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SUPPORTING INFORMATION

Active Electropositive α-Chlorine：Trichloroacetonitrile as an Electrophilic Chlorination Reagent

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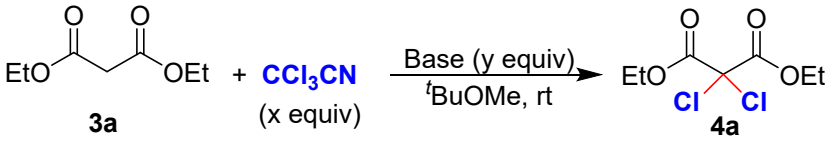
1. General information

Commercial grade reagents were used without further purification. Solvents were dried and distilled following usual protocols. Flash chromatography was carried out using 200-300 mesh silica gel. All experiments were monitored by analytical thin layer chromatography (TLC). ^{1}H and ^{13}C spectra were recorded on a Bruck Avance NEO-500 MHz spectrometer (500 MHz for ^{1}H NMR, 125 MHz for ^{13}C NMR). All chemical shifts were recorded in ppm relative to chloroform (δ = 7.26) for ^{1}H NMR and to chloroform (δ = 77.16) for the ^{13}C NMR measurements. High resolution mass spectra (HRMS) were obtained using Thermo Scientific Q Exactive instrument by the ESI (Quadrupole-Orbitrap) ionization sources. The substrates **1m-1n**, **1q**, **1r**, **1t**, **3a-3f**, **3h-3j** and **3l-3o** were commercially available. The substrates **1a-1b**,[1] **1c**,[2] **1d**,[3] **1e**,[4] **1f**,[5] **1g**,[6] **1h**,[7] **1i**,[8] **1j-1l**,[9] **1o**,[10] **1p**,[11] **1s**,[12] **3g**,[4] **3k**[13] and **3p**[5] were synthesized according to the literatures and the NMR data are identical to those previously reported. Compounds **2a-2b**,[14] **2c**,[15] **2d**,[14] **2i**,[16] **2j**,[17] **2k**,[18] **2l**,[19] **2m-2n**,[20] **2o**,[21] **2p**,[22] **2q**,[23] **2r**,[24] **2s**,[25] **4a-4b**,[24] **4c**,[26] **4d**,[27] **4e**,[23] **4f**,[28] **4h-4i**,[24] **4j**,[17] **4l**,[20] **4m**,[29] **4n**,[30] **5a**,[31] **5b**,[32] **7**,[17] **8**[33] and **10**[34] are known and the NMR data are identical to those previously reported. Compounds **2e-2h**, **4f** and **4k** are unknown and their analysis data are as follows.

2. Optimization of dichlorination

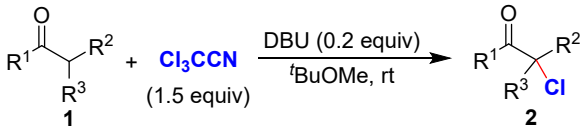
Table S1. Optimization of dichlorination.[a]



Entry	x	Base (y equiv)	Time (h)	Yield (%)
1	1	DBU (0.2)	4.5	mess
2	1	K_2CO_3 (2)	5	46
3	1.5	K_2CO_3 (2)	5	65
4	**2**	**K_2CO_3 (2)**	**1.5**	**76**
5	3	K_2CO_3 (2)	0.5	74

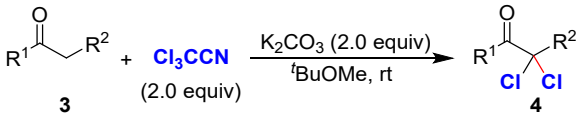
[a]Reaction conditions: **3a** (0.2 mmol), Cl_3CCN (x equiv), base (y equiv), ^{t}BuOMe (1.0 mL), rt.

3. General procedure for monochlorination of 1



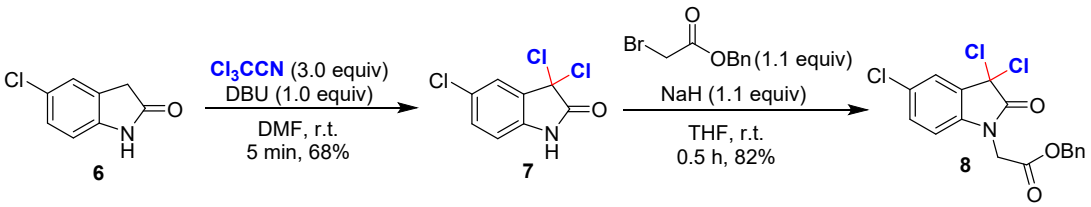
DBU (0.04 mmol) and Cl_3CCN (0.3 mmol) were added into a solution of **1** (0.2 mmol) in ^{t}BuOMe (1 mL), then the mixture was allowed to stir at room temperature and until the complete disappearance of **1** indicated by TLC. To the mixture was added water (1.0 mL) and extracted with EtOAc (3×2.0 mL). The organic layer was washed with brine (3×6.0 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by silica gel flash column chromatography to obtain the desired product **2**.

4. General procedure for dichlorination of 3



K_2CO_3 (0. 4 mmol) and Cl_3CCN (0.4 mmol) were added into a solution of **3** (0.2 mmol) in ^{t}BuOMe (1 mL), then the mixture was allowed to stir at room temperature and until the complete disappearance of **3** indicated by TLC. To the mixture was added water (1.0 mL) and extracted with EtOAc (3×2.0 mL). The organic layer was washed with brine (3×6.0 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by silica gel flash column chromatography to obtain the desired product **4**.

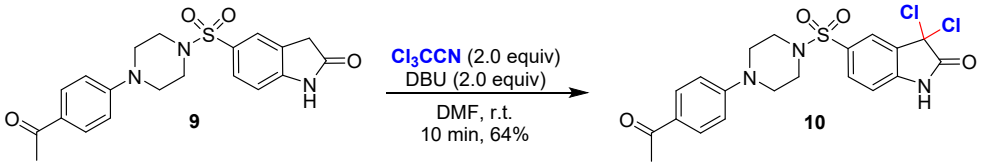
5. Synthesis of 8



Step 1: DBU (0.25 mmol) and Cl_3CCN (0.75 mmol) were added into a solution of **6** (0.25 mmol) in DMF (1.5 mL), then the mixture was allowed to stir at room temperature and until the complete disappearance of **6** indicated by TLC. To the mixture was added distilled water (1.5 mL) and extracted with CH_2Cl_2 (3×3.0 mL). The organic layer was washed with water (3×9.0 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (EtOAc/PE = 1/12) to obtain the desired product **7** with 68% yield.

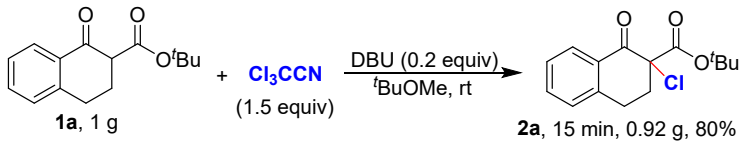
Step 2: To a solution of **7** (0.28 mmol) in anhydrous THF (2.5 mL) was added NaH (0.31 mmol, 60% in mineral oil) at 0 °C under argon. The resulting brown suspension was stirred at 0 °C for 15 min and benzyl bromoacetate (0.31 mmol) was added. The reaction mixture was stirred at room temperature for 0.5 h, then water (2.5 mL) and EtOAc (5.0 mL) were added. The phases were separated, and the aqueous phase was extracted three times with EtOAc. The combined organic layer was washed with brine (15.0 mL), dried over $MgSO_4$, filtrated off and evaporated in vacuo. The residue was purified by silica gel flash column chromatography (EtOAc/PE = 1/15) to obtain the desired product **8** with 82% yield.

6. Synthesis of 10



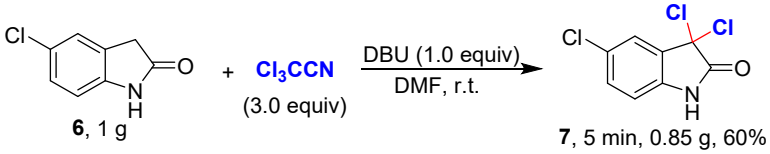
DBU (0.2 mmol) and Cl_3CCN (0.2 mmol) were added into a solution of **9** (0.1 mmol) in DMF (1 mL), then the mixture was allowed to stir at room temperature and until the complete disappearance of **9** indicated by TLC. To the mixture was added water (1.0 mL) and extracted with CH_2Cl_2 (3×2.0 mL). The organic layer was washed with water (6×3.0 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (MeOH/CH_2Cl_2 = 1/90) to obtain the desired product **10** with 64% yield.

7. Gram-Scale Synthesis of 2a



DBU (0.8 mmol) and Cl_3CCN (6.2 mmol) were added into a solution of **1a** (4.1 mmol) in ^{t}BuOMe (10 mL), then the mixture was allowed to stir at room temperature and until the complete disappearance of **1a** indicated by TLC. To the mixture was added water (10 mL) and extracted with EtOAc (3×20 mL). The organic layer was washed with brine (3×60 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (EtOAc/PE = 1/10) to obtain the desired product **2a** with 80% yield.

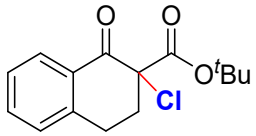
8. Gram-Scale Synthesis of 7



DBU (6 mmol) and Cl_3CCN (18 mmol) were added into a solution of **6** (6.0 mmol) in DMF (15 mL), then the mixture was allowed to stir at room temperature and until the complete disappearance of **6** indicated by TLC. To the mixture was added distilled water (15 mL) and extracted with CH_2Cl_2 (3×30 mL). The organic layer was washed with water (3×90 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (EtOAc/PE = 1/12) to obtain the desired product **7** with 60% yield.

9. Spectral Data

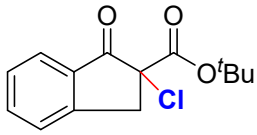
tert-butyl 2-chloro-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate



2a

Colorless oil liquid; 86% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.53 (td, *J* = 7.4, 1.5 Hz, 1H), 7.37 – 7.34 (m, 1H), 7.27 – 7.26 (m, 1H), 3.28 – 3.22 (m, 1H), 3.05 – 2.92 (m, 2H), 2.54 – 2.49 (m, 1H), 1.46 (s, 9H). The NMR data is identical to that previously reported.[14]

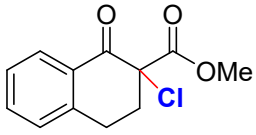
tert-butyl 2-chloro-1-oxo-2,3-dihydro-1H-indene-2-carboxylate



2b

Colorless oil liquid; 85% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.6 Hz, 1H), 7.69 (td, *J* = 7.5, 1.4 Hz, 1H), 7.49 – 7.44 (m, 2H), 4.02 (d, *J* = 17.6 Hz, 1H), 3.54 (d, *J* = 17.7 Hz, 1H), 1.43 (s, 9H). The NMR data is identical to that previously reported.[14]

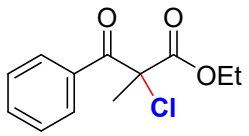
methyl 2-chloro-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate



2c

Colorless oil liquid; 96% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.55 (td, *J* = 7.4, 1.5 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 7.4 Hz, 1H), 3.85 (s, 3H), 3.32 – 3.26 (m, 1H), 3.04 – 2.97 (m, 2H), 2.56 – 2.51 (m, 1H). The NMR data is identical to that previously reported.[15]

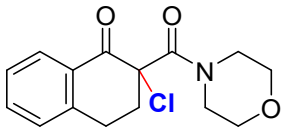
ethyl 2-chloro-2-methyl-3-oxo-3-phenylpropanoate



2d

Colorless oil liquid; 71% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 – 7.98 (m, 2H), 7.58 – 7.54 (m, 1H), 7.46 – 7.42 (m, 2H), 4.25 – 4.16 (m, 2H), 2.01 (s, 3H), 1.09 (t, *J* = 7.2 Hz, 3H). The NMR data is identical to that previously reported.[14]

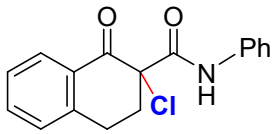
2-chloro-2-(morpholine-4-carbonyl)-3,4-dihydronaphthalen-1(2H)-one



2e

Colorless oil liquid; 92% yield; 1H NMR (500 MHz, CDCl3) δ 7.99 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.53 (td, *J* = 7.5, 1.7 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.26 (d, *J* = 7.6 Hz, 1H), 3.71 – 3.69 (m, 8H), 3.25 (t, *J* = 6.0 Hz, 2H), 2.99 (dt, *J* = 14.5, 6.2 Hz, 1H), 2.59 (dt, *J* = 14.6, 5.8 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 189.93, 164.89, 142.74, 134.36, 130.70, 128.86, 128.76, 127.15, 77.36, 70.51, 66.72, 36.16, 26.49. HRMS (ESI) calcd for $C_{15}H_{17}O_3NCl^+$ ($[M+H]^+$) 294.0891, 295.0925, 296.0862; found 294.0890, 295.0924, 296.0862.

2-chloro-1-oxo-N-phenyl-1,2,3,4-tetrahydronaphthalene-2-carboxamide

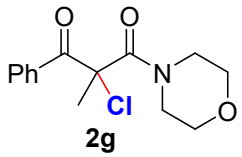


2f

Colorless oil liquid; 98% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.93 (s, 1H), 8.11 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.61 – 7.54 (m, 2H), 7.55 (td, *J* = 7.4, 1.5 Hz, 1H), 7.35 (q, *J* = 8.0 Hz, 3H), 7.29 (d, *J* = 7.8 Hz, 1H), 7.17 – 7.13 (m, 1H), 3.32 – 3.26 (m, 1H), 3.13 – 3.04

(m, 2H), 2.69 – 2.64 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 189.88, 164.77, 143.51, 137.15, 134.95, 129.72, 129.28, 129.14, 128.92, 127.41, 125.16, 120.31, 69.27, 34.25, 25.52. HRMS (ESI) calcd for $C_{17}H_{15}O_2NCl^+$ ([M+H]$^+$) 300.0786, 300.0819, 302.0756; found 300.0785, 300.0819, 302.0755.

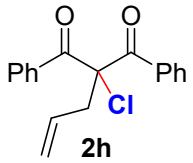
2-chloro-2-methyl-1-morpholino-3-phenylpropane-1,3-dione



2g

Colorless oil liquid; 57% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 – 7.99 (m, 2H), 7.62 – 7.61 (m, 1H), 7.50 – 7.46 (m, 2H), 3.73 – 3.14 (m, 8H), 2.11 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.48, 166.74, 134.30, 132.98, 129.67, 128.98, 72.52, 66.57, 65.87, 47.01, 43.76, 28.12. HRMS (ESI) calcd for $C_{14}H_{17}O_3NCl^+$ ([M+H]$^+$) 282.0891, 283.0925, 284.0862; found 282.0890, 283.0924, 284.0861.

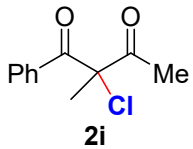
2-allyl-2-chloro-1,3-diphenylpropane-1,3-dione



2h

Colorless oil liquid; 72% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 – 7.90 (m, 4H), 7.51 – 7.47 (m, 2H), 7.36 (t, J = 7.8 Hz, 4H), 5.87 – 5.78 (m, 1H), 5.13 (dd, J = 10.2, 1.2 Hz, 1H), 5.00 – 4.95 (m, 1H), 3.32 (d, J = 7.2 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.66, 134.21, 133.78, 130.59, 129.92, 128.76, 120.60, 79.50, 43.41. HRMS (ESI) calcd for $C_{18}H_{16}O_2Cl^+$ ([M+H]$^+$) 299.0833, 300.0867, 301.0804; found 299.0833, 300.0868, 301.0805.

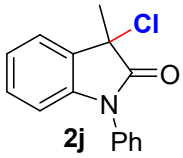
2-chloro-2-methyl-1-phenylbutane-1,3-dione



2i

Colorless oil liquid; 81% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 – 7.90 (m, 2H), 7.58 – 7.55 (m, 1H), 7.46 – 7.43 (m, 2H), 2.39 (s, 3H), 1.95 (s, 3H). The NMR data is identical to that previously reported.[16]

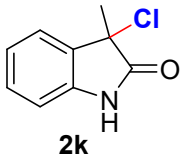
3-chloro-3-methyl-1-phenylindolin-2-one



2j

Colorless oil liquid; 98% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 – 7.49 (m, 3H), 7.45 – 7.41 (m, 3H), 7.29 – 7.25 (m, 1H), 7.16 (td, *J* = 7.5, 1.0 Hz, 1H), 6.85 – 6.83 (m, 1H), 2.01 (s, 3H). The NMR data is identical to that previously reported.[17]

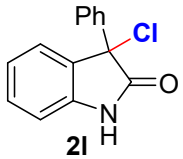
3-chloro-3-methylindolin-2-one



2k

Colorless oil liquid; 78% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.44 (s, 1H), 7.41 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.29 (td, *J* = 7.6, 1.4 Hz, 1H), 7.11 (td, *J* = 7.6, 1.1 Hz, 1H), 6.99 (d, *J* = 7.8 Hz, 1H), 1.93 (s, 3H). The NMR data is identical to that previously reported.[18]

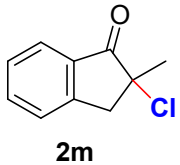
3-chloro-3-phenylindolin-2-one



2l

Colorless oil liquid; 31% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.77 (s, 1H), 7.56 – 7.54 (m, 2H), 7.39 – 7.35 (m, 5H), 7.14 (t, *J* = 7.6 Hz, 1H), 6.98 (d, *J* = 7.8 Hz, 1H). The NMR data is identical to that previously reported.[19]

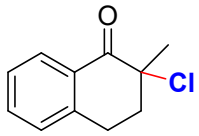
2-chloro-2-methyl-2,3-dihydro-1H-inden-1-one



2m

Colorless oil liquid; 72% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.9 Hz, 1H), 7.67 (t, *J* = 7.2 Hz, 1H), 7.44 (t, *J* = 6.8 Hz, 2H), 3.66 (d, *J* = 18.0 Hz, 1H), 3.46 (d, *J* = 17.7 Hz, 1H), 1.81 (s, 3H). The NMR data is identical to that previously reported.[20]

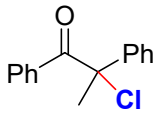
2-chloro-2-methyl-3,4-dihydronaphthalen-1(2H)-one



2n

Colorless oil liquid; 62% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (dd, J = 8.0, 1.7 Hz, 1H), 7.50 (td, J = 7.5, 1.6 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 7.25 (d, J = 7.8 Hz, 1H), 3.42 – 3.36 (m, 1H), 2.92 – 2.86 (m, 1H), 2.52 – 2.48 (m, 1H), 2.36 – 2.30 (m, 1H), 1.83 (s, 3H). The NMR data is identical to that previously reported.[20]

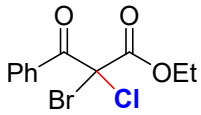
2-chloro-1,2-diphenylpropan-1-one



2o

Colorless oil liquid; 51% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 – 7.74 (m, 2H), 7.51 – 7.48 (m, 2H), 7.42 – 7.29 (m, 4H), 7.27 – 7.24 (m, 2H), 2.04 (s, 3H). The NMR data is identical to that previously reported.[21]

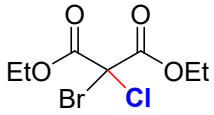
ethyl 2-bromo-2-chloro-3-oxo-3-phenylpropanoate



2p

White solid, 41% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 – 8.03 (m, 2H), 7.63 – 7.60 (m, 1H), 7.50 – 7.46 (m, 2H), 4.31 (q, J = 7.2 Hz, 2H), 1.18 (t, J = 7.2 Hz, 3H). The NMR data is identical to that previously reported.[22]

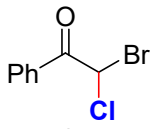
diethyl 2-bromo-2-chloromalonate



2q

Colorless oil liquid; 80% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.38 – 4.33 (m, 4H), 1.35 – 1.31 (m, 6H). The NMR data is identical to that previously reported.[23]

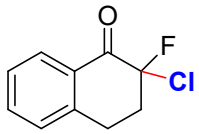
2-bromo-2-chloro-1-phenylethan-1-one



2r

Colorless oil liquid; 50% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 – 8.07 (m, 2H), 7.68 – 7.63 (m, 1H), 7.54 – 7.50 (m, 2H), 6.79 – 6.64 (m, 1H). The NMR data is identical to that previously reported.[24]

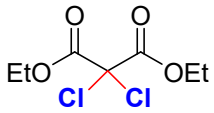
2-chloro-2-fluoro-3,4-dihydronaphthalen-1(2H)-one



2s

White solid; 57% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, J = 8.0 Hz, 1H), 7.58 (t, J = 7.6 Hz, 1H), 7.40 (t, J = 7.6 Hz, 1H), 7.30 (d, J = 7.8 Hz, 1H), 3.38 – 3.32 (m, 1H), 3.14 – 3.09 (m, 1H), 2.84 – 2.78 (m, 1H), 2.74 – 2.67 (m, 1H). The NMR data is identical to that previously reported.[25]

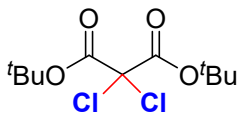
diethyl 2,2-dichloromalonate



4a

Colorless oil liquid; 76% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.25 – 4.18 (m, 4H), 1.32 (t, J = 7.2 Hz, 3H), 1.27 (t, J = 7.0 Hz, 3H). The NMR data is identical to that previously reported.[24]

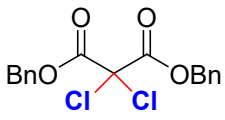
di-tert-butyl 2,2-dichloromalonate



4b

White solid; 48% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.51 (dd, J = 3.5, 1.6 Hz, 18H). The NMR data is identical to that previously reported.[24]

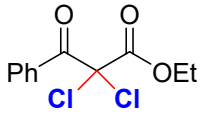
dibenzyl 2,2-dichloromalonate



4c

Colorless oil liquid; 60% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 10H), 5.16 (d, J = 8.0 Hz, 4H). The NMR data is identical to that previously reported.[26]

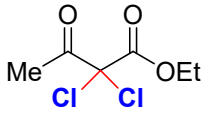
ethyl 2,2-dichloro-3-oxo-3-phenylpropanoate



4d

Colorless oil liquid; 64% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 – 7.73 (m, 2H), 7.58 – 7.55 (m, 1H), 7.53 – 7.50 (m, 2H), 4.24 – 4.19 (m, 2H), 1.10 (td, J = 7.2, 1.7 Hz, 3H). The NMR data is identical to that previously reported.[27]

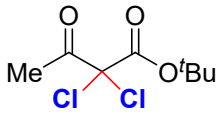
ethyl 2,2-dichloro-3-oxobutanoate



4e

White solid; 46% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.25 (q, J = 7.2 Hz, 2H), 2.28 (s, 3H), 1.35 (t, J = 7.2 Hz, 3H). The NMR data is identical to that previously reported.[23]

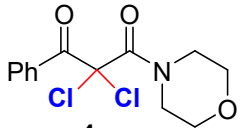
tert-butyl 2,2-dichloro-3-oxobutanoate



4f

Colorless oil liquid; 45% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.32 (s, 3H), 1.56 (s, 9H). The NMR data is identical to that previously reported.[28]

2,2-dichloro-1-morpholino-3-phenylpropane-1,3-dione

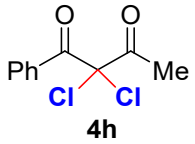


4g

Colorless oil liquid; 85% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, J = 7.6 Hz, 2H), 7.63 (t, J = 7.3 Hz, 1H), 7.48 (t, J = 7.9 Hz, 2H), 3.64 (dd, J = 16.0, 5.4 Hz, 4H), 3.45

(s, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.37, 162.10, 134.56, 131.31, 130.53, 128.85, 85.27, 66.57, 65.81, 47.61, 44.53. HRMS (ESI) calcd for $C_{13}H_{14}O_3NCl_2^+$ ($[M+H]^+$) 302.0345, 303.0379, 304.0316; found 302.0346, 303.0383, 304.0313.

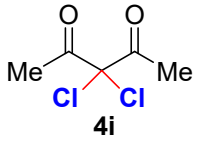
2,2-dichloro-1-phenylbutane-1,3-dione



4h

Colorless oil liquid; 96% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 – 7.83 (m, 2H), 7.70 – 7.66 m, 1H), 7.54 (t, J = 7.3 Hz, 2H), 2.50 (d, J = 1.2 Hz, 3H). The NMR data is identical to that previously reported.[24]

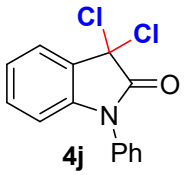
3,3-dichloropentane-2,4-dione



4i

Yellow oil liquid; 88% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.75 (t, J = 1.4 Hz, 3H), 2.66 (t, J = 1.2 Hz, 3H). The NMR data is identical to that previously reported.[24]

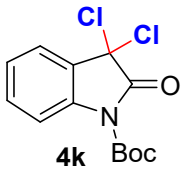
3,3-dichloro-1-phenylindolin-2-one



4j

White solid liquid; 82% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (dd, J = 7.6, 1.5 Hz, 1H), 7.57 – 7.53 (m, 2H), 7.47 – 7.43 (m, 3H), 7.34 (td, J = 7.8, 1.4 Hz, 1H), 7.22 (td, J = 7.6, 1.1 Hz, 1H), 6.82 (d, J = 7.9 Hz, 1H). The NMR data is identical to that previously reported.[17]

tert-butyl 3,3-dichloro-2-oxoindoline-1-carboxylate

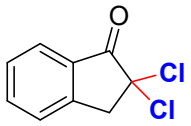


4k

Colorless oil liquid; 47% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (dt, J = 8.2, 0.8 Hz, 1H), 7.68 (dd, J = 7.6, 1.7 Hz, 1H), 7.47 – 7.43 (m, 1H), 7.30 (td, J = 7.6, 1.1 Hz, 1H),

1.66 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.51, 148.49, 137.09, 132.32, 128.27, 126.01, 124.98, 115.80, 86.02, 74.49, 28.13. HRMS (ESI) calcd for $C_{13}H_{14}O_3NCl_2^+$ ($[M+H]^+$) 302.0345, 303.0379, 304.0316; found 302.0344, 303.0378, 304.0315.

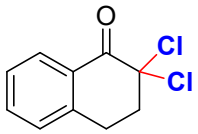
2,2-dichloro-2,3-dihydro-1H-inden-1-one



4l

Colorless oil liquid; 49% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, J = 7.8 Hz, 1H), 7.74 (t, J = 7.5 Hz, 1H), 7.51 (t, J = 7.6 Hz, 1H), 7.44 (d, J = 7.8 Hz, 1H), 4.06 (s, 2H). The NMR data is identical to that previously reported.[20]

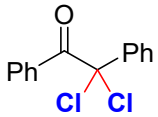
2,2-dichloro-3,4-dihydronaphthalen-1(2H)-one



4m

White solid; 62% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (dd, J = 7.9, 1.5 Hz, 1H), 7.56 (td, J = 7.6, 1.6 Hz, 1H), 7.39 (t, J = 7.4 Hz, 1H), 7.28 (d, J = 7.6 Hz, 1H), 3.21 (t, J = 6.0 Hz, 2H), 2.96 (t, J = 6.1 Hz, 2H). The NMR data is identical to that previously reported.[29]

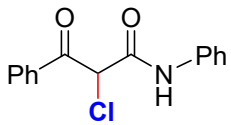
2,2-dichloro-1,2-diphenylethan-1-one



4n

White solid; 62% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (dd, J = 8.4, 1.2 Hz, 2H), 7.67 – 7.64 (m, 2H), 7.48 – 7.40 (m, 4H), 7.31 (t, J = 7.4 Hz, 2H). The NMR data is identical to that previously reported.[30]

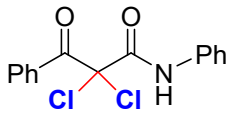
2-chloro-3-oxo-N,3-diphenylpropanamide



5a

White solid; 51% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (s, 1H), 8.09 (d, *J* = 7.8 Hz, 2H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.55 – 7.51 (m, 4H), 7.35 (t, *J* = 7.8 Hz, 2H), 7.17 (t, *J* = 7.4 Hz, 1H), 5.80 (s, 1H). The NMR data is identical to that previously reported.[31]

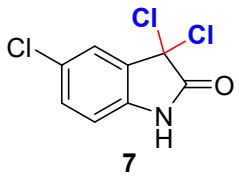
2,2-dichloro-3-oxo-N,3-diphenylpropanamide



5b

White solid; 56% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 – 7.92 (m, 2H), 7.53 – 7.47 (m, 3H), 7.41 (s, 1H), 7.34 – 7.27 (m, 4H), 7.18 (t, *J* = 7.4 Hz, 1H). The NMR data is identical to that previously reported.[32]

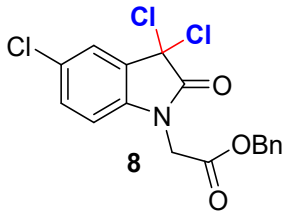
3,3,5-trichloroindolin-2-one



7

White solid; 68% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.29 (s, 1H), 7.61 (d, *J* = 2.1 Hz, 1H), 7.35 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 1H). The NMR data is identical to that previously reported.[17]

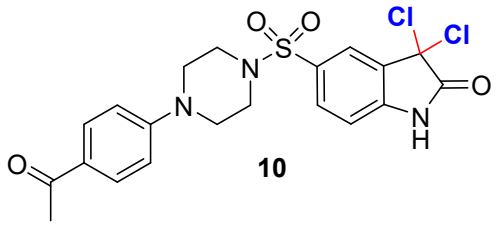
benzyl 2-(3,3,5-trichloro-2-oxoindolin-1-yl)acetate



8

White solid; 82% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 2.2 Hz, 1H), 7.35 – 7.33 (m, 3H), 7.32 – 7.27 (m, 3H), 6.63 (d, *J* = 8.6 Hz, 1H), 5.19 (s, 2H), 4.51 (s, 2H). The NMR data is identical to that previously reported.[33]

5-((4-(4-acetylphenyl)piperazin-1-yl)sulfonyl)-3,3-dichloroindolin-2-one

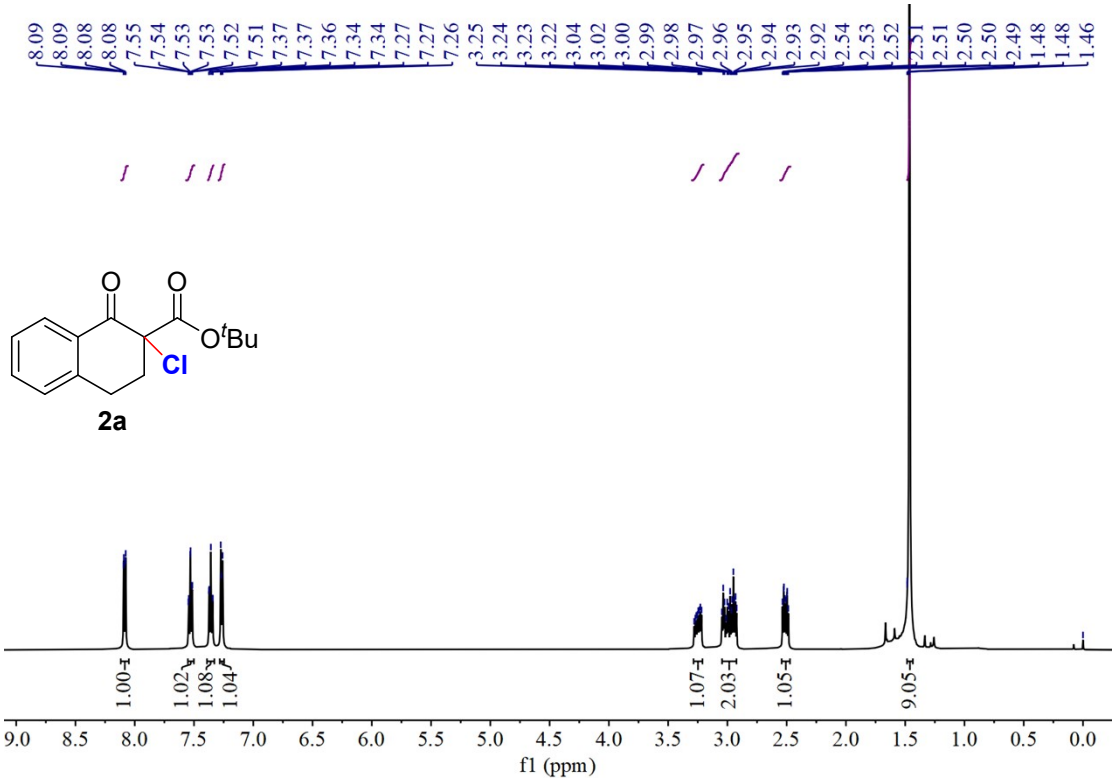


10

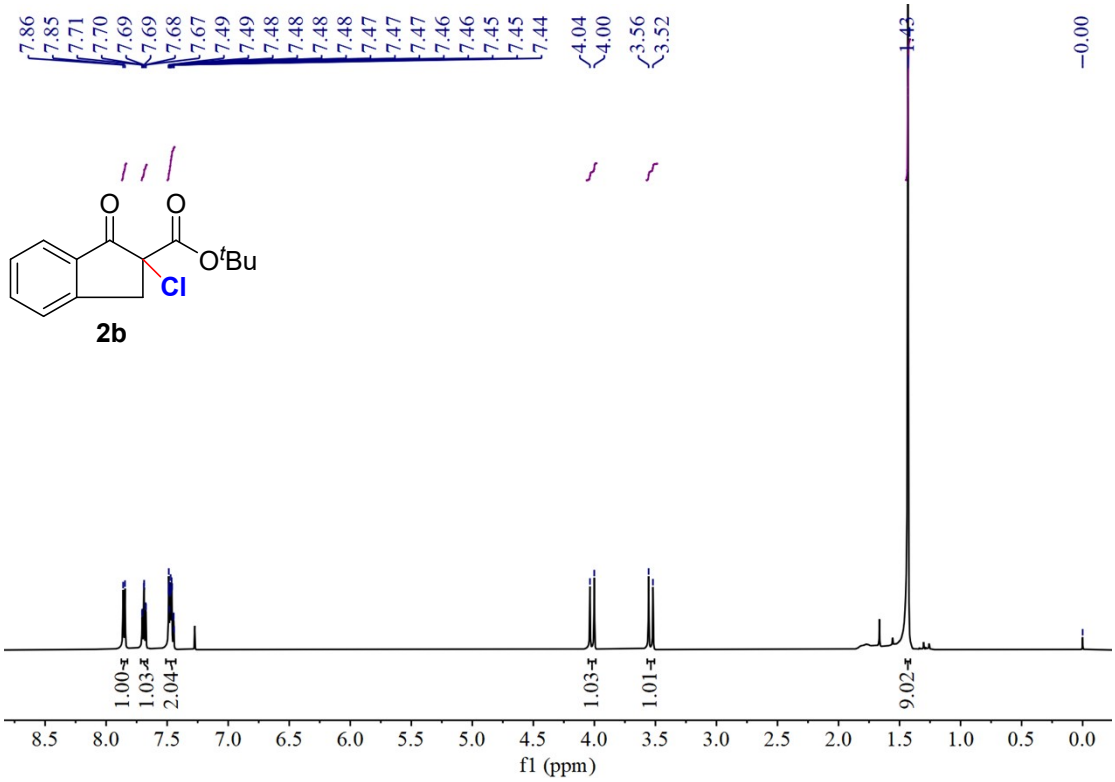
White solid; 64% yield; ^{1}H NMR (500 MHz, DMSO) δ 11.90 (s, 1H), 7.96 (d, *J* = 2.0 Hz, 1H), 7.84 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.80 – 7.77 (m, 2H), 7.22 (d, *J* = 8.2 Hz, 1H), 6.97 – 6.94 (m, 2H), 3.44 (t, J=4.2 Hz, 4H), 3.05 (t, *J* = 5.0 Hz, 4H), 2.44 (s, 3H). The NMR data is identical to that previously reported.[34]

10. Copies of NMR Spectra

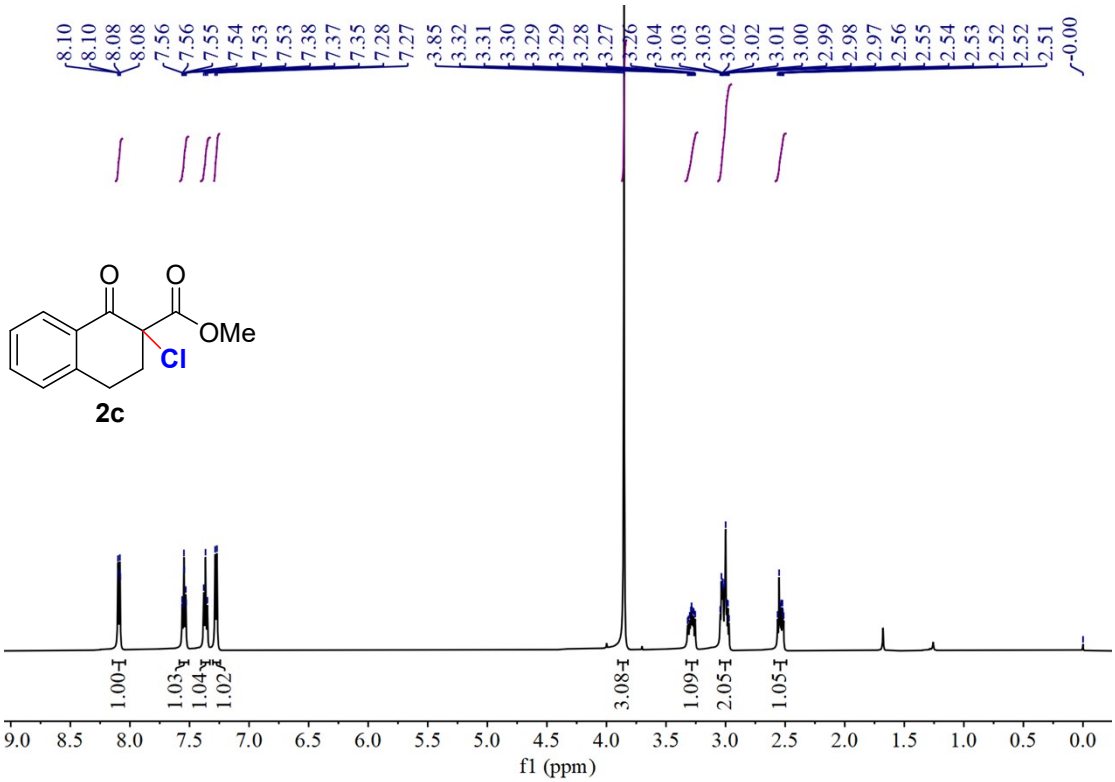
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2a**



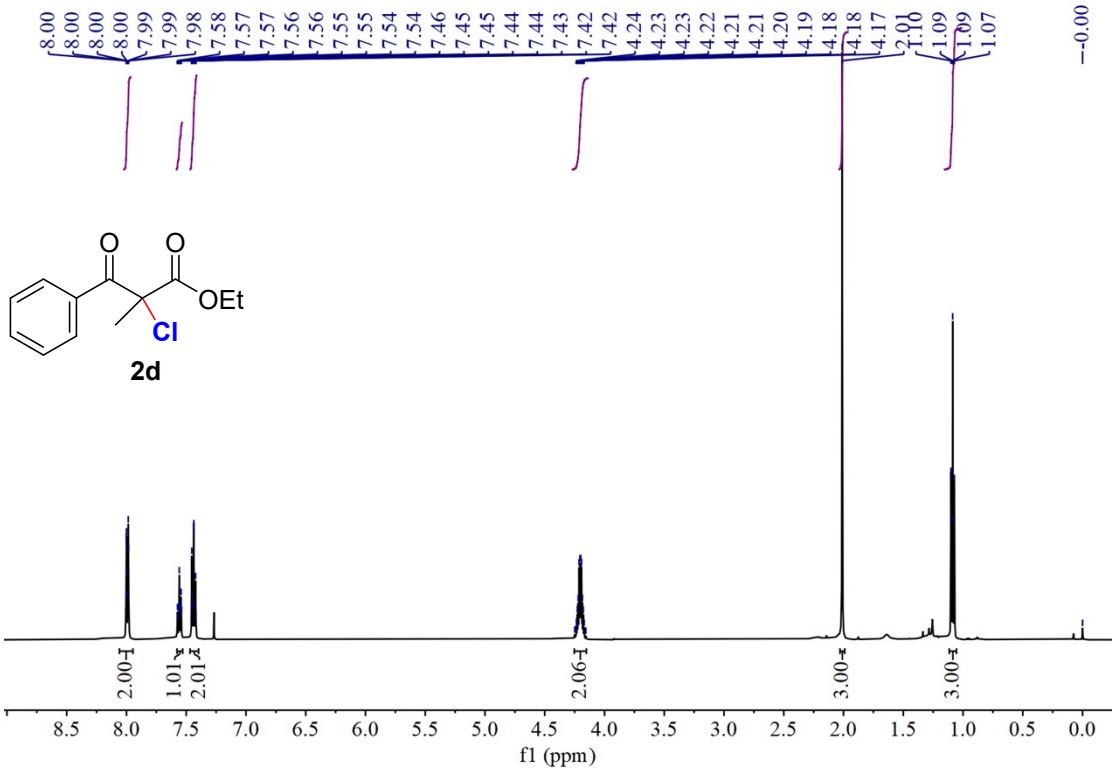
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2b**



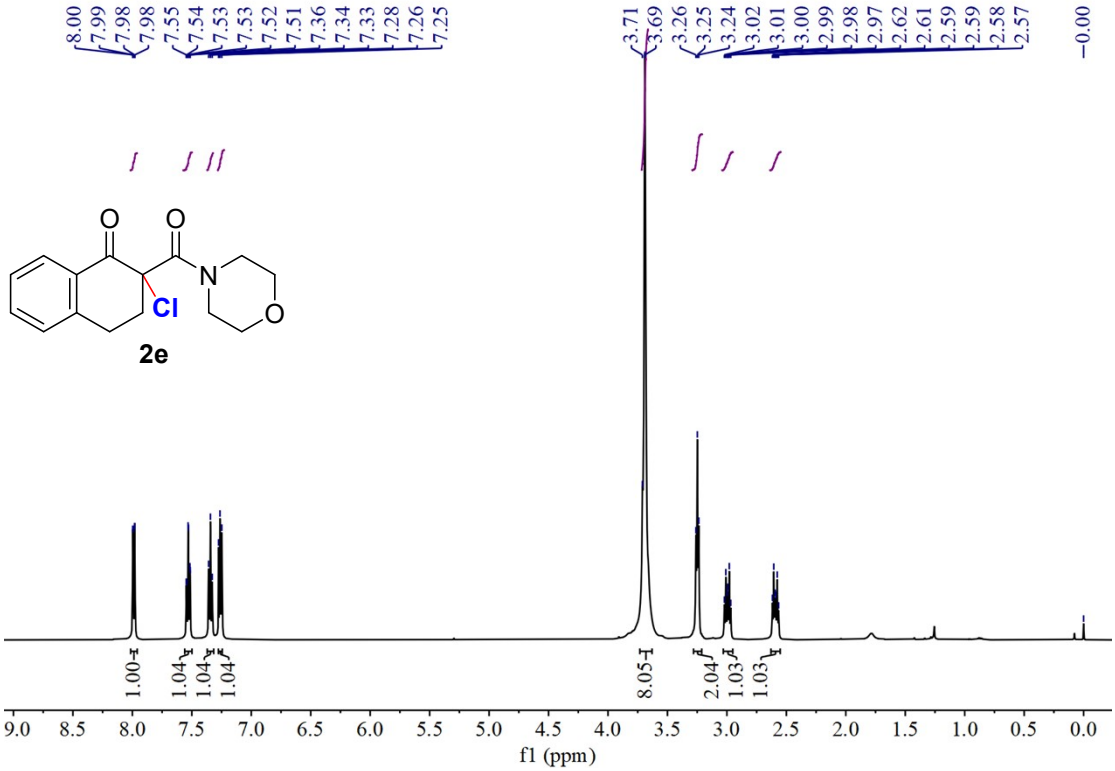
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2c**



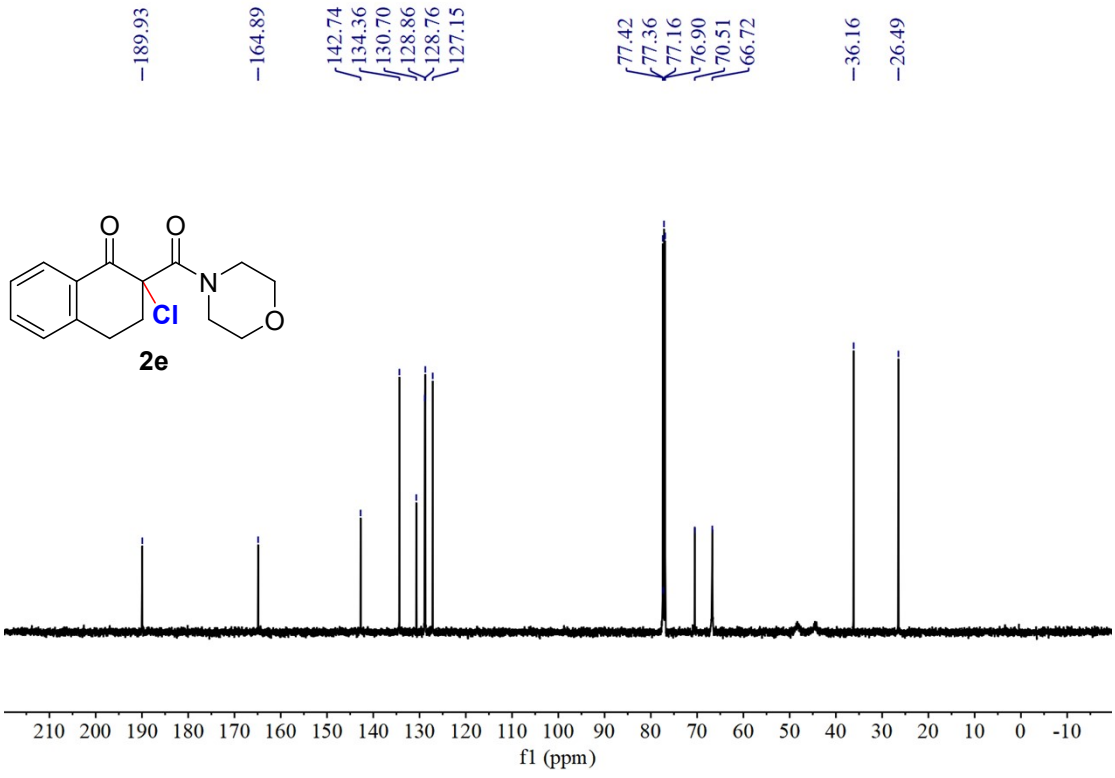
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2d**



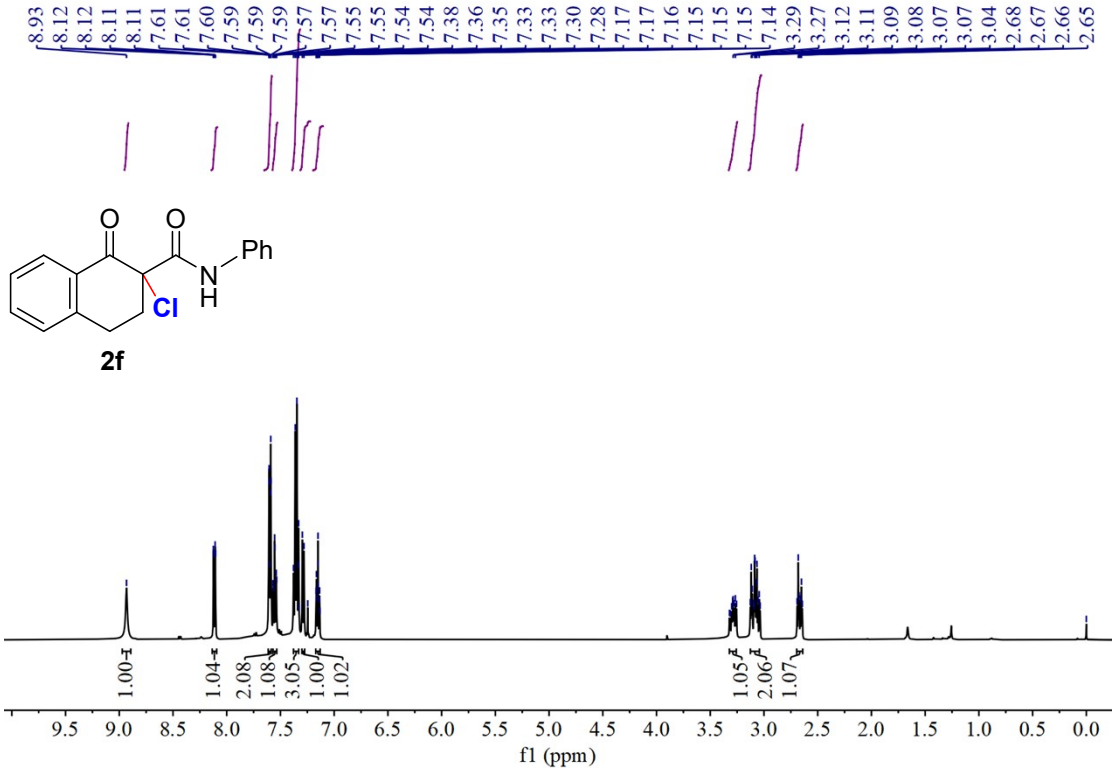
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2e**



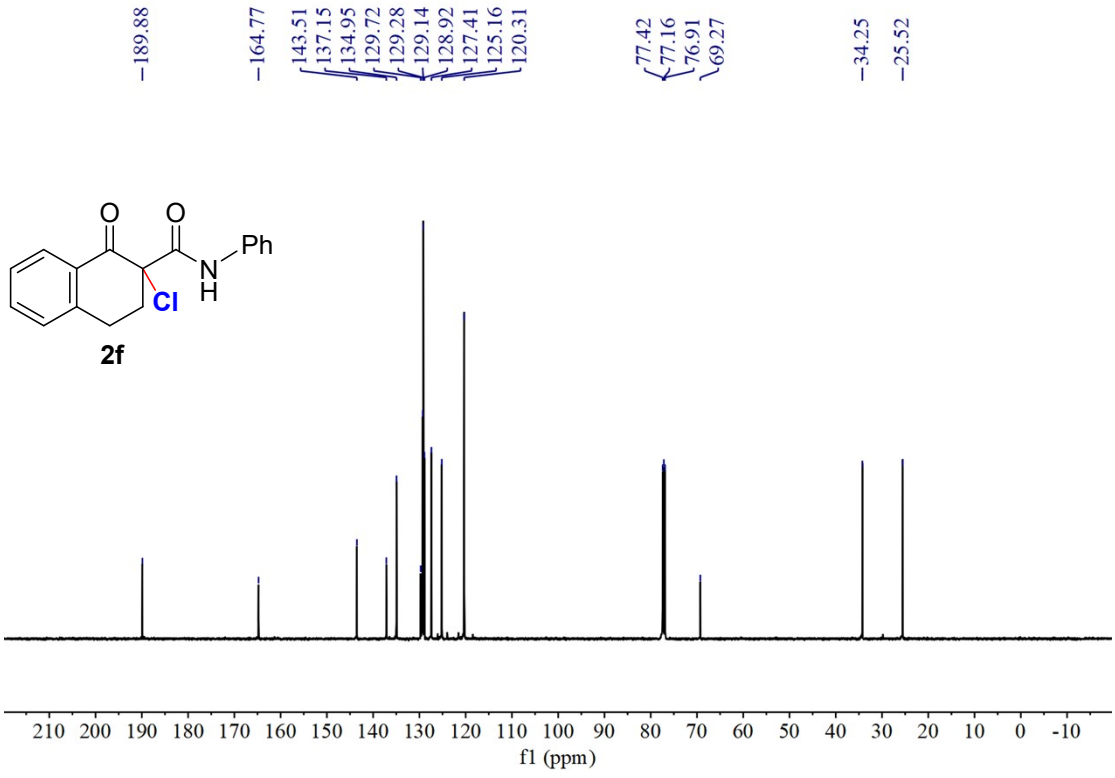
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **2e**



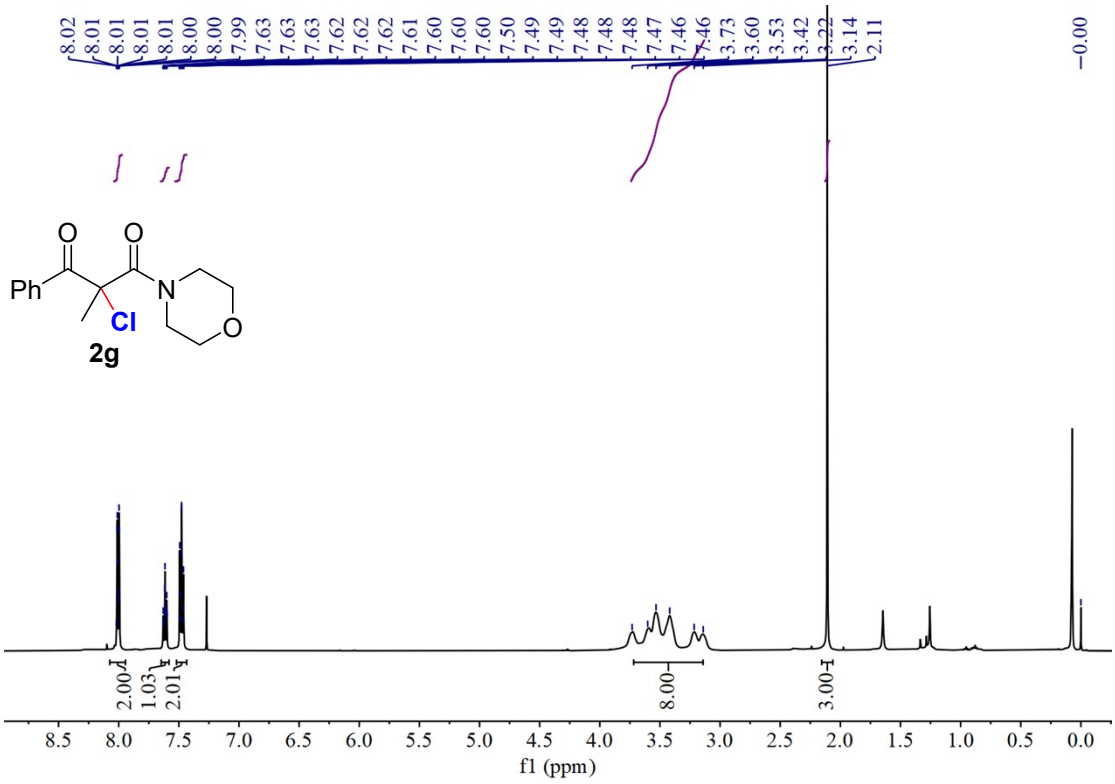
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2f**



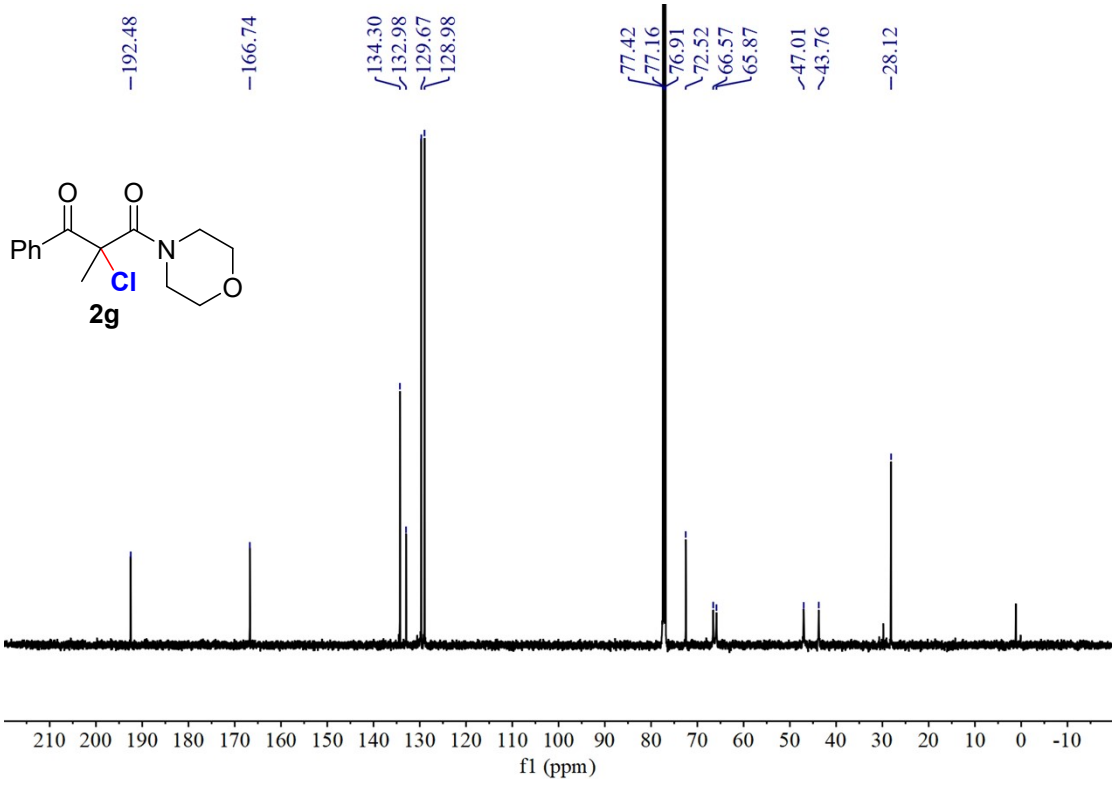
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **2f**



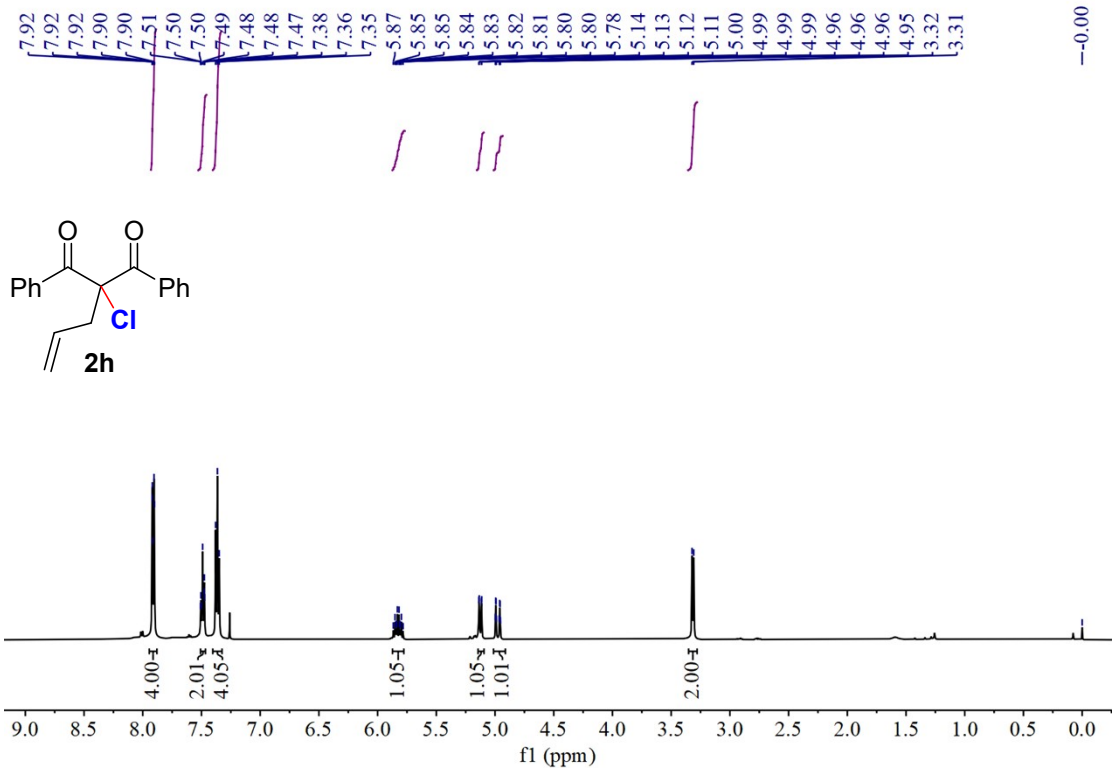
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2g**



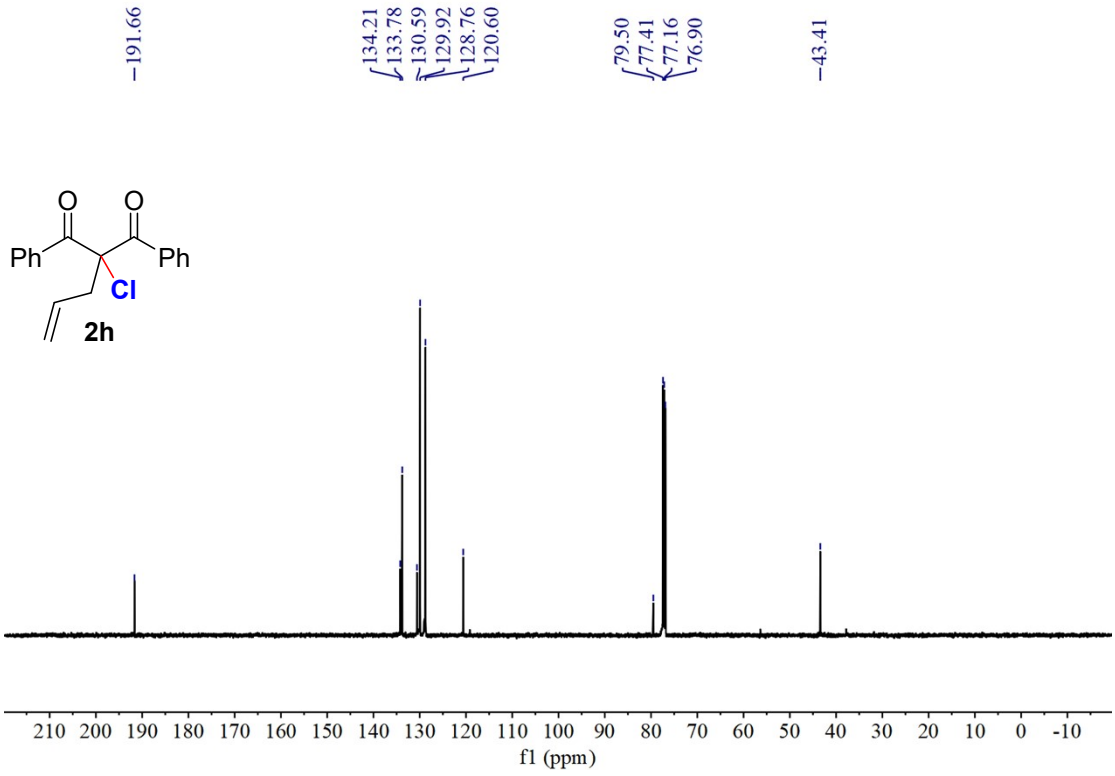
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **2g**



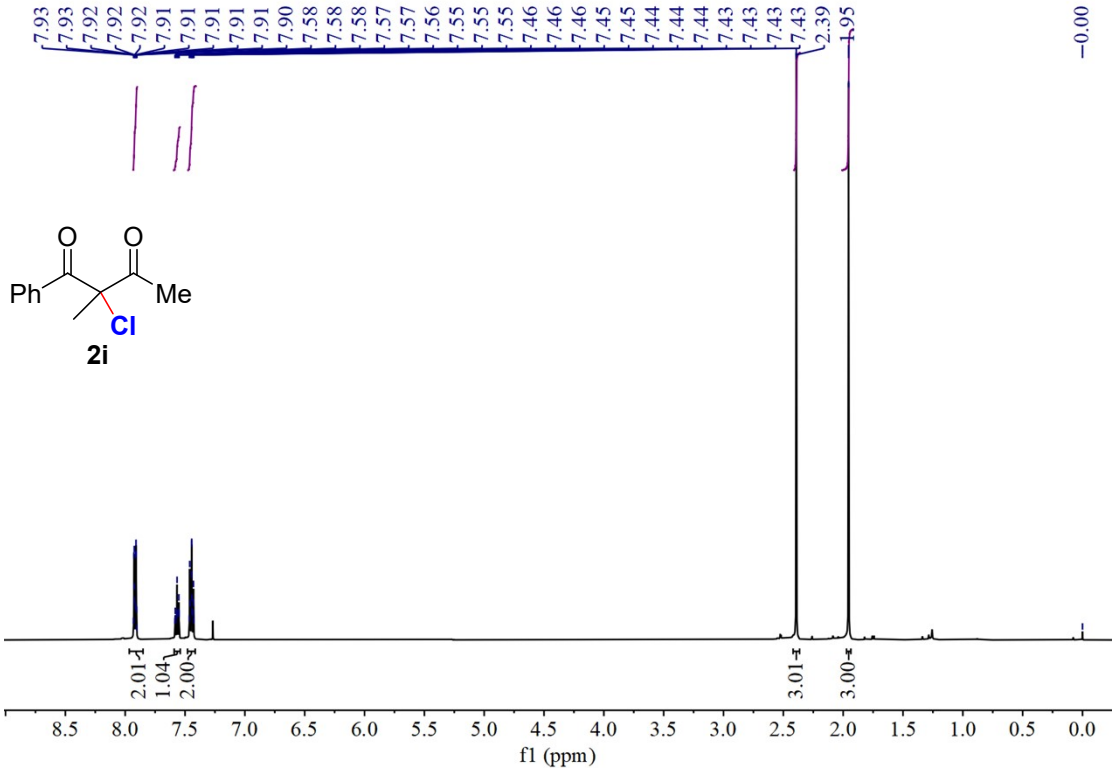
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2h**



^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **2h**



^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2i**



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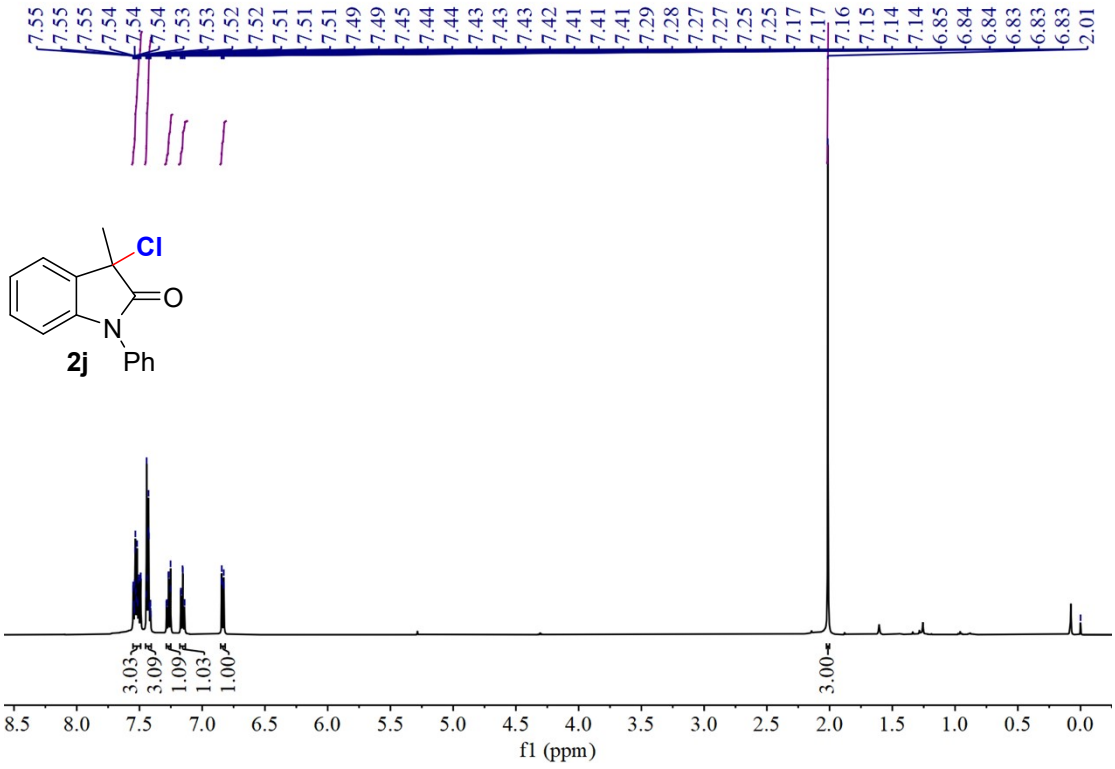
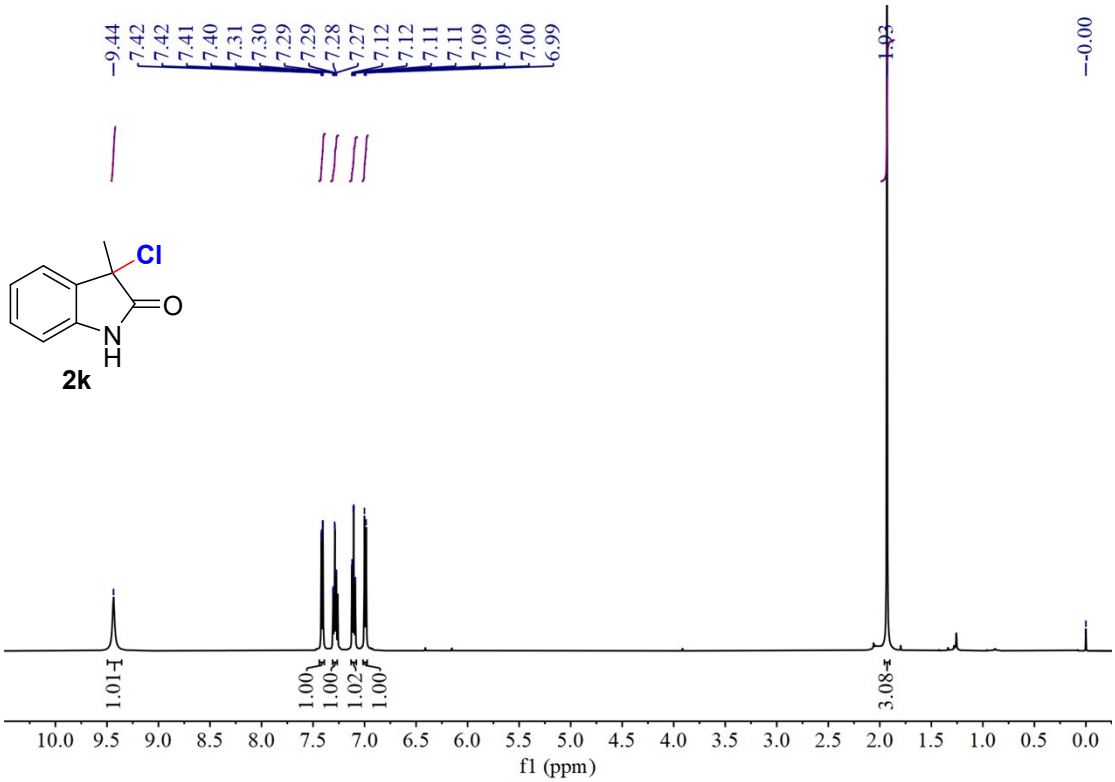
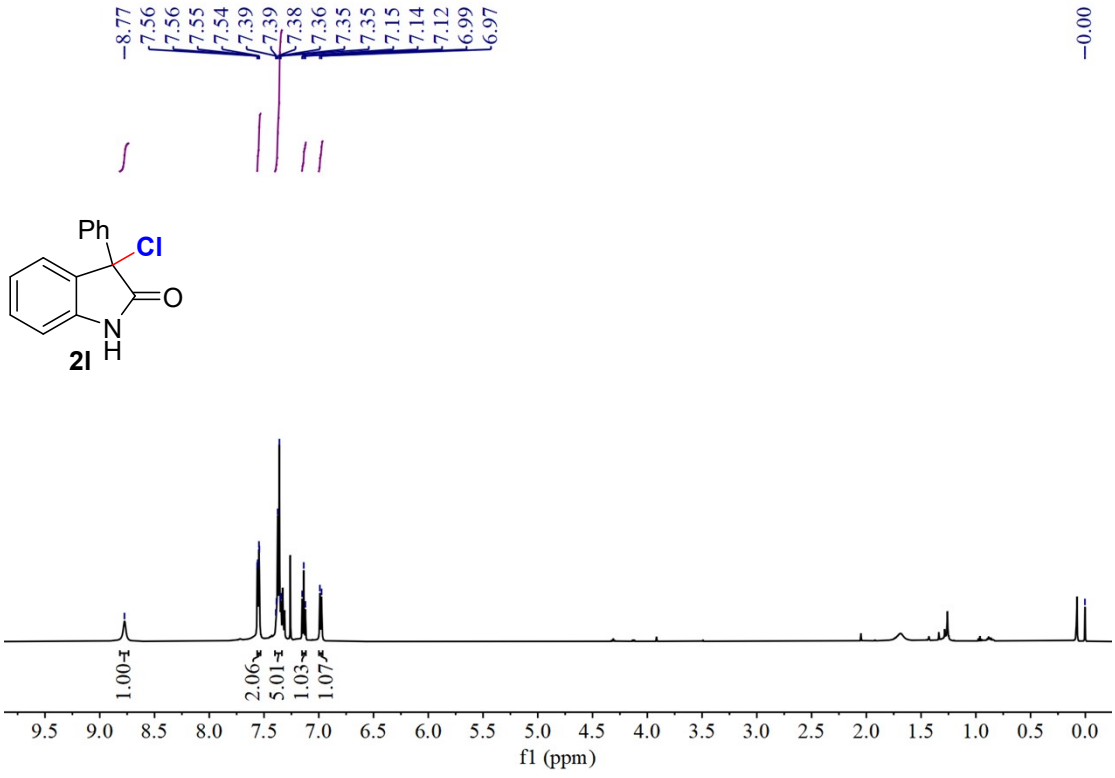


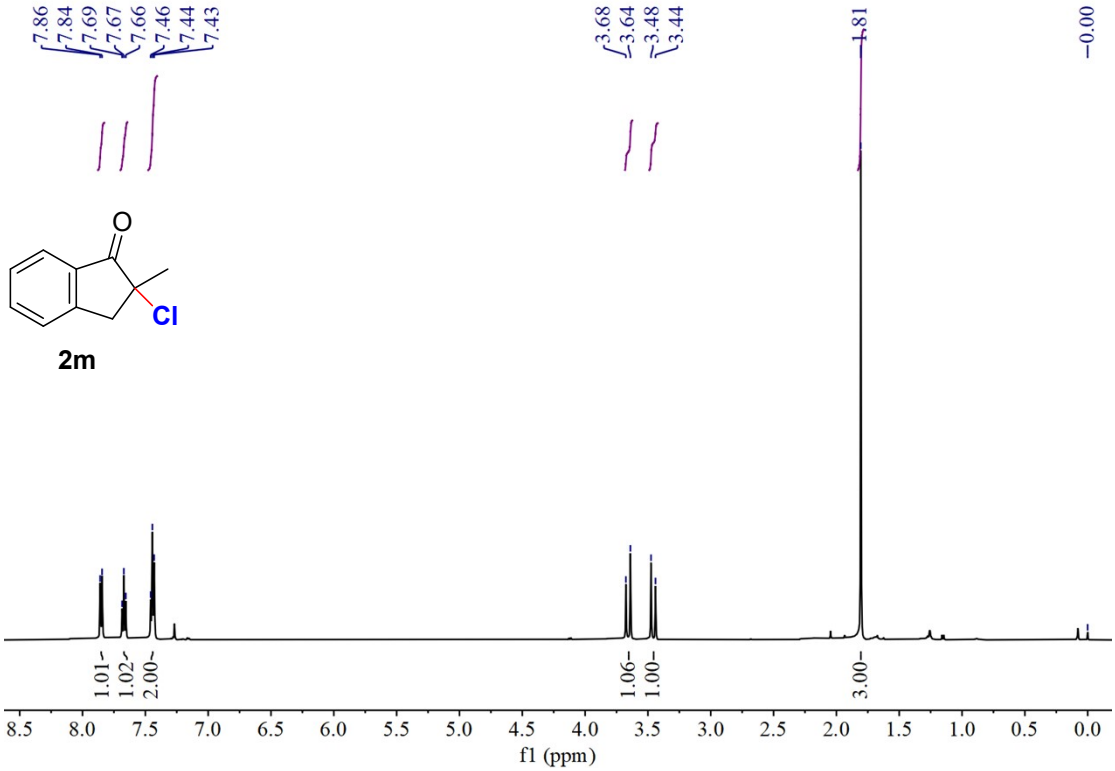
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2k**



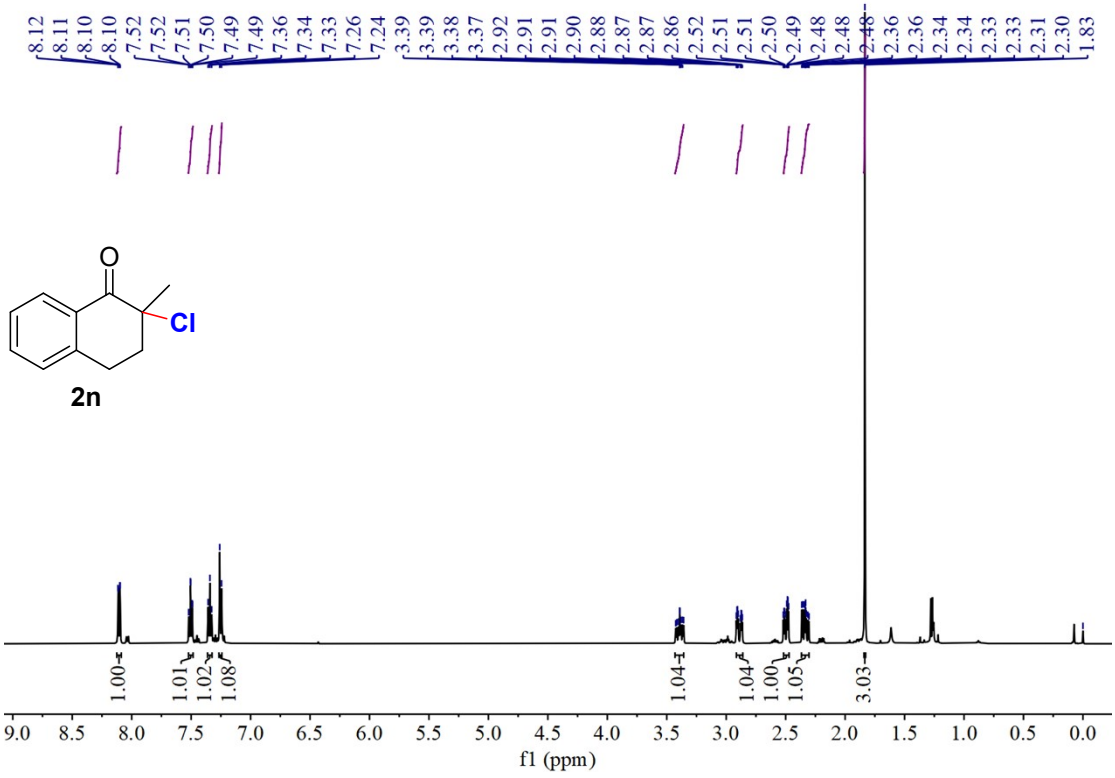
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2l**



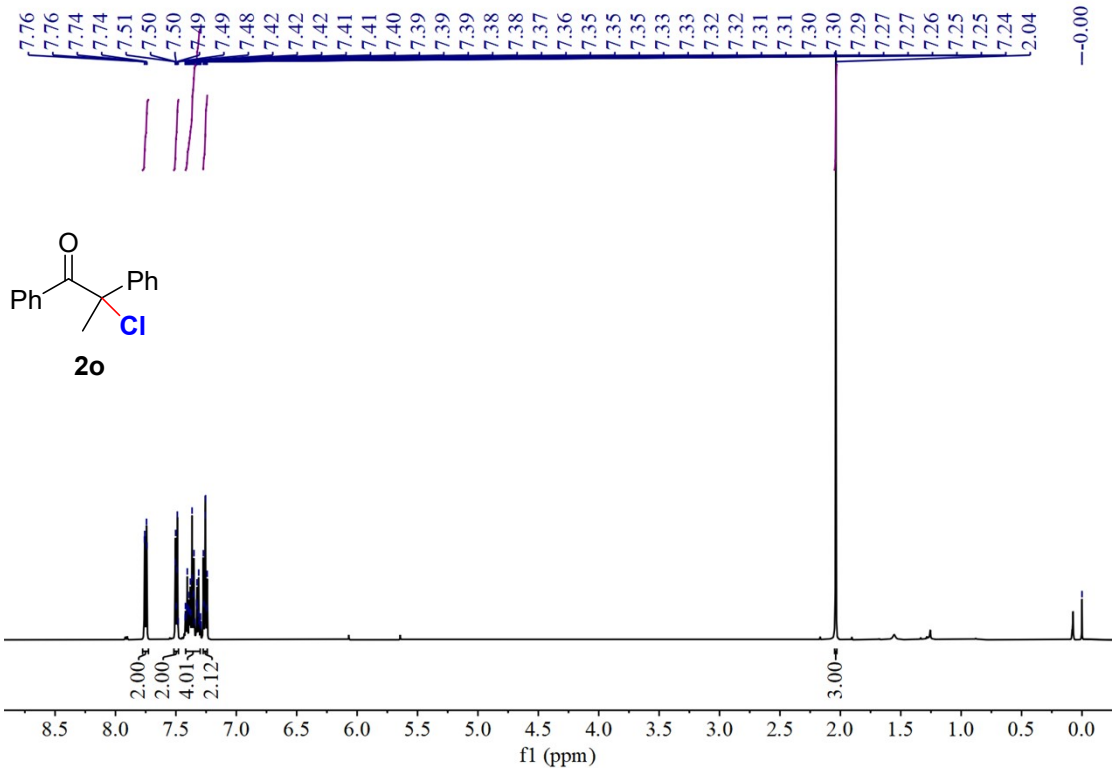
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2m**



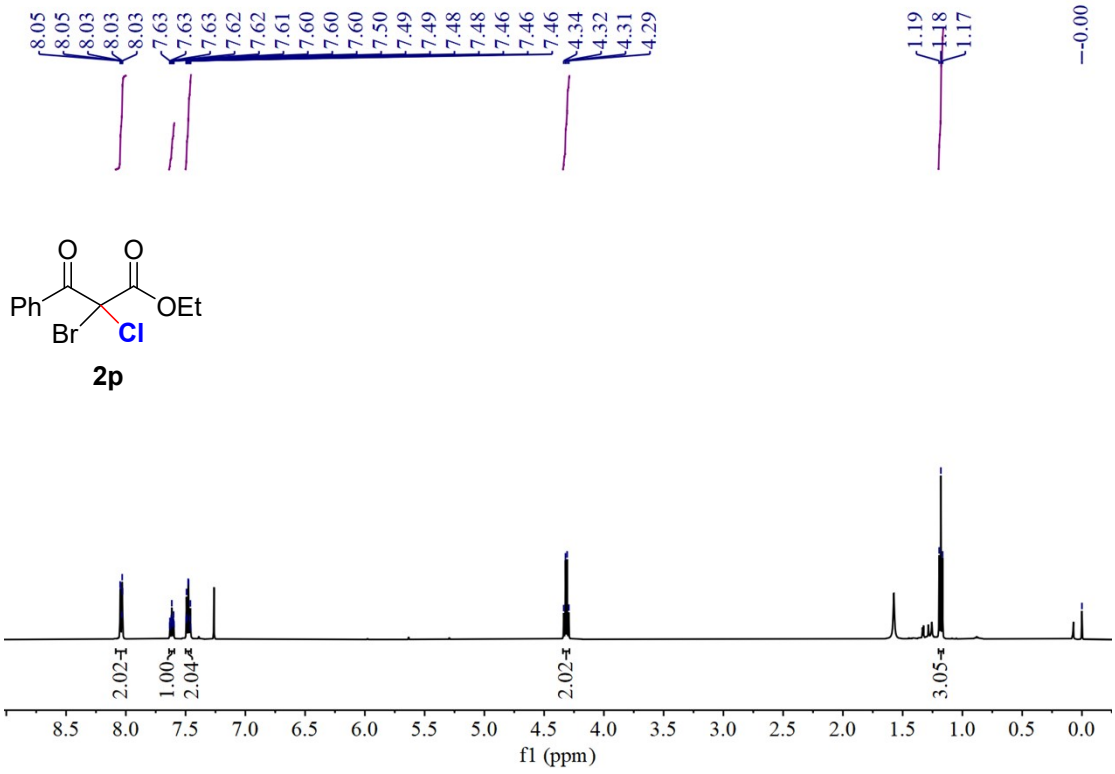
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2n**



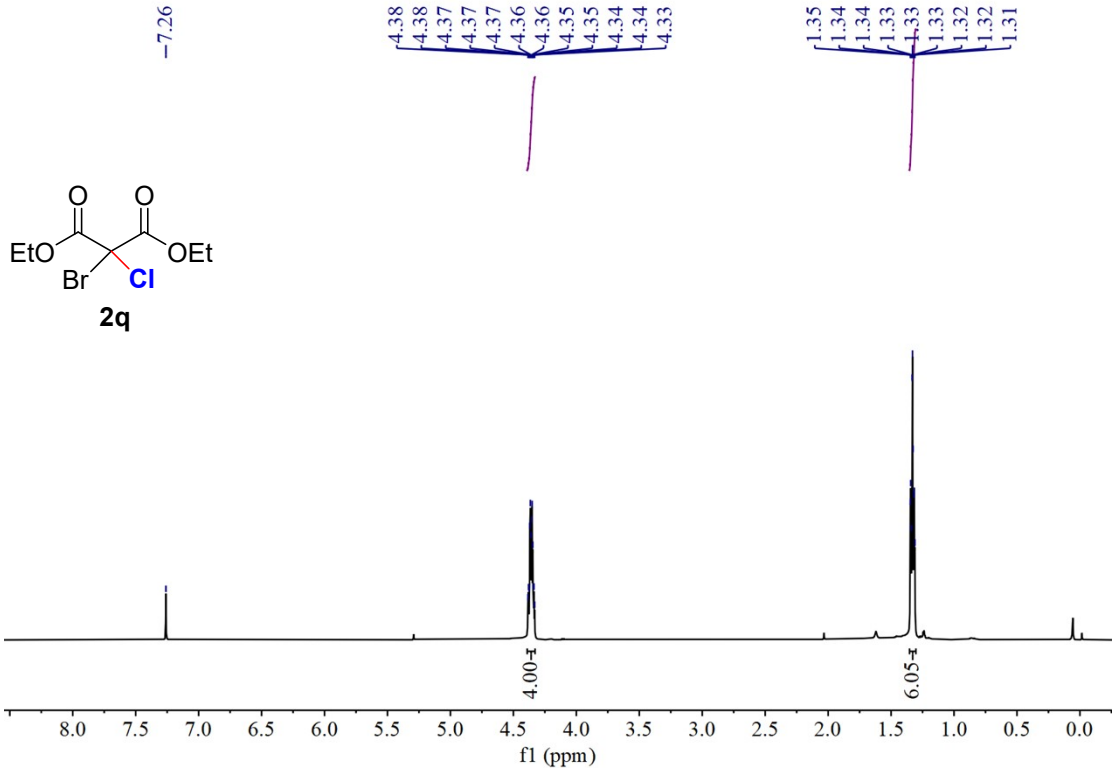
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2o**



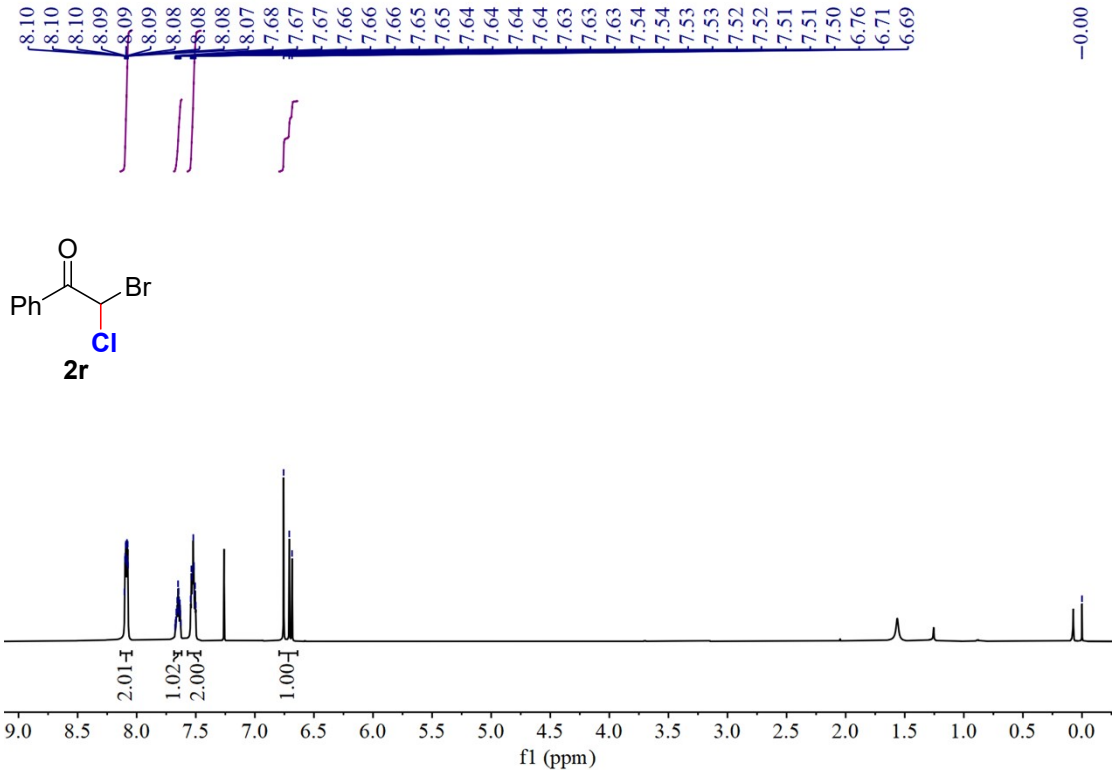
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2p**



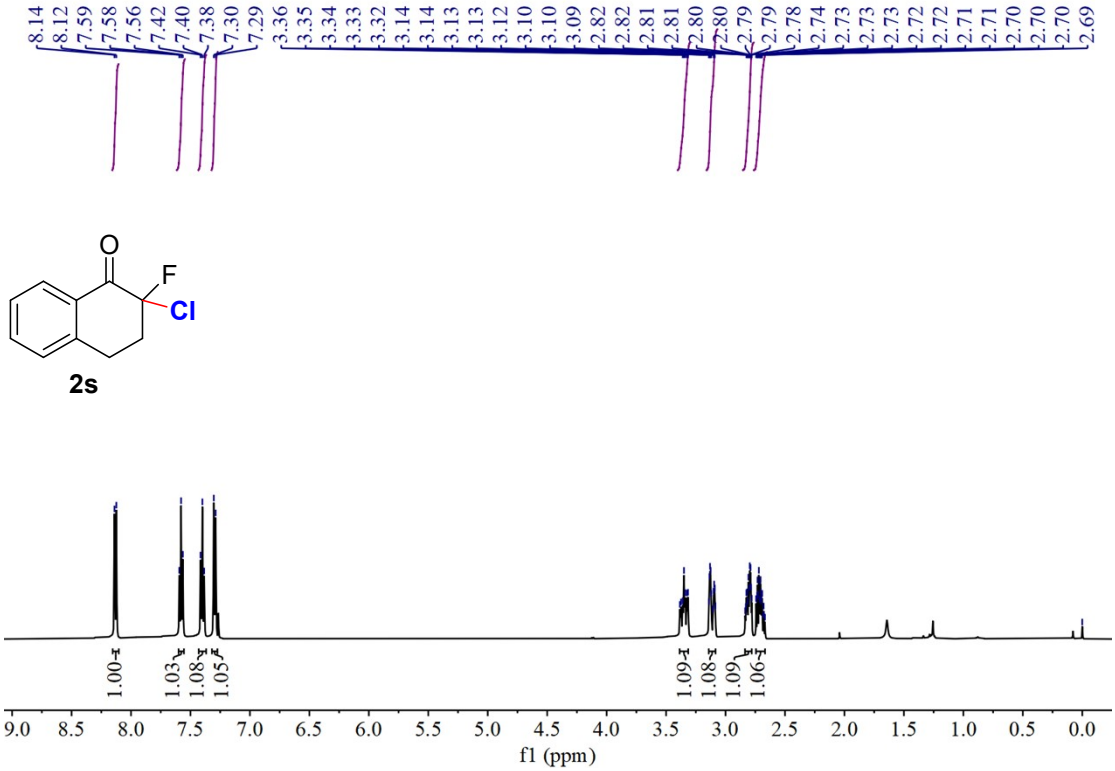
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2q**



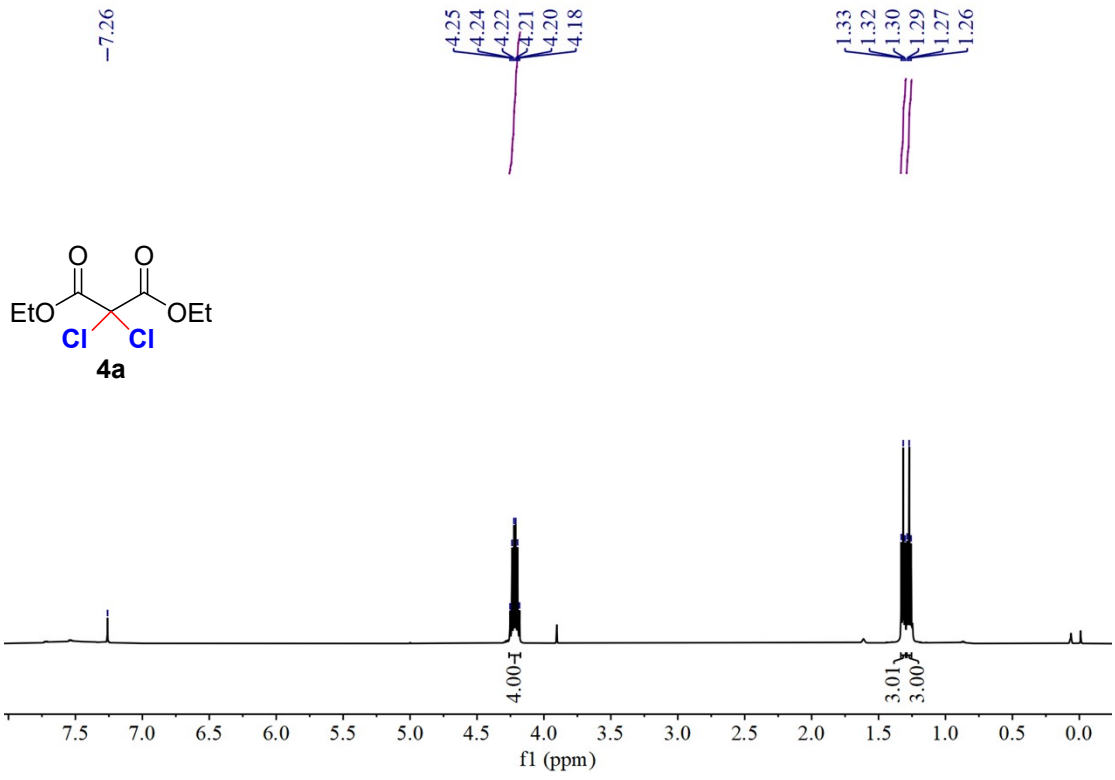
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2r**



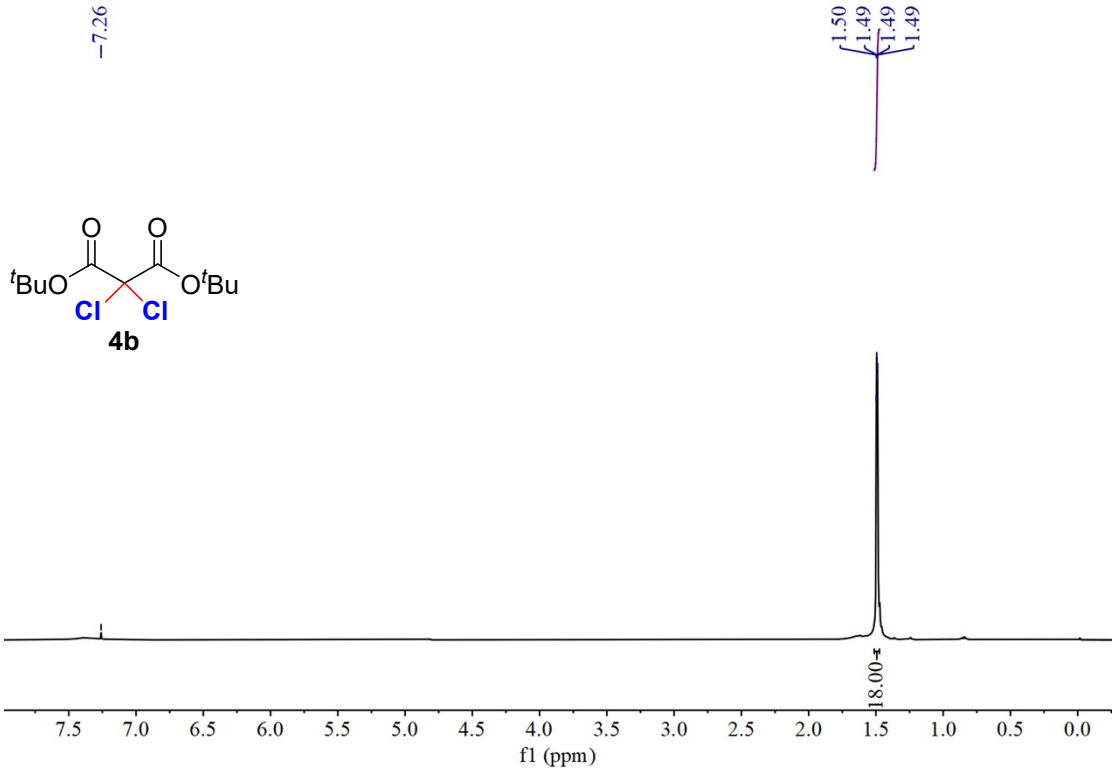
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2s**



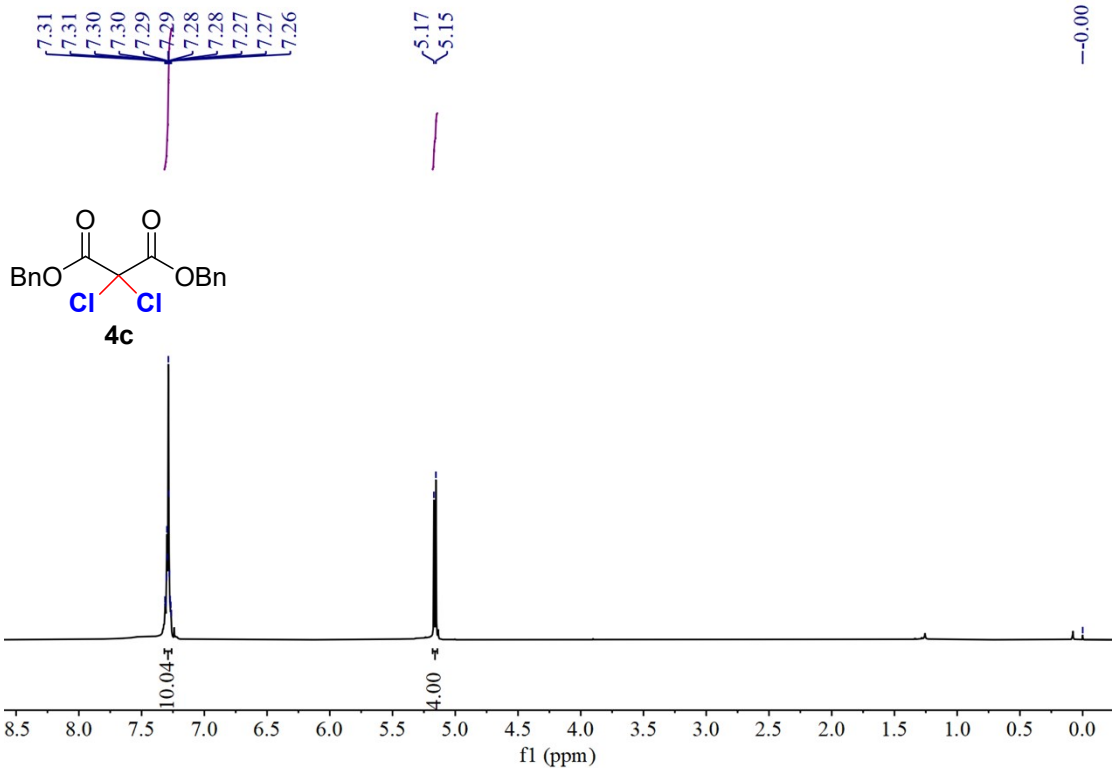
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **4a**



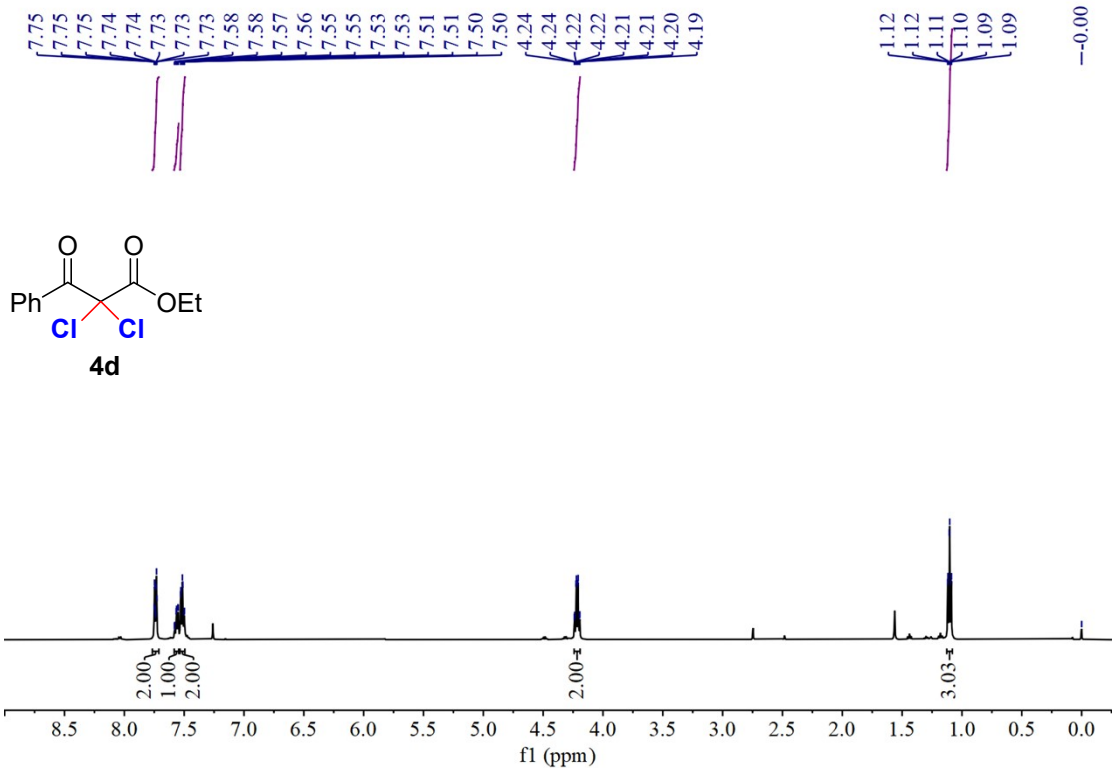
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **4b**



^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **4c**

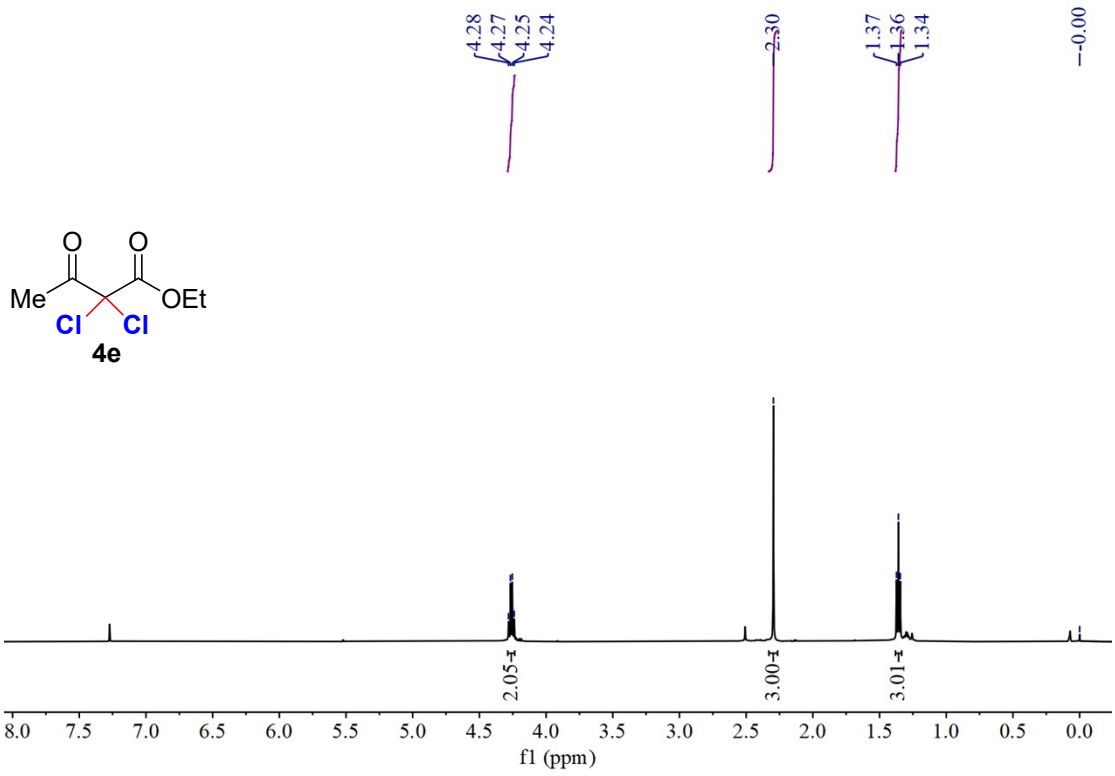


^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **4d**



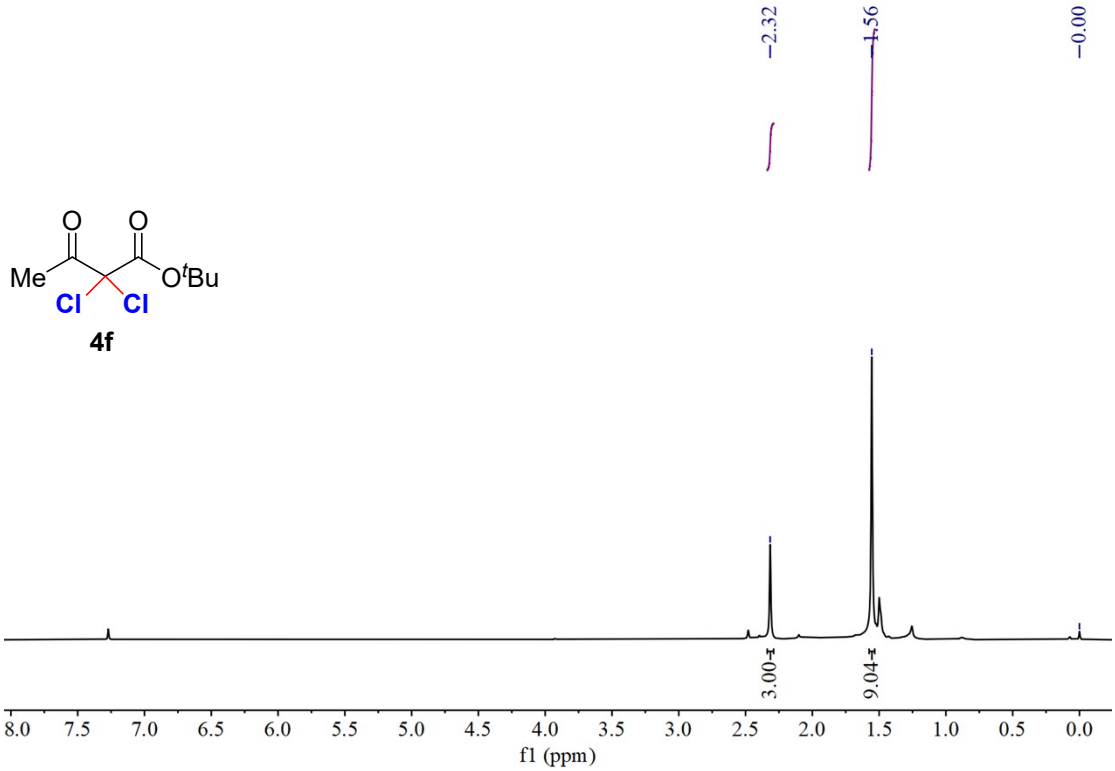
4d

^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **4e**

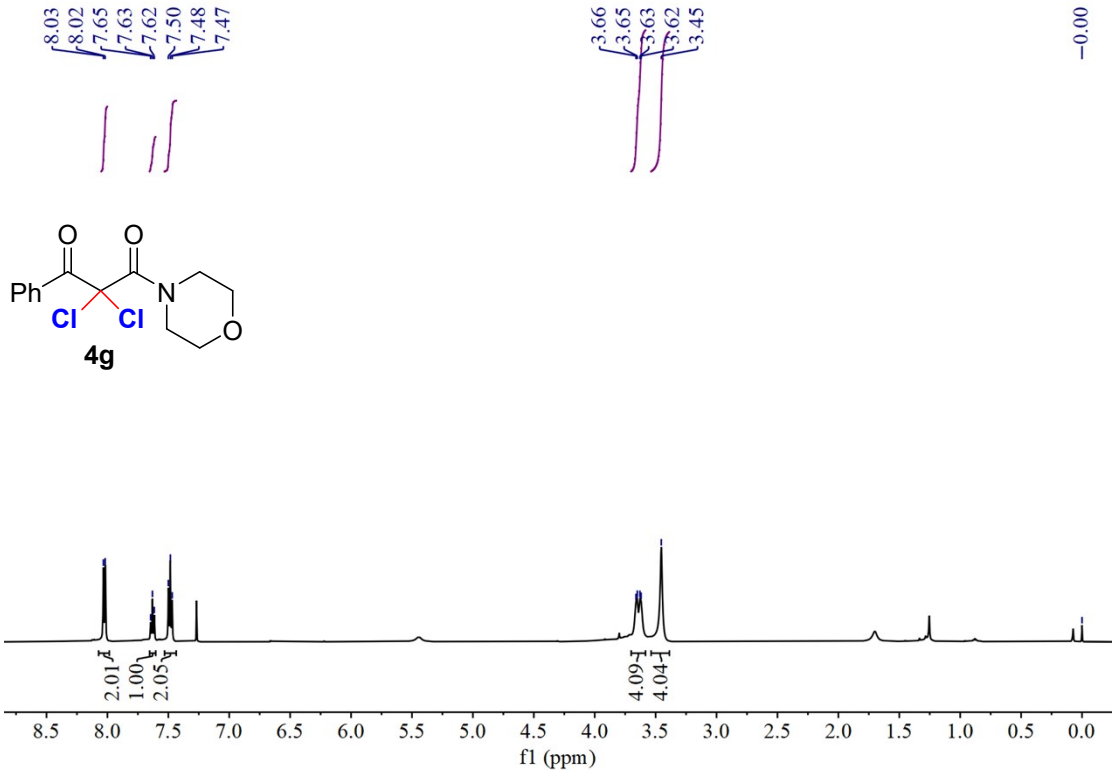


4e

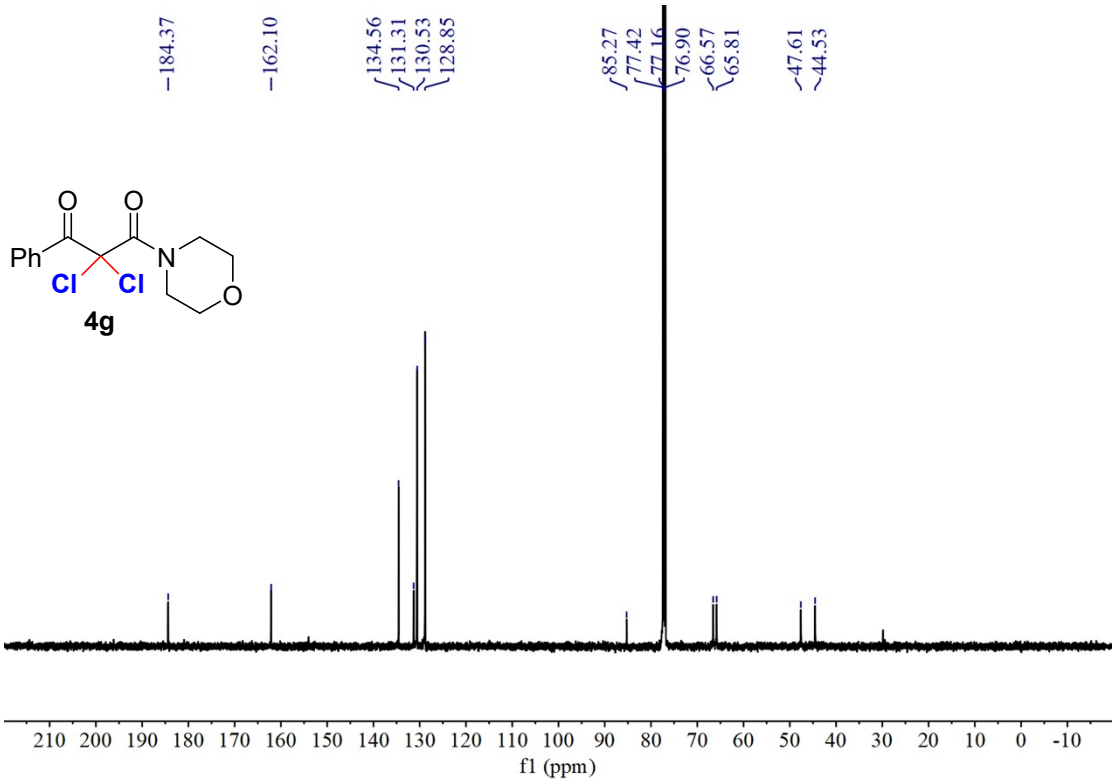
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **4f**



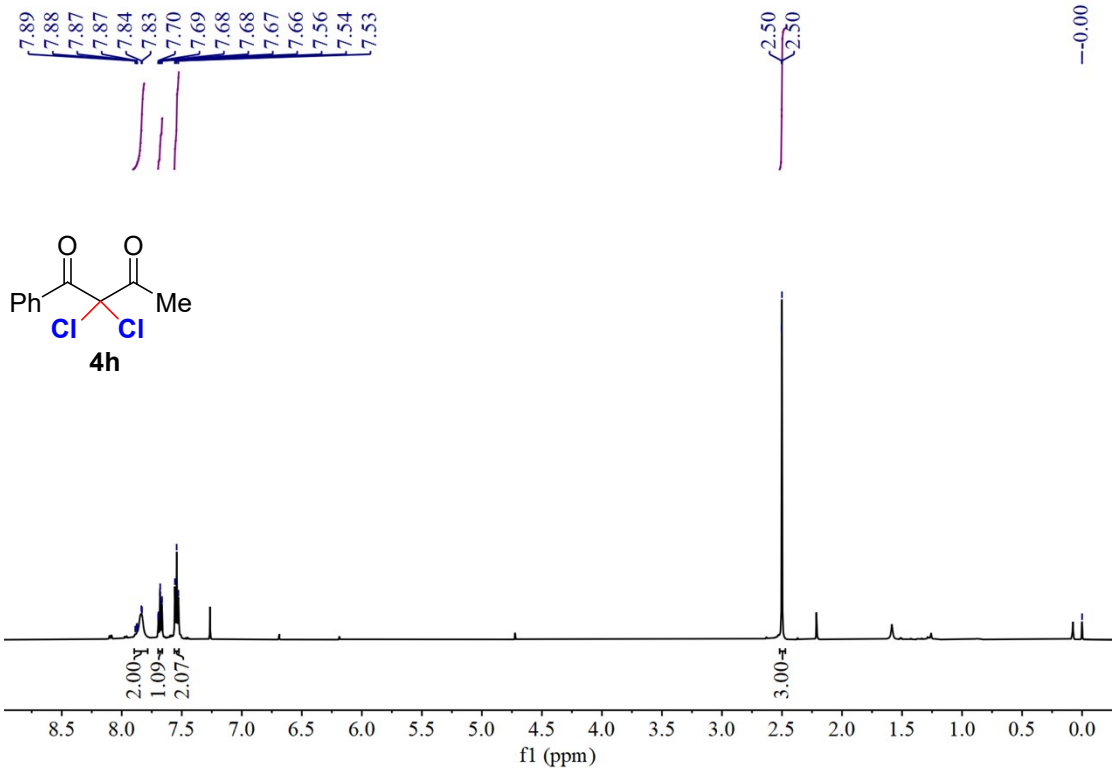
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **4g**



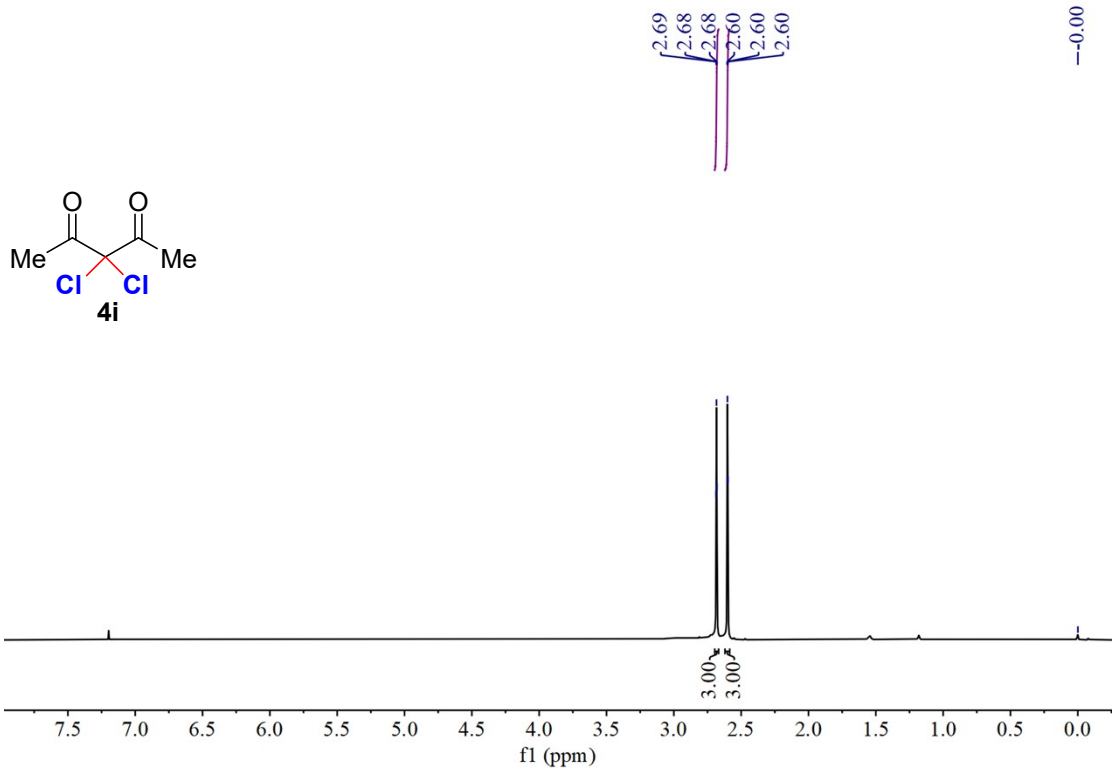
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **4g**



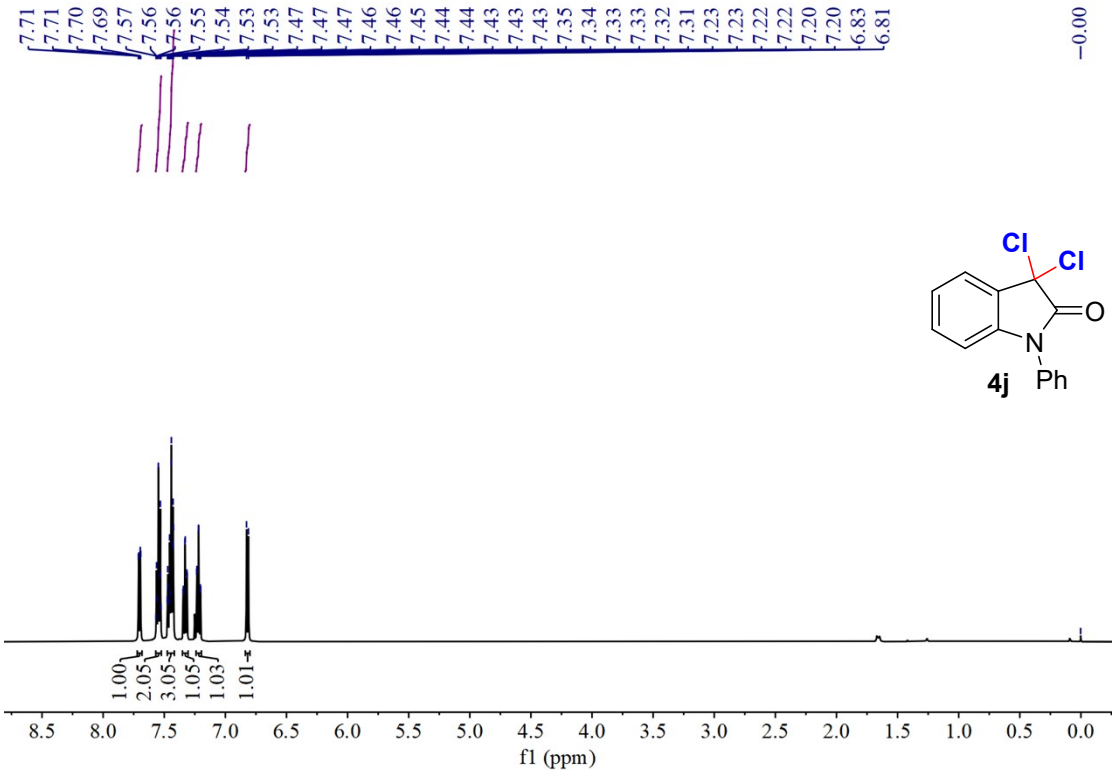
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **4h**



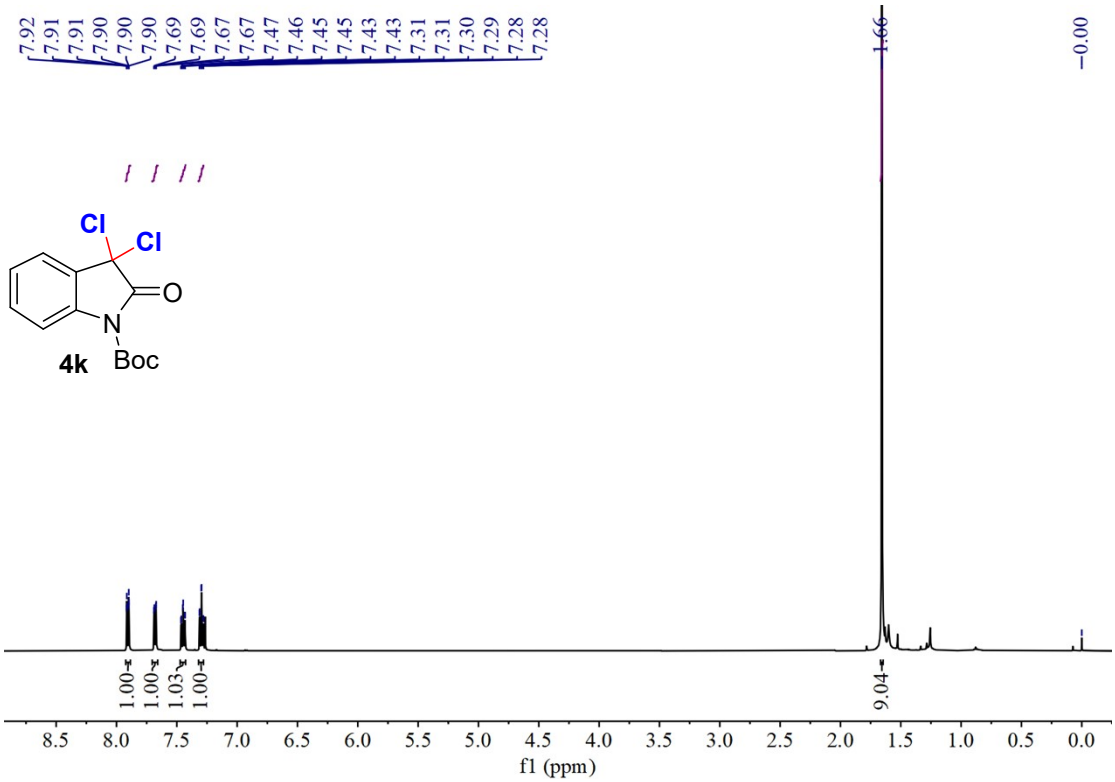
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **4i**



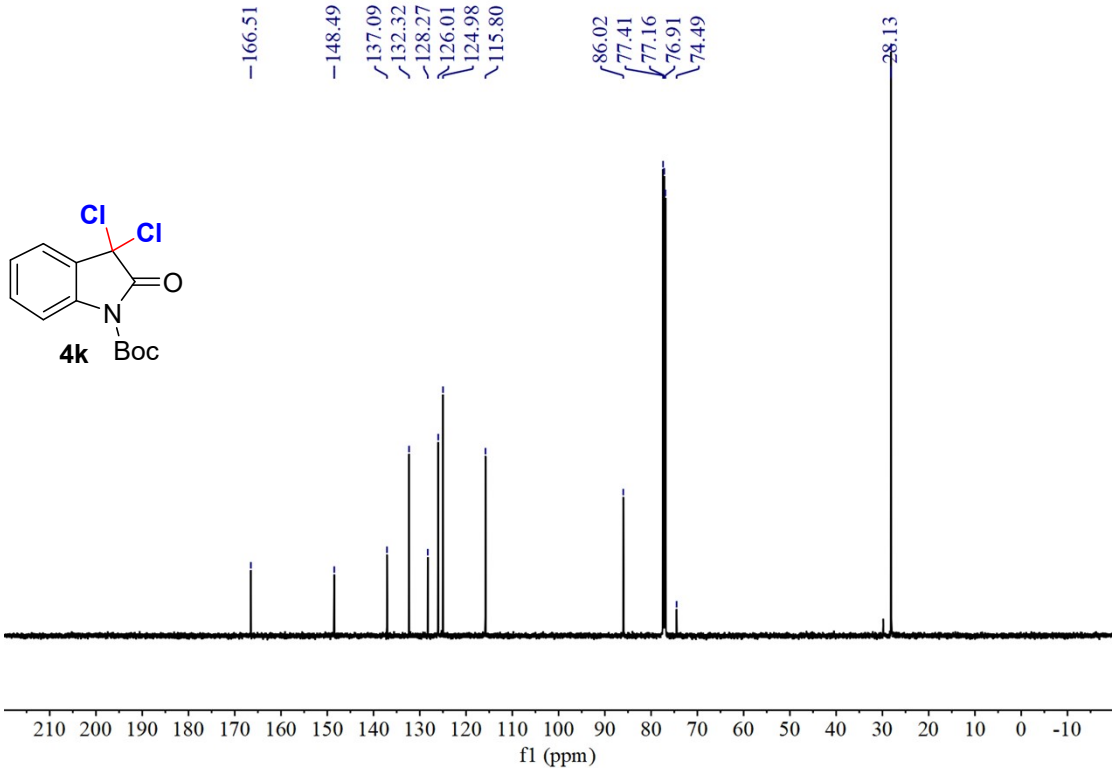
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **4j**



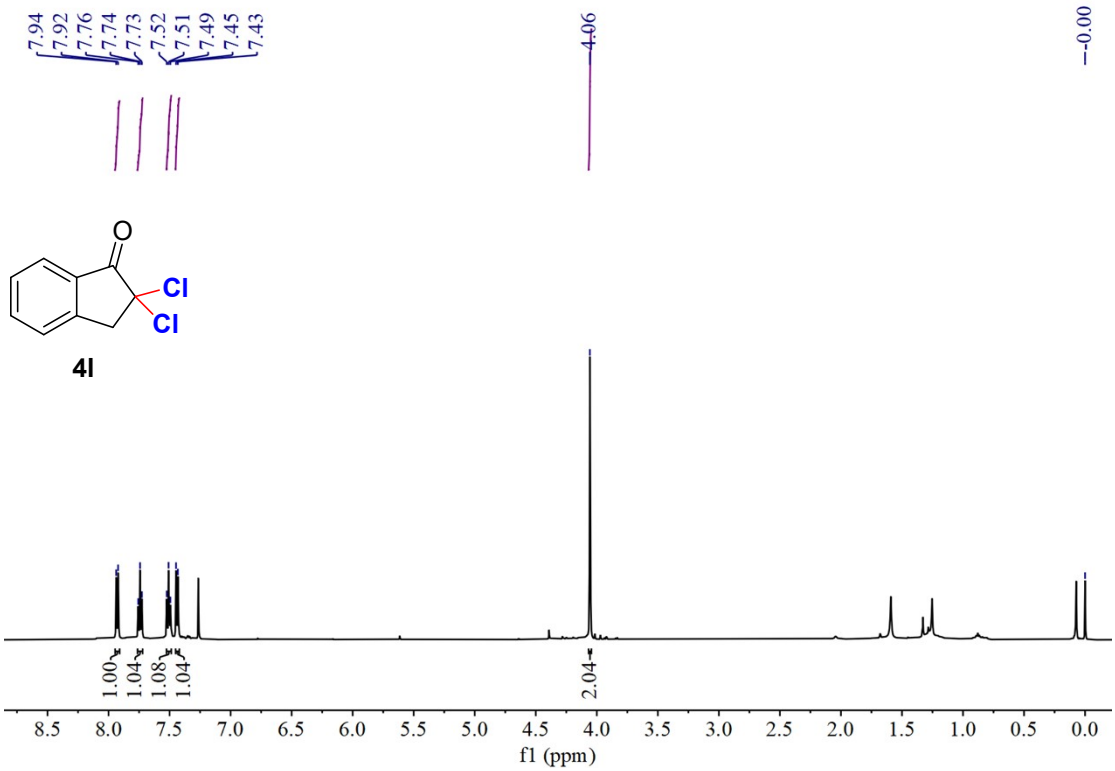
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **4k**



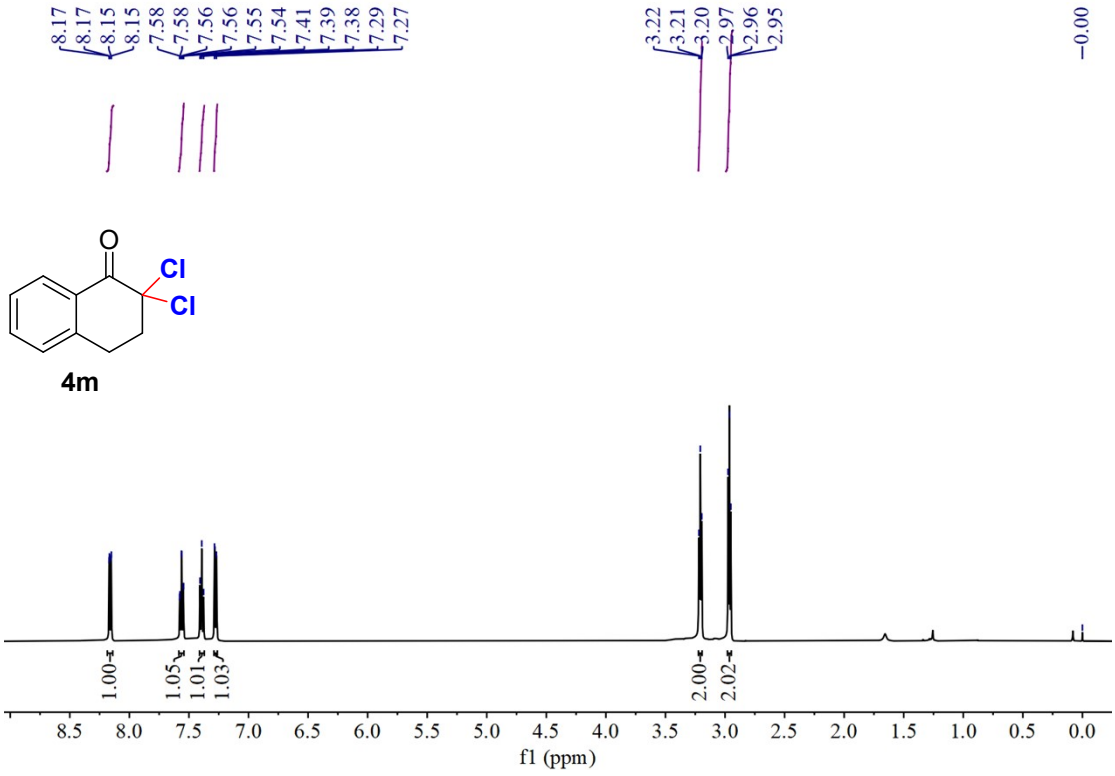
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **4k**



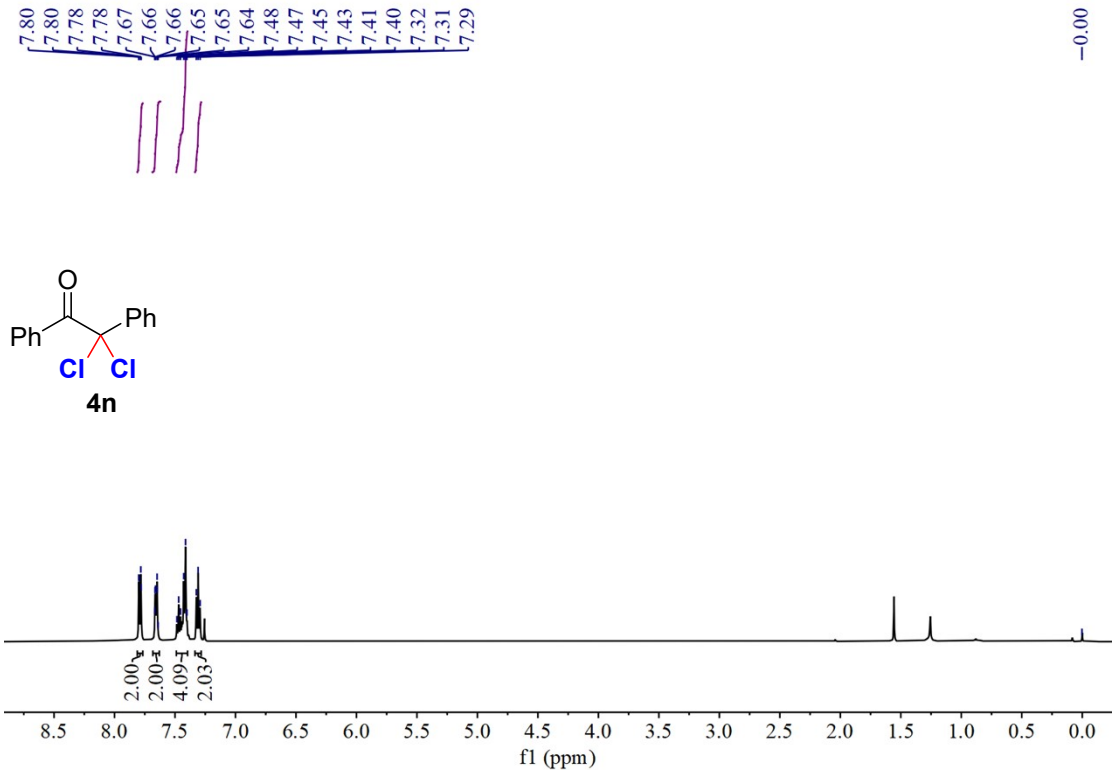
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **4l**



^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **4m**

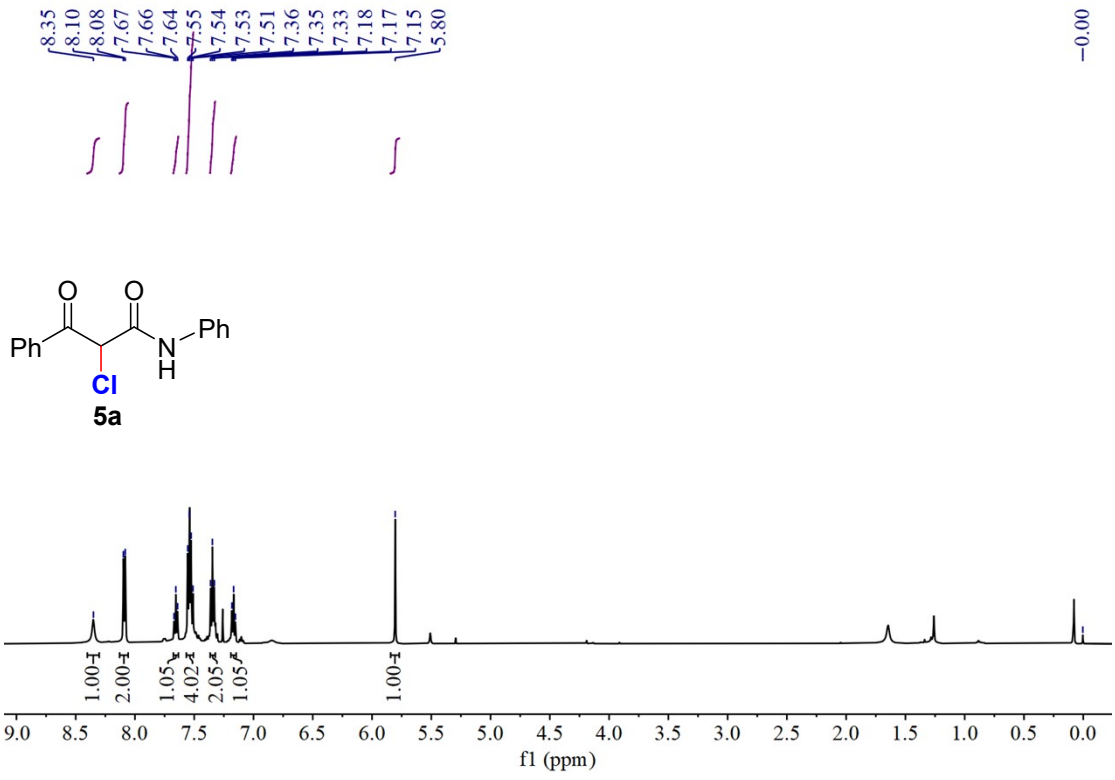


^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **4n**



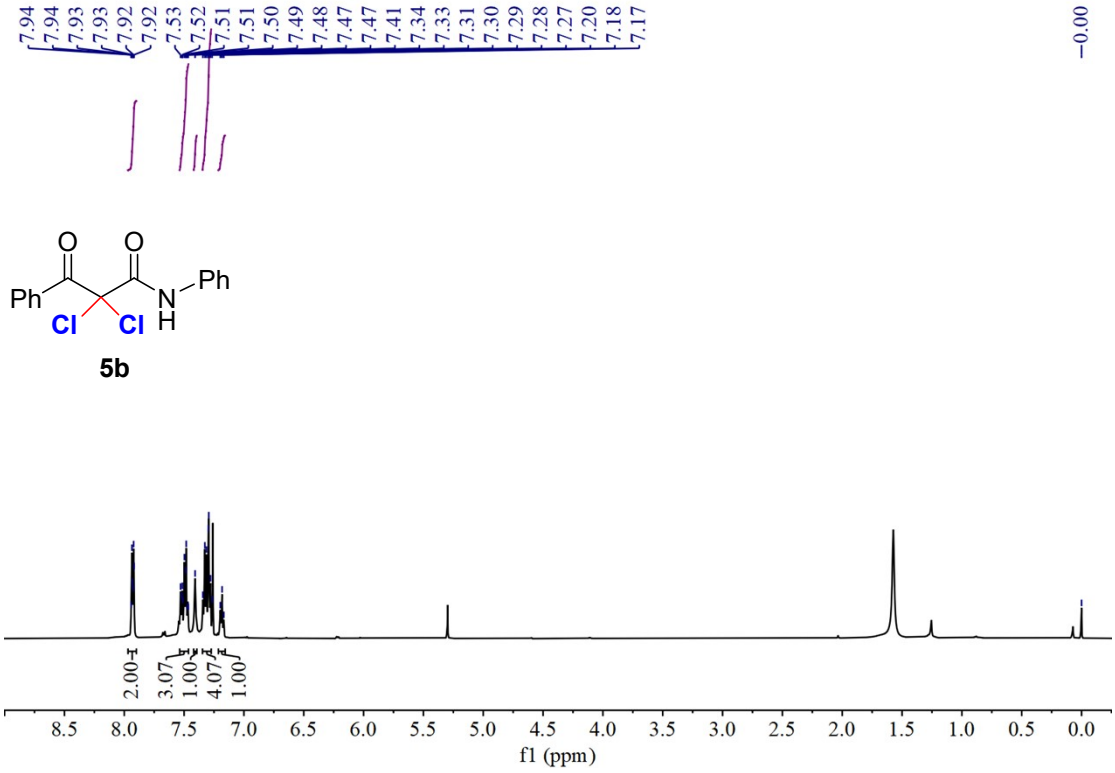
4n

^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **5a**



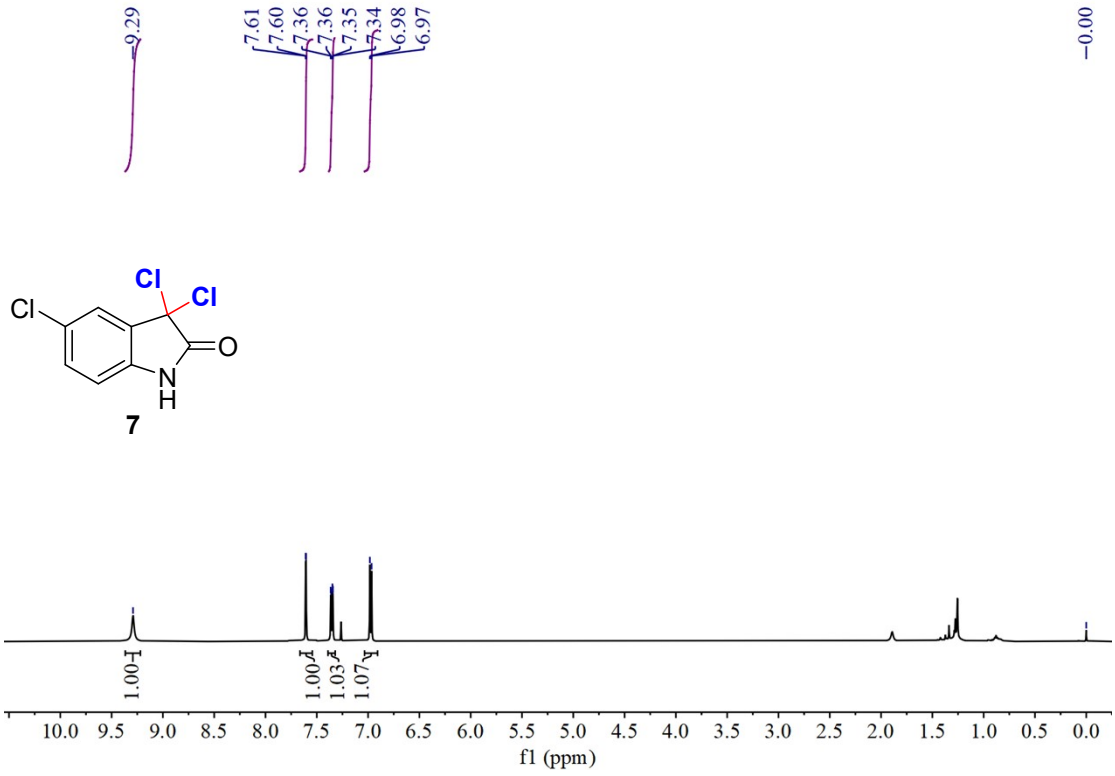
5a

^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **5b**



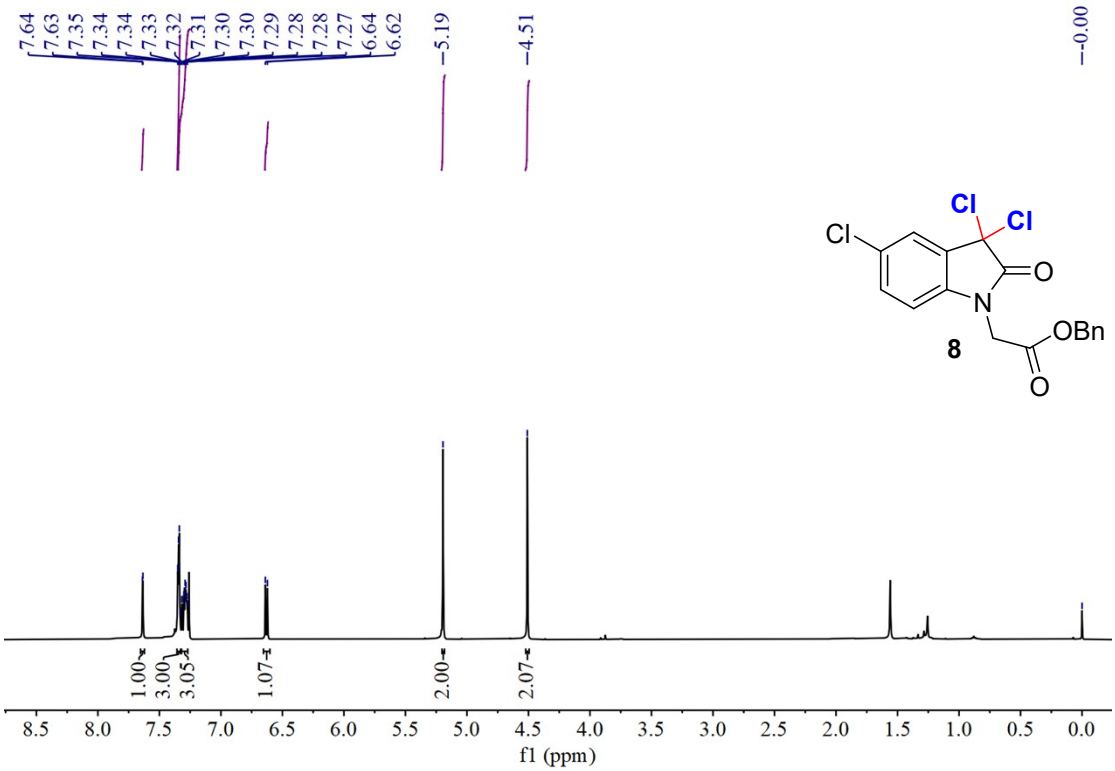
5b

^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **7**

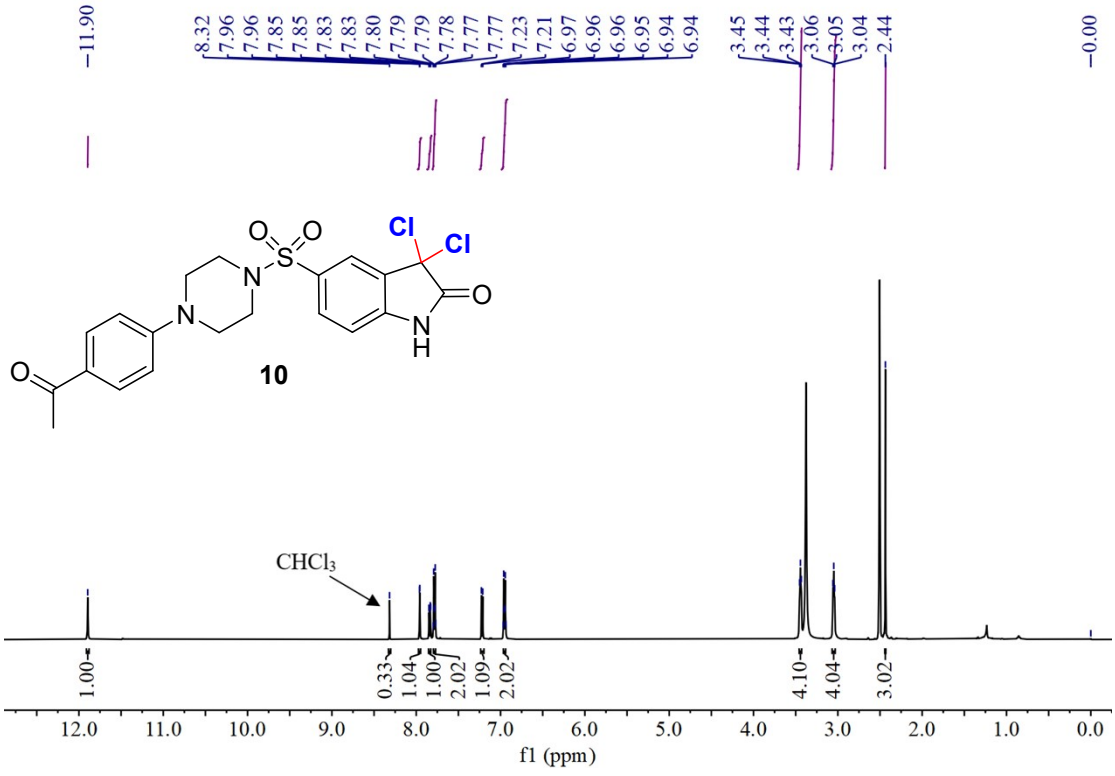


7

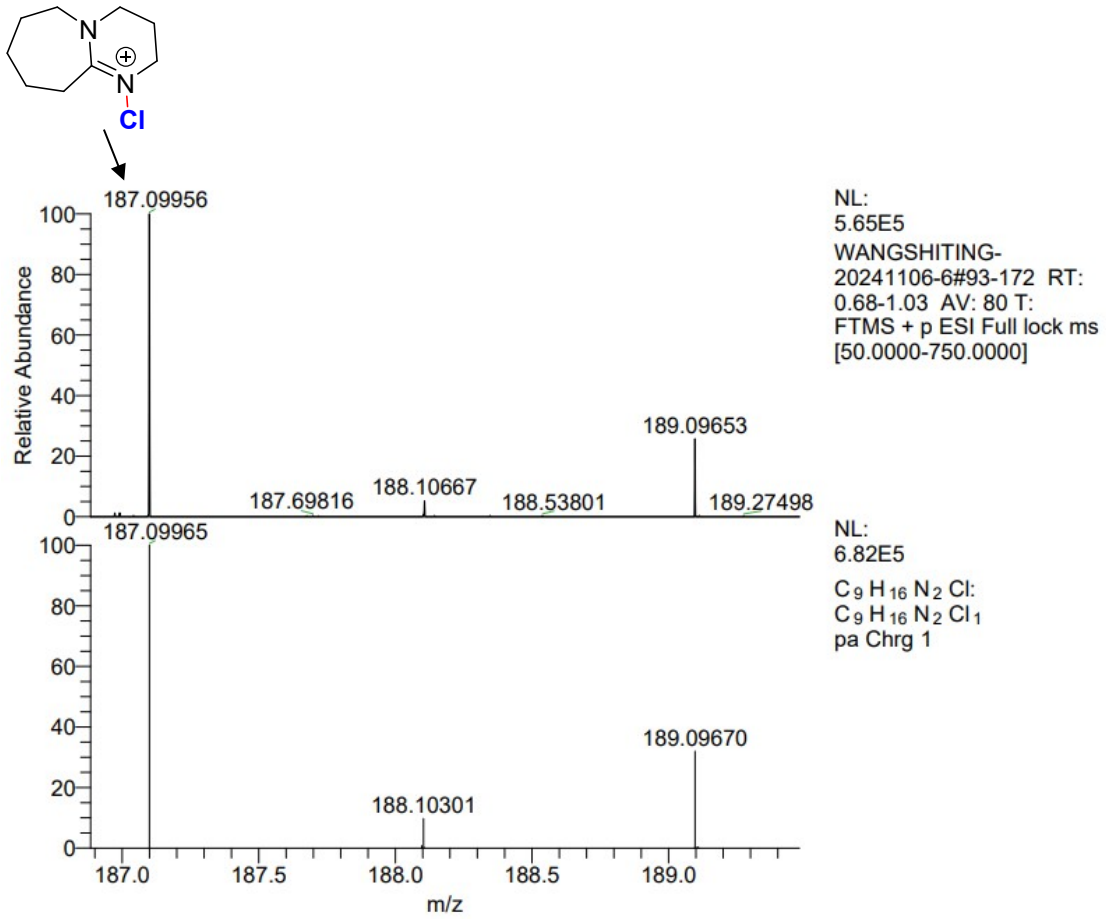
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **8**



^{1}H NMR (500 MHz, DMSO) spectrum of **10**



11. HRMS Spectrum of Intermediate B



12. References

[1] (a) J. E. Taylor, M. D. Jones, J. M. J. Williams and S. D. Bull, Friedel−Crafts Acylation of Pyrroles and Indoles using 1, 5-Diazabicyclo [4.3. 0] non-5-ene (DBN) as a Nucleophilic Catalyst. Org. Lett., 2010, **12**, 5740; (b) T. A. Moss, D. R. Fenwick and D. J. Dixon, Enantio-and diastereoselective catalytic alkylation reactions with aziridines. J. Am. Chem., Soc. 2008, **130**, 10076.

[2] M. R. Smith, H. S. Rzepa, A. J. P. White, D. Billen and K. K. Hii, Delineating origins of stereocontrol in asymmetric Pd-catalyzed α-hydroxylation of 1, 3-ketoesters. J. Org. Chem., 2010, **75**, 3085.

[3] D. Guijarro and M. Yus, Synthesis of substituted cyclopropanes from 1, 3-diols through the corresponding cyclic sulfates. Tetrahedron, 1995, 51, 11445.

[4] K. Dechira, A. Taleb, A. Benmaati and H. H. Zahmani, Eco-friendly Access to β-ketoamides: One-step Catalyst-and Solvent-free Amidation of β-ketoesters Under Microwave Irradiation. Orent. J. Chem., 2018, **34**, 152.

[5] (a) C. D. Fusco, S. Meninno, C. Tedesco and A. Lattanzi, Enantioselective α-hydroxylation of β-ketoamides. Org. Biomol. Chem., 2013, **11**, 896; (b) C. X. Pan, X. H. Zeng, Y. F. Guan, X. L. Jiang, L. Li and H. B. Zhang, Design and synthesis of brazilin-like compounds. Synlett, 2011, **2011**, 425.

[6] S. Santra, U. Maji and J. Guin, Enantioselective α-amination of acyclic 1, 3-dicarbonyls catalyzed by N-heterocyclic carbene. Org. Lett., 2020, **22**, 468.

[7] P. Li, X. Wang, G. Wang, L. Zhao, Y. Hong, X. Hu, F. Zi and H. Cheng, Synthesis and evaluation of ion-imprinted composite membranes of Cr (VI) based on β-diketone functional monomers. RSC Advances, 2021, **11**, 38915.

[8] A. Bertogg, L, Hintermann, D. P. Huber, M. Perseghini, M. Sanna and A. Togni, Substrate range of the titanium TADDOLate catalyzed asymmetric fluorination of activated carbonyl compounds. Helv. Chim. Acta., 2012, **95**, 353.

[9] (a) J. Groβkopf, A. A. Heidecker and T. Bach, Photochemical Deracemization of 3-Substituted Oxindoles. Angew. Chem. Int. Ed., 2023, **62**, e202305274; (b) D. P. Phillips, A. R. Hudson, B. Nguyen, T. L. Lau, M. H. McNeill, J. E. Dalgard, J. H.

Chen, R. J. Penuliar, T. A. Miller and L. Zhi, Copper-catalyzed N-arylation of oxindoles. Tetrahedron Lett., 2006, **47**, 7137; (c) J. T. Xia and X. P. Hu, Copper-catalyzed asymmetric propargylic alkylation with oxindoles: diastereo-and enantioselective construction of vicinal tertiary and all-carbon quaternary stereocenters. Org. Lett., 2020, **22**, 1102.

[10] Z. Li and V. Gevorgyan, Double duty for cyanogen bromide in a cascade synthesis of cyanoepoxides. Angewandte Chemie International Edition. Angew. Chem. Int. Ed., 2011, **50**, 2808.

[11] M. Kirihara, S. Ogawa, T. Noguchi, K. Okubo, Y. Monma, I. Shimizu, R. Shimosaki, A. Hatano and Y. Hirai, Chemoselective bromination of active methylene and methyne compounds by potassium bromide, hydrochloric acid and hydrogen peroxide. Synlett, 2006, **2006**, 2287.

[12] Z. Jiao, J. J. Beiger, Y. Jin, S. Ge, J. Zhou, and J. F. Hartwig, Palladium-catalyzed enantioselective α-arylation of α-fluoroketones. J. Am. Chem. Soc., 2016, **138**, 15980.

[13] S. De, M. K. Das, S. Bhunia and A. Bisai, Unified Approach to the Spiro (pyrrolidinyl-oxindole) and Hexahydropyrrolo [2, 3-b] indole Alkaloids: Total Syntheses of Pseudophrynamines 270 and 272A. Org. Lett., 2015, **17**, 5922.

[14] Y. K. Kang, H. H. Kim, K. O. Koh and D. Y. Kim, Catalytic enantioselective chlorination of cyclic β-keto esters in the presence of chiral Pd (II) complexes. Tetrahedron Lett., 2012, **53**, 3811.

[15] M. Majdecki, P. Grodek and J. Jurczak, Stereoselective α-Chlorination of β-Keto Esters in the Presence of Hybrid Amide-Based Cinchona Alkaloids as Catalysts. J. Org. Chem., 2021, **86**, 995.

[16] R. Akula, M. Galligana and H. Ibrahim, Umpolung of halide reactivity: efficient (diacetoxyiodo) benzene-mediated electrophilic α-halogenation of 1, 3-dicarbonyl compounds. Chem. Commun., 2009, 6991.

[17] X. Li, B. Wang, D. Li, J. Zhao, J. Qu and Y. Zhou, KI-Mediated Chlorine Gas-Free Synthesis of 3,3-Dichloro-2-oxindole Derivatives. Eur. J. Org. Chem., 2023, **26**, e202201452.

[18] T. Zheng, Z. Li, Y. Luo, J. Zhang and J. Xu, A direct and efficient 3-halooxidation of indoles using DMSO as oxygen source. Tetrahedron, 2023, **133**, 133274.

[19] S. Ma, X. Q. Han, S. Krishnan, S. C. Virgil and B. M. Stoltz, Catalytic Enantioselective Stereoablative Alkylation of 3-Halooxindoles: Facile Access to Oxindoles with C3 All-Carbon Quaternary Stereocenters. Angew. Chem. Int. Ed., 2009, **48**, 8037.

[20] H. F. Shi, J. R. Zhang, X. M. Li, J. He, Y. Sun, J. Wu and Y. Du, Thianthrene/TfOH-catalyzed electrophilic halogenations using N-halosuccinimides as the halogen source. *Chem. Sci.*, **2024**, *15*, 13058.

[21] K. M. Aitken and R. Alan Aitken, Rearrangement during halogenation of 2-hydroxy-1,2-diphenylpropan-1-one (α-methylbenzoin). Tetrahedron, 2008, **64**, 5217.

[22] N. Shariff, S. Mathi, C. Rameshkumar and L. Emmanuvel, Tetrabutylammonium dichlorobromide: an efficient and mild reagent for geminal bromochlorination of α-diazo carbonyl compounds. Tetrahedron Lett., 2015, **56**, 934.

[23] M. L. Meketa, Y. R. Mahajan and S. M. Weinreb, An efficacious method for the halogenation of β-dicarbonyl compounds under mildly acidic conditions. Tetrahedron Lett., 2005, **46**, 4749.

[24] D. W. Tu, J. Luo, W. G. Jiang and Q. Tang, Solvent-free preparation of α,α-dichloroketones with sulfuryl chloride. Tetrahedron Lett., 2021, **81**, 153335.

[25] K. Shibatomi, H. Yamamoto, Stereoselective synthesis of α,α-chlorofluoro carbonyl compounds leading to the construction of fluorinated chiral quaternary carbon centers. Angew. Chem. Int. Ed., 2008, **47**, 5796.

[26] J. S. Tao, T. N. Tuck and G. K. Murphy, Geminal dichlorination of phenyliodonium ylides of β-dicarbonyl compounds through double ligand transfer from (dichloroiodo) benzene. Synthesis, 2016, **48**, 772.

[27] Y. J. Mei, P. A. Bentley and J. Du, Thiourea catalysis of NCS in the synthesis of α-chloroketones. Tetrahedron Lett., 2008, **49**, 3802.

[28] V. Giannopoulos and I. Smonou, Asymmetric Reduction of α,α-Dichloro-β-Keto Esters by NADPH-Dependent Ketoreductases. Eur. J. Org. Chem., 2022, e202200410.

[29] Y. Peng, Z. Wang, Y. Chen, W. Xu, Y. Hu, Z. Chen, J. Xu and Q. Wu, Photoinduced Promiscuity of Cyclohexanone Monooxygenase for the Enantioselective Synthesis of α-Fluoroketones. Angew. Chem. Int. Ed., 2022, **61**, e202211199.

[30] J. A. Nobrega, S. M. C. Gonçalves and C. Peppe, Selective Preparation of α, α-dichloroketones with Copper (II) chloride. Synthetic Commun., 2002, **32**, 3711.

[31] I. Pravst, M. Zupan and S. Stavber, Halogenation of ketones with N-halosuccinimides under solvent-free reaction conditions. Tetrahedron, 2008, **64**, 5191.

[32] A. J. Hodgkinson and B. Staskun, Conversion of 2,2-dichloroacetoacetanilides into 4-(hydroxymethyl)-2 (1H)-quinolones. J. Org. Chem., 1969, **34**, 1709.

[33] Y. X. Jian, P. Liang, X. Y. Li, H. Shao and X. Ma, Controllable transformation of indoles using iodine (iii) reagent. Org. Biomol. Chem., 2023, **21**, 179.

[34] J. Xiao, W. Westbroek, O. Motabar, W. A. Lea, X. Hu, A. Velayati, W. Zheng, N. Southall, A. M. Gustafson, E. Goldin, E. Sidransky, K. Liu, A. Simeonov, R. J. Tamargo, A. Ribes, L. Matalonga, M. Ferrer and J. J. Marugan, Controllable transformation of indoles using iodine (iii) reagent. J. Med. Chem., 2012, **55**, 7546.