Pd-Catalyzed Synthesis of Deuterated Olefins from (Hetero)Arenes and Ketones via Cross-Coupling Approach

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1.0 General information

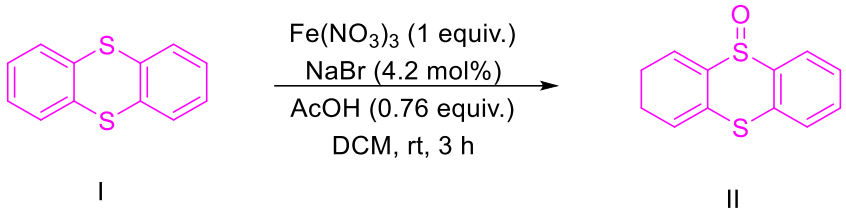
All chemicals were purchased from Aldrich, TCI, GLR Innovations, BLD Pharm, and Avra synthesis in analytical grade and were used as supplied. All reaction were carried out under inert atmosphere using oven dried reaction tubes. Dry solvents were prepared by distilling over sodium metal with benzophenone, Calcium hydride and stored over molecular sieves 4 Å under N_2 atmosphere. All compounds were purified by column chromatography using silica gel (60-120 mesh). Thin layer chromatography was performed on 0.25 mm thick aluminum-baked silica gel plates purchased from Merck and visualized with ultraviolet (λ = 254 nm). ^{1}H, $^{13}C\{^{1}H\}$, ^{19}F NMR and ^{2}H spectra were recorded on JEOL ECZ500R/S1 (500, 126, 471, 77 MHz respectively) instrument. ^{1}H signals are referenced to residual $CHCl_3$ at 7.26 ppm. ^{13}C signals are referenced to $CDCl_3$ at 77.16 ppm. IR spectra were recorded on Bruker Alpha II compact FT-IR spectrophotometer (only characteristic IR peaks were reported). High resolution mass spectra quadrupole time-of-flight (HRMS-QTOF) was obtained in ESI mode. The single-crystal XRD data was collected and integrated using a Bruker SMART APEX CCD diffractometer with a Mo-Kα (λ = 0.71073 Å) sealed tube. Melting point were recorder on OptiMelt Automated Melting Point System.

2.0 Synthesis of starting materials

2.1 Synthesis of aryl thianthrenium salts **1**

Step 1:

Oxidation of thianthrene (TT) **I** was performed according to the reported procedure.[1]

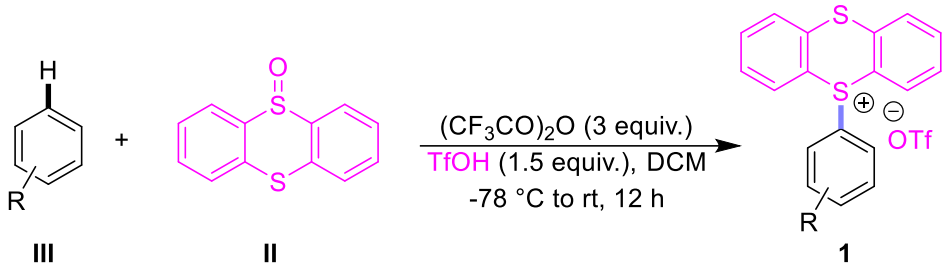


I II

All the aryl thianthrenium salts **1** were prepared according to the reported procedure.[1]

Step 2:

Method 1:

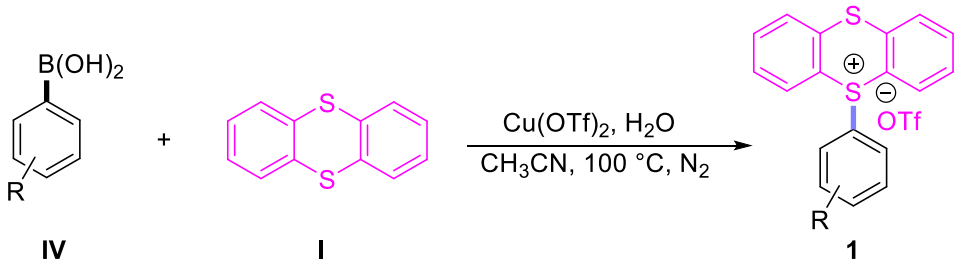


III II 1

Under an ambient atmosphere, 25 mL round bottom (RB) flask equipped with a magnetic stir bar was charged with arene **III** (3.0 mmol, 1 equiv.), thianthrene *S*-oxide (TTS) **II** (696.0 mg, 3.0 mmol, 1 equiv.) and MeCN (6.0 mL, 0.5 M). The reaction mixture was cooled to −78 °C and then $(CF_3CO)_2O$ (1.8 g, 9.0 mmol, 3 equiv.) was added slowly in a dropwise manner, followed by the addition of TfOH (450.0 mg, 4.5 mmol, 1.5 equiv.). The reaction mixture was warmed to room temperature and stirred for 12 h. The reaction was monitored by TLC, after completion of the reaction, the reaction mixture was diluted with DCM (5 mL), followed by addition of excess amount of DCM (30 mL) and extracted with saturated $NaHCO_3$ solution (20 mL), this procedure was repeated three times. The combined organic layers were dried over Na_2SO_4, filtered, and the solvent was removed under reduced pressure by using rotary evaporator. The residue was purified by column chromatography on silica gel eluting with DCM/MeOH (~30:1 (v/v)) to afford the aryl thianthrenium salt **1**.[1]

All thianthrenium salts except **1h**, **1n**, **1o**, **1p** and **1r** were prepared by method 1.

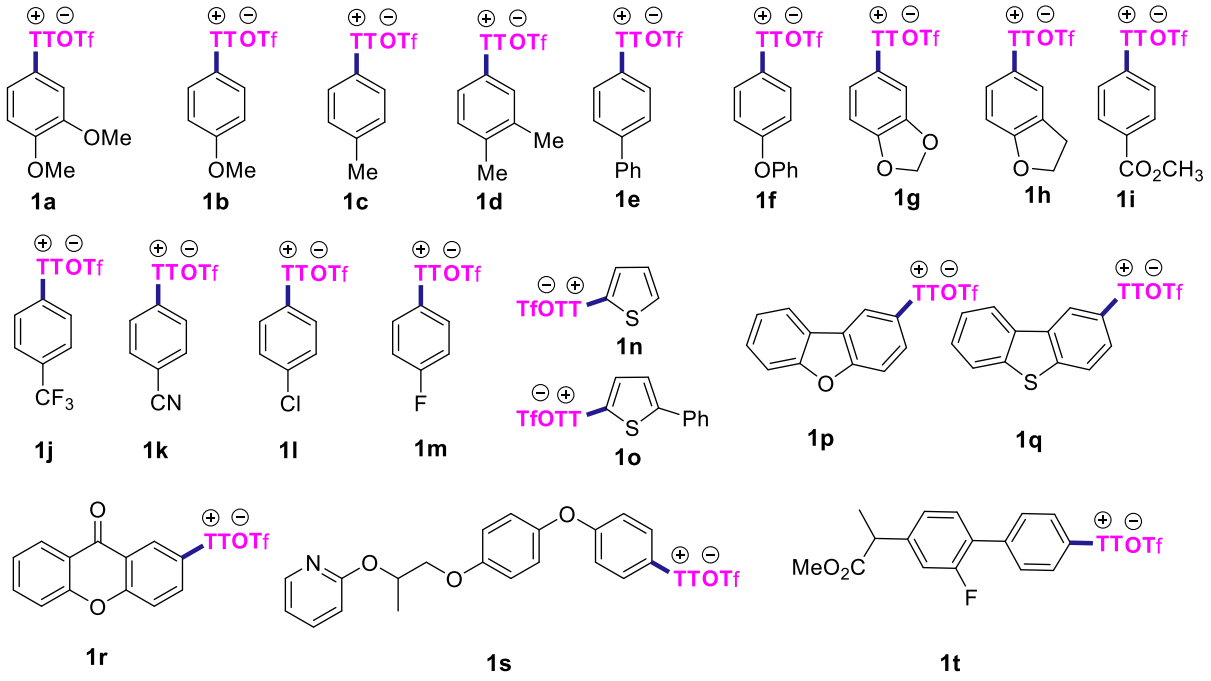
Method 2:



IV I 1

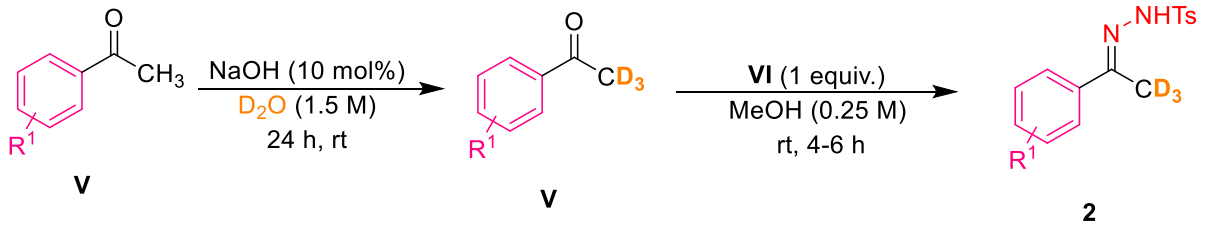
A 10 mL Schlenk tube were charged with aryl boron or heterocyclic boron **IV** (1.0 mmol, 1.0 equiv), **I** (324 mg, 1.5 mmol, 1.5 equiv) and the reaction tube was moved to a glove box (argon atmosphere), followed by the addition of $Cu(OTf)_2$ (724 mg, 2.0 mmol, 2.0 equiv). After removal of the Schlenk tube out of the glove box, H_2O (36 μL, 2.0 mmol, 2.0 equiv) and MeCN (1.0 mL) were added under a inert atmosphere. The reaction mixture was stirred at 100 °C for 3.0 hours. The reaction was monitored by TLC, after completion of reaction. Reaction mixture was cooled to room temperature, followed by the addition of ammonia solution (100 mL, 25%–28% solution in water), and the water phase was extracted with DCM (2 x 30 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was dissolved in DCM (4.0 mL), and precipitated by adding the solution into the stirring Et_2O (50 mL). The solid was collected by filtration to afford the arylthianthrenium salts **1** without further purification.[2]

Aryl thianthrenium salts **1i**, **1j**, **1k**, and **1m** were prepared by method 2.



2.2 Synthesis of deuterated *N*-tosylhydrazones

Method 3:



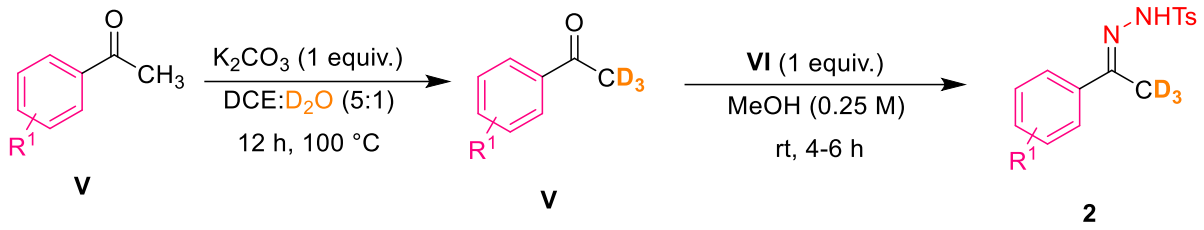
Under an ambient atmosphere, 25 mL round bottom (RB) flask was equipped with magnetic stir bar, acetophenone **V** (1.5 mmol, 1 equiv.) was added, followed by the addition of NaOH (6.0 mg, 10 mol%) under inert atmosphere. The RB flask was sealed with rubber septa and D_2O (1 mL) was added under

inert atmosphere. Then, the reaction was stirred at room temperature for 24 h. After completion of reaction, the reaction mixture was extracted with Et_2O (3x10 mL). The organic layers were dried over Na_2SO_4, filtered, and the solvent was removed under reduced pressure by using rotary evaporator and the crude deuterated acetophenone **V** was used for next step without any further purification.

To a stirred solution of tosylhydrazide **VI** (1.5 mmol, 1.0 equiv.) in MeOH (0.25 M), solution of corresponding acetophenone **V** in MeOH (0.5 M) was added. The reaction mixture was stirred at room temperature until complete conversion was observed by TLC. Solvent was removed under reduced pressure by rotary evaporator and crude compound was recrystallized with hot methanol to get the desired product.

Note: **2a**, **2b, 2c, 2d, 2f, 2g, 2h, 2j, 2o** and **2p** were prepared according to method 3.

Method 4:

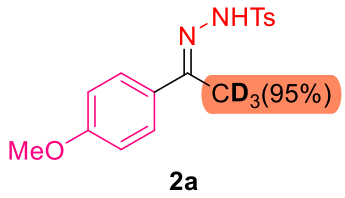


To a 25 mL round bottom (RB) flask equipped with a magnetic stir bar, acetophenone **V** (1.5 mmol, 1 equiv.) was added, followed by the addition of K_2CO_3 (20.7 mg, 1.0 equiv.) under inert atmosphere. Then, the mixture of solvent DCE:D_2O (5:1) (5 mL DCE: 1mL D_2O) was added to the reaction tube under inert atmosphere. Then, the reaction tube was sealed and reaction mixture was stirred at 100 °C for 12 hours. After completion of reaction, the reaction mixture was extracted with Et_2O (3*10 mL). The organic layers were dried over Na_2SO_4, filtered, and the solvent was removed under reduced pressure by using rotary evaporator and deuterated acetophenone **V** was used for next step without further purification.

To a stirred solution of tosylhydrazide **VI** (1.5 mmol, 1.0 equiv.) in MeOH (0.5 M), solution of corresponding acetophenone **V** in MeOH (0.5 M) was added. The reaction mixture was stirred at room temperature until complete conversion was observed by TLC. Solvent was removed under reduced pressure by rotary evaporator and crude compound was recrystallized with hot methanol to get the desired product.

Note: **2i, 2l, 2m** and **2n** were prepared according to method 4.

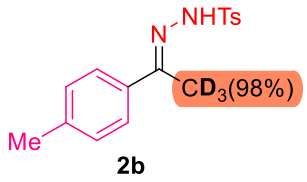
(*E*)-N'-(1-(4-methoxyphenyl)ethylidene-2,2,2-d3)-4-methylbenzenesulfonohydrazide (**2a**)



2a

2a was prepared according to the general procedure **4** in 85% (408.0 mg) isolated yield. White solid. **TLC** (30% ethyl acetate in hexanes): R_f = 0.4; **M.P.** 164-166 ºC; **IR** (KBr): 3204, 1597, 1572, 1511, 1398, 1338, 1310, 1302, 1247, 1184, 1165, 1091, 1038, 1012 cm^{-1}; **^{1}H NMR** (500 MHz, DMSO-d6): δ 10.34 (bs, 1H), 7.93 (d, J = 8.2 Hz, 2H), 7.81 (d, J = 8.2 Hz, 2H), 7.76 (d, J = 8.2 Hz, 2H), 7.40 (d, J = 8.2 Hz, 2H), 3.84 (s, 3H), 2.35 (s, 3H), 2.09 (s, 0.15H); **^{13}C NMR** (126 MHz, DMSO-d6): δ 165.8, 151.6, 143.4, 141.6, 136.1, 129.5, 129.2, 127.5, 126.2, 52.2, 21.5; **^{2}H NMR** (77 MHz, $CDCl_3$): δ 2.10; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{16}D_3N_2O_3S$ 322.1299, Found 322.1299.

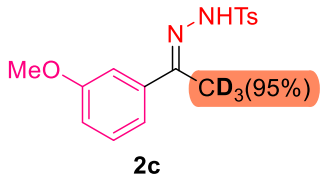
(*E*)-N'-(1-(4-methylphenyl)ethylidene-2,2,2- d3)-4-methylbenzenesulfonohydrazide (**2b**)



2b

2b was prepared according to the general procedure **4** in 82% (375.1 mg) isolated yield. White solid. **TLC** (20% ethyl acetate in hexanes): R_f = 0.3; **M.P.** 148-150 ºC; **IR** (KBr): 3387, 3259, 1961, 1598, 1494, 1305, 1289, 1185, 1154, 1089, 118, 834, 814 cm^{-1}; **^{1}H NMR** (500 MHz,DMSO-d6): δ 10.61 (bs, 1H), 7.82 (d, J = 8.2 Hz, 2H), 7.56 (m, 4H), 7.38 (m, 2H), 2.39 (s, 3H), 2.15(s, 3H)), 2.11 (s, 0.06H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 151.9, 143.4, 136.5(8), 136.1, 131.3, 129.5, 127.9, 127.5, 122.8, 21.02, 14.12; **^{2}H NMR** (77 MHz, $CDCl_3$): δ 2.13; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{16}D_3N_2O_2S$ 306.1350, Found 306.1351.

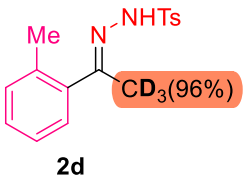
(E)-N'-(1-(3-methoxyphenyl)ethylidene-2,2,2-d3)-4-methylbenzenesulfonohydrazide (**2c**)



2c

2c was prepared according to the general procedure **4** in 72% (351.0 mg) isolated yield. White solid. **TLC** (20% ethyl acetate in hexanes): R_f = 0.3; **M.P.** 156-160 ºC; **IR** (KBr): 3390, 3257, 1960, 1594, 1498, 1420, 131, 1289, 1185, 1154, 1089, 1018, 839, 814 cm^{-1}; **^{1}H NMR** (500 MHz, DMSO-d6): δ 10.67 (bs, 1H), 7.79 (d, J = 8.2 Hz, 2H), 7.36 (d, J = 8.1 Hz, 2H), 7.23-7.22 (m, 1H), 7.15 (d, J = 7.8 Hz, 1H) 7.09-7.08 (m, 1H), 6.91-6.89 (m, 1H), 3.70 (s, 3H), 2.30 (s, 3H)), 2.11 (s, 0.14H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ159.6, 153.5, 143.9, 139.3, 136.6, 129.9, 128.1, 118.9, 115.5, 111.6, 55.5, 21.5; **^{2}H-NMR** (77 MHz,$CDCl_3$); 2.04; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for Calcd for $C_{16}H_{16}D_3N_2O_3S$ 322.1299, Found 322.1299.

(*E*)-N'-(1-(2-methylphenyl)ethylidene-2,2,2- d3)-4-methylbenzenesulfonohydrazide (**2d**)

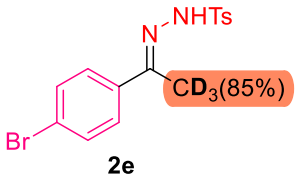


2d

2d was prepared according to the general procedure **4** in 70% (321.3 mg) isolated yield. White solid. **TLC** (20% ethyl acetate in hexanes): R_f = 0.3; **M.P.** 138-140 ºC; **IR** (KBr): 3387, 3259, 1961, 1598, 1494, 1419, 1305, 1289, 1185, 1154, 1089, 1018, 834, 814 cm^{-1}; **^{1}H NMR** (500 MHz,DMSO-d6): δ 10.44 (bs,

1H), 7.74 (d, J = 8.2 Hz, 2H), 7.40-7.37 (m, 3H), 7.21-7.13 (m, 3H), 2.36 (s, 3H), 2.10 (s, 0.13H), 2.00 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 155.9, 143.2, 138.7, 136.4, 135.4, 130.6, 129.4, 128.2, 127.7, 127.5, 125.6, 21.0, 19.8; **^{2}H NMR** (77 MHz, $CDCl_3$): δ 2.14; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{16}D_3N_2O_2S$ 306.1350, Found 306.1352.

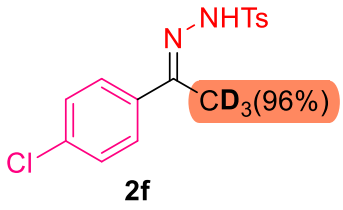
(E)-N'-(1-(4-bromophenyl)ethylidene-2,2,2-d3)-4-methylbenzenesulfonohydrazide (**2e**)



2e

2e was prepared according to the general procedure **4** in 82% (400.0 mg) isolated yield. White solid. **TLC** (20% ethyl acetate in hexanes): R_f = 0.3; **M.P.** 151-153 ºC; **IR** (KBr): 3390, 3257, 1965, 1591, 1493, 1420, 1315, 1287, 1183, 1152, 1090, 1017, 834, 814 cm^{-1}; **^{1}H NMR** (500 MHz,DMSO-d6): δ 10.66 (bs, 1H), 7.77 (d, J = 8.2 Hz, 2H), 7.52 (s, 4H), 7.35 (d, J = 8.1 Hz, 2H), 2.30 (s, 3H)), 2.09 (s, 0.46H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 152.4, 143.9, 137.0, 136.6, 131.8, 130.0, 128.4, 128.0, 123.3, 21.5; **^{2}H NMR** (77 MHz, $CDCl_3$): δ 2.16; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{12}D_3BrO_2SN_2$ 370.0299, Found 370.0295.

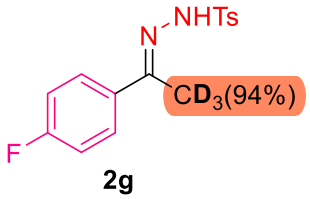
(*E*)-N'-(1-(4-chlorophenyl)ethylidene-2,2,2- d3)-4-methylbenzenesulfonohydrazide (**2f**)



2f

2f was prepared according to the general procedure **4** in 82% (400.0 mg) isolated yield. White solid. **TLC** (20% ethyl acetate in hexanes): R_f = 0.3; **M.P.** 151-153 ºC; **IR** (KBr): 3390, 3257, 1965, 1591, 1493, 1420, 1315, 1287, 1183, 1152, 1090, 1017, 834, 814 cm^{-1}; **^{1}H NMR** (500 MHz,DMSO-d6): δ 10.66 (bs, 1H), 7.80 (d, J = 8.2 Hz, 2H), 7.59 (d, J = 8.2 Hz, 2H), 7.43-7.38 (m, 4H), 2.37 (s, 3H),), 2.13 (s, 0.13H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 143.4, 139.4, 136.1, 133.2, 130.3, 129.5, 129.1, 125.6, 124.6, 21.1; **^{2}H NMR** (77 MHz, $CDCl_3$): δ 2.16; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{13}D_3ClO_2SN_2$ 326.0804, Found 326.0803.

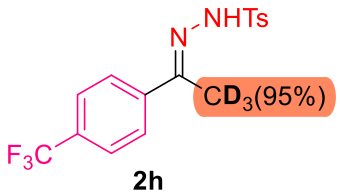
(E)-N'-(1-(4-fluorophenyl)ethylidene-2,2,2- d3)-4-methylbenzenesulfonohydrazide (**2g**)



2g

2g was prepared according to the general procedure **4** in 84% (389.3 mg) isolated yield. White solid. **TLC** (20% ethyl acetate in hexanes): R_f = 0.3; **M.P.** 148-150 ºC; **IR** (KBr): 3390, 3257, 1960, 1594, 1498, 1420, 131, 1289, 1185, 1154, 1089, 1018, 839, 814 cm^{-1}; **^{1}H NMR** (500 MHz,DMSO-d6): δ 8.38 (bs, 1H), 7.80 (d, J = 8.2 Hz, 2H), 7.67 (d, J = 8.2 Hz, 2H), 7.41 (d, J = 8.2 Hz, 2H), 7.14 (d, J = 8.2 Hz, 2H), 2.38 (s, 3H),), 2.12 (s, 0.17H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 151 (d, J = 247 Hz), 139.4, 136.1, 133.2(d, J = 14.8 Hz), 130.3, 129.5(d, J = 4.0 Hz), 129.1, 125.6, 124.6, 21.8; **^{2}H NMR** (77 MHz, $CDCl_3$): δ 2.11; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{13}D_3FO_2SN_2$ 310.1099, Found 310.1098.

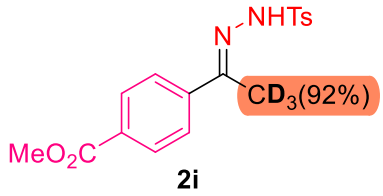
(*E*)-4-Methyl-N'-(1-(4-(trifluoromethyl)phenyl)ethylidene-2,2,2- d3)benzenesulfonohydrazide (**2h**)



2h

2h was prepared according to the general procedure **4** in 78% (420.5 mg) isolated yield. White solid. **TLC** (20% ethyl acetate in hexanes): R_f = 0.3; **M.P.** 179-181 ºC; **IR** (KBr): 3387, 3259, 1961, 1598, 1494, 1419, 1305, 1289, 1185, 1154, 1089, 1018, 834, 814 cm^{-1}; **^{1}H-NMR** (500 MHz, DMSO-d6): 10.40 (bs, 1H), 7.74 (d, *J* = 8.3 Hz, 2H), 7.47 (dd, *J* = 5.1, 0.6 Hz, 2H), 7.37-7.32 (m, 4H), 6.99-6.98 (m, 2H), 2.33 (s, 3H)), 2.13 (s, 0.15H); **^{13}C-NMR** (126 MHz, DMSO-d6): 154.6, 154.1, 143.8, 143.0, 136.5, 129.8, 129.1, 128.1, 128.0 (q, *J* = 250 Hz), 21.5; **^{19}F NMR** (471 MHz, $CDCl_3$): -62.33; **^{2}H NMR** (77 MHz, $CDCl_3$): δ 2.10; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{13}D_3F_3O_2SN_2$ 360.1067, Found 360.1068.

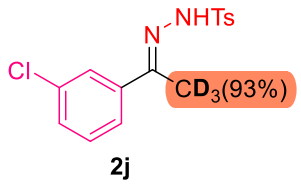
Methyl (*E*)-4-(1-(2-tosylhydrazineylidene)ethyl-2,2,2- d3)benzoate (**2i**)



2i

2i was prepared according to the general procedure **4** in 76% (397.8 mg) isolated yield. White solid. **TLC** (20% ethyl acetate in hexanes): R_f = 0.3; **M.P.** 168-180 ºC; **IR** (KBr): 3207, 1712, 1597, 1511, 1435, 1396, 1310, 1278, 1248, 1155, 1083, 1053 cm^{-1}; **^{1}H NMR** (500 MHz,DMSO-d6): δ 10.7 (bs, 1H), 7.92 (d, *J* = 8.3 Hz, 2H), 7.82 (d, *J* = 8.3 Hz, 2H), 7.53 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 8.2 Hz, 2H), 3.84 (s, 3H), 2.34 (s, 3H)), 2.19 (s, 0.24H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 165.8, 151.6, 143.4, 141.6, 136.9, 129.9, 129.6, 129.1, 127.5, 126.1, 52.1, 20.9; **^{2}H NMR** (77 MHz, $CDCl_3$): δ 2.10; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{16}D_3O_4SN_2$ 350.1248, Found 350.1248.

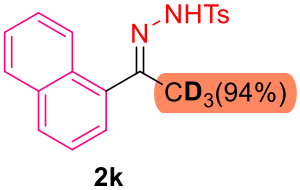
(*E*)-*N*'-(1-(3-chlorophenyl)ethylidene-2,2,2- d3)-4-methylbenzenesulfonohydrazide (**2j**)



2j

2j was prepared according to the general procedure **4** in 72% (351.0 mg) isolated yield. White solid. **TLC** (20% ethyl acetate in hexanes): R_f = 0.3; **M.P.** 156-160 ºC; **IR** (KBr): 3390, 3257, 1960, 1594, 1498, 1420, 131, 1289, 1185, 1154, 1089, 1018, 839, 814 cm^{-1}; **^{1}H NMR** (500 MHz, DMSO-d6): δ 10.67 (bs, 1H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.59-7.56 (m, 2H), 7.47-7.39 (m, 4H), 2.36 (s, 3H)), 2.12 (s, 0.20H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ151.5, 143.5, 139.5, 136.1, 133.2, 130.3, 129.5, 129.1, 127.1, 125.6, 124.6, 21.0; **^{2}H-NMR** (77 MHz,$CDCl_3$); 2.04; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{13}D_3ClO_2SN_2$ 326.0804, Found 326.0803.

(*E*)-4-Methyl-N'-(1-(naphthalen-2-yl)ethylidene-2,2,2- d3)benzenesulfonohydrazide (**2k**)

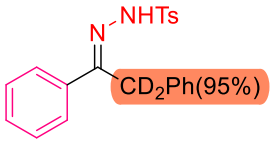


2k

2k was prepared according to the general procedure **4** in 69% (353.9 mg) isolated yield. White solid. **TLC** (20% ethyl acetate in hexanes): R_f = 0.3; **M.P.** 188-190 ºC; **IR** (KBr): 3217, 2000, 1597, 1333, 1305, 1103, 1155 cm^{-1}; **^{1}H NMR** (500 MHz,DMSO-d6): δ 10.60 (bs, 1H), 8.14 (m, 1H),

7.96-7.84 (m, 6H), 7.53-7.52 (m, 2H), 7.47 (d, J = 8.2 Hz, 2H), 2.35 (s, 3H)), 2.25 (s, 0.17H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 152.8, 143.4, 136.2, 134.7, 133.2, 132.6, 129.5, 128.5, 127.8, 127.6, 127.4, 126.9, 126.5, 126.2, 123.0, 21.02; **^{2}H-NMR** (77 MHz,$CDCl_3$): 2.14; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{16}D_3O_2SN_2$ 342.1350, Found 342.1349.

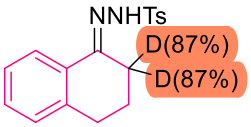
(*E*)-4-Methyl-N'-(1-(naphthalen-2-yl)ethylidene-2,2,2-d3)benzenesulfonohydrazide (**2l**)



2l

2l was prepared according to the general procedure **4** in 75% (412.8 mg) isolated yield. White solid. **TLC** (20% ethyl acetate in hexanes): R_f = 0.3; **M.P.** 164-166 ºC; **IR** (KBr): 3217, 2000, 1597, 1333, 1305, 1103, 1155 cm^{-1}; **^{1}H NMR** (500 MHz,DMSO-d6): δ 10.95 (bs, 1H), 7.82 (d, J = 8.2 Hz, 2H), 7.62-7.61 (m, 2H), 7.43 (d, J = 8.2 Hz, 2H), 7.33-7.30 (m, 3H), 7.24-7.21 (m, 2H), 7.15-7.05 (m, 3H), 2.39 (s, 3H)), 2.30 (s, 0.11H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 153.0, 143.4, 142.8, 136.5, 136.2, 135.7, 135.2, 129.5, 128.5, 128.3, 128.1, 127.4, 126.3, 21.0; **^{2}H-NMR** (77 MHz,$CDCl_3$): 2.10 **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{21}H_{19}D_2O_2SN_2$ 367.1444, Found 367.1443.

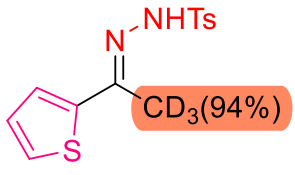
(Z)-N'-(3,4-dihydronaphthalen-1(2H)-ylidene-2,2-d2)-4-methylbenzenesulfonohydrazide



2m

2m was prepared according to the general procedure **4** in 70% (331.8 mg) isolated yield. White solid. **TLC** (20% ethyl acetate in hexanes): R_f = 0.3; **M.P.** 169-171 ºC; **IR** (KBr): 3219, 2005, 1599, 1339, 1315, 1109, 1078 cm^{-1}; **^{1}H NMR** (500 MHz,DMSO-d6): δ 10.38 (bs, 1H), 7.82 (d, J = 8.2 Hz, 2H), 7.76-7.74 (m, 1H), 7.42-7.40 (m, 2H), 7.25-7.23 (m, 1H), 7.19-7.14 (m, 2H), 2.69 (t, J = 8.2 Hz, 2H), 2.49(m, 0.25H), 2.37 (s, 3H)), 1.79 (m, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 146.5, 143.0, 138.6, 137.6, 131.1, 129.3 128.7, 128.2, 126.1, 124.6, 29.9, 26.1, 24.0, 21.3 cm^{-1}; **^{2}H-NMR** (77 MHz,$CDCl_3$): 2.49 **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{17}D_2O_2SN_2$ 317.1287, Found 317.1289.

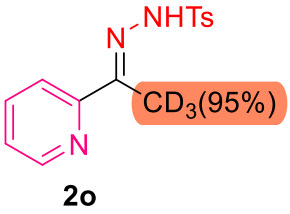
(E)-4-methyl-N'-(1-(thiophen-2-yl)ethylidene-2,2,2- d3)benzenesulfonohydrazide (**2n**)



2n

2n was prepared according to the general procedure **4** in 84% (374.2 mg) isolated yield. White solid. **TLC** (30% ethyl acetate in hexanes): R_f = 0.4; **M.P.** 200-202 ºC; **IR** (KBr): 3390, 3215, 2254, 2170, 2109, 1415, 1354, 1314, 1187, 1085, 1046 cm^{-1}; **^{1}H-NMR** (500 MHz, DMSO-d6): δ 10.75 (bs, 1H), 7.82-7.80 (m, 4H), 7.74-7.73 (m, 1H), 7.40 (d, J = 8.2 Hz, 2H), 2.38 (s, 3H), 2.11 (s, 0.18H); **^{13}C-NMR** (126 MHz, DMSO-d6): δ 143.4, 141.2, 136.0, 129.5, 129.4, 127.6, 127.4, 126.6, 125.2, 20.9; **^{2}H-NMR** (77 MHz,$CDCl_3$): 2.14; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{13}H_{12}D_3N_2S_2O_2$ 298.0758, Found 298.0760..

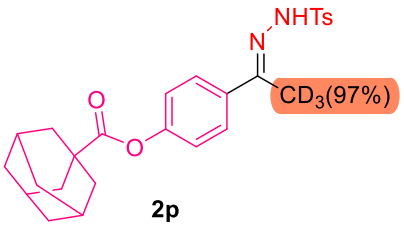
(*E*)-4-methyl-N'-(1-(pyridin-2-yl)ethylidene-2,2,2- d3)benzenesulfonohydrazide (**2o**)



2o

2o was prepared according to the general procedure **4** in 79% (346.0 mg) isolated yield. White solid. **TLC** (30% ethyl acetate in hexanes): R_f = 0.4; **M.P.** 137-139 ºC; **IR** (KBr): 3629, 3387, 3207, 2222, 2165, 2106, 1410, 1344, 1304, 1186, 1089, 1046 cm^{-1}; **^{1}H-NMR** (500 MHz, DMSO-d6): δ 10.72 (bs, 1H), 8.70-8.69 (m, 1H), 8.56-8.55 (m, 1H), 7.99-7.98 (m, 1H), 7.69-7.64 (m, 1H), 7.42-7.41 (m, 2H), 7.40-7.39(m, 2H), 2.38 (s, 3H), 2.20 (s, 0.15H); **^{13}C-NMR** (126 MHz, DMSO-d6): δ 150.0, 149.7, 146.8, 143.4, 142.8, 136.0, 135.1, 129.4, 127.6, 123.5, 20.9; **^{2}H-NMR** (77 MHz,$CDCl_3$): **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{13}D_3N_3SO_2$ 293.1146, Found 293.1149.

(*E*)-4-((3,4-dimethoxyphenyl)(2-tosylhydrazineylidene)methyl)phenyladamantane-1-carboxylate (**2p**)

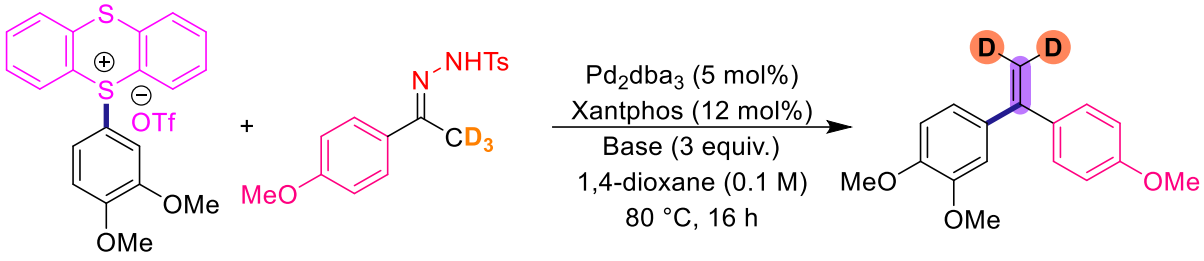


2p

2p was prepared according to the general procedure **4** in 80% (562.8 mg) isolated yield. White solid. **TLC** (20% ethyl acetate in hexanes): R_f = 0.3; **M.P.** 198-200 ºC; **IR** (KBr): 3217, 2000, 1712, 1597, 1511, 1435, 1396, 1333, 1305, 1103, 1155 cm^{-1}; **^{1}H-NMR** (500 MHz, DMSO-d6): δ 10.35 (bs, 1H), 8.14-8.12 (m, 2H), 7.64 (d, J = 5.7 Hz, 2H), 7.52-7.48 (m, 2H), 7.24-7.22 (m, 2H), 2.38-2.36 (m, 6H), 2.09 (s, 0.09H), 2.02 (s, 3H), 1.97 (s, 6H), 1.71 (s, 3H); **^{13}C-NMR** (126 MHz, DMSO-d6): δ 175.6, 151.5, 142.8, 136.9, 135.2, 129.4, 127.6, 127.5, 127.1, 121.6, 38.1, 35.8, 27.2, 20.9(8), 20.9(5); **^{2}H-NMR** (77 MHz,$CDCl_3$): **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{26}H_{27}D_3O_4SN_2$ 470.2187, Found 470.2189.

3.0 Optimization for the synthesis of deuterated olefins **3aa**

3.1 Base optimization



1a **2a** **3aa**

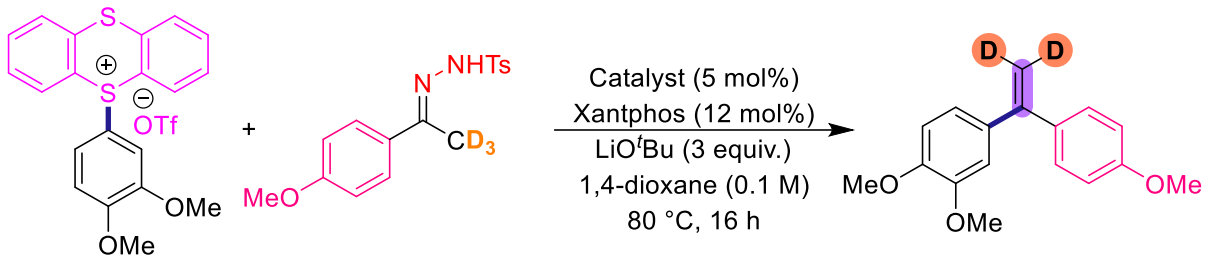
In a glove box, oven dried 10 mL reaction tube was charged with a magnetic stir bar, aryl thianthrenium salt **1a** (50.2 mg, 0.10 mmol, 1 equiv.) was added followed by the addition of *N*-tosylhydrazones **2a** (48.1 mg, 0.15 mmol, 1.5 equiv.), base (0.3 mmol, 3 equiv.), Xantphos (7.0 mg, 0.012 mmol, 12 mol%) and Pd_2dba_3 (4.5 mg, 0.005 mmol, 5 mol%). The reaction tube was taken out

from the glove box, dry 1,4-dioxane (0.1 M, 1.0 mL) was added under inert atmosphere and closed the reaction tube with stopper. The resulting reaction mixture was stirred at 80 ºC for 16 h until the complete consumption of starting material was observed, which was monitored by the TLC analysis. The reaction mixture was diluted with EtOAc (5 mL) and filtered through celite and concentrated under reduced pressure, and the product yield **3aa** was calculated by ^{1}H NMR using CH_2Br_2 as an internal standard.

Entry	Base	Yield of **3aa** (%)[a]
1	Cs_2CO_3	15
2	K_2CO_3	23
3	**LiO^{t}Bu**	**86**
4	$KHCO_3$	trace

Reaction conditions; **1a** (0.1 mmol, 1.0 equiv.), **2a** (0.15 mmol, 1.5 equiv.), Pd_2dba_3 (0.005 mmol, 5 mol%), xantphos (0.012 mmol, 12 mol%), base (0.3 mmol, 3 equiv.), dry 1,4-dioxane (0.1 M, 1.0 mL). [a]Yield determined by ^{1}H NMR using CH_2Br_2 as internal standard.

3.2 Catalyst optimization



1a **2a** **3aa**

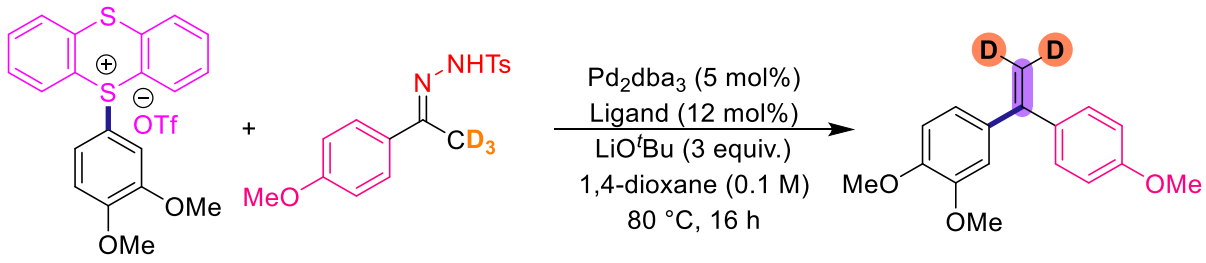
In a glove box, oven dried 10 mL reaction tube was charged with a magnetic stir bar, aryl thianthrenium salt **1a** (50.2 mg, 0.10 mmol, 1 equiv.) was added followed by the addition of *N*-tosylhydrazones **2a** (48.1 mg, 0.15 mmol, 1.5 equiv.), LiO^{t}Bu (24 mg, 0.3 mmol, 3 equiv.), Xantphos (7.0 mg, 0.012 mmol, 12 mol%) and catalyst (0.005 mmol, 5 mol%). The reaction tube was taken out from the glove box, dry 1,4-dioxane (0.1 M, 1.0 mL) was added under inert atmosphere and closed the reaction tube with stopper. The resulting reaction mixture was stirred at 80 ºC for 16 h until the complete consumption of starting material was observed, which was monitored by the TLC analysis. The reaction mixture was diluted with EtOAc (5 mL) and filtered through celite and concentrated under reduced pressure, and the product yield **3aa** was calculated by ^{1}H NMR using CH_2Br_2 as an internal standard.

Entry	Catalyst	Yield of **3aa** (%)[a]
1[b]	$Pd(OAc)_2$	60

2	$[(\eta^3\text{-}C_3H_5)PdCl]_2$	45
3	**Pd_2dba_3**	**86**
4[b]	$Pd(PPh_3)_4$	47

Reaction conditions: **1a** (0.1 mmol, 1.0 equiv.), **2a** (0.15 mmol, 1.5 equiv.), catalyst (0.005 mmol, 5 mol%), Xantphos (0.012 mmol, 12 mol%), LiO^{t}Bu (0.3 mmol, 3 equiv.), dry 1,4-dioxane (0.1 M, 1.0 mL). [a]Yield determined by ^{1}H NMR using CH_2Br_2 as internal standard. [b]Catalyst (0.01 mmol, 10 mol% was used).

3.3 Ligand optimization



1a **2a** **3aa**

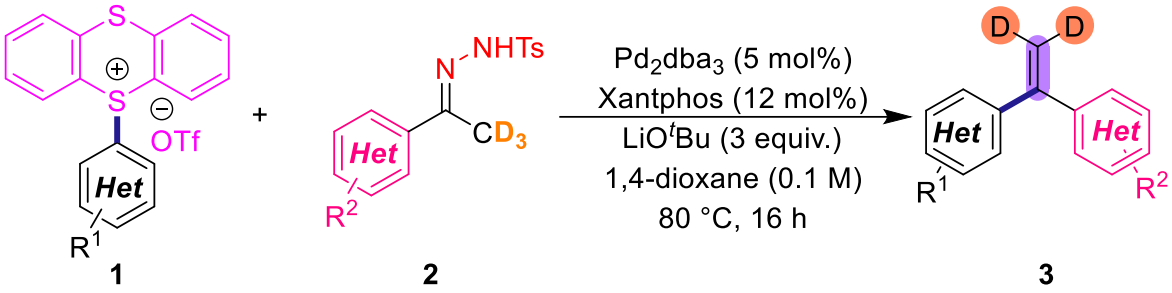
In a glove box, oven dried 10 mL reaction tube was charged with a magnetic stir bar, aryl thianthrenium salt **1a** (50.2 mg, 0.10 mmol, 1 equiv.) was added followed by the addition of *N*-tosylhydrazones **2a** (48.1 mg, 0.15 mmol, 1.5 equiv.), LiO^{t}Bu (24 mg, 0.3 mmol, 3 equiv.), ligand (0.012 mmol, 12 mol%) and Pd_2dba_3 (4.5 mg, 0.005 mmol, 5 mol%). The reaction tube was taken out from the glove box, dry 1,4-dioxane (0.1 M, 1.0 mL) was added under inert atmosphere and closed the reaction tube with stopper. The resulting reaction mixture was stirred at 80 ºC for 16 h until the complete consumption of starting material was observed, which was monitored by the TLC analysis. The reaction mixture was diluted with EtOAc (5 mL) and filtered through celite and concentrated under reduced pressure, and the product yield **3aa** was calculated by ^{1}H NMR using CH_2Br_2 as an internal standard.

Entry	Deviation from standard condition	Yield of **3aa (%)**[a]
1[b]	Ruphos	32
2[b]	Johnphos	18
3	**Xantphos**	**86**
4	Sphos	75

Reaction conditions: **1a** (0.1 mmol, 1.0 equiv.), **2a** (0.15 mmol, 1.5 equiv.), Pd_2dba_3 (0.005 mmol, 5 mol%), ligand (0.012 mmol, 12 mol%), LiO^{t}Bu (0.3 mmol, 3 equiv.), dry 1,4-dioxane (0.1 M, 1.0 mL). [a]Yield determined by ^{1}H NMR using CH_2Br_2 as internal standard. [b]Ligand (0.024 mmol, 24 mol% was used).

4.0 General procedure

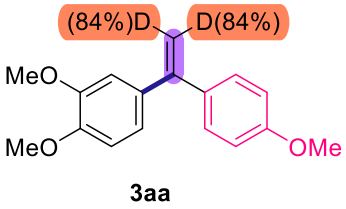
4.1 General procedure for the synthesis of deuterated olefins **3** from deuterated *N*-tosylhydrazones **2** derived from deuterated aryl-alkyl ketones



In a glove box, oven dried 10 mL reaction tube was charged with a magnetic stir bar, aryl thianthrenium salt **1** (0.2 mmol, 1.0 equiv.) was added followed by the addition of *N*-tosylhydrazones **2** (0.3 mmol, 1.5 equiv.), LiO^{t}Bu (48.0 mg, 0.6 mmol, 3.0 equiv.) Xantphos (14.0 mg, 0.024 mmol, 12 mol%) and Pd_2dba_3 (9.1 mg, 0.01 mmol, 5 mol%). The reaction tube was taken out from the glove box, dry 1,4-dioxane (0.1 M, 2.0 mL) was added under inert atmosphere and closed the reaction tube with stopper. The resulting reaction mixture was stirred at 80 ºC for 16 h until the complete consumption of starting material was observed, which was monitored by the TLC analysis. The reaction mixture was diluted with EtOAc (5 mL) and filtered through celite and concentrated under reduced pressure and the crude product was purified by column chromatography using EtOAc:hexanes to afford the compound **3**.

1,2-Dimethoxy-4-(1-(4-methoxyphenyl)vinyl-2,2-D_2)benzene (**3aa**)

3aa was prepared according to the general procedure **4.1** in 84% (45.6 mg) isolated yield. White solid.

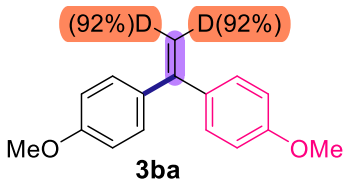


3aa

M.P. 107-109 ºC; **TLC** (10% ethyl acetate in hexanes): R_f = 0.5; **IR** (KBr): 2197, 2173, 2009, 1652, 1602, 1510, 1461, 1286, 1176, 1115, 1029 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.28 (d, J = 8.0 Hz, 2H), 6.86-6.78 (m, 5H), 5.30 (s, 0.16H), 5.29 (s, 0.16H), 3.90 (s, 3H), 3.83(6) (s, 3H), 3.83(1) (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 159.4, 148.8(8) 148.8(6), 134.7, 134.2, 129.5, 121.0, 113.6, 112.0, 111.6, 110.8, 56.0(5), 56.0(1), 55.4; **^{2}H NMR** (77 MHz, $CHCl_3$): δ 5.24; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{17}D_2O_3$ 273.1454, Found 273.1455.

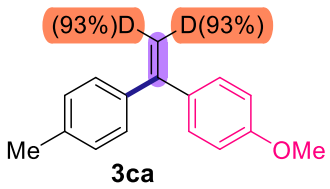
4,4'-(Ethene-1,1-diyl-2,2-d2)bis(methoxybenzene) (**3ba**)

3ba was prepared according to the general procedure **4.1** in 73% (35.3 mg) isolated yield. White solid. **M.P.** 137-138 ºC; **TLC** (10% ethyl acetate in hexanes): R_f = 0.6; **IR**(KBr): 2940, 2840, 1789, 1729, 998 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.27 (d, J = 8.9 Hz, 4H), 6.86 (d, J = 9.0 Hz, 4H), 5.27 (s, 0.08H), 3.82 (s, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 159.4, 149.1, 129.5, 113.6, 111.8, 55.4; **^{2}H NMR** (77 MHz, $CHCl_3$): δ 5.29; **HRMS** (ESI/Q-TOF) *m/z*: $[M]^+$ Calcd for $C_{16}H_{14}D_2O_2$ 242.1276, Found 241.1271.



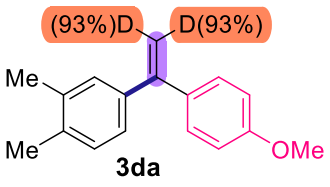
1-Methoxy-4-(1-(p-tolyl)vinyl-2,2-d2)benzene (**3ca**)

3ca was prepared according to the general procedure **4.1** in 78% (35.2 mg) isolated yield. White solid. **M.P.** 66-68 ºC; **TLC** (10% ethyl acetate in hexanes): R_f = 0.8; **IR** (KBr): 2197, 2173, 2009, 1652, 1602, 1510, 1461, 1286, 1176, 1115, 1029 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.28 (d, J = 8.8 Hz, 2H), 7.25 (d, J = 8.1 Hz, 2H), 7.14 (d, J = 7.9 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 5.34 (s, 0.07H), 5.32 (s, 0.07H), 3.83 (s, 3H), 2.37 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 159.3, 149.2, 138.9, 137.5, 134.2, 129.4, 128.9, 128.2, 113.5, 55.3, 21.2; **^{2}H NMR** (77 MHz, $CHCl_3$): δ 5.36; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{15}D_2O$ 227.1399, Found 227.1397.



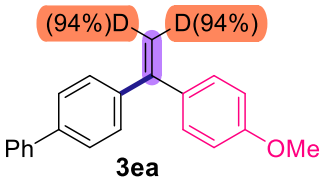
4-(1-(4-Methoxyphenyl)vinyl-2,2-d2)-1,2-dimethylbenzene (**3da**)

3da was prepared according to the general procedure **4.1** in 72% (34.5 mg) isolated yield. Colourless oil. **TLC** (10% ethyl acetate in hexanes): R_f = 0.8; **IR**(KBr): 2919, 2834, 2198, 2170, 1979, 1653, 1607, 1507, 1400, 1246, 1110, 1038 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.29-7.28 (m, 2H) 7.13-7.08 (m, 3H), 6.87-6.86 (m, 2H), 5.32 (s, 0.07H), 5.31 (s, 0.07H), 3.83 (s, 3H), 2.28 (s, 3H), 2.26 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 159.3, 149.4, 139.4, 136.3, 136.2, 134.2, 129.6, 129.4, 128.2, 125.9, 113.5, 55.4, 19.9, 19.6; **^{2}H NMR** (77 MHz,$CHCl_3$): δ 5.36; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{17}D_2O$ 241.1556, Found 241.1562.



4-(1-(4-Methoxyphenyl)vinyl-2,2-d2)-1,1'-biphenyl (**3ea**)

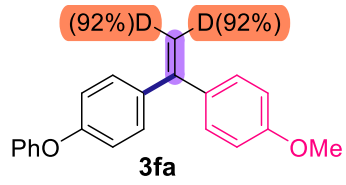
3ea was prepared according to the general procedure **4.1** in 72% (42.9 mg) isolated yield. White solid. **M.P.** 117-119 ºC; **TLC** (10% ethyl acetate in hexanes): R_f = 0.7; **IR:** 2212, 2174, 1508, 1233 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.63-7.61 (m, 2H), 7.57 (d, J = 8.5 Hz, 2H), 7.45-7.41 (m, 4H), 7.33-7.31 (m, 3H), 6.88 (d, J =8.9 Hz, 2H) 5.41 (s, 0.06H), 5.40 (s, 0.06H), 3.84 (s, 3H); **^{13}C**



NMR (126 MHz, $CDCl_3$): δ 159.4, 149.2, 140.8, 140.6, 140.2, 134.0, 129.6, 128.9, 128.8, 127.4, 127.1, 126.9, 113.6, 55.4; **^{2}H NMR** (77 MHz,$CHCl_3$): δ 5.43; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{21}H_{17}D_2O$ 289.1556, Found 289.1558.

1-Methoxy-4-(1-(4-phenoxyphenyl)vinyl-2,2-d2)benzene (**3fa**)

3fa was prepared according to the general procedure **4.1** in 72% (43.7 mg) isolated yield. White solid.

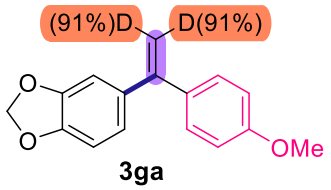


3fa

M.P. 125-127 ºC; **TLC** (10% ethyl acetate in hexanes): R_f = 0.6; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.36-7.33 (m, 2H) 7.29 (m, 4H), 7.13-7.10 (m, 1H), 7.05-7.04 (m, 2H), 6.96 (d, J = 8.7 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 5.25 (s, 008H), 5.24 (s, 0.08H), 3.75 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 159.5, 157.2, 157.1, 148.8, 148.7, 136.8, 134.1, 129.9, 129.7, 129.5, 123.5, 119.2, 113.7, 55.4; **^{2}H NMR** (77 MHz, $CHCl_3$): δ 5.24; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{21}H_{17}D_2O_2$ 305.1505, Found 305.1506.

5-(1-(4-Methoxyphenyl)vinyl-2,2-d2)benzo[d][1,3]dioxole (**3ga**)

3ga was prepared according to the general procedure **4.1** in 69% (35.3 mg) isolated yield. White solid.

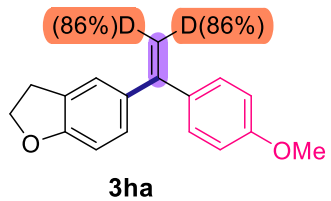


3ga

M.P. 101-102 ºC; **TLC** (10% ethyl acetate in hexanes): R_f = 0.6; **IR** (KBr): 2929, 1647, 1610, 1575, 1525, 1315, 1248, 1113, 967, 827 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.28-7.26 (m, 2H), 6.87-6.82 (m, 4H), 6.77-6.75 (m, 1H), 5.96 (s, 2H), 5.28 (s, 0.09H), 5.27 (s, 0.09H), 3.82 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 159.4, 149.0, 147.5, 147.3, 134.1, 129.5, 122.1, 113.6, 108.8, 108.0, 101.2, 55.4; **^{2}H NMR** (77 MHz,$CHCl_3$): δ 5.31; **HRMS** (ESI/Q-TOF) *m/z*: $[M]^+$ Calcd for $C_{16}H_{13}D_2O_3$ 256.1068, Found 256.1078.

5-(1-(4-Methoxyphenyl)vinyl-2,2-d2)-2,3-dihydrobenzofuran (**3ha**)

3ha was prepared according to the general procedure **4.1** in 72% (36.6 mg) isolated yield. White solid.

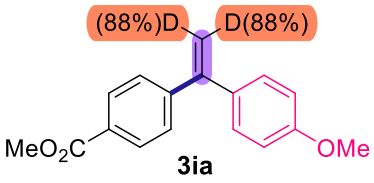


3ha

M.P. 92-94 ºC; **TLC** (10% ethyl acetate in hexanes): R_f = 0.6; **IR** (KBr): 2935, 1655, 1610, 1578, 1525, 1467, 1449, 1378, 1173, 1031, 967, 827 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.29-7.27 (m, 2H), 7.17 (s, 1H), 7.16-7.10 (m, 1H), 6.87-6.85 (m, 2H), 6.74(d, J = 8.2 Hz, 1H) 5.25 (s, 0.14H), 5.24 (s, 0.14H), 4.58 (t, J = 8.6 Hz, 2H), 3.82 (s, 3H), 3.19 (t, J = 8.6 Hz, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 160.0, 159.3, 149.5, 134.6, 129.6, 128.4, 126.9, 125.0, 113.5, 111.5, 108.9, 71.5, 55.4, 29.7; **^{2}H NMR** (77 MHz,$CHCl_3$): δ 5.25; **HRMS** (ESI/Q-TOF) *m/z*: $[M]^+$ Calcd for $C_{17}H_{14}D_2O_2$ 254.1276, Found 254.1280.

1-(4-(1-(4-Methoxyphenyl)vinyl)phenyl)ethan-1-one (**3ia**)

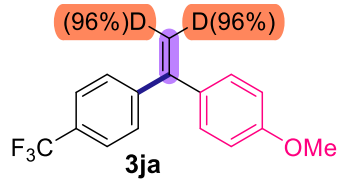
3ia was prepared according to the general procedure **4.1** in 62% (33.4 mg) isolated yield. White solid.



M.P. 124-125 ºC; **TLC** (10% ethyl acetate in hexanes): R_f = 0.4; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.92 (d, J = 8.6 Hz, 2H), 7.30 (d, J = 8.3 Hz, 2H), 7.15 (d, J = 8.9 Hz, 2H), 6.97 (d, J = 8.8 Hz, 2H), 5.39 (s, 0.12H), 5.34 (s, 0.13H), 3.84 (s, 3H), 3.74 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 167.0, 154.6, 148.8, 148.7, 146.5, 133.4, 129.6, 129.4, 128.4, 113.8, 55.4, 52.2; **^{2}H NMR** (77 MHz, $CHCl_3$): δ 5.38; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{15}D_2O_3$ 271.1298 Found 271.1297.

1-Methoxy-4-(1-(4-(trifluoromethyl)phenyl)vinyl-2,2-d2)benzene (**3ja**)

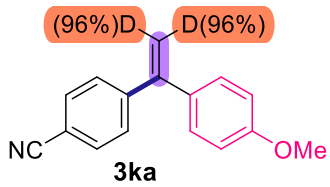
3ja was prepared according to the general procedure **4.1** in 60% (33.6 mg) isolated yield. White solid.



M.P. 78-79 ºC; **TLC** (10% ethyl acetate in hexanes): R_f = 0.8; **IR**(KBr): 2836, 1654, 1619, 1512, 1445, 1410, 1325, 1252, 1228, 1166, 1060, 1023 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.58 (d, J = 8.7 Hz, 2H), 7.43 (d, J = 8.7 Hz, 2H), 7.24 (d, J = 8.7 Hz, 2H), 6.88 (d, J = 8.8 Hz, 2H), 5.47 (s, 0.04H), 5.38 (s, 0.04H), 3.83 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 159.6, 148.4, 145.5, 133.2, 129.6 (q, J = 273.4 Hz), 129.5, 128.7, 125.3, 125.2, 113.8, 55.4; **^{2}H NMR** (77 MHz,$CHCl_3$): δ 5.46; **HRMS** (ESI/Q-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{16}H_{11}D_2F_3ONa$ 303.0936, Found 303.0925.

4-(1-(4-Methoxyphenyl)vinyl-2,2-d2)benzonitrile (**3ka)**

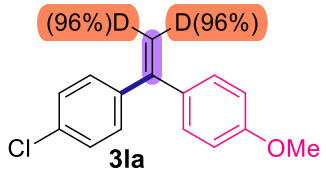
3ka was prepared according to the general procedure **4.1** in 67% (31.7 mg) isolated yield. Yellow oil.



TLC (10% ethyl acetate in hexanes): R_f = 0.6; **IR** (KBr): 2933, 2842, 1602, 1508, 1324, 1249, 1169, 1128, 1064 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.61 (d, J = 8.2 Hz, 2H), 7.43 (d, J = 8.3 Hz, 2H), 7.21 (d, J = 8.7 Hz, 2H), 6.88 (d, J = 8.7 Hz, 2H), 5.50 (s, 0.04H), 5.41 (s, 0.04H), 3.83 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 159.8, 148.2, 147.6, 139.3, 132.2, 129.4, 129.0, 119.0, 113.9, 111.4, 55.5; **^{2}H NMR** (77 MHz, $CHCl_3$): δ 5.48; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{12}D_2NO$ 238.1195, Found 238.1193.

1-Chloro-4-(1-(4-methoxyphenyl)vinyl-2,2-d2)benzene (**3la**)

3la was prepared according to the general procedure **4.1** in 78% (38.3 mg) isolated yield. White solid.

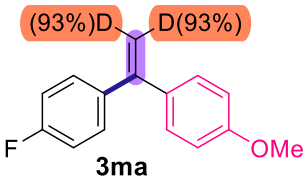


M.P. 60-62 ºC; **TLC** (10% ethyl acetate in hexanes): R_f = 0.8; **IR** (KBr): 2963, 2938, 2842, 1512, 1461, 1411, 1252, 1228, 1181, 1136, 1074, 1028 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.31-7.26 (m, 4H), 7.26-7.24 (m, 2H), 6.87 (d, J = 8.8 Hz, 2H), 5.37 (s, 0.04H), 5.31 (s, 0.04H), 3.83 (s,

3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 159.6, 148.4, 140.3, 133.6, 133.5, 129.7, 129.4, 128.4, 113.7, 55.4; **^{2}H NMR** (77 MHz, $CDCl_3$): δ 5.30; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{12}D_2ClO$ 247.0853, Found 247.0855.

1-Fluoro-4-(1-(4-methoxyphenyl)vinyl-2,2-d2)benzene (**3ma**)

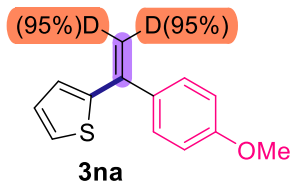
3ma was prepared according to the general procedure **4.1** in 59% (27.1 mg) isolated yield. Colourless oil. **TLC** (10% ethyl acetate in hexanes): R_f = 0.8; **IR**(KBr): 2943, 2908, 2840, 1758, 994 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.32-7.29 (m, 2H), 7.26-7.25 (m, 2H), 7.01 (t, J = 8.7 Hz, 2H), 6.87(d, J = 8.9 Hz, 2H), 5.36 (s, 0.07H), 5.29 (s, 0.07H), 3.83 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 162.6 (d, J = 246 Hz), 159.5, 148.4, 138.9 (d, J = 4.0 Hz), 133.9, 130.0 (d, J = 8.2 Hz), 129.4, 115.1 (d, J = 21.5 Hz), 113.7, 55.4; **^{19}F-NMR** (471 MHz, $CDCl_3$): δ -114.7; **^{2}H NMR** (77 MHz, $CDCl_3$): δ 5.33, 5.32; **HRMS** (ESI/Q-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{15}H_{11}D_2FONa$ 253.0968, Found 258.0964.



3ma

2-(1-(4-Methoxyphenyl)vinyl-2,2-d2)thiophene (**3na**)

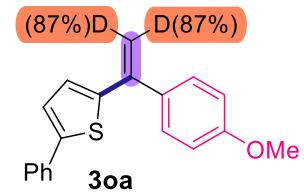
3na was prepared according to the general procedure **4.1** in 67% (29.2 mg) isolated yield. Colourless oil. **TLC** (10% ethyl acetate in hexanes): R_f = 0.4; **IR** (KBr): 2930, 2837, 2195, 1708, 1603, 1507, 1461, 1438, 1415, 1378, 1181, 1168. 1097, 1029 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.38 (d, J = 8.7 Hz, 2H), 7.23 (dd, J = 5.1,1.2 Hz, 1H), 6.99-6.97 (m, 1H), 6.94 (dd, J = 3.5, 1.2 Hz, 1H), 6.89 (d, J = 8.8 Hz, 2H), 5.49 (s, 0.05H), 5.18 (s, 0.05H), 3.84 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 159.6, 145.2, 133.6, 133.5, 129.5, 127.3, 126.3, 125.0, 113.5, 55.3; **^{2}H NMR** (77 MHz, $CDCl_3$): δ 5.54, 5.51; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{13}H_{11}OD_2S$ 219.0807, Found 219.0804.



3na

2-(1-(4-Methoxyphenyl)vinyl-2,2-d2)-5-phenylthiophene (**3oa**)

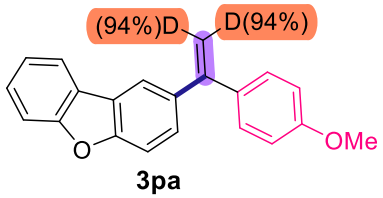
3oa was prepared according to the general procedure **4.1** in 58% (34.1 mg) isolated yield. White solid. **M.P.** 96-98 ºC; **TLC** (10% ethyl acetate in hexanes): R_f = 0.7; **IR**(KBr): 3058, 2955, 2929, 2832, 2192, 1606, 1509, 1462, 14440, 1409, 1289, 1250, 1213, 1178, 1071, 1031 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.61-7.59 (m, 2H), 7.41 (d, J = 8.8 Hz, 2H), 7.38-7.35 (m, 2H), 7.28 (d, J = 7.4 Hz, 1H), 7.19 (d, J = 3.7 Hz, 1H), 6.92-6.89 (m, 3H), 5.52 (s, 0.13H), 5.18 (s, 0.13H), 3.84 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 159.7, 144.5, 143.8, 142.9, 134.4, 133.4, 129.7, 129.0, 127.6, 127.4, 125.8, 123.3, 113.7, 55.4; **^{2}H NMR** (77 MHz,$CHCl_3$): δ 5.58, 5.25; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{15}D_2OS$ 295.1120, Found 295.1122.



3oa

2-(1-(4-Methoxyphenyl)vinyl-2,2-d2)dibenzo[b,d]furan (**3pa**)

3pa was prepared according to the general procedure **4.1** in 69% (41.6 mg) isolated yield. White solid.

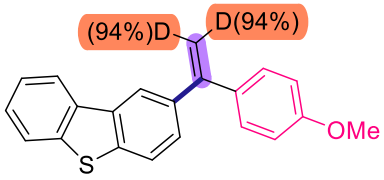


3pa

M.P. 134-136 ºC; **TLC** (10% ethyl acetate in hexanes): R_f = 0.6; **IR**(KBr): 2927, 2833, 2197, 1607, 1508, 1465, 1434, 1331, 1301, 1246, 1178, 1112, 1033 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.93-7.92 (m, 2H), 7.59-7.52(m, 2H), 7.47-7.45 (m, 2H), 7.35-7.33(m, 3H), 6.91-6.89 (m, 2H), 5.47 (s, 0.06H), 5.43 (s, 0.06H), 3.85 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 159.5, 149.5, 149.4, 139.9, 135.7, 135.6, 129.5, 127.4, 126.9, 124.5, 123.0, 122.5, 121.8, 121.4, 113.7, 113.0, 111.2, 55.4; **^{2}H NMR** (77 MHz,$CDCl_3$): δ 5.45; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{21}H_{15}D_2O_2$ 303.1349, Found 303.1347.

2-(1-(4-Methoxyphenyl)vinyl-2,2-d2)dibenzo[b,d]thiophene (**3qa**)

3qa was prepared according to the general procedure **4.1** in 76% (48.3 mg) isolated yield. White solid.

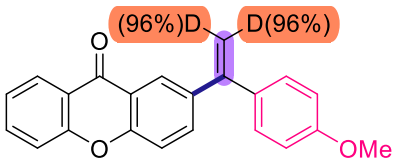


3qa

M.P. 140-142 ºC; **TLC** (10% ethyl acetate in hexanes): R_f = 0.6; **IR**(KBr): 2930, 2835, 2190, 1609, 1510, 1435, 1309, 1250, 1115, 1039 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.12-8.11 (m, 2H), 7.86-7.80 (m, 2H), 7.46-7.44 (m, 3H), 7.35-7.33 (m, 2H), 6.90-6.89 (m, 2H), 5.48 (s, 0.06H), 5.45 (s, 0.06H), 3.84 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 159.5, 149.4, 139.9, 138.9, 138.5, 135.7, 135.6, 134.1, 129.5, 127.4, 126.9, 124.5, 123.0, 122.5, 121.8, 121.4, 113.7, 55.4; **^{2}H NMR** (77 MHz,$CDCl_3$): δ 5.53; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{21}H_{15}OD_2S$ 319.1120, Found 319.1125.

2-(1-(4-Methoxyphenyl)vinyl-2,2-d2)-9H-xanthen-9-one (**3ra**)

3ra was prepared according to the general procedure **4.1** in 92% (60.7 mg) isolated yield. Brown oil.

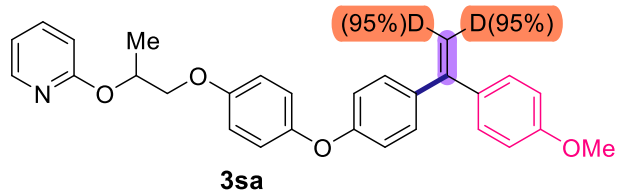


3ra

TLC (10% ethyl acetate in hexanes): R_f = 0.4; **IR** (KBr): 3365, 2865, 1649, 1469, 1015, 855 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.36-8.34 (m, 2H), 7.73-7.67 (m, 2H), 7.52-7.50 (m, 1H), 7.47-7.45 (m, 1H), 7.40-7.39 (m, 1H), 7.27-7.26 (m, 2H), 6.88 (d, J = 8.9, 2H), 5.46 (s, 0.04H), 5.45 (s, 0.04H), 3.83 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 177.3, 159.7, 156.3, 155.8, 148.0, 138.0, 135.1, 135.0, 133.5, 129.5, 126.9, 126.0, 124.1, 121.9, 121.6, 118.1, 117.9, 113.9, 55.4; **^{2}H NMR** (77 MHz, $CDCl_3$): δ 5.42; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{22}H_{15}D_2O_3$ 331.1298 Found 331.1306.

2-((1-(4-(4-(1-(4-Methoxyphenyl)vinyl-2,2-d2)phenoxy)phenoxy)propan-2-yl)oxy)pyridine (**3sa)**

3sa was prepared according to the general procedure **4.1** in 74% (67.3 mg) isolated yield. White solid.

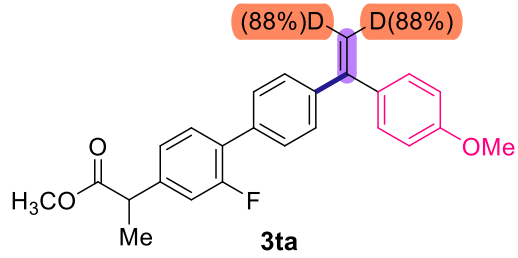


3sa

M.P. 115-117 ºC; **TLC** (20% ethyl acetate in hexanes): R_f = 0.4; **IR** (KBr): 3018, 1729, 1602, 1497, 1470, 1437, 1373, 1249, 1219 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.16-8.14 (m, 1H), 7.58-7.55 (m, 1H), 7.29-7.27 (m, 3H), 7.00-6.86 (m, 10H), 6.75-6.73 (m, 1H), 5.59-5.58 (m, 1H), 5.31 (s, 0.05H), 5.29 (s, 0.05H), 4.20 (q, J = 4.5 Hz, 1H), 4.08 (q, J = 5.0 Hz, 1H), 3.82 (s, 3H), 1.48 (d, J = 6.4 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 163.3, 159.5, 158.4, 155.5, 150.3, 149.0, 146.9, 138.3, 136.2, 134.2, 129.6, 129.5, 122.0, 117.2, 116.9, 115.9, 113.6, 112.3, 111.8, 71.2, 69.4, 55.4, 17.1; **^{2}H NMR** (77 MHz, $CDCl_3$): δ 5.29; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{29}H_{26}D_2NO_4$ 456.2138, Found 456.2136.

Methyl 2-(2-fluoro-4'-(1-(4-methoxyphenyl)vinyl-2,2-d2)-[1,1'-biphenyl]-4-yl)propanoate (**3ta**)

3ta was prepared according to the general procedure **4.1** in 51% (39.9 mg) isolated yield. White solid.

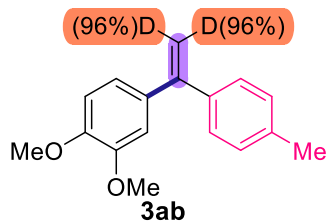


3ta

M.P. 120-122 ºC; **TLC** (10% ethyl acetate in hexanes): R_f = 0.2; **IR** (KBr): 2910, 2858, 1737, 1595, 1438, 1024, 909 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.51-7.49 (m, 2H), 7.43-7.40 (m, 3H), 7.31 (d, J = 8.9, 2H), 7.16-7.11 (m, 2H), 6.88 (d, J = 8.9 Hz, 2H), 5.42 (s, 0.12H), 5.40 (s, 0.12H), 3.87 (s, 3H), 3.77 (q, J = 7.2 Hz, 1H), 3.69 (s, 3H), 1.53 (q, J = 7.2 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 174.5, 159.9 (d, J = 245 Hz), 159.8, 149.2, 141.8 (d, J = 10.9 Hz), 134.9, 134.0, 130.8 (d, J = 6.0 Hz), 129.6, 129.5(9), 128.7 (d, J = 4.8 Hz), 128.5, 123.2 (d, J = 5.2 Hz), 115.4 (d, J = 33.1 Hz), 114.0, 113.7, 55.4, 52.3, 45.1, 18.5; **^{19}F NMR** (471 MHz, $CDCl_3$): δ -117.2; **^{2}H NMR** (77 MHz, $CHCl_3$): δ 5.39; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{22}D_2FO_3$ 393.1830 Found 393.1833.

1,2-Dimethoxy-4-(1-(p-tolyl)vinyl-2,2-d2)benzene (**3ab**)

3ab was prepared according to the general procedure **4.1** in 85% (43.5 mg) isolated yield. White solid.



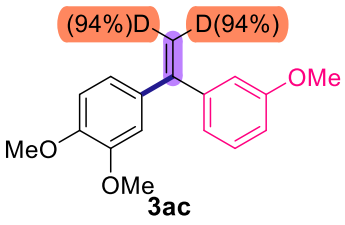
3ab

M.P. 72-73 ºC; **TLC** (10% ethyl acetate in hexanes): R_f = 0.7; **IR** (KBr): 2199, 2175, 2007, 1654, 1515. 1468, 1289, 1180, 1030 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.24 (m, 1H), 7.15 (d, J = 8.4 Hz, 2H), 709-7.08 (m, 1H), 6.92 (m, 2H), 6.84 (d, J = 8.1 Hz, 1H), 5.34 (s, 0.04H), 5.33 (s, 0.04H), 3.89 (s, 3H), 3.84 (s, 3H), 2.37 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 149.5, 148.8, 148.6, 138.7, 137.7, 128.9, 128.3, 121.0, 119.3, 111.5, 110.8, 56.0(5), 56.0(2),

21.3; **^{2}H NMR** (77 MHz,$CHCl_3$): δ 5.36; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{17}D_2O_2$ 257.1505, Found 257.1505.

1,2-Dimethoxy-4-(1-(3-methoxyphenyl)vinyl2,2-d2)benzene (**3ac**)

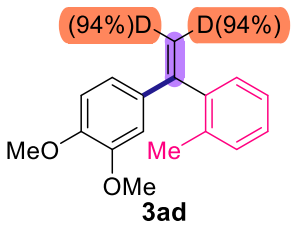
3ac was prepared according to the general procedure **4.1** in 78% (42.2 mg) isolated yield. Colourless liquid. **TLC** (10% ethyl acetate in hexanes): R_f = 0.5; **IR** (KBr): 2195, 2185, 1679, 1535, 1470, 1295, 1185, 1035 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.25-7.23 (m, 1H), 6.95-6.93 (m, 1H), 6.90-6.86 (m, 4H), 6.83-6.79 (m, 1H), 5.40 (s, 0.06H), 5.38 (s, 0.06H), 3.90 (s, 3H), 3.84 (s, 3H), 3.79 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 159.4, 149.6, 148.8, 148.5, 143.1, 134.2, 129.1, 121.0, 114.0, 113.3(9), 111.4, 110.7, 55.9(9), 55.9(6), 55.3; **HRMS** (ESI/Q-TOF) *m/z*: **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{17}D_2O_3$ 273.1454, Found 273.1456.



3ac

1,2-Dimethoxy-4-(1-(o-tolyl)vinyl-2,2-d2)benzene (**3ad**)

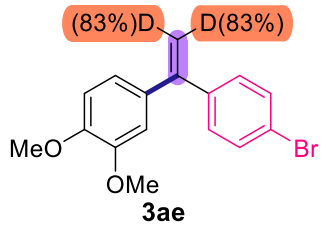
3ad was prepared according to general procedure **4.1** in 70% (35.9 mg) isolated yield. White solid. **M.P.** 70-72 ºC; **TLC** (10% ethyl acetate in hexanes): R_f = 0.6; **IR** (KBr): 2939, 2845, 1585, 1520, 1493, 1460, 1451, 1255, 1236 ; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.24-7.19 (m, 4H), 6.81 (s, 1H), 6.77 (d, J = 8.2 Hz, 2H), 5.71 (s, 0.06H), 5.13 (s, 0.06H), 3.90 (s, 3H), 3.87 (s, 3H), 2.11 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 148.9, 148.8, 141.7, 136.3, 130.1, 130.0, 128.6, 128.4, 127.6, 125.7, 119.5, 110.8, 109.4, 55.9(8), 55.9(5); **^{2}H NMR** (77 MHz,$CHCl_3$): δ 5.72, 5.14; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{17}D_2O_2$ 257.1505, Found 257.1505.



3ad

4-(1-(4-Bromophenyl)vinyl-2,2-d2)-1,2-dimethoxybenzene (**3ae**)

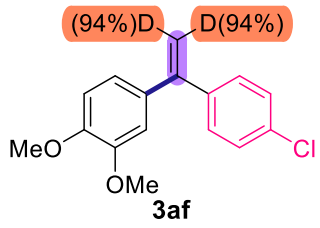
3ae was prepared according to the general procedure **4.1** in 62% (41.3 mg) isolated yield. White solid. **M.P.** 100-102 ºC; **TLC** (10% ethyl acetate in hexanes): R_f = 0.7; **IR** (KBr): 2935, 2842, 1650, 1603, 1510, 1487, 1440, 1248, 1228, 1012 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.45 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 6.87-6.82 (m, 3H), 5.40 (s, 0.17H), 5.35 (s, 0.17H), 3.89 (s, 3H), 3.83 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 149.1, 148.7, 140.6, 133.8, 131.3, 130.0, 126.5, 120.9, 114.1, 111.3, 110.8, 56.0(3), 56.0(0); **^{2}H NMR** (77 MHz, $CDCl_3$): δ 5.43; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{14}D_2BrO_2$ 321.0454, Found 321.0454.



3ae

4-(1-(4-Chlorophenyl)vinyl-2,2-d2)-1,2-dimethoxybenzene (**3af**)

3af was prepared according to the general procedure **4.1** in 72% (39.7 mg) isolated yield. White solid.

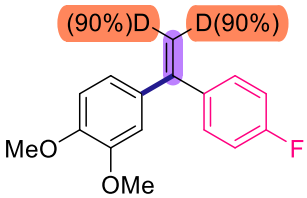


3af

M.P. 64-66 ºC; **TLC** (10% ethyl acetate in hexanes): R_f = 0.7; **IR** (KBr): 2963, 2938, 2845, 1515, 1460, 1411, 1252, 1229, 1180, 1140, 1075, 1028 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.45 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 6.87-6.82 (m, 3H), 5.42(s, 0.06H), 5.37 (s, 0.06H), 3.92 (s, 3H), 3.86 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 149.1, 148.7, 148.5, 134.2, 129.4, 128.4, 127.8, 126.6, 121.0, 111.3, 110.9, 56.0(4), 56.0(2); **^{2}H NMR** (77 MHz, $CDCl_3$): δ 5.40; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{14}D_2ClO_2$ 277.0959, Found 277.0954.

4-(1-(4-Fluorophenyl)vinyl-2,2-d2)-1,2-dimethoxybenzene (**3ag**)

3ag was prepared according to the general procedure **4.1** in 84% (43.6 mg) isolated yield. White solid.

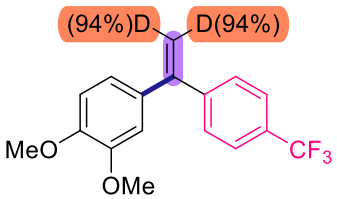


3ag

M.P. 98-100 ºC; **TLC** (10% ethyl acetate in hexanes): R_f = 0.6; **IR** (KBr): 2950, 2910, 2859, 1758, 994 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.33-7.30 (m, 2H), 7.02 (t, J = 8.7 Hz, 2H), 6.87-6.82 (m, 3H), 5.36 (s, 0.1H), 5.33 (s, 0.1H), 3.90 (s, 3H), 3.83 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 162.6 (d, J = 247.0 Hz), 149.0, 148.8, 148.7, 137.7 (d, J = 3.4 Hz), 134.2, 130.0 (d, J = 8.9 Hz), 120.9, 115.2 (d, J = 21.5 Hz), 111.4, 110.8, 56.0(6), 55.0(1); **^{19}F NMR** (471 MHz, $CDCl_3$): δ -114.2; ; **^{2}H NMR** (77 MHz, $CHCl_3$): δ 5.36; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{14}D_2FO_2$ 261.1254, Found 261.1256.

1,2-Dimethoxy-4-(1-(4-(trifluoromethyl)phenyl)vinyl-2,2-d2)benzene (**3ah**)

3ah was prepared according to the general procedure **4.1** in 86% (53.3 mg) isolated yield. White solid.

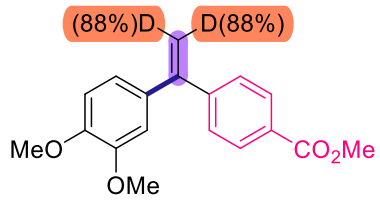


3ah

M.P. 120-122 ºC; **TLC** (10% ethyl acetate in hexanes): R_f = 0.6; **IR** (KBr): 2840, 1650, 1615, 1516, 1464, 1445, 1415, 1330, 1255, 1228, 1169, 1069, 1023 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.59 (d, J = 8.0 Hz, 2H), 7.47-7.45 (m, 2H), 6.84 (m, 3H), 5.50 (s, 0.06H), 5.43 (s, 0.06H), 3.90 (s, 3H), 3.84 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 149.1, 148.8, 148.6, 145.2, 133.5, 129.9 (q, J = 274 Hz), 128.7, 125.2(6), 125.2(3), 121.0, 111.2, 110.9, 5, 55.9; **^{19}F NMR** (471 MHz, $CDCl_3$): -62.33; **^{2}H NMR** (77 MHz, $CDCl_3$): δ 5.43; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{14}D_2F_3O_2$ 311.1222, Found 311.1225.

Methyl 4-(1-(3,4-dimethoxyphenyl)vinyl-2,2-d2)benzoate (**3ai**)

3ai was prepared according to the general procedure **4.1** in 82% (49.1 mg) isolated yield. White solid.

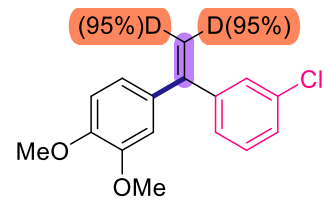


3ai

M.P. 133-135 ºC; **TLC** (10% ethyl acetate in hexanes): R_f = 0.4; **IR**(KBr): 2960, 2834, 1735, 1647, 1615, 1599, 1442, 1272, 1139, 1023 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.01-7.99 (m, 2H), 7.42-7.41 (m, 2H), 6.85-6.82 (m, 3H), 5.49 (s, 0.12H), 5.45 (s, 0.12H), 3.92 (s, 3H), 3.90 (s, 3H), 3.82 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 167.0, 149.1, 149.0, 148.7, 146.3, 133.7, 129.6, 128.4, 121.0, 114.8, 111.3, 110.8, 56.0, 55.9, 55.2; **^{2}H NMR** (77 MHz, $CDCl_3$): δ 5.47; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{17}D_2O_4$ 301.1403, Found 301.1405.

4-(1-(3-Chlorophenyl)vinyl-2,2-d2)-1,2-dimethoxybenzene (**3aj**)

3aj was prepared according to the general procedure **4.1** in 76% (40.7 mg) isolated yield. White solid.

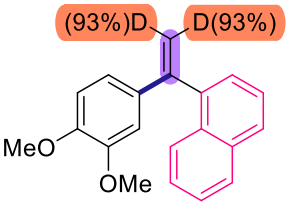


3aj

M.P. 92-94 ºC; **TLC** (10% ethyl acetate in hexanes): R_f = 0.6; **IR** (KBr): 2930, 2830, 1608, 1515, 1469, 1435, 1247, 1228, 1024 cm^{1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.35 (s, 1H), 7.28-7.21 (m, 3H), 6.85-6.84 (m, 3H), 5.42 (s, 0.05H), 5.38 (s, 0.05H), 3.90 (s, 3H), 3.84 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 148.0, 147.7, 147.4, 142.5, 134.1, 133.1, 128.4, 127.4, 126.8, 125.5, 119.9, 110.3, 109.8, 54.9(8), 54.9(6); **^{2}H NMR** (77 MHz, $CDCl_3$): δ 5.40, 5.37; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{14}D_2ClO_2$ 277.0959, Found 277.0959.

1-(1-(3,4-Dimethoxyphenyl)vinyl-2,2-d2)naphthalene (**3ak**)

3ak was prepared according to the general procedure **4.1** in 82% (47.7 mg) isolated yield. White solid.

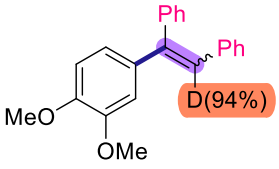


D_2-**3ak**

M.P. 80-90 ºC; **TLC** (10% ethyl acetate in hexanes): R_f = 0.6; **IR** (KBr): 3056, 2960, 2835, 1731, 1647, 1599, 1514, 1442, 1272, 1219, 1177, 1138, 1023 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.86-7.81 (m, 4H), 7.52-7.47 (m, 3H), 6.97-6.93 (m, 2H), 6.86 (d, J = 8.3 Hz, 1H), 5.50 (s, 0.07H), 5.49 (s, 0.07H), 3.92 (s, 3H), 3.83 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 149.6, 148.9, 148.7, 139.0, 134.4, 133.3, 133.0, 128.3, 127.7, 127.6. 127.3, 126.5, 126.2, 126.0, 121.1, 111.5, 110.8, 56.0, 55.9; **^{2}H NMR** (77 MHz, $CDCl_3$): δ 5.53; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{20}H_{17}D_2O_2$ 293.1505, Found 293.1505.

(1-(3,4-dimethoxyphenyl)ethene-1,2-diyl-2-d)dibenzene (**3al**)

3al was prepared according to the general procedure **4.1** in 79% (50.1 mg) isolated yield. White solid.

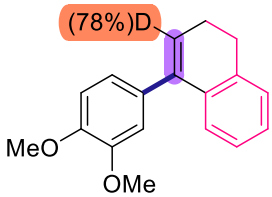


3al
dr = 1:1

M.P. 120-122 ºC; **TLC** (10% ethyl acetate in hexanes): R_f = 0.6; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.36-7.33 (m, 4H), 7.22-7.21 (m, 5H), 7.15-7.09 (m, 2H), 6.82-6.70 (m, 2H), 3.91-3.89 (s, 3H), 3.84-3.83 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 149.0, 148.9, 148.7, 148.4, 143.3, 142.3(8), 142.3(4), 140.4, 137.6, 137.5, 136.5, 132.8, 130.5, 129.5(9), 129.5(4), 128.7, 128.3, 128.1, 128.0, 127.7, 127.6, 127.5, 126.9, 126.8, 126.6, 122.9, 120.6, 113.6, 111.3, 110.8(7), 110.8(4), 56.0, 55.9(7), 55.9(1); **^{2}H NMR** (77 MHz, $CDCl_3$): δ 6.47; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ .Calcd for $C_{22}H_{20}DO_2$ 318.1599, Found 318.1597.

4-(3,4-Dimethoxyphenyl)-1,2-dihydronaphthalene-3-d (**3am**)

3am was prepared according to the general procedure **4.1** in 73% (38.8 mg) isolated yield. Colourless liquid.

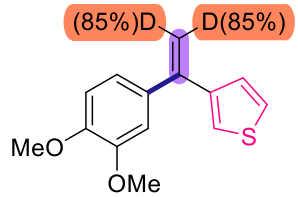


3am

TLC (10% ethyl acetate in hexanes): R_f = 0.6; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.22-7.03 (m, 4H), 6.92-6.86 (m, 3H), 6.06 (t, J = 4.7 Hz, 0.22H), 3.91 (s, 3H), 3.85 (s, 3H), 2.84 (t, J = 7.8 Hz, 2H), 2.41-2.37 (m, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 148.6, 148.3, 139.6, 136.9, 135.3, 133.6, 127.6, 127.1, 126.3, 125.5, 121.0, 112.1, 111.1, 56.0(3), 55.9, 28.3, 23.4; **^{2}H NMR** (77 MHz,$CDCl_3$): δ 6.12, **HRMS** (ESI/Q-TOF) *m/z*: **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{18}DO_2$ 268.1442, Found 268.1446.

3-(1-(3,4-Dimethoxyphenyl)vinyl-2,2-d2)thiophene (**3an**)

3an was prepared according to the general procedure **4.1** in 64% (31.7 mg) isolated yield. White solid.

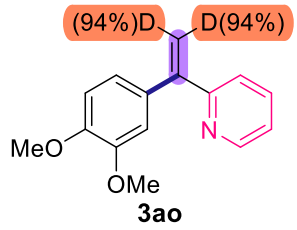


3an

M.P. 67-69 ºC; **TLC** (10% ethyl acetate in hexanes): R_f = 0.4; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.24-7.23 (m, 1H), 7.02-6.95 (m, 4H), 6.86 (d, J = 7.7 Hz, 1H), 5.52 (s, 0.15H), 5.21 (s, 0.15H), 3.91 (s, 3H), 3.87 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 149.1, 148.6, 145.1, 143.1, 133.9, 127.6, 126.4, 125.2, 120.9, 112.8, 111.7, 110.8, 56.1, 56.0; **^{2}H NMR** (77 MHz, $CDCl_3$): δ 5.54, 5.19; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{13}D_2O_2S$ 249.0913, Found 249.0917.

2-(1-(3,4-Dimethoxyphenyl)vinyl-2,2-d2)pyridine (**3ao**)

3ao was prepared according to the general procedure **4.1** in 65% (31.5 mg) isolated yield. White solid.

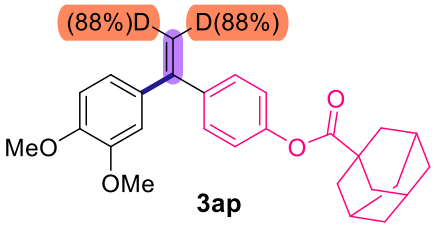


3ao

M.P. 76-77 ºC; **TLC** (20% ethyl acetate in hexanes): R_f = 0.3; **IR** (KBr): 3018, 1729, 1602, 1497, 1470, 1437, 1373, 1249, 1219 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.62 (d, J = 1.8 Hz, 1H), 8.55 (dd, J = 2.3, 0.7 Hz, 1H), 7.62-7.60 (m, 1H), 7.27-7.24 (m, 1H), 6.83 (s, 3H), 5.49 (s, 0.06H), 5.40 (s, 0.06H), 3.88 (s, 3H), 3.82 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 149.3, 149.2, 148.9, 148.8, 146.5, 137.4, 135.8, 133.2, 123.2, 120.9, 111.1, 111.0, 56.0(7), 56.0(3); **^{2}H NMR** (77 MHz,$CDCl_3$): δ 5.34; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{14}D_2NO_2$ 244.1301, Found 244.1300.

4-(1-(3,4-Dimethoxyphenyl)vinyl)phenyl adamantane-1-carboxylate (**3ap**)

3ap was prepared according to the general procedure **4.1** in 43% (36.1 mg) isolated yield. White solid.

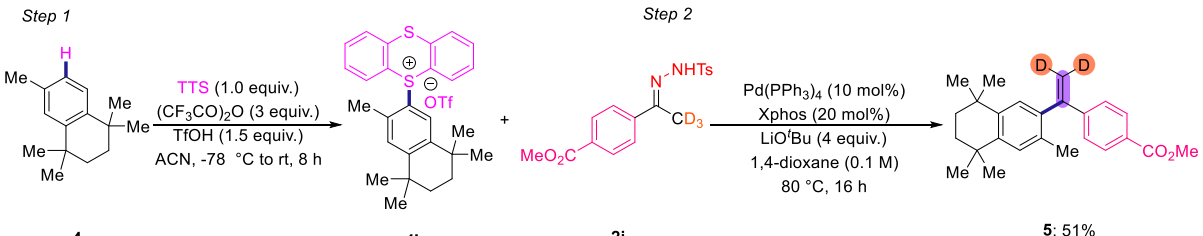


3ap

M.P. 115-117 ºC; **TLC** (10% ethyl acetate in hexanes): R_f = 0.4; **IR** (KBr): 2910, 2895, 1748, 1597, 1535, 1419, 1258, 1227, 1190, 1162, 1048, 789 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.34 (d, J = 8.7 Hz, 2H), 7.01 (d, J = 8.7 Hz, 2H), 6.89-6.81 (m, 3H), 5.37 (s, 0.12H), 5.34 (s, 0.12H), 3.96 (s, 3H), 3.89 (s, 3H), 2.12-2.10 (m, 3H), 2.08-2.03 (m, 6H), 1.77-1.74 (m, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 176.4, 150.8, 149.0, 148.9, 148.6, 139.0, 134.2, 129.3, 121.2, 121.0, 113.3, 111.4, 110.8, 56.0, 55.9, 41.1, 38.8, 36.5(6), 36.5(4), 27.9; **^{2}H NMR** (77 MHz,$CDCl_3$): δ 5.34; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{27}H_{29}D_2O_4$ 421.2342, Found 421.2345.

5.0 Synthesis of biologically active molecules

5.1 Synthesis of deuterium analog of retinoid X acceptor agonist **5**



4 **4'** **2i**

5; 51%
D = 94%
Bexarotene D_2-analog

Step-1:

Under an ambient atmosphere, 25 mL round bottom (RB) flask equipped with a magnetic stir bar was charged with arene **6** (40.4 mg, 0.2 mmol, 1 equiv.), thianthrene *S*-oxide (TTS) **II** (46.4 mg, 0.2 mmol,

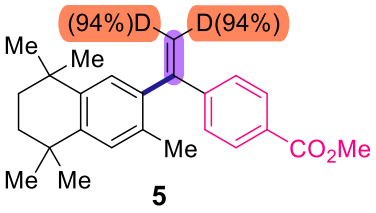
1 equiv.) and MeCN (1.0 mL, 0.2 M). The reaction mixture was cooled to –78 °C and then $(CF_3CO)_2O$ (0.6 mmol, 3 equiv.) was added slowly in a dropwise manner, followed by the addition of TfOH (0.3 mmol, 1.5 equiv.). The reaction mixture was warmed to room temperature and stirred for 12 h. The reaction was washed with Et_2O (10 mL). Then, 1,4 dioxane (0.1 M, 2.0 mL) was added followed by the addition of LiO^tBu (64.0 mg, 0.8 mmol, 4.0 equiv.) to neutralize the reaction mixture and reaction was stirred at room temperature for 3 h. Then, the reaction mixture was concentrated under reduced pressure and used for next step without purification.

Step 2:

The above obtained crude reaction mixture was taken into the glove box and charged with magnetic stir bar, *N*-tosylhydrazones **2i** (104.7 mg, 0.3 mmol, 1.5 equiv.), Xphos (19.0 mg, 0.04 mmol, 20 mol%) and $Pd(PPh_3)_4$ (21.1 mg, 0.02 mmol, 10 mol%). The RB flask was taken out from the glove box, dry 1,4-dioxane (0.1 M, 2.0 mL) under inert atmosphere and RB flask was closed with stopper. The resulting reaction mixture was stirred at 80 ºC for 16 h until the complete consumption of starting material was observed, which was monitored by the TLC analysis. The reaction mixture was diluted with EtOAc (5 mL) and filtered through celite and concentrated under reduced pressure and the crude product was purified by column chromatography using EtOAc:hexanes to afford the compound **7** with 51% yield and 94% deuterium incorporation.

Methyl 4-(1-(3,5,5,8,8-pentamethyl-5,6,7,8-tetrahydronaphthalen-2-yl)vinyl-2,2-d2)benzoate (**5**)

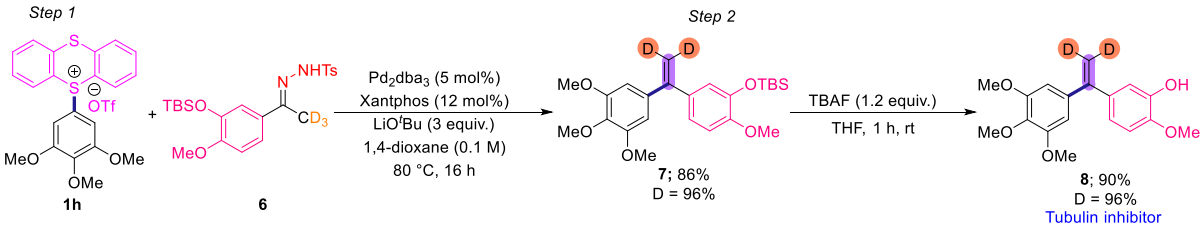
5 was prepared according to the general procedure **5.1** in 51% (37.1 mg) isolated yield. White solid.



5

M.P. 160-162 ºC; **TLC** (10% ethyl acetate in hexanes): R_f = 0.5; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.95 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.6 Hz, 2H), 7.12 (s, 1H), 7.07 (s, 1H), 5.80 (s, 0.06H), 5.32 (s, 0.06H), 3.90 (s, 1H), 1.90 (s, 1H), 1.69 (s, 4H), 1.30 (s, 6H), 1.27 (s, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 167.1, 149.2, 145.7, 144.5, 142.4, 138.1, 132.8, 129.7, 129.0, 128.2, 128.1, 126.7, 52.7, 35.3, 35.2, 34.1, 34.0, 32.0(6), 32.0(2), 20.1; **^{2}H NMR** (77 MHz, $CDCl_3$): δ 5.78, 5.19; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{29}D_2O_2$ 365.2444, Found 365.2449.

5.2 Synthesis of deuterium analog of tubulin inhibitor **8**

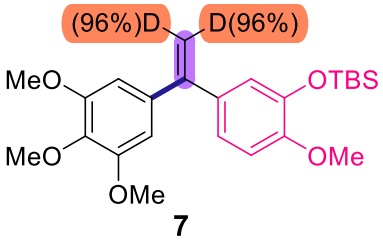


Step 1:

In a glove box, oven dried 10 mL reaction tube was charged with a magnetic stir bar, aryl thianthrenium salt **1h** (106.4 mg, 0.2 mmol, 1.0 equiv.) was added followed by the addition of *N*-tosylhydrazones **6** (136.4 mg, 0.3 mmol, 1.5 equiv.), Xantphos (14.0 mg, 0.024 mmol, 12 mol%), LiO^{t}Bu (48.0 mg, 0.6 mmol, 3.0 equiv.) and Pd_2dba_3 (9.1 mg, 0.01 mmol, 5 mol%). The reaction tube was taken out from the glove box, dry 1,4-dioxane (0.1 M, 2.0 mL) was added under inert atmosphere and closed the reaction tube with stopper. The resulting reaction mixture was stirred at 80 ºC for 16 h until the complete consumption of starting material was observed, which was monitored by the TLC analysis. The reaction mixture was diluted with EtOAc (5 mL) and filtered through celite and concentrated under reduced pressure and the crude product was purified by column chromatography using EtOAc:hexanes to afford the compound **7** with 86% yield and 96% deuterium incorporation.

tert-Butyl(2-methoxy-5-(1-(3,4,5-trimethoxyphenyl)vinyl-2,2-d2)phenoxy)dimethylsilane (**7**)

7 was prepared according to the general procedure **5.2** in 86% isolated yield. Brown oil. **TLC** (20% ethyl acetate in hexanes): R_f = 0.4; **IR** (KBr): 2939, 2835, 1585, 1515, 1465, 1456, 1397, 1285, 1254, 1010 cm^{-1} **^{1}H NMR** (500 MHz, $CDCl_3$): δ 6.91-6.79 (m, 3H), 6.55 (s, 2H), 5.34 (s, 0.04H), 5.30 (s, 0.04H), 3.87 (s, 3H), 3.82 (s, 3H), 3.81 (s, 6H), 0.97 (s, 6H), 0.14 (s, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 152.9, 150.9, 149.6, 144.6, 137.8, 137.6, 134.2, 121.8, 121.0, 111.6, 105.8, 61.0, 56.2, 55.6, 25.8, 18.5, -4.4; **^{2}H NMR** (77 MHz, $CDCl_3$): δ 5.34; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{33}D_2O_5Si$ 433.2374, Found 433.2375.



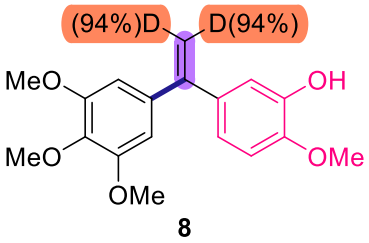
7

Step 2:

In an oven dried 10 mL round bottom (RB) flask was charged with a magnetic stir bar, olefin **7** (43.4 mg, 0.1 mmol, 1.0 equiv.) was added followed by the addition of TBAF (1M) (0.12 mmol, 1.2 equiv., 0.12 mL) was added and closed the RB flask with stopper. The resulting reaction mixture was stirred at room temperature for 6 h until the complete consumption of starting material was observed, which was monitored by the TLC analysis. The reaction mixture was diluted with EtOAc (5 mL) and filtered through celite and concentrated under reduced pressure and the crude product was purified by column chromatography using EtOAc:hexanes to afford the compound **8** with 90% yield and 96% deuterium incorporation.

2-Methoxy-5-(1-(3,4,5-trimethoxyphenyl)vinyl)phenol (**8**)

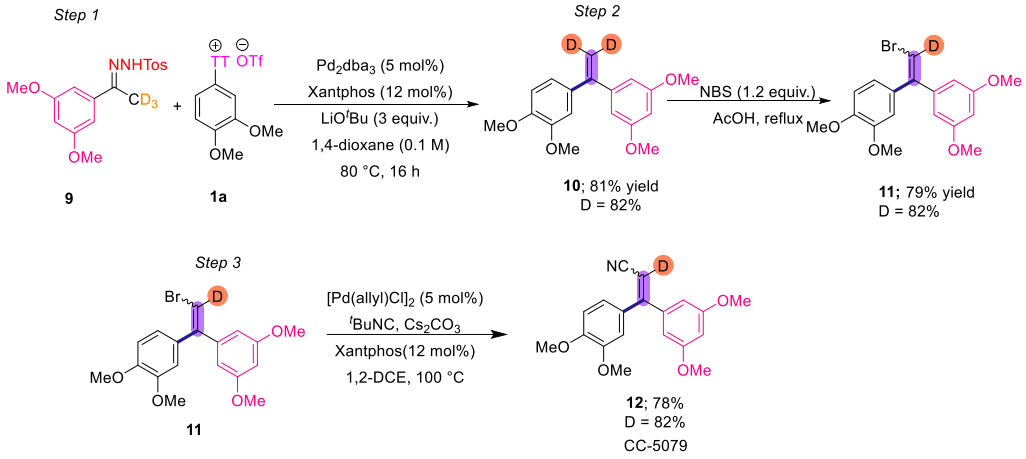
8 was prepared according to the general procedure **5.2** in 90% (28.5 mg) isolated yield. White solid.



8

TLC (30% ethyl acetate in hexanes): $R_f = 0.4$; **IR** (KBr): 3417, 2937, 2837, 1579, 1506, 1460, 1411, 1346, 1281, 1254, 1005 cm^{-1} **^{1}H NMR** (500 MHz, $CDCl_3$): δ 6.97-6.96 (m, 1H), 6.84-6.83 (m, 1H), 6.83-6.82 (m, 1H), 6.55 (s, 2H), 5.58 (bs, 1H), 5.37 (s, 0.06H), 5.30(s, 0.06H), 3.91 (s, 3H), 3.87 (s, 3H), 3.81 (s, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 152.9, 149.7, 146.5, 145.3, 137.8, 137.5, 134.8, 120.3, 114.6, 113.0, 110.2, 105.8, 61.0, 56.2, 56.1; **^{2}H NMR** (77 MHz, $CDCl_3$): δ 5.43; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{21}O$ 317.1384, Found 317.1385.

5.3 Synthesis of deuterium analog of anti-tumor drug CC-5079 **12**



Step1:

In a glove box, oven dried 50 mL round bottom (RB) flask was charged with a magnetic stir bar, aryl thianthrenium salt **1a** (501.2 mg, 1.0 mmol, 1.0 equiv.) was added followed by the addition of *N*-tosylhydrazones **9** (526.5 mg, 1.5 mmol, 1.5 equiv.), Xantphos (70.0 mg, 0.12 mmol, 12 mol%), LiO^{t}Bu (240.0 mg, 3.0 mmol, 3.0 equiv.) and Pd_2dba_3 (45.0 mg, 0.5 mmol, 5 mol%). The RB was taken out from the glove box, dry 1,4-dioxane (0.1 M, 10.0 mL) was added under inert atmosphere and closed the reaction tube with stopper. The resulting reaction mixture was stirred at 80 ºC for 16 h until the complete consumption of starting material was observed, which was monitored by the TLC analysis. The reaction mixture was diluted with EtOAc (15 mL) and filtered through celite and concentrated under reduced pressure and the crude product was purified by column chromatography using EtOAc:hexanes to afford the compound **10** with 81% yield and 82% deuterium incorporation.

Step 2:

In a 10 ml round bottom flask *N*-bromosuccinimide (0.72 mmol, 126.0 mg, 1.2 equiv.) was added to a suspension of 4-(1-(3,5-dimethoxyphenyl)vinyl-2,2-d_2)-1,2-dimethoxybenzene (0.60 mmol, 181.2mg,

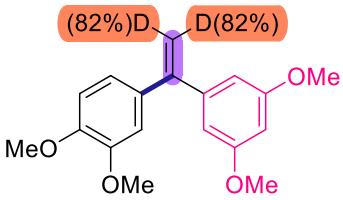
1.0 equiv.) in AcOH (6 mL) and reaction mixture was stirred at 70 °C for 4 hours. After the completion of reaction monitored by TLC, the reaction mixture was cooled down to room temperature. The reaction mixture was neutralized by slow addition of NaOH/$NaHCO_3$ (1:1) and extracted by EtOAc dried over anhydrous Na_2SO_4 and concentrated under reduced pressure and the crude product was purified by column chromatography using EtOAc:hexanes to afford the compound **11** with 79% yield.

Step 3:

In a glove box, oven dried 10 mL reaction tube was charged with a magnetic stir bar, crude 4-(2-bromo-1-(3,5-dimethoxyphenyl)vinyl-2-d)-1,2-dimethoxybenzene (0.2 mmol, 1.0 equiv.) was added followed by the addition of Cs_2CO_3 (195.0 mg, 0.6 mmol, 3 equiv.), Xantphos (14.0 mg, 0.024 mmol, 12 mol%) and $[(\eta^3\text{-}C_3H_5)PdCl]_2$ (3.6 mg, 0.01 mmol, 5 mol%). The reaction tube was taken out from the glove box, anhydrous 1,2-DCE (0.1 M, 2.0 mL) was added and then addition of tert-butyl isocyanide (36.0 µL, 0.3 mmol, 1.5 equiv.) under inert atmosphere and closed the reaction tube with stopper. The resulting reaction mixture was stirred at 100 ºC for 10 h until the complete consumption of starting material was observed, which was monitored by the TLC analysis. The reaction mixture was diluted with EtOAc (5 mL) and filtered through celite and concentrated under reduced pressure and the crude product was purified by column chromatography using EtOAc:hexanes to afford the compound **12** with 78% yield and 82 % deuterium incorporation.

4-(1-(3,5-dimethoxyphenyl)vinyl-2,2-d2)-1,2-dimethoxybenzene (**10**)

10 was prepared according to the general procedure **5.3** in 81% (244.6 mg) isolated yield. Brown oil.

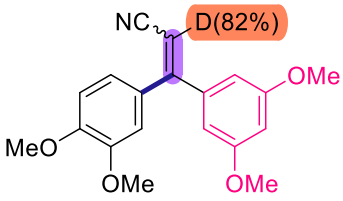


10

TLC (20% ethyl acetate in hexanes): R_f = 0.4; **IR** (KBr): 2197, 2173, 2009, 1652, 1602, 1510, 1461, 1286, 1176, 1115, 1029 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 6.89-6.81 (m, 3H), 6.51-6.49 (m, 2H), 6.45-6.44 (m, 1H), 5.40 (d, J = 1.3 Hz, 1H), 5.36 (d, J = 1.3 Hz, 1H), 3.89 (s, 3H), 3.84 (s, 3H), 3.76 (s, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 160.5, 149.6, 148.9, 148.5, 143.8, 134.0, 121.0, 111.4, 110.7, 106.6(6), 106.6(3), 55.9(9), 55.9(4), 55.3; **^{2}H NMR** (77 MHz, $CDCl_3$): δ 5.39; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{29}D_2O_4$ 303.1560, Found 303.1560.

3-(3,4-dimethoxyphenyl)-3-(3,5-dimethoxyphenyl)acrylonitrile-d (**12**)

12 was prepared according to the general procedure **5.3** in 78% (50.7 mg) isolated yield. White solid.

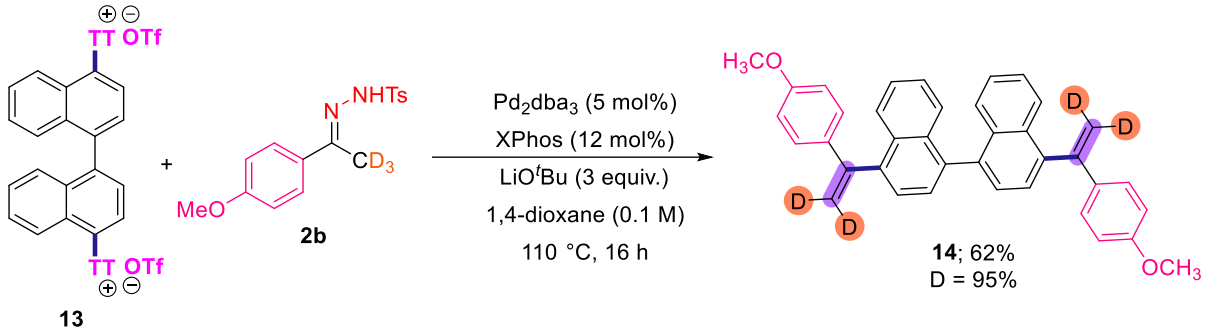


12

M.P. 104-106 ºC; **TLC** (20% ethyl acetate in hexanes): R_f = 0.3; **IR** (KBr): 2197, 2173, 2009, 1652, 1602, 1510, 1461, 1286, 1176, 1115, 1029 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 6.88 (s, 1H), 6.79 (s, 2H), 6.56-6.43 (m, 3H), 5.90 (s, 0.18H), 3.91 (s, 3H), 3.88 (s, 3H), 3.85 (s, 3H), 3.82 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 161.3, 161.2, 160.1, 157.3, 151.5, 149.3, 139.9, 139.8, 128.8(9), 128.8(1), 121.5, 117.2, 111.0, 110.9, 106.8, 106.7, 103.0,

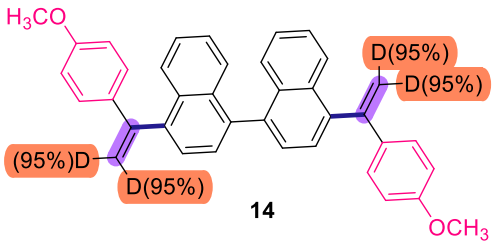
100.3, 94.8, 56.5, 56.1(5), 56.1(0), 55.8; **^{2}H NMR** (77 MHz, $CDCl_3$): δ 5.90; **HRMS** (ESI/Q-TOF) *m/z*: $[M]^+$ Calcd for $C_{19}H_{18}DO_4$ 326.1367, Found 326.1377.

6.0 Synthesis of *bis*-olefins **14** from *bis*-thianthrenium salts **13**



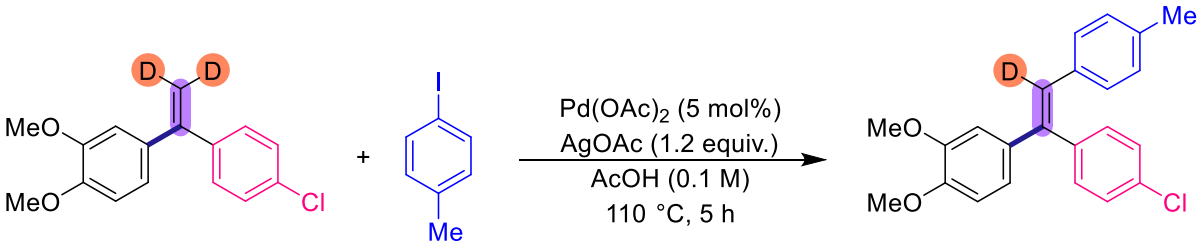
In a glove box, oven dried 10 mL reaction tube was charged with a magnetic stir bar, aryl thianthrenium salt **1a** (112.4 mg, 0.1 mmol, 1.0 equiv.) was added followed by the addition of *N*-tosylhydrazones **2a** (96.3 mg, 0.3 mmol, 1.5 equiv.), Xphos (19.0 mg, 0.04 mmol, 20 mol%), LiO^{t}Bu (48.0 mg, 0.6 mmol, 3.0 equiv.) and Pd_2dba_3 (9.1 mg, 0.01 mmol, 5 mol%). The reaction tube was taken out from the glove box, dry 1,4-dioxane (0.1 M, 2.0 mL) was added under inert atmosphere and closed the reaction tube with stopper. The resulting reaction mixture was stirred at 110 ºC for 16 h until the complete consumption of starting material was observed, which was monitored by the TLC analysis. The reaction mixture was diluted with EtOAc (5 mL) and filtered through celite and concentrated under reduced pressure and the crude product was purified by column chromatography using EtOAc:hexanes to afford the compound **14** with 62% yield and 95% deuterium incorporation.

14 was prepared according to the general procedure 6.0 in 62% (32.3 mg) isolated yield. White solid.



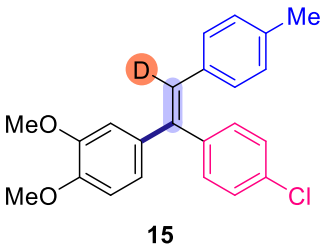
M.P. 114-116 ºC; **TLC** (20% ethyl acetate in hexanes): R_f = 0.4; **IR** (KBr) 2930, 1510, 1462, 1352, 1258, 1229, 1139, 1073, 1025, 909 cm^{-1}**^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.91-7.89 (m, 2H), 7.55-7.47 (m, 6H), 7.38-7.27 (m, 8H), 6.87-6.84 (m 4H), 5.79 (s, 0.11H), 5.33 (s, 0.11H), 3.81 (s, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 159.4, 147.7, 140.0, 138.4, 133.9, 133.2, 132.1, 128.0, 127.6, 127.2, 127.0, 126.9, 126.8, 125.8, 113.9, 55.4; **HRMS** (ESI/Q-TOF) *m/z*: $[M]^+$ Calcd for $C_{38}H_{26}D_4O_2$, 522.2489 Found. 522.2497.

7.0 Synthesis of tri-substituted olefin **15**



In a glove box, 10 mL reaction tube equipped with magnetic stir bar, **3af** (55.2 mg, 0.2 mmol, 1.0 equiv.) was added followed by the aryl iodide **VII** (52.0 mg, 0.24 mmol, 1.2 equiv.) $Pd(OAc)_2$ (2.2 mg, 0.01 mmol, 5 mol%) and AgOAc (40.0 mg, 0.24 mmol, 1.2 equiv.). The reaction tube was taken out from the glove box, AcOH (0.1 M, 20.0 mL) was added under inert atmosphere and closed the reaction tube with stopper. The resulting reaction mixture was stirred at 110 ºC for 5 h until the complete consumption of starting material was observed, which was monitored by the TLC analysis. The reaction mixture was quenched with $NaHCO_3$ solution and extracted with EtOAc and the crude product was purified by column chromatography using EtOAc:hexanes to afford the compound **15** with 89% yield (64.9 mg).

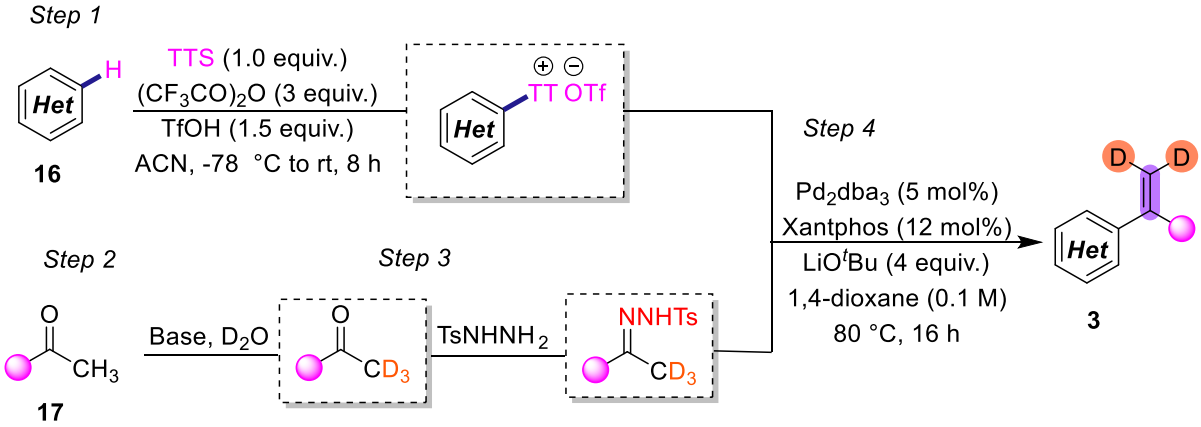
15 was prepared according to the general procedure **7.0** in 89% (64.9 mg) isolated yield. White solid.



M.P. 155-157 ºC; **TLC** (10% ethyl acetate in hexanes): R_f = 0.4; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.27-7.26 (m, 4H), 6.95-6.94 (m, 4H), 6.84-6.83 (m, 1H), 6.74-6.73 (m 1H), 6.68-6.67 (m, 1H), 3.91 (s, 3H), 3.70 (s, 3H), 2.27 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 149.0, 148.4, 142.1, 140.1, 136.8, 134.3, 133.1, 132.4, 131.9, 129.3, 128.7(9), 128.7(7), 128.3, 122.7, 113.4, 111.3, 55.9(8), 55.9(6), 21.3; **^{2}H NMR** (77 MHz, $CDCl_3$): δ 6.65 ; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{21}ClDO_2$, 366.1366 Found. 366.1368

Note: C-D chemical shift merges with aromatic peak so not able to calculate deuterium retention.

8.0 General procedure for semi-one-pot synthesis



Step 1:

Under an ambient atmosphere, 25 mL round bottom (RB) flask equipped with a magnetic stir bar was charged with arene **III** (0.2 mmol, 1 equiv.), thianthrene *S*-oxide (TTS) **II** (46.4 mg, 0.2 mmol, 1 equiv.) and MeCN (1.0 mL, 0.2 M). The reaction mixture was cooled to −78 °C and then $(CF_3CO)_2O$ (0.6 mmol, 3 equiv.) was added slowly in a dropwise manner, followed by the addition of TfOH (0.3 mmol, 1.5 equiv.). The reaction mixture was warmed to room temperature and stirred for 12 h. After that, the LiO^tBu (16.0 mg, 0.2 mmol, 1.0 equiv.) was added to neutralize the reaction mixture for 2 h. and washed with Et_2O (3x10 mL) and dried over high vaccum and crude product was used without further purification.

Step 2:

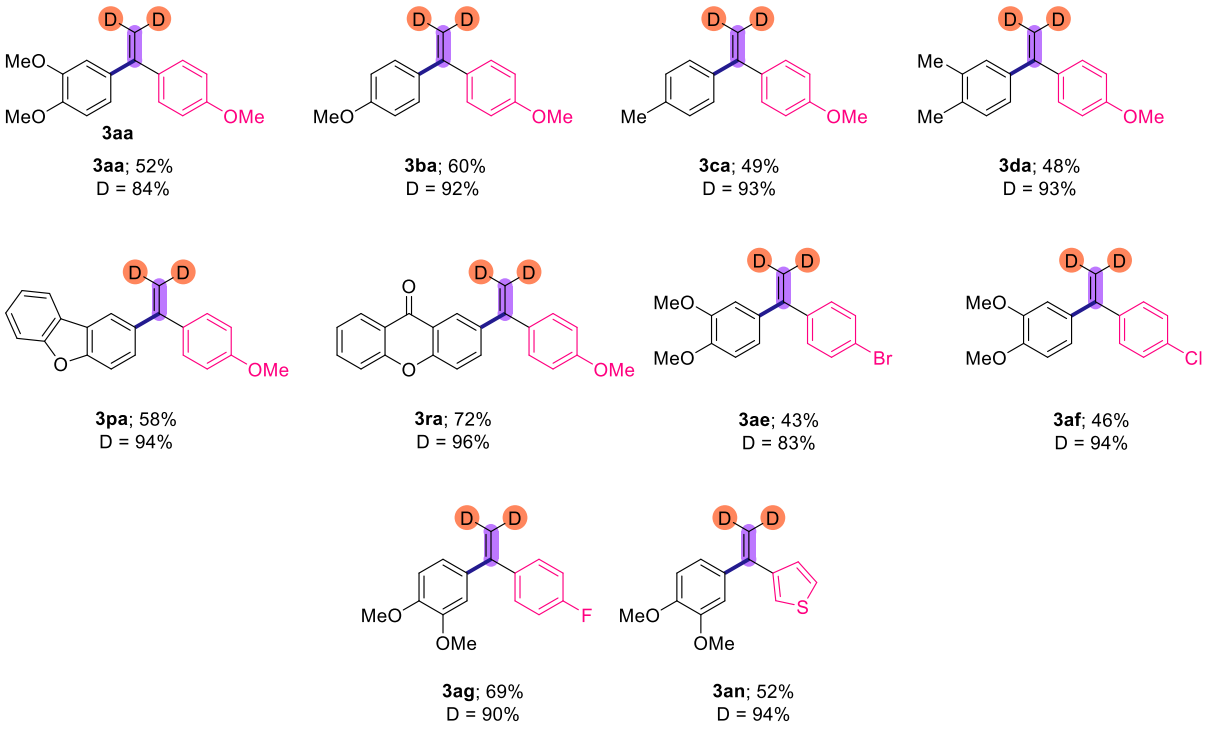
Under an ambient atmosphere, another 10 mL round bottom (RB) flask was equipped with magnetic stir bar, acetophenone **17** (0.3 mmol, 1 equiv.) was added, followed by the addition of NaOH (1.2 mg, 10 mol%) under inert atmosphere. The RB flask was sealed with rubber septa and D_2O (0.3 mL) was added under inert atmosphere. Then, the reaction was stirred at room temperature for 24 h. After completion of reaction, the reaction mixture was extracted with Et_2O (3x10 mL). The organic layers were dried over Na_2SO_4, filtered, and the solvent was removed under reduced pressure by using rotary evaporator and the crude deuterated acetophenone **17** was used for next step without any further purification.

Step 3:

To a stirred solution of tosylhydrazide **VI** (0.3 mmol, 1.0 equiv.) in MeOH (0.25 M), solution of corresponding acetophenone **2** in MeOH (0.5 M) was added. The reaction mixture was stirred at room temperature until complete conversion was observed by TLC. Solvent was removed under reduced pressure by rotary evaporator and crude compound was recrystallized with hot methanol to get the desired product and used for next step without further purification.

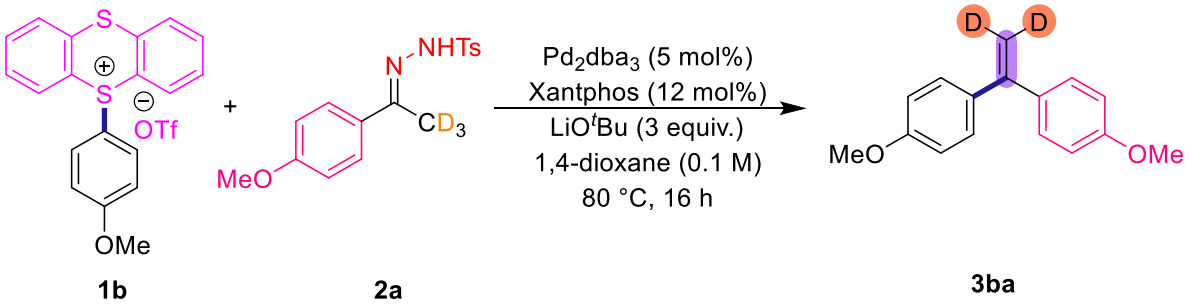
Step 4:

The crude compound obtained reaction mixture obtained from step 1 was taken into glove box and *N*-tosylhydrazones D_3-**2** obtained from step 3 was added, followed by the addition of Xantphos (14.0 mg, 0.024 mmol, 12 mol%), LiO^tBu (48.0mg, 0.6 mmol, 3.0 equiv.) and Pd_2dba_3 (4.6 mg, 0.01 mmol, 5 mol%). The RB flask was taken out from the glove box, dry 1,4-dioxane (0.1 M, 2.0 mL) was added under inert atmosphere and RB flask was closed with stopper. The resulting reaction mixture was stirred at 80 ºC for 16 h until the complete consumption of starting material was observed, which was monitored by the TLC analysis. The reaction mixture was diluted with EtOAc (5 mL) and filtered through celite and concentrated under reduced pressure and the crude product was purified by column chromatography using EtOAc:hexanes to afford the compound **3**.



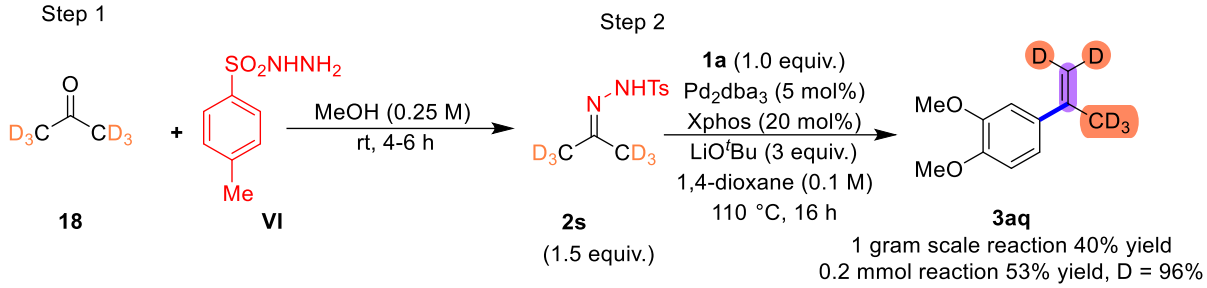
9.0 Scale up reactions

9.1 1.0 mmol reaction of thianthrenium salt **1b** with deuterated *N*-tosylhydrazone **2a** for the synthesis of **3ba**



In a glove box, 50 mL round bottom flask (RB) equipped with magnetic stir bar, aryl thianthrenium salt **1** (472.0 mg, 1.0 mmol, 1.0 equiv.) was added followed by the addition of LiO^{t}Bu (240.0 mg, 3.0 mmol, 3.0 equiv.), *N*-tosylhydrazones **2a** (481.5 mg, 1.5 mmol, 1.5 equiv.) Xantphos (70.0 mg, 0.12 mmol, 12 mol%) and Pd_2dba_3 (45.5 mg, 0.05 mmol, 5 mol%). The reaction tube was taken out from the glove box, dry 1,4-dioxane (0.1 M, 10.0 mL) was added under inert atmosphere and closed the reaction tube with stopper. The resulting reaction mixture was stirred at 80 ºC for 16 h until the complete consumption of starting material was observed, which was monitored by the TLC analysis. The reaction mixture was diluted with EtOAc (5 mL) and filtered through celite and concentrated under reduced pressure and the crude product was purified by column chromatography using EtOAc:hexanes to afford the compound **3ba** with 68% yield (164.5 mg).

9.2 Semi-one-pot synthesis of 3aq with different mmol/gram reaction: 1.0, 0.2 mmol 1.0 gram reaction of in-situ generated thianthrenium salt **1a** with deuterated acetone-D6 **18** via in-situ generated deuterated *N*-tosylhydrazone **2q**



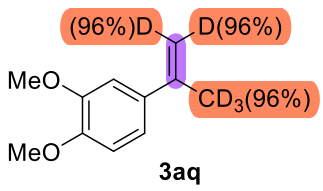
1 gram scale reaction:

Step 1: To a stirred solution of tosylhydrazide **VI** (558 mg, 3.0 mmol, 1.0 equiv.) in MeOH (0.25 M), corresponding D_6-acetone **18** (220 µL, 3.0 mmol, 1.0 equiv.) was added in dropwise manner. The reaction mixture was stirred at room temperature until complete conversion was observed by TLC. Solvent was removed under reduced pressure by rotary evaporator and crude compound was recrystallized with hot methanol to get the desired product **2q** and transferred into a 50 mL round bottom flask (RB) and used for next step without further purification.

Step 2: In a glove box, 50 mL round bottom flask (RB) charged with a *N*-tosylhydrazones **2q** was taken and magnetic stir bar, aryl thianthrenium salt **1a** (2.0 mmol, 1.0 equiv.) [*1a was prepared from corresponding arene following procedure 9.0 step 1,* **11** (2.0 mmol, 1.0 equiv.)] was added followed by the addition of LiO^{t}Bu (480.0 mg, 6.0 mmol, 3.0 equiv.) Xphos (190.0 mg, 0.24 mmol, 12 mol%) and Pd_2dba_3 (91.0 mg, 0.1 mmol, 5 mol%). The reaction tube was taken out from the glove box, dry 1,4-dioxane (0.1 M, 20.0 mL) was added under inert atmosphere and closed the reaction tube with stopper. The resulting reaction mixture was stirred at 110 ºC for 16 h until the complete consumption of starting material was observed, which was monitored by the TLC analysis. The reaction mixture was diluted with EtOAc (5 mL) and filtered through celite and concentrated under reduced pressure and the crude product was purified by column chromatography using EtOAc:hexanes to afford the compound **3as** with 40% yield (146.5 mg).

1,2-Dimethoxy-4-(prop-1-en-2-yl-d5)benzene (**3aq**)

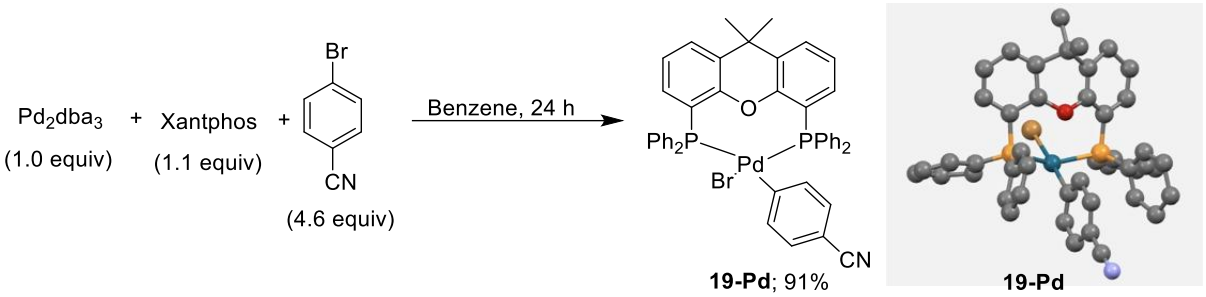
3aq was prepared according to the general procedure **4.3** in 40% (146.5 mg) isolated yield. Colourless oil. **TLC** (10% ethyl acetate in hexanes): R_f = 0.7; **IR** (KBr): 2927, 2850, 1520, 1503, 1439, 1269, 1250, 1026 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.02-7.00 (m, 1H), 6.91-6.88 (m, 2H), 5.29 (s, 0.04H), 5.01 (s, 0.04H), 3.88(5) (s, 3H), 3.88(2) (s, 3H), 2.10(s, 0.13H); **^{13}C NMR** (126 MHz,



$CDCl_3$): δ 149.1, 148.7, 120.9, 118.1, 111.4, 110.8, 55.9(6), 55.9(0); **^{2}H NMR** (77 MHz, $CHCl_3$): δ 5.32, 5.04, 2.12; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{11}H_{10}D_5O_2$ 184.1380, Found 184.1380. For 0.2 mmol scale reaction, the same above procedure was followed and product **3as** was obtained with 53% yield 96% deuterium incorporation.

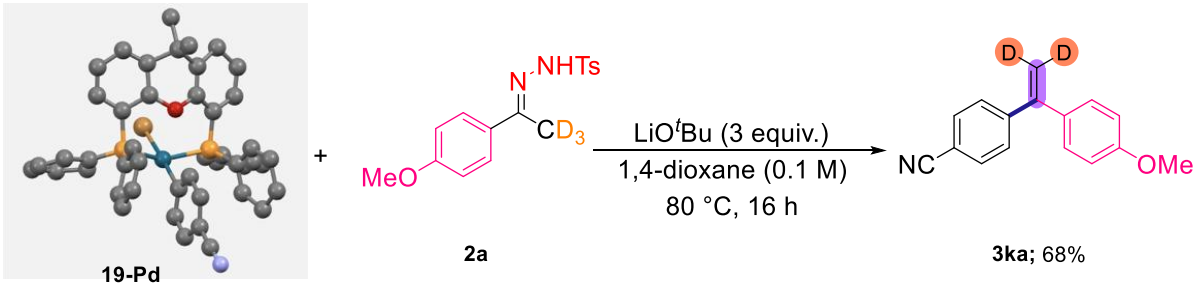
10.0 Mechanistic studies

10.1 Synthesis of **19-Pd** complex



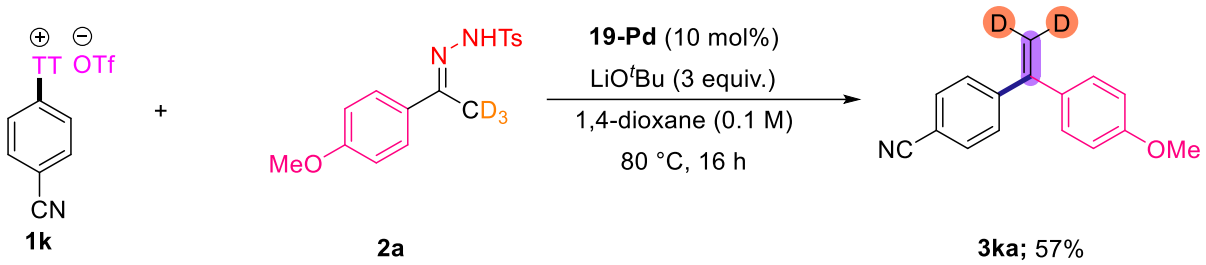
The palladium complex was prepared according to the modified reported literature. A solution of Xantphos (128 mg, 0.22 mmol, 1.1 equiv), $Pd_2(dba)_3$ (92 mg, 0.10 mmol, 0.20 mmol Pd, 1.0 equiv), and 4-bromobenzonitrile (168 mg, 0.92 mmol, 4.6 equiv) in benzene (6 mL) was stirred at room temperature for 24 h. The mixture was then filtered through a pad of Celite and concentrated in vacuo. Ether (6 mL) was then added to the residue and yellow crystalline solid was allowed to form upon standing for 1 h. The solid was then filtered, washed with ether, and dried under vacuum to give 157 mg (91%) of complex **22**-Pd.[7]

10.2 Stoichiometric reaction of **19**-Pd complex



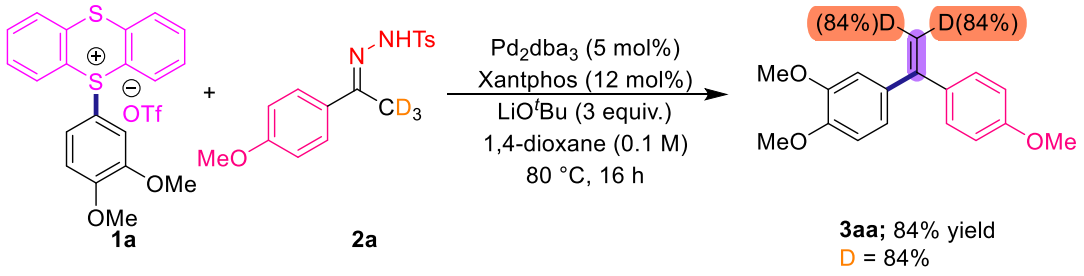
In a glove box, oven dried 15 mL reaction tube was charged with a magnetic stir bar, **19-Pd** complex (86.5 mg, 0.1 mmol, 10 mol%) was added followed by the addition of LiO^tBu (24.0 mg, 0.3 mmol, 3.0 equiv.) and *N*-tosylhydrazones **2a** (48.1 mg, 0.15 mmol, 1.5 equiv.). The reaction tube was taken out of glove box and to the reaction mixture anhydrous 1,4-dioxane (0.1 M, 1.0 mL) was added under inert atmosphere and closed the reaction tube with stopper. The resulting reaction mixture was stirred for 16 h at 80 ºC. Next the reaction mixture was filtered through celite and concentrated under reduced pressure, and purified by column chromatography to get the product **3ka** with 68% yield.

10.3 Catalytic reaction of **19**-Pd complex



In a glove box, oven dried 10 mL reaction tube was charged with a magnetic stir bar, **19-Pd** complex (8.6 mg, 0.01 mmol, 10 mol%) and **1k** (46.5 mg, 0.1 mmol, 1 equiv.) were added followed by the addition of LiO^{t}Bu (24.0 mg, 0.3 mmol, 3.0 equiv.) and *N*-tosylhydrazones **2a** (48.1 mg, 0.15 mmol, 1.5 equiv.). The reaction tube was taken out of glove box and to the reaction mixture anhydrous 1,4-dioxane (0.1 M, 1.0 mL) was added under inert atmosphere and closed the reaction tube with stopper. The resulting reaction mixture was stirred for 16 h at 80 ºC. Next the reaction mixture was filtered through celite and concentrated under reduced pressure, and purified by column chromatography to get the product **3ka** with 57% yield.

10.4 Calculation of deuterium incorporation taking $CDCl_3$ as internal standard



The reaction was performed following **procedure 4.1** and deuterium incorporation was calculated by adding $CDCl_3$ (0.8 mmol, 64 µL) for 0.1 mmol (27.2 mg) of product **3aa** to lock the sample.

Giving the integration to $CDCl_3$ as 1.00

Olefin C-D integration comes out to be: 0.21

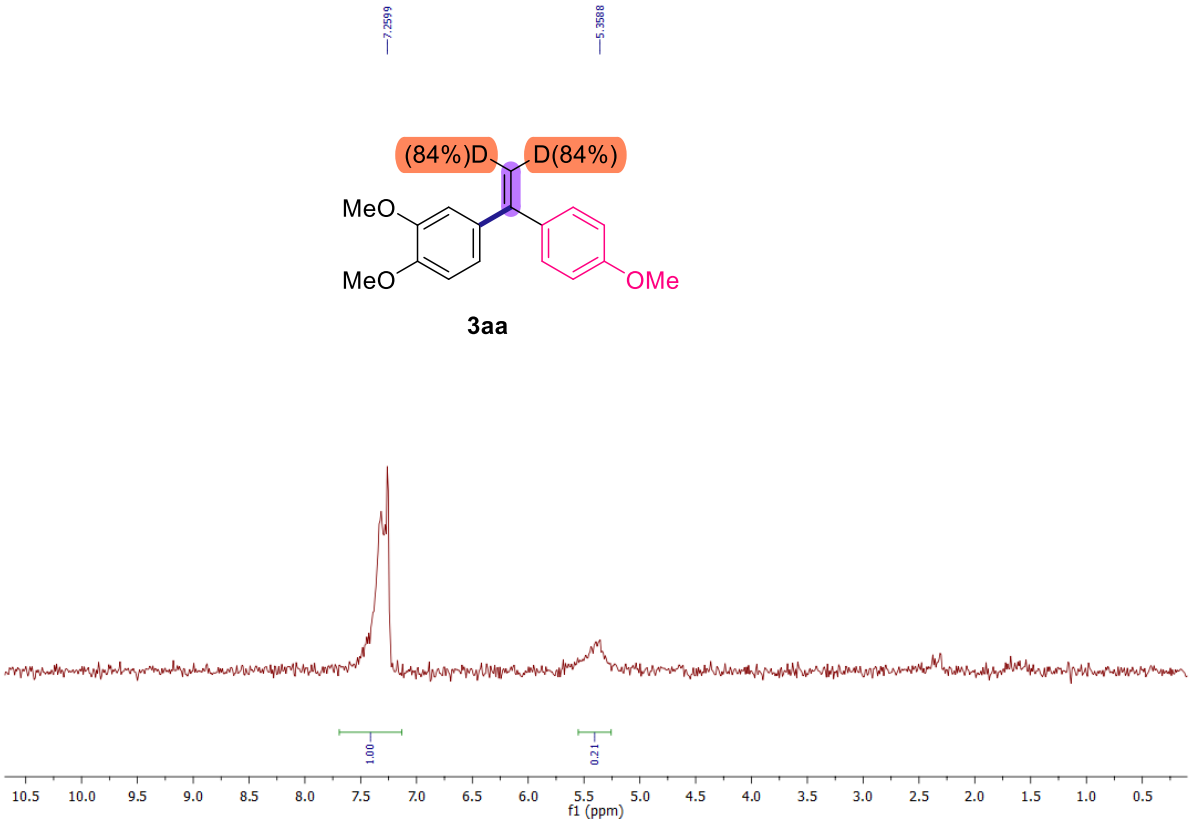
Deuterium incorporation = (Integration of C-D peak × Equivalents of $CDCl_3$ added) × 100/ Number of olefinic proton

Percentage deuterium incorporation = (0.21×8) × 100/ 2

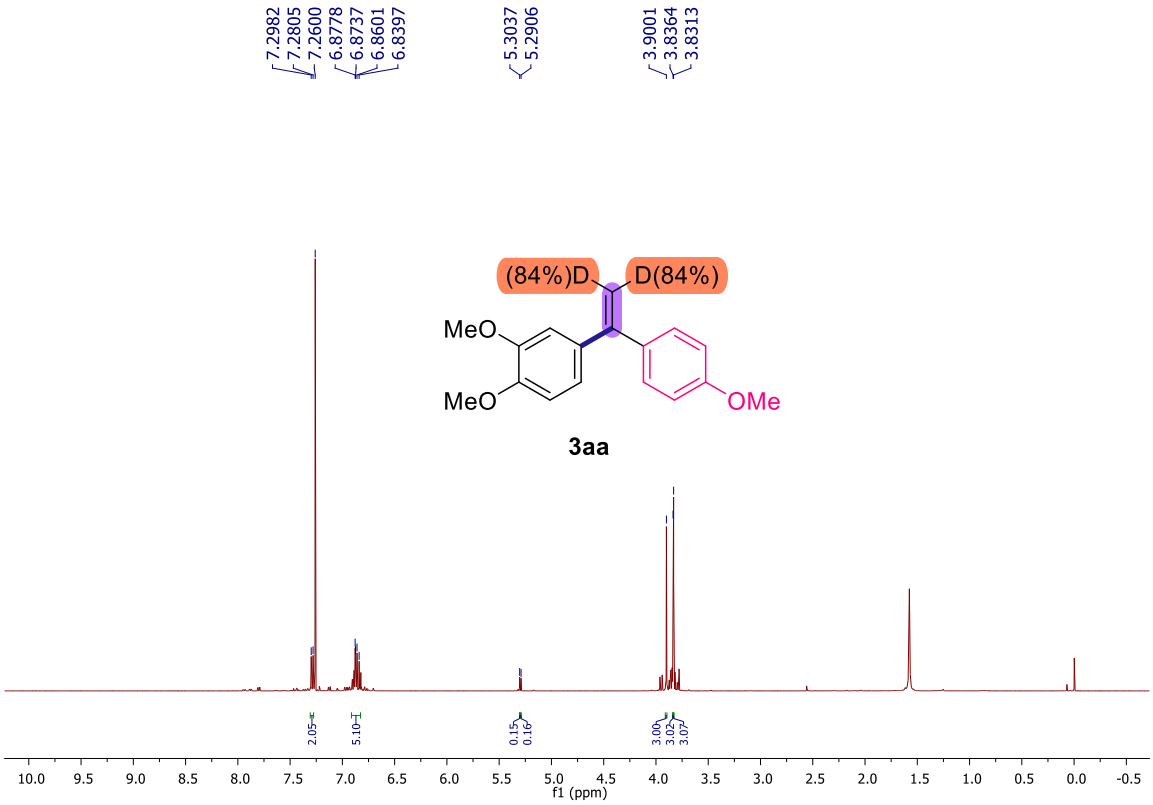
Percentage deuterium incorporation = 84%

1,2-Dimethoxy-4-(1-(4-methoxyphenyl)vinyl-2,2-d2)benzene (**3aa**)

^{2}H NMR (77 MHz, $CDCl_3$, 24 °C)



^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)



11.0 References

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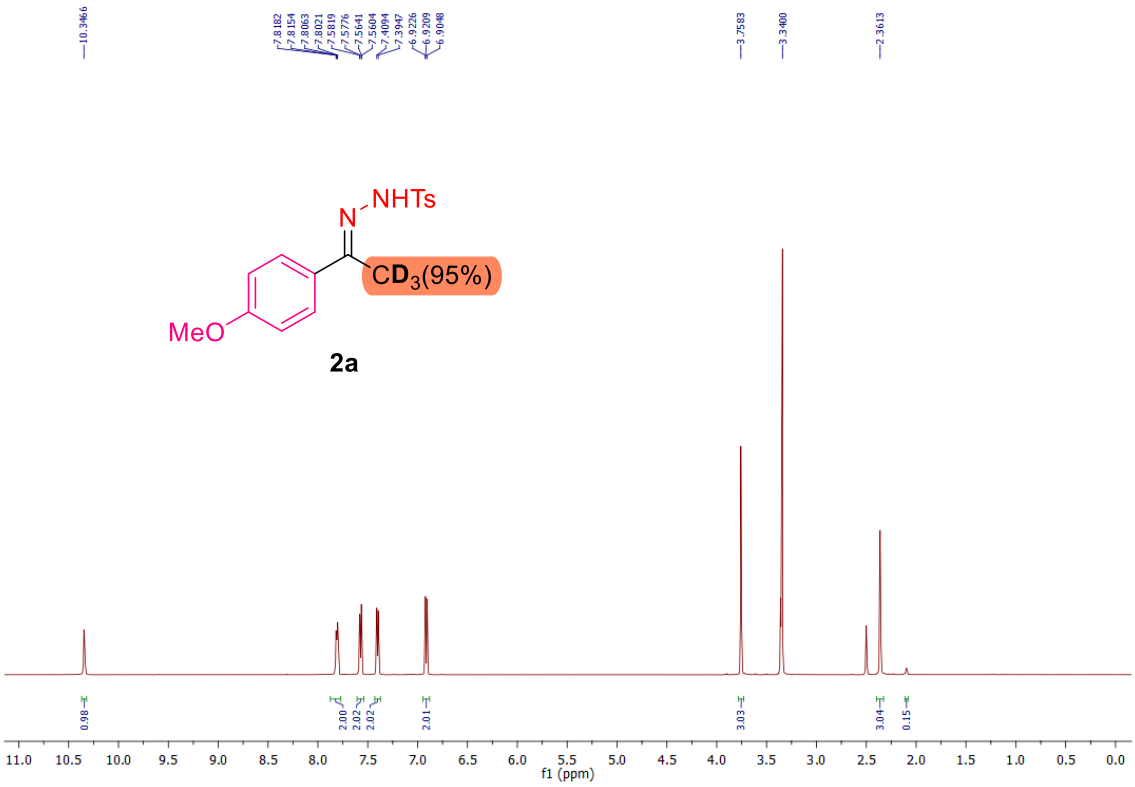
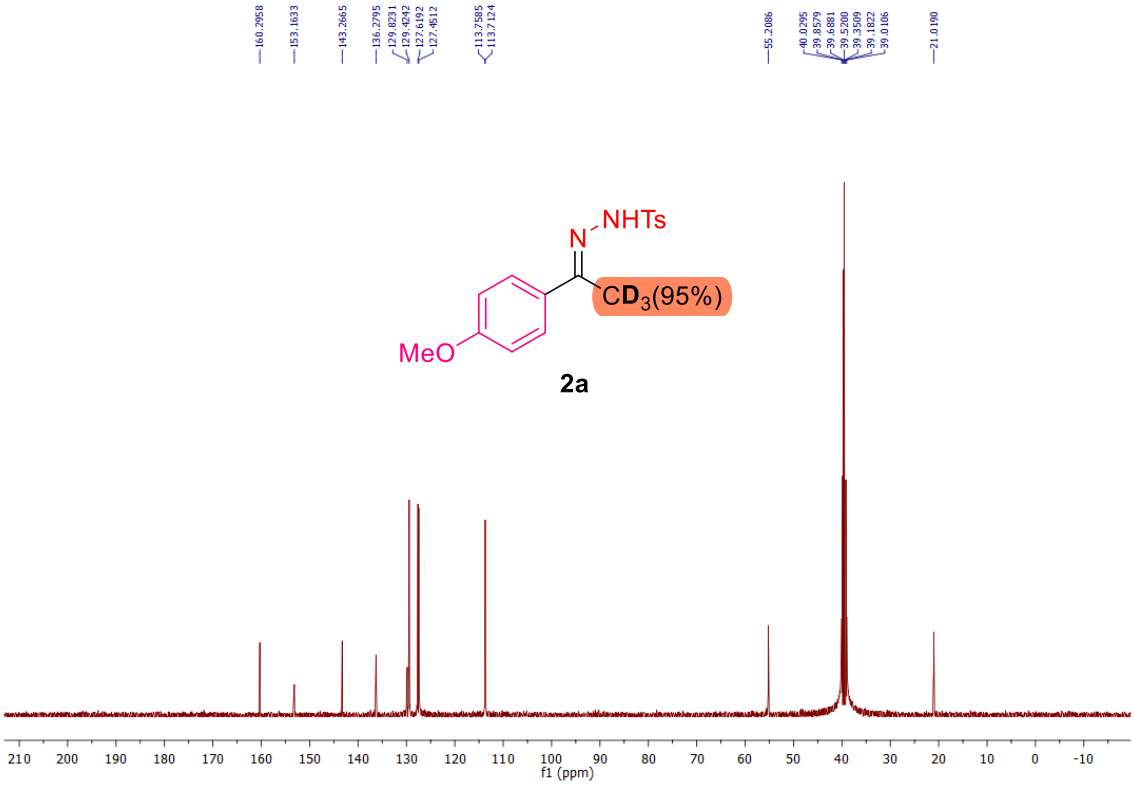
12.0 Spectral data

(*E*)-N'-(1-(4-methoxyphenyl)ethylidene-2,2,2-d3)-4-methylbenzenesulfonohydrazide (**2a**)

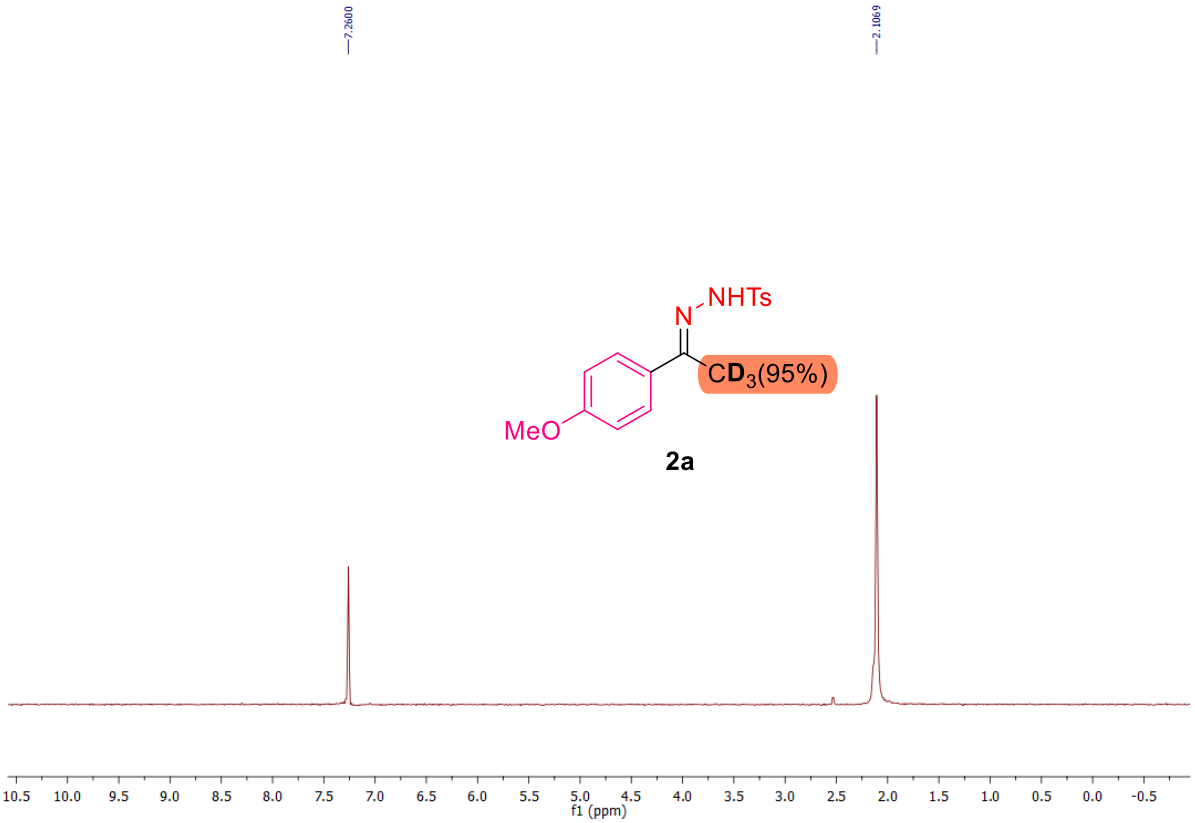
^{1}H NMR (500 MHz, DMSO-d$_6$, 24 °C)



^{13}C{^{1}H} NMR (126 MHz, DMSO D$_6$, 24 °C)

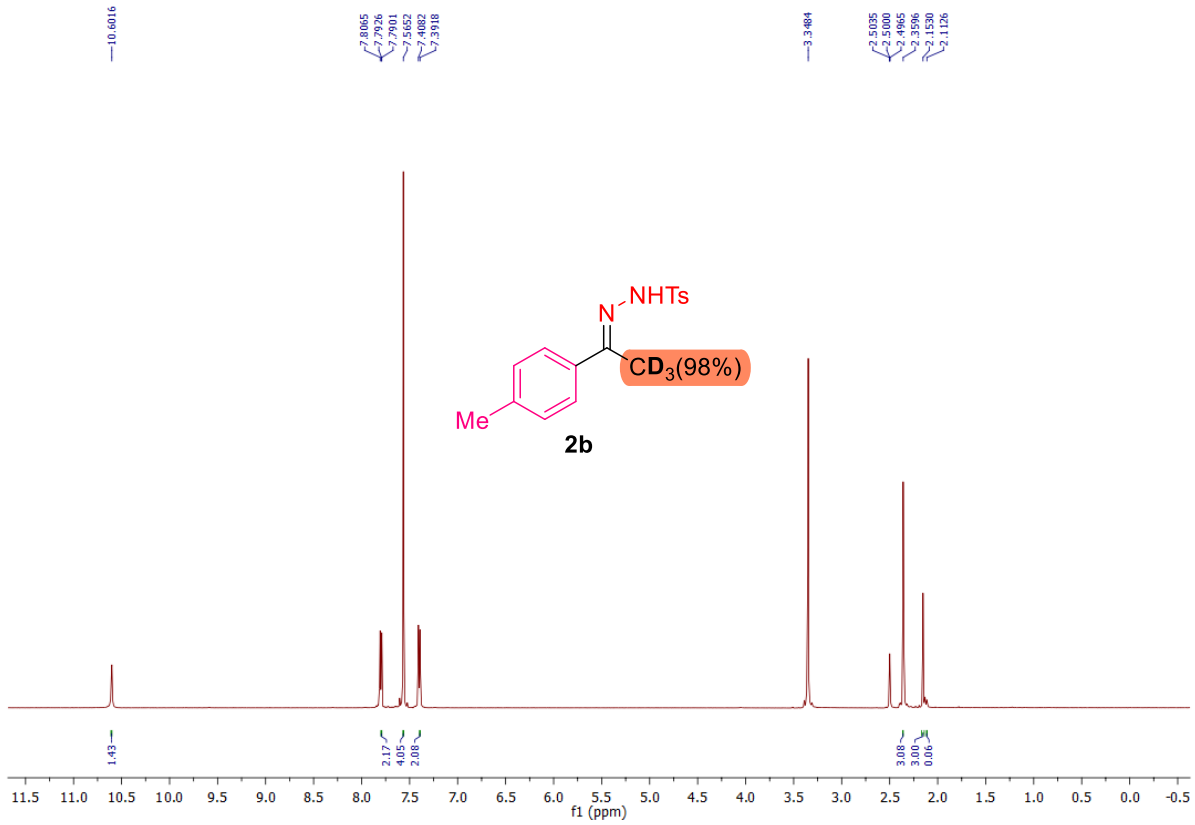


^{2}H NMR (77 MHz, $CDCl_3$, 24 °C)

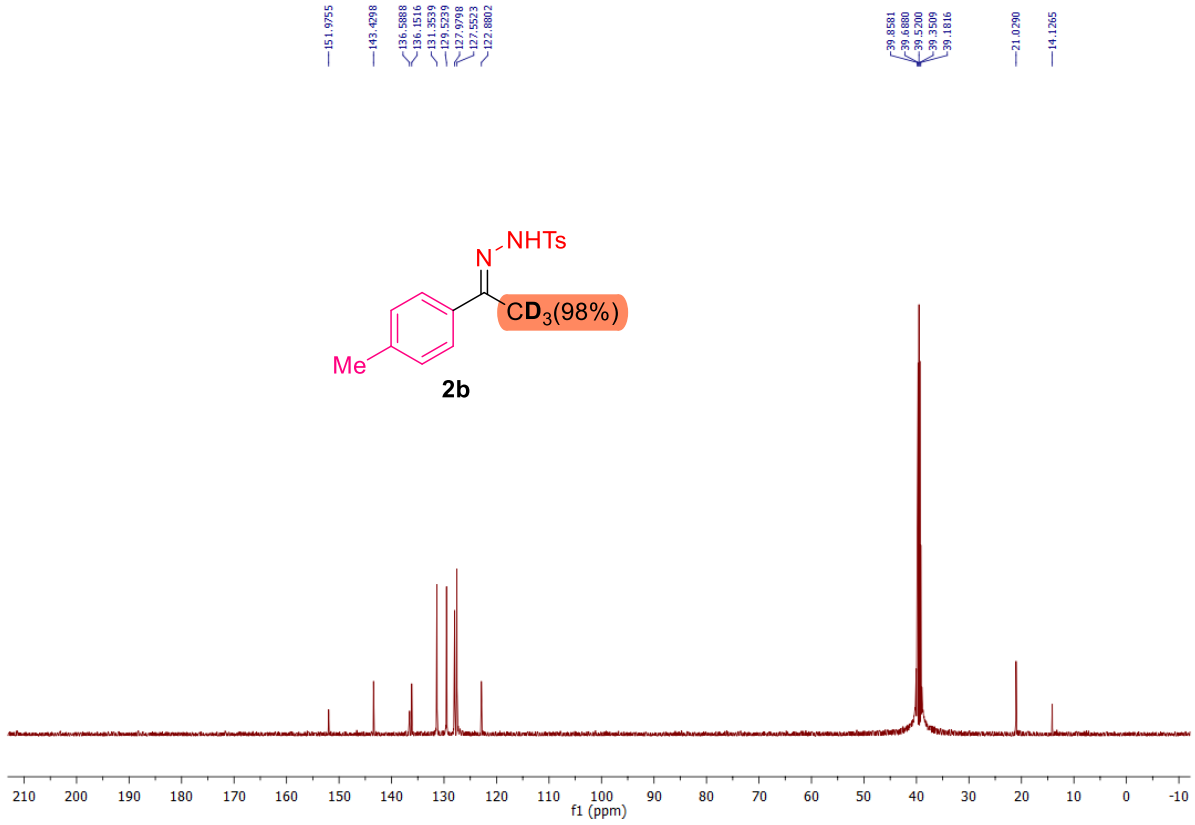


(*E*)-N'-(1-(4-methylphenyl)ethylidene-2,2,2-d3)-4-methylbenzenesulfonohydrazide (**2b**)

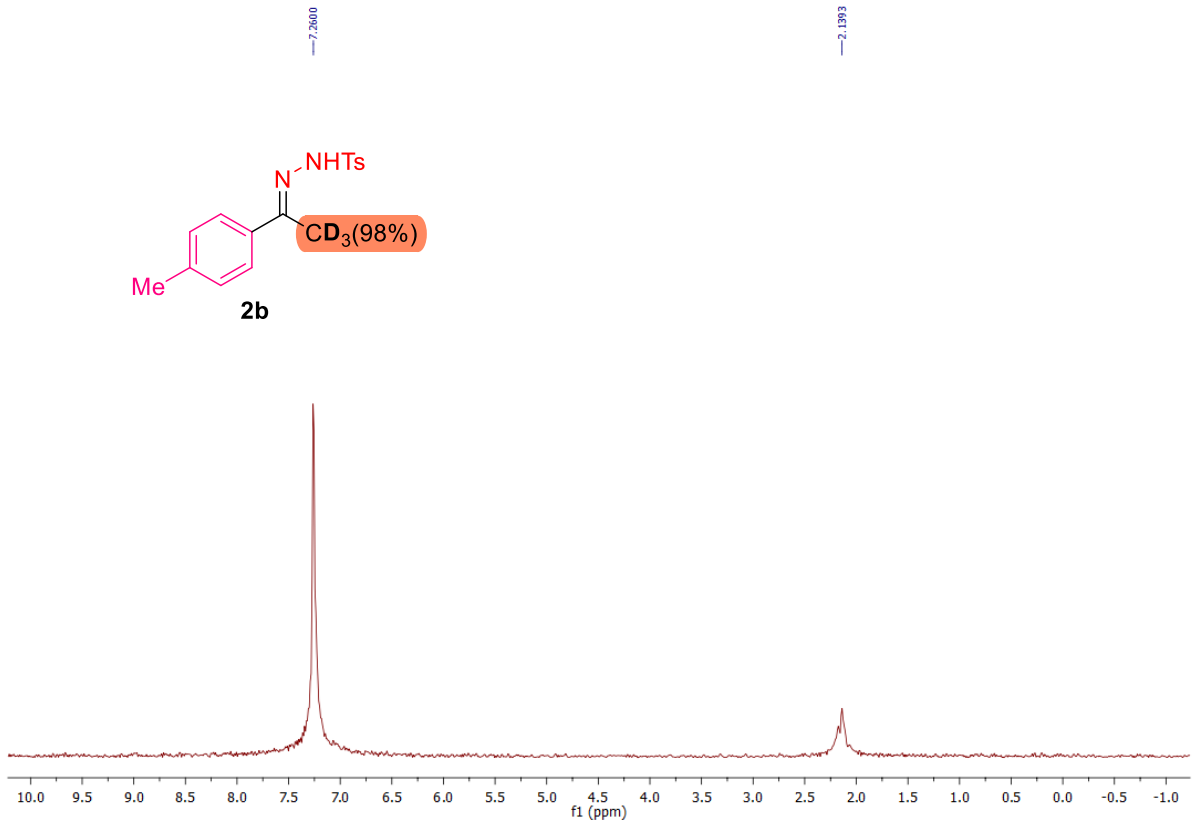
^{1}H NMR (500 MHz, DMSO D_6, 24 °C)



$^{13}C\{^{1}H\}$ NMR (126 MHz, DMSO D_6, 24 °C)

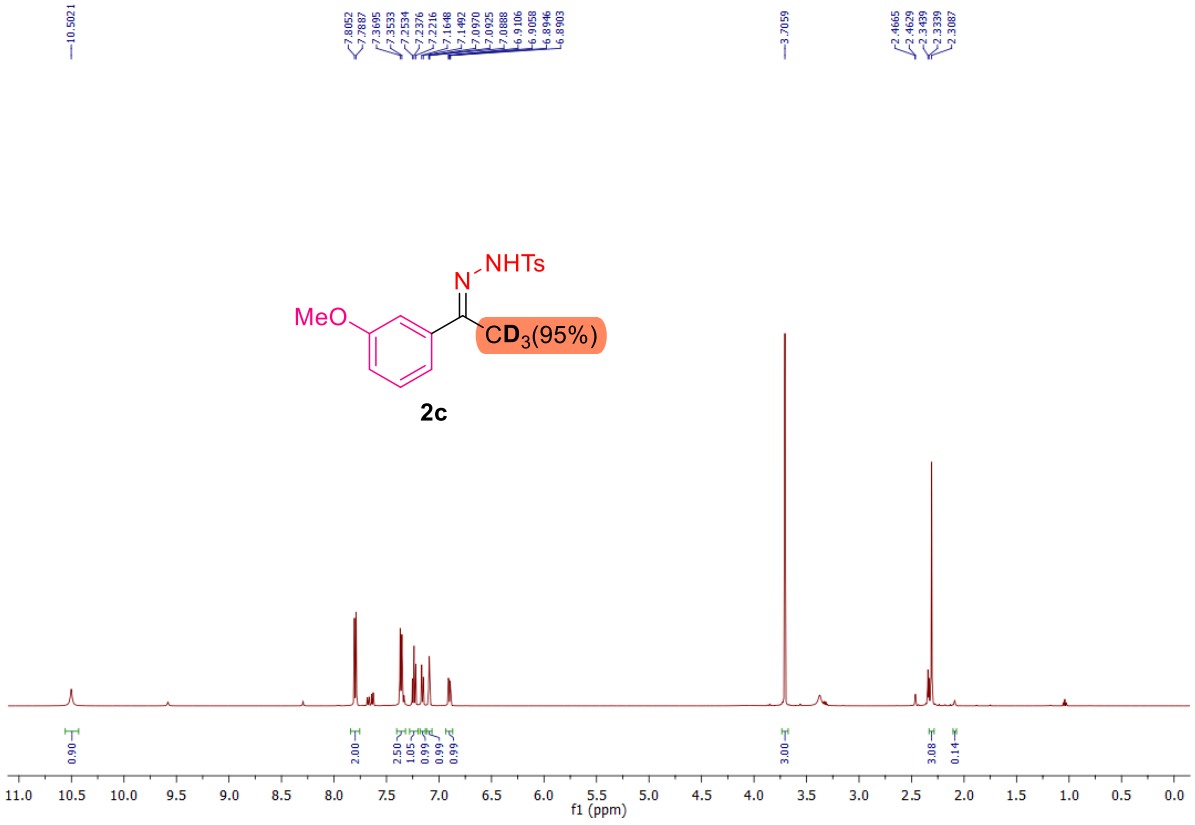


^{2}H NMR (77 MHz, $CDCl_3$, 24 °C)

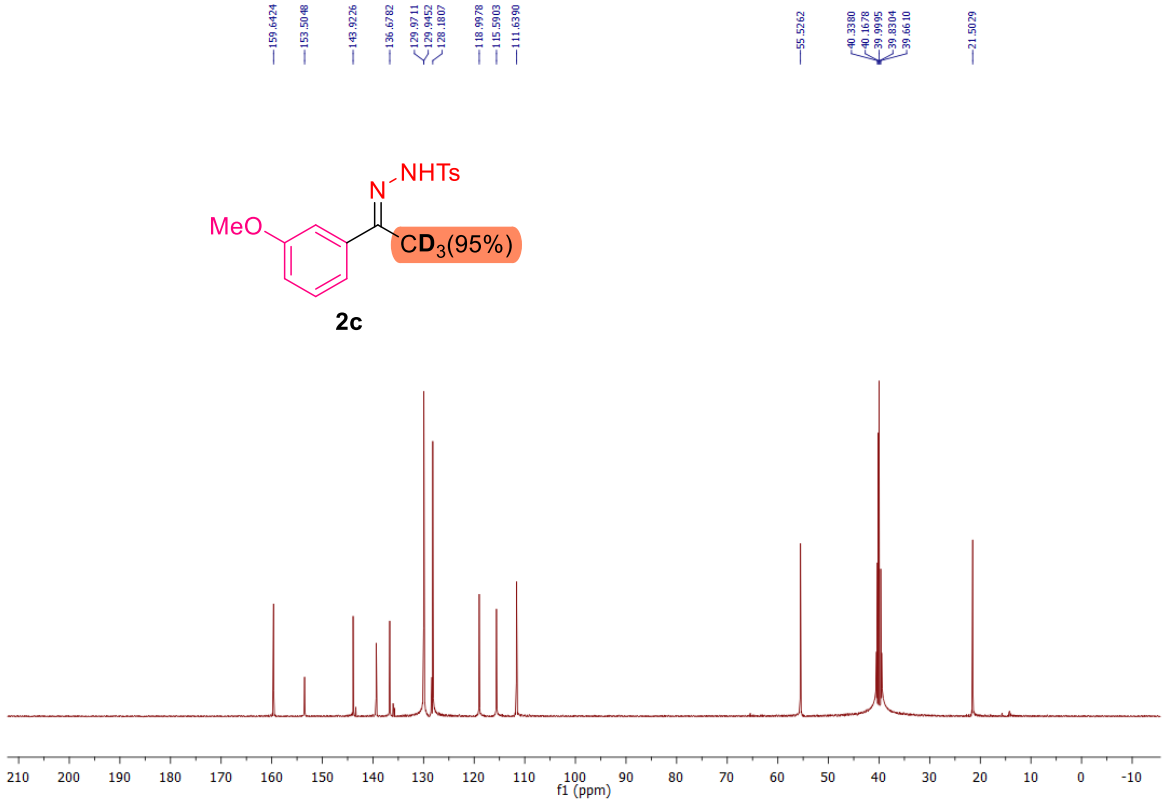


(E)-N'-(1-(3-methoxyphenyl)ethylidene-2,2,2-d3)-4-methylbenzenesulfonohydrazide (**2c**)

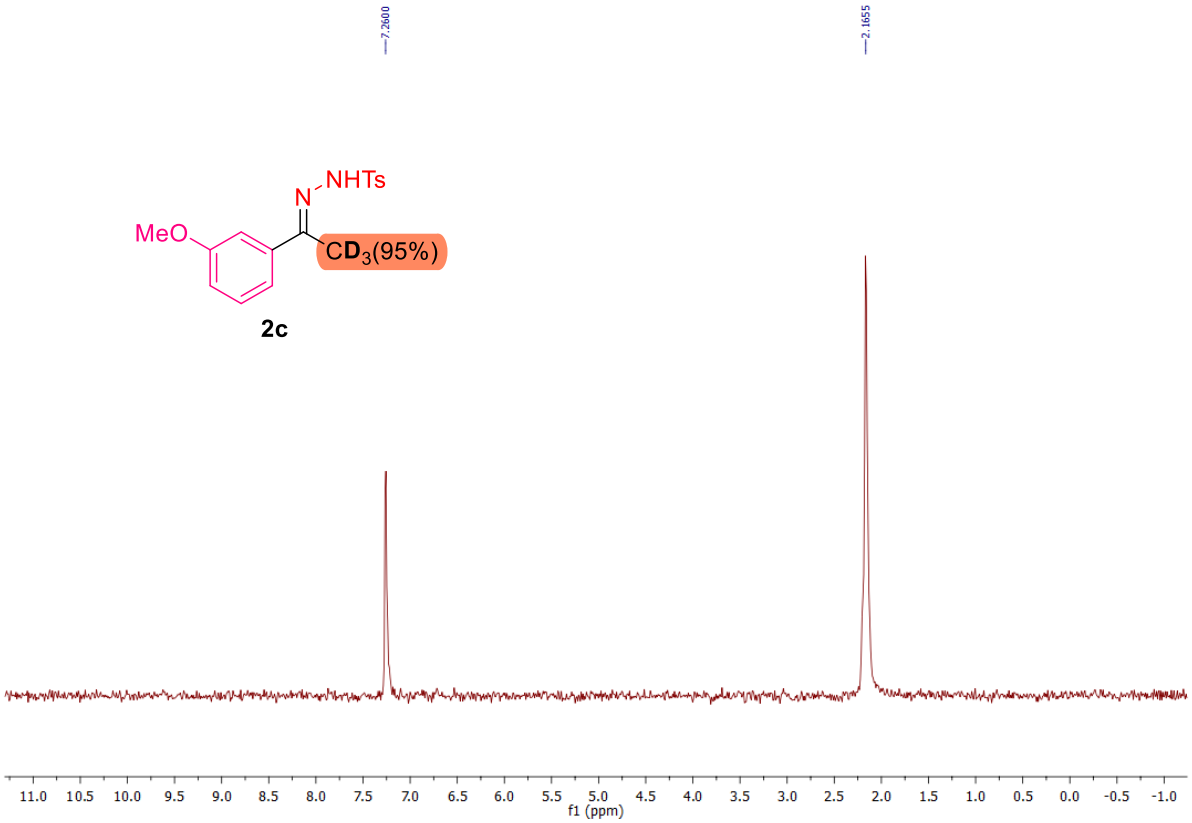
^{1}H NMR (500 MHz, DMSO D_6, 24 °C)



^{13}C{^{1}H} NMR (126 MHz, DMSO D_6, 24 °C)

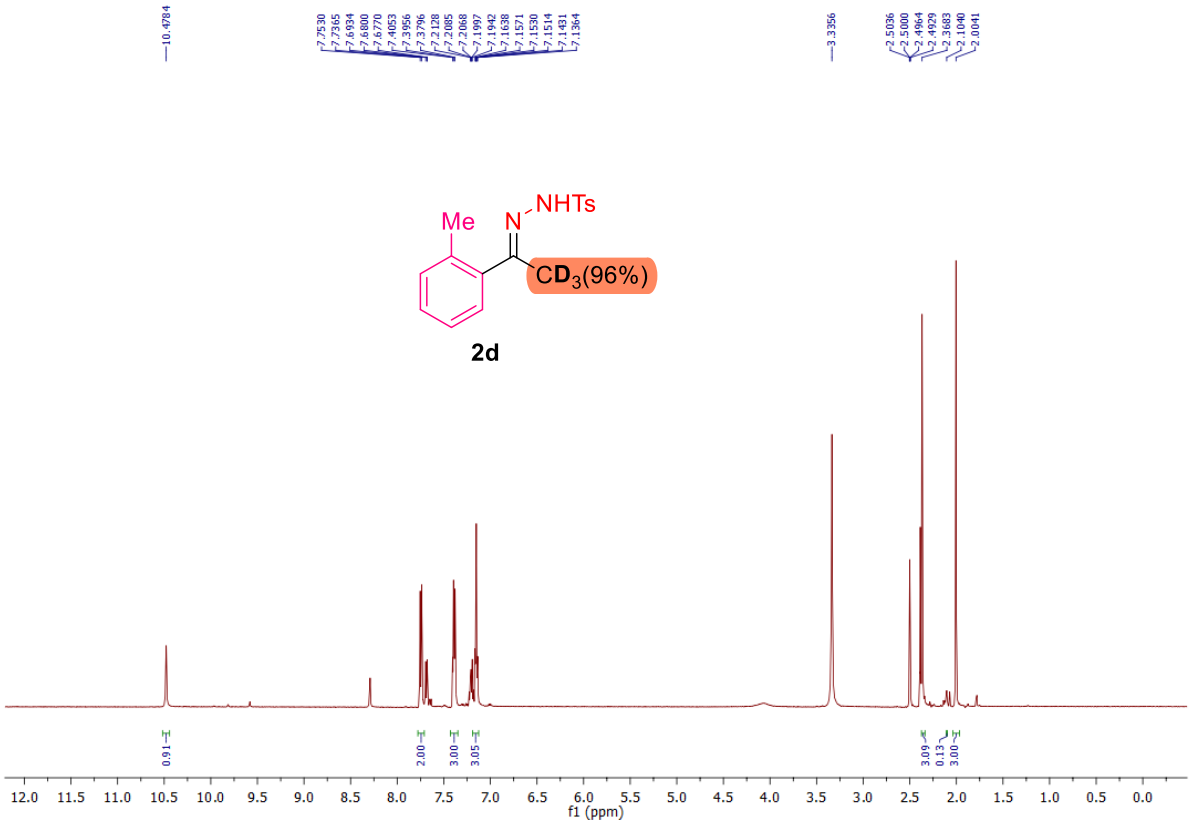


^{2}H NMR (77 MHz, $CDCl_3$, 24 °C)

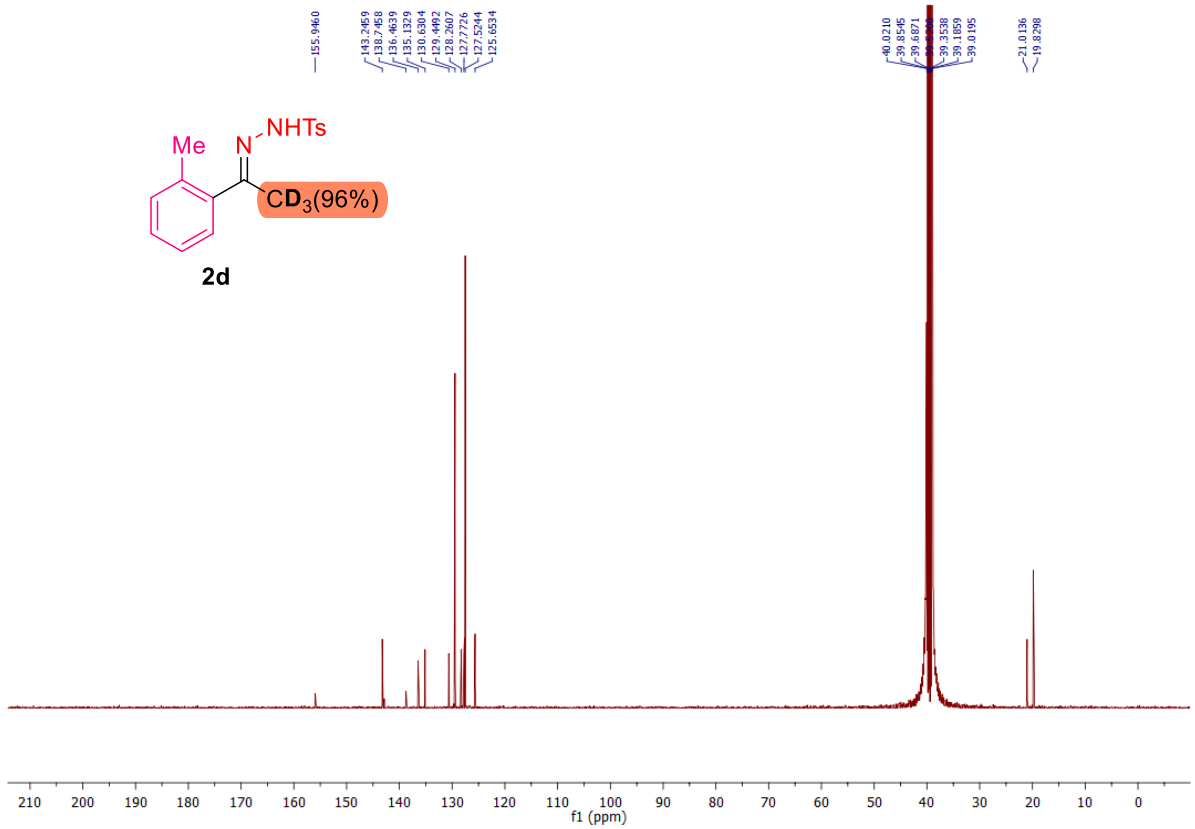


(*E*)-N'-(1-(2-methylphenyl)ethylidene-2,2,2-d3)-4-methylbenzenesulfonohydrazide (**2d**)

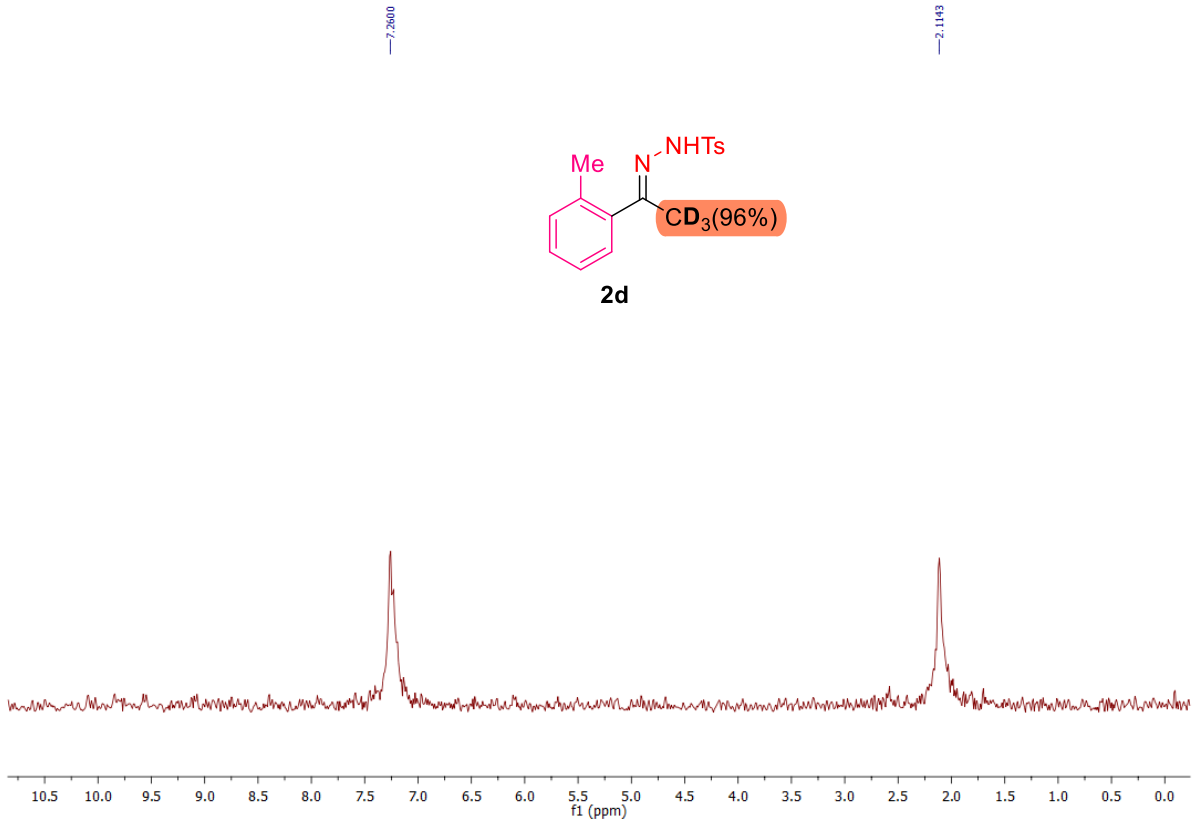
^{1}H NMR (500 MHz, DMSO D_6, 24 °C)



$^{13}C\{^{1}H\}$ NMR (126 MHz, DMSO D_6, 24 °C)

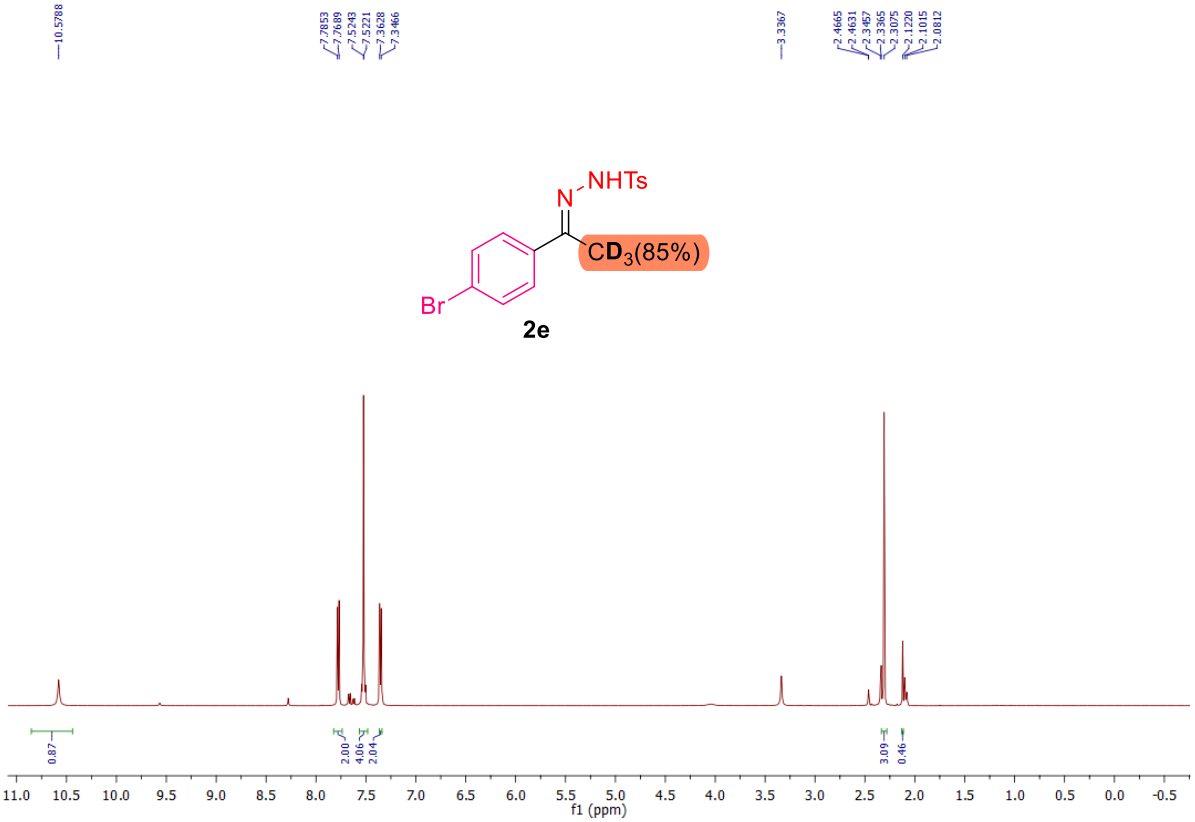


^{2}H NMR (77 MHz, $CDCl_3$, 24 °C)

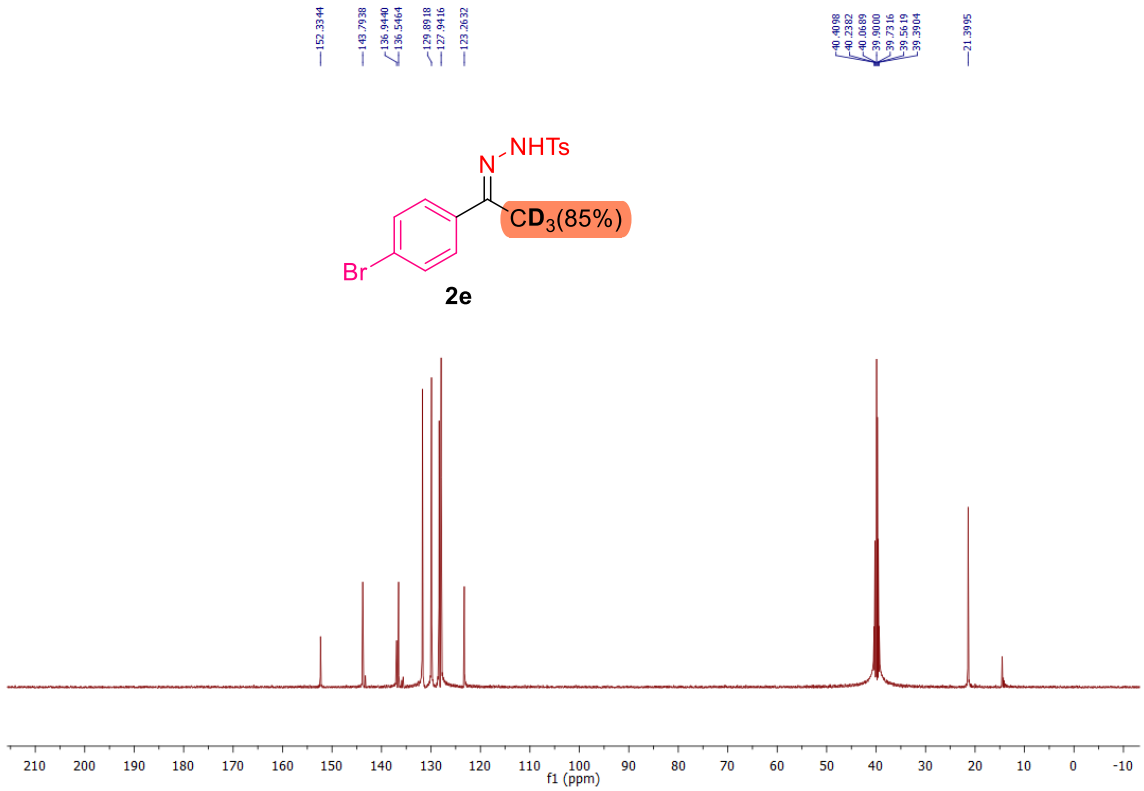


(*E*)-N'-(1-(2-methylphenyl)ethylidene-2,2,2- d3)-4-methylbenzenesulfonohydrazide (**2e**)

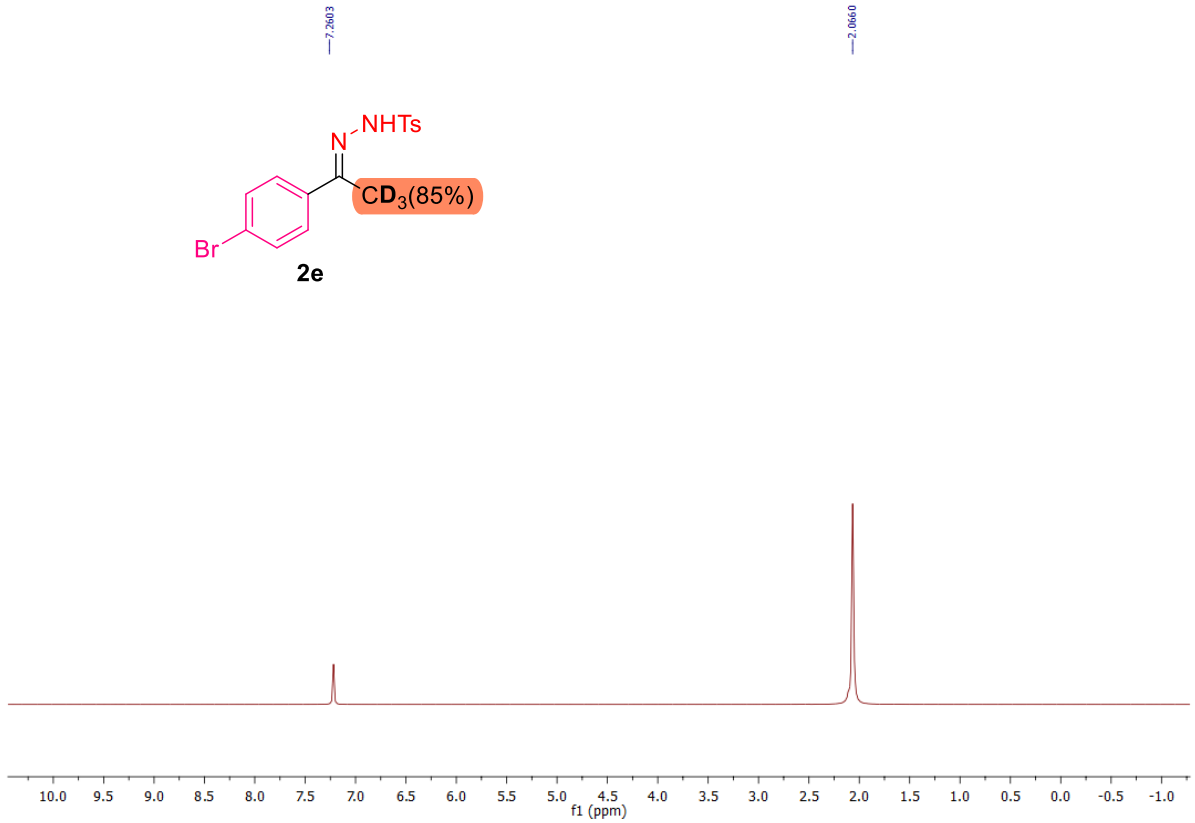
^{1}H NMR (500 MHz, DMSO D_6, 24 °C)



^{13}C{^{1}H} NMR (126 MHz, DMSO D_6, 24 °C)

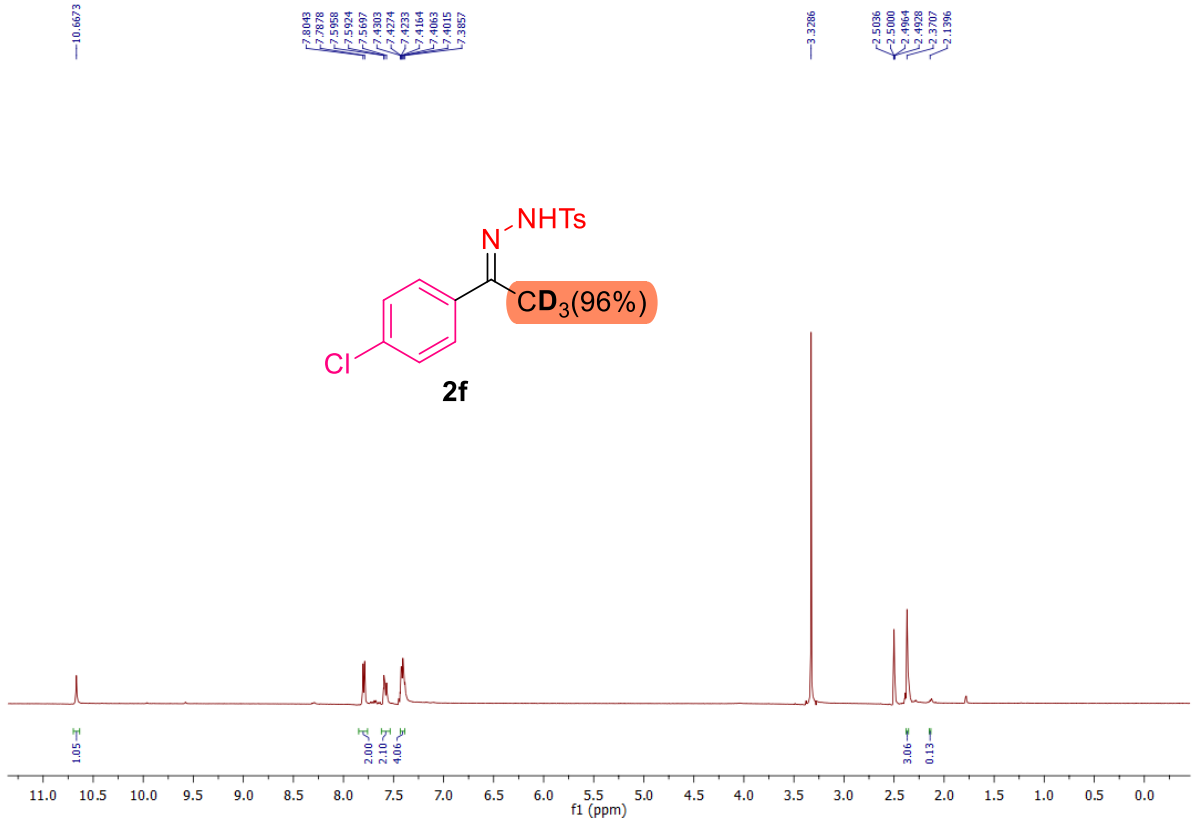


^{2}H NMR (77 MHz, $CDCl_3$, 24 °C)

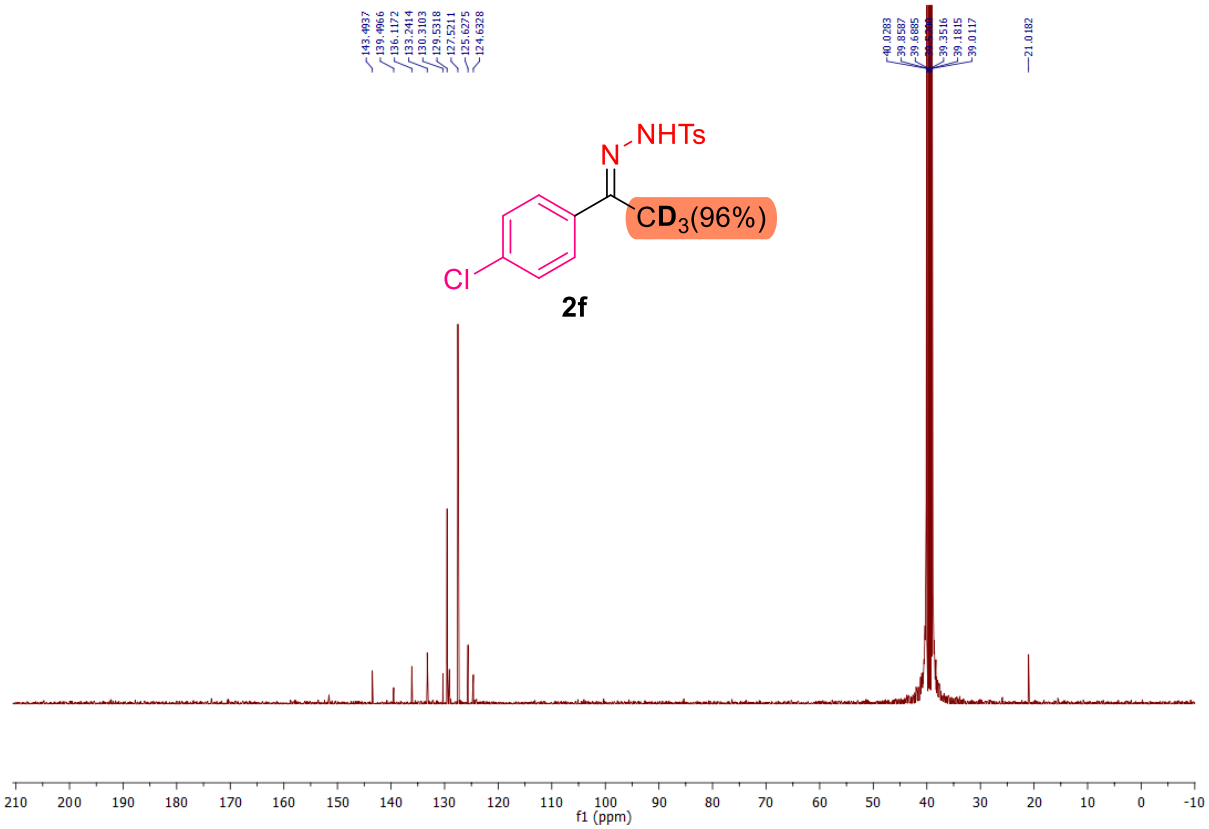


(*E*)-N'-(1-(4-chlorophenyl)ethylidene-2,2,2-d3)-4-methylbenzenesulfonohydrazide (**2f**)

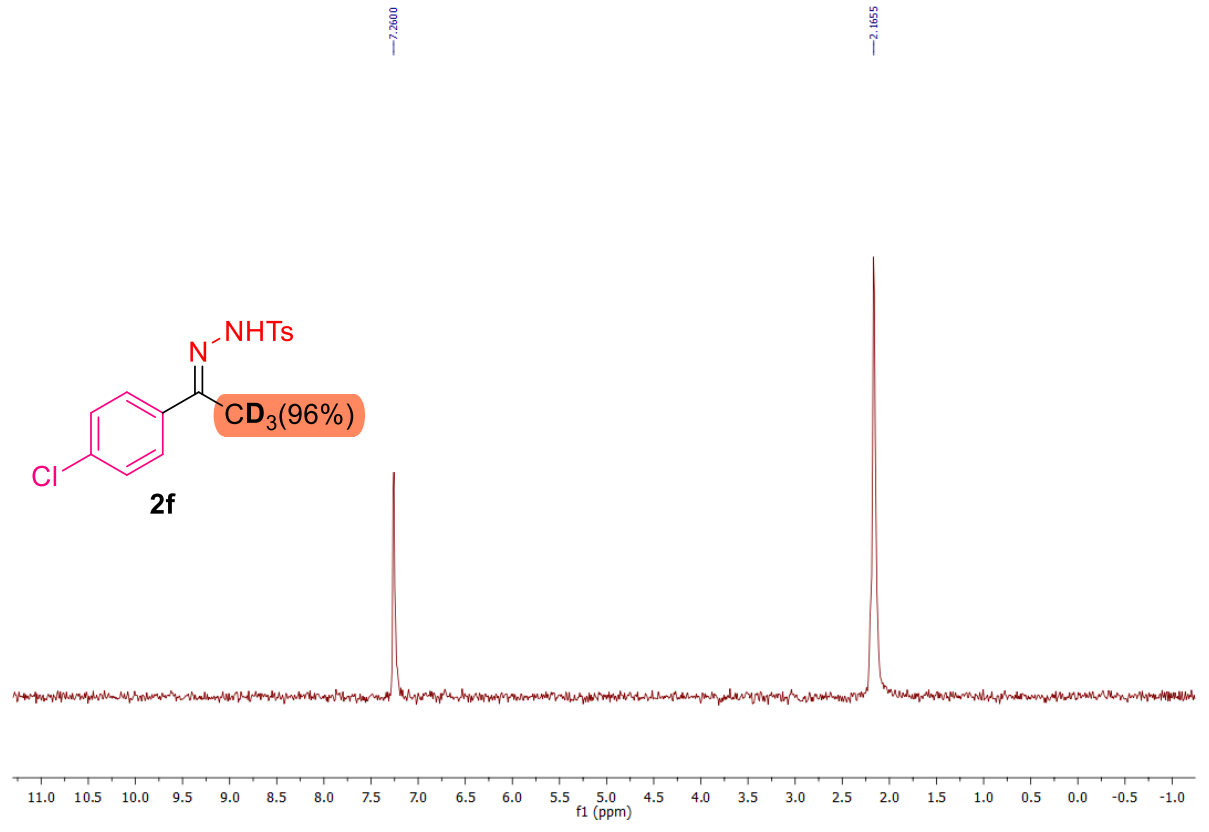
^{1}H NMR (500 MHz, DMSO D_6, 24 °C)



$^{13}C\{^{1}H\}$ NMR (126 MHz, DMSO D_6, 24 °C)

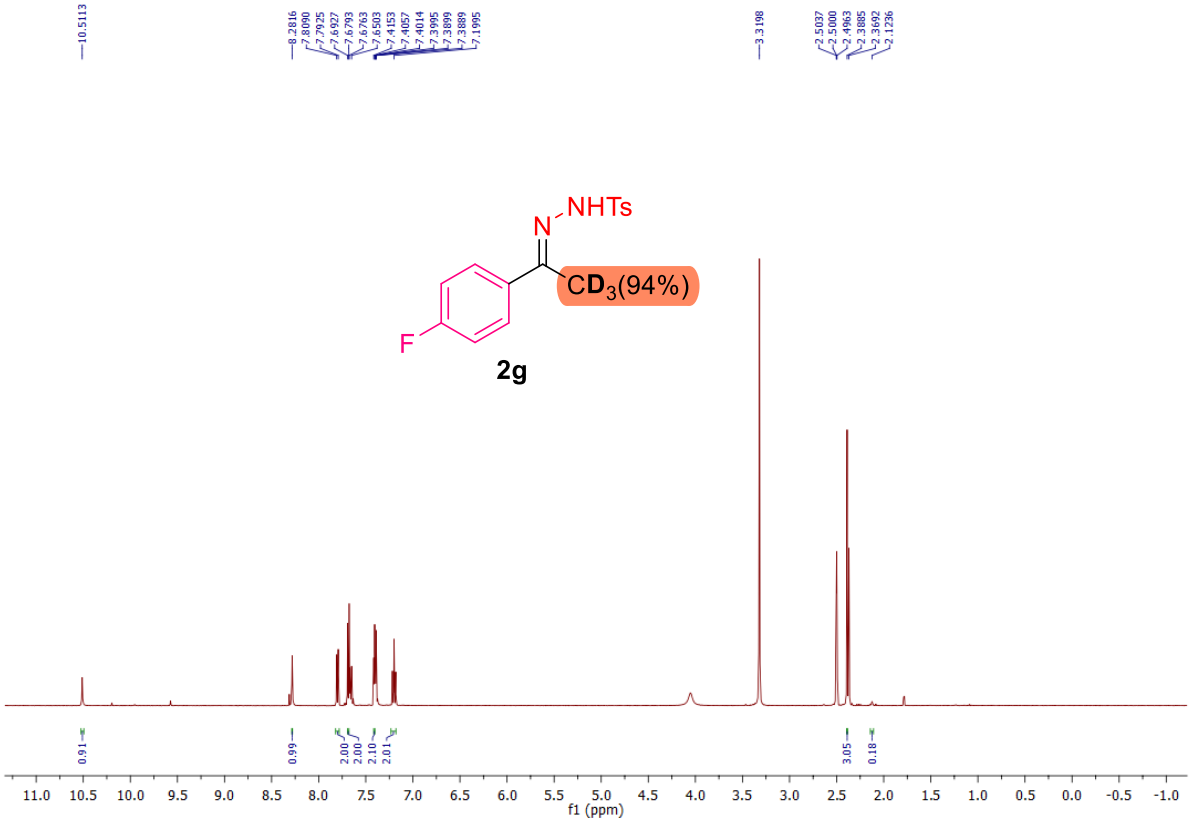


^{2}H NMR (77 MHz, $CDCl_3$, 24 °C)

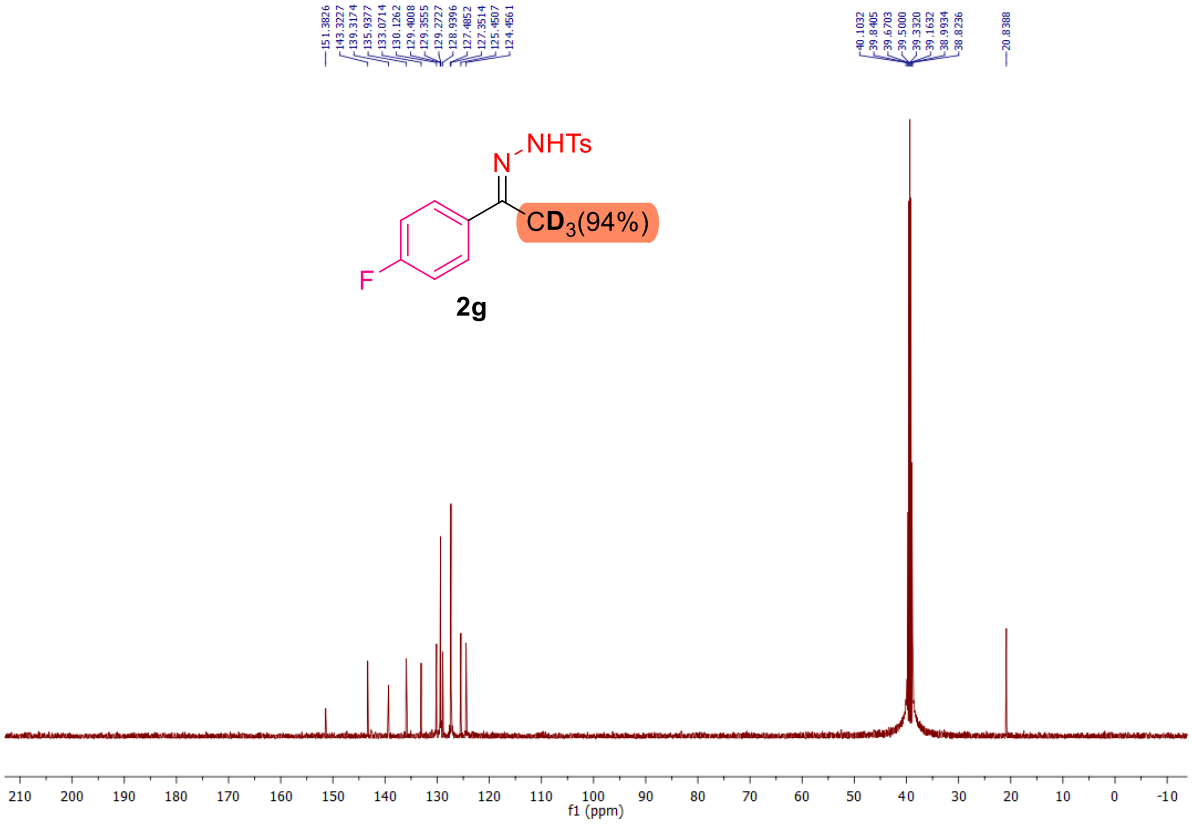


(*E*)-N'-(1-(4-fluorophenyl)ethylidene-2,2,2-d3)-4-methylbenzenesulfonohydrazide (**2g**)

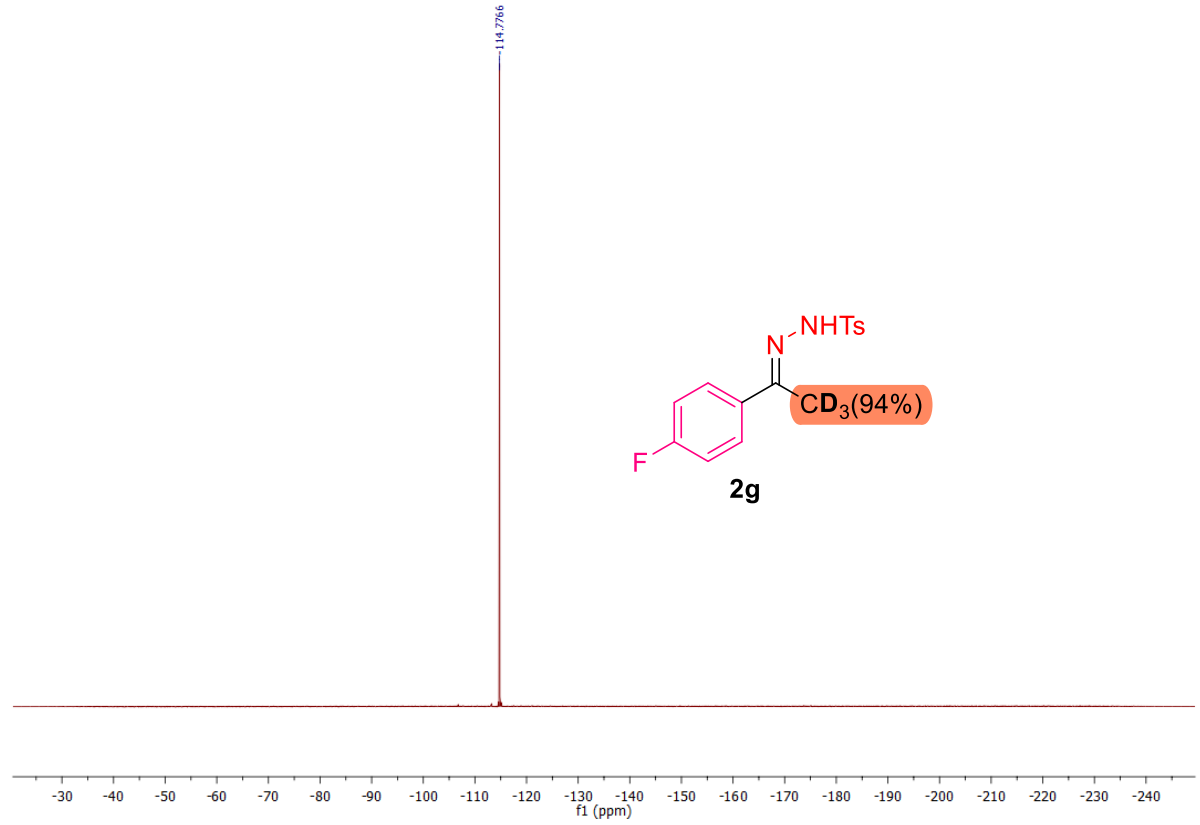
^{1}H NMR (500 MHz, DMSO D_6, 24 °C)



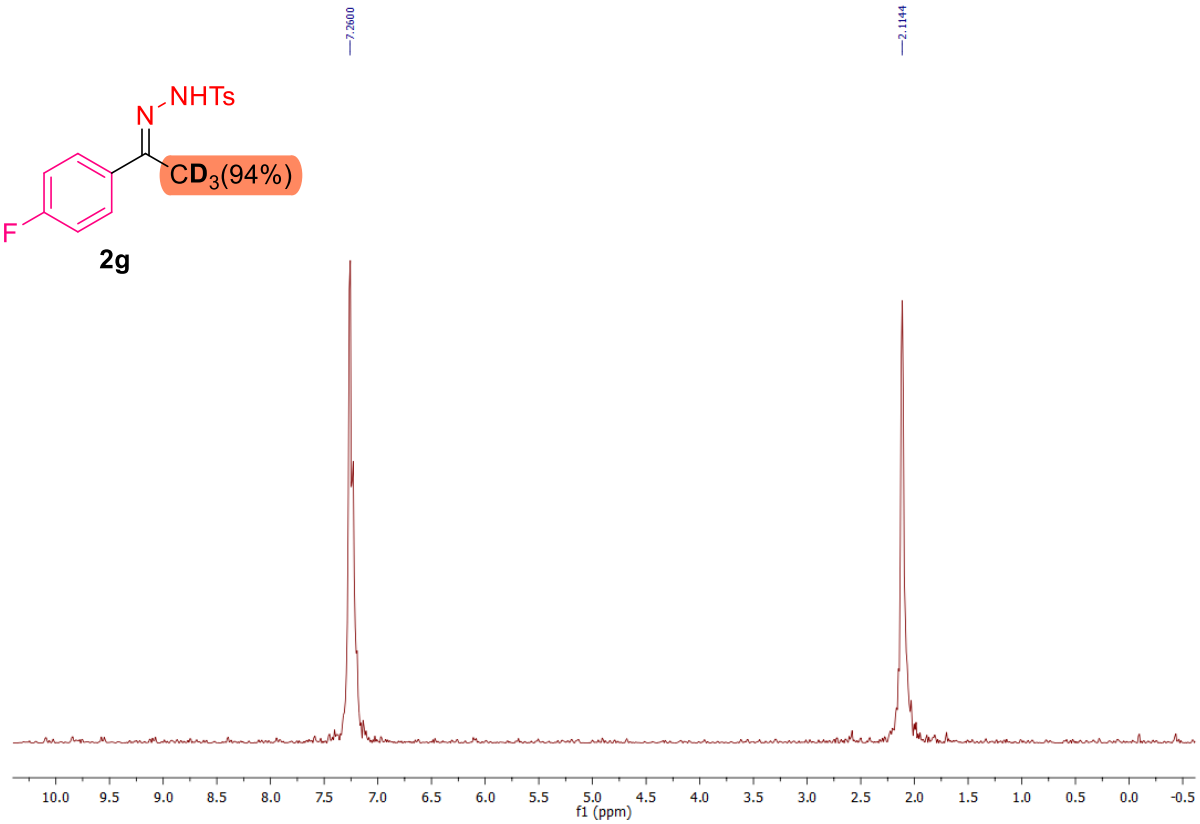
^{13}C{^{1}H} NMR (126 MHz, DMSO D_6, 24 °C)



^{19}F NMR (471 MHz, DMSO D_6, 24 °C)

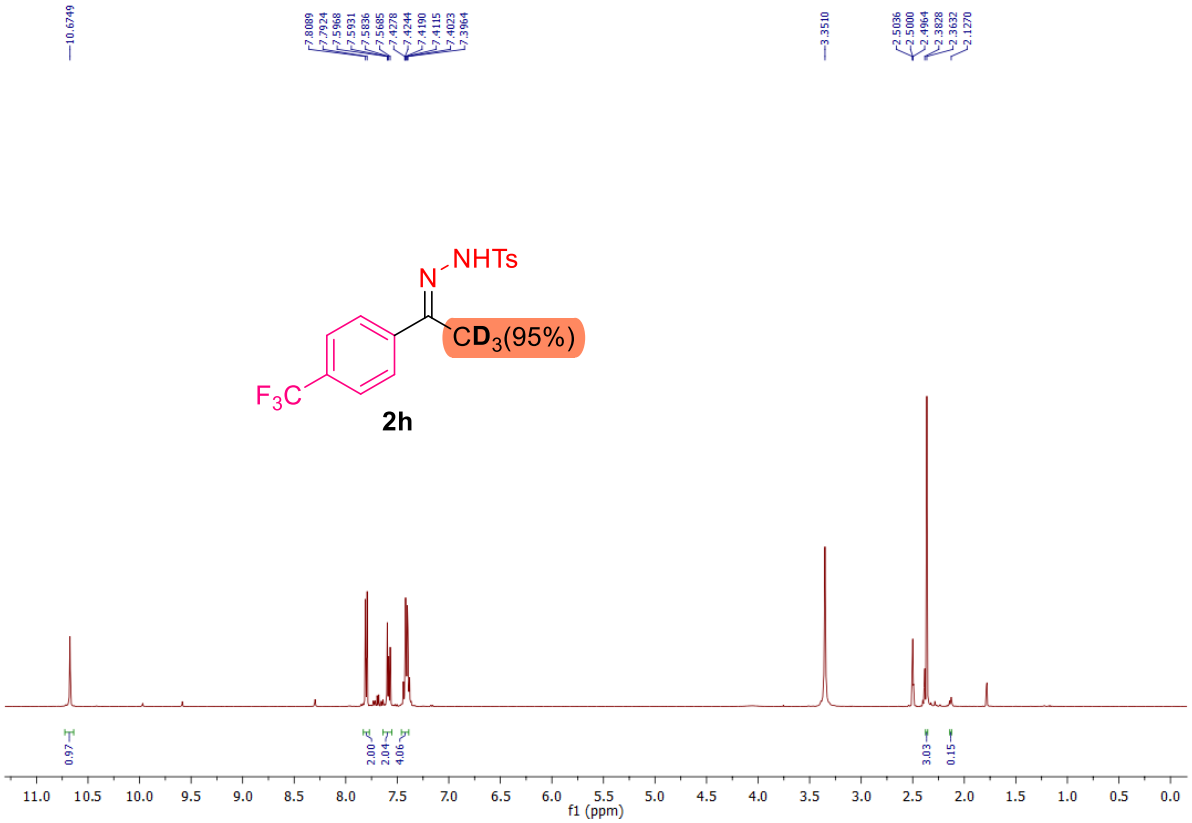


^{2}H NMR (77 MHz, $CDCl_3$, 24 °C)

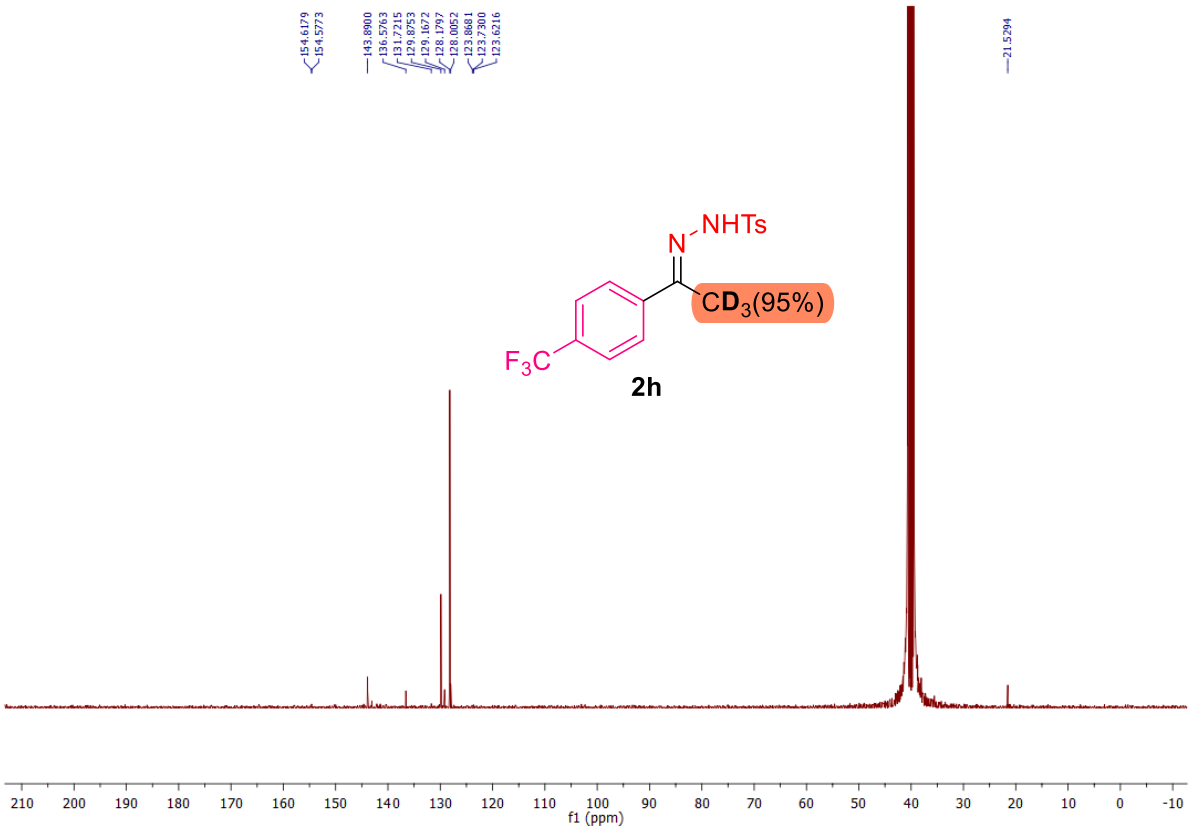


(*E*)-4-Methyl-N'-(1-(4-(trifluoromethyl)phenyl)ethylidene-2,2,2-d3)benzenesulfonohydrazide (**2h**)

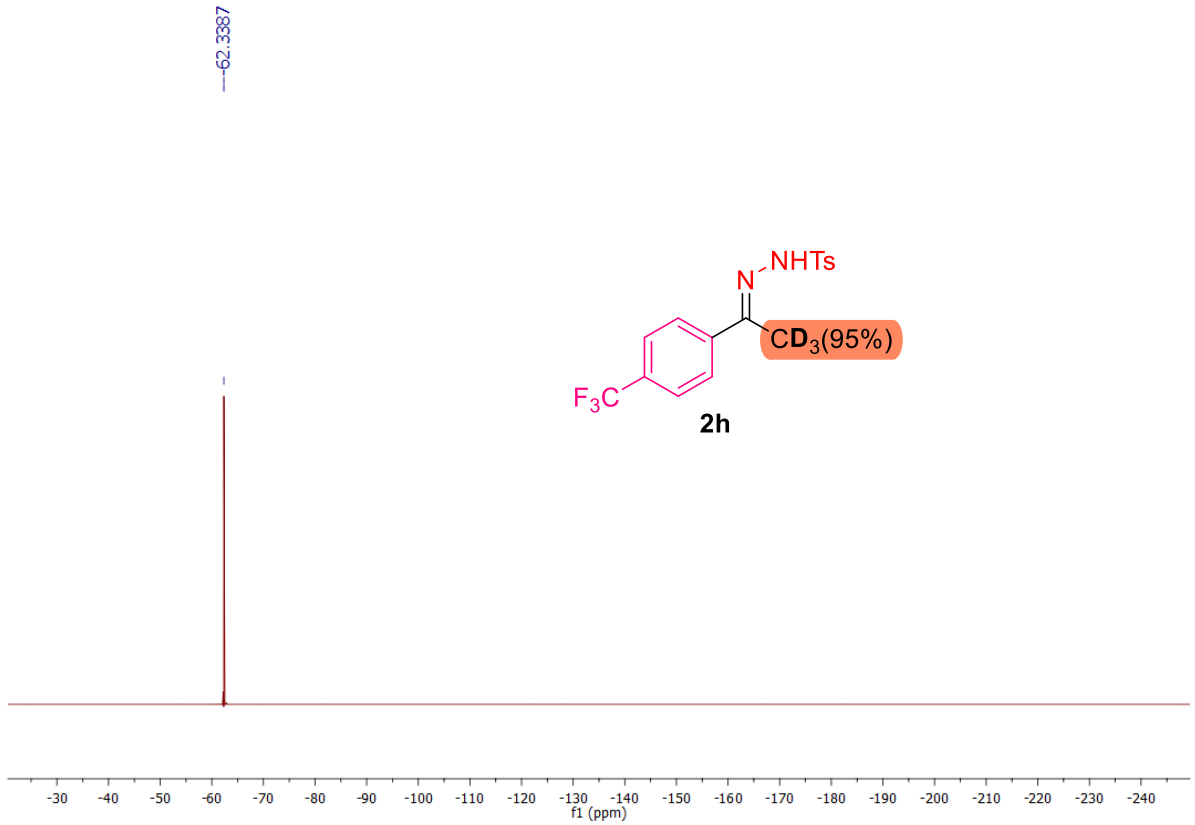
^{1}H NMR (500 MHz, DMSO D_6, 24 °C)



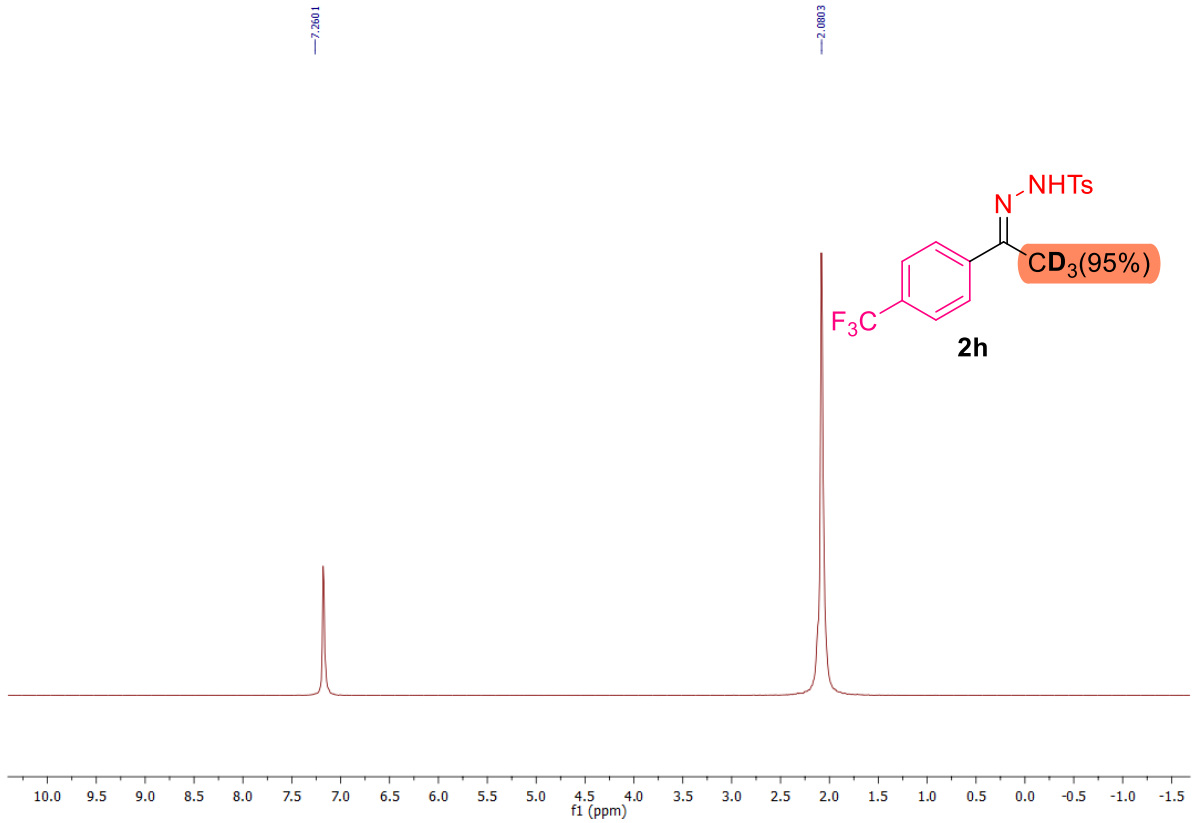
^{13}C{^{1}H} NMR (126 MHz, DMSO D_6, 24 °C)



^{19}F NMR (471 MHz, $CDCl_3$, 24 °C)

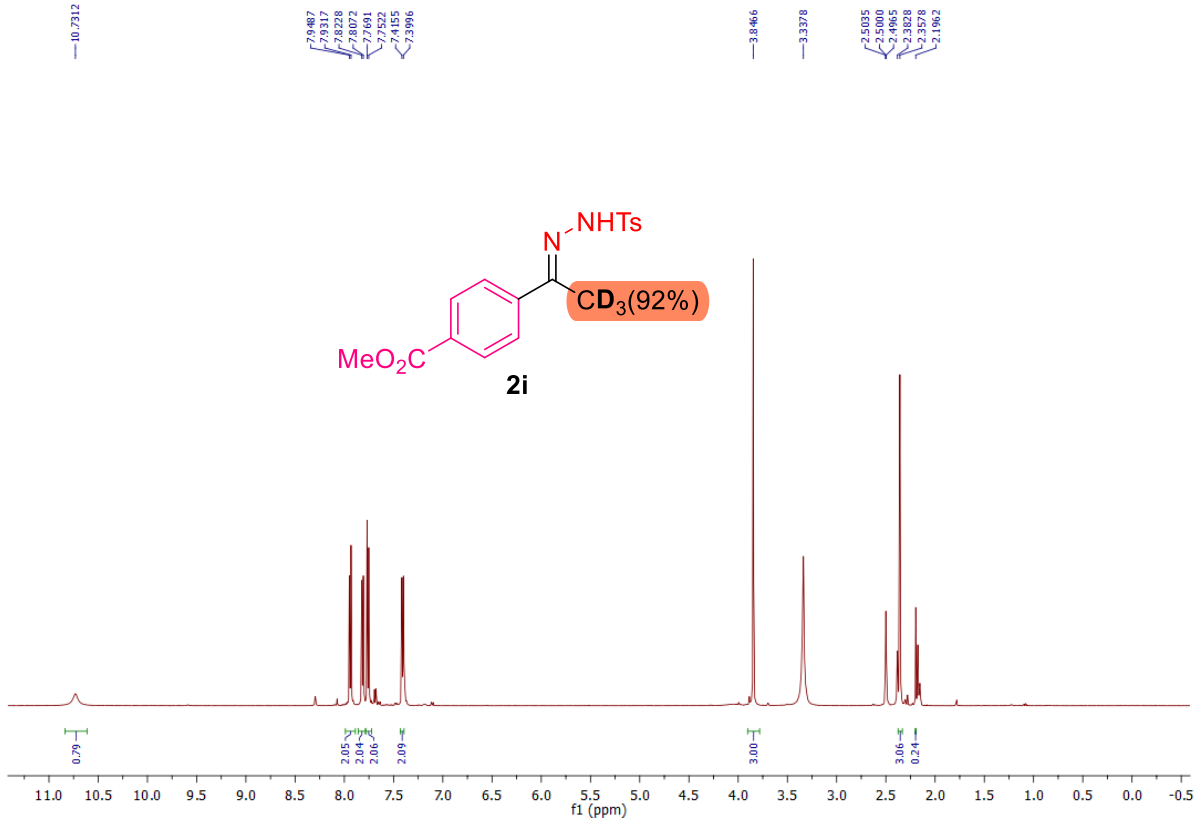


^{2}H NMR (77 MHz, $CDCl_3$, 24 °C)

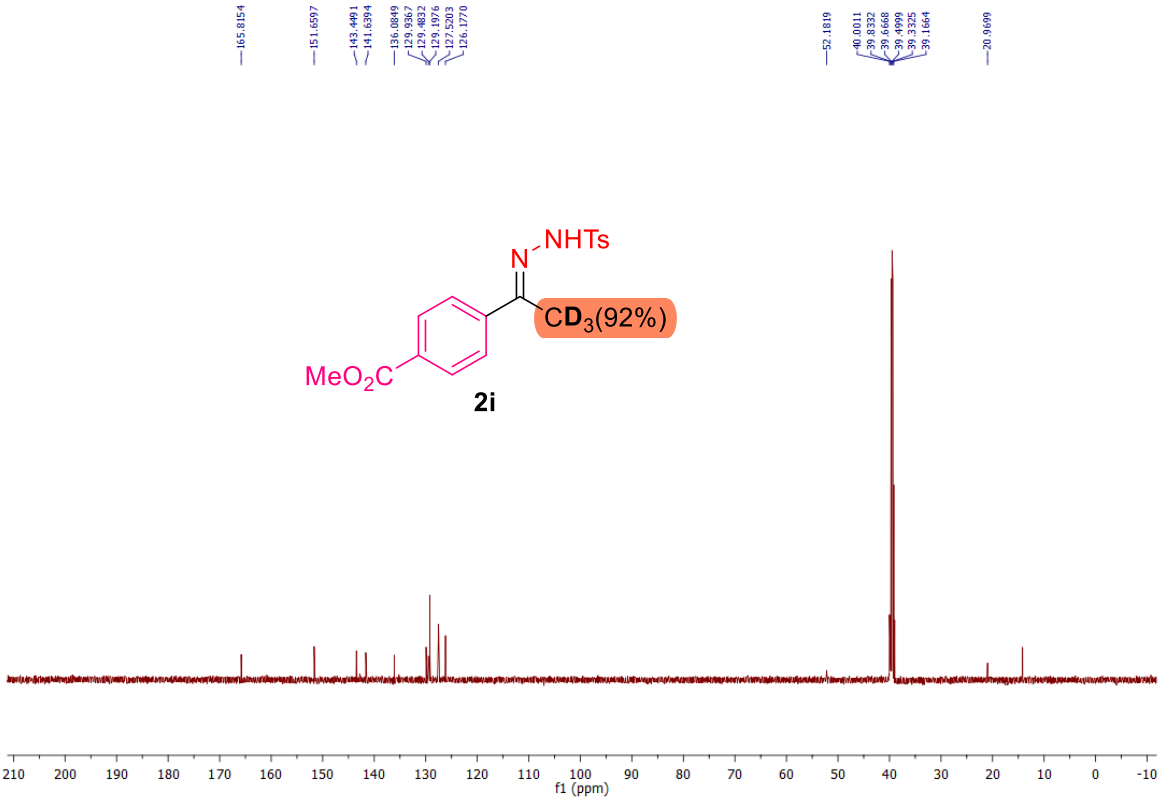


Methyl (E)-4-(1-(2-tosylhydrazineylidene)ethyl-2,2,2-d3)benzoate (**2i**)

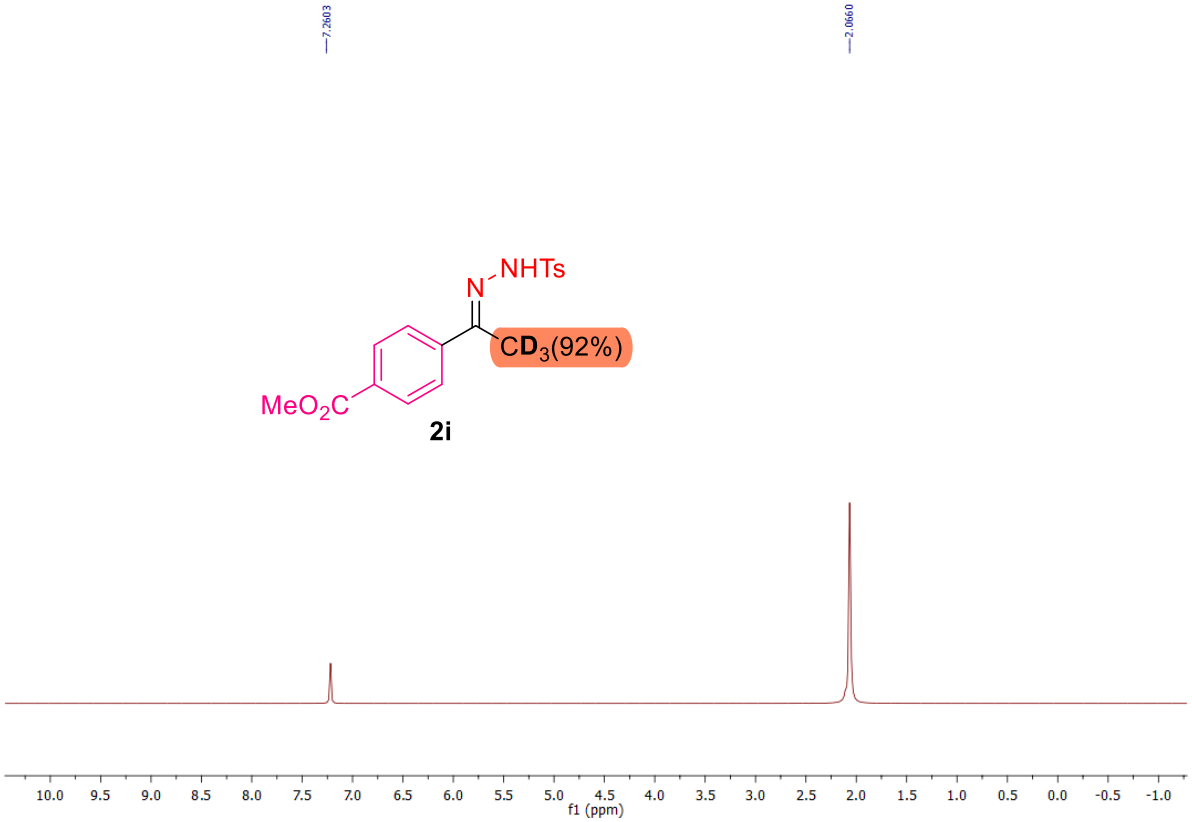
^{1}H NMR (500 MHz, DMSO D_6, 24 °C)



^{13}C{^{1}H} NMR (126 MHz, DMSO D_6, 24 °C)

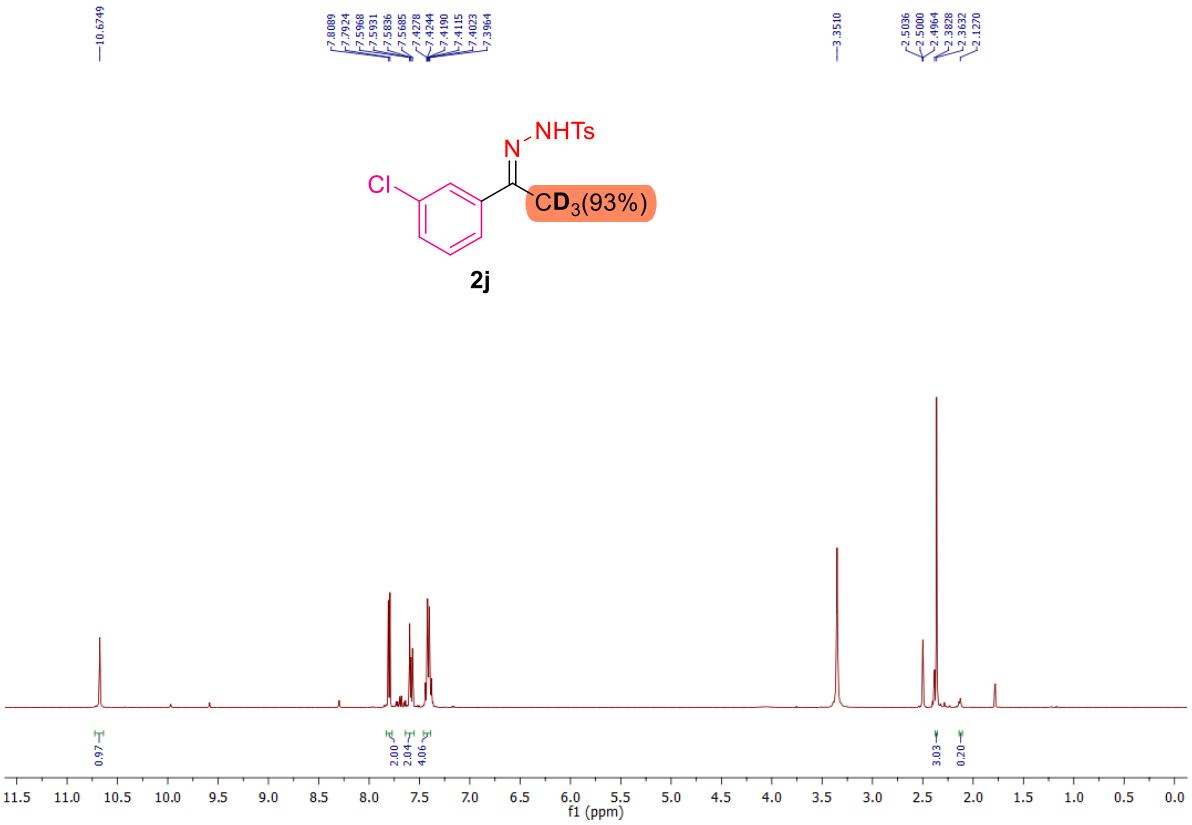


^{2}H NMR (77 MHz, $CDCl_3$, 24 °C)

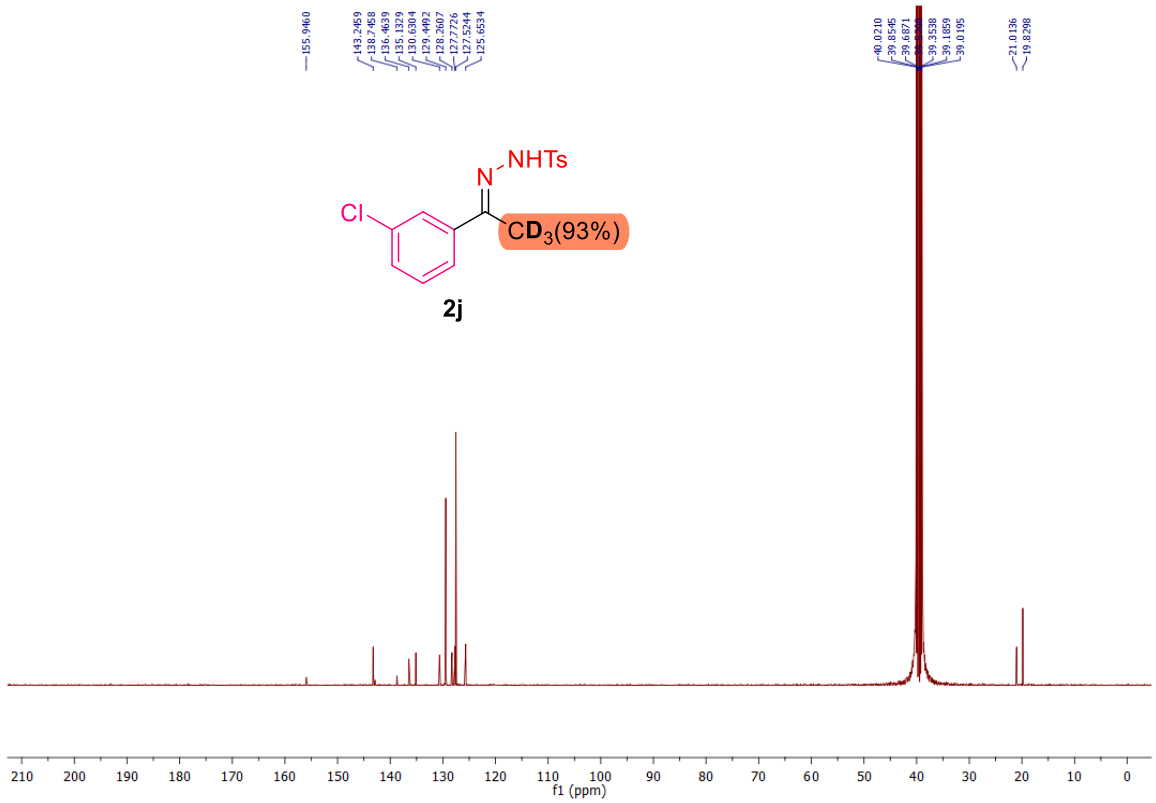


(*E*)-N'-(1-(3-chlorophenyl)ethylidene-2,2,2-d3)-4-methylbenzenesulfonohydrazide **(2j)**

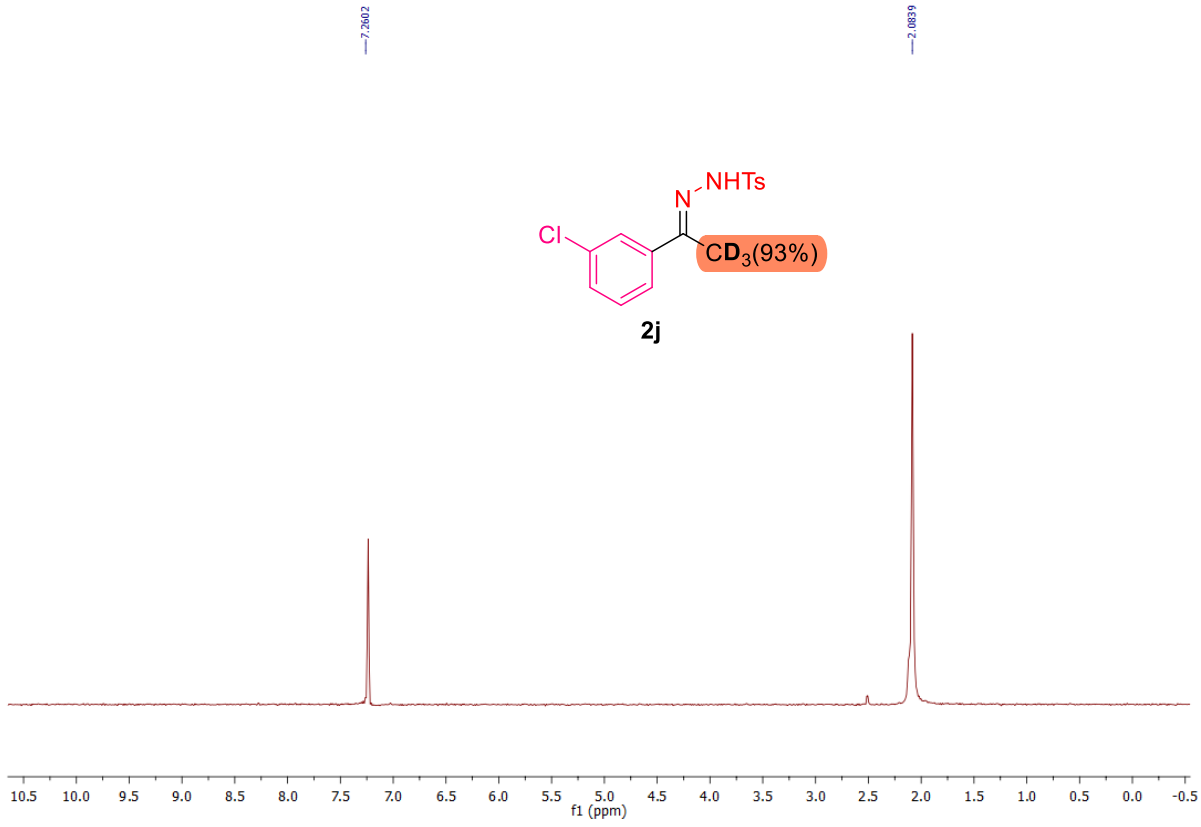
^{1}H NMR (500 MHz, DMSO D_6, 24 °C)



$^{13}C\{^{1}H\}$ NMR (126 MHz, DMSO D_6, 24 °C)

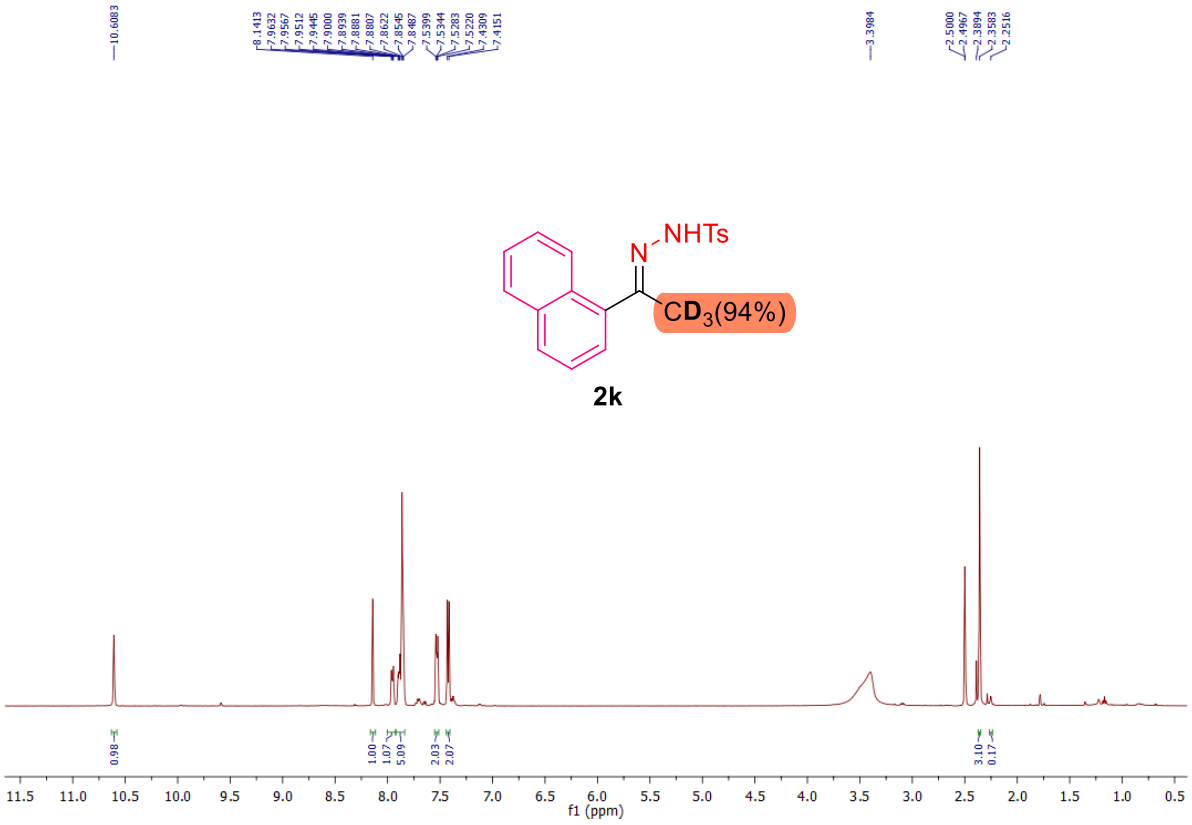


^{2}H NMR (77 MHz, $CDCl_3$, 24 °C)

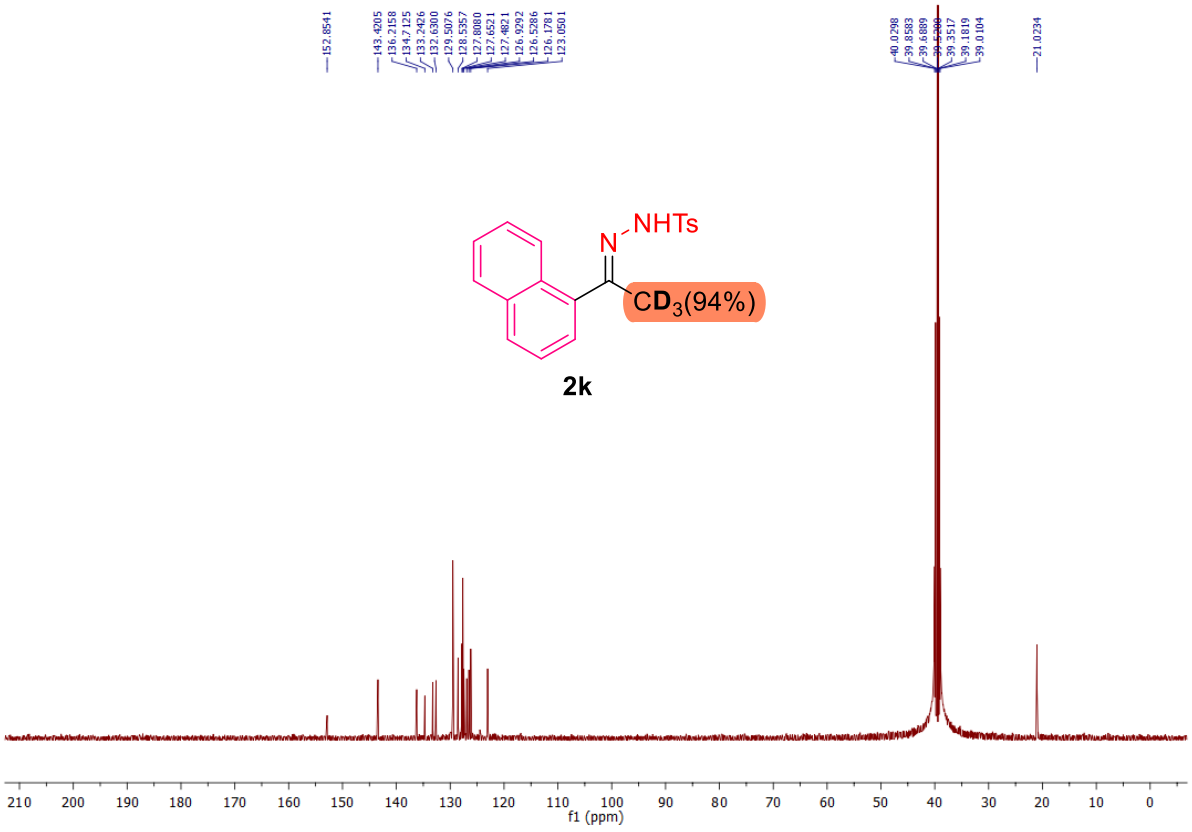


(*E*)-4-methyl-N'-(1-(naphthalen-1-yl)ethylidene-2,2,2-d3)benzenesulfonohydrazide **(2k)**

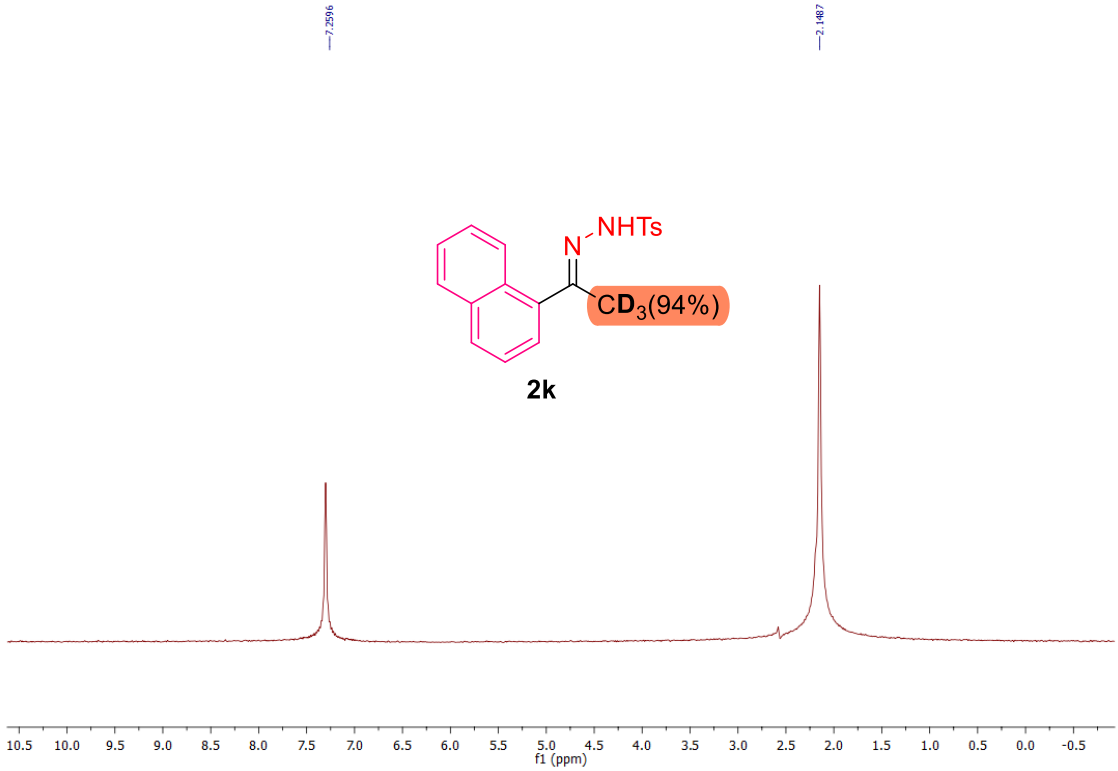
^{1}H NMR (500 MHz, DMSO D_6, 24 °C)



^{13}C{^{1}H} NMR (126 MHz, DMSO D_6, 24 °C)

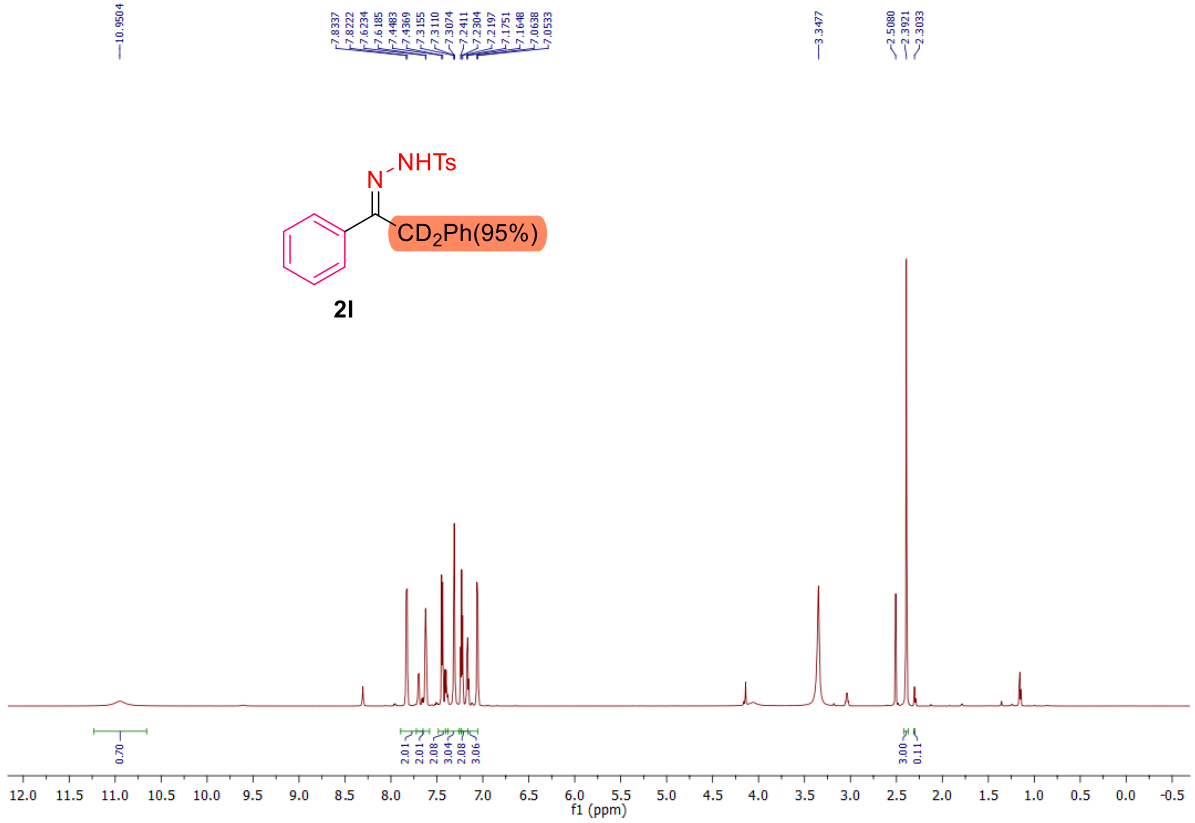


^{2}H NMR (77 MHz, $CDCl_3$, 24 °C)

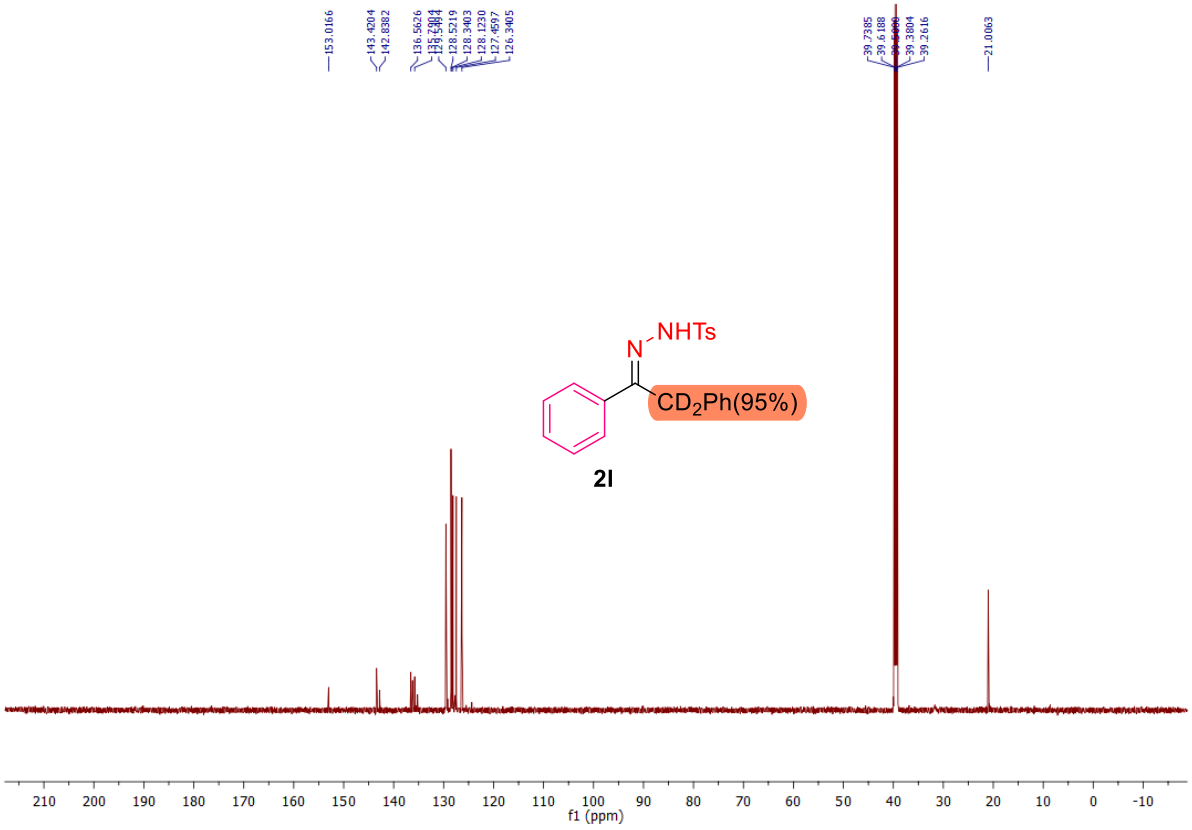


(*E*)-4-Methyl-N'-(1-(naphthalen-2-yl)ethylidene-2,2,2-d3)benzenesulfonohydrazide (**2l**)

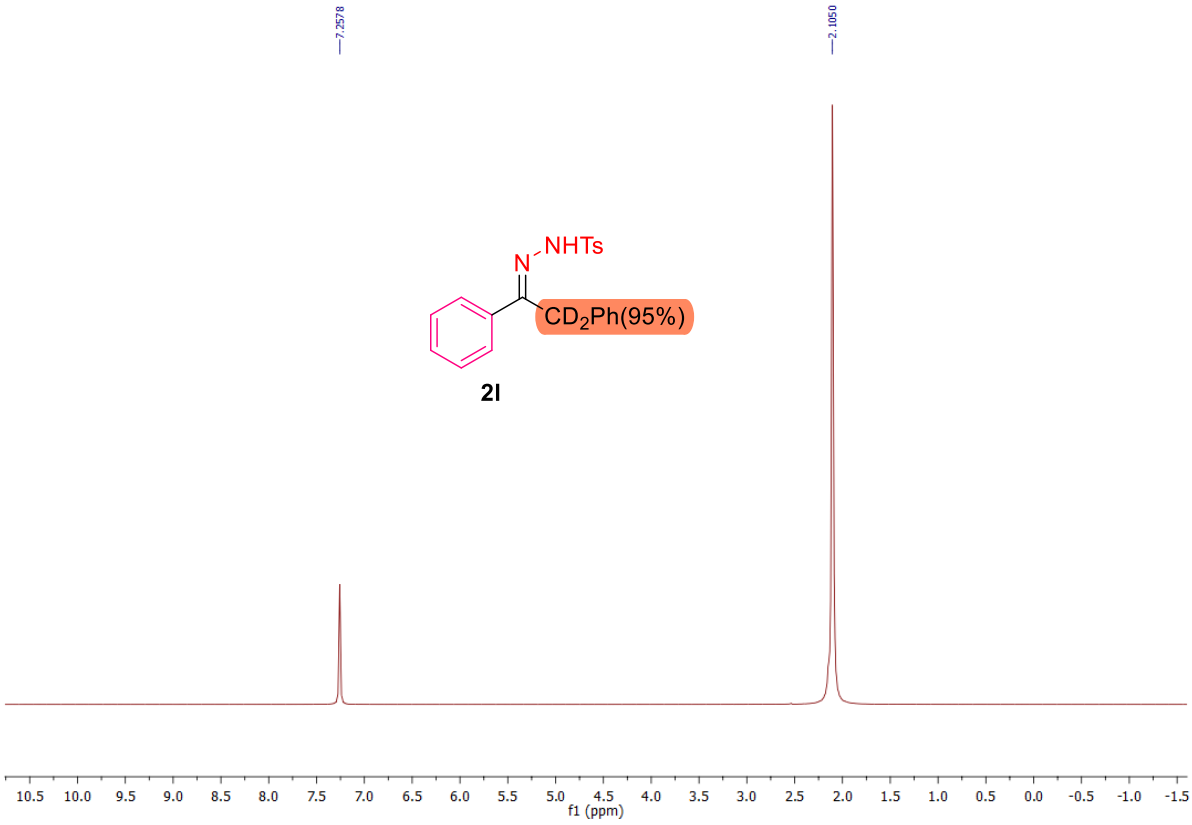
^{1}H NMR (500 MHz, DMSO D_6, 24 °C)



$^{13}C\{^{1}H\}$ NMR (126 MHz, DMSO D_6, 24 °C)

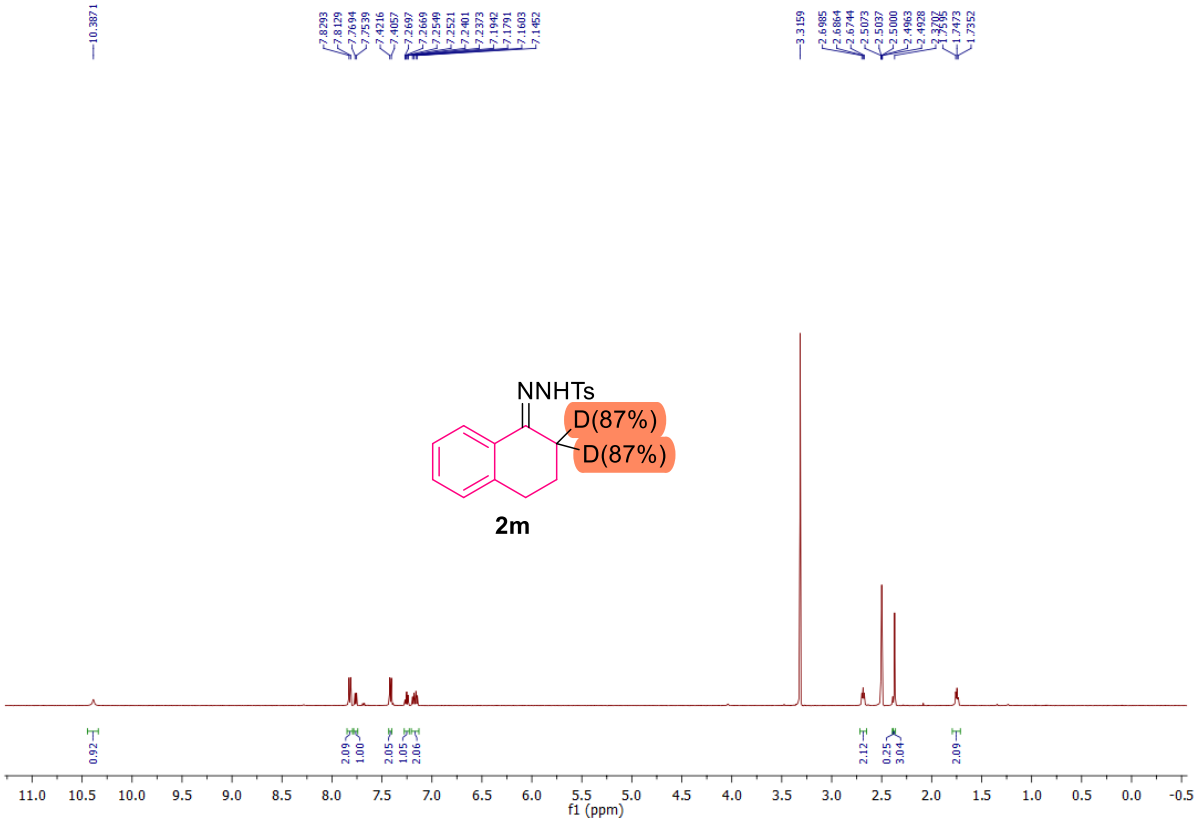


^{2}H NMR (77 MHz, $CDCl_3$, 24 °C)

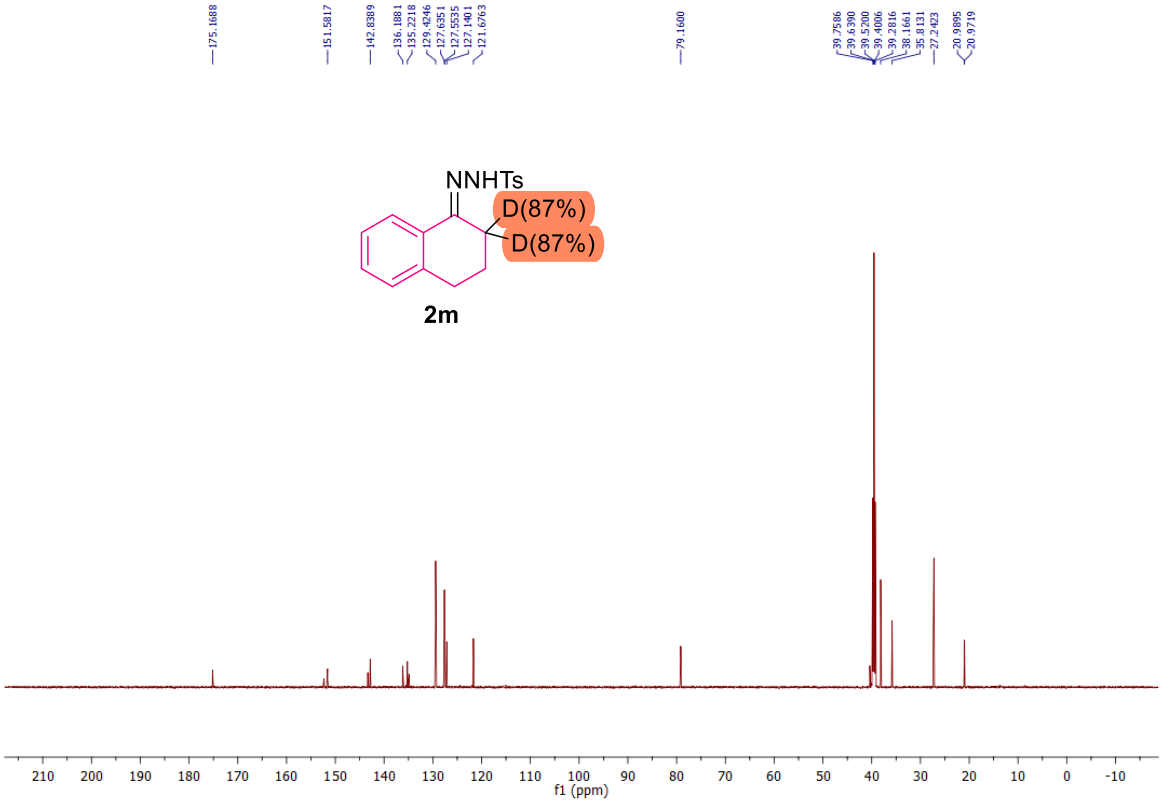


(Z)-N'-(3,4-dihydronaphthalen-1(2H)-ylidene-2,2-d2)-4-methylbenzenesulfonohydrazide

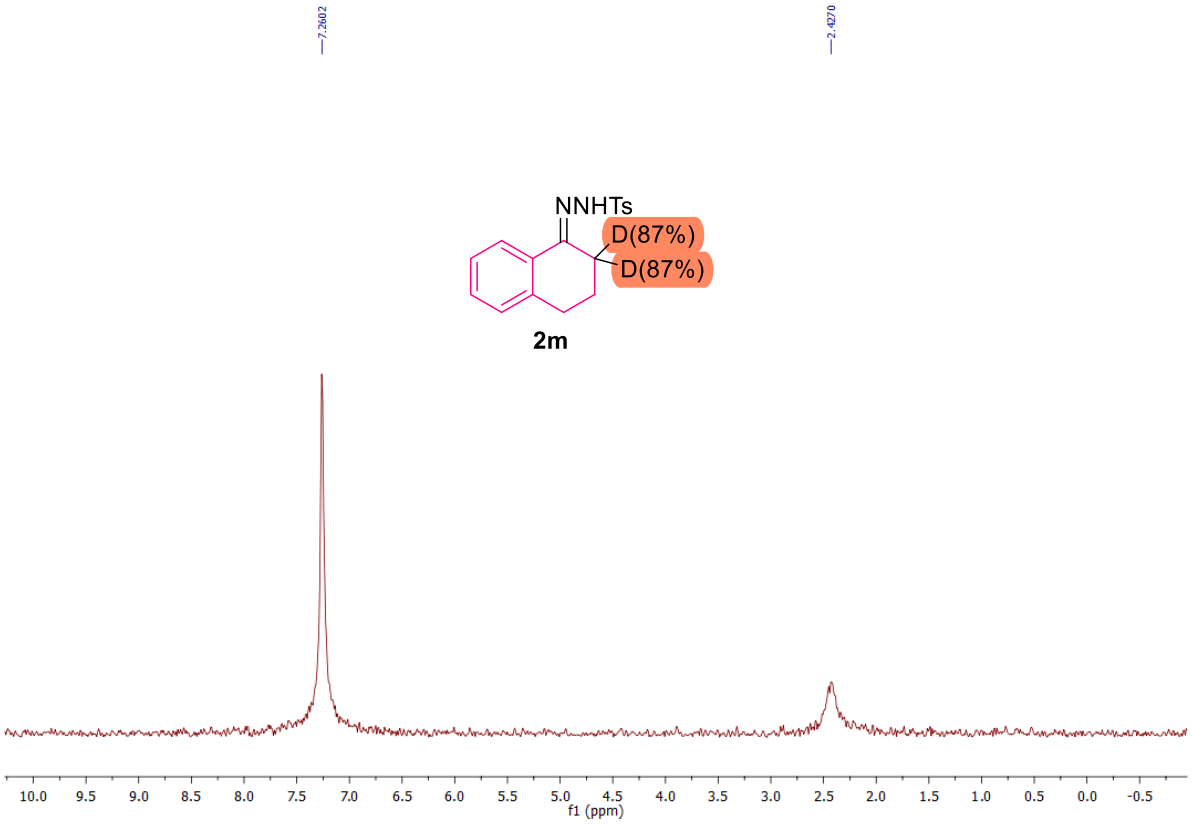
^{1}H NMR (500 MHz, DMSO D_6, 24 °C)



^{13}C{^{1}H} NMR (126 MHz, DMSO D_6, 24 °C)

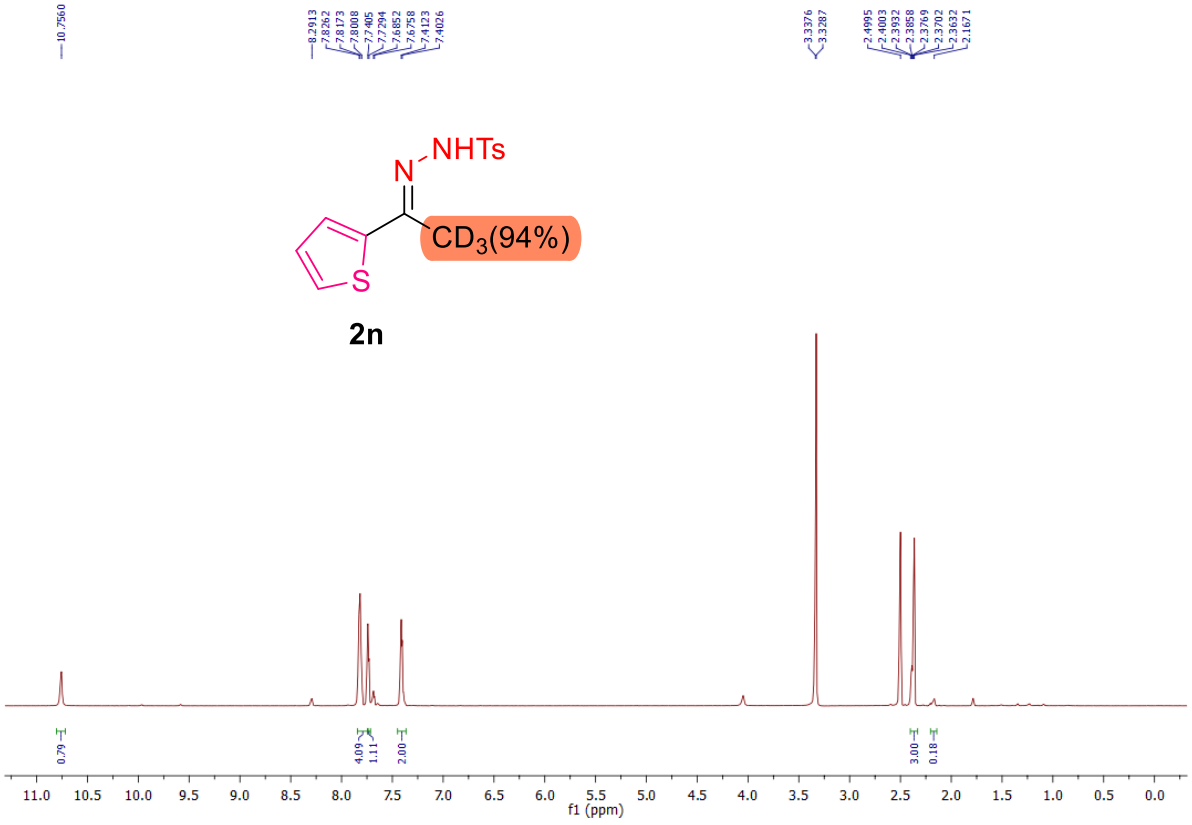


^{2}H NMR (77 MHz, $CDCl_3$, 24 °C)

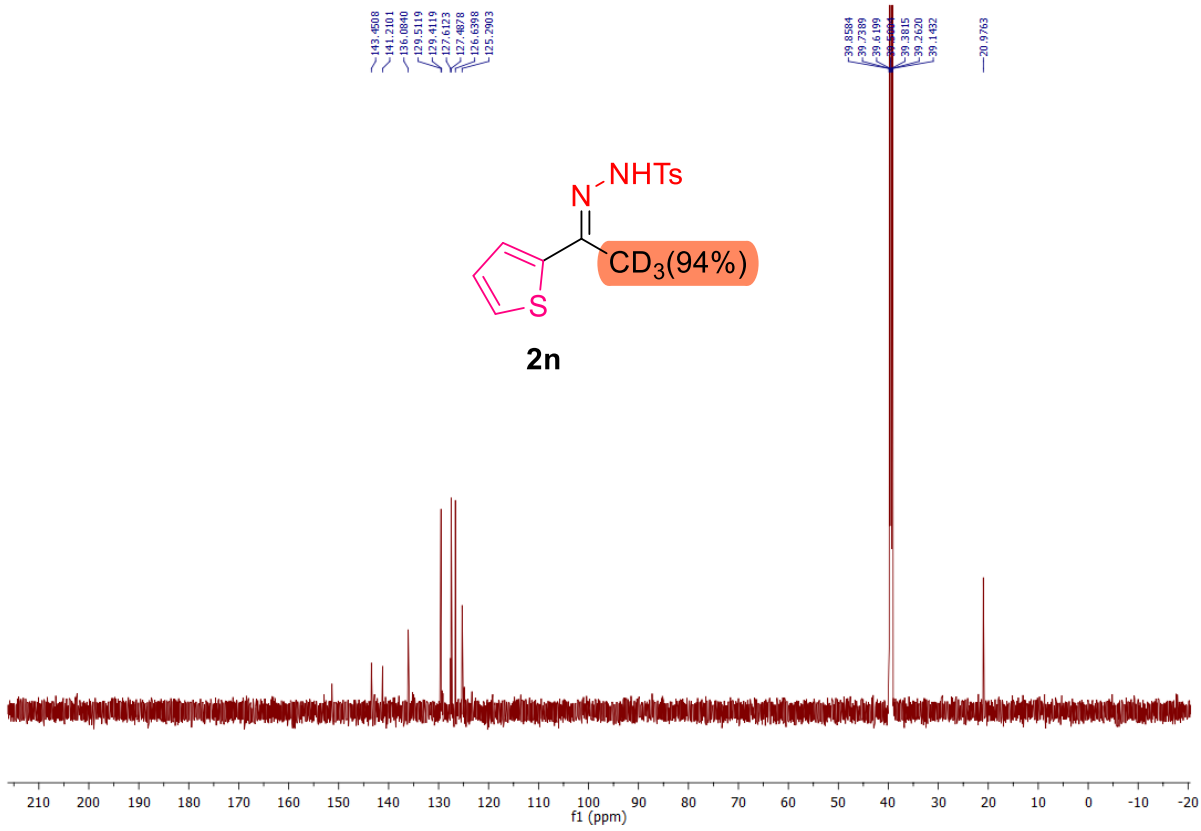


(*E*)-4-methyl-N'-(1-(thiophen-2-yl)ethylidene-2,2,2-d3)benzenesulfonohydrazide (**2n**)

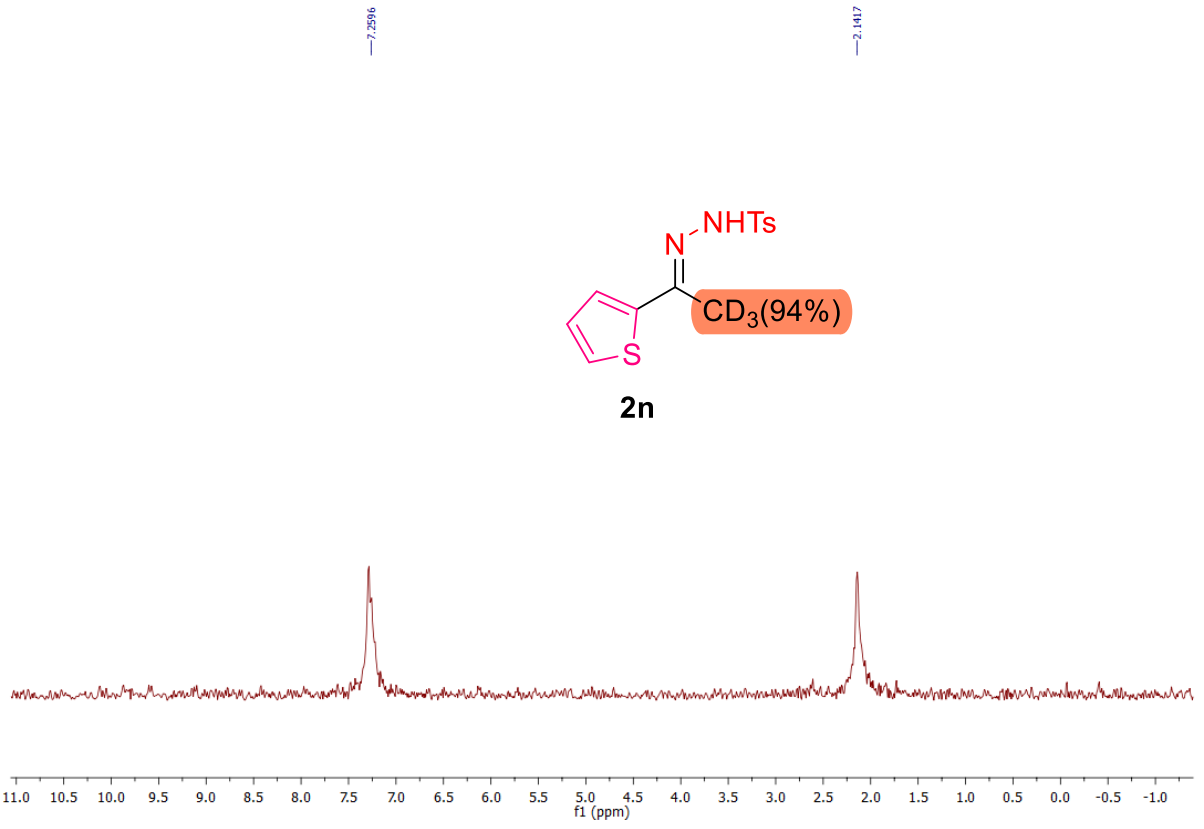
^{1}H NMR (500 MHz, DMSO D_6, 24 °C)



$^{13}C\{^{1}H\}$ NMR (126 MHz, DMSO D_6, 24 °C)

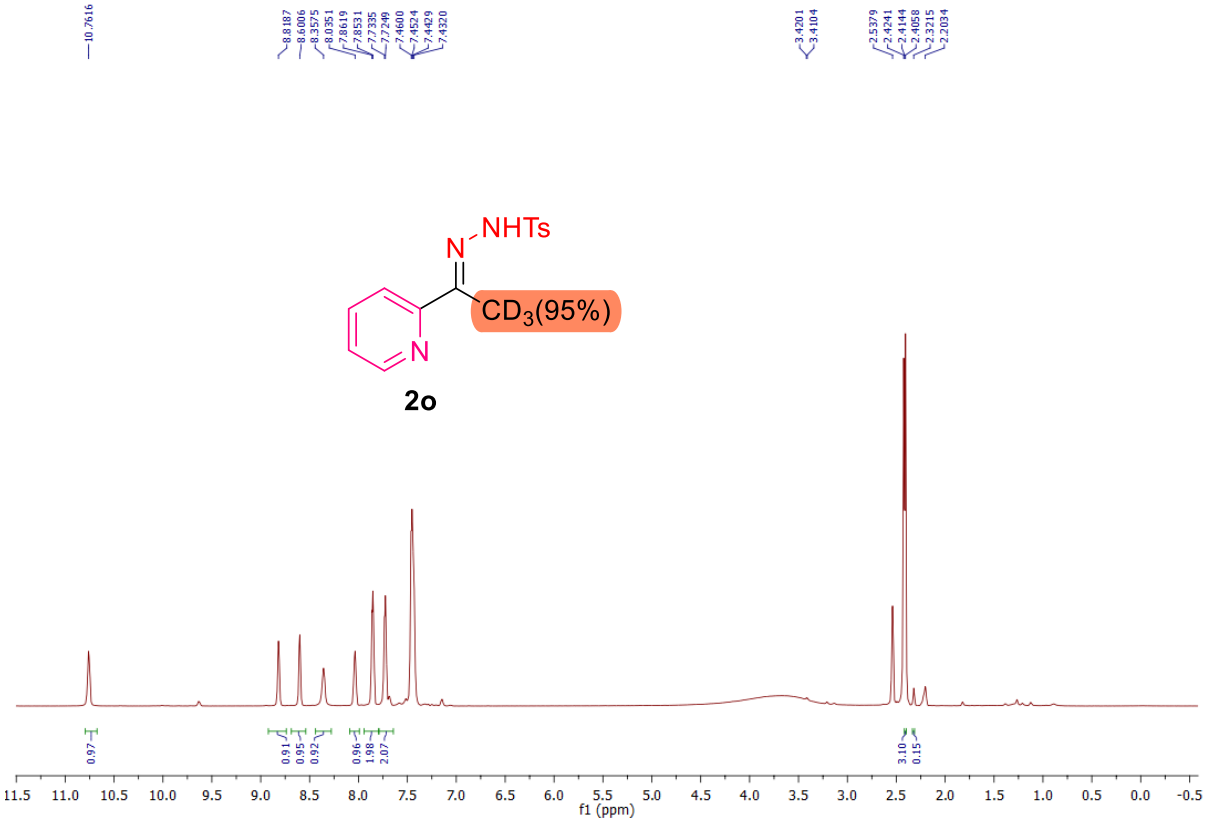


^{2}H NMR (77 MHz, $CDCl_3$, 24 °C)

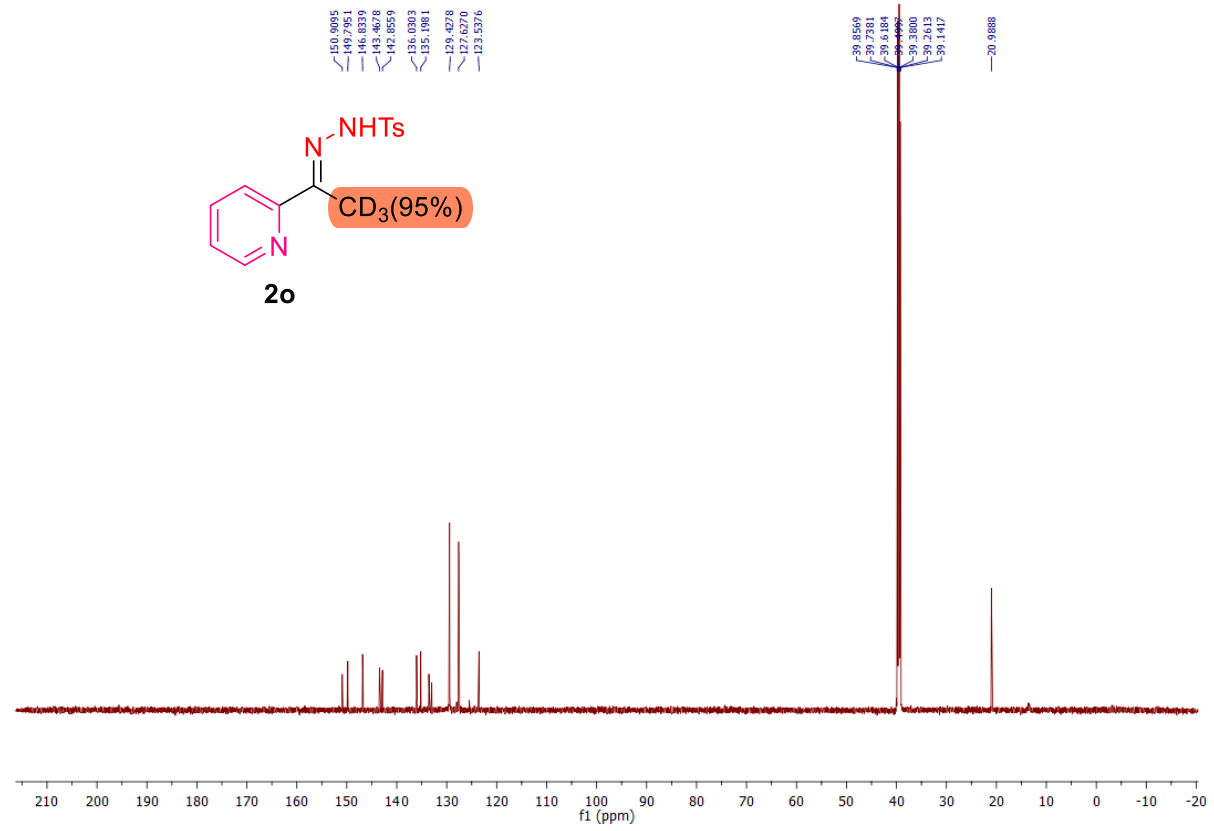


(*E*)-4-methyl-N'-(1-(pyridin-2-yl)ethylidene-2,2,2-d3)benzenesulfonohydrazide (**2o**)

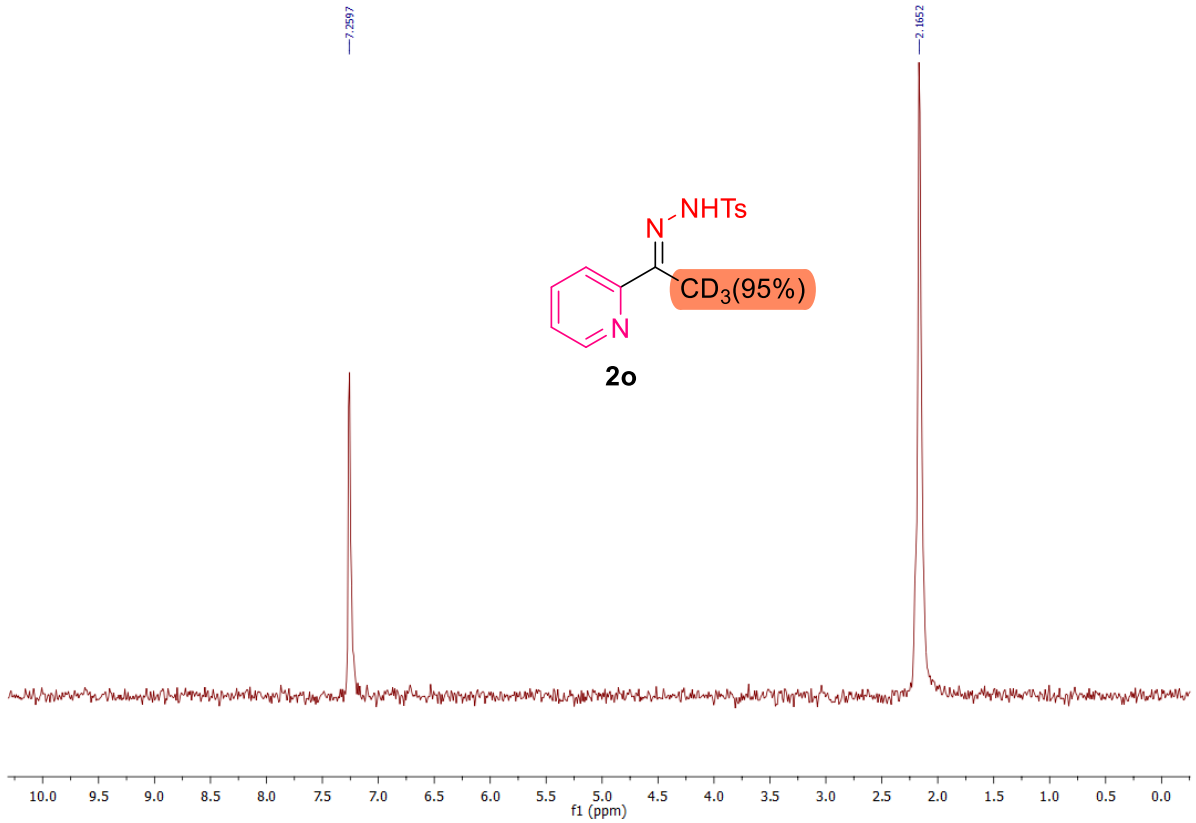
^{1}H NMR (500 MHz, DMSO D_6, 24 °C)



^{13}C{^{1}H} NMR (126 MHz, DMSO D_6, 24 °C)

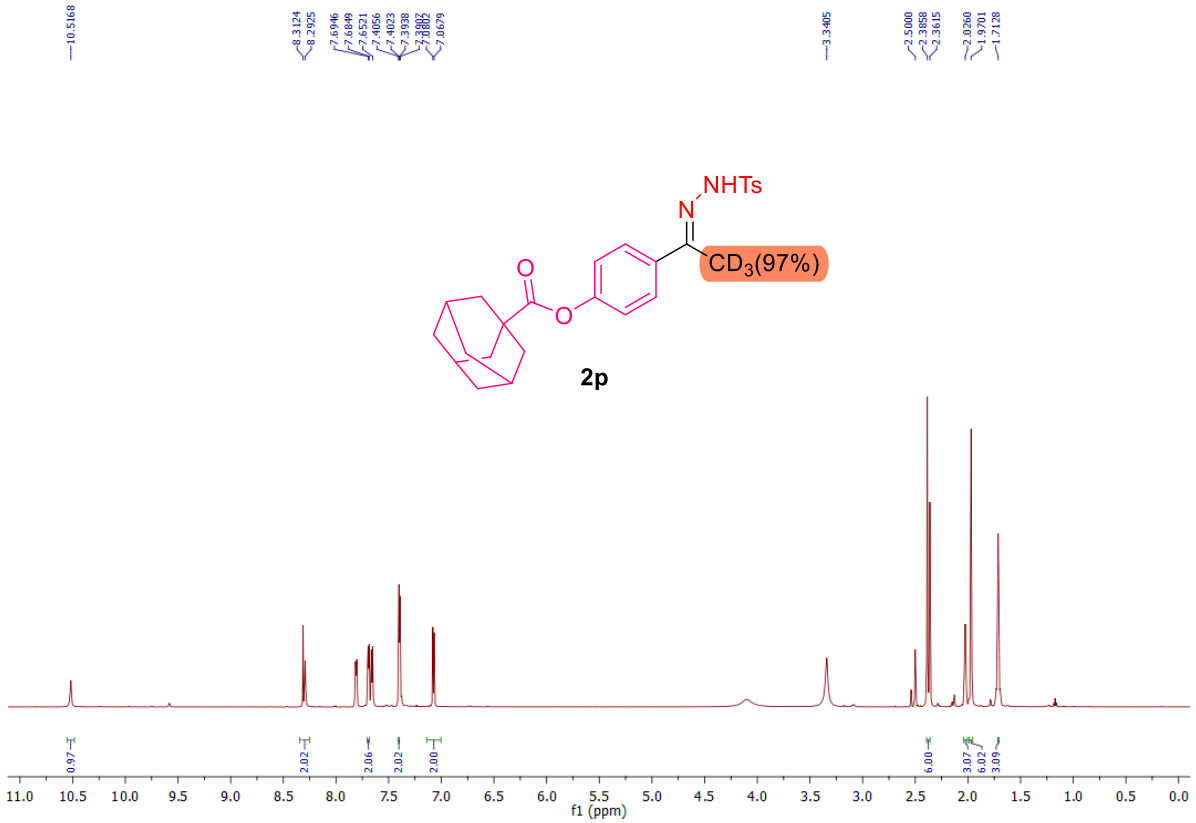


^{2}H NMR (77 MHz, $CDCl_3$, 24 °C)

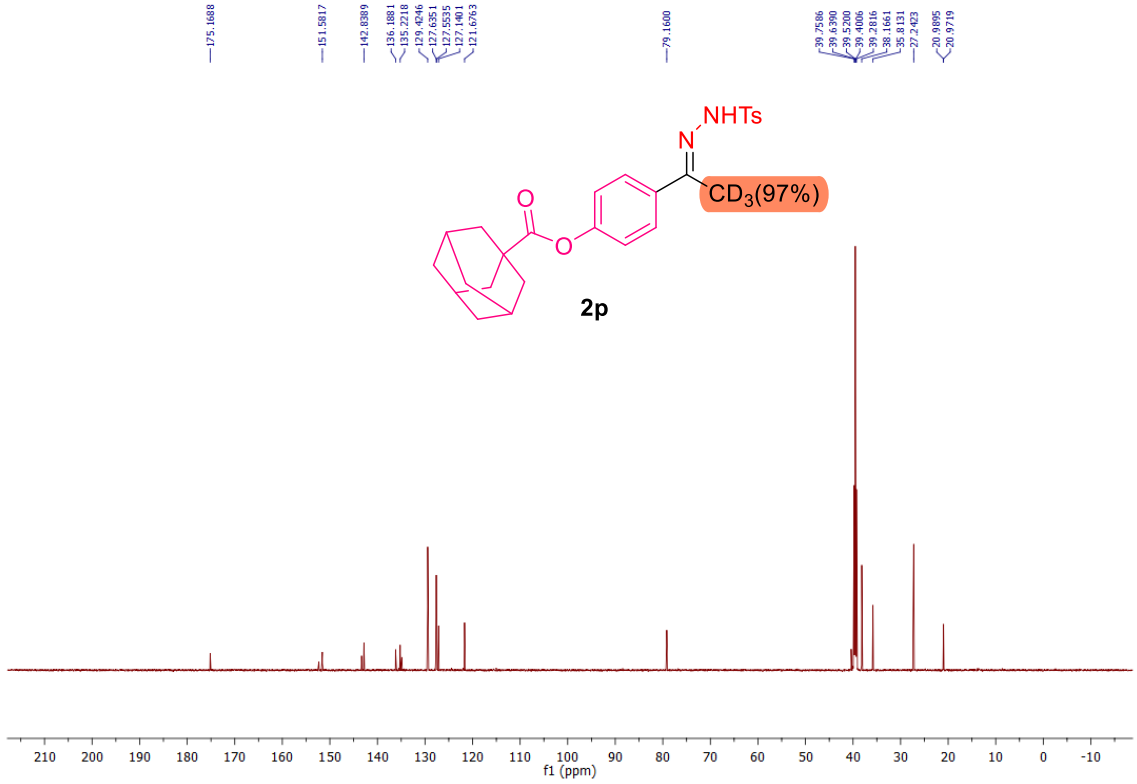


(*E*)-4-((3,4-dimethoxyphenyl)(2-tosylhydrazineylidene)methyl)phenyl adamantane-1-carboxylate(**2p**)

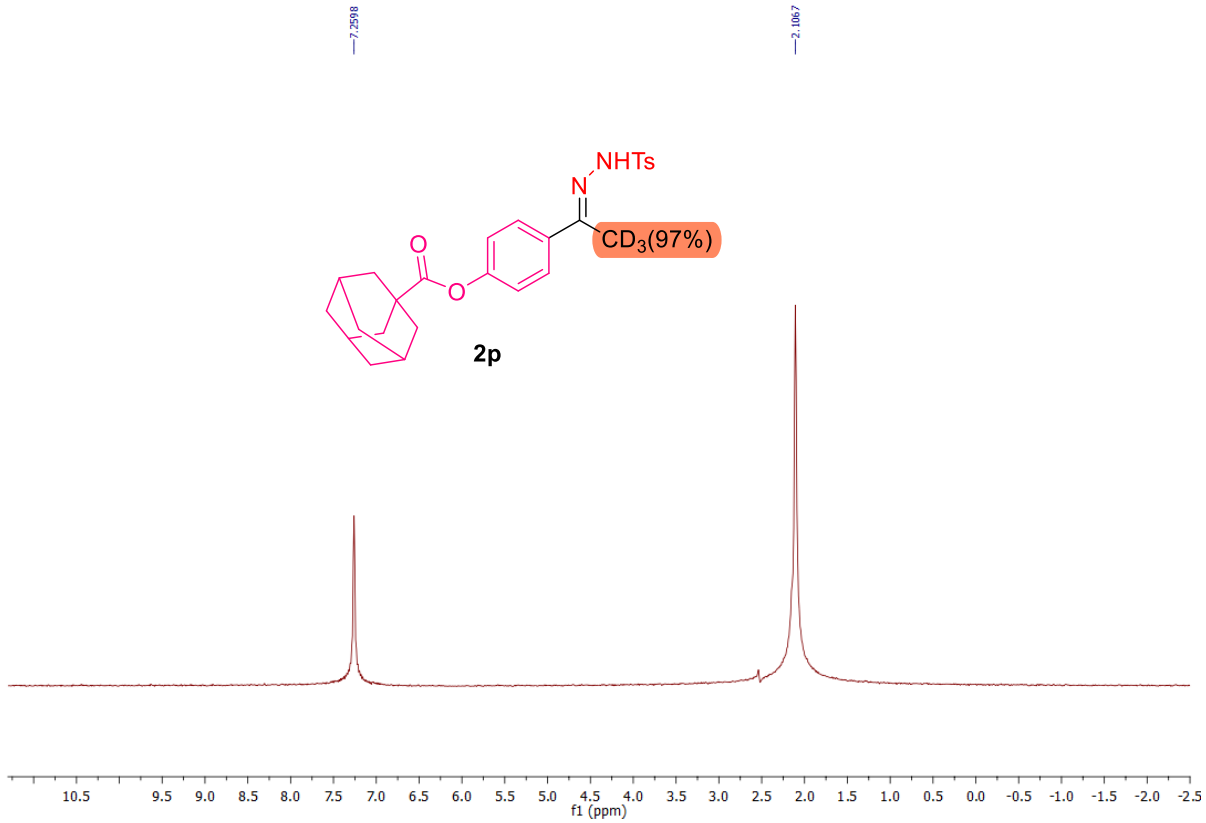
^{1}H NMR (500 MHz, DMSO D_6, 24 °C)



$^{13}C\{^{1}H\}$ NMR (126 MHz, DMSO D_6, 24 °C)

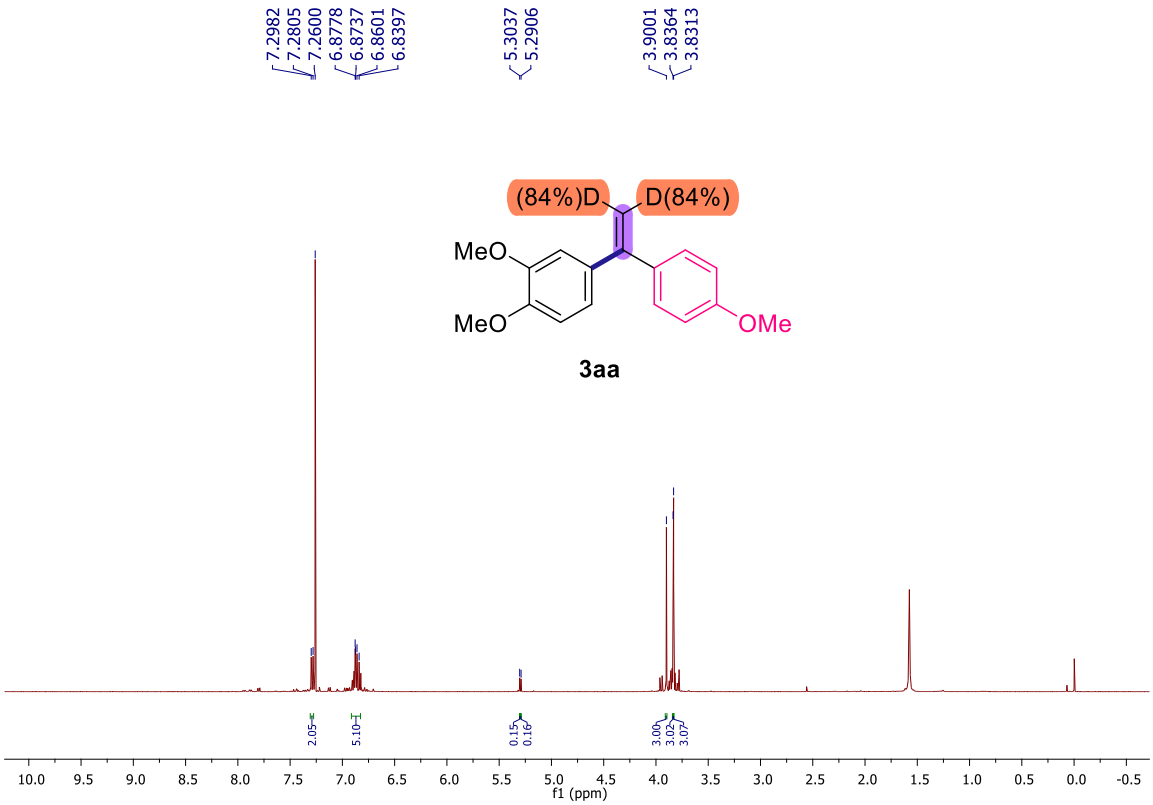


^{2}H NMR (77 MHz, $CDCl_3$, 24 °C)

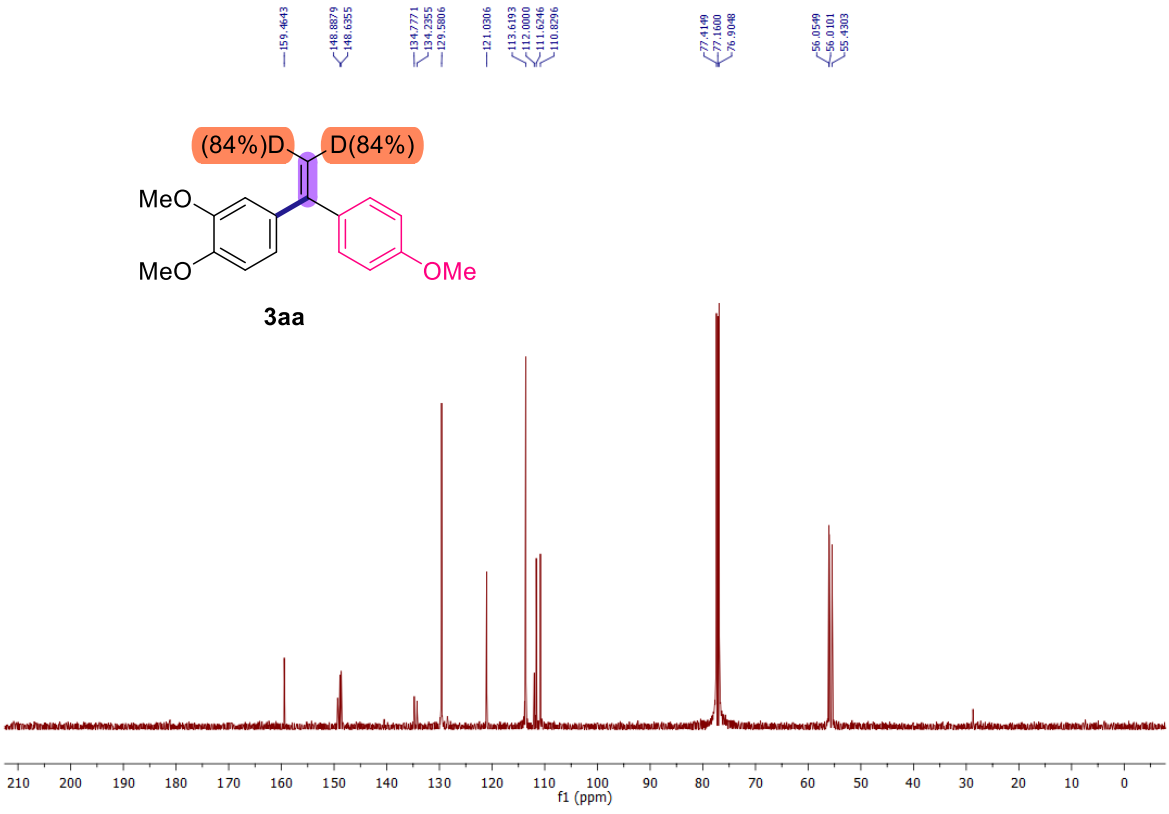


1,2-Dimethoxy-4-(1-(4-methoxyphenyl)vinyl-2,2-d2)benzene (**3aa**)

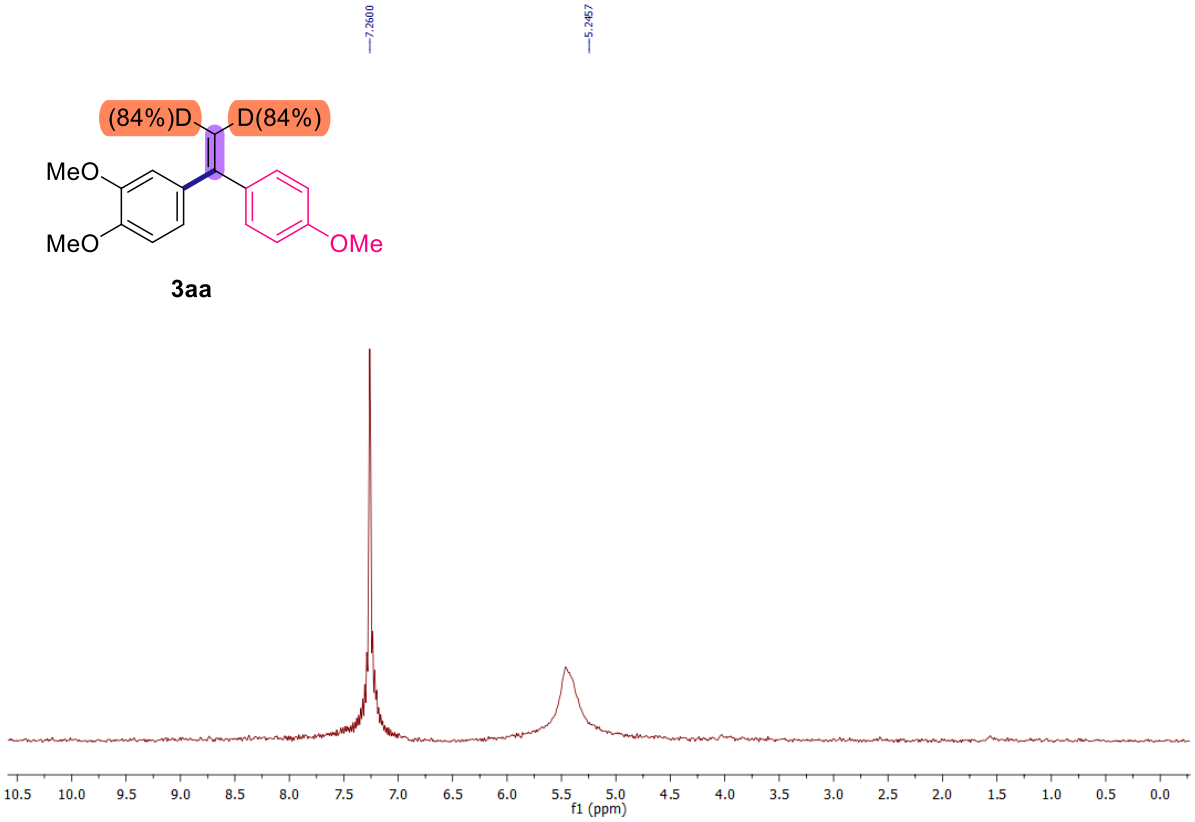
^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)



^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 24 °C)

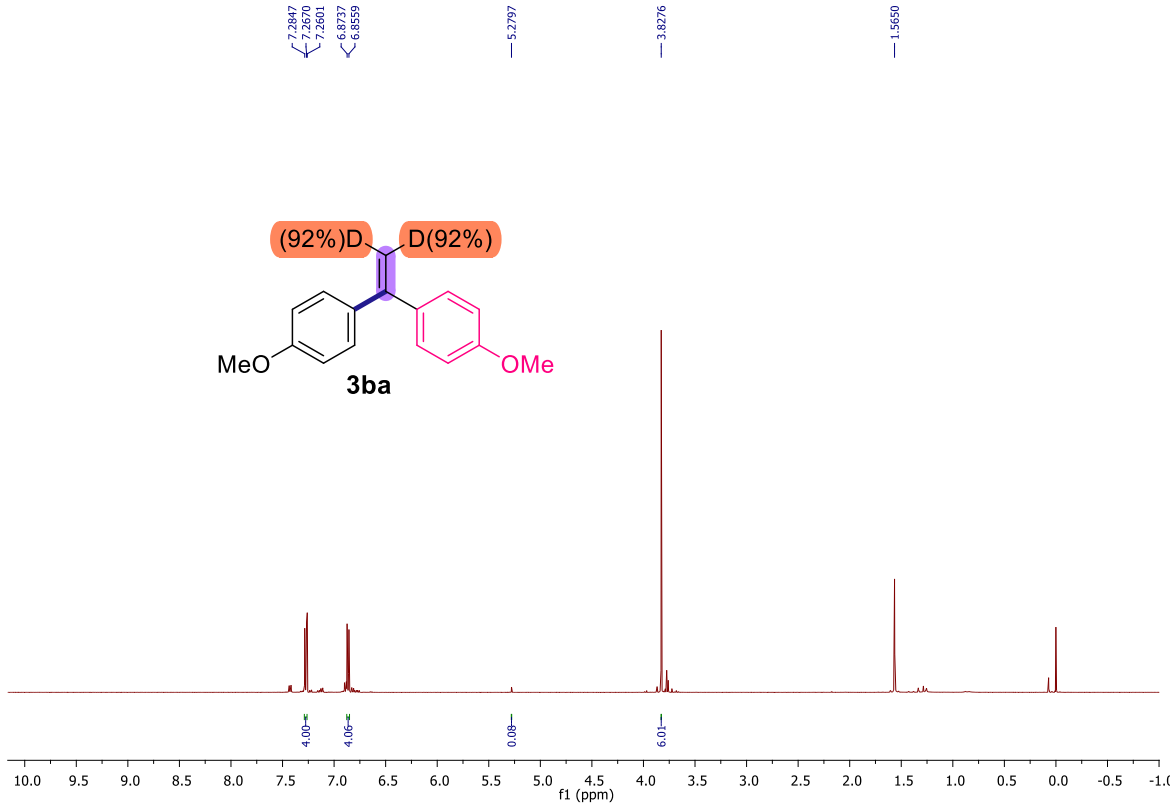


^{2}H NMR (77 MHz, $CHCl_3$, 24 °C)

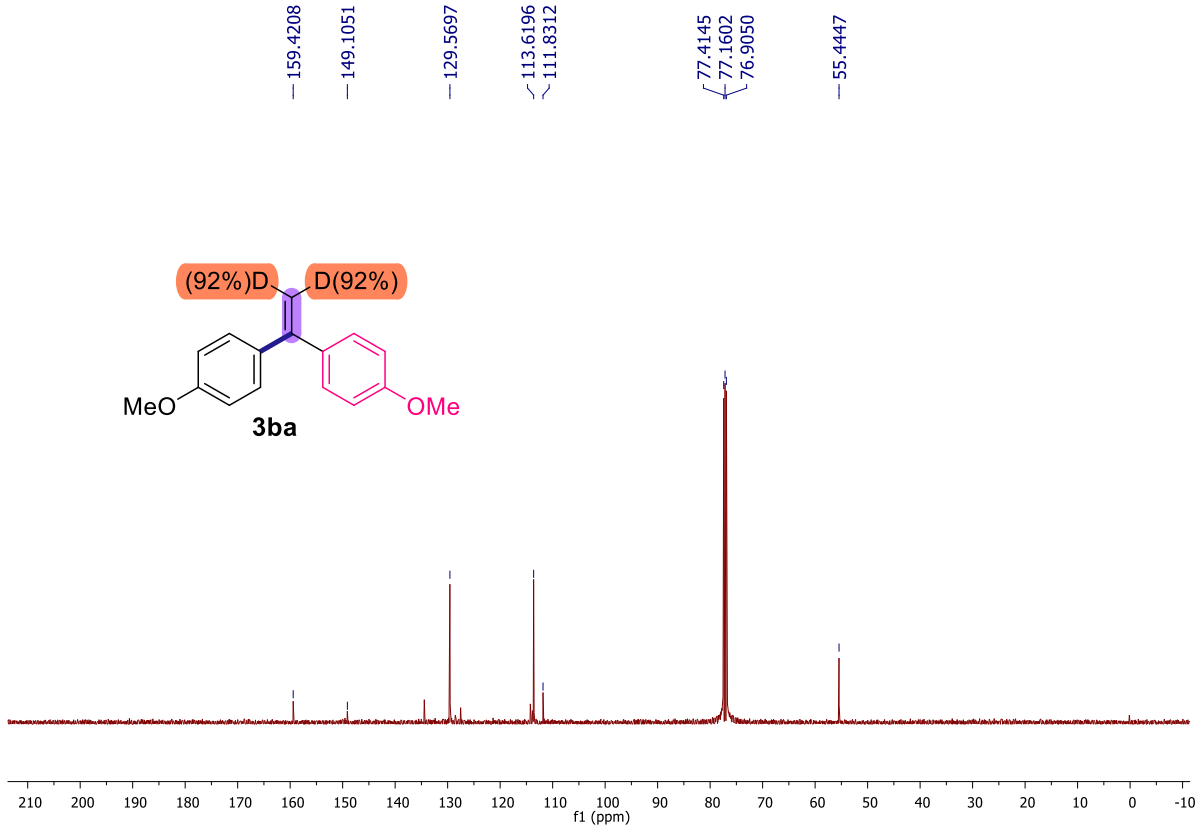


4,4'-(Ethene-1,1-diyl-2,2-d_2)bis(methoxybenzene) (**3ba**)

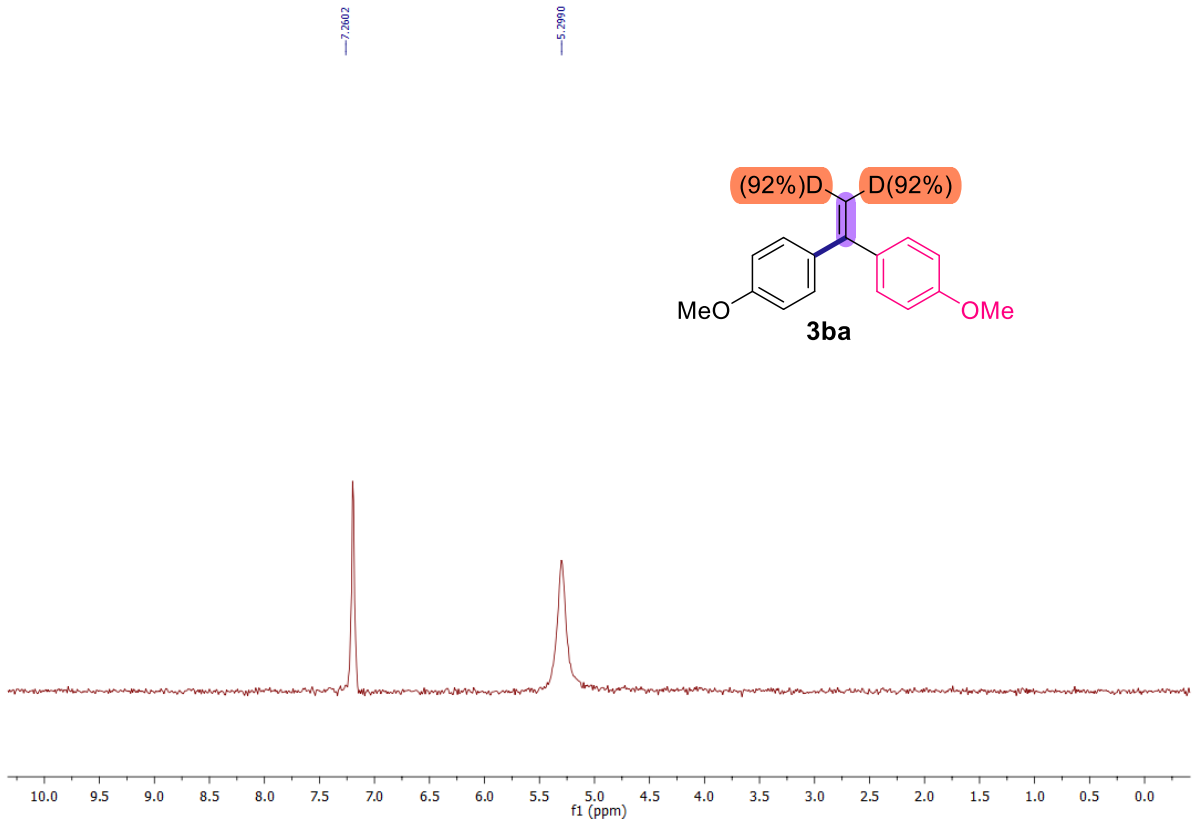
^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)



$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 24 °C)

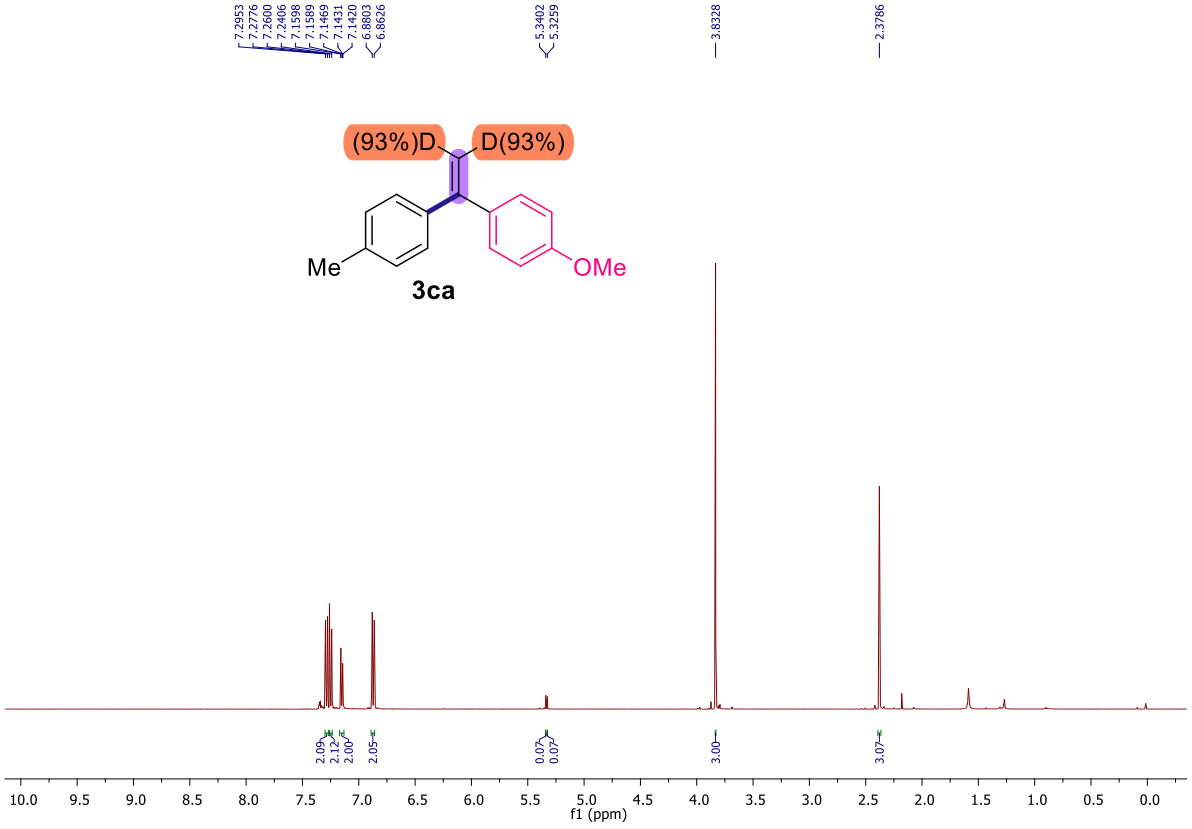


^{2}H NMR (94 MHz, $CHCl_3$, 24 °C)

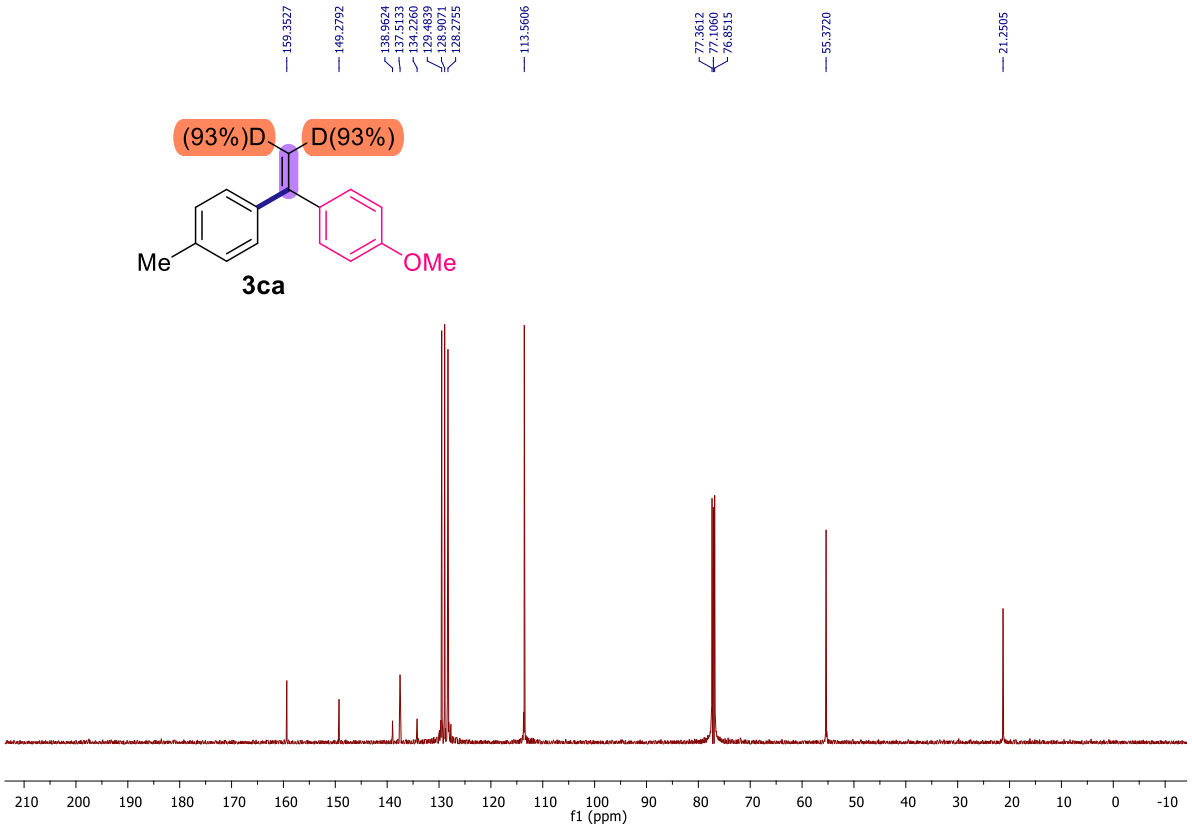


1-Methoxy-4-(1-(p-tolyl)vinyl-2,2-d2)benzene (**3ca**)

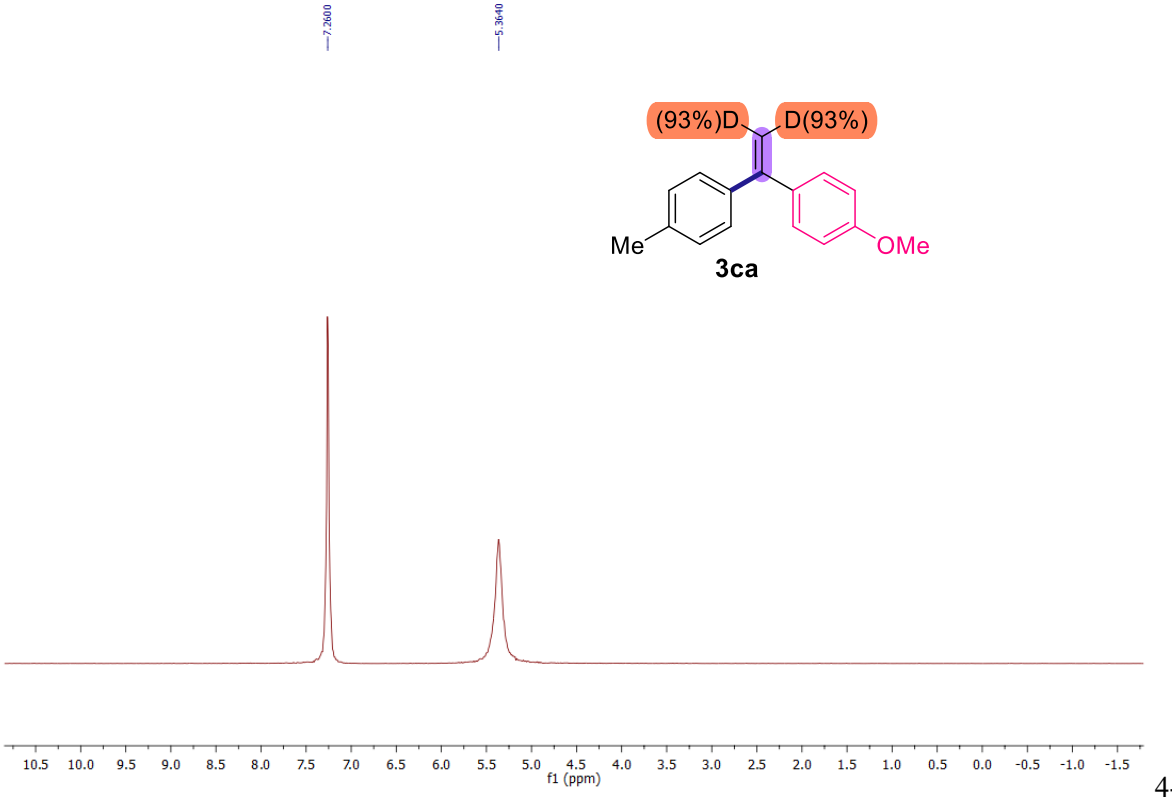
^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)



^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 24 °C)



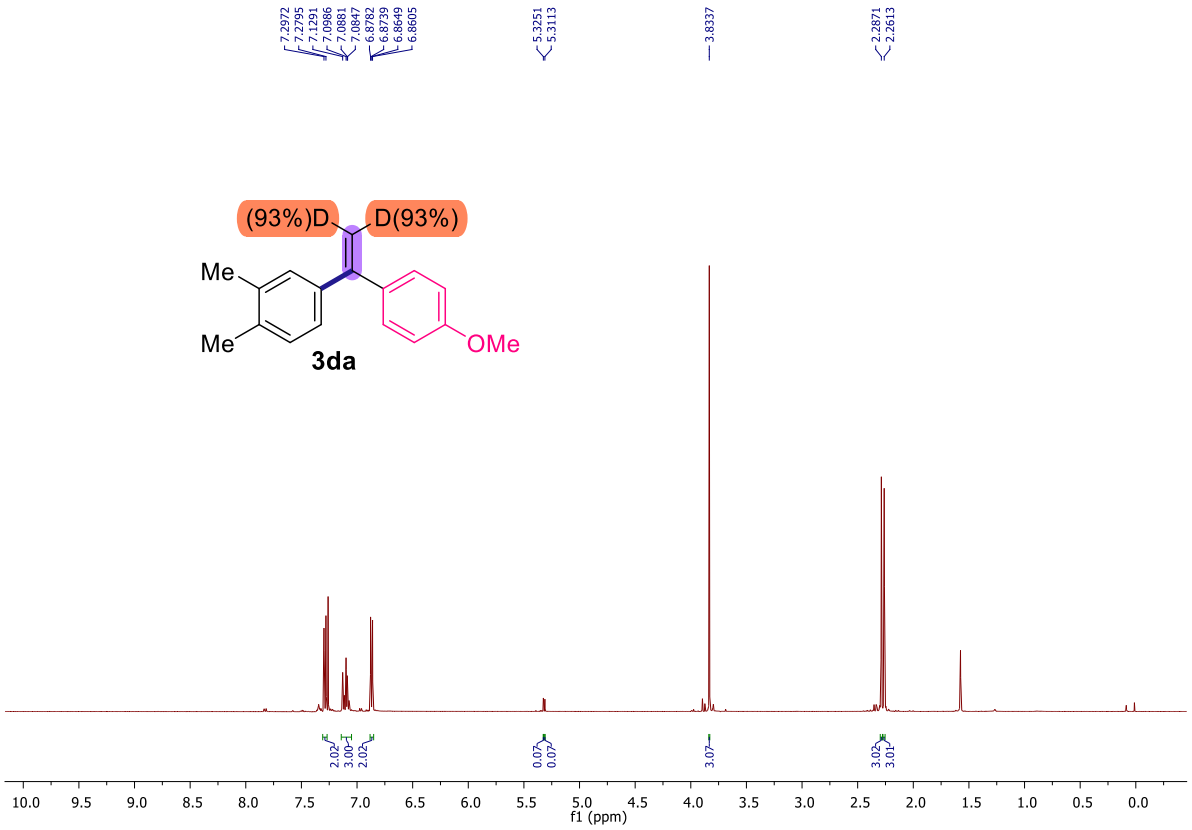
^{2}H NMR (77 MHz, $CHCl_3$, 24 °C)



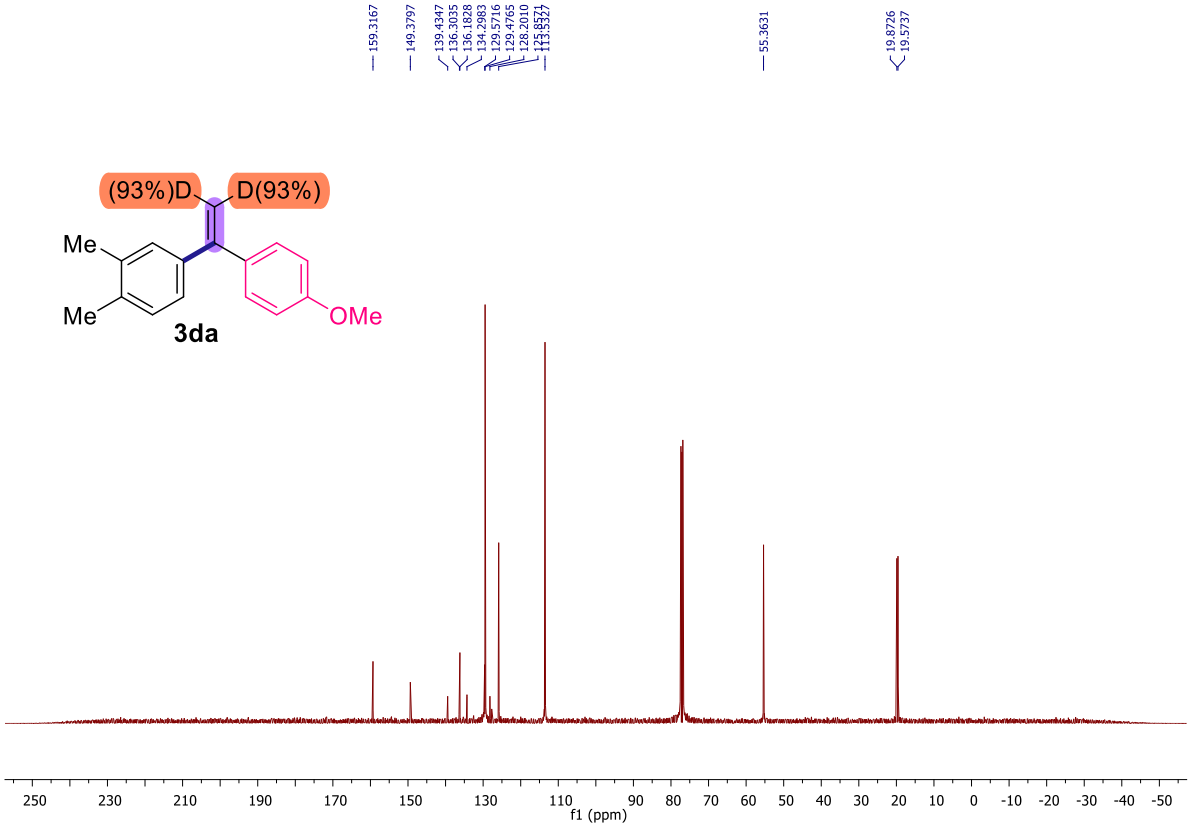
4-

4-(1-(4-Methoxyphenyl)vinyl-2,2-d2)-1,2-dimethylbenzene (**3da**)

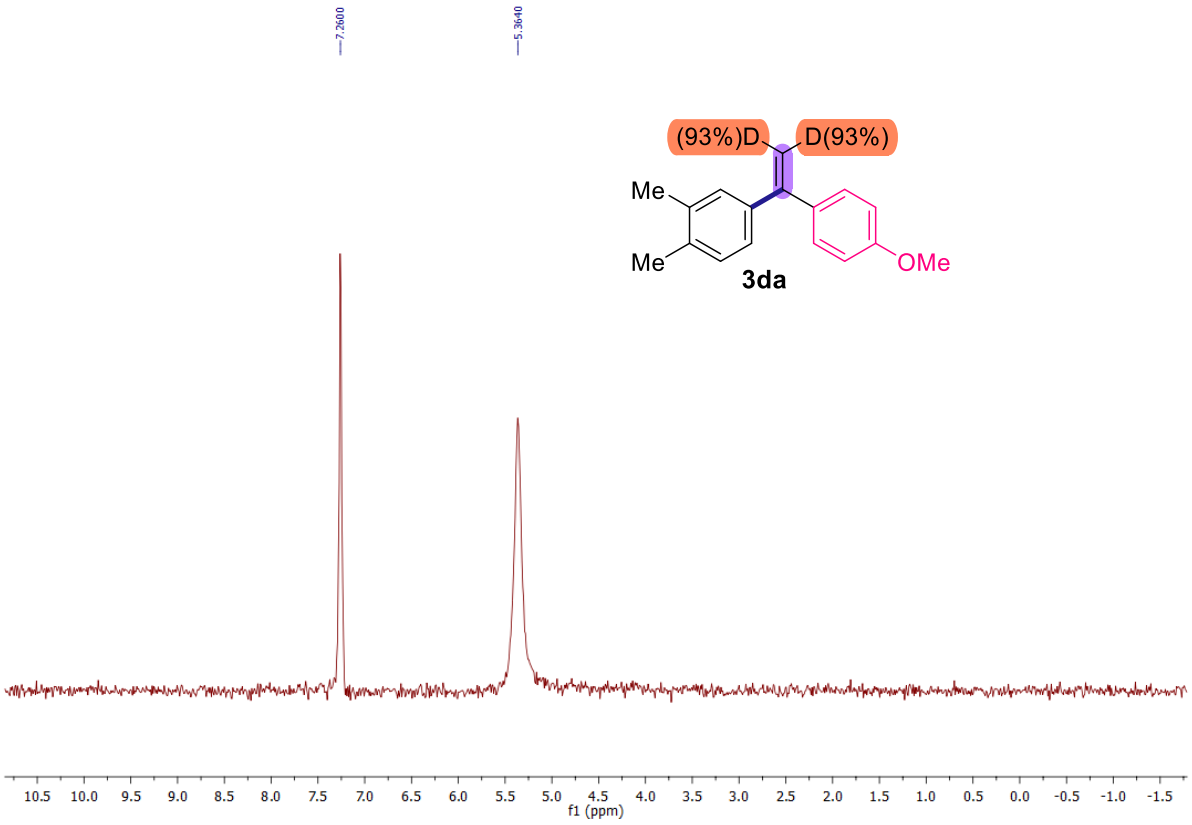
^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)



$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 24 °C)

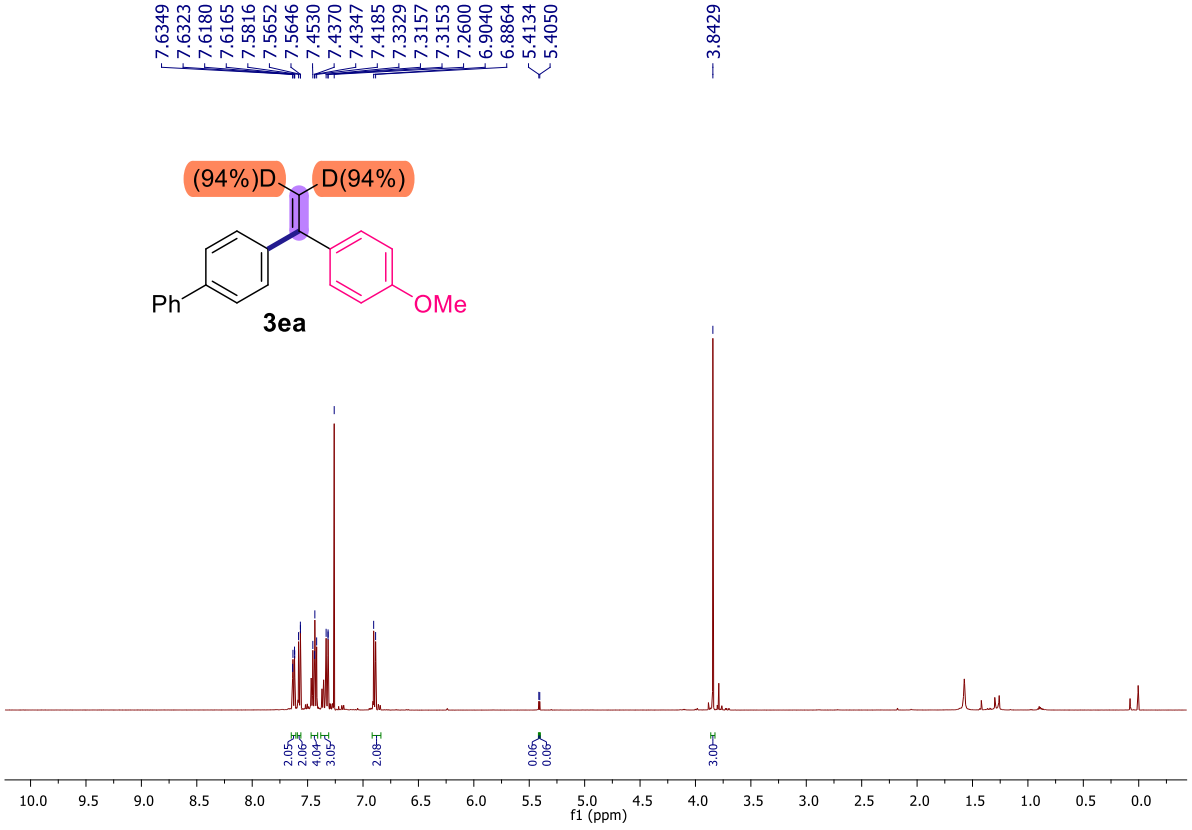


^{2}H NMR (94 MHz, $CHCl_3$, 24 °C)

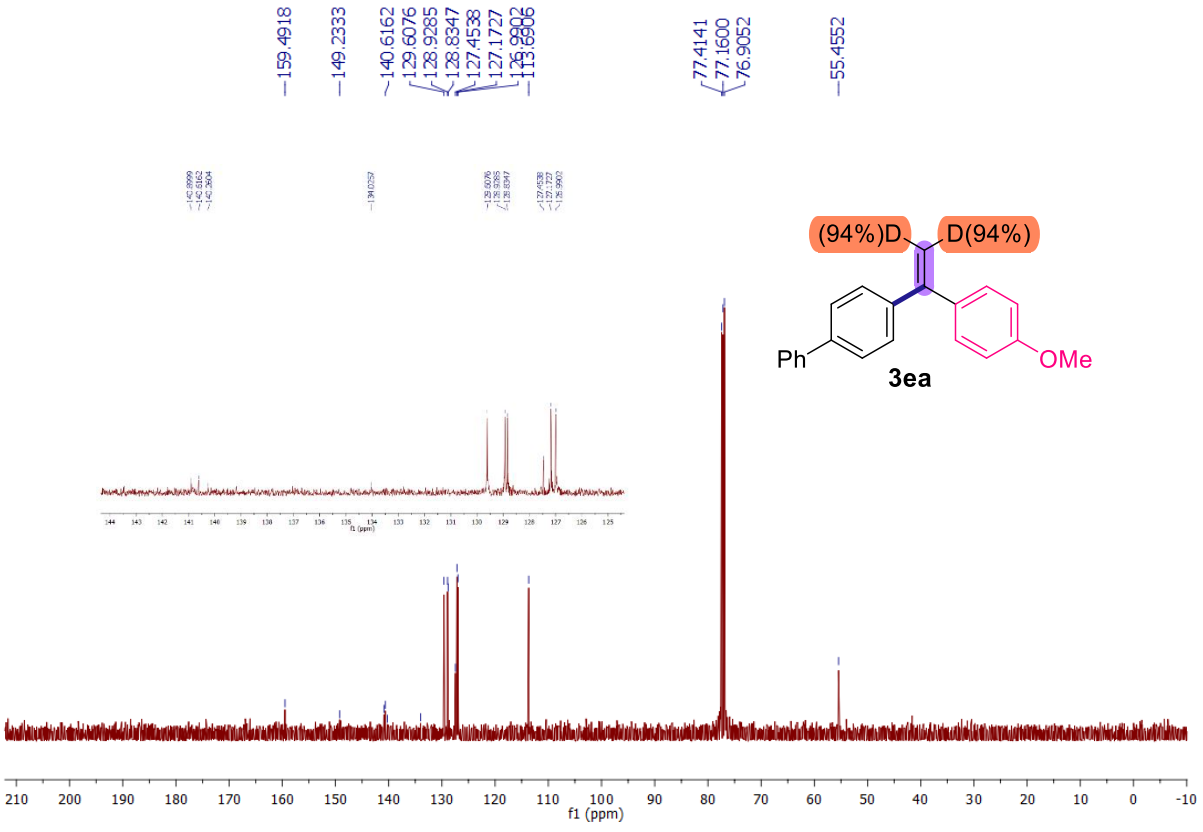


4-(1-(4-Methoxyphenyl)vinyl-2,2-d2)-1,1'-biphenyl (**3ea**)

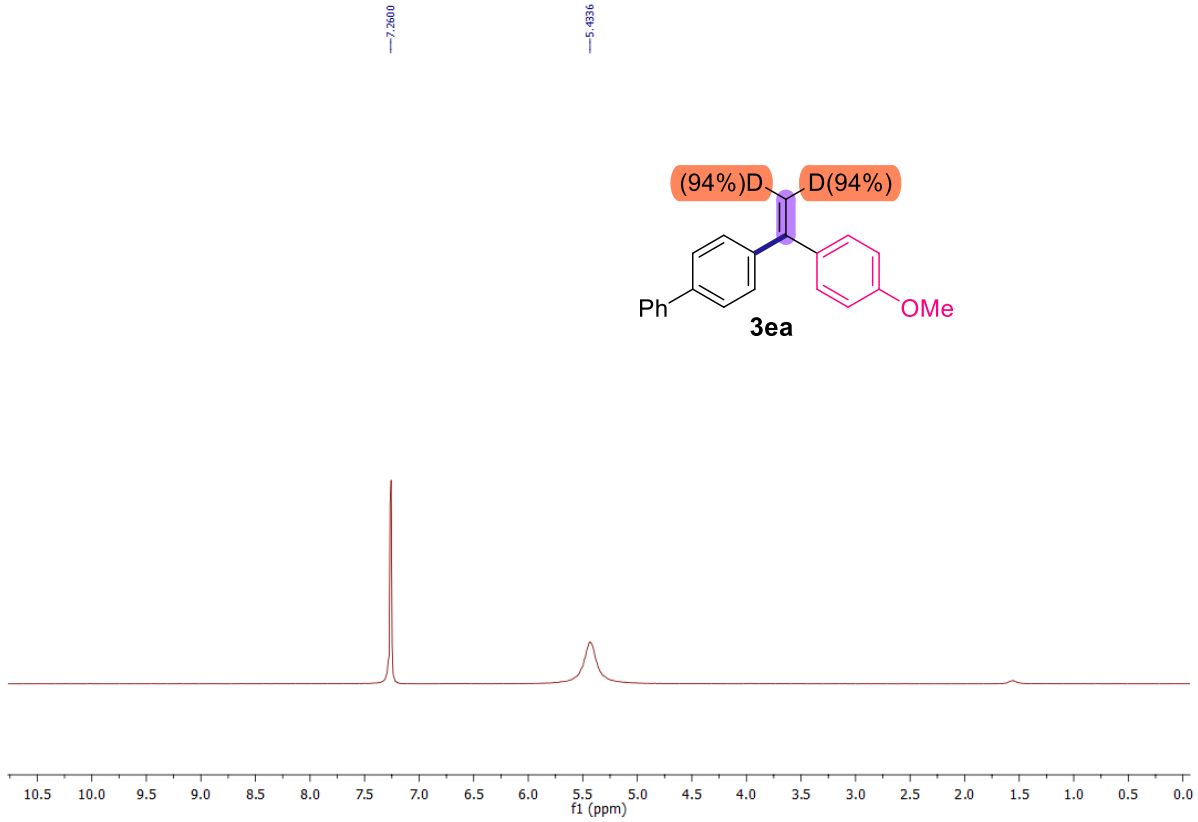
^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)



^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 24 °C)

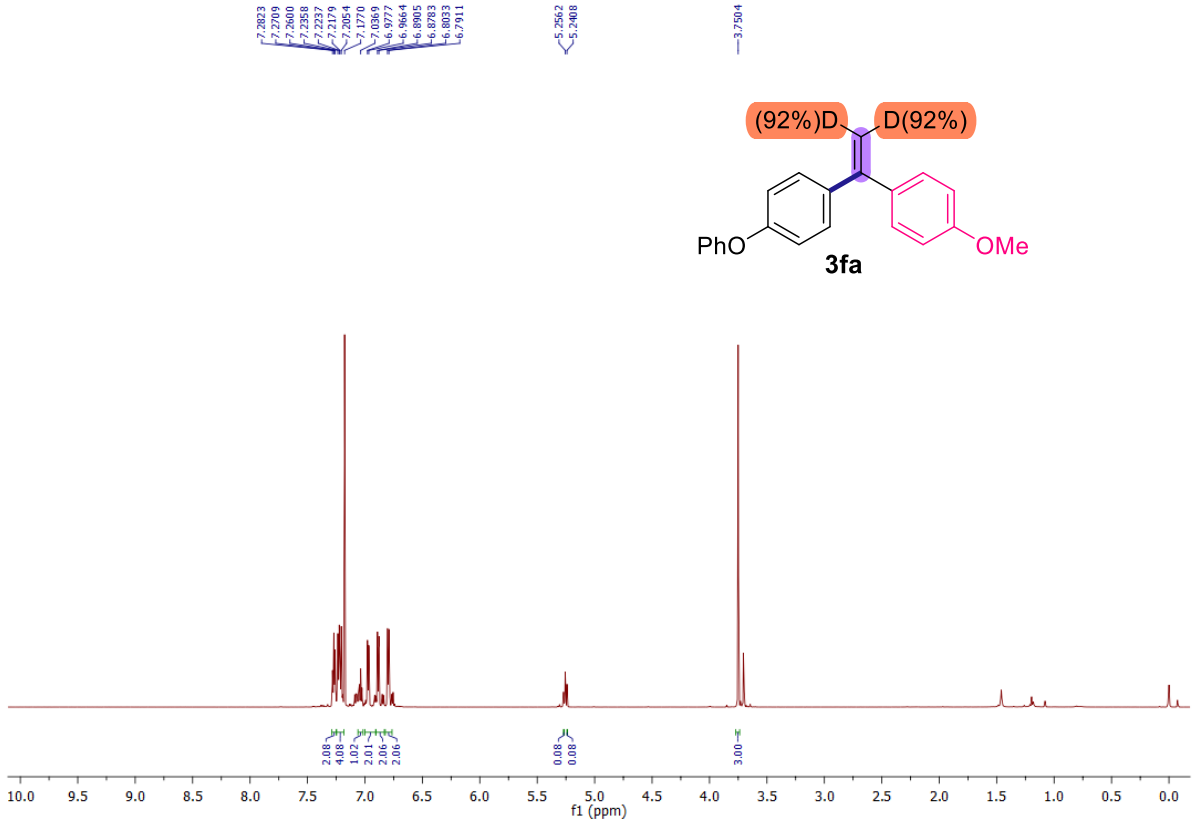


^{2}H NMR (94 MHz, $CHCl_3$, 24 °C)

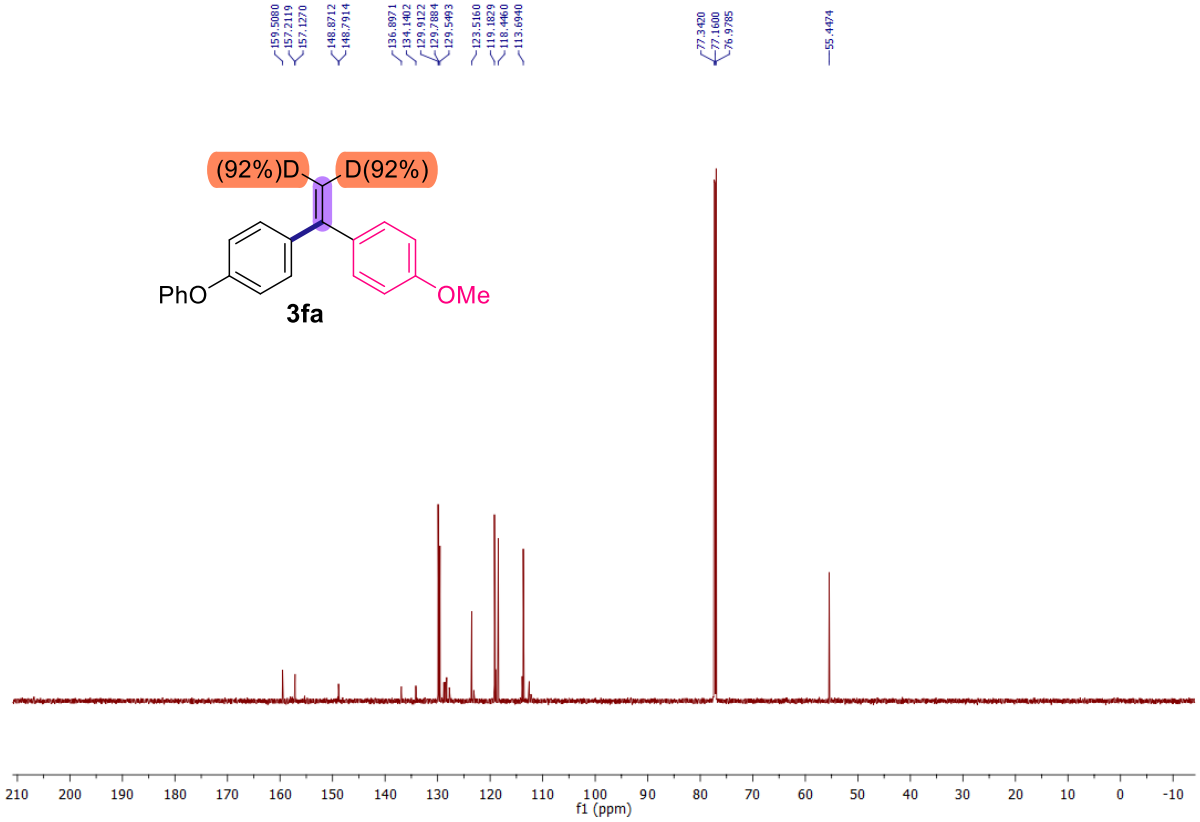


1-Methoxy-4-(1-(4-phenoxyphenyl)vinyl-2,2-d2)benzene (**3fa**)

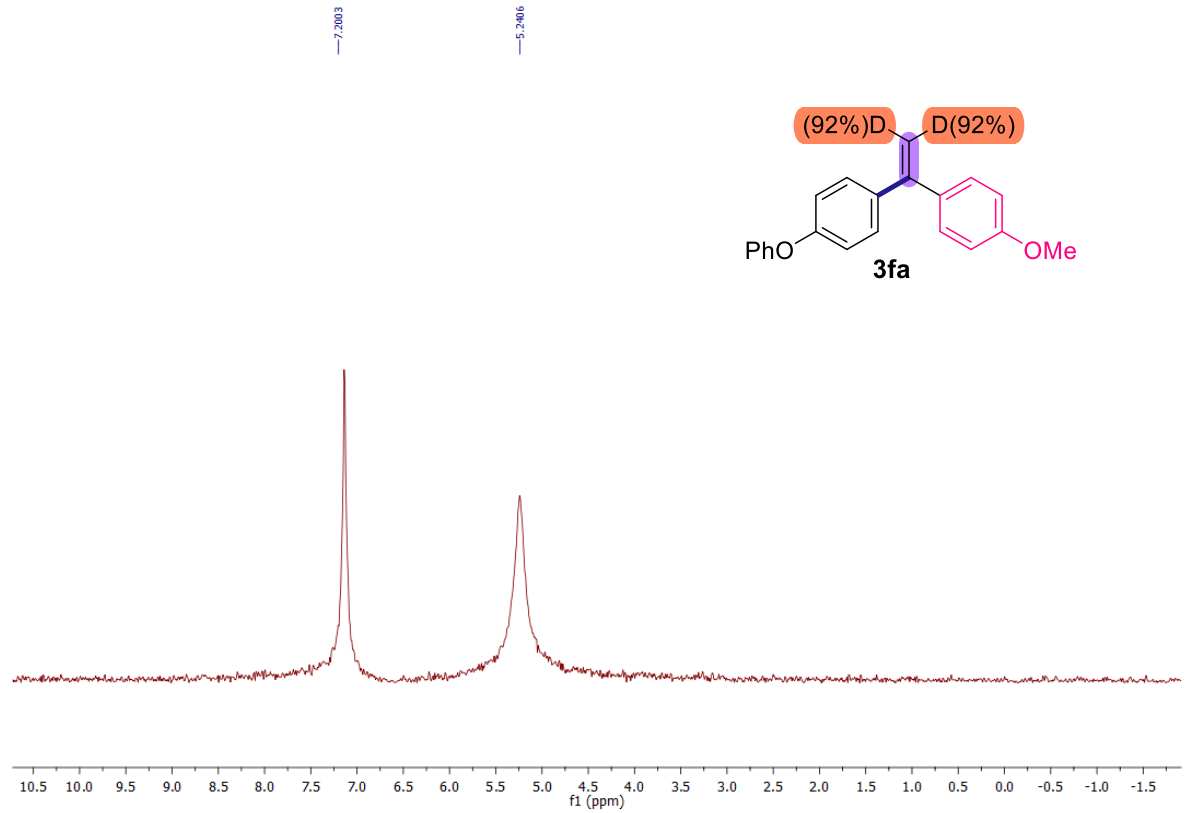
^{1}H NMR (500 MHz, CDCl3, 24 °C)



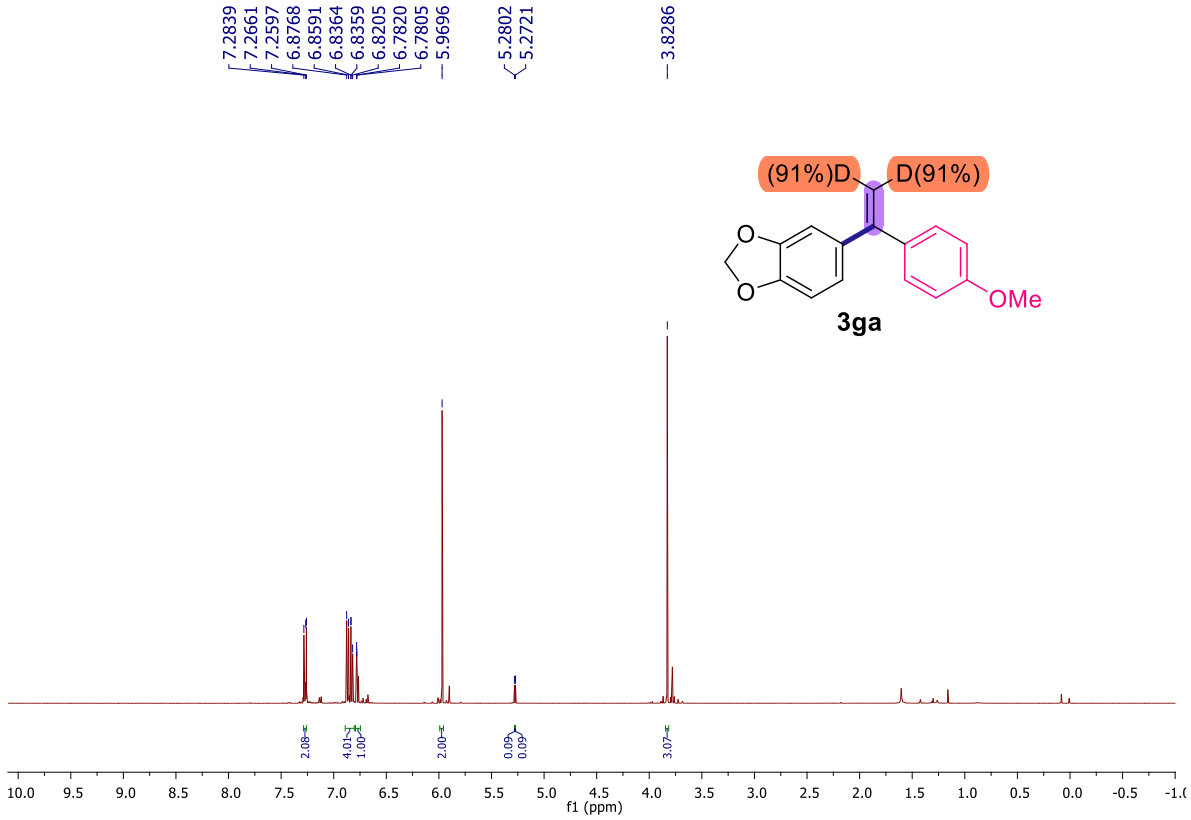
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 24 °C)



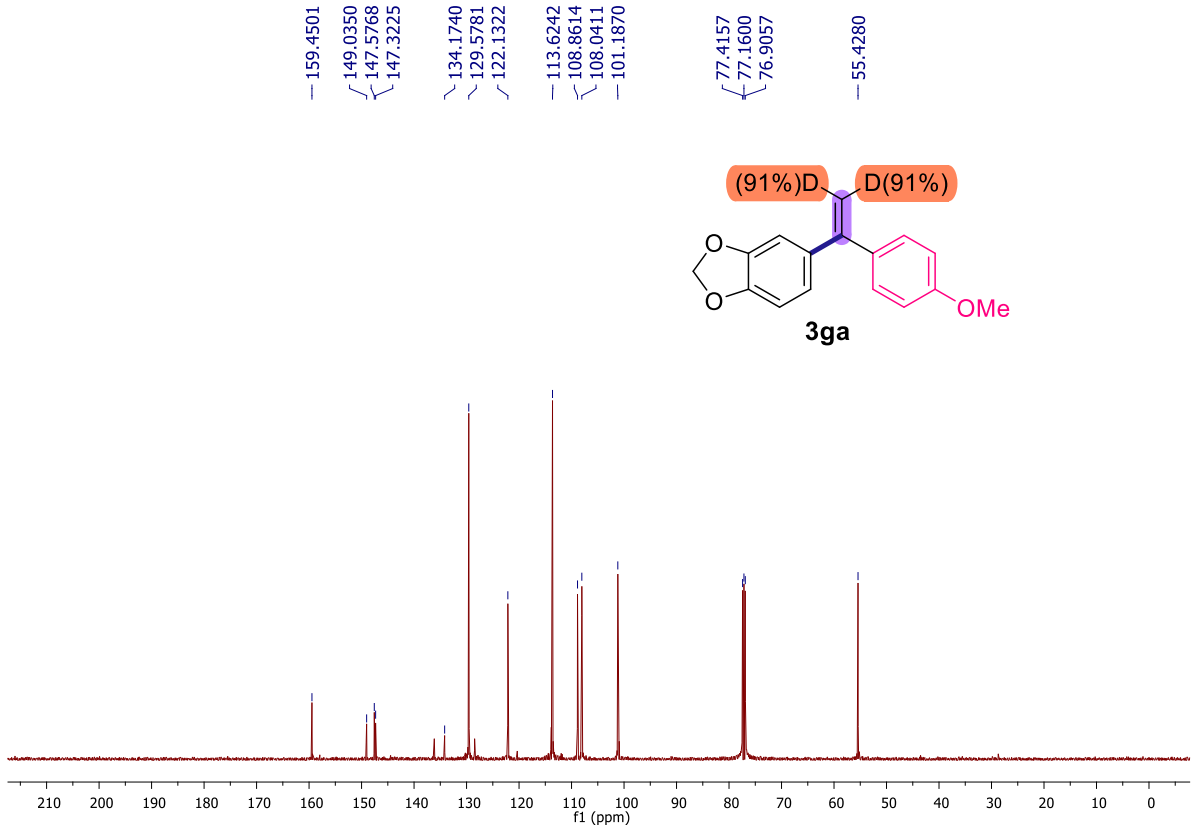
^{2}H NMR (77 MHz, $CHCl_3$, 24 °C)



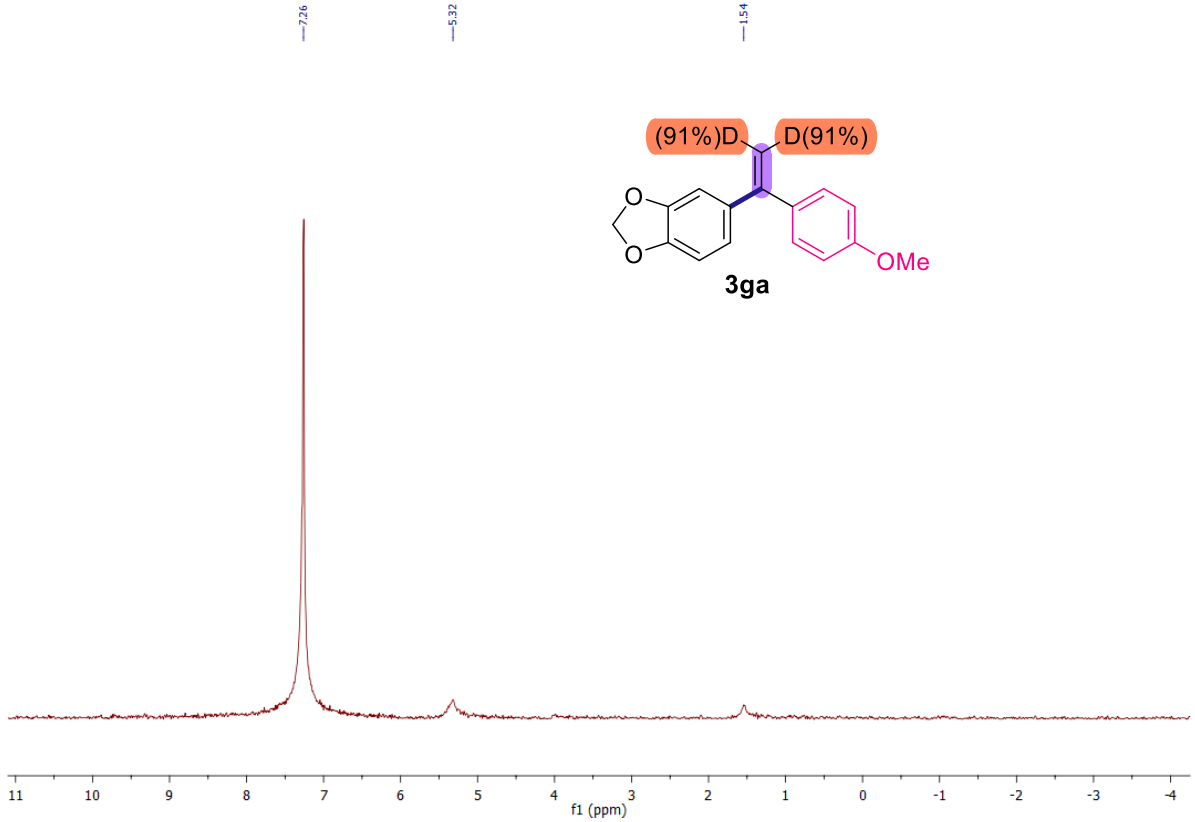
5-(1-(4-Methoxyphenyl)vinyl-2,2-d2)benzo[d][1,3]dioxole (**3ga**)



$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 24 °C)

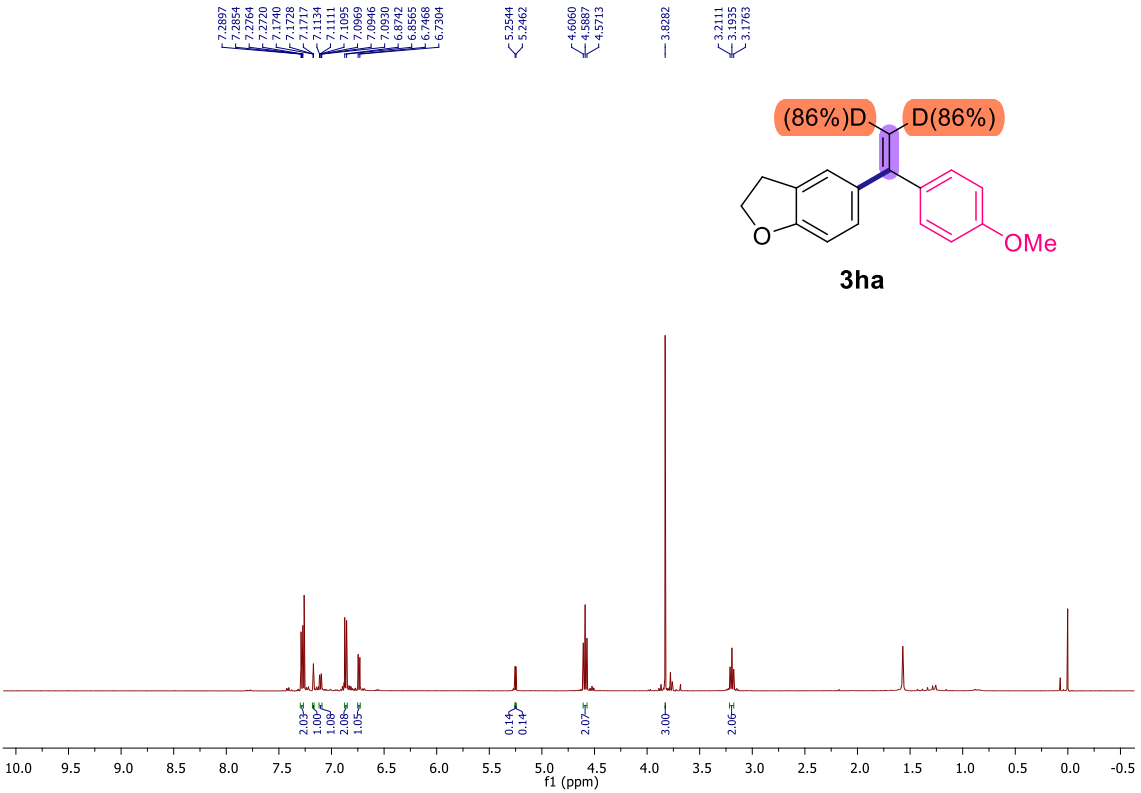


^{2}H NMR (94 MHz, $CHCl_3$, 24 °C)

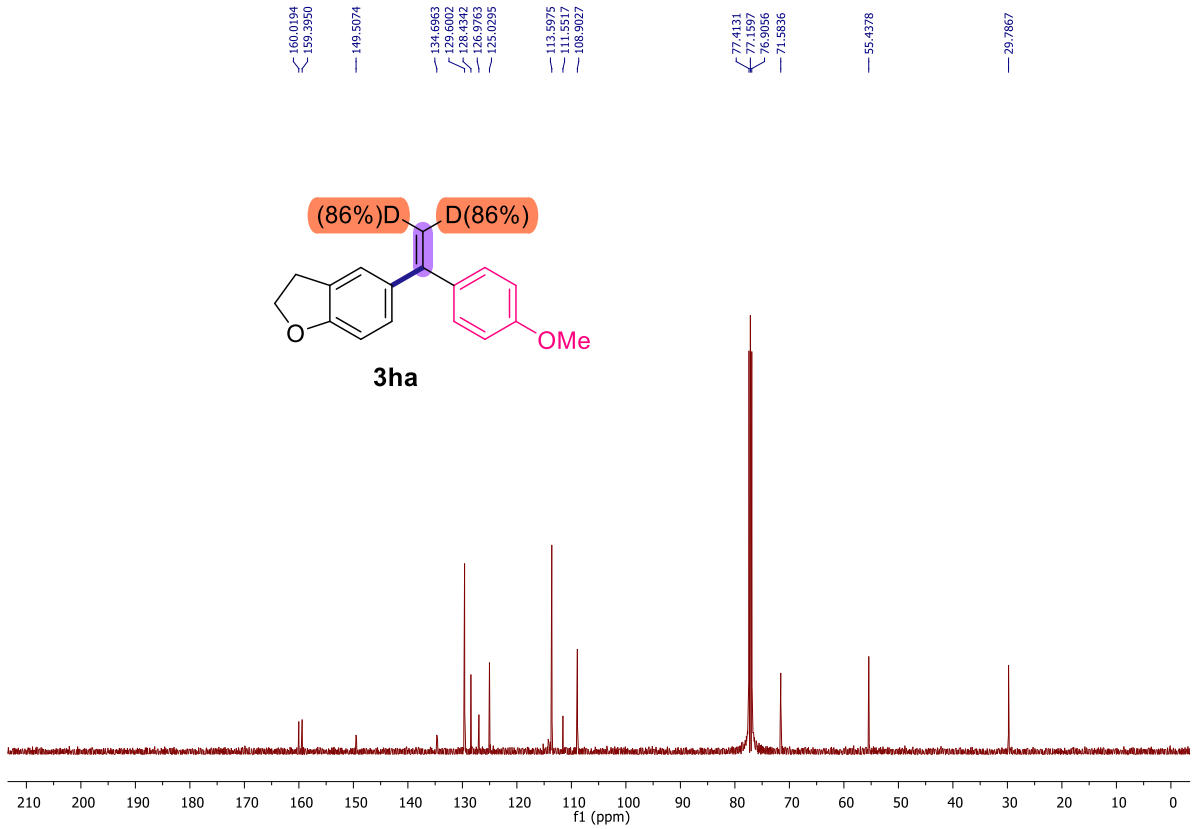


5-(1-(4-Methoxyphenyl)vinyl-2,2-d2)-2,3-dihydrobenzofuran (**3ha**)

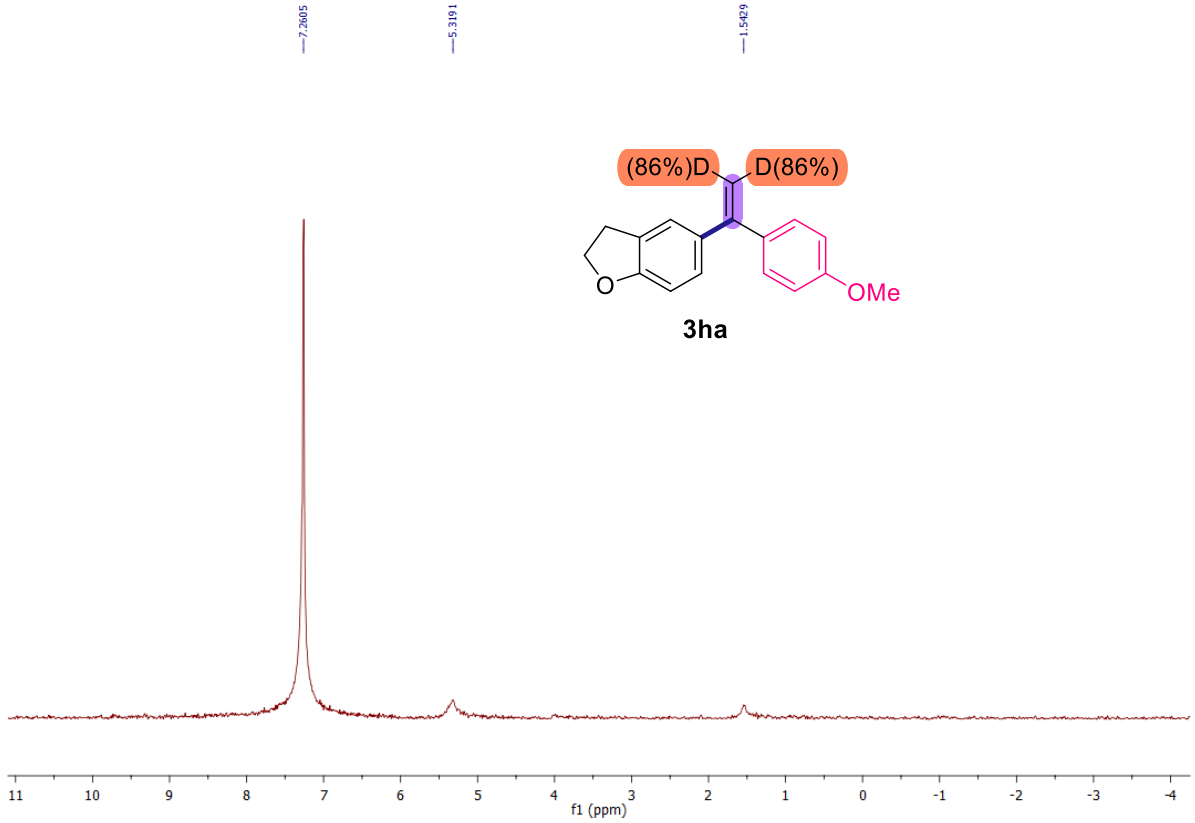
^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)



$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 24 °C)

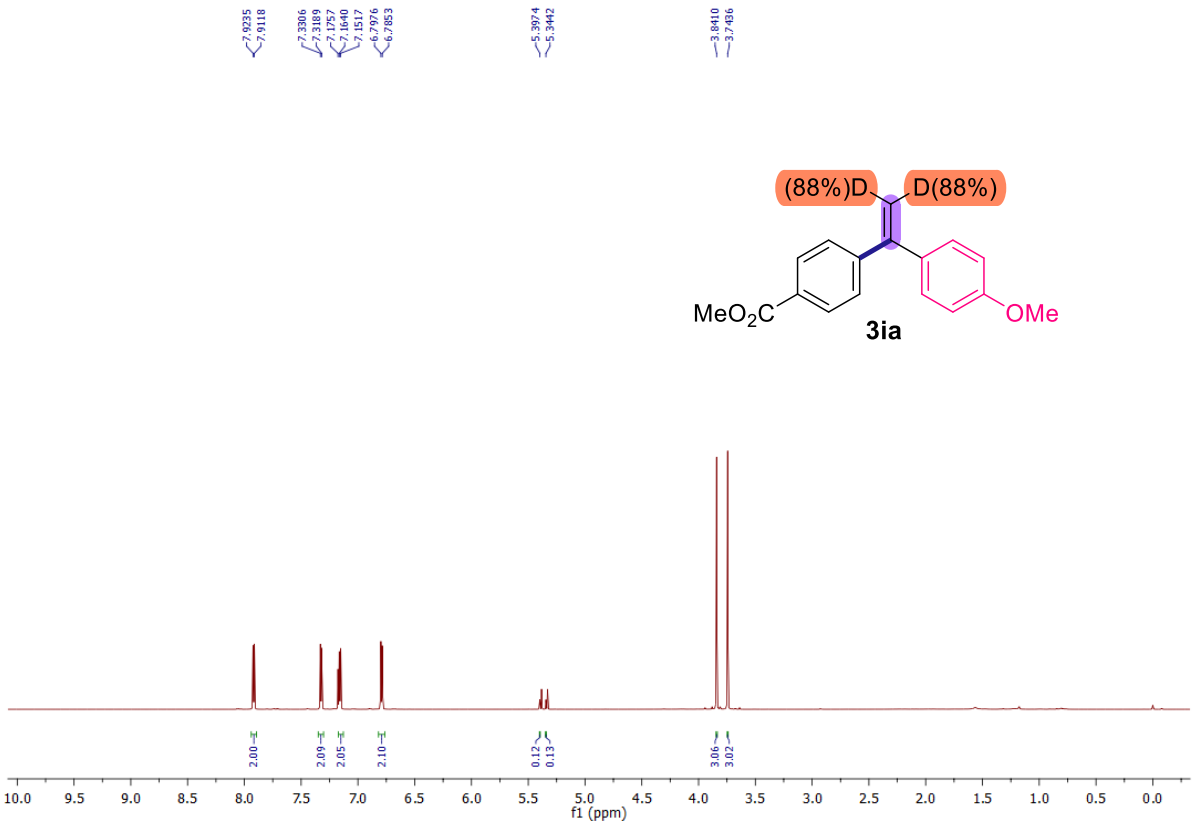


^{2}H NMR (77 MHz, $CDCl_3$, 24 °C)

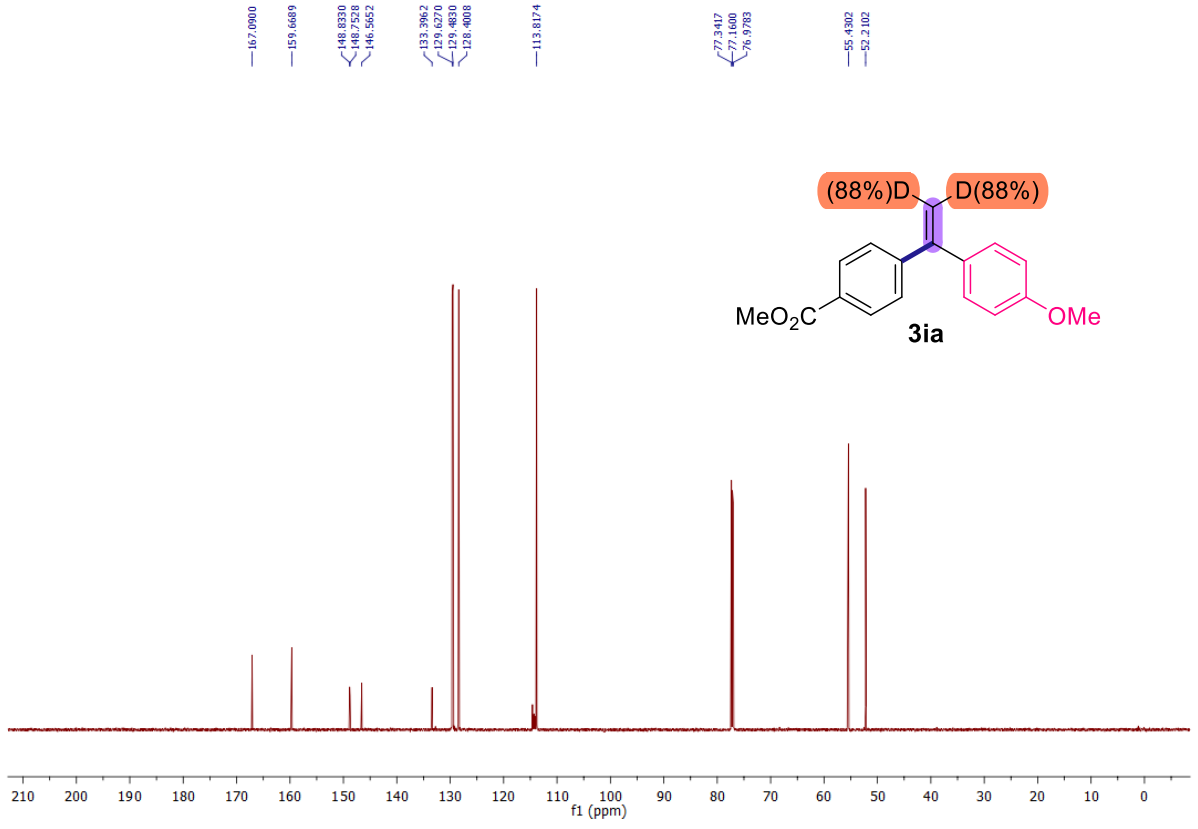


1-(4-(1-(4-Methoxyphenyl)vinyl)phenyl)ethan-1-one (**3ia**)

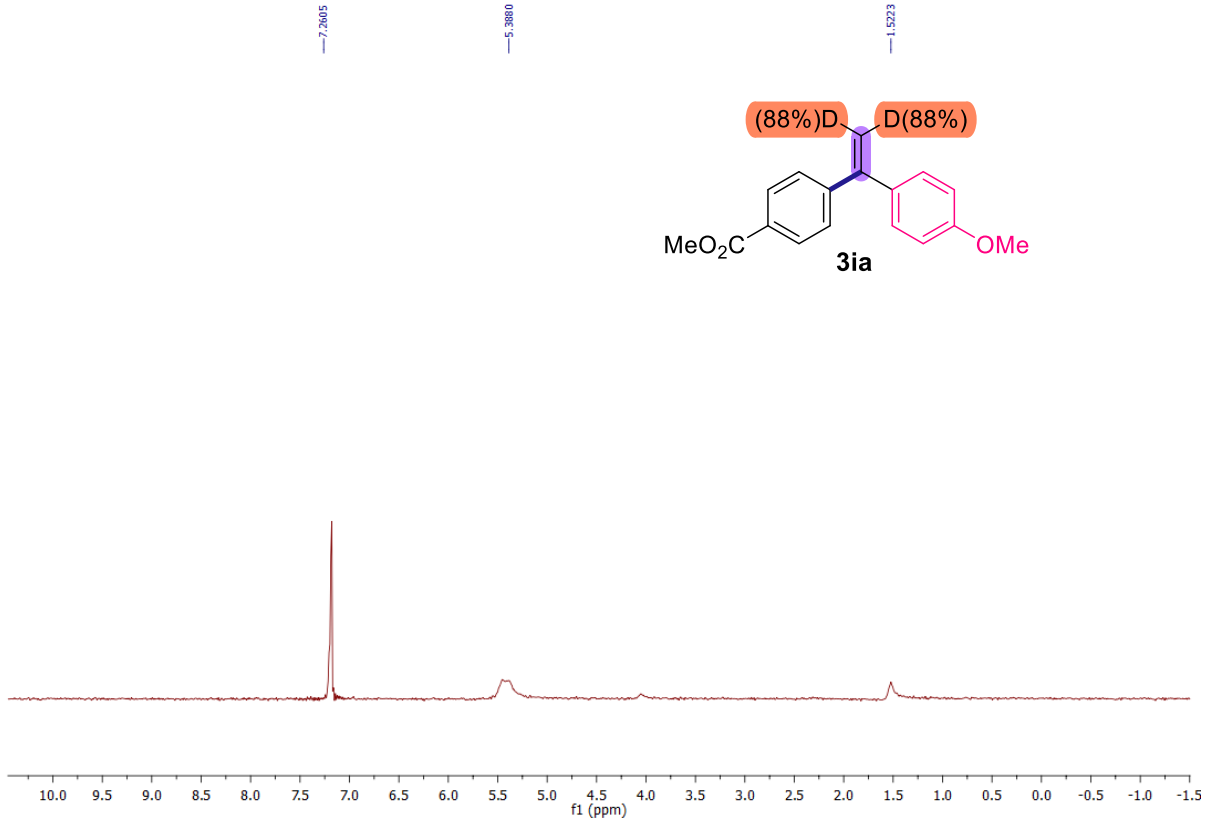
^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)



^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 24 °C)

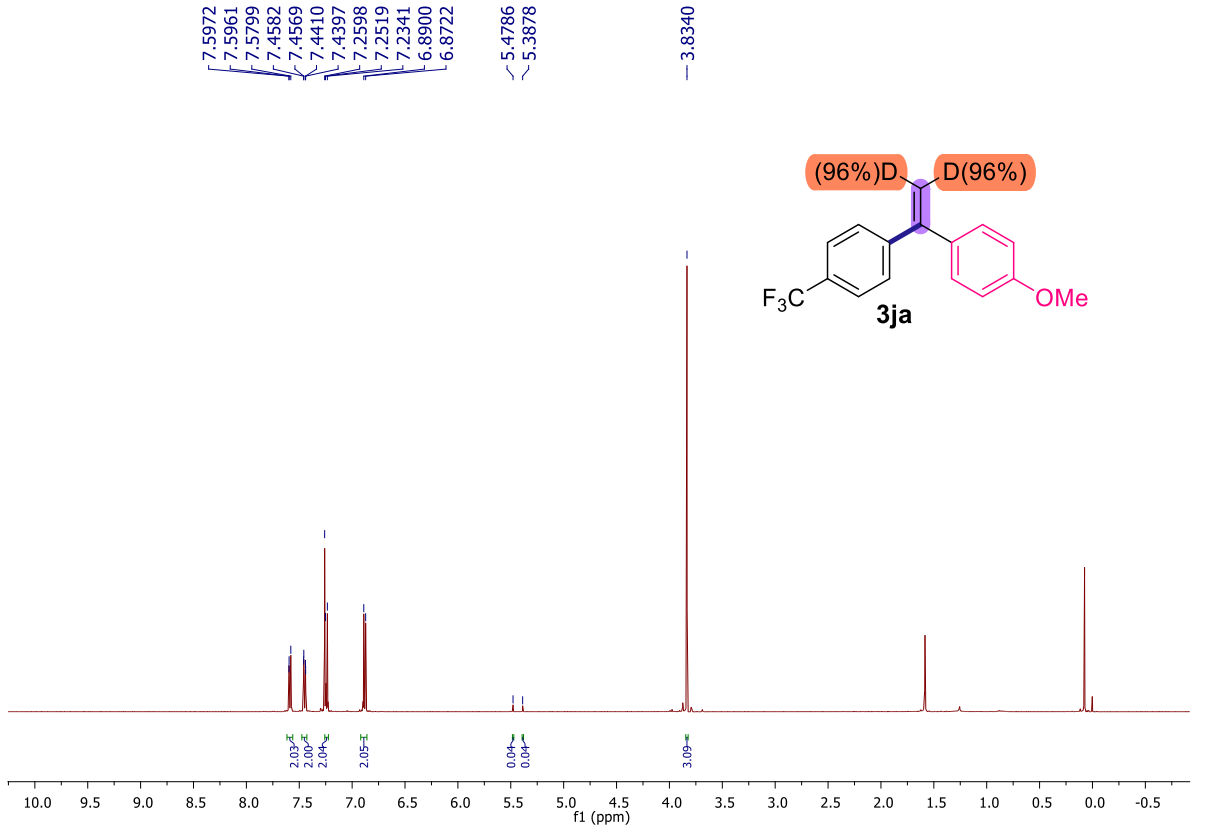


^{2}H NMR (77 MHz, $CDCl_3$, 24 °C)

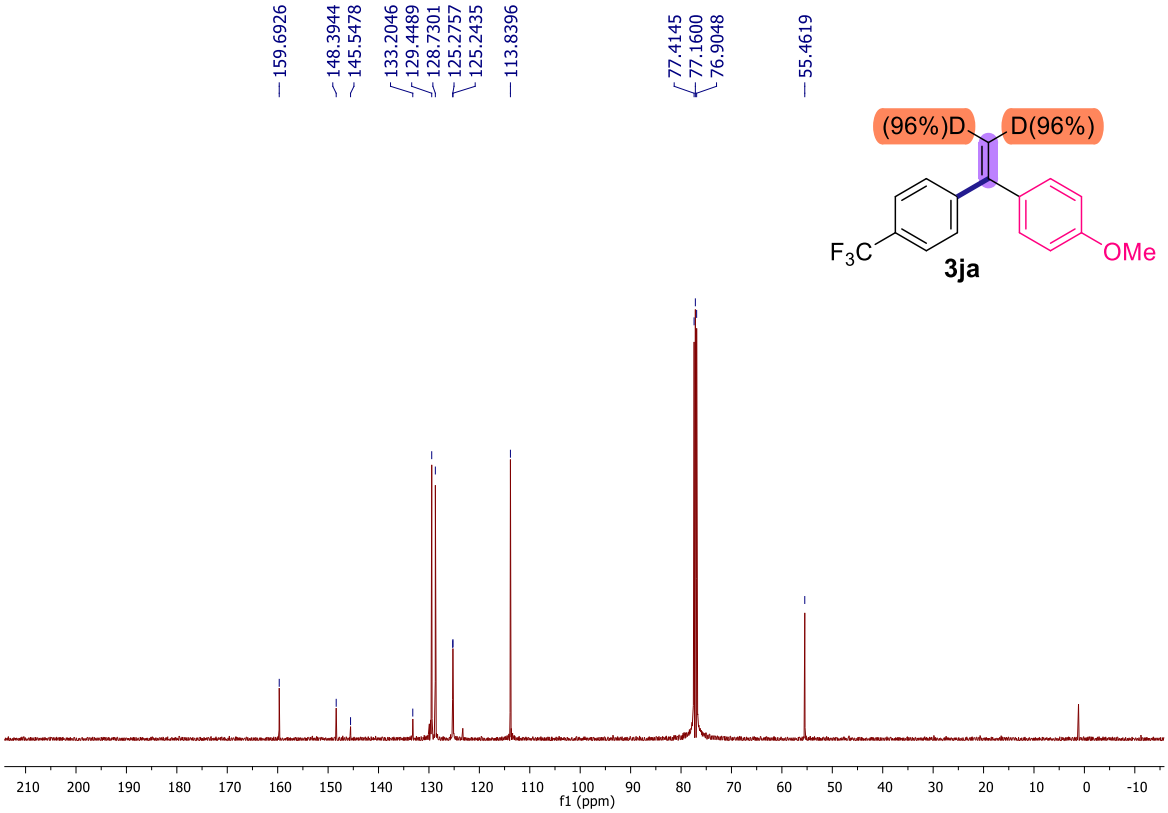


1-Methoxy-4-(1-(4-(trifluoromethyl)phenyl)vinyl-2,2-d2)benzene (**3ja**)

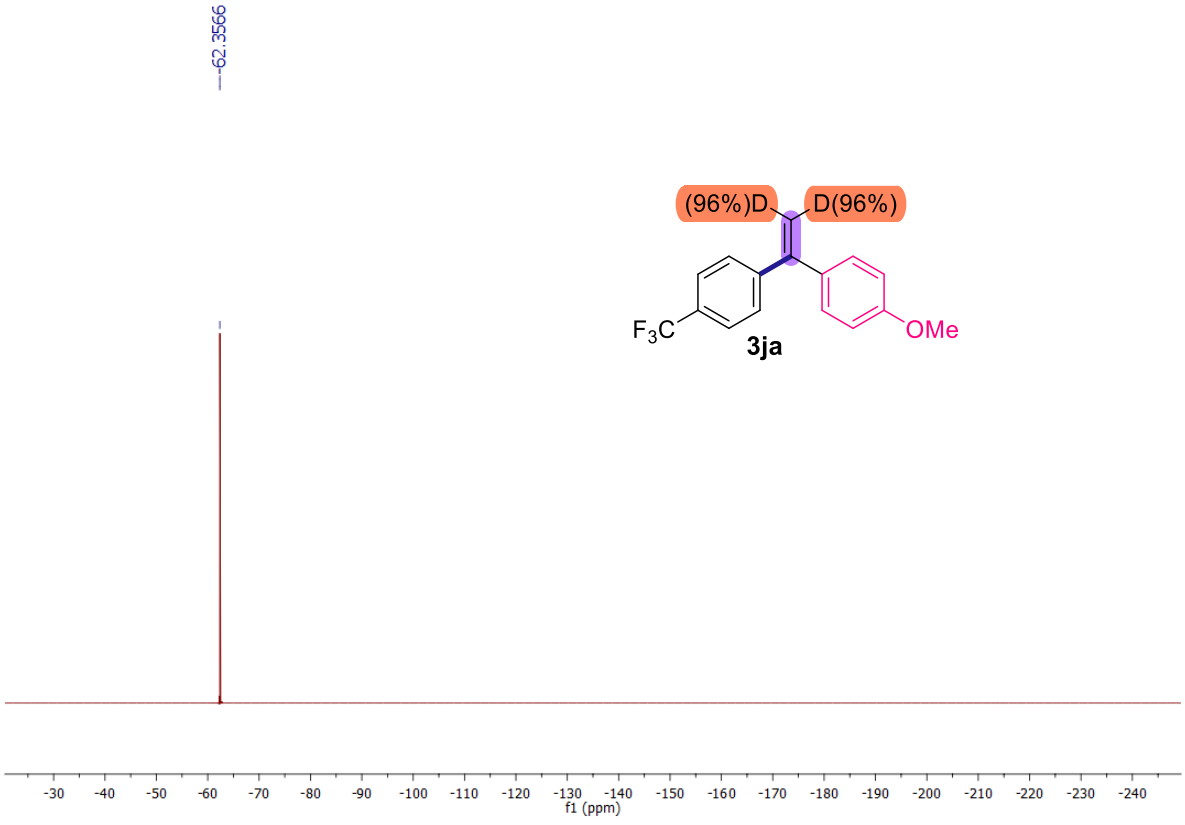
^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)



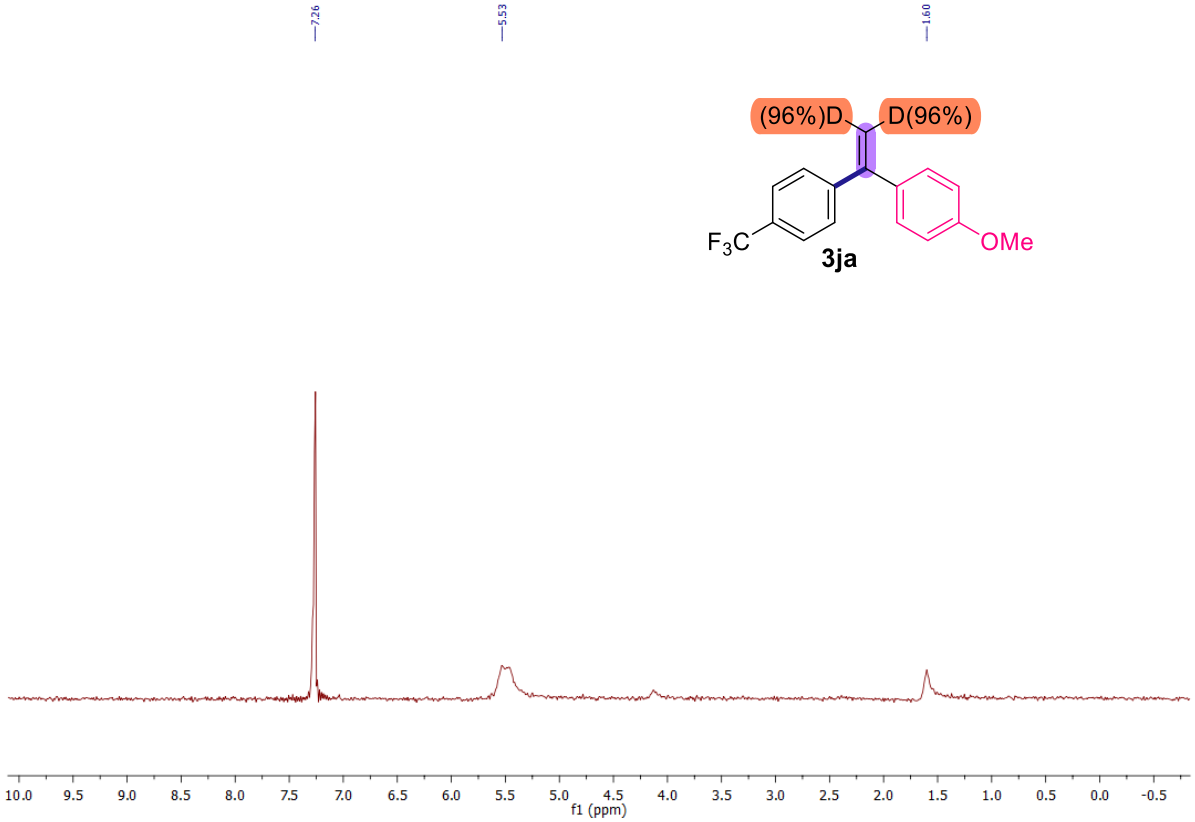
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 24 °C)



^{19}F NMR (471 MHz, $CDCl_3$, 24 °C)

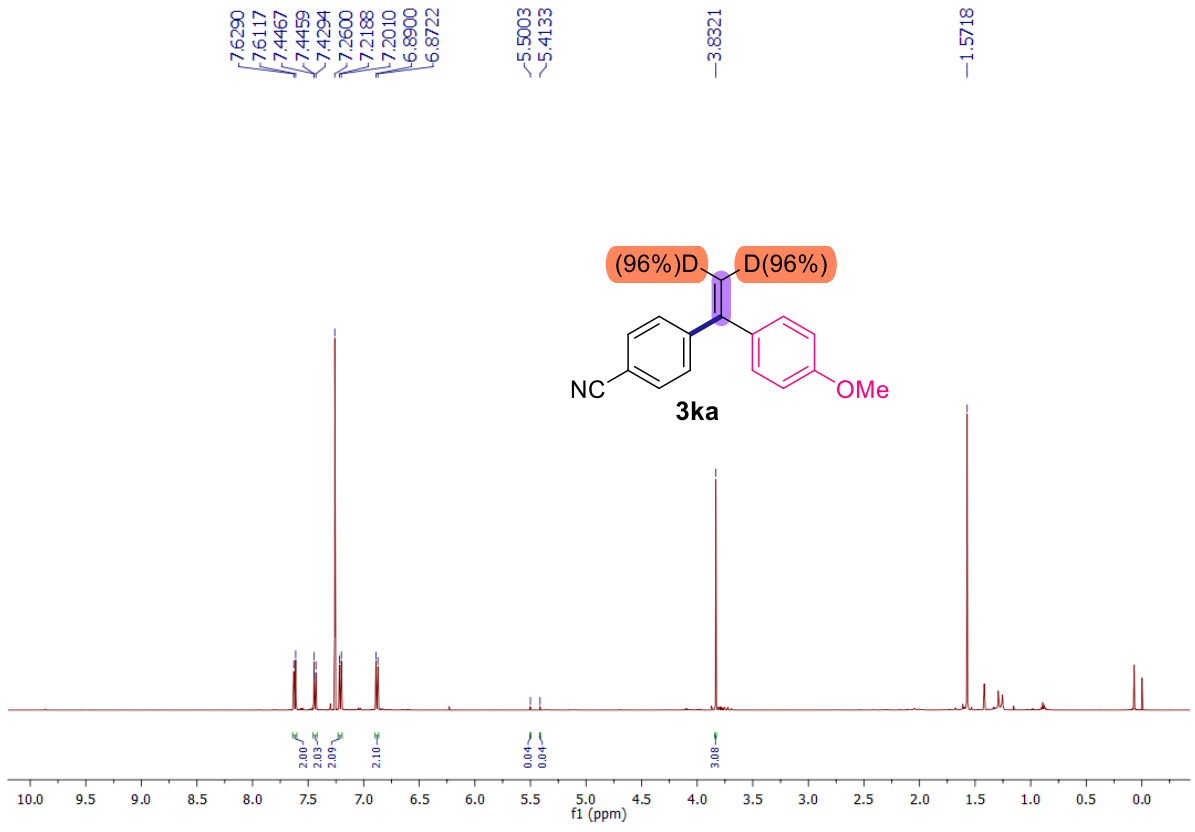


^{2}H NMR (77 MHz, $CDCl_3$, 24 °C)

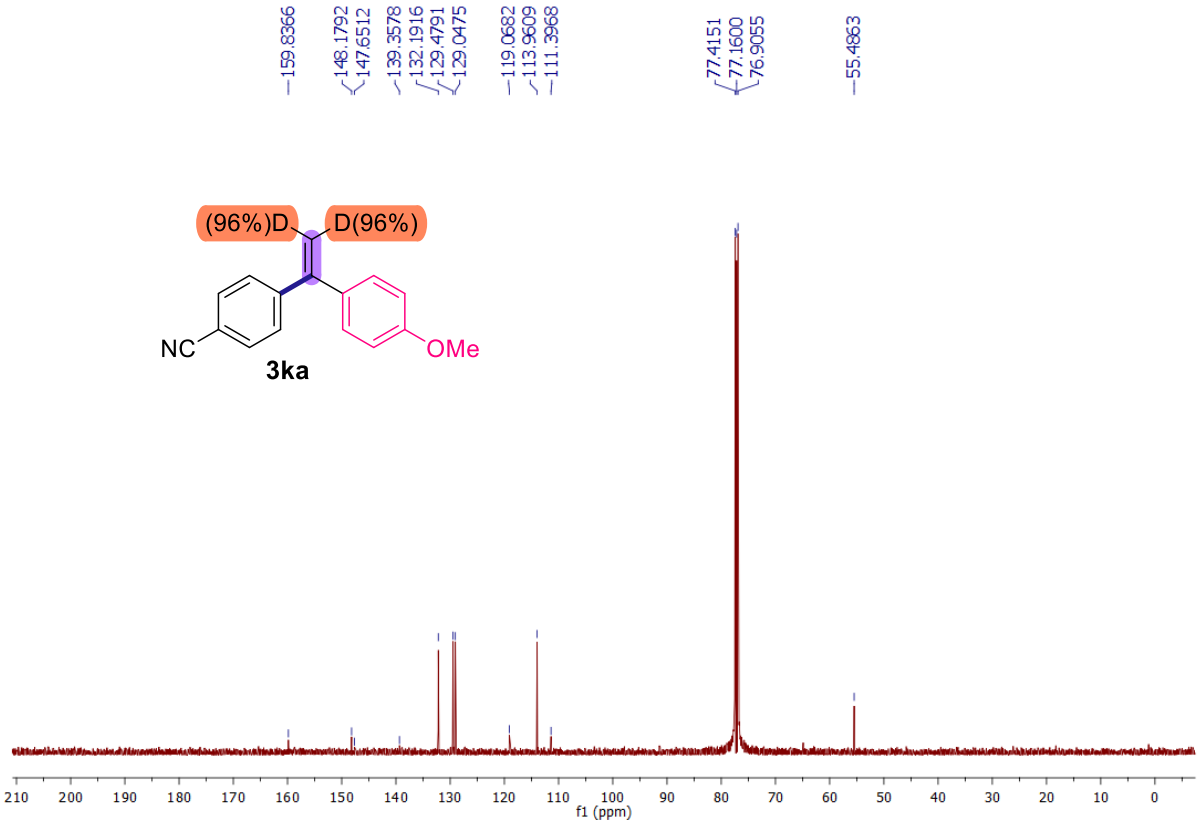


4-(1-(4-Methoxyphenyl)vinyl-2,2-d2)benzonitrile (**3ka**)

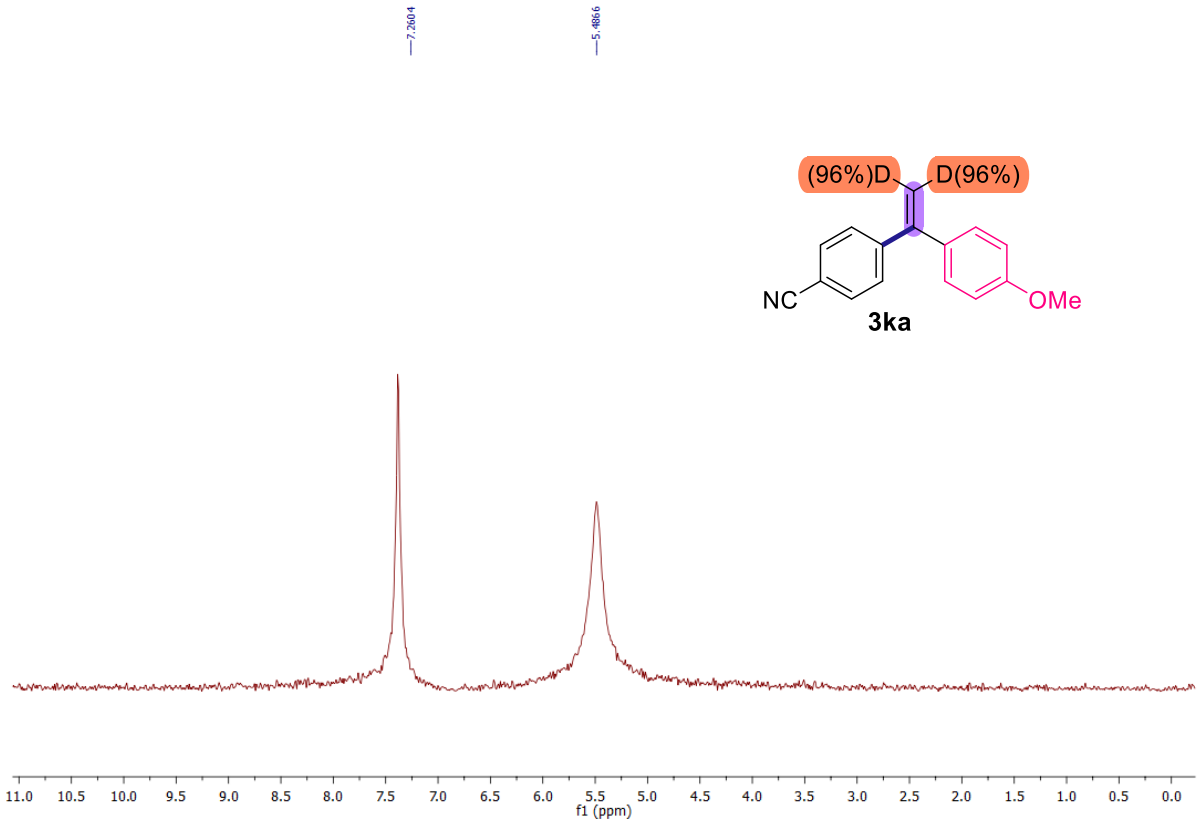
^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)



$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 24 °C)

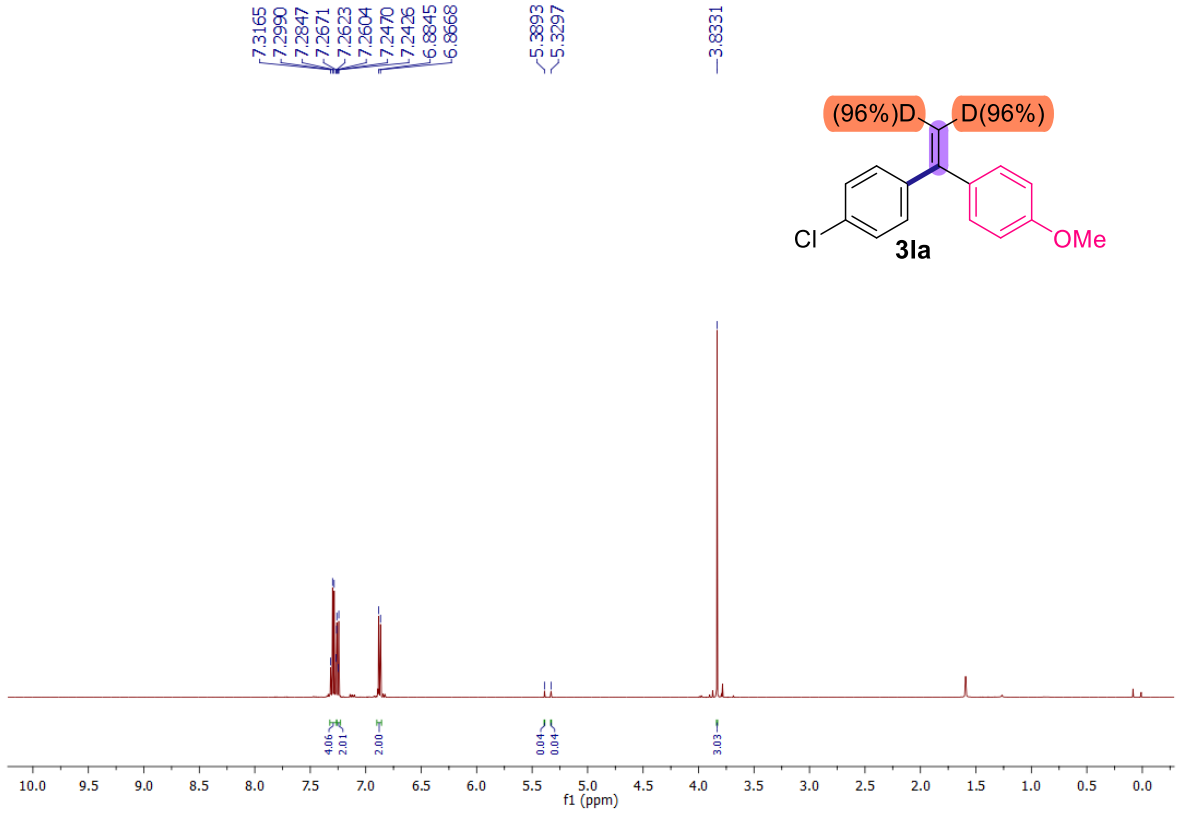


^{2}H NMR (77 MHz, $CHCl_3$, 24 °C)

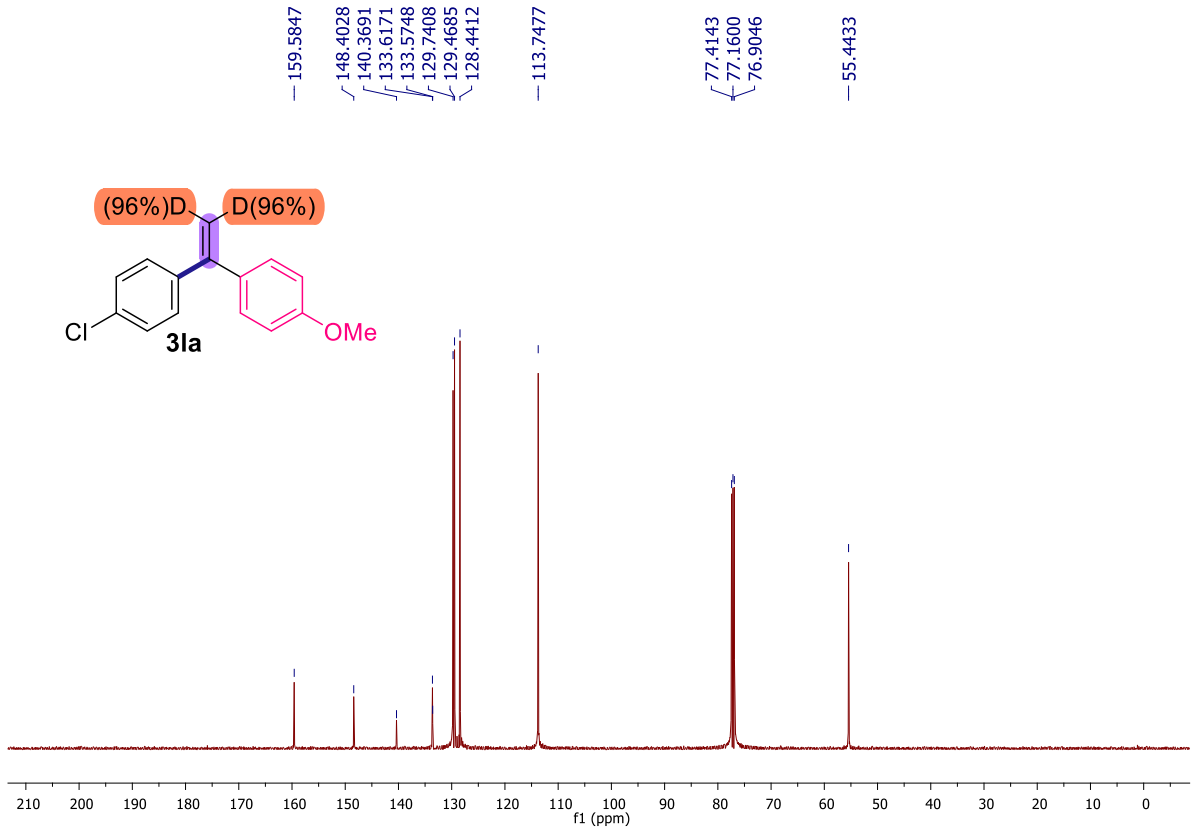


1-Chloro-4-(1-(4-methoxyphenyl)vinyl-2,2-d2)benzene (**3la**)

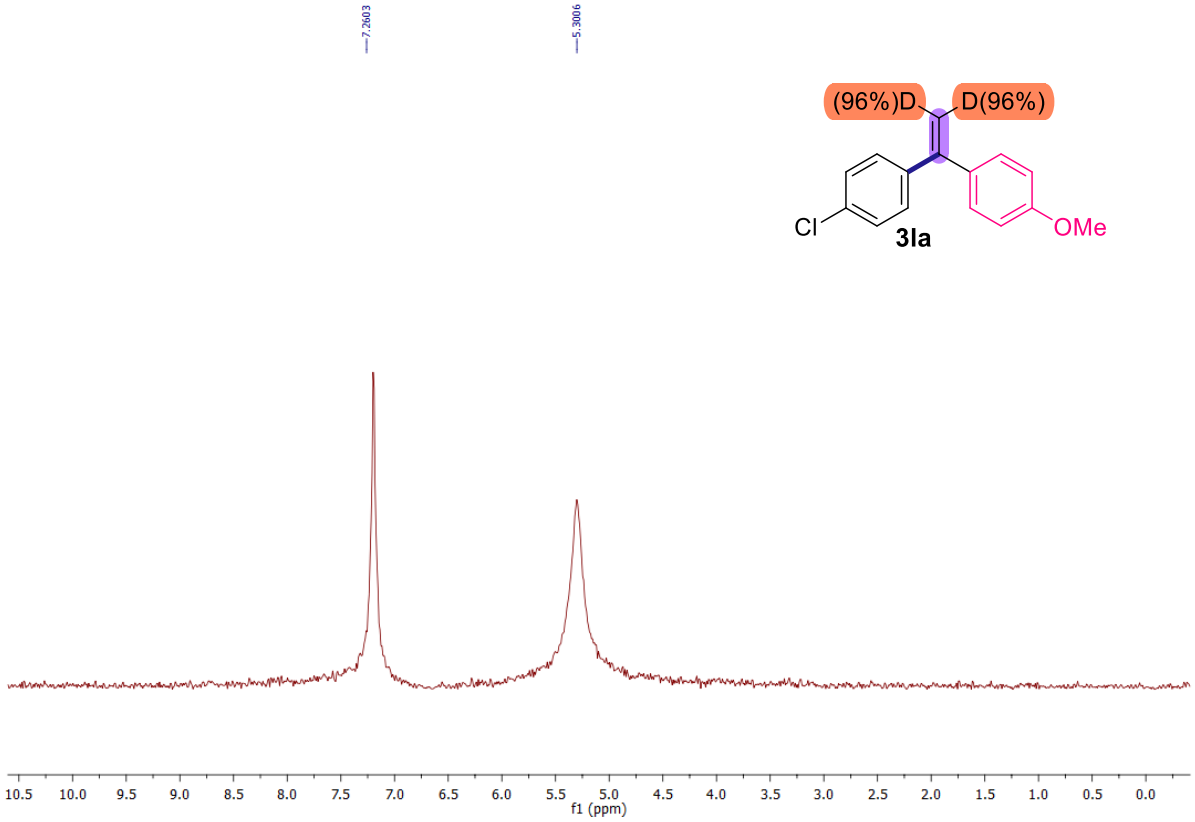
^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)



^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 24 °C)

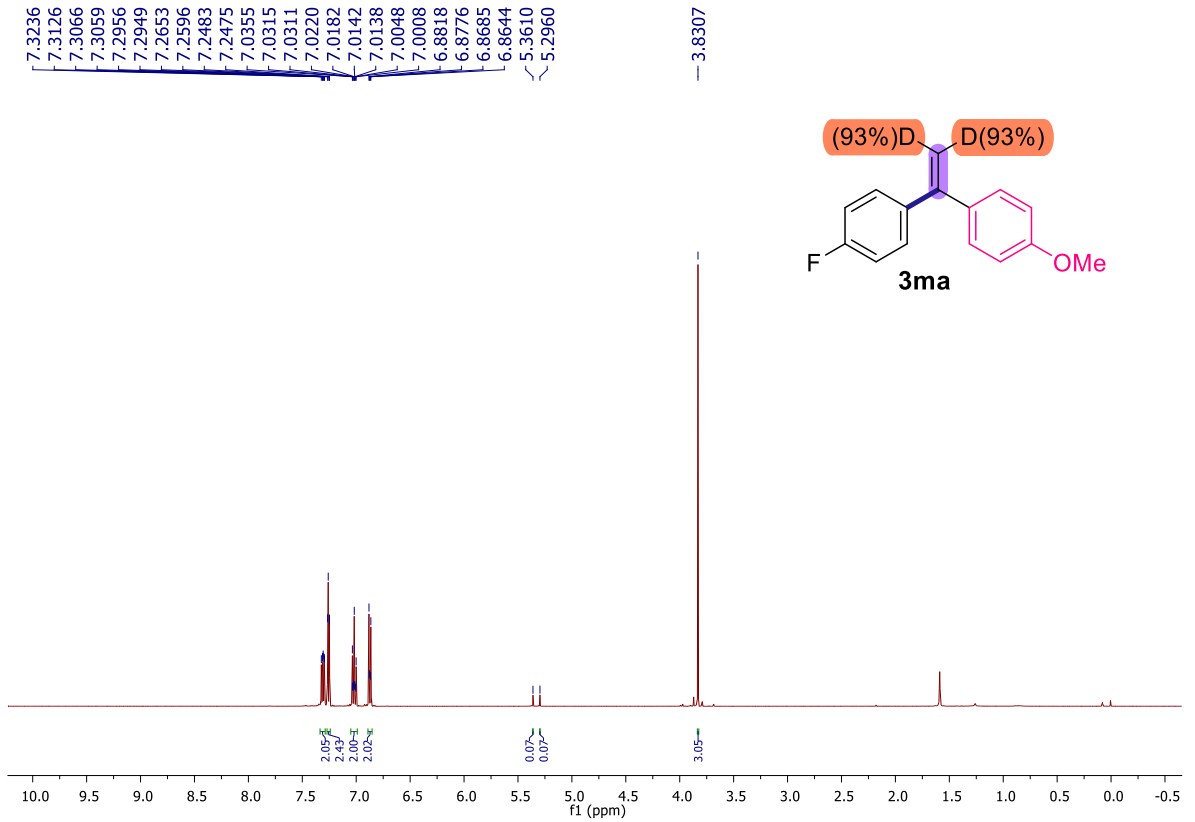


^{2}H NMR (77 MHz, $CDCl_3$, 24 °C)

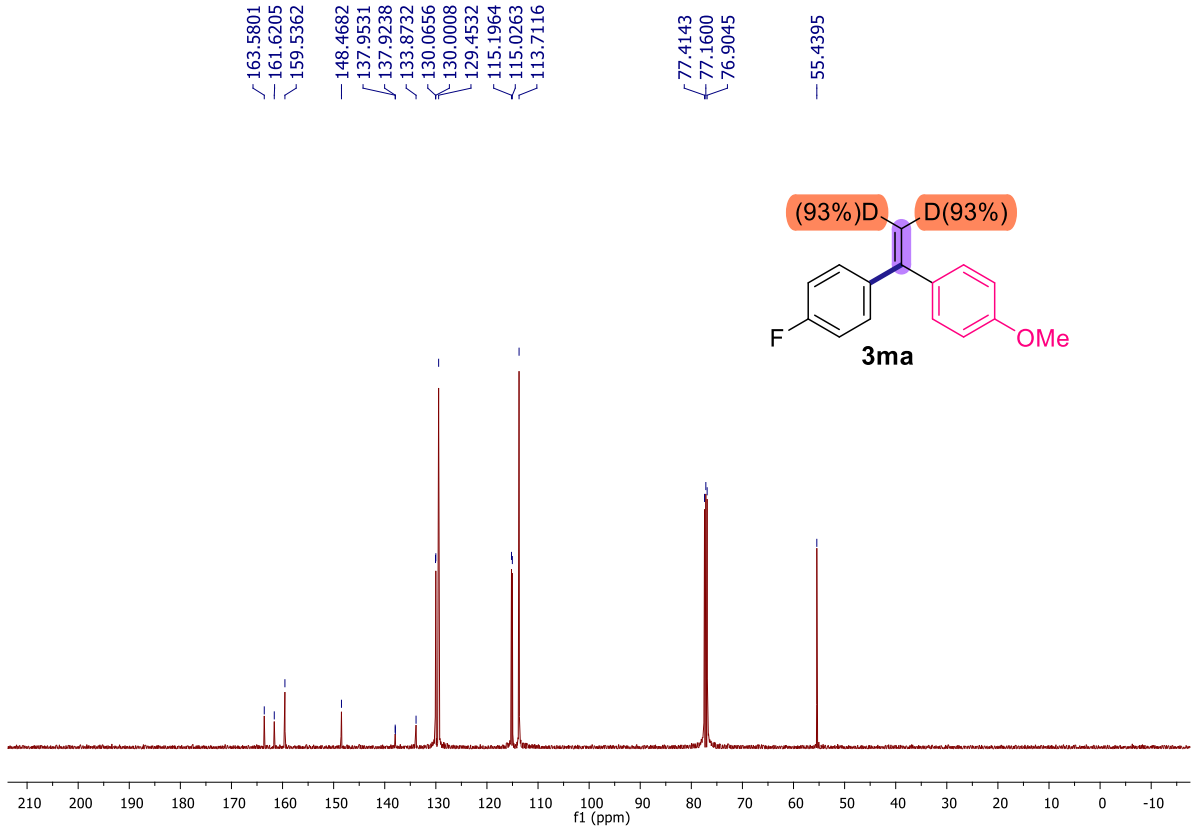


1-Fluoro-4-(1-(4-methoxyphenyl)vinyl-2,2-d2)benzene (**3ma**)

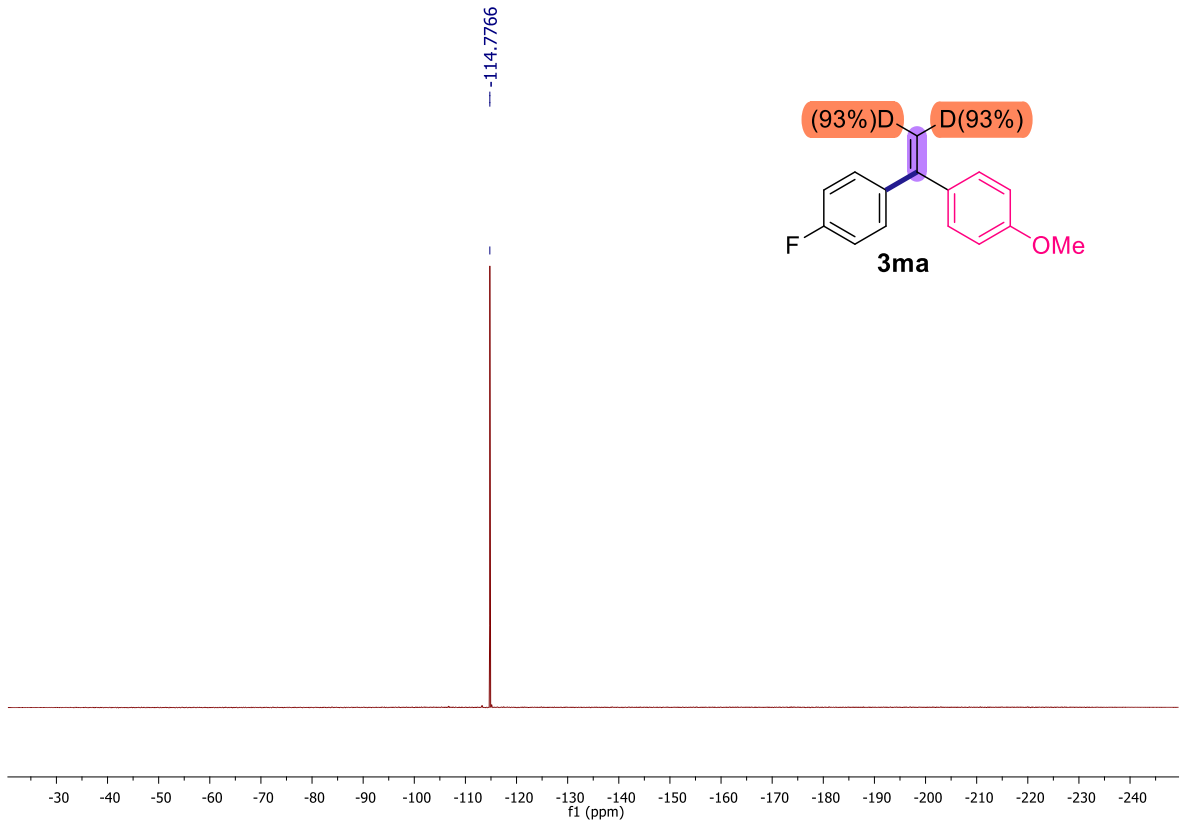
^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)



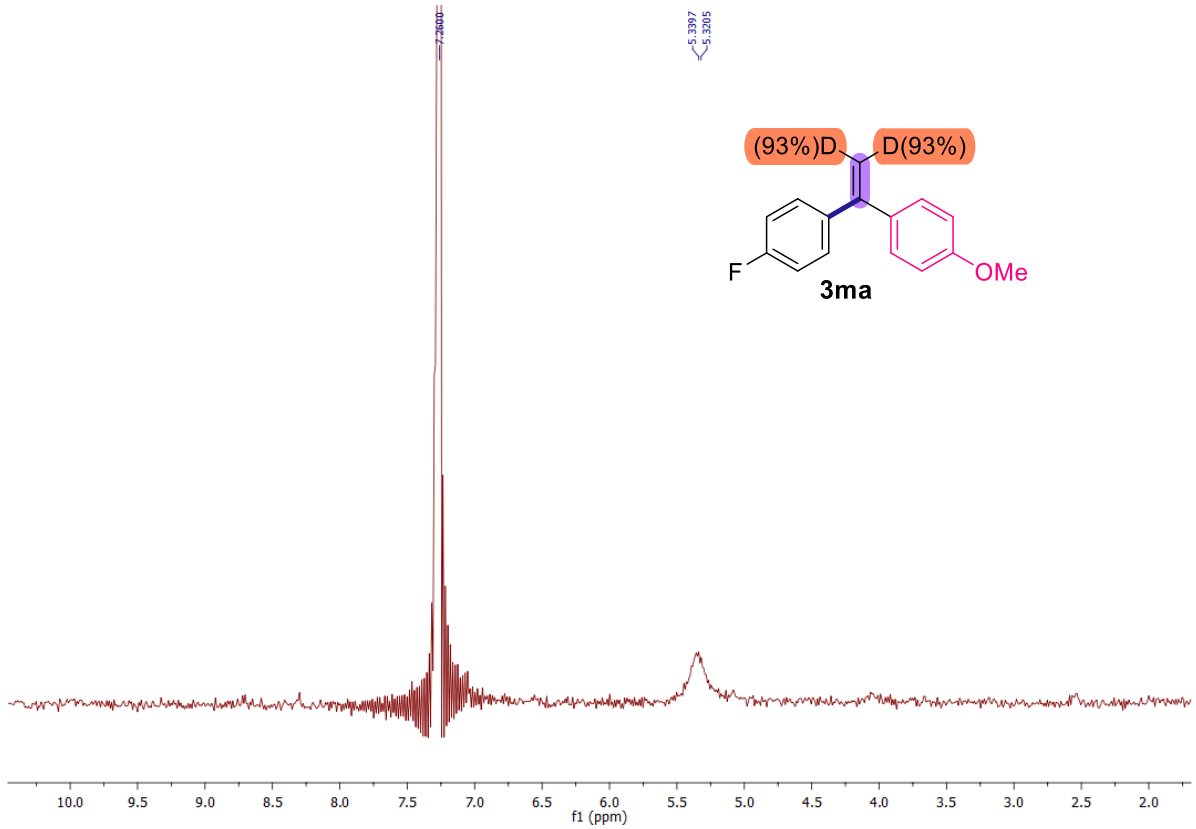
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 24 °C)



^{19}F NMR (471 MHz, $CDCl_3$, 24 °C)

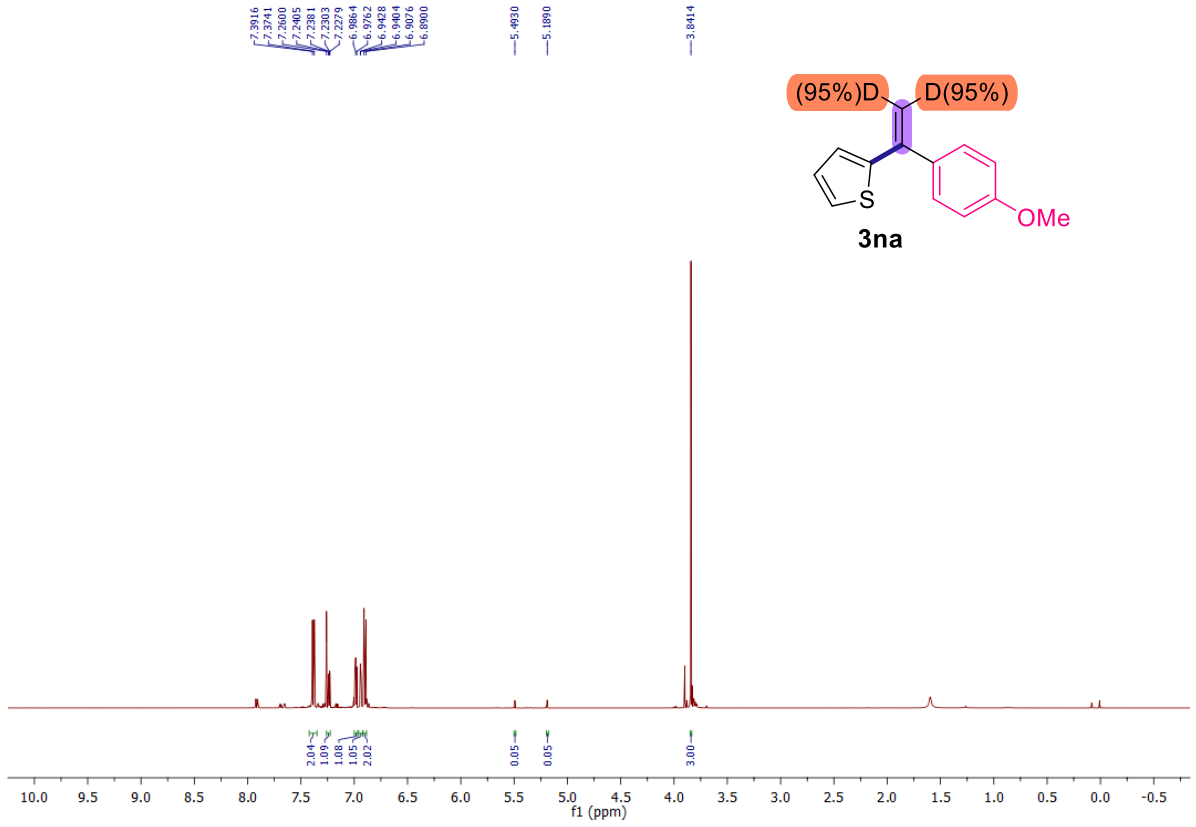


^{2}H NMR (94 MHz, $CDCl_3$, 24 °C)

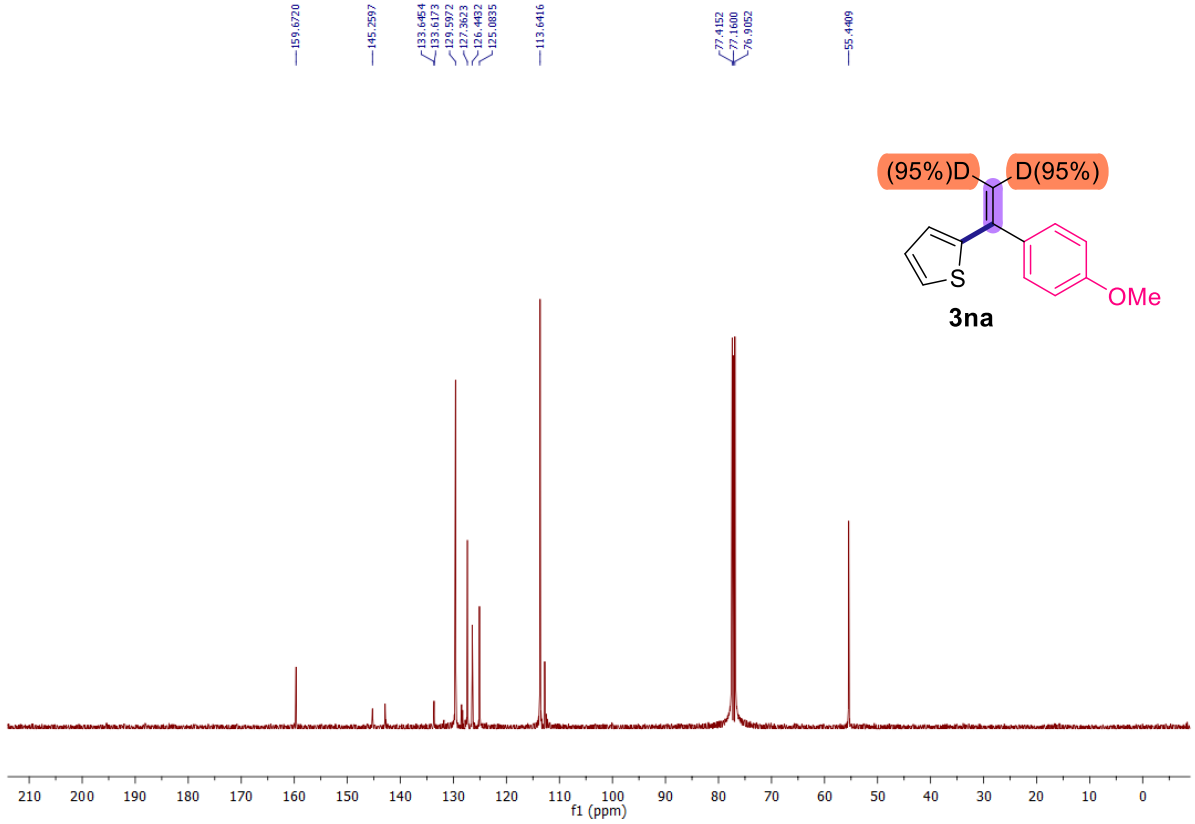


2-(1-(4-Methoxyphenyl)vinyl-2,2-d2)thiophene (**3na**)

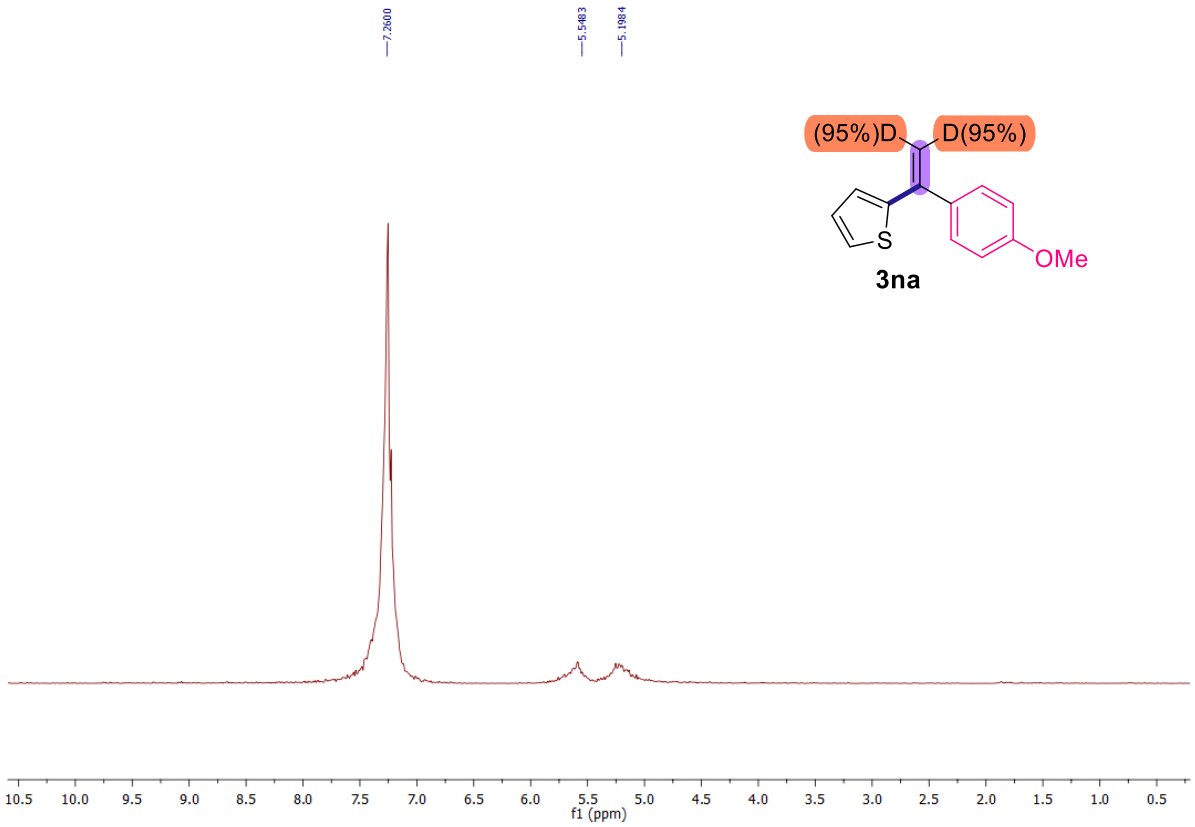
^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)



$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 24 °C)

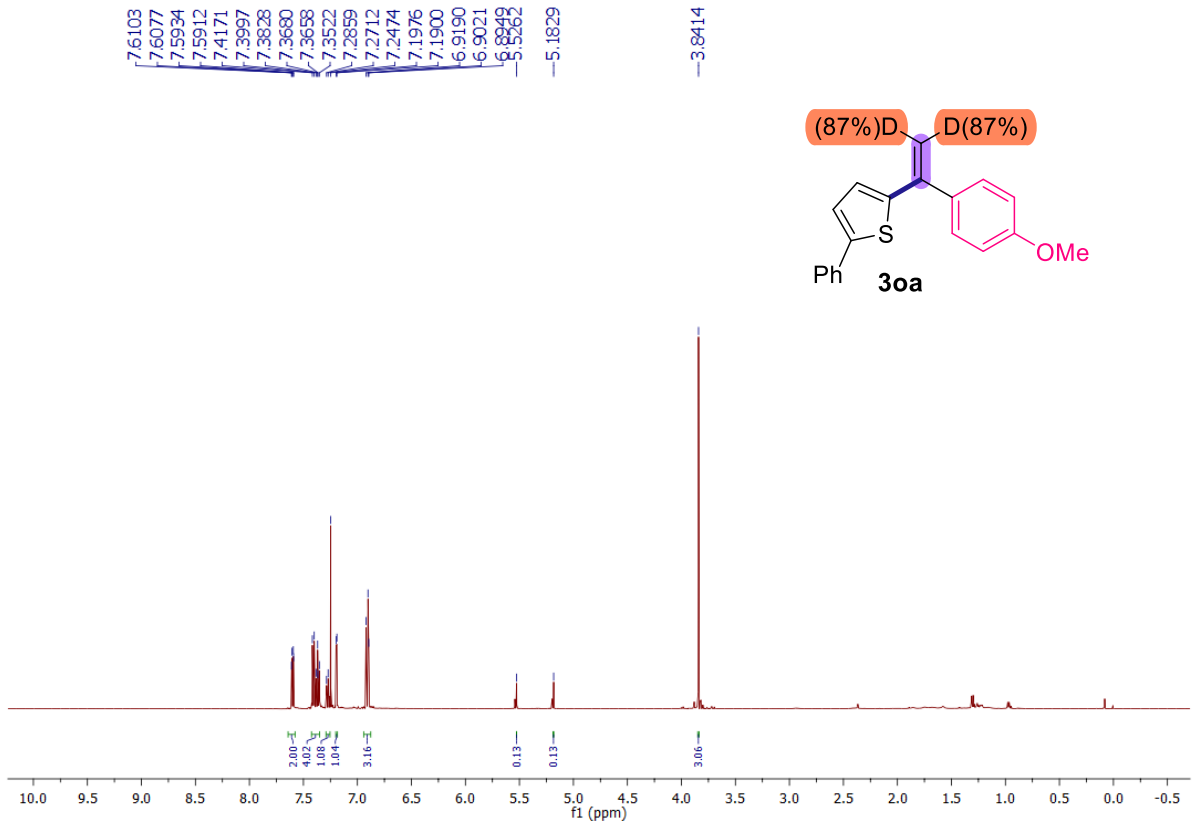


^{2}H NMR (77 MHz, $CDCl_3$, 24 °C)

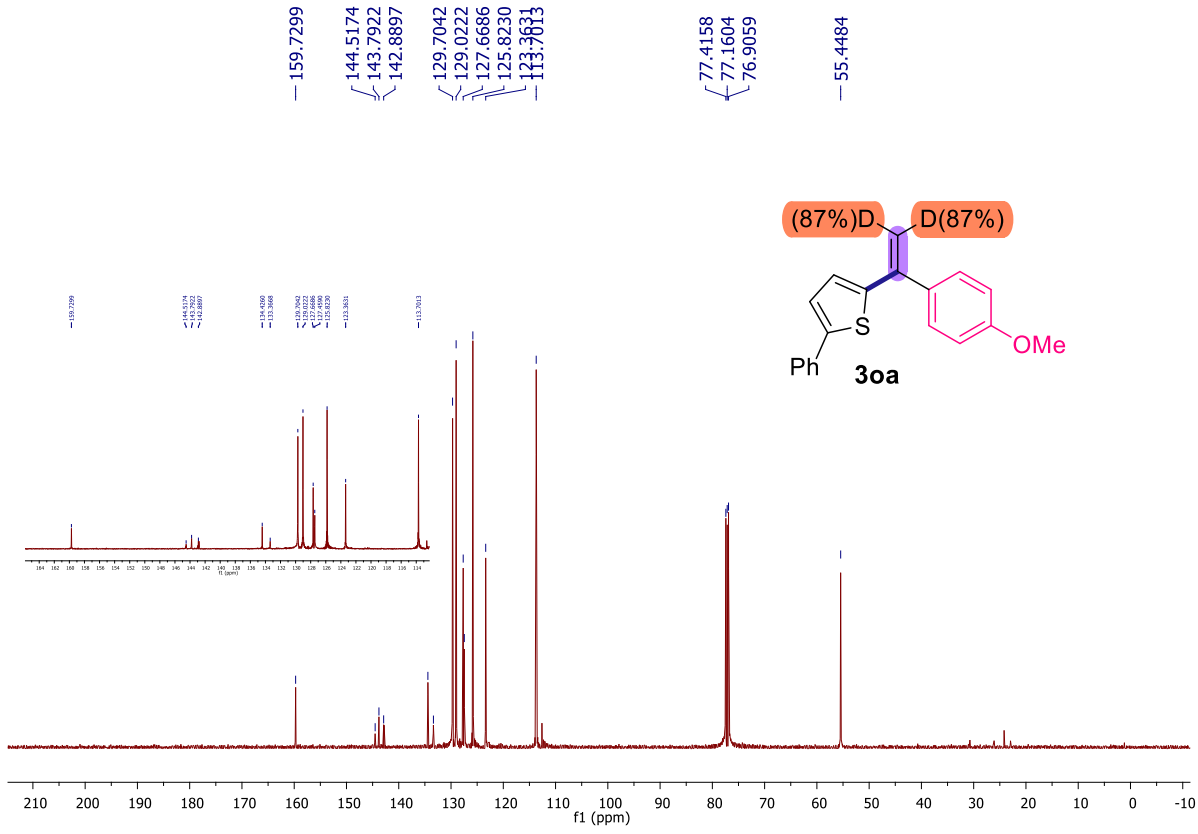


2-(1-(4-Methoxyphenyl)vinyl-2,2-d2)-5-phenylthiophene (**3oa**)

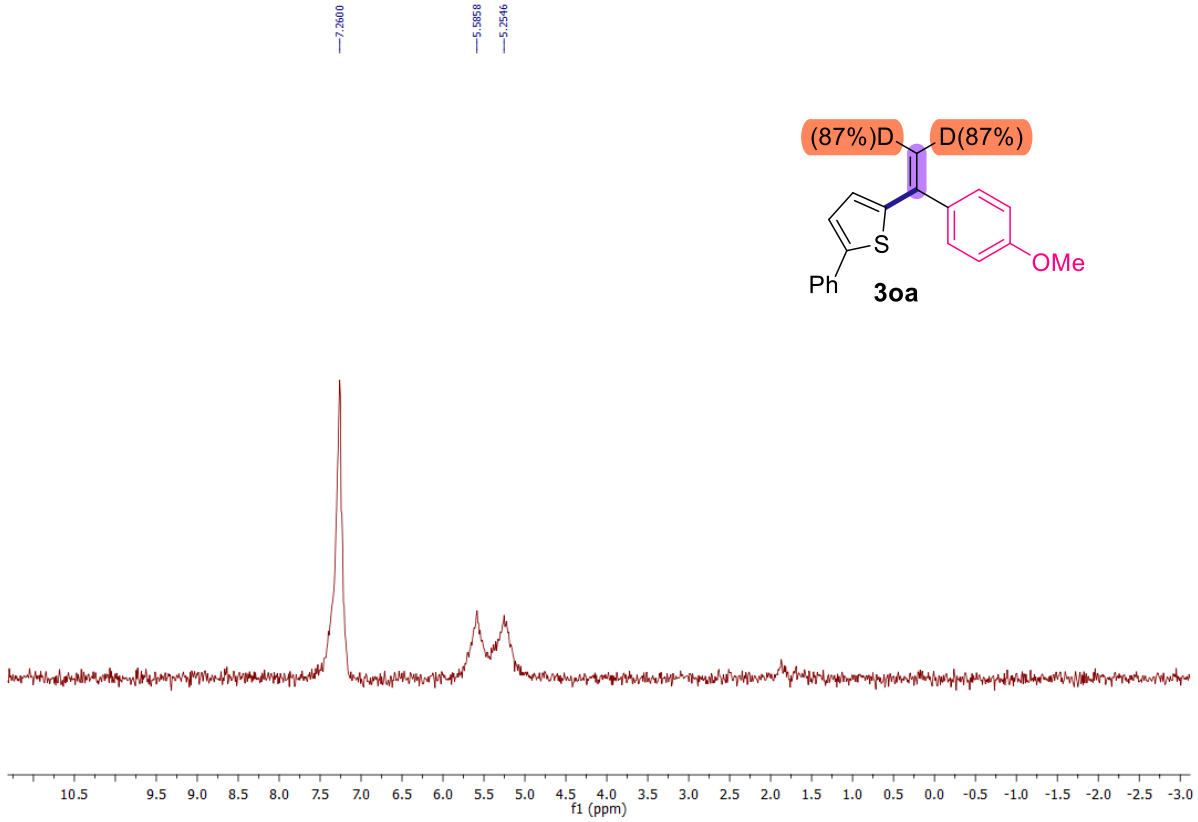
^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)



^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 24 °C)

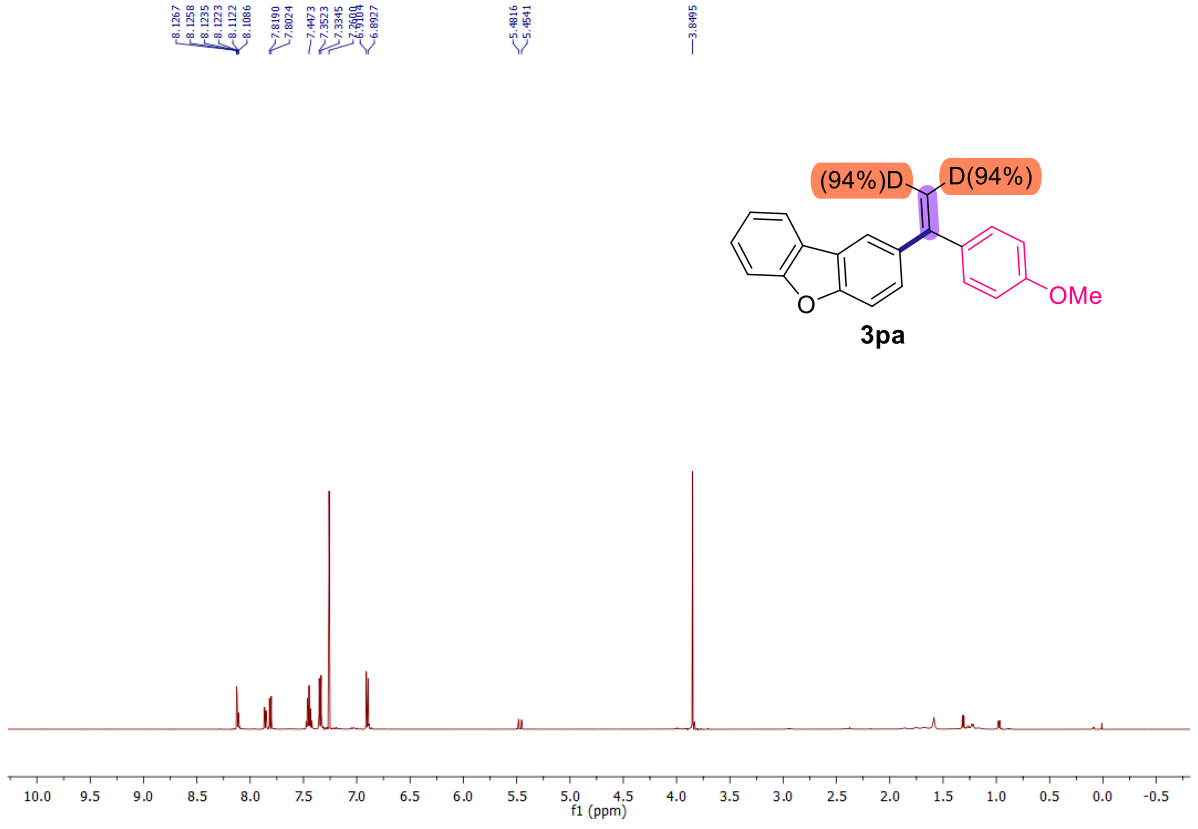


^{2}H NMR (77 MHz, $CDCl_3$, 24 °C)

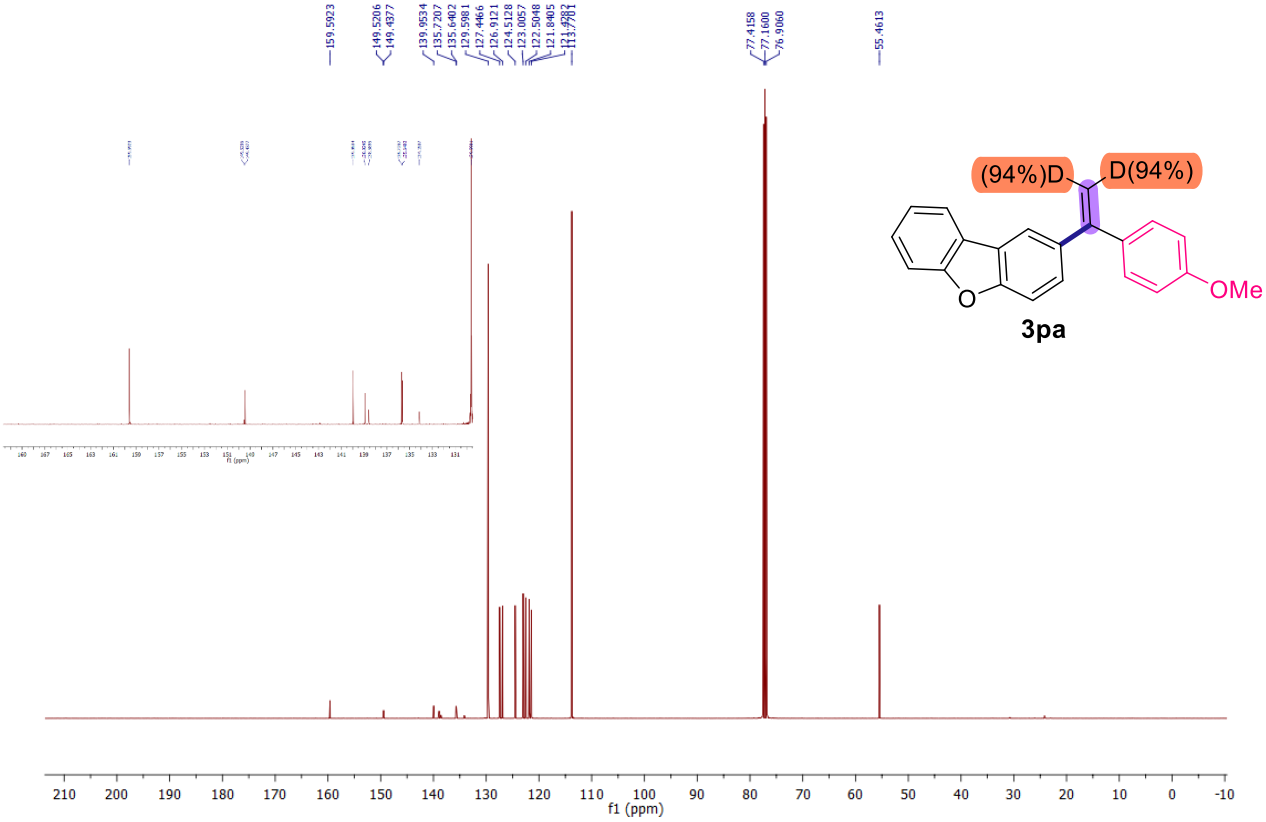


2-(1-(4-Methoxyphenyl)vinyl-2,2-d2)dibenzo[b,d]furan (**3pa**)

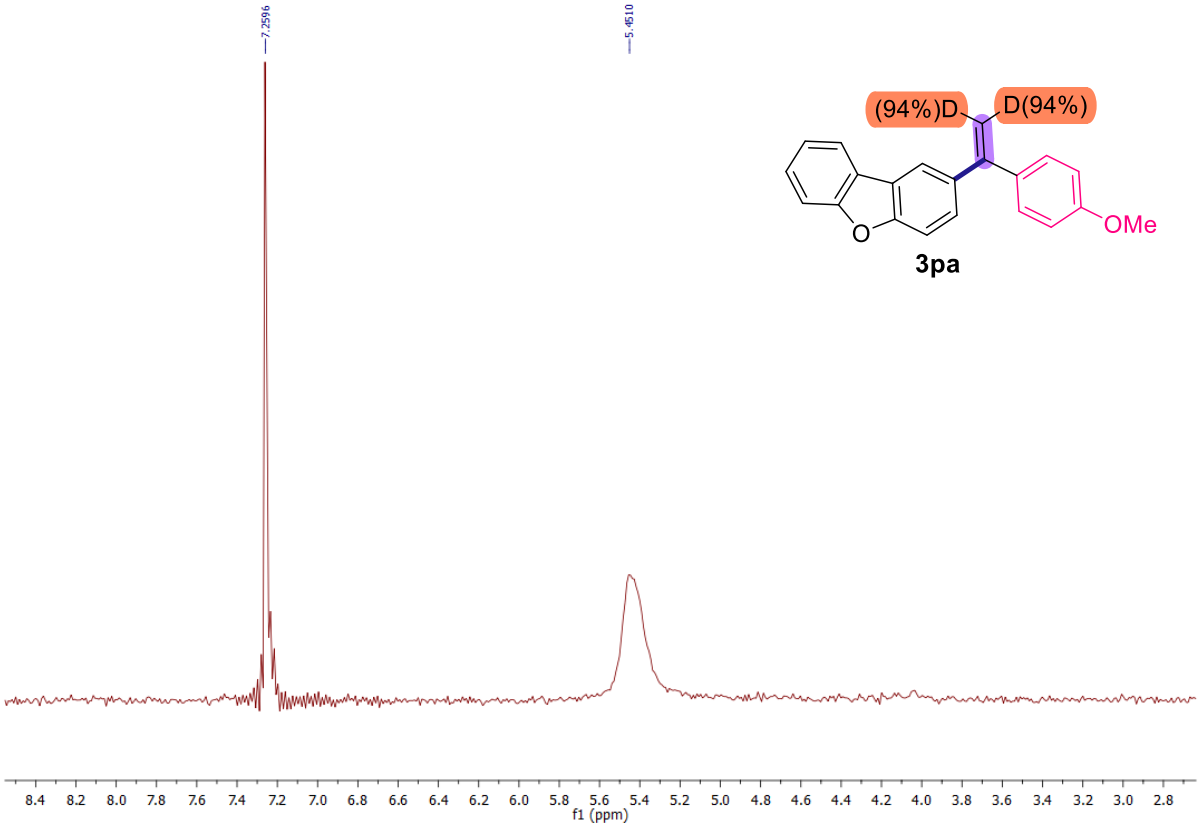
^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)



$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 24 °C)

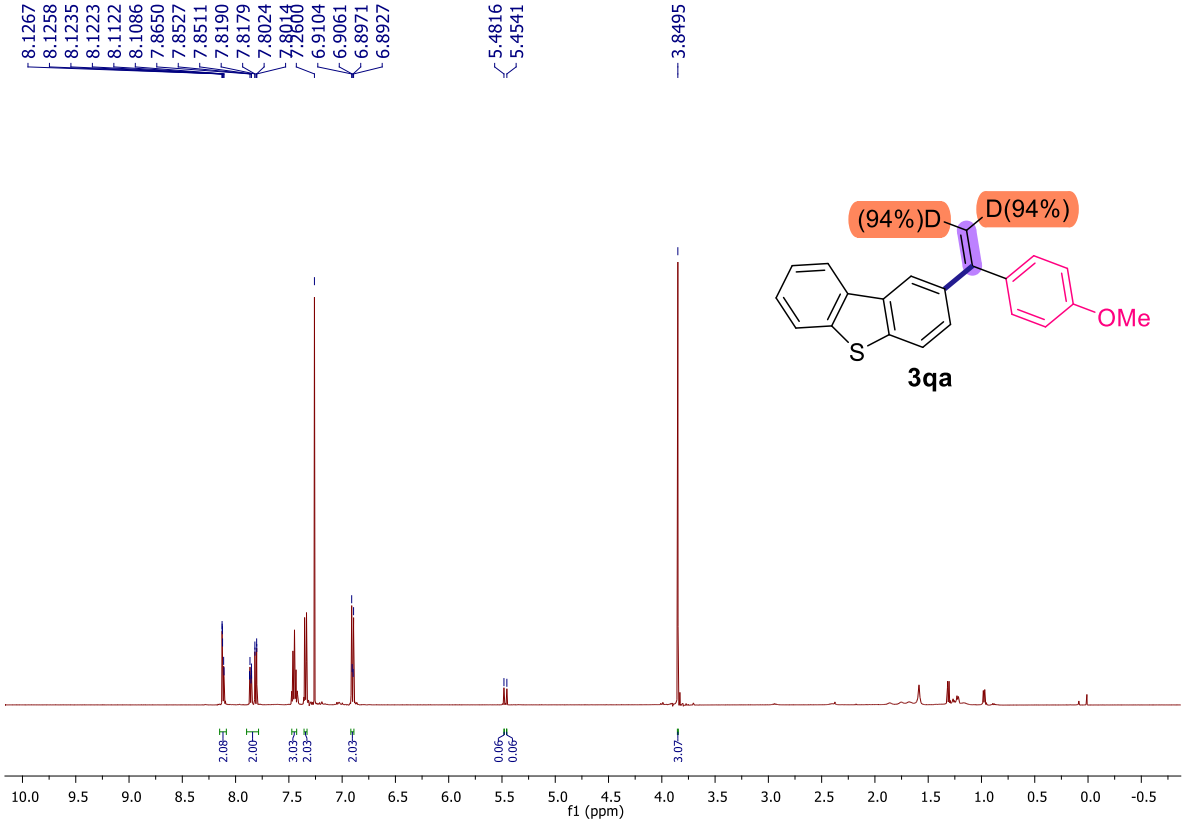


^{2}H NMR (94 MHz, $CHCl_3$, 24 °C)

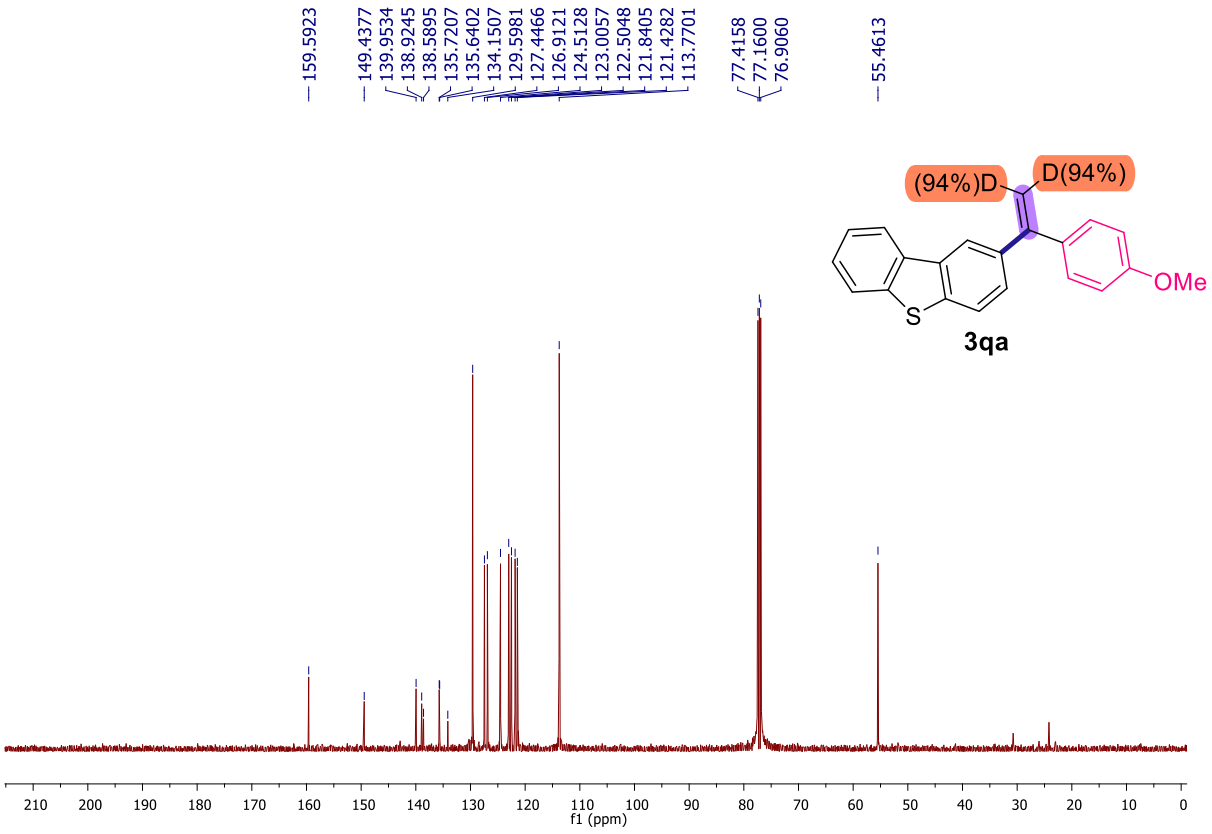


2-(1-(4-Methoxyphenyl)vinyl-2,2-d2)dibenzo[b,d]thiophene (**3qa**)

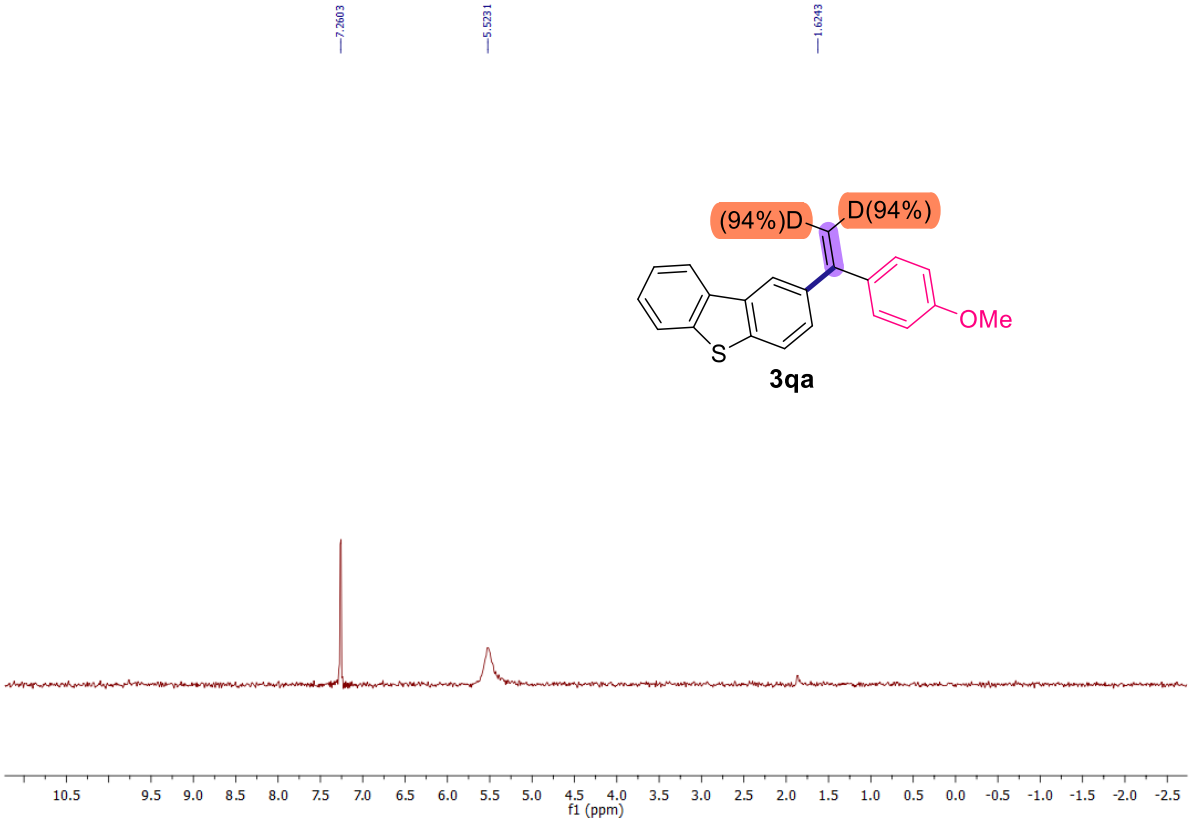
^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)



^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 24 °C)

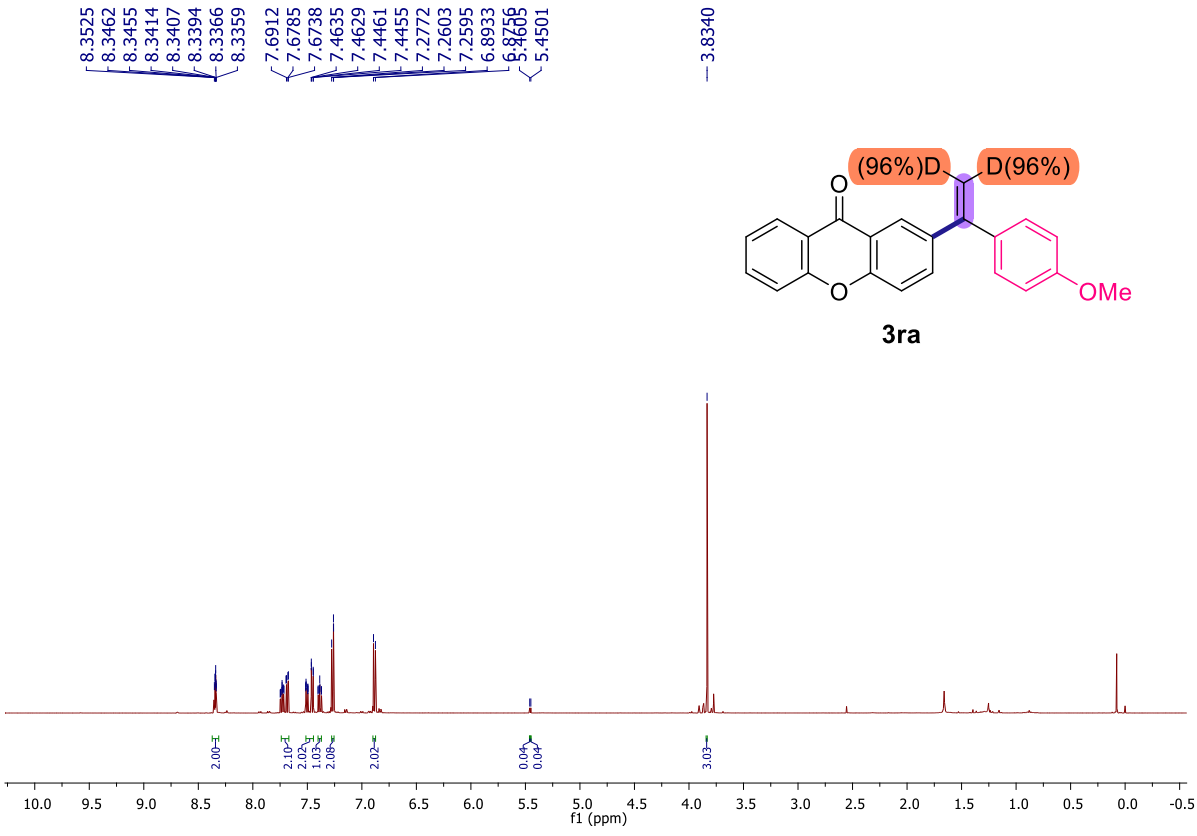


^{2}H NMR (94 MHz, $CHCl_3$, 24 °C)

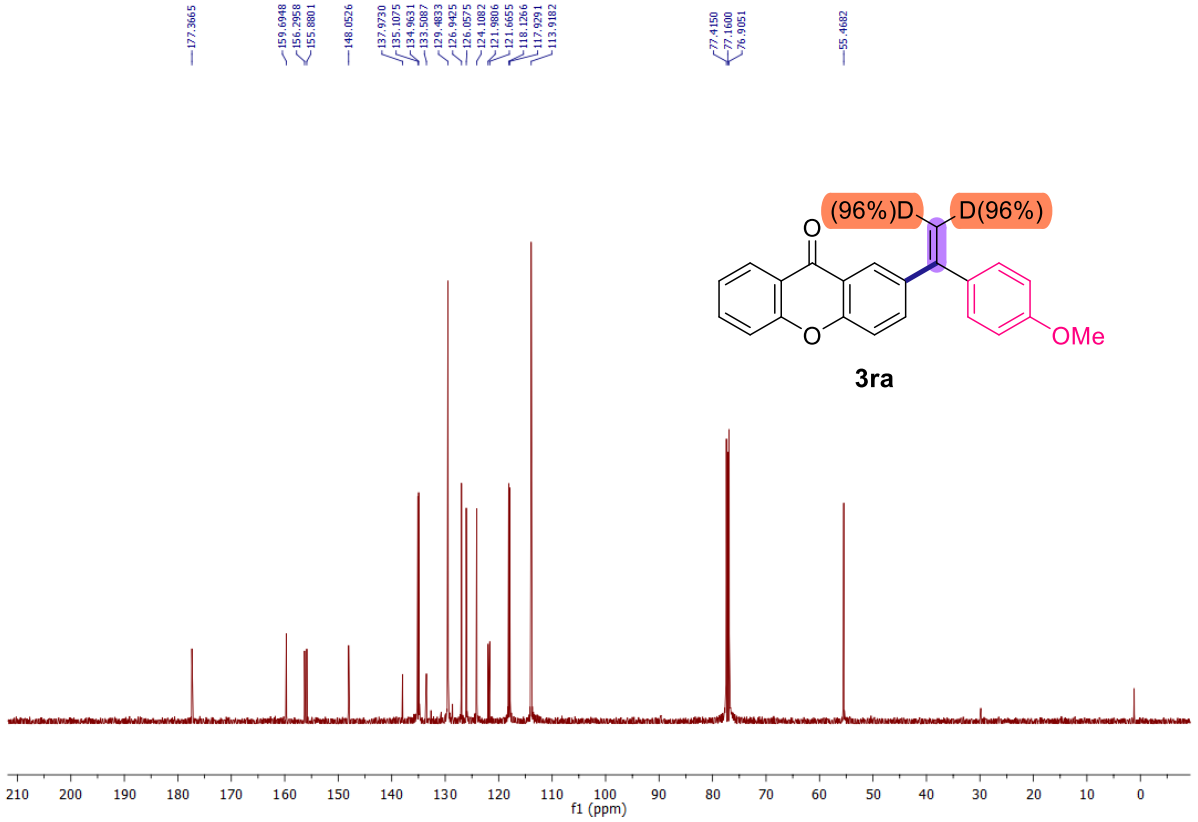


2-(1-(4-Methoxyphenyl)vinyl-2,2-d2)-9H-xanthen-9-one (**3ra**)

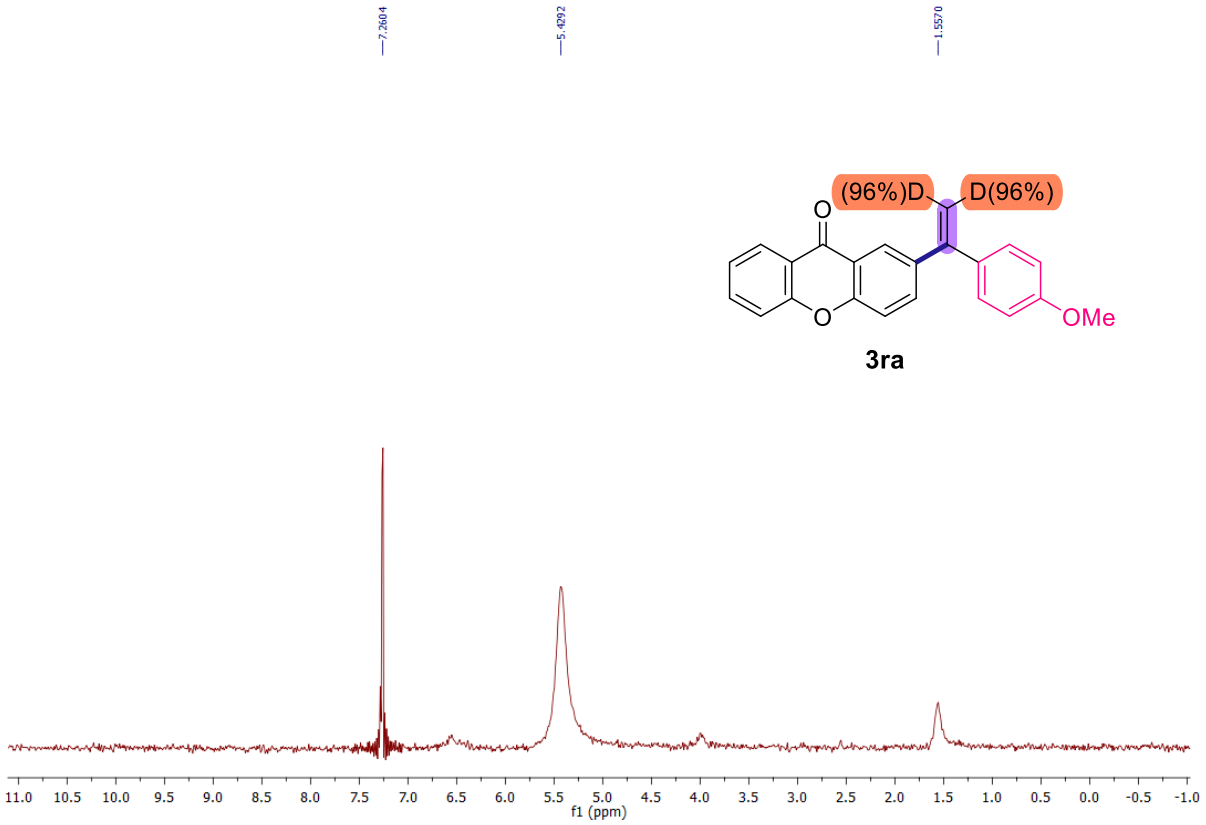
^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)



$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 24 °C)

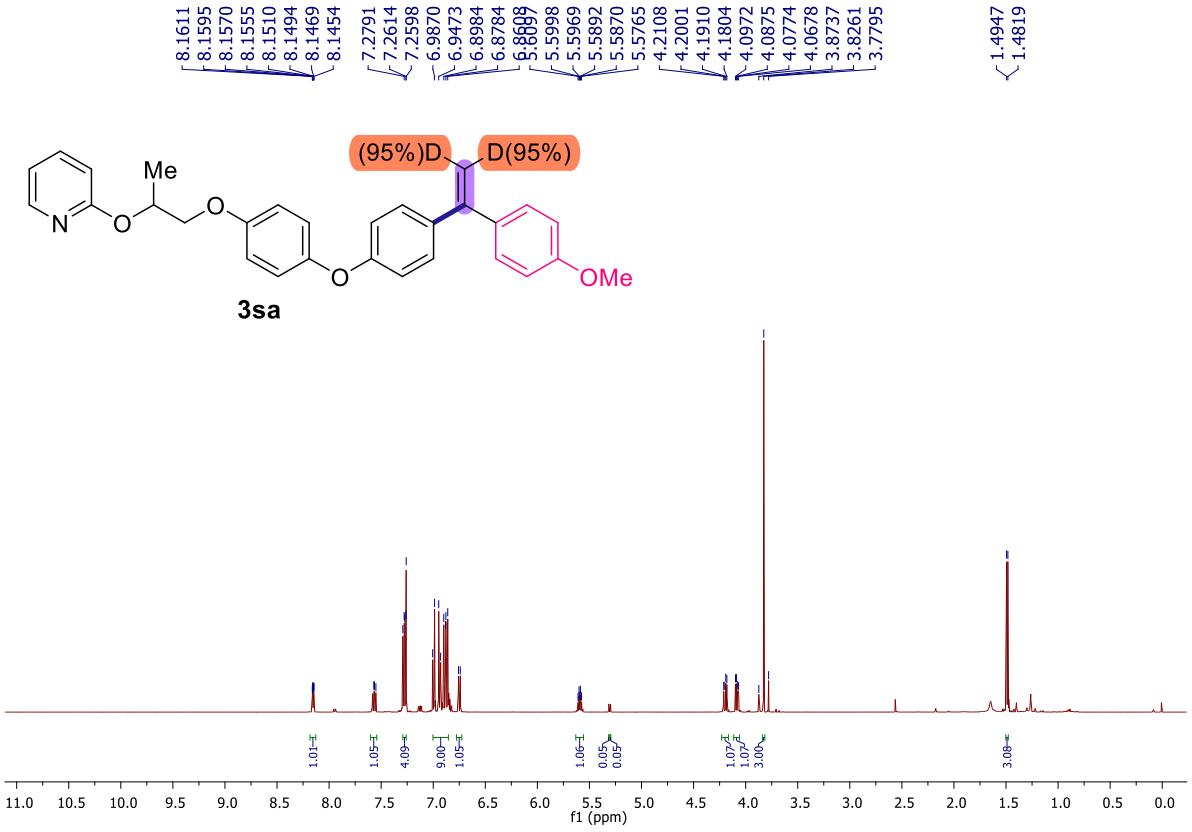


^{2}H NMR (77 MHz, $CDCl_3$, 24 °C)

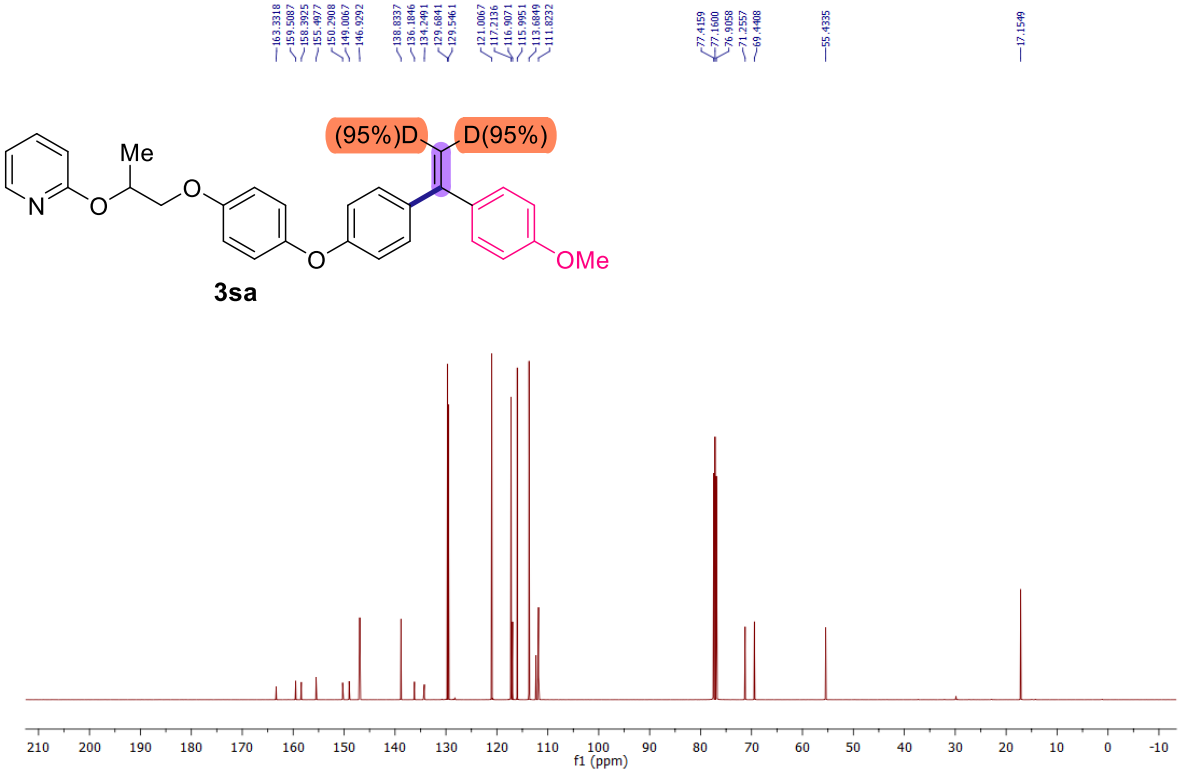


2-((1-(4-(4-(1-(4-Methoxyphenyl)vinyl-2,2-d2)phenoxy)phenoxy)propan-2-yl)oxy)pyridine (**3sa**)

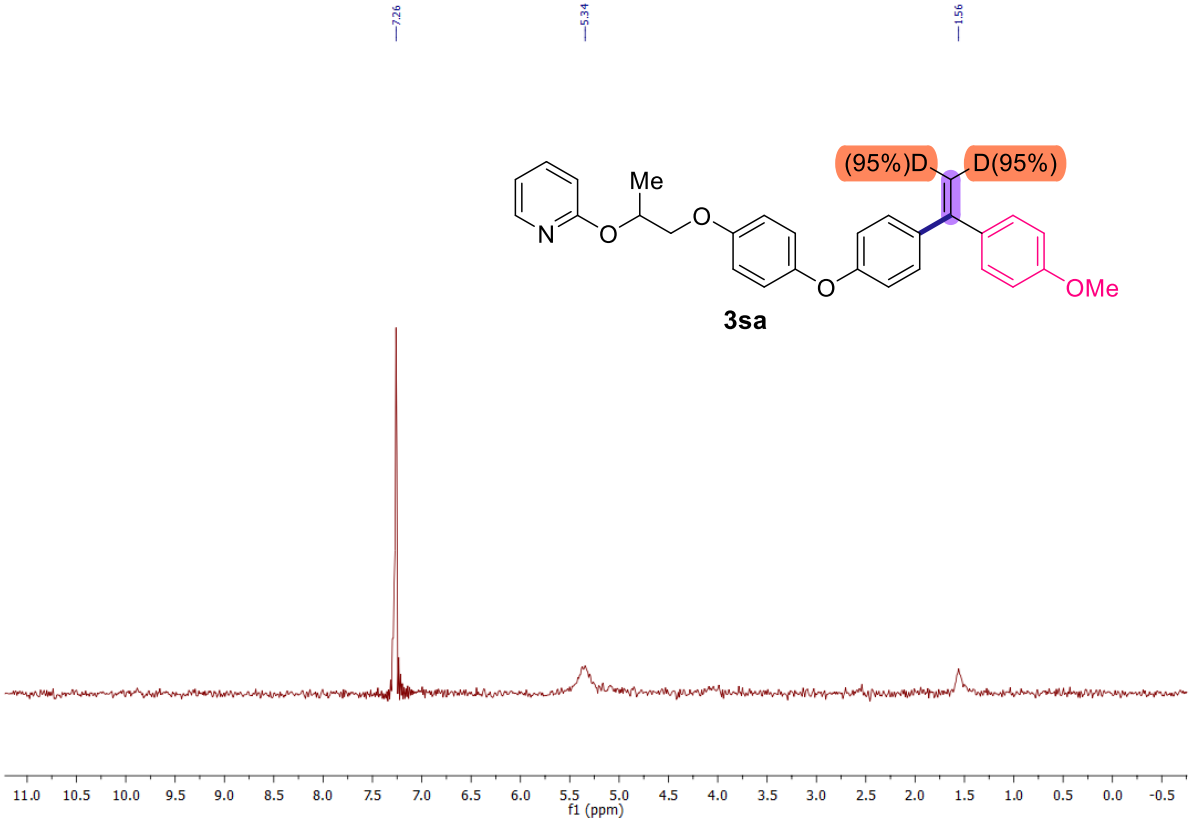
^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)



^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 24 °C)

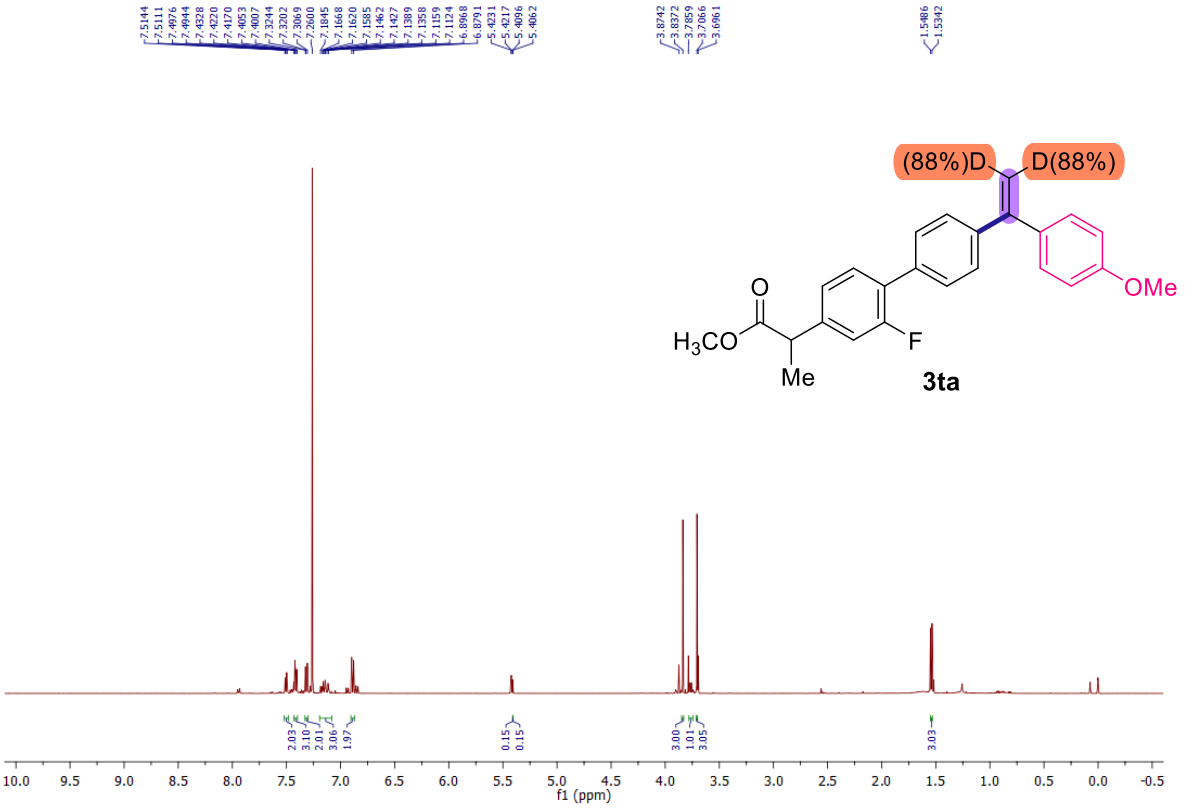


^{2}H NMR (77 MHz, $CDCl_3$, 24 °C)

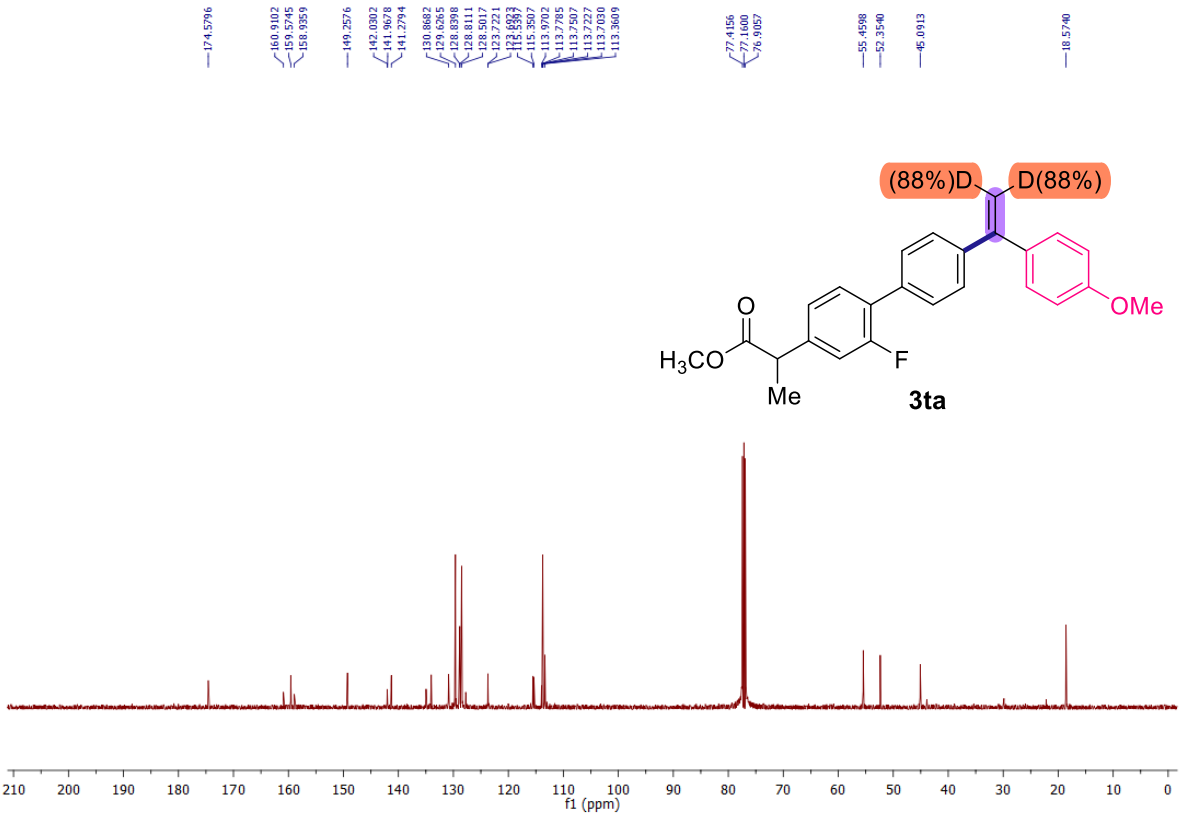


Methyl 2-(2-fluoro-4'-(1-(4-methoxyphenyl)vinyl-2,2-d2)-[1,1'-biphenyl]-4-yl)propanoate (**3ta**)

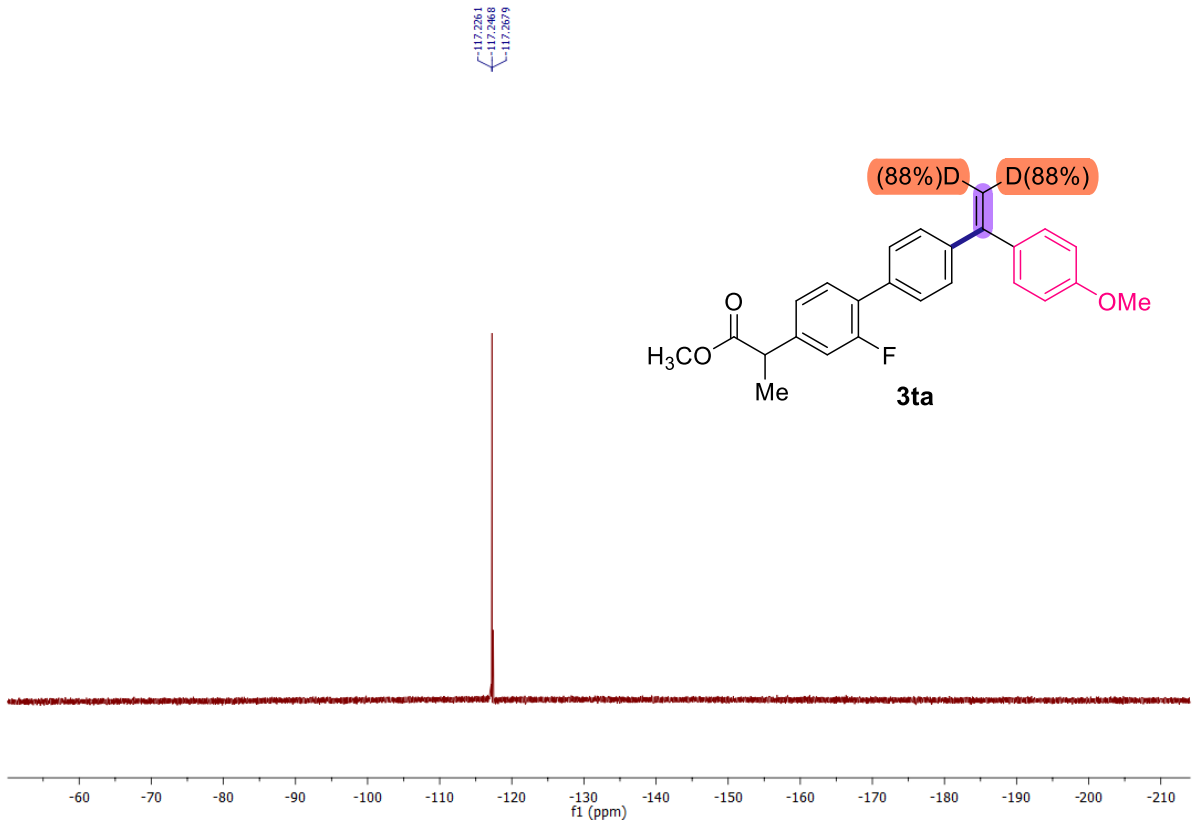
^{1}H NMR (500 MHz, CDCl3, 24 °C)



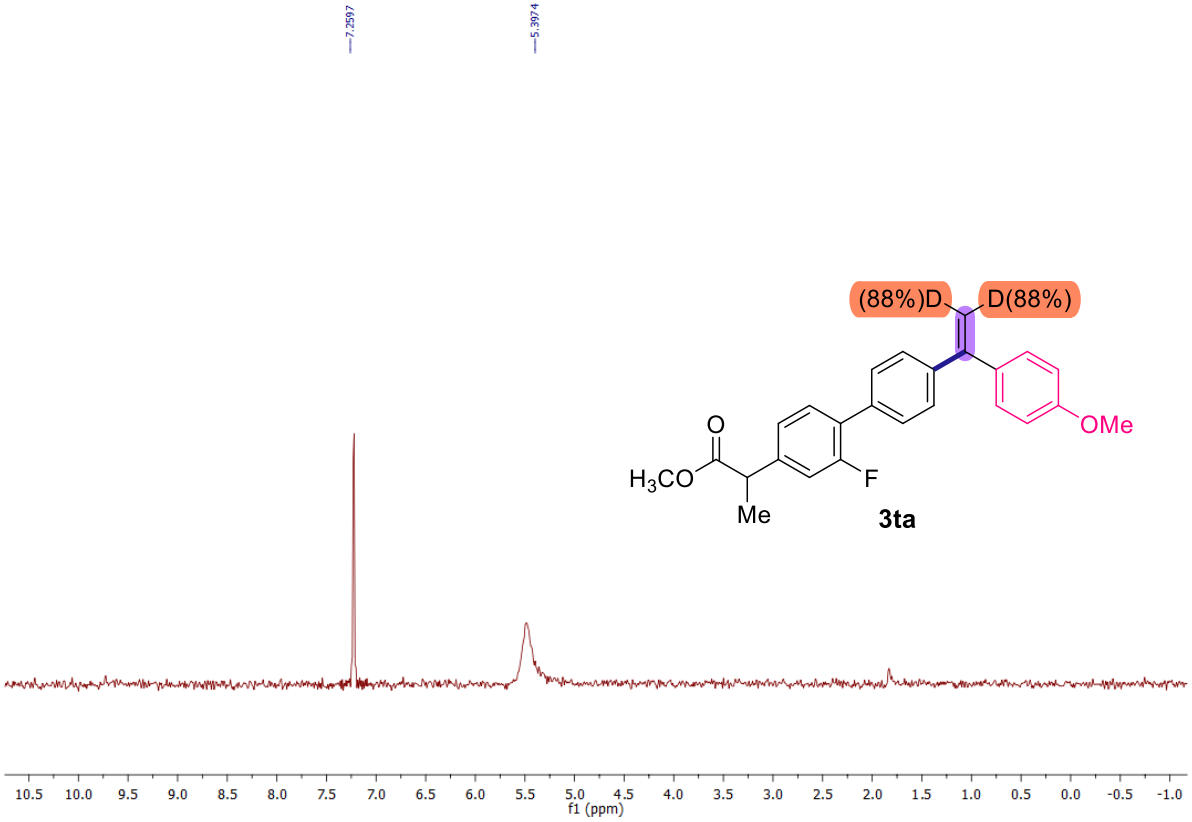
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 24 °C)



^{19}F NMR(471 MHz, $CDCl_3$)

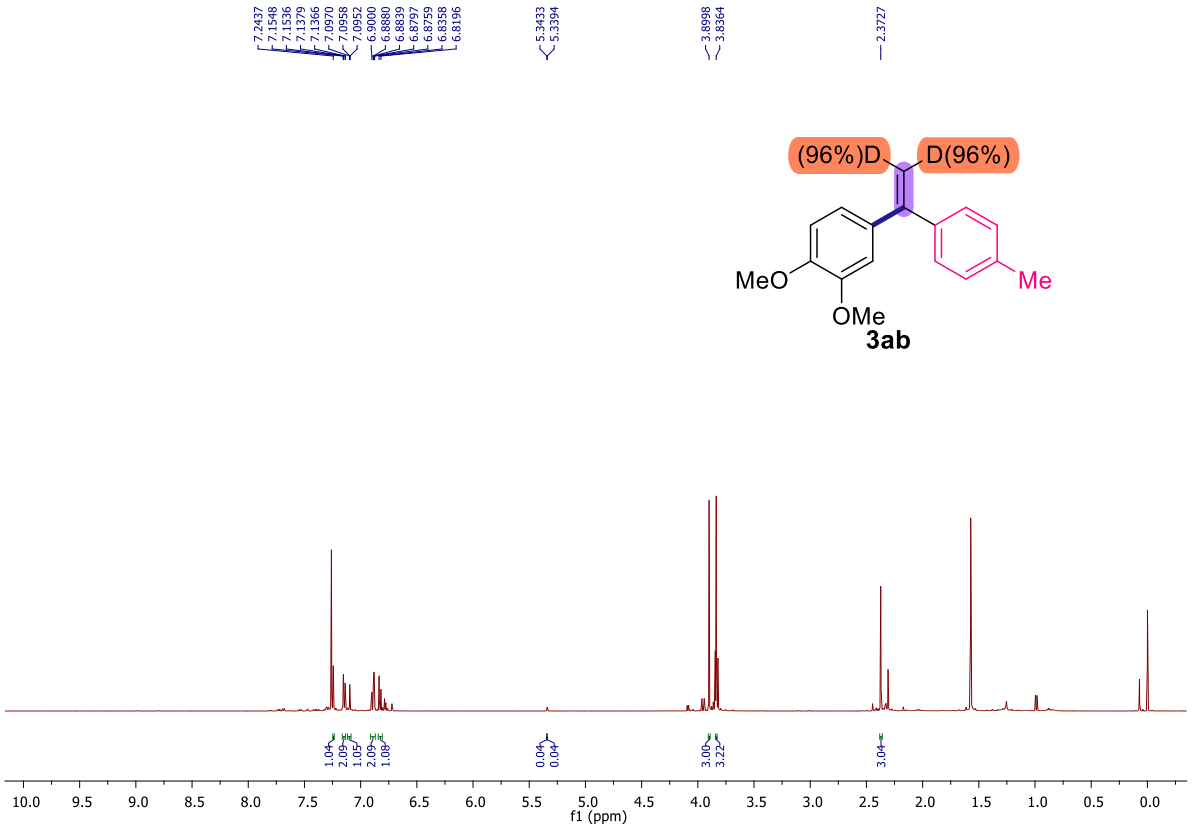


^{2}H NMR (77 MHz, $CHCl_3$, 24 °C)

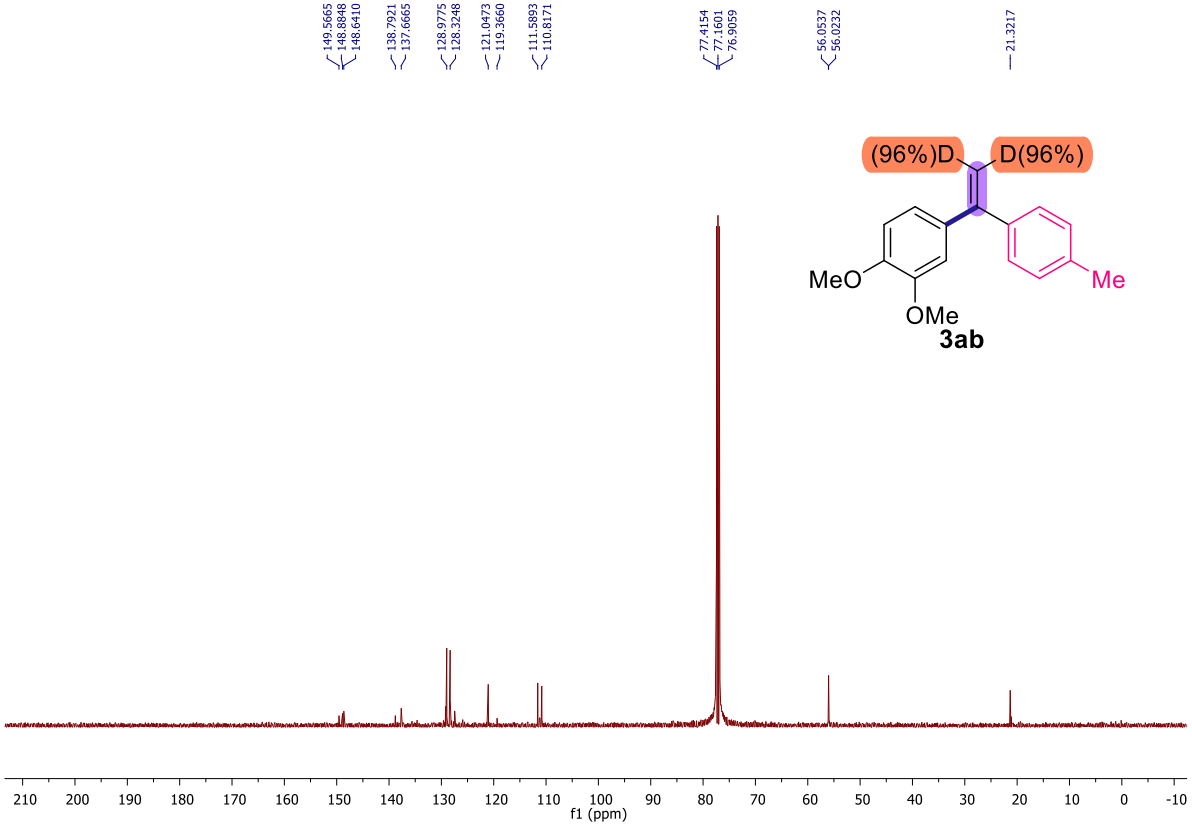


1,2-Dimethoxy-4-(1-(p-tolyl)vinyl-2,2-d2)benzene (**3ab**)

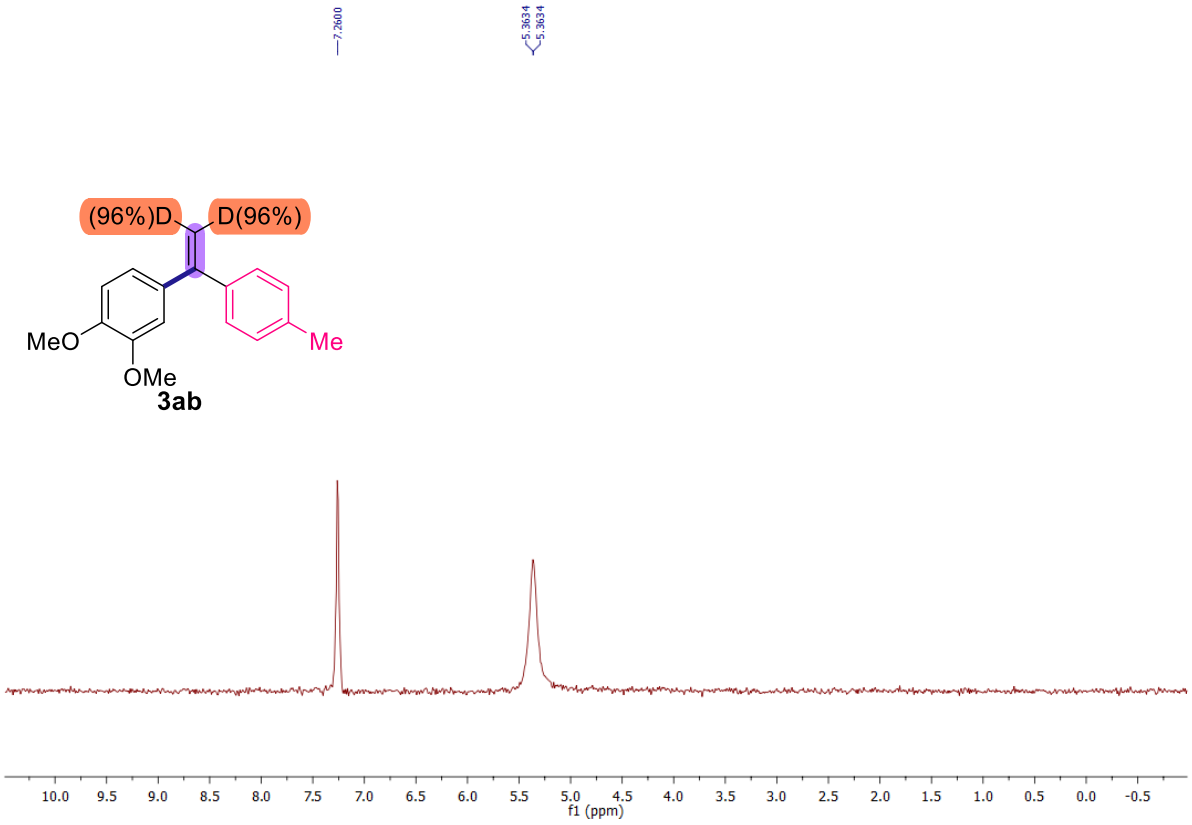
^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)



$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 24 °C)

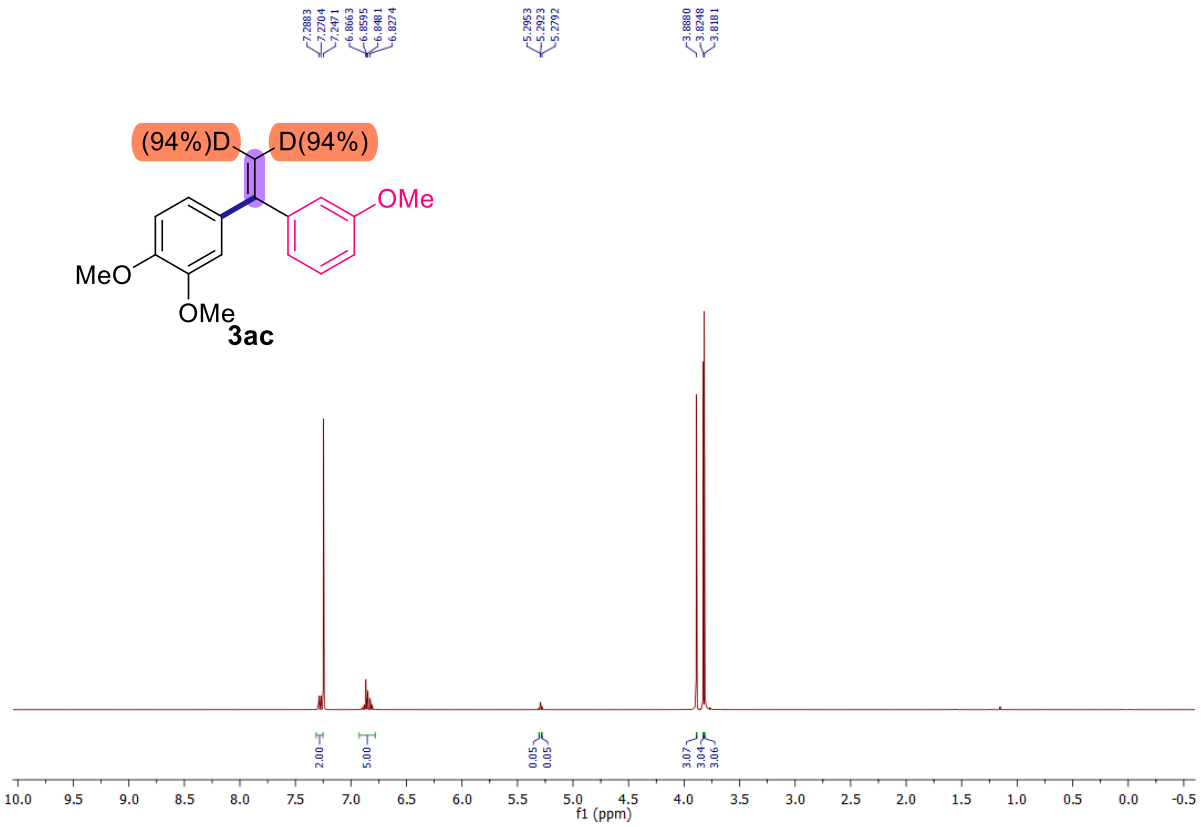


^{2}H NMR (77 MHz, $CHCl_3$, 24 °C)

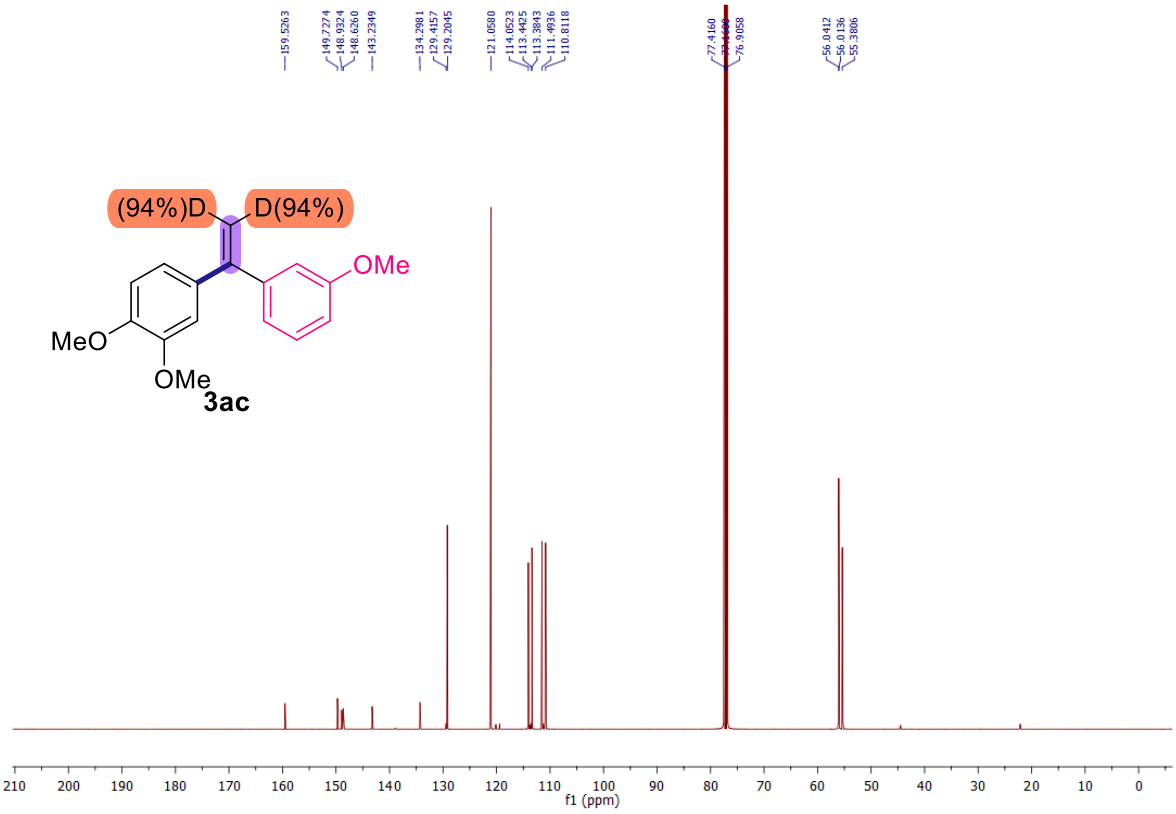


1,2-Dimethoxy-4-(1-(3-methoxyphenyl)vinyl2,2-d2)benzene (**3ac**)

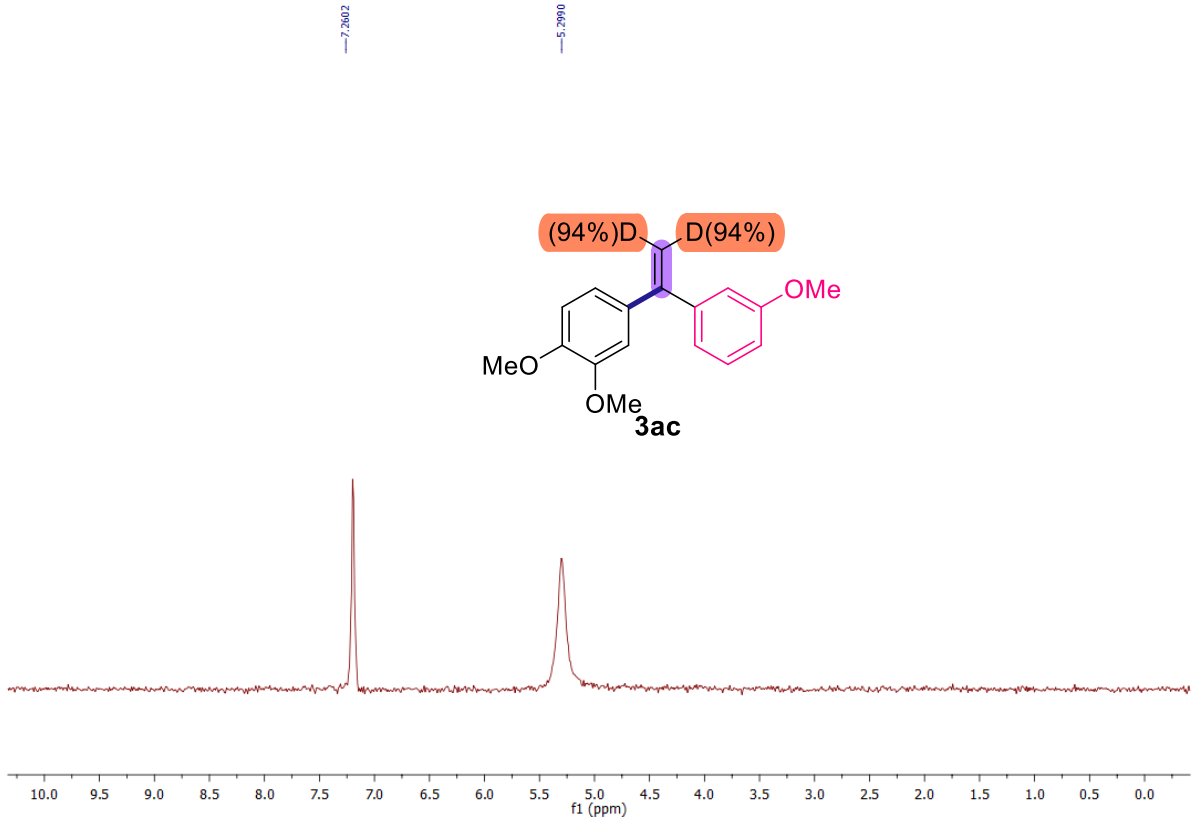
^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)



^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 24 °C)

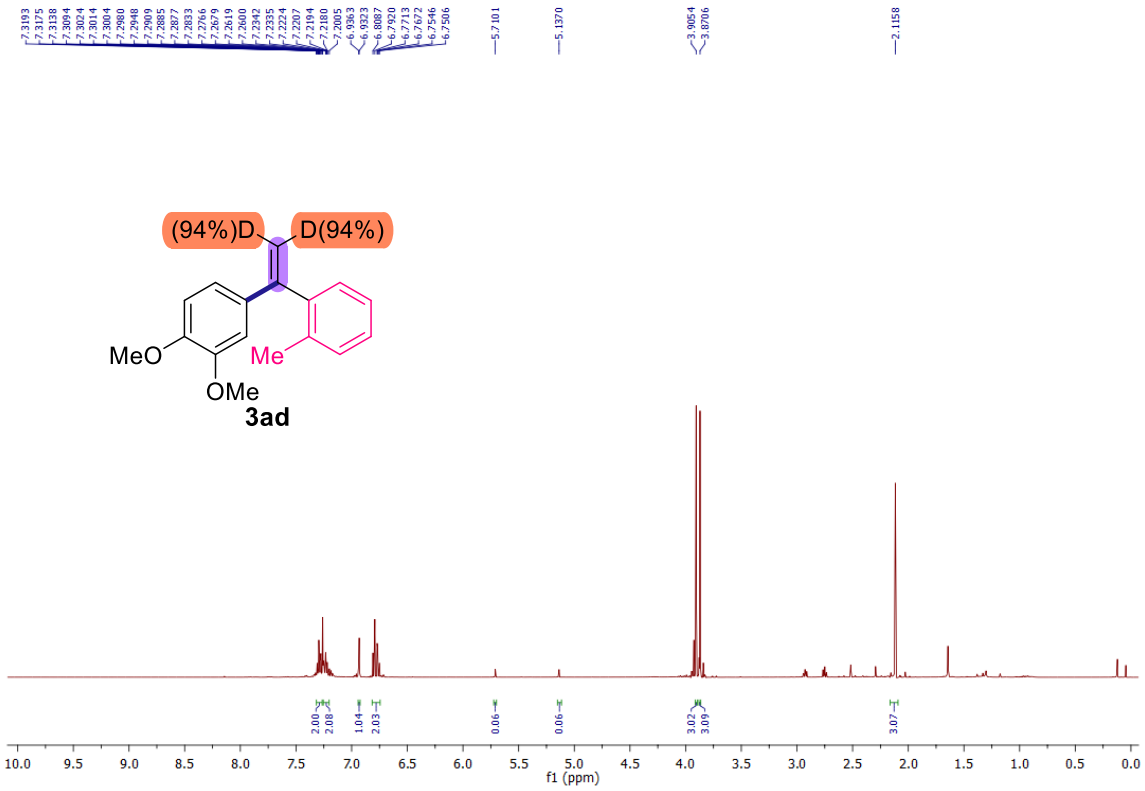


^{2}H NMR (77 MHz, $CHCl_3$, 24 °C)

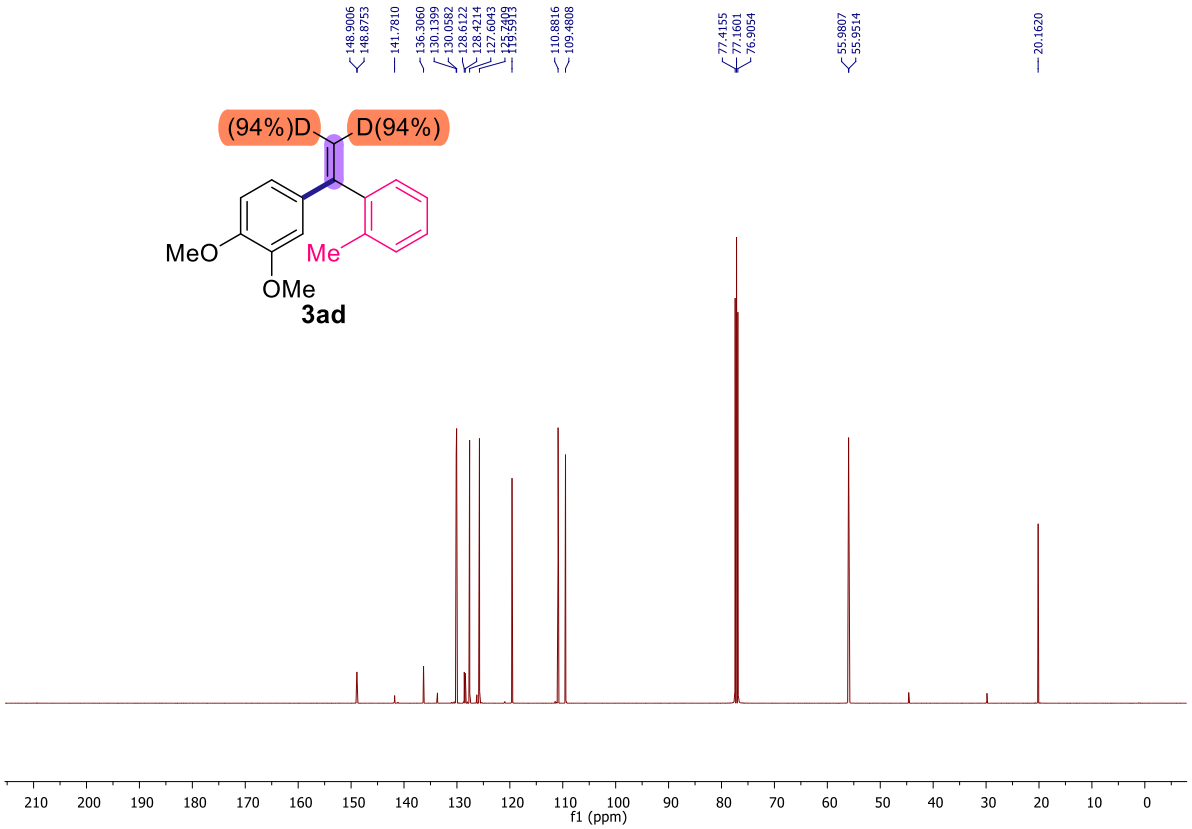


1,2-Dimethoxy-4-(1-(o-tolyl)vinyl-2,2-d2)benzene (**3ad**)

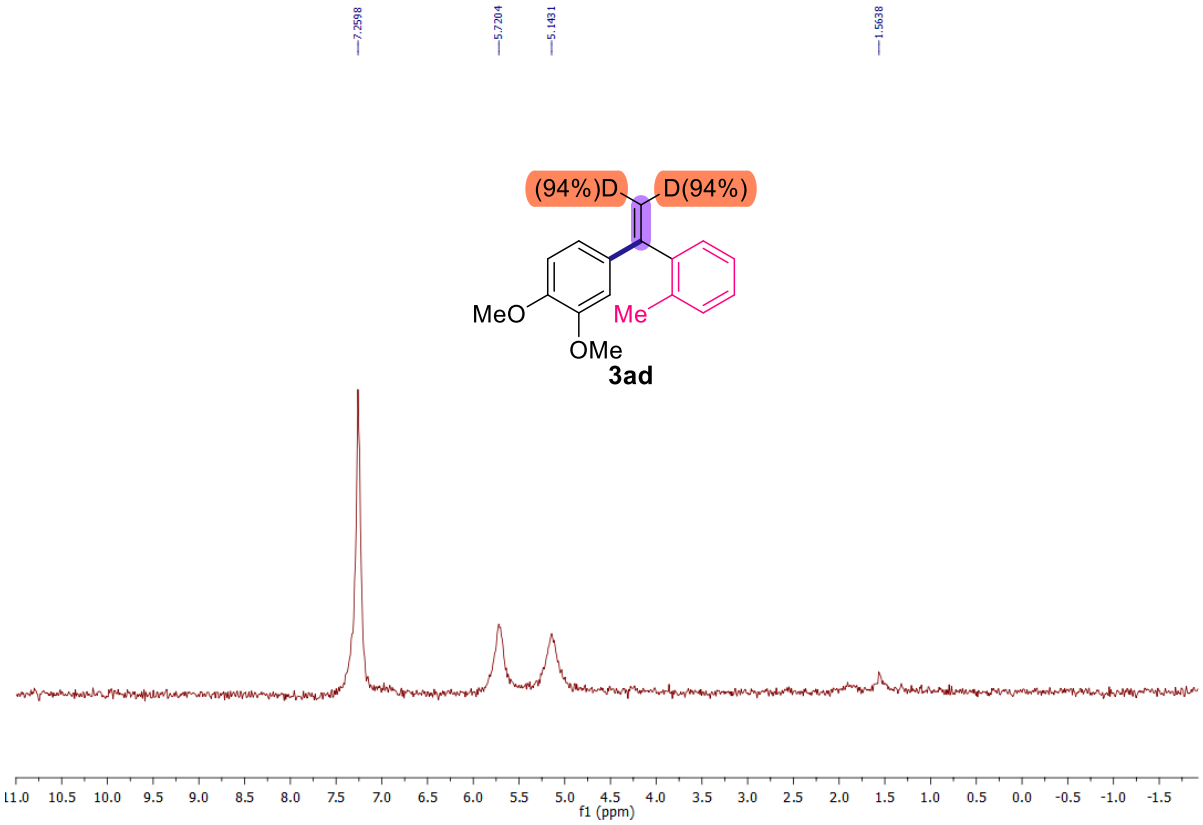
^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)



$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 24 °C)

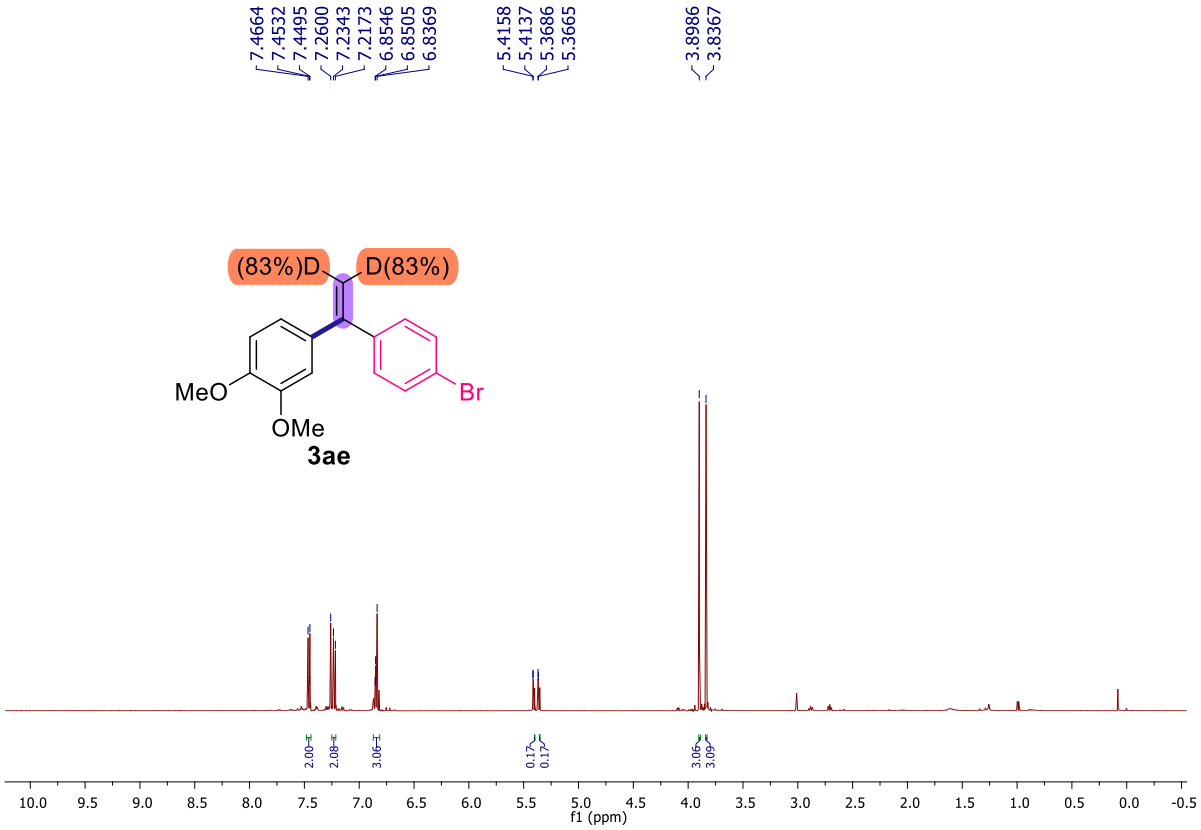


^{2}H NMR (77 MHz, $CHCl_3$, 24 °C)

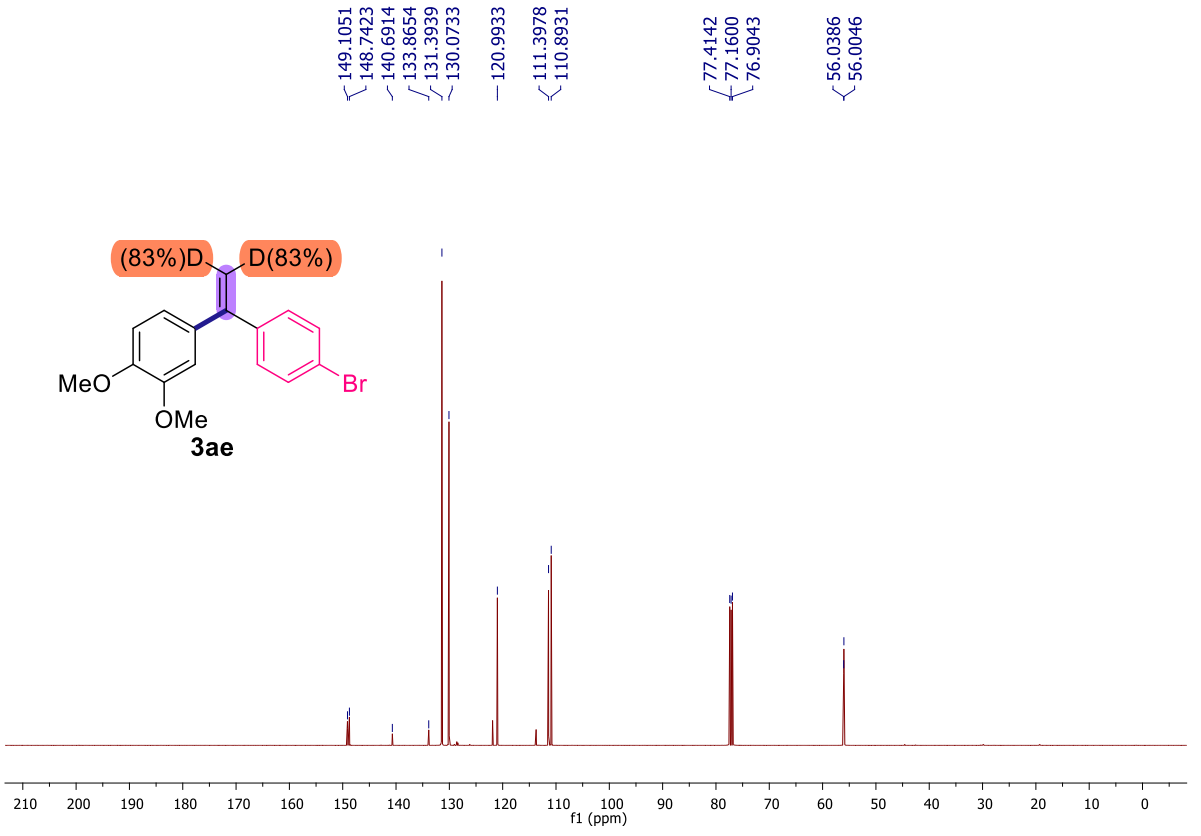


4-(1-(4-Bromophenyl)vinyl-2,2-d2)-1,2-dimethoxybenzene **(3ae)**

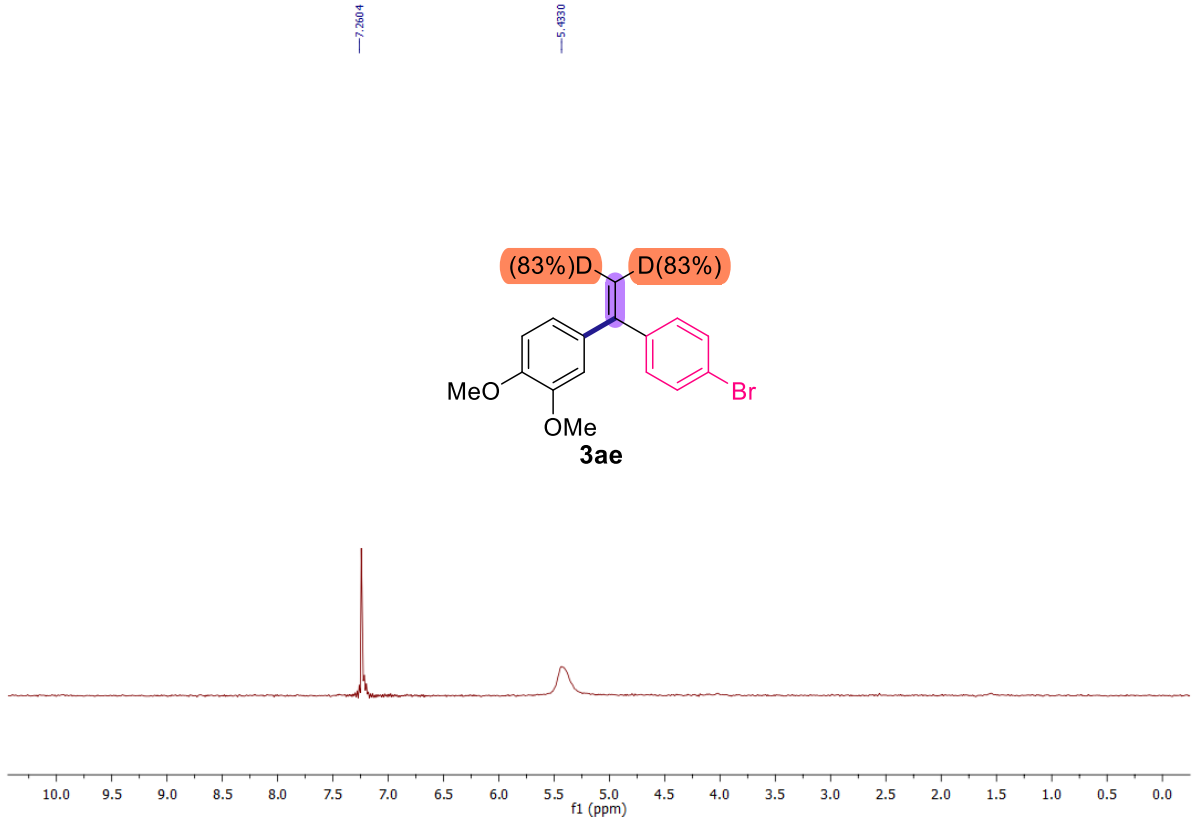
^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)



^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 24 °C)

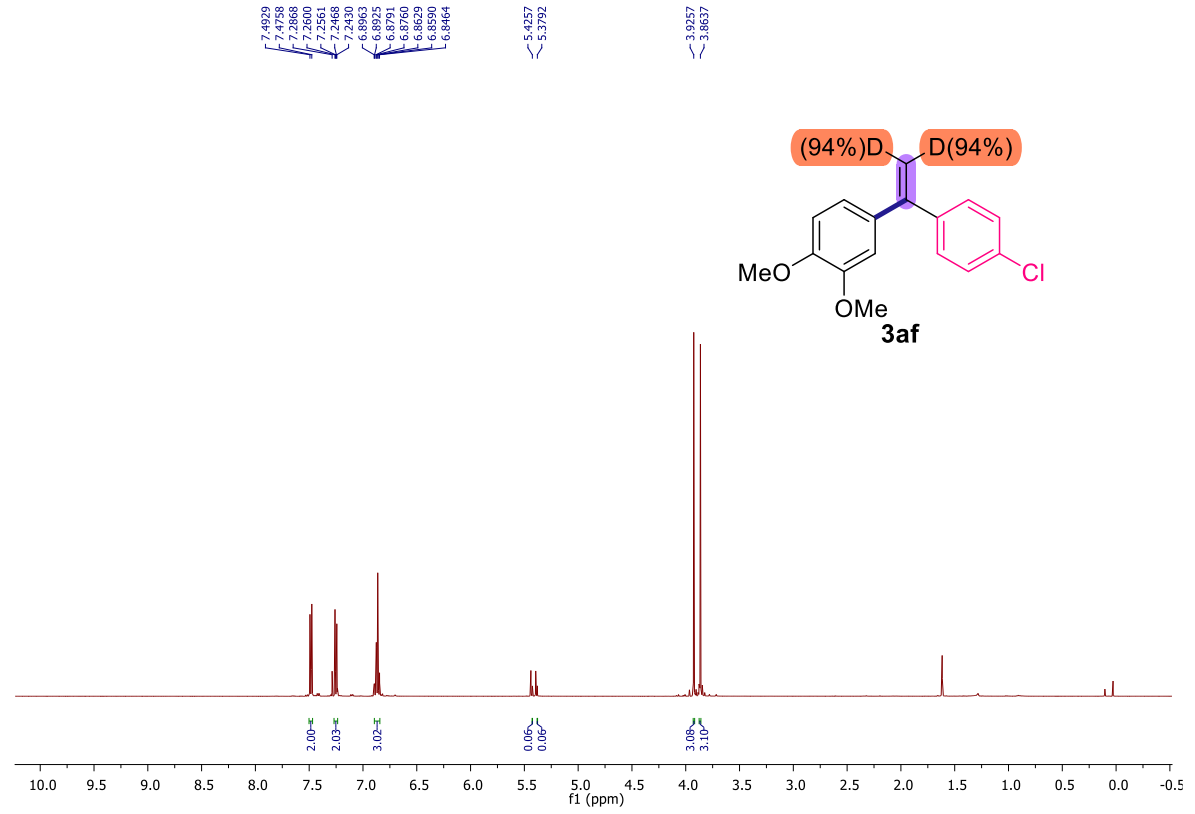


^{2}H NMR (77 MHz, $CDCl_3$, 24 °C)

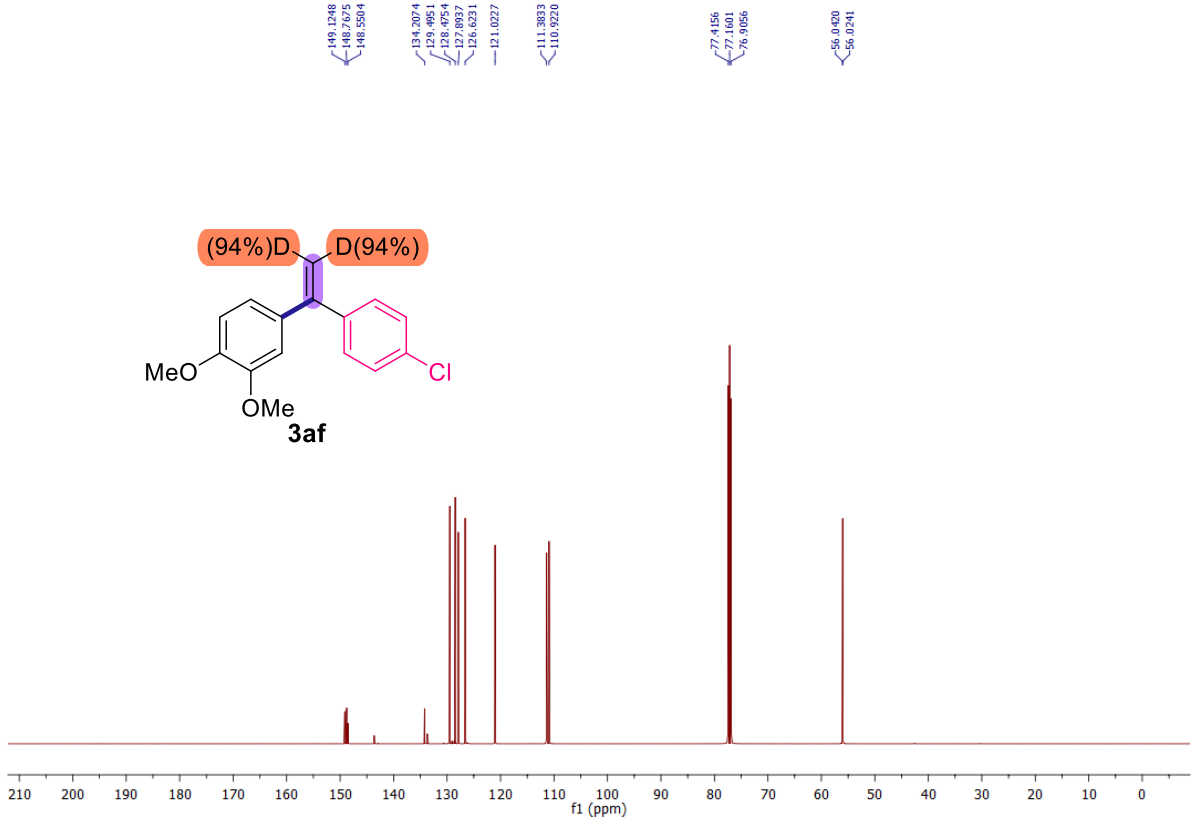


4-(1-(4-Chlorophenyl)vinyl-2,2-d2)-1,2-dimethoxybenzene (**3af**)

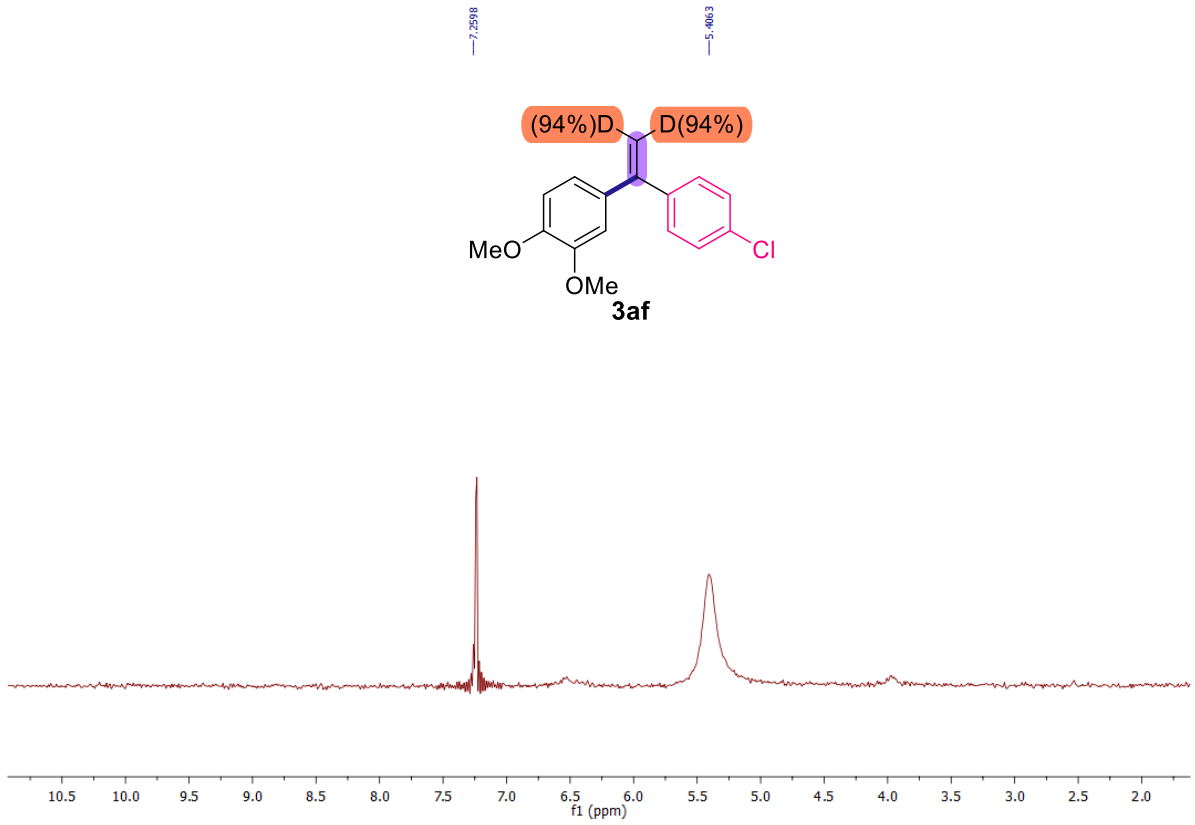
^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)



$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 24 °C)

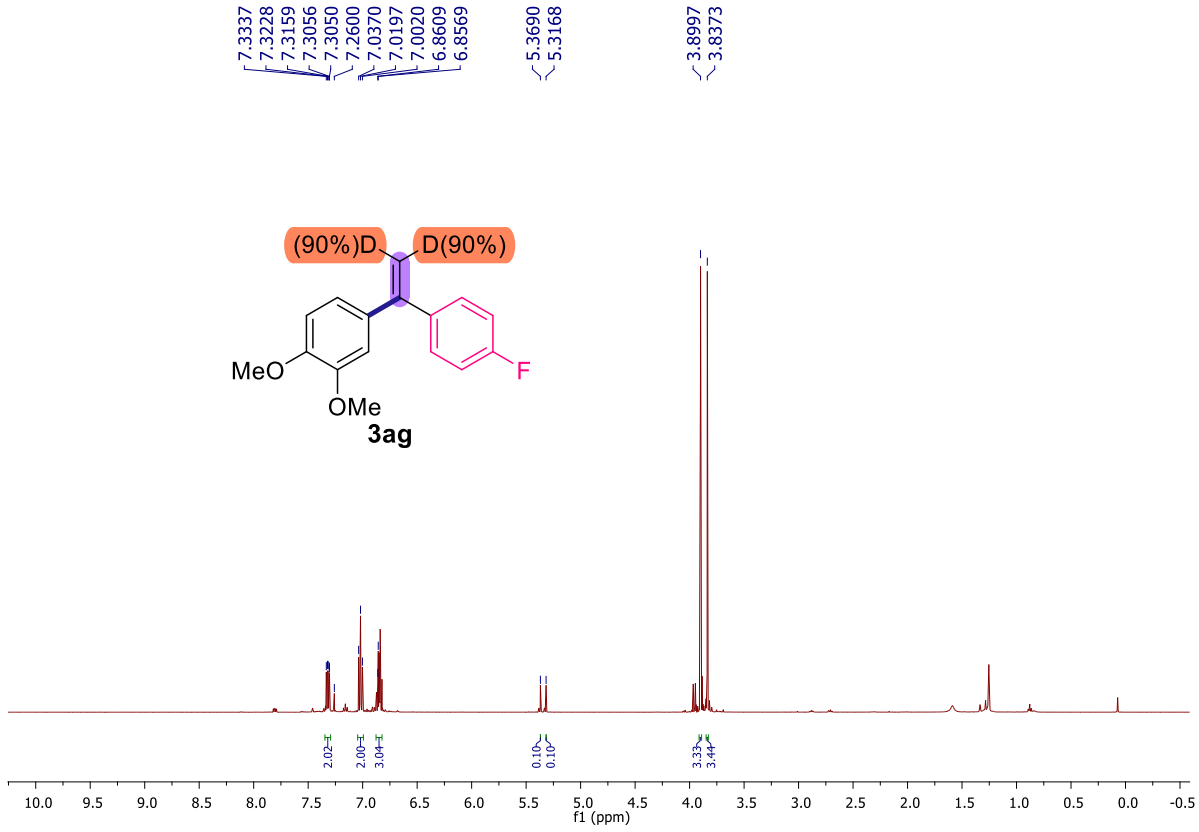


^{2}H NMR (77 MHz, $CDCl_3$, 24 °C)

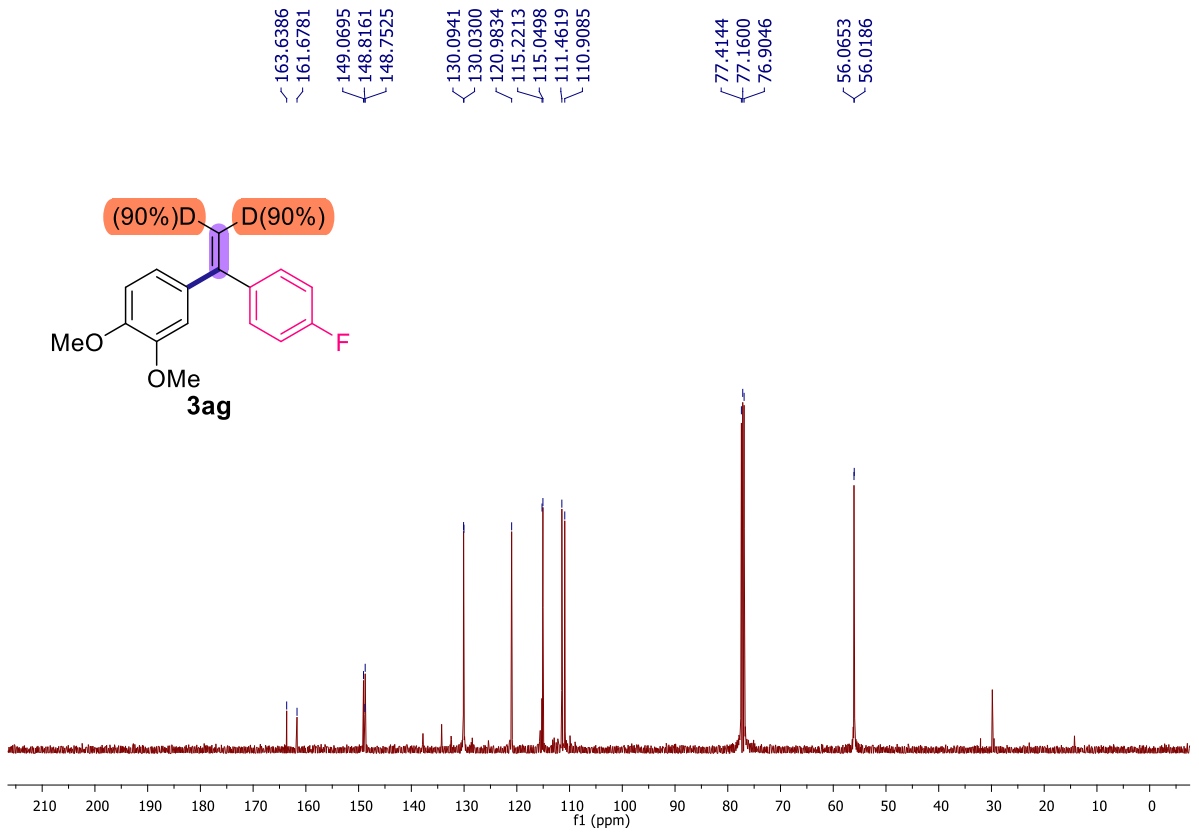


4-(1-(4-Fluorophenyl)vinyl-2,2-d2)-1,2-dimethoxybenzene (**3ag**)

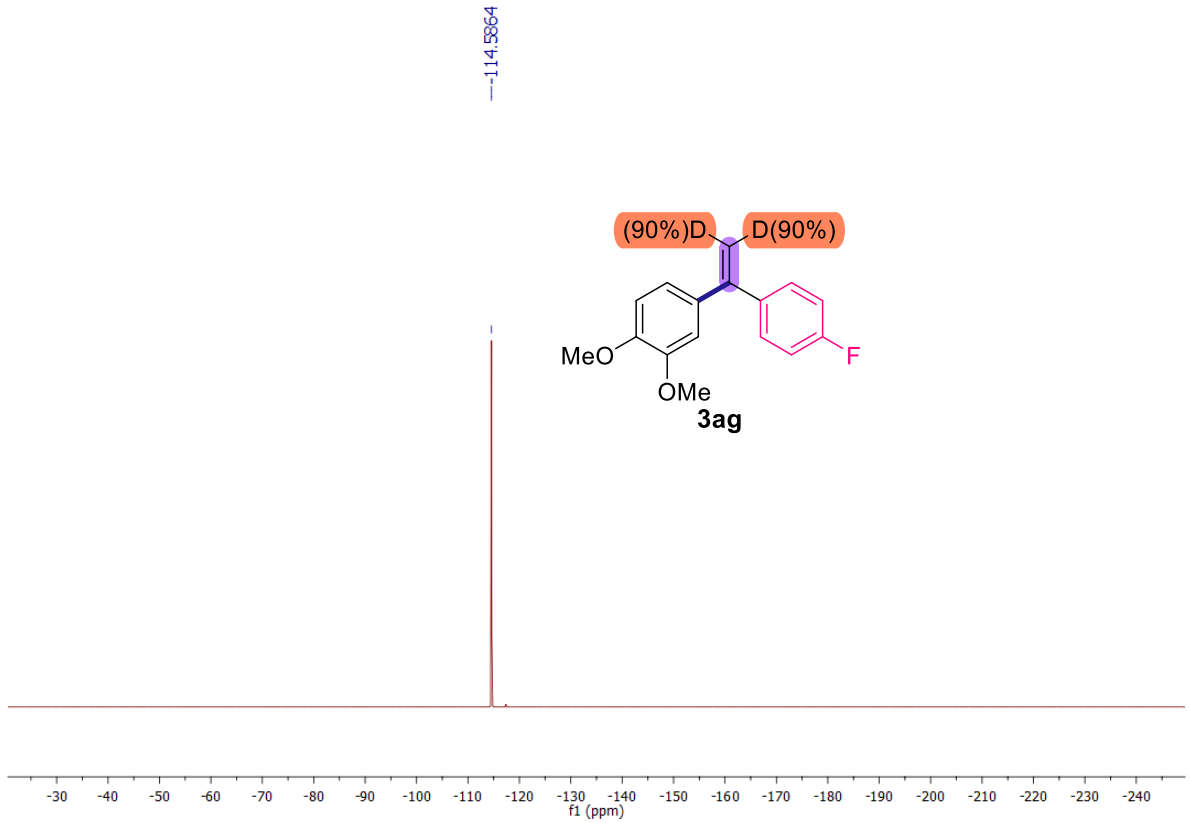
^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)



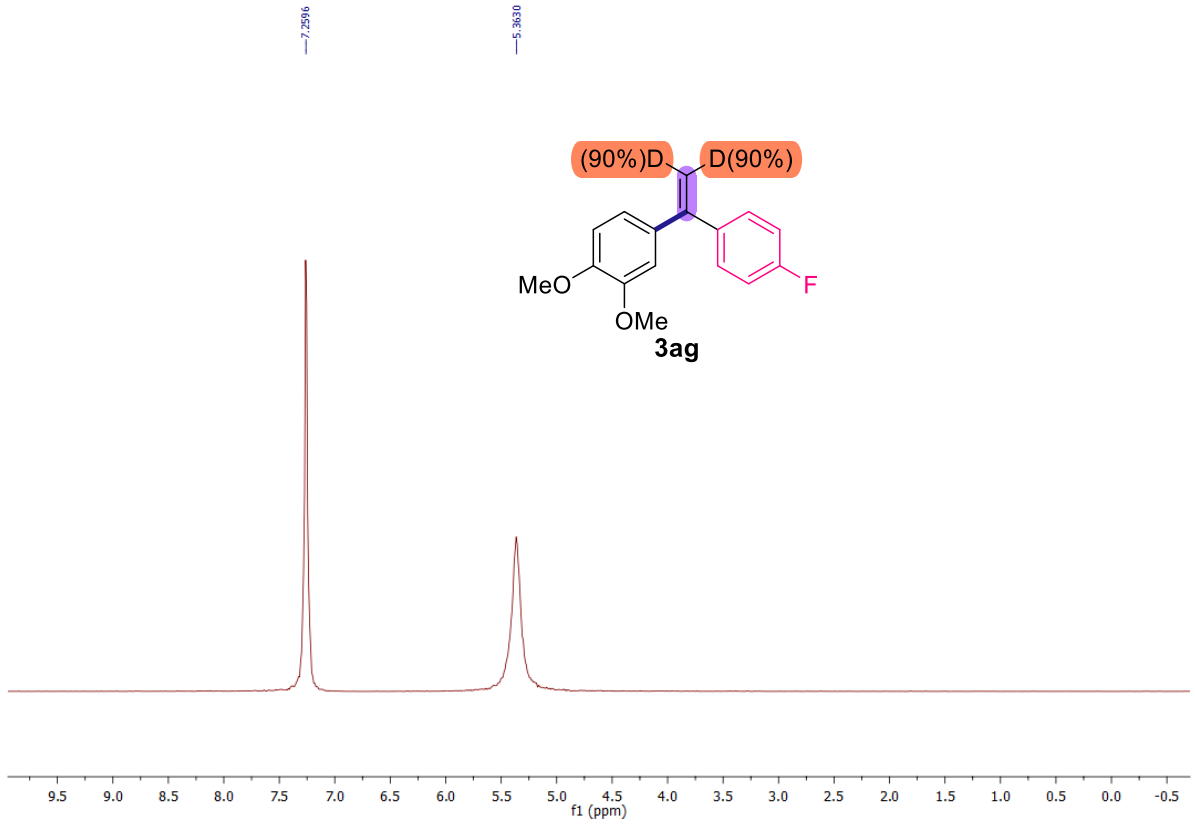
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 24 °C)



^{19}F NMR (471 MHz, $CDCl_3$, 24 °C)

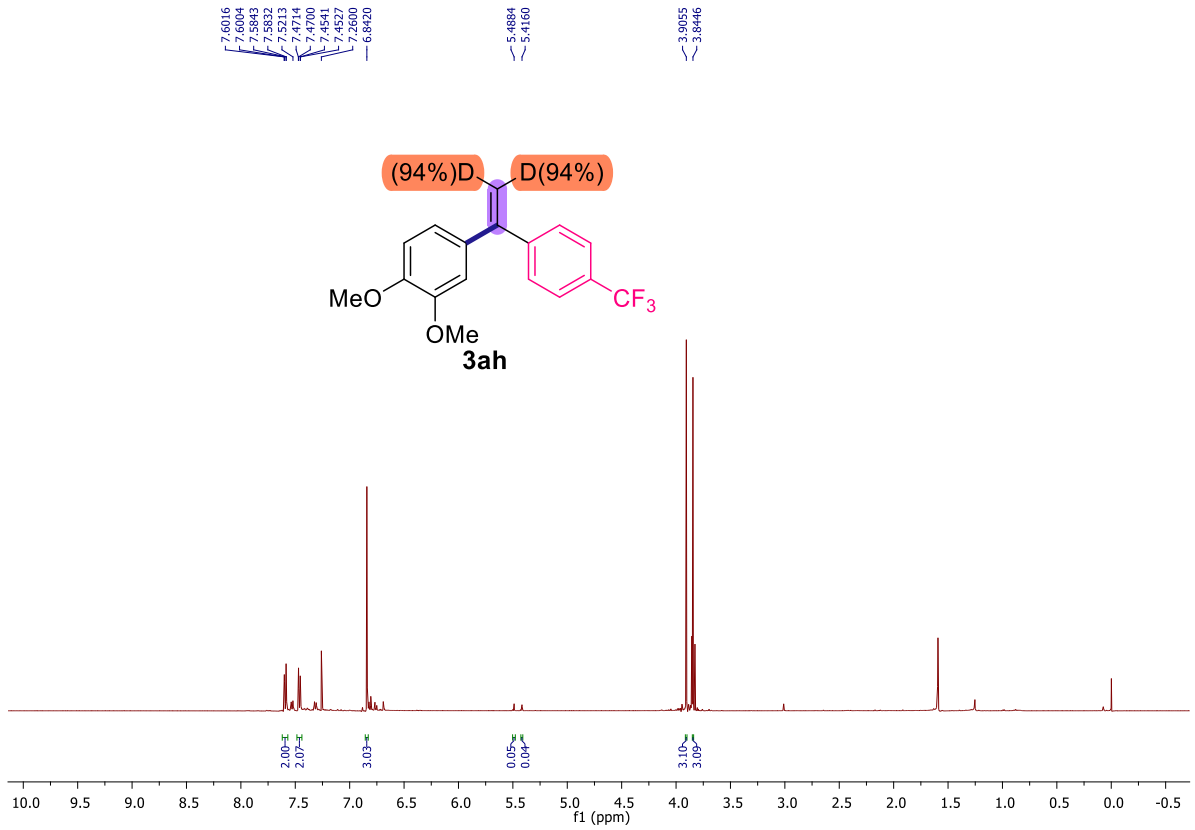


^{2}H NMR (77 MHz, $CDCl_3$, 24 °C)

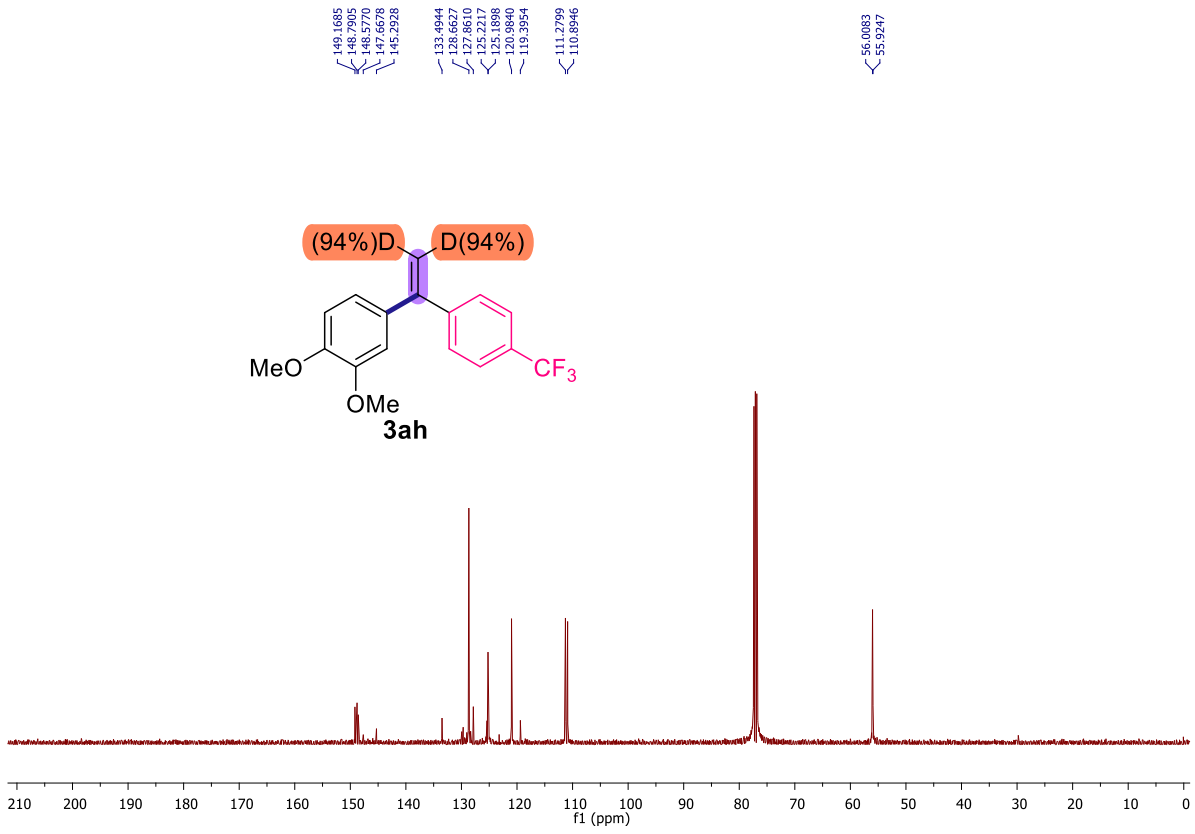


1,2-Dimethoxy-4-(1-(4-(trifluoromethyl)phenyl)vinyl-2,2-d2)benzene (**3ah**)

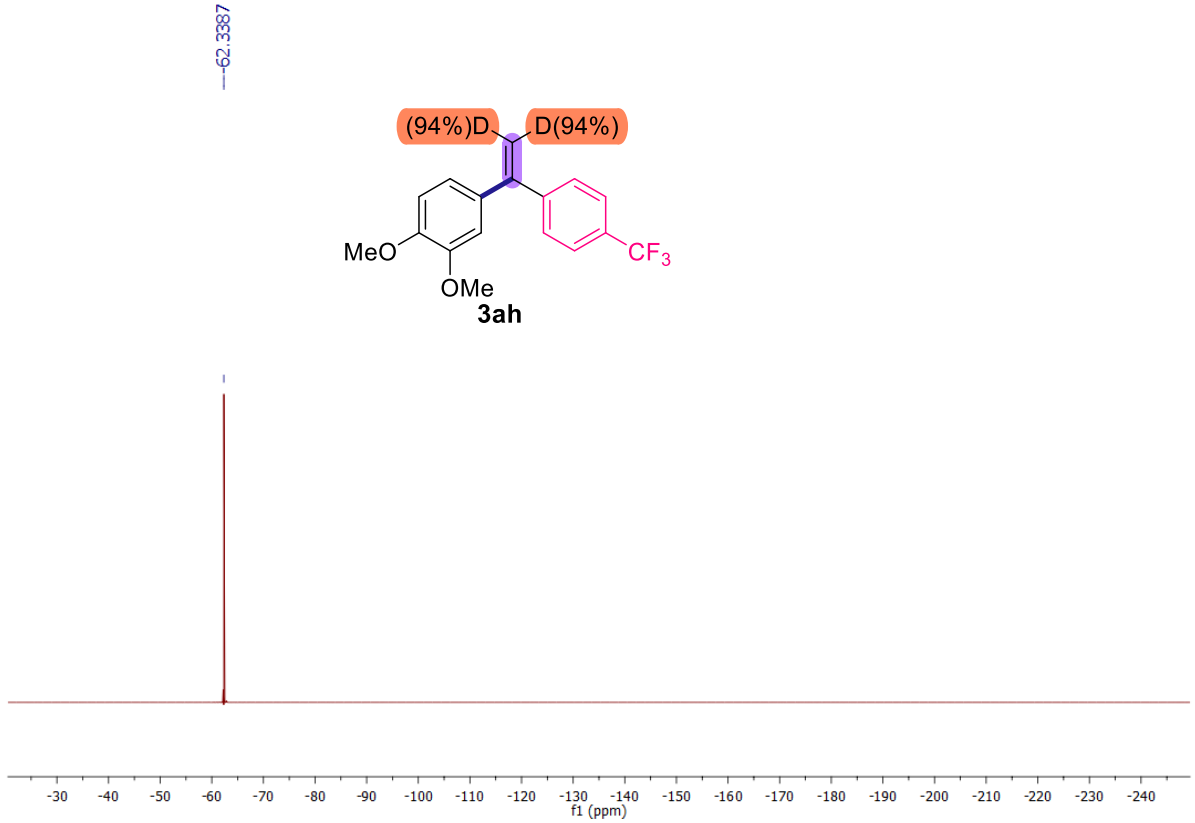
^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)



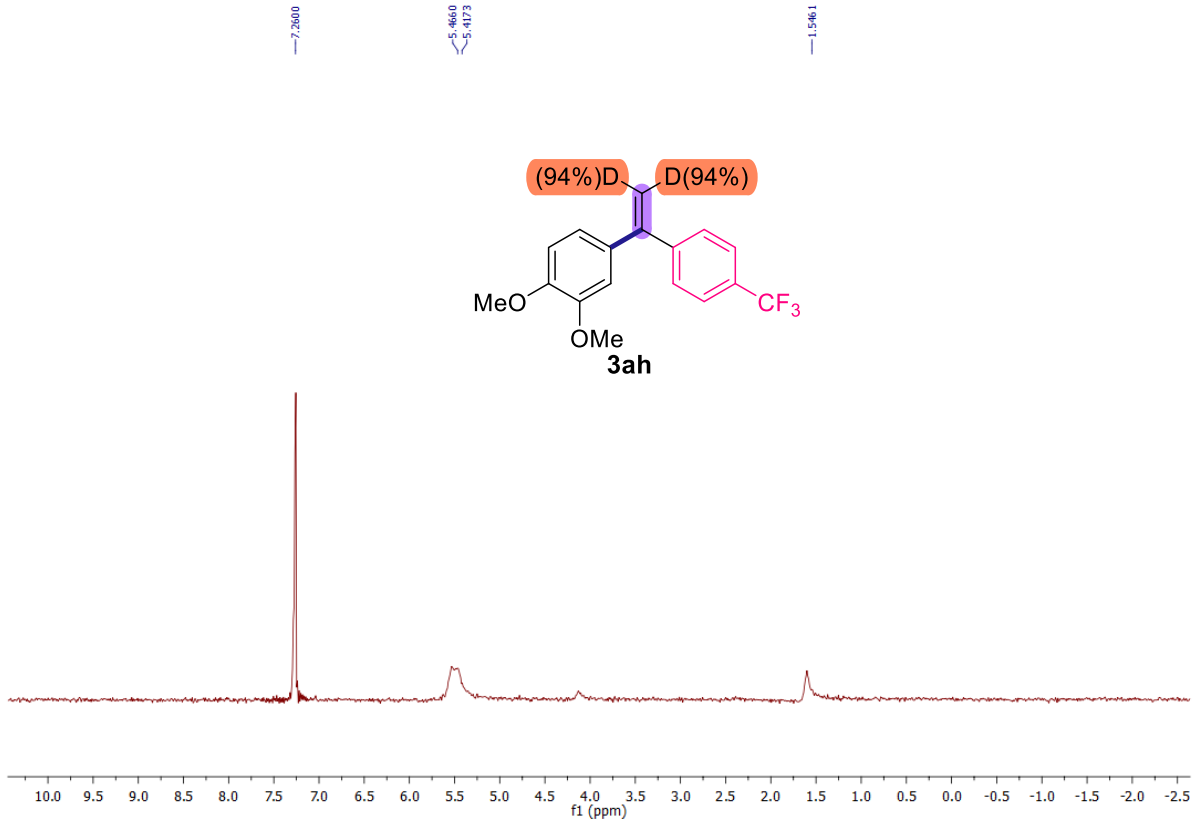
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 24 °C)



^{19}F NMR (471 MHz, $CDCl_3$, 24 °C)

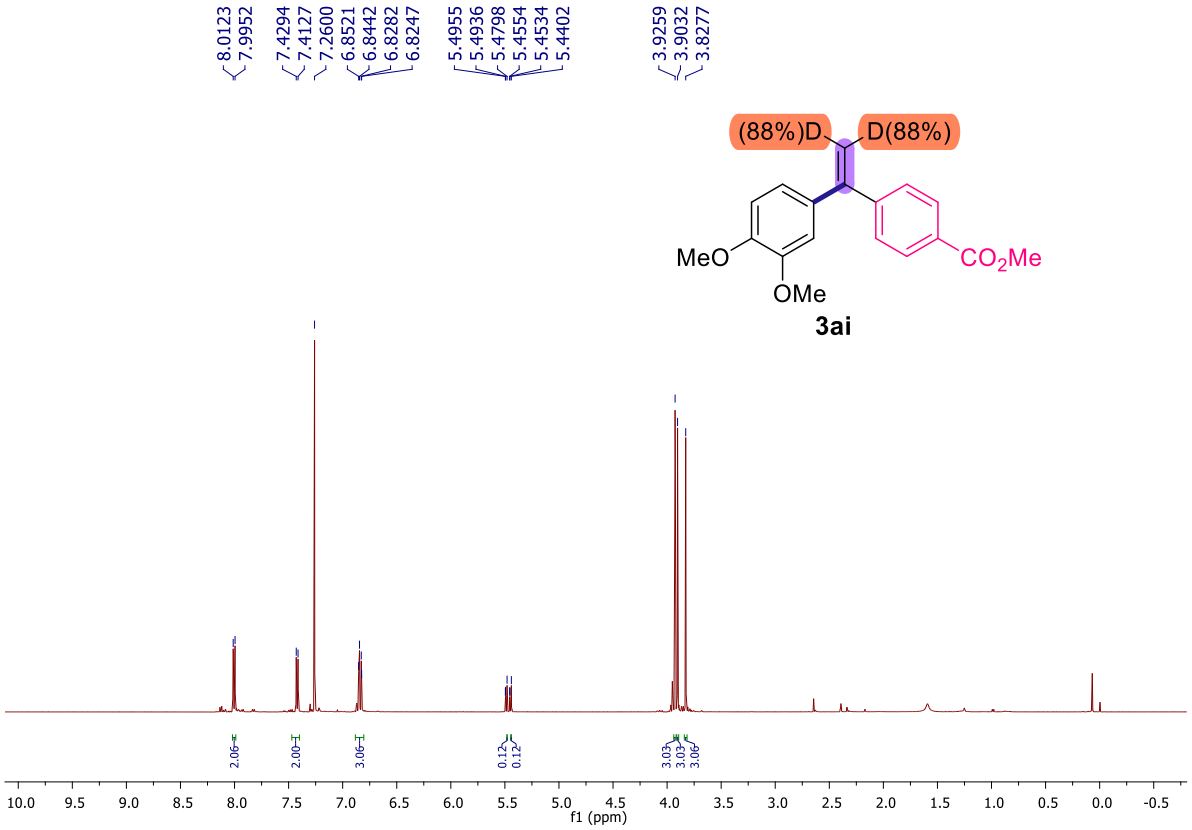


^{2}H NMR (77 MHz, $CHCl_3$, 24 °C)

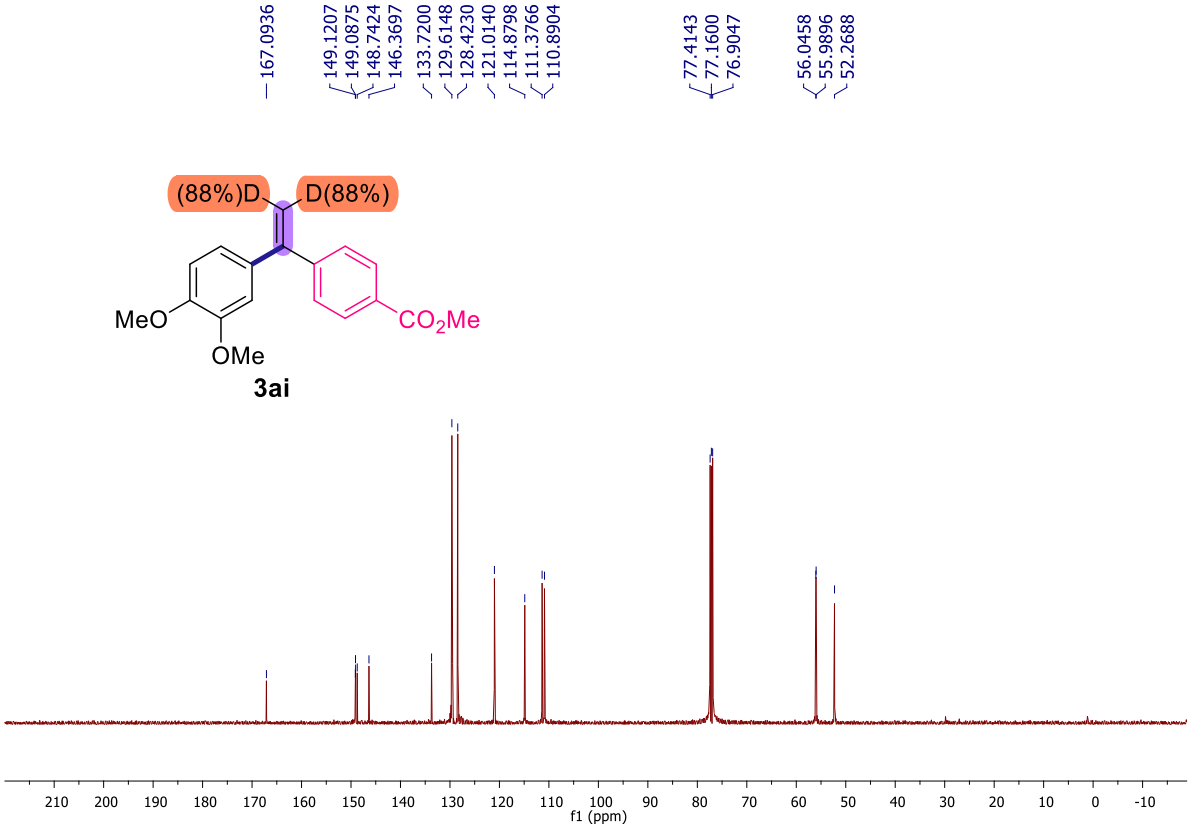


Methyl 4-(1-(3,4-dimethoxyphenyl)vinyl-2,2-d2)benzoate (**3ai**)

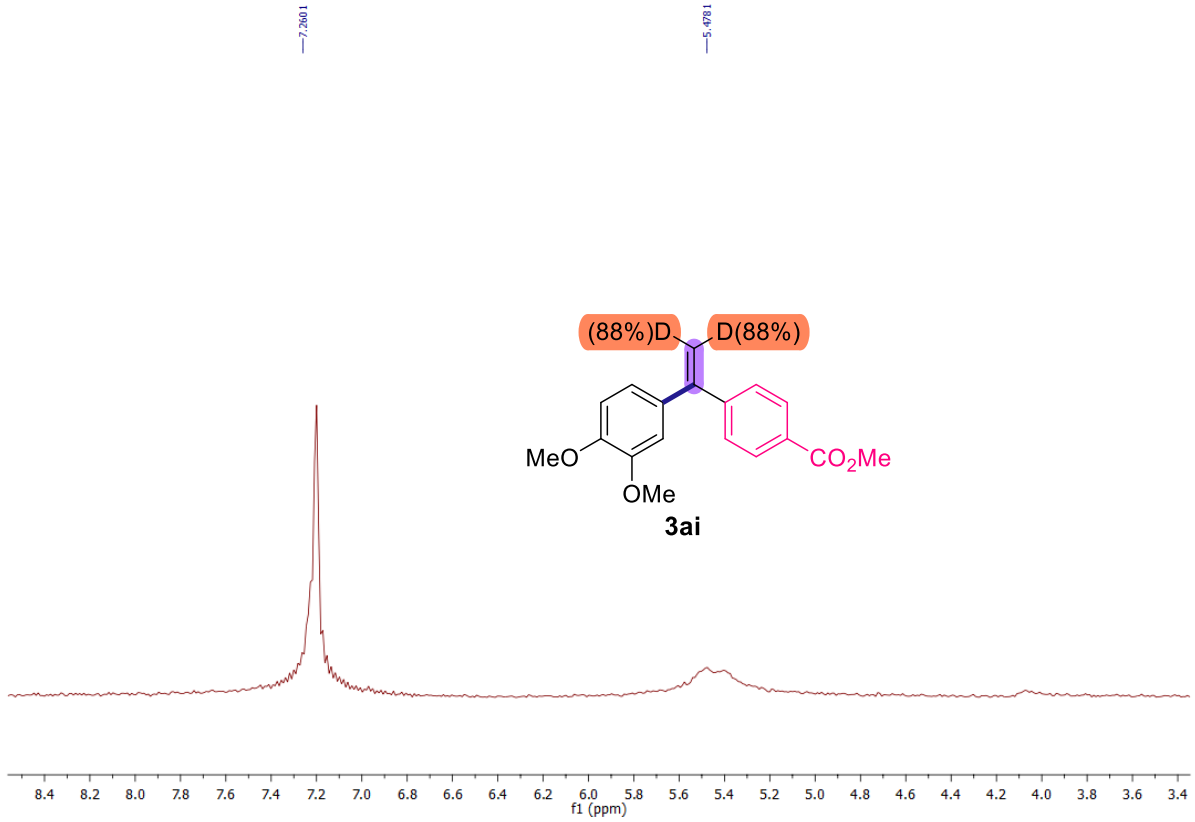
^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)



^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 24 °C)

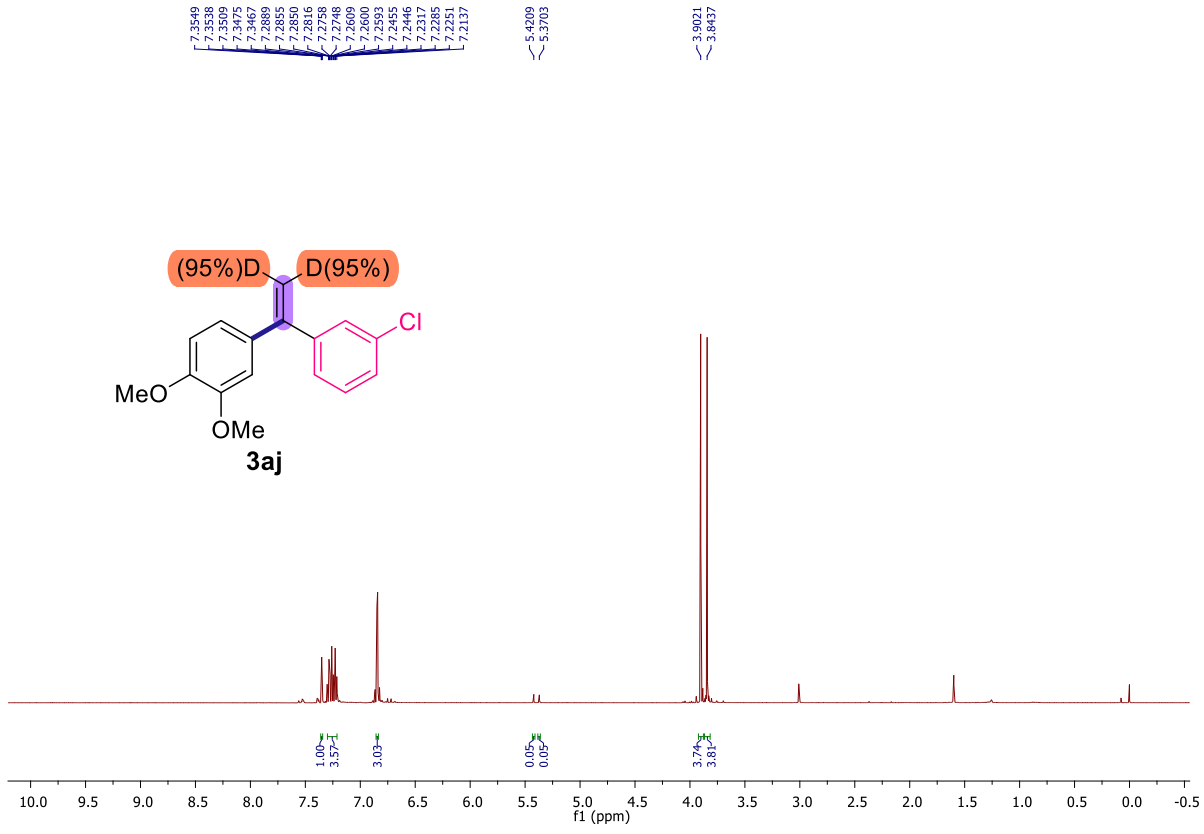


^{2}H NMR (77 MHz, $CHCl_3$, 24 °C)

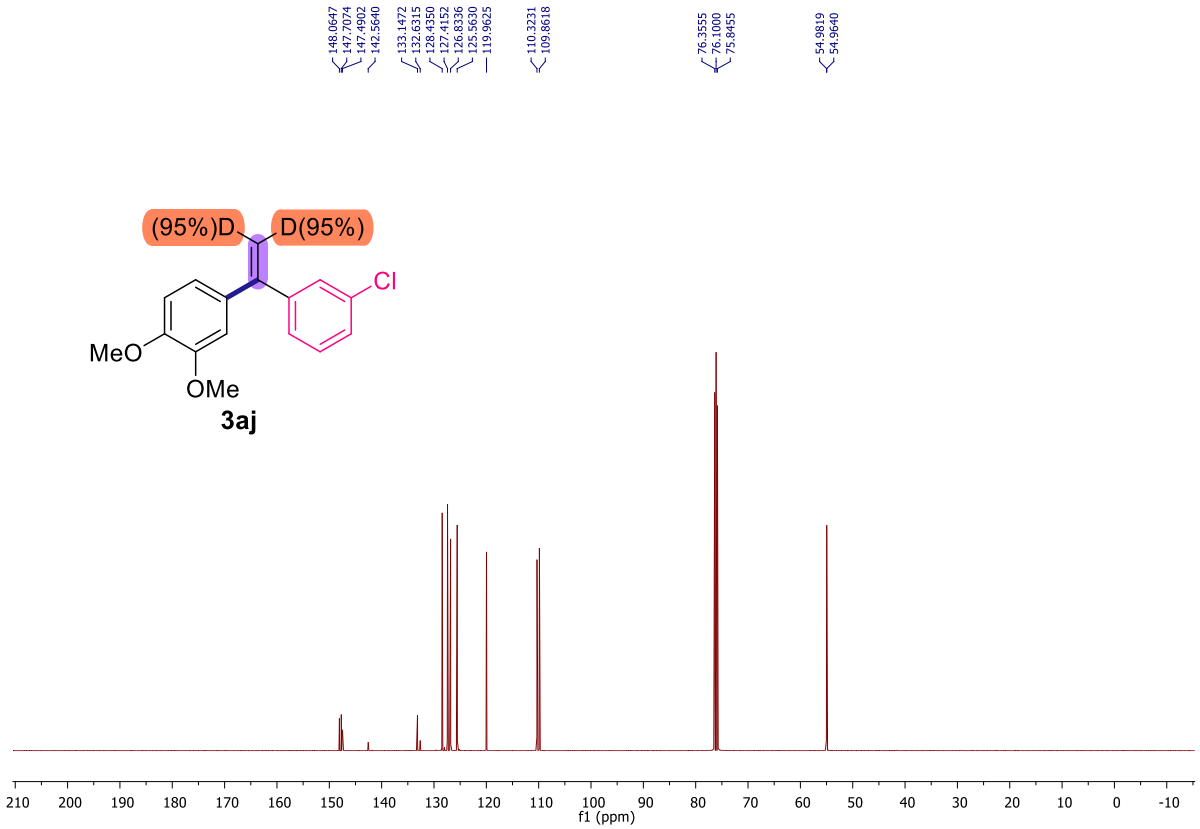


4-(1-(3-Chlorophenyl)vinyl-2,2-d2)-1,2-dimethoxybenzene (**3aj**)

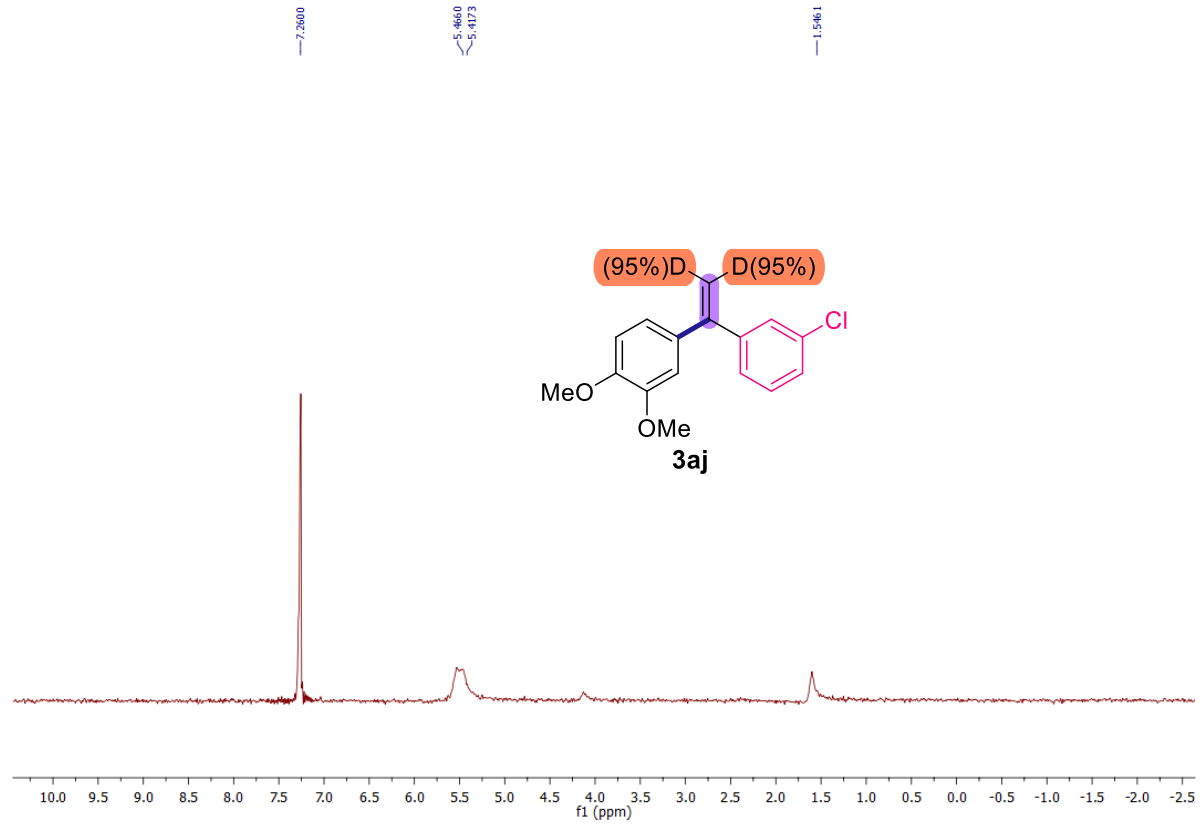
^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)



$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 24 °C)

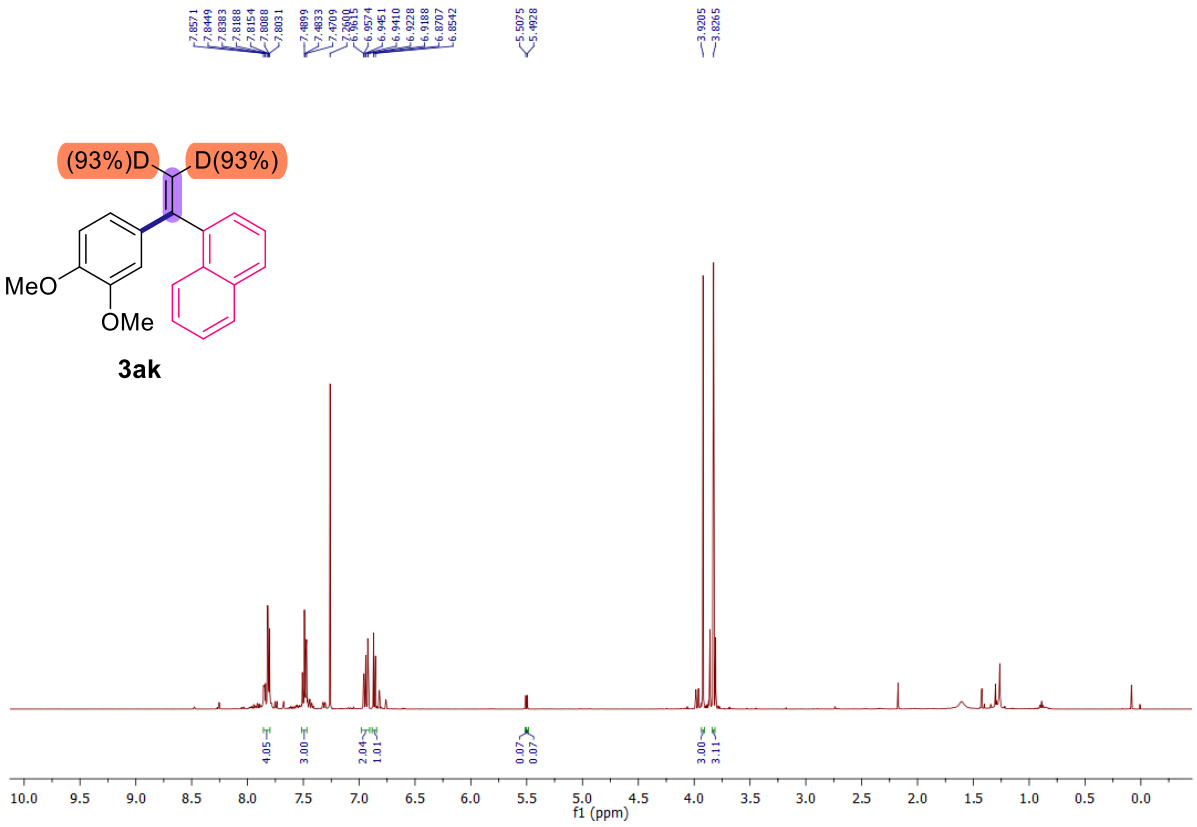


^{2}H NMR (77 MHz, $CHCl_3$, 24 °C)

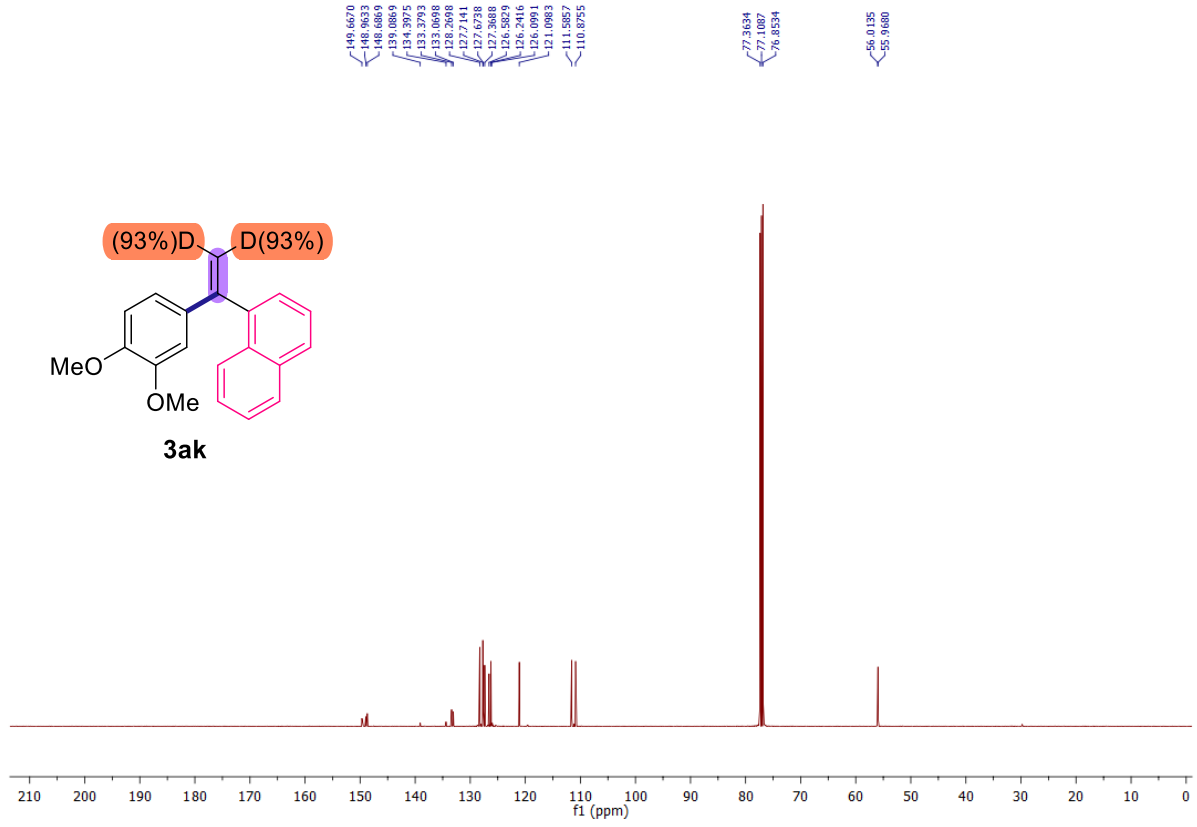


1-(1-(3,4-Dimethoxyphenyl)vinyl-2,2-d2)naphthalene (**3ak**)

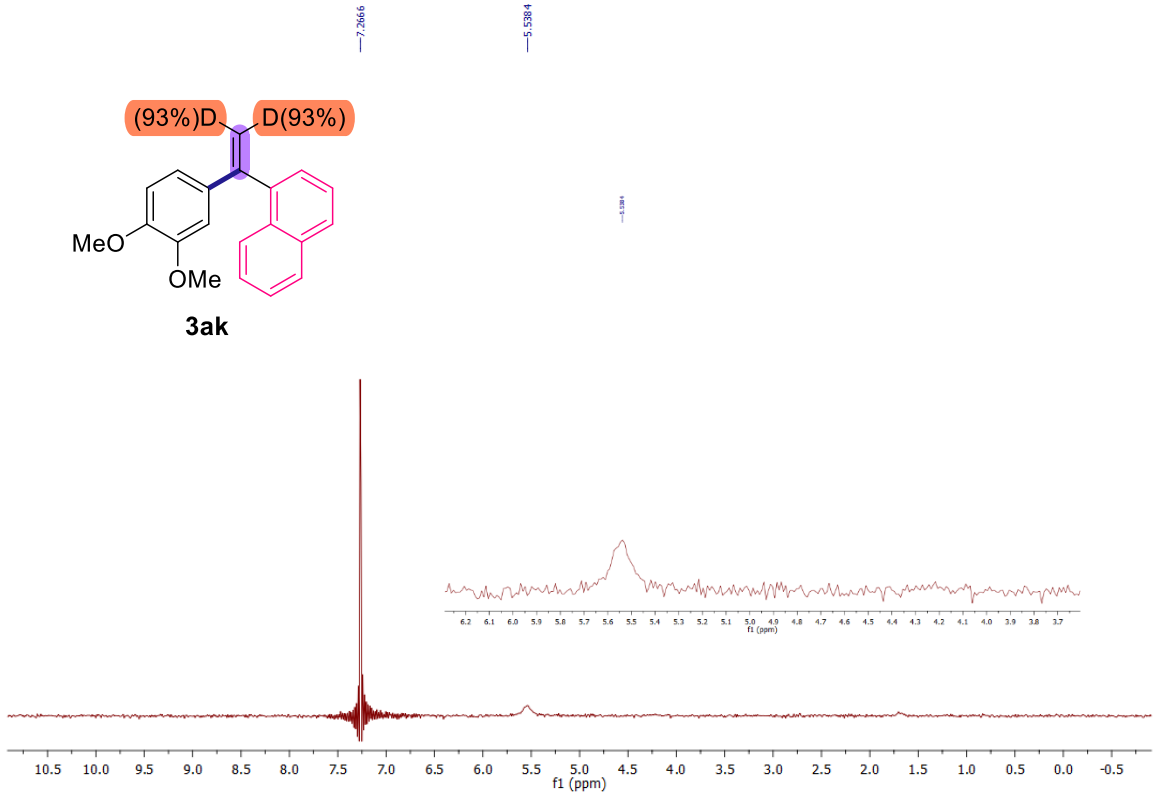
^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)



^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 24 °C)

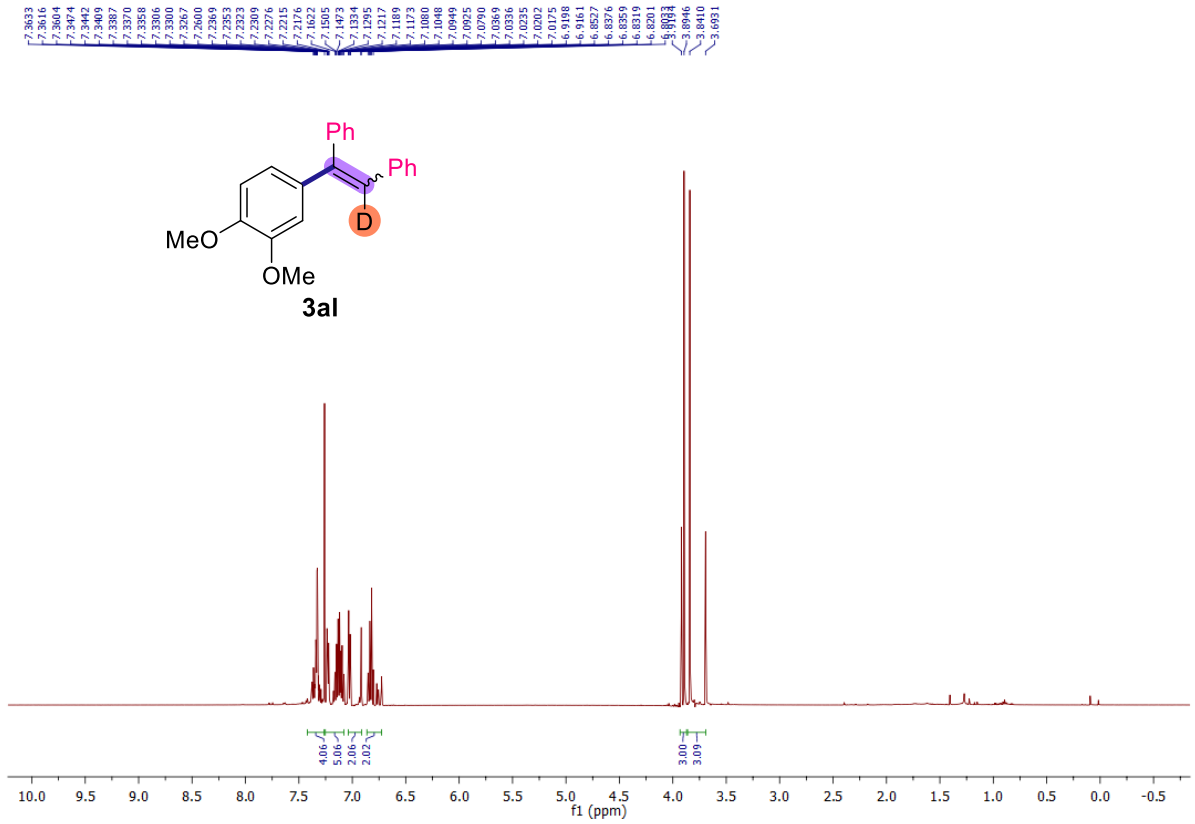


^{2}H NMR (77 MHz, $CDCl_3$, 24 °C)

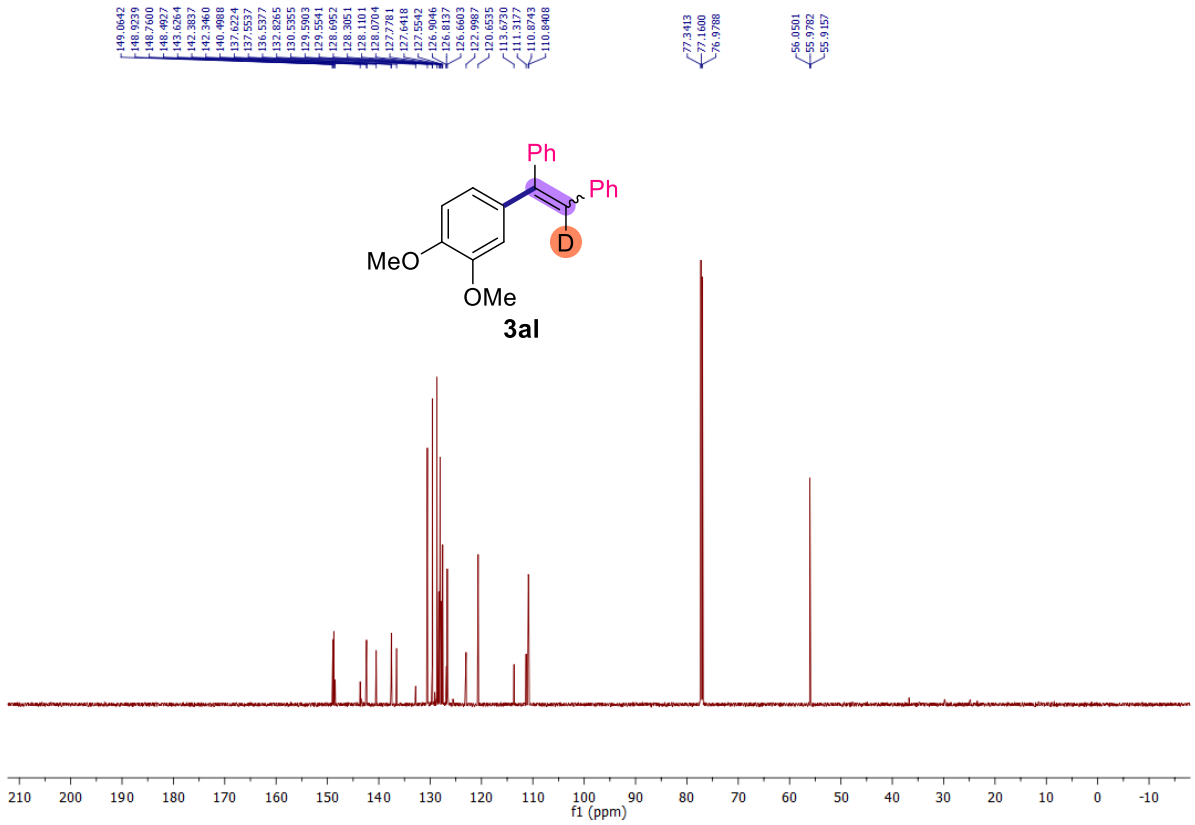


(1-(3,4-Dimethoxyphenyl)ethene-1,2-diyl-2-d)dibenzene (**3al**)

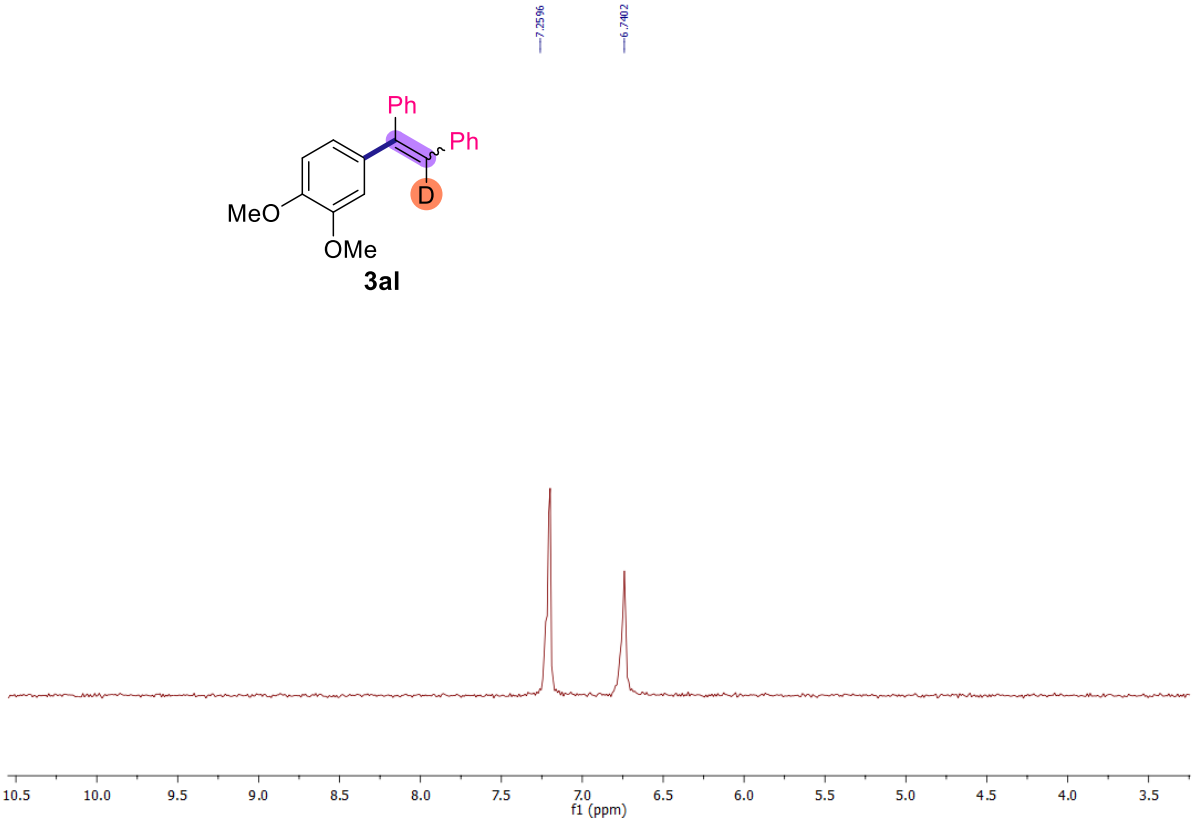
^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)



$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 24 °C)

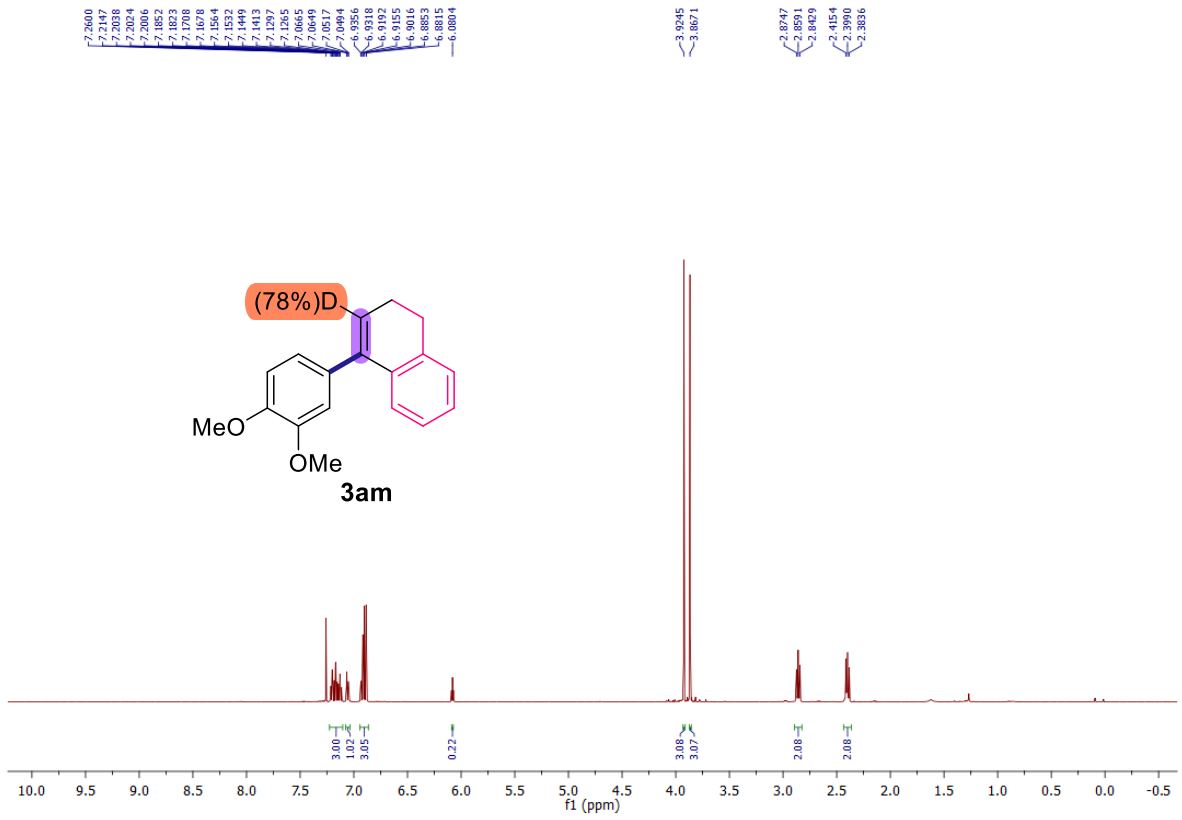


^{2}H NMR (94 MHz, $CHCl_3$, 24 °C)

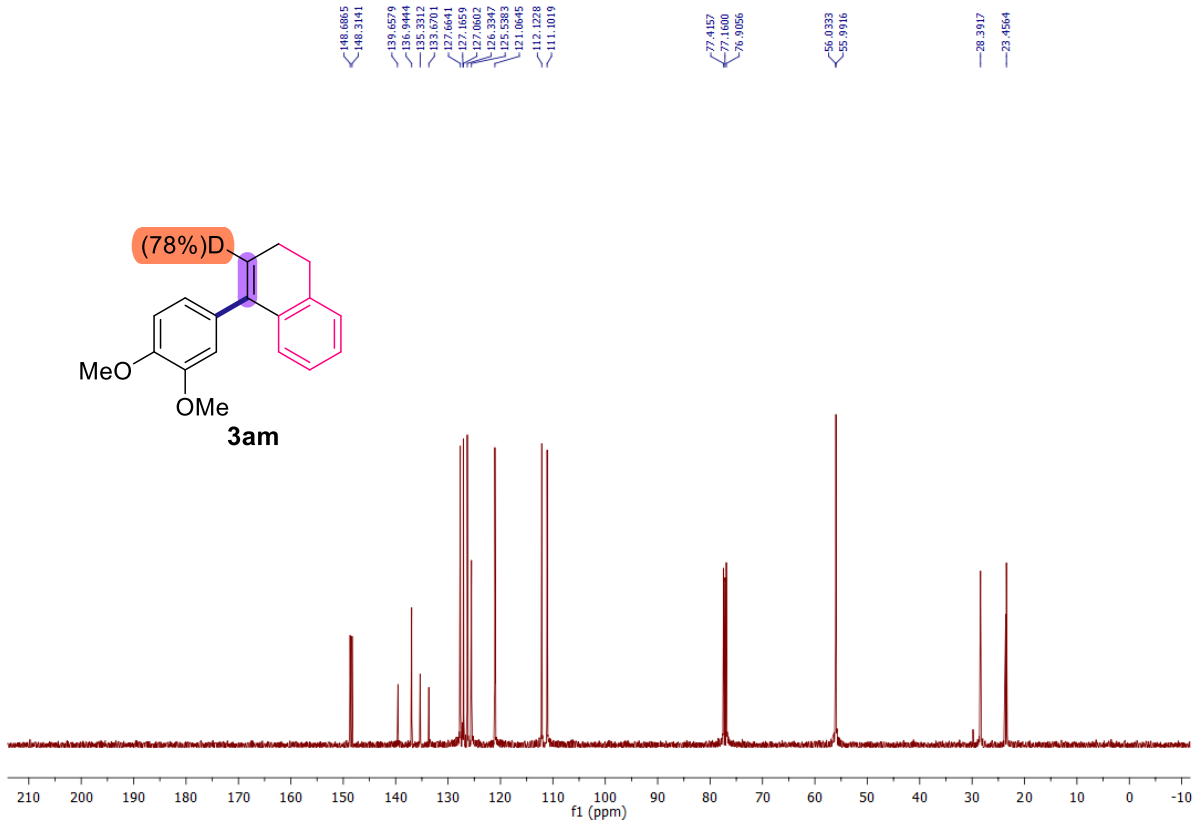


4-(3,4-Dimethoxyphenyl)-1,2-dihydronaphthalene-3-d (**3am**)

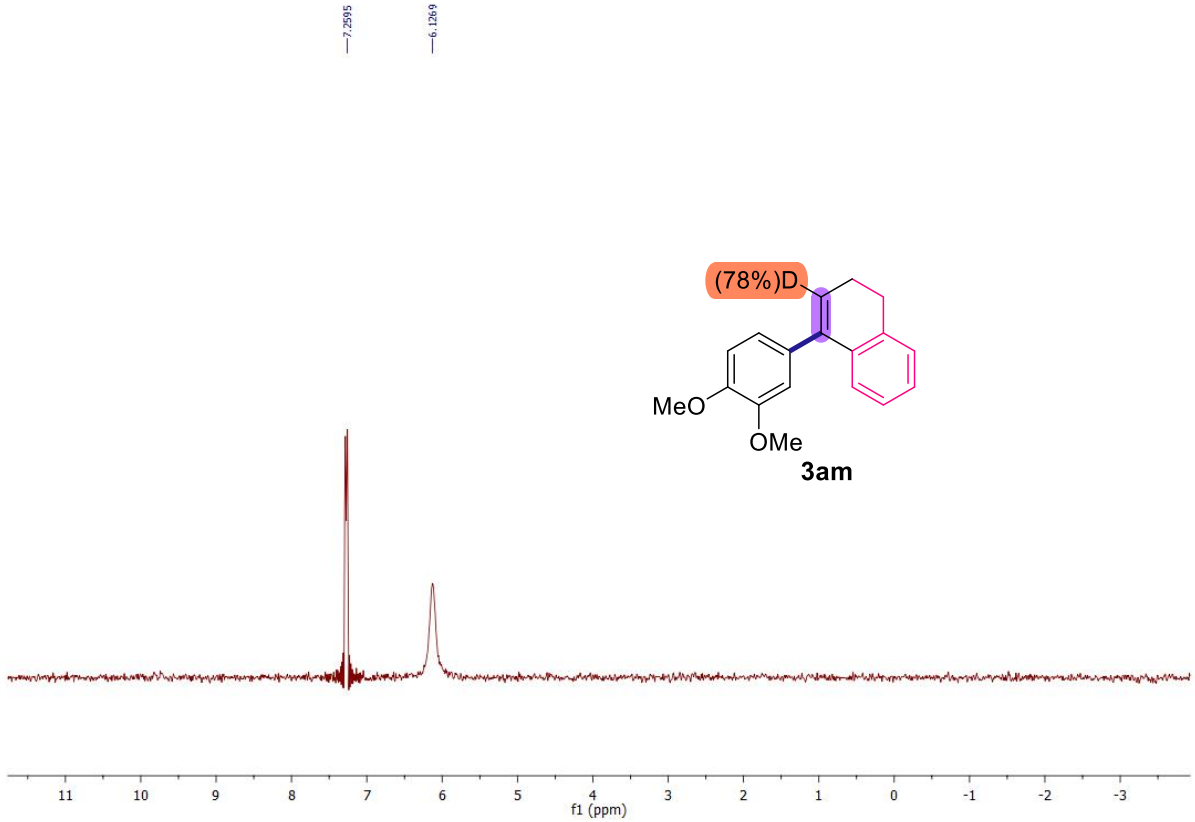
^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)



^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 24 °C)

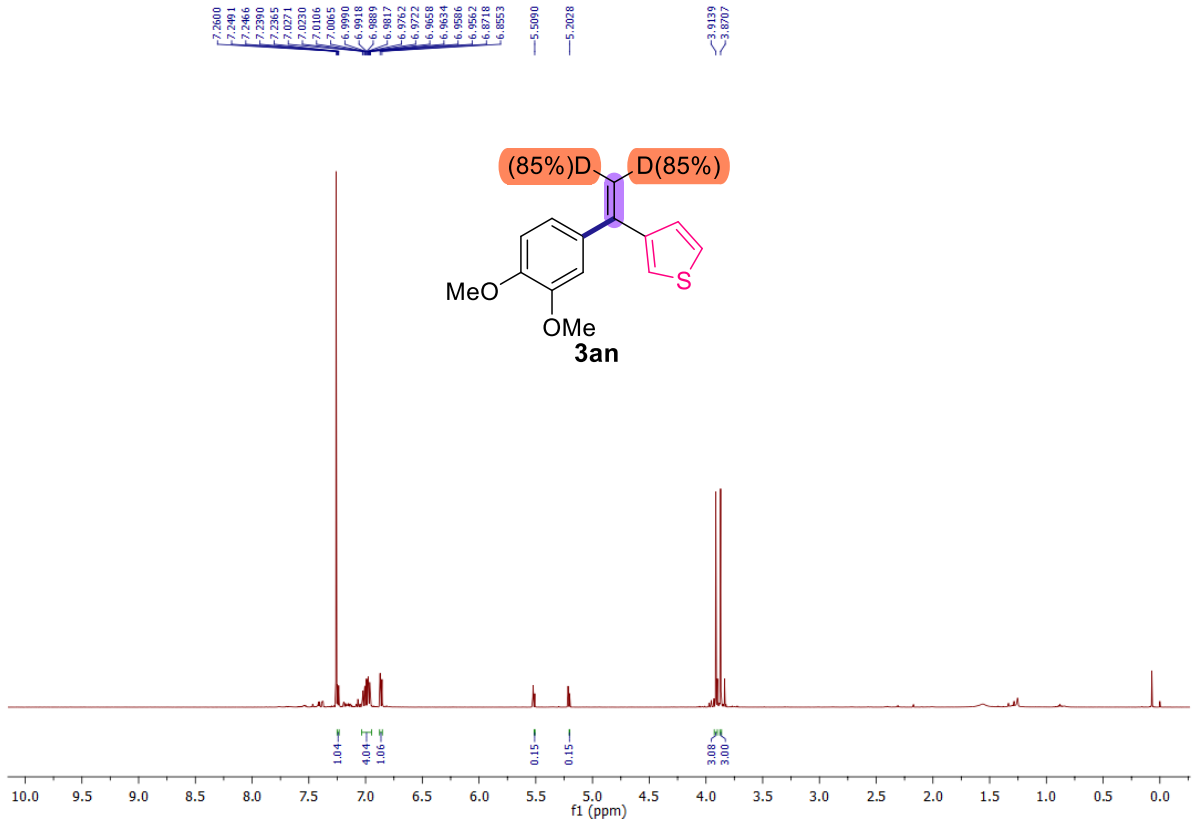


^{2}H NMR (94 MHz, $CHCl_3$, 24 °C)

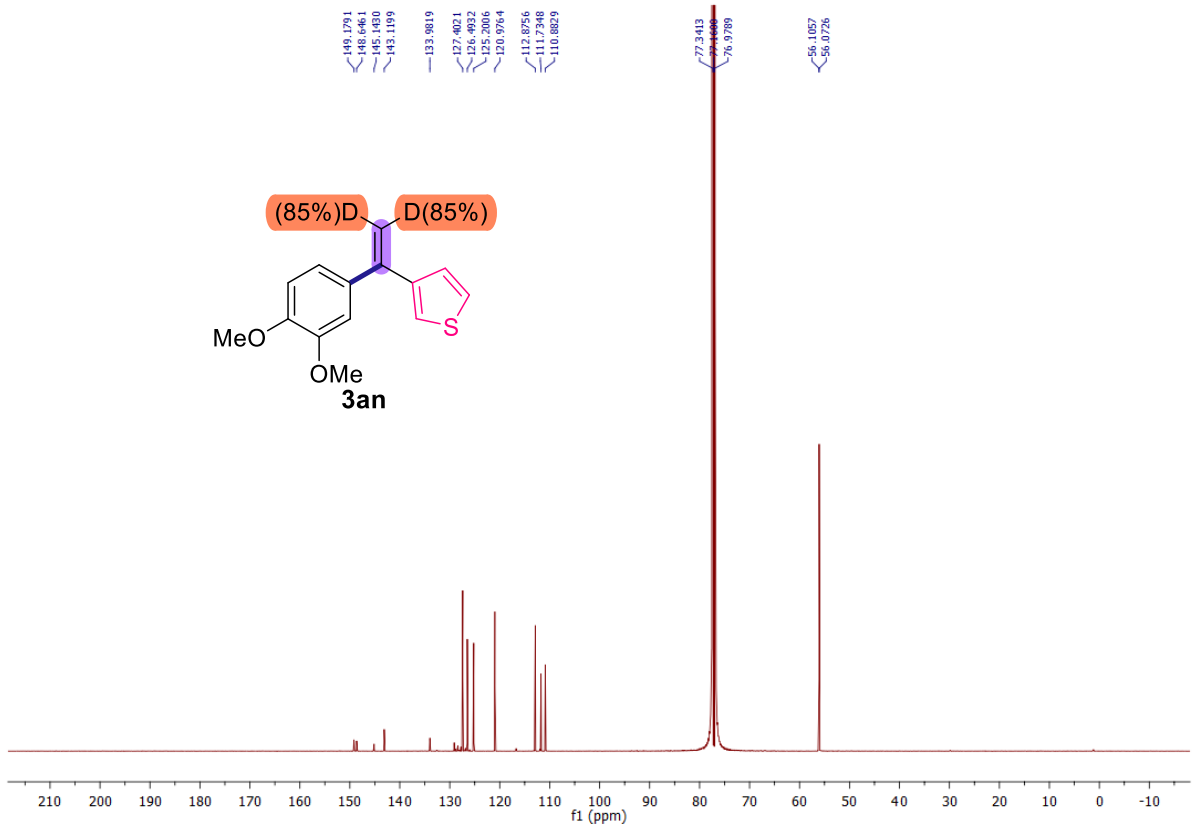


3-(1-(3,4-Dimethoxyphenyl)vinyl-2,2-d2)thiophene

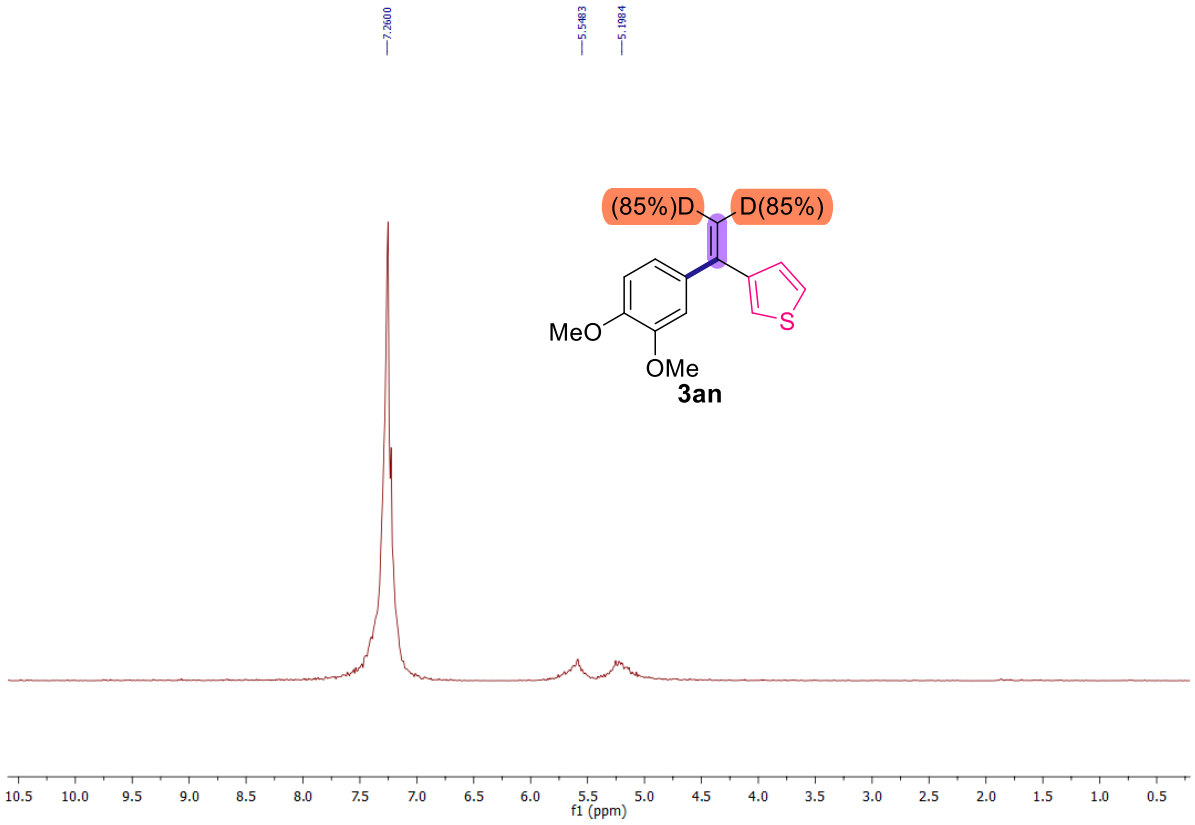
^{1}H NMR (500 MHz, $CDCl_3$, 24 °C) (**3an**)



$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 24 °C)

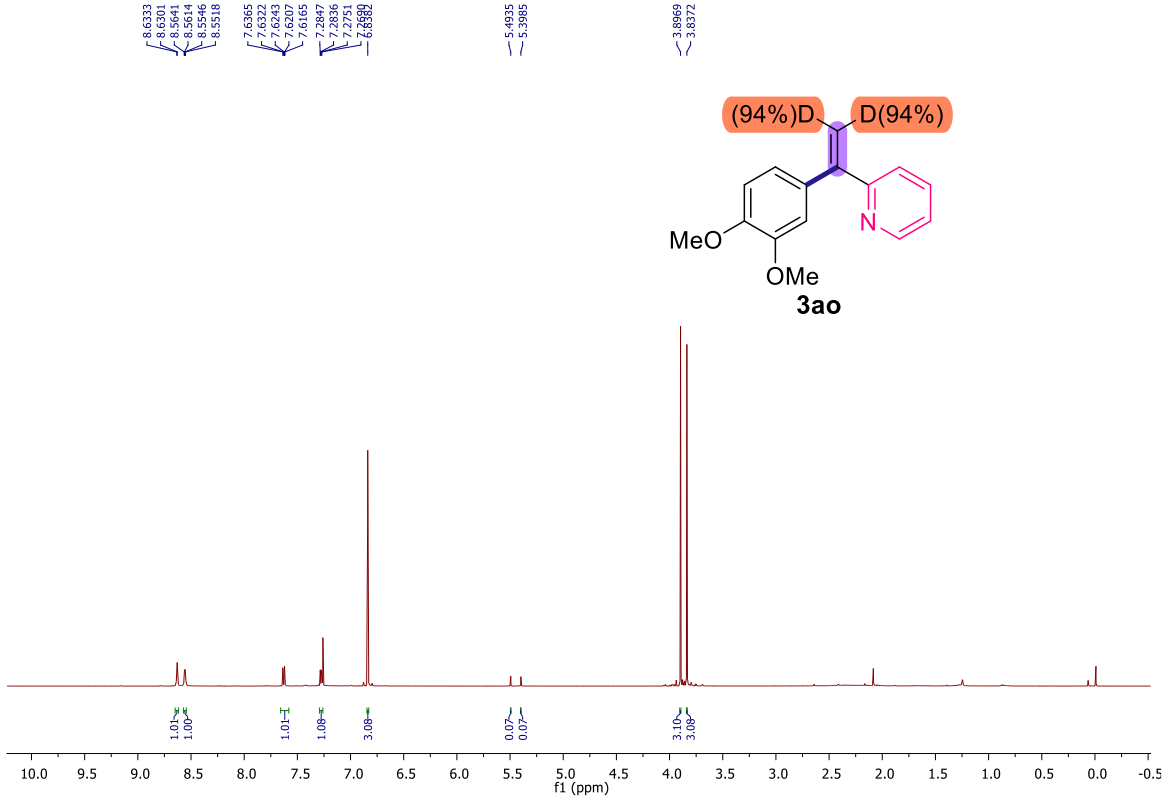


^{2}H NMR (77 MHz, $CDCl_3$, 24 °C)

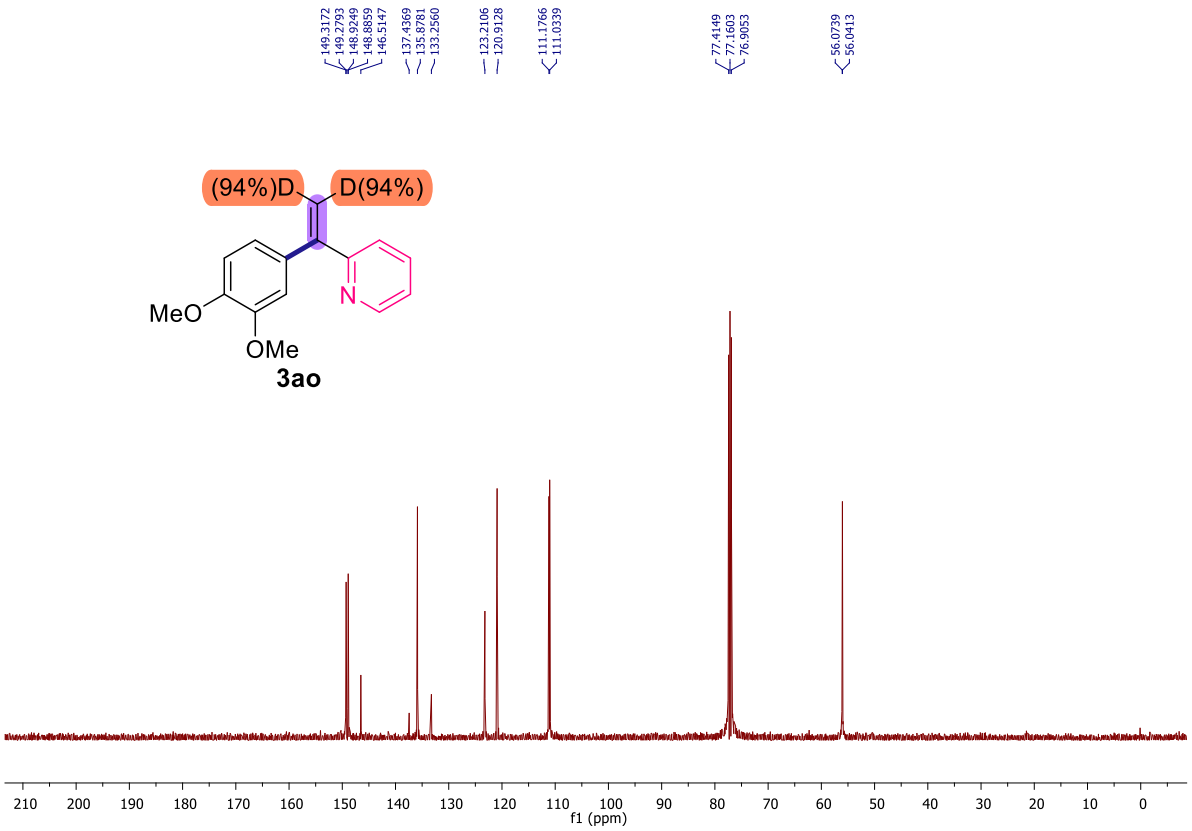


2-(1-(3,4-Dimethoxyphenyl)vinyl-2,2-d2)pyridine (**3ao**)

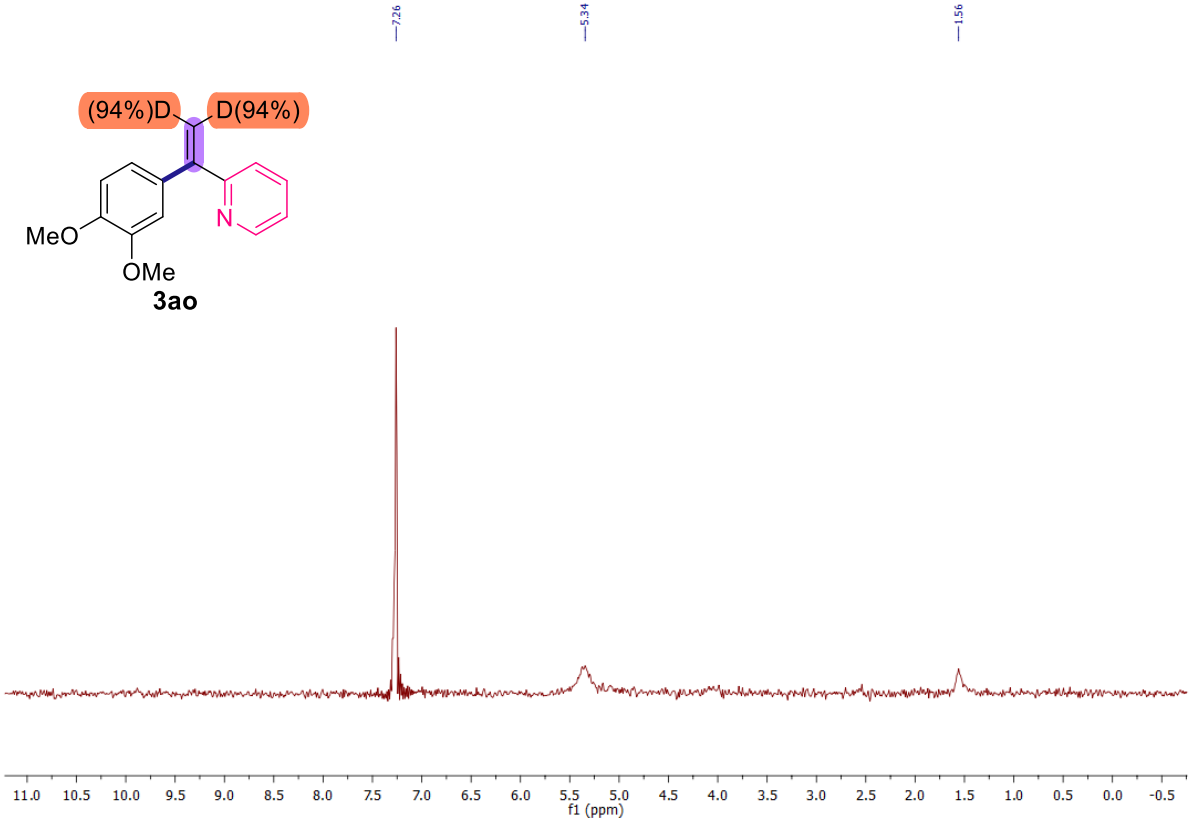
^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)



^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 24 °C)

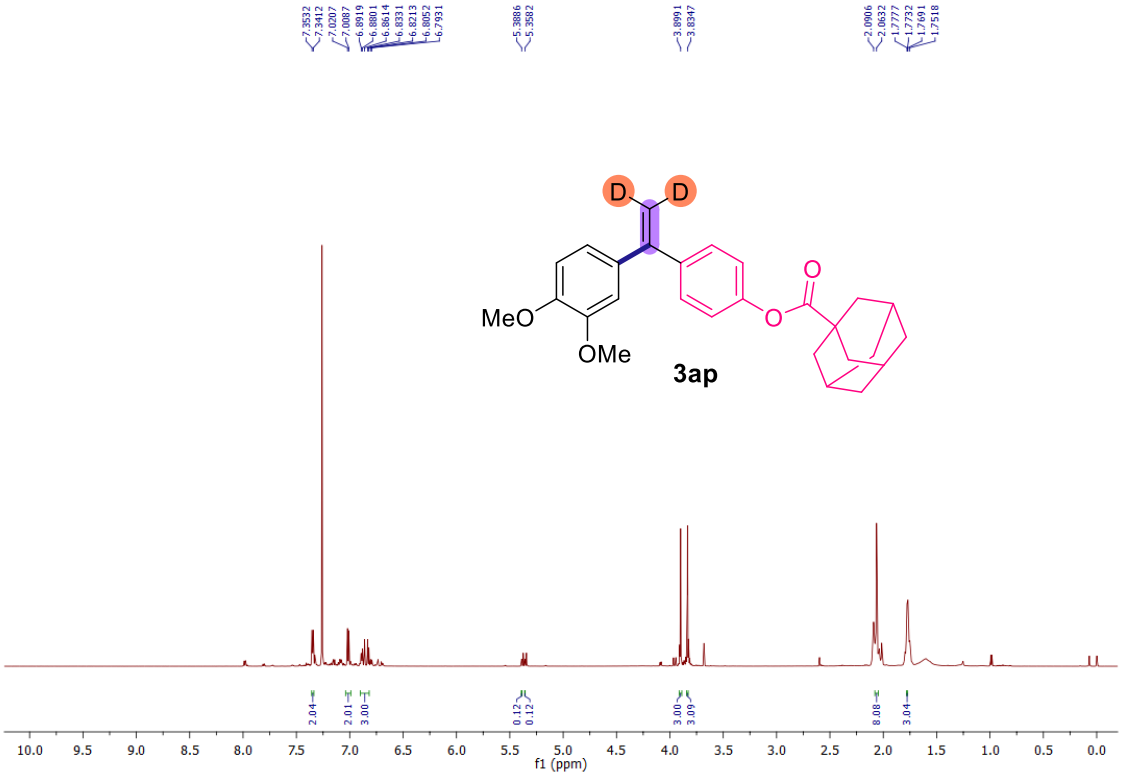


^{2}H NMR (77 MHz, $CDCl_3$, 24 °C)

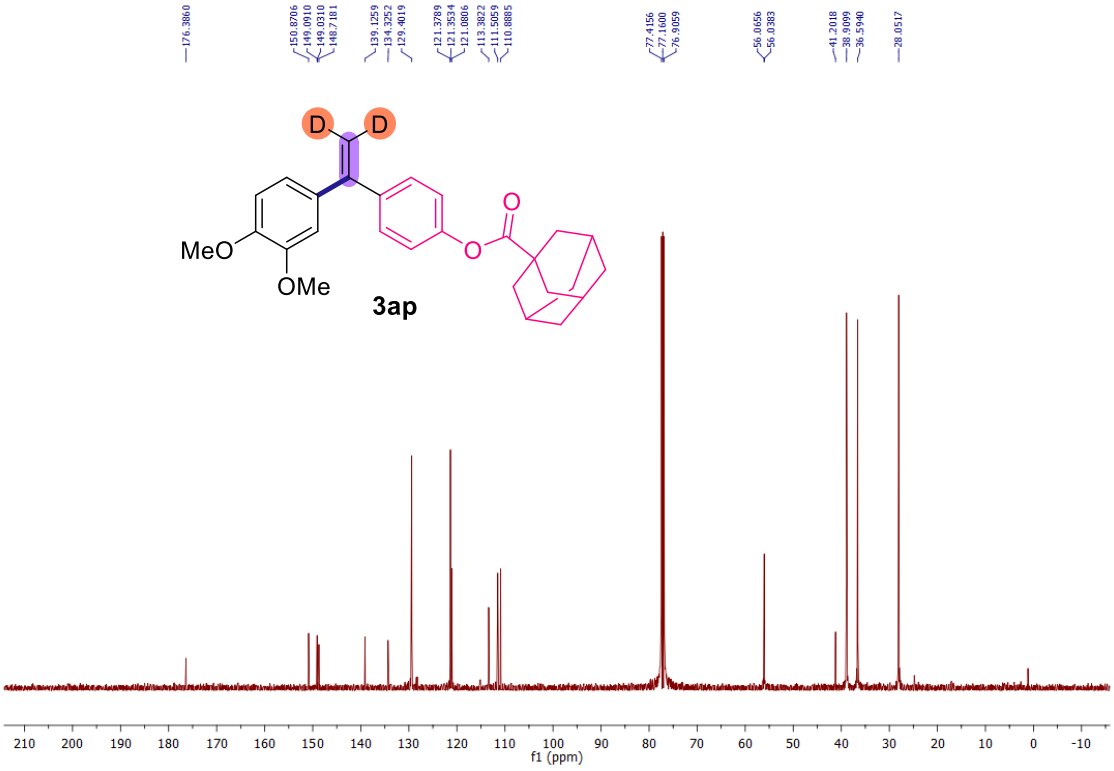


4-(1-(3,4-Dimethoxyphenyl)vinyl)phenyl adamantane-1-carboxylate (**3ap**)

^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)

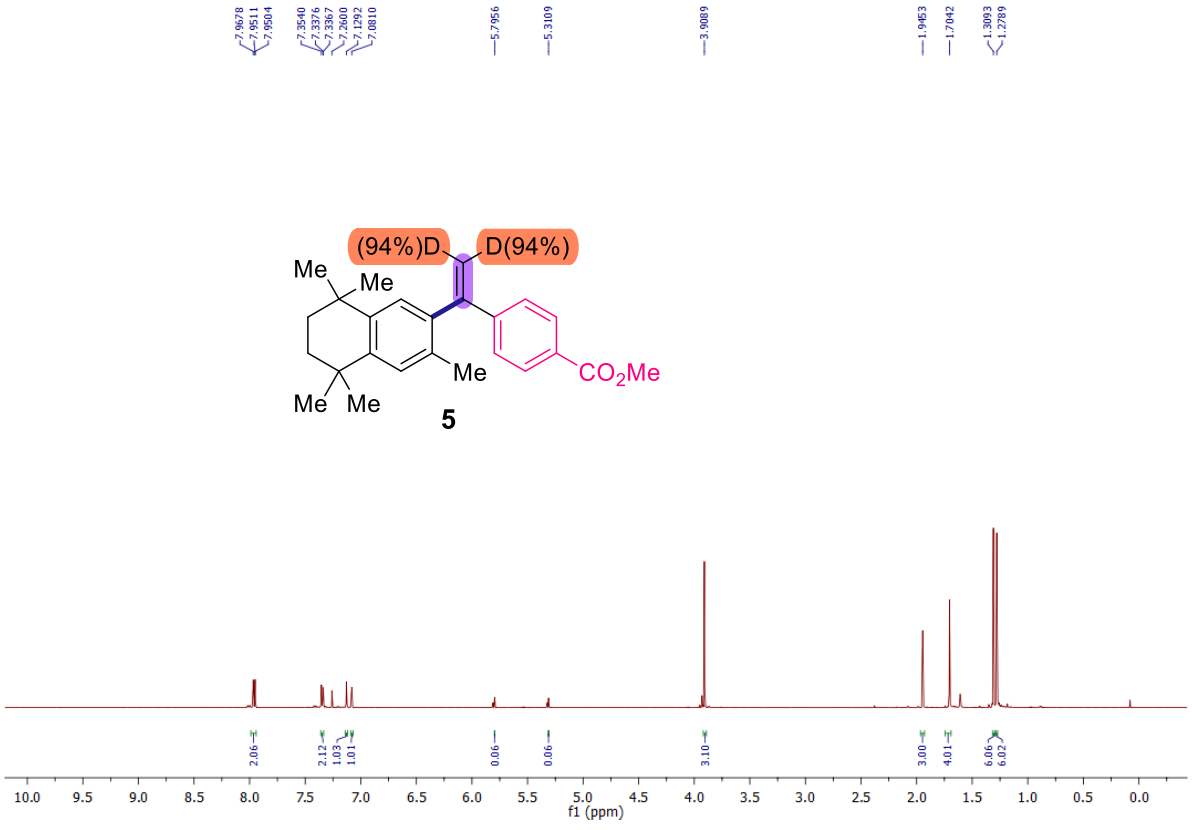


$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 24 °C)

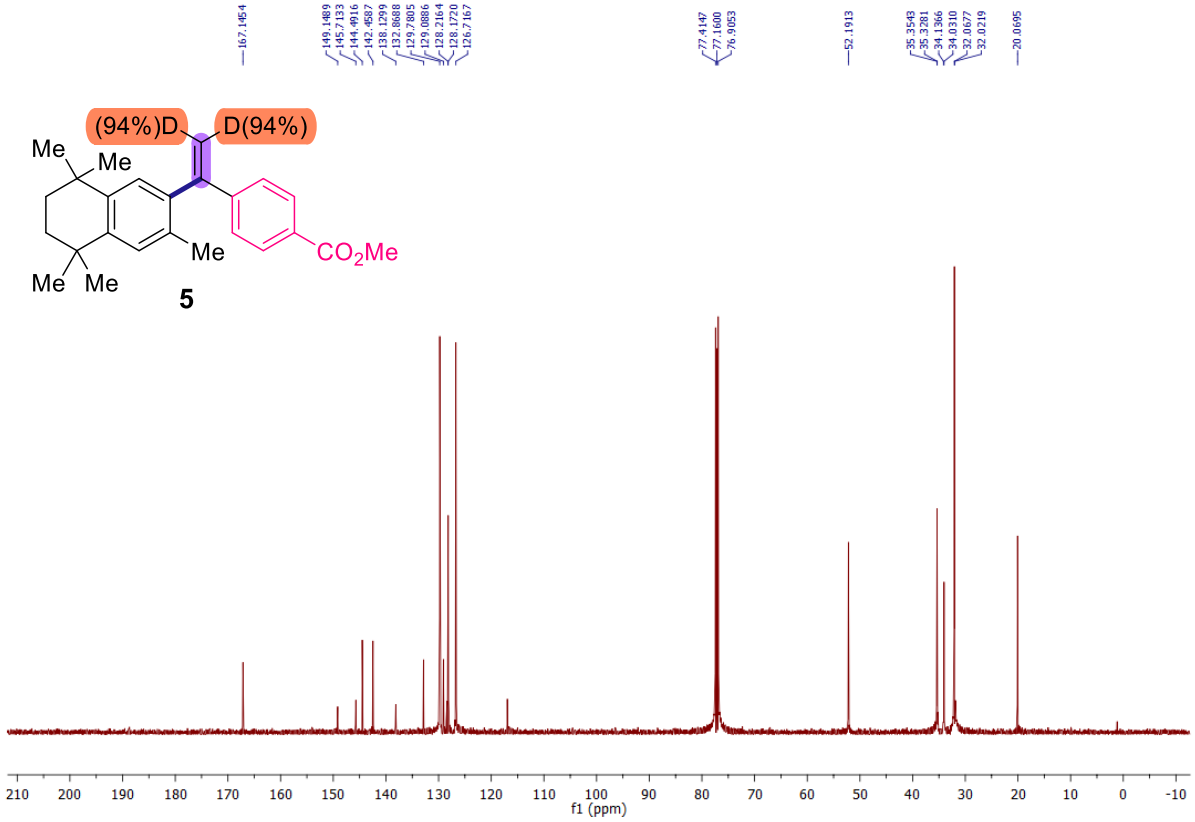


Methyl 4-(1-(3,5,5,8,8-pentamethyl-5,6,7,8-tetrahydronaphthalen-2-yl)vinyl-2,2-d2)benzoate (**5**)

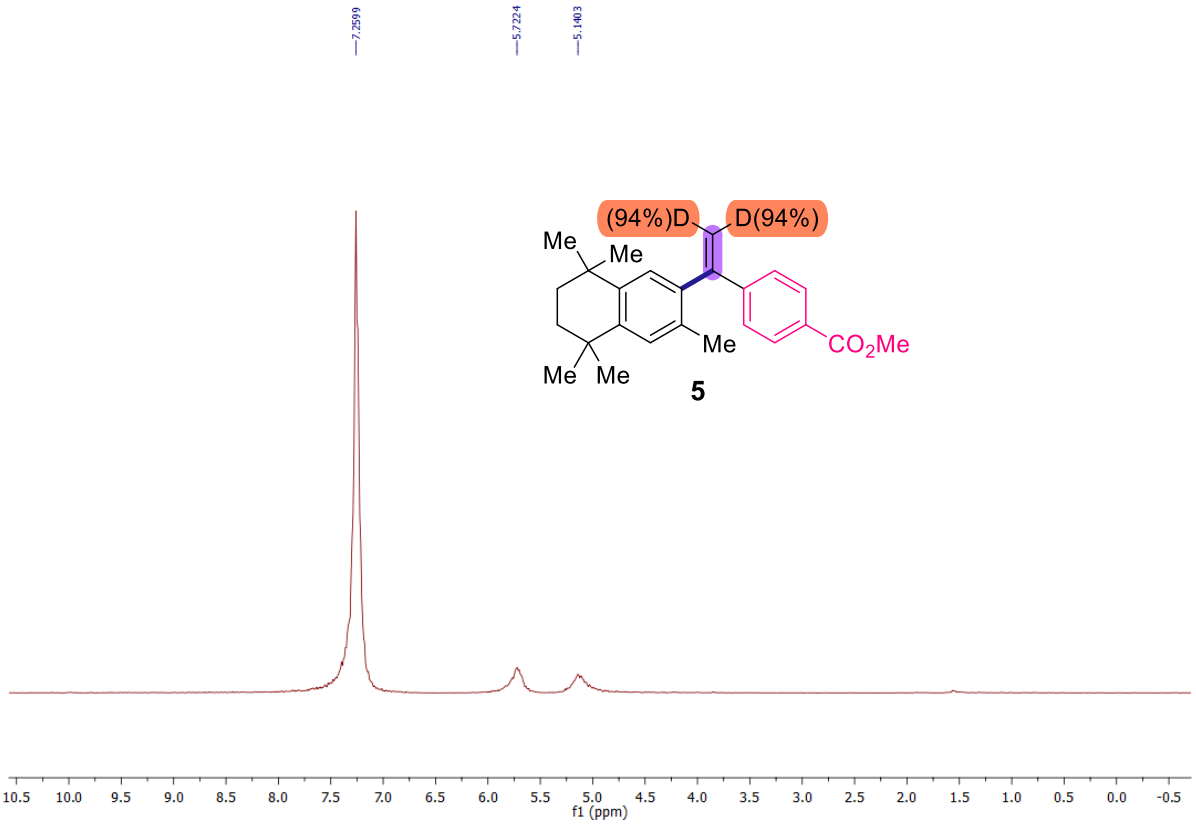
^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)



$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 24 °C)

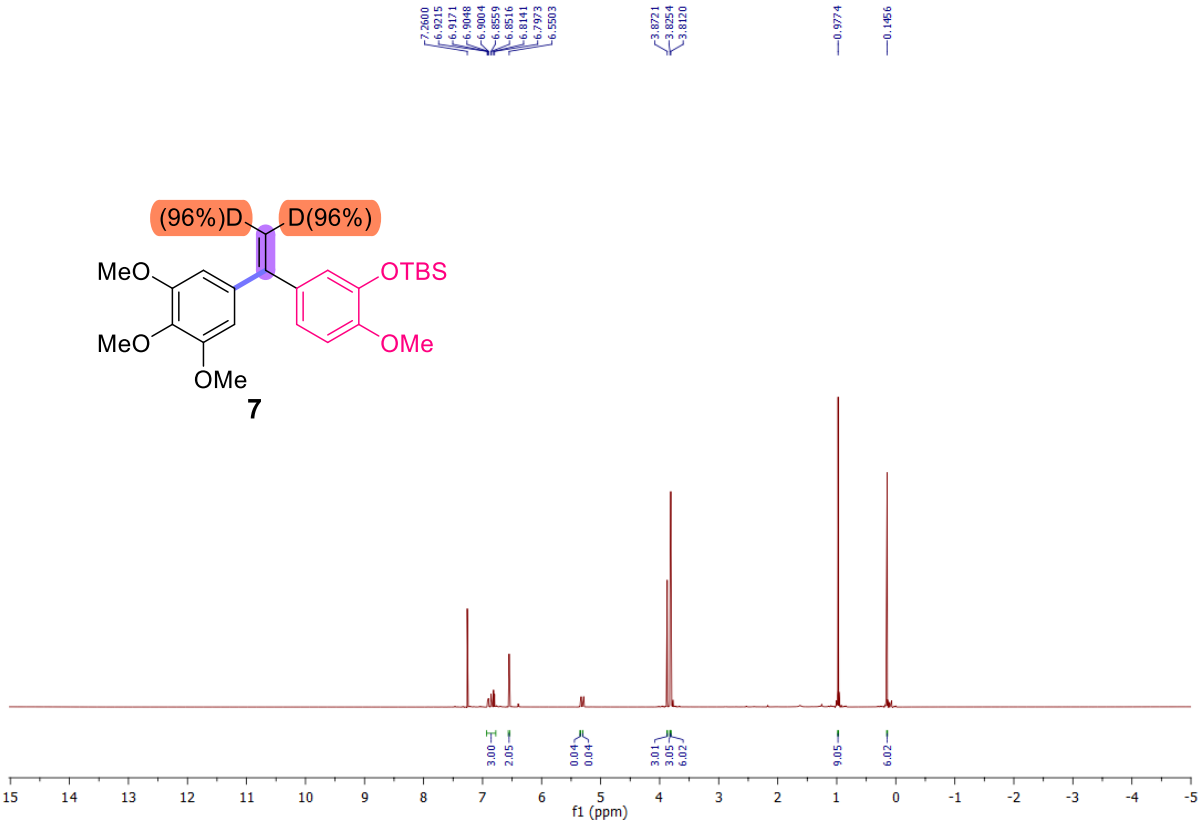


^{2}H NMR (77 MHz, $CHCl_3$, 24 °C)

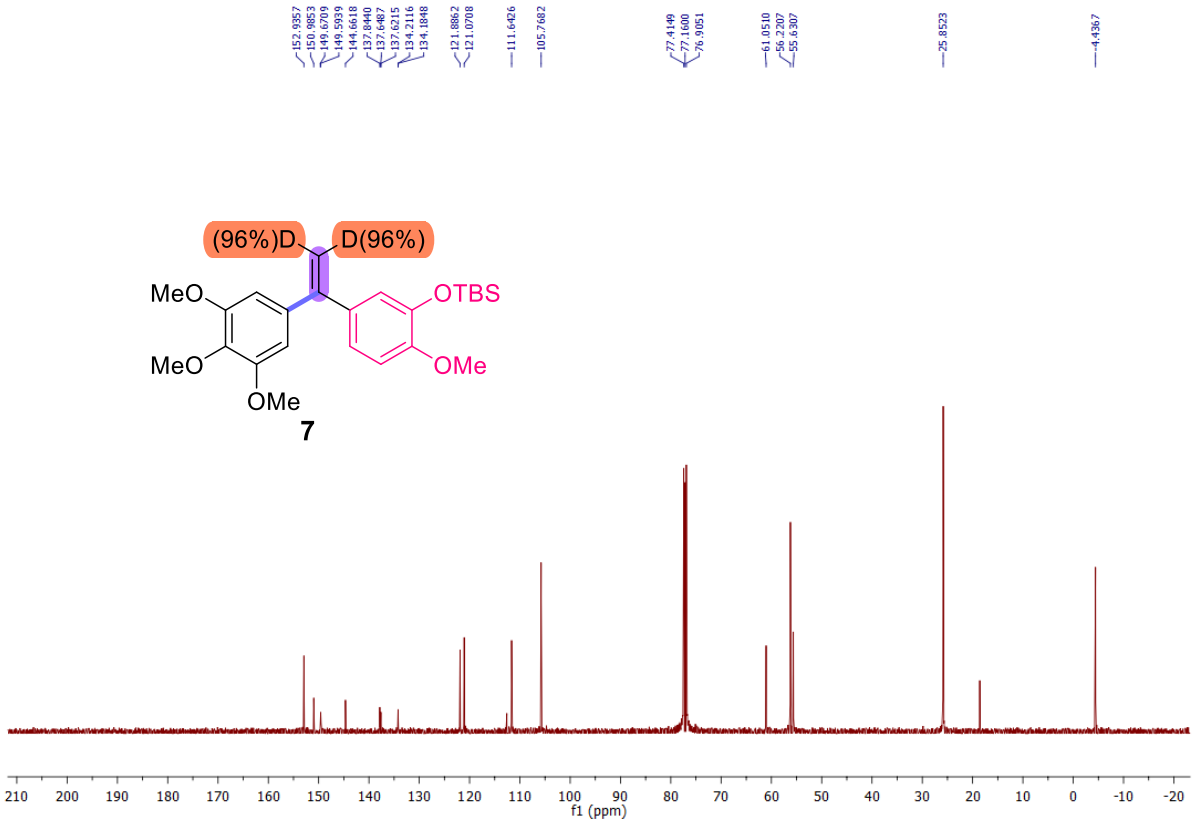


tert-Butyl(2-methoxy-5-(1-(3,4,5-trimethoxyphenyl)vinyl-2,2-d2)phenoxy)dimethylsilane (**7**)

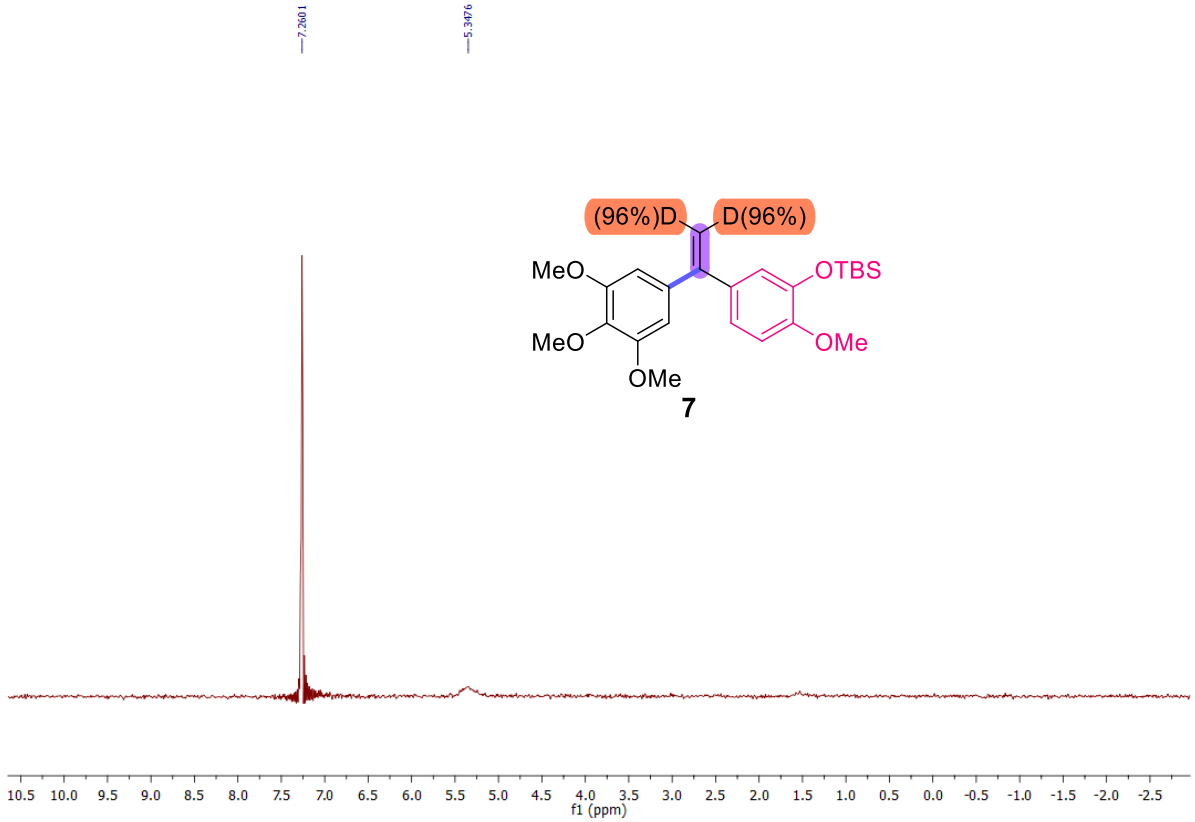
^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)



^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 24 °C)

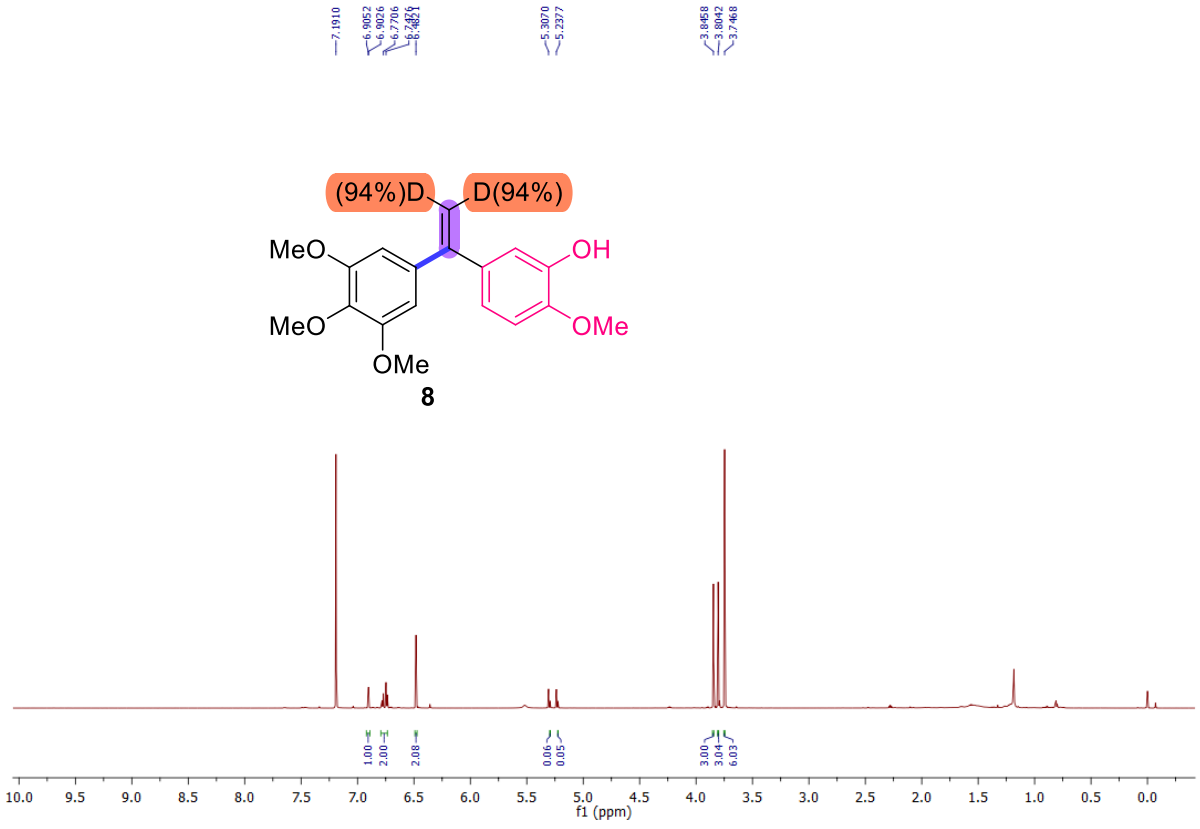


^{2}H NMR (77 MHz, $CHCl_3$, 24 °C)

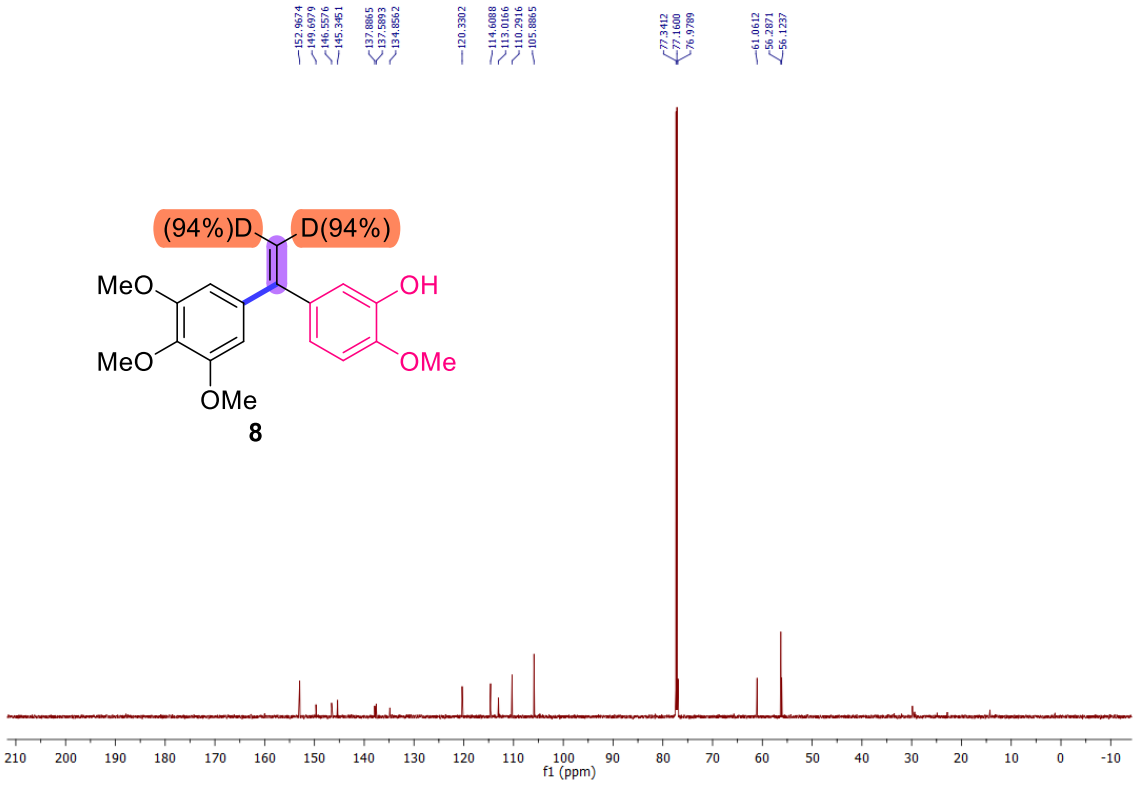


2-Methoxy-5-(1-(3,4,5-trimethoxyphenyl)vinyl-2,2-d2)phenol (**8**)

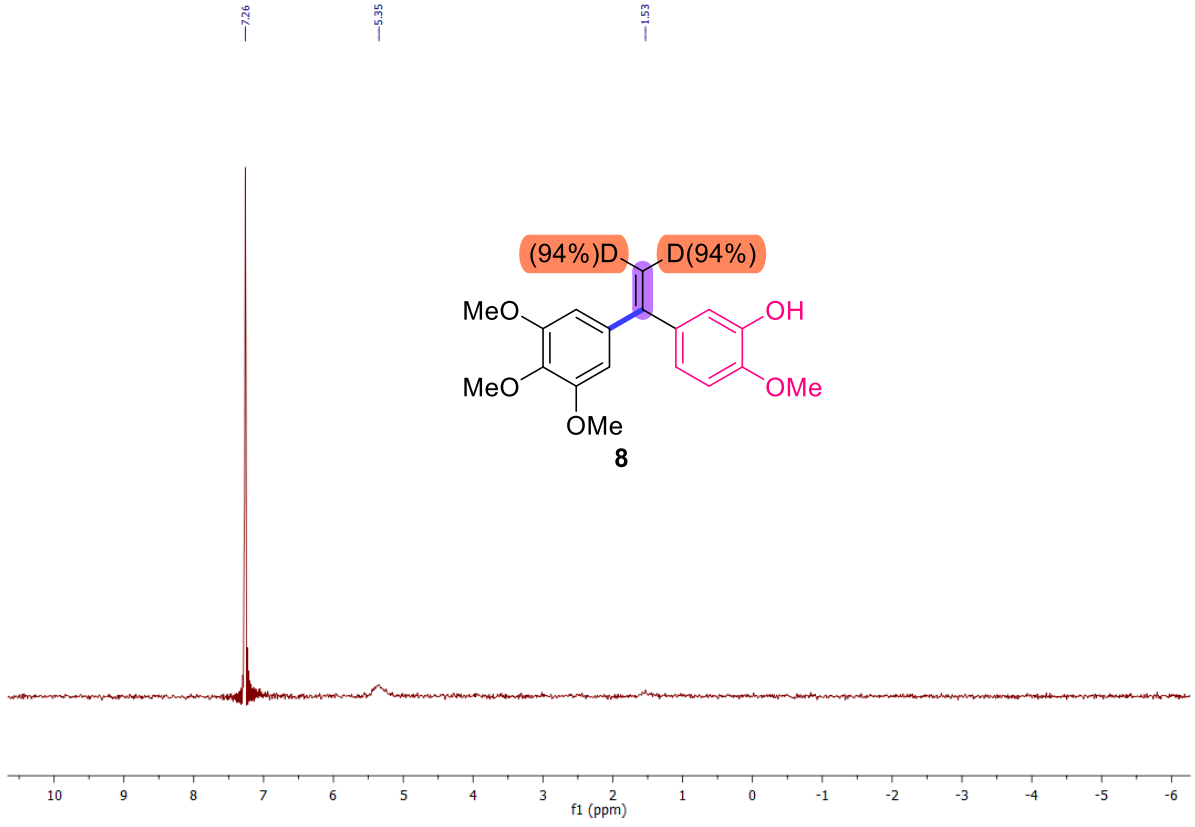
^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)



$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 24 °C)

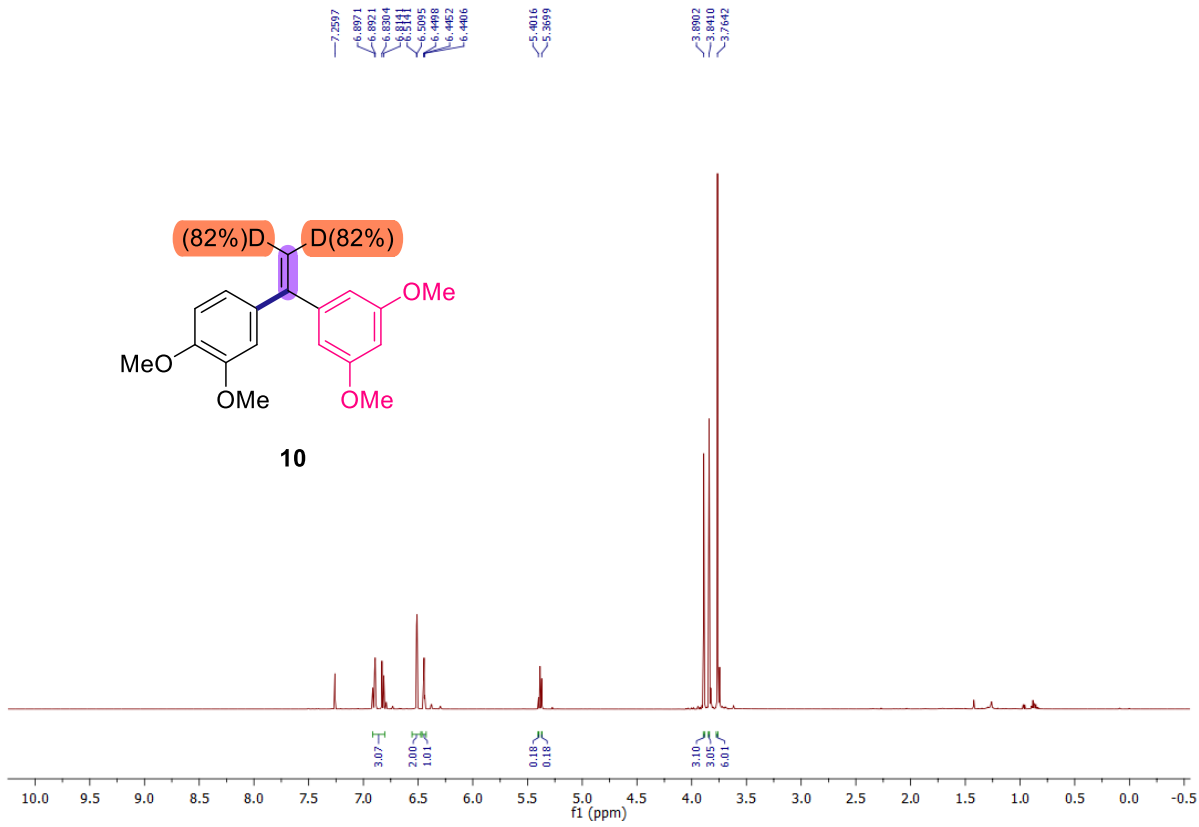


^{2}H NMR (77 MHz, $CHCl_3$, 24 °C)

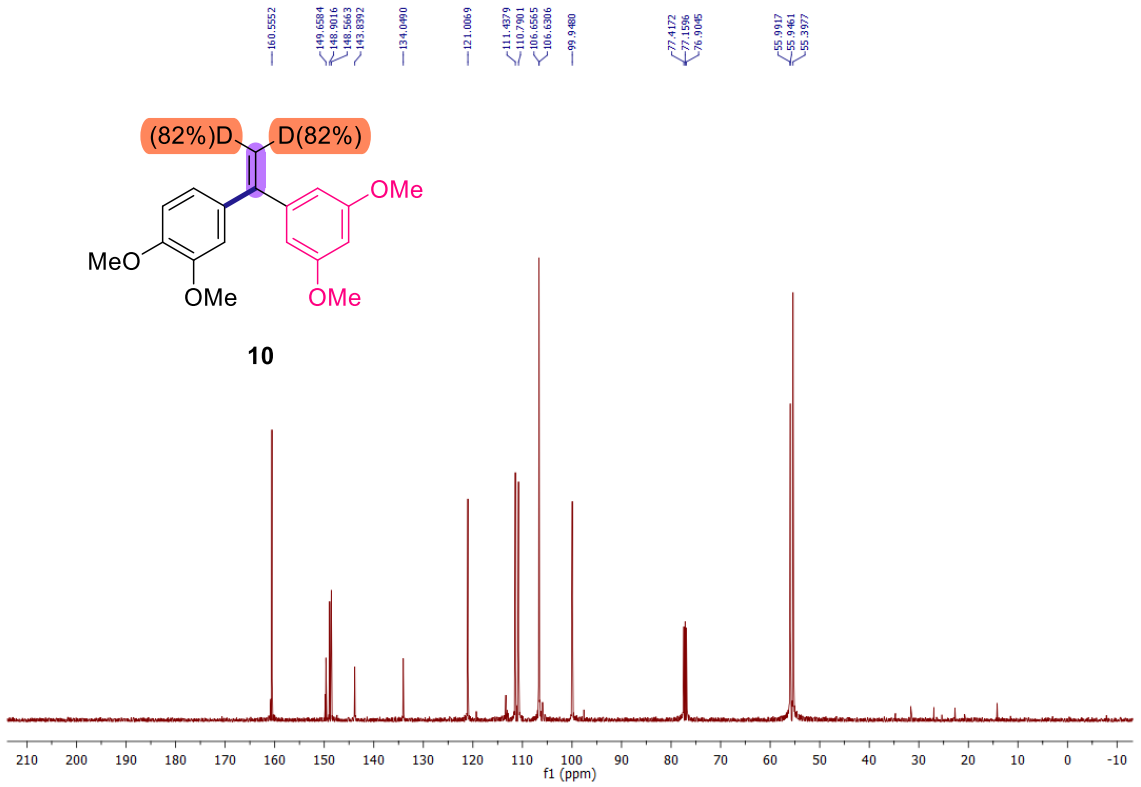


4-(1-(3,5-Dimethoxyphenyl)vinyl-2,2-d2)-1,2-dimethoxybenzene (**10**)

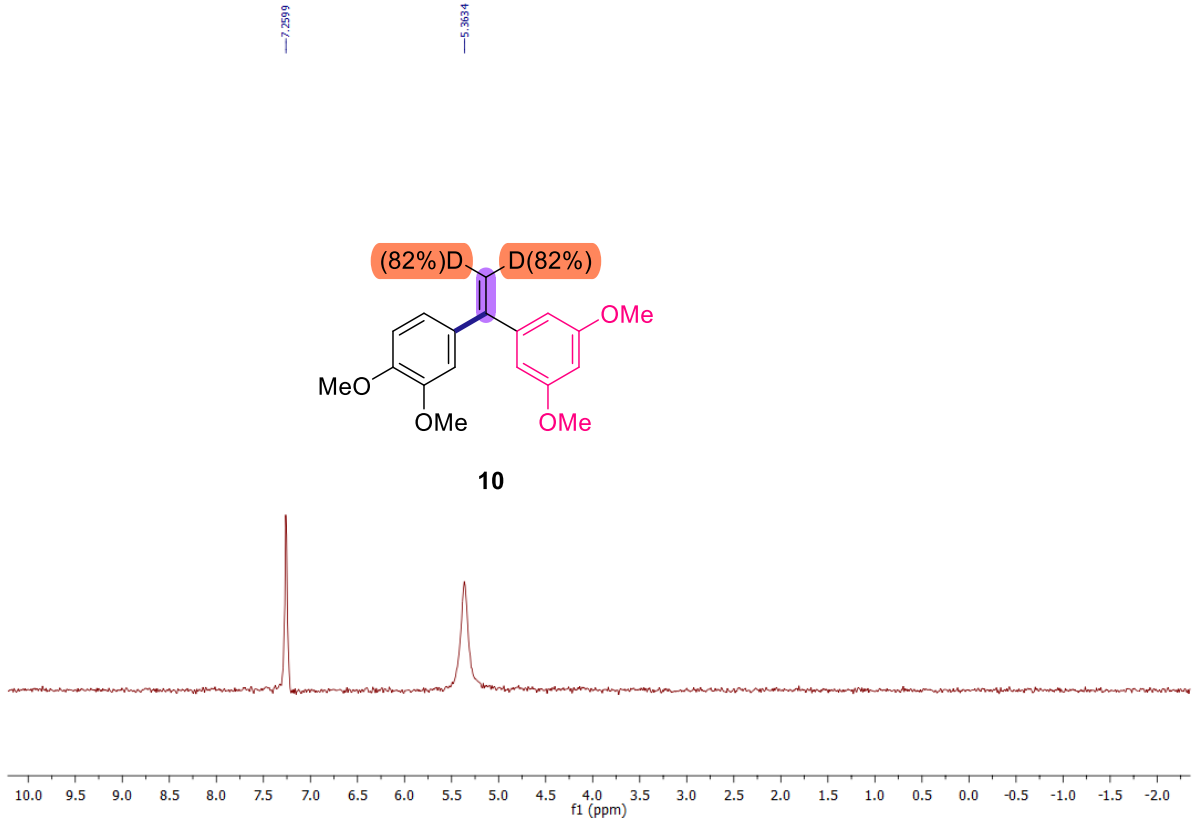
^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)



^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 24 °C)

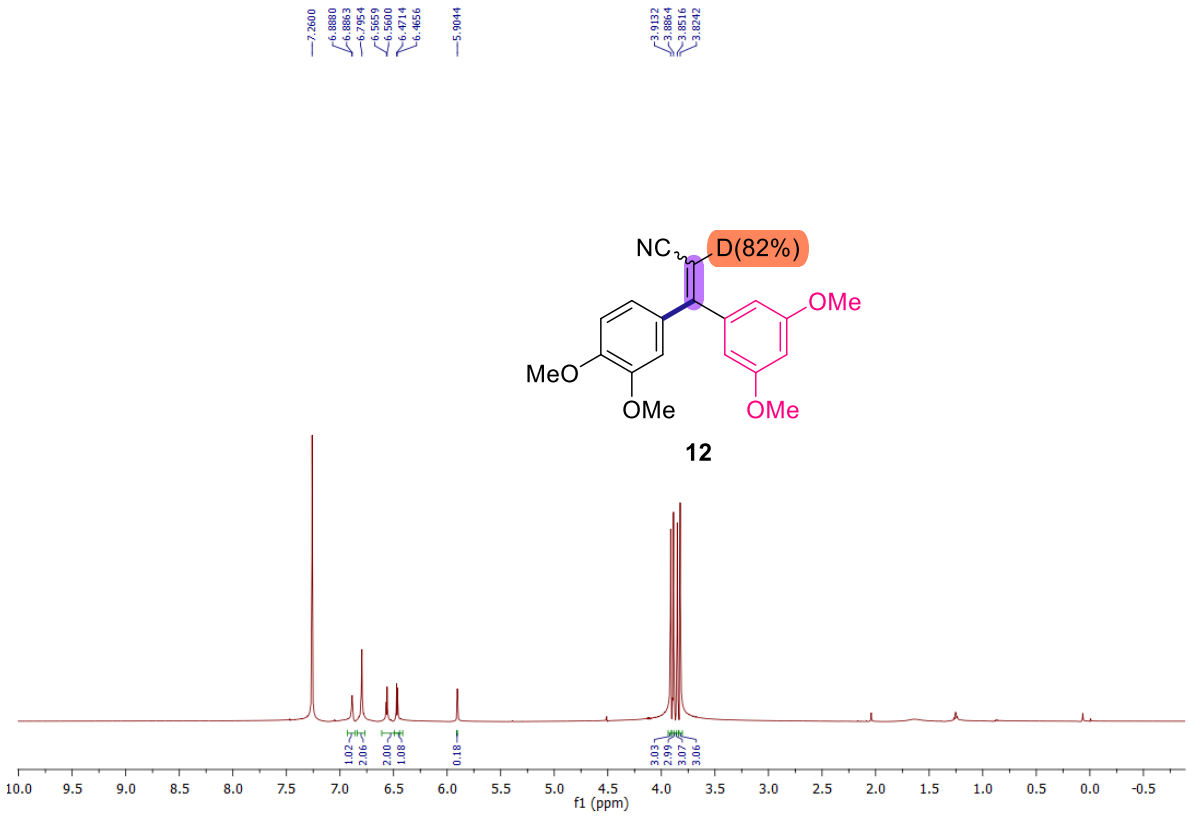


^{2}H NMR (77 MHz, $CHCl_3$, 24 °C)

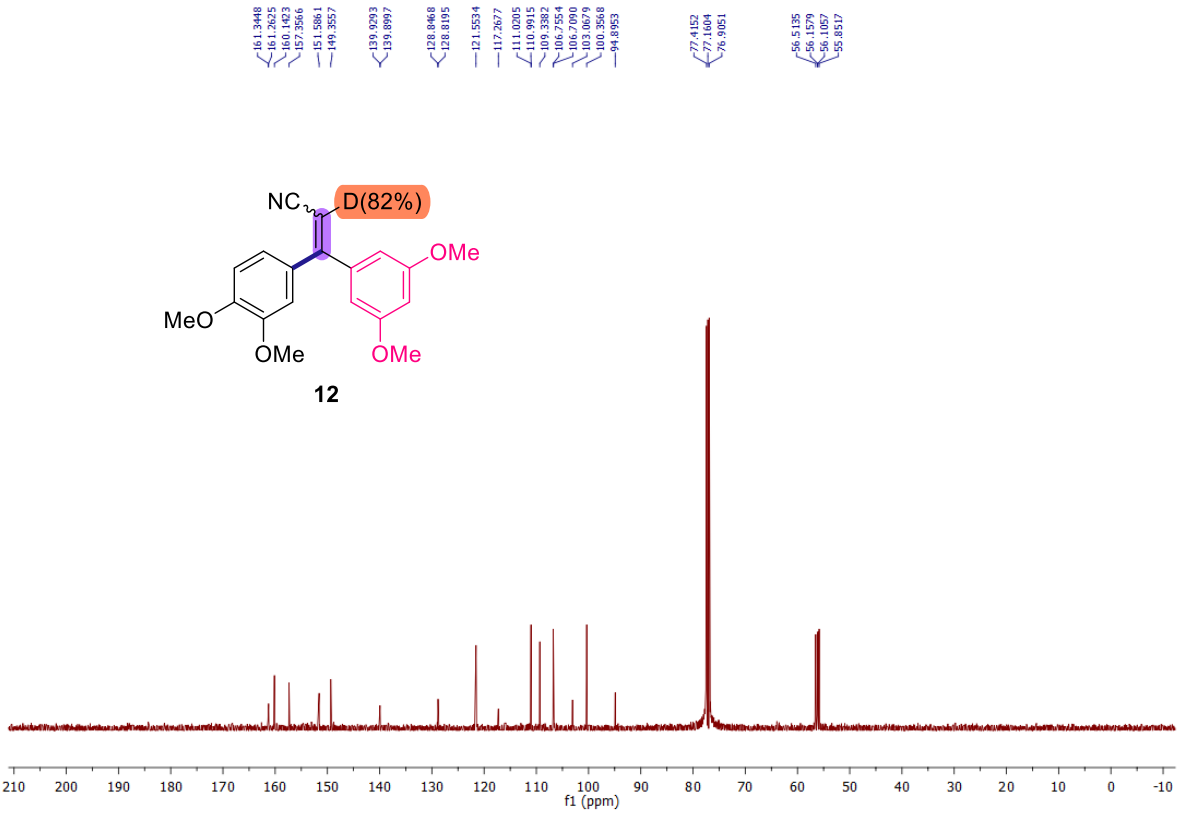


(3,4-Dimethoxyphenyl)-3-(3,5-dimethoxyphenyl)acrylonitrile-d (**12**)

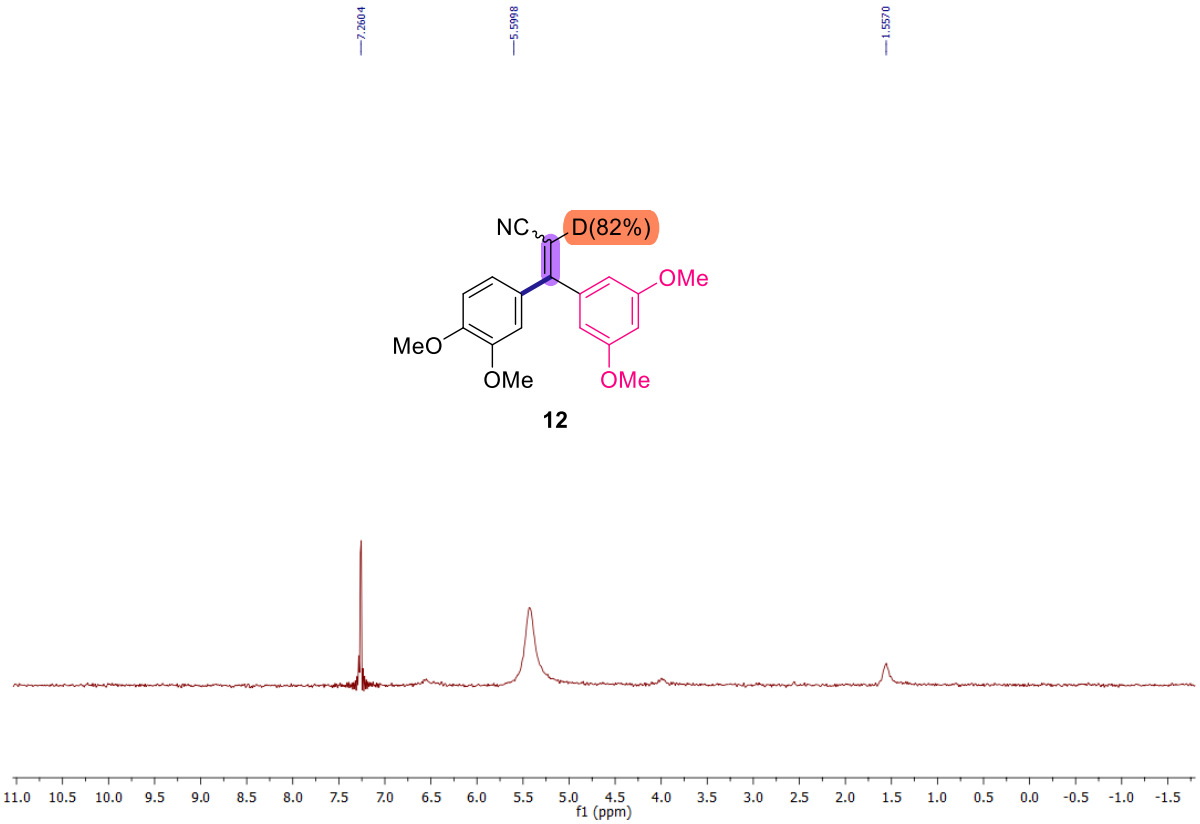
^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)



$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 24 °C)

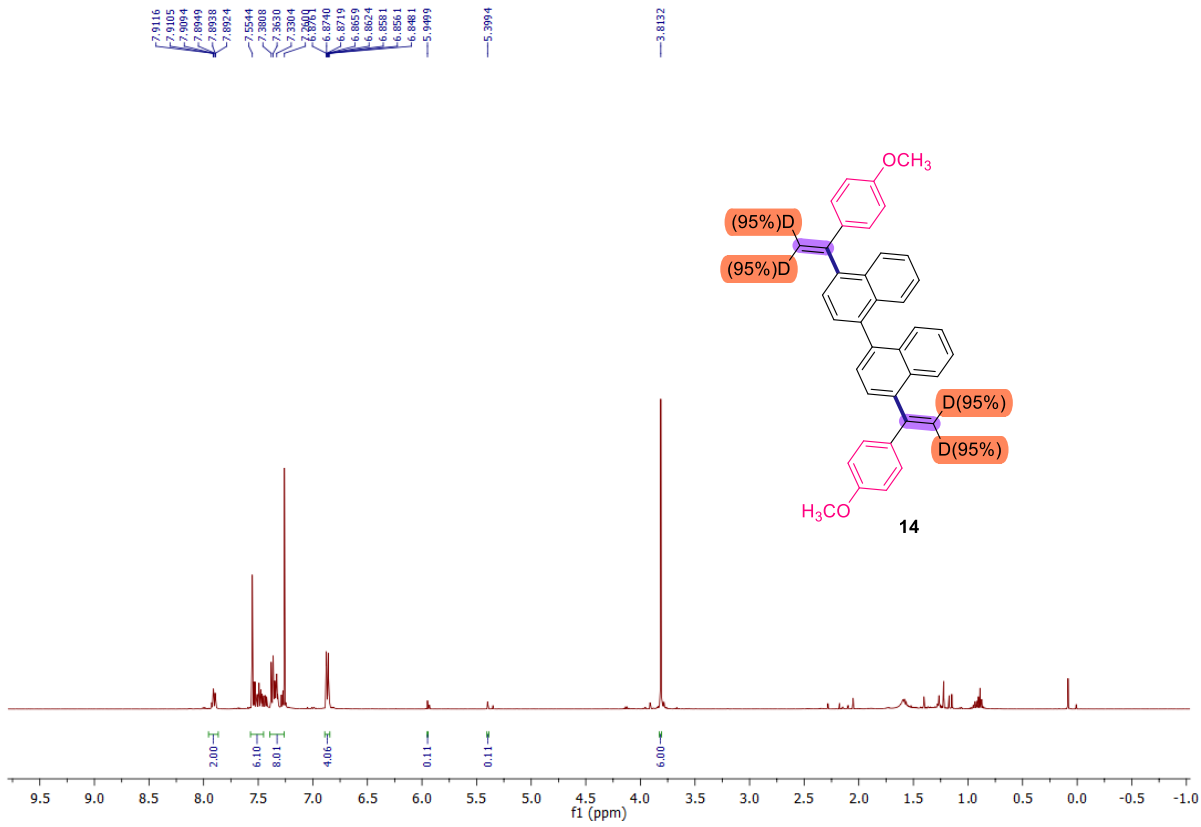


^{2}H NMR (77 MHz, $CHCl_3$, 24 °C)

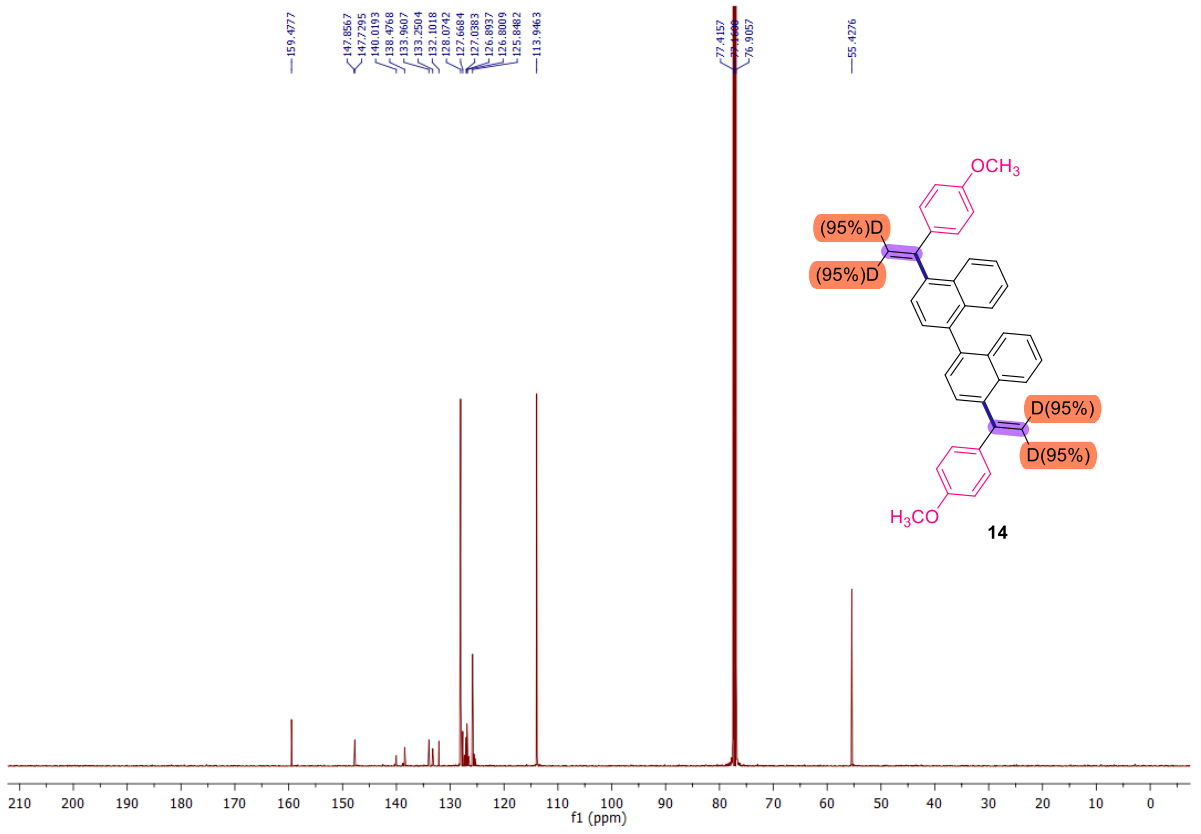


4,4'-*bis*(1-(4-Methoxyphenyl)vinyl-2,2-d2)-1,1'-binaphthalene **(14)**

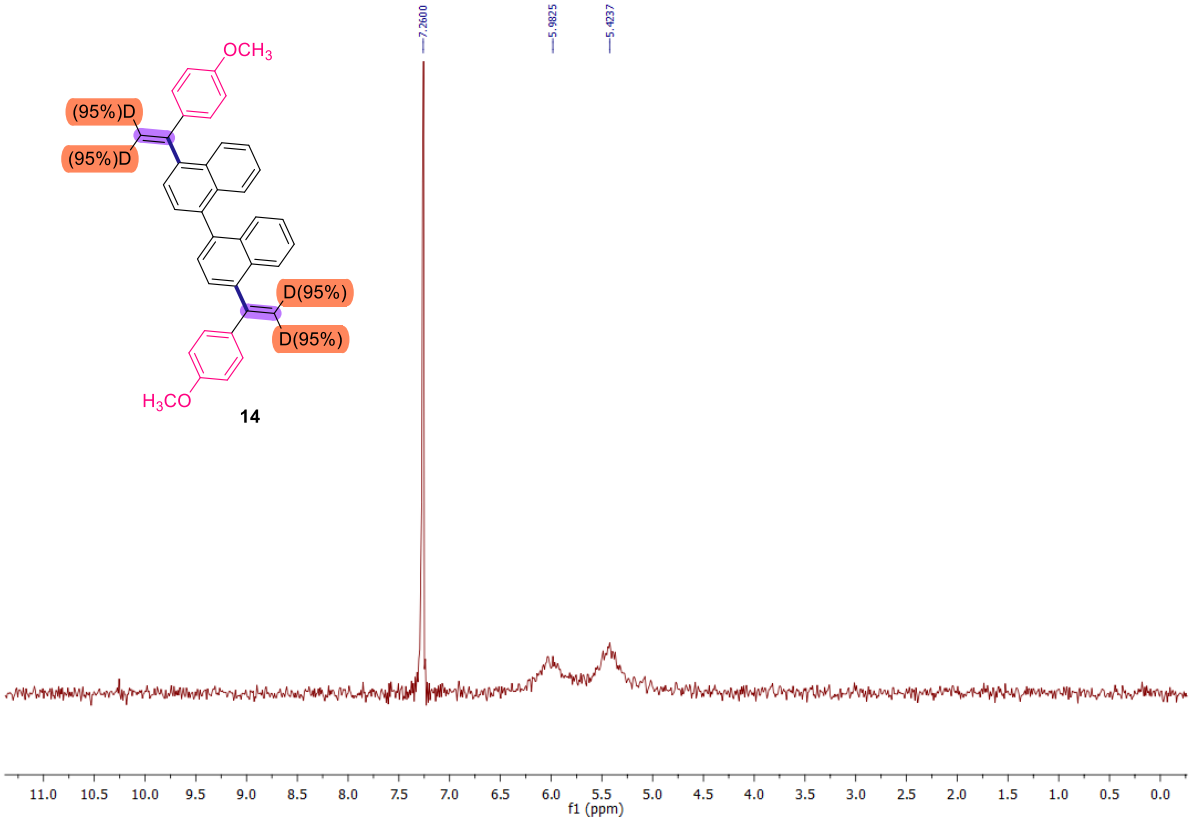
^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)



^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 24 °C)

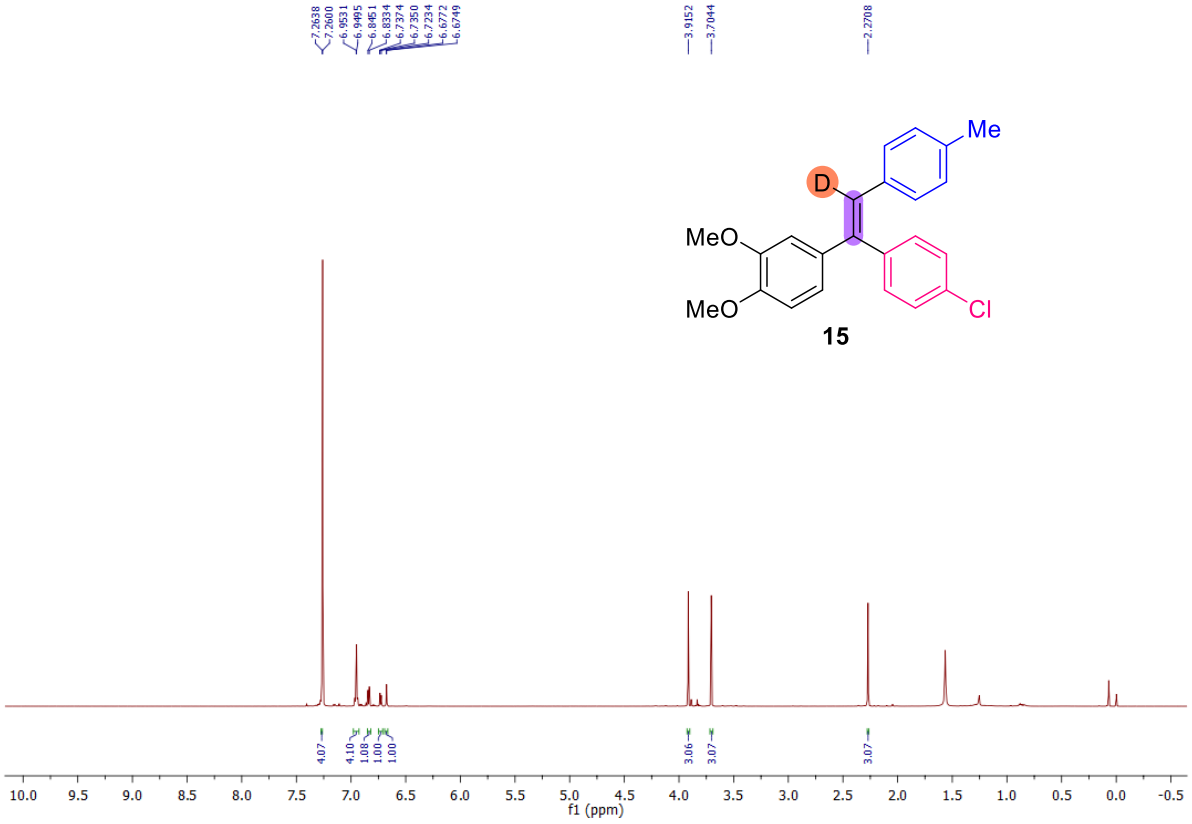


^{2}H NMR (77 MHz, $CHCl_3$, 24 °C)

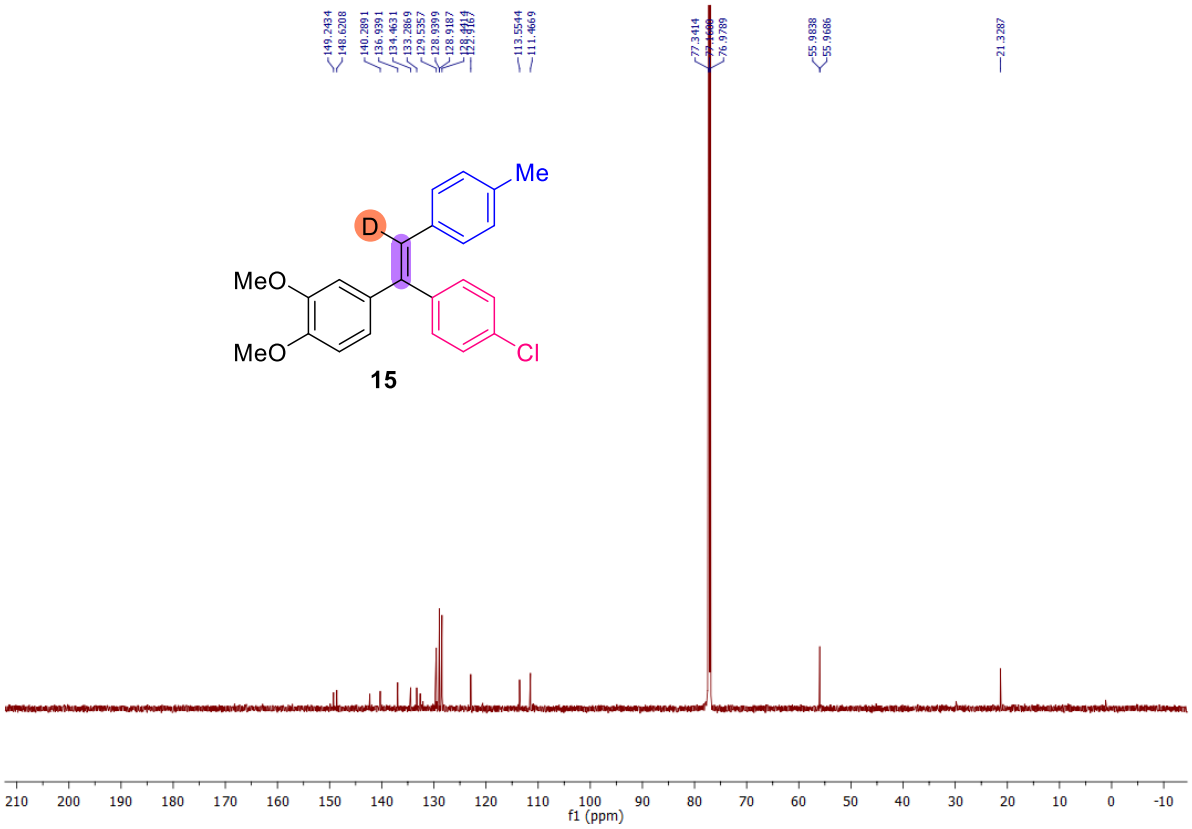


(*E*)-4-(1-(4-Chlorophenyl)-2-(p-tolyl)vinyl-2-d)-1,2-dimethoxybenzene (**15**)

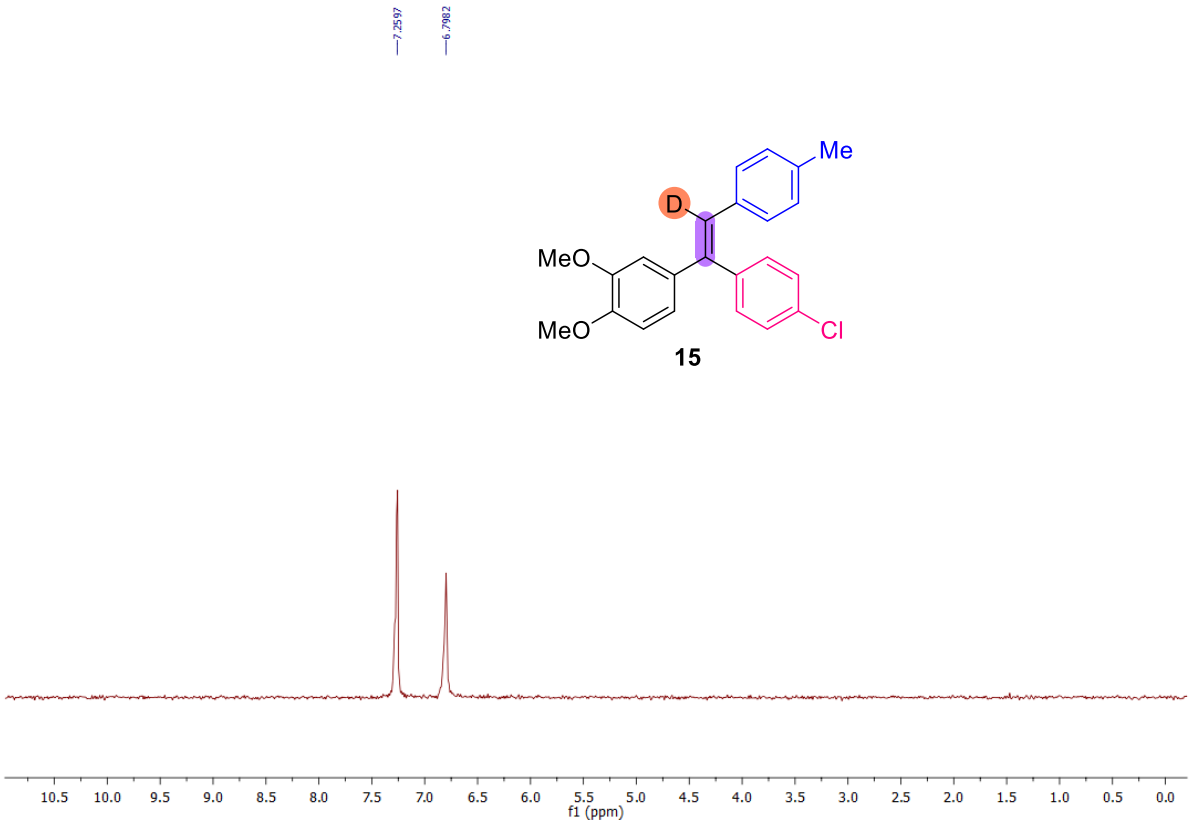
^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)



$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 24 °C)

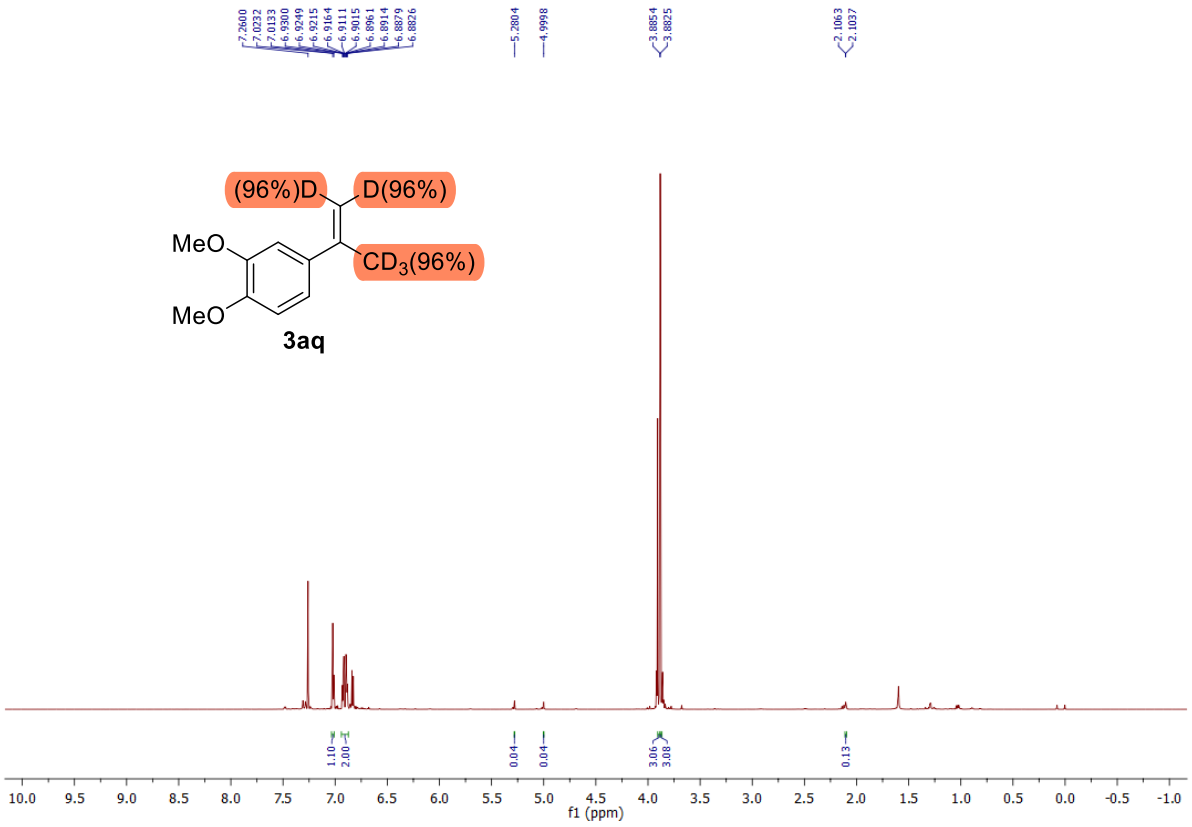


^{2}H NMR (77 MHz, $CHCl_3$, 24 °C)

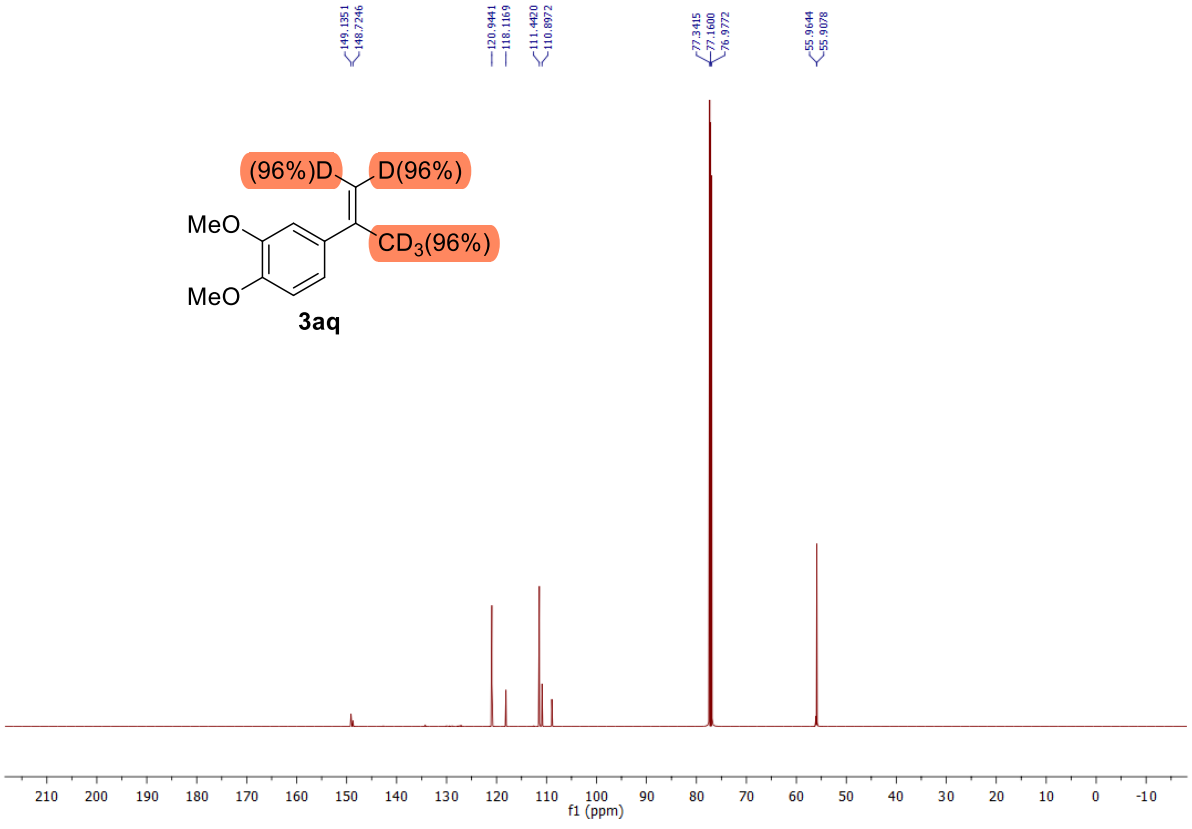


1,2-Dimethoxy-4-(prop-1-en-2-yl-d5)benzene (**3aq**)

^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)



^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 24 °C)



^{2}H NMR (77 MHz, $CHCl_3$, 24 °C)