Supporting information

Bulky iodotriazolium tetrafluoroborates as highly active halogen-bonding-donor catalysts

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Contents

Instrumentation and Chemicals

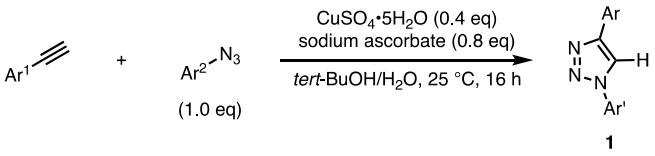
All manipulations of oxygen- and moisture-sensitive materials were conducted under argon or nitrogen atmosphere in a flame dried Schlenk flask. Nuclear magnetic resonance spectra were taken on a JEOL ECA spectrometer using tetramethylsilane for ^{1}H NMR as an internal standard (δ = 0 ppm) when $CDCl_3$ was used as a solvent, using CD_2Cl_2 for ^{1}H NMR as an internal standard (δ = 5.32 ppm) when CD_2Cl_2 was used as a solvent, using $CDCl_3$ for ^{13}C NMR as an internal standard (δ = 77.16 ppm) when $CDCl_3$ was used as a solvent, using CD_2Cl_2 for ^{13}C NMR as an internal standard (δ = 53.84 ppm) when CD_2Cl_2 was used as a solvent, and using hexafluorobenzene for ^{19}F NMR as an internal standard (δ = 0 ppm) when $CDCl_3$ and CD_2Cl_2 was used as a solvent. ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, br = broad, m = multiplet), coupling constants (Hz), and integration. High-resolution mass spectra (HRMS) were measured by a JEOL JMS-T100LC AccuTOF. Infrared (IR) spectra were measured by an FT/IR-4100ST spectrometer. Melting points were determined using a YANAKO MP-500D. Flash column chromatography was carried out using silica gel (Fuji Silysia PSQ 100B). *n*-Butyllithium in *n*-hexane 1.6 mol/L was purchased from Kanto Chemical Co., Inc. (04937-05, 1.5–1.7 mol/L). 2-Ethynylpyridine was purchased from Tokyo Chemical Industry Co., Ltd. (E0340, >97%). Copper chloride (I) was purchased from Kanto Chemical Co., Inc. (07524-30, >95%). Carbon tetrabromide was purchased from Tokyo Chemical Industry Co., Ltd. (T0038, >99%). Copper (II) sulfate pentahydrate was purchased from Kanto Chemical Co., Inc. (07516-01, >99%). L(+)-Ascorbic acid sodium salt was purchased from Wako Pure Chemical Industries, Ltd. (196-01252, >98%). *tert*-Butyl alcohol was purchased from Tokyo Chemical Industry Co., Ltd. (B0706, >99%). Iodine was purchased from nacalai tesque (19220-95, >99.8%). Hexachloroethane was purchased from Tokyo Chemical Industry Co., Ltd. (H0060, >99%). Trimethyloxonium tetrafluoroborate was purchased from Tokyo Chemical Industry Co., Ltd. (T1507, >95%). Dichloromethane was purchased from Kanto Chemical Co., Inc., distilled from calcium hydride and stored under nitrogen. Unless otherwise noted, commercially available reagents were used without purification.

2-Ethynyl-1,3,5-trimethylbenzene,[1] 2-ethynyl-1,3-diisopropylbenzene,[1] 2-azide-1,3,5-trimethylbenzene,[2] 2-azide-1,3-diisopropylbenzene,[2] *N*-(4-methoxybenzylidene)aniline,[3] *N*-(4-methylbenzylidene)aniline,[3] *N*-benzylideneaniline,[3] *N*-(4-trifluoromethylbenzylidene)aniline,[3] *N*-(4-bromobenzylidene)aniline,[3] *N*-(2,2-dimethylpropylidene)aniline,[3] 2-(*tert*-

butyldimethylsilyloxy)-1,3-butadiene,[4] 2-(*tert*-butyldimethylsilyloxy)-1-phenyl-1,3-butadiene,[5] and trimethyl[(1-phenylvinyl)oxy)silane[6] were prepared according to the literature.

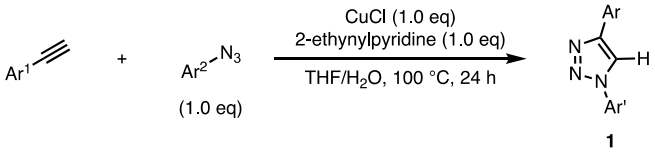
Experimental Procedure

General procedure for preparation of 1,2,3-triazoles 1: Type A



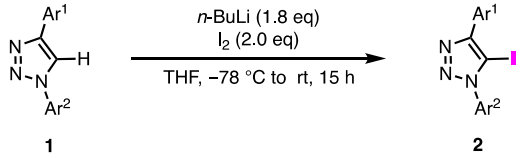
Following the reported procedure,[7] the reaction was performed in a 50-mL Schlenk flask equipped with a magnetic stirring bar and a septum. Aryl acetylene (4.8 mmol), aryl azide (4.8 mmol), copper (II) sulfate pentahydrate (0.48 g, 1.9 mmol), L-sodium ascorbate (0.77 g, 3.9 mmol), 2-methyl-2-propanol (4.8 mL), and water (4.8 mL) were added, and the mixture was stirred at 25 °C for 16 h. The resulting mixture was extracted with ethyl acetate three times. The combined organic layers were washed with aqueous ammonia, water, and brine, dried over sodium sulfate, and concentrated *in vacuo*. Purification by flash silica gel column chromatography gave 1,2,3-triazole **1a** and **1c**.

General procedure for preparation of 1,2,3-triazoles 1: Type B



Following the reported procedure,[8] the reaction was performed in a 50-mL Schlenk flask equipped with a magnetic stirring bar and a septum. Aryl acetylene (4.8 mmol), aryl azide (4.8 mmol), copper(I) chloride (0.48 g, 4.8 mmol), and 2-ethynylpyridine (0.49 g, 4.8 mmol) were dissolved in tetrahydrofuran (12 mL) and water (12 mL), and the mixture was stirred at 100 °C for 24 h. The resulting mixture was filtered through a pad of Celite and rinsed with the additional ethyl acetate. The organic layers were washed with aqueous ammonia, water, and brine, dried over sodium sulfate, and concentrated *in vacuo*. Purification by flash silica gel column chromatography gave 1,2,3-triazole **1b**, **1d**, and **1e**.

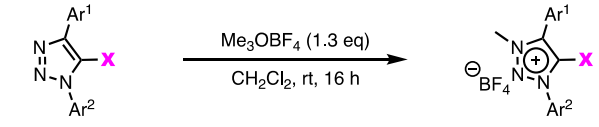
General procedure for preparation of 5-iodo-1,2,3-triazoles 2



1 **2**

The reaction was performed in a 50-mL Schlenk flask equipped with a magnetic stirring bar and a septum. 1,2,3-Triazole **1** (1.0 mmol) was dissolved in tetrahydrofuran (10 mL) under a nitrogen atmosphere, and the mixture was cooled to –78 °C. To a stirred solution *n*-butyllithium (1.6 M in hexane, 1.1 mL, 1.8 mmol) was added dropwise at –78 °C, and the mixture was stirred at –78 °C for 20 min. And then, to the reaction mixture iodine (1.0 M in tetrahydrofuran, 2.0 mL, 2.0 mmol) was added at –78 °C. After the resulting mixture was stirred at –78 °C for 1 h, the mixture was warmed to room temperature and stirred for 15 h. The reaction was quenched with saturated aqueous solution of ammonium chloride (3.0 mL) and saturated aqueous solution of sodium thiosulfate (3.0 mL). The resulting mixture was extracted with ethyl acetate. The combined organic layers were washed with water and brine, dried over sodium sulfate, and concentrated *in vacuo*. Purification by flash silica gel column chromatography gave the corresponding 5-iodo-1,2,3-triazole **2**.

General procedure for preparation of 5-halo-1,2,3-triazolium tetrafluoroborates 3

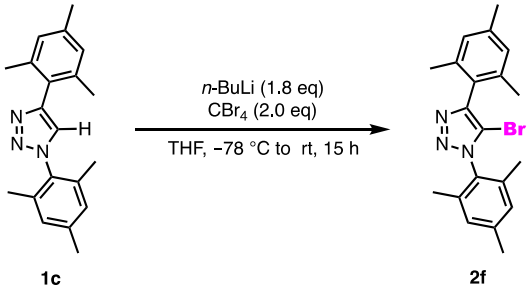


2
(X = I, Br, and Cl)

3

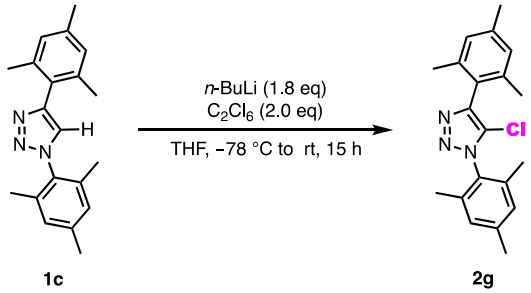
The reaction was performed in a 20-mL Schlenk flask equipped with a magnetic stirring bar and a septum. 5-Halo-1,2,3-triazole **2** (1.0 mmol) and trimethyloxonium tetrafluoroborate (0.20 g, 1.3 mmol) was dissolved in dichloromethane (7.5 mL) at a nitrogen atmosphere, and the mixture was stirred at room temperature for 16 h. And then, the solvent was removed under reduced pressure, affording an yellowish solid. The crude product was washed with diethyl ether and dried to give the corresponding 5-halo-3-methyl-1,2,3-triazolium tetrafluoroborate **3**.

Procedure for preparation of 5-bromo-1,2,3-triazole 2f



The reaction was performed in a 50-mL Schlenk flask equipped with a magnetic stirring bar and a septum. **1c** (0.31 g, 1.0 mmol) was dissolved in tetrahydrofuran (10 mL) under a nitrogen atmosphere, and the mixture was cooled to –78 °C. To a stirred solution *n*-butyllithium (1.6 M in hexane, 1.1 mL, 1.8 mmol) was added dropwise at –78 °C, and the mixture was stirred at –78 °C for 20 min. And then, to the reaction mixture carbon tetrabromide (1.0 M in tetrahydrofuran, 2.0 mL, 2.0 mmol) was added at –78 °C. After the resulting mixture was stirred at –78 °C for 1 h, the mixture was warmed to room temperature and stirred for 15 h. The reaction was quenched with saturated aqueous solution of ammonium chloride (3.0 mL) and saturated aqueous solution of sodium thiosulfate (3.0 mL). The resulting mixture was extracted with ethyl acetate. The combined organic layers were washed with water and brine, dried over sodium sulfate, and concentrated *in vacuo.* Purification by flash silica gel column chromatography gave the corresponding 5-bromo-1,2,3-triazole **2f** in 13% yield.

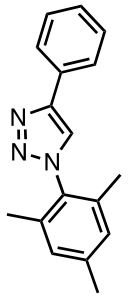
Procedure for preparation of 5-chloro-1,2,3-triazole 2g



The reaction was performed in a 50-mL Schlenk flask equipped with a magnetic stirring bar and a septum. **1c** (0.31 g, 1.0 mmol) was dissolved in tetrahydrofuran (10 mL) under

a nitrogen atmosphere, and the mixture was cooled to −78 °C. To a stirred solution *n*-butyllithium (1.6 M in hexane, 1.1 mL, 1.8 mmol) was added dropwise at −78 °C, and the mixture was stirred at −78 °C for 20 min. And then, to the reaction mixture hexachloroethane (1.0 M in tetrahydrofuran, 2.0 mL, 2.0 mmol) was added at −78 °C. After the resulting mixture was stirred at −78 °C for 1 h, the mixture was warmed to room temperature and stirred for 15 h. The reaction was quenched with saturated aqueous solution of ammonium chloride (3.0 mL) and saturated aqueous solution of sodium thiosulfate (3.0 mL). The resulting mixture was extracted with ethyl acetate. The combined organic layers were washed with water and brine, dried over sodium sulfate, and concentrated *in vacuo*. Purification by flash silica gel column chromatography gave the corresponding 5-chloro-1,2,3-triazole **2g** in 59% yield.

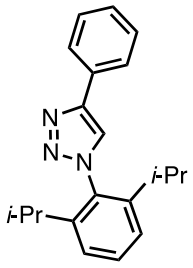
4-Phenyl-1-(2,4,6-trimethylphenyl)-1*H*-1,2,3-triazole (1a, CAS Registry Number 1119516-47-0).



White solid (0.98 g, 77%); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.99–7.90 (m, 2H), 7.83 (s, 1H), 7.46 (dd, *J* = 7.7, 7.5 Hz, 2H), 7.36 (tt, *J* = 7.5, 1.3 Hz, 1H), 7.01 (s, 2H), 2.36 (s, 3H), 2.02 (s, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 147.7, 140.2, 135.2, 133.6, 130.6, 129.2, 129.0, 128.4, 125.9, 121.6, 21.3, 17.4 ppm.

1a

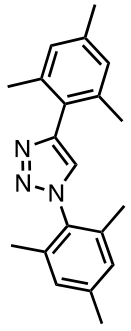
1-(2,6-Diisopropylphenyl)-4-phenyl-1*H*-1,2,3-triazole (1b, CAS Registry Number 1254815-47-8).



White solid (0.71 g, 48%); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.95 (dd, *J* = 7.8, 1.2 Hz, 2H), 7.87 (s, 1H), 7.51 (t, *J* = 7.8 Hz, 1H), 7.48 (dd, *J* = 7.8, 7.4 Hz, 2H), 7.38 (tt, *J* = 7.4, 1.2 Hz, 1H), 7.31 (d, *J* = 7.8 Hz, 2H), 2.34 (sep, *J* = 6.8 Hz, 2H), 1.17 (d, *J* = 6.8 Hz, 6H), 1.15 (d, *J* = 6.8 Hz, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 147.6, 146.3, 133.4, 131.0, 130.5, 129.1, 128.5, 125.9, 124.0, 122.6, 28.5, 24.4, 24.2 ppm.

1b

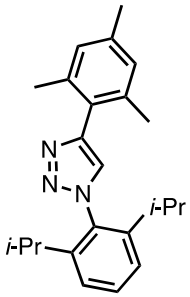
1,4-Bis(2,4,6-trimethylphenyl)-1*H*-1,2,3-triazole (1c, CAS Registry Number 1251555-83-5).



White solid (0.56 g, 38%); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.48 (s, 1H), 7.02 (s, 2H), 6.98 (s, 2H), 2.37 (s, 3H), 2.33 (s, 3H), 2.18 (s, 6H), 2.04 (s, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 145.5, 140.1, 138.4, 137.9, 135.2, 133.7, 129.2, 128.5, 127.2, 124.6, 21.3, 21.3, 20.8, 17.3 ppm.

1c

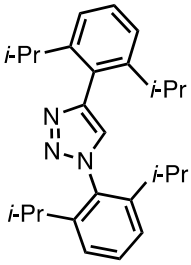
1-(2,6-Diisopropylphenyl)-4-(2,4,6-trimethylphenyl)-1*H*-1,2,3-triazole (1d, CAS Registry Number 1263862-49-2).



1d

White solid (0.92 g, 55%); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.53 (s, 1H), 7.51 (t, *J* = 7.7 Hz, 1H), 7.32 (d, *J* = 7.7 Hz, 2H), 6.99 (s, 2H), 2.40 (sep, *J* = 6.8 Hz, 2H), 2.34 (s, 3H), 2.20 (s, 6H), 1.22 (d, *J* = 6.8 Hz, 6H), 1.14 (d, *J* = 6.8 Hz, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 146.3, 145.3, 138.4, 137.9, 133.5, 130.9, 128.6, 127.1, 126.0, 124.0, 28.7, 24.4, 23.9, 21.3, 20.8 ppm.

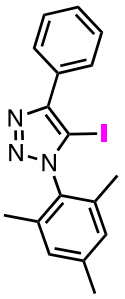
1,4-Bis(2,6-diisopropylphenyl)-1*H*-1,2,3-triazole (1e, CAS Registry Number 1263862-50-5).



1e

White solid (1.2 g, 61%); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.56 (s, 1H), 7.52 (t, *J* = 7.8 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 7.8 Hz, 2H), 7.26 (d, *J* = 7.8 Hz, 2H), 2.82 (sep, *J* = 6.8 Hz, 2H), 2.43 (sep, *J* = 6.8 Hz, 2H), 1.24 (d, *J* = 6.8 Hz, 6H), 1.21–1.15 (m, 12H), 1.13 (d, *J* = 6.8 Hz, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 148.9, 146.2, 144.7, 133.5, 130.9, 129.5, 127.9, 126.5, 124.0, 122.7, 30.7, 28.7, 24.5, 24.1, 24.1, 23.8 ppm.

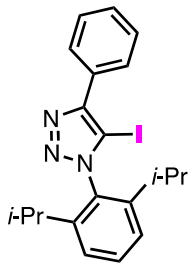
5-Iodo-4-phenyl-1-(2,4,6-trimethylphenyl)-1*H*-1,2,3-triazole (2a, CAS Registry Number 1949755-98-9).



2a

White solid (0.27 g, 70%); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.12 (dd, *J* = 7.7, 1.2 Hz, 2H), 7.51 (dd, *J* = 7.7, 7.5 Hz, 2H), 7.43 (tt, *J* = 7.5, 1.2 Hz, 1H), 7.04 (s, 2H), 2.39 (s, 3H), 1.95 (s, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 149.5, 140.9, 136.0, 133.2, 130.3, 129.3, 128.8, 128.7, 127.4, 79.4, 21.4, 17.6 ppm.

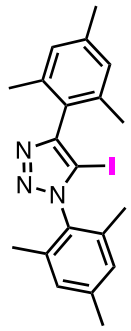
1-(2,6-Diisopropylphenyl)-5-iodo-4-phenyl-1*H*-1,2,3-triazole (2b).



2b

White solid (0.34 g, 78%); Mp. 138.5–139.0 °C; R_f 0.42 (hexane/ethyl acetate = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.16 (d, *J* = 7.5 Hz, 2H), 7.52 (t, *J* = 7.8 Hz, 1H), 7.48 (dd, *J* = 7.5, 7.4 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.31 (d, *J* = 7.8 Hz, 2H), 2.15 (sep, *J* = 6.8 Hz, 2H), 1.20 (d, *J* = 6.8 Hz, 6H), 1.12 (d, *J* = 6.8 Hz, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 148.9, 146.5, 132.8, 131.3, 130.1, 128.6, 128.6, 127.1, 124.0, 80.8, 28.7, 24.9, 23.0 ppm; IR (KBr): 3449.0, 3073.0, 2963.1, 2926.5, 2867.6, 2380.7, 1596.8, 1578.5, 1468.5, 1396.2, 1361.5, 1346.1, 1325.8, 1150.3, 1093.4, 1056.8, 1031.7, 997.0, 978.7, 937.3, 918.9, 698.3, 578.5, 493.7, 414.6 cm^{-1}; APCI-HRMS (*m/z*): $[M+H]^+$ calcd for $C_{20}H_{23}N_3I$ 432.0937, found 432.0950.

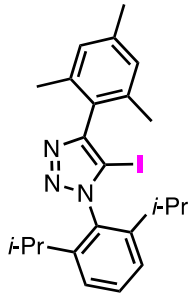
5-Iodo-1,4-bis(2,4,6-trimethylphenyl)-1*H*-1,2,3-triazole (2c).



2c

White solid (0.28 g, 65%); Mp. 235.0–236.0 °C; R_f 0.45 (hexane/ethyl acetate = 3/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.05 (s, 2H), 6.98 (s, 2H), 2.40 (s, 3H), 2.35 (s, 3H), 2.09 (s, 6H), 1.98 (s, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 151.6, 140.7, 139.0, 138.1, 135.8, 133.2, 129.3, 128.4, 126.6, 84.1, 21.4, 21.4, 20.2, 17.4 ppm; IR (KBr): 3449.1, 2956.3, 2919.7, 2853.2, 1654.6, 1606.4, 1563.0, 1542.8, 1458.9, 1383.7, 1212.0, 1129.1, 1083.8, 1033.7, 985.4, 855.3, 728.9, 471.5 cm^{-1}; ESI-HRMS (*m/z*): $[M+H]^+$ calcd for $C_{20}H_{23}N_3I$ 432.0937, found 432.0927.

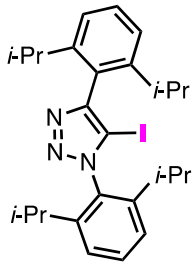
1-(2,6-Diisopropylphenyl)-5-iodo-4-(2,4,6-trimethylphenyl)-1*H*-1,2,3-triazole (2d).



2d

White solid (0.38 g, 81%); Mp. 182.0–182.8 °C; R_f 0.51 (hexane/ethyl acetate = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) 7.55 (t, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 7.8 Hz, 2H), 6.99 (s, 2H), 2.36 (s, 3H), 2.24 (sep, *J* = 6.8 Hz, 2H), 2.10 (s, 6H), 1.23 (d, *J* = 6.8 Hz, 6H), 1.18 (d, *J* = 6.8 Hz, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 151.4, 146.6, 139.0, 138.1, 133.1, 131.4, 128.4, 126.6, 124.2, 85.7, 29.0, 24.8, 23.2, 21.4, 20.2 ppm; IR (KBr): 2961.2, 2925.5, 2869.6, 1638.2, 1473.4, 1466.6, 1458.9, 1451.2, 1400.1, 1384.6, 1213.9, 1108.9, 981.6, 854.3, 802.2, 760.8, 746.3, 736.7, 597.8, 553.5, 466.7 cm^{-1}; ESI-HRMS (*m/z*): $[M+H]^+$ calcd for $C_{23}H_{29}N_3I$ 474.1406, found 474.1390.

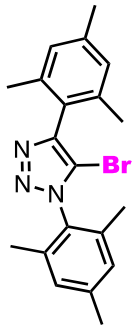
1,4-Bis(2,6-diisopropylphenyl)-5-iodo-1*H*-1,2,3-triazole (2e).



2e

White solid (0.48 g, 93%); Mp. 172.0–172.8 °C; R_f 0.55 (hexane/ethyl acetate = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.55 (t, *J* = 7.8 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 7.8 Hz, 2H), 2.63 (sep, *J* = 6.8 Hz, 2H), 2.26 (sep, *J* = 6.8 Hz, 2H), 1.28–1.11 (m, 24H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 150.8, 149.0, 146.5, 133.2, 131.4, 130.0, 127.6, 124.2, 122.9, 87.4, 31.1, 29.0, 24.7, 24.3, 23.9, 23.2 ppm; IR (KBr): 3855.0, 3650.6, 3630.3, 3449.1, 2963.1, 2867.6, 2382.6, 1596.8, 1473.4, 1381.8, 1361.5, 1321.9, 1215.9, 1151.3, 1059.7, 987.4, 801.3, 754.0 cm^{-1}; APCI-HRMS (*m/z*): $[M+H]^+$ calcd for $C_{26}H_{35}N_3I$ 516.1876, found 516.1867.

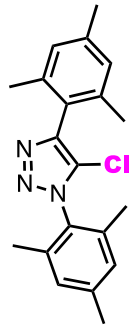
5-Bromo-1,4-bis(2,4,6-trimethylphenyl)-1*H*-1,2,3-triazole (2f).



2f

White solid (0.050 g, 13%); Mp. 173.5–174.2 °C; R_f 0.33 (hexane/ethyl acetate = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.05 (s, 2H), 6.98 (s, 2H), 2.39 (s, 3H), 2.35 (s, 3H), 2.12 (s, 6H), 2.01 (s, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 145.6, 140.8, 139.1, 138.2, 135.9, 131.9, 129.4, 128.5, 125.6, 113.2, 21.4, 21.4, 20.1, 17.3 ppm; IR (KBr): 2960.2, 2920.7, 2854.1, 2732.6, 1735.6, 1613.2, 1560.1, 1535.1, 1470.5, 1438.6, 1400.1, 1375.0, 1322.9, 1289.2, 1218.8, 1198.5, 1158.0, 1132.9, 1082.8, 1033.7, 980.6, 946.9, 728.9, 853.4, 756.9, 728.9, 574.7, 500.4, 484.1, 473.4 cm^{-1}; APCI-HRMS (*m/z*): $[M+H]^+$ calcd for $C_{20}H_{23}N_3Br$ 384.1075, found 384.1093.

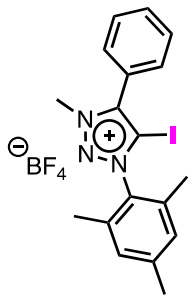
5-Chloro-1,4-bis(2,4,6-trimethylphenyl)-1*H*-1,2,3-triazole (2g).



2g

White solid (0.20 g, 59%); Mp. 194.2–195.0 °C; R_f 0.37 (hexane/ethyl acetate = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.05 (s, 2H), 6.98 (s, 2H), 2.38 (s, 3H), 2.35 (s, 3H), 2.14 (s, 6H), 2.03 (s, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 142.3, 140.9, 139.1, 138.3, 135.9, 131.0, 129.3, 128.5, 125.6, 125.1, 21.4, 21.4, 20.1, 17.3 ppm; IR (KBr): 2920.7, 2380.7, 2346.0, 2284.3, 1735.6, 1612.2, 1474.3, 1225.5, 1199.5, 1162.9, 1086.7, 1034.6, 981.6, 946.9, 900.6, 853.3, 730.9, 578.5, 490.8 cm^{-1}; APCI-HRMS (*m/z*): $[M+H]^+$ calcd for $C_{20}H_{23}N_3Cl$ 340.1581, found 340.1577.

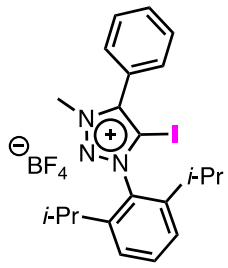
5-Iodo-3-methyl-1-(2,4,6-trimethylphenyl)-4-phenyl-1*H*-1,2,3-triazolium tetrafluoroborate (3a).



3a

White solid (0.46 g, 93%); ^{1}H NMR (500 MHz, CD_2Cl_2) δ: 7.78–7.64 (m, 5H), 7.16 (s, 2H), 4.41 (s, 3H), 2.43 (s, 3H), 2.07 (s, 6H) ppm; ^{13}C NMR (125 MHz, CD_2Cl_2) δ: 148.4, 143.9, 135.6, 132.9, 131.6, 130.6, 130.4, 130.3, 122.2, 90.5, 40.6, 21.5, 17.6 ppm; ^{19}F NMR (470 MHz, CD_2Cl_2) δ: 9.7 ppm; IR (KBr): 3639.9, 3568.6, 3040.2, 2924.5, 2379.7, 1609.3, 1557.2, 1483.9, 1450.2, 1382.7, 1324.9, 1290.1, 1221.7, 1186.0, 1062.6, 853.3, 784.9, 749.2, 731.9, 718.4, 697.1, 545.8, 520.7 cm^{-1}; ESI-HRMS (*m/z*): $[M–BF_4]^+$ calcd for $C_{18}H_{19}N_3I$ 404.0618, found 404.0605.

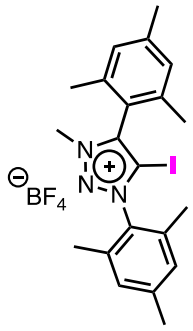
1-(2,6-Diisopropylphenyl)-5-iodo-3-methyl-4-phenyl-1*H*-1,2,3-triazolium tetrafluoroborate (3b).



3b

White solid (0.48 g, 90%); ^{1}H NMR (500 MHz, CD_2Cl_2) δ: 7.81–7.77 (m, 2H), 7.75–7.69 (m, 4H), 7.47 (d, *J* = 7.8 Hz, 2H), 4.44 (s, 3H), 2.20 (sep, *J* = 6.8 Hz, 2H), 1.30 (d, *J* = 6.8 Hz, 6H), 1.19 (d, *J* = 6.8 Hz, 6H) ppm; ^{13}C NMR (125 MHz, CD_2Cl_2) δ: 148.2, 146.4, 133.8, 133.0, 131.2, 130.7, 130.3, 125.5, 122.1, 91.7, 40.6, 29.5, 25.2, 23.1 ppm; ^{19}F NMR (470 MHz, CD_2Cl_2) δ: 9.5 ppm; IR (KBr): 3064.3, 2972.7, 2932.2, 2871.5, 2379.7, 2346.9, 1993.1, 1910.2, 1828.2, 1607.4, 1580.4, 1556.3, 1487.8, 1452.2, 1386.6, 1366.3, 1331.6, 1293.0, 1222.7, 1187.9, 935.3, 812.9, 764.5, 757.9, 697.1, 678.8, 612.3, 520.7, 473.5, 424.3 cm^{-1}; ESI-HRMS (*m/z*): $[M–BF_4]^+$ calcd for $C_{21}H_{25}N_3I$ 446.1088, found 446.1115.

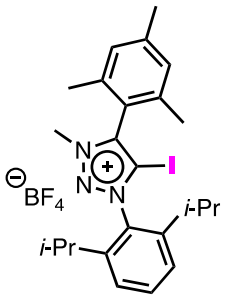
5-Iodo-3-methyl-1,4-bis(2,4,6-trimethylphenyl)-1*H*-1,2,3-triazolium tetrafluoroborate (3c).



3c

White solid (0.39 g, 74%); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.10 (s, 2H), 7.08 (s, 2H), 4.25 (s, 3H), 2.42 (s, 3H), 2.39 (s, 3H), 2.09 (s, 6H), 2.04 (s, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 148.4, 143.4, 143.3, 138.3, 135.0, 131.1, 130.1, 129.7, 117.4, 91.8, 39.6, 21.5, 21.5, 19.6, 17.3 ppm; ^{19}F NMR (470 MHz, $CDCl_3$) δ: 8.7 ppm; IR (KBr): 2923.6, 2383.6, 1611.2, 1544.7, 1458.9, 1282.7, 1323.9, 1288.2, 1219.8, 1060.7, 852.4, 774.3, 732.8, 563.1, 517.8 cm^{-1}; ESI-HRMS (*m/z*): $[M–BF_4]^+$ calcd for $C_{21}H_{25}N_3I$ 446.1088, found 446.1113.

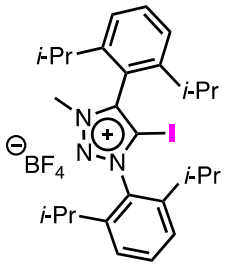
1-(2,6-Diisopropylphenyl)-5-iodo-3-methyl-4-(2,4,6-trimethylphenyl)-1*H*-1,2,3-triazolium tetrafluoroborate (3d).



3d

White solid (0.40 g, 69%); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.69 (t, *J* = 7.8 Hz, 1H), 7.43 (d, *J* = 7.8 Hz, 2H), 7.11 (s, 2H), 4.31 (s, 3H), 2.40 (s, 3H), 2.19–2.06 (m, 8H), 1.28 (d, *J* = 6.8 Hz, 6H), 1.22 (d, *J* = 6.8 Hz, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 148.5, 145.8, 143.5, 138.3, 133.6, 130.8, 129.9, 125.2, 117.3, 93.4, 39.9, 29.5, 24.8, 23.1, 21.5, 19.6 ppm; ^{19}F NMR (470 MHz, $CDCl_3$) δ: 8.3 ppm; IR (KBr): 2967.9, 2929.3, 2378.8, 1612.2, 1458.9, 1387.5, 1318.1, 1285.3, 1214.9, 1063.6, 860.1, 811.9, 763.7, 520.7 cm^{-1}; ESI-HRMS (*m/z*): $[M–BF_4]^+$ calcd for $C_{24}H_{31}N_3I$ 488.1557, found 488.1538.

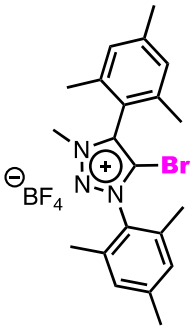
1,4-Bis(2,6-diisopropylphenyl)-5-iodo-3-methyl-1*H*-1,2,3-triazolium tetrafluoroborate (3e).



3e

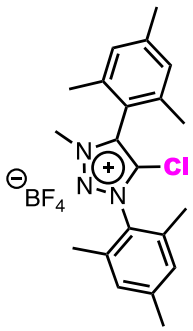
White solid (0.53 g, 86%); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.74–7.65 (m, 2H), 7.44 (d, *J* = 7.7 Hz, 2H), 7.43 (d, *J* = 7.7 Hz, 2H), 4.35 (s, 3H), 2.26 (sep, *J* = 6.8 Hz, 2H), 2.16 (sep, *J* = 6.8 Hz, 2H), 1.32–1.22 (m, 24H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 149.4, 148.1, 145.7, 133.9, 133.7, 130.8, 125.3, 124.9, 117.8, 95.0, 40.3, 32.4, 29.6, 24.9, 24.7, 24.1, 23.2 ppm; ^{19}F NMR (470 MHz, $CDCl_3$) δ: 8.1 ppm; IR (KBr): 3423.0, 2965.0, 2383.6, 2228.3, 1465.6, 1389.5, 1368.3, 1283.4, 1066.4, 810.9, 790.7, 757.9, 630.6, 592.0, 571.8, 545.8, 513.9, 500.4, 479.2, 469.6, 460.9, 455.1, 445.5, 435.8, 410.8 cm^{-1}; ESI-HRMS (*m/z*): $[M–BF_4]^+$ calcd for $C_{27}H_{37}N_3I$ 530.2027, found 530.2022.

5-Bromo-3-methyl-1,4-bis(2,4,6-trimethylphenyl)-1*H*-1,2,3-triazolium tetrafluoroborate (3f).



3f

White solid (0.050 g, 79%); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.12 (s, 2H), 7.10 (s, 2H), 4.31 (s, 3H), 2.42 (s, 3H), 2.39 (s, 3H), 2.17 (s, 6H), 2.11 (s, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 143.6, 143.5, 143.3, 138.7, 135.3, 130.2, 129.8, 129.5, 119.3, 116.4, 40.5, 21.5, 21.5, 19.8, 17.4 ppm; ^{19}F NMR (470 MHz, $CDCl_3$) δ: 8.6 ppm; IR (KBr): 3449.1, 2922.6, 2382.6, 1611.2, 1561.1, 1458.9, 1382.7, 1325.8, 849.5, 800.3, 563.1, 520.7 cm^{-1}; ESI-HRMS (*m/z*): $[M–BF_4]^+$ calcd for $C_{21}H_{25}N_3Br$ 398.1226, found 398.1250.

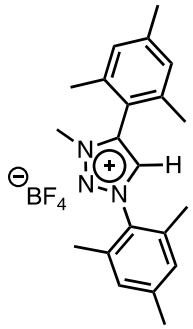


3g

5-Chloro-3-methyl-1,4-bis(2,4,6-trimethylphenyl)-1*H*-1,2,3-triazolium tetrafluoroborate (3g).

White solid (0.20 g, 78%); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.12 (s, 2H), 7.10 (s, 2H), 4.31 (s, 3H), 2.42 (s, 3H), 2.40 (s, 3H), 2.19 (s, 6H), 2.14 (s, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 143.7, 143.6, 140.2, 138.9, 135.5, 131.4, 130.2, 129.8, 128.5, 115.8, 40.1, 21.5, 21.4, 19.6, 17.1 ppm; ^{19}F NMR (470 MHz, $CDCl_3$) δ: 8.6 ppm; IR (KBr): 3423.0, 2923.6, 2384.6, 2346.9, 1611.2, 1576.5, 1293.0, 1229.4, 1057.8, 859.1, 755.0, 616.1, 565.0, 520.7 cm^{-1}; ESI-HRMS (*m/z*): $[M-BF_4]^+$ calcd for $C_{21}H_{25}N_3Cl$ 354.1732, found 354.1729.

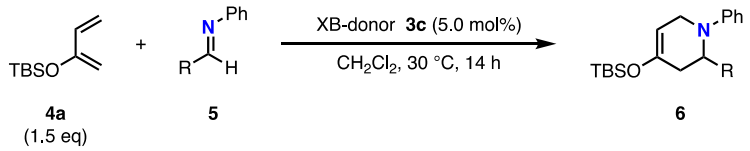
3-Methyl-1,4-bis(2,4,6-trimethylphenyl)-1*H*-1,2,3-triazolium tetrafluoroborate (3h, CAS Registry Number 1263862-40-3)



3h

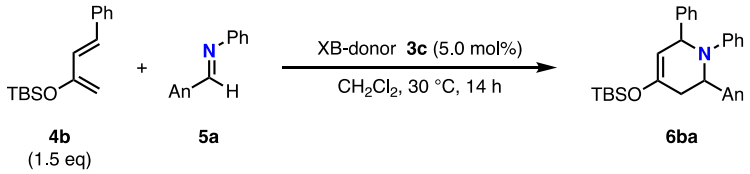
White solid (0.11 g, 82%); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.49 (s, 1H), 7.07 (s, 2H), 7.05 (s, 2H), 4.15 (s, 3H), 2.38 (s, 3H), 2.36 (s, 3H), 2.13 (s, 6H), 2.11 (s, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 143.0, 142.8, 142.8, 138.3, 134.5, 131.7, 131.4, 130.0, 129.6, 117.3, 38.2, 21.5, 21.4, 20.0, 17.2 ppm; ^{19}F NMR (470 MHz, $CDCl_3$) δ: 8.6 ppm.

General procedure for the reaction of 4a and 5



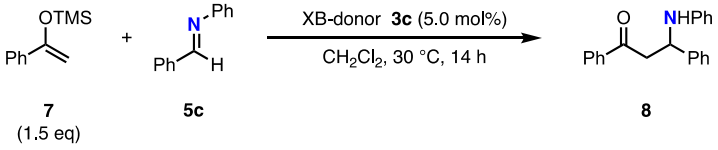
To a 1-mL vial were added sequentially **4a** (55 mg, 0.30 mmol), **5** (0.20 mmol), XB-donor **3c** (5.3 mg, 0.010 mmol), and dichloromethane (0.20 mL). The vial was purged with argon, and the reaction mixture was stirred at 30 °C for 14 h. And then, the solvent was removed under reduced pressure, affording an yellowish oil. Purification by flash silica gel column chromatography gave the corresponding product **6**.

Procedure for the reaction of 4b and 5a



To a 1-mL vial were added sequentially **4b** (78 mg, 0.30 mmol), **5a** (42 mg, 0.20 mmol), XB-donor **3c** (5.3 mg, 0.010 mmol), and dichloromethane (0.20 mL). The vial was purged with argon, and the reaction mixture was stirred at 30 °C for 14 h. And then, the solvent was removed under reduced pressure, affording an yellowish oil. Purification by flash silica gel column chromatography using hexane/ethyl acetate = 20/1 as an eluent gave **6ba** in 80% yield (0.075 g, dr = 3.3:1).

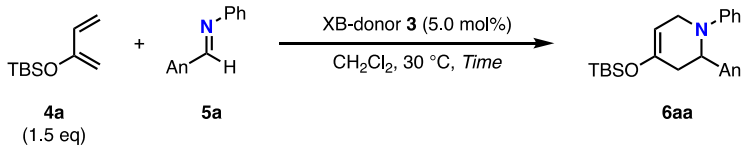
Procedure for the reaction of 7 and 5c



To a 1-mL vial were added sequentially **7** (57 mg, 0.30 mmol), **5c** (36 mg, 0.20 mmol), XB-donor **3c** (5.3 mg, 0.010 mmol), and dichloromethane (0.20 mL). The vial was

purged with argon, and the reaction mixture was stirred at 30 °C for 14 h. And then, the solvent was removed under reduced pressure, affording an yellowish oil. Purification by flash silica gel column chromatography using hexane/ethyl acetate = 10/1 as an eluent gave **8** in 39% yield (0.024 g).

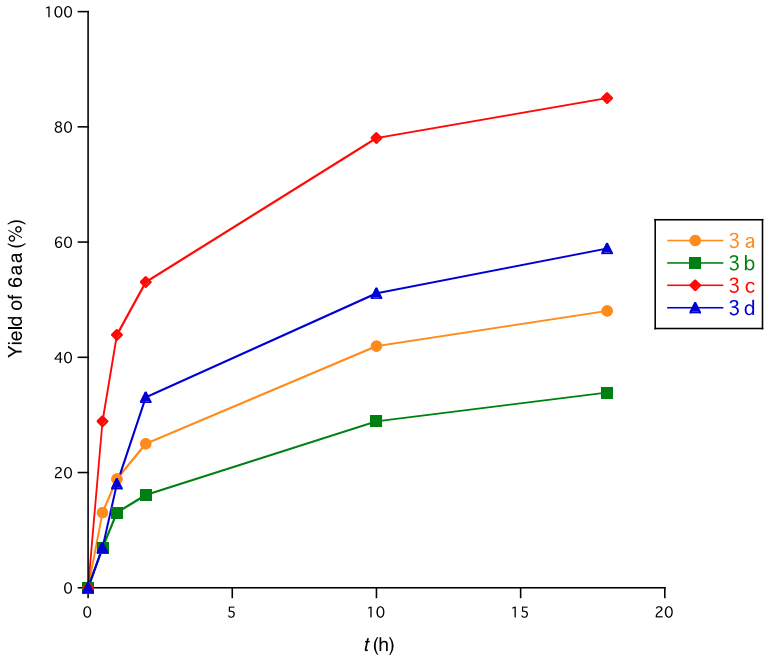
Table S1. Reaction profile using various XB-donors **3**.[a,b]



4a (1.5 eq) **5a** **6aa**

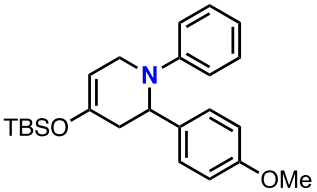
3 / *Time* (h)	0	0.5	1	2	10	18
3a	0%	13%	19%	25%	42%	48%
3b	19%	7%	13%	16%	29%	34%
3c	25%	29%	44%	53%	78%	85%
3d	42%	7%	18%	33%	51%	59%

[a] Standard conditions: **4a** (0.30 mmol), **5a** (0.20 mmol), XB-donor **3** (10 μmol) in CH_2Cl_2 (0.20 mL) at 30 °C. [b] Yields were determined by ^1H NMR.



Characterization Data of Products

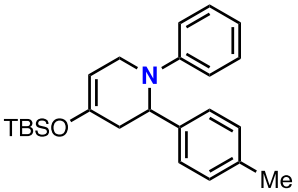
4-(*tert*-Butyldimethylsilyloxy)-2-(4-methoxyphenyl)-1-phenyl-4,5-didehydropiperidine (6aa).



6aa

Yellow solid (0.071 g, 90%); Mp. 64.0–65.0 °C; R_f 0.29 (hexane/ethyl acetate = 20/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.22 (dd, *J* = 8.7, 7.5 Hz, 2H), 7.12 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.80–6.74 (m, 3H), 5.17–5.10 (m, 1H), 4.96 (dd, *J* = 5.9, 3.6 Hz, 1H), 3.92 (ddd, *J* = 16, 3.6, 3.6 Hz, 1H), 3.76 (s, 3H), 3.60 (ddd, *J* = 16, 3.9, 2.5 Hz, 1H), 2.94–2.82 (m, 1H), 2.40 (d, *J* = 16 Hz, 1H), 0.92 (s, 9H), 0.12 (s, 3H), 0.09 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 158.5, 149.7, 148.0, 133.8, 129.2, 128.2, 118.2, 115.4, 113.6, 101.0, 56.4, 55.3, 43.9, 35.5, 25.8, 18.1, –4.3, –4.3 ppm; IR (KBr): 3036.4, 3003.6, 2953.5, 2932.2, 2887.9, 2857.0, 1719.2, 1676.8, 1595.8, 1510.0, 1460.8, 1377.9, 1307.5, 1250.6, 1217.8, 1198.5, 1180.2, 1113.7, 1034.6, 879.4, 833.1, 809.9, 797.4, 777.2, 753.1, 693.3, 564.1, 529.4 cm^{-1}; ESI-HRMS (*m/z*): $[M+H]^+$ calcd for $C_{24}H_{34}NO_2Si$ 396.2359, found 396.2378.

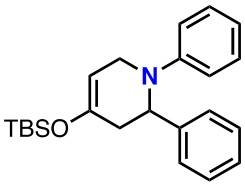
4-(*tert*-Butyldimethylsilyloxy)-2-(4-methylphenyl)-1-phenyl-4,5-didehydropiperidine (6ab).



6ab

Yellow solid (0.061 g, 81%); Mp. 54.6–55.0 °C; R_f 0.51 (hexane/ethyl acetate = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.24 (dd, *J* = 8.5, 7.2 Hz, 2H), 7.11 (d, *J* = 8.2 Hz, 2H), 7.06 (d, *J* = 8.2 Hz, 2H), 6.89 (d, *J* = 8.5 Hz, 2H), 6.78 (t, *J* = 7.2 Hz, 1H), 5.19–5.12 (m,1H), 4.98 (dd, *J* = 5.7, 3.3 Hz, 1H), 3.96 (ddd, *J* = 16, 3.3, 3.3 Hz, 1H), 3.64 (ddd, *J* = 16, 4.7, 2.9 Hz, 1H), 2.94–2.85 (m, 1H), 2.44 (dd, *J* = 17, 1.4 Hz, 1H), 2.31 (s, 3H), 0.93 (s, 9H), 0.13 (s, 3H), 0.09 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 149.6, 147.9, 138.7, 136.4, 129.2, 129.0, 127.0, 118.1, 115.2, 101.0, 56.5, 44.1, 35.5, 25.8, 21.1, 18.1, –4.3, –4.3 ppm; IR (KBr): 2956.3, 2929.3, 2857.0, 2801.1, 1675.8, 1595.8, 1500.4, 1460.8, 1389.5, 1373.1, 1253.5, 1216.9, 1198.5, 1175.4, 1033.7, 992.2, 938.2, 879.4, 839.8, 821.5, 518.8, 449.3 cm^{-1}; ESI-HRMS (*m/z*): $[M+H]^+$ calcd for $C_{24}H_{34}NOSi$ 380.2410, found 380.2405.

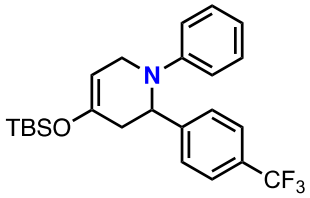
4-(*tert*-Butyldimethylsilyloxy)-1,2-diphenyl-4,5-didehydropiperidine (6ac, CAS Registry Number 919080-26-5).



6ac

Yellow oil (0.045 g, 62%); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.31—7.16 (m, 7H), 6.88 (d, *J* = 8.1 Hz, 2H), 6.78 (t, *J* = 7.2 Hz, 1H), 5.24–5.15 (m, 1H), 4.99 (dd, *J* = 5.7, 3.4 Hz, 1H), 4.00 (ddd, *J* = 16, 3.4, 3.4 Hz, 1H), 3.68 (ddd, *J* = 16, 5.0, 3.2, Hz, 1H), 3.00–2.87 (m, 1H), 2.45 (dd, *J* = 17, 1.2 Hz, 1H), 0.93 (s, 9H), 0.12 (s, 3H), 0.07 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 149.5, 147.8, 141.9, 129.2, 128.3, 127.1, 126.9, 118.1, 115.1, 101.0, 56.8, 44.2, 35.6, 25.8, 18.1, –4.3, –4.4 ppm.

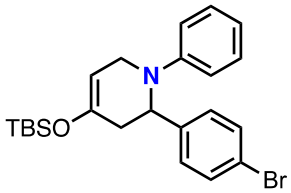
4-(*tert*-Butyldimethylsilyloxy)-2-(4-trifluoromethylphenyl)-1-phenyl-4,5-didehydropiperidine (6ad).



6ad

Yellow oil (0.062 g, 71%); R_f 0.48 (hexane/ethyl acetate = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.51 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 7.24 (dd, *J* = 8.7, 7.4 Hz, 2H), 6.85 (dd, *J* = 8.7, 0.8 Hz, 2H), 6.80 (tt, *J* = 7.4, 0.8 Hz, 1H), 5.22–5.17 (m, 1H), 4.99 (dd, *J* = 5.8, 3.5 Hz, 1H), 4.00 (ddd, *J* = 16, 3.5, 3.5 Hz, 1H), 3.66 (ddd, *J* = 16, 4.8, 3.2 Hz, 1H), 2.99–2.90 (m, 1H), 2.42 (dd, *J* = 16, 1.3 Hz, 1H), 0.91 (s, 9H), 0.12 (s, 3H), 0.06 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 149.2, 147.5, 146.2, 129.4, 129.2 (q, *J* = 32 Hz), 127.4, 125.3 (q, *J* = 3.8 Hz), 124.3 (q, *J* = 272 Hz), 118.6, 115.0, 100.8, 56.6, 44.3, 35.6, 25.7, 18.1, –4.3, –4.4 ppm; ^{19}F NMR (470 MHz, $CDCl_3$) δ: 99.3 ppm; IR (KBr): 3063.4, 2956.3, 2931.3, 1895.6, 2858.0, 1686.4, 1617.9, 1597.7, 1504.2, 1473.4, 1414.5, 1377.9, 1325.8, 1258.3, 1220.7, 1165.8, 1126.2, 1068.4, 1038.5, 1165.8, 1126.2, 1068.4, 1038.5, 1017.3, 990.3, 781.0, 749.2, 689.4, 661.5, 608.4 cm^{-1}; ESI-HRMS (*m/z*): $[M+H]^+$ calcd for $C_{24}H_{31}F_3NOSi$ 434.2127, found 434.2133.

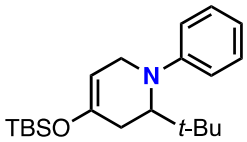
2-(4-Bromophenyl)-4-(*tert*-butyldimethylsilyloxy)-1-phenyl-4,5-didehydropiperidine (6ae).



6ae

Yellow solid (0.062 g, 70%); Mp. 40.0–40.2 °C; R_f 0.43 (hexane/ethyl acetate = 20/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.35 (d, *J* = 8.6 Hz, 2H), 7.21 (dd, *J* = 8.8, 7.3 Hz, 2H), 7.06 (d, *J* = 8.6 Hz, 2H), 6.83 (dd, *J* = 8.8, 0.9 Hz, 2H), 6.77 (tt, *J* = 7.3, 0.9 Hz, 1H), 5.13–5.07 (m, 1H), 4.95 (dd, *J* = 5.7, 3.4 Hz, 1H), 3.93 (ddd, *J* = 16, 3.4, 3.4 Hz, 1H), 3.60 (ddd, *J* = 16, 4.9, 3.1 Hz, 1H), 2.94–2.84 (m,1H), 2.36 (dd, *J* = 17, 1.2 Hz, 1H), 0.90 (s, 9H), 0.11 (s, 3H), 0.06 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 149.3, 147.6, 140.9, 131.4, 129.3, 128.9, 120.8, 118.5, 115.3, 100.9, 56.5, 44.2, 35.5, 25.8, 18.1, –4.3, –4.3 ppm; IR (KBr): 3064.3, 3036.4, 3021.9, 2956.3, 2929.3, 2886.0, 2857.0, 2811.7, 1673.0, 1595.8, 1576.5, 1560.1, 1498.4, 1488.8, 1473.4, 1390.4, 1374.0, 1348.0, 1294.0, 1259.3, 1217.8, 1197.6, 1177.3, 1151.3, 1074.2, 1031.7, 1010.5, 991.2, 938.2, 924.7, 876.5, 824.4, 795.5, 750.2, 710.6, 693.3, 659.5, 552.5, 535.2 cm^{-1}; ESI-HRMS (*m/z*): $[M+H]^+$ calcd for $C_{23}H_{31}NOSiBr$ 444.1358, found 444.1374.

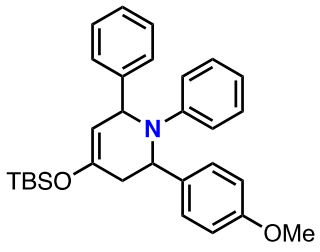
2-(*tert*-Butyl)-4-(*tert*-butyldimethylsilyloxy)-1-phenyl-4,5-didehydropiperidine (6ag).



6ag

Yellow oil (0.024 g, 35%); R_f 0.51 (hexane/ethyl acetate = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.19 (dd, *J* = 8.6, 7.2 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 6.66 (t, *J* = 7.2 Hz, 1H), 4.82 (dd, *J* = 5.6, 3.2 Hz, 1H), 3.98 (d, *J* = 7.5 Hz, 1H), 3.88–3.82 (m, 2H), 2.50–2.41 (m, 1H), 2.07 (d, *J* = 17 Hz, 1H), 0.93 (s, 9H), 0.91 (s, 9H), 0.16 (s, 3H), 0.14 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 151.8, 148.8, 129.1, 116.7, 114.4, 100.2, 59.8, 44.4, 39.3, 29.9, 28.9, 25.9, 18.2, –4.1, –4.3 ppm; IR (KBr): 3059.5, 2957.3, 2896.6, 2858.0, 2801.1, 1691.3, 1596.8, 1502.3, 1472.4, 1403.0, 1369.2, 1320.0, 1254.5, 1227.5, 1197.6, 1033.7, 990.3, 940.1, 877.5, 838.9, 792.6, 778.1, 748.2, 720.3, 690.4, 408.8 cm^{-1}; ESI-HRMS (*m/z*): $[M+H]^+$ calcd for $C_{21}H_{36}NOSi$ 346.2566, found 346.2554.

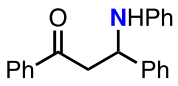
4-(*tert*-Butyldimethylsilyloxy)-2-(4-methoxyphenyl)-1,6-diphenyl-4,5-didehydropiperidine (6ba, CAS Registry Number 919080-14-1).



6ba

Colorless oil (0.075 g, 80%, dr = 3.3:1); major diastereomer; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.31 (d, *J* = 8.7 Hz, 2H), 7.28–7.23 (m, 3H), 7.07 (d, *J* = 8.7 Hz, 2H), 7.00 (dd, *J* = 8.7, 8.7 Hz, 2H), 6.78–6.72 (m, 3H), 6.79–6.59 (m, 2H), 5.20–5.14 (m, 2H), 5.14–5.10 (m, 1H), 3.74 (s, 3H), 2.98 (dd, *J* = 16, 5.7 Hz, 1H), 2.42 (dd, *J* = 16, 4.0 Hz, 1H), 0.82 (s, 9H), –0.01 (s, 3H), –0.07 (s, 3H) ppm; minor diastereomer; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.22–7.11 (m, 7H), 6.91 (dd, *J* = 7.8, 7.8 Hz, 2H), 6.79–6.59 (m, 5H), 4.99–4.95 (m, 1H), 4.71 (dd, *J* = 4.5, 2.5 Hz, 1H), 4.60 (dd, *J* = 9.8, 4.1 Hz, 1H), 3.68 (s, 3H), 2.68 (dddd, *J* = 17, 9.8, 2.5, 2.5 Hz, 1H), 2.36 (ddd, *J* = 17, 4.1, 1.9, Hz, 1H), 0.91 (s, 9H), 0.15 (s, 6H) ppm.

1,3-Diphenyl-3-(*N*-phenylamino)propan-1-one (8, CAS Registry Number 742-43-8).



8

White solid (0.024 g, 39%); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.90 (dd, *J* = 8.2, 1.2 Hz, 2H), 7.55 (tt, *J* = 7.5, 1.2 Hz, 1H), 7.48–7.39 (m, 4H), 7.32 (dd, *J* = 7.5, 7.5 Hz, 2H), 7.23 (tt, *J* = 7.5, 1.2 Hz, 1H), 7.08 (dd, *J* = 8.5, 7.4 Hz, 2H), 6.66 (tt, *J* = 7.4, 0.9 Hz, 1H), 6.58–6.52 (dd, *J* = 8.5, 0.9 Hz, 2H), 5.00 (dd, *J* = 7.7, 5.2 Hz, 1H), 4.55 (br, 1H), 3.51 (dd, *J* = 16, 5.2 Hz, 1H), 3.42 (dd, *J* = 16, 7.7 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 198.4, 147.1, 143.1, 136.8, 133.6, 129.2, 129.0, 128.8, 128.4, 127.5, 126.5, 117.9, 113.9, 54.9, 46.4 ppm.

Theoretical Study

The geometries of the isolated cation of **3a-3e** were optimized by using density functional theory (DFT) at the M06-2X/LANL2DZ for I and 6-31+G(d,p) for the other atoms. The optimized structures, HOMO, and LUMO of the isolated cation of **3a-3e** are shown in Figure S1, S2, and S3, respectively. All DFT calculations were carried out with *Gaussian 09* package.[9]

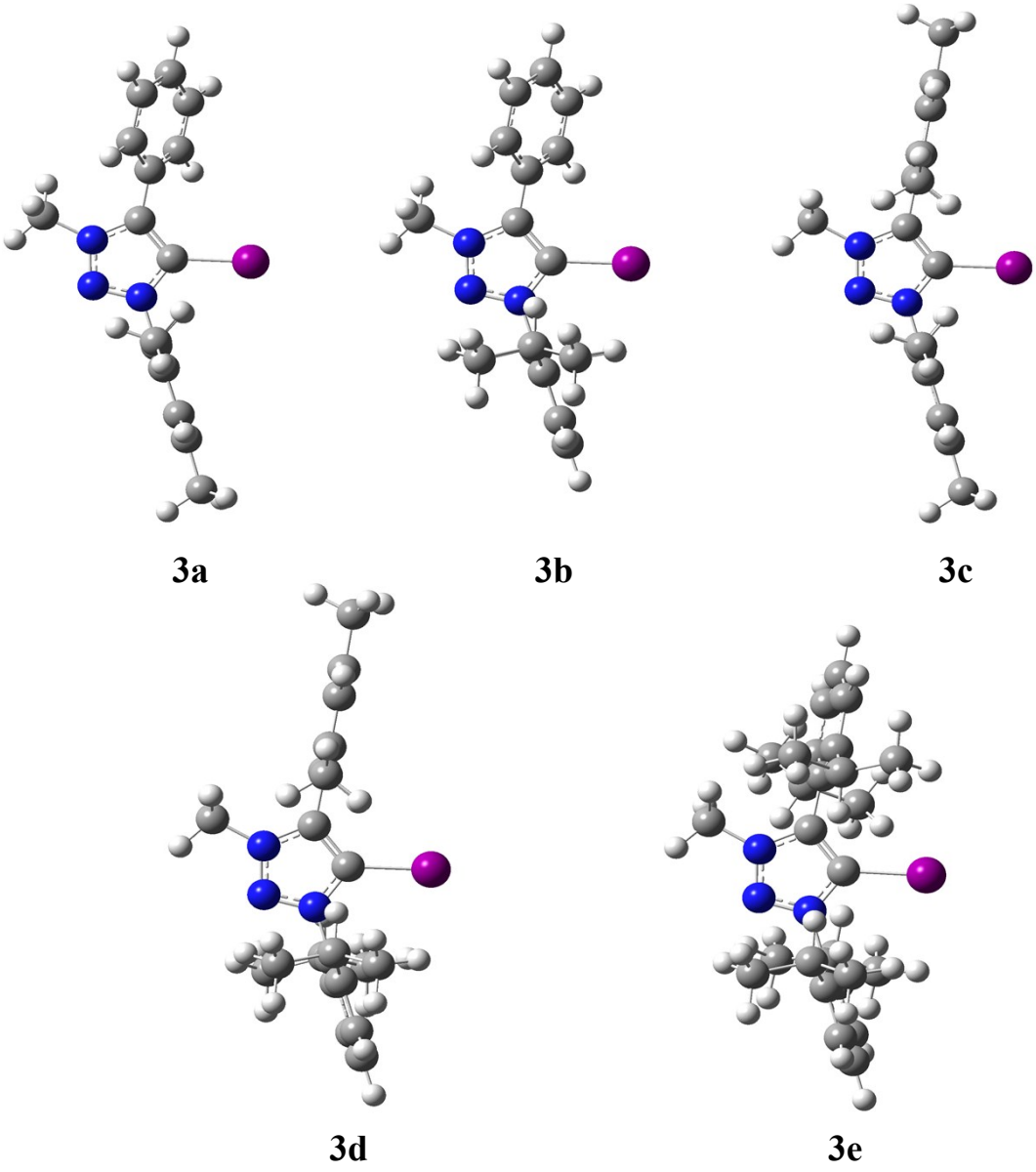
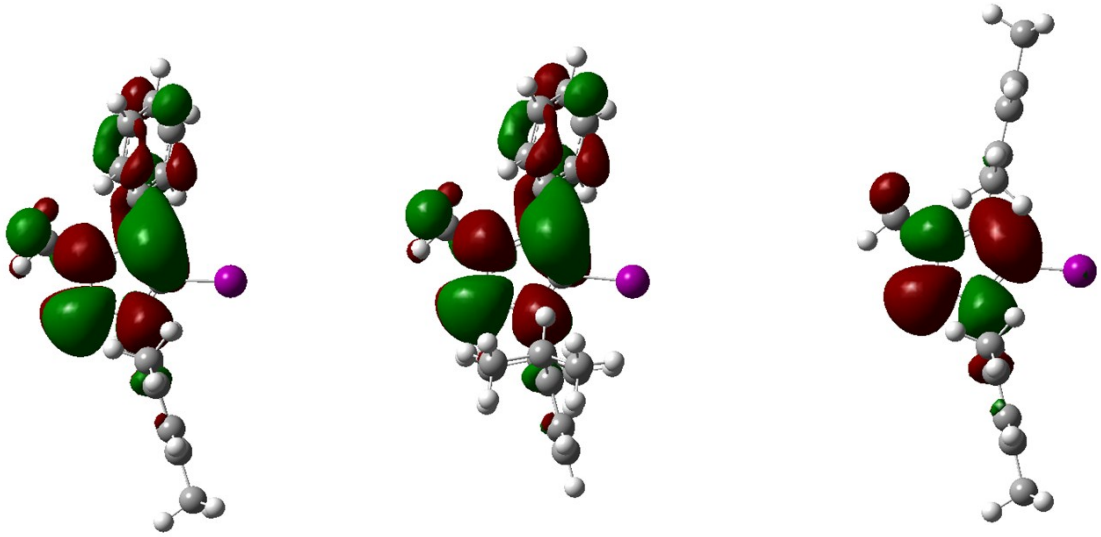
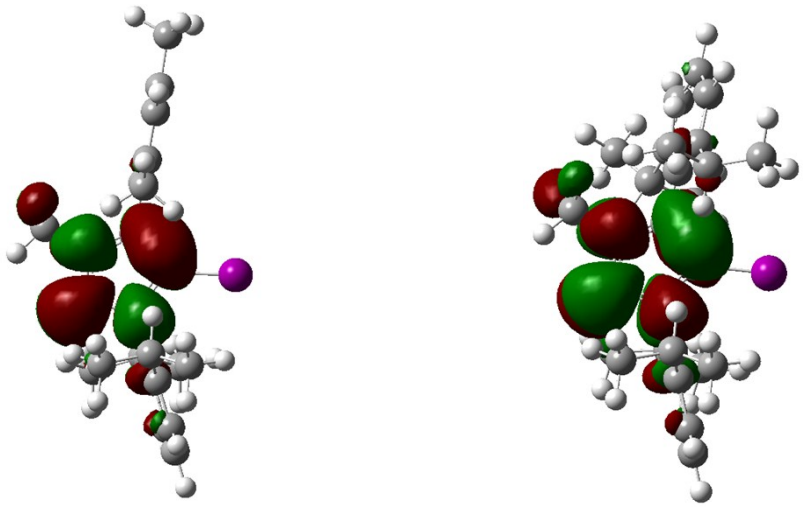


Fig. S1 DFT-optimized structure of cationic parts in **3a-3e**.

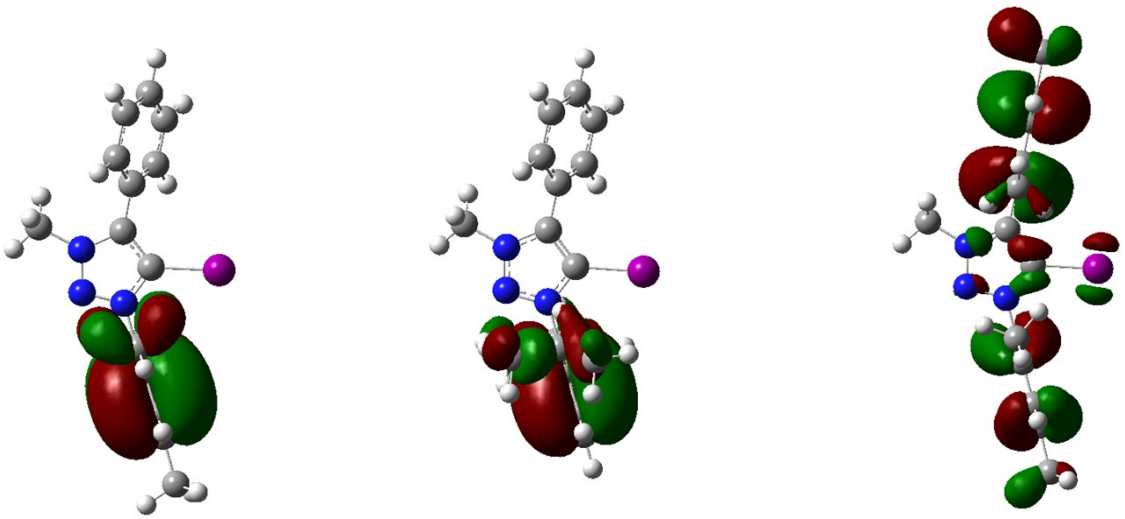


3a **3b** **3c**

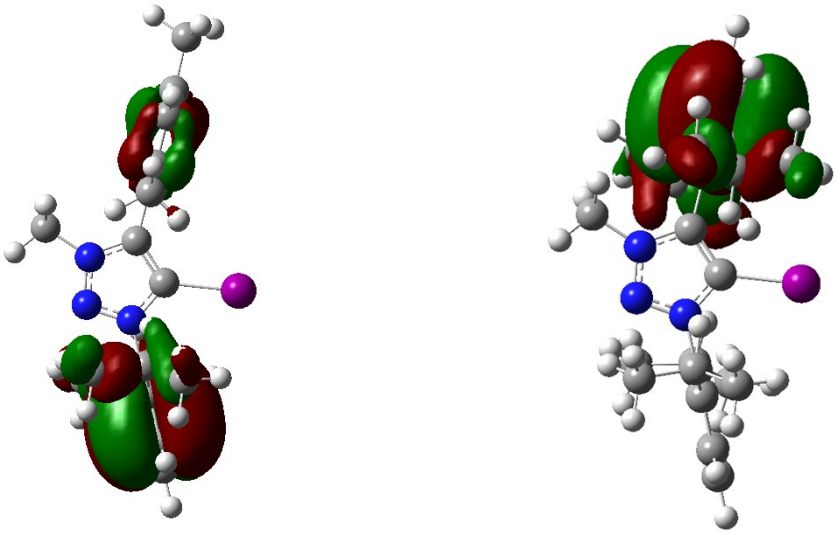


3d **3e**

Fig. S2 LUMO of cationic parts in **3a-3e**.



3a **3b** **3c**



3d **3e**

Fig. S3 HOMO of cationic parts in **3a**-**3e**.

Moreover, we optimized the structures of imine **5a** and the halogen-bonding complex **3c-5a** by the DFT calculation analysis. According to the previous report by Huber,[10] we used the M06-2X/def2-TZVPP and corresponding pseudopotential for iodine which included the D3 dispersion correction by Grimme[11] and the SMD solvation model[12] with the predefined parameters for dichloromethane.

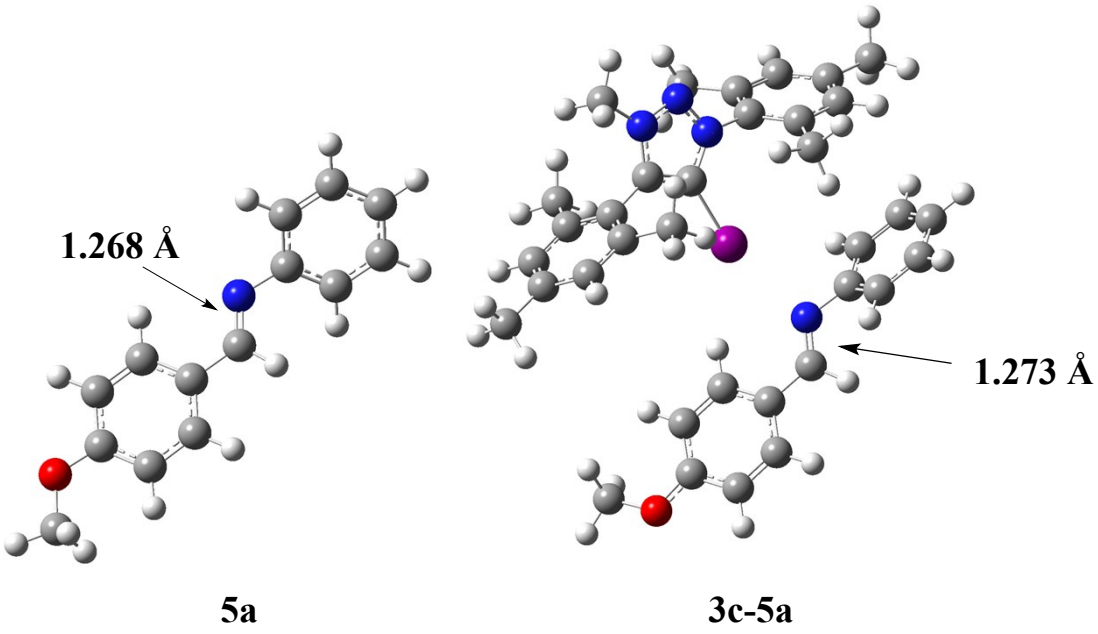


Fig. S4 The optimized structures of Imine **5a** and the calculated halogen-bonding complex **3c-5a**.

Cartesian coordinates of the reported structures

3a

C	-0.41551900	0.08153000	0.02857500
C	-1.57406800	0.83167800	0.10146300
N	0.60729700	0.97532100	0.12400500
N	0.17625300	2.20587400	0.24847000
N	-1.12738000	2.11536600	0.23750600
C	-1.92742200	3.33549700	0.38462600
H	-2.80476500	3.09766800	0.98518000
H	-1.30230700	4.07498300	0.88172200
H	-2.23033100	3.69492900	-0.59910600
C	-2.99178300	0.44547800	0.06139000
C	-3.83990900	0.97499300	-0.91791800
C	-3.48171100	-0.46736900	1.00186500
C	-5.17765300	0.59336900	-0.95058200
C	-4.82079700	-0.84419300	0.96249200
C	-5.66674900	-0.31442500	-0.01118100
H	-5.83557500	0.99666900	-1.71275700
H	-5.20399200	-1.54924500	1.69217300
C	2.02827600	0.70341900	0.08203800
C	2.67536400	0.41532600	1.28451000
C	2.65427100	0.72478700	-1.16585700
C	4.04042200	0.14301900	1.20706600
C	4.01880700	0.44489400	-1.18349600
C	4.72571000	0.15707900	-0.01121700
H	4.58199100	-0.08480300	2.12137700
H	4.54378100	0.45154400	-2.13527700
I	-0.15073800	-1.94734000	-0.22253100
H	-2.81950700	-0.87170800	1.76228200
H	-3.45178300	1.66267300	-1.66459000
H	-6.70981600	-0.61175200	-0.04014600
C	1.92878400	0.39717500	2.59234300
H	1.42980300	1.35356900	2.77845200
H	1.16624800	-0.39049000	2.60452100
H	2.61323300	0.20843500	3.42018800
C	1.88249200	1.03002100	-2.42264100

H	1.08690500	0.29451400	-2.58889400
H	1.42099700	2.02159800	-2.37316500
H	2.54139900	1.00896800	-3.29131900
C	6.20693600	-0.10675400	-0.05983500
H	6.75992100	0.83769100	-0.02748800
H	6.53019500	-0.71166800	0.78968100
H	6.48682300	-0.62366200	-0.98040600

3b

C	-0.51584300	-0.01070800	-0.03285700
C	-1.62816300	0.16664300	0.76812700
N	0.55725000	0.17382000	0.78376300
N	0.20160400	0.44755000	2.01293100
N	-1.10573800	0.43983300	2.00087500
C	-1.82768200	0.68972000	3.25236000
H	-2.72288800	0.06902900	3.26007700
H	-1.16101800	0.42192900	4.07006100
H	-2.09862900	1.74401200	3.31445100
C	-3.06654500	0.09161700	0.47579500
C	-3.90065300	1.18026400	0.75647700
C	-3.59355400	-1.07209600	-0.09452600
C	-5.26036100	1.09859300	0.47331000
C	-4.95447500	-1.14561000	-0.37608700
C	-5.78631800	-0.06326900	-0.09122700
H	-5.90653900	1.94363500	0.68536000
H	-5.36545800	-2.04888400	-0.81384700
C	1.96041000	0.09569800	0.42833600
C	2.57982400	-1.15571800	0.52451100
C	2.58172500	1.27066500	-0.01001700
C	3.92950500	-1.20253000	0.17031900
C	3.93184000	1.16196800	-0.34910800
C	4.59551100	-0.05776500	-0.25722400
H	4.46629600	-2.14349200	0.22986300
H	4.47068000	2.04021000	-0.68903600
I	-0.35739100	-0.42516300	-2.04486600

H	-2.94391600	-1.91654000	-0.30732100
H	-3.48593900	2.09519400	1.17118100
H	-6.84673200	-0.12366500	-0.31268500
C	1.85272500	-2.38687800	1.03655000
H	0.77241700	-2.22336400	0.92698700
C	1.85404200	2.60211400	-0.07000700
H	0.77396000	2.40617400	-0.09847000
C	2.15162400	3.41627500	1.19839700
H	1.60731900	4.36494000	1.17840800
H	1.86907300	2.86827600	2.10249300
H	3.22129800	3.63992600	1.26242500
C	2.19776100	3.39990300	-1.33147200
H	3.23565100	3.74479400	-1.31729400
H	2.04644700	2.80428100	-2.23641100
H	1.56263500	4.28767600	-1.39161700
C	2.14918300	-2.58345400	2.53112200
H	1.86689100	-1.70300300	3.11642900
H	1.60435200	-3.45027700	2.91637000
H	3.21878900	-2.75890100	2.68446600
C	2.19811600	-3.64751700	0.23760000
H	2.04951100	-3.49726300	-0.83559000
H	3.23551000	-3.95329200	0.40075300
H	1.56288100	-4.47622900	0.56153900
H	5.64530000	-0.11743600	-0.52593800

3c

C	-0.0579200	0.0685310	0.0003090
C	1.0939970	0.8255450	0.0005990
N	-1.0884480	0.9588290	0.0008900
N	-0.6642580	2.1998330	0.0015080
N	0.6388210	2.1123220	0.0013330
C	1.4542600	3.3283710	0.0017660
H	2.0814220	3.3339680	-0.8903250
H	0.7721300	4.1763280	0.0020770
H	2.0814530	3.3333600	0.8938380
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3e

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5a

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3c-5a

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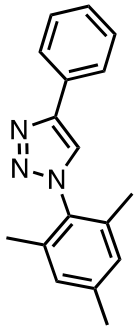
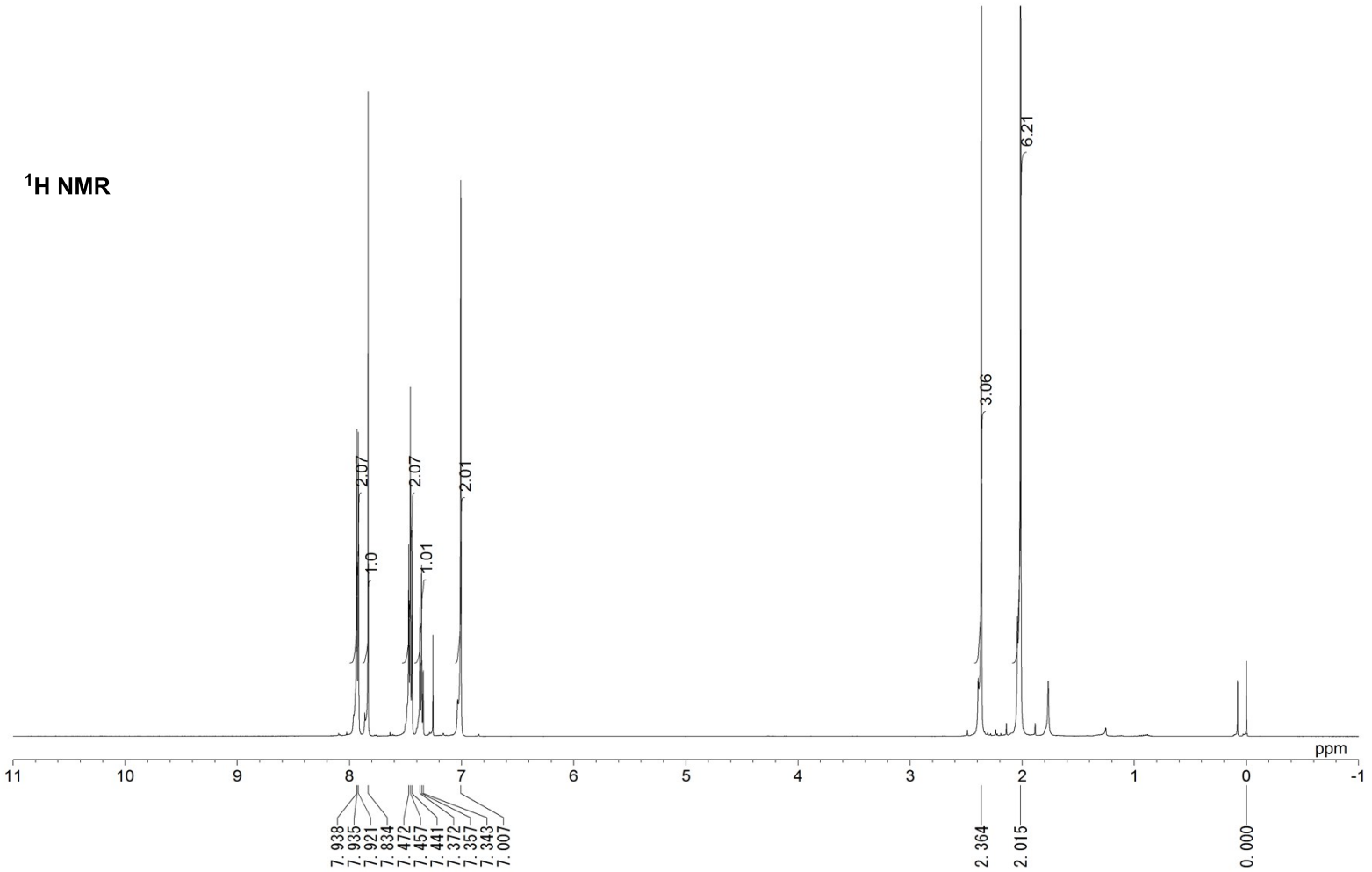
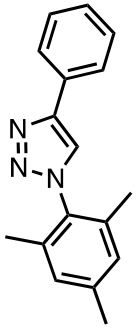
NMR Spectra Data



1a

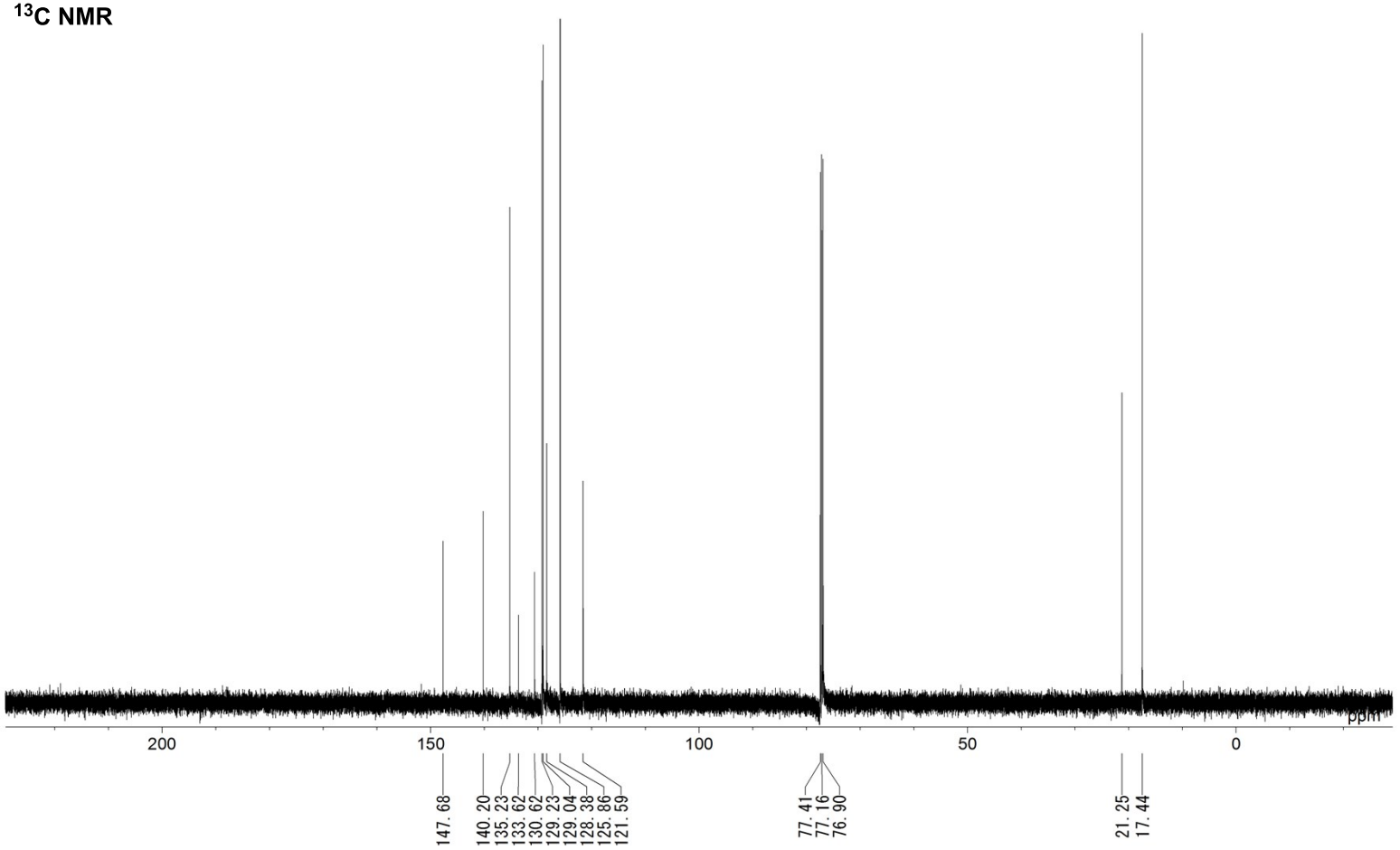
^{1}H NMR





1a

^{13}C NMR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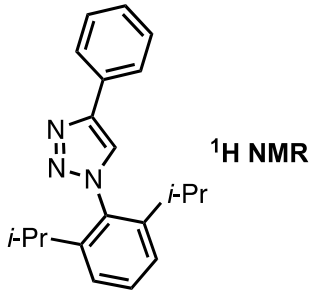
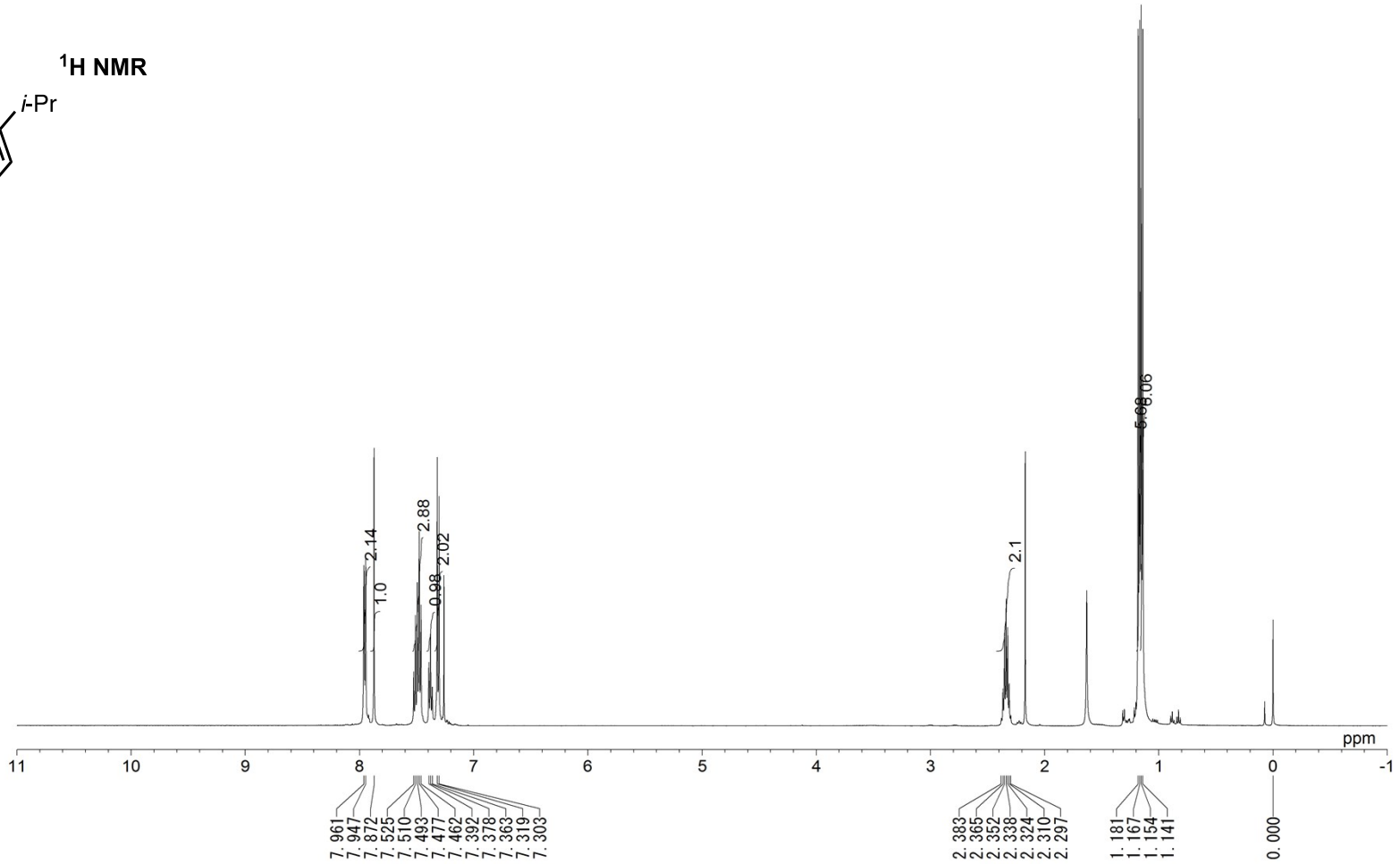


^{1}H NMR

1b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3
2
1
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7.525
7.510
7.493
7.477
7.462
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7.378
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7.319
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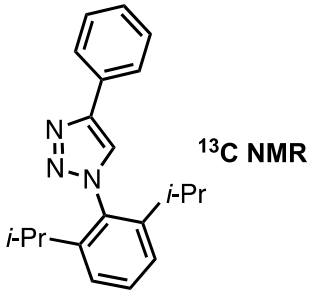
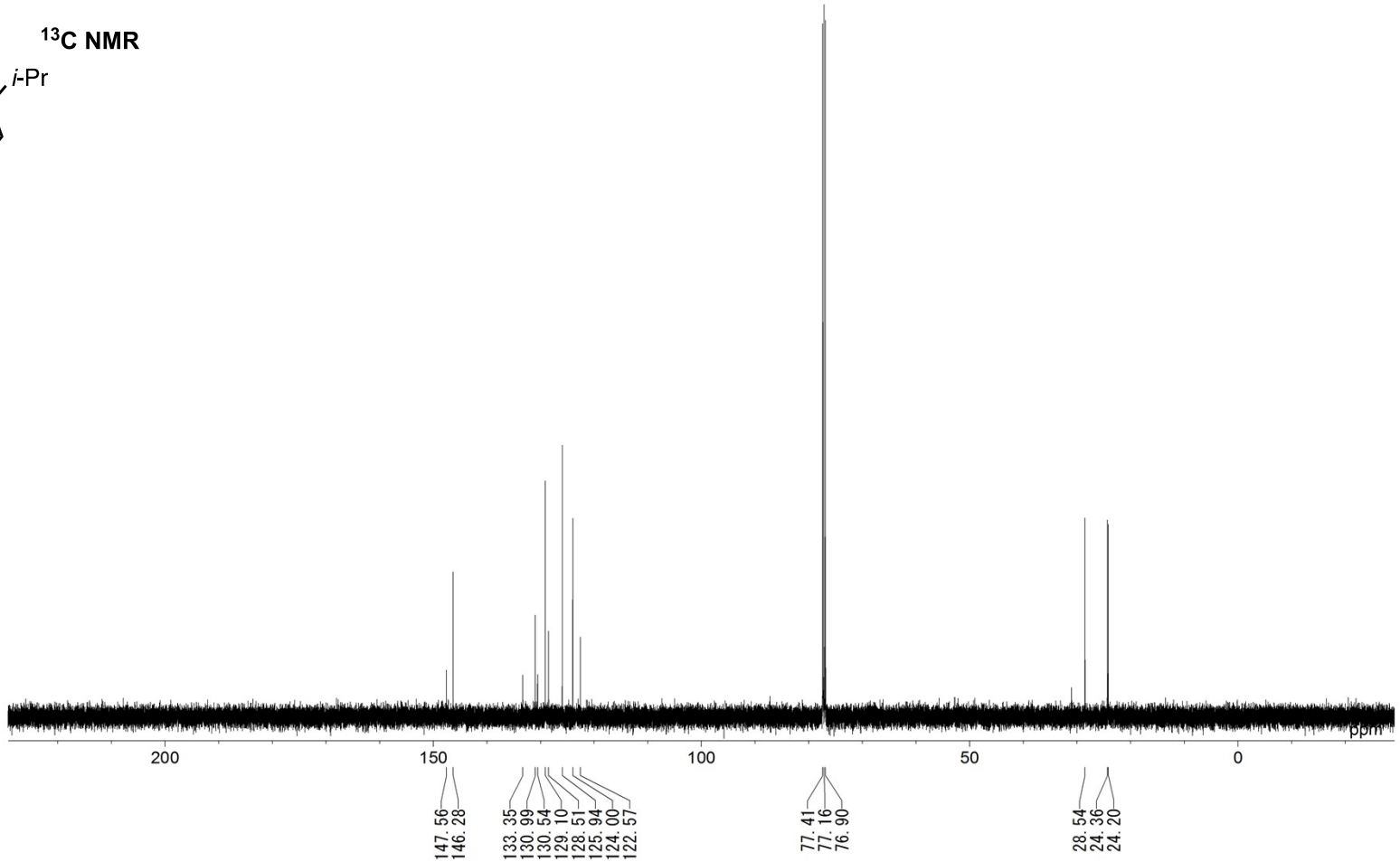

i-Pr
i-Pr

^{13}C NMR

1b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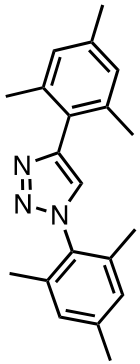
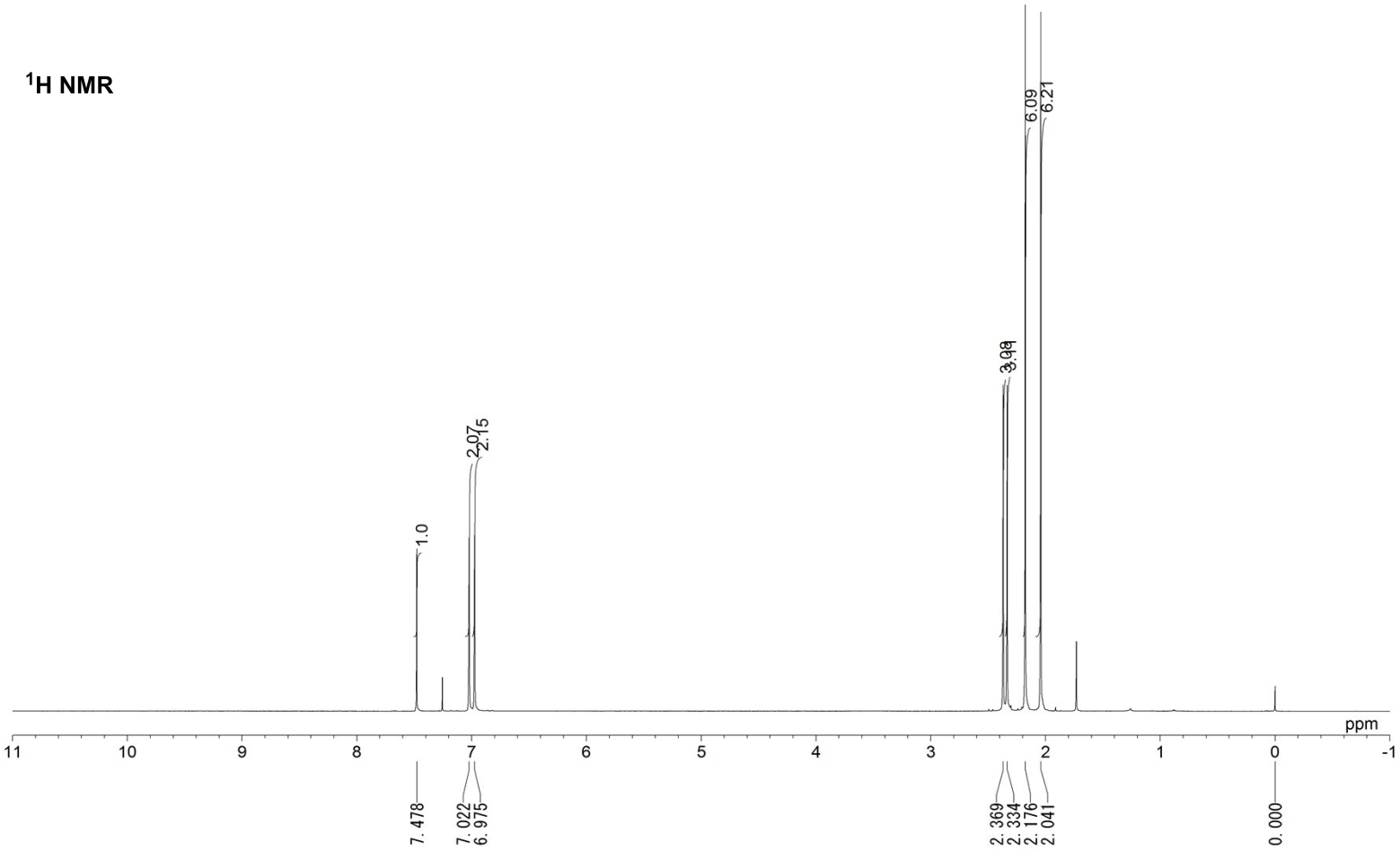


1c

^{1}H NMR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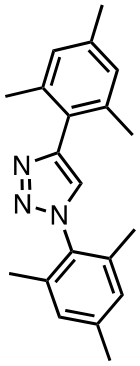
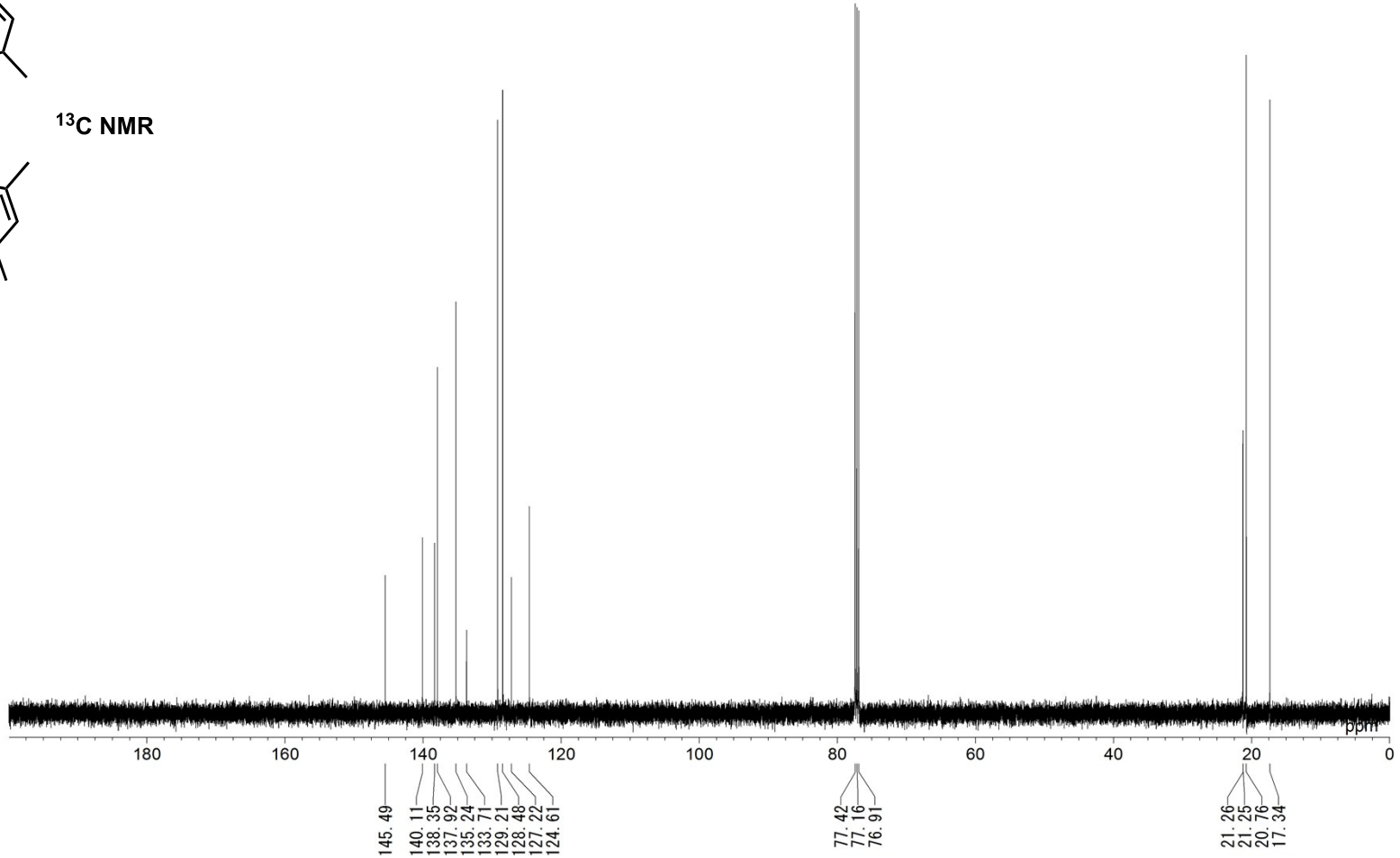
0.000



1c

^{13}C NMR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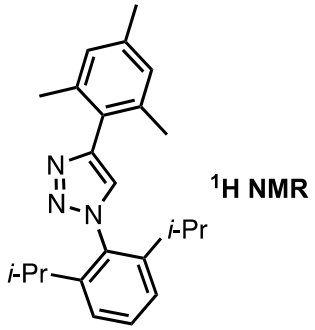
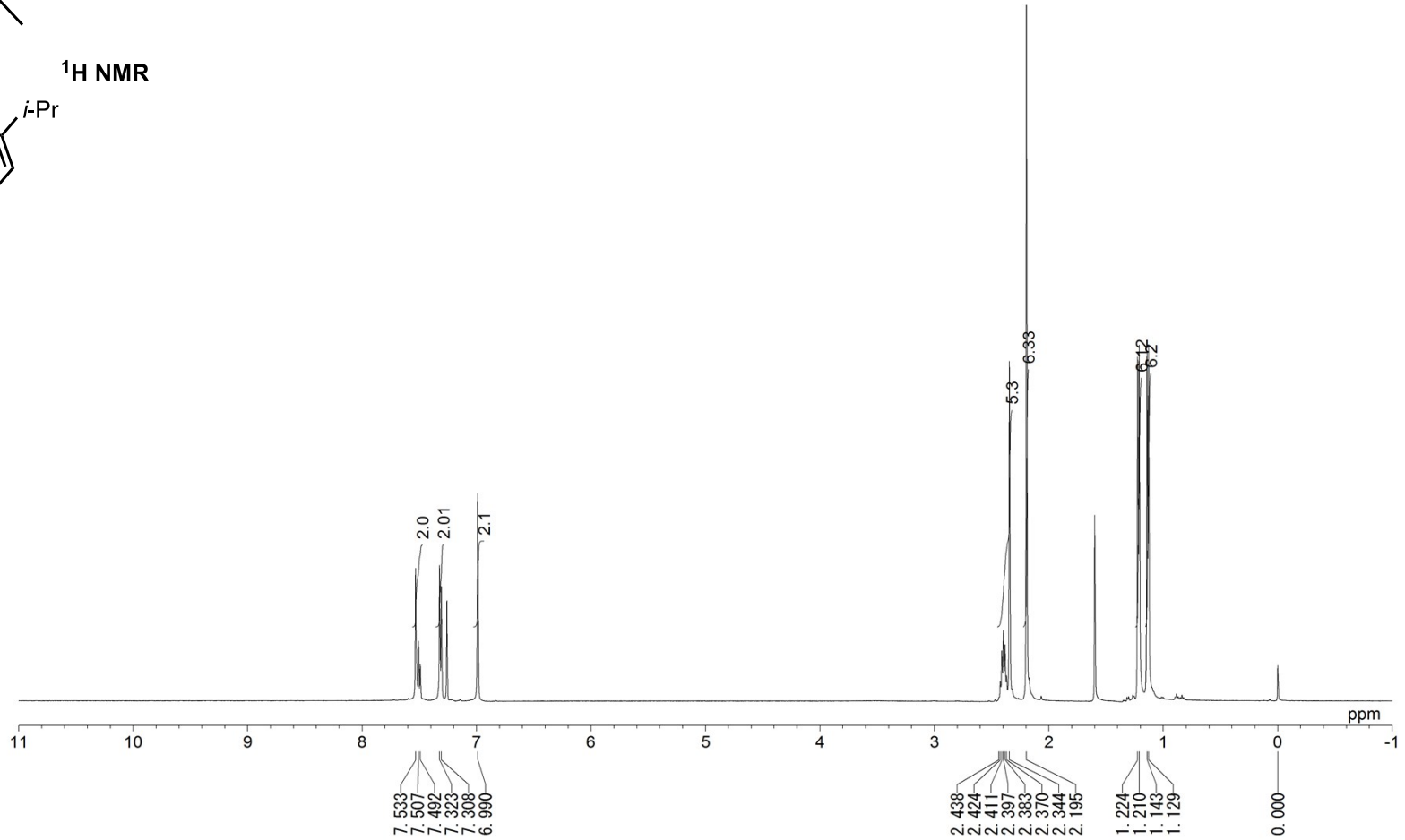
160
140
120
100
80
60
40
20
0
145. 49
140. 11
138. 35
137. 92
135. 24
133. 71
129. 21
128. 48
127. 22
124. 61
77. 42
77. 16
76. 91
21. 26
21. 25
20. 76
17. 34


N
N
N
i-Pr
i-Pr

^{1}H NMR

1d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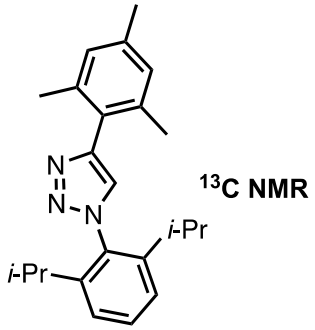
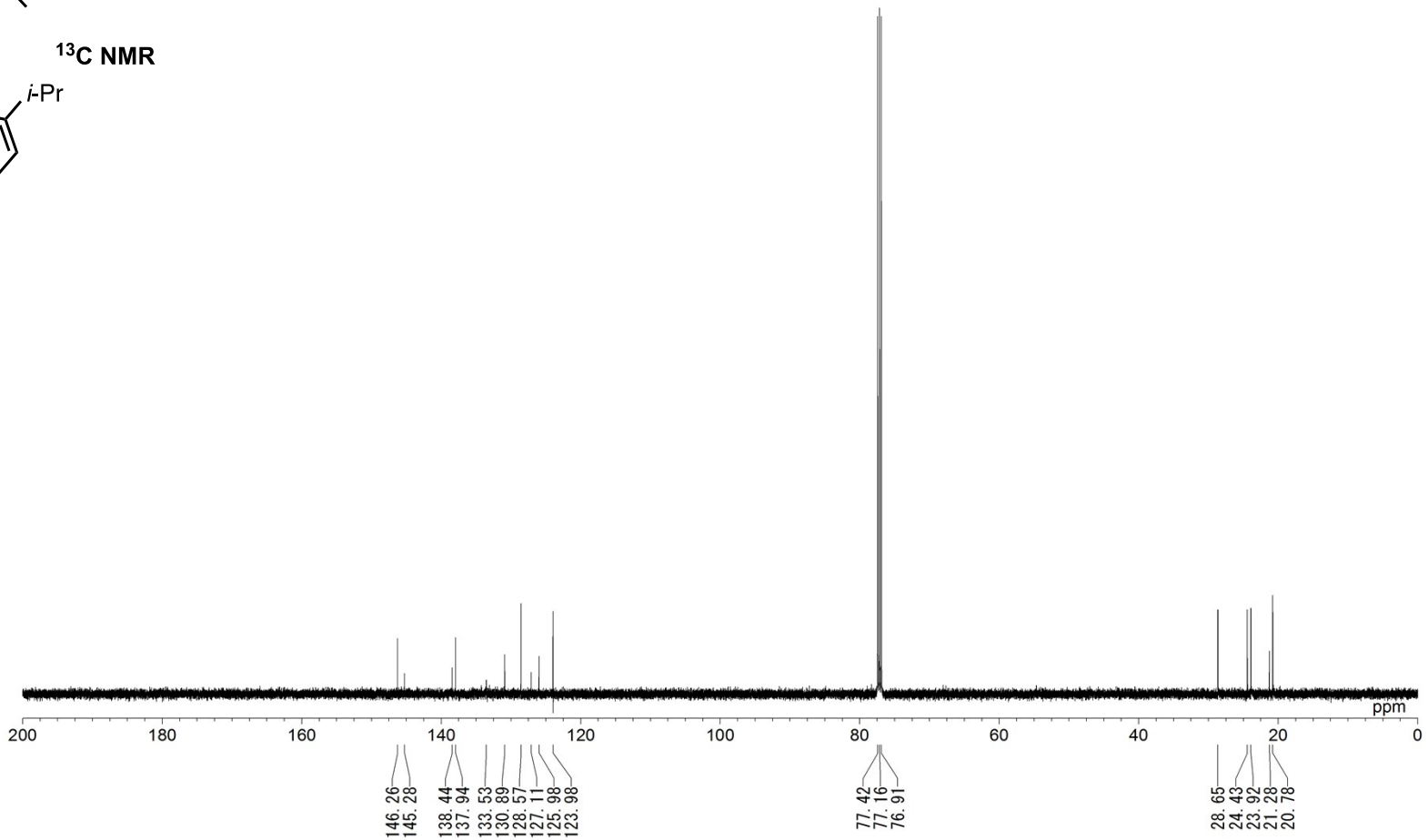
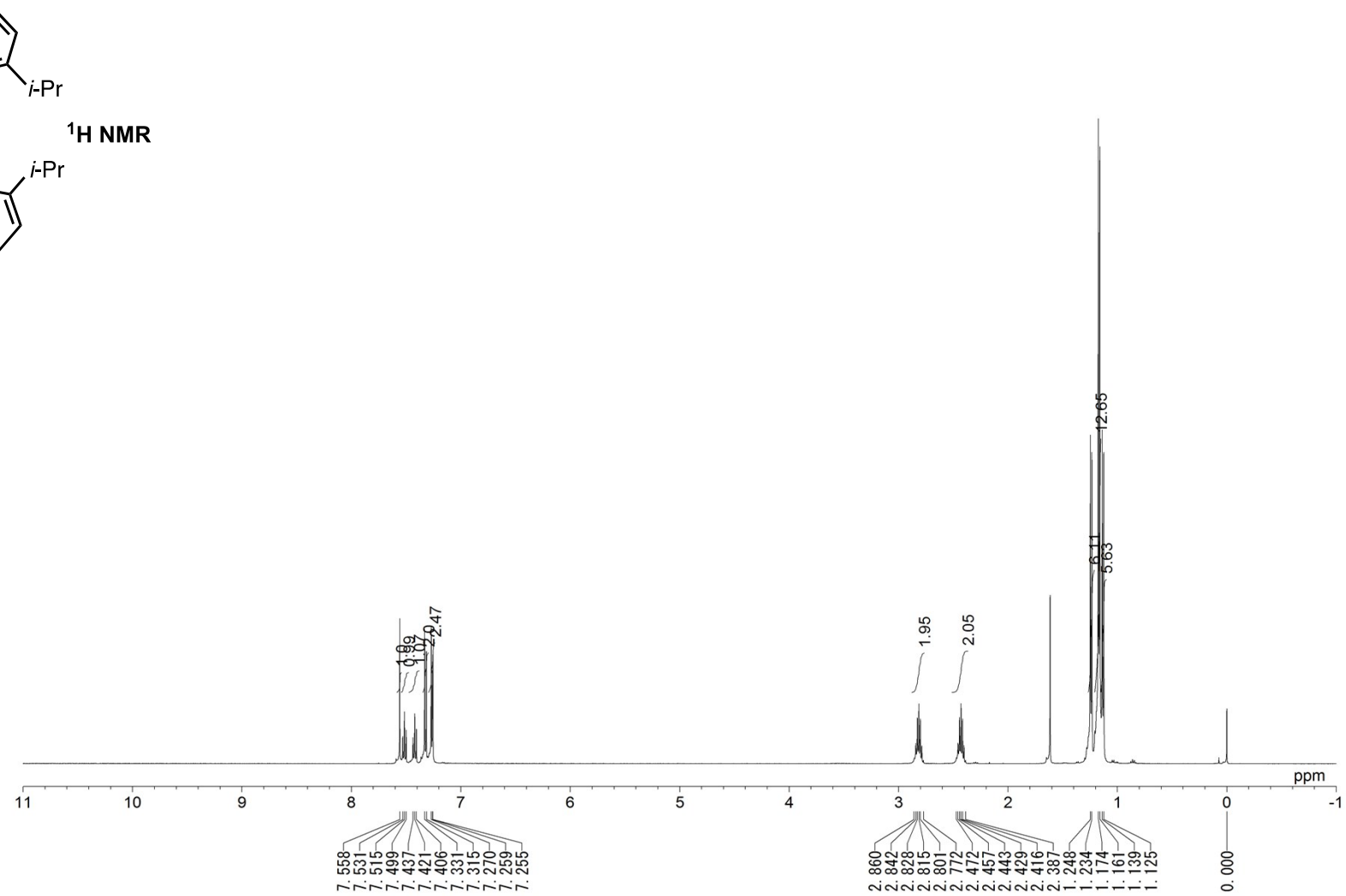
2.01
2.1
5.3
6.33
6.12
6.2
ppm
11
10
9
8
7
6
5
4
3
2
1
0
-1
7.533
7.507
7.492
7.323
7.308
6.990
2.438
2.424
2.411
2.397
2.383
2.370
2.344
2.195
1.224
1.210
1.143
1.129
0.000

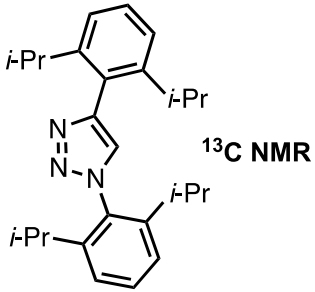

N
N
N
i-Pr
i-Pr

^{13}C NMR

1d

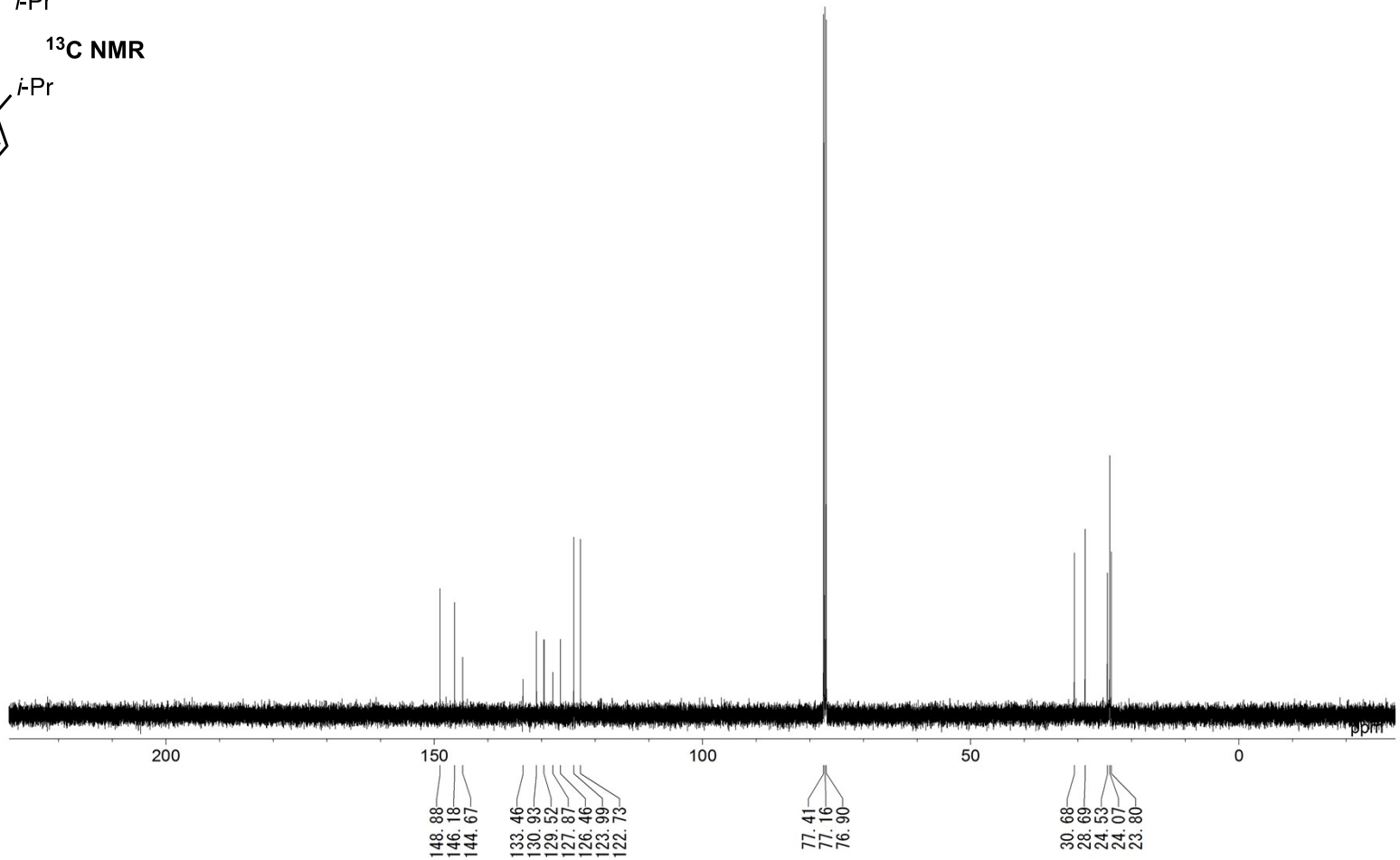

ppm
200
180
160
140
120
100
80
60
40
20
0
146.26
145.28
138.44
137.94
133.53
130.89
128.57
127.11
125.98
123.98
77.42
77.16
76.91
28.65
24.43
23.92
21.28
20.78


i-Pr
i-Pr
1H NMR
1.95
2.05
12.65
6.11
5.63
2.47
ppm
11
10
9
8
7
6
5
4
3
2
1
0
-1
7.558
7.531
7.515
7.499
7.437
7.421
7.406
7.331
7.315
7.270
7.259
7.255
2.860
2.842
2.828
2.815
2.801
2.772
2.472
2.457
2.443
2.429
2.416
2.387
1.248
1.234
1.174
1.161
1.139
1.125
0.000


i-Pr
i-Pr
N
N
N
i-Pr
i-Pr

^{13}C NMR

1e


ppm
200
150
100
50
0
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146. 18
144. 67
133. 46
130. 93
129. 52
127. 87
126. 46
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122. 73
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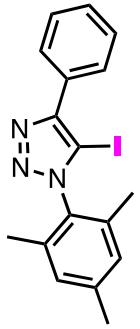
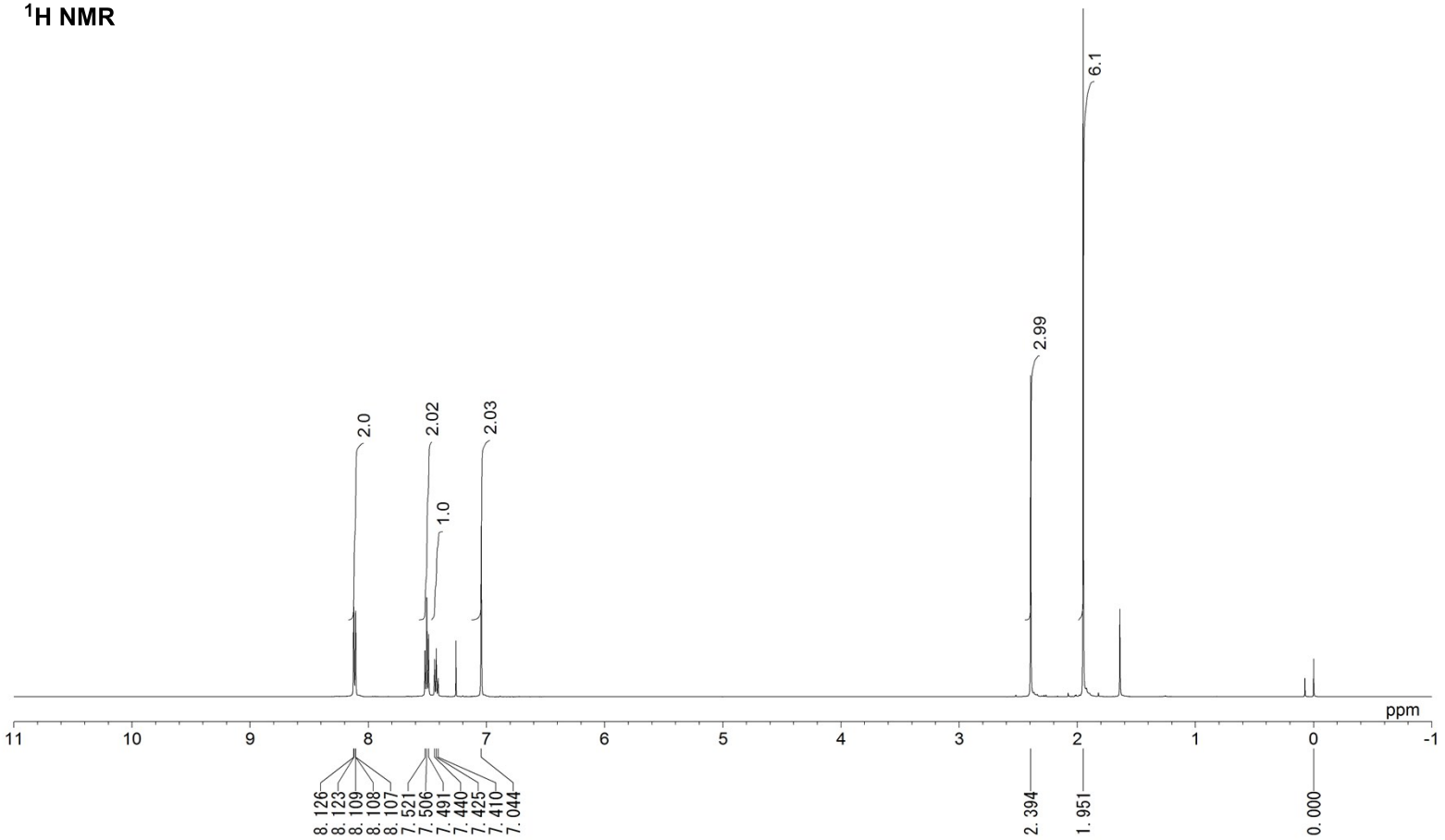
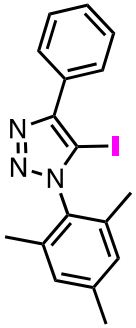
76. 90
30. 68
28. 69
24. 53
24. 07
23. 80



2a

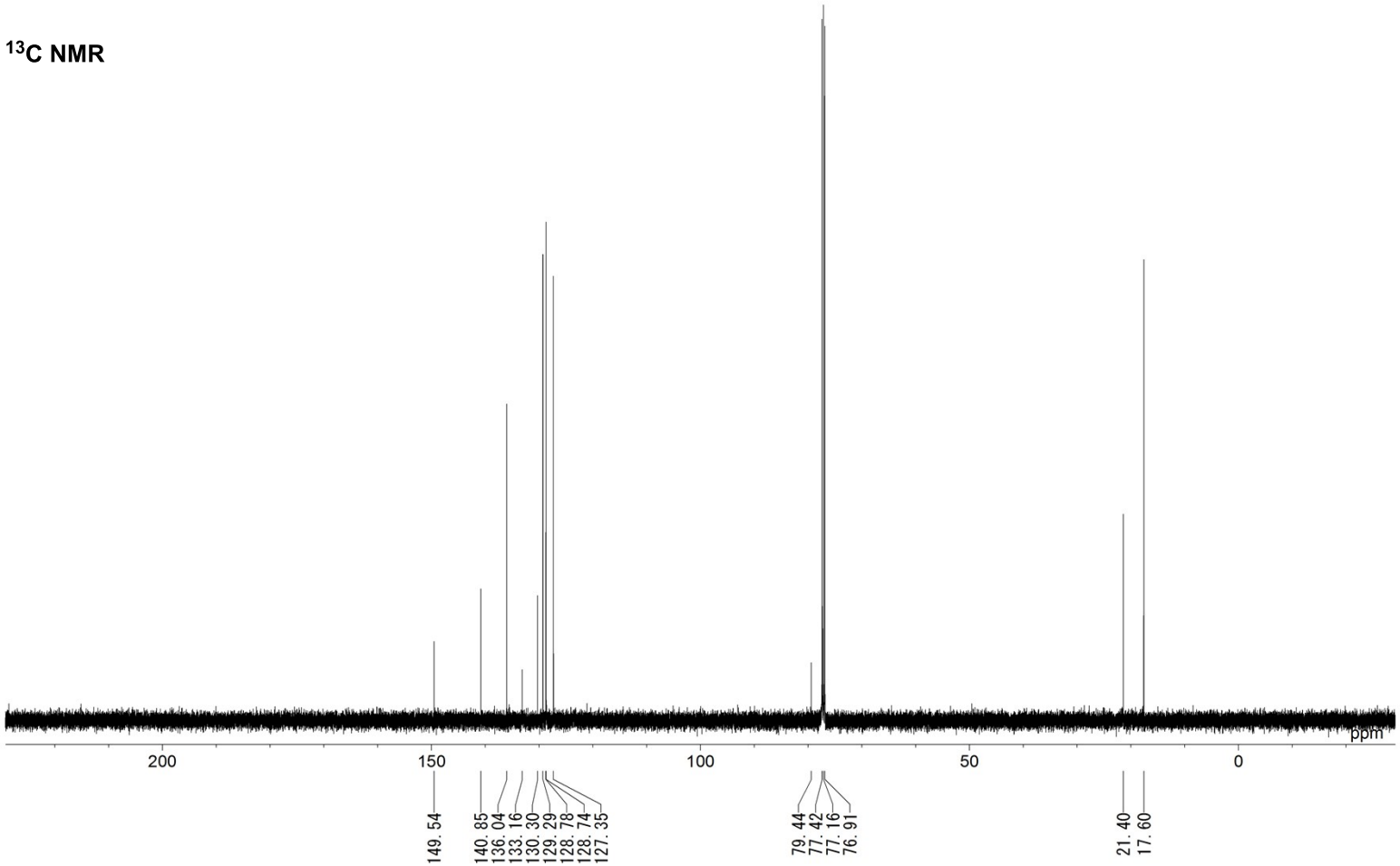
^{1}H NMR


2.0
2.02
1.0
2.03
2.99
6.1
ppm
11
10
9
8
7
6
5
4
3
2
1
0
-1
8.126
8.123
8.109
8.108
8.107
7.521
7.506
7.491
7.440
7.425
7.410
7.044
2.394
1.951
0.000



2a

^{13}C NMR


200
150
100
50
0
ppm
149.54
140.85
136.04
133.16
130.30
129.29
128.78
128.74
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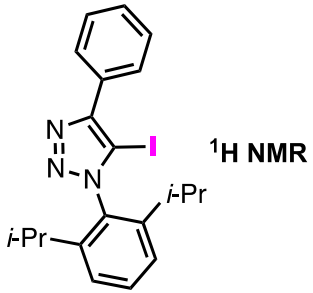
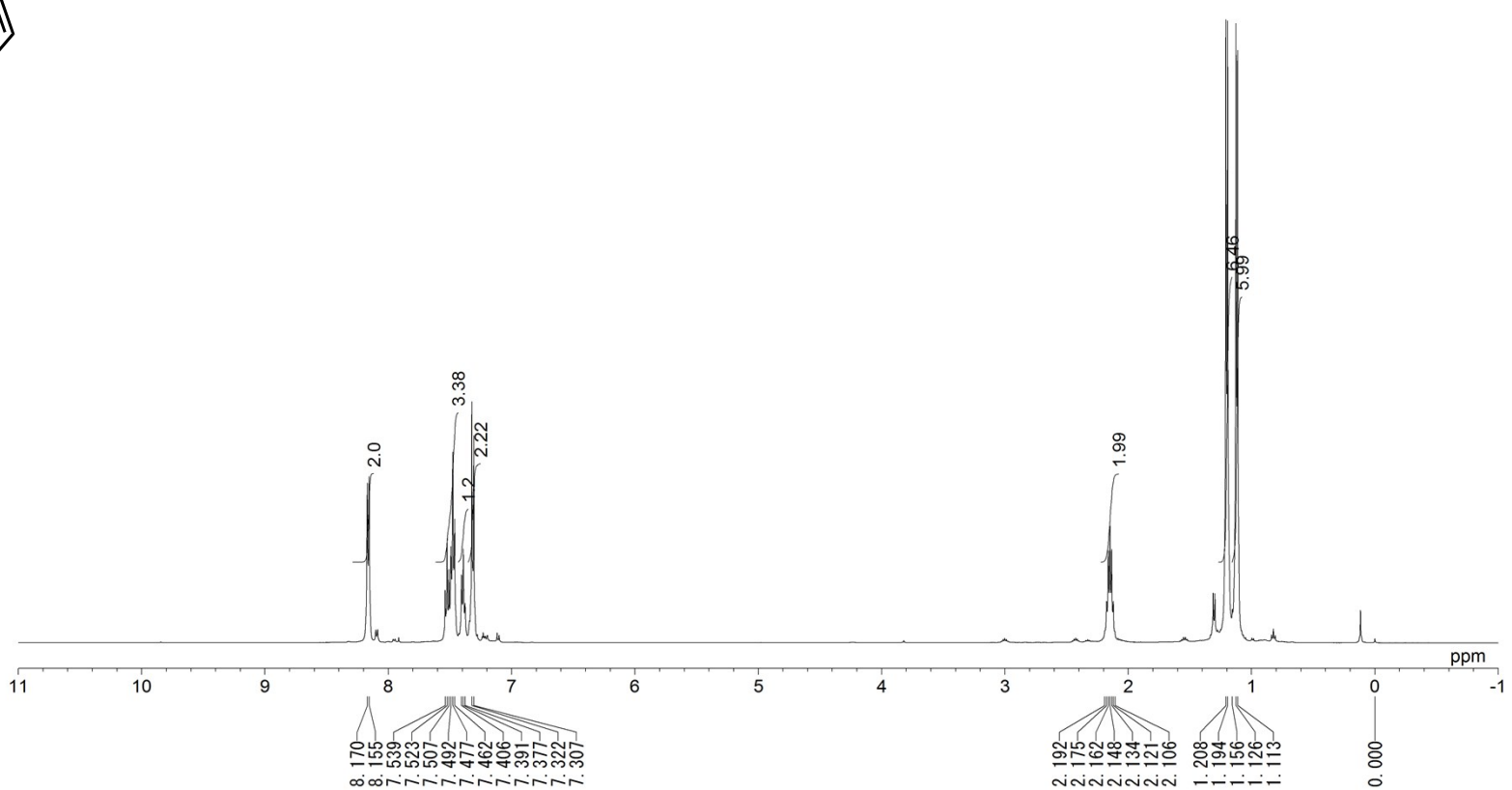
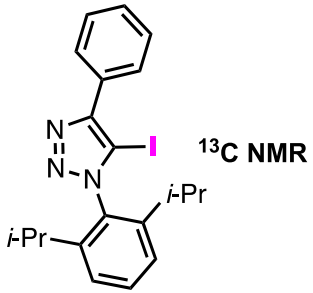
79.44
77.42
77.16
76.91
21.40
17.60



2b

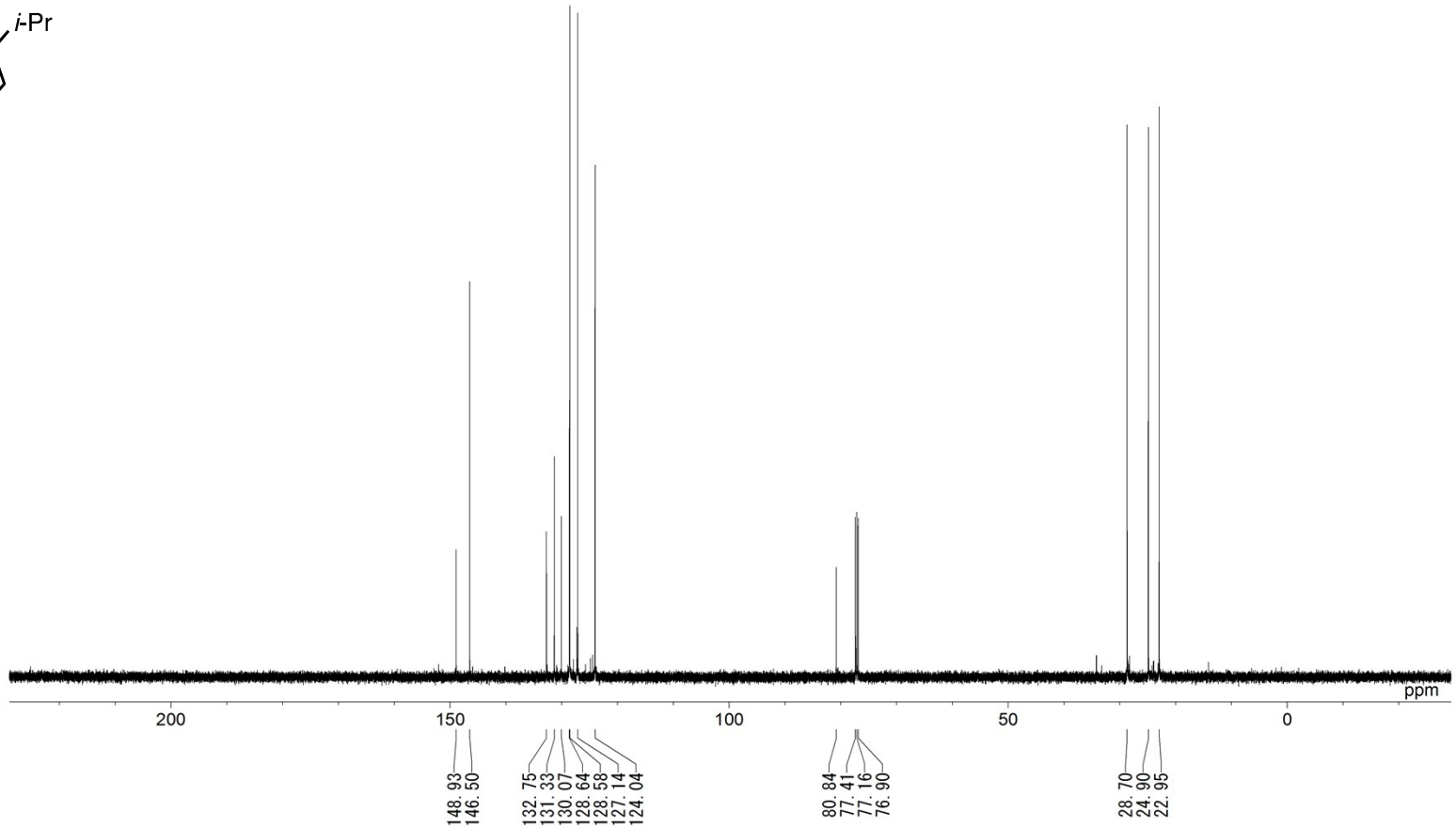
^{1}H NMR

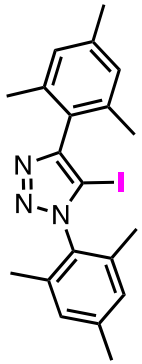

2.0
3.38
2.22
1.2
1.99
6.46
5.99
ppm
11
10
9
8
7
6
5
4
3
2
1
0
-1
8.170
8.155
7.539
7.523
7.507
7.492
7.477
7.462
7.406
7.391
7.377
7.322
7.307
2.192
2.175
2.162
2.148
2.134
2.121
2.106
1.208
1.194
1.156
1.126
1.113
0.000


N
N
N
I
i-Pr
i-Pr

^{13}C NMR

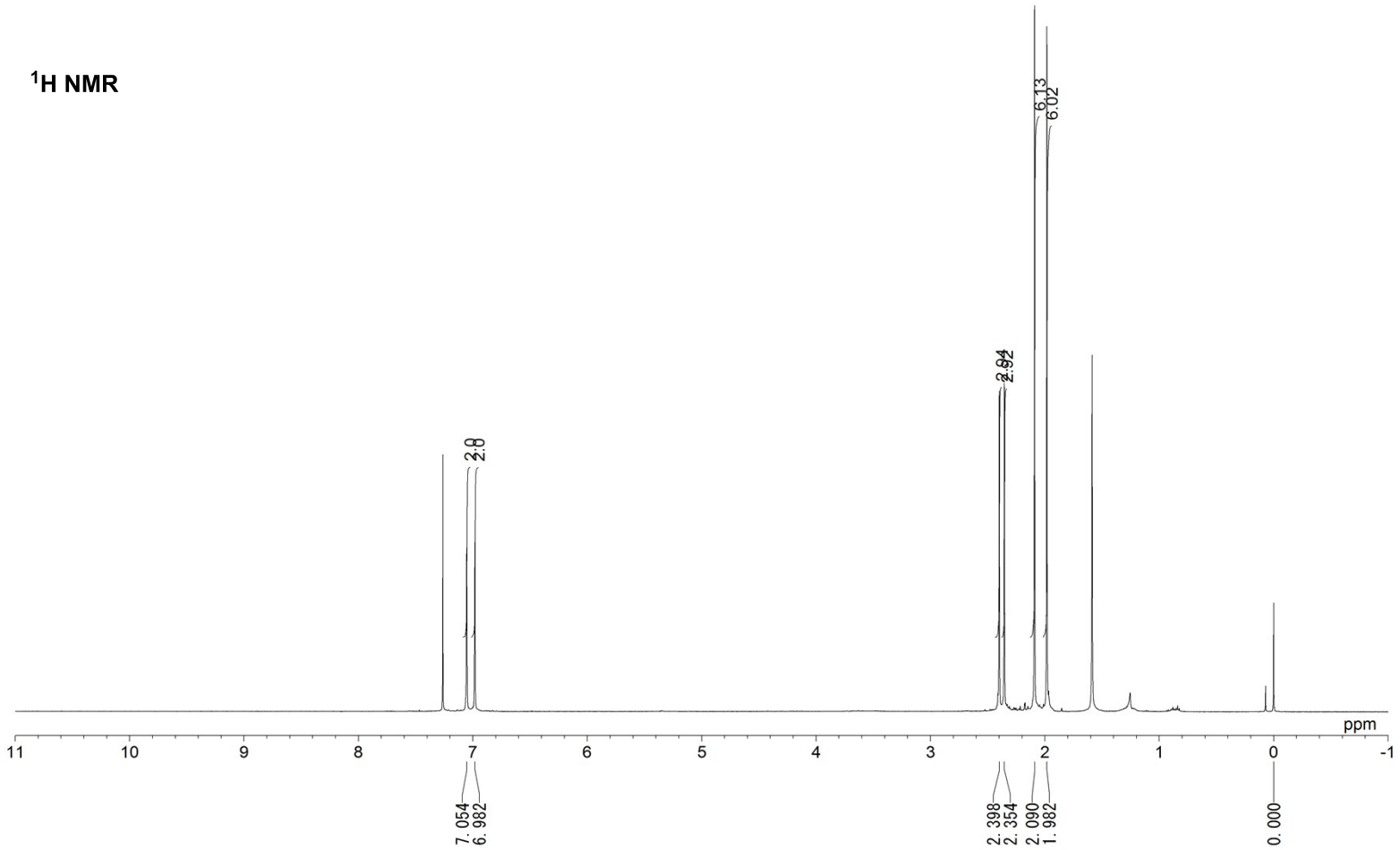
2b

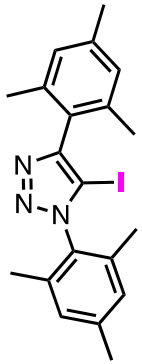

ppm
200
150
100
50
0
148. 93
146. 50
132. 75
131. 33
130. 07
128. 64
128. 58
127. 14
124. 04
80. 84
77. 41
77. 16
76. 90
28. 70
24. 90
22. 95



2c

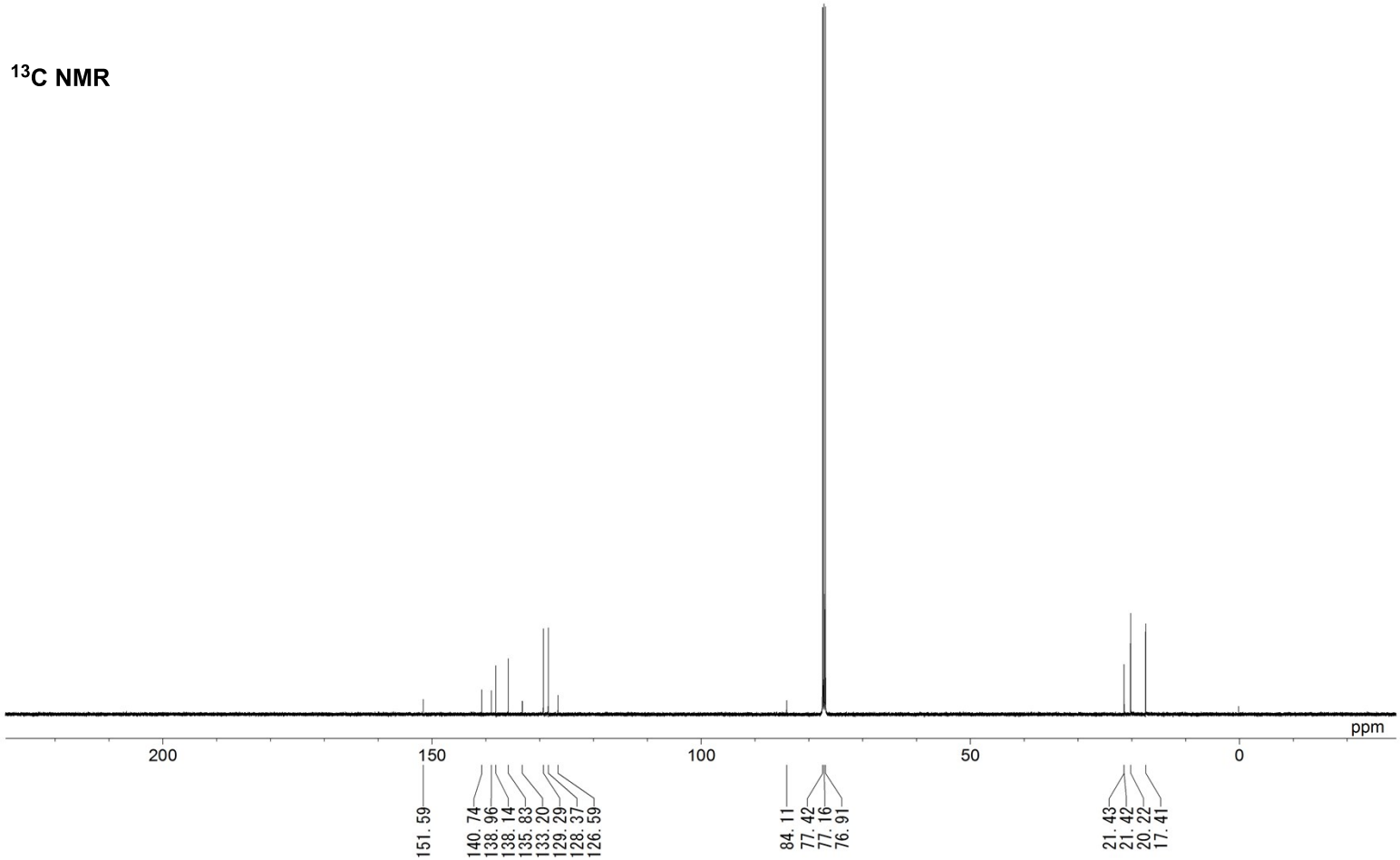
^{1}H NMR

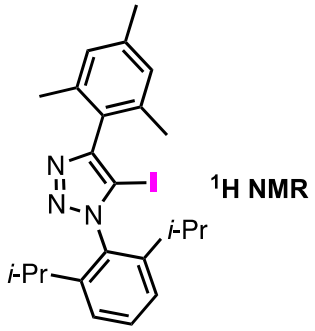

6.13
6.02
2.94
2.94
2.0
2.0
ppm
11
10
9
8
7
6
5
4
3
2
1
0
-1
7.054
6.982
2.398
2.354
2.090
1.982
0.000



2c

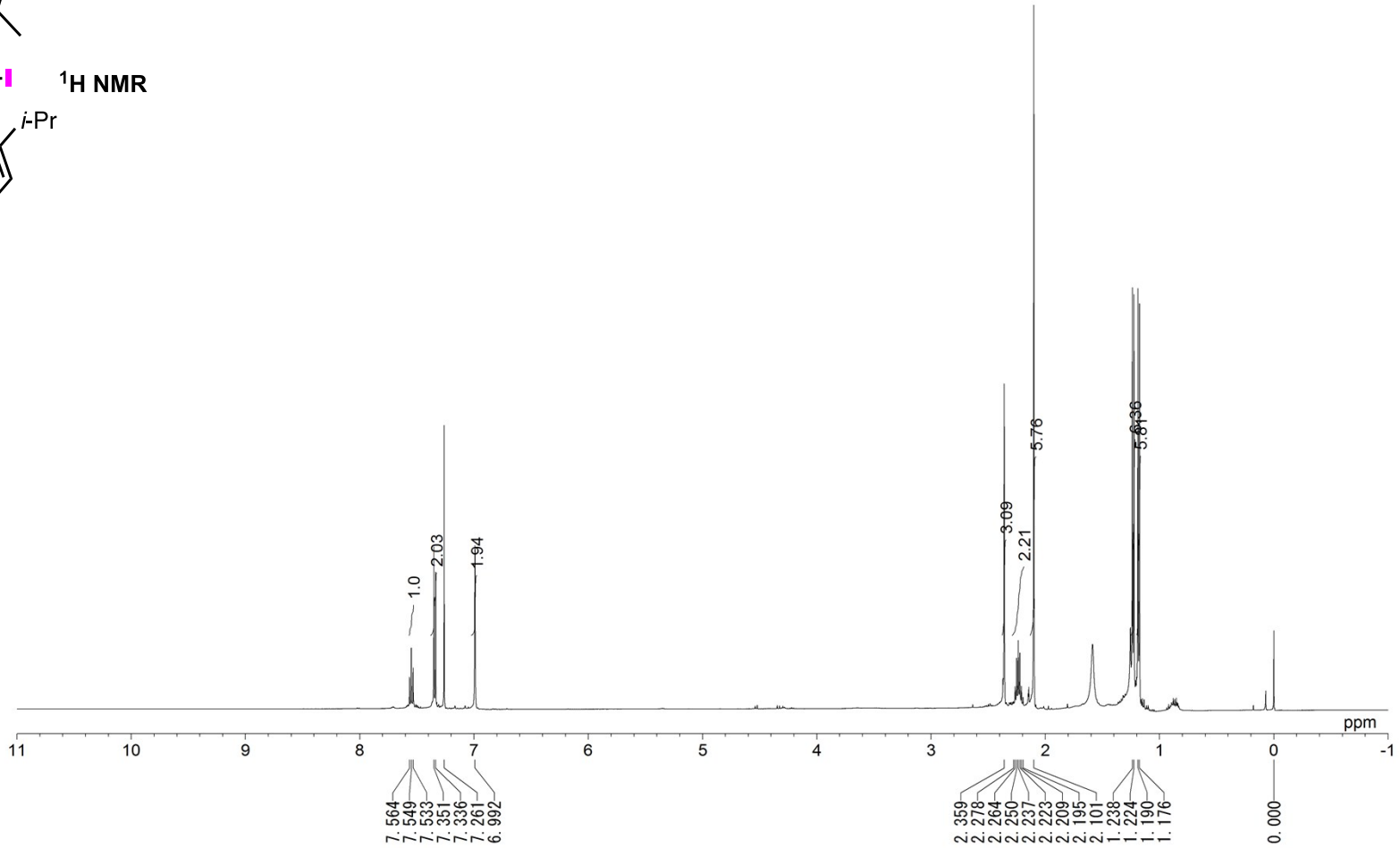
^{13}C NMR

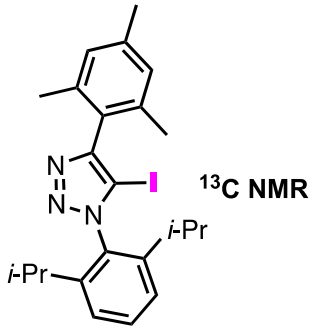

ppm
200
150
100
50
0
151.59
140.74
138.96
138.14
135.83
133.20
129.29
128.37
126.59
84.11
77.42
77.16
76.91
21.43
21.42
20.22
17.41


N
N
N
I
i-Pr
i-Pr

^{1}H NMR

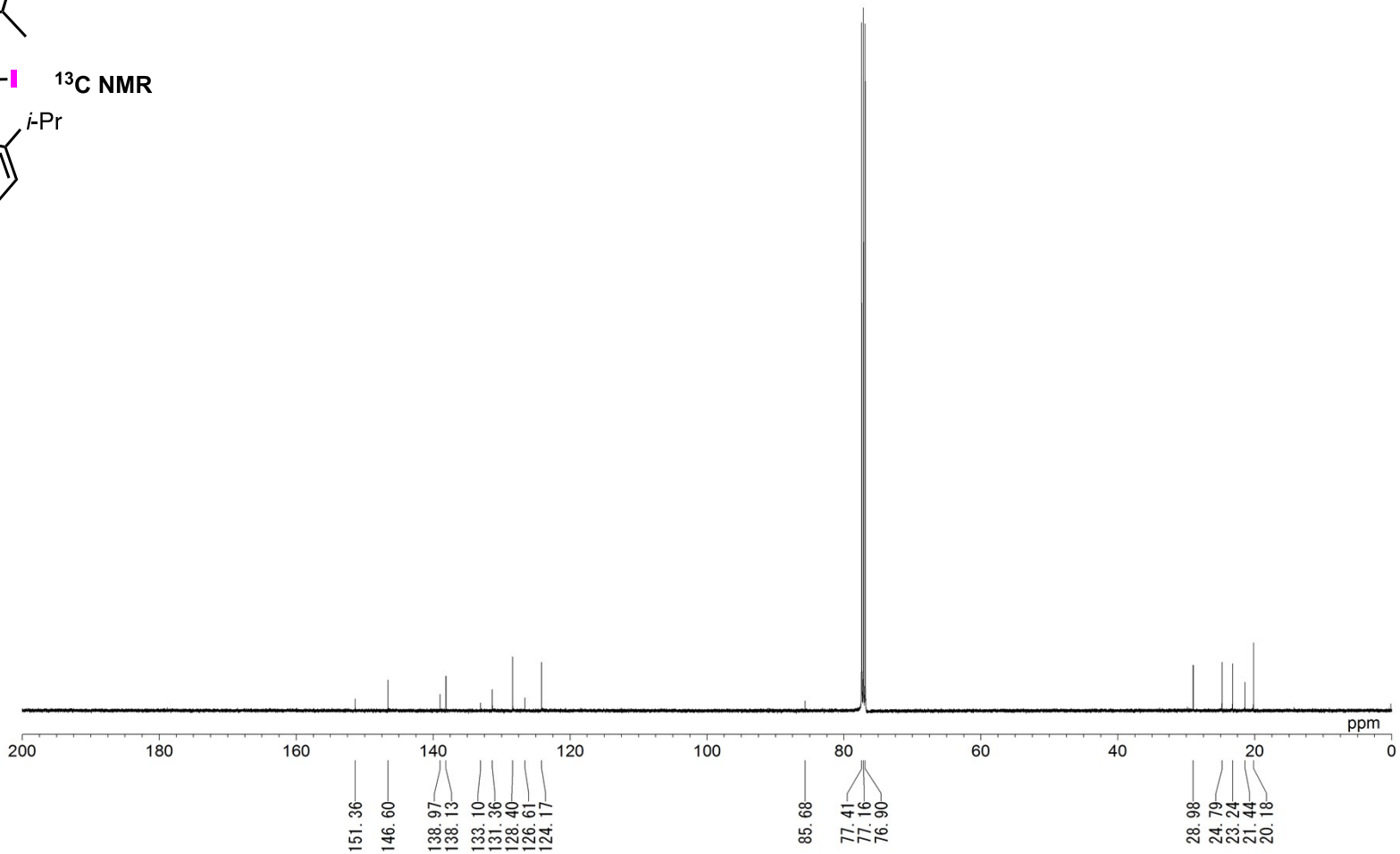
2d

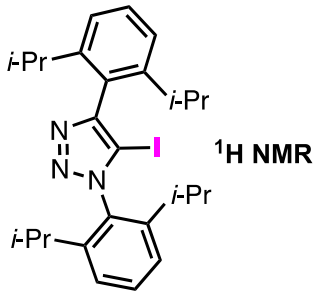

1.0
2.03
1.94
3.09
2.21
5.76
5.81
5.86
ppm
11
10
9
8
7
6
5
4
3
2
1
0
-1
7.564
7.549
7.533
7.351
7.336
7.261
6.992
2.359
2.278
2.264
2.250
2.237
2.223
2.209
2.195
2.101
1.238
1.224
1.190
1.176
0.000


N
N
N
I
i-Pr
i-Pr

^{13}C NMR

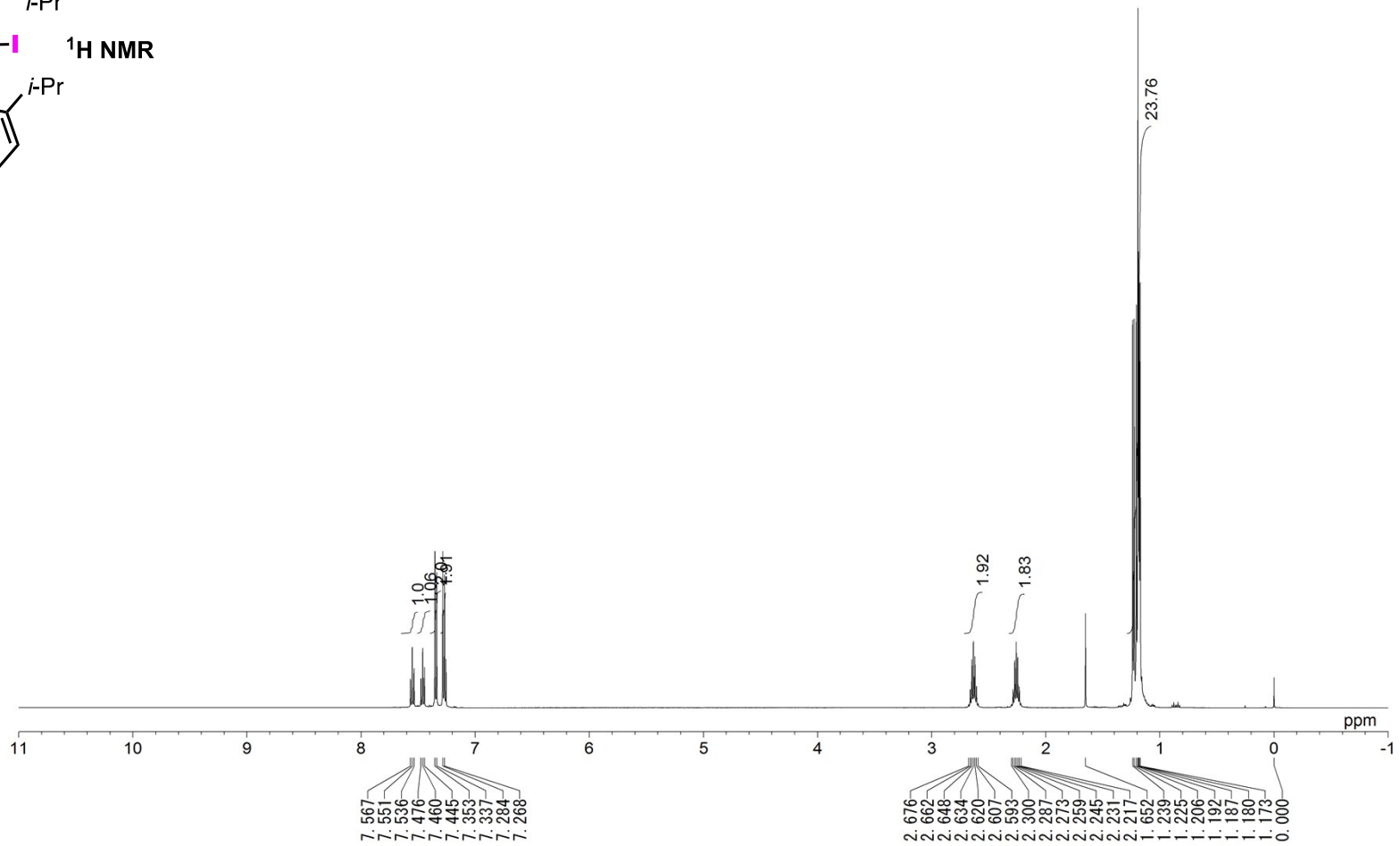
2d

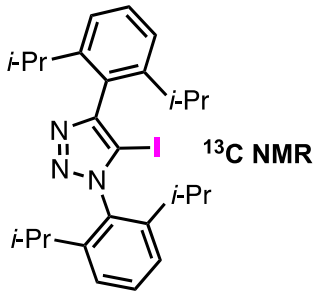

ppm
200
180
160
140
120
100
80
60
40
20
0
151. 36
146. 60
138. 97
138. 13
133. 10
131. 36
128. 40
126. 61
124. 17
85. 68
77. 41
77. 16
76. 90
28. 98
24. 79
23. 24
21. 44
20. 18


i-Pr
i-Pr
N
N
N
I
i-Pr
i-Pr

^{1}H NMR

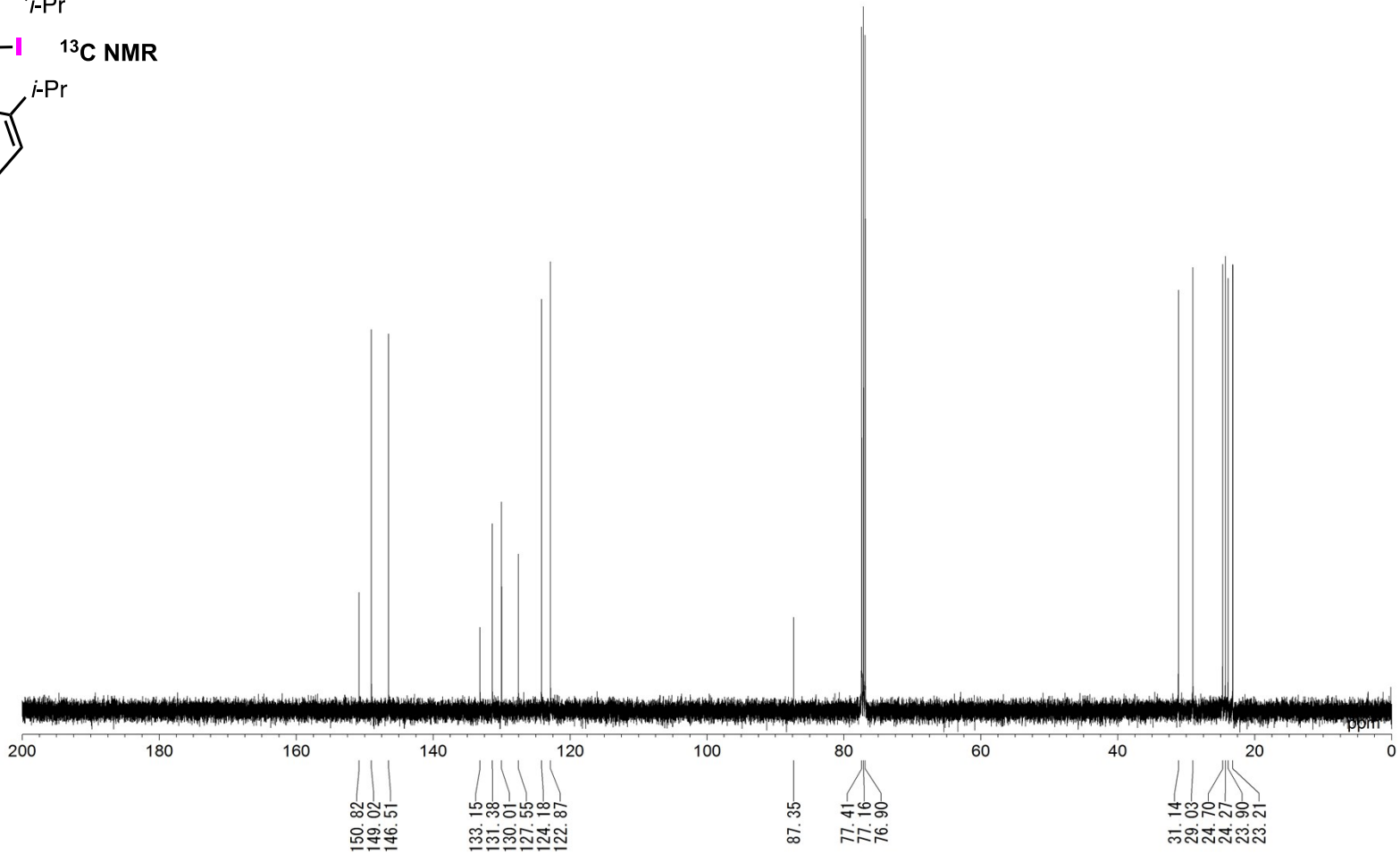
2e

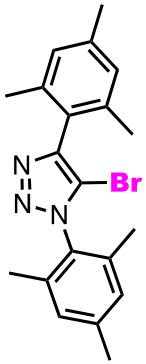

23.76
1.92
1.83
1.0
1.06
2.01
ppm
11
10
9
8
7
6
5
4
3
2
1
0
-1
7.567
7.551
7.536
7.476
7.460
7.445
7.353
7.337
7.284
7.268
2.676
2.662
2.648
2.634
2.620
2.607
2.593
2.300
2.287
2.273
2.259
2.245
2.231
2.217
1.652
1.239
1.225
1.206
1.192
1.187
1.180
1.173
0.000


i-Pr
i-Pr
N
N
N
I
i-Pr
i-Pr

^{13}C NMR

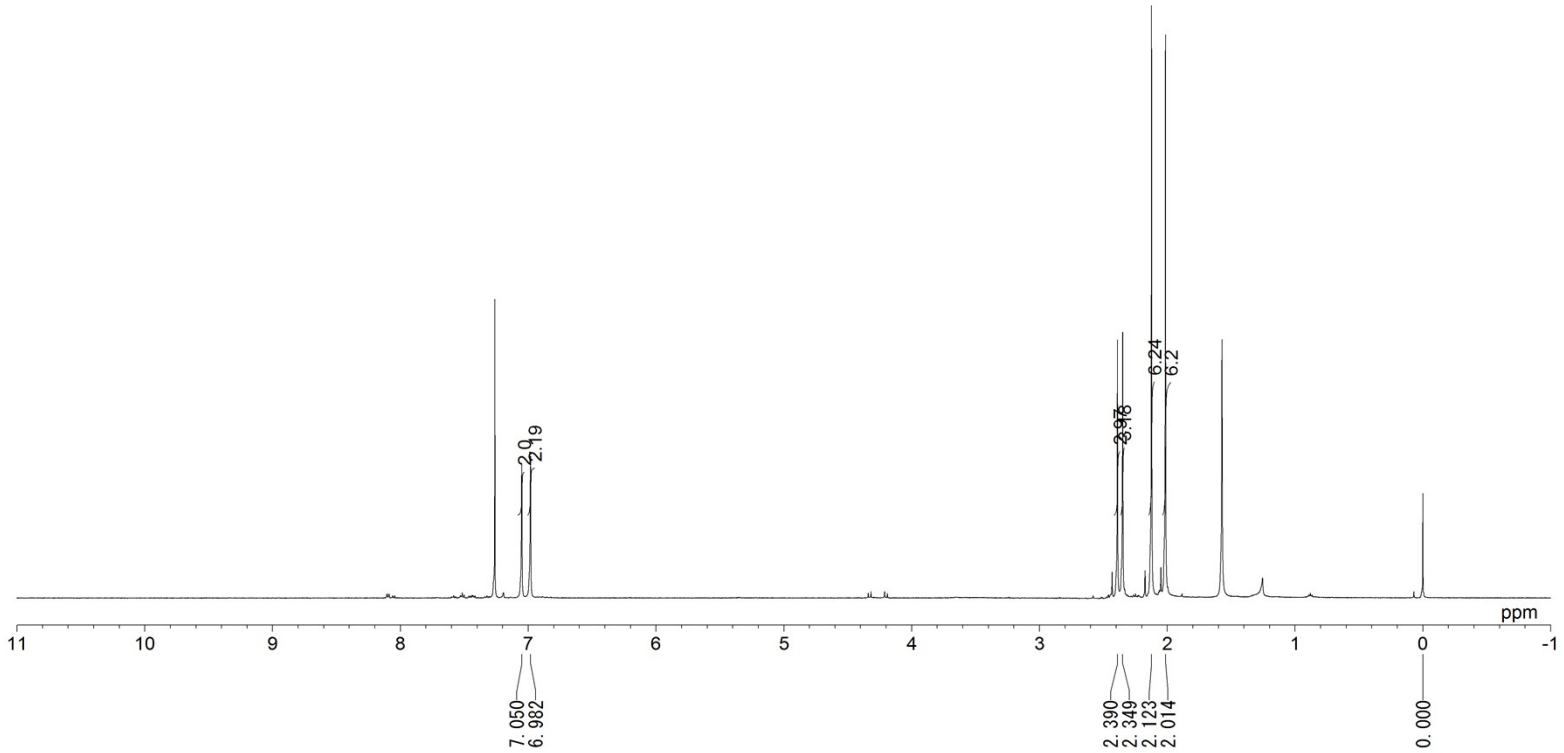
2e

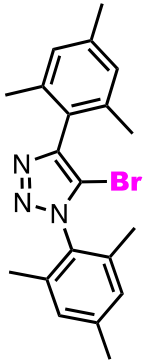

ppm
200
180
160
140
120
100
80
60
40
20
0
150.82
149.02
146.51
133.15
131.38
130.01
127.55
124.18
122.87
87.35
77.41
77.16
76.90
31.14
29.03
24.70
24.27
23.90
23.21


Br
N
N
N

2f

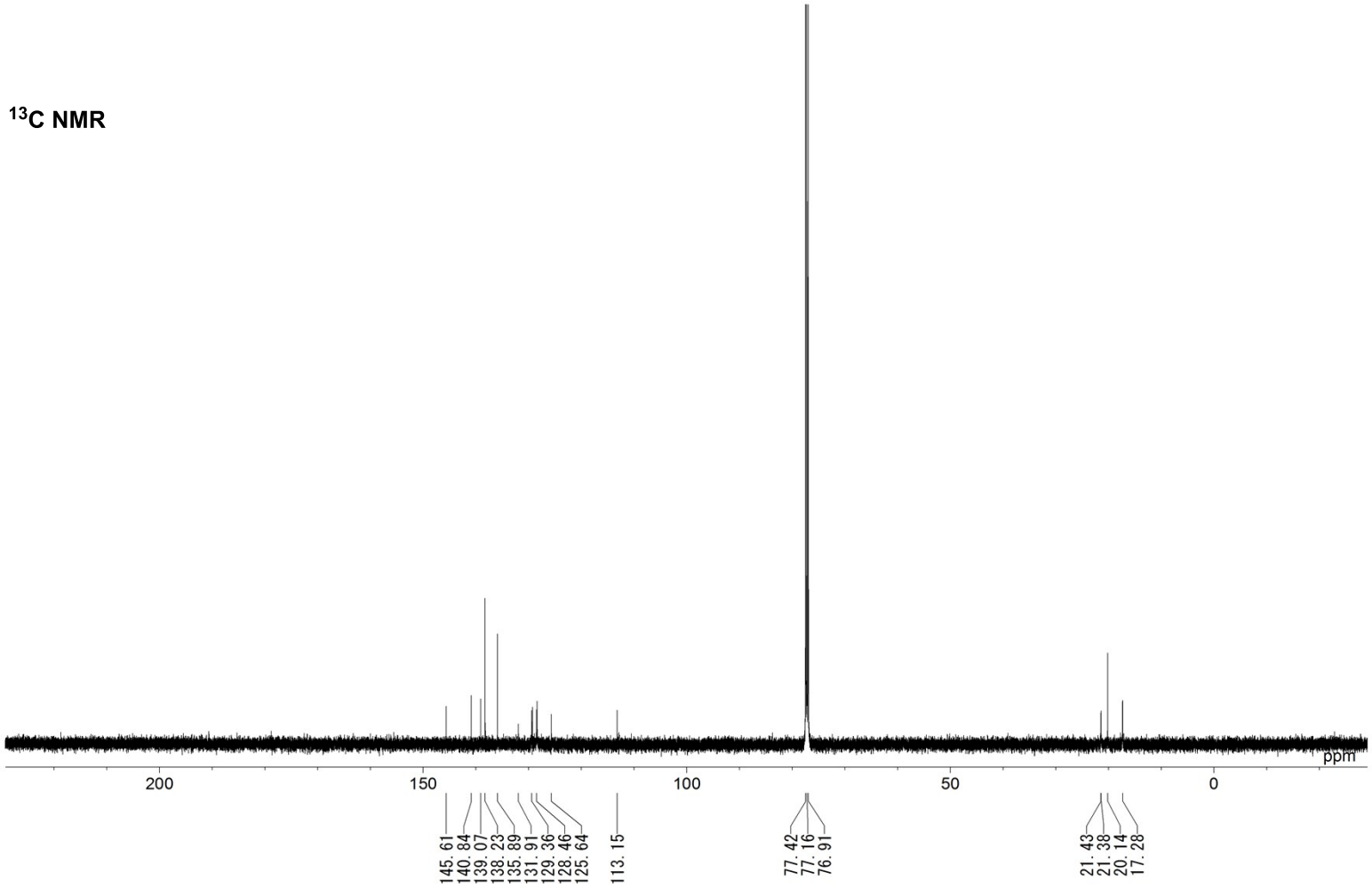
^{1}H NMR


6.24
6.2
2.07
2.06
2.0
2.19
ppm
11
10
9
8
7
6
5
4
3
2
1
0
-1
7.050
6.982
2.390
2.349
2.123
2.014
0.000

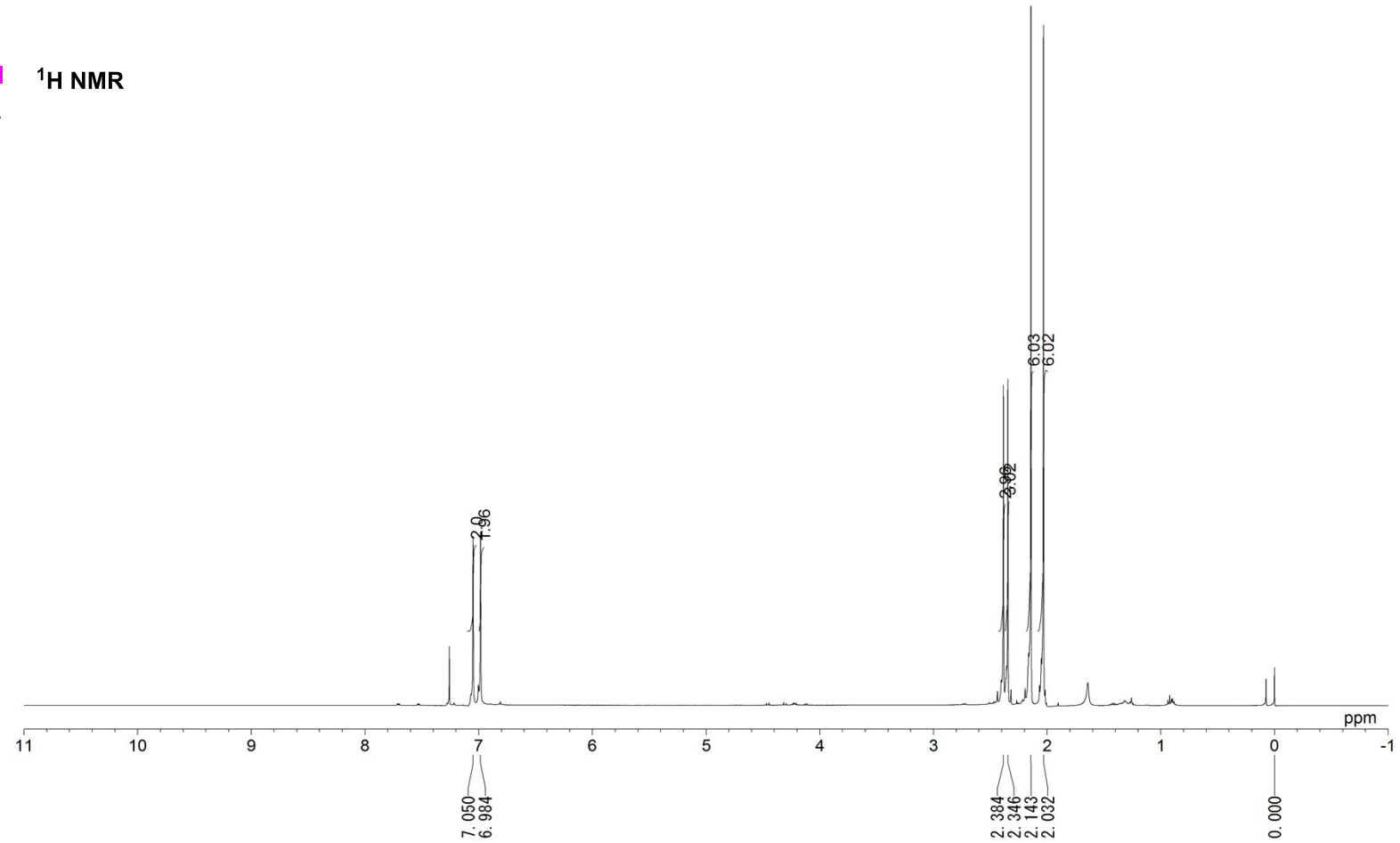

N
N
N
Br

^{13}C NMR

2f


ppm
200
150
100
50
0
145. 61
140. 84
139. 07
138. 23
135. 89
131. 91
129. 36
128. 46
125. 64
113. 15
77. 42
77. 16
76. 91
21. 43
21. 38
20. 14
17. 28

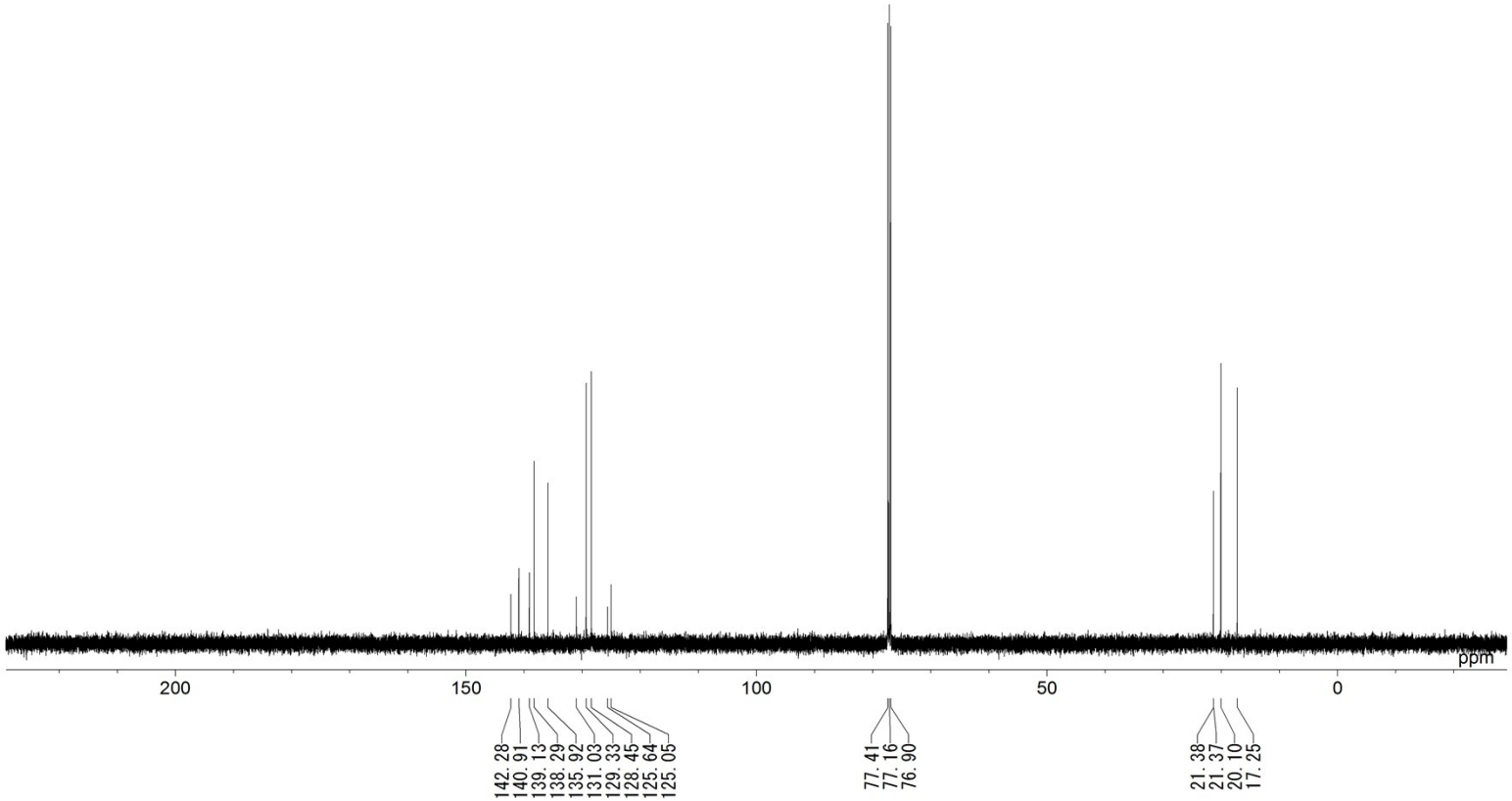
^{1}H NMR

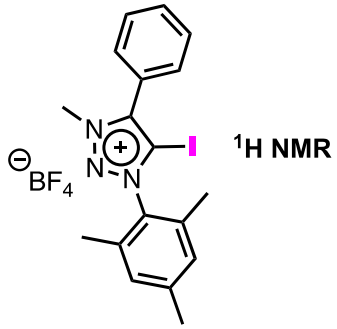

6.03
6.02
2.00
1.96
ppm
11
10
9
8
7
6
5
4
3
2
1
0
-1
7.050
6.984
2.384
2.346
2.143
2.032
0.000


Cl
N
N
N

2g

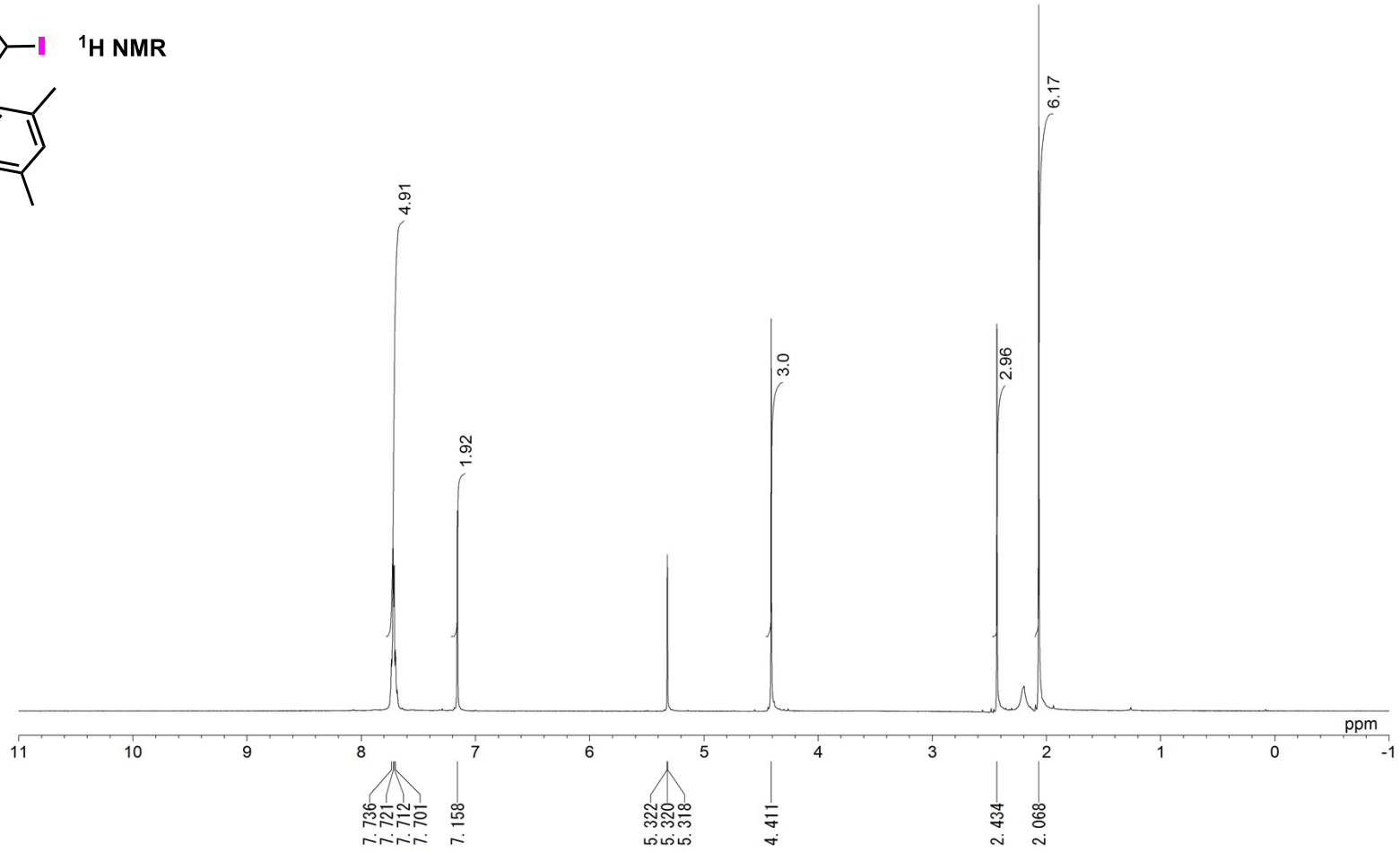
^{13}C NMR

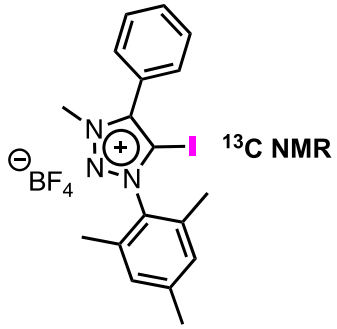

ppm
200
150
100
50
0
142. 28
140. 91
139. 13
138. 29
135. 92
131. 03
129. 33
128. 45
125. 64
125. 05
77. 41
77. 16
76. 90
21. 38
21. 37
20. 10
17. 25



3a

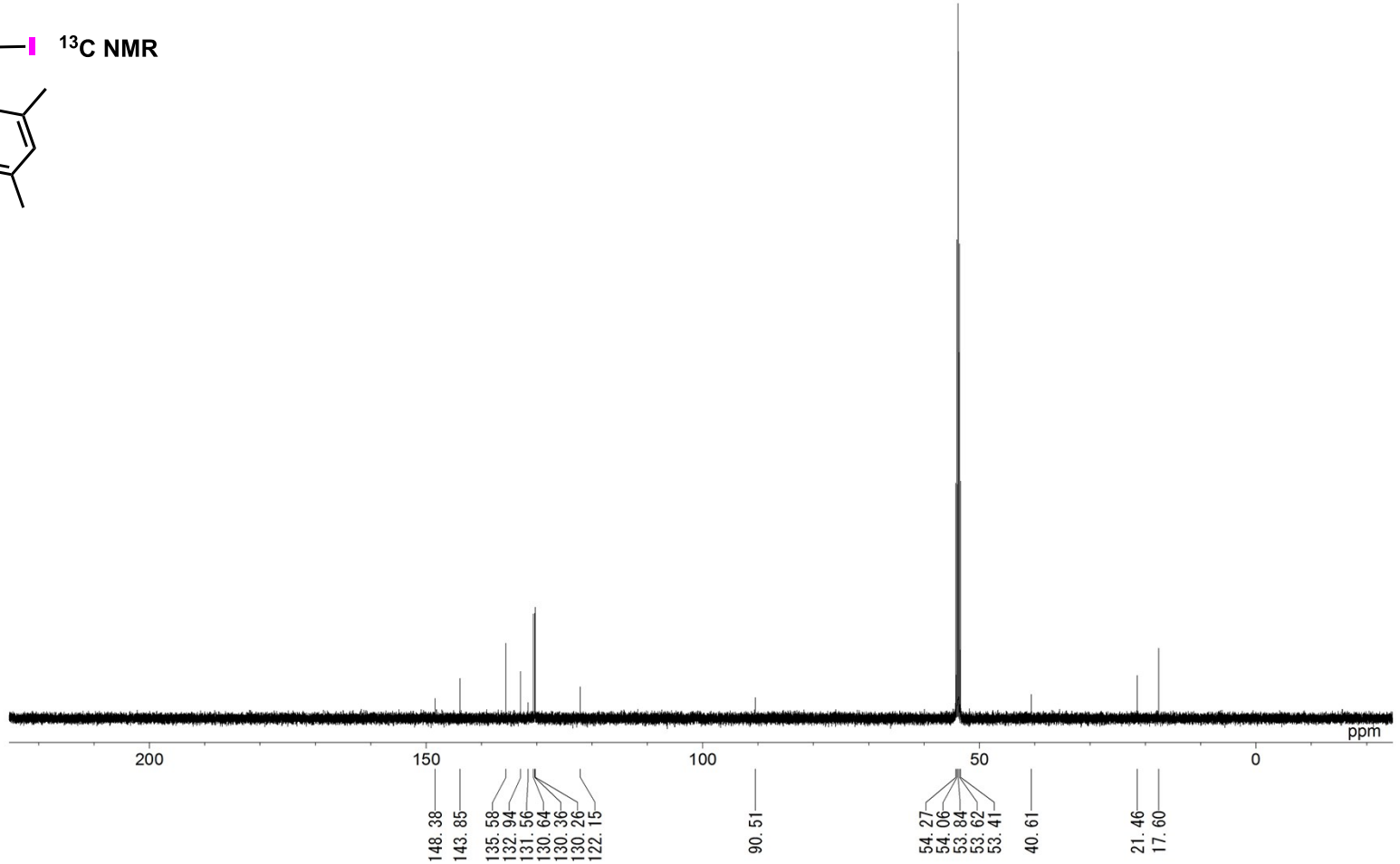
^{1}H NMR


4.91
1.92
3.0
2.96
6.17
ppm
11
10
9
8
7
6
5
4
3
2
1
0
-1
7.736
7.721
7.712
7.701
7.158
5.322
5.320
5.318
4.411
2.434
2.068



3a

^{13}C NMR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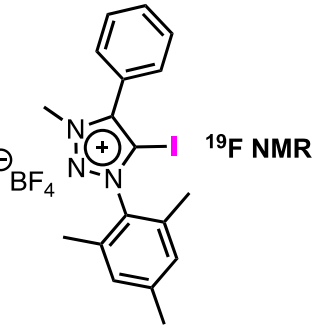
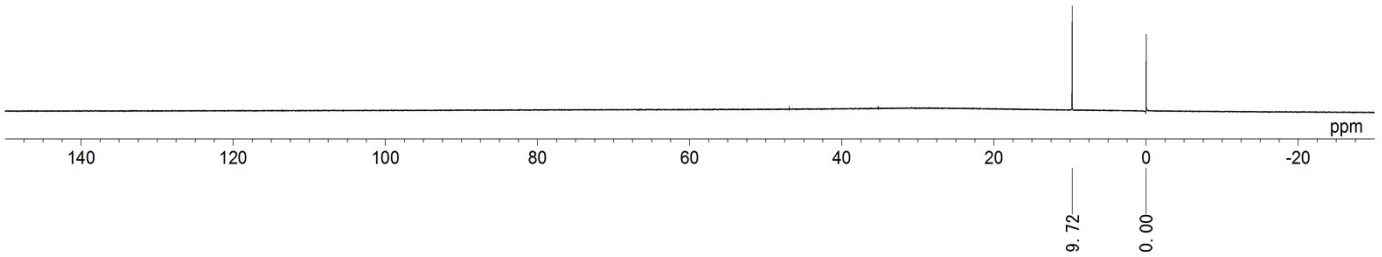
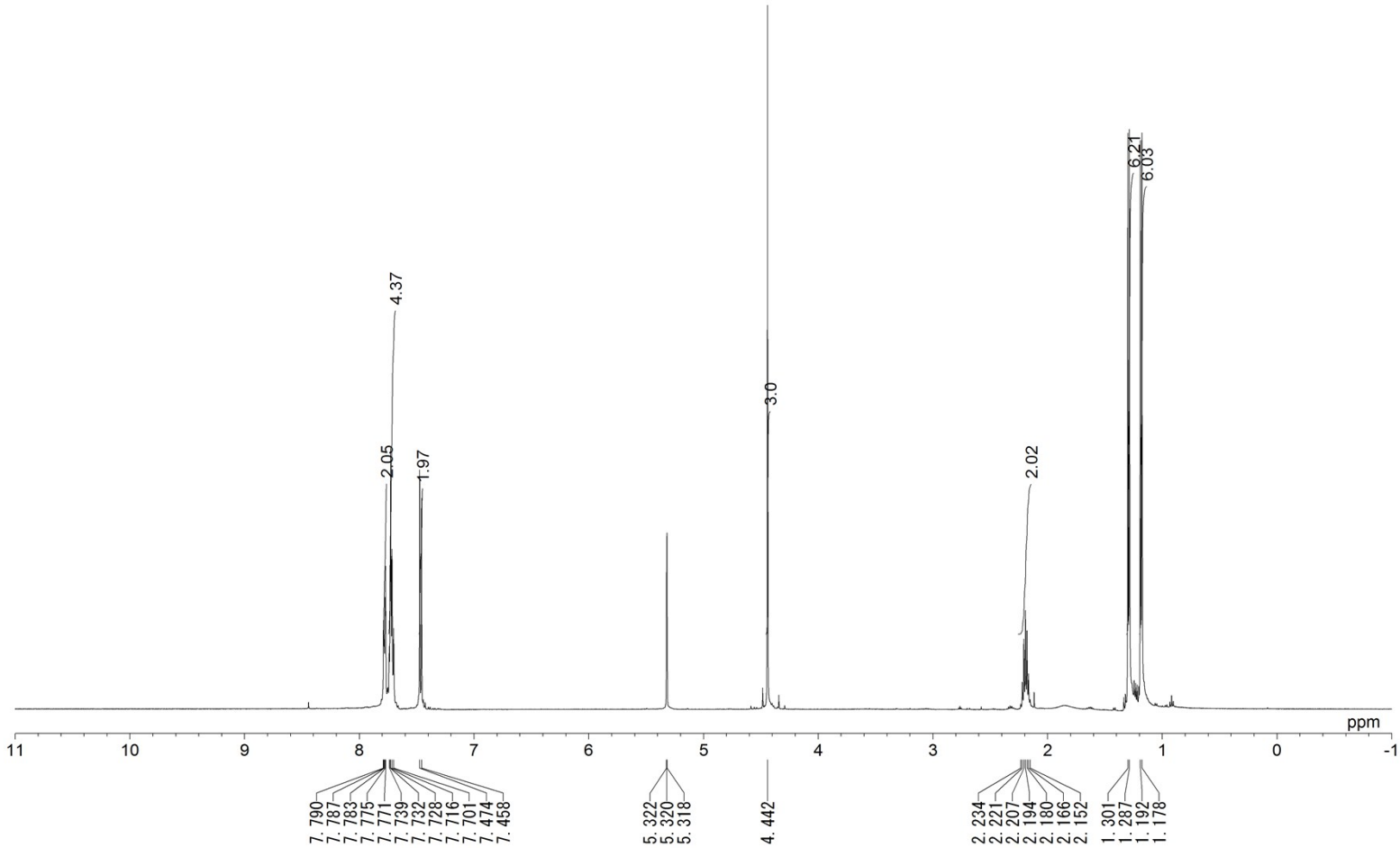
100
50
0
148. 38
143. 85
135. 58
132. 94
131. 56
130. 64
130. 36
130. 26
122. 15
90. 51
54. 27
54. 06
53. 84
53. 62
53. 41
40. 61
21. 46
17. 60

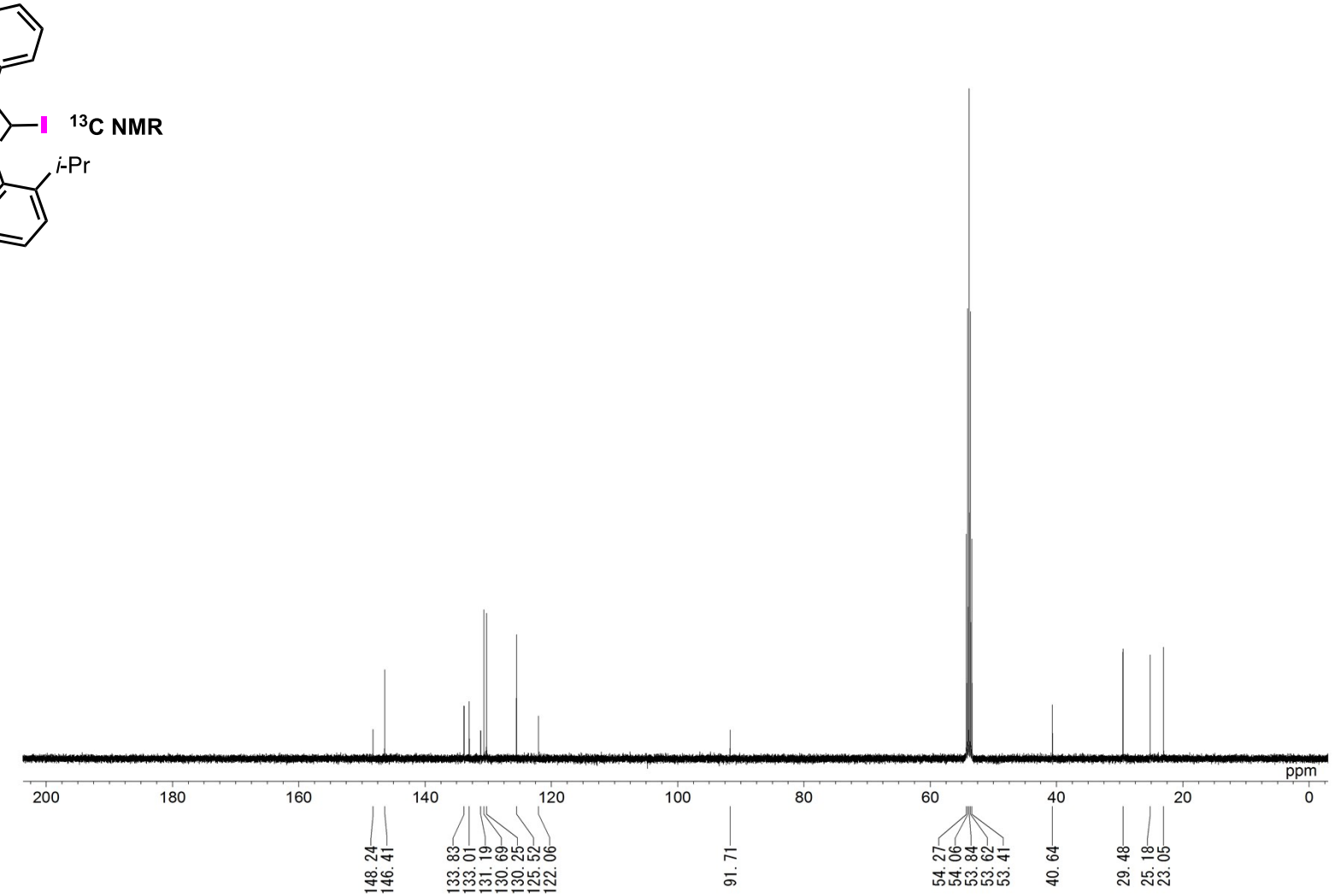


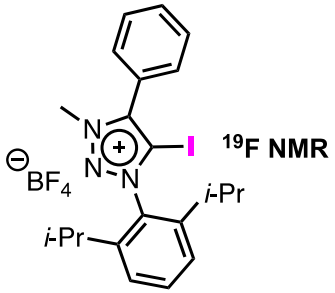
3a

^{19}F NMR

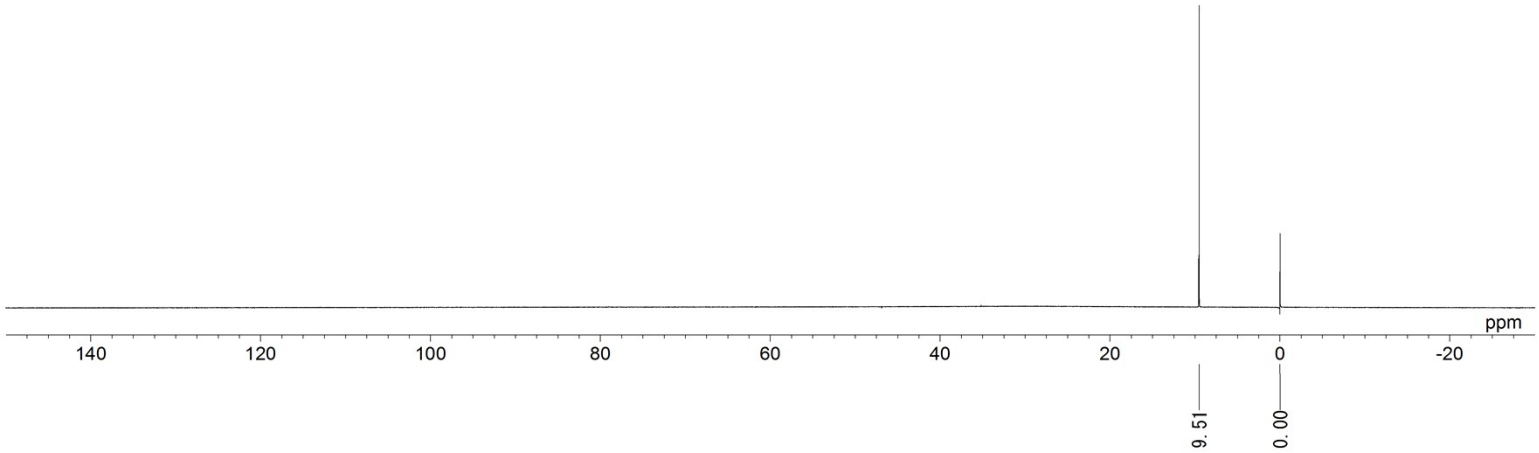


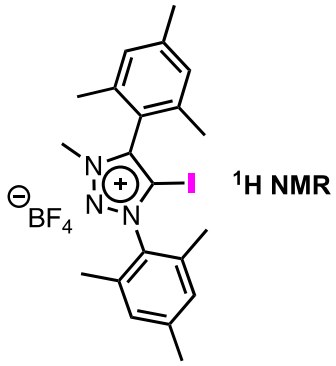

4.37
2.05
1.97
3.0
2.02
6.21
6.03
ppm
11
10
9
8
7
6
5
4
3
2
1
0
-1
7. 790
7. 787
7. 783
7. 775
7. 771
7. 739
7. 732
7. 728
7. 716
7. 701
7. 474
7. 458
5. 322
5. 320
5. 318
4. 442
2. 234
2. 221
2. 207
2. 194
2. 180
2. 166
2. 152
1. 301
1. 287
1. 192
1. 178


^{13}C NMR
i-Pr
ppm
200
180
160
140
120
100
80
60
40
20
0
148. 24
146. 41
133. 83
133. 01
131. 19
130. 69
130. 25
125. 52
122. 06
91. 71
54. 27
54. 06
53. 84
53. 62
53. 41
40. 64
29. 48
25. 18
23. 05



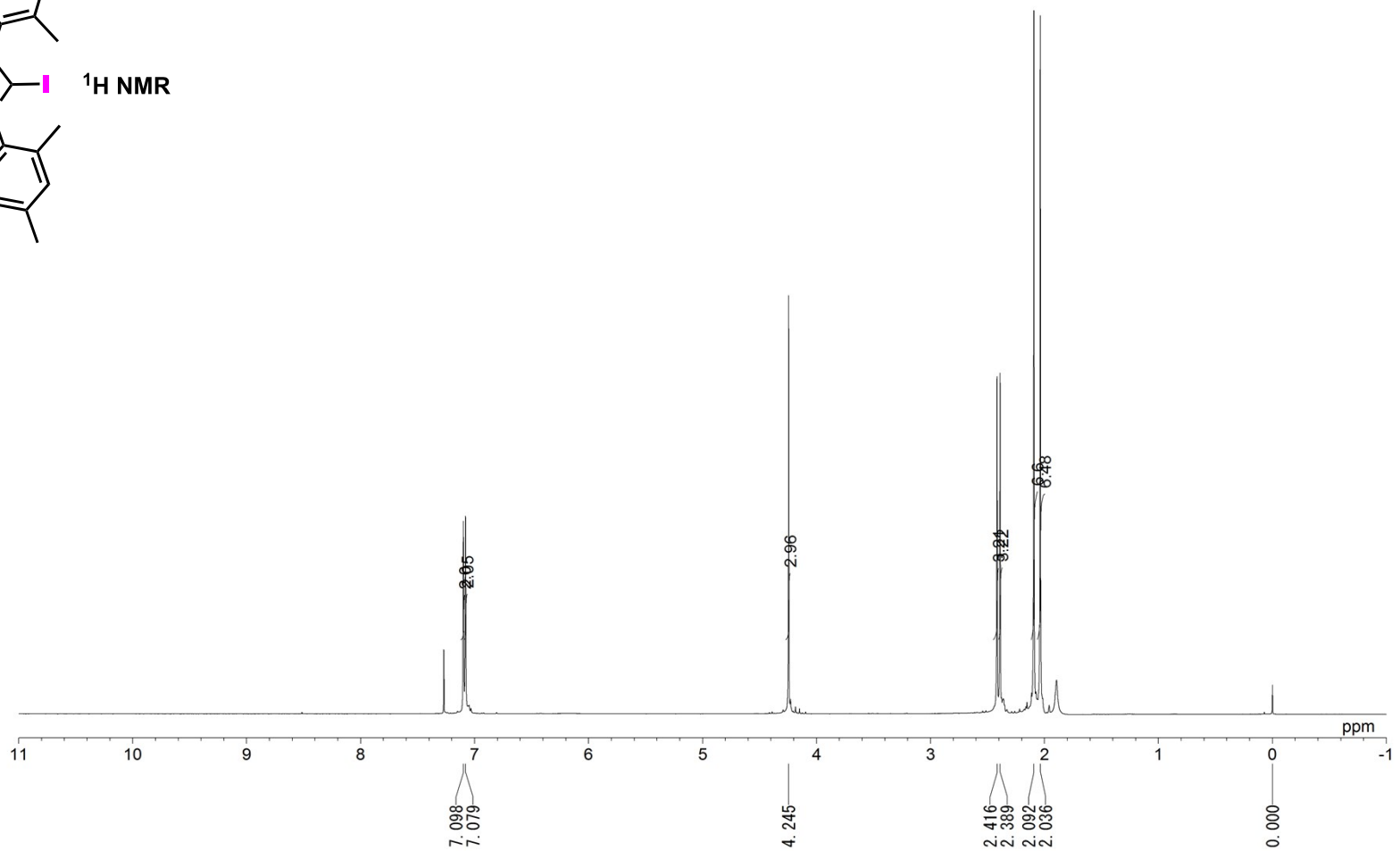
3b

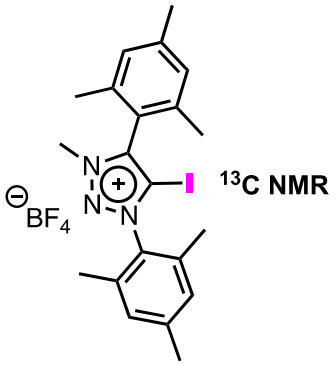




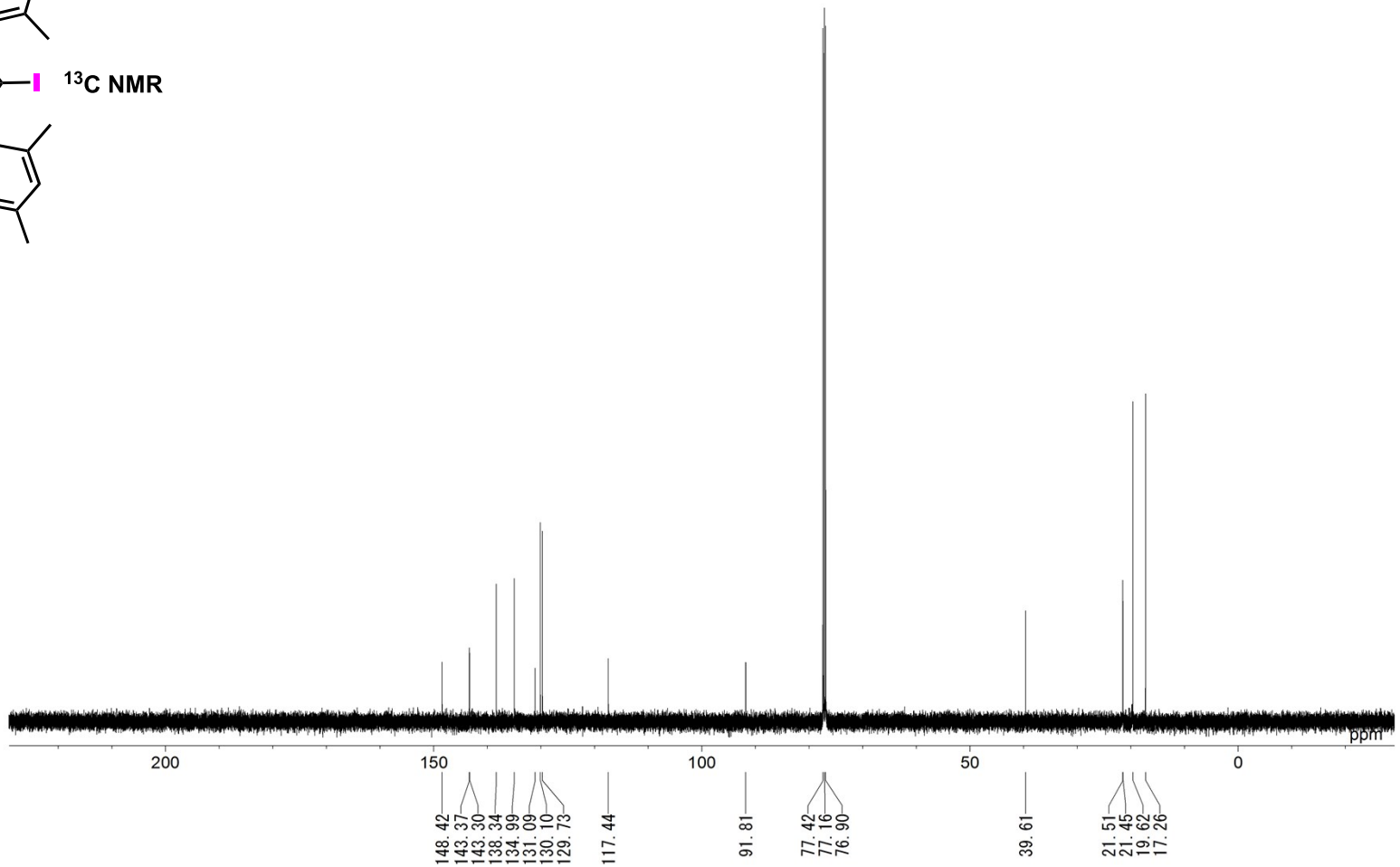
3c

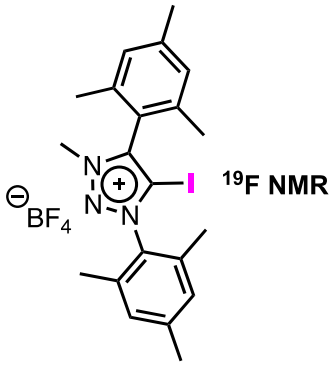
^{1}H NMR


2.96
6.6
6.48
ppm
11
10
9
8
7
6
5
4
3
2
1
0
-1
7.098
7.079
4.245
2.416
2.389
2.092
2.036
0.000


^{13}C NMR
$\ominus$BF$_4$

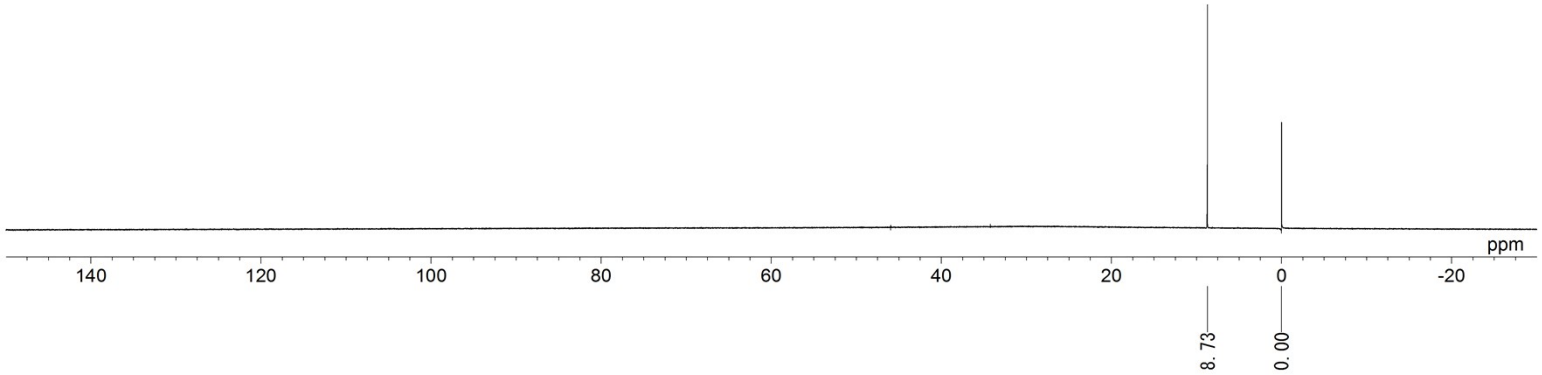
3c

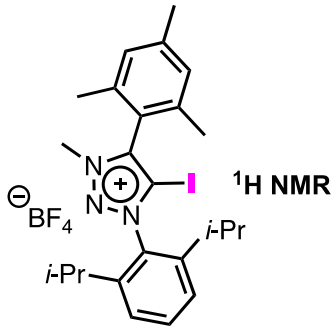

ppm
200
150
100
50
0
148. 42
143. 37
143. 30
138. 34
134. 99
131. 09
130. 10
129. 73
117. 44
91. 81
77. 42
77. 16
76. 90
39. 61
21. 51
21. 45
19. 62
17. 26



3c

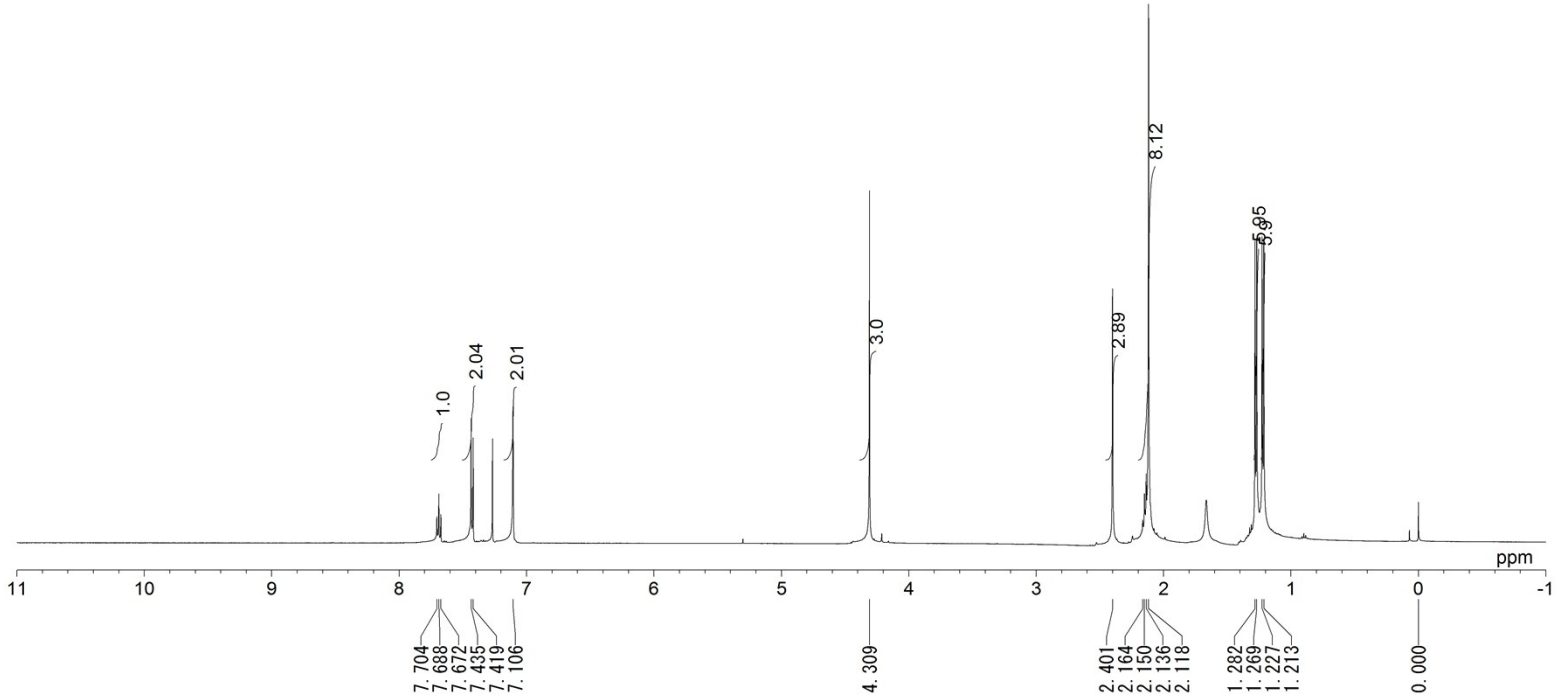
^{19}F NMR

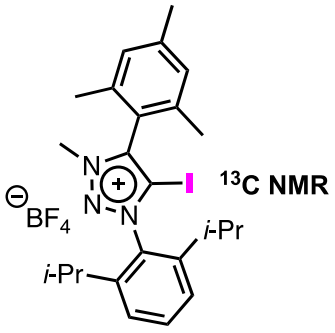



$^{\ominus}BF_4$
N
N
N
i-Pr
i-Pr

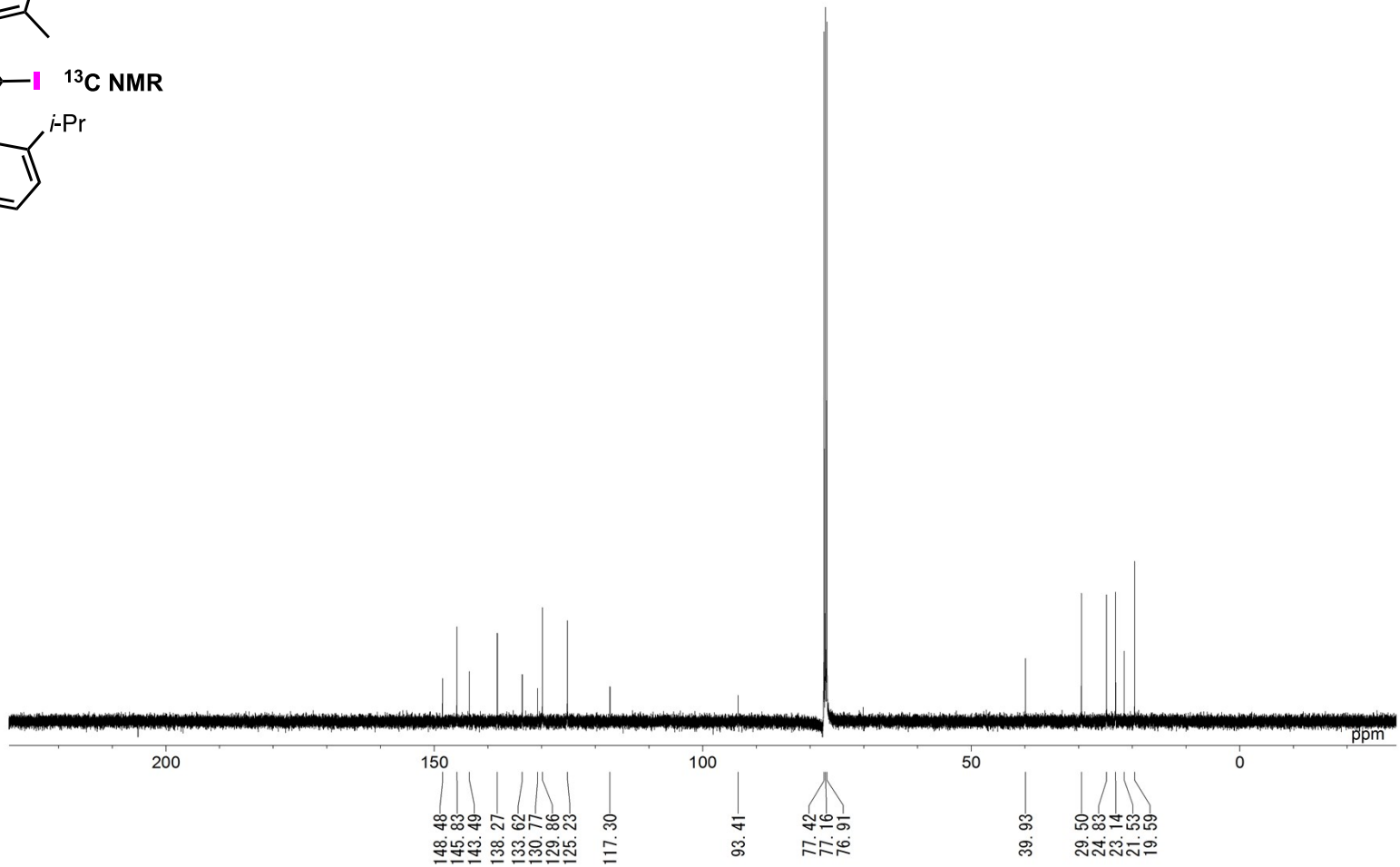
^{1}H NMR

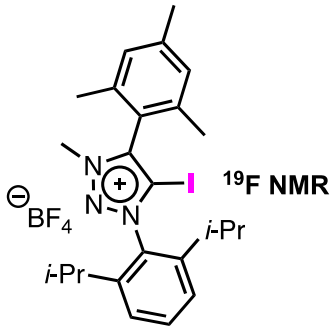
3d


1.0
2.04
2.01
3.0
2.89
8.12
5.95
5.99
ppm
11
10
9
8
7
6
5
4
3
2
1
0
-1
7.704
7.688
7.672
7.435
7.419
7.106
4.309
2.401
2.164
2.150
2.136
2.118
1.282
1.269
1.227
1.213
0.000

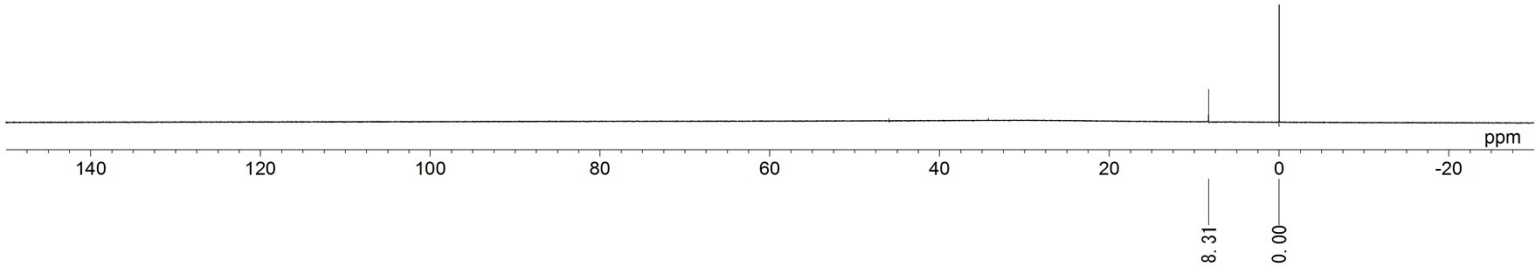

^{13}C NMR
$\ominus$BF$_4$
i-Pr
i-Pr

3d


ppm
200
150
100
50
0
148. 48
145. 83
143. 49
138. 27
133. 62
130. 77
129. 86
125. 23
117. 30
93. 41
77. 42
77. 16
76. 91
39. 93
29. 50
24. 83
23. 14
21. 53
19. 59


^{19}F NMR
$\ominus$BF$_4$
i-Pr
i-Pr

3d


ppm
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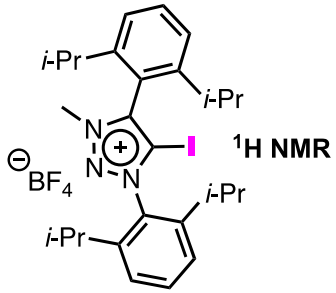
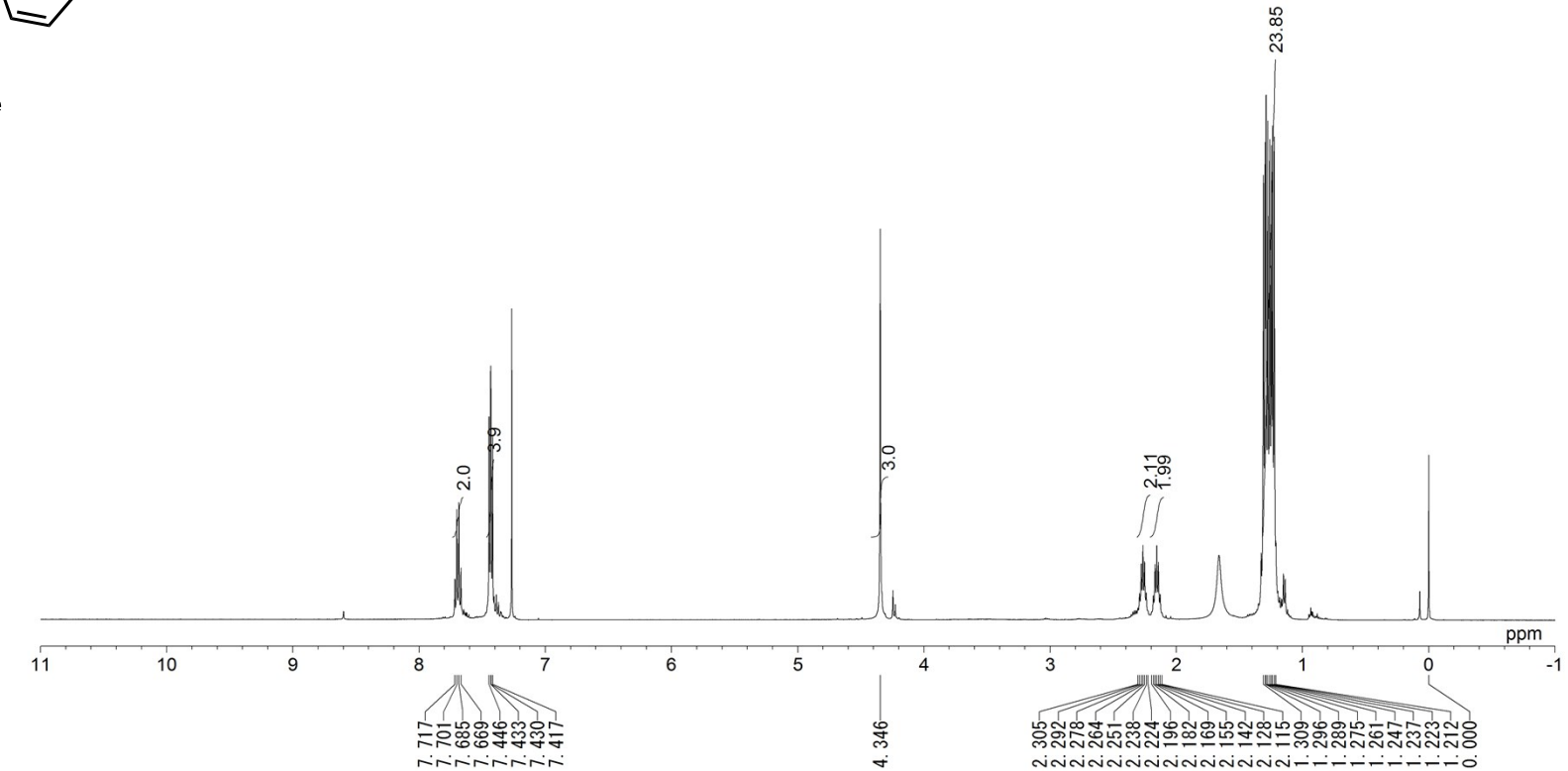
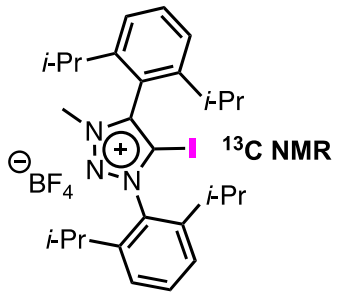
120
100
80
60
40
20
0
-20
8. 31
0. 00


i-Pr
i-Pr
N
N
BF4
i-Pr
i-Pr

^{1}H NMR

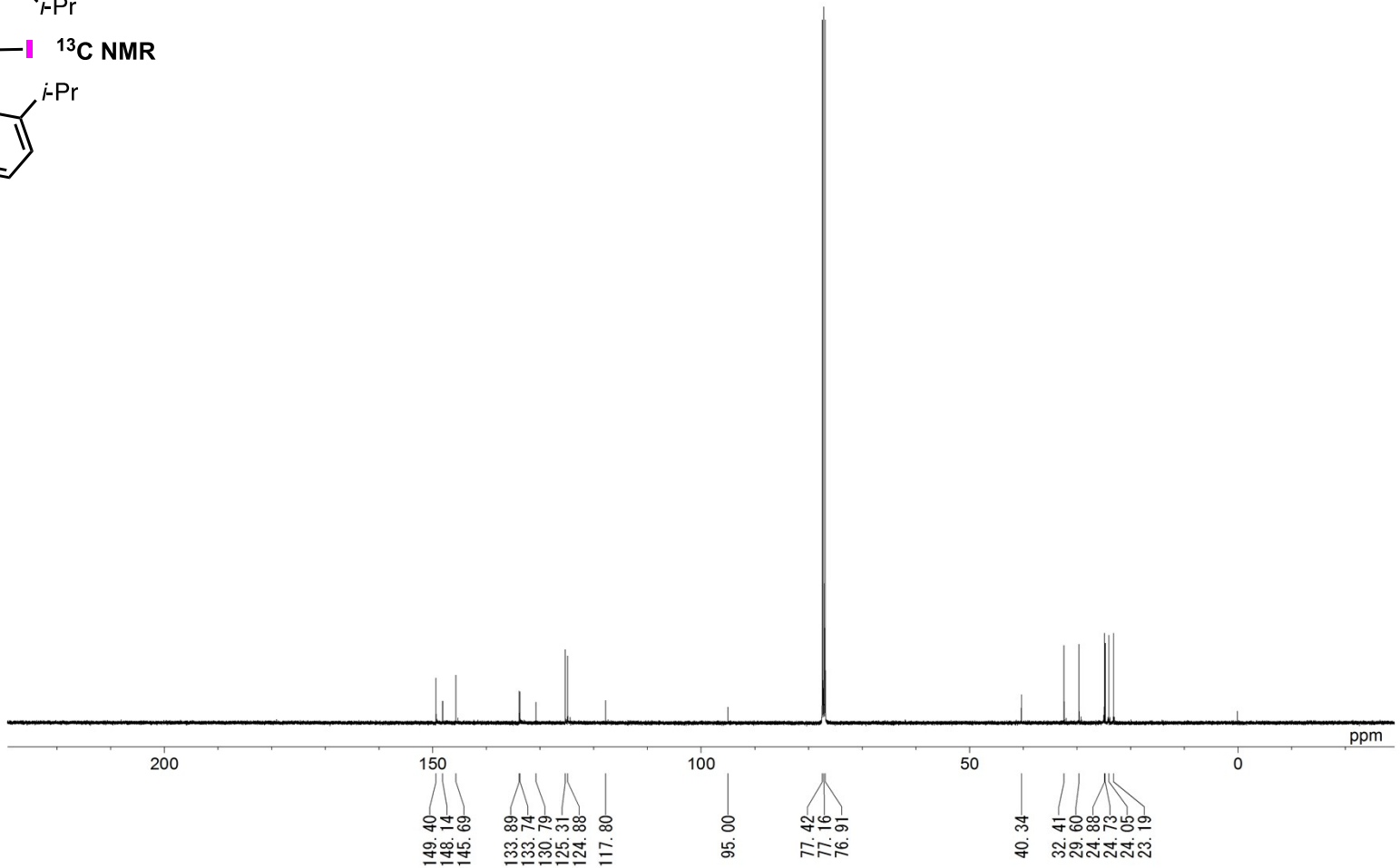
3e

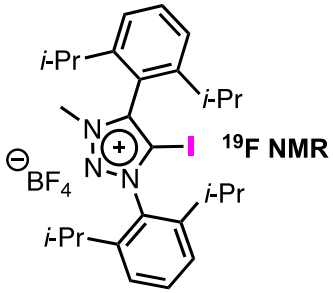

23.85
2.0
3.9
3.0
2.11
1.99
ppm
11
10
9
8
7
6
5
4
3
2
1
0
-1
7.717
7.701
7.685
7.669
7.446
7.433
7.430
7.417
4.346
2.305
2.292
2.278
2.264
2.251
2.238
2.224
2.196
2.182
2.169
2.155
2.142
2.128
2.115
1.309
1.296
1.289
1.275
1.261
1.247
1.237
1.223
1.212
0.000


i-Pr
i-Pr
N
N
N
BF4
i-Pr
i-Pr

^{13}C NMR

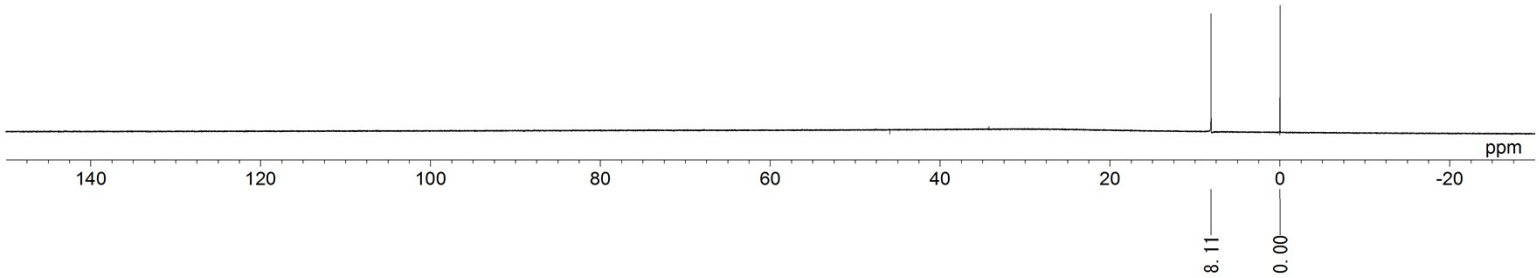
3e

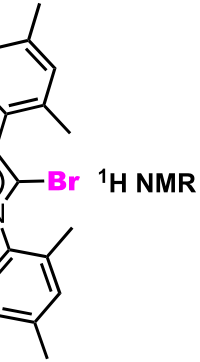

ppm
200
150
100
50
0
149. 40
148. 14
145. 69
133. 89
133. 74
130. 79
125. 31
124. 88
117. 80
95. 00
77. 42
77. 16
76. 91
40. 34
32. 41
29. 60
24. 88
24. 73
24. 05
23. 19



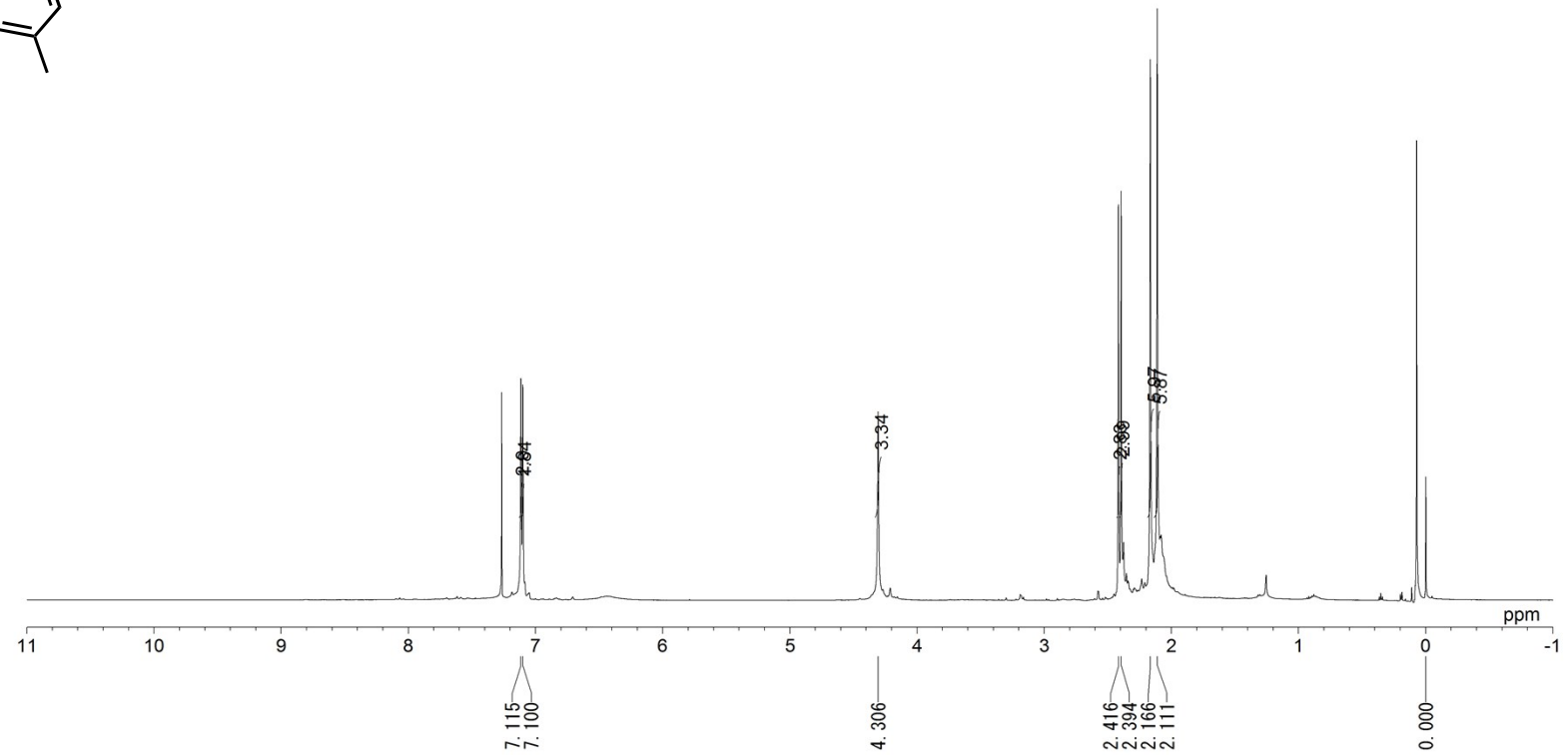
^{19}F NMR

3e




Br

^{1}H NMR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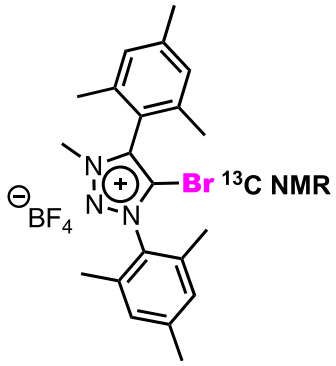
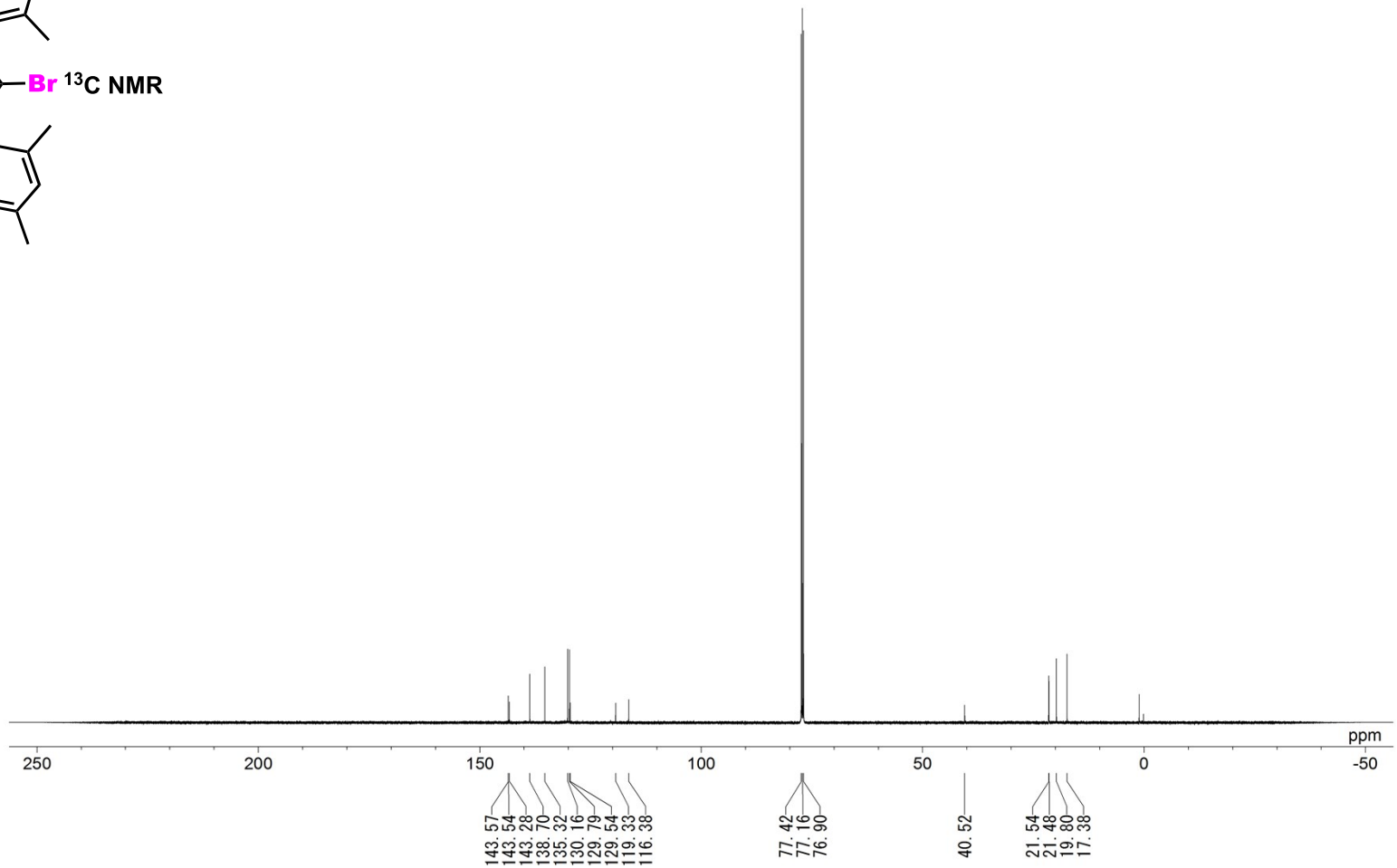
5.87
ppm
11
10
9
8
7
6
5
4
3
2
1
0
-1
7.115
7.100
4.306
2.416
2.394
2.166
2.111
0.000


Br
BF4

^{13}C NMR

3f


ppm
250
200
150
100
50
0
-50
143.57
143.54
143.28
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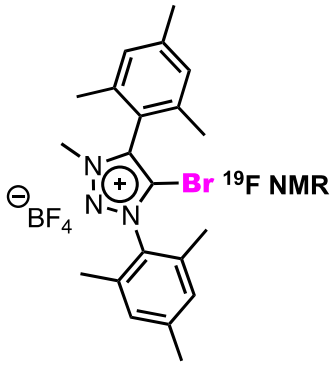
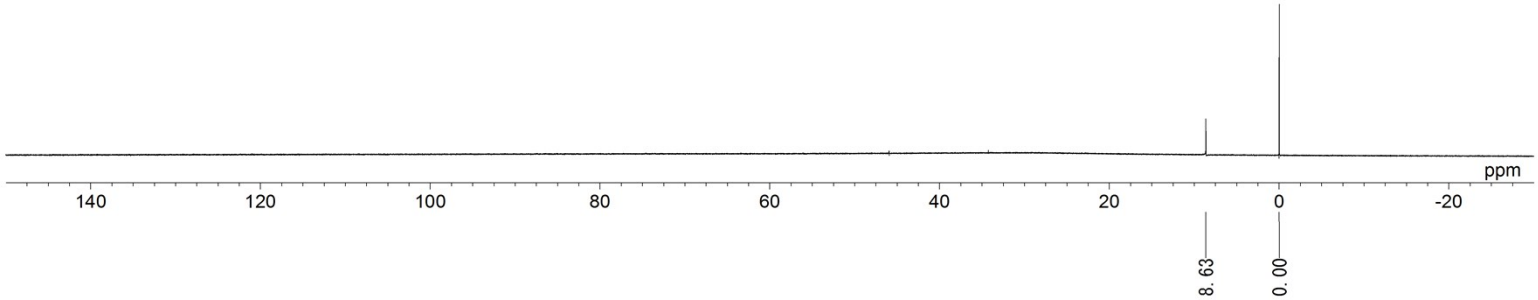
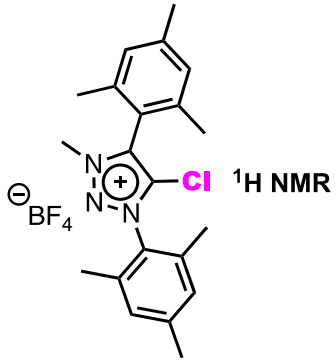
135.32
130.16
129.79
129.54
119.33
116.38
77.42
77.16
76.90
40.52
21.54
21.48
19.80
17.38



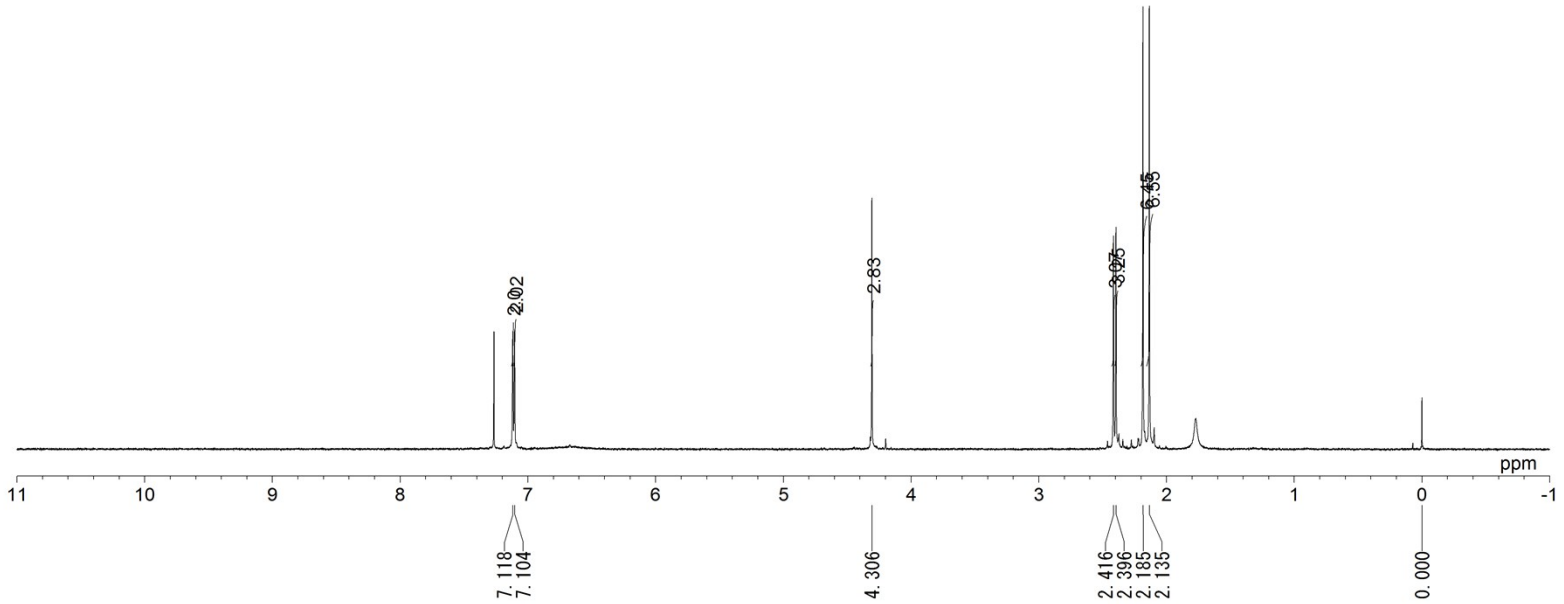
3f

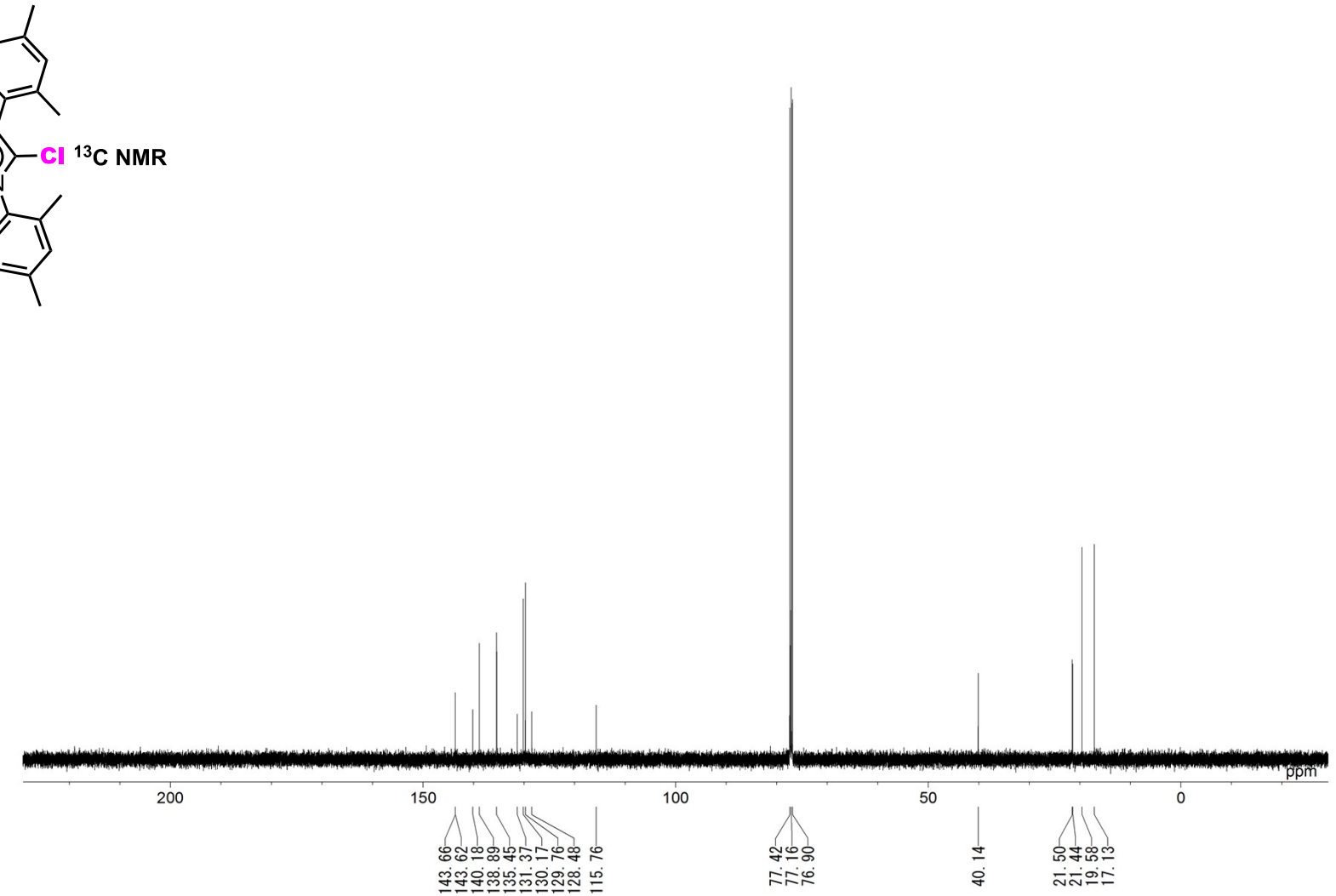



Cl
BF4

^{1}H NMR

3g


2.02
2.00
2.83
3.07
3.05
6.45
6.43
ppm
11
10
9
8
7
6
5
4
3
2
1
0
-1
7.118
7.104
4.306
2.416
2.396
2.185
2.135
0.000


Cl
13C NMR
ppm
200
150
100
50
0
143. 66
143. 62
140. 18
138. 89
135. 45
131. 37
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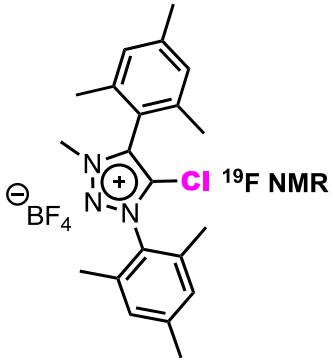
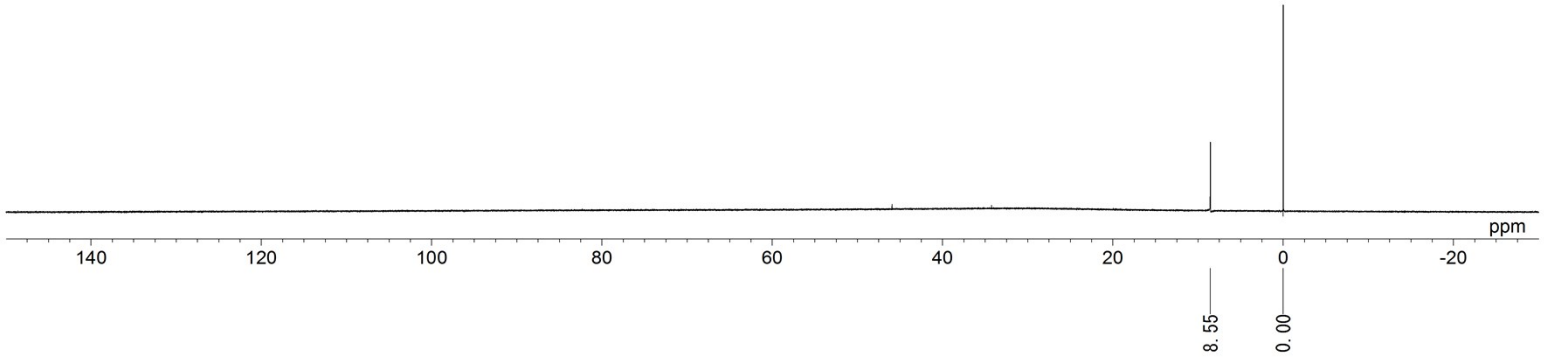
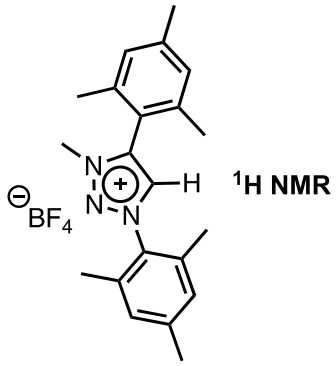
129. 76
128. 48
115. 76
77. 42
77. 16
76. 90
40. 14
21. 50
21. 44
19. 58
17. 13



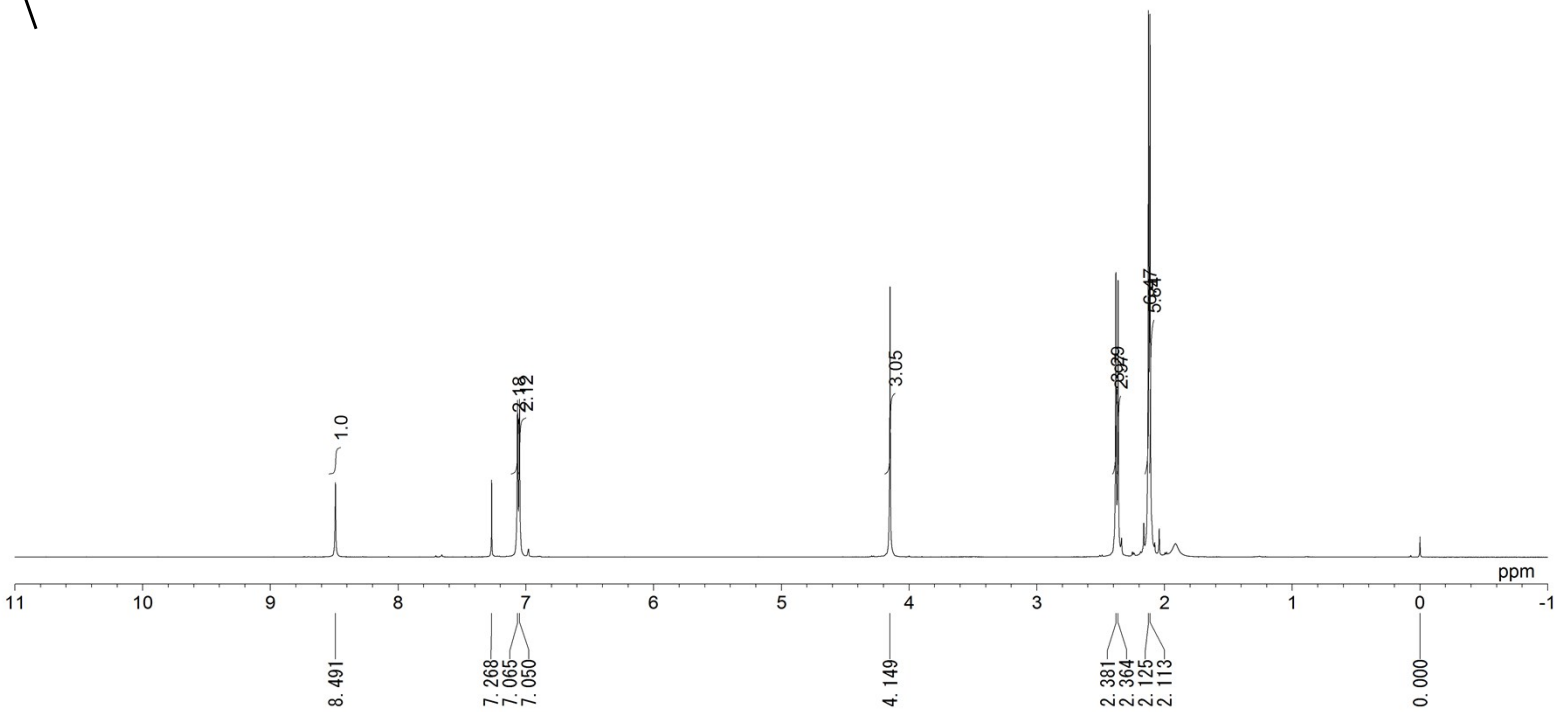
3g

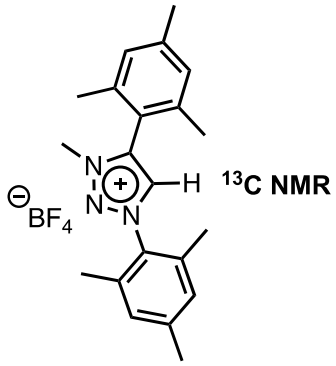




3h

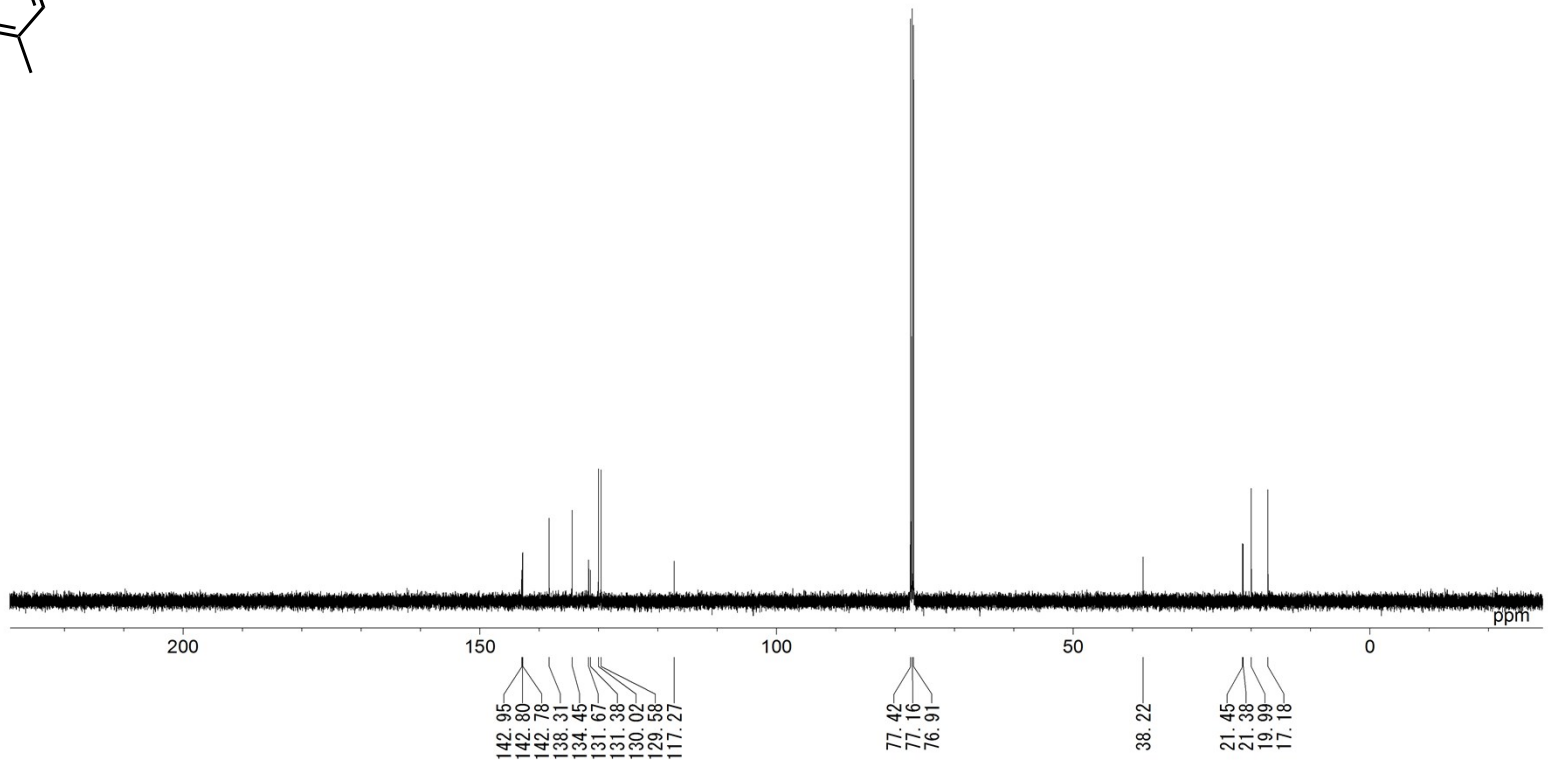
^{1}H NMR


1.0
2.12
3.05
5.47
ppm
11
10
9
8
7
6
5
4
3
2
1
0
-1
8.491
7.268
7.065
7.050
4.149
2.381
2.364
2.125
2.113
0.000



3h

^{13}C NMR


ppm
200
150
100
50
0
142. 95
142. 80
142. 78
138. 31
134. 45
131. 67
131. 38
130. 02
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117. 27
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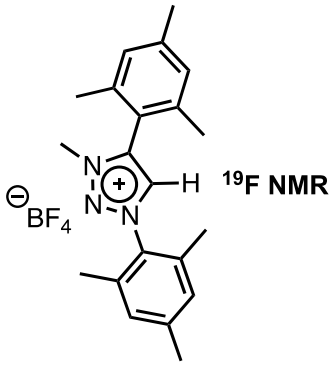
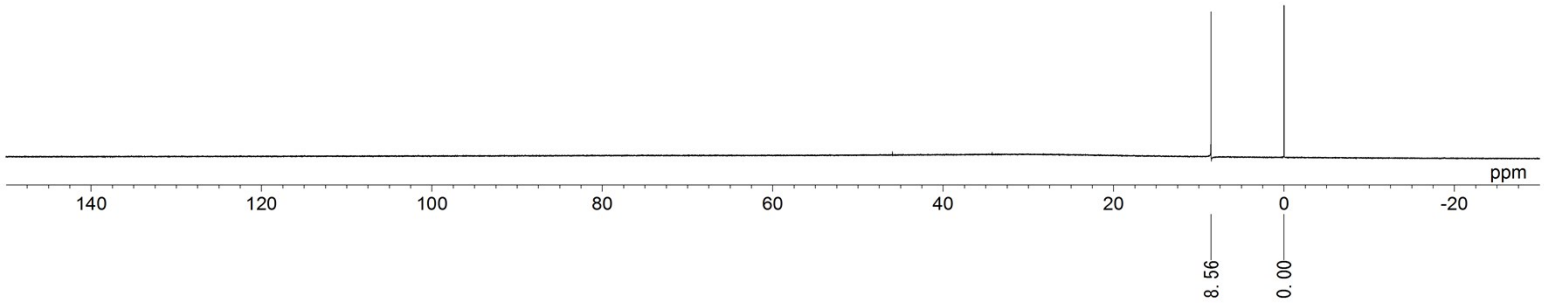
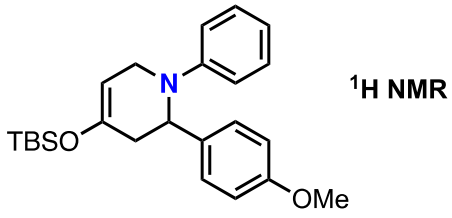
21. 45
21. 38
19. 99
17. 18



3h

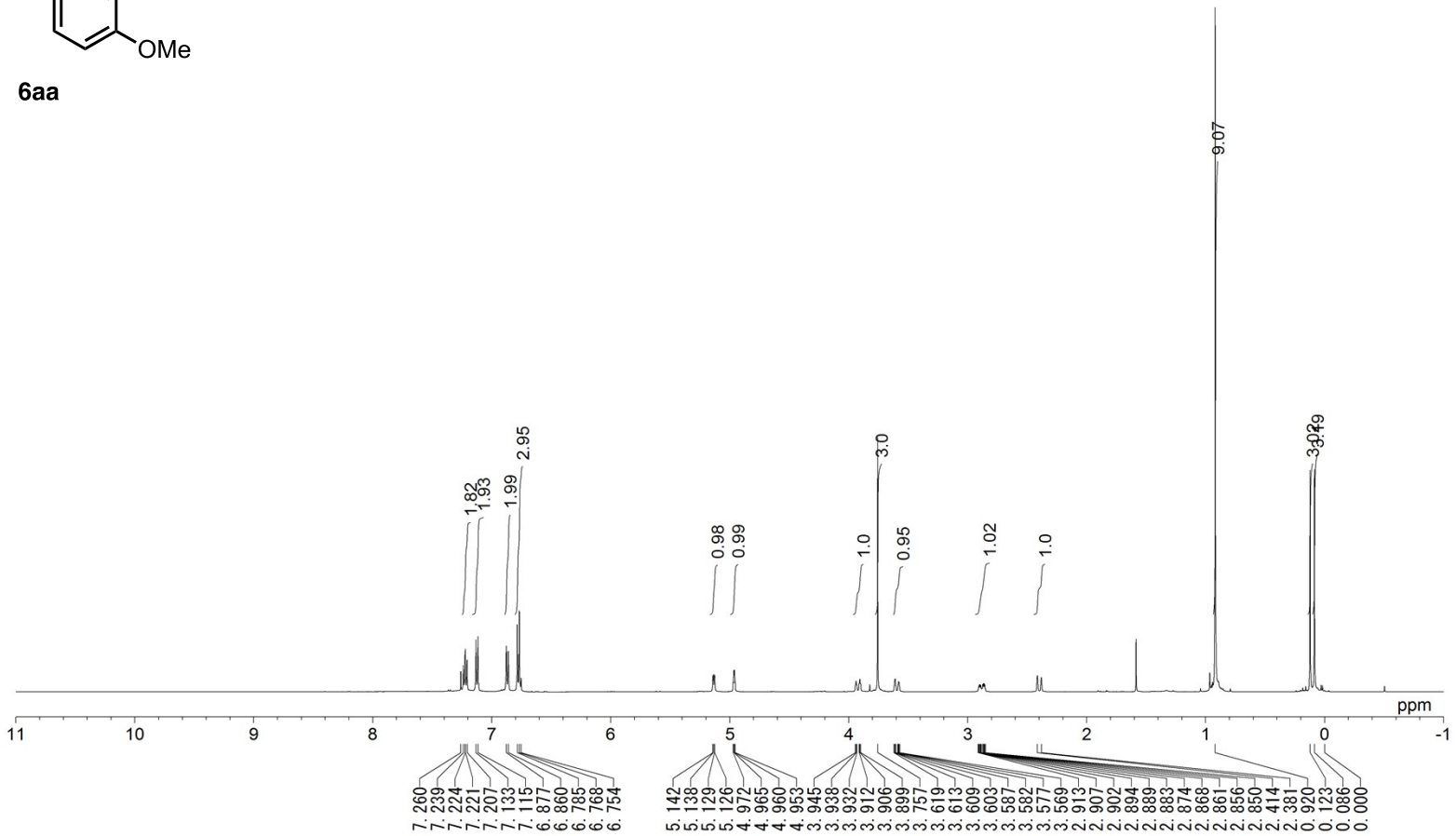
^{19}F NMR




N
TBSO
OMe

6aa

^{1}H NMR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0.99
0.95
ppm
11
10
9
8
7
6
5
4
3
2
1
0
-1
7.260
7.239
7.224
7.221
7.207
7.133
7.115
6.877
6.860
6.785
6.768
6.754
5.142
5.138
5.129
5.126
4.972
4.965
4.960
4.953
3.945
3.938
3.932
3.912
3.906
3.899
3.757
3.619
3.613
3.609
3.603
3.587
3.582
3.577
3.569
2.913
2.907
2.902
2.894
2.889
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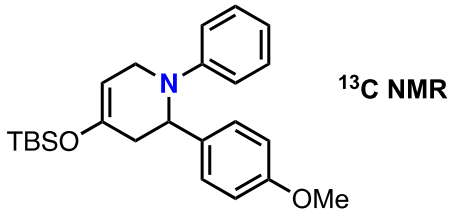
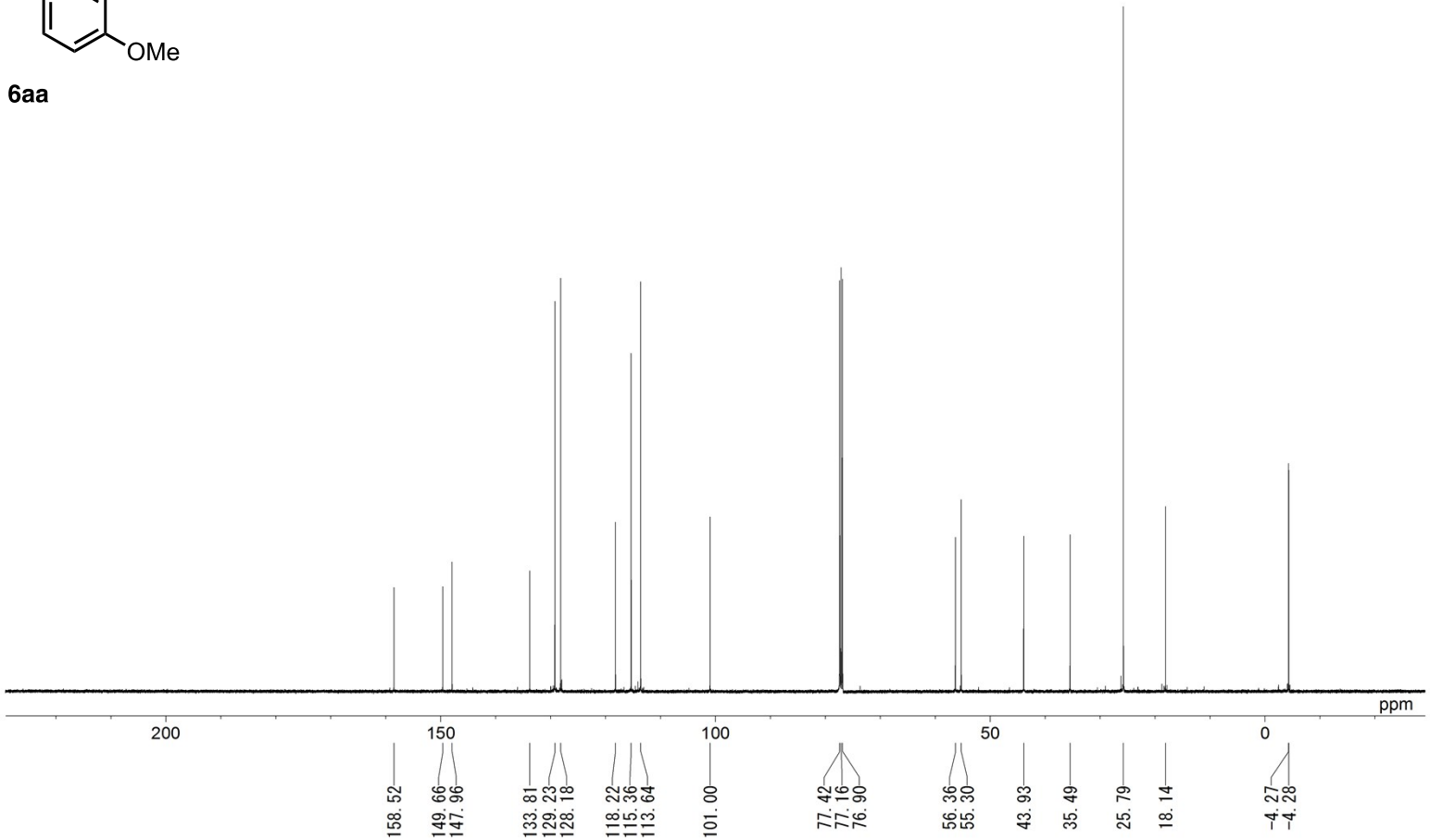

N
TBSO
OMe

6aa

^{13}C NMR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55.30
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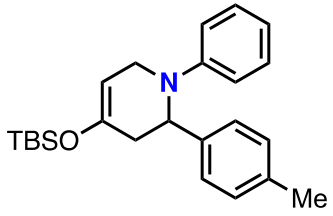
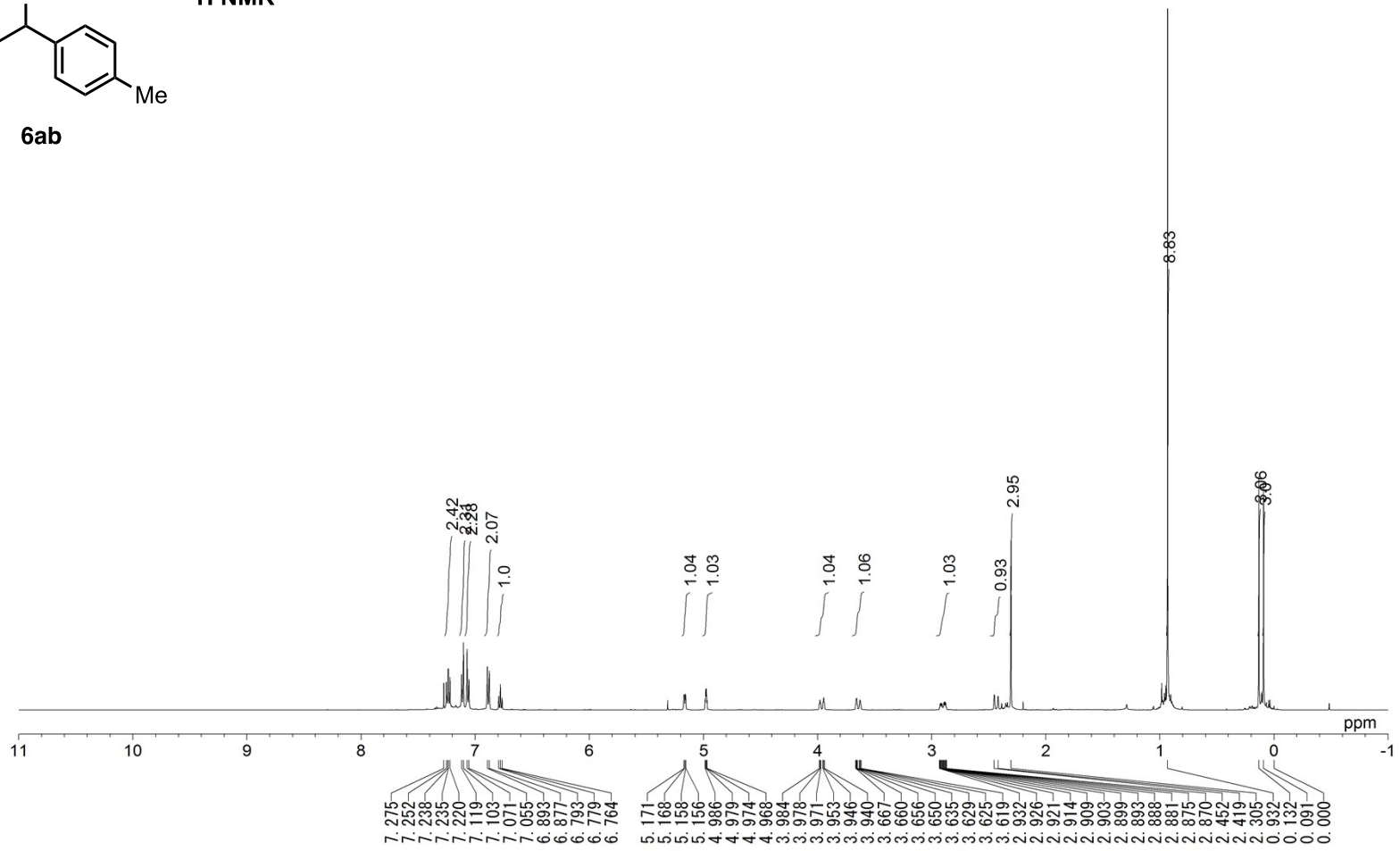
-4.28


N
TBSO
Me

6ab

^{1}H NMR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1.0
1.04
1.03
1.04
1.06
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0.93
ppm
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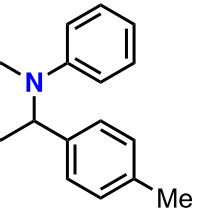
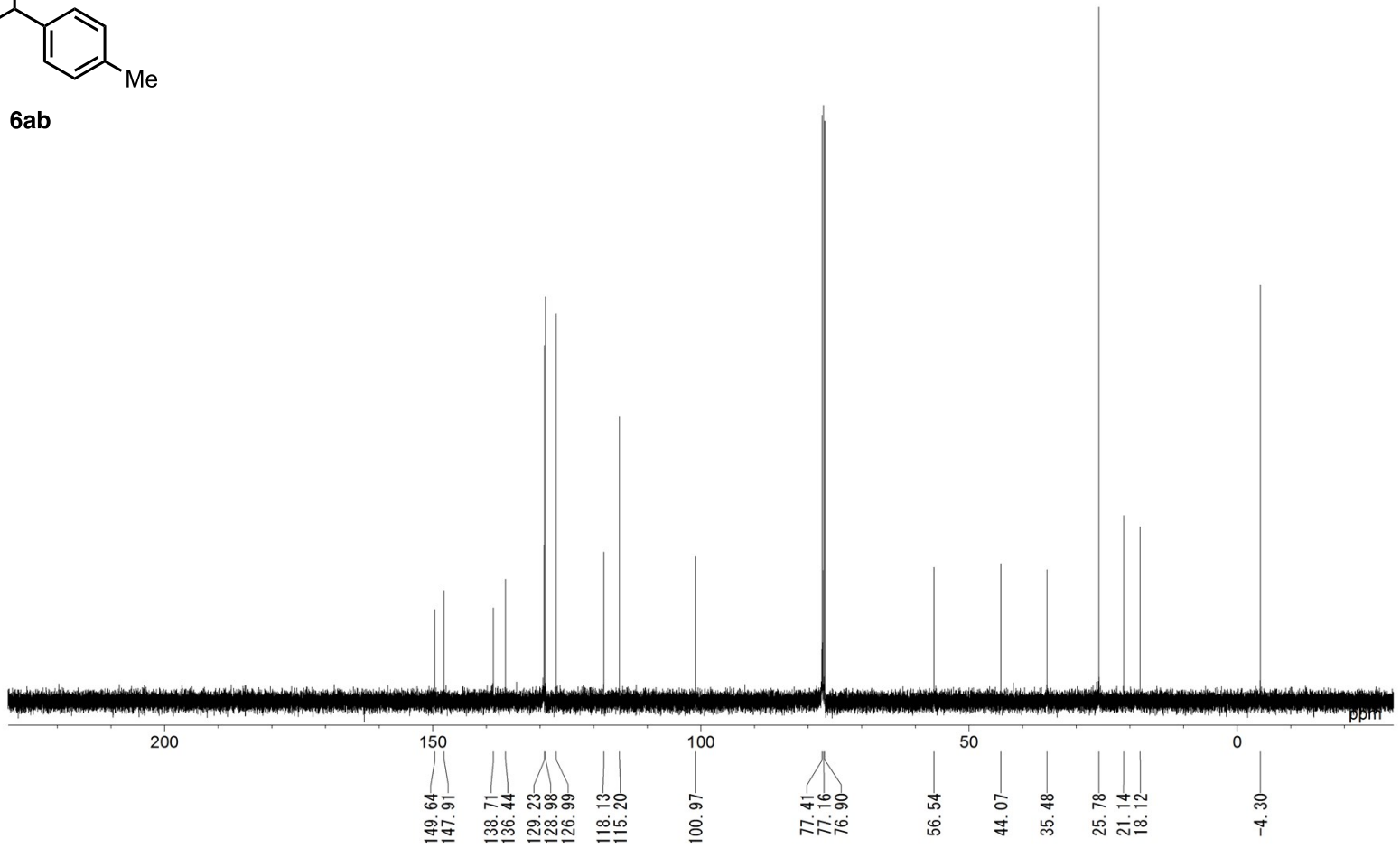
10
9
8
7
6
5
4
3
2
1
0
-1


N
Me

6ab

^{13}C NMR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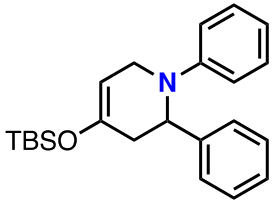
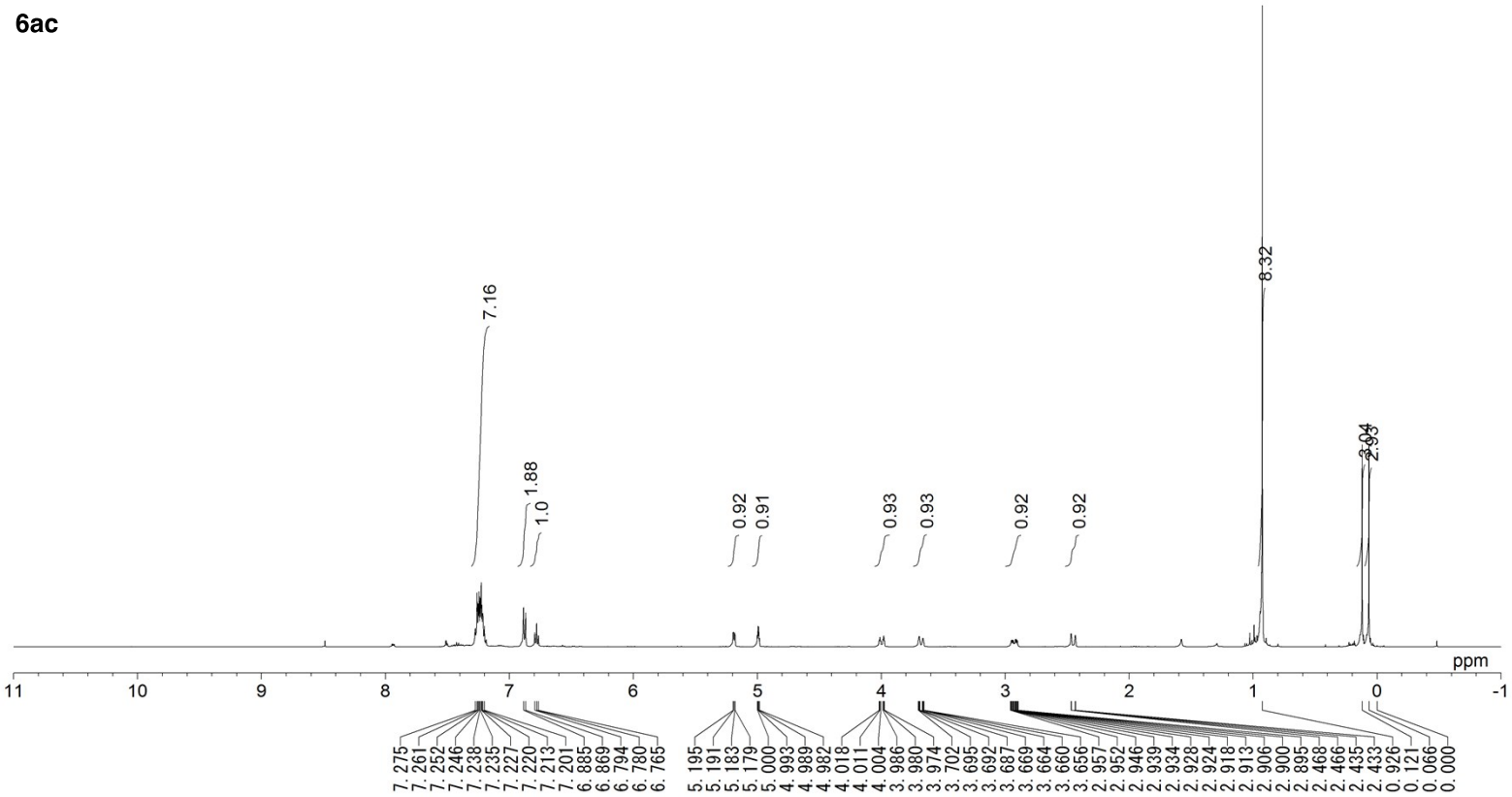
-4.30


N
TBSO

6ac

^{1}H NMR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0.91
0.93
0.93
0.92
0.92
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2.04
2.03
ppm
11
10
9
8
7
6
5
4
3
2
1
0
-1
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7.261
7.252
7.246
7.238
7.235
7.227
7.220
7.213
7.201
6.885
6.869
6.794
6.780
6.765
5.195
5.191
5.183
5.179
5.000
4.993
4.989
4.982
4.018
4.011
4.004
3.986
3.980
3.974
3.702
3.695
3.692
3.687
3.669
3.664
3.660
3.656
2.957
2.952
2.946
2.939
2.934
2.928
2.924
2.918
2.913
2.906
2.900
2.895
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2.466
2.435
2.433
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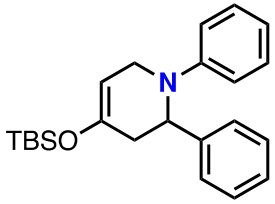
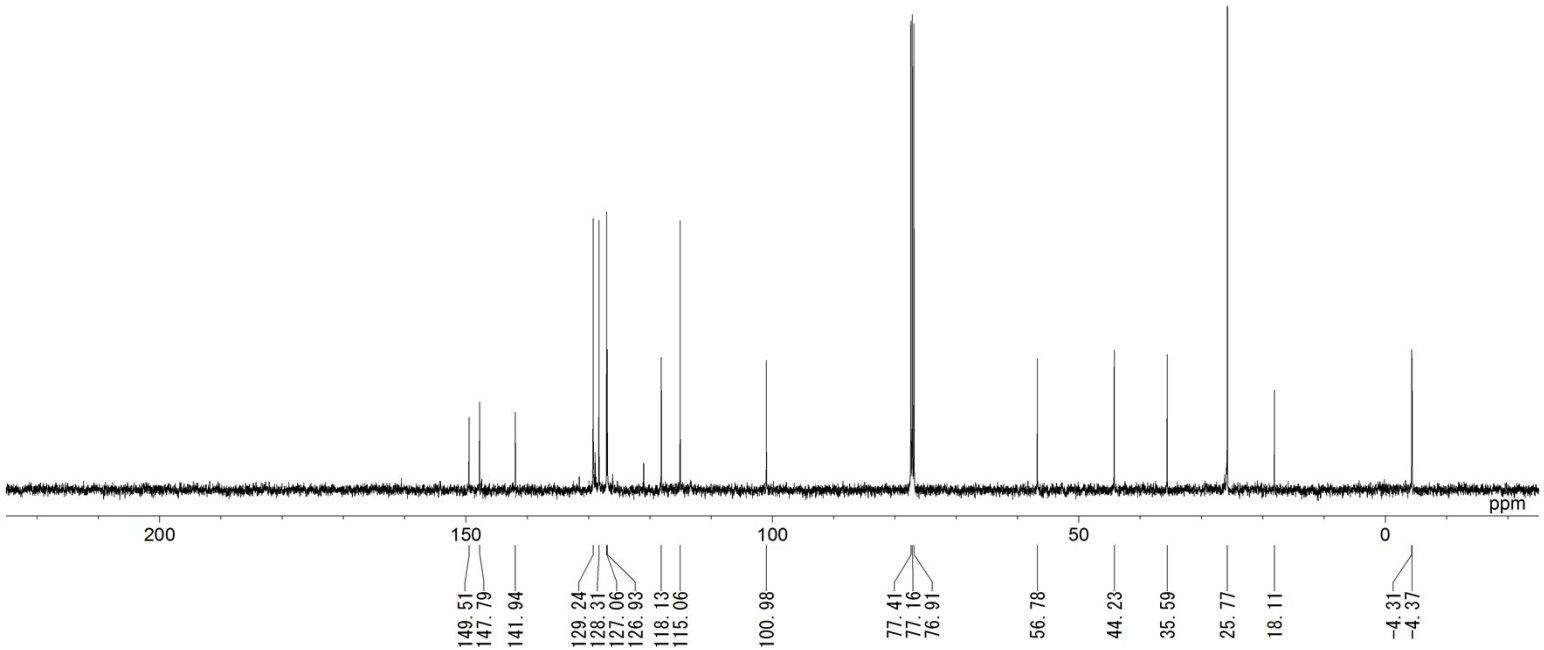
0.121
0.066
0.000


N
TBSO

6ac

^{13}C NMR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100
50
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128.31
127.06
126.93
118.13
115.06
100.98
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77.16
76.91
56.78
44.23
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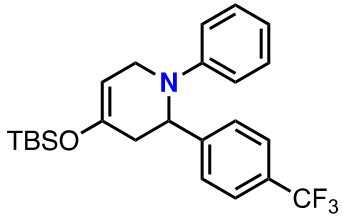
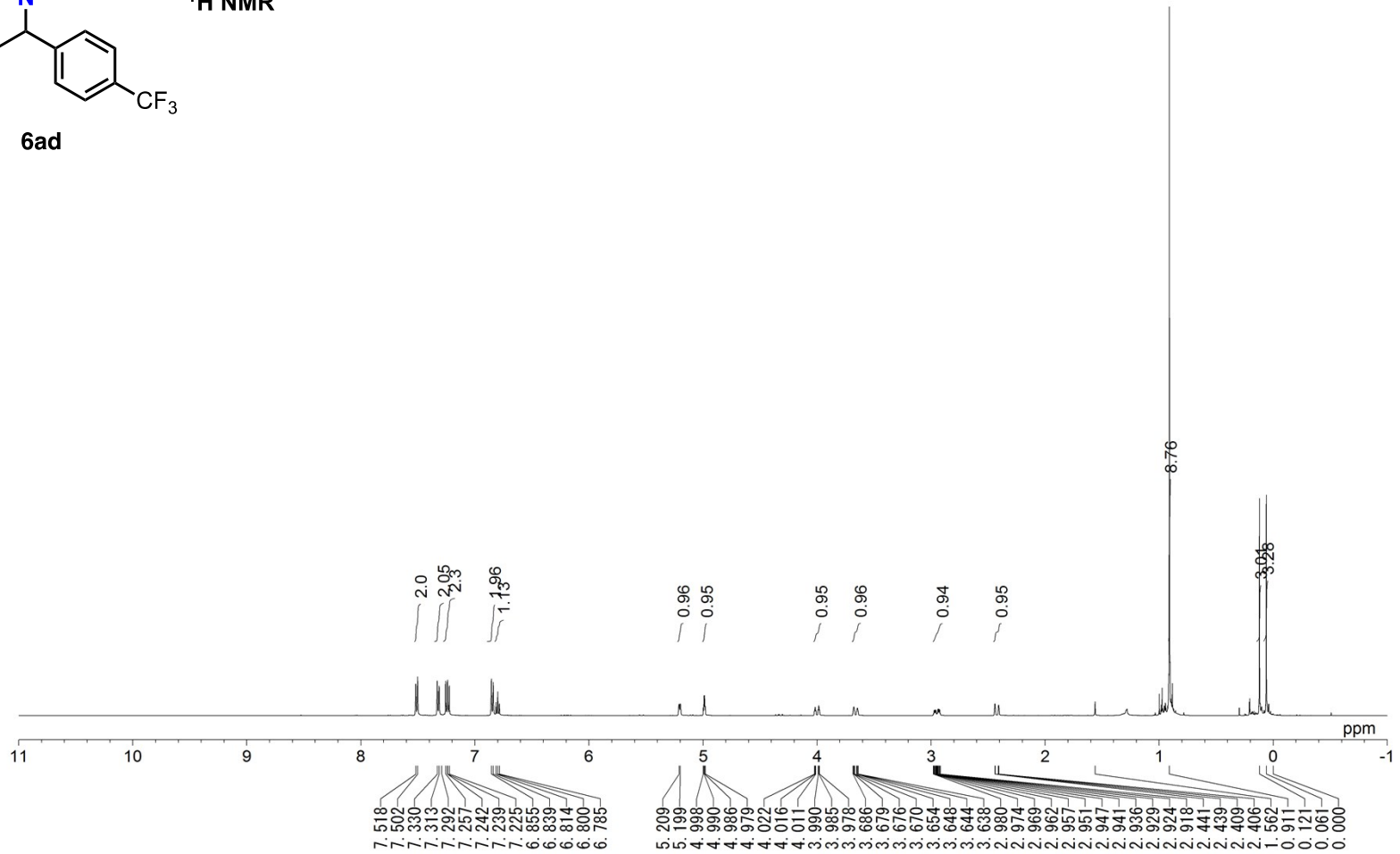
25.77
18.11
-4.31
-4.37


TBSO
N
CF3

6ad

^{1}H NMR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1.13
0.96
0.95
0.95
0.96
0.94
0.95
ppm
11
10
9
8
7
6
5
4
3
2
1
0
-1
7.518
7.502
7.330
7.313
7.292
7.257
7.242
7.239
7.225
6.855
6.839
6.814
6.800
6.785
5.209
5.199
4.998
4.990
4.986
4.979
4.022
4.016
4.011
3.990
3.985
3.978
3.686
3.679
3.676
3.670
3.654
3.648
3.644
3.638
2.980
2.974
2.969
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2.941
2.936
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2.406
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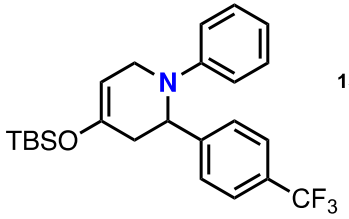
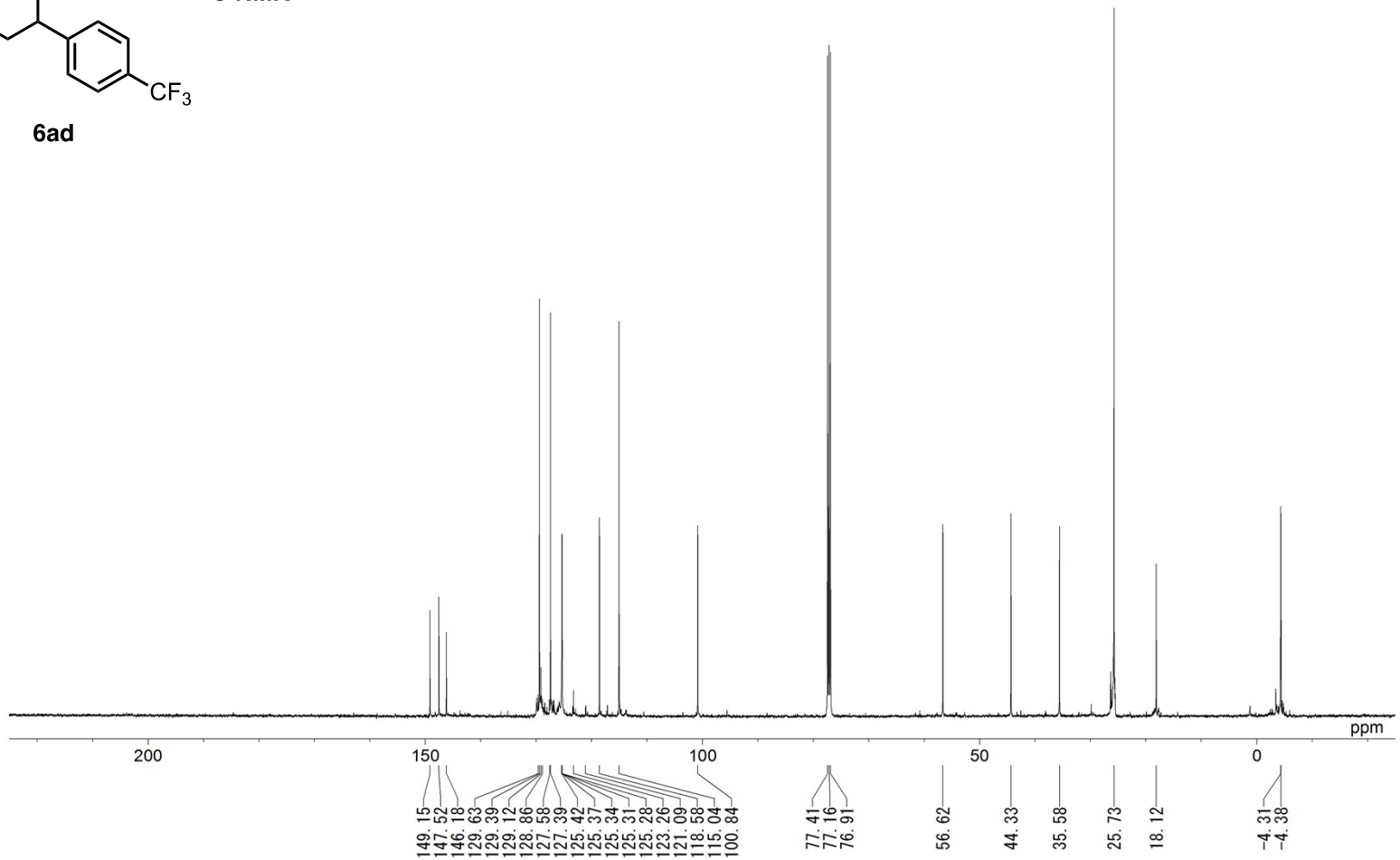
0.000


N
TBSO
CF3

6ad

^{13}C NMR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128.86
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127.39
125.42
125.37
125.34
125.31
125.28
123.26
121.09
118.58
115.04
100.84
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77.16
76.91
56.62
44.33
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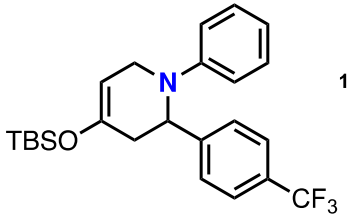
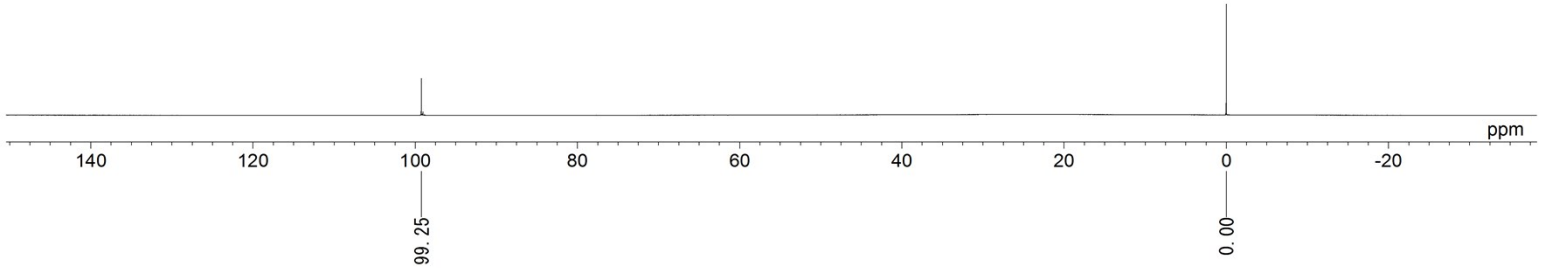
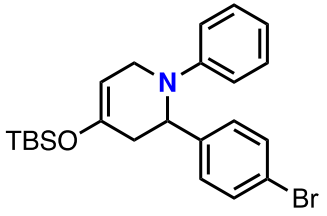
18.12
-4.31
-4.38



6ad

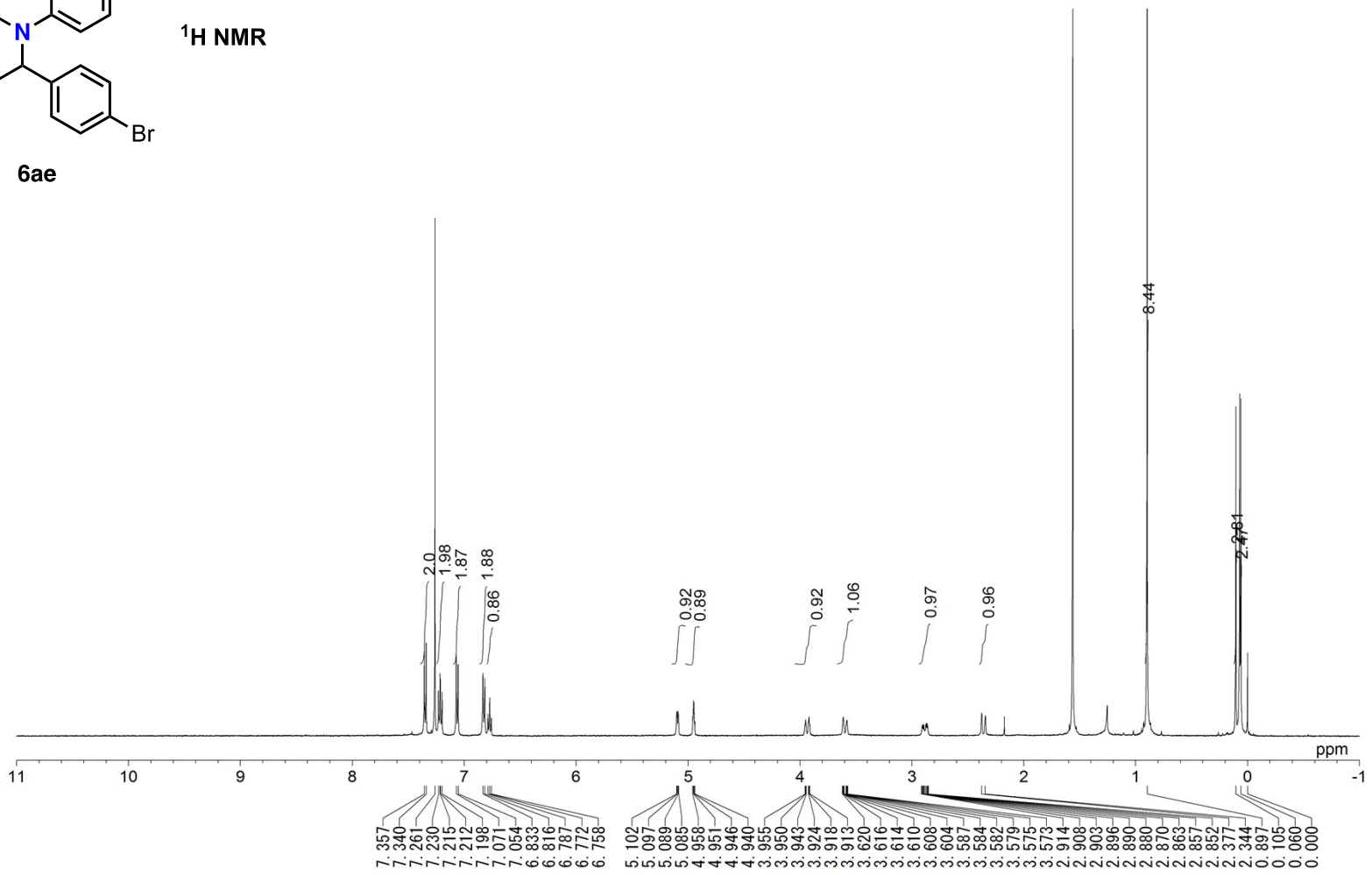
^{19}F NMR




N
TBSO
Br

6ae

^{1}H NMR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1.98
1.87
1.88
0.86
0.92
0.89
0.92
1.06
0.97
0.96
8.44
2.81
2.47
ppm
11
10
9
8
7
6
5
4
3
2
1
0
-1
7.357
7.340
7.261
7.230
7.215
7.212
7.198
7.071
7.054
6.833
6.816
6.787
6.772
6.758
5.102
5.097
5.089
5.085
4.958
4.951
4.946
4.940
3.955
3.950
3.943
3.924
3.918
3.913
3.620
3.616
3.614
3.610
3.608
3.604
3.587
3.584
3.582
3.579
3.575
3.573
2.914
2.908
2.903
2.896
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2.863
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2.344
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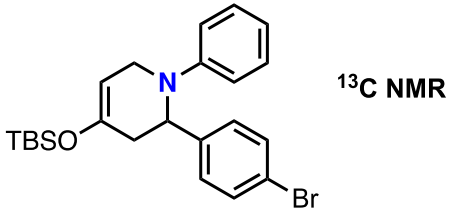
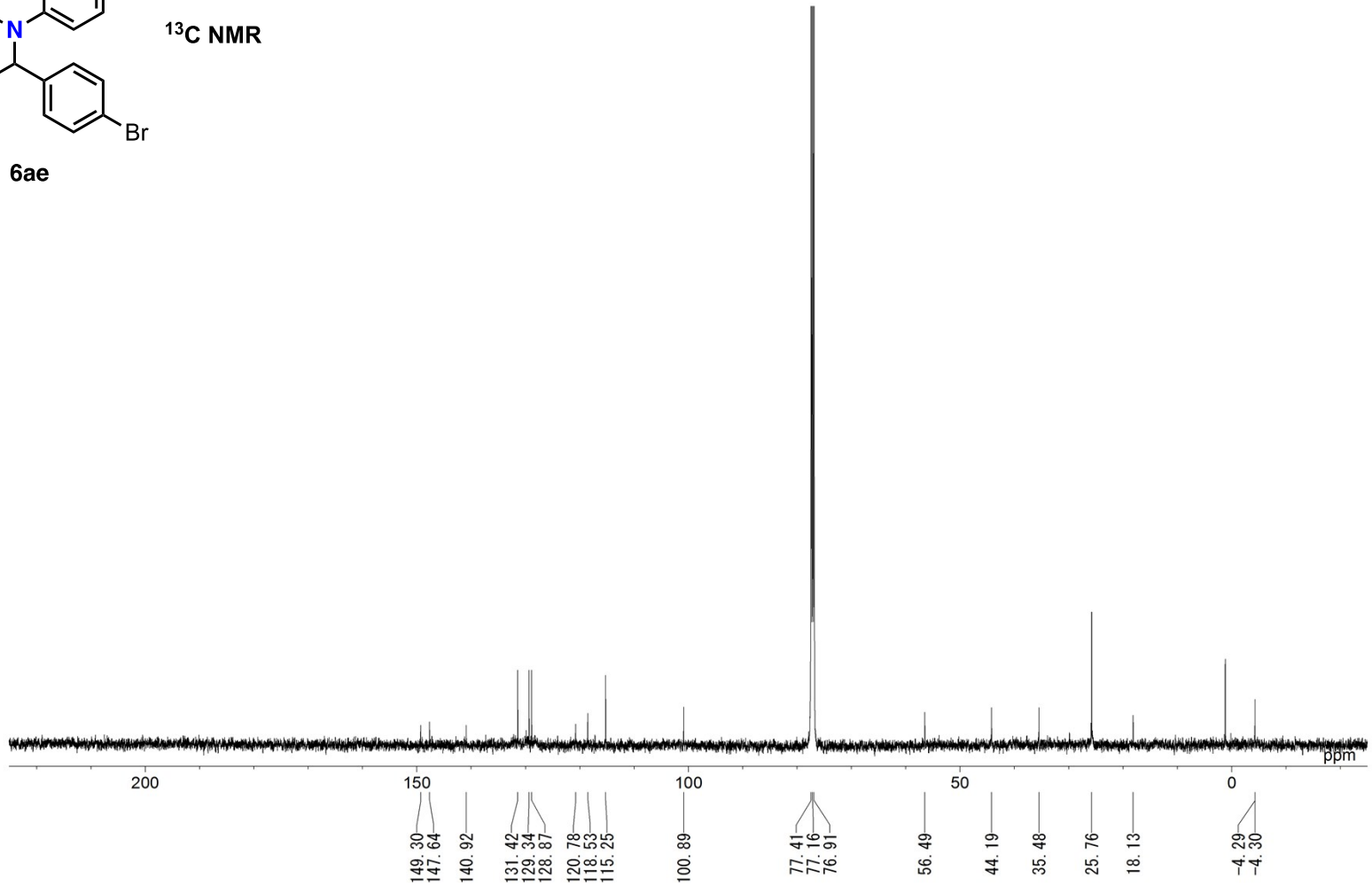
0.000


N
TBSO
Br

6ae

^{13}C NMR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50
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140.92
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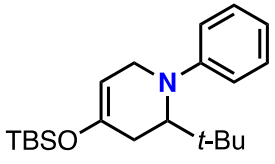
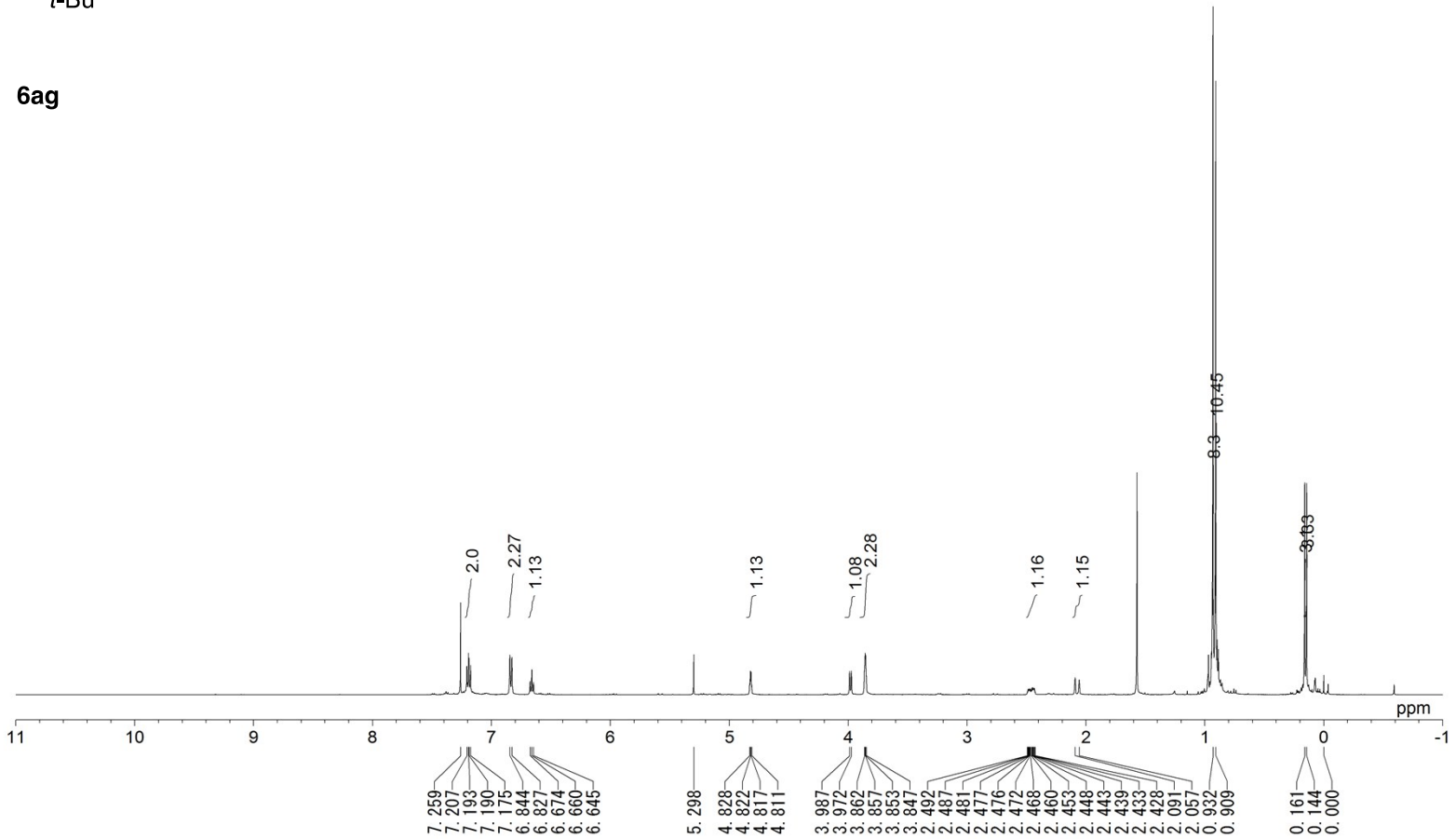
129.34
128.87
120.78
118.53
115.25
100.89
77.41
77.16
76.91
56.49
44.19
35.48
25.76
18.13
-4.29
-4.30


N
TBSO
t-Bu

^{1}H NMR

6ag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1.13
1.13
1.08
2.28
1.16
1.15
8.3
10.45
3.03
ppm
11
10
9
8
7
6
5
4
3
2
1
0
-1
7.259
7.207
7.193
7.190
7.175
6.844
6.827
6.674
6.660
6.645
5.298
4.828
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4.817
4.811
3.987
3.972
3.862
3.857
3.853
3.847
2.492
2.487
2.481
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2.476
2.472
2.468
2.460
2.453
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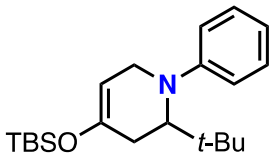
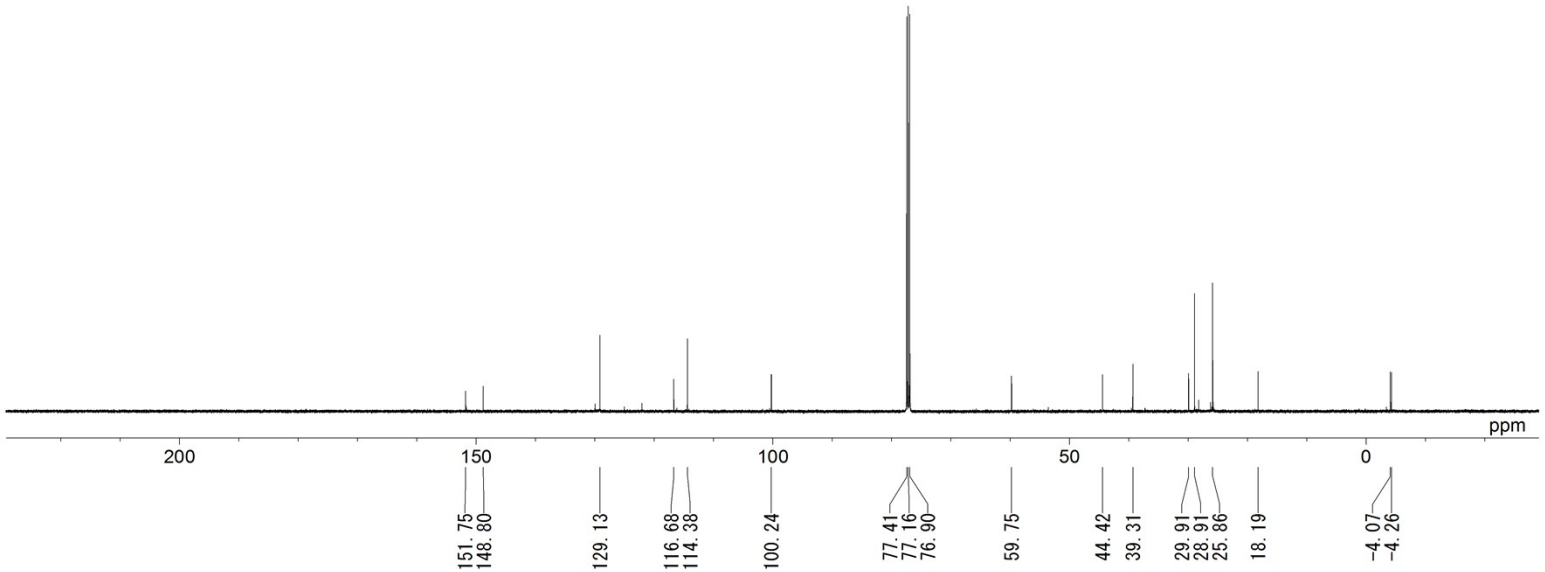

N
TBSO
t-Bu

^{13}C NMR

6ag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100
50
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151.75
148.80
129.13
116.68
114.38
100.24
77.41
77.16
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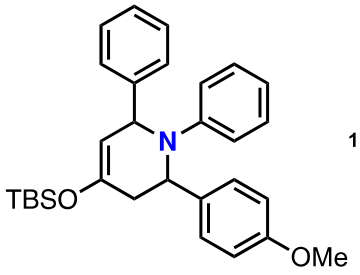
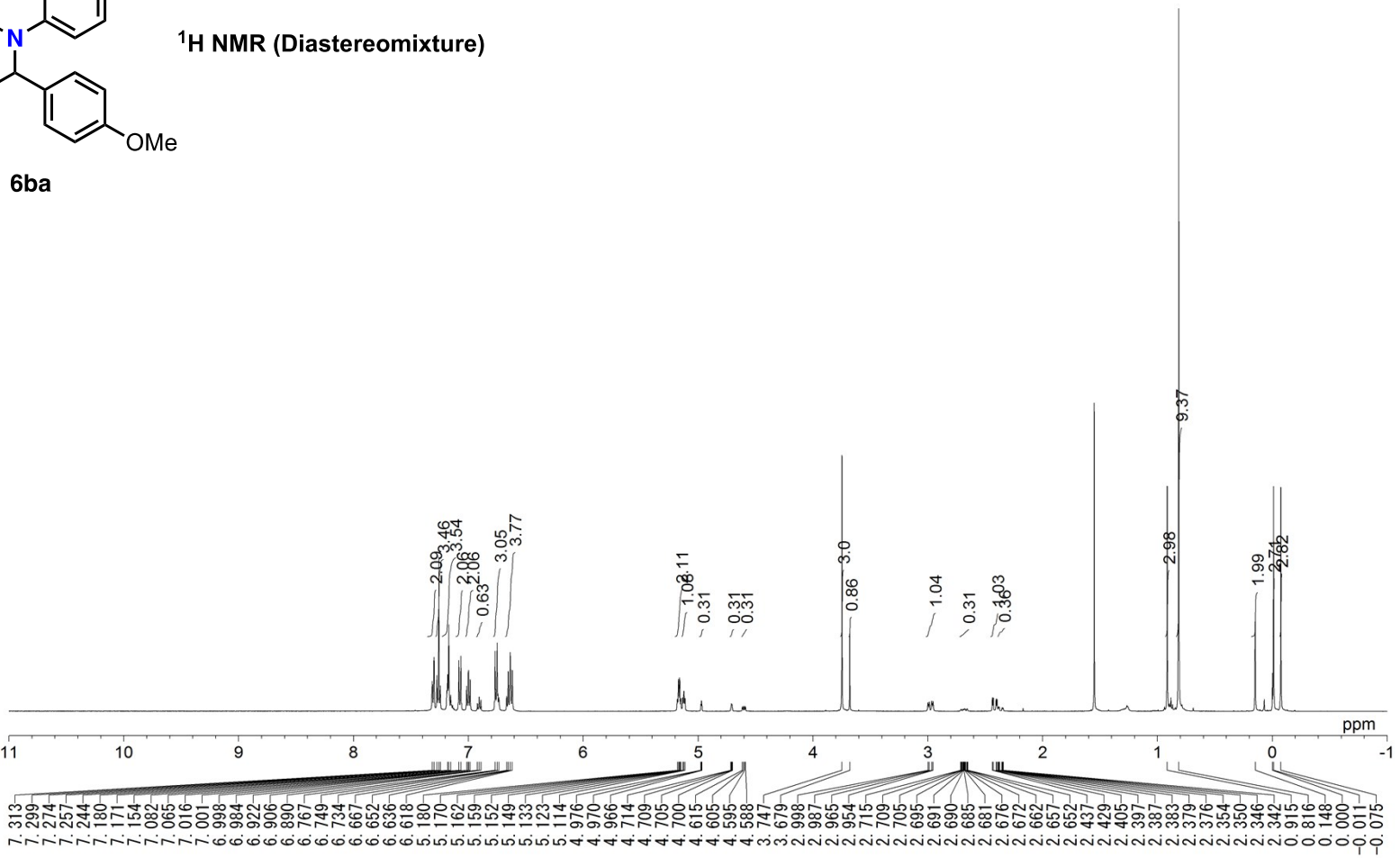
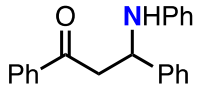
18.19
-4.07
-4.26



6ba

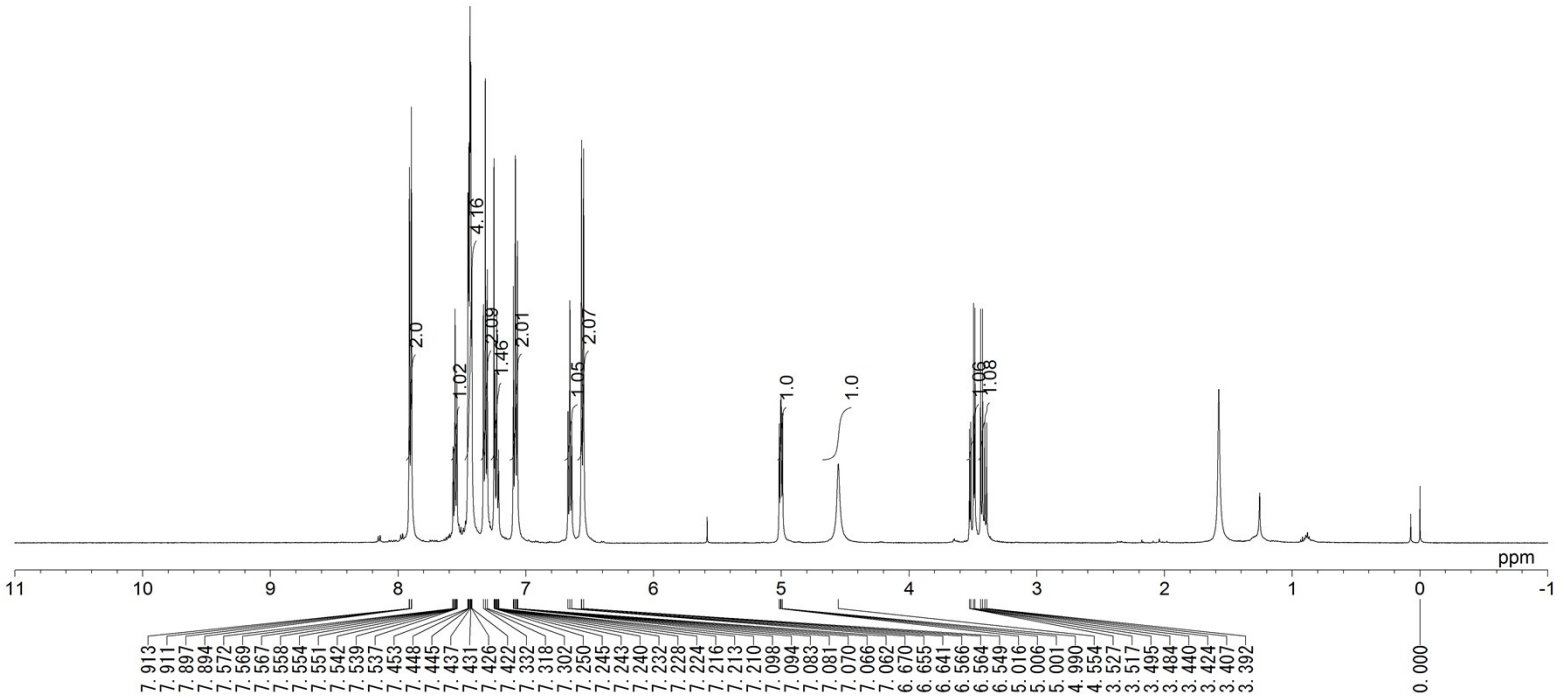
^{1}H NMR (Diastereomixture)




O
NHPh
Ph
Ph

8

^{1}H NMR


2.0
1.02
4.16
2.09
1.46
2.01
1.05
2.07
1.0
1.0
1.06
1.08
ppm
11
10
9
8
7
6
5
4
3
2
1
0
-1
7.913
7.911
7.897
7.894
7.572
7.569
7.567
7.558
7.554
7.551
7.542
7.539
7.537
7.453
7.448
7.445
7.437
7.431
7.426
7.422
7.332
7.318
7.302
7.250
7.245
7.243
7.240
7.232
7.228
7.224
7.216
7.213
7.210
7.098
7.094
7.083
7.081
7.070
7.066
7.062
6.670
6.655
6.641
6.566
6.564
6.549
5.016
5.006
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3.440
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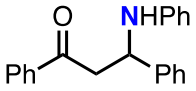
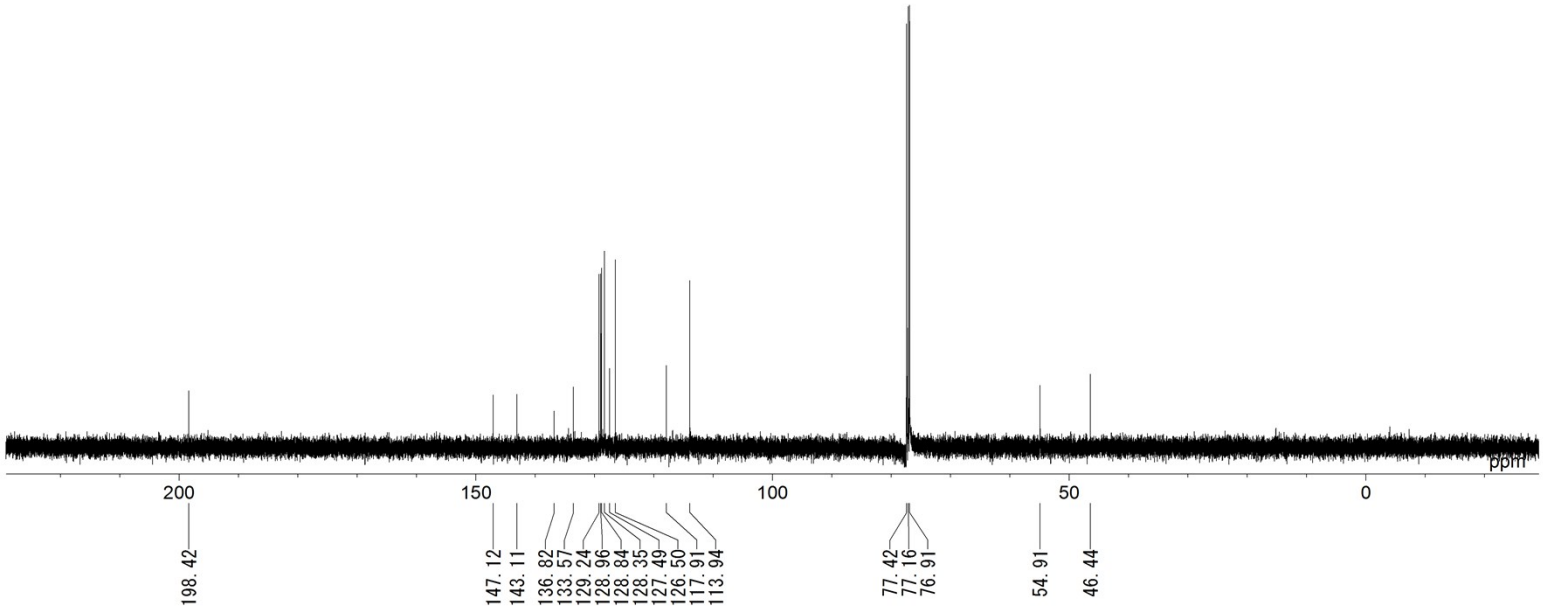
3.392
0.000


O
NHPh
Ph
Ph

8

^{13}C NMR


ppm
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143.11
136.82
133.57
129.24
128.96
128.84
128.35
127.49
126.50
117.91
113.94
77.42
77.16
76.91
54.91
46.44

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[2] S. W. Kwok, J. R. Fotsing, R. J. Fraser, V. O. Rodionov and V. V. Fokin, *Org. Lett.*, 2010, **12**, 4217.

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