaporator under reduced pressure to yield compound **8**.



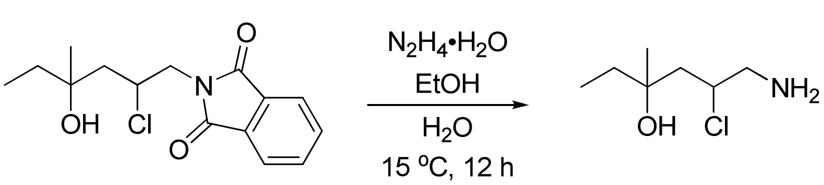
8 **9**, 91%

8 (0.5 mmol, 1.0 equiv.), EtOH (5 mL), and KOH (84 mg, 3.0 equiv.) were added into a stainless steel autoclave reactor equipped with a pressure gauge. The autoclave was then sealed, purged three times and pressurized with carbon dioxide (35 bar). The autoclave was heated to 65 °C in an oil bath while stirring for 16 hours. After the reaction, the autoclave was cooled to ambient temperature and depressurized. The reaction solution was diluted with 30 mL of CH_2Cl_2 and concentrated by rotary evaporator under reduced pressure and the residue was purified by column chromatography on silica gel (PE/EA =40/60-20/80) to yield **9**.



2i, 0.5 mmol **10**, 85%

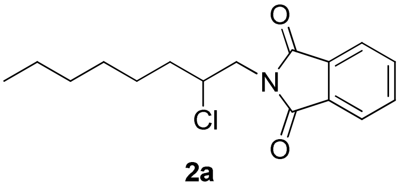
2i (0.5 mmol, 1 equiv.), $N_2H_4·H_2O$ (5 mmol, 10 equiv.), EtOH (6 mL), and H_2O (27 mg, 3 equiv.) were added into a flame-dried Schlenk tube with a stirring bar under a nitrogen atmosphere. The reaction mixture was stirred at 15 °C for 12 hours. The reaction solution was clarified by filtration. 30 mL of petroleum ether was added to the filtrate. The solution was clarified by filtration and concentrated by rotary evaporator under reduced pressure. The reaction solution was washed by water and extraction with (20 mL × 3) CH_2Cl_2. The organic layer was dried over magnesium sulfate, filtered, and concentrated by rotary evaporator under reduced pressure to yield compound **10**.



2l, 0.5 mmol **11**, 72%

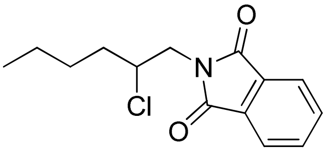
2l (0.5 mmol, 1 equiv.), $N_2H_4{\cdot}H_2O$ (5 mmol, 10 equiv.), EtOH (6 mL), and H_2O (27 mg, 3 equiv.) were added into a flame-dried Schlenk tube with a stirring bar under a nitrogen atmosphere. The reaction mixture was stirred at 15 ^{o}C for 12 hours. The reaction solution was clarified by filtration. 30 mL of petroleum ether was added to the filtrate. The solution was clarified by filtration and concentrated by rotary evaporator under reduced pressure. The reaction solution was washed by water and extraction with (20 mL × 3) CH_2Cl_2. The organic layer was dried over magnesium sulfate, filtered, and concentrated by rotary evaporator under reduced pressure to yield compound **11**.

Characterization Data for the Products:



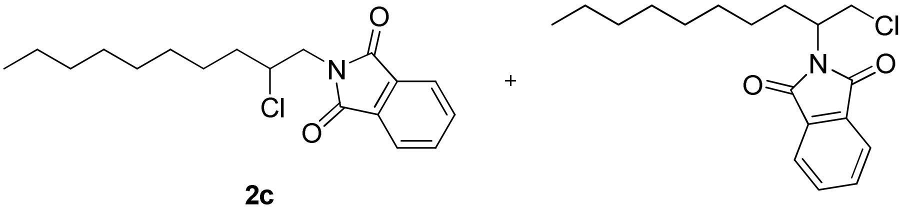
2a

Following the general procedure for monosubstituted unactivated alkenes, **2a** was obtained as a white solid (100 mg, 68% yield, regio 10:1). Mp: 65.3-66.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 5.3, 3.0 Hz, 2H), 7.74 (dd, *J* = 5.5, 3.1 Hz, 2H), 4.39 – 4.23 (m, 1H), 4.02 (dd, *J* = 14.1, 8.9 Hz, 1H), 3.85 (dd, *J* = 14.1, 5.1 Hz, 1H), 1.86 – 1.70 (m, 2H), 1.65 – 1.56 (m, 1H), 1.50 – 1.40 (m, 1H), 1.35 – 1.24 (m, 6H), 0.88 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.06, 134.16, 131.86, 123.50, 59.50, 44.33, 35.74, 31.62, 28.71, 26.16, 22.54, 14.04. HRMS (ESI) calcd for $[C_{16}H_{20}ClNO_2Na]^+$ ($[M+Na]^+$): 316.1075, found: 316.1076.



2b

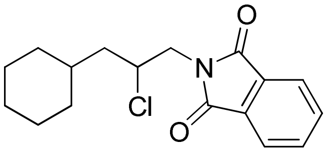
Following the general procedure for monosubstituted unactivated alkenes, **2b** was obtained as a white solid (89 mg, 67% yield, regio 9:1). Mp: 67.9-68.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.74 (dd, *J* = 5.5, 3.0 Hz, 2H), 4.37 – 4.23 (m, 1H), 4.02 (dd, *J* = 14.0, 8.9 Hz, 1H), 3.85 (dd, *J* = 14.1, 5.1 Hz, 1H), 1.88 – 1.68 (m, 2H), 1.64 – 1.56 (m, 1H), 1.48 – 1.30 (m, 3H), 0.92 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.05, 134.16, 131.85, 123.50, 59.48, 44.33, 35.44, 28.33, 22.18, 13.91. HRMS (ESI) calcd for $[C_{14}H_{16}ClNO_2Na]^+$ ($[M+Na]^+$): 288.0762, found: 288.0763.



2c

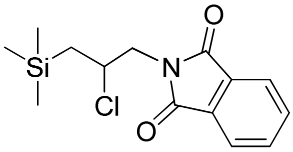
2cc, regioisomer of **2c**

Following the general procedure for monosubstituted unactivated alkenes, **2c** and **2cc** were obtained as a white solid (108 mg, 67% yield, regio 10:1, mixture of regioisomers). Mp: 60.4-61.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.74 (dd, *J* = 5.4, 3.1 Hz, 2H), 4.53 – 4.39 (m, 0.09H), 4.35 – 4.26 (m, 0.92H), 4.21 – 4.12 (m, 0.09H), 4.02 (dd, *J* = 14.0, 8.8 Hz, 0.93H), 3.85 (dd, *J* = 14.1, 5.2 Hz, 0.93H), 3.76 (dd, *J* = 11.2, 5.0 Hz, 0.09H), 1.86 – 1.69 (m, 2H), 1.49 – 1.40 (m, 1H), 1.39 – 1.17 (m, 11H), 0.88 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.06, 134.16, 131.86, 123.50, 59.50, 44.34, 35.74, 31.83, 29.39, 29.18, 29.05, 26.20, 22.65, 14.11. HRMS (ESI) calcd for $[C_{18}H_{24}ClNO_2Na]^+$ ($[M+Na]^+$): 344.1388, found: 344.1388.



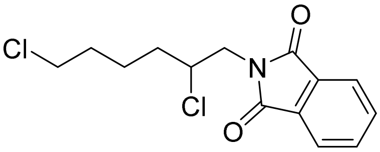
2d

Following the general procedure for monosubstituted unactivated alkenes, **2d** was obtained as a clean oil (110 mg, 72% yield, regio 11:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.74 (dd, *J* = 5.4, 3.1 Hz, 2H), 4.49 – 4.35 (m, 1H), 4.00 (dd, *J* = 14.1, 8.9 Hz, 1H), 3.83 (dd, *J* = 14.1, 4.9 Hz, 1H), 1.85 – 1.62 (m, 7H), 1.39 – 1.27 (m, 2H), 1.22 – 0.82 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.08, 134.16, 131.85, 123.50, 57.12, 44.70, 43.33, 34.51, 33.75, 31.95, 26.45, 26.21, 25.95. HRMS (ESI) calcd for $[C_{17}H_{20}ClNO_2Na]^+$ ($[M+Na]^+$): 328.1075, found: 328.1076.



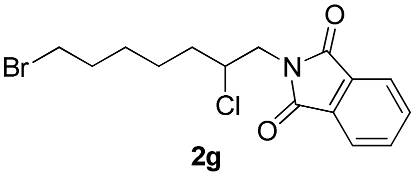
2e

Following the general procedure for monosubstituted unactivated alkenes, **2e** was obtained as a white solid (75 mg, 64% yield, regio 5.4:1). Mp: 51.9-52.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1H NMR (400 MHz, CDCl3) δ 7.86 (dd, J = 5.4, 3.1 Hz, 2H), 7.73 (dd, J = 5.5, 3.1 Hz, 2H), 4.55 – 4.38 (m, 1H), 4.00 (dd, J = 14.1, 9.4 Hz, 1H), 3.79 (dd, J = 14.1, 4.4 Hz, 1H), 1.28 – 1.16 (m, 2H), 0.12 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.26, 134.33, 132.05, 123.67, 58.16, 47.10, 25.54, -0.68. HRMS (ESI) calcd for $[C_{14}H_{18}ClNO_2SiNa]^+$ ($[M+Na]^+$): 318.0688, found: 318.0687.



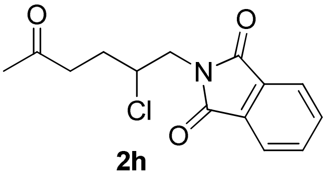
2f

Following the general procedure for monosubstituted unactivated alkenes, **2f** was obtained as a clean oil (103 mg, 72% yield, regio 6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.75 (dd, *J* = 5.5, 3.1 Hz, 2H), 4.39 – 4.24 (m, 1H), 4.03 (dd, *J* = 14.1, 8.5 Hz, 1H), 3.86 (dd, *J* = 14.1, 5.4 Hz, 1H), 3.55 (t, *J* = 6.3 Hz, 2H), 1.89 – 1.75 (m, 4H), 1.74 – 1.57 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.03, 134.24, 131.80, 123.55, 58.98, 44.61, 44.18, 34.92, 31.95, 23.66. HRMS (ESI) calcd for $[C_{14}H_{15}Cl_2NO_2Na]^+$ ($[M+Na]^+$): 322.0372, found: 322.0375.



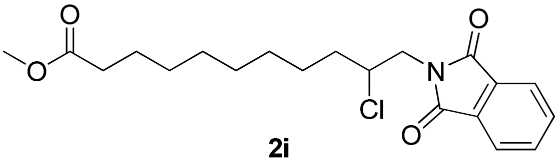
2g

Following the general procedure for monosubstituted unactivated alkenes, **2g** was obtained as a clean oil (126 mg, 70% yield, regio 9:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.75 (dd, *J* = 5.5, 3.1 Hz, 2H), 4.37 – 4.24 (m, 1H), 4.02 (dd, *J* = 14.1, 8.6 Hz, 1H), 3.86 (dd, *J* = 14.1, 5.4 Hz, 1H), 3.41 (t, *J* = 6.7 Hz, 2H), 1.93 – 1.81 (m, 3H), 1.77 – 1.62 (m, 2H), 1.56 – 1.42 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.04, 134.22, 131.80, 123.53, 59.20, 44.23, 35.44, 33.62, 32.51, 27.59, 25.38. HRMS (ESI) calcd for $[C_{15}H_{17}BrClNO_2Na]^+$ ($[M+Na]^+$): 380.0023, found: 380.0025.



2h

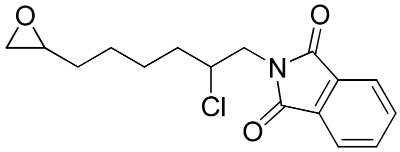
Following the general procedure for monosubstituted unactivated alkenes, **2h** was obtained as a white solid (91 mg, 65% yield, regio 8:1, mixture of regioisomers). Mp: 101.1-102.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.83 (m, 2H), 7.79 – 7.71 (m, 2H), 4.46 – 4.40 (m, 0.12H), 4.40 – 4.27 (m, 0.88H), 4.23 – 4.17 (m, 0.12H), 4.02 (dd, *J* = 14.1, 8.2 Hz, 0.89H), 3.88 (dd, *J* = 14.1, 5.9 Hz, 0.86H), 3.80 (dd, *J* = 11.2, 5.2 Hz, 0.12H), 2.86 – 2.74 (m, 0.90H), 2.74 – 2.63 (m, 0.89H), 2.53 – 2.44 (m, 0.28H), 2.36 – 2.26 (m, 0.25H), 2.24 – 2.16 (m, 3.29H), 2.10 (s, 0.36H), 1.94 – 1.81 (m, 1.21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.13, 206.72, 168.30, 167.95, 134.26, 134.24, 131.76, 131.53, 123.55, 123.48, 58.49, 52.97, 43.96, 43.78, 40.01, 39.76, 30.06, 29.94, 29.11, 24.24. HRMS (ESI) calcd for $[C_{14}H_{14}ClNO_3Na]^+$ ($[M+Na]^+$): 302.0554, found: 302.0556.



2i

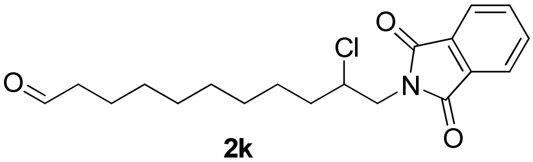
Following the general procedure for monosubstituted unactivated alkenes, **2i** was obtained as a white solid (103 mg, 54% yield, regio 9:1, BRSM: 90%). Mp: 73.0-74.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.74 (dd,

J = 5.5, 3.0 Hz, 2H), 4.38 – 4.23 (m, 1H), 4.01 (dd, J = 14.1, 8.8 Hz, 1H), 3.85 (dd, J = 14.1, 5.2 Hz, 1H), 3.67 (s, 3H), 2.30 (t, J = 7.5 Hz, 2H), 1.86 – 1.58 (m, 5H), 1.50 – 1.41 (m, 1H), 1.35 – 1.28 (m, 8H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 174.29, 168.03, 134.17, 131.83, 123.49, 59.44, 51.44, 44.30, 35.68, 34.07, 29.20, 29.09, 29.05, 28.93, 26.14, 24.90. HRMS (ESI) calcd for $[C_{20}H_{26}ClNO_4Na]^+$ ($[M+Na]^+$): 402.1443, found: 402.1443.



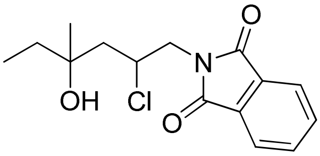
2j

Following the general procedure for monosubstituted unactivated alkenes, **2j** was obtained as a white solid (88 mg, 57% yield, regio 7:1, dr = 1:1). Mp: 68.3-69.7 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.88 (dd, J = 5.4, 3.1 Hz, 2H), 7.75 (dd, J = 5.5, 3.0 Hz, 2H), 4.37 – 4.24 (m, 1H), 4.02 (dd, J = 14.1, 8.6 Hz, 1H), 3.86 (dd, J = 14.0, 5.4 Hz, 1H), 2.97 – 2.86 (m, 1H), 2.79 – 2.69 (m, 1H), 2.47 (dd, J = 5.0, 2.7 Hz, 1H), 1.90 – 1.79 (m, 1H), 1.76 – 1.67 (m, 2H), 1.60 – 1.41 (m, 5H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 168.04, 134.21, 131.81, 123.52, 59.20, 59.19, 52.13, 52.11, 47.08, 47.05, 44.24, 35.53, 32.26, 32.21, 25.98, 25.46, 25.43. HRMS (ESI) calcd for $[C_{16}H_{18}ClNO_3Na]^+$ ($[M+Na]^+$): 330.0867, found: 330.0868.



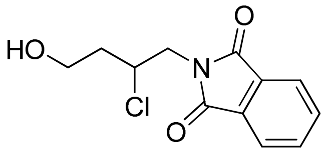
2k

Following the general procedure for monosubstituted unactivated alkenes, **2k** was obtained as a white solid (1.75 equiv. of NCP was added) (112 mg, 64% yield, regio 9:1). Mp: 66.2-68.2 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.76 (s, 1H), 7.88 (dd, J = 5.2, 3.2 Hz, 2H), 7.74 (dd, J = 5.2, 2.9 Hz, 2H), 4.37 – 4.24 (m, 1H), 4.02 (dd, J = 14.0, 8.8 Hz, 1H), 3.85 (dd, J = 14.0, 5.1 Hz, 1H), 2.42 (td, J = 7.3, 1.2 Hz, 2H), 1.85 – 1.71 (m, 2H), 1.65 – 1.59 (m, 3H), 1.35 – 1.24 (m, 9H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 202.94, 168.07, 134.19, 131.84, 123.51, 59.43, 44.31, 43.89, 35.67, 29.20, 29.18, 29.09, 28.92, 26.13, 22.05. HRMS (ESI) calcd for $[C_{19}H_{24}ClNO_3Na]^+$ ($[M+Na]^+$): 372.1337, found: 372.1338.



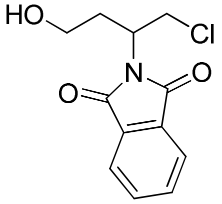
2l

Following the general procedure for monosubstituted unactivated alkenes, **2l** was obtained as a clean oil (74 mg, 50% yield, regio 17:1, dr=1:0.8, mixture of diastereomers). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.81 (m, 2H), 7.81 – 7.69 (m, 2H), 4.63 – 4.49 (m, 1H), 4.15 – 3.95 (m, 2H), 2.08 – 1.99 (m, 2H), 1.66 – 1.49 (m, 2H), 1.29 (s, 1.61H), 1.24 (s, 1.28H), 0.93 (td, J = 7.5, 5.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.25, 168.19, 134.22, 134.19, 131.84, 131.82, 123.53, 123.52, 72.45, 72.37, 55.75, 55.67, 46.56, 46.21, 45.02, 44.97, 35.93, 34.34, 27.05, 25.80, 8.32, 8.14. HRMS (ESI) calcd for $[C_{15}H_{18}ClNO_3Na]^+$ ($[M+Na]^+$): 318.0867, found: 318.0868.



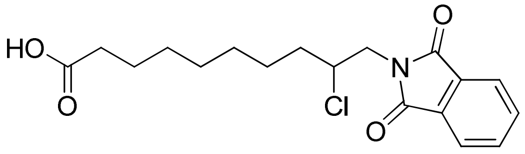
2m

+



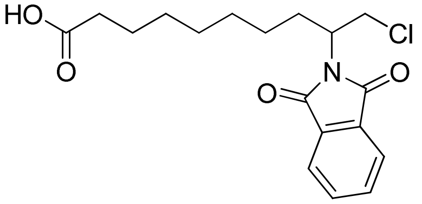
2mm, regioisomer of **2m**

Following the general procedure for monosubstituted unactivated alkenes, **2m** and **2mm** were obtained as a clean oil (64 mg, 50% yield, regio 7:1, mixture of regioisomers). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.82 (m, 2H), 7.79 – 7.70 (m, 2H), 4.73 – 4.64 (m, 0.12H), 4.56 – 4.45 (m, 0.88H), 4.31 – 4.21 (m, 0.14H), 4.13 – 4.04 (m, 0.94H), 3.97 – 3.84 (m, 2.67H), 3.78 – 3.69 (m, 0.15H), 3.64 – 3.56 (m, 0.13H), 2.18 – 2.07 (m, 1H), 1.97 – 1.90 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.60, 168.09, 134.25, 131.78, 131.60, 123.55, 123.51, 59.25, 56.29, 50.71, 44.24, 43.94, 38.09, 33.05. HRMS (ESI) calcd for $[C_{12}H_{12}ClNO_3Na]^+$ ($[M+Na]^+$): 276.0398, found: 276.0398.



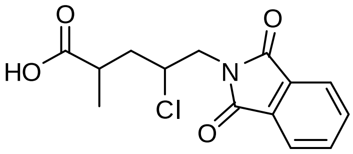
2n

+

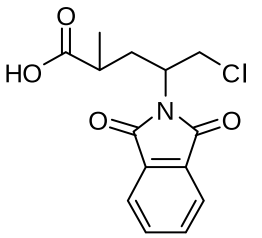


2nn, regioisomer of **2n**

Following the general procedure for monosubstituted unactivated alkenes, **2n** and **2nn** were obtained as a white solid (99 mg, 56% yield, regio 9:1, mixture of regioisomers). Mp: 77.3-78.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.83 (m, 2H), 7.77 – 7.70 (m, 2H), 4.52 – 4.41 (m, 0.10H), 4.36 – 4.23 (m, 0.90H), 4.19 – 4.13 (m, 0.10H), 4.02 (dd, J = 14.1, 8.8 Hz, 0.89H), 3.85 (dd, J = 14.1, 5.2 Hz, 0.87H), 3.76 (dd, J = 11.2, 5.0 Hz, 0.10H), 2.35 (t, J = 7.5 Hz, 2H), 1.84 – 1.69 (m, 2H), 1.68 – 1.55 (m, 3H), 1.44 – 1.20 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.81, 168.09, 134.20, 131.82, 123.53, 59.41, 44.30, 35.64, 33.98, 29.00, 28.89, 28.79, 26.09, 24.58. HRMS (ESI) calcd for $[C_{18}H_{22}ClNO_4Na]^+$ ($[M+Na]^+$): 374.1130, found: 374.1129.

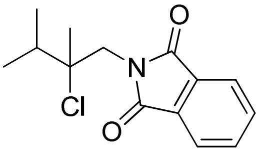


2o



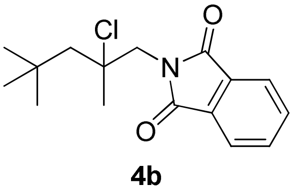
2oo, regioisomer of **2o**

Following the general procedure for monosubstituted unactivated alkenes, **2o** and **2oo** were obtained as a white solid (80 mg, 54% yield, regio 8:1, dr=1.5:1, mixture of regioisomers and diastereomers). Mp: 109.3-111.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.83 (m, 2H), 7.76 – 7.70 (m, 2H), 4.63 – 4.53 (m, 0.11H), 4.47 – 4.30 (m, 0.88H), 4.15 – 3.96 (m, 1.15H), 3.93 – 3.86 (m, 0.86H), 3.83 – 3.73 (m, 0.14H), 2.93 – 2.80 (m, 0.86H), 2.68 – 2.59 (m, 0.11H), 2.50 – 2.38 (m, 0.15H), 2.26 – 2.18 (m, 0.84H), 1.92 – 1.84 (m, 0.37H), 1.77 – 1.66 (m, 0.60H), 1.28 (d, *J* = 7.2 Hz, 1.78H), 1.23 (d, *J* = 7.0 Hz, 1.16H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.64, 181.32, 168.03, 134.29, 134.24, 131.76, 131.74, 123.61, 123.59, 57.36, 56.55, 44.30, 44.18, 39.25, 38.22, 36.56, 36.40, 18.12, 15.55. HRMS (ESI) calcd for $[C_{14}H_{14}ClNO_4Na]^+$ ($[M+Na]^+$): 318.0504, found: 318.0502.



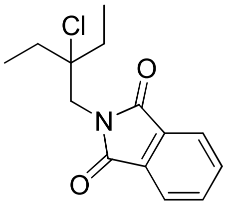
4a

Following the general procedure for 1,1-disubstituted unactivated alkenes, **4a** was obtained as a clean oil (97 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.74 (dd, *J* = 5.4, 3.1 Hz, 2H), 4.11 (d, *J* = 14.1 Hz, 1H), 3.94 (d, *J* = 14.1 Hz, 1H), 2.02 (dt, *J* = 13.3, 6.7 Hz, 1H), 1.53 (s, 3H), 1.20 (d, *J* = 6.6 Hz, 3H), 1.11 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.47, 134.15, 131.90, 123.47, 76.83, 46.99, 37.69, 26.47, 18.35, 18.02. HRMS (ESI) calcd for $[C_{14}H_{16}ClNO_2Na]^+$ ($[M+Na]^+$): 288.0762, found: 288.0762.



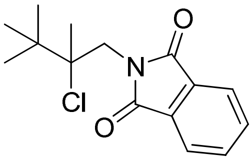
4b

Following the general procedure for 1,1-disubstituted unactivated alkenes, **4b** was obtained as a white solid (109 mg, 74% yield). Mp: 74.6-76.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.75 (dd, *J* = 5.5, 3.1 Hz, 2H), 4.05 (d, *J* = 14.0 Hz, 1H), 3.91 (d, *J* = 14.0 Hz, 1H), 2.00 (d, *J* = 15.3 Hz, 1H), 1.87 (d, *J* = 15.3 Hz, 1H), 1.68 (s, 3H), 1.12 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.44, 134.16, 131.91, 123.53, 72.92, 54.29, 50.80, 32.30, 31.60, 29.84. HRMS (ESI) calcd for $[C_{16}H_{20}ClNO_2Na]^+$ ($[M+Na]^+$): 316.1075, found: 316.1076.



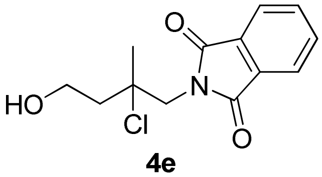
4c

Following the general procedure for 1,1-disubstituted unactivated alkenes, **4c** was obtained as a clean oil (100 mg, 75% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.74 (dd, *J* = 5.5, 3.1 Hz, 2H), 3.99 (s, 2H), 1.85 (ddt, *J* = 23.8, 14.6, 7.3 Hz, 4H), 1.09 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.45, 134.14, 131.86, 123.44, 77.14, 46.14, 32.00, 8.74. HRMS (ESI) calcd for $[C_{14}H_{16}ClNO_2Na]^+$ ($[M+Na]^+$): 288.0762, found: 288.0762.



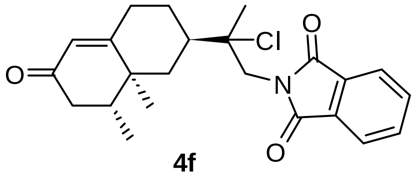
4d

Following the general procedure for 1,1-disubstituted unactivated alkenes, **4d** was obtained as a white solid (77 mg, 55% yield). Mp: 106.5-107.8 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.74 (dd, *J* = 5.5, 3.1 Hz, 2H), 4.26 (dd, *J* = 14.1, 0.5 Hz, 1H), 3.93 (d, *J* = 14.1 Hz, 1H), 1.54 (s, 3H), 1.22 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.53, 134.06, 132.01, 123.45, 80.61, 45.13, 39.37, 26.31, 24.69. HRMS (ESI) calcd for $[C_{15}H_{18}ClNO_2Na]^+$ ($[M+Na]^+$): 302.0918, found: 302.0921.



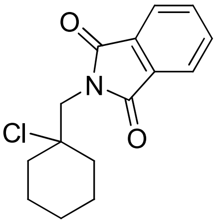
4e

Following the general procedure for 1,1-disubstituted unactivated alkenes, **4e** was obtained as a white solid (64 mg, 44% yield, white solid). Mp: 90.5-91.7 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.76 (dd, *J* = 5.5, 3.0 Hz, 2H), 4.13 – 3.89 (m, 4H), 2.10 (td, *J* = 6.4, 2.5 Hz, 2H), 1.65 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.56, 134.37, 131.72, 123.63, 70.92, 59.47, 48.69, 43.97, 29.08. HRMS (ESI) calcd for $[C_{13}H_{14}ClNO_2Na]^+$ ($[M+Na]^+$): 290.0554, found: 290.0554.



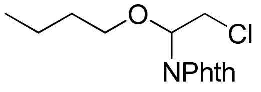
4f

Following the general procedure for 1,1-disubstituted unactivated alkenes, **4f** was obtained as a light yellow solid (1.75 equiv. of NCP was added) (106 mg, 53% yield, dr=1:1, mixture of diastereomers). Mp: 62.4-63.7 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.90 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.77 (dd, *J* = 5.4, 3.0 Hz, 2H), 5.79 (s, 0.48H), 5.78 (s, 0.48H), 4.14 – 4.02 (m, 2H), 2.59 – 2.38 (m, 3H), 2.35 – 2.24 (m, 2H), 2.22 – 2.14 (m, 1H), 2.10 – 2.04 (m, 2H), 1.72 (s, 1H), 1.59 (s, 1.43H), 1.58 (s, 1.46H), 1.51 – 1.41 (m, 1H), 1.12 (s, 1.51H), 1.10 (s, 1.50H), 1.05 (d, *J* = 6.8 Hz, 1.49H), 1.00 (d, *J* = 6.8 Hz, 1.50H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 199.52, 199.40, 169.68, 169.64, 168.48, 168.43, 134.32, 131.81, 124.63, 124.54, 123.60, 123.59, 75.47, 75.20, 46.89, 46.80, 42.06, 40.46, 39.56, 39.47, 39.25, 39.21, 32.54, 32.48, 28.13, 27.84, 26.69, 26.60, 17.08, 16.81, 15.10, 15.03. HRMS (ESI) calcd for $[C_{23}H_{26}ClNO_3Na]^+$ ($[M+Na]^+$): 422.1493, found: 422.1492.



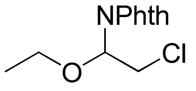
4g

Following the general procedure for 1,1-disubstituted unactivated alkenes, **4g** was obtained as a white solid (78 mg, 56% yield, regio 8:1). Mp: 100.1-101.9 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.88 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.75 (dd, *J* = 5.5, 3.1 Hz, 2H), 3.99 (s, 2H), 2.01 – 1.91 (m, 2H), 1.78 – 1.59 (m, 7H), 1.22 – 1.07 (m, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 168.44, 134.16, 131.89, 123.49, 74.15, 49.72, 37.83, 25.01, 21.77. HRMS (ESI) calcd for $[C_{15}H_{16}ClNO_2Na]^+$ ($[M+Na]^+$): 300.0762, found: 300.0763.



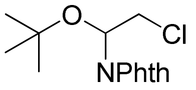
6a

Following the general procedure for heteroatom substituted alkenes, **6a** was obtained as a light yellow oil (117 mg, 83% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.90 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.78 (dd, *J* = 5.5, 3.1 Hz, 2H), 5.53 (dd, *J* = 8.3, 5.7 Hz, 1H), 4.31 (dd, *J* = 11.2, 8.3 Hz, 1H), 4.01 (dd, *J* = 11.2, 5.7 Hz, 1H), 3.56 (t, *J* = 6.5 Hz, 2H), 1.61 – 1.51 (m, 2H), 1.36 – 1.29 (m, 2H), 0.87 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 167.76, 134.50, 131.51, 123.78, 81.24, 69.79, 41.96, 31.28, 19.08, 13.73. HRMS (ESI) calcd for $[C_{14}H_{16}ClNO_3Na]^+$ ($[M+Na]^+$): 304.0711, found: 304.0711.



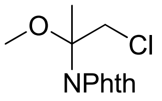
6b

Following the general procedure for heteroatom substituted alkenes, **6b** was obtained as a light yellow oil (108 mg, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.78 (dd, *J* = 5.5, 3.1 Hz, 2H), 5.54 (dd, *J* = 8.4, 5.6 Hz, 1H), 4.32 (dd, *J* = 11.3, 8.4 Hz, 1H), 4.00 (dd, *J* = 11.3, 5.6 Hz, 1H), 3.70 – 3.57 (m, 2H), 1.22 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.77, 134.51, 131.52, 123.78, 80.98, 65.52, 41.95, 14.82. HRMS (ESI) calcd for $[C_{12}H_{12}ClNO_3Na]^+$ ($[M+Na]^+$): 276.0398, found: 276.0399.



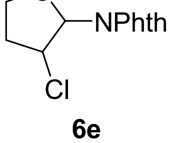
6c

Following the general procedure for heteroatom substituted alkenes, **6c** was obtained as a white solid (117 mg, 83% yield). Mp: 90.0-91.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.77 (dd, *J* = 5.5, 3.1 Hz, 2H), 5.70 (dd, *J* = 8.8, 5.5 Hz, 1H), 4.26 (dd, *J* = 11.1, 8.8 Hz, 1H), 3.80 (dd, *J* = 11.1, 5.5 Hz, 1H), 1.26 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.44, 134.35, 131.69, 123.63, 76.47, 75.37, 43.33, 27.92. HRMS (ESI) calcd for $[C_{14}H_{16}ClNO_3Na]^+$ ($[M+Na]^+$): 304.0711, found: 304.0710.



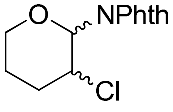
6d

Following the general procedure for heteroatom substituted alkenes, **6d** was obtained as a light yellow solid (69 mg, 54% yield). Mp: 72.4-73.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.75 (dd, *J* = 5.4, 3.1 Hz, 2H), 4.66 (d, *J* = 11.3 Hz, 1H), 3.68 (d, *J* = 11.2 Hz, 1H), 3.33 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.72, 134.39, 131.44, 123.37, 91.64, 51.09, 48.59, 21.15. HRMS (ESI) calcd for $[C_{12}H_{12}ClNO_3Na]^+$ ($[M+Na]^+$): 276.0398, found: 276.0398.



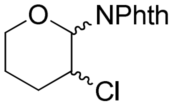
6e

Following the general procedure for heteroatom substituted alkenes, **6e** was obtained as a white solid (106 mg, 84% yield, dr=2:1, mixture of diastereomers). Mp: 94.5-95.9 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.90 – 7.84 (m, 2H), 7.79 – 7.73 (m, 2H), 6.16 (d, *J* = 6.8 Hz, 0.22H), 5.97 (d, *J* = 3.8 Hz, 0.77H), 5.08 – 4.96 (m, 0.83H), 4.67 – 4.57 (m, 0.25H), 4.53 – 4.45 (m, 0.26H), 4.30 (dd, *J* = 13.9, 7.5 Hz, 0.89H), 4.16 (dd, *J* = 15.1, 6.9 Hz, 0.90H), 3.98 (dd, *J* = 16.5, 7.8 Hz, 0.26H), 2.95 (dq, *J* = 13.7, 6.9 Hz, 0.89H), 2.82 – 2.74 (m, 0.25H), 2.62 – 2.54 (m, 0.26H), 2.31 (dt, *J* = 13.0, 6.1 Hz, 0.89H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 167.50, 167.32, 134.53, 134.32, 131.72, 123.70, 123.56, 88.00, 82.47, 68.95, 68.62, 58.15, 56.83, 36.69, 34.68. HRMS (ESI) calcd for $[C_{12}H_{10}ClNO_3Na]^+$ ($[M+Na]^+$): 274.0241, found: 274.0241.



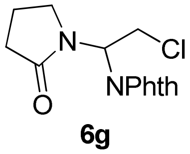
6f

Following the general procedure for heteroatom substituted alkenes, **6f** was obtained as a white solid (82 mg, 62% yield). Mp: 142.8-144.5 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.90 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.76 (dd, *J* = 5.5, 3.1 Hz, 2H), 5.22 (d, *J* = 9.7 Hz, 1H), 4.98 (ddd, *J* = 11.3, 9.8, 4.7 Hz, 1H), 4.17 – 4.03 (m, 1H), 3.78 – 3.61 (m, 1H), 2.58 – 2.46 (m, 1H), 1.99 – 1.84 (m, 2H), 1.81 – 1.72 (m, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 167.14, 134.45, 131.54, 123.78, 82.96, 68.55, 53.51, 34.65, 26.37. HRMS (ESI) calcd for $[C_{13}H_{12}ClNO_3Na]^+$ ($[M+Na]^+$): 288.0398, found: 288.0398.



6ff, diastereomer of **6f**

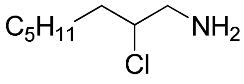
Following the general procedure for heteroatom substituted alkenes, **6ff** was obtained as a white solid (38 mg, 25% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.88 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.75 (dd, *J* = 5.5, 3.0 Hz, 2H), 5.79 (d, *J* = 3.5 Hz, 1H), 4.36 (dt, *J* = 6.8, 3.6 Hz, 1H), 4.29 – 4.21 (m, 1H), 3.77 – 3.68 (m, 1H), 2.59 – 2.49 (m, 1H), 2.28 – 2.14 (m, 2H), 1.71 – 1.65 (m, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 167.34, 134.32, 131.57, 123.64, 81.74, 67.50, 56.86, 30.61, 21.59.



6g

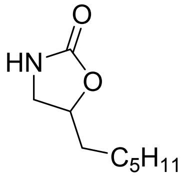
Following the general procedure for heteroatom substituted alkenes, **6g** was obtained as a light yellow oil (117 mg, 80% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.88 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.77 (dd, *J* = 5.5, 3.1 Hz, 2H), 6.50 (t, *J* = 8.0 Hz, 1H), 4.26 (dd, *J* = 11.2, 8.3 Hz, 1H), 4.10 (dd, *J* = 11.2, 7.7 Hz, 1H), 3.68 (t, *J* = 7.0 Hz, 2H), 2.48 –

2.32 (m, 2H), 2.13 – 2.00 (m, 2H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 175.56, 167.49, 134.59, 131.39, 123.82, 58.41, 44.63, 40.11, 30.42, 18.40. HRMS (ESI) calcd for [$C_{14}H_{13}ClN_2O_3Na$]$^+$ ([M+Na]$^+$): 315.0507, found: 315.0507.



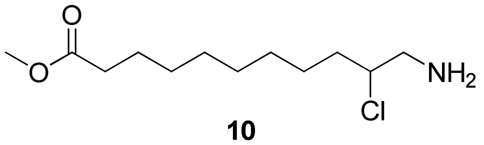
8

Following the general procedure for synthetic applications, **8** was obtained as a light yellow oil. ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.95 – 3.82 (m, 1H), 2.97 (dd, J = 13.8, 3.6 Hz, 1H), 2.83 (dd, J = 13.8, 7.8 Hz, 1H), 1.76 – 1.64 (m, 2H), 1.44 – 1.21 (m, 8H), 0.88 (t, J = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 67.22, 48.92, 35.70, 31.65, 28.82, 26.45, 22.58, 14.06. HRMS (ESI) calcd for [$C_8H_{19}ClN$]$^+$ ([M+H]$^+$): 164.1201, found: 164.1203.



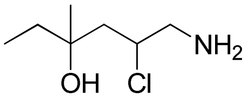
9

Following the general procedure for synthetic applications, **9** was obtained as a white solid (78 mg, 91% yield). Mp: 81.0-82.8 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.22 (s, 1H), 4.72 – 4.54 (m, 1H), 3.66 (t, J = 8.4 Hz, 1H), 3.23 (t, J = 7.8 Hz, 1H), 1.85 – 1.73 (m, 1H), 1.68 – 1.59 (m, 1H), 1.52 – 1.42 (m, 1H), 1.37 – 1.25 (m, 7H), 0.89 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 160.41, 77.20, 46.02, 34.92, 31.62, 28.93, 24.56, 22.51, 14.02. HRMS (ESI) calcd for [$C_9H_{17}NO_2Na$]$^+$ ([M+Na]$^+$): 194.1151, found: 194.1151.



10

Following the general procedure for synthetic applications, **10** was obtained as a clean oil (106 mg, 85% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.92 – 3.81 (m, 1H), 3.66 (s, 3H), 2.97 (dd, J = 13.7, 3.3 Hz, 1H), 2.83 (dd, J = 13.7, 7.8 Hz, 1H), 2.30 (t, J = 7.5 Hz, 2H), 1.75 – 1.57 (m, 5H), 1.44 – 1.37 (m, 1H), 1.33 – 1.27 (m, 8H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 174.28, 67.12, 51.44, 48.88, 35.64, 34.06, 29.21, 29.12, 29.06, 29.04, 26.42, 24.89. HRMS (ESI) calcd for [$C_{12}H_{25}ClNO_2$]$^+$ ([M+H]$^+$): 250.1568, found: 250.1570.

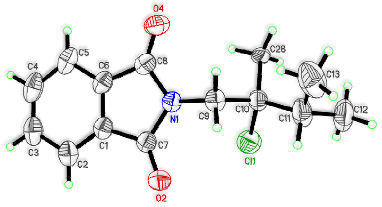


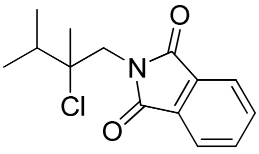
11

Following the general procedure for synthetic applications, **11** was obtained as a clean oil (59 mg, 72% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ 4.24 – 4.04 (m, 1H), 3.16 – 2.94 (m, 2H), 2.21 – 2.12 (broad, 2H), 2.08 – 1.94 (m, 2H), 1.61 – 1.48 (m, 2H), 1.21 (s, 1.63H), 1.20 (s, 1.34H), 0.92 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 70.89, 70.63, 60.34, 60.15, 48.55, 48.42, 46.37, 46.12, 35.20, 33.40, 26.20, 24.87, 7.46, 7.20. HRMS (ESI) calcd for $[C_7H_{17}ClNO]^+$ ($[M+H]^+$): 166.0993, found: 166.0993.

Single crystal data of 4a, 4g, 6e, and 6g.

Single crystal of **4a, 4g, 6e,** and **6g** suitable for X-ray diffraction were mounted in Paratone oil onto a glass fiber and frozen under a nitrogen cold stream. The data was collected at 220.0(1) K using a Agilent SuperNova, Dual, Cu at zero, Atlas fitted with Cu Kα radiation (λ = 1.54184 Å). Data collection and unit cell refinement were executed by using CrysAlisPro software. Data processing and absorption correction, giving minimum and maximum transmission factors, were accomplished with CrysAlisPro. The structure was solved with the SHELXT-2014 and refined with the SHELXL-2014 using Least Squares minimisation. All non-hydrogen atoms were refined with anisotropic displacement parameters. All carbon bound hydrogen atom positions were determined by geometry and refined by a riding model. CCDC 1579087 for **4a,** 1579238 for **4g**, 1579242 for **6e**, and 1579241 for **6g** contain the supplementary crystallographic data. Crystal data and structure refinements of **4a**, **4g**, **6e**, and **6g** are listed in Table S1, S2, S3, and S4, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



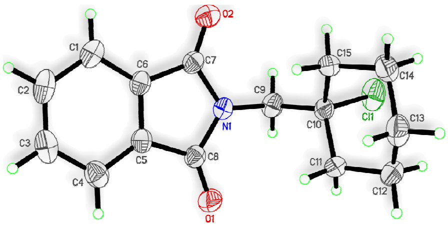


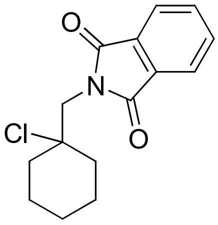
4a

Table S1. Crystal data and structure refinement for data.

Identification code	data
Empirical formula	C14 H16 Cl N O2
Formula weight	265.73

Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
space group	P-1	
Unit cell dimensions	a = 11.325(4) Å	alpha = 61.937(13) deg.
	b = 12.043(3) Å	beta = 82.653(16) deg.
	c = 12.775(4) Å	gamma = 64.028(12) deg.
Volume	1375.5(7) $Å^3$	
Z	2	
Calculated density	1.283 Mg/m^3	
Absorption coefficient	0.271 mm^{-1}	
F(000)	560	
Crystal size	0.169 x 0.238 x 0.193 mm	
Theta range for data collection	3.32 to 27.46 deg.	
Limiting indices	-14<=h<=14, -15<=k<=15, -16<=l<=16	
Reflections collected / unique	15409 / 6208 [R(int) = 0.0383]	
Completeness to theta = 27.46	98.4 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6208 / 3 / 331	
Goodness-of-fit on F^2	0.995	
Final R indices [I>2sigma(I)]	R1 = 0.0998, wR2 = 0.3139	
R indices (all data)	R1 = 0.1170, wR2 = 0.3447	
Largest diff. peak and hole	1.424 and -0.620 e. $Å^{-3}$	



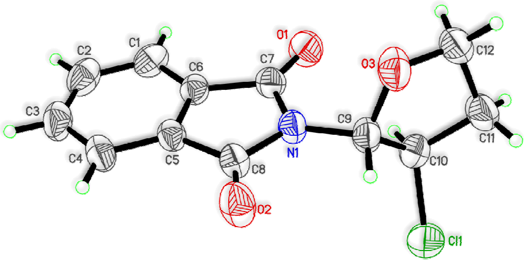


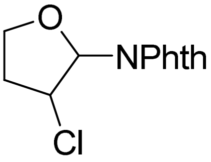
4g

Table S2. Crystal data and structure refinement for data.

Identification code	data
Empirical formula	C15 H16 Cl N O2
Formula weight	277.74
Temperature	293(2) K
Wavelength	0.71073 Å

Crystal system	Orthorhombic	
space group	Pbca	
Unit cell dimensions	a = 16.501(3) Å	alpha = 90 deg.
	b = 7.2983(15) Å	beta = 90 deg.
	c = 22.711(5) A	gamma = 90 deg.
Volume	2735.0(10) $Å^3$	
Z	8	
Calculated density	1.349 Mg/ m^3	
Absorption coefficient	0.276 mm^{-1}	
F(000)	1168	
Crystal size	0.173 x 0.105 x 0.085 mm	
Theta range for data collection	2.47 to 27.48 deg.	
Limiting indices	-21<=h<=21, -9<=k<=9, -29<=l<=29	
Reflections collected / unique	19947 / 3124 [R(int) = 0.0302]	
Completeness to theta = 27.48	99.5 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3124 / 0 / 172	
Goodness-of-fit on F^2	1.191	
Final R indices [I>2sigma(I)]	R1 = 0.0537, wR2 = 0.1221	
R indices (all data)	R1 = 0.0573, wR2 = 0.1244	
Largest diff. peak and hole	0.323 and -0.427 $e.A^{-3}$	



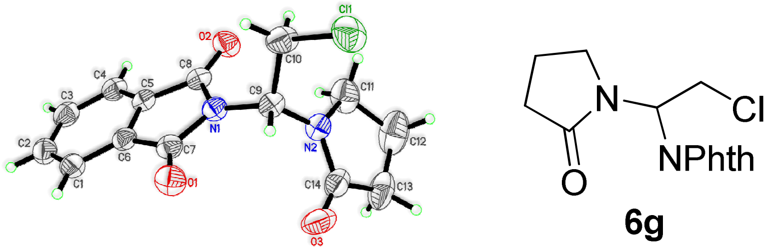


6e

Table S3. Crystal data and structure refinement for data.

Identification code	data
Empirical formula	C12 H10 Cl N O3
Formula weight	251.66
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
space group	P-1

Unit cell dimensions	a = 7.3183(15) Å	alpha = 108.07(3) deg.
	b = 8.0932(16) Å	beta = 97.49(3) deg.
	c = 10.816(2) Å	gamma = 104.80(3) deg.
Volume	573.3(2) $Å^3$	
Z	2	
Calculated density	1.458 Mg/m^3	
Absorption coefficient	0.328 mm^{-1}	
F(000)	260	
Crystal size	0.223 x 0.278 x 0.165 mm	
Theta range for data collection	2.80 to 27.48 deg.	
Limiting indices	-9<=h<=9, -10<=k<=10, -14<=l<=14	
Reflections collected / unique	6029 / 2592 [R(int) = 0.0202]	
Completeness to theta = 27.48	98.6 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2592 / 1 / 154	
Goodness-of-fit on F^2	1.099	
Final R indices [I>2sigma(I)]	R1 = 0.0652, wR2 = 0.1713	
R indices (all data)	R1 = 0.0788, wR2 = 0.1828	
Largest diff. peak and hole	0.406 and -0.276 $e.A^{-3}$	



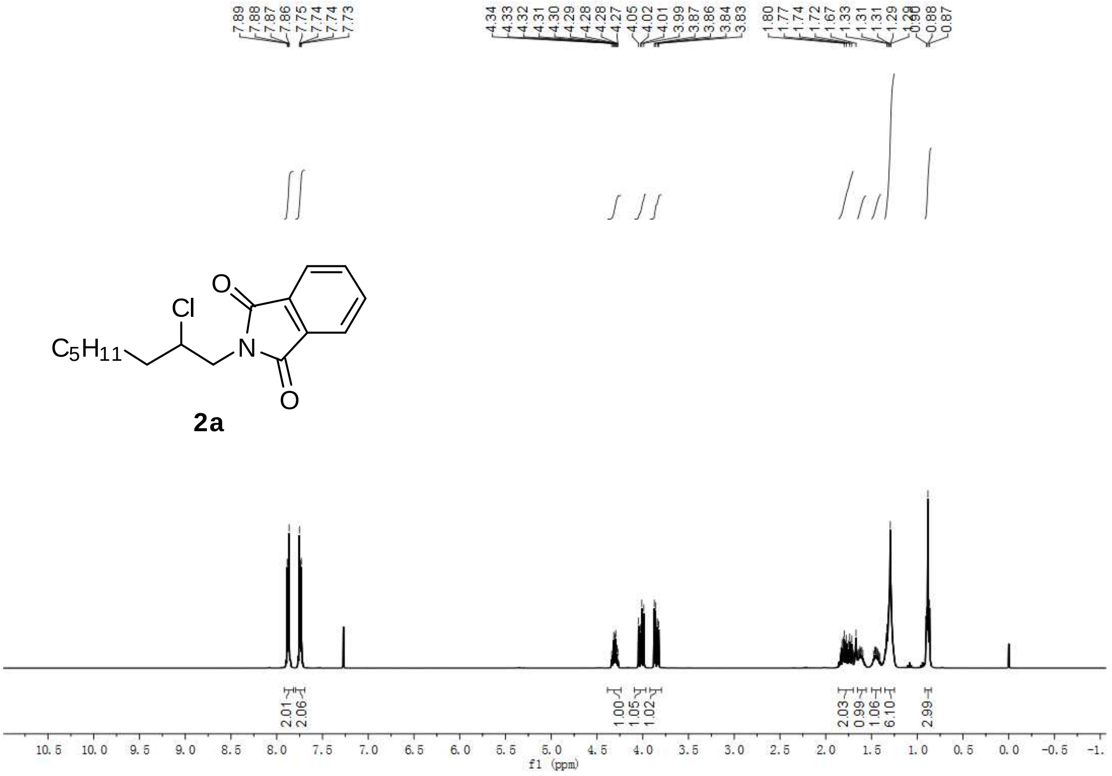
6g

Table S4. Crystal data and structure refinement for data.

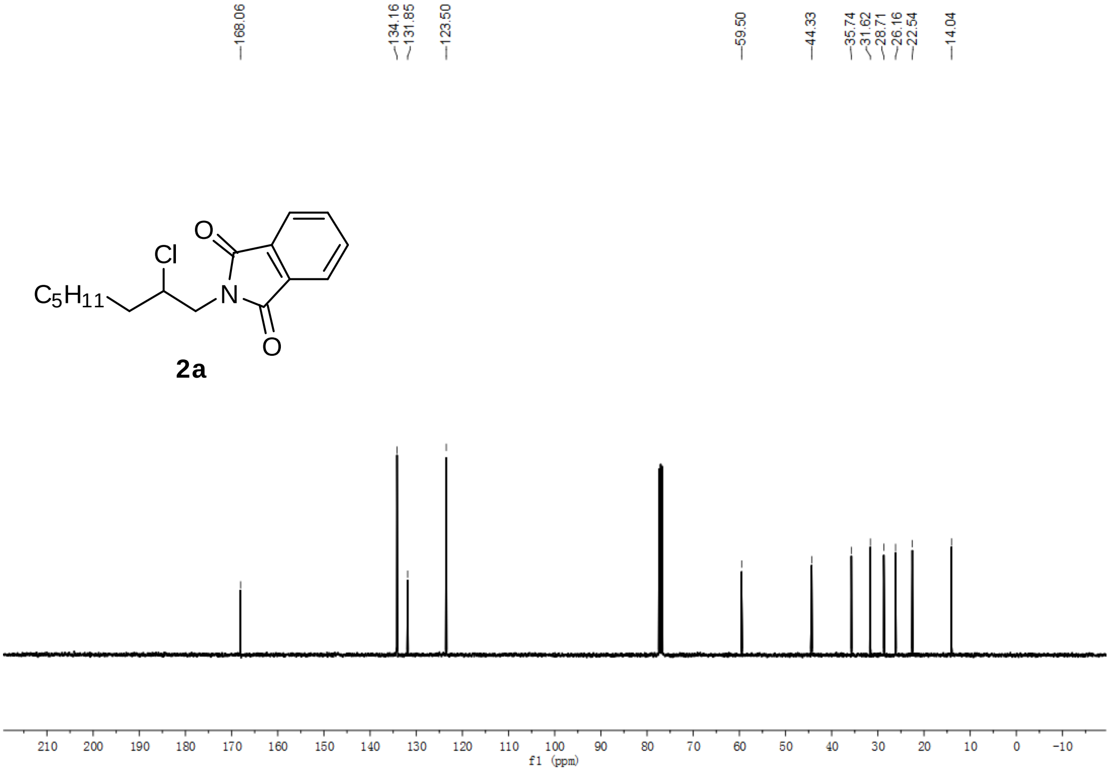
Identification code	data	
Empirical formula	C14 H13 Cl N2 O3	
Formula weight	292.71	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
space group	P-1	
Unit cell dimensions	a = 16.319(3) Å	alpha = 90 deg.
	b = 6.1182(12) Å	beta = 108.57(3) deg.
	c = 14.399(3) Å	gamma = 90 deg.

Volume	1362.8(5) Å ^{3}
Z	4
Calculated density	1.427 Mg/m^3
Absorption coefficient	0.289 mm^{-1}
F(000)	608
Crystal size	0.089 x 0.083 x 0.079 mm
Theta range for data collection	3.58 to 27.48 deg.
Limiting indices	-20<=h<=21, -7<=k<=7, -18<=l<=15
Reflections collected / unique	10900 / 3117 [R(int) = 0.0682]
Completeness to theta = 27.48	99.6 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3117 / 0 / 181
Goodness-of-fit on F^2	0.949
Final R indices [I>2sigma(I)]	R1 = 0.0583, wR2 = 0.1581
R indices (all data)	R1 = 0.0765, wR2 = 0.1691
Largest diff. peak and hole	0.282 and -0.343 e.A^{-3}

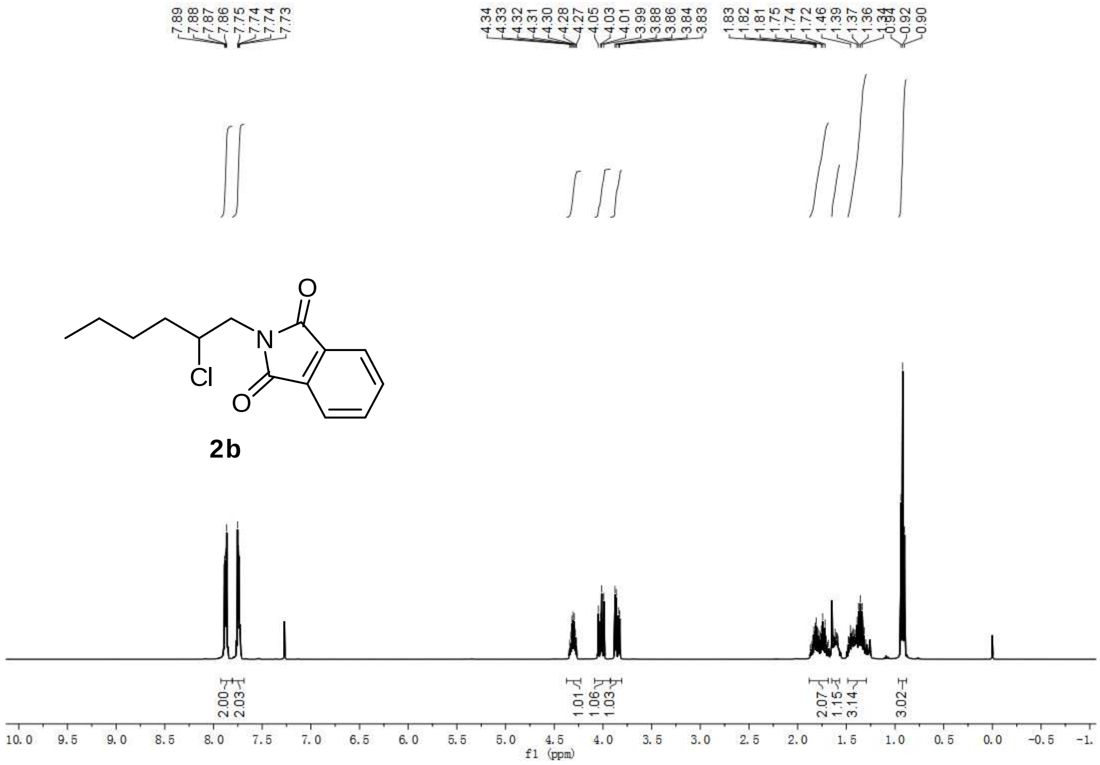
NMR Spectra



2a



2a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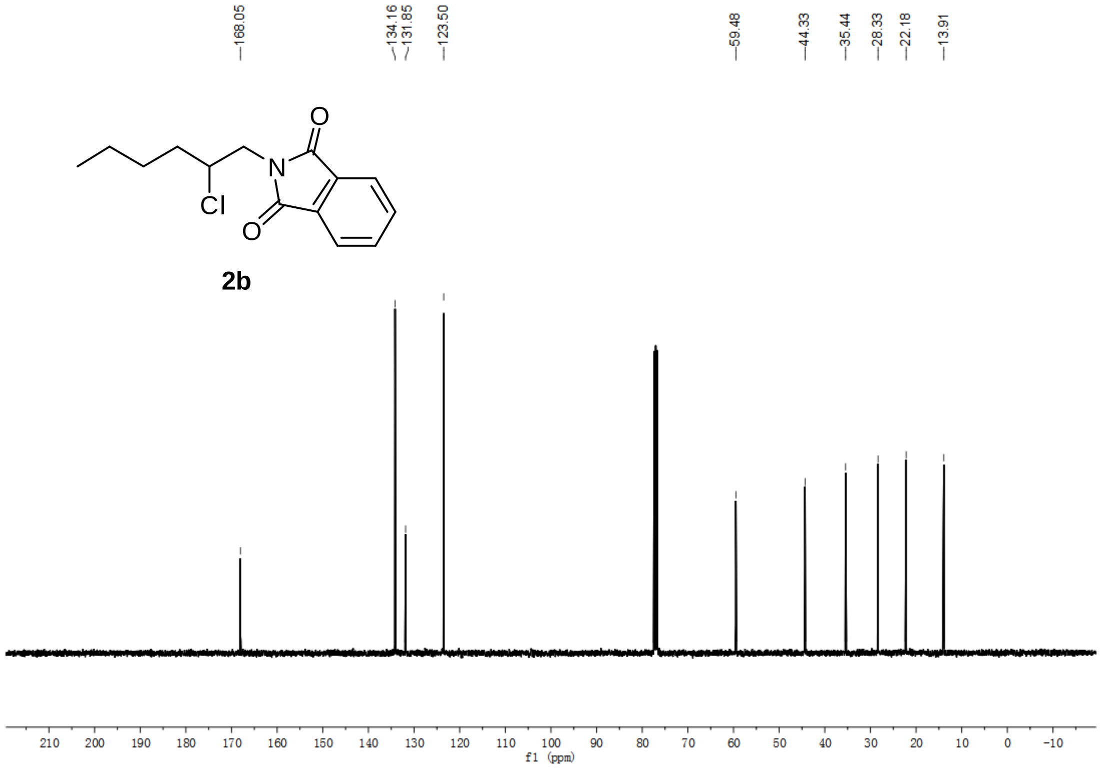
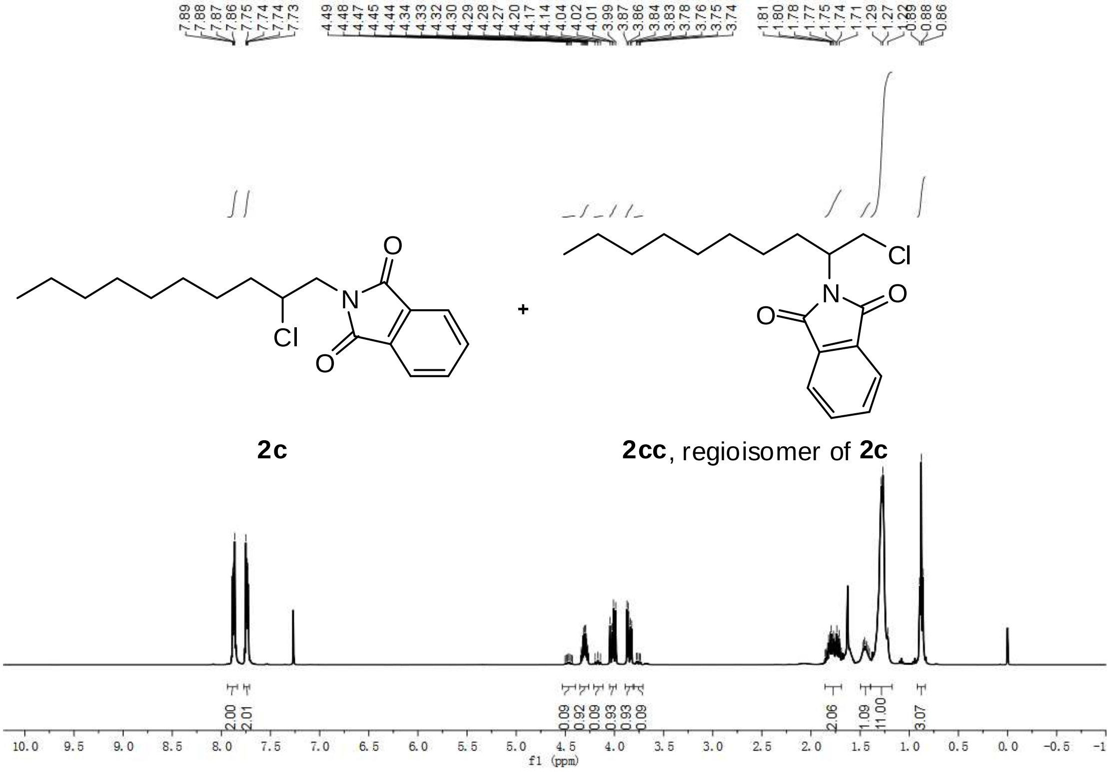
7.87
7.86
7.75
7.74
7.74
7.73
4.34
4.33
4.32
4.31
4.30
4.28
4.27
4.05
4.03
4.01
3.99
3.88
3.86
3.84
3.83
1.83
1.82
1.81
1.75
1.74
1.72
1.46
1.39
1.37
1.36
1.34
0.94
0.92
0.90
O
N
Cl
O
2.00
2.03
1.01
1.06
1.03
2.07
1.15
3.14
3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.
f1 (ppm)

2b


168.05
134.16
131.85
123.50
59.48
44.33
35.44
28.33
22.18
13.91
O
N
Cl
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

2b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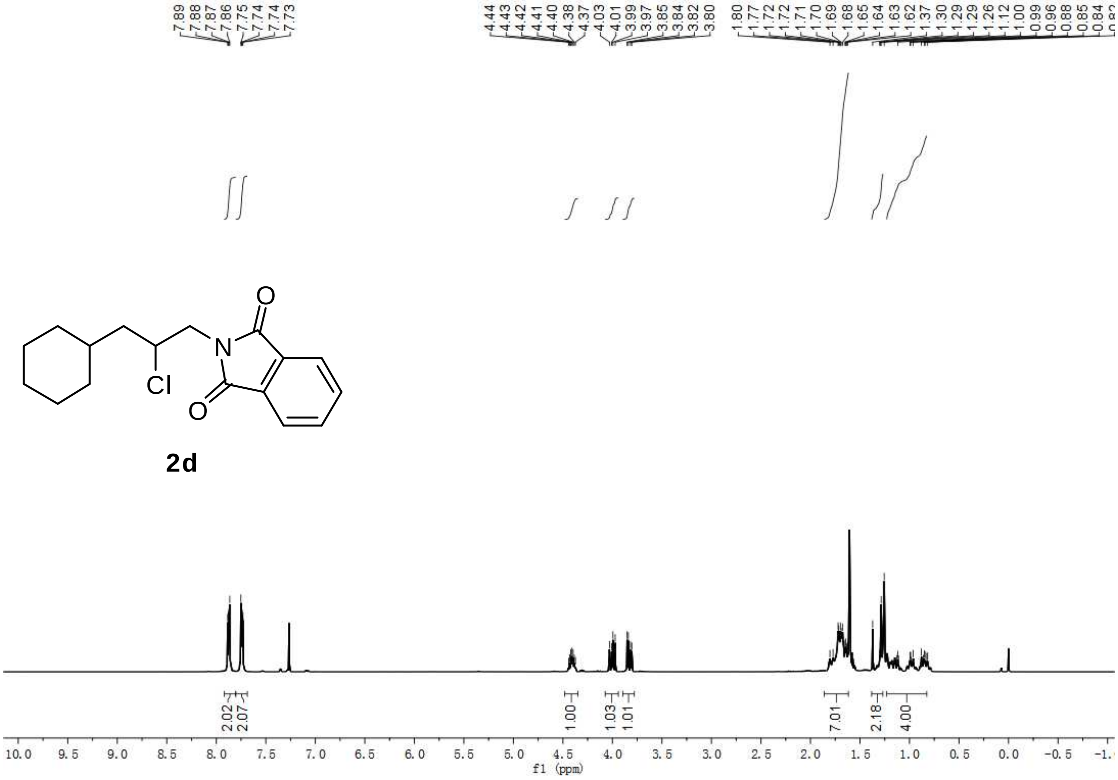
7.88
7.87
7.86
7.75
7.74
7.74
7.73
4.49
4.48
4.47
4.45
4.44
4.34
4.33
4.32
4.30
4.29
4.28
4.27
4.20
4.17
4.14
4.04
4.02
4.01
3.99
3.87
3.86
3.84
3.83
3.78
3.76
3.75
3.74
1.81
1.80
1.78
1.77
1.75
1.74
1.71
1.29
1.27
1.22
0.89
0.88
0.86
O
N
Cl
O
+
Cl
N
O
O
2c
2cc, regioisomer of 2c
2.00
2.01
0.09
0.92
0.09
0.93
0.93
0.09
2.06
1.09
11.00
3.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1
f1 (ppm)


168.06
134.16
131.86
123.50
59.50
44.34
35.74
31.83
29.39
29.18
29.05
26.20
22.65
14.11
O
N
Cl
O
+
Cl
N
O
O
2c
2cc, regioisomer of 2c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)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7.74
7.74
7.73
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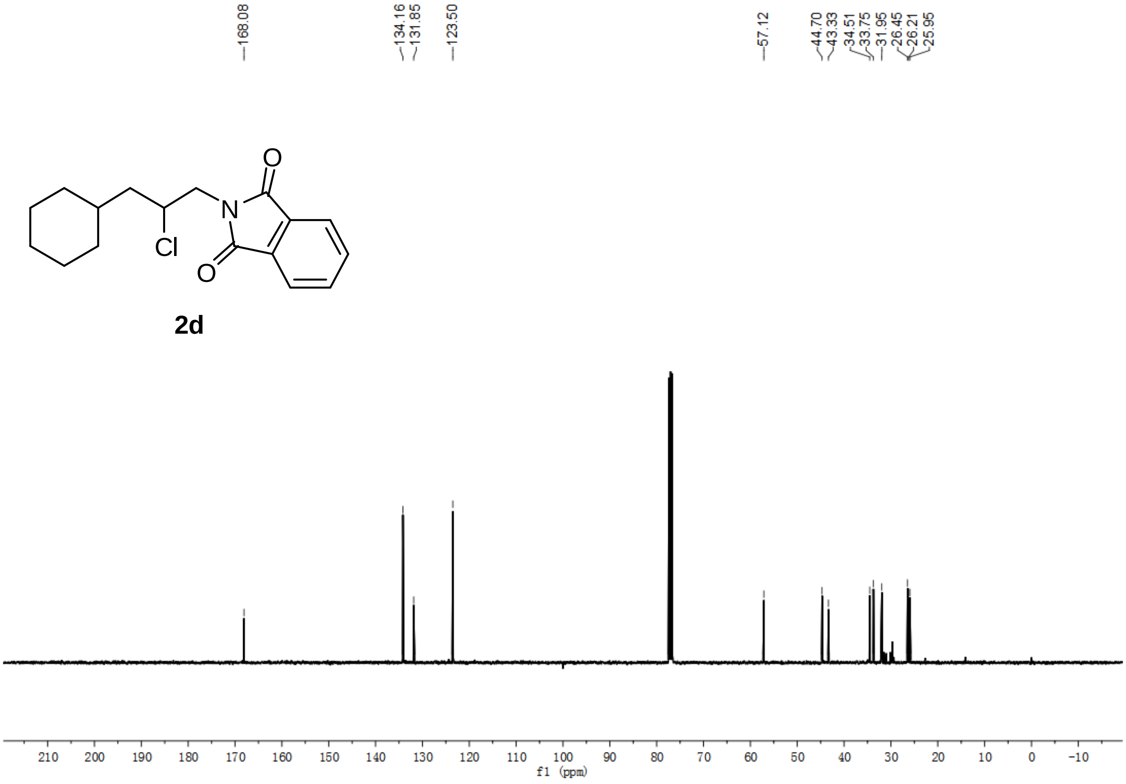
4.42
4.41
4.40
4.38
4.37
4.03
4.01
3.99
3.97
3.85
3.84
3.82
3.80
1.80
1.77
1.72
1.72
1.71
1.70
1.69
1.68
1.65
1.64
1.63
1.62
1.37
1.30
1.29
1.29
1.26
1.12
1.00
0.99
0.96
0.88
0.85
0.84
0.8
O
N
Cl
O
2d
2.02
2.07
1.00
1.03
1.01
7.01
2.18
4.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.
f1 (ppm)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131.85
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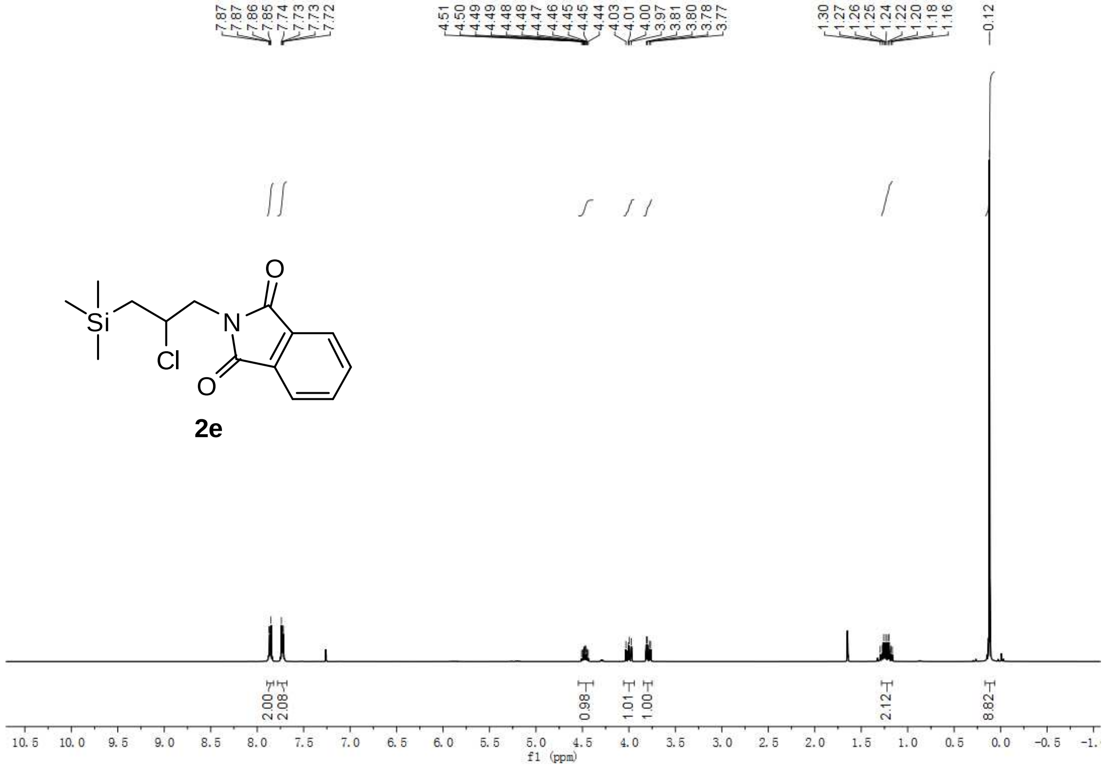
57.12
44.70
43.33
34.51
33.75
31.95
26.45
26.21
25.95
O
N
Cl
O
2d
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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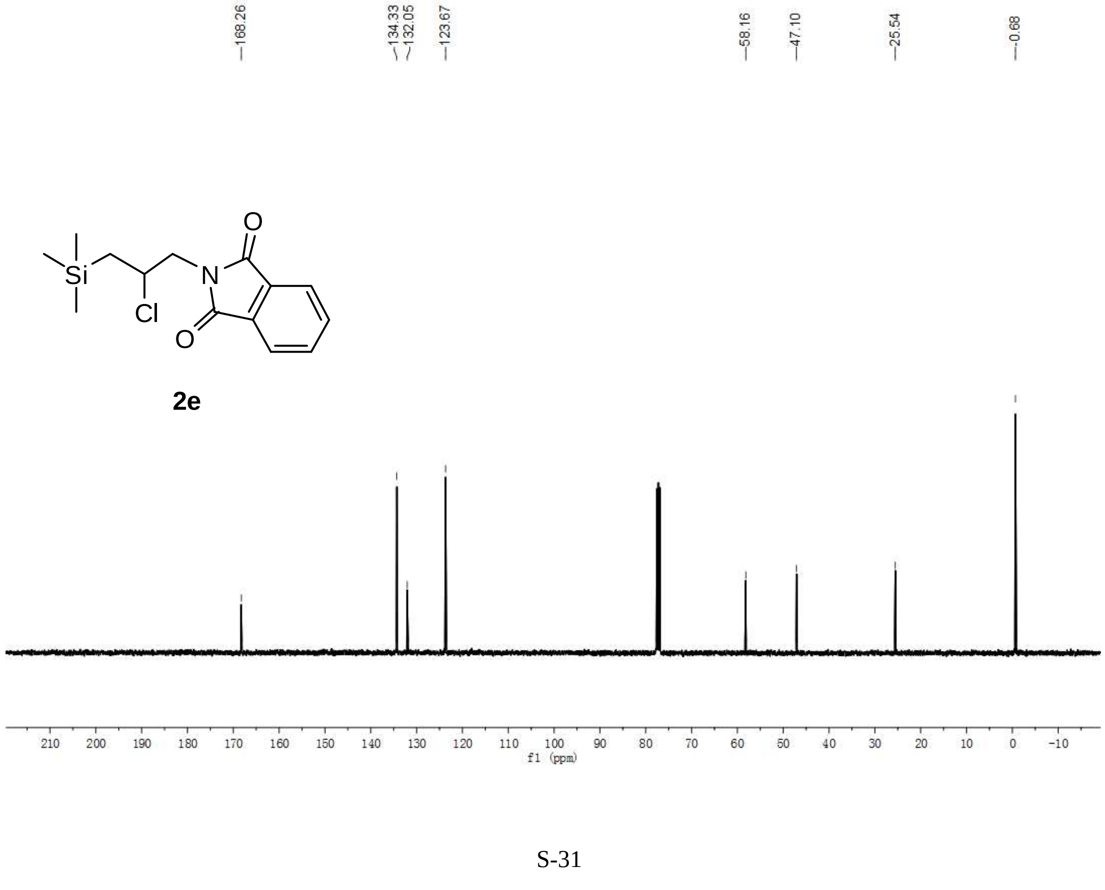
7.74
7.73
7.73
7.72
4.51
4.50
4.49
4.49
4.48
4.48
4.47
4.46
4.45
4.45
4.44
4.03
4.01
4.00
3.97
3.81
3.80
3.78
3.77
1.30
1.27
1.26
1.25
1.24
1.22
1.20
1.18
1.16
0.12
Si
N
O
O
Cl
2e
2.00
2.08
0.98
1.01
1.00
2.12
8.82
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)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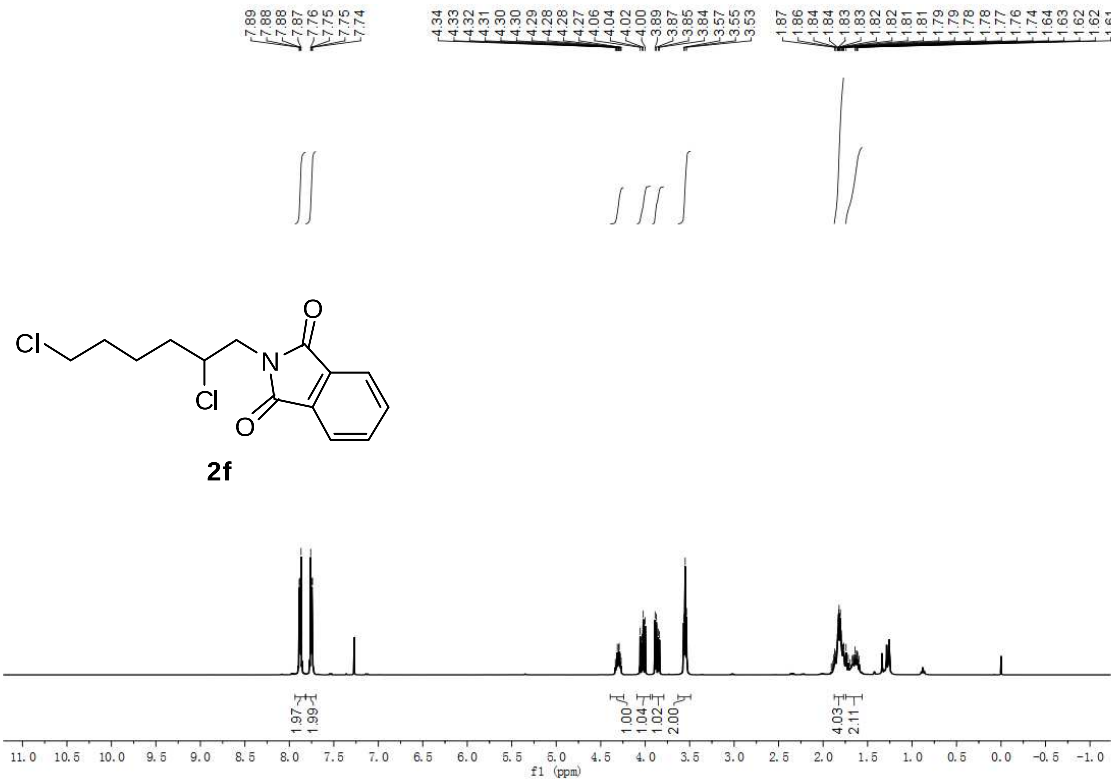
132.05
123.67
58.16
47.10
25.54
-0.68
Si
N
O
O
Cl
2e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.88
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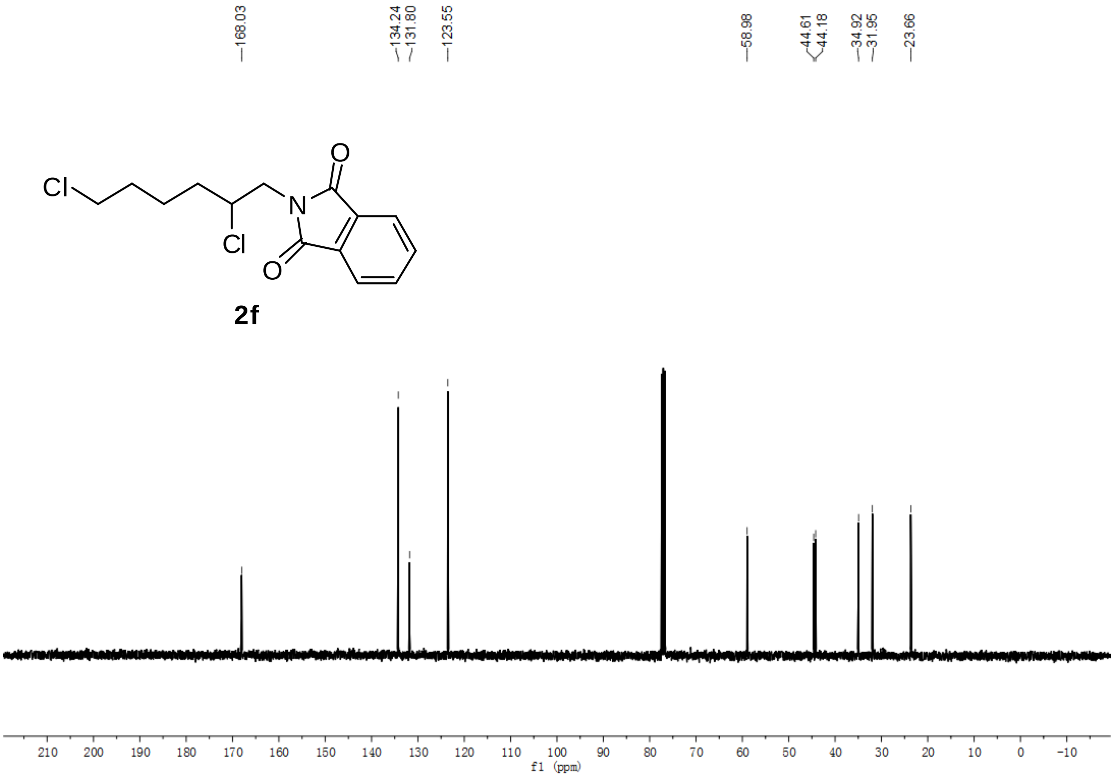
7.75
7.75
7.74
4.34
4.33
4.32
4.31
4.30
4.29
4.28
4.28
4.27
4.06
4.04
4.02
4.00
3.89
3.87
3.85
3.84
3.57
3.55
3.53
1.87
1.86
1.84
1.83
1.83
1.82
1.82
1.81
1.81
1.79
1.79
1.78
1.78
1.77
1.76
1.74
1.64
1.63
1.62
1.62
Cl
Cl
N
O
O
2f
1.97
1.99
1.00
1.04
1.02
2.00
4.03
2.11
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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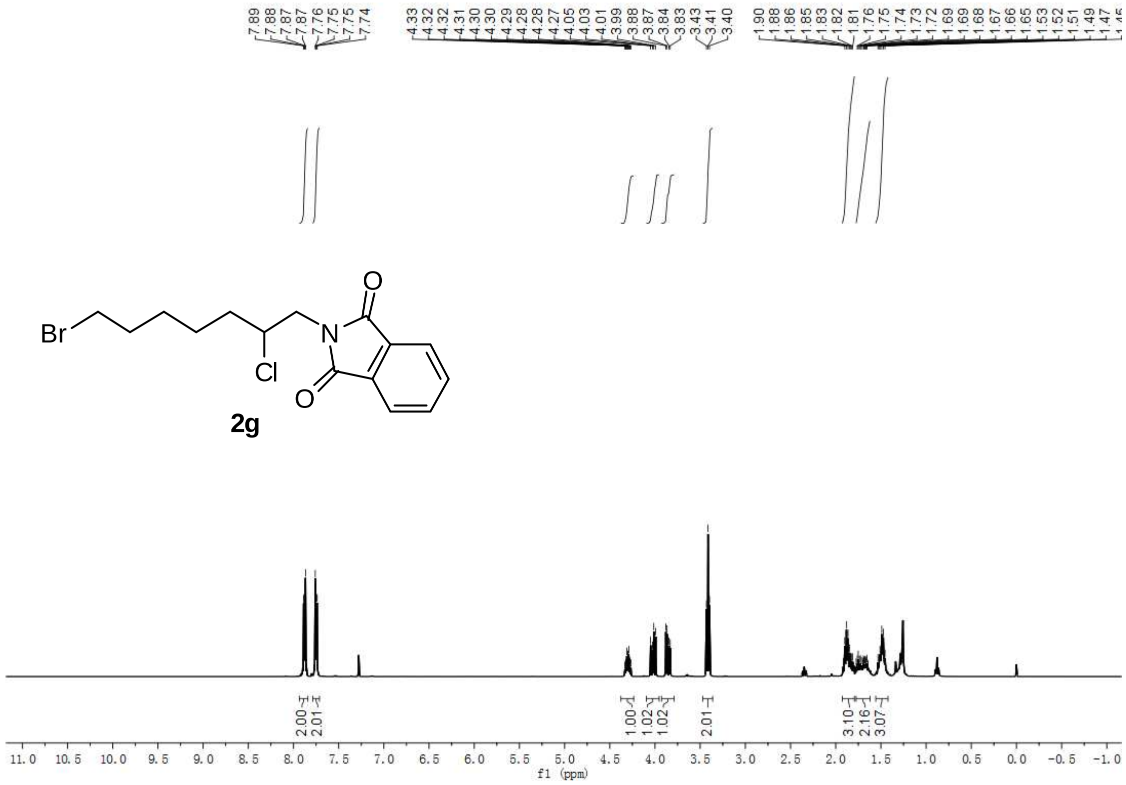
131.80
123.55
58.98
44.61
44.18
34.92
31.95
23.66
Cl
Cl
N
O
O
2f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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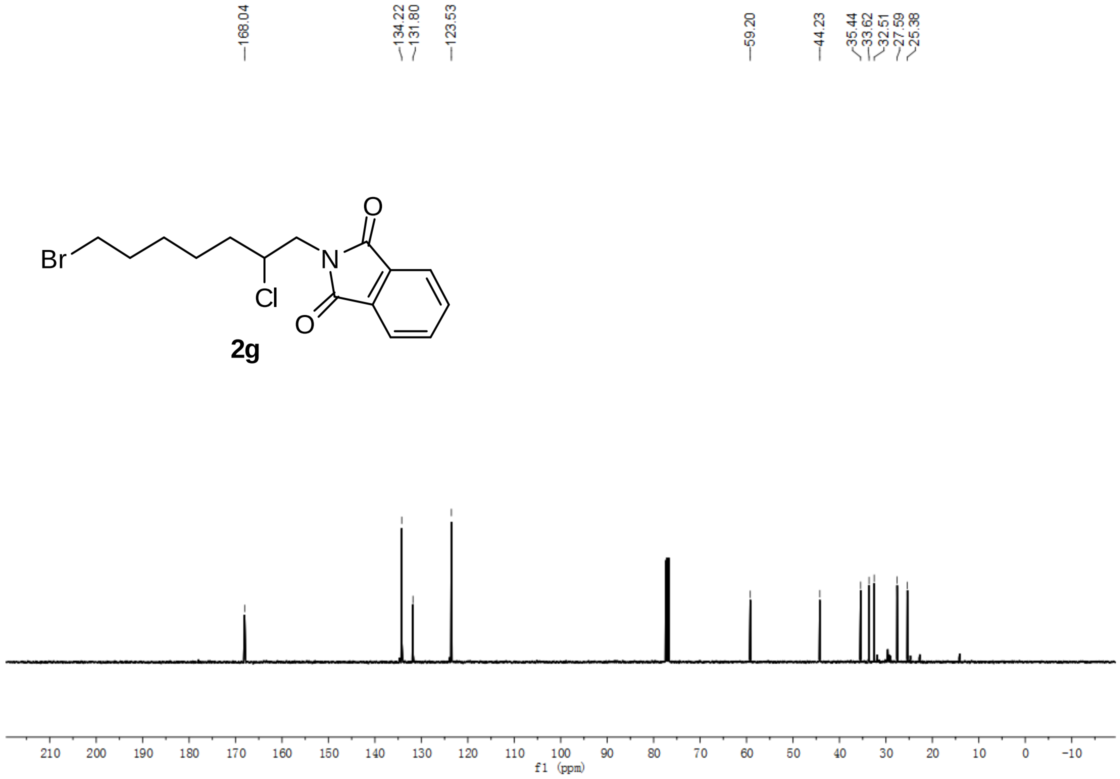
7.75
7.75
7.74
4.33
4.32
4.32
4.31
4.30
4.30
4.29
4.28
4.28
4.27
4.05
4.03
4.01
3.99
3.88
3.87
3.84
3.83
3.43
3.41
3.40
1.90
1.88
1.86
1.85
1.83
1.82
1.81
1.76
1.75
1.74
1.73
1.72
1.69
1.69
1.68
1.67
1.66
1.65
1.53
1.52
1.51
1.49
1.47
Br
N
O
O
Cl
2g
2.00
2.01
1.00
1.02
1.02
2.01
3.10
2.16
3.07
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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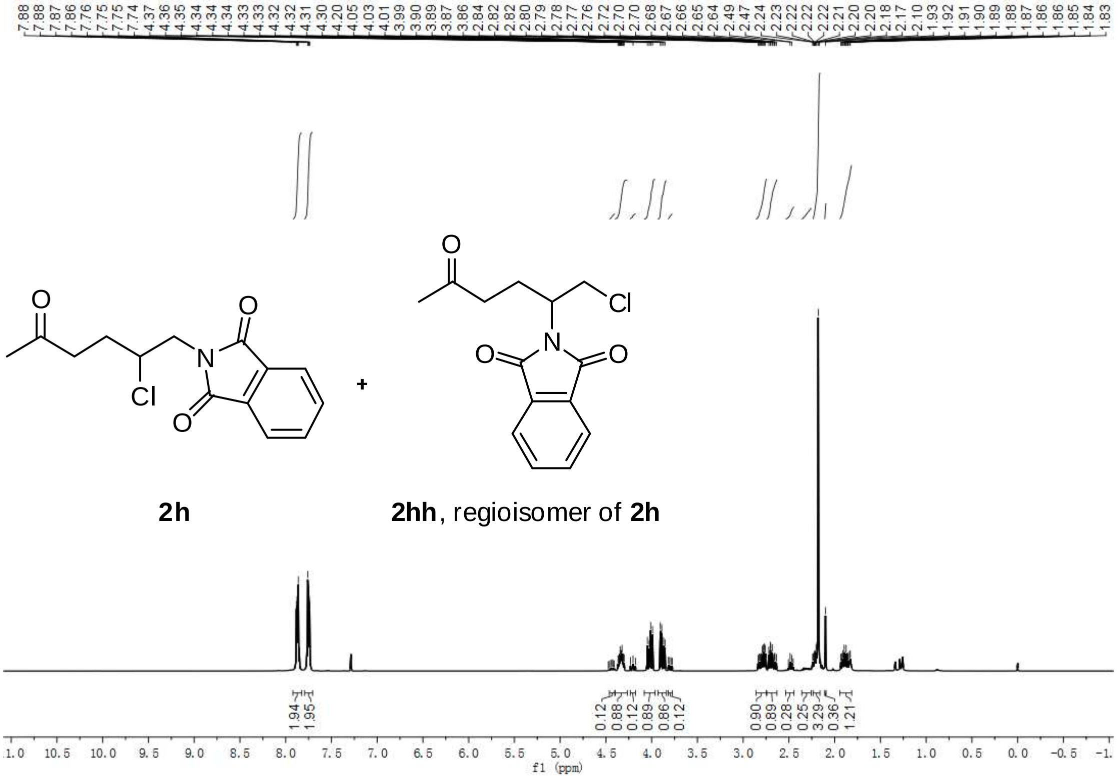
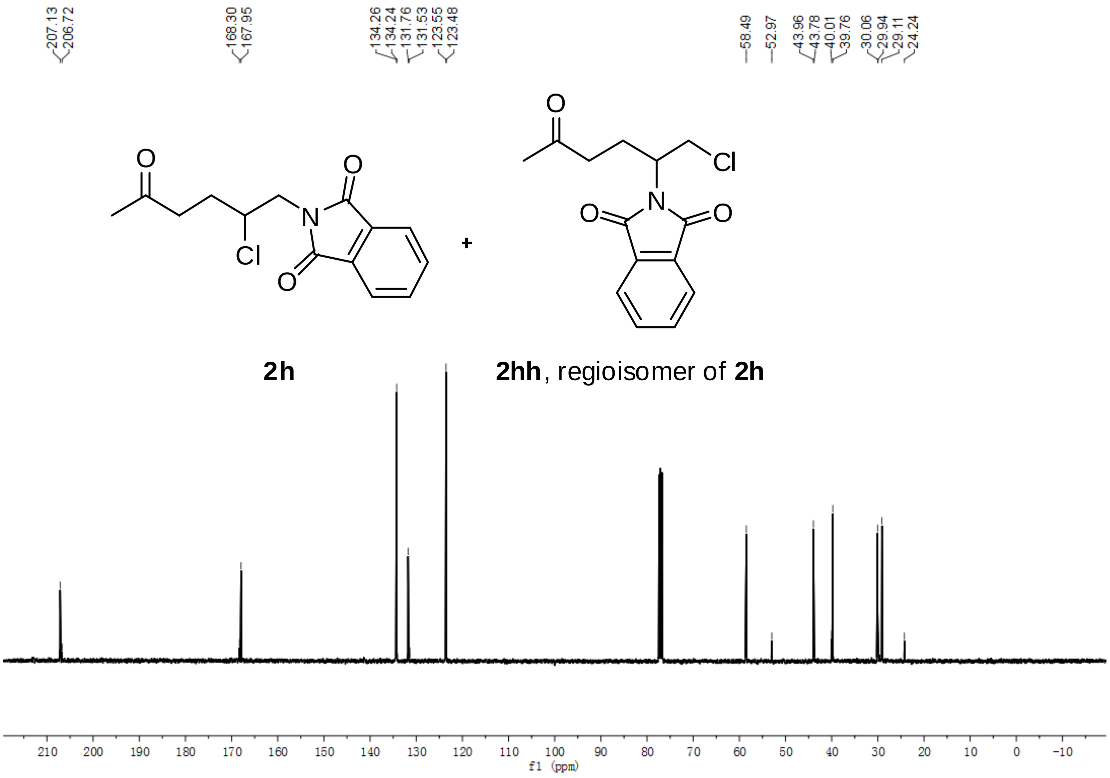
134.22
131.80
123.53
59.20
44.23
35.44
33.62
32.51
27.59
25.38
Br
N
O
O
Cl
2g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



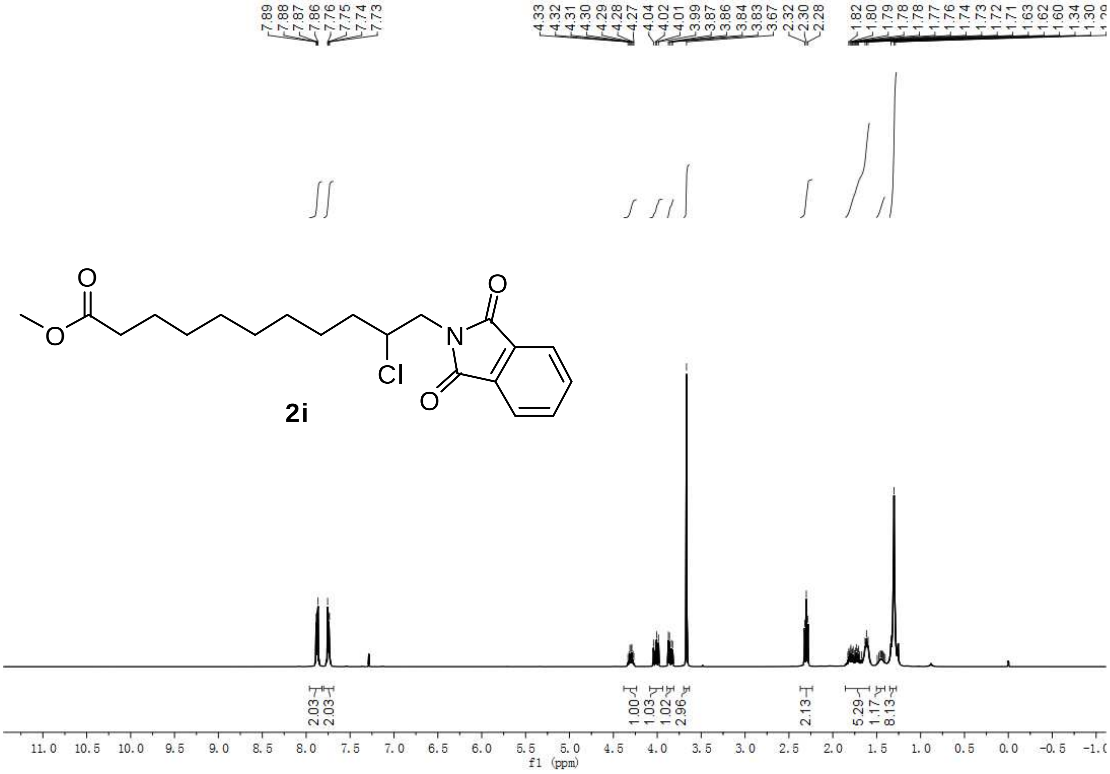
2h

2hh, regioisomer of **2h**



2h

2hh, regioisomer of **2h**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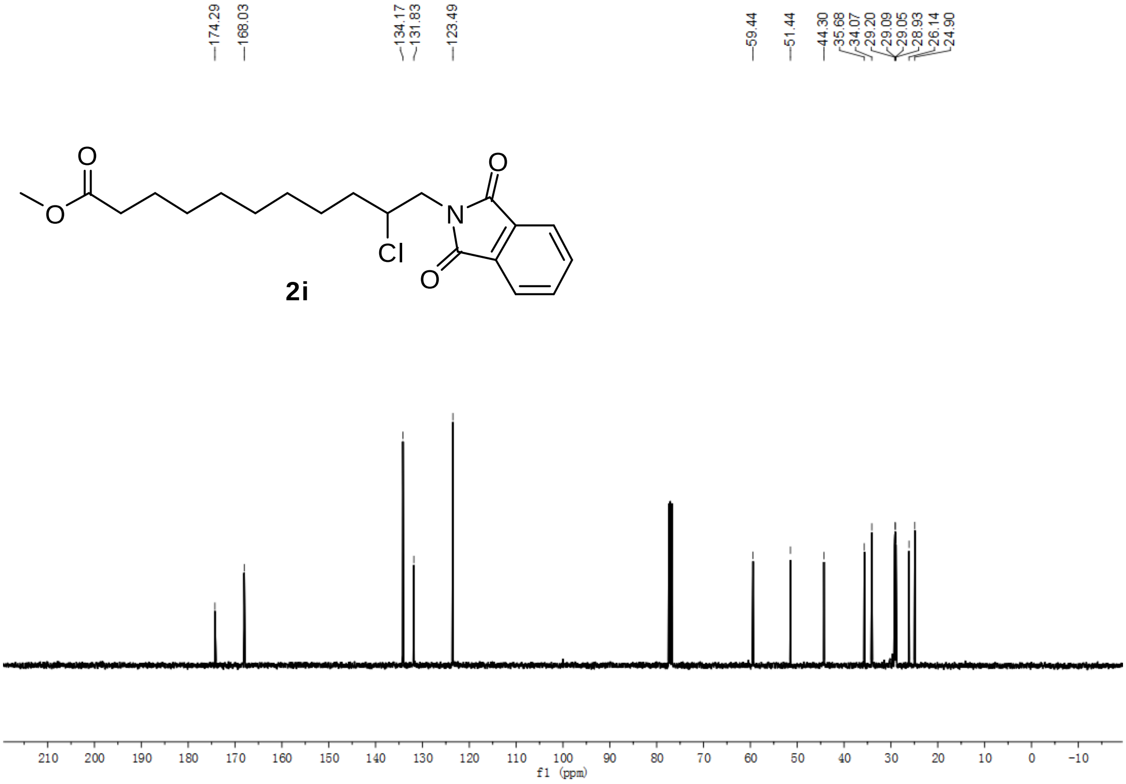
7.86
7.76
7.75
7.74
7.73
4.33
4.32
4.31
4.30
4.29
4.28
4.27
4.04
4.02
4.01
3.99
3.87
3.86
3.84
3.83
3.67
2.32
2.30
2.28
1.82
1.80
1.79
1.78
1.78
1.76
1.74
1.73
1.72
1.71
1.63
1.62
1.60
1.34
1.30
O
O
N
O
O
Cl
2i
2.03
2.03
1.00
1.03
1.02
2.96
2.13
5.29
1.17
8.13
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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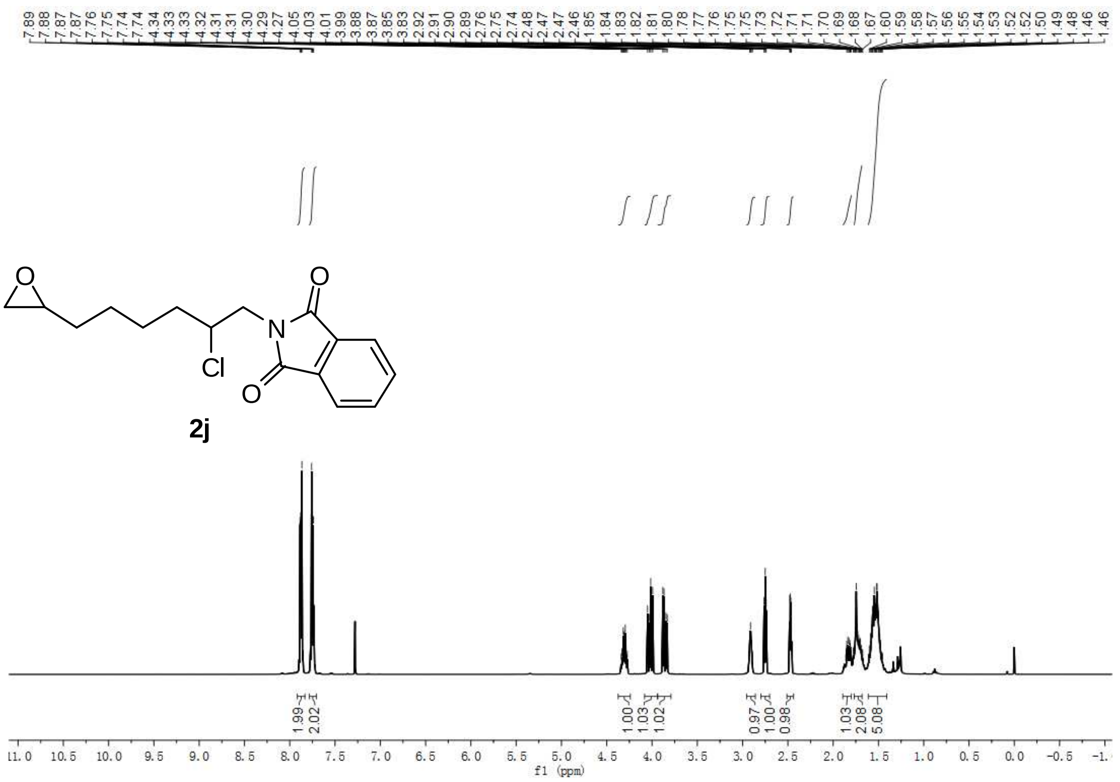
134.17
131.83
123.49
59.44
51.44
44.30
35.68
34.07
29.20
29.09
29.05
28.93
26.14
24.90
O
O
N
O
O
Cl
2i
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


2j

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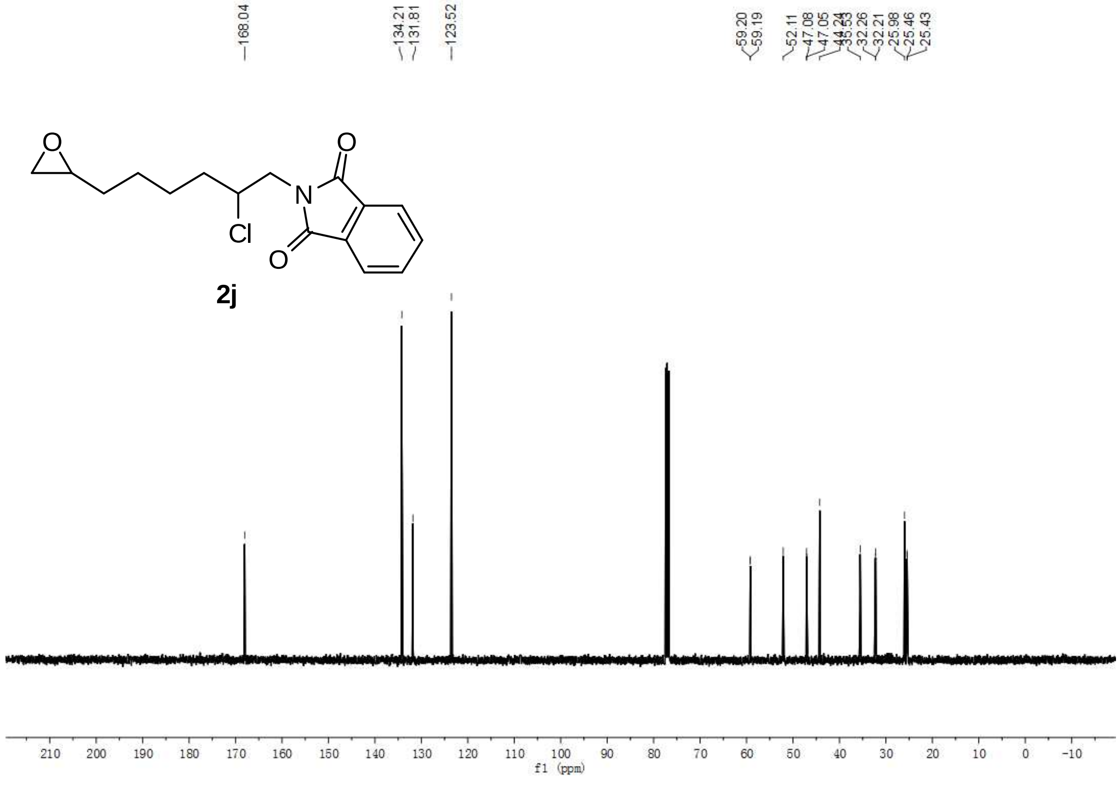
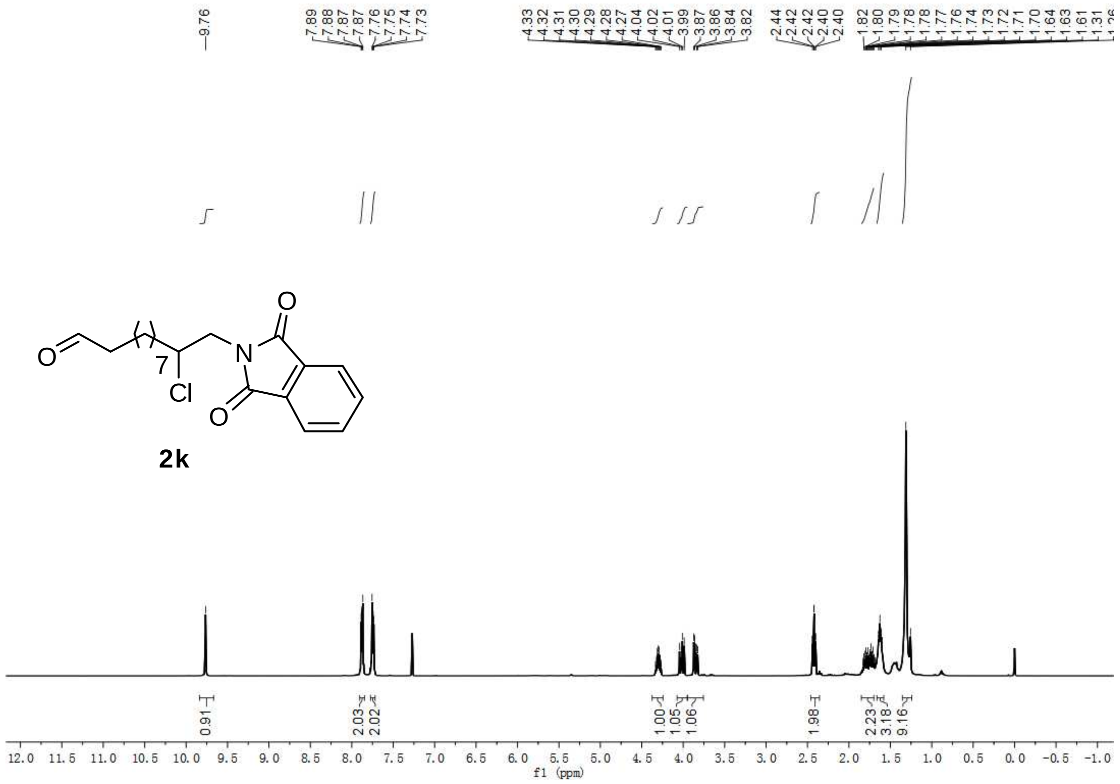
7.88
7.87
7.87
7.76
7.75
7.74
7.74
4.34
4.33
4.33
4.32
4.31
4.31
4.30
4.29
4.27
4.05
4.03
4.01
3.99
3.88
3.87
3.85
3.83
2.92
2.91
2.90
2.89
2.76
2.75
2.74
2.48
2.47
2.47
2.46
1.85
1.84
1.83
1.82
1.81
1.80
1.78
1.77
1.76
1.75
1.75
1.73
1.72
1.71
1.71
1.70
1.69
1.68
1.67
1.60
1.59
1.58
1.57
1.56
1.55
1.54
1.53
1.52
1.52
1.50
1.49
1.48
1.46
1.46
O
N
O
Cl
O
1.99
2.02
1.00
1.03
1.02
0.97
1.00
0.98
1.03
2.08
5.08
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.
f1 (ppm)


2j

168.04
134.21
131.81
123.52
59.20
59.19
52.11
47.08
47.05
44.24
35.53
32.26
32.21
25.98
25.46
25.43
O
N
O
Cl
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.87
7.87
7.76
7.75
7.74
7.73
4.33
4.32
4.31
4.30
4.29
4.28
4.27
4.04
4.02
4.01
3.99
3.87
3.86
3.84
3.82
2.44
2.42
2.42
2.40
2.40
1.82
1.80
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1.77
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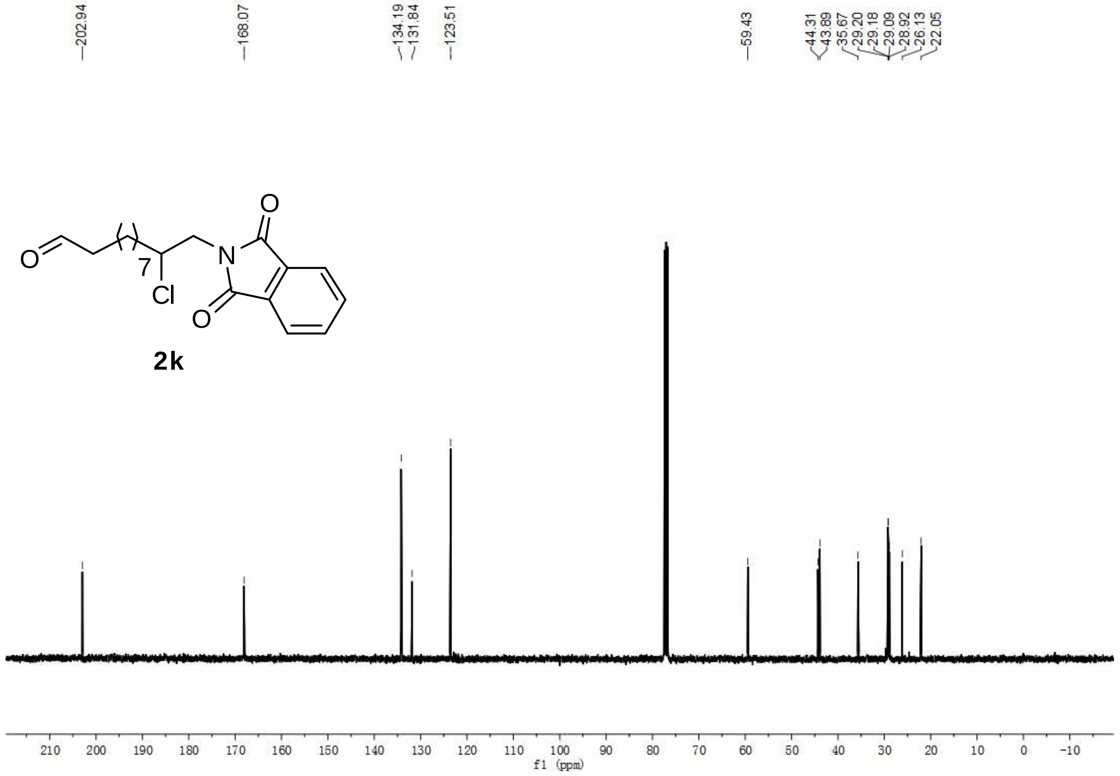
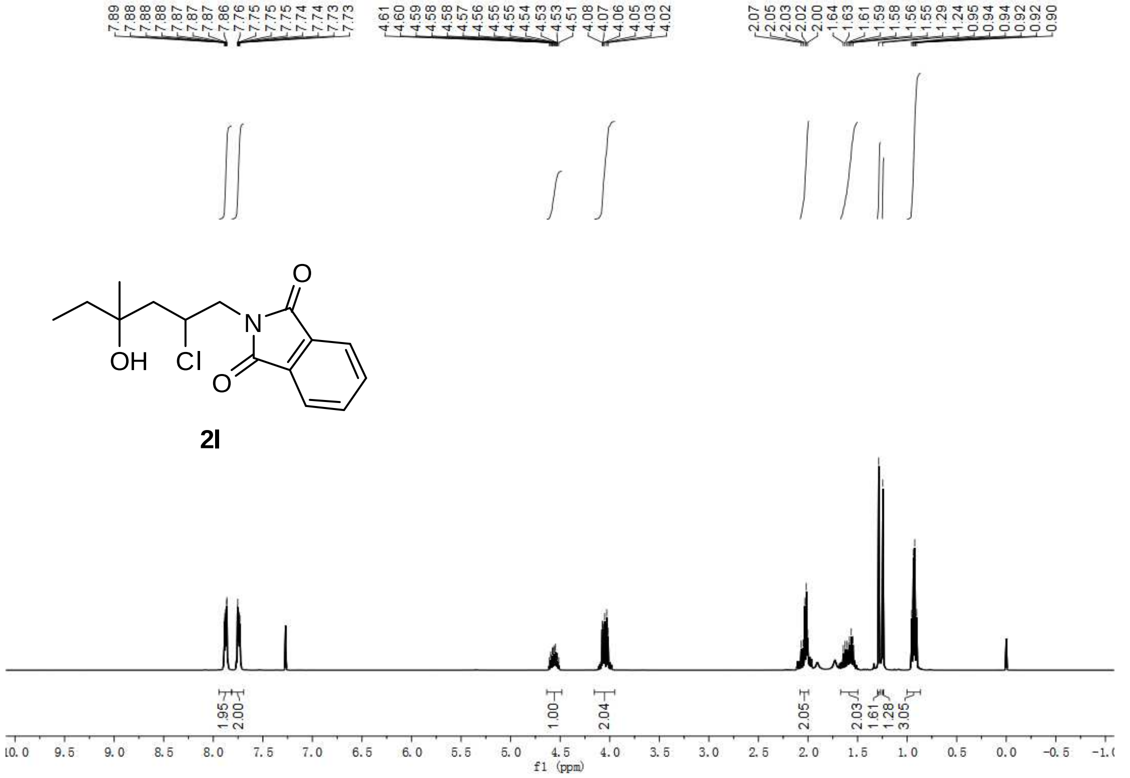
1.73
1.72
1.71
1.70
1.64
1.63
1.61
1.31
O
N
O
O
7
Cl
2k
0.91
2.03
2.02
1.00
1.05
1.06
1.98
2.23
3.18
9.16
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


202.94
168.07
134.19
131.84
123.51
59.43
44.31
43.89
35.67
29.20
29.18
29.09
28.92
26.13
22.05
O
N
O
O
7
Cl
2k
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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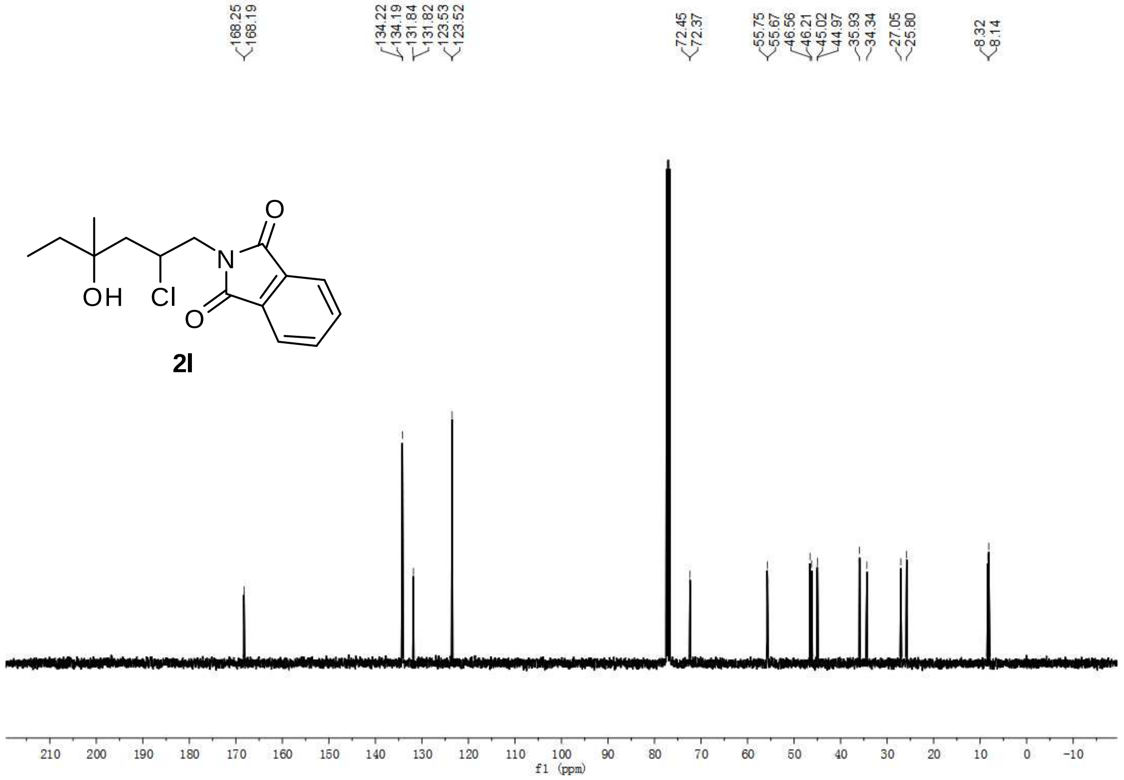
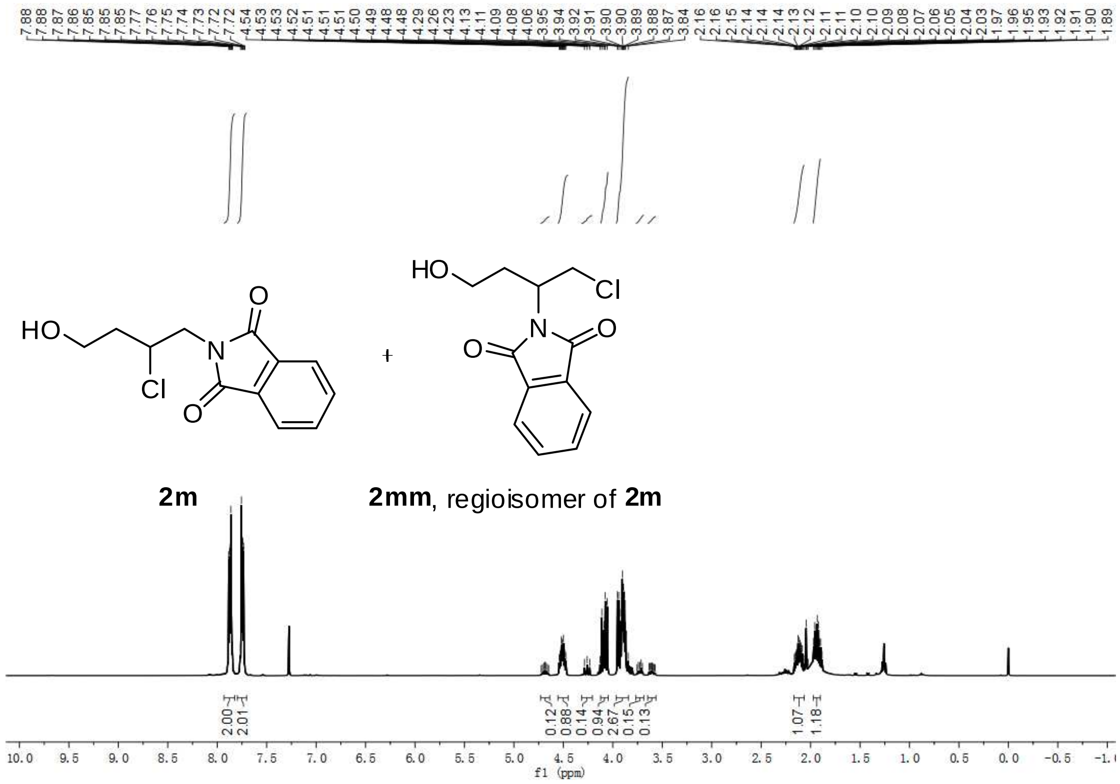
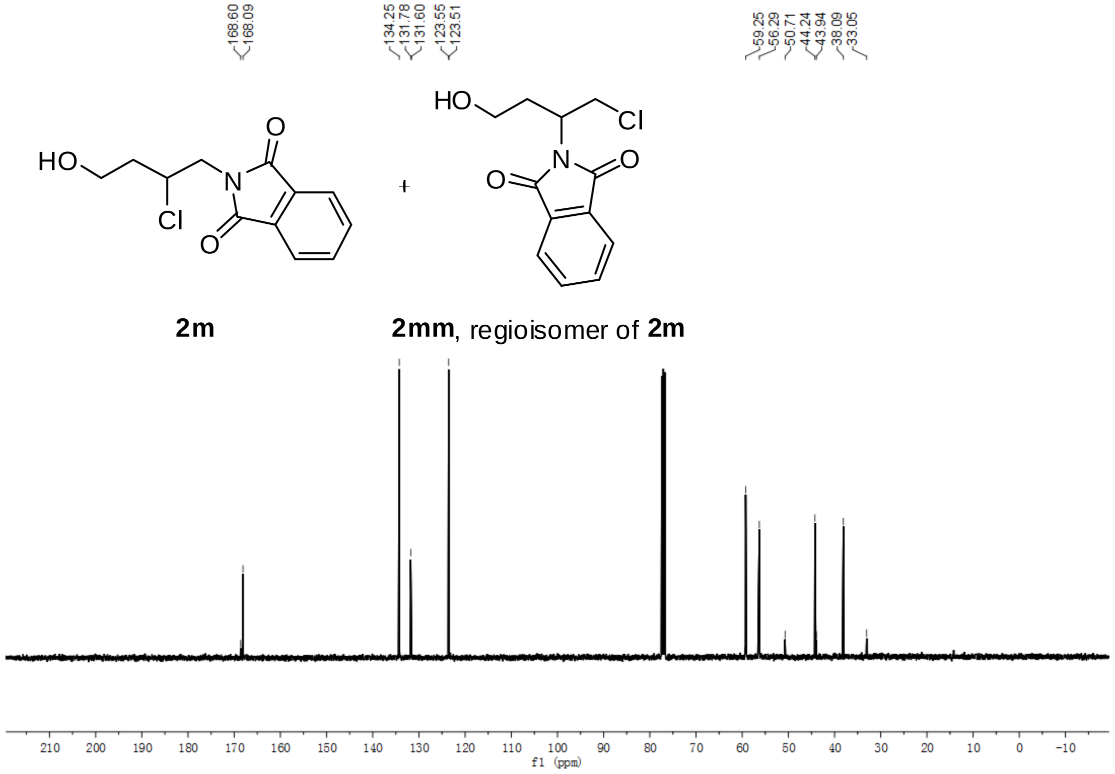
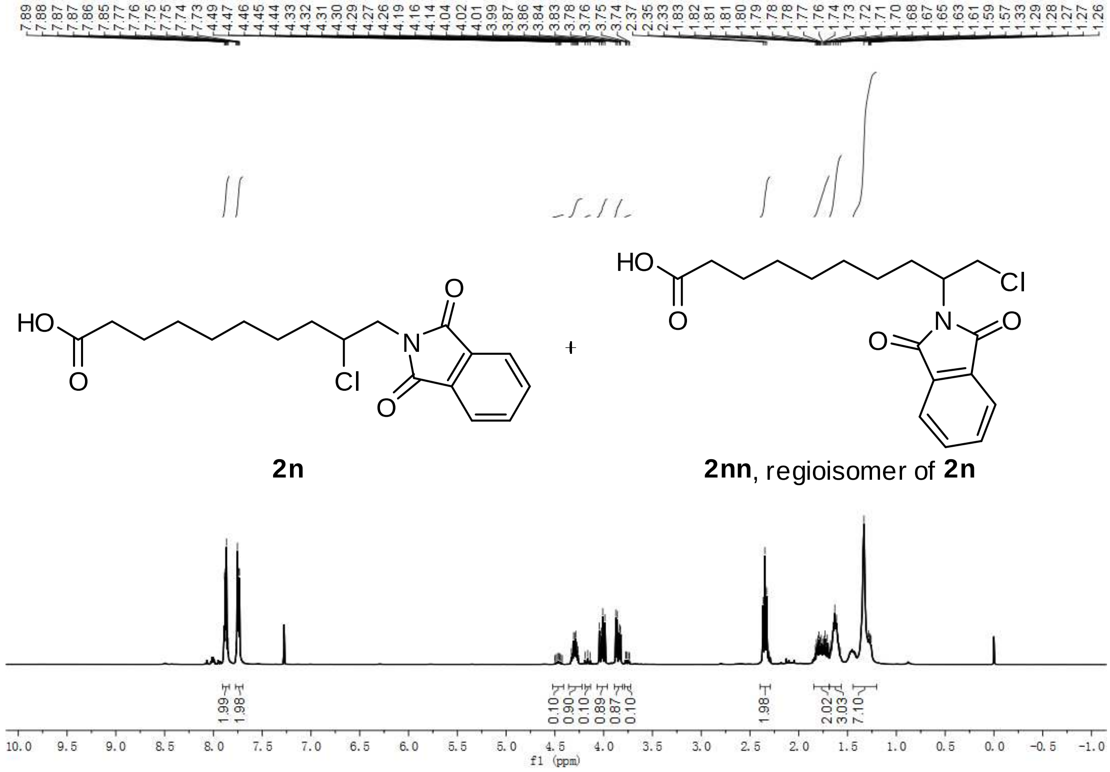
4.61 4.60 4.59 4.58 4.58 4.57 4.56 4.55 4.55 4.54 4.53 4.53 4.51 4.08 4.07 4.06 4.05 4.03 4.02
2.07 2.05 2.03 2.02 2.00 1.64 1.63 1.61 1.59 1.58 1.56 1.55 1.29 1.24 0.95 0.94 0.94 0.92 0.92 0.90
O
N
OH
Cl
O
2l
1.95
2.00
1.00
2.04
2.05
2.03
1.61
1.28
3.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


168.25 168.19
134.22 134.19 131.84 131.82 123.53 123.52
72.45 72.37
55.75 55.67 46.56 46.21 45.02 44.97 35.93 34.34 27.05 25.80
8.32 8.14
O
N
OH
Cl
O
2l
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

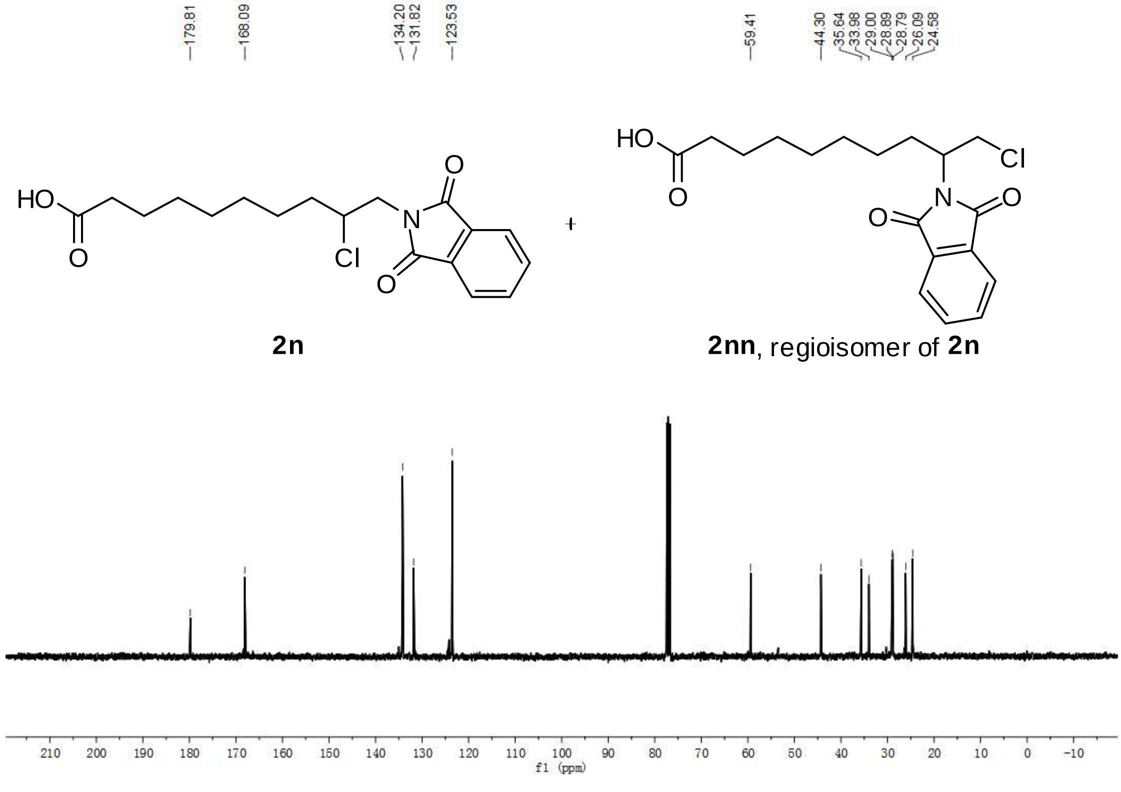

7.88
7.88
7.87
7.86
7.85
7.85
7.77
7.76
7.75
7.74
7.73
7.72
7.72
4.54
4.53
4.53
4.52
4.51
4.51
4.50
4.49
4.48
4.48
4.29
4.26
4.23
4.13
4.11
4.09
4.08
4.06
3.95
3.94
3.92
3.91
3.90
3.90
3.89
3.88
3.87
3.84
2.16
2.15
2.14
2.14
2.14
2.13
2.12
2.11
2.11
2.10
2.10
2.09
2.08
2.07
2.06
2.05
2.04
2.03
1.97
1.96
1.95
1.93
1.92
1.91
1.90
1.89
HO
Cl
N
O
O
+
HO
Cl
N
O
O
2m
2mm, regioisomer of 2m
2.00
2.01
0.12
0.88
0.14
0.94
2.67
0.15
0.13
1.07
1.18
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


168.60
168.09
134.25
131.78
131.60
123.55
123.51
59.25
56.29
50.71
44.24
43.94
38.09
33.05
HO
Cl
N
O
O
+
HO
Cl
N
O
O
2m
2mm, regioisomer of 2m
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



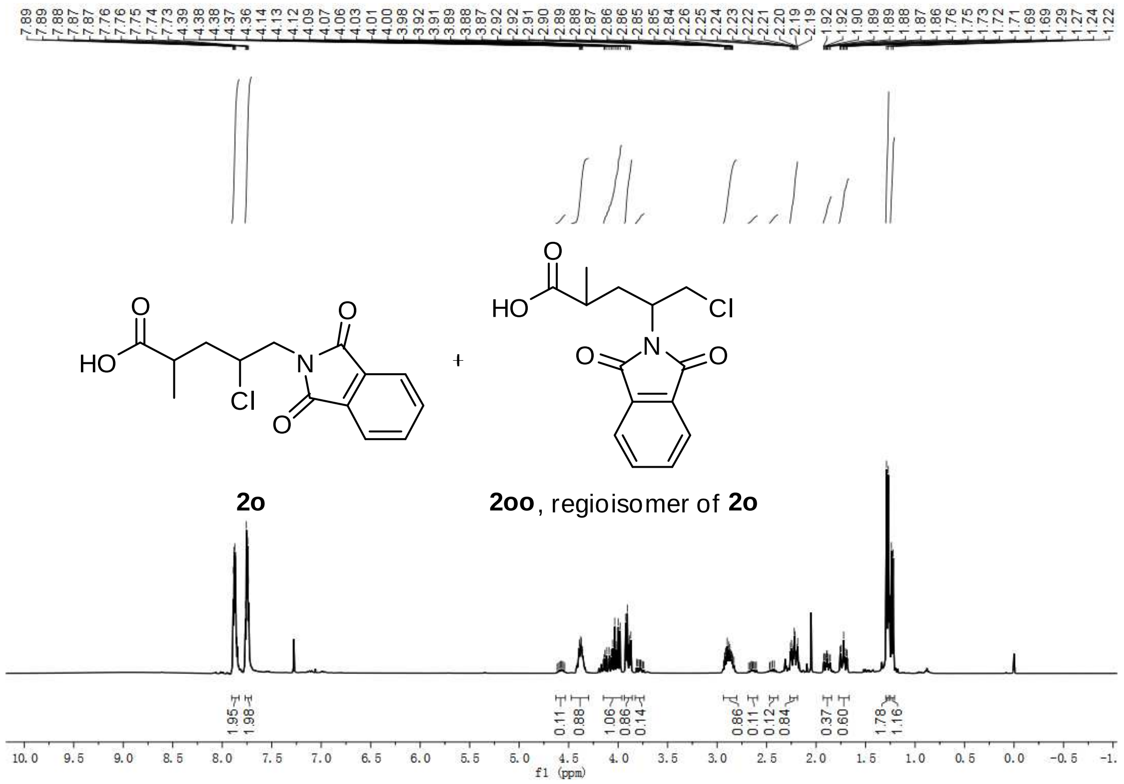
2n

2nn, regioisomer of **2n**

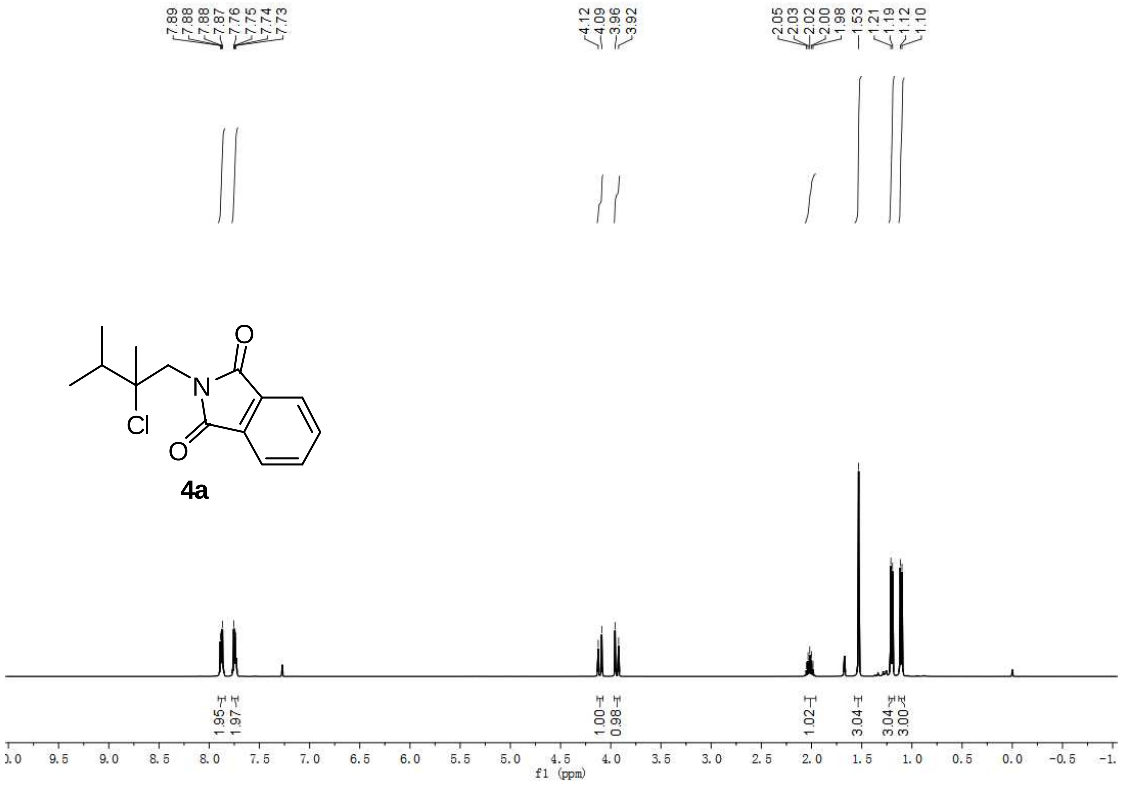


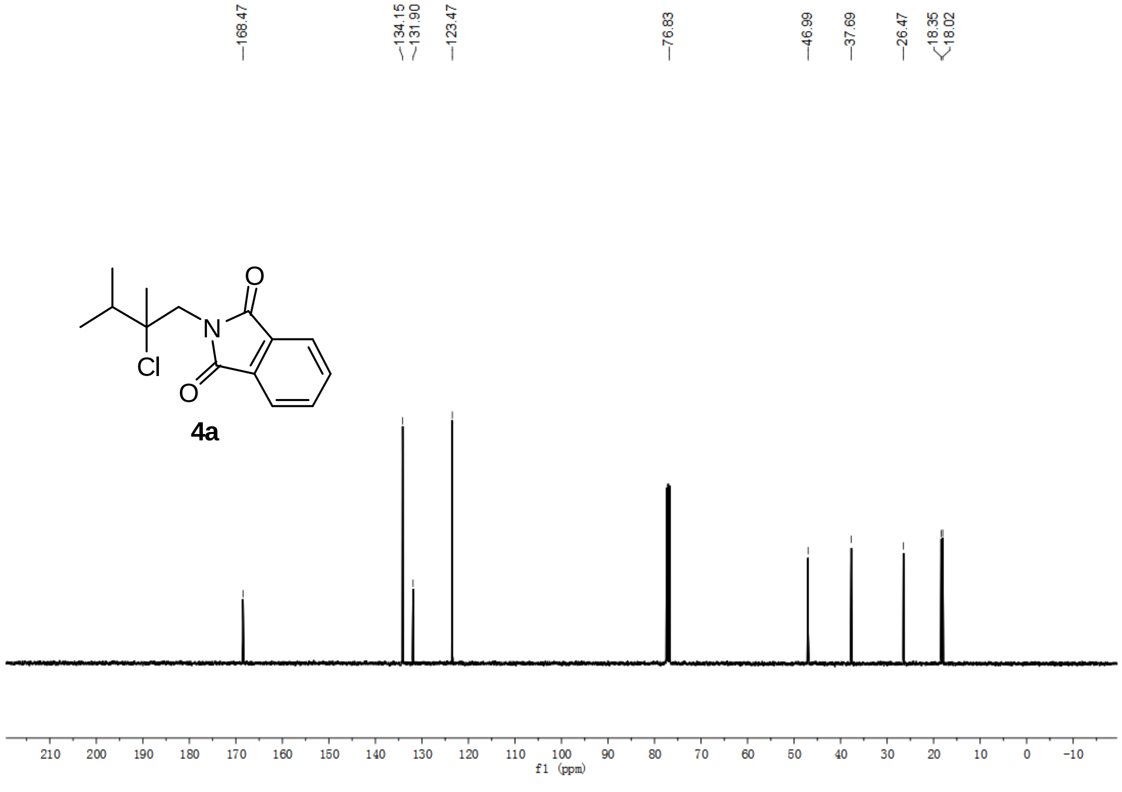
2n

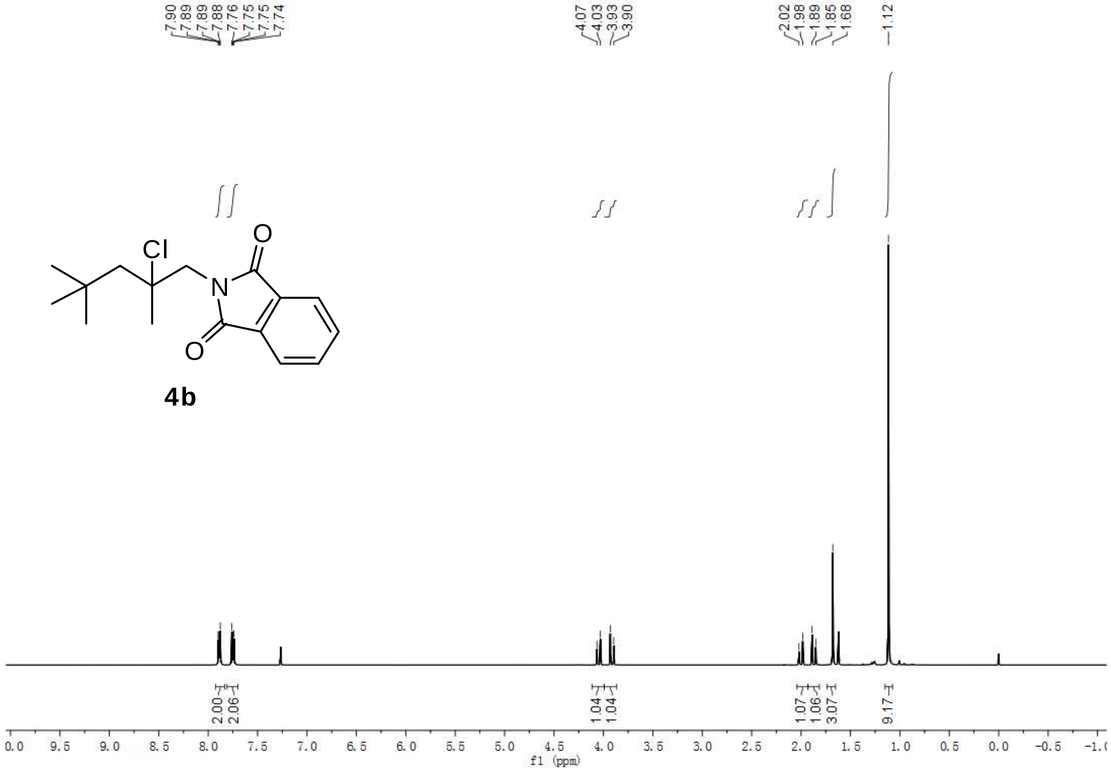
2nn, regioisomer of **2n**

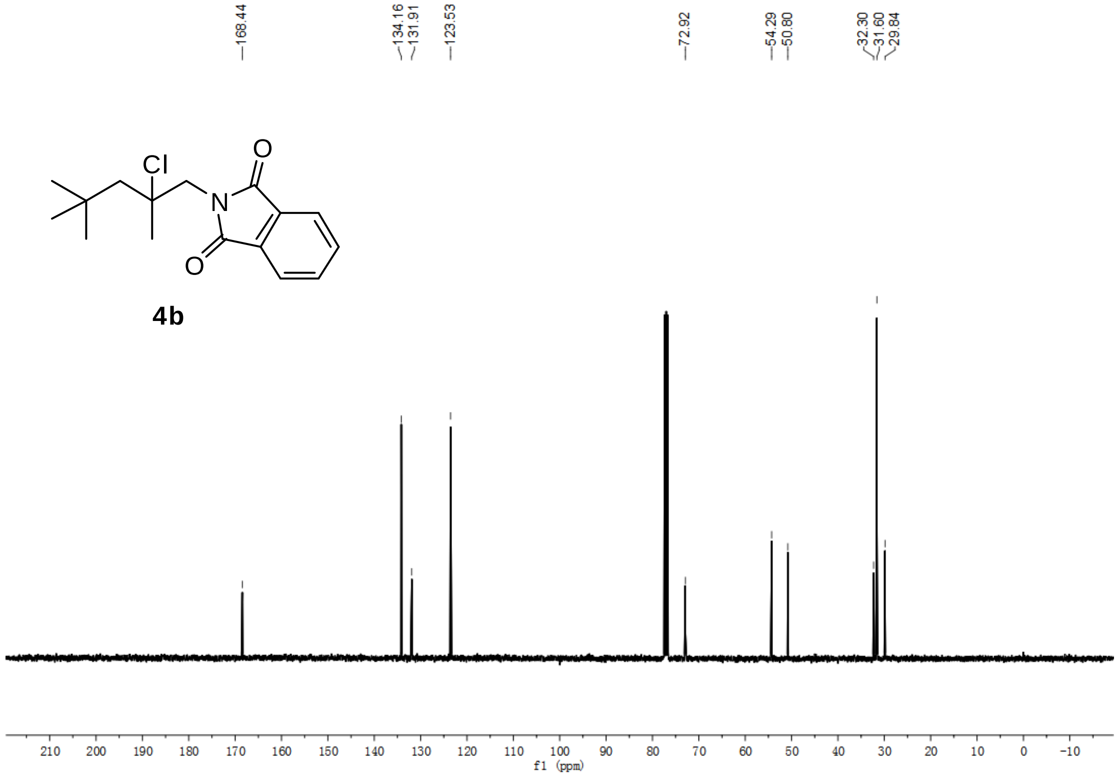

7.89
7.89
7.88
7.87
7.87
7.76
7.76
7.75
7.74
7.73
4.39
4.38
4.38
4.37
4.36
4.14
4.13
4.12
4.09
4.07
4.06
4.03
4.01
4.00
3.98
3.92
3.91
3.89
3.88
3.87
2.92
2.92
2.91
2.90
2.89
2.88
2.87
2.86
2.86
2.85
2.85
2.84
2.26
2.25
2.24
2.23
2.22
2.21
2.20
2.19
2.19
1.92
1.92
1.90
1.89
1.89
1.88
1.87
1.86
1.76
1.75
1.73
1.72
1.71
1.69
1.69
1.29
1.27
1.24
1.22
O
HO
N
O
Cl
O
+
O
HO
Cl
N
O
O
2o
2oo, regioisomer of 2o
1.95
1.98
0.11
0.88
1.06
0.86
0.14
0.86
0.11
0.12
0.84
0.37
0.60
1.78
1.16
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.
f1 (ppm)

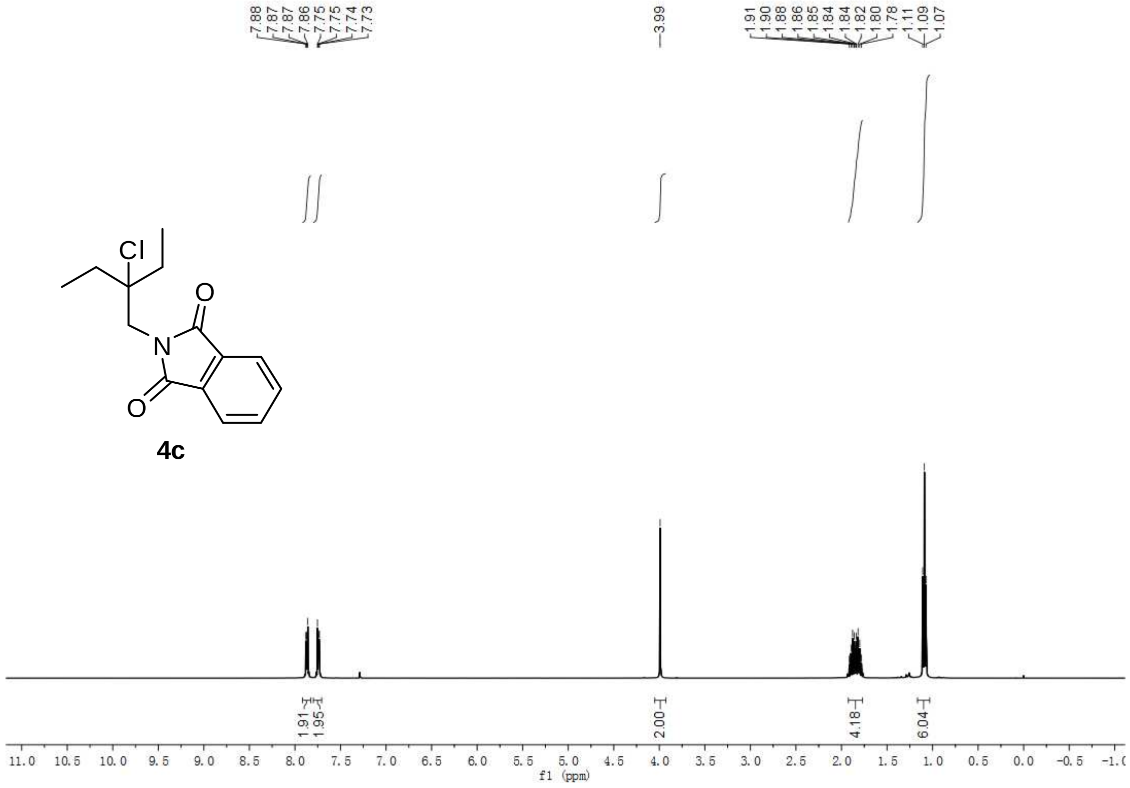

181.64
181.32
168.03
134.29
134.24
131.76
131.74
123.61
123.59
57.36
56.55
44.30
44.18
39.25
38.22
36.56
36.40
18.12
15.55
O
HO
N
O
Cl
O
+
O
HO
Cl
N
O
O
2o
2oo, regioisomer of 2o
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

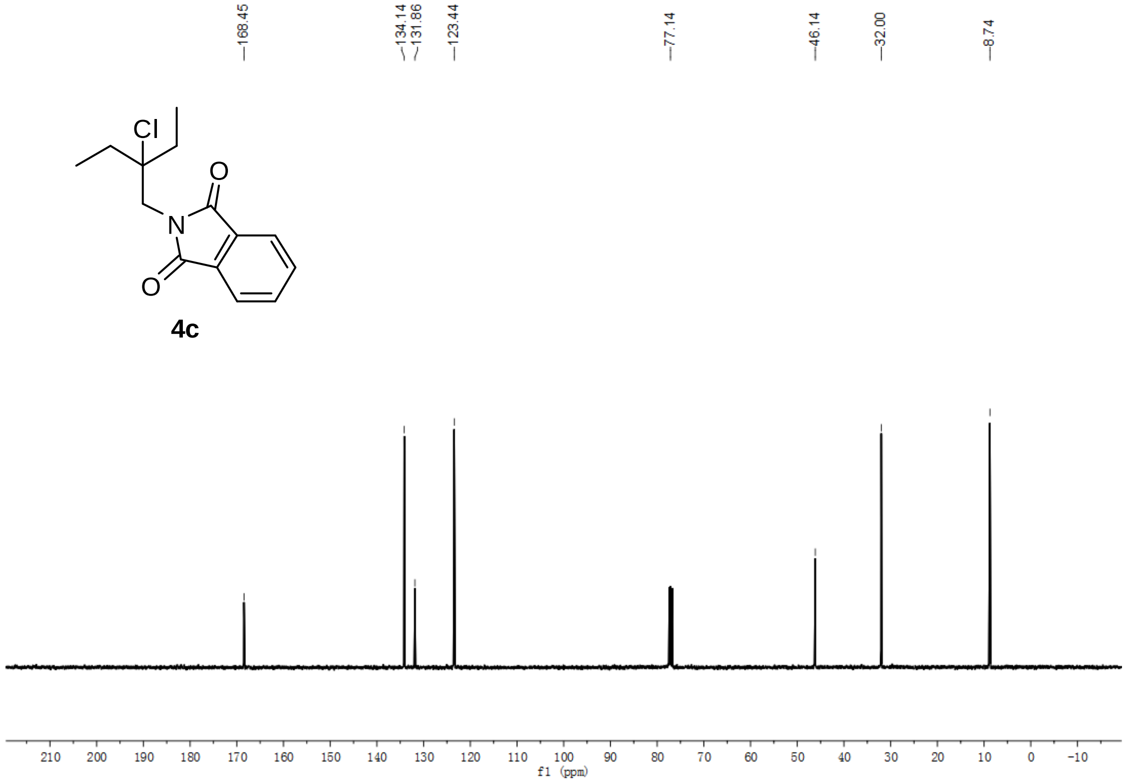

7.89
7.88
7.88
7.87
7.76
7.75
7.74
7.73
4.12
4.09
3.96
3.92
2.05
2.03
2.02
2.00
1.98
1.53
1.21
1.19
1.12
1.10
O
N
Cl
O
4a
1.95
1.97
1.00
0.98
1.02
3.04
3.04
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


168.47
134.15
131.90
123.47
76.83
46.99
37.69
26.47
18.35
18.02
O
N
Cl
O
4a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.90
7.89
7.89
7.88
7.76
7.75
7.75
7.74
4.07
4.03
3.93
3.90
2.02
1.98
1.89
1.85
1.68
1.12
Cl
N
O
O
4b
2.00
2.06
1.04
1.04
1.07
1.06
3.07
9.17
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.(
f1 (ppm)


168.44
134.16
131.91
123.53
72.92
54.29
50.80
32.30
31.60
29.84
Cl
N
O
O
4b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.88
7.87
7.87
7.86
7.75
7.75
7.74
7.73
3.99
1.91
1.90
1.88
1.86
1.85
1.84
1.84
1.82
1.80
1.78
1.11
1.09
1.07
Cl
O
N
O
4c
1.91
1.95
2.00
4.18
6.04
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)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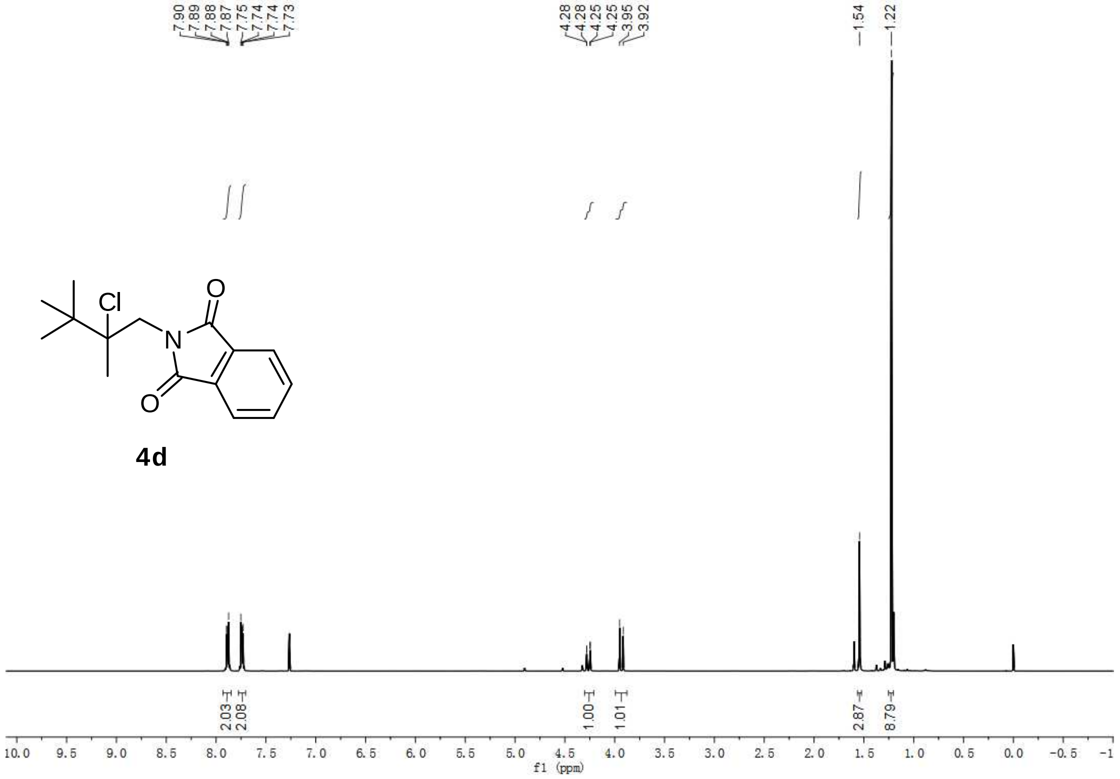
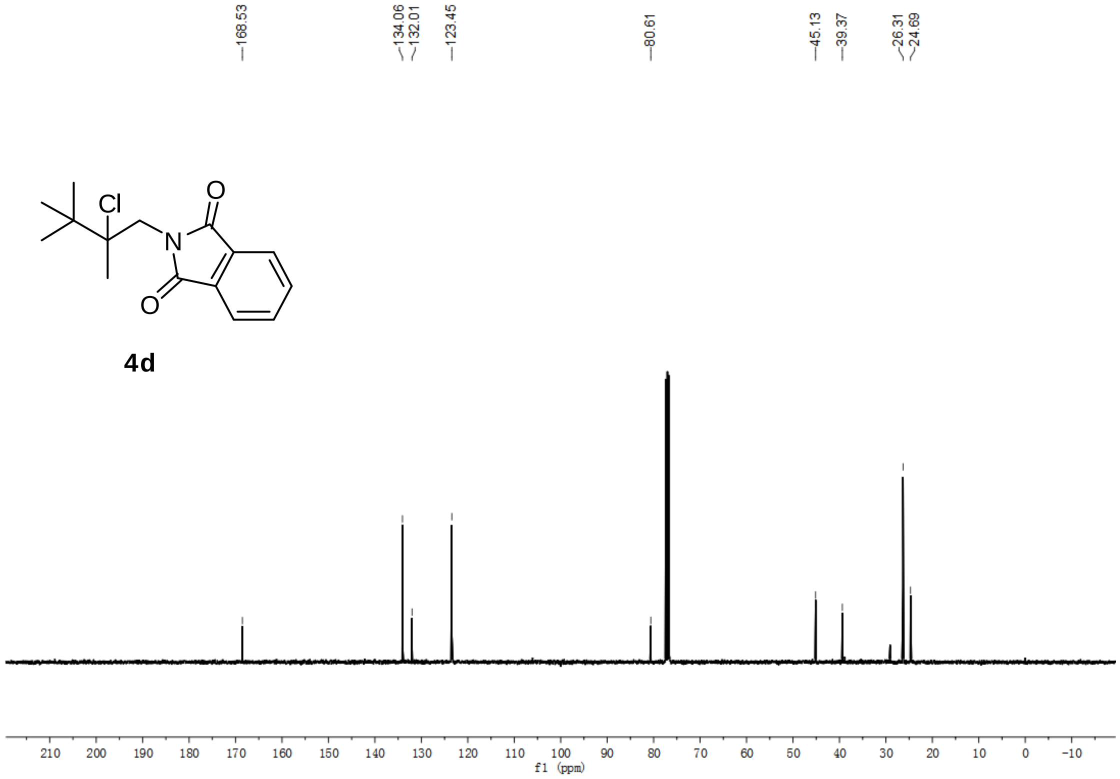
134.14
131.86
123.44
77.14
46.14
32.00
8.74
Cl
O
N
O
4c
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.90
7.89
7.88
7.87
7.75
7.74
7.74
7.73
4.28
4.28
4.25
4.25
3.95
3.92
1.54
1.22
Cl
N
O
O
4d
2.03
2.08
1.00
1.01
2.87
8.79
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)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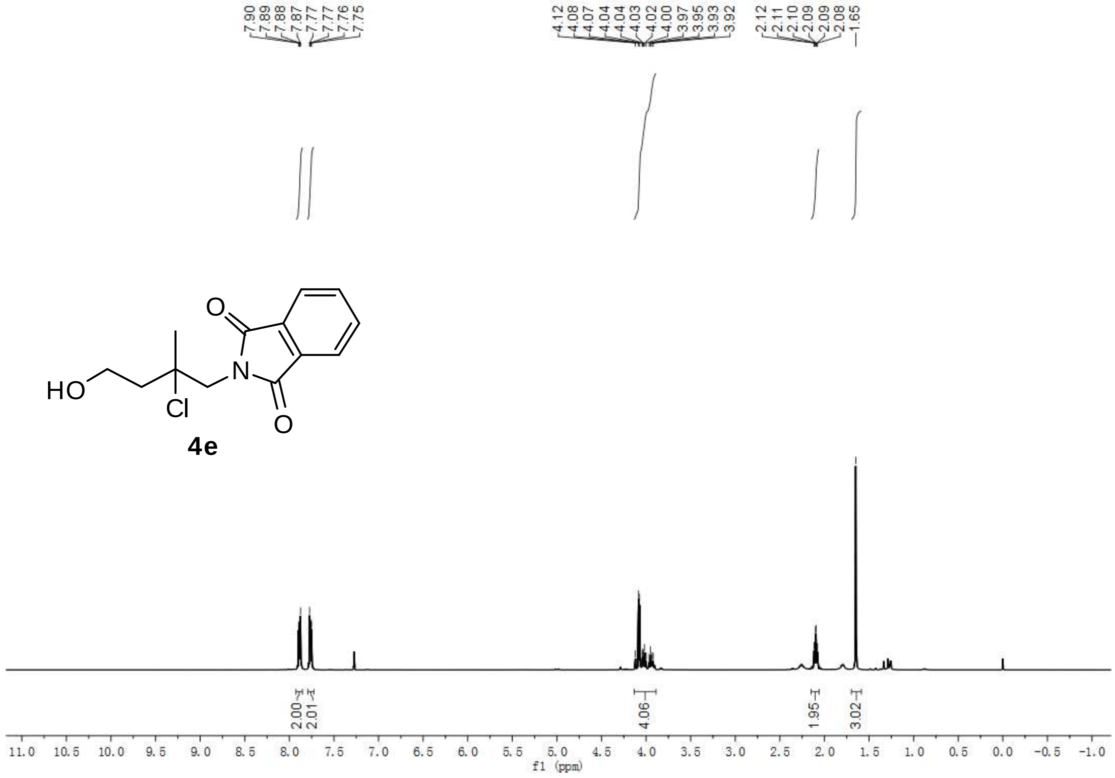
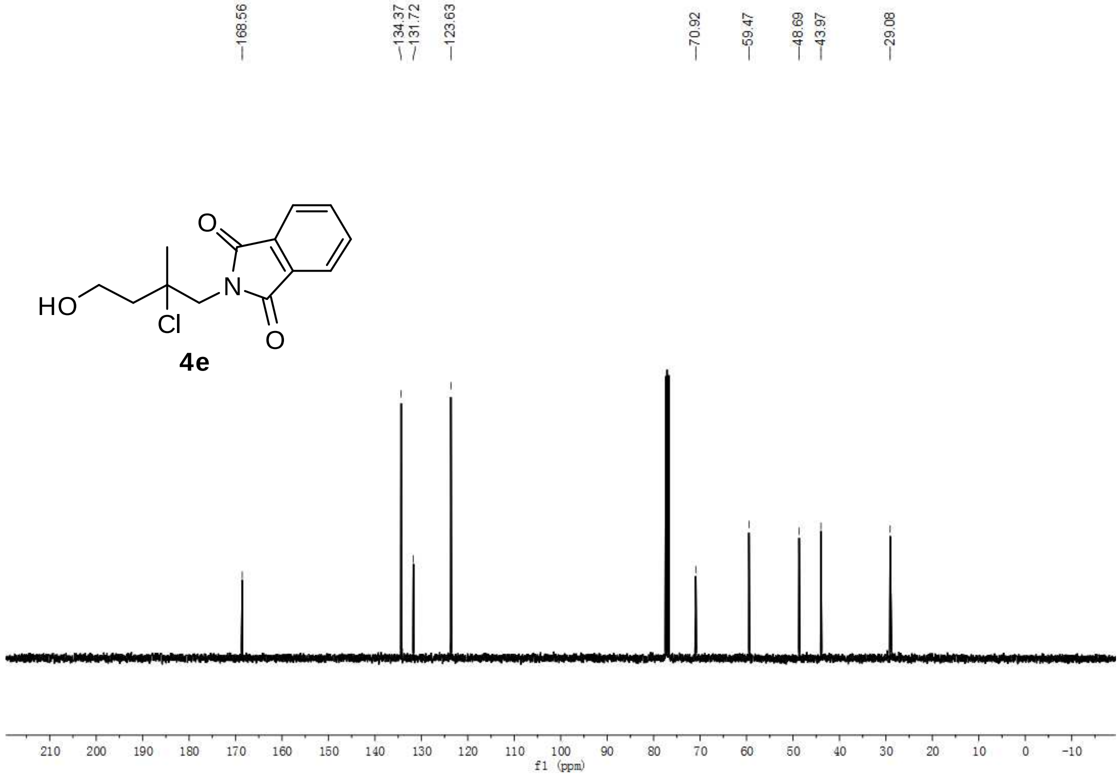
134.06
132.01
123.45
80.61
45.13
39.37
26.31
24.69
Cl
N
O
O
4d
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.90
7.89
7.88
7.87
7.77
7.77
7.76
7.75
4.12
4.08
4.07
4.04
4.04
4.03
4.02
4.00
3.97
3.95
3.93
3.92
2.12
2.11
2.10
2.09
2.09
2.08
1.65
HO
Cl
N
O
O
4e
2.00
2.01
4.06
1.95
3.02
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)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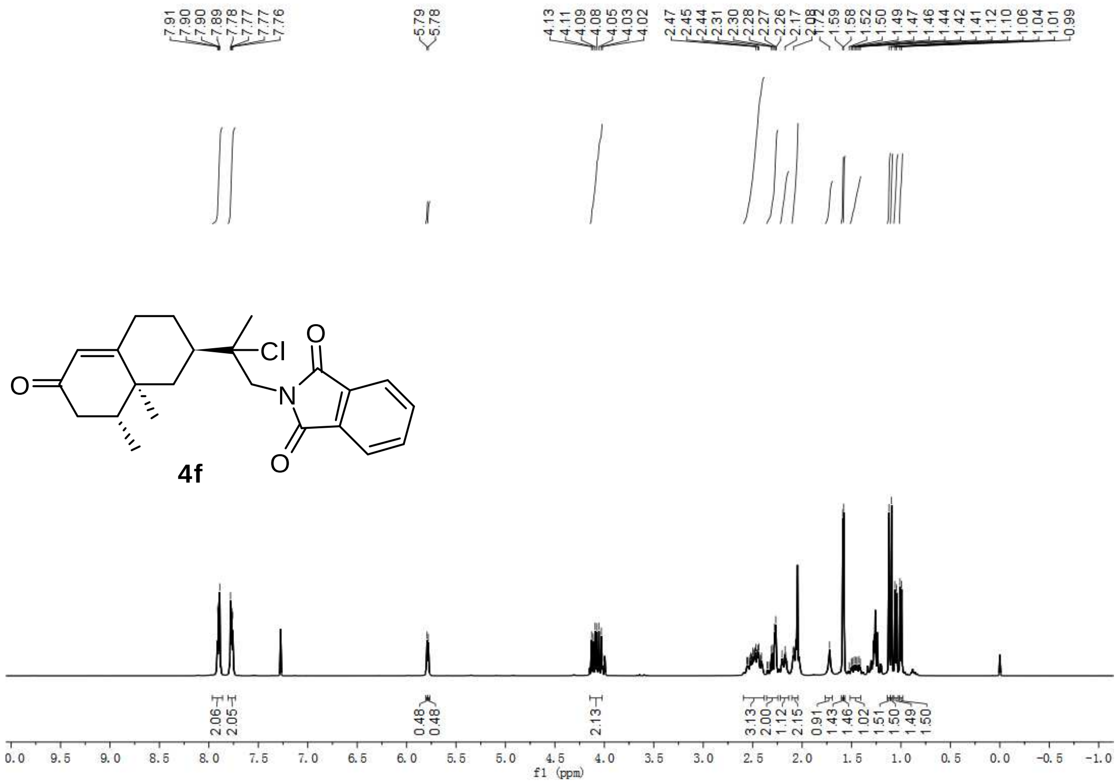
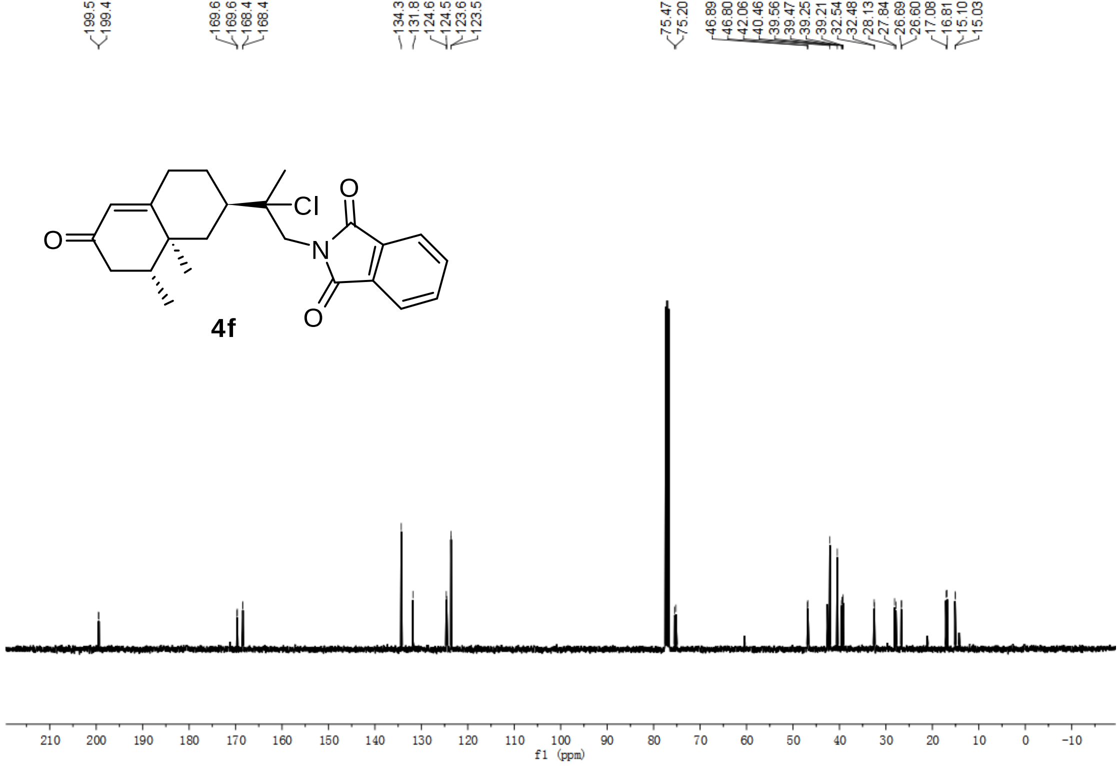
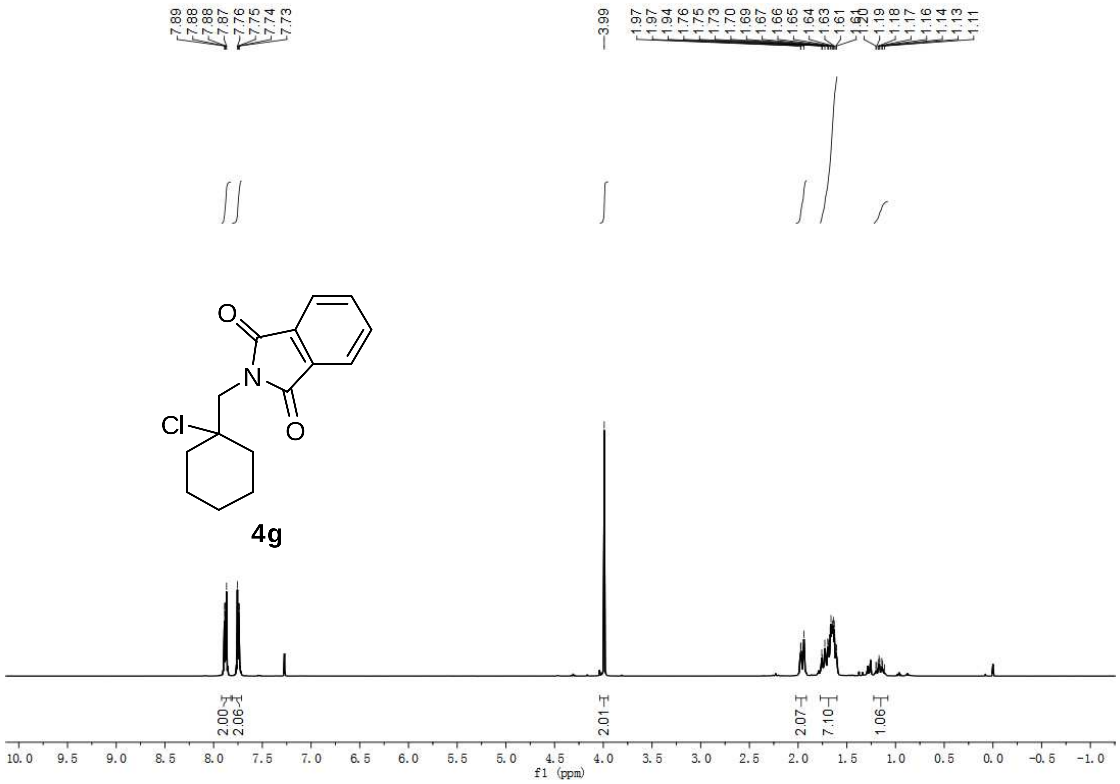
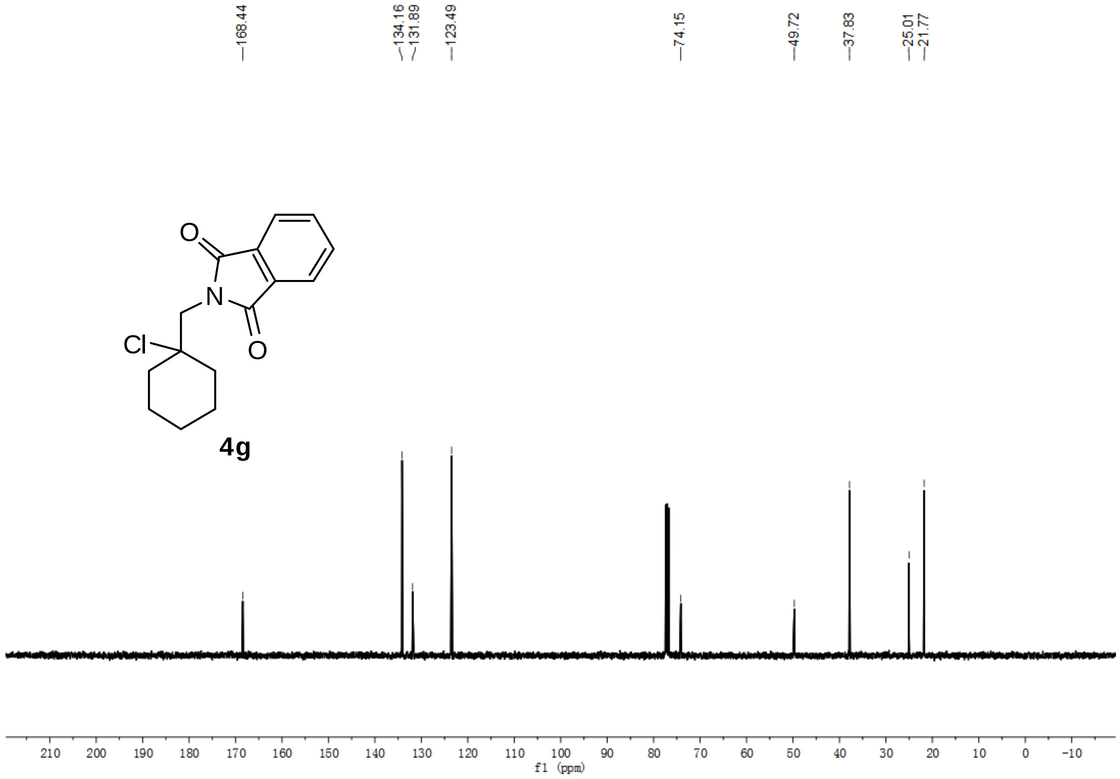
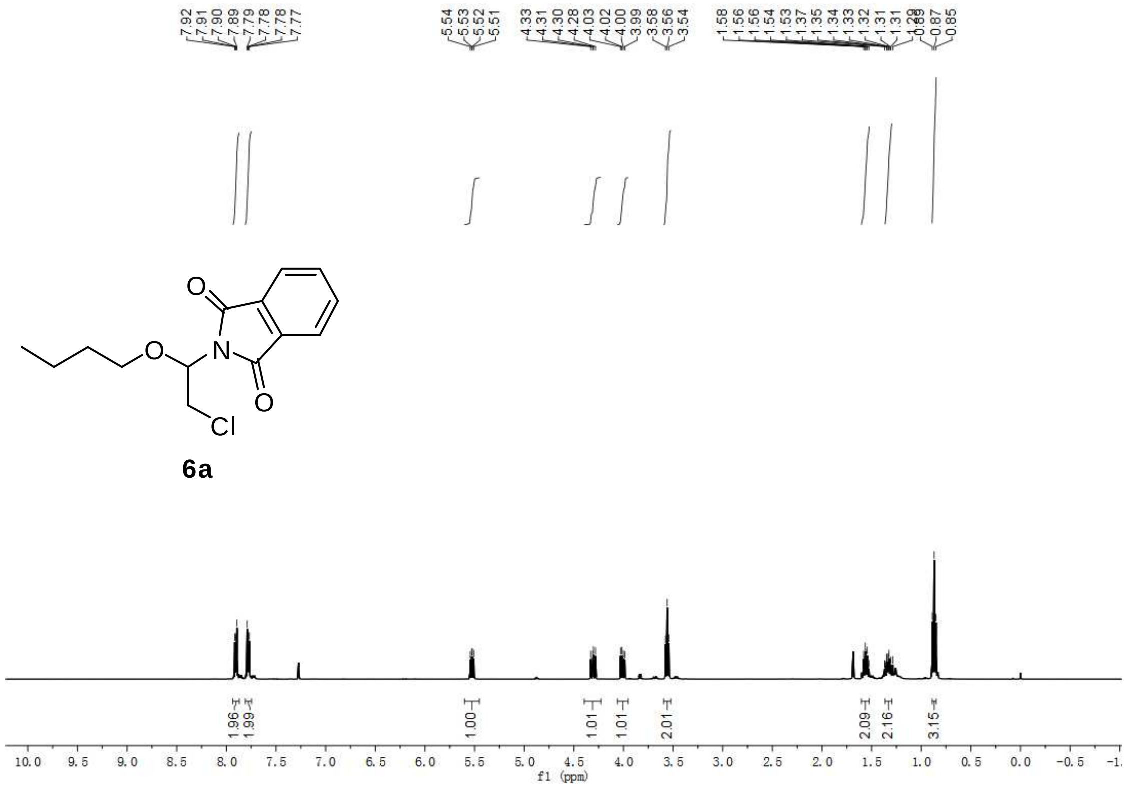
134.37
131.72
123.63
70.92
59.47
48.69
43.97
29.08
HO
Cl
N
O
O
4e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

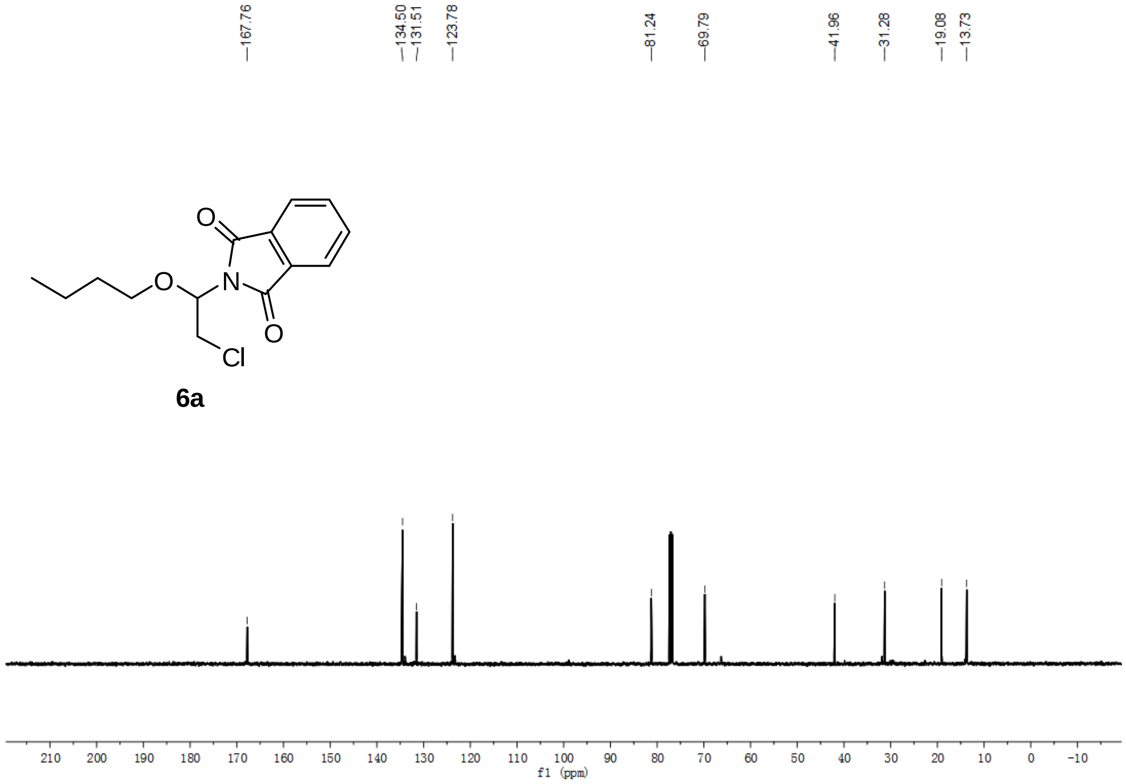

7.91
7.90
7.90
7.89
7.78
7.77
7.77
7.76
5.79
5.78
4.13
4.11
4.09
4.08
4.05
4.03
4.02
2.47
2.45
2.44
2.31
2.30
2.28
2.27
2.26
2.17
2.08
1.72
1.59
1.58
1.52
1.50
1.49
1.47
1.46
1.44
1.42
1.41
1.12
1.10
1.06
1.04
1.01
0.99
O
Cl
O
N
O
4f
2.06
2.05
0.48
0.48
2.13
3.13
2.00
1.12
2.15
0.91
1.43
1.46
1.02
1.51
1.50
1.49
1.50
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

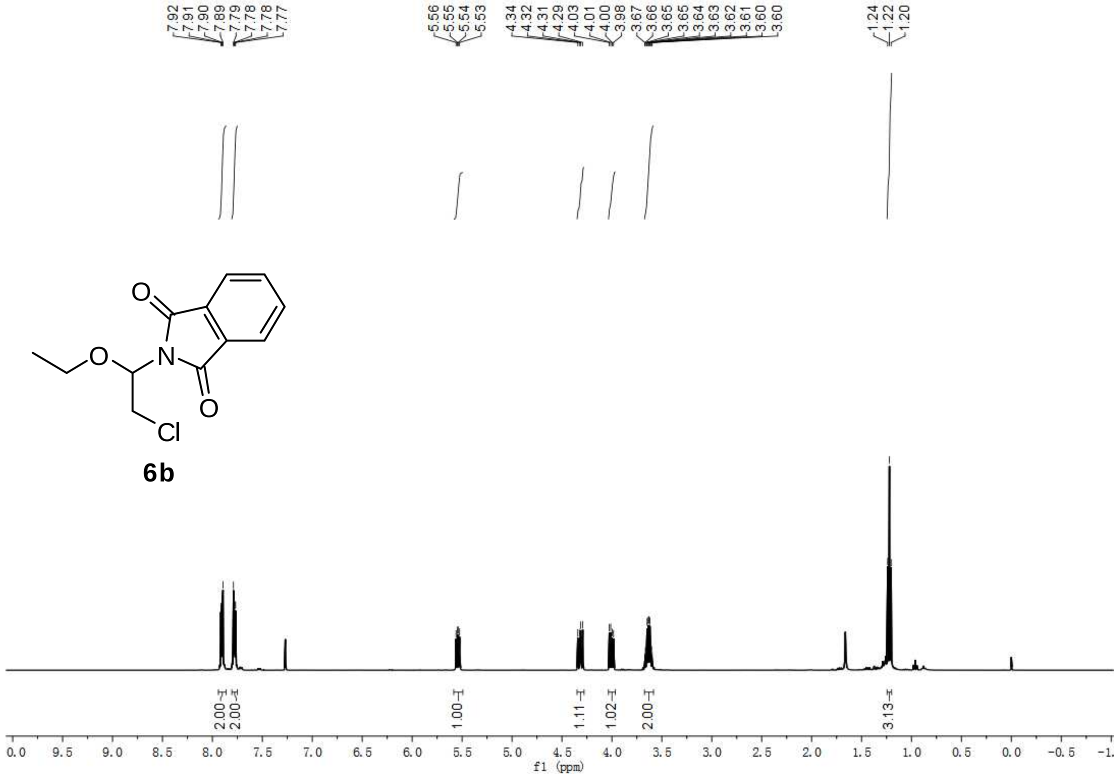

199.52
199.40
169.68
169.64
168.48
168.43
134.32
131.81
124.63
124.54
123.60
123.59
75.47
75.20
46.89
46.80
42.06
40.46
39.56
39.47
39.25
39.21
32.54
32.48
28.13
27.84
26.69
26.60
17.08
16.81
15.10
15.03
O
Cl
O
N
O
4f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

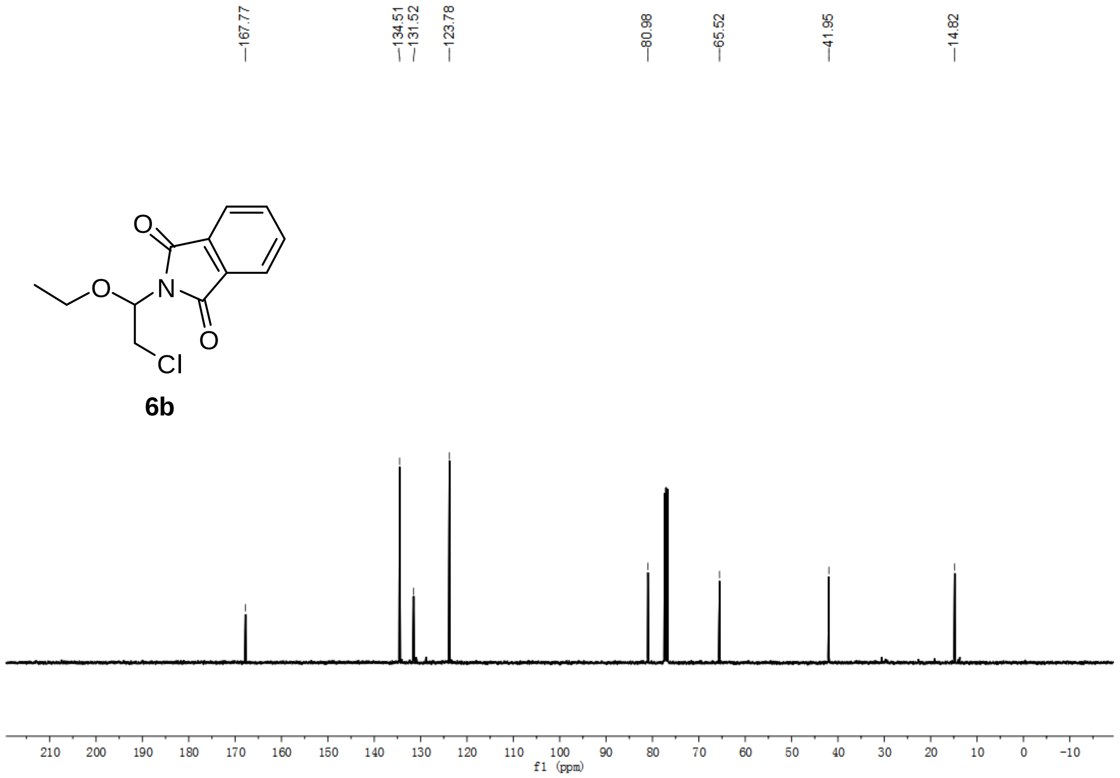

7.89
7.88
7.88
7.87
7.76
7.75
7.74
7.73
3.99
1.97
1.97
1.94
1.76
1.75
1.73
1.70
1.69
1.67
1.66
1.65
1.64
1.63
1.61
1.61
1.20
1.19
1.18
1.17
1.16
1.14
1.13
1.11
O
N
O
Cl
4g
2.00
2.06
2.01
2.07
7.10
1.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

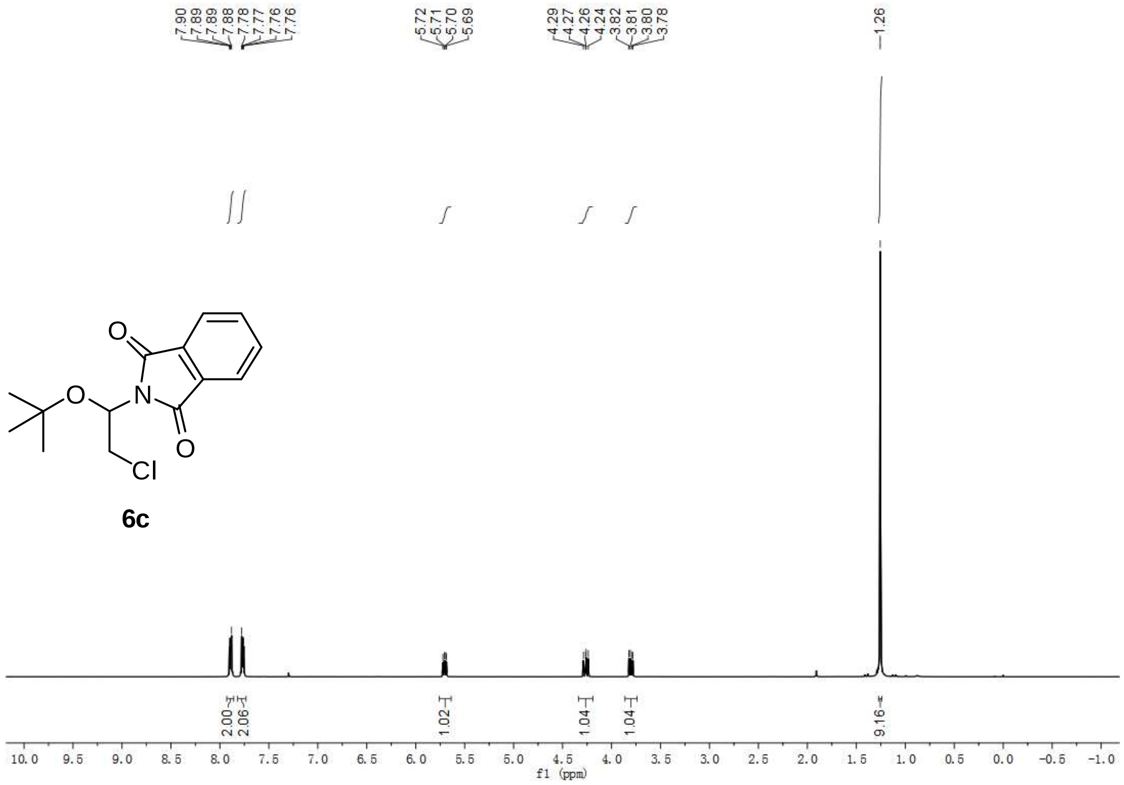

168.44
134.16
131.89
123.49
74.15
49.72
37.83
25.01
21.77
O
N
O
Cl
4g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.92
7.91
7.90
7.89
7.79
7.78
7.78
7.77
5.54
5.53
5.52
5.51
4.33
4.31
4.30
4.28
4.03
4.02
4.00
3.99
3.58
3.56
3.54
1.58
1.56
1.56
1.54
1.53
1.37
1.35
1.34
1.33
1.32
1.31
1.31
1.29
0.89
0.87
0.85
O
N
O
O
Cl
6a
1.96
1.99
1.00
1.01
1.01
2.01
2.09
2.16
3.15
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)


167.76
134.50
131.51
123.78
81.24
69.79
41.96
31.28
19.08
13.73
O
N
O
O
Cl
6a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

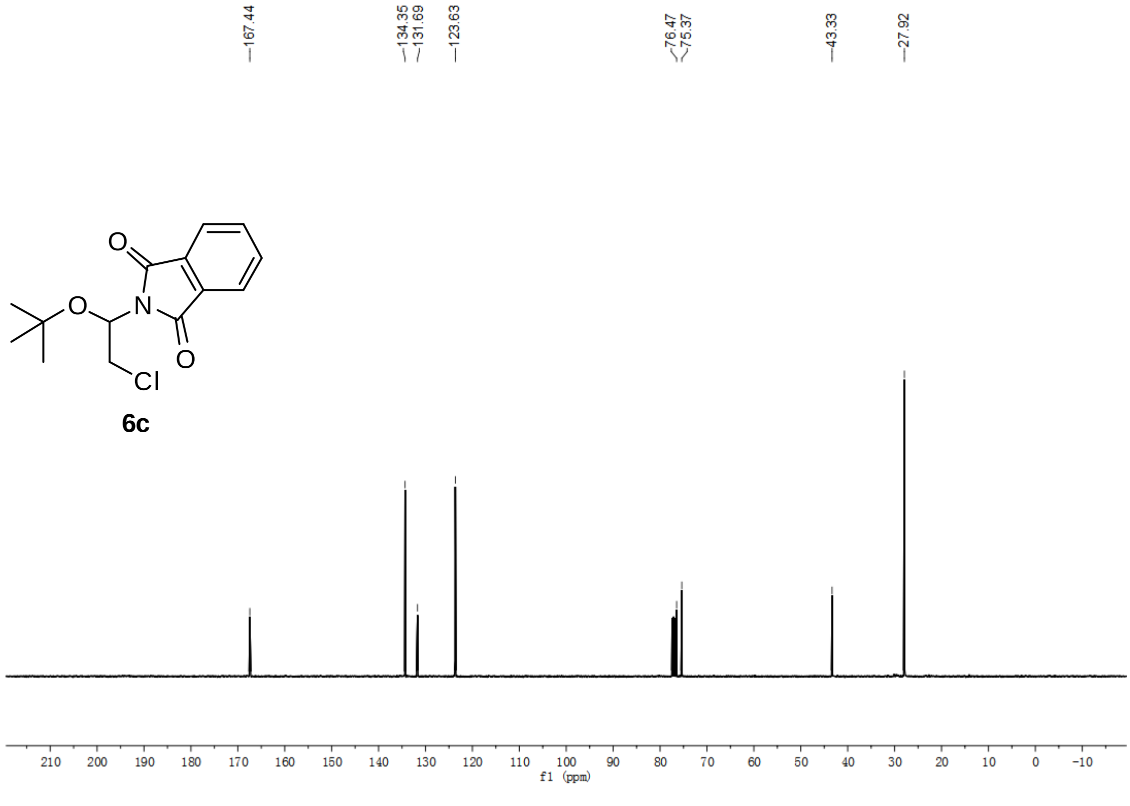

7.92
7.91
7.90
7.89
7.79
7.78
7.78
7.77
5.56
5.55
5.54
5.53
4.34
4.32
4.31
4.29
4.03
4.01
4.00
3.98
3.67
3.66
3.65
3.65
3.64
3.63
3.62
3.61
3.60
3.60
1.24
1.22
1.20
6b
2.00
2.00
1.00
1.11
1.02
2.00
3.13
f1 (ppm)


167.77
134.51
131.52
123.78
80.98
65.52
41.95
14.82
6b
f1 (ppm)



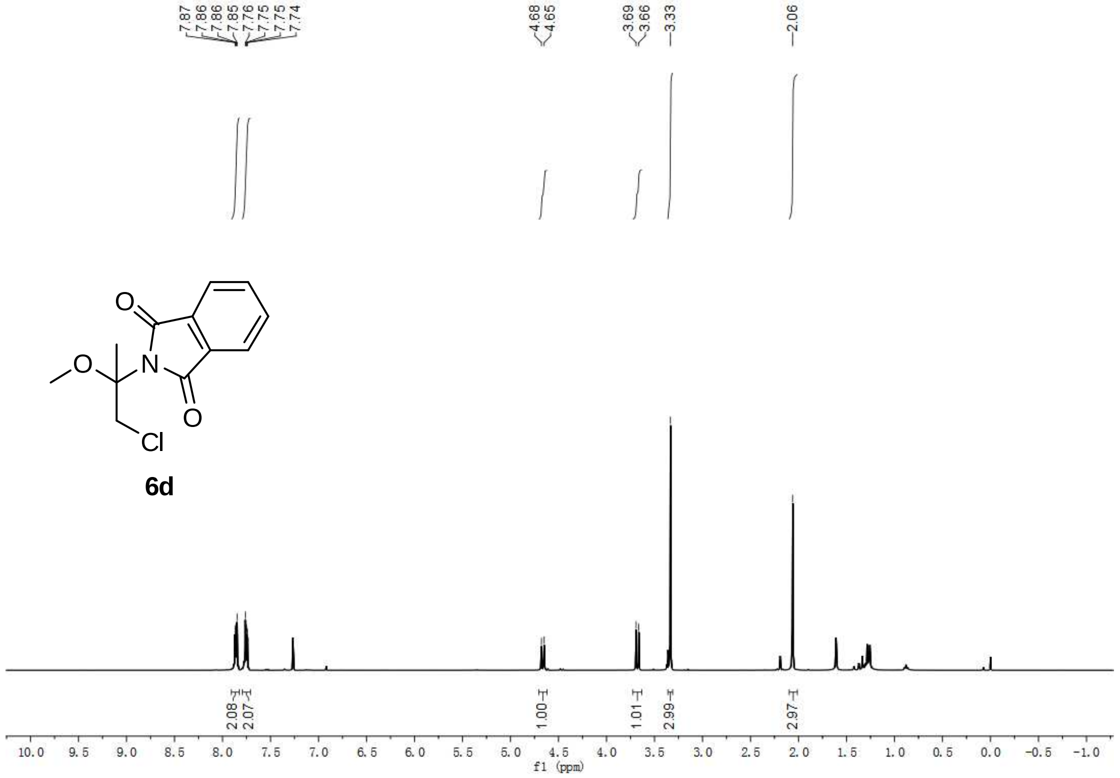
7.90
7.89
7.89
7.88
7.78
7.77
7.76
7.76
5.72
5.71
5.70
5.69
4.29
4.27
4.26
4.24
3.82
3.81
3.80
3.78
1.26
O
N
O
Cl
2.00
2.06
1.02
1.04
1.04
9.16
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
f1 (ppm)

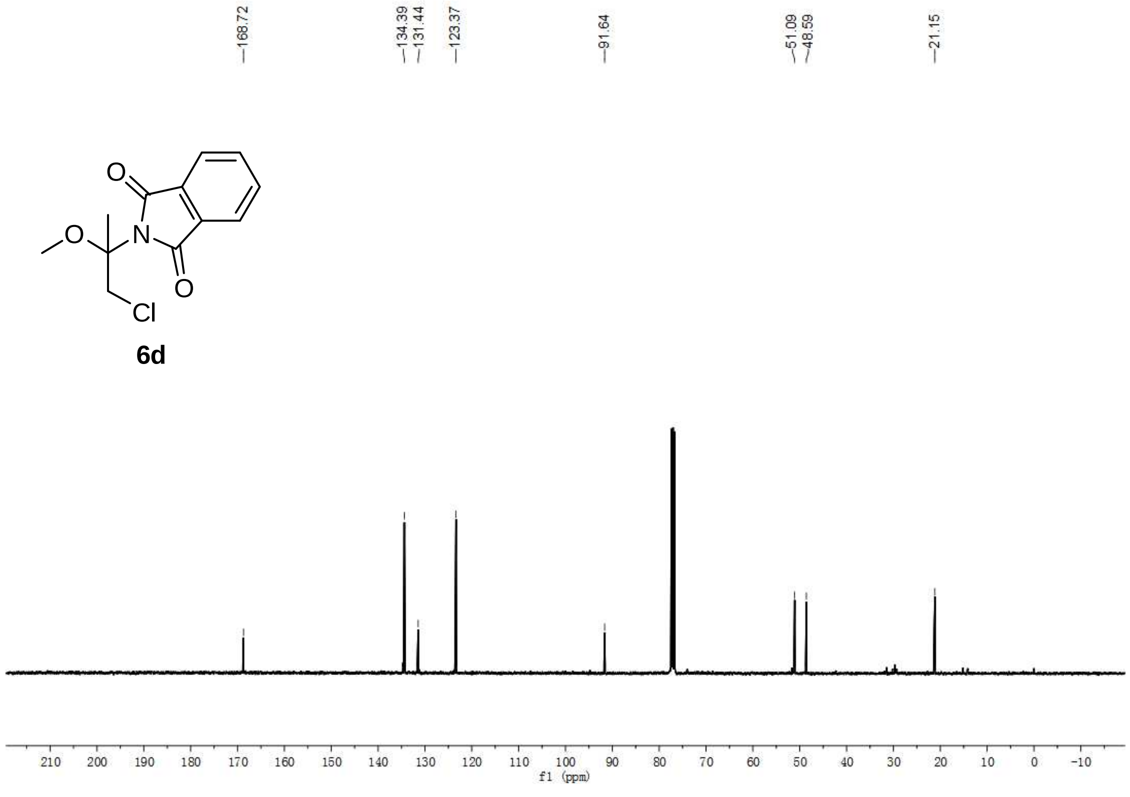
6c

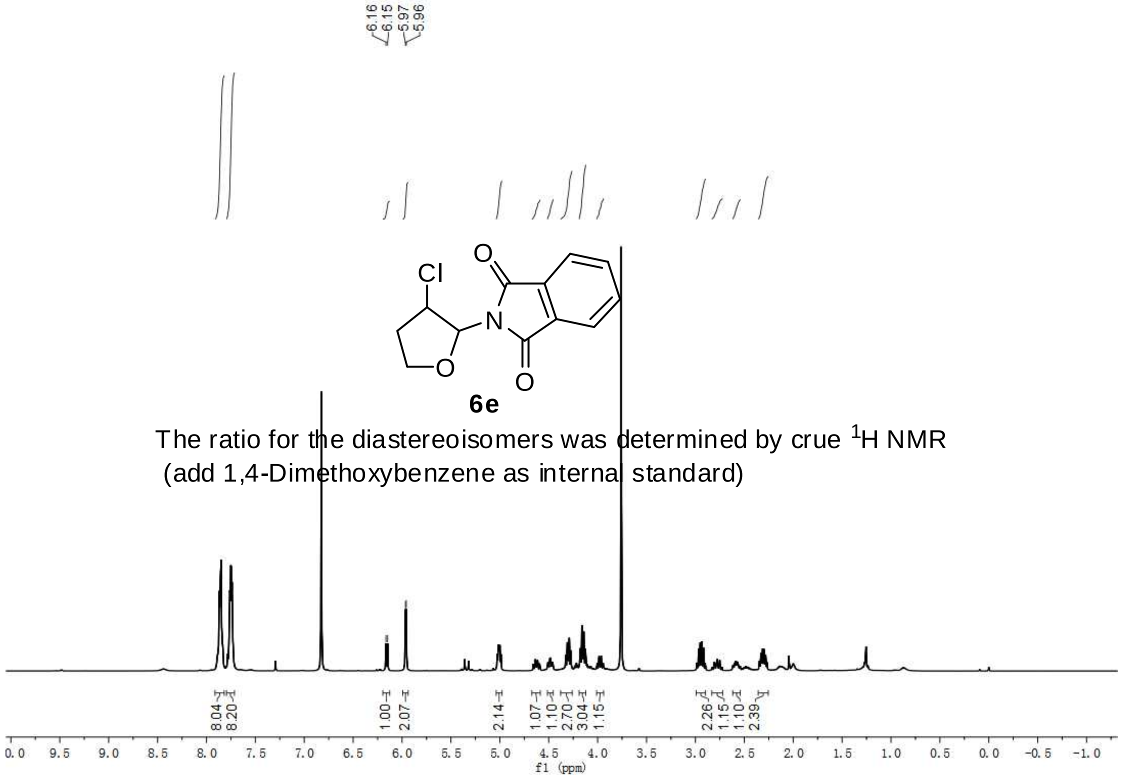


167.44
134.35
131.69
123.63
76.47
75.37
43.33
27.92
O
N
O
Cl
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

6c

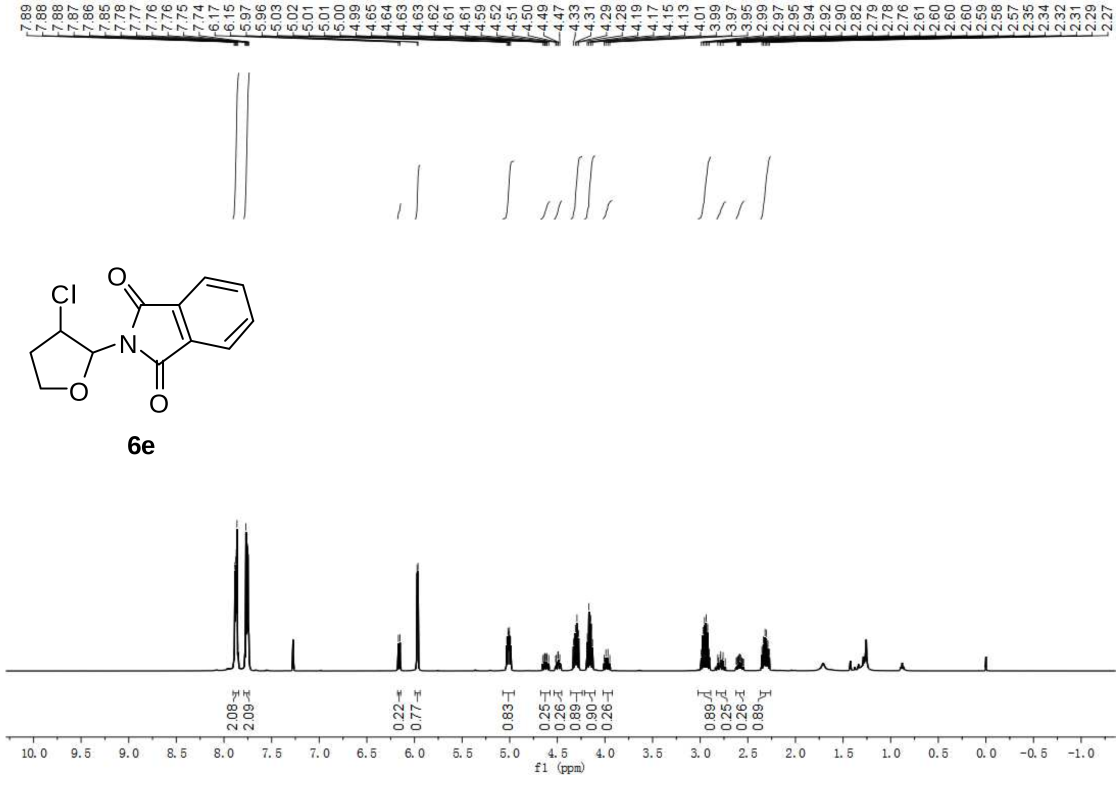

7.87
7.86
7.86
7.85
7.76
7.75
7.75
7.74
4.68
4.65
3.69
3.66
3.33
2.06
O
O
N
O
Cl
6d
2.08
2.07
1.00
1.01
2.99
2.97
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


168.72
134.39
131.44
123.37
91.64
51.09
48.59
21.15
O
O
N
O
Cl
6d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

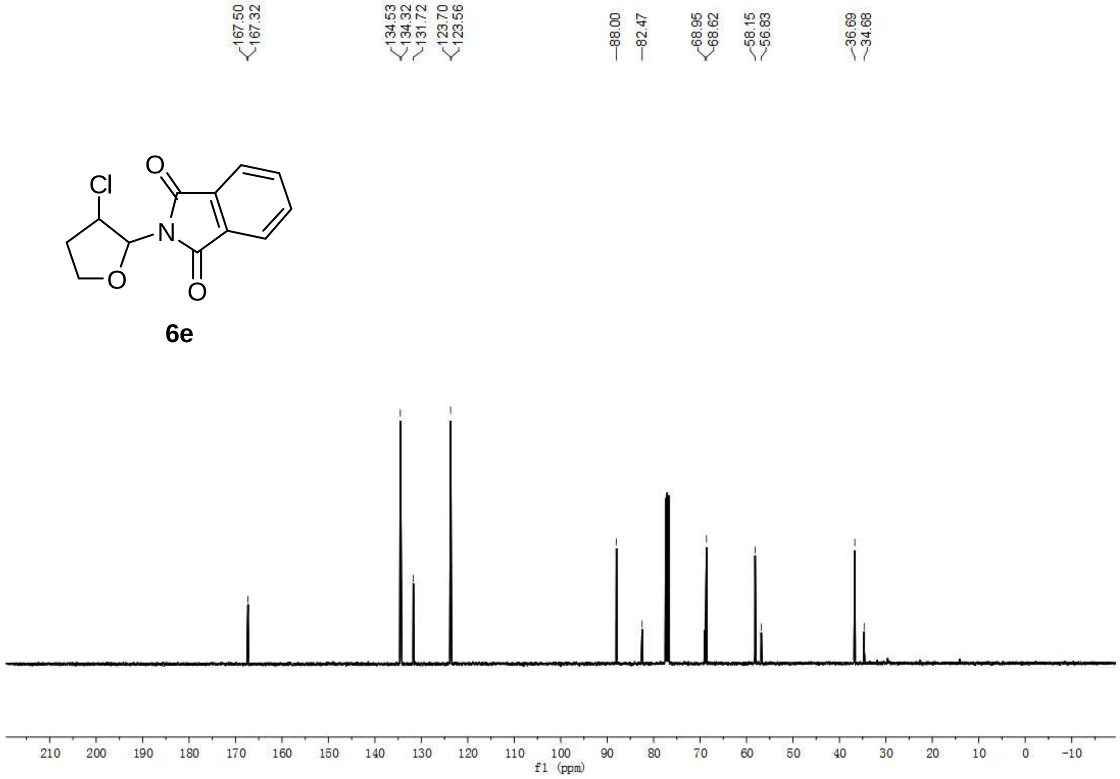


6e

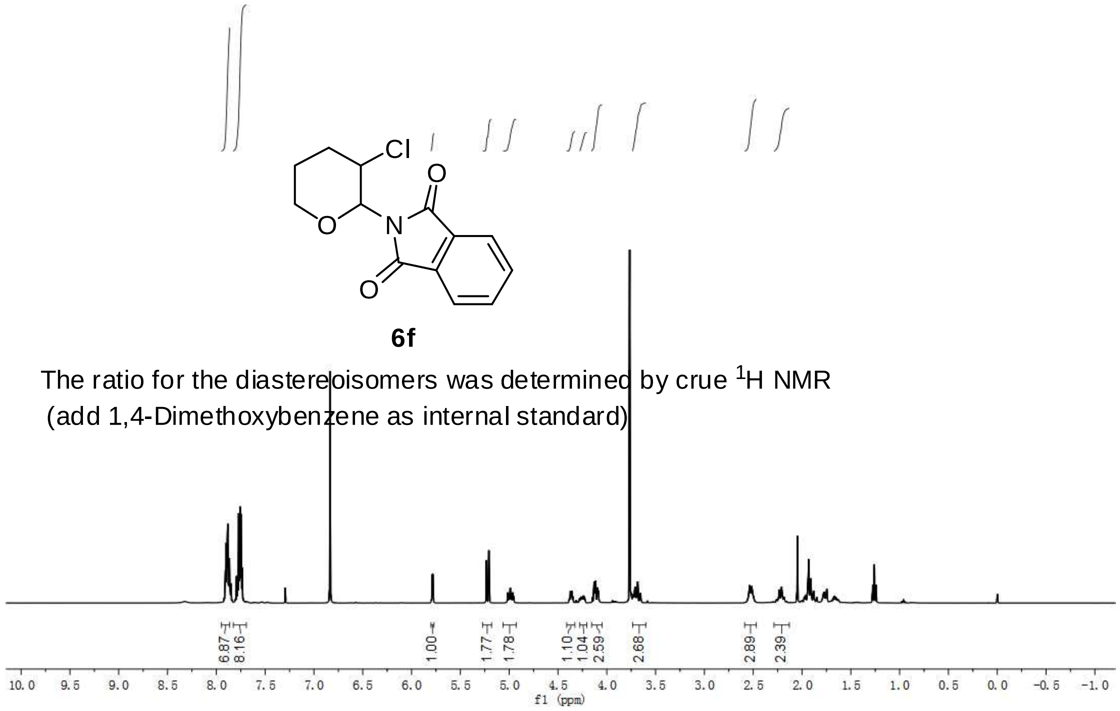
The ratio for the diastereoisomers was determined by crue ^{1}H NMR (add 1,4-Dimethoxybenzene as internal standard)



6e

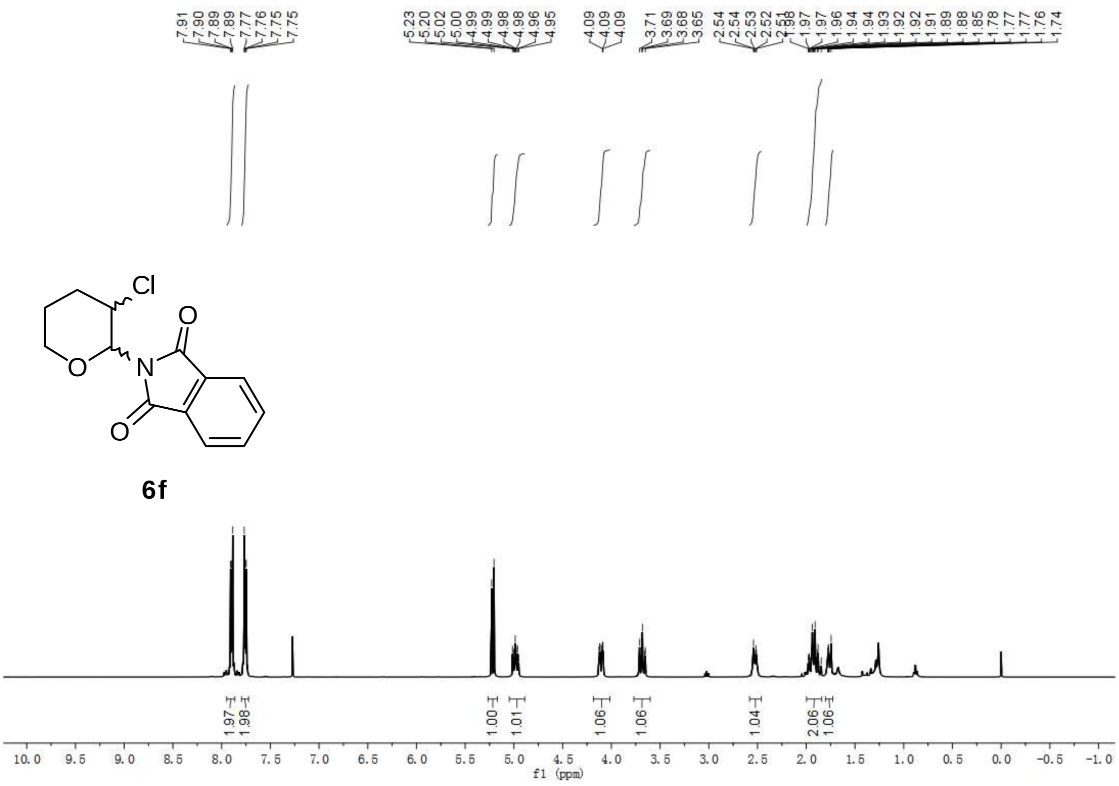


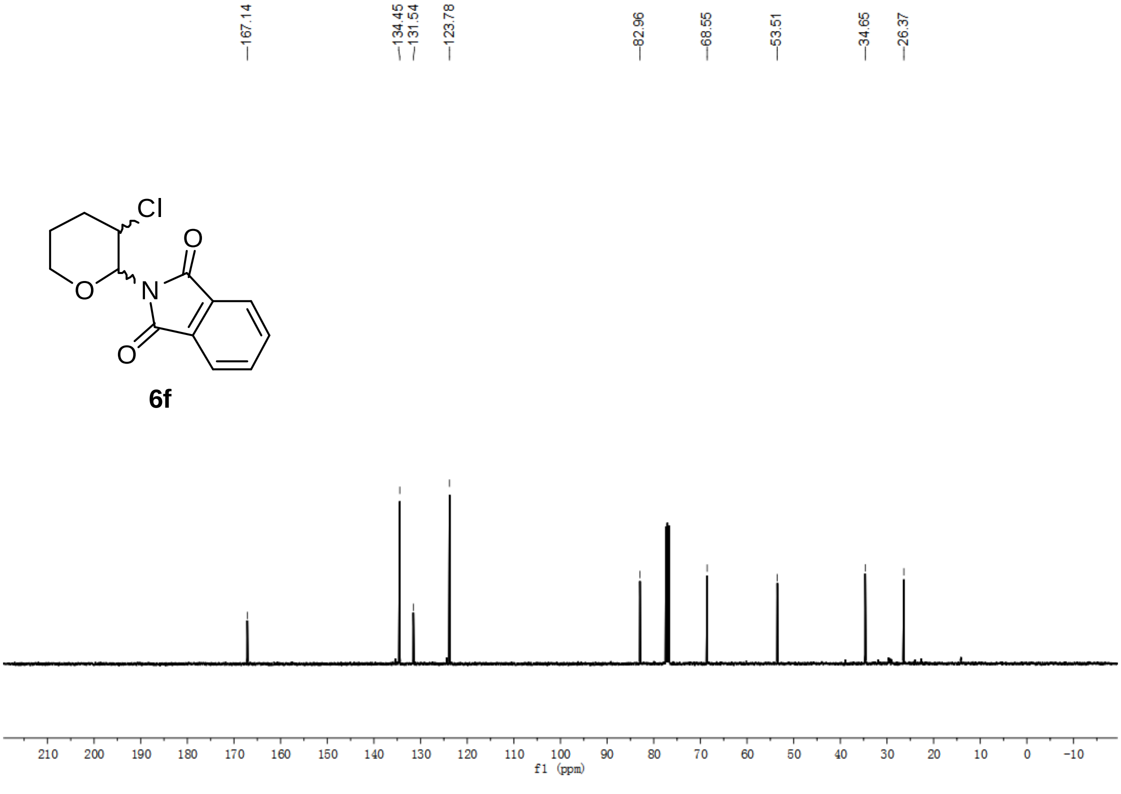
6e

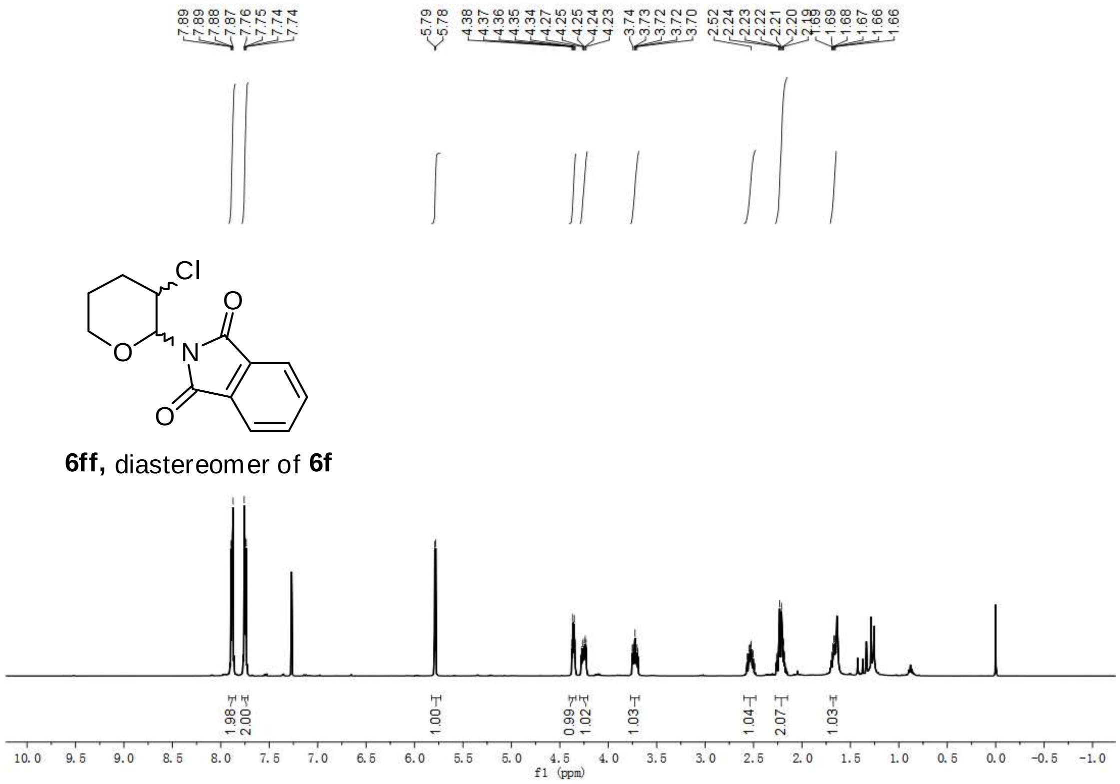


6f

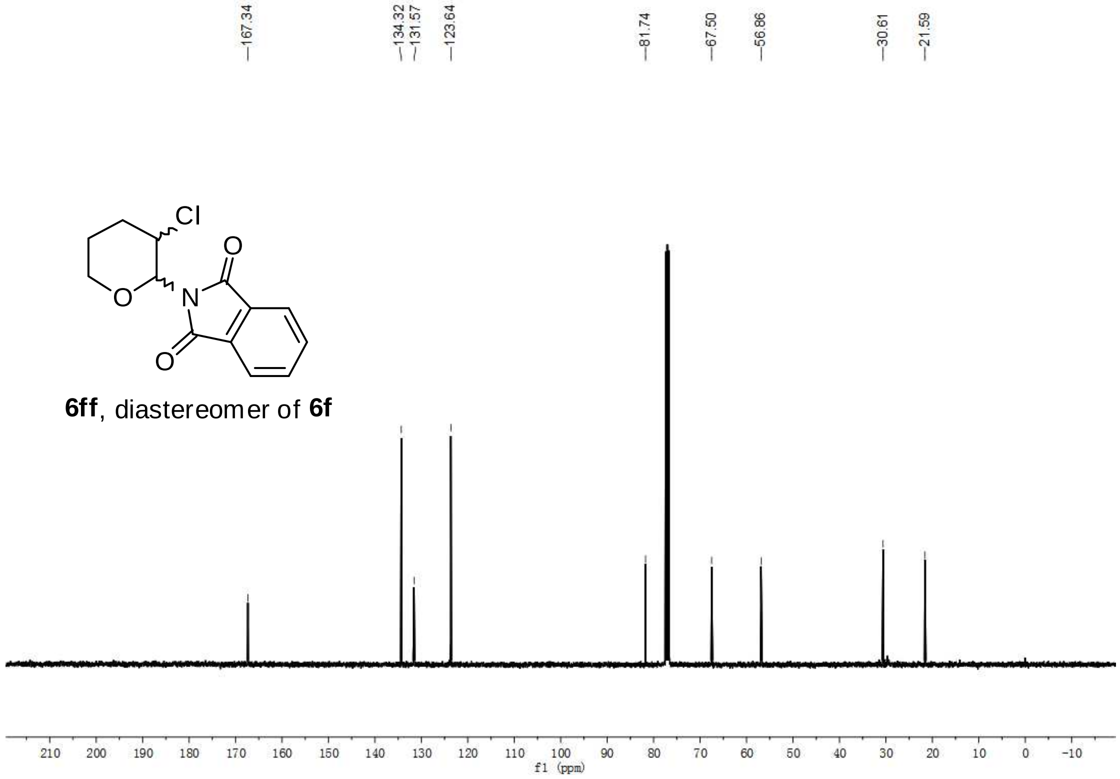
The ratio for the diastereoisomers was determined by crue ^{1}H NMR
(add 1,4-Dimethoxybenzene as internal standard)


7.91
7.90
7.89
7.89
7.77
7.76
7.75
7.75
5.23
5.20
5.02
5.00
4.99
4.99
4.98
4.98
4.96
4.95
4.09
4.09
4.09
3.71
3.69
3.68
3.65
2.54
2.54
2.53
2.52
2.51
1.98
1.97
1.97
1.96
1.94
1.94
1.93
1.92
1.92
1.91
1.89
1.88
1.85
1.78
1.77
1.76
1.74
Cl
O
N
O
O
6f
1.97
1.98
1.00
1.01
1.06
1.06
1.04
2.06
1.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

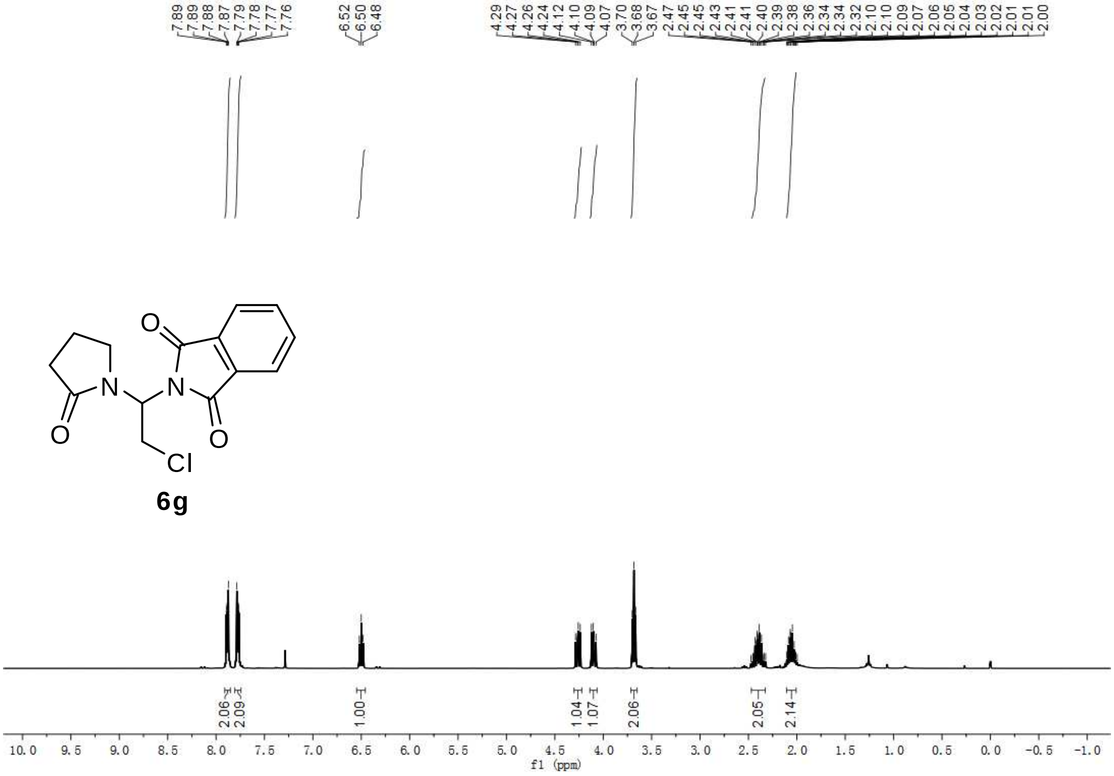

167.14
134.45
131.54
123.78
82.96
68.55
53.51
34.65
26.37
Cl
O
N
O
O
6f
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



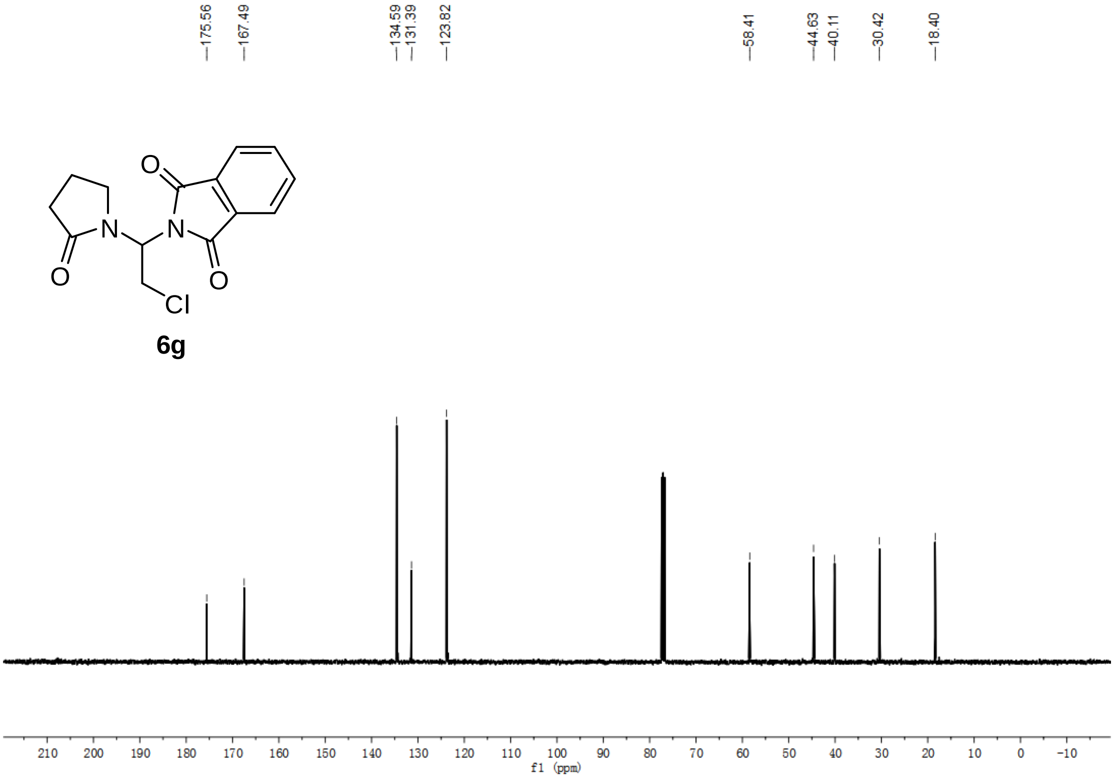
6ff, diastereomer of **6f**



6ff, diastereomer of **6f**

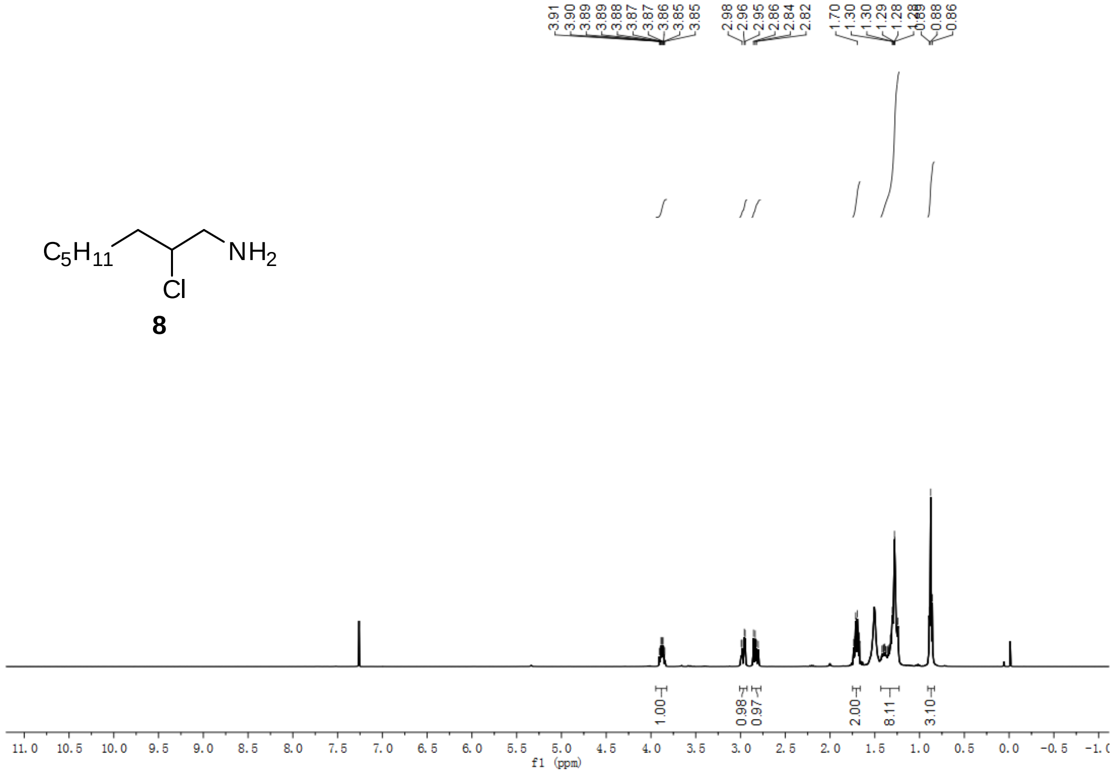

7.89
7.89
7.88
7.87
7.79
7.78
7.77
7.76
6.52
6.50
6.48
4.29
4.27
4.26
4.24
4.12
4.10
4.09
4.07
3.70
3.68
3.67
2.47
2.45
2.45
2.43
2.41
2.41
2.40
2.39
2.38
2.36
2.34
2.34
2.32
2.10
2.09
2.07
2.06
2.05
2.04
2.03
2.02
2.01
2.01
2.00
O
O
N
N
O
O
Cl
2.06
2.09
1.00
1.04
1.07
2.06
2.05
2.14
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

6g

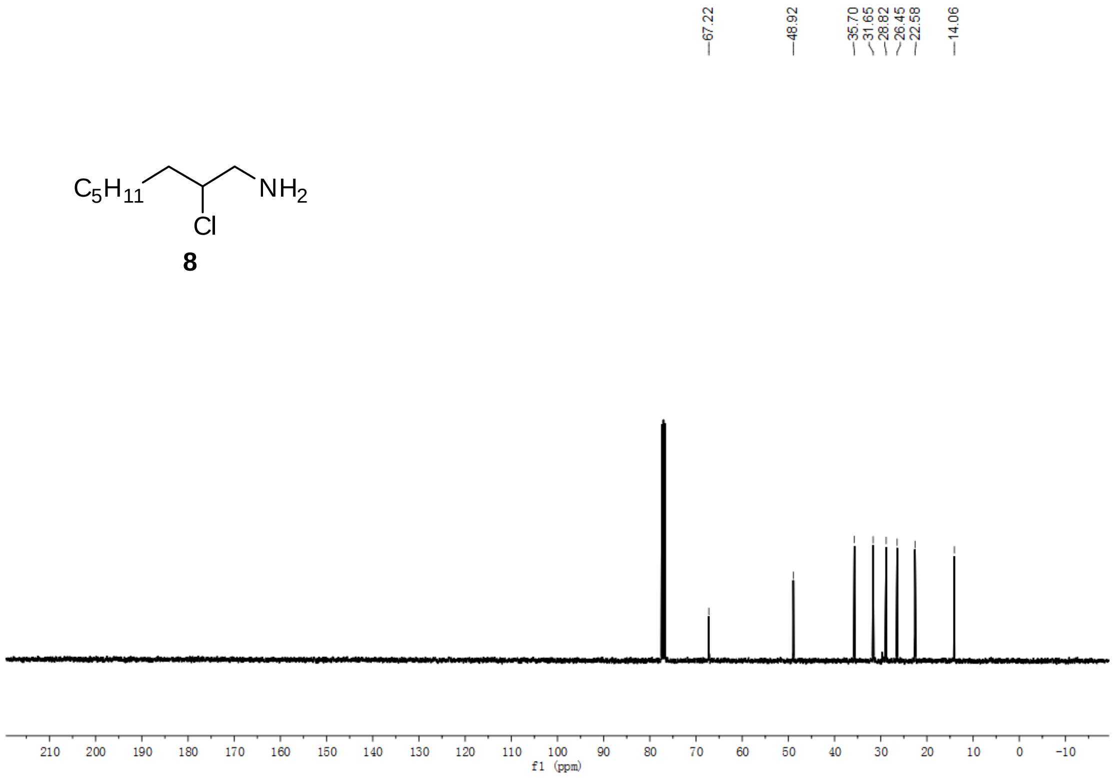

175.56
167.49
134.59
131.39
123.82
58.41
44.63
40.11
30.42
18.40
O
O
N
N
O
O
Cl
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

6g

8

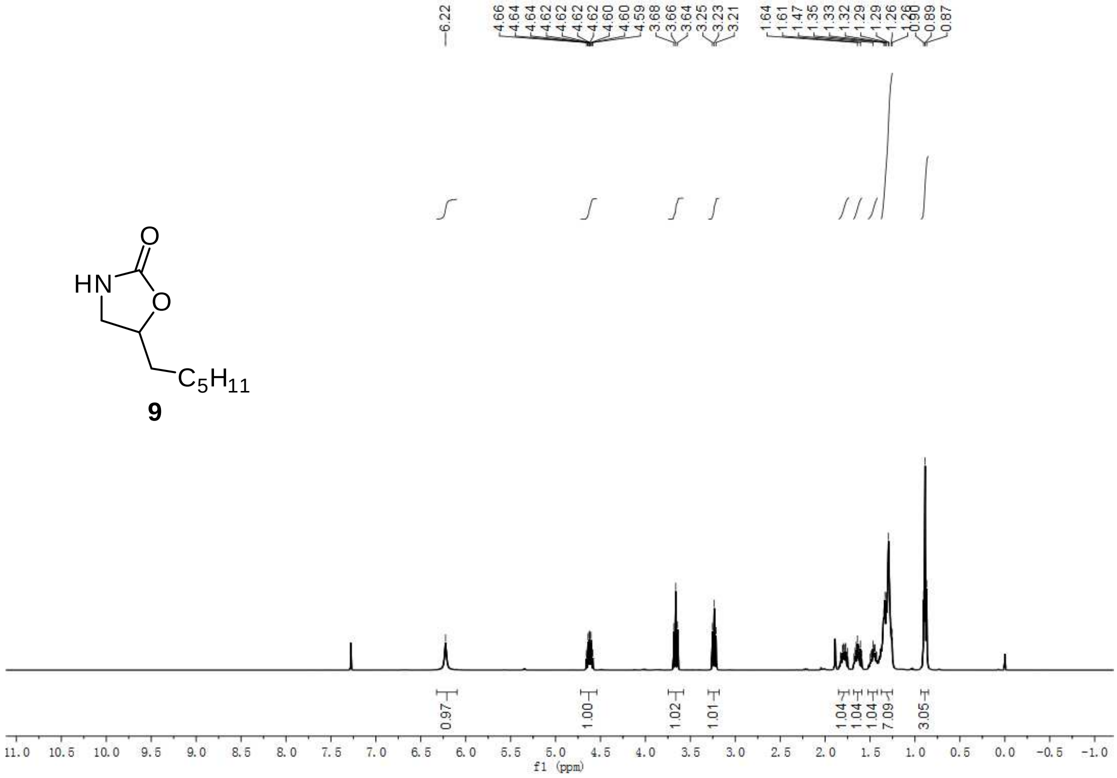

3.91
3.90
3.89
3.89
3.88
3.87
3.87
3.86
3.85
3.85
2.98
2.96
2.95
2.86
2.84
2.82
1.70
1.30
1.30
1.29
1.28
1.28
0.89
0.88
0.86
1.00
0.98
0.97
2.00
8.11
3.10
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)

8


67.22
48.92
35.70
31.65
28.82
26.45
22.58
14.06
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

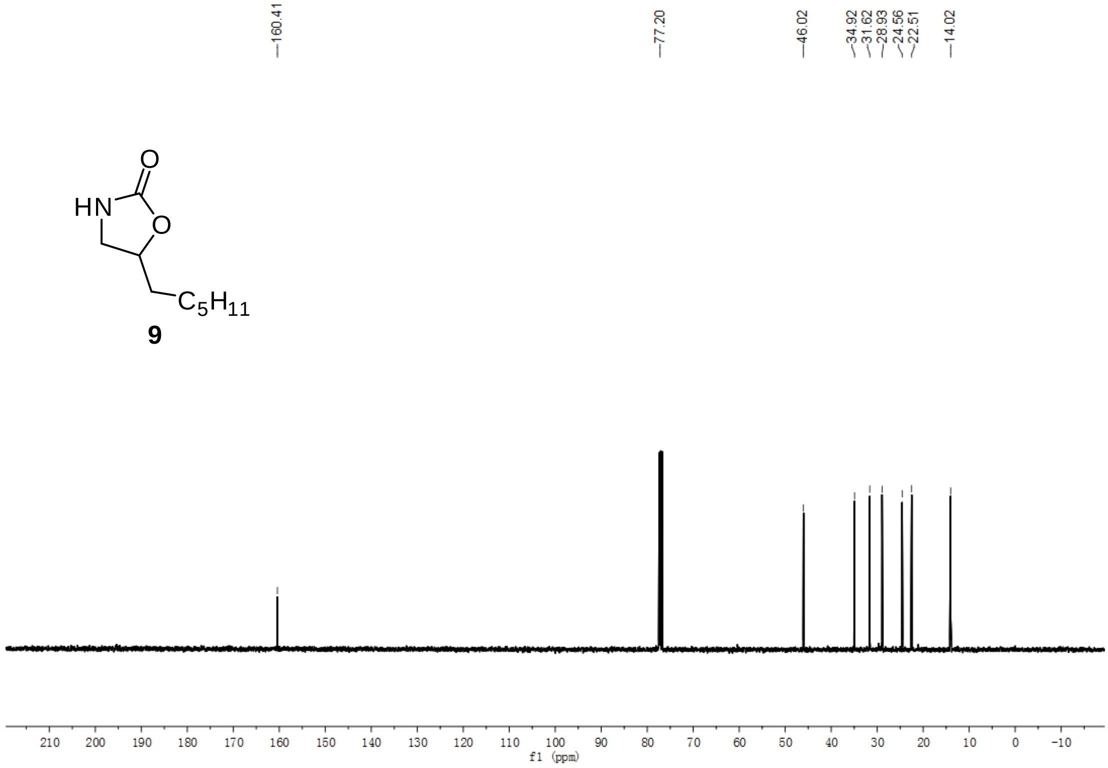
O
HN
O
C5H11

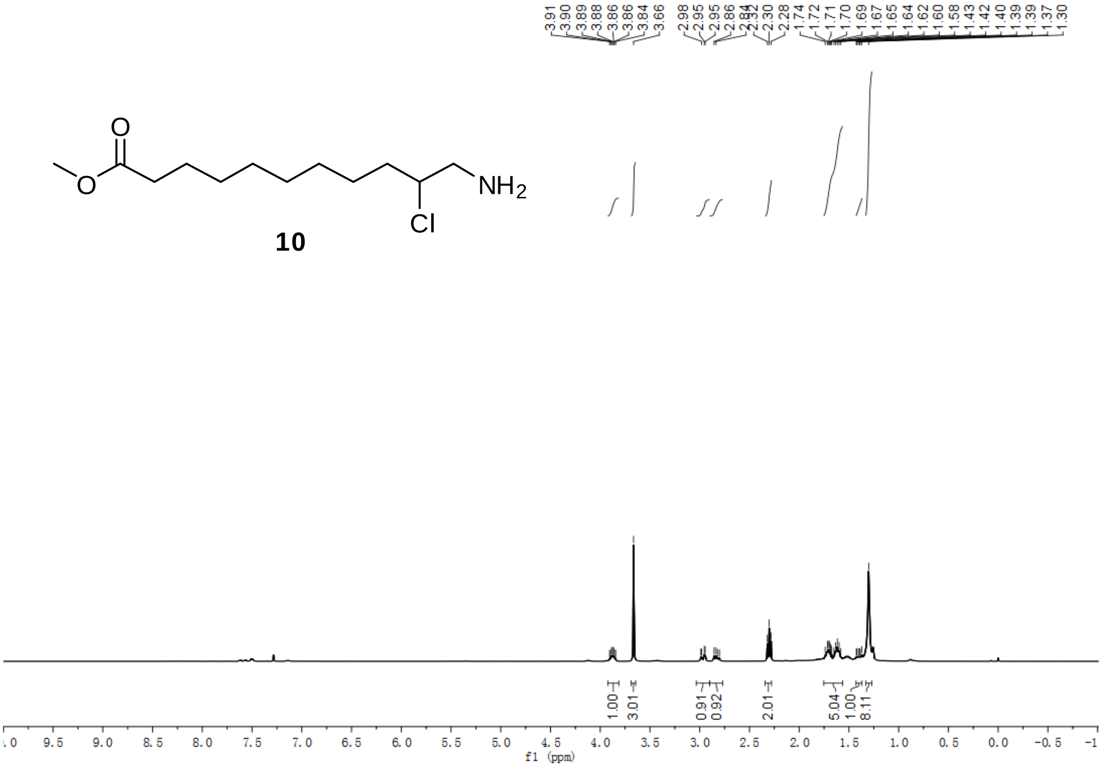
9


6.22
4.66
4.64
4.62
4.62
4.62
4.62
4.60
4.60
4.59
3.68
3.66
3.64
3.25
3.23
3.21
1.64
1.61
1.47
1.35
1.33
1.32
1.29
1.29
1.26
1.26
0.90
0.89
0.87
0.97
1.00
1.02
1.01
1.04
1.04
1.04
7.09
3.05
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

O
HN
O
C5H11

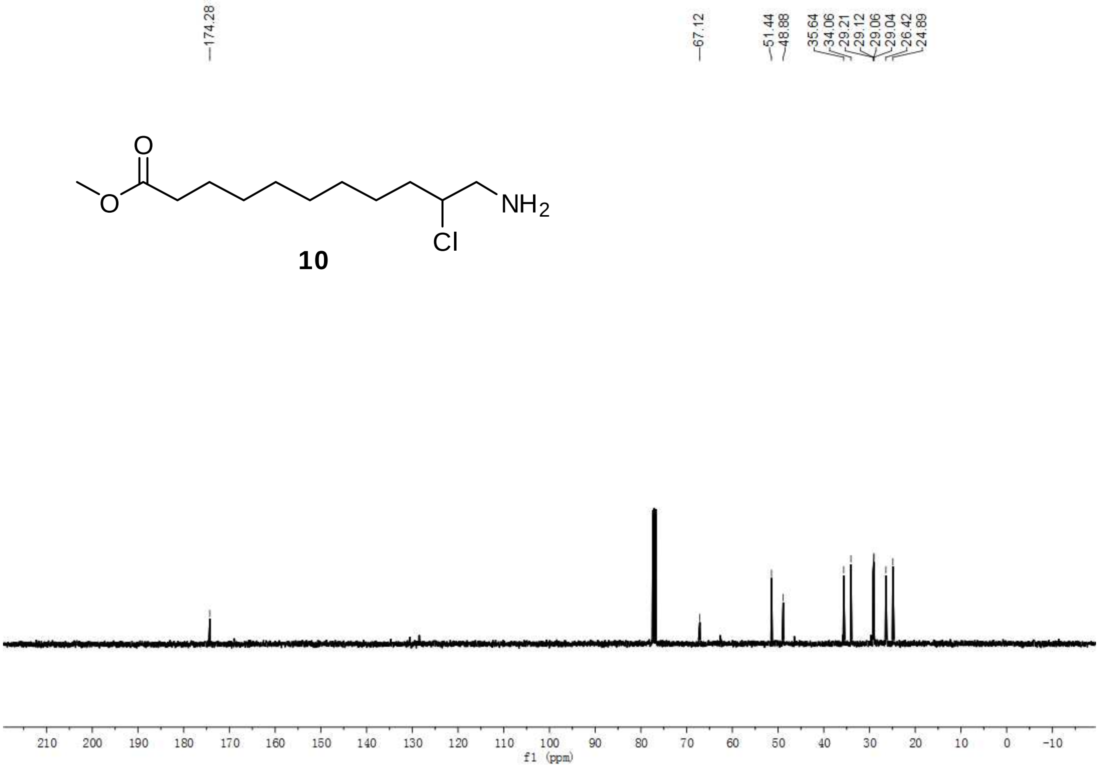
9


160.41
77.20
46.02
34.92
31.62
28.93
24.56
22.51
14.02
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


O
O
NH2
Cl

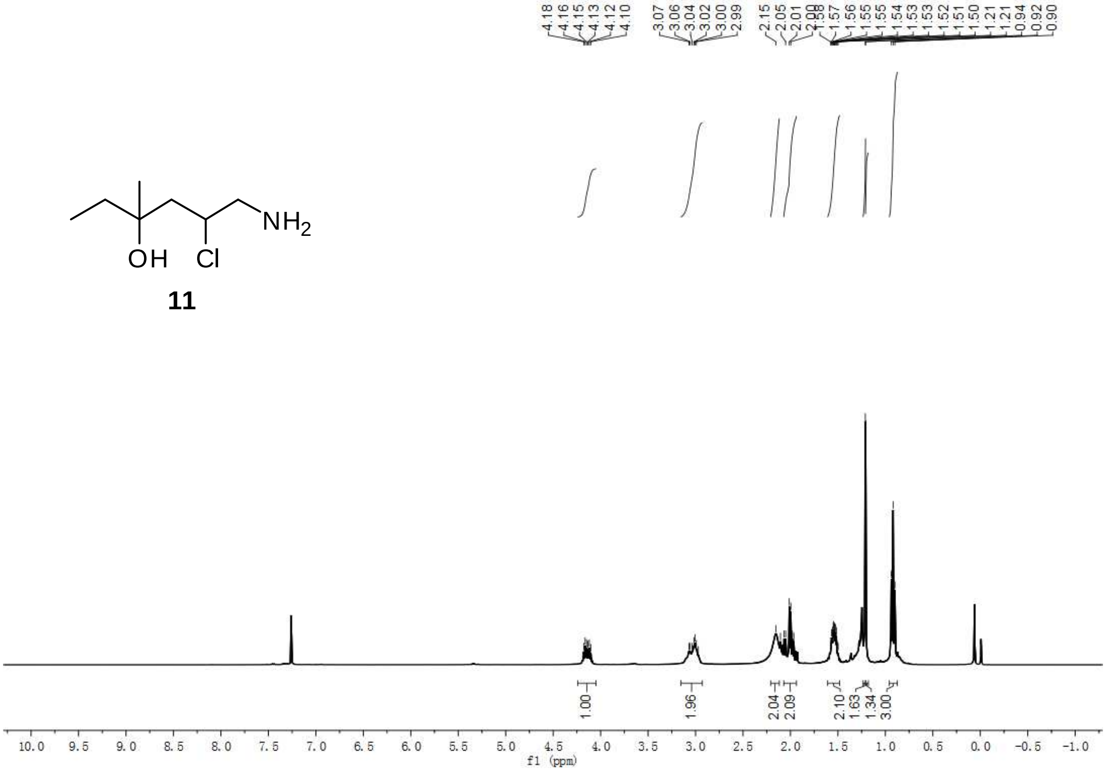
10

3.91
3.90
3.89
3.88
3.86
3.86
3.84
3.66
2.98
2.95
2.95
2.86
2.84
2.32
2.30
2.28
1.74
1.72
1.71
1.70
1.69
1.67
1.65
1.64
1.62
1.60
1.58
1.43
1.42
1.40
1.39
1.37
1.30
1.00
3.01
0.91
0.92
2.01
5.04
1.00
8.11
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

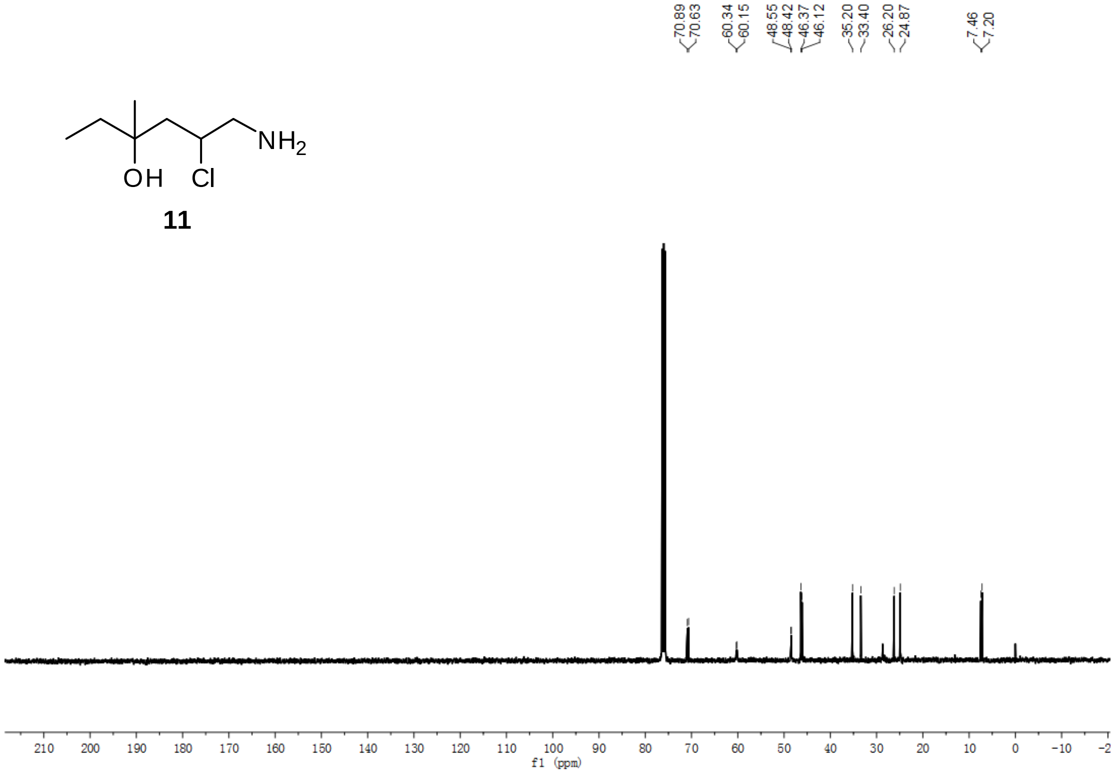

O
O
NH2
Cl

10

174.28
67.12
51.44
48.88
35.64
34.06
29.21
29.12
29.06
29.04
26.42
24.89
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



11
4.18
4.16
4.15
4.13
4.12
4.10
3.07
3.06
3.04
3.02
3.00
2.99
2.15
2.05
2.01
2.00
1.98
1.57
1.56
1.55
1.55
1.54
1.53
1.53
1.52
1.51
1.50
1.21
1.21
0.94
0.92
0.90
1.00
1.96
2.04
2.09
2.10
1.63
1.34
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)



11
70.89
70.63
60.34
60.15
48.55
48.42
46.37
46.12
35.20
33.40
26.20
24.87
7.46
7.20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-2
f1 (ppm)