Supporting Information

A General, Versatile and Divergent Synthesis of Selectively Deuterated Amines

Morgan Lecomte, Mounsef Lahboubi, Pierre Thilmany, Adil El Bouzakhi and Gwilherm Evano*

Laboratoire de Chimie Organique, Service de Chimie et PhysicoChimie Organiques, Université libre de Bruxelles, Avenue F. D. Roosevelt 50, CP160/06, 1050 Brussels, Belgium.

General Information.

All reactions were carried out in oven-dried glassware under an argon atmosphere employing standard techniques in handling air-sensitive materials.

All reagents and solvents were reagent grade. Acetonitrile, dichloromethane and *N,N*-dimethylformamide were freshly distilled from calcium hydride under argon. Tetrahydrofuran and 1,2-dimethoxyethane was freshly distilled from sodium/benzophenone under argon. 1,4-Dioxane (99.5%, Extra Dry over Molecular Sieve, AcroSeal®) and toluene (99.5%, Extra Dry over Molecular Sieve, AcroSeal®) were purchased from ACROS Organics and used as supplied.

Copper(I) iodide (99,999% purity), trifluoromethanesulfonic acid-*d* (98% D), triethylsilane (99% purity) and triethyl(silane-*d*) (97% D) were purchased from Sigma-Aldrich and used as supplied unless otherwise stated. Trifluoromethanesulfonic acid (98+% purity) was purchased from Alfa Aesar and used as supplied. Deuterium oxide (99.9% D) was purchased from Eurisotop and used as supplied. Finely powdered anhydrous cesium carbonate was used for copper-mediated coupling reactions. All other reagents were used as supplied.

Reactions were magnetically stirred and monitored by thin layer chromatography using Merck-Kiesegel 60F_{254} plates or Macherey-Nagel Pre Coated TLC-sheets Alugram® Xtra Sil/UV_{254}. Flash chromatography was performed with silica gel 60 (particle size 35-70 µm) supplied by Merck or silica gel 60 (particle size 15 - 40 µm) supplied by Macherey-Nagel. Yields refer to chromatographically and spectroscopically pure compounds unless otherwise stated.

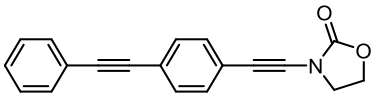
Proton NMR spectra were recorded using an internal deuterium lock at ambient temperature on Bruker 300, Varian 400 MHz or JEOL 400 and 600 MHz spectrometers. Internal reference of δ_H 7.26 was used for $CDCl_3$, δ_H 3.31 was used for CD_3OH and δ_H 3.31 was used for CD_3OD. Data are presented as follows: chemical shift (in ppm on the δ scale relative to $\delta_{TMS} = 0$), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint. = quintuplet, sext. = sextuplet, m = multiplet, br. = broad, app. = apparent), coupling constant (*J*/Hz) and integration. Resonances that are either partially or fully obscured are denoted obscured (obs.). Carbon-13 NMR spectra were recorded at 75 or 100 MHz using $CDCl_3$ (δ_C 77.16), CD_2Cl_2 (δ_C 53.84), CD_3OH (δ_C 49.00) and CD_3OD (δ_C 49.00) as internal references. Fluorine-19 NMR spectra were recorded at 376 MHz using CF_3CH_2OH (δ_F -77.59) as internal reference. Deuterium NMR spectra were recorded at 92 MHz using $C_2D_2Cl_4$ (δ_D 6.00) as internal reference.

Melting points were recorded on a Stuart Scientific Analogue SMP11. Infrared spectra were recorded on a Bruker Alpha (ATR). High resolution mass spectra (HRMS) in positive mode were recorded using a 6520 series quadrupole time-of-flight (Q-TOF) mass spectrometer (Agilent) fitted with a multimode ion source.

Freshly prepared trifluoromethanesulfonic acid-*d*:[S1]

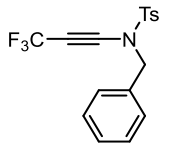
An oven dried 25 mL round bottom flask was successively charged with deuterium oxide (99.9%, 1.5 mL, 82.83 mmol) and trifluoromethanesulfonic anhydride (15 mL, 88.61 mmol). The resulting colorless mixture was stirred and refluxed for 1 hour until persistence of a dark color, then fractionally distilled to afford trifluoromethanesulfonic acid-*d* (>99% D) that could be used without further purification.

Experimental Procedure and Characterization Data: Unreported Starting Ynamides



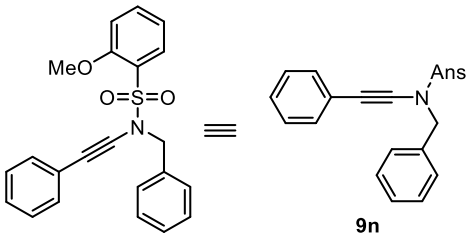
9c

3-{[4-(Phenylethynyl)phenyl]ethynyl}oxazolidin-2-one 9c. This compound was prepared according to a previously reported procedure.[S2] A 25 mL round bottom flask was successively charged with 2-oxazolidinone (2.16 g, 24.8 mmol), {[4-(phenylethynyl)phenyl]ethynyl}copper (1.46 g, 5.52 mmol) and acetonitrile (14 mL). The resulting bright yellow slurry was then treated with *N,N,N',N'*-tetramethylethylenediamine (830 µL, 5.52 mmol) and the reaction mixture was vigorously stirred at rt and under an atmosphere of oxygen (balloon). After complete disappearance of the alkynylcopper reagent (complete dissolution to a deep blue homogeneous reaction mixture: typically 24-48 h), the crude reaction mixture was filtered over a plug of silica gel (washed with EtOAc) and concentrated under reduced pressure. The residue was finally purified by flash chromatography over silica gel (cyclohexane/CH_2Cl_2: gradient from 30/70 to 0/100) to afford the desired ynamide as a white solid. Yield: 50% (790 mg, 2.75 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.56-7.31 (m, 9H), 4.54-4.44 (m, 2H), 4.06-3.96 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.9, 131.7, 131.6, 131.5, 128.6, 128.5, 123.1 (2C), 122.1, 91.3, 89.1, 80.8, 71.2, 63.2, 47.1; ESIHRMS *m/z* calcd for $C_{19}H_{14}NO_2$ $[M+H]^+$ 288.1019, found 288.1025.

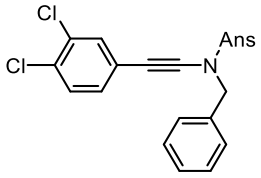


9k

***N*-(*p*-Toluenesulfonyl)-*N*-benzyl-trifluoromethylethynylamine 9k**. This compound was prepared according to a previously reported procedure.[S3] A 250 mL round bottom flask was charged with copper iodide (800 mg, 4.20 mmol), potassium carbonate (1.16 g, 8.40 mmol), *N,N,N',N'*-tetramethylethylenediamine (625 µL, 4.20 mmol) and *N*,*N*-dimethylformamide (12.9 mL). The resulting deep blue mixture was vigorously stirred at rt under air atmosphere for 15 minutes. Trimethyl(trifluoromethyl)silane (830 µL, 5.60 mmol) was next added and the resulting deep green mixture was stirred for an additional 5 minutes under air atmosphere, then cooled to 0 °C. A solution of *N*-(p-toluenesulfonyl)-*N*-benzyl-ethynylamine (799 mg, 2.80 mmol) and trimethyl(trifluoromethyl)silane (830 µL, 5.60 mmol) in *N*,*N*-dimethylformamide (12.9 mL), previously cooled to 0 °C, was then added in one portion. The reaction mixture was stirred at 0 °C for 30 minutes under air atmosphere, allowed to warm to rt, and stirred for an additional 24 hours before being quenched with water (30 mL). The layers were separated and the aqueous layer was extracted with Et_2O (3x). The combined organic layers were washed with water (3x), brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was finally purified by flash column chromatography (petroleum ether/EtOAc: 95/5) to afford the desired trifluoromethylated ynamide as an off white solid. Yield: 38% (372 mg, 1.05 mmol). Mp: 37 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 8.4 Hz, 2H), 7.36-7.30 (m, 5H), 7.25-7.21 (m, 2H), 4.55 (s, 2H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.8, 134.3, 133.2, 130.2, 129.0, 128.9, 128.9, 127.9, 115.6 (q, J_{C-F} = 256.8 Hz), 81.5 (q, J_{C-F} = 6.2 Hz), 60.9 (q, J_{C-F} = 54.0 Hz), 55.4, 21.9; ^{19}F (376 MHz, $CDCl_3$): δ -48.7; IR (ATR): ν_{max} 2880, 2254, 1598, 1368, 1170, 1127, 1088, 942, 813, 714, 663 cm^{-1}; ESIHRMS *m/z* calcd for $C_{17}H_{18}F_3N_2O_2S$ $[M+NH_4]^+$ 371.1036, found 371.1040.



***N*-(*o*-Anisylsulfonyl)-*N*-benzyl-phenylethynylamine 9n**. This compound was prepared according to a previously reported procedure.[S4] A pressure tube was charged with *N*-(*o*-anisylsulfonyl)-*N*-benzylamine **16**. (2.50 g, 9.00 mmol), potassium carbonate (2.50 g, 18.0 mmol), copper sulfate pentahydrate (225 mg, 900 µmol), 1,10-phenanthroline (324 mg, 1.80 mmol) and (bromoethynyl)benzene (1.80 g, 9.90 mmol). The tube was fitted with a rubber septum, evacuated under high vacuum and backfilled with argon three times. Dry toluene (20 mL) was next added, the rubber septum was replaced by a Teflon-coated screw cap and the mixture was heated at 70 °C for 48 hours. The reaction mixture was then cooled to rt, filtered over a plug of silica gel (washed with EtOAc) and concentrated under reduced pressure. The crude residue was finally purified by flash column chromatography over silica gel (petroleum ether/EtOAc: 80/20) affording the desired ynamide as a dark orange solid. Yield: 98% (3.3 g, 8.8 mmol). Mp: 75 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.02 (dd, J = 7.8 and 1.7 Hz, 1H), 7.59 (ddd, J = 8.4, 7.5 and 1.7 Hz, 1H), 7.38-7.29 (m, 5H), 7.22-7.14 (m, 5H), 7.08 (app. td, J = 7.5 and 0.9 Hz, 1H), 7.01 (d, J = 8.4 Hz, 1H), 4.75 (s, 2H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.3, 135.7, 135.4, 132.1, 131.1, 128.9, 128.6, 128.3, 128.2, 127.5, 126.2, 123.3, 120.4, 112.4, 82.8, 71.5, 56.2, 56.0; IR (ATR): ν_{max} 3031, 2945, 2234, 1592, 1481, 1357, 1282, 1162, 1069, 1017, 911, 804, 779, 752, 731, 695 cm^{-1}; ESIHRMS m/z calcd for $C_{22}H_{20}NO_3S$ $[M+H]^+$ 378.1158, found 378.1141.



***N*-(*o*-Anisylsulfonyl)-(3,4-dichlorophenyl)ethynylamine 9o**. This compound was prepared according to a previously reported procedure.[S4] A pressure tube was charged with the *N*-(*o*-anisylsulfonyl)-*N*-benzylamine **16**. (881 mg, 3.18 mmol), potassium carbonate (879 mg, 6.36 mmol), copper sulfate pentahydrate (79 mg, 318 µmol), 1,10-phenanthroline (115 mg, 636 µmol) and 4-(bromoethynyl)-1,2-dichlorobenzene (875 mg, 3.50 mmol). The tube was fitted with a rubber septum, evacuated under high vacuum and backfilled with argon three times. Dry toluene (3.2 mL) was next added, the rubber septum was replaced by a Teflon-coated screw cap and the mixture was heated at 70 °C for 48 hours. The reaction mixture was then cooled to rt, filtered over a plug of silica gel (washed with EtOAc) and concentrated under reduced pressure. The crude residue was finally purified by flash column chromatography over silica gel (petroleum ether/EtOAc: 80/20) affording the desired ynamide as a yellow solid. Yield: 69% (1.0 g, 2.2 mmol). Mp: 84 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.01 (dd, J = 8.1 and 1.8 Hz, 1H), 7.61 (ddd, J = 8.4, 7.5 and 1.7 Hz, 1H), 7.35-7.29 (m, 5H), 7.26 (obs. d, J = 8.3 Hz, 1H), 7.21 (d, J = 1.9 Hz, 1H), 7.10 (ddd, J = 7.9, 7.5 and 1.0 Hz, 1H), 7.02 (d, J = 8.4 Hz, 1H), 6.97 (dd, J = 8.4 and 1.9 Hz, 1H), 4.73 (s, 2H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 157.7, 136.3, 135.6, 132.6, 132.5, 132.1, 131.8, 130.6, 130.3, 129.0, 128.9, 128.7, 126.1, 123.7, 120.7, 113.0, 85.3, 69.9, 56.6, 56.2; IR (ATR): ν_{max} 3114, 3067, 2238, 1482, 1355, 1283, 1161, 1070, 1017, 830, 819, 806, 758, 721, 693, 610 cm^{-1}; ESIHRMS m/z calcd for $C_{22}H_{18}Cl_2NO_3S$ $[M+H]^+$ 446.0379, found 446.0387.

Experimental Procedure and Characterization Data: Reduction/Reductive Deuteration of Ynamides

General procedure I: synthesis of amines

To a vigorously stirred solution of the ynamide (400 µmol) in dichloromethane (1.5 mL) under an argon atmosphere was added triethylsilane (320 µL, 2.0 mmol). Trifluoromethanesulfonic acid (88 µL, 1.0 mmol) was then added dropwise at 0 °C and the mixture was stirred at rt overnight. The resulting yellow/brown reaction mixture was then poured into a 1M aqueous solution of NaOH. The layers were separated and the aqueous layer was extracted with dichloromethane (2x). Combined organic layers were dried over $MgSO_4$, filtered and concentrated. The crude residue was finally purified by flash column chromatography over silica gel to give the desired amine.

General procedure II: synthesis of α-deuterated amines

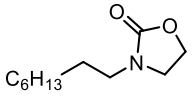
To a vigorously stirred solution of the ynamide (300 µmol) in dichloromethane (1.1 mL) under an argon atmosphere was added triethyl(silane-*d*) (240 µL, 1.5 mmol). Trifluoromethanesulfonic acid (66 µL, 750 µmol) was then added dropwise at 0 °C and the mixture was stirred at rt overnight. The resulting yellow/brown reaction mixture was then poured into a 1M aqueous solution of NaOH. The layers were separated and the aqueous layer was extracted with dichloromethane (2x). Combined organic layers were dried over $MgSO_4$, filtered and concentrated. The crude residue was finally purified by flash column chromatography over silica gel to give the desired α,α-deuterated amine.

General procedure III: synthesis of β-deuterated amines

To a vigorously stirred solution of the ynamide (300 µmol) in dichloromethane (1.1 mL) under an argon atmosphere was added triethylsilane (240 µL, 1.5 mmol). Trifluoromethanesulfonic acid-*d* (66 µL, 750 µmol) was then added dropwise at 0 °C and the mixture was stirred at rt overnight. The resulting yellow/brown reaction mixture was then poured into a 1M aqueous solution of NaOH. The layers were separated and the aqueous layer was extracted with dichloromethane (2x). Combined organic layers were dried over $MgSO_4$, filtered and concentrated. The crude residue was finally purified by flash column chromatography over silica gel to give the desired β,β-deuterated amine.

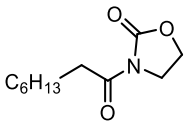
General procedure IV: synthesis of α,β-deuterated amines

To a vigorously stirred solution of the ynamide (300 µmol) in dichloromethane (1.1 mL) under an argon atmosphere was added triethyl(silane-*d*) (240 µL, 1.5 mmol). Trifluoromethanesulfonic acid-*d* (66 µL, 750 µmol) was then added dropwise at 0 °C and the mixture was stirred at rt overnight. The resulting yellow/brown reaction mixture was then poured into a 1M aqueous solution of NaOH. The layers were separated and the aqueous layer was extracted with dichloromethane (2x). Combined organic layers were dried over $MgSO_4$, filtered and concentrated. The crude residue was finally purified by flash column chromatography over silica gel to give the desired α,α,β,β-deuterated amine.



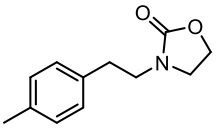
13a

3-Octyloxazolidin-2-one 13a. Prepared according to general procedure I starting from 350 µmol of the corresponding ynamide. Yield: 72% (50 mg, 251 µmol). Solvent system for flash column chromatography: cyclohexane/EtOAc: 50/50; White solid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.33-4.26 (m, 2H), 3.57-3.49 (m, 2H), 3.23 (t, J = 7.3 Hz, 2H), 1.52 (quint., J = 7.1 Hz, 2H), 1.35-1.19 (m, 10H), 0.86 (app. t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.6, 61.7, 44.6, 44.4, 31.8, 29.3, 29.2, 27.5, 26.7, 22.7, 14.2; ESIHRMS *m/z* calcd for $C_{11}H_{22}NO_2$ $[M+H]^+$ 200.1645, found 200.1645.



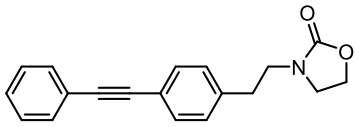
14a

3-Octanoyloxazolidin-2-one 14a. Solvent system for flash column chromatography: cyclohexane/EtOAc: 90/10; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.38 (t, J = 8.1 Hz, 2H), 3.98 (t, J = 8.1 Hz, 2H), 2.87 (t, J = 7.6 Hz, 2H), 1.62 (quint., J = 7.4 Hz, 2H), 1.37-1.19 (m, 8H), 0.85 (app. t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.7, 153.6, 62.1, 42.6, 35.1, 31.7, 29.1, 29.1, 24.3, 22.6, 14.1; IR (ATR): ν_{max} 2956, 2927, 2857, 1779, 1700, 1387, 1363, 1335, 1273, 1225, 1131, 1098, 1040, 1008, 761, 702; ESIHRMS *m/z* calcd for $C_{11}H_{20}NO_3$ $[M+H]^+$ 214.1438, found 214.1436.



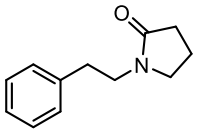
13b

3-(4-Methylphenethyl)oxazolidin-2-one 13b. Prepared according to general procedure I. Yield: 77% (63 mg, 307 µmol). Solvent system for flash column chromatography: cyclohexane/EtOAc: 50/50; White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11 (app. s, 4H), 4.27-4.21 (m, 2H), 3.53-3.48 (m, 2H), 3.44-3.38 (m, 2H), 2.84 (t, J = 7.4 H, 2H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.5, 136.3, 135.4, 129.5, 128.7, 61.8, 45.8, 45.2, 33.8, 21.2; ESIHRMS *m/z* calcd for $C_{12}H_{16}NO_2$ $[M+H]^+$ 206.1176, found 206.1175.



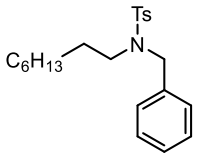
13c

3-[4-(Phenylethynyl)phenethyl]oxazolidin-2-one 13c. Prepared according to general procedure I starting from 350 µmol of the corresponding ynamide. Yield: 42% (43 mg, 148 µmol). Solvent system for flash column chromatography: cyclohexane/EtOAc: 30/70; Pale yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.56-7.46 (m, 4H), 7.38-7.31 (m, 3H), 7.22 (d, J = 8.2 Hz, 2H), 4.29-4.20 (m, 2H), 3.53 (t, J = 7.3 Hz, 2H), 3.44-3.35 (m, 2H), 2.91 (t, J = 7.3 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.5, 138.8, 132.0, 131.7, 128.9, 128.5, 128.4, 123.3, 121.8, 89.5, 89.2, 61.9, 45.5, 45.3, 34.2; ESIHRMS *m/z* calcd for $C_{19}H_{18}NO_2$ $[M+H]^+$ 292.1332, found 292.1306.



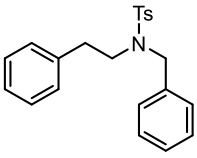
13d

1-Phenethylpyrrolidin-2-one 13d. Prepared according to general procedure I. Yield: 62% (47 mg, 248 µmol). Solvent system for flash column chromatography: cyclohexane/EtOAc: 20/80; White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.27 (m, 2H), 7.23-7.19 (m, 3H), 3.53 (t, J = 7.2 Hz, 2H), 3.24 (t, J = 7.2 Hz, 2H), 2.84 (t, J = 7.6 Hz, 2H), 2.34 (t, J = 8.0 Hz, 2H), 1.94 (quint., J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.0, 139.0, 128.8, 128.7, 126.6, 47.8, 44.1, 34.0, 31.1, 18.2; ESIHRMS *m/z* calcd for $C_{12}H_{16}NO$ $[M+H]^+$ 190.1226, found 190.1226. This compound has been previously reported.[S5]



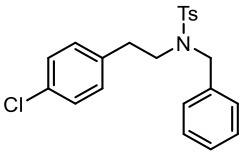
13e

***N*-Benzyl-*N*-octyl-*p*-toluenesulfonamide 13e**. Prepared according to general procedure I. Yield: 74% (110 mg, 294 µmol). Solvent system for flash column chromatography: cyclohexane/EtOAc: 90/10; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 8.3 Hz, 2H), 7.34-7.25 (m, 7H), 4.31 (s, 2H), 3.07 (t, J = 7.6 Hz, 2H), 2.44 (s, 3H), 1.35-1.00 (m, 12H), 0.85 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.2, 137.4, 136.8, 129.8, 128.6, 128.4, 127.8, 127.3, 51.9, 48.2, 31.8, 29.2, 29.1, 28.0, 26.7, 22.7, 21.6, 14.2; ESIHRMS *m/z* calcd for $C_{22}H_{32}NO_2S$ $[M+H]^+$ 374.2148, found 374.2153.



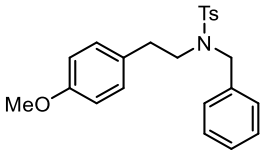
13f

***N*-Benzyl-*N*-phenethyl-*p*-toluenesulfonamide 13f**. Prepared according to general procedure I starting from 250 µmol of the corresponding ynamide. Yield: 79% (72 mg, 197 µmol). Solvent system for flash column chromatography: cyclohexane/EtOAc: 90/10; White solid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.74 (d, J = 8.1 Hz, 2H), 7.36-7.26 (m, 7H), 7.24-7.15 (m, 3H), 6.96-6.93 (m, 2H), 4.34 (s, 2H), 3.31-3.25 (m, 2H), 2.64-2.59 (m, 2H), 2.44 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.4, 138.6, 137.2, 136.4, 129.9, 128.8, 128.8, 128.6, 128.6, 128.0, 127.4, 126.5, 52.4, 49.6, 35.4, 21.7; ESIHRMS *m/z* calcd for $C_{22}H_{24}NO_2S$ $[M+H]^+$ 366.1522, found 366.1526. This compound has been previously reported.[S6]



13g

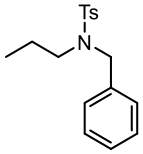
***N*-Benzyl-*N*-(*p*-chlorophenethyl)-*p*-toluenesulfonamide 13g.** Prepared according to general procedure I. Yield: 84% (134 mg, 335 µmol). Solvent system for flash column chromatography: cyclohexane/EtOAc: 90/10; White solid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.71 (d, J = 8.3 Hz, 2H), 7.35-7.28 (m, 5H), 7.28-7.23 (m, 2H), 7.15 (d, J = 8.4 Hz, 2H), 6.85 (d, J = 8.4 Hz , 2H), 4.31 (s, 2H), 3.28-3.19 (m, 2H), 2.63-2.55 (m, 2H), 2.44 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.5, 137.0, 136.8, 136.2, 132.3, 130.2, 129.9, 128.8, 128.7, 128.6, 128.1, 127.3, 52.6, 49.5, 34.9, 21.7; ESIHRMS *m/z* calcd for $C_{22}H_{23}ClNO_2S$ $[M+H]^+$ 400.1133, found 400.1109.



13h

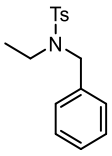
***N*-Benzyl-*N*-(*p*-methoxyphenethyl)-*p*-toluenesulfonamide 13h**. Prepared according to general procedure I. Yield: 80% (126 mg, 319 µmol). Solvent system for flash column chromatography: cyclohexane/EtOAc: 90/10; White solid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.75 (d, J = 8.3 Hz, 2H), 7.36-7.27 (m, 7H), 6.87 (d, J = 8.6 Hz, 2H), 6.75 (d, J = 8.6 Hz, 2H), 4.34 (s, 2H), 3.76 (s, 3H), 3.31-3.21 (m, 2H),

2.62-2.53 (m, 2H), 2.44 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.3, 143.3, 137.1, 136.4, 130.6, 129.8, 129.7, 128.7, 128.6, 127.9, 127.3, 114.0, 55.3, 52.3, 49.8, 34.4, 21.6; ESIHRMS *m/z* calcd for $C_{23}H_{26}NO_3S$ $[M+H]^+$ 396.1628, found 396.1635.



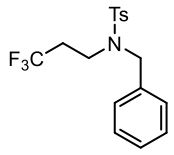
13i

***N*-Benzyl-*N*-propyl-*p*-toluenesulfonamide 13i**. Prepared according to general procedure I starting from 134 µmol of the corresponding ynamide. Yield: 89% (36 mg, 119 µmol). Solvent system for flash column chromatography: cyclohexane/EtOAc: 90/10; Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.73 (d, J = 8.3 Hz, 2H), 7.35-7.26 (m, 7H), 4.32 (s, 2H), 3.09-3.01 (m, 2H), 2.44 (s, 3H), 1.34 (sext., J = 7.5 Hz, 2H), 0.70 (t, J = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.2, 137.3, 136.8, 129.8, 128.6, 128.3, 127.8, 127.3, 52.0, 50.0, 21.7, 21.5, 11.3; ESIHRMS *m/z* calcd for $C_{17}H_{22}NO_2S$ $[M+H]^+$ 304.1366, found 304.1350.



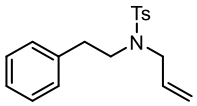
13j

***N*-Benzyl-*N*-(ethyl)-4-methylbenzenesulfonamide 13j**. Prepared according to general procedure I starting from 175 µmol of the corresponding ynamide. Yield: 50% (25 mg, 87 µmol). Solvent system for flash column chromatography: petroleum ether/EtOAc: 95/5; Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, J = 8.3 Hz, 2H), 7.35-7.26 (m, 7H), 4.34 (s, 2H), 3.19 (q, J = 7.2 Hz, 2H), 2.44 (s, 3H), 0.92 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.3, 137.5, 136.7, 129.9, 128.7, 128.4, 127.9, 127.3, 51.2, 42.4, 21.7, 13.4. This compound has been previously reported.[S7]



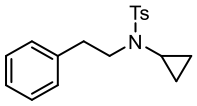
13k

***N*-Benzyl-*N*-(3,3,3-trifluoropropyl)-4-methylbenzenesulfonamide 13k**. Prepared according to general procedure I starting from 140 µmol of the corresponding ynamide. Yield: 40% (20 mg, 56 µmol). Solvent system for flash column chromatography: petroleum ether/EtOAc: 95/5; Yellow solid; Mp: 77 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, J = 8.2 Hz, 2H), 7.38-7.31 (m, 5H), 7.30-7.26 (m, 2H), 4.30 (s, 2H), 3.29-3.23 (m, 2H), 2.46 (s, 3H), 2.23-2.09 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.0, 136.1, 135.7, 130.1, 129.0, 128.6, 128.5, 127.4, 125.7 (q, J_{C-F} = 277.0 Hz), 53.2, 41.6 (q, J_{C-F} = 4.2 Hz), 33.9 (q, J_{C-F} = 28.0 Hz), 21.7; ^{19}F (376 MHz, $CDCl_3$): δ -66.4 (t, J = 10.7 Hz); IR (ATR): ν_{max} 2926, 1459, 1324, 1246, 1180, 1153, 1127, 1090, 972, 814, 735, 697, 667 cm^{-1}; ESIHRMS m/z calcd for $C_{17}H_{19}F_3NO_2S$ $[M+H]^+$ 358.1083, found 358.1085.



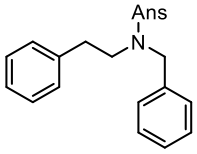
13l

***N*-Allyl-*N*-phenethyl-*p*-toluenesulfonamide 13l**. Prepared according to general procedure I. Yield: 75% (94 mg, 298 µmol). Solvent system for flash column chromatography: cyclohexane/EtOAc: 90/10; White solid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.70 (d, J = 8.2 Hz, 2H), 7.32-7.25 (m, 4H), 7.25-7.18 (m, 1H), 7.18-7.11 (m, 2H), 5.64 (ddt, J = 16.6, 10.1 and 6.5 Hz, 1H), 5.24-5.12 (m, 2H), 3.81 (d, J = 6.5 Hz, 2H), 3.39-3.29 (m, 2H), 2.90-2.79 (m, 2H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.3, 138.7, 137.2, 133.3, 129.8, 128.9, 128.6, 127.2, 126.6, 119.1, 51.1, 48.9, 35.5, 21.6; ESIHRMS *m/z* calcd for $C_{18}H_{22}NO_2S$ $[M+H]^+$ 316.1366, found 316.1368.



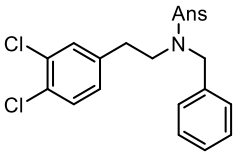
13m

***N*-Cyclopropyl-*N*-(2-phenylethyl)4-methylbenzenesulfonamide 13m**. Prepared according to general procedure I starting from 640 µmol of the corresponding ynamide. Yield: 50% (100 mg, 317 µmol). Solvent system for flash column chromatography: petroleum ether/EtOAc: 95/5; Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, J = 8.3 Hz, 2H), 7.33-7.26 (m, 4H), 7.24-7.16 (m, 3H), 3.42-3.36 (m, 2H), 2.94-2.88 (m, 2H), 2.43 (s, 3H), 2.07 (tt, J = 6.7 and 3.6 Hz, 1H), 0.77-0.72 (m, 2H), 0.69-0.63 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.5, 139.1, 135.9, 129.7, 129.1, 128.6, 127.8, 126.6, 53.0, 35.7, 30.9, 21.7, 7.6; IR (ATR): ν_{max} 2940, 1455, 1337, 1158, 1099, 1028, 961, 867, 822, 756, 713, 698, 653 cm^{-1}; ESIHRMS *m/z* calcd for $C_{18}H_{22}NO_2S$ $[M+H]^+$ 316.1366, found 316.1370.



13n

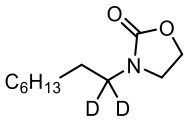
***N*-Benzyl-*N*-phenethyl-*o*-anisolesulfonamide 13n**. Prepared according to general procedure I starting from 450 µmol of the corresponding ynamide. Yield: 81% (139 mg, 364 µmol). Solvent system for flash column chromatography: cyclohexane/EtOAc: 60/40; Pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (dd, J = 7.9 and 1.7 Hz, 1H), 7.57-7.49 (m, 1H), 7.35-7.24 (m, 5H), 7.23-7.13 (m, 3H), 7.06 (td, J = 7.7 and 1.0 Hz, 1H), 6.98 (d, J = 8.4, 1H), 6.95-6.93 (m, 2H), 4.49 (s, 2H), 3.86 (s, 3H), 3.43-3.34 (m, 2H), 2.66-2.58 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.8, 138.8, 137.1, 134.5, 131.5, 129.0, 128.8, 128.7, 128.5, 128.5, 127.8, 126.5, 120.5, 112.2, 56.0, 52.2, 49.0, 35.1; ESIHRMS *m/z* calcd for $C_{22}H_{24}NO_3S$ $[M+H]^+$ 382.1471, found 382.1473.



13o

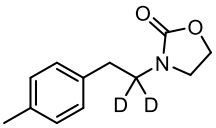
***N*-Benzyl-*N*-(3,4-dichlorophenethyl)-2-methoxybenzenesulfonamide 13o**. Prepared according to general procedure I starting from 500 µmol of the corresponding ynamide. Yield: 65% (146 mg, 325 µmol). Solvent system for flash column chromatography: petroleum ether/EtOAc: 80/20; White solid; ^{1}H

NMR (400 MHz, $CDCl_3$): δ 7.96 (dd, J = 8.0 and 1.7 Hz, 1H), 7.53 (ddd, J = 8.4, 7.5 and 1.7 Hz, 1H), 7.34-7.24 (m, 5H), 7.20 (d, J = 8.3 Hz, 1H), 7.04 (app. td, J = 7.5 and 1.0 Hz, 1H), 6.98-6.95 (m, 2H), 6.77 (dd, J = 8.3 and 2.0 Hz, 1H), 4.46 (s, 2H), 3.87 (s, 3H), 3.38 (t, J =7.6 Hz, 2H), 2.58 (t, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.6, 139.0, 136.7, 134.6, 132.2, 131.4, 130.7, 130.4, 130.3, 128.7, 128.5 (2C), 128.2, 127.9, 120.5, 112.3, 56.0, 52.4, 48.6, 34.4; ESIHRMS *m/z* calcd for $C_{22}H_{22}Cl_2NO_3S$ $[M+H]^+$ 450.0692, found 450.0675.



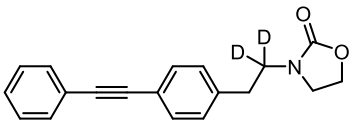
13a$_{d\alpha 2}$

3-(Octyl-1,1-*d*$_2$)oxazolidin-2-one 13a$_{d\alpha 2}$. Prepared according to general procedure II. Yield: 86% (52 mg, 257 µmol), α deuteration: 99% (calculated by integration of the residual signal in the ^{1}H NMR spectra). Solvent system for flash column chromatography: cyclohexane/EtOAc: 60/40; Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.34-4.25 (m, 2H), 3.58-3.48 (m, 2H), 1.57-1.45 (m, 2H), 1.37-1.15 (m, 10H), 0.86 (app. t, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.6, 61.7, 44.5, 31.9, 29.3, 29.3, 27.3, 26.7, 22.7, 14.2, (1C-D missing); IR (ATR): ν_{max} 2925, 2856, 1746, 1484, 1422, 1269, 1041, 762 cm^{-1}; ESIHRMS *m/z* calcd for $C_{11}H_{20}D_2NO_2$ $[M+H]^+$ 202.1771, found 202.1771.



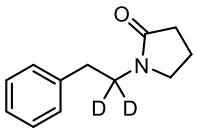
13b$_{d\alpha 2}$

3-[2-(*p*-Tolyl)ethyl-1,1-*d*$_2$]oxazolidin-2-one 13b$_{d\alpha 2}$. Prepared according to general procedure II. Yield: 74% (46 mg, 222 µmol), α deuteration: 99% (calculated by integration of the residual signal in the ^{1}H NMR spectra). Solvent system for flash column chromatography: petroleum ether/EtOAc: 50/50; White solid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.11 (app. s, 4H), 4.28-4.20 (m, 2H), 3.45-3.36 (m, 2H), 2.83 (s, 2H), 2.32 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.5, 136.3, 135.3, 129.4, 128.6, 61.8, 45.1, 33.5, 21.1, (1C-D missing); IR (ATR): ν_{max} 2919, 1733, 1474, 1429, 1268, 1038, 809, 754 cm^{-1}; ESIHRMS m/z calcd for $C_{12}H_{14}D_2NO_2$ $[M+H]^+$ 208.1301, found 208.1300.



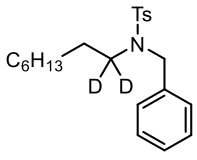
13c$_{d\alpha 2}$

3-{2-[4-(Phenylethynyl)phenyl]ethyl-1,1-*d*$_2$}oxazolidin-2-one 13c$_{d\alpha 2}$. Prepared according to general procedure II. Yield: 36% (32 mg, 109 µmol), α deuteration: 97% (calculated by integration of the residual signal in the ^{1}H NMR spectra). Solvent system for flash column chromatography: cyclohexane/EtOAc: 40/60; Pale yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.56-7.46 (m, 4H), 7.38-7.31 (m, 3H), 7.22 (d, J = 8.2 Hz, 2H), 4.29-4.21 (m, 2H), 3.44-3.35 (m, 2H), 2.90 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.5, 138.9, 132.0, 131.7, 128.9, 128.5, 128.4, 123.4, 121.8, 89.6, 89.2, 61.9, 45.3, 34.0, (1C-D missing); IR (ATR): ν_{max} 1738, 1473, 1434, 1271, 1037, 830, 760, 695 cm^{-1}; ESIHRMS m/z calcd for $C_{19}H_{16}D_2NO_2$ $[M+H]^+$ 294.1458, found 294.1464.



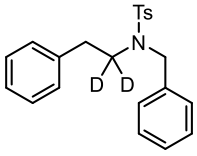
13d$_{dα2}$

1-(2-Phenylethyl-1,1-*d*$_2$)pyrrolidin-2-one 13d$_{dα2}$. Prepared according to general procedure II. Yield: 71% (41 mg, 214 µmol), α deuteration: 97% (calculated by integration of the residual signal in the ^{1}H NMR spectra). Solvent system for flash column chromatography: cyclohexane/EtOAc: 30/70; White solid; ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 7.33-7.18 (m, 5H), 3.24 (t, *J* = 7.0 Hz, 2H), 2.83 (s, 2H), 2.35 (t, *J* = 8.0 Hz, 2H), 1.94 (quint., *J* = 7.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 175.0, 139.0, 128.8, 128.7, 126.6, 47.7, 33.8, 31.2, 18.2, (1C-D missing); ESIHRMS *m/z* calcd for $C_{12}H_{14}D_2NO$ $[M+H]^+$ 192.1352, found 192.1351.



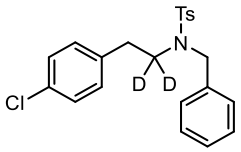
13e$_{dα2}$

***N*-Benzyl-4-methyl-*N*-(octyl-1,1-*d*$_2$)benzenesulfonamide 13e$_{dα2}$**. Prepared according to general procedure II. Yield: 74% (83 mg, 221 µmol), α deuteration: 99% (calculated by integration of the residual signal in the ^{1}H NMR spectra). Solvent system for flash column chromatography: cyclohexane/EtOAc: 90/10; White solid; ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 7.73 (d, *J* = 8.3 Hz, 2H), 7.35-7.25 (m, 7H), 4.31 (s, 2H), 2.44 (s, 3H), 1.33-1.00 (m, 12H), 0.85 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 143.2, 137.4, 136.8, 129.8, 128.6, 128.4, 127.8, 127.3, 51.9, 31.8, 29.2, 29.1, 27.8, 26.7, 22.7, 21.6, 14.2, (1C-D missing); IR (ATR): ν_{max} 2928, 2856, 1455, 1340, 1159, 1096, 887, 814, 757, 730, 699 cm^{-1}; ESIHRMS *m/z* calcd for $C_{22}H_{30}D_2NO_2S$ $[M+H]^+$ 376.2274, found 376.2280.



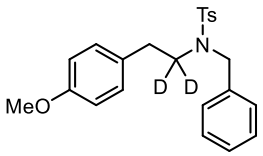
13f$_{dα2}$

***N*-Benzyl-4-methyl-*N*-(2-phenylethyl-1,1-*d*$_2$)benzenesulfonamide 13f$_{dα2}$**. Prepared according to general procedure II starting from 250 µmol of the corresponding ynamide. Yield: 60% (55 mg, 150 µmol), α deuteration: 98% (calculated by integration of the residual signal in the ^{1}H NMR spectra). Solvent system for flash column chromatography: cyclohexane/EtOAc: 90/10; White solid; ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 7.74 (d, *J* = 8.2 Hz, 2H), 7.38-7.26 (m, 7H), 7.24-7.14 (m, 3H), 6.98-6.91 (m, 2H), 4.33 (s, 2H), 2.61 (s, 2H), 2.44 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 143.4, 138.6, 137.2, 136.4, 129.9, 128.8 (2C), 128.6 (2C), 128.0, 127.3, 126.5, 52.3, 35.2, 21.7, (1C-D missing); IR (ATR): ν_{max} 2361, 1455, 1338, 1158, 1106, 1068, 820, 774, 752, 729, 702, 658 cm^{-1}; ESIHRMS m/z calcd for $C_{22}H_{22}D_2NO_2S$ $[M+H]^+$ 368.1648, found 368.1655.



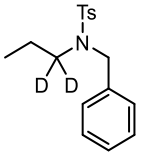
13g$_{d\alpha 2}$

***N*-Benzyl-*N*-[2-(4-chlorophenyl)ethyl-1,1-*d*$_2$]-4-methylbenzenesulfonamide 13g$_{d\alpha 2}$.** Prepared according to general procedure II. Yield: 78% (94 mg, 234 µmol), α deuteration: 98% (calculated by integration of the residual signal in the ^{1}H NMR spectra). Solvent system for flash column chromatography: cyclohexane/EtOAc: 90/10; White solid; ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 7.71 (d, *J* = 8.3 Hz, 2H), 7.35-7.22 (m, 7H), 7.15 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.3 Hz , 2H), 4.31 (s, 2H), 2.58 (s, 2H), 2.44 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 143.5, 137.0, 136.9, 136.2, 132.3, 130.1, 129.9, 128.8, 128.7, 128.6, 128.1, 127.3, 52.5, 34.6, 21.7, (1C-D missing); IR (ATR): ν_{max} 2937, 1491, 1332, 1159, 1108, 1089, 913, 840, 818, 742, 711, 660 cm^{-1}; ESIHRMS *m/z* calcd for $C_{22}H_{21}D_2ClNO_2S$ $[M+H]^+$ 402.1258, found 402.1266.



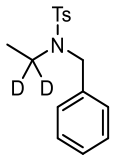
13h$_{d\alpha 2}$

***N*-Benzyl-*N*-[2-(4-methoxyphenyl)ethyl-1,1-*d*$_2$]-4-methylbenzenesulfonamide 13h$_{d\alpha 2}$.** Prepared according to general procedure II starting from 220 µmol of the corresponding ynamide. Yield: 69% (60 mg, 151 µmol), α deuteration: 98% (calculated by integration of the residual signal in the ^{1}H NMR spectra). Solvent system for flash column chromatography: cyclohexane/EtOAc: 90/10; White solid; ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 7.74 (d, *J* = 8.3 Hz, 2H), 7.36-7.26 (m, 7H), 6.86 (d, *J* = 8.7 Hz, 2H), 6.74 (d, *J* = 8.7 Hz, 2H), 4.33 (s, 2H), 3.75 (s, 3H), 2.55 (s, 2H), 2.44 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 158.3, 143.4, 137.2, 136.4, 130.6, 129.9, 129.7, 128.7, 128.6, 128.0, 127.3, 114.0, 55.4, 52.3, 34.2, 21.6, (1C-D missing); IR (ATR): ν_{max} 2933, 1512, 1333, 1249, 1159, 1035, 816, 746, 723, 701 cm^{-1}; ESIHRMS *m/z* calcd for $C_{23}H_{24}D_2NO_3S$ $[M+H]^+$ 398.1753, found 398.1722.



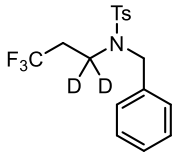
13i$_{d\alpha 2}$

***N*-Benzyl-4-methyl-*N*-(propyl-1,1-*d*$_2$)benzenesulfonamide 13i$_{d\alpha 2}$.** Prepared according to general procedure II starting from 140 µmol of the corresponding ynamide. Yield: 80% (34 mg, 112 µmol), α deuteration: 99% (calculated by integration of the residual signal in the ^{1}H NMR spectra). Solvent system for flash column chromatography: cyclohexane/EtOAc: 90/10; Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 7.73 (d, *J* = 8.1 Hz, 2H), 7.37-7.24 (m, 7H), 4.32 (s, 2H), 2.44 (s, 3H), 1.33 (q, *J* = 7.4 Hz, 2H), 0.70 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 143.2, 137.4, 136.8, 129.8, 128.6, 128.3, 127.8, 127.3, 51.9, 21.6, 21.3, 11.2, (1C-D missing); IR (ATR): ν_{max} 2928, 1455, 1320, 1154, 814, 762, 727, 694, 662 cm^{-1}; ESIHRMS *m/z* calcd for $C_{17}H_{20}D_2NO_2S$ $[M+H]^+$ 306.1491, found 306.1498.



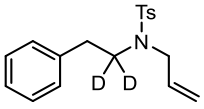
13j$_{dα2}$

***N*-Benzyl-*N*-(ethyl-1,1-*d*$_2$)-4-methylbenzenesulfonamide 13j$_{dα2}$**. Prepared according to general procedure II starting from 350 µmol of the corresponding ynamide. Yield: 32% (32 mg, 111 µmol), α deuteration: >99% (calculated by integration of the residual signal in the ^{1}H NMR spectra). Solvent system for flash column chromatography: petroleum ether/EtOAc: 95/5; Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.74 (d, *J* = 8.3 Hz, 2H), 7.35-7.27 (m, 7H), 4.33 (s, 2H), 2.44 (s, 3H), 0.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 143.3, 137.6, 136.7, 129.8, 128.7, 128.4, 127.8, 127.3, 51.1, 21.7, 13.2, (1C-D missing); IR (ATR): ν_{max} 2977, 2936, 1598, 1495, 1455, 1336, 1157, 1093, 942, 855, 812, 756, 719, 673, 646 cm^{-1}; ESIHRMS *m/z* calcd for $C_{16}H_{18}D_2NO_2S$ $[M+H]^+$ 292.1335, found 292.1344.



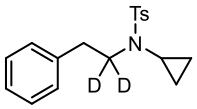
13k$_{dα2}$

***N*-Benzyl-*N*-(3,3,3-trifluoropropyl-1,1-*d*$_2$)-4-methylbenzenesulfonamide 13k$_{dα2}$**. Prepared according to general procedure II starting from 250 µmol of the corresponding ynamide. Yield: 36% (32 mg, 89 µmol), α deuteration: 99% (calculated by integration of the residual signal in the ^{1}H NMR spectra). Solvent system for flash column chromatography: petroleum ether/EtOAc: 95/5; Pale yellow solid; Mp: 77 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.74 (d, *J* = 8.3 Hz, 2H), 7.38-7.31 (m, 5H), 7.29-7.26 (m, 2H), 4.30 (s, 2H), 2.46 (s, 3H), 2.15 (q, *J* = 10.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 144.0, 136.1, 135.7, 130.1, 129.0, 128.6, 128.5, 127.4, 125.7 (q, J_{C-F} = 277.0 Hz), 53.1, 33.7 (q, J_{C-F} = 28.0 Hz), 21.7, (1C-D missing); ^{19}F (376 MHz, $CDCl_3$): *δ* -66.4 (t, *J* = 10.7 Hz); IR (ATR): ν_{max} 2930, 1367, 1327, 1276, 1259, 1190, 1154, 1135, 981, 867, 815, 729, 697, 665 cm^{-1}; ESIHRMS *m/z* calcd for $C_{17}H_{17}D_2F_3NO_2S$ $[M+H]^+$ 360.1209, found 360.1211.



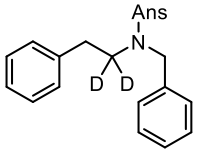
13l$_{dα2}$

***N*-Allyl-4-methyl-*N*-(2-phenylethyl-1,1-*d*$_2$)benzenesulfonamide 13l$_{dα2}$**. Prepared according to general procedure II. Yield: 80% (76 mg, 239 µmol), α deuteration: 96% (calculated by integration of the residual signal in the ^{1}H NMR spectra). Solvent system for flash column chromatography: cyclohexane/EtOAc: 90/10; White solid; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.69 (d, *J* = 8.2 Hz, 2H), 7.32-7.25 (m, 4H), 7.24-7.18 (m, 1H), 7.14 (d, *J* = 7.7 Hz, 2H), 5.63 (ddt, *J* = 16.7, 10.1 and 6.6 Hz, 1H), 5.22-5.13 (m, 2H), 3.80 (d, *J* = 6.5 Hz, 2H), 2.83 (s, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 143.3, 138.7, 137.2, 133.3, 129.8, 128.9, 128.6, 127.2, 126.6, 119.1, 51.0, 48.7-47.9 (m_{C-D}), 35.3, 21.6; IR (ATR): ν_{max} 3028, 1339, 1305, 1160, 1093, 933, 861, 746, 701, 667 cm^{-1}; ESIHRMS *m/z* calcd for $C_{18}H_{20}D_2NO_2S$ $[M+H]^+$ 318.1491, found 318.1496.



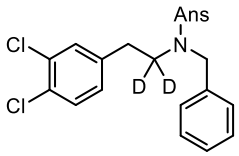
13m$_{dα2}$

***N*-Cyclopropyl-*N*-(2-phenylethyl-1,1-*d*$_2$)4-methylbenzenesulfonamide 13m$_{dα2}$**. Prepared according to general procedure II starting from 640 µmol of the corresponding ynamide. Yield: 46% (93 mg, 292 µmol), α deuteration: >99% (calculated by integration of the residual signal in the ^{1}H NMR spectra). Solvent system for flash column chromatography: petroleum ether/EtOAc: 95/5; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.75 (d, *J* = 8.3 Hz, 2H), 7.33-7.26 (m, 4H), 7.24-7.16 (m, 3H), 2.90 (s, 2H), 2.43 (s, 3H), 2.07 (tt, *J* = 7.0 and 3.7 Hz, 1H), 0.77-0.71 (m, 2H), 0.69-0.63 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 143.5, 139.1, 135.9, 129.7, 129.0, 128.6, 127.8, 126.6, 35.5, 30.8, 21.7, 7.6, (1C-D missing); IR (ATR): ν_{max} 3028, 1599, 1496, 1455, 1370, 1338, 1161, 1093, 1027, 818, 747, 711, 689, 649 cm^{-1}; ESIHRMS *m/z* calcd for $C_{18}H_{20}D_2NO_2S$ $[M+H]^+$ 318.1491, found 318.1502.



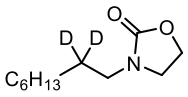
13n$_{dα2}$

***N*-Benzyl-2-methoxy-*N*-(2-phenylethyl-1,1-*d*$_2$)benzenesulfonamide 13n$_{dα2}$**. Prepared according to general procedure II starting from 800 µmol of the corresponding ynamide. Yield: 67% (206 mg, 537 µmol), α deuteration: >99% (calculated by integration of the residual signal in the ^{1}H NMR spectra). Solvent system for flash column chromatography: petroleum ether/EtOAc: 80/20; White solid; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.02 (dd, *J* = 8.0 and 1.8 Hz, 1H), 7.53 (ddd, *J* = 8.4, 7.5 and 1.8 Hz, 1H), 7.35-7.24 (m, 5H), 7.22-7.12 (m, 3H), 7.06 (app. td, *J* = 7.8 and 1.0 Hz, 1H), 6.99 (d, *J* = 8.3 Hz, 1H), 6.96-6.93 (m, 2H), 4.49 (s, 2H), 3.86 (s, 3H), 2.62 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 156.8, 138.8, 137.1, 134.4, 131.4, 128.9, 128.8, 128.7, 128.5, 128.5, 127.8, 126.4, 120.5, 112.3, 56.0, 52.1, 48.5-48.1 (m_{C-D}), 35.0; IR (ATR): ν_{max} 2920, 2851, 2256, 1590, 1466, 1331, 1280, 1154, 1134, 1072, 1020, 910, 866, 803, 755, 734, 700 cm^{-1}; ESIHRMS *m/z* calcd for $C_{22}H_{22}D_2NO_3S$ $[M+H]^+$ 384.1597, found 384.1562.



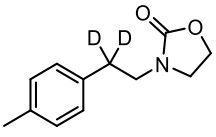
13o$_{dα2}$

***N*-Benzyl-*N*-[2-(3,4-dichlorophenyl)ethyl-1,1-*d*$_2$]-2-methoxybenzenesulfonamide 13o$_{dα2}$**. Prepared according to general procedure II starting from 800 µmol of the corresponding ynamide. Yield: 66% (238 mg, 526 µmol), α deuteration: >99% (calculated by integration of the residual signal in the ^{1}H NMR spectra). Solvent system for flash column chromatography: petroleum ether/EtOAc: 80/20; White solid; Mp: 96 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.94 (dd, *J* = 7.9 and 1.8 Hz, 1H), 7.50 (ddd, *J* = 8.3, 7.5 and 1.8 Hz, 1H), 7.31-7.22 (m, 5H), 7.18 (d, *J* = 8.3 Hz, 1H), 7.02 (app. td, *J* = 7.6 and 1.0 Hz, 1H), 6.96-6.93 (m, 2H), 6.75 (dd, *J* = 8.3 and 2.0 Hz, 1H), 4.44 (s, 2H), 3.84 (s, 3H), 2.55 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 156.6, 139.0, 136.7, 134.5, 132.2, 131.3, 130.7, 130.4, 130.3, 128.7, 128.5 (2C), 128.2, 127.9, 120.5, 112.3, 60.0, 52.3, 48.3-47.8 (m_{C-D}), 34.2; IR (ATR): ν_{max} 3376, 2945, 2841, 2361, 2333, 1590, 1480, 1332, 1280, 1155, 1133, 1072, 1020, 867, 804, 757, 700 cm^{-1}; ESIHRMS *m/z* calcd for $C_{22}H_{20}D_2Cl_2NO_3S$ $[M+H]^+$ 452.0817, found 452.0822.



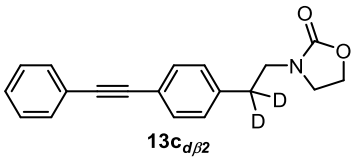
13a$_{d\beta2}$

3-(Octyl-2,2-*d*$_2$)oxazolidin-2-one 13a$_{d\beta2}$. Prepared according to general procedure III starting from 1.0 mmol of the corresponding ynamide and using freshly prepared trifluoromethanesulfonic acid-*d*. Yield: 73% (146 mg, 726 µmol), β deuteration: 88% (calculated by integration of the residual signal in the ^{1}H NMR spectra). Solvent system for flash column chromatography: petroleum ether/EtOAc: 70/30; Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 4.34-4.28 (m, 2H), 3.57-3.51 (m, 2H), 3.23 (s, 2H), 1.34-1.22 (m, 10H), 0.90-0.85 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 158.6, 61.7, 44.7, 44.3, 31.9, 29.3, 29.3, 26.6, 22.8, 14.2, (1C-D missing); IR (ATR): ν_{max} 2923, 2855, 1747, 1485, 1427, 1262, 1043, 763 cm^{-1}; ESIHRMS *m/z* calcd for $C_{11}H_{20}D_2NO_2$ $[M+H]^+$ 202.1771, found 202.1768.



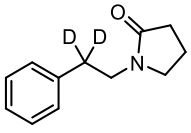
13b$_{d\beta2}$

3-[2-(*p*-Tolyl)ethyl-2,2-*d*$_2$]oxazolidin-2-one 13b$_{d\beta2}$. Prepared according to general procedure III starting from 853 µmol of the corresponding ynamide and using freshly prepared trifluoromethanesulfonic acid-*d*. Yield: 71% (126 mg, 608 µmol), β deuteration: 91% (calculated by integration of the residual signal in the ^{1}H NMR spectra). Solvent system for flash column chromatography: petroleum ether/EtOAc: 60/40; White solid; Mp: 77 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.11 (app. s, 4H), 4.26-4.21 (m, 2H), 3.49 (s, 2H), 3.43-3.38 (m, 2H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 158.5, 136.3, 135.3, 129.5, 128.6, 61.8, 45.7, 45.2, 34.0-32.5 (m_{C-D}), 21.2; IR (ATR): ν_{max} 1734, 1474, 1434, 1261, 1038, 754 cm^{-1}; ESIHRMS *m/z* calcd for $C_{12}H_{14}D_2NO_2$ $[M+H]^+$ 208.1301, found 208.1300.



13c$_{d\beta2}$

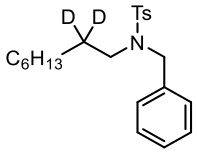
3-{2-[4-(Phenylethynyl)phenyl]ethyl-2,2-*d*$_2$}oxazolidin-2-one 13c$_{d\beta2}$. Prepared according to general procedure III. Yield: 43% (38 mg, 130 µmol), β deuteration: 82% (calculated by integration of the residual signal in the ^{1}H NMR spectra). Solvent system for flash column chromatography: cyclohexane/EtOAc: 40/60; Pale yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 7.58-7.43 (m, 4H), 7.39-7.30 (m, 3H); 7.22 (d, *J* = 8.1 Hz, 2H), 4.31-4.21 (m, 2H), 3.52 (obs. s, 2H), 3.44-3.36 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 158.8, 138.7, 132.0, 131.7, 128.8, 128.5, 128.4, 123.3, 121.8, 89.6, 89.2, 62.1, 45.4, 45.4, 34.3-33.0 (m_{C-D}), IR (ATR): ν_{max} 2919, 1739, 1474, 1437, 1265, 1039, 760, 695 cm^{-1}; ESIHRMS *m/z* calcd for $C_{19}H_{16}D_2NO_2$ $[M+H]^+$ 294.1458, found 294.1463.



13d$_{d\beta2}$

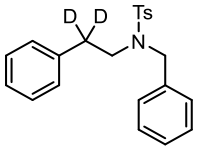
1-(2-Phenylethyl-2,2-*d*$_2$)pyrrolidin-2-one 13d$_{d\beta2}$. Prepared according to general procedure III starting from 540 µmol of the corresponding ynamide and using freshly prepared trifluoromethanesulfonic acid-*d*.

Yield: 54% (56 mg, 293 µmol), β deuteration: 84% (calculated by integration of the residual signal in the ^{1}H NMR spectra). Solvent system for flash column chromatography: cyclohexane/EtOAc: 30/70; White solid; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.28-7.23 (m, 2H), 7.15-7.20 (m, 3H) 3.48 (obs. s, 2H), 3.21 (t, *J* = 7.2 Hz, 2H), 2.31 (t, *J* = 8.4 Hz, 2H), 1.90 (quint., *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 175.0, 138.9, 128.8, 128.6, 126.6, 47.8, 44.1, 34.1-33.2 (m_{C-D}), 31.2, 18.2; IR (ATR): ν_{max} 2921, 1672, 1495, 1427, 1286, 741, 702, 622 cm^{-1}; ESIHRMS *m/z* calcd for $C_{12}H_{14}D_2NO$ $[M+H]^+$ 192.1352, found 192.1349.



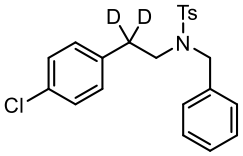
13e$_{dβ2}$

***N*-Benzyl-4-methyl-*N*-(octyl-2,2-*d*$_2$)benzenesulfonamide 13e$_{dβ2}$**. Prepared according to general procedure III starting from 270 µmol of the corresponding ynamide and using freshly prepared trifluoromethanesulfonic acid-*d*. Yield: 53% (54 mg, 144 µmol), β deuteration: 83% (calculated by integration of deuterium signal in ^{2}H NMR spectra with $C_2D_2Cl_4$ as a reference). Solvent system for flash column chromatography: cyclohexane/EtOAc: 90/10; White solid; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.73 (d, *J* = 8.4 Hz, 2H), 7.33-7.25 (m, 7H), 4.31 (s, 2H), 3.06 (s, 2H), 2.44 (s, 3H), 1.33-1.05 (m, 10H), 0.86 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 143.2, 137.4, 136.8, 129.8, 128.6, 128.4, 127.8, 127.3, 52.0, 48.0, 31.8, 29.2, 29.1, 27.4-27.0 (m_{C-D}), 26.5, 22.7, 21.7, 14.2; ^{2}H NMR (92 MHz, $CHCl_3$): *δ* 1.33 (s, 2D); IR (ATR): ν_{max} 2924, 2856, 1455, 1336, 1159, 1092, 949, 815, 756, 699 cm^{-1}; ESIHRMS *m/z* calcd for $C_{22}H_{30}D_2NO_2S$ $[M+H]^+$ 376.2274, found 376.2278.



13f$_{dβ2}$

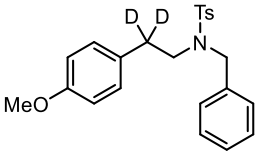
***N*-Benzyl-4-methyl-*N*-(2-phenylethyl-2,2-*d*$_2$)benzenesulfonamide 13f$_{dβ2}$**. Prepared according to general procedure III. Yield: 72% (79 mg, 215 µmol), β deuteration: 87% (calculated by integration of the residual signal in the ^{1}H NMR spectra). Solvent system for flash column chromatography: cyclohexane/EtOAc: 90/10; White solid; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.75 (d, *J* = 8.2 Hz, 2H), 7.38-7.28 (m, 7H), 7.25-7.14 (m, 3H), 6.96 (d, *J* = 8.0 Hz, 2H), 4.35 (s, 2H), 3.28 (s, 2H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 143.4, 138.5, 137.1, 136.4, 129.9, 128.7 (2C), 128.6 (2C), 128.0, 127.3, 126.5, 52.4, 49.5, 35.0-34.5 (m_{C-D}), 21.6; IR (ATR): ν_{max} 3031, 1495, 1451, 1334, 1157, 817, 804, 747, 701, 655 cm^{-1}; ESIHRMS *m/z* calcd for $C_{22}H_{22}D_2NO_2S$ $[M+H]^+$ 368.1648, found 368.1651.



13g$_{dβ2}$

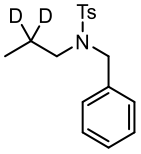
***N*-Benzyl-*N*-(2-(4-chlorophenyl)ethyl-2,2-*d*$_2$)-4-methylbenzenesulfonamide 13g$_{dβ2}$**. Prepared according to general procedure III. Yield: 75% (91 mg, 226 µmol), β deuteration: 93% (calculated by integration of the residual signal in the ^{1}H NMR spectra). Solvent system for flash column chromatography: cyclohexane/EtOAc: 90/10; White solid; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.71 (d, *J* = 8.2 Hz, 2H), 7.35-7.29 (m, 5H), 7.28-7.23 (m, 2H), 7.15 (app. dt, *J* = 8.3 and 2.0 Hz, 2H), 6.85 (app. dt, *J* = 8.4 and 2.0 Hz, 2H), 4.31 (s, 2H), 3.22 (s, 2H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 143.5, 137.0,

136.9, 136.2, 132.3, 130.1, 129.9, 128.8, 128.7, 128.6, 128.1, 127.3, 52.6, 49.4, 34.8-33.9 (m_{C-D}), 21.7; IR (ATR): ν_{max} 2951, 1491, 1332, 1159, 1108, 1089, 914, 819, 778, 742, 710, 661 cm^{-1}; ESIHRMS *m/z* calcd for $C_{22}H_{21}D_2ClNO_2S$ $[M+H]^+$ 402.1258, found 402.1210.



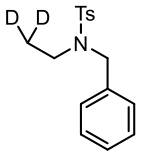
13h$_{d\beta2}$

***N*-Benzyl-*N*-(2-(4-methoxyphenyl)ethyl-2,2-*d*$_2$)-4-methylbenzenesulfonamide 13h$_{d\beta2}$**. Prepared according to general procedure III. Yield: 65% (78 mg, 196 µmol), β deuteration: 85% (calculated by integration of the residual signal in the ^{1}H NMR spectra). Solvent system for flash column chromatography: cyclohexane/EtOAc: 90/10; White solid; ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 7.74 (d, *J* = 8.3 Hz, 2H), 7.37-7.26 (m, 7H), 6.90-6.82 (m, 2H), 6.74 (d, *J* = 8.9 Hz, 1H*), 4.33 (s, 2H), 3.76 (s, 3H), 3.23 (s, 2H), 2.44 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 158.3, 143.4, 137.2, 136.4, 130.5, 129.8, 129.7, 128.7, 128.6, 128.0, 127.3, 114.0, 55.3, 52.4, 49.7, 34.6-33.3 (m_{C-D}), 21.6; IR (ATR): ν_{max} 2955, 1609, 1495, 1332, 1245, 1157, 1032, 950, 783, 745, 725, 658 cm^{-1}; ESIHRMS *m/z* calcd for $C_{23}H_{24}D_2NO_3S$ $[M+H]^+$ 398.1753, found 398.1737.



13i$_{d\beta2}$

***N*-Benzyl-4-methyl-*N*-(propyl-2,2-*d*$_2$)benzenesulfonamide 13i$_{d\beta2}$**. Prepared according to general procedure III starting from 140 µmol of the corresponding ynamide. Yield: 72% (31 mg, 101 µmol), β deuteration: 87% (calculated by integration of the residual signal in the ^{1}H NMR spectra). Solvent system for flash column chromatography: cyclohexane/EtOAc: 95/5; Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 7.73 (d, *J* = 8.2 Hz, 2H), 7.37-7.23 (m, 7H), 4.31 (s, 2H), 3.03 (s, 2H), 2.44 (s, 3H), 0.68 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 143.3, 137.3, 136.8, 129.8, 128.6, 128.3, 127.8, 127.3, 52.0, 49.8, 21.7, 11.1, (1C-D missing); IR (ATR): ν_{max} 2927, 1494, 1454, 1322, 1310, 1152, 1122, 1094, 947, 814, 728, 657 cm^{-1}; ESIHRMS *m/z* calcd for $C_{17}H_{20}D_2NO_2S$ $[M+H]^+$ 306.1491, found 306.1496.

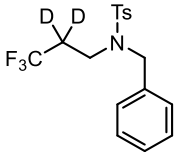


13j$_{d\beta2}$

***N*-Benzyl-*N*-(ethyl-2,2-*d*$_2$)-4-methylbenzenesulfonamide 13j$_{d\beta2}$**. Prepared according to general procedure III starting from 350 µmol of the corresponding ynamide. Yield: 46% (47 mg, 161 µmol), β deuteration: 85% (calculated by integration of the residual signal in the ^{1}H NMR spectra). Solvent system for flash column chromatography: petroleum ether/EtOAc: 95/5; Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.74 (d, *J* = 8.3 Hz, 2H), 7.35-7.27 (m, 7H), 4.33 (s, 2H), 3.17 (obs. d, *J* = 6.8 Hz, 2H), 2.44 (s, 3H), 0.93-0.86 (m, 1.30H: 1.00H from the desired deuterated product and 0.30H from the residual non deuterated molecule); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 143.3, 137.5, 136.7, 129.8, 128.7, 128.4, 127.8,

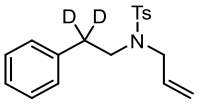
* 1H missing due to partial deuteration.

127.3, 51.2, 42.3, 21.7, 13.4-12.6 (m_{C-D}); IR (ATR): ν_{max} 2938, 1599, 1495, 1455, 1333, 1158, 1089, 944, 811, 753, 711, 692, 650 cm^{-1}; ESIHRMS *m/z* calcd for $C_{16}H_{18}D_2NO_2S$ $[M+H]^+$ 292.1335, found 292.1341.



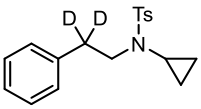
13k$_{d\beta2}$

***N*-Benzyl-*N*-(3,3,3-trifluoropropyl-2,2-*d*$_2$)-4-methylbenzenesulfonamide 13k$_{d\beta2}$**. Prepared according to general procedure III starting from 250 µmol of the corresponding ynamide. Yield: 48% (43 mg, 120 µmol), β deuteration: 90% (calculated by integration of the residual signal in the ^{1}H NMR spectra). Solvent system for flash column chromatography: petroleum ether/EtOAc: 95/5; Pale yellow solid; Mp: 79 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.38-7.32 (m, 5H), 7.30-7.26 (m, 2H), 4.30 (s, 2H), 3.25 (obs. s, 2H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.0, 136.1, 135.7, 130.1, 129.0, 128.6, 128.5, 127.4, 125.6 (q, J_{C-F} = 276.8 Hz), 53.2, 41.5 (q, J_{C-F} = 4.2 Hz), 21.7, (1C-D missing); ^{19}F (376 MHz, $CDCl_3$): δ -66.6; IR (ATR): ν_{max} 2929, 1456, 1325, 1310, 1168, 1153, 1059, 937, 815, 733, 697, 663 cm^{-1}; ESIHRMS *m/z* calcd for $C_{17}H_{17}D_2F_3NO_2S$ $[M+H]^+$ 360.1209, found 360.1213.



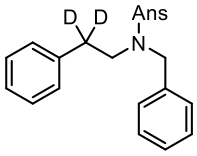
13l$_{d\beta2}$

***N*-Allyl-4-methyl-*N*-(2-phenylethyl-2,2-*d*$_2$)benzenesulfonamide 13l$_{d\beta2}$**. Prepared according to general procedure III. Yield: 72% (69 mg, 217 µmol), β deuteration: 91% (calculated by integration of the residual signal in the ^{1}H NMR spectra). Solvent system for flash column chromatography: cyclohexane/EtOAc: 90/10; White solid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.32-7.25 (m, 4H), 7.24-7.18 (m, 1H), 7.18-7.12 (m, 2H), 5.64 (ddt, *J* = 16.6, 10.1 and 6.5 Hz, 1H), 5.23-5.12 (m, 2H), 3.81 (d, *J* = 6.3 Hz, 2H), 3.33 (s, 2H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.3, 138.6, 137.2, 133.3, 129.8, 128.9, 128.6, 127.2, 126.6, 119.1, 51.1, 48.8, 35.5-34.4 (m_{C-D}), 21.6; IR (ATR): ν_{max} 3026, 1496, 1449, 1335, 1155, 1089, 983, 919, 815, 761, 738, 700, 666 cm^{-1}; ESIHRMS *m/z* calcd for $C_{18}H_{20}D_2NO_2S$ $[M+H]^+$ 318.1491, found 318.1494.



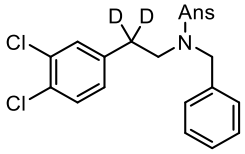
13m$_{d\beta2}$

***N*-Cyclopropyl-*N*-(2-phenylethyl-2,2-*d*$_2$)4-methylbenzenesulfonamide 13m$_{d\beta2}$**. Prepared according to general procedure III starting from 640 µmol of the corresponding ynamide. Yield: 55% (111 mg, 350 µmol), β deuteration: 86% (calculated by integration of the residual signal in the ^{1}H NMR spectra). Solvent system for flash column chromatography: petroleum ether/EtOAc: 95/5; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.1 Hz, 2H), 7.33-7.26 (m, 4H), 7.24-7.16 (m, 3H), 3.38 (obs. s, 2H), 2.43 (s, 3H), 2.07 (tt, *J* = 7.0 and 3.8 Hz, 1H), 0.77-0.71 (m, 2H), 0.70-0.63 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.5, 139.0, 135.8, 129.7, 129.0, 128.6, 127.8, 126.6, 52.9, 30.9, 21.7, 7.6, (1C-D missing); IR (ATR): ν_{max} 3024, 2923, 1599, 1496, 1449, 1336, 1159, 1124, 1112, 1094, 1027, 863, 823, 740, 714, 699, 652 cm^{-1}; ESIHRMS *m/z* calcd for $C_{18}H_{20}D_2NO_2S$ $[M+H]^+$ 318.1491, found 318.1497.



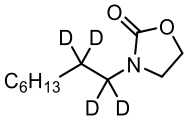
13n$_{dβ2}$

***N*-Benzyl-2-methoxy-*N*-(2-phenylethyl-2,2-*d*$_2$)benzenesulfonamide 13n$_{dβ2}$** Prepared according to general procedure III starting from 800 µmol of the corresponding ynamide. Yield: 71% (218 mg, 569 µmol), β deuteration: 95% (calculated by integration of the residual signal in the ^{1}H NMR spectra). Solvent system for flash column chromatography: petroleum ether/EtOAc: 80/20; White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (dd, *J* = 7.8 and 1.8 Hz, 1H), 7.55-7.50 (ddd, *J* = 8.4, 7.5 and 1.8 Hz, 1H), 7.34-7.24 (m, 5H), 7.22-7.11 (m, 3H), 7.06 (td, *J* = 7.6 and 1.0 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 6.96-6.92 (m, 2H), 4.49 (s, 2H), 3.86 (s, 3H), 3.37 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.8, 138.8, 137.1, 134.5, 131.5, 128.9, 128.8, 128.7, 128.5, 128.5, 127.8, 126.5, 120.5, 112.3, 56.0, 52.2, 48.9, 34.3-33.7(m_{C-D}); IR (ATR): ν_{max} 3026, 2921, 1590, 1466, 1328, 1280, 1154, 1134, 1111, 1068, 1020, 938, 806, 759, 735, 700 cm^{-1}; ESIHRMS *m/z* calcd for $C_{22}H_{22}D_2NO_3S$ $[M+H]^+$ 384.1597, found 384.1562.



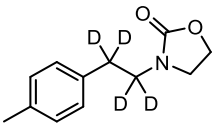
13o$_{dβ2}$

***N*-Benzyl-*N*-[2-(3,4-dichlorophenyl)ethyl-2,2-*d*$_2$]-2-methoxybenzenesulfonamide 13o$_{dβ2}$** Prepared according to general procedure III starting from 800 µmol of the corresponding ynamide. Yield: 71% (256 mg, 568 µmol), β deuteration: 94% (calculated by integration of the residual signal in the ^{1}H NMR spectra). Solvent system for flash column chromatography: petroleum ether/EtOAc: 80/20; White solid, Mp: 94 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (dd, *J* =7.8 and 1.8 Hz, 1H), 7.50 (ddd, *J* = 8.4, 7.5 and 1.7 Hz, 1H), 7.32-7.21 (m, 5H), 7.18 (d, *J* = 8.3 Hz, 1H), 7.02 (td, *J* = 7.8 and 1.0 Hz, 1H), 6.96-6.93 (m, 2H), 6.75 (dd, *J* = 8.3 and 2.0 Hz, 1H), 4.44 (s, 2H), 3.84 (s, 3H), 3.34 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.6, 139.0, 136.7, 134.5, 132.2, 131.3, 130.6, 130.4, 130.3, 128.7, 128.5, 128.4, 128.2, 127.9, 120.5, 112.3, 56.0, 52.4, 48.5, 34.1-33.5 (m_{C-D}); IR (ATR): ν_{max} 3064, 2940, 1590, 1480, 1329, 1280, 1154, 1133, 1020, 939, 805, 757, 700 cm^{-1}; ESIHRMS *m/z* calcd for $C_{22}H_{20}D_2Cl_2NO_3S$ $[M+H]^+$ 452.0817, found 452.0821.



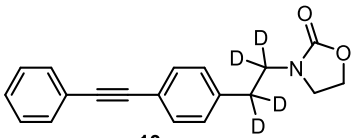
13a$_{dα2β2}$

3-(Octyl-1,1,2,2-*d*$_4$)oxazolidin-2-one 13a$_{dα2β2}$. Prepared according to general procedure IV starting from 1.0 mmol of the corresponding ynamide and using freshly prepared trifluoromethanesulfonic acid-*d*. Yield: 68% (139 mg, 684 µmol), α and β deuteration: >99% and 91% (calculated by integration of the residual signals in the ^{1}H NMR spectra). Solvent system for flash column chromatography: petroleum ether/EtOAc: 70/30; Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.34-4.28 (m, 2H), 3.57-3.51 (m, 2H), 1.34-1.22 (m, 10H), 0.90-0.85 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.6, 61.8, 44.6, 31.9, 29.3 (2C), 26.5, 22.8, 14.2, (2C-D missing); IR (ATR): ν_{max} 2924, 2855, 1746, 1483, 1422, 1269, 1041, 762 cm^{-1}; ESIHRMS *m/z* calcd for $C_{11}H_{18}D_4NO_2$ $[M+H]^+$ 204.1896, found 204.1891.



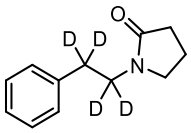
13b$_{d\alpha 2\beta 2}$

3-[2-(*p*-Tolyl)ethyl-1,1,2,2-*d*$_4$]oxazolidin-2-one 13b$_{d\alpha 2\beta 2}$. Prepared according to general procedure IV starting from 853 µmol of the corresponding ynamide and using freshly prepared trifluoromethanesulfonic acid-*d*. Yield: 66% (117 mg, 559 µmol), α and β deuteration: >99% and 87% (calculated by integration of the residual signals in the ^{1}H NMR spectra). Solvent system for flash column chromatography: petroleum ether/EtOAc: 60/40; White solid; Mp: 79 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11 (app. s, 4H), 4.26-4.21 (m, 2H), 3.43-3.38 (m, 2H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.5, 136.3, 135.3, 129.5, 128.6, 61.8, 45.1, 33.8-32.5 ($m_{C\text{-}D}$), 21.2, (1C-D missing); IR (ATR): ν_{max} 2919, 1733, 1474, 1431, 1267, 1034, 803, 755 cm^{-1}; ESIHRMS *m/z* calcd for $C_{12}H_{12}D_4NO_2$ $[M+H]^+$ 210.1427, found 210.1424.



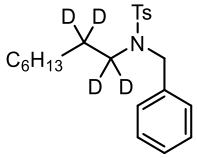
13c$_{d\alpha 2\beta 2}$

3-{2-[4-(Phenylethynyl)phenyl]ethyl-1,1,2,2-*d*$_4$}oxazolidin-2-one 13c$_{d\alpha 2\beta 2}$. Prepared according to general procedure IV. Yield: 39% (35 mg, 118 µmol), α and β deuteration: 99% and 84% (calculated by integration of the residual signals in the ^{1}H NMR spectra). Solvent system for flash column chromatography: cyclohexane/EtOAc: 40/60; Pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.50 (m, 2H), 7.48 (d, *J* = 8.3 Hz, 2H), 7.38-7.32 (m, 3H), 7.22 (d, *J* = 8.3 Hz, 2H), 4.28-4.22 (m, 2H), 3.43-3.36 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.6, 138.8, 132.0, 131.7, 128.9, 128.5, 128.4, 123.4, 121.8, 89.6, 89.2, 62.0, 45.3, 33.9-32.7 ($m_{C\text{-}D}$), (1C-D missing); IR (ATR): ν_{max} 2919, 1739, 1473, 1434, 1272, 1034, 760, 695 cm^{-1}; ESIHRMS *m/z* calcd for $C_{19}H_{14}D_4NO_2$ $[M+H]^+$ 296.1583, found 296.1588.



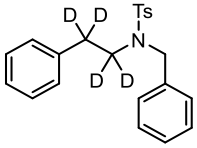
13d$_{d\alpha 2\beta 2}$

1-(2-Phenylethyl-1,1,2,2-*d*$_4$)pyrrolidin-2-one 13d$_{d\alpha 2\beta 2}$. Prepared according to general procedure IV starting from 540 µmol of the corresponding ynamide and using freshly prepared trifluoromethanesulfonic acid-*d*. Yield: 57% (60 mg, 310 µmol), α and β deuteration: 99% and 85% (calculated by integration of the residual signals in the ^{1}H NMR spectra). Solvent system for flash column chromatography: cyclohexane/EtOAc: 30/70; White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.25 (m, 2H), 7.21-7.17 (m, 3H), 3.22 (t, *J* = 6.8 Hz, 2H), 2.32 (t, *J* = 8.4 Hz, 2H), 1.91 (quint., *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.0, 138.9, 128.8, 128.6, 126.6, 47.7, 43.9-43.1 ($m_{C\text{-}D}$), 33.9-33.1 ($m_{C\text{-}D}$), 31.1, 18.2; IR (ATR): ν_{max} 2916, 1673, 1423, 1293, 891, 740, 701, 623 cm^{-1}; ESIHRMS *m/z* calcd for $C_{12}H_{12}D_4NO$ $[M+H]^+$ 194.1477, found 194.1476.



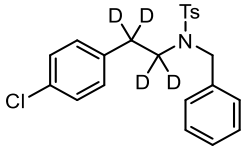
13e$_{d\alpha 2\beta 2}$

***N*-Benzyl-4-methyl-*N*-(octyl-1,1,2,2-*d*$_4$)benzenesulfonamide 13e**$_{d\alpha 2\beta 2}$. Prepared according to general procedure IV starting from 270 µmol of the corresponding ynamide and using freshly prepared trifluoromethanesulfonic acid-*d*. Yield: 57% (58 mg, 154 µmol), α deuteration: >99% (calculated by integration of the residual signal in the ^{1}H NMR spectra) and α deuteration: 84% (calculated by integration of the deuterium signal in ^{2}H NMR spectra with $C_2D_2Cl_4$ as a reference). Solvent system for flash column chromatography: cyclohexane/EtOAc: 90/10; White solid; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.73 (d, *J* = 8.0 Hz, 2H), 7.33-7.24 (m, 7H), 4.31 (s, 2H), 2.44 (s, 3H), 1.29-1.05 (m, 10H), 0.85 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 143.2, 137.4, 136.8, 129.8, 128.6, 128.4, 127.8, 127.3, 51.9, 31.8, 29.2, 29.1, 26.5, 22.7, 21.6, 14.2, (2C-D missing); ^{2}H NMR (92 MHz, $CHCl_3$): *δ* 1.33 (s, 2D); IR (ATR): ν_{max} 2925, 2856, 1455, 1340, 1161, 866, 815, 729, 699 cm^{-1}; ESIHRMS *m/z* calcd for $C_{22}H_{28}D_4NO_2S$ $[M+H]^+$ 378.2399, found 378.2383.



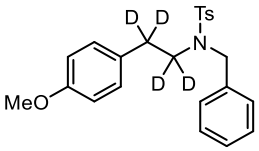
13f$_{d\alpha 2\beta 2}$

***N*-Benzyl-4-methyl-*N*-(2-phenylethyl-1,1,2,2-*d*$_4$)benzenesulfonamide 13f**$_{d\alpha 2\beta 2}$. Prepared according to general procedure IV starting from 220 µmol of the corresponding ynamide. Yield: 77% (63 mg, 170 µmol), α and β deuteration: 98% and 88% (calculated by integration of the residual signals in the ^{1}H NMR spectra). Solvent system for flash column chromatography: cyclohexane/EtOAc: 90/10; White solid; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.75 (d, *J* = 8.2 Hz, 2H), 7.37-7.27 (m, 7H), 7.25-7.13 (m, 3H), 6.95 (d, *J* = 8.0 Hz, 2H), 4.34 (s, 2H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 143.4, 138.5, 137.1, 136.4, 129.9, 128.7 (2C), 128.6 (2C), 128.0, 127.3, 126.5, 52.3, 49.2-48.4 ($m_{C\text{-}D}$), 35.2-34.1 ($m_{C\text{-}D}$), 21.6; IR (ATR): ν_{max} 3023, 1495, 1338, 1153, 1097, 821, 771, 744, 726, 700, 653 cm^{-1}; ESIHRMS *m/z* calcd for $C_{22}H_{20}D_4NO_2S$ $[M+H]^+$ 370.1773, found 370.1775.



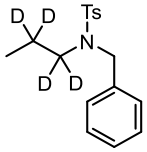
13g$_{d\alpha 2\beta 2}$

***N*-Benzyl-*N*-[2-(4-chlorophenyl)ethyl-1,1,2,2-*d*$_4$]-4-methylbenzenesulfonamide 13g**$_{d\alpha 2\beta 2}$. Prepared according to general procedure IV. Yield: 75% (91 mg, 225 µmol), α and β deuteration: 99% and 95% (calculated by integration of the residual signals in the ^{1}H NMR spectra). Solvent system for flash column chromatography: cyclohexane/EtOAc: 90/10; White solid; ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 7.72 (d, *J* = 8.2 Hz, 2H), 7.35-7.22 (m, 7H), 7.15 (app. dt, *J* = 8.4 and 2.0 Hz, 2H), 6.85 (app. dt, *J* = 8.4 and 2.0 Hz, 2H), 4.31 (s, 2H), 2.44 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 143.5, 137.0, 136.9, 136.2, 132.3, 130.1, 129.9, 128.8, 128.7, 128.6, 128.1, 127.3, 52.5, 21.7, (2C-D missing); IR (ATR): ν_{max} 1490, 1333, 1162, 1089, 1073, 933, 863, 818, 768, 735, 706, 658 cm^{-1}; ESIHRMS *m/z* calcd for $C_{22}H_{19}D_4ClNO_2S$ $[M+H]^+$ 404.1384, found 404.1392.



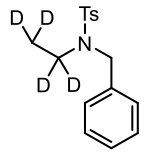
13h$_{d\alpha 2\beta 2}$

***N*-Benzyl-*N*-[2-(4-methoxyphenyl)ethyl-1,1,2,2-*d*$_4$]-4-methylbenzenesulfonamide 13h$_{d\alpha 2\beta 2}$.** Prepared according to general procedure IV starting from 220 µmol of the corresponding ynamide. Yield: 61% (54 mg, 135 µmol), α and β deuteration: >99% and 89% (calculated by integration of the residual signals in the ^{1}H NMR spectra). Solvent system for flash column chromatography: cyclohexane/EtOAc: 90/10; Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, J = 8.2 Hz, 2H), 7.36-7.26 (m, 7H), 6.89-6.84 (m, 2H), 6.74 (d, J = 8.5 Hz, 1H[†]), 4.33 (s, 2H), 3.76 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.3, 143.4, 137.2, 136.4, 130.5, 129.9, 129.7, 128.7, 128.6, 128.0, 127.3, 114.0, 55.3, 52.3, 49.5-48.6 ($m_{C\text{-}D}$), 34.3-33.2 ($m_{C\text{-}D}$), 21.6; IR (ATR): ν_{max} 2957, 1513, 1495, 1333, 1246, 1158, 1033, 816, 734, 722, 705, 656 cm^{-1}; ESIHRMS *m/z* calcd for $C_{23}H_{22}D_4NO_3S$ $[M+H]^+$ 400.1879, found 400.1891.



13i$_{d\alpha 2\beta 2}$

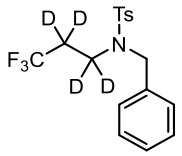
***N*-Benzyl-4-methyl-*N*-(propyl-1,1,2,2-d$_4$)benzenesulfonamide 13i$_{d\alpha 2\beta 2}$.** Prepared according to general procedure IV starting from 140 µmol of the corresponding ynamide. Yield: 79% (34 mg, 111 µmol), α and β deuteration: >99% and 92% (calculated by integration of the residual signals in the ^{1}H NMR spectra). Solvent system for flash column chromatography: cyclohexane/EtOAc: 95/5; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 8.2 Hz, 2H), 7.35-7.25 (m, 7H), 4.31 (s, 2H), 2.44 (s, 3H), 0.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.2, 137.4, 136.8, 129.8, 128.6, 128.3, 127.8, 127.3, 52.0, 49.6-48.8 ($m_{C\text{-}D}$), 21.7, 21.2-20.2 ($m_{C\text{-}D}$), 11.0; IR (ATR): ν_{max} 2968, 1320, 1153, 1115, 814, 762, 727, 694, 655 cm^{-1}; ESIHRMS *m/z* calcd for $C_{17}H_{18}D_4NO_2S$ $[M+H]^+$ 308.1617, found 308.1624.



13j$_{d\alpha 2\beta 2}$

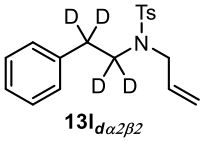
***N*-Benzyl-*N*-(ethyl-1,1,2,2-*d*$_4$)-4-methylbenzenesulfonamide 13j$_{d\alpha 2\beta 2}$.** Prepared according to general procedure IV starting from 350 µmol of the corresponding ynamide. Yield: 50% (51 mg, 173 µmol), α and β deuteration: >99% and 92% (calculated by integration of the residual signals in the ^{1}H NMR spectra). Solvent system for flash column chromatography: petroleum ether/EtOAc: 95/5; Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, J = 8.3 Hz, 2H), 7.35-7.26 (m, 7H), 4.33 (s, 2H), 2.44 (s, 3H), 0.90-0.85 (m, 1.16H: 1.00H from the desired deuterated product and 0.16H from the residual non deuterated molecule); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.3, 137.5, 136.7, 129.8, 128.7, 128.3, 127.8, 127.3, 51.1, 21.6, 13.2-12.1 ($m_{C\text{-}D}$), (1C-D missing); IR (ATR): ν_{max} 2960, 1598, 1496, 1455, 1336, 1304, 1158, 1097, 1076, 944, 860, 812, 751, 702, 693, 652 cm^{-1}; ESIHRMS *m/z* calcd for $C_{16}H_{16}D_4NO_2S$ $[M+H]^+$ 294.1460, found 294.1470.

[†] 1H missing due to partial deuteration.



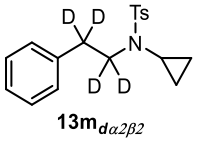
13k$_{d\alpha 2\beta 2}$

***N*-Benzyl-*N*-(3,3,3-trifluoropropyl-1,1,2,2-*d*$_4$)-4-methylbenzenesulfonamide 13k$_{d\alpha 2\beta 2}$**. Prepared according to general procedure IV starting from 250 µmol of the corresponding ynamide. Yield: 49% (44 mg, 123 µmol), α and β deuteration: >99% and 91% (calculated by integration of the residual signals in the ^{1}H NMR spectra). Solvent system for flash column chromatography: petroleum ether/EtOAc: 95/5; Pale yellow solid; Mp: 81 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, J = 8.3 Hz, 2H), 7.37-7.31 (m, 5H), 7.29-7.26 (m, 2H), 4.29 (s, 2H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.0, 136.1, 135.7, 130.1, 129.0, 128.6, 128.5, 127.4, 125.6 (q, $J_{C\text{-}F}$ = 276.7 Hz), 53.1, 21.7, (2C-D missing); ^{19}F (376 MHz, $CDCl_3$): δ -66.6; IR (ATR): ν_{max} 2960, 1457, 1327, 1309, 1192, 1170, 1153, 1103, 1011, 868, 815, 772, 727, 696, 659 cm^{-1}; ESIHRMS *m/z* calcd for $C_{17}H_{15}D_4F_3NO_2S$ $[M+H]^+$ 362.1334, found 362.1338.



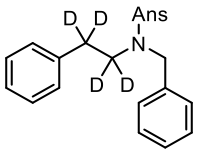
13l$_{d\alpha 2\beta 2}$

***N*-Allyl-4-methyl-*N*-(2-phenylethyl-1,1,2,2-*d*$_4$)benzenesulfonamide 13l$_{d\alpha 2\beta 2}$**. Prepared according to general procedure IV. Yield: 72% (69 mg, 216 µmol), α and β deuteration: 99% and 92% (calculated by integration of the residual signals in the ^{1}H NMR spectra). Solvent system for flash column chromatography: cyclohexane/EtOAc: 90/10; White solid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.70 (d, J = 8.2 Hz, 2H), 7.33-7.25 (m, 4H), 7.25-7.18 (m, 1H), 7.18-7.11 (m, 2H), 5.64 (ddt, J = 16.7, 10.1 and 6.5 Hz, 1H), 5.24-5.12 (m, 2H), 3.81 (d, J = 6.4 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.3, 138.6, 137.2, 133.3, 129.8, 128.9, 128.6, 127.2, 126.6, 119.1, 51.0, 48.8-47.7 ($m_{C\text{-}D}$), 35.4-34.2 ($m_{C\text{-}D}$), 21.6; IR (ATR): ν_{max} 2924, 1336, 1288, 1160, 1093, 922, 862, 814, 735, 700, 665 cm^{-1}; ESIHRMS *m/z* calcd for $C_{18}H_{18}D_4NO_2S$ $[M+H]^+$ 320.1617, found 320.1617.



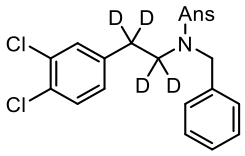
13m$_{d\alpha 2\beta 2}$

***N*-Cyclopropyl-*N*-(2-phenylethyl-1,1,2,2-*d*$_4$)4-methylbenzenesulfonamide 13m$_{d\alpha 2\beta 2}$**. Prepared according to general procedure IV starting from 640 µmol of the corresponding ynamide. Yield: 50% (102 mg, 320 µmol). α and β deuteration: >99% and 88% (calculated by integration of the residual signals in the ^{1}H NMR spectra). Solvent system for flash column chromatography: petroleum ether/EtOAc: 95/5; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, J = 8.3 Hz, 2H), 7.33-7.26 (m, 4H), 7.24-7.16 (m, 3H), 2.43 (s, 3H), 2.07 (tt, J = 7.0 and 3.8 Hz, 1H), 0.77-0.72 (m, 2H), 0.69-0.63 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.5, 139.0, 135.9, 129.7, 129.0, 128.6, 127.8, 126.6, 30.8, 21.7, 7.6, (2 C-D missing); IR (ATR): ν_{max} 3026, 2924, 1599, 1496, 1450, 1369, 1338, 1307, 1236, 1161, 1096, 1027, 814, 769, 738, 711, 689, 647 cm^{-1}; ESIHRMS *m/z* calcd for $C_{18}H_{18}D_4NO_2S$ $[M+H]^+$ 320.1617, found 320.1626.



13n$_{d\alpha 2\beta 2}$

***N*-Benzyl-2-methoxy-*N*-(2-phenylethyl-1,1,2,2-*d*$_4$)benzenesulfonamide 13n$_{d\alpha 2\beta 2}$.** Prepared according to general procedure IV starting from 800 µmol of the corresponding ynamide. Yield: 68% (210 mg, 545 µmol), α and β deuteration: 97% and 95% (calculated by integration of the residual signals in the ^{1}H NMR spectra). Solvent system for flash column chromatography: petroleum ether/EtOAc: 80/20; White solid; ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 8.01 (dd, *J* = 7.8 and 1.8 Hz, 1H), 7.55-7.50 (ddd, *J* = 8.4, 7.5 and 1.8 Hz, 1H), 7.32-7.24 (m, 5H), 7.22-7.14 (m, 3H), 7.06 (td, *J* = 7.8 and 0.9 Hz, 1H), 7.00-6.92 (m, 3H), 4.48 (s, 2H), 3.86 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): *δ* 156.8, 138.7, 137.0, 134.4, 131.4, 129.0, 128.8, 128.7, 128.5, 128.5, 127.8, 126.4, 120.4, 112.2, 56.0, 52.1, (2 C-D missing); IR (ATR): ν_{max} 3027, 2918, 1591, 1480, 1331, 1280, 1154, 1134, 1073, 1020, 870, 804, 757, 733, 700 cm^{-1}.



13o$_{d\alpha 2\beta 2}$

***N*-Benzyl-*N*-[2-(3,4-dichlorophenyl)ethyl-1,1,2,2-*d*$_4$]-2-methoxybenzenesulfonamide 13o$_{d\alpha 2\beta 2}$.** Prepared according to general procedure IV starting from 800 µmol of the corresponding ynamide. Yield: 71% (258 mg, 568 µmol), α and β deuteration: 99% and 94% (calculated by integration of the residual signals in the ^{1}H NMR spectra). Solvent system for flash column chromatography: petroleum ether/EtOAc: 80/20; White solid; Mp: 92 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.96 (dd, *J* = 7.8 and 1.8 Hz, 1H), 7.52 (ddd, *J* = 8.3, 7.5 and 1.8 Hz, 1H), 7.34-7.24 (m, 5H), 7.19 (d, *J* = 8.3 Hz, 1H), 7.03 (td, *J* = 7.6 and 1.0 Hz, 1H), 6.98-6.95 (m, 2H), 6.77 (dd, *J* = 8.3 and 2.0 Hz, 1H), 4.46 (s, 2H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 156.6, 138.9, 136.7, 134.5, 132.1, 131.2, 130.6, 130.3 (2C), 128.6, 128.4, 128.4, 128.1, 127.8, 120.4, 112.2, 55.9, 52.2, 48.9-47.9 ($m_{C\text{-}D}$), 33.9-33.3 ($m_{C\text{-}D}$); IR (ATR): ν_{max} 3067, 3027, 2942, 1591, 1480, 1331, 1280, 1155, 1133, 1072, 1020, 804, 756, 737, 702, 682 cm^{-1}; ESIHRMS *m/z* calcd for $C_{22}H_{18}D_4Cl_2NO_3S$ $[M+H]^+$ 454.0943, found 454.0942.

Experimental Procedure and Characterization Data: Synthesis of Deuterated Biologically Relevant Amines

General procedure V: Pd-catalyzed double cross-coupling of aryl chlorides and methanol[S8]
An oven-dried 15 mL pressure tube was charged with *t*BuBrettPhos (8 mg, 16 µmol), sodium *tert*-butoxide (111 mg, 1.15 mmol) and the sulfonamide (470 µmol), fitted with a rubber septum, evacuated under high vacuum and backfilled with argon three times before adding methanol (190 µL, 4.70 mmol). In a glovebox, an oven-dried 10 mL round bottom flask was charged with *t*BuBrettPhos Pd G3 (14 mg, 16 µmol), fitted with a rubber septum and then taken outside the glovebox. Dry 1,4-dioxane (1.0 mL) was next added and the resulting mixture was stirred at rt for 1 minute until the formation of a homogeneous solution that was successively added to the pressure tube via cannula. The rubber septum was next replaced by a Teflon-coated screw cap and the resulting reaction mixture was stirred at 50 °C for 48 hours. The reaction mixture was then cooled to rt, filtered over a plug of silica gel (washed with EtOAc) and concentrated under reduced pressure. The crude residue was finally purified by flash column chromatography over silica gel to afford the desired methyl protected catechol.

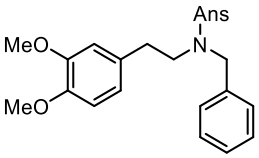
General procedure VI: Ni-catalyzed *o*-anisylsulfonyl deprotection[S9]
A 50 mL round bottom flask was charged with the sulfonamide (260 µmol) and nickel(II) acetylacetonate (3 mg, 13 µmol), fitted with a rubber septum, evacuated under high vacuum and backfilled with argon three times before adding Et_2O (7.0 mL). Isopropylmagnesium chloride (2.0 M in Et_2O, 585 µL, 1.17 mmol) was then added dropwise and the reaction mixture was stirred at rt for 3 hours before being quenched with a saturated aqueous solution of NH_4Cl. The layers were separated and the aqueous layer was extracted with EtOAc (2x). The combined organic layers were washed with a saturated aqueous solution of NH_4Cl (3x), water (1x) and brine (1x), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude residue was then dissolved in Et_2O and an excess of HCl (6.7 M in Et_2O) was added dropwise at 0 °C. The white precipitate was recovered by filtration, carefully washed with Et_2O (3x) and dried under high vacuum to afford the desired amine hydrochloride that was used without further purification in the next step.

General procedure VII: Reductive *o*-anisylsulfonyl deprotection
To a solution of naphthalene (290 mg, 2.27 mmol) in 1,2-dimethoxyethane (4.5 mL) under argon was added sodium (52 mg, 2.27 mmol) in small portions. The resulting mixture was sonicated for a few minutes until persistence of a deep blue/green color and subsequently stirred at rt for 1 to 2 hours (until complete disappearance of sodium). The resulting solution was then added dropwise via cannula to a solution of the sulfonamide (100 mg, 227 µmol) in 1,2-dimethoxyethane (1.0 mL) at -78 °C under argon. The reaction mixture was then allowed to warm to rt and stirred until completion (TLC analysis revealed complete disappearance of the starting material after typically 5-10 minutes). The mixture was then poured into a saturated aqueous solution of $NaHCO_3$, the layers were separated, and the aqueous layer was extracted with Et_2O (3x). The organic layers were combined, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude residue was then dissolved in Et_2O and an excess of HCl (6.7 M in Et_2O) was added dropwise at 0°C. The white precipitate was recovered by filtration, carefully washed with Et_2O (3x) and dried under high vacuum to afford the desired deprotected amine hydrochloride that was used without further purification in the next step.

General procedure VIII: Hydrogenative benzyl deprotection
A glass vial was charged with the *N*-benzylamine hydrochloride (160 µmol), palladium on charcoal (10%, 50 mg) and methanol (3.0 mL). The vial was placed in an autoclave, purged with N_2, pressurized with H_2 (10 bars) and stirred at rt for 24 hours. After the reactor was depressurized and purged with N_2, the reaction mixture was filtered over a plug of Celite® (washed with methanol) and concentrated under reduced pressure to afford the desired unprotected amine hydrochloride without further purification.

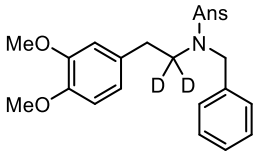
General procedure IX: Methyl ether deprotection[S10]

A solution of dimethoxyphenylamine hydrochloride (450 µmol) and sodium hypophosphite monohydrate (49 mg, 462 µmol) in concentrated hydrobromic acid (45%, 3.0 mL) was refluxed for 2 hours under argon. The reaction mixture was diluted with water (10 mL) and concentrated under reduced pressure. The residue was diluted with water (10 mL) and concentrated two more times before being dried under high vacuum to afford the desired amine hydrobromide without further purification.



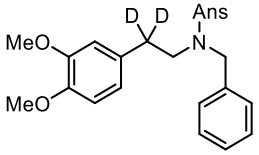
S1

***N*-Benzyl-*N*-(3,4-dimethoxyphenethyl)-2-methoxybenzenesulfonamide S1**. Prepared according to general procedure V starting from 334 µmol of **13o**. Yield: 83% (122 mg, 276 µmol). Solvent system for flash column chromatography: petroleum ether/EtOAc: 60/40; Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (dd, *J* = 7.8 and 1.7 Hz, 1H), 7.51 (ddd, *J* = 8.4, 7.5 and 1.8 Hz, 1H), 7.32-7.22 (m, 5H), 7.04 (td, *J* = 7.6 and 0.9 Hz, 1H), 6.97 (dd, *J* = 8.4 and 0.8 Hz, 1H), 6.69 (d, *J* = 8.3 Hz, 1H), 6.49 (dd, *J* = 8.3 and 2.0 Hz, 1H), 6.45 (d, *J* = 2.0 Hz, 1H), 4.47 (s, 2H), 3.86 (s, 3H), 3.81 (s, 3H), 3.78 (s, 3H), 3.39-3.36 (m, 2H), 2.61-2.57 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.8, 148.9, 147.6, 137.0, 134.4, 131.4 (2C), 128.8, 128.6, 128.5, 127.7, 120.7, 120.4, 112.2, 112.0, 111.2, 56.0 (2C), 55.9, 52.1, 49.1, 34.8; IR (ATR): ν_{max} 2937, 2836, 1515, 1480, 1330, 1280, 1263, 1240, 1155, 1027, 804, 754, 733, 720, 701 cm^{-1} ; ESIHRMS *m/z* calcd for $C_{24}H_{28}NO_5S$ $[M+H]^+$ 442.1683, found 442.1680.



S1$_{d\alpha 2}$

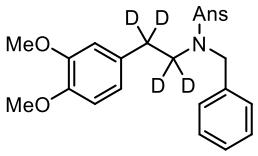
***N*-Benzyl-*N*-[2-(3,4-dimethoxyphenyl)ethyl-1,1-*d*$_2$]-2-methoxybenzenesulfonamide S1**$_{d\alpha 2}$. Prepared according to general procedure V starting from 350 µmol of **13o**$_{d\alpha 2}$**.** Yield: 56% (87 mg, 196 µmol). Solvent system for flash column chromatography: petroleum ether/EtOAc: 60/40; Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (dd, *J* = 7.9 and 1.8 Hz, 1H), 7.51 (ddd, *J* = 1.8, 7.5 and 8.3 Hz, 1H), 7.32-7.23 (m, 5H), 7.04 (td, *J* = 7.7 and 1.0 Hz, 1H), 6.97 (dd, *J* = 8.4 and 0.9 Hz, 1H), 6.69 (d, *J* = 8.3 Hz, 1H), 6.49 (dd, *J* = 8.0 and 2.0 Hz, 1H), 6.45 (d, *J* = 2.0 Hz, 1H), 4.47 (s, 2H), 3.86 (s, 3H), 3.81 (s, 3H), 3.78 (s, 3H), 2.58 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.8, 148.9, 147.6, 137.0, 134.4, 131.4 (2C), 128.8, 128.6, 128.5, 127.7, 120.7, 120.4, 112.2, 112.0, 111.3, 56.0 (2C), 55.9, 52.0, 48.7-48.3 ($m_{C\text{-}D}$), 34.6; IR (ATR): ν_{max} 2944, 2836, 2361, 1590, 1515, 1480, 1330, 1280, 1263, 1155, 1027, 866, 804, 759, 732, 700 cm^{-1}.



S1$_{d\beta 2}$

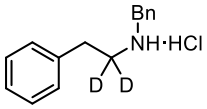
***N*-Benzyl-*N*-[2-(3,4-dimethoxyphenyl)ethyl-2,2-*d*$_2$]-2-methoxybenzenesulfonamide S1**$_{d\beta 2}$. Prepared according to general procedure V starting from 380 µmol of **13o**$_{d\beta 2}$**.** Yield: 50% (84 mg, 189

μmol). Solvent system for the flash column chromatography: petroleum ether/EtOAc: 60/40; Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.00 (d, *J* = 8.0 Hz, 1H), 7.52 (app. t, *J* = 7.6 Hz, 1H), 7.32-7.24 (m, 5H), 7.04 (app. t, *J* = 7.6 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 6.69 (d, *J* = 8.0 Hz, 1H), 6.49 (app. d, *J* = 8.0 Hz, 1H), 6.45-6.44 (m, 1H), 4.47 (s, 2H), 3.86 (s, 3H), 3.82 (s, 3H), 3.79 (s, 3H), 3.36 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 156.8, 148.9, 147.6, 137.0, 134.4, 131.4, 131.3, 128.8, 128.6, 128.5, 127.8, 120.7, 120.4, 112.3, 112.0, 111.3, 56.0 (2C), 55.9, 52.2, 49.0, 34.5-33.8 (m_{C-D}); IR (ATR): ν_{max} 2938, 2837, 1590, 1516, 1480, 1328, 1280, 1243, 1154, 1027, 805, 761, 701 cm^{-1}.



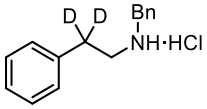
S1$_{dα2β2}$

***N*-Benzyl-*N*-[2-(3,4-dimethoxyphenyl)ethyl-1,1,2,2-*d*$_4$]-2-methoxybenzenesulfonamide S1**$_{dα2β2}$. Prepared according to general procedure V starting from 470 μmol of **13o**$_{dα2β2}$**.**Yield: 44% (92 mg, 207 μmol). Solvent system for the flash column chromatography: petroleum ether/EtOAc: 60/40; Brown oil; ^{1}H (400 MHz, $CDCl_3$): *δ* 7.99 (dd, *J* = 7.8 and 1.7 Hz, 1H), 7.51 (ddd, *J* = 8.3, 7.5 and 1.7 Hz, 1H), 7.32-7.21 (m, 5H), 7.03 (td, *J* = 7.7 and 1.0 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 6.69 (d, *J* = 8.3 Hz, 1H), 6.51-6.47 (m, 1H), 6.46-6.44 (m, 1H), 4.47 (s, 2H), 3.86 (s, 3H), 3.81 (s, 3H), 3.78 (s, 3H); ^{13}C (100 Hz, $CDCl_3$): *δ* 156.7, 148.9, 147.6, 137.0, 134.4, 131.3, 131.3, 128.8, 128.6, 128.4, 127.7, 120.6, 120.4, 112.2, 111.9, 111.2, 56.0 (2C), 55.9, 52.0, 48.7-47.9 (m_{C-D}), 34.3-33.6 (m_{C-D}); IR (ATR): ν_{max} 2939, 2837, 1590, 1515, 1480, 1329, 1280, 1244, 1155, 1072, 1027, 869, 804, 758, 731, 702 cm^{-1}; ESIHRMS *m/z* calcd for $C_{24}H_{24}D_4NO_5S$ $[M+H]^+$ 446.1934, found 446.1942.



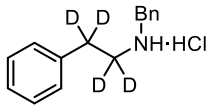
S2$_{dα2}$

***N*-Benzyl-(2-phenylethyl-1,1-*d*$_2$)amine hydrochloride S2**$_{dα2}$. Prepared according to general procedure VI starting from 335 μmol of **13n**$_{dα2}$. Yield: 75% (62 mg, 250 μmol); White solid; ^{1}H (400 MHz, CD_3OH): *δ* 8.90 (br. s, 1H), 7.55-7.51 (m, 2H), 7.46-7.42 (m, 3H), 7.33-7.22 (m, 5H), 4.23 (s, 2H), 3.03 (s, 2H); ^{13}C (100 Hz, CD_3OH): *δ* 137.7, 132.5, 130.9, 130.5, 130.1, 129.8, 129.6, 128.0, 52.3, 32.9, (1 C-D missing, obscured by the signal of CD_3OH); ESIHRMS *m/z* calcd for $C_{15}H_{16}D_2N$ $[M+H]^+$ 214.1559, found 214.1558.



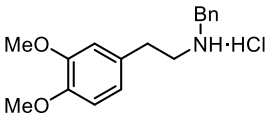
S2$_{dβ2}$

***N*-Benzyl-(2-phenylethyl-2,2-*d*$_2$)amine hydrochloride S2**$_{dβ2}$. Prepared according to general procedure VI starting from 450 μmol of **13n**$_{dβ2}$. Yield: 46% (52 mg, 207 μmol); White solid; ^{1}H (400 MHz, CD_3OH): *δ* 8.90 (br. s, 1H), 7.56-7.52 (m, 2H), 7.48-7.42 (m, 3H), 7.35-7.22 (m, 5H), 4.24 (s, 2H), 3.26 (s, 2H); ^{13}C (100 Hz, CD_3OH): *δ* 137.6, 132.5, 130.9, 130.5, 130.1, 129.8, 129.6, 128.1, 52.4, 49.6, 33.0-32.3 (m_{C-D}); ESIHRMS *m/z* calcd for $C_{15}H_{16}D_2N$ $[M+H]^+$ 214.1559, found 214.1557.



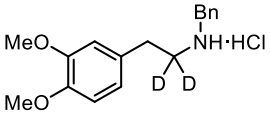
S2$_{dα2β2}$

***N*-Benzyl-(2-phenylethyl-1,1,2,2-*d*$_4$)amine hydrochloride S2$_{dα2β2}$**. Prepared according to general procedure VI starting from 215 µmol of **13n$_{dα2β2}$**. Yield: 86% (40 mg, 186 µmol); White solid; ^{1}H NMR (400 MHz, CD_3OH): *δ* 7.54-7.50 (m, 2H), 7.47-7.42 (m, 3H), 7.34-7.22 (m, 5H), 4.22 (s, 2H); ^{13}C NMR (100 MHz, CD_3OH): *δ* 137.6, 132.5, 130.9, 130.5, 130.1, 129.8, 129.6, 128.1, 52.3, 32.8-31.9 (m_{C-D}), (1 C-D missing, obscured by the signal of CD_3OH); ESIHRMS *m/z* calcd for $C_{15}H_{14}D_4N$ $[M+H]^+$ 216.1685, found 216.1683.



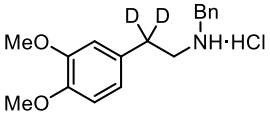
S3

***N*-Benzyl-2-(3,4-dimethoxyphenyl)ethan-1-amine hydrochloride S3**. Prepared according to general procedure VII starting from 450 µmol of **S1**. Yield: 68% (94 mg, 305 µmol); Pale yellow solid; Mp: 164 °C; ^{1}H NMR (400 MHz, CD_3OH): *δ* 8.81 (br. s, 1H), 7.53-7.50 (m, 2H), 7.48-7.43 (m, 3H), 6.92-6.88 (m, 2H), 6.82 (dd, *J* = 8.0 and 2.0 Hz, 1H), 4.23 (br. s, 2H), 3.82 (s, 3H), 3.79 (s, 3H), 3.25 (br. s, 2H), 3.00-2.94 (m, 2H); ^{13}C NMR (100 MHz, CD_3OH): *δ* 150.6, 149.6, 132.5, 130.9, 130.5, 130.4, 130.1, 122.0, 113.6, 113.3, 56.4 (2C), 52.4, 49.9, 32.7; IR (ATR): ν_{max} 3401, 2922, 2839, 2791, 2757, 2663, 2625, 2363, 2342, 1518, 1456, 1439, 1417, 1267, 1244, 1212, 1144, 1027, 797, 750, 697, 627, 609 cm^{-1}; ESIHRMS *m/z* calcd for $C_{17}H_{22}NO_2$ $[M+H]^+$ 272.1645, found 272.1647.



S3$_{dα2}$

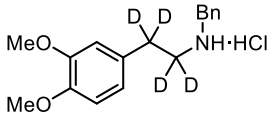
***N*-Benzyl-2-(3,4-dimethoxyphenyl)ethan-1,1-*d*$_2$-1-amine hydrochloride S3$_{dα2}$**. Prepared according to general procedure VII starting from 726 µmol of **S1$_{dα2}$**. Yield: 67% (151 mg, 487 µmol); Pale yellow solid; Mp: 170 °C; ^{1}H (400 MHz, CD_3OH): *δ* 8.77 (br. s, 1H), 7.53-7.49 (m, 2H), 7.47-7.44 (m, 3H), 6.90 (d, *J* = 8.2 Hz, 1H), 6.88 (d, *J* = 2.1 Hz, 1H), 6.81 (dd, *J* = 8.2 and 2.1 Hz, 1H), 4.22 (t, *J* = 6.1 Hz, 2H), 3.82 (s, 3H), 3.80 (s, 3H), 2.95 (s, 2H); ^{13}C NMR (100 MHz, CD_3OH): *δ* 150.7, 149.7, 132.5, 130.9, 130.6, 130.3, 130.2, 122.0, 113.5, 113.3, 56.4 (2C), 52.3, 32.5, (1 C-D missing); IR (ATR): ν_{max} 3410, 2937, 2839, 2760, 2672, 2626, 2363, 2342, 1591, 1519, 1457, 1440, 1423, 1264, 1240, 1159, 1144, 1027, 852, 806, 767, 750, 697, 625 cm^{-1}; ESIHRMS *m/z* calcd for $C_{17}H_{20}D_2NO_2$ $[M+H]^+$ 274.1771, found 274.1772.



S3$_{dβ2}$

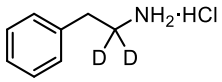
***N*-Benzyl-2-(3,4-dimethoxyphenyl)ethan-2,2-*d*$_2$-1-amine hydrochloride S3$_{dβ2}$**. Prepared according to general procedure VII starting from 676 µmol of **S1$_{dβ2}$**. Yield: 86% (179 mg, 578 µmol); Pale yellow solid; ^{1}H NMR (400 MHz, CD_3OH): *δ* 8.83 (br. s, 1H), 7.56-7.50 (m, 2H), 7.47-7.41 (m, 3H), 6.92-6.87 (m, 2H), 6.82 (dd, *J* = 8.3 and 2.0 Hz, 1H), 4.23 (br. t, *J* = 5.6 Hz, 2H), 3.81 (s, 3H), 3.78 (s, 3H), 3.25

(br. t, *J* = 5.5 Hz, 2H); ^{13}C NMR (100 MHz, CD_3OH): *δ* 150.6, 149.6, 132.5, 130.9, 130.5, 130.3, 130.1, 122.0, 113.5, 113.3, 56.4 (2C), 52.4, 49.8, 32.6-31.8 ($m_{C\text{-}D}$).



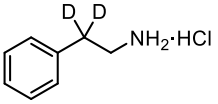
S3$_{d\alpha 2\beta 2}$

***N*-Benzyl-2-(3,4-dimethoxypheny)ethan-1,1,2,2-*d*$_4$-1-amine hydrochloride S3**$_{d\alpha 2\beta 2}$. Prepared according to general procedure VII starting from 606 µmol of **S1**$_{d\alpha 2\beta 2}$. Yield: 54% (103 mg, 330 µmol); Brown solid; ^{1}H NMR (400 MHz, CD_3OH): *δ* 8.83 (br. s, 1H), 7.54-7.51 (m, 2H), 7.45-7.42 (m, 3H), 6.90-6.86 (m, 2H), 6.81 (dd, *J* = 8.0 and 1.9 Hz, 1H), 4.22 (br. t, *J* = 6.0 Hz, 2H), 3.80 (s, 3H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, CD_3OH): *δ* 150.6, 149.5, 132.5, 130.9, 130.5, 130.3, 130.1, 122.0, 113.5, 113.2, 56.4 (2C), 52.3, 32.4-31.7 ($m_{C\text{-}D}$), (1 C-D missing); IR (ATR): ν_{max} 3401, 2922, 2839, 2791, 2757, 2663, 2625, 2363, 2342, 1518, 1455, 1439, 1417, 1267, 1244, 1212, 1144, 1027, 797, 749, 697, 627, 609 cm^{-1}; ESIHRMS *m/z* calcd for $C_{17}H_{18}D_4NO_2$ $[M+H]^+$ 276.1896, found 276.1901.



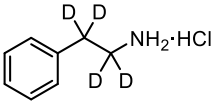
17$_{d\alpha 2}$

(2-Phenylethyl-1,1-*d*$_2$)amine hydrochloride 17$_{d\alpha 2}$. Prepared according to general procedure VIII starting from 249 µmol of **S2**$_{d\alpha 2}$. Yield: 63% (25 mg, 156 µmol), α deuteration: >99% (calculated by integration of the residual signal in the ^{1}H NMR spectra); White solid; ^{1}H NMR (400 MHz, CD_3OH): *δ* 7.35-7.30 (m, 2H), 7.29-7.22 (m, 3H), 2.94 (s, 2H); ^{13}C NMR (100 MHz, CD_3OH): *δ* 138.1, 129.8, 129.7, 128.0, 42.0-41.3 ($m_{C\text{-}D}$), 34.7; IR (ATR): ν_{max} 3405, 3025, 2991, 1637, 1229, 900, 742, 697, 655 cm^{-1}; ESIHRMS *m/z* calcd for $C_8H_{10}D_2N$ $[M+H]^+$ 124.1090 found 124.1096.



17$_{d\beta 2}$

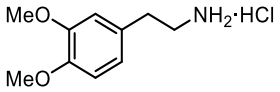
(2-Phenylethyl-2,2-*d*$_2$)amine hydrochloride 17$_{d\beta 2}$. Prepared according to general procedure VIII starting from 206 µmol of **S2**$_{d\beta 2}$. Yield: 91% (30 mg, 188 µmol), β deuteration: 84% (calculated by integration of the residual signal in the ^{1}H NMR spectra); White solid; ^{1}H NMR (400 MHz, CD_3OH): *δ* 7.36-7.31 (m, 2H), 7.29-7.24 (m, 3H), 3.14 (obs. s, 2H); ^{13}C NMR (100 MHz, CD_3OH): *δ* 137.9, 129.8, 129.6, 128.0, 42.1, 34.7-34.0 ($m_{C\text{-}D}$); IR (ATR): ν_{max} 3438, 3406, 3025, 2991, 1602, 1511, 1497, 1464, 1385, 1148, 927, 785, 736, 695 cm^{-1}; ESIHRMS *m/z* calcd for $C_8H_{10}D_2N$ $[M+H]^+$ 124.1090 found 124.1095.



17$_{d\alpha 2\beta 2}$

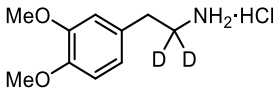
(2-Phenylethyl-1,1,2,2-*d*$_4$)amine hydrochloride 17$_{d\alpha 2\beta 2}$. Prepared according to general procedure VIII starting from 159 µmol of **S2**$_{d\alpha 2\beta 2}$. Yield: 85% (22 mg, 136 µmol), α and β deuteration: >99% and 95% (calculated by integration of the residual signals in the ^{1}H NMR spectra); White solid; ^{1}H NMR (400 MHz,

CD_3OH): δ 7.36-7.31 (m, 2H), 7.29-7.23 (m, 3H); ^{13}C NMR (100 MHz, CD_3OH): δ 137.9, 129.8, 129.6, 128.0, 42.0-41.3 (m_{C-D}), 34.3-33.7 (m_{C-D}); IR (ATR): ν_{max} 3419, 3025, 2980, 2928, 1602, 1513, 1467, 1449, 1227, 1177, 1075, 904, 875, 649, 618, 607 cm^{-1}; ESIHRMS *m/z* calcd for $C_8H_8D_4N$ $[M+H]^+$ 126.1215 found 126.1221.



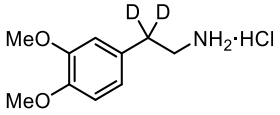
S4

2-(3,4-Dimethoxyphenyl)ethanamine hydrochloride S4. Prepared according to general procedure VIII starting from 305 µmol of **S3**. Yield: 89% (59 mg, 271 µmol); Pale yellow solid, Mp: 128 °C; ^1H NMR (400 MHz, CD_3OH): δ 6.92-6.89 (m, 2H), 6.83 (dd, *J* = 8.4 and 2.4 Hz, 1H), 3.83 (s, 3H), 3.80 (s, 3H), 3.17 (app. t, *J* = 7.2 Hz, 2H), 2.92 (app. t, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, CD_3OH): δ 150.5, 149.4, 130.6, 122.1, 113.5, 113.2, 56.4 (2C), 42.3, 34.1; IR (ATR): ν_{max} 3404, 2937, 2362, 2341, 1634, 1595, 1518, 1466, 1422, 1265, 1236, 1157, 1144, 1024, 867, 808, 765, 667, 631 cm^{-1}; ESIHRMS *m/z* calcd for $C_{10}H_{16}NO_2$ $[M+H]^+$ 182.1176 found 182.1169. This compound has been previously reported.[S11]



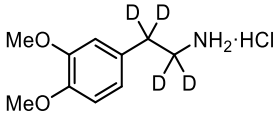
S4$_{d\alpha 2}$

2-(3,4-Dimethoxyphenyl)ethan-1,1-*d*$_2$-1-amine hydrochloride S4$_{d\alpha 2}$. Prepared according to general procedure VIII starting from 468 µmol of **S3$_{d\alpha 2}$**. Yield: 97% (100 mg, 455 µmol); Pale yellow solid; Mp: 125 °C ; ^1H NMR (400 MHz, CD_3OH): δ 6.91-6.88 (m, 2H), 6.82 (dd, *J* = 8.2 and 2.0 Hz, 1H), 3.82 (s, 3H), 3.79 (s, 3H), 2.90 (s, 2H); ^{13}C NMR (100 MHz, CD_3OH): δ 150.5, 149.4, 130.6, 122.1, 113.5, 113.2, 56.4 (2C), 42.1-41.3 (m_{C-D}), 34.0; IR (ATR): ν_{max} 3416, 3396, 2942, 2840, 1612, 1517, 1265, 1235, 1157, 1143, 1024, 811, 764, 655, 620 cm^{-1}; ESIHRMS *m/z* calcd for $C_{10}H_{14}D_2NO_2$ $[M+H]^+$, 184.1301 found 183.1299.



S4$_{d\beta 2}$

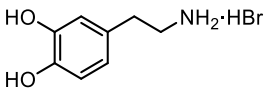
2-(3,4-Dimethoxyphenyl)ethan-2,2-*d*$_2$-1-amine hydrochloride S4$_{d\beta 2}$. Prepared according to general procedure VIII starting from 548 µmol of **S3$_{d\beta 2}$**Yield: 90% (108 mg, 492 µmol); White solid; Mp: 124 °C; ^1H NMR (400 MHz, CD_3OH): δ 6.91-6.87 (m, 2H), 6.82 (dd, *J* = 8.2 and 2.0 Hz, 1H), 3.82 (s, 3H), 3.78 (s, 3H), 3.16 (obs. s, 2H); ^{13}C NMR (100 MHz, CD_3OH): δ 150.5, 149.4, 130.6, 122.1, 113.5, 113.2, 56.4 (2C), 42.2, 34.2-33.1 (m_{C-D}); IR (ATR): ν_{max} 3394, 2944, 1614, 1518, 1466, 1265, 1244, 1172, 1143, 1023, 805, 765, 629 cm^{-1}.



S4$_{d\alpha 2\beta 2}$

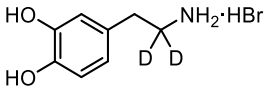
2-(3,4-Dimethoxypheny)ethan-1,1,2,2-*d*$_4$-1-amine hydrochloride S4$_{d\alpha 2\beta 2}$. Prepared according to general procedure VIII starting from 321 µmol of **S3$_{d\alpha 2\beta 2}$**. Yield: 80% (57 mg, 257 µmol); Pale yellow solid; Mp: 124 °C; ^1H NMR (400 MHz, CD_3OH): δ 6.92-6.89 (m, 2H), 6.82 (dd, *J* =8.0 and 2.0 Hz, 1H),

3.83 (s, 3H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, CD_3OH): δ 150.5, 149.4, 130.6, 122.1, 113.5, 113.2, 56.4 (2C), 42.1-41.3 (m_{C-D}), 34.0-33.0 (m_{C-D}); IR (ATR): ν_{max} 3409, 2995, 2941, 2836, 1609, 1590, 1516, 1465, 1415, 1264, 1243, 1208, 1168, 1142, 1026, 804, 763 cm^{-1}; ESIHRMS *m/z* calcd for $C_{10}H_{12}D_4NO_2$ $[M+H]^+$, 186.1427 found 186.1429.



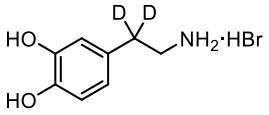
19

2-(3,4-Dihydroxyphenyl)ethylamine hydrobromide 19. Prepared according to general procedure IX starting from 921 µmol of **S4**. Yield: 97% (210 mg, 897 µmol); Brown solid; Mp: 130 °C ; ^{1}H NMR (400 MHz, CD_3OD): δ 6.77-6.73 (m, 2H), 6.61 (dd, *J* = 8.0 and 2.0 Hz, 1H), 3.12 (t, *J* = 7.6 Hz, 2H), 2.83 (t, *J* = 8.0 Hz, 2H), ^{13}C NMR (100 MHz, CD_3OD): δ 146.5, 145.4, 129.3, 121.1, 116.8, 116.7, 42.2, 33.8; IR (ATR): ν_{max} 3370, 3031, 2505, 2421, 1516, 1282, 1187, 1153, 1128, 1120, 1060, 974, 934, 875, 807, 780 cm^{-1}.



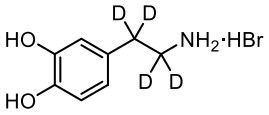
$19_{d\alpha 2}$

2-(3,4-Dihydroxyphenyl)ethyl-1,1-*d*$_2$-amine hydrobromide $19_{d\alpha 2}$. Prepared according to general procedure IX starting from 1.46 mmol of **$S4_{d\alpha 2}$**. Yield: quant. (343 mg, 1.45 mmol), α deuteration: 99% (calculated by integration of the residual signal in the ^{1}H NMR spectra); Brown solid; ^{1}H NMR (400 MHz, CD_3OD): δ 6.79-6.74 (m, 2H), 6.62 (dd, *J* = 8.0 and 2.0 Hz, 1H), 2.83 (s, 2H); ^{13}C NMR (100 MHz, CD_3OD): δ 146.4, 145.3, 129.3, 121.2, 116.8, 116.7, 42.0-41.4 (m_{C-D}), 33.6; IR (ATR): ν_{max} 3419, 3062, 3033, 2952, 2277, 1626, 1528, 1450, 1362, 1288, 1188, 1118, 954, 865, 812, 783, 610 cm^{-1}; ESIHRMS *m/z* calcd for $C_8H_{10}D_2NO_2$ $[M+H]^+$ 156.0988, found 156.0992.



$19_{d\beta 2}$

2-(3,4-Dihydroxyphenyl)ethyl-2,2-*d*$_2$-amine hydrobromide $19_{d\beta 2}$. Prepared according to general procedure IX starting from 450 µmol of **$S4_{d\beta 2}$**. Yield: quant. (107 mg, 453 µmol), β deuteration: 87% (calculated by integration of the residual signal in the ^{1}H NMR spectra); Brown solid; ^{1}H NMR (400 MHz, CD_3OD): δ 6.79-6.75 (m, 2H), 6.61 (dd, *J* = 8.0 and 2.4 Hz, 1H), 3.11 (s, 2H); ^{13}C NMR (100 MHz, CD_3OD): δ 146.4, 145.2, 129.3, 121.2, 116.8, 116.7, 42.1, 33.8-32.8 (m_{C-D}); IR (ATR): ν_{max} 3400, 3065, 2950, 2530, 2315, 1629, 1527, 1439, 1285, 1180, 1121, 959, 869, 812, 783 cm^{-1}; ESIHRMS *m/z* calcd for $C_8H_{10}D_2NO_2$ $[M+H]^+$ 156.0988, found 156.0992.

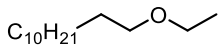


$19_{d\alpha 2\beta 2}$

2-(Dihydroxyphenyl)ethyl-1,1,2,2-*d*$_4$-amine hydrobromide $19_{d\alpha 2\beta 2}$. Prepared according to general procedure IX starting from 262 µmol of **$S4_{d\alpha 2\beta 2}$**. Yield: quant. (63 mg, 265 µmol), α and β deuteration: 99% and 91% (calculated by integration of the residual signals in the ^{1}H NMR spectra); Brown solid; ^{1}H

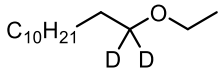
NMR (400 MHz, CD_3OD): δ 6.79-6.77 (m, 2H), 6.62 (dd, J = 8.0 and 2.0 Hz, 1H); ^{13}C NMR (100 MHz, CD_3OD): δ 146.1, 144.9, 129.3, 121.2, 116.7, 116.6, 42.0-41.2 (m_{C-D}), 33.0-32.2 (m_{C-D}); IR (ATR): ν_{max} 3392, 3028, 2991, 1637, 1528, 1439, 1179, 1121, 604 cm^{-1}; ESIHRMS *m/z* calcd for $C_8H_8D_4NO_2$ $[M+H]^+$ 158.1114, found 158.1114.

Experimental Procedure and Characterization Data: Reduction/Reductive Deuteration of Ynol Ethers



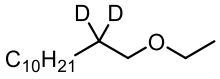
22

1-Ethoxydodecane 22. To a vigorously stirred solution of 1-ethoxydodec-1-yne **21** (197 mg, 936 µmol) in dichloromethane (3.5 mL) under an argon atmosphere was added triethylsilane (745 µL, 4.68 mmol). Trifluoromethanesulfonic acid (205 µL, 2.34 mmol) was then added dropwise at 0 °C and the mixture was stirred at rt overnight. The resulting reaction mixture was then poured into a 1M aqueous solution of NaOH. The layers were separated and the aqueous layer was extracted with dichloromethane (2x). Combined organic layers were dried over $MgSO_4$, filtered and concentrated. The crude reaction mixture was diluted in a 1:1:1 mixture of tetrahydrofuran, methanol and water (3.5 mL) before lithium hydroxide (112 mg, 4.66 mmol) was added. The resulting mixture was stirred at rt for 5 hours before being quenched by addition of a 1M aqueous solution of NaOH. The layers were separated, the aqueous layer was extracted with EtOAc (2x) and the combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was finally purified by flash column chromatography (petroleum ether) to afford the desired ether as a colorless oil. Yield: 40% (80 mg, 376 µmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.46 (q, J = 6.8 Hz, 2H), 3.40 (t, J = 6.8 Hz, 2H), 1.60-1.53 (m, 2H), 1.34-1.23 (m, 18H), 1.20 (t, J = 7.0 Hz, 3H), 0.88 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 71.0, 66.2, 32.1, 30.0, 29.8, 29.8, 29.8 (2C), 29.7, 29.5, 26.4, 22.8, 15.4, 14.3. This compound has been previously reported.[S12]



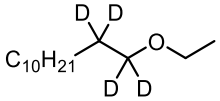
22$_{d\alpha 2}$

1-Ethoxydodecane-1,1-d_2 22 $_{d\alpha 2}$. To a vigorously stirred solution of 1-ethoxydodec-1-yne **21** (180 mg, 855 µmol) in dichloromethane (3.2 mL) under an argon atmosphere was added triethyl(silane-*d*) (690 µL, 4.28 mmol). Trifluoromethanesulfonic acid (190 µL, 2.14 mmol) was then added dropwise at 0 °C and the mixture was stirred at rt overnight. The resulting reaction mixture was then poured into a 1M aqueous solution of NaOH. The layers were separated and the aqueous layer was extracted with dichloromethane (2x). Combined organic layers were dried over $MgSO_4$, filtered and concentrated. The crude reaction mixture was diluted in a 1:1:1 mixture of tetrahydrofuran, methanol and water (3.2 mL) before lithium hydroxide (102 mg, 4.28 mmol) was added. The resulting mixture was stirred at rt for 5 hours before being quenched by addition of a 1M aqueous solution of NaOH. The layers were separated, the aqueous layer was extracted with EtOAc (2x) and the combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was finally purified by flash column chromatography (petroleum ether) to afford the desired α,α-deuterated ether as a colorless oil. Yield: 27% (50 mg, 231 µmol), α deuteration: 92% (calculated by integration of the residual signal in the ^{1}H NMR spectra). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.46 (q, J = 7.0 Hz, 2H), 1.57-1.53 (m, 2H), 1.35-1.25 (m, 18H), 1.20 (t, J = 7.2 Hz, 3H), 0.87 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 70.4-69.9 ($m_{C\text{-}D}$), 66.1, 32.1, 29.8, 29.8, 29.8 (3C), 29.7, 29.5, 26.3, 22.8, 15.4, 14.3; IR (ATR): ν_{max} 2957, 2924, 2854, 1466, 1393, 1379, 1180, 1158, 1118, 721 cm^{-1}.



$22_{d\beta2}$

1-Ethoxydodecane-2,2-*d*$_2$ $22_{d\beta2}$. To a vigorously stirred solution of 1-ethoxydodec-1-yne **21** (97 mg, 461 µmol) in dichloromethane (1.8 mL) under an argon atmosphere was added triethylsilane (370 µL, 2.31 mmol). Freshly prepared trifluoromethanesulfonic acid-*d* (100 µL, 1.15 mmol) was then added dropwise at 0 °C and the mixture was stirred at rt overnight. The resulting reaction mixture was then poured into a 1M aqueous solution of NaOH. The layers were separated and the aqueous layer was extracted with dichloromethane (2x). Combined organic layers were dried over $MgSO_4$, filtered and concentrated. The crude reaction mixture was diluted in a 1:1:1 mixture of tetrahydrofuran, methanol and water (1.8 mL) before lithium hydroxide (57 mg, 2.40 mmol) was added. The resulting mixture was stirred at rt for 5 hours before being quenched by addition of a 1M aqueous solution of NaOH. The layers were separated, the aqueous layer was extracted with EtOAc (2x) and the combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was finally purified by flash column chromatography (petroleum ether) to afford the desired β,β-deuterated ether as a colorless oil. Yield: 44% (44 mg, 203 µmol), β deuteration: 86% (calculated by integration of the residual signal in the ^{1}H NMR spectra). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 3.46 (q, *J* = 7.0 Hz, 2H), 1.57-1.53 (m, 2H), 1.35-1.25 (m, 18H), 1.20 (t, *J* = 7.2 Hz, 3H), 0.87 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 70.8, 66.2, 32.1, 29.8, 29.8, 29.8 (2C), 29.6, 29.5, 26.2, 22.8, 15.4, 14.2 (1 C-D missing); IR (ATR): ν_{max} 2957, 2924, 2854, 1466, 1376, 1352, 1119, 721 cm^{-1}.

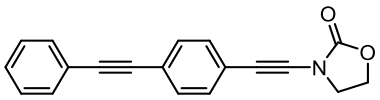


$22_{d\alpha2\beta2}$

1-Ethoxydodecane-1,1,2,2-*d*$_4$ $22_{d\alpha2\beta2}$. To a vigorously stirred solution of 1-ethoxydodec-1-yne **21** (178 mg, 847 µmol) in dichloromethane (3.1 mL) under an argon atmosphere was added triethyl(silane-*d*) (680 µL, 4.24 mmol). Trifluoromethanesulfonic acid-*d* (190 µL, 2.12 mmol) was then added dropwise at 0 °C and the mixture was stirred at rt overnight. The resulting reaction mixture was then poured into a 1M aqueous solution of NaOH. The layers were separated and the aqueous layer was extracted with dichloromethane (2x). Combined organic layers were dried over $MgSO_4$, filtered and concentrated. The crude reaction mixture was diluted in a 1:1:1 mixture of tetrahydrofuran, methanol and water (3.1 mL) before lithium hydroxide (101 mg, 4.24 mmol) was added. The resulting mixture was stirred at rt for 5 hours before being quenched by addition of a 1M aqueous solution of NaOH. The layers were separated, the aqueous layer was extracted with EtOAc (2x) and the combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was finally purified by flash column chromatography (petroleum ether) to afford the desired α,α,β,β-deuterated ether as a colorless oil. Yield: 27% (50 mg, 229 µmol), α and β deuteration: 98% and 62% (calculated by integration of the residual signals in the ^{1}H NMR spectra). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 3.46 (q, *J* = 7.2 Hz, 2H), 1.31-1.25 (m, 18H), 1.20 (t, *J* = 7.0 Hz, 3H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 66.1, 32.1, 29.8, 29.8, 29.8 (2C), 29.6, 29.5, 26.1, 22.8, 15.4, 14.3 (2 C-D missing); IR (ATR): ν_{max} 2957, 2924, 2855, 1466, 1394, 1379, 1134, 1084, 997, 770, 721.

Supporting Information

^{1}H and ^{13}C NMR Spectra



9c

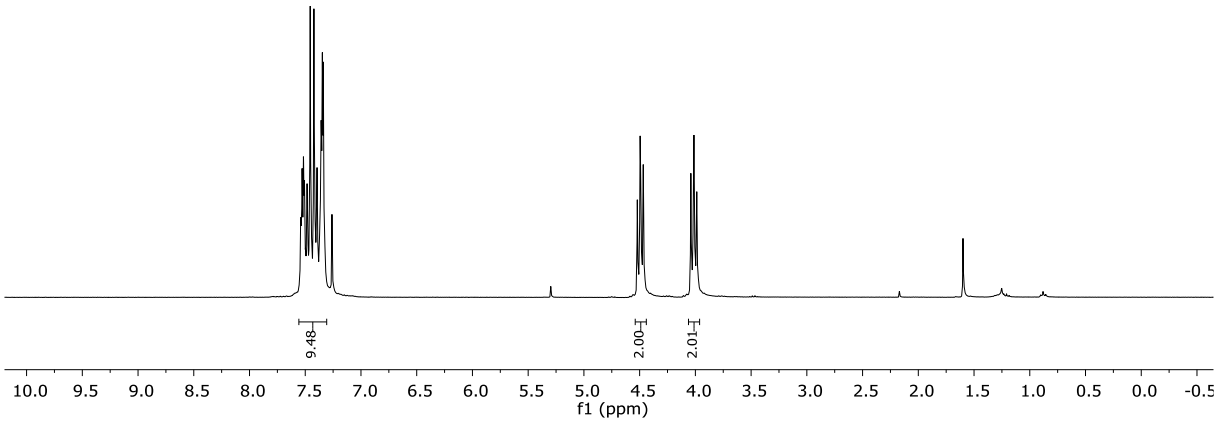


Figure S1. ^{1}H NMR spectrum of **9c**.

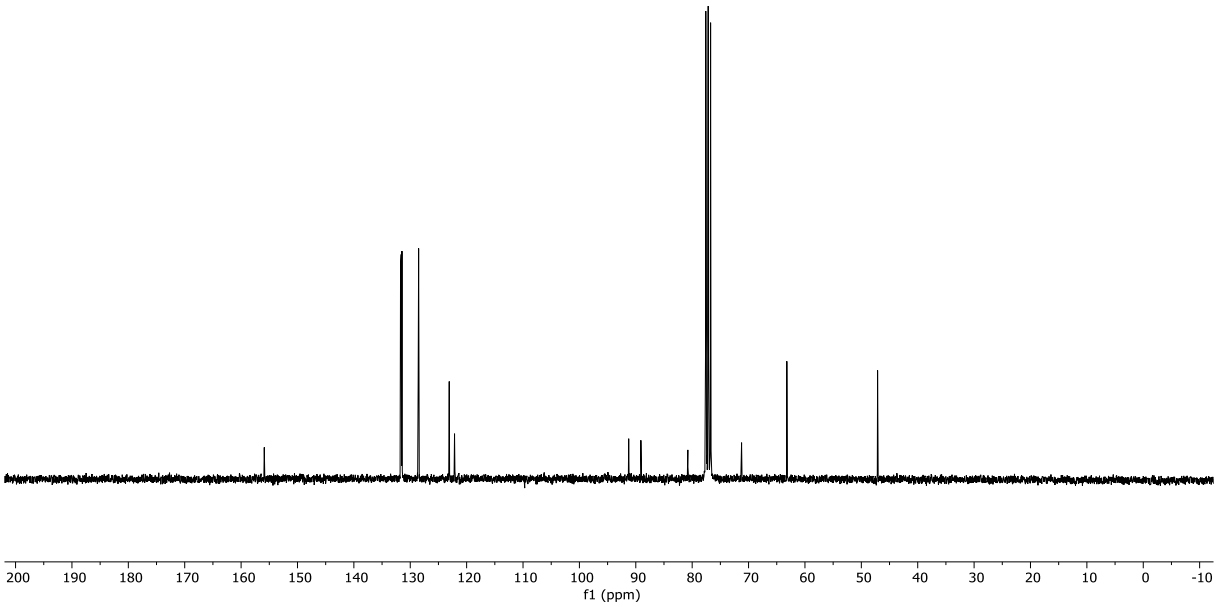
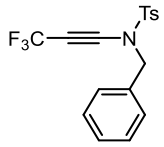


Figure S2. ^{13}C NMR spectrum of **9c**.



9k

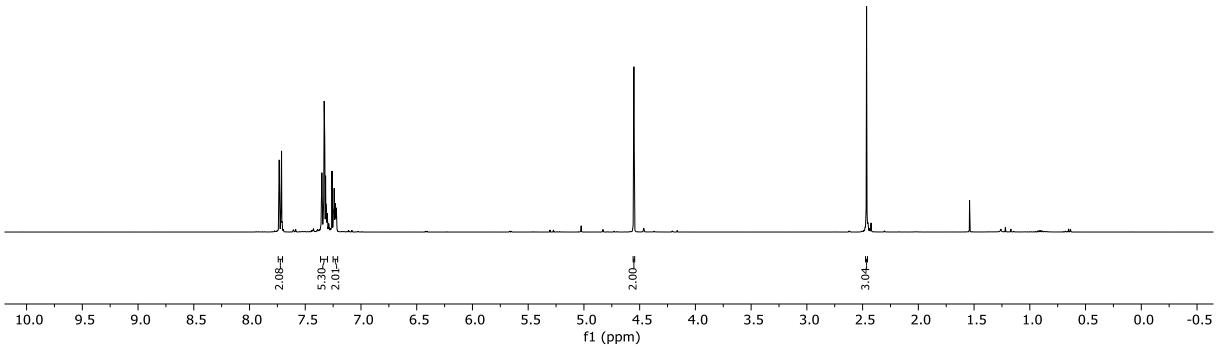


Figure S3. ^{1}H NMR spectrum of **9k**.

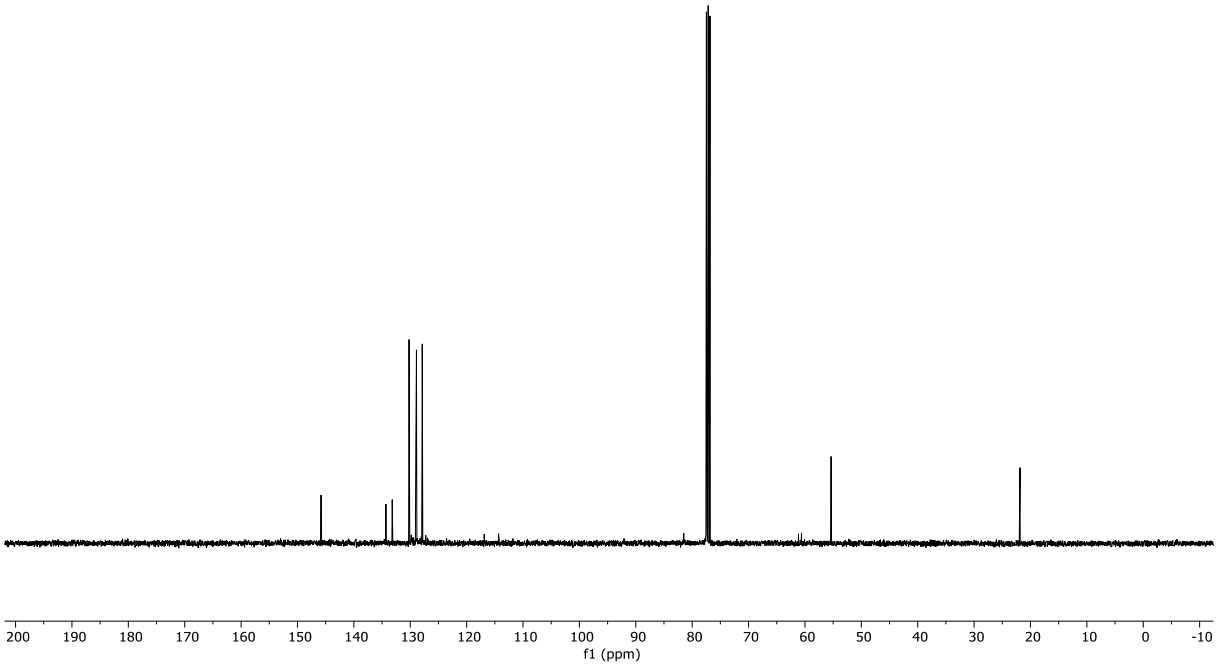


Figure S4.^{13}C NMR spectrum of **9k**.

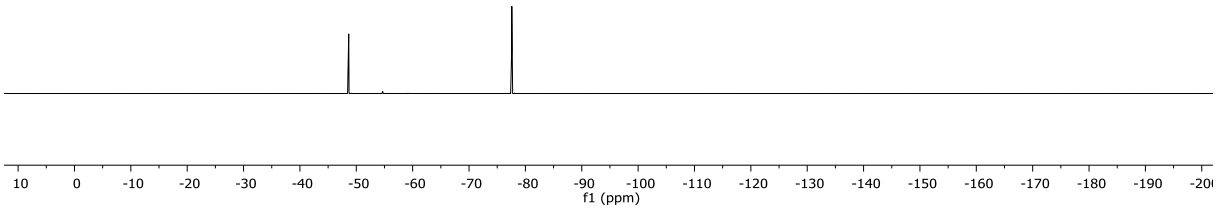


Figure S5. ^{19}F NMR spectrum of **9k**.

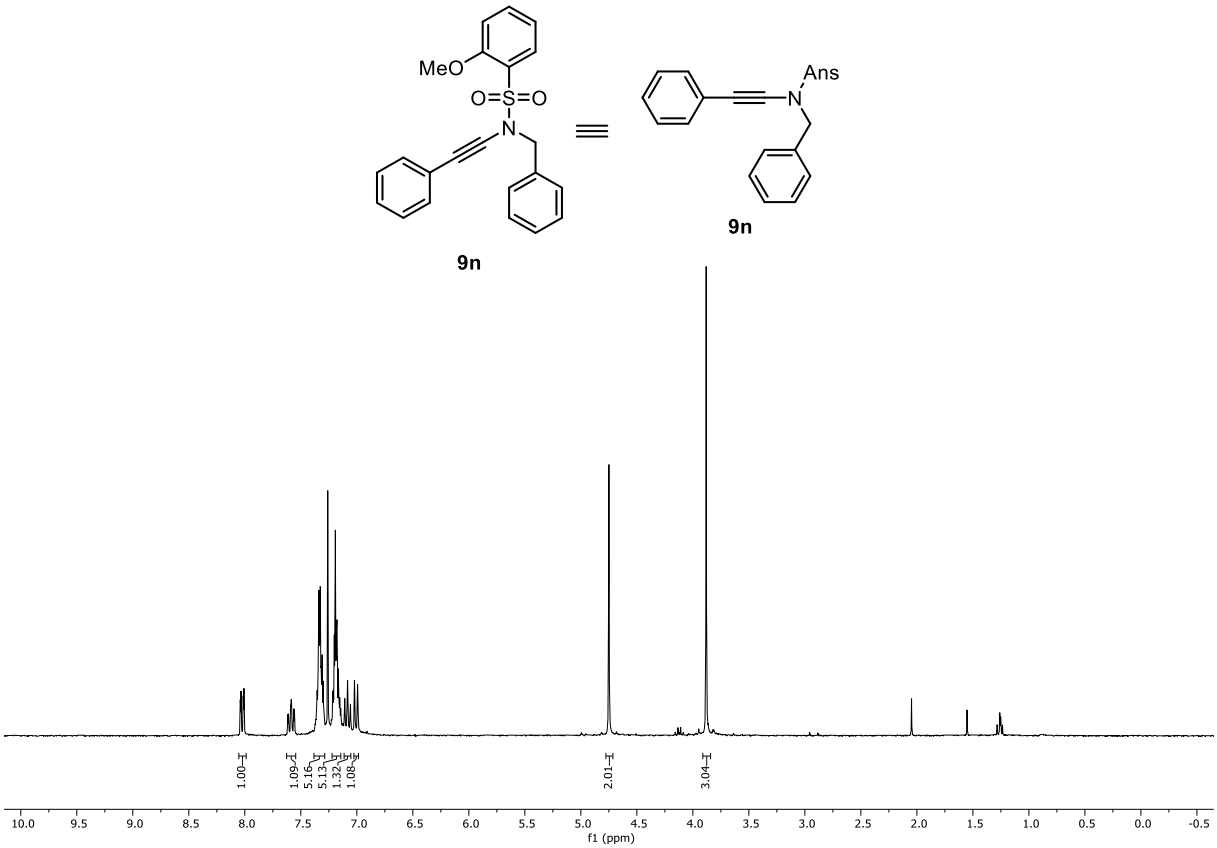


Figure S6. ^{1}H NMR spectrum of **9n**.

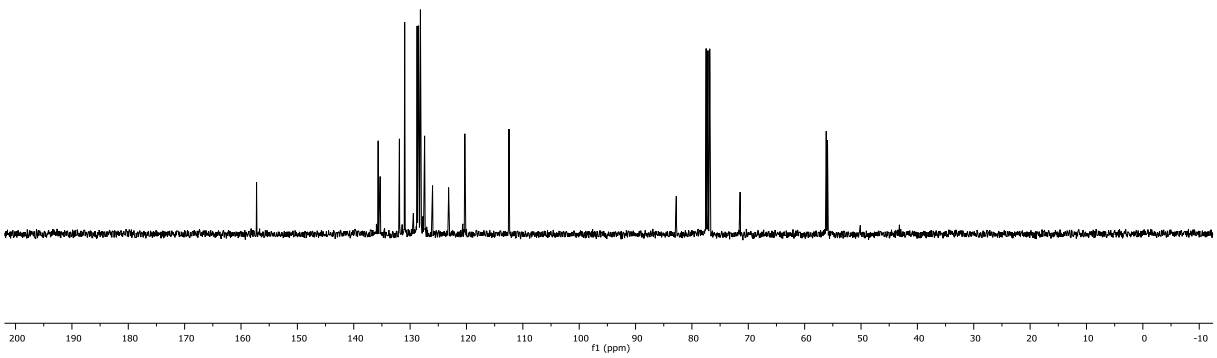
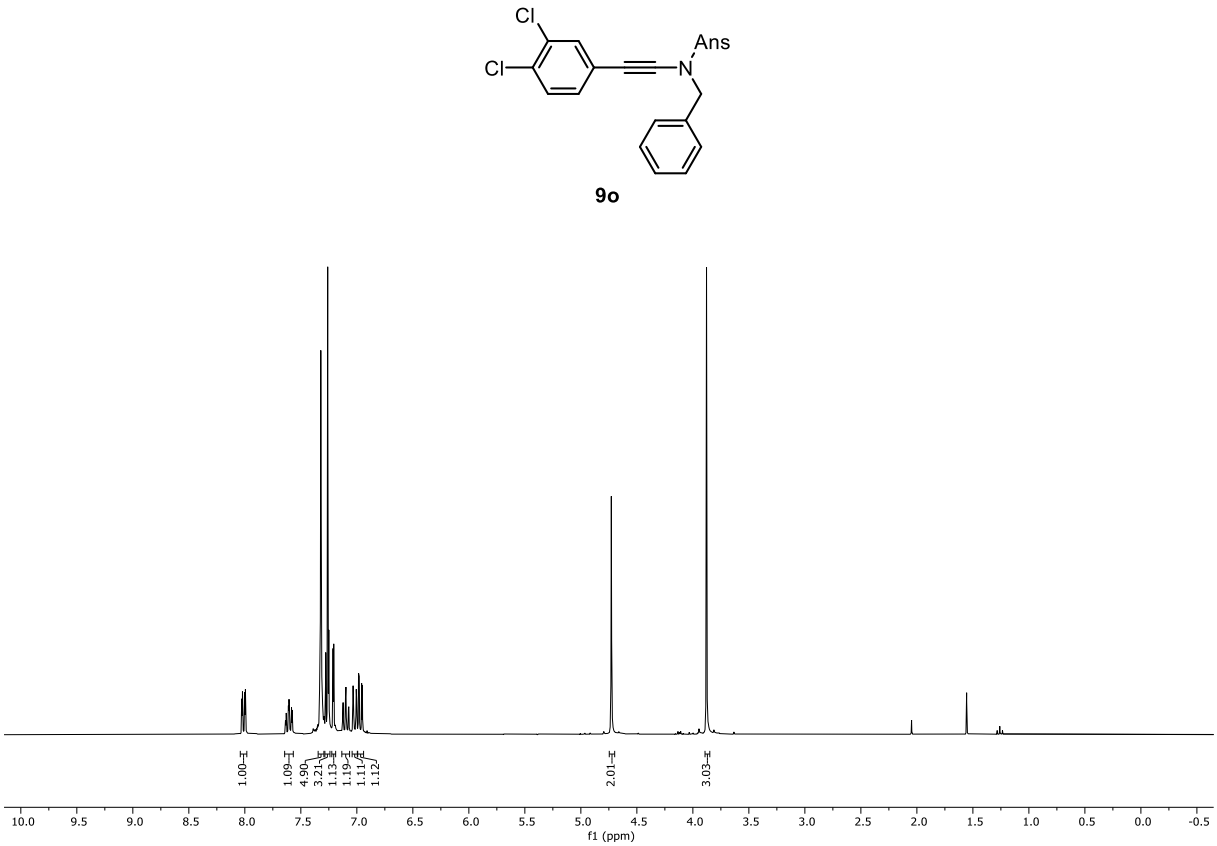


Figure S7. ^{13}C NMR spectrum of **9n**.



9o

Figure S8. ^{1}H NMR spectrum of **9o**.

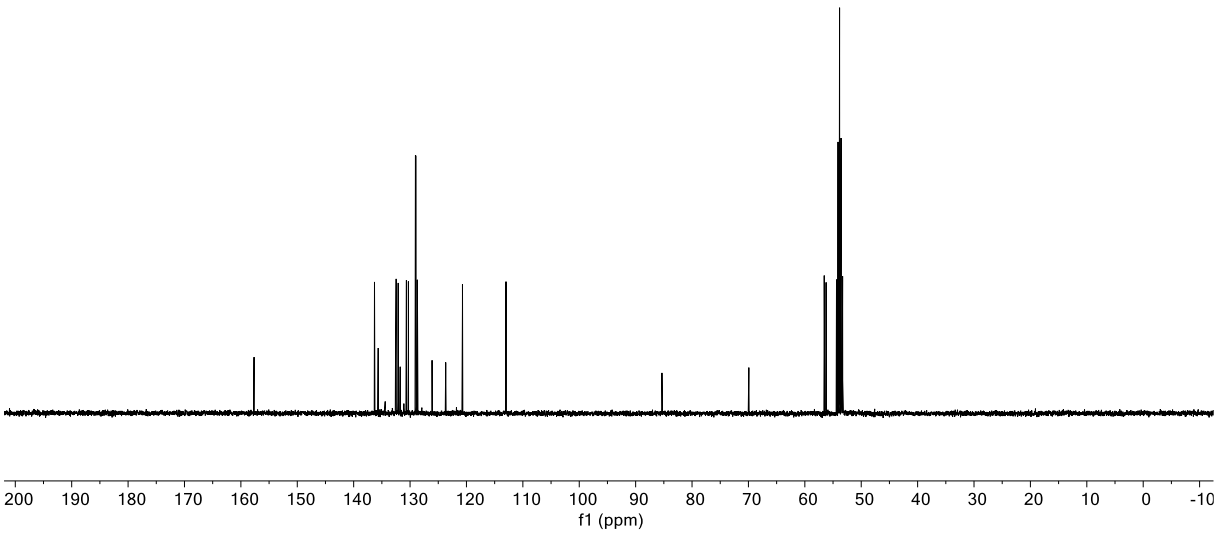
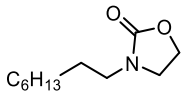


Figure S9. ^{13}C NMR spectrum of **9o**.



13a

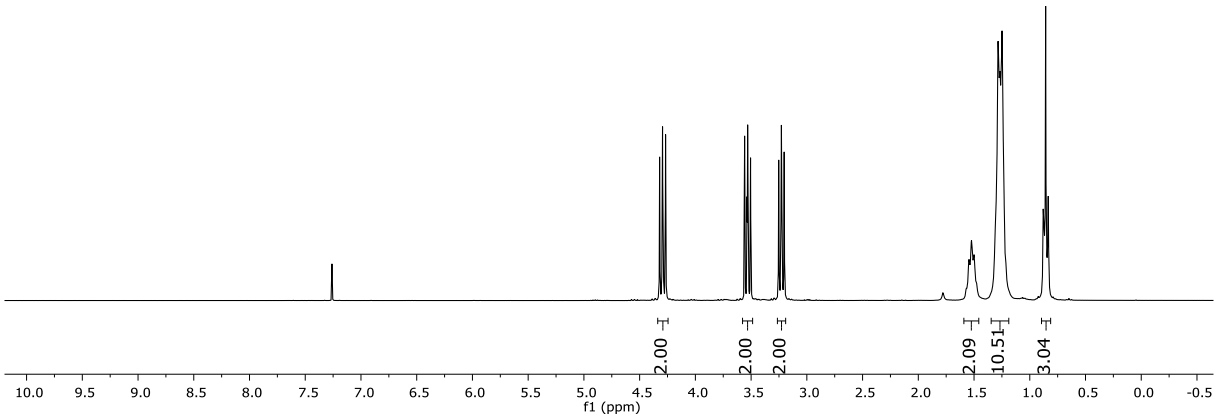


Figure S10. ^{1}H NMR spectrum of **13a**.

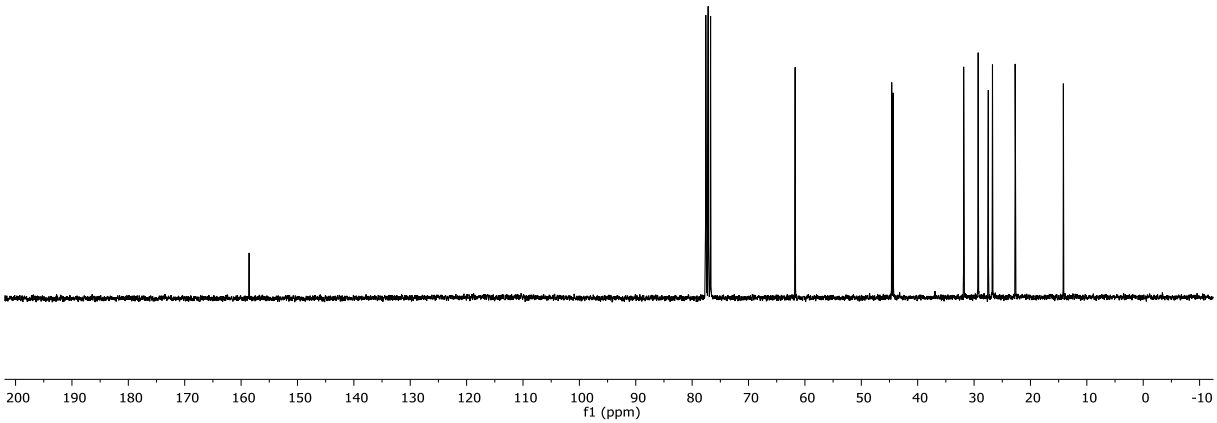
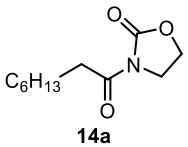


Figure S11. ^{13}C NMR spectrum of **13a**.



14a

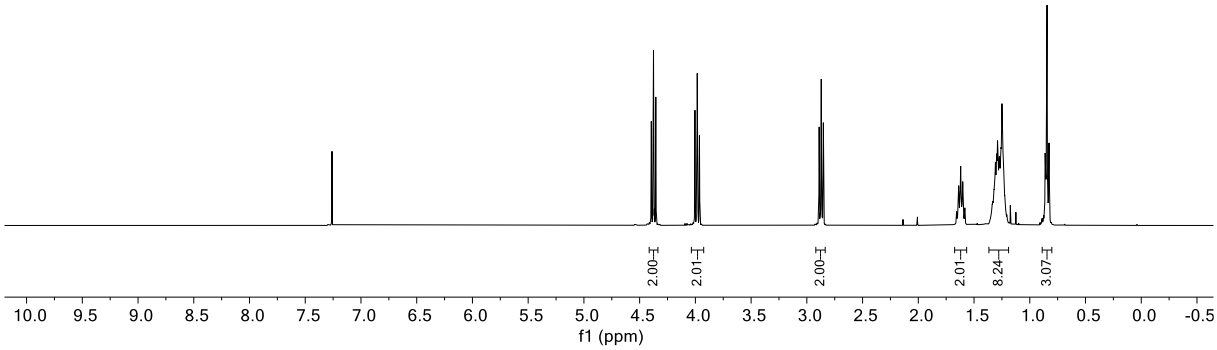


Figure S12. ^{1}H NMR spectrum of **14a.**

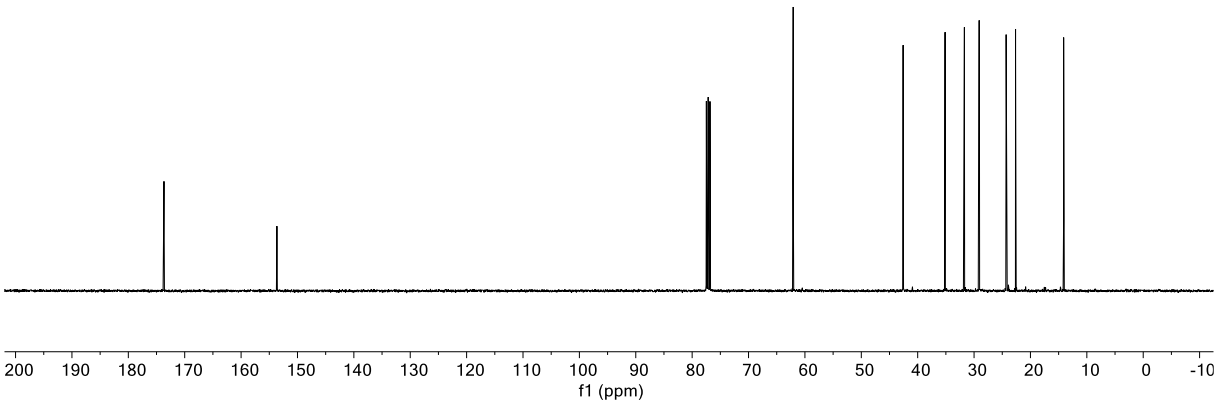


Figure S13. ^{13}C NMR spectrum of **14a.**

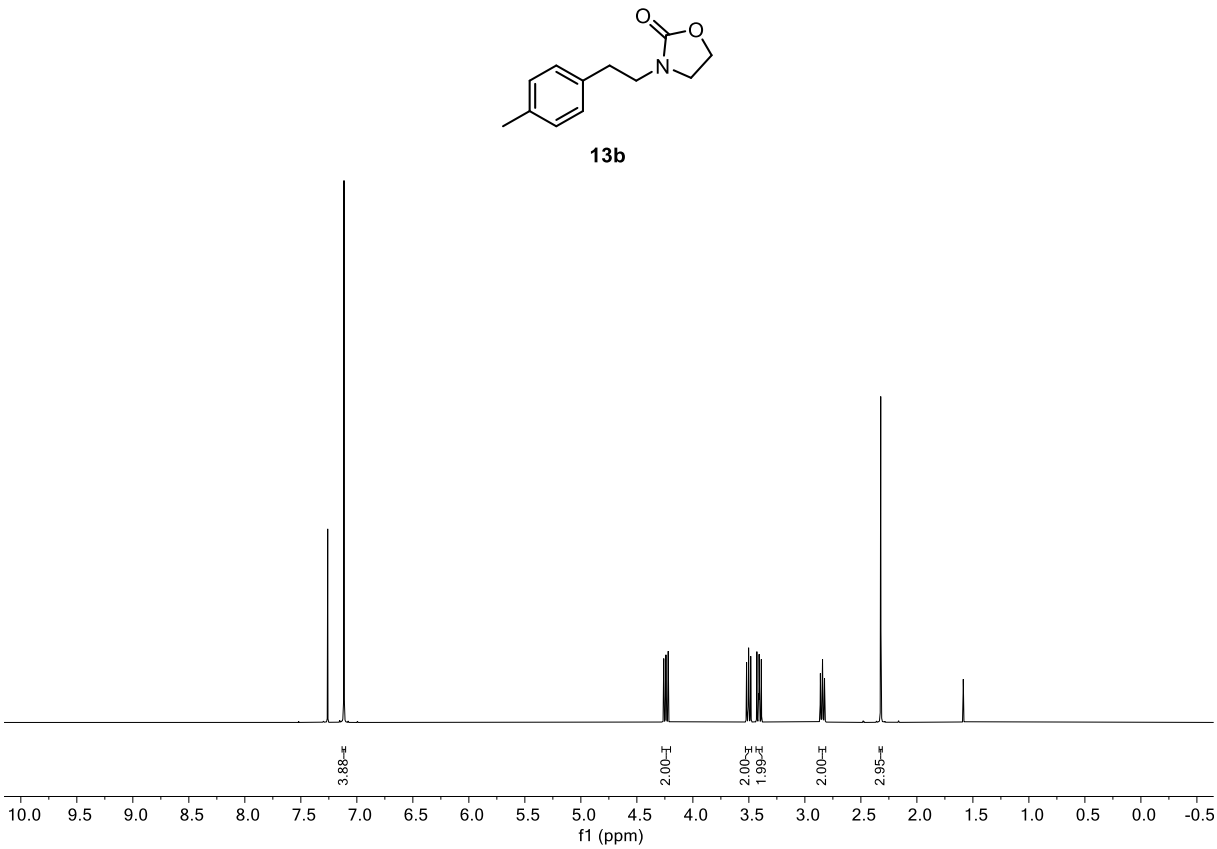


Figure S14. ^{1}H NMR spectrum of **13b**.

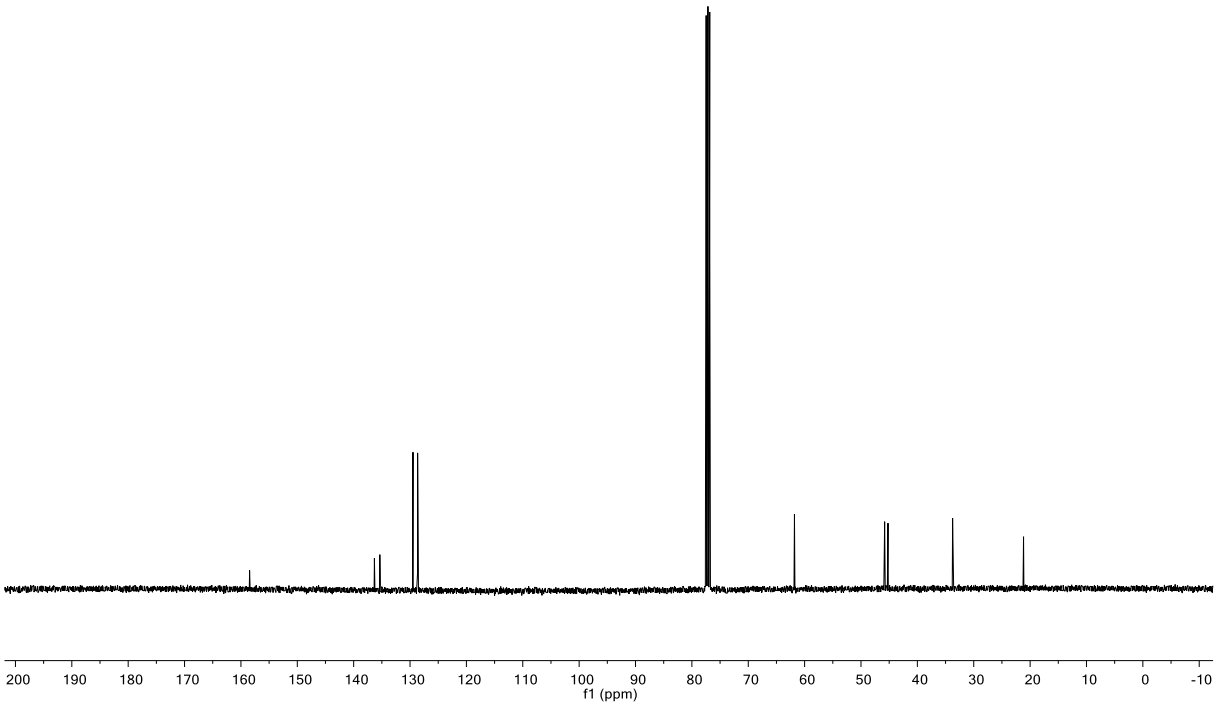
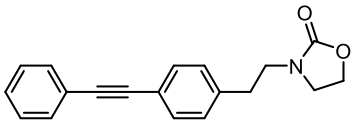


Figure S15. ^{13}C NMR spectrum of **13b**.



13c

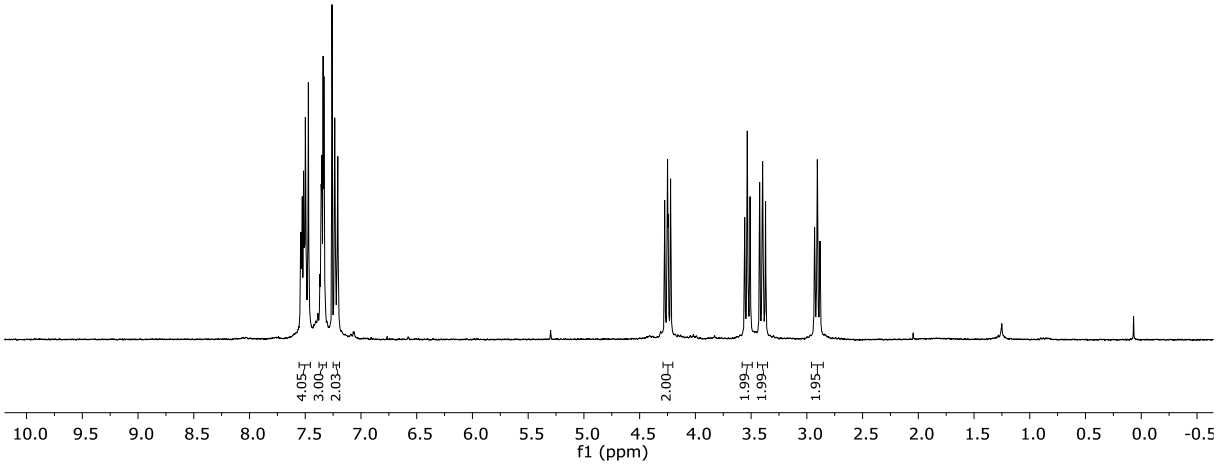


Figure S16. ^{1}H NMR spectrum of **13c**.

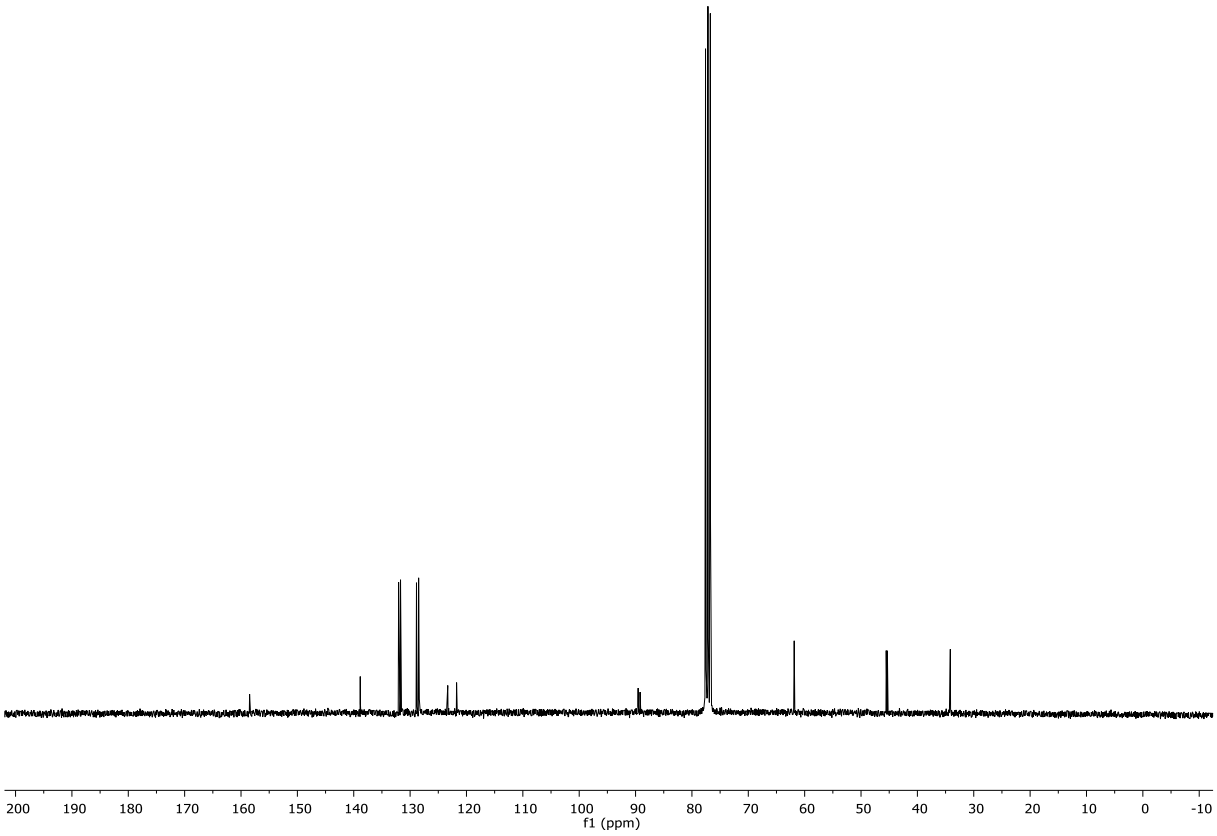
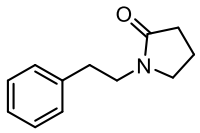


Figure S17. ^{13}C NMR spectrum of **13c**.



13d

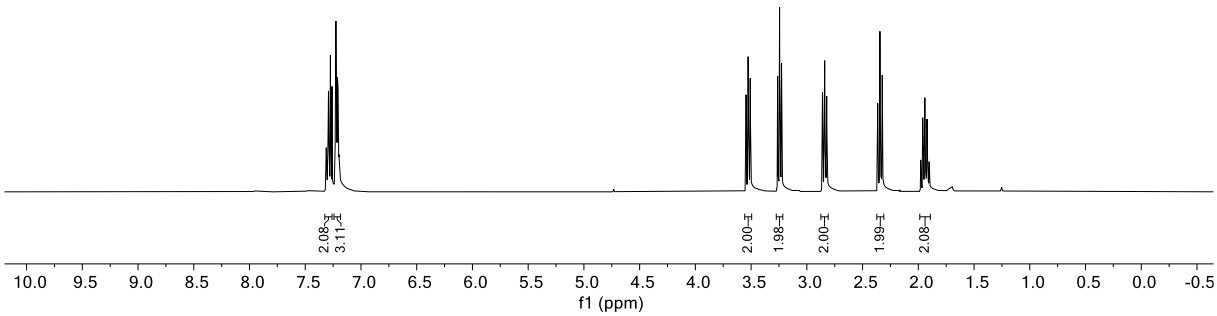


Figure S18. ^{1}H NMR spectrum of **13d**.

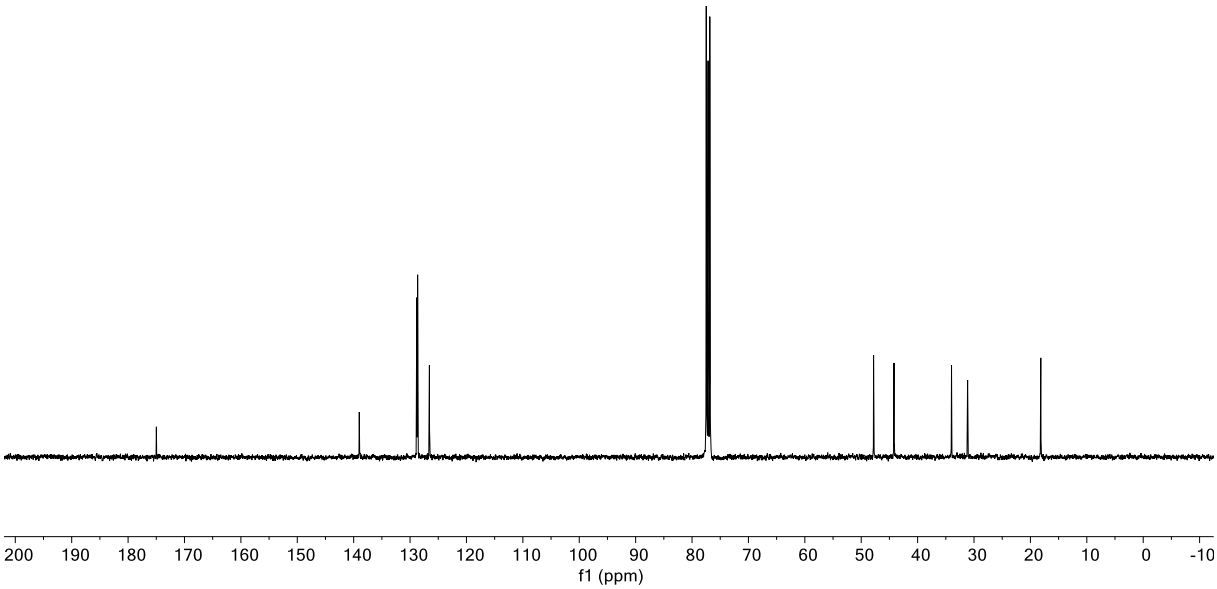
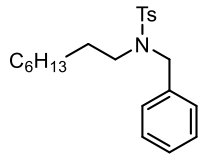


Figure S19. ^{13}C NMR spectrum of **13d**.



13e

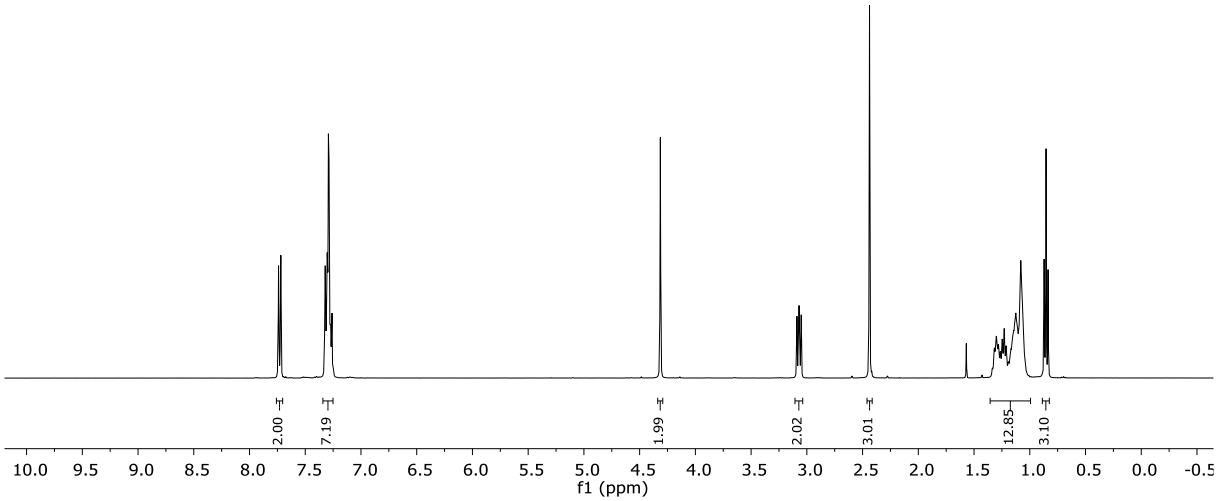


Figure S20. ^{1}H NMR spectrum of **13e**.

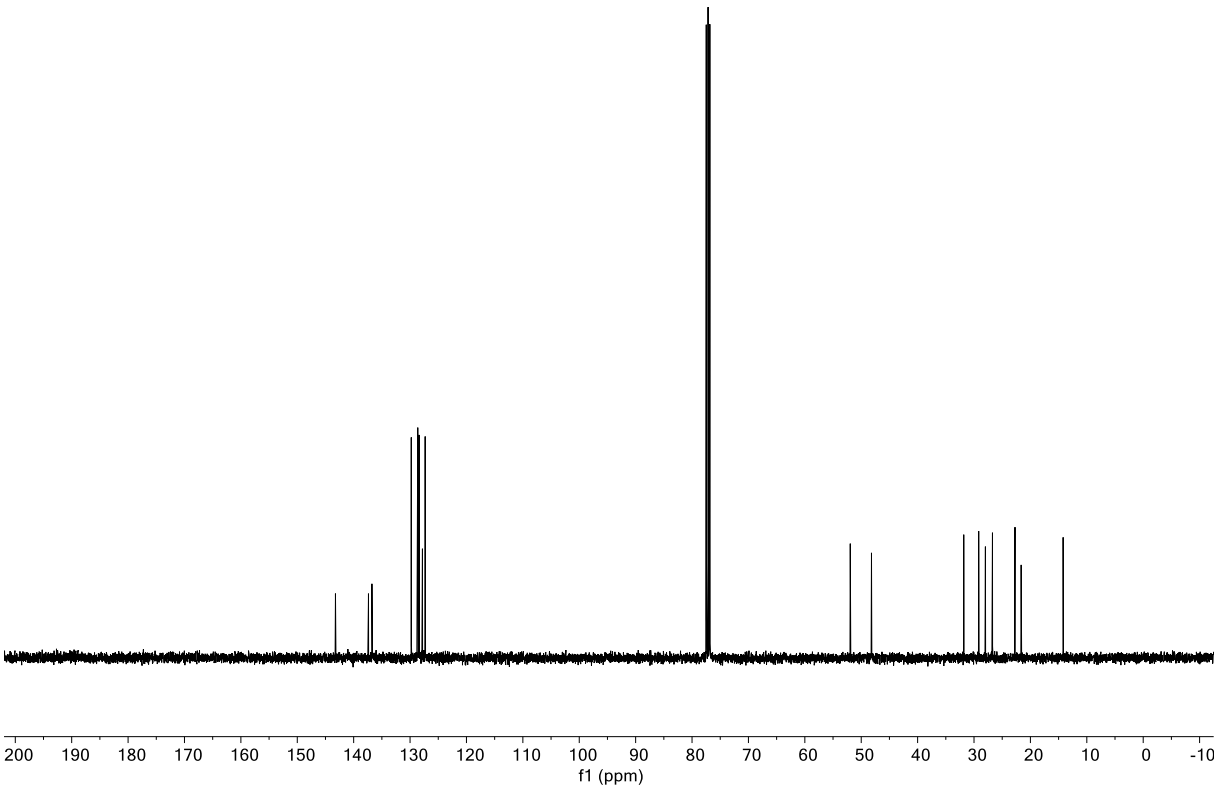
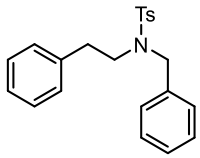


Figure S21. ^{13}C NMR spectrum of **13e**.



13f

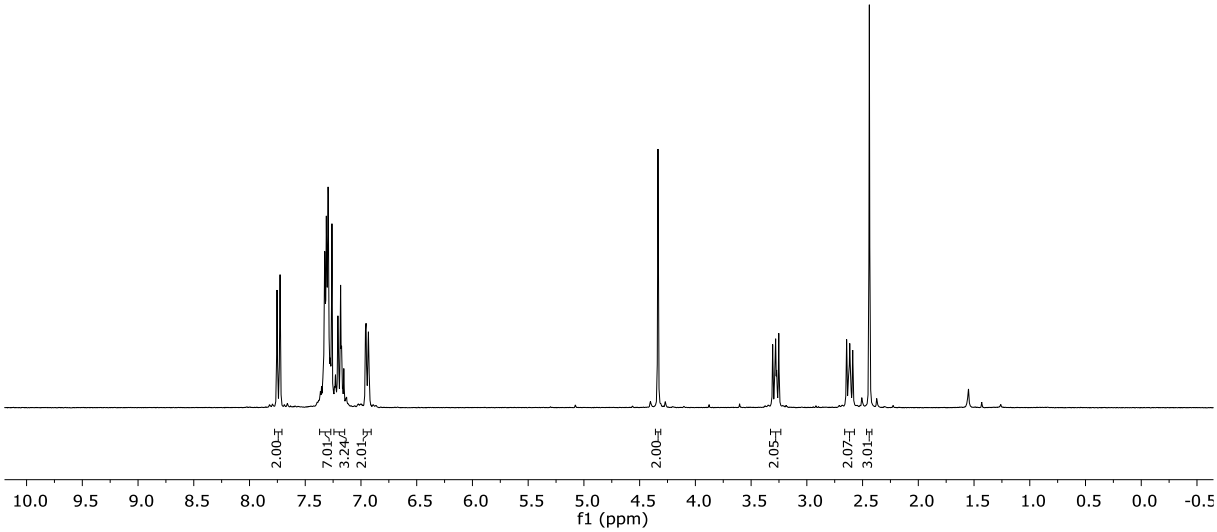


Figure S22. ^{1}H NMR spectrum of **13f**.

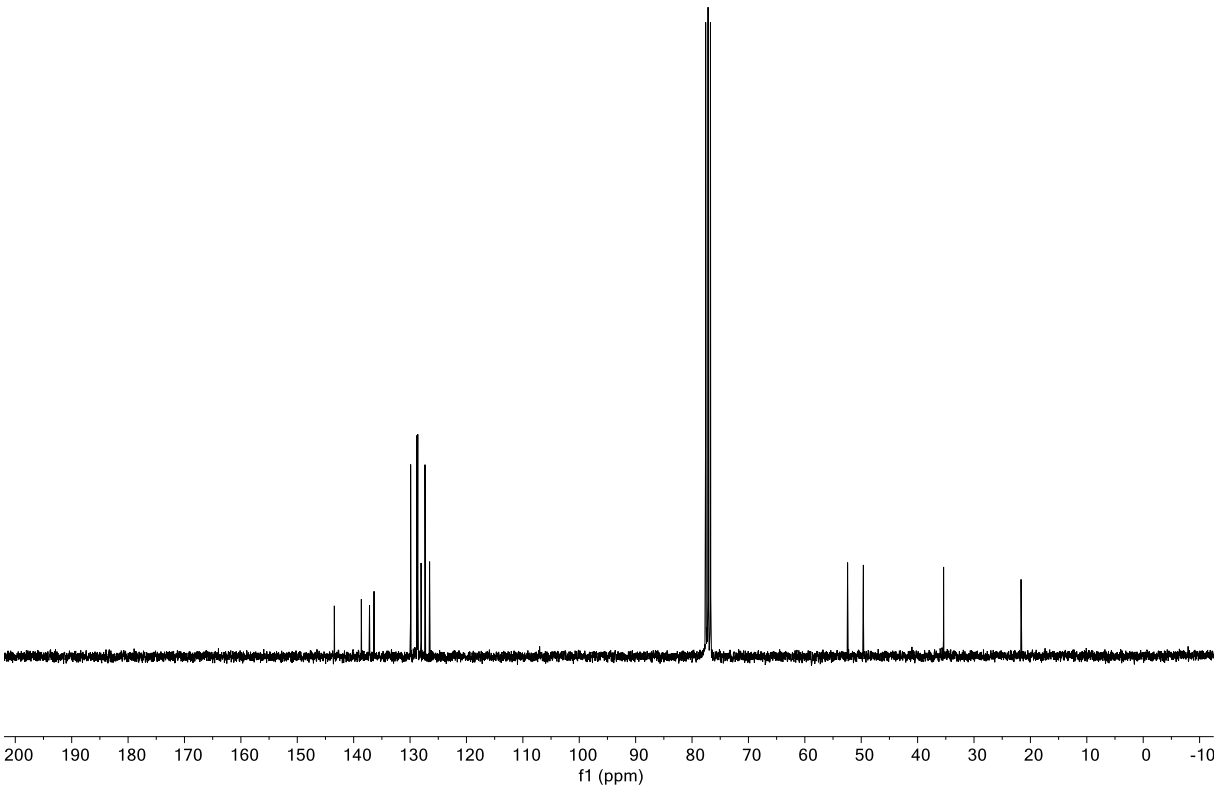
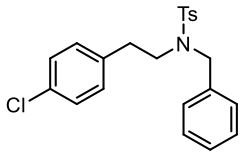


Figure S23. ^{1}H NMR spectrum of **13f**.



13g

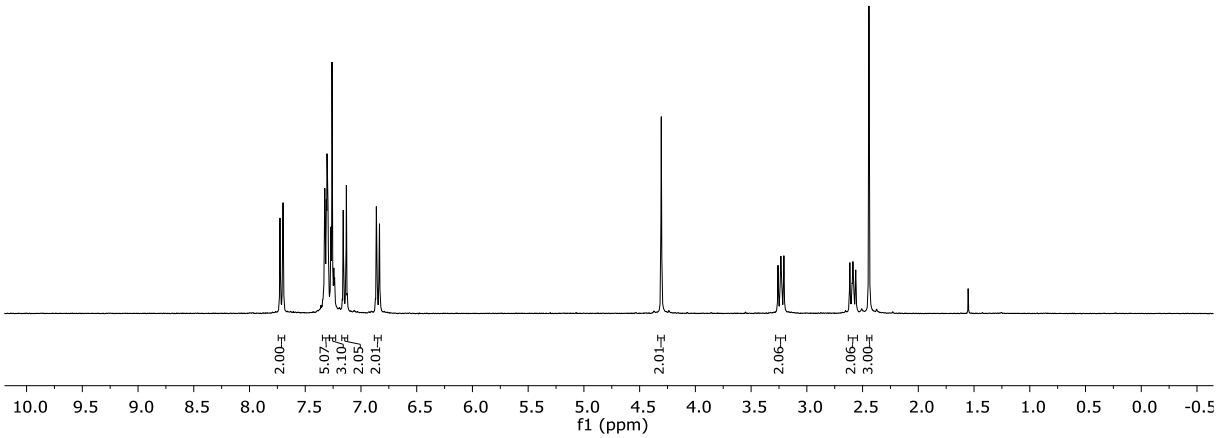


Figure S24. ^{1}H NMR spectrum of **13g**.

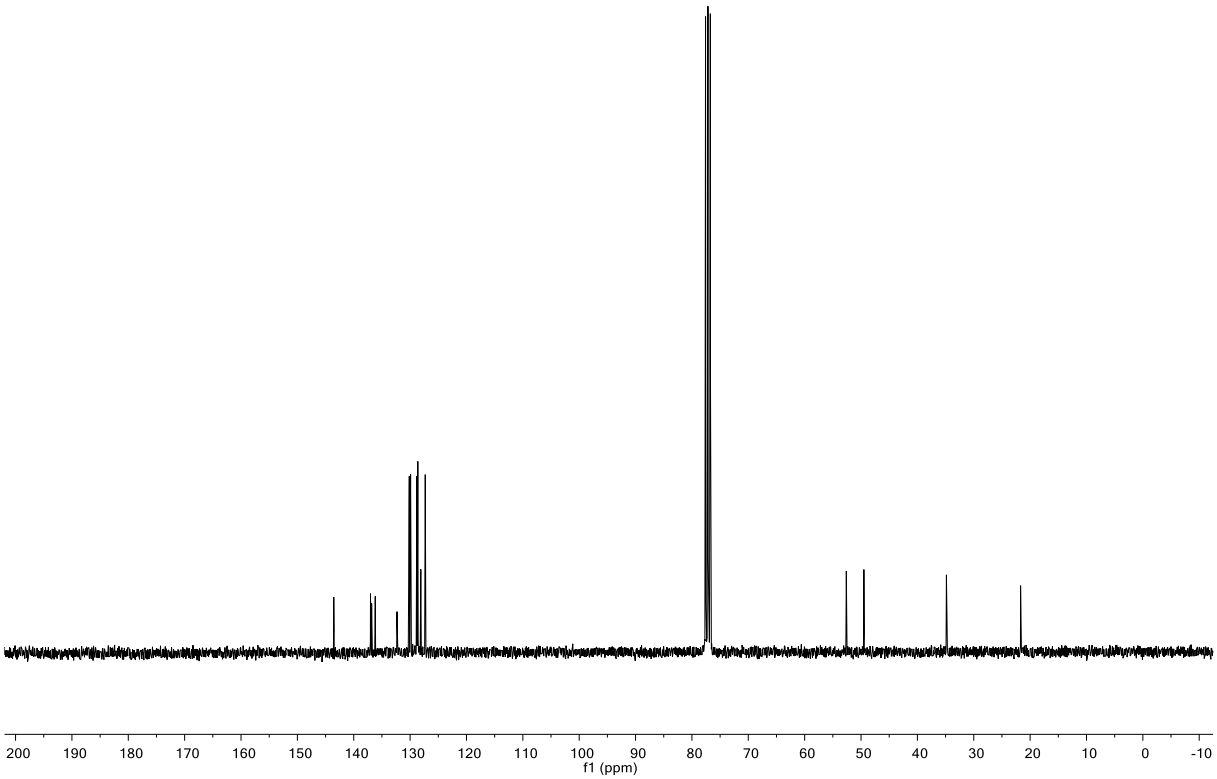
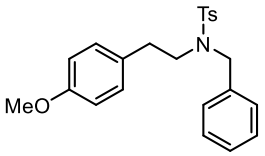


Figure S25. ^{13}C NMR spectrum of **13g**.



13h

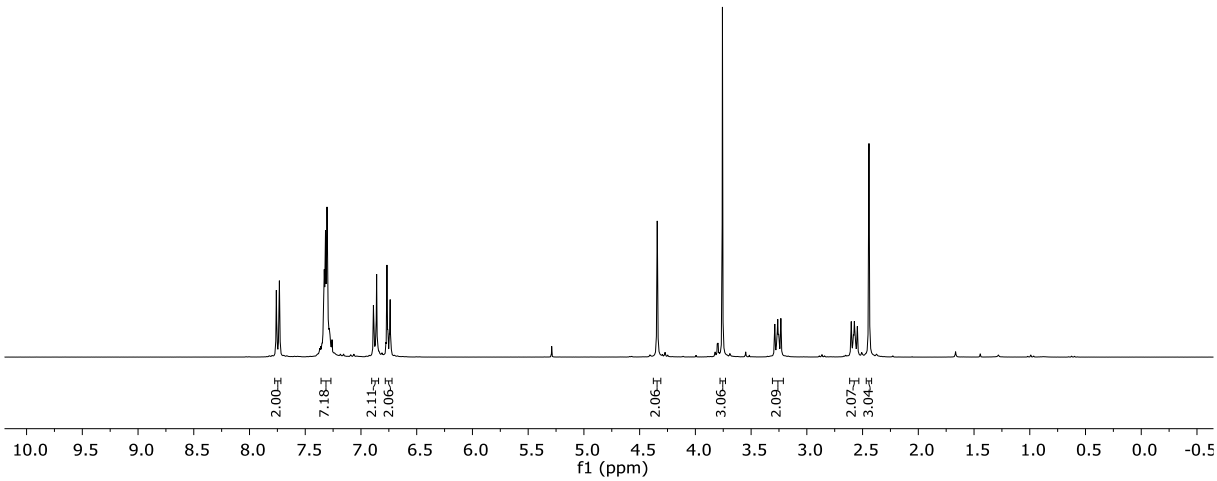


Figure S26. ^{1}H NMR spectrum of **13h**.

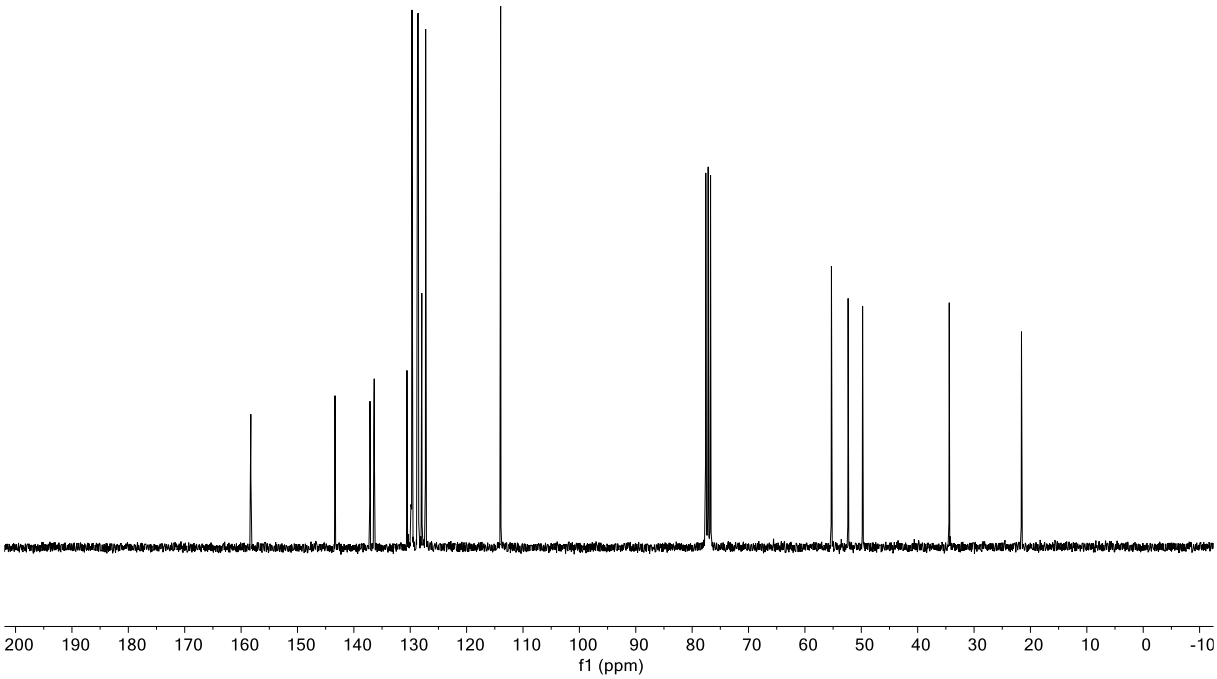
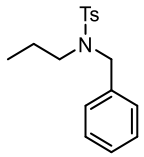


Figure S27. ^{13}C NMR spectrum of **13h**.



13i

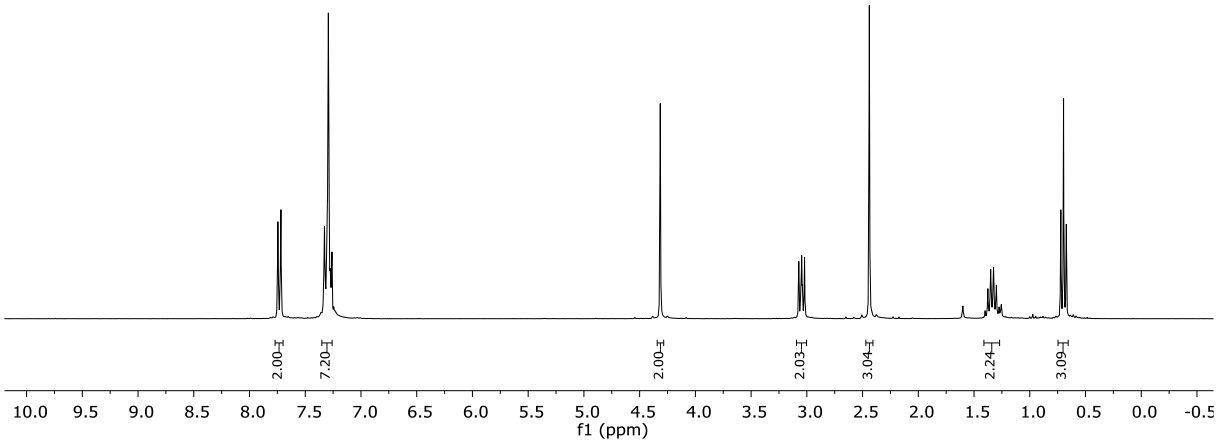


Figure S28. ^{1}H NMR spectrum of **13i**.

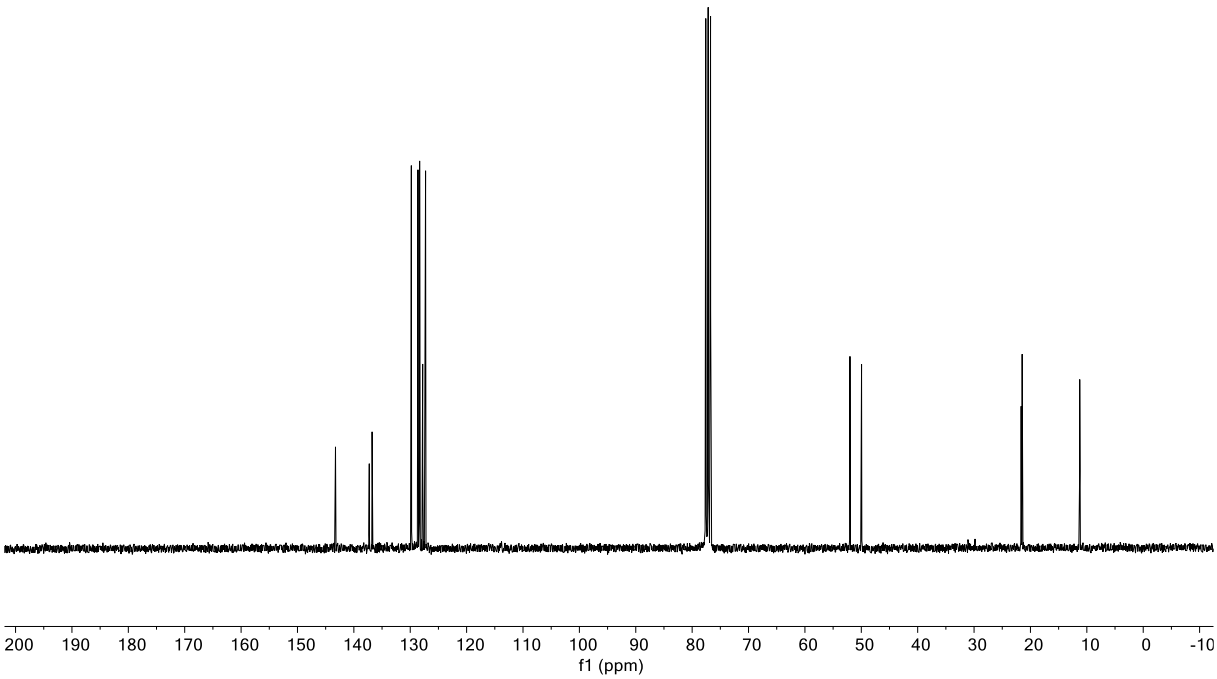
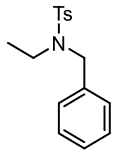


Figure S29. ^{13}C NMR spectrum of **13i**.



13j

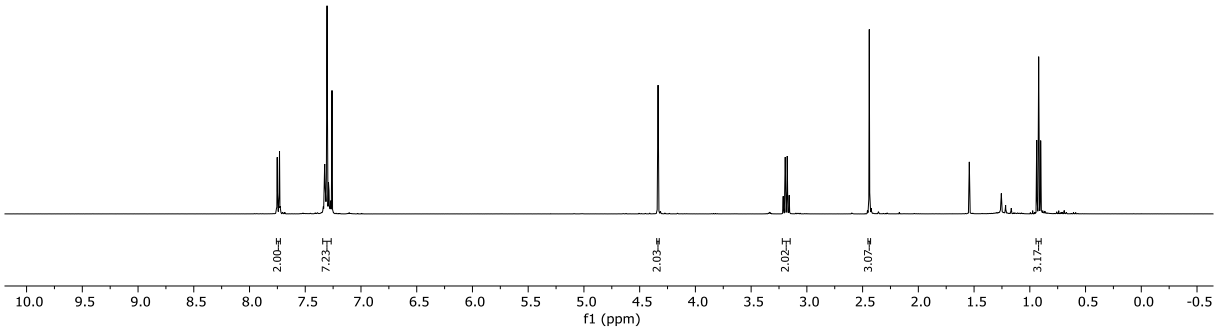


Figure S30. ^{1}H NMR spectrum of **13j**.

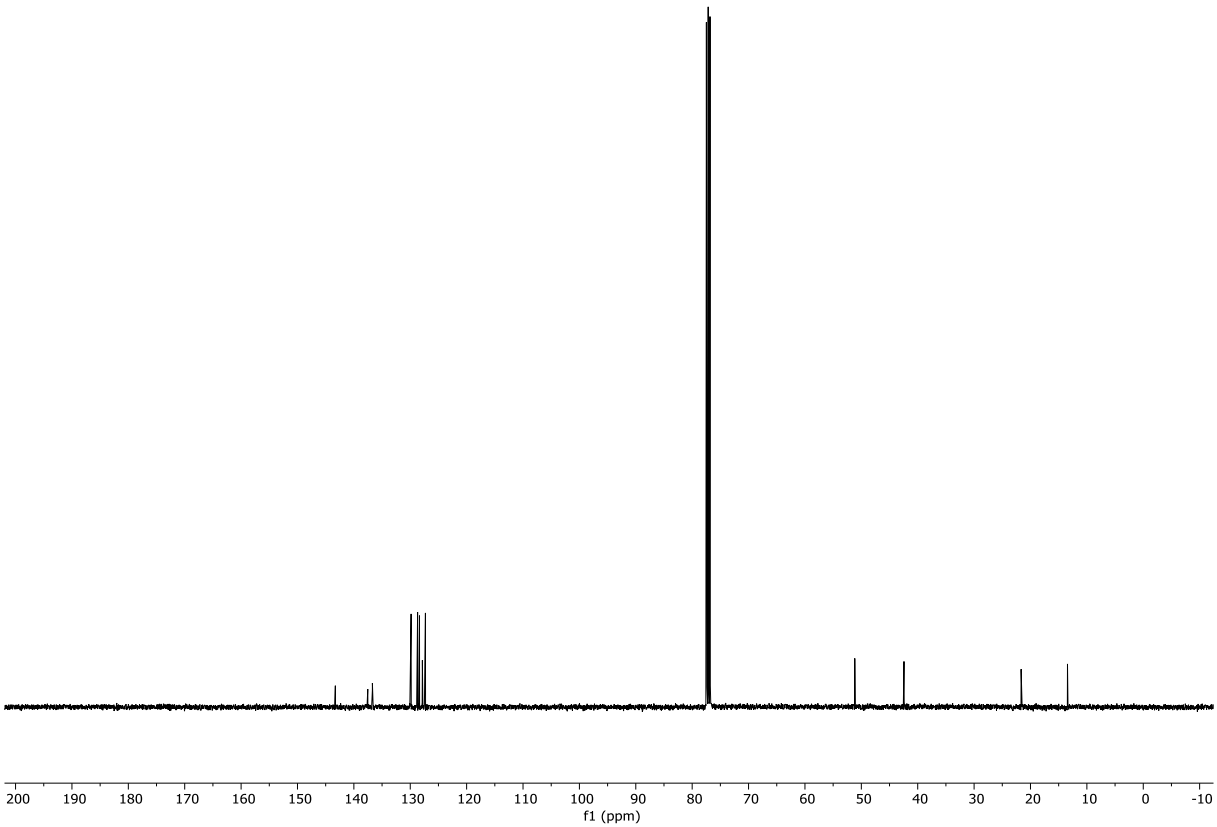
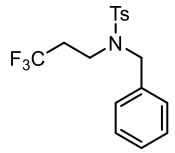


Figure S31. ^{13}C NMR spectrum of **13j**.



13k

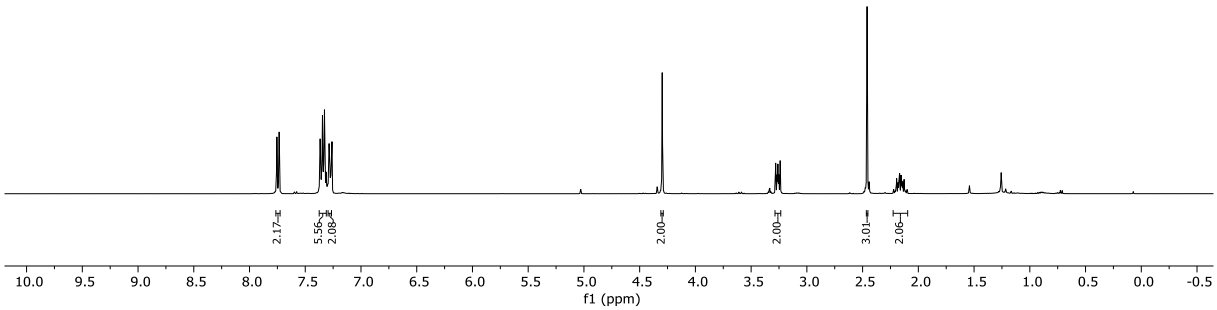


Figure S32. ^{1}H NMR spectrum of **13k**.

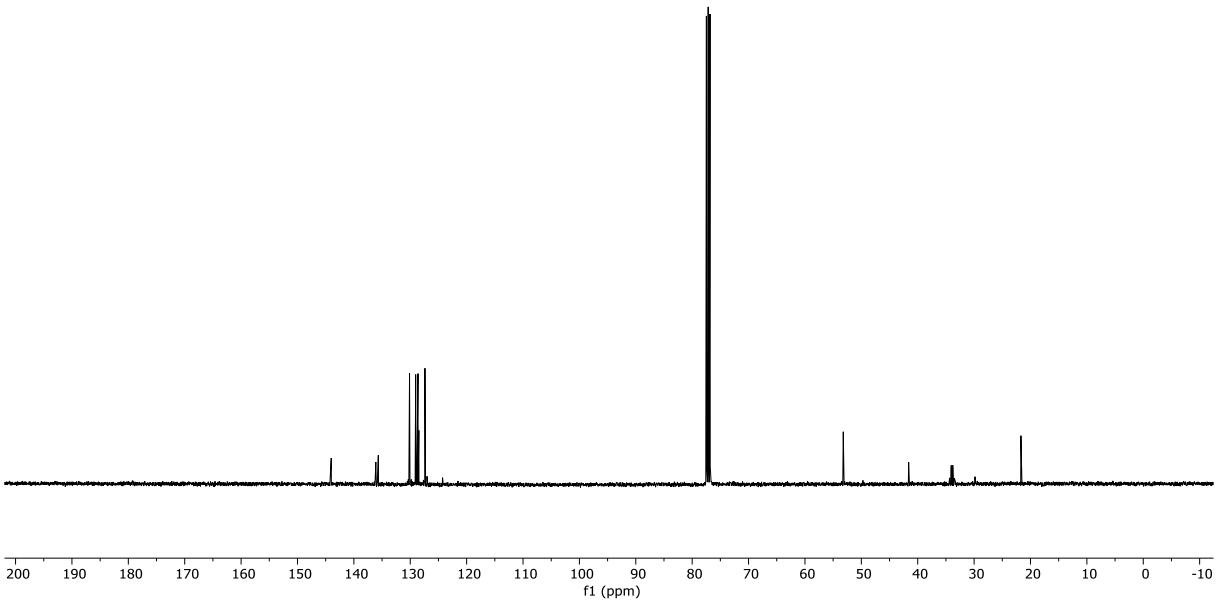


Figure S33. ^{13}C NMR spectrum of **13k**.

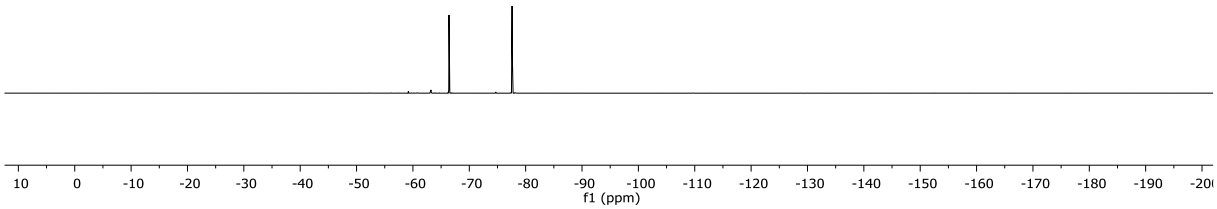
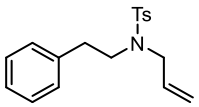


Figure S34. ^{19}F NMR spectrum of **13k**.



13l

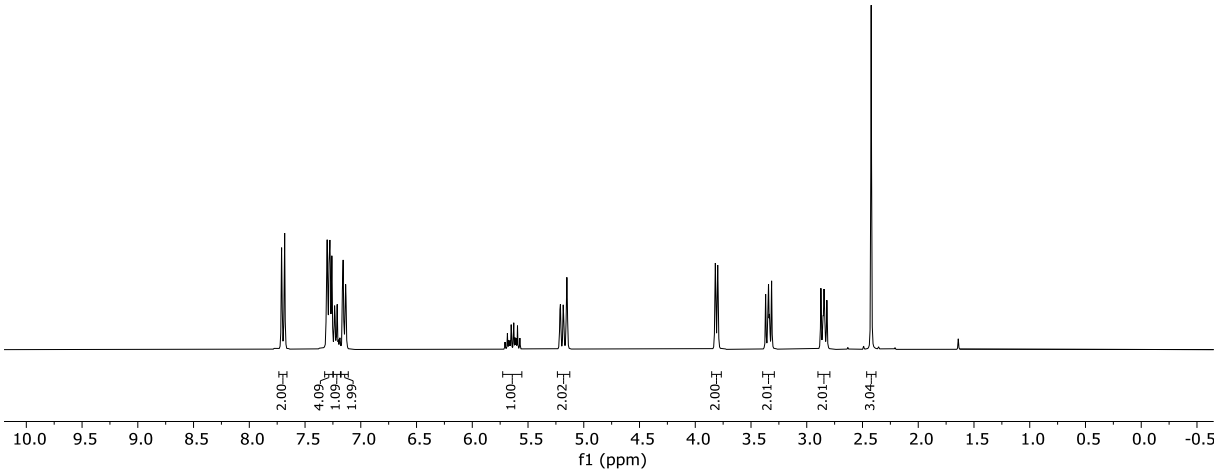


Figure S35. ^{1}H NMR spectrum of **13l**.

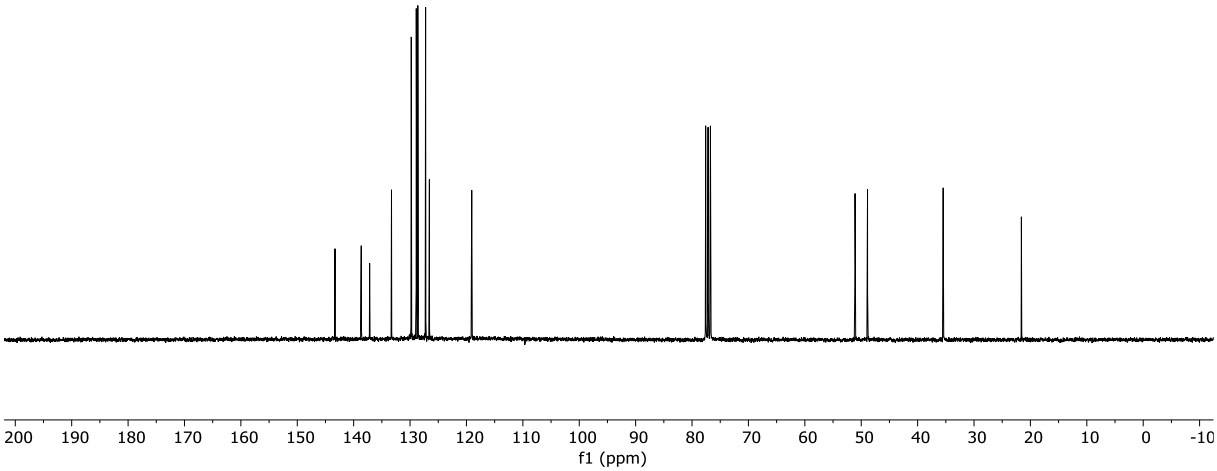
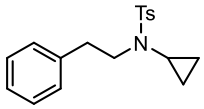


Figure S36. ^{13}C NMR spectrum of **13l**.



13m

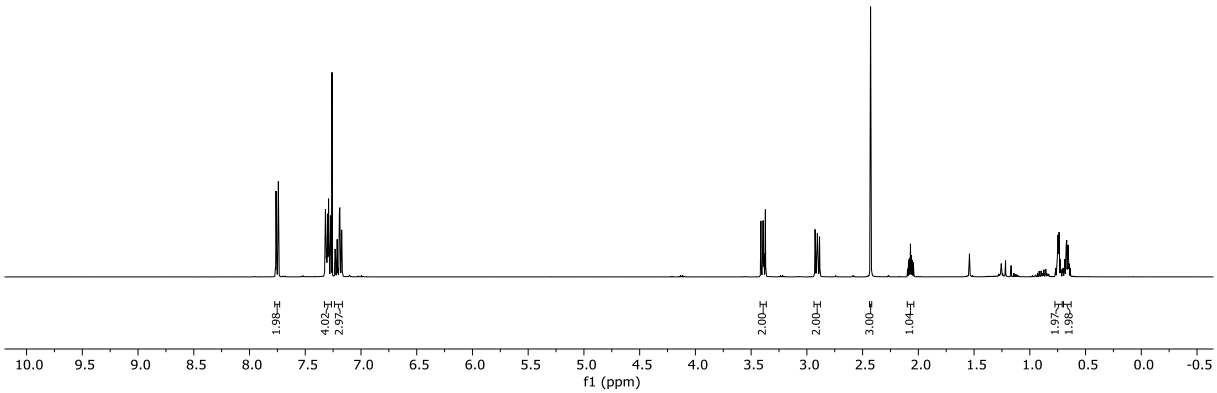


Figure S37. ^{1}H NMR spectrum of **13m**.

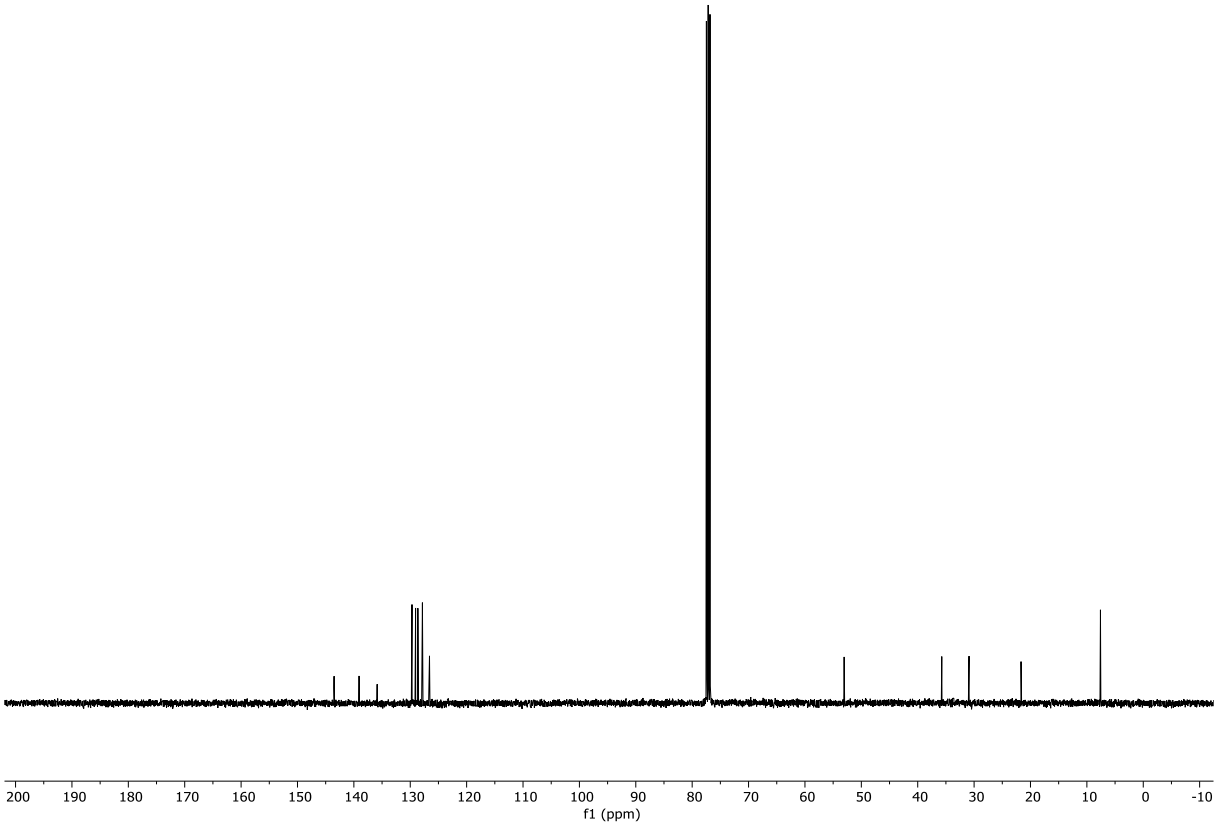
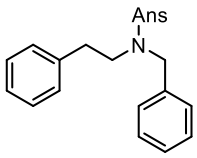


Figure S38. ^{13}C NMR spectrum of **13m**.



13n

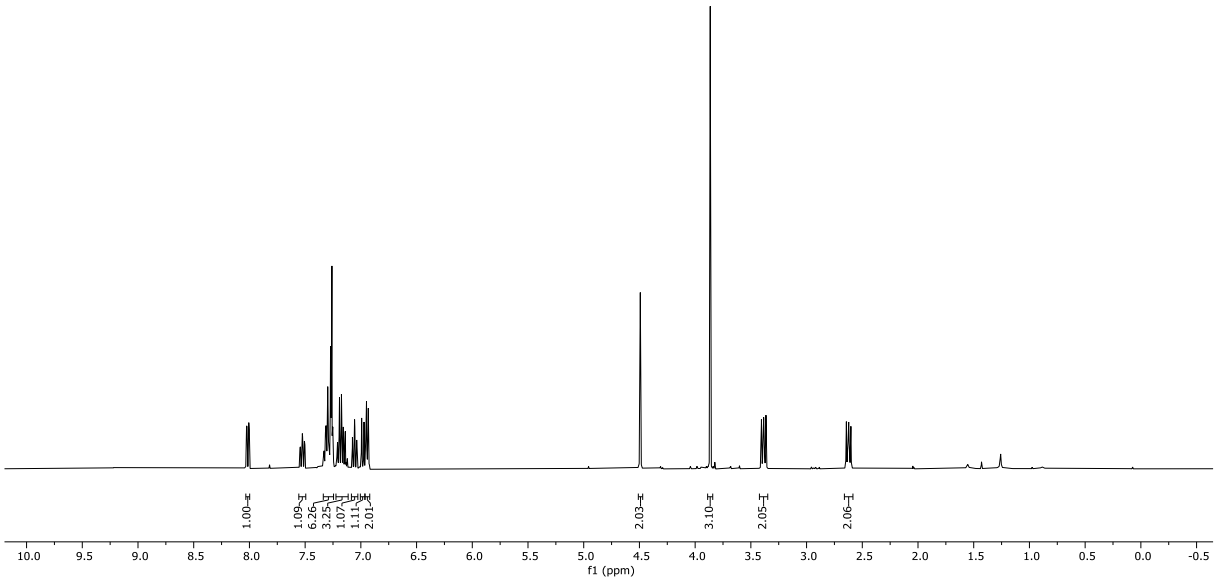


Figure S39. ^{1}H NMR spectrum of **13n**.

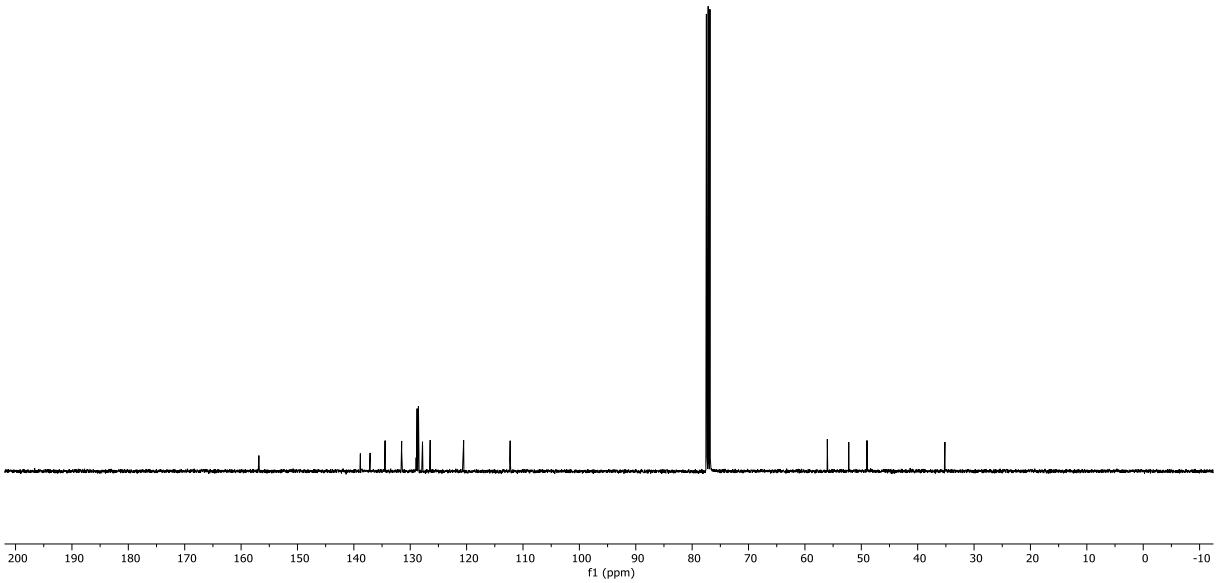
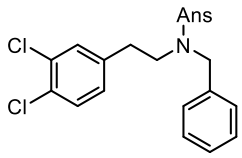


Figure S40. ^{13}C NMR spectrum of **13n**.



13o

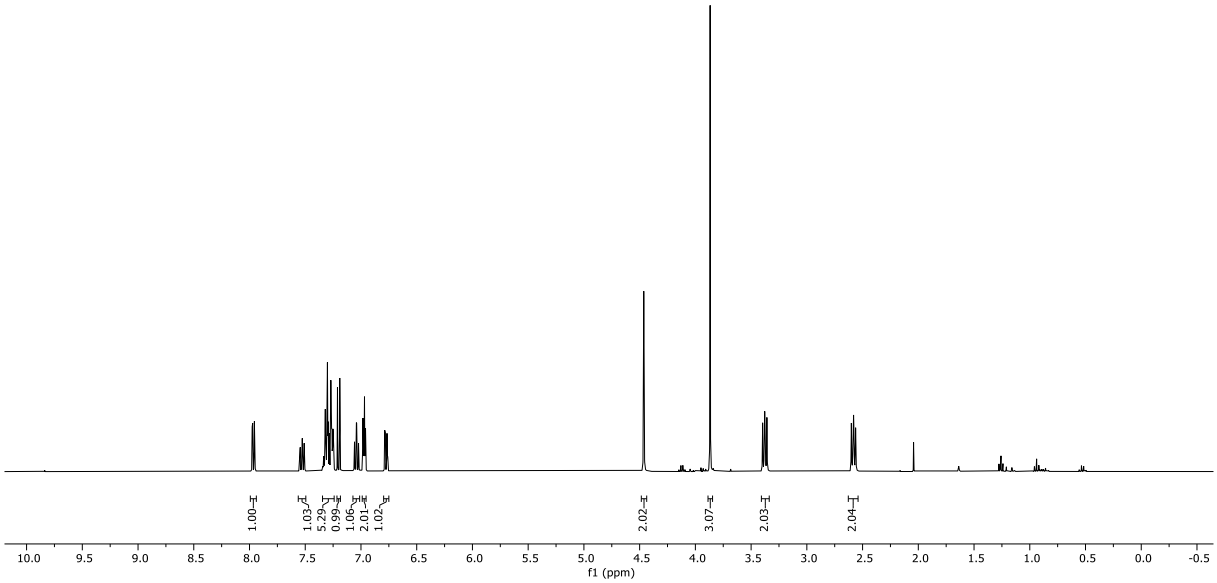


Figure S41. ^{1}H NMR spectrum of **13o**.

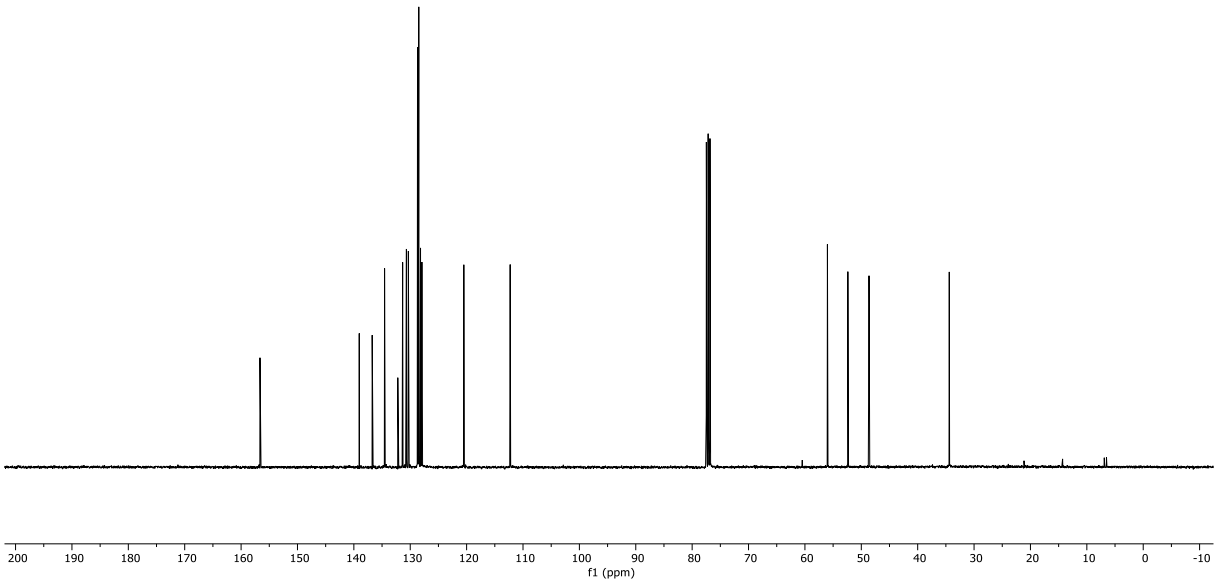
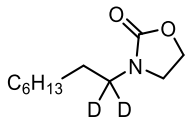


Figure S42. ^{13}C NMR spectrum of **13o**.



13a$_{d\alpha 2}$

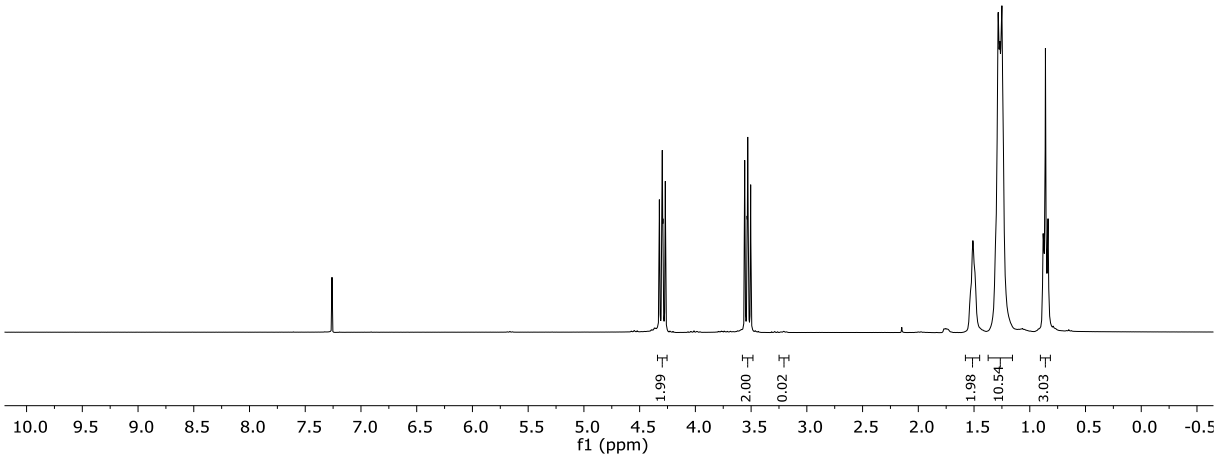


Figure S43. ^{1}H NMR spectrum of **13a**$_{d\alpha 2}$.

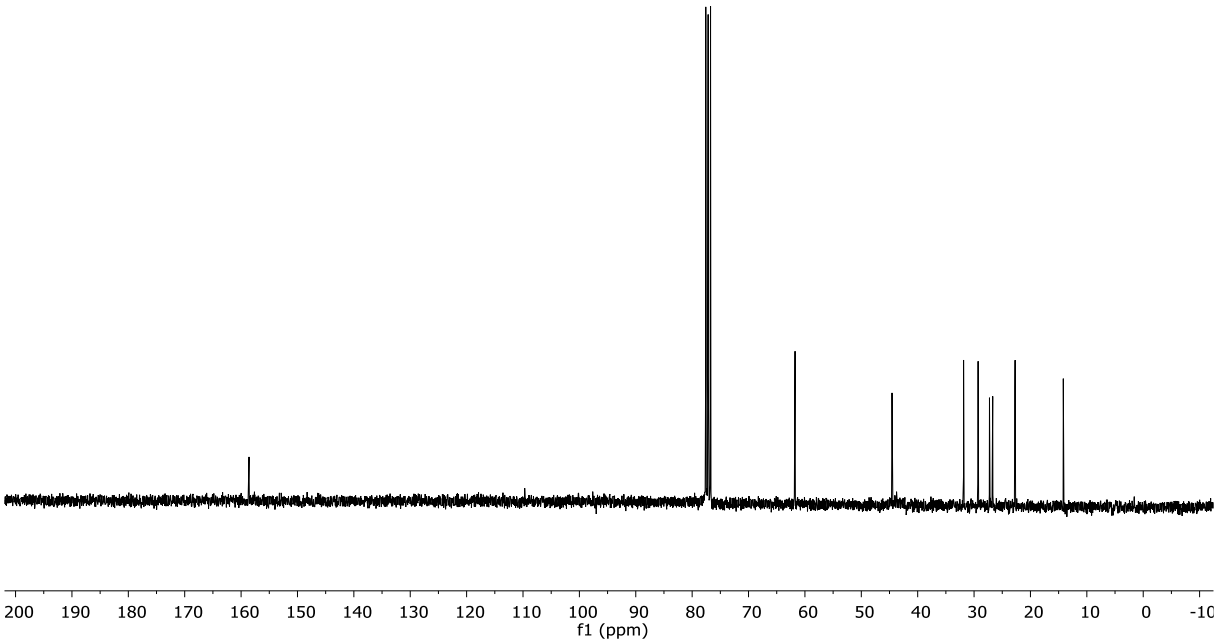


Figure S44. ^{13}C NMR spectrum of **13a**$_{d\alpha 2}$.

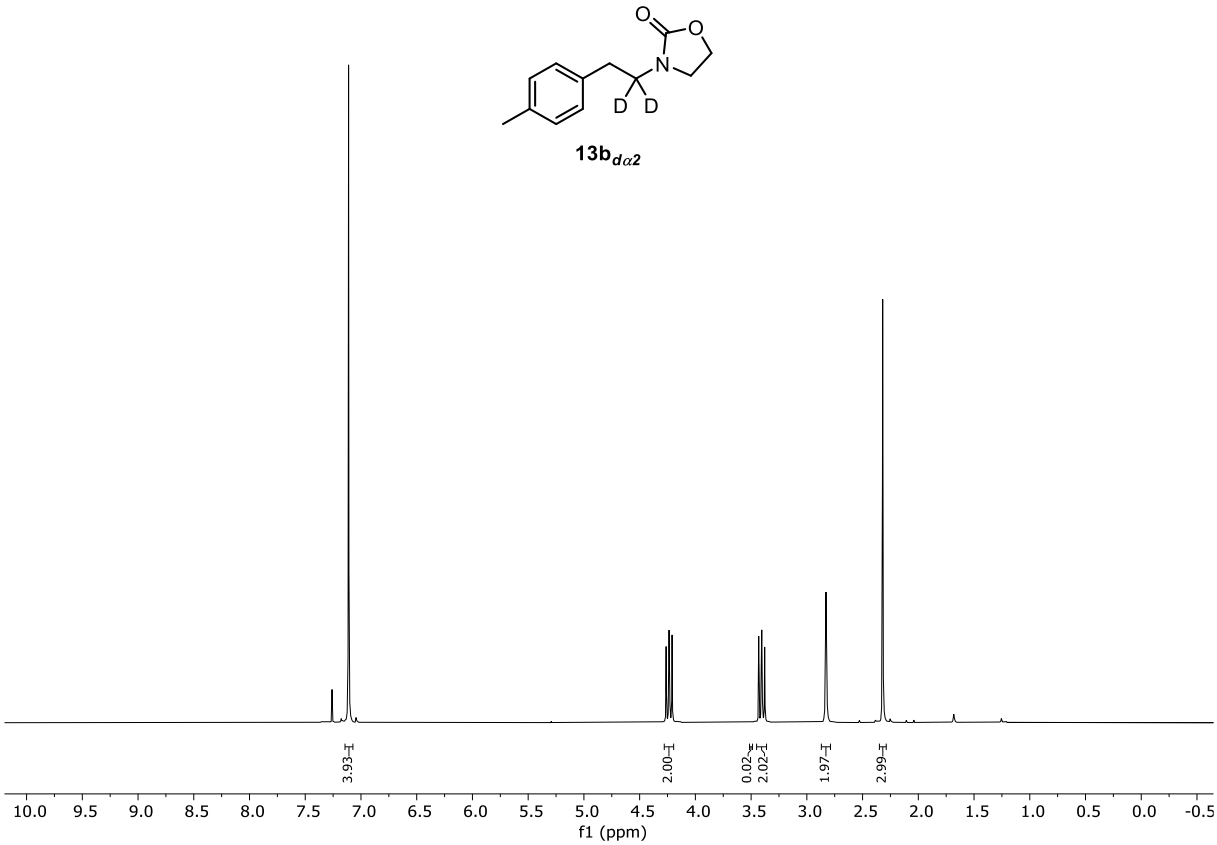


Figure S45. ^{1}H NMR spectrum of **13b$_{d\alpha2}$**.

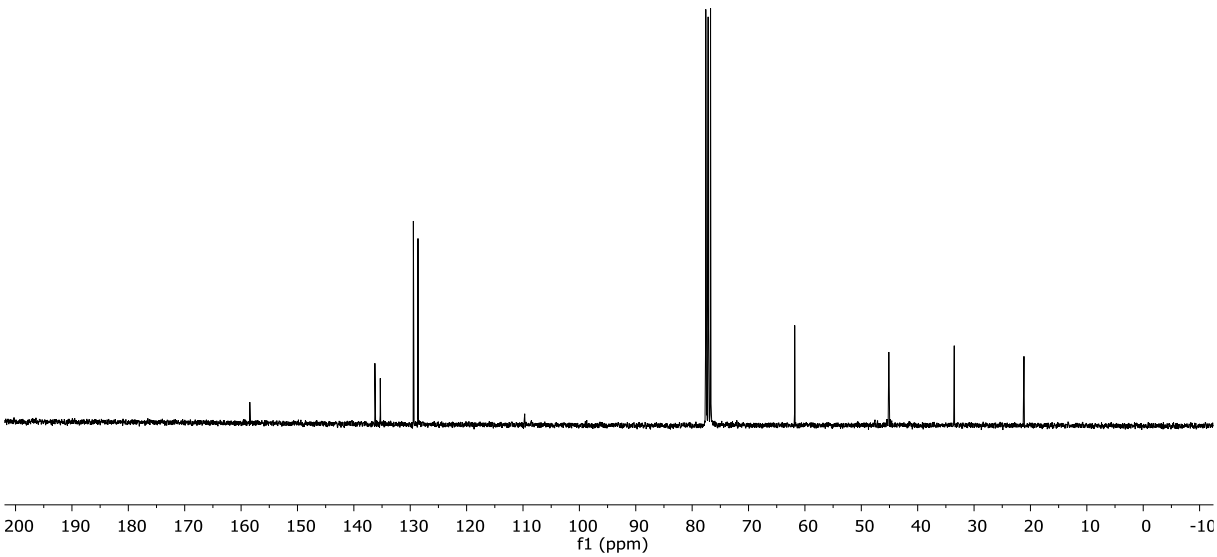
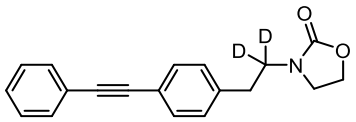


Figure S46. ^{13}C NMR spectrum of **13b$_{d\alpha2}$**.



13c$_{d\alpha 2}$

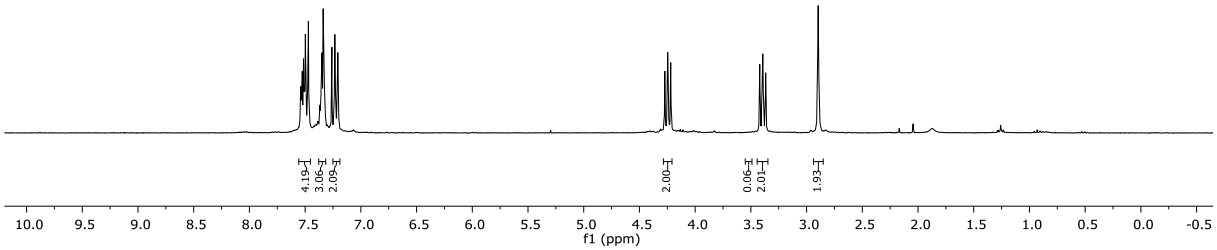


Figure S47. ^{1}H NMR spectrum of **13c$_{d\alpha 2}$**.

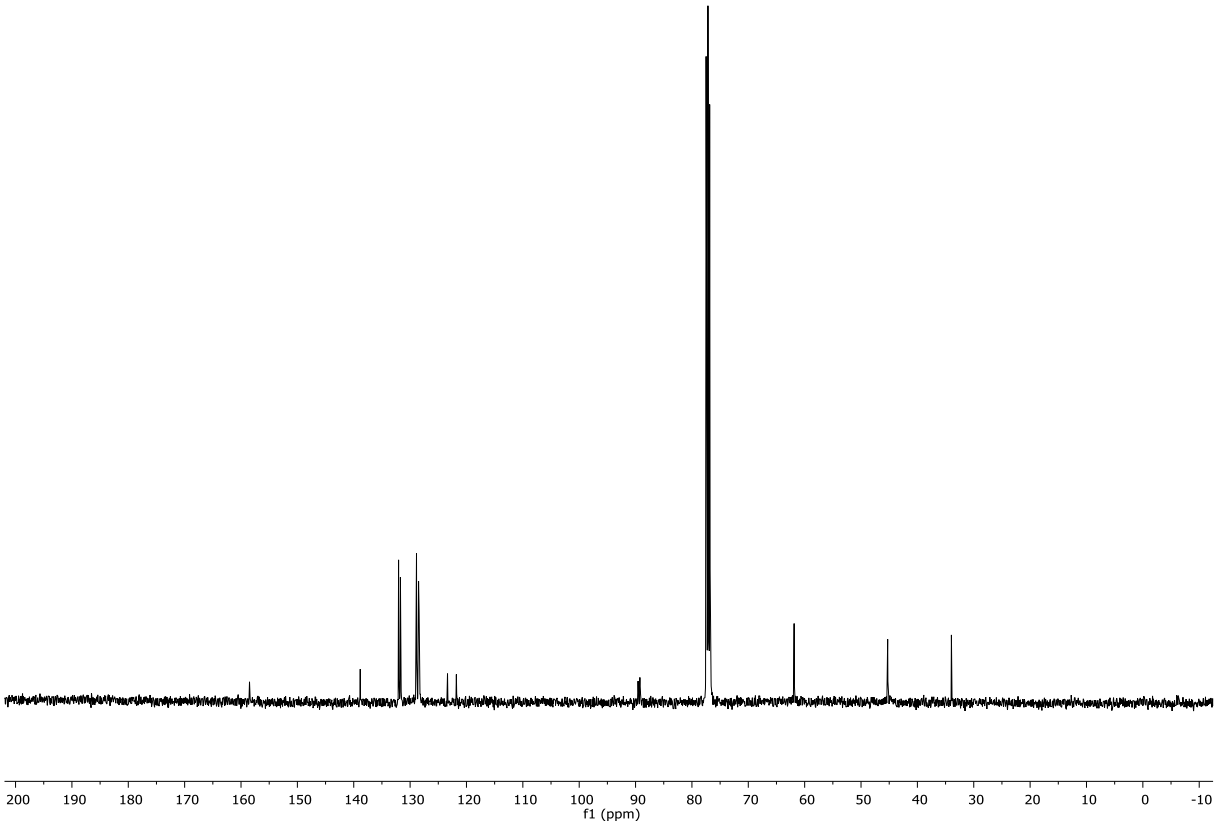
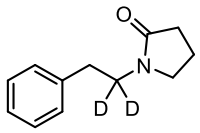


Figure S48. ^{13}C NMR spectrum of **13c$_{d\alpha 2}$**.



13d$_{d\alpha 2}$

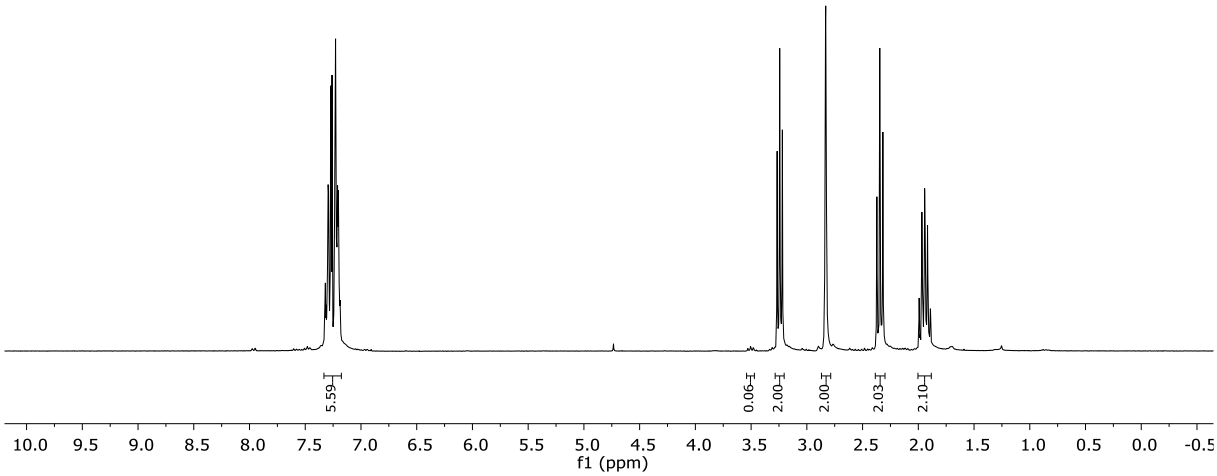


Figure S49. ^{1}H NMR spectrum of **13d$_{d\alpha 2}$**.

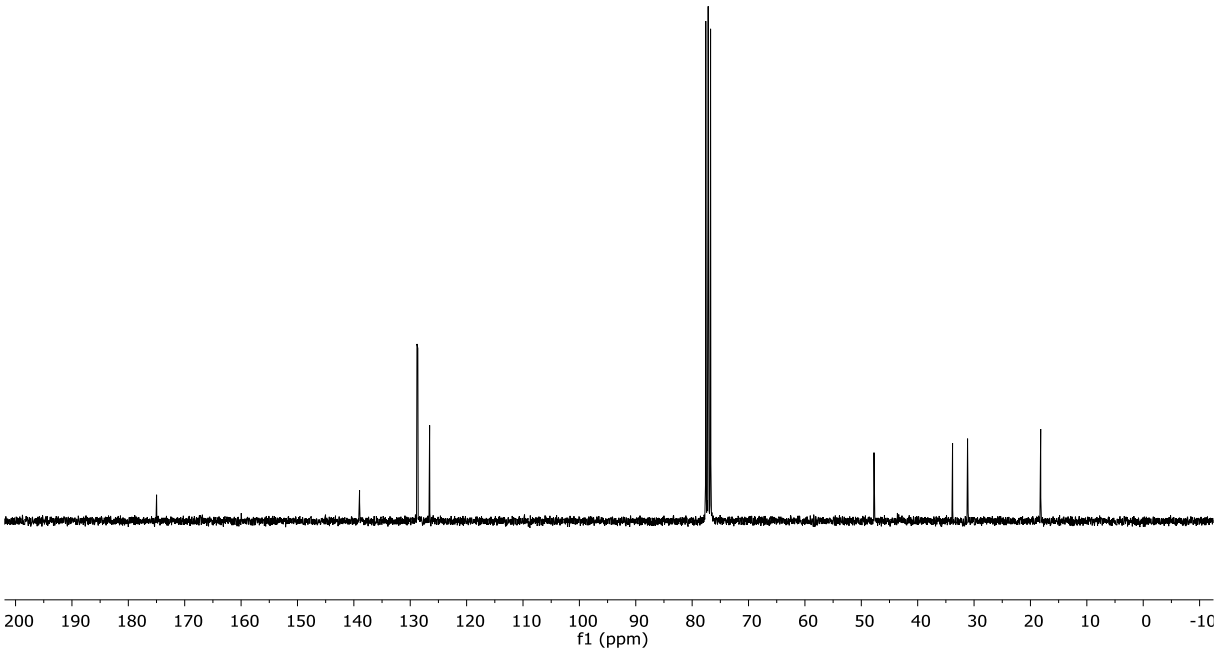
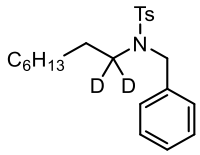


Figure S50. ^{13}C NMR spectrum of **13d$_{d\alpha 2}$**.



13e$_{d\alpha 2}$

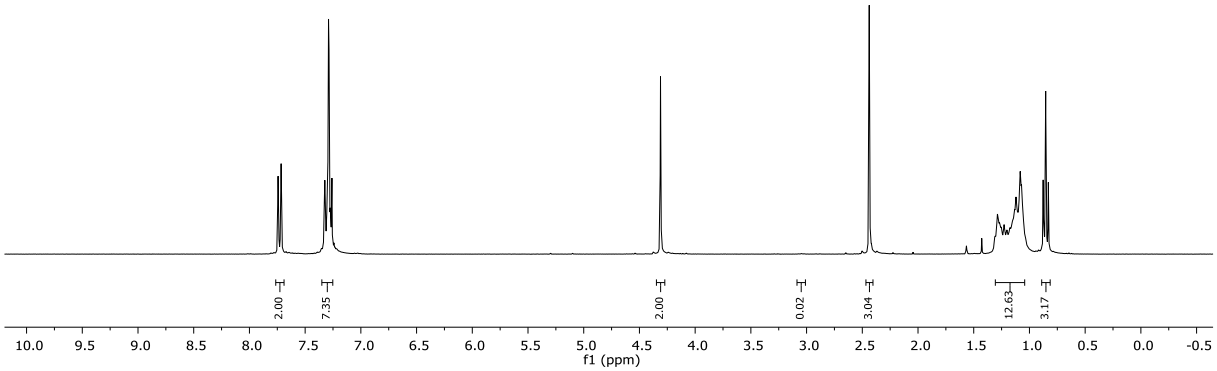


Figure S51. ^{1}H NMR spectrum of **13e$_{d\alpha 2}$**.

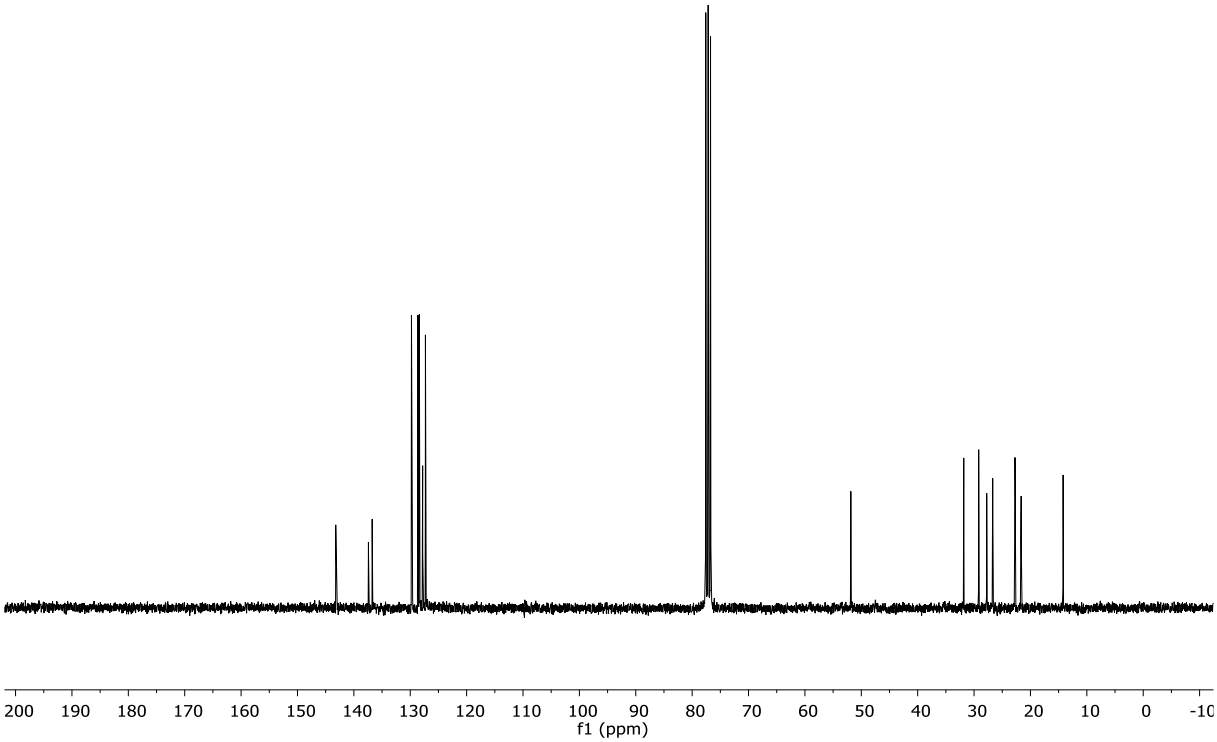
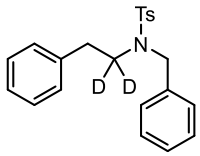


Figure S52. ^{13}C NMR spectrum of **13e$_{d\alpha 2}$**.



13f$_{d\alpha2}$

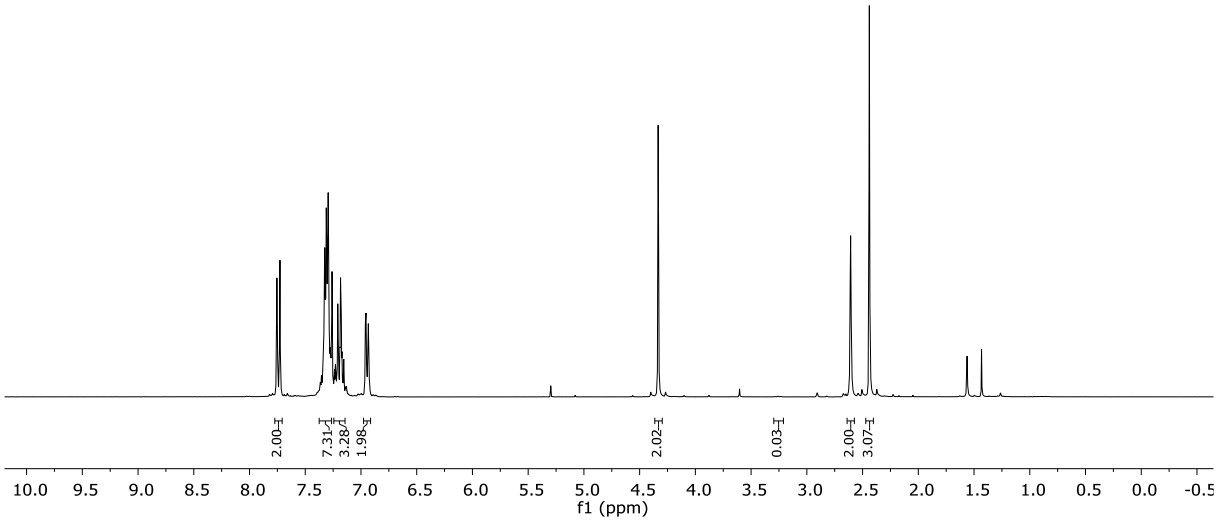


Figure S53. ^{1}H NMR spectrum of **13f$_{d\alpha2}$**.

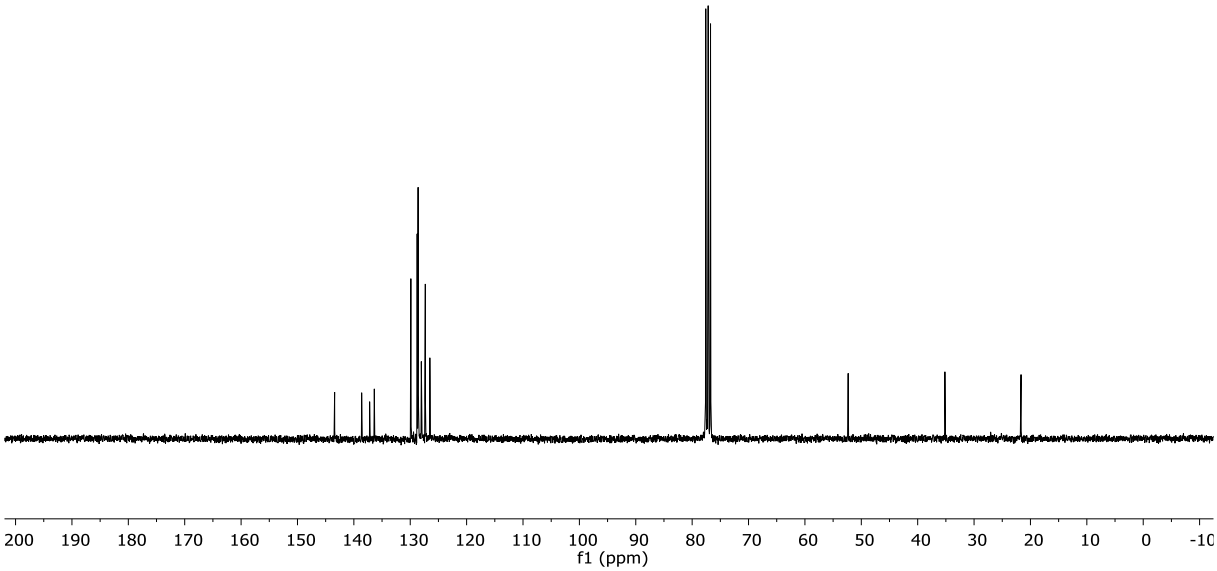
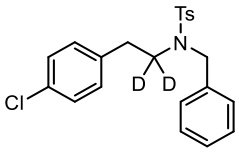


Figure S54. ^{13}C NMR spectrum of **13f$_{d\alpha2}$**.



13g$_{d\alpha 2}$

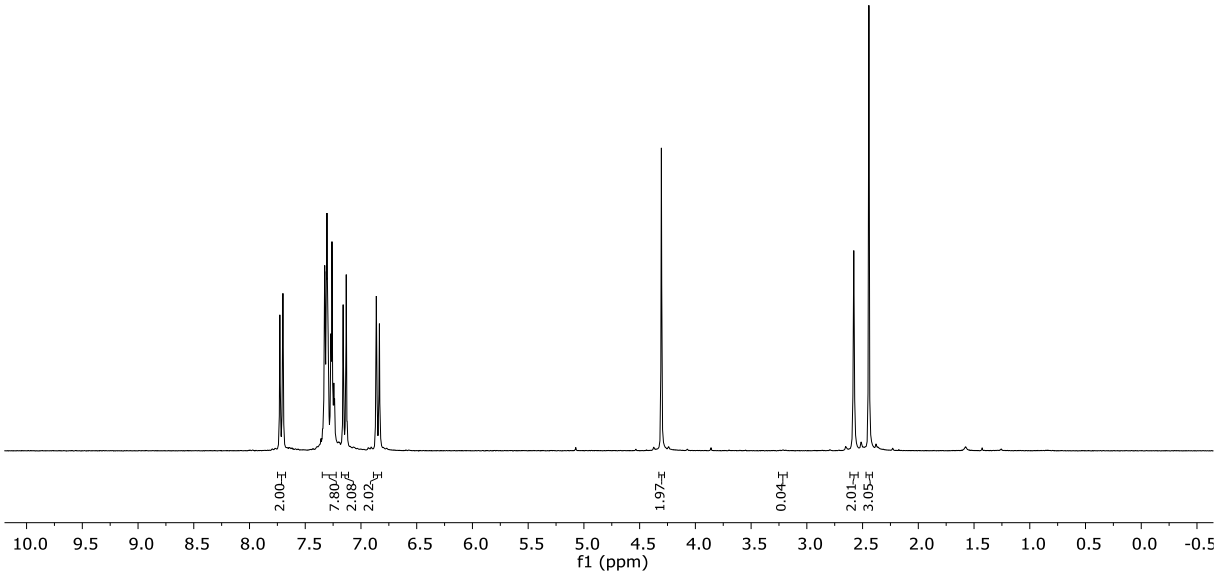


Figure S55. ^{1}H NMR spectrum of **13g$_{d\alpha 2}$**.

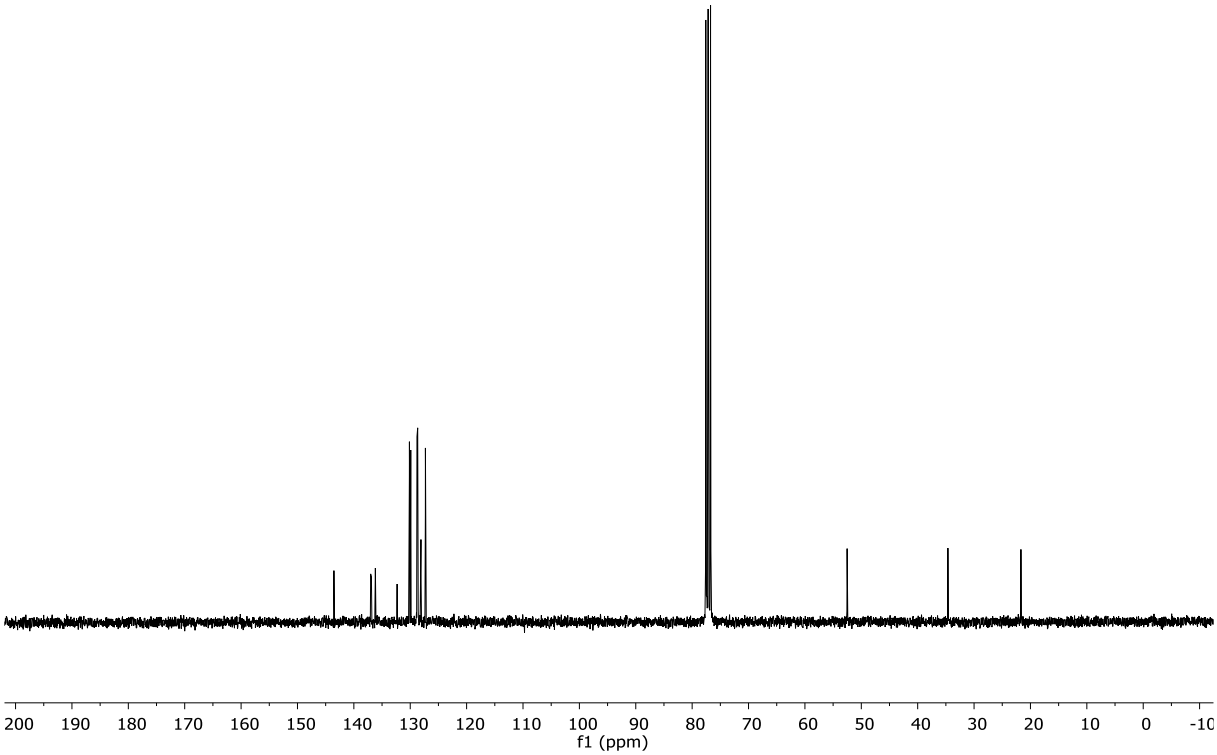
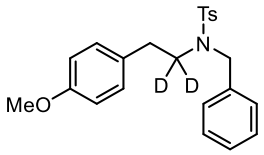


Figure S56. ^{13}C NMR spectrum of **13g$_{d\alpha 2}$**.



13h$_{d\alpha2}$

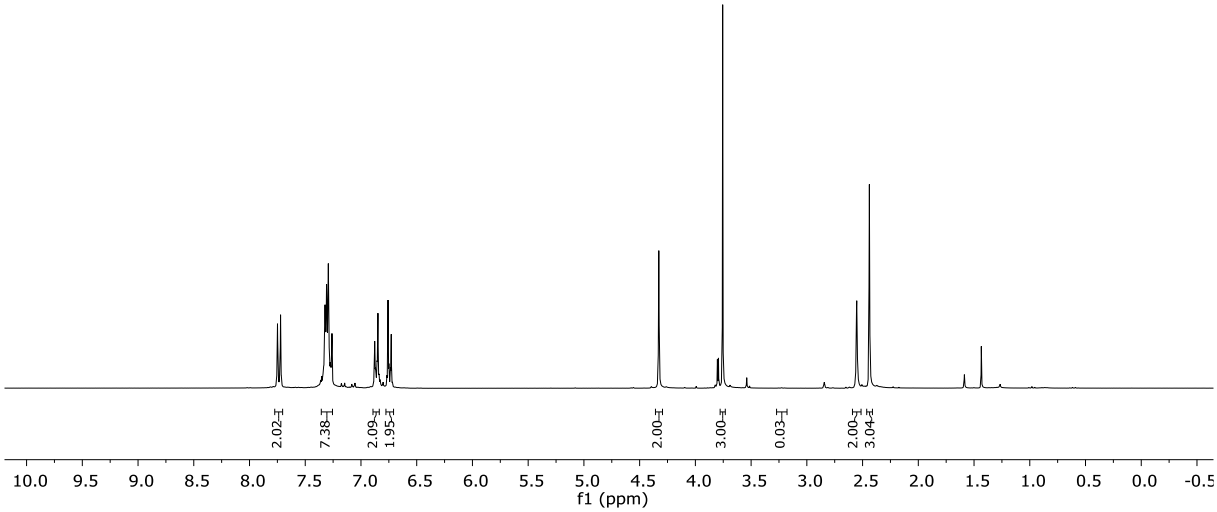


Figure S57. ^{1}H NMR spectrum of **13h$_{d\alpha2}$**.

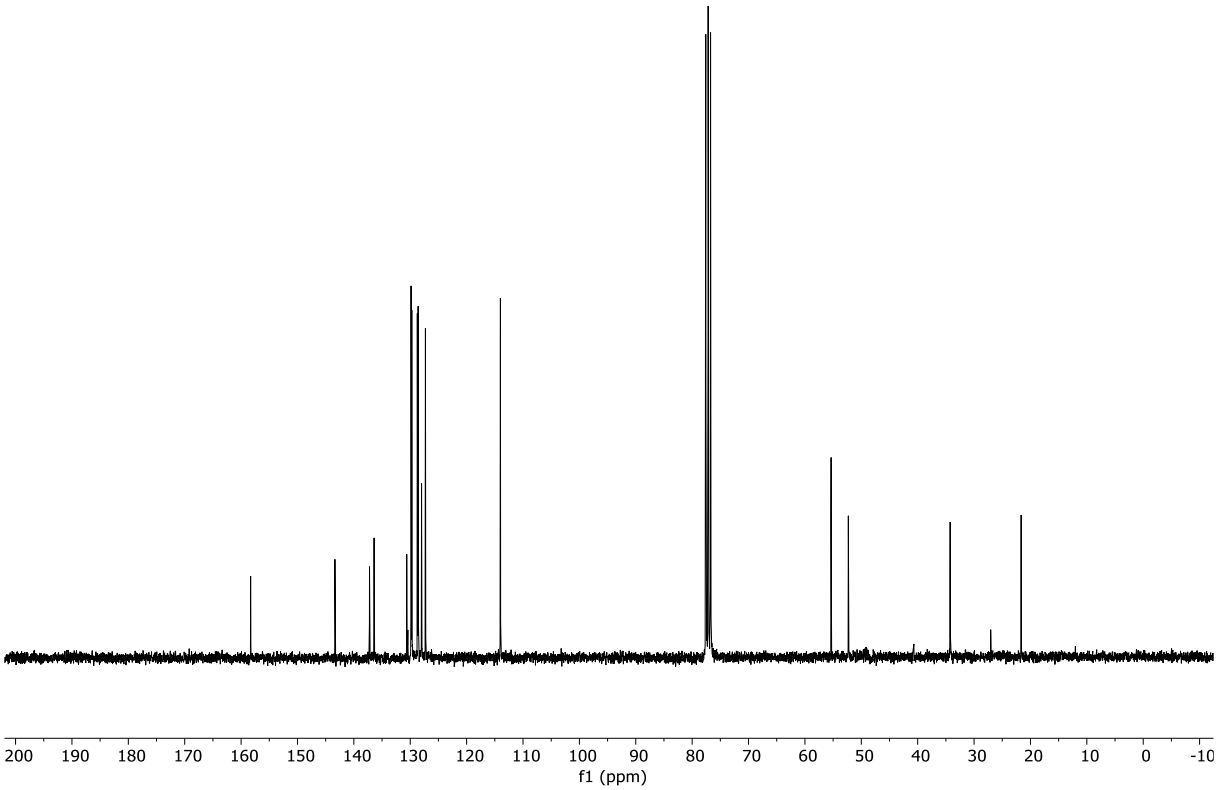
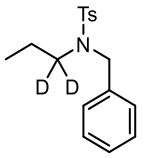


Figure S58. ^{13}C NMR spectrum of **13h$_{d\alpha2}$**.



13i$_{d\alpha2}$

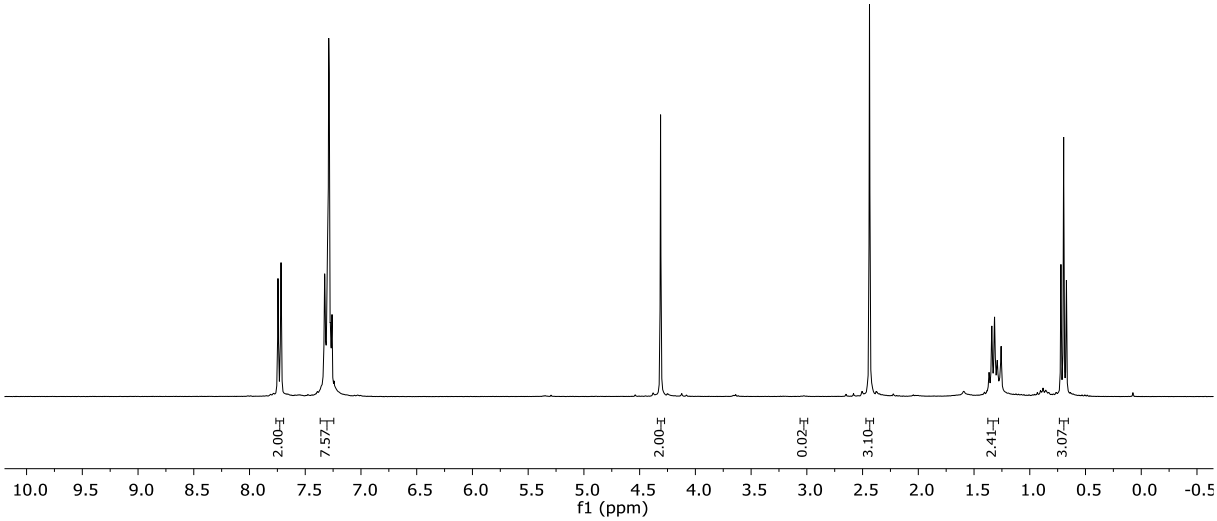


Figure S59. ^{1}H NMR spectrum of **13i$_{d\alpha2}$**.

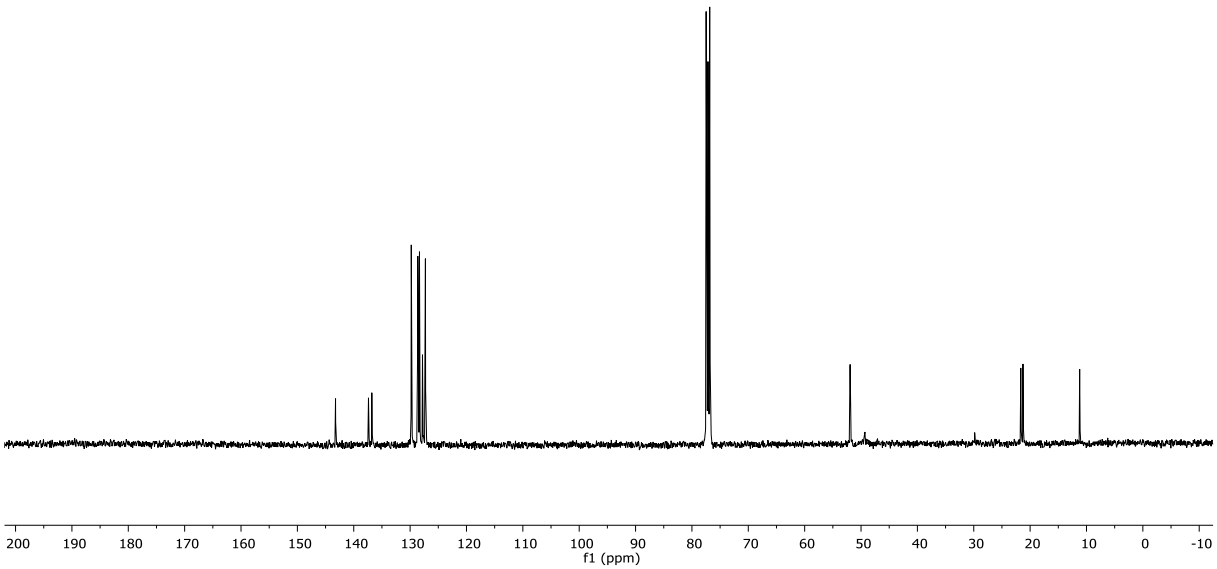
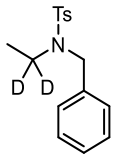


Figure S60. ^{13}C NMR spectrum of **13i$_{d\alpha2}$**.



13j$_{d\alpha2}$

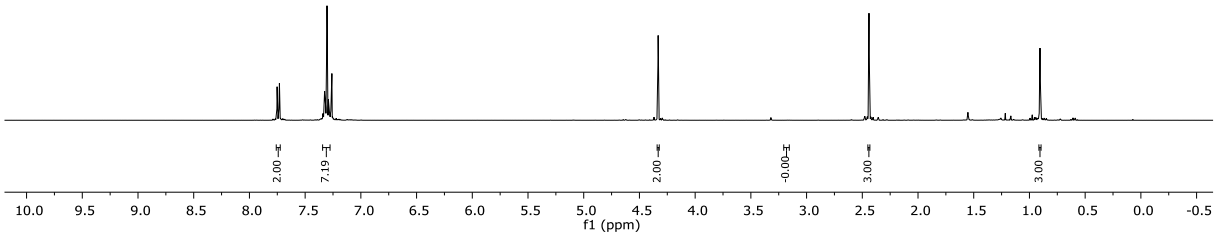


Figure S61. ^{1}H NMR spectrum of **13j$_{d\alpha2}$**.

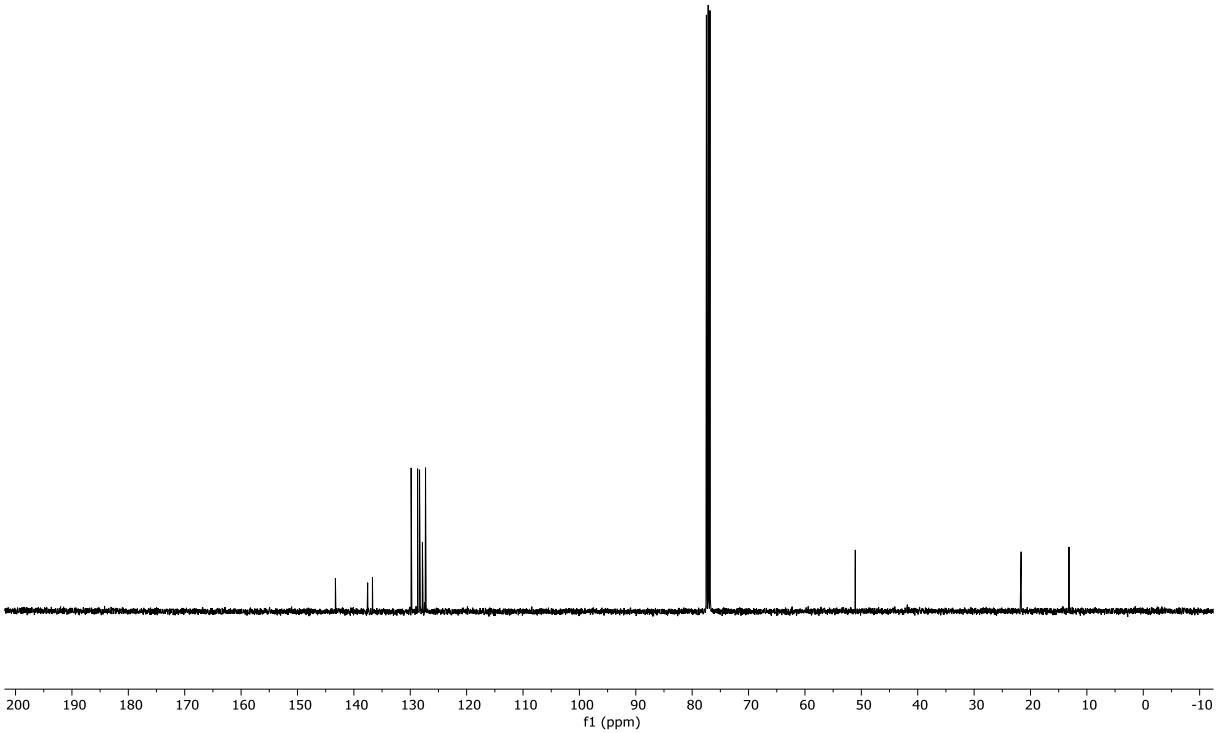
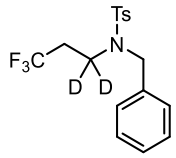


Figure S62. ^{13}C NMR spectrum of **13j$_{d\alpha2}$**.



13k$_{d\alpha2}$

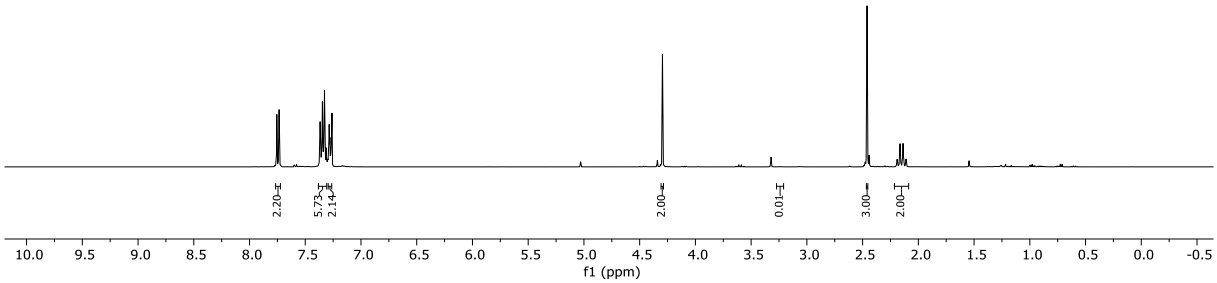


Figure S63. ^{1}H NMR spectrum of **13k$_{d\alpha2}$**.

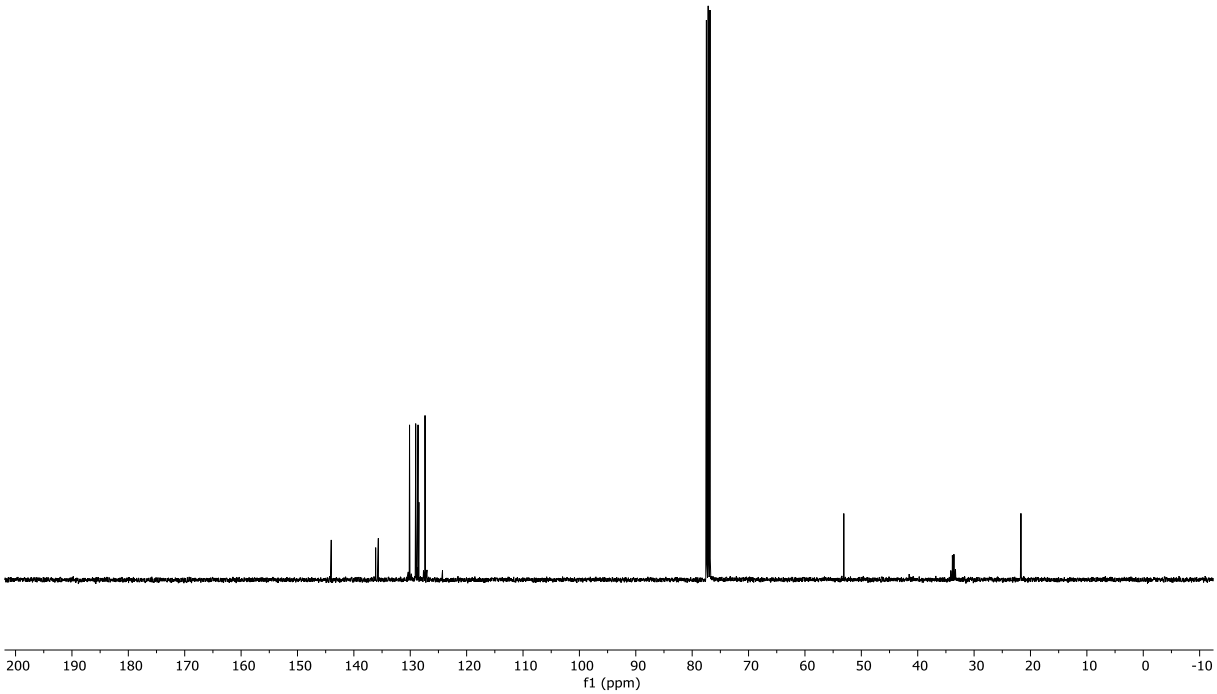


Figure S64. ^{13}C NMR spectrum of **13k$_{d\alpha2}$**.

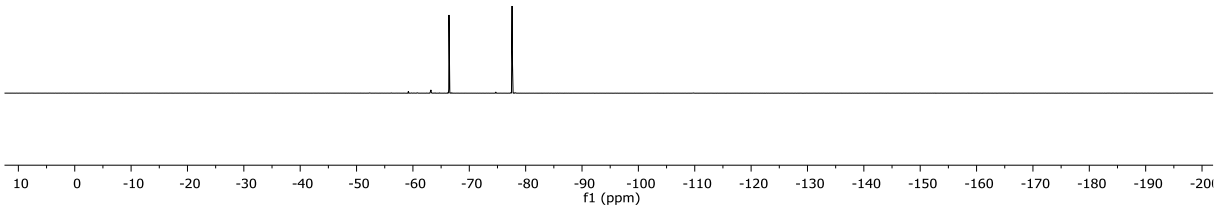
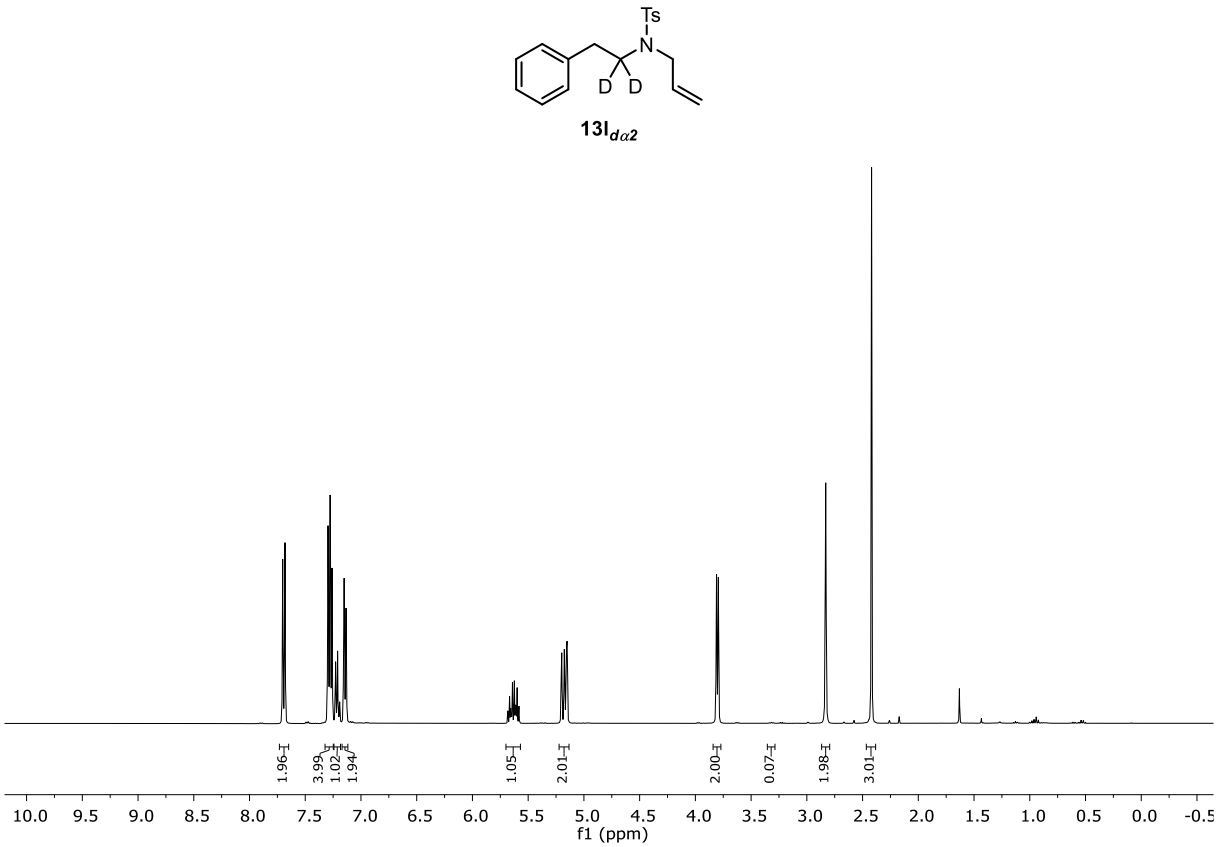


Figure S65. ^{19}F NMR spectrum of **13k**$_{d\alpha 2}$.



13l$_{d\alpha2}$

Figure S66. ^{1}H NMR spectrum of **13l$_{d\alpha2}$**.

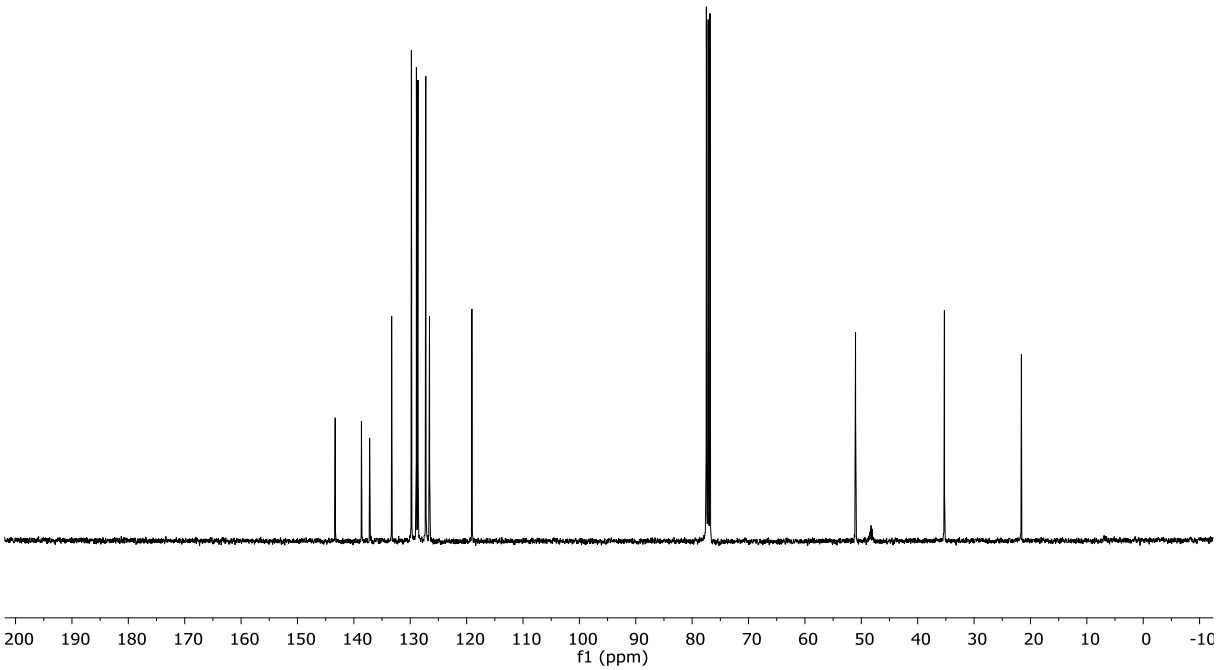
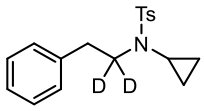


Figure S67. ^{13}C NMR spectrum of **13l$_{d\alpha2}$**.



13m$_{d\alpha2}$

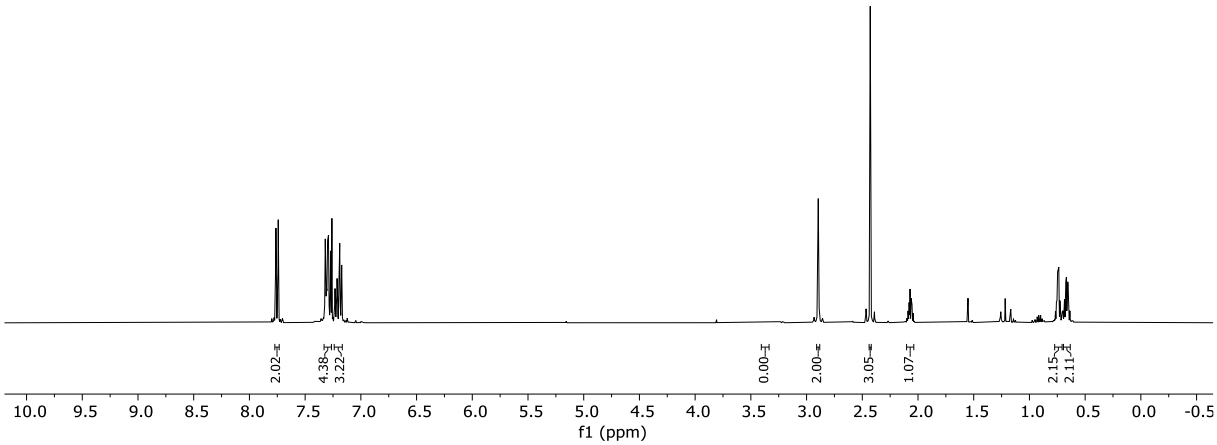


Figure S68. ^{1}H NMR spectrum of **13m$_{d\alpha2}$**.

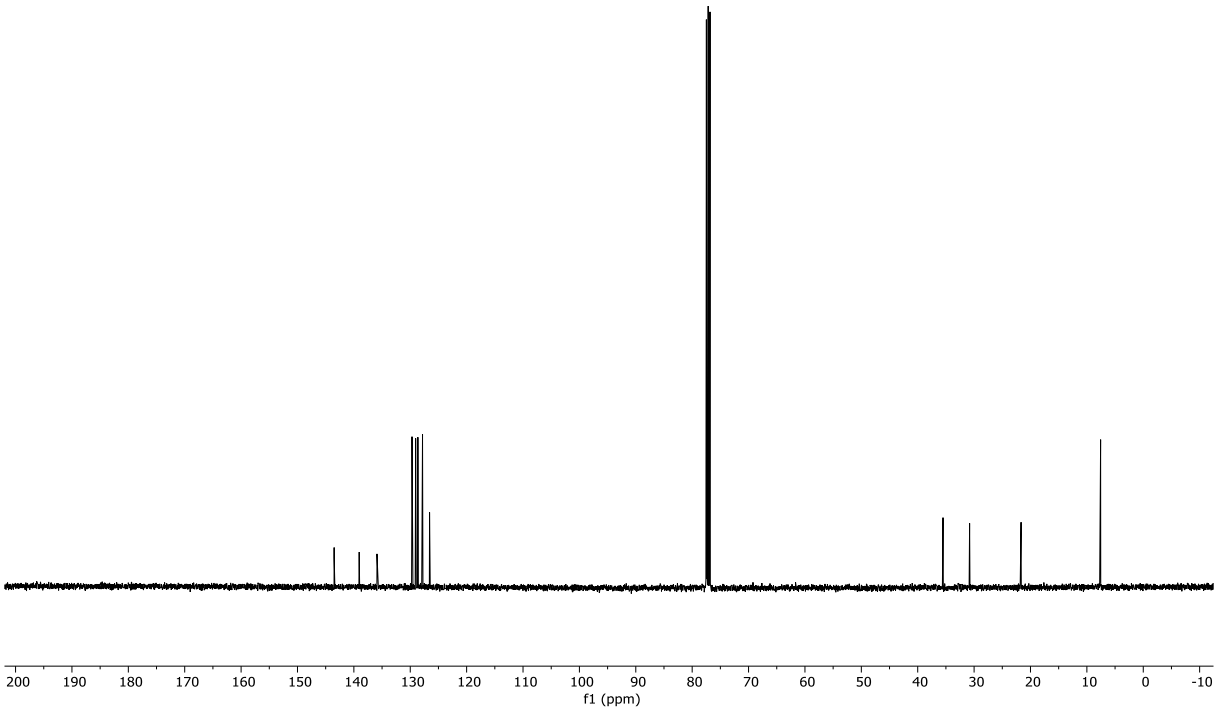


Figure S69. ^{13}C NMR spectrum of **13m$_{d\alpha2}$**.

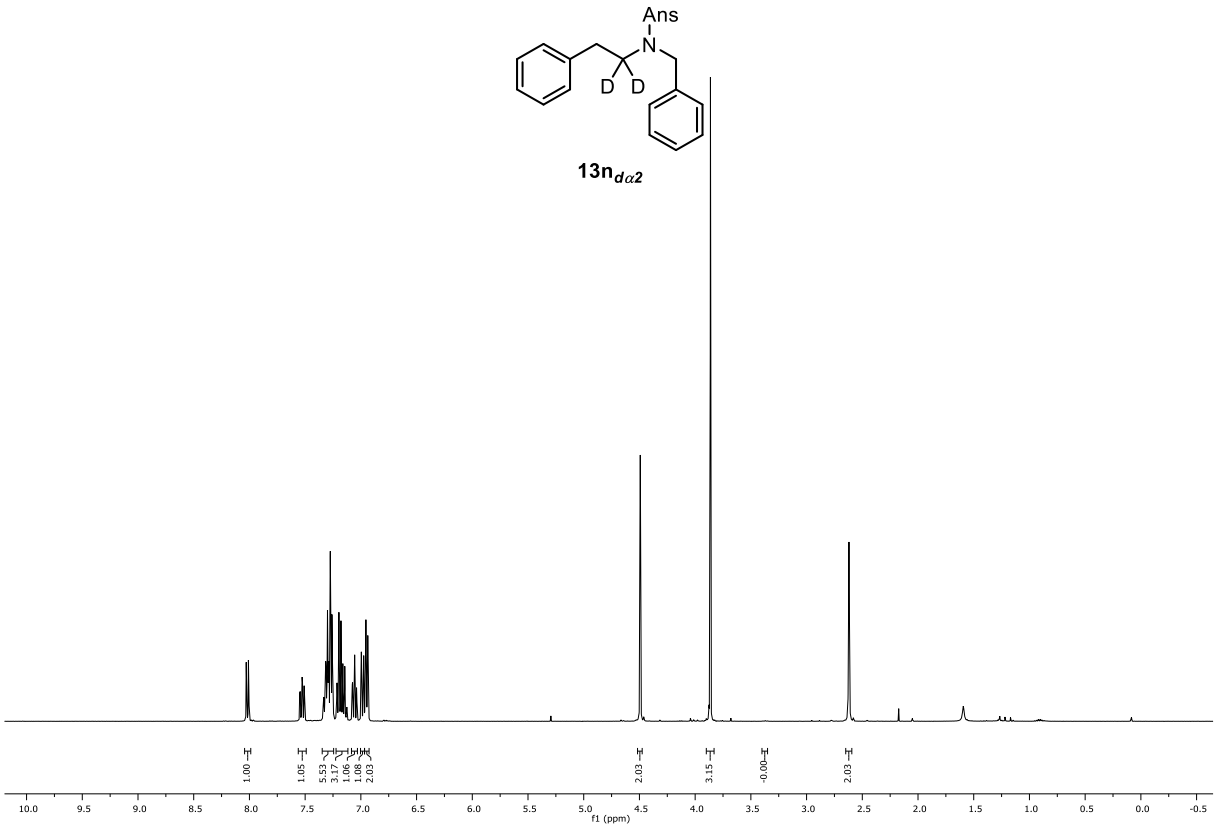


Figure S70. ^{1}H NMR spectrum of **13n$_{d\alpha2}$**.

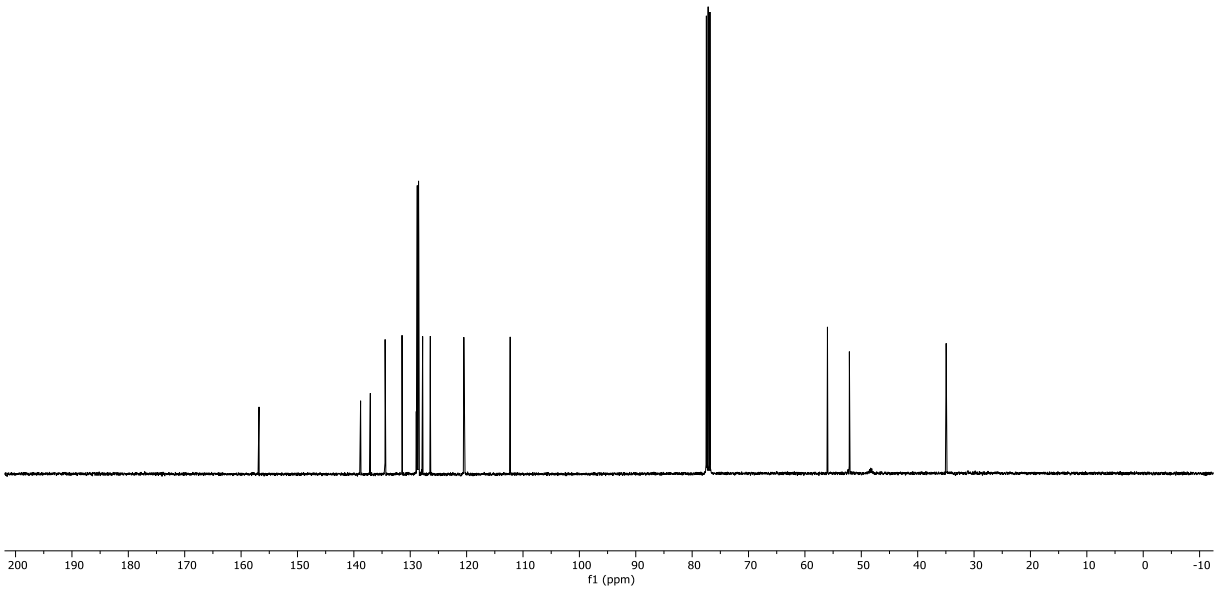
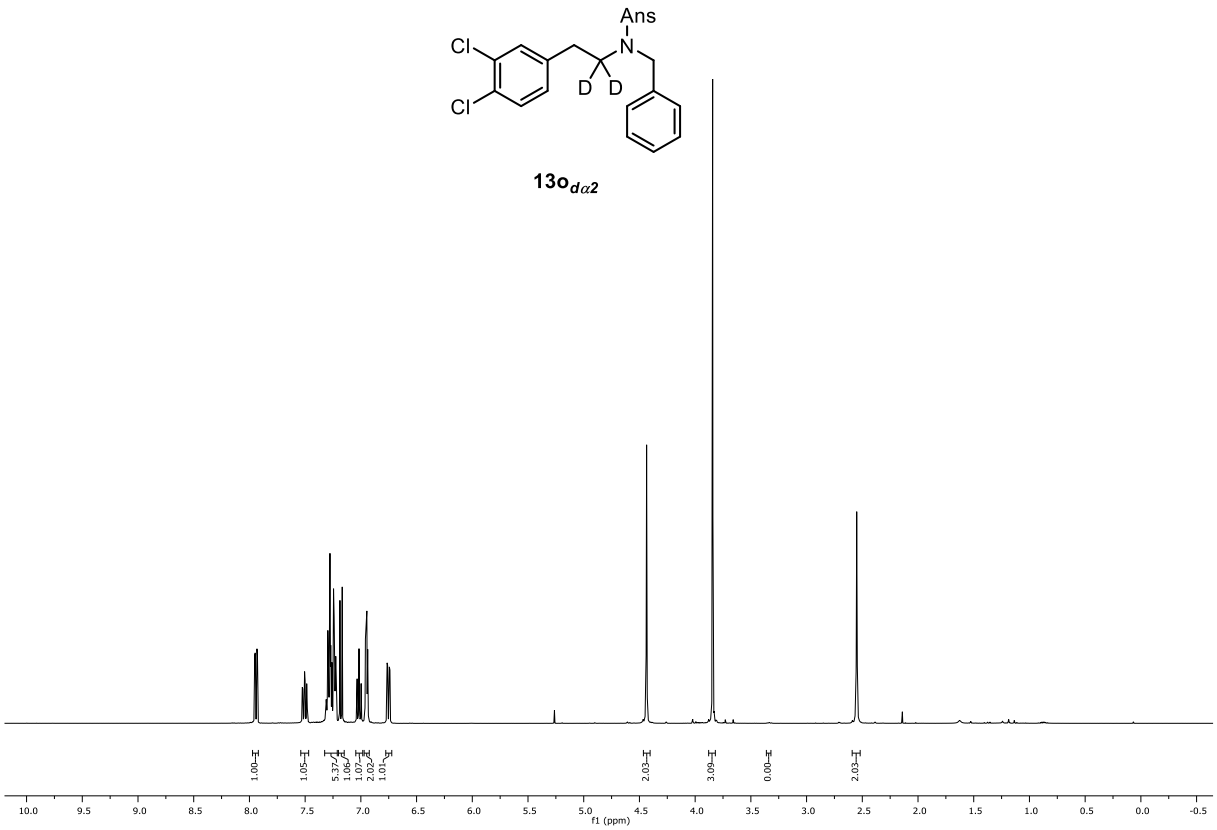


Figure S71. ^{13}C NMR spectrum of **13n$_{d\alpha2}$**.



13o$_{d\alpha 2}$

Figure S72. ^{1}H NMR spectrum of **13o**$_{d\alpha 2}$.

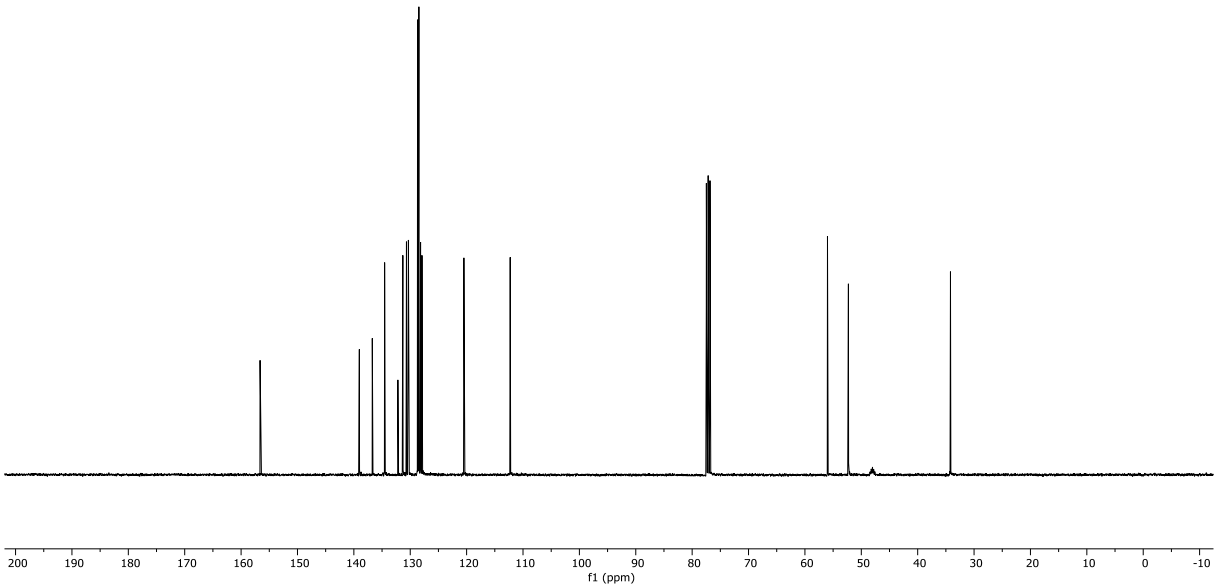
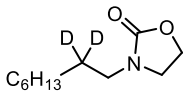


Figure S73. ^{13}C NMR spectrum of **13o**$_{d\alpha 2}$.



13a$_{d\beta2}$

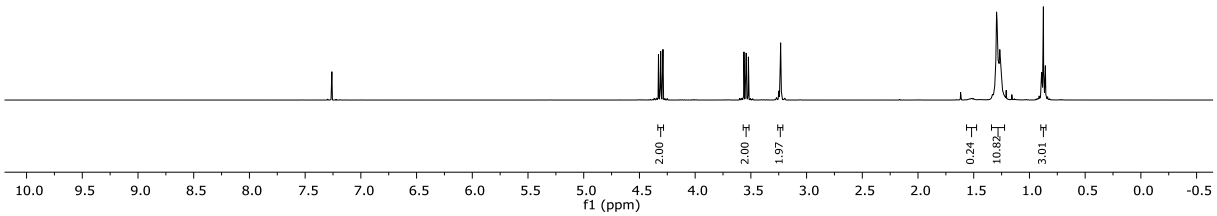


Figure S74. ^{1}H NMR spectrum of **13a**$_{d\beta2}$.

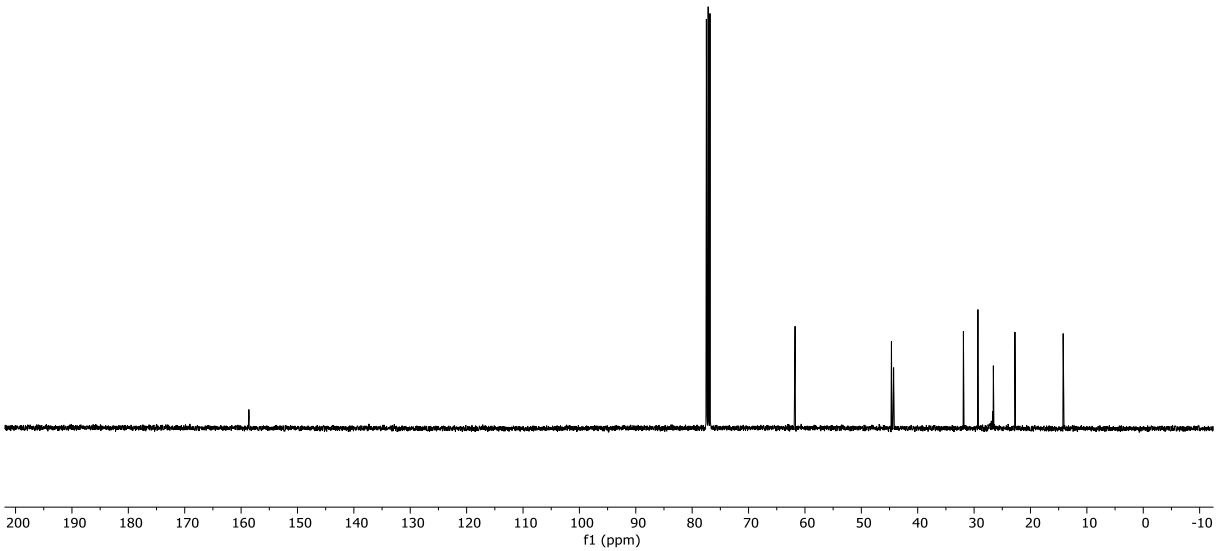
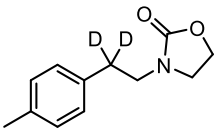


Figure S75. ^{13}C NMR spectrum of **13a**$_{d\beta2}$.



13b$_{d\beta 2}$

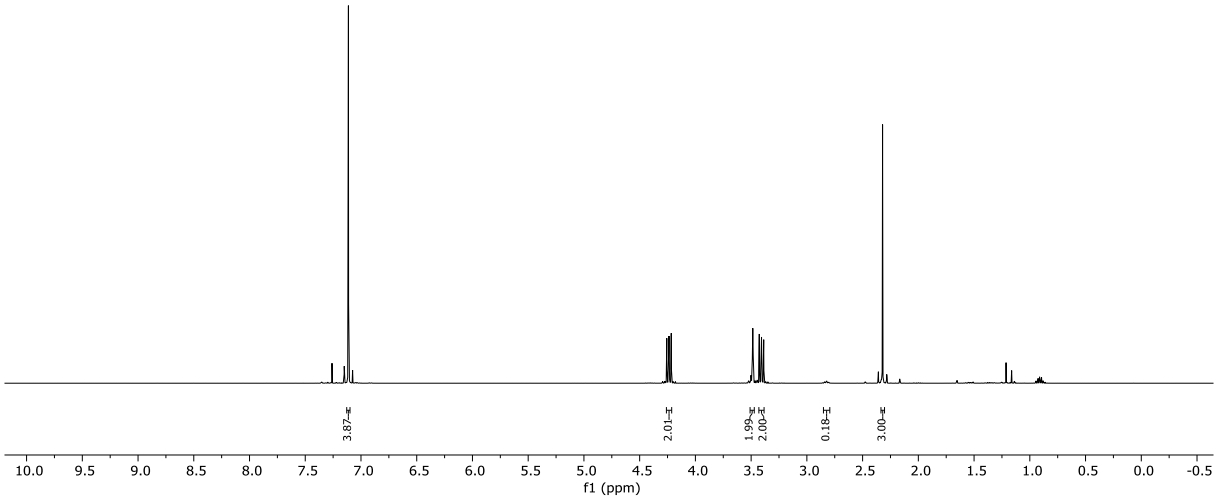


Figure S76. ^{1}H NMR spectrum of **13b**$_{d\beta 2}$.

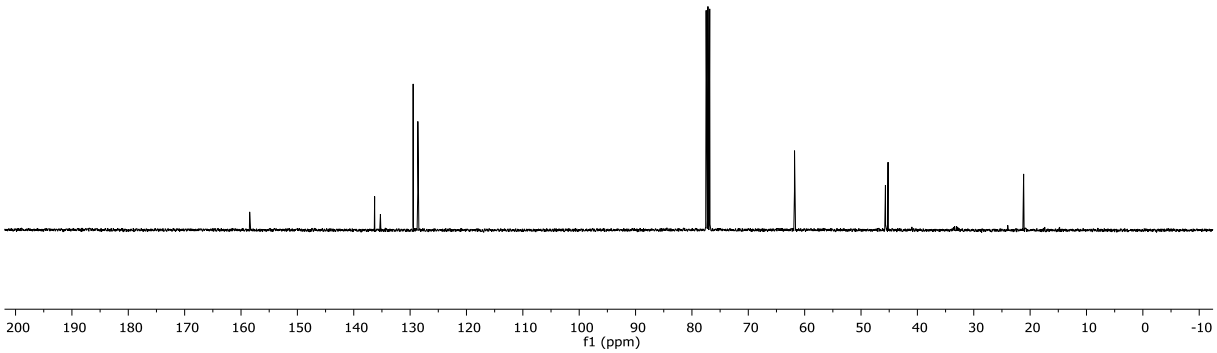
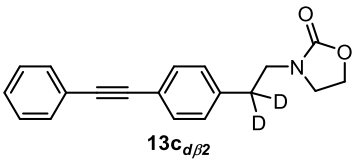


Figure S77. ^{13}C NMR spectrum of **13b**$_{d\beta 2}$.



13c$_{d\beta2}$

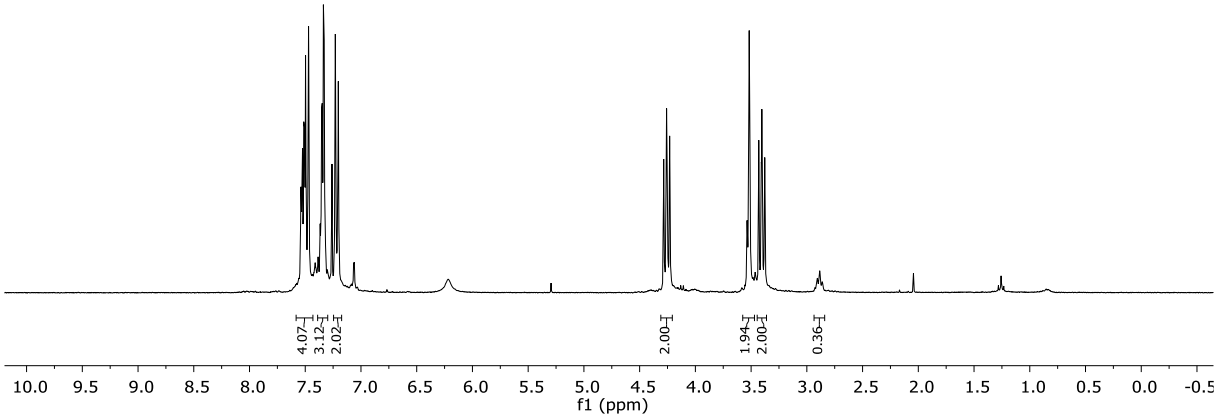


Figure S78. ^{1}H NMR spectrum of **13c**$_{d\beta2}$.

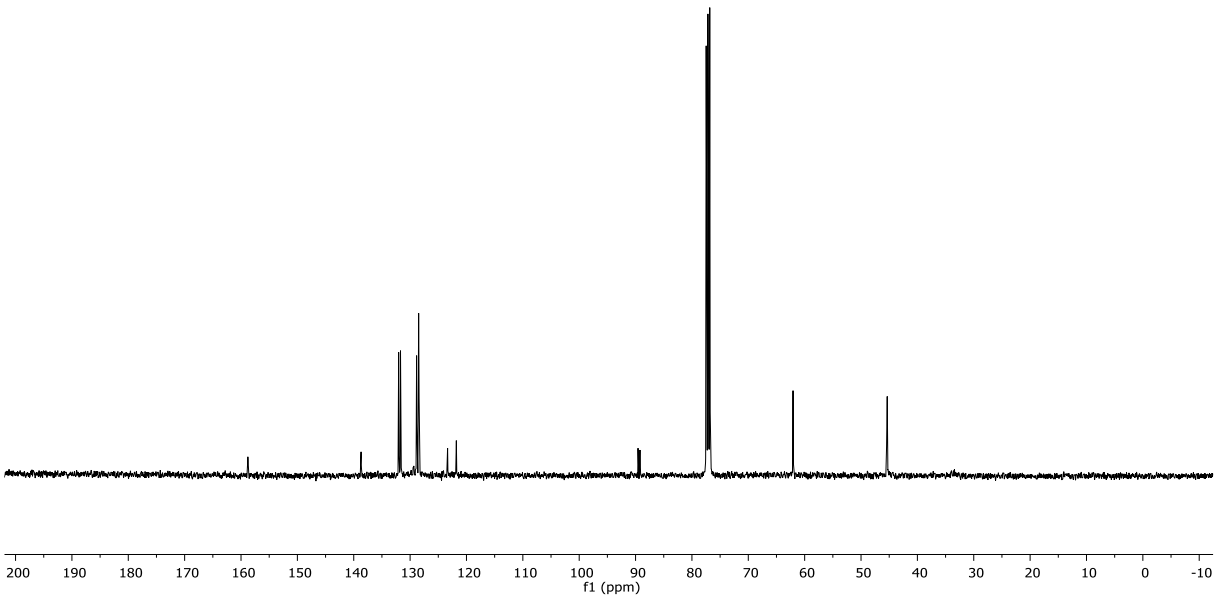
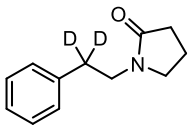


Figure S79. ^{13}C NMR spectrum of **13c**$_{d\beta2}$.



13d$_{d\beta 2}$

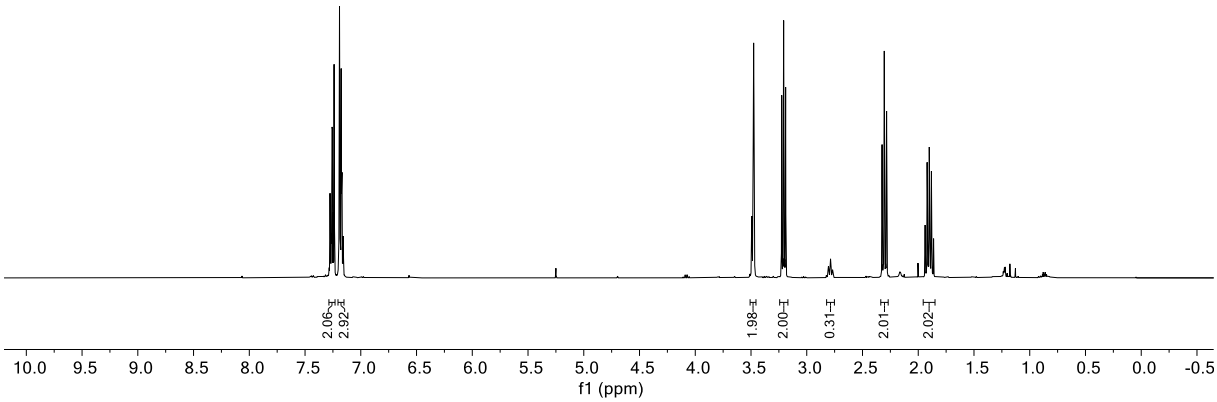


Figure S80. ^{1}H NMR spectrum of **13d**$_{d\beta 2}$.

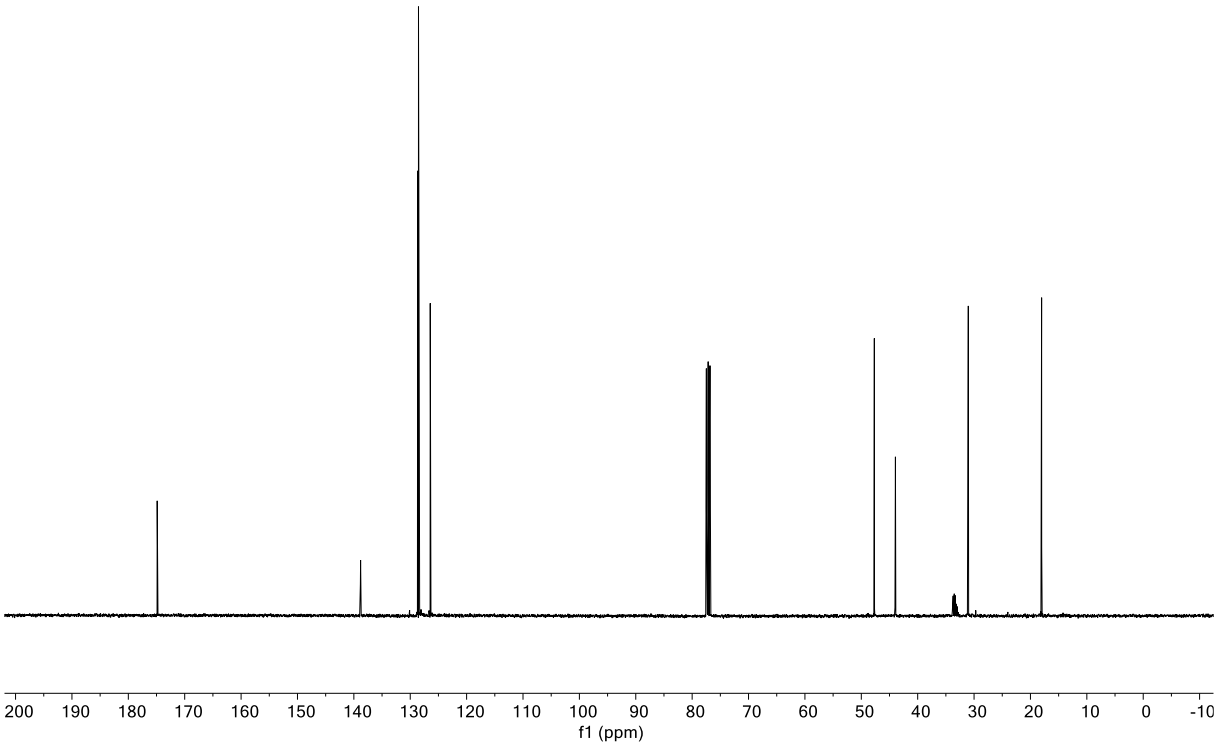
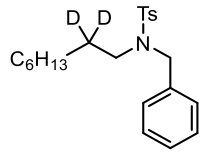


Figure S81. ^{13}C NMR spectrum of **13d**$_{d\beta 2}$.



13e$_{d\beta2}$

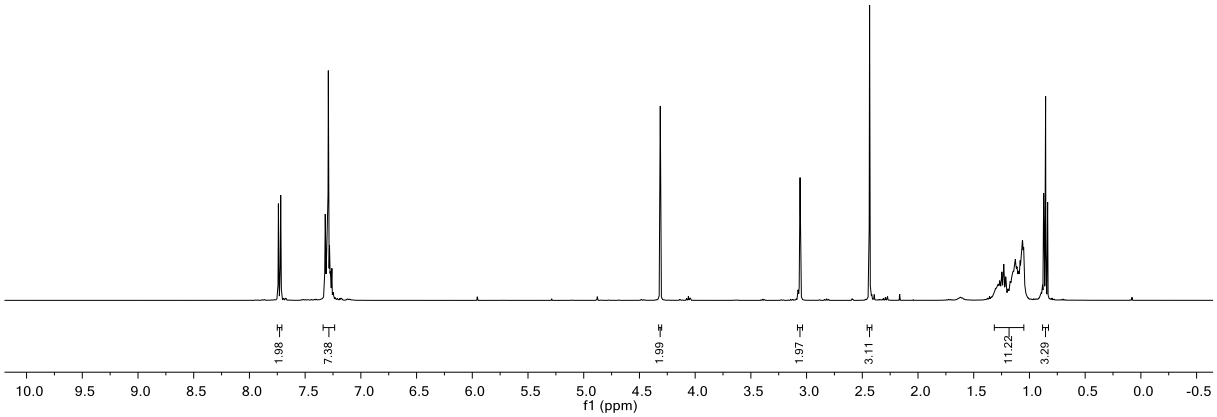


Figure S82. ^{1}H NMR spectrum of **13e$_{d\beta2}$**.

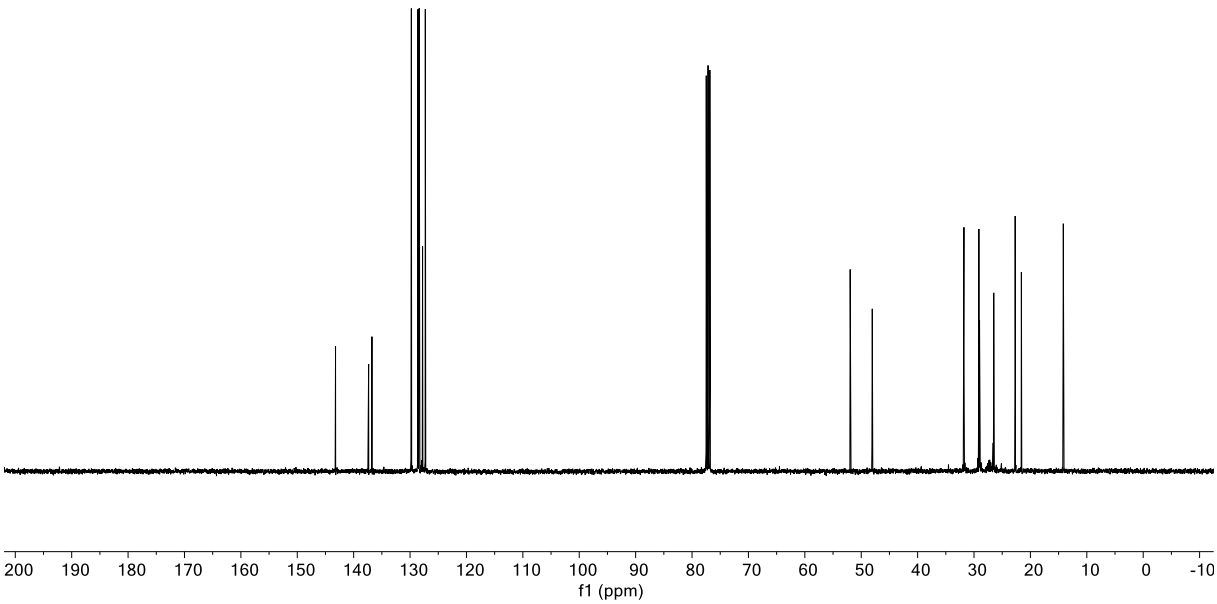


Figure S83. ^{13}C NMR spectrum of **13e$_{d\beta2}$**.

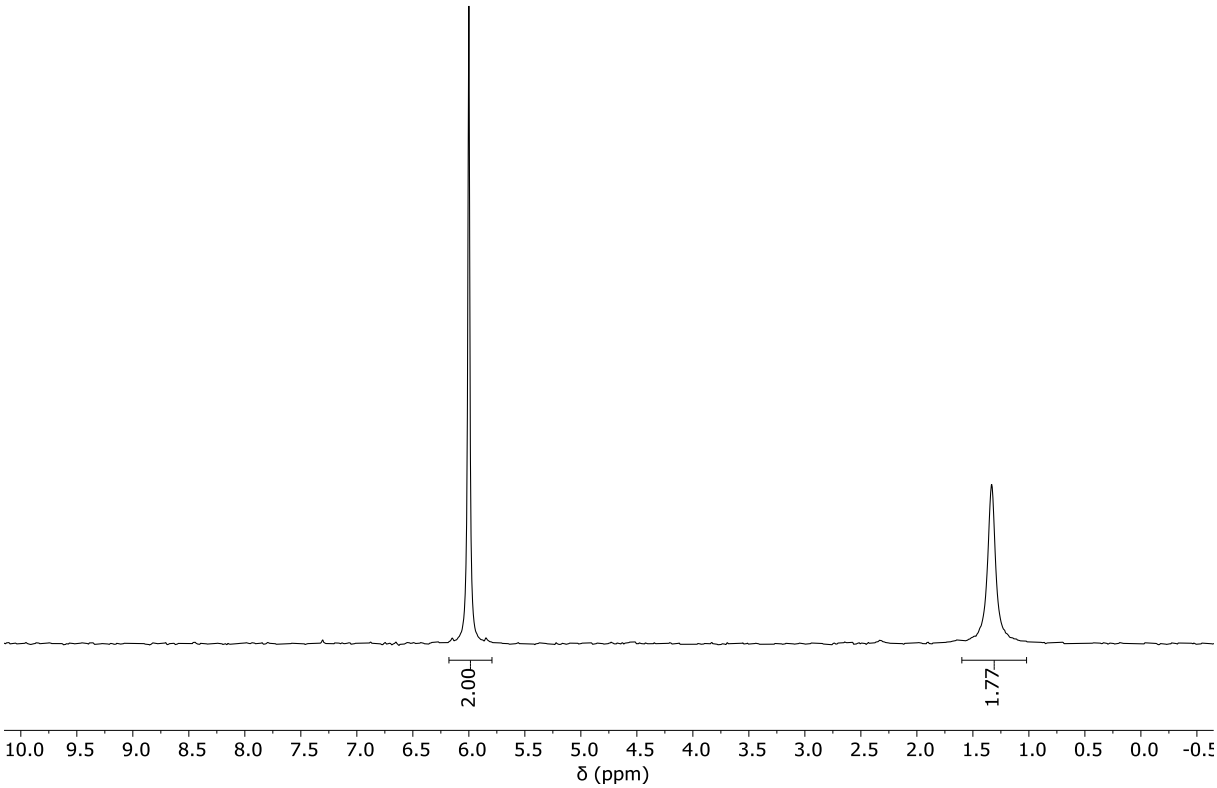
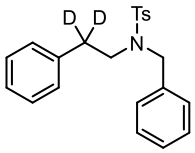


Figure S84. ^{2}H NMR spectrum of **13e**$_{d\beta 2}$.



13f$_{d\beta2}$

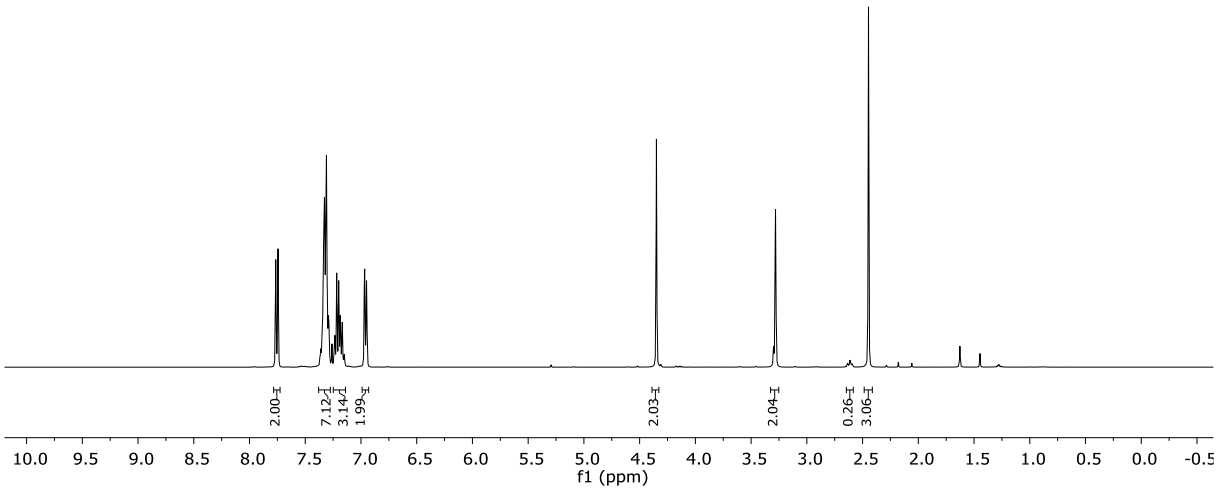


Figure S85. ^{1}H NMR spectrum of **13f**$_{d\beta2}$.

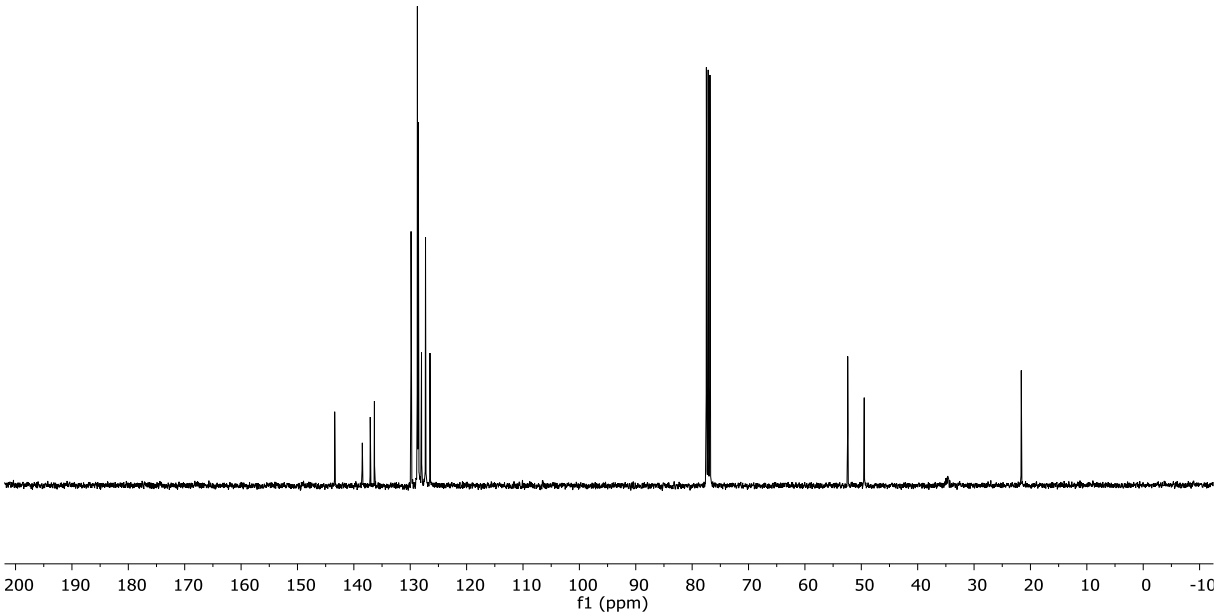
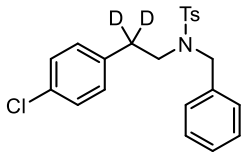


Figure S86. ^{13}C NMR spectrum of **13f**$_{d\beta2}$.



13g$_{d\beta 2}$

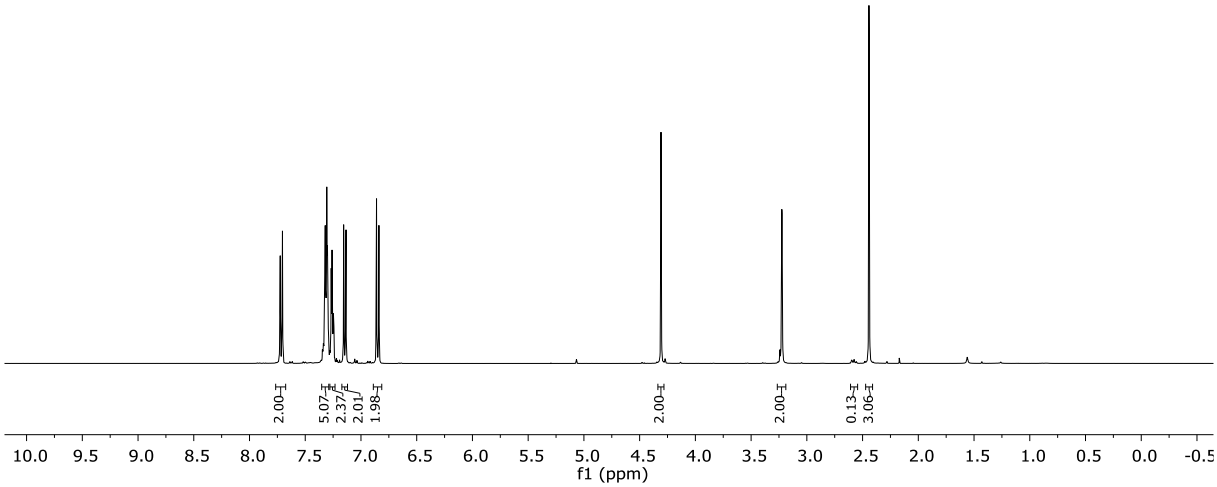


Figure S87. ^{1}H NMR spectrum of **13g**$_{d\beta 2}$.

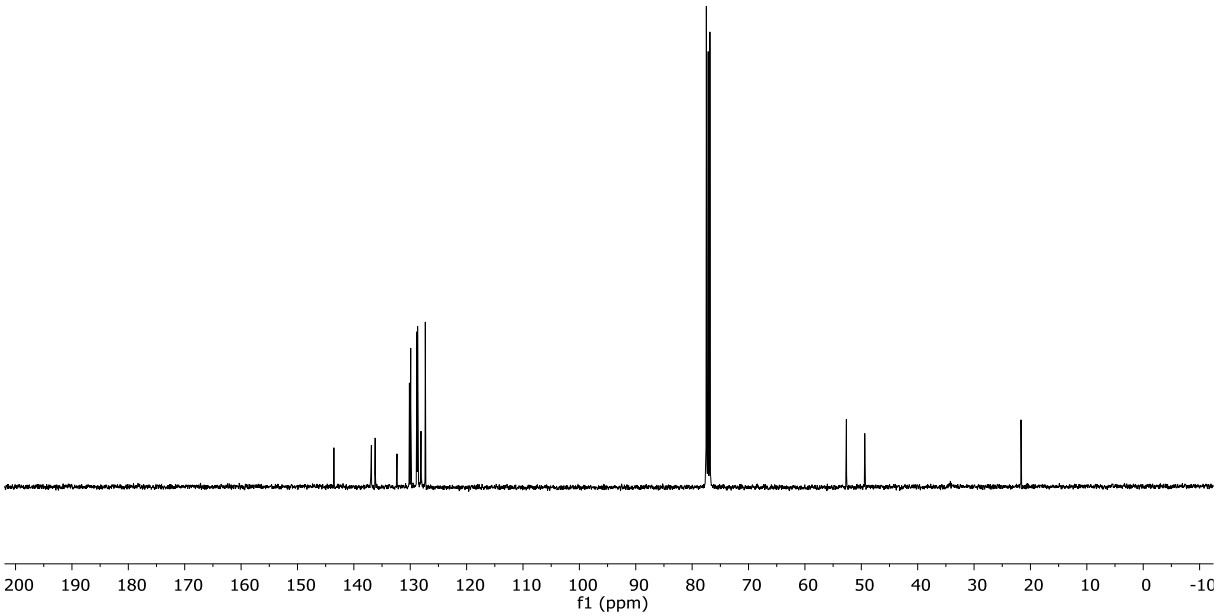
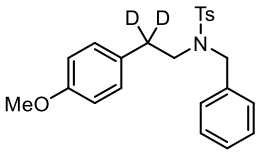


Figure S88. ^{13}C NMR spectrum of **13g**$_{d\beta 2}$.



13h$_{d\beta2}$

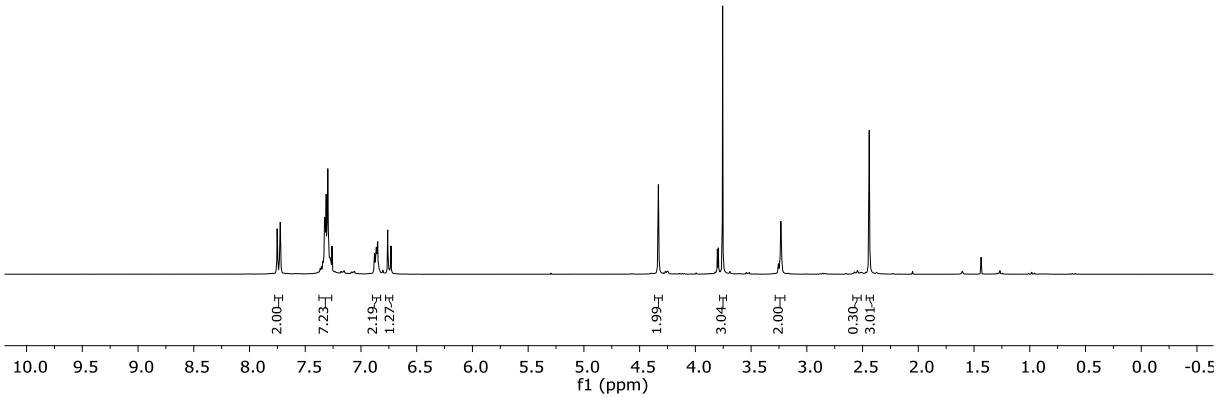


Figure S89. ^{1}H NMR spectrum of **13h$_{d\beta2}$**.

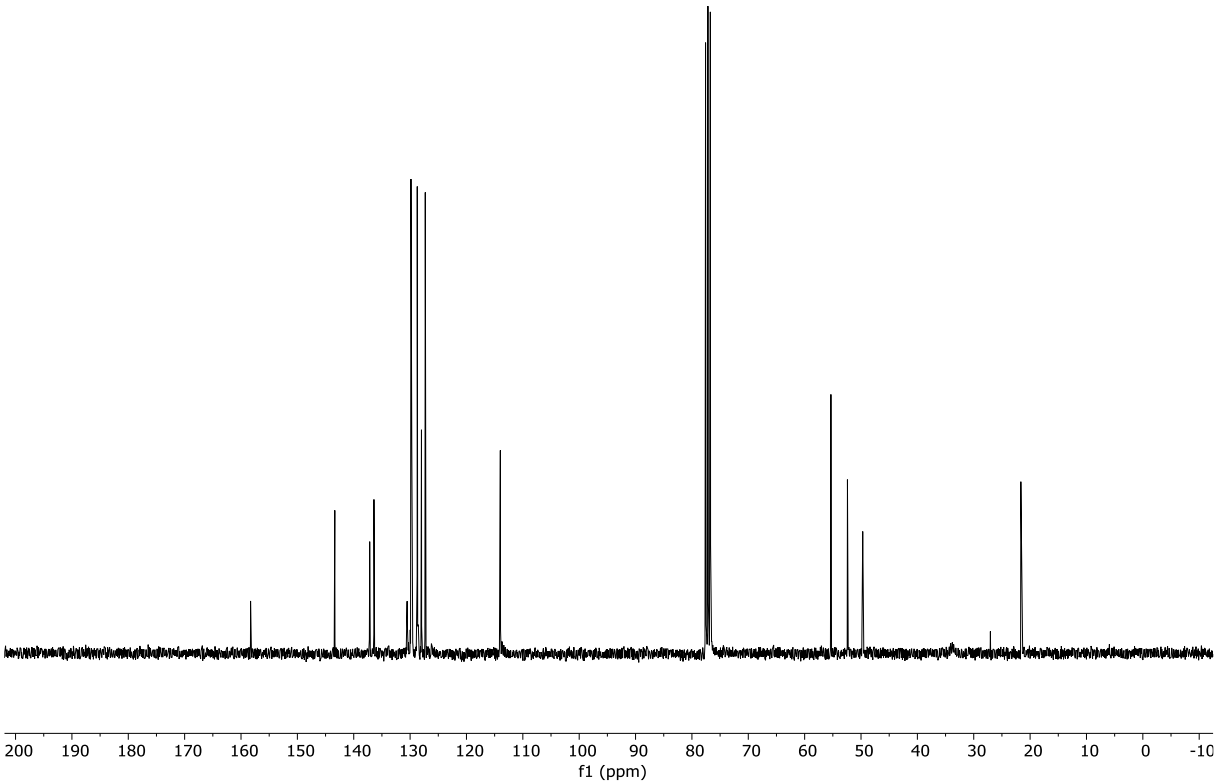
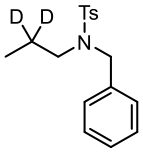


Figure S90. ^{13}C NMR spectrum of **13h$_{d\beta2}$**.



13i$_{d\beta 2}$

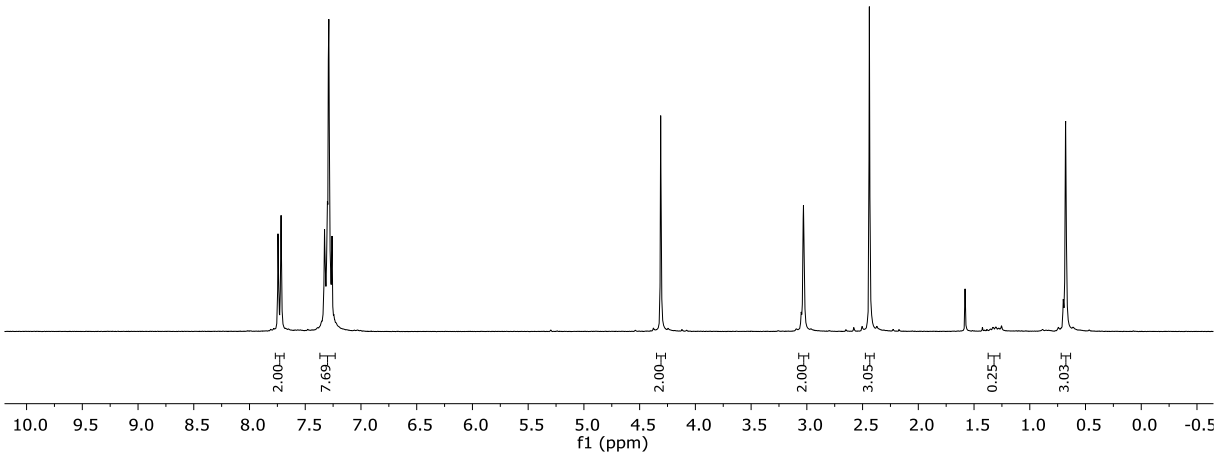


Figure S91. ^{1}H NMR spectrum of **13i**$_{d\beta 2}$.

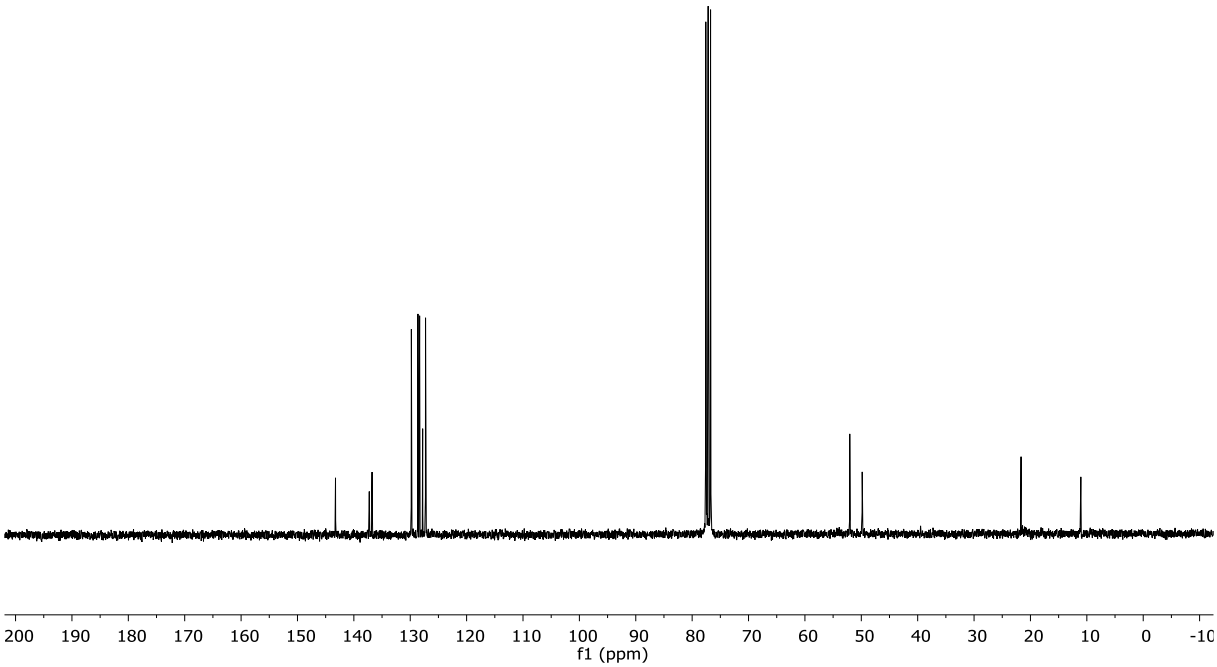
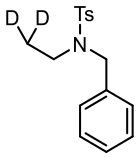


Figure S92. ^{13}C NMR spectrum of **13i**$_{d\beta 2}$.



13j$_{d\beta2}$

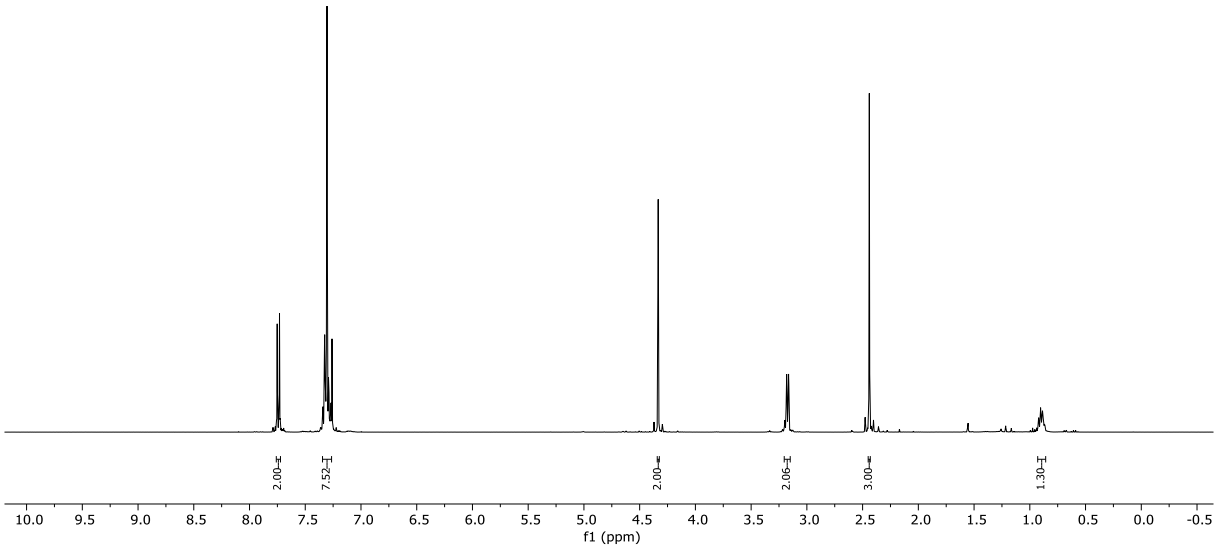


Figure S93. ^{1}H NMR spectrum of **13j$_{d\beta2}$**.

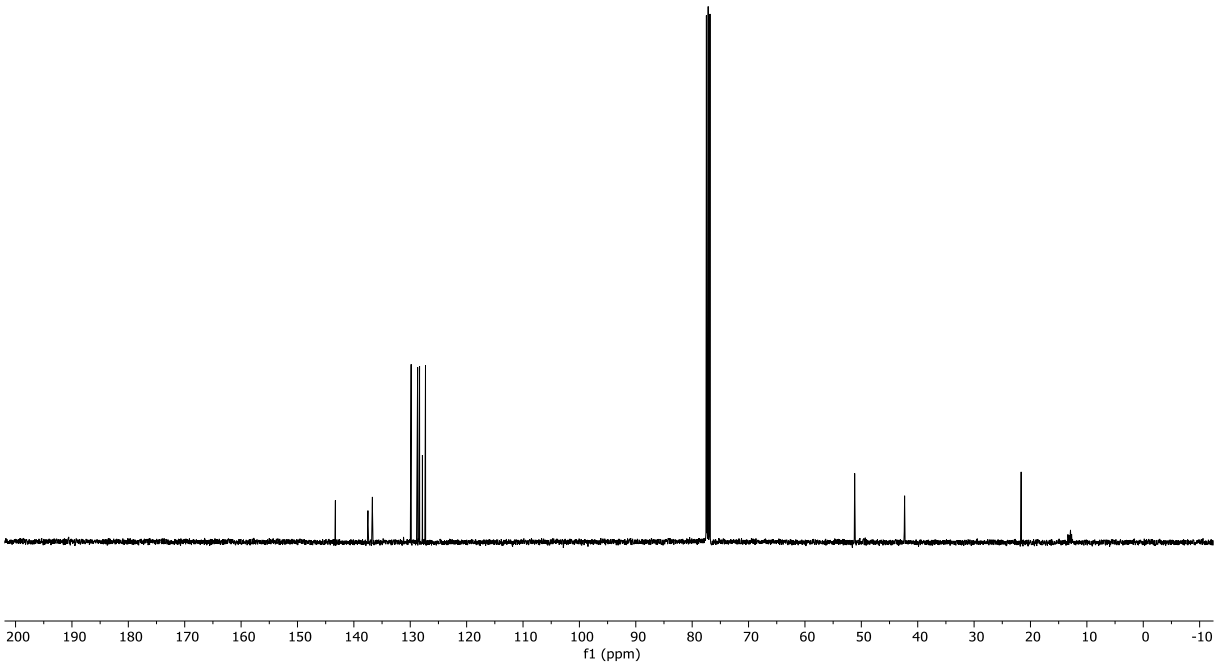
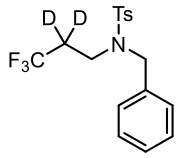


Figure S94. ^{13}C NMR spectrum of **13j$_{d\beta2}$**.



13k$_{d\beta2}$

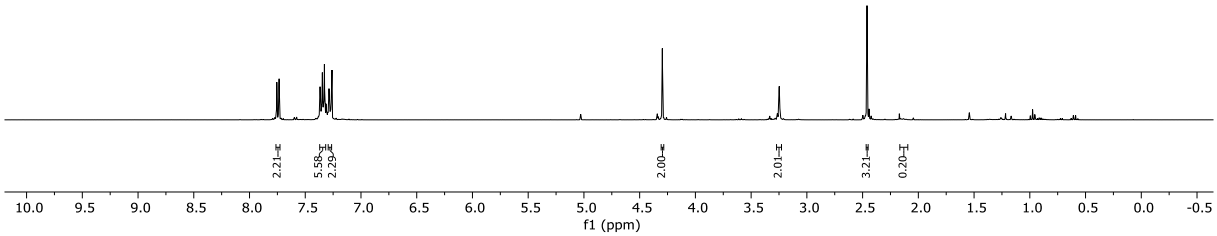


Figure S95. ^{1}H NMR spectrum of **13k$_{d\beta2}$**.

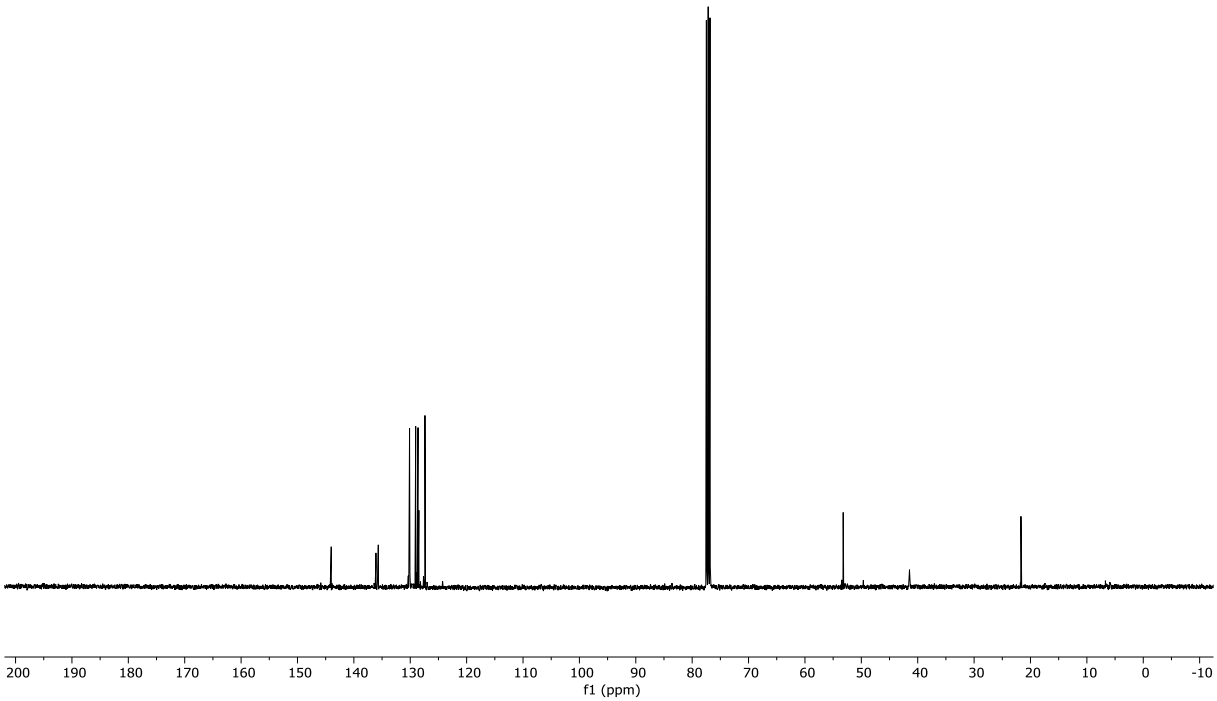


Figure S96. ^{13}C NMR spectrum of **13k$_{d\beta2}$**.

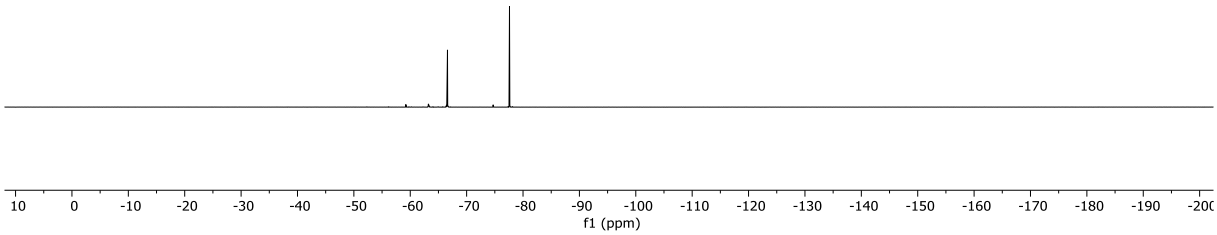
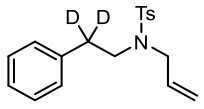


Figure S97. ^{19}F NMR spectrum of **13k**$_{d\beta 2}$.



13l$_{d\beta2}$

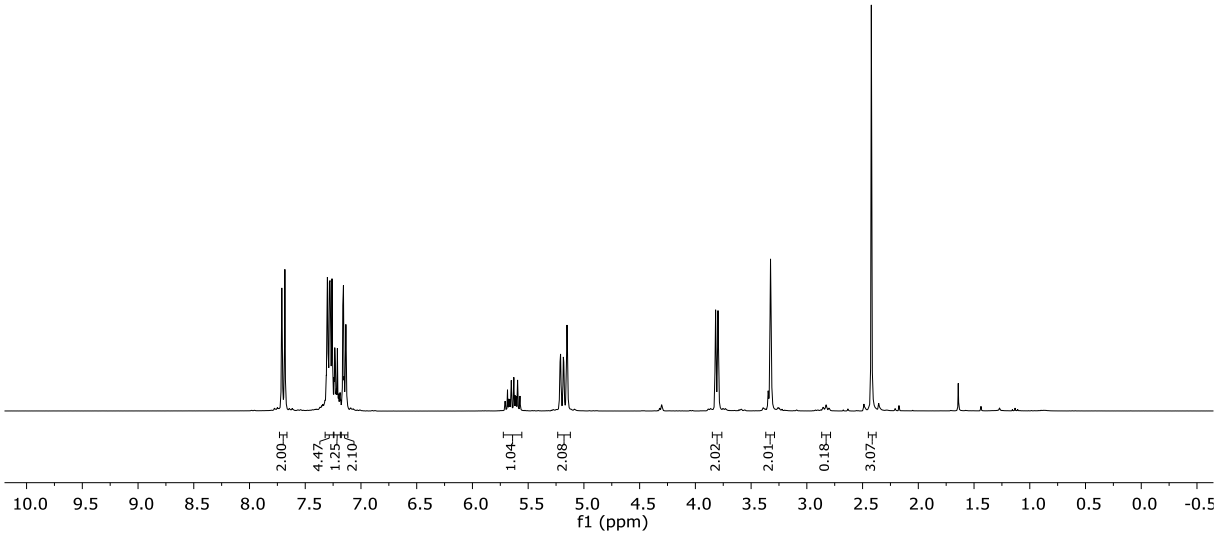


Figure S98. ^{1}H NMR spectrum of **13l$_{d\beta2}$**.

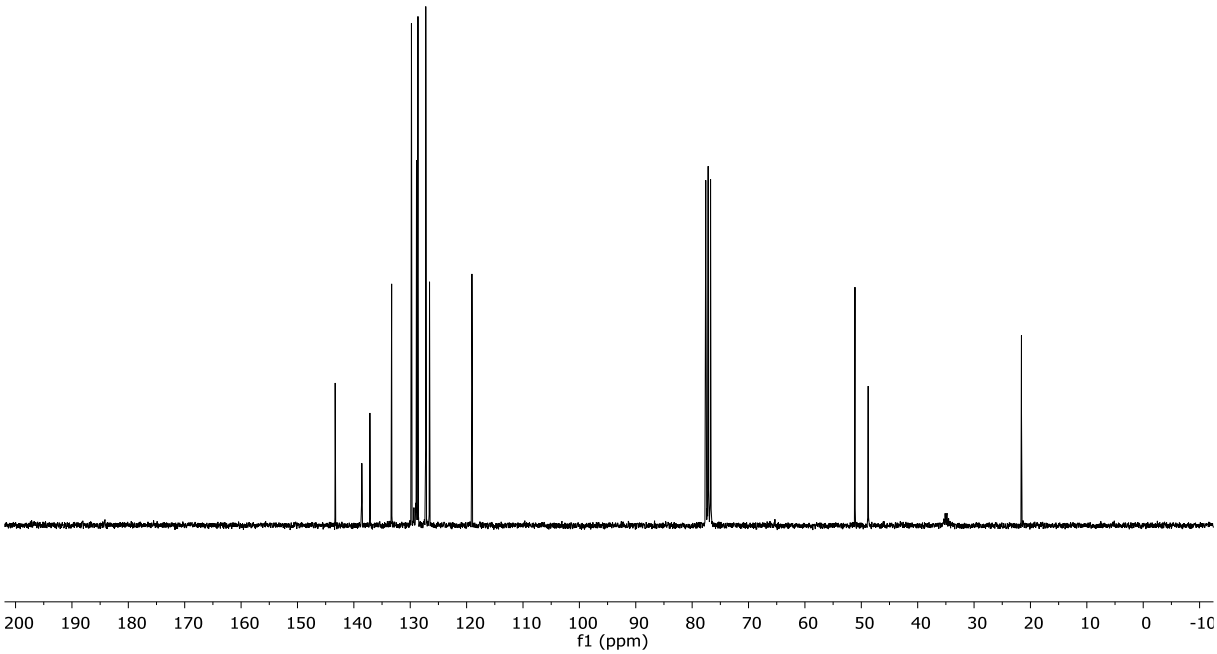
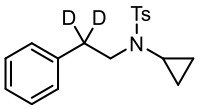


Figure S99. ^{13}C NMR spectrum of **13l$_{d\beta2}$**.



13m$_{d\beta2}$

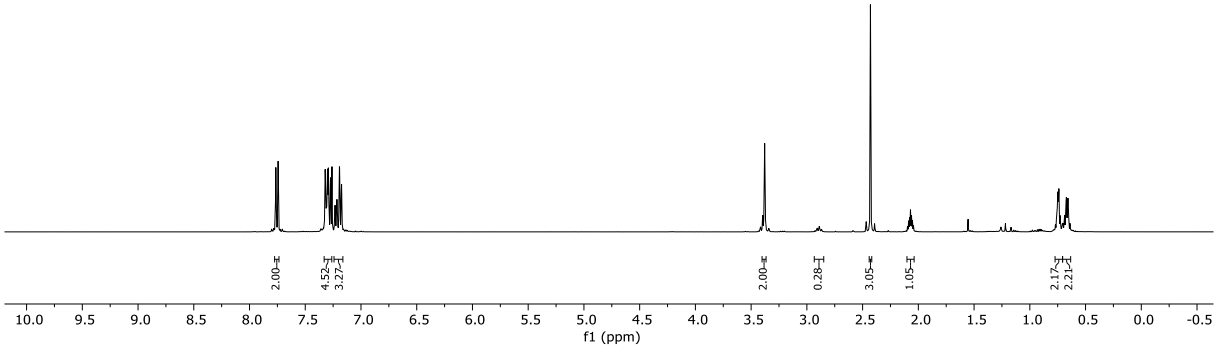


Figure S100. ^{1}H NMR spectrum of **13m**$_{d\beta2}$.

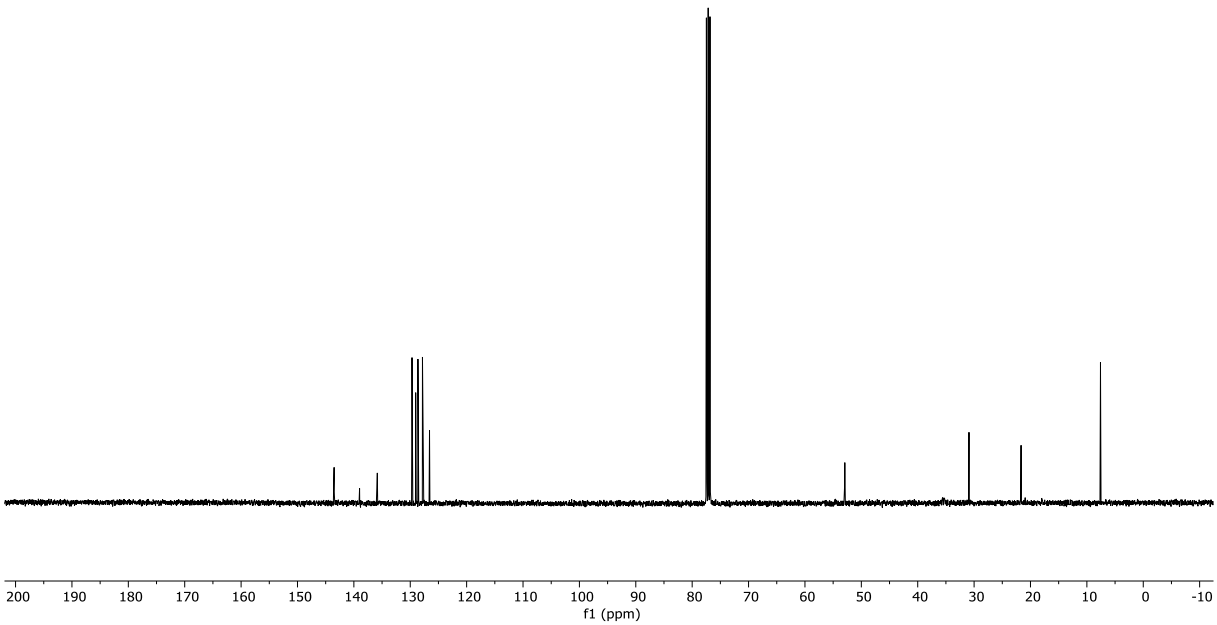


Figure S101. ^{13}C NMR spectrum of **13m**$_{d\beta2}$.

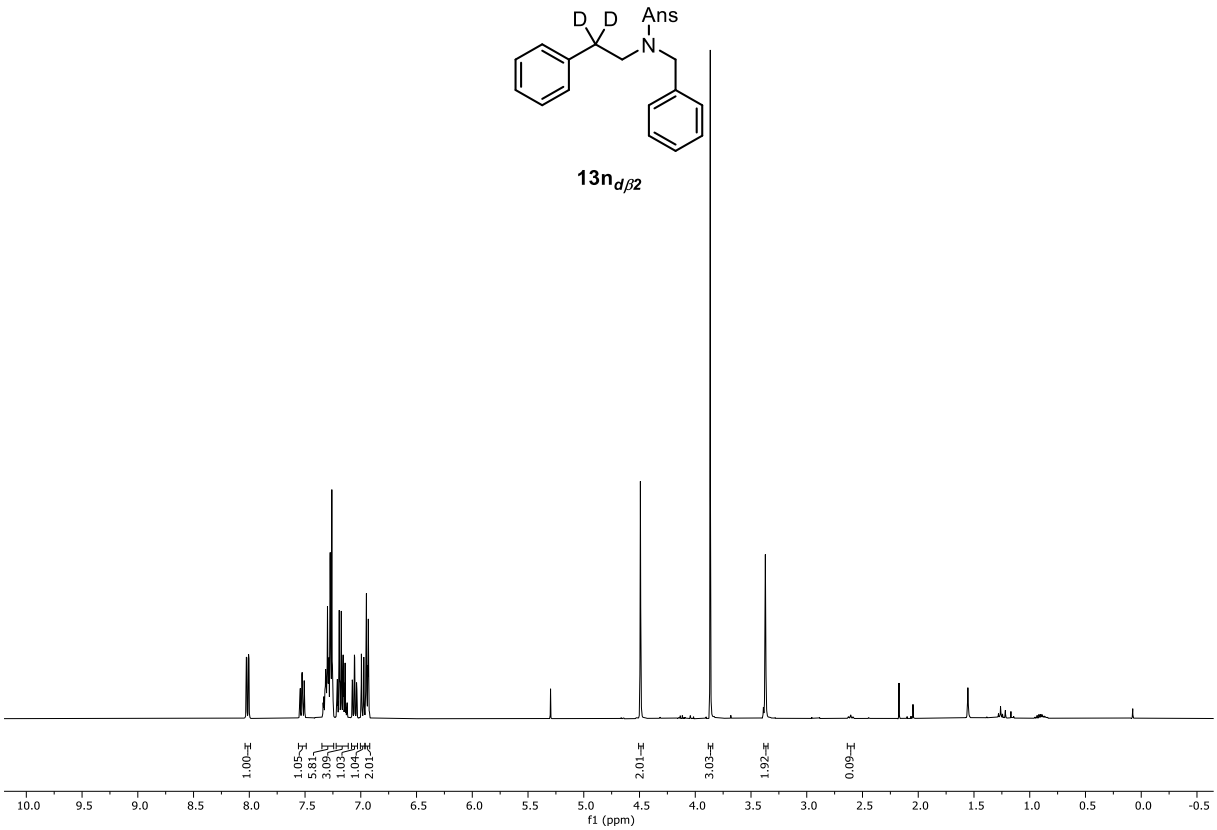


Figure S102. ^{1}H NMR spectrum of **13n$_{d\beta2}$**.

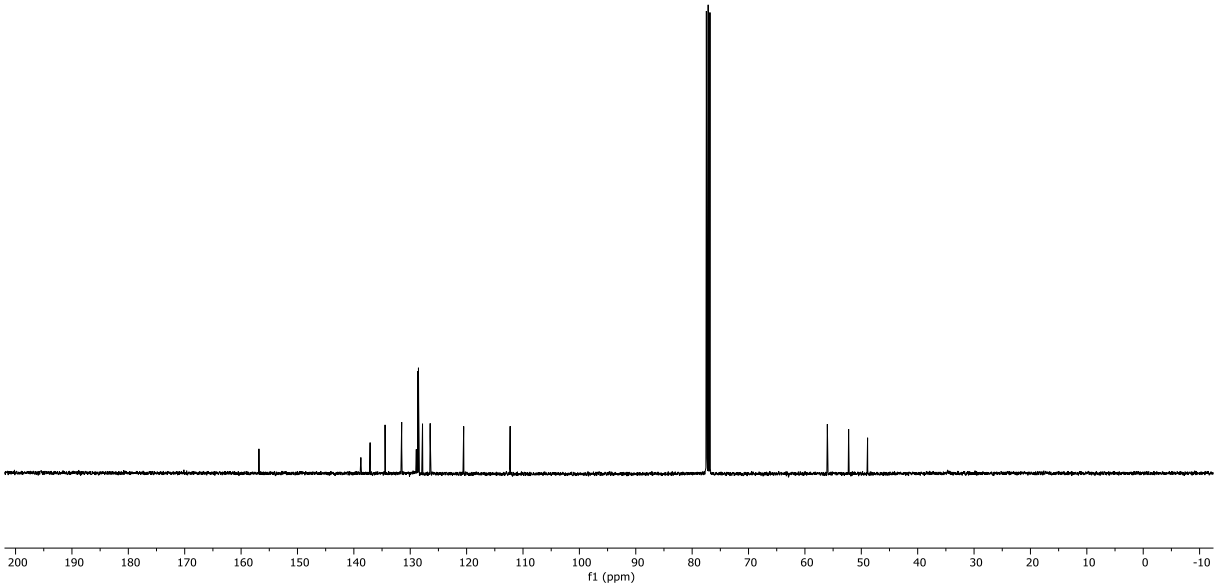


Figure S103. ^{13}C NMR spectrum of **13n$_{d\beta2}$**.

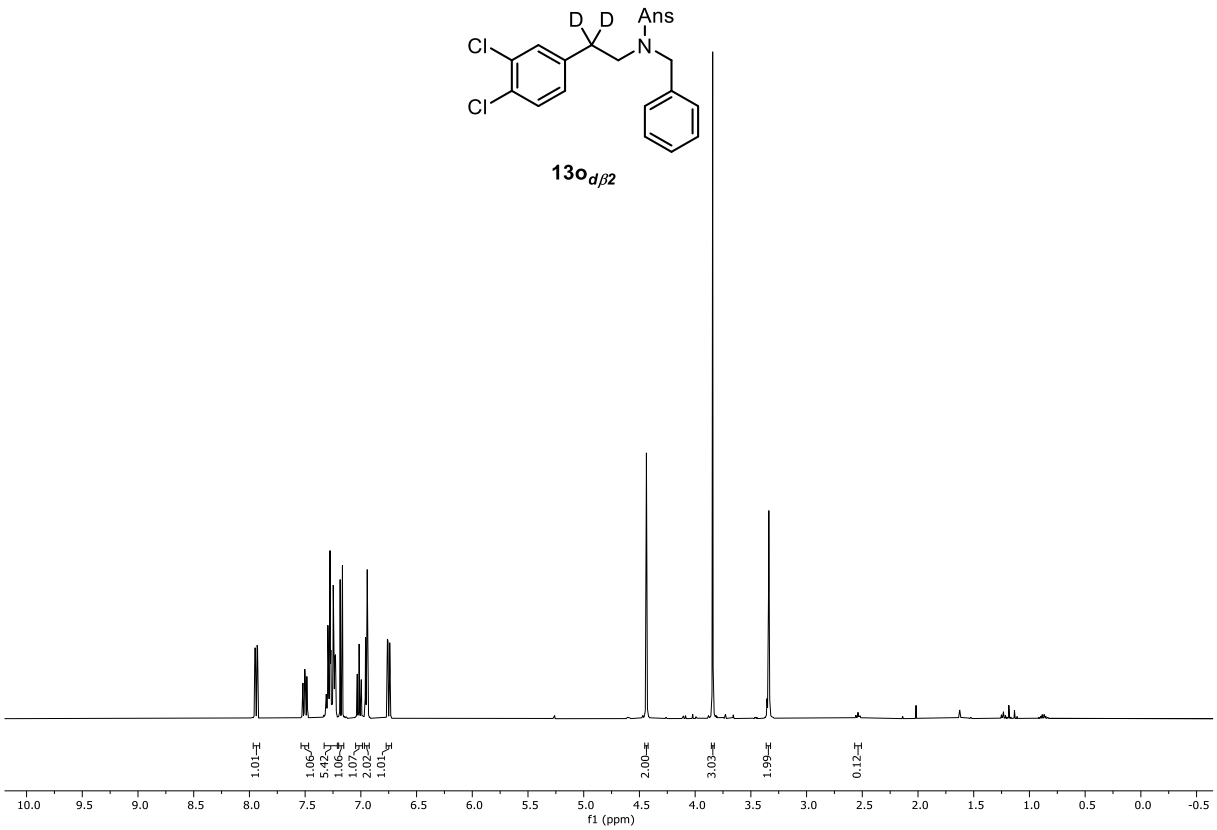


Figure S104. ^{1}H NMR spectrum of **13o**$_{d\beta2}$.

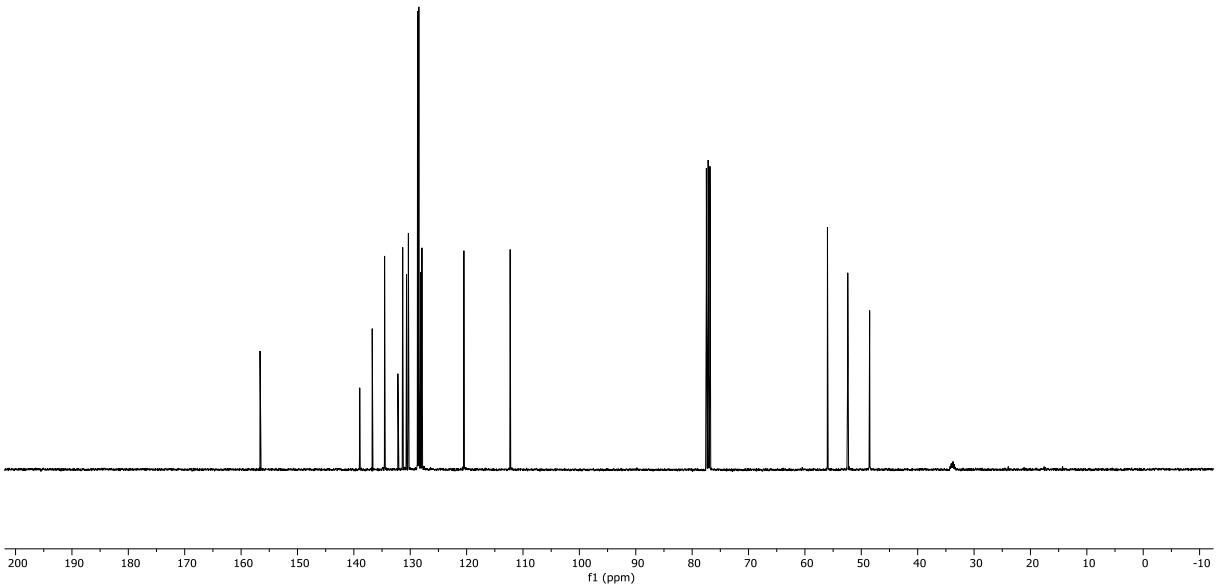
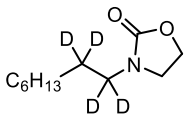


Figure S105. ^{13}C NMR spectrum of **13o**$_{d\beta2}$.



13a$_{d\alpha 2\beta 2}$

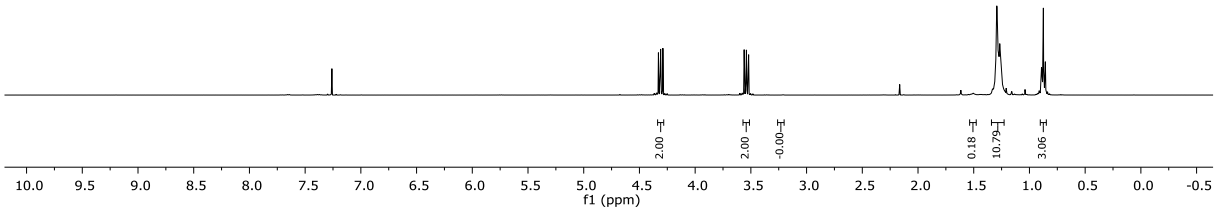


Figure S106. ^{1}H NMR spectrum of **13a**$_{d\alpha 2\beta 2}$.

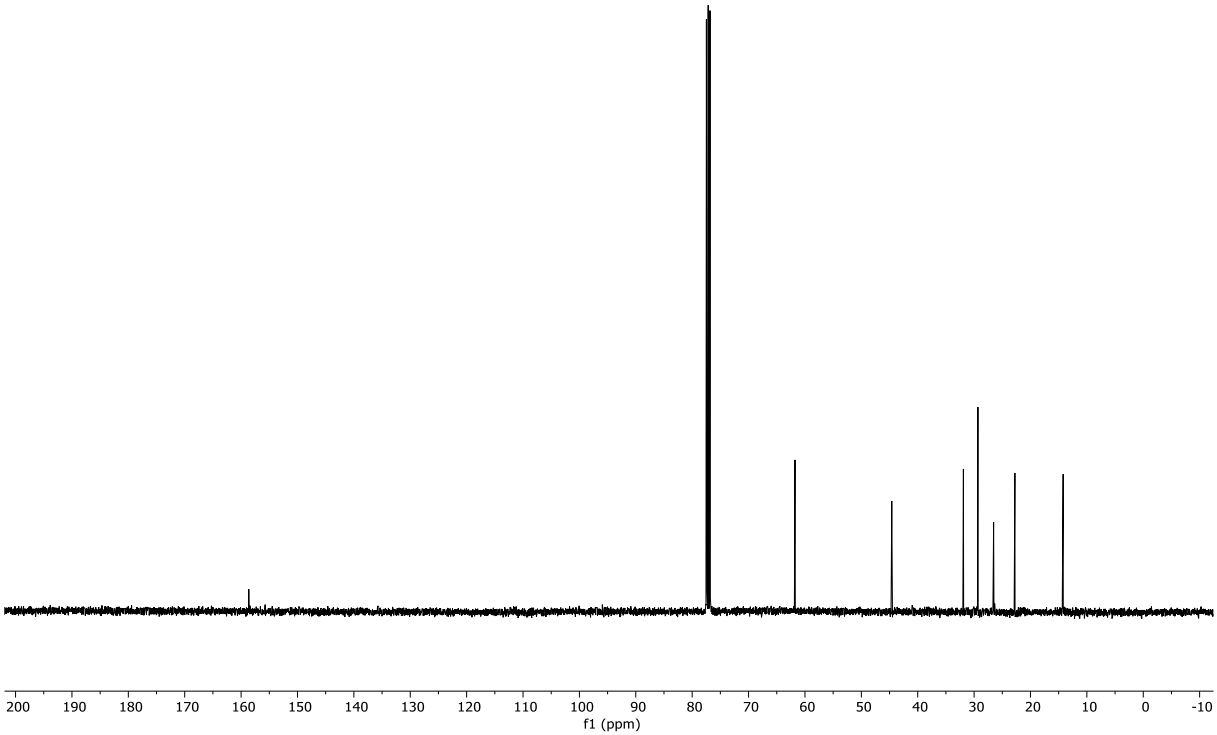
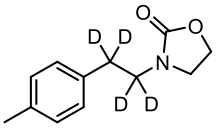


Figure S107. ^{13}C NMR spectrum of **13a**$_{d\alpha 2\beta 2}$.



13b$_{d\alpha 2\beta 2}$

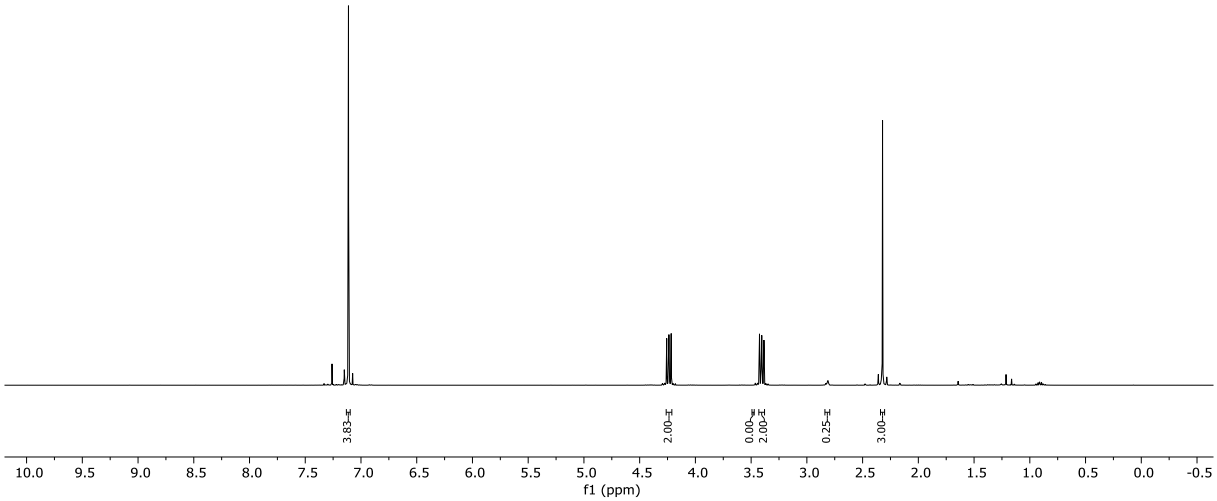


Figure S108. ^{1}H NMR spectrum of **13b**$_{d\alpha 2\beta 2}$.

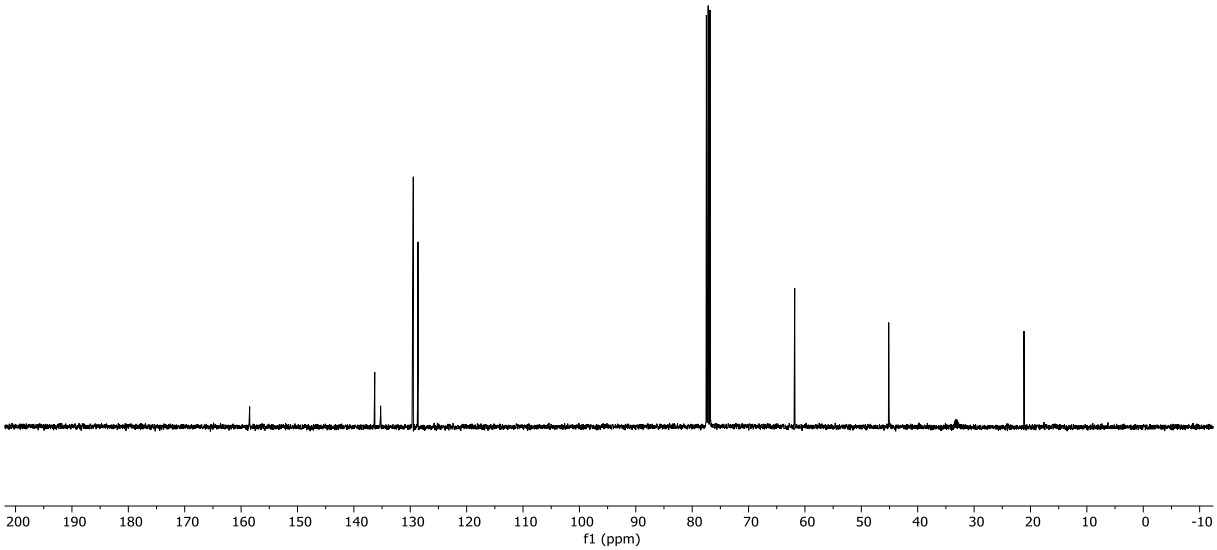
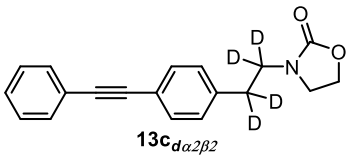


Figure S109. ^{13}C NMR spectrum of **13b**$_{d\alpha 2\beta 2}$.



13c$_{d\alpha 2\beta 2}$

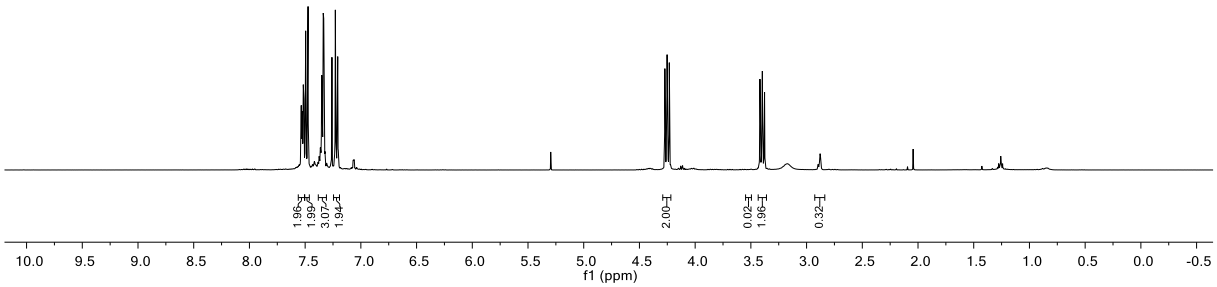


Figure S110. ^{1}H NMR spectrum of **13c**$_{d\alpha 2\beta 2}$.

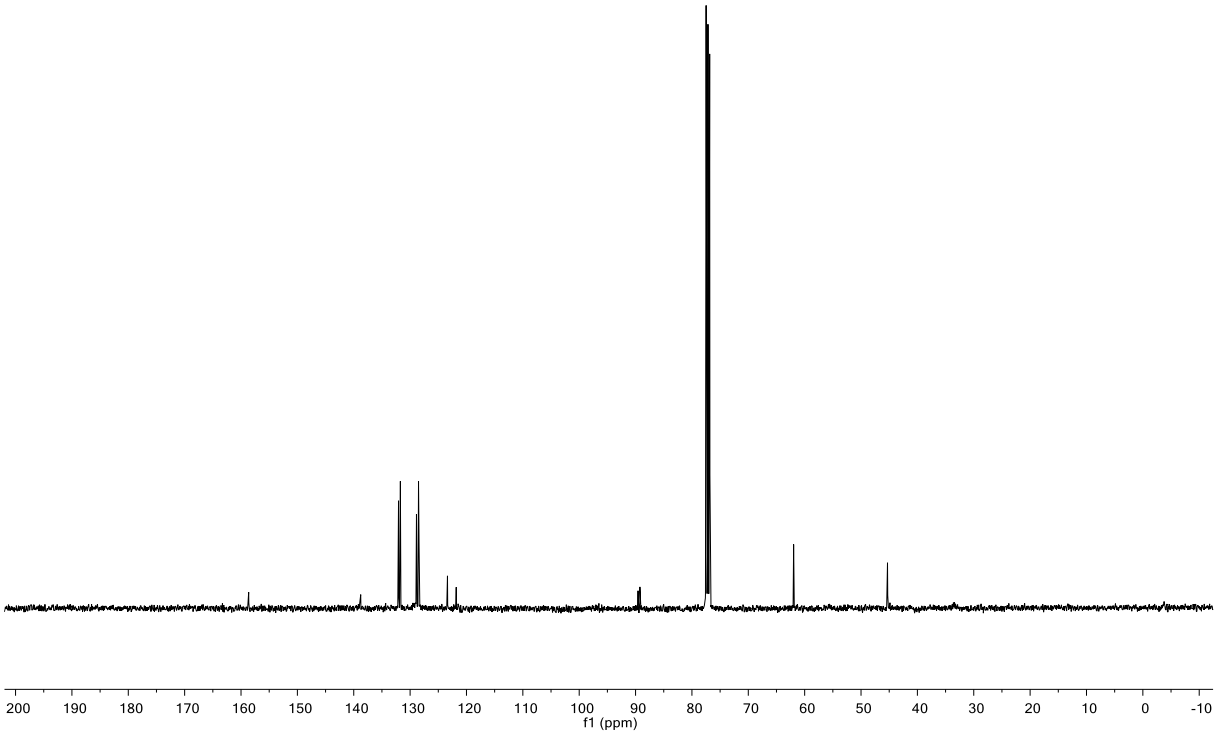
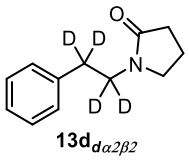


Figure S111. ^{13}C NMR spectrum of **13c**$_{d\alpha 2\beta 2}$.



13d$_{d\alpha 2\beta 2}$

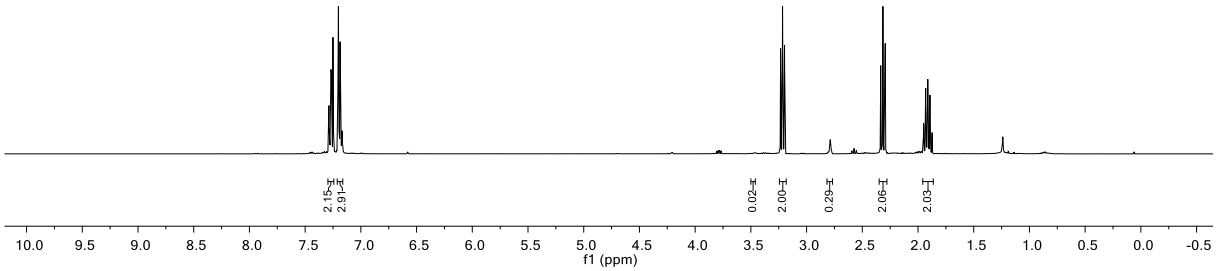


Figure S112. ^{1}H NMR spectrum of **13d**$_{d\alpha 2\beta 2}$.

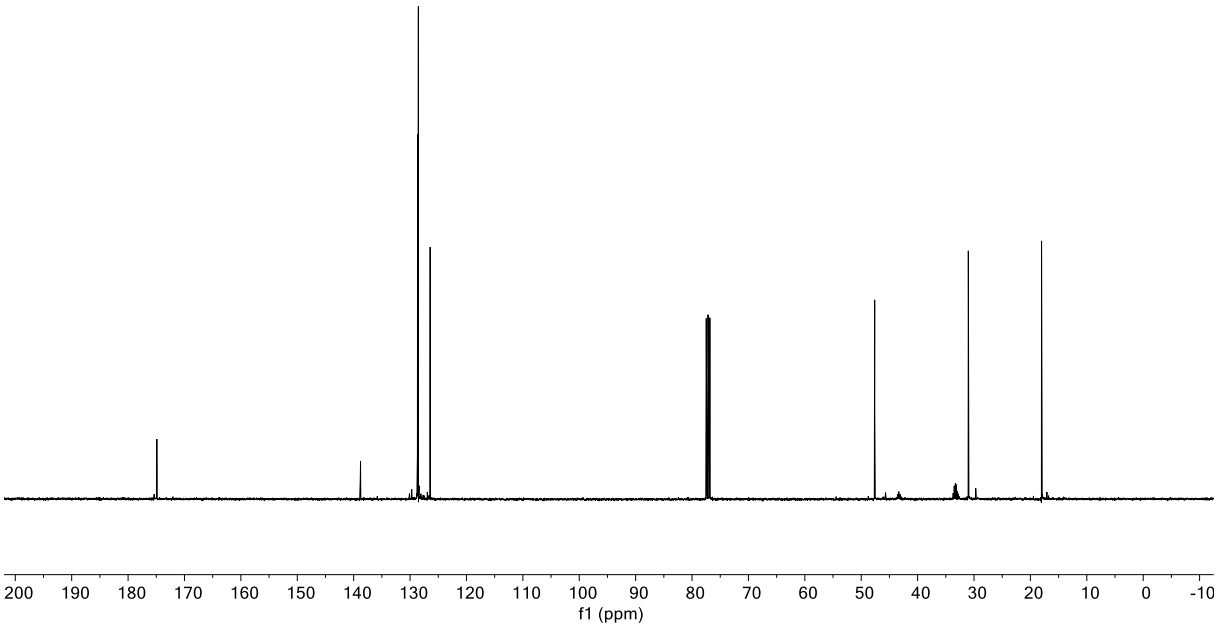
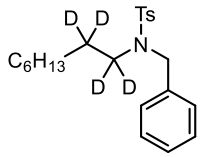


Figure S113. ^{13}C NMR spectrum of **13d**$_{d\alpha 2\beta 2}$.



13e$_{d\alpha 2\beta 2}$

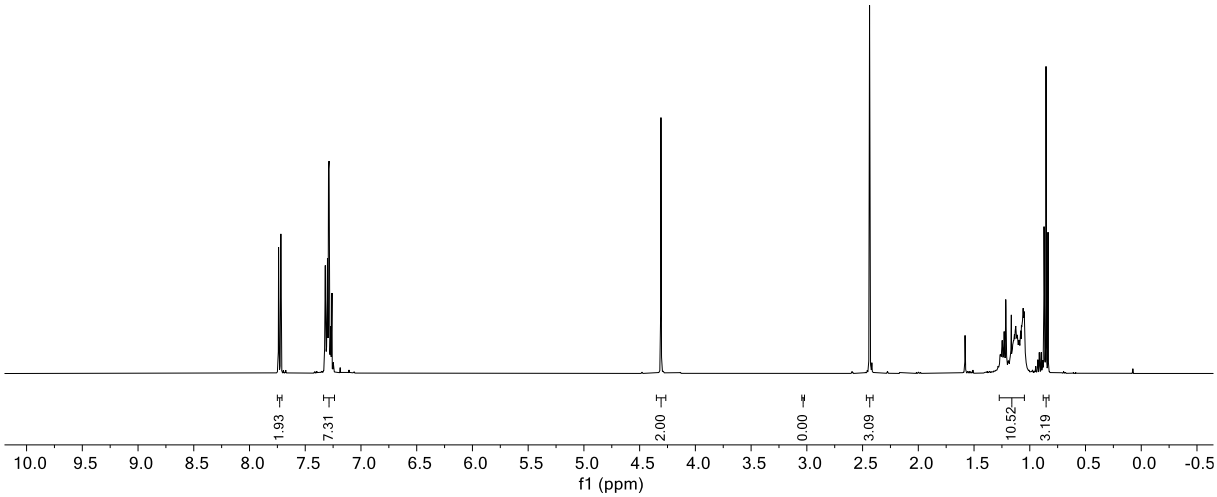


Figure S114. ^{1}H NMR spectrum of **13e**$_{d\alpha 2\beta 2}$.

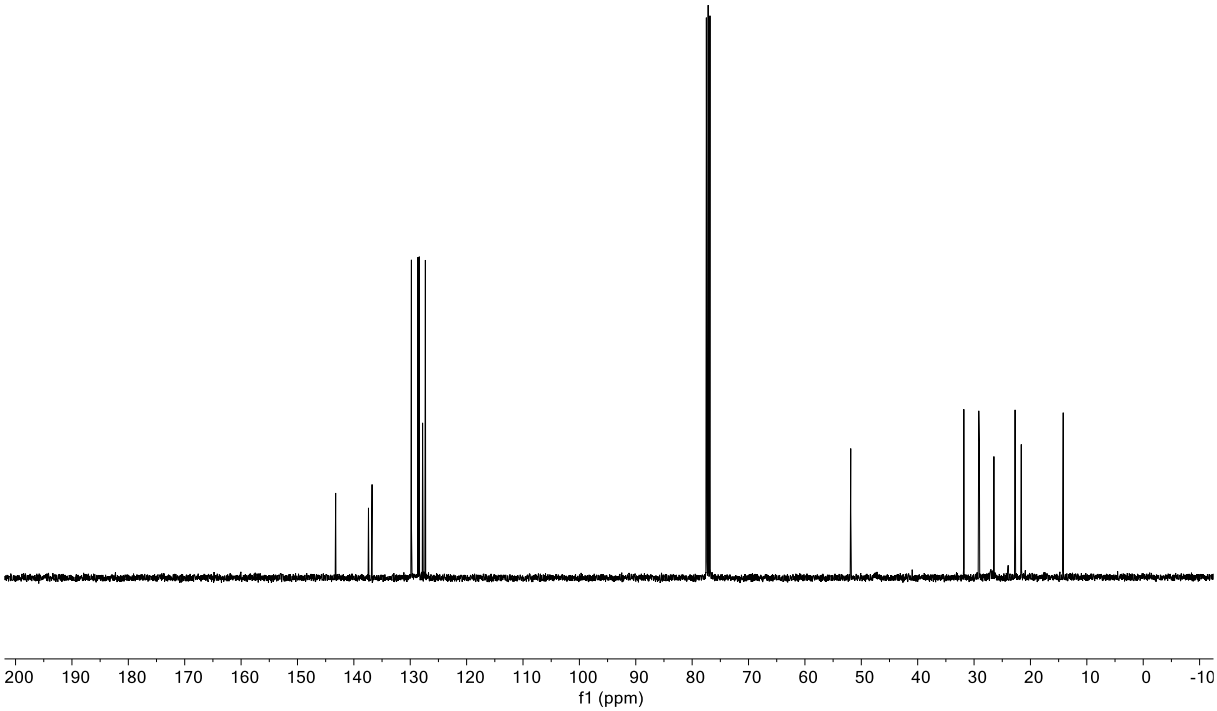


Figure S115. ^{13}C NMR spectrum of **13e**$_{d\alpha 2\beta 2}$.

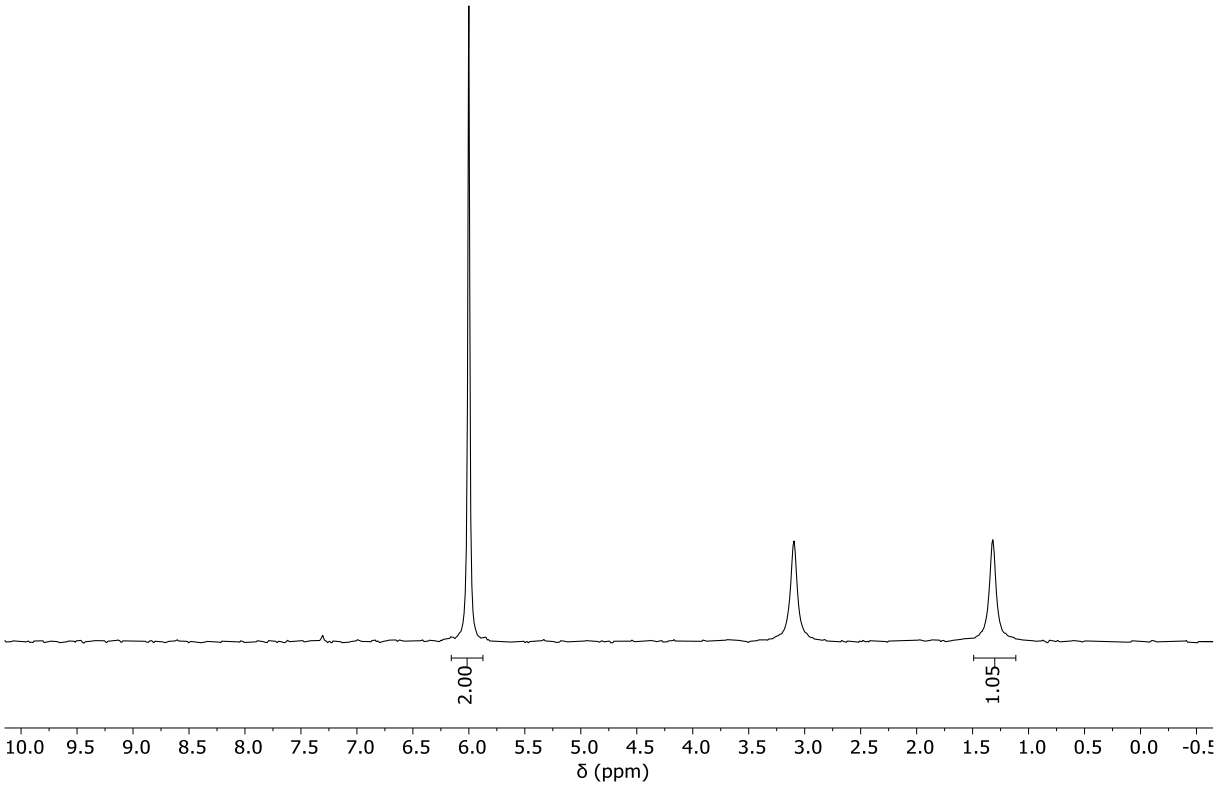
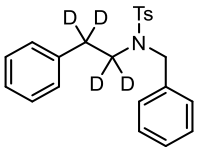


Figure S116. ^{2}H NMR spectrum of **13e**$_{d\alpha 2\beta 2}$.



13f$_{d\alpha 2\beta 2}$

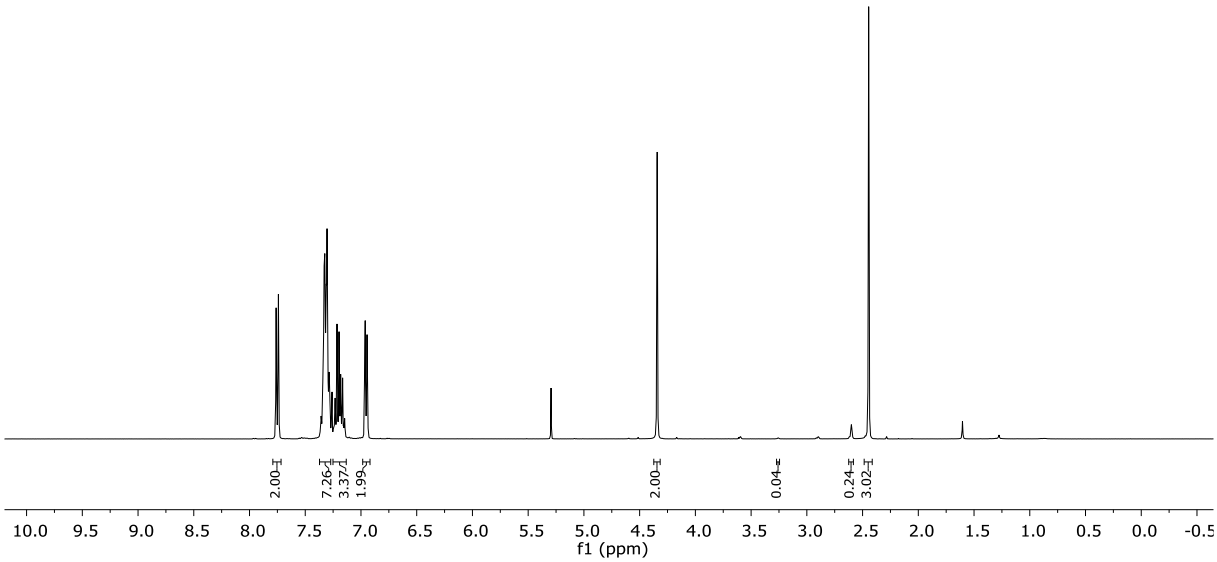


Figure S117. ^{1}H NMR spectrum of **13f**$_{d\alpha 2\beta 2}$.

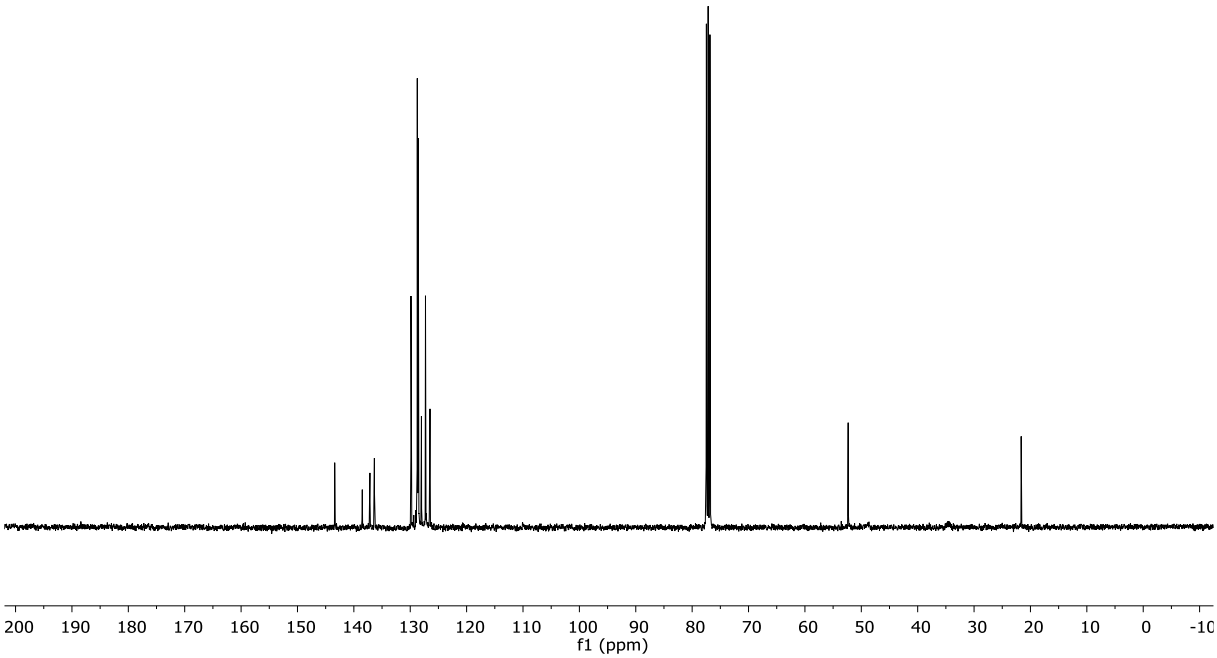
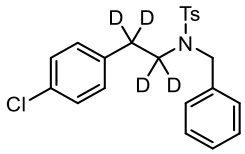


Figure S118. ^{13}C NMR spectrum of **13f**$_{d\alpha 2\beta 2}$.



13g$_{d\alpha 2\beta 2}$

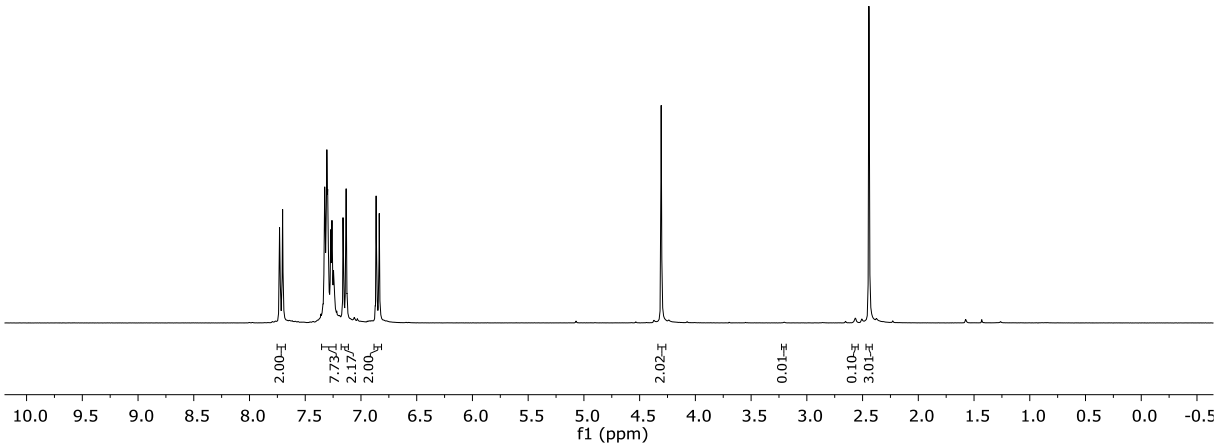


Figure S119. ^{1}H NMR spectrum of **13g**$_{d\alpha 2\beta 2}$.

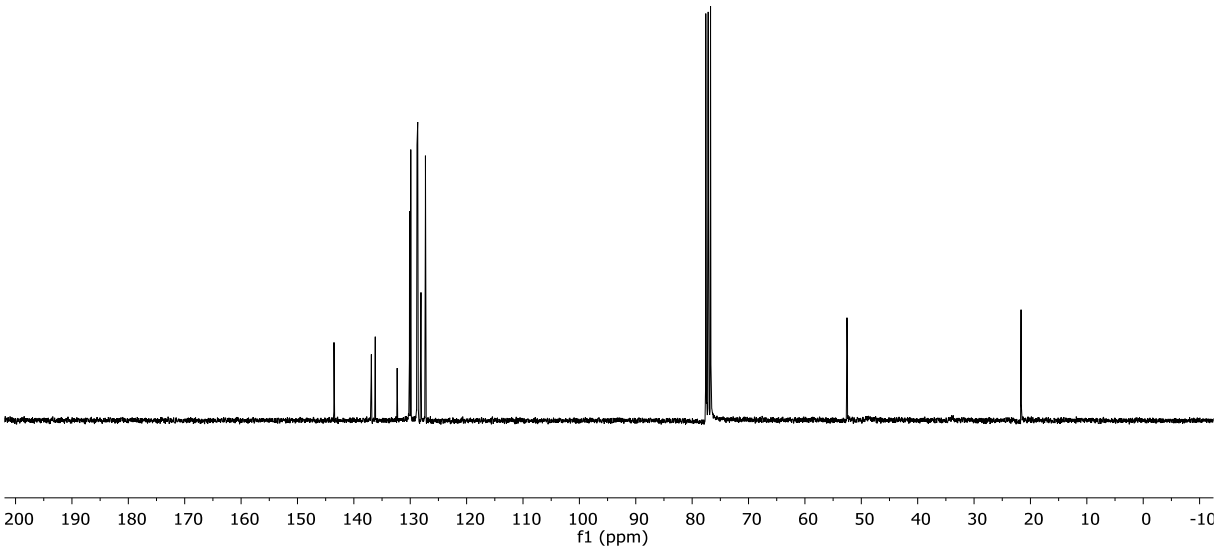
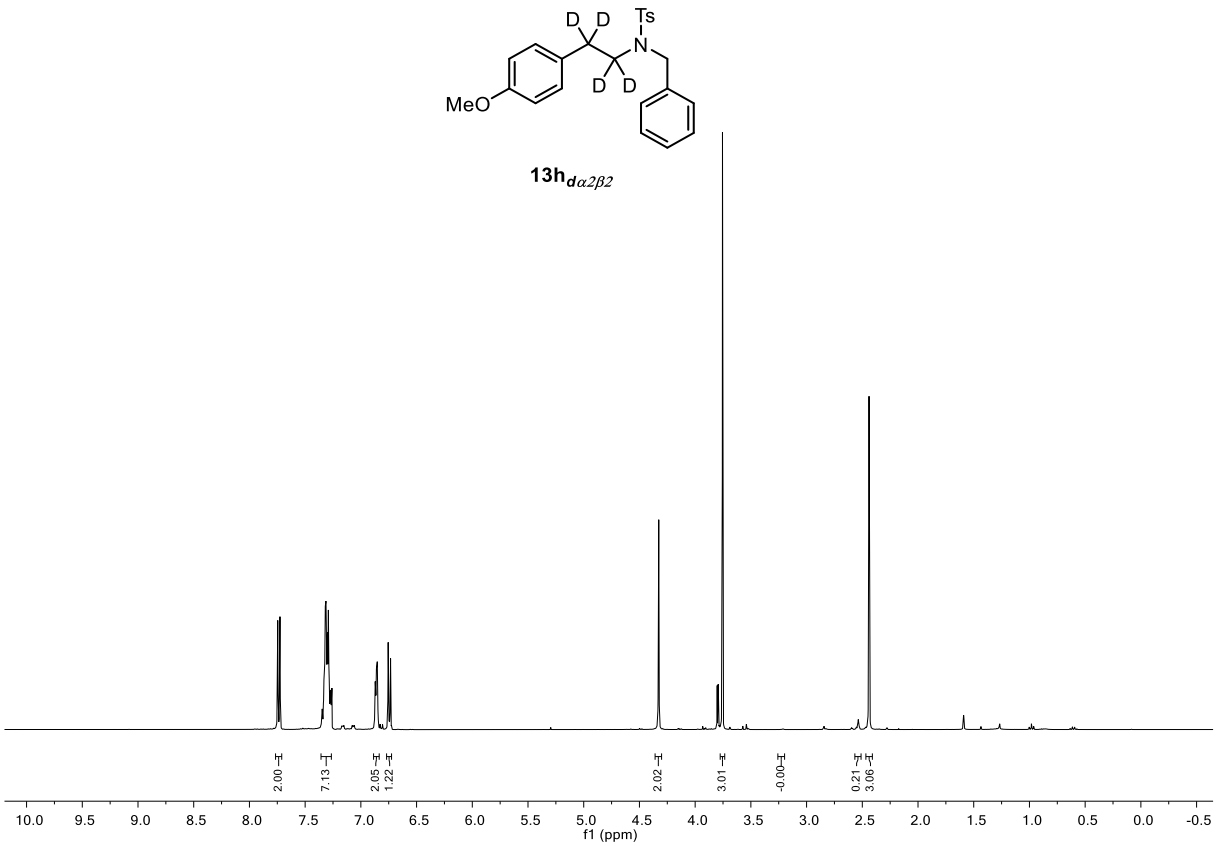


Figure S120. ^{13}C NMR spectrum of **13g**$_{d\alpha 2\beta 2}$.



13h$_{d\alpha 2\beta 2}$

Figure S121. ^{1}H NMR spectrum of **13h**$_{d\alpha 2\beta 2}$.

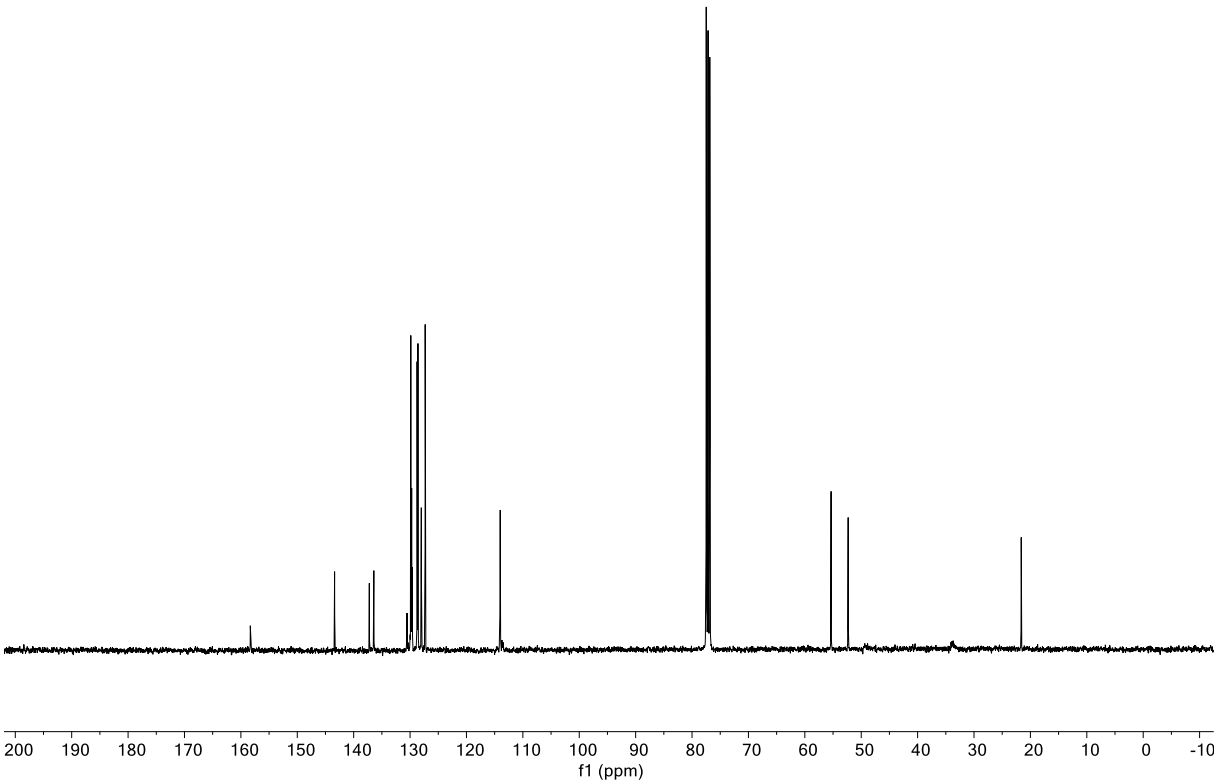
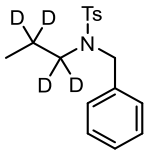


Figure S122. ^{13}C NMR spectrum of **13h**$_{d\alpha 2\beta 2}$.



13i$_{d\alpha 2\beta 2}$

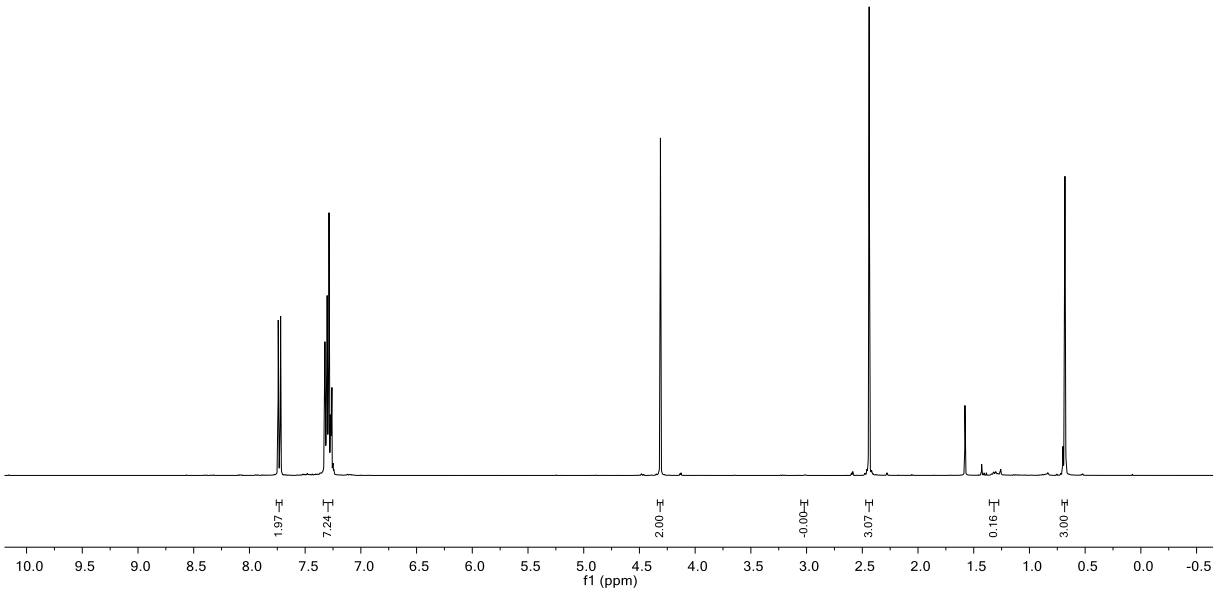


Figure S123. ^{1}H NMR spectrum of **13i**$_{d\alpha 2\beta 2}$.

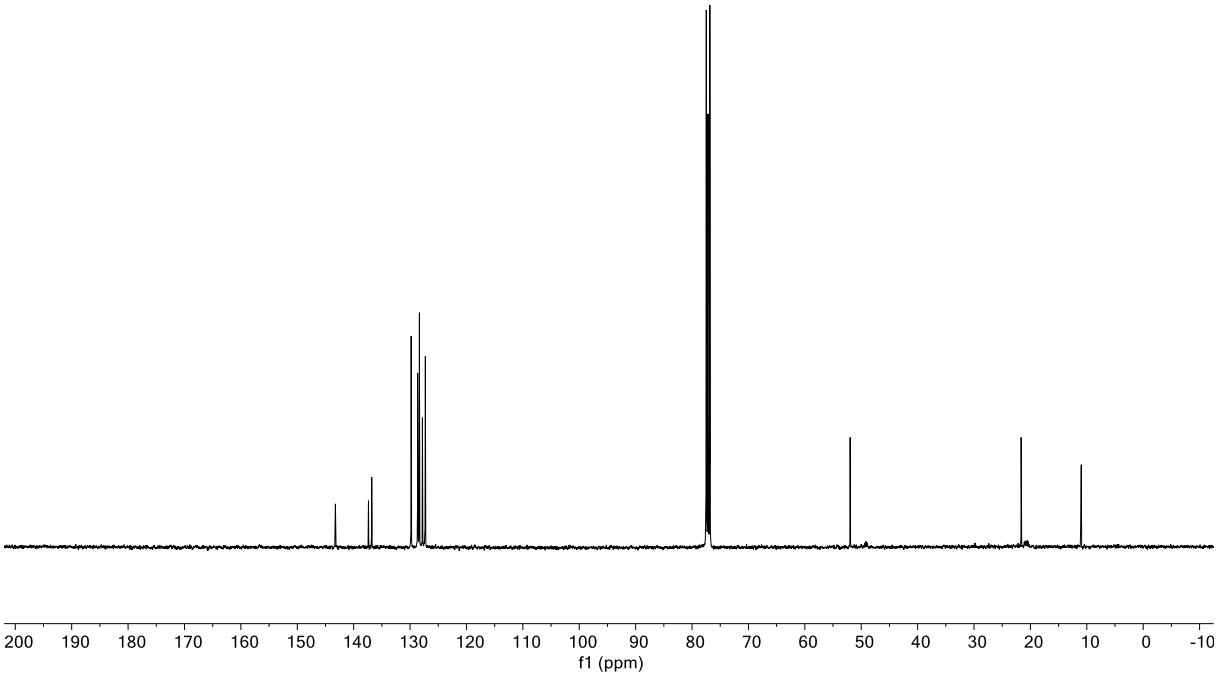
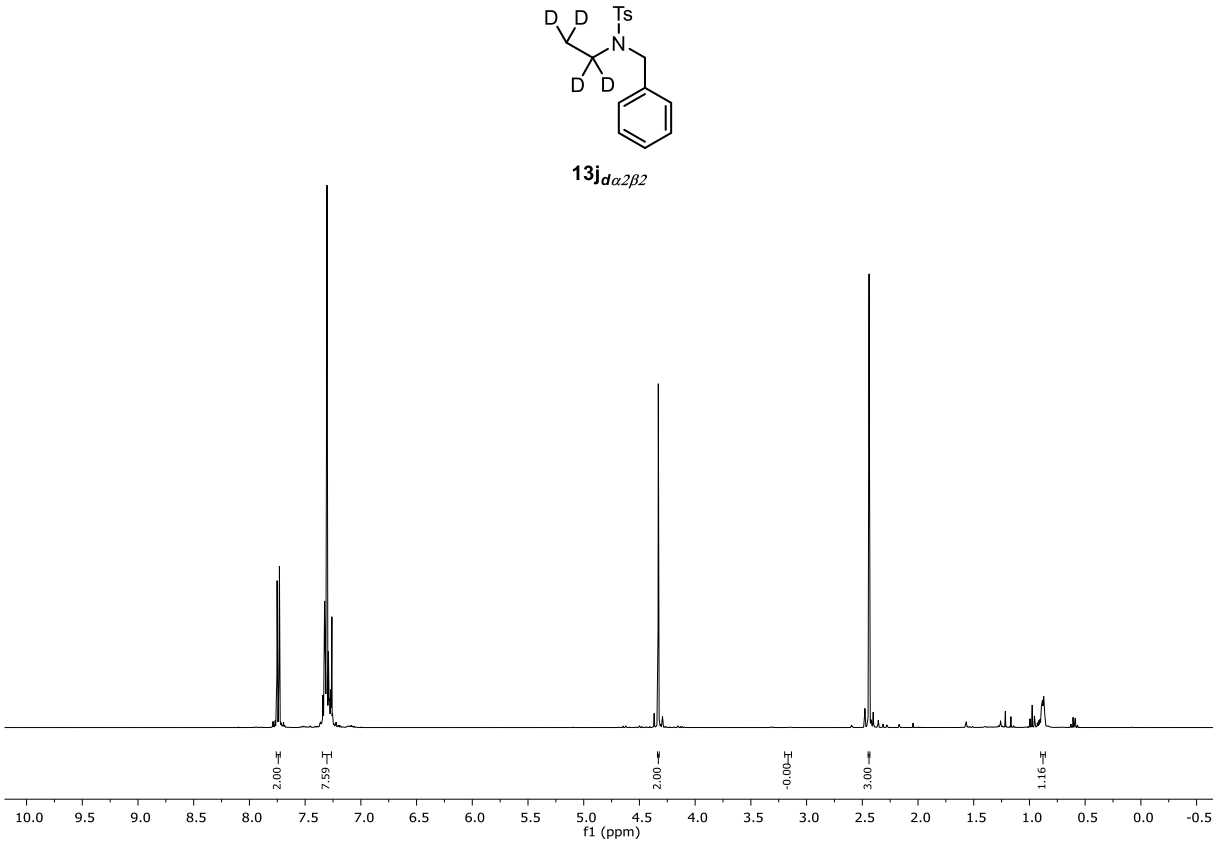


Figure S124. ^{13}C NMR spectrum of **13i**$_{d\alpha 2\beta 2}$.



13j$_{d\alpha 2\beta 2}$

Figure S125. ^{1}H NMR spectrum of **13j**$_{d\alpha 2\beta 2}$.

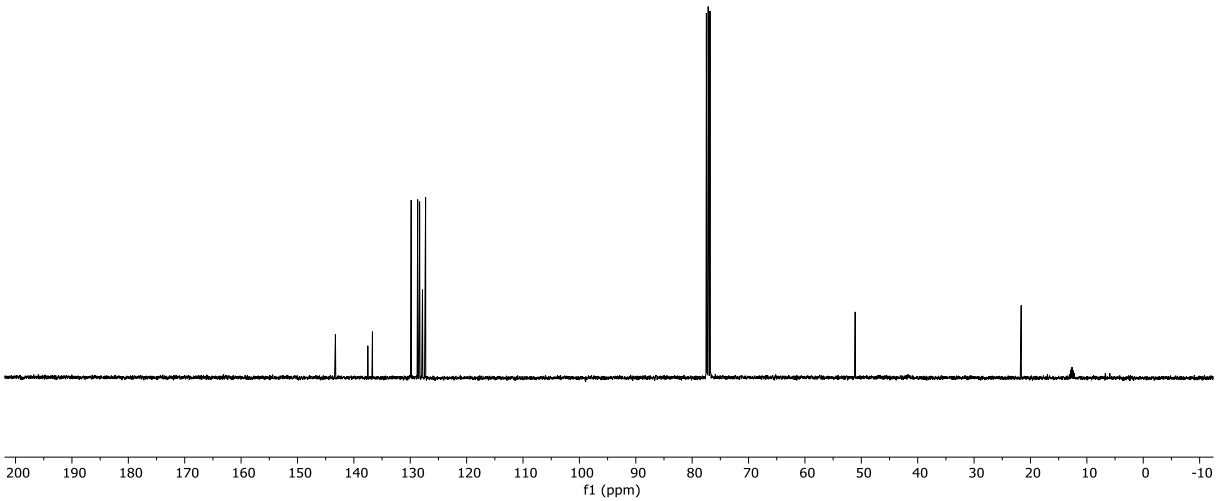
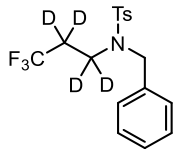


Figure S126. ^{13}C NMR spectrum of **13j**$_{d\alpha 2\beta 2}$.



13k$_{d\alpha 2\beta 2}$

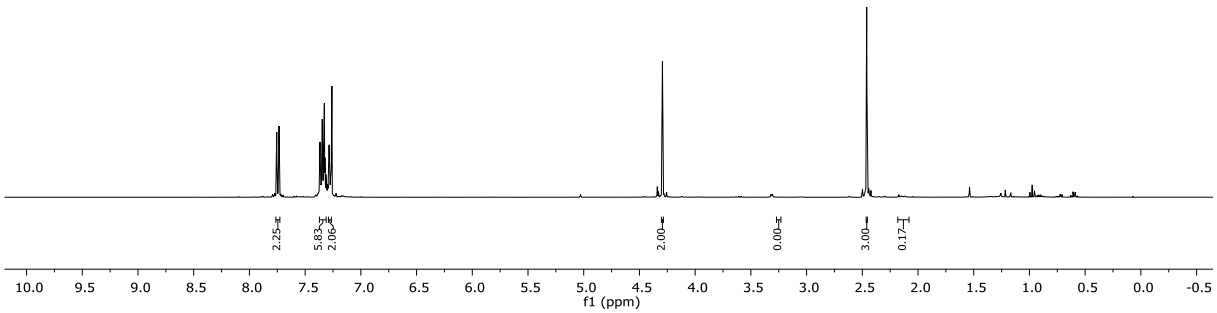


Figure S127. ^{1}H NMR spectrum of **13k**$_{d\alpha 2\beta 2}$.

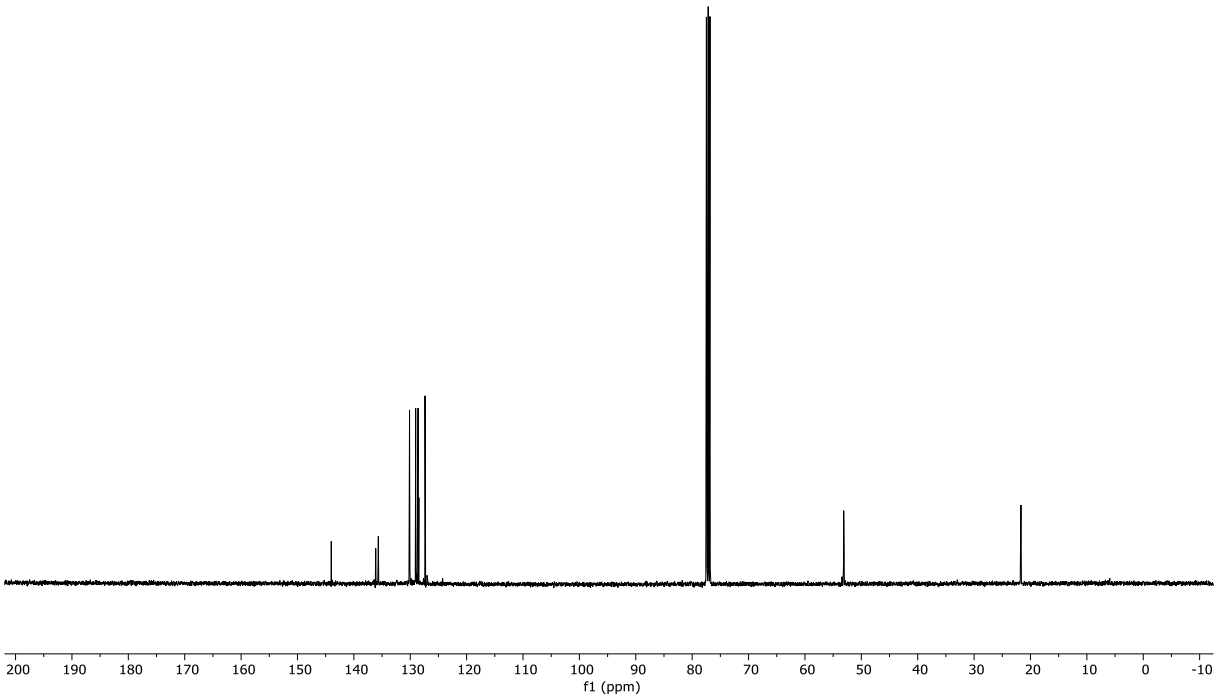


Figure S128. ^{13}C NMR spectrum of **13k**$_{d\alpha 2\beta 2}$.

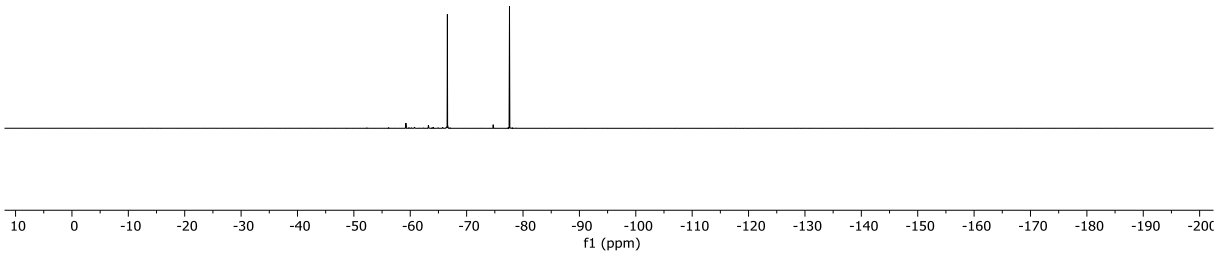
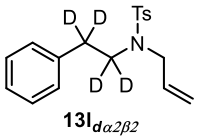


Figure S129. ^{19}F NMR spectrum of **13k**$_{d\alpha 2\beta 2}$.



13l*d*α2β2

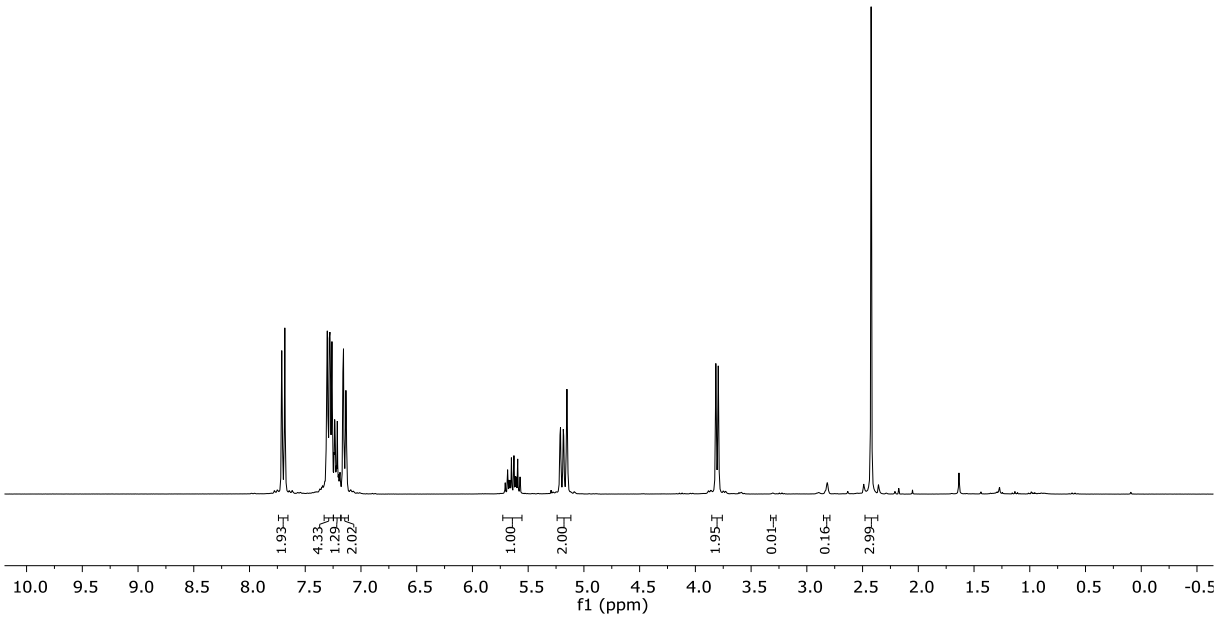


Figure S130. ^{1}H NMR spectrum of **13l*d*α2β2**.

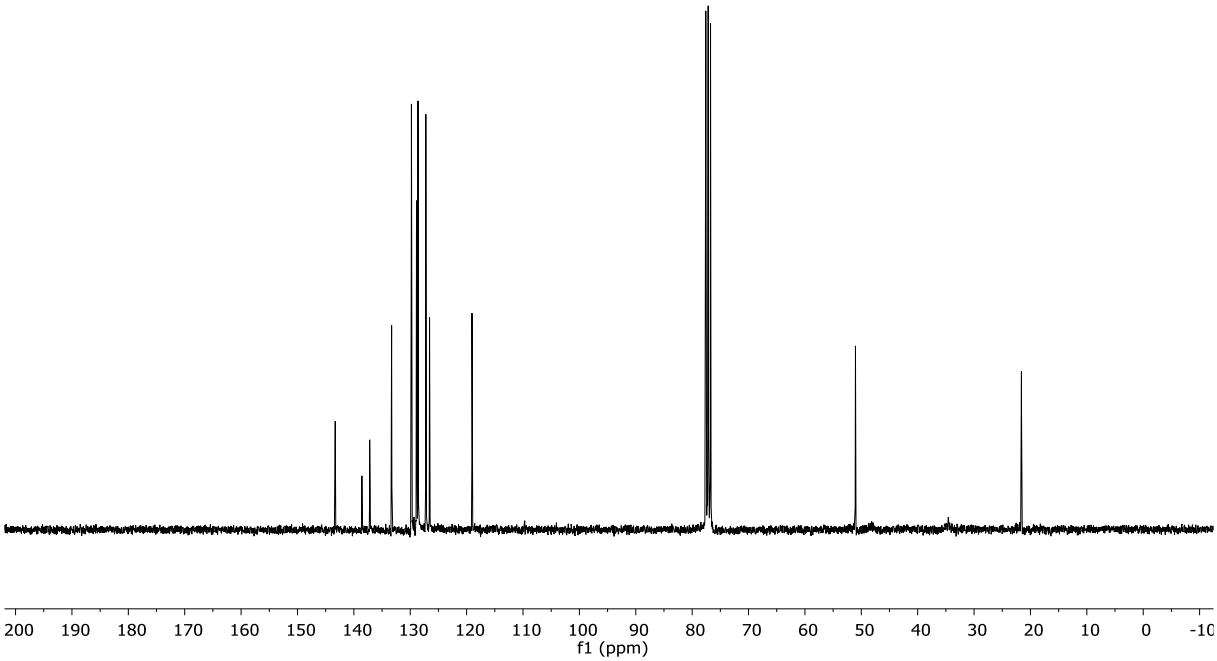
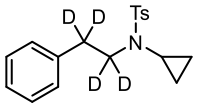


Figure S131. ^{13}C NMR spectrum of **13l*d*α2β2**.



13m$_{d\alpha 2\beta 2}$

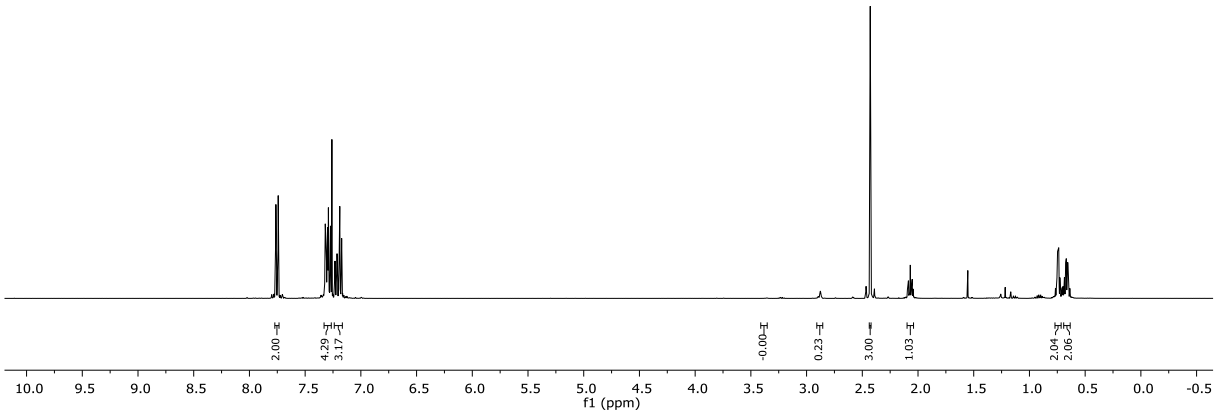


Figure S132. ^{1}H NMR spectrum of **13m**$_{d\alpha 2\beta 2}$.

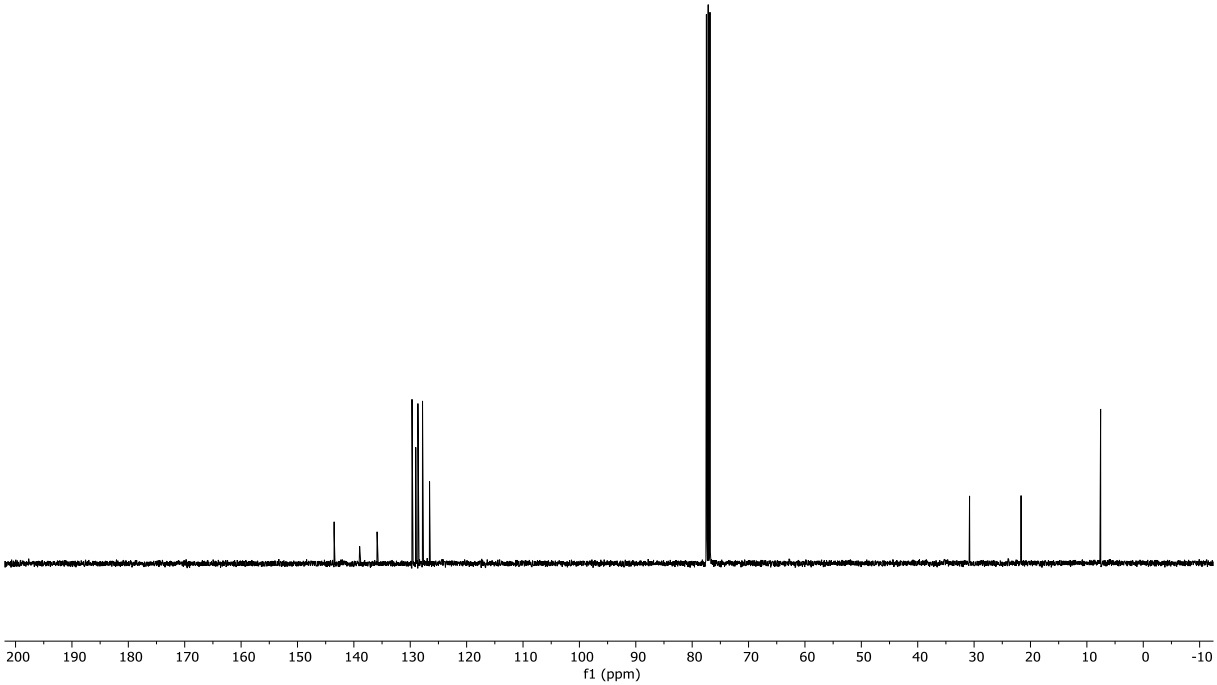
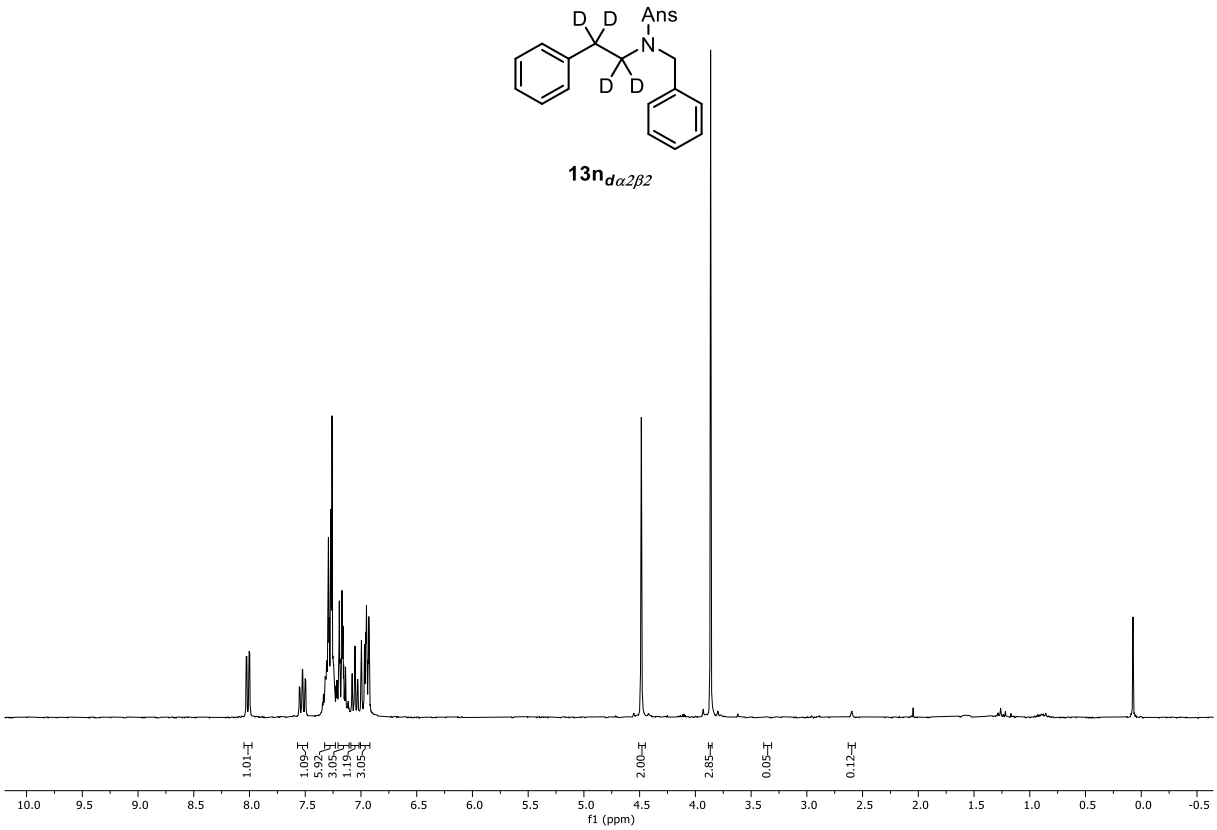


Figure S133. ^{13}C NMR spectrum of **13m**$_{d\alpha 2\beta 2}$.



13n$_{d\alpha 2\beta 2}$

Figure S134. ^{1}H NMR spectrum of **13n**$_{d\alpha 2\beta 2}$.

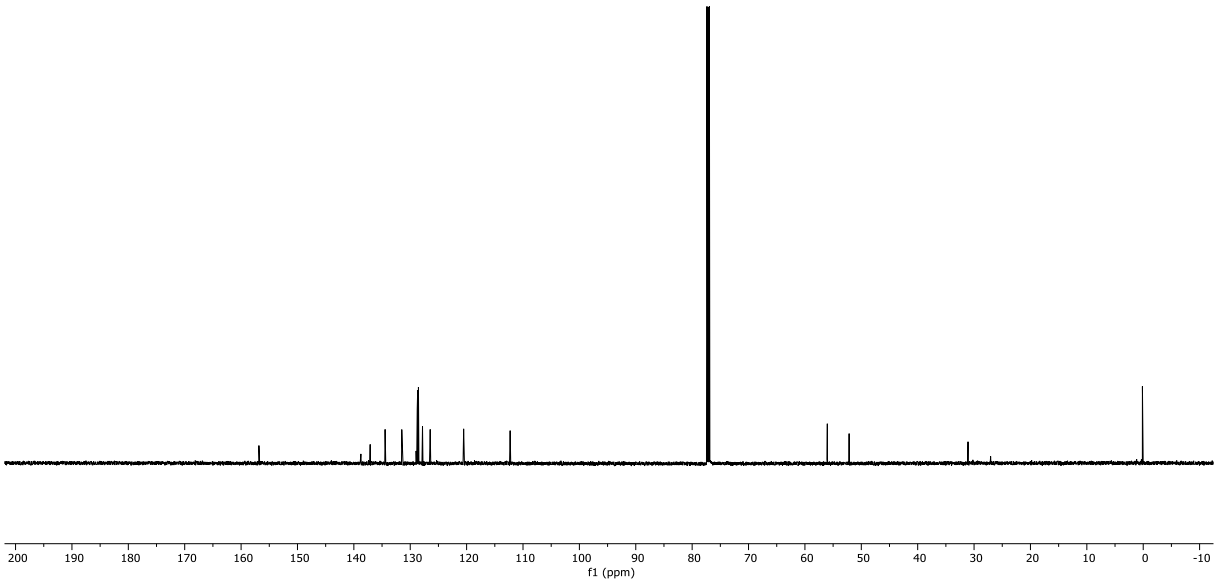
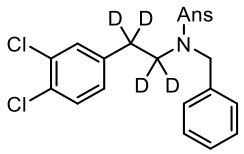


Figure S135. ^{13}C NMR spectrum of **13n**$_{d\alpha 2\beta 2}$.



13o$_{d\alpha 2\beta 2}$

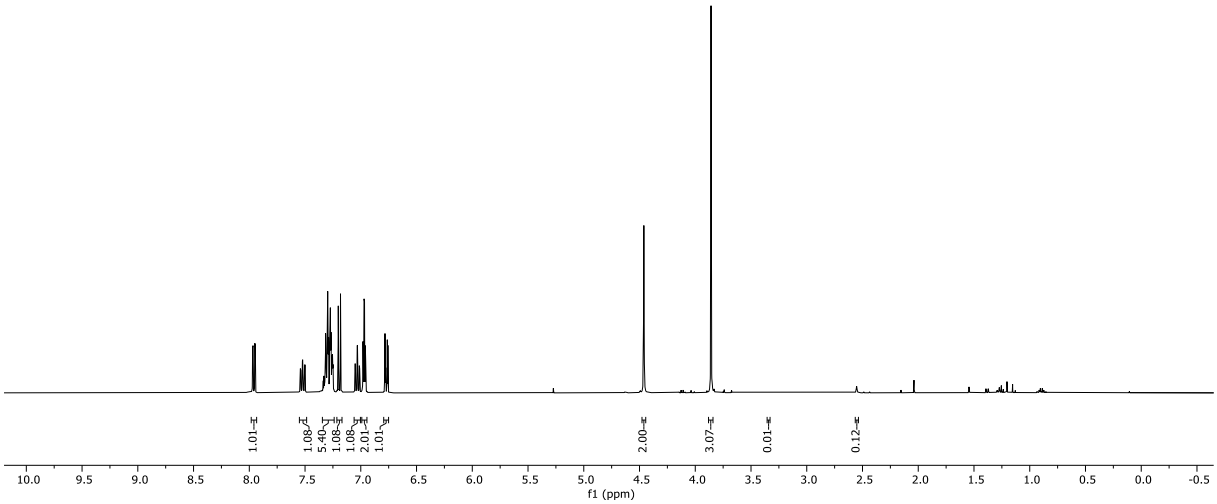


Figure S136. ^{1}H NMR spectrum of **13o**$_{d\alpha 2\beta 2}$.

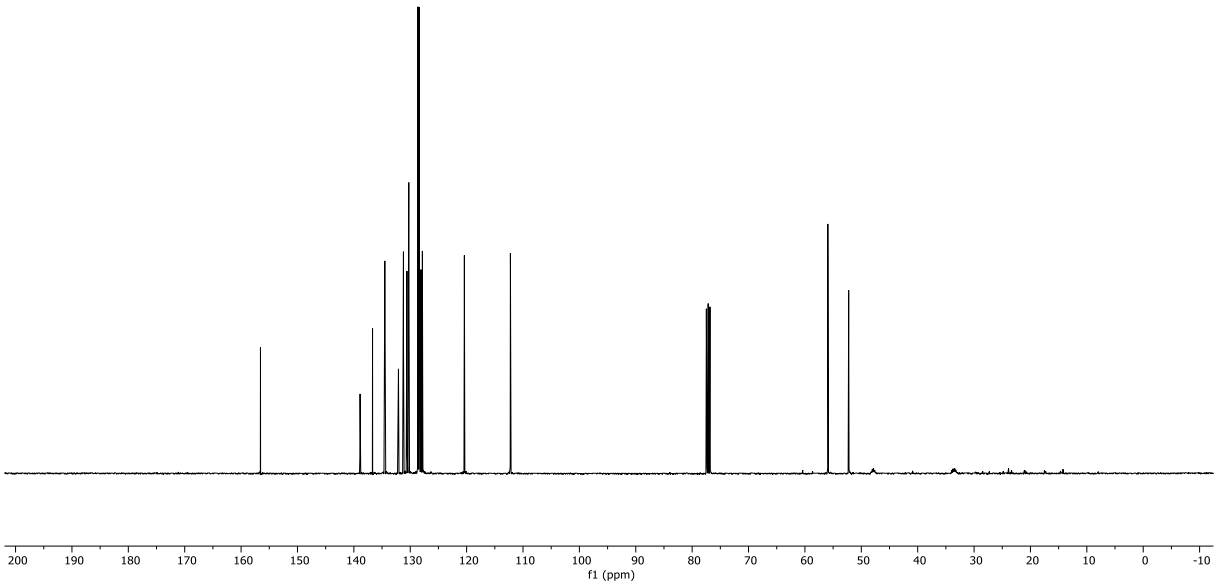
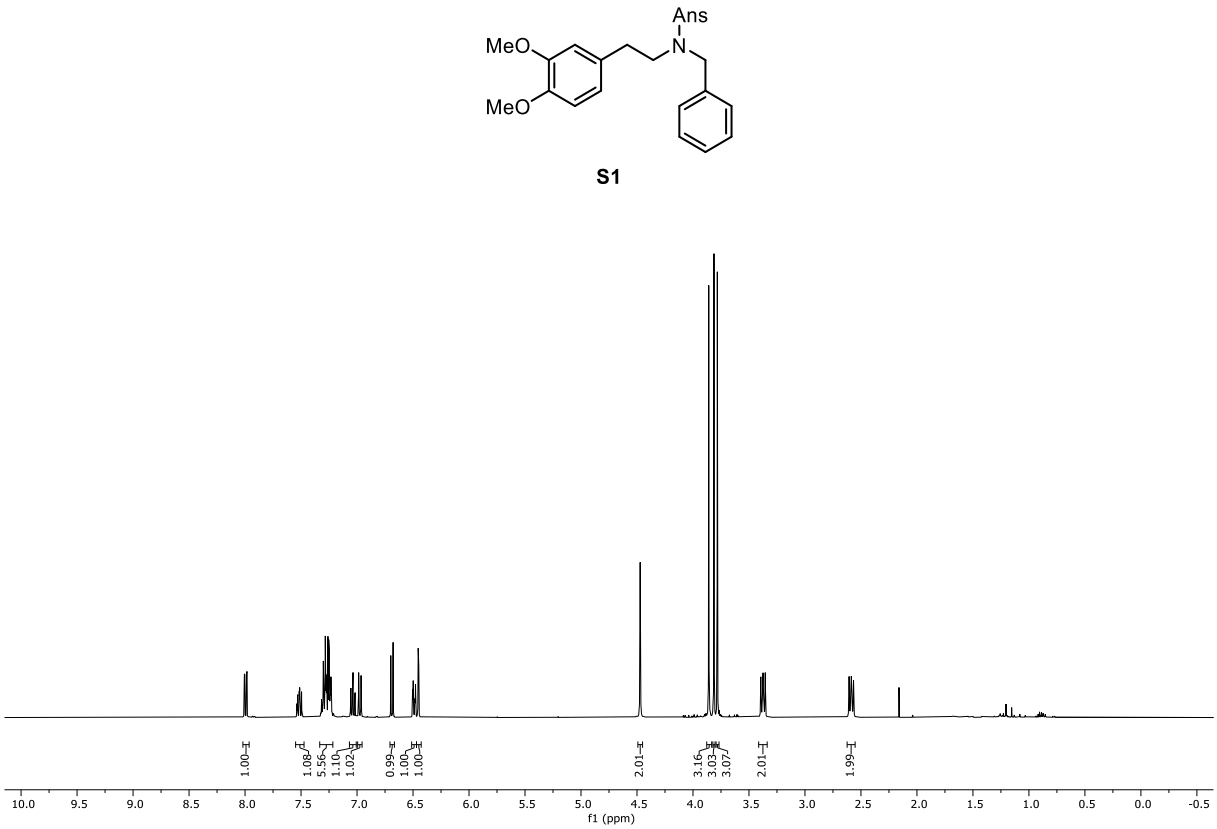


Figure S137. ^{13}C NMR spectrum of **13o**$_{d\alpha 2\beta 2}$.



S1

Figure S138. ^{1}H NMR spectrum of **S1**.

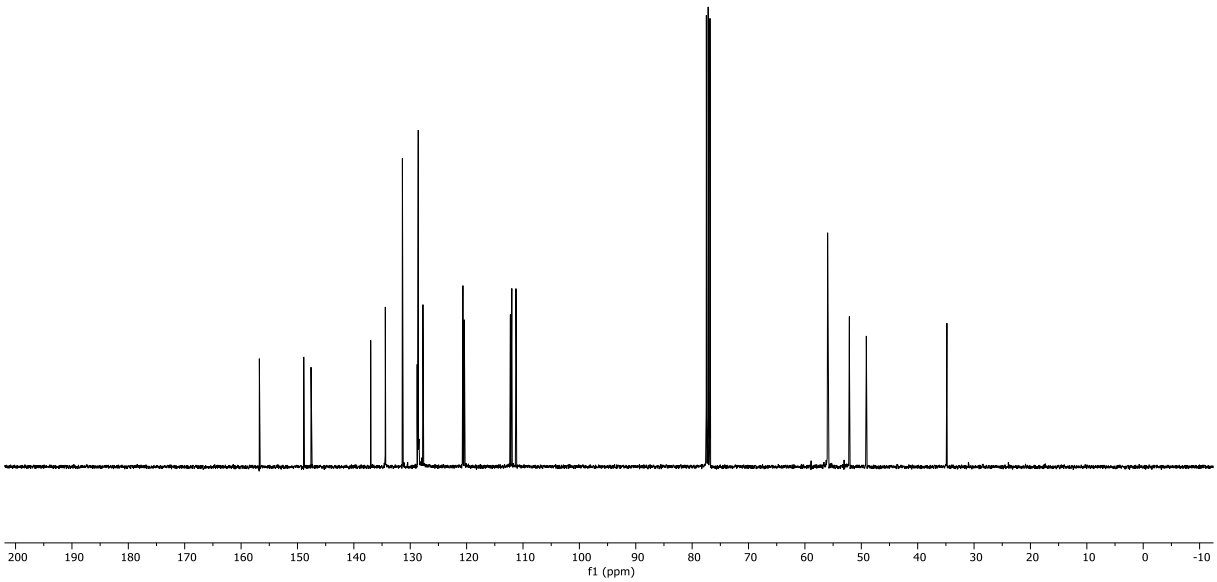
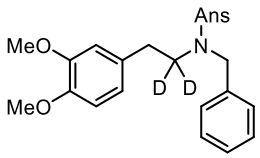


Figure S139. ^{13}C NMR spectrum of **S1**.



S1$_{d\alpha 2}$

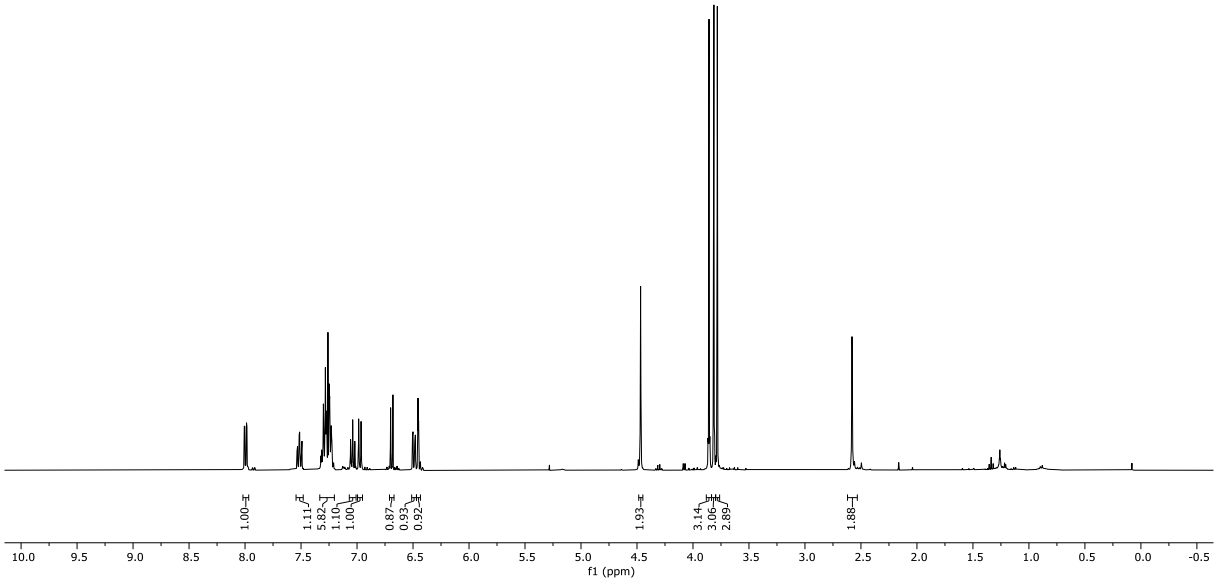


Figure S140. ^{1}H NMR spectrum of **S1**$_{d\alpha 2}$.

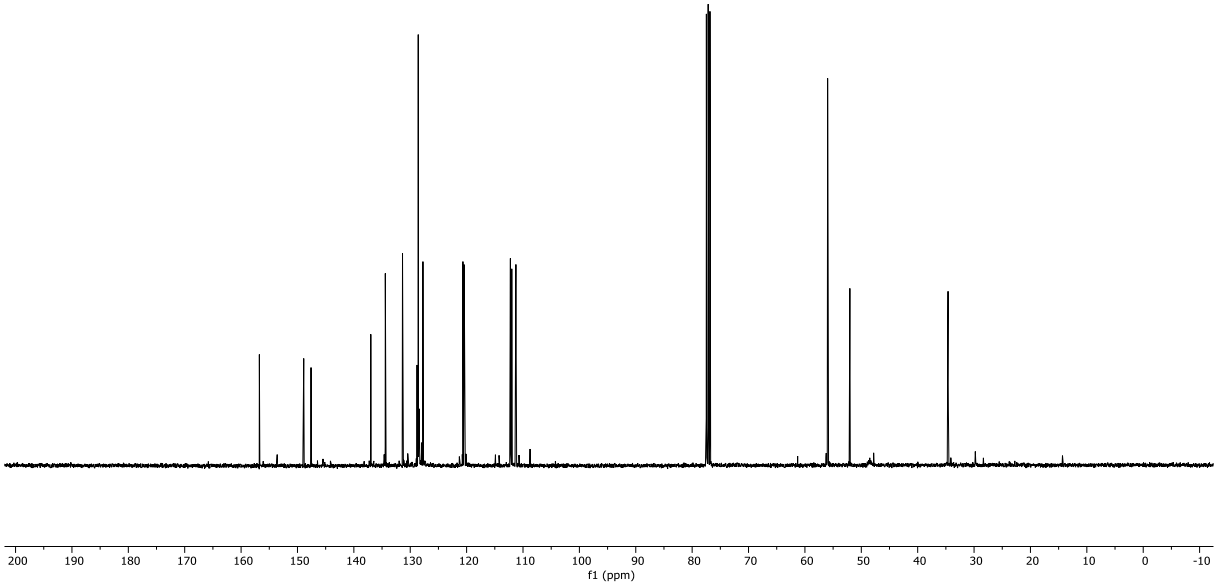
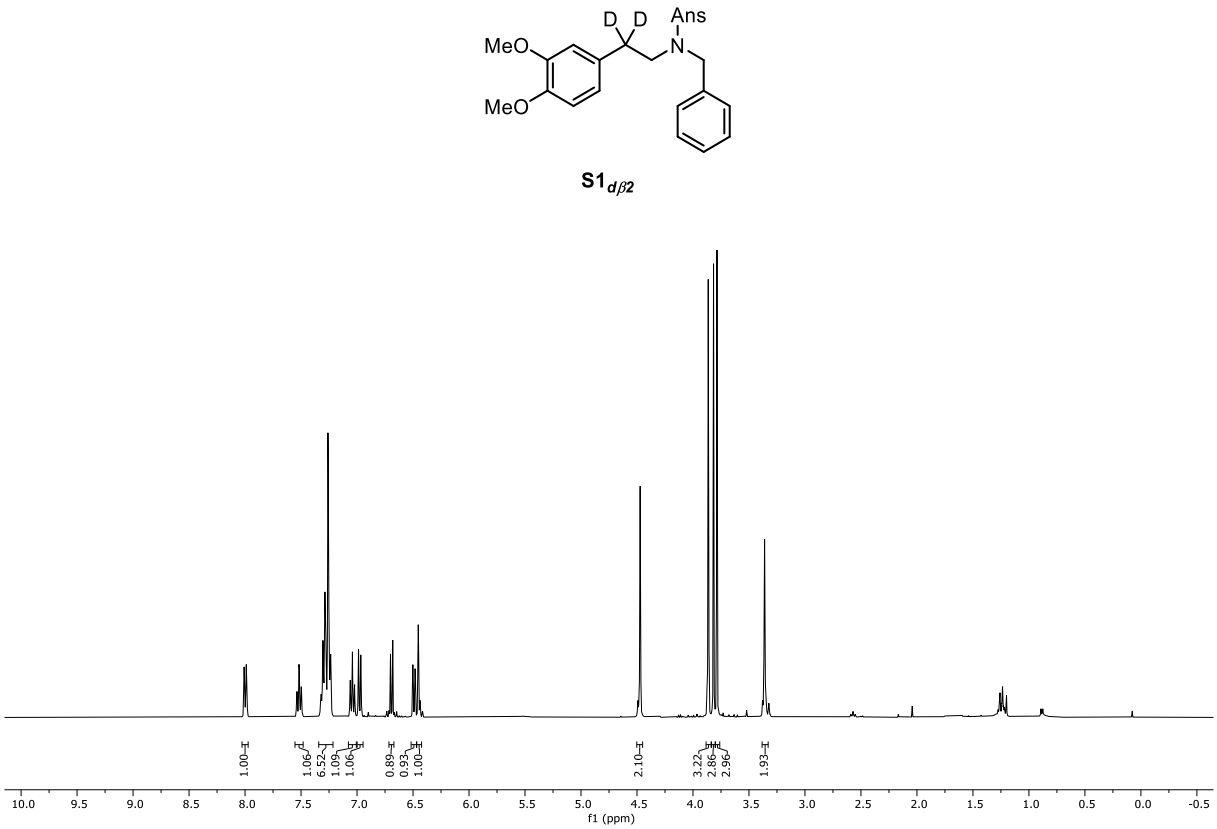


Figure S141. ^{13}C NMR spectrum of **S1**$_{d\alpha 2}$.



S1$_{d\beta 2}$

Figure S142. ^{1}H NMR spectrum of **S1**$_{d\beta 2}$.

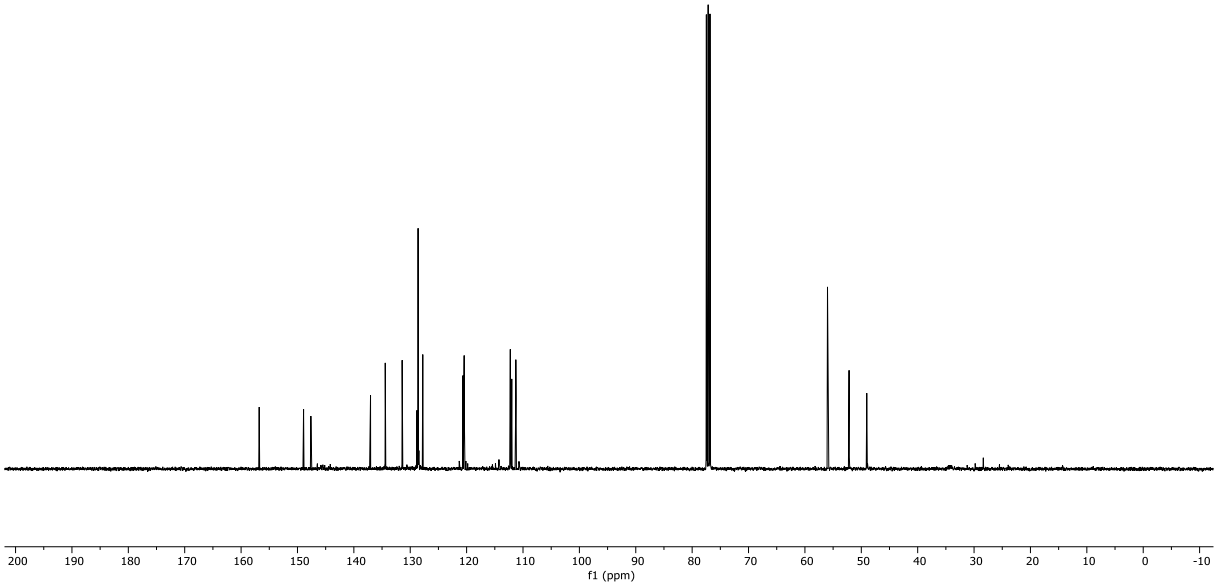
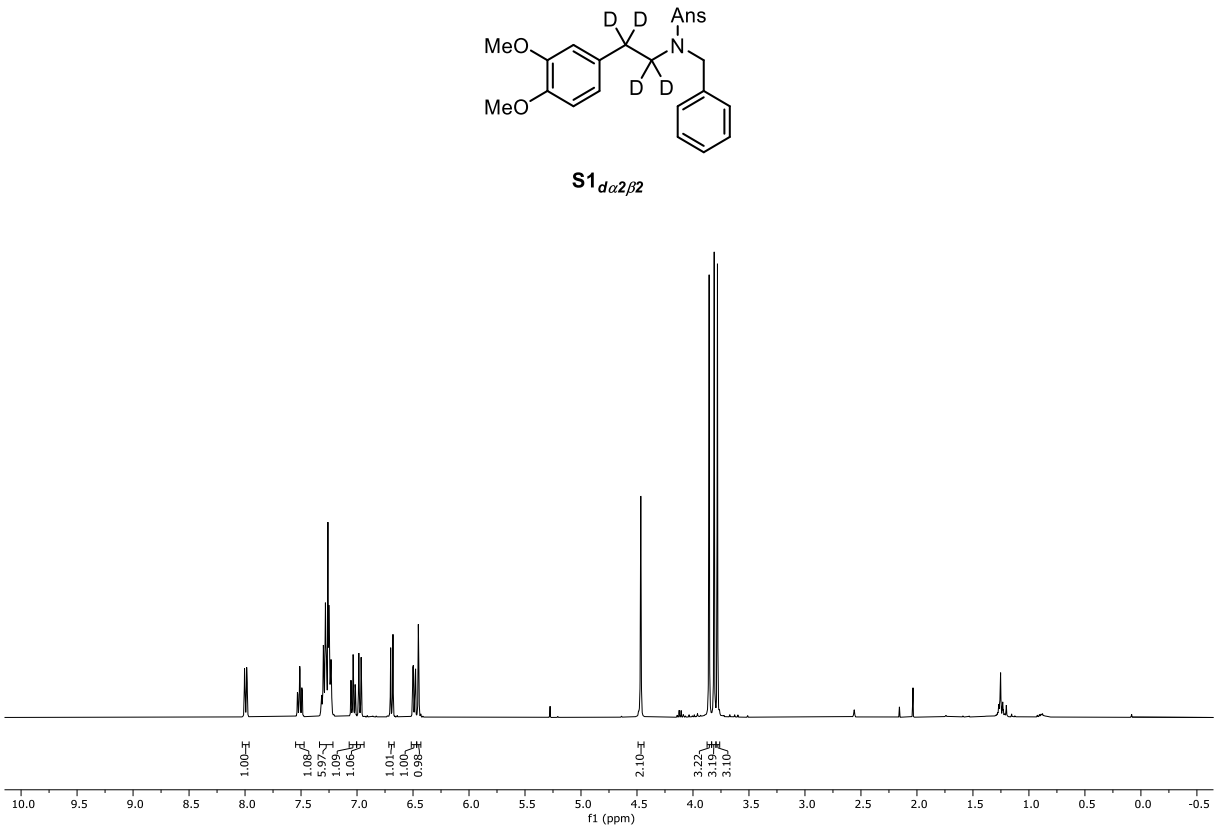


Figure S143. ^{13}C NMR spectrum of **S1**$_{d\beta 2}$.



S1$_{d\alpha2\beta2}$

Figure S144. ^{1}H NMR spectrum of **S1**$_{d\alpha2\beta2}$.

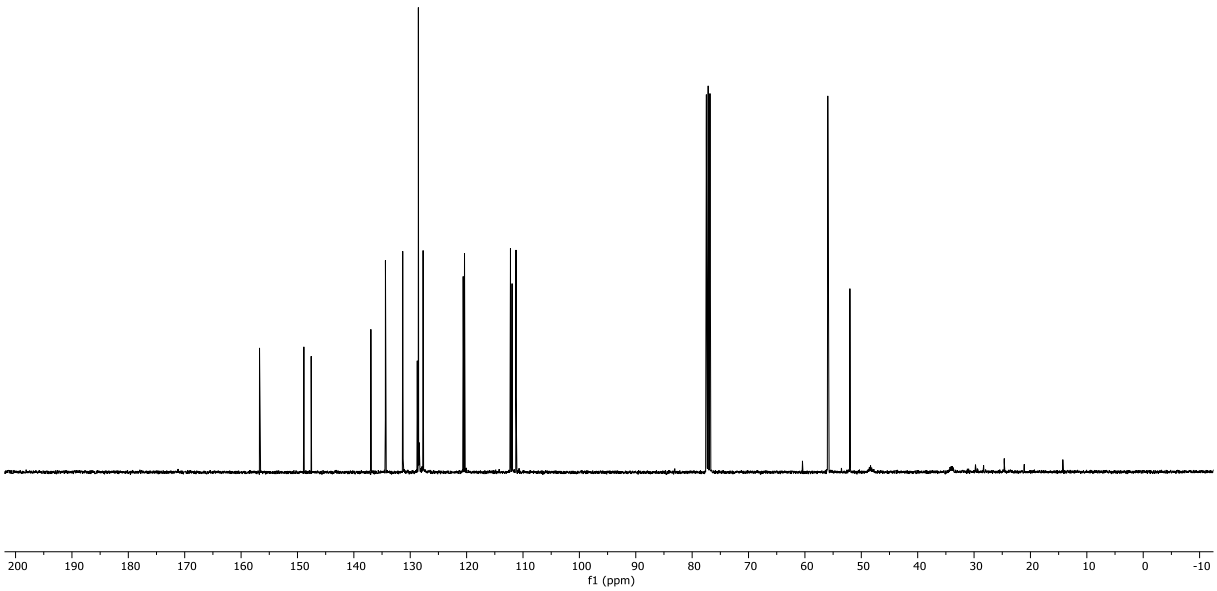
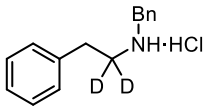


Figure S145. ^{13}C NMR spectrum of **S1**$_{d\alpha2\beta2}$.



S2$_{d\alpha 2}$

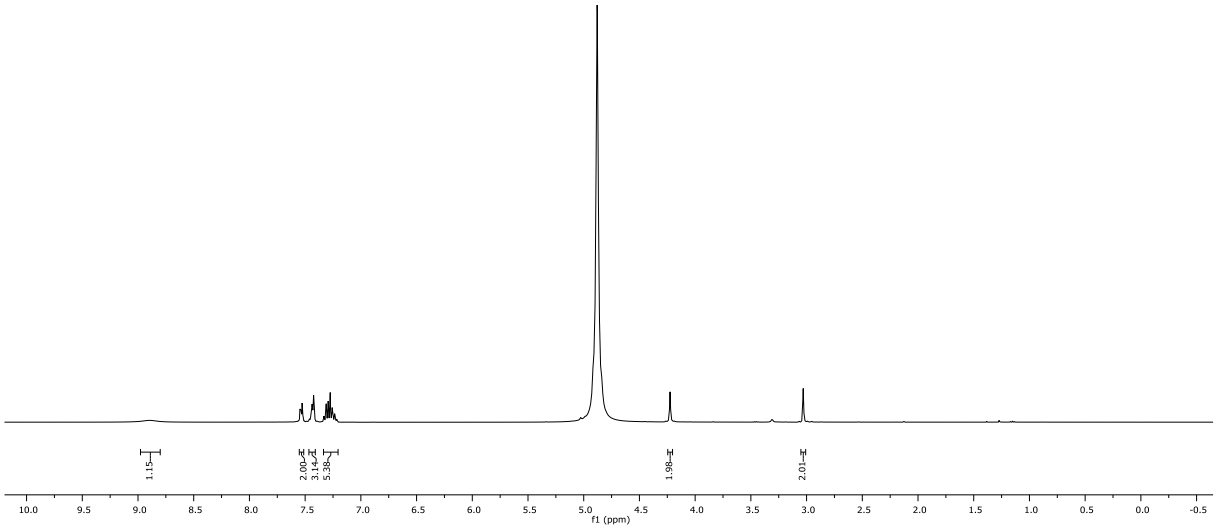


Figure S146. ^{1}H NMR spectrum of **S2$_{d\alpha 2}$**.

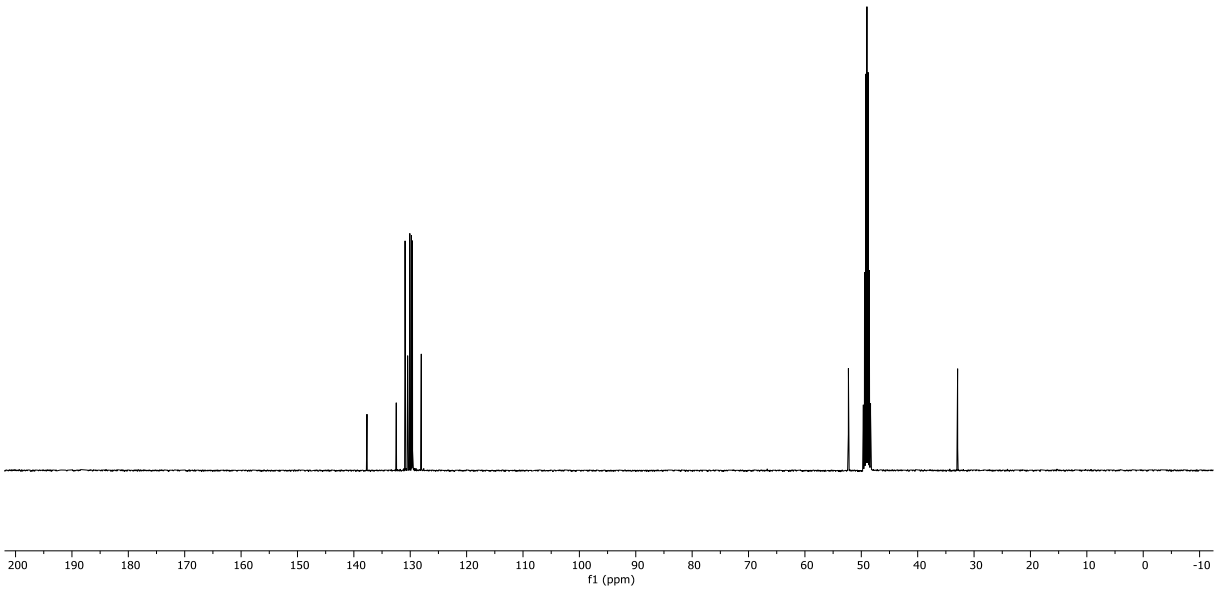


Figure S147. ^{13}C NMR spectrum of **S2$_{d\alpha 2}$**.

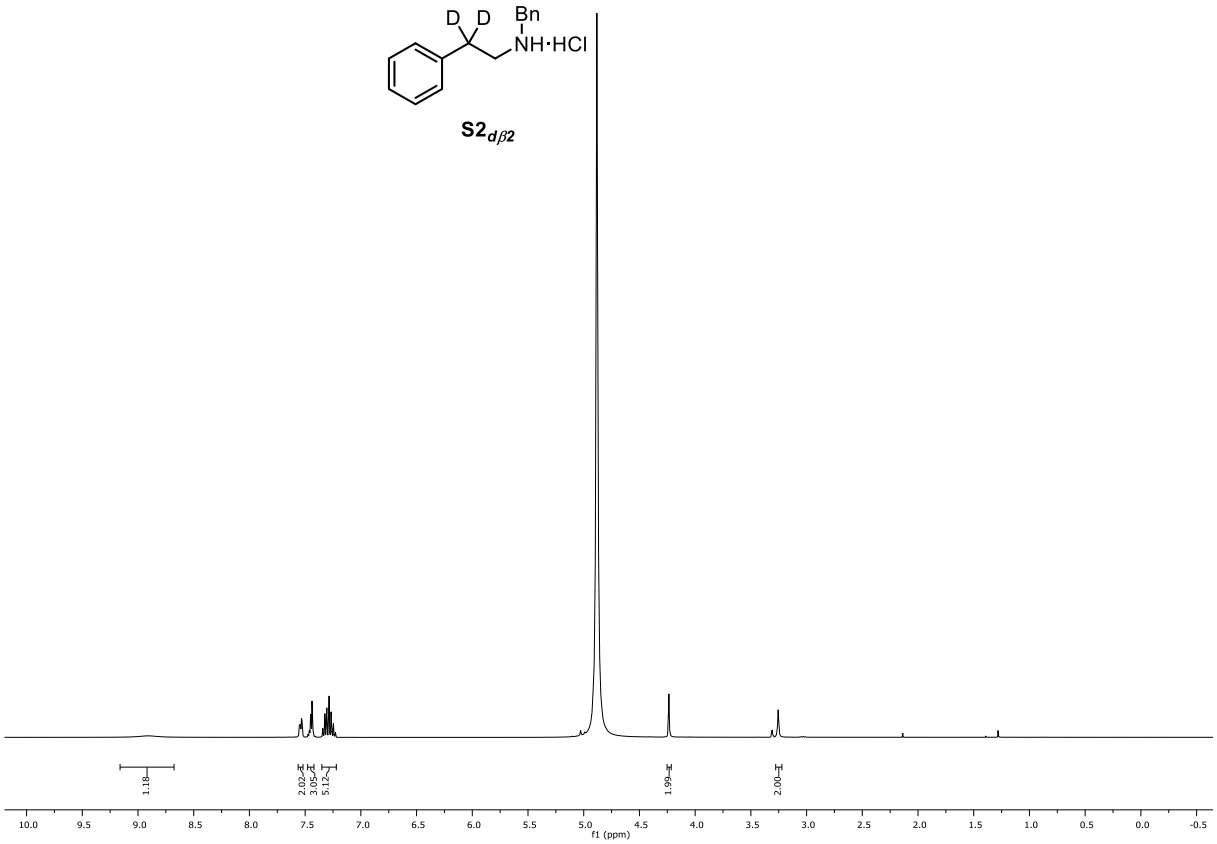


Figure S148. ^{1}H NMR spectrum of **S2*dβ2***.

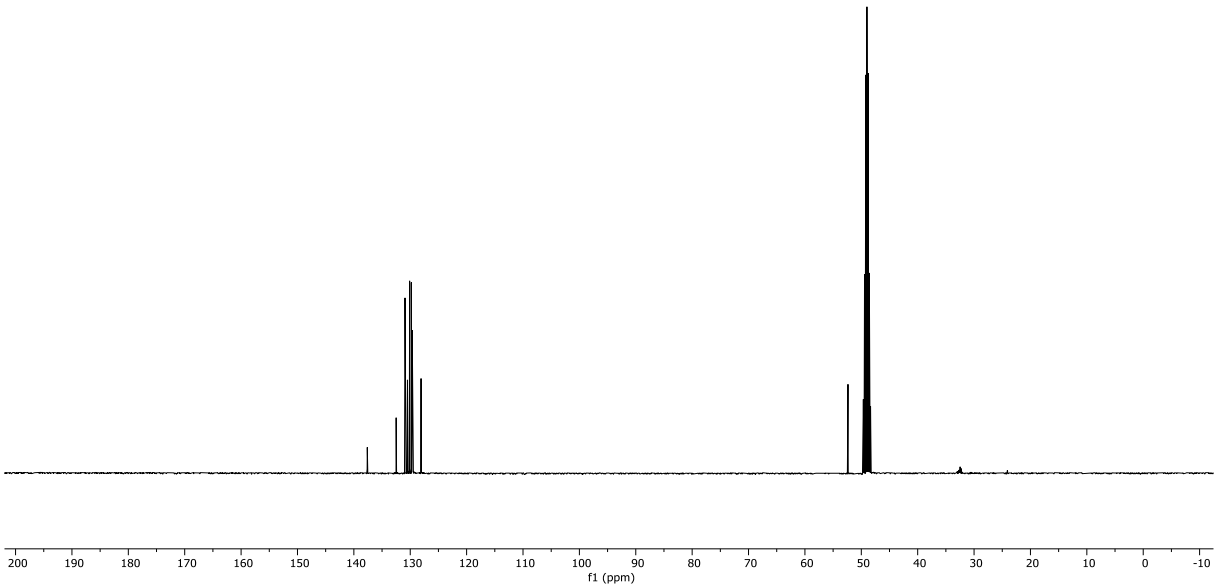
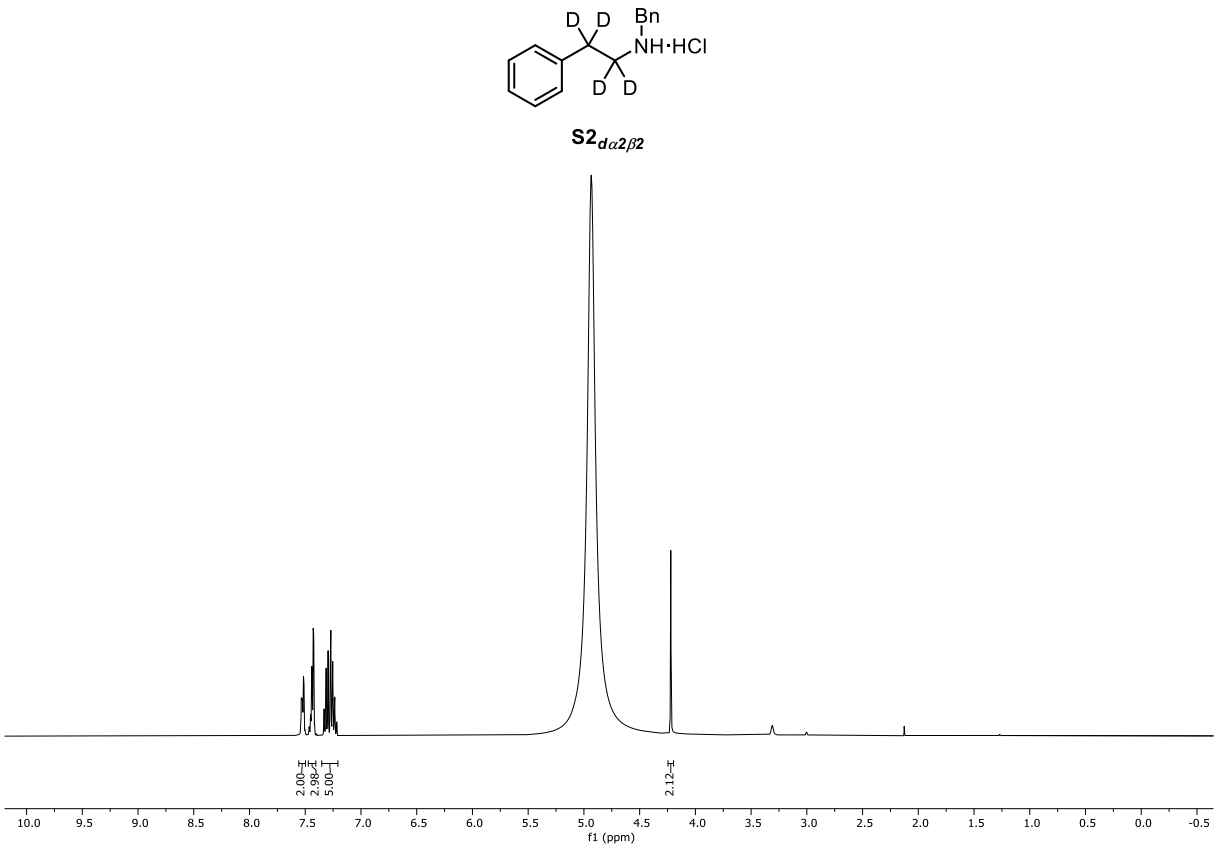


Figure S149. ^{13}C NMR spectrum of **S2*dβ2***.



S2$_{d\alpha 2\beta 2}$

Figure S150. ^{1}H NMR spectrum of **S2**$_{d\alpha 2\beta 2}$.

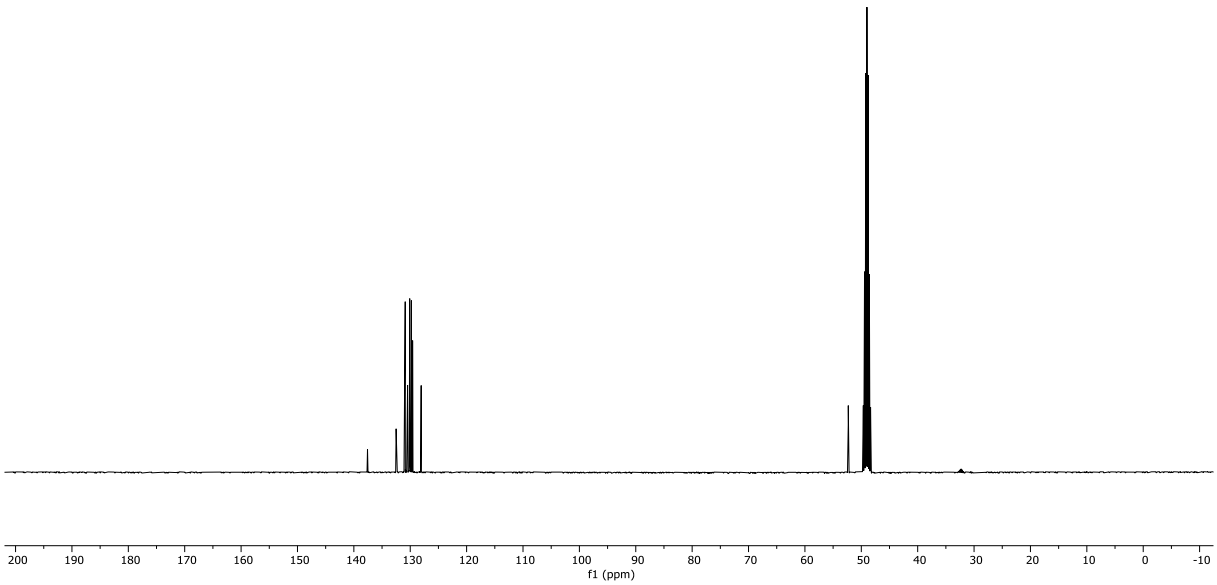


Figure S151. ^{13}C NMR spectrum of **S2**$_{d\alpha 2\beta 2}$.

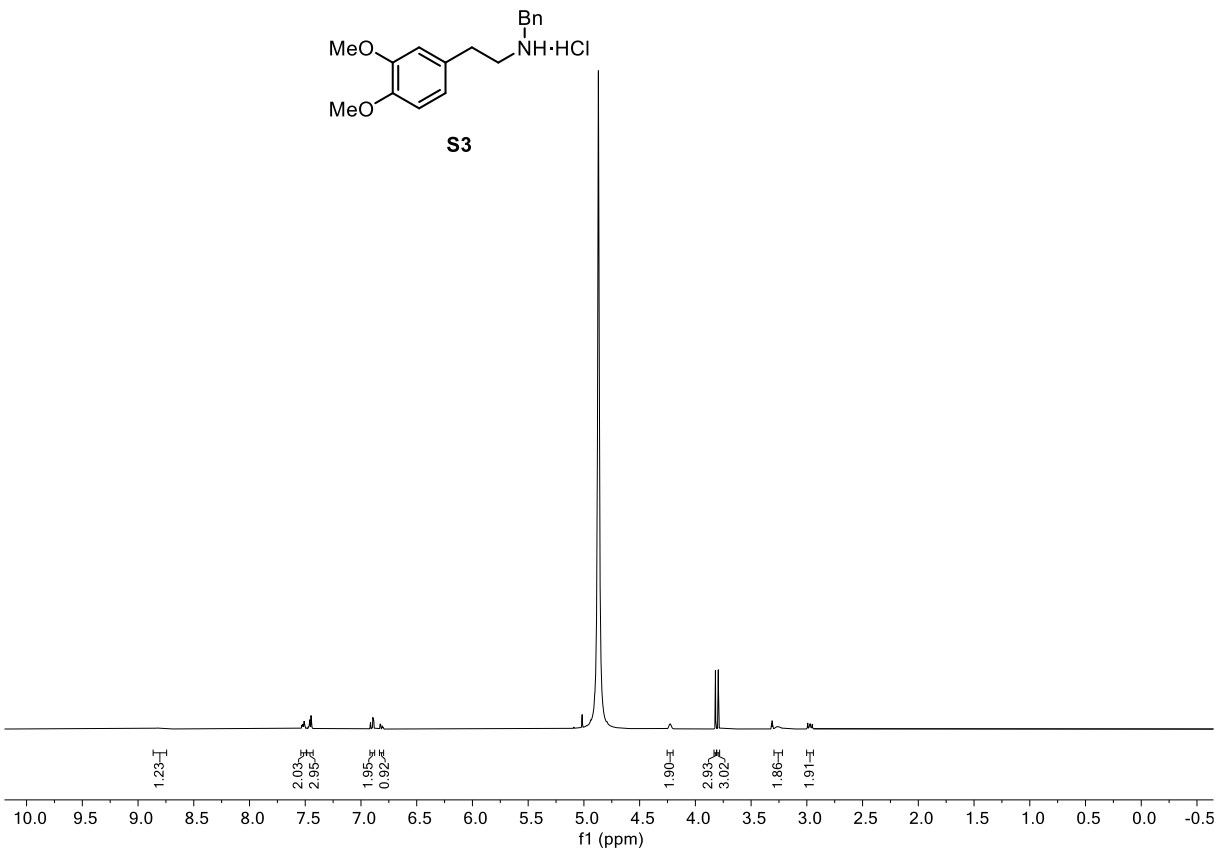


Figure S152. ^{1}H NMR spectrum of **S3**.

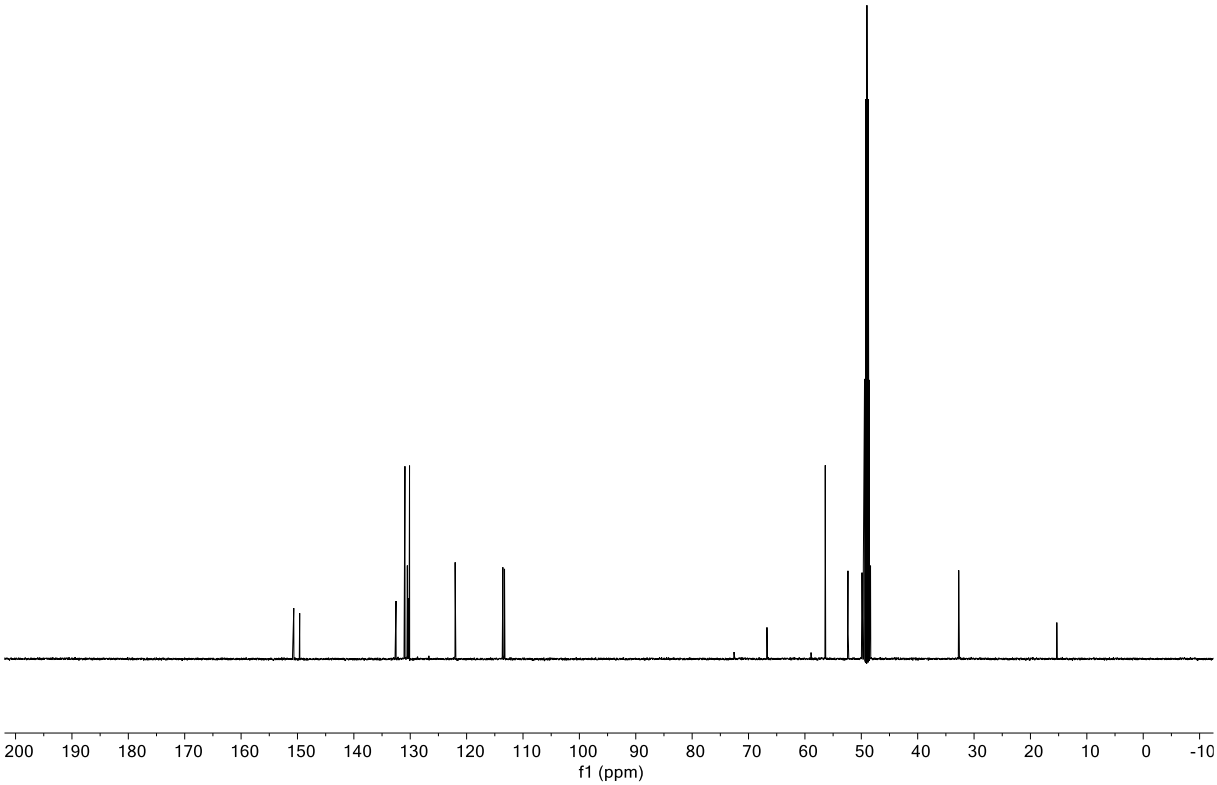
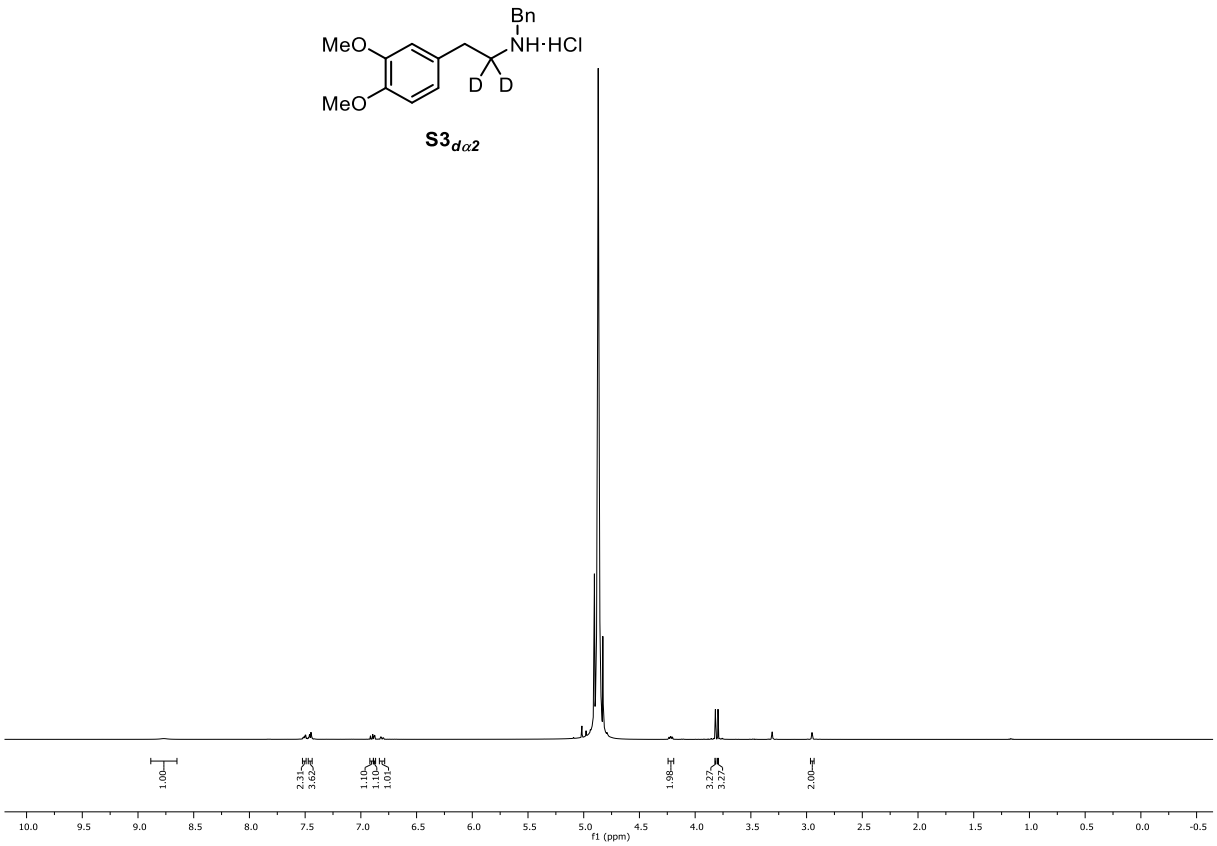


Figure S153. ^{13}C NMR spectrum of **S3**.



S3$_{d\alpha 2}$

Figure S154. ^{1}H NMR spectrum of **S3$_{d\alpha 2}$**.

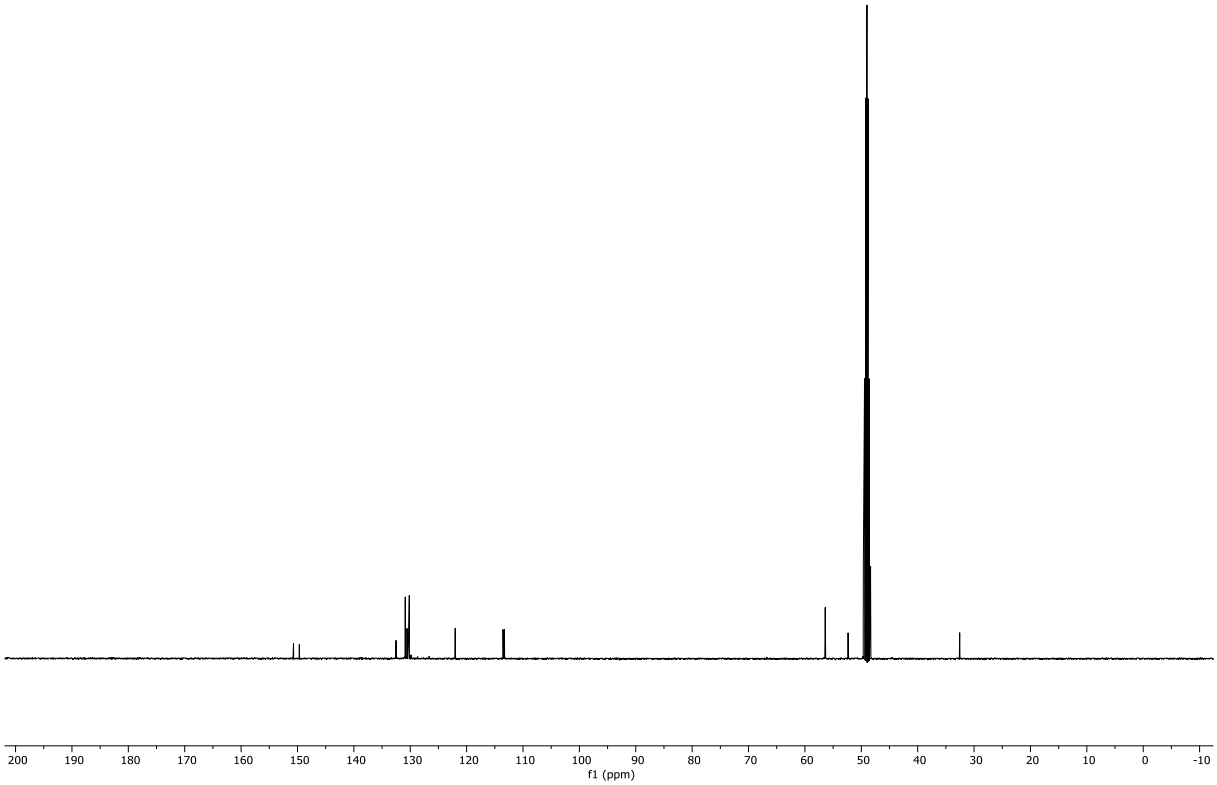


Figure S155. ^{13}C NMR spectrum of **S3$_{d\alpha 2}$**.

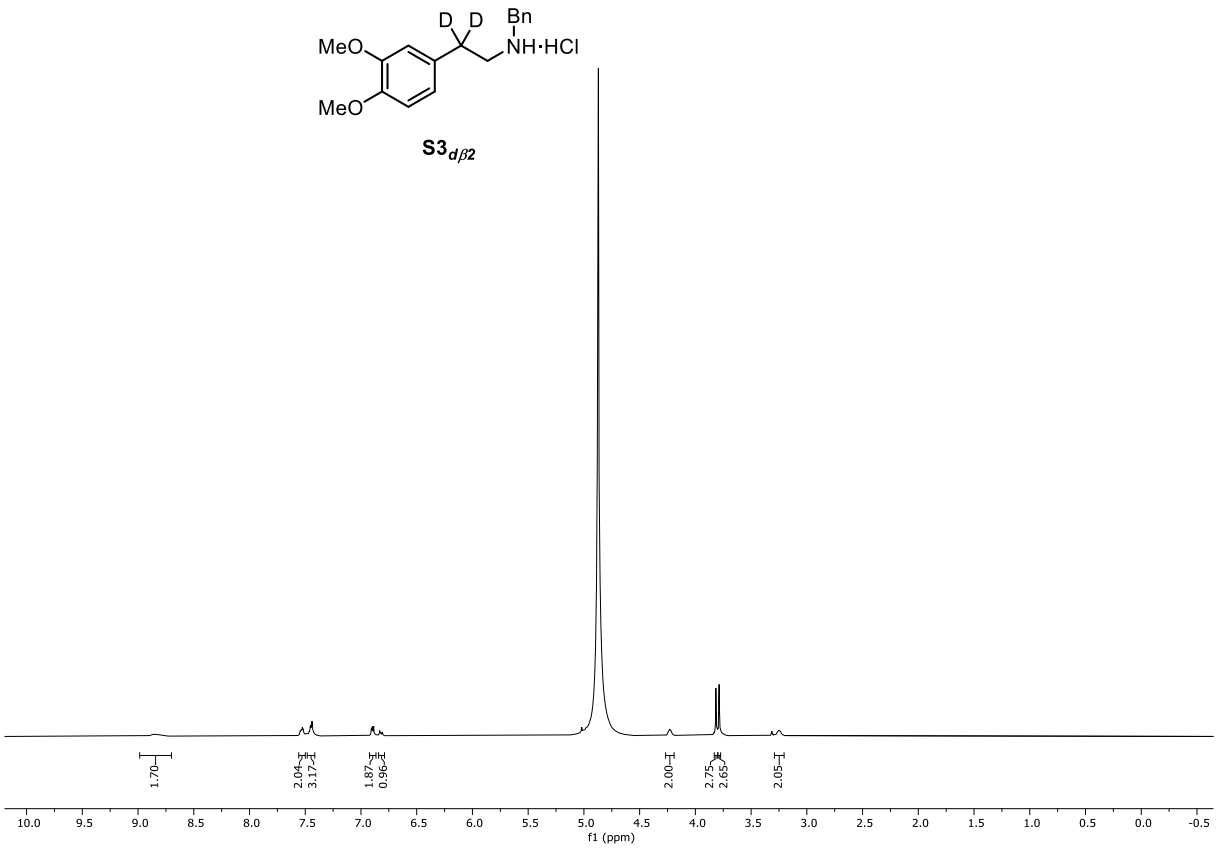


Figure S156. ^{1}H NMR spectrum of **S3*dβ2***.

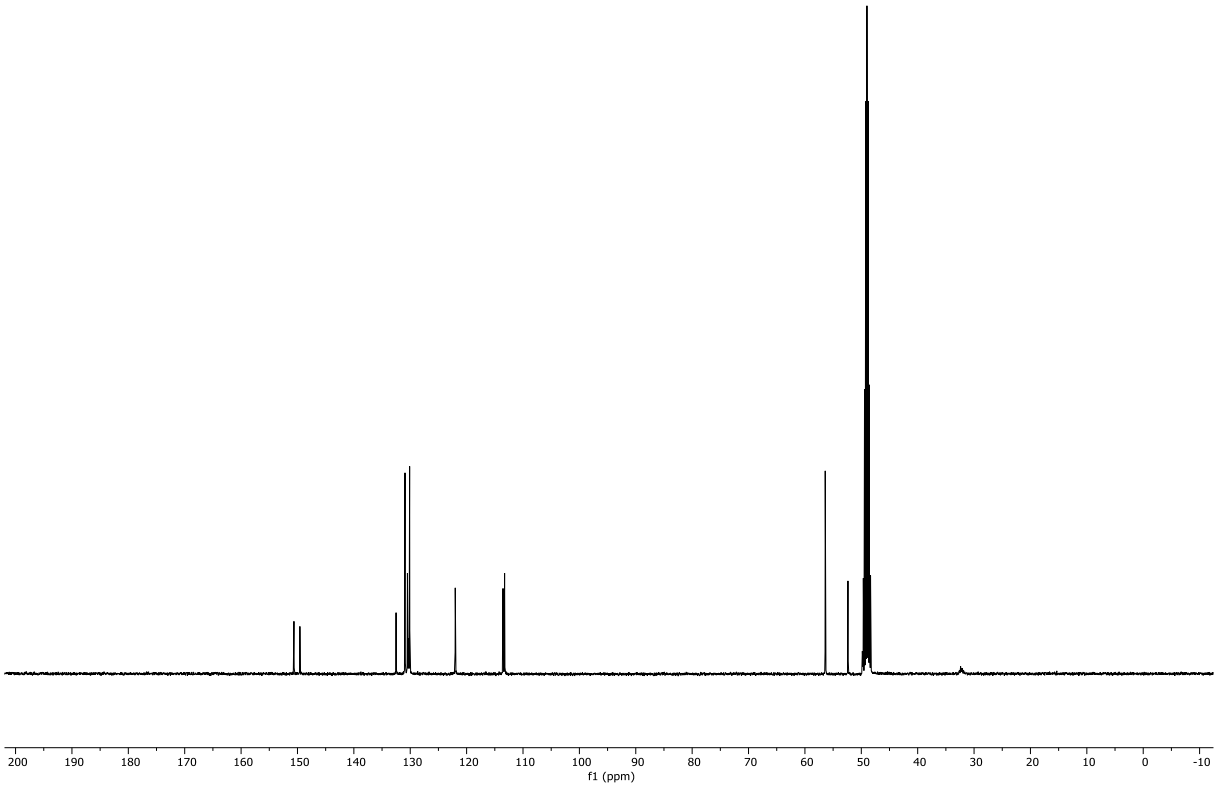
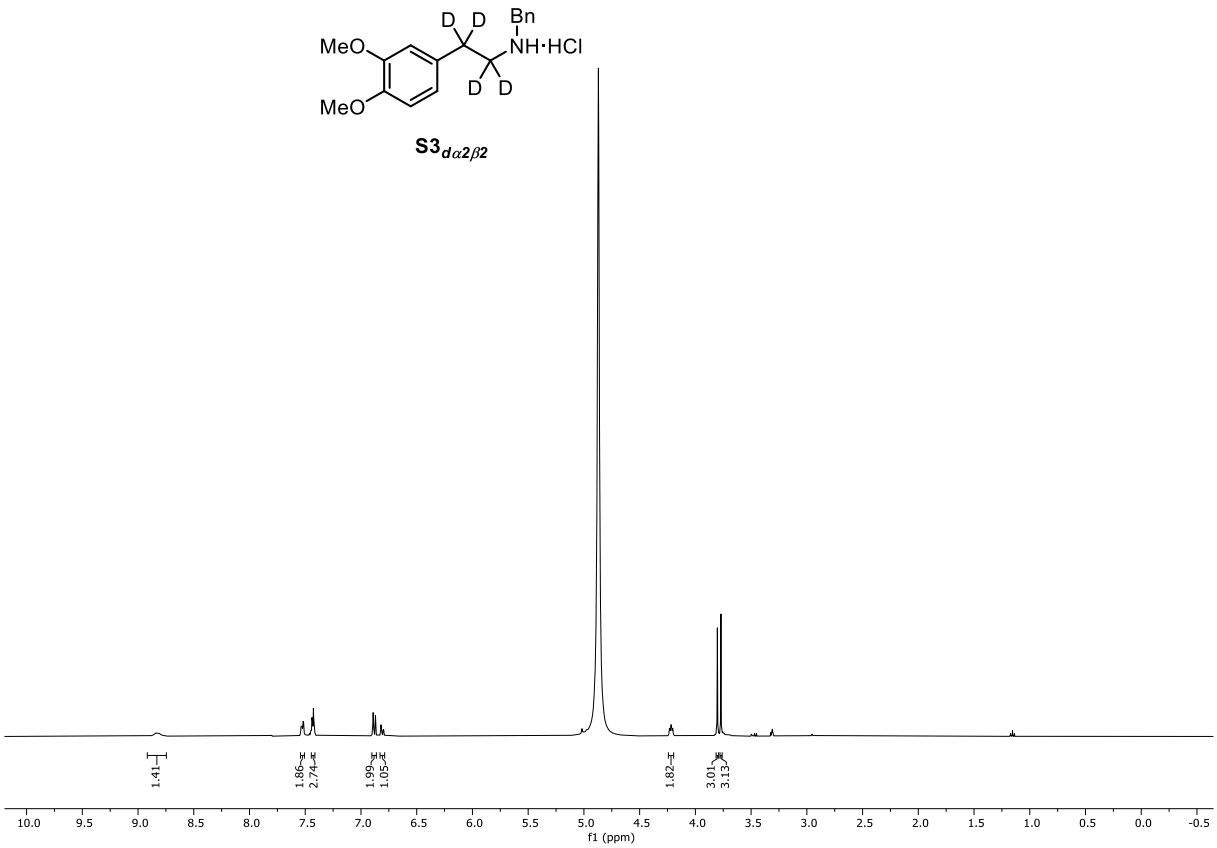


Figure S157. ^{13}C NMR spectrum of **S3*dβ2***.



S3$_{d\alpha 2\beta 2}$

Figure S158. ^{1}H NMR spectrum of **S3**$_{d\alpha 2\beta 2}$.

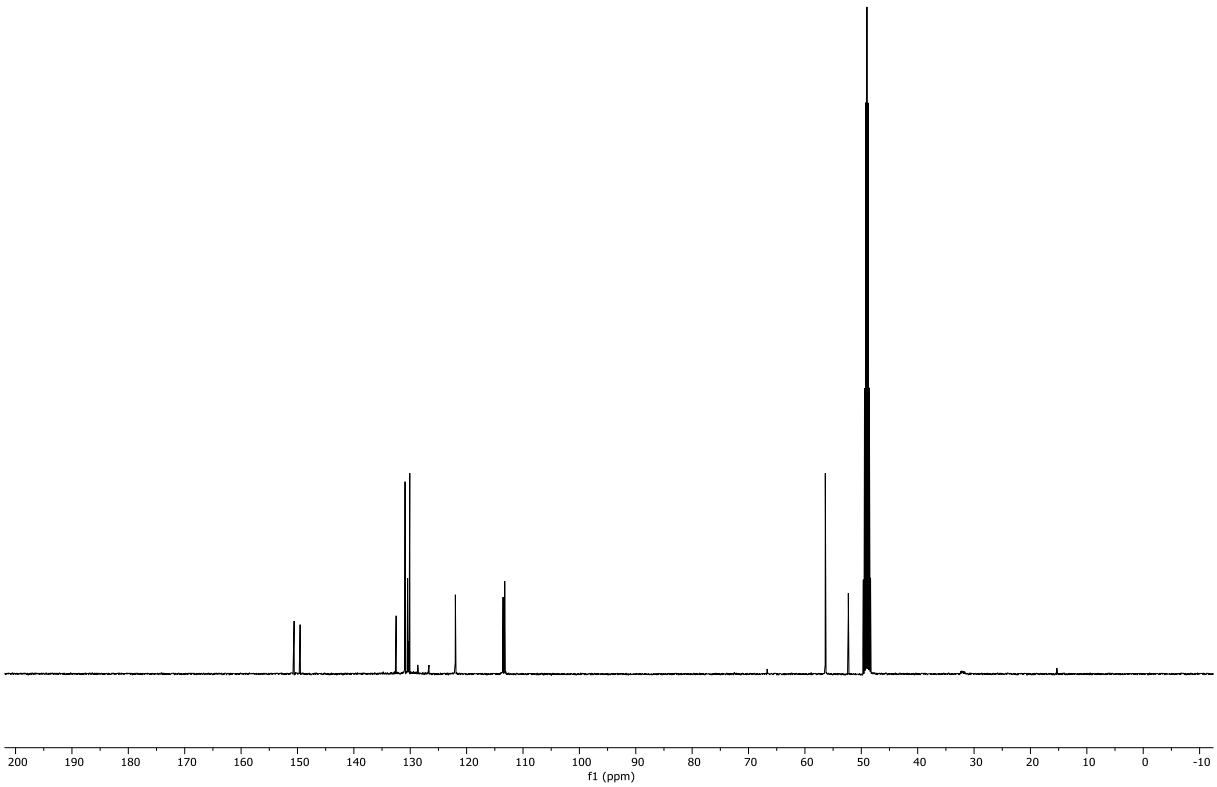


Figure S159. ^{13}C NMR spectrum of **S3**$_{d\alpha 2\beta 2}$.

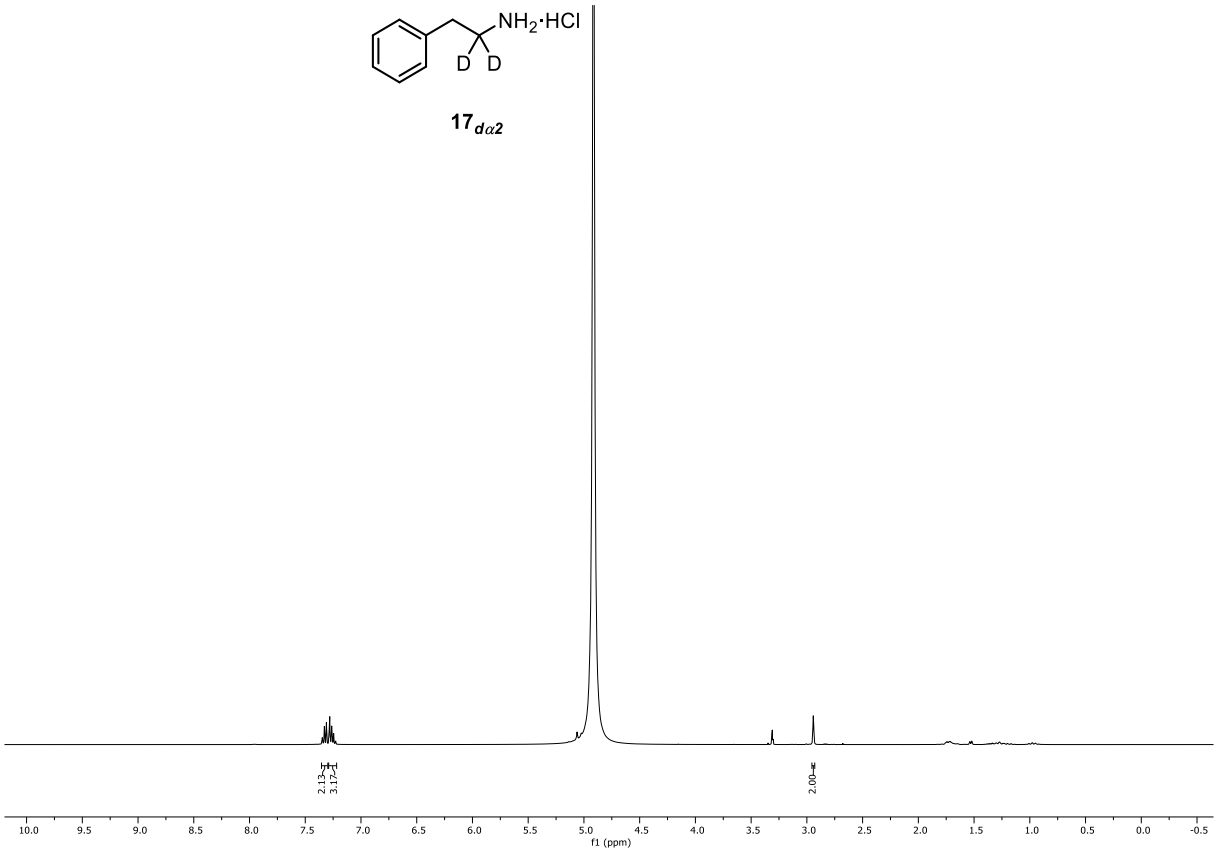


Figure S160. ^{1}H NMR spectrum of **17*dα2***.

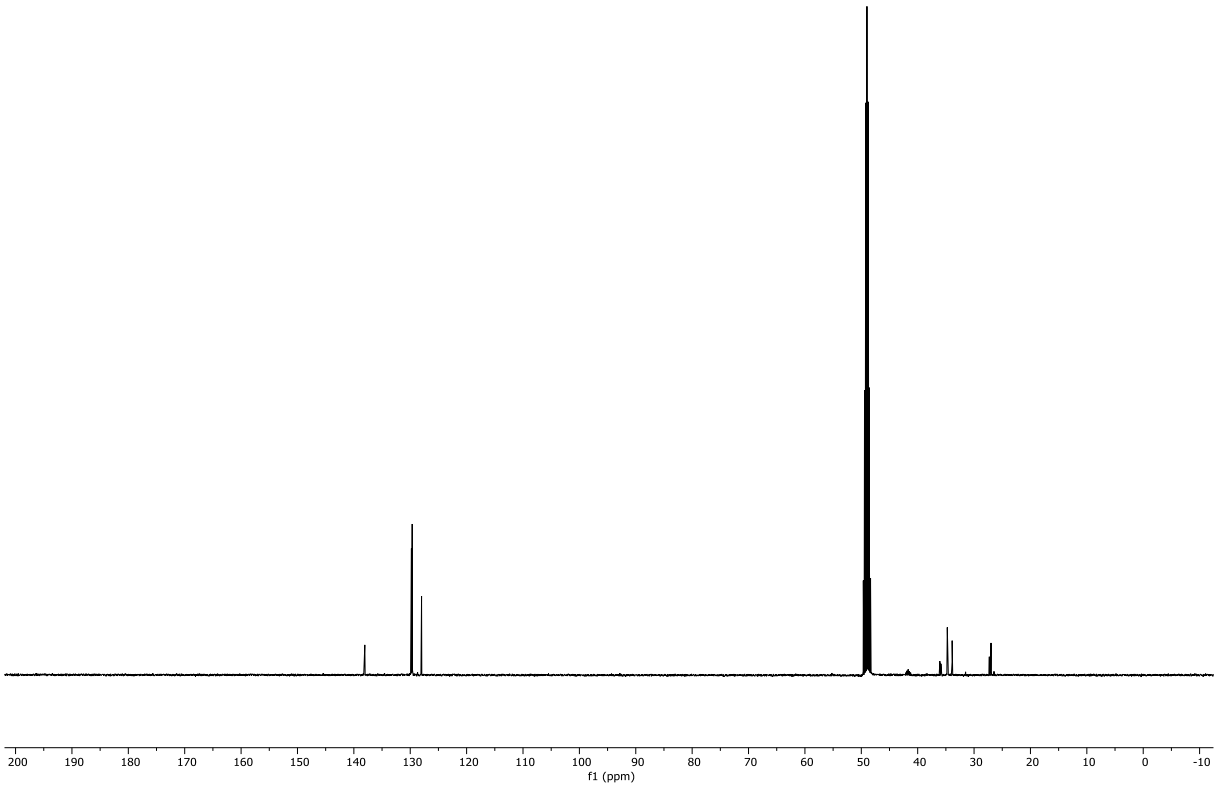


Figure S161. ^{13}C NMR spectrum of **17*dα2***.

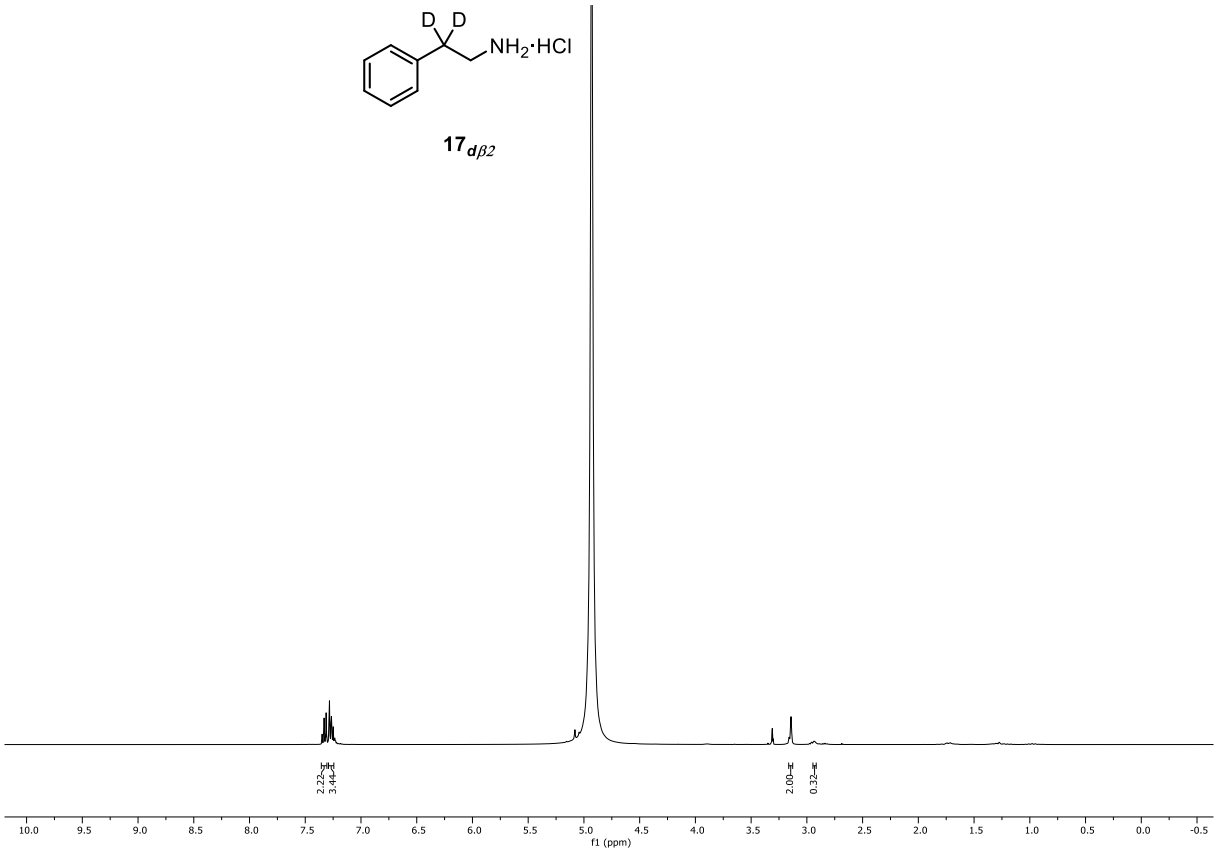


Figure S162. ^{1}H NMR spectrum of **17**$_{d\beta 2}$.

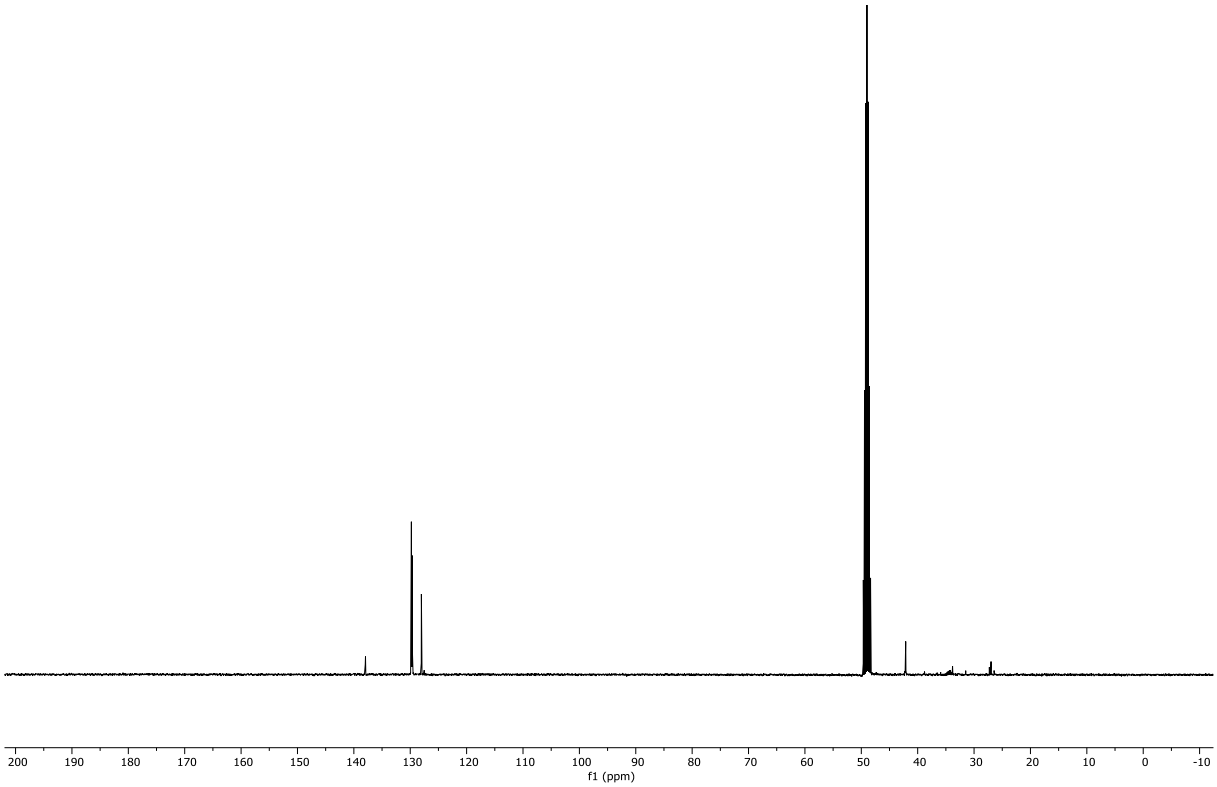


Figure S163. ^{13}C NMR spectrum of **17**$_{d\beta 2}$.

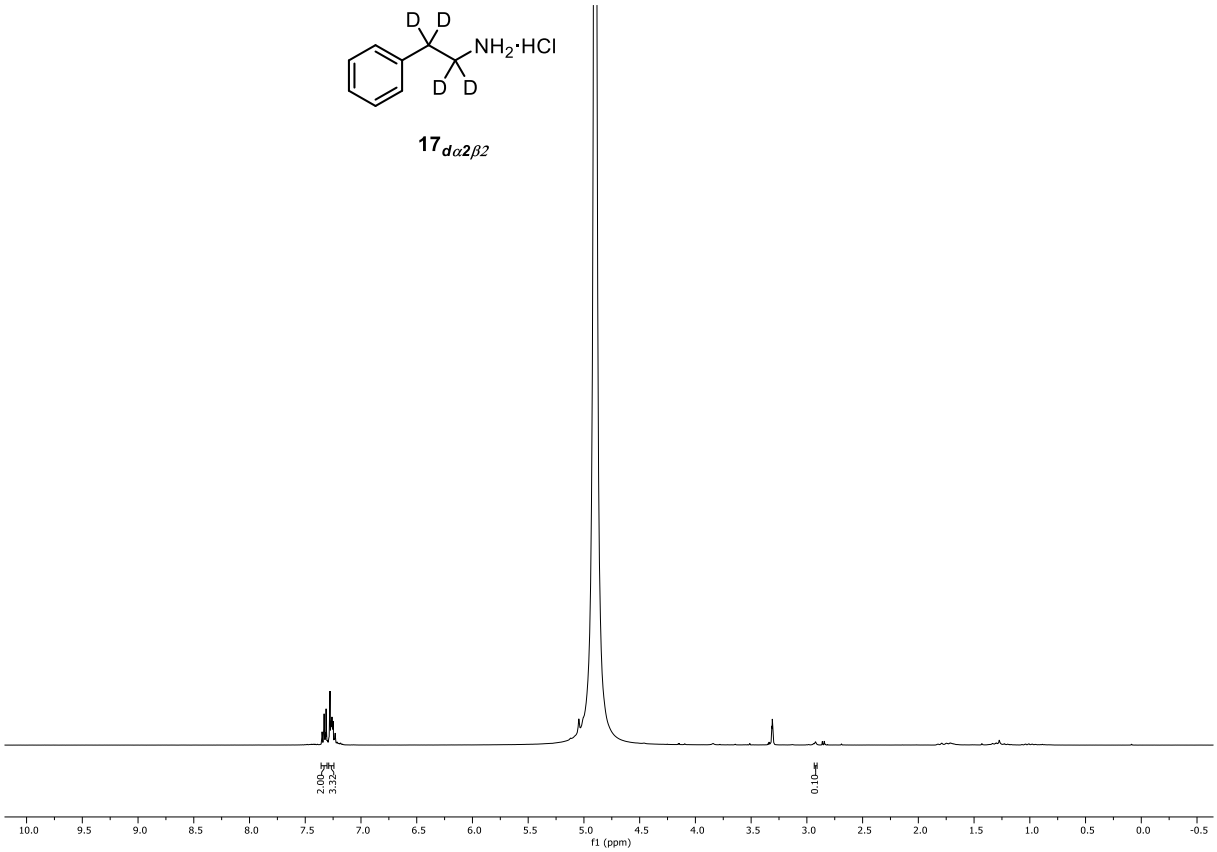


Figure S164. ^{1}H NMR spectrum of **17**$_{d\alpha 2\beta 2}$.

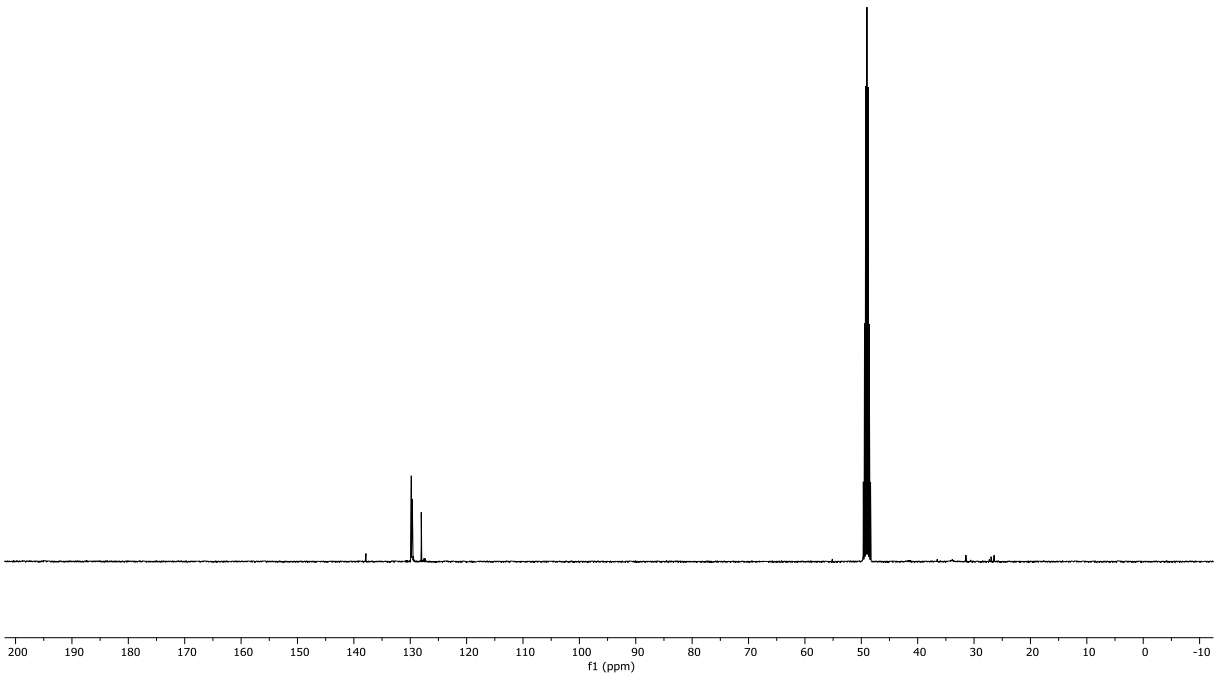


Figure S165. ^{13}C NMR spectrum of **17**$_{d\alpha 2\beta 2}$.

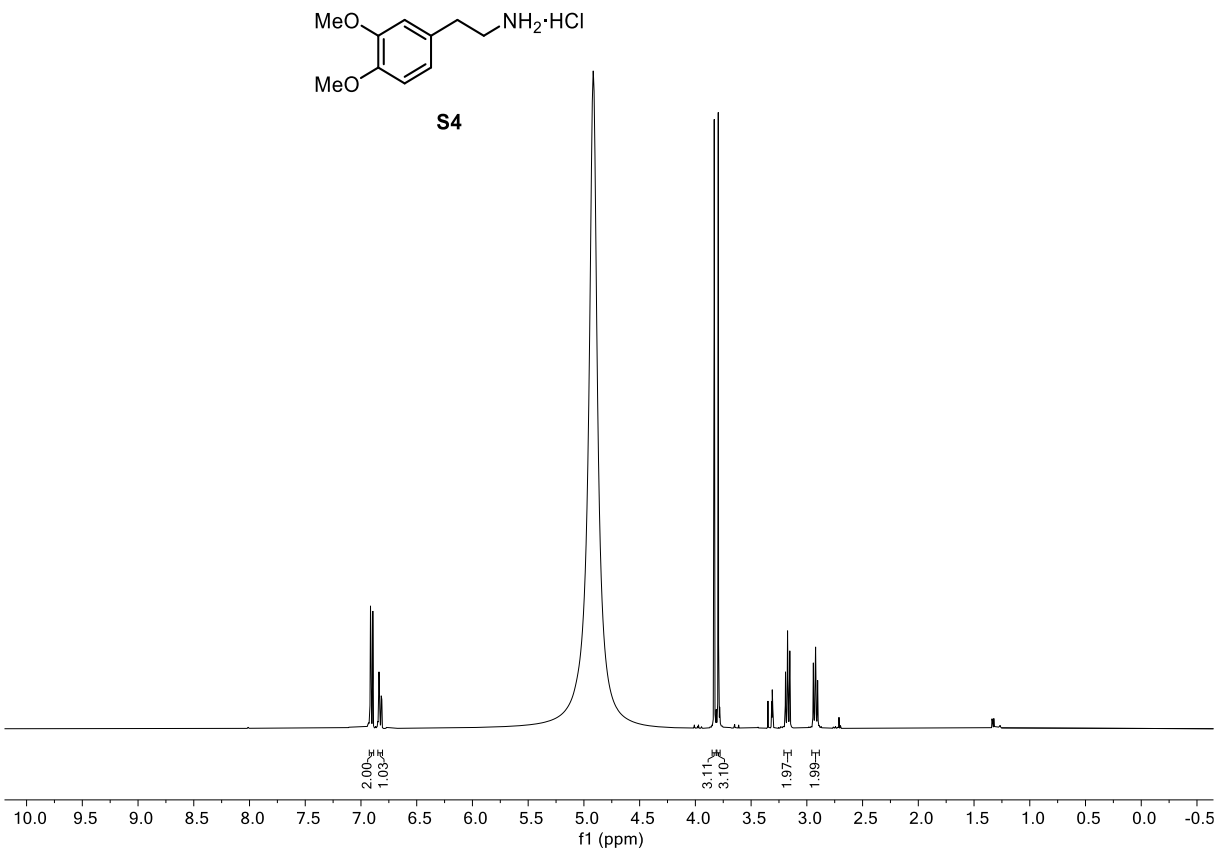


Figure S166. ^{1}H NMR spectrum of **S4.**

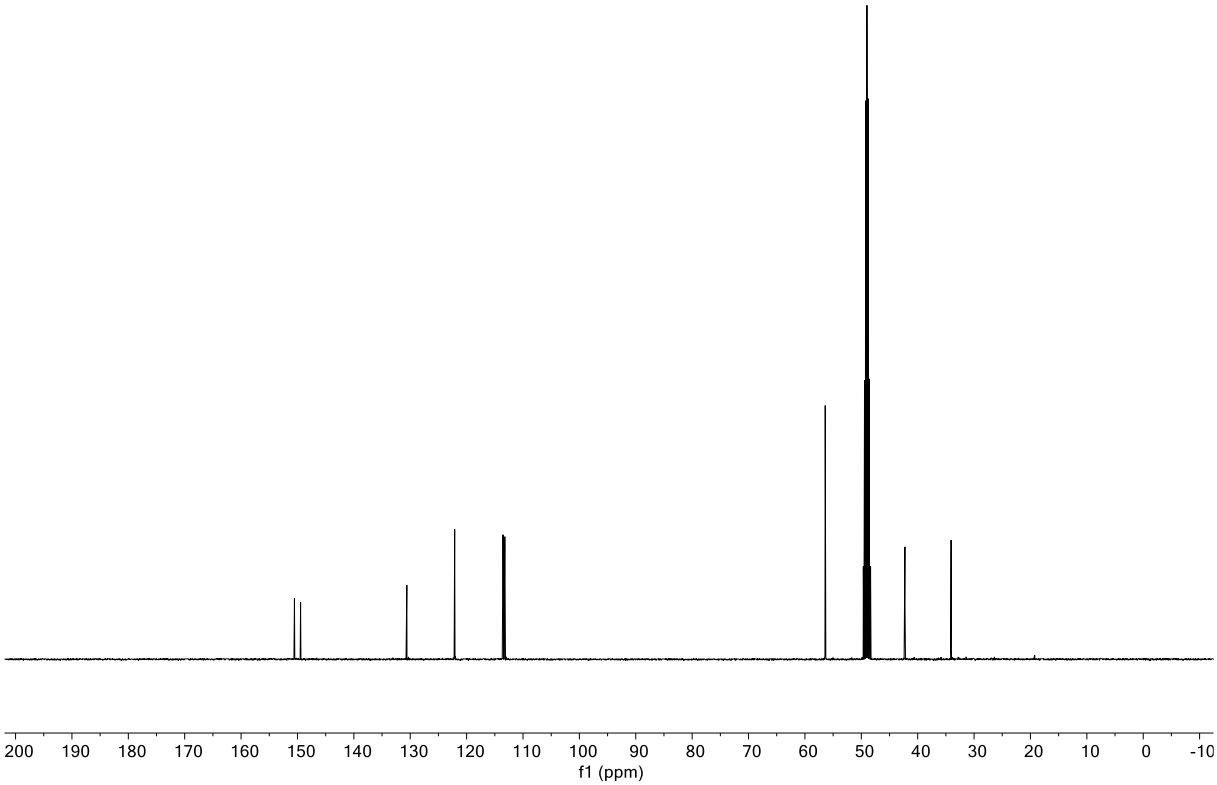


Figure S167. ^{13}C NMR spectrum of **S4.**

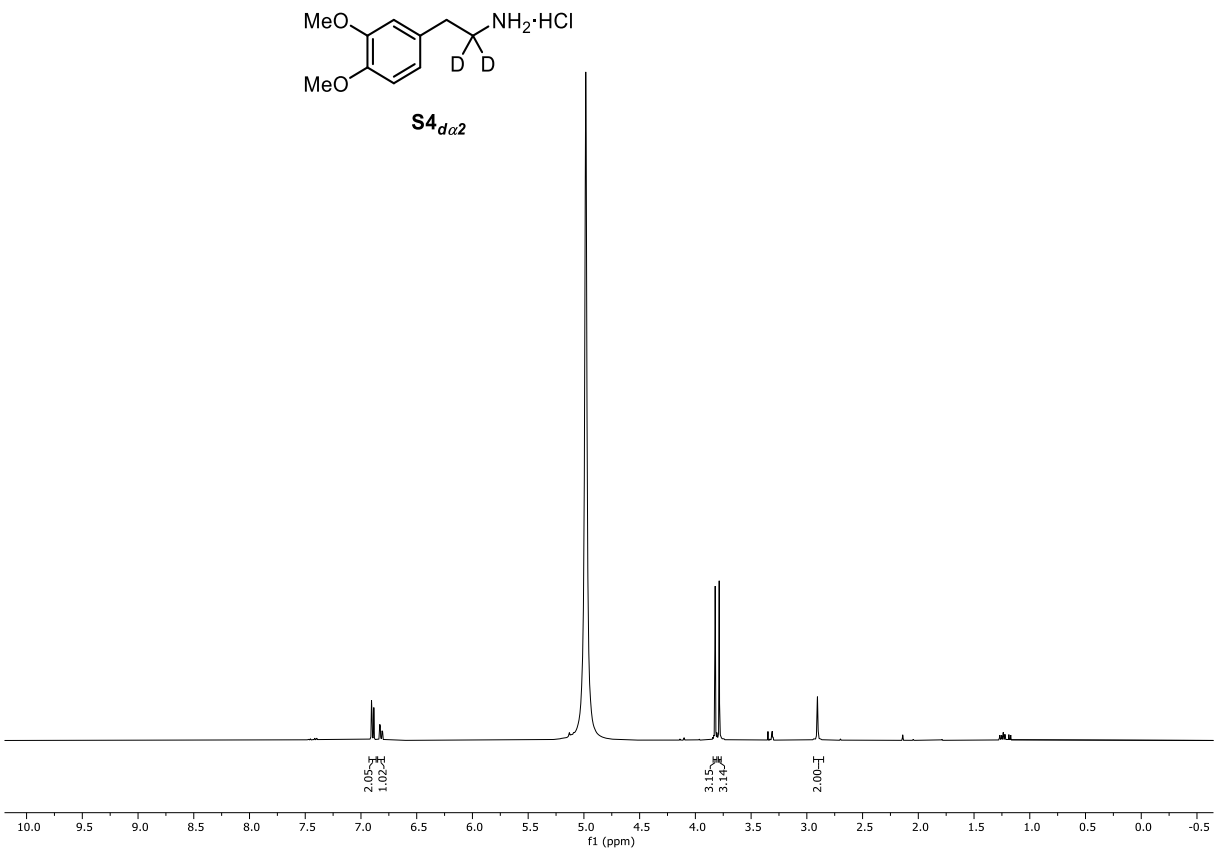


Figure S168. ^{1}H NMR spectrum of **S4*dα2***.

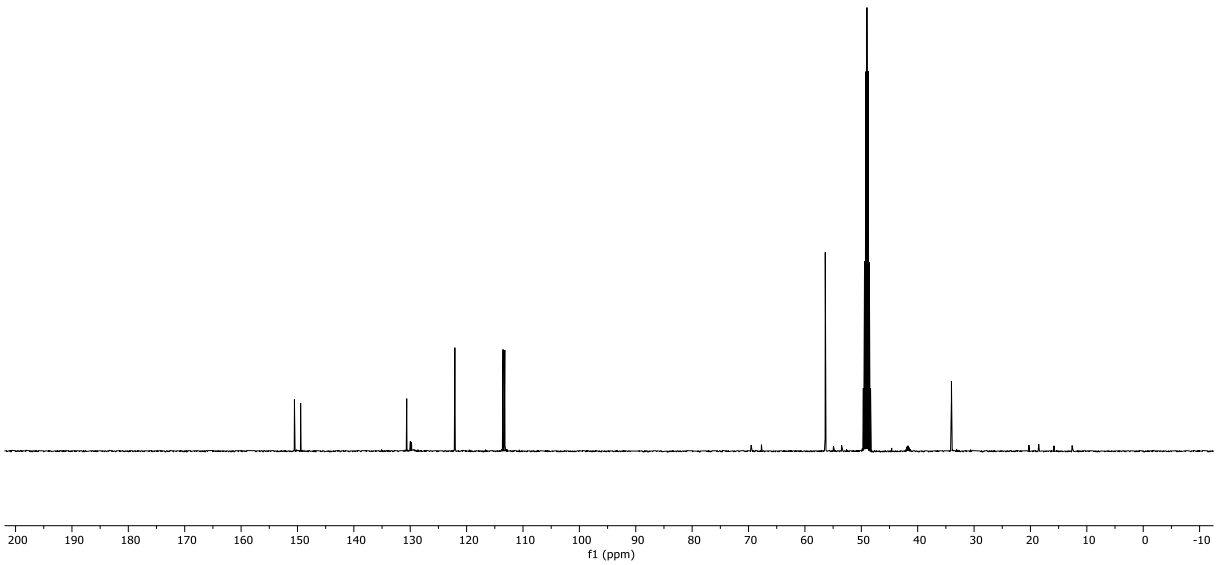


Figure S169. ^{13}C NMR spectrum of **S4*dα2***.

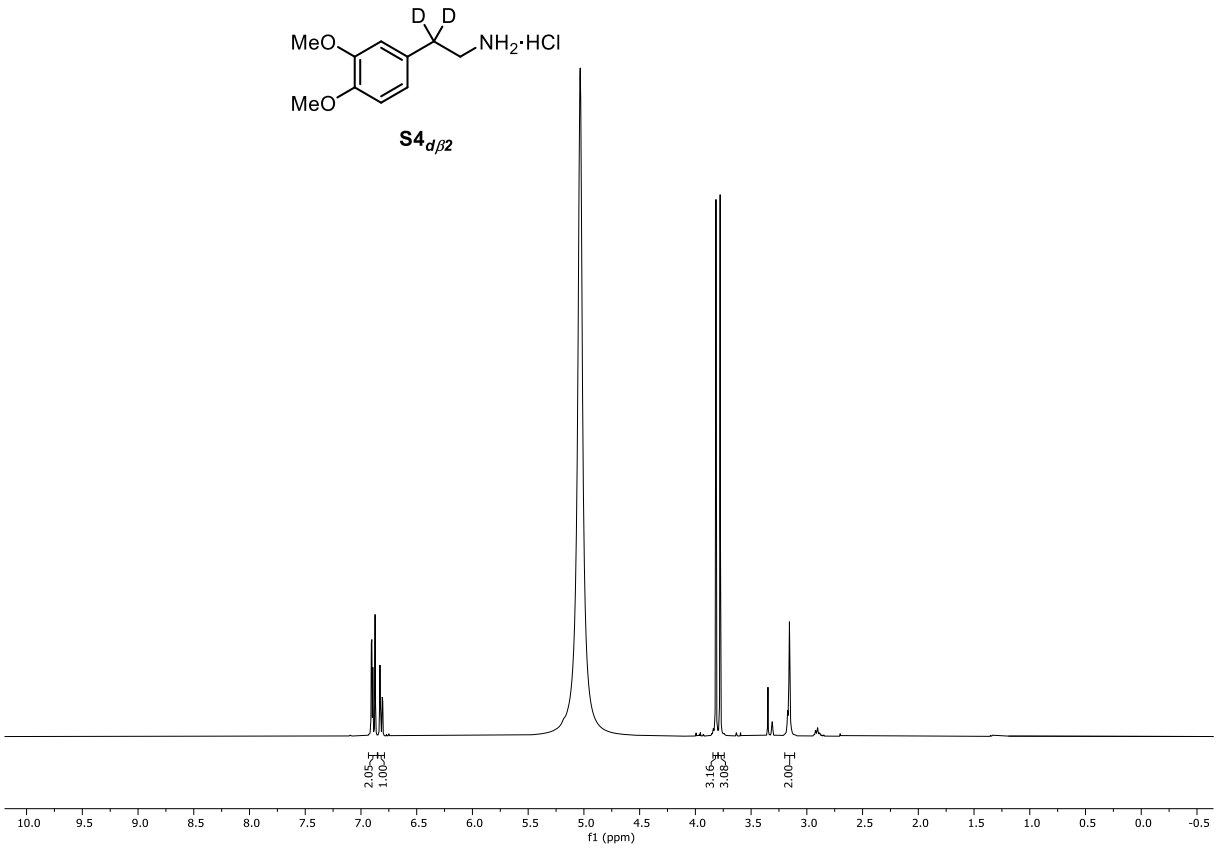


Figure S170. ^{1}H NMR spectrum of **S4*dβ2***.

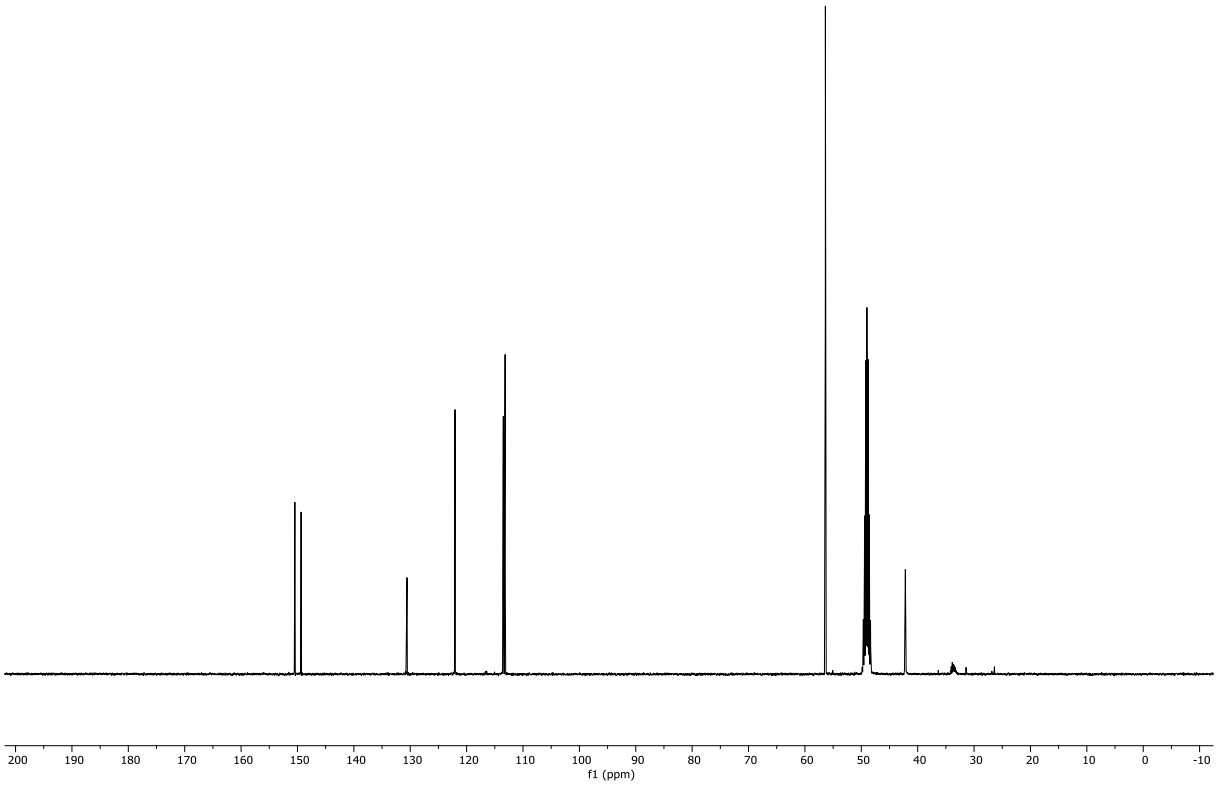


Figure S171. ^{13}C NMR spectrum of **S4*dβ2***.

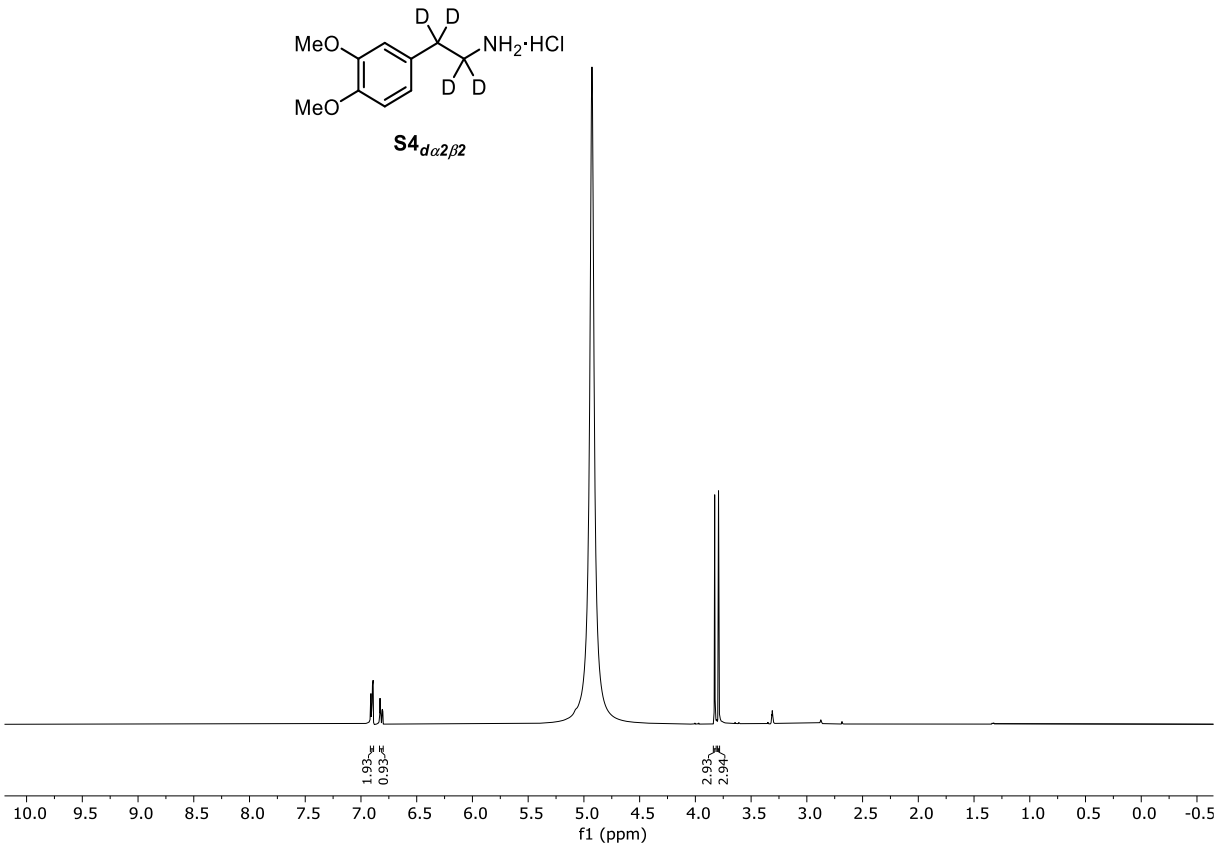


Figure S172. ^{1}H NMR spectrum of **S4**$_{d\alpha 2\beta 2}$.

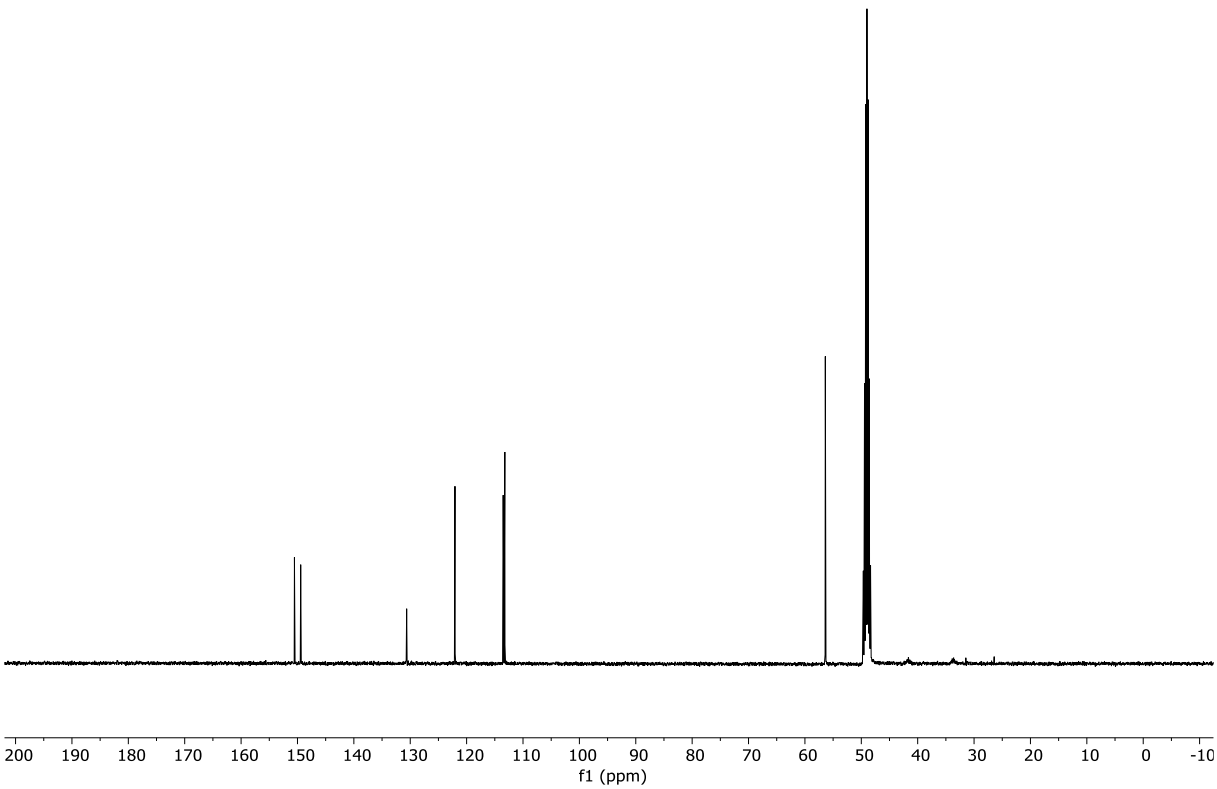
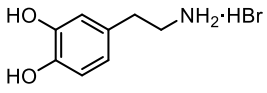


Figure S173. ^{13}C NMR spectrum of **S4**$_{d\alpha 2\beta 2}$.



19

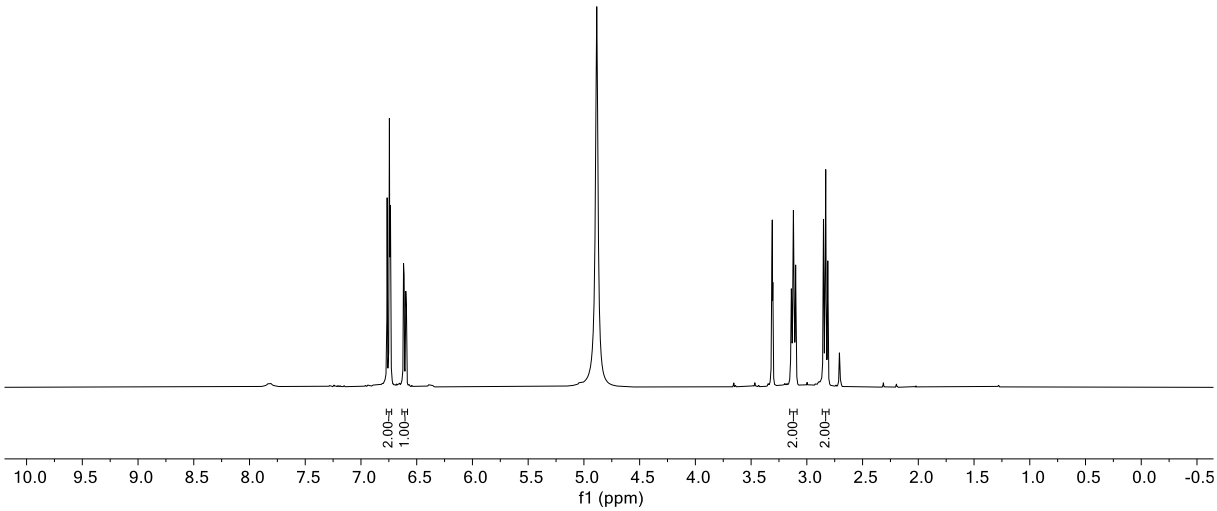


Figure S174. ^{1}H NMR spectrum of **19**.

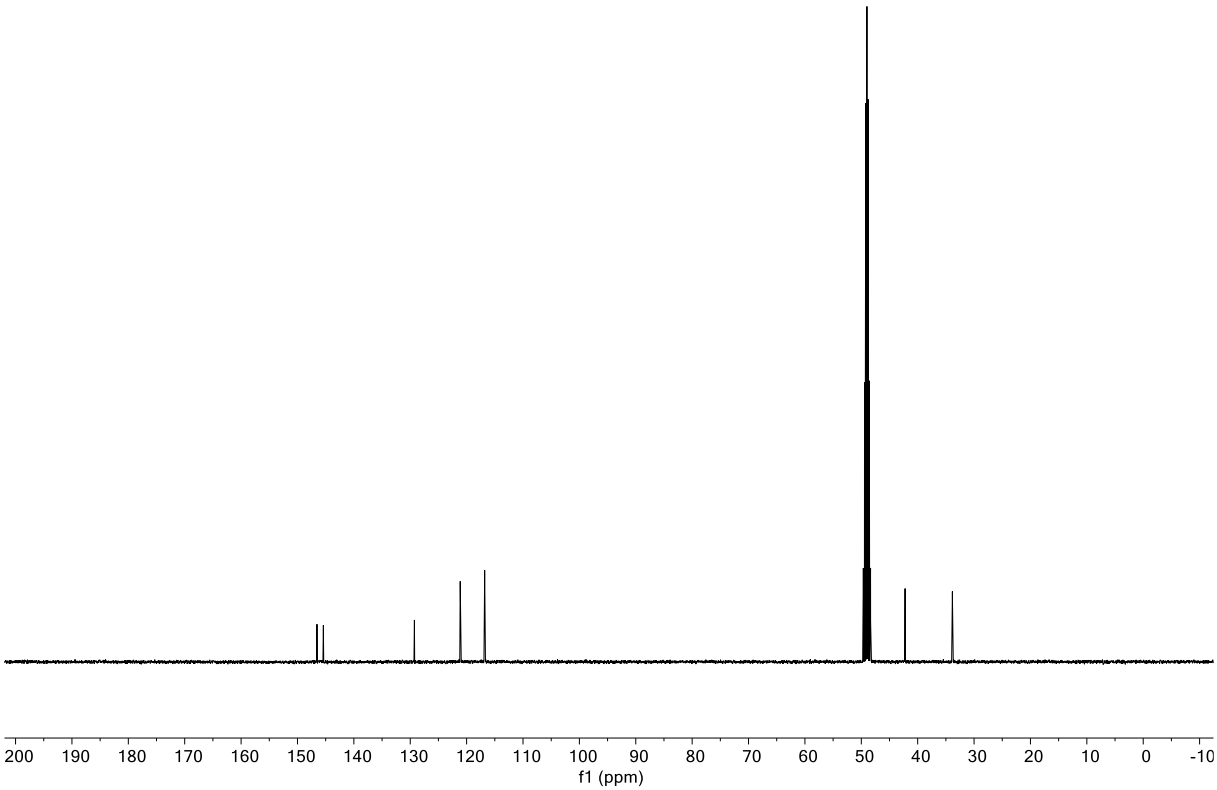
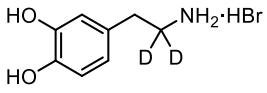


Figure S175. ^{13}C NMR spectrum of **19**.



19$_{d\alpha 2}$

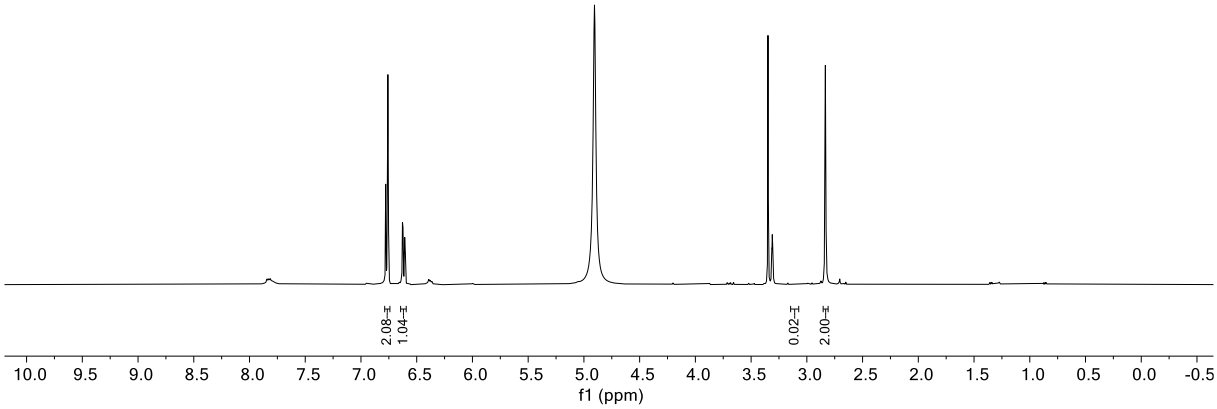


Figure S176. ^{1}H NMR spectrum of **19**$_{d\alpha 2}$.

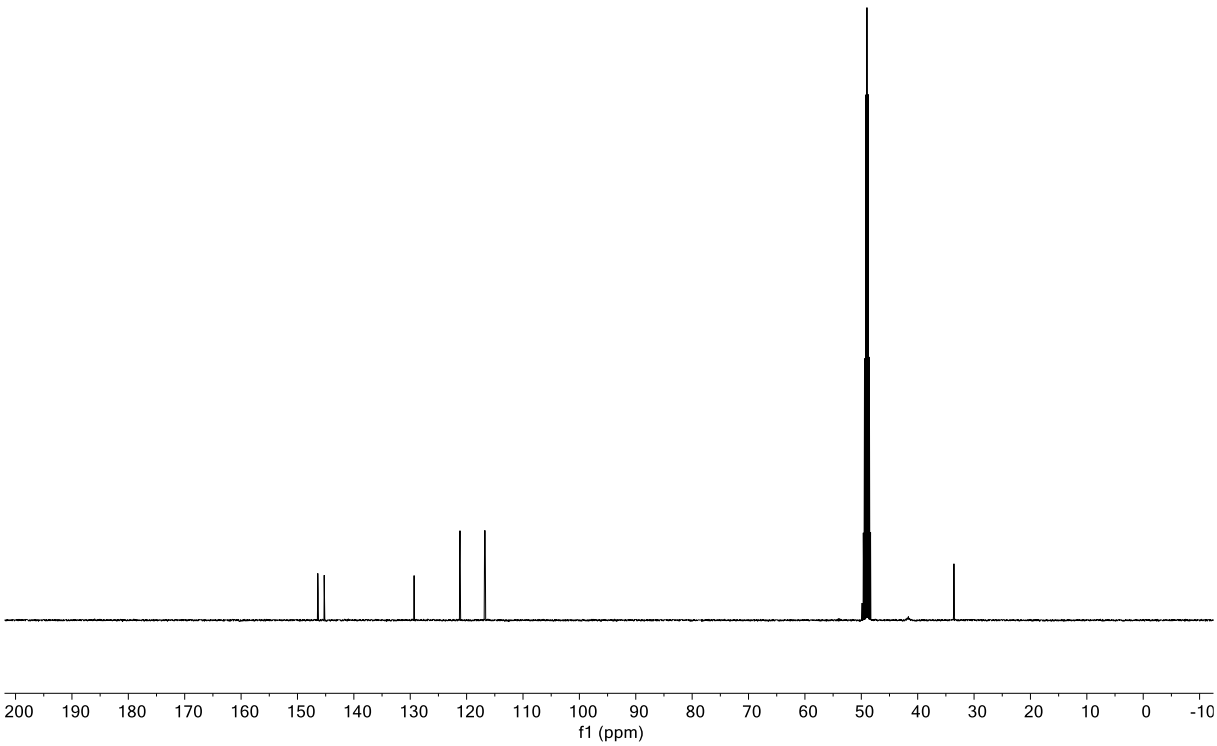
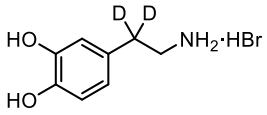


Figure S177. ^{13}C NMR spectrum of **19**$_{d\alpha 2}$.



19$_{d\beta 2}$

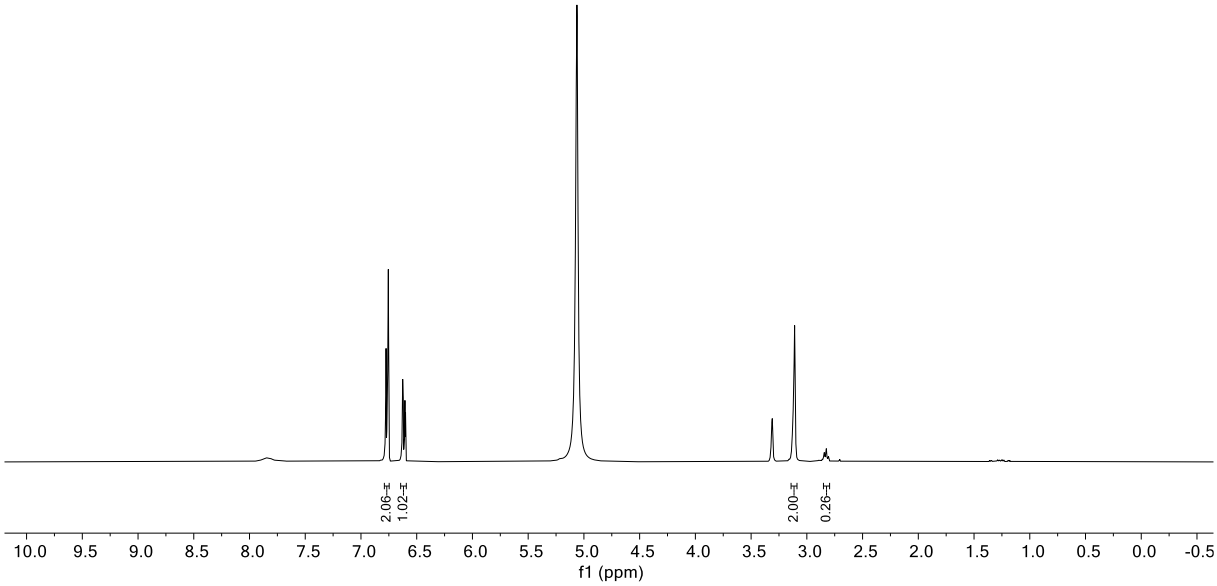


Figure S178. ^{1}H NMR spectrum of **19**$_{d\beta 2}$.

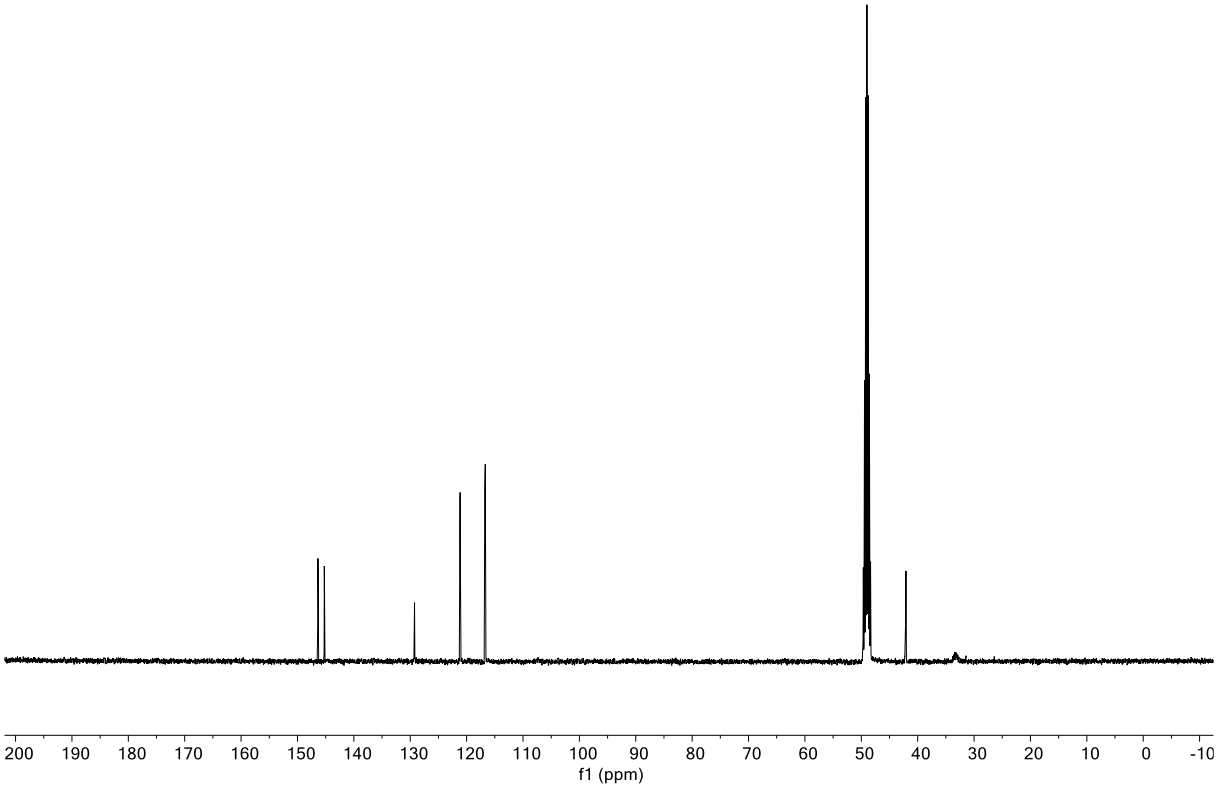


Figure S179. ^{13}C NMR spectrum of **19**$_{d\beta 2}$.

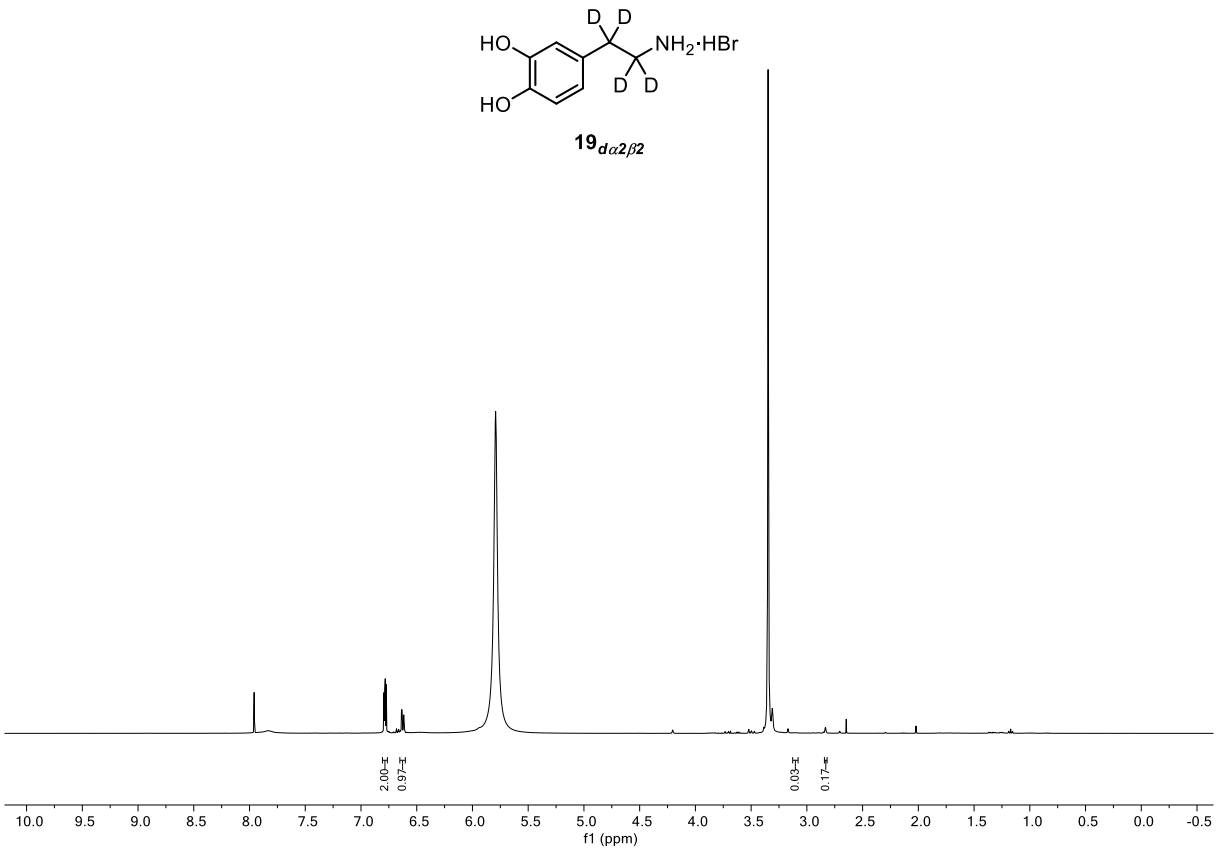


Figure S180. ^{1}H NMR spectrum of **19**$_{d\alpha2\beta2}$.

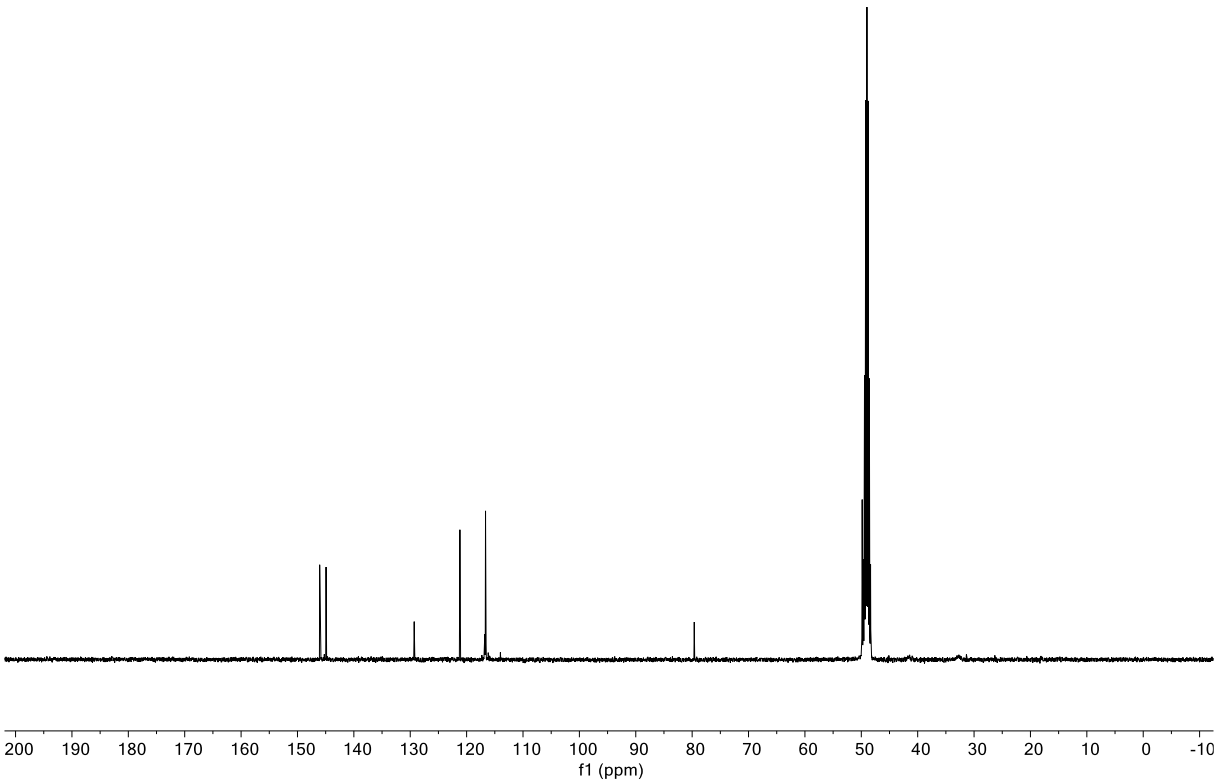
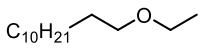


Figure S181. ^{13}C NMR spectrum of **19**$_{d\alpha2\beta2}$.



22

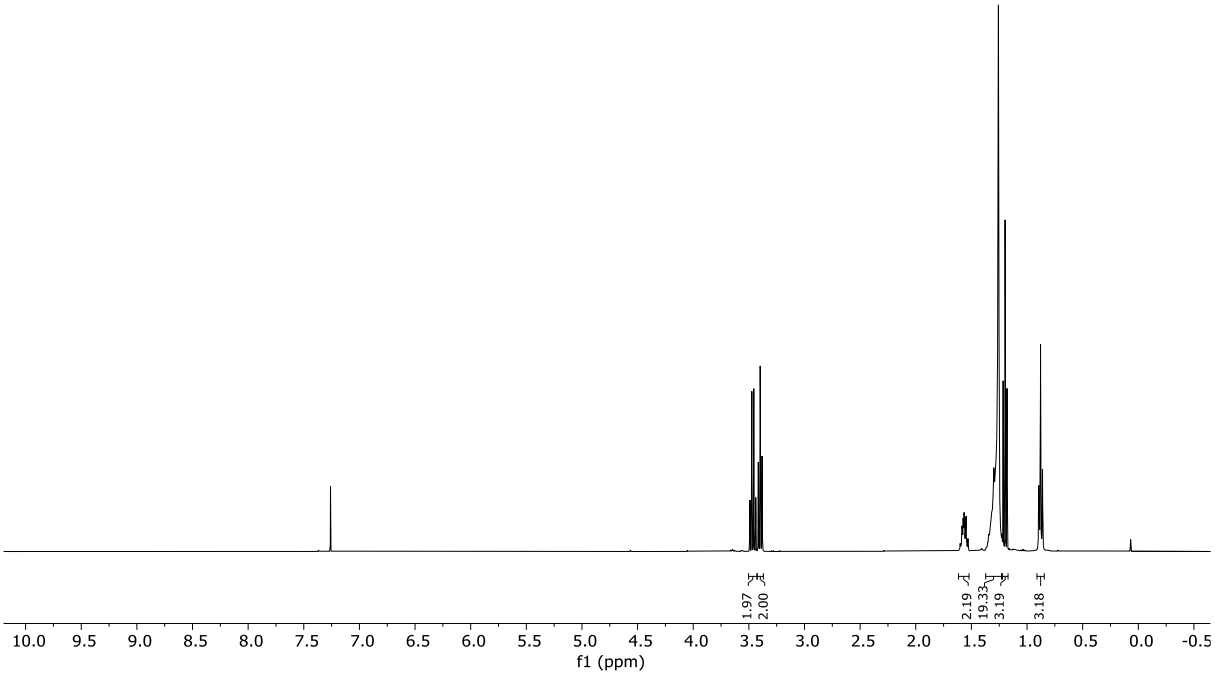


Figure S182. ^{1}H NMR spectrum of **22**.

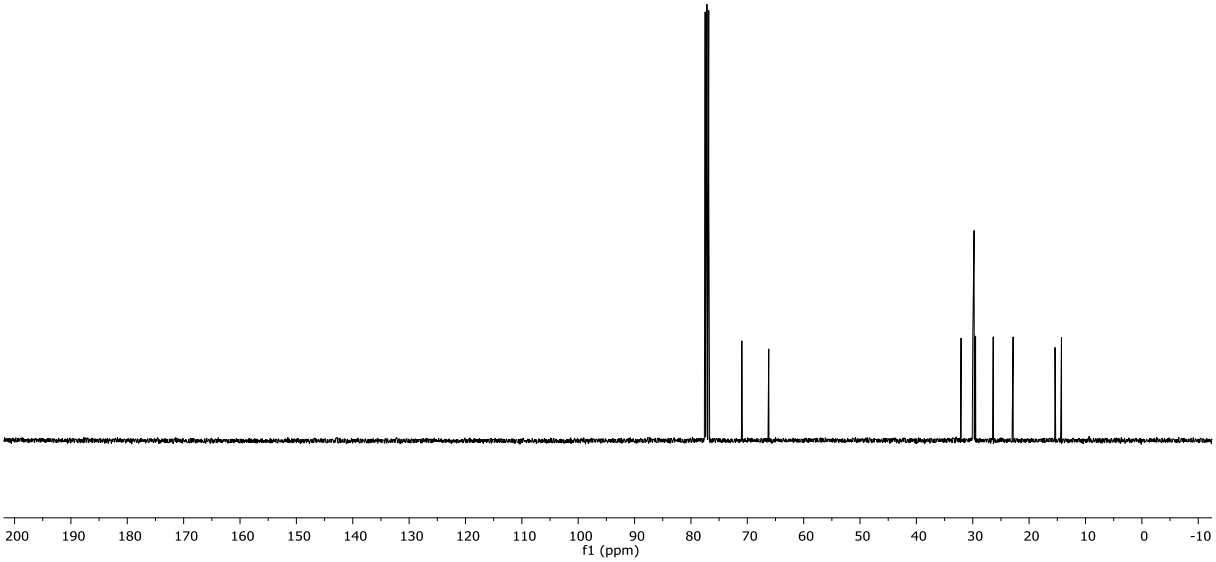


Figure S183. ^{13}C NMR spectrum of **22**.

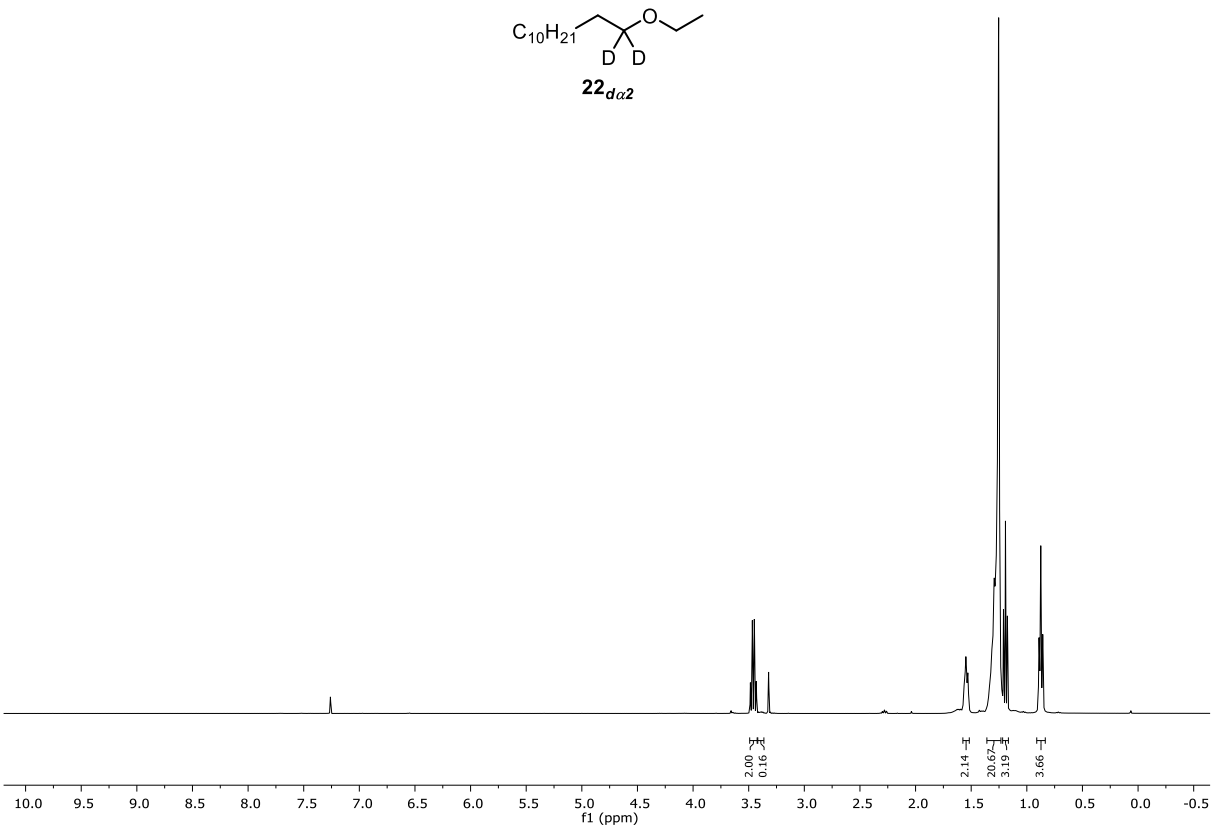


Figure S184. ^{1}H NMR spectrum of **22$_{d\alpha2}$**.

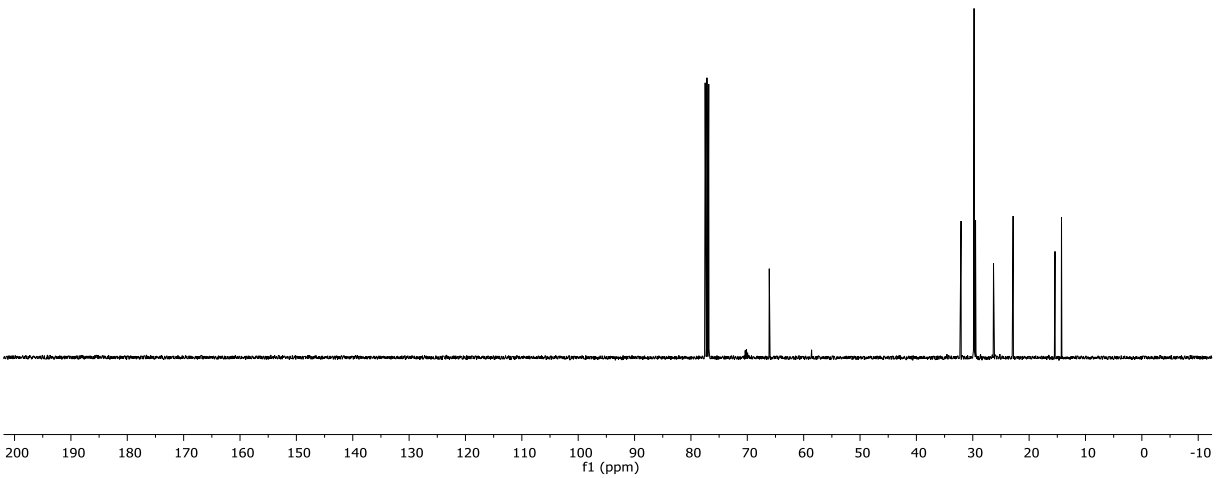
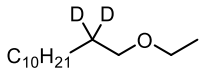


Figure S185. ^{13}C NMR spectrum of **22$_{d\alpha2}$**.



22$_{d\beta2}$

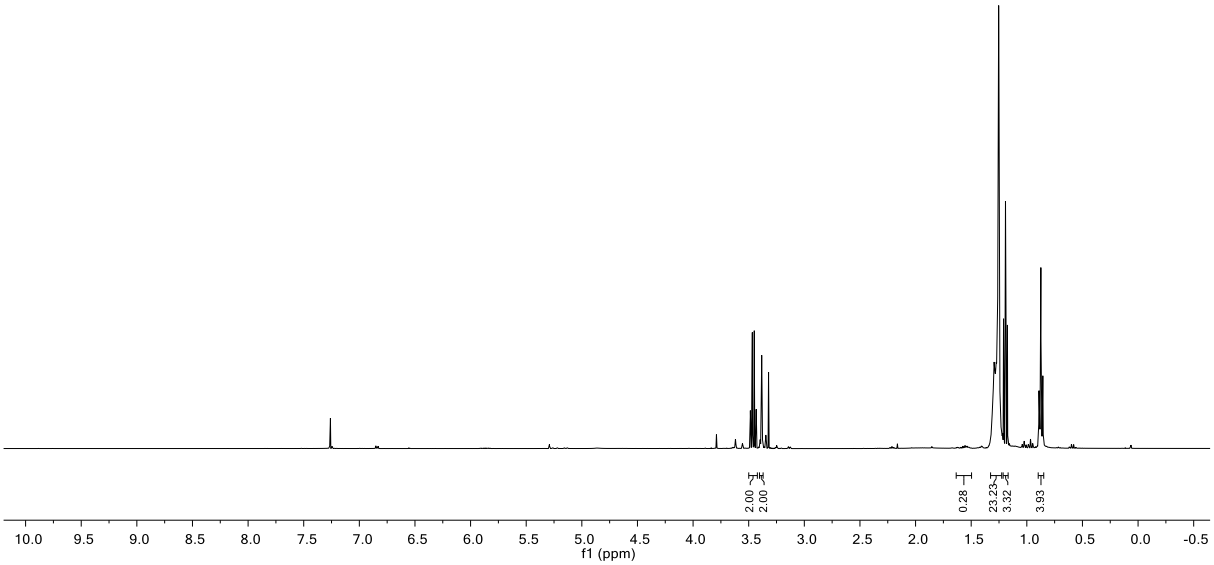


Figure S186. ^{1}H NMR spectrum of **22**$_{d\beta2}$.

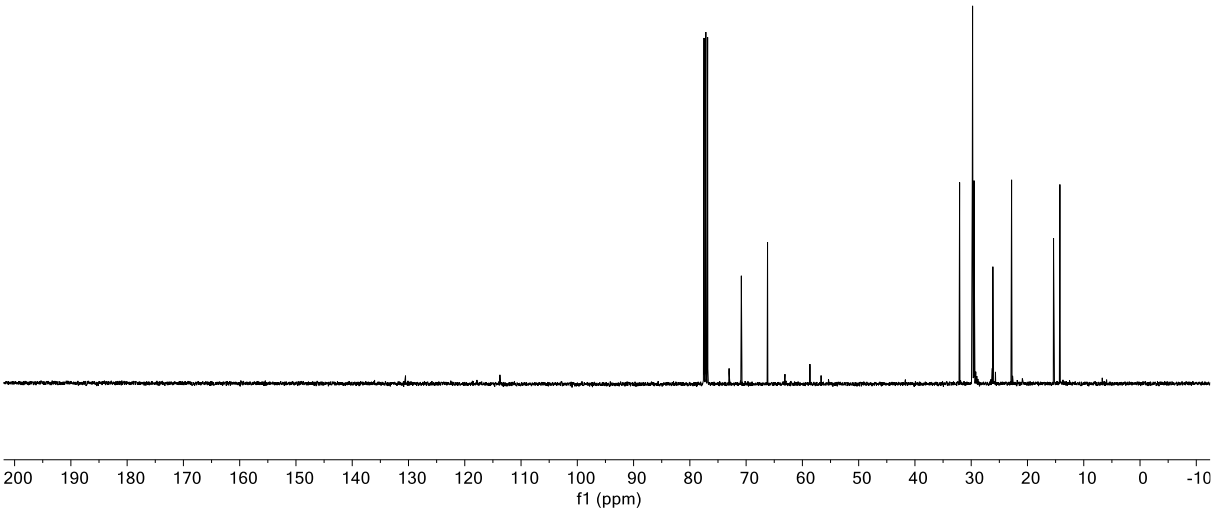
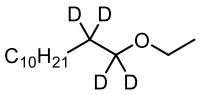


Figure S187. ^{13}C NMR spectrum of **22**$_{d\beta2}$.



22$_{d\alpha 2\beta 2}$

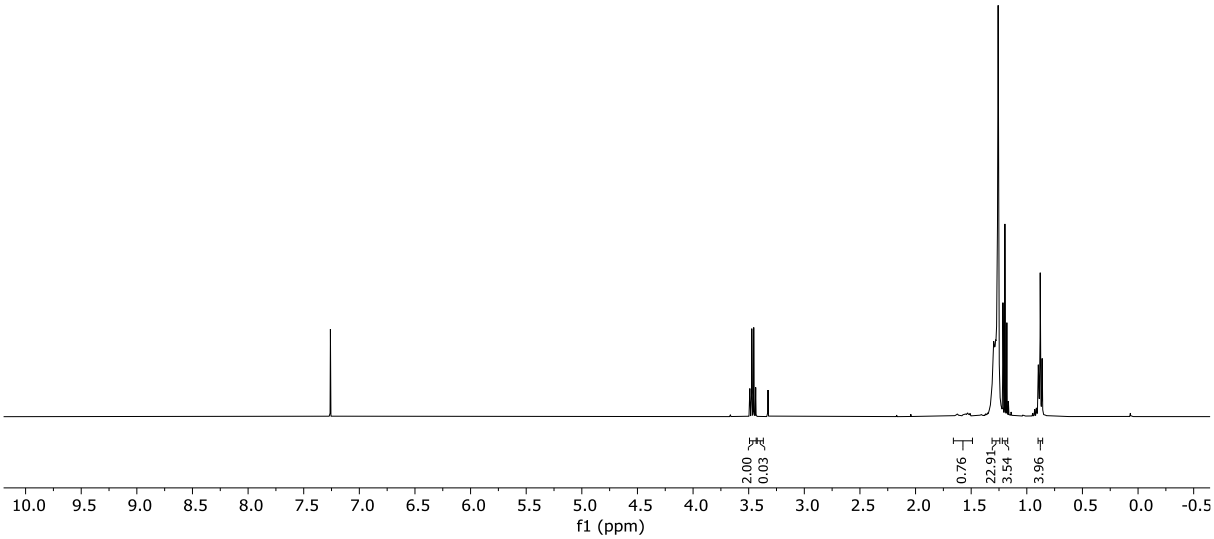


Figure S188. ^{1}H NMR spectrum of **22**$_{d\alpha 2\beta 2}$.

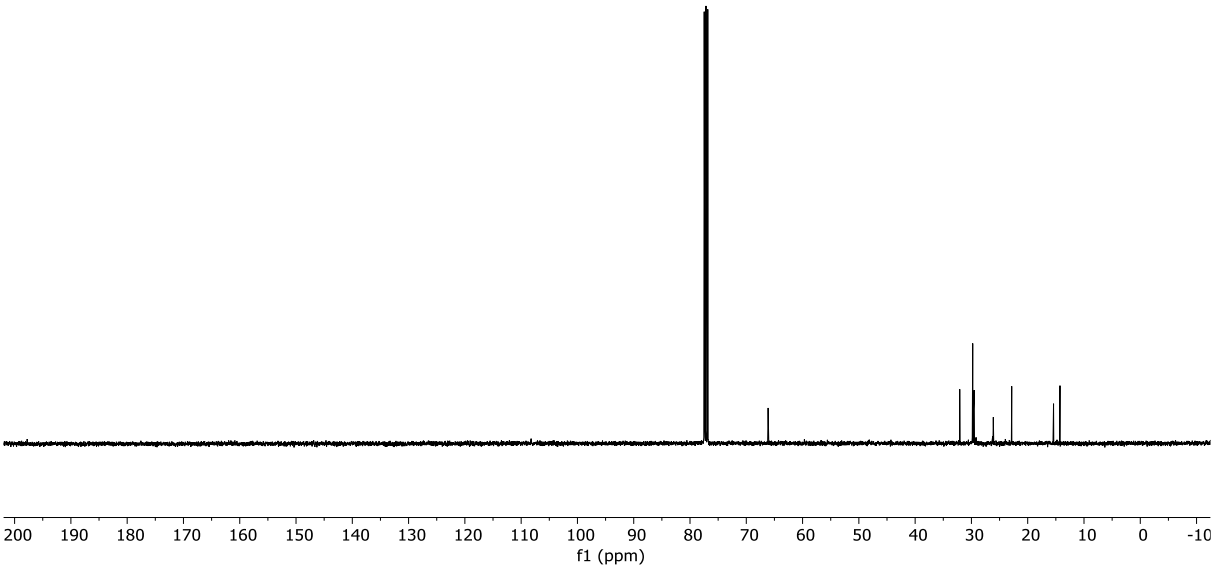


Figure S189. ^{13}C NMR spectrum of **22**$_{d\alpha 2\beta 2}$.

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