Supporting Information

Visible-light-induced regioselective amideperoxidation of alkenes

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Contents

General experimental information

Commercial reagents were used without further purification. Oxime esters, cyanoarene-based photocatalyst were prepared based on literature procedures. The light source used for illuminating the reaction vessel consists of blue LEDs (λmax = 420 nm) purchased from Taobao (https://shop35740806.taobao.com/). A clip fan was placed over the reaction vials to cool down the reaction system during the whole process of the reaction. The ^{1}H NMR spectra were recorded at 400 MHz or 500 MHz. The ^{13}C NMR spectra were recorded at 100 MHz or 125 MHz. The ^{19}F NMR spectra were recorded at 376 MHz. Chemical shifts were expressed in parts per million (δ), and were reported as s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), m (multiplet), brs (broad singlet), etc. The coupling constants J were given in Hz. High resolution mass spectra (HRMS) were obtained via ESI mode by using a MicrOTOF mass spectrometer. The conversion of starting materials was monitored by thin layer chromatography (TLC) using silica gel plates (silica gel 400 mesh), and components were visualized by observation under UV light (254 and 365 nm).

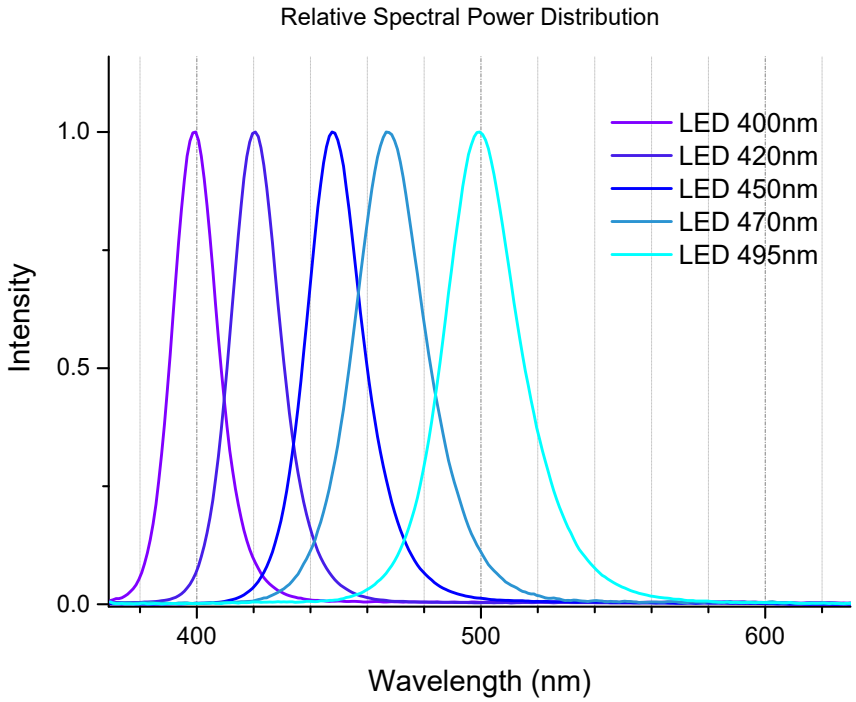
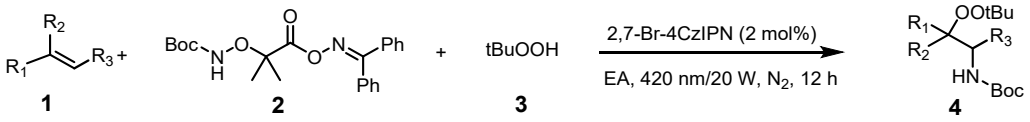


Figure S1. Emission spectra of the used light sources

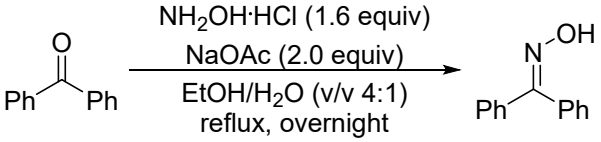
General procedure for peroxylfunctionalization of alkenes



In 15 ml Schlenk tube equipped with a stirring bar, oxime ester (**2**, 0.6 mmol, 240 mg), alkene (0.4 mmol, 1.0 equiv., if solid) and 2,7-Br-4CzIPN (2 mol%) were charged under air, then Schlenk tube was evacuated and re-filled with N_2 for three times. EtOAc (4.0 mL, 0.1 M), appropriate alkene (0.4 mmol, 1.0 equiv., if liquid) and tBuOOH (1.2 mmol, 108 mg) were added under N_2 counter flow. The Schlenk tube was tightly sealed and stirred under irradiation with 20 W blue LEDs (λ_{max} = 420 nm) using the described set-up at room temperature for 12 hours. After irradiation, the resulting homogenous solution was transferred to a 50 mL round bottom flask with aid of EtOAc (3 × 5 mL). SiO_2 were added to this solution and the volatiles were removed under reduced pressure, affording a powder which was loaded on column. Purification by flash column chromatography on SiO_2, using PE: EtOAc mixtures afforded the corresponding peroxyl-functionalization products.

Preparation of Starting Materials

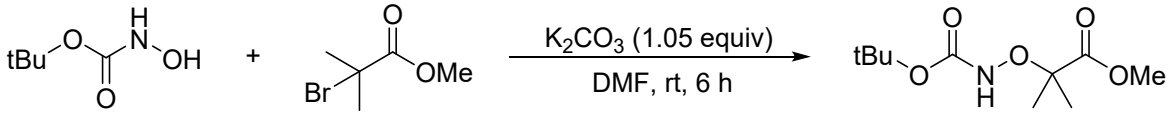
General procedure for the preparation of oxime



Following a literature report.[S1] In a 250 mL round-bottom flask equipped with a condenser, aromatic ketones (9.1 g, 50 mmol, 1.0 equiv.) were dissolved in the EtOH/H_2O mixture (v/v 4:1, 125 mL). Then, hydroxylamine hydrochloride (5.52 g, 80 mmol, 1.6 equiv.) and NaOAc (8.2 g, 100 mmol, 2.0 equiv.) were added in one portion. The reaction mixture was refluxed (oil bath) overnight and the consumption of the starting material was monitored by TLC. After the. transformation completed, the reaction was cooled to room temperature and concentrated under reduced pressure to remove ethanol as much as possible. Then the obtained white solid was diluted with and brine, extracted with ethyl acetate (80 mL × 3) and dried over anhydrous $MgSO_4$. Evaporation of the solvent afforded the product in quantitative yield. This product was sufficiently pure as determined by NMR and was used without further purification for the preparation of oxime ether or ester.

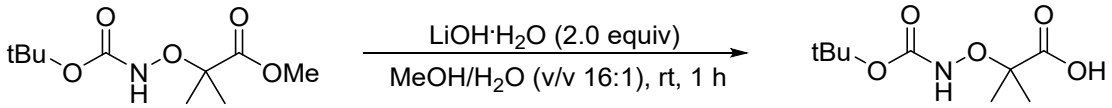
Note: The oximes did not show appreciable decomposition when stored in the fridge at -20 °C.

General procedure for the preparation of α-oxyester



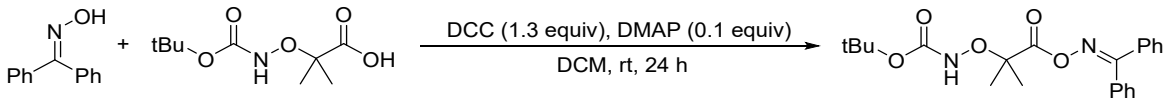
Following a literature report.[S2] Treat a solution of tert-butyl hydroxycarbamate (5.3 g, 40 mmol, 1.0 equiv.) in DMF (10 mL) with K_2CO_3 (5.8 g, 42 mmol, 1.05 equiv.) and methyl 2-bromo-2-methylpropanoate (7.6 g, 42 mmol, 1.05 equiv.). Stir the reaction mixture at room temperature for 6 h. The mixture was filtered through a piece of filter paper washing with DCM (100 mL). Then the mixed liquid was extracted with brine (40 mL × 3). After the organic phase dried over anhydrous MgSO4, the solvent was removed under reduced pressure, and then the residue was purified by flash column chromatography (PE/EA = 50:1) to afford α-oxyester (6.9 g, yield 74%).

General procedure for the preparation of 2-methylpropanoic acid



Following a literature report.[S2] The α-oxyester (6.9 g, 29.6 mmol, 1.0 equiv.) was solubilised in MeOH/H_2O (296 mL, 0.1 M, v/v = 16:1) and treated with LiOH·H_2O (2.5 g, 59.2 mmol, 2.0 equiv.). The reaction was stirred at rt for 1 h. The mixture was evaporated and diluted with EtOAc and 1 N HCl until pH = 2. The layers were separated and the aqueous layer was extracted with EtOAc. The combined organic layers were dried over anhydrous $MgSO_4$. Evaporation of the solvent afforded the product in quantitative yield (6.5 g). This product was sufficiently pure as determined from NMR and was used without further purification for the preparation of 2-methylpropanoic acid.

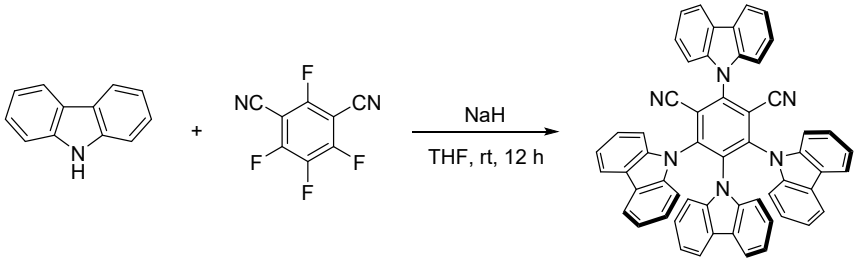
General procedure for the preparation of oxime ester 2



Following a literature report.[S2] Ketoxime esters were prepared following a previously reported procedure. Ketoxime (394 mg, 2.0 mmol) from previous step and aliphatic carboxylic acid (338 mg, 2.0 mmol) were dissolved in CH_2Cl_2 (20 mL). The reaction bath is lowered to 0 °C in a low-temperature stirring reaction bath. Then, DCC (536 mg, 2.6 mmol, 1.3 equiv.) and DMAP (10 mol%, 24.4 mg, 0.2 mmol) was added sequentially. The mixture was stirred at room temperature under argon atmosphere until the reaction was complete as monitored by TLC analysis. The mixture was diluted with distilled water (25 mL) and the DCM layer was separated, dried over anhydrous Na_2SO_4 and concentrated. The crude mass was treated with pentane (3 mL) and sonicated for 15 minutes. The resultant solid was filtered and dried under vacuum to obtain the pure oxime esters. In some cases, final compound 6a was purified by flash column chromatography using PE/EA as eluent.

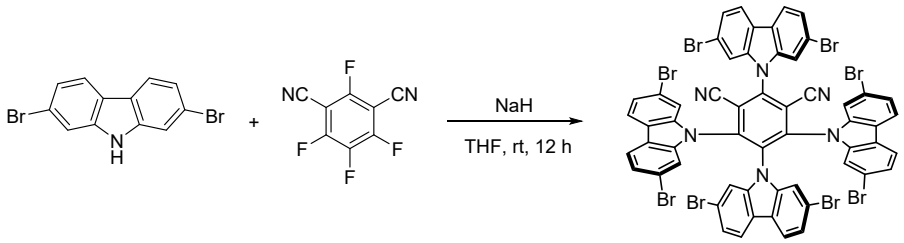
Note: oxime ester **2** did not show appreciable decomposition when stored in the fridge at 4 °C.

2,4,5,6-Tetrakis(carbazole-9-yl)-4,6-dicyanobenzene (Exemplified by 4CzIPN)



Sodium hydride (60% suspension in mineral oil, 300 mg, 7.5 equiv) was added slowly to a stirred solution of carbazole (835 mg, 5 mmol, 5.0 equiv) in dry THF (100 mL, 0.05 M) under a N_2 atmosphere at rt.[S3] After 30 min, 2,4,5,6- tetrafluoroisophthalonitrile (200 mg, 1 mmol, 1.0 equiv) was added. After stirring at rt for 12 h, 2 mL water was added to the reaction mixture to quench the excess of NaH. The resulting mixture was then concentrated under reduced pressure. The crude product was purified by recrystallization from PE/DCM then filtered. The brown liquid filtrate was concentrated and recrystallized as before. The combined solids were then purified by column chromatography on silica gel with PE/DCM as eluent to give 4CzIPN as bright yellow powder (584 mg, 74%).

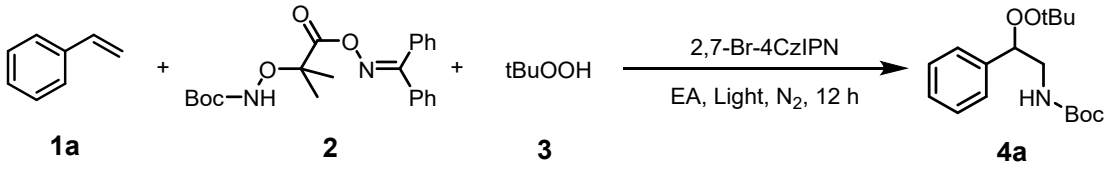
2,4,5,6-tetrakis (2,7-dibromo-9H-carbazol-9-yl) isophthalonitrile (2,7-Br-4CzIPN)



Following our previously reported procedure.[S4] Sodium hydride (60% suspension in mineral oil, 300 mg, 7.5 equiv.) was added slowly to a stirred solution of 2,7-Dibromo-9H-carbazole (1.625 g, 5 mmol, 5.0 equiv) in dry THF (100 mL, 0.05 M) under a N_2 atmosphere at rt. After 2 h, 2,4,5,6-tetrafluoroisophthalonitrile (200 mg, 1.0 mmol, 1.0 equiv) was added. After stirring at rt for 12 h, 2 mL water was added to the reaction mixture to quench the excess of NaH. The resulting mixture was then concentrated under reduced pressure. The solid residue was washed with H_2O, EtOH and acetone to yield 2,4,5,6-tetrakis(2,7-dibromo-9H-carbazol-9- yl)isophthalonitrile (2,7-Br-4CzIPN) as a greenish yellow solid (1.31 g, 93%).

Optimization of the reaction conditions

Table S1. Screening of reaction conditions 1

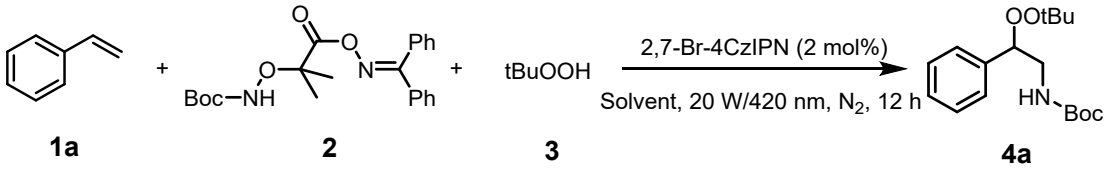


1a **2** **3** **4a**

Entry	Photocatalyst	Light	Yield (%)
1	2,7-Br-4CzIPN /2 mol%	36W/450nm	43
2	2,7-Br-4CzIPN /2 mol%	20W/450nm	42
3	2,7-Br-4CzIPN /2 mol%	10W/450nm	38
4	2,7-Br-4CzIPN /2 mol%	5W/450nm	16
5	2,7-Br-4CzIPN /2 mol%	20W/495nm	6
6	2,7-Br-4CzIPN /2 mol%	20W/470nm	43
7	2,7-Br-4CzIPN /2 mol%	20W/450nm	59
8	2,7-Br-4CzIPN /2 mol%	20W/420nm	67
9	2,7-Br-4CzIPN /2 mol%	20W/400nm	66
10	2,7-Br-4CzIPN /0.5 mol%	20W/420nm	49
11	2,7-Br-4CzIPN /1 mol%	20W/420nm	58
12	2,7-Br-4CzIPN /4 mol%	20W/420nm	56
13	4CzIPN /2 mol%	20W/450nm	27
14	$[Ru(bpy)_3](PF_6)_2$ /2 mol%	20W/450nm	0
15	3DPAFIPN /2 mol%	20W/450nm	0
16	/	20W/420nm	0
17	2,7-Br-4CzIPN /2 mol%	/	0

[a] Reaction conditions: **1a** (0.4 mmol), **2** (0.8 mmol), tBuOOH (5−6 M in decane, 1.6 mmol, 4.0 equiv) in 4 mL dry EA under an N_2 atmosphere at room temperature. [b] Yields were determined by ^1H NMR with 1,3,5-trimethoxy-benzene as an internal standard.

Table S2. Screening of reaction conditions 2

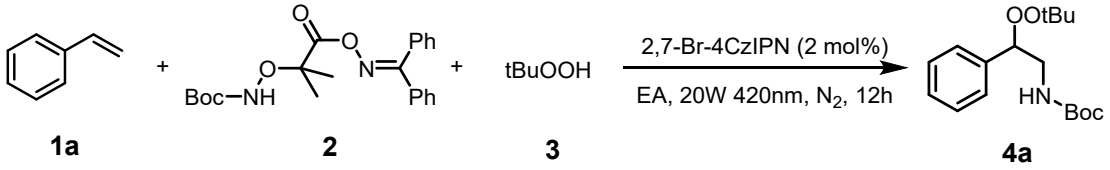


1a **2** **3** **4a**

Entry	Solvent	Equiv	Molarity	Yield (%)
1	EA	1:2:4	0.1 M	67
2	EA	2:1:4	0.1 M	24
3	EA	1:1.5:3	0.1 M	72
4	EA	1:1.25:2.5	0.1 M	61
5	EA	1:1.5:3	0.05 M	55
6	EA	1:1.5:3	0.2 M	59
7	THF	1:1.5:3	0.1 M	9
8	DCE	1:1.5:3	0.1 M	21
9	MeCN	1:1.5:3	0.1 M	16
10	DMSO	1:1.5:3	0.1 M	trace
11	DME	1:1.5:3	0.1 M	12
12	DCM	1:1.5:3	0.1 M	31
13	Dioxane	1:1.5:3	0.1 M	23
14	EtOH	1:1.5:3	0.1 M	13
15	Acetone	1:1.5:3	0.1 M	37
16	Toluene	1:1.5:3	0.1 M	43
17	DMF	1:1.5:3	0.1 M	30
18	DMC	1:1.5:3	0.1 M	55

[a] Reaction conditions: **1a** (0.4 mmol), **2** and tBuOOH (5−6 M in decane) in dry solvent under an N_2 atmosphere at room temperature. [b] Yields were determined by ^{1}H NMR with 1,3,5-trimethoxy-benzene as an internal standard.

Table S3. Screening of reaction conditions 3

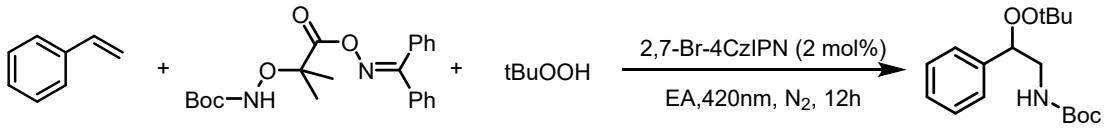


1a 2 3 4a

Entry	variation from the standard conditions	Yield (%)
1	EA (add 0.2 mL H_2O)	72
2	use 70% aq **3**	72
3	air instead of N_2	22

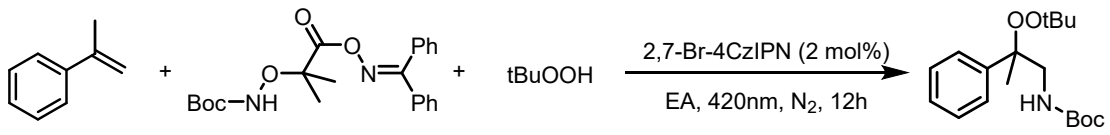
[a] standard conditions: 1a (0.4 mmol), 2 (0.6 mmol), tBuOOH (1.2 mmol, 5−6 M in decane), and 2,7-Br-4CzIPN (0.008 mmol) under irradiation of 20 W/420 nm LED in N_2 at room temperature for 12 h. [b] Yields were determined by ^{1}H NMR with 1,3,5-trimethoxy-benzene as an internal standard.

Procedure of Gram-Scale Experiment



1a 10 mmol | **2** 15 mmol | **3** 30 mmol | **4a** 2.02 g, 65% yield

In 250 ml Schlenk tube equipped with a stirring bar, oxime ester **2** (15 mmol, 1.5 equiv, 6 g), and 2,7-Br-4CzIPN (2 mol%, 282.4 mg) were charged under air, then Schlenk tube was evacuated and re-filled with N_2 for three times. Dry EtOAc (100 mL, 0.1 M), styrene **1a** (10 mmol, 1.0 equiv.,1.04 g) and tBuOOH (30 mmol, 2.70 g) were added under N_2 counter flow. The Schlenk tube was tightly sealed and stirred under irradiation with 20 W blue LEDs (λ_{max} = 420 nm) at room temperature for 12 hours. After irradiation, the crude product was purified by column chromatography isolation on silica gel (petroleum ether: ethyl acetate = 40:1 v/v) to afford colorless oil tert-butyl (2-(tert-butylperoxy)-2-phenylethyl)carbamate **4a** in 65% yield (2.02 g).



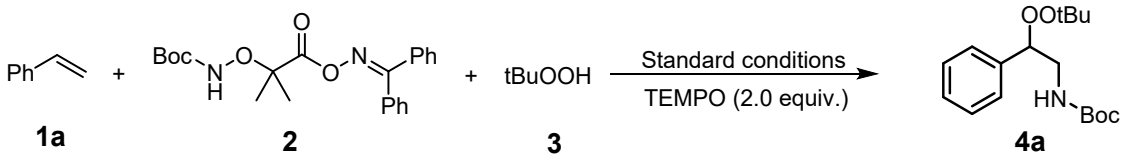
1o 10 mmol | **2** 15 mmol | **3** 30 mmol | **4o** 2.49 g, 77% yield

In 250 ml Schlenk tube equipped with a stirring bar, oxime ester (15 mmol, 1.5 equiv, 6 g), and 2,7-Br-4CzIPN (2 mol%, 282 mg) were charged under air, then Schlenk tube was evacuated and re-filled with N_2 for three times. Dry EtOAc (100 mL, 0.1 M), 2-phenyl-1-propene **1o** (10 mmol, 1.0 equiv.,1.18 g) and tBuOOH (30 mmol, 2.70 g) were added under N_2 counter flow. The Schlenk tube was tightly sealed and stirred under irradiation with 20 W blue LEDs (λ_{max} = 420 nm) at room temperature for 12 hours. After irradiation, the crude product was purified by column chromatography isolation on silica gel (petroleum ether: ethyl acetate = 40:1 v/v) to afford colorless oil tert-butyl (2-(tert-butylperoxy)-2-phenylpropyl)carbamate **4o** in 77% yield (2.49 g).

Mechanistic studies

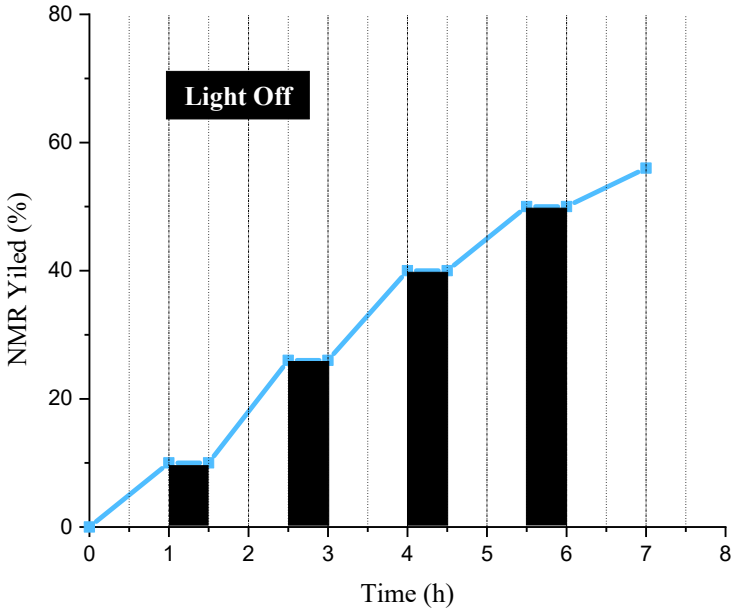
Radical probe experiment

In an 15 ml Schlenk tube equipped with a stirring bar, oxime esters **2** (0.6 mmol), TEMPO (0.8 mmol), and 2,7-Br4CzIPN (0.008 mmol) were charged under air, then the vessel was evacuated and re-filled with N_2 for three times. EtOAc (4.0 mL, 0.1 M), tBuOOH (0.6 mmol) and styrene **1a** (0.4 mmol) were added under N_2 counter flow. The vessel was sealed with the screw cap, then irradiated at 420 nm for 12 hours. After irradiation, the resulting homogenous solution was checked by TLC analysis, the corresponding product cannot be observed.



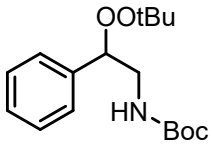
1a **2** **3** **4a**

On/off visible light irradiation experiment



The result indicates that continuous irradiation with visible light should be required in the reaction, and radical-chain propagation is not a key pathway in the present transformation.

Experimental data for the described substances



4a

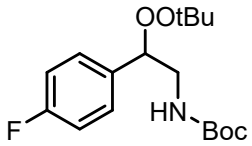
tert-butyl (2-(tert-butylperoxy)-2-phenylethyl)carbamate (4a)

84.0 mg, (PE/EA = 30:1), colorless oil, yield: 68%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.30 (m, 5H), 5.02 (dd, J = 8.0, 4.0 Hz, 1H), 4.88 (brs, 1H), 3.54-3.51 (m, 1H), 3.46-3.40 (m, 1H), 1.43 (s, 9H), 1.23 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 138.9, 128.8, 128.5, 127.3, 85.0, 81.2, 79.8, 45.1, 28.8, 26.8.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{17}H_{27}NNaO_4$: 332.1838, found: 332.1839.



4b

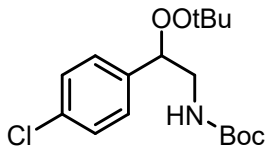
tert-butyl (2-(tert-butylperoxy)-2-(4-fluorophenyl)ethyl)carbamate (4b)

94.2 mg, (PE/EA = 30:1), colorless oil, yield: 72%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31-7.30 (m, 2H), 7.04-7.01 (m, 2H), 4.99 (dd, J = 8.0, 4.0 Hz, 1H), 4.86 (brs, 1H), 3.53-3.48 (m, 1H), 3.40-3.35 (m, 1H), 1.42 (s, 9H), 1.22 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 162.7 (d, $^{1}J_{C\text{-}F}$ = 244.6 Hz), 155.8, 134.5 (d, $^{4}J_{C\text{-}F}$ = 3.6 Hz), 128.7 (d, $^{3}J_{C\text{-}F}$ = 8.1 Hz), 115.4 (d, $^{2}J_{C\text{-}F}$ = 21.7 Hz), 84.1, 80.9, 79.6, 44.7, 28.4, 26.5.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{17}H_{26}FNNaO_4$: 350.1744, found: 350.1740.



4c

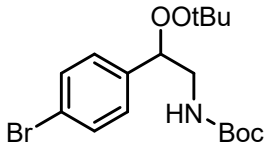
tert-butyl (2-(tert-butylperoxy)-2-(4-chlorophenyl)ethyl)carbamate (4c)

101.6 mg, (PE/EA = 30:1), colorless oil, yield: 74%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32-7.27 (m, 4H), 4.98 (dd, J = 8.0, 4.0 Hz, 1H), 4.85 (brs, 1H), 3.52-3.47 (m, 1H), 3.37-3.32 (m, 1H), 1.42 (s, 9H), 1.22 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 155.9, 137.3, 133.9, 128.7, 128.3, 84.1, 81.0, 79.6, 44.6, 28.5, 26.5.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{17}H_{26}ClNNaO_4$: 366.1448, found: 366.1445.



4d

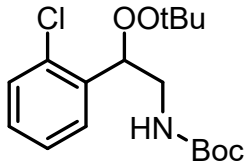
tert-butyl (2-(4-bromophenyl)-2-(tert-butylperoxy)ethyl)carbamate (4d)

123.9 mg, (PE/EA = 30:1), yellow oil, yield: 80%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 8.1 Hz, 2H), 7.23 (d, J = 8.1 Hz, 2H), 4.98 (dd, J = 8.0, 4.0 Hz, 1H), 4.85 (brs, 1H), 3.52-3.46 (m, 1H), 3.37-3.30 (m, 1H), 1.42 (s, 9H), 1.22 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 137.8, 131.6, 128.7, 122.1, 84.1, 81.0, 79.7, 44.6, 28.5, 26.5.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{17}H_{26}BrNNaO_4$: 410.0943, found: 410.0946.



4e

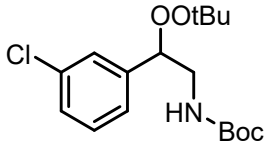
tert-butyl (2-(tert-butylperoxy)-2-(2-chlorophenyl)ethyl)carbamate (4e)

96.1 mg, (PE/EA = 30:1), colorless oil, yield: 70%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 7.3 Hz, 1H), 7.31 (d, J = 7.8 Hz, 1H), 7.24-7.17 (m, 2H), 5.40 (dd, J = 8.0, 4.0 Hz, 1H), 4.81 (brs, 1H), 3.56-3.50 (m, 1H), 3.40-3.33 (m, 1H), 1.37 (s, 9H), 1.22 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 136.4, 132.6, 129.0, 128.4, 128.1, 126.9, 81.5, 81.1, 79.4, 43.3, 28.5, 26.5.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{17}H_{26}ClNNaO_4$: 366.1448, found: 366.1443.



4f

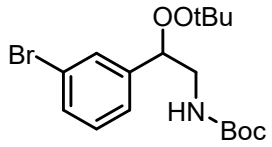
tert-butyl (2-(tert-butylperoxy)-2-(3-chlorophenyl)ethyl)carbamate (4f)

93.3 mg, (PE/EA = 30:1), colorless oil, yield: 68%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (s, 1H), 7.29-7.21 (m, 3H), 4.99 (dd, J = 8.0, 4.0 Hz, 1H), 4.86 (brs, 1H), 3.53-3.48 (m, 1H), 3.36-3.29 (m, 1H), 1.42 (s, 9H), 1.23 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 140.9, 134.4, 129.8, 128.3, 127.1, 125.1, 84.1, 81.1, 79.7, 44.7, 28.5, 26.5.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{17}H_{26}ClNNaO_4$: 366.1448, found: 366.1441.



4g

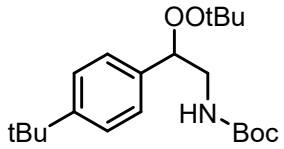
tert-butyl (2-(3-bromophenyl)-2-(tert-butylperoxy)ethyl)carbamate (4g)

105.3 mg, (PE/EA = 30:1), yellow oil, yield: 68%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.42 (d, J = 9.3 Hz, 1H), 7.28-7.19 (m, 2H), 4.98 (dd, J = 8.0, 4.0 Hz, 1H), 4.86 (brs, 1H), 3.52-3.46 (m, 1H), 3.36-3.29 (m, 1H), 1.42 (s, 9H), 1.23 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 141.2, 131.2, 130.1, 130.0, 125.5, 122.6, 84.1, 81.1, 79.7, 44.7, 28.5, 26.5.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{17}H_{26}BrNNaO_4$: 410.0943, found: 410.0945.



4h

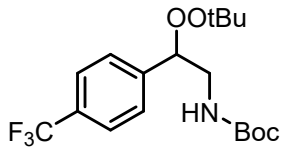
tert-butyl (2-(4-(tert-butyl)phenyl)-2-(tert-butylperoxy)ethyl)carbamate (4h)

111.0 mg, (PE/EA = 50:1), yellow oil, yield: 76%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, J = 7.8 Hz, 2H), 7.17 (d, J = 7.8 Hz, 2H), 4.90 (t, J=6.8 Hz, 1H), 4.78 (brs, 1H), 3.45-3.33 (m, 2H), 1.33 (s, 9H), 1.22 (s, 9H), 1.15 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 151.1, 135.3, 126.7, 125.4, 84.5, 80.9, 79.4, 44.7, 34.7, 31.5, 28.5, 26.6.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{21}H_{35}NNaO_4$: 388.2464, found: 388.2452.



4i

tert-butyl (2-(tert-butylperoxy)-2-(4-(trifluoromethyl)phenyl)ethyl)carbamate (4i)

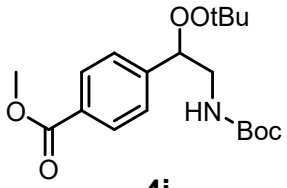
92.0 mg, (PE/EA = 40:1), colorless oil, yield: 61%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.2 Hz, 2H), 7.47 (d, J = 8.2 Hz, 2H), 5.08 (t, J= 4.6 Hz, 1H), 4.86 (brs, 1H), 3.56-3.49 (m, 1H), 3.37-3.30 (m, 1H), 1.42 (s, 9H), 1.24 (s, 9H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.54

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 143.0, 130.3 (q, $^{2}J_{C\text{-}F}$ = 32.0 Hz), 127.2, 125.4 (q, $^{3}J_{C\text{-}F}$ = 3.6 Hz), 124.3 (q, $^{1}J_{C\text{-}F}$ = 271.1 Hz), 84.2, 81.2, 79.8, 44.7, 28.5, 26.5.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{26}F_3NNaO_4$: 400.1712, found: 400.1717.



4j

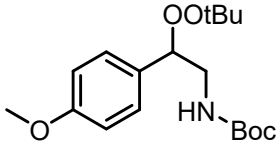
methyl 4-(2-((tert-butoxycarbonyl)amino)-1-(tert-butylperoxy)ethyl)benzoate (4j)

104.2 mg, (PE/EA = 30:1), colorless oil, yield: 71%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 8.2 Hz, 2H), 7.42 (d, J = 8.2 Hz, 2H), 5.08 (dd, J = 8.0, 4.0 Hz, 1H), 4.88 (brs, 1H), 3.90 (s, 3H), 3.56-3.49 (m, 1H), 3.37-3.30 (m, 1H), 1.42 (s, 9H), 1.22 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 155.8, 143.9, 129.8, 129.7, 126.8, 84.3, 81.0, 79.6, 52.2, 44.6, 28.4, 26.4.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{19}H_{29}NNaO_6$: 390.1893, found: 390.1899.



4k

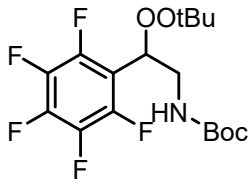
tert-butyl (2-(tert-butylperoxy)-2-(4-methoxyphenyl)ethyl)carbamate (4k)

101.8 mg, (PE/EA = 30:1), colorless oil, yield: 75%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, J = 8.4 Hz, 2H), 6.88 (d, J = 8.4 Hz, 2H), 4.94 (dd, J = 8.0, 4.0 Hz, 1H), 4.86 (brs, 1H), 3.80 (s, 3H), 3.51-3.42 (m, 2H), 1.43 (s, 9H), 1.22 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 156.0, 130.5, 128.4, 113.9, 84.3, 80.8, 79.4, 55.4, 44.6, 28.5, 26.6.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{29}NNaO_5$: 362.1943, found: 362.1938.



4l

tert-butyl (2-(tert-butylperoxy)-2-(perfluorophenyl)ethyl)carbamate (4l)

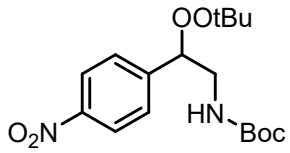
103.7 mg, (PE/EA = 30:1), colorless oil, yield: 65%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.39 (dd, J = 8.0, 4.0 Hz, 1H), 4.90 (brs, 1H), 3.69-3.54 (m, 2H), 1.42 (s, 9H), 1.19 (s, 9H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -141.51, -153.92, -162.03.

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 81.1, 79.7, 76.3, 41.6, 28.1, 26.0.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{17}H_{22}F_5NNaO_4$: 422.1367, found: 422.1356.



4m

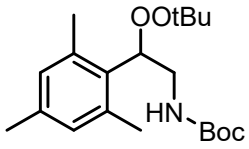
tert-butyl (2-(tert-butylperoxy)-2-(4-nitrophenyl)ethyl)carbamate (4m)

65.1 mg, (PE/EA = 30:1), yellow oil, yield: 46%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 8.0 Hz, 2H), 7.54 (d, J = 8.0 Hz, 2H), 5.14 (dd, J = 8.0, 4.0 Hz, 1H), 4.87 (brs, 1H), 3.57-3.50 (m, 1H), 3.34-3.27 (m, 1H), 1.42 (s, 9H), 1.24 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 147.8, 146.5, 127.7, 123.7, 84.0, 81.4, 80.0, 44.6, 28.5, 26.5.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{17}H_{22}N_2NaO_6$: 377.1689, found: 377.1681.



4n

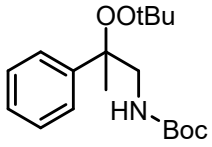
tert-butyl (2-(tert-butylperoxy)-2-mesitylethyl)carbamate (4n)

101.1 mg, (PE/EA = 30:1), colorless oil, yield: 72%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81 (s, 2H), 5.44 (dd, J = 8.0, 4.0 Hz, 1H), 4.93 (brs, 1H), 3.63-3.56 (m, 1H), 3.47-3.42 (m, 1H), 2.38 (s, 6H), 2.25 (s, 3H), 1.44 (s, 9H), 1.23 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 137.3, 136.8, 131.6, 130.0, 82.9, 80.6, 79.3, 43.4, 28.5, 26.6, 21.0, 20.9.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{20}H_{33}NNaO_4$: 374.2307, found: 374.2315.



4o

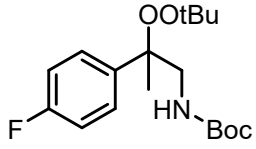
tert-butyl (2-(tert-butylperoxy)-2-phenylpropyl)carbamate (4o)

107.2 mg, (PE/EA = 40:1), colorless oil, yield: 83%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.28 (m, 5H), 4.86 (brs, 1H), 3.73-3.63 (m, 2H), 1.54 (s, 3H), 1.42 (s, 9H), 1.31 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 142.9, 128.2, 127.3, 125.8, 83.6, 79.6, 79.2, 47.2, 28.5, 26.8, 23.7.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{29}NNaO_4$: 346.1994, found: 346.1985.



4p

tert-butyl (2-(tert-butylperoxy)-2-(4-fluorophenyl)propyl)carbamate (4p)

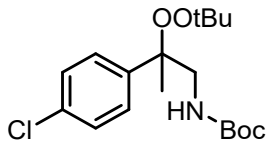
106.3 mg, (PE/EA = 30:1), colorless oil, yield: 78%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.36 (m, 2H), 7.03-6.98 (m, 2H), 4.82 (brs, 1H), 3.68-3.56 (m, 2H), 1.49 (s, 3H), 1.39 (s, 9H), 1.27 (s, 9H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -115.86.

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4 (d, $^{1}J_{C\text{-}F}$ = 244 Hz), 156.5, 138.9, 128.0 (d, $^{3}J_{C\text{-}F}$ = 8 Hz), 115.3 (d, $^{2}J_{C\text{-}F}$ = 21 Hz), 83.7, 80.0, 79.6, 47.58, 28.8, 27.1, 24.0.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{28}FNNaO_4$: 364.1900, found: 364.1912.



4q

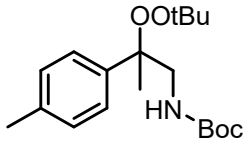
tert-butyl (2-(tert-butylperoxy)-2-(4-chlorophenyl)propyl)carbamate (4q)

114.2 mg, (PE/EA = 30:1), colorless oil, yield: 80%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 8.7 Hz, 2H), 7.29 (d, J = 8.7 Hz, 2H), 4.81 (brs, 1H), 3.67-3.55 (m, 2H), 1.48 (s, 3H), 1.39 (s, 9H), 1.27 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 141.5, 133.1, 128.3, 127.4, 83.5, 79.8, 79.4, 47.2, 28.5, 26.8, 23.6.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{28}ClNNaO_4$: 380.1605, found: 380.1609.



4r

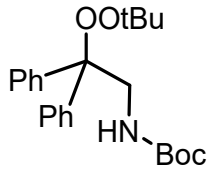
tert-butyl (2-(tert-butylperoxy)-2-(p-tolyl)propyl)carbamate (4r)

106.5 mg, (PE/EA = 30:1), colorless oil, yield: 79%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 8.1 Hz, 2H), 7.14 (d, J = 8.1 Hz, 2H), 4.83 (brs, 1H), 3.69-3.59 (m, 2H), 2.33 (s, 3H), 1.50 (s, 3H), 1.40 (s, 9H), 1.28 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 139.9, 136.9, 128.9, 125.8, 83.5, 79.5, 79.1, 47.2, 28.5, 26.8, 23.6, 21.2.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{19}H_{31}NNaO_4$: 360.2151, found: 360.2139.



4s

tert-butyl (2-(tert-butylperoxy)-2,2-diphenylethyl)carbamate (4s)

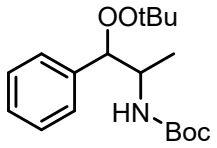
127.8 mg, (PE/EA = 40:1), colorless oil, yield: 83%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.28 (m, 10H), 5.01 (brs, 1H), 4.23 (d, J = 5.7 Hz, 2H), 1.37 (s,

9H), 1.30 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 142.0, 128.0, 127.5, 127.1, 86.9, 80.1, 79.1, 46.1, 28.4, 26.8.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{23}H_{31}NNaO_4$: 408.2151, found: 408.2158.



4t

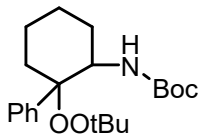
tert-butyl (1-(tert-butylperoxy)-1-phenylpropan-2-yl)carbamate (4t)

49.1 mg, (PE/EA = 40:1), colorless oil, yield: 38%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.28 (m, 5H), 5.10 (d, J = 8.0 Hz, 1H), 4.88 (brs, 1H), 4.00-3.93 (m, 1H), 1.45 (s, 9H), 1.26 (s, 9H), 1.02 (d, J = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 138.9, 128.2, 127.5, 126.7, 87.0, 80.9, 79.3, 51.3, 28.6, 26.6, 14.5.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{29}NNaO_4$: 346.1994, found: 346.1991.



4u

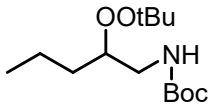
tert-butyl (2-(tert-butylperoxy)-2-phenylcyclohexyl)carbamate (4u)

72.6 mg, (PE/EA = 40:1), colorless oil, yield: 50%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 8.0 Hz, 2H), 7.14 (t, J = 8.1 Hz, 2H), 7.22 (d, J = 8.0 Hz, 1H), 4.58 (d, J = 9.9 Hz, 1H), 4.12-4.06 (m, 1H), 2.42-2.36 (m, 1H), 2.07-2.00 (m, 1H), 1.82-1.78 (m, 2H), 1.67-1.60 (m, 4H), 1.40-1.31(m, 2H), 1.21 (s, 9H), 1.15 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 142.7, 127.5, 127.2, 127.0, 83.0, 79.1, 78.8, 51.4, 29.8, 28.3, 28.0, 26.8, 20.9, 20.5.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{21}H_{33}NNaO_4$: 386.2307, found: 386.2312.



4v

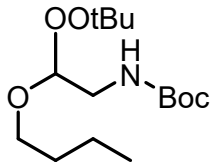
tert-butyl (2-(tert-butylperoxy)pentyl)carbamate (4v)

64.9 mg, (PE/EA = 50:1), colorless oil, yield: 58%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.96-4.90 (m, 1H), 3.96 (brs, 1H), 3.47-3.40 (m, 1H), 3.24-3.17 (m, 1H), 1.56-1.49 (m, 2H), 1.44 (s, 9H), 1.41-1.36 (m, 2H), 1.24 (s, 9H), 0.92 (t, J = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 82.6, 80.3, 79.2, 43.0, 29.9, 28.6, 26.6, 19.2, 14.3.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{14}H_{29}NNaO_4$: 298.1994, found: 298.1988.



4w

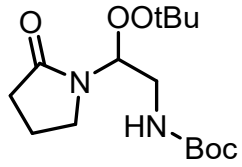
tert-butyl (2-butoxy-2-(tert-butylperoxy)ethyl)carbamate (4w)

103.7 mg, (PE/EA = 40:1), colorless oil, yield: 85%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.88 (t, J = 7.2 Hz, 1H), 4.73 (brs, 1H), 3.93-3.87 (m, 1H), 3.58-3.52 (m, 1H), 3.30 (t, J = 5.3 Hz, 2H), 1.60-1.53 (m, 2H), 1.44 (s, 9H), 1.40-1.34 (m, 2H), 1.25 (s, 9H), 0.91 (t, J = 9.2 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 156.0, 104.1, 80.7, 79.5, 69.8, 41.9, 32.1, 28.4, 26.6, 19.3, 13.9.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{15}H_{31}NNaO_5$: 328.2100, found: 328.2089.



4x

tert-butyl (2-(tert-butylperoxy)-2-(2-oxopyrrolidin-1-yl)ethyl)carbamate (4x)

84.7 mg, (PE/EA = 30:1), colorless oil, yield: 67%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.65 (t, J = 6.7 Hz, 1H), 4.74 (brs, 1H), 3.53-3.30 (m, 4H), 2.45-2.33 (m, 2H), 2.02-1.95 (m, 2H), 1.41 (s, 9H), 1.21 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 176.6, 155.8, 84.0, 81.2, 79.8, 42.8, 39.5, 31.7, 28.3, 26.4, 18.4.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{15}H_{28}N_2NaO_5$: 339.1896, found: 339.1898.

References

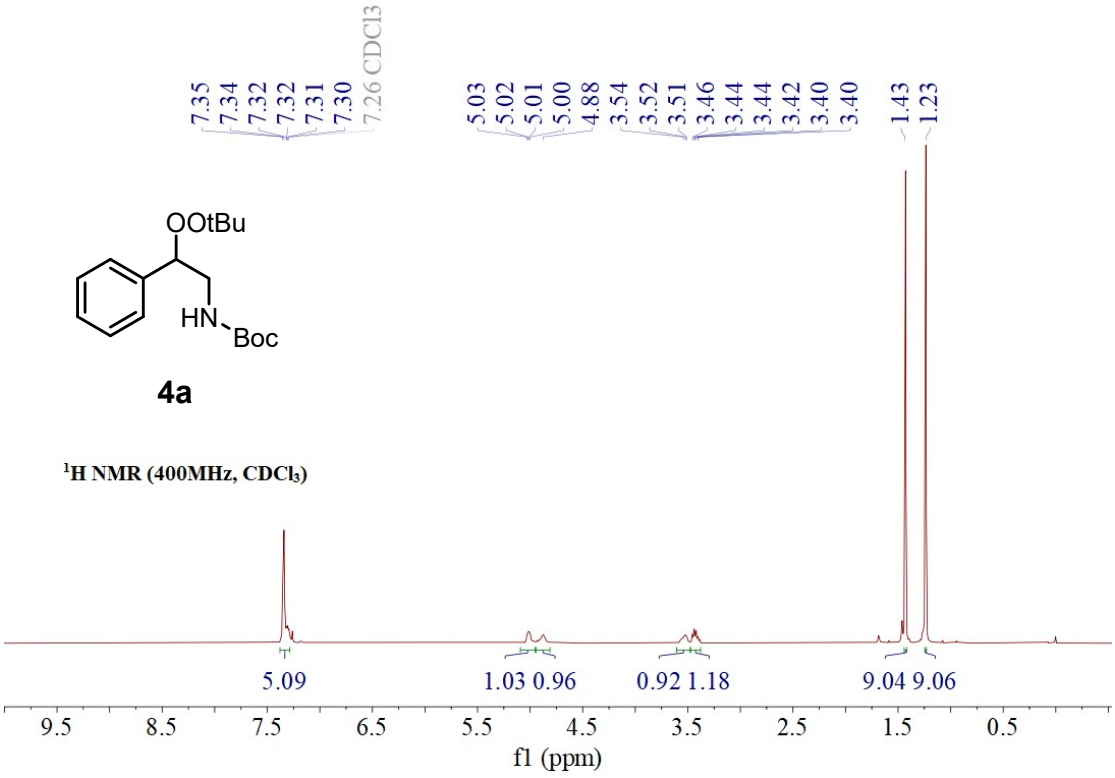
[S1] T. Patra, M. Das, C.-G. Daniliuc, F. Glorius, *Nat. Catal.*, 2021, **4**, 54.

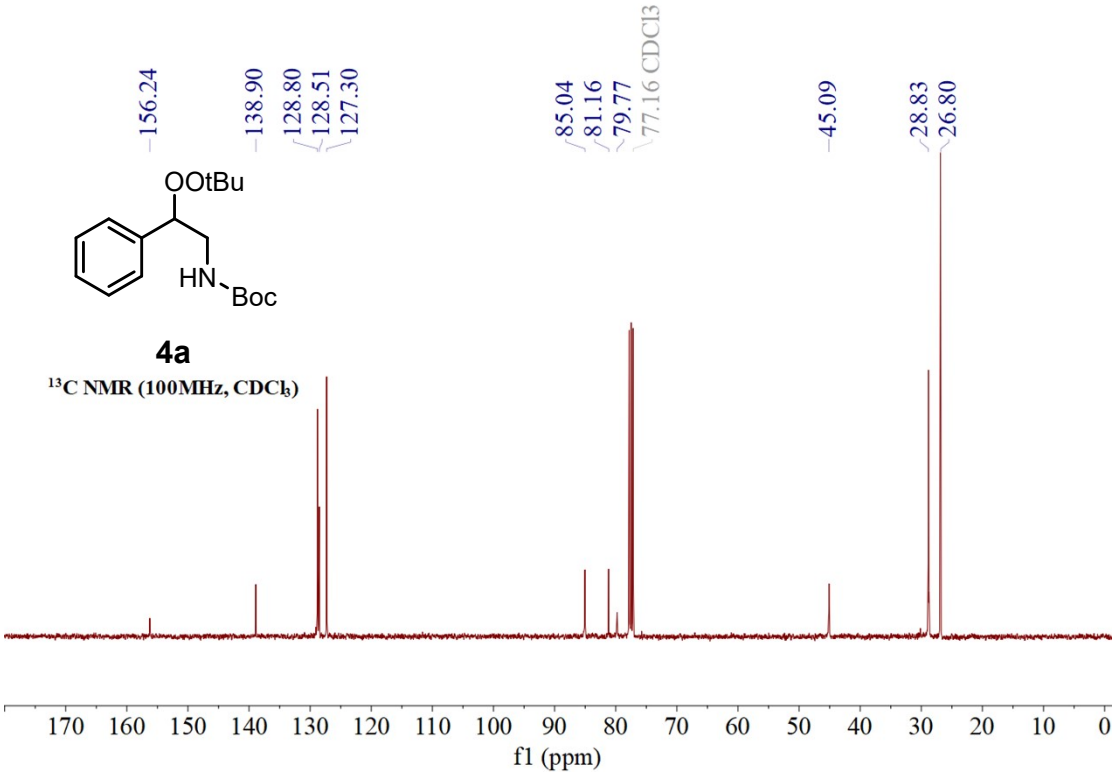
[S2] Y. Zheng, Z.-J. Wang, Z.-P. Ye, K. Tang, Z.-Z. Xie, J.-A. Xiao, H.-Y. Xiang, K. Chen, X.-Q. Chen, H. Yang, *Angew. Chem. Int. Ed.* 2022, **61**, e202212292.

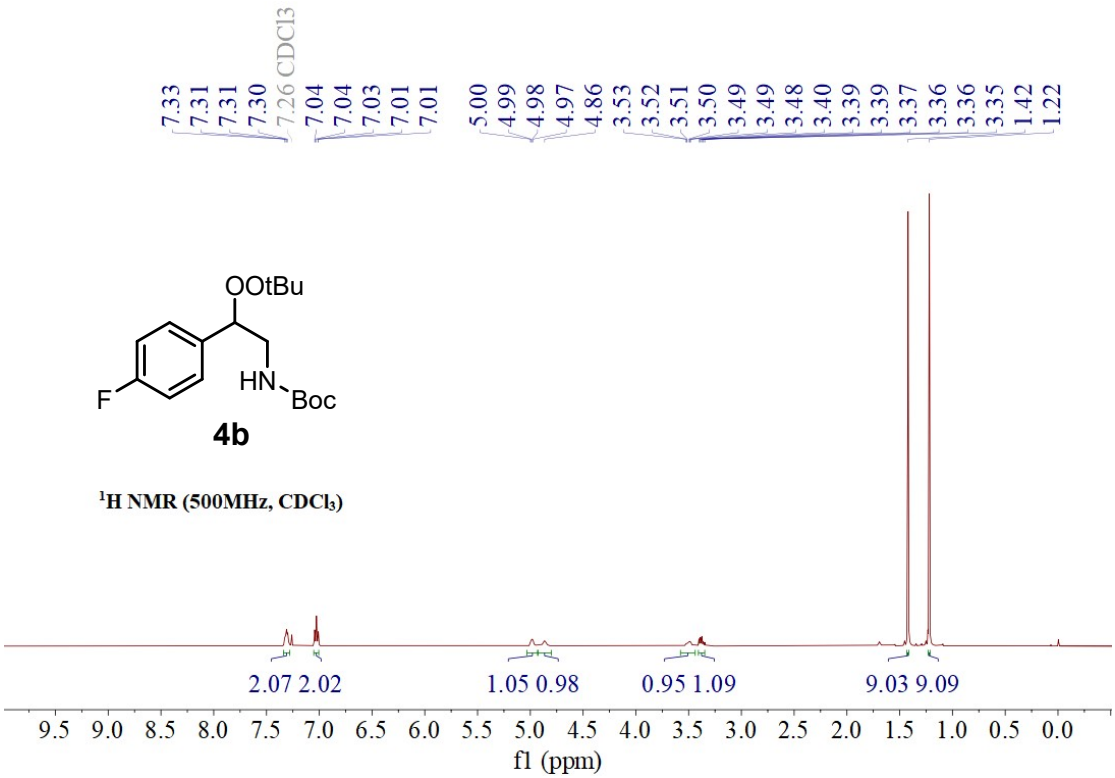
[S3] J. Luo, J. Zhang, *ACS Catal.*, 2016, **6**, 873.

[S4] C. Gao, J. Zeng, X. Zhang, Y. Liu, Z.-P. Zhan, *Org. Lett.*, 2023, **25**, 3146-3151.

Copies of ^{1}H and ^{13}C NMR spectra

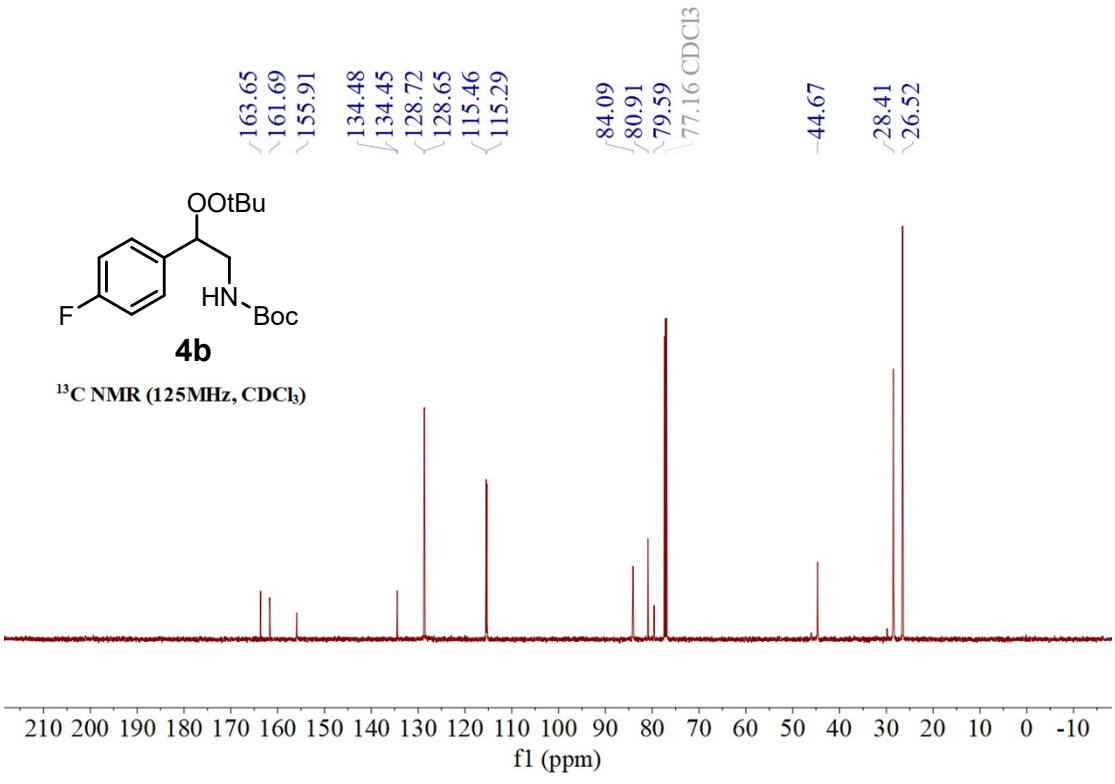






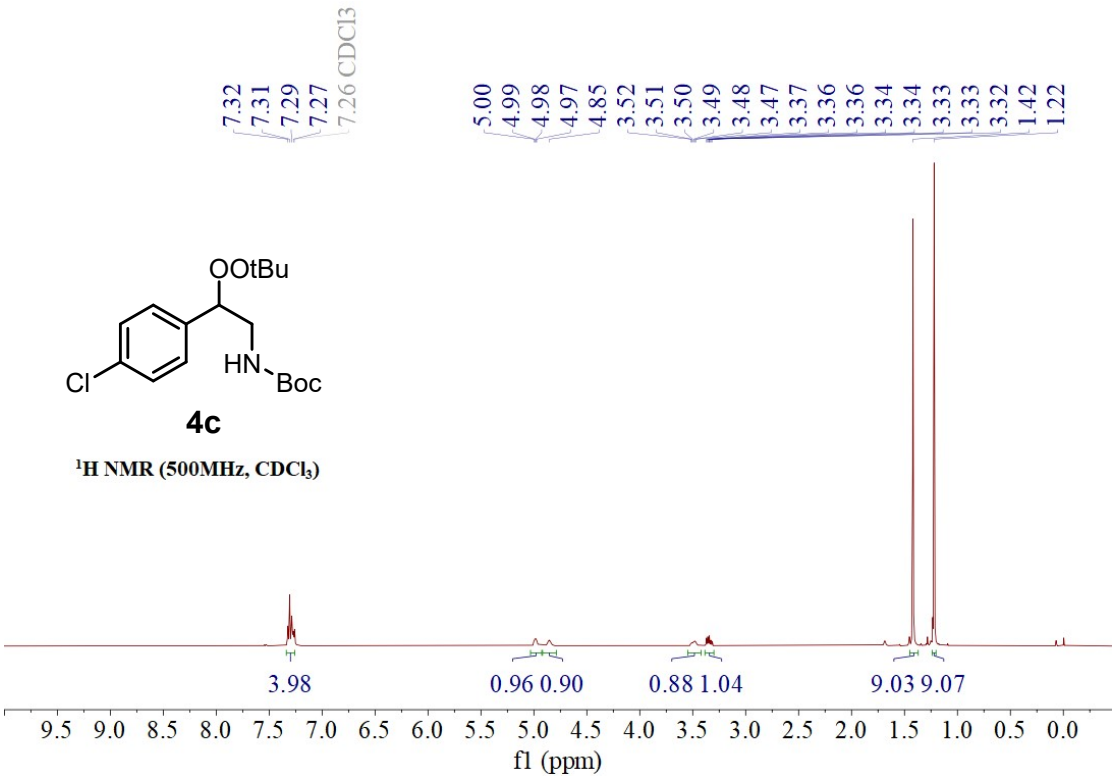
4b

^{1}H NMR (500MHz, $CDCl_3$)



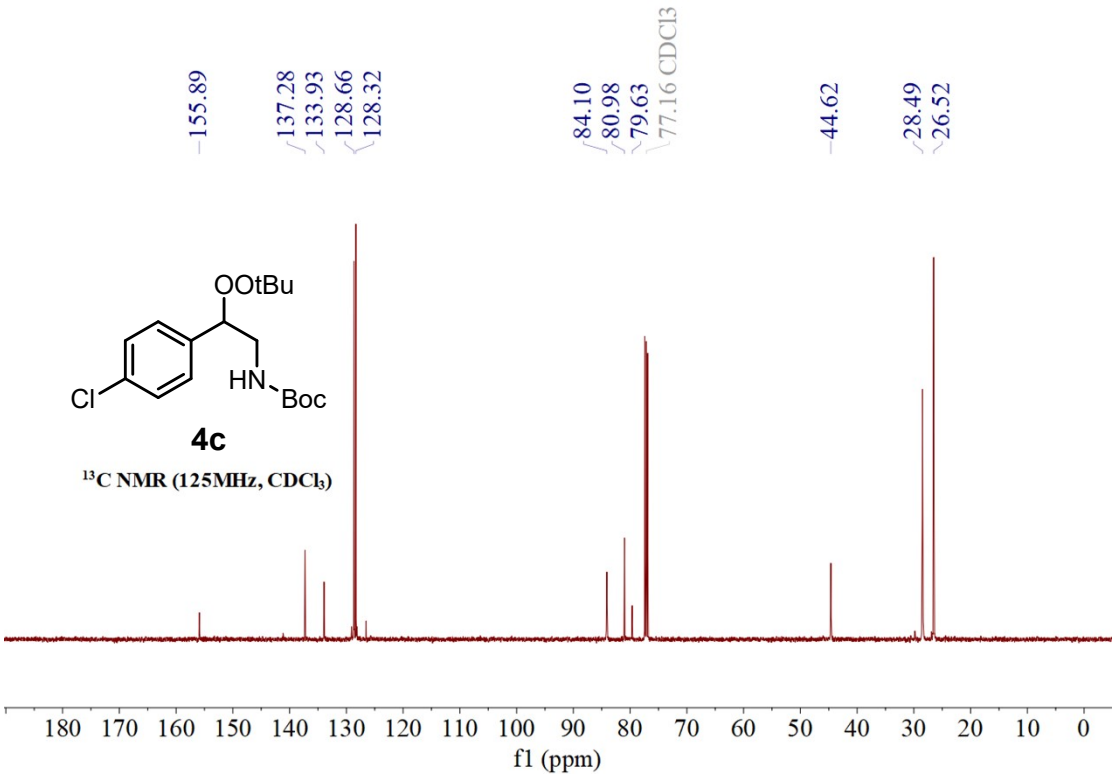
4b

^{13}C NMR (125MHz, $CDCl_3$)



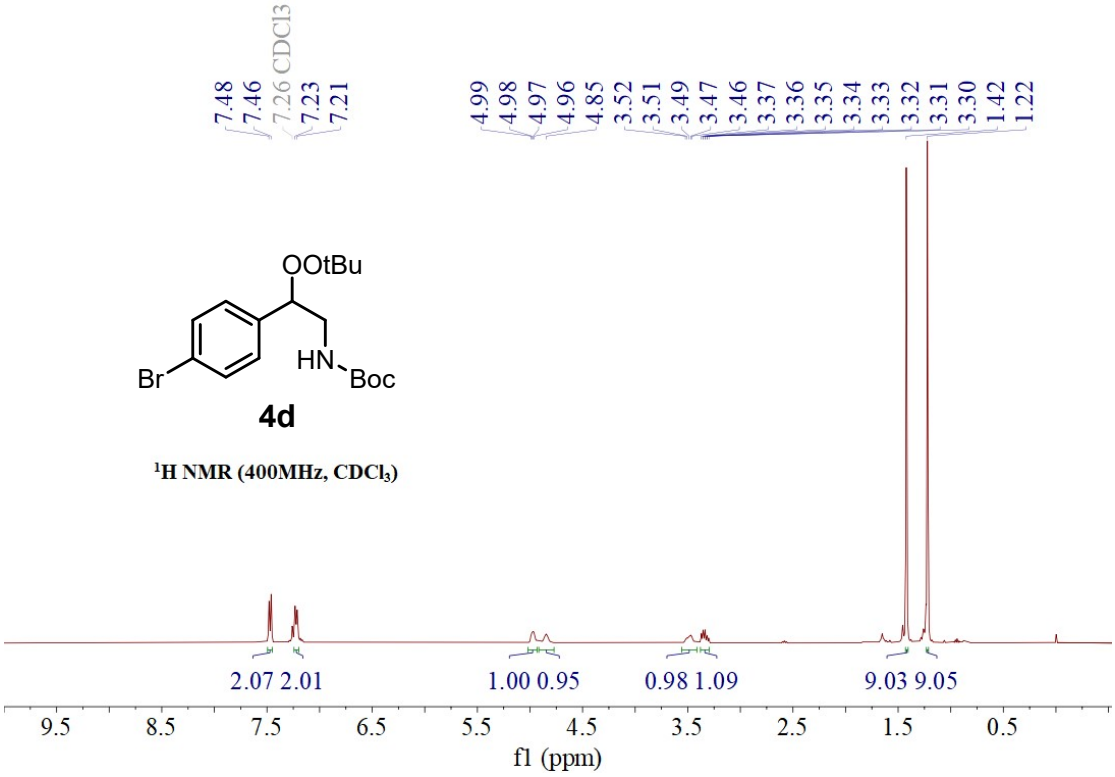
4c

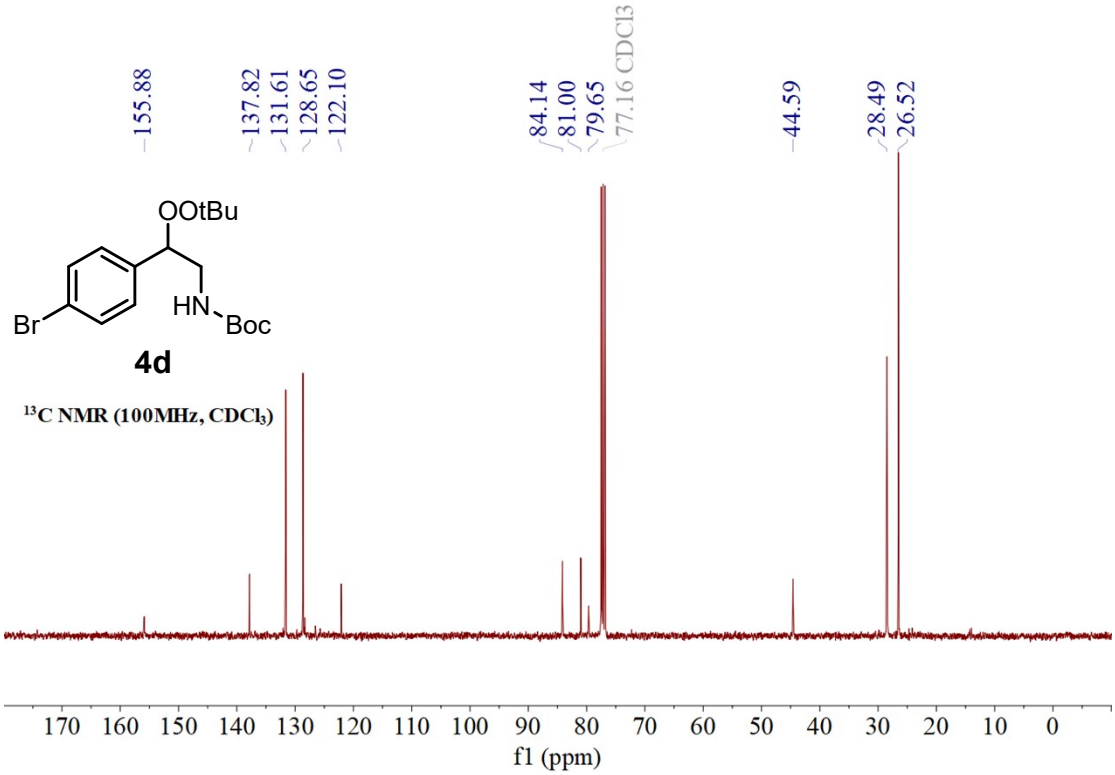
^{1}H NMR (500MHz, $CDCl_3$)

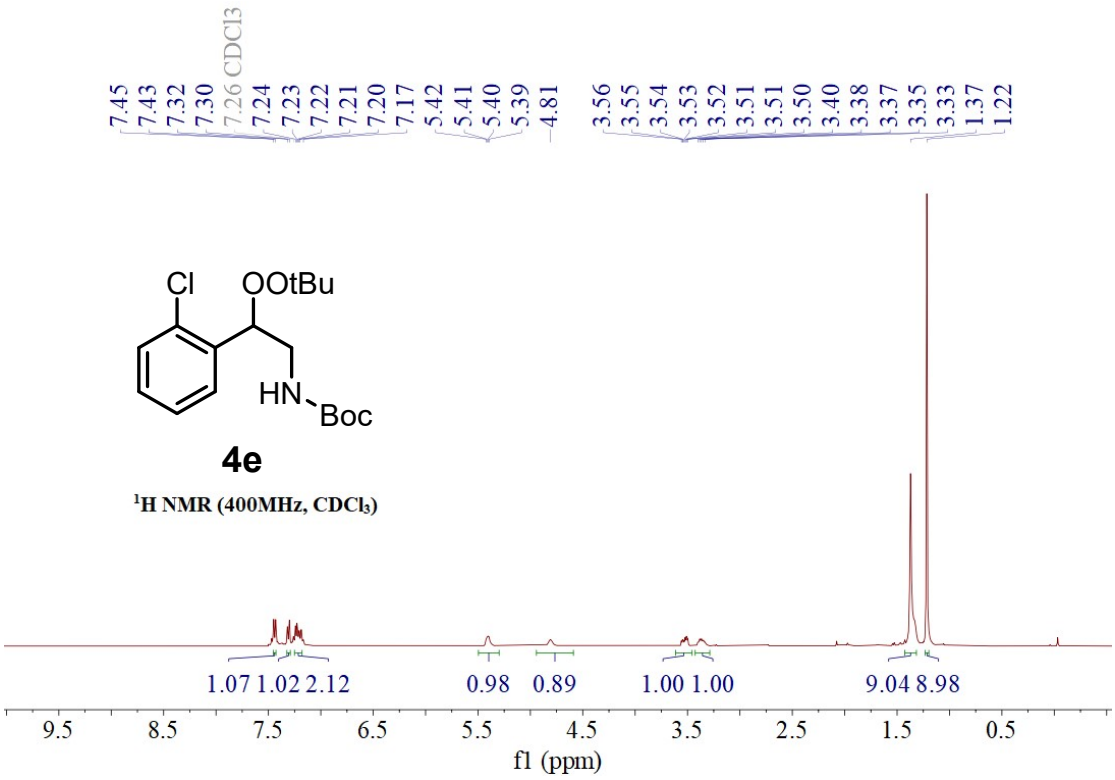


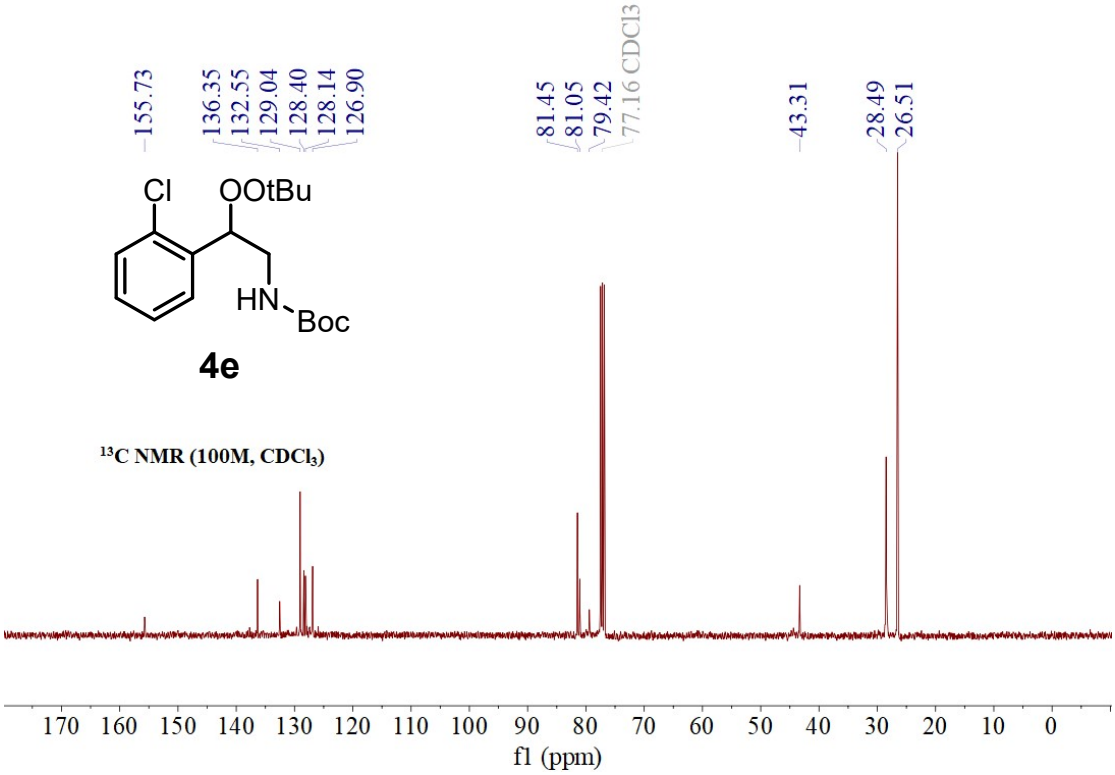
4c

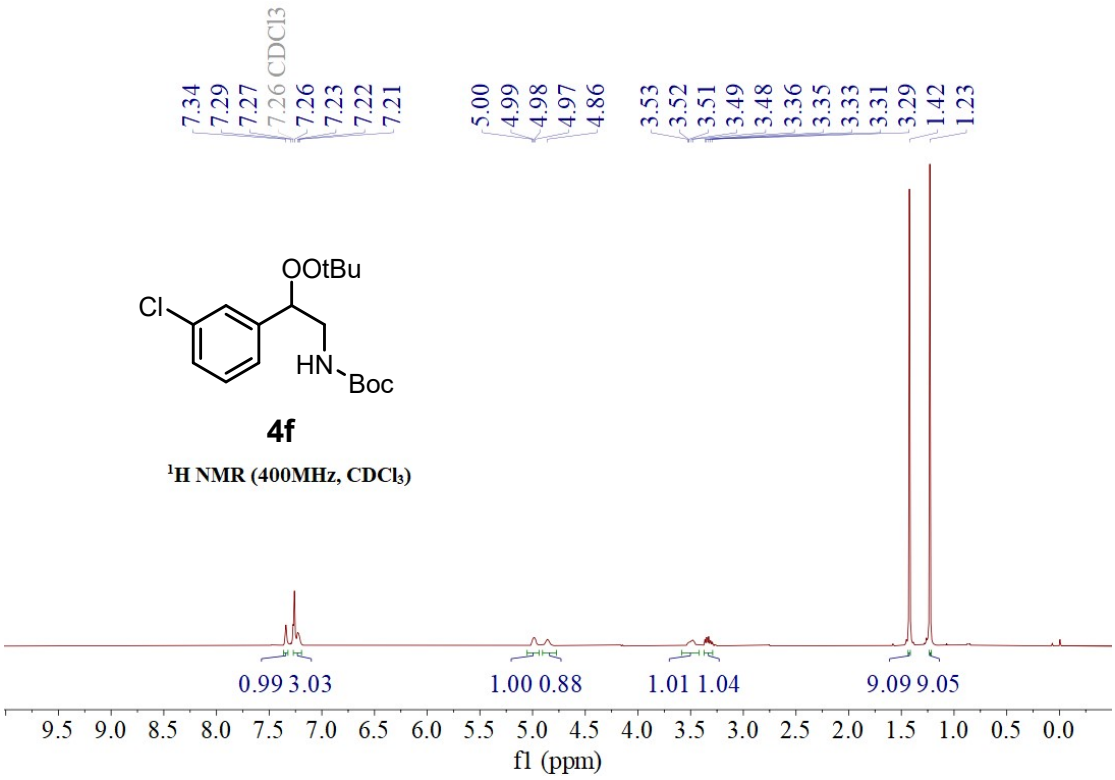
^{13}C NMR (125MHz, $CDCl_3$)


7.48
7.46
7.26 CDCl3
7.23
7.21
4.99
4.98
4.97
4.96
4.85
3.52
3.51
3.49
3.47
3.46
3.37
3.36
3.35
3.34
3.33
3.32
3.31
3.30
1.42
1.22
OOtBu
HN
Boc
Br
4d
1H NMR (400MHz, CDCl3)
2.07 2.01
1.00 0.95
0.98 1.09
9.03 9.05
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)


155.88
137.82
131.61
128.65
122.10
84.14
81.00
79.65
77.16 CDCl3
44.59
28.49
26.52
OOtBu
HN
Boc
Br
4d
13C NMR (100MHz, CDCl3)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

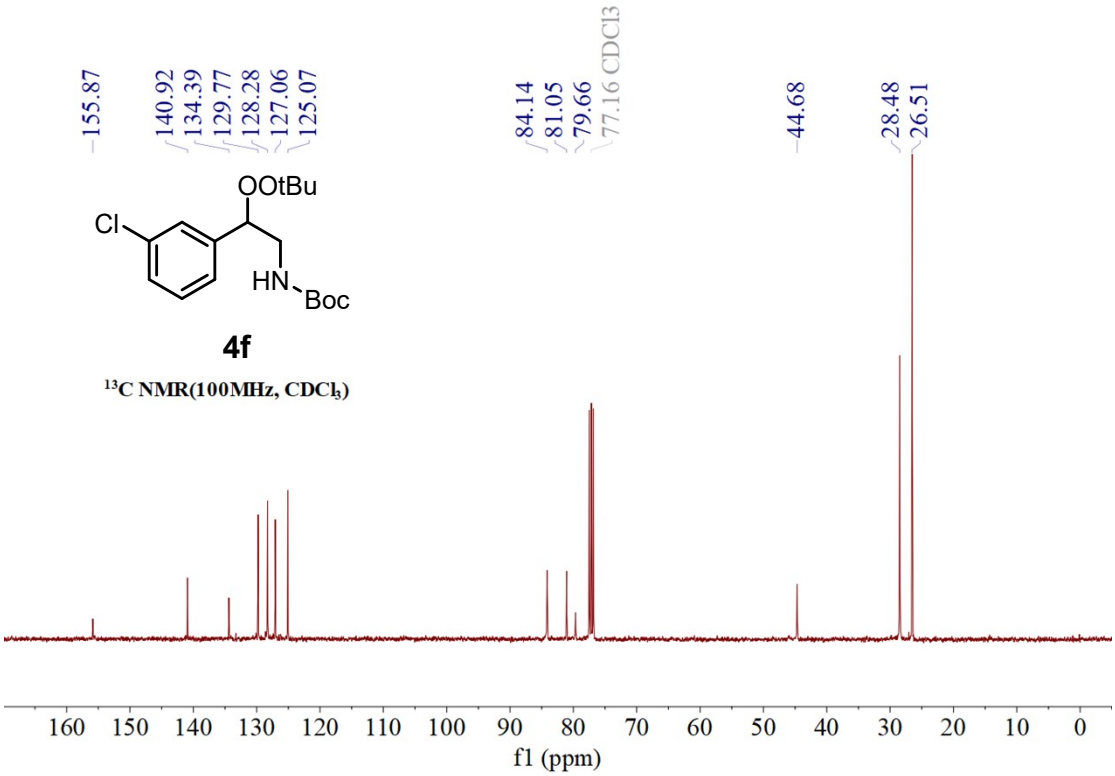

7.45
7.43
7.32
7.30
7.26 CDCl3
7.24
7.23
7.22
7.21
7.20
7.17
5.42
5.41
5.40
5.39
4.81
3.56
3.55
3.54
3.53
3.52
3.51
3.51
3.50
3.40
3.38
3.37
3.35
3.33
1.37
1.22
Cl
OOtBu
HN
Boc
4e
1H NMR (400MHz, CDCl3)
1.07 1.02 2.12
0.98 0.89
1.00 1.00
9.04 8.98
9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5
f1 (ppm)


155.73
136.35
132.55
129.04
128.40
128.14
126.90
81.45
81.05
79.42
77.16 CDCl3
43.31
28.49
26.51
Cl
OOtBu
HN
Boc
4e
13C NMR (100M, CDCl3)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



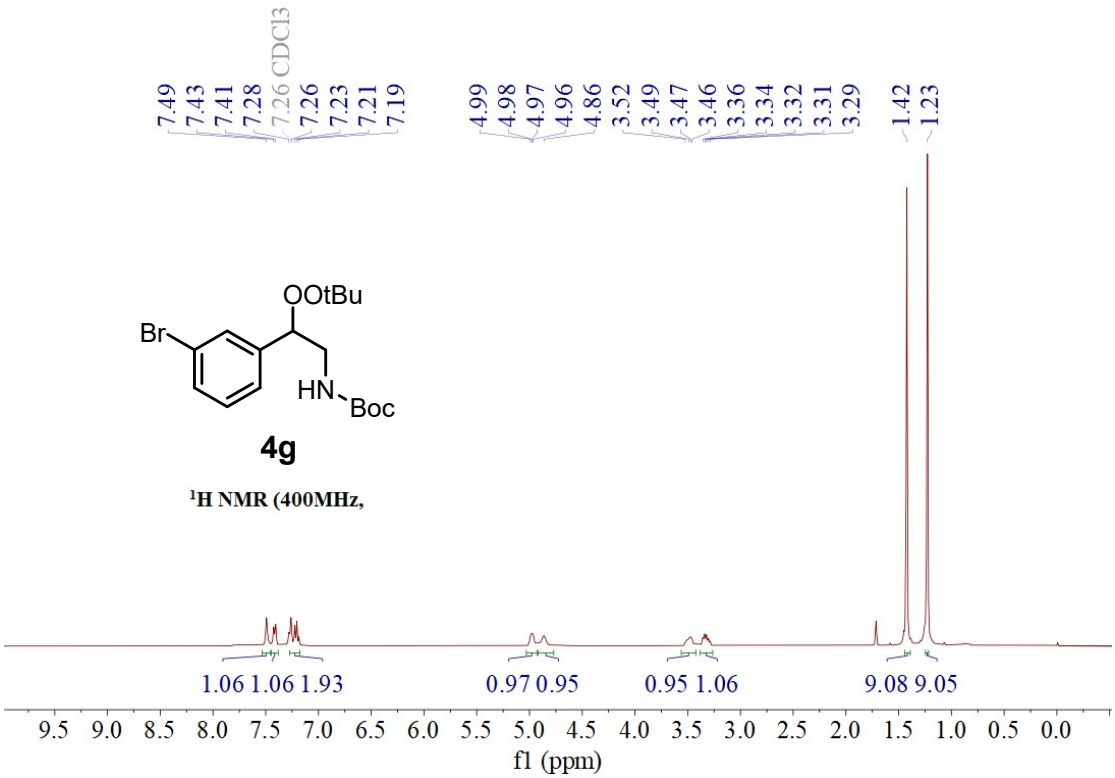
4f

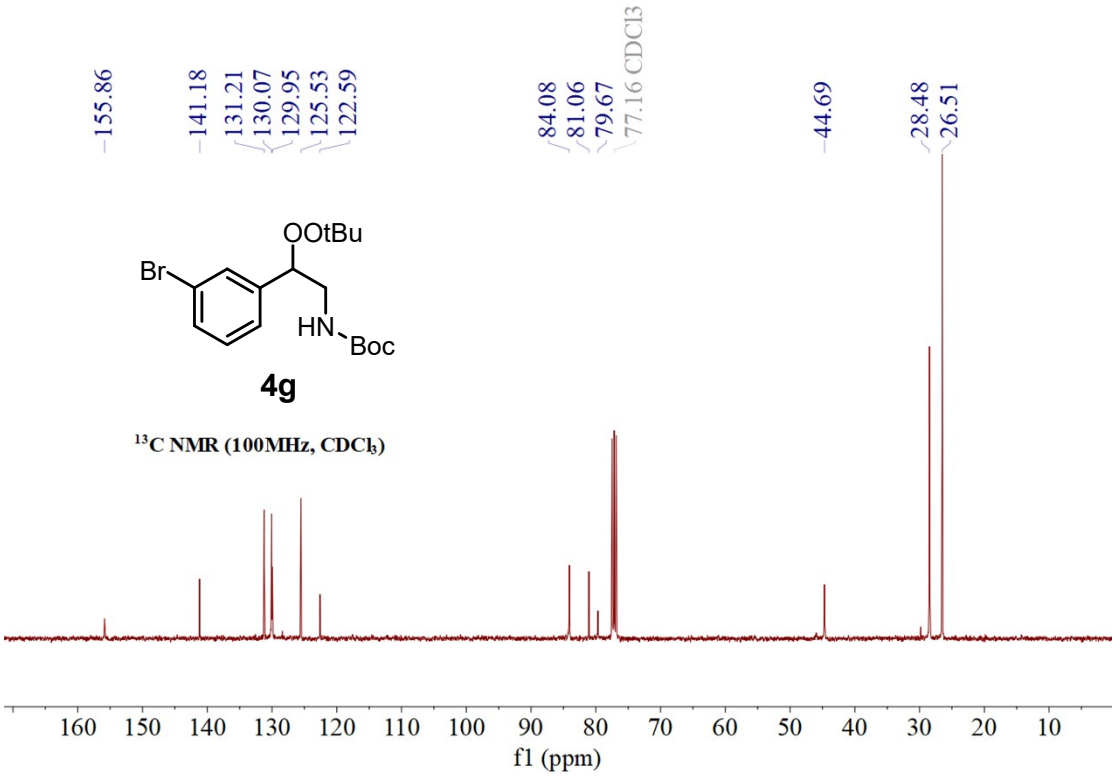
^{1}H NMR (400MHz, $CDCl_3$)

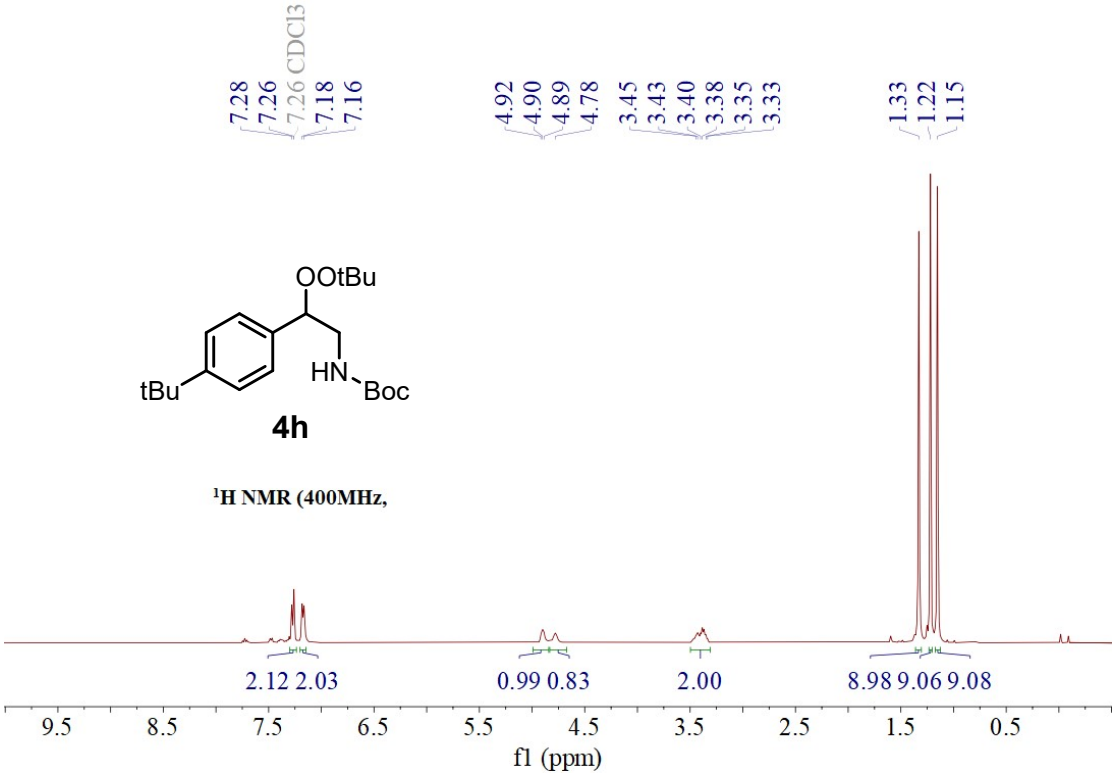


4f

^{13}C NMR(100MHz, $CDCl_3$)

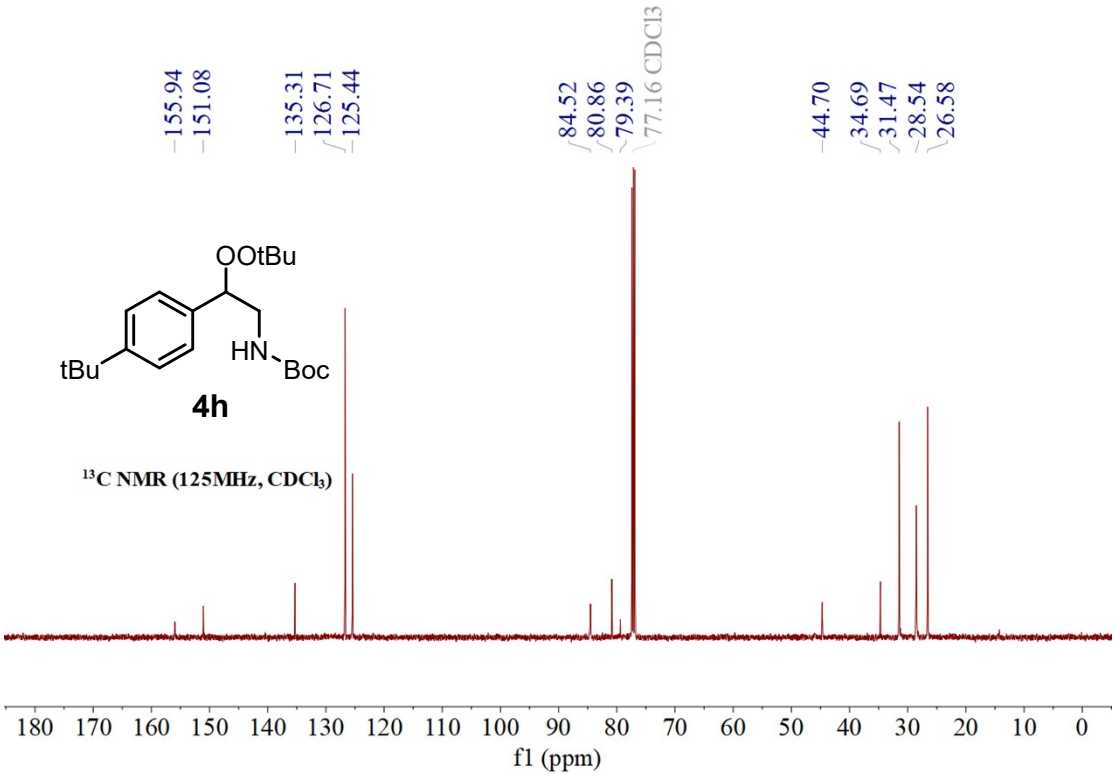

7.49
7.43
7.41
7.28
7.26 CDCl3
7.26
7.23
7.21
7.19
4.99
4.98
4.97
4.96
4.86
3.52
3.49
3.47
3.46
3.36
3.34
3.32
3.31
3.29
1.42
1.23
OOtBu
Br
HN
Boc
4g
1H NMR (400MHz,
1.06 1.06 1.93
0.97 0.95
0.95 1.06
9.08 9.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


155.86
141.18
131.21
130.07
129.95
125.53
122.59
84.08
81.06
79.67
77.16 CDCl3
44.69
28.48
26.51
OOtBu
Br
HN
Boc
4g
13C NMR (100MHz, CDCl3)
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)



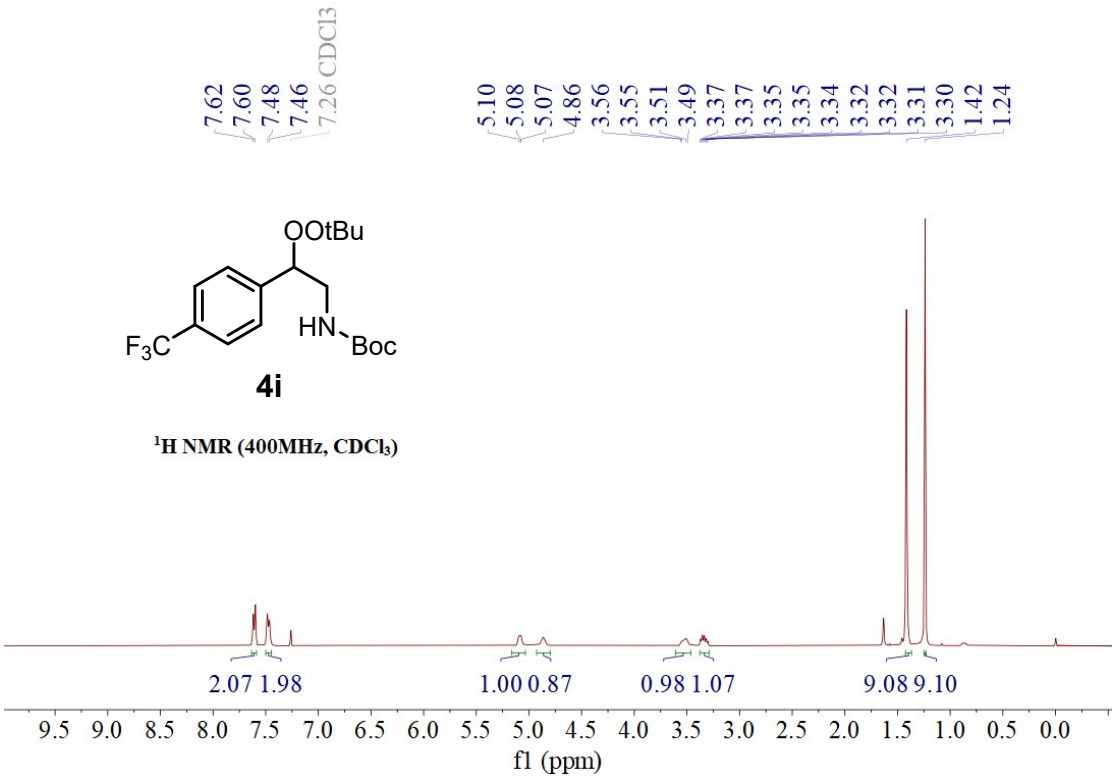
4h

^{1}H NMR (400MHz,



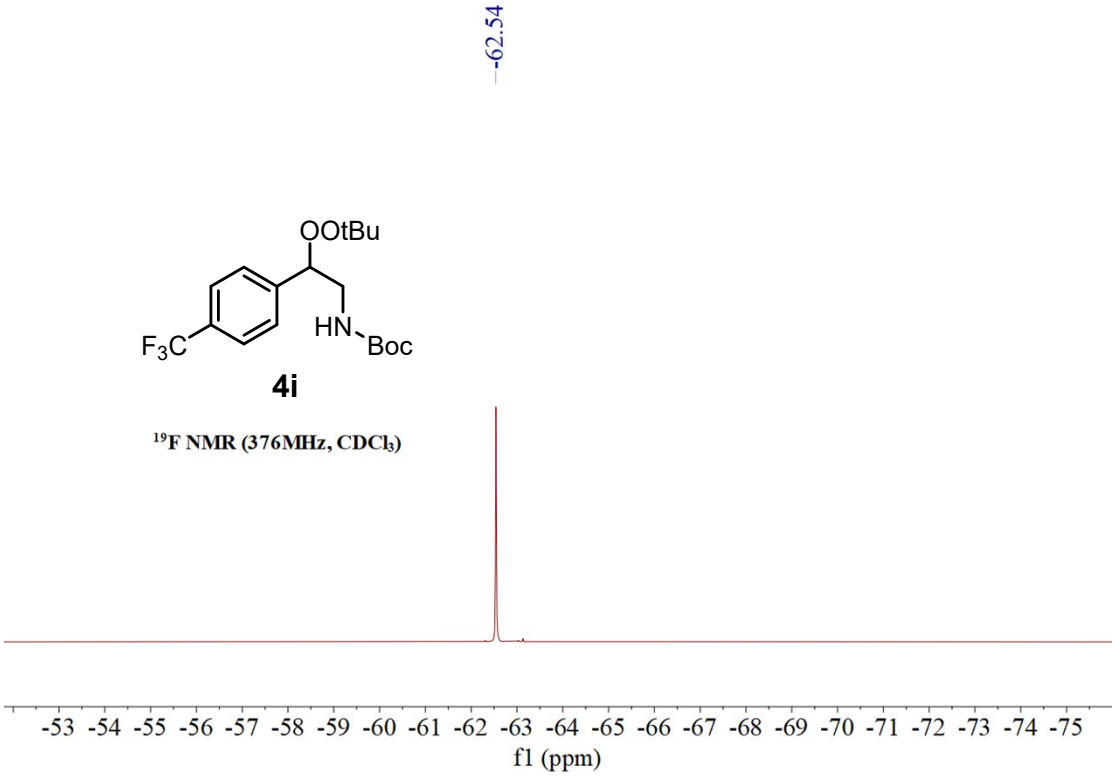
4h

^{13}C NMR (125MHz, $CDCl_3$)



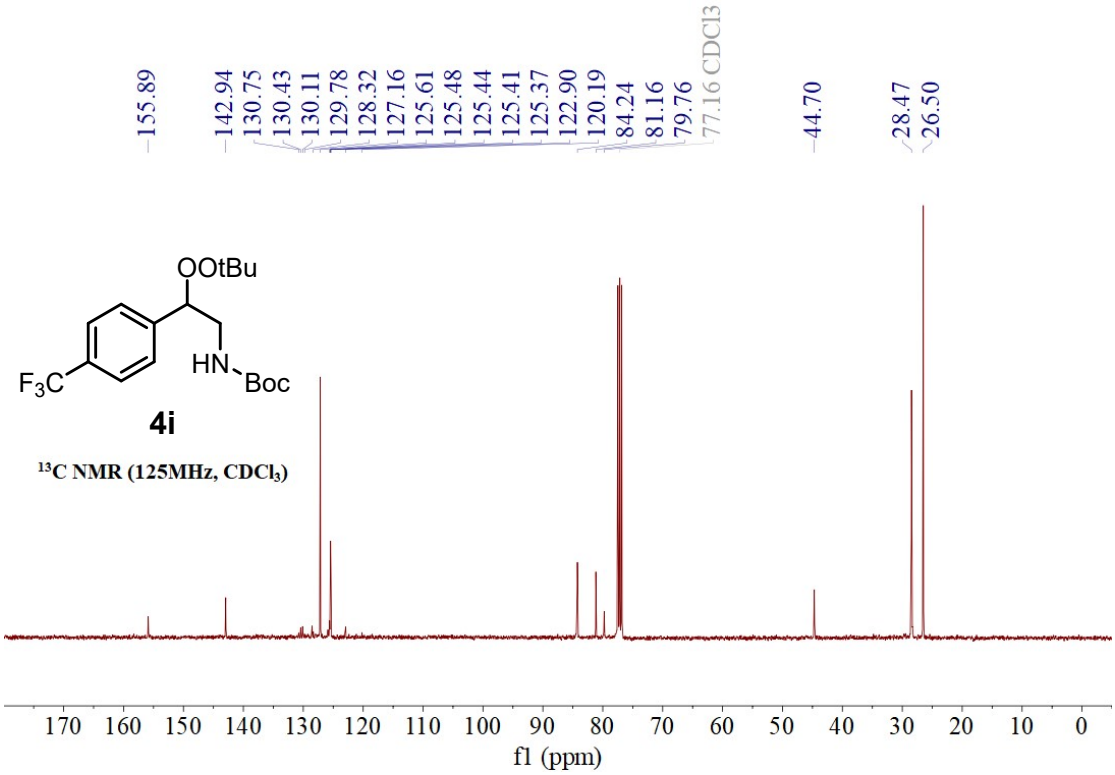
4i

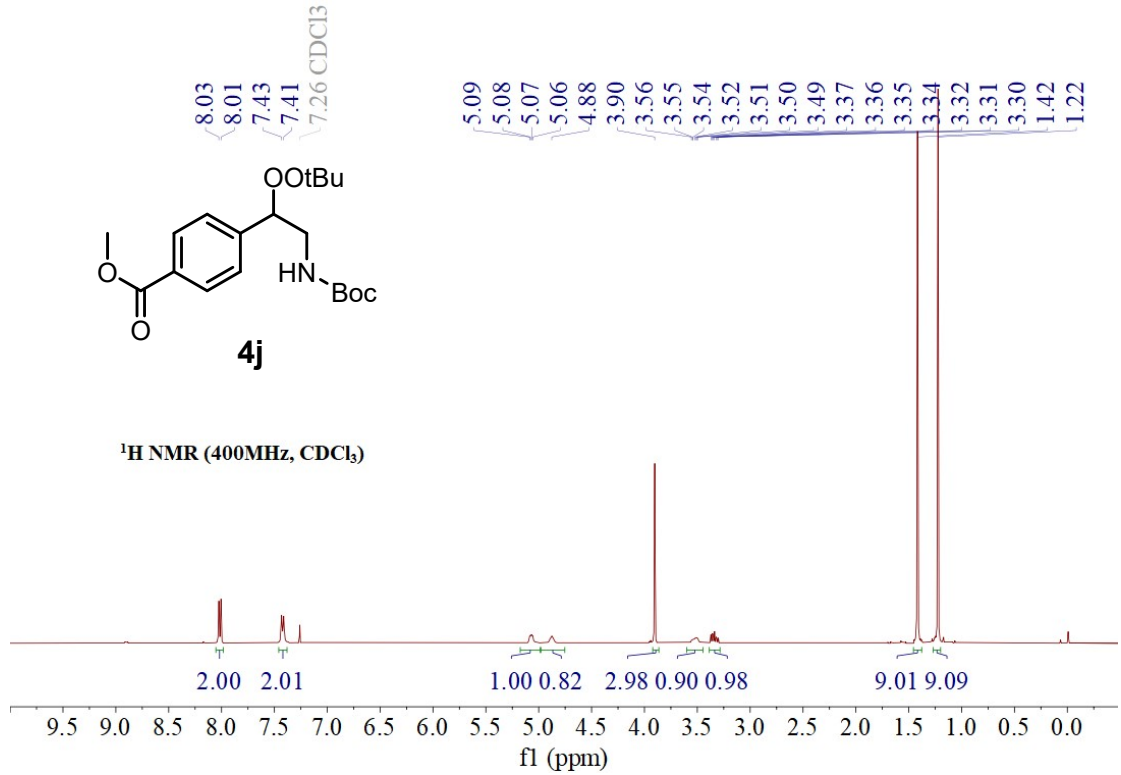
^{1}H NMR (400MHz, $CDCl_3$)

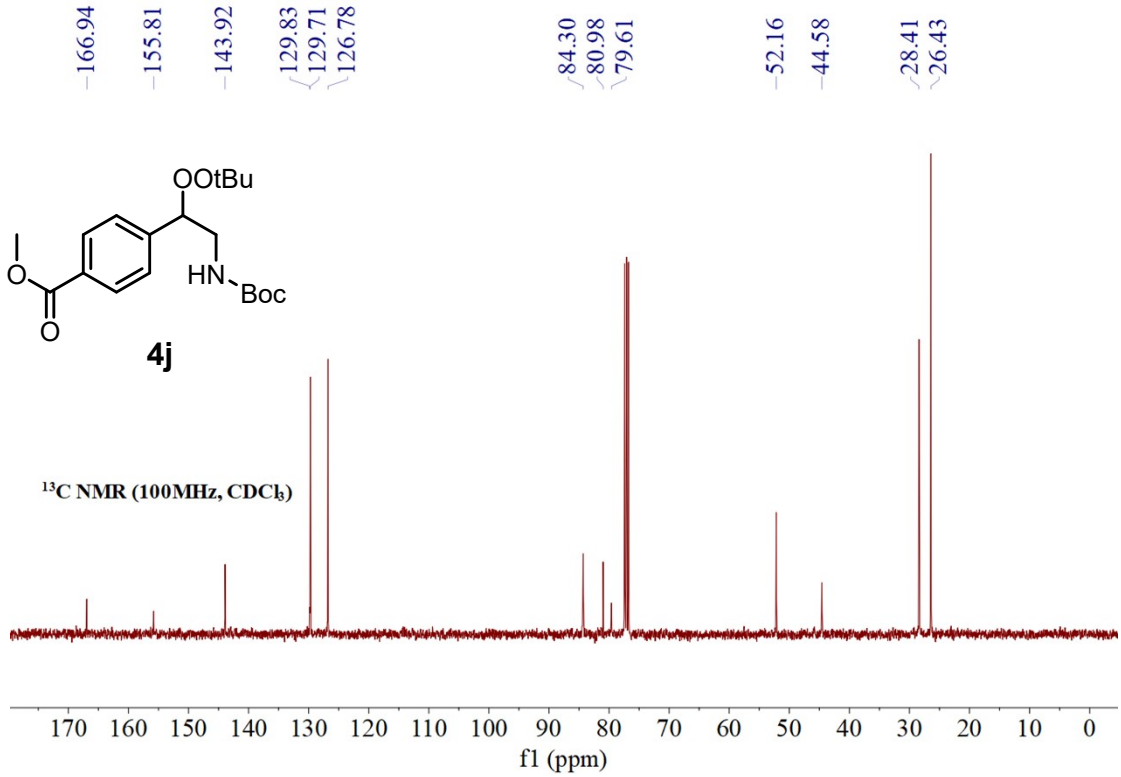


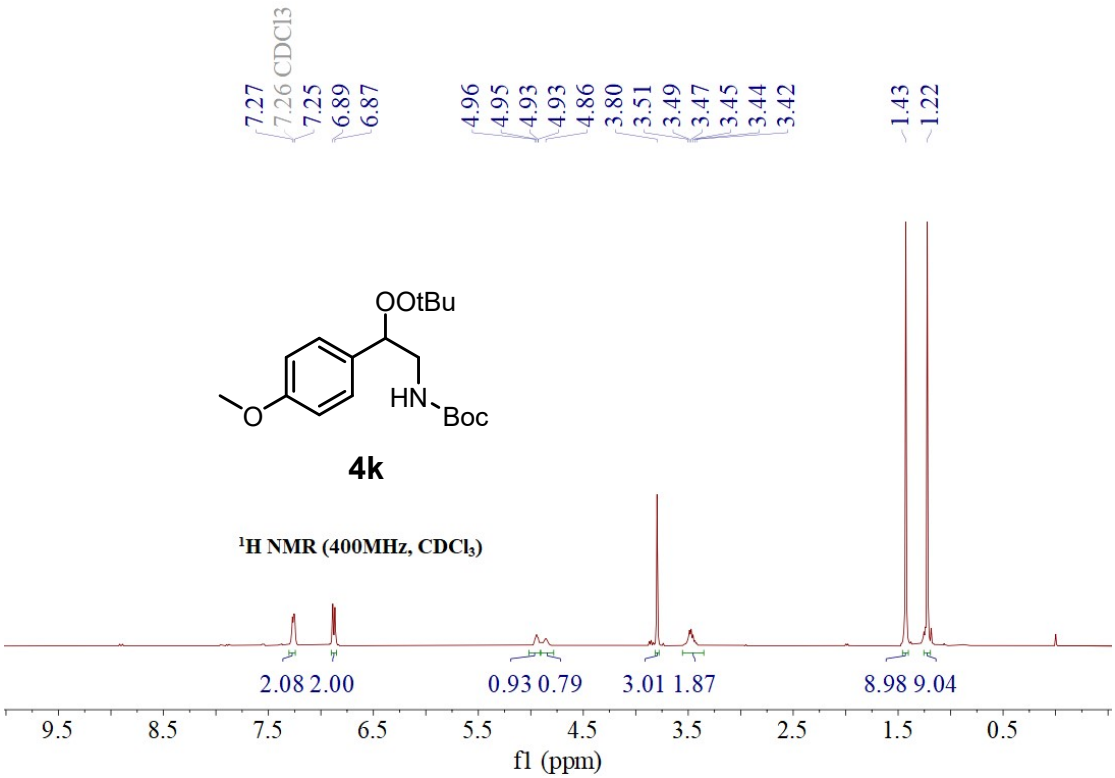
4i

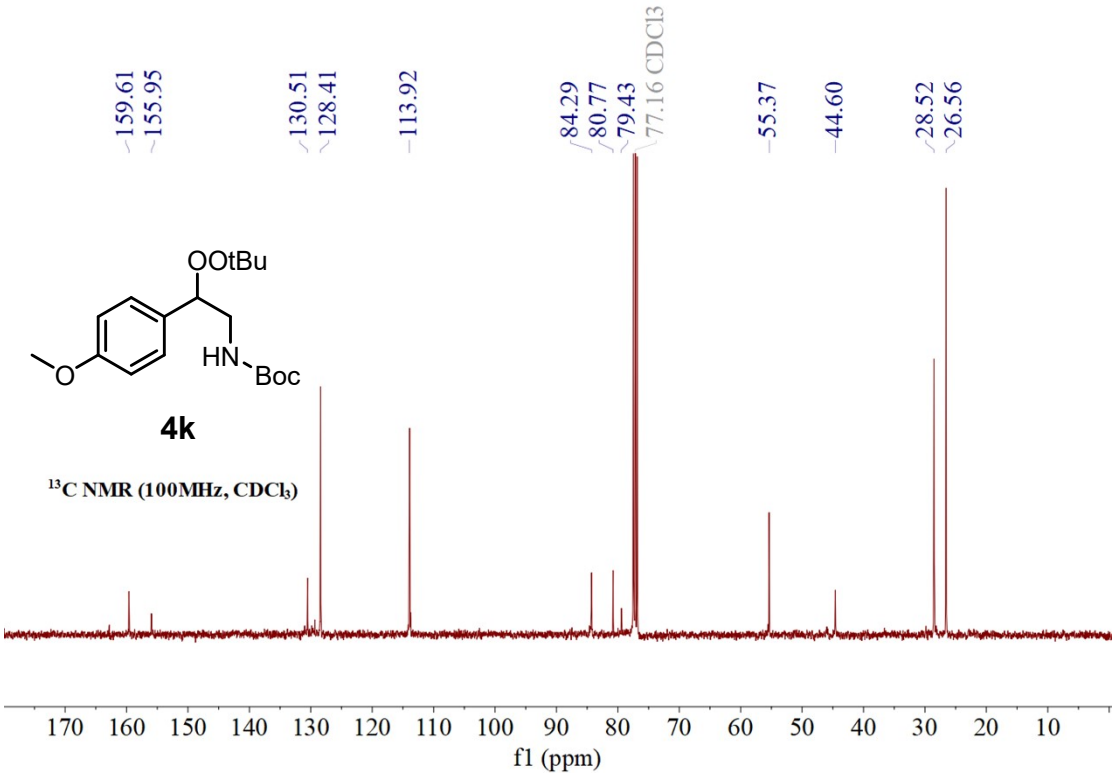
^{19}F NMR (376MHz, $CDCl_3$)

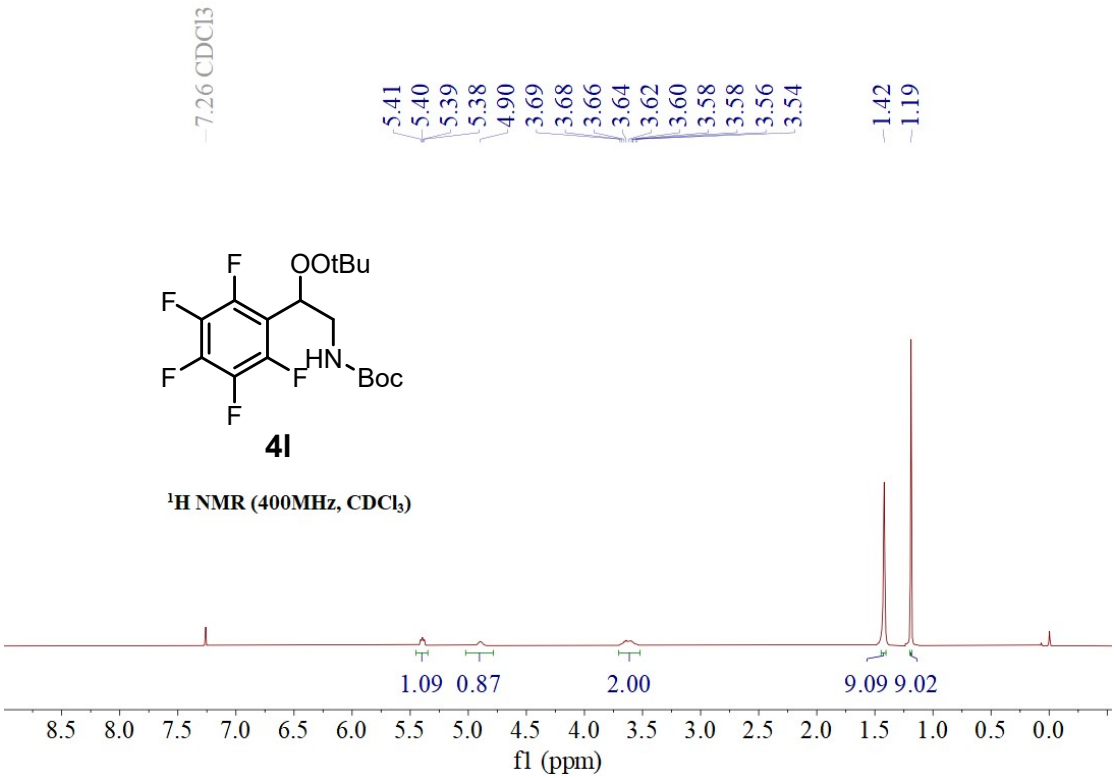

155.89
142.94
130.75
130.43
130.11
129.78
128.32
127.16
125.61
125.48
125.44
125.41
125.37
122.90
120.19
84.24
81.16
79.76
77.16 CDCl3
44.70
28.47
26.50
OOtBu
HN
Boc
F3C
4i
13C NMR (125MHz, CDCl3)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

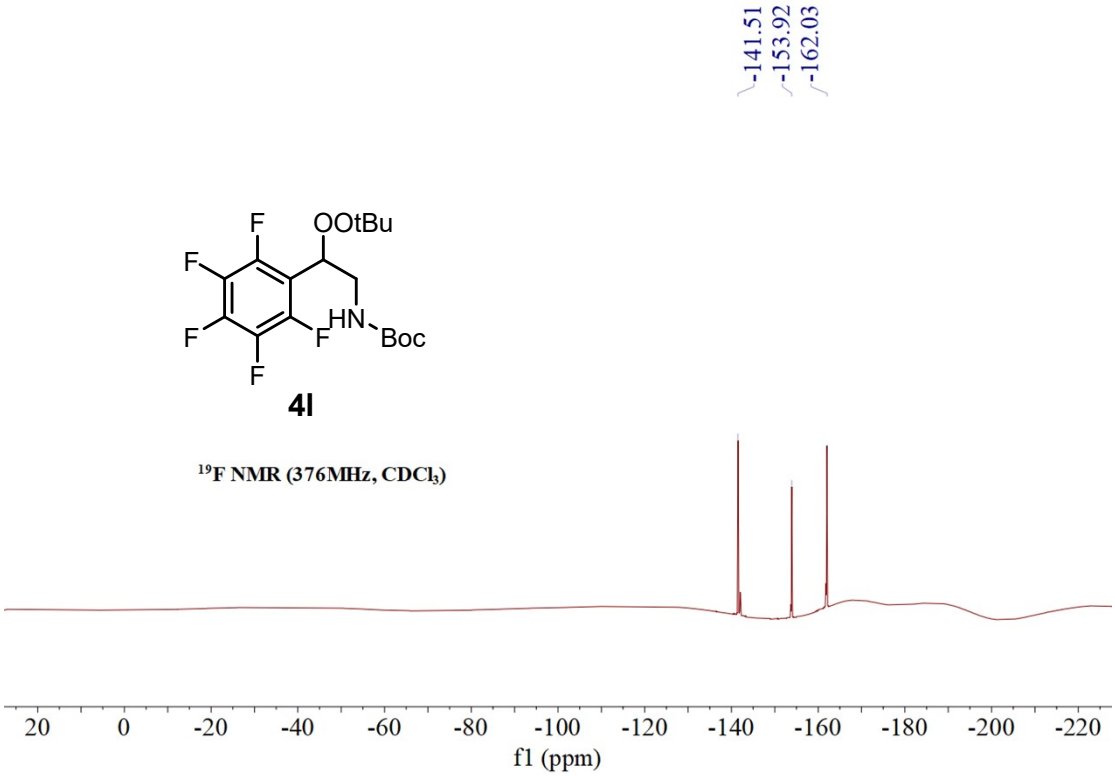

8.03
8.01
7.43
7.41
7.26 CDCl3
5.09
5.08
5.07
5.06
4.88
3.90
3.56
3.55
3.54
3.52
3.51
3.50
3.49
3.37
3.36
3.35
3.34
3.32
3.31
3.30
1.42
1.22
OOtBu
HN
Boc
O
O
4j
1H NMR (400MHz, CDCl3)
2.00 2.01
1.00 0.82
2.98 0.90 0.98
9.01 9.09
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

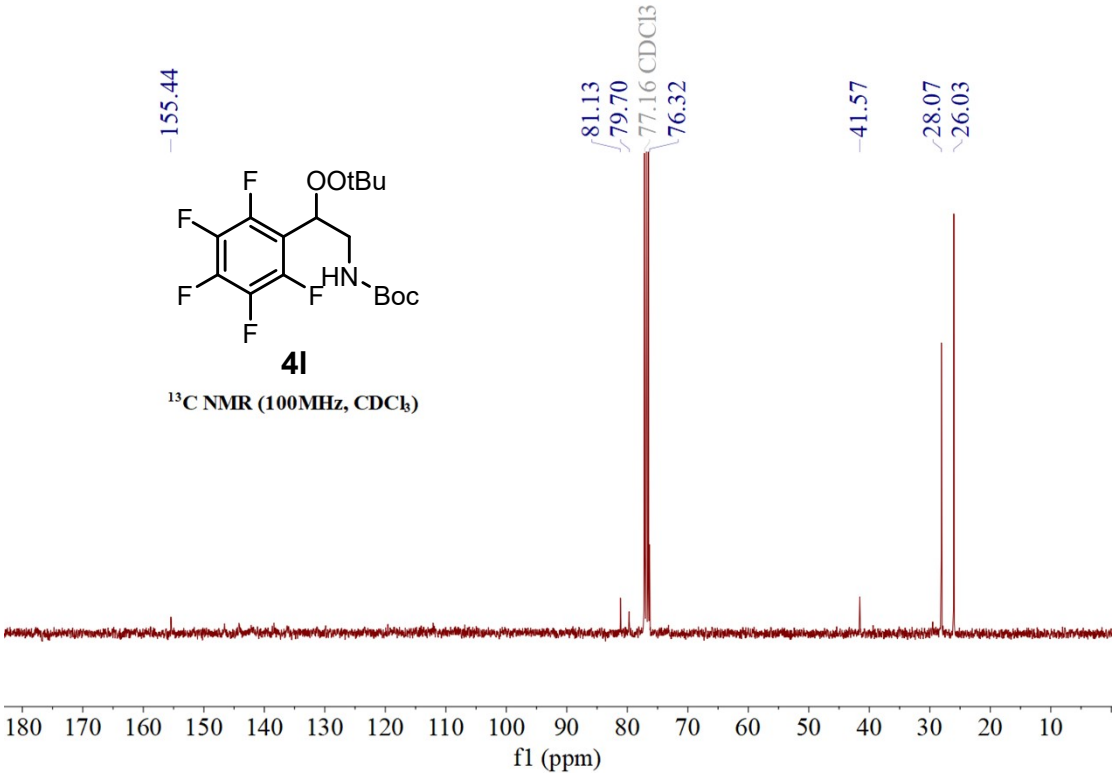

166.94
155.81
143.92
129.83
129.71
126.78
84.30
80.98
79.61
52.16
44.58
28.41
26.43
OOtBu
HN
Boc
O
O
4j
13C NMR (100MHz, CDCl3)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

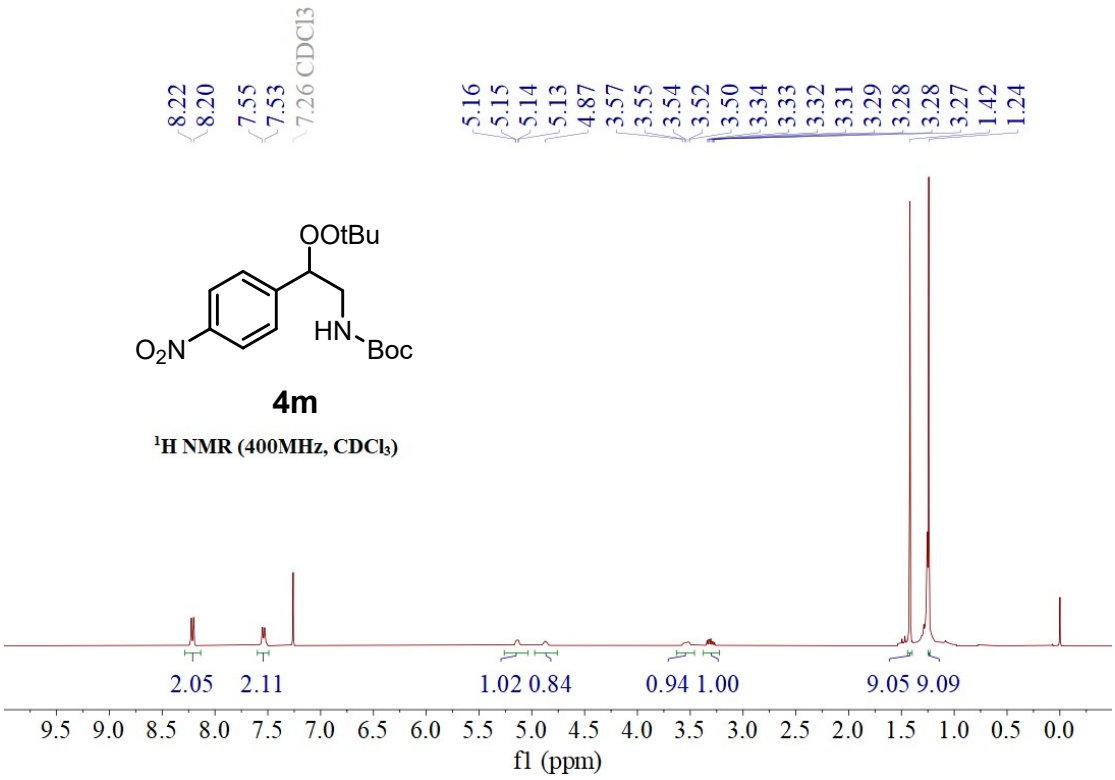

7.27
7.26 CDCl3
7.25
6.89
6.87
4.96
4.95
4.93
4.93
4.86
3.80
3.51
3.49
3.47
3.45
3.44
3.42
1.43
1.22
OOtBu
HN
Boc
O
4k
1H NMR (400MHz, CDCl3)
2.08 2.00
0.93 0.79
3.01 1.87
8.98 9.04
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)


159.61
155.95
130.51
128.41
113.92
84.29
80.77
79.43
77.16 CDCl3
55.37
44.60
28.52
26.56
OOtBu
HN
Boc
O
4k
13C NMR (100MHz, CDCl3)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.26 CDCl3
5.41
5.40
5.39
5.38
4.90
3.69
3.68
3.66
3.64
3.62
3.60
3.58
3.58
3.56
3.54
1.42
1.19
F
OOtBu
F
HN
Boc
F
F
F
4l
1H NMR (400MHz, CDCl3)
1.09
0.87
2.00
9.09
9.02
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
f1 (ppm)

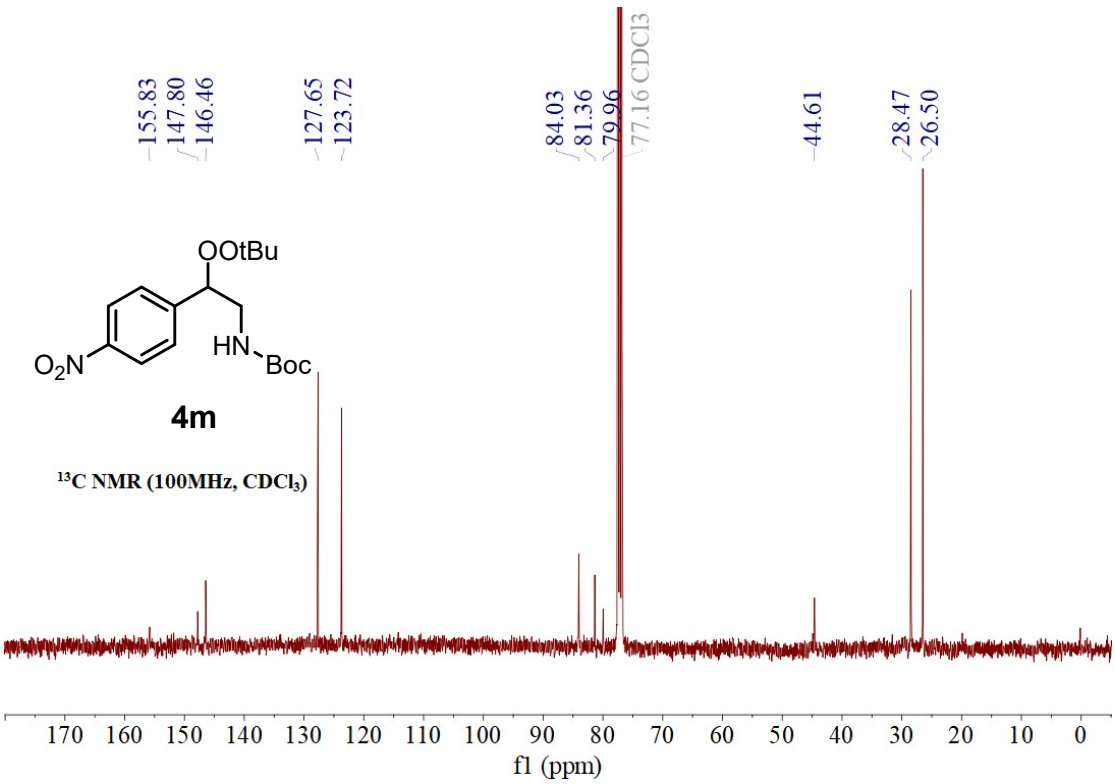

-141.51
-153.92
-162.03
F
OOtBu
F
HN
Boc
F
F
F
4l
19F NMR (376MHz, CDCl3)
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
f1 (ppm)


155.44
81.13
79.70
77.16 CDCl3
76.32
41.57
28.07
26.03
F
OOtBu
F
HN
F
Boc
F
F
4l
13C NMR (100MHz, CDCl3)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)



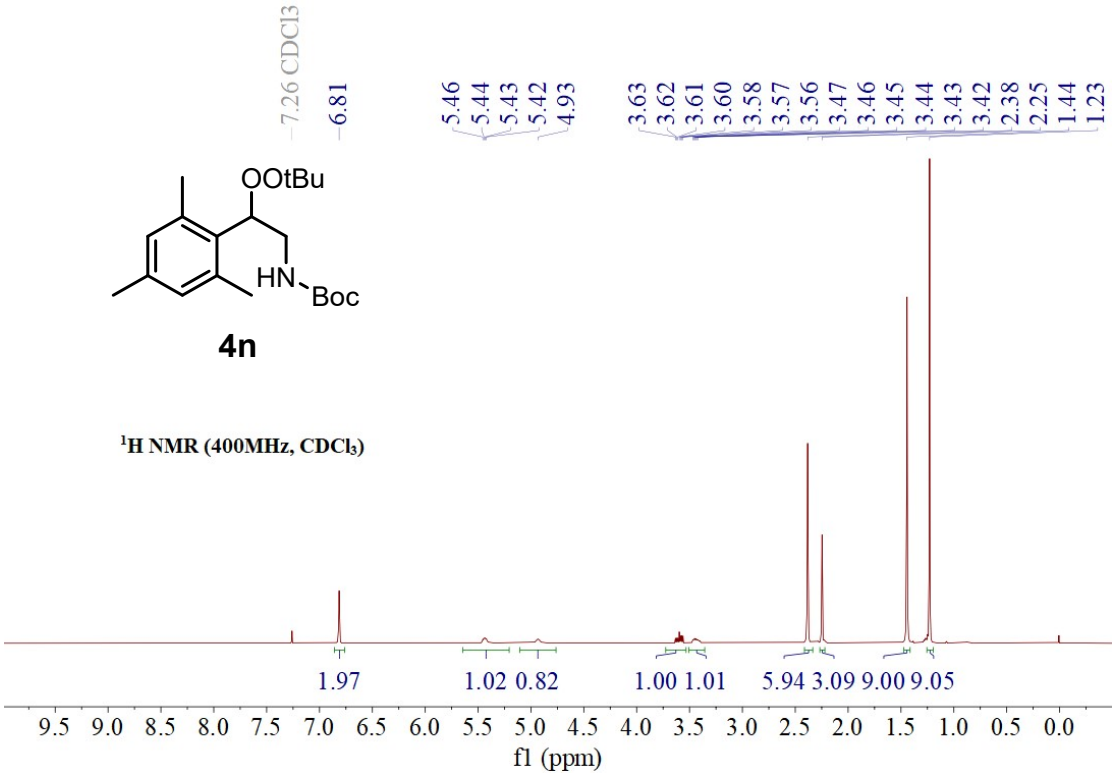
4m

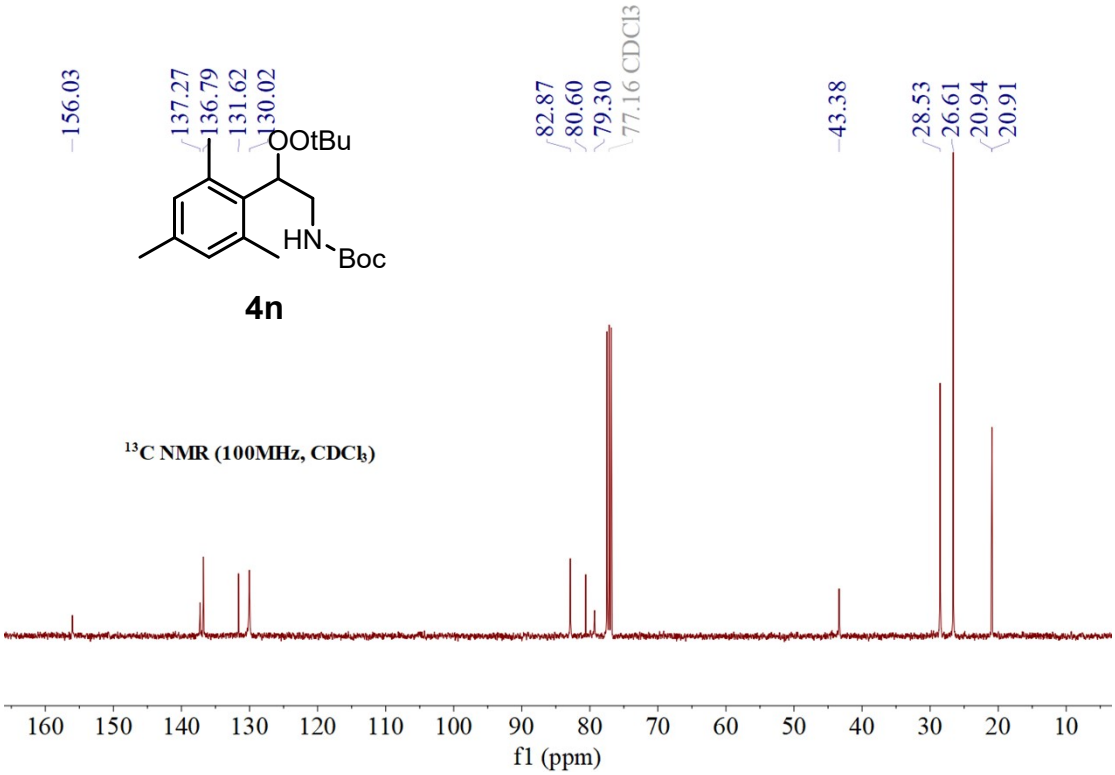
^{1}H NMR (400MHz, $CDCl_3$)

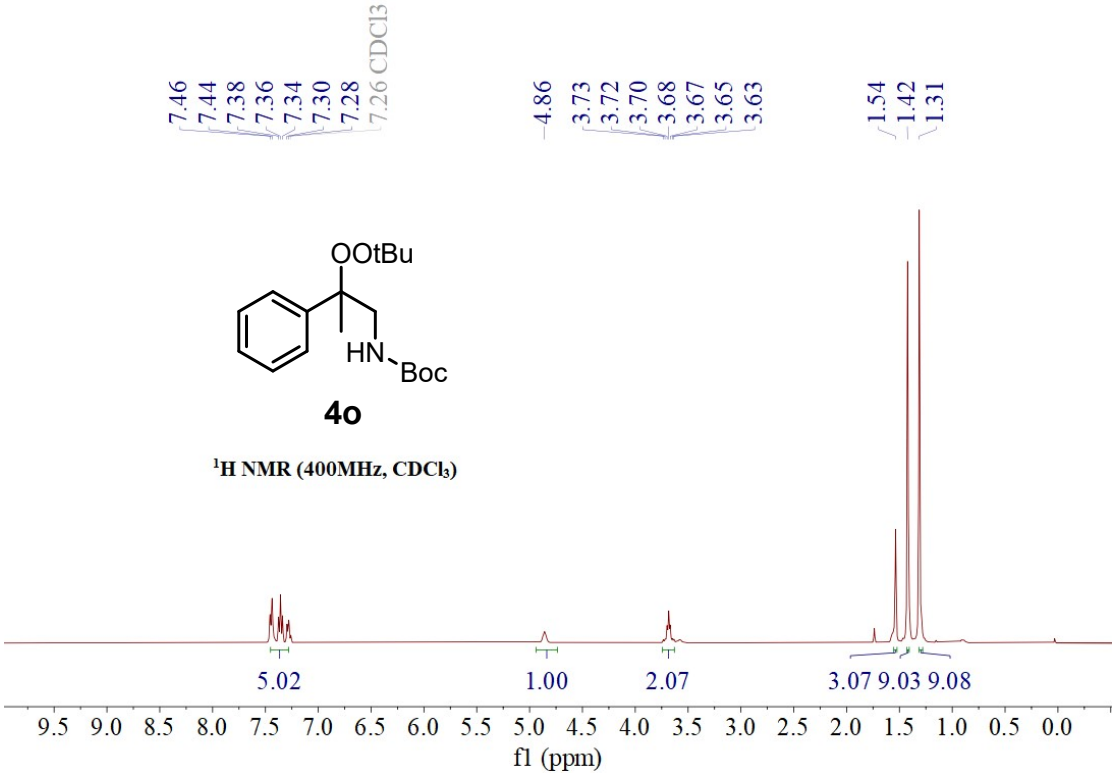


4m

^{13}C NMR (100MHz, $CDCl_3$)

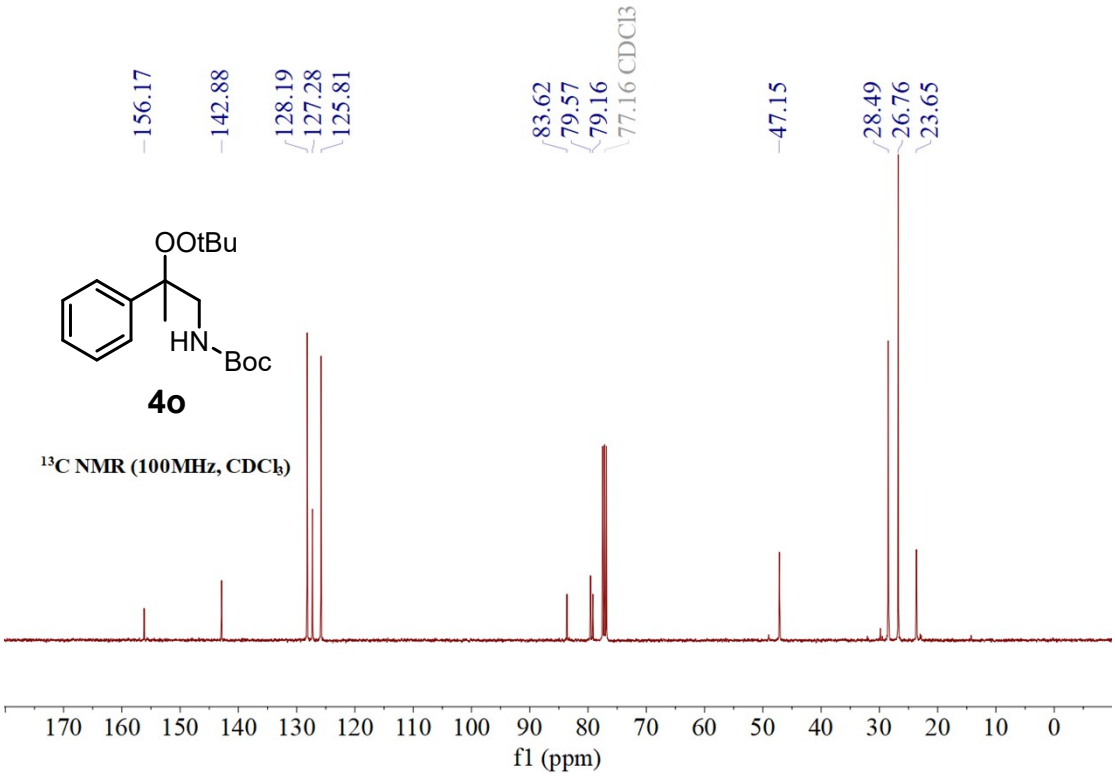

7.26 CDCl3
6.81
5.46
5.44
5.43
5.42
4.93
3.63
3.62
3.61
3.60
3.58
3.57
3.56
3.47
3.46
3.45
3.44
3.43
3.42
2.38
2.25
1.44
1.23
OOtBu
HN
Boc
4n
1H NMR (400MHz, CDCl3)
1.97
1.02 0.82
1.00 1.01
5.94 3.09 9.00 9.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


156.03
137.27
136.79
131.62
130.02
82.87
80.60
79.30
77.16 CDCl3
43.38
28.53
26.61
20.94
20.91
OOtBu
HN
Boc
4n
13C NMR (100MHz, CDCl3)
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)



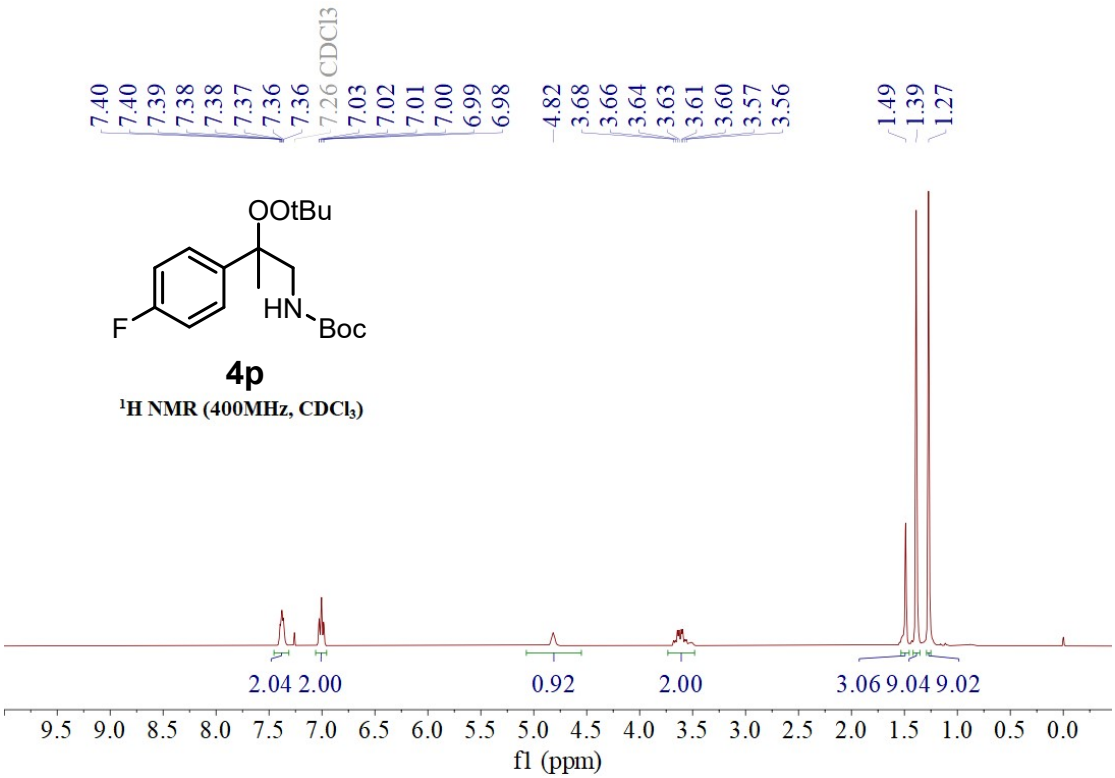
4o

^{1}H NMR (400MHz, $CDCl_3$)



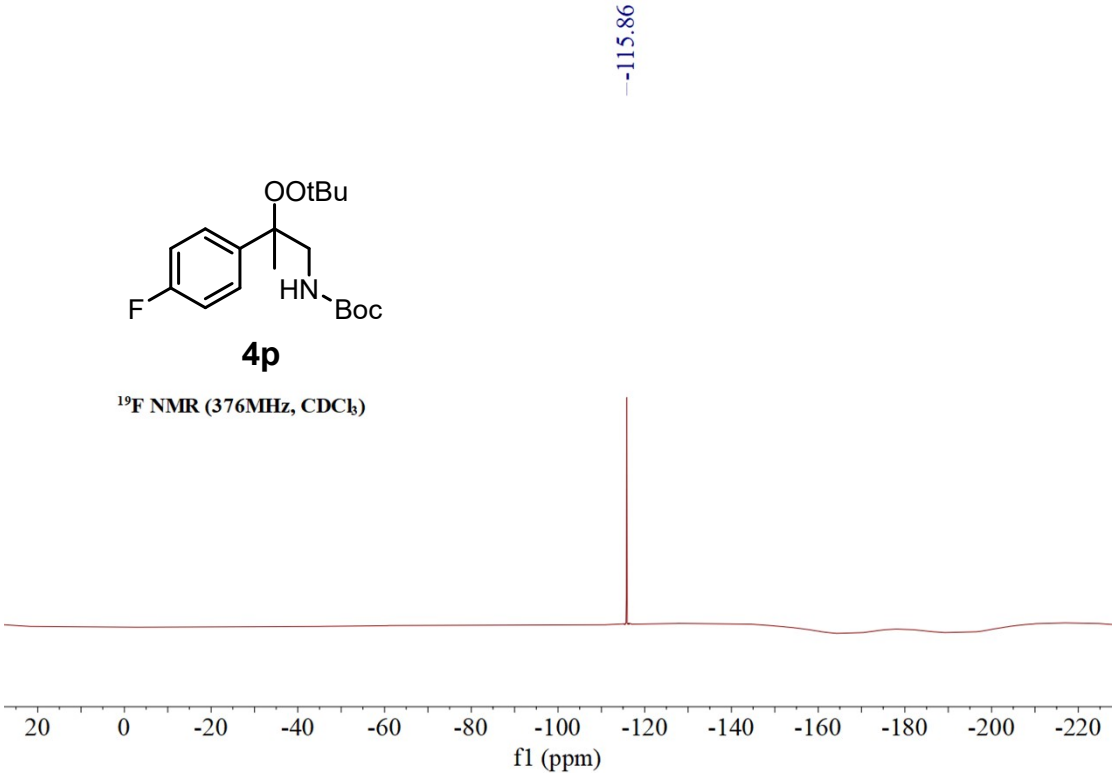
4o

^{13}C NMR (100MHz, $CDCl_3$)



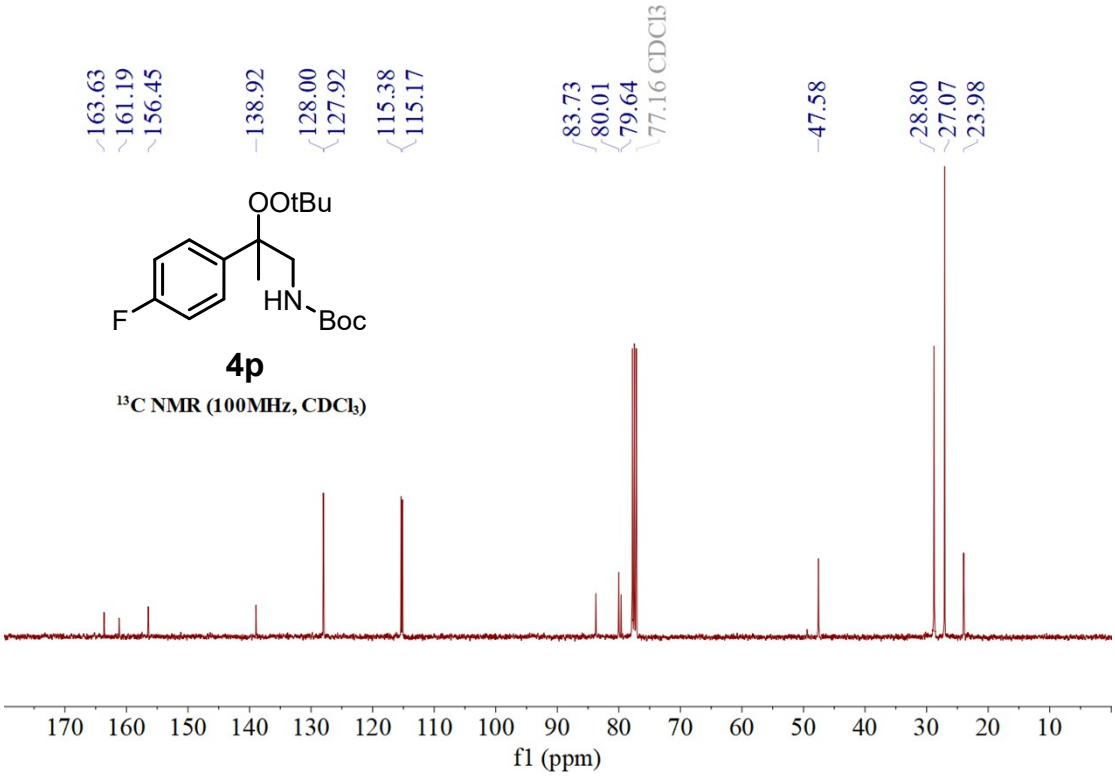
4p

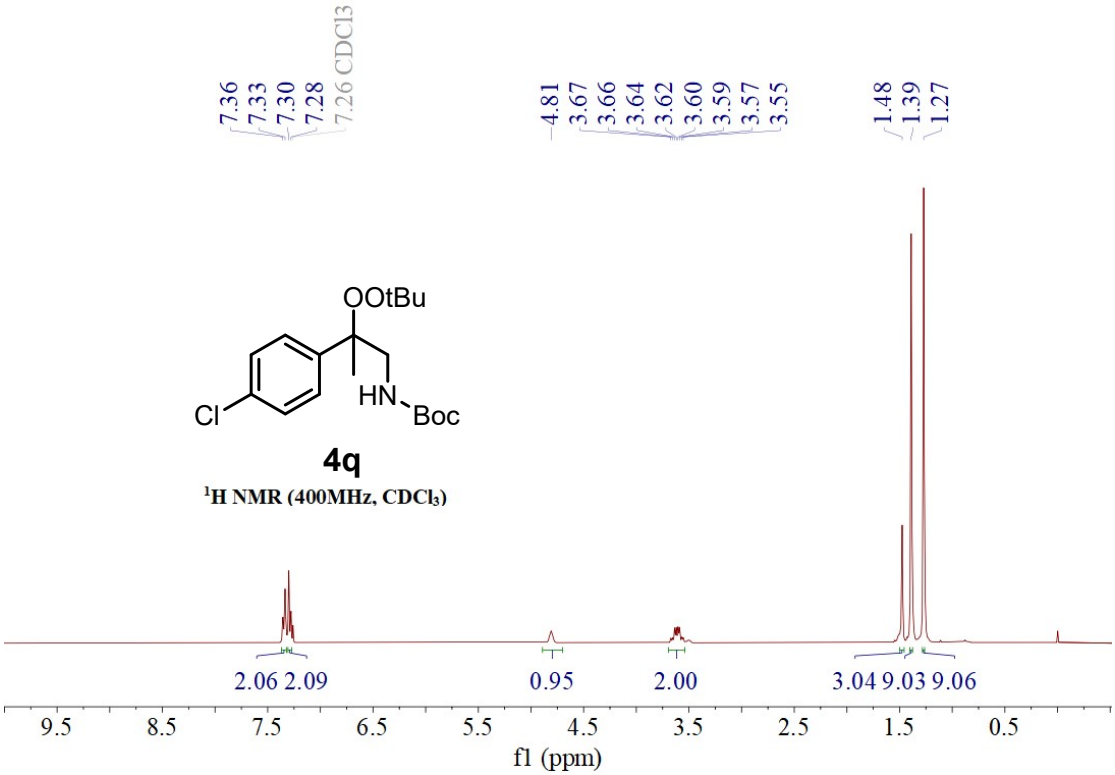
^{1}H NMR (400MHz, $CDCl_3$)



4p

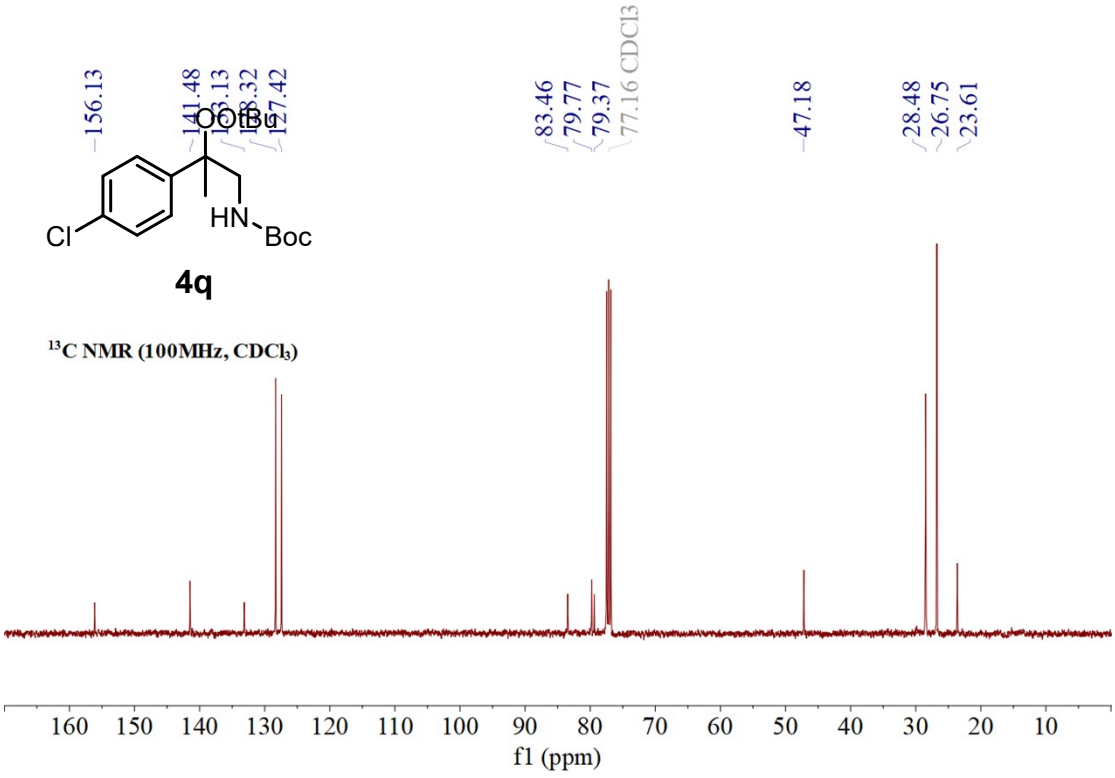
^{19}F NMR (376MHz, $CDCl_3$)


163.63
161.19
156.45
138.92
128.00
127.92
115.38
115.17
83.73
80.01
79.64
77.16 CDCl3
47.58
28.80
27.07
23.98
OOtBu
HN
Boc
F
4p
13C NMR (100MHz, CDCl3)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)



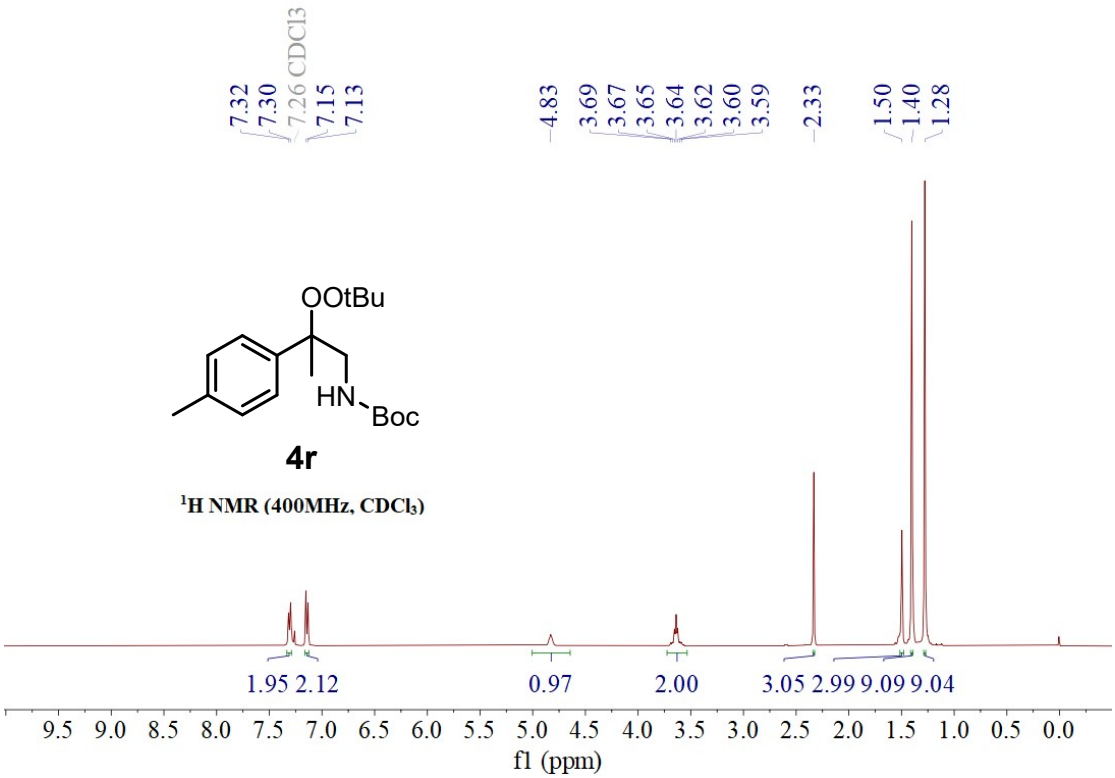
4q

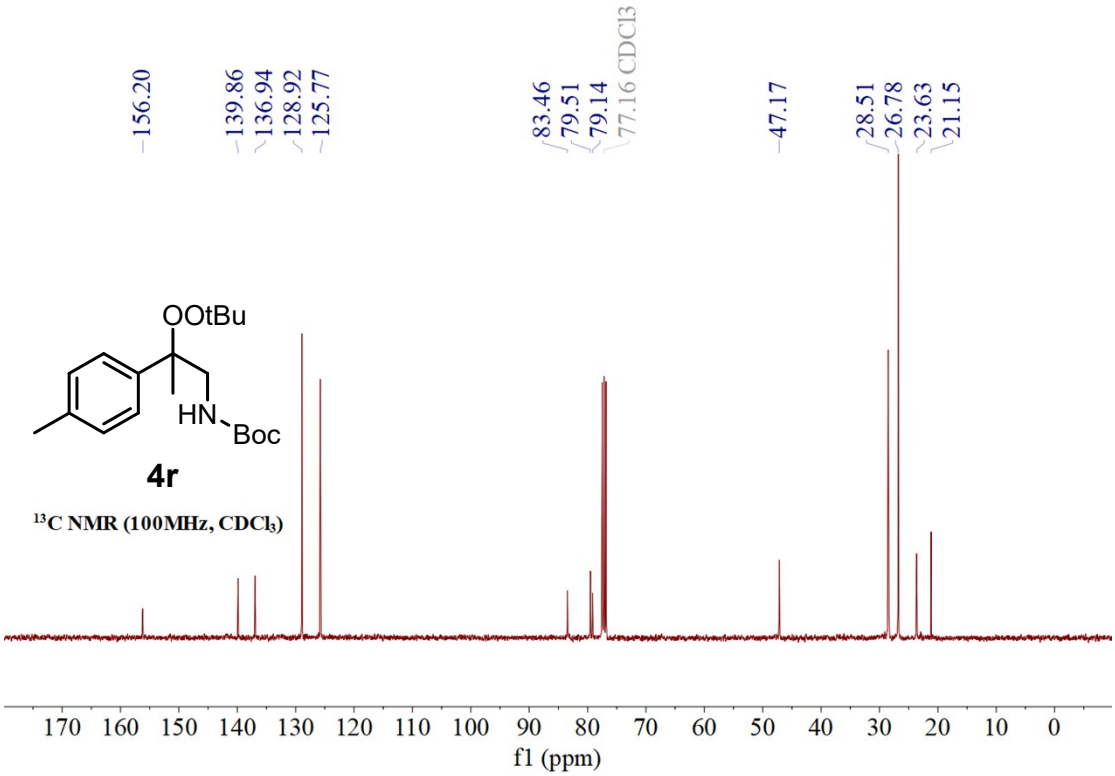
^{1}H NMR (400MHz, $CDCl_3$)

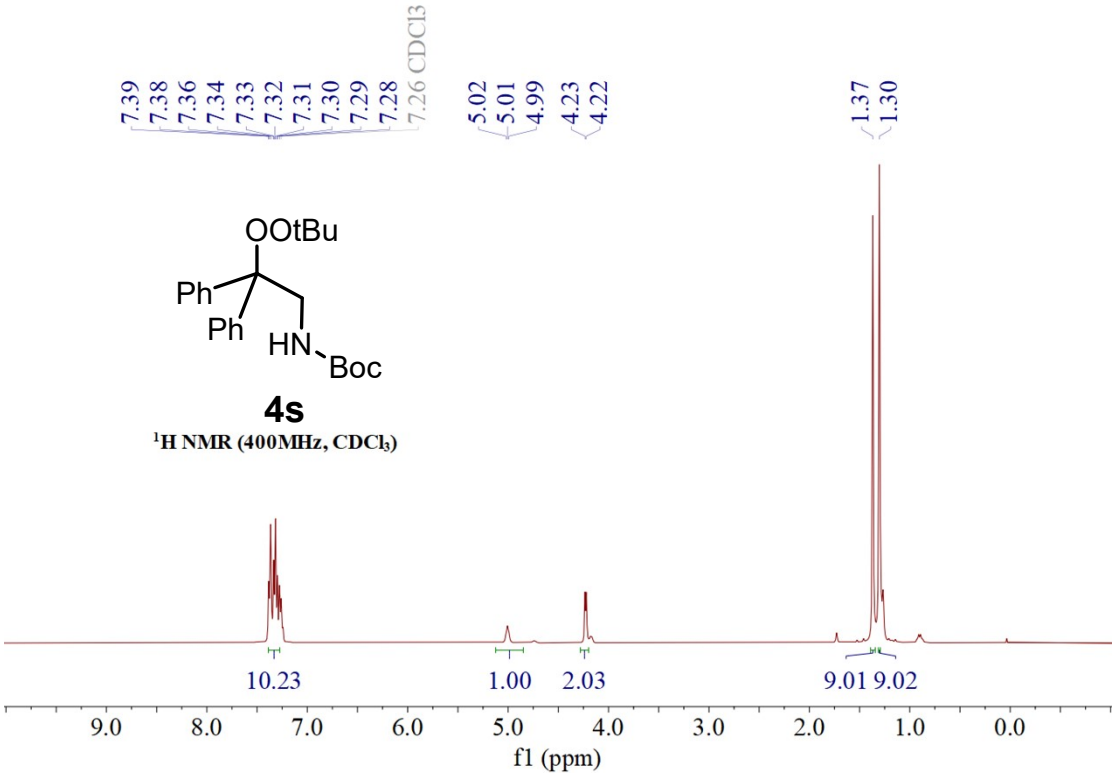


4q

^{13}C NMR (100MHz, $CDCl_3$)

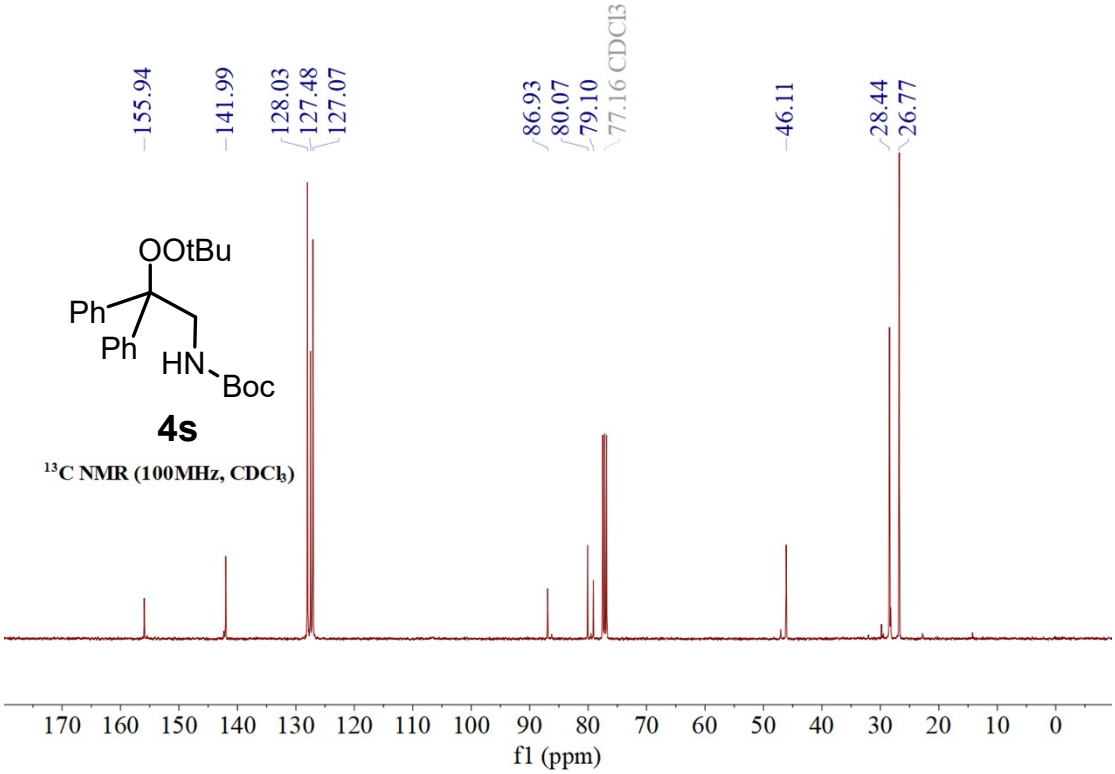

7.32
7.30
7.26 CDCl3
7.15
7.13
4.83
3.69
3.67
3.65
3.64
3.62
3.60
3.59
2.33
1.50
1.40
1.28
OOtBu
HN
Boc
4r
1H NMR (400MHz, CDCl3)
1.95 2.12
0.97
2.00
3.05 2.99 9.09 9.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


156.20
139.86
136.94
128.92
125.77
83.46
79.51
79.14
77.16 CDCl3
47.17
28.51
26.78
23.63
21.15
OOtBu
HN
Boc
4r
13C NMR (100MHz, CDCl3)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



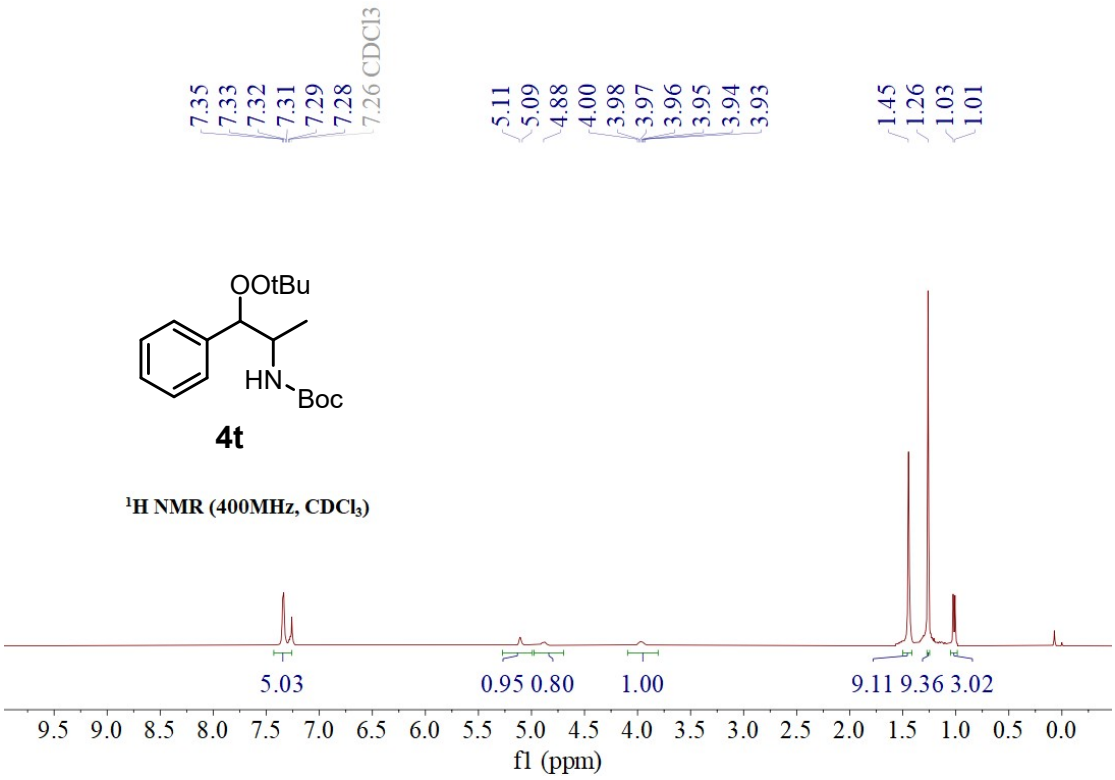
4s

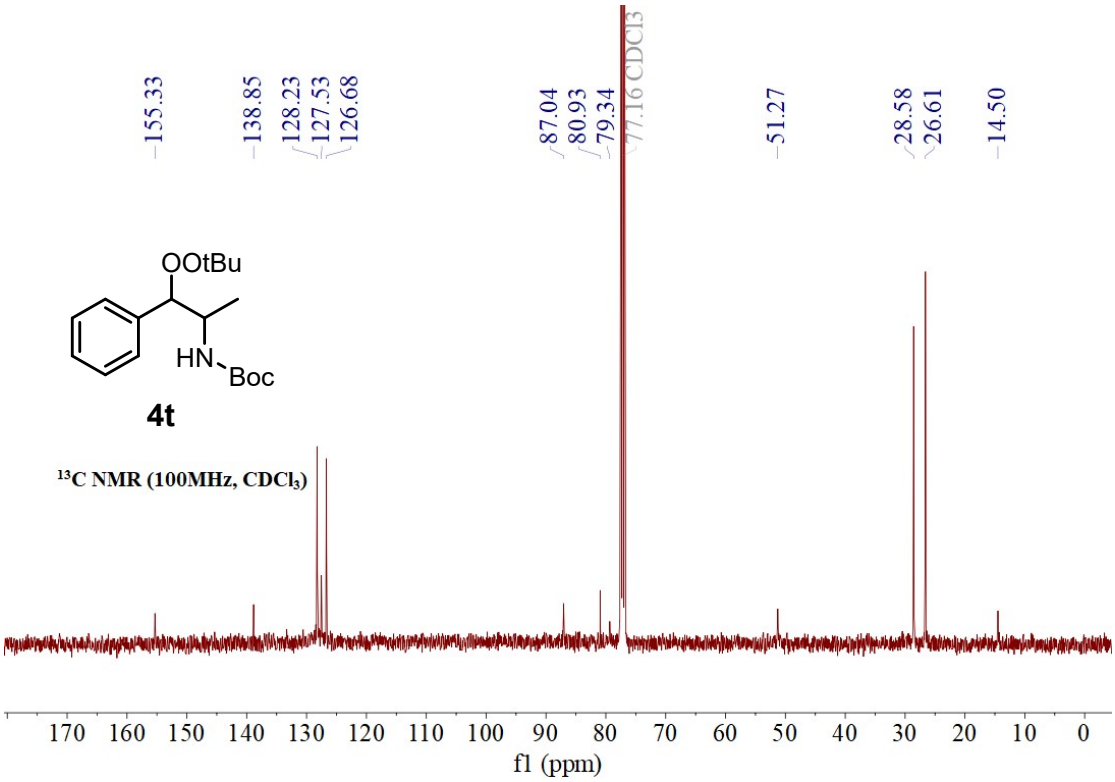
^{1}H NMR (400MHz, $CDCl_3$)

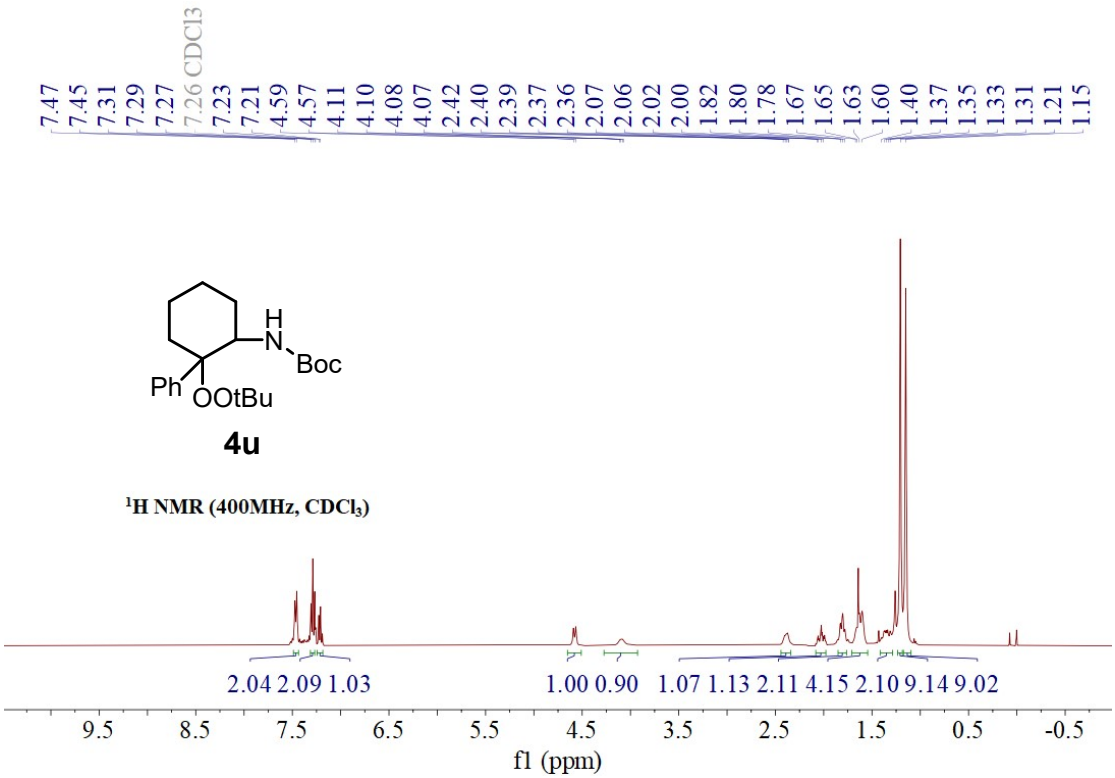


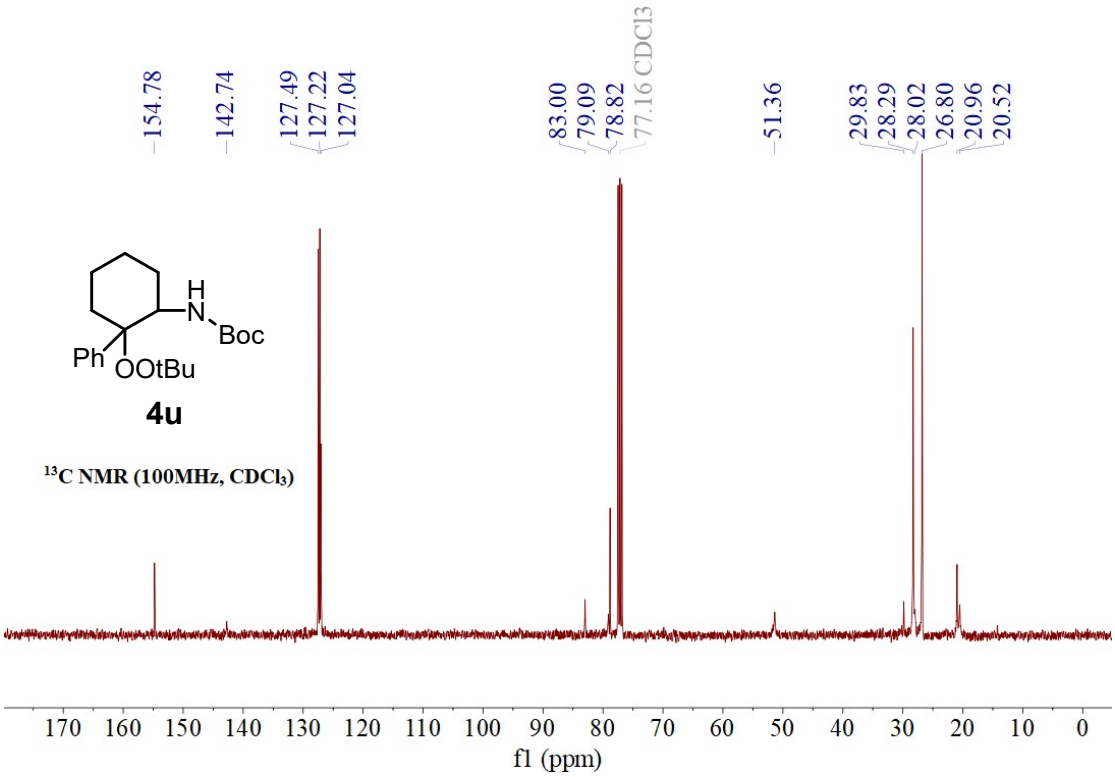
4s

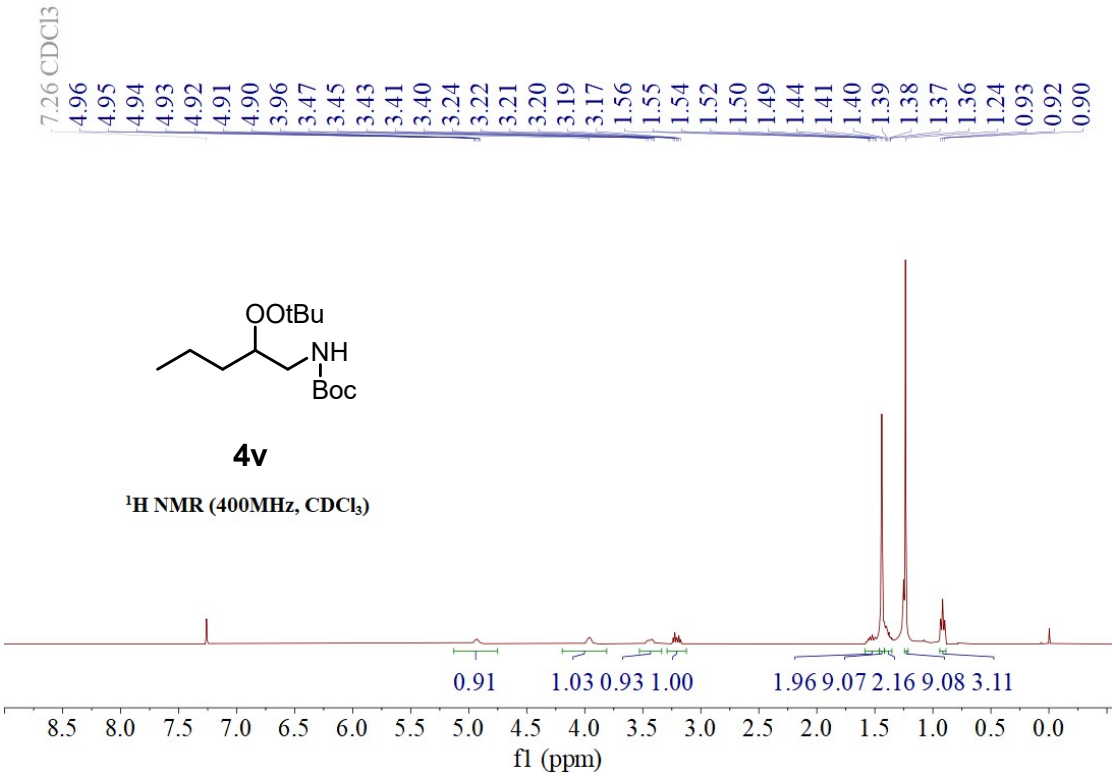
^{13}C NMR (100MHz, $CDCl_3$)


7.35
7.33
7.32
7.31
7.29
7.28
7.26 CDCl3
5.11
5.09
4.88
4.00
3.98
3.97
3.96
3.95
3.94
3.93
1.45
1.26
1.03
1.01
OOtBu
HN
Boc
4t
¹H NMR (400MHz, CDCl₃)
5.03
0.95 0.80
1.00
9.11 9.36 3.02
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
f1 (ppm)


155.33
138.85
128.23
127.53
126.68
87.04
80.93
79.34
77.16 CDCl3
51.27
28.58
26.61
14.50
OOtBu
HN
Boc
4t
¹³C NMR (100MHz, CDCl₃)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

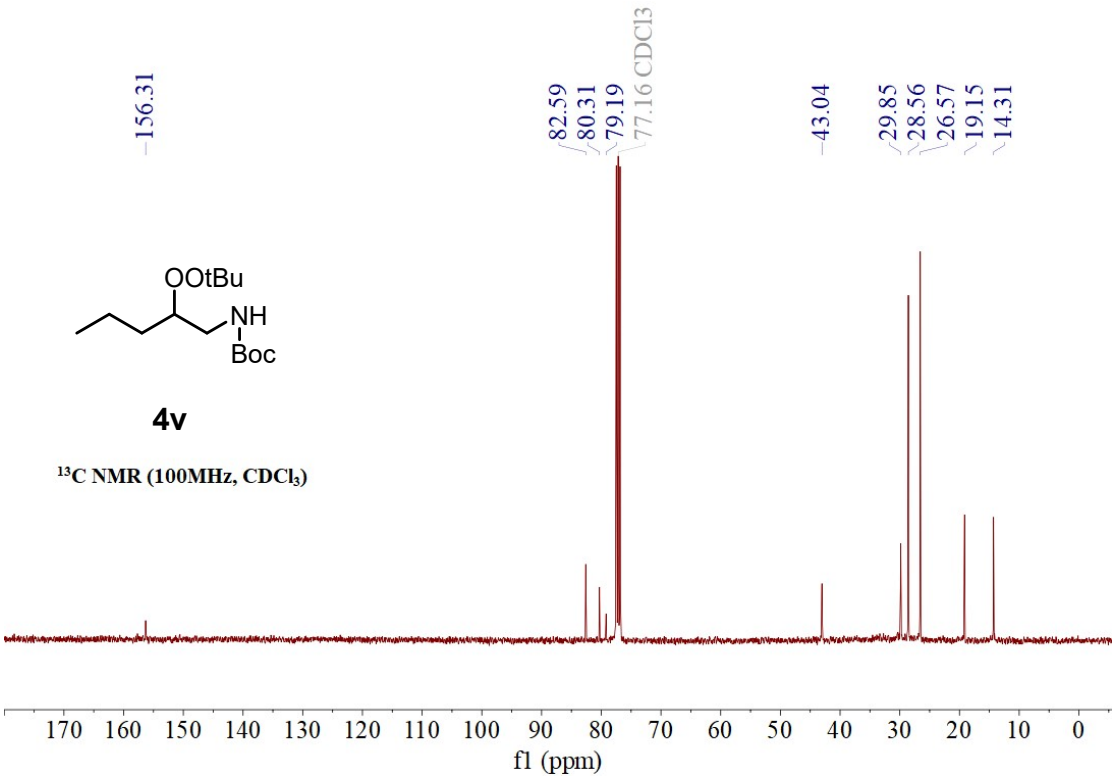

7.47 7.45 7.31 7.29 7.27 7.26 CDCl3 7.23 7.21 4.59 4.57 4.11 4.10 4.08 4.07 2.42 2.40 2.39 2.37 2.36 2.07 2.06 2.02 2.00 1.82 1.80 1.78 1.67 1.65 1.63 1.60 1.40 1.37 1.35 1.33 1.31 1.21 1.15
H
N
Boc
Ph
OOtBu
4u
¹H NMR (400MHz, CDCl₃)
2.04 2.09 1.03
1.00 0.90 1.07 1.13 2.11 4.15 2.10 9.14 9.02
9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.5
f1 (ppm)


154.78 142.74 127.49 127.22 127.04 83.00 79.09 78.82 77.16 CDCl3 51.36 29.83 28.29 28.02 26.80 20.96 20.52
H
N
Boc
Ph
OOtBu
4u
¹³C NMR (100MHz, CDCl₃)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



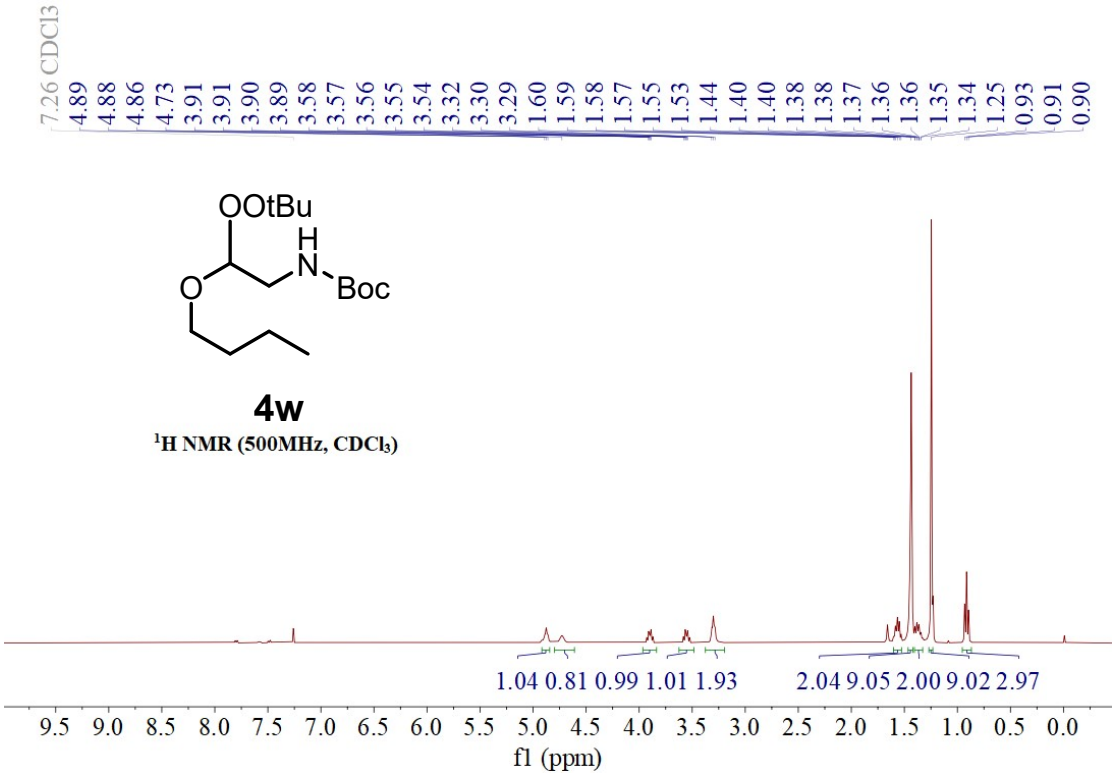
4v

^{1}H NMR (400MHz, $CDCl_3$)



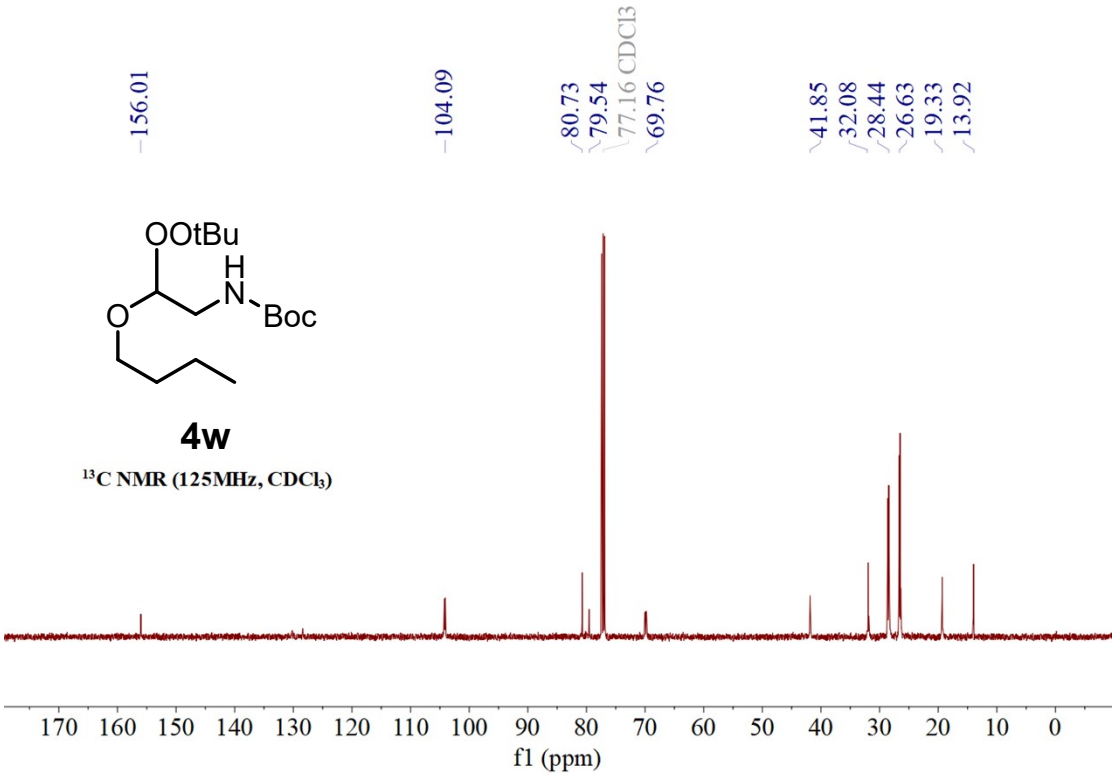
4v

^{13}C NMR (100MHz, $CDCl_3$)



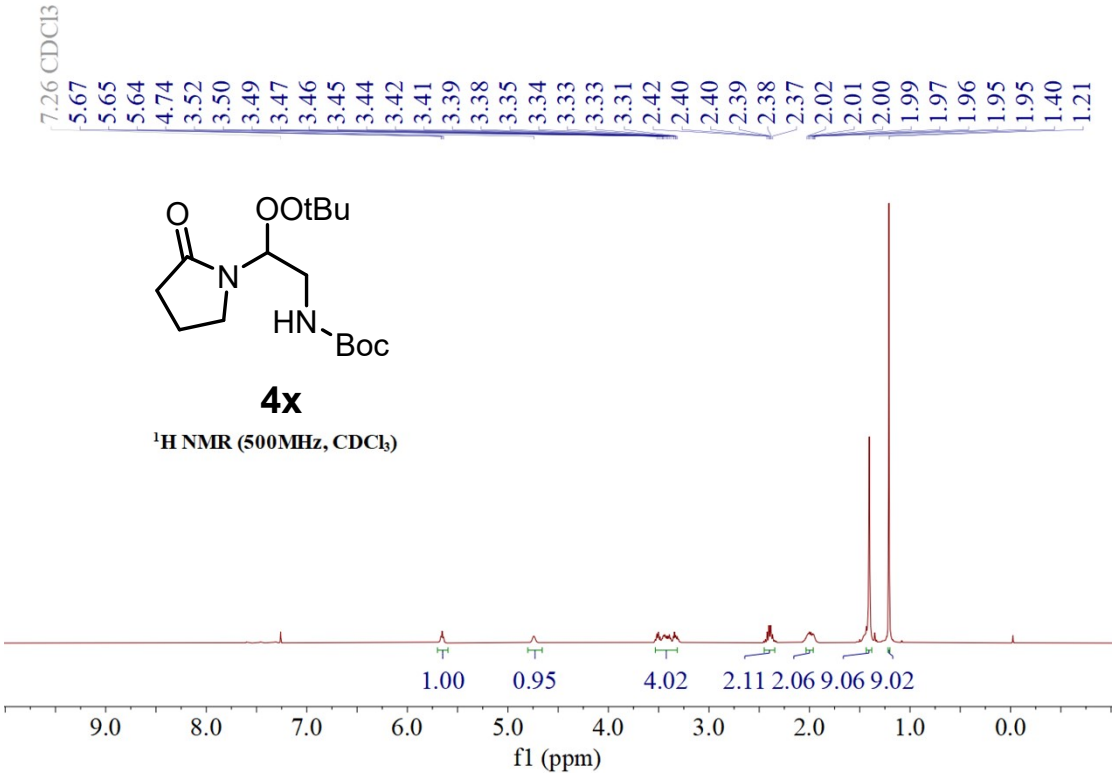
4w

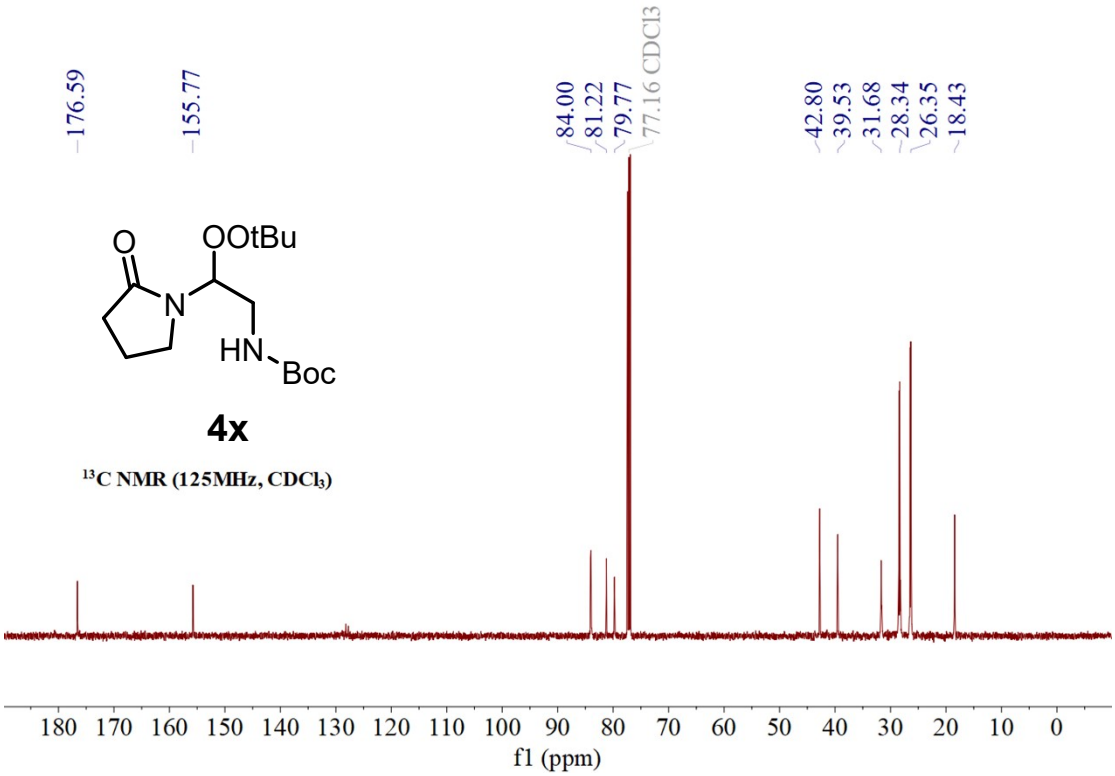
^{1}H NMR (500MHz, $CDCl_3$)



4w

^{13}C NMR (125MHz, $CDCl_3$)


7.26 CDCl3
5.67
5.65
5.64
4.74
3.52
3.50
3.49
3.47
3.46
3.45
3.44
3.42
3.41
3.39
3.38
3.35
3.34
3.33
3.33
3.31
2.42
2.40
2.40
2.39
2.38
2.37
2.02
2.01
2.00
1.99
1.97
1.96
1.95
1.95
1.40
1.21
O
OOtBu
N
HN
Boc
4x
1H NMR (500MHz, CDCl3)
1.00
0.95
4.02
2.11
2.06
9.06
9.02
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


176.59
155.77
84.00
81.22
79.77
77.16 CDCl3
42.80
39.53
31.68
28.34
26.35
18.43
O
OOtBu
N
HN
Boc
4x
13C NMR (125MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)