Supporting Information

Transition Metal Free C-C Bond Cleavage/Borylation of Cycloketone Oxime Esters

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General Information

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Advance III-400 in solvents as indicated. Chemical shift are reported in ppm referenced to the solvent resonance ($CDCl_3$: ^{1}H NMR: $\delta = 7.26$; ^{13}C NMR: $\delta = 77.00$). IR spectra were recorded on a Bruker Tensor 27 spectrometer and only major peaks are given in cm^{-1}. HRMS were obtained on a Q-TOF micro spectrometer or Orbitrap mass spectrometer. All reactions were conducted in oven-dried Schlenk-tube under an atmosphere of nitrogen, unless otherwise stated. Reagents were purchased at commercial quality and were used without further purification. Column chromatography was carried out on silica gel.

Starting Materials

All of cyclobutanone oxime esters **1** were synthesized from the corresponding cyclobutanones and carboxylic acids according to the literature.[1] The substituted cyclobutanones were prepared according to the reported procedure.[2] All of the NMR spectra of the known compounds were in full accordance with the data in the literatures.[3]

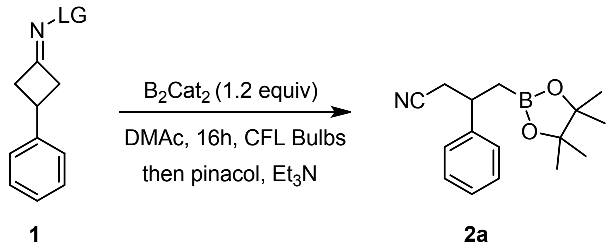
Optimization of Reaction Conditions

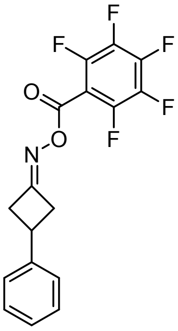
General Procedure

A 10 mL oven-dried Schlenk-tube equipped with a magnetic stir bar was charged with **1** (0.20 mmol, 1.0 equiv.) under a nitrogen atmosphere, boron source and additives. Then 2.0 mL solvent were added by syringe. The tube was then sealed and the mixture was stirred under the irradiation of two 23 W compact fluorescent light (CFL) bulbs or without irradiation at room temperature for 16 h. Pinacol (0.8 mmol, 4.0 equiv.) dissolved in Et_3N (0.7 mL) were added to the reaction mixture and stirred for 1 h. The mixture was then quenched with H_2O and transferred to a separatory funnel with EtOAc (5 mL). The aqueous layer was extracted with EtOAc (3 x 10 mL), and then the organic phases were combined and washed with brine (20 mL), dried over Na_2SO_4, and evaporated under reduced pressure. Then the internal standard dibromomethane (0.2 mmol) was added into the crude product mixture for the NMR yield study.

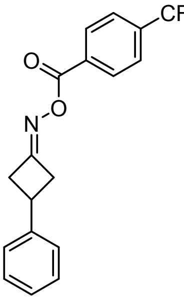
Table S1 Optimization of the reaction conditions.

Leaving Group[a]





1a



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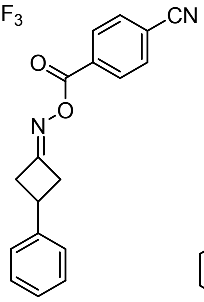

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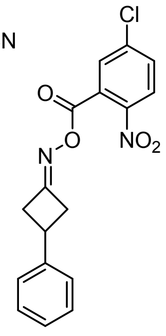

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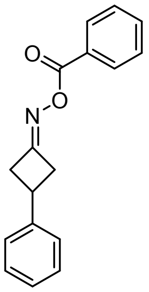

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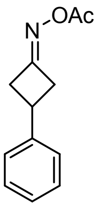
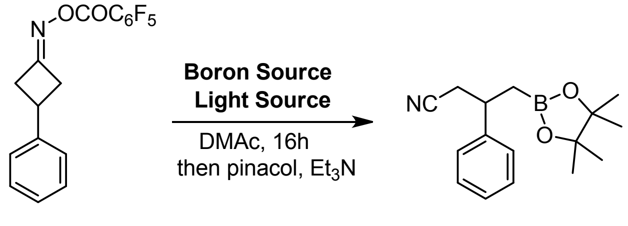


1a-5

Entry	**1**	Yield[b] (%)
1	**1a**	52
2	**1a-1**	48
3	**1a-2**	10
4	**1a-3**	15
5	**1a-4**	trace
6	**1a-5**	trace

[a] Reaction conditions: **1** (0.2 mmol, 1.0 equiv.), B_2cat_2 (0.24 mmol, 1.2 equiv.), in 2.0 mL of DMAc at room temperature were irradiated by two 23 W compact fluorescent light (CFL) bulbs for 16 h under N_2; pinacol (0.8 mmol, 4.0 equiv.) dissolved in Et_3N (0.7 mL) were added to the reaction mixture and stirred for 1 h. [b] NMR yields using CH_2Br_2 as internal standard.

Boron Source[a]

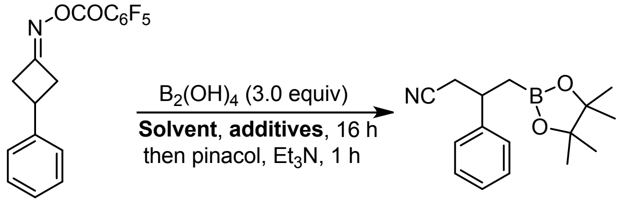


1a **2a**

Entry	Boron source (equiv.)	Light source	Yield[b] (%)
1	B_2Cat_2 (1.2)	23 W CFL	52
2	B_2Cat_2 (2.0)	23 W CFL	54
3	B_2pin_2 (2.0)	23 W CFL	7[c]
4	$B_2(OH)_4$ (2.0)	23 W CFL	61
5	B_2Cat_2 (2.0)	-	28[d]
6	$B_2(OH)_4$ (2.0)	-	60[d]
7	$B_2(OH)_4$ (2.0)	-	61[e]
8	$B_2(OH)_4$ (3.0)	-	77[e]
9	$B_2(OH)_4$ (4.0)	-	73[e]

[a] Reaction conditions: **1a** (0.20 mmol, 1.0 equiv.), Boron sources (1.2-4.0 equiv.), in 2.0 mL of DMAc at room temperature were irradiated by two 23 W compact fluorescent light (CFL) bulbs for 16 h under N_2; then pinacol (0.8 mmol, 4.0 equiv.) dissolved in Et_3N (0.7 mL), were added to the reaction mixture and stirred for 1 h. [b] NMR Yields using CH_2Br_2 as internal standard. [c] Without workup with pinacol and Et_3N. [d] In the dark. [e] under ambient light.

Solvents and Additives[a]



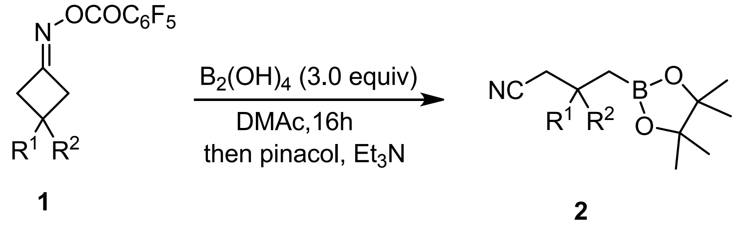
1a **2a**

Entry	Solvent	Additives (equiv.)	Yield[b] (%)
1	NMP	-	66
2	DMF	-	52
3	MeCN	-	20
4	acetone	-	15
5	DCM	-	NR
6	DCM	DMAc (1.0)	trace
7	DMAc	4-phenylpyridine (1.0)	56
8	DMAc	4-cyanopyridine (1.0)	trace[c]
9	DMAc	DMAP (1.0)	63
10	DMAc	Cs_2CO_3 (1.0)	26

[a] Reaction conditions: **1a** (0.20 mmol, 1.0 equiv.), $B_2(OH)_4$ (0.60 mmol, 3.0 equiv.), additives, in 2.0 mL of solvent at room temperature for 16 h under N_2; then pinacol (0.8 mmol, 4.0 equiv.) dissolved in Et_3N (0.7 mL), was added to the reaction mixture and stirred for 1 h. [b] NMR yields using CH_2Br_2 as internal standard. [c] 3-Phenylbutanenitrile was observed as a major product.

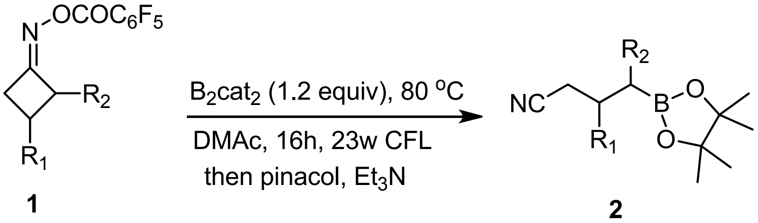
Representative Procedure for the Borylation of Cyclobutanone Oximes

*For Cyclobutanone Oxime Esters **1a-t***



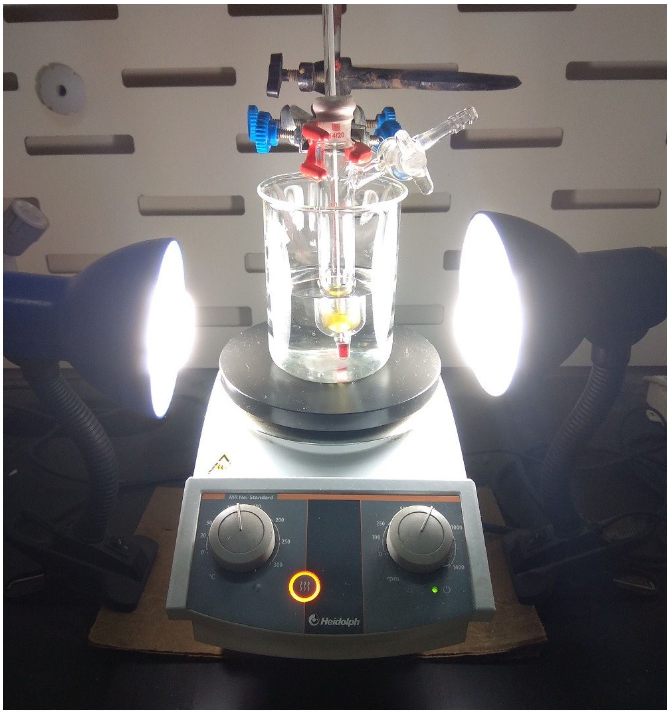
A 10 mL oven-dried Schlenk-tube equipped with a magnetic stir bar under a nitrogen atmosphere was charged with **1** (0.20 mmol, 1.0 equiv.), $B_2(OH)_4$ (0.60 mmol, 3.0 equiv.). Then 2.0 mL of DMAc were added by syringe. The tube was then sealed and the mixture was stirred at room temperature for 16 h. Pinacol (0.8 mmol, 4.0 equiv.) dissolved in Et_3N (0.7 mL) were added to the reaction mixture and stirred for 1 h. The mixture was then quenched with H_2O and transferred to a separatory funnel with EtOAc (10 mL). The aqueous layer was extracted with EtOAc (3 x 10 mL), the organic phases were combined and washed with brine (20 mL), dried over Na_2SO_4, and evaporated under reduced pressure. The resulting residue was purified by column chromatography on silica gel (gradient eluent of EtOAc/petroleum ether: 1/15 to 1/5) to give the corresponding products **2a-t** in Table 2, **7a-c** in Figure 2.

For Cyclobutanone Oxime Esters ***1u*** *and* ***1v***

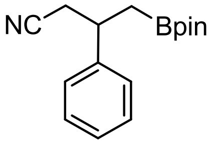


A 10 mL oven-dried Schlenk-tube equipped with a magnetic stir bar under a nitrogen atmosphere was charged with **1** (0.20 mmol, 1.0 equiv.), B_2Cat_2 (0.24 mmol, 1.2 equiv.) and additives. Then 2.0 mL of DMAc were added by syringe. The tube was then sealed and the mixture was stirred under the irradiation of two 23 W compact fluorescent light (CFL) bulbs at 80 °C for 16 h. Pinacol (0.8 mmol, 4.0 equiv.) dissolved in Et_3N (0.7 mL) were added to the reaction mixture and stirred for 1 h. The mixture was then quenched with H_2O and transferred to a separatory funnel with EtOAc (10 mL). The aqueous layer was extracted with EtOAc (3 x 10 mL), then the organic phases were combined and washed with brine (20 mL), dried over Na_2SO_4, and evaporated under reduced pressure. The resulting residue was purified by column chromatography on silica gel (gradient eluent of EtOAc/petroleum ether: 1/15 to 1/5) to give the corresponding products **2u** and **2v** in eqs (1) and (2).

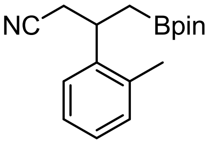
Picture of Reaction Set-Up



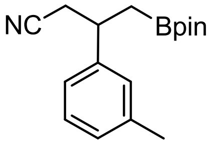
Characterization of Products 2



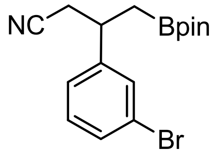
3-Phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanenitrile (2a): Colorless oil (75%, 40.7 mg); R_f 0.35 (EtOAc/petroleum ether = 1:10); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.36 – 7.18 (m, 5H), 3.30 – 3.20 (m, 1H), 2.66 (d, J = 7.2 Hz, 2H), 1.42 – 1.30 (m, 2H), 1.12 (s, 6H), 1.09 (s, 6H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 143.3, 128.6, 127.2, 127.0, 118.7, 83.4, 38.0, 26.9, 24.7, 24.6 ppm; IR (neat): υ_{max} 2977, 2927, 2245, 1369, 1141, 699 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{23}BNO_2$ [M+H]$^+$ 272.1816, found 272.1810.



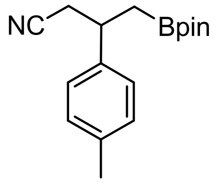
4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(*o*-tolyl)butanenitrile (2b): Colorless oil (71%, 41 mg); R_f 0.35 (EtOAc/petroleum ether = 1:10); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.25 – 7.08 (m, 4H), 3.60 – 3.50 (m, 1H), 2.60 (d, J = 6.8 Hz, 2H), 2.40 (s, 3H), 1.43 – 1.32 (m, 2H), 1.07 (s, 6H), 1.03 (s, 6H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 141.4, 135.6, 130.4, 126.8, 126.5, 125.3, 118.8, 83.3, 32.7, 26.2, 24.6, 24.5, 19.6; IR (neat): υ_{max} 2926, 2246, 1370, 1142, 733, 702 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{25}BNO_2$ [M+H]$^+$ 286.1973, found 286.1967.



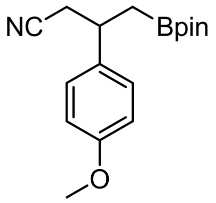
4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(m-tolyl)butanenitrile (2c): Colorless oil (78%, 44.4 mg); R_f 0.35 (EtOAc/petroleum ether = 1:10); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.19 (t, J = 7.5 Hz, 1H), 7.06 – 7.02 (m, 3H), 3.26 – 3.10 (m, 1H), 2.65 (d, J = 6.8 Hz, 2H), 2.33 (s, 3H), 1.42 – 1.27 (m, 2H), 1.12 (s, 6H), 1.10 (s, 6H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 143.3, 138.1, 128.5, 127.9, 127.7, 123.9, 118.8, 83.4, 37.9, 26.7, 24.7, 24.6, 21.4 ppm; IR (neat): υ_{max} 2977, 2927, 2245, 1368, 1141, 702 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{25}BNO_2$ [M+H]$^+$ 286.1973, found 286.1970.



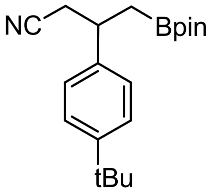
3-(3-Bromophenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanenitrile (2d): Colorless oil (60%, 42 mg); R_f 0.30 (EtOAc/petroleum ether = 1:10); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.42 – 7.35 (m, 2H), 7.23 – 7.17 (m, 2H), 3.28 – 3.10 (m, 1H), 2.68 (dd, *J* = 16.8, 6.8 Hz, 1H), 2.64 (dd, *J* = 16.8, 7.2 Hz, 1H), 1.39 – 1.30 (m, 2H), 1.14 (s, 6H), 1.11 (s, 6H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 145.6, 130.3, 130.2, 125.6, 122.6, 118.4, 83.6, 37.8, 26.4, 24.7, 24.6 ppm; IR (neat): υ_{max} 2977, 2928, 2360, 2246, 1372, 1143 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{22}BBrNO_2$ [M+H]$^+$ 350.0921, found 350.0920.



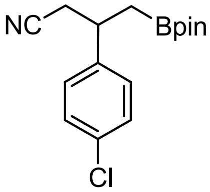
4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(p-tolyl)butanenitrile (2e): Colorless oil (78%, 44.5 mg); R_f 0.35 (EtOAc/petroleum ether = 1:10); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.14 (m, 4H), 3.29 – 3.17 (m, 1H), 2.66 (dd, *J* = 16.4, 7.0 Hz, 1H), 2.66 (dd, *J* = 16.4, 7.2 Hz, 1H), 2.32 (s, 3H), 1.38 – 1.28 (m, 2H), 1.13 (s, 6H), 1.11 (s, 6H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 140.4, 136.7, 129.3, 126.8, 118.8, 83.4, 37.6, 26.9, 24.7, 24.6, 21.0 ppm; IR (KBr): υ_{max} 2977, 2927, 2245, 1368, 1142, 813 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{25}BNO_2$ [M+H]$^+$ 286.1973, found 286.1965.



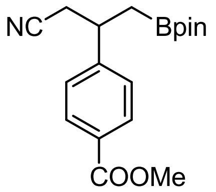
3-(4-Methoxyphenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanenitrile (2f): Colorless oil (72%, 44 mg); R_f 0.30 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.18 (dd, *J* = 6.8, 2.0 Hz, 2H), 6.85 (dd, *J* = 6.8, 2.0 Hz, 2H), 3.78 (s, 3H), 3.28 – 3.17 (m, 1H), 2.64 (dd, *J* = 16.4, 6.8 Hz, 2H), 2.59 (dd, *J* = 16.8, 7.2 Hz, 2H), 1.34 – 1.29 (m, 2H), 1.13 (s, 6H), 1.11 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.6, 135.5, 128.0, 118.8, 113.9, 83.4, 55.3, 37.2, 27.2, 24.7, 24.6; IR (neat): υ_{max} 2926, 2242, 1514, 1372, 1250, 1143 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{25}BNO_3$ [M+H]$^+$ 302.1922, found 302.1923.



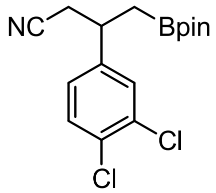
3-(4-(*tert*-Butyl)phenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanenitrile (2g): White solid (76%, 49.7 mg); R_f 0.35 (EtOAc/petroleum ether = 1:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 – 7.30 (m, 2H), 7.20 – 7.17 (m, 2H), 3.30 – 3.17 (m, 1H), 2.65 (d, *J* = 6.8 Hz, 2H), 1.42 – 1.31 (m, 2H), 1.29 (s, 9H), 1.10 (s, 6H), 1.09 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.0, 140.3, 126.6, 125.4, 118.9, 83.3, 37.5, 34.4, 31.3, 26.8, 25.0, 24.6 ppm; IR (neat): υ_{max} 2966, 2241, 1367, 1144, 832 cm^{-1}. HRMS (ESI) calcd for $C_{20}H_{31}BNO_2$ [M+H]$^+$ 328.2442, found 328.2459.



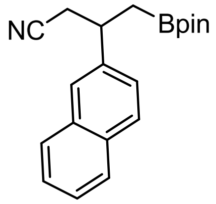
3-(4-Chlorophenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanenitrile (2h): Colorless oil (61%, 37.2 mg); R_f 0.30 (EtOAc/petroleum ether = 1:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29 (dd, *J* = 6.6, 2.0 Hz, 2H), 7.20 (dd, *J* = 6.8, 2.0 Hz, 2H), 3.31 – 3.20 (m, 1H), 2.65 (dd, *J* = 16.8, 6.4 Hz, 1H), 2.60 (dd, *J* = 16.4, 7.2 Hz, 1H), 1.39 – 1.30 (m, 2H), 1.15 (s, 6H), 1.13 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.8, 132.9, 128.7, 128.4, 118.4, 83.5, 37.4, 26.7, 25.0, 24.7, 24.5 ppm; IR (neat): υ_{max} 2978, 2930, 2245, 1370, 1141, 826 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{21}BClNaNO_2$ [M+Na]$^+$ 328.1246, found 328.1257.



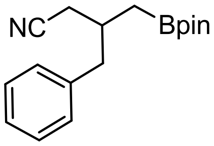
Methyl-4-(1-cyano-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)benzoate (2i): Colorless oil (30%, 22.6 mg); R_f 0.3 (EtOAc/petroleum ether = 1:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 3.89 (s, 3H), 3.35 – 3.27 (m, 1H), 2.69 (dd, *J* = 18.8, 6.6 Hz, 1H), 2.64 (dd, *J* = 16.8, 7.4 Hz, 1H), 1.41 – 1.28 (m, 2H), 1.11 (s, 6H), 1.08 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.7, 148.5, 130.0, 129.1, 127.1, 118.2, 83.5, 52.0, 38.0, 26.4, 24.7, 24.5 ppm; IR (KBr): υ_{max} 2978, 2245, 1718, 1276, 1141, 844 cm^{-1}. HRMS (ESI) calcd for $C_{18}H_{25}BNO_4$ $[M+H]^+$ 330.1871, found 330.1863.



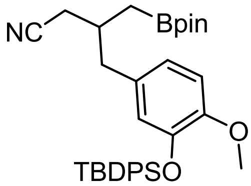
3-(3,4-Dichlorophenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanenitrile (2j): Colorless oil (48%, 31.1 mg); R_f 0.3 (EtOAc/petroleum ether = 1:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39 – 7.20 (m, 3H), 3.92 – 3.81 (m, 1H), 2.79 (dd, *J* = 16.8, 6.0 Hz, 1H), 2.69 (dd, *J* = 16.8, 6.0 Hz, 1H), 1.47 – 1.33 (m, 2H), 1.15 (s, 6H), 1.10 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.7, 133.4, 131.9, 129.2, 127.5, 125.8, 118.0, 83.6, 34.3, 24.8, 24.7, 24.5 ppm; IR (neat): υ_{max} 2923, 2247, 1371, 1141, 845 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{21}BCl_2NO_2$ $[M+H]^+$ 340.1037, found 340.1048.



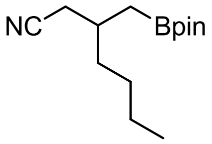
3-(Naphthalen-2-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanenitrile (2k): Colorless oil (75%, 48.2 mg); R_f 0.35 (EtOAc/petroleum ether = 1:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 7.6 Hz, 1H), 7.78 – 7.74 (m, 1H), 7.59 – 7.43 (m, 4H), 4.27 – 4.12 (m, 1H), 2.90 (dd, *J* = 16.8, 6.0 Hz, 1H), 2.77 (dd, *J* = 16.6, 7.0 Hz, 1H),1.63 – 1.50 (m, 2H), 1.08 (s, 6H), 0.99 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.2, 133.9, 130.9, 129.1, 127.7, 126.3, 125.6, 125.4, 123.3, 122.6, 118.7, 83.4, 31.9, 26.1, 24.6, 24.5 ppm; IR (neat): υ_{max} 2976, 2360, 2245, 1141, 778, 734 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{24}BNNaO_2$ [M+Na]$^+$ 344.1792, found 344.1789.



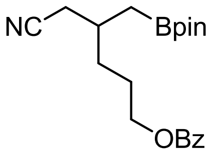
3-Benzyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanenitrile (2l): Colorless oil (65%, 37.1 mg); R_f 0.35 (EtOAc/petroleum ether = 1:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30 (t, *J* = 7.2 Hz, 2H), 7.25 – 7.15 (m, 3H), 2.78 (dd, *J* = 13.8, 5.8 Hz, 1H), 2.63 (dd, *J* = 13.6, 8.0 Hz, 1H), 2.41 – 2.18 (m, 3H), 1.25 (s, 12H), 1.01 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.2, 129.2, 128.5, 126.5, 118.9, 83.4, 42.1, 33.8, 24.9, 24.8, 23.1 ppm; IR (KBr): υ_{max} 2977, 2926, 2245, 1371, 1141, 700 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{25}BNO_2$ [M+H]$^+$ 286.1973, found 286.1970.



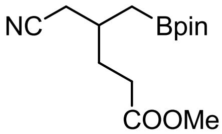
3-(3-((*tert*-Butyldiphenylsilyl)oxy)-4-methoxybenzyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanenitrile (2m): White solid (42%, 45.6 mg); R_f 0.3 (EtOAc/petroleum ether = 1:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 – 7.66 (m, 4H), 7.39 – 7.30 (m, 6H), 6.63 (d, *J* = 8.0 Hz, 1H), 6.55 (d, *J* = 2.0 Hz, 1H), 6.43 (dd, *J* = 8.0, 2.0 Hz, 1H), 3.54 (s, 3H), 2.64 (dd, *J* = 13.8, 5.8 Hz, 1H), 2.46 (dd, *J* = 13.6, 8.4 Hz, 1H), 2.32 – 2.18 (m, 2H), 2.18 – 2.05 (m, 1H), 1.24 (s, 12H), 1.11 (s, 9H), 0.94 (dd, *J* = 7.0, 3.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.4, 143.6, 135.4, 133.6, 132.4, 129.5, 127.4, 121.0, 120.1, 119.0, 113.1, 83.4, 55.3, 41.7, 33.8, 26.7, 24.9, 24.8, 22.9, 19.7 ppm; IR (neat): υ_{max} 2928, 2856, 2246, 1514, 1112, 800 cm^{-1}; HRMS (ESI) calcd for $C_{34}H_{44}BNNaO_4Si$ [M+Na]$^+$ 592.3025, found 592.3035.



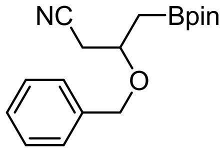
3-((4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)heptanenitrile (2n): Colorless oil (62%, 31.1 mg); R_f 0.4 (EtOAc/petroleum ether = 1:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.40 (d, *J* = 6.0 Hz, 2H), 2.0 – 1.90 (m, 1H), 1.48 – 1.36 (m, 2H), 1.36 – 1.28 (m, 4H), 1.24 (s, 12H), 0.96 – 0.89 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 119.2, 83.3, 35.6, 31.6, 28.9, 24.8, 23.9, 22.6, 14.0 ppm; IR (neat): υ_{max} 2958, 2927, 2857, 2360, 2245, 1373, 1144 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{27}BNO_2$ $[M+H]^+$ 252.2129, found 252.2127.



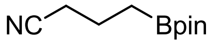
5-Cyano-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)pentyl benzoate (2o): Colorless oil (70%, 50.0 mg); R_f 0.3 (EtOAc/petroleum ether = 1:10); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.06 – 7.95 (m, 2H), 7.62 – 7.47 (m, 1H), 7.47 – 7.37 (m, 2H), 4.31 (t, *J* = 6.6 Hz, 2H), 2.45 (d, *J* = 6.4 Hz, 2H), 2.12 – 1.97 (m, 1H), 1.87 – 1.73 (m, 2H), 1.67 – 1.46 (m, 2H), 1.22 (s, 12H), 1.01 – 0.98 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.5, 132.9, 130.2, 129.5, 128.3, 118.8, 83.4, 64.63, 32.3, 31.4, 26.1, 24.8, 23.9 ppm; IR (neat): υ_{max} 2977, 2245, 1716, 1270, 721 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{28}BNNaO_4$ $[M+Na]^+$ 380.2004, found 380.2008.



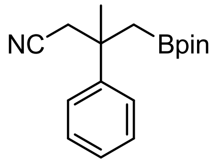
Methyl-5-cyano-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)pentanoate (2p): Colorless oil (38%, 21.4 mg); R_f 0.3 (EtOAc/petroleum ether = 1:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.68 (s, 3H), 2.44 (d, *J* = 6.0 Hz, 2H), 2.35 (t, *J* = 7.6 Hz, 2H), 2.05 – 1.95 (m, 1H), 1.87 – 1.66 (m, 2H), 1.24 (s, 12H), 1.03 – 0.90 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.4, 118.7, 83.5, 51.7, 31.5, 31.1, 31.0, 24.8, 23.71 ppm; IR (neat): υ_{max} 2977, 2927, 2245, 1734, 1371, 1141, 845 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{24}BNNaO_4$ $[M+Na]^+$ 304.1691, found 304.1691.



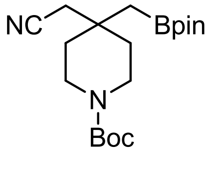
3-(Benzyloxy)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanenitrile (2q): Colorless oil (58%, 34.9 mg); R_f 0.3 (EtOAc/petroleum ether = 1:10); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.39 – 7.26 (m, 5H), 4.59 (dd, *J* = 25.4, 11.4 Hz, 2H), 3.98 – 3.90 (m, 1H), 2.69 (dd, *J* = 16.8, 5.2 Hz, 1H), 2.64 (dd, *J* = 16.8, 6.4 Hz, 1H), 1.37 – 1.27 (m, 2H), 1.24 (s, 12H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 137.8, 128.4, 127.8, 127.7, 118.0, 83.6, 72.4, 71.2, 25.0, 24.8, 24.7 ppm; IR (KBr): υ_{max} 2978, 2249, 1371, 1142, 697 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{24}BNNaO_3$ [M+Na]$^+$ 324.1741, found 324.1732.



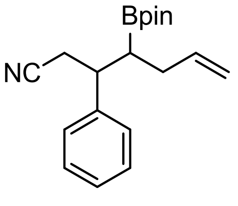
4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)butanenitrile (2r): Colorless oil (85%, 33.1 mg); R_f 0.4 (EtOAc/petroleum ether = 1:10); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.36 (t, *J* = 7.2 Hz, 2H), 1.83 – 1.70 (m, 2H), 1.24 (s, 12H), 0.94 (t, *J* = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 119.9, 83.4, 24.8, 20.4, 19.1 ppm; IR (neat): υ_{max} 2978, 2929, 2360, 2245, 1373, 1320, 1143, 780 cm^{-1}. HRMS (ESI) calcd for $C_{10}H_{19}BNO_2$ [M+H]$^+$ 196.1503, found 196.1496.



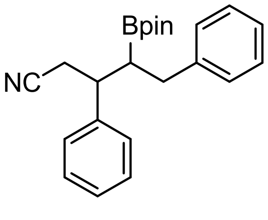
3-Methyl-3-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanenitrile (2s): White solid (76%, 43.3 mg); R_f 0.35 (EtOAc/petroleum ether = 1:10); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.39 – 7.28 (m, 4H), 7.24 – 7.19 (m, 1H), 2.83 (dd, *J* = 23.2, 16.4 Hz, 2H), 1.60 (s, 3H), 1.43 (dd, *J* = 24.4, 15.6 Hz, 2H), 1.08 (s, 6H), 1.06 (s, 6H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 146.2, 128.4, 126.6, 125.4, 118.7, 83.2, 38.4, 32.5, 28.1, 24.6, 24.5 ppm; IR (neat): υ_{max} 2975, 2248, 1334, 700 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{25}BNO_2$ [M+H]$^+$ 286.1973, found 286.1969.



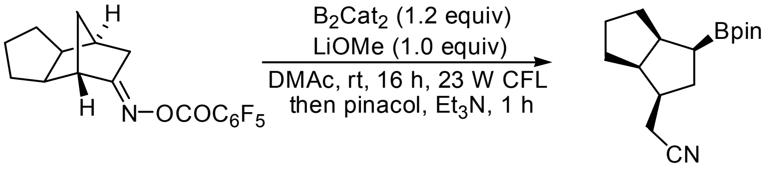
tert**-Butyl-4-(cyanomethyl)-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)piperidine-1-carboxylate (2t):** Colorless oil (34%, 24.8 mg); R_f 0.3 (EtOAc/petroleum ether = 1:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.52 (m, 2H), 3.31 – 3.19 (m, 2H), 2.56 (s, 2H), 1.54 (t, J = 5.7 Hz, 4H), 1.45 (s, 9H), 1.24 (s, 12H), 1.10 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.8, 118.1, 83.4, 79.6, 36.1, 33.1, 28.4, 25.0, 24.8, 22.7, 14.1 ppm; IR (neat): υ_{max} 2924, 2246, 1690, 1365, 1143 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{34}BN_2O_4$ [M+H]$^+$ 365.2606, found 365.2616.



3-Phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hept-6-enenitrile (2u): Colorless oil (40%, 24.9 mg); R_f 0.30 (EtOAc/petroleum ether = 1:10); the title compound as a 1.6:1 mixture of inseparable diastereomers; ^{1}H NMR (400 MHz, $CDCl_3$): δ = ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.26 (m, 3H), 7.25 – 7.20 (m, 2H), 5.90 – 5.60 (m, 1H), 5.15– 4.85 (m, 2H), 3.11 – 2.94 (m, 1H), 2.84 – 2.63 (m, 2H), 2.38 – 2.17 (m, 1H), 2.08 – 1.90 (m, 2 H), 1.68 – 1.57 (m, 1H), 1.27 (s, 7.5H), 0.97 (s, 4.5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.0, 141.6, 136.9, 136.7, 128.8, 128.6, 127.9, 127.6, 127.4, 127.3, 118.8, 118.6, 116.3, 116.1, 83.75, 83.3, 42.8, 42.7, 33.7, 25.0, 24.8, 24.6, 24.5, 23.7 ppm; IR (neat): υ_{max} 3734, 2924, 2245, 1373, 1141, 700 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{27}BNO_2$ [M+H]$^+$ 312.2129, found 312.2130.

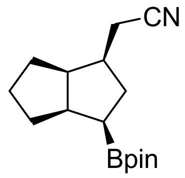


3,5-Diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanenitrile (2v): White solid (42%, 30.3 mg); R_f 0.30 (EtOAc/petroleum ether = 1:10); the title compound as a 1.9:1 mixture of inseparable diastereomers; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 – 7.27 (m, 5H), 7.25 – 7.07 (m, 5H), 3.12 – 3.01 (m, 1H), 2.96 –2.54 (m, 4H), 2.02 – 1.88 (m, 1H), 1.14 (s, 3.9H), 1.09 (s, 3.9H), 0.85 (s, 2.1H), 0.77 (s, 2.1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.8, 141.6, 140.7, 140.4, 128.9, 128.8, 128.6, 128.3, 128.1, 128.0, 127.5, 127.4, 126.2, 126.0, 118.7, 118.5, 83.6, 83.2, 43.8, 43.7, 35.8, 35.7, 24.9, 24.7, 24.5, 24.4, 24.3, 24.1 ppm; IR (neat): υ_{max} 2925, 2245, 1139, 1018, 798, 698 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{29}BNO_2$ $[M+H]^+$ 362.2286, found 362.2282.

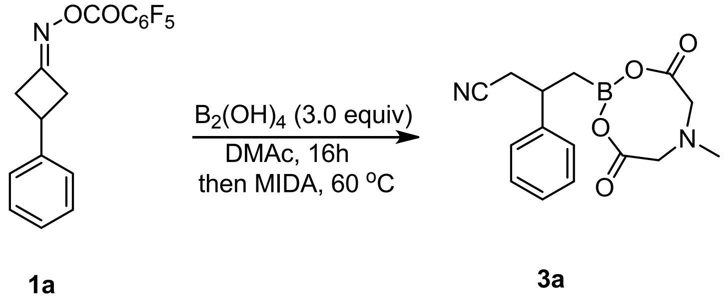


1w **2w**, 25%

A 10 mL oven-dried Schlenk-tube equipped with a magnetic stir bar under a nitrogen atmosphere was charged with **1w** (0.20 mmol, 1.0 equiv.), B_2Cat_2 (0.24 mmol, 1.2 equiv) and LiOMe (0.20 mmol, 1.0 equiv.). Then 2.0 mL of DMAc were added by syringe. The tube was then sealed and the mixture was stirred under the irradiation of two 23 W compact fluorescent light (CFL) bulbs at room temperature for 16 h. Pinacol (0.8 mmol, 4.0 equiv.) dissolved in Et_3N (0.7 mL) were added to the reaction mixture and stirred for 1 h. The mixture was then quenched with H_2O and transferred to a separatory funnel with EtOAc (10 mL). The aqueous layer was extracted with EtOAc (3 x 10 mL), then the organic phases were combined and washed with brine (20 mL), dried over Na_2SO_4, and evaporated under reduced pressure. The resulting residue was purified by column chromatography on silica gel (gradient eluent of EtOAc/petroleum ether: 1/15 to 1/5) to give the corresponding products **2w** in eq (3).



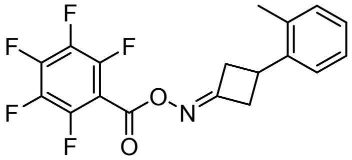
2-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)octahydropentalen-1-yl)acetonitrile (2w): Colorless oil (25%, 13.8 mg); R_f 0.4 (EtOAc/petroleum ether = 1:10); ^1H NMR (400 MHz, $CDCl_3$): δ = 2.60 – 2.48 (m, 1H), 2.47 – 2.33 (m, 2H), 2.08 (m, 1H), 1.97 – 1.97 (m, 1H), 1.74 – 1.65 (m, 1H), 1.60 – 1.44 (m, 6H), 1.24 (s, 12H), 0.93 – 0.84 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 119.3, 83.0, 49.9, 46.9, 45.5, 36.9, 33.1, 32.1, 24.8, 24.7, 24.6, 21.9 ppm; IR (neat): υ_{max} 2934, 2360, 2343, 1507, 1144, 668 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{26}BNNaO_2$ $[M+Na]^+$ 298.1949, found 298.1961.



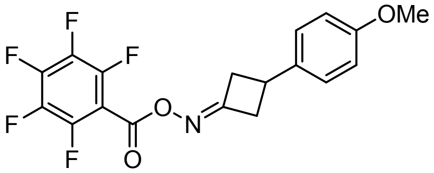
A 10 mL oven-dried Schlenk-tube equipped with a magnetic stir bar under a nitrogen atmosphere was charged with **1a** (0.20 mmol, 1.0 equiv.), $B_2(OH)_4$ (0.6 mmol, 3.0 equiv.). Then 2.0 mL of DMAc were added by syringe. The tube was then sealed and the mixture was stirred at room temperature for 16 h. Methyliminodiacetic acid (MIDA, 0.8 mmol, 4.0 equiv.) was added to the reaction mixture and stirred at 60 °C for 24 h. The mixture was then quenched with H_2O and transferred to a separatory funnel with EtOAc (10 mL). The aqueous layer was extracted with EtOAc (3 x 10 mL), the organic phases were combined and washed with brine (20 mL), dried over Na_2SO_4, and evaporated under reduced pressure. The resulting residue was purified by column chromatography on silica gel (gradient eluent of EtOAc) to give the corresponding product **3a** in Scheme 1.

4-(6-Methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-3-phenylbutanenitrile (3a): White solid (60%, 36 mg); R_f 0.3 (EtOAc); ^1H NMR (400 MHz, DMSO-*d6*): $\delta = 7.33 - 7.22$ (m, 5H), 4.18 (dd, $J = 19.8, 17.0$ Hz, 2H), 3.96 (dd, $J = 32.2, 17.0$ Hz, 2H), 3.10 – 3.03 (m, 1H), 2.82 – 2.78 (m, 5H), 1.04 – 1.02 (m, 2H); ^{13}C NMR (100 MHz, DMSO-*d6*): $\delta = 169.4$, 169.3, 145.8, 128.8, 127.6, 127.1, 120.0, 62.0, 61.9, 46.0, 38.2, 25.9 ppm; IR (neat): υ_{max} 2920, 2247, 1741, 1309, 1022, 859, 697cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{18}BN_2O_4$ $[M+H]^+$ 301.1354, found 301.1357.

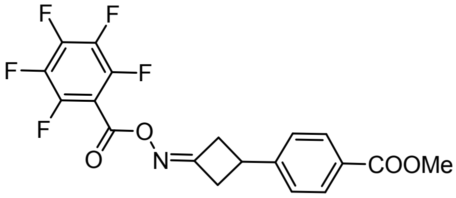
Characterization of Substrates



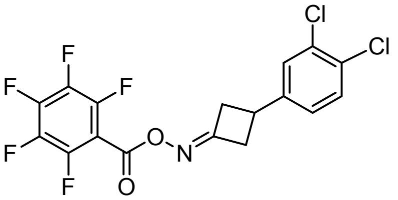
3-(*o*-Tolyl)cyclobutanone *O*-perfluorobenzoyl oxime (1b): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.30 – 7.12 (m, 4H), 3.83 – 3.77 (m, 1H), 3.59 – 3.52 (m, 2H), 3.31 – 3.16 (m, 2H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.9, 156.4, 146.6, 144.1 139.6, 139.0, 136.3, 135.9, 130.5, 126.9, 126.2, 124.5, 38.2, 37.8, 30.0, 19.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -137.02 – -137.13 (m, 2F), -147.61 – -147.72 (m, 1F), -159.78 – -159.94 (m, 2F) ppm; IR (neat): υ_{max} 2930, 2250, 1745, 1494, 994, 753 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{13}F_5NO_2^+$ $[M+H]^+$ 370.0861, found 370.0866.



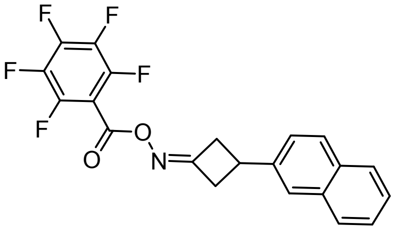
3-(4-Methoxyphenyl)cyclobutanone *O*-perfluorobenzoyl oxime (1f): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.23 – 7.14 (m, 2H), 6.90 – 6.88 (m, 2H), 3.81 (s, 3H), 3.68 – 3.62 (m, 1H), 3.58 – 3.48 (m, 2H), 3.26 – 3.09 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 168.2, 158.5, 156.6, 146.7, 144.0, 138.8, 136.6, 134.6, 127.3, 114.1, 55.3, 39.9, 39.5, 31.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -137.02 – -137.13 (m, 2F), -147.60 – -147.71 (m, 1F), -159.76 – -159.92 (m, 2F) ppm; IR (neat): υ_{max} 2924, 2358, 1742, 1494, 1000, 827 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{12}F_5NNaO_3^+$ $[M+Na]^+$ 408.0630, found 408.0628.



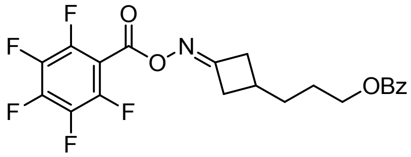
Methyl 4-(3-(((perfluorobenzoyl)oxy)imino)cyclobutyl)benzoate (1i): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.03 (d, *J* = 8.2 Hz, 2H), 7.35 (t, *J* = 10.7 Hz, 2H), 3.92 (s, 3H), 3.84 – 3.68 (m, 1H), 3.68 – 3.51 (m, 2H), 3.35 – 3.06 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.29, 166.66, 156.50, 147.64, 146.73, 144.04, 142.19, 136.46, 130.09, 129.0, 126.3, 52.1, 39.5, 39.1, 32.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -136.97 (m, 2F), -147.30 – -147.47 (m, 1F), -159.64 – -159.86 (m, 2F) ppm; IR (neat): υ_{max} 2960, 1714, 1491, 1001, 704 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{13}F_5NO_4^+$ [M+H]$^+$ 414.0759, found 414.0763.



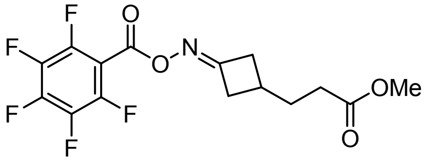
3-(2,3-Dichlorophenyl)cyclobutanone *O*-perfluorobenzoyl oxime (1j): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.40 (m, 1H), 7.28 – 7.18 (m, 2H), 3.99 (m, 1H), 3.69 – 3.47 (m, 2H), 3.33 – 3.08 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.0, 156.4, 144.1, 142.3, 141.3, 139, 136.4, 133.7, 132.1, 129.1, 128.9, 127.4, 127.3, 124.6, 53.0, 38.2, 37.5, 31.3, 27.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -135.42 – -137.07 (m, 2F), -145.92 – -147.65 (m, 1F), -158.11 – -159.82 (m, 2F) ppm; IR (neat): υ_{max} 2928, 2253, 1759, 1495, 1324, 1200, 728 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_9Cl_2F_5NO_2^+$ [M+H]$^+$ 423.9925, found 423.9932.



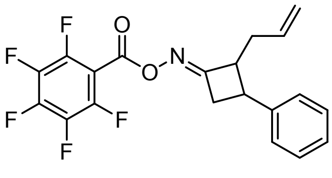
3-(Naphthalen-1-yl)cyclobutanone *O*-perfluorobenzoyl oxime (1k): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.07 – 7.71 (m, 3H), 7.52 (m, 4H), 4.34 (m, 1H), 3.84 – 3.59 (m, 2H), 3.49 – 3.26 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.9, 156.6, 146. 7, 144.1, 142.2, 137.2, 133.9, 131.1, 129.0, 127.8, 126.4, 126.0, 125.3, 123.3, 122.3, 38.4, 37.8, 30.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -136.88 – -136.97 (m, 2F), -147.38 – -147.58 (m, 1F), -159.69 – -159.81 (m, 2F) ppm; IR (neat): υ_{max} 2924, 2361, 1760, 1497, 1325, 1203, 1002, 699 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{13}F_5NO_2^+$ [M+H]$^+$ 406.0861, found 406.0855.



3-(3-(((Perfluorobenzoyl)oxy)imino)cyclobutyl)propyl benzoate (1o): ^{1}H NMR (400 MHz, CDCl$_3$) δ = 8.03 (d, *J* = 7.2 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 4.34 (t, *J* = 6.1 Hz, 2H), 3.23 (m, 2H), 2.81 – 2.60 (m, 2H), 2.50 (m, 1H), 1.87 – 1.63 (m, 4H). ^{13}C NMR (100 MHz, CDCl$_3$) δ = 168.9, 166.5, 156.6, 146.6, 144.0, 142.1, 138.9, 136.0, 133.0, 130.1, 129.5, 128.4, 64.3, 37.6, 37.2, 32.43, 27.86, 26.60; ^{19}F NMR (376 MHz, CDCl$_3$) δ = -136.15 – -137.30 (m, 2F), -147.82 – -147.99 (m, 1F), -159.63 – -160.26 (m, 2F) ppm; IR (neat): υ_{max} 2940, 2253, 1715, 1497, 1274, 906, 710 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{17}F_5NO_4^+$ [M+H]$^+$ 442.1072, found 442.1070.

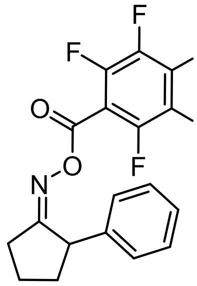


Methyl 3-(3-(((perfluorobenzoyl)oxy)imino)cyclobutyl)propanoate (1p): ^{1}H NMR (400 MHz, CDCl$_3$) δ = 3.66 (d, *J* = 7.5 Hz, 3H), 3.20 (m, 2H), 2.77 – 2.57 (m, 2H), 2.54 – 2.38 (m, 1H), 2.32 (t, *J* = 7.4 Hz, 2H), 1.89 (m, 2H). ^{13}C NMR (100 MHz, CDCl$_3$) δ = 173.2, 168.5, 156.5, 146.6, 144.0, 51.7, 37.4, 37.0, 31.7, 30.9, 27.60. ^{19}F NMR (376 MHz, CDCl$_3$) δ = -136.26 – -137.23 (m, 2F), -147.72 (m, 1F), -159.80 – -160.12 (m, 2F) ppm; IR (neat): υ_{max} 2954, 2253, 1738, 1505, 1207, 851 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{12}F_5NNaO_4^+$ [M+Na]$^+$ 388.0579, found 388.0579.

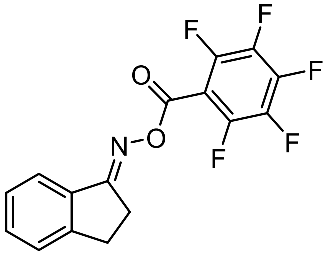


2-Allyl-3-phenylcyclobutanone *O*-perfluorobenzoyl oxime (1u): ^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.50 – 7.15 (m, 5H), 5.86 (m, 1H), 5.12 (m, 2H), 3.58 – 3.42 (m, 2H), 3.40 – 3.30 (m, 1H), 3.08 (m, 1H), 2.77 – 2.53 (m, 2H). ^{13}C NMR (100 MHz, CDCl$_3$) δ = 170.8, 156.6, 146.6, 144.3, 144.0, 142.1, 139.0, 136.5, 134.0, 128.7, 127.0, 126.5, 117.8, 53.0, 38.6, 37.0, 35.5; ^{19}F NMR (376 MHz, CDCl$_3$) δ = -137.08 – -

137.20 (m, 2F), -147.74 – -147.85 (m, 1F), -159.64 – -159.98 (m, 2F) ppm; IR (neat): υ$_{max}$ 2924, 1757, 1495, 1324, 1204, 994 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{15}F_5NO_2^+$ $[M+H]^+$ 396.1017, found 396.1017.

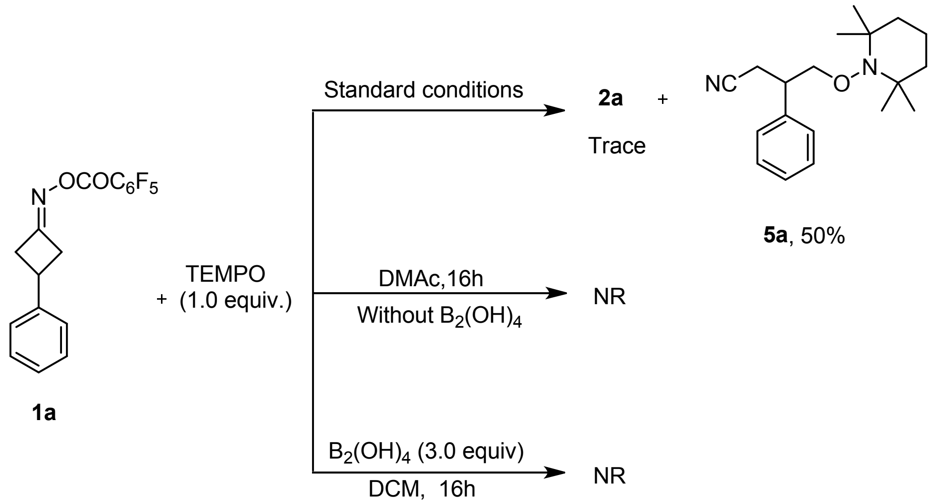


2-Phenylcyclopentan-1-one *O*-perfluorobenzoyl oxime (1x) : ^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.33 (t, *J* = 7.5 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 7.1 Hz, 1H), 4.00 (t, J=7.4 Hz, 1H), 2.89 (m, 1H), 2.72 (m, 1H), 2.34 (m, 1H) 2.02 (m, 1H), 1.84 (m, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ = 178.9, 156.7, 144.5, 143.9, 142.0, 139.6, 138.9, 136.5, 136.4, 136.2, 128.6, 127.8, 126.9, 107.2, 49.4, 34.7, 30.4, 22.4; ^{19}F NMR (376 MHz, CDCl$_3$) δ = -137.17 – -137.33 (m, 2F), -148.16 – -148.27 (m, 1F), -160.04 – -160.15 (m, 2F) ppm; IR (neat): υ$_{max}$ 2970, 1651, 1523, 1048, 808 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{13}F_5NO_2^+$ $[M+H]^+$ 370.0861, found 370.0854.



2,3-Dihydro-1H-inden-1-one *O*-perfluorobenzoyl oxime (1y) : ^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.94 (d, *J* = 7.8 Hz, 1H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.35 (t, J=7.6 Hz, 1H), 3.14 – 3.08 (m, 4H); ^{13}C NMR (100 MHz, CDCl$_3$) δ = 172.6, 152.6, 150.3, 146.8, 144.7, 144.2, 142.1, 139.0, 138.9, 136.5, 133.5, 132.7, 127.4, 125.7, 123.4, 107.3, 107.1, 28.5, 28.2; ^{19}F NMR (376 MHz, CDCl$_3$) δ = -136.99 – -137.07 (m, 2F), -147.76 – -147.89 (m, 1F), -159.86 – -160.02 (m, 2F) ppm; IR (neat): υ$_{max}$ 1637, 1526, 1465, 982, 732 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_9F_5NO_2^+$ $[M+H]^+$ 342.0548, found 342.0544.

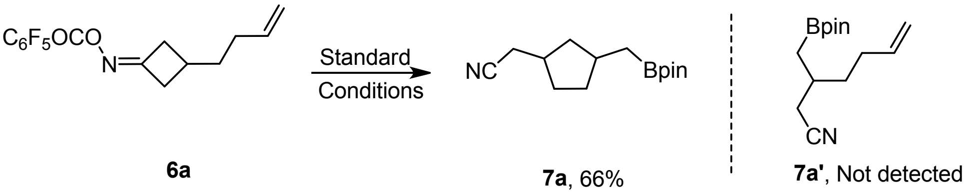
Investigation of the Reaction Mechanism



When TEMPO, a typical radical scavenger was added to the reaction of **1a** with boron source, no **2a** was obtained. While the alkyl-TEMPO adduct **5a** was isolated in 50% yield. In addition, the reaction of TEMPO with **1a** in the absence of boron source or DMAc results no reaction. These results suggest that alkyl radical intermediate might be involved, $B_2(OH)_4$ and solvent played the important roles in this transformation.

3-Phenyl-4-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-butyronitrile (5a):[3]

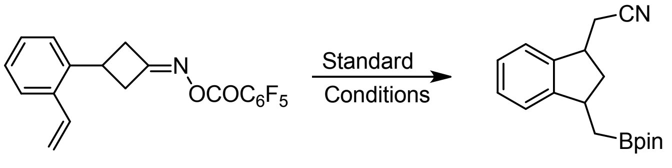
Colorless oil (50%, 30 mg); R_f 0.35 (EtOAc/petroleum ether = 1:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36-7.24 (m, 5H), 3.98 (d, *J* = 6.4 Hz, 2H), 3.26-3.20 (m, 1H), 2.92 (dd, *J* = 16.8, 6.0 Hz, 1H), 2.74 (dd, *J* = 16.8, 8.0 Hz, 1H), 1.42 (d, *J* = 7.6 Hz, 4H), 1.26 (s, 2H), 1.11-1.07 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.2, 128.7, 127.6, 127.5, 118.7, 78.1, 60.0, 42.0, 39.7, 33.0, 25.0, 21.1, 20.2, 20.1, 17.0 ppm; IR (neat): υ_{max} 2926, 2246, 1454, 1360, 1261, 799, 760, 698 cm^{-1};



Treatment of a radical-clock substrate **6a** under the standard conditions furnished the ring-closing product **7a** in 66% yield with no linear coupling product detected.

2-(3-((4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)cyclopentyl)acetonite (7a): Colorless oil (66%, 33 mg); R_f 0.4 (EtOAc/petroleum ether = 1:10); ^{1}H NMR

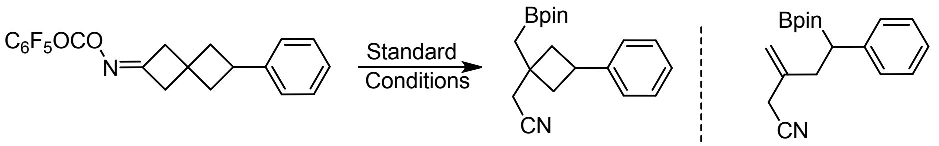
(400 MHz, $CDCl_3$): δ = 2.37 – 2.28 (m, 2H), 2.27 – 2.01 (m, 2H), 2.00 – 1.79 (m, 2H), 1.54 – 1.35 (m, 2H), 1.34 – 1.27 (m, 1H), 1.24 (s, 12H), 1.21 – 1.10 (m, 1H), 0.88 – 0.82 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 119.5, 83.0, 41.9, 40.1, 36.3, 36.2, 35.2, 35.0, 34.6, 33.7, 32.4, 31.1, 25.0, 24.8, 23.4, 23.2 ppm; IR (neat): υ_{max} 2926, 2247, 1735, 1371, 1144, 847 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{27}BNO_2$ $[M+H]^+$ 250.1973, found 250.1970.



6b **7b**, 66%, d.r. = 1:1

Similarly, oxime ester **6b** with an *o*-vinylphenyl substituent at the 3-position reacted well to deliver the cyanoalkyl boronic ester **7b** in 66% yield via a ring-opening/cyclization/borylation cascade.

2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3-dihydro-1H-inden-1-yl)acetonitrile (7b): Colorless oil (66%, 37 mg); R_f 0.35 (EtOAc/petroleum ether = 1:10); the title compound as a 1:1 mixture of inseparable diastereomers; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.31 – 7.26 (m, 1H), 7.26 – 7.17 (m, 3H), 3.56 – 3.48 (m, 0.5H), 3.40 (m, 0.5H), 3.33 – 3.22 (m, 0.5H), 2.83 (m, 0.5H), 2.77 – 2.65 (m, 0.5H), 2.63 – 2.46 (m, 1.5H), 2.24 – 2.12 (m, 0.5H), 2.08 – 1.98 (m, 0.5H), 1.40 (m, 1.5H), 1.28 (s, 6H), 1.23 (s, 6H), 1.00 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ =148.8, 148.6, 142.9, 142.89, 127.8, 127.5, 126.8, 126.6, 124.0, 123.7, 123.5, 122.5, 119.0, 118.8, 83.3, 41.8, 40.4, 40.0, 39.8, 39.1, 38.5, 24.9, 24.7, 23.1, 22.30 ppm; IR (neat): υ_{max} 2979, 2922, 2244, 1362, 1142, 763 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{25}BNO_2$ $[M+H]^+$ 298.1973, found 298.1970.

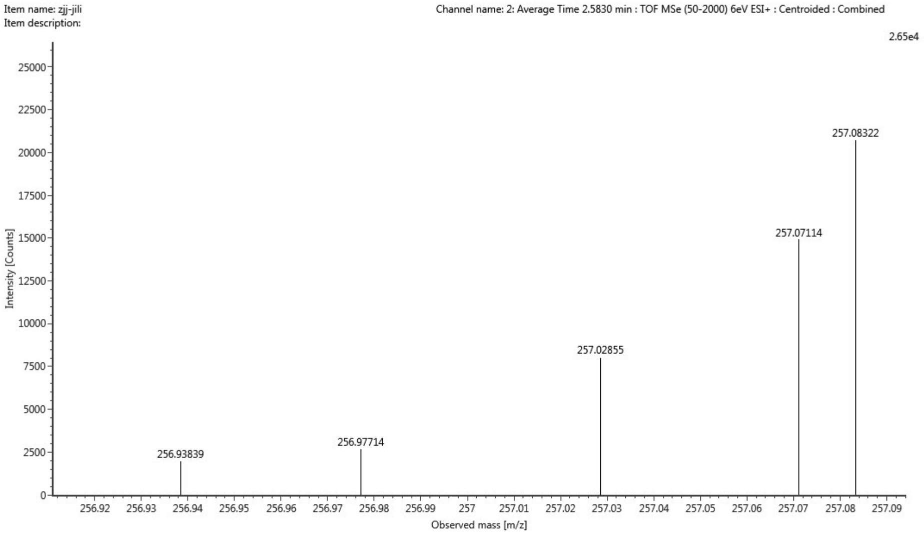


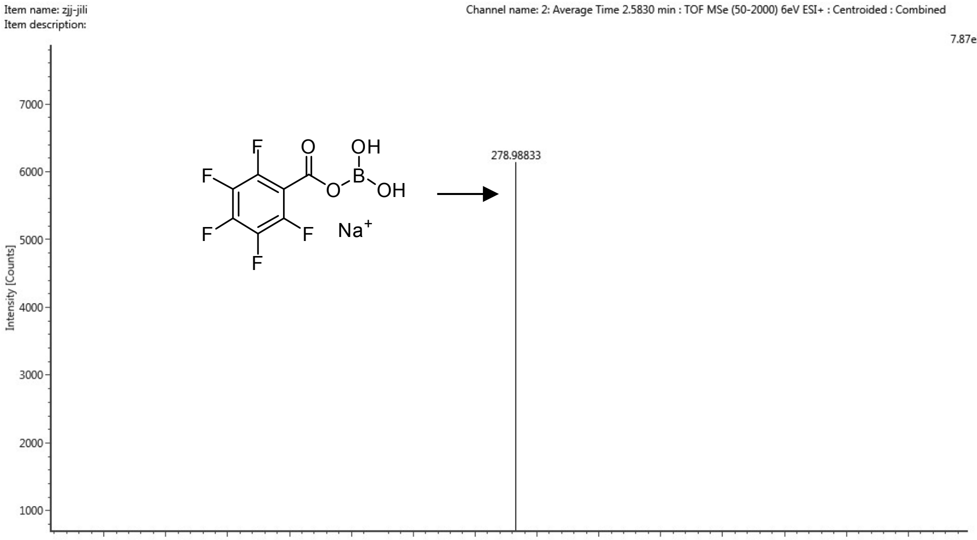
6c **7c**, 58% **7c'**, Not detected

Treatment of a radical-block substrate **6c** under the standard conditions furnished the unexpected product **7c** in 58% yield with no further ring-opened product detected.

2-(3-Phenyl-1-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)cyclobutyl)acetonitrile (7c): Colorless oil (58%, 36 mg); R_f 0.35 (EtOAc/petroleum ether = 1:10); the title compound as a 1.3:1 mixture of inseparable diastereomers; ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.36 – 7.12 (m, 5H), 3.63 – 3.45 (m, 1H), 2.78 (s, 1H), 2.62 (s, 1H), 2.49 – 2.36 (m, 1H), 2.36 – 2.10 (m, 3H), 1.38 (m, 2H), 1.26 (s, 6H), 1.23 (s, 6H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 145.0, 144.9, 128.4, 128.3, 128.2, 126.5, 126.4, 126.3, 126.1, 126.0, 125.9, 119.2, 118.8, 83.4, 83.3, 40.78, 40.58, 39.9, 39.8, 34.68, 33.7, 32.9, 30.2, 28.7, 24.8 ppm. IR (neat): υ_{max} 2929, 2244, 1363, 1142, 699 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{27}BNO_2$ [M+H]$^+$ 312.2129, found 312.2134.

HRMS of ArCOOB(OH)$_2$





UV-Vis spectrum of Cyclobutanone Oxime 1u and B_2Cat_2.

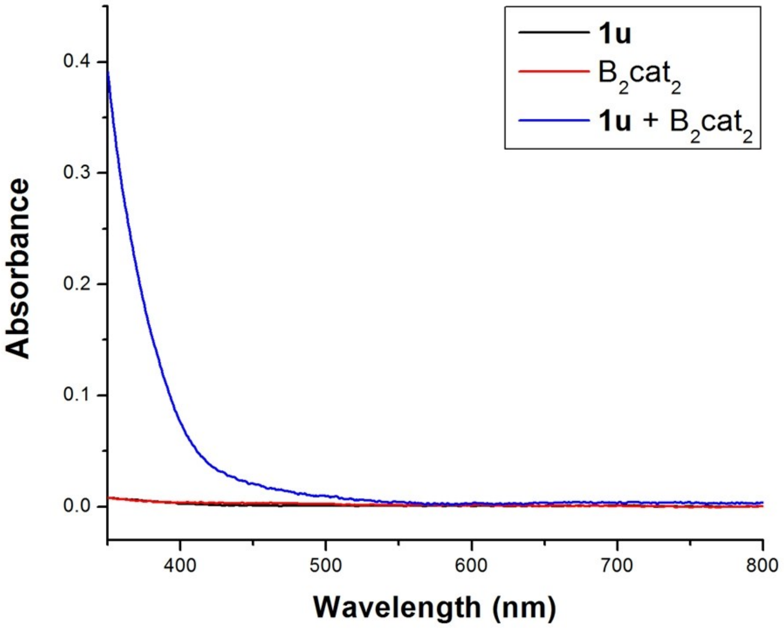


Fig 1. UV-Vis data from Cyclobutanone Oxime **1u** and B_2Cat_2.

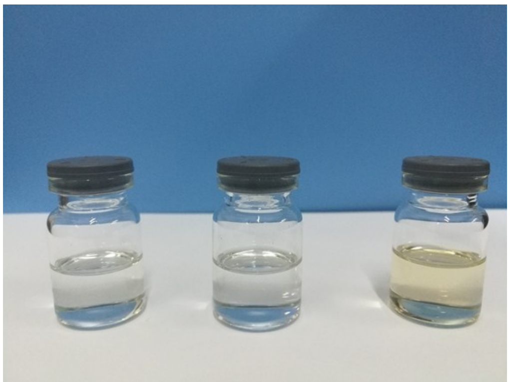
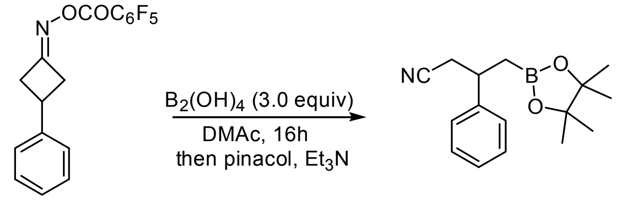


Fig 2. (left) Cyclobutanone Oxime **1u** in DMAc at 0.1 M (center) B_2Cat_2 in DMAc at 0.1 M (right) mixture of **1u** and B_2Cat_2 in DMAc at 0.1 M.

Fig 1 shows the UV-Vis spectrum of cyclobutanone oxime **1u**, B_2Cat_2, and mixture of **1u** and B_2Cat_2. All data was measured in solvent of DMAc at 0.1 M with respect to **1u** and 0.125 M with respect to B_2Cat_2. From the results of measurement, the mixture of **1u** and B_2cat_2 have a clearly absorbance within the visible range, but nearly no absorbance were present in the separate compounds. Furthermore, there was no visible color change when **1u** and B_2Cat_2 were dissolved in DMAc separately, but the mixture of them have a very pale yellow color just like showed in Fig 2. These results implied that direct photolysis of B_2Cat_2 accounts partly for the formation of **2u** and **2v**.

Representative Procedure for Synthesis of 2a on Gram Scale

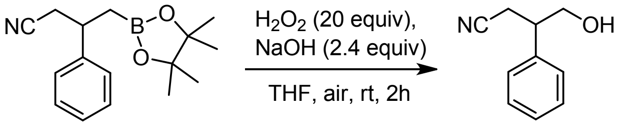


1a 2.0 mmol, 0.71g

2a 67%, 0.36g

A 50 mL oven-dried Schlenk-tube equipped with a magnetic stir bar under a nitrogen atmosphere was charged with **1a** (2 mmol, 1.0 equiv.), $B_2(OH)_4$ (6 mmol, 3.0 equiv.). Then 20 mL solvent were added by syringe. The tube was then sealed and the mixture was stirred at room temperature for 16 h. Pinacol (8 mmol, 4.0 equiv.) was dissolved in Et_3N (7 mL), added to the reaction mixture and stirred for 1 h. The mixture was then quenched with H_2O (10 mL) and transferred to a separatory funnel with EtOAc (15 mL). The aqueous layer was extracted with EtOAc (3 x 20 mL), and then the organic phases were combined and washed with brine (50 mL), dried over Na_2SO_4, and evaporated under reduced pressure. The resulting residue was purified by column chromatography on silica gel (gradient eluent of EtOAc/petroleum ether: 1/15 to 1/10) to give the corresponding product **2a** in 67% yield.

Representative Procedure for the Oxidation/Hydrolysis of 2a



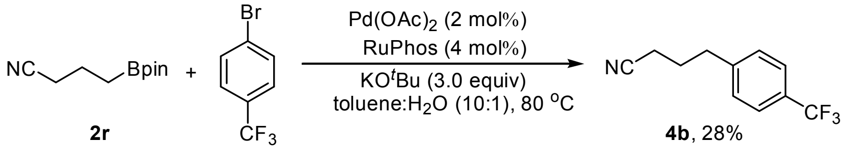
2a **4a**

According to a literature procedure[4]**: 2a** (0.2 mmol) was dissolved in THF (4.0 mL), then NaOH (1M, 0.5 mL, 2.4 equiv.) and H_2O_2 (30% H_2O solution, 0.16 mL, 20.0 equiv.) were added sequentially. After the mixture was stirred at room temperature for 2 hours, the aqueous layer was extracted with EtOAc (3 x 10 mL), the organic phases were combined and washed with brine (20 mL), dried over Na_2SO_4, and evaporated under reduced pressure. The resulting residue was purified by column chromatography on silica gel (gradient eluent of EtOAc/petroleum ether: 1/3 to 1/1) to give colorless oil **4a** in 80% yield.

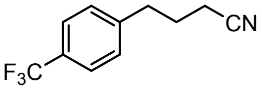
4-hydroxy-3-phenylbutanenitrile (4a): Colorless oil (80%, 25.6 mg); R_f 0.30

(EtOAc/petroleum ether = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 – 7.26 (m, 4H), 7.25 (s, 1H), 3.96 – 3.85 (m, 2H), 3.23 – 3.16 (m, 1H), 2.86 (dd, *J* = 16.8, 6.4 Hz, 1H), 2.73 (dd, *J* = 17.0, 7.8 Hz, 1H), 1.59 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.66, 129.09, 127.97, 127.48, 118.46, 65.22, 44.22, 20.45 ppm. IR (neat): υ_{max} 2923, 2360, 2248, 1020, 699 cm^{-1}; HRMS (ESI) calcd for $C_{10}H_{12}NO$ [M+H]$^+$ 162.0913, found 162.0917.

Representative Procedure for the Cross Coupling of Cyanoalkylboronic Esters

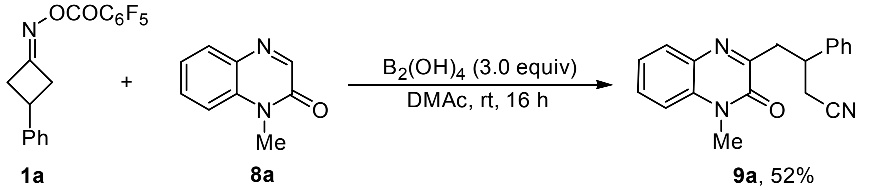


A 10 mL oven-dried Schlenk-tube equipped with a magnetic sir bar was charged with **2r** (0.2 mmol, 1.0 equiv), $Pd(OAc)_2$ (0.004 mmol, 2 mol%), RuPhos (0.008 mmol, 4 mol%) and KO*^{t}*Bu (0.6 mmol, 3.0 equiv). Then, the tube was evacuated and backfilled with nitrogen (three times). After that, 2 mL of solvent (toluene:H_2O=10:1, 0.1 M) followed by 4-bromobenzotrifluoride (0.2 mmol, 1.0 equiv) were added by syringe under nitrogen. The tube was then sealed and the mixture was stirred for 24 h at 80 °C. The mixture was then cooled down to room temperature, quenched with water and the aqueous layer was extracted with EtOAc (3 x 10 mL), the organic phases were washed with brine (20 mL), dried over Na_2SO_4, and evaporated under reduced pressure. The resulting residue was purified by column chromatography on silica gel to give product **4b** in 28% yield.



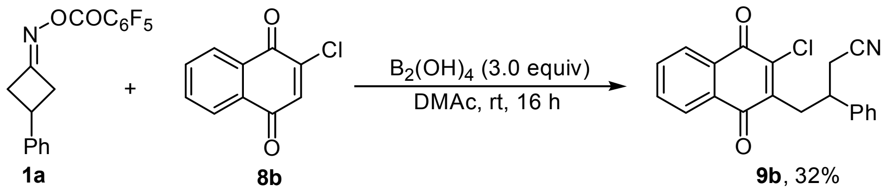
4-(4-(trifluoromethyl)phenyl)butanenitrile (4b): (known compound)[5] ^{1}H NMR (400 MHz, CDCl3) δ = 7.58 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 2.86 (t, J = 7.6 Hz, 2H), 2.35 (t, J = 6.8 Hz, 2H), 2.01 (q, 2H). ^{13}C NMR (100 MHz, CDCl3) δ = 143.8, 128.8, 125.7, 125.6, 119.1, 34.1, 26.6, 16.5; ^{19}F NMR (376 MHz, CDCl3) δ = -62.47.

Synthetic Applications



General procedure: A 10 mL oven-dried Schlenk-tube equipped with a magnetic stir bar under a nitrogen atmosphere was charged with **1a** (0.20 mmol, 1.0 equiv.), **8a** (0.30 mmol, 1.5 equiv.), $B_2(OH)_4$ (0.6 mmol, 3.0 equiv.). Then 2.0 mL DMAc were added by syringe. The tube was then sealed and the mixture was stirred at room temperature for 16 h. The mixture was then quenched with H_2O and transferred to a separatory funnel with EtOAc (10 mL). The aqueous layer was extracted with EtOAc (3 x 10 mL), then the organic phases were combined and washed with brine (20 mL), dried over Na_2SO_4, and evaporated under reduced pressure. The resulting residue was purified by column chromatography on silica gel (gradient eluent of EtOAc/petroleum ether: 1/3 to 1/1) to give faint yellow solid **9a** in 52% yield.

4-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)-3-phenylbutanenitrile (9a):[6a] faint yellow solid (52%, 31.5 mg); R_f 0.2 (EtOAc/petroleum ether = 1:2); ^1H NMR (400 MHz, $CDCl_3$) δ = 7.83 (dd, J = 7.9, 1.0 Hz, 1H), 7.58 – 7.51 (m, 1H), 7.43 – 7.28 (m, 6H), 7.26 – 7.20 (m, 1H), 3.95 – 3.84 (m, 1H), 3.69 (s, 3H), 3.41 (m, 2H), 2.82 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 154.8, 141.6, 133.0, 132.4, 130.1, 129.8, 128.8, 127.4, 127.3, 123.7, 118.5, 113.6, 38.8, 38.5, 29.1, 24.30 ppm.



General procedure: A 10 mL oven-dried Schlenk-tube equipped with a magnetic stir bar under a nitrogen atmosphere was charged with **1a** (0.20 mmol, 1.0 equiv.), **8b** (0.30 mmol, 1.5 equiv.), $B_2(OH)_4$ (0.6 mmol, 3.0 equiv.). Then 2.0 mL DMAc were added by syringe. The tube was then sealed and the mixture was stirred at room temperature for 16 h. The mixture was then quenched with H_2O and transferred to a separatory funnel with EtOAc (10 mL). The aqueous layer was extracted with EtOAc

(3 x 10 mL), then the organic phases were combined and washed with brine (20 mL), dried over Na_2SO_4, and evaporated under reduced pressure. The resulting residue was purified by column chromatography on silica gel (gradient eluent of EtOAc/petroleum ether: 1/10 to 1/5) to give yellow liquid **9b** in 32% yield.

4-(3-Chloro-1,4-dioxo-1,4-dihydro-naphthalen-2-yl)-3-phenyl-butyronitrile (9b):[6b] Yellow liquid (32%, 19.0 mg); R_f 0.3 (EtOAc/petroleum ether = 1:5); ^1H NMR (400MHz, $CDCl_3$): δ = 8.12 – 8.05 (m, 2H), 7.75 – 7.73 (m, 2H), 7.32 – 7.24 (m, 5H), 3.56 – 3.48 (m, 1H), 3.31 – 3.22 (m, 2H), 2.75 (d, J = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 182.2, 177.2, 144.8, 140.1, 134.4, 134.1, 131.3, 131.1, 128.9, 127.9, 127.2, 127.1, 127.0, 118.1, 40.8, 34.4, 24.1 ppm.

References

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2 H.-J. Xu, F.-F. Zhu, Y.-Y. Shen, X. Wan and Y.-S. Feng, *Tetrahedron*, 2012, **68**, 4145.

3 Y.-R. Gu, X.-H. Duan, L. Yang and L.-N. Guo, *Org. Lett.*, 2017, **19**, 5908.

4 G.-H. Wang, L. Liu, H. Wang, Y.-S. D, J. Zhang, S. Mao and P.-F. Li, *J. Am. Chem. Soc.*, 2017, **139**, 91.

5 M. Shimogaki, M. Fujita and T. Sugimura, *Angew. Chem.*, *Int. Ed.*, 2016, **55**, 15797.

6 (a) Y.-R. Gu, X.-H. Duan, L. Yang and L.-N. Guo, *Org. Lett.*, 2017, **19**, 5908; (b) L. Yang, P. Gao, X.-H. Duan, Y.-R. Gu and L.-N. Guo, *Org. Lett.*, 2018, **20**, 1034.

DFT Computational Study

All of relevant geometries were fully optimized by using M06-2X density functional theory (DFT) in conjunction with self-consistent reaction field (SCRF) method. The standard 6-31+G(d,p) basis set were used in computations. After geometry optimization, harmonic vibrational analyses were performed at the same level to confirm that each minimum has no imaginary frequency or each transition state (TS) has only one imaginary frequency. The minimum energy path (MEP) was also traced by using intrinsic reaction coordinate (IRC) method to ensure that each TS structure correctly links with two minima. The implicit CPCM solvent model was adopted to evaluate solvent effect on the reaction in n,n-dimethylacetamide (DMAc, $\varepsilon = 37.781$). To describe the reaction in the solvent, the contribution of the transitional entropy is negligible because the translational motion would be quenched in the solvent. Therefore, the reported relative Gibbs free energy of each species was obtained by using the formula $\Delta G(\mathrm{T}) = \Delta H(\mathrm{T}) + \mathrm{T}(\Delta S_{\mathrm{rot}}(\mathrm{T}) + \Delta S_{\mathrm{vib}}(\mathrm{T}))$. All computations were fulfilled with Gaussian 09 program.[6] All 3-D structures were generated by CYLview program.[7]

[6] Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, (2009).

[7] CYLview, 1.0b; Legault, C. Y. Université de Sherbrooke, 2009, (http://www.cylview.org).

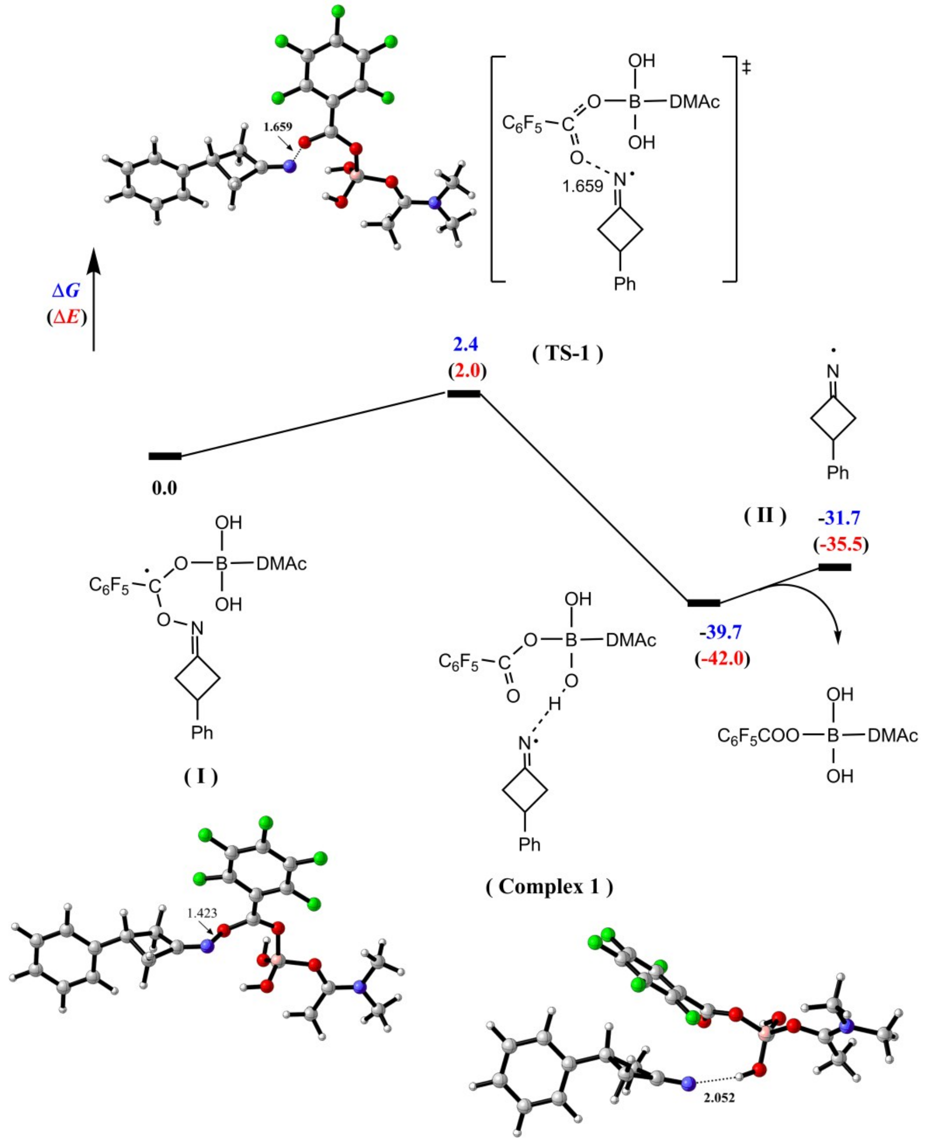


Figure S2. Relative energy (kcal/mol) profile in the N-O bond cleavage process.

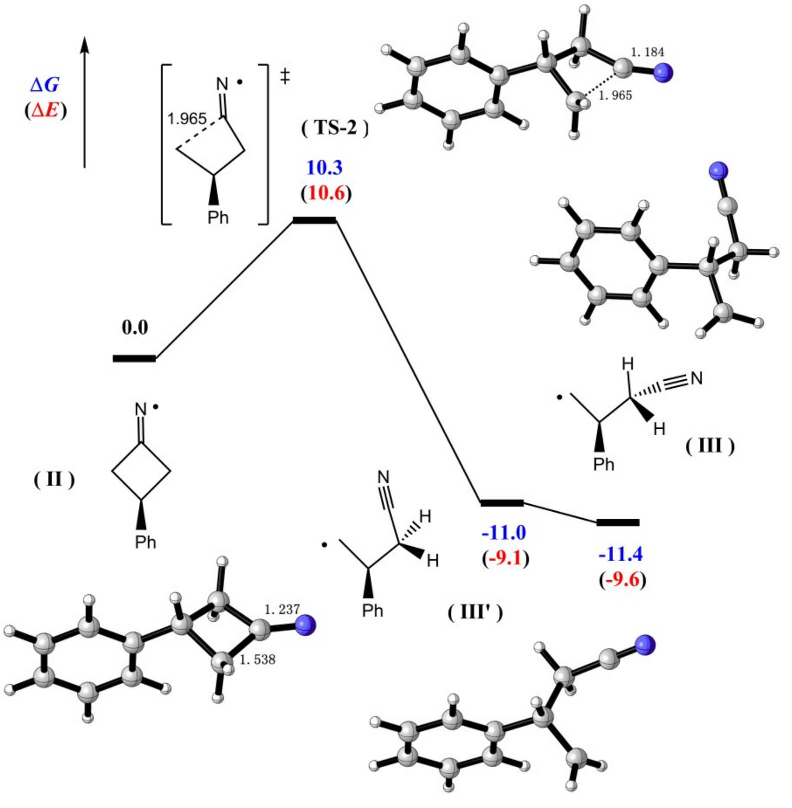


Figure S3. Relative energy (kcal/mol) profile in the C-C bond cleavage process.

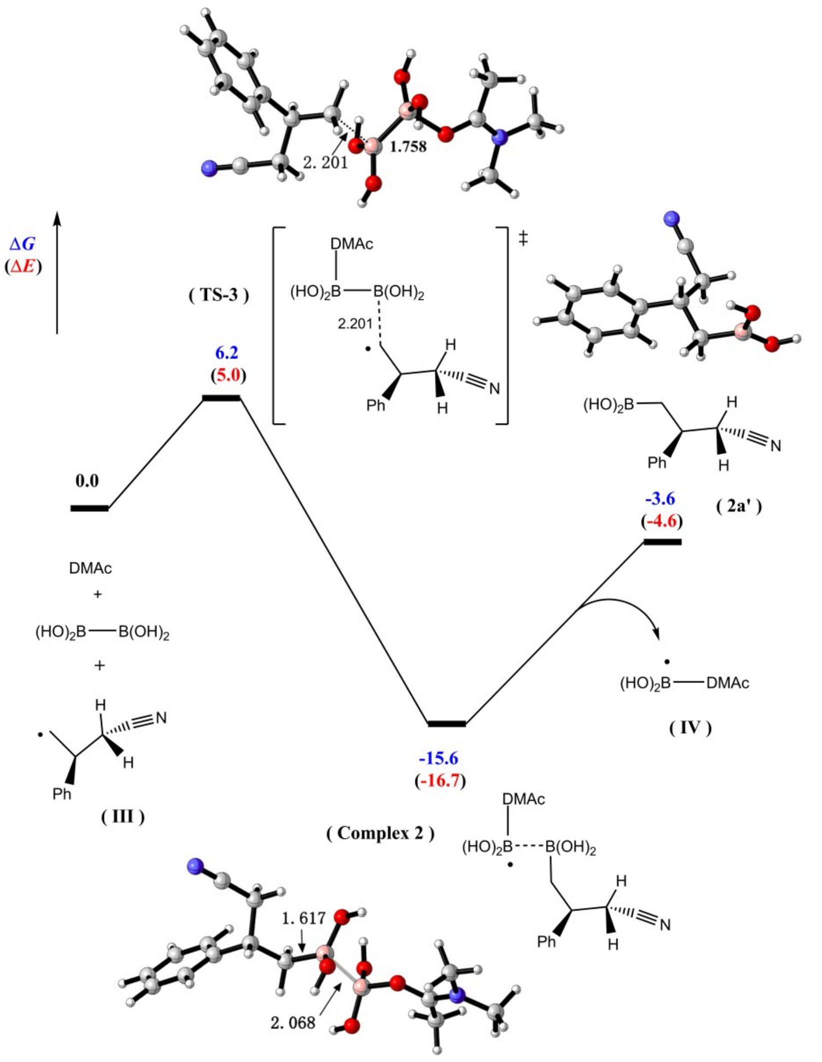
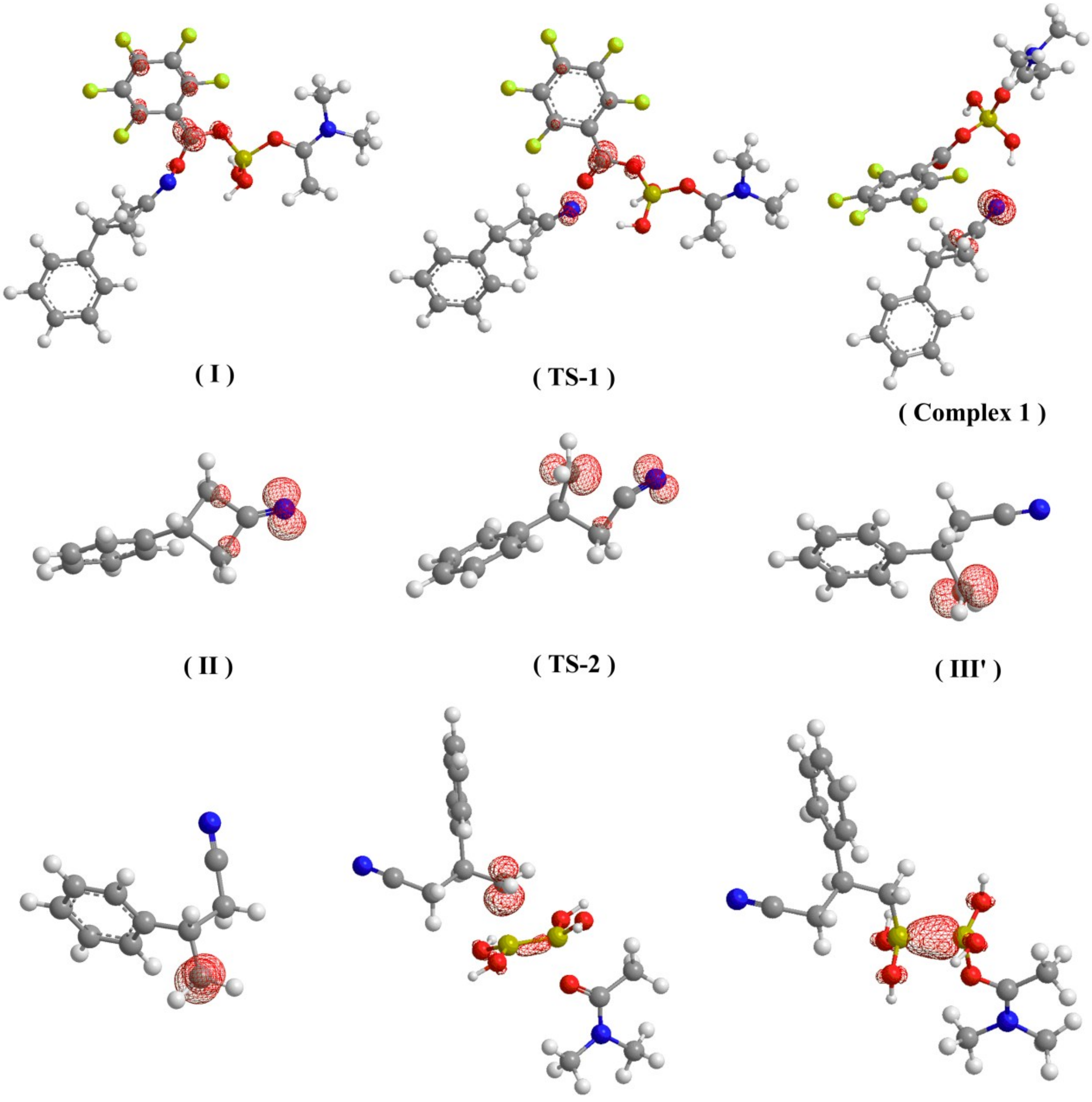


Figure S4. Relative energy (kcal/mol) profile in the formation of product and precursor.



(I) (TS-1) (Complex 1)

(II) (TS-2) (III')

(III) (TS-3) (Complex 2)

Figure S5. Spin density contours (isovalue=0.015) for some radical structures.

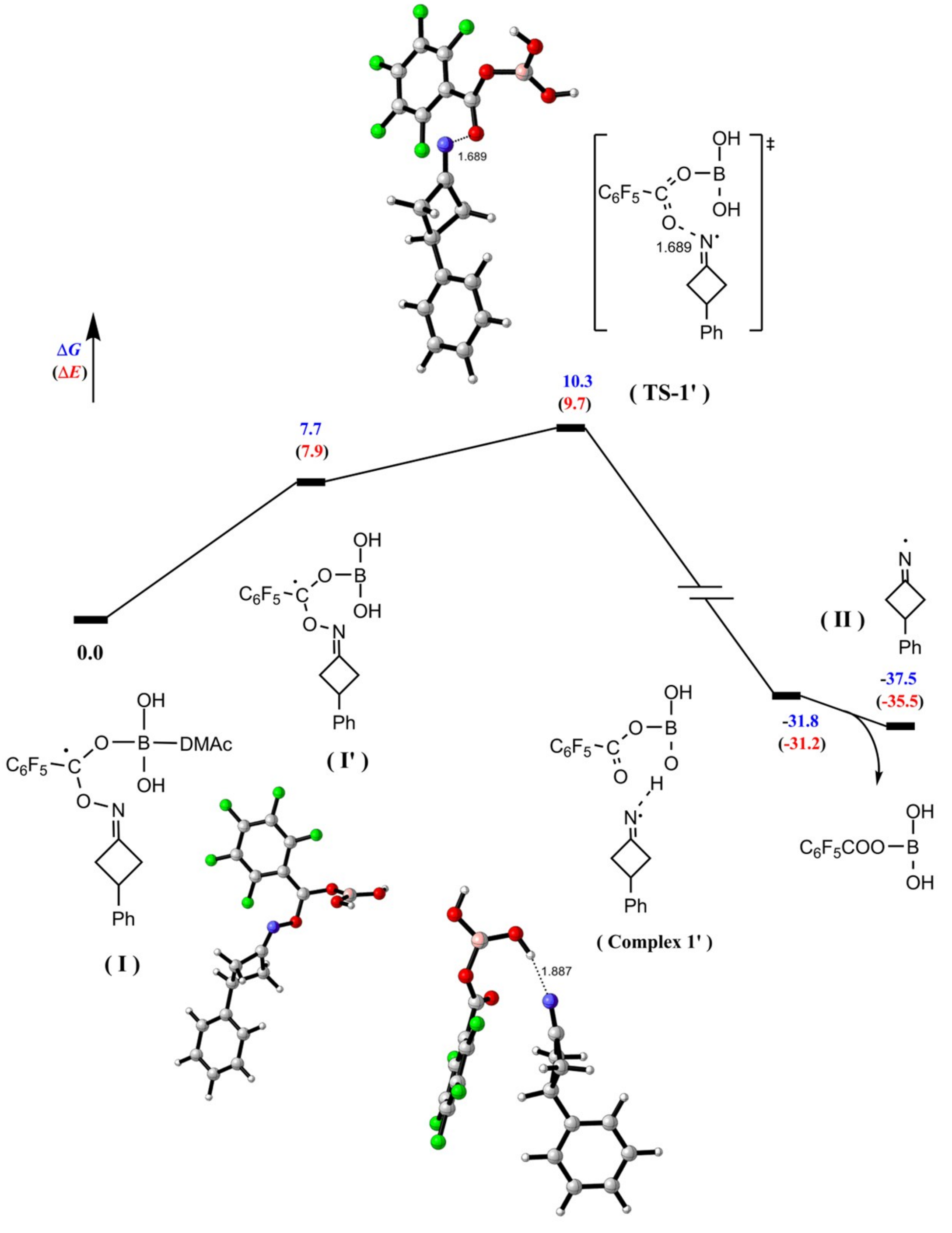


Figure S6. Relative energy (kcal/mol) profile in the N-O bond cleavage process without the explicit DMAc solvent.

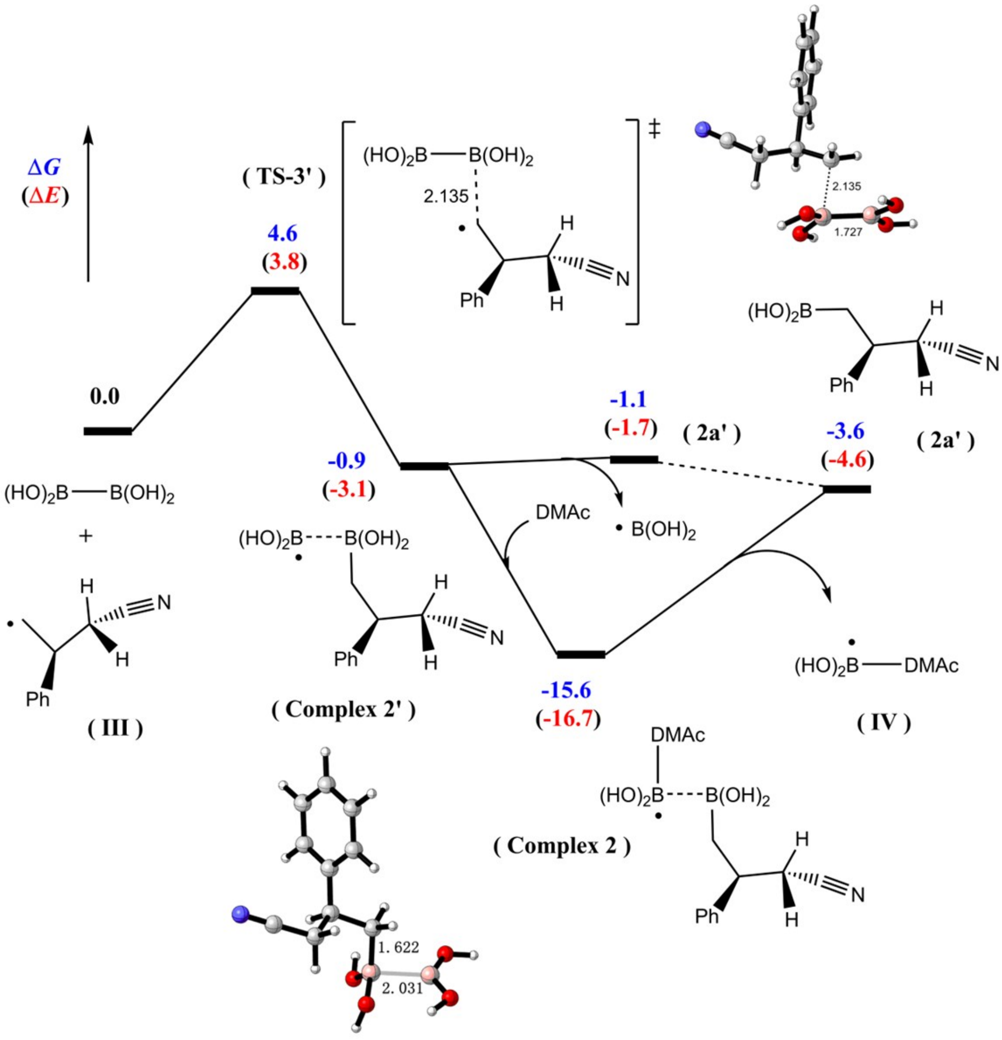
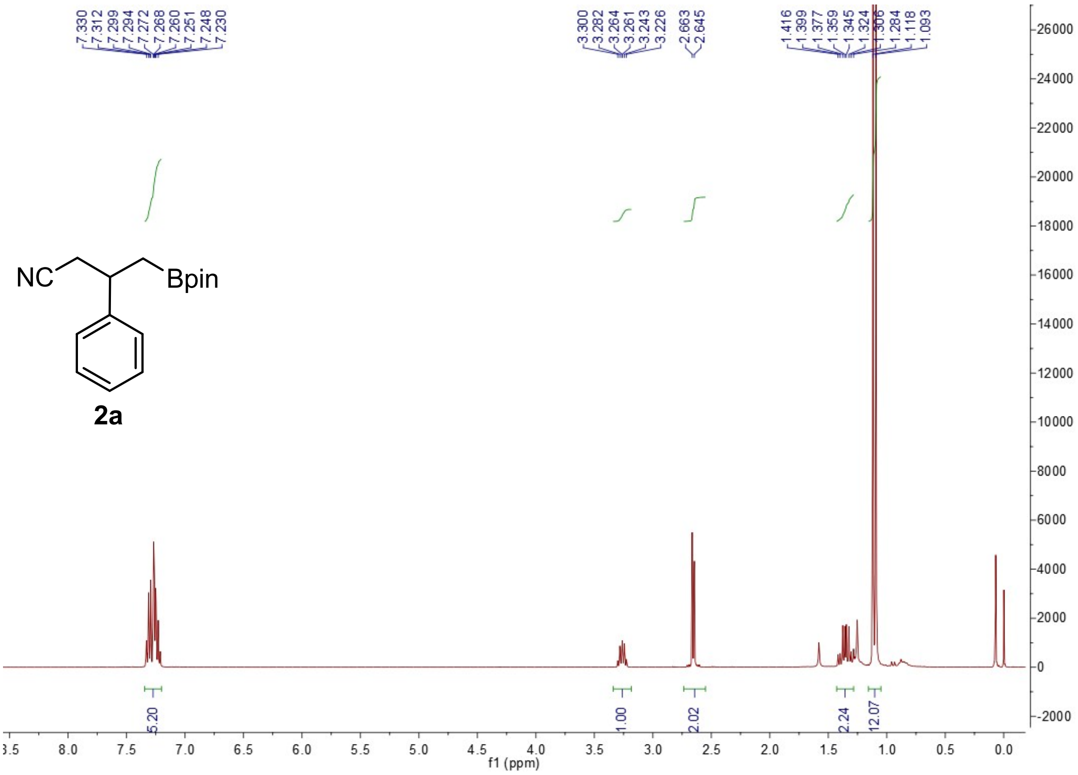
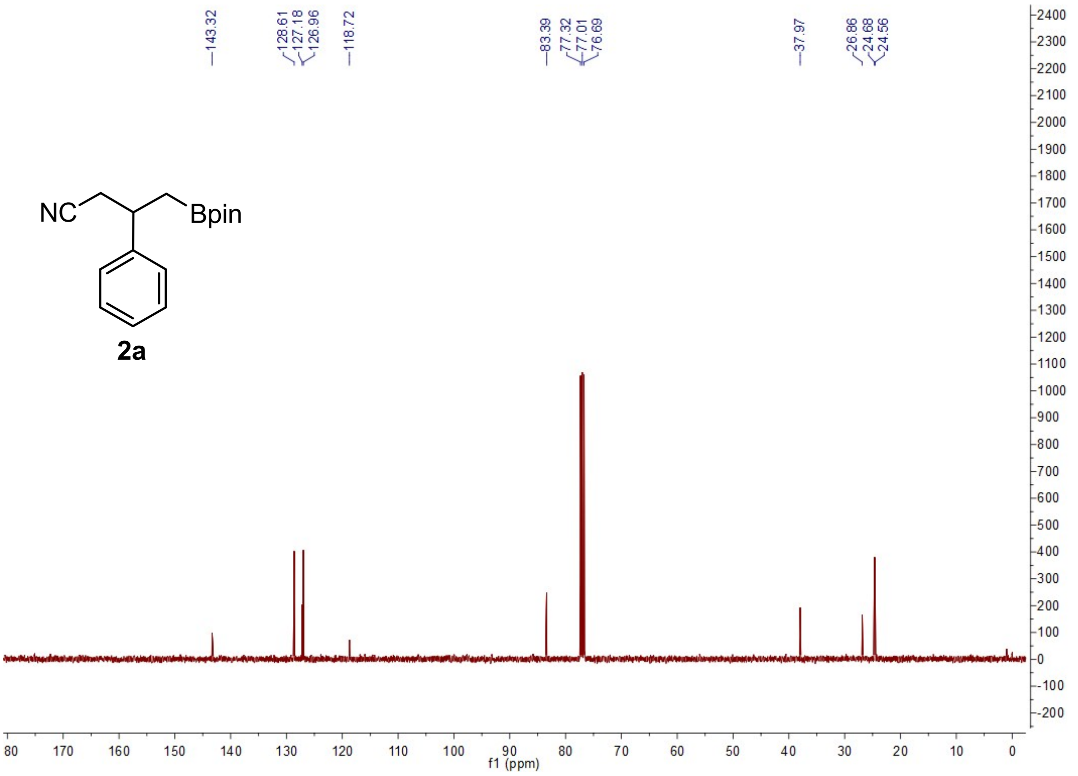
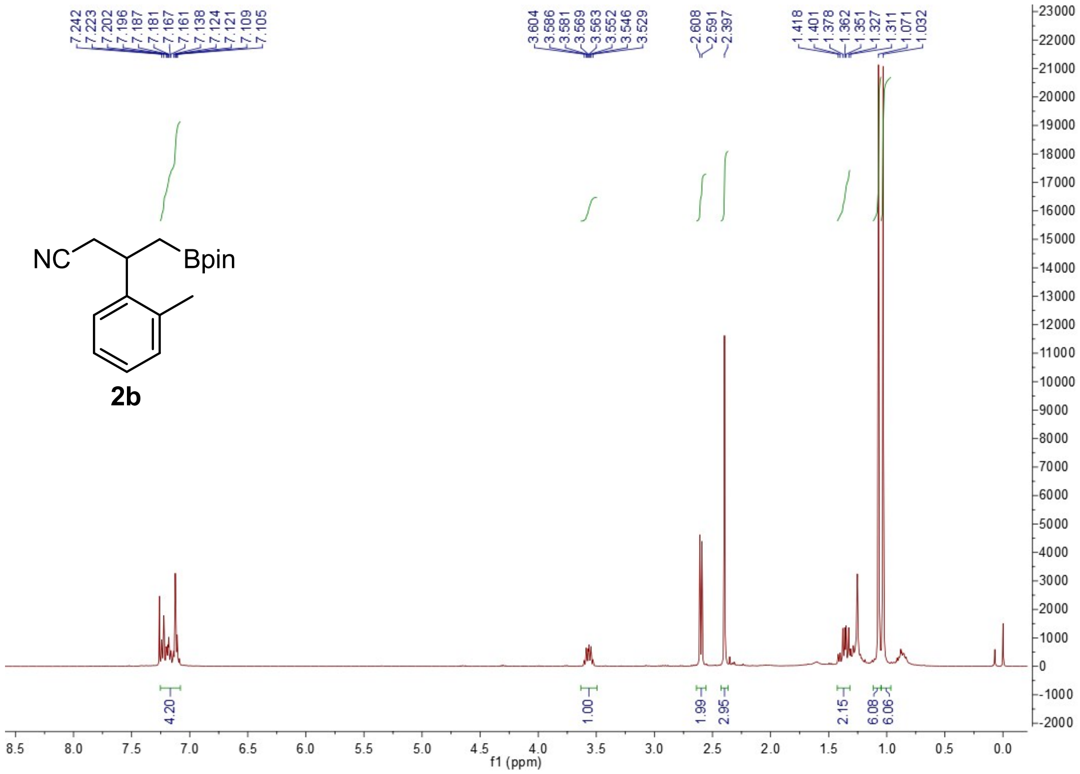


Figure S7. Relative energy (kcal/mol) profile in the formation of product without the explicit DMAc solvent.

^{1}H NMR and ^{13}C NMR Spectra of the Products 2



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3.586
3.581
3.569
3.563
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3.529
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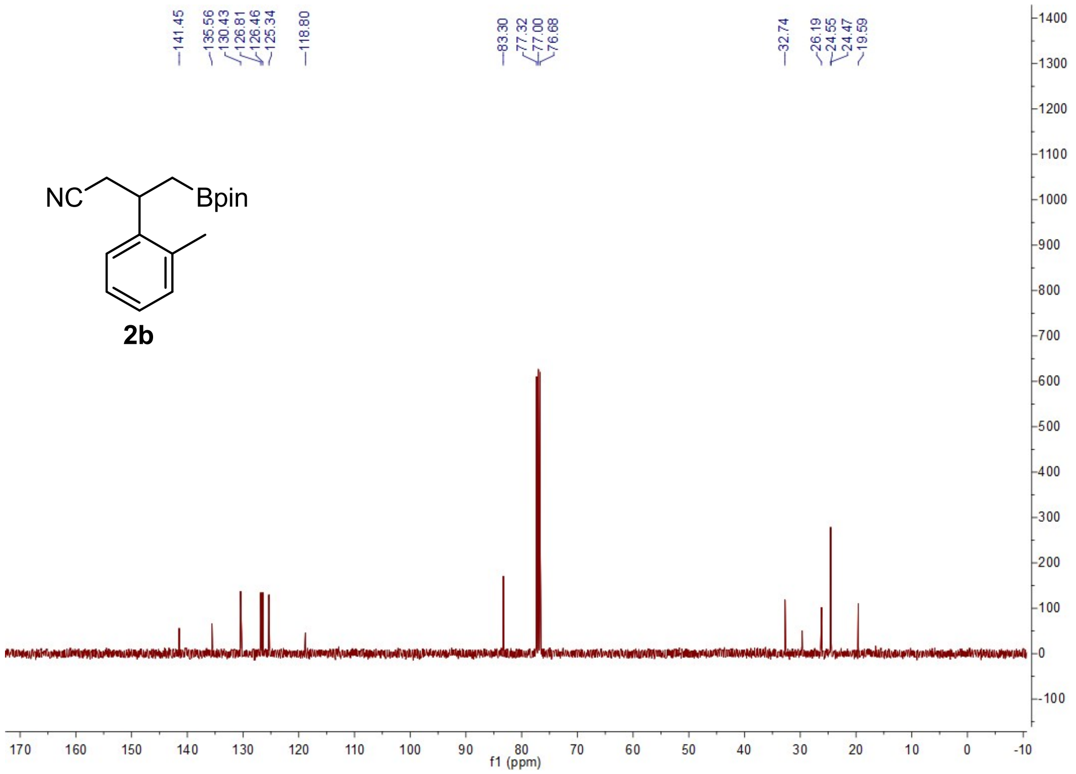
f1 (ppm)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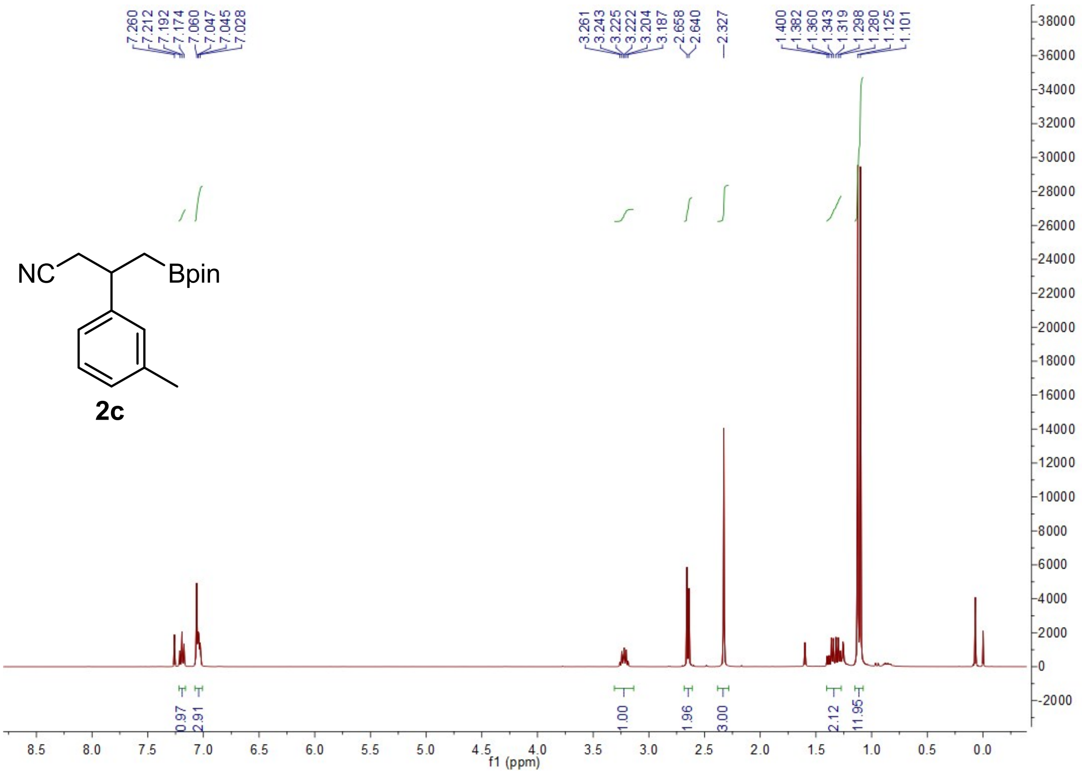
2b
f1 (ppm)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34000
32000
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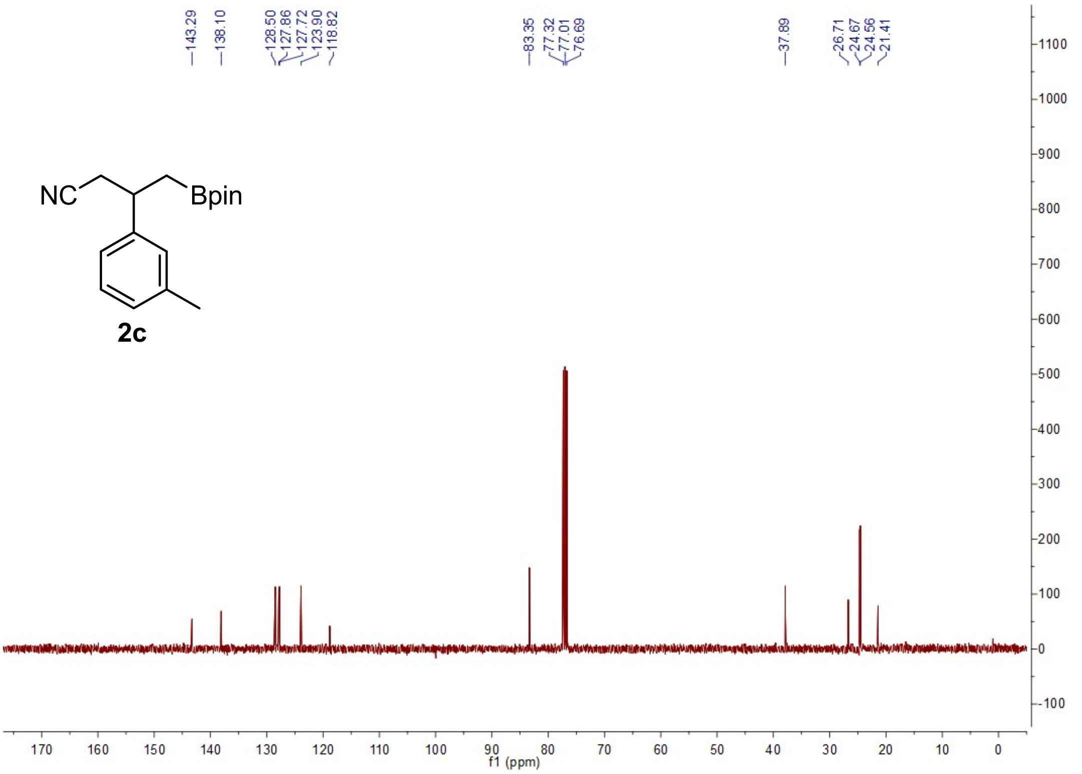
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110
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50
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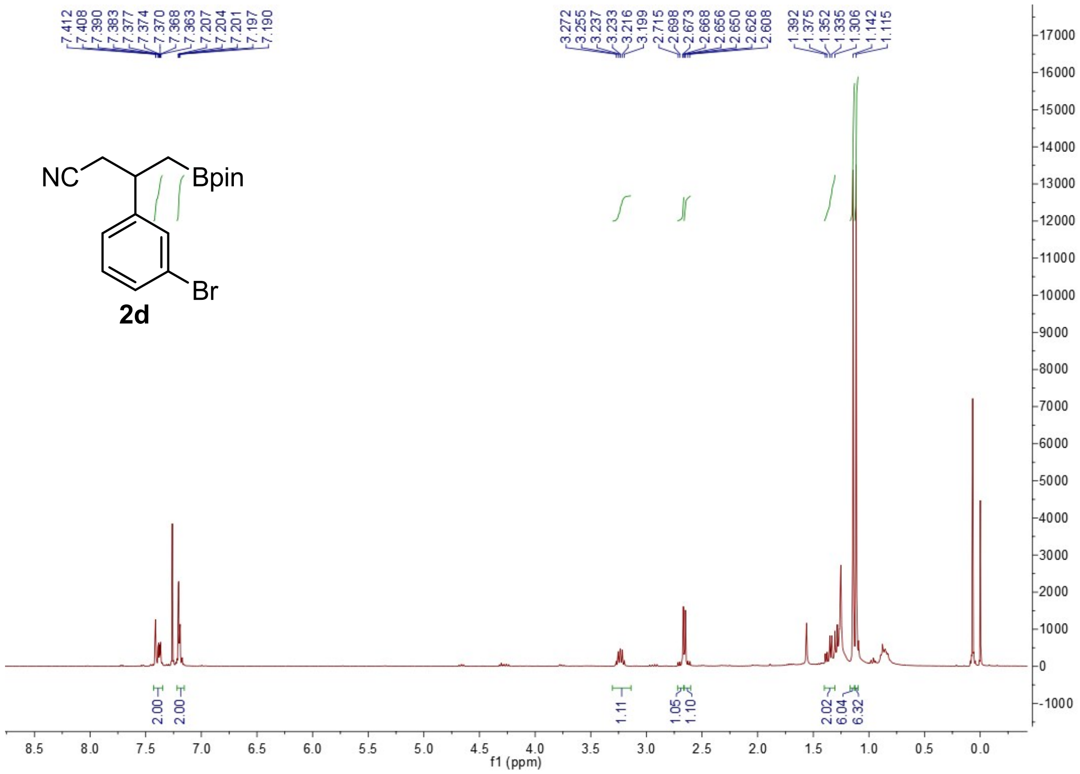
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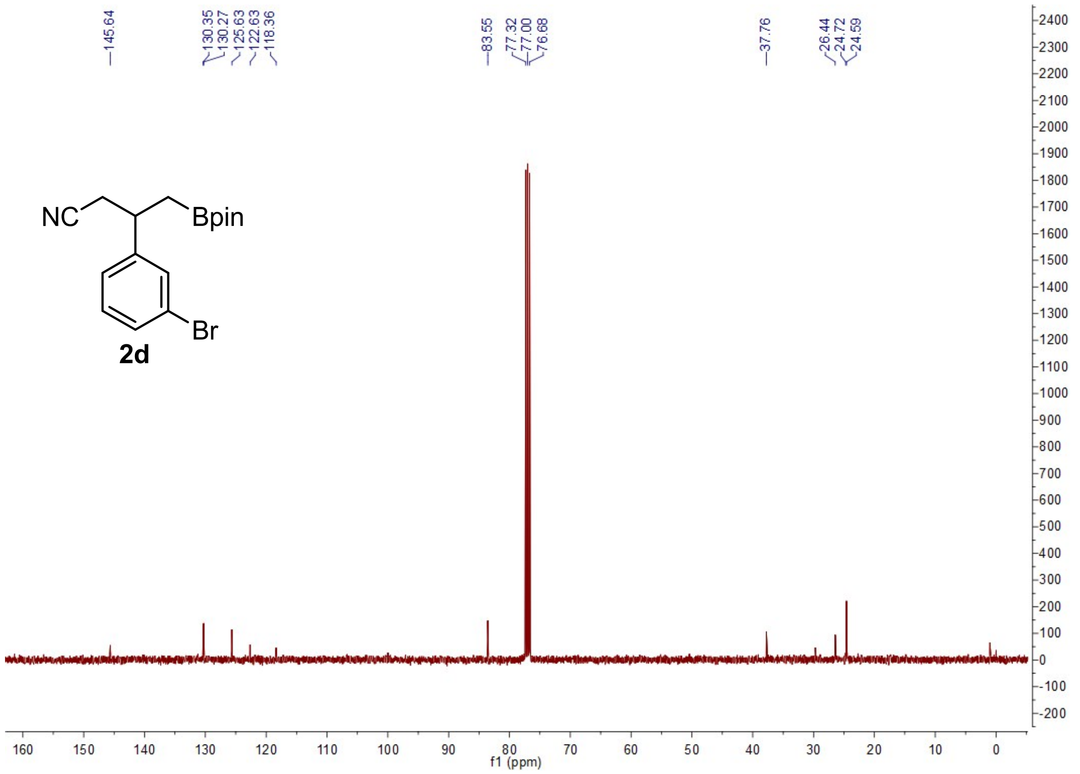
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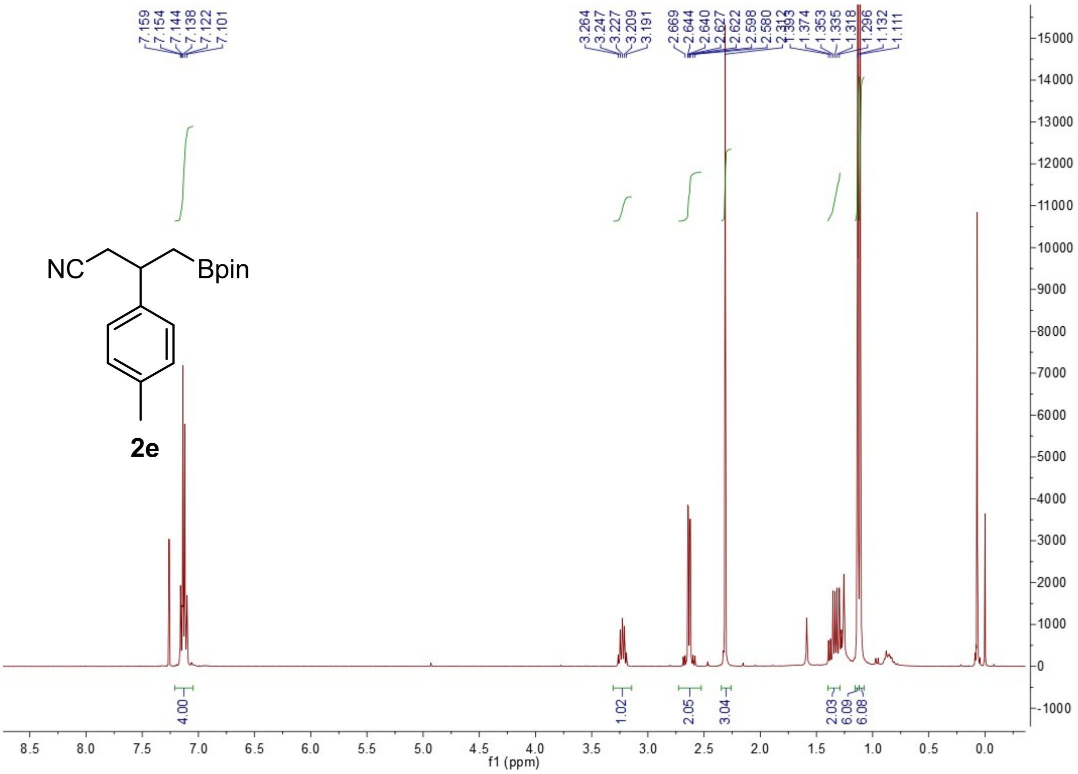
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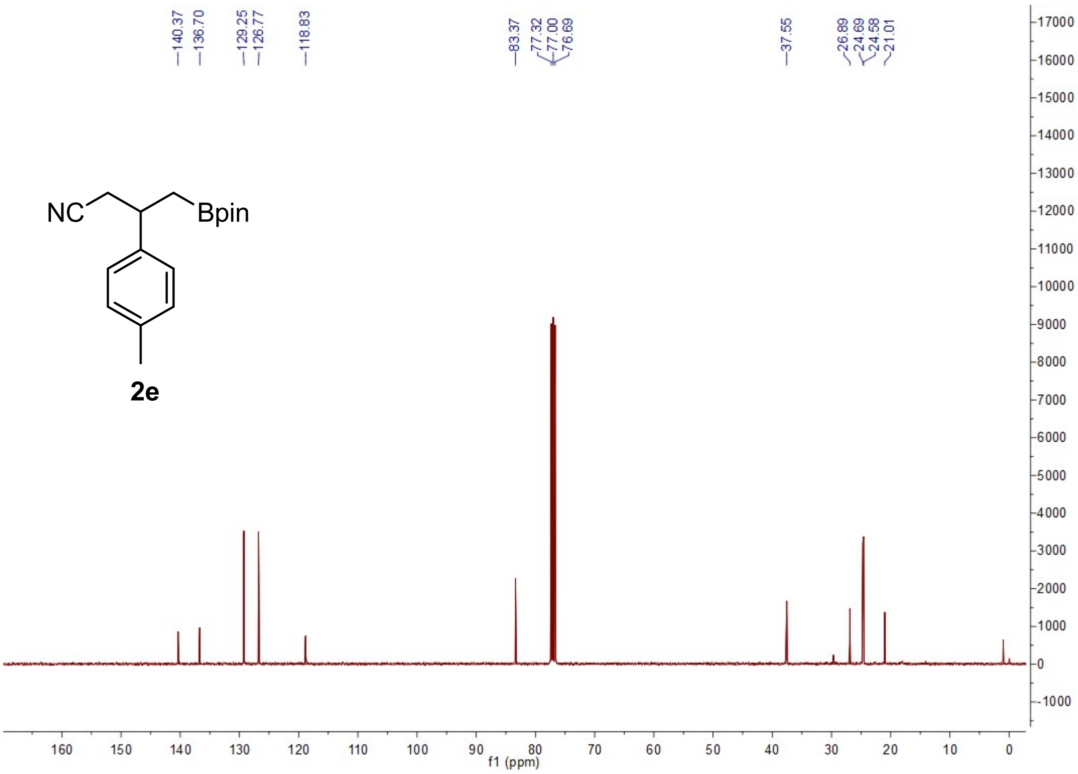
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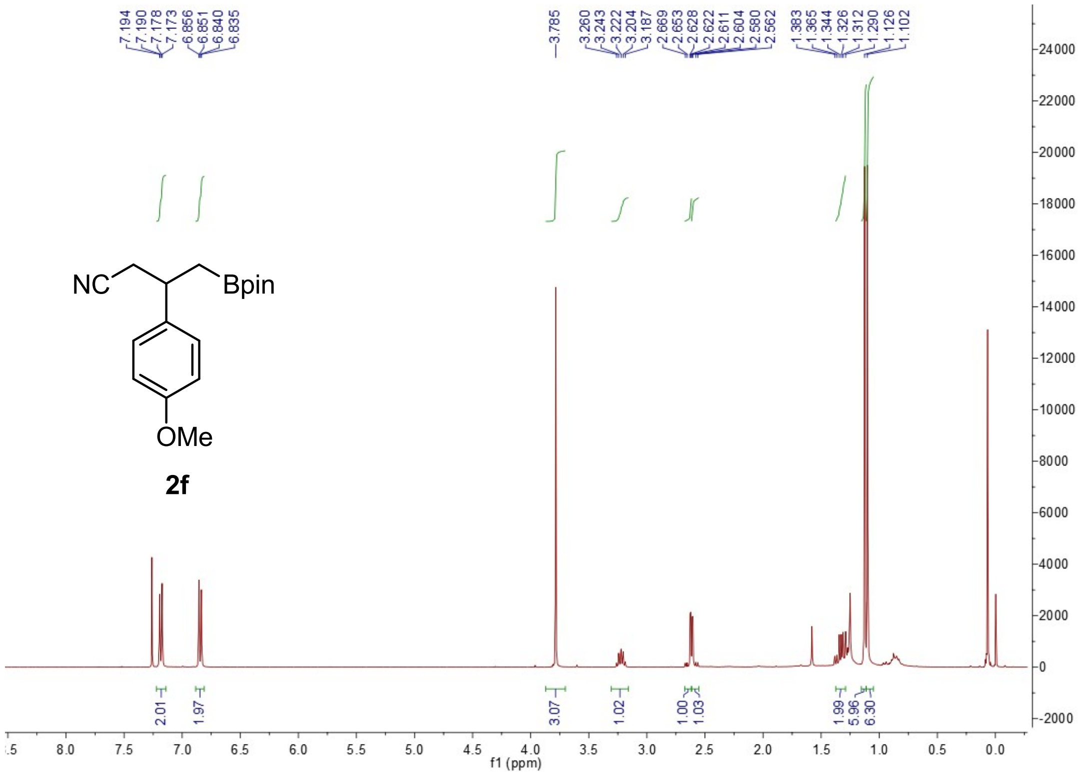
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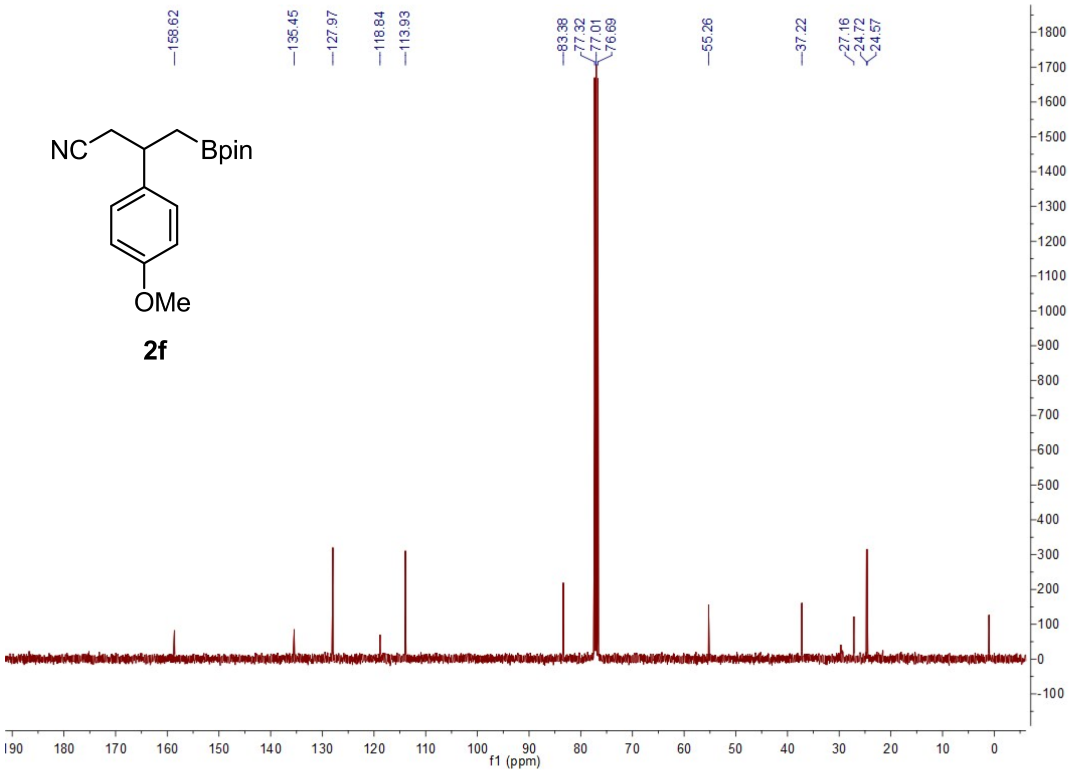
f1 (ppm)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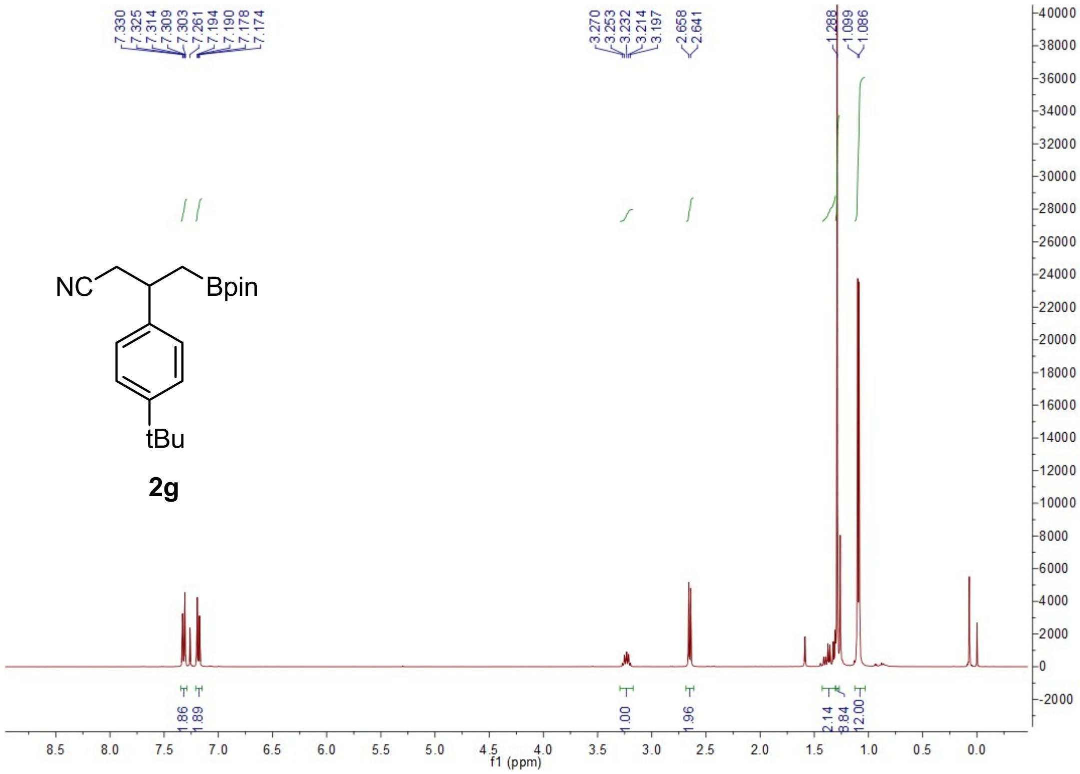
2f
f1 (ppm)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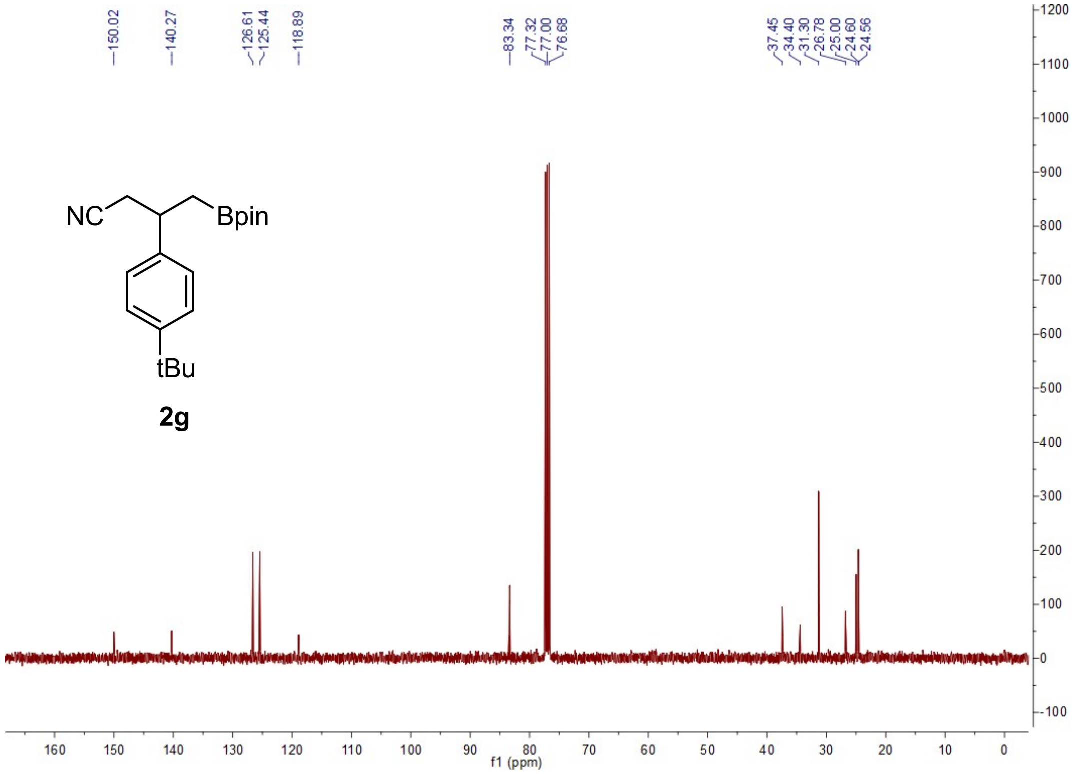
f1 (ppm)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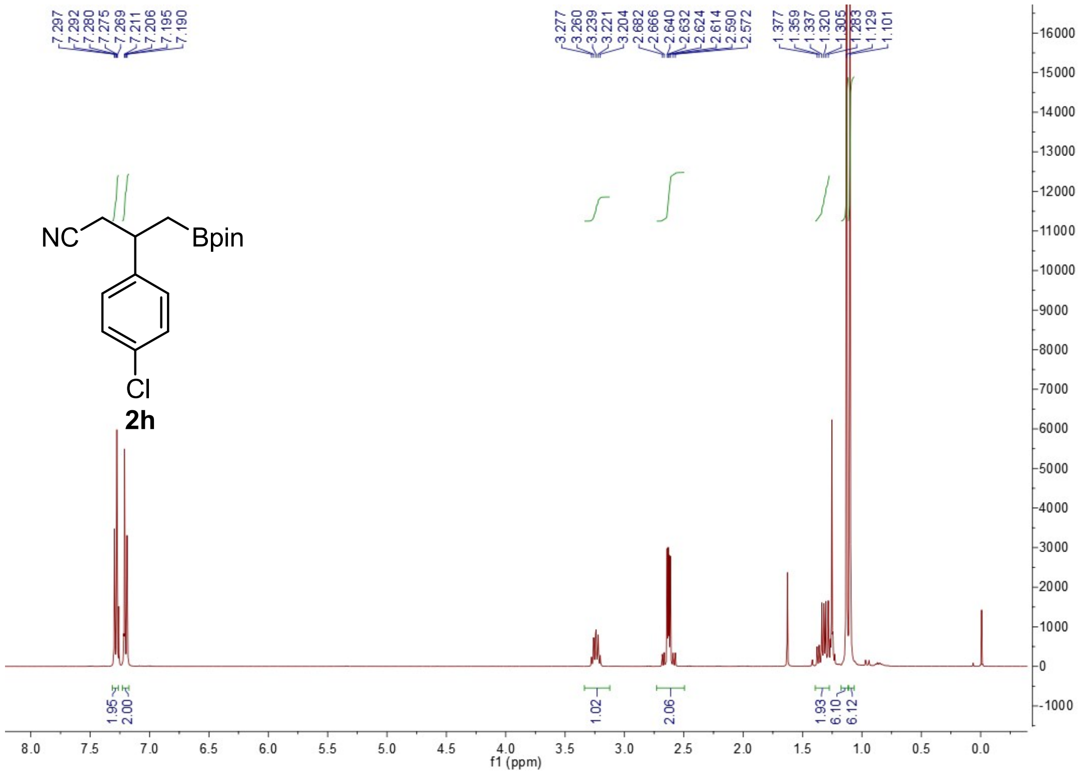
2g
f1 (ppm)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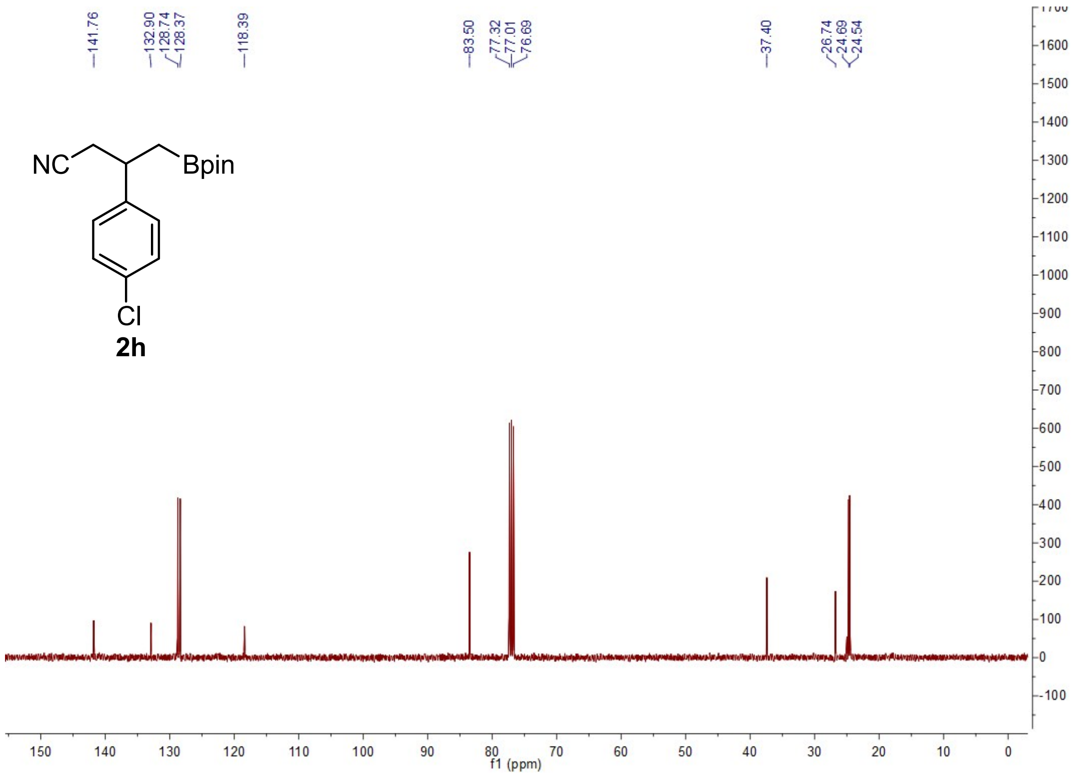
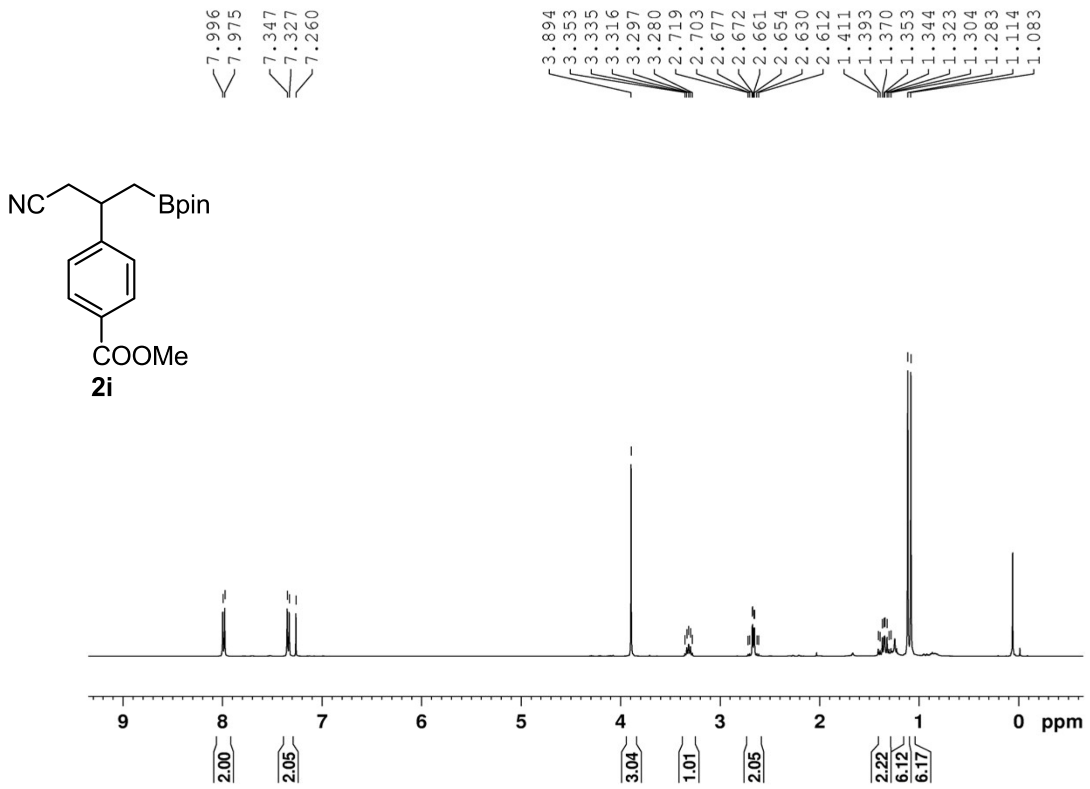
7.292
7.280
7.275
7.269
7.211
7.206
7.195
7.190
3.277
3.260
3.239
3.221
3.204
2.682
2.666
2.640
2.632
2.624
2.614
2.590
2.572
1.377
1.359
1.337
1.320
1.305
1.283
1.129
1.101
NC
Bpin
Cl
1.95
2.00
1.02
2.06
1.93
6.10
6.12
f1 (ppm)

2h


141.76
132.90
128.74
128.37
118.39
83.50
77.32
77.01
76.69
37.40
26.74
24.69
24.54
NC
Bpin
Cl
f1 (ppm)

2h


7.996
7.975
7.347
7.327
7.260
3.894
3.353
3.335
3.316
3.297
3.280
2.719
2.703
2.677
2.672
2.661
2.654
2.630
2.612
1.411
1.393
1.370
1.353
1.344
1.323
1.304
1.283
1.114
1.083
NC
Bpin
COOMe
2i
9
8
7
6
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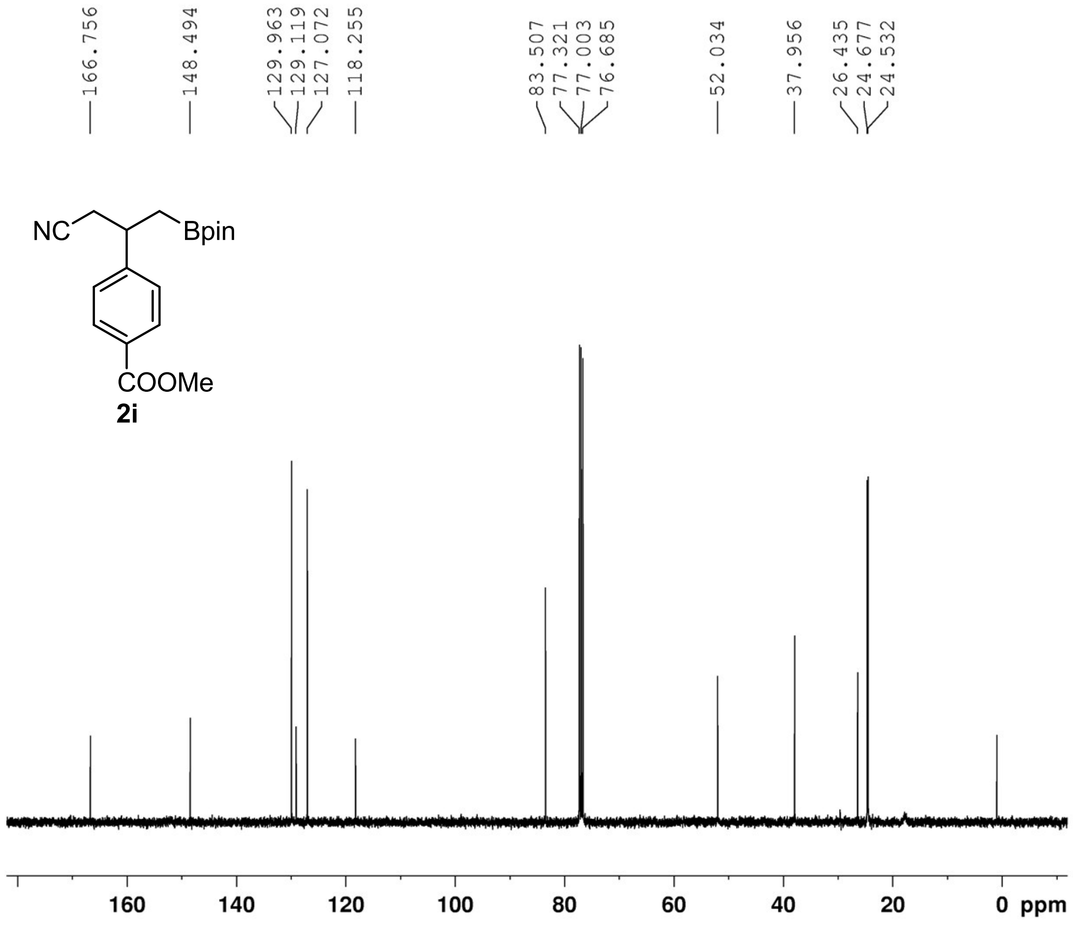
1.01
2.05
2.22
6.12
6.17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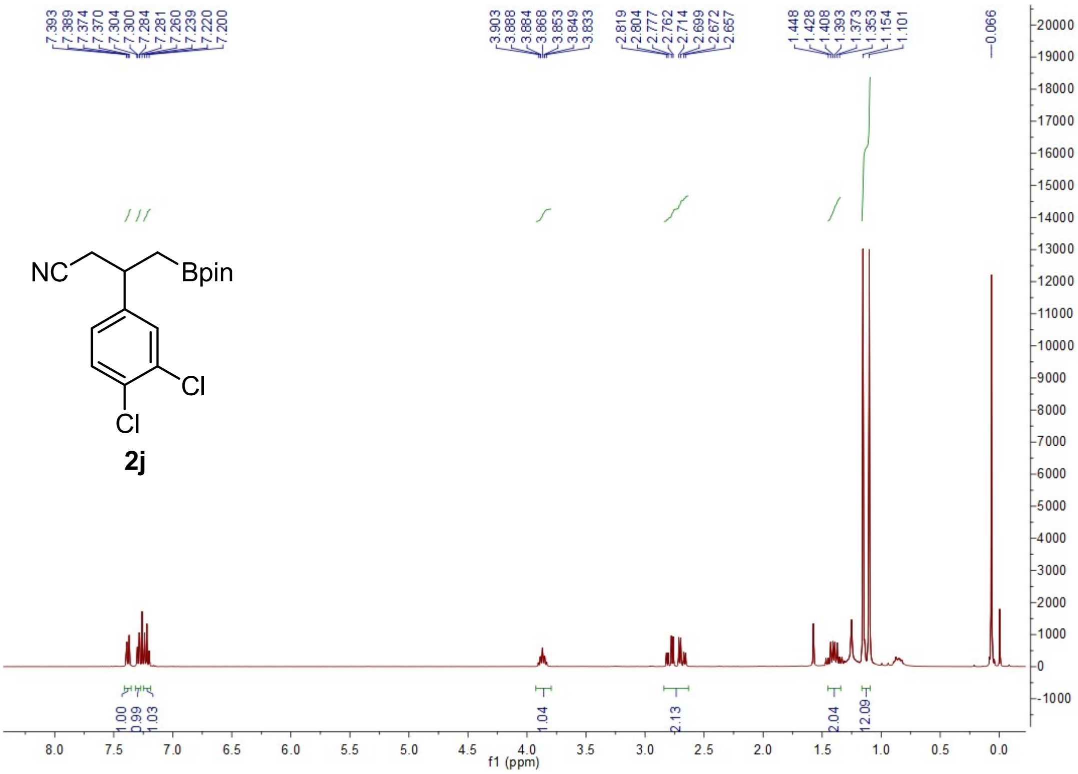
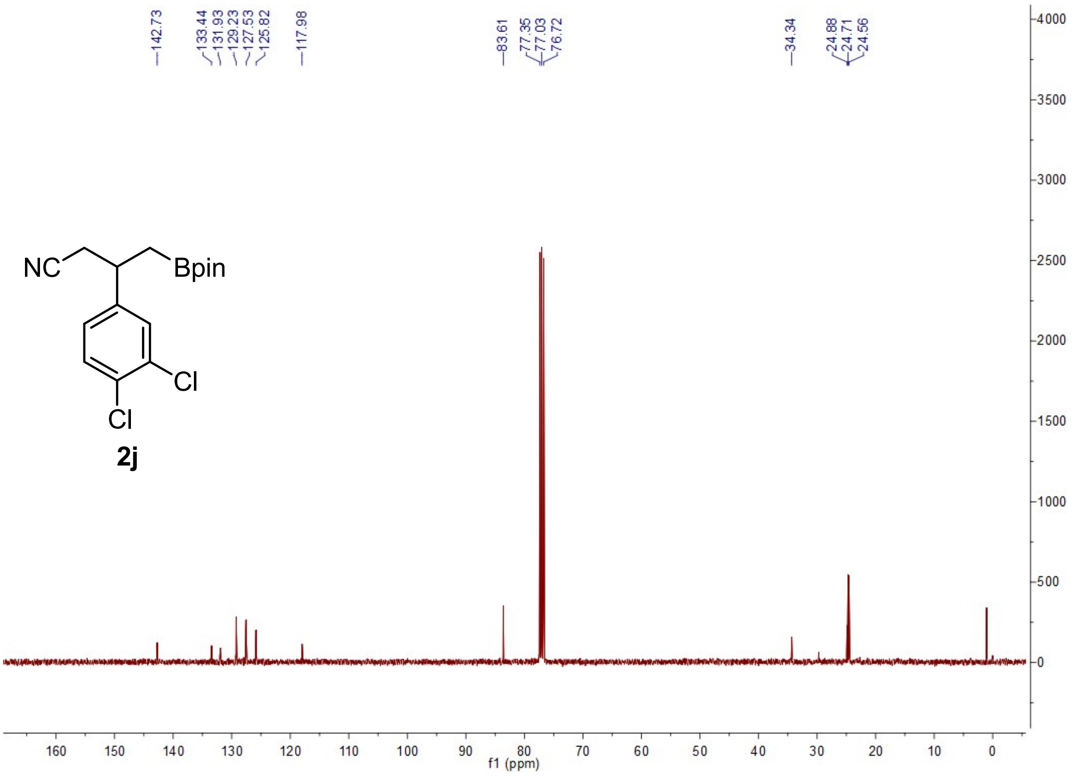
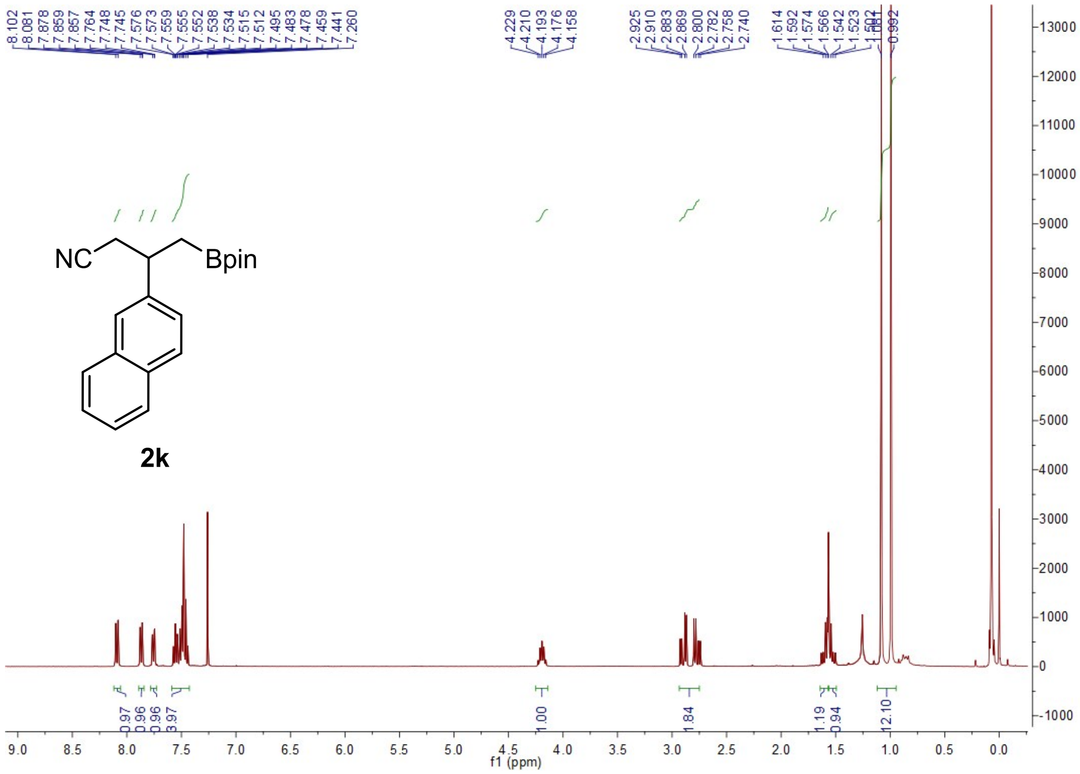
148.494
129.963
129.119
127.072
118.255
83.507
77.321
77.003
76.685
52.034
37.956
26.435
24.677
24.532
NC
Bpin
COOMe
2i
160
140
120
100
80
60
40
20
0 ppm


7.393
7.389
7.374
7.370
7.304
7.300
7.284
7.281
7.260
7.239
7.220
7.200
3.903
3.888
3.884
3.868
3.853
3.849
3.833
2.819
2.804
2.777
2.762
2.714
2.699
2.672
2.657
1.448
1.428
1.408
1.393
1.373
1.353
1.154
1.101
0.066
NC
Bpin
Cl
Cl
2j
1.00
0.99
1.03
1.04
2.13
2.04
12.09
f1 (ppm)


142.73
133.44
131.93
129.23
127.53
125.82
117.98
83.61
77.35
77.03
76.72
34.34
24.88
24.71
24.56
NC
Bpin
Cl
Cl
2j
f1 (ppm)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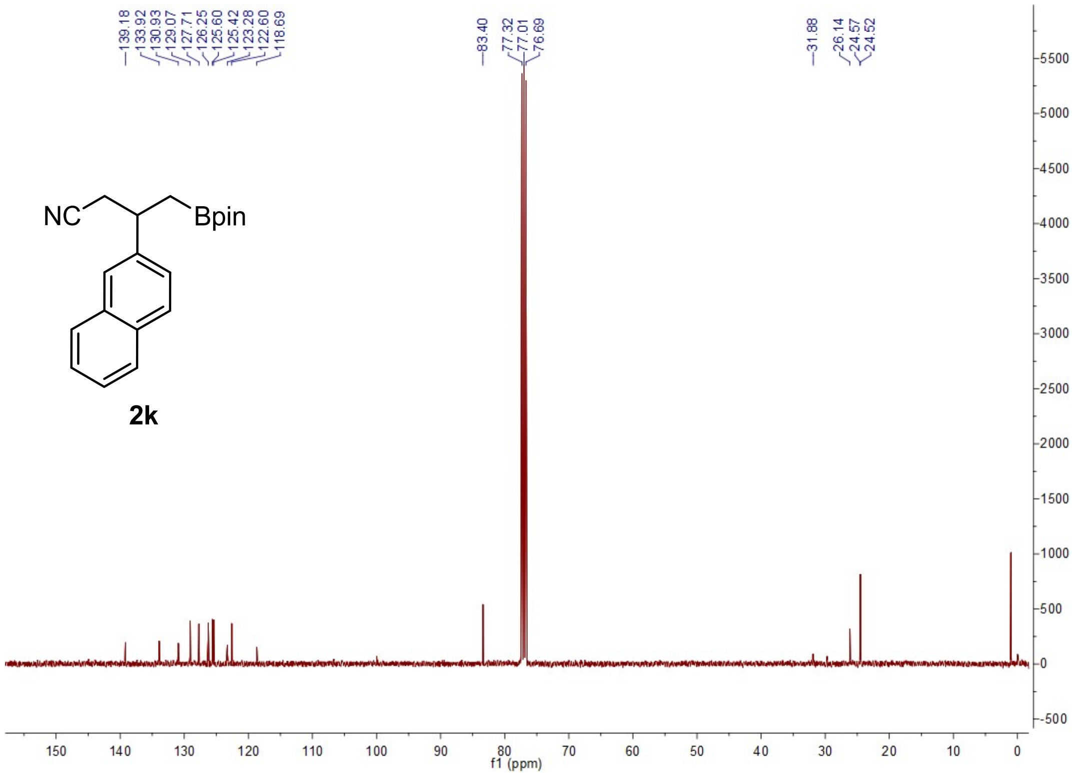
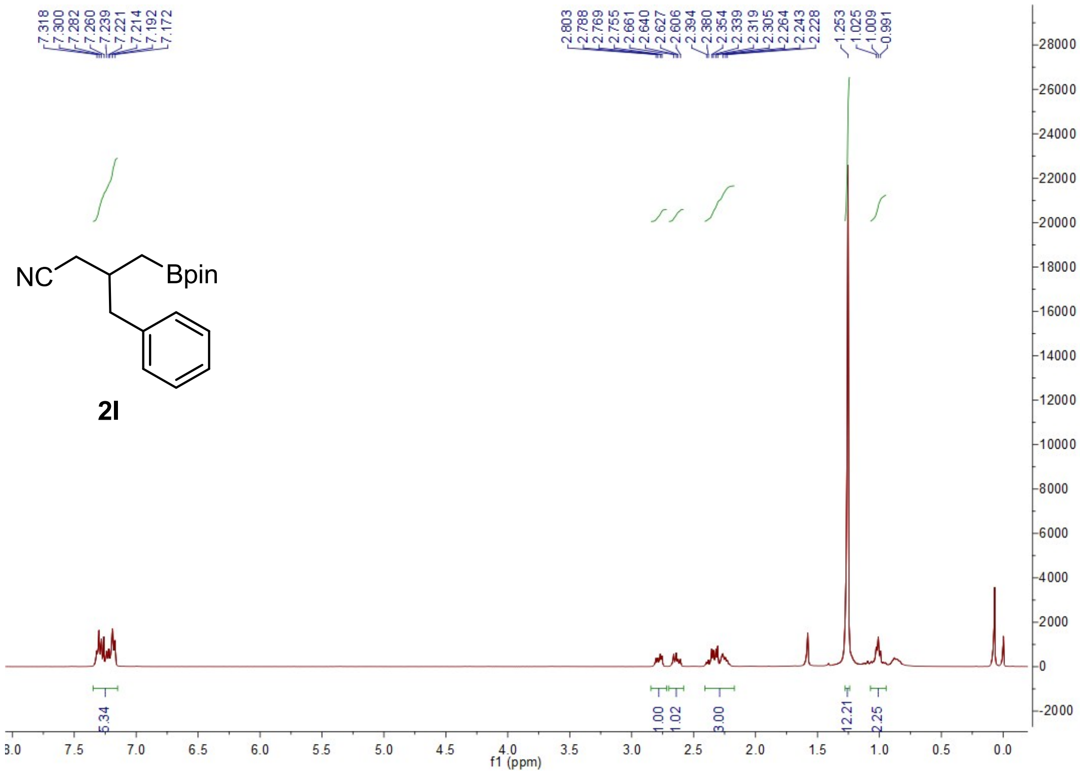
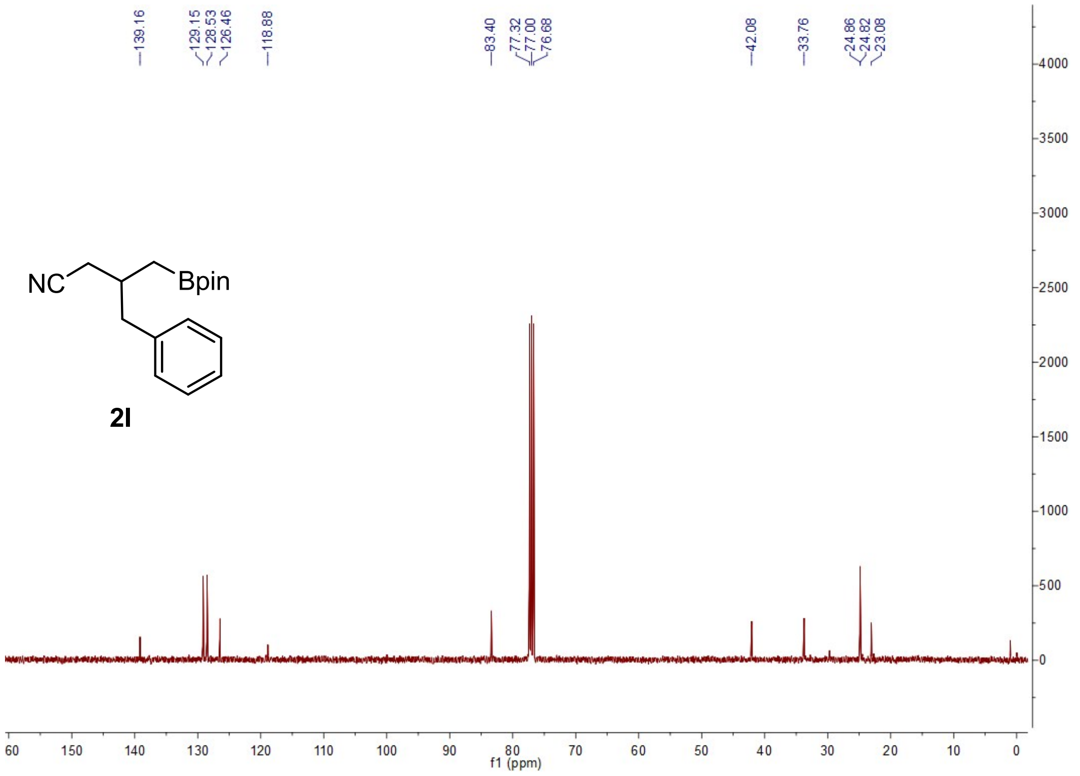
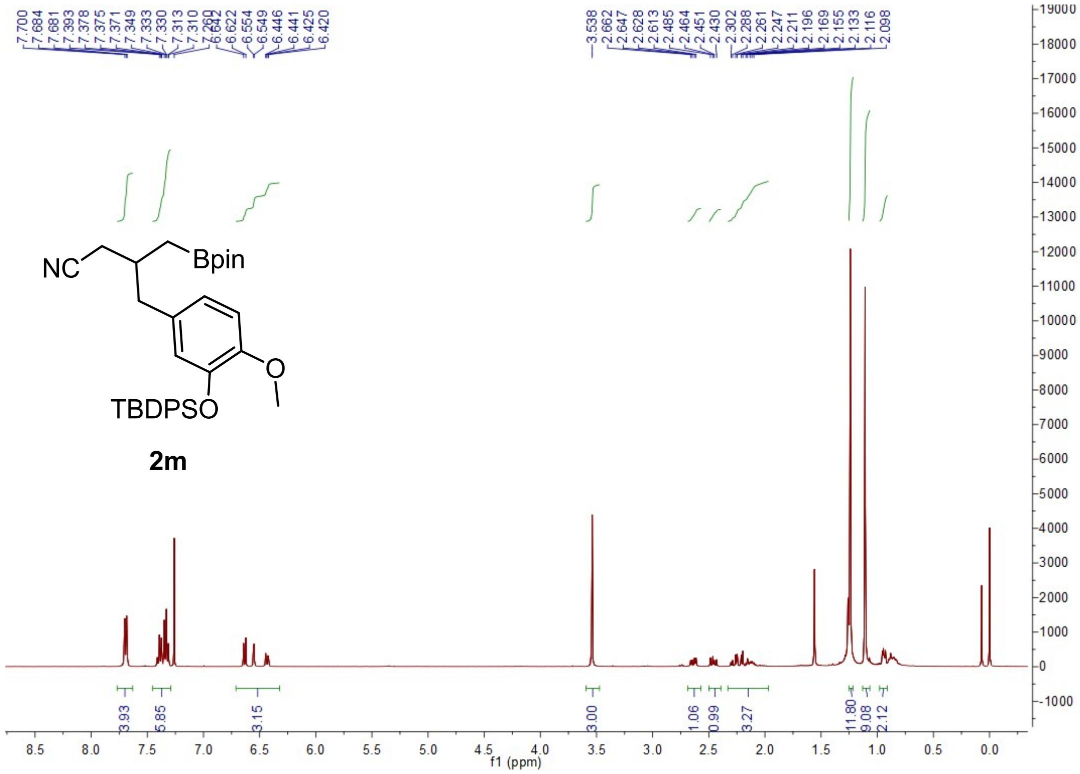
8.081
7.878
7.859
7.857
7.764
7.748
7.745
7.576
7.573
7.559
7.555
7.552
7.538
7.534
7.515
7.512
7.495
7.483
7.478
7.459
7.441
7.260
4.229
4.210
4.193
4.176
4.158
2.925
2.910
2.883
2.869
2.800
2.782
2.758
2.740
1.614
1.592
1.574
1.566
1.542
1.523
1.502
1.081
0.992
NC
Bpin
2k
0.97
0.96
0.96
3.97
1.00
1.84
1.19
0.94
12.10
f1 (ppm)

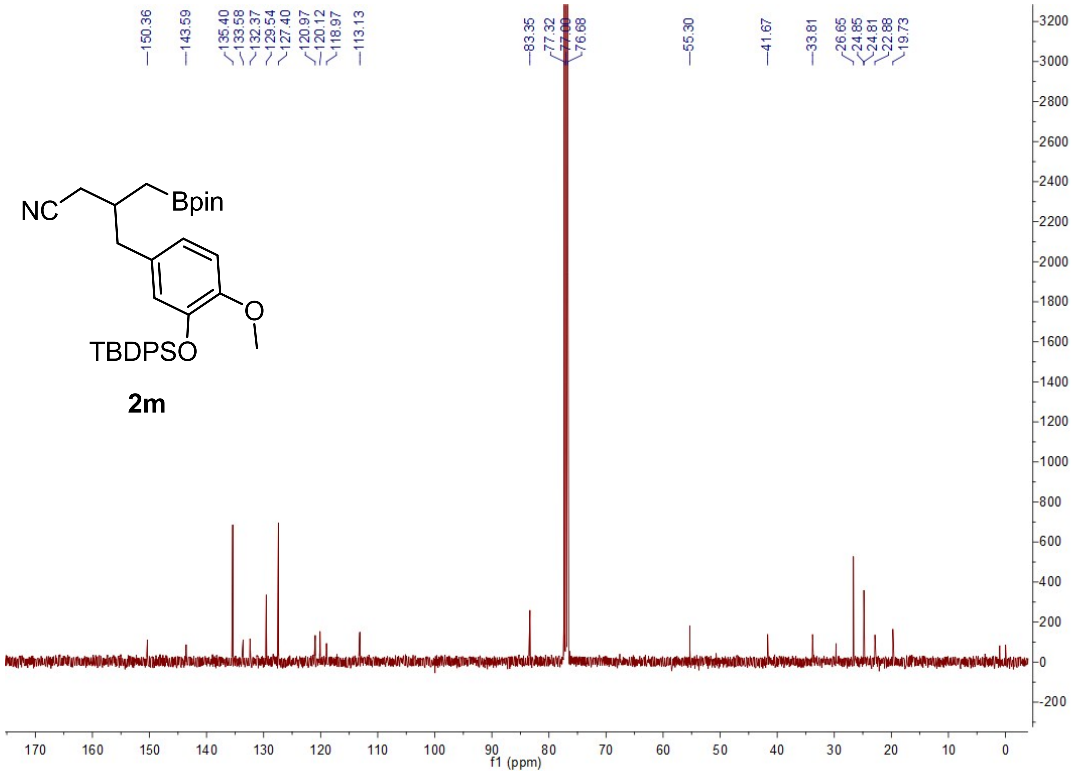

139.18
133.92
130.93
129.07
127.71
126.25
125.60
125.42
123.28
122.60
118.69
83.40
77.32
77.01
76.69
31.88
26.14
24.57
24.52
NC
Bpin
2k
f1 (ppm)


7.318
7.300
7.282
7.260
7.239
7.221
7.214
7.192
7.172
2.803
2.788
2.769
2.755
2.661
2.640
2.627
2.606
2.394
2.380
2.354
2.339
2.319
2.305
2.264
2.243
2.228
1.253
1.025
1.009
0.991
NC
Bpin
2l
5.34
1.00
1.02
3.00
12.21
2.25
f1 (ppm)
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
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000

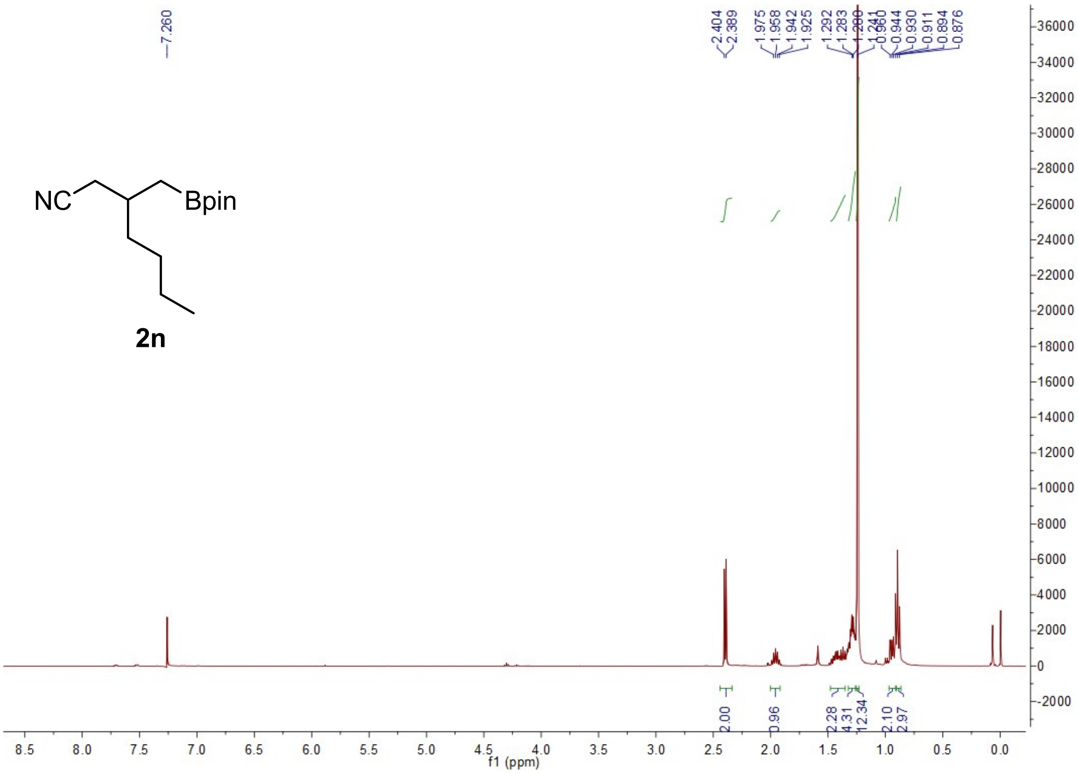

139.16
129.15
128.53
126.46
118.88
83.40
77.32
77.00
76.68
42.08
33.76
24.86
24.82
23.08
NC
Bpin
2l
f1 (ppm)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
4000
3500
3000
2500
2000
1500
1000
500
0

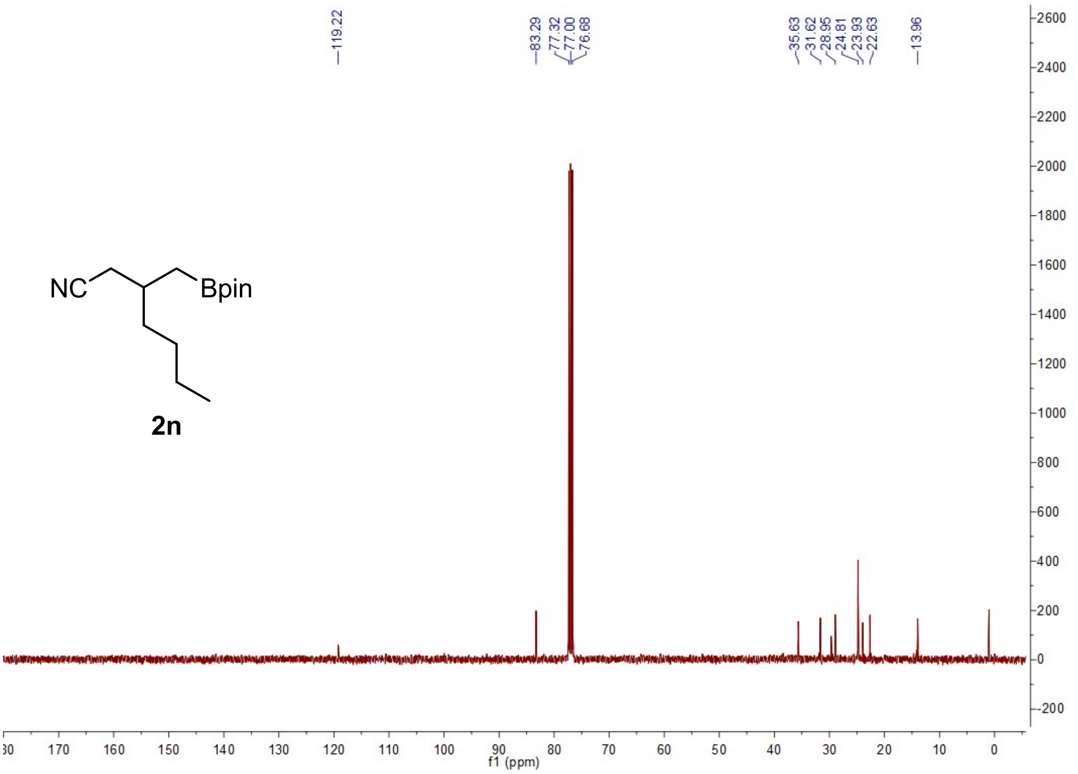

7.700 7.684 7.681 7.393 7.378 7.375 7.371 7.349 7.333 7.330 7.313 7.310 7.260 6.642 6.622 6.554 6.549 6.446 6.441 6.425 6.420
3.538 2.662 2.647 2.628 2.613 2.485 2.464 2.451 2.430 2.302 2.288 2.261 2.247 2.211 2.196 2.169 2.155 2.133 2.116 2.098
NC
Bpin
O
TBDPSO
3.93
5.85
3.15
3.00
1.06
0.99
3.27
11.80
9.08
2.12
f1 (ppm)

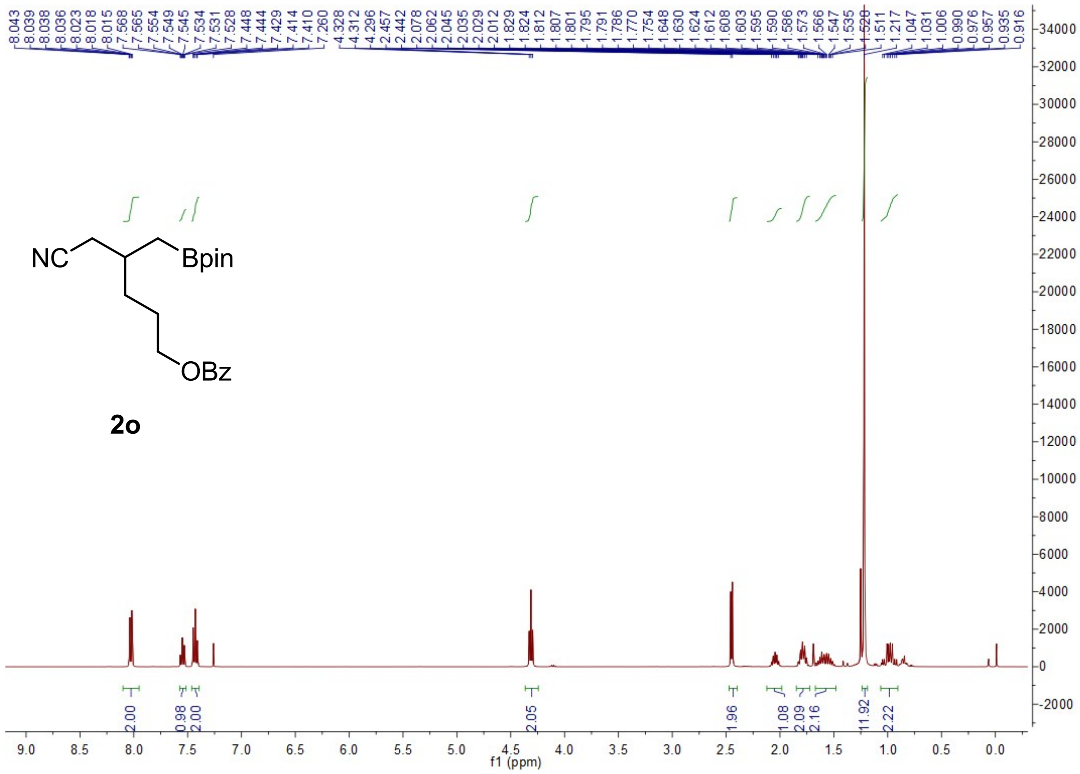
2m

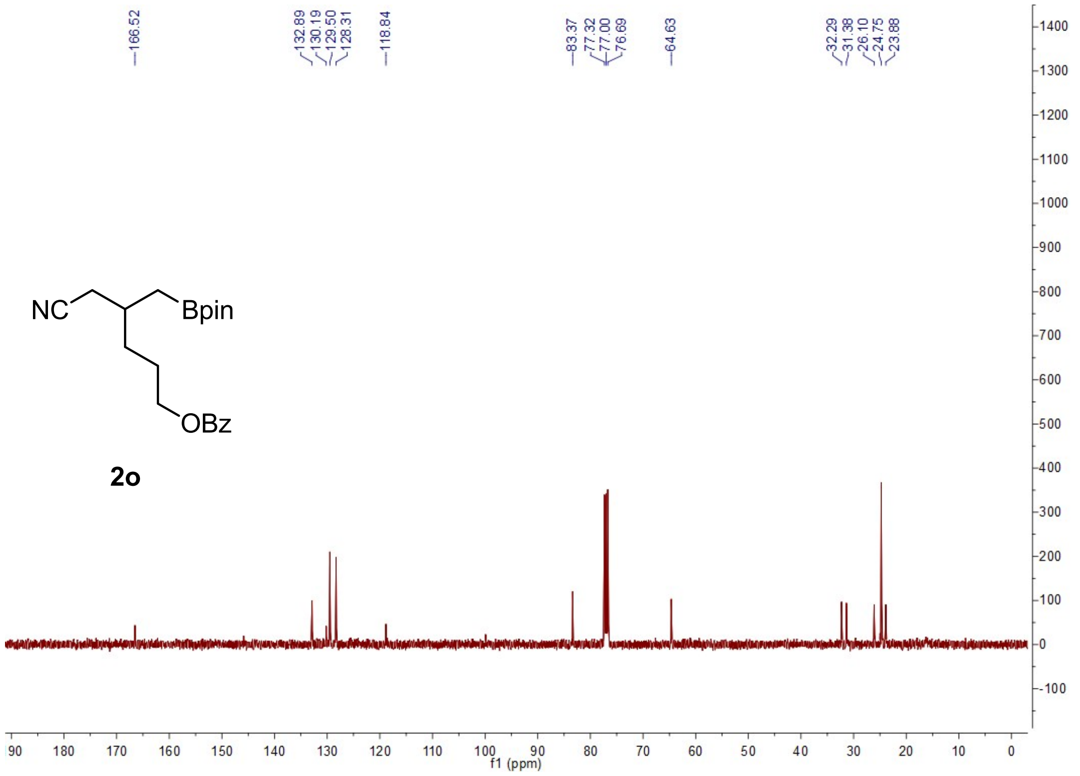

150.36 143.59 135.40 133.58 132.37 129.54 127.40 120.97 120.12 118.97 113.13
83.35 77.32 77.00 76.68 55.30 41.67 33.81 26.65 24.85 24.81 22.88 19.73
NC
Bpin
O
TBDPSO
f1 (ppm)

2m


2n
NC
Bpin
7.260
2.404
2.389
1.975
1.958
1.942
1.925
1.292
1.283
1.280
1.241
0.960
0.944
0.930
0.911
0.894
0.876
2.00
0.96
2.28
4.31
12.34
2.10
2.97
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
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)


2n
NC
Bpin
119.22
83.29
77.32
77.00
76.68
35.63
31.62
28.95
24.81
23.93
22.63
13.96
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
30
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.043
8.039
8.038
8.036
8.023
8.018
8.015
7.568
7.565
7.554
7.549
7.545
7.534
7.531
7.528
7.448
7.444
7.429
7.414
7.410
7.260
4.328
4.312
4.296
2.457
2.442
2.078
2.062
2.045
2.035
2.029
2.012
1.829
1.824
1.812
1.807
1.801
1.795
1.791
1.786
1.770
1.754
1.648
1.630
1.624
1.612
1.608
1.603
1.595
1.590
1.586
1.573
1.566
1.547
1.535
1.520
1.511
1.217
1.047
1.031
1.006
0.990
0.976
0.957
0.935
0.916
NC
Bpin
OBz
2o
2.00
0.98
2.00
2.05
1.96
1.08
2.09
2.16
11.92
2.22
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)
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000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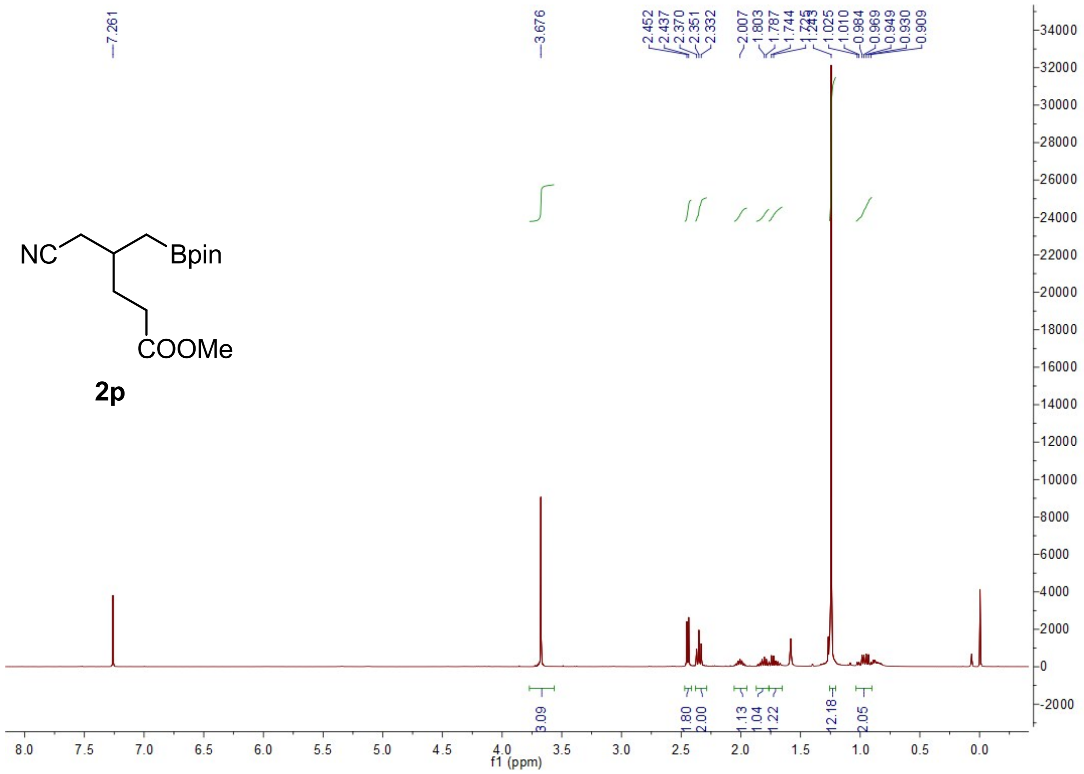
132.89
130.19
129.50
128.31
118.84
83.37
77.32
77.00
76.69
64.63
32.29
31.38
26.10
24.75
23.88
NC
Bpin
OBz
2o
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100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3.676
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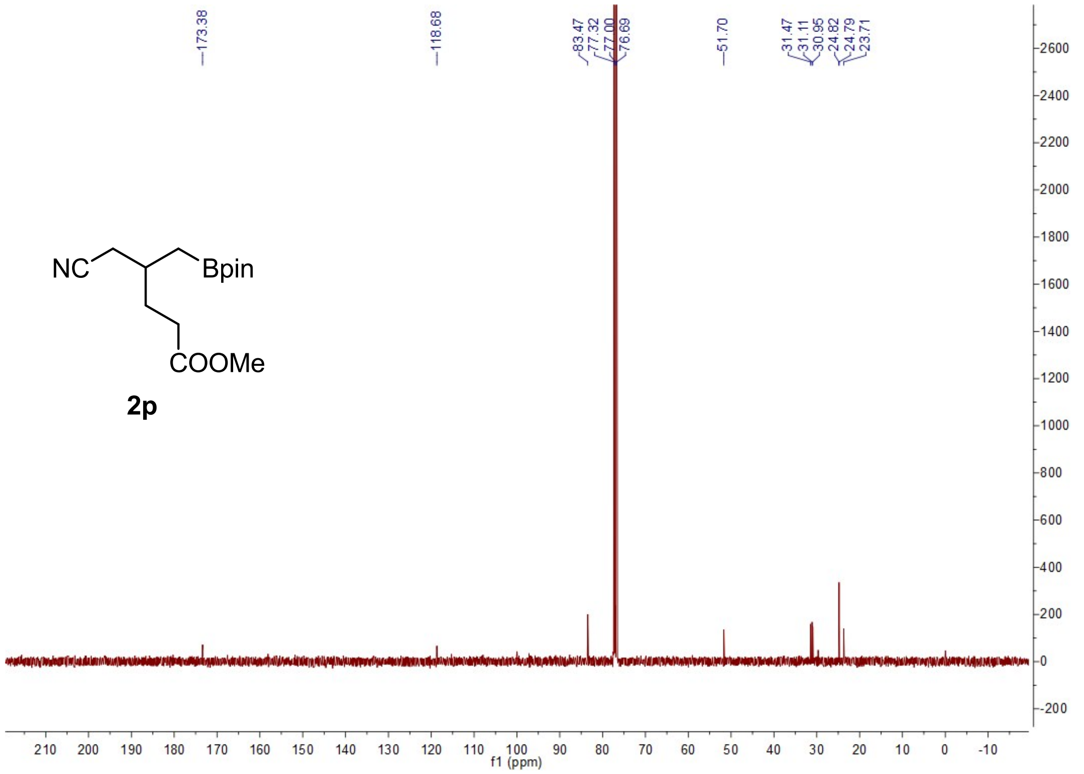
2.370
2.351
2.332
2.007
1.803
1.787
1.744
1.725
1.243
1.025
1.010
0.984
0.969
0.949
0.930
0.909
NC
Bpin
COOMe
2p
3.09
1.80
2.00
1.13
1.04
1.22
12.18
2.05
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000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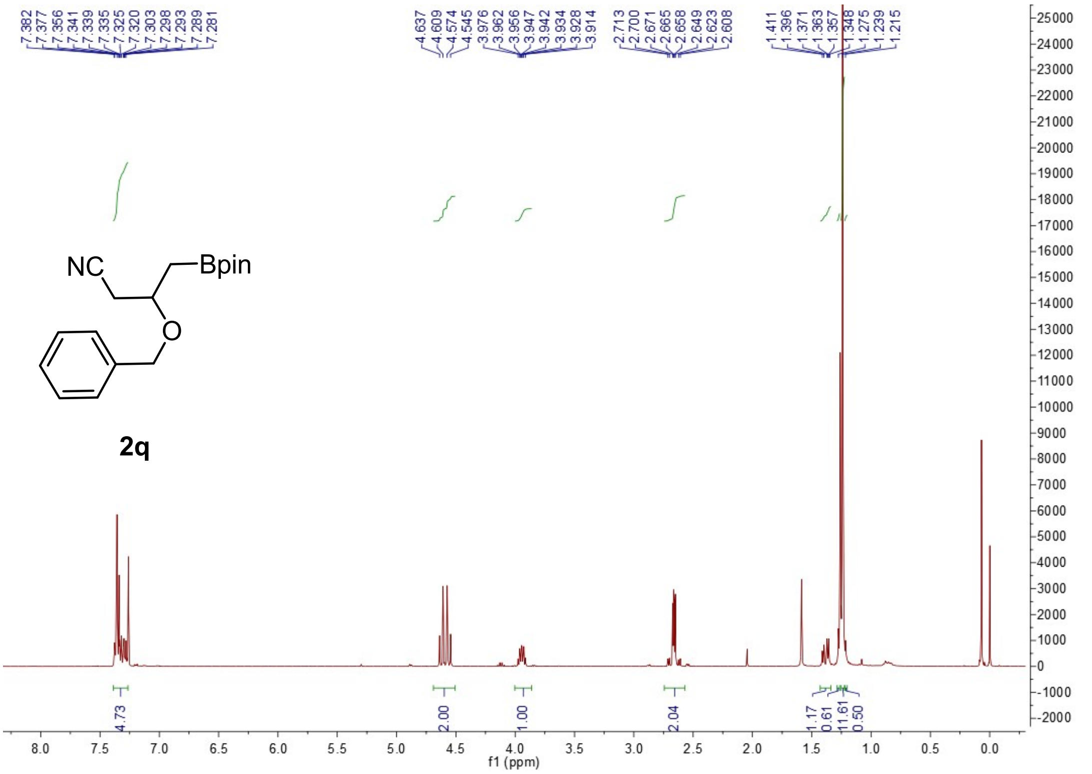
83.47
77.32
77.00
76.69
51.70
31.47
31.11
30.95
24.82
24.79
23.71
NC
Bpin
COOMe
2p
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200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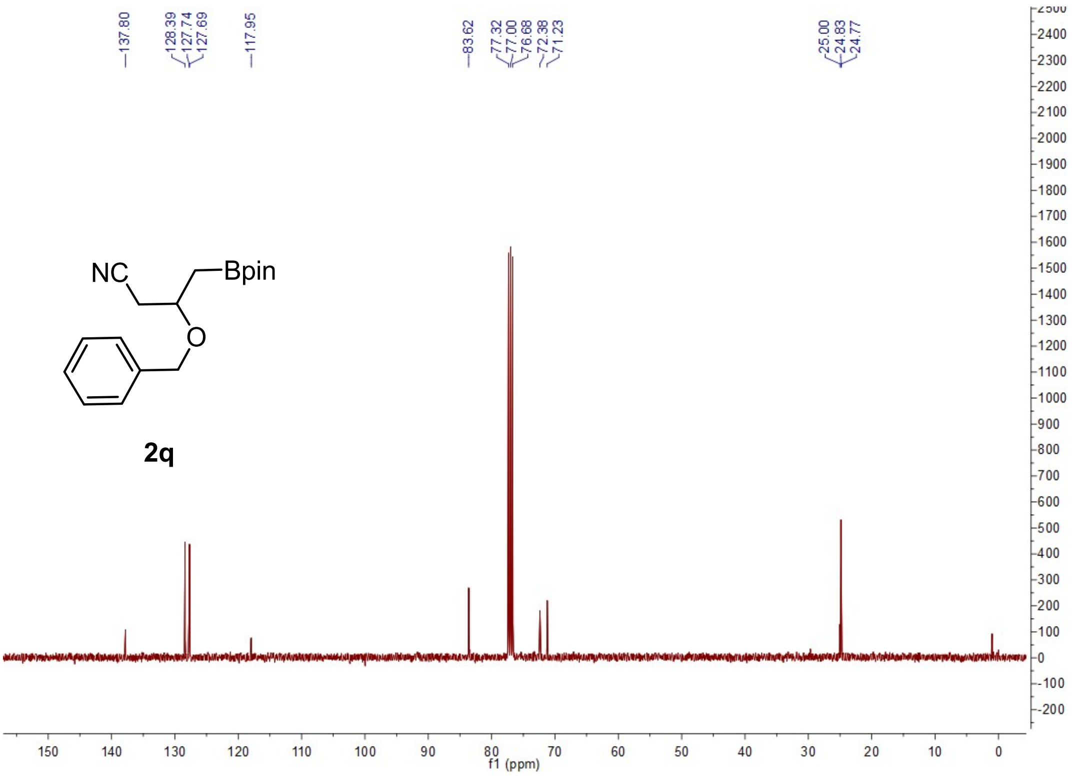
7.377
7.356
7.341
7.339
7.335
7.325
7.320
7.303
7.298
7.293
7.289
7.281
4.637
4.609
4.574
4.545
3.976
3.962
3.956
3.947
3.942
3.934
3.928
3.914
2.713
2.700
2.671
2.665
2.658
2.649
2.623
2.608
1.411
1.396
1.371
1.363
1.357
1.348
1.275
1.239
1.215
NC
Bpin
O
2q
4.73
2.00
1.00
2.04
1.17
0.61
11.61
0.50
f1 (ppm)


137.80
128.39
127.74
127.69
117.95
83.62
77.32
77.00
76.68
72.38
71.23
25.00
24.83
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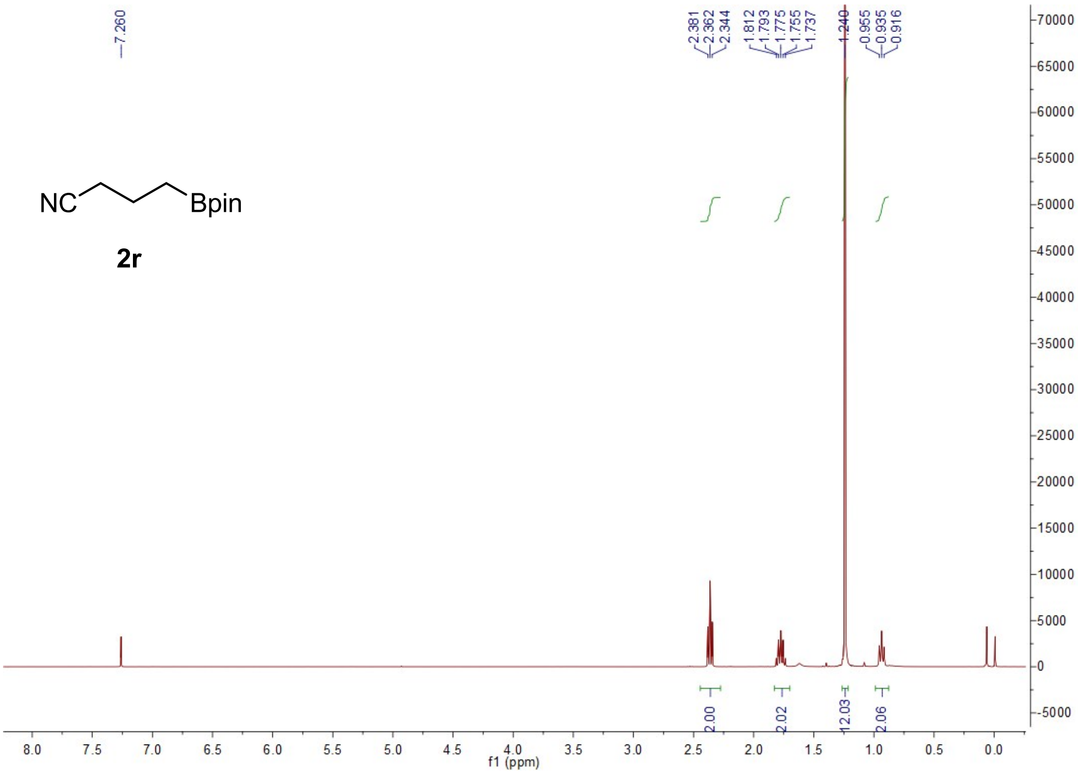
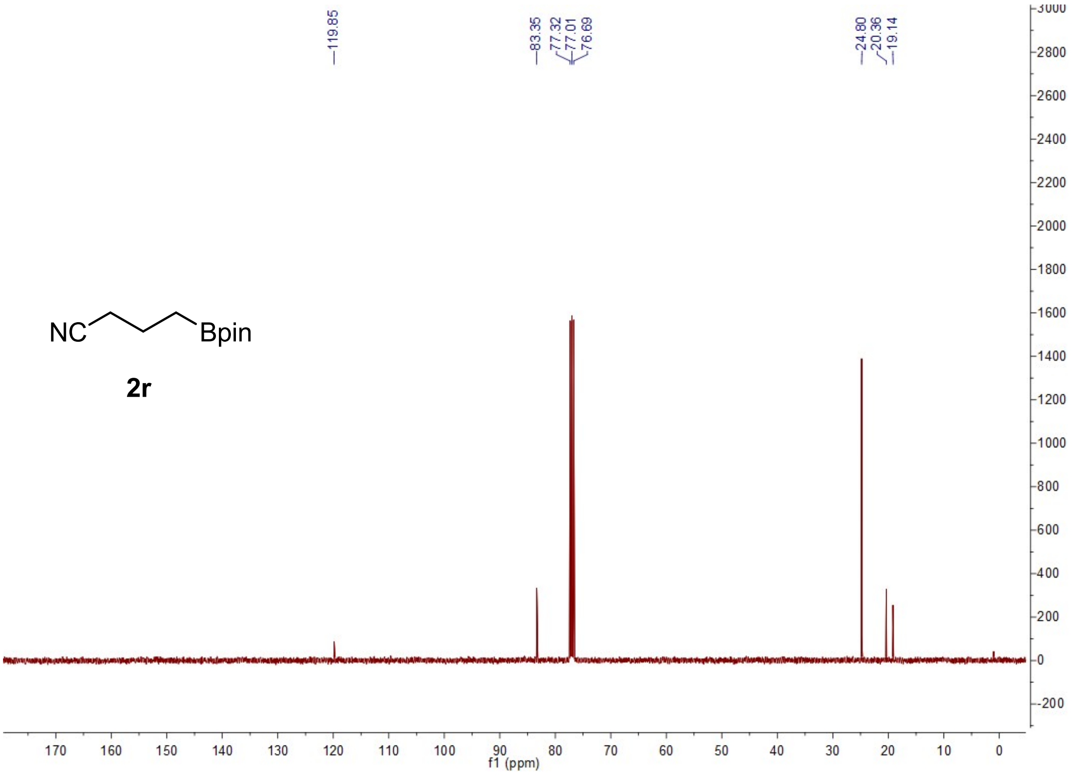
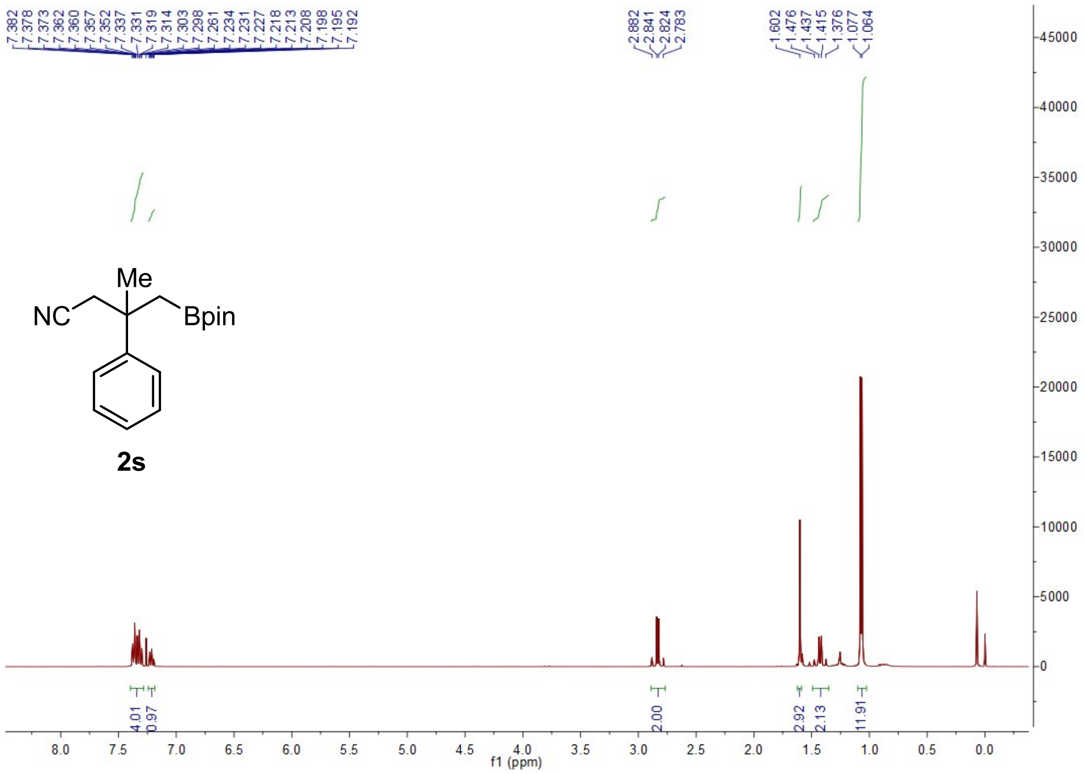
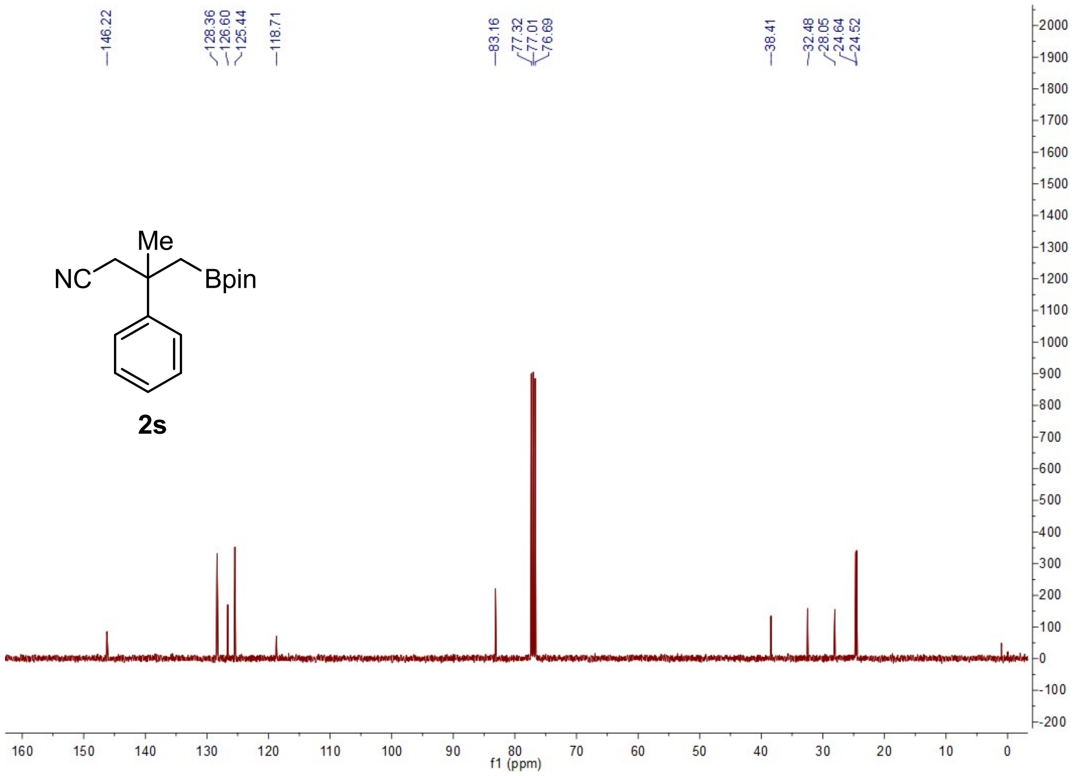
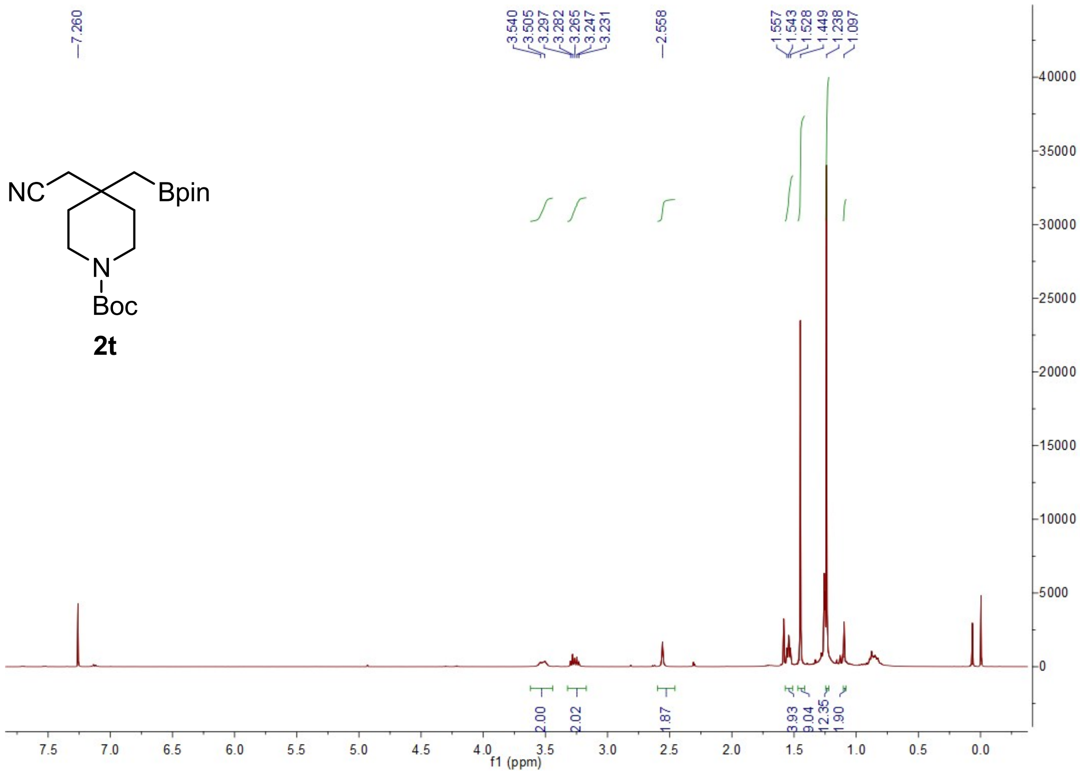
Bpin
O
2q
f1 (ppm)


NC
Bpin
2r
7.260
2.381
2.362
2.344
1.812
1.793
1.775
1.755
1.737
1.249
0.955
0.935
0.916
2.00
2.02
12.03
2.06
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)
70000 65000 60000 55000 50000 45000 40000 35000 30000 25000 20000 15000 10000 5000 0 -5000

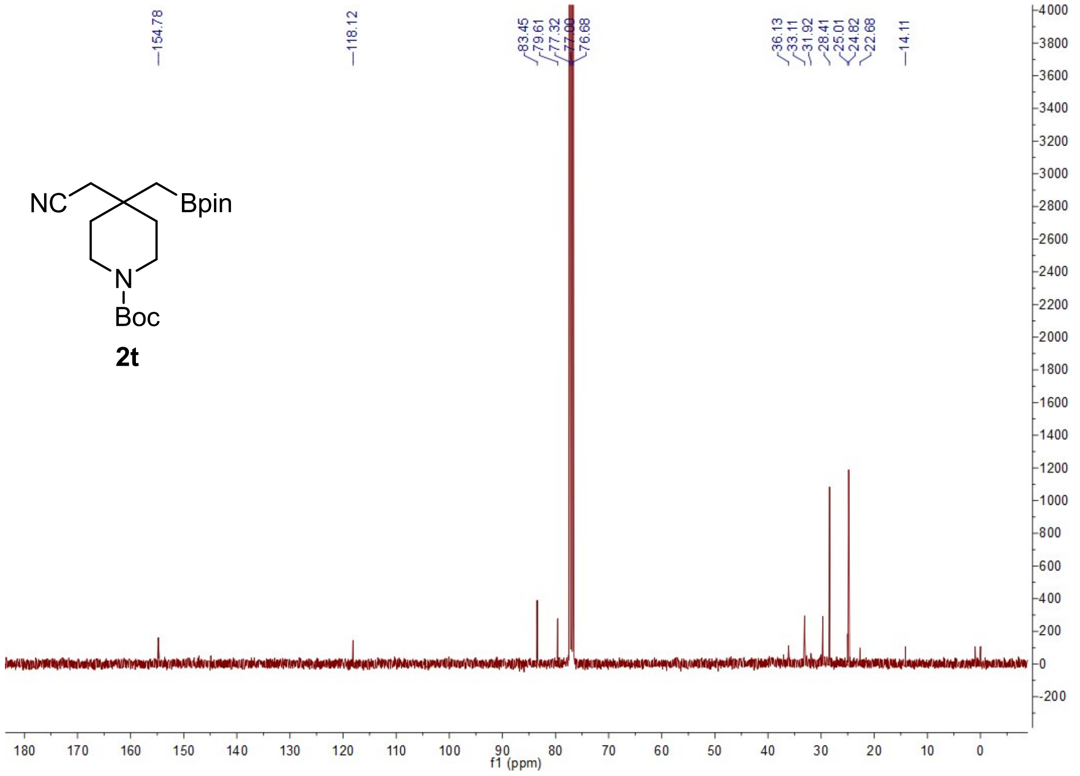

NC
Bpin
2r
119.85
83.35
77.32
77.01
76.69
24.80
20.36
19.14
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
3000 2800 2600 2400 2200 2000 1800 1600 1400 1200 1000 800 600 400 200 0 -200


7.382
7.378
7.373
7.362
7.360
7.357
7.352
7.337
7.331
7.319
7.314
7.303
7.298
7.261
7.234
7.231
7.227
7.218
7.213
7.208
7.198
7.195
7.192
2.882
2.841
2.824
2.783
1.602
1.476
1.437
1.415
1.376
1.077
1.064
Me
NC
Bpin
2s
4.01
0.97
2.00
2.92
2.13
11.91
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)
45000
40000
35000
30000
25000
20000
15000
10000
5000
0

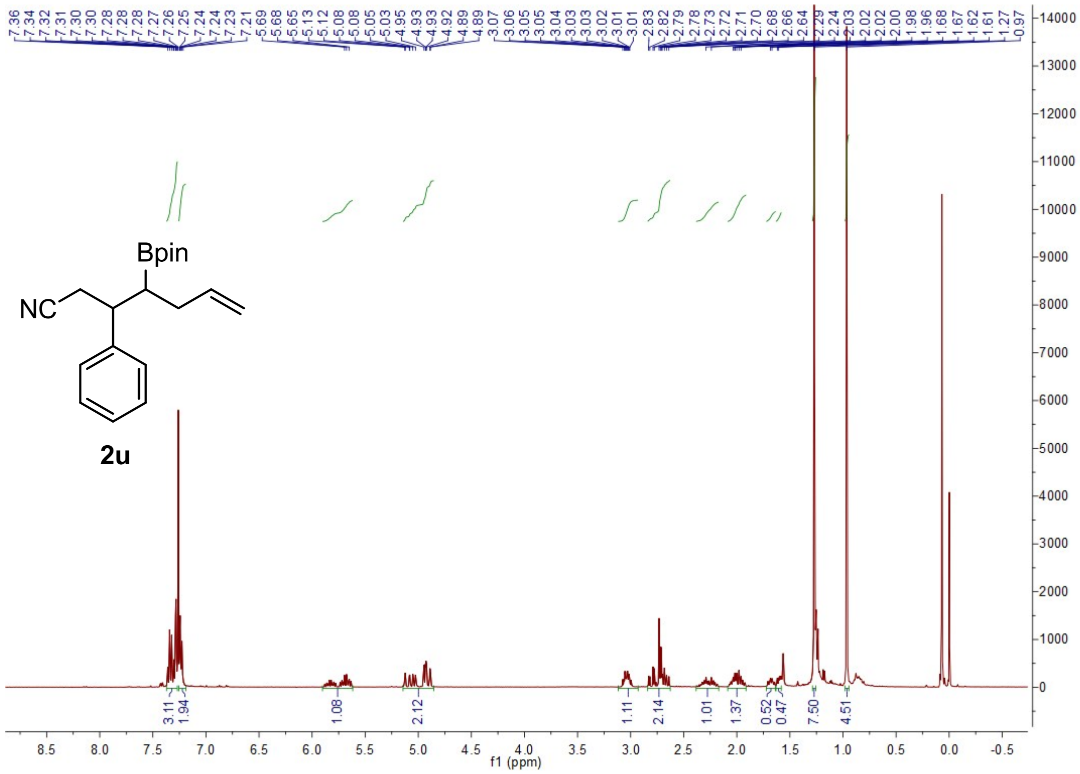

146.22
128.36
126.60
125.44
118.71
83.16
77.32
77.01
76.69
38.41
32.48
28.05
24.64
24.52
Me
NC
Bpin
2s
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200


7.260
3.540
3.505
3.297
3.282
3.265
3.247
3.231
2.558
1.557
1.543
1.528
1.449
1.238
1.097
NC
Bpin
N
Boc
2.00
2.02
1.87
3.93
9.04
12.35
1.90
f1 (ppm)

2t


154.78
118.12
83.45
79.61
77.32
77.00
76.68
36.13
33.11
31.92
28.41
25.01
24.82
22.68
14.11
NC
Bpin
N
Boc
f1 (ppm)

2t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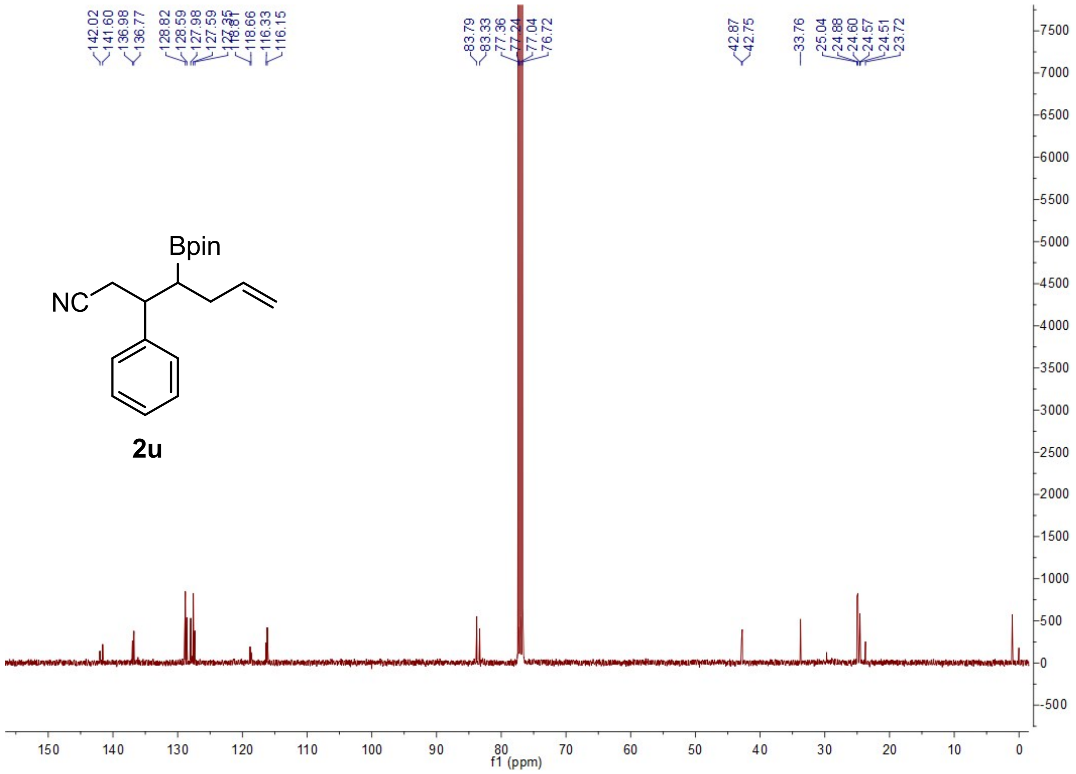
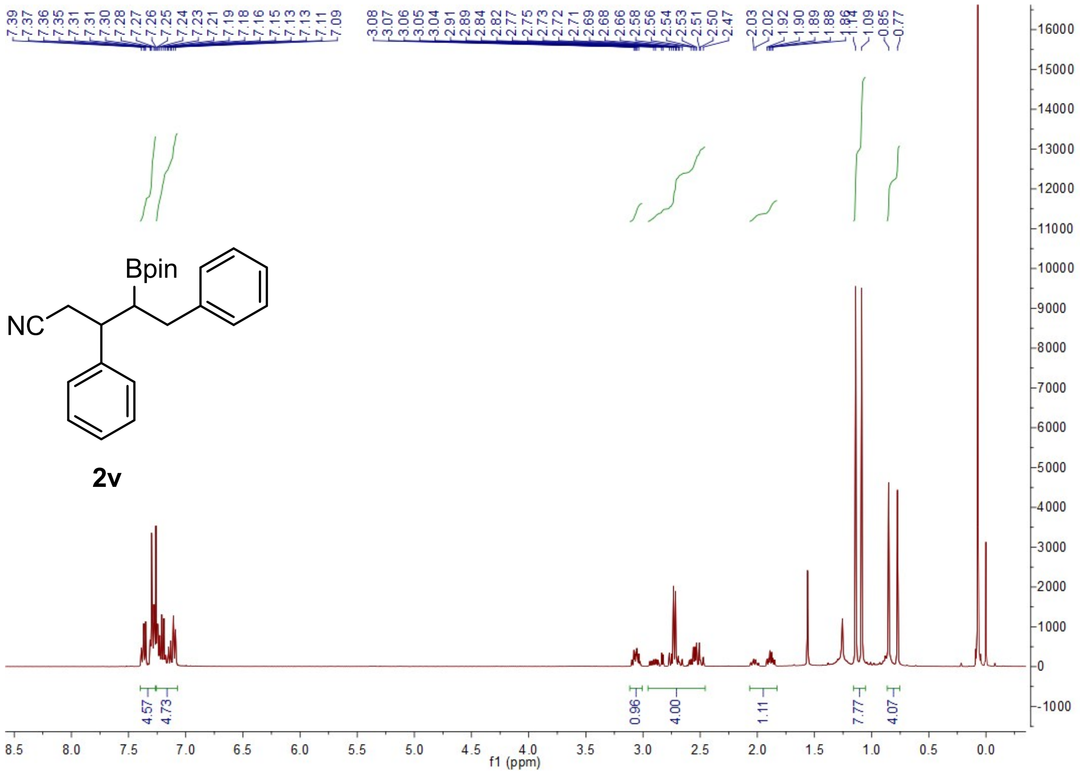
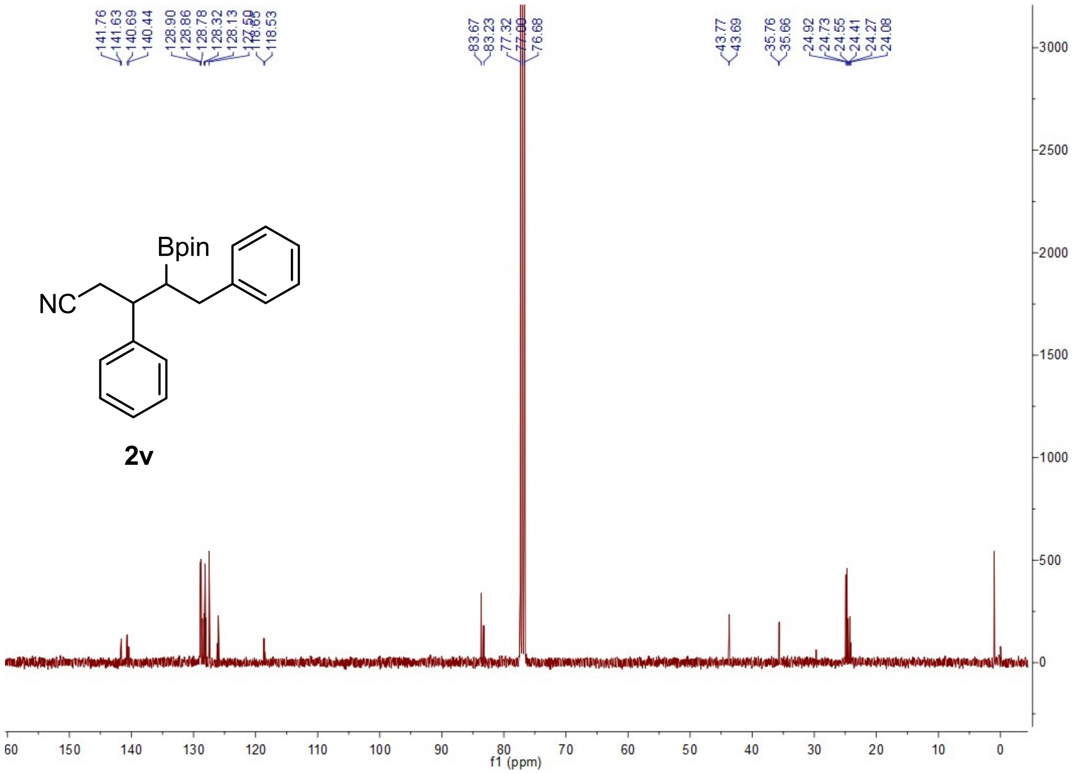
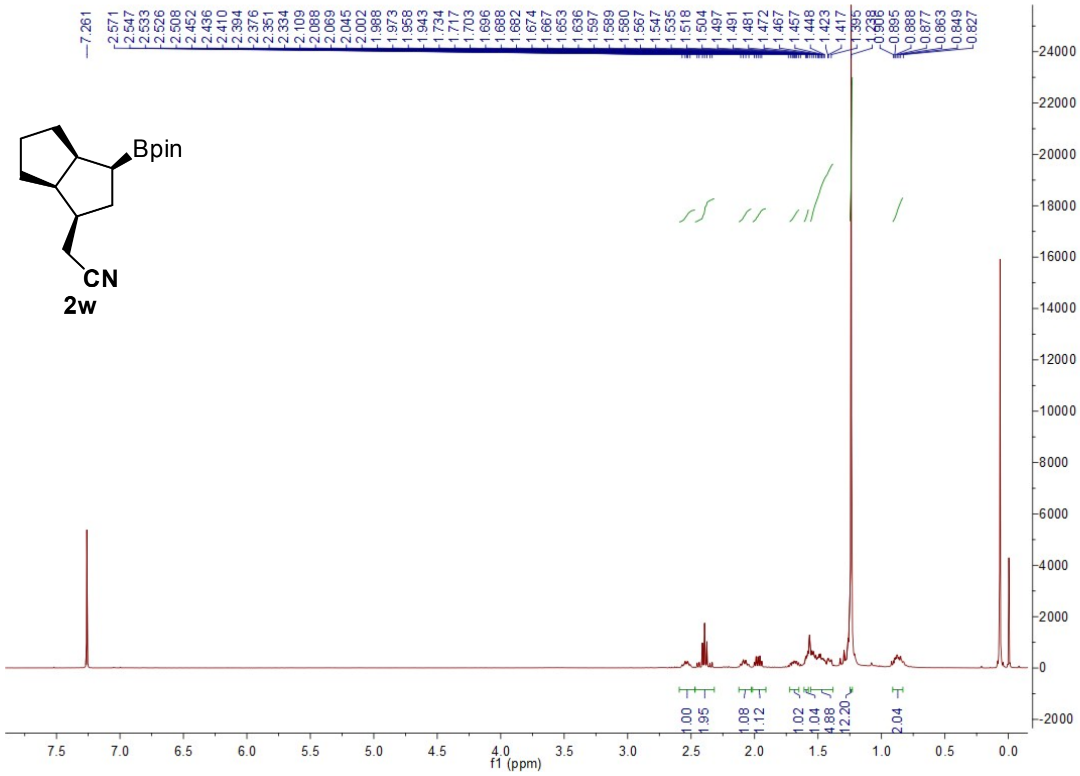
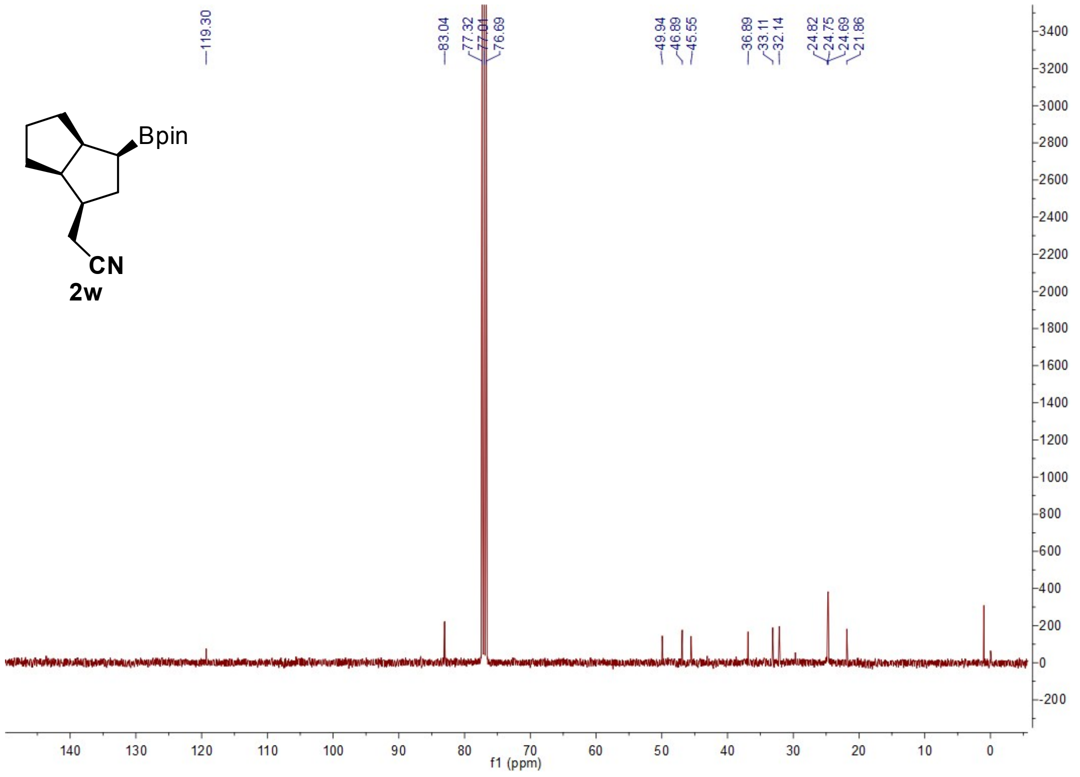
7.34
7.32
7.31
7.30
7.30
7.28
7.28
7.28
7.27
7.26
7.25
7.24
7.24
7.23
7.21
5.69
5.68
5.65
5.13
5.12
5.08
5.08
5.05
5.03
4.95
4.93
4.93
4.89
4.89
3.07
3.06
3.05
3.05
3.04
3.03
3.03
3.02
3.01
3.01
2.83
2.82
2.79
2.78
2.73
2.72
2.71
2.70
2.68
2.66
2.64
2.29
2.24
2.03
2.02
2.02
2.00
1.98
1.96
1.68
1.67
1.62
1.61
1.27
0.97
Bpin
NC
2u
3.11
1.94
1.08
2.12
1.11
2.14
1.01
1.37
0.52
0.47
7.50
4.51
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0


142.02
141.60
136.98
136.77
128.82
128.59
127.98
127.59
127.35
118.81
118.66
116.33
116.15
83.79
83.33
77.36
77.24
77.04
76.72
42.87
42.75
33.76
25.04
24.88
24.60
24.57
24.51
23.72
Bpin
NC
2u
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500

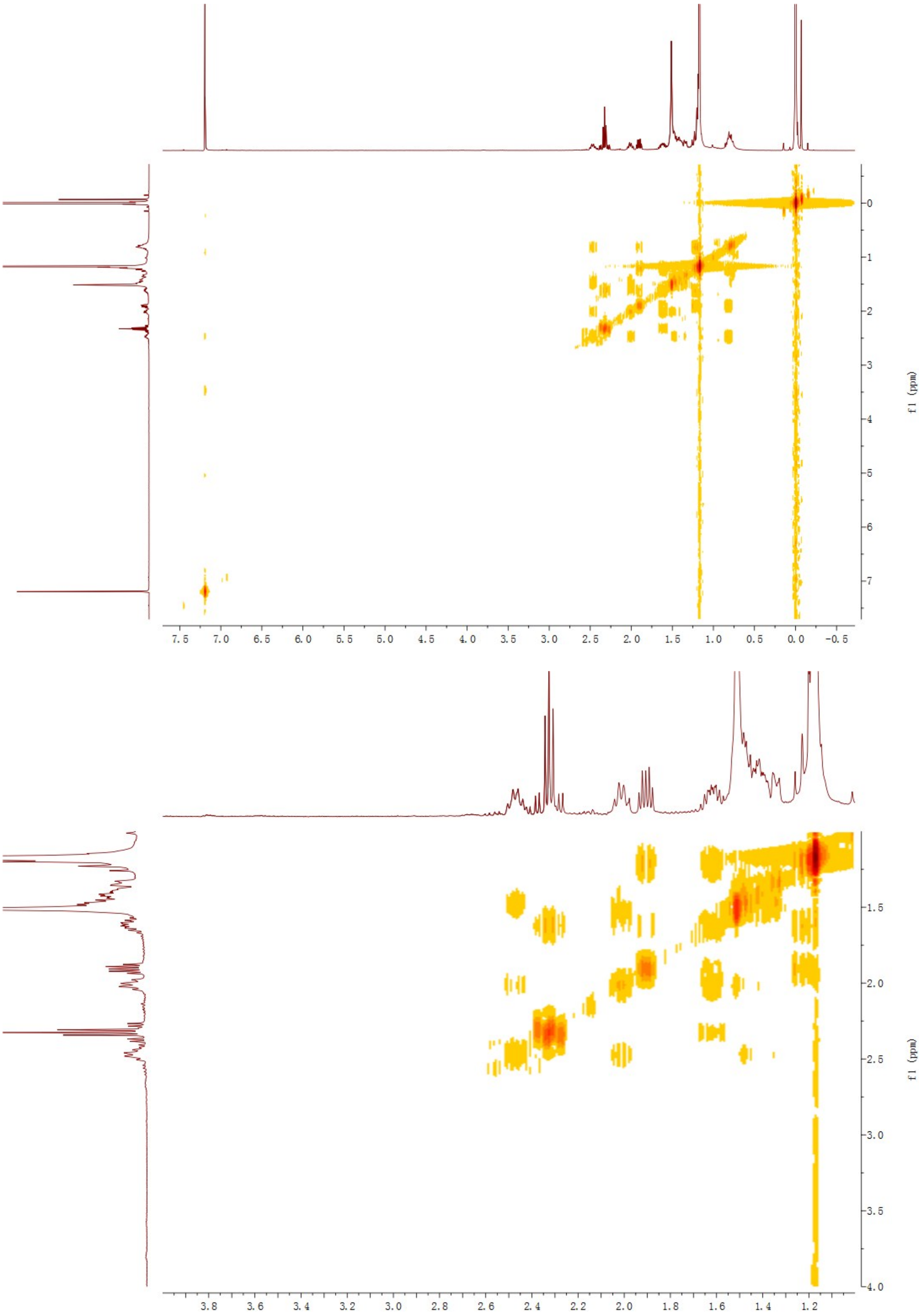

7.39
7.37
7.36
7.35
7.31
7.30
7.28
7.27
7.26
7.25
7.24
7.23
7.21
7.19
7.18
7.16
7.15
7.13
7.13
7.11
7.09
3.08
3.07
3.06
3.05
3.04
2.91
2.89
2.84
2.82
2.77
2.75
2.73
2.72
2.71
2.69
2.68
2.66
2.58
2.56
2.54
2.53
2.51
2.50
2.47
2.03
2.02
1.92
1.90
1.89
1.88
1.86
1.14
1.09
0.85
0.77
Bpin
NC
2v
4.57
4.73
0.96
4.00
1.11
7.77
4.07
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)
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000


141.76
141.63
140.69
140.44
128.90
128.86
128.78
128.32
128.13
127.50
125.85
118.53
83.67
83.23
77.32
77.00
76.68
43.77
43.69
35.76
35.66
24.92
24.73
24.55
24.41
24.27
24.08
Bpin
NC
2v
60
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
3000
2500
2000
1500
1000
500
0


7.261
2.571
2.547
2.533
2.526
2.508
2.452
2.436
2.410
2.394
2.376
2.351
2.334
2.109
2.088
2.069
2.045
2.002
1.988
1.973
1.958
1.943
1.734
1.717
1.703
1.696
1.688
1.682
1.674
1.667
1.653
1.636
1.597
1.589
1.580
1.567
1.547
1.535
1.518
1.504
1.497
1.491
1.481
1.472
1.467
1.457
1.448
1.423
1.417
1.395
1.238
0.906
0.895
0.888
0.877
0.863
0.849
0.827
Bpin
CN
2w
1.00
1.95
1.08
1.12
1.02
1.04
4.88
12.20
2.04
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)
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000

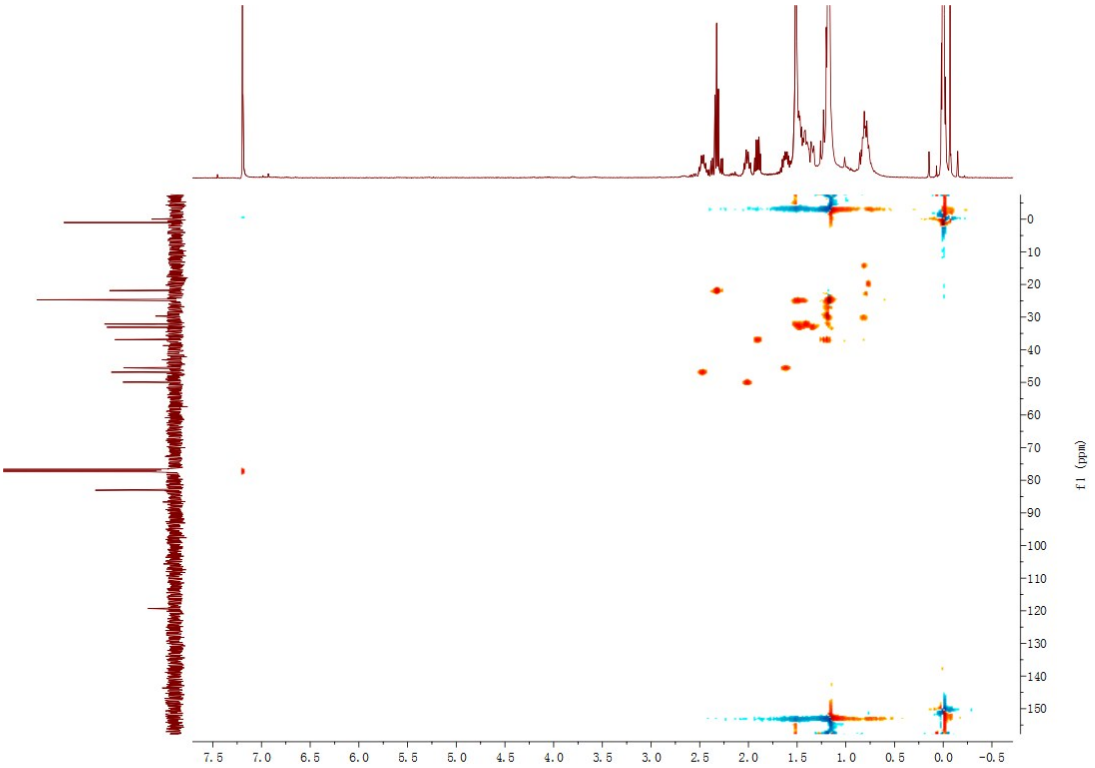

119.30
83.04
77.32
77.01
76.69
49.94
46.89
45.55
36.89
33.11
32.14
24.82
24.75
24.69
21.86
Bpin
CN
2w
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200

H-H COSY of **2w**

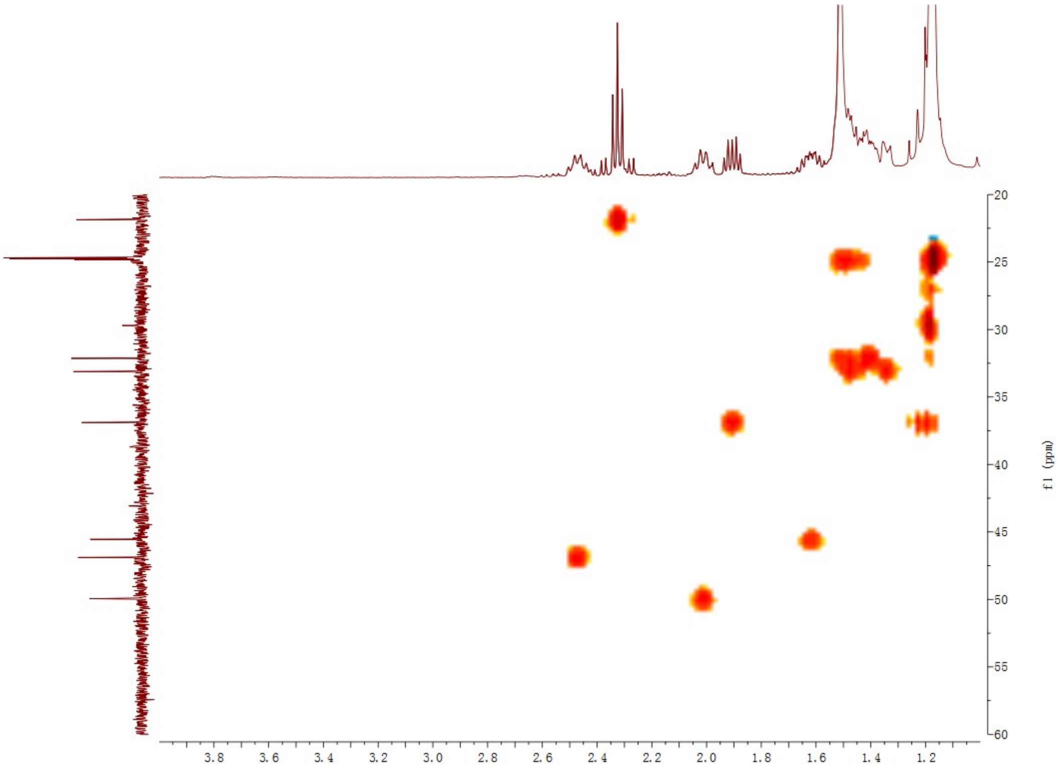


7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.5
2.0
2.5
3.0
3.5
4.0
f1 (ppm)

HSQC of **2w**

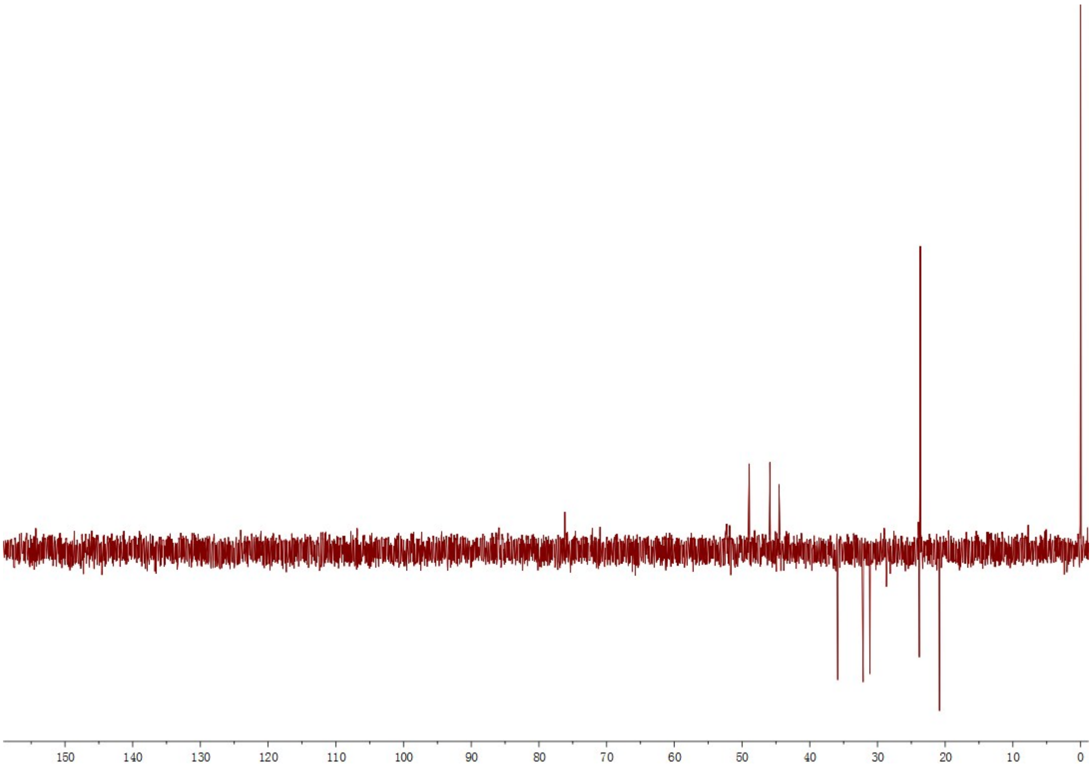


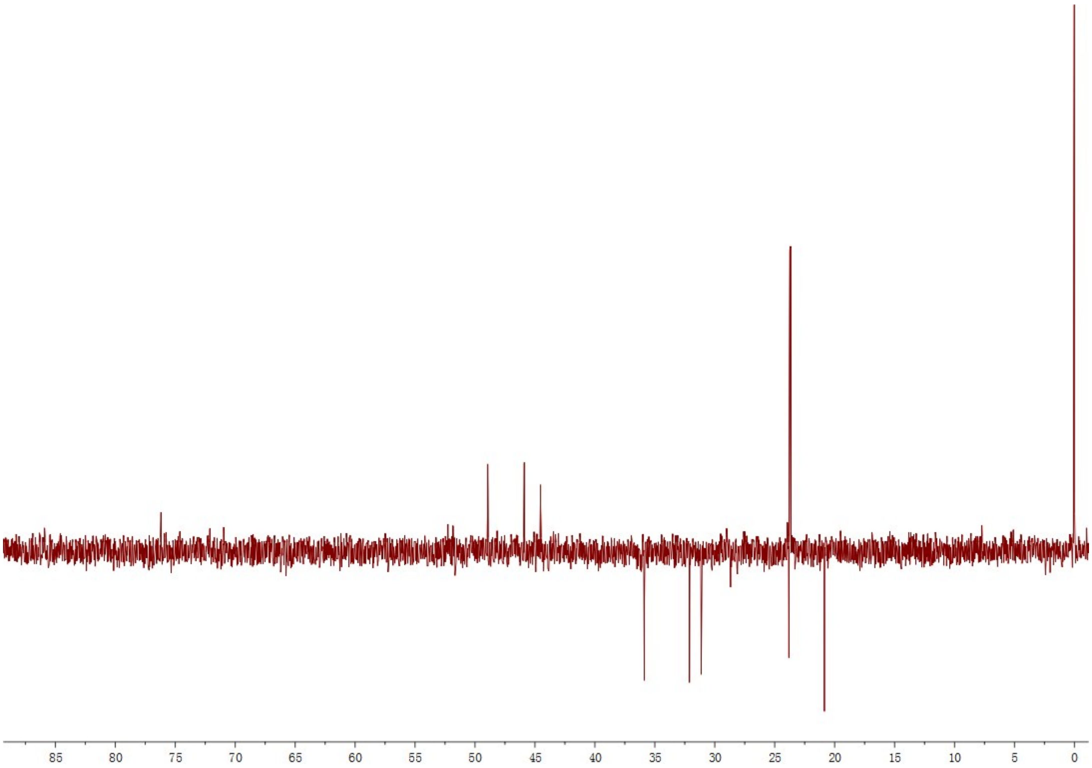
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

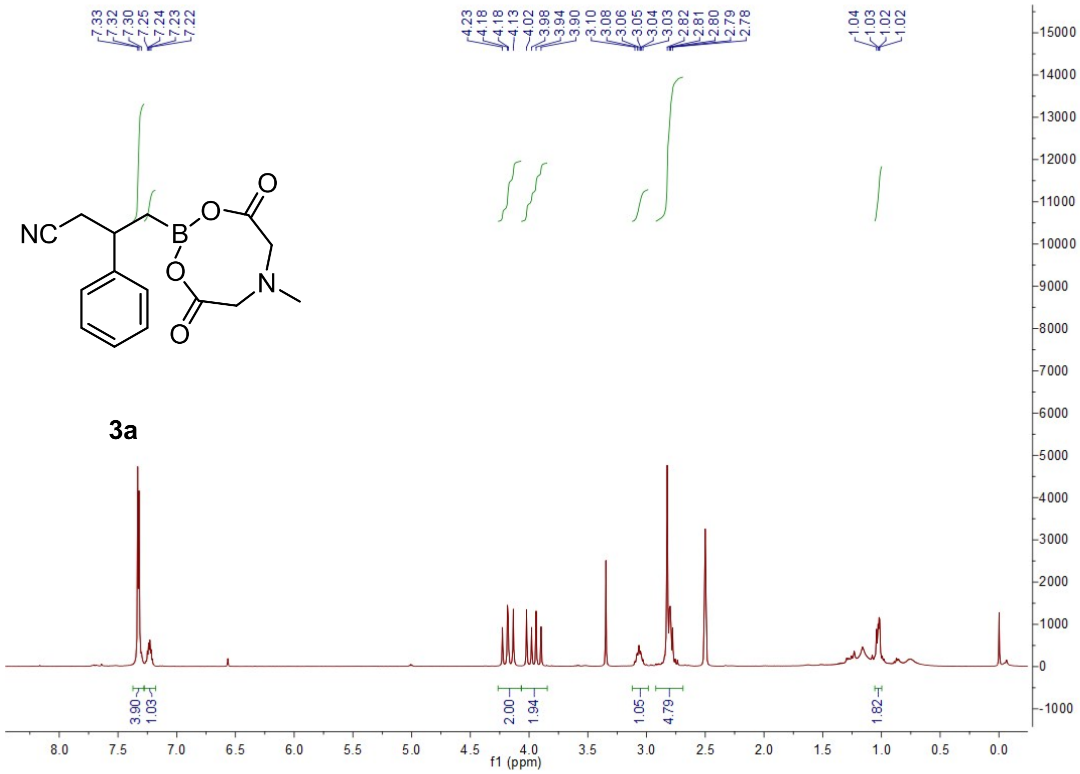


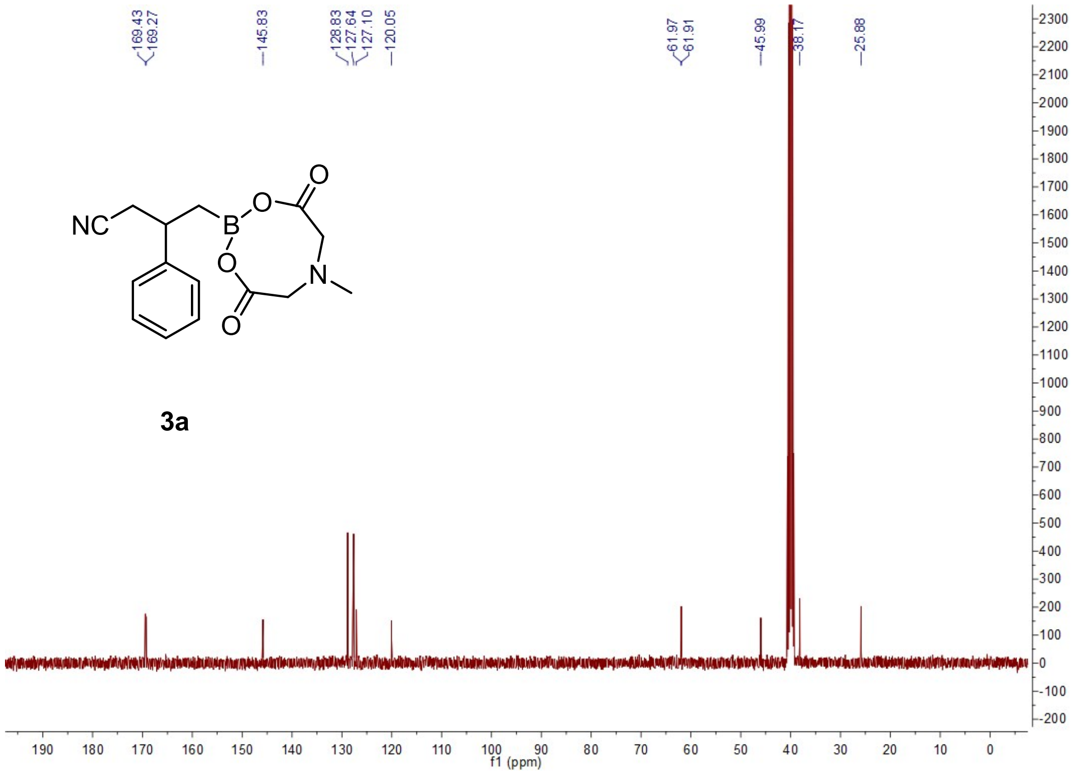
20
25
30
35
40
45
50
55
60
f1 (ppm)
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2

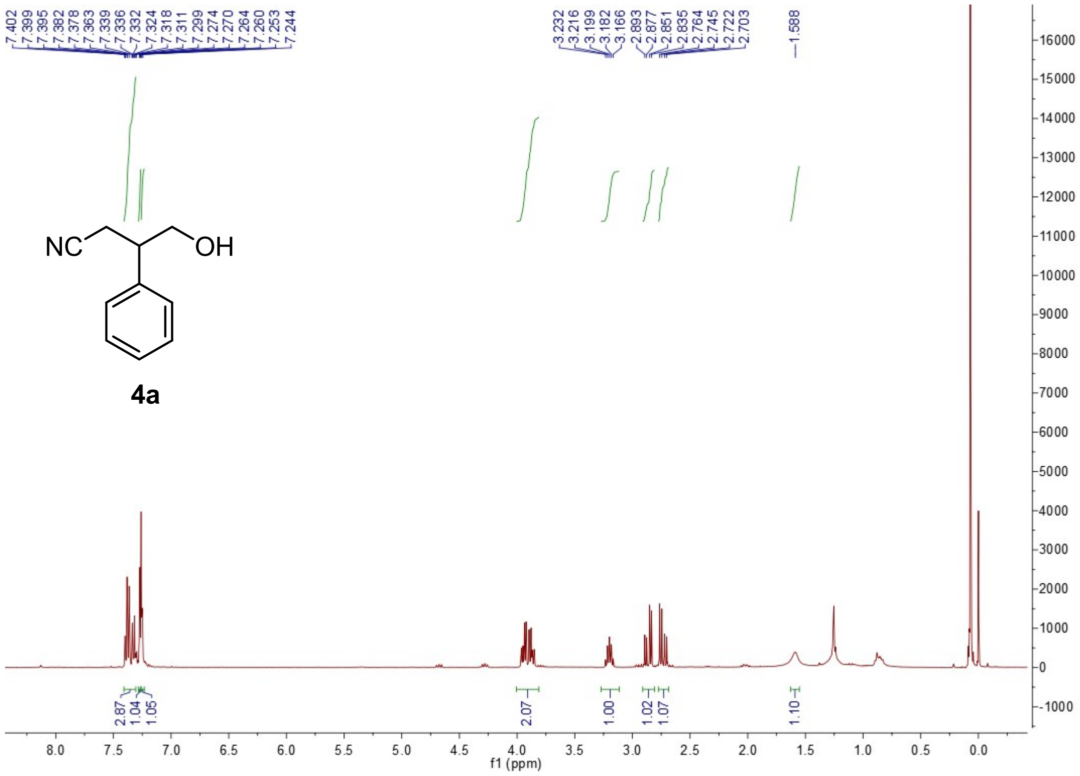
DEPT 135 of **2w**



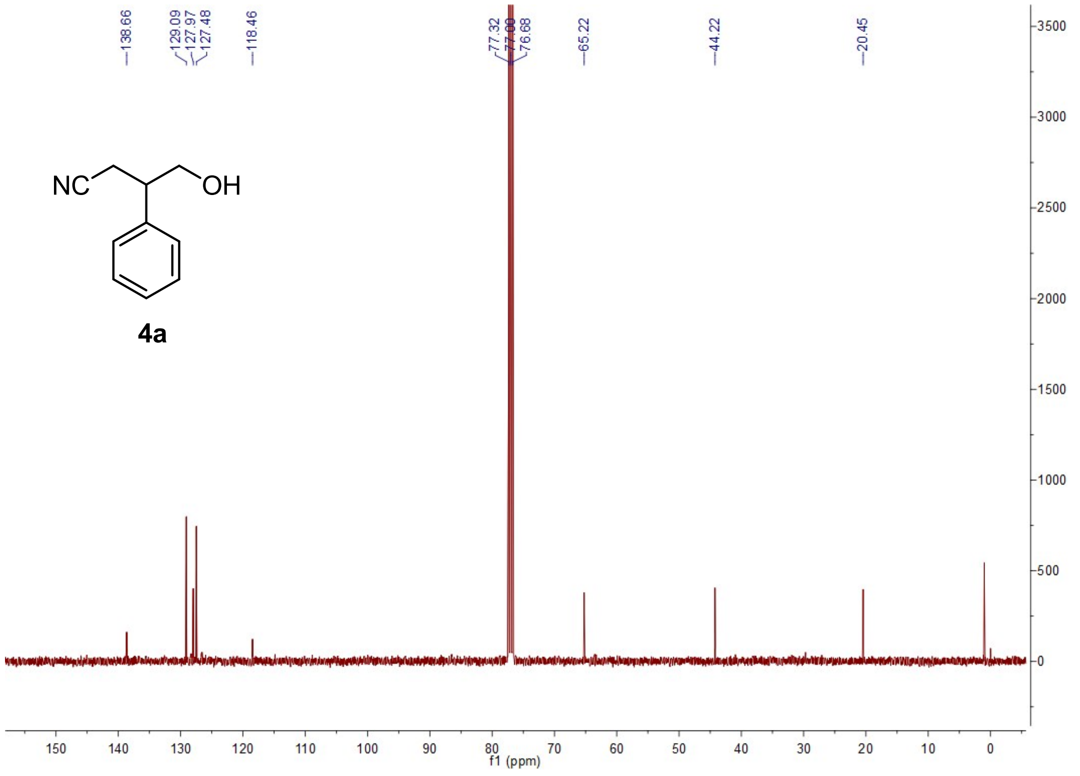



7.33
7.32
7.30
7.25
7.24
7.23
7.22
4.23
4.18
4.18
4.13
4.02
3.98
3.94
3.90
3.10
3.08
3.06
3.05
3.04
3.03
2.82
2.81
2.80
2.79
2.78
1.04
1.03
1.02
1.02
NC
B
O
O
O
O
N
3a
3.90
1.03
2.00
1.94
1.05
4.79
1.82
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000

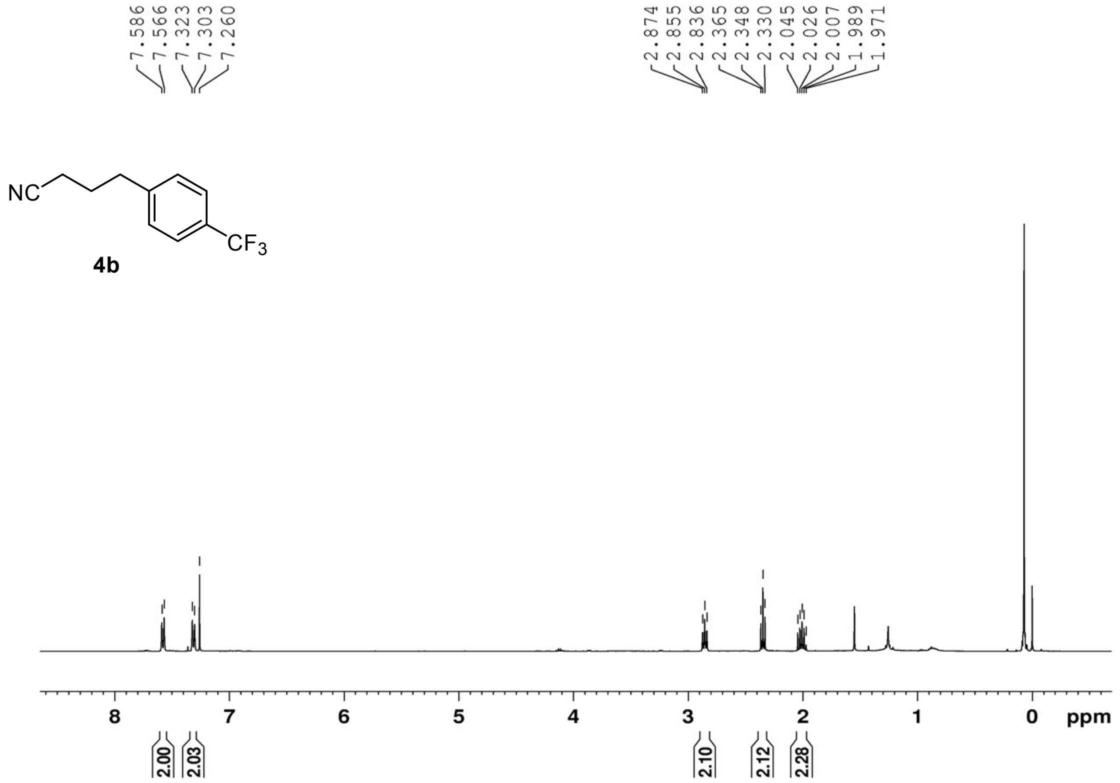

169.43
169.27
145.83
128.83
127.64
127.10
120.05
61.97
61.91
45.99
38.17
25.88
NC
B
O
O
O
O
N
3a
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200

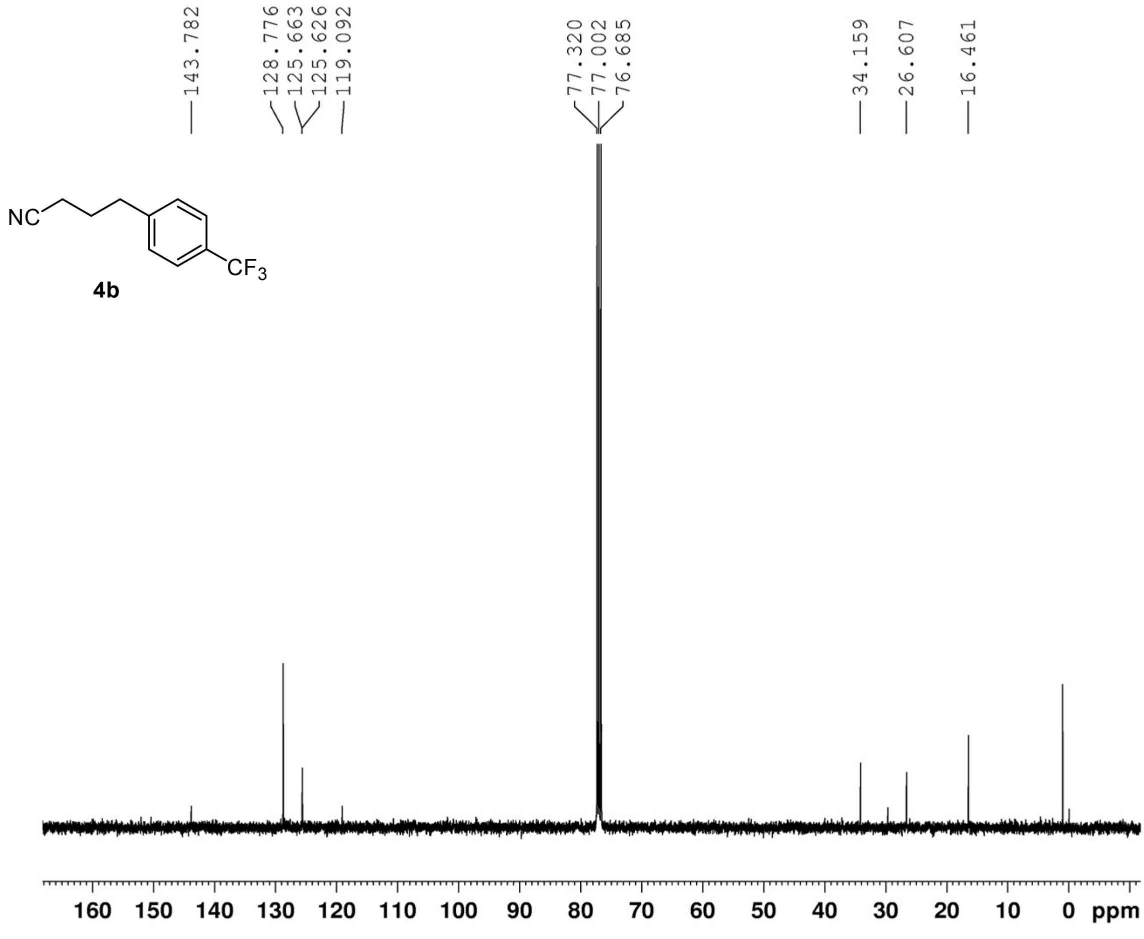

7.402
7.399
7.395
7.382
7.378
7.363
7.339
7.336
7.332
7.324
7.318
7.311
7.299
7.274
7.270
7.264
7.260
7.253
7.244
3.232
3.216
3.199
3.182
3.166
2.893
2.877
2.851
2.835
2.764
2.745
2.722
2.703
1.588
NC
OH
2.87
1.04
1.05
2.07
1.00
1.02
1.07
1.10
f1 (ppm)

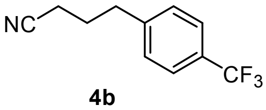
4a


138.66
129.09
127.97
127.48
118.46
77.32
77.00
76.68
65.22
44.22
20.45
NC
OH
f1 (ppm)

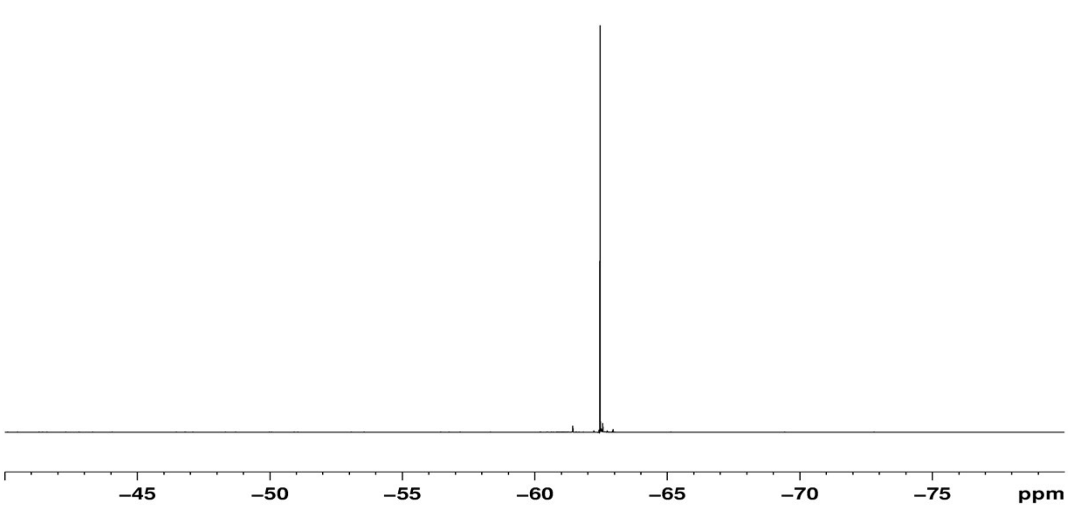
4a

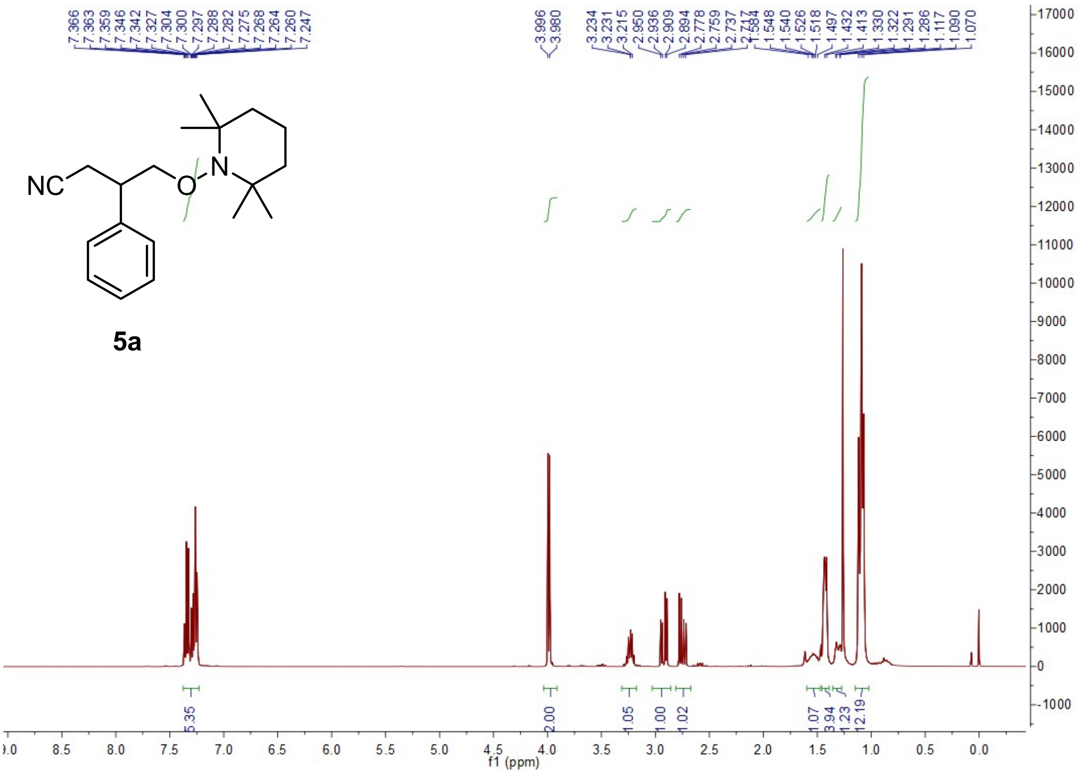

7.586
7.566
7.323
7.303
7.260
2.874
2.855
2.836
2.365
2.348
2.330
2.045
2.026
2.007
1.989
1.971
NC
CF3
4b
8
7
6
5
4
3
2
1
0
ppm
2.00
2.03
2.10
2.12
2.28

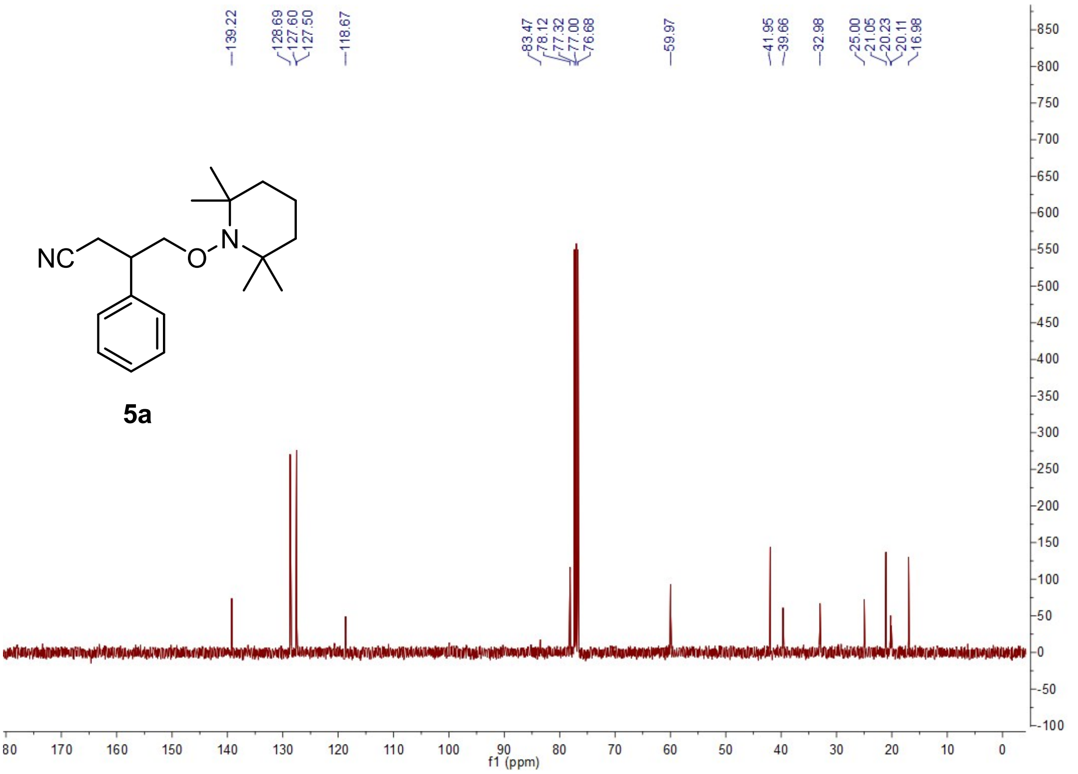

143.782
128.776
125.663
125.626
119.092
77.320
77.002
76.685
34.159
26.607
16.461
NC
CF3
4b
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

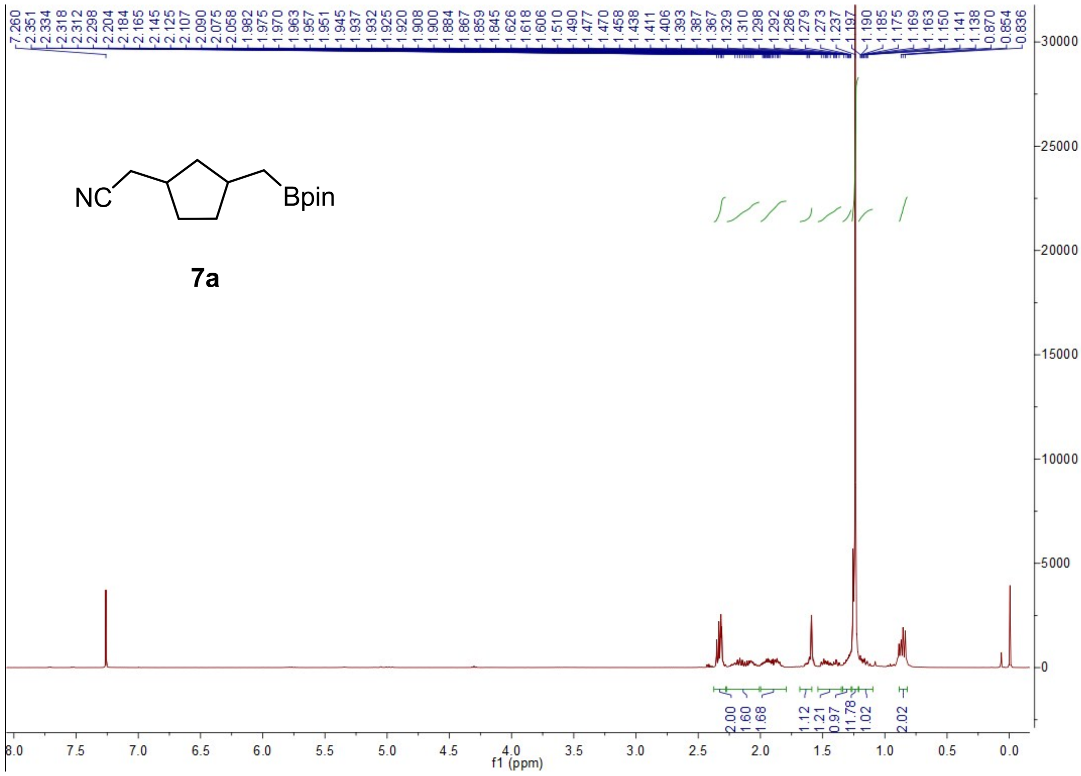


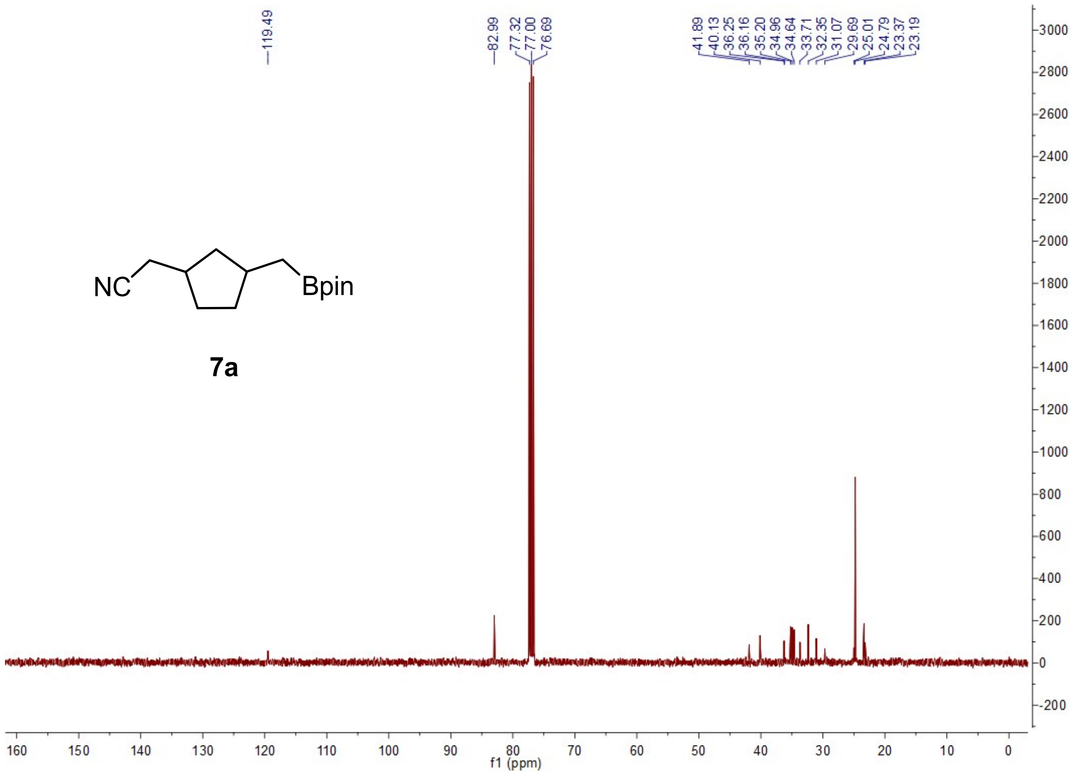
4b

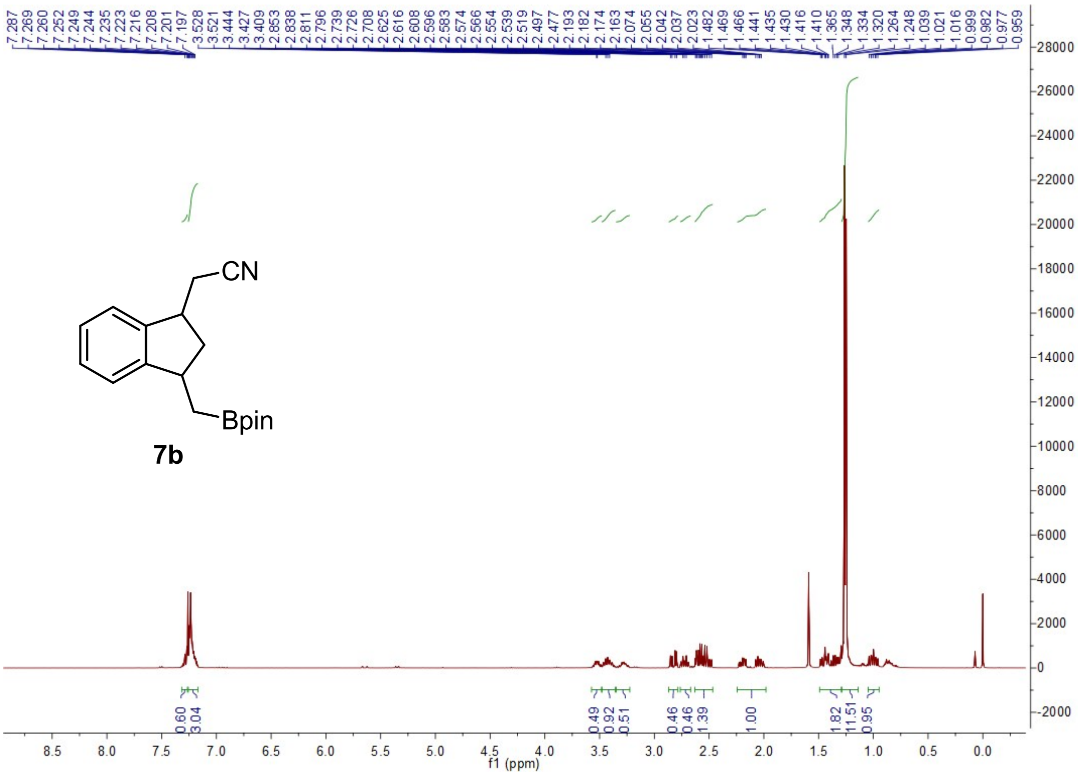


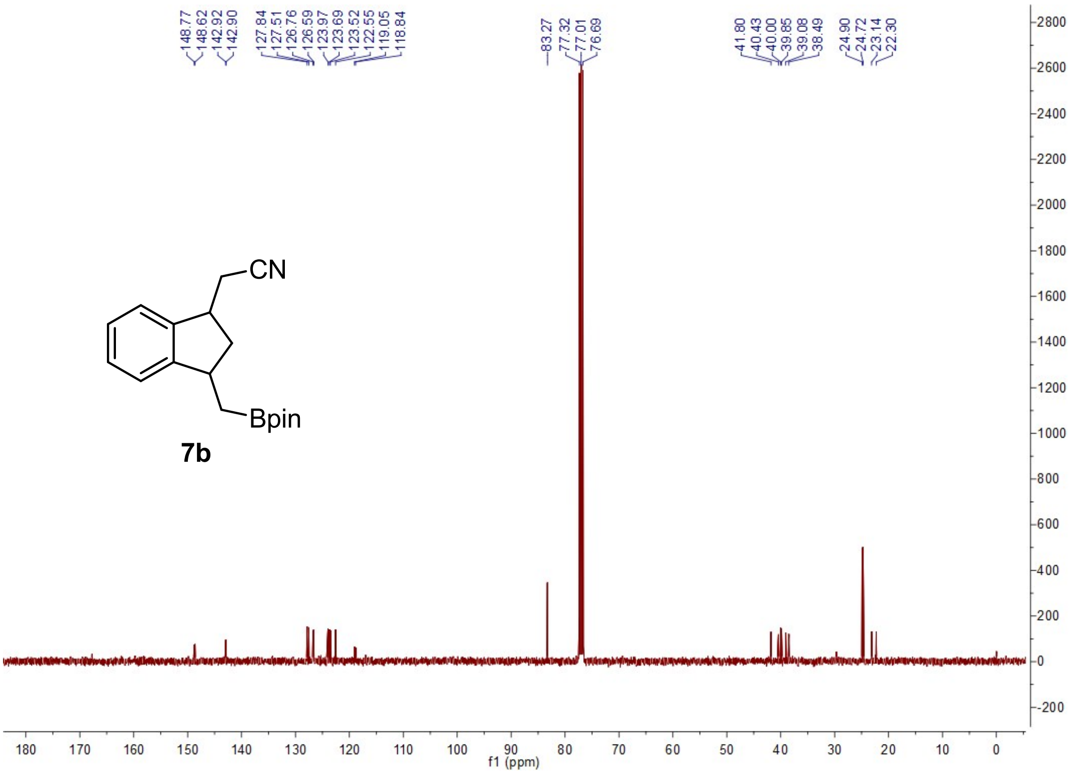

7.366
7.363
7.359
7.346
7.342
7.327
7.304
7.300
7.297
7.288
7.282
7.275
7.268
7.264
7.260
7.247
3.996
3.980
3.234
3.231
3.215
2.950
2.936
2.909
2.894
2.778
2.759
2.737
2.717
1.584
1.548
1.540
1.526
1.518
1.497
1.432
1.413
1.330
1.322
1.291
1.286
1.117
1.090
1.070
NC
O
N
5a
5.35
2.00
1.05
1.00
1.02
1.07
3.94
1.23
12.19
f1 (ppm)
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
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

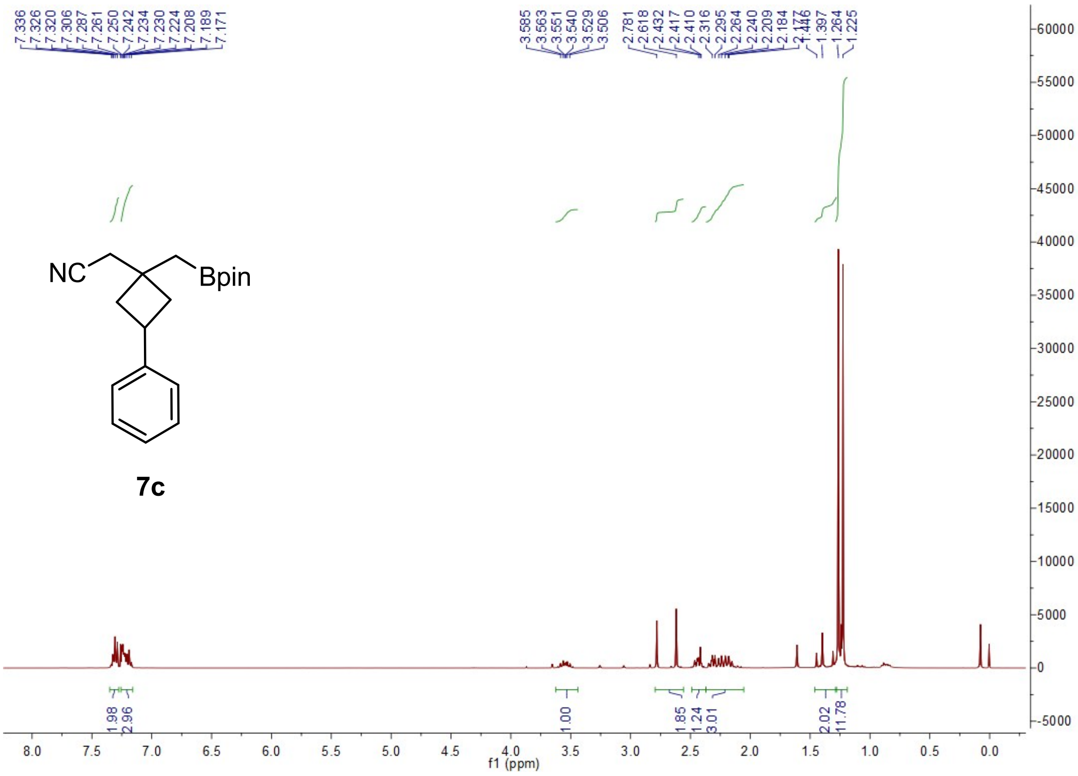

139.22
128.69
127.60
127.50
118.67
83.47
78.12
77.32
77.00
76.68
59.97
41.95
39.66
32.98
25.00
21.05
20.23
20.11
16.98
NC
O
N
5a
f1 (ppm)
850
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
-100
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

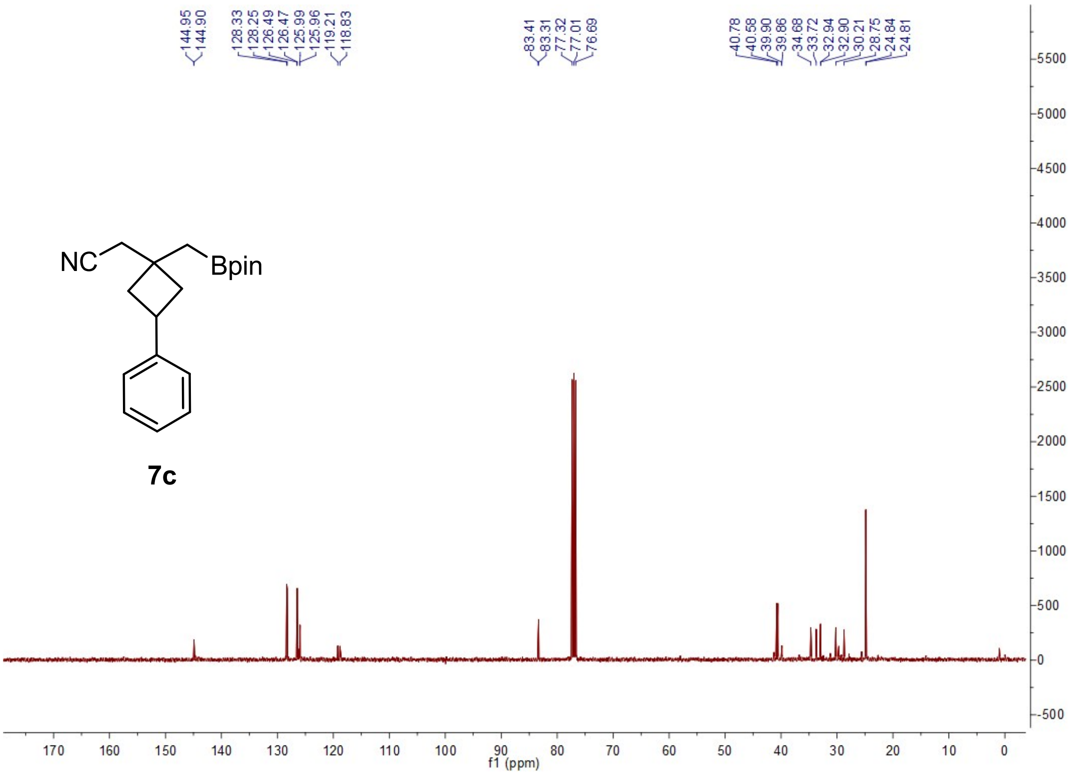

7.260
2.351
2.334
2.318
2.312
2.298
2.204
2.184
2.165
2.145
2.125
2.107
2.090
2.075
2.058
1.982
1.975
1.970
1.963
1.957
1.951
1.945
1.937
1.932
1.925
1.920
1.908
1.900
1.884
1.867
1.859
1.845
1.626
1.618
1.606
1.510
1.490
1.477
1.470
1.458
1.438
1.411
1.406
1.393
1.387
1.367
1.329
1.310
1.298
1.292
1.286
1.279
1.273
1.237
1.197
1.190
1.185
1.175
1.169
1.163
1.150
1.141
1.138
0.870
0.854
0.836
NC
Bpin
7a
2.00
1.60
1.68
1.12
1.21
0.97
11.78
1.02
2.02
30000
25000
20000
15000
10000
5000
0
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)

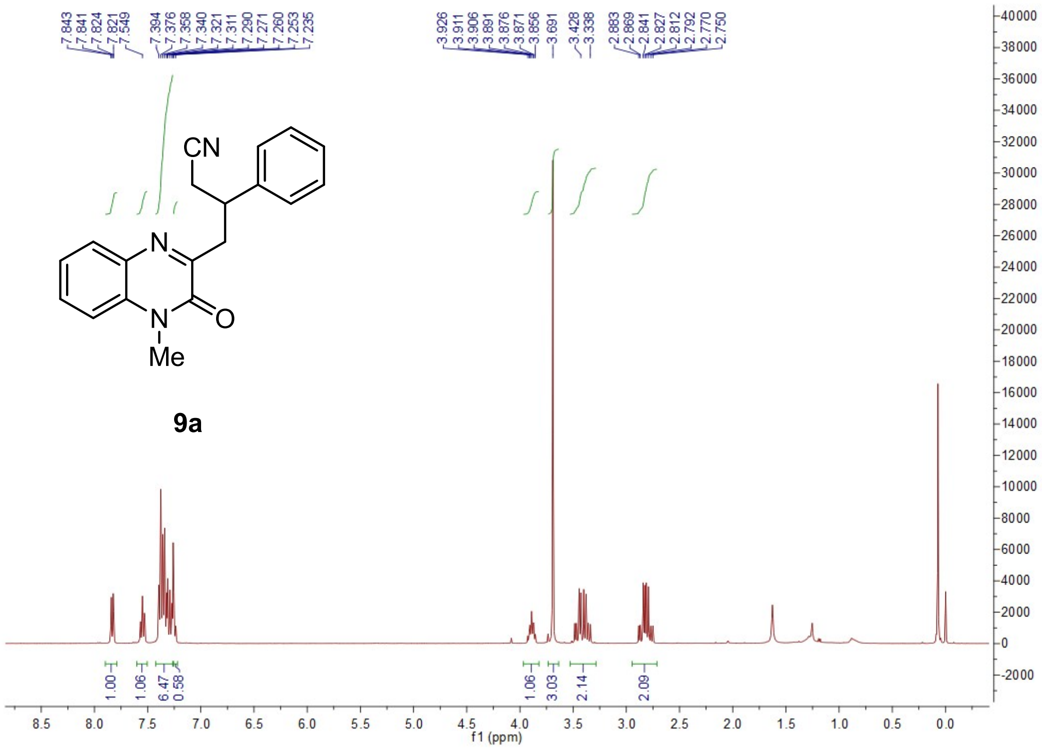

119.49
82.99
77.32
77.00
76.69
41.89
40.13
36.25
36.16
35.20
34.96
34.64
33.71
32.35
31.07
29.69
25.01
24.79
23.37
23.19
NC
Bpin
7a
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

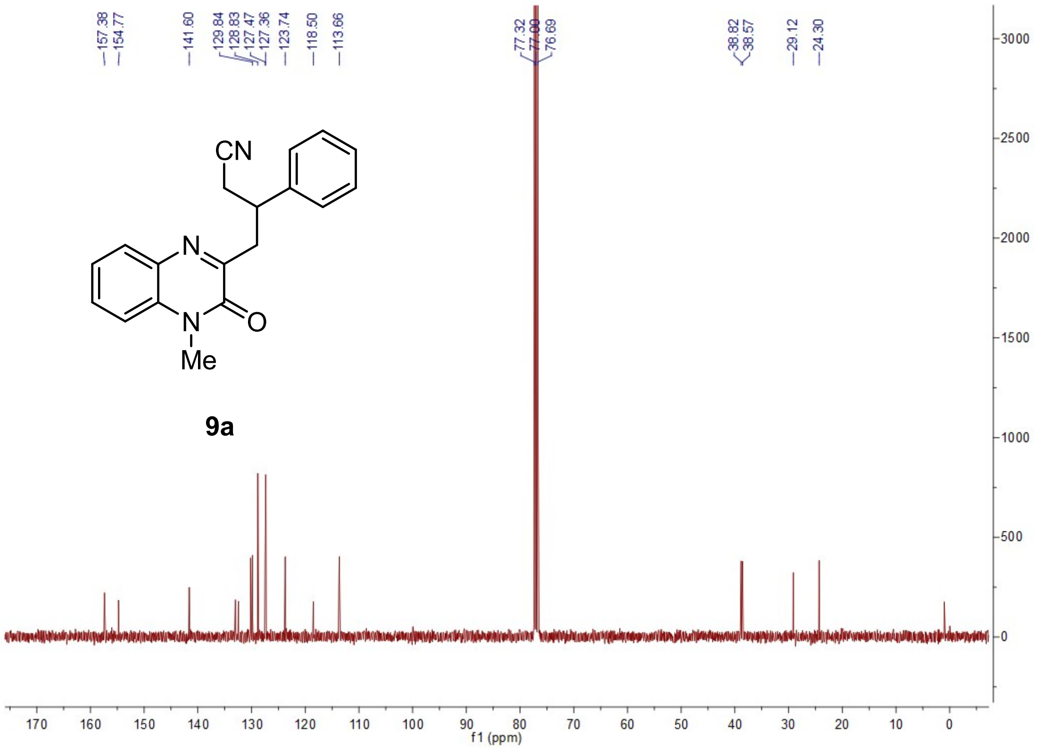

7.287
7.269
7.260
7.252
7.249
7.244
7.235
7.223
7.216
7.208
7.201
7.197
3.528
3.521
3.444
3.427
3.409
2.853
2.838
2.811
2.796
2.739
2.726
2.708
2.625
2.616
2.608
2.596
2.583
2.574
2.566
2.554
2.539
2.519
2.497
2.477
2.193
2.182
2.174
2.163
2.074
2.055
2.042
2.037
2.023
1.482
1.469
1.466
1.441
1.435
1.430
1.416
1.410
1.365
1.348
1.334
1.320
1.264
1.248
1.039
1.021
1.016
0.999
0.982
0.977
0.959
CN
Bpin
7b
0.60
3.04
0.49
0.92
0.51
0.46
0.46
1.39
1.00
1.82
11.51
0.95
f1 (ppm)

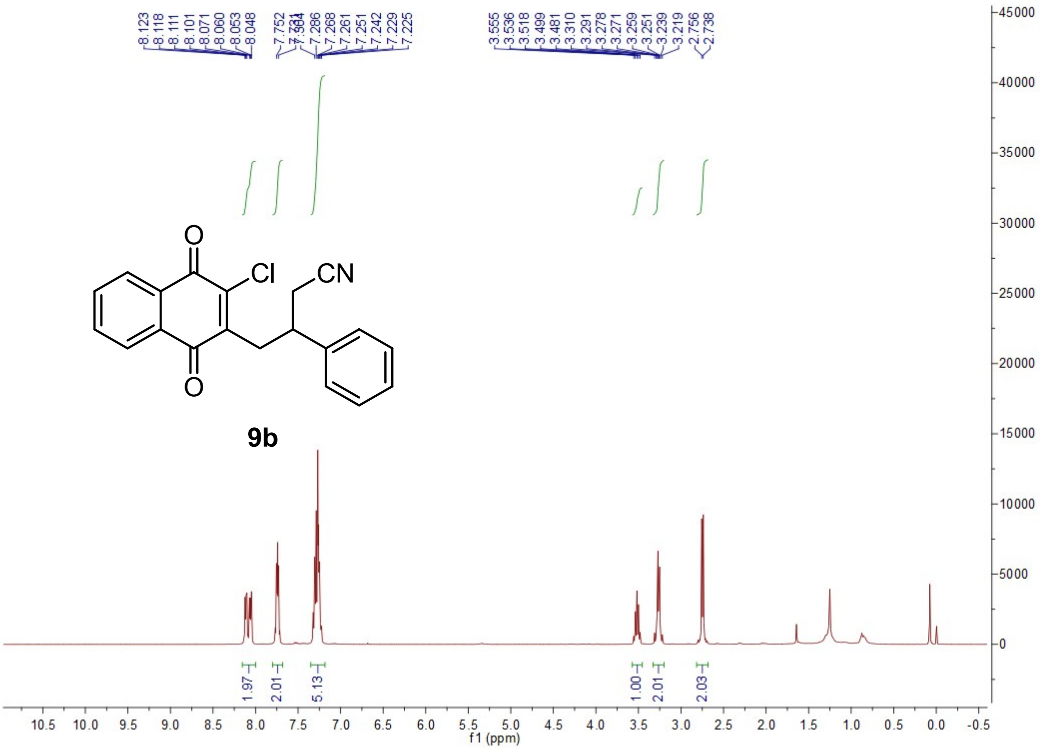

148.77
148.62
142.92
142.90
127.84
127.51
126.76
126.59
123.97
123.69
123.52
122.55
119.05
118.84
83.27
77.32
77.01
76.69
41.80
40.43
40.00
39.85
39.08
38.49
24.90
24.72
23.14
22.30
CN
Bpin
7b
f1 (ppm)


7.336
7.326
7.320
7.306
7.287
7.261
7.250
7.242
7.234
7.230
7.224
7.208
7.189
7.171
3.585
3.563
3.551
3.540
3.529
3.506
2.781
2.618
2.432
2.417
2.410
2.316
2.295
2.264
2.240
2.209
2.184
2.177
1.446
1.397
1.264
1.225
NC
Bpin
7c
1.98
2.96
1.00
1.85
1.24
3.01
2.02
11.78
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)
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000


144.95
144.90
128.33
128.25
126.49
126.47
125.99
125.96
119.21
118.83
83.41
83.31
77.32
77.01
76.69
40.78
40.58
39.90
39.86
34.68
33.72
32.94
32.90
30.21
28.75
24.84
24.81
NC
Bpin
7c
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500

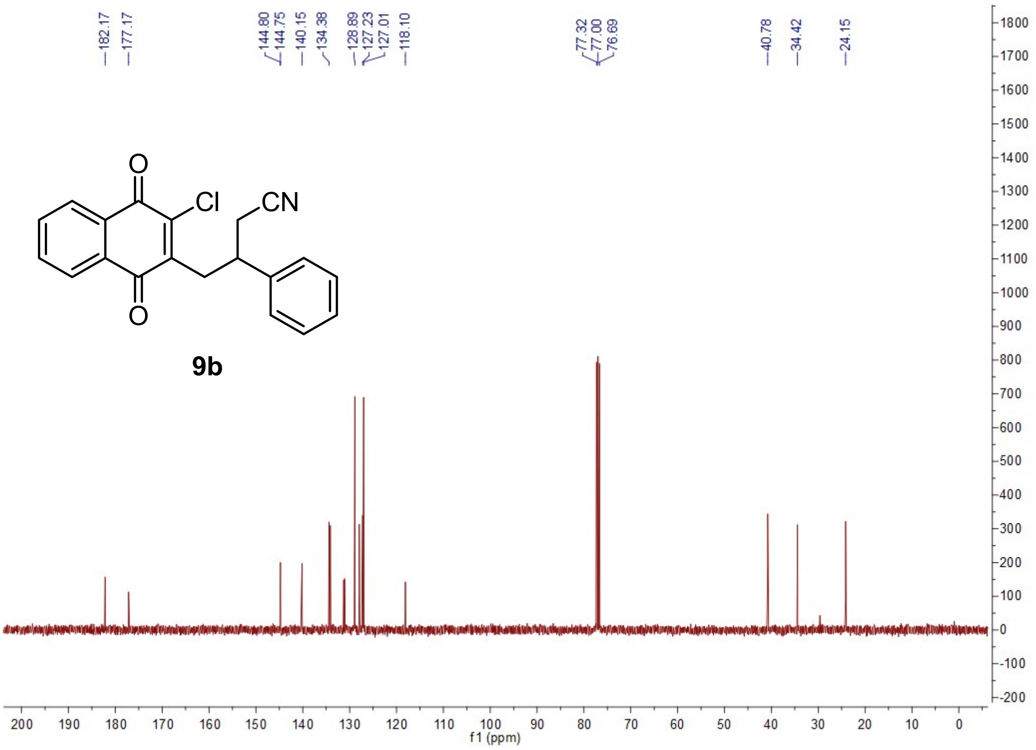

7.843
7.841
7.824
7.821
7.549
7.394
7.376
7.358
7.340
7.321
7.311
7.290
7.271
7.260
7.253
7.235
3.926
3.911
3.906
3.891
3.876
3.871
3.856
3.691
3.428
3.338
2.883
2.869
2.841
2.827
2.812
2.792
2.770
2.750
CN
N
N
O
Me
9a
1.00
1.06
6.47
0.58
1.06
3.03
2.14
2.09
f1 (ppm)


157.38
154.77
141.60
129.84
128.83
127.47
127.36
123.74
118.50
113.66
77.32
77.00
76.69
38.82
38.57
29.12
24.30
CN
N
N
O
Me
9a
f1 (ppm)



9b

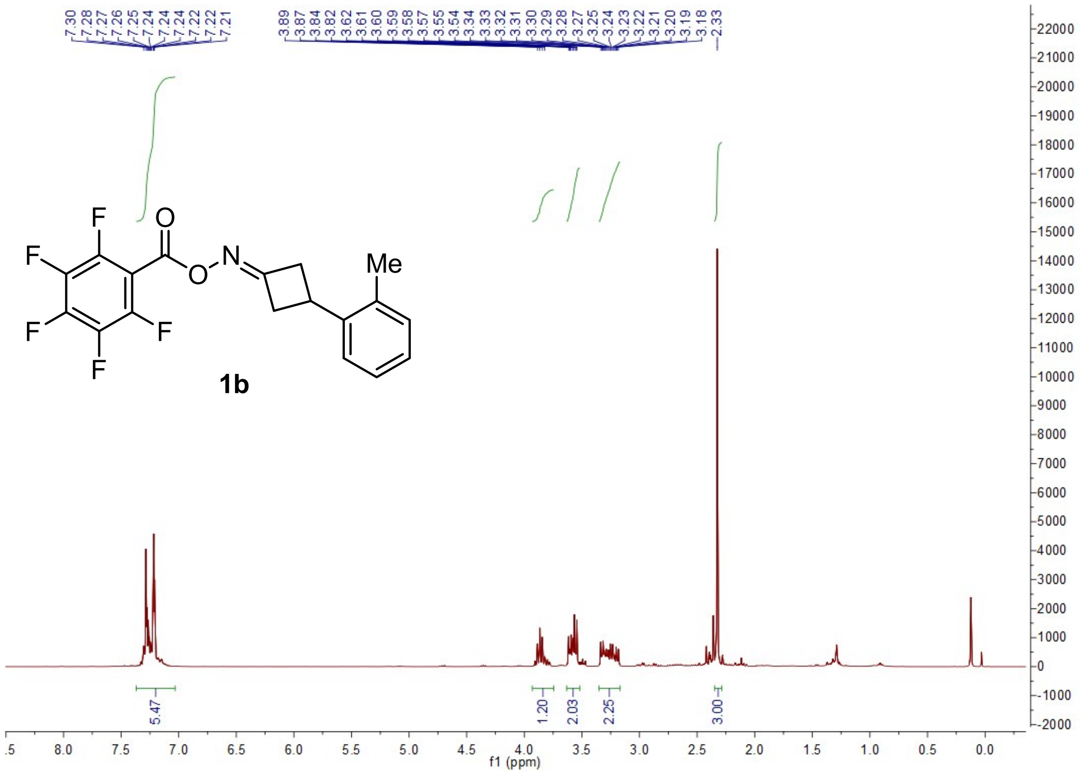
8.123
8.118
8.111
8.101
8.071
8.060
8.053
8.048
7.752
7.286
7.268
7.261
7.251
7.242
7.229
7.225
3.555
3.536
3.518
3.499
3.481
3.310
3.291
3.278
3.271
3.259
3.251
3.239
3.219
2.756
2.738
1.97
2.01
5.13
1.00
2.01
2.03
Cl
CN
O
f1 (ppm)

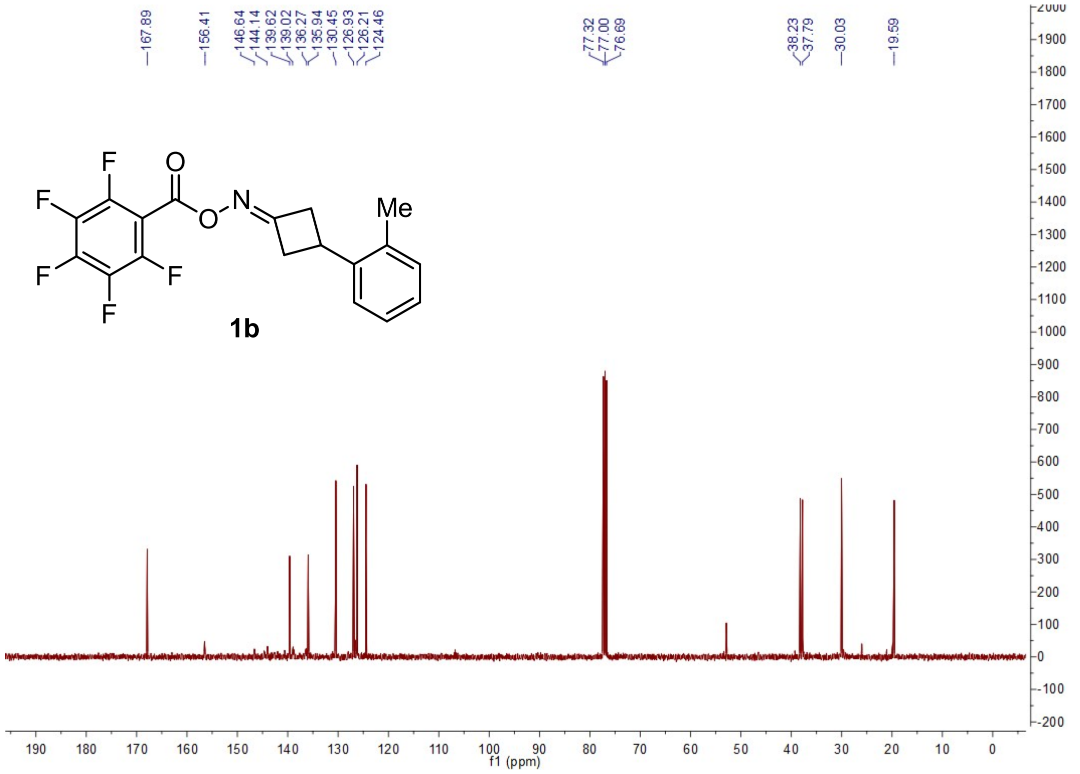


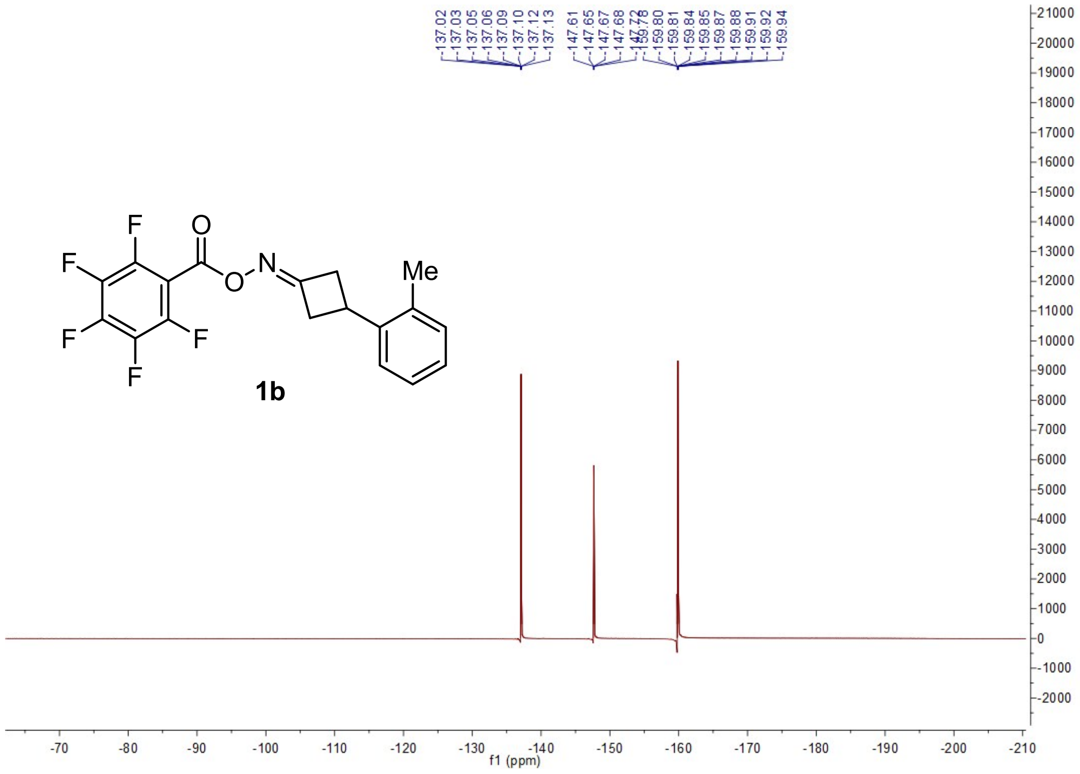
9b

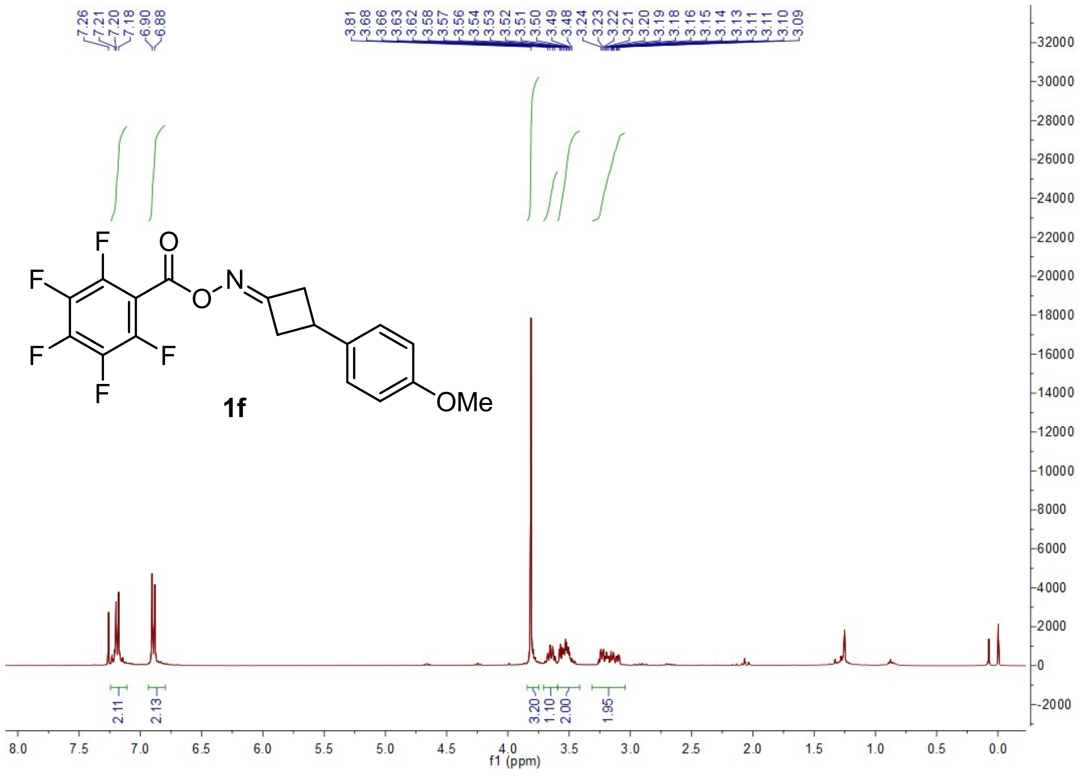
182.17
177.17
144.80
144.75
140.15
134.38
128.89
127.23
127.01
118.10
77.32
77.00
76.69
40.78
34.42
24.15
Cl
CN
O
f1 (ppm)

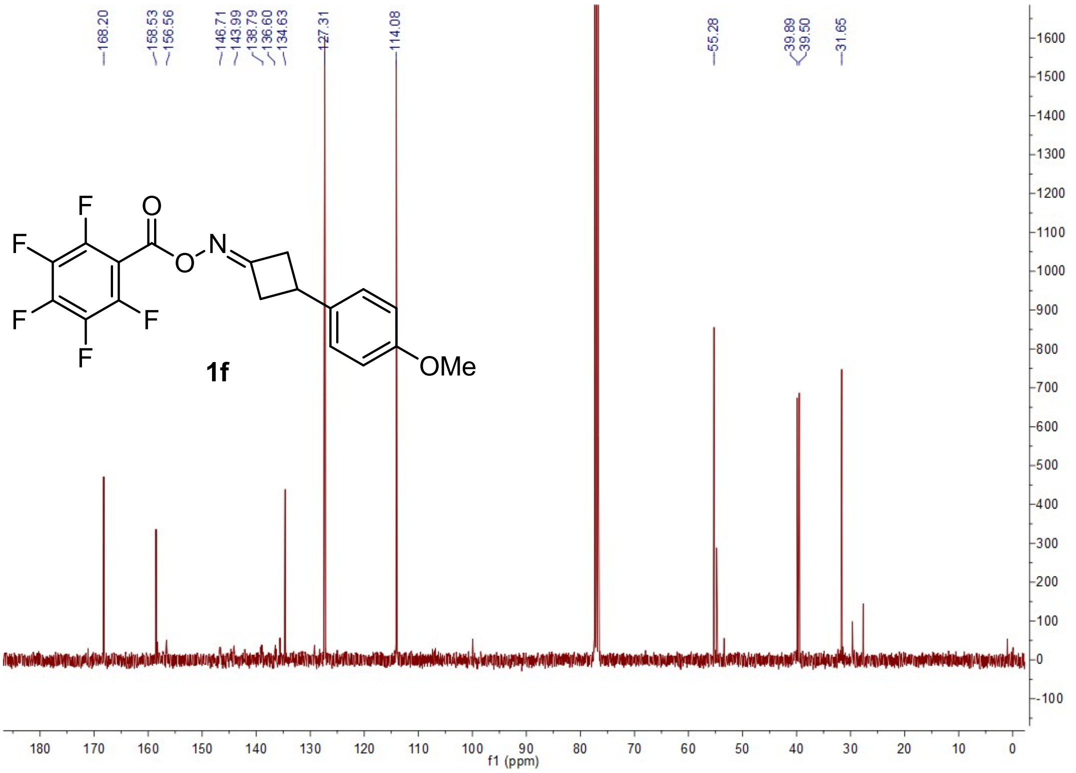
^{1}H NMR , ^{13}C NMR and ^{19}F Spectra of the Substrates

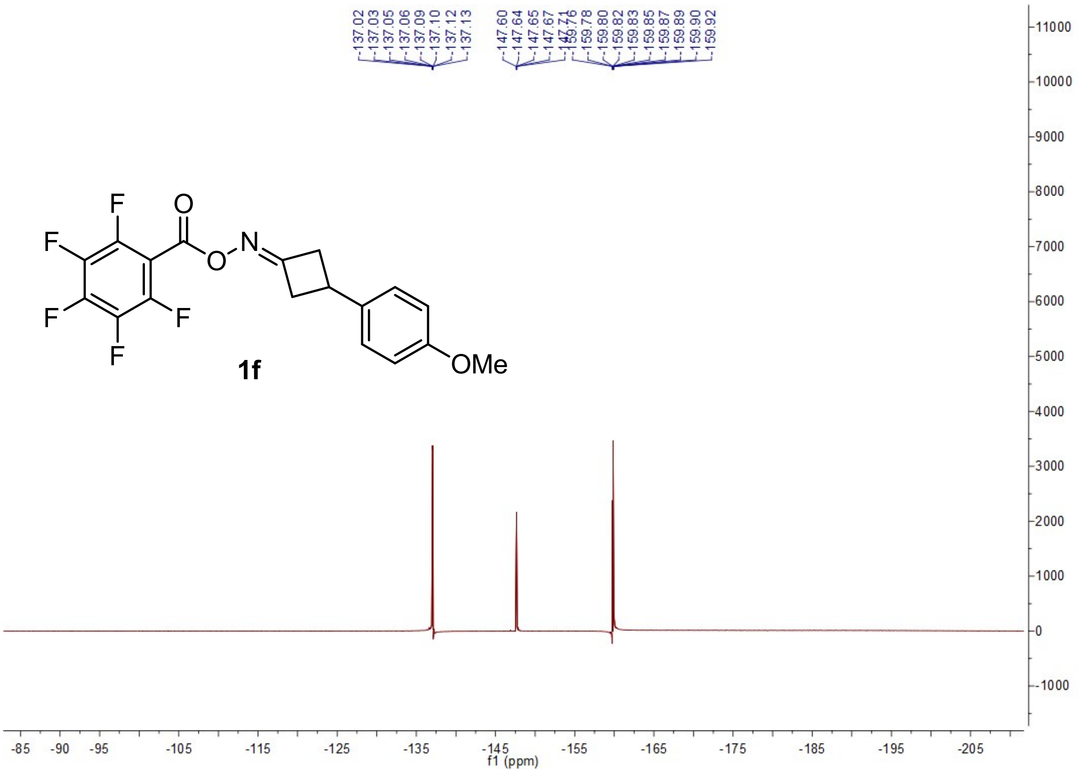


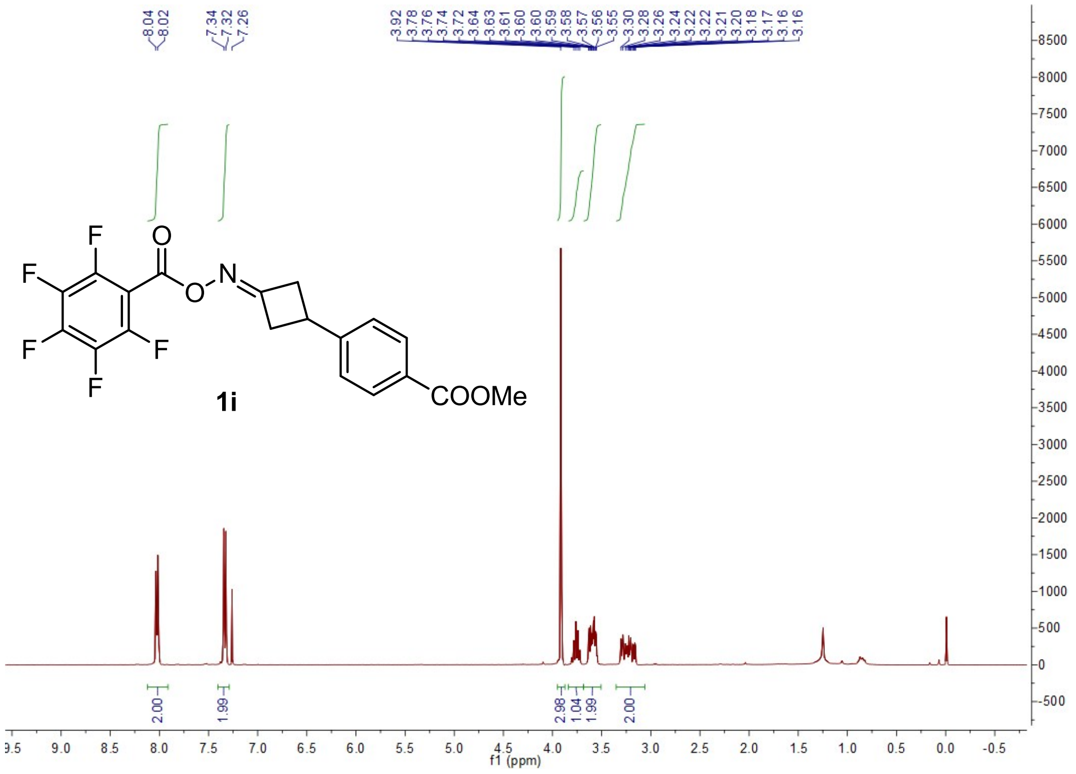


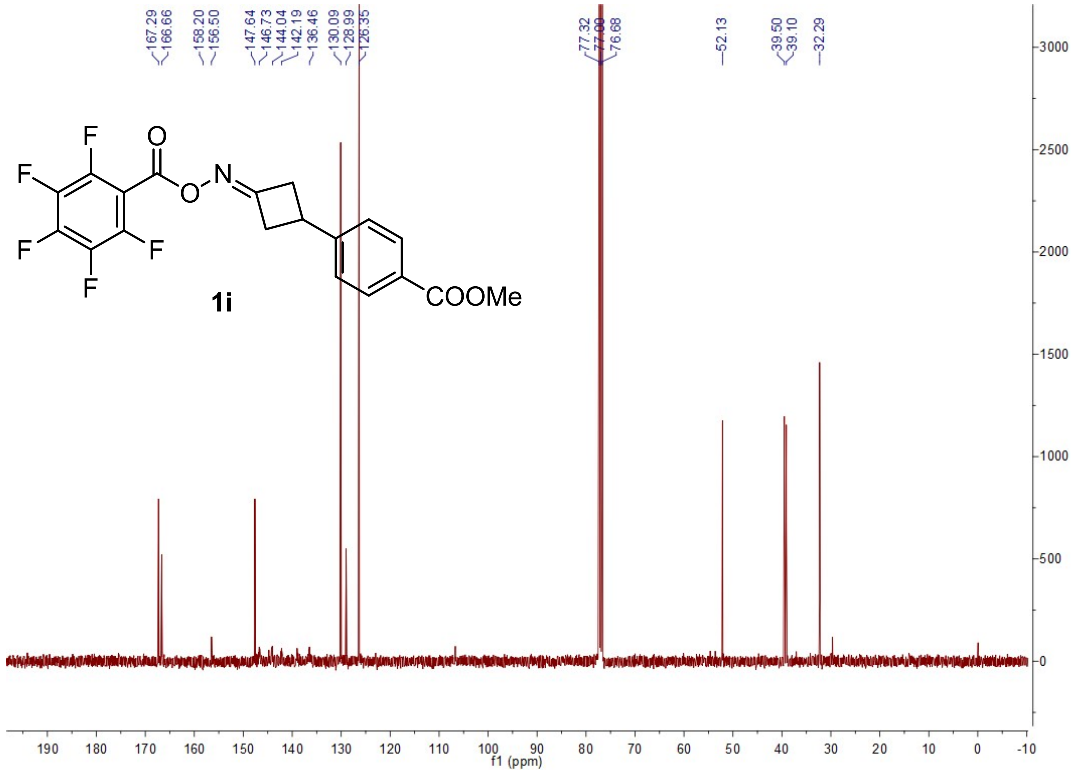

-137.02
-137.03
-137.05
-137.06
-137.09
-137.10
-137.12
-137.13
-147.61
-147.65
-147.67
-147.68
-147.72
-159.78
-159.80
-159.81
-159.84
-159.85
-159.87
-159.88
-159.91
-159.92
-159.94
F
F
F
F
F
O
O
N
Me
1b
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

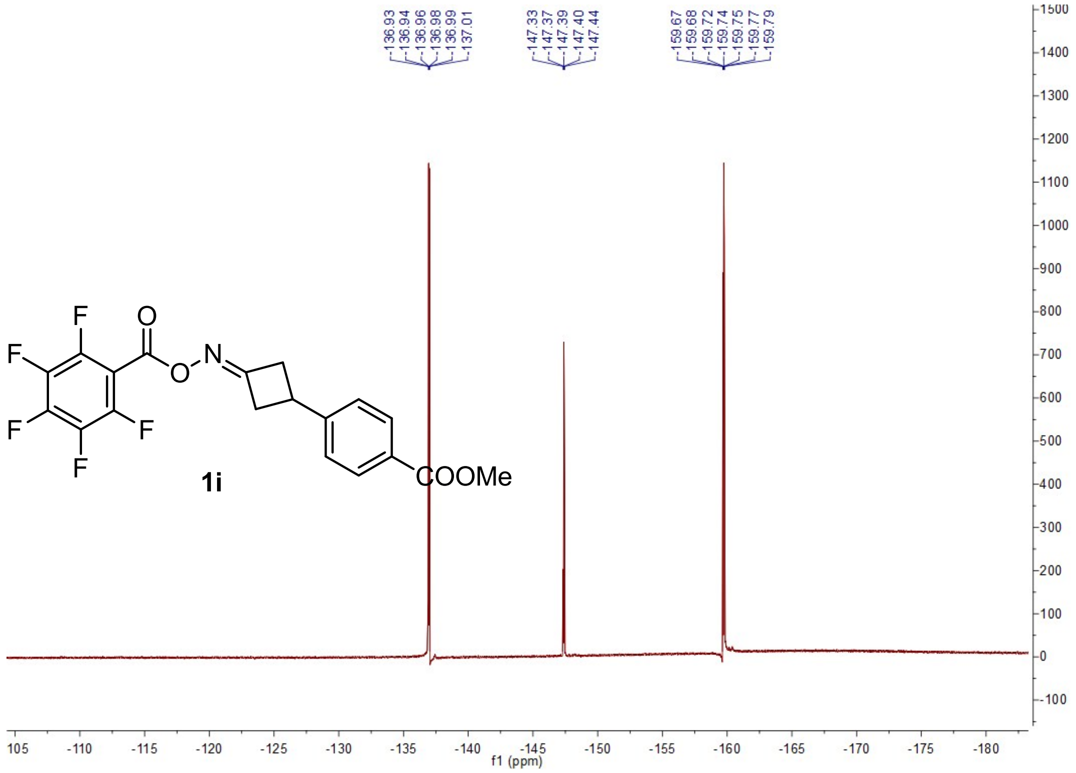

7.26
7.21
7.20
7.18
6.90
6.88
3.81
3.68
3.66
3.63
3.62
3.58
3.57
3.56
3.54
3.53
3.52
3.51
3.50
3.49
3.48
3.24
3.23
3.22
3.21
3.20
3.19
3.18
3.16
3.15
3.14
3.13
3.11
3.11
3.10
3.09
F
F
F
F
F
O
O
N
OMe
1f
2.11
2.13
3.20
1.10
2.00
1.95
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
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)


168.20
158.53
156.56
146.71
143.99
138.79
136.60
134.63
127.31
114.08
55.28
39.89
39.50
31.65
F
F
F
F
F
O
O
N
OMe
1f
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

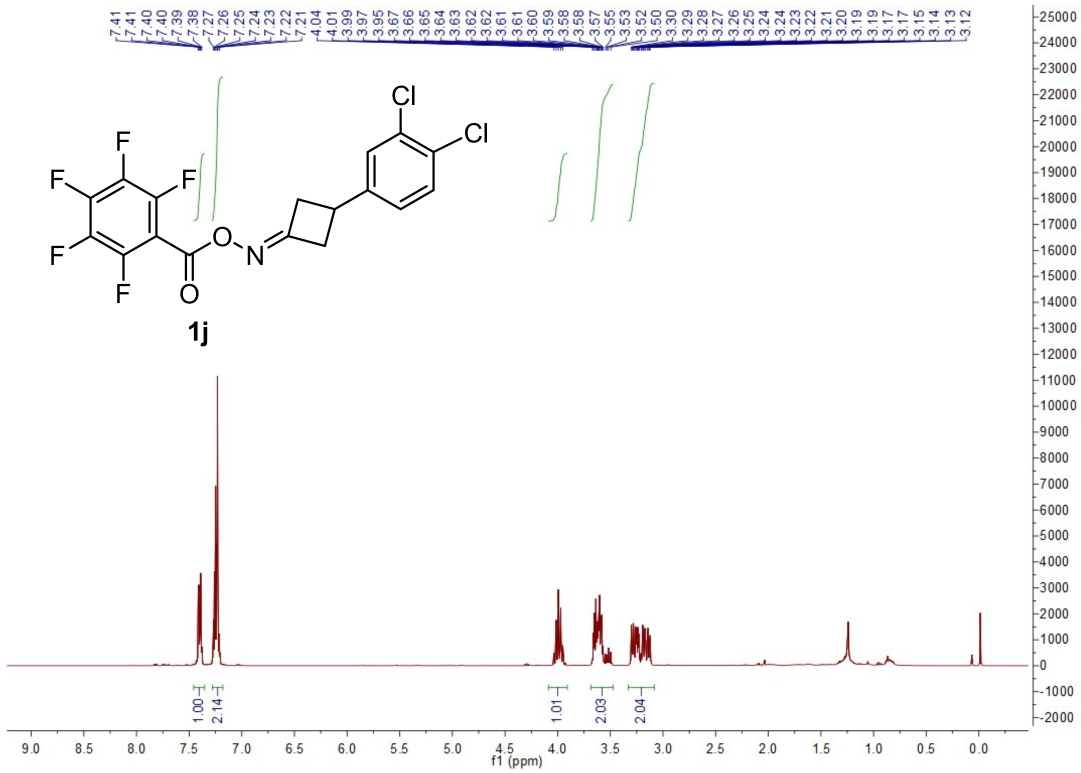

137.02
137.03
137.05
137.06
137.09
137.10
137.12
137.13
147.60
147.64
147.65
147.67
147.71
159.76
159.78
159.80
159.82
159.83
159.85
159.87
159.89
159.90
159.92
F
F
F
F
F
O
O
N
OMe
1f
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-85 -90 -95 -105 -115 -125 -135 -145 -155 -165 -175 -185 -195 -205
f1 (ppm)


8.04
8.02
7.34
7.32
7.26
3.92
3.78
3.76
3.74
3.72
3.64
3.63
3.61
3.60
3.59
3.58
3.57
3.56
3.55
3.30
3.28
3.26
3.24
3.22
3.22
3.21
3.20
3.18
3.17
3.16
3.16
F
F
F
F
F
O
O
N
COOMe
1i
2.00
1.99
2.98
1.04
1.99
2.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500

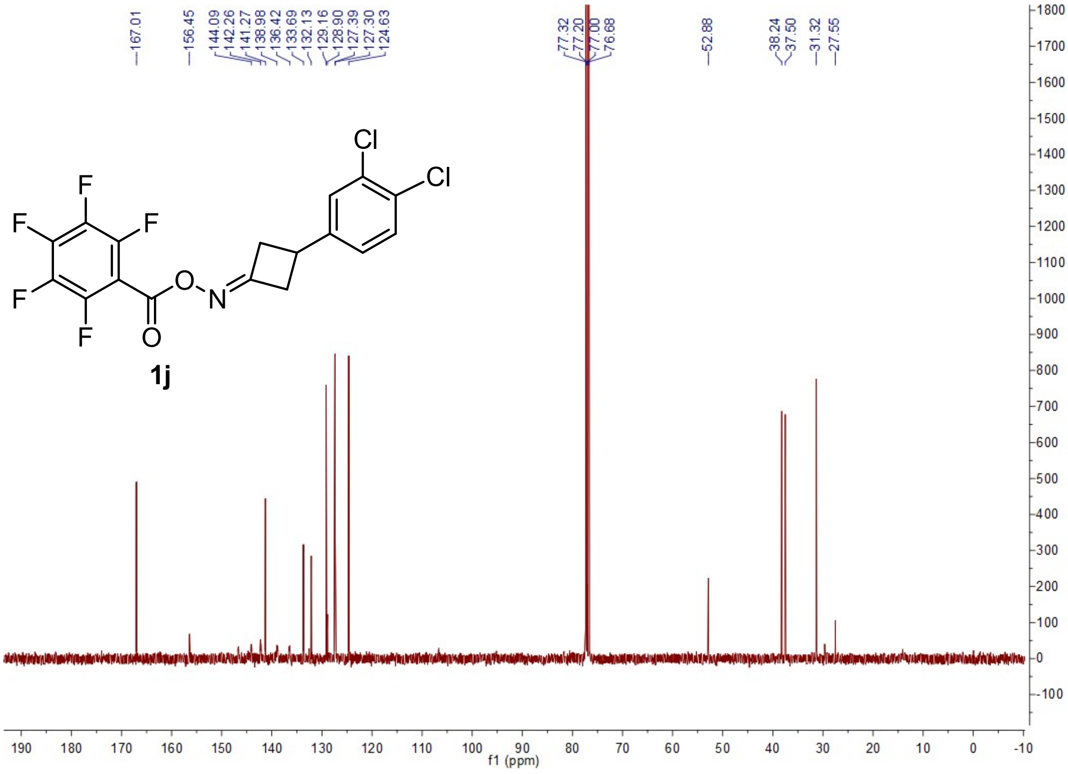

167.29
166.66
158.20
156.50
147.64
146.73
144.04
142.19
136.46
130.09
128.99
126.35
77.32
77.00
76.68
52.13
39.50
39.10
32.29
F
F
F
F
F
O
O
N
COOMe
1i
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
3000
2500
2000
1500
1000
500
0


-136.93
-136.94
-136.96
-136.98
-136.99
-137.01
-147.33
-147.37
-147.39
-147.40
-147.44
-159.67
-159.68
-159.72
-159.74
-159.75
-159.77
-159.79
F
O
N
COOMe
f1 (ppm)

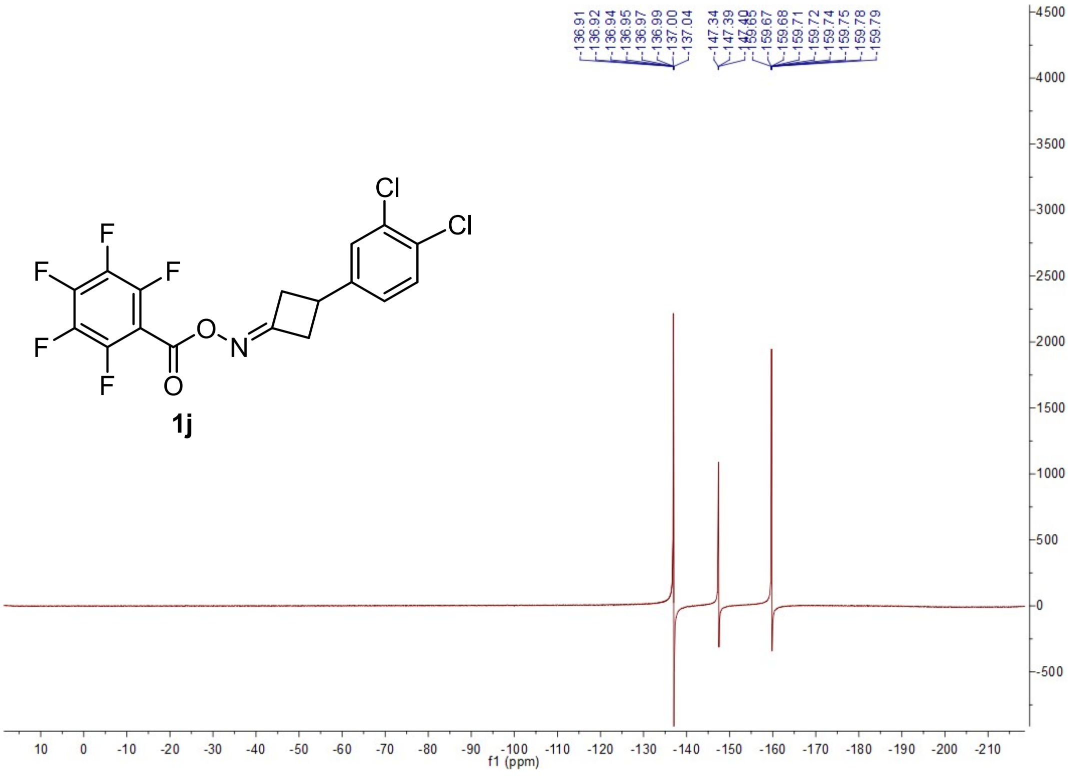
1i


7.41
7.41
7.40
7.39
7.38
7.27
7.26
7.25
7.24
7.23
7.22
7.21
4.04
4.01
3.99
3.97
3.95
3.67
3.66
3.65
3.64
3.63
3.62
3.61
3.60
3.59
3.58
3.57
3.55
3.53
3.52
3.50
3.30
3.29
3.28
3.27
3.26
3.25
3.24
3.23
3.22
3.21
3.20
3.19
3.17
3.15
3.14
3.13
3.12
Cl
F
O
N
1.00
2.14
1.01
2.03
2.04
f1 (ppm)

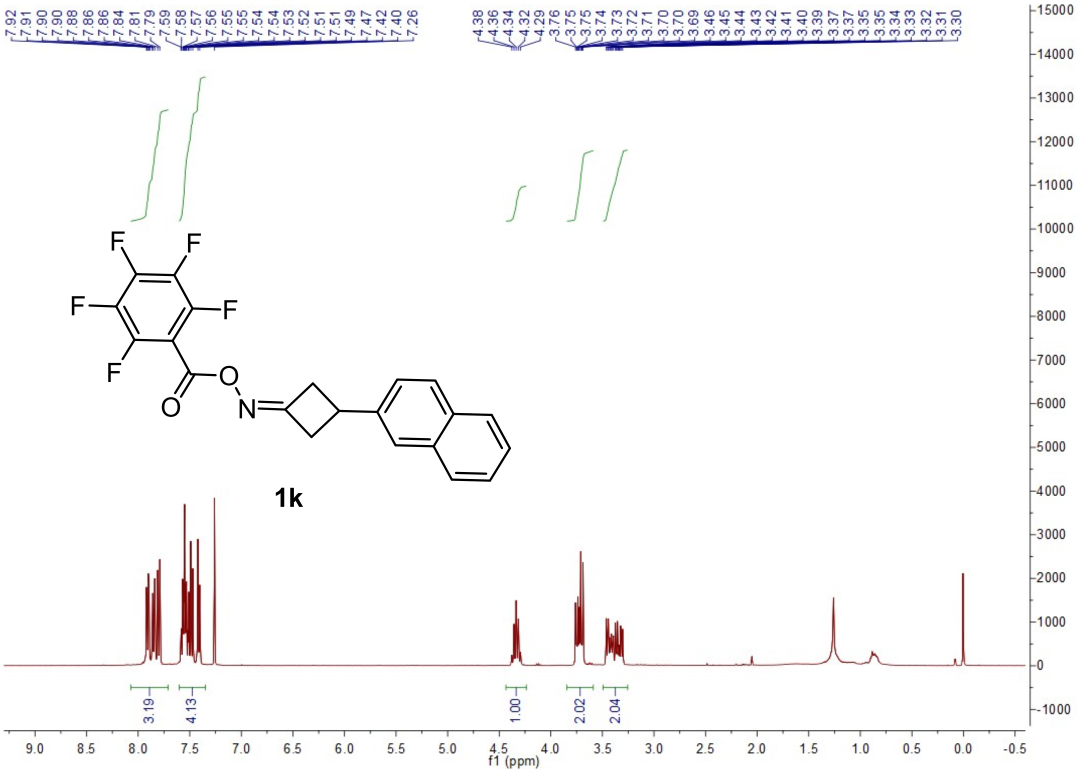
1j

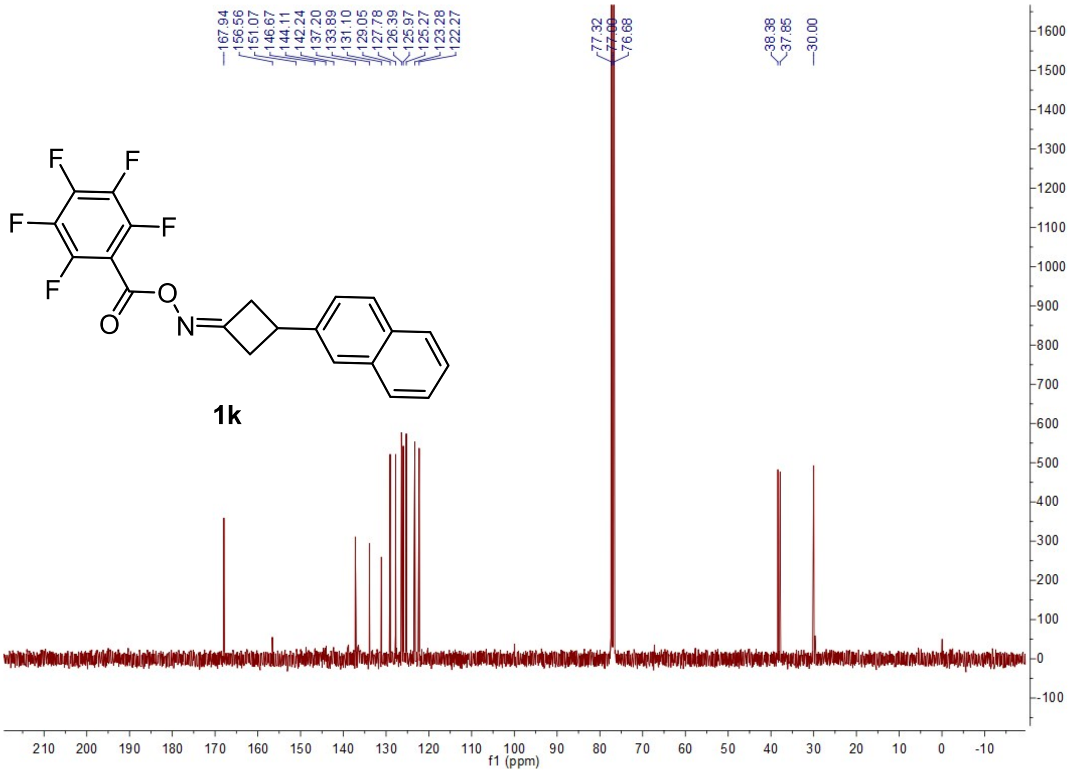


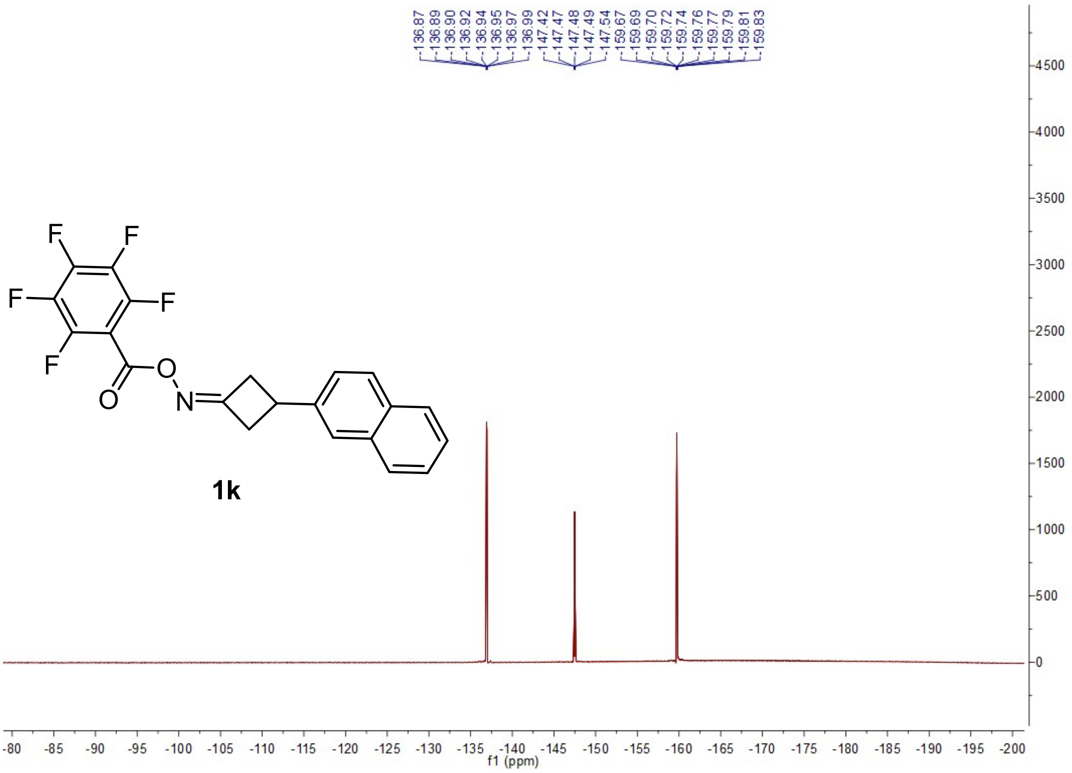
-167.01
-156.45
144.09
142.26
141.27
138.98
136.42
133.69
132.13
129.16
128.90
127.39
127.30
124.63
77.32
77.20
77.00
76.68
-52.88
38.24
37.50
-31.32
-27.55
F
F
F
F
F
O
O
N
Cl
Cl
1j
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



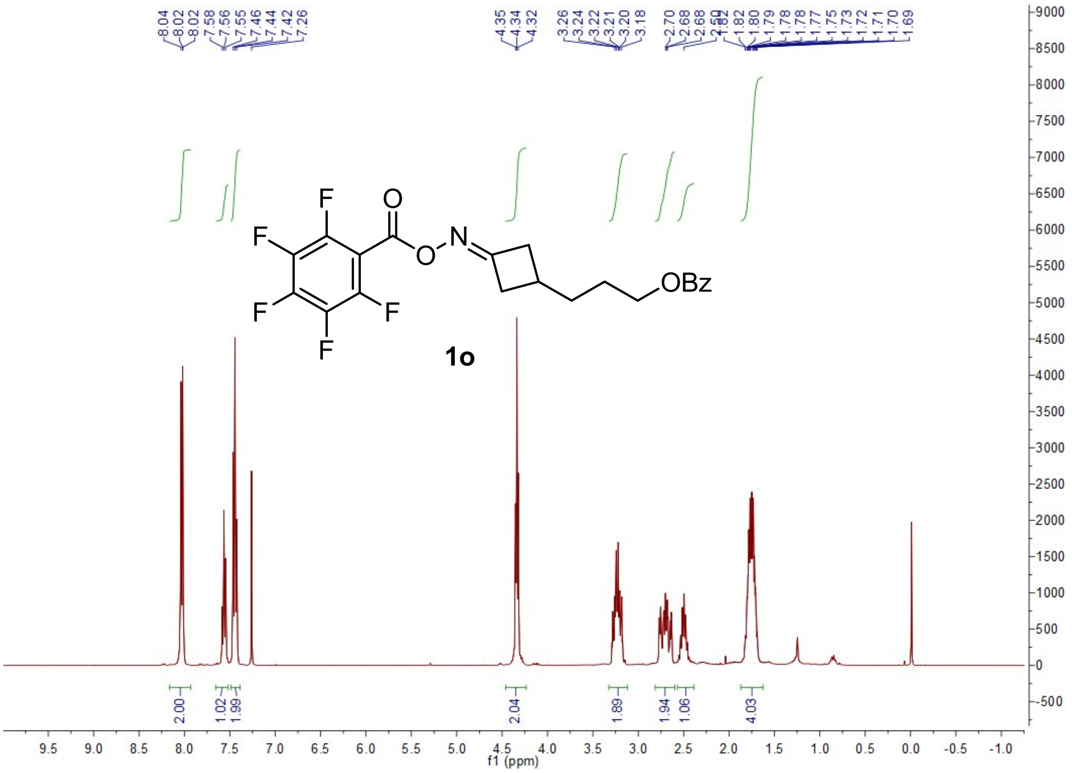
-136.91
-136.92
-136.94
-136.95
-136.97
-136.99
-137.00
-137.04
-147.34
-147.39
-147.40
-159.65
-159.67
-159.68
-159.71
-159.72
-159.74
-159.75
-159.78
-159.79
F
F
F
F
F
O
O
N
Cl
Cl
1j
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


7.92
7.91
7.90
7.90
7.88
7.86
7.86
7.84
7.81
7.79
7.59
7.58
7.57
7.56
7.55
7.55
7.54
7.54
7.53
7.52
7.51
7.51
7.49
7.47
7.42
7.40
7.26
4.38
4.36
4.34
4.32
4.29
3.76
3.75
3.75
3.74
3.73
3.72
3.71
3.70
3.70
3.69
3.46
3.45
3.44
3.43
3.42
3.41
3.40
3.39
3.37
3.37
3.35
3.35
3.34
3.33
3.32
3.31
3.30
F
F
F
F
F
O
O
N
1k
3.19
4.13
1.00
2.02
2.04
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000

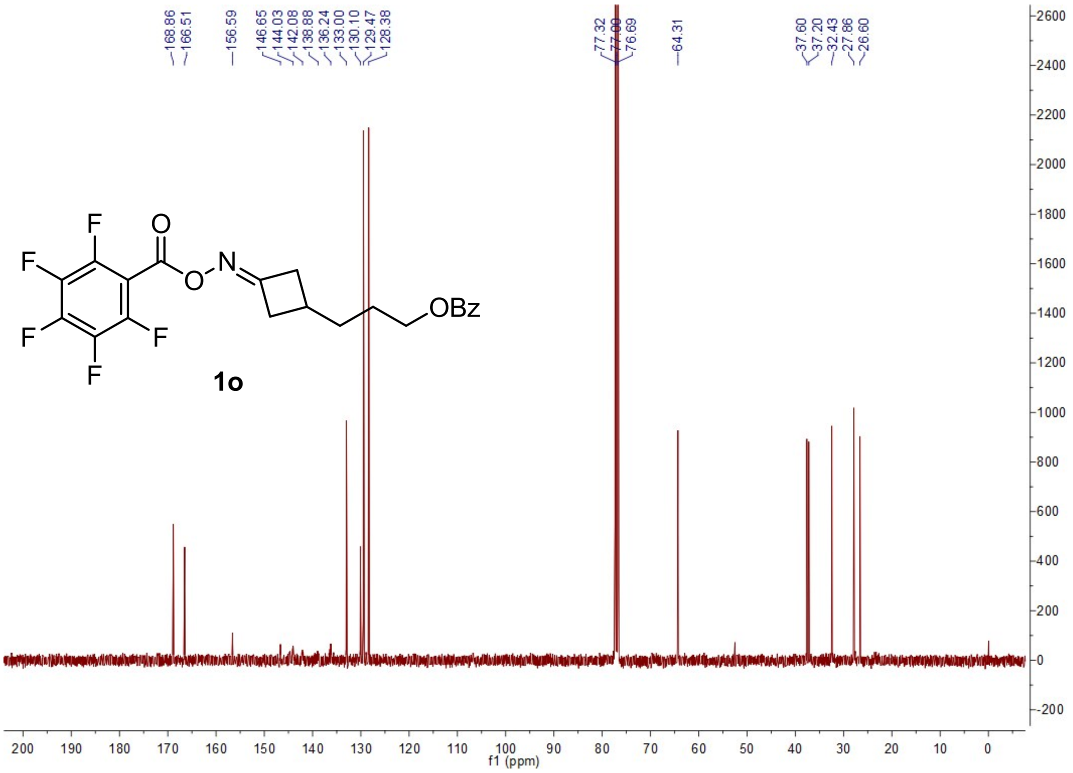

167.94
156.56
151.07
146.67
144.11
142.24
137.20
133.89
131.10
129.05
127.78
126.39
125.97
125.27
123.28
122.27
77.32
77.00
76.68
38.38
37.85
30.00
F
F
F
F
F
O
O
N
1k
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100


-136.87
-136.89
-136.90
-136.92
-136.94
-136.95
-136.97
-136.99
-147.42
-147.47
-147.48
-147.49
-147.54
-159.67
-159.69
-159.70
-159.72
-159.74
-159.76
-159.77
-159.79
-159.81
-159.83
F
F
F
F
F
O
O
N
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180 -185 -190 -195 -200
f1 (ppm)

1k


8.04
8.02
8.02
7.58
7.56
7.55
7.46
7.44
7.42
7.26
4.35
4.34
4.32
3.26
3.24
3.22
3.21
3.20
3.18
2.70
2.68
2.68
2.50
1.82
1.82
1.80
1.79
1.78
1.78
1.77
1.75
1.73
1.72
1.71
1.70
1.69
F
F
F
F
F
O
O
N
OBz
2.00
1.02
1.99
2.04
1.89
1.94
1.06
4.03
9000
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

1o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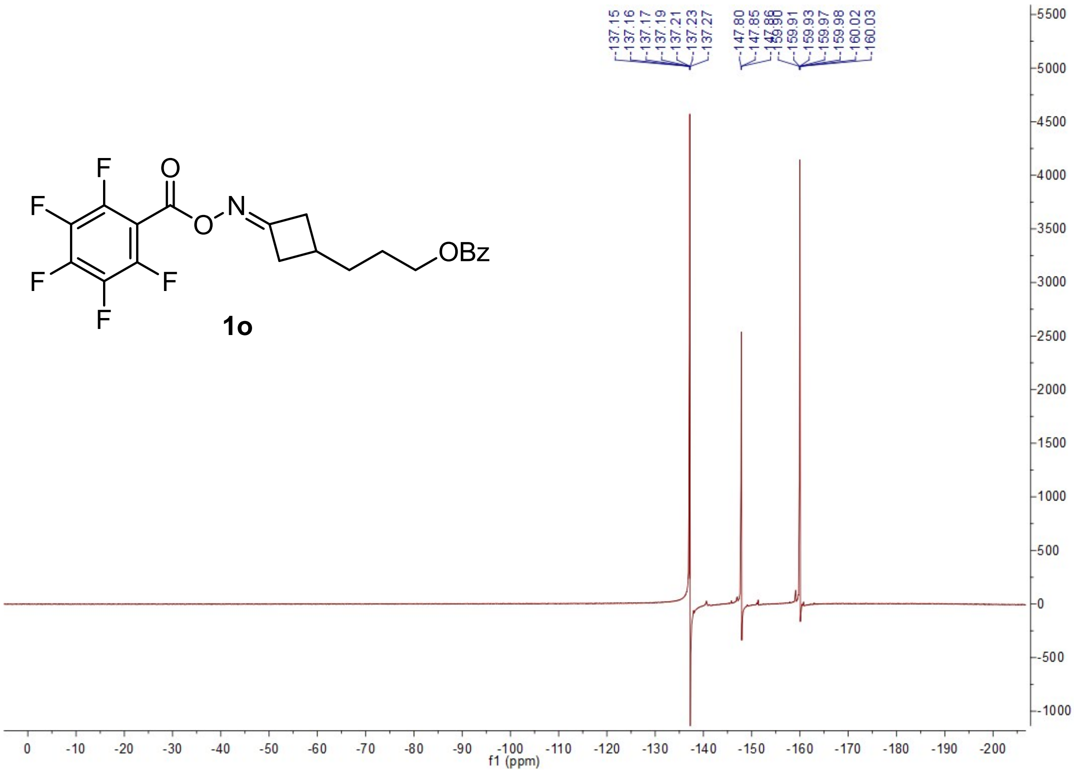
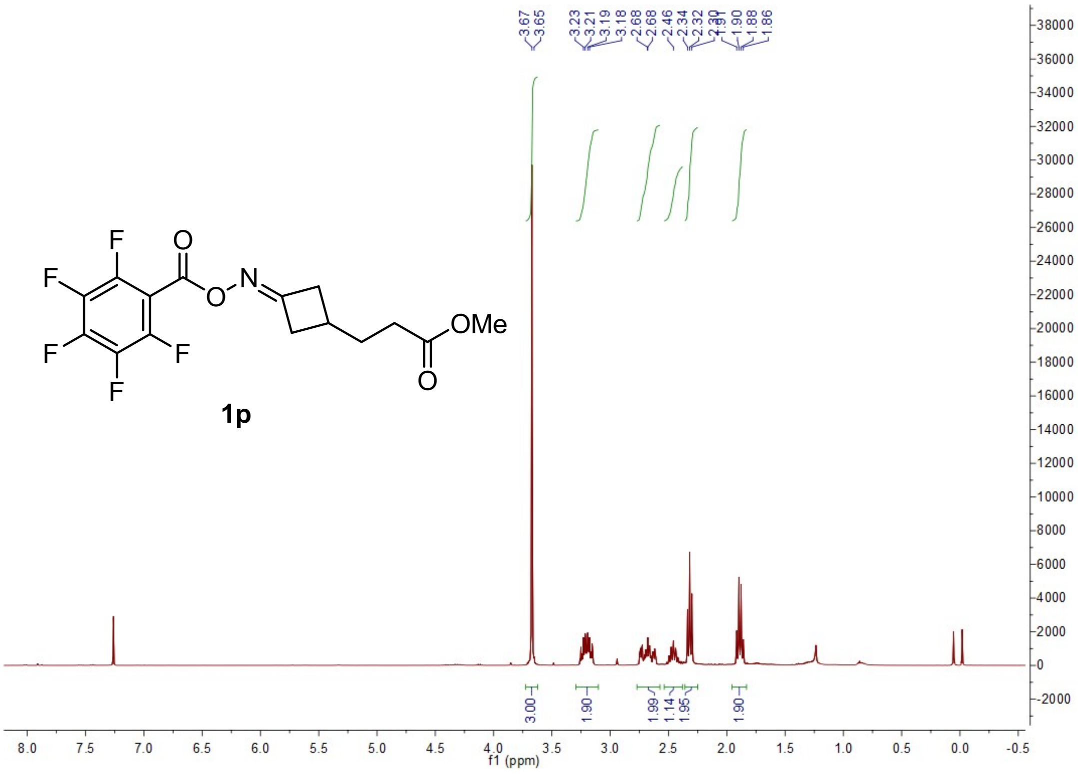
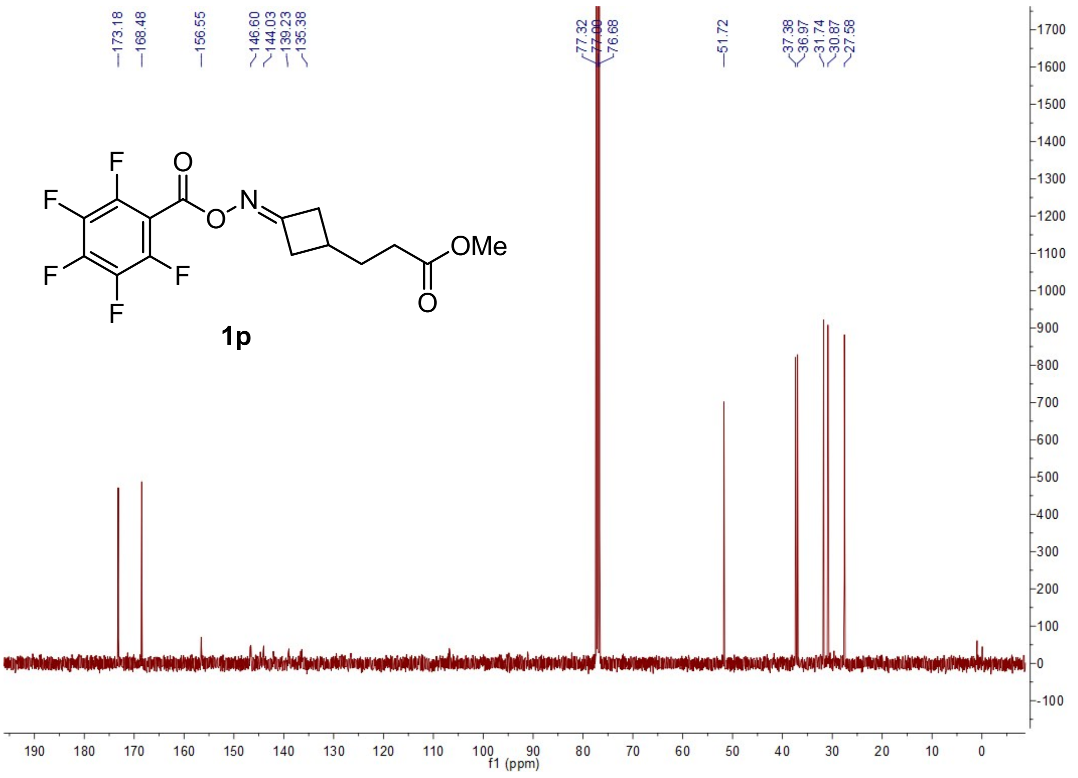
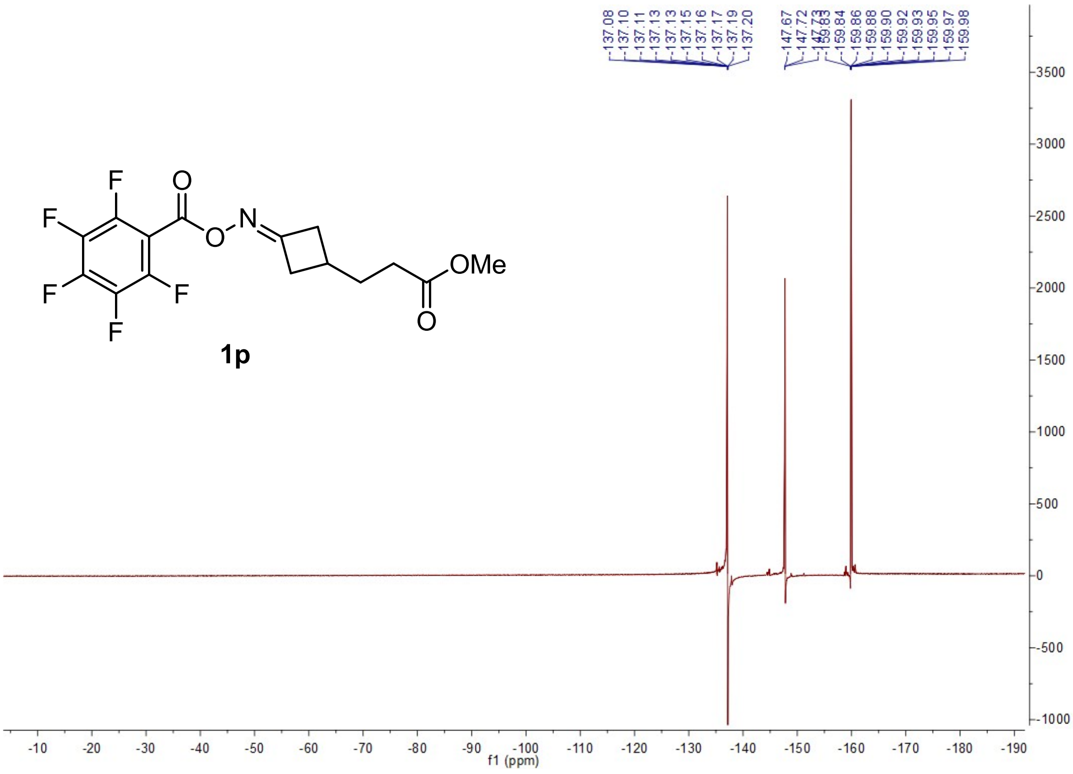
166.51
156.59
146.65
144.03
142.08
138.88
136.24
133.00
130.10
129.47
128.38
77.32
77.00
76.69
64.31
37.60
37.20
32.43
27.86
26.60
F
F
F
F
F
O
O
N
OBz
1o
f1 (ppm)

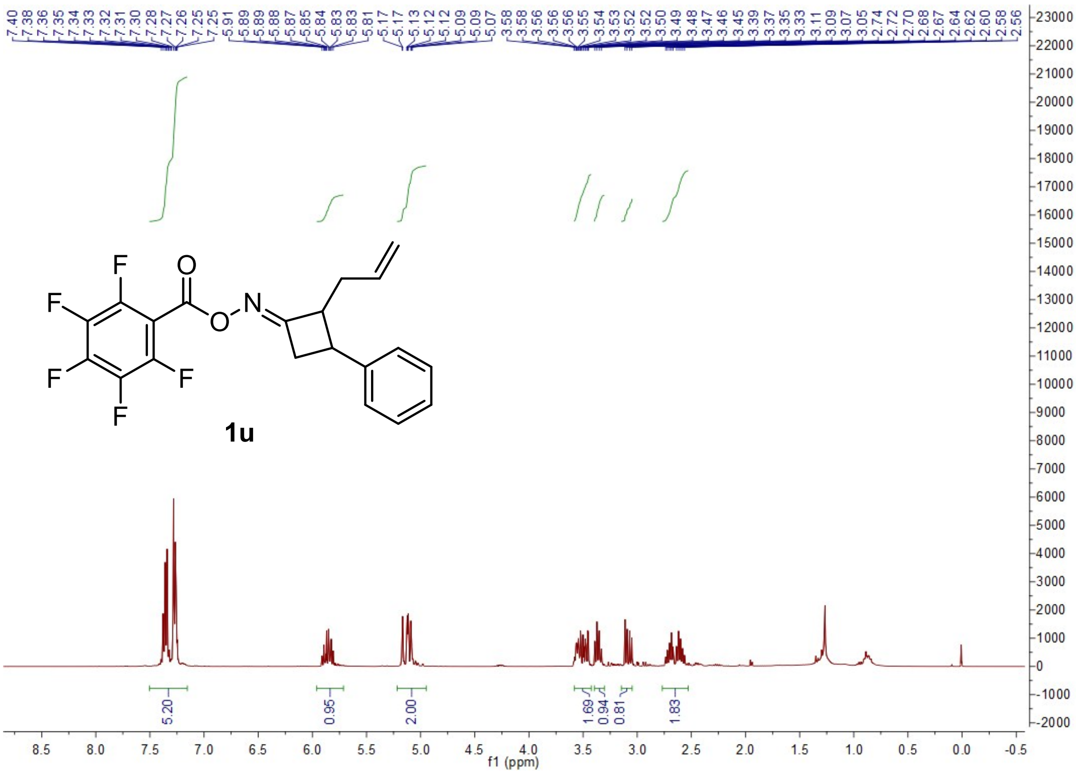

-137.15
-137.16
-137.17
-137.19
-137.21
-137.23
-137.27
-147.80
-147.85
-147.86
-159.90
-159.91
-159.93
-159.97
-159.98
-160.02
-160.03
F
F
F
F
F
O
O
N
OBz
1o
f1 (ppm)


3.67
3.65
3.23
3.21
3.19
3.18
2.68
2.46
2.34
2.32
2.30
1.91
1.90
1.88
1.86
F
F
F
F
F
O
O
N
OMe
O
1p
3.00
1.90
1.99
1.14
1.95
1.90
38000
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

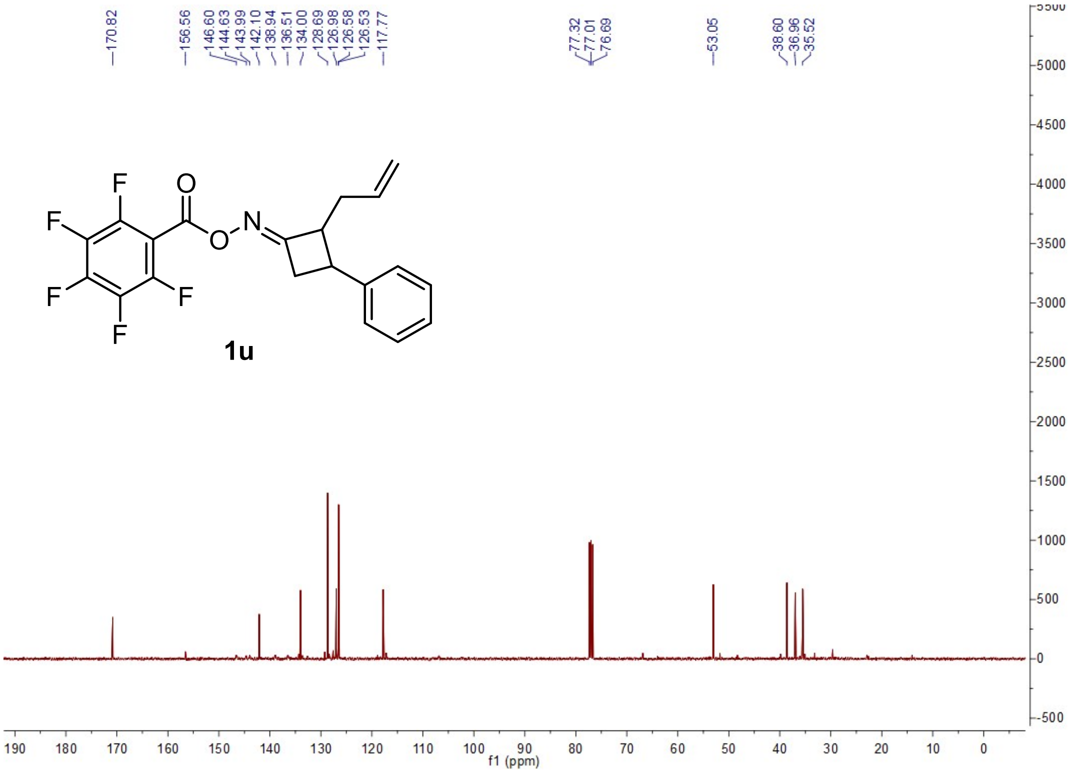

173.18
168.48
156.55
146.60
144.03
139.23
135.38
77.32
77.00
76.68
51.72
37.38
36.97
31.74
30.87
27.58
F
F
F
F
F
O
O
N
OMe
O
1p
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

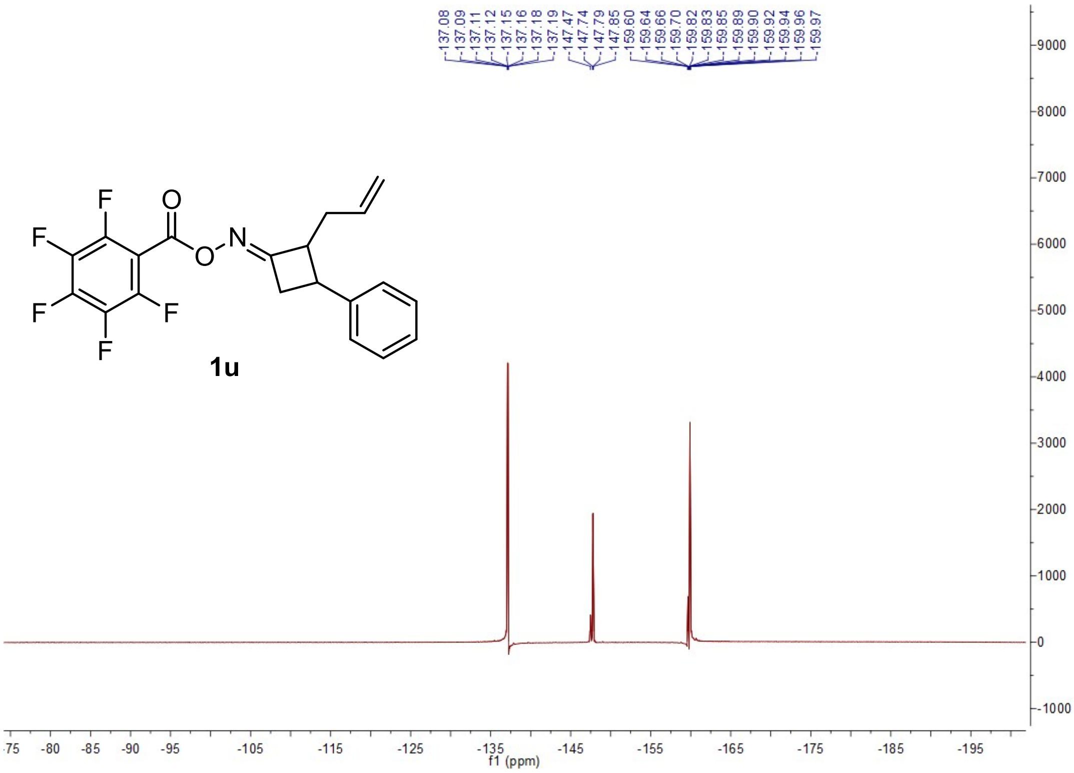

-137.08
-137.10
-137.11
-137.13
-137.13
-137.15
-137.16
-137.17
-137.19
-137.20
-147.67
-147.72
-147.73
-159.83
-159.84
-159.86
-159.88
-159.90
-159.92
-159.93
-159.95
-159.97
-159.98
F
F
F
F
F
O
O
N
OMe
O
3500
3000
2500
2000
1500
1000
500
0
-500
-1000
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

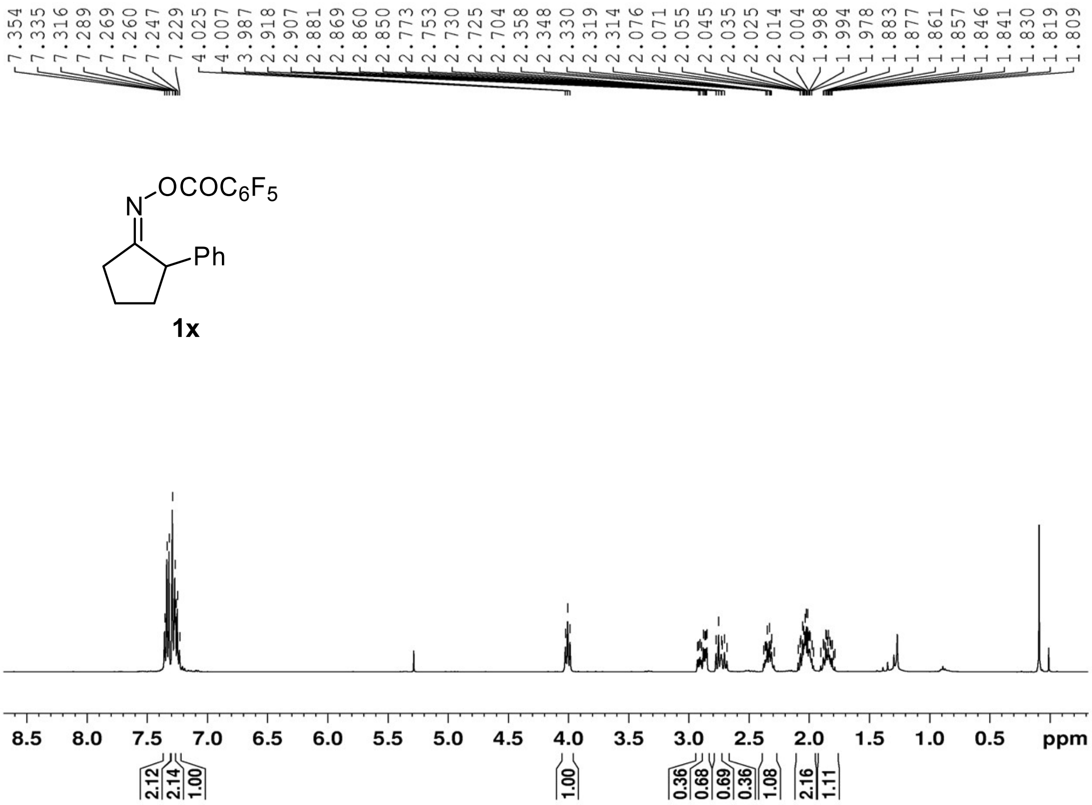
1p


7.40
7.38
7.36
7.35
7.34
7.33
7.32
7.31
7.30
7.28
7.27
7.26
7.25
7.25
5.91
5.89
5.89
5.88
5.87
5.85
5.84
5.83
5.83
5.81
5.17
5.17
5.13
5.12
5.12
5.09
5.09
5.07
3.58
3.58
3.56
3.56
3.55
3.54
3.53
3.52
3.52
3.50
3.49
3.48
3.47
3.46
3.45
3.39
3.37
3.35
3.33
3.11
3.09
3.07
3.05
2.74
2.72
2.70
2.68
2.67
2.64
2.62
2.60
2.58
2.56
F
F
F
F
F
O
O
N
5.20
0.95
2.00
1.69
0.94
0.81
1.83
23000
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

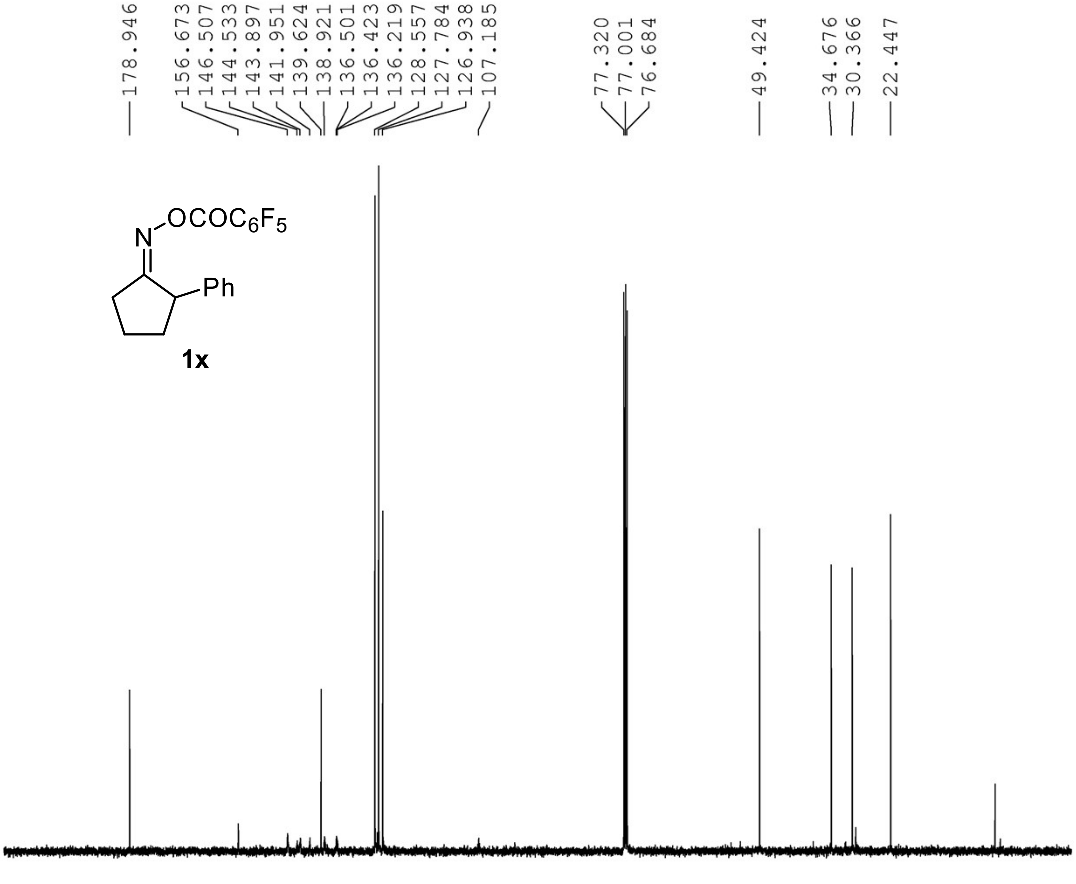
1u


170.82
156.56
146.60
144.63
143.99
142.10
138.94
136.51
134.00
128.69
126.98
126.58
126.53
117.77
77.32
77.01
76.69
53.05
38.60
36.96
35.52
F
F
F
F
F
O
O
N
1u
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

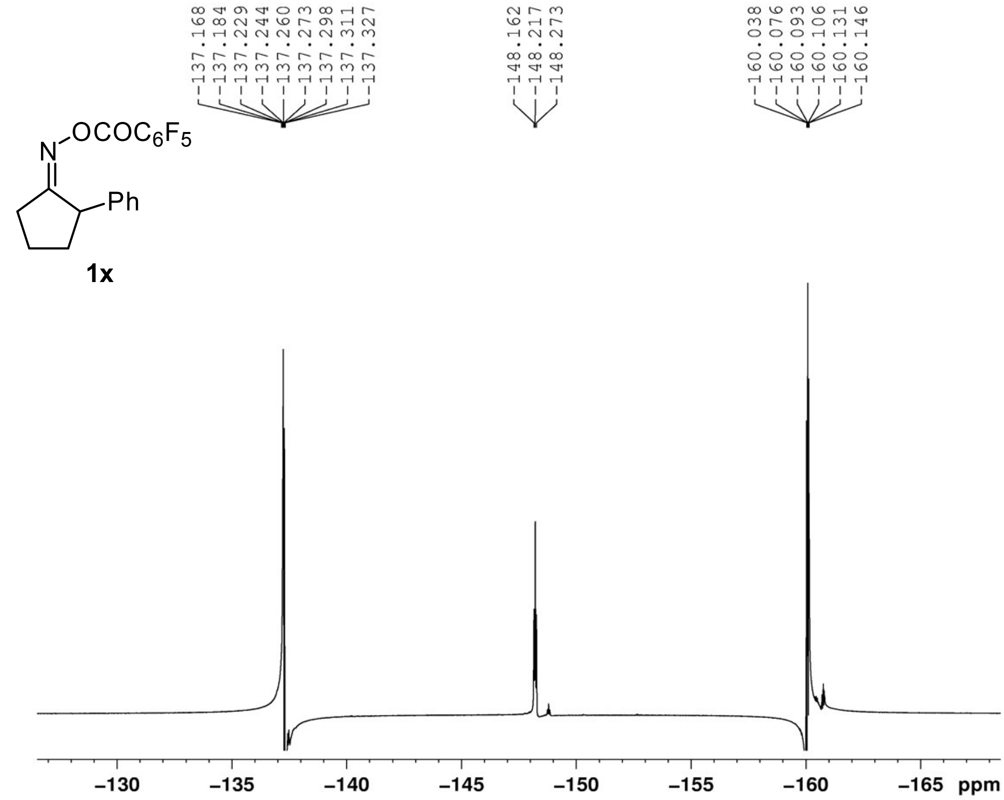

-137.08
-137.09
-137.11
-137.12
-137.15
-137.16
-137.18
-137.19
-147.47
-147.74
-147.79
-147.85
-159.60
-159.64
-159.66
-159.70
-159.82
-159.83
-159.85
-159.89
-159.90
-159.92
-159.94
-159.96
-159.97
F
F
F
F
F
O
O
N
1u
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-75
-80
-85
-90
-95
-105
-115
-125
-135
-145
-155
-165
-175
-185
-195
f1 (ppm)


7.354
7.335
7.316
7.289
7.269
7.260
7.247
7.229
4.025
4.007
3.987
2.918
2.907
2.881
2.869
2.860
2.850
2.773
2.753
2.730
2.725
2.704
2.358
2.348
2.330
2.319
2.314
2.076
2.071
2.055
2.045
2.035
2.025
2.014
2.004
1.998
1.994
1.978
1.883
1.877
1.861
1.857
1.846
1.841
1.830
1.819
1.809
N
OCOC6F5
Ph
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
ppm
2.12
2.14
1.00
1.00
0.36
0.68
0.69
0.36
1.08
2.16
1.11

1x

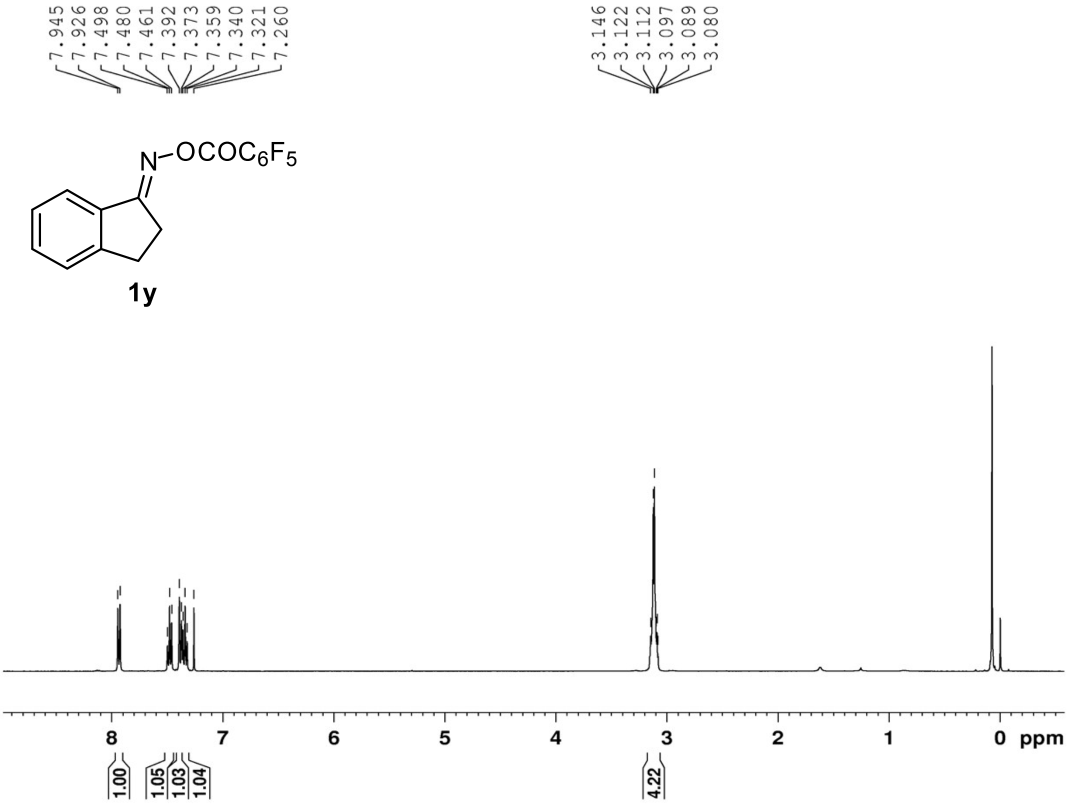

178.946
156.673
146.507
144.533
143.897
141.951
139.624
138.921
136.501
136.423
136.219
128.557
127.784
126.938
107.185
77.320
77.001
76.684
49.424
34.676
30.366
22.447
N
OCOC6F5
Ph
200
180
160
140
120
100
80
60
40
20
0
ppm

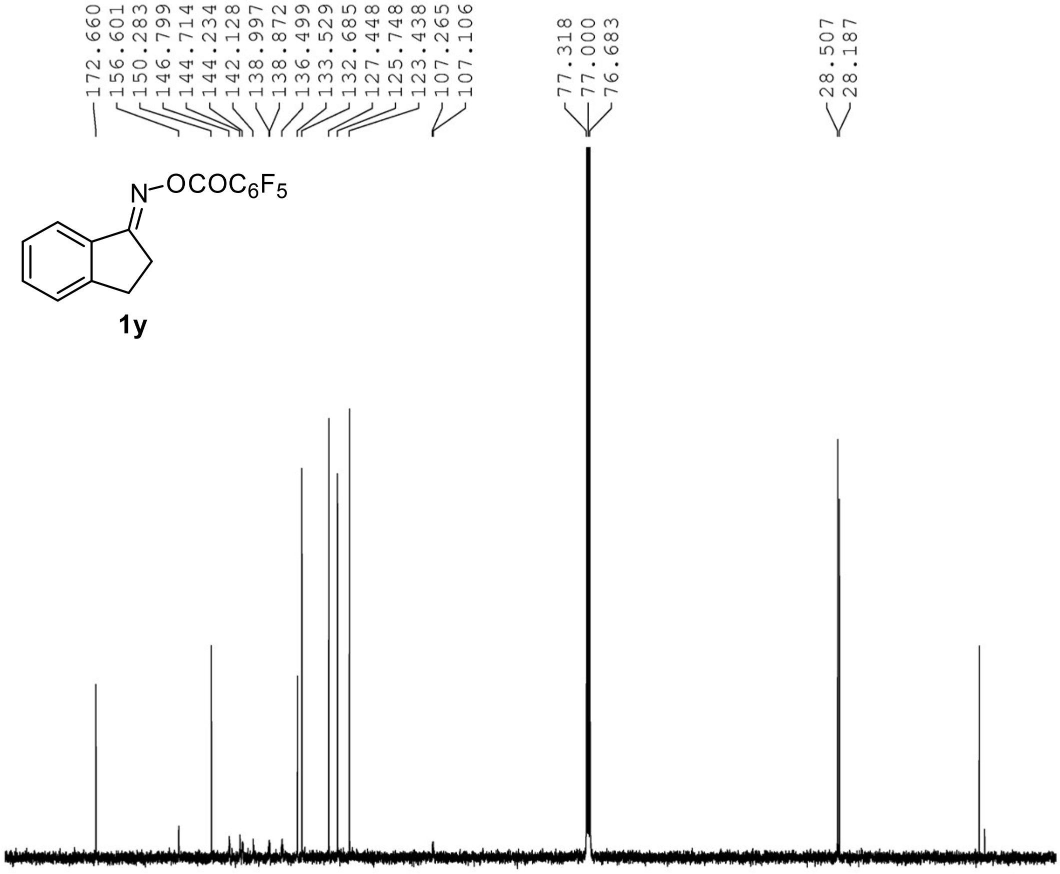
1x

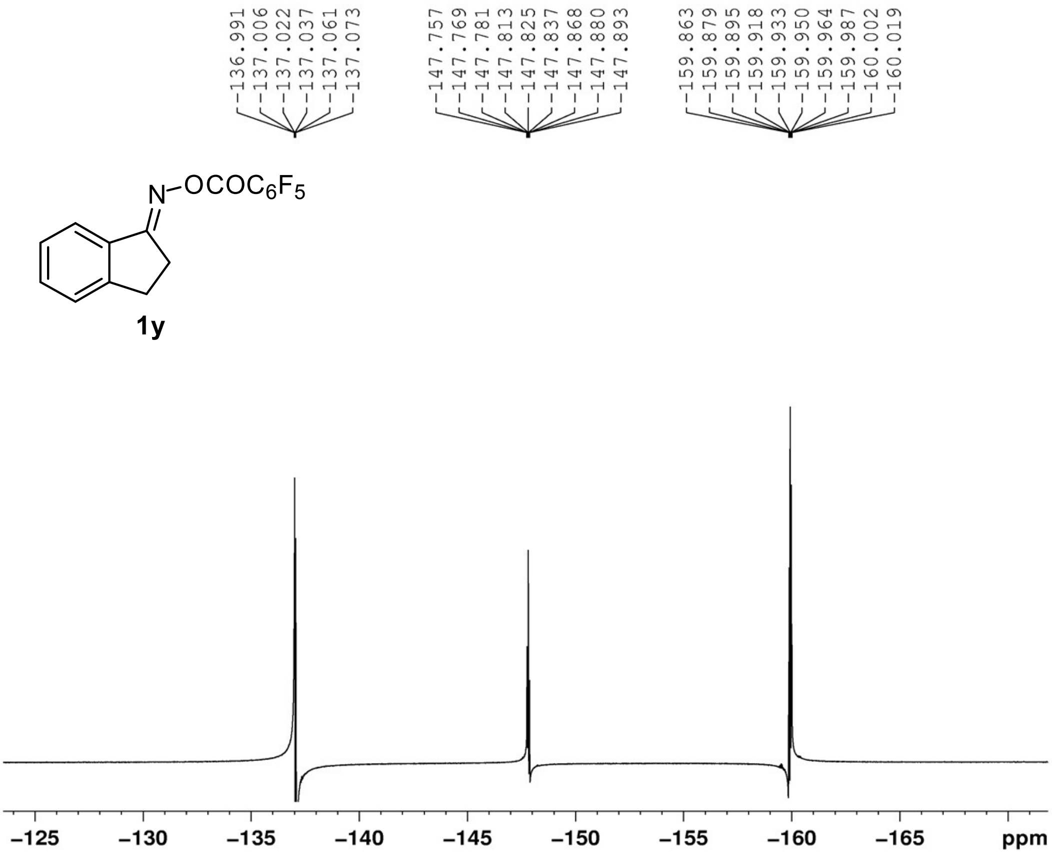


1x

N
OCOC6F5
Ph
-137.168
-137.184
-137.229
-137.244
-137.260
-137.273
-137.298
-137.311
-137.327
-148.162
-148.217
-148.273
-160.038
-160.076
-160.093
-160.106
-160.131
-160.146
−130
−135
−140
−145
−150
−155
−160
−165
ppm


7.945
7.926
7.498
7.480
7.461
7.392
7.373
7.359
7.340
7.321
7.260
3.146
3.122
3.112
3.097
3.089
3.080
N–OCOC6F5
1y
8
7
6
5
4
3
2
1
0 ppm
1.00
1.05
1.03
1.04
4.22


172.660
156.601
150.283
146.799
144.714
144.234
142.128
138.997
138.872
136.499
133.529
132.685
127.448
125.748
123.438
107.265
107.106
77.318
77.000
76.683
28.507
28.187
N–OCOC6F5
1y
180
160
140
120
100
80
60
40
20
0 ppm



N–OCOC6F5
-136.991
-137.006
-137.022
-137.037
-137.061
-137.073
-147.757
-147.769
-147.781
-147.813
-147.825
-147.837
-147.868
-147.880
-147.893
-159.863
-159.879
-159.895
-159.918
-159.933
-159.950
-159.964
-159.987
-160.002
-160.019
–125
–130
–135
–140
–145
–150
–155
–160
–165
ppm

1y