Electronic Supplementary Information

A new, *substituted* palladacycle for ppm level Pd-catalyzed Suzuki-Miyaura cross couplings in water

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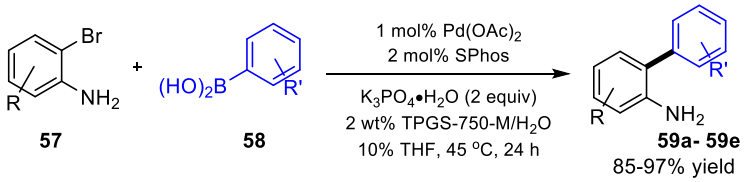
1. General information

Reagents were purchased from Sigma-Aldrich, Combi-Blocks, Alfa Aeser, or Acros Organics and used without further purifications. Palladium acetate was supplied generously by Johnson Matthey. ^{1}H and ^{13}C NMR spectra were recorded on either a Varian Unity Inova 400 MHz (400 MHz for ^{1}H, 100 MHz for ^{13}C), a Varian Unity Inova 500 MHz (500 MHz for ^{1}H, 125 MHz for ^{13}C) or on a Varian Unity Inova 600 MHz spectrometer (600 MHz for ^{1}H); d_6-DMSO, CD_3OD, CD_3CN and $CDCl_3$ were used as a solvent. Residual peaks for $CHCl_3$ in $CDCl_3$ (1 H = 7.26 ppm, ^{13}C = 77.20 ppm), $(CH_3)_2SO$ in $(CD_3)_2SO$ (1 H = 2.50 ppm, ^{13}C = 39.52 ppm), CH_3CN in CD_3CN (^{1}H = 1.98 ppm, ^{13}C = 0.49 and 117.47 ppm) or MeOH in MeOD (^{1}H = 4.78 ppm, ^{13}C = 49.00 ppm) have been assigned. The chemical shifts are reported in ppm, the coupling constants *J* are given in Hz. The peak patterns are indicated as follows: bs, broad singlet; s, singlet; d, doublet; t, triplet; q, quartet; p, pentate; m, multiplet. Thin layer chromatography (TLC) was performed using Silica Gel 60 F254 plates (Merck, 0.25 mm thick). Flash chromatography was done in glass columns using Silica Gel 60 (EMD, 40-63 μm). GCMS data were recorded on a 5975C Mass Selective Detector, coupled with a 7890A Gas Chromatograph (Agilent Technologies). Cryo-electron microscopy was performed at material research laboratory (MRL-UCSB) using FEI Tecnai G2 Sphera Microscope with CCD camera (Gatan Ultrascan 1000 2Kx2K). TPGS-750-M is either prepared or supplied by PHT International (it is also available from Sigma-Aldrich, catalog #733857). The desired 2 wt% TPGS-750-M solution in HPLC water (which was degassed with argon prior to use) was prepared by dissolving 2 g of TPGS-750-M solid to 98 g of HPLC water and stored under argon.

Compounds **3**,[1] **4**,[2] **6**,[3] **21**,[4] **27**,[5] **29**,[6] **30**,[7] **52**,[8] **54**,[9] **60**,[10] **67**,[11] **68**,[12] were confirmed by comparing with literature NMR. All other new compounds were characterized by ^{1}H-, ^{13}C-, ^{19}F-, ^{31}P-NMR and HRMS.

2. Preparation of pre-catalysts: general procedure

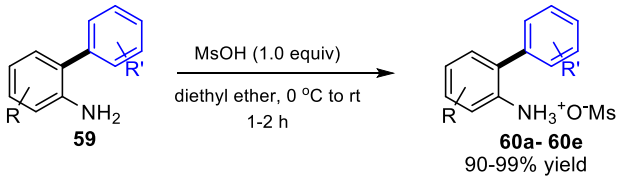
a. Synthesis of biarylamines (59a- 59e)



Scheme S1. Synthesis of substituted biarylamines.

In a 25 mL round bottom flask containing Teflon coated magnet were added 4.0 mmol of Ar-Br (**57**), 5.0 mmol of Ar-B(OH)$_2$ (**58**), 1 mol % Pd(OAc)$_2$, 2 mol % SPhos and 8.0 mmol of K_3PO_4•H_2O. The flask was degassed and backfilled with argon (this procedure was repeated 3 times). Finally, 7.2 mL of aqueous 2 wt % TPGS-750-M solution and 0.8 mL of THF were added and the reaction mixture was stirred at 45 °C for 24 h. After completion, the reaction mixture was extracted with EtOAc, the combined organic layers were washed with brine and then dried over anhydrous $MgSO_4$, and then the solvent was evaporated in vacuo. The crude product was purified by flash chromatography on silica gel using hexanes/EtOAc as eluent to afford compounds **59a- 59e**.

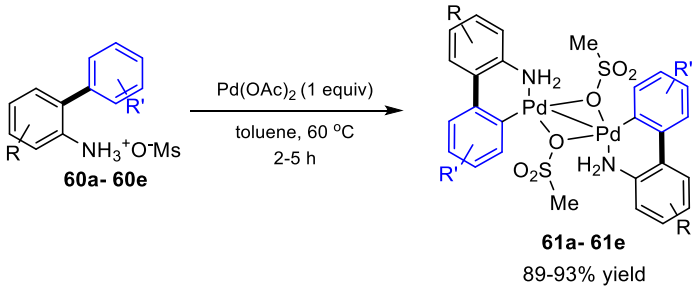
b. Preparation of mesylate salts from biarylamines (60a- 60e)



Scheme S2. Synthesis of mesylate salts of substituted biarylamines.

In a 25 mL round bottom flask containing Teflon coated magnet was dissolved 3.0 mmol of biarylamine (**59**) in dry Et_2O. The flask is then cooled to 0 °C. Methanesulfonic acid (3.0 mmol) was added dropwise at 0 °C, and after complete addition, the reaction mixture was stirred at rt until a white precipitate forms (generally, 1-2 h). The white precipitate was filtered, washed with Et_2O and dried under vacuum overnight to give the corresponding mesylate salts, **60a- 60e** as white solids.

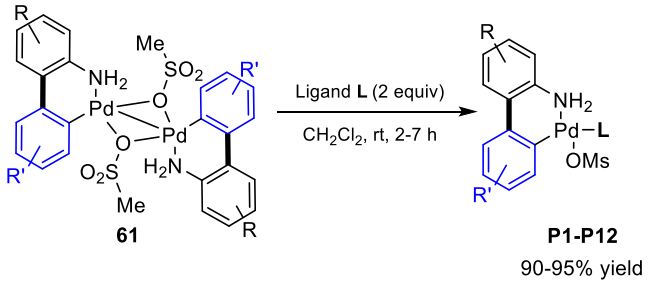
c. Preparation of Pd dimers from mesylate salts (61a- 61e)



Scheme S3. Synthesis of Pd dimers from mesylate salts of substituted biarylamines.

To a 10 mL round bottom flask containing a Teflon-coated magnet were added 2.0 mmol of mesylate salt (**60a- 60e**), 2.0 mmol of $Pd(OAc)_2$ and the flask was degassed and refilled with argon (repeated 3 times). Finally, 6 mL dry toluene was added under argon and the reaction mixture was stirred at 60 °C for 2-5 h until a clear solution formed. The reaction mixture was cooled to rt, and at this point, in some cases product precipitated out. It was filtered and washed with toluene, and dried under vacuum, while in some cases, where product remained soluble in toluene, the toluene was evaporated to 90% of its volume and dry hexanes was added to precipitate product. This product was then filtered and dried under vacuum to give the desired dimers of palladium as **61a- 61e**.

d. Preparation of palladacycle pre-catalysts (P1- P12) from Pd dimers

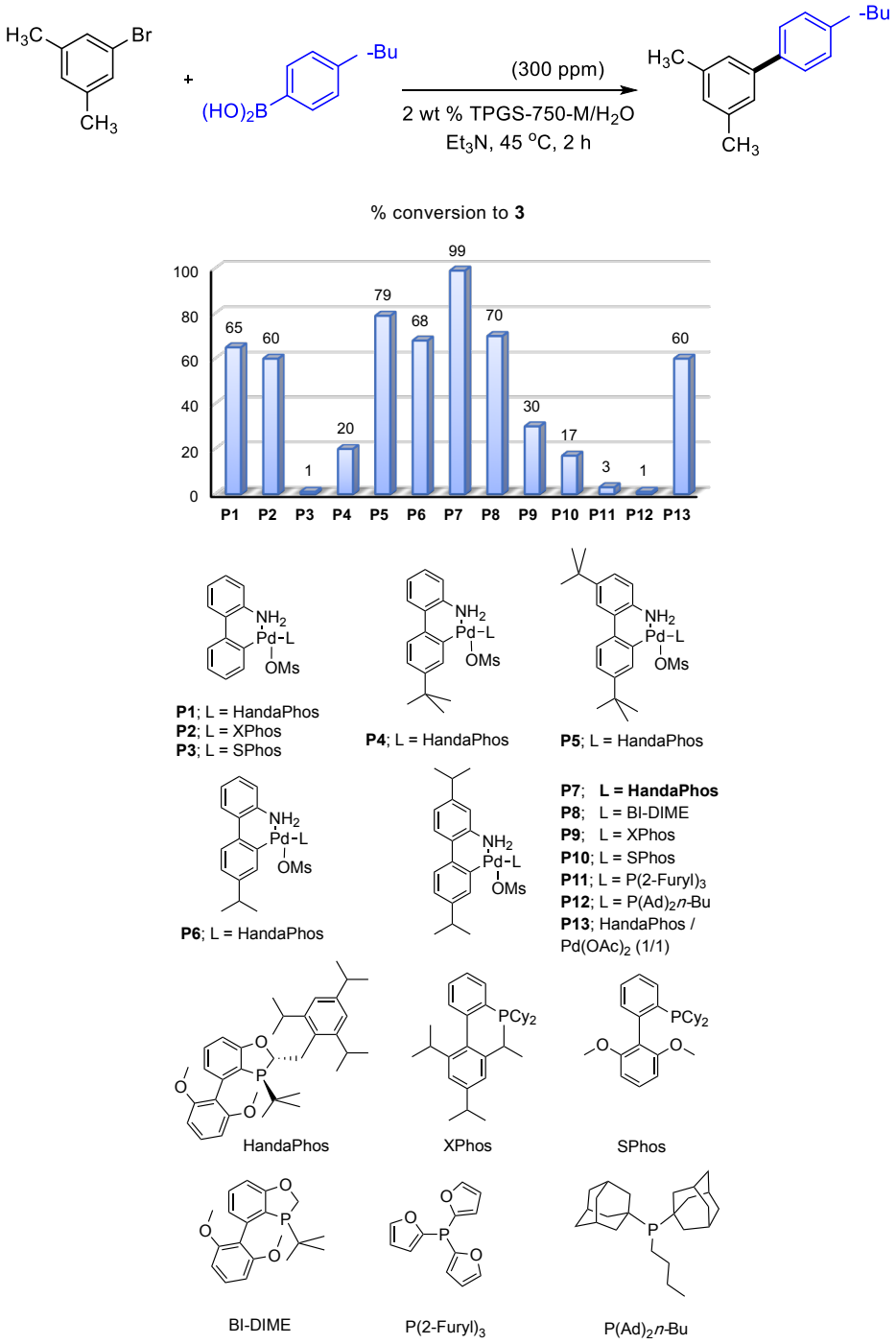


Scheme S4. Synthesis of palladacycle pre-catalysts.

To a 10 mL round bottom flask containing Teflon coated magnet were added 1.0 mmol of Pd dimer (**61a- 61e**), 2.0 mmol of ligand (**L**) and the flask was degassed and refilled with argon (repeated 3 times). Finally, 4 mL dry DCM was added under argon and the reaction mixture was stirred at rt for 2-7 h until the solution becomes clear. The DCM was evaporated to 90% of its volume and dry pentanes was added to triturate the resulting oil.

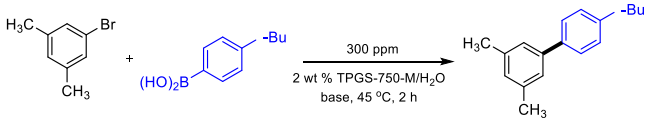
The solvent was again evaporated to give a free flowing solid (more pentane triturations were repeated until a free flowing solid has been obtained). The solid was then filtered, washed with pentanes, and dried under vacuum overnight to give the desired palladacycles **P1- P12**.

3. Optimization study:



Scheme S5. Comparison of reactivity of palladacycles (300 ppm Pd in water).

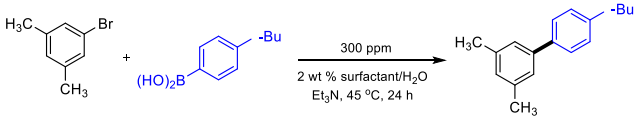
4. Base screenings



base	GC conv (%)
Et_3N	99
iPr_2NEt	80
$K_3PO_4•H_2O$	98
K_2CO_3	78

Scheme S6. Suzuki-Miyaura couplings in different bases.

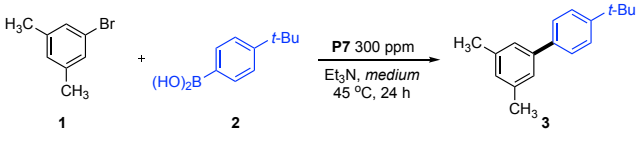
5. Surfactant study:

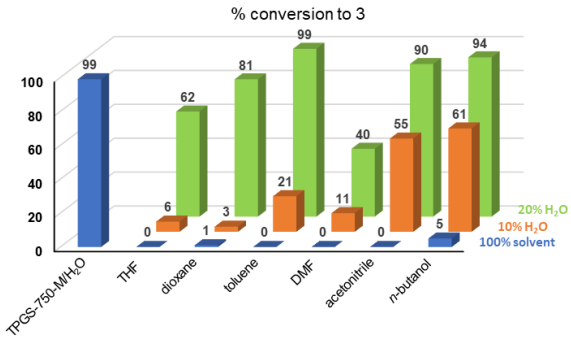


surfactant	GC conv (%)
TPGS-750-M	99
Nok	92
Triton-X-100	77
solutol	71
pluronic	69
Brij-30	68
PTS-600	62
cremophor EL	50

Scheme S7. Suzuki-Miyaura couplings in different surfactant solutions.

6. Couplings in water and aqueous organic solvents:





Scheme S8. Couplings in water and in aqueous organic solvents

7. Preparation of a stock solution:

In total 10,000 ppm of Pd catalyst solution was prepared by dissolving the corresponding pre-catalyst or $Pd(OAc)_2$/HandaPhos in 3.3 mL dry and degassed THF. This stock solution was used to carry out several (~30) reactions (stock solution can either be used freshly or can be stored up to a few weeks under argon in a freezer). For 300 ppm catalyst loading, 100 μL of this stock solution was used.

8. General procedure for Suzuki-Miyaura couplings of aryl iodides and bromides:

From the stock solution above, the desired amount (e.g., 100 μL for 300 ppm Pd) of solution was added to a Teflon coated magnet containing 1-dram screw cap vial and covered with a rubber septum. The THF from this solution was evacuated under low pressure (~20 min). The aryl/vinyl halide (0.5 mmol; if solid or added after an evacuation/backfill sequence if liquid), 0.6 mmol boronic acid were added to this vial. The vial was evacuated and backfilled with argon (this procedure was repeated three times). Aqueous 2 wt % TPGS-750-M solution (1.0 mL) followed by Et_3N (1.0 mmol) were added under argon. The vial was quickly replaced with the screw cap and stirred at 45 ^oC until completion (as monitored by TLC or GC-MS). The products were then separated by either filtration, decantation of the aqueous layer, or extraction with a minimum amount of MTBE or EtOAc. The organic layer was adsorbed on silica and purified using flash column chromatography.

9. General procedure for Suzuki-Miyaura couplings of aryl chlorides:

The similar stock solution as noted above was prepared in which 100 μL corresponds to 500 ppm Pd. An aryl chloride (0.5 mmol, if solid or added after evacuation/backfill sequence if liquid) and boronic acid (0.6 mmol) were added to a 1-dram screw cap vial containing Teflon coated magnet. The vial was evacuated and backfilled with argon (this procedure was repeated three times). From the stock solution, 100 μL were added, along with aqueous 2 wt % TPGS-750-M (0.9 mL) and Et_3N (1.0 mmol) sequentially under argon. The vial was quickly replaced with the screw cap and stirred at 45 ^oC until completion (as monitored by TLC or GC-MS). The products were then separated by either filtration, decantation of the aqueous layer, or extraction with a minimum

amount of MTBE or EtOAc. The organic layer was adsorbed on silica and purified using flash column chromatography.

10. General procedure for the synthesis of boscalid:

From the stock solution above, the desired amount (e.g., 166 μL for 500 ppm Pd) of solution was added to a 1-dram screw cap vial containing a Teflon coated magnet and covered with a rubber septum. The THF from this solution was evacuated under low pressure (~20 min). Compound **42** (1-chloro-2-nitrobenzene, 1.0 mmol, 157.5 mg) and compound **43** (4-chlorophenylboronic acid, 1.2 mmol, 187.6 mg) were added to this vial. The vial was evacuated and backfilled with argon (this procedure was repeated three times). Aqueous 2 wt % TPGS-750-M solution (2.0 mL) and Et_3N (2.0 equiv, 2.0 mmol, 279 μL) were added sequentially under argon. The vial was quickly replaced with the screw cap and stirred at 45 ^oC for 24 h (24 h were required for the completion as monitored by GC-MS analysis of a separate reaction). After 24 h, CIP (carbonyl iron powder, 5 equiv, 5.0 mmol, 279 mg) and NH_4Cl (3 equiv, 3.0 mmol, 160 mg), was added and the reaction was stirred for 12 h at 45 ^oC. Subsequently, 2-chloronicotynyl chloride (1.2 equiv, 1.2 mmol, 211.1 mg) was added in two portions with a 1.5 h break in between, after which the reaction was stirred at 45 ^oC for 8 h. The product was then separated by extraction with a minimum amount of EtOAc. The organic layer was adsorbed on silica and purified using flash column chromatography to afford 80% (275 mg) overall yield of boscalid.

11. ICP-MS data (12, 24 and 36 synthesized using current conditions and literature conditions):

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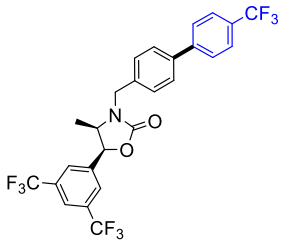
250 Mass. Ave.
Cambridge, Massachusetts 02139

Sample #: REILJO3-002-EXP006 **Test #:** 1 **Received:** 04/11/2018 **Completed:** 04/12/2018

ICP-MS: Palladium = 6 ppm

Services
ICP-MS



prepared using current conditions

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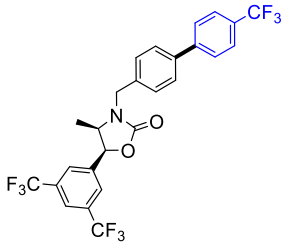
Sample #: REILLJO3-002-EXP032 Test #: 1 Received: 10/23/2018 Completed: 10/23/2018

ICP-MS Palladium : 349 ppm

Services
ICP-MS



prepared using literature conditions

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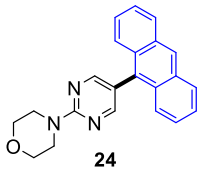
CIB001

Sample #: REILJO3-002-EXP005 **Test #:** 1 **Received:** 04/11/2018 **Completed:** 04/12/2018

ICP-MS: Palladium = 2 ppm

Services
ICP-MS



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prepared using current conditions

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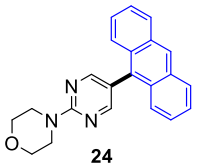
Sample #: REILLJO3-002-EXP033 Test #: 1 Received: 10/23/2018 Completed: 10/23/2018

ICP-MS Palladium : 57 ppm

Services
ICP-MS



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prepared using literature conditions

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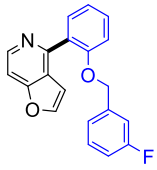
Sample #: REILJO3-002-EXP007 Test #: 1 Received: 04/11/2018 Completed: 04/12/2018

ICP-MS: Palladium = < 1 ppm

Services
ICP-MS



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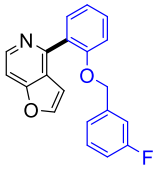
CIB001

Sample #: REILLJO3-002-EXP031 Test #: 1 Received: 10/23/2018 Completed: 10/23/2018

ICP-MS Palladium : 3049 ppm

Services
ICP-MS



36

prepared using literature conditions

12. References:

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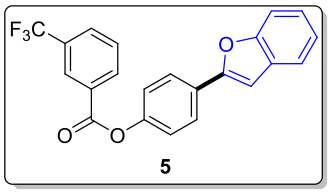
11. Y. Qiao, T. Si, M. -H. Yang and R. A. Altman, *J. Org. Chem.*, 2014, **79**, 7122-7131.
12. M. Begala, P. Caboni, M. J. Matos and G. L. Delogu, *Tetrahedron Lett*., 2018, **59**, 1711-1714.

13. Compound characterization data

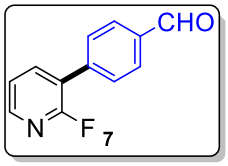


5

^{1}H NMR (500 MHz, chloroform-*d*) δ 8.42 (s, 1H), 8.34 (d, *J* = 7.9 Hz, 1H), 7.90 – 7.83 (m, 3H), 7.62 (t, *J* = 7.8 Hz, 1H), 7.53 (d, *J* = 7.5 Hz, 1H), 7.48 – 7.43 (m, 1H), 7.28 – 7.21 (m, 3H), 7.19 – 7.16 (m, 2H), 6.97 (d, *J* = 0.9 Hz, 1H).

^{13}C NMR (126 MHz, chloroform-*d*) δ 163.76, 155.02, 154.95, 150.70, 133.40, 130.32, 130.23, 130.20, 129.36, 128.68, 127.13, 127.10, 126.20, 124.45, 123.05, 122.03, 120.99, 111.21, 101.61.

HRMS: $C_{22}H_{13}F_3O_3$ ESI-MS [M^+] calcd: 382.0817; found: 382.0813.



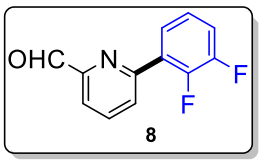
7

^{1}H NMR (500 MHz, chloroform-*d*) δ 10.09 (s, 1H), 8.28 (dt, *J* = 4.8, 1.5 Hz, 1H), 8.00 (d, *J* = 8.3 Hz, 2H), 7.94 (ddd, *J* = 9.7, 7.3, 1.9 Hz, 1H), 7.79 – 7.73 (m, 2H), 7.35 (ddd, *J* = 7.2, 4.8, 1.7 Hz, 1H).

^{13}C NMR (126 MHz, chloroform-*d*) δ 191.62, 161.22, 159.30, 147.53, 147.41, 140.74, 140.71, 139.87, 139.83, 135.98, 129.99, 129.49, 129.46, 122.75, 122.53, 122.02, 121.99.

^{19}F NMR (376 MHz, chloroform-*d*) δ -70.32.

HRMS: $C_{12}H_8NO$ ESI-MS [M^+] calcd: 201.0590; found: 201.0585.



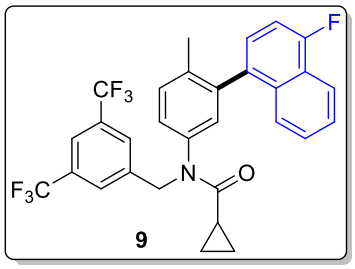
8

^{1}H NMR (500 MHz, chloroform-*d*) δ 10.15 (s, 1H), 8.04 (dt, *J* = 6.6, 2.2 Hz, 1H), 8.01 – 7.95 (m, 2H), 7.91 – 7.86 (m, 1H), 7.30 – 7.24 (m, 2H).

^{13}C NMR (126 MHz, chloroform-*d*): δ 193.40, 152.87, 137.74, 128.50, 128.42, 125.55 (m), 124.42 (m), 120.50, 118.16, 118.02.

^{19}F NMR (376 MHz, chloroform-*d*): δ -137.86 – 137.91 (m), -142.91–142.97 (m).

HRMS: $C_{12}H_7F_2NO$ ESI-MS [M^+] calcd: 219.0496; found: 219.0496.



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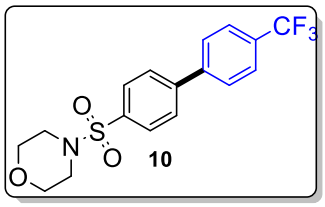
^{1}H NMR (500 MHz, chloroform-*d*) δ 8.19 (d, *J* = 8.4 Hz, 1H), 7.76 (s, 1H), 7.70 (s, 2H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.27 (d, *J* = 7.1 Hz, 1H), 7.19

(dd, J = 7.8, 4.4 Hz, 2H), 7.14 (dd, J = 8.1, 2.0 Hz, 1H), 7.00 (d, J = 1.8 Hz, 1H), 5.14 (d, J = 14.7 Hz, 1H), 4.99 (d, J = 14.6 Hz, 1H), 2.03 (s, 3H), 1.57 (m, 2H), 1.18 – 1.02 (m, 2H), 0.73 (m, 3H).

^{13}C NMR (126 MHz, chloroform-*d*) δ 173.95, 159.45, 157.44, 141.24, 140.30, 139.46, 137.30, 134.13 (d, J = 4.3 Hz), 132.92, 132.88, 131.51, 131.40, 131.31 – 131.18 (m), 130.16, 128.93 – 128.87 (m), 128.87, 128.82, 127.26, 127.24, 126.28, 126.26, 126.24, 126.21, 125.26, 125.24, 124.30, 123.82, 123.69, 122.13, 121.44, 121.41, 121.38, 121.35, 121.32, 121.01, 120.97, 109.01, 108.85, 52.38, 19.63, 12.86, 8.97, 8.90.

^{19}F NMR (376 MHz, chloroform-*d*) δ -62.85, -123.29.

HRMS: $cC_{30}H_{23}F_7NO$ ESI-MS [M+H] calcd: 546.1668; found: 546.1669.

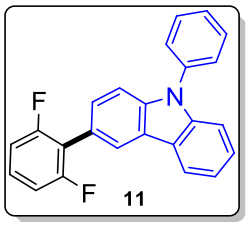


^{1}H NMR (500 MHz, chloroform-*d*) δ 7.86 (td, J = 8.6, 1.7 Hz, 2H), 7.80 – 7.74 (m, 4H), 7.72 (d, J = 8.3 Hz, 2H), 3.77 (t, 4H), 3.06 (t, 4H).

^{13}C NMR (126 MHz, chloroform-*d*) δ 144.46, 142.68, 134.75, 130.75, 130.49, 128.56, 127.99, 127.74, 126.10, 126.07, 126.04, 126.01, 125.11, 122.94, 66.10, 46.00.

^{19}F NMR (376 MHz, chloroform-*d*) δ -62.63.

HRMS: $C_{17}H_{16}F_3NO_3S$ ESI-MS [M^+] calcd: 371.0803; found: 371.0805.

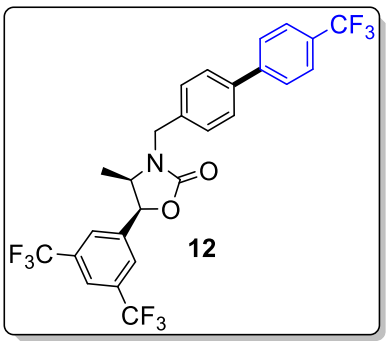


^{1}H NMR (500 MHz, chloroform-*d*) δ 8.18 (s, 1H), 8.08 (d, J = 7.7 Hz, 1H), 7.51 (s, 4H), 7.45 – 7.37 (m, 3H), 7.37 – 7.29 (m, 2H), 7.26 – 7.19 (m, 2H), 6.97 (s, 2H).

^{13}C NMR (126 MHz, chloroform-*d*) δ 161.33, 159.41, 141.25, 140.58, 137.54, 129.92, 128.36, 128.28, 128.20, 128.10, 127.61, 127.14, 126.18, 123.37, 123.27, 122.35, 120.47, 120.42, 120.15, 111.72, 111.67, 111.56, 111.51, 109.90, 109.59.

^{19}F NMR (376 MHz, chloroform-*d*) δ -114.62.

HRMS: $C_{24}H_{15}F_2N$ ESI-MS [M^+] calcd: 355.1172; found: 355.1165.



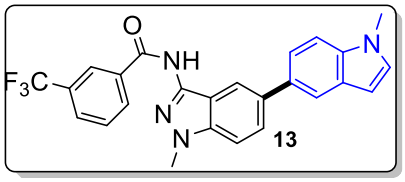
12

^{1}H NMR (500 MHz, chloroform-*d*) δ 7.90 (s, 1H), 7.78 (d, *J* = 1.6 Hz, 2H), 7.75 – 7.68 (m, 4H), 7.65 – 7.61 (m, 2H), 7.48 – 7.43 (m, 2H), 5.70 (d, *J* = 8.1 Hz, 1H), 4.97 (d, *J* = 15.2 Hz, 1H), 4.16 (d, *J* = 15.3 Hz, 1H), 4.11 – 4.04 (m, 1H), 0.80 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (126 MHz, chloroform-*d*) δ 156.84, 143.89, 139.77, 137.89, 135.59, 132.39, 132.12, 129.81, 128.75, 127.87, 127.35, 126.35, 126.35, 126.33, 125.84, 125.81, 125.78, 124.04, 122.69, 122.66, 122.63, 122.59, 53.95, 45.79, 14.45.

^{19}F NMR (376 MHz, chloroform-*d*) δ -62.51, -62.98.

HRMS: $C_{26}H_{18}F_9NO_2Na$ ESI-MS [M+Na] calcd: 570.1091; found: 570.1091.



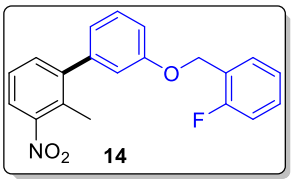
13

^{1}H NMR (500 MHz, chloroform-*d*) δ 8.67 (s, 1H), 8.30 (s, 1H), 8.25 (s, 1H), 8.17 (d, *J* = 7.8 Hz, 1H), 7.90 (d, *J* = 1.7 Hz, 1H), 7.84 (d, *J* = 7.9 Hz, 1H), 7.78 (dd, *J*= 8.8, 1.7 Hz, 1H), 7.64 (t, *J* = 7.8 Hz, 1H), 7.55 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.44 – 7.36 (m, 2H), 7.09 (d, *J* = 3.1 Hz, 1H), 6.54 (dd, *J* = 3.1, 0.8 Hz, 1H), 4.02 (s, 3H), 3.84 (s, 3H).

^{13}C NMR (126 MHz, chloroform-*d*): δ 140.68, 138.62, 136.10, 135.60, 134.84, 132.90, 130.63, 129.40 (d), 128.98, 128.63 (m), 128.06, 124.61 (m), 121.80, 120.64 (m), 119.64, 117.37, 109.37, 109.02, 101.28, 35.47, 32.93.

^{19}F NMR (376 MHz, chloroform-*d*): δ -62.72

HRMS: $C_{25}H_{19}F_3N_4ONa$ ESI-MS [M+Na] calcd: 471.1409; found: 471.1415.

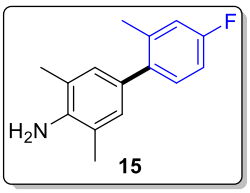


^{1}H NMR (500 MHz, chloroform-*d*) δ 7.81 (d, *J* = 8.1 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.41 – 7.32 (m, 3H), 7.19 (t, *J* = 7.1 Hz, 1H), 7.11 (t, *J* = 9.2 Hz, 1H), 7.05 (dd, *J* = 8.9, 1.7 Hz, 1H), 6.93 – 6.88 (m, 2H), 5.19 (s, 2H), 2.35 (s, 3H).

^{13}C NMR (126 MHz, chloroform-*d*) δ 161.46, 159.50, 158.47, 151.23, 144.66, 141.43, 133.72, 130.12, 129.88, 129.82, 129.74, 129.71, 129.60, 126.13, 124.33, 124.30, 123.96, 123.85, 123.15, 122.10, 115.90, 115.51, 115.34, 114.16, 63.86, 63.82, 16.87.

^{19}F NMR (376 MHz, chloroform-*d*) δ -118.48.

HRMS: $C_{20}H_{16}FNO_3$ ESI-MS [M^+] calcd: 337.1114; found: 337.1113.

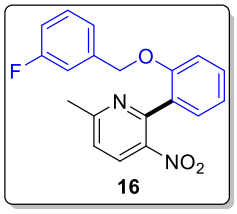


^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.19 (t, *J* = 7.2 Hz, 1H), 6.97 (d, *J* = 9.9 Hz, 1H), 6.93 (d, *J* = 7.5 Hz, 3H), 3.74 (s, 2H), 2.31 (s, 3H), 2.27 (s, 6H).

^{13}C NMR (126 MHz, chloroform-*d*) δ 162.55, 160.61, 141.50, 138.23, 138.20, 137.77, 137.70, 131.30, 131.23, 130.88, 130.60, 129.19, 121.52, 116.63, 116.46, 112.36, 112.20, 20.83, 17.74, 17.45.

^{19}F NMR (376 MHz, chloroform-*d*) δ -117.20.

HRMS: $C_{16}H_{16}FN$ ESI-MS [M+H] calcd: 230.1345; found: 230.1342.

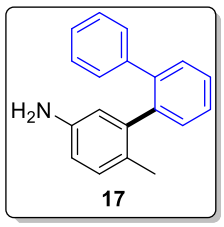


^{1}H NMR (500 MHz, chloroform-*d*) δ 8.16 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.64 (d, *J* = 7.5 Hz, 1H), 7.40 (t, *J* = 7.9 Hz, 1H), 7.27 (d, *J* = 8.3 Hz, 2H), 7.18 (t, *J* = 7.7 Hz, 1H), 7.06 – 6.86 (m, 4H), 5.00 (s, 2H), 2.71 (s, 3H).

^{13}C NMR (126 MHz, chloroform-*d*) δ 163.85, 162.81, 161.89, 155.24, 150.18, 144.85, 139.18, 139.12, 132.18, 130.89, 130.57, 130.01, 129.94, 127.44, 122.41, 122.39, 122.05, 121.98, 114.75, 114.58, 113.96, 113.79, 112.27, 69.82, 69.81, 24.81.

^{19}F NMR (376 MHz, chloroform-*d*) δ -112.94.

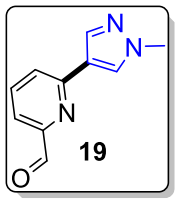
HRMS: $C_{19}H_{16}FN_2O_3$ ESI-MS [M+H] calcd: 339.1145; found: 339.1142.



^{1}H NMR (500 MHz, chloroform-*d*) δ 7.48 – 7.38 (m, 3H), 7.30 (d, *J* = 7.3 Hz, 1H), 7.20 (s, 5H), 6.87 (d, *J* = 7.6 Hz, 1H), 6.57 (d, *J* = 9.1 Hz, 2H), 3.52 (s, 2H), 1.78 (s, 3H).

^{13}C NMR (126 MHz, chloroform-*d*) δ 143.14, 142.12, 141.45, 140.81, 140.43, 130.66, 130.52, 129.92, 129.37, 127.71, 127.46, 127.00, 126.47, 126.43, 117.84, 114.55, 19.01.

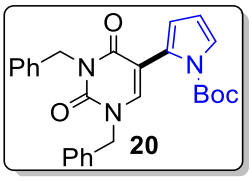
HRMS: $C_{19}H_{18}N$ ESI-MS [M+H] calcd: 260.1439; found: 260.1447.



^{1}H NMR (500 MHz, chloroform-*d*) δ 9.99 (s, 1H), 7.96 (s, 1H), 7.94 (s, 1H), 7.75 (t, *J* = 7.7 Hz, 1H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.58 (s, 1H), 3.92 (s, 3H).

^{13}C NMR (126 MHz, chloroform-*d*) δ 193.84, 152.68, 152.65, 137.67, 137.51, 129.27, 123.39, 122.75, 118.81, 39.27.

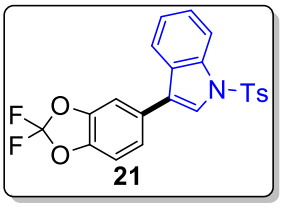
HRMS: $C_{10}H_9N_3O$ ESI-MS [M^+] calcd: 187.0746; found: 187.0746.



^{1}H NMR (500 MHz, chloroform-*d*) δ 7.58 (d, *J* = 6.7 Hz, 2H), 7.40 – 7.26 (m, 9H), 7.19 (s, 1H), 6.16 (t, *J* = 3.3 Hz, 1H), 6.09 (dd, *J* = 3.3, 1.8 Hz, 1H), 5.19 (s, 2H), 4.97 (s, 2H), 1.39 (s, 9H).

^{13}C NMR (126 MHz, chloroform-*d*) δ 161.98, 151.66, 148.81, 138.44, 136.82, 135.49, 129.52, 129.09, 128.56, 128.46, 128.31, 128.03, 127.59, 126.98, 125.43, 123.09, 115.01, 110.39, 110.16, 83.66, 65.37, 52.28, 44.93, 27.66.

HRMS: $C_{27}H_{27}N_3O_4Na$ ESI-MS [M^+] calcd: 480.1899; found: 480.1889.

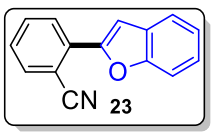


^{1}H NMR (500 MHz, chloroform-*d*) δ 8.08 (d, *J* = 8.3 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.74 – 7.66 (m, 2H), 7.40 (ddd, *J* = 8.4, 7.1, 1.3 Hz, 1H), 7.36 – 7.29 (m, 3H), 7.29 – 7.24 (m, 2H), 7.16 (dd, *J* = 7.8, 0.9 Hz, 1H), 2.37 (s, 3H).

^{13}C NMR (126 MHz, chloroform-*d*) δ 145.20, 144.24, 143.15, 135.38, 135.13, 133.71, 131.67, 130.00, 129.84, 129.64, 129.25, 128.89, 126.91, 126.80, 125.16, 123.74, 123.25, 123.11, 122.69, 119.93, 113.93, 113.53, 109.83, 109.18, 21.58.

^{19}F NMR (376 MHz, chloroform-*d*) δ -50.68.

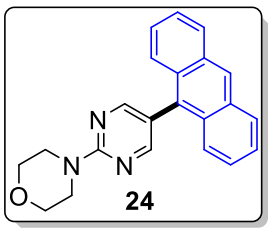
HRMS: $C_{22}H_{15}F_2NO_4$SESI-MS [M^+] calcd: 427.0690; found: 427.0707.



^{1}H NMR (500 MHz, chloroform-*d*) δ 8.12 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.78 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.74 – 7.66 (m, 3H), 7.56 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.44 (ddd, *J* = 7.5, 3.9, 1.4 Hz, 1H), 7.40 – 7.35 (m, 1H), 7.32 – 7.25 (m, 1H).

^{13}C NMR (126 MHz, chloroform-*d*): δ 134.40, 134.31, 133.84, 133.19, 133.03, 128.74, 128.15, 127.59, 127.03, 125.70, 123.37, 121.93, 118.84, 11.27, 106.78.

HRMS: $C_{15}H_9NO$ ESI-MS [M^+] calcd: 219.0684; found: 219.0692.



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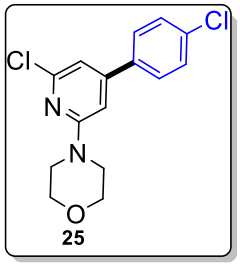
^{1}H NMR (500 MHz, chloroform-*d*) δ 8.55 (s, 1H), 8.44 (d, *J* = 1.6 Hz, 2H), 8.10 – 8.06 (m, 2H), 7.79 (dt, *J* = 8.8, 1.1 Hz, 2H), 7.51 (ddd, *J* = 8.3, 6.6, 1.2 Hz, 2H), 7.44 (ddd, *J* = 8.7, 6.5, 1.4 Hz, 2H), 3.98 (dd, *J* = 5.7, 4.0 Hz, 4H), 3.92 – 3.88 (m, 4H).

^{13}C NMR (126 MHz, chloroform-*d*) δ 159.52, 131.41, 131.06, 130.08, 128.61, 127.50, 125.96, 125.94, 125.30, 120.57, 66.91, 44.37.

HRMS: $C_{22}H_{20}N_3OH$ ESI-MS [M+H] calcd: 342.1606; found: 342.1615.

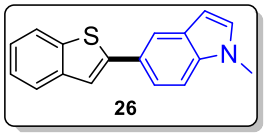


25

^{1}H NMR (500 MHz, chloroform-*d*) δ 7.50 (d, *J* = 8.6 Hz, 2H), 7.44 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 1.1 Hz, 1H), 6.60 (d, *J* = 1.1 Hz, 1H), 3.86 – 3.81 (m, 4H), 3.62 – 3.57 (m, 4H).

^{13}C NMR (126 MHz, chloroform-*d*): δ 159.59, 151.65, 150.29, 136.80, 135.35, 129.21, 128.28, 114.11, 111.16, 102.46, 66.59, 45.41.

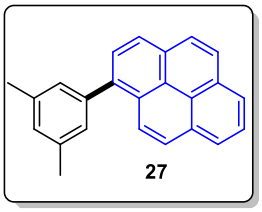
HRMS: $C_{15}H_{14}Cl_2N_2O$ ESI-MS [M^+] calcd: 308.0483; found: 308.0487.



^{1}H NMR (500 MHz, chloroform-*d*) δ 7.90 (d, *J* = 1.7 Hz, 1H), 7.74 (d, *J* = 7.7 Hz, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.54 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.44 – 7.42 (m, 1H), 7.30 – 7.16 (m, 4H), 7.00 (d, *J* = 3.0 Hz, 1H), 6.46 (d, *J* = 3.1 Hz, 1H), 3.74 (s, 3H).

^{13}C NMR (126 MHz, chloroform-*d*): δ 146.16, 141.09, 139.24, 129.85, 128.84, 125.88, 124.30, 123.90, 123.63, 123.10, 122.13, 120.69, 119.17, 117.97, 109.61, 101.56, 32.97.

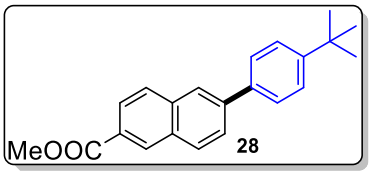
HRMS: $C_{17}H_{13}NS$ ESI-MS [M^+] calcd: 263.0769; found: 263.0772.



^{1}H NMR (500 MHz, chloroform-*d*) δ 8.25 – 8.16 (m, 4H), 8.11 (d, *J* = 1.1 Hz, 2H), 8.06 – 7.98 (m, 3H), 7.29 – 7.27 (m, 2H), 7.17 – 7.14 (m, 1H), 2.48 (s, 6H).

^{13}C NMR (126 MHz, chloroform-*d*): δ 141.13, 138.10, 137.85, 131.50, 131.02, 130.44, 128.86, 128.51, 128.44, 127.55, 127.44, 127.29, 127.27, 125.94, 125.52, 124.989, 124.95, 124.73, 124.58, 21.46.

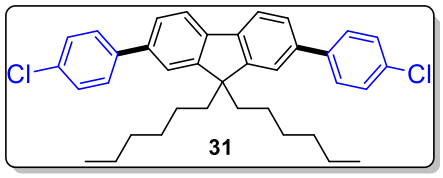
HRMS: $C_{24}H_{18}$ ESI-MS [M^+] calcd: 306.1409; found: 306.1410.



^{1}H NMR (500 MHz, chloroform-*d*) δ 8.64 (d, *J* = 1.8 Hz, 1H), 8.12 – 8.06 (m, 2H), 8.03 (d, *J* = 8.6 Hz, 1H), 7.94 (d, *J* = 8.6 Hz, 1H), 7.83 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.69 (dd, *J* = 8.6, 2.3 Hz, 2H), 7.58 – 7.52 (m, 2H), 7.28 (s, 1H), 4.01 (s, 3H), 1.41 (s, 9H).

^{13}C NMR (126 MHz, chloroform-*d*): δ 167.26, 150.98, 140.82, 137.60, 135.86, 131.53, 130.81, 129.78, 128.33, 127.20, 127.11, 126.38, 125.93, 125.63, 125.25, 52.22, 34.63, 31.35.

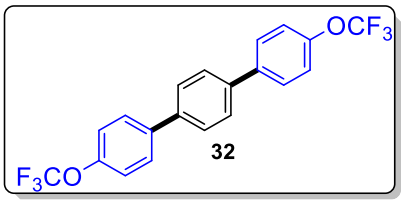
HRMS: $C_{22}H_{22}O_2$ ESI-MS [M^+] calcd: 318.1620; found: 318.1615.



^{1}H NMR (500 MHz, chloroform-*d*) δ 7.78 (d, *J* = 7.8 Hz, 1H), 7.64 – 7.59 (m, 2H), 7.58 – 7.52 (m, 2H), 7.48 – 7.43 (m, 2H), 2.09 – 2.01 (m, 2H), 1.17 – 1.01 (m, 6H), 0.77 (t, *J* = 7.0 Hz, 3H), 0.72 (dd, *J* = 10.3, 5.8 Hz, 2H).

^{13}C NMR (126 MHz, chloroform-*d*): δ 151.79, 140.20, 140.07, 138.94, 133.20, 128.90, 128.41, 125.96, 121.31, 120.16, 55.34, 40.39, 31.44, 29.66, 23.79, 22.55, 13.98.

HRMS: $C_{37}H_{40}Cl_2$ ESI-MS [M^+] calcd: 554.2507; found: 554.2494.

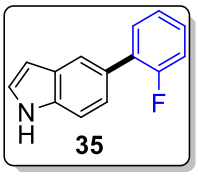


^{1}H NMR (500 MHz, chloroform-*d*) δ 7.65 (d, *J* = 6.1 Hz, 8H), 7.32 (d, *J* = 8.3 Hz, 4H).

^{13}C NMR (126 MHz, chloroform-*d*): δ 148.80, 139.17 (d), 128.34, 127.57, 121.54, 121.30, 119.50.

^{19}F NMR (376 MHz, chloroform-*d*) δ -57.73.

HRMS: $C_{20}H_{12}F_6O_2$ ESI-MS [M^+] calcd: 398.0741; found: 398.0753.

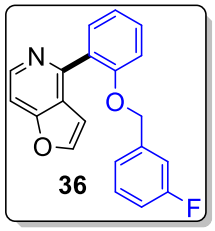


^{1}H NMR (500 MHz, chloroform-*d*) δ 8.15 (s, 1H), 7.88 (s, 1H), 7.56 (tt, *J* = 7.8, 1.8 Hz, 1H), 7.46 (d, *J* = 1.9 Hz, 2H), 7.36 – 7.30 (m, 1H), 7.28 – 7.19 (m, 3H), 6.65 (p, *J* = 1.6 Hz, 1H).

^{13}C NMR (126 MHz, chloroform-*d*) δ 160.91, 158.95, 135.31, 131.26, 131.23, 130.37, 130.27, 128.14, 128.08, 127.60, 124.84, 124.27, 124.24, 123.47, 123.45, 121.38, 121.36, 116.10, 115.91, 110.95, 103.05.

^{19}F NMR (376 MHz, chloroform-*d*) δ -118.18.

HRMS: $C_{14}H_{10}FN$ ESI-MS [M^+] calcd: 211.0797; found: 211.0799

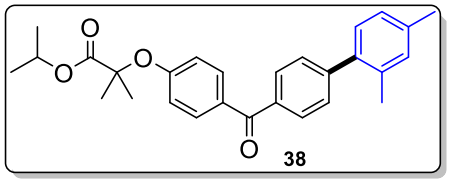


^{1}H NMR (500 MHz, chloroform-*d*) δ 8.54 (d, *J* = 5.7 Hz, 1H), 7.54 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.52 (d, *J* = 2.2 Hz, 1H), 7.37 (dd, *J* = 5.7, 1.0 Hz, 1H), 7.34 (ddd, *J* = 8.2, 7.4, 1.8 Hz, 1H), 7.15 – 7.06 (m, 2H), 7.01 (dd, *J* = 8.3, 1.0 Hz, 1H), 6.88 – 6.77 (m, 3H), 6.67 (dd, *J* = 2.2, 1.0 Hz, 1H), 4.98 (s, 2H).

^{13}C NMR (126 MHz, chloroform-*d*) δ 163.76, 161.80, 159.40, 155.74, 151.81, 144.72, 144.26, 139.50, 131.61, 130.19, 129.80, 129.74, 124.33, 122.15, 122.12, 121.79, 114.52, 114.35, 113.86, 113.68, 113.57, 106.95, 105.98, 70.05.

^{19}F NMR (376 MHz, chloroform-*d*) δ -113.14.

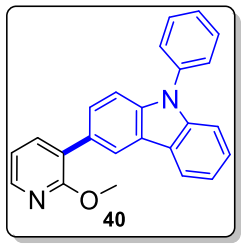
HRMS: $C_{20}H_{14}FNO_2Na$ ESI-MS [M+Na] calcd: 342.0906; found: 342.0919



^{1}H NMR (500 MHz, chloroform-*d*) δ 7.82 (t, *J* = 7.7 Hz, 4H), 7.43 (d, *J* = 7.9 Hz, 2H), 7.20 – 7.08 (m, 3H), 6.90 (d, *J* = 8.3 Hz, 2H), 5.15 – 5.06 (m, 1H), 2.39 (s, 3H), 2.29 (s, 3H), 1.69 (s, 6H), 1.23 (d, *J* = 6.2 Hz, 6H).

^{13}C NMR (126 MHz, chloroform-*d*): δ 195.28, 173.18, 159.50, 1456.91, 138.06, 137.56, 136.32, 135.04, 132.01, 131.29, 130.76, 129.68, 129.56, 129.15, 126.64, 117.20, 79.38, 69.38, 69.31, 25.39, 21.54, 21.08, 20.38.

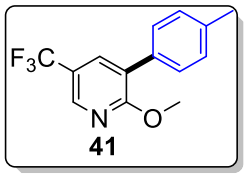
HRMS: $C_{28}H_{30}O_4Na$ ESI-MS [M+Na] calcd: 453.2042; found: 453.2032



^{1}H NMR (500 MHz, chloroform-*d*) δ 8.34 – 8.31 (m, 1H), 8.22 – 8.17 (m, 2H), 7.75 (dd, *J* = 7.2, 1.3 Hz, 1H), 7.67 – 7.59 (m, 6H), 7.52 – 7.43 (m, 4H), 7.34 – 7.30 (m, 1H), 7.04 (ddd, *J* = 7.4, 4.9, 1.3 Hz, 1H), 4.03 (s, 3H).

^{13}C NMR (126 MHz, chloroform-*d*) δ 161.09, 145.11, 141.28, 140.34, 138.76, 137.64, 129.90, 128.56, 127.53, 127.32, 127.10, 126.06, 125.48, 123.41, 121.01, 120.36, 120.04, 117.15, 109.87, 109.47, 53.58.

HRMS: $C_{24}H_{19}N_2O$ ESI-MS [M+H] calcd: 351.1497; found: 351.1509

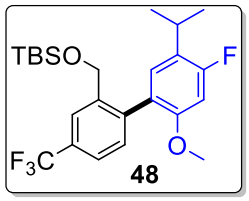


^{1}H NMR (500 MHz, chloroform-*d*) δ 8.43 (s, 1H), 7.80 (s, 1H), 7.47 (d, *J* = 7.4 Hz, 2H), 7.28 (d, *J* = 7.8 Hz, 2H), 4.04 (s, 3H), 2.43 (s, 3H).

^{13}C NMR (126 MHz, chloroform-*d*) δ 162.96, 143.08, 143.05, 143.01, 138.23, 135.10, 135.08, 132.29, 129.15, 128.96, 124.92, 120.56, 54.24, 21.24.

^{19}F NMR (376 MHz, chloroform-*d*) δ -61.44.

HRMS: $C_{14}H_{12}F_3NO$ ESI-MS [M+N] calcd: 267.0871; found: 267.0867.

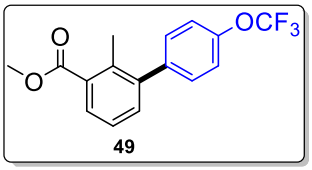


^{1}H NMR (500 MHz, chloroform-*d*) δ 7.91 (s, 1H), 7.54 (d, *J* = 6.8 Hz, 1H), 7.25 (d, *J* = 7.9 Hz, 1H), 6.96 (d, *J* = 8.6 Hz, 1H), 6.66 (d, *J* = 12.1 Hz, 1H), 3.71 (s, 3H), 3.21 (p, *J* = 6.9 Hz, 1H), 1.24 (d, *J* = 6.9 Hz, 6H), 0.90 (s, 9H), -0.00 (s, 6H).

^{13}C NMR (126 MHz, chloroform-*d*) δ 167.19, 165.24, 160.68, 160.60, 146.53, 144.74, 135.91, 135.22, 134.96, 134.35, 134.29, 132.47, 132.35, 130.97, 129.15, 128.81, 128.68, 128.67, 128.64, 128.63, 104.64, 104.42, 67.71, 61.10, 32.05, 31.29, 28.26, 23.78, -0.00.

^{19}F NMR (376 MHz, chloroform-*d*) δ -62.57, -116.72.

HRMS: $C_{20}H_{23}F_4O_2Si$ ESI-MS [M-C_4H_9] calcd: 399.1404; found: 399.1424.

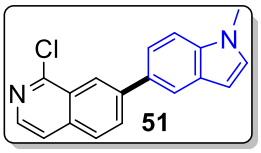


^{1}H NMR (500 MHz, chloroform-*d*) δ 7.84 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.35 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.34 – 7.31 (m, 3H), 7.31 – 7.28 (m, 2H), 7.28 (s, 1H), 3.94 (s, 3H), 2.42 (s, 3H).

^{13}C NMR (126 MHz, chloroform-*d*) δ 168.66, 142.34, 140.18, 136.59, 133.13, 131.57, 130.73, 129.55, 125.38, 120.66, 52.05, 18.40.

^{19}F NMR (376 MHz, chloroform-*d*) δ -57.82.

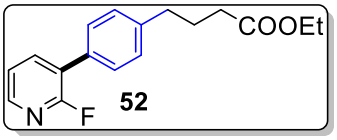
HRMS: $C_{16}H_{13}F_3O_3$ ESI-MS $[M^+]$+ calcd: 310.0817; found: 310.0814.



^{1}H NMR (500 MHz, chloroform-*d*) δ 8.56 (s, 1H), 8.26 (d, *J* = 5.6 Hz, 1H), 8.11 (d, *J* = 8.5 Hz, 1H), 8.00 (s, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.68 – 7.58 (m, 2H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.14 (d, *J* = 2.9 Hz, 1H), 6.61 (d, *J* = 2.9 Hz, 1H), 3.86 (s, 3H).

13C NMR (126 MHz, chloroform-*d*) δ 151.59, 143.01, 140.91, 136.68, 136.36, 131.48, 131.35, 129.94, 129.16, 127.48, 127.30, 123.57, 121.45, 120.59, 120.05, 109.87, 101.62, 33.01.

HRMS: $C_{18}H_{13}ClN_2$ ESI-MS $[M^+]$ calcd: 292.0767; found: 292.0773.

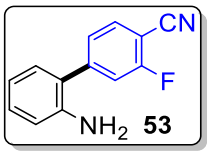


^{1}H NMR (500 MHz, chloroform-*d*) δ 8.19 (dt, *J* = 4.8, 1.5 Hz, 1H), 7.87 (ddd, *J* = 9.5, 7.4, 1.9 Hz, 1H), 7.51 (dd, *J* = 8.2, 1.7 Hz, 2H), 7.30 (dd, *J* = 8.8, 2.1 Hz, 2H), 7.28 – 7.26 (m, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 2.79 – 2.66 (m, 2H), 2.37 (t, *J* = 7.4 Hz, 2H), 2.01 (p, *J* = 7.5 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, chloroform-*d*) δ 173.37, 161.42, 146.12, 146.00, 141.96, 140.49, 140.46, 128.88, 128.82, 128.80, 121.79, 121.75, 60.32, 34.85, 33.66, 26.39, 14.25.

^{19}F NMR (376 MHz, chloroform-*d*) δ -71.14 (d, *J* = 9.4 Hz).

HRMS: $C_{17}H_{18}FNO_2$ ESI-MS [M^+] calcd: 287.1322; found: 287.1312.

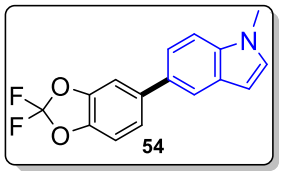


^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.70 (t, *J* = 7.3 Hz, 1H), 7.41 (dd, *J* = 15.3, 9.0 Hz, 2H), 7.23 (t, *J* = 7.7 Hz, 1H), 7.11 (d, *J* = 7.6 Hz, 1H), 6.87 (t, *J* = 7.5 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 3.80 (s, 2H).

^{13}C NMR (126 MHz, chloroform-*d*) δ 164.37, 162.30, 147.50, 147.44, 143.21, 133.75, 130.11, 125.52, 125.49, 124.24, 119.13, 117.03, 116.88, 116.32, 113.99, 99.85, 99.73.

^{19}F NMR (376 MHz, chloroform-*d*) δ -105.85.

HRMS: $C_{13}H_9FN_2$ ESI-MS [M^+] calcd: 212.0750; found: 212.0752.

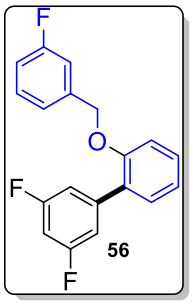


^{1}H NMR (500 MHz, chloroform-*d*) δ 7.78 (t, *J* = 1.3 Hz, 1H), 7.40 (d, *J* = 1.3 Hz, 2H), 7.34 (dt, *J* = 6.9, 1.4 Hz, 2H), 7.12 (ddd, *J* = 6.7, 2.9, 1.1 Hz, 2H), 6.56 (dd, *J* = 3.2, 1.0 Hz, 1H), 3.85 (s, 3H).

^{13}C NMR (126 MHz, chloroform-*d*): δ 144.19, 142.49, 139.33, 136.34, 131.74, 131.64, 129.79, 128.97, 122.47, 121.18, 119.42, 109.60, 109.35, 108.70, 101.36, 32.95.

^{19}F NMR (376 MHz, chloroform-*d*): δ -49.96.

HRMS: $C_{16}H_{11}F_2NO_2$ ESI-MS [M^+] calcd: 287.0785; found: 287.0785.

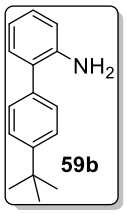


^{1}H NMR (500 MHz, chloroform-*d*) δ 7.38 – 7.31 (m, 3H), 7.16 – 7.07 (m, 4H), 7.07 – 6.99 (m, 3H), 6.81 (tt, *J* = 9.0, 2.4 Hz, 1H), 5.12 (s, 2H).

^{13}C NMR (126 MHz, chloroform-*d*) δ 163.93, 163.65, 163.55, 161.97, 161.69, 161.59, 155.13, 141.60, 141.52, 141.44, 139.41, 139.35, 130.70, 130.15, 130.09, 129.65, 129.55, 122.21, 122.19, 121.66, 114.79, 114.62, 113.85, 113.67, 113.29, 112.61, 112.56, 112.45, 112.40, 102.52, 102.32, 102.12, 69.79, 69.77.

^{19}F NMR (376 MHz, chloroform-*d*) δ -111.02 – -111.23 (m), -112.64 – -112.83 (m).

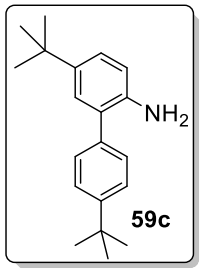
HRMS: $C_{19}H_{13}F_3O$ ESI-MS [M^+] calcd: 314.0919; found: 314.0921.



^{1}H NMR (500 MHz, chloroform-*d*) δ 7.51 – 7.47 (m, 2H), 7.43 – 7.40 (m, 2H), 7.19 – 7.14 (m, 2H), 6.85 (td, *J* = 7.4, 1.2 Hz, 1H), 6.79 (dd, *J* = 8.5, 1.3 Hz, 1H), 3.75 (s, 2H), 1.39 (s, 9H).

^{13}C NMR (126 MHz, chloroform-*d*) δ 150.01, 143.57, 136.46, 130.47, 128.69, 128.26, 127.63, 125.70, 118.63, 115.55, 34.59, 31.39.

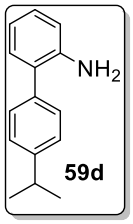
HRMS: $C_{16}H_{19}NH$ ESI-MS [M+H] calcd: 226.1596; found: 226.1598.



^{1}H NMR (500 MHz, chloroform-*d*) δ 7.51 – 7.40 (m, 4H), 7.27 (d, *J* = 1.5 Hz, 1H), 7.25 – 7.15 (m, 2H), 6.81 (d, *J* = 8.2 Hz, 1H), 4.01 (s, 2H), 1.37 (d, *J* = 1.4 Hz, 9H), 1.32 (d, *J* = 1.4 Hz, 9H).

^{13}C NMR (126 MHz, chloroform-*d*) δ 149.99, 136.82, 128.81, 127.50, 125.66, 125.18, 115.88, 34.57, 34.04, 31.56, 31.38.

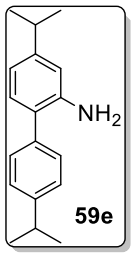
HRMS: $C_{20}H_{28}N$ ESI-MS [M+H] calcd: 282.2222; found: 282.2220.



^{1}H NMR (500 MHz, chloroform-*d*) δ 7.45 – 7.39 (m, 2H), 7.37 – 7.33 (m, 2H), 7.21 – 7.15 (m, 2H), 6.86 (td, *J* = 7.4, 1.2 Hz, 1H), 6.81 – 6.77 (m, 1H), 3.79 (s, 2H), 3.00 (p, *J* = 6.9 Hz, 1H), 1.35 (d, *J* = 6.9 Hz, 6H).

^{13}C NMR (126 MHz, chloroform-*d*) δ 147.76, 143.64, 136.90, 130.49, 129.00, 128.29, 127.69, 126.87, 118.61, 115.55, 33.90, 24.05.

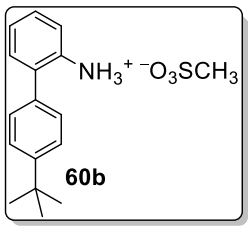
HRMS: $C_{15}H_{17}NH$ ESI-MS [M+H] calcd: 212.1439; found: 212.1439.



^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.47 (d, *J* = 5.5 Hz, 2H), 7.37 (d, *J* = 6.0 Hz, 2H), 7.16 (dd, *J* = 7.7, 2.7 Hz, 1H), 6.79 (d, *J* = 7.7 Hz, 1H), 6.72 (s, 1H), 3.74 (s, 2H), 3.03 (dt, *J* = 13.5, 6.7 Hz, 1H), 2.93 (dt, *J* = 13.4, 6.6 Hz, 1H), 1.39 (d, *J* = 2.8 Hz, 3H), 1.38 (d, *J* = 2.8 Hz, 3H), 1.36 (d, *J* = 2.8 Hz, 3H), 1.35 (d, *J* = 2.8 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 149.26, 147.53, 143.50, 137.04, 130.49, 129.11, 126.85, 125.42, 116.98, 113.76, 33.95, 33.93, 24.11, 24.05.

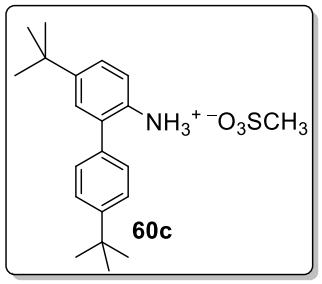
HRMS: $C_{18}H_{23}NH$ ESI-MS [M+H] calcd: 254.1909; found: 254.1907.



^{1}H NMR (500 MHz, Methanol-d_4) δ 7.62 (d, *J* = 8.2 Hz, 2H), 7.58 – 7.51 (m, 3H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.42 (d, *J* = 8.3 Hz, 2H), 4.90 (s, 3H), 2.68 (s, 3H), 1.40 (s, 9H).

^{13}C NMR (126 MHz, Methanol-d_4) δ 151.64, 137.03, 133.36, 131.60, 129.20, 128.71, 128.54, 127.69, 125.93, 123.67, 38.17, 34.21, 30.35.

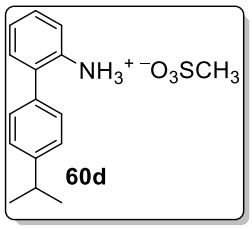
HRMS: $C_{16}H_{20}N$ ESI-MS [M-OMs] calcd: 226.1596; found: 226.1591.



^{1}H NMR (500 MHz, methanol-d_4) δ 7.60 (m, 3H), 7.48 (s, 1H), 7.45 – 7.36 (m, 3H), 2.71 (s, 3H), 1.39 (d, J = 8.0 Hz, 18H).

^{13}C NMR (126 MHz, methanol-d_4) δ 152.73, 152.67, 151.59, 151.55, 136.57, 133.83, 133.82, 128.54, 128.51, 125.90, 125.74, 125.00, 123.34, 38.14, 34.30, 34.19, 30.36, 30.24.

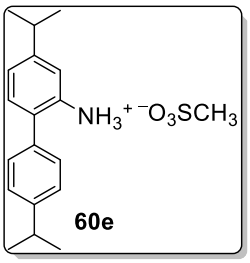
HRMS: $C_{20}H_{28}N$ ESI-MS [M-OMs] calcd: 282.2222; found: 282.2217



^{1}H NMR (500 MHz, methanol-d_4) δ 7.59 – 7.43 (m, 6H), 7.42 – 7.36 (m, 2H), 2.98 (d, J = 6.9 Hz, 1H), 2.69 (d, J = 0.8 Hz, 3H), 1.32 (d, J = 6.9 Hz, 6H).

^{13}C NMR (126 MHz, methanol-d_4) δ 149.53, 137.10, 133.70, 131.63, 129.19, 128.76, 128.69, 127.66, 127.01, 123.48, 38.09, 33.82, 22.93.

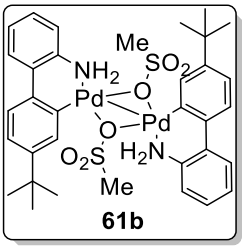
HRMS: $C_{15}H_{17}NH$ ESI-MS [M-OMs] calcd: 212.1439; found: 212.1440.



^{1}H NMR (500 MHz, methanol-d_4) δ 7.47 – 7.39 (m, 4H), 7.38 – 7.34 (m, 3H), 3.08 – 2.95 (m, 2H), 2.70 (s, 3H), 1.32 (dd, J = 8.7, 6.9 Hz, 12H).

^{13}C NMR (126 MHz, methanol-d_4) δ 150.29, 149.30, 134.48, 133.73, 131.56, 128.79, 127.44, 127.30, 126.95, 121.40, 38.11, 33.81, 33.55, 22.96, 22.75.

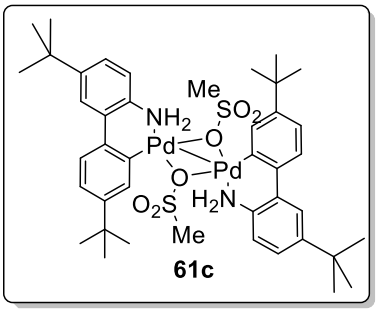
HRMS: $C_{18}H_{24}N$ ESI-MS [M-OMs] calcd: 254.1909; found: 254.1913.



^{1}H NMR (500 MHz, acetonitrile-d_3) δ 7.61 (d, J = 7.4 Hz, 1H), 7.44 – 7.36 (m, 2H), 7.33 – 7.18 (m, 4H), 6.30 (s, 2H), 2.59 (s, 3H), 1.36 (s, 9H).

^{13}C NMR (126 MHz, acetonitrile-d_3) δ 150.40, 138.71, 135.49, 134.15, 133.32, 127.84, 127.74, 126.30, 124.80, 123.56, 120.62, 98.61, 39.25, 34.32, 30.80.

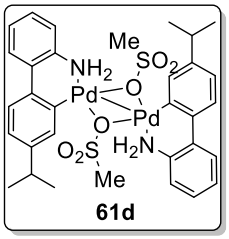
HRMS: $C_{33}H_{39}N_2O_3Pd_2S$ ESI-MS [M-OMs] calcd: 757.0769; found: 757.0763.



^{1}H NMR (500 MHz, acetonitrile-d_3) δ 7.64 (s, 2H), 7.44 (d, J = 8.0 Hz, 2H), 7.31 (q, J = 8.2 Hz, 4H), 7.27 – 7.19 (m, 4H), 6.10 (s, 4H), 2.66 (s, 6H), 2.66 (s, 6H), 1.39 (dd, J = 12.3, 1.0 Hz, 36H).

^{13}C NMR (126 MHz, acetonitrile-d_3) δ 150.39, 149.55, 138.24, 134.52, 133.21, 132.77, 125.07, 124.94, 124.69, 123.58, 120.08, 39.10, 34.42 (d, J = 23.9 Hz), 30.80, 30.77.

HRMS: $C_{41}H_{55}N_2O_3Pd_2S$ ESI-MS [M-OMs] calcd: 867.2003; found: 867.2000.

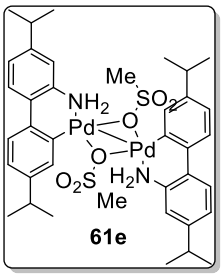


61d

^{1}H NMR (500 MHz, acetonitrile-d_3) δ 7.61 (dt, J = 7.4, 1.3 Hz, 1H), 7.40 (dd, J = 9.9, 7.5 Hz, 2H), 7.28 (dtd, J = 8.7, 7.4, 6.1 Hz, 2H), 7.08 (d, J = 7.8 Hz, 2H), 6.30 (s, 2H), 2.92 (p, J = 6.9 Hz, 1H), 2.60 (s, 3H), 1.30 (d, J = 6.9 Hz, 6H).

^{13}C NMR (126 MHz, acetonitrile-d_3) δ 148.19, 139.28, 138.85, 135.59, 134.55, 127.79, 127.68, 126.23, 125.12, 124.52, 120.66, 39.26, 33.61, 23.48.

HRMS: $C_{31}H_{35}N_2O_3Pd_2S$ ESI-MS [M-OMs] calcd: 727.0455; found: 727.0451.

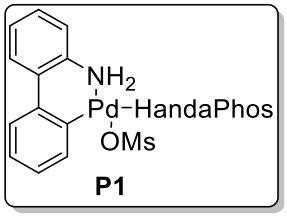


61e

^{1}H NMR (500 MHz, acetonitrile-d_3) δ 7.52 (d, J = 8.0 Hz, 1H), 7.38 (d, J = 7.7 Hz, 1H), 7.30 (s, 1H), 7.17 (dd, J = 8.0, 1.9 Hz, 1H), 7.09 – 7.01 (m, 2H), 6.28 (s, 2H), 3.00 – 2.87 (m, 2H), 2.60 (s, 3H), 1.29 (d, J = 6.9 Hz, 12H).

^{13}C NMR (126 MHz, acetonitrile-d_3) δ 149.06, 147.94, 143.61, 136.32, 135.38, 134.57, 134.48, 127.75, 124.87, 124.48, 124.18, 118.75, 117.47, 39.28, 33.65, 33.61, 23.49, 23.34.

HRMS: $C_{37}H_{47}N_2O_3Pd_2S$ ESI-MS [M-OMs] calcd: 811.1377; found: 811.1372.

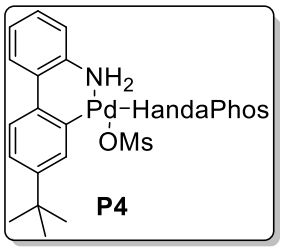


^{1}H NMR (500 MHz, chloroform-*d*): δ 7.64 (d, *J* = 9.5 Hz, 1H), 7.37-7.29 (m, 3H), 7.26-7.25 (m, 1H, 7.19-7.35 (m, 2H), 7.02-6.99 (m, 2H), 6.88-6.85 (m, 2H), 6.77 (d, *J* = 8.5 Hz, 1H), 6.60 (t, *J* = 7.5 Hz, 1H), 6.55-6.52 (m, 2H), 6.43 (t, *J* = 7.5 Hz, 1H), 4.57 (m, 1H), 4.20 (m, 1H), 3.97 (s, 3H), 3.62 (m, 3H), 2.76 (m, 1H), 2.62 (m, 3H), 2.02 (t, *J* = 4.0 Hz, 2H), 1.93-1.15 (m, 9H), 1.05-0.955 (m, 10H), 0.86-0.79 (m, 8H).

^{13}C NMR (126 MHz, chloroform-*d*): δ 158.36, 157.40, 146.71, 139.58, 139.36, 135.82, 135.44, 132.74, 130.09, 128.47, 127.26, 126.75, 126.24, 126.17, 125.96, 125.37, 121.39, 120.09, 111.14, 104.49, 103.79, 81.32, 81.16, 55.94, 55.51, 40.07, 33.96, 33.85, 32.51, 30.91, 29.70, 28.98, 26.79, 23.96, 23.77.

^{31}P NMR (162 MHz, chloroform-*d*) δ 59.40.

HRMS: $C_{47}H_{57}NO_3PPd$ ESI-MS [M-OMs] calcd: 820.3128; found: 820.3129.



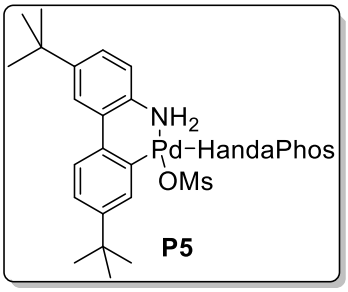
^{1}H NMR (500 MHz, chloroform-*d*) δ 7.99 (d, *J* = 5.2 Hz, 1H), 7.85 – 7.76 (m, 2H), 7.68 – 7.58 (m, 2H), 7.54 – 7.44 (m, 3H), 7.40 – 7.27 (m, 4H), 7.03 (dd, *J* = 18.7, 8.3 Hz, 2H), 5.05 (d, *J* = 11.5 Hz, 1H), 4.71 – 4.63 (m, 1H), 4.51 (s, 3H), 4.10 (s, 3H), 3.25 (p, *J* = 6.9 Hz, 1H), 3.08 (s, 3H), 2.89 (dd, *J* = 15.6, 4.8 Hz, 1H), 2.78 – 2.65 (m, 2H), 1.82 (d, *J* = 27.1 Hz, 3H), 1.69 – 1.64 (m, 9H), 1.40 (s, 9H), 1.32 – 1.24 (m, 9H).

^{13}C NMR (126 MHz, chloroform-*d*) δ 164.31, 164.25, 158.55, 157.22, 150.96, 150.93, 150.03, 146.66, 139.61, 138.86, 138.80, 138.63, 138.60, 136.83, 135.57, 135.55, 132.94, 132.87, 132.41, 129.98, 129.87, 129.77, 128.80, 128.12, 127.10, 127.04, 126.97, 126.31, 126.02, 125.14, 123.52, 119.90, 119.89, 118.81, 114.71, 114.42, 111.66, 111.63, 104.53, 103.82, 77.27, 77.01, 76.76,

55.60, 55.51, 40.01, 34.81, 34.66, 34.33, 34.10, 33.87, 33.38, 33.31, 32.10, 31.93, 31.44, 31.38, 31.11, 30.33, 29.97, 29.70, 28.72, 27.98, 27.84, 25.88, 23.95, 23.83, 22.69, 22.44, 20.86, 14.12.

^{31}P NMR (162 MHz, chloroform-*d*) δ 56.64.

HRMS: $C_{51}H_{65}NO_3PPd$ ESI-MS [M-OMs] calcd: 876.3755; found: 876.3751.

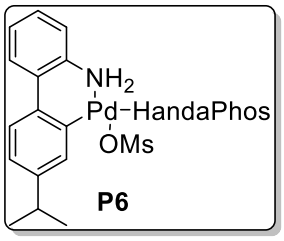


^{1}H NMR (500 MHz, chloroform-*d*) δ 7.41 (d, *J* = 8.8 Hz, 1H), 7.33 – 7.21 (m, 3H), 7.16 (s, 1H), 7.11 (d, *J* = 8.1 Hz, 1H), 7.02 (d, *J* = 21.9 Hz, 3H), 6.91 – 6.87 (m, 1H), 6.81 (d, *J* = 7.7 Hz, 2H), 6.54 (d, *J* = 8.1 Hz, 2H), 4.61 (d, *J* = 11.3 Hz, 1H), 4.10 (s, 1H), 4.06 (s, 3H), 3.71 (s, 1H), 3.62 (s, 3H), 2.81 – 2.70 (m, 2H), 2.65 (s, 3H), 2.51 (d, *J* = 11.4 Hz, 1H), 1.31 – 1.17 (m, 8H), 1.14 (d, *J* = 6.0 Hz, 6H), 1.08 (s, 3H), 1.02 (s, 9H), 0.90 (s, 9H), 0.81 (s, 9H), 0.64 (d, *J* = 14.1 Hz, 1H).

^{13}C NMR (126 MHz, chloroform-*d*) δ 158.48, 157.33, 147.97, 146.81, 139.23, 138.46, 137.00, 132.80, 132.79, 132.72, 132.28, 130.07, 127.17, 127.10, 126.38, 124.86, 124.14, 123.33, 121.32, 119.33, 118.86, 111.67, 111.64, 104.49, 103.86, 81.97, 81.82, 55.66, 55.56, 39.94, 34.50, 34.39, 34.15, 34.09, 33.99, 33.76, 33.68, 31.20, 31.16, 30.92, 29.69, 29.44, 29.34, 27.59, 24.05, 23.86, 23.56.

^{31}P NMR (162 MHz, chloroform-*d*) δ 57.76 (d, *J* = 8.3 Hz).

HRMS: $C_{57}H_{73}NO_3PPd$ ESI-MS [M-OMs] calcd: 932.4363; found: 932.4361.

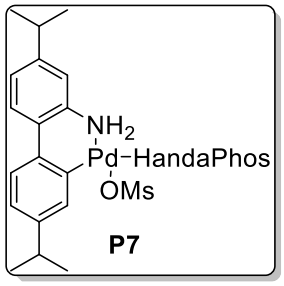


^{1}H NMR (500 MHz, chloroform-*d*): δ 7.56 (d, *J* = 8.0 Hz, 1H), 7.35-7.29 (m, 2H), 7.19-7.17 (m, 2H), 7.12 (dt, *J* = 7.5, 1.5 Hz, 1H), 7.06 (d, *J* = 8.0 Hz, 1H), 6.99-6.94 (m, 1H), 6.89-6.84 (m, 3H), 6.79 (d, J = 8.5 Hz, 1H), 6.62 (dd, *J* = 6.0, 2.0 Hz, 1H), 6.58-6.52 (m, 2H), 4.57 (d, *J* = 11.0 Hz, 1H), 4.19 (q, *J* = 4.0 Hz, 1H), 3.97 (s, 3H), 3.62 (s, 3H), 2.76 (m, 1H), 2.62 (s, 3H), 2.46-2.42 (m, 1H), 2.38-2.33 (m, 1H), 2.21 (m, 1H), 1.22-1.13 (m, 10H), 0.99-0.90 (m, 10H), 0.87-0.79 (m, 10H).

^{13}C NMR (126 MHz, chloroform-*d*): δ 164.31, 158.48, 157.35, 148.43, 146.67, 139.53, 138.94, 138.09, 136.93, 135.47, 134.84, 134.76, 132.35, 130.04, 128.07, 127.06, 126.46, 125.22, 123.67, 121.26, 119.96, 111.26, 104.46, 103.77, 81.81, 81.66, 55.61, 55.50, 40.00, 34.29, 34.15, 33.85, 33.59, 33.19, 33.12, 30.91, 29.69, 29.35, 26.57, 24.53, 23.94, 23.80, 23.58, 22.40.

^{31}P NMR (162 MHz, chloroform-*d*): δ 58.65

HRMS: $C_{50}H_{63}NO_3PPd$ ESI-MS [M-OMs] calcd: 862.3599; found: 862.3594.



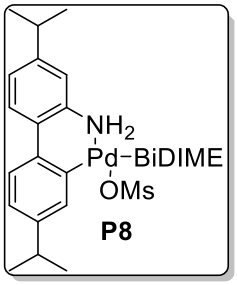
P7

^{1}H NMR (500 MHz, chloroform-*d*): δ 7.50 (dd, *J* = 8.0, 3.5 Hz, 1H), 7.31 (t, *J* = 8.0 Hz, 2H), 7.18 (s, 1H), 7.09 (d, *J* = 8.0 Hz, 1H), 7.03 (d, *J* = 7.5 Hz, 1H), 6.88-6.78 (m, 5 H), 6.63-6.52 (m, 3H), 4.56 (d, *J* = 6.0 Hz, 1H), 4.18 (q, *J* = 4.0 Hz, 1H), 3.98 (s, 3H), 3.72-3.65 (m, 1H), 3.61 (s, 3H), 2.85-2.73 (m, 2H), 2.61 (s, 3H), 2.45 (dd, *J* = 15.5, 4.5 Hz, 1H), 2.38-2.32 (m, 1H), 2.20-2.15 (m, 1H), 1.17-0.08 (m, 39 H)

^{13}C NMR (126 MHz, chloroform-*d*): δ 164.36, 164.30, 158.50, 157.35, 149.10, 148.19, 148.17, 146.66, 138.96, 138.90, 137.91, 137.00, 135.21, 135.18, 134.86, 134.79, 132.33, 130.07, 129.96, 129.85, 127.09, 126.52, 126.46, 126.25, 123.59, 122.84, 121.23, 121.08, 118.86, 118.49, 114.81, 114.51, 111.29, 111.26, 104.07, 103.79, 81.86, 81.71, 55.65, 55.51, 40.06, 34.25, 34.10, 33.87, 33.69, 33.64, 33.54, 33.46, 29.70, 26.60, 24.65, 24.31, 23.97, 23.84, 23.33, 22.41.

^{31}P NMR (162 MHz, chloroform-*d*): δ 59.06

HRMS: $C_{53}H_{69}NO_3PPd$ ESI-MS [M-OMs] calcd: 904.4069; found: 904.4070.



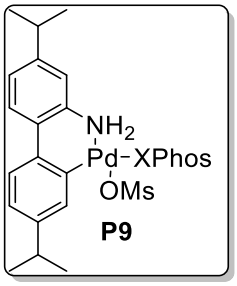
P8

^{1}H NMR (500 MHz, chloroform-*d*): δ 7.52-7.45 (m, 2H), 7.42-7.38 (m, 2H), 7.23-7.21 (m, 2H), 7.07 (d, *J* = 7.5 Hz, 1H), 6.98-6.90 (m, 3H), 6.82 (d, *J* = 7.0 Hz, 2H), 6.61 (d, *J* = 8.5 Hz, 1H), 4.35 (d, *J* = 12.5 Hz, 1H), 4.25 (s, 1H), 4.40 (s, 3H), 3.70 (s, 3H), 2.94 (t, *J* = 7.0 Hz, 1H), 2.59 (s, 3H), 2.48 (t, *J* = 7.0 Hz, 1H), 1.29-1.25 (m, 6 H), 0.98-095 (m, 6 H), 0.91-0.87 (m, 9 H).

^{13}C NMR (126 MHz, chloroform-*d*): δ 164.93, 158.00, 157.37, 149.16, 149.02, 136.36, 135.17, 134.79, 134.07, 133.98, 132.65, 130.02, 126.87, 126.21, 126.15, 125.97, 124.18, 122.96, 119.10, 110.86, 104.78, 103.52, 68.68, 68.50, 56.03, 55.31, 39.81, 34.43, 34.29, 33.65, 33.55, 25.73, 25.68, 23.94, 23.81, 23.67, 22.94.

^{31}P NMR (162 MHz, chloroform-*d*): δ 37.89.

HRMS: $C_{37}H_{45}NO_3PPd$ ESI-MS [M-OMs] calcd: 688.2186; found: 688.2159.



P9

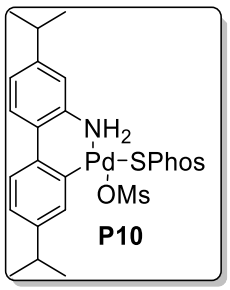
^{1}H NMR (500 MHz, chloroform-*d*): δ 7.79 (m, 1H), 7.69 (s, 1H), 7.55 (t, *J* = 4.5 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 7.06-7.02 (m, 2H), 6.98-6.91 (m, 2H), 6.70 (s, 1H), 6.45 (dd, *J* = 11.5, 4.5 Hz, 1H), 3.56-3.51 (m, 1H), 2.97-2.81 (m, 3H), 2.65-2.61 (m, 1H), 2.46 (s, 3H), 2.42-2.38 (m, 1H), 2.18-2.02 (m, 3H), 1.97 (d, *J* = 7.0 Hz, 2H), 1.92-1.79 (m, 5 H), 1.68 (d, *J* = 7.0 Hz, 3H), 1.60 (d, *J* = 7.0 Hz, 3H), 1.52-1.46 (m, 3H), 1.37-1.26 (m, 15H), 1.19-1.01 (m, 10 H), 0.95 (t, *J* = 7.0 HZ, 1H), 0.89 (d, *J* = 7.0 Hz, 3H), 0.66 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (126 MHz, chloroform-*d*) δ 154.81, 154.62, 149.53, 148.71, 148.52, 145.65, 145.49, 138.90, 136.99, 136.41, 136.03, 134.47, 134.19, 133.99, 133.93, 132.92, 132.83, 132.03, 131.27, 127.85, 127.16, 126.58, 125.45, 125.34, 125.31, 124.47, 123.71, 123.35, 120.28, 119.26, 39.13,

36.05, 35.82, 34.41, 33.96, 33.81, 32.75, 31.72, 31.54, 31.05, 29.45, 29.41, 29.15, 28.10, 28.03, 27.82, 27.76, 27.50, 27.39, 26.74, 26.65, 26.43, 26.32, 25.99, 25.90, 25.79, 25.59, 24.46, 24.27, 24.22, 23.98, 23.95, 23.66, 23.20.

^{31}P NMR (162 MHz, chloroform-*d*) δ 35.40.

HRMS: $C_{51}H_{17}NPPd$ ESI-MS [M-OMs] calcd: 833.4377; found: 833.4357.

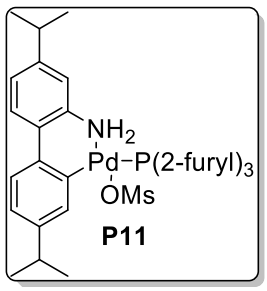


^{1}H NMR (500 MHz, chloroform-*d*) δ 8.77 (s, 1H), 7.87 (s, 1H), 7.77 (t, *J* = 7.6 Hz, 1H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.62 (d, *J* = 7.9 Hz, 1H), 7.56 (d, *J* = 2.8 Hz, 1H), 7.49 (s, 1H), 7.36 (d, *J* = 7.7 Hz, 1H), 7.26 (dd, *J* = 15.0, 7.6 Hz, 2H), 7.10 (dd, *J* = 30.7, 10.7 Hz, 3H), 4.26 (s, 3H), 3.48 (s, 3H), 3.33 – 3.20 (m, 2H), 3.13 (s, 1H), 2.97 (s, 3H), 2.80 (s, 1H), 2.59 (s, 1H), 2.34 – 2.03 (m, 7H), 1.82 (d, *J* = 12.4 Hz, 3H), 1.58 (dd, *J* = 12.6, 6.9 Hz, 14H), 1.33 – 1.21 (m, 4H), 1.18 (t, *J* = 7.0 Hz, 3H), -0.01 (s, 1H).

^{13}C NMR (126 MHz, chloroform-*d*) δ 148.65, 148.05, 143.10, 139.27, 137.17, 136.86, 136.74, 134.00, 131.81, 131.38, 127.09, 126.13, 124.72, 123.01, 119.66, 106.64, 104.86, 103.42, 56.42, 55.23, 39.49, 35.24, 35.01, 34.24, 34.10, 33.85, 30.06, 28.65, 27.74, 27.62, 26.78, 26.08, 25.77, 25.22, 24.14, 24.00, 23.84, 22.31, 14.05.

^{31}P NMR (162 MHz, chloroform-*d*) δ 43.05.

HRMS: $C_{44}H_{57}NO_2PPd$ ESI-MS [M-OMs] calcd: 763.3178; found: 763.3156.

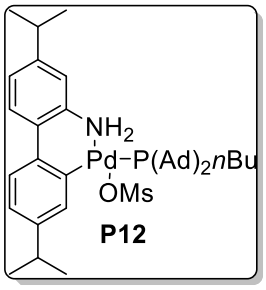


^{1}H NMR (500 MHz, chloroform-*d*) δ 7.58 (s, 3H), 7.41 (d, *J* = 7.9 Hz, 1H), 7.20 (d, *J* = 3.3 Hz, 2H), 7.16 (d, *J* = 7.7 Hz, 1H), 7.06 (d, *J* = 7.9 Hz, 1H), 6.79 (d, *J* = 14.4 Hz, 3H), 6.50 (d, *J* = 8.4 Hz, 1H), 6.36 (s, 3H), 2.96 – 2.83 (m, 1H), 2.57 (s, 3H), 2.46 – 2.31 (m, 1H), 1.23 (d, *J* = 6.9 Hz, 6H), 0.83 (d, *J* = 6.7 Hz, 6H).

^{13}C NMR (126 MHz, chloroform-*d*) δ 149.24, 148.73, 148.69, 147.97, 147.94, 141.50, 140.88, 140.24, 136.68, 135.62, 135.51, 135.24, 134.96, 134.93, 127.46, 126.24, 124.88, 124.70, 124.22, 123.66, 119.40, 119.38, 111.44, 111.38, 39.32, 33.76, 33.47, 23.86, 23.56.

^{31}P NMR (162 MHz, chloroform-*d*) δ -22.50.

HRMS: $C_{51}H_{65}NO_3PPd$ ESI-MS [M-OMs] calcd: 876.3755; found: 876.3751.



P12

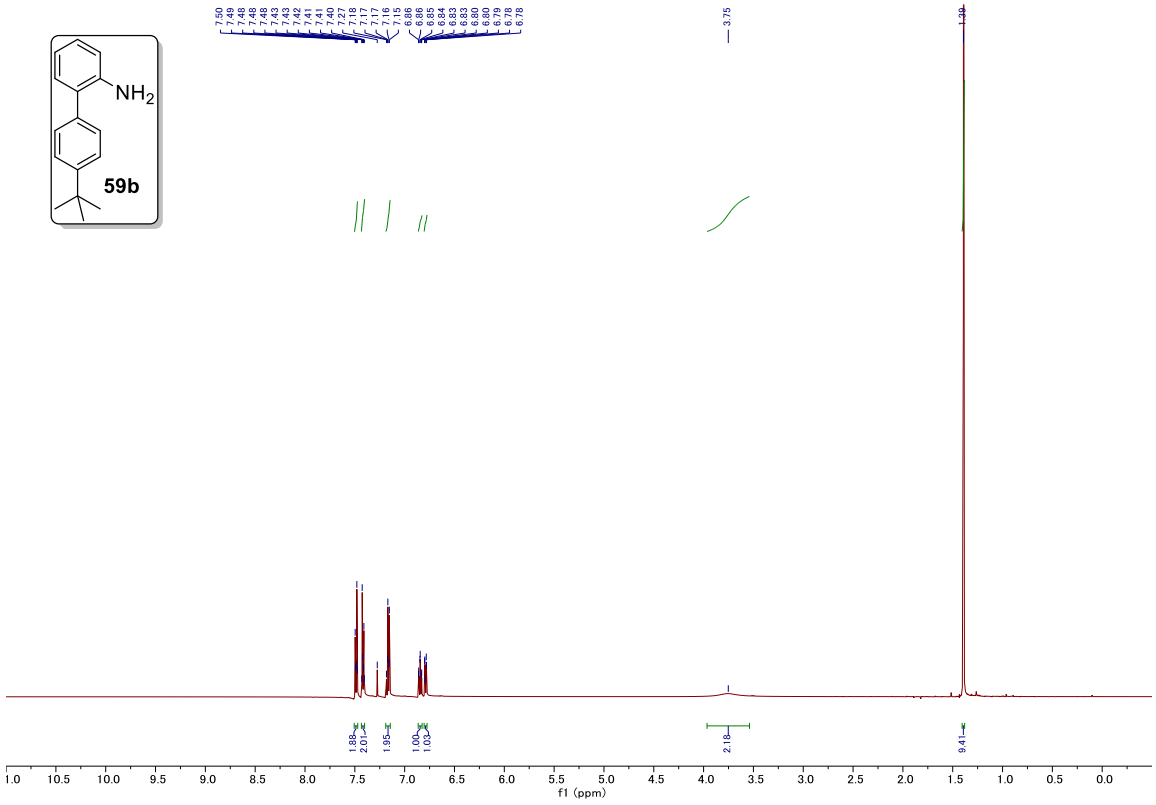
^{1}H NMR (500 MHz, chloroform-*d*) δ 7.19 (dt, *J* = 5.0, 2.7 Hz, 2H), 7.05 – 6.99 (m, 2H), 6.92 (d, *J* = 7.7 Hz, 1H), 6.82 (d, *J* = 7.5 Hz, 1H), 4.08 (dd, *J* = 8.0, 4.1 Hz, 1H), 2.85 (dtt, *J* = 9.4, 7.0, 4.2 Hz, 1H), 2.76 (d, *J* = 2.5 Hz, 3H), 2.72 (dd, *J* = 7.8, 5.5 Hz, 1H), 2.13 (s, 6H), 2.03 – 1.91 (m, 9H), 1.72 (dq, *J* = 27.2, 11.9, 11.5 Hz, 12H), 1.37 – 1.28 (m, 2H), 1.19 (ddd, *J* = 12.5, 7.6, 4.5 Hz, 12H), 1.02 – 0.94 (m, 1H), 0.88 – 0.79 (m, 2H), 0.78 (d, *J* = 11.1 Hz, 1H), 0.55 – 0.25 (m, 5H).

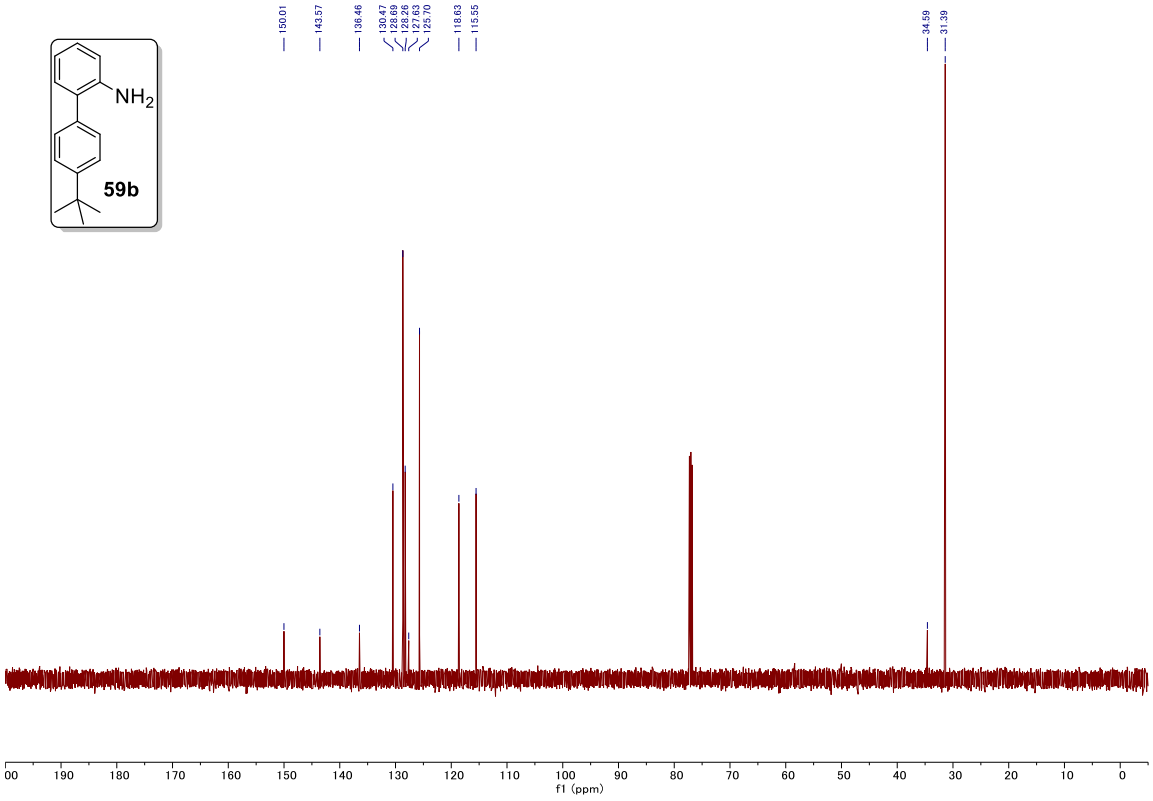
^{13}C NMR (126 MHz, chloroform-*d*) δ 149.12, 147.61, 137.82, 137.59, 136.65, 136.63, 135.59, 135.54, 126.64, 124.65, 123.48, 122.19, 117.75, 41.19, 41.08, 40.90, 40.82, 40.62, 40.49, 40.15, 40.12, 39.83, 37.11, 36.68, 36.67, 36.60, 36.58, 36.49, 36.48, 33.98, 33.74, 29.96, 29.69, 28.90, 28.83, 28.70, 28.68, 28.63, 27.78, 27.71, 27.67, 25.34, 25.25, 24.15, 23.99, 23.81, 17.97, 17.80, 13.80.

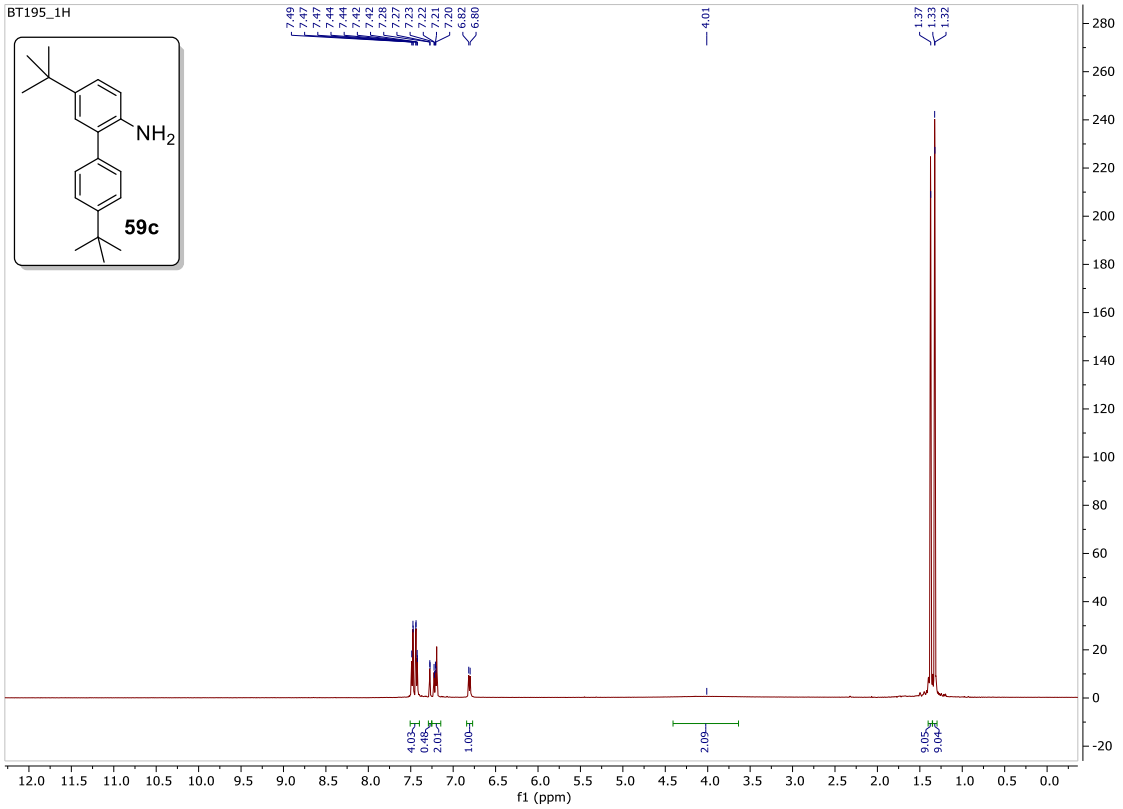
^{31}P NMR (162 MHz, chloroform-*d*) δ 48.07.

HRMS: $C_{42}H_{61}NPPd$ ESI-MS [M-OMs] calcd: 716.3593; found: 716.3600.

14. NMR spectra of new compounds



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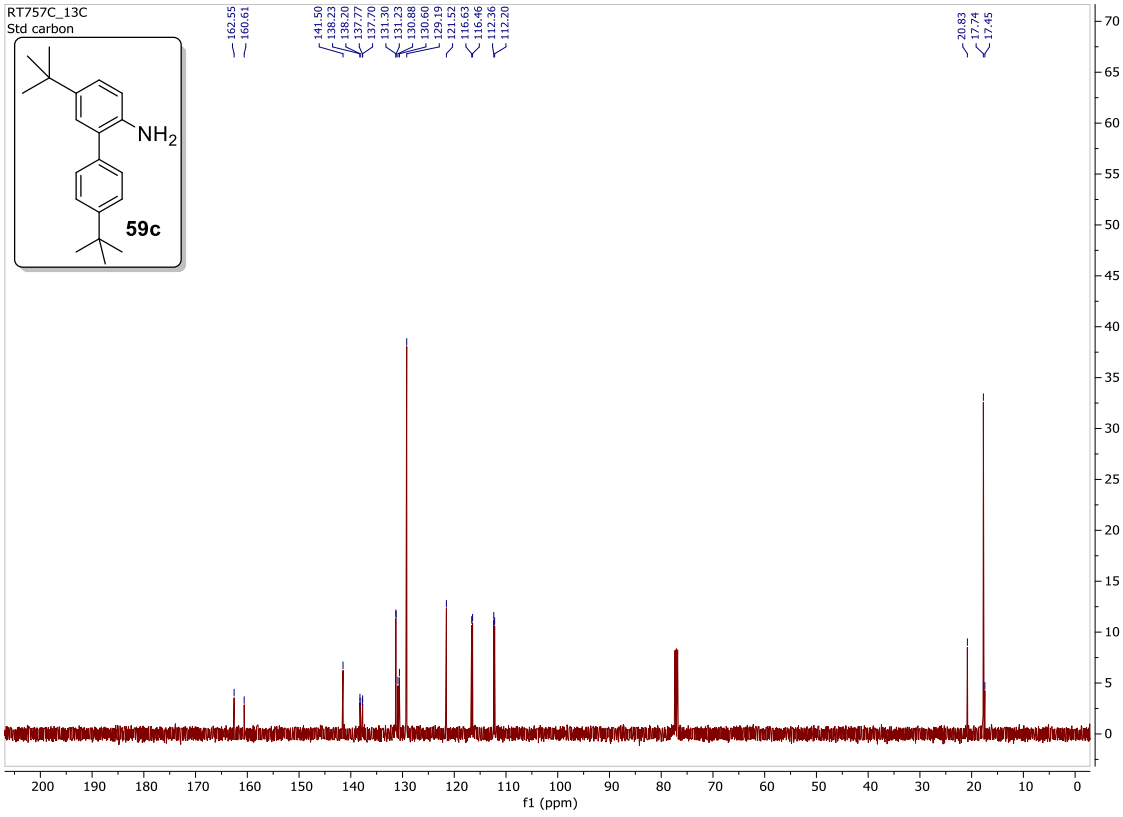
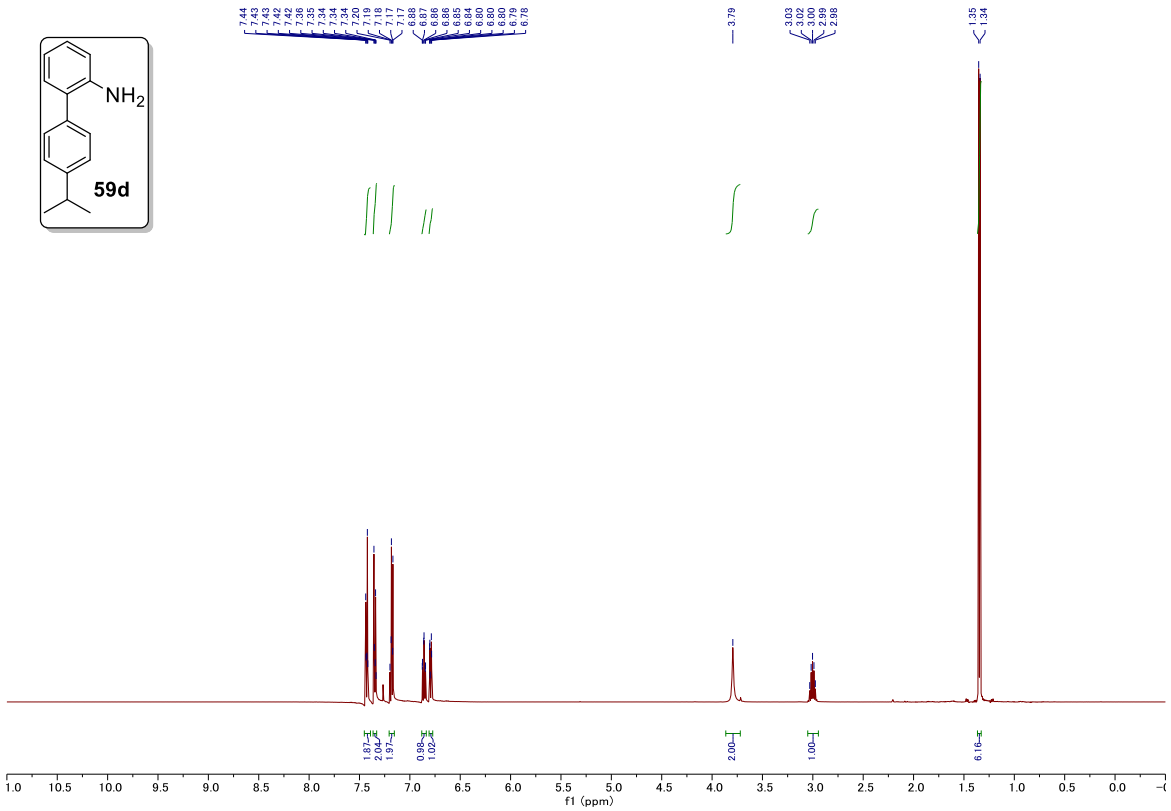
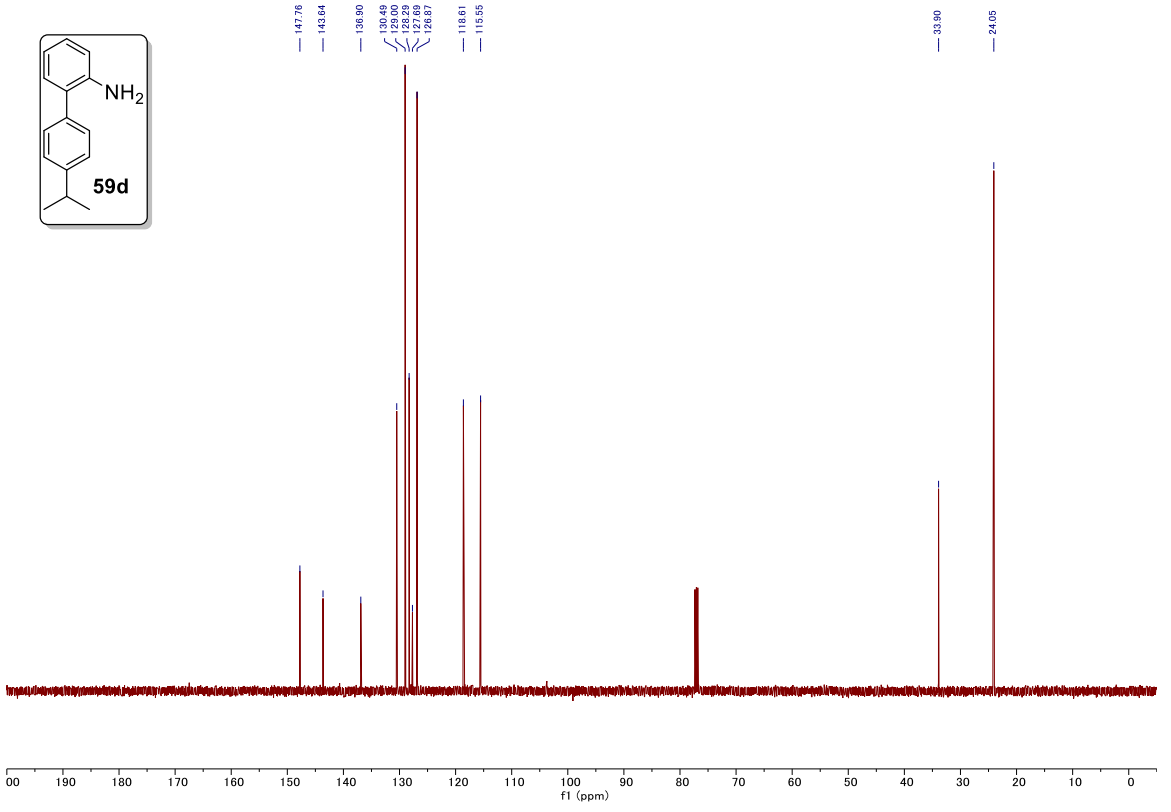
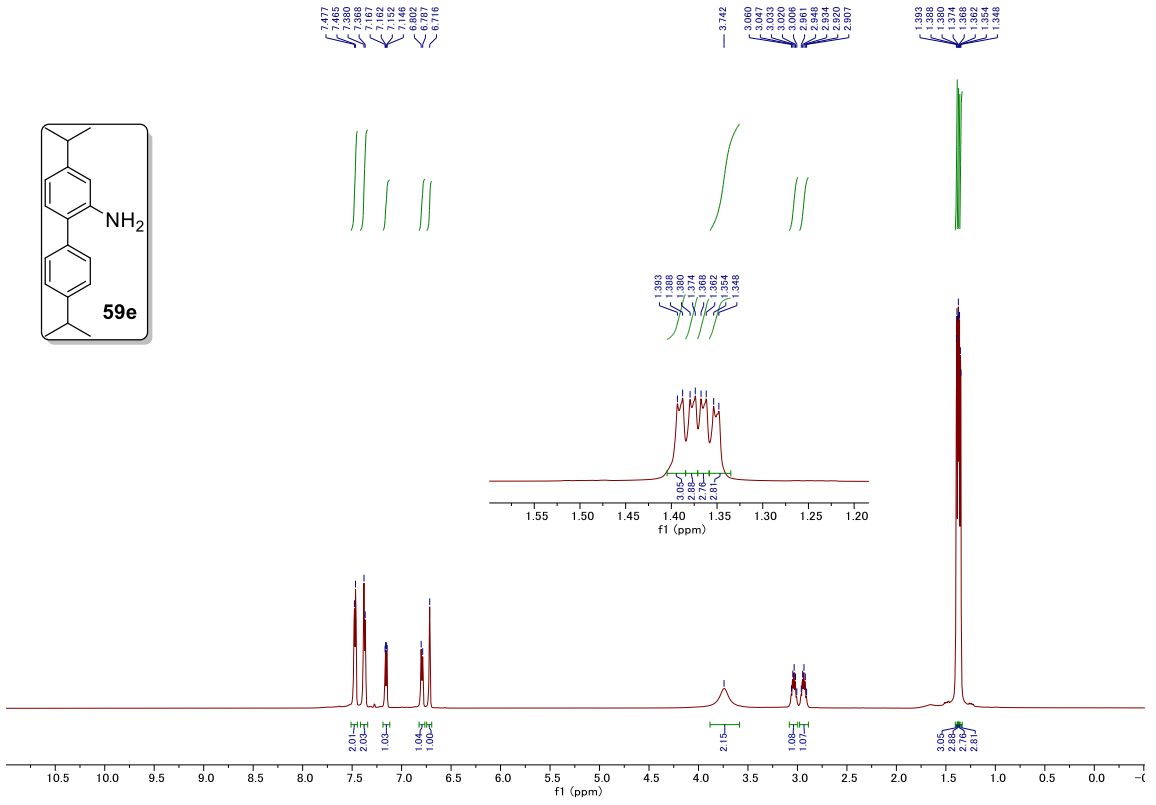
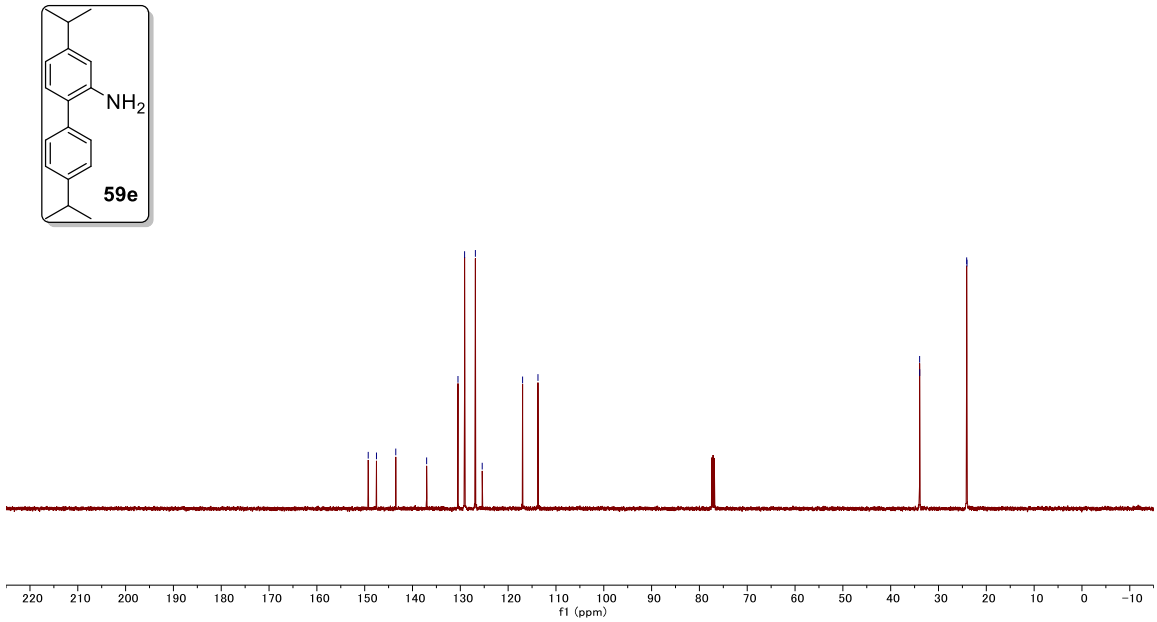
NH2
59c
7.49
7.47
7.47
7.44
7.44
7.42
7.42
7.28
7.27
7.23
7.22
7.21
7.20
6.82
6.80
4.01
1.37
1.33
1.32
4.03
0.46
2.01
1.00
2.09
9.05
9.04
f1 (ppm)

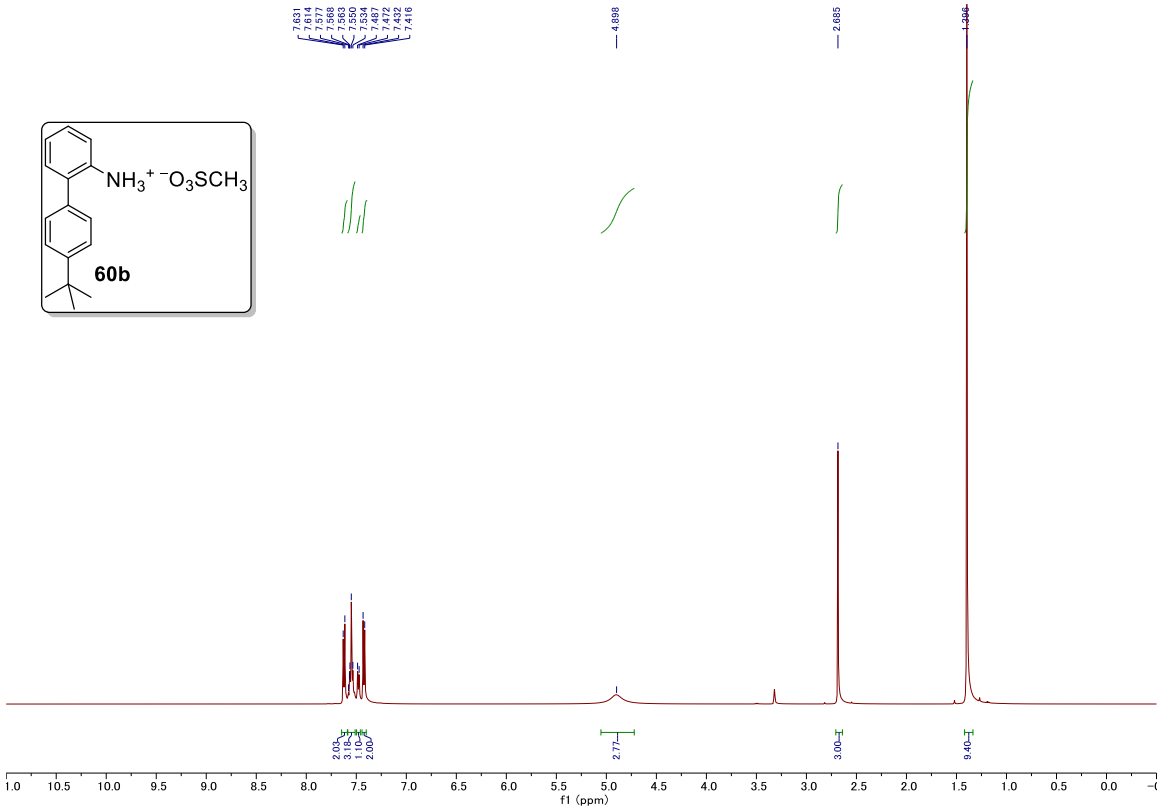

RT757C_13C
Std carbon
NH2
59c
162.55
160.61
141.50
138.23
138.20
137.77
137.70
131.30
131.23
130.88
130.60
129.19
121.52
116.63
116.46
112.36
112.20
20.83
17.74
17.45
f1 (ppm)


NH2
59d
7.44
7.43
7.43
7.42
7.42
7.42
7.36
7.35
7.34
7.34
7.34
7.34
7.20
7.19
7.18
7.17
7.17
6.89
6.87
6.86
6.86
6.85
6.84
6.80
6.80
6.80
6.79
6.78
3.79
3.03
3.02
3.00
2.99
2.98
1.35
1.34
1.87
2.04
1.97
0.98
1.02
2.00
1.00
6.16
f1 (ppm)


NH2
59d
147.76
143.64
136.90
130.49
129.00
128.29
127.69
126.87
118.61
115.55
33.80
24.05
f1 (ppm)


NH2
59e
f1 (ppm)


NH2
59e
f1 (ppm)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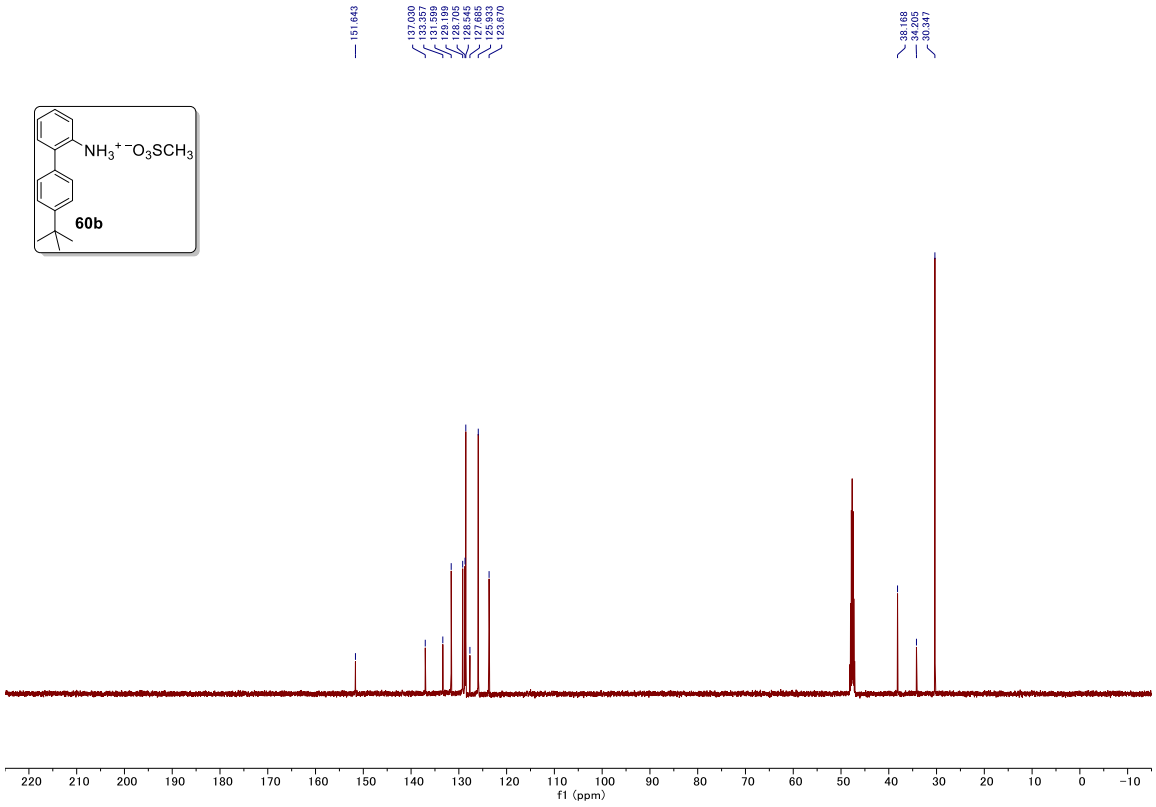
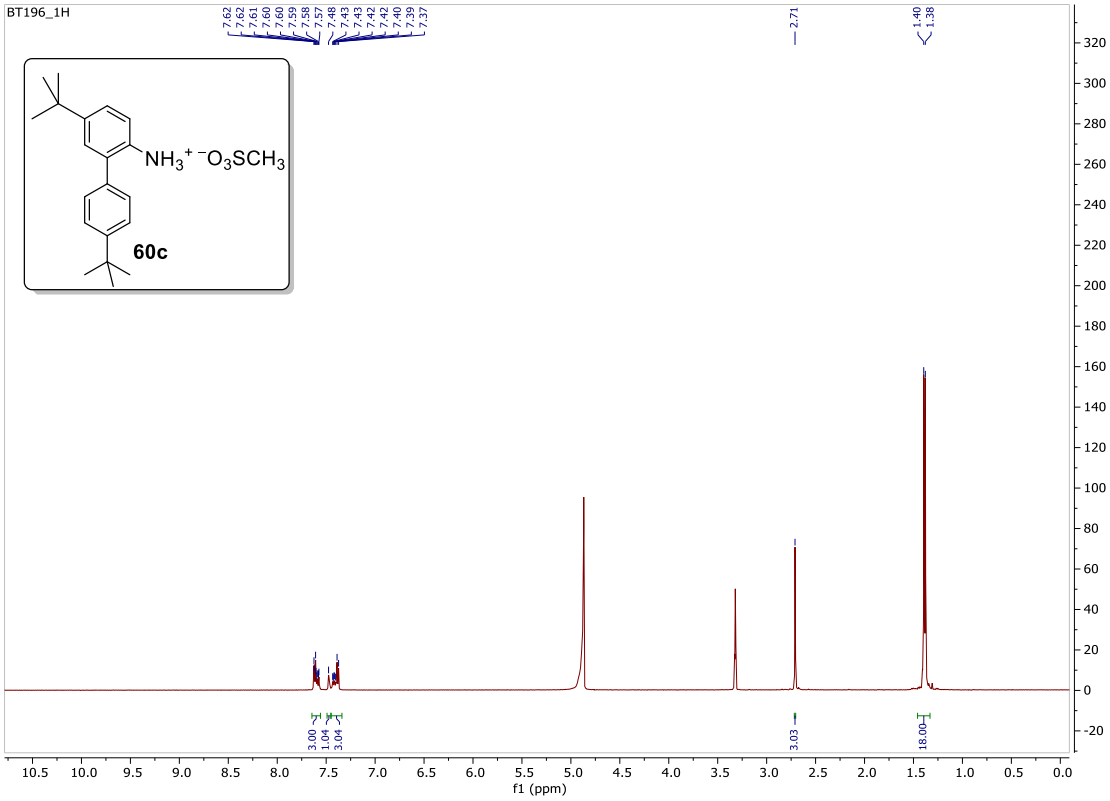
7.614
7.577
7.568
7.563
7.550
7.534
7.487
7.472
7.423
7.416
4.898
2.685
1.396
NH3+ −O3SCH3
60b
2.03
3.18
1.10
2.00
2.77
3.00
9.40
f1 (ppm)


151.643
137.030
133.357
131.599
129.199
128.705
128.545
127.685
125.933
123.670
38.168
34.705
30.347
NH3+ −O3SCH3
60b
f1 (ppm)


BT196_1H
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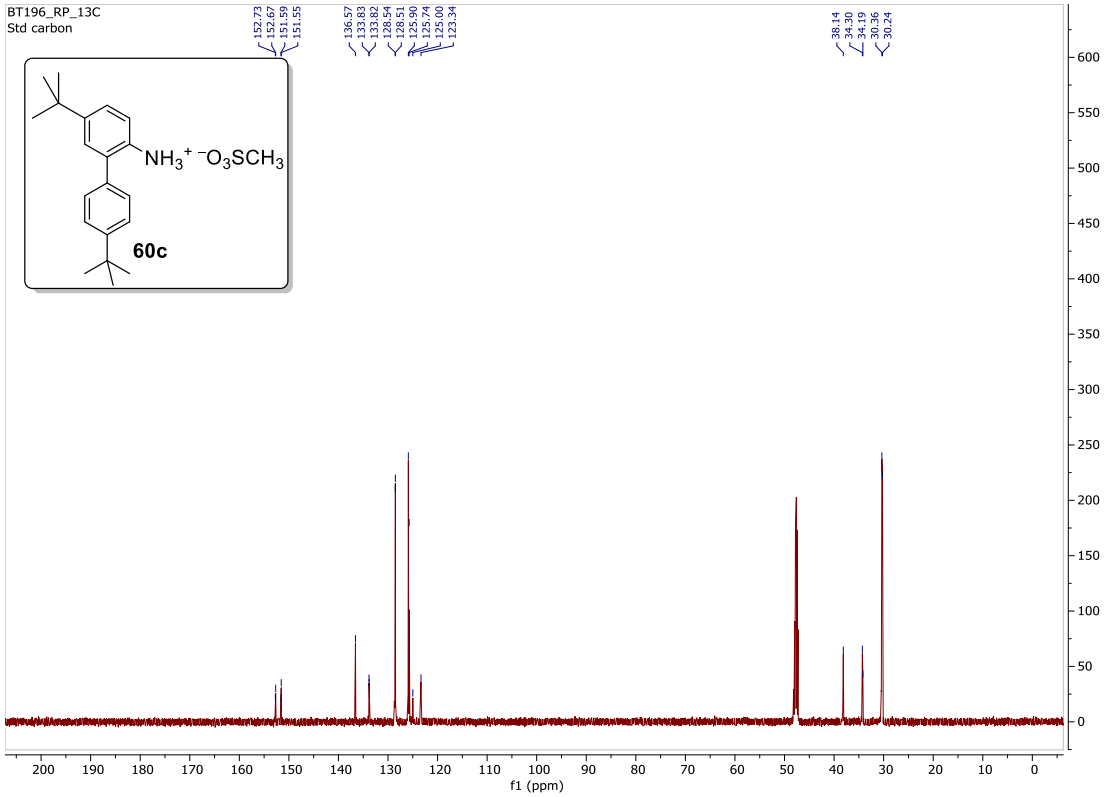
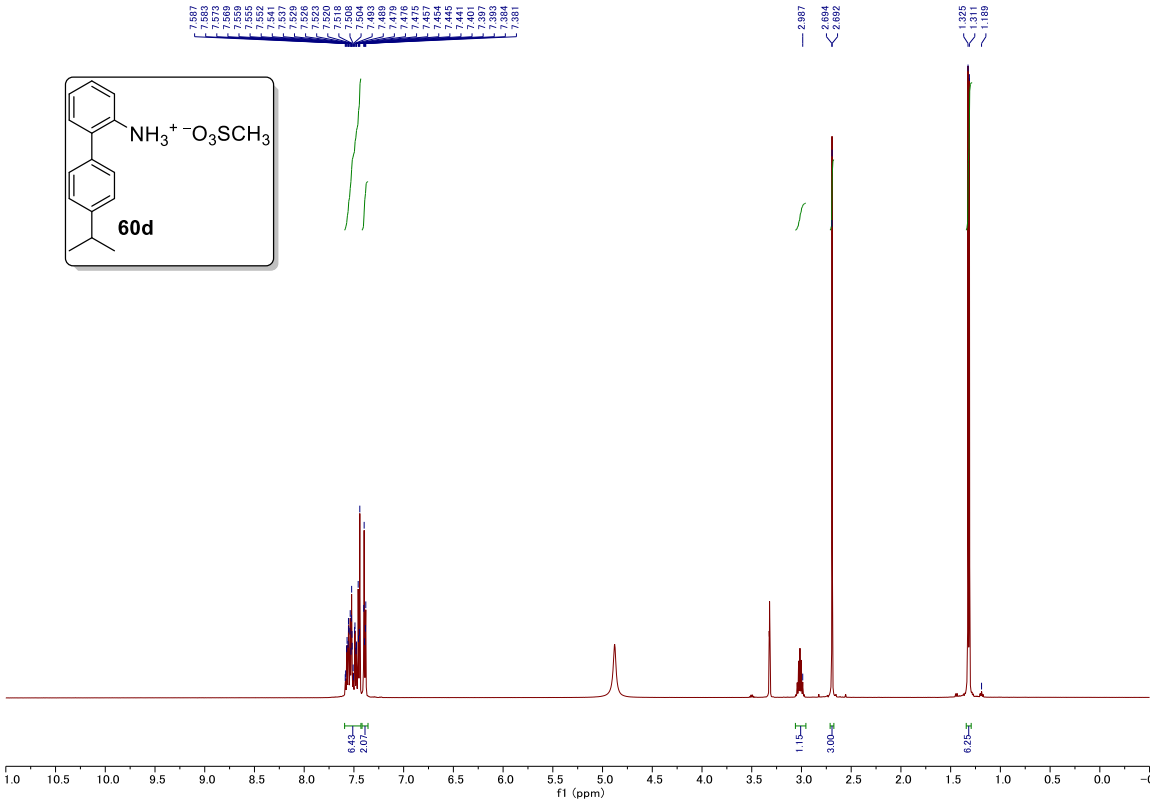
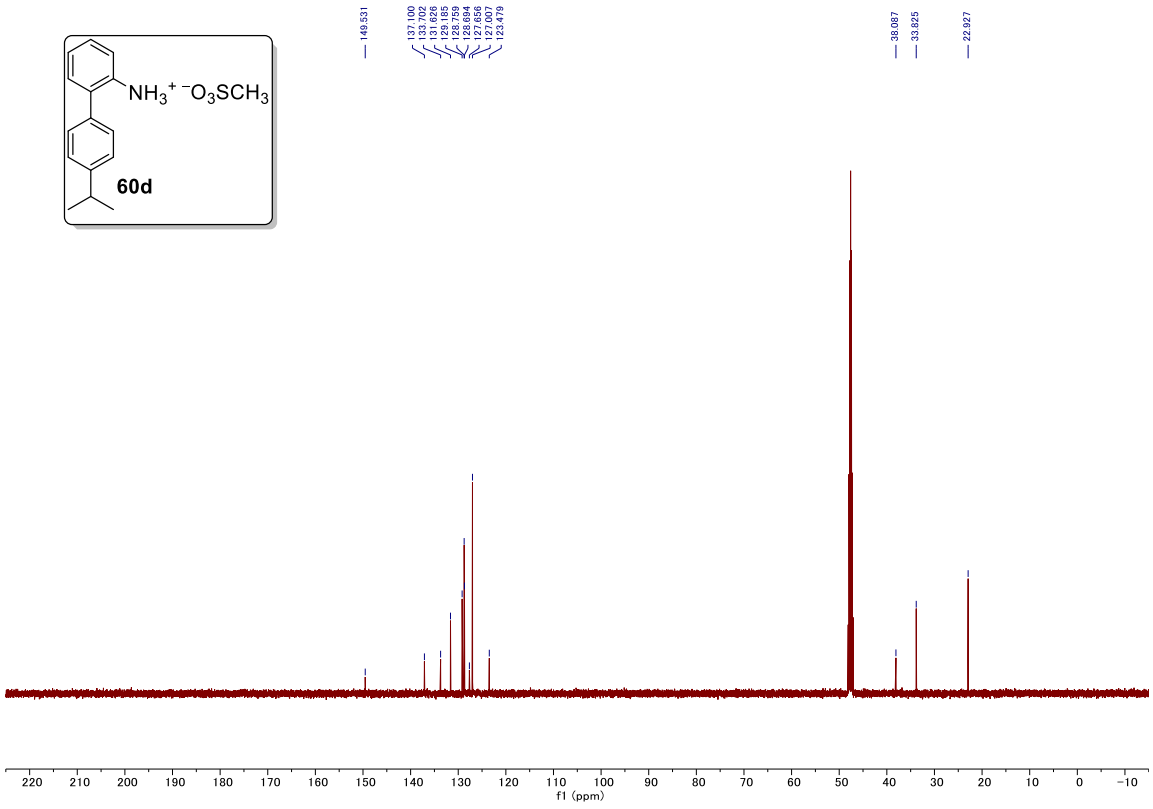
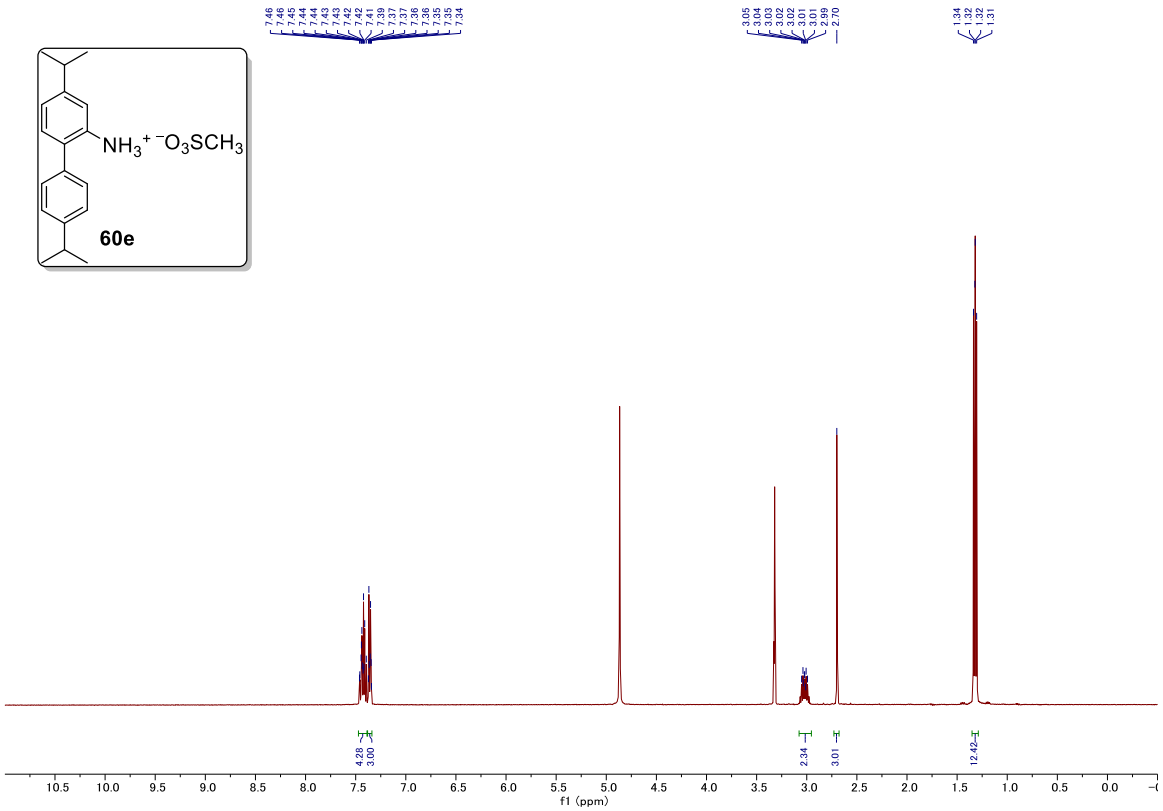
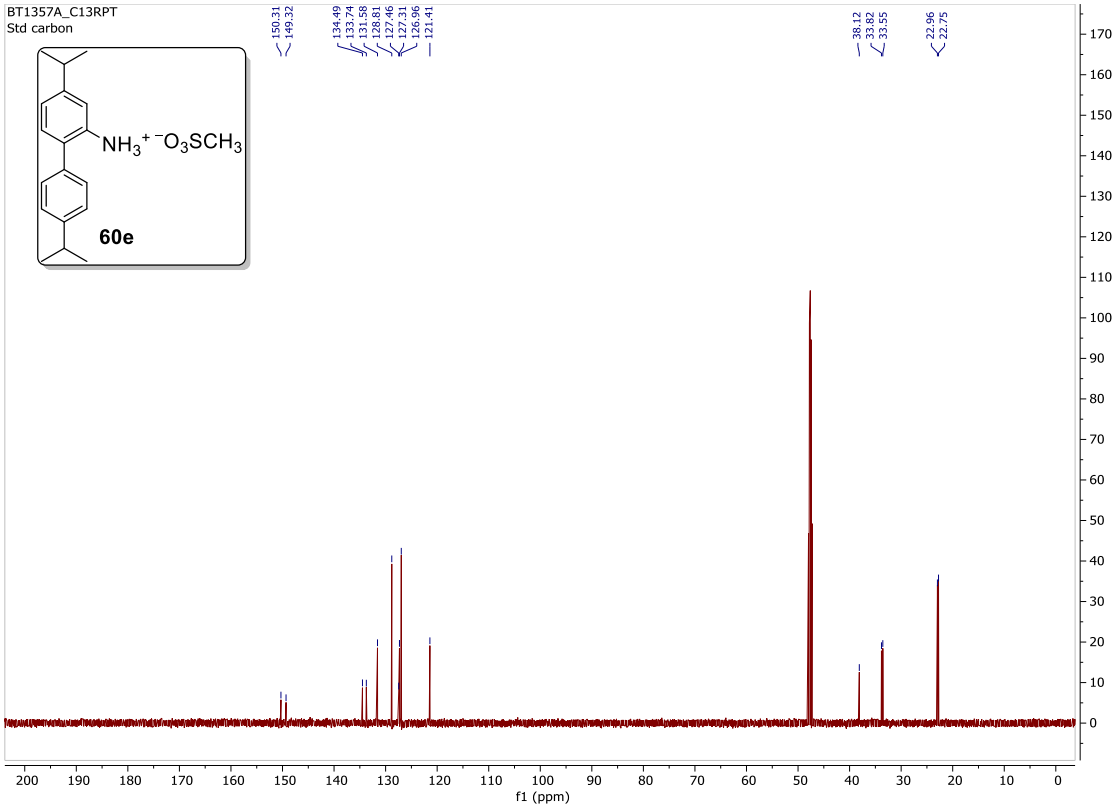
7.62
7.61
7.60
7.60
7.59
7.58
7.57
7.48
7.43
7.43
7.42
7.42
7.40
7.39
7.37
2.71
1.40
1.38
NH3+ −O3SCH3
60c
3.00
1.04
3.04
3.03
18.00
f1 (ppm)


BT196_RP_13C
Std carbon
152.73
152.67
151.59
151.55
136.57
133.83
133.82
128.54
128.51
125.90
125.74
125.00
123.34
38.14
34.30
34.19
30.36
30.24
NH3+ −O3SCH3
60c
f1 (ppm)


NH3+ −O3SCH3
60d
f1 (ppm)


NH3+ −O3SCH3
60d
f1 (ppm)


7.46
7.46
7.45
7.44
7.44
7.43
7.43
7.42
7.42
7.41
7.39
7.37
7.37
7.36
7.36
7.35
7.35
7.34
3.05
3.04
3.03
3.02
3.02
3.01
3.01
2.99
2.70
1.34
1.32
1.32
1.31
NH3+ −O3SCH3
60e
4.28
3.00
2.34
3.01
12.42
f1 (ppm)


BT1357A_C13RPT
Std carbon
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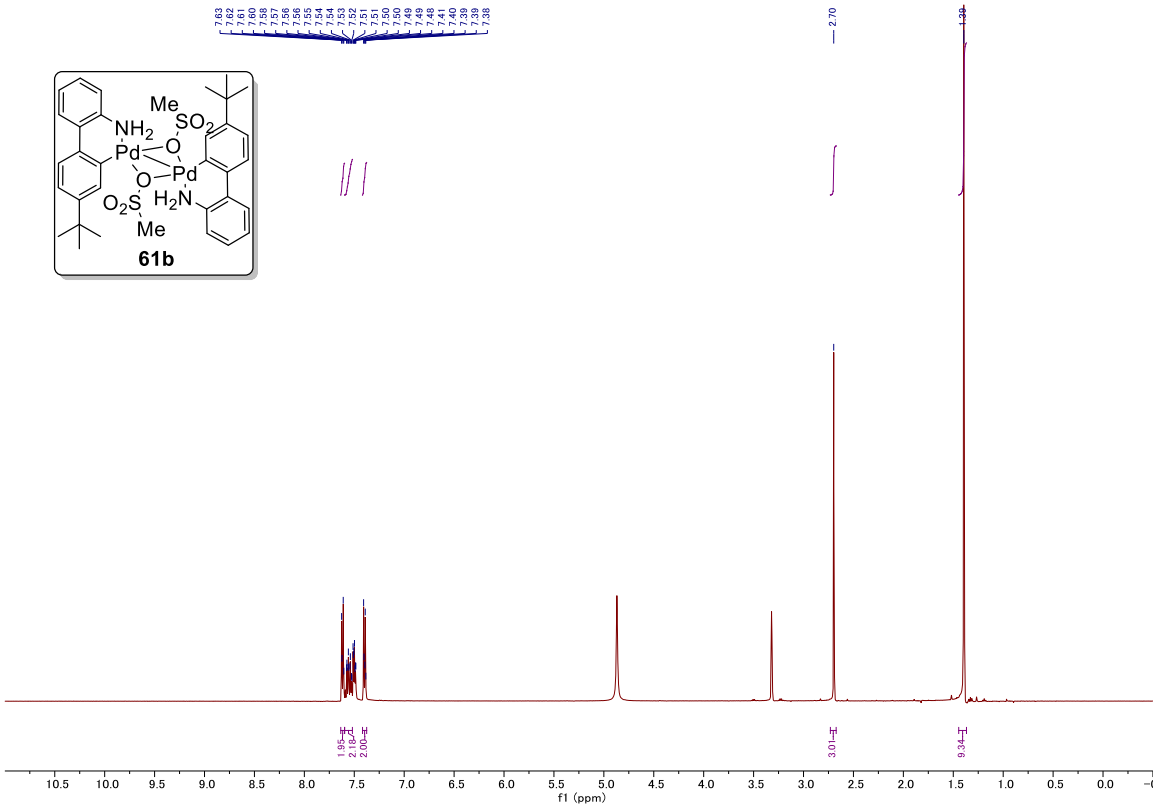
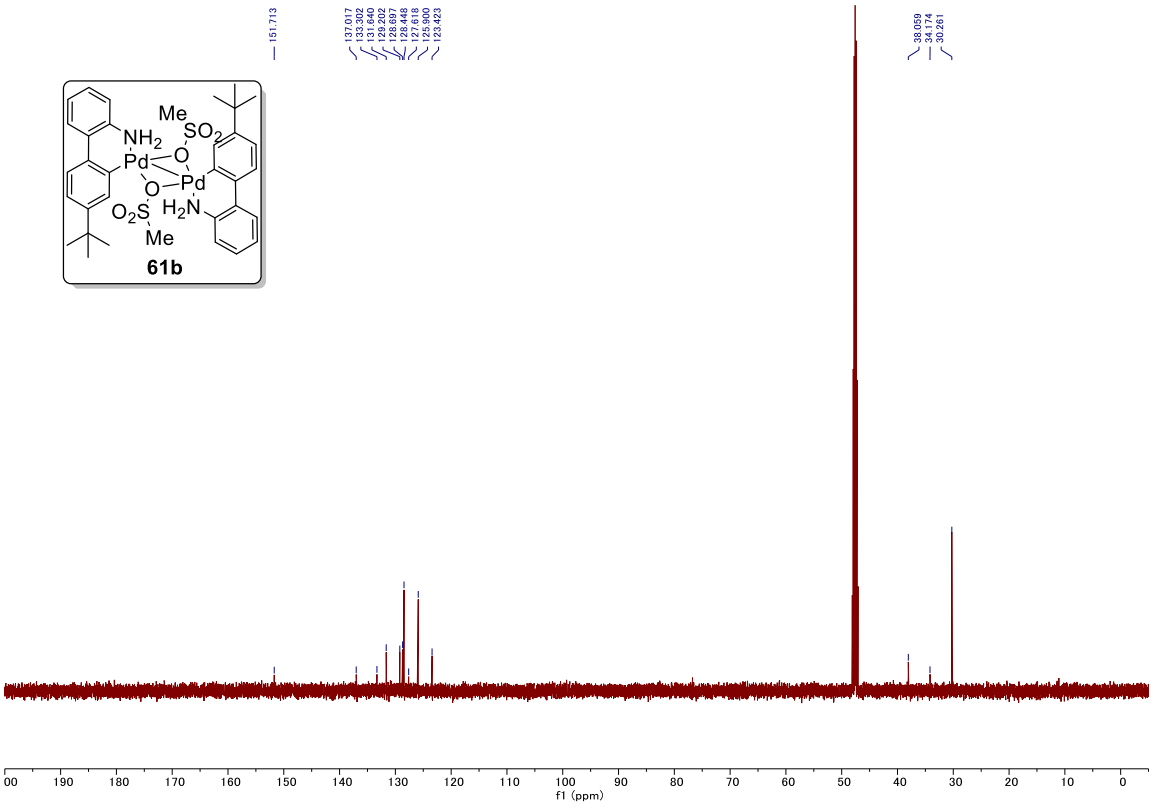
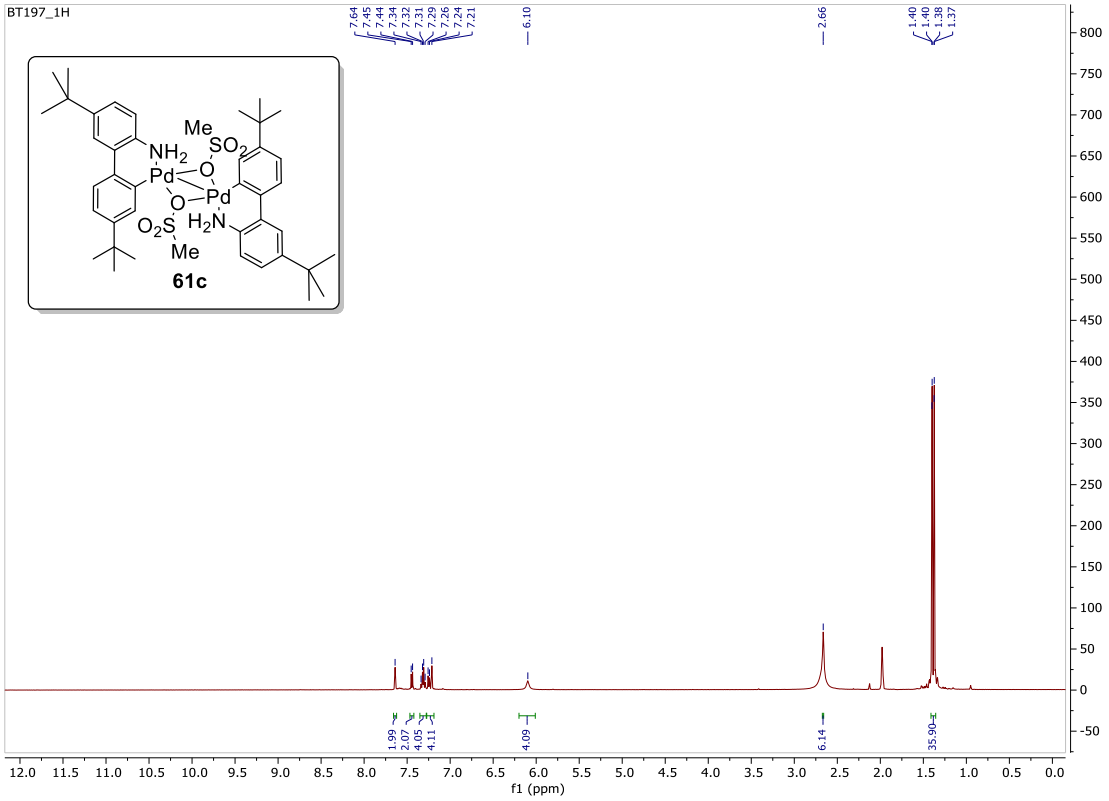
149.32
134.49
133.74
131.58
128.81
127.46
127.31
126.96
121.41
38.12
33.82
33.55
22.96
22.75
NH3+ −O3SCH3
60e
f1 (ppm)


Me
SO2
NH2
Pd
O
Pd
O
O2S
H2N
Me
61b
f1 (ppm)


Me
SO2
NH2
Pd
O
Pd
O
O2S
H2N
Me
61b
f1 (ppm)


BT197_1H
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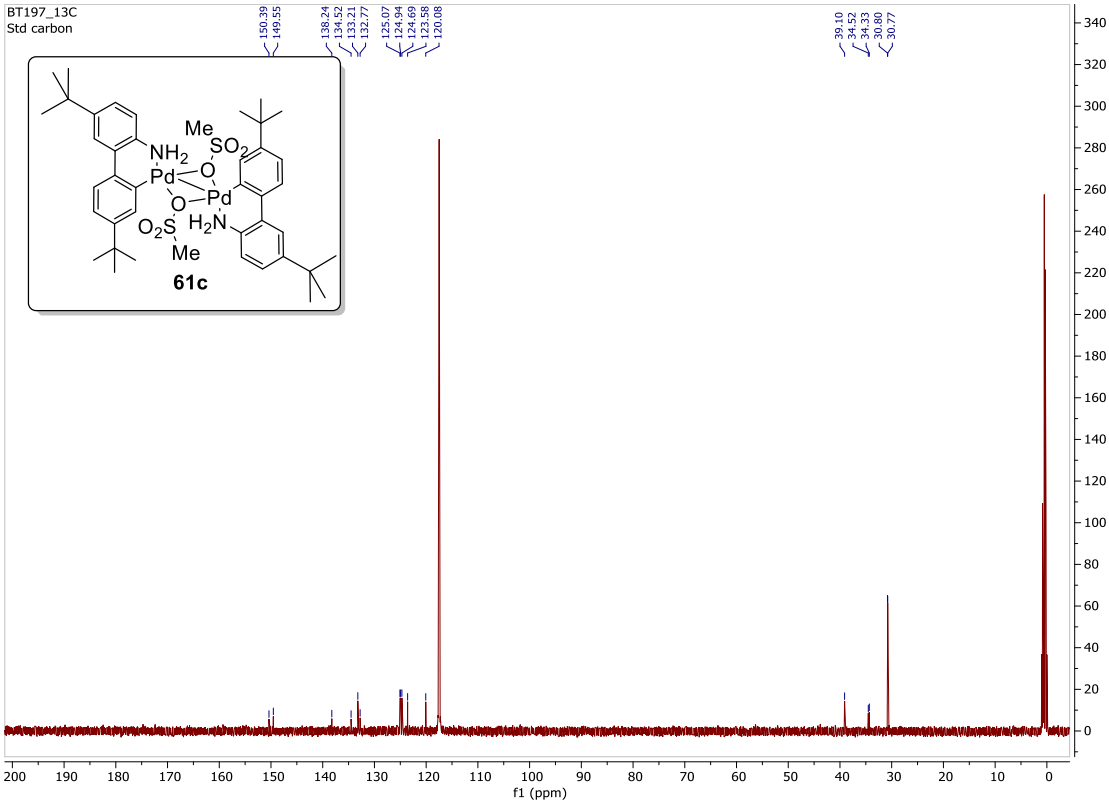
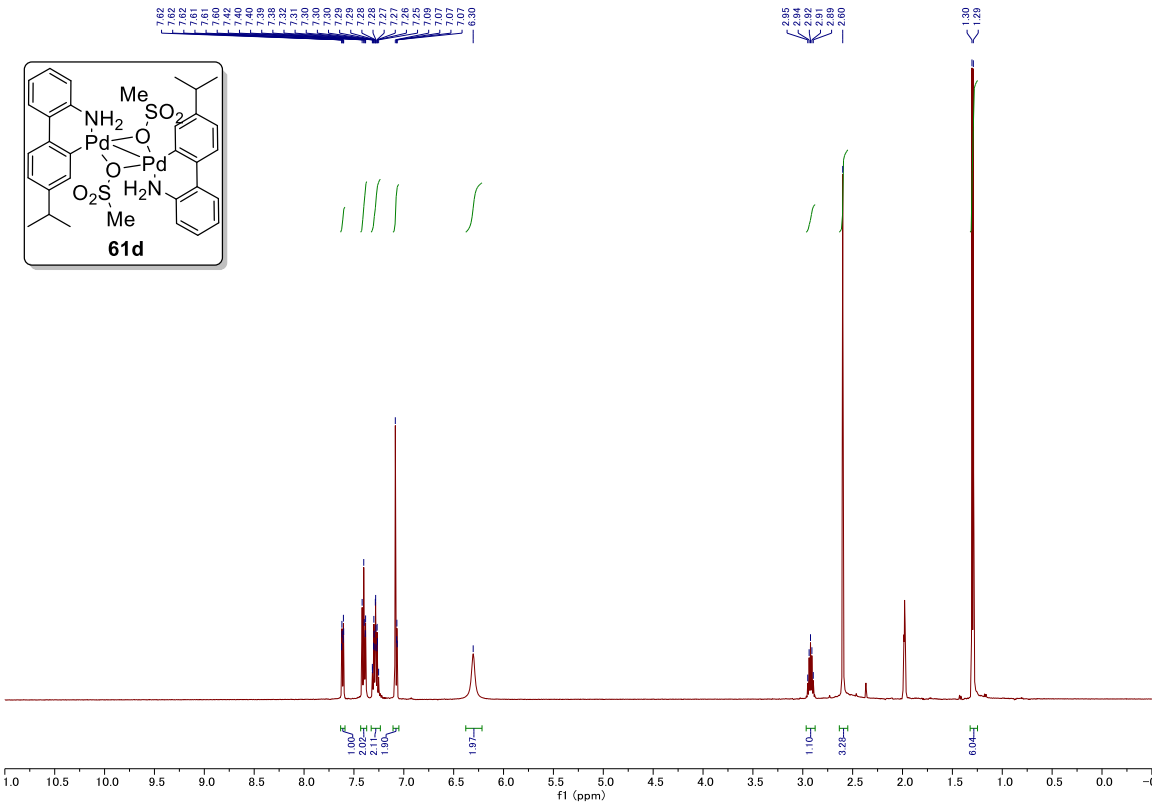
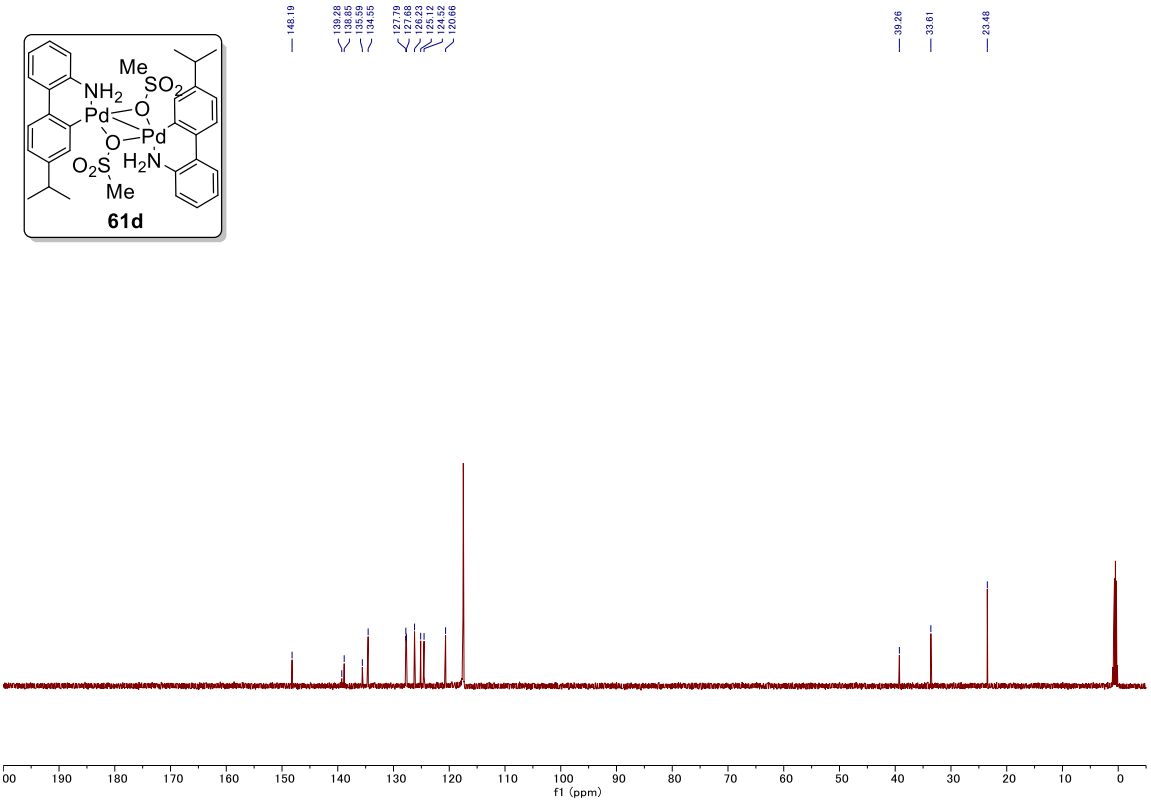
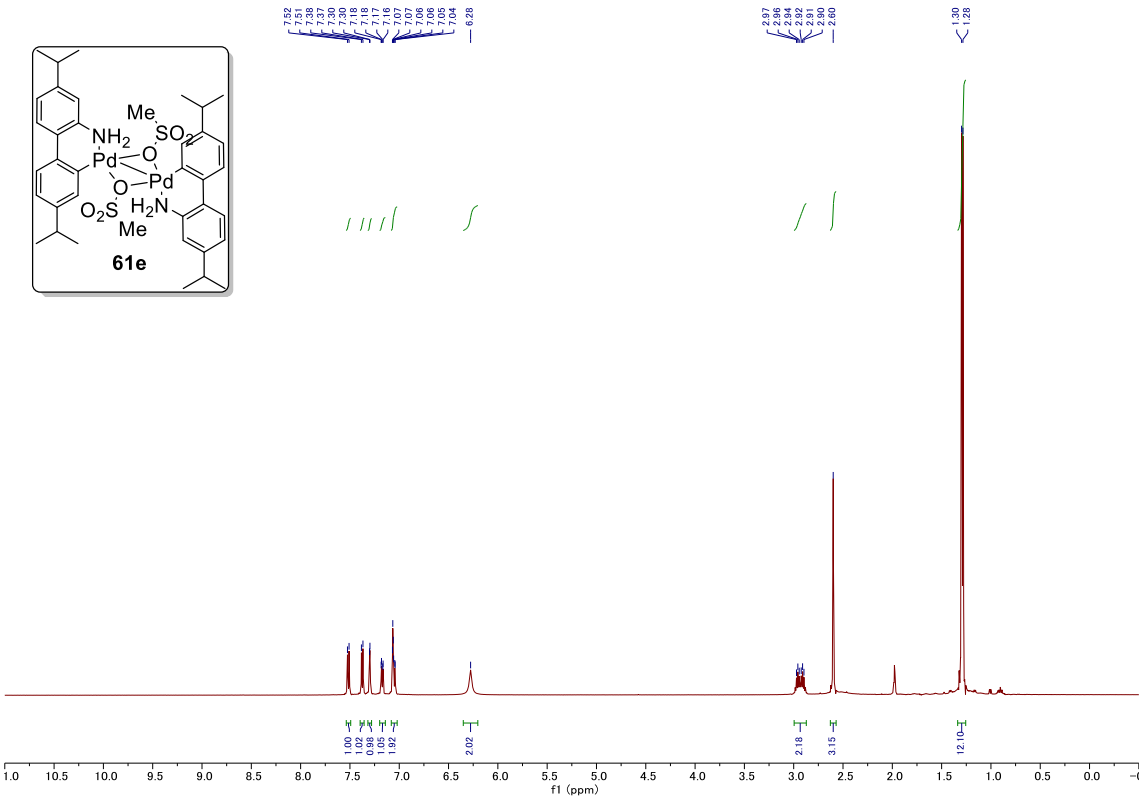
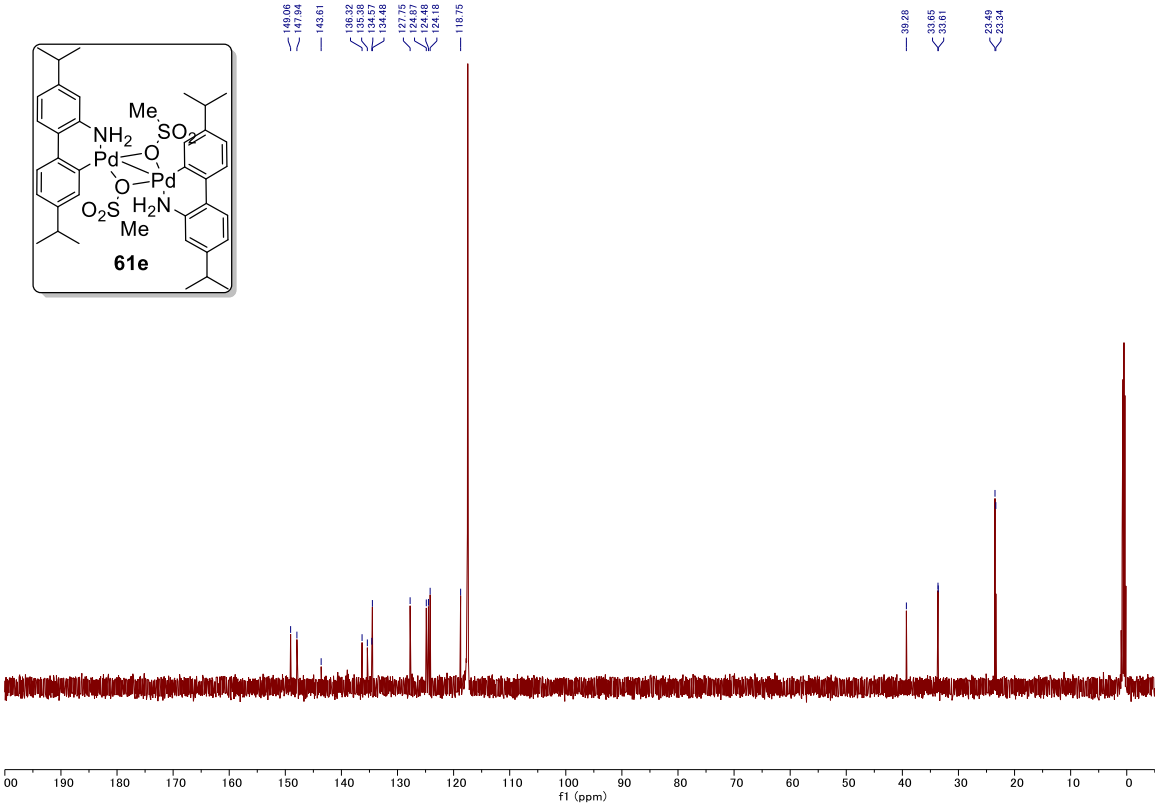
7.45
7.44
7.34
7.32
7.31
7.29
7.26
7.24
7.21
6.10
2.66
1.40
1.40
1.38
1.37
Me
SO2
NH2
Pd
O
O
Pd
O2S
H2N
Me
61c
1.99
2.07
4.05
4.11
4.09
6.14
35.90
f1 (ppm)

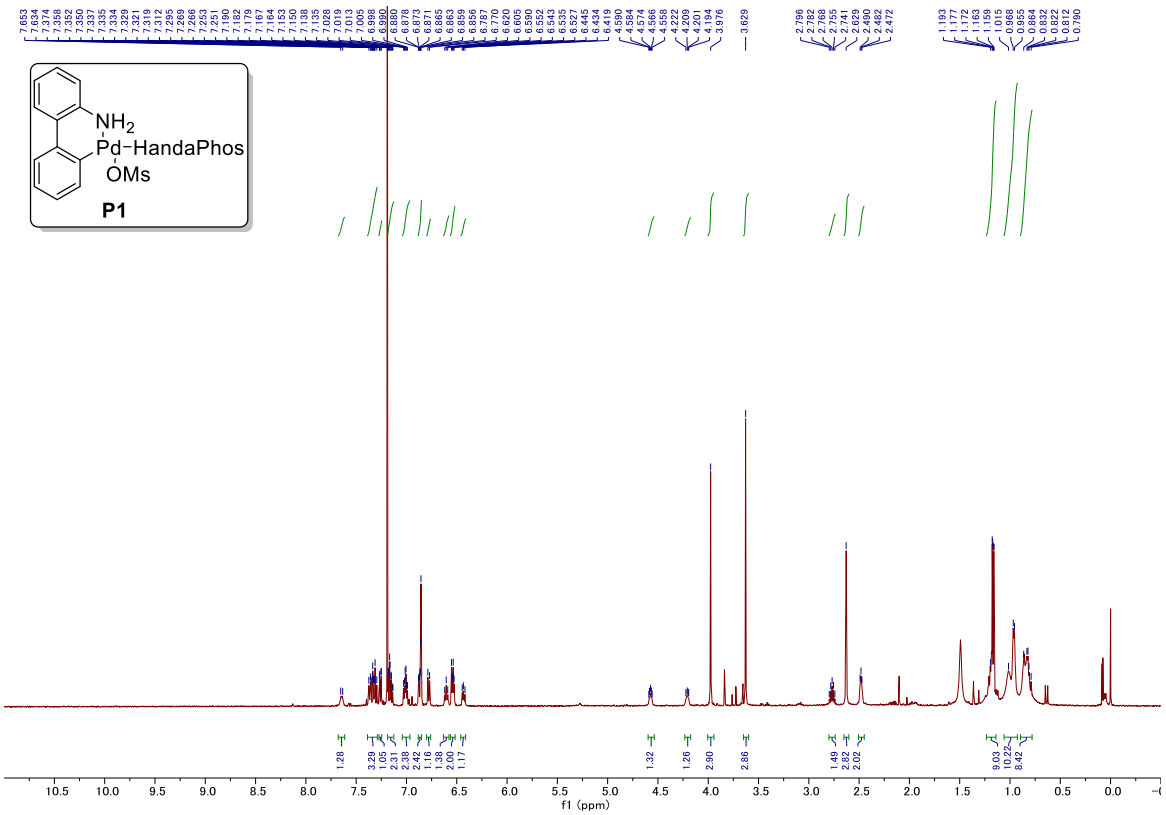

BT197_13C
Std carbon
150.39
149.55
138.24
134.52
133.21
132.77
125.07
124.94
124.69
123.58
120.08
39.10
34.52
34.33
30.80
30.77
Me
SO2
NH2
Pd
O
O
Pd
O2S
H2N
Me
61c
f1 (ppm)

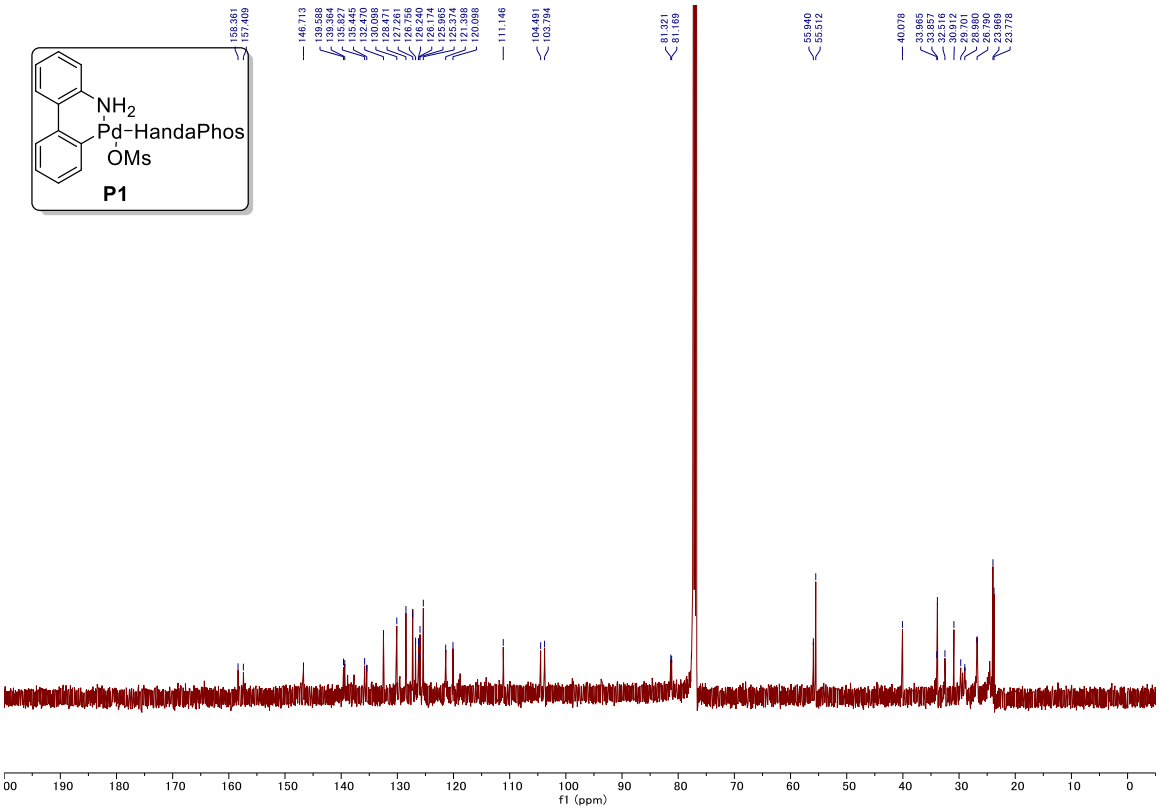

61d
f1 (ppm)

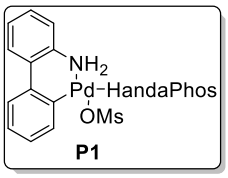

61d
f1 (ppm)


Me
NH2
SO2
Pd
O
O
Pd
O2S
H2N
Me
61e
f1 (ppm)

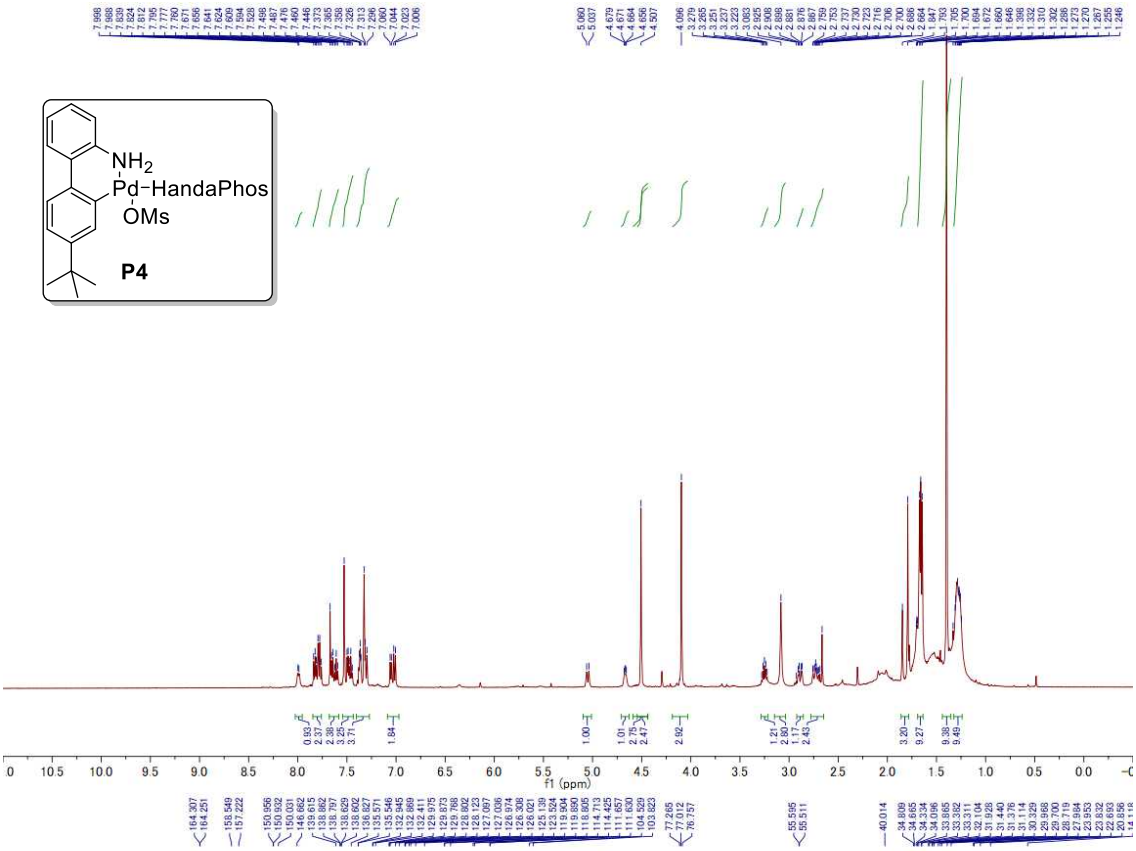

Me
NH2
SO2
Pd
O
O
Pd
O2S
H2N
Me
61e
f1 (ppm)

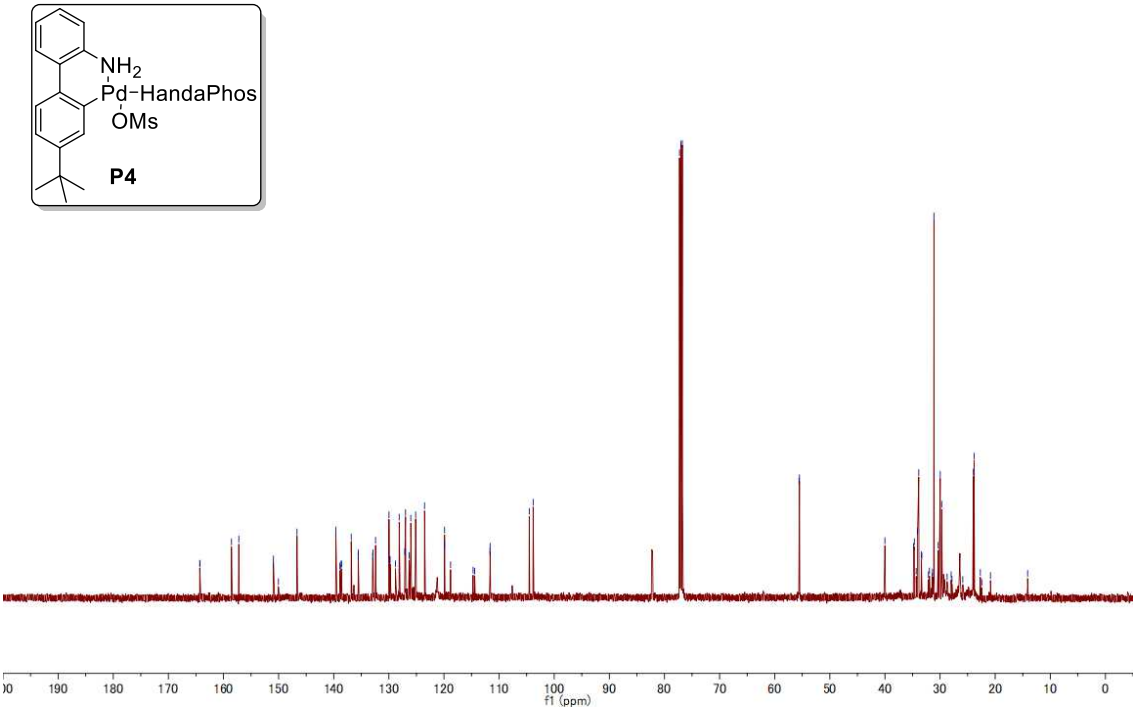

NH2
Pd–HandaPhos
OMs
P1
f1 (ppm)

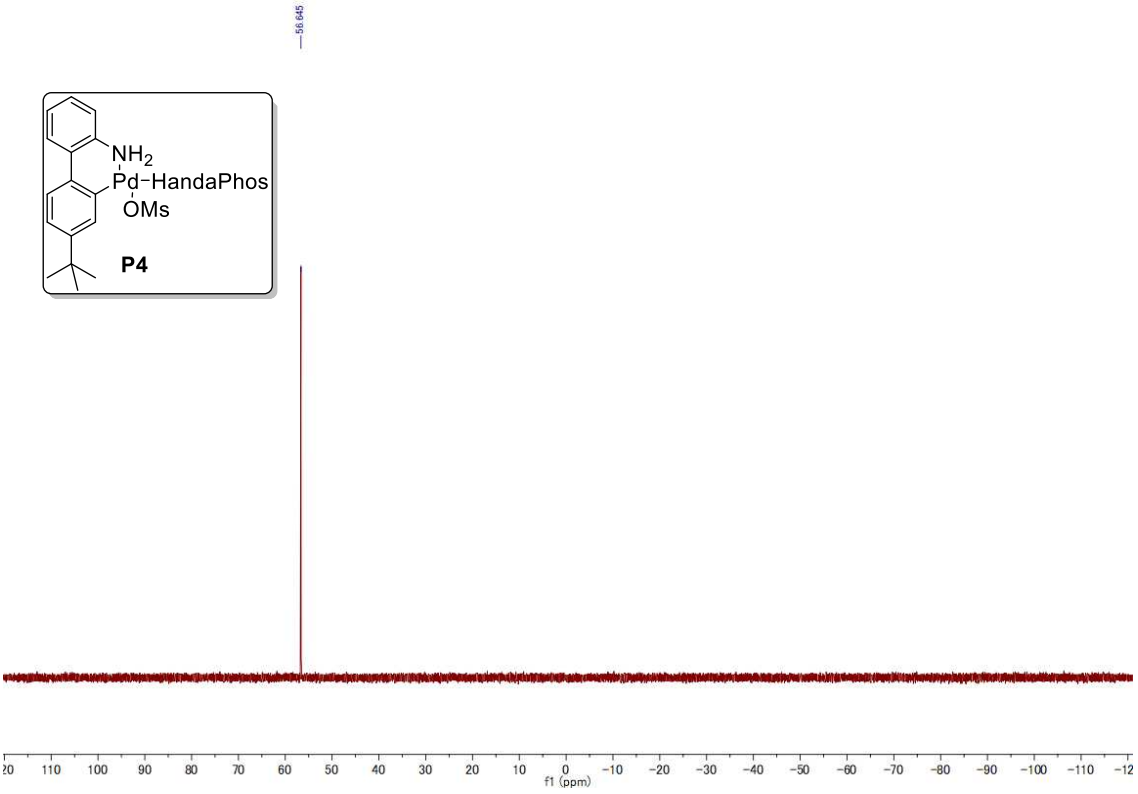

NH2
Pd–HandaPhos
OMs
P1
f1 (ppm)


NH2
Pd–HandaPhos
OMs
P1

59.402
20
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
f1 (ppm)


NH2
Pd-HandaPhos
OMs
P4
f1 (ppm)


NH2
Pd-HandaPhos
OMs
P4
f1 (ppm)


56.645
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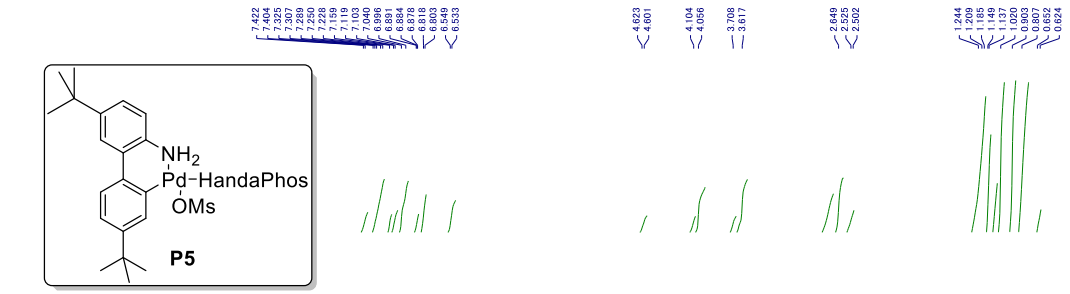
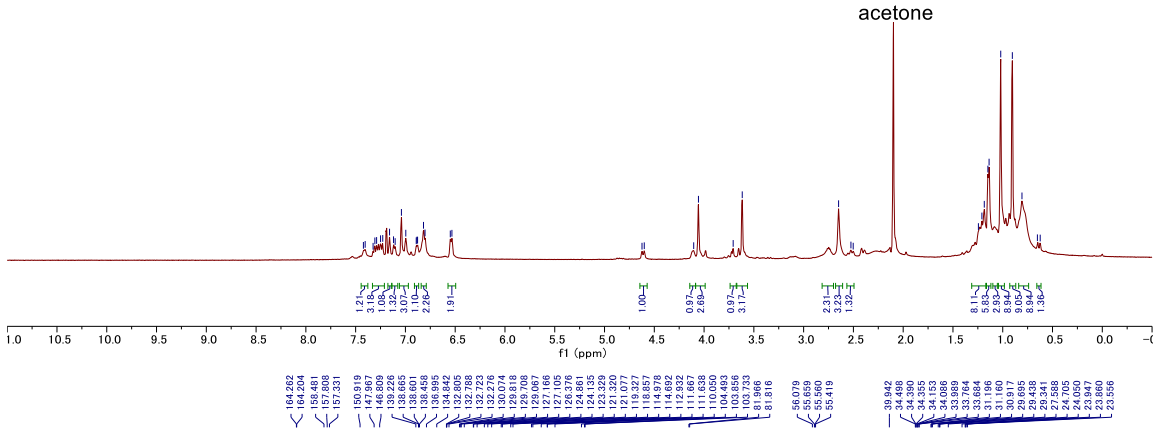
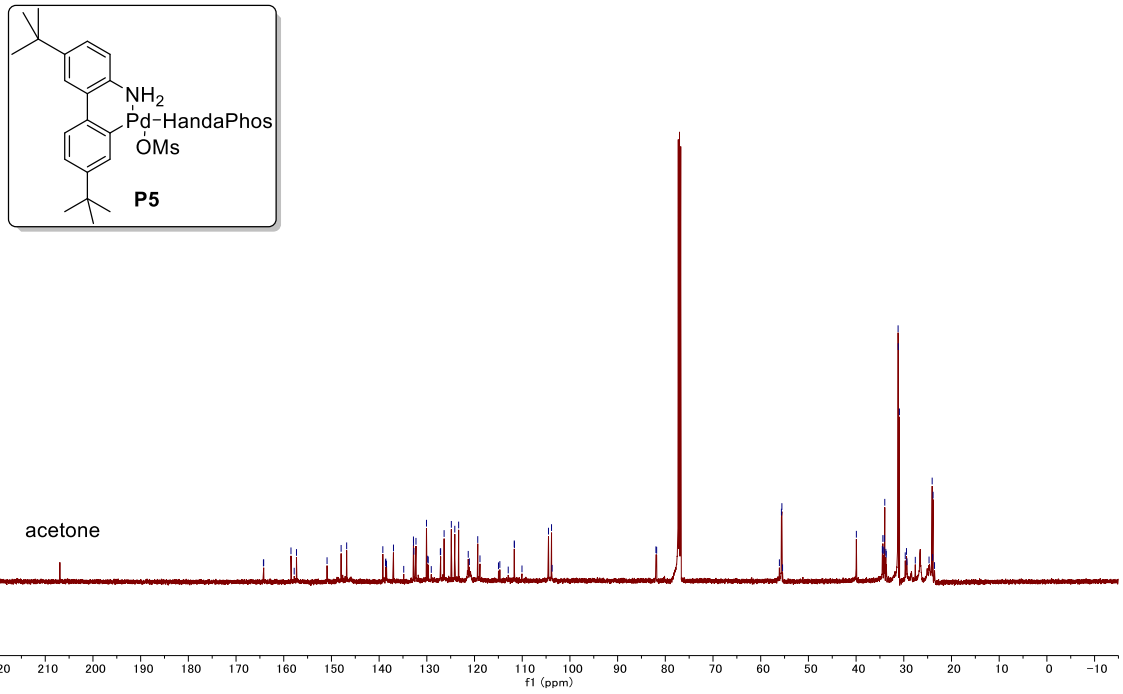
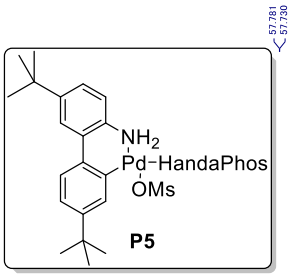
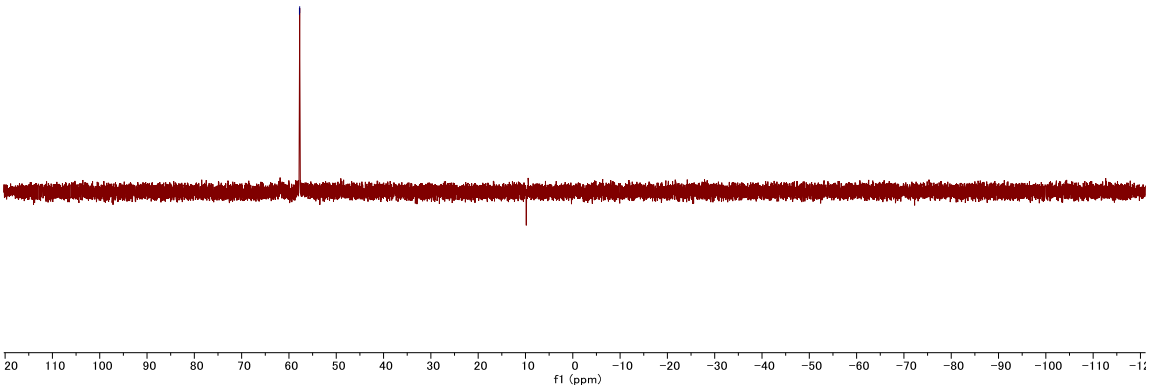
Pd-HandaPhos
OMs
P4
f1 (ppm)

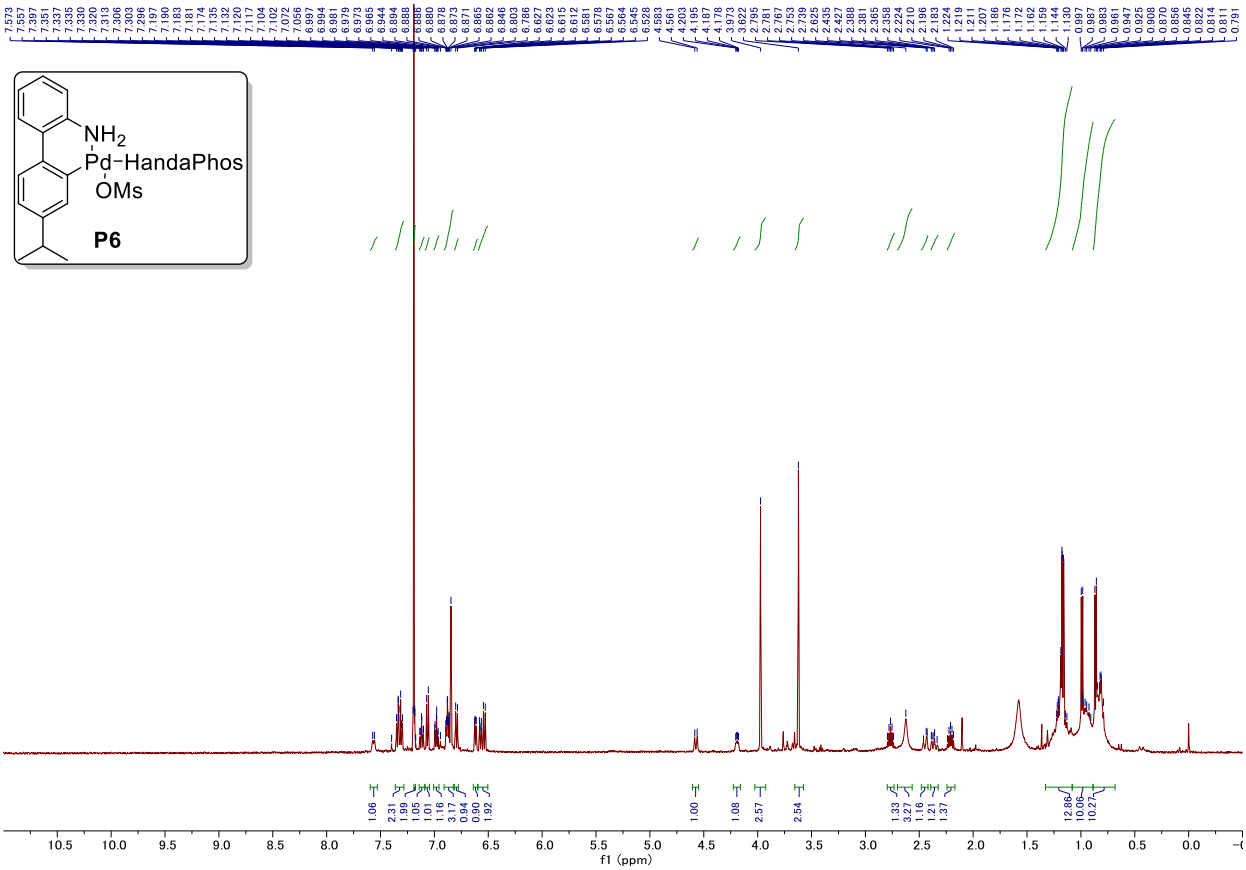

NH2
Pd-HandaPhos
OMs
P5

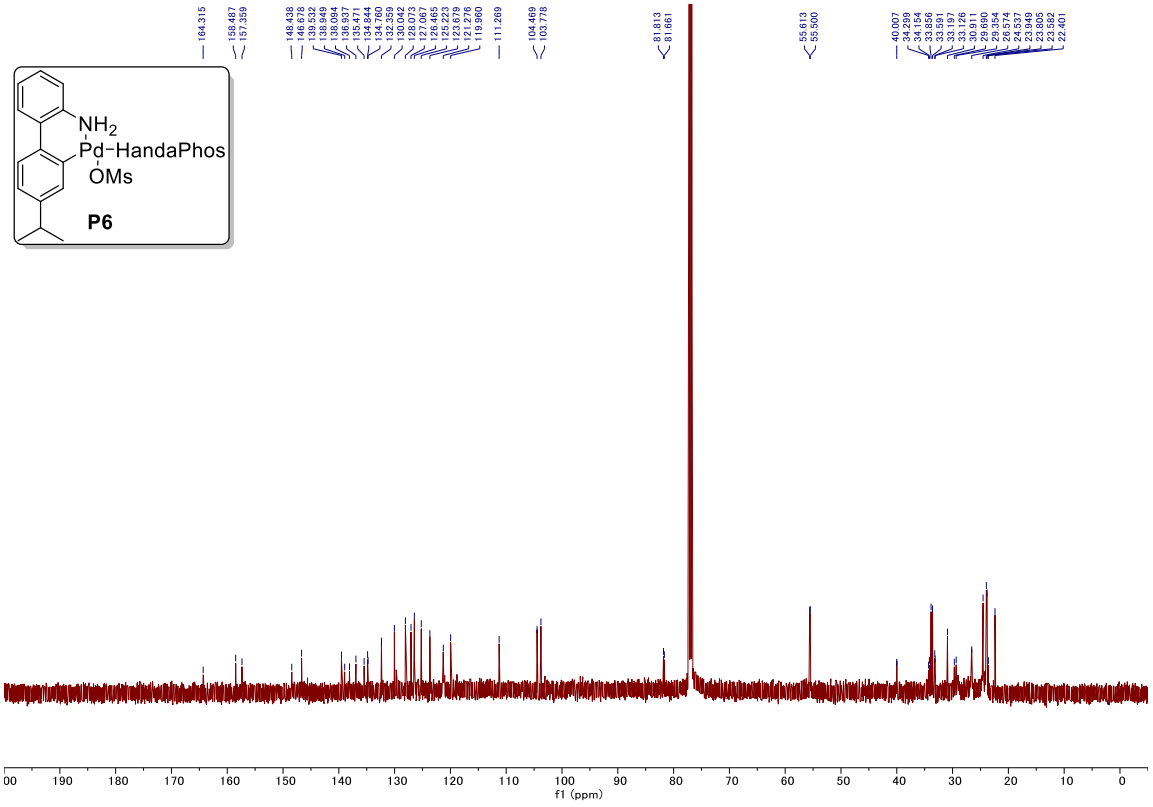

acetone
f1 (ppm)

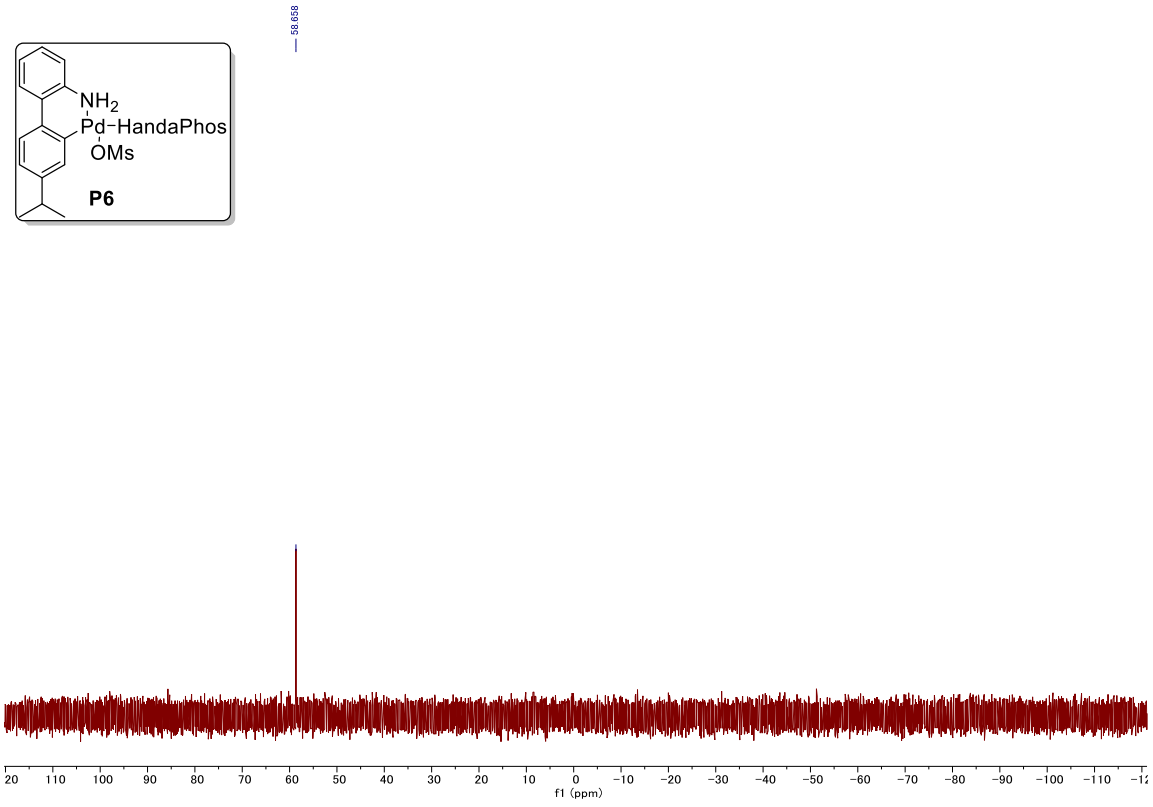

NH2
Pd-HandaPhos
OMs
P5
acetone
f1 (ppm)

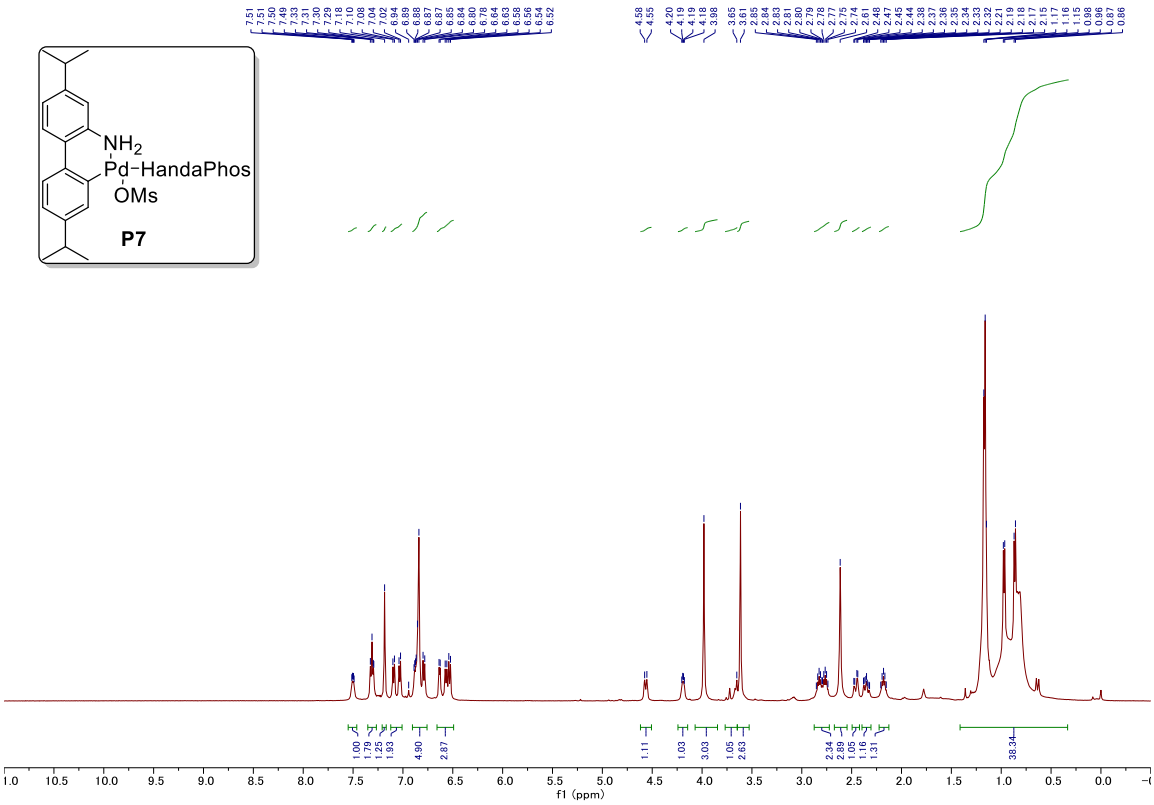

NH2
Pd-HandaPhos
OMs
P5

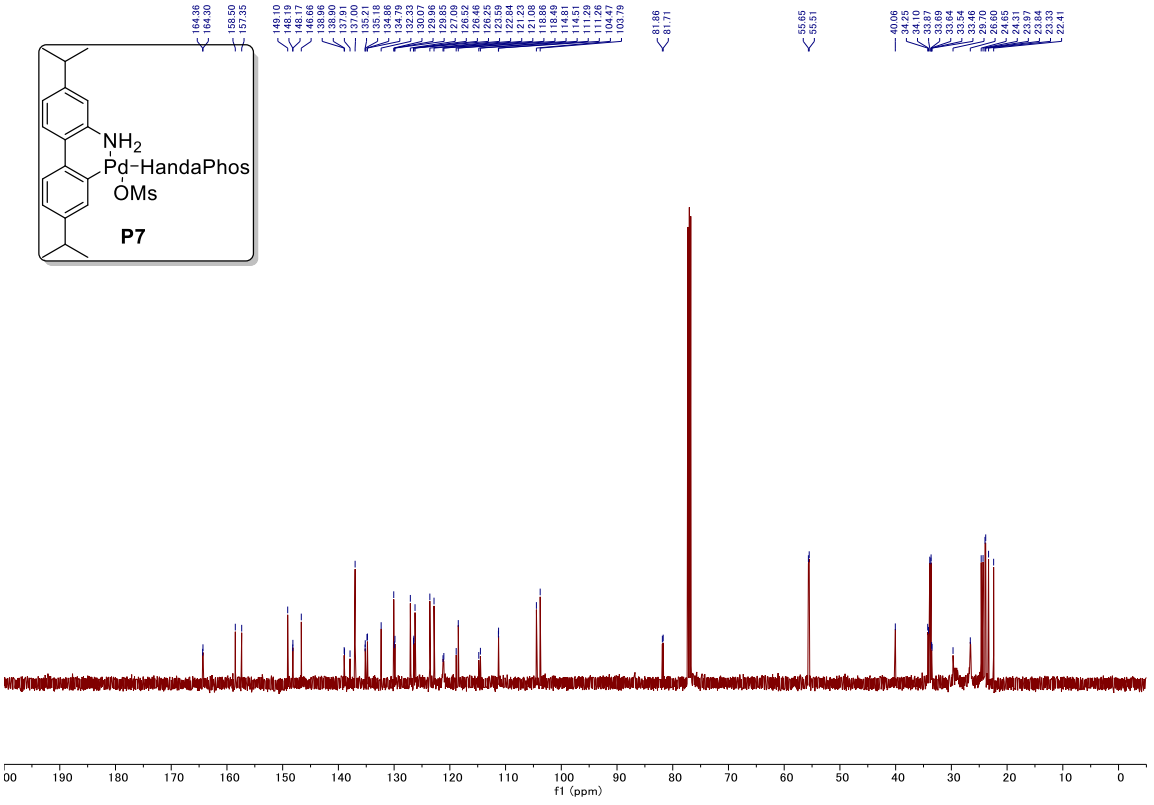

f1 (ppm)

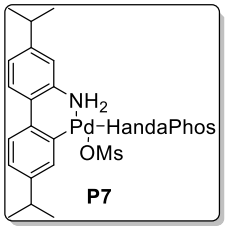

NH2
Pd-HandaPhos
OMs
P6
f1 (ppm)


NH2
Pd-HandaPhos
OMs
P6
f1 (ppm)

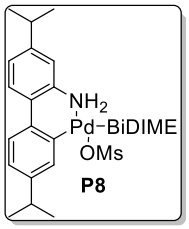

NH2
Pd-HandaPhos
OMs
P6
f1 (ppm)


NH2
Pd-HandaPhos
OMs
P7
f1 (ppm)

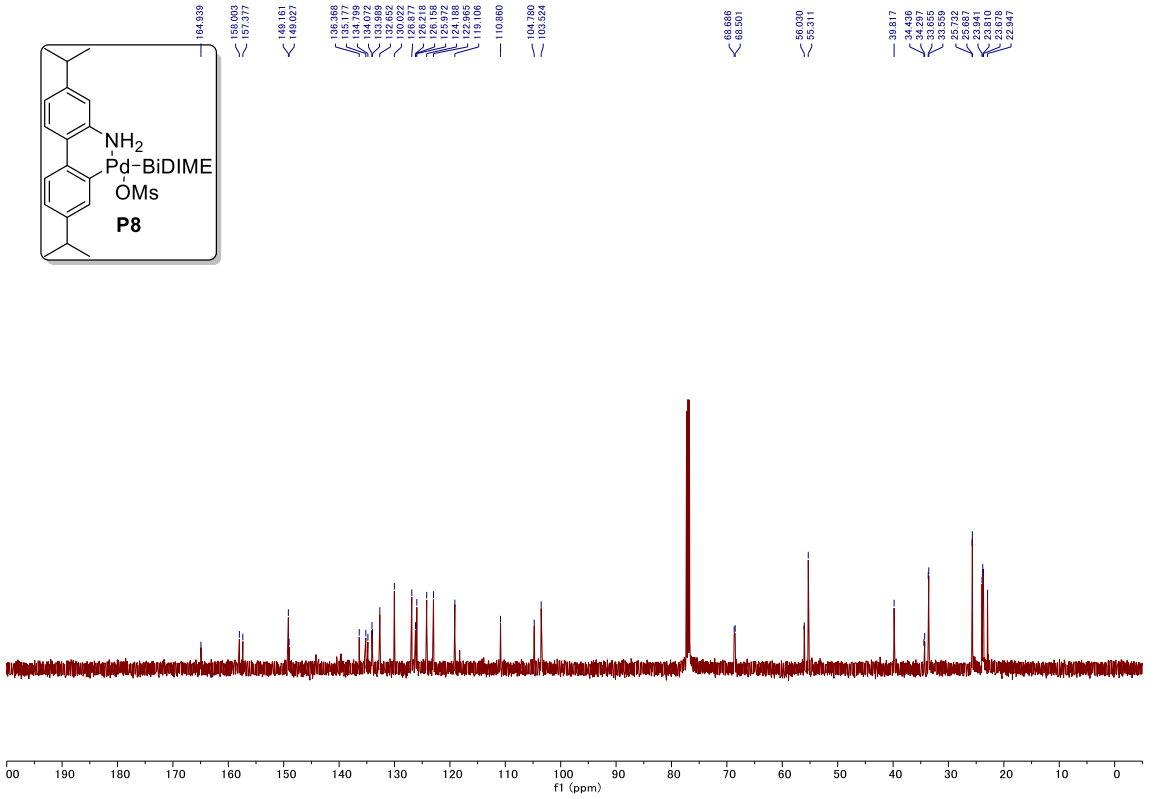

NH2
Pd-HandaPhos
OMs
P7
f1 (ppm)

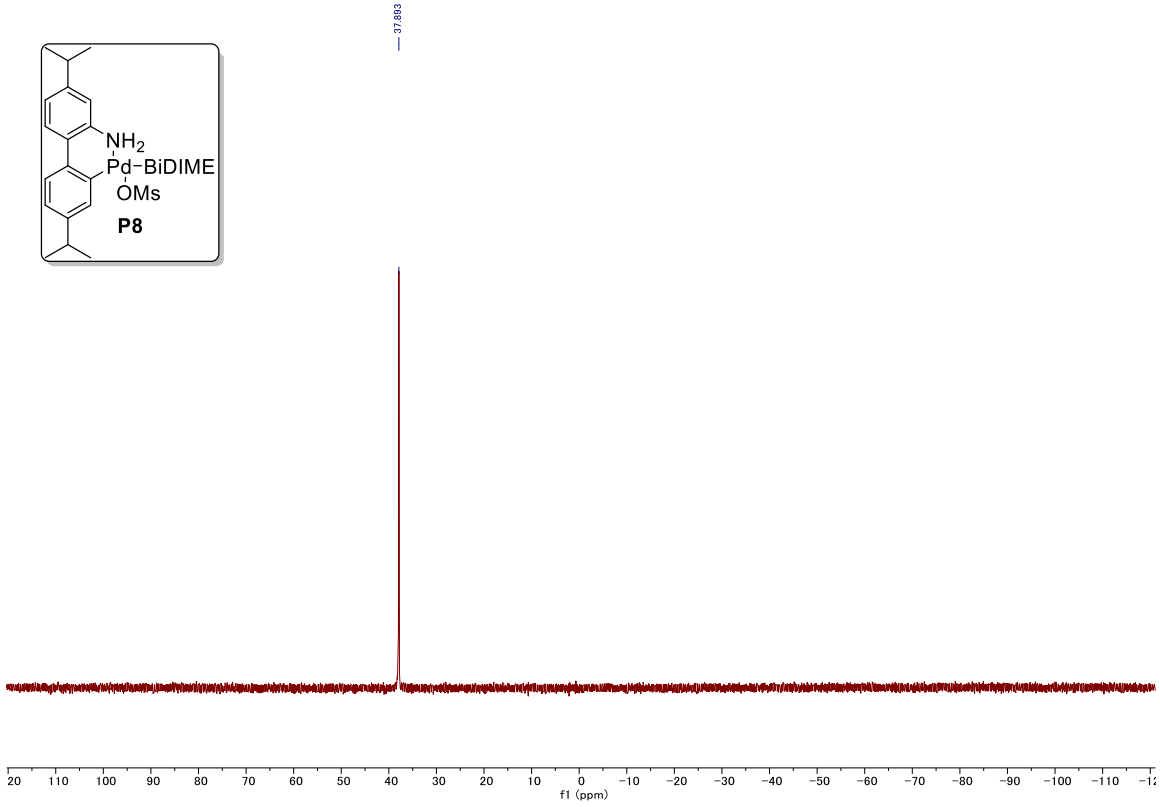

NH2
Pd-HandaPhos
OMs
P7

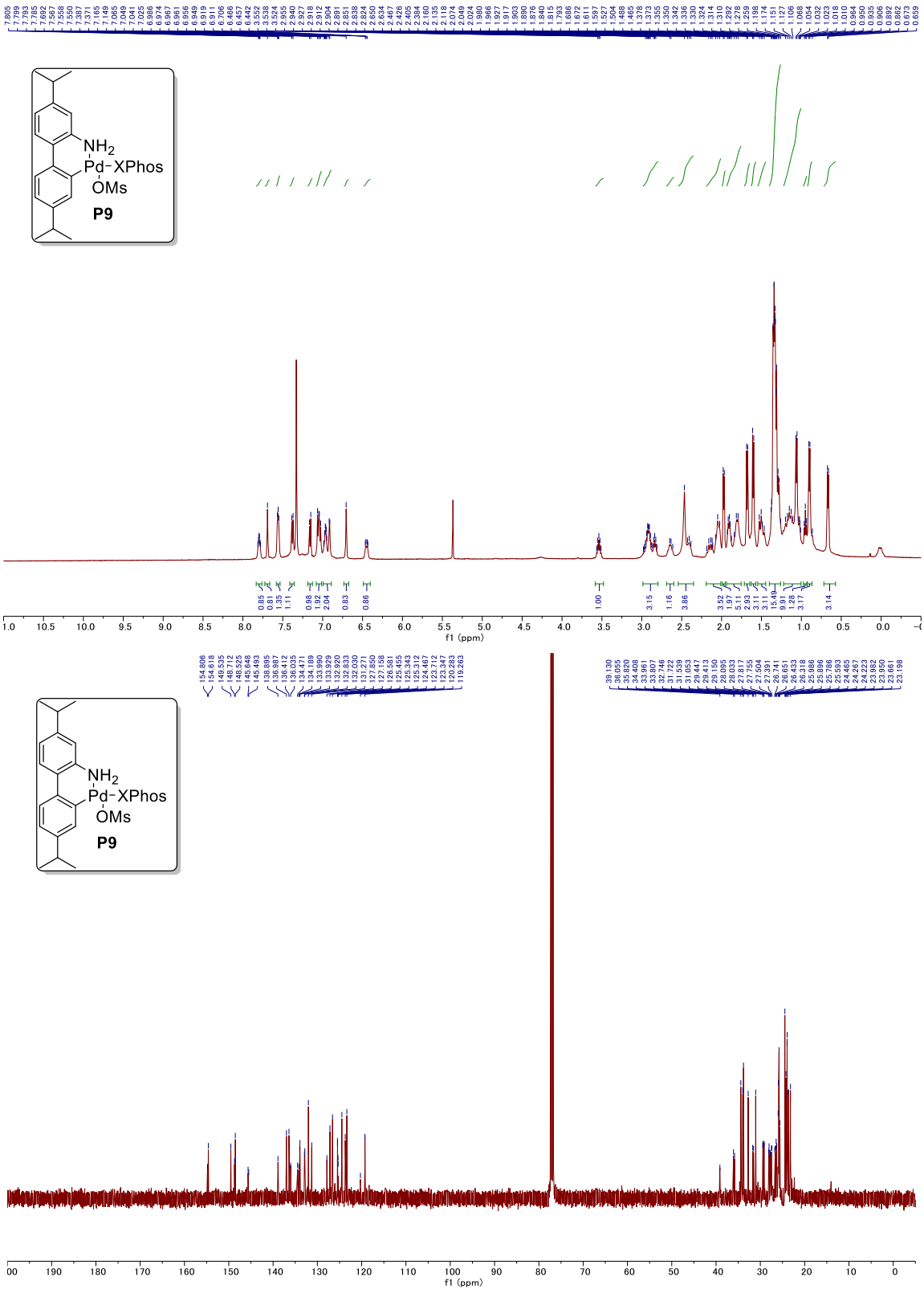
59.060
f1 (ppm)

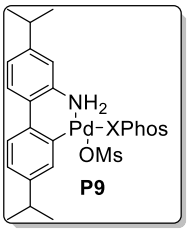

NH2
Pd-BiDIME
OMs
P8

7.526
7.511
7.487
7.471
7.445
7.425
7.420
7.409
7.403
7.392
7.386
7.345
7.274
7.237
7.232
7.219
7.088
7.073
6.990
6.974
6.965
6.957
6.935
6.918
6.901
6.825
6.811
6.622
6.605
4.369
4.344
4.258
4.002
3.708
2.960
2.946
2.931
2.596
2.498
2.484
2.469
1.298
1.294
1.285
1.280
1.274
1.268
0.989
0.984
0.974
0.969
0.959
0.951
0.915
0.910
0.902
0.884
0.878
0.871
2.29
2.24
1.04
1.02
3.07
1.83
0.91
0.95
0.83
2.70
3.28
0.94
3.00
0.97
6.62
6.27
9.25
f1 (ppm)

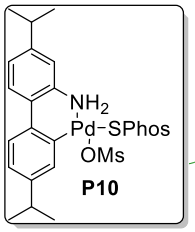

164.939
158.003
157.377
149.161
149.027
136.368
135.177
134.799
134.072
133.989
132.652
130.022
128.677
126.218
126.158
125.972
124.488
122.955
119.106
110.860
104.780
103.524
68.686
68.501
56.030
55.311
39.817
34.436
34.297
33.655
33.558
25.732
25.687
23.941
23.810
23.678
22.947
NH2
Pd-BiDIME
OMs
P8
f1 (ppm)


37.893
NH2
Pd-BiDIME
OMs
P8
f1 (ppm)

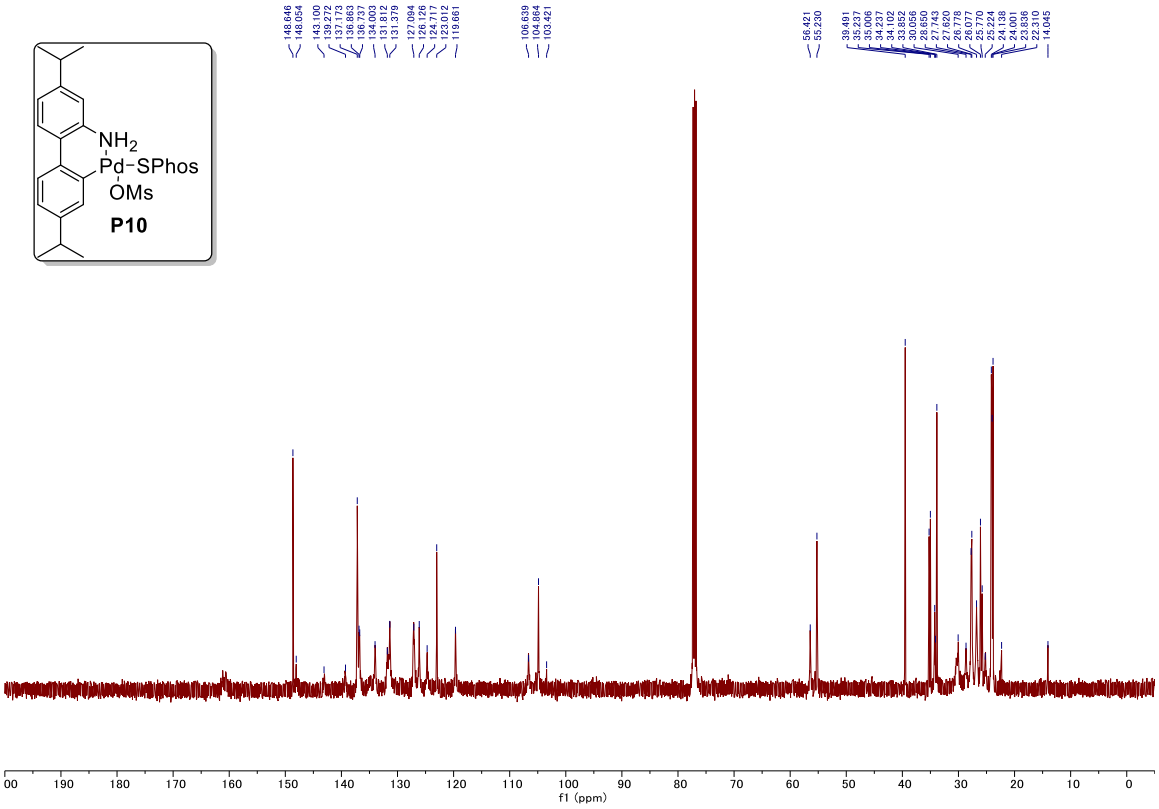

NH2
Pd-XPhos
OMs
P9
f1 (ppm)
NH2
Pd-XPhos
OMs
P9
f1 (ppm)

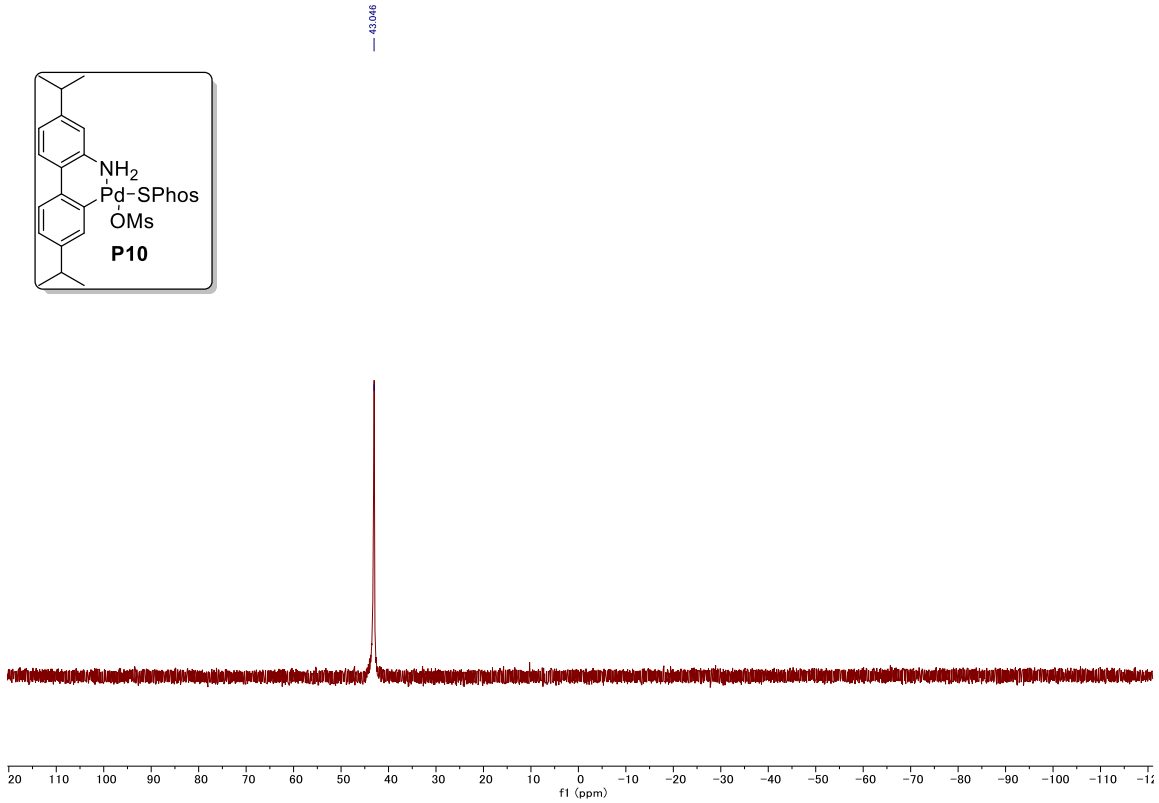

NH2
Pd-XPhos
OMs
P9

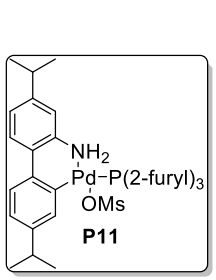
35.396
f1 (ppm)


NH2
Pd-SPhos
OMs
P10

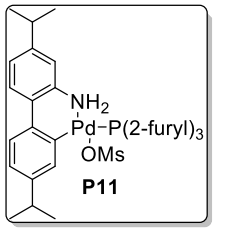
f1 (ppm)


148.646
148.054
143.100
139.272
137.773
136.863
136.737
134.003
131.812
131.379
127.094
124.195
124.117
123.012
119.661
106.639
104.864
103.421
56.421
55.230
39.491
35.237
35.006
34.237
34.102
33.852
30.656
30.650
27.743
27.620
26.778
26.077
25.770
25.224
24.138
24.001
23.936
23.310
14.045
NH2
Pd-SPhos
OMs
P10
f1 (ppm)

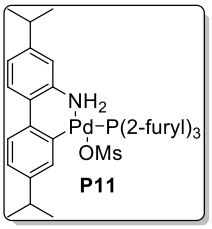

43.046
NH2
Pd-SPhos
OMs
P10
f1 (ppm)


NH2
Pd–P(2-furyl)3
OMs
P11

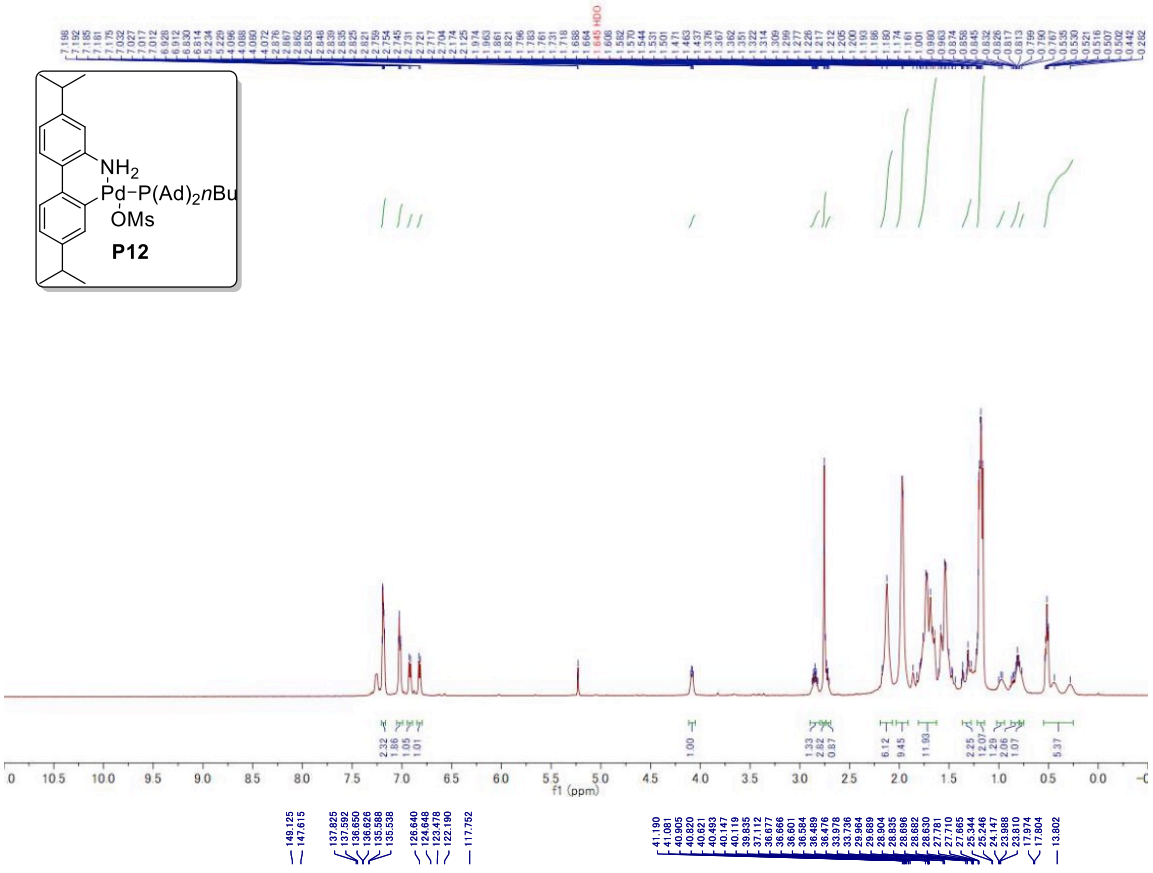
f1 (ppm)

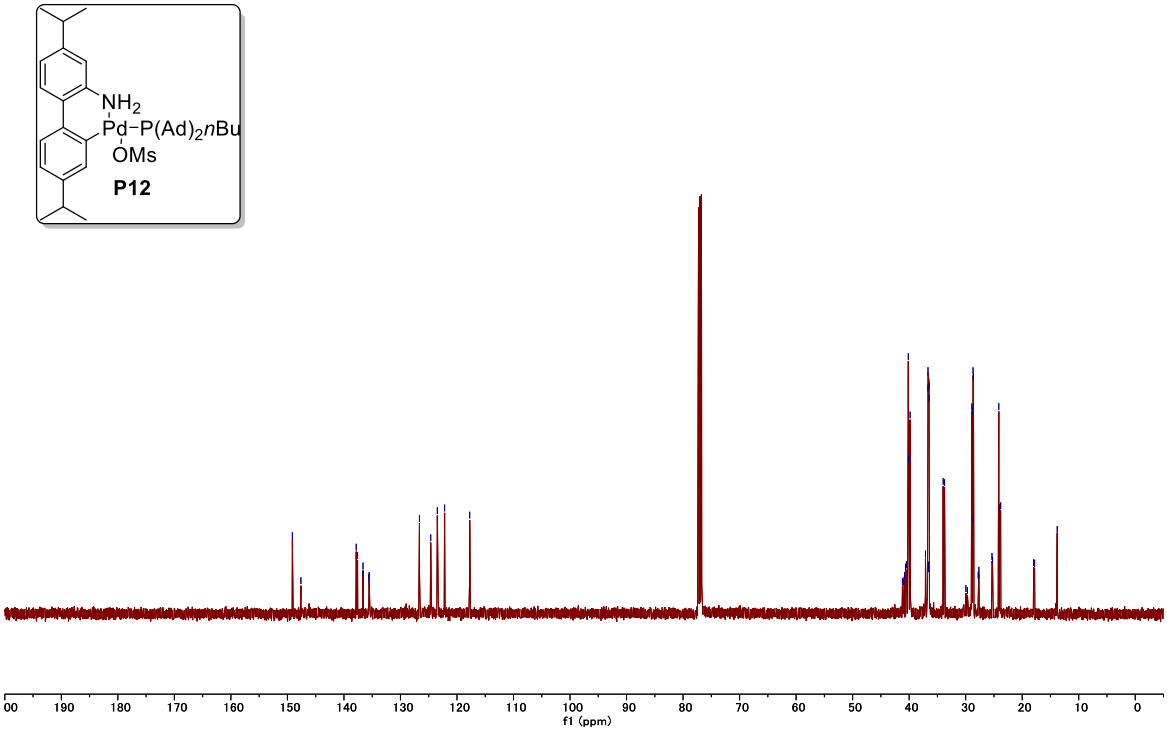

NH2
Pd–P(2-furyl)3
OMs
P11

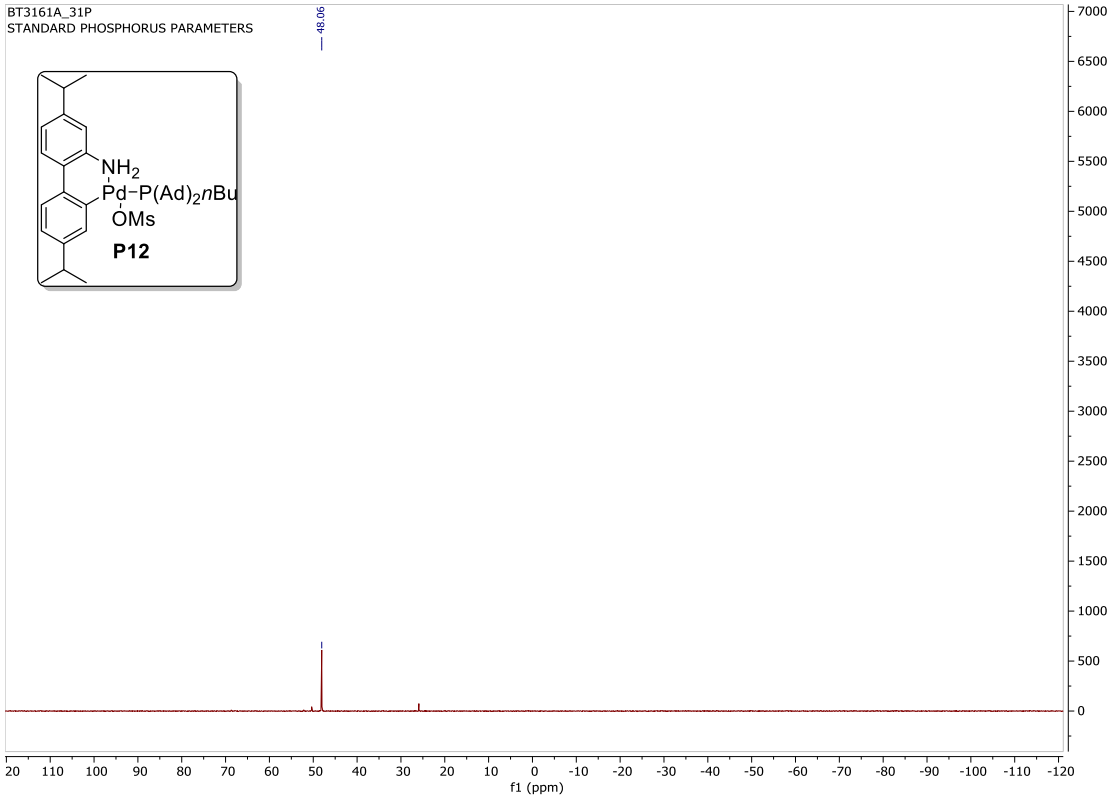
f1 (ppm)

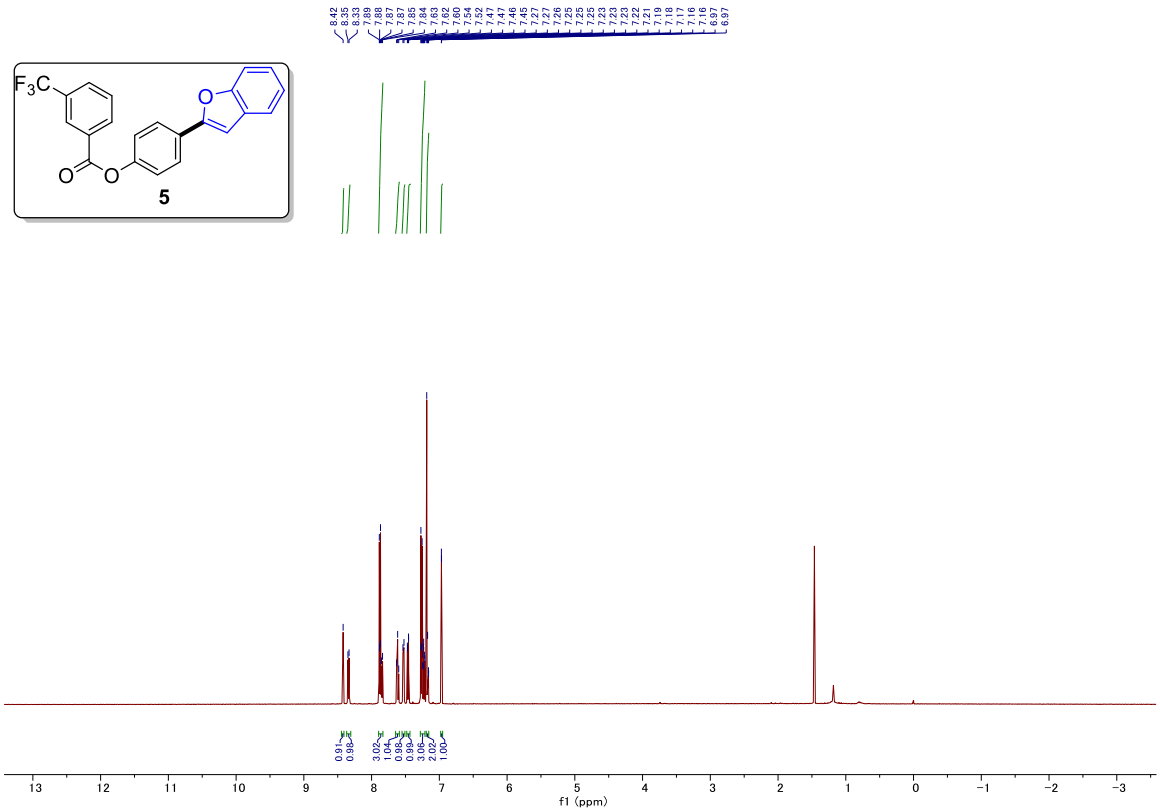

NH2
Pd–P(2-furyl)3
OMs
P11

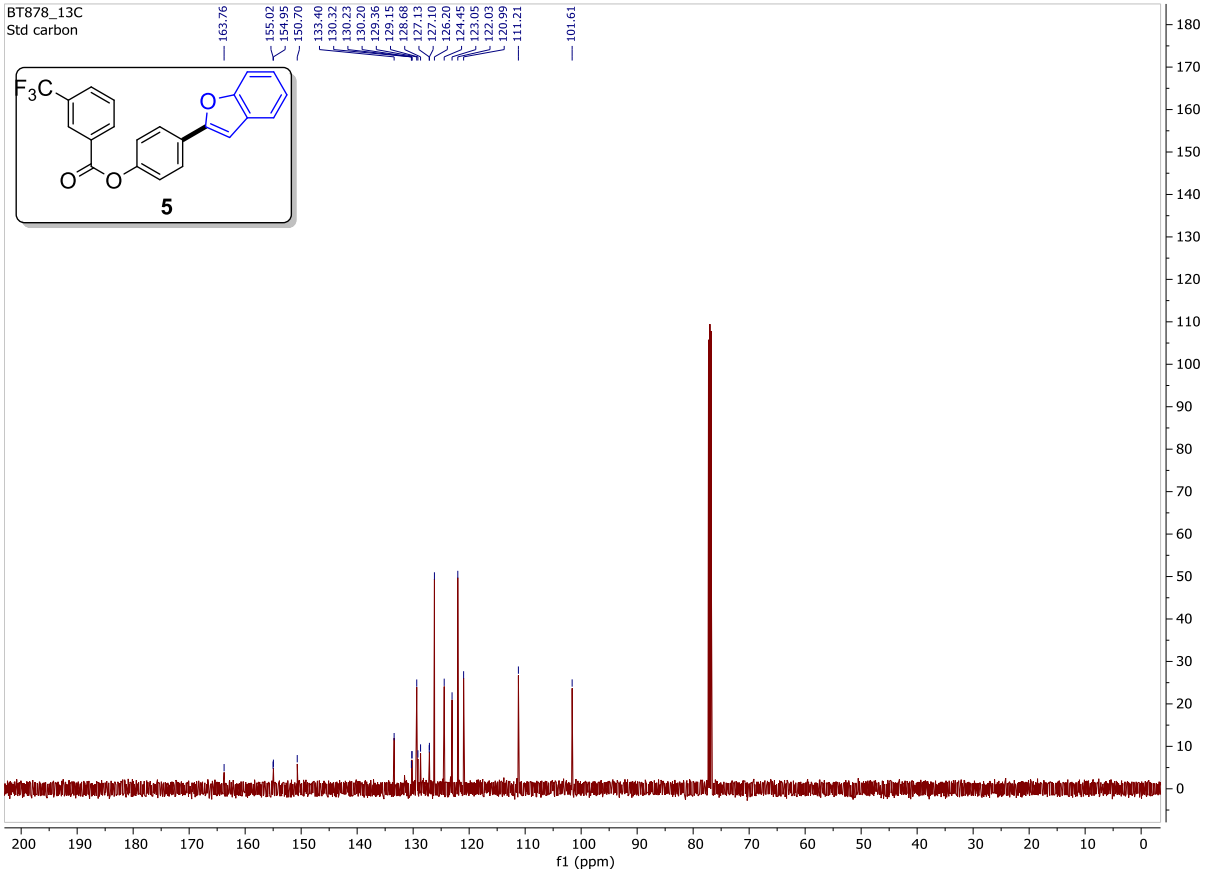
-22.504
20 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110
f1 (ppm)

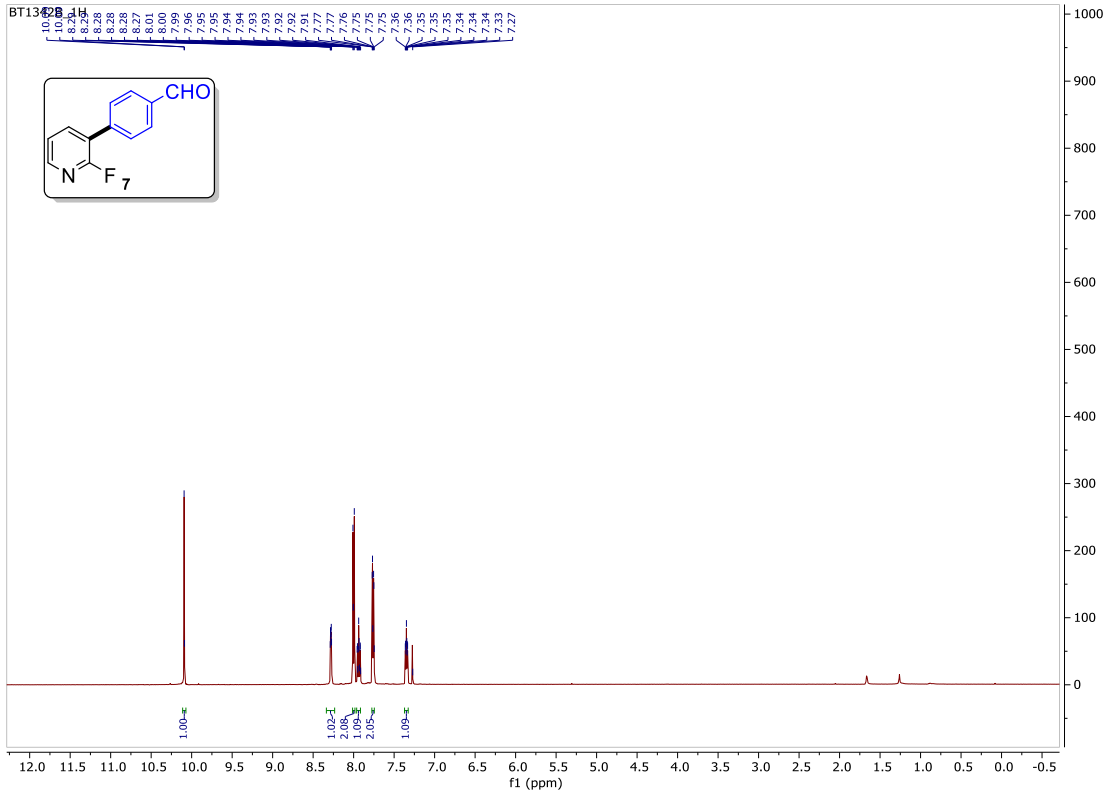

NH2
Pd–P(Ad)2nBu
OMs
P12
f1 (ppm)

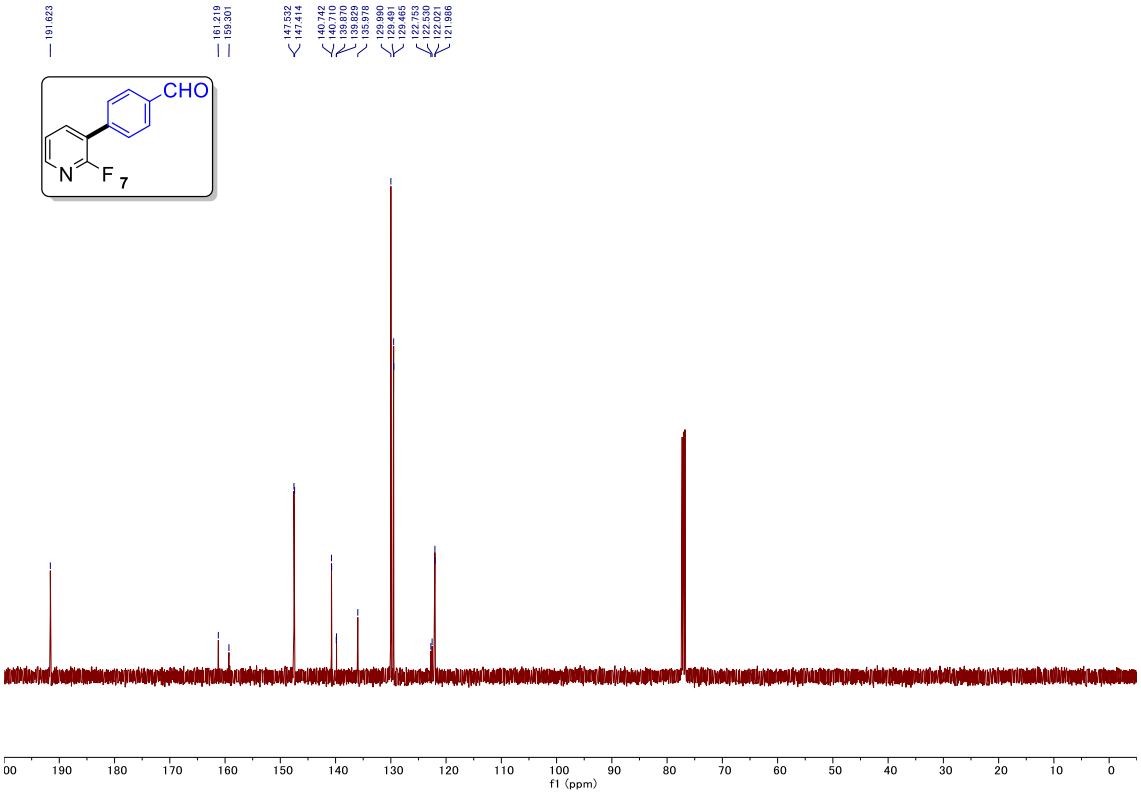

NH2
Pd–P(Ad)2nBu
OMs
P12
f1 (ppm)

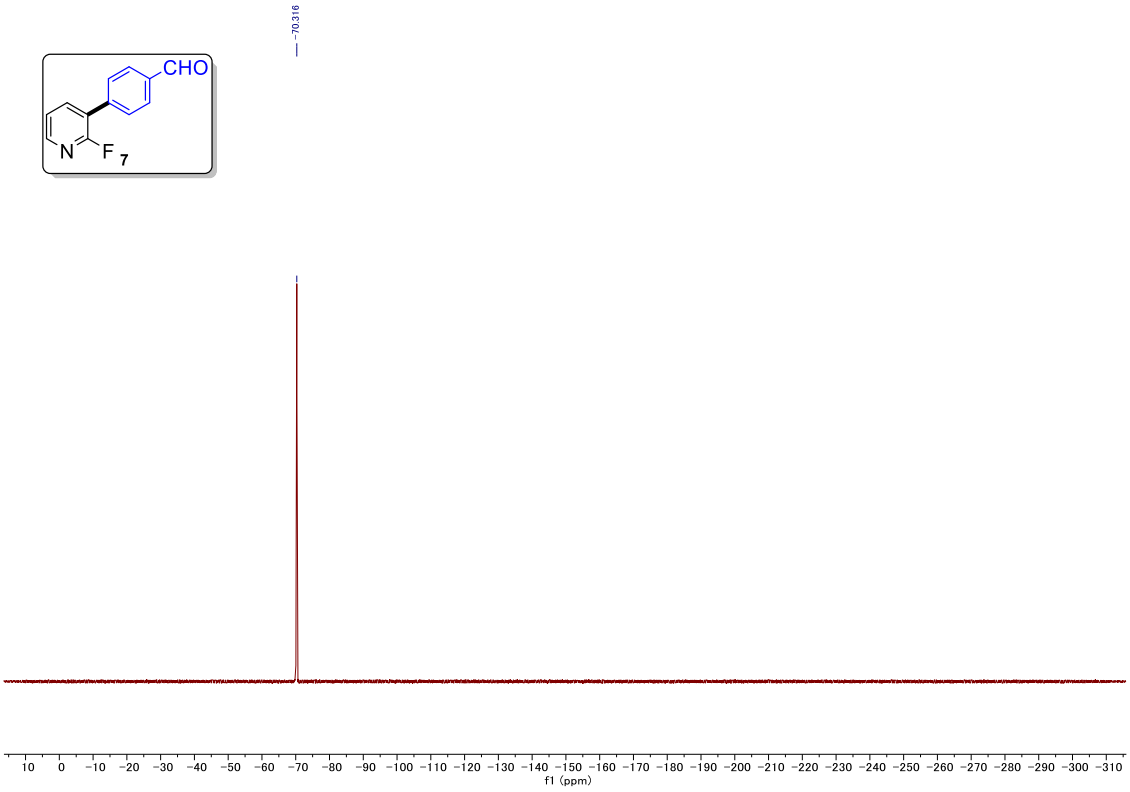

BT3161A_31P
STANDARD PHOSPHORUS PARAMETERS
48.06
NH2
Pd–P(Ad)2nBu
OMs
P12
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
20 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120
f1 (ppm)

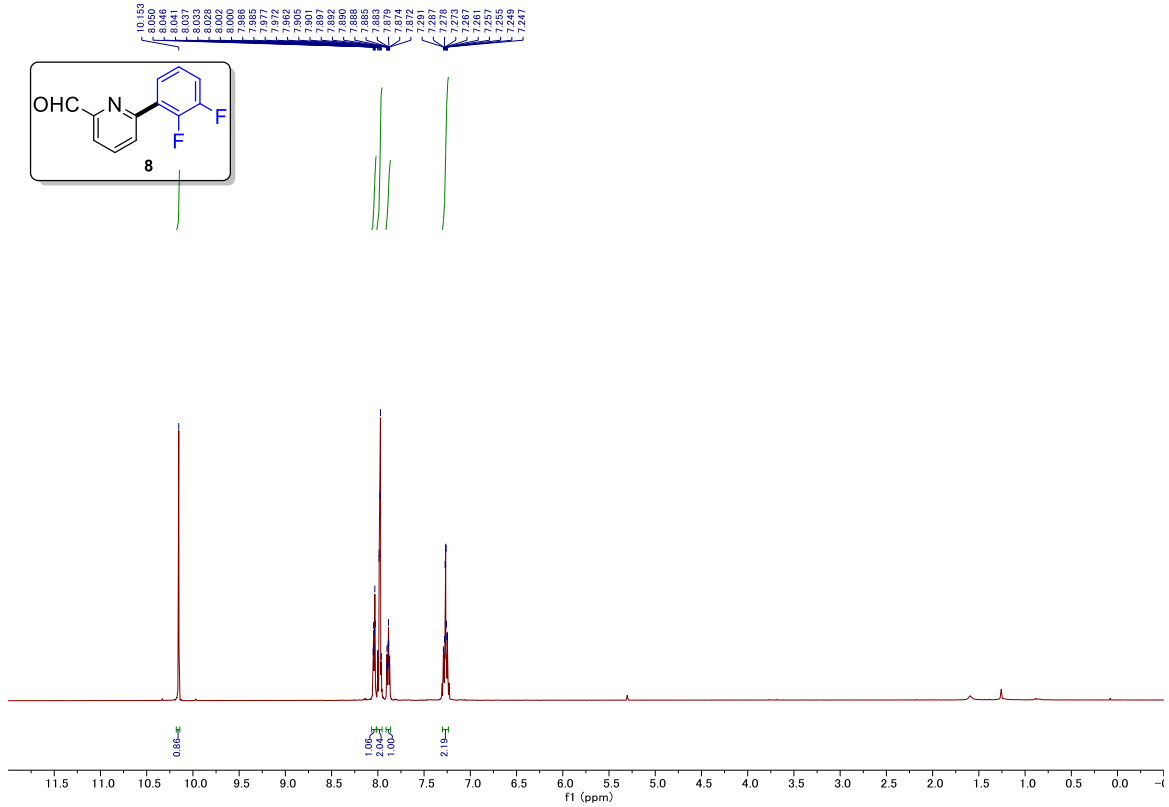

F3C
O
O
O
5
f1 (ppm)

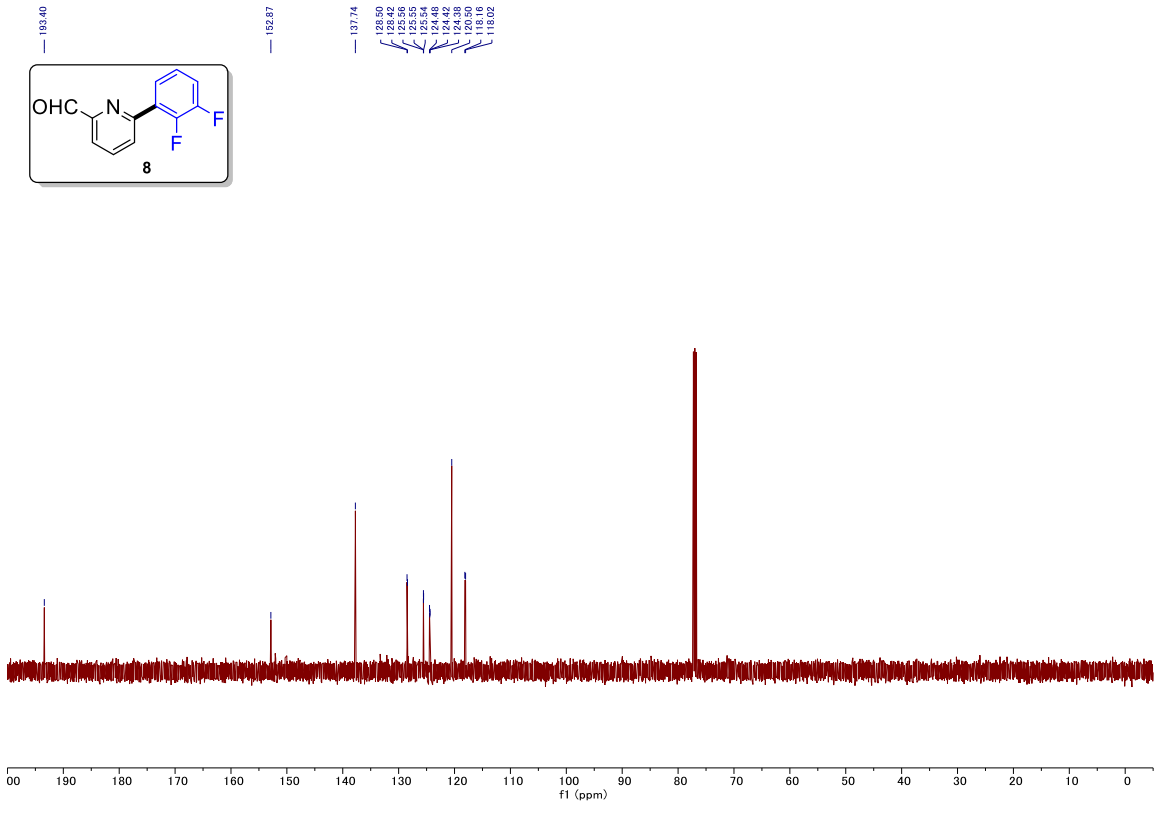

BT878_13C
Std carbon
F3C
O
O
O
5
f1 (ppm)

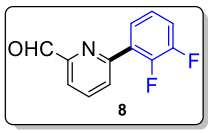

BT1328_1H
CHO
F 7
1.00
1.02
2.08
1.09
2.05
1.09
f1 (ppm)


191.623
161.219
159.301
147.532
147.414
140.742
140.710
139.870
139.838
135.978
129.980
129.491
129.465
122.753
122.650
122.021
121.986
CHO
F 7
f1 (ppm)


-70.316
CHO
N
F
7
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270 -280 -290 -300 -310
f1 (ppm)

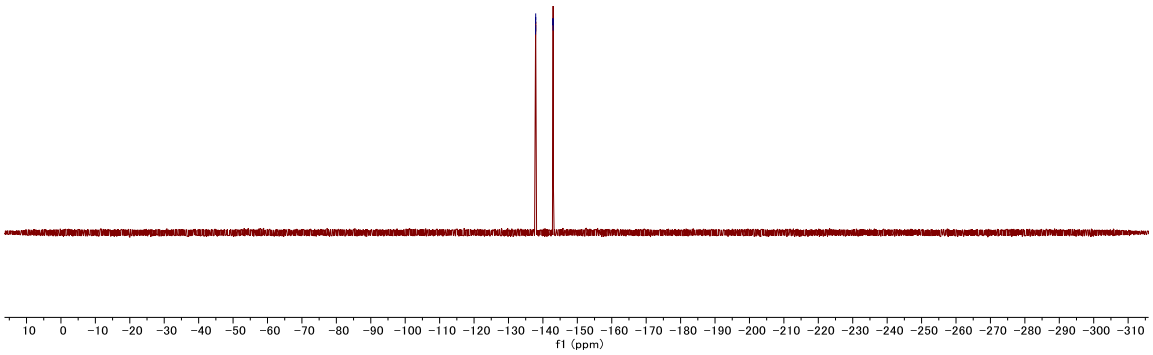

10.153
8.050
8.046
8.041
8.037
8.033
8.028
8.002
8.000
7.986
7.985
7.977
7.972
7.969
7.905
7.901
7.897
7.892
7.890
7.888
7.885
7.883
7.879
7.874
7.872
7.291
7.287
7.278
7.273
7.267
7.261
7.257
7.255
7.249
7.247
OHC
N
F
F
8
0.86
1.06
2.04
1.00
2.19
f1 (ppm)

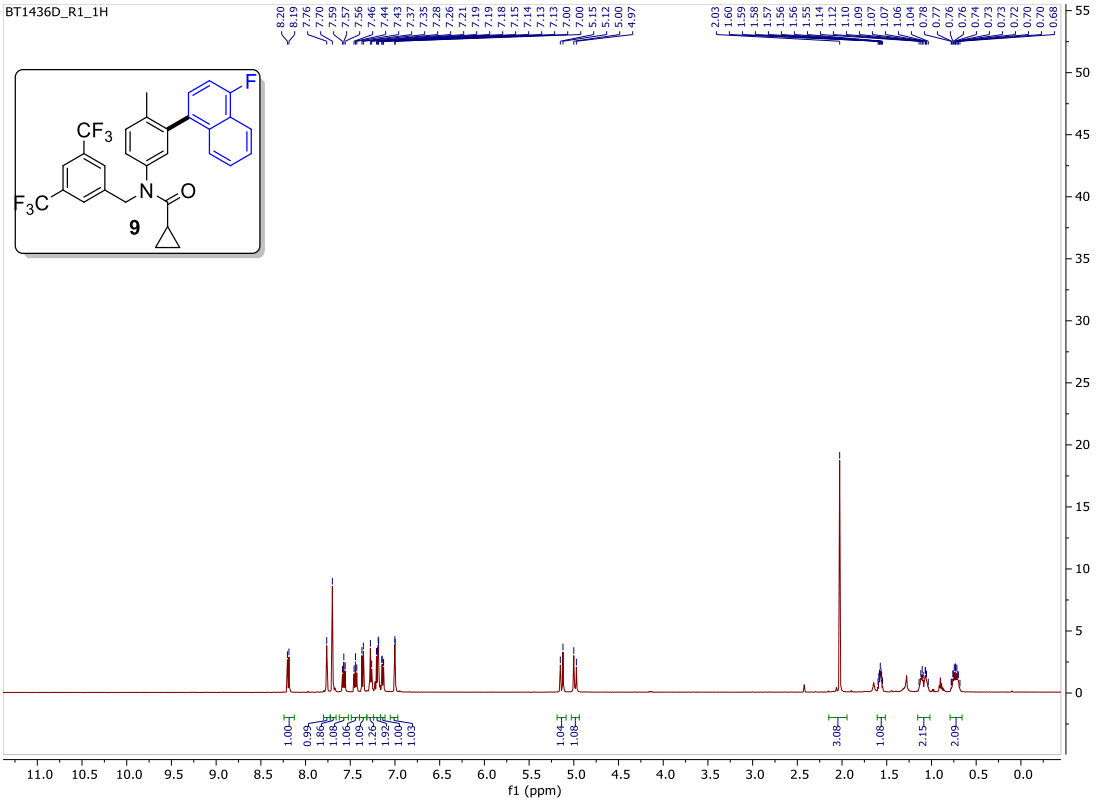

193.40
152.87
137.74
128.50
128.42
125.56
125.55
125.54
124.44
124.42
124.38
120.50
118.16
118.02
OHC
N
F
F
8
f1 (ppm)

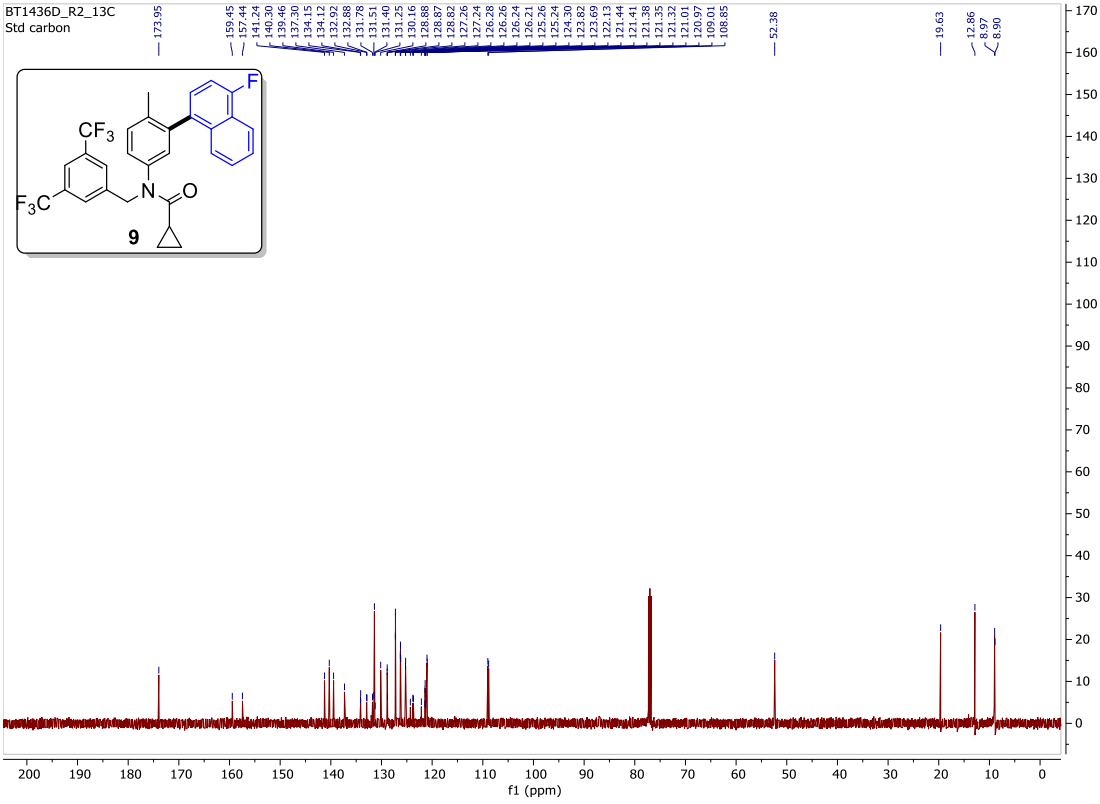

OHC
N
F
F

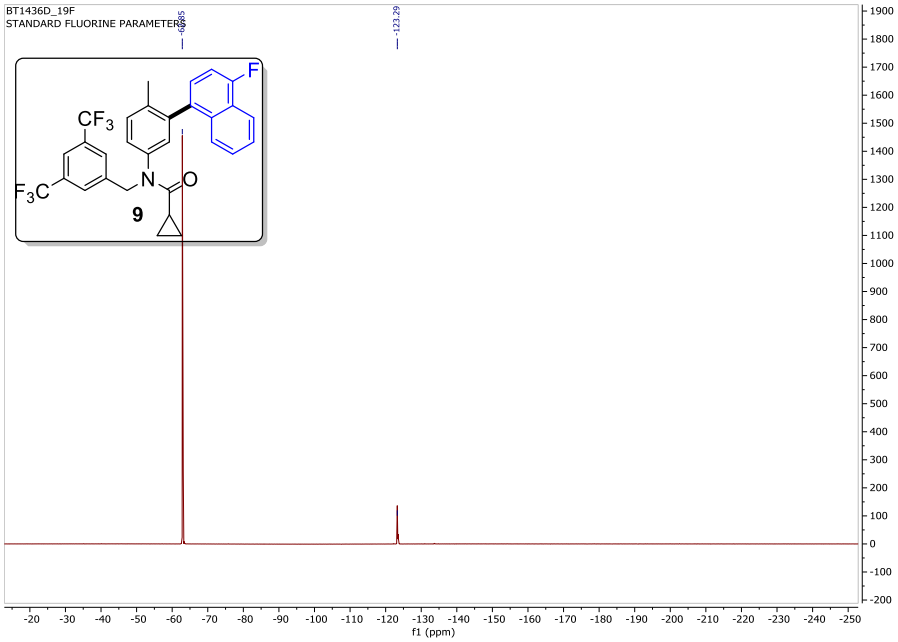
8

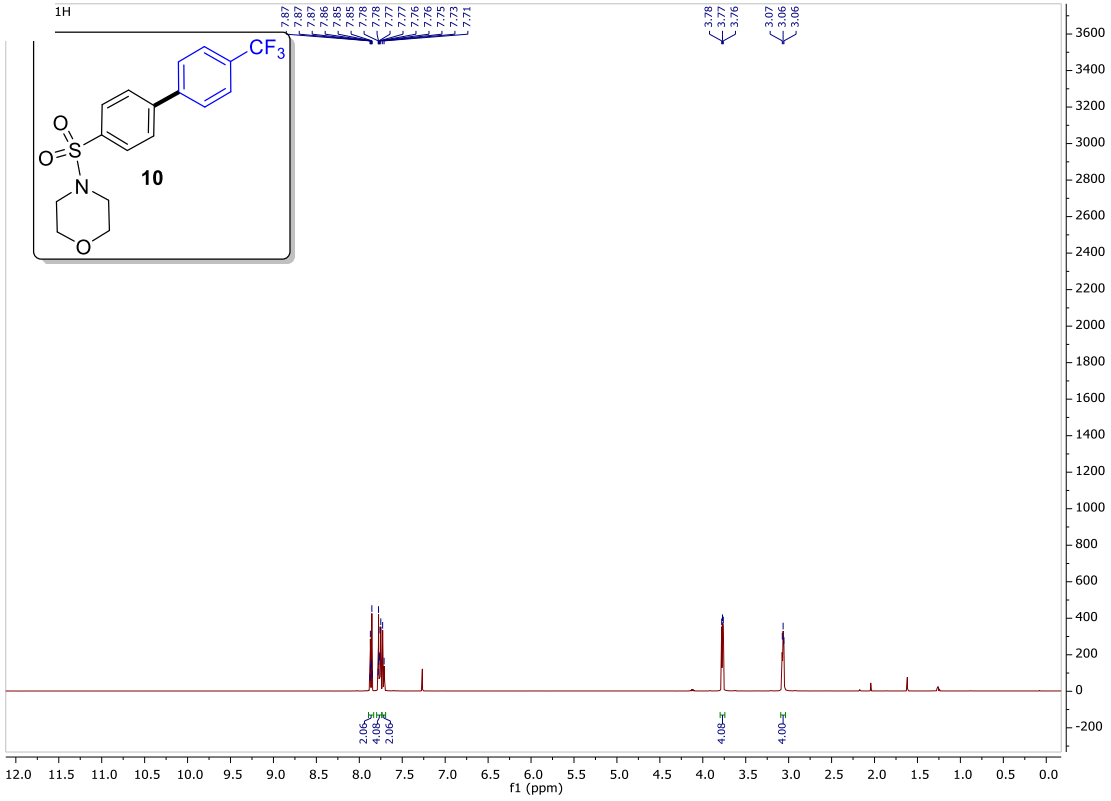

-137.861
-137.878
-137.891
-137.905
-137.917
-142.918
-142.919
-142.957
-142.976

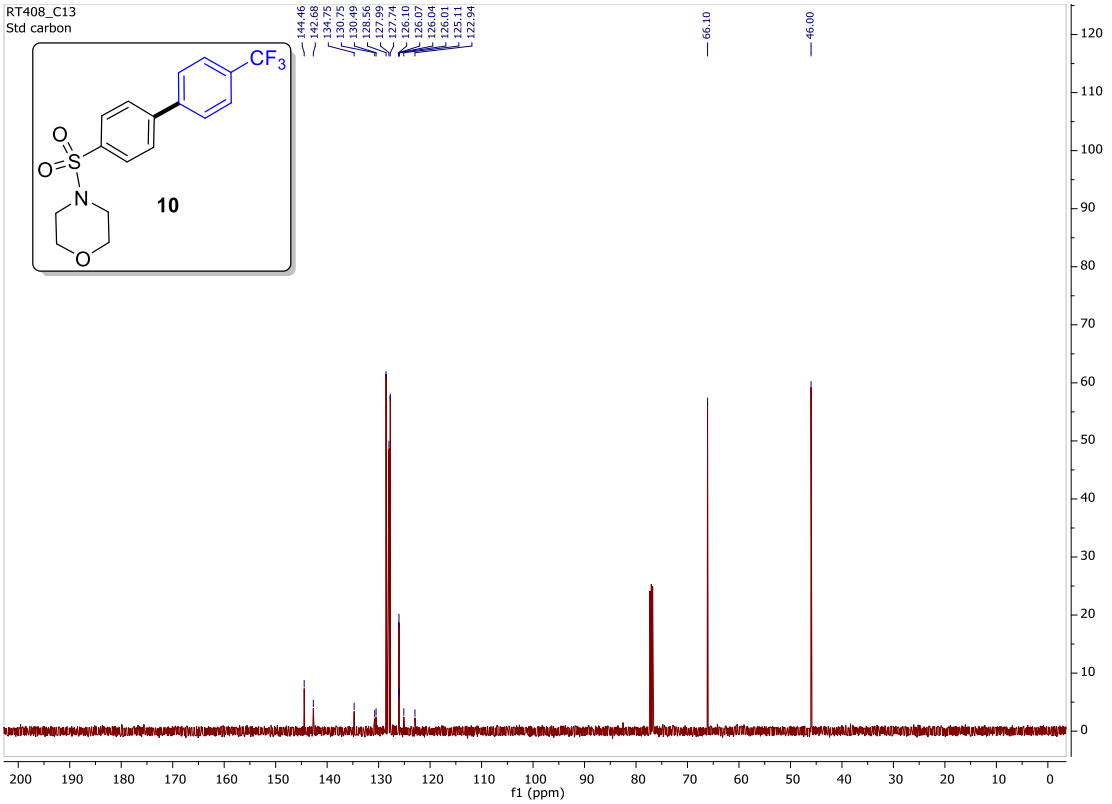

10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −220 −230 −240 −250 −260 −270 −280 −290 −300 −310
f1 (ppm)

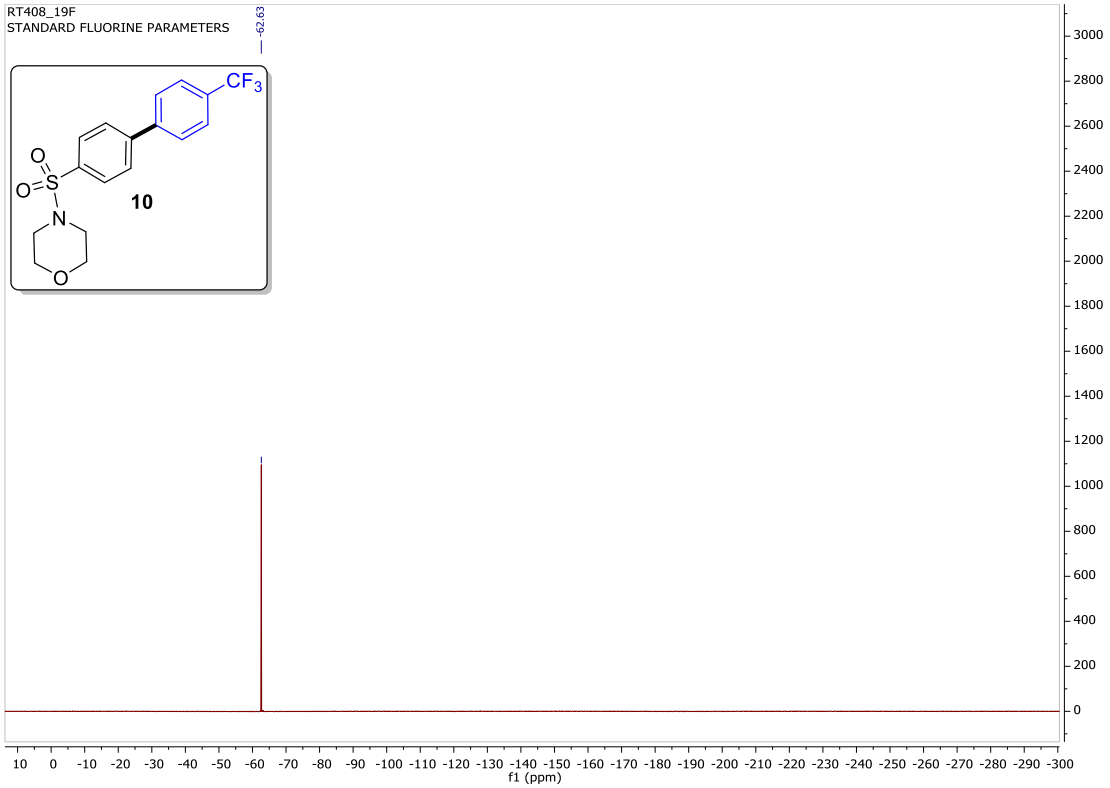

BT1436D_R1_1H
F
CF3
F3C
N
O
9
f1 (ppm)

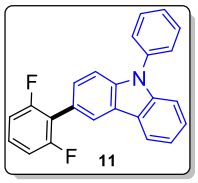

BT1436D_R2_13C
Std carbon
F
CF3
F3C
N
O
9
f1 (ppm)

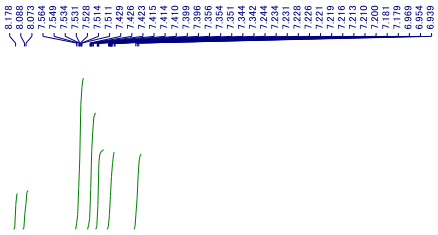

BT1436D_19F
STANDARD FLUORINE PARAMETERS
-60.95
-123.29
F
CF3
F3C
N
O
9
f1 (ppm)


1H
10
f1 (ppm)


RT408_C13
Std carbon
10
f1 (ppm)


RT408_19F
STANDARD FLUORINE PARAMETERS
-62.63
CF3
O
O
S
N
O
10
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270 -280 -290 -300
f1 (ppm)


F
N
F
11


8.178
8.088
8.073
7.564
7.549
7.534
7.531
7.528
7.514
7.511
7.499
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7.423
7.415
7.414
7.410
7.399
7.396
7.356
7.354
7.351
7.344
7.342
7.244
7.234
7.231
7.228
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7.221
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7.216
7.213
7.210
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7.179
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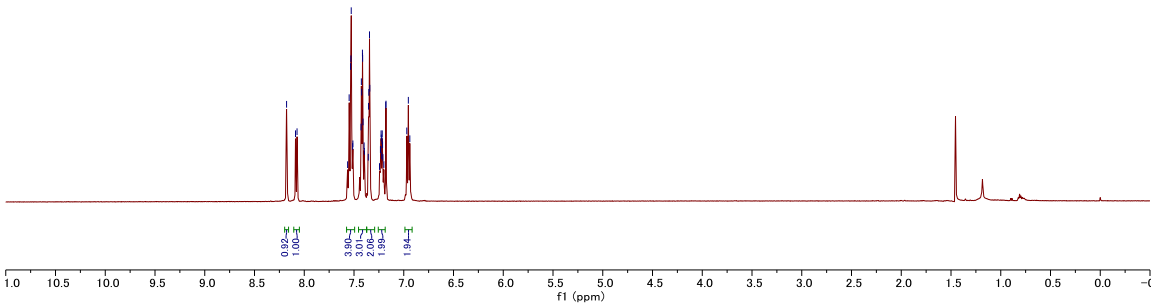
6.954
6.939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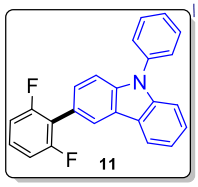
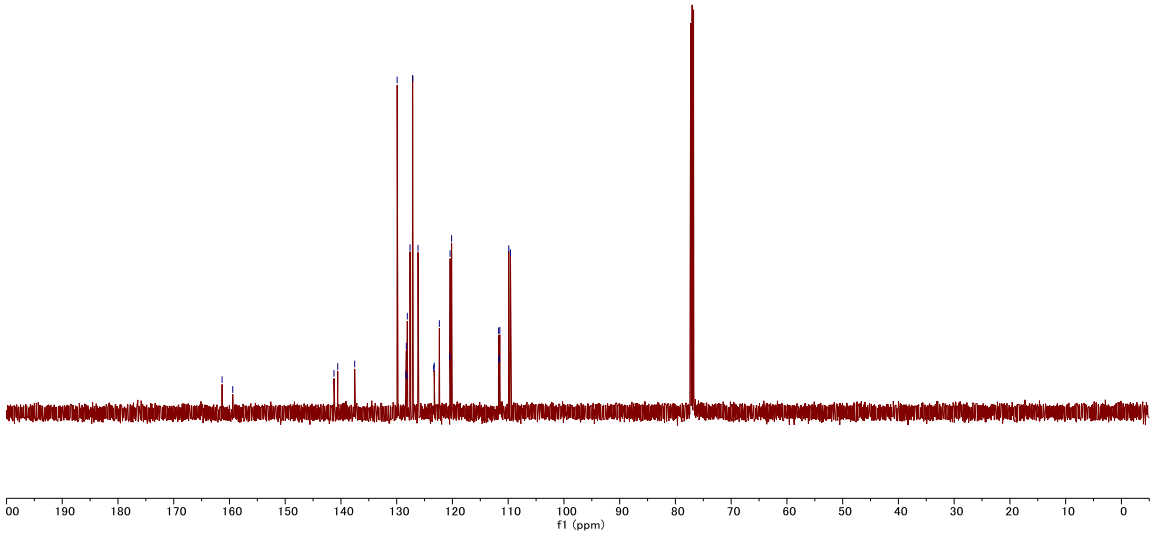
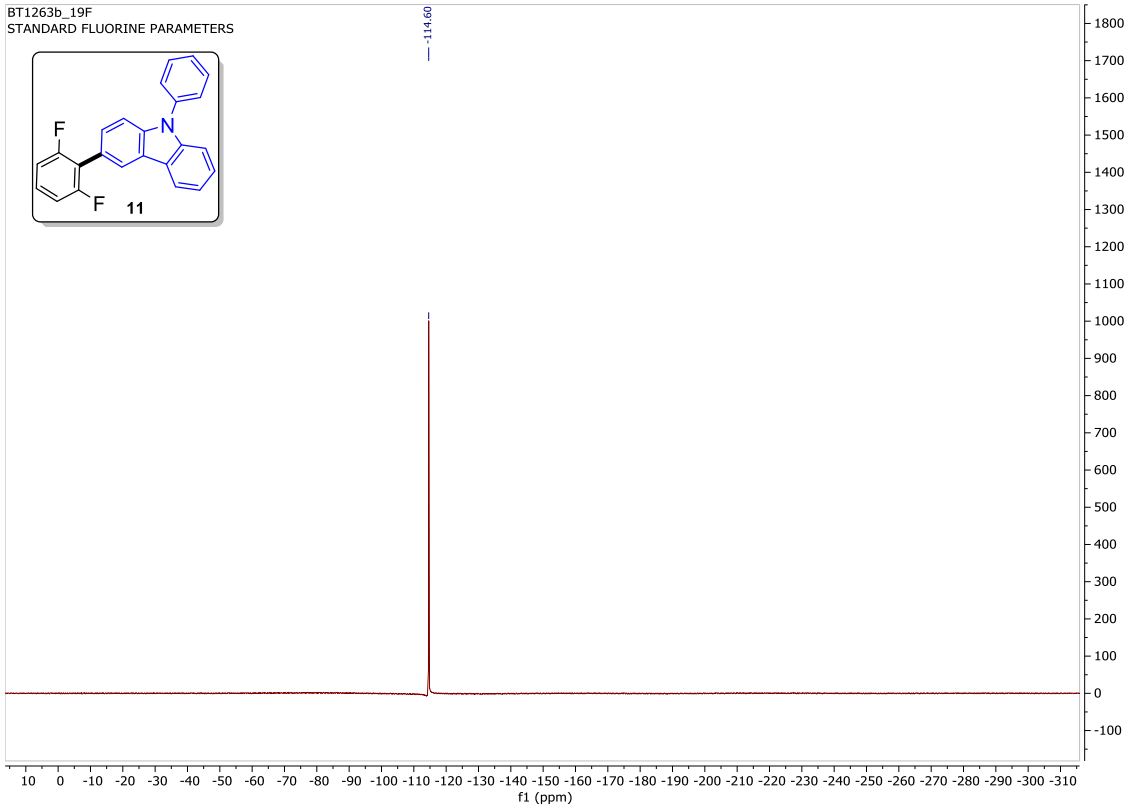
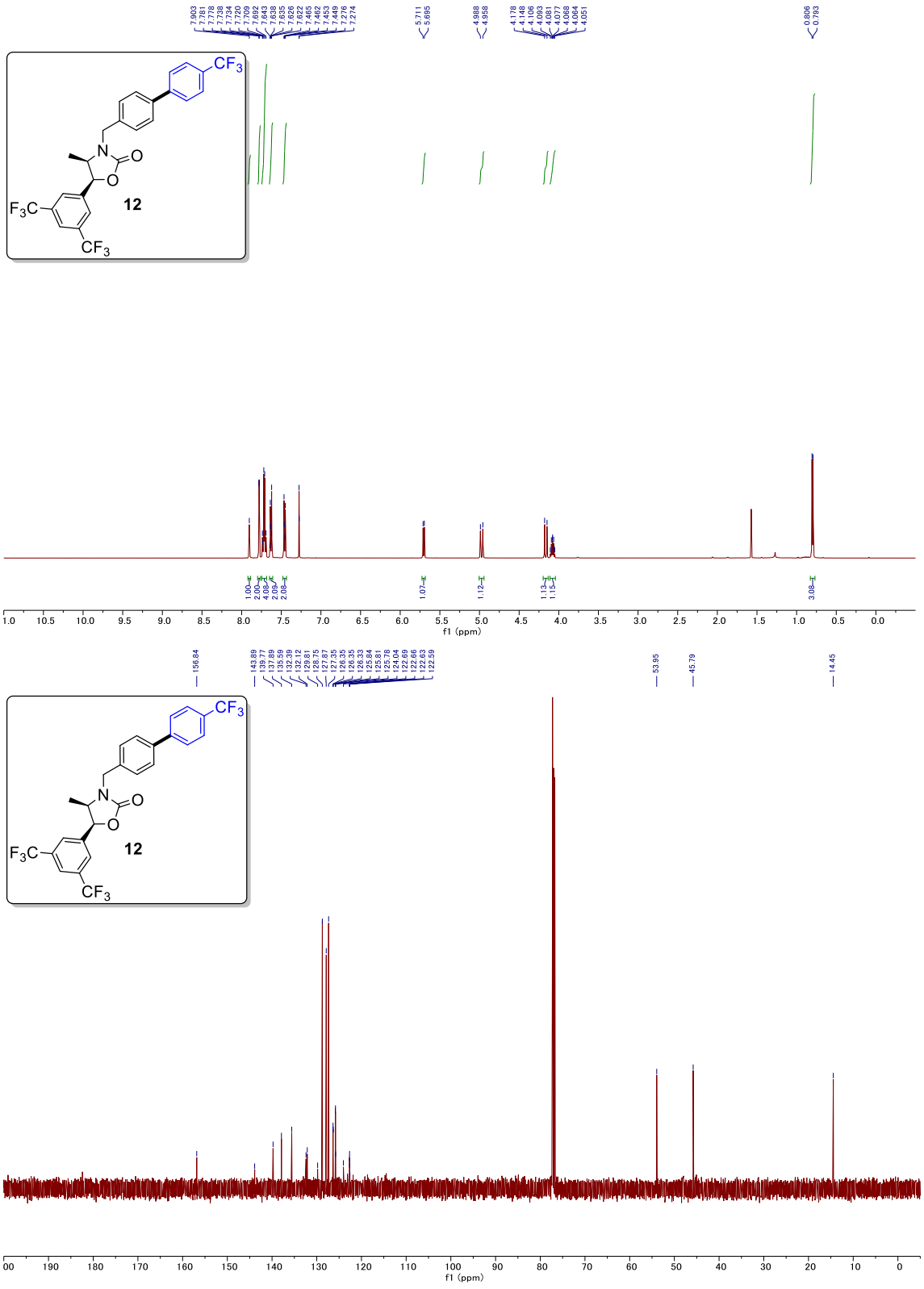
1.00
3.90
3.01
2.06
1.93
1.94
f1 (ppm)

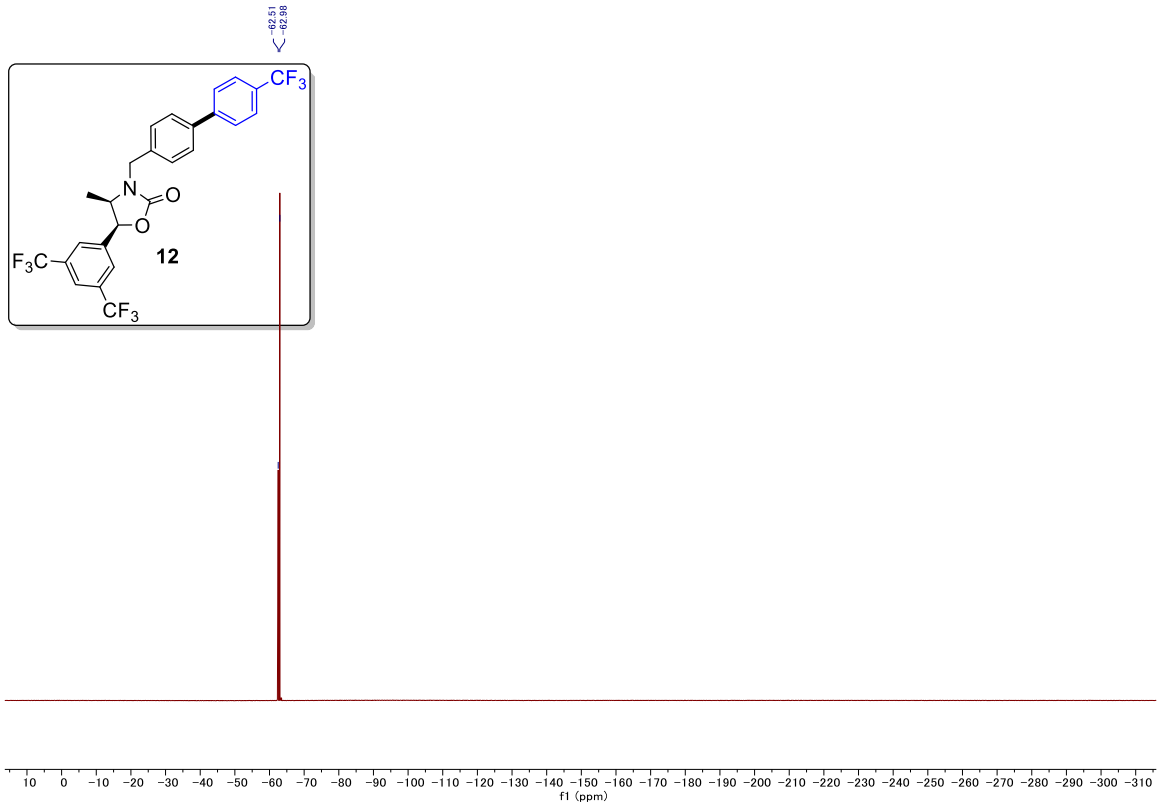

F
N
F
11

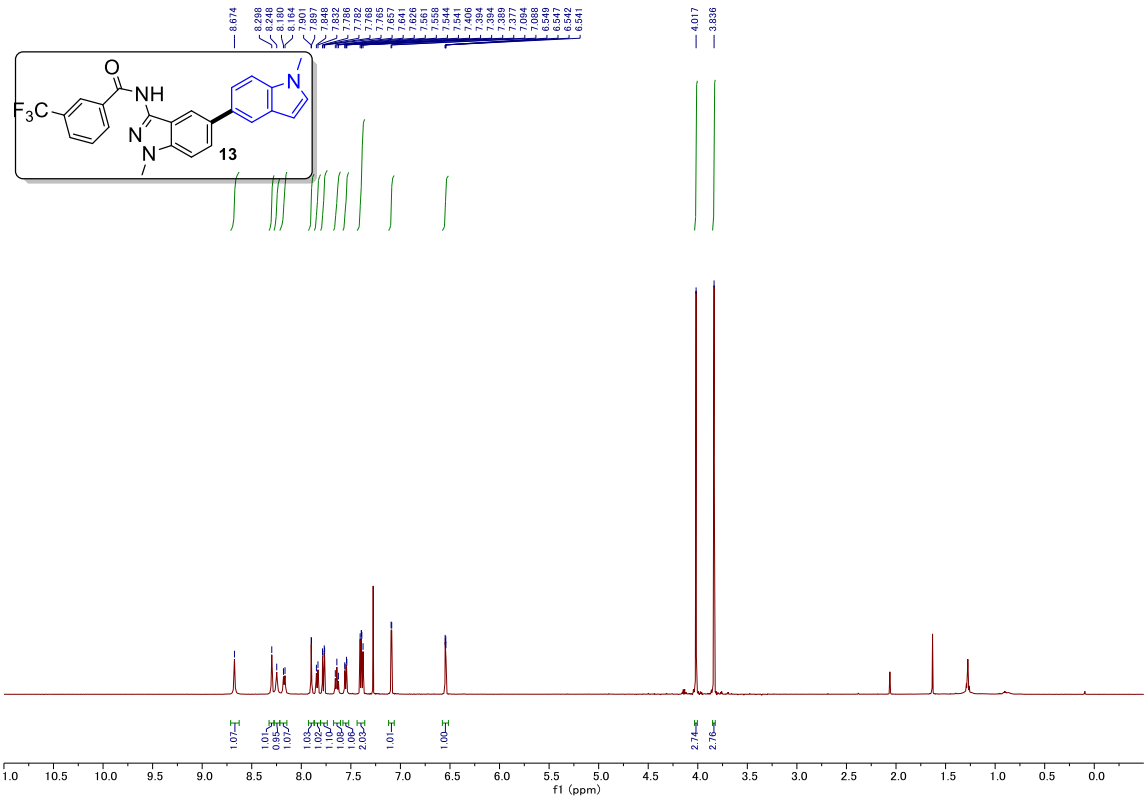

161.327
159.415
141.254
140.576
137.538
129.921
129.892
128.278
128.196
128.103
127.611
127.139
126.175
123.371
123.269
122.346
120.474
120.419
120.154
111.721
111.670
111.583
111.505
109.896
109.589

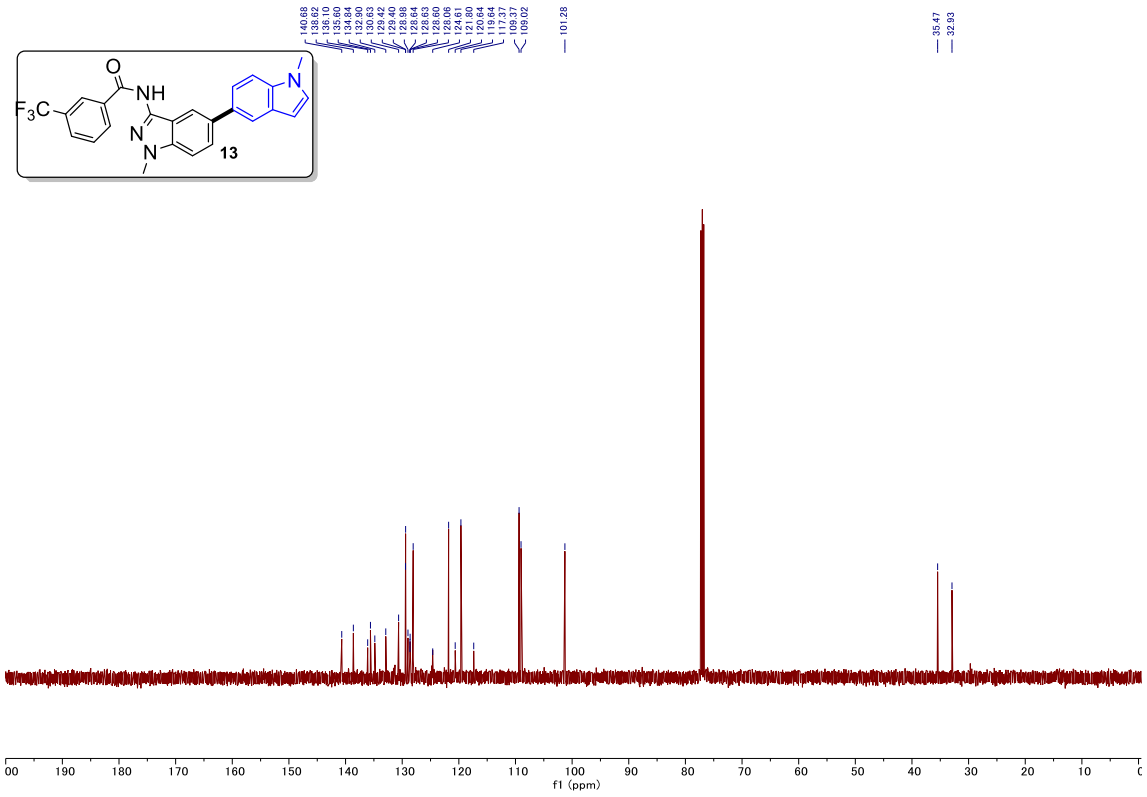

f1 (ppm)

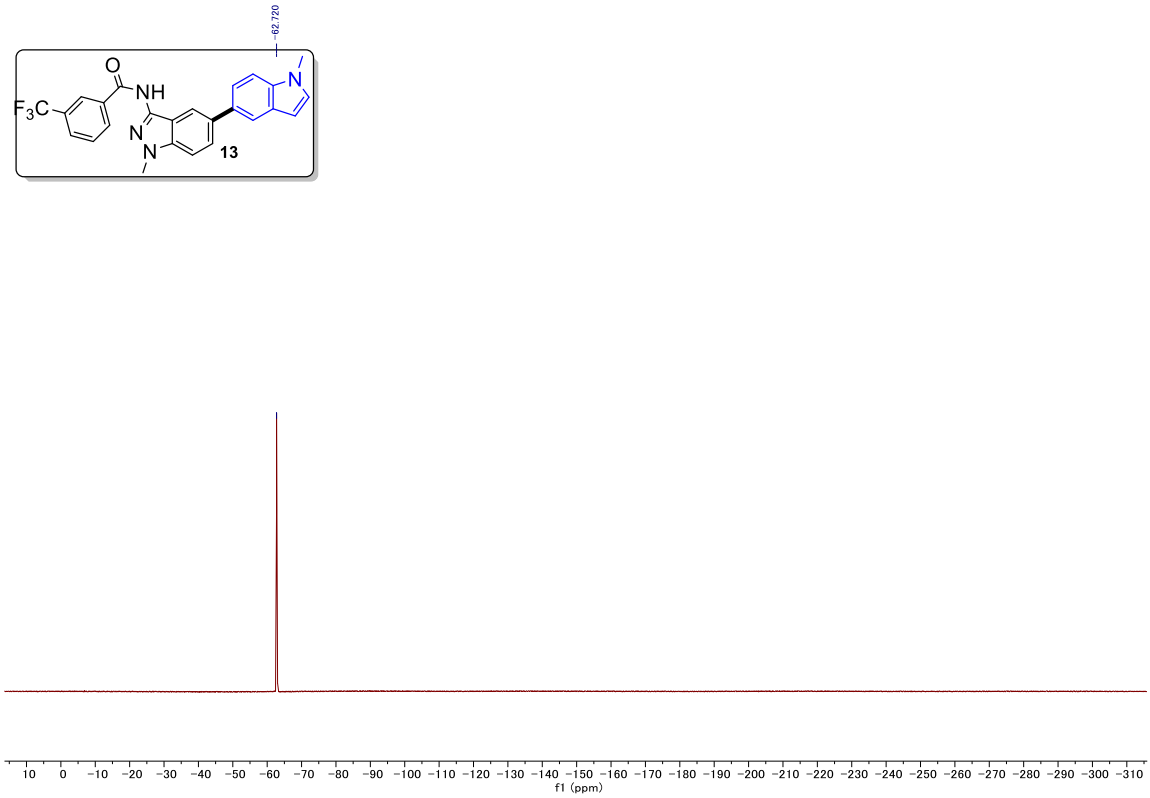

BT1263b_19F
STANDARD FLUORINE PARAMETERS
-114.60
F
N
F
11
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270 -280 -290 -300 -310
f1 (ppm)

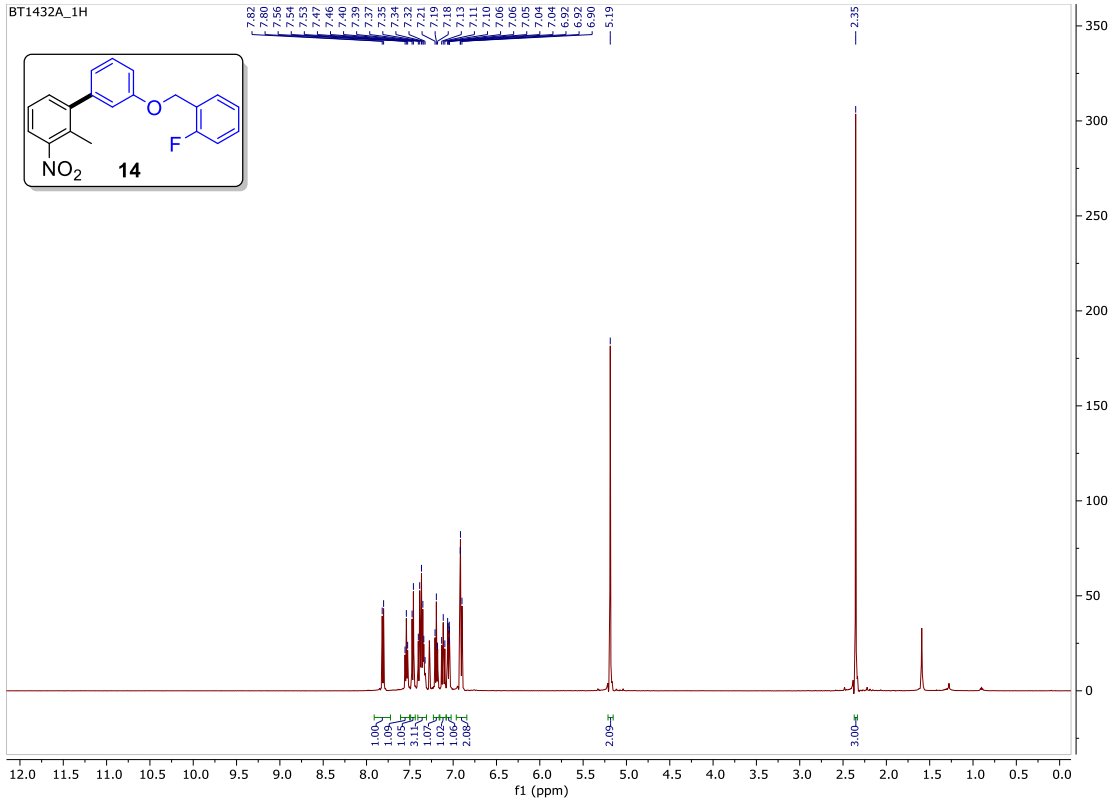

12
f1 (ppm)
12
f1 (ppm)

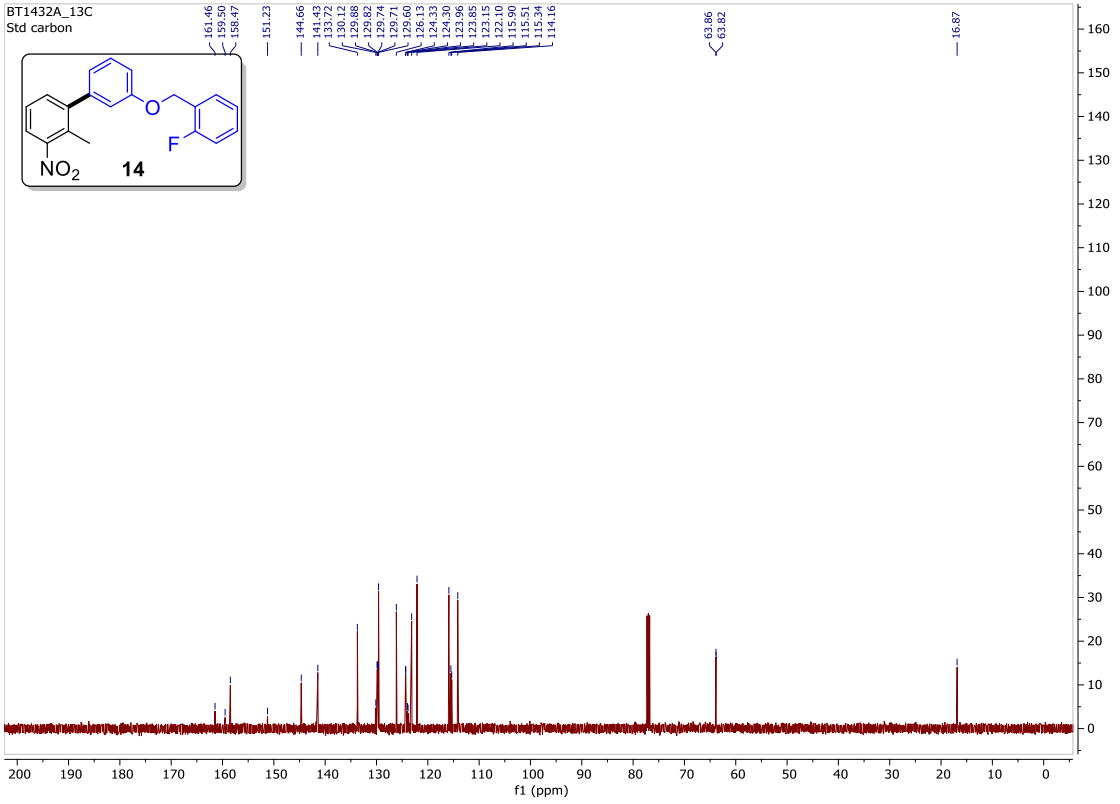

-62.51
-62.98
CF3
N
O
O
12
F3C
CF3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270 -280 -290 -300 -310
f1 (ppm)

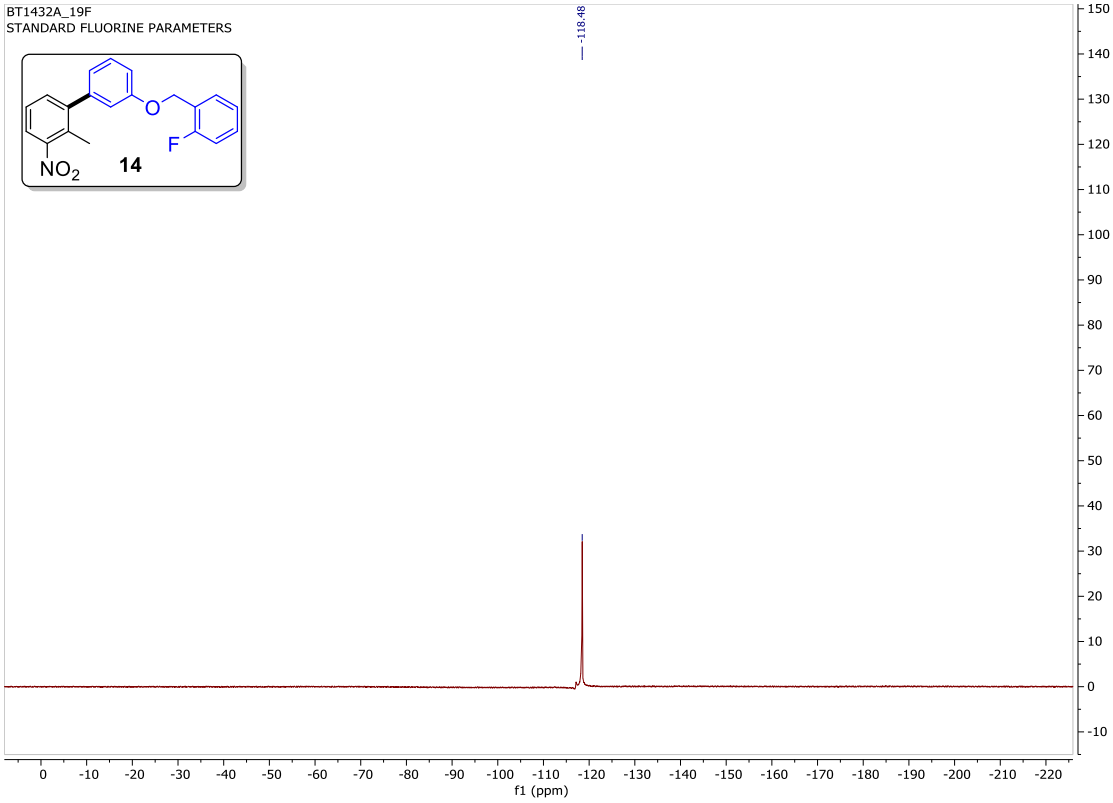

8.674
8.298
8.248
8.180
8.164
8.101
7.897
7.848
7.832
7.788
7.782
7.768
7.765
7.657
7.641
7.626
7.561
7.558
7.544
7.541
7.406
7.394
7.389
7.377
7.094
7.088
6.549
6.547
6.542
6.541
4.017
3.836
1.07
1.01
0.95
1.07
1.03
1.02
1.10
1.08
1.06
2.03
1.01
1.00
2.74
2.76
f1 (ppm)
13

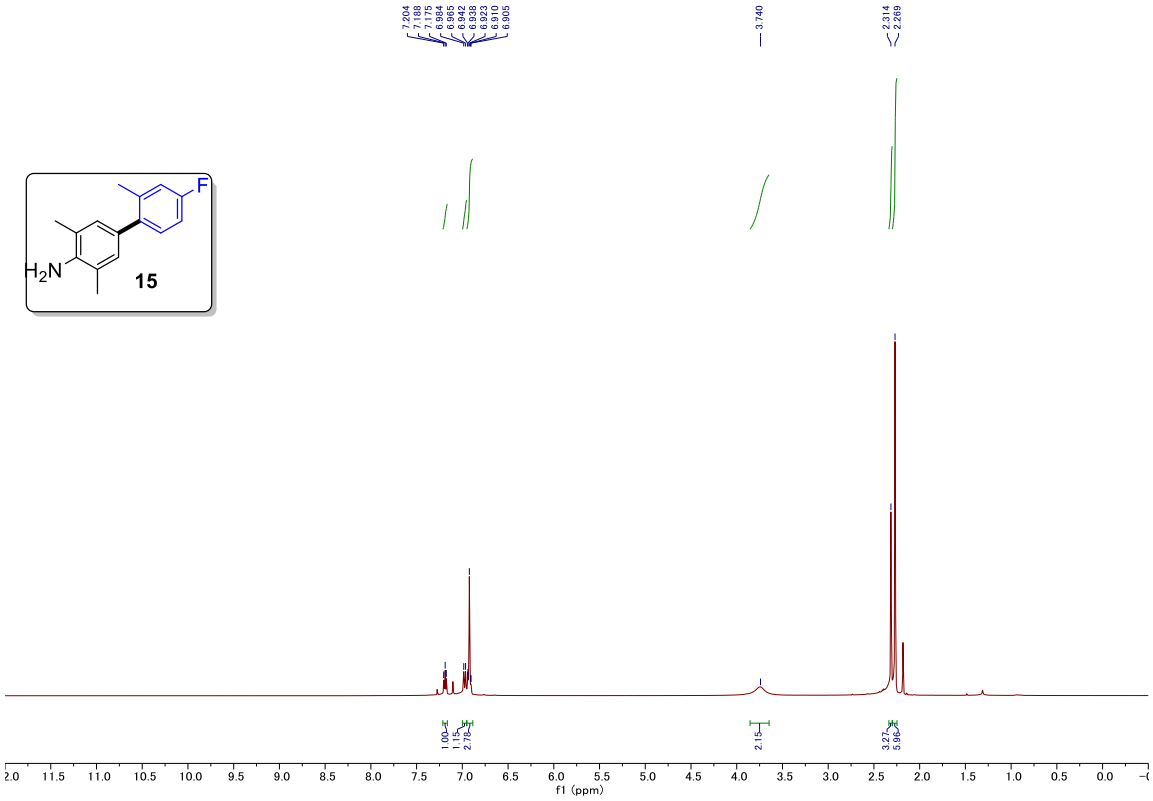

140.68
139.62
136.10
135.60
134.84
132.90
130.63
129.42
129.40
128.98
128.64
128.63
128.60
128.06
124.61
122.80
120.64
119.64
117.37
109.37
105.02
101.28
35.47
32.93
f1 (ppm)
13

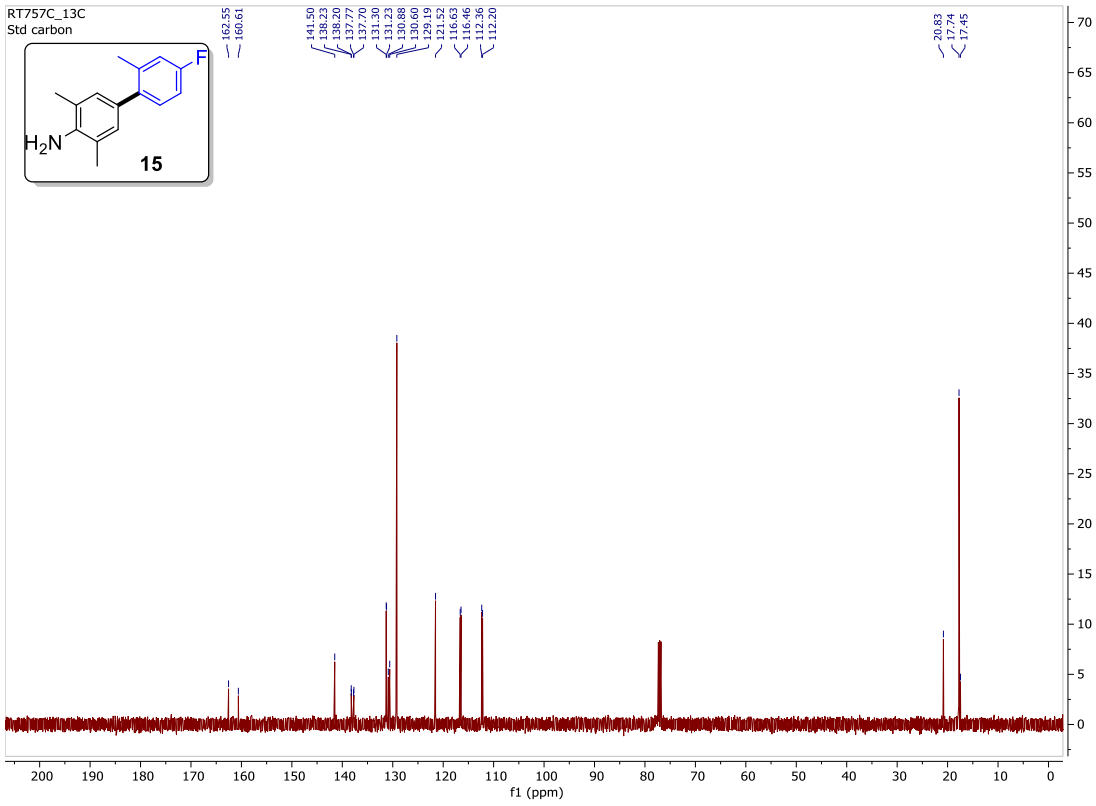

-62.720
O
NH
F3C
N
N
13
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270 -280 -290 -300 -310
f1 (ppm)

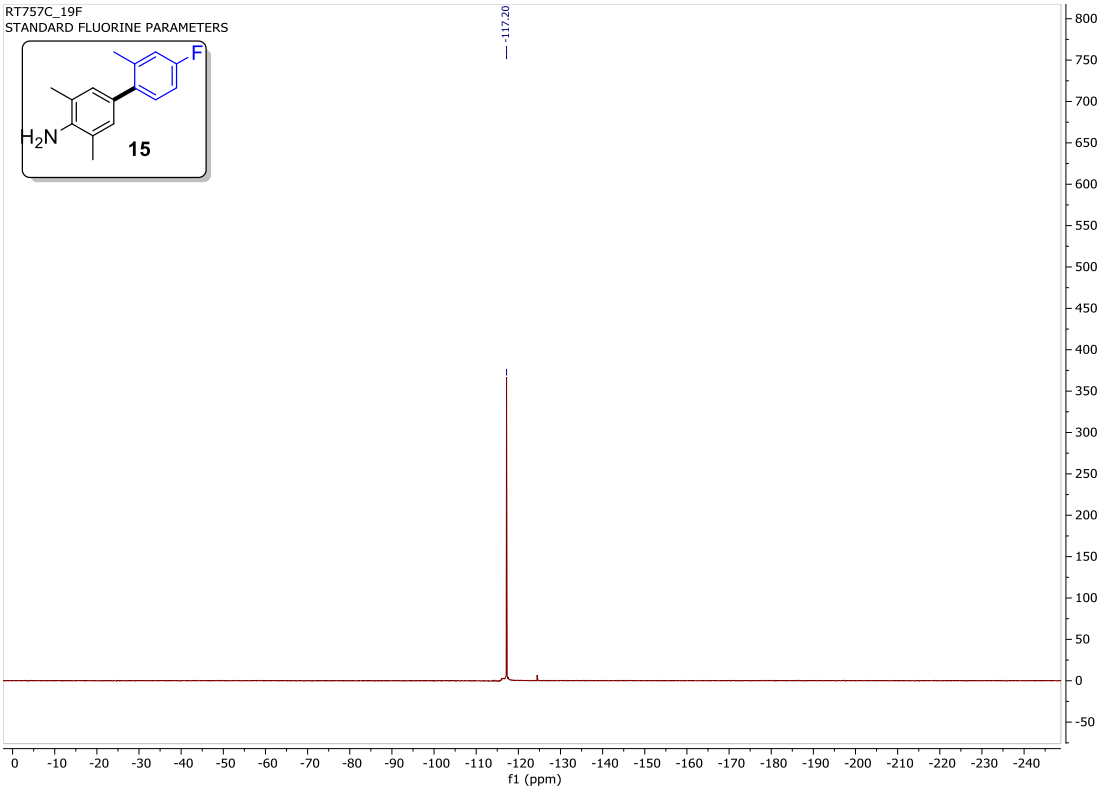

BT1432A_1H
NO2
14
f1 (ppm)

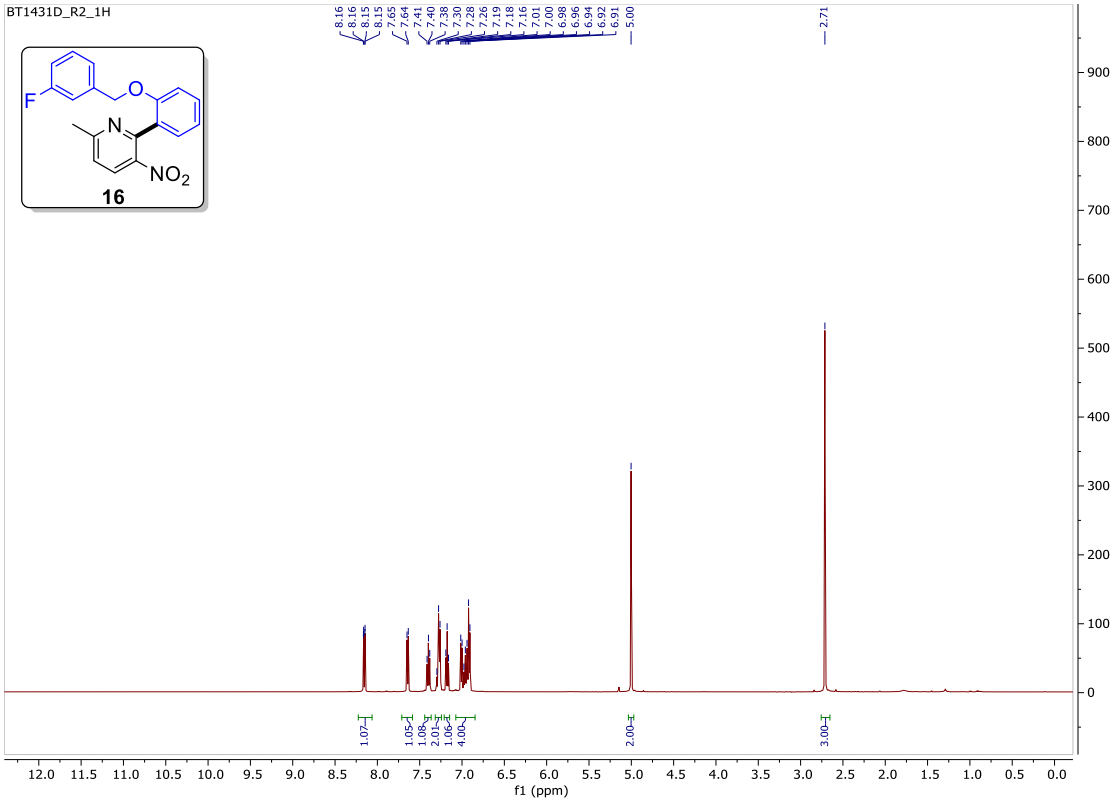

BT1432A_13C
Std carbon
NO2
14
f1 (ppm)

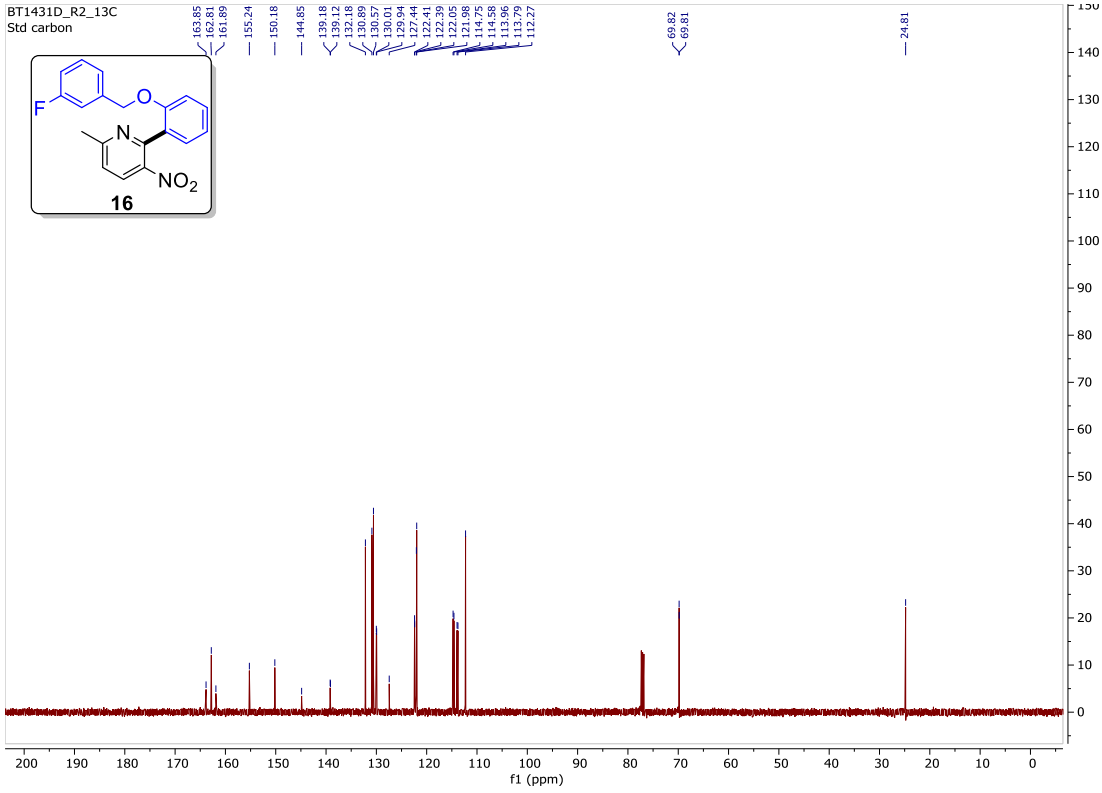

BT1432A_19F
STANDARD FLUORINE PARAMETERS
-118.48
O
F
NO2
14
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

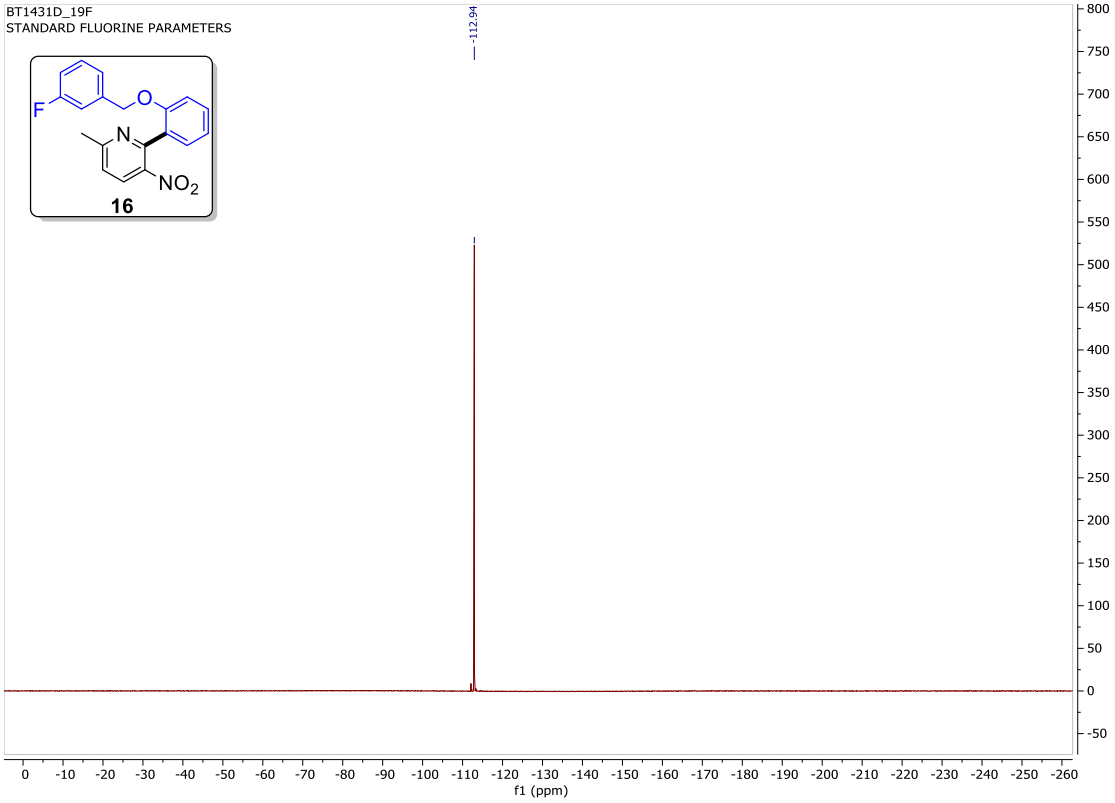

7.204
7.188
7.175
6.984
6.965
6.948
6.938
6.923
6.910
6.905
3.740
2.314
2.269
F
H2N
15
1.00
1.15
2.78
2.15
3.27
5.96
f1 (ppm)

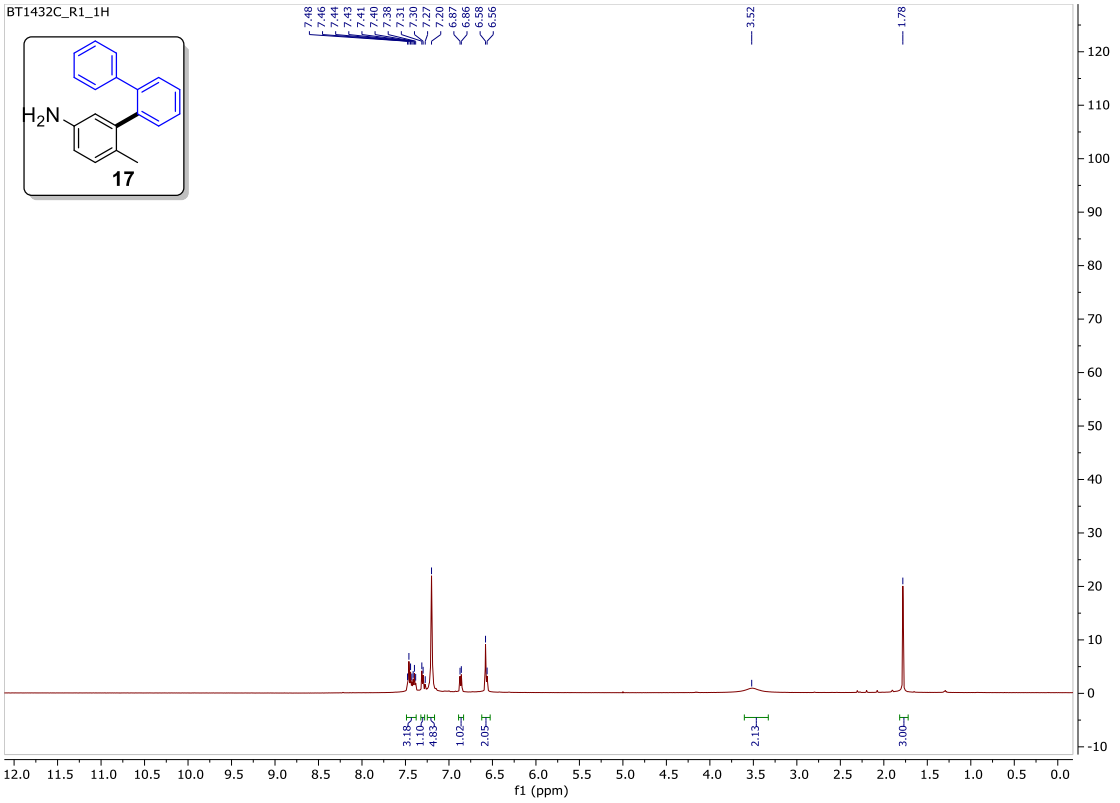

RT757C_13C
Std carbon
162.55
160.61
141.50
138.23
138.20
137.77
137.70
131.30
131.23
130.88
130.60
129.13
121.52
116.63
116.46
112.36
112.20
20.83
17.74
17.45
F
H2N
15
f1 (ppm)

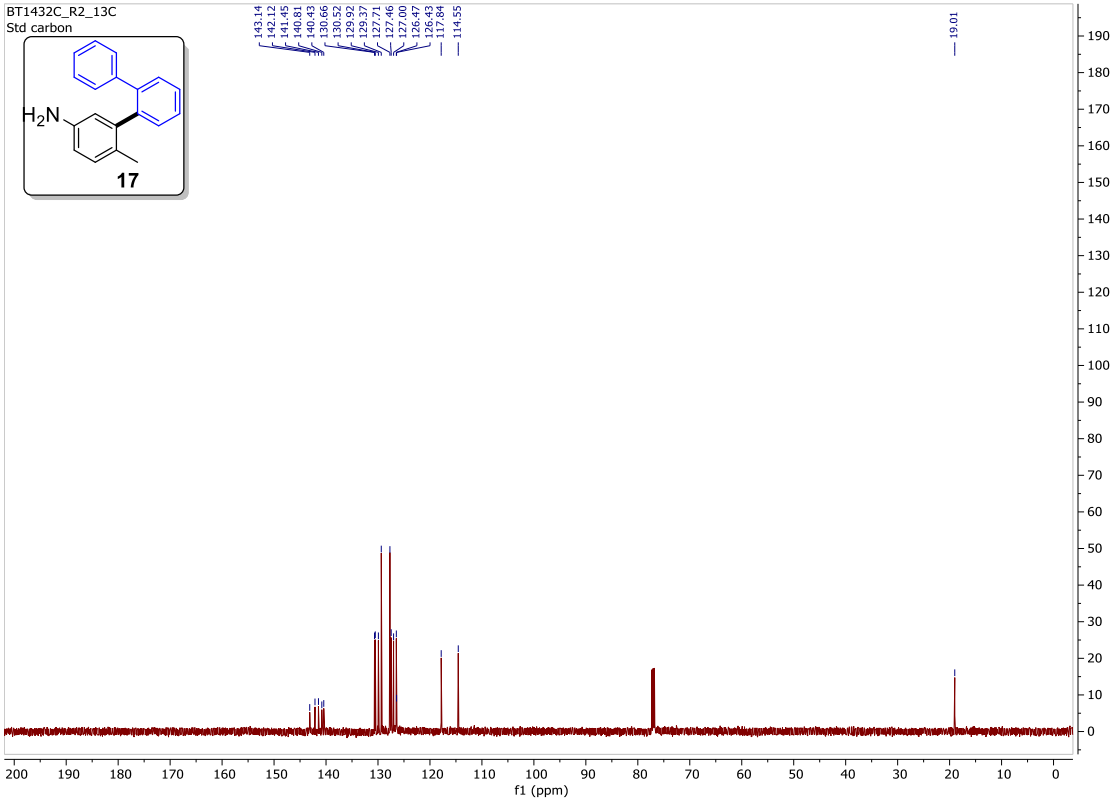

RT757C_19F
STANDARD FLUORINE PARAMETERS
F
H2N
15
-117.20
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)

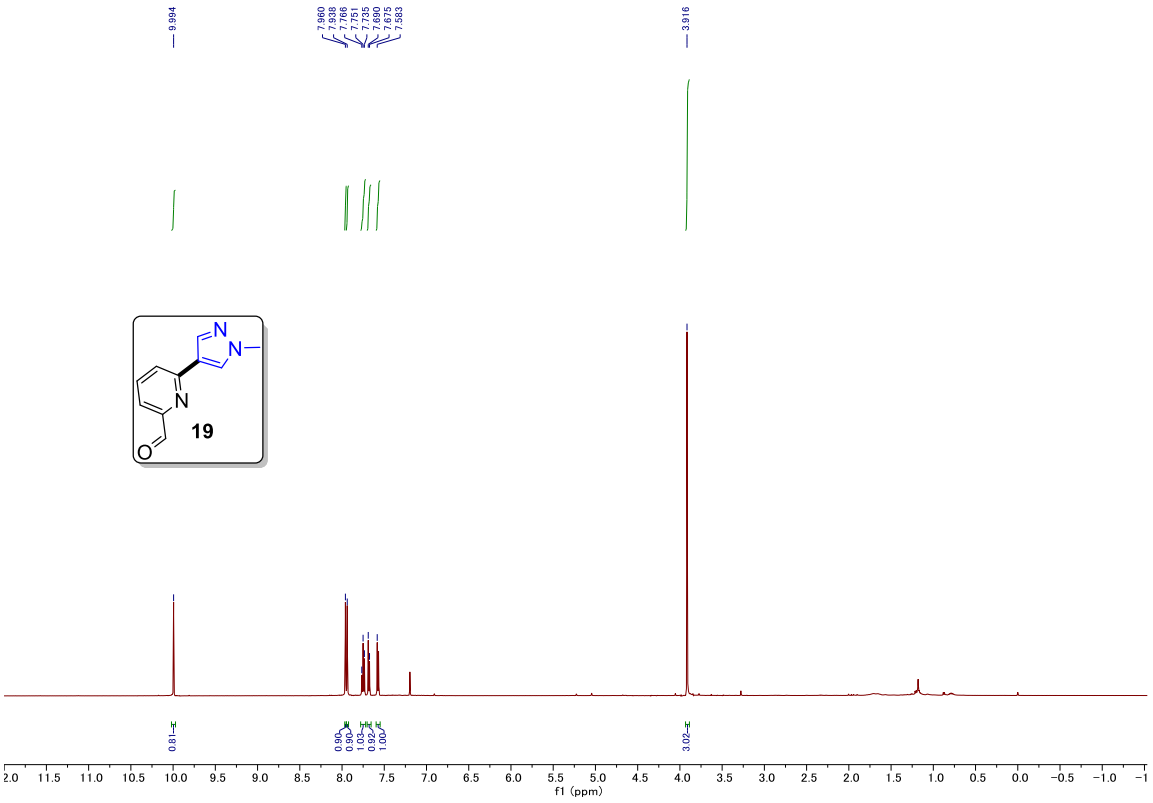

BT1431D_R2_1H
16
f1 (ppm)

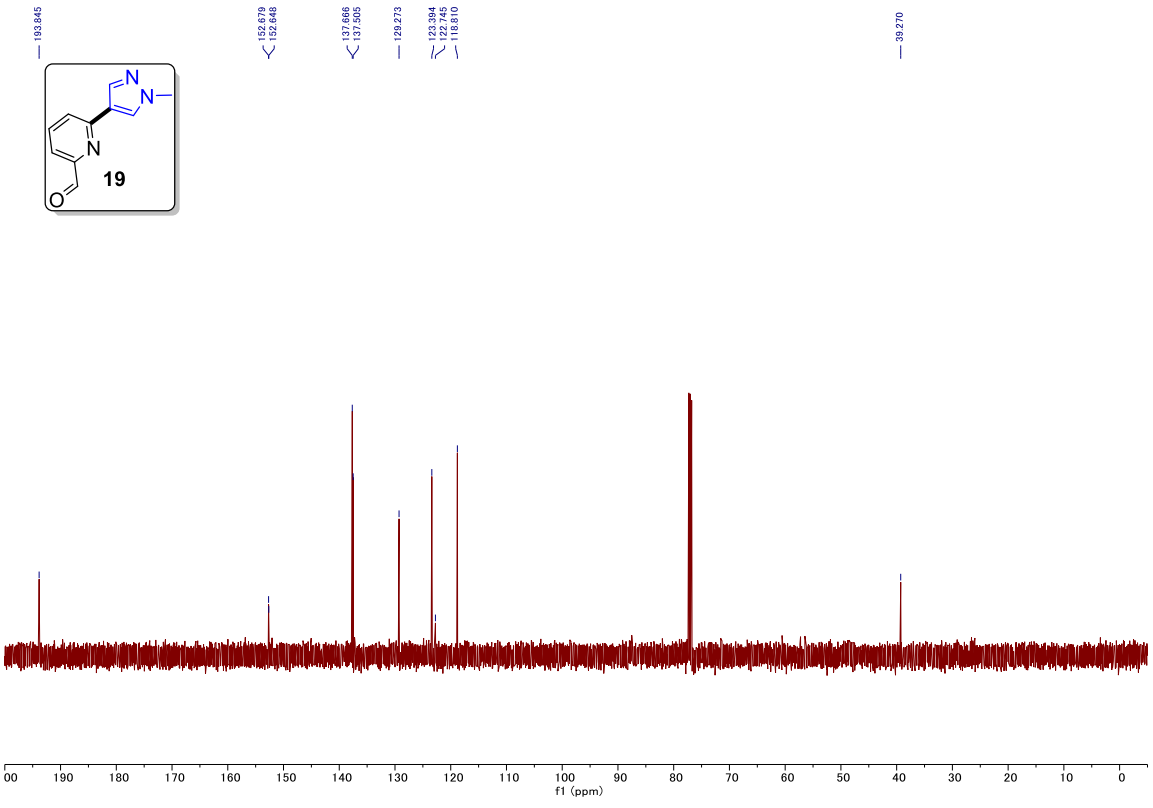

BT1431D_R2_13C
Std carbon
16
f1 (ppm)

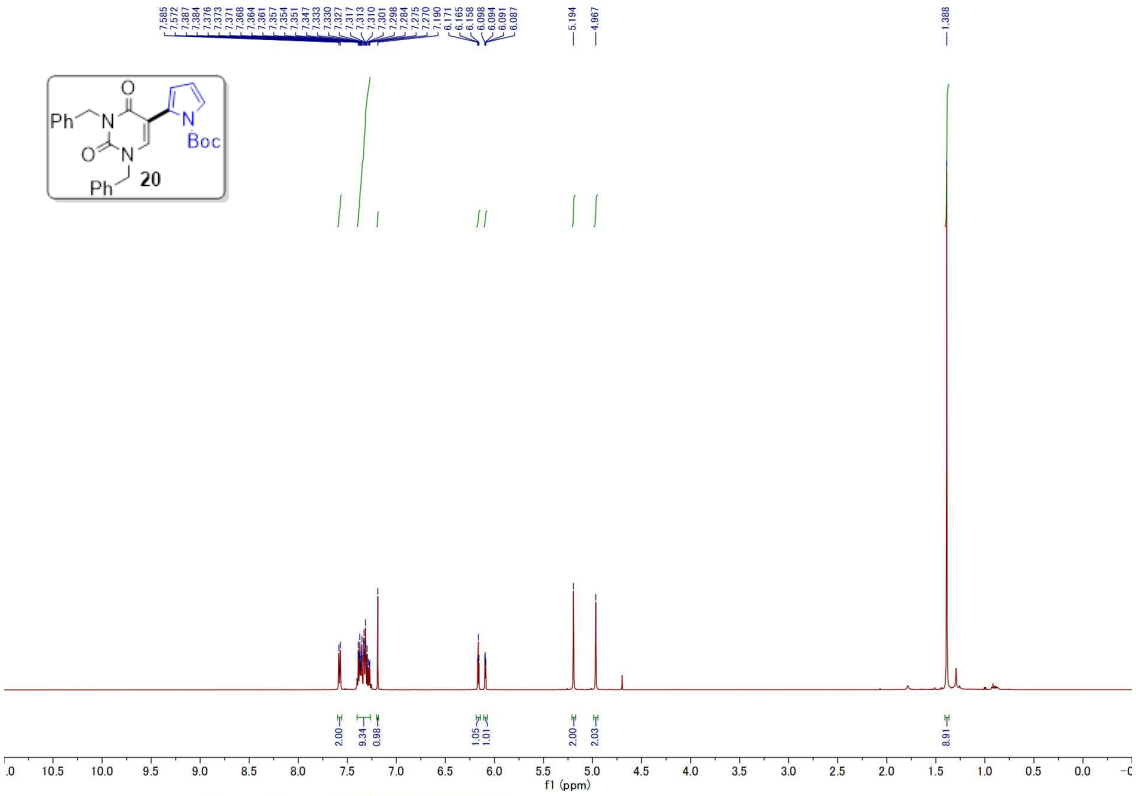

BT1431D_19F
STANDARD FLUORINE PARAMETERS
-112.94
F
O
N
NO2
16
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260
f1 (ppm)

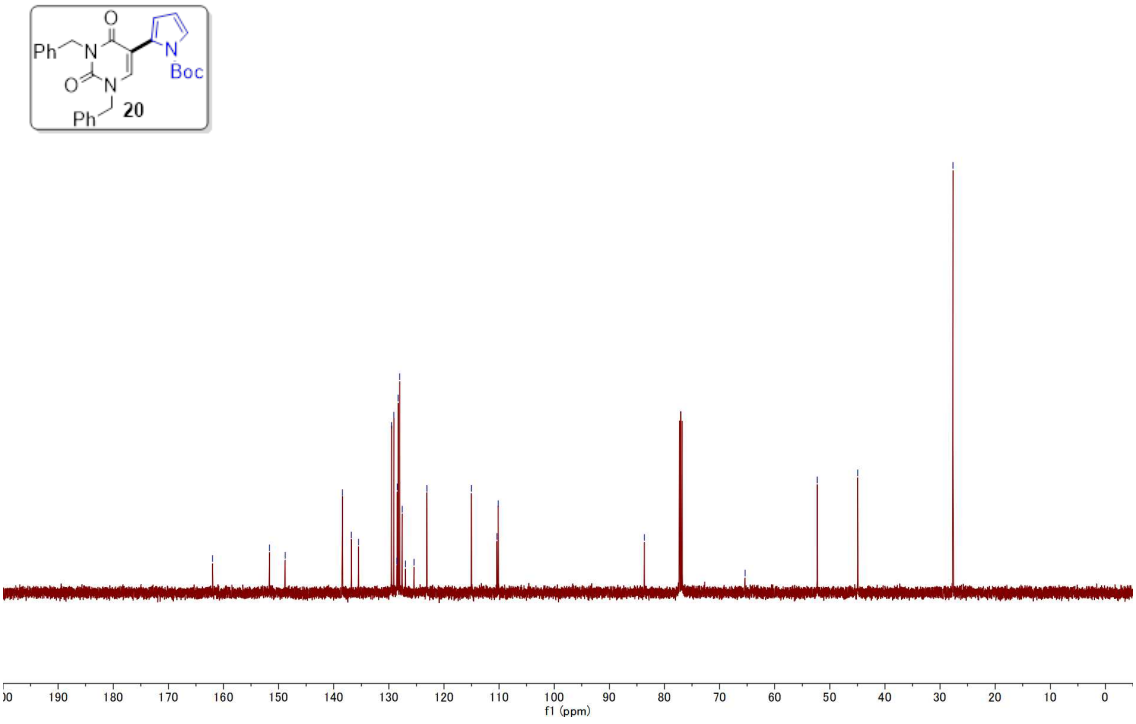

BT1432C_R1_1H
7.48
7.46
7.44
7.43
7.41
7.40
7.38
7.31
7.30
7.27
7.20
6.87
6.86
6.58
6.56
3.52
1.78
H_2N
17
3.18
1.10
4.83
1.02
2.05
2.13
3.00
f1 (ppm)

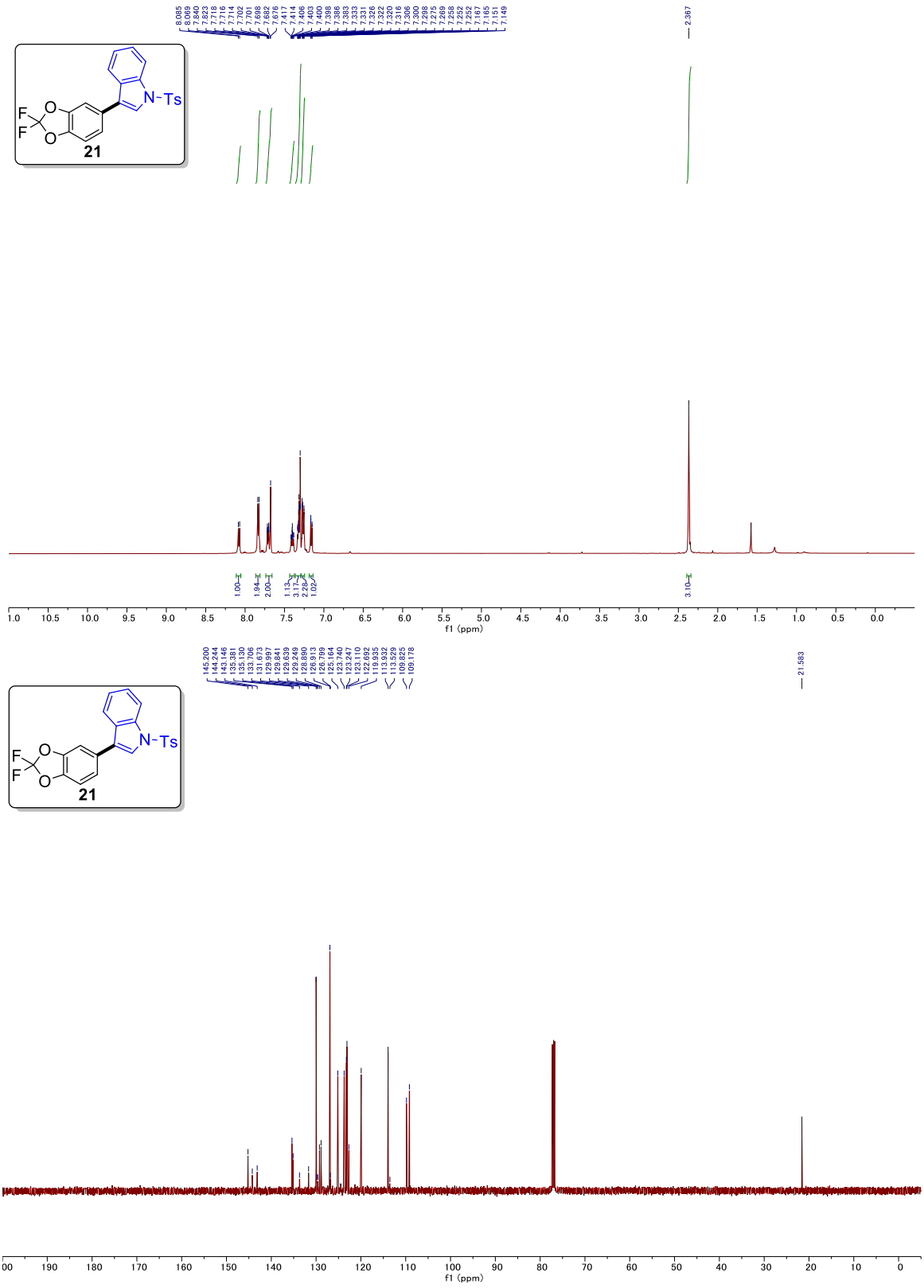

BT1432C_R2_13C
Std carbon
143.14
142.12
141.45
140.81
140.43
130.66
130.52
129.92
129.37
127.71
127.46
127.00
126.47
126.43
117.84
114.55
19.01
H_2N
17
f1 (ppm)

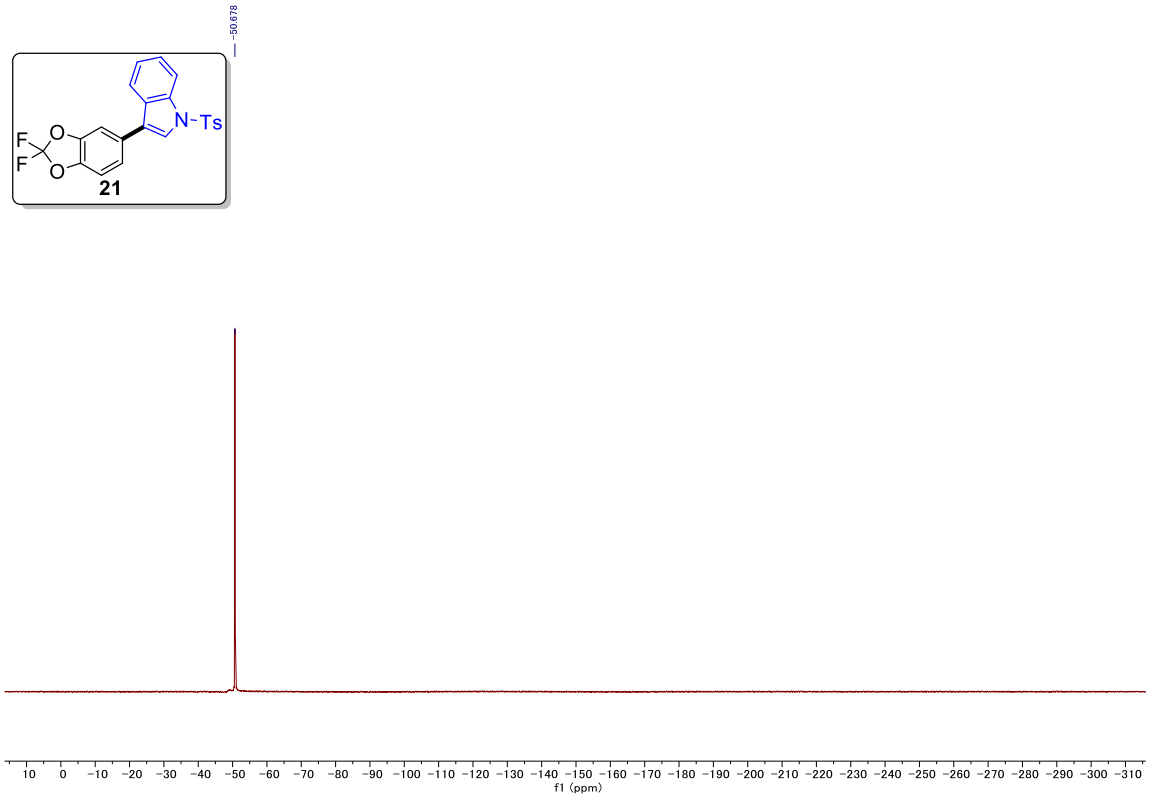

9.994
7.960
7.938
7.766
7.751
7.735
7.690
7.675
7.583
3.916
19
0.61
0.90
0.90
1.03
0.92
1.00
3.02
f1 (ppm)

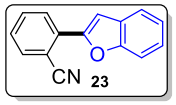

193.845
152.679
152.648
137.666
137.505
129.273
123.394
122.745
118.810
39.270
19
f1 (ppm)

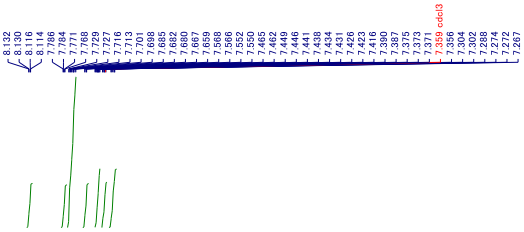

Ph
N
O
N
Boc
Ph
20
f1 (ppm)


Ph
N
O
N
Boc
Ph
20
f1 (ppm)


N-Ts
F
F
O
O
21
f1 (ppm)


-50.678
N-Ts
F
F
O
O
21
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270 -280 -290 -300 -310
f1 (ppm)


CN
23


8.132
8.130
8.115
8.114
7.786
7.784
7.771
7.768
7.729
7.727
7.716
7.713
7.701
7.698
7.685
7.682
7.669
7.667
7.659
7.568
7.566
7.552
7.550
7.465
7.462
7.449
7.446
7.441
7.438
7.434
7.431
7.426
7.423
7.416
7.390
7.387
7.375
7.373
7.371
7.359
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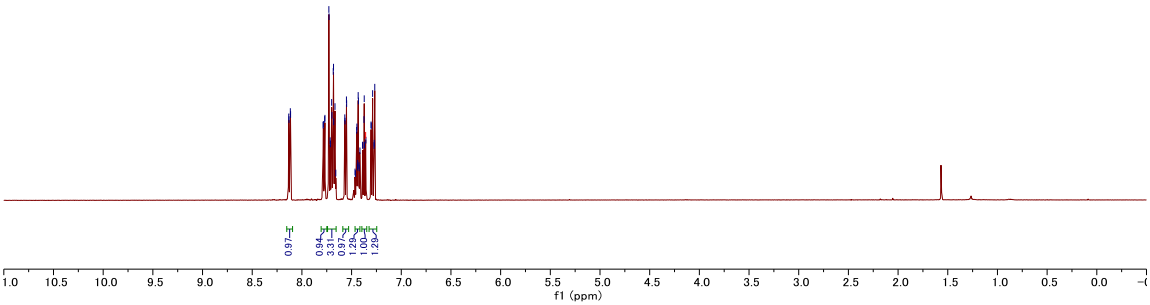
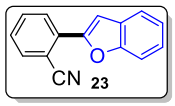
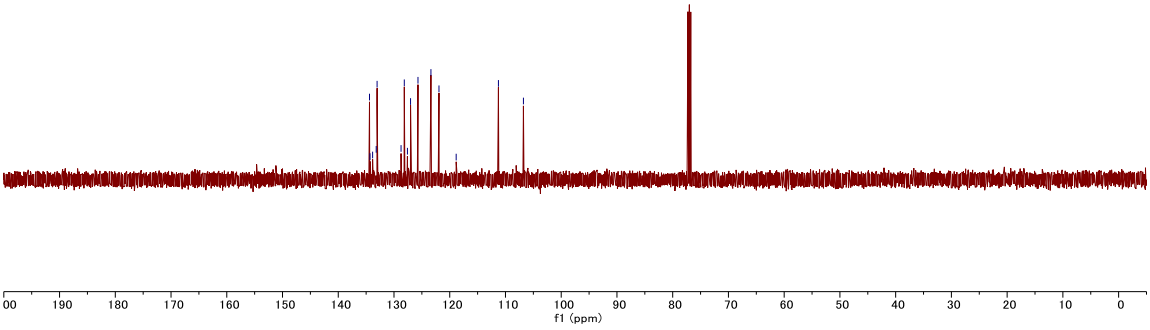
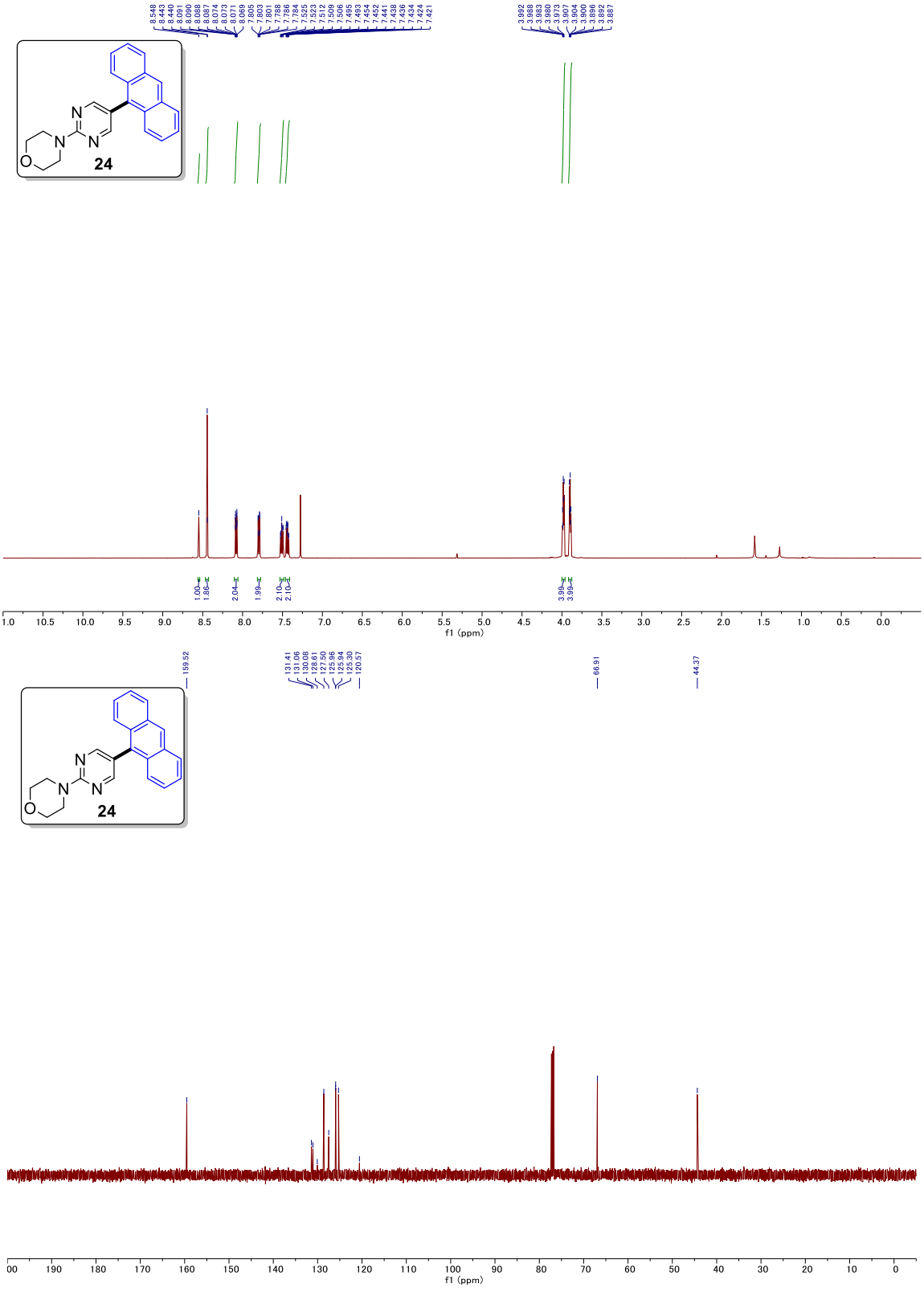
7.302
7.288
7.274
7.272
7.267
cdcl3

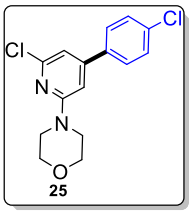

0.97
0.94
3.31
0.97
1.29
1.00
1.29
f1 (ppm)


CN
23

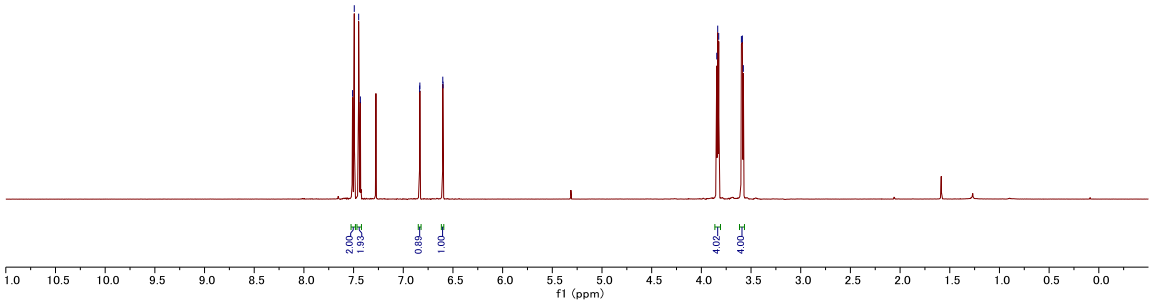

134.40
134.31
133.84
133.19
133.03
128.74
128.15
127.59
127.03
125.70
123.37
121.83
118.84
111.27
106.78

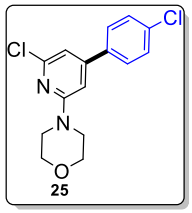

f1 (ppm)


24
f1 (ppm)
24
f1 (ppm)

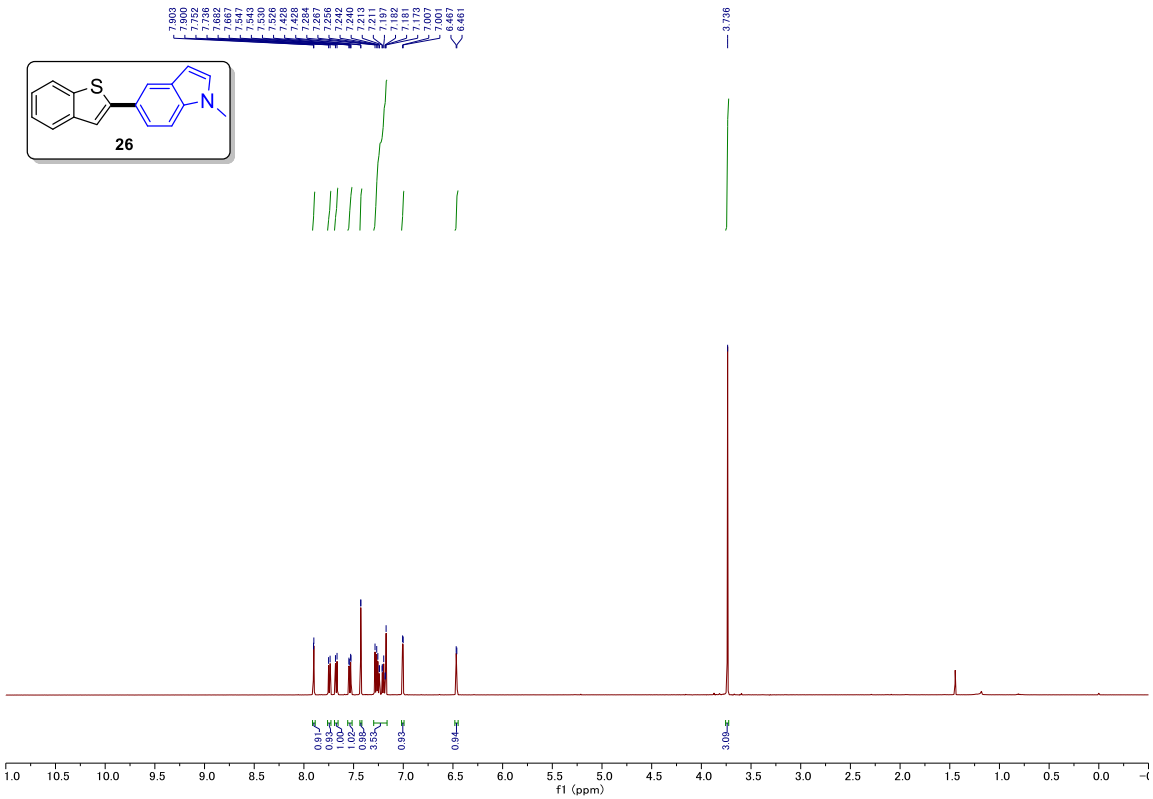

Cl
Cl
N
N
O
25

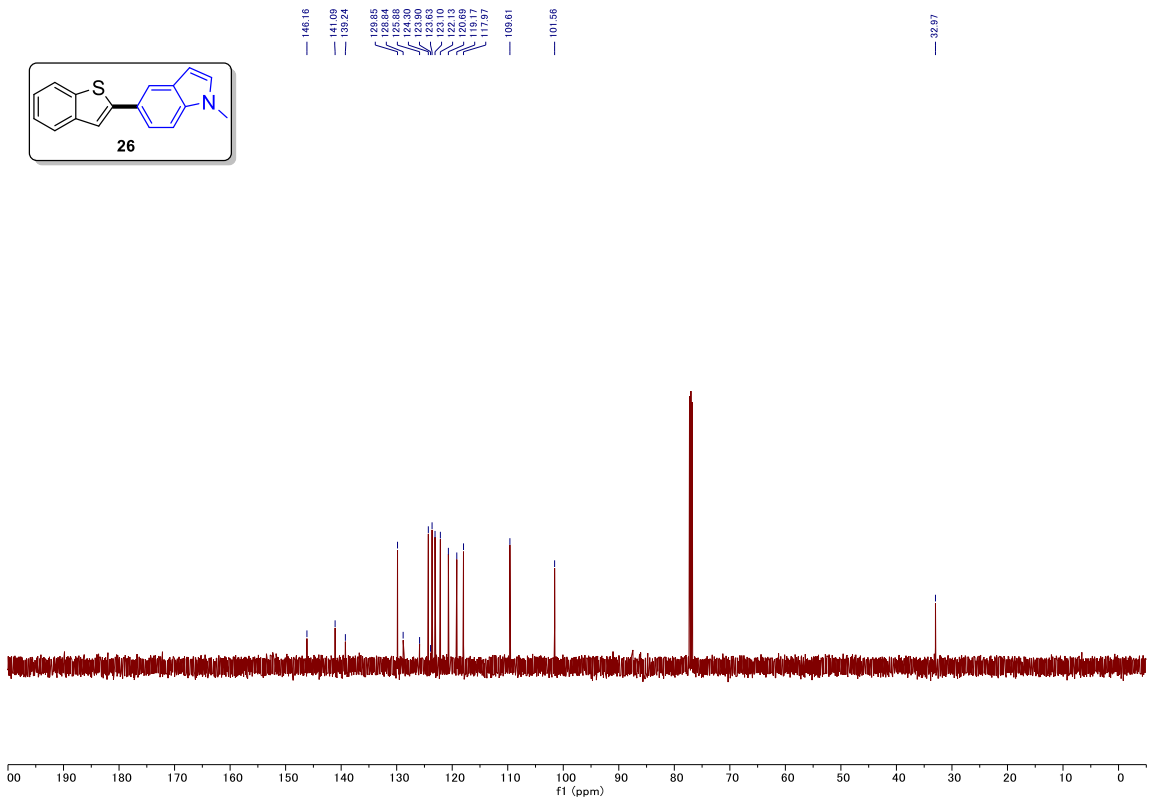

7.510
7.498
7.449
7.432
6.835
6.833
6.602
6.600
3.845
3.835
3.825
3.597
3.587
3.577

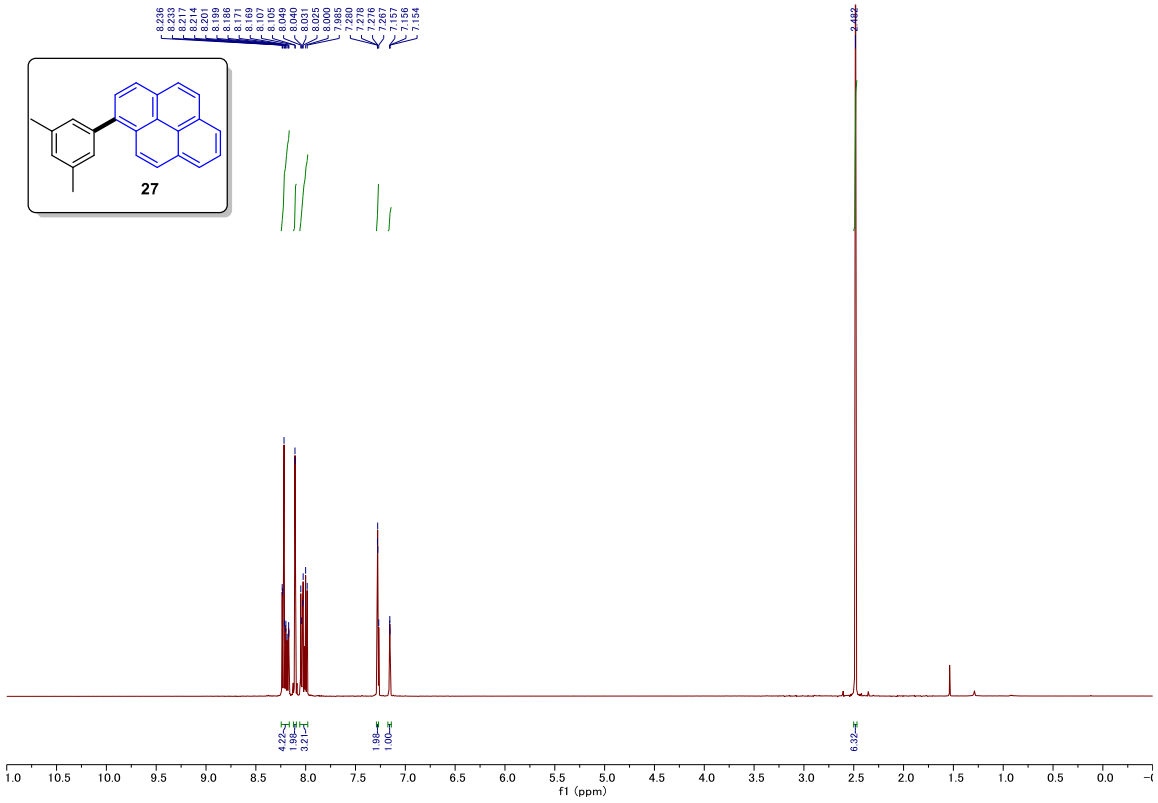

2.00
1.93
0.89
1.00
4.02
4.00
f1 (ppm)

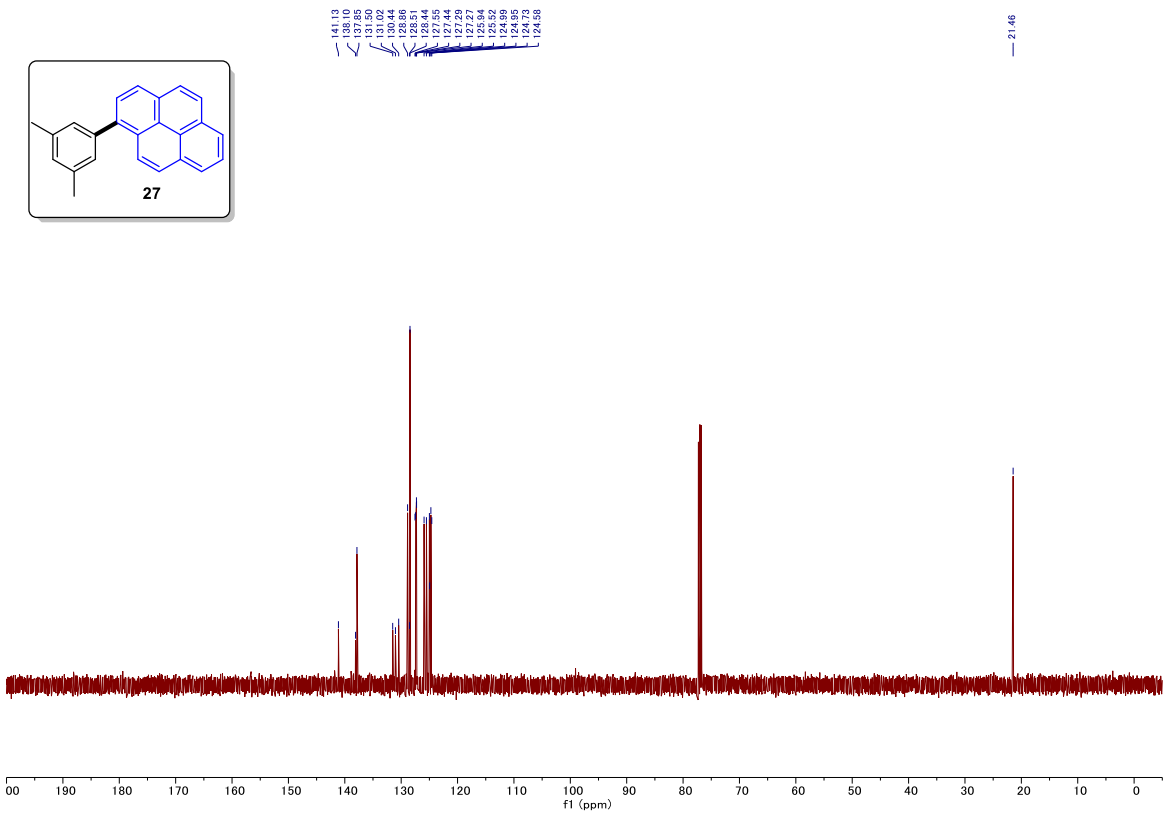

Cl
Cl
N
N
O
25

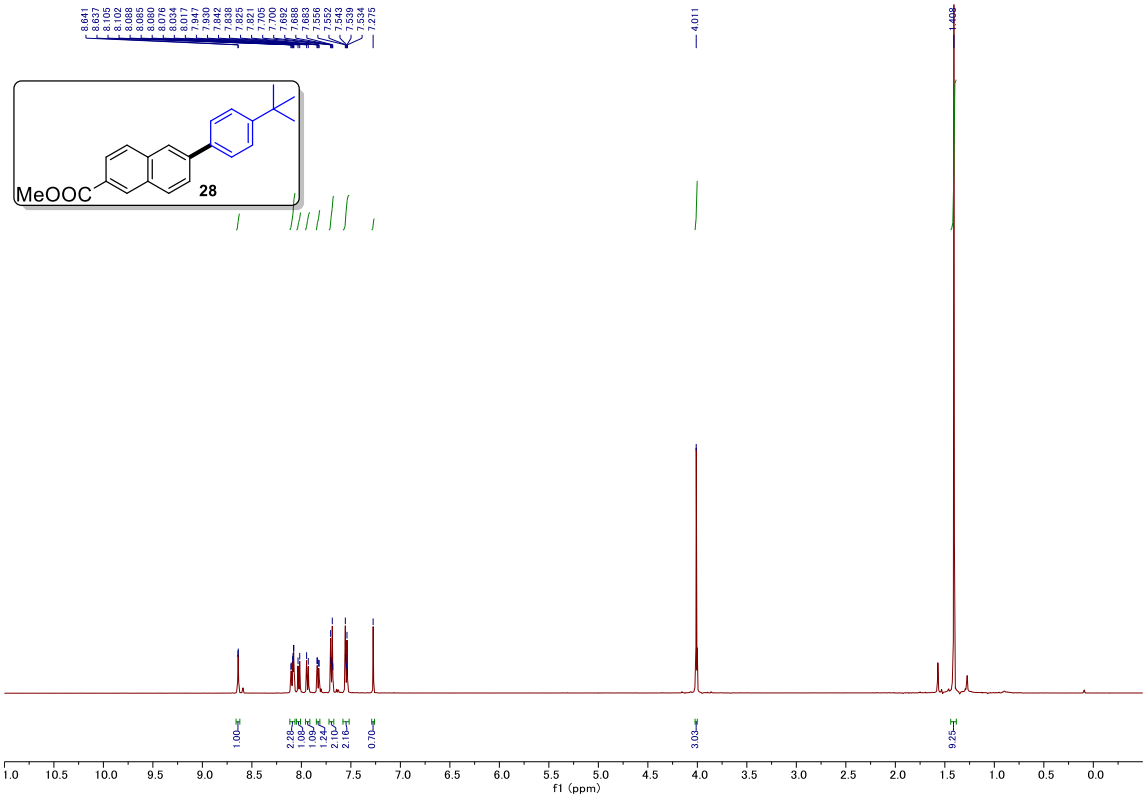
159.59
151.65
150.29
136.80
135.35
129.21
128.28
114.11
111.16
102.46
66.59
45.41
f1 (ppm)

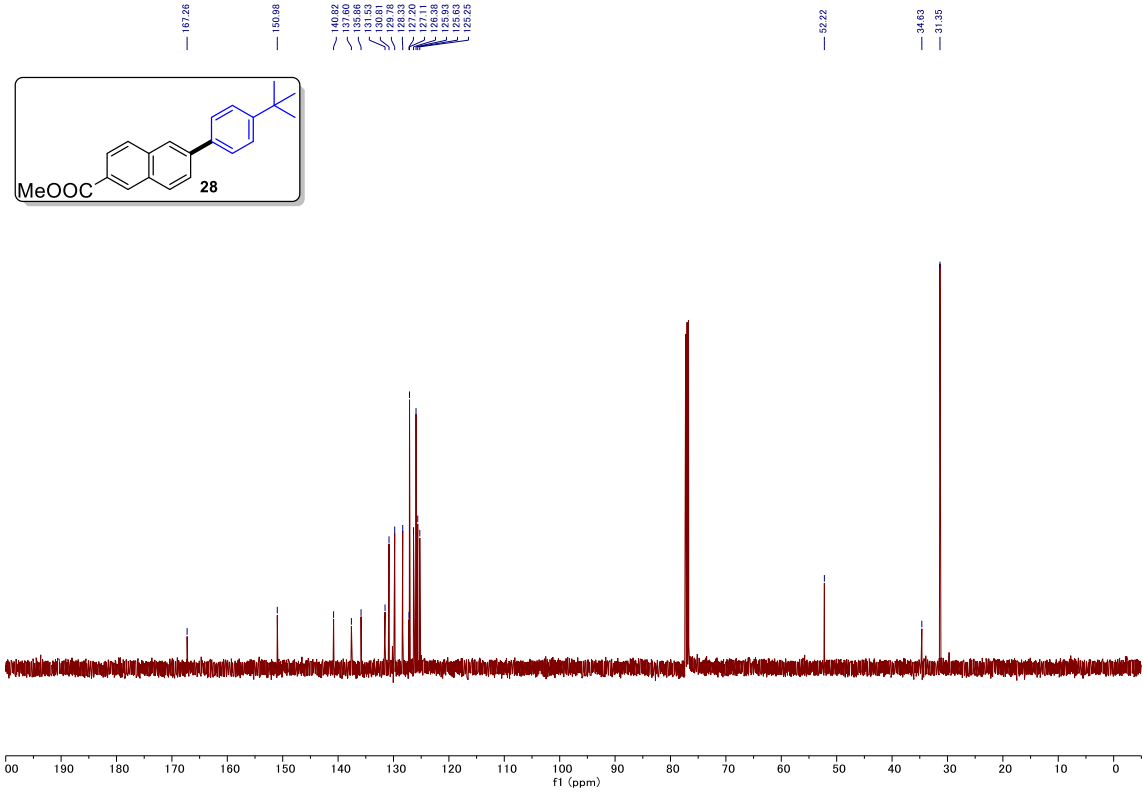

7.903
7.900
7.732
7.736
7.682
7.667
7.547
7.543
7.530
7.526
7.428
7.424
7.264
7.267
7.256
7.242
7.240
7.213
7.211
7.197
7.182
7.181
7.173
7.007
7.001
6.467
6.461
3.736
S
N
26
0.91
0.83
1.00
1.02
0.98
3.53
0.93
0.94
3.06
f1 (ppm)

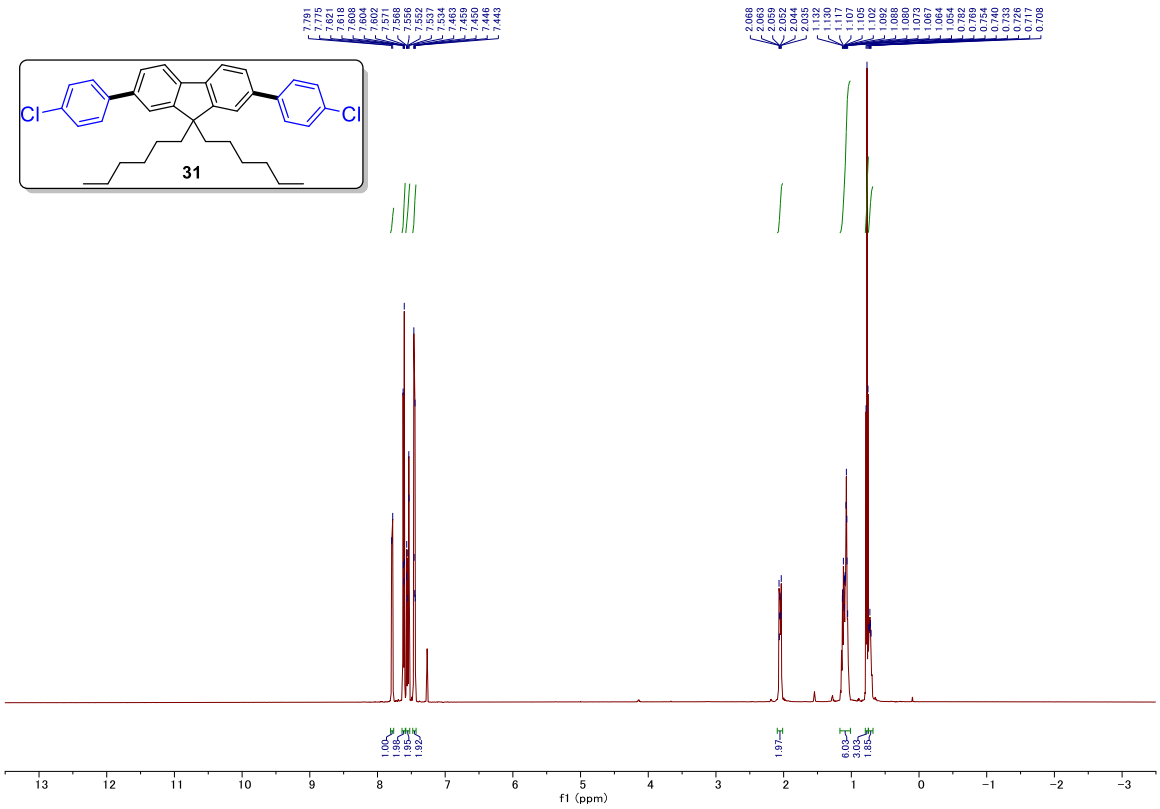

146.16
141.09
139.24
128.85
128.84
125.88
124.30
123.90
123.63
123.10
122.13
120.69
119.17
117.97
109.61
101.56
32.97
S
N
26
f1 (ppm)

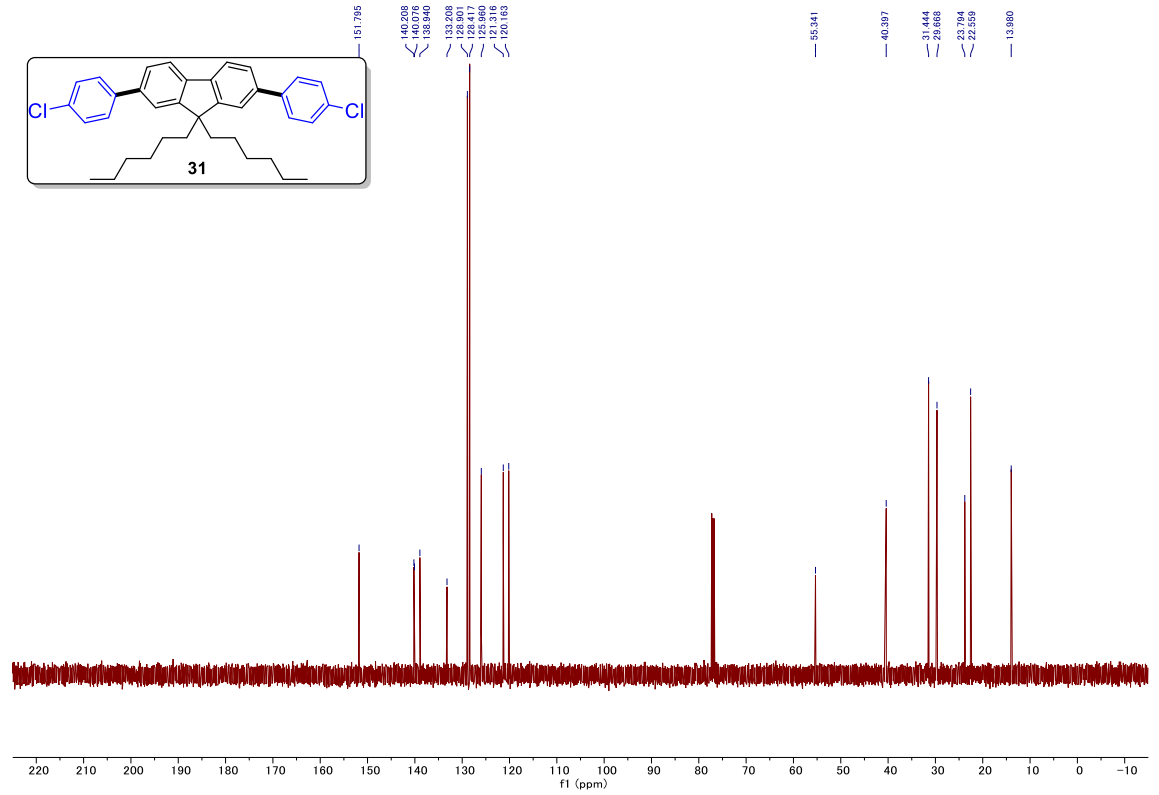

8.236
8.233
8.217
8.214
8.201
8.199
8.196
8.171
8.169
8.107
8.105
8.048
8.040
8.031
8.025
8.000
7.985
7.280
7.278
7.276
7.267
7.157
7.156
7.154
2.482
27
4.22
1.98
3.21
1.98
1.00
6.32
f1 (ppm)

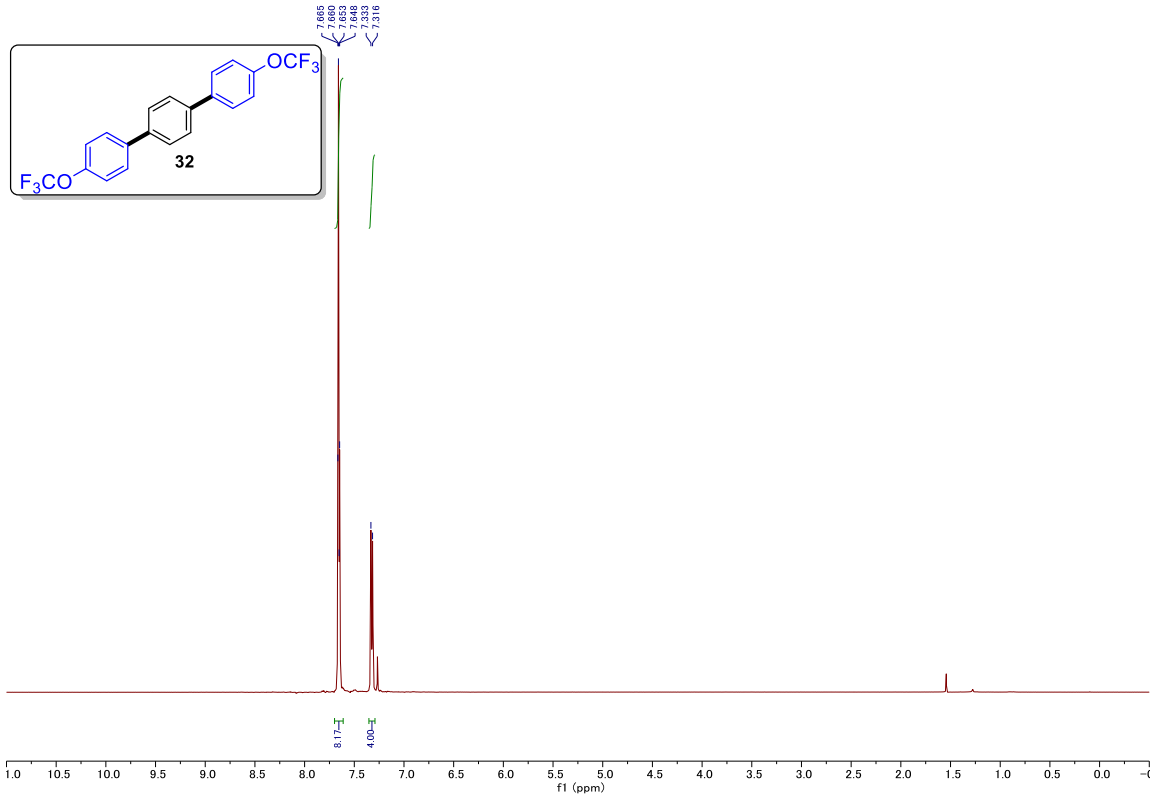

141.13
138.10
137.85
131.56
131.02
130.44
128.86
128.51
128.44
127.55
127.44
127.29
127.27
125.64
125.52
124.99
124.95
124.73
124.58
21.46
27
f1 (ppm)

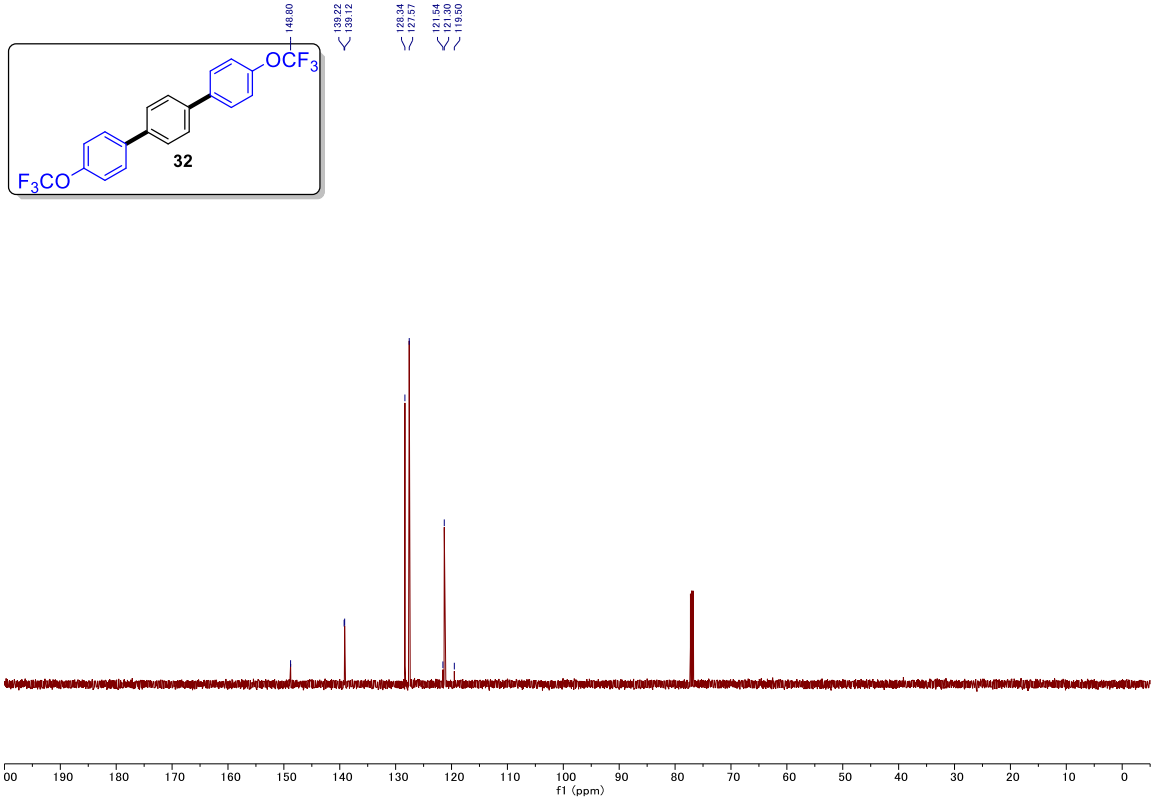

MeOOC
28
f1 (ppm)

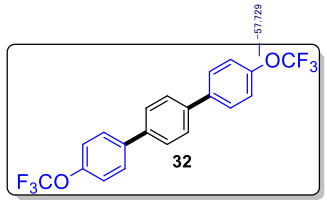

MeOOC
28
f1 (ppm)

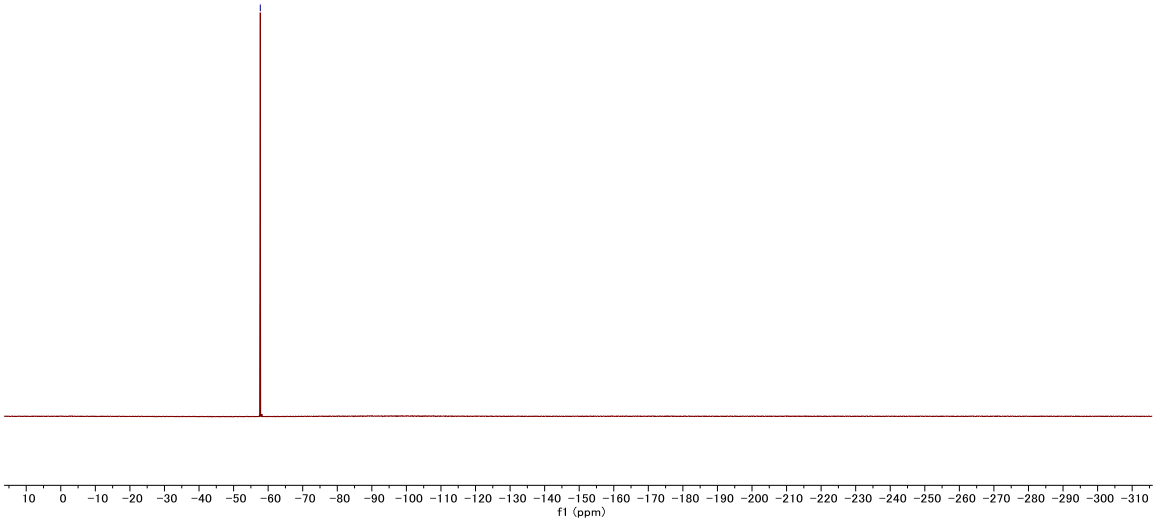

Cl
Cl
31
f1 (ppm)

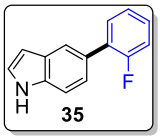

Cl
Cl
31
f1 (ppm)

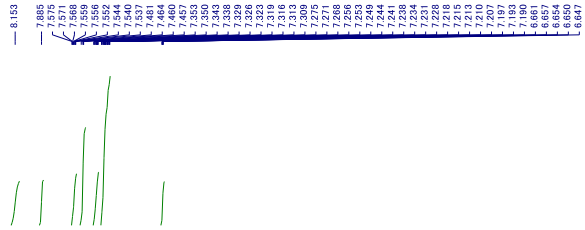

7.665
7.660
7.653
7.648
7.333
7.316
OCF3
F3CO
32
8.17
4.00
f1 (ppm)

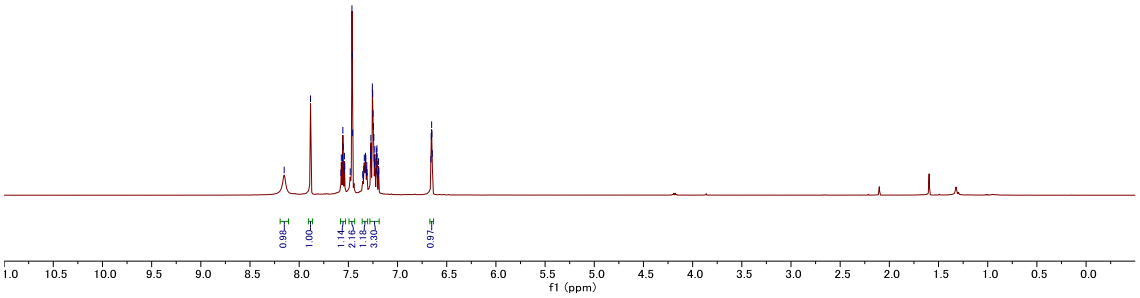

148.80
139.22
139.12
128.34
127.57
121.54
121.30
119.50
OCF3
F3CO
32
f1 (ppm)

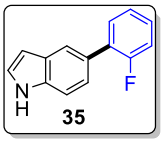

-57.729
OCF3
F3CO
32


10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −220 −230 −240 −250 −260 −270 −280 −290 −300 −310
f1 (ppm)

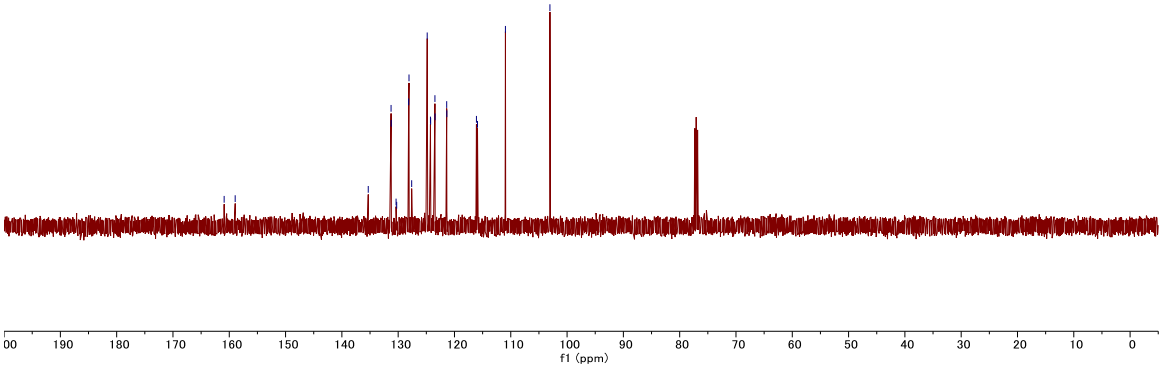

N
H
F
35

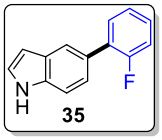

8.153
7.885
7.575
7.571
7.568
7.559
7.556
7.552
7.544
7.540
7.537
7.481
7.464
7.460
7.457
7.353
7.350
7.343
7.338
7.329
7.326
7.323
7.319
7.316
7.313
7.309
7.275
7.271
7.268
7.256
7.253
7.249
7.244
7.241
7.238
7.234
7.231
7.228
7.218
7.215
7.213
7.210
7.207
7.197
7.193
7.190
7.661
6.657
6.654
6.650
6.647


0.98
1.00
1.14
2.16
1.18
3.35
0.97
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

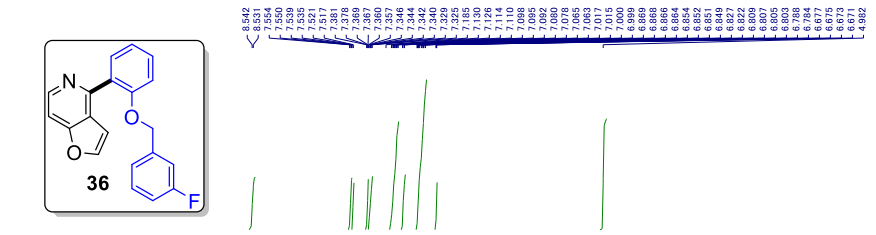

N
H
F
35

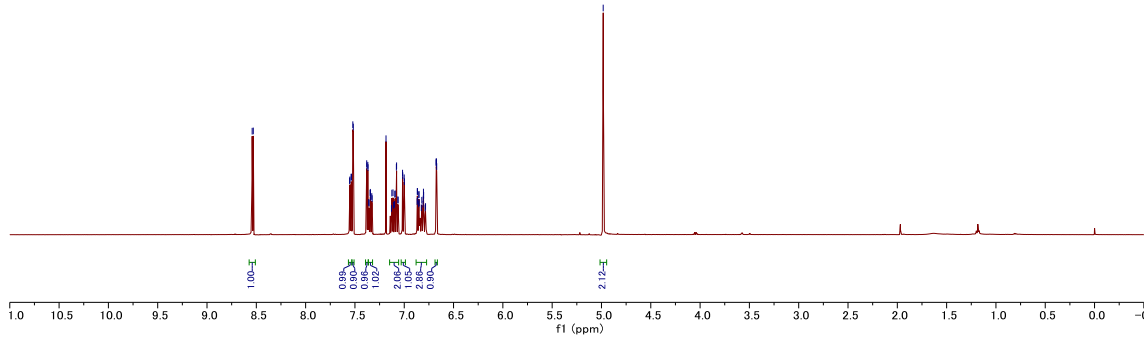

160.91
158.95
135.31
131.26
131.23
130.37
130.27
128.14
128.08
127.80
124.84
124.27
124.24
123.47
123.45
121.38
121.36
116.10
115.91
110.95
103.05

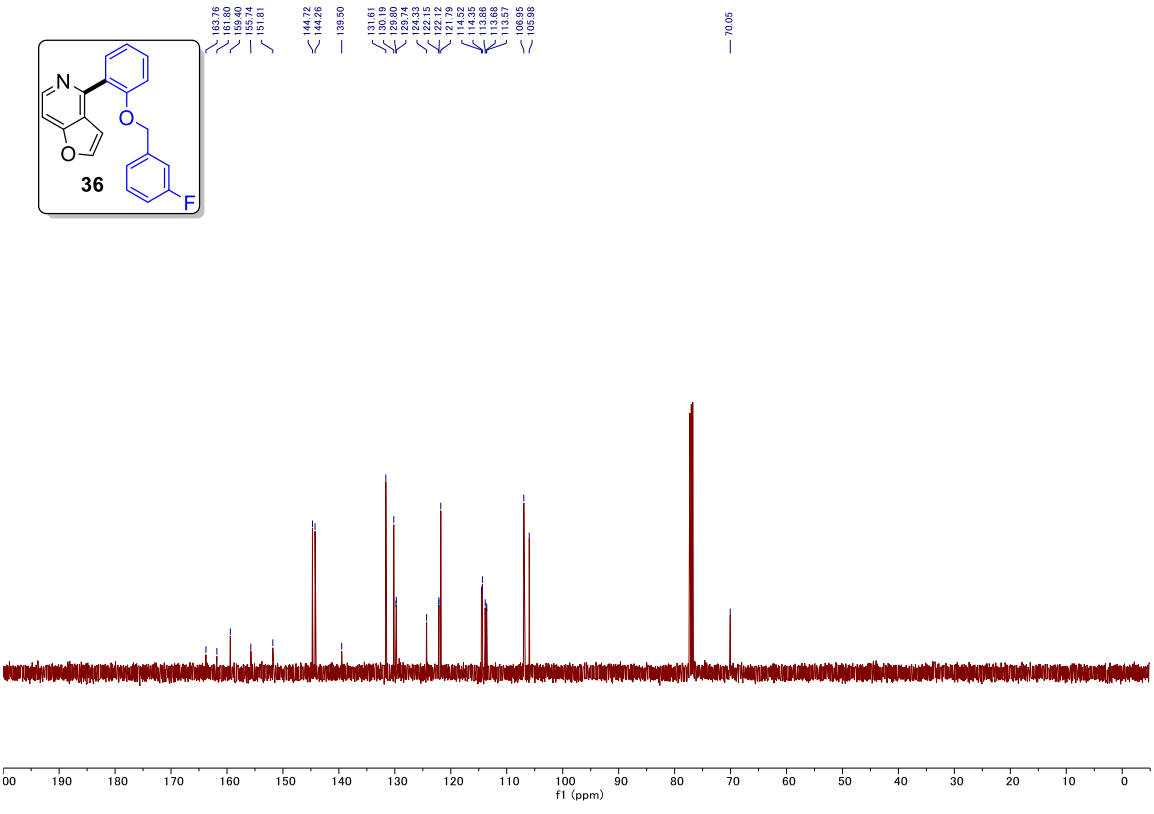

00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

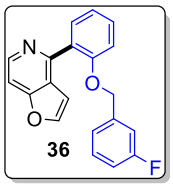

N
H
F
35

-118.177
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270 -280 -290 -300 -310
f1 (ppm)


8.542
8.531
7.554
7.550
7.539
7.535
7.521
7.517
7.383
7.378
7.369
7.367
7.360
7.357
7.346
7.344
7.342
7.340
7.329
7.325
7.185
7.130
7.126
7.114
7.110
7.098
7.095
7.092
7.080
7.078
7.065
7.063
7.017
7.015
7.000
6.999
6.889
6.888
6.886
6.884
6.854
6.852
6.851
6.849
6.827
6.822
6.809
6.807
6.805
6.803
6.788
6.784
6.677
6.675
6.673
6.671
4.982
36
N
O
O
F

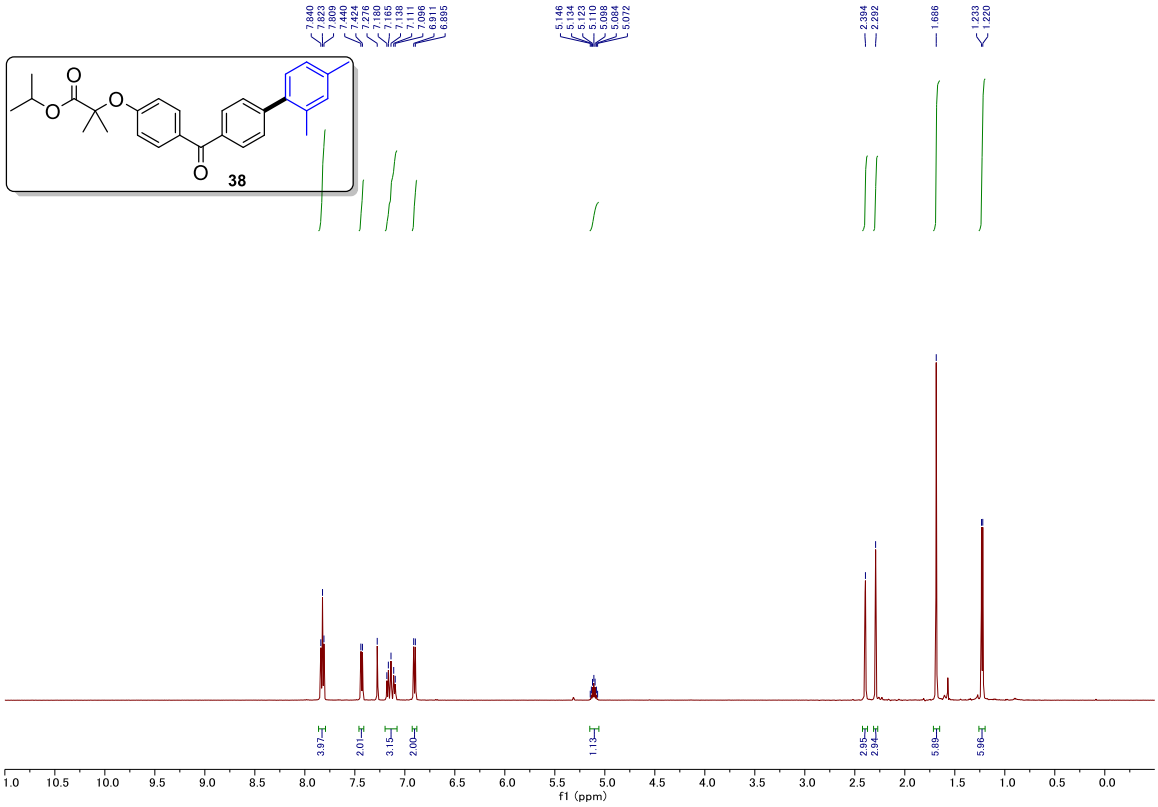

1.00
0.99
0.96
0.96
1.02
2.06
1.05
1.00
0.96
2.12
f1 (ppm)

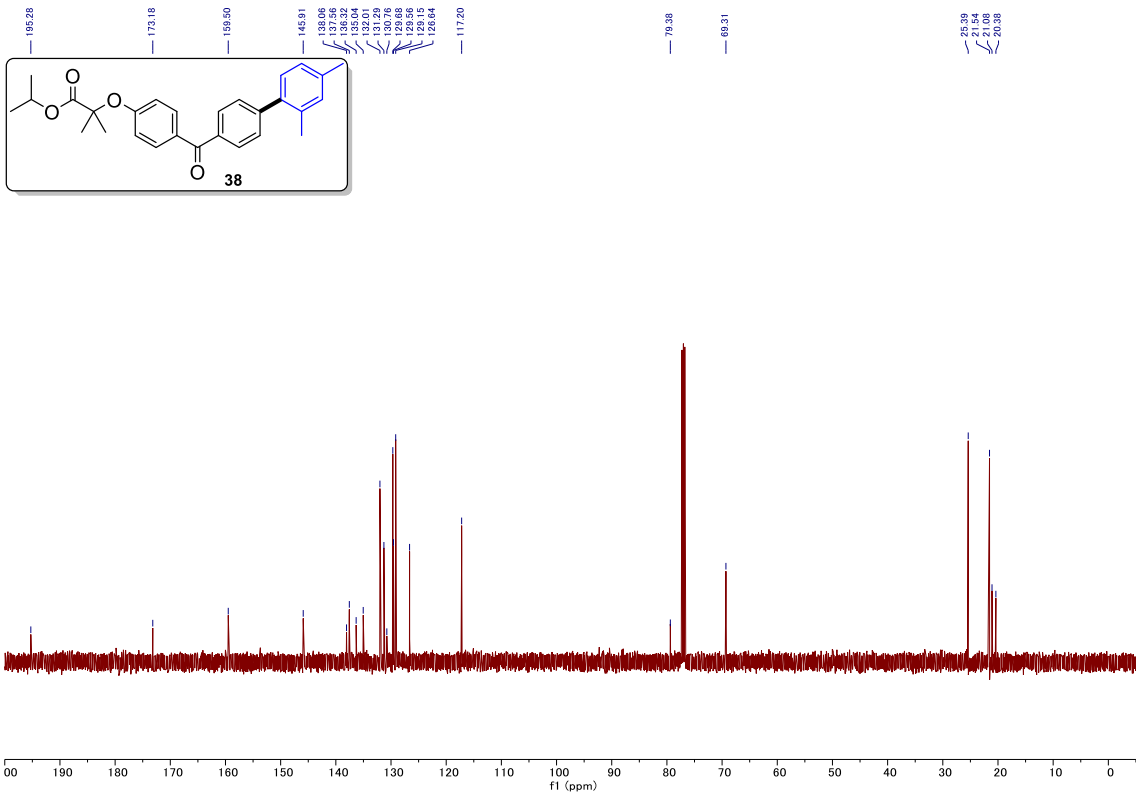

163.76
161.80
159.40
155.74
151.81
144.72
144.26
139.50
131.61
130.19
129.80
129.74
124.33
122.15
122.12
121.79
114.52
114.35
113.86
113.68
113.57
106.95
105.98
70.05
36
N
O
O
F
f1 (ppm)

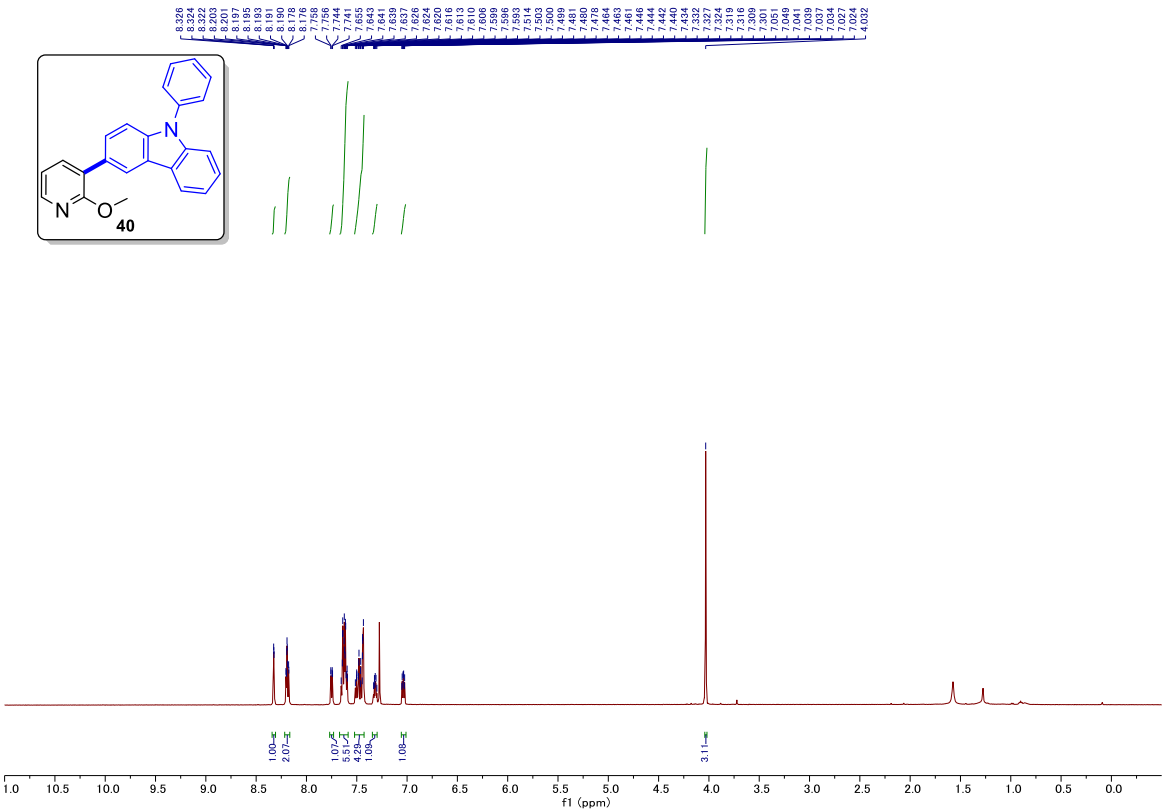

N
O
O
F

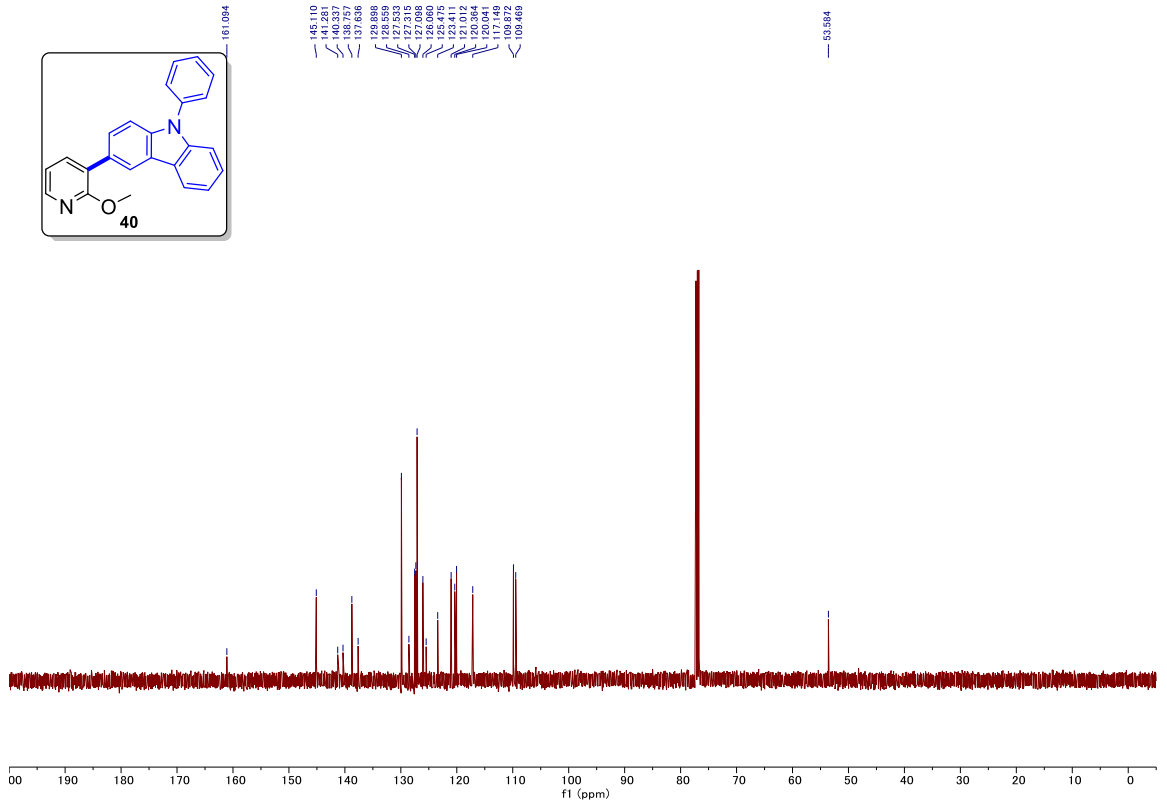
36

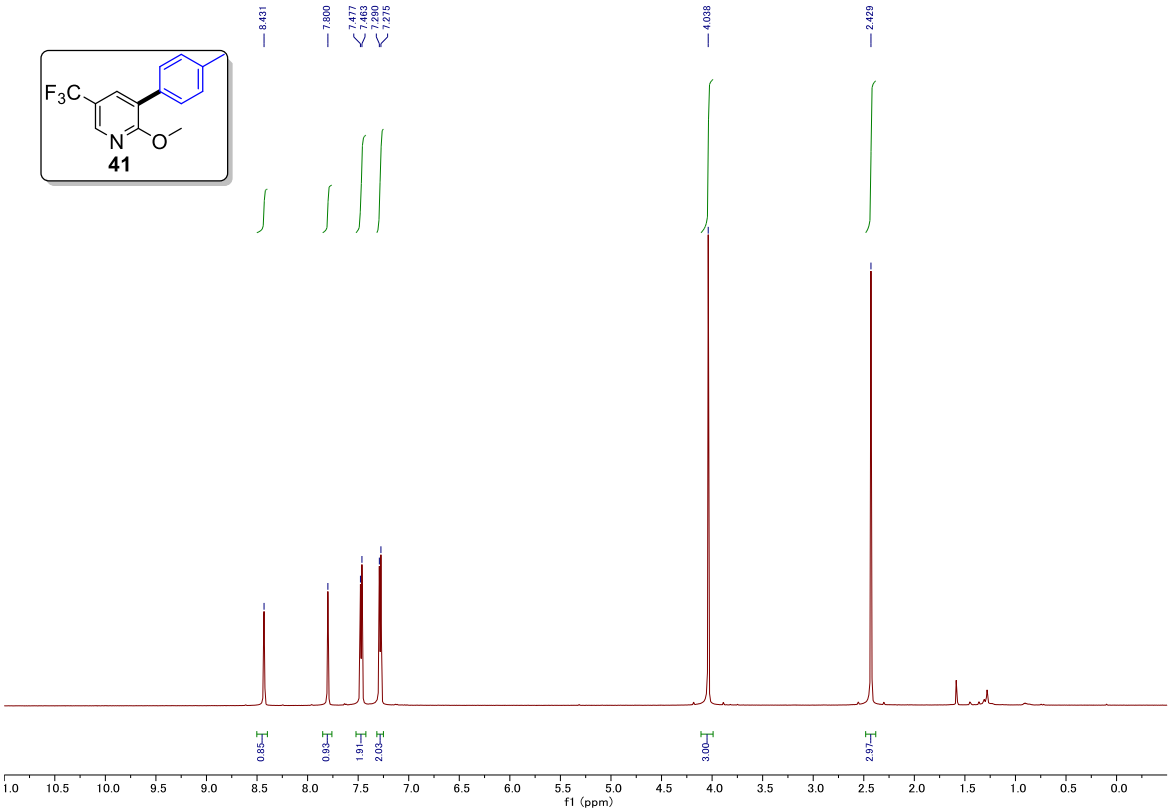
−113.125
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −220 −230 −240 −250 −260 −270 −280 −290 −300 −310
f1 (ppm)

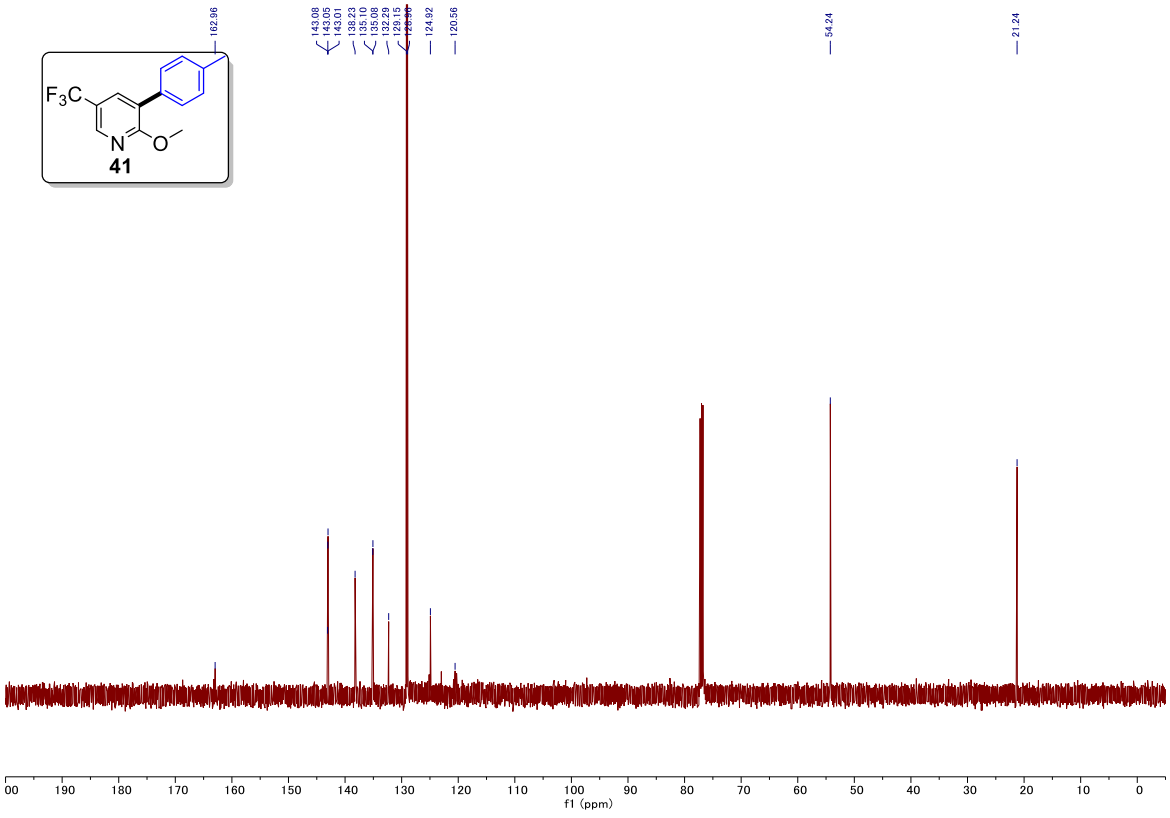

7.840
7.823
7.809
7.440
7.424
7.226
7.180
7.165
7.138
7.111
7.066
6.911
6.895
5.146
5.134
5.123
5.110
5.098
5.084
5.072
2.394
2.292
1.686
1.233
1.220
38
3.97
2.01
3.15
2.00
1.13
2.95
2.94
5.89
5.96
f1 (ppm)

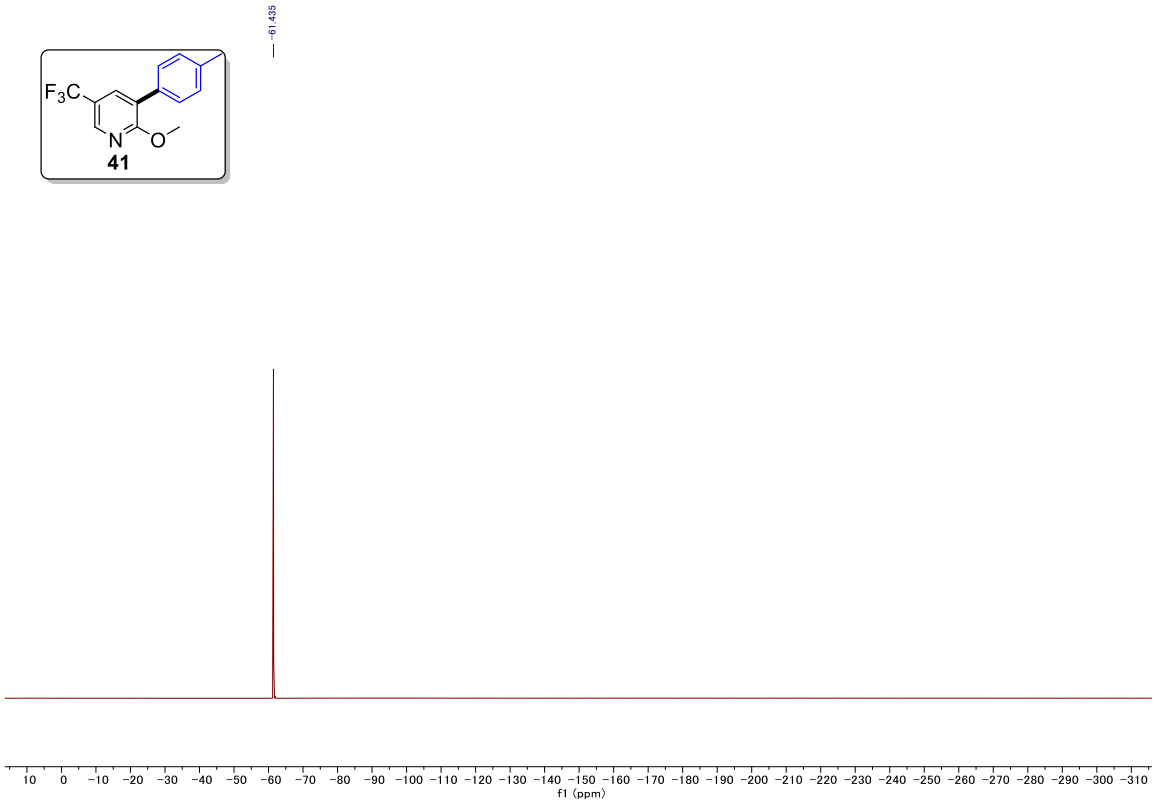

195.28
173.18
159.50
145.91
138.06
137.56
136.32
135.04
132.01
131.29
130.76
129.68
129.56
129.15
126.64
117.20
79.38
69.31
25.39
21.54
21.08
20.38
38
f1 (ppm)

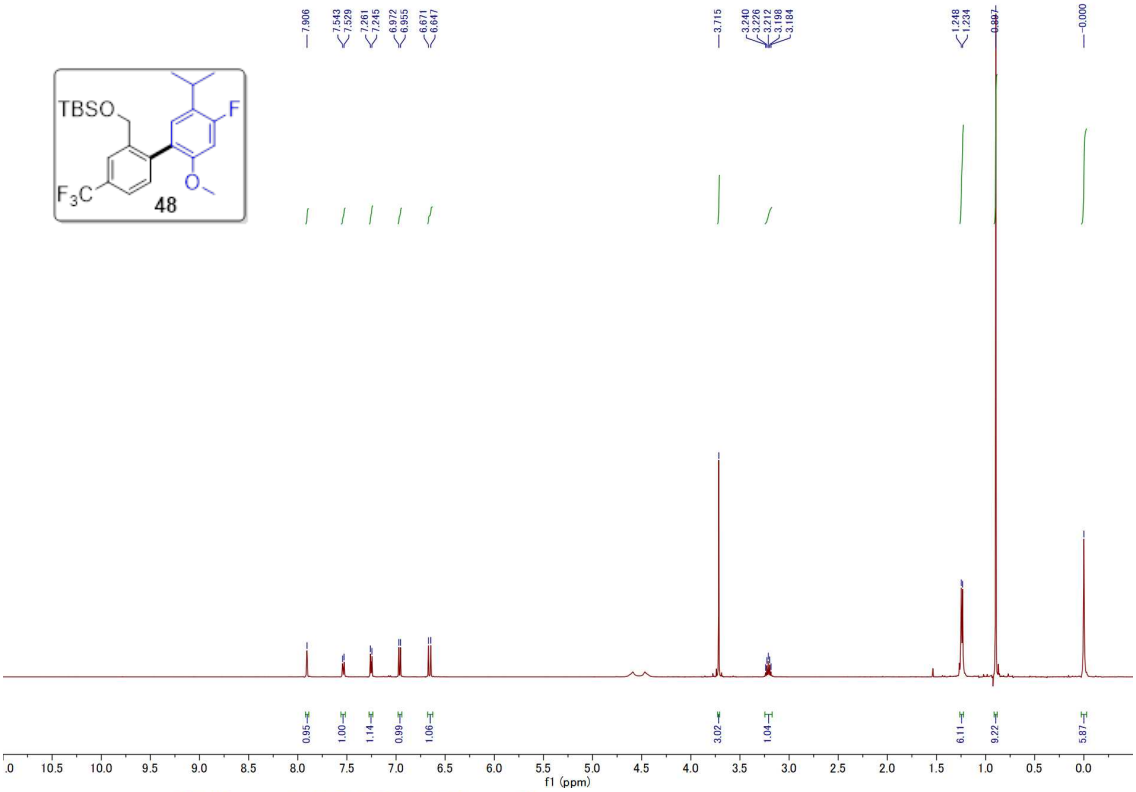

40
f1 (ppm)

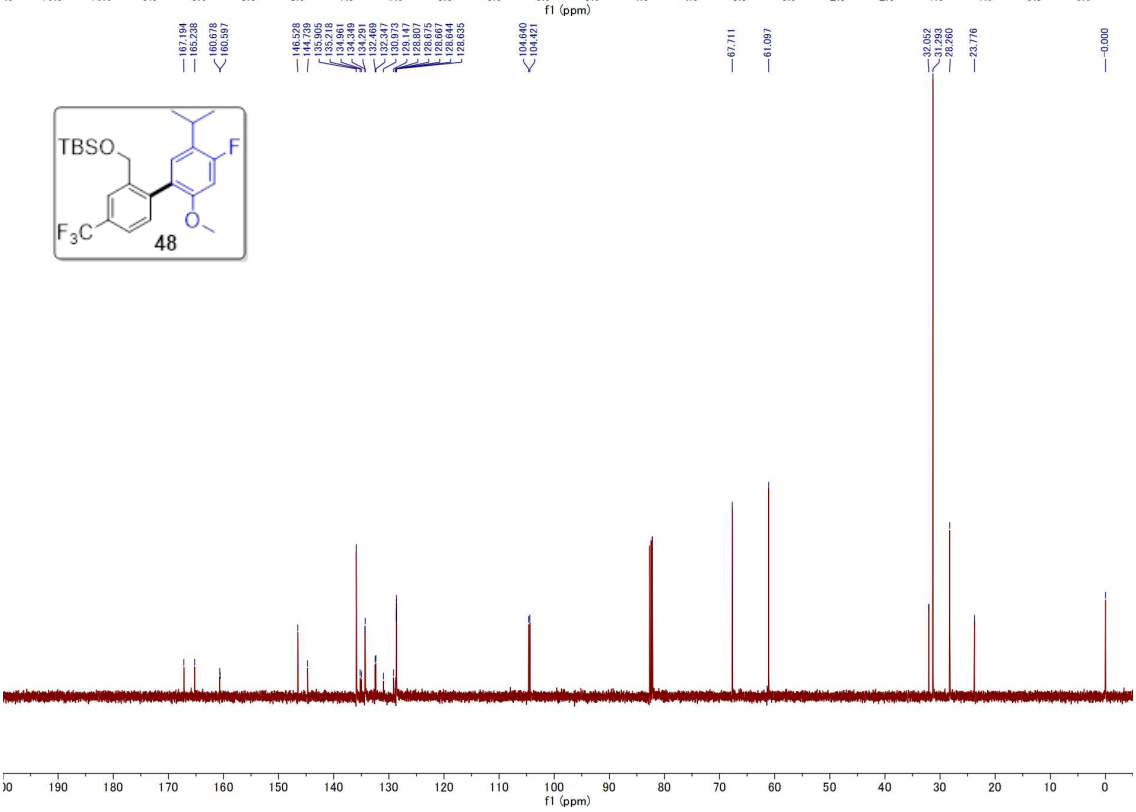

40
f1 (ppm)

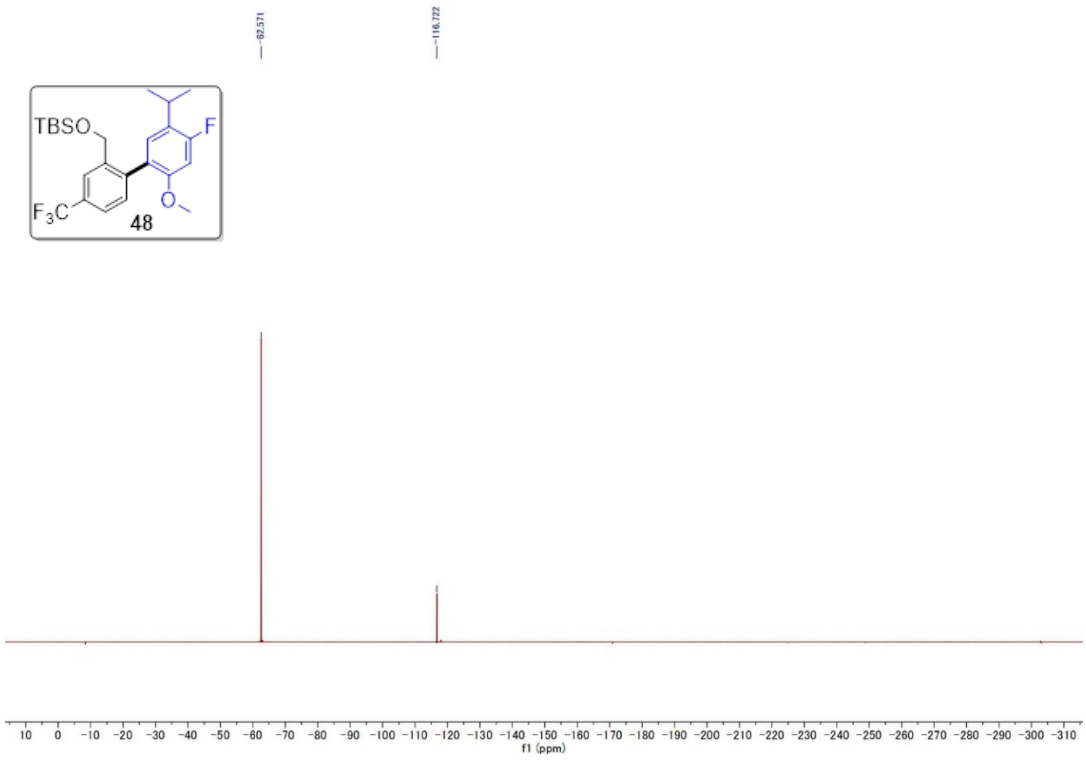

8.431
7.800
7.477
7.463
7.290
7.275
4.038
2.429
0.85
0.93
1.91
2.03
3.00
2.97
F3C
N
O
41
f1 (ppm)

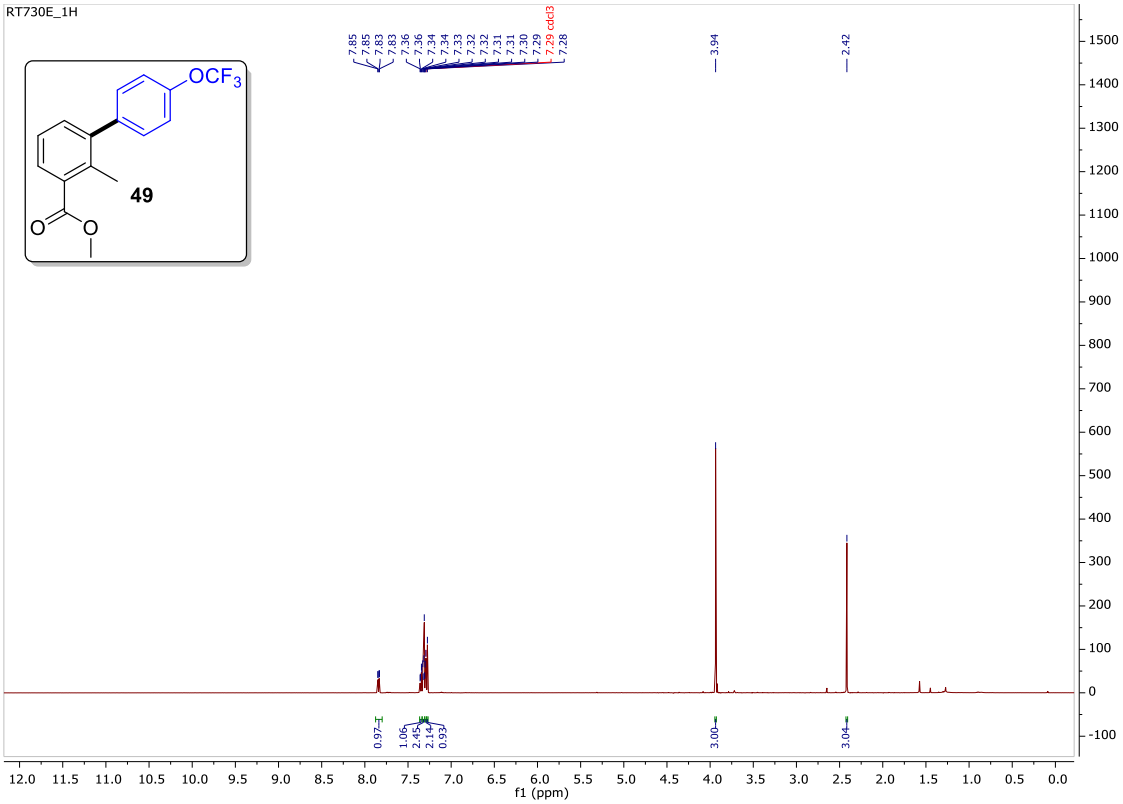

162.96
143.08
143.05
143.01
138.23
135.10
135.08
132.29
129.15
128.80
124.92
120.56
54.24
21.24
F3C
N
O
41
f1 (ppm)

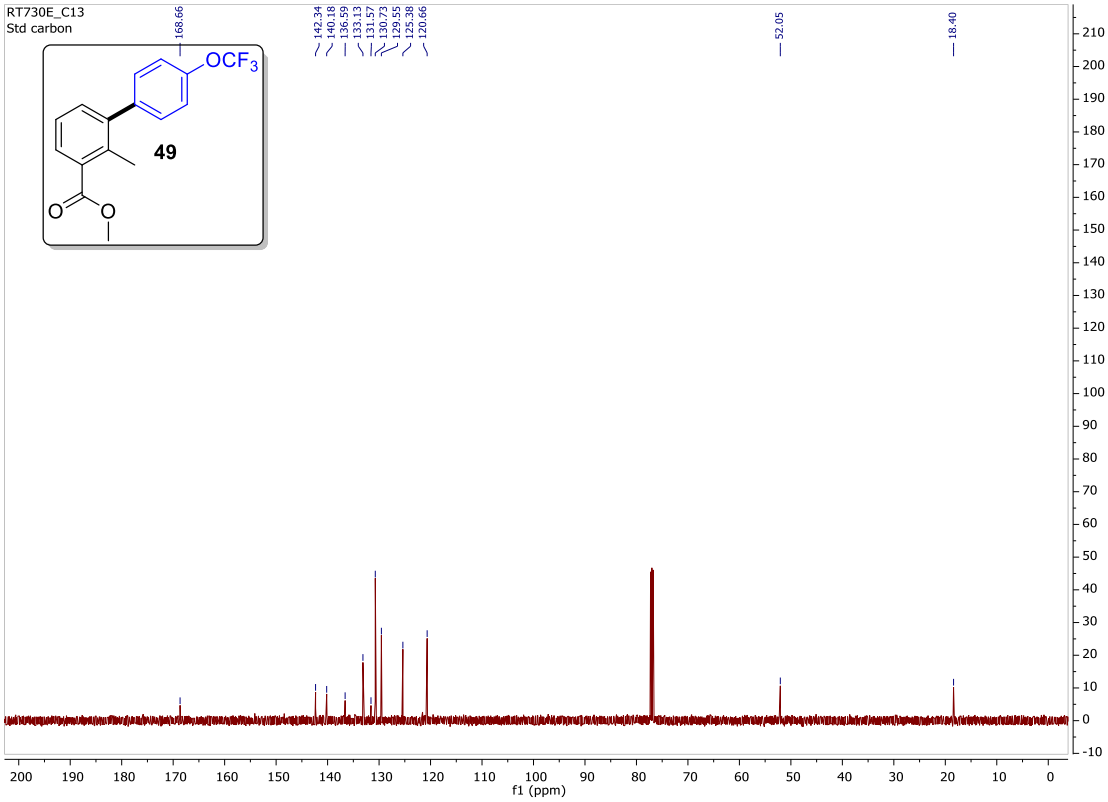

-61.435
F3C
N
O
41
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270 -280 -290 -300 -310
f1 (ppm)

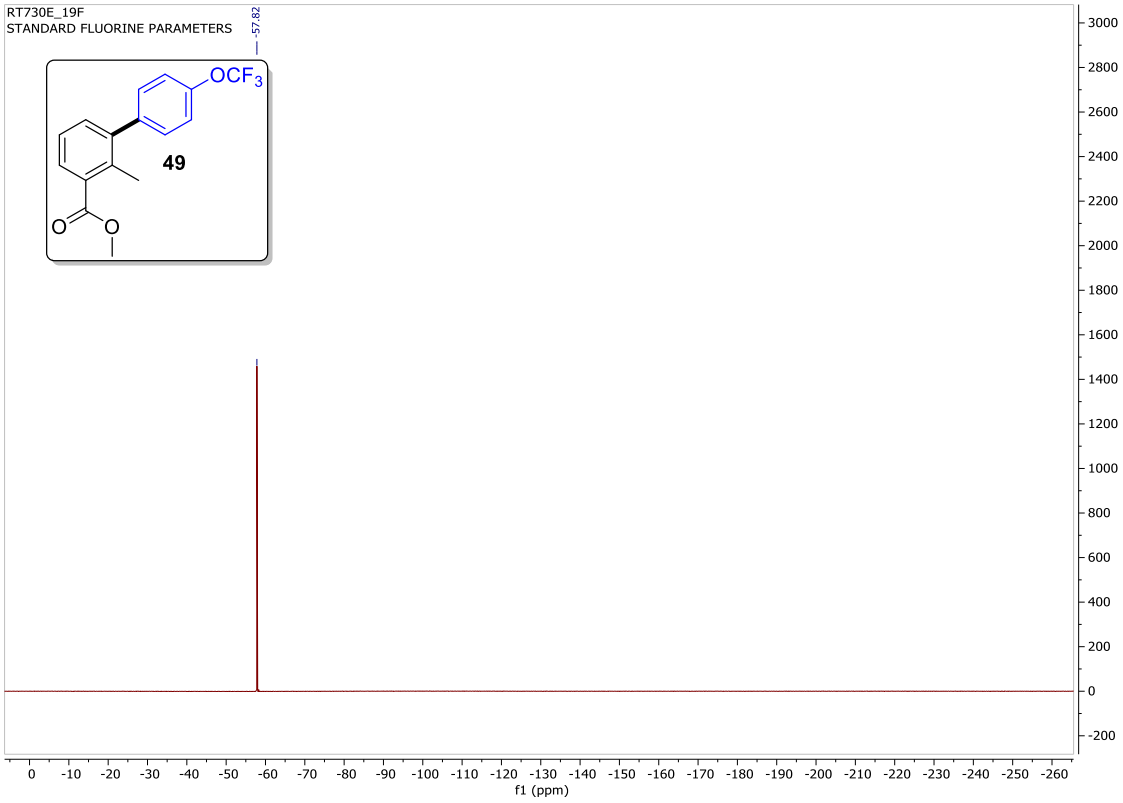

TBSO
F
F3C
O
48
f1 (ppm)

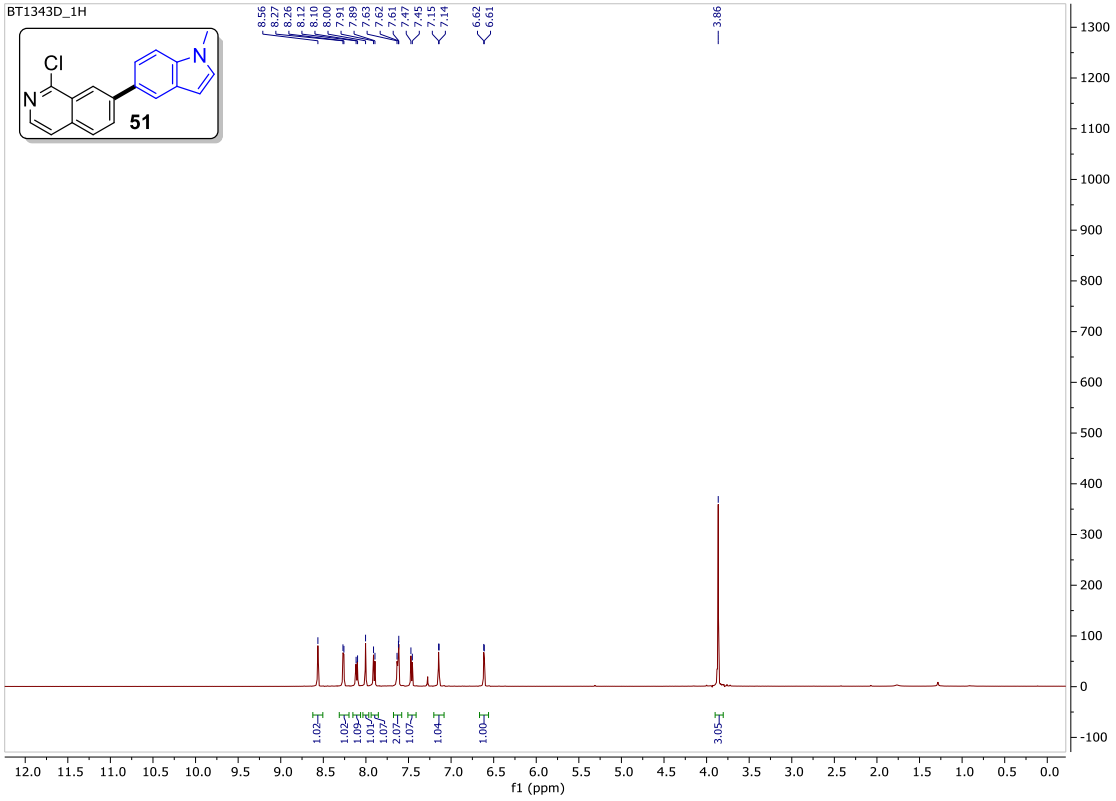

TBSO
F
F3C
O
48
f1 (ppm)

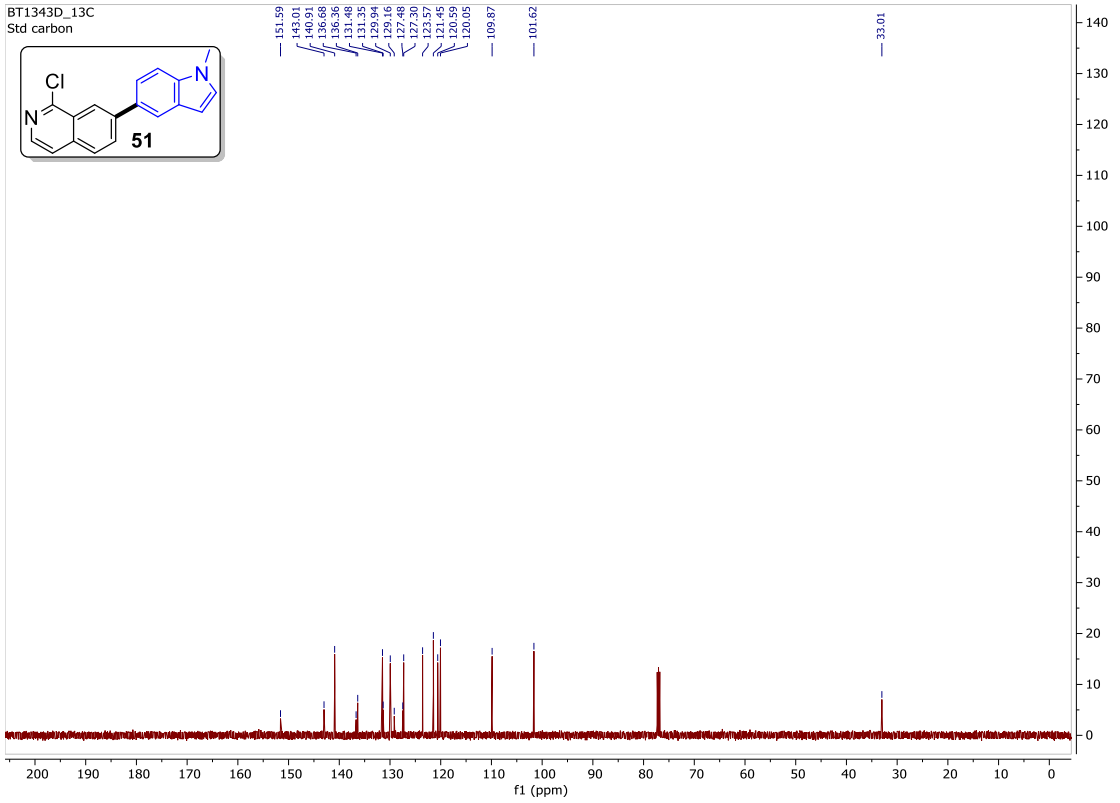

-62.571
-116.722
TBSO
F
F3C
O
48
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270 -280 -290 -300 -310
f1 (ppm)

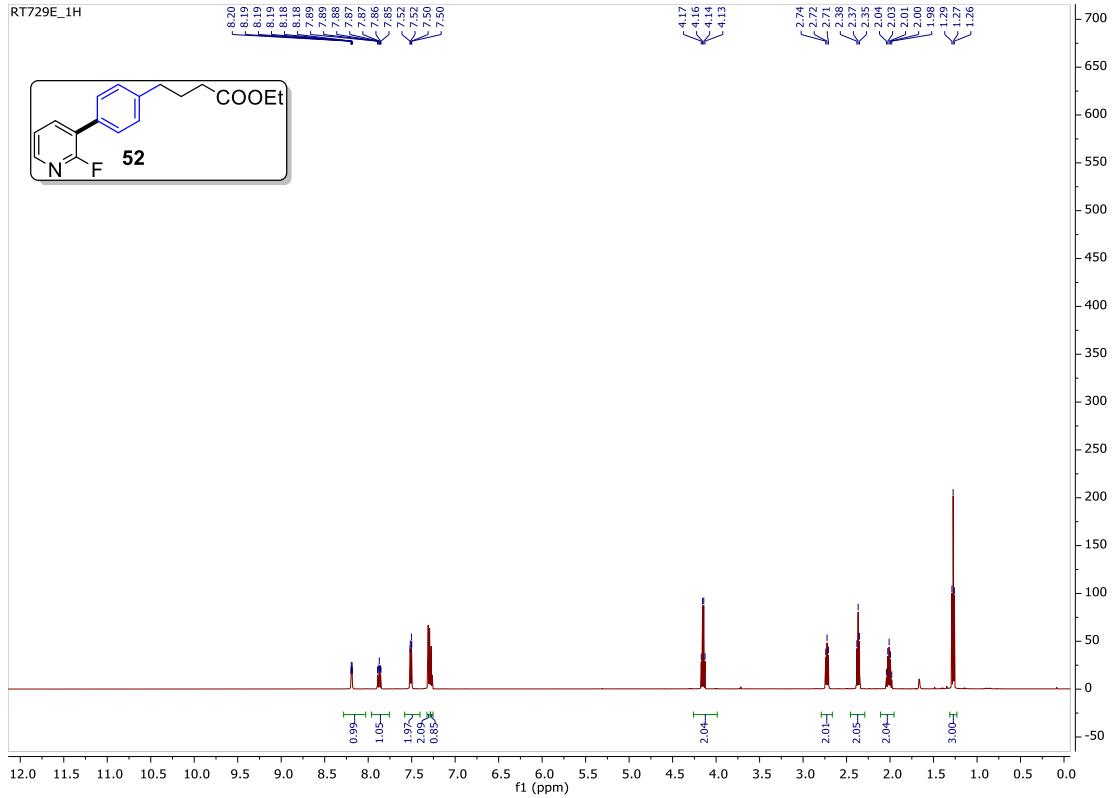

RT730E_1H
OCF3
49
O
O
7.85
7.85
7.83
7.83
7.36
7.36
7.34
7.34
7.33
7.32
7.32
7.31
7.31
7.30
7.29
7.29 cdcl3
7.28
3.94
2.42
0.97
1.06
2.45
2.14
0.93
3.00
3.04
f1 (ppm)

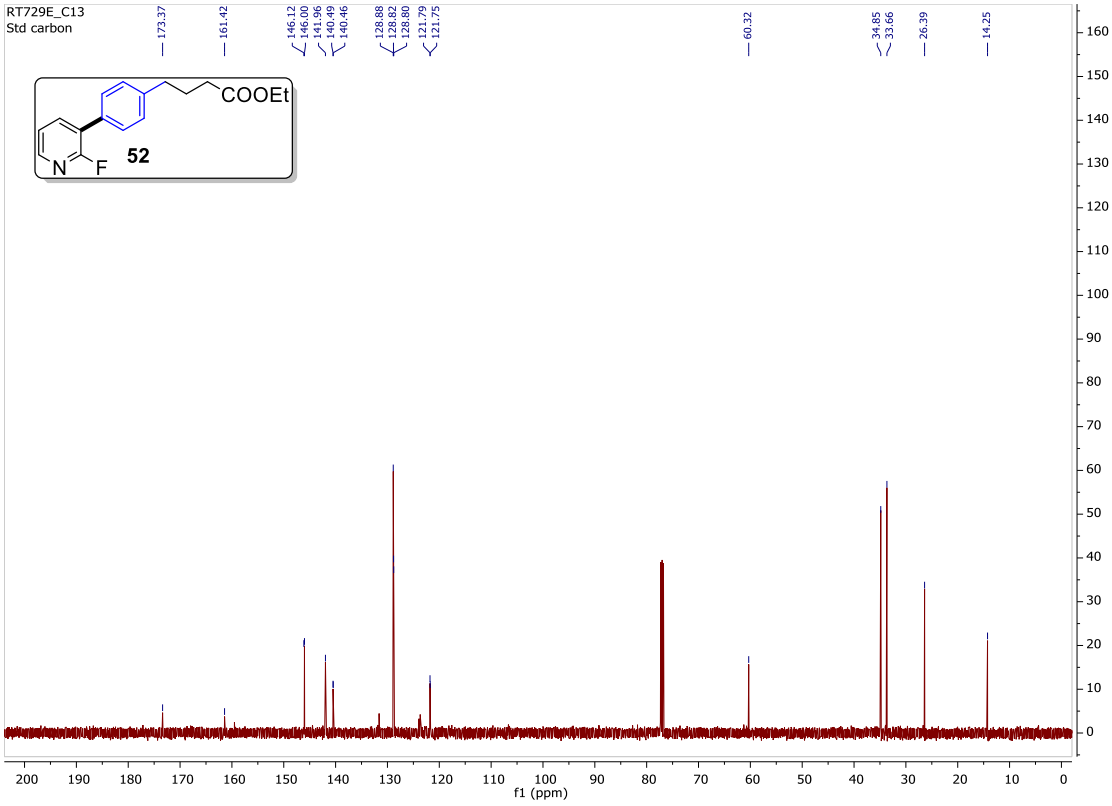

RT730E_C13
Std carbon
OCF3
49
O
O
168.66
142.34
140.18
136.59
133.13
131.57
130.73
129.55
125.38
120.66
52.05
18.40
f1 (ppm)

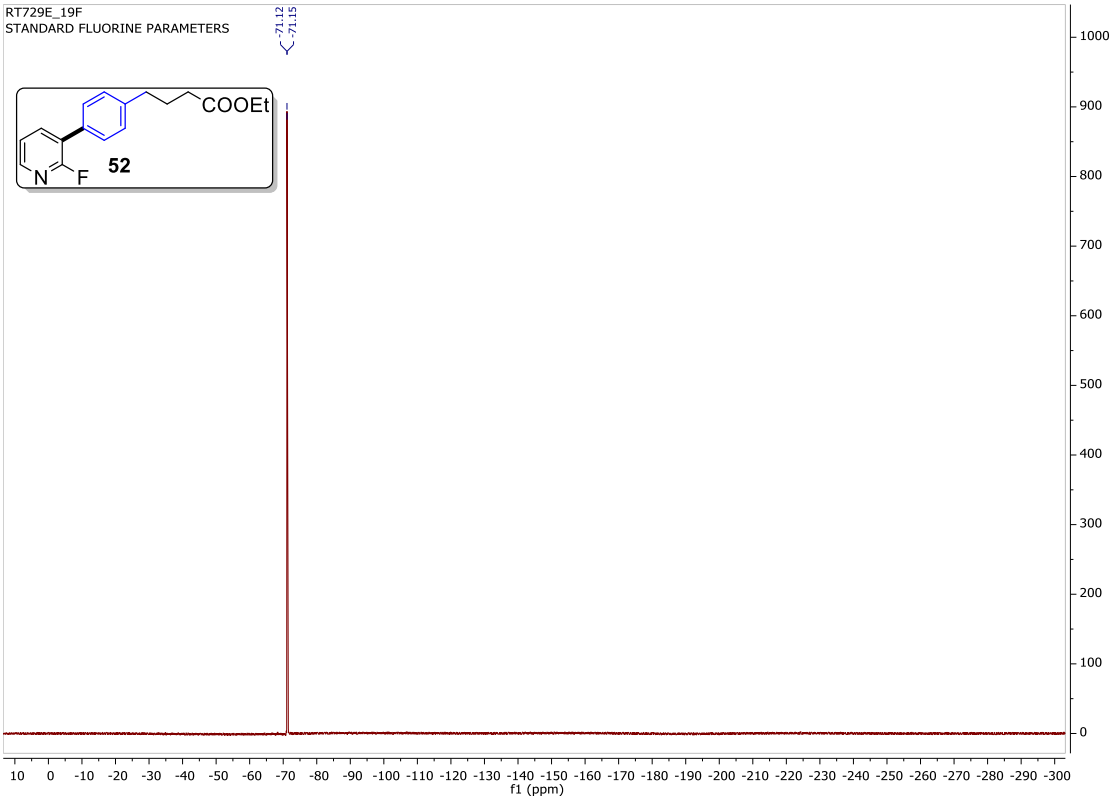

RT730E_19F
STANDARD FLUORINE PARAMETERS
-57.82
OCF3
49
O
O
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260
f1 (ppm)

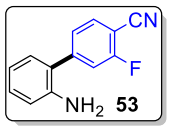

BT1343D_1H
Cl
N
N
51
8.56
8.27
8.26
8.12
8.10
8.00
7.91
7.89
7.63
7.62
7.61
7.47
7.45
7.15
7.14
6.62
6.61
3.86
1.02
1.02
1.09
1.01
1.07
2.07
1.07
1.04
1.00
3.05
f1 (ppm)

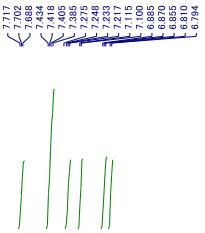

BT1343D_13C
Std carbon
Cl
N
N
51
151.59
143.01
140.91
136.68
136.36
131.48
131.35
129.94
129.16
127.48
127.30
123.57
121.45
120.59
120.05
109.87
101.62
33.01
f1 (ppm)

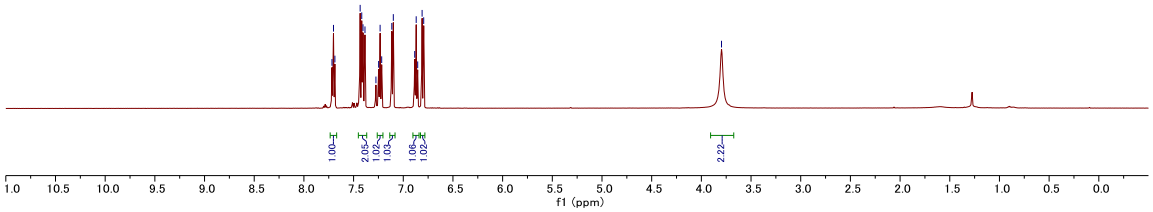

RT729E_1H
COOEt
N
F
52
f1 (ppm)

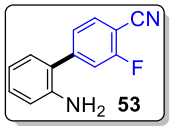

RT729E_C13
Std carbon
COOEt
N
F
52
f1 (ppm)


RT729E_19F
STANDARD FLUORINE PARAMETERS
-71.12
-71.15
COOEt
N
F
52
1000
900
800
700
600
500
400
300
200
100
0
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270 -280 -290 -300
f1 (ppm)

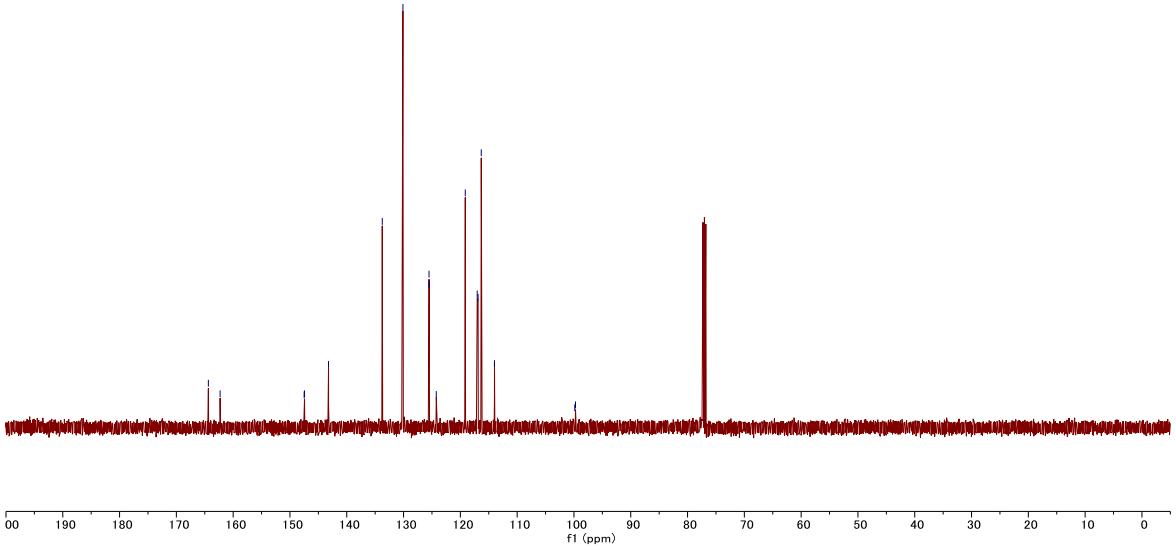

CN
F
NH2 53

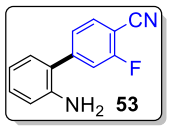

7.717
7.702
7.688
7.434
7.418
7.405
7.385
7.275
7.248
7.233
7.217
7.115
7.100
6.885
6.870
6.855
6.810
6.794
3.797


1.00
2.05
1.02
1.03
1.06
1.02
2.22
f1 (ppm)

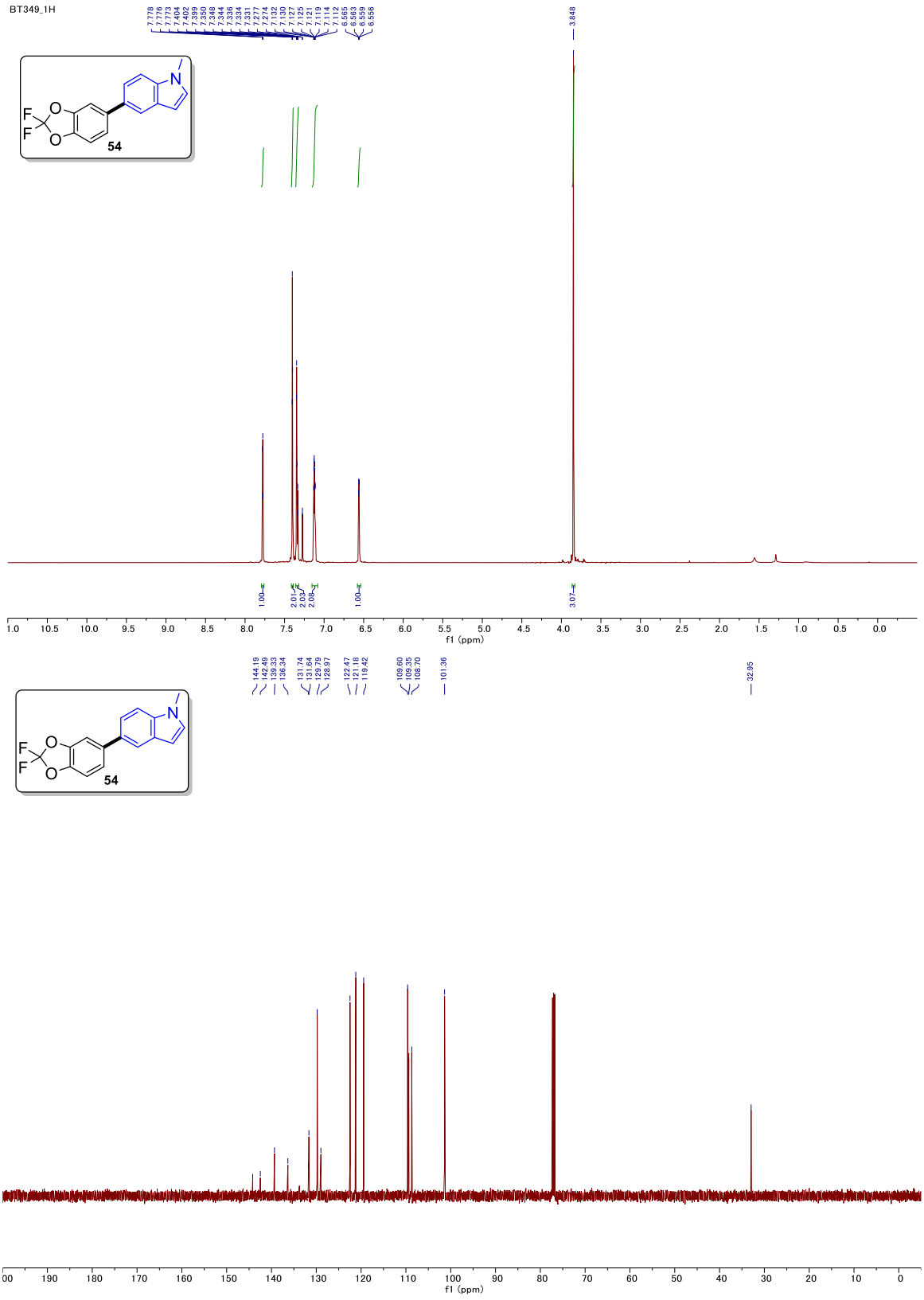

CN
F
NH2 53

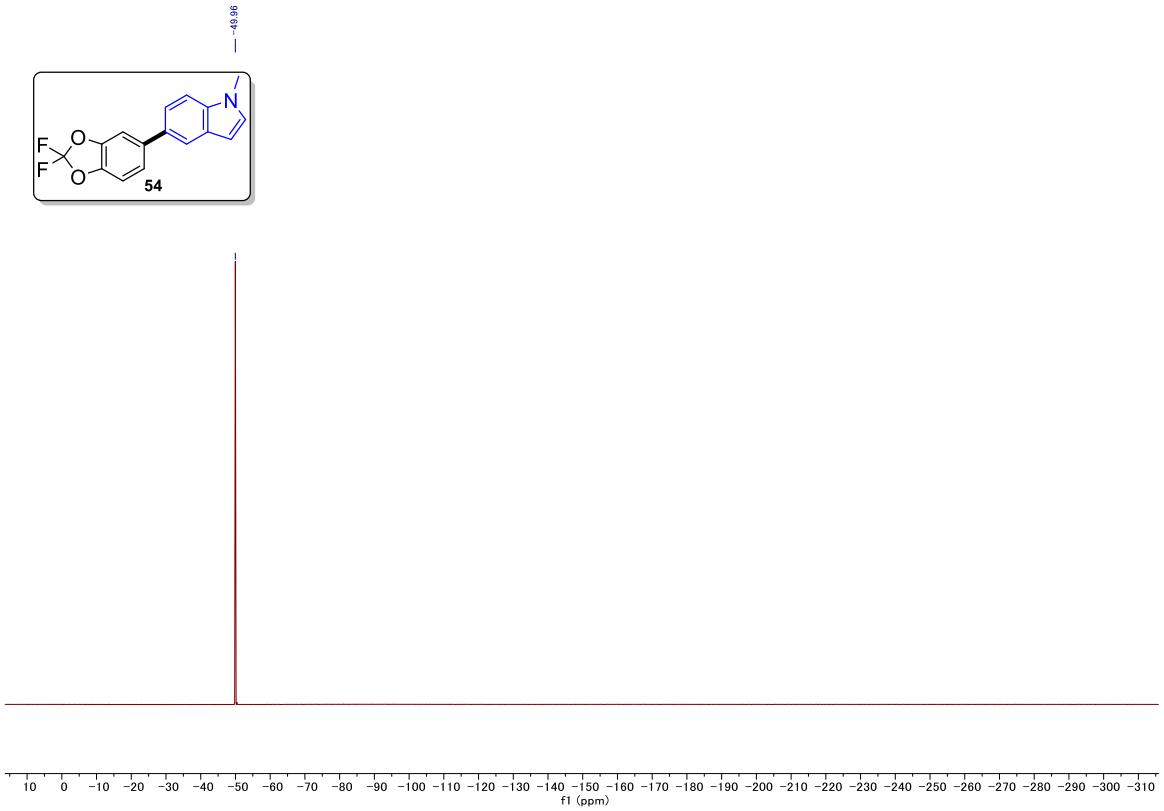

164.366
162.300
147.502
147.437
143.214
133.751
130.112
125.517
125.491
124.941
119.135
117.034
116.878
116.321
113.994
99.853
99.728

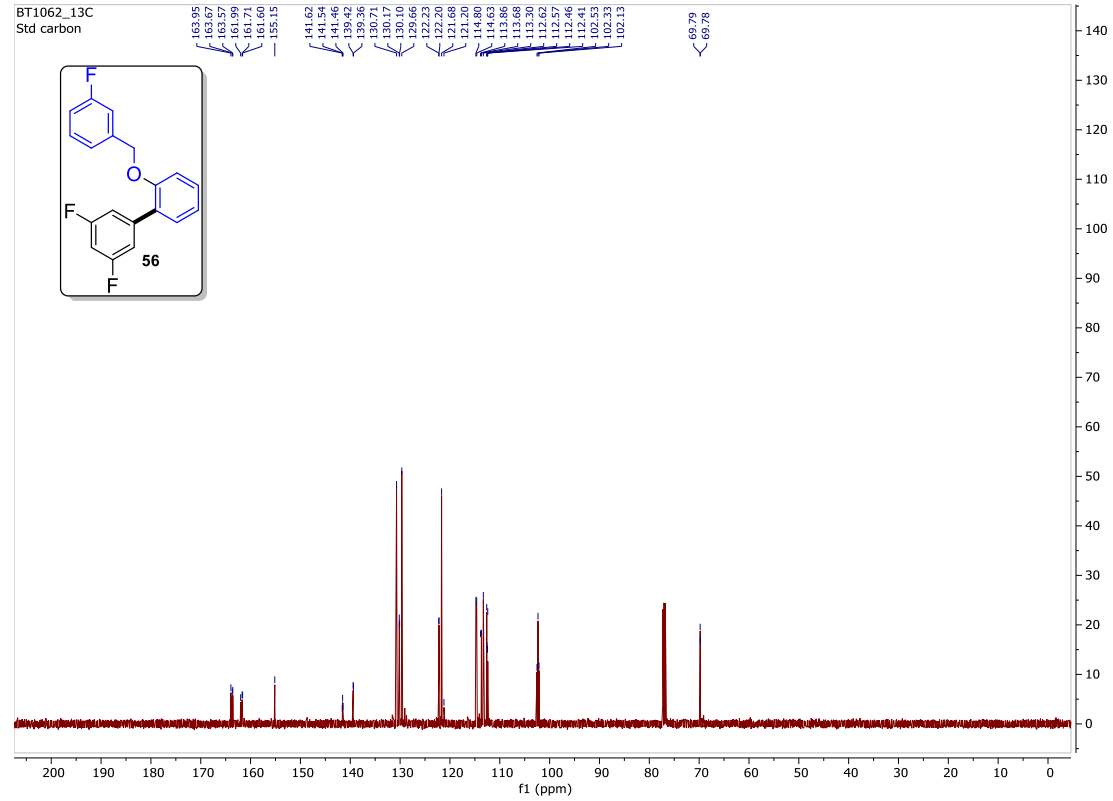

f1 (ppm)

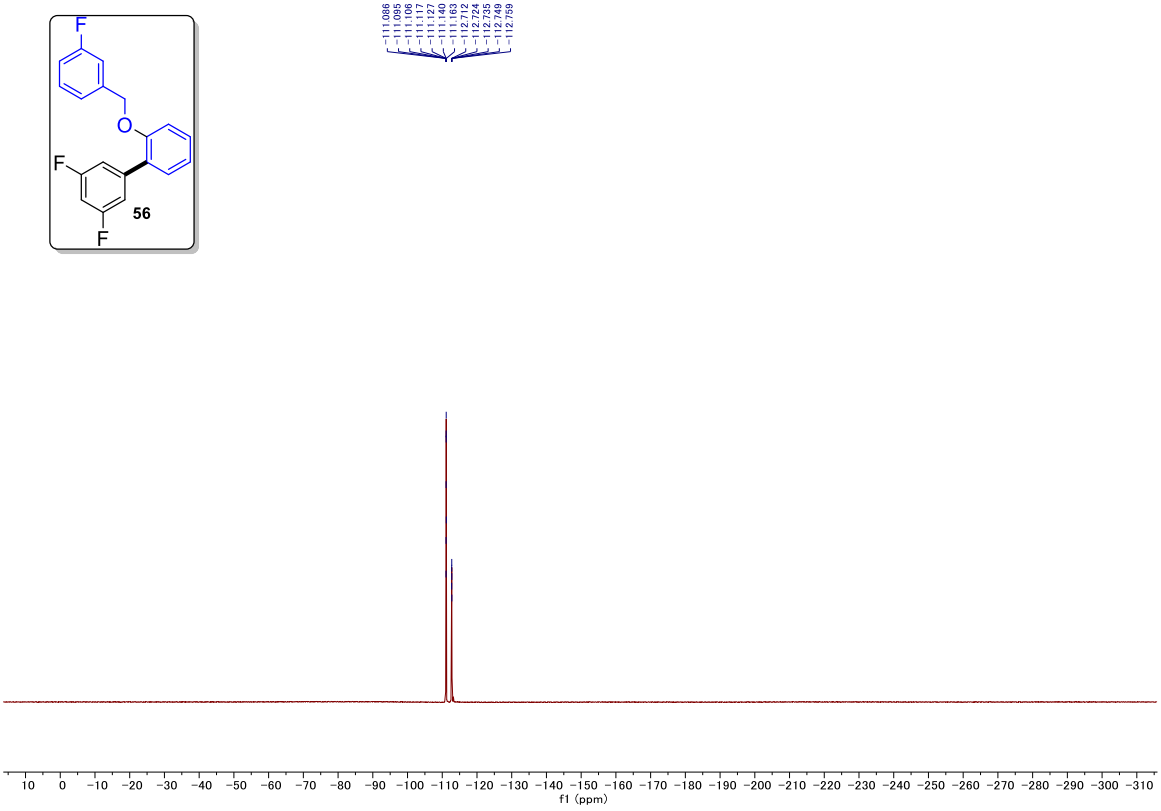

CN
F
NH2
53

-105.852
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270 -280 -290 -300 -310
f1 (ppm)


BT349_1H
54
f1 (ppm)
54
f1 (ppm)


-49.96
F
F
O
O
N
54
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270 -280 -290 -300 -310
f1 (ppm)


BT1062_13C
Std carbon
163.95
163.67
163.57
161.99
161.71
161.60
155.15
141.62
141.54
141.46
139.42
139.36
130.71
130.17
130.10
129.66
122.23
122.20
121.68
121.20
114.80
114.63
113.86
113.68
113.30
112.62
112.57
112.46
112.41
102.53
102.33
102.13
69.79
69.78
F
O
F
F
56
f1 (ppm)


−111.086
−111.095
−111.105
−111.117
−111.127
−111.140
−111.163
−112.712
−112.724
−112.735
−112.749
−112.759
F
O
F
F
56
f1 (ppm)