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Supporting Information for the Paper

Catalyst-Free Bis(Triflyl)ethylation/Benzannulation Reaction: Rapid Access to Carbazole-based Superacidic Carbon Acids from Alkynols

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Dedicated to Prof. Benito Alcaide on the occasion of his retirement

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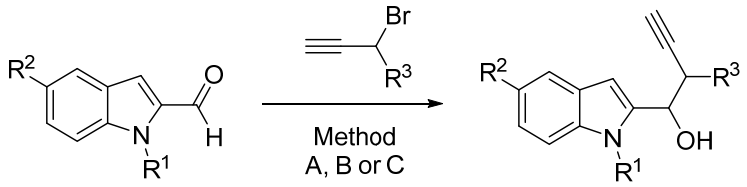
General Methods: NMR spectra were recorded at 25 ºC on a Bruker Avance AVIII-700 with cryoprobe, Bruker AMX-500, Bruker Avance III Nanobay 400, or Bruker Avance-300 spectrometers. NMR spectra were recorded in the corresponding deuterated solvent. Data are reported as follows: chemical shifts (in ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, br = broad), and coupling constants (*J*, in Hz). Chemical shifts are given in ppm relative to deuterated solvent used, $CDCl_3$ (^{1}H, 7.27 ppm; ^{13}C, 77.0 ppm); C_6D_6 (^{1}H, 7.16 ppm; ^{13}C, 128.0 ppm); CD_3COCD_3 (^{1}H, 20.5 ppm; ^{13}C, 29.84 ppm). Chemical shifts in ^{19}F are given in ppm relative to (trifluoromethyl)benzene ($C_6H_5CF_3$) in $CDCl_3$ (^{19}F, –63.7 ppm). Chemical shifts in ^{23}Na are given in ppm relative to NaCl in D_2O (^{23}Na, 0.00 ppm). Low- and high-resolution mass spectra were taken on an AGILENT 6520 Accurate-Mass QTOF LC/MS or Waters Xevo G2-XS Tof mass spectrometers using the electronic impact (EI) or electrospray modes (ES) unless otherwise stated. Column chromatography was carried out using silica gel 60, 0.04-0.06 mm, for flash chromatography (230-400 mesh ASTM) provided by Scharlau.

Experimental Section

Metal-promoted reaction between propargyl bromide or 3-bromo-1-butyne with indole-2-carbaldehydes. General procedure for the synthesis of alkynols **5b** and **I-IV**.



5b R^1 = Me, R^2 = Me, R^3 = H (73%)
I R^1 = Me, R^2 = OMe, R^3 = H (50%)
II R^1 = Me, R^2 = Cl, R^3 = H (70%)
III R^1 = Me, R^2 = Me, R^3 = Me (56%)
IV R^1 = Boc, R^2 = H, R^3 = H (93%)

Method A. Propargyl bromide (0.3 mL, 4 mmol, 2.6 equiv.) was added at room temperature to a suspension of zinc powder (11.61 mmol, 7.5 equiv.) in anhydrous THF (3.6 mL). The reaction mixture was activated by a gentle heating until a few bubbles were formed. When the formation of bubbles stopped, the reaction mixture was cooled at –15 °C and propargyl bromide (1.3 mL, 17 mmol, 11 equiv.) was added. The mixture was further stirred at –15 ºC for 30 minutes and cooled to –78 ºC. Afterwards, a solution of the appropriate indole-2-carbaldehyde (1.55 mmol, 1 equiv.) in THF was added dropwise at –78 ºC. Then, the reaction mixture was allowed to slowly warm at room temperature and stirred overnight. After disappearance of the starting material (TLC), the mixture was washed with a solution of NH_4Cl (aq. sat.) (20 mL), extracted with Et_2O (3 × 15 mL) and washed with brine (3 x 15 mL), dried ($MgSO_4$), and concentrated under reduced pressure. Chromatography of the residue using ethyl acetate/*n*-hexane mixtures gave analytically pure compounds **5b**, **I** and **II**.

Method B. 3-Bromo-1-butyne (3.63 mmol, 1.4 equiv.) was added dropwise to a solution of 1,5-dimethyl-1*H*-indole-2-carbaldehyde (2.6 mmol, 1 equiv.) in a mixture of solvents THF/H_2O/NH_4Cl (3:3:5, 33mL) and zinc powder (5.2 mmol, 2 equiv.) at 0 ºC. The reaction was stirred at room

temperature until disappearance of the starting material (TLC). Then, the mixture was extracted with ethyl acetate (2 x 25 mL). The organic extract was washed with brine, dried ($MgSO_4$), and concentrated under reduced pressure. Chromatography of the residue using ethyl acetate/*n*-hexane mixtures gave analytically pure compound **III**.

Method C. Propargyl bromide (2 equiv.) was added at room temperature to a suspension of zinc powder (5 equiv) in anhydrous THF (6.0 mL). The reaction mixture was activated by a gentle heating until a few bubbles were formed. When the formation of bubbles stopped, the reaction mixture was cooled at –15 °C and propargyl bromide (8 equiv.) was added. The mixture was further stirred at –15 ºC for 30 minutes and cooled to −78 °C. Afterwards, a solution of the appropriate indole-2-carbaldehyde (3.7 mmol) in THF (9.0 mL) was added dropwise at –78 °C. Then, the reaction mixture was allowed to slowly warm at room temperature and stirred overnight. The reaction mixture was quenched with a saturated solution of NH_4Cl in water (20 mL) and extracted with EtOAc (3 × 15 mL). After washing the combined organic layer with brine (15 mL), it was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Column chromatography of the residue on silica gel using EtOAc/hexane mixtures gave the corresponding homopropargyl alcohol **IV**.

1-(1,5-Dimethyl-1*H*-indol-2-yl)but-3-yn-1-ol 5b. *Method A*. From 268 mg (1.55 mmol) of the corresponding aldehyde, and after flash chromatography of the residue using *n*-hexane/ethyl acetate (5:1) as eluent gave compound **5b** (240 mg, 73%) as an orange-coloured oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38 (1H, s, CH_{Ar}), 7.22 (1H, d, *J* = 8.4 Hz, CH_{Ar}), 7.07 (1H, dd, *J* = 8.4, 1.4 Hz, CH_{Ar}), 6.46 (1H, s, CH_{Ar}), 5.05 (1H, q, *J* = 6.1 Hz, C*H*OH), 3.80 (3H, s, NCH_3), 2.96–2.92 (2H, m, CH_2), 2.44 (3H, s, CH_3), 2.21 (1H, d, *J* = 6.4 Hz, OH), 2.15 (1H, t, *J* = 2.6 Hz, C≡C*H*); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.6 (C_{Ar}), 136.3 (C_{Ar}), 128.8 (C_{Ar}), 127.1 (C_{Ar}), 123.6 (CH_{Ar}), 120.4 (CH_{Ar}), 108.8 (CH_{Ar}), 98.7 (CH_{Ar}), 80.3 (*C*≡CH), 71.4 (C≡*C*H), 65.1 (CHOH), 30.0 (NCH_3), 26.4 (CH_2), 21.3 (CH_3); IR ($CHCl_3$): ν = 2926 (Ar), 1469 (C-O), 1292 (OH) cm^{-1}; HRMS (ES): calcd for $C_{14}H_{16}NO$ [*M* + H]$^+$: 214.12264; found: 214.12264.

1-(5-Methoxy-1-methyl-1*H*-indol-2-yl)but-3-yn-1-ol I. *Method A.* From 264 mg (1.4 mmol) of the corresponding aldehyde, and after flash chromatography of the residue using *n*-hexane/ethyl acetate (5:1) as eluent gave compound **I** (160 mg, 50%) as an orange-coloured oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.21 (1H, d, *J* = 8.9 Hz, CH_{Ar}), 7.06 (1H, d, *J* = 2.3 Hz, CH_{Ar}), 6.90 (1H, dd, *J* = 8.9, 2.4 Hz, CH_{Ar}), 6.46 (1H, s, CH_{Ar}), 5.02 (1H, t, *J* = 6.2 Hz, C*H*-OH), 3.85 (3H, s, O-CH_3), 3.78 (3H, s, N-CH_3) 2.93-2.91 (2H, m, CH_2), 2.35 (1H, brs, OH), 2.15 (1H, t, *J* = 2.6 Hz, C≡C*H*); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.1 (C_{Ar}), 140.0 (C_{Ar}), 133.3 (C_{Ar}), 127.1 (C_{Ar}), 112.4 (CH_{Ar}), 109.9 (CH_{Ar}), 102.4 (CH_{Ar}), 98.8 (CH_{Ar}), 80.3 (*C*≡CH), 71.6 (C≡*C*H), 65.2 (CH-OH), 56.8 (O-CH_3), 30.2 (N-CH_3), 26.5 (CH_2); IR ($CHCl_3$): ν = 3281 (C≡CH), 2993 (Ar), 1484 (C-O), 1211 (C-OH) cm^{-1}; HRMS (ES): calcd for $C_{14}H_{16}NO_2$ [*M* + H]$^+$: 230.11756; found: 230.11699.

1-(5-Chloro-1-methyl-1*H*-indol-2-yl)but-3-yn-1-ol II. *Method A.* From 600 mg (3.1 mmol) of the corresponding aldehyde, and after flash chromatography of the residue using *n*-hexane/ethyl acetate (5:1) as eluent gave compound **II** (505 mg, 70%) as an yellow-coloured oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.54 (1H, d, *J* = 0.9 Hz, CH_{Ar}), 7.22-7.15 (2H, m, CH_{Ar}), 6.44 (1H, s, H_{Ar}), 5.00-4.99 (1H, m, C*H*-OH), 3.76 (3H, s, N-CH_3), 2.90 (2H, dd, *J* = 6.3, 2.6 Hz, CH_2), 2.49 (1H, brs, OH), 2.16 (1H, t, *J* = 2.6 Hz, C≡C*H*); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.8 (C_{Ar}), 136.2 (C_{Ar}), 127.8 (C_{Ar}), 125.2 (C_{Ar}), 122.3 (CH_{Ar}), 120.1 (CH_{Ar}), 110.1 (CH_{Ar}), 98.9 (CH_{Ar}), 80.0 (*C*≡CH), 71.8 (C≡*C*H), 65.0 (CH-OH), 30.2 (N-CH_3), 26.4 (CH_2); IR ($CHCl_3$): ν = 3293 (C≡CH), 1473 (C-OH) cm^{-1}; HRMS (ES): calcd for $C_{13}H_{13}ClNO$ [*M* + H]$^+$: 234.06802; found: 234.06814.

1-(1,5-Dimethyl-1*H*-indol-2-yl)-2-methylbut-3-yn-1-ol III. *Method B.* From 450 mg (2.6 mmol) of the corresponding aldehyde, and after flash chromatography of the residue using *n*-hexane/ethyl acetate (5:1) as eluent gave compound **III** in a ratio 83:17 (330 mg, 56%) as an yellow-coloured oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.29 (1H, s, CH_{Ar}, M+m), 7.11 (1H, d, *J* = 8.4 Hz, CH_{Ar}, M+m), 6.97 (1H, dd, *J* = 8.4, 1.2 Hz, CH_{Ar}, M+m), 6.47 (0.15H, s, CH_{Ar}, m), 6.39 (0.85H, s, CH_{Ar}, M), 4.71

(0.16H, d, *J* = 7.1 Hz, C*H*-OH, m), 4.59 (0.84H, d, *J* = 6.4 Hz, C*H*-OH, M), 3.69 (2.52H, s, N-CH_3, M), 3.66 (0.48H, s, N-CH_3, m), 3.07 (0.81H, pd, *J* = 7.0, 2.3 Hz, C*H*-CH_3, M), 2.96 (0.19H, ddd, *J* = 14.0, 7.0, 2.4 Hz, C*H*-CH_3, m), 2.36 (3H, s, C-CH_3, M+m), 2.18 (0.78H, d, *J* = 2.4 Hz, C≡CH, M), 2.02 (0.22H, *J* = 2.5 Hz, C≡CH, m), 1.28 (0.5H, d, *J* = 7.0 Hz, CH-C*H*$_3$, m), 1.19 (2.5H, d, *J* = 7.0 Hz, CH-C*H*$_3$, M); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.6 (C_{Ar}, m), 138.8 (C_{Ar}, M), 136.3 (C_{Ar}, M), 136.1 (C_{Ar}, m), 128.8 (C_{Ar}, M+m), 127.3 (C_{Ar}, m), 127.2 (C_{Ar}, M), 123.5 (CH_{Ar}, M), 123.4 (CH_{Ar}, m), 120.4 (CH_{Ar}, m), 120.4 (CH_{Ar}, M), 108.8 (CH_{Ar}, M+m), 99.9 (CH_{Ar}, M), 99.5 (CH_{Ar}, m), 85.5 (*C*≡CH, m), 85.1 (*C*≡CH, M), 72.0 (C≡*C*H, M), 71.0 (C≡*C*H, m), 70.3 (CH-OH, M), 69.8 (CH-OH, m), 32.5 (N-CH_3, M), 32.4 (N-CH_3, m), 30.3 (CH-OH, M), 30.1 (CH-OH, m), 21.6 (CH_3, m), 21.3 (CH_3, M), 18.2 (CH_3, M), 16.9 (CH_3, m); IR ($CHCl_3$): ν = 3290 (C≡CH), 2932 (Ar), 1542 (C-OH) cm^{-1}; HRMS (ES): calcd for $C_{15}H_{18}NO$ [*M* + H]$^+$: 228.13829; found: 228.13870.

***tert*-Butyl 2-(1-hydroxybut-3-yn-1-yl)-1*H*-indole-1-carboxylate IV.** *Method C*. From the corresponding aldehyde [D. Uredi, D. R. Motati, E. B. Watkins, *Org. Lett.* **2018**, *20*, 6336] (900 mg, 3.67 mmol), compound **IV** was obtained in 93% yield (975 mg, 3.42 mmol) as a colourless oil after column chromatography on silica gel (EtOAc/hexane = 1 :3). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 7.99 (1H, d, *J* = 8.0 Hz), 7.53 (1H, d, *J* = 8.0 Hz), 7.29 (1H, dd, *J* = 8.0, 7.2 Hz), 7.22 (1H, dd, *J* = 8.0, 7.2 Hz), 6.72 (1H, s), 5.28 (1H, t, *J* = 6.4 Hz), 4.25 (1H, brs), 2.94 (1H, ddd, *J* = 17.2, 6.4, 2.8 Hz), 2.87 (1H, ddd, *J* = 17.2, 6.4, 2.8 Hz), 2.06 (1H, t, *J* = 2.8 Hz), 1.72 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* = 151.5, 141.4, 136.3, 128.8, 124.6, 123.1, 121.0, 115.7, 108.5, 85.3, 80.5, 70.7, 66.4, 28.2, 25.6; IR (neat): *ν* = 3471, 3293, 2975, 1795, 1723, 1455, 1332, 1158, 749 cm^{-1}; HRMS (ESI-TOF): calcd for $C_{17}H_{19}NNaO_3$ [*M*+Na]$^+$: 308.1263; found: 308.1258.

Palladium-catalyzed reaction between iodoarenes and terminal alkynes 5b and I–IV. General procedure for the synthesis of aryl-substituted alkynes 5a and 5c–n. $PdCl_2(PPh_3)_2$ (0.00352 mmol, 1% mol), CuI (0.00703 mmmol, 2% mol), were sequentially added to a solution of the corresponding terminal alkyne (0.352 mmol, 1 equiv.) in Et_3N (0.7 mL) at room temperature. After

five minutes, the appropriate iodoarene (0.703 mmol, 2 equiv.) in Et_3N (0.7 mL) was added under argon atmosphere. The reaction mixture was stirred at room temperature. After completion of the reaction as indicated by TLC, the mixture was poured into water (5 mL) and extracted with ethyl acetate (3 x 5 mL). The organic layer was washed with water (2 x 10 mL) and brine (2 x 10 mL), dried over $MgSO_4$, and concentrated under reduced pressure. Chromatography of the residue eluting with *n*-hexane/ethyl acetate mixtures gave analytically pure compounds. Spectroscopic and analytical data for compounds **5a, 5c–n** follow.

1-(1,5-Dimethyl-1*H*-indol-2-yl)-4-(4-methoxyphenyl)but-3-yn-1-ol 5a. From 75 mg (0.35 mmol) of alkyne **5b**, and after flash chromatography of the residue using *n*-hexane/ethyl acetate (3:1) as eluent gave compound **5a** (60 mg, 53%) as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.39 (1H, m, CH_{Ar}), 7.36 (2H, *AA'*XX', 2 CH_{Ar} PMP), 7.23 (1H, d, *J* = 8.4 Hz, CH_{Ar}), 7.07 (1H, dd, *J* = 8.3, 1.4 Hz, CH_{Ar}), 6.83 (2H, AA'*XX'*, 2 CH_{Ar} PMP), 6.52 (1H, brs, CH_{Ar}), 5.10 (1H, t, *J* = 6.2 Hz, C*H*OH), 3.83 (3H, s, CH_3), 3.81 (3H, s, CH_3), 3.14 (2H, dd, *J* = 6.3, 2.0 Hz, CH_2), 2.46 (3H, s, CCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.5 (C_{Ar}), 140.1 (C_{Ar}), 136.4 (C_{Ar}), 133.1 (2xCH_{Ar}), 128.8 (C_{Ar}), 127.3 (C_{Ar}), 123.6 (CH_{Ar}), 120.5 (CH_{Ar}), 115.3 (C_{Ar}), 113.9 (2xCH_{Ar}), 108.8 (CH_{Ar}), 98.8 (CH_{Ar}), 83.9 (*C*≡C), 83.5 (C≡*C*), 65.6 (CHOH), 55.3 (OCH_3), 30.2 (NCH_3), 27.7 (CH_2), 21.3 (C*C*H_3); IR ($CHCl_3$): ν = 2922 (Ar), 1503 (C-OH), 1207 (C-H) cm^{-1}; HRMS (ES): calcd for $C_{21}H_{22}NO_2$ [*M* + H]$^+$: 320.16451; found: 320.16607.

1-(1,5-Dimethyl-1*H*-indol-2-yl)-4-phenylbut-3-yn-1-ol 5c. From 90 mg (0.42 mmol) of alkyne **5b**, and after flash chromatography of the residue using *n*-hexane/ethyl acetate (3:1) as eluent gave compound **5c** (80 mg, 66%) as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42-7.36 (3H, m, CH_{Ar}), 7.27-7.15 (4H, m, CH_{Ar}), 7.04 (1H, d, *J* = 8.4 Hz, CH_{Ar}), 6.47 (1H, s, CH_{Ar}), 5.04 (1H, t, *J* = 6.2 Hz, C*H*OH), 3.75 (3H, s, NCH_3), 3.09 (2H, d, *J* = 5.8 Hz, CH_2), 2.43 (3H, s, CCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.9 (C_{Ar}), 136.3 (C_{Ar}), 131.7 (2xCH_{Ar}), 128.7 (C_{Ar}), 128.2 (2xCH_{Ar}), 128.0 (CH_{Ar}) 127.2 (C_{Ar}), 123.6 (CH_{Ar}), 123.1 (C_{Ar}), 120.5 (CH_{Ar}), 108.8 (CH_{Ar}), 98.8 (CH_{Ar}), 85.5 (*C*≡C),

83.6 (C≡*C*), 65.5 (CHOH), 30.1 (NCH_3), 27.6 (CH_2), 21.3 (C*C*H_3); IR ($CHCl_3$): ν = 2920 (Ar), 1489 (C-OH) cm^{-1}; HRMS (ES): calcd for $C_{20}H_{20}NO$ $[M + H]^+$: 290.15290; found: 290.15394.

4-(2,4-Dimethoxyphenyl)-1-(1,5-dimethyl-1*H*-indol-2-yl)but-3-yn-1-ol 5d. From 120 mg (0.56 mmol) of alkyne **5b**, and after flash chromatography of the residue using *n*-hexane/ethyl acetate (3:1) as eluent gave compound **5d** (73 mg, 37%) as a yellow oil; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.40 (1H, brs, CH_{Ar}), 7.34–7.29 (1H, m, CH_{Ar}), 7.22 (1H, d, *J* = 8.4 Hz, CH_{Ar}), 7.07 (1H, d, *J* = 8.4 Hz, CH_{Ar}), 6.53 (1H, brs, CH_{Ar}), 6.46–6.43 (2H, m, CH_{Ar}), 5.11 (1H, t, *J* = 6.1 Hz, C*H*OH), 3.85 (3H, s, NCH_3), 3.82 (6H, s, 2xOCH_3), 3.20–3.15 (2H, m, CH_2), 2.92 (1H, brs, OH), 2.47 (3H, s, CCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.3 (C_{Ar}), 160.9 (C_{Ar}), 140.0 (C_{Ar}), 136.3 (C_{Ar}), 133.8 (CH_{Ar}), 128.6 (C_{Ar}), 127.3 (C_{Ar}), 123.4 (CH_{Ar}), 120.4 (CH_{Ar}), 108.7 (CH_{Ar}), 104.7 (C_{Ar}), 104.6 (CH_{Ar}) 98.8 (CH_{Ar}), 98.3 (CH_{Ar}), 88.3 (*C*≡C), 80.1 (C≡*C*), 65.4 (CHOH), 55.7 (OCH_3), 55.3 (OCH_3), 30.1 (NCH_3), 28.0 (CH_2), 21.3 (C*C*H_3); IR ($CHCl_3$): ν = 2920 (Ar), 1210 (C-O) cm^{-1}; HRMS (ES): calcd for $C_{22}H_{24}NO_3$ $[M + H]^+$: 350.17507; found: 350.17672.

1-(1,5-Dimethyl-1*H*-indol-2-yl)-4-(thiophen-2-yl)but-3-yn-1-ol 5e. From 150 mg (0.7 mmol) of the alkyne **5b**, and after flash chromatography of the residue using *n*-hexane/ethyl acetate (3:1) as eluent gave compound **5e** (191 mg, 92%) as a yellow oil; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.40 (1H, brs, CH_{Ar}), 7.24–7.17 (3H, m, CH_{Ar}), 7.08 (1H, d, *J* = 8.4 Hz, CH_{Ar}), 6.96 (1H, dd, *J* = 5.0, 3.8 Hz, CH_{Ar}), 6.50 (1H, brs, CH_{Ar}), 5.13–5.11 (1H, m, C*H*OH), 3.83 (3H, s, NCH_3), 3.19–3.16 (2H, m, CH_2), 2.46 (3H, s, CCH_3), 2.30 (1H, brs, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.8 (C_{Ar}), 136.4 (C_{Ar}), 131.8 (CH_{Ar}), 128.8 (C_{Ar}), 127.2 (C_{Ar}), 126.8 (CH_{Ar}), 126.6 (CH_{Ar}) 123.7 (CH_{Ar}), 123.3 (C_{Ar}), 120.5 (CH_{Ar}), 108.8 (CH_{Ar}), 98.8 (CH_{Ar}), 89.7 (*C*≡C), 76.7 (C≡*C*), 65.4 (CHOH), 30.2 (NCH_3), 27.9 (CH_2), 21.4 (CCH_3); IR ($CHCl_3$): ν = 2920 (Ar) cm^{-1}; HRMS (ES): calcd for $C_{18}H_{18}NOS$ $[M + H]^+$: 296.11036; found: 296.11007.

1-(1-Methyl-1*H*-indol-2-yl)-4-(thiophen-2-yl)but-3-yn-1-ol 5f. From 80 mg (0.4 mmol) of the corresponding alkyne, and after flash chromatography of the residue using *n*-hexane/ethyl acetate (3:1) as eluent gave compound **5f** (38 mg, 34%) as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.74 (1H, d, *J* = 7.9 Hz, CH_{Ar}), 7.50–7.19 (5H, m, CH_{Ar}), 7.07 (1H, dd, *J* = 5.1, 3.7 Hz, CH_{Ar}), 6.68 (1H, s, CH_{Ar}), 5.21 (1H, brs, C*H*OH), 3.91 (3H, s, NCH_3), 3.28-3.26 (2H, m, CH_2), 2.57 (1H, brs, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.8 (C_{Ar}), 137.9 (C_{Ar}), 131.8 (CH_{Ar}), 127.0 (C_{Ar}), 126.8 (CH_{Ar}), 126.6 (CH_{Ar}), 123.1 (C_{Ar}), 122.0 (CH_{Ar}), 120.9 (CH_{Ar}), 119.6 (CH_{Ar}), 109.1 (CH_{Ar}), 99.4 (CH_{Ar}), 89.6 (*C*≡C), 76.8 (C≡*C*), 65.4 (CHOH), 30.2 (NCH_3), 27.9 (CH_2).; IR ($CHCl_3$): ν = 2921 (Ar) cm^{-1}; HRMS (ES): calcd for $C_{17}H_{16}NOS$ [*M* + H]$^{+}$: 282.09471; found: 282.09604.

4-(4-Methoxyphenyl)-1-(1-methyl-1*H*-indol-2-yl)but-3-yn-1-ol 5g. Described in J. Wang, H.-T. Zhu, Y.-F. Qiu, Y. Niu, S. Chen, Y.-X. Li, X.-Y. Liu, *Org. Lett.* **2015**, *17*, 3186.

1-(3-Iodo-1-metyl-1*H*-indol-2-yl)-4(4-methoxyphenyl)but-3-yn-1-ol 5g-I. From 50 mg (0.154 mmol) of the corresponding alkyne, and after flash chromatography of the residue using *n*-hexane/ethyl acetate (3:1) as eluent gave compound **5g-I** (35 mg, 54%) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): *δ* = 7.64-7.61 (1H, m, H_{Ar}), 7.37-7.32 (2H, *AA'*XX', 2 CH_{ArPMP}), 7.20-7.13 (1H, m, H_{Ar}), 6.91-6.88 (2H, m, H_{Ar}), 6.57-6.53 (2H, AA'*XX'*, 2 CH_{ArPMP}), 5.35 (1H, t, *J* = 7.2 Hz, C*H*-OH), 3.34 (3H, s, O-CH_3), 3.15 (3H, s, N-CH_3), 2.91-2.72 (2H, m, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* = 160.4 (C_{Ar}), 139.7 (C_{Ar}), 139.3 (C_{Ar}), 134.1 (2xCH_{Ar}), 131.0 (C_{Ar}), 123.9 (CH_{Ar}), 122.5 (CH_{Ar}), 121.5 (CH_{Ar}), 116.7 (C_{Ar}), 114.9 (2xCH_{Ar}), 110.3 (CH_{Ar}), 84.8 (C≡), 84.2 (C≡), 69.7 (CH-OH), 55.3 (O-CH_3), 31.8 (N-CH_3), 28.7 (CH_2).

4-(2,4-Dimethoxyphenyl)-1-(1-methyl-1*H*-indol-2-yl)but-3-yn-1-ol 5h. From 190 mg (0.95 mmol) of the corresponding alkyne, and after flash chromatography of the residue using *n*-hexane/ethyl acetate (3:1) as eluent gave compound **5h** (160 mg, 47%) as yellow solid; mp 123.9-125.4 ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.62 (1H, d, *J* = 7.8 Hz, CH_{Ar}), 7.37–7.20 (3H, m, CH_{Ar}),

7.14–7.08 (1H, m, CH_{Ar}), 6.62 (1H, s, CH_{Ar}), 6.46–6.43 (2H, m, CH_{Ar}), 5.14 (1H, t, *J* = 3.3 Hz, C*H*OH), 3.86 (3H, s, OCH_3), 3.85 (3H, s, OCH_3), 3.82 (3H, s, NCH_3), 3.27–3.10 (2H, m, CH_2), 2.88 (1H, brs, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.3 (C_{Ar}), 160.9 (C_{Ar}), 139.9 (C_{Ar}), 137.9 (C_{Ar}), 133.8 (C_{Ar}), 127.1 (C_{Ar}), 121.8 (C_{Ar}), 120.8 (C_{Ar}), 119.5 (C_{Ar}), 109.1 (C_{Ar}), 104.7 (C_{Ar}), 104.6 (C_{Ar}), 99.4 (C_{Ar}), 98.3 (C_{Ar}), 88.2 (*C*≡C), 80.2 (C≡*C*), 65.3 (CHOH), 55.7 (OCH_3), 55.4 (OCH_3), 30.1 (NCH_3), 27.9 (CH_2); IR ($CHCl_3$): ν = 2919 (Ar), 1210 (C-H) cm^{-1}; HRMS (ES): calcd for $C_{21}H_{22}NO_3$ $[M + H]^+$: 335.15942; found: 336.15826.

1-(5-Methoxy-1-methyl-1*H*-indol-2-yl)-4-(4-methoxyphenyl)but-3-yn-1-ol 5i. From 138 mg (0.6 mmol) of alkyne **I**, and after flash chromatography of the residue using *n*-hexane/ethyl acetate (3:1) as eluent gave compound **5i** (147 mg, 73%) as a yellow oil; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.36 (2H, *AA'*XX', 2CH_{Ar}PMP), 7.22 (1H, d, *J* = 9.0 Hz, CH_{Ar}), 7.08–7.07 (1H, m, CH_{Ar}), 6.91 (1H, dd, *J* = 8.9, 2.4 Hz, CH_{Ar}), 6.83 (2H, AA'*XX'*, 2CH_{Ar}PMP), 6.52 (1H, brs, CH_{Ar}), 5.09 (1H, s, C*H*OH), 3.86 (3H, s, NCH_3), 3.82 (3H, s, OCH_3), 3.81 (3H, s, CH_3), 3.14–3.12 (2H, m, CH_2), 2.45 (1H, brs, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.4 (C_{Ar}), 154.1 (C_{Ar}), 140.5 (C_{Ar}), 133.2 (C_{Ar}), 133.1 (2xCH_{Ar}), 127.3 (C_{Ar}), 115.1 (C_{Ar}), 113.8 (2xCH_{Ar}), 112.2 (CH_{Ar}), 109.9 (CH_{Ar}), 102.4 (CH_{Ar}), 98.9 (CH_{Ar}), 83.9 (*C*≡C), 83.5 (C≡*C*), 65.5 (CHOH), 55.8 (OCH_3), 55.2 (OCH_3), 30.3 (NCH_3), 27.6 (CH_2); IR ($CHCl_3$): ν = 2928 (Ar), 1575 (C-O), 1290 (C-O) cm^{-1}; HRMS (ES): calcd for $C_{21}H_{22}NO_3$ $[M + H]^+$: 336.15942; found: 336.15825.

4-(2,4-Dimethoxyphenyl)-1-(5-methoxy-1-methyl-1*H*-indol-2-yl)but-3-yn-1-ol 5j. From 115 mg (0.51 mmol) of alkyne **I**, and after flash chromatography of the residue using *n*-hexane/ethyl acetate (3:1) as eluent gave compound **5j** (115 mg, 63%) as a yellow oil; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.31 (1H, d, *J* = 9.1 Hz, CH_{Ar}), 7.21 (1H, d, *J* = 8.9 Hz, CH_{Ar}), 7.07 (1H, d, *J* = 2.3 Hz, CH_{Ar}), 6.90 (1H, dd, *J* = 8.9, 2.4 Hz, CH_{Ar}), 6.52 (1H, s, CH_{Ar}), 6.45–6.42 (2H, m, CH_{Ar}), 5.10 (1H, t, *J* = 6.1 Hz, C*H*OH), 3.85 (3H, s, OCH_3), 3.84 (3H, s, OCH_3), 3.82 (3H, s, OCH_3), 3.81 (3H, s, NCH_3), 3.16 (2H,

t, J = 6.4 Hz, CH_2), 2.91 (1H, brs, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.2 (C_{Ar}), 160.9 (C_{Ar}), 154.0 (C_{Ar}), 140.5 (C_{Ar}), 133.8 (CH_{Ar}), 133.2 (C_{Ar}), 127.3 (C_{Ar}), 112.0 (CH_{Ar}), 109.8 (CH_{Ar}), 104.7 (C_{Ar}), 104.6 (CH_{Ar}), 102.4 (CH_{Ar}), 98.9 (CH_{Ar}), 98.3 (CH_{Ar}), 88.2 (*C*≡C), 80.1 (C≡*C*), 65.3 (CHOH), 55.8 (OCH_3), 55.7 (OCH_3) 55.4 (OCH_3), 30.2 (NCH_3), 28.0 (CH_2); IR ($CHCl_3$): ν = 2996 (Ar), 1485 (C-O), 1245 (C-O) cm^{-1}; HRMS (ES): calcd for $C_{22}H_{24}NO_4$ [M + H]$^+$: 366.16998; found: 366.17012.

1-(5-Chloro-1-methyl-1*H*-indol-2-yl)-4-(4-methoxyphenyl)but-3-yn-1-ol 5k. From 250 mg (1.07 mmol) of alkyne **II**, and after flash chromatography of the residue using *n*-hexane/ethyl acetate (3:1) as eluent gave compound **5k** (150 mg, 41%) as a yellow oil; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.57−7.56 (1H, m, CH_{Ar}), 7.35 (2H, AA'*XX'* 2CH_{Ar} PMP), 7.22−7.16 (2H, m, CH_{Ar}), 6.80 (2H, *AA'*XX' 2CH_{Ar} PMP), 6.54 (1H, brs, CH_{Ar}), 5.09 (1H, d, J = 5.3 Hz, C*H*OH), 3.83 (3H, s, OCH_3), 3.81 (3H, s, NCH_3), 3.15-3.12 (2H, m, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.5 (C_{Ar}), 141.2 (C_{Ar}), 136.3 (C_{Ar}), 133.1 (2xCH_{Ar}), 128.0 (C_{Ar}), 125.2 (C_{Ar}), 122.2 (CH_{Ar}), 120.2 (CH_{Ar}), 115.0 (C_{Ar}), 113.9 (2xCH_{Ar}), 110.1 (CH_{Ar}), 99.0 (CH_{Ar}), 83.8 (*C*≡C), 83.5 (C≡*C*), 65.4 (CHOH), 55.3 (OCH_3), 30.4 (NCH_3), 27.6 (s, CH_2); IR ($CHCl_3$): ν = 2925 (Ar), 1256 (C-O) cm^{-1}; HRMS (ES): calcd for $C_{20}H_{19}ClNO_2$ [M + H]$^+$: 340.10988; found: 340.10950.

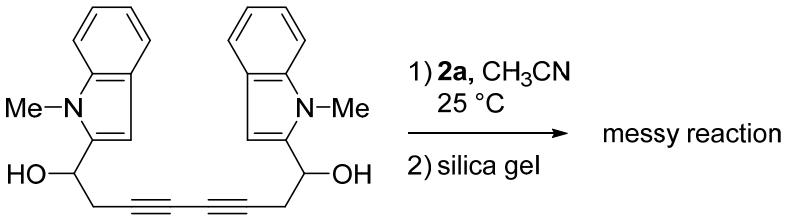
1-(5-Chloro-1-methyl-1*H*-indol-2-yl)-4-(2,4-dimethoxyphenyl)but-3-yn-1-ol 5l. From 250 mg (1.07 mmol) of alkyne **II**, and after flash chromatography of the residue using *n*-hexane/ethyl acetate (3:1) as eluent gave compound **5l** (108 mg, 27%) as a yellow oil; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.55 (1H, d, J = 1.6 Hz, CH_{Ar}), 7.31-7.15 (3H, m, CH_{Ar}), 6.55 (1H, s, CH_{Ar}), 6.45−6.42 (2H, m, CH_{Ar}), 5.10 (1H, brs, C*H*OH), 3.84 (3H, s, OCH_3), 3.83 (3H, s, OCH_3), 3.82 (3H, s, NCH_3), 3.16 (2H, dd, J = 6.1, 4.9 Hz, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.3 (C_{Ar}), 161.0 (C_{Ar}) 141.3 (C_{Ar}), 136.3 (C_{Ar}), 133.8 (CH_{Ar}), 128.0 (C_{Ar}), 125.1 (C_{Ar}), 122.1 (CH_{Ar}), 120.1 (CH_{Ar}), 110.1 (CH_{Ar}), 104.6 (CH_{Ar}), 104.5 (C_{Ar}), 99.1 (CH_{Ar}), 98.3 (CH_{Ar}), 87.8 (*C*≡C), 80.5 (C≡*C*), 65.2 (C*H*OH), 55.8 (OCH_3), 55.4 (OCH_3), 30.4 (NCH_3), 28.0 (CH_2); IR ($CHCl_3$): ν = 1037 (Ar) cm^{-1}; HRMS (ES): calcd for $C_{21}H_{21}ClNO_3$ [M + H]$^+$: 370.12045; found: 370.12225.

4-(2,4-Dimethoxyphenyl)-1-(1,5-dimethyl-1*H*-indol-2-yl)-2-methylbut-3-yn-1-ol 5m. From 165 mg (0.72 mmol) of alkyne **5b**, and after flash chromatography of the residue using *n*-hexane/ethyl acetate (3:1) as eluent gave compound **5m** (168 mg, 64%) as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.28 (1H, s, CH_{Ar}, M+m), 7.23-7.20 (0.6H, m, CH_{Ar}, M), 7.14–7.08 (1.4H, m, CH_{Ar}, M+m), 6.96-6.93 (1H, dd, *J* = 8.4, 1.7 Hz, CH_{Ar}, M+m), 6.60 (0.4H, s, CH_{Ar}, m), 6.43 (0.6H, s, CH_{Ar}, M), 6.35-6.28 (2H, m, CH_{Ar}, M+m), 4.83 (0.4H, d, *J* = 6.1 Hz, C*H*OH, m), 4.64 (0.6H, d, *J* = 6.7 Hz, C*H*OH, M), 3.74 (1.7H, s, CH_3, M+m), 3.72 (1.6H, s, CH_3, M+m), 3.70 (1.8H, s, CH_3, M+m), 3.68 (1.4H, s, CH_3, M+m), 3.65 (2.5H, s, CH_3, M+m), 3.31-3.17 (1H, m, C*H*CH_3, M+m), 2.35 (3H, s, CC*H*$_3$, M+m), 1.27 (1.3H, d, *J* = 7.02 Hz, CC*H*$_3$, m), 1.23 (1.7H, d. *J* = 6.9 Hz, CC*H*$_3$, M); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.3 (C_{Ar}, M), 161.2 (C_{Ar}, m), 160.9 (C_{Ar}, M), 160.7 (C_{Ar}, m) 139.8 (C_{Ar}, m), 139.0 (C_{Ar}, M), 136.4 (C_{Ar}, M), 136.0 (C_{Ar}, m), 133.8 (CH_{Ar}, m), 133.4 (CH_{Ar}, M), 128.5 (C_{Ar}, M+m), 127.5 (C_{Ar}, m), 127.4 (C_{Ar}, M), 123.2 (CH_{Ar}, M), 123.1 (CH_{Ar}, m), 120.3 (CH_{Ar}, m), 120.3 (CH_{Ar}, M), 108.7 (CH_{Ar}, M+m), 104.9 (C_{Ar}, m), 104.6 (C_{Ar}, M), 104.6 (CH_{Ar}, M), 104.5 (CH_{Ar}, m), 100.1 (CH_{Ar}, M), 99.6 (CH_{Ar}, m), 98.3 (CH_{Ar}, M+m), 93.3 (*C*≡C, m), 93.2 (*C*≡C, M), 80.5 (C≡*C*, M), 79.5 (C≡*C*, m), 70.9 (CHOH, M), 69.9 (CHOH, m), 55.7 (OCH_3, M), 55.6 (OCH_3, m), 55.4 (OCH_3, M), 55.3 (OCH_3, m), 34.0 (NCH_3, M), 33.8 (NCH_3, m), 30.3 (*C*HCH_3, M), 30.2 (*C*HCH_3, m), 21.3 (2 x C*C*H$_3$, M+m), 18.1 (CH*C*H$_3$, M), 16.7 (CH*C*H$_3$, m); IR ($CHCl_3$): ν = 1210 (C-O), 1034 (Ar) cm^{-1}; HRMS (ES): calcd for $C_{23}H_{26}NO_3$ [*M* + H]$^+$: 364.19072; found: 364.19049.

***tert*-Butyl 2-(1-hydroxy-4-(4-methoxyphenyl)but-3-yn-1-yl)-1*H*-indole-1-carboxylate 5n.** From *tert*-butyl 2-(1-hydroxybut-3-yn-1-yl)-1*H*-indole-1-carboxylate **IV** (856 mg, 3.00 mmol) and *p*-iodoanisole (702 mg, 3.0 mmol), this compound was obtained in 61% yield (721 mg, 1.84 mmol) as a yellow oil after column chromatography on silica gel (EtOAc/hexane = 1 : 6). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 8.00 (1H, dd, *J* = 8.0, 0.8 Hz), 7.53 (1H, dd, *J* = 8.0, 0.8 Hz), 7.31-7.20 (4H, m), 6.78-6.75 (3H, m), 5.35 (1H, dd, *J* = 6.8, 6.4 Hz), 3.76 (3H, s), 3.15 (1H, dd, *J* = 16.8, 6.8 Hz), 3.06 (1H, dd, *J* = 16.8, 6.4 Hz), 1.72 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* = 159.2, 151.2, 141.9, 136.4,

133.0, 128.9, 124.4, 123.1, 120.9, 115.7, 115.6, 113.8, 108.5, 85.2, 84.6, 82.7, 66.9, 55.2, 28.2, 26.8; IR (neat): ν = 3453, 2955, 1724, 110, 1334, 1245, 1165, 837, 746 cm^{-1}; HRMS (ESI-TOF): calcd for $C_{24}H_{25}NNaO_4$ $[M+Na]^+$: 414.1681; found: 414.1674.

1,8-Bis(1-methyl-1*H*-indol-2-yl)octa-3,5-diyne-1,8-diol 5g-dimer. $Cu(OAc)_2$ (1.4 g, 8 mmol) was added at room temperature to a solution of the alkyne **5g** (720 mg, 3.8 mmol) in CH_3CN (86 mL) and Et_3N (0.64 mL, 4.58 mmol). The reaction was stirred at 80ºC room temperature for 2 hours. After disappearance of the starting material (TLC), the mixture was extracted with AcOEt (3 × 25 mL) and washed with brine (3 x 25 mL), dried ($MgSO_4$), and concentrated under reduced pressure. Chromatography of the residue using ethyl acetate/*n*-hexane (1:2) mixtures gave 620 mg (88%) of analytically pure compound **5g-dimer**. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.60 (2H, d, J = 7.8 Hz, H_{Ar}), 7.32 (2H, d, J = 8.2 Hz, H_{Ar}), 7.25-7.20 (2H, m, H_{Ar}), 7.14-7.09 (2H, m, H_{Ar}), 6.53 (2H, s, H_{Ar}), 5.06 (2H, s, 2xC*H*-OH), 3.82 (6H, s, 2xCH_3), 3.02 (4H, d, J = 6.0 Hz, 2xCH_2), 2.17 (2H, s, 2xOH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.5 (2xC_{Ar}), 138.0 (2xC_{Ar}), 127.0 (2xC_{Ar}), 122.2 (2xCH_{Ar}), 120.9 (2xCH_{Ar}), 119.7 (2xCH_{Ar}), 109.2 (2xCH_{Ar}), 99.5 (2xCH_{Ar}), 74.0 (2xC≡), 68.0 (2xC≡), 65.3 (2xCH-OH), 30.1 (2xCH_3), 27.4 (2xCH_2); IR ($CHCl_3$): ν = 1469 (C–O) cm^{-1}; HRMS (ES): calcd for $C_{26}H_{25}N_2O_2$ $[M + H]^+$: 397.19303; found: 397.19105.



5g-dimer

General procedure for the reaction between alkynols 5 and pyridinium salt 2a. Preparation of bis(triflyl)indoles 7b and 7c and bis(triflyl)carbazoles 6a and 6d-m. 2-(2-Fluoropyridin-1-ium-1-yl)-1,1-bis[(trifluoromethyl)sulfonyl]ethan-1-ide **2a** (0.24 mmol, 1 equiv.) was added at room temperature to a solution of the appropriate alkynol **5** (0.24 mmol, 1 equiv.) in acetonitrile (9.8 mL). The reaction was stirred at room temperature until disappearance of the starting material (TLC). Then,

the mixture was concentrated under reduced pressure. Chromatography of the residue eluting with toluene/ethyl acetate mixtures gave analytically pure compounds. Spectroscopic and analytical data for compounds **7b**, **7c** and **6a**, **6d-m** follow.

2-(1,5-Dimethyl-2-(1-hydroxybut-3-yn-1yl)-1*H*-indol-3-yl)-1,1-bis((trifluoromethyl)sulfonyl)ethan-1-ide triethylammonium salt 7b-Et$_3$N. From 50 mg (0.234 mmol) of indole **5b**, and after flash chromatography, with neutral silica gel, of the residue using toluene/ethyl acetate (1:1) as eluent gave compound **7b-Et$_3$N** (61 mg, 45%) as a yellow oil. Compound **7b-Et$_3$N** has been characterized as a triethylammonium salt (78% in ^{1}H NMR); ^{1}H NMR (300 MHz, CD_3COCD_3): δ = 8.00 (1H, s, CH_{Ar}), 7.12 (1H, d, *J* = 8.3 Hz, CH_{Ar}), 6.91 (1H, d, *J* = 8.4 Hz, CH_{Ar}), 5.48–5.43 (1H, m, C*H*OH), 3.88 (2H, brs, CH_2), 3.84 (3H, s, NCH_3), 3.48-3.39 (5H, m, CH_2), 2.94 (2H, brs, OH), 2.92-2.73 (2H, m, CH_2), 2.37 (3H, s, CCH_3), 2.28 (1H, brs, C≡CH), 1.39 (7H, t, *J* = 7.3 Hz, CH_3); ^{13}C NMR (175 MHz, CD_3COCD_3): δ = 137.4 (C_{Ar}), 137.3 (C_{Ar}), 128.8 (C_{Ar}), 127.4 (2xC_{Ar}), 123.4 (CH_{Ar}), 121.4 (CH_{Ar}), 122.3 (q, *J* = 329.8 Hz, CF_3), 122.2 (q, *J* = 325.5 Hz, CF_3), 108.7 (CH_{Ar}), 70.9 (*C*≡CH, CHOH), 66.2 (C≡*C*H), 48.0 (3 x CH_2), 47.9 (CH_2), 31.5 (NCH_3), 23.7 (CH_2), 21.8 (C*C*H$_3$), 9.26 (3 x CH_3); ^{19}F NMR (282 MHz, CD_3COCD_3): δ = –79.88 (s, 3F, CF_3), –82.00 (s, 3F, CF_3); IR ($CHCl_3$): ν = 1337 (SO_2), 1183 (CF_3), 1044 (SO_2) cm^{-1}; HRMS (ES): calcd for $C_{18}H_{18}F_6NO_5S_2$ [*M* + H]$^+$: 506.05251; found: 506.05347.

2-(1,5-Dimethyl-2-(1-hydroxy-4-phenylbut-3-yn-1-yl)-1*H*-indol-3-yl)-1,1-bis((trifluoromethyl)sulfonyl)ethan-1-ide triethylammonium salt 7c-Et$_3$N. From 20 mg (0.069 mmol) of indole **5c**, and after flash chromatography, with neutral silica gel, of the residue using toluene/ethyl acetate (1:1) as eluent gave compound **7c-Et$_3$N** (35 mg, 74%) as a yellow oil. Compound **7c** has been characterized as a triethylammonium salt; ^{1}H NMR (300 MHz, CD_3COCD_3): δ = 8.03 (1H, s, CH_{Ar}), 7.30–7.28 (5H, m, CH_{Ar}), 7.12 (1H, d, *J* = 8.2 Hz, CH_{Ar}), 6.90 (1H, d, *J* = 8.3 Hz, CH_{Ar}), 5.59 (1H, brs, C*H*OH), 3.95 (2H, brs, CH_2), 3.89–3.88 (3H, m, NCH_3), 3.48-3.40 (6H, m, CH_2), 3.14-2.98 (2H, m, CH_2), 2.36 (3H, s, CCH_3), 1.41–1.36 (9H, m, CH_3); IR ($CDCl_3$): ν = 1378

(SO_2), 1178 (CF_3) cm^{-1}; HRMS (ES): calcd for $C_{24}H_{22}F_6NO_5S_2$ [*M* + H]$^+$: 582.08381; found: 582.08587. Compound **7c** is unstable in solution and a good quality ^{13}C NMR spectrum cannot be recorded.

2-(4-(4-Methoxyphenyl)-6,9-dimethyl-9*H*-carbazol-3-yl)-1,1-bis((trifluoromethyl)sulfonyl)ethan-1-ide sodium salt 6a-Na. From 60 mg (0.19 mmol) of indole **5a**, and after flash chromatography of the residue using toluene/ethyl acetate (2:1) as eluent gave compound **6a-Na** (65 mg, 56%) as a pink oil; ^1H NMR (300 MHz, CD_3COCD_3): δ = 8.00 (1H, d, *J* = 8.2 Hz, CH_{Ar}), 7.88 (1H, s, CH_{Ar}), 7.73 (1H, d, *J* = 8.2 Hz, CH_{Ar}), 7.30 (2H, AA'*XX'*, 2CH_{Ar} PMP), 7.23-7.16 (2H, m, CH_{Ar}), 7.05 (2H, *AA'*XX', 2CH_{Ar} PMP), 3.89 (3H, s, OCH_3), 3.61 (2H, brs, CH_2), 3.13 (3H, s, NCH_3), 2.48 (3H, s, CH_3); ^{13}C NMR (175 MHz, CD_3COCD_3): δ = 160.0 (C_{Ar}), 141.3 (C_{Ar}), 140.0 (C_{Ar}), 139.6 (C_{Ar}), 132.9 (2 x CH_{Ar}), 131.5 (C_{Ar}), 128.3 (C_{Ar}), 127.0 (CH_{Ar}), 124.6 (C_{Ar}), 123.8 (C_{Ar}), 122.6 (q, J_{CF} = 329.7 Hz, 2 x CF_3), 122.0 (C_{Ar}), 121.0 (CH_{Ar}), 120.1 (CH_{Ar}), 118.8 (CH_{Ar}), 114.2 (2xCH_{Ar}), 109.2 (CH_{Ar}), 65.3 (CTf_2), 55.5 (OCH_3), 32.1 (NCH_3+CH_2), 21.4 (C*C*H_3); ^{19}F NMR (282 MHz, CD_3COCD_3): δ = –79.62 (s, 6F, 2 x CF_3); ^{23}Na NMR (132 MHz, CD_3COCD_3): δ =– 8.51 (s, Na); IR ($CHCl_3$): ν = 1333 (SO_2), 1175 (CF_3), 1032 (SO_2) cm^{-1}; HRMS (ES): calcd for $C_{25}H_{22}F_6NO_5S_2$ [*M* + H]$^+$: 594.08381; found: 594.08568.

2-(4-(2,4-Dimethoxyphenyl)-6,9-dimethyl-9*H*-carbazol-3-yl)-1,1-bis((trifluoromethyl)sulfonyl)ethan-1-ide triethylammonium salt 6d-Et$_3$N (100% as triethylammonium salt by ^{1}H NMR). From 37 mg (0.10 mmol) of indole **5d**, and after flash chromatography, with neutral silica gel, of the residue using toluene/ethyl acetate (2:1) as eluent gave compound **6d-Et$_3$N** (41 mg, 56%) as a pink oil; ^1H NMR (300 MHz, CD_3COCD_3): δ = 7.98 (1H, d, *J* = 8.2 Hz, CH_{Ar}), 7.87 (1H, s, CH_{Ar}), 7.71 (1H, d, *J* = 8.2 Hz, CH_{Ar}), 7.23-7.13 (3H, m, CH_{Ar}), 6.71-6.63 (2H, m, CH_{Ar}), 3.90 (3H, s, OCH_3), 3.68 (3H, s, OCH_3), 3.68 (1H, *A*B, *J* = 18.2 Hz, CH_2), 3.55 (1H, A*B*, *J* = 18.2 Hz, CH_2), 3.42 (6H, q, *J* = 7.3 Hz, CH_2), 3.21 (3H, s, OCH_3), 2.47 (3H, s, CCH_3), 1.37 (9H, t, *J* = 7.3 Hz, CH_3); ^{13}C NMR (175 MHz, CD_3COCD_3): δ = 161.9 (C_{Ar}), 160.1 (C_{Ar}), 141.2

(C_{Ar}), 140.4 (C_{Ar}), 140.2 (C_{Ar}), 133.6 (CH_{Ar}), 128.1 (CH_{Ar}), 126.8 (C_{Ar}), 123.9 (C_{Ar}), 122.6 (q, J_{CF} = 329.5 Hz, 2xCF_3), 121.9 (C_{Ar}), 121.0 (C_{Ar}), 120.8 (C_{Ar}), 120.3 (CH_{Ar}), 120.1 (CH_{Ar}), 118.5 (CH_{Ar}), 109.1 (CH_{Ar}), 105.3 (CH_{Ar}), 99.1 (CH_{Ar}), 65.0 (CTf_2), 55.8 (OCH_3), 55.6 (OCH_3), 48.0 (3 x CH_2), 31.8 (CH_2), 31.2 (NCH_3), 21.4 (C*C*H_3), 9.3 (3 x CH_3); ^{19}F NMR (282 MHz, CD_3COCD_3): δ = –79.33 (s, 6F, 2xCF_3); IR ($CHCl_3$): ν = 1338 (SO_2), 1176 (CF_3), 1034 (SO_2) cm^{-1}; HRMS (ES): calcd for $C_{26}H_{24}F_6NO_6S_2$ [*M* + H]$^+$: 624.09437; found: 624.09675.

2-(6,9-Dimethyl-4-(thiophen-2-yl)-9*H*-carbazol-3-yl)-1,1-bis((trifluoromethyl)sulfonyl)ethan-1-ide sodium salt 6e-Na (100% as sodium salt, by ^{1}H NMR) . From 65 mg (0.22 mmol) of indole **5e**, and after flash chromatography of the residue using toluene/ethyl acetate (3:1) to toluene/ethyl acetate 2:1 as eluent gave compound **6e-Na** (47 mg, 36%) as a brown oil; ^{1}H NMR (300 MHz, CD_3COCD_3): δ = 8.07 (1H, d, *J* = 8.2 Hz, CH_{Ar}), 7.90 (1H, s, CH_{Ar}), 7.73 (1H, d, *J* = 8.2 Hz, CH_{Ar}), 7.64 (1H, dd, *J* = 5.3, 1.1 Hz, CH_{Ar}), 7.27 (1H, d, *J* = 8.3 Hz, CH_{Ar}), 7.23–7.21 (2H, m, CH_{Ar}), 7.13 (1H, d, *J* = 2.8 Hz, CH_{Ar}), 3.74 (2H, brs, CH_2), 3.29 (3H, s, NCH_3), 2.48 (3H, s, CCH_3); ^{13}C NMR (175 MHz, CD_3COCD_3): δ = 141.7 (C_{Ar}), 141.3 (C_{Ar}), 140.6 (C_{Ar}), 139.7 (C_{Ar}), 130.2 (CH_{Ar}), 128.7 (C_{Ar}), 127.9 (CH_{Ar}), 127.4 (CH_{Ar}), 127.3 (CH_{Ar}), 123.5 (C_{Ar}), 122.6 (q, J_{CF} = 330.6 Hz, 2xCF_3), 122.1 (C_{Ar}), 120.8 (CH_{Ar}), 120.3 (CH_{Ar}), 120.2 (CH_{Ar}), 116.2 (C_{Ar}), 109.4 (CH_{Ar}), 60.5 (C), 32.0 (CH_2), 31.1 (NCH_3), 21.4 (CCH_3); ^{19}F NMR (282 MHz, CD_3COCD_3): δ = –79.31 (s, 6F, 2CF_3); ^{23}Na NMR (132 MHz, CD_3COCD_3): δ =– 8.51 (s, Na); IR ($CHCl_3$): ν = 1335 (SO_2), 1178 (CF_3), 1035 (SO_2) cm^{-1}; HRMS (ES): calcd for $C_{22}H_{18}F_6NO_4S_3$ [*M* + H]$^+$: 570.02967; found: 570.03143.

2-(9-Methyl-4-(thiophen-2-yl)-9*H*-carbazol-3-yl)-1,1-bis((trifluoromethyl)sulfonyl)ethan-1-ide triethylammonium salt 6f-Et_3N. From 45 mg (0.16 mmol) of indole **5f**, and after flash chromatography, with neutral silica gel, of the residue using toluene/ethyl acetate (2:1) as eluent gave compound **6f-Et_3N** (44 mg, 42%) as a brown oil. Compound **6f-Et_3N** has been characterized as a triethylammonium salt (88% in ^{1}H NMR); ^{1}H NMR (300 MHz, CD_3COCD_3): δ = 8.12 (2H, dd, *J* = 8.0, 4.3 Hz, CH_{Ar}), 7.76 (1H, d, *J* = 8.2 Hz, CH_{Ar}), 7.66 (1H, dd, *J* = 5.2, 1.1 Hz, CH_{Ar}), 7.39 (2H, d,

J = 3.7 Hz, CH_{Ar}), 7.25–7.13 (3H, m, CH_{Ar}), 3.76 (2H, brs, CH_2), 3.44 (5H, q, J = 7.3 Hz, CH_2), 3.33 (3H, s, NCH_3), 1.39 (8H, t, J = 7.3 Hz, CH_3); ^{13}C NMR (175 MHz, CD_3COCD_3): δ = 142.9 (C_{Ar}), 142.0 (C_{Ar}), 140.4 (C_{Ar}), 139.6 (C_{Ar}), 130.3 (CH_{Ar}), 128.0 (CH_{Ar}), 127.5 (CH_{Ar}), 126.0 (CH_{Ar}), 123.4 (C_{Ar}), 122.6 (q, J_{CF} = 329.3 Hz, 2xCF_3), 122.3 (C_{Ar}), 121.1 (CH_{Ar}), 120.3 (CH_{Ar}), 120.2 (CH_{Ar}), 119.7 (CH_{Ar}), 116.3 (C_{Ar}), 109.6 (CH_{Ar}), 65.1 (CTf_2), 47.9 (3 x CH_2), 32.1 (CH_2), 31.1 (NCH_3), 9.3 (3 x CH_3); ^{19}F NMR (282 MHz, CD_3COCD_3): δ = –79.30 (s, 6F, 2xCF_3); ^{23}Na NMR (132 MHz, CD_3COCD_3): δ = –8.51 (s, Na); IR ($CHCl_3$): ν = 1335 (SO_2), 1178 (CF_3), 1035 (SO_2) cm^{-1}; HRMS (ES): calcd for $C_{21}H_{16}F_6NO_4S_3$ [M + H]$^+$: 556.01402; found: 556.01650.

2-(4-(4-Methoxyphenyl)-9-methyl-9*H*-carbazol-3-yl)-1,1-bis((trifluoromethyl)sulfonyl)ethan-1-ide sodium salt 6g-Na. From 30 mg (0.098 mmol) of indole **5g**, and after flash chromatography of the residue using *n*-hexane/ethyl acetate (1:1) as eluent gave compound **6g-Na** (37 mg, 63%) as a brown oil; ^{1}H NMR (500 MHz, CD_3COCD_3): δ = 8.09 (1H, d, J = 7.7 Hz, CH_{Ar}), 8.05 (1H, d, J = 8.2 Hz, CH_{Ar}), 7.76 (1H, d, J = 8.2 Hz, CH_{Ar}), 7.37–7.31 (4H, m, CH_{Ar}), 7.16–7.13 (1H, m, CH_{Ar}), 7.07–7.05 (2H, m, CH_{Ar}), 3.90 (3H, s, OCH_3), 3.62 (2H, s, CH_2), 3.17 (3H, s, NCH_3); ^{13}C NMR (125 MHz, CD_3COCD_3): δ = 160.1 (C_{Ar}), 142.9 (C_{Ar}), 139.8 (C_{Ar}), 139.7 (C_{Ar}), 133.0 (2xCH_{Ar}), 131.5 (C_{Ar}), 125.7 (CH_{Ar}), 124.7 (C_{Ar}), 123.7 (C_{Ar}), 122.6 (q, J_{CF} = 329.1 Hz, 2xCF_3), 122.1 (C_{Ar}), 121.2 (CH_{Ar}), 120.2 (CH_{Ar}), 119.4 (CH_{Ar}), 118.8 (CH_{Ar}), 114.2 (2xCH_{Ar}), 109.5 (CH_{Ar}), 65.3 (CTf_2), 55.5 (OCH_3), 32.1 (CH_2), 32.0 (NCH_3); ^{19}F NMR (282 MHz, CD_3COCD_3): δ = –79.63 (s, 6F, 2x CF_3); ^{23}Na NMR (132 MHz, CD_3COCD_3): δ = – 8.40; IR ($CHCl_3$): ν = 1338 (SO_2), 1185 (CF_3), 1035 (SO_2) cm^{-1}; HRMS (ES): calcd for $C_{24}H_{20}F_6NO_5S_2$ [M + H]$^+$: 580.06816; found: 580.06858.

2-(4-(2,4-Dimethoxyphenyl)-9-methyl-9*H*-carbazol-3-yl)-1,1-bis((trifluoromethyl)sulfonyl)ethan-1-ide sodium salt 6h-Na. From 80 mg (0.24 mmol) of indole **5h**, and after flash chromatography of the residue using toluene/ethyl acetate (1:1) as eluent gave compound **6h-Na** (75 mg, 50%) as a brown oil; ^{1}H NMR (300 MHz, CD_3COCD_3): δ = 8.08 (1H, d, J = 7.7 Hz, CH_{Ar}), 8.02 (1H, d, J = 8.2 Hz, CH_{Ar}), 7.74 (1H, d, J = 8.2 Hz, CH_{Ar}), 7.37–7.31 (2H, m,

CH_{Ar}), 7.17-7.10 (2H, m, CH_{Ar}), 6.71–6.64 (2H, m, CH_{Ar}), 3.90 (3H, s, OCH_3), 3.68 (3H, s, OCH_3), 3.72 (*A*B, *J* = 18.0 Hz, 1H, CH_2), 3.59 (A*B*, *J* = 18.4 Hz, 1H, CH_2), 3.24 (3H, s, NCH_3); ^{13}C NMR (175 MHz, CD_3COCD_3): δ = 162.0 (C_{Ar}), 160.1 (C_{Ar}), 142.7 (C_{Ar}), 140.1 (C_{Ar}), 140.0 (C_{Ar}), 133.6 (CH_{Ar}), 125.5 (CH_{Ar}), 125.4 (C_{Ar}), 123.7 (C_{Ar}), 122.5 (q, J_{CF} = 330.7 Hz, 2xCF_3), 122.0 (C_{Ar}), 121.1 (CH_{Ar}), 120.9 (C_{Ar}), 120.1 (CH_{Ar}), 119.2 (CH_{Ar}), 118.6 (CH_{Ar}), 109.3 (CH_{Ar}), 105.2 (CH_{Ar}), 99.1 (CH_{Ar}), 64.7 (CTf_2), 55.7 (OCH_3), 55.6 (OCH_3), 31.6 (CH_2), 31.1 (NCH_3); ^{19}F NMR (282 MHz, CD_3COCD_3): δ = –79.32 (s, 6F, 2x CF_3); ^{23}Na NMR (132 MHz, CD_3COCD_3): δ = – 8.40; IR ($CHCl_3$): ν = 1337 (SO_2), 1195 (CF_3), 1038 (SO_2) cm^{-1}; HRMS (ES): calcd for $C_{25}H_{22}F_6NO_6S_2$ [*M* + H]$^+$: 610.07872; found: 610.07866.

2-(6-Methoxy-4-(4-methoxyphenyl)-9-methyl-9*H*-carbazol-3-yl)-1,1-bis((trifluoromethyl)sulfonyl)ethan-1-ide triethylammonium salt 6i-Et$_3$N. From 51 mg (0.15 mmol) of indole **5i**, and after flash chromatography, with neutral silica gel, of the residue using toluene/ethyl acetate (2:1) to toluene/ethyl acetate 1:1 as eluent gave compound **6i-Et$_3$N** (32 mg, 30%) as a brown oil. Compound **6i-Et$_3$N** has been characterized as a triethylammonium salt (56% in ^{1}H NMR); ^{1}H NMR (300 MHz, CD_3COCD_3): δ = 8.01 (1H, d, *J* = 8.2 Hz, CH_{Ar}), 7.72 (1H, d, *J* = 8.2 Hz, CH_{Ar}), 7.66 (1H, d, *J* = 2.5 Hz, CH_{Ar}), 7.30 (2H, d, *J* = 7.1 Hz, CH_{Ar}), 7.24 (1H, d, *J* = 8.8 Hz, CH_{Ar}), 7.05 (2H, dd, *J* = 7.3, 1.4 Hz, CH_{Ar}), 6.99 (1H, dd, *J* = 8.8, 2.5 Hz, CH_{Ar}), 3.89 (3H, s, OCH_3), 3.88 (3H, s, OCH_3), 3.61 (2H, brs, CH_2), 3.46 (3H, dd, *J* = 14.5, 7.2 Hz, CH_2), 3.13 (3H, s, NCH_3), 1.41 (5H, t, *J* = 7.3 Hz, CH_3); ^{13}C NMR (175 MHz, CD_3COCD_3): δ = 160.0 (C_{Ar}), 154.6 (C_{Ar}), 140.2 (C_{Ar}), 139.7 (C_{Ar}), 137.9 (C_{Ar}), 132.9 (2xCH_{Ar}), 131.5 (C_{Ar}), 124.7 (C_{Ar}), 124.0 (C_{Ar}), 122.6 (q, *J* = 278.4 Hz, 2xCF_3), 122.1 (C_{Ar}), 120.8 (CH_{Ar}), 118.9 (CH_{Ar}), 114.7 (CH_{Ar}), 114.2 (2xCH_{Ar}), 110.2 (CH_{Ar}), 103.2 (CH_{Ar}), 65.4 (CTf_2), 56.1 (OCH_3), 55.5 (OCH_3), 47.9 (3 x CH_2), 32.1 (NCH_3), 32.1 (CH_2), 9.2 (3 x CH_3); ^{19}F NMR (282 MHz, CD_3COCD_3): δ = –79.30 (s, 6F, 2CF_3); ^{23}Na NMR (132 MHz, CD_3COCD_3): δ = – 8.36 (s, Na); IR ($CHCl_3$): ν = 1336 (SO_2), 1173 (CF_3), 1032 (SO_2) cm^{-1}; HRMS (ES): calcd for $C_{25}H_{22}F_6NO_6S_2$ [*M* + H]$^+$: 610.07872; found: 610.07986.

2-(4-(2,4-Dimethoxyphenyl)-6-methoxy-9-methyl-9*H*-carbazol-3-yl)-1,1-bis((trifluoromethyl)sulfonyl)ethan-1-ide triethylammonium salt 6j-Et$_3$N. From 58 mg (0.16 mmol) of indole **5j**, and after flash chromatography, with neutral silica gel, of the residue using toluene/ethyl acetate (1:1) as eluent gave compound **6j-Et$_3$N** (55 mg, 47%) as a brown oil. Compound **6j-Et$_3$N** has been characterized as a triethylammonium salt (66% in ^{1}H NMR); ^{1}H NMR (300 MHz, CD_3COCD_3): δ = 7.99 (1H, d, *J* = 8.2 Hz, CH_{Ar}), 7.70 (1H, d, *J* = 8.2 Hz, CH_{Ar}), 7.65 (1H, d, *J* = 2.4 Hz, CH_{Ar}), 7.24 (1H, d, *J* = 8.8 Hz, CH_{Ar}), 7.14 (1H, d, *J* = 8.2 Hz, CH_{Ar}), 6.98 (1H, dd, *J* = 8.8, 2.5 Hz, CH_{Ar}), 6.70 (1H, d, *J* = 2.3 Hz, CH_{Ar}), 6.65 (1H, dd, *J* = 8.2, 2.4 Hz, CH_{Ar}), 3.89 (3H, s, OCH_3), 3.88 (3H, s, OCH_3), 3.68 (1H, *A*B, *J* = 18.0 Hz, CH_2), 3.55 (1H, A*B*, *J* = 18.4 Hz, CH_2), 3.68 (3H, s, OCH_3), 3.41 (4H, q, *J* = 7.3 Hz, CH_2), 3.20 (3H, s, NCH_3), 1.37 (6H, t, *J* = 7.3 Hz, CH_3); ^{13}C NMR (175 MHz, CD_3COCD_3): δ = 161.9 (C_{Ar}), 160.1 (C_{Ar}), 154.5 (C_{Ar}), 140.6 (C_{Ar}), 140.2 (C_{Ar}), 137.8 (C_{Ar}), 133.6 (CH_{Ar}), 124.0 (C_{Ar}), 122.6 (q, *J* = 329.4 Hz, 2xCF_3), 122.0 (C_{Ar}), 121.0 (C_{Ar}), 120.6 (CH_{Ar}), 120.3 (C_{Ar}), 118.7 (CH_{Ar}), 114.5 (CH_{Ar}), 110.0 (CH_{Ar}), 105.2 (CH_{Ar}), 103.3 (CH_{Ar}), 99.1 (CH_{Ar}), 65.0 (C-Tf_2), 56.1 (OCH_3), 55.7 (OCH_3), 55.6 (OCH_3), 48.0 (3 x CH_2), 31.7 (CH_2), 31.2 (NCH_3), 9.2 (3 x CH_3); ^{19}F NMR (282 MHz, CD_3COCD_3): δ = –79.26 (s, 6F, 2CF_3); ^{23}Na NMR (132 MHz, CD_3COCD_3): δ = – 8.49 (s, Na); IR ($CHCl_3$): ν = 1332 (SO_2), 1170 (CF_3), 1034 (SO_2) cm^{-1}; HRMS (ES): calcd for $C_{26}H_{24}F_6NO_7S_2$ [*M* + H]$^+$: 640.08929; found: 640.08845.

2-(6-Chloro-4-(4-methoxyphenyl)-9-methyl-9*H*-carbazol-3-yl)-1,1-bis((trifluoromethyl)sulfonyl)ethan-1-ide triethylammonium salt 6k-Et$_3$N. From 65 mg (0.19 mmol) of indole **5k**, and after flash chromatography, with neutral silica gel, of the residue using toluene/ethyl acetate (1:1) as eluent gave compound **6k-Et$_3$N** (62 mg, 45%) as a brown oil; ^{1}H NMR (300 MHz, CD_3COCD_3): δ = 8.12–8.08 (2H, m, CH_{Ar}), 7.79 (1H, d, *J* = 8.3 Hz, CH_{Ar}), 7.38–7.30 (4H, m, CH_{Ar}), 7.06 (2H, d, *J* = 8.8 Hz, CH_{Ar}), 3.90 (3H, s, OCH_3), 3.62 (2H, s, CH_2), 3.45–3.39 (6H, dd, *J* = 13.4, 6.4 Hz, CH_2), 3.17 (3H, s, NCH_3), 1.40 (9H, t, *J* = 7.3 Hz, CH_3); ^{13}C NMR (175 MHz, CD_3COCD_3): δ = 160.1 (C_{Ar}), 141.3 (C_{Ar}), 140.9 (C_{Ar}), 140.2 (C_{Ar}), 132.9 (2 x CH_{Ar}), 131.0 (C_{Ar}),

125.4 (CH_{Ar}), 125.0 (C_{Ar}), 124.8 (C_{Ar}), 124.4 (C_{Ar}), 122.6 (q, J = 329.6 Hz, 2 x CF_3), 121.7 (CH_{Ar}), 121.2 (C_{Ar}), 119.8 (CH_{Ar}), 119.2 (CH_{Ar}), 114.3 (2 x CH_{Ar}), 110.9 (CH_{Ar}), 55.5 (OCH_3), 47.8 (3 x CH_2), 32.3 (NCH_3), 32.2 (CH_2), 9.2 (3 x CH_3); ^{19}F NMR (282 MHz, CD_3COCD_3): δ = –79.31 (s, 6F, $2CF_3$); IR ($CHCl_3$): ν = 1334 (SO_2), 1174 (CF_3), 1032 (SO_2) cm^{-1}; HRMS (ES): calcd for $C_{24}H_{19}ClF_6NO_5S_2$ [M + H]$^+$: 614.02919; found: 614.02771.

2-(6-Chloro-4-(2,4-dimethoxyphenyl)-9-methyl-9*H*-carbazol-3-yl)-1,1-bis((trifluoromethyl)sulfonyl)ethan-1-ide triethylammonium salt 6l-Et$_3$N. From 54 mg (0.15 mmol) of indole **5l**, and after flash chromatography, with neutral silica gel, of the residue using toluene/ethyl acetate (2:1 → 1:1) as eluent gave compound **6l-Et$_3$N** (41 mg, 38%) as a brown oil. Compound **6l-Et$_3$N** has been characterized as a triethylammonium salt (51% in ^{1}H NMR); ^{1}H NMR (300 MHz, CD_3COCD_3): δ = 8.10 (1H, d, J = 1.2 Hz, CH_{Ar}), 8.06 (1H, d, J = 8.3 Hz, CH_{Ar}), 7.77 (1H, d, J = 8.3 Hz, CH_{Ar}), 7.37–7.30 (2H, m, CH_{Ar}), 7.15 (1H, d, J = 8.2 Hz, CH_{Ar}), 6.71–6.64 (2H, m, CH_{Ar}), 3.90 (3H, s, OCH_3), 3.68 (3H, s, OCH_3), 3.68 (1H, *A*B, J = 18.1 Hz, CH_2), 3.55 (1H, A*B*, J = 18.3 Hz, CH_2), 3.44 (3H, q, J = 7.3 Hz, CH_2), 3.25 (3H, s, NCH_3), 1.39 (5H, t, J = 7.3 Hz, CH_3); ^{13}C NMR (175 MHz, CD_3COCD_3): δ = 162.1 (C_{Ar}), 160.0 (C_{Ar}), 141.4 (C_{Ar}), 141.1 (C_{Ar}), 140.6 (C_{Ar}), 133.5 (CH_{Ar}), 125.3 (CH_{Ar}), 124.9 (C_{Ar}), 124.2 (C_{Ar}), 122.6 (q, J = 329.2 Hz, 2 x CF_3), 121.5 (CH_{Ar}), 121.3 (C_{Ar}), 121.1 (C_{Ar}), 119.7 (CH_{Ar}, C_{Ar}), 119.0 (CH_{Ar}), 110.7 (CH_{Ar}), 105.3 (CH_{Ar}), 99.1 (CH_{Ar}), 64.8 (CTf_2), 55.8 (OCH_3), 55.6 (OCH_3), 48.0 (3 x CH_2), 31.8 (CH_2), 31.4 (NCH_3), 9.3 (3 x CH_3); ^{19}F NMR (282 MHz, CD_3COCD_3): δ = –79.30 (s, 6F, $2CF_3$); IR ($CHCl_3$): ν = 1334 (SO_2), 1207 (CF_3), 1033 (SO_2) cm^{-1}; HRMS (ES): calcd for $C_{25}H_{20}ClF_6NNaO_6S_2$ [M + Na]$^+$: 666.0217; found: 666.02062.

2-(4-(2,4-Dimethoxyphenyl)-2,6,9-trimethyl-9*H*-carbazol-3-yl)-1,1-bis((trifluoromethyl)sulfonyl)ethan-1-ide sodium salt 6m-Na. From 51 mg (0.14 mmol) of indole **5m**, and after flash chromatography, with neutral silica gel, of the residue using toluene/ethyl acetate (2:1) as eluent gave compound **6m-Na** (39 mg, 42%) as a yellow oil; ^{1}H NMR (700 MHz,

CD_3COCD_3): δ = 7.82 (1H, s, CH_{Ar}), 7.73 (1H, s, CH_{Ar}), 7.49 (1H, brs, CH_{Ar}), 7.15–7.12 (2H, m, CH_{Ar}), 6.61–6.59 (2H, m, CH_{Ar}), 3.88 (3H, s, OCH_3), 3.82–3.73 (2H, m, CH_2), 3.62 (3H, s, OCH_3), 3.05 (3H, s, NCH_3), 2.76 (3H, s, CCH_3), 2.45 (3H, s, CCH_3); ^{13}C NMR (175 MHz, CD_3COCD_3): δ = 161.7 (C_{Ar}), 160.4 (C_{Ar}), 141.3 (C_{Ar}), 139.5 (C_{Ar}), 137.0 (C_{Ar}), 135.2 (CH_{Ar}), 130.1 (C_{Ar}), 129.8 (C_{Ar}), 129.0 (C_{Ar}), 127.7 (C_{Ar}), 126.6 (CH_{Ar}), 123.7 (C_{Ar}), 122.4 (q, J = 329.9 Hz, 2 x CF_3), 121.0 (CH_{Ar}), 120.8 (C_{Ar}), 120.0 (CH_{Ar}), 109.0 (CH_{Ar}), 104.3 (CH_{Ar}), 98.3 (CH_{Ar}), 60.4 (CTf_2), 55.6 (OCH_3), 55.5 (OCH_3), 31.3 (NCH_3), 30.3 (CH_2), 22.1 (C*C*H_3), 21.4 (C*C*H_3); ^{19}F NMR (282 MHz, CD_3COCD_3): δ = –79.12 (s, 6F, 2 x CF_3); ^{23}Na NMR (132 MHz, CD_3COCD_3): δ = – 8.39 (s, Na); IR ($CHCl_3$): ν = 1338 (SO_2), 1159 (CF_3), 1029 (SO_2) cm^{-1}; HRMS (ES): calcd for $C_{27}H_{26}F_6NO_6S_2$ $[M + H]^+$: 638.11002; found: 638.10932.

***tert*-Butyl 3-(2,2-bis((trifluoromethyl)sulfonyl)ethyl)-4-(4-methoxyphenyl)-9*H*-carbazole-9-carboxylate triethylammonium salt (6n-Et$_3$N).** From *N*-Boc-indole **5n** (97.9 mg, 0.250 mmol) and 2-fluoropyridinium salt **2a** (101 mg, 0.259 mmol), compound **6n** was obtained in 49% yield (79.3 mg, 0.103 mmol) as a yellow oil. Isolation of this compound was achieved as follows; after completed consumption of the starting indole **6n** (by TLC), Et_3N (0.5 mL) was added to the reaction mixture at room temperature. The resulting mixture was concentrated under reduced pressure to give a crude material as a brown oil. Desired carbazole salt was isolated as a brown oil after removal of neutral byproducts from the crude material by pipetting technique with a mixed solvent (EtOAc/hexane = 10 : 1, 3 x 5 mL) as a washing solvent. This compound was a mixture of two rotarmers in a ratio of 1.5 : 1 in CD_3CN at room temperature. ^1H NMR (600 MHz, CD_3CN): δ for major rotamer = 8.01-7.96 (1H, m), 7.69 (1H, d, J = 8.2 Hz), 7.52 (2H, d, J = 8.2 Hz), 7.11 (1H, brt, J = 7.1 Hz), 7.03-7.00 (1H, m), 6.93-6.87 (2H, m), 6.64 (2H, d, J = 8.8 Hz), 3.51 (3H, s), 3.38 (2H, s), 2.82-2.73 (6H, m), 0.98 (9H, s), 0.90 (9H, t, J = 7.2 Hz), δ for minor rotamer = 7.71 (1H, d, J = 7.6 Hz), 7.58 (1H, d, J = 8.8 Hz), 7.03-7.00 (1H, m), 6.93-6.87 (2H, m), 6.80 (2H, d, J = 8.8 Hz), 6.70-6.62 (2H, m), 6.19 (1H, d, J = 7.0 Hz), 3.59 (3H, s), 3.22 (2H, s), 2.82-2.73 (6H, m), 1.43 (9H, s), 0.90 (2H, t, J = 7.2 Hz); ^{19}F

NMR (376 MHz, CD_3CN): δ for major rotamer = –80.1 (6F, s), δ for minor rotamer = –80.2 (6F, s); ^{13}C NMR (150 MHz, CD_3CN): δ for major rotamer = 7.0, 25.7, 30.0, 45.8, 53.8, 62.7, 82.3, 112.6, 113.2, 116.9, 118.6, 120.0 (q, J_{CF} = 327 Hz), 121.5, 123.2, 123.9, 124.3, 125.5, 127.5, 129.6, 129.8, 133.6, 136.9, 138.9, 149.0, 157.6, δ for minor rotamer = 7.0, 26.4, 29.1, 45.8, 53.9, 62.6, 82.8, 112.5, 113.3, 114.6, 120.0 (q, J_{CF} = 327 Hz), 120.4, 121.2, 122.4, 124.7, 125.2, 126.3, 129.2, 130.1, 133.7, 135.6, 137.8, 138.1, 149.9, 158.2; IR (neat): ν = 3130, 2983, 1726, 1332, 1151, 1031, 593, 577 cm^{-1}; HRMS (ESI-TOF): calcd for $C_{28}H_{24}F_6NO_7S_2$ $[M]^-$: 664.0898; found: 664.0906.

3-(2,2-Bis(trifluoromethyl)sulfonyl)ethyl)-4-(4-methoxyphenyl)-9-methyl-9*H*-carbazol-1-ol triethylammonium salt 8. From 30 mg (0.07 mmol) of indole **5g-I**, and after flash chromatography, with neutral silica gel, of the residue using *n*-hexane/ethyl acetate (1:1) as eluent gave compound **8** (18 mg, 37%) as a yellow oil; ^1H NMR (300 MHz, $CDCl_3$): δ = 8.08 (1H, d, J = 1.0 Hz, H_{Ar}), 7.75-7.69 (2H, m, H_{Ar}), 7.56 (1H, dd, J = 8.5, 1.5 Hz, H_{Ar}), 7.22-7.13 (2H, *AA'*XX', 2 CH_{ArPMP}), 7.14 (1H, d, J = 8.5 Hz, H_{Ar}), 7.05 – 6.96 (2H, AA'*XX'*, 2 CH_{ArPMP}), 3.92 (3H, s, O-CH_3), 3.98 (2H, br, CH_2), 3.09-3.05 (6H, m, N-CH_3 + CH_3 Et_3N), 1.24 (6H, t, J = 6.3 Hz, CH_2 Et_3N). ^{13}C NMR (100 MHz, $CDCl_3$): δ =159.4 (C_{Ar}), 140.3 (C_{Ar}), 139.2 (C_{Ar}), 134.9 (C_{Ar}), 131.9 (2xCH_{Ar}), 130.70 (d, J_{CF} = 321.6 Hz, 2xCF_3), 129.2 (C_{Ar}), 128.8 (CH_{Ar}), 128.7 (C_{Ar}), 127.4 (CH_{Ar}), 123.7 (C_{Ar}), 121.7 (C_{Ar}), 120.7 (CH_{Ar}), 119.8 (CH_{Ar}), 113.4 (2xCH_{Ar}), 108.3 (CH_{Ar}), 99.8 (C_{Ar}), 55.3 (O-CH_3), 46.7 (CH_2 Et_3N), 32.7 (CH_2), 32.0 (N-CH_3), 8.3 (CH_3). ^{19}F NMR (282 MHz, $CDCl_3$): δ = –78.73 (s, 6F, 2 x CF_3).

1-Methoxy-4-(3-(*p*-tolyloxy)prop-1-yn-1-yl)benzene 9a. To a solution of 1-methyl-4-(prop-2-yn-1-yloxy)benzene [L. Alonso-Marañón, M. M. Martínez, L. A. Sarandeses, J. P. Sestelo, *Org. Biomol. Chem.* **2015**, *13*, 379.] (1.47 g, 10.0 mmol) in Et_3N (30 mL), $(Ph_3P)_2PdCl_2$ (71 mg, 0.10 mmol) and CuI (39 mg, 0.20 mmol) were added. After being stirred for 10 min at room temperature, *p*-iodoanisole (2.81 g, 12.0 mmol) was added to the reaction mixture. This mixture was stirred for additional 1 h at the same temperature, then it was poured into water (100 mL). After extraction with Et_2O (3 x 25 mL) and washing the combined organic layer with 1 M hydrochloric acid (2 x 25 mL)

and brine (25 mL), the mixture was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The resulting residue was purified by column chromatography on silica gel (EtOAc/hexane = 1 : 15) to give this compound as light brown crystals in 92% yield (2.33 g, 9.23 mmol). Mp. 111-113 °C (from EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37 (2H, brd, J = 8.8 Hz), 7.10 (2H, brd, J = 8.8 Hz), 6.93 (2H, brd, J = 8.8 Hz), 6.82 (2H, brd, J = 8.8 Hz), 4.86 (2H, s), 3.79 (3H, s), 2.29 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.9, 155.8, 133.3, 130.6, 129.9, 114.9, 114.5, 113.9, 87.0, 82.8, 57.0, 55.3, 20.5; IR (neat): ν = 2226, 1601, 1504, 1219, 1024, 830, 813, 538 cm^{-1}; HRMS (ESI-TOF): calcd for $C_{17}H_{17}O_2$ $[M+H]^+$: 253.1229; found: 253.1227.

1-(But-2-yn-1-yloxy)-4-methylbenzene 9b. To a solution of 1-methyl-4-(prop-2-yn-1-yloxy)benzene [L. Alonso-Marañón, M. M. Martínez, L. A. Sarandeses, J. P. Sestelo, *Org. Biomol. Chem.* **2015**, *13*, 379.] (733 mg, 5.01 mmol) in THF (25 mL), a 1.55 M solution of *n*-BuLi in hexane (4.8 mL, 7.5 mmol) was slowly added at –78 °C. After being stirred for 2 h at the same temperature, the reaction mixture was treated with iodomethane (0.95 mL, 15 mmol) for 1 h at room temperature. Then, the resulting mixture was quenched with a saturated solution of NH_4Cl in water (25 mL), extracted with Et_2O (3 x 25 mL), dried over anhydrous Na_2SO_4, and evaporated. Thus obtained residue was purified by column chromatography on silica gel (EtOAc/hexane = 1 : 16) to give this compound as a pale yellow oil in 91% yield (728 mg, 4.54 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.07 (2H, brd, J = 8.4 Hz), 6.86 (2H, brd, J = 8.4 Hz), 4.61 (2H, q, J = 2.4 Hz), 2.29 (2H, s), 1.85 (2H, t, J = 2.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.8, 130.5, 129.8, 114.7, 83.5, 74.3, 56.5, 20.5, 3.7; IR (neat): ν = 3027, 2920, 2225, 1607, 1508, 1219, 1016, 818 cm^{-1}; HRMS (ESI-TOF): calcd for $C_{11}H_{13}O$ $[M+H]^+$: 161.0966; found: 161.0966.

3-(2,2-Bis((trifluoromethyl)sulfonyl)ethyl)-4-(4-methoxyphenyl)-6-methyl-2*H*-chromene triethylamine salt (10a-Et$_3$N). From propargyl ether **8a** (63.7 mg, 0.252 mmol) and 2-fluoropyridinium salt **2a** (102 mg, 0.261 mmol), compound **10a-Et$_3$N** was obtained in 95% yield (153 mg, 0.237 mmol) as a yellow oil. Isolation of this compound was achieved as follows; after completed

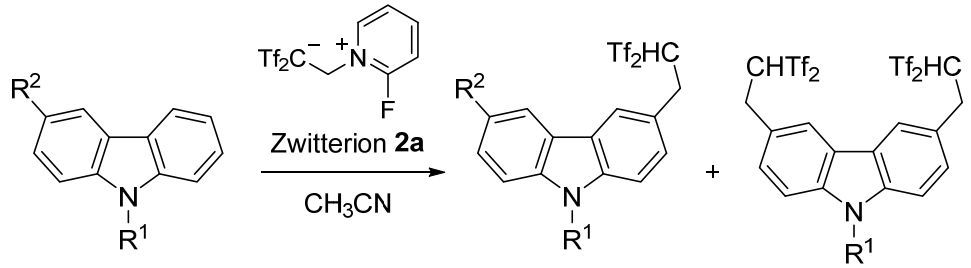
consumption of the starting ether **8a** (by TLC), Et_3N (0.5 mL) was added to the reaction mixture at room temperature. The resulting mixture was concentrated under reduced pressure to give a crude material as a brown oil. Desired salt was isolated after removal of neutral compounds from this oily material by pipetting technique with hexane (5.0 mL) as a washing solvent. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.13 (2H, d, J = 8.6 Hz), 6.93 (2H, d, J = 8.6 Hz), 9.83 (1H, d, J = 8.0 Hz), 6.71 (1H, d, J = 8.0 Hz), 6.36 (1H, s), 5.32 (1H, br, N*H*), 4.98 (2H, s), 3.85 (3H, s), 3.20 (2H, brs), 3.06 (6H, q, J = 7.2 Hz), 2.10 (3H, s), 1.28 (9H, t, J = 7.2 Hz); ^{19}F NMR (376 MHz, CD_3CN): δ = –79.7 (6F, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.5, 151.2, 131.3, 130.4, 129.9, 129.5, 128.9, 128.2, 126.3, 125.8, 121.2 (q, J_{CF} = 327 Hz), 114.8, 113.5, 66.9, 59.9, 55.1, 46.7, 28.6, 20.6, 8.5; IR (neat): ν = 3130, 1608, 1335, 1164, 1035, 590cm^{-1}; HRMS (ESI-TOF): calcd for $C_{21}H_{17}F_6O_6S_2$ $[M]^-$: 543.0371; found: 543.0380.

1-(9*H*-Carbazol-9-yl)ethan-1-one 11b. To a solution of 9*H*-carbazole (2.51 g, 15.0 mmol) and acetic anhydride (5.0 mL, 52.9 mmol) in $CHCl_3$ (25 mL), concentrated H_2SO_4 (2 drops) was added at room temperature. After being heated for 5 h under reflux, the reaction mixture was evaporated. Thus obtained solid material was dissolved in Et_2O (40 mL), then the resulting solution was washed with saturated $NaHCO_3$ aqueous solution (40 mL x 2) and water (40 mL x 2). After removal of solvents under reduced pressure, 1-(9*H*-carbazol-9-yl)ethan-1-one **11b** was obtained in 69% yield (2.17 g, 10.4 mmol). This material was used for further experiment without additional purification. The structure of this compound was confirmed by comparison of reported NMR data [Bjørsvik, H.-R.; Elumalai, V. *Eur. J. Org. Chem.* **2016**, 5474]. ^{1}H NMR (400 MHz, $CDCl_3$) δ2.90 (s, 3H), 7.37-7.43 (m, 2H), 7.49 (ddd, J = 8.4, 7.3, 1.4 Hz, 2H), 8.00 (brd, J = 7.3 Hz, 2H), 8.23 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ27.3, 115.8, 119.4, 123.2, 125.9, 126.9, 138.1, 169.6.

Reaction of carbazoles with $Tf_2C=CH_2$

The results for the bis(triflyl)ethylation reactions of carbazole derivatives **11** are summarized in the following figure. As mentioned in the manuscript, electron-deficient **11a** and **11b** required heating

conditions to form the products **12a** and **12b**. In particular, the reaction of *N*-acetly substrate **11b** gave the desired product **12b** in poor yield due to notably low nucleophilicity of this starting carbazole. In the 1:1 reaction of *N*-ethyl carbazole **11c** with **2a**, the monoalkylated product **12c** was obtained in 66% yield, accompanying with formation of a considerable amount of the dialkylated product **14c**. The product **14c** was selectively formed by similar reaction using 2 equiv of **2a**.



[a] Based on NMR data of crude materials using $PhCF_3$ as an internal standard.

3-(2,2-Bis((trifluoromethyl)sulfonyl)ethyl)-6-bromo-9-ethyl-9*H*-carbazole 12a. To a solution of 3-bromo-9-ethyl-9*H*-carbazole **11a** (54.5 mg, 0.199 mmol) in CH_3CN (2.0 mL), 2-fluoropyridinium salt **2a** (81.8 mg, 0.210 mmol) was added at room temperature. After being stirred for 5 h at 90 °C, the reaction mixture was concentrated under reduced pressure. The resulting solid was purified by washing the crude material with hexane (2.0 mL x 3) to give **12a** in 89% yield (99.7 mg, 0.176 mmol). Greenish crystals (from $CHCl_3$); Mp. 145-146 °C, IR (ATR) ν 2980, 2938, 1629, 1596, 1482, 1438, 1391, 1377, 1225, 1207, 1151, 1108, 1097, 867, 817, 806, 701, 644, 583, 511, 484, 459 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.43 (t, J = 7.2 Hz, 3H), 3.99 (d, J = 5.7 Hz, 2H), 4.34 (q, J = 7.2 Hz, 2H), 5.16 (t, J = 5.7 Hz, 1H), 7.29 (d, J = 8.6 Hz, 1H), 7.37-7.43 (m, 2H), 7.58 (dd, J = 8.6, 1.9 Hz, 1H), 7.98 (s, 1H), 8.21 (d, J = 1.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 30.7, 37.8, 80.5, 109.5, 110.2, 112.0, 119.2 (q, J_{CF} = 330 Hz), 121.4, 122.4, 123.3, 123.5, 124.0, 127.0, 129.0, 139.0,

139.9; ^{19}F NMR (376 Hz, $CDCl_3$) δ –73.5 (s, 6F); MS (ESI-TOF) *m*/*z* 563 $[M–H]^–$; HRMS calcd for $C_{18}H_{13}BrF_6NO_4S_2$ $[M–H]^–$, 563.9374; found, 563.9377.

1-(3-(2,2-Bis((trifluoromethyl)sulfonyl)ethyl)-9*H*-carbazol-9-yl)ethan-1-one 12b. According to the synthetic procedure for **12a**, 9-acetyl-9*H*-carbazole **11b** (21.2 mg, 0.101 mmol) was treated by 2-fluoropyridinium salt **2a** (80.1 mg, 0.206 mmol) in CH_3CN (1.0 mL) for 8 h at 90 °C in a sealed tube. After chromatographic purification (hexane/EtOAc = 3 : 1 to 1 : 2) followed by acidification using 10% hydrochloric acid, 22.6 mg of a mixture containing 4-substituted product **12b** (37.7 μmol, 37% yield), 3-substituted one **12b'** (3.8 μmol, 3.8% yield), and 4,7-disubstituted product **14c** (3.8 μmol, 3.8% yield) in a ratio of 1 : 0.10 : 0.10 was obtained. Analytically pure **12b** was isolated by repeating the column chromatography.

For **12b**. Colorless crystals (from $CHCl_3$); Mp. 159-160 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.89 (s, 3H), 3.98 (d, *J* = 5.8 Hz, 2H), 5.16 (t, *J* = 5.8 Hz, 1H), 7.40 (dd, *J* = 8.6, 2.0 Hz, 1H), 7.40-7.46 (m, 1H), 7.53 (ddd, *J* = 8.4, 7.2, 1.3 Hz, 1H), 7.94 (d, *J* = 2.0 Hz, 1H), 8.02 (dd, *J* = 7.7, 0.6 Hz, 1H), 8.13 (d, *J* = 8.4 Hz, 1H), 8.32 (d, *J* = 8.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.7, 30.5, 80.2, 116.0, 117.3, 119.2(q, J_{CF} = 330 Hz), 120.2, 120.6, 123.9, 125.6, 127.1, 127.8, 128.0, 128.4, 138.5, 138.9, 170.0; ^{19}F NMR (376 Hz, $CDCl_3$) δ –73.4 (s, 6F); IR (ATR) ν 2883, 1679, 1491, 1453, 1438, 1391, 1377, 1367, 1326, 1304, 1234, 1193, 1110, 1095, 813, 778, 755, 702, 651, 583, 512, 483 cm^{-1}; MS (ESI-TOF) *m*/*z* 500 $[M–H]^–$; HRMS calcd for $C_{18}H_{12}F_6NO_5S_2$ $[M–H]^–$, 500.0061; found, 500.0067.

3-(2,2-Bis((trifluoromethyl)sulfonyl)ethyl)-9-ethyl-9*H*-carbazole 12c. According to the synthetic procedure for **12a**, 9-ethyl-9*H*-carbazole **11c** (38.8 mg, 0.199 mmol) was treated by 2-fluoropyridinium salt **2a** (80.6 mg, 0.207 mmol) in CH_3CN (2.0 mL) for 3 h at room temperature. The product **12c** was isolated in 66% yield (63.9 mg, 0.131 mmol) after column chromatography on neutral silica gel (hexane/EtOAc = 5 : 1 to 1 : 2) and the following acidification with 10% hydrochloric acid.

Greenish crystals (from $CHCl_3$); Mp. 94-95 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.44 (t, J = 7.2 Hz, 3H), 4.01 (d, J = 5.7 Hz, 2H), 4.38 (q, J = 7.2 Hz, 2H), 5.17 (t, J = 5.7 Hz, 1H), 7.27 (ddd, J = 7.8, 7.1, 0.8 Hz, 1H), 7.39 (dd, J = 8.5, 1.6 Hz, 1H), 7.41 (d, J = 8.5 Hz, 1H), 7.43 (brd, J = 8.2 Hz, 1H), 7.51 (ddd, J = 8.2, 7.1, 1.0 Hz, 1H), 8.03 (brs, 1H), 8.11 (brd, J = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 30.8, 37.7, 80.8, 108.8, 109.2, 119.3, 119.3 (q, J_{CF} = 330 Hz), 120.6, 121.2, 122.3, 123.0, 123.5, 126.2, 126.3, 139.6, 140.4; ^{19}F NMR (376 Hz, $CDCl_3$) δ –73.5 (s, 6F); MS (ESI-TOF) m/z 486 $[M–H]^–$; IR (ATR) ν 2968, 2947, 1603, 1493, 1470, 1392, 1375, 1332, 1227, 1203, 1113, 1100, 741, 700, 641, 583, 484 $cm^{–1}$; HRMS calcd for $C_{18}H_{14}F_6NO_4S_2$ $[M–H]^–$, 486.0268; found, 486.0265.

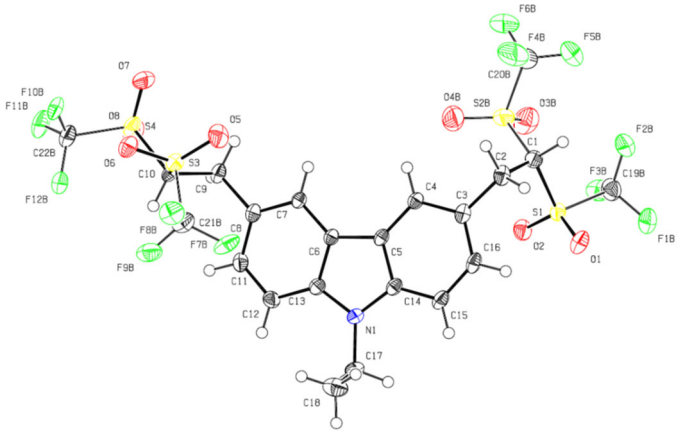
3,6-Bis(2,2-bis((trifluoromethyl)sulfonyl)ethyl)-9-ethyl-9*H*-carbazole 14c. According to the synthetic procedure for **12a**, the 1 : 2 reaction of 9-ethyl-9*H*-carbazole **11c** (20.3 mg, 0.104 mmol) and 2-fluoropyridinium salt **2b** (82.8 mg, 0.213 mmol) in CH_3CN (1.0 mL) was conducted for 3 h at room temperature. The product **14c** was isolated in 89% yield (72.2 mg, 92.6 μmol) by washing the crude material with 5% $CHCl_3$ in hexane (0.5 mL x 3). Its structure was also confirmed by an X-ray crystallographic analysis.

Greenish crystals (from $CHCl_3$/hexane); Mp. 149 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.44 (t, J = 7.2 Hz, 3H), 4.01 (d, J = 5.6 Hz, 4H), 4.37 (q, J = 7.2 Hz, 2H), 5.17 (d, J = 5.6, 1.3 Hz, 2H), 7.41 (d, J = 10.3 Hz, 2H), 7.42-7.45 (m, 2H), 8.03 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 30.7, 37.9, 80.6, 109.5, 119.3(q, J_{CF} = 330 Hz), 121.4, 122.9, 123.6, 127.0, 140.1; ^{19}F NMR (376 Hz, $CDCl_3$) δ –73.4 (s, 6F); MS (ESI-TOF) m/z 777 $[M–H]^–$; IR (ATR) ν 2972, 2945, 1606, 1494, 1486, 1386, 1377, 1237, 1199, 1102, 806, 731, 699, 642, 579, 511, 481, 457 $cm^{–1}$; HRMS calcd for $C_{22}H_{16}F_{12}NO_8S_4$ $[M–H]^–$, 777.9567; found, 777.9562. Anal. Calcd for $C_{22}H_{17}F_{12}NO_8S_4$: C, 33.89; H, 2.20; N, 1.80. Found: C, 33.85; H, 2.31; N, 1.96.

X-ray crystallographic data for 14c

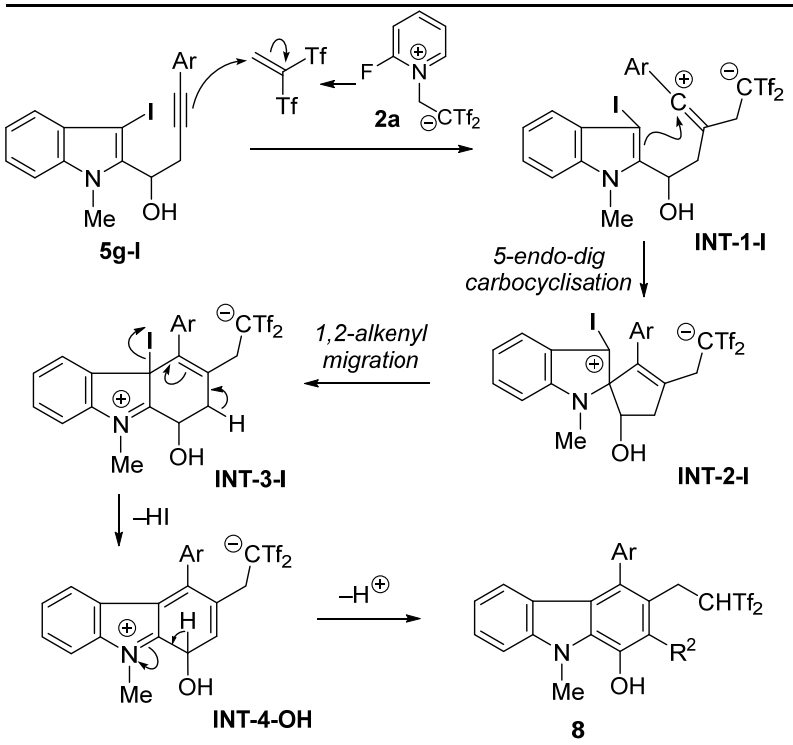
Crystallographic data by the X-ray diffraction study has been deposited with Cambridge Crystallographic Data Center (CCDC) as supplementary publication No. CCDC 1911534. This data can be obtained free of charge from the CCDC *via* www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystal data and structure refinement for **14c**



$C_{22}H_{17}F_{12}NO_8S_4$	V = 1469.2 (3) Å^3
M_r = 779.60	Z = 2
Triclinic, $P\bar{1}$	$F(000)$ = 784
a = 10.7413 (12) Å	D_x = 1.762 Mg m^{-3}
b = 11.0944 (12) Å	Mo $K\alpha$ radiation, λ = 0.71073 Å
c = 13.5068 (14) Å	μ = 0.45 mm^{-1}
α = 86.340 (1)°	T = 150 K
β = 69.593 (1)°	Block, colourelss
γ = 76.912 (1)°	0.28 × 0.21 × 0.09 mm
Bruker D8 goniometer diffractometer	5179 independent reflections
Radiation source: rotating-anode X-ray tube, Bruker TXS fine-focus Turbo X-ray Source	4412 reflections with $I > 2\sigma(I)$
Bruker Helios multilayered confocal mirror monochromator	R_{int} = 0.024
Detector resolution: 8.333 pixels mm^{-1}	θ_{max} = 25.0°, θ_{min} = 1.6°

ω scans	h = -12→12
Absorption correction: numerical Crystal Faces plugin in Bruker *APEX2* software	k = -13→13
T_{min} = 0.884, T_{max} = 0.961	l = -16→16
14293 measured reflections	
Refinement on F^2	1179 restraints
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.049	H-atom parameters constrained
$wR(F^2)$ = 0.132	$w = 1/[\sigma^2(F_o^2) + (0.0654P)^2 + 3.6706P]$, where $P = (F_o^2 + 2F_c^2)/3$
S = 0.99	$(\Delta/\sigma)_{max}$ = 0.001
5179 reflections	$\Delta\rangle_{max}$ = 1.08 e Å^{-3}
597 parameters	$\Delta\rangle_{min}$ = -0.73 e Å^{-3}



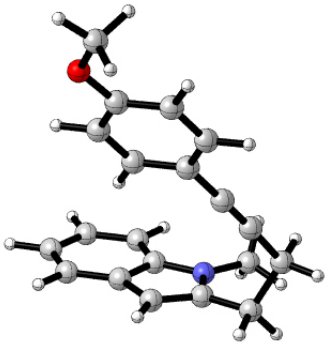
Scheme S1 Mechanistic explanation for the formation of 1-hydroxycarbazole **8**.

DFT calculations

All calculations were carried out by using *Gaussian 09* program, revision D.01.[i] Molecular geometries of **13**, **TS1**, **TS2**, and **TS3** were optimized and characterised by frequency analysis using hybrid density functional theory (M06-2X)[ii] and the 6-31+G(d) basis set as implemented in the *Gaussian 09* program. Single imaginary frequency was obtained in all transition states, which were supported by the intrinsic reaction coordinate (IRC) calculations. Each geometry of intermediates **INT-1'**, **INT-2'** and **INT-3'** was obtained by optimisation of the IRC geometries. Molecular geometries and energy of $Tf_2C{=}CH_2$ were used the reported one under the same level of calculation.[iii]

Reaction profile of model molecule 13

Table S1. Coordinates and energies for optimised geometry of 13

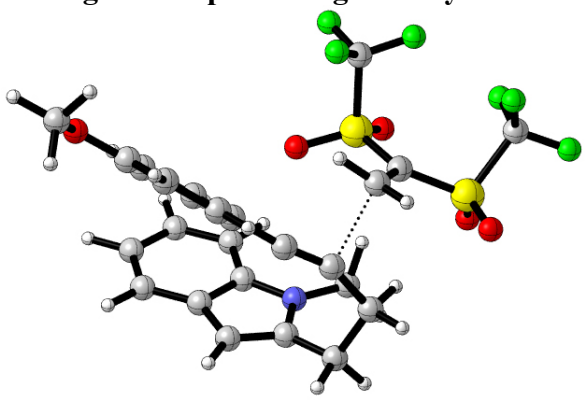


Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.608173	2.473311	1.085335
2	1	0	-2.050202	2.861199	1.934053
3	6	0	-2.665764	1.089139	0.846777
4	6	0	1.074754	-1.734661	-0.096628
5	6	0	0.062641	-2.401615	-0.094489
6	6	0	-2.528478	-1.167875	0.777306
7	6	0	-3.402963	0.615795	-0.269532
8	6	0	-4.073069	1.479931	-1.144632
9	1	0	-4.626236	1.105905	-2.001684
10	6	0	-3.996511	2.841480	-0.882562
11	1	0	-4.501951	3.539978	-1.543305
12	7	0	-3.312724	-0.757842	-0.288434
13	6	0	-3.951951	-1.596523	-1.284180
14	1	0	-4.972463	-1.244992	-1.456847
15	1	0	-3.401986	-1.576188	-2.231066
16	1	0	-4.003910	-2.623829	-0.922587
17	6	0	-3.270958	3.334568	0.222460
18	1	0	-3.231343	4.406143	0.396057
19	6	0	-2.175059	-2.603870	0.998904
20	1	0	-1.718828	-2.688191	1.989274
21	1	0	-3.070755	-3.235850	1.003483
22	6	0	-1.190730	-3.161018	-0.055747
23	1	0	-0.979972	-4.210475	0.176526
24	1	0	-1.653966	-3.146324	-1.049542
25	6	0	-2.121421	-0.068747	1.493117
26	1	0	-1.491204	-0.095415	2.372672
27	6	0	2.253687	-0.914296	-0.096513
28	6	0	2.146036	0.478873	0.072022
29	6	0	3.526695	-1.471624	-0.257882
30	6	0	3.275740	1.279495	0.078036

31	1	0	1.163945	0.926029	0.199174
32	6	0	4.670687	-0.673842	-0.253852
33	1	0	3.627445	-2.545111	-0.388540
34	6	0	4.546046	0.707985	-0.084277
35	1	0	3.199160	2.354798	0.207750
36	1	0	5.640738	-1.139710	-0.382257
37	8	0	5.591702	1.572705	-0.063053
38	6	0	6.898168	1.038749	-0.220688
39	1	0	7.576740	1.889174	-0.170632
40	1	0	7.131334	0.333210	0.584042
41	1	0	7.002637	0.541383	-1.190973

E(RM062X) = -903.138694339
Zero-point correction= 0.342621 (Hartree/Particle)
Sum of electronic and thermal Enthalpies = -902.775532
Sum of electronic and thermal Free Energies = -902.847448

Table S2. Coordinates and energies for optimised geometry of TS1

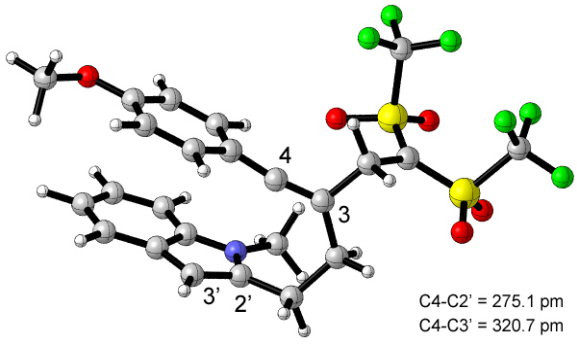


Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.085237	-2.767459	0.922986
2	1	0	5.043084	-2.614538	0.431963
3	6	0	2.91099	-2.907116	0.162732
4	6	0	1.311641	0.152176	-1.794146
5	6	0	0.295264	-0.454443	-2.130612
6	6	0	-1.039238	1.09127	-1.368125
7	1	0	-1.435509	1.253341	-2.366592
8	1	0	-0.262458	1.773849	-1.041142
9	6	0	-1.856304	0.498452	-0.419662
10	6	0	1.248199	-3.035146	-1.364226
11	6	0	1.677016	-3.094959	0.836382
12	6	0	1.585642	-3.152634	2.232677
13	1	0	0.631096	-3.287419	2.733896
14	6	0	2.761941	-3.008823	2.955699
15	1	0	2.727182	-3.039465	4.040871
16	7	0	0.68182	-3.184647	-0.11035
17	8	0	-3.418902	-0.11745	-2.385136
18	8	0	-3.524183	-1.594056	-0.33032
19	8	0	-2.179115	-0.416972	2.035673
20	8	0	0.139037	0.290195	1.257244
21	16	0	-3.331607	-0.287188	-0.939098
22	16	0	-1.309896	0.429475	1.233519
23	6	0	-0.713362	-3.425876	0.206863
24	1	0	-0.784367	-4.210289	0.965385

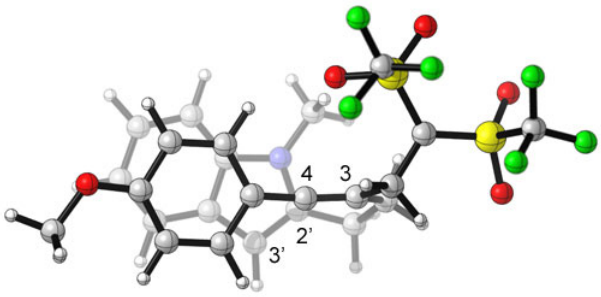
25	1	0	-1.202784	-2.522428	0.587364
26	1	0	-1.242948	-3.767848	-0.683214
27	6	0	4.000855	-2.816917	2.307199
28	1	0	4.901025	-2.705815	2.905172
29	6	0	-1.603499	2.161908	1.853013
30	6	0	-4.715033	0.764871	-0.268594
31	9	0	-2.885976	2.481205	1.732942
32	9	0	-1.248649	2.223649	3.128978
33	9	0	-0.872541	3.020786	1.148941
34	9	0	-4.770644	0.675065	1.052047
35	9	0	-4.533352	2.030425	-0.622731
36	9	0	-5.850736	0.318735	-0.790366
37	6	0	0.416367	-2.899	-2.598614
38	1	0	1.093196	-2.84169	-3.455272
39	1	0	-0.235239	-3.766425	-2.756694
40	6	0	-0.474507	-1.631412	-2.561321
41	1	0	-0.934642	-1.459764	-3.539579
42	1	0	-1.293402	-1.788313	-1.849386
43	6	0	2.606229	-2.872892	-1.237214
44	1	0	3.294302	-2.704857	-2.05576
45	6	0	2.383014	0.947924	-1.32736
46	6	0	2.958193	0.687756	-0.06227
47	6	0	2.893544	1.993701	-2.114232
48	6	0	4.012815	1.455658	0.387067
49	1	0	2.566305	-0.124946	0.542648
50	6	0	3.945615	2.777471	-1.660176
51	1	0	2.456254	2.189854	-3.088728
52	6	0	4.510631	2.506092	-0.405196
53	1	0	4.473594	1.268995	1.352112
54	1	0	4.318155	3.582234	-2.282101
55	8	0	5.536773	3.198539	0.123583
56	6	0	6.083185	4.278399	-0.626178
57	1	0	6.88845	4.683524	-0.015673
58	1	0	6.48494	3.923316	-1.580149
59	1	0	5.326662	5.049746	-0.800222

E(RM062X) = -2752.51045978
Zero-point correction = 0.428920 (Hartree/Particle)
Sum of electronic and thermal Enthalpies = -2752.045190
Sum of electronic and thermal Free Energies = -2752.151447

Table S3. Coordinates and energies for optimised geometry of INT-1'



Side view



Top view

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	-5.430989	1.283677	-0.214976
2	1	0	-5.965172	1.403888	-1.154314
3	6	0	-4.138672	1.821651	-0.060831
4	6	0	-0.900991	0.354263	-1.003942
5	6	0	0.221789	0.995925	-1.014457
6	6	0	1.481188	0.15759	-1.315539
7	1	0	1.964298	0.598698	-2.192375
8	1	0	1.191326	-0.860743	-1.583532
9	6	0	2.455821	0.173619	-0.16133
10	6	0	-2.072212	2.71793	-0.224078
11	6	0	-3.449635	1.62075	1.166835
12	6	0	-4.033729	0.938244	2.247293
13	1	0	-3.502505	0.788229	3.182584
14	6	0	-5.305946	0.42577	2.062745
15	1	0	-5.781551	-0.120952	2.871851
16	7	0	-2.200709	2.182257	1.04761
17	8	0	3.645283	2.087992	-1.37373
18	8	0	4.227255	1.739489	1.063196
19	8	0	3.074945	-0.633758	2.273669
20	8	0	0.712857	-0.942387	1.401842
21	16	0	3.808689	1.192052	-0.223912
22	16	0	2.155105	-0.836893	1.157408
23	6	0	-1.167523	2.145847	2.068645
24	1	0	-1.639403	2.076946	3.049822
25	1	0	-0.502265	1.284924	1.926594
26	1	0	-0.585512	3.069187	2.03679
27	6	0	-5.996722	0.586531	0.837684
28	1	0	-6.987683	0.154689	0.728027
29	6	0	2.558183	-2.567888	0.594261
30	6	0	5.280034	0.172994	-0.736838
31	9	0	3.823492	-2.649459	0.189657
32	9	0	2.375406	-3.420516	1.601905
33	9	0	1.764755	-2.929359	-0.417584
34	9	0	5.669563	-0.632425	0.248346
35	9	0	4.975343	-0.56639	-1.80398
36	9	0	6.293341	0.979447	-1.053995
37	6	0	-0.809187	3.350428	-0.715142
38	1	0	-0.99646	3.656975	-1.748341
39	1	0	-0.586026	4.265038	-0.151545
40	6	0	0.438901	2.452983	-0.672616
41	1	0	1.198372	2.84802	-1.355111
42	1	0	0.90049	2.46232	0.32251
43	6	0	-3.248758	2.537183	-0.915755
44	1	0	-3.42288	2.841381	-1.939978
45	6	0	-1.975714	-0.473944	-0.949661
46	6	0	-2.321982	-1.120634	0.282608

47	6	0	-2.840313	-0.621611	-2.081684
48	6	0	-3.461414	-1.872076	0.368015
49	1	0	-1.653756	-1.007099	1.131452
50	6	0	-3.992164	-1.354501	-1.990119
51	1	0	-2.577059	-0.121219	-3.008654
52	6	0	-4.321374	-1.968919	-0.751618
53	1	0	-3.755759	-2.364723	1.288258
54	1	0	-4.649698	-1.443061	-2.845907
55	8	0	-5.427181	-2.664013	-0.558029
56	6	0	-6.411419	-2.741057	-1.596062
57	1	0	-7.233041	-3.312519	-1.170174
58	1	0	-6.75109	-1.737072	-1.864733
59	1	0	-6.005757	-3.260068	-2.467808

E(RM062X) = -2752.54294858
Zero-point correction= 0.431591 (Hartree/Particle)
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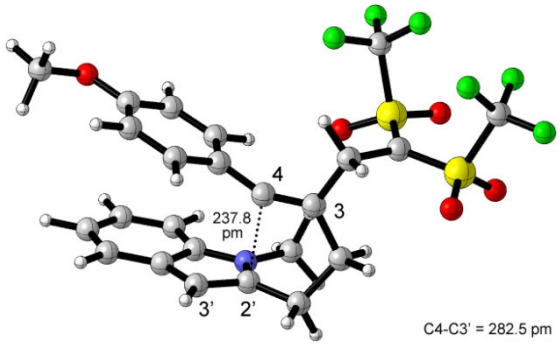
Sum of electronic and thermal Free Energies= -2752.179844

Table S4. Coordinates and energies for optimised geometry of TS2



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	5.356102	-1.340872	-0.529732
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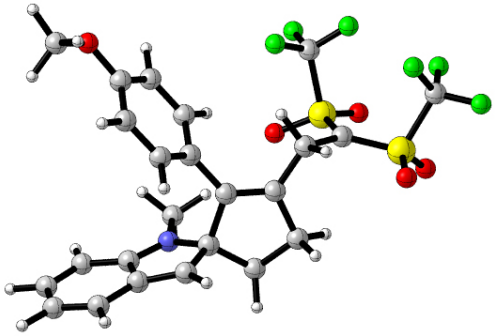
3	6	0	4.076042	-1.87968	-0.265469
4	6	0	1.000985	-0.678622	-0.933183
5	6	0	-0.200711	-1.181818	-0.912777
6	6	0	-1.36616	-0.229532	-1.218267
7	1	0	-1.825146	-0.566739	-2.152732
8	1	0	-0.979486	0.777049	-1.395094
9	6	0	-2.424631	-0.24107	-0.139459
10	6	0	1.983464	-2.736917	-0.255522
11	6	0	3.509011	-1.721775	1.033937
12	6	0	4.203985	-1.076099	2.075287
13	1	0	3.769824	-0.954974	3.062667
14	6	0	5.451834	-0.568816	1.779616
15	1	0	6.010842	-0.054117	2.555627
16	7	0	2.259214	-2.275864	1.026499

17	8	0	-3.710449	-1.897393	-1.607367
18	8	0	-4.428488	-1.716981	0.809971
19	8	0	-3.154915	0.421098	2.309297
20	8	0	-0.706459	0.503522	1.654512
21	16	0	-3.86331	-1.098678	-0.38665
22	16	0	-2.124092	0.602774	1.290627
23	6	0	1.310998	-2.261627	2.128424
24	1	0	1.857009	-2.157897	3.066485
25	1	0	0.603106	-1.431615	2.021587
26	1	0	0.76702	-3.208506	2.153234
27	6	0	6.024781	-0.690725	0.484083
28	1	0	7.006219	-0.263539	0.300946
29	6	0	-2.265994	2.414929	0.871731
30	6	0	-5.182192	0.120396	-0.871678
31	9	0	-3.466627	2.693019	0.368995
32	9	0	-2.084341	3.14251	1.973152
33	9	0	-1.33987	2.763373	-0.025209
34	9	0	-5.517382	0.890413	0.161036
35	9	0	-4.746746	0.897491	-1.864259
36	9	0	-6.268134	-0.531792	-1.287552
37	6	0	0.73739	-3.485431	-0.60657
38	1	0	0.873936	-3.862444	-1.623713
39	1	0	0.612507	-4.357663	0.045286
40	6	0	-0.520665	-2.60586	-0.552163
41	1	0	-1.301911	-2.992356	-1.214979
42	1	0	-0.955619	-2.586156	0.455677
43	6	0	3.112254	-2.551948	-1.049063
44	1	0	3.183964	-2.831929	-2.092453
45	6	0	1.967194	0.308912	-0.88128
46	6	0	2.231469	0.963778	0.354383
47	6	0	2.762502	0.631179	-2.015452
48	6	0	3.231359	1.903478	0.442182
49	1	0	1.616763	0.720112	1.215837
50	6	0	3.753097	1.580652	-1.935855
51	1	0	2.578607	0.112019	-2.951783
52	6	0	4.005255	2.211148	-0.693862
53	1	0	3.45457	2.409732	1.375415
54	1	0	4.34357	1.818069	-2.812058
55	8	0	4.965551	3.115472	-0.511028
56	6	0	5.827635	3.449252	-1.600729
57	1	0	6.527556	4.181264	-1.203642
58	1	0	6.368796	2.56245	-1.942756
59	1	0	5.255301	3.888412	-2.42225

E(RM062X) = -2752.54125143
Zero-point correction = 0.431279 (Hartree/Particle)
Sum of electronic and thermal Enthalpies = -2752.074638

Sum of electronic and thermal Free Energies = -2752.176969

Table S5. Coordinates and energies for optimised geometry of INT-2'

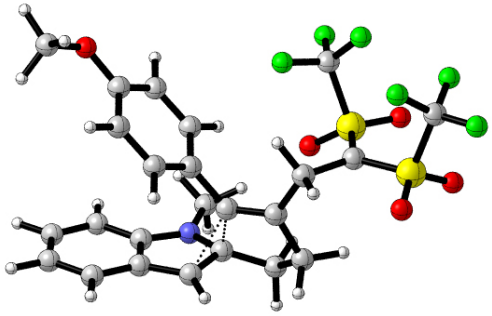


Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	5.760898	-2.150417	-1.166241
2	1	0	5.868648	-2.490242	-2.191028
3	6	0	4.447727	-2.024208	-0.590762
4	6	0	1.278565	-0.721591	-0.429736
5	6	0	0.016572	-1.13852	-0.596103
6	6	0	-1.151373	-0.272721	-0.982391
7	1	0	-1.439203	-0.51172	-2.012498
8	1	0	-0.852925	0.780261	-0.979178
9	6	0	-2.375199	-0.502021	-0.110356
10	6	0	2.186381	-1.89871	-0.029424
11	6	0	4.301985	-1.571436	0.787281
12	6	0	5.444388	-1.248593	1.5755
13	1	0	5.346264	-0.916836	2.602845
14	6	0	6.660971	-1.381769	0.971386
15	1	0	7.555168	-1.142234	1.539212
16	7	0	3.026704	-1.522698	1.114173
17	8	0	-3.264727	-1.996891	-1.989749
18	8	0	-4.333488	-2.266049	0.283767
19	8	0	-3.517264	-0.327613	2.263632
20	8	0	-1.023651	0.062192	2.035177
21	16	0	-3.665779	-1.417966	-0.702177
22	16	0	-2.373982	0.103827	1.461276
23	6	0	2.472575	-1.057373	2.377542
24	1	0	2.988695	-0.146607	2.689926
25	1	0	1.414256	-0.831238	2.226441
26	1	0	2.578965	-1.82843	3.145395
27	6	0	6.830291	-1.830935	-0.394686
28	1	0	7.83749	-1.907813	-0.789048
29	6	0	-2.652429	1.94152	1.311723
30	6	0	-5.027009	-0.253765	-1.207771
31	9	0	-3.818491	2.195162	0.720227
32	9	0	-2.658703	2.497263	2.523789

33	9	0	-1.681764	2.50954	0.590885
34	9	0	-5.61231	0.288285	-0.141445
35	9	0	-4.537757	0.724312	-1.971631
36	9	0	-5.949609	-0.916278	-1.908266
37	6	0	1.176017	-3.03862	0.290684
38	1	0	1.552962	-4.015595	-0.016878
39	1	0	1.027864	-3.060058	1.373902
40	6	0	-0.131367	-2.625281	-0.405443
41	1	0	-0.249748	-3.117087	-1.379574
42	1	0	-1.01038	-2.881247	0.194472
43	6	0	3.194449	-2.231831	-1.072676
44	1	0	2.911085	-2.574629	-2.062595
45	6	0	1.83372	0.648238	-0.531461
46	6	0	1.446815	1.636536	0.388699
47	6	0	2.764145	0.990628	-1.515764
48	6	0	1.964936	2.921016	0.315275
49	1	0	0.724787	1.385281	1.161724
50	6	0	3.297887	2.277994	-1.599982
51	1	0	3.075047	0.250443	-2.249141
52	6	0	2.895031	3.249272	-0.679691
53	1	0	1.66109	3.68806	1.021808
54	1	0	4.01152	2.504236	-2.383641
55	8	0	3.347676	4.529768	-0.672377
56	6	0	4.286093	4.906471	-1.668806
57	1	0	4.513442	5.95548	-1.483788
58	1	0	5.202707	4.312018	-1.58873
59	1	0	3.858424	4.793958	-2.670836

E(RM062X) = -2752.57118299
Zero-point correction = 0.431651 (Hartree/Particle)
Sum of electronic and thermal Enthalpies = -2752.103669
Sum of electronic and thermal Free Energie s= -2752.209060

Table S6. Coordinates and energies for optimised geometry of TS3



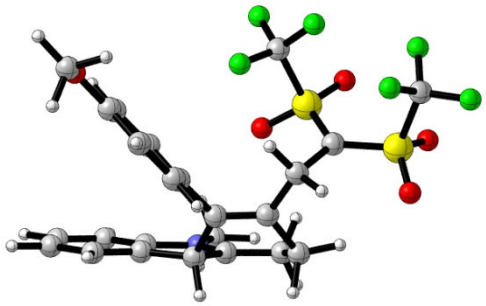
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.9279	-1.662263	-1.675798
2	1	0	4.815189	-1.885002	-2.732538
3	6	0	3.865016	-1.910069	-0.780401

4	6	0	1.219655	-1.004364	-0.495314
5	6	0	-0.052803	-1.369472	-0.745679
6	6	0	-1.141236	-0.405818	-1.131159
7	1	0	-1.486061	-0.66391	-2.139827
8	1	0	-0.734407	0.609088	-1.184655
9	6	0	-2.348801	-0.496806	-0.213584
10	6	0	1.882884	-2.31977	0.313736
11	6	0	4.000391	-1.610899	0.604073
12	6	0	5.190444	-1.0574	1.114557
13	1	0	5.30615	-0.821935	2.167008
14	6	0	6.212607	-0.835118	0.21382
15	1	0	7.146129	-0.41492	0.576524
16	7	0	2.842428	-1.911762	1.254899
17	8	0	-3.595884	-1.579768	-2.172317
18	8	0	-4.635925	-1.816947	0.119832
19	8	0	-3.357822	-0.332323	2.222104
20	8	0	-0.84709	-0.46114	1.907392
21	16	0	-3.82675	-1.049486	-0.823908
22	16	0	-2.171801	-0.068853	1.410595
23	6	0	2.553179	-1.62832	2.652981
24	1	0	3.110703	-0.74258	2.964492
25	1	0	1.48642	-1.419775	2.760054
26	1	0	2.826869	-2.476798	3.285223
27	6	0	6.093965	-1.134968	-1.169799
28	1	0	6.934517	-0.936801	-1.826325
29	6	0	-2.051865	1.79033	1.455499
30	6	0	-4.906495	0.426735	-1.164191
31	9	0	-3.162559	2.343539	0.971862
32	9	0	-1.885182	2.196425	2.714727
33	9	0	-1.015924	2.216009	0.730739
34	9	0	-5.307789	0.994267	-0.029143
35	9	0	-4.235162	1.32916	-1.881767
36	9	0	-5.982953	0.050211	-1.855916
37	6	0	0.682628	-3.174662	0.647335
38	1	0	0.950698	-4.233884	0.673916
39	1	0	0.283398	-2.879241	1.621362
40	6	0	-0.337325	-2.819337	-0.448656
41	1	0	-0.187765	-3.429155	-1.350945
42	1	0	-1.367995	-2.97064	-0.119938
43	6	0	2.554284	-2.40333	-0.961176
44	1	0	2.134587	-2.860889	-1.848408
45	6	0	1.851684	0.324279	-0.478004
46	6	0	1.854695	1.08306	0.70347
47	6	0	2.484804	0.844416	-1.609256
48	6	0	2.47797	2.3199	0.747457
49	1	0	1.337969	0.704005	1.581357

50	6	0	3.109122	2.089636	-1.583624
51	1	0	2.496403	0.263875	-2.528711
52	6	0	3.112706	2.828258	-0.394588
53	1	0	2.479478	2.915357	1.655349
54	1	0	3.58769	2.462904	-2.481352
55	8	0	3.699253	4.041318	-0.255204
56	6	0	4.359752	4.596334	-1.384398
57	1	0	4.75904	5.554188	-1.054185
58	1	0	5.179443	3.949053	-1.714029
59	1	0	3.656257	4.755096	-2.208423

E(RM062X) = -2752.56022051
Zero-point correction = 0.430559 (Hartree/Particle)
Sum of electronic and thermal Enthalpies = -2752.094486
Sum of electronic and thermal Free Energies = -2752.197949

Table S7. Coordinates and energies for optimised geometry of INT-3'



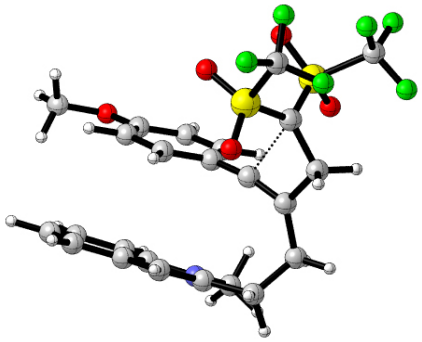
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.782922	-0.37141	-0.963131
2	1	0	4.685546	0.375078	-1.745856
3	6	0	3.764403	-1.280133	-0.716569
4	6	0	1.343321	-0.413963	-1.278981
5	6	0	0.085751	-0.8242	-1.51226
6	6	0	-1.131039	0.048917	-1.321311
7	1	0	-1.68907	0.110526	-2.261582
8	1	0	-0.834859	1.069035	-1.063262
9	6	0	-2.078249	-0.535287	-0.279016
10	6	0	1.89376	-2.668792	-0.574069
11	6	0	3.915442	-2.218732	0.30202
12	6	0	5.035003	-2.30173	1.113094
13	1	0	5.128506	-3.041814	1.901036
14	6	0	6.048645	-1.373809	0.861337
15	1	0	6.94615	-1.392072	1.470856
16	7	0	2.735185	-3.029069	0.348228
17	8	0	-3.625488	-1.207884	-2.208289
18	8	0	-4.197855	-2.104091	0.083123
19	8	0	-2.595561	-1.128128	2.241255
20	8	0	-0.194162	-0.884959	1.487618

21	16	0	-3.61699	-1.052197	-0.74844
22	16	0	-1.608873	-0.526979	1.34481
23	6	0	2.545454	-4.075837	1.34879
24	1	0	2.600991	-3.624674	2.341095
25	1	0	1.572669	-4.540662	1.202747
26	1	0	3.334247	-4.820624	1.230319
27	6	0	5.925865	-0.426674	-0.160314
28	1	0	6.730755	0.281621	-0.328969
29	6	0	-1.600679	1.258511	1.885977
30	6	0	-4.810601	0.356584	-0.511968
31	9	0	-2.80276	1.806891	1.709482
32	9	0	-1.287388	1.330482	3.18068
33	9	0	-0.707227	1.96603	1.193957
34	9	0	-5.052692	0.562763	0.78114
35	9	0	-4.303868	1.474356	-1.037547
36	9	0	-5.966898	0.088033	-1.121402
37	6	0	0.527393	-3.189295	-0.818112
38	1	0	0.57769	-4.230607	-1.159688
39	1	0	-0.033775	-3.170076	0.124324
40	6	0	-0.15292	-2.278221	-1.855591
41	1	0	0.256266	-2.49763	-2.850953
42	1	0	-1.221415	-2.500721	-1.888761
43	6	0	2.427188	-1.506409	-1.359762
44	1	0	2.544885	-1.819374	-2.410481
45	6	0	1.733303	0.967944	-0.905294
46	6	0	2.290796	1.255273	0.351595
47	6	0	1.539575	2.024542	-1.795139
48	6	0	2.634569	2.550996	0.700664
49	1	0	2.438991	0.454893	1.07267
50	6	0	1.876466	3.338729	-1.458967
51	1	0	1.114292	1.823811	-2.775719
52	6	0	2.427108	3.602543	-0.203553
53	1	0	3.056471	2.774853	1.6761
54	1	0	1.707223	4.130087	-2.179752
55	8	0	2.789604	4.838561	0.229693
56	6	0	2.58056	5.934882	-0.647288
57	1	0	2.923442	6.818152	-0.109856
58	1	0	3.161328	5.816038	-1.568583
59	1	0	1.518162	6.042908	-0.892098

E(RM062X) = -2752.59679436
Zero-point correction = 0.433036 (Hartree/Particle)
Sum of electronic and thermal Enthalpies = -2752.128424
Sum of electronic and thermal Free Energies = -2752.232305

Reaction profile of cyclobutene-forming reaction of INT-1'

Table S8. Coordinates and energies for transition state of cyclobutene-forming reaction

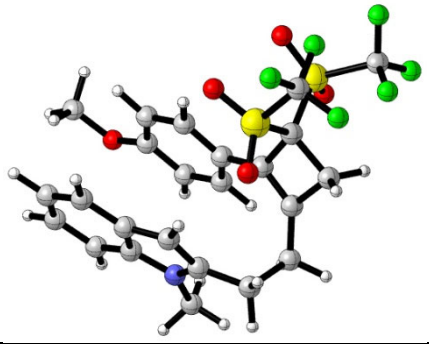


Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.522093	-0.394481	2.128945
2	1	0	-4.341376	-0.452292	3.199289
3	6	0	-3.825256	-1.236435	1.244586
4	6	0	-0.208005	-0.791754	-0.489328
5	6	0	0.347361	-1.966498	-0.693083
6	6	0	1.825005	-1.85933	-0.454906
7	1	0	2.39573	-2.112855	-1.354424
8	1	0	2.157109	-2.526677	0.347058
9	6	0	1.979218	-0.386962	-0.069704
10	6	0	-2.500975	-2.703218	0.146918
11	6	0	-4.084748	-1.141115	-0.148256
12	6	0	-4.993517	-0.214695	-0.676454
13	1	0	-5.162108	-0.127343	-1.746198
14	6	0	-5.653616	0.612779	0.220185
15	1	0	-6.360236	1.347094	-0.157523
16	7	0	-3.289846	-2.060931	-0.793303
17	8	0	1.802126	0.33045	-2.547952
18	8	0	2.387884	2.103171	-0.827622
19	8	0	1.453882	1.37441	1.84387
20	8	0	1.404358	-1.112679	2.320293
21	16	0	2.435533	0.721053	-1.289017
22	16	0	1.960778	0.030605	1.596329
23	6	0	-3.315378	-2.297994	-2.224092
24	1	0	-4.337069	-2.174052	-2.589538
25	1	0	-2.660747	-1.600587	-2.760071
26	1	0	-3.005226	-3.322996	-2.433397
27	6	0	-5.42726	0.51885	1.611819
28	1	0	-5.969888	1.179384	2.282984
29	6	0	3.714424	0.092675	2.230504
30	6	0	4.23963	0.428886	-1.665197
31	9	0	4.407662	-0.93488	1.741432
32	9	0	4.302995	1.228263	1.873058
33	9	0	3.703805	0.012582	3.558156

34	9	0	4.990521	0.670881	-0.595824
35	9	0	4.430451	-0.834468	-2.045331
36	9	0	4.615257	1.238697	-2.650847
37	6	0	-1.473117	-3.726323	-0.2165
38	1	0	-1.028546	-4.081017	0.718052
39	6	0	-0.355653	-3.223266	-1.15142
40	1	0	0.4007	-4.008755	-1.245404
41	1	0	-0.748459	-3.046918	-2.157447
42	6	0	-2.808999	-2.231589	1.400158
43	1	0	-2.338035	-2.55292	2.320385
44	6	0	-1.068029	0.287312	-0.511102
45	6	0	-1.400205	0.895676	-1.759715
46	6	0	-1.617346	0.819609	0.686471
47	6	0	-2.286132	1.939448	-1.80102
48	1	0	-0.94843	0.508809	-2.668271
49	6	0	-2.471462	1.899075	0.651244
50	1	0	-1.347391	0.366973	1.635812
51	6	0	-2.835255	2.443914	-0.596181
52	1	0	-2.581708	2.401505	-2.737097
53	1	0	-2.881142	2.290531	1.57379
54	8	0	-3.69339	3.44889	-0.741047
55	6	0	-4.288098	4.030519	0.421753
56	1	0	-4.964784	4.796682	0.049135
57	1	0	-4.84715	3.273688	0.979707
58	1	0	-3.520143	4.483419	1.054704
59	1	0	-1.941181	-4.595806	-0.695294

E(RM062X) = -2752.53290220
Zero-point correction= 0.430624 (Hartree/Particle)
Sum of electronic and thermal Enthalpies = -2752.066816
Sum of electronic and thermal Free Energies = -2752.169706

Table S9. Coordinates and energies for cyclobutene product



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.520153	-1.207989	-2.239227
2	1	0	2.938177	-1.480478	-3.116381
3	6	0	3.100194	-1.603117	-0.957814
4	6	0	-0.207657	-0.084419	0.894465

5	6	0	-0.459943	-1.042169	1.814468
6	6	0	-1.947848	-1.096223	1.566002
7	1	0	-2.542748	-0.637781	2.362961
8	1	0	-2.394896	-2.0517	1.27662
9	6	0	-1.647918	-0.108165	0.393485
10	6	0	2.110996	-2.384353	0.920058
11	6	0	3.878303	-1.224465	0.165829
12	6	0	5.054544	-0.474947	0.044775
13	1	0	5.633217	-0.181442	0.916777
14	6	0	5.440626	-0.094768	-1.232986
15	1	0	6.342247	0.498356	-1.362461
16	7	0	3.26538	-1.714727	1.295473
17	8	0	-1.826497	2.200169	1.645798
18	8	0	-2.389346	2.197834	-0.833021
19	8	0	-1.197698	-0.137477	-2.302321
20	8	0	-1.26621	-2.323642	-1.021665
21	16	0	-2.407089	1.564703	0.474862
22	16	0	-1.742069	-0.967219	-1.241007
23	6	0	3.81643	-1.572606	2.627677
24	1	0	4.855211	-1.916332	2.641104
25	1	0	3.785936	-0.526002	2.951177
26	1	0	3.246381	-2.179902	3.330896
27	6	0	4.680428	-0.457297	-2.365728
28	1	0	5.011892	-0.138875	-3.350504
29	6	0	-3.548535	-1.169837	-1.669686
30	6	0	-4.233576	1.304494	0.932922
31	9	0	-4.145367	-1.963318	-0.794612
32	9	0	-4.14826	0.014466	-1.693379
33	9	0	-3.596744	-1.715597	-2.873214
34	9	0	-4.532917	0.007746	0.905114
35	9	0	-4.437091	1.773257	2.149519
36	9	0	-4.987289	1.953975	0.066334
37	6	0	1.155592	-2.955022	1.919365
38	1	0	0.436135	-3.576666	1.377238
39	6	0	0.385159	-1.870513	2.721027
40	1	0	-0.252879	-2.362715	3.461278
41	1	0	1.094994	-1.245163	3.271492
42	6	0	1.983731	-2.341589	-0.446868
43	1	0	1.154278	-2.755438	-1.004723
44	6	0	0.939256	0.765332	0.563104
45	6	0	1.825696	1.116839	1.597267
46	6	0	1.192728	1.256584	-0.718624
47	6	0	2.946697	1.886141	1.345969
48	1	0	1.62136	0.795321	2.615018
49	6	0	2.317277	2.038227	-0.984986
50	1	0	0.519766	1.020981	-1.536568

51	6	0	3.213283	2.333018	0.043645
52	1	0	3.637308	2.148892	2.142362
53	1	0	2.489391	2.384006	-1.997615
54	8	0	4.354061	3.048304	-0.116695
55	6	0	4.680992	3.47945	-1.429571
56	1	0	5.646808	3.977202	-1.349432
57	1	0	4.760364	2.623128	-2.108649
58	1	0	3.933235	4.185556	-1.807041
59	1	0	1.667583	-3.609509	2.634431

E(RM062X) = -2752.57924435
Zero-point correction = 0.431587 (Hartree/Particle)
Sum of electronic and thermal Enthalpies = -2752.112327
Sum of electronic and thermal Free Energies = -2752.213022

NBO and QTAIM analyses

With DFT optimised geometries and wavefunctions of **INT-1'** and **TS2**, detailed bond analyses by applying Bader's Quantum Theory of Atoms in Molecules (QTAIM)[iv] and Natural Bond Orbital (NBO) theory[v] were conducted. In QTAIM analysis of **INT-1'**, three bond paths between aryl vinyl-type carbocation moiety and indole moiety were obtained. Even at the stage of **INT-1'**, the cationic C4 atom interacts with the C2' atom (the indole 2-position) rather than the C3' atom (the indole 3-position). The electron density ρ of 0.0157 *e* bohr^{-3} and the Laplasian $\nabla^2\rho$ of +0.0485 *e* bohr^{-5} at the C4–C2' bond critical point (BCP) indicate that this interatomic interaction has a slight charge-transfer character. Indeed, in the picture of NBO analysis, a $\pi_{C2'\text{-}C3'}/\pi^*_{C3\text{-}C4}$ interaction with second-order perturbation energies *E(2)* of 2.72 kcal mol^{-1} was computed. Not surprisingly, this orbital interaction is enhanced to 19.18 kcal mol^{-1} at the **TS2** geometry.

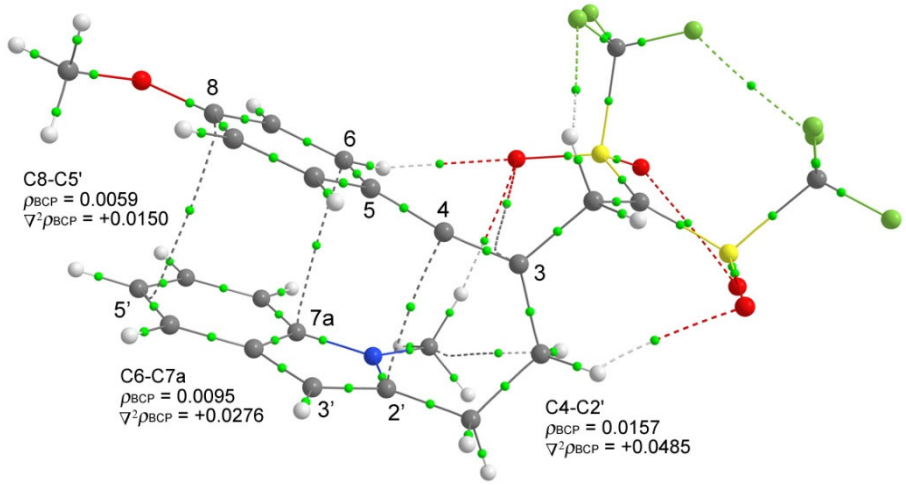
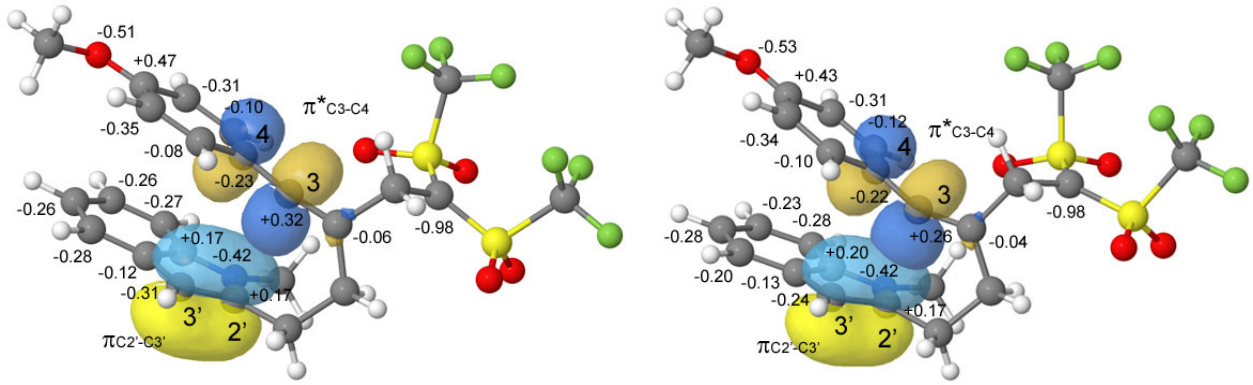


Figure S1. Bond paths (dash lines) and BCPs (green spheres) in QTAIM analysis of **INT-1'**. AIM parameters ρ and $\nabla^2\rho$ are given in *e* bohr^{-3} and *e* bohr^{-5} units, respectively.



INT-1' [*E(2)* = 2.72 kcal mol^{-1}] **TS2** [*E(2)* = 19.18 kcal mol^{-1}]

Figure S2. Second-order perturbation interactions and NPA charges (in *e*) in **INT-1'** and **TS2**

References

i. For *Gaussian 09*, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

ii. Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215.

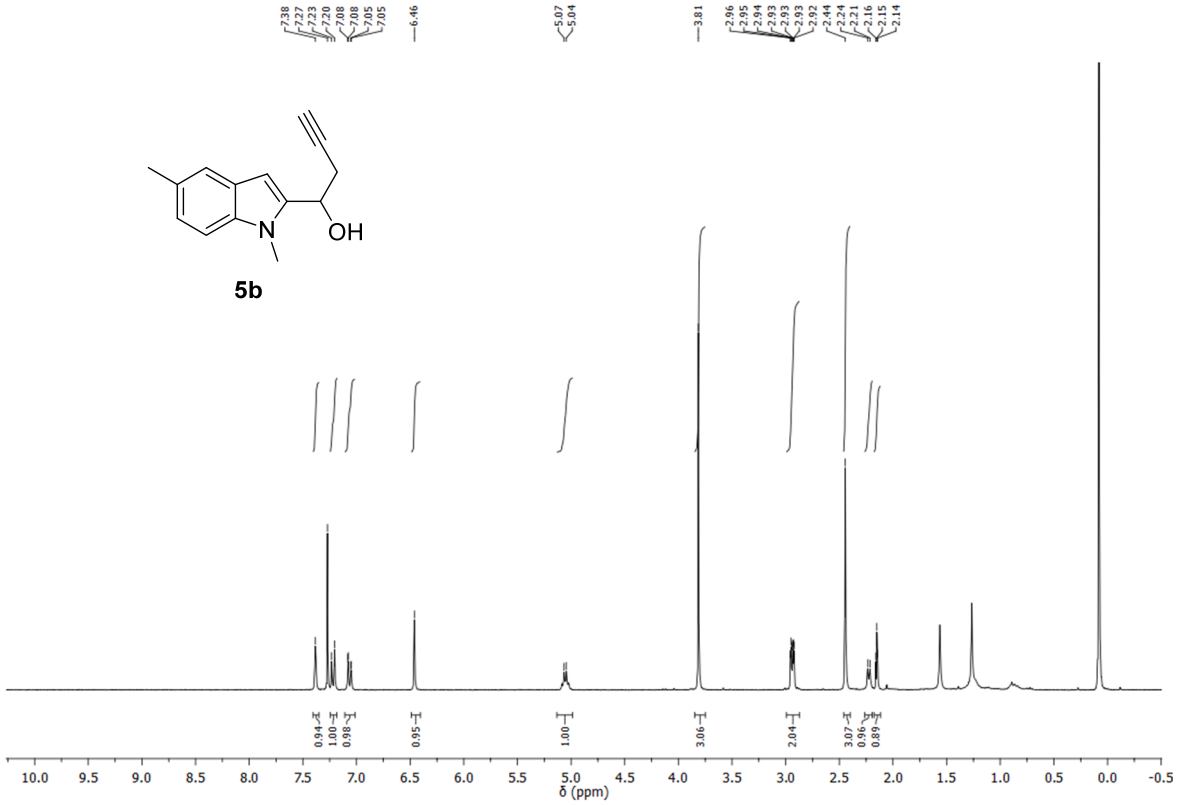
iii. B. Alcaide, P. Almendros, I. Fernández, C. Lázaro-Milla, *Chem. Commun.* **2015**, *51*, 3395.

iv. For *AIMAll* (Ver. 17.11.14), T. A. Keith, TK Gristmill Software, Overland Park KS, 2017.

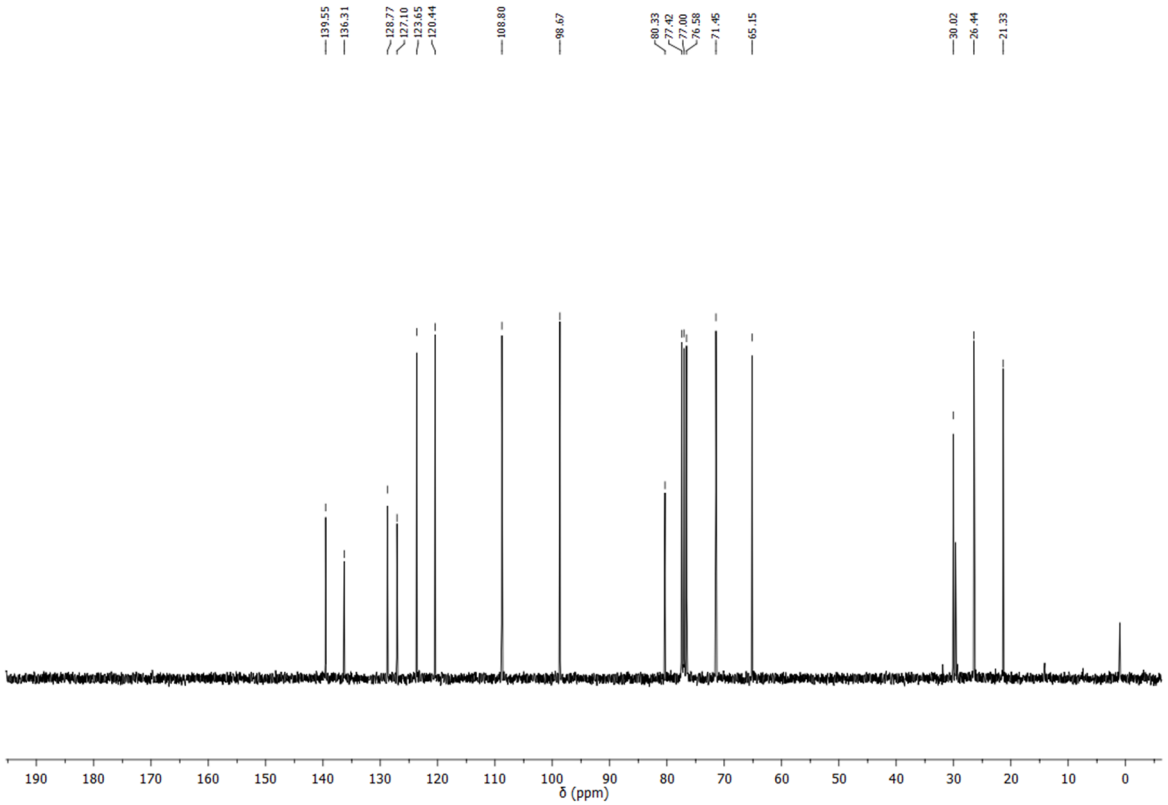
v. For *NBO 6.0*, E. D. Glendening, J, K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, C. R. Landis, F. Weinhold, Theoretical Chemistry Institute, University of Wisconsin, Madison, 2013.

^{1}H NMR, ^{13}C NMR, ^{19}F NMR and ^{23}Na NMR Spectra

^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC)



^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC)



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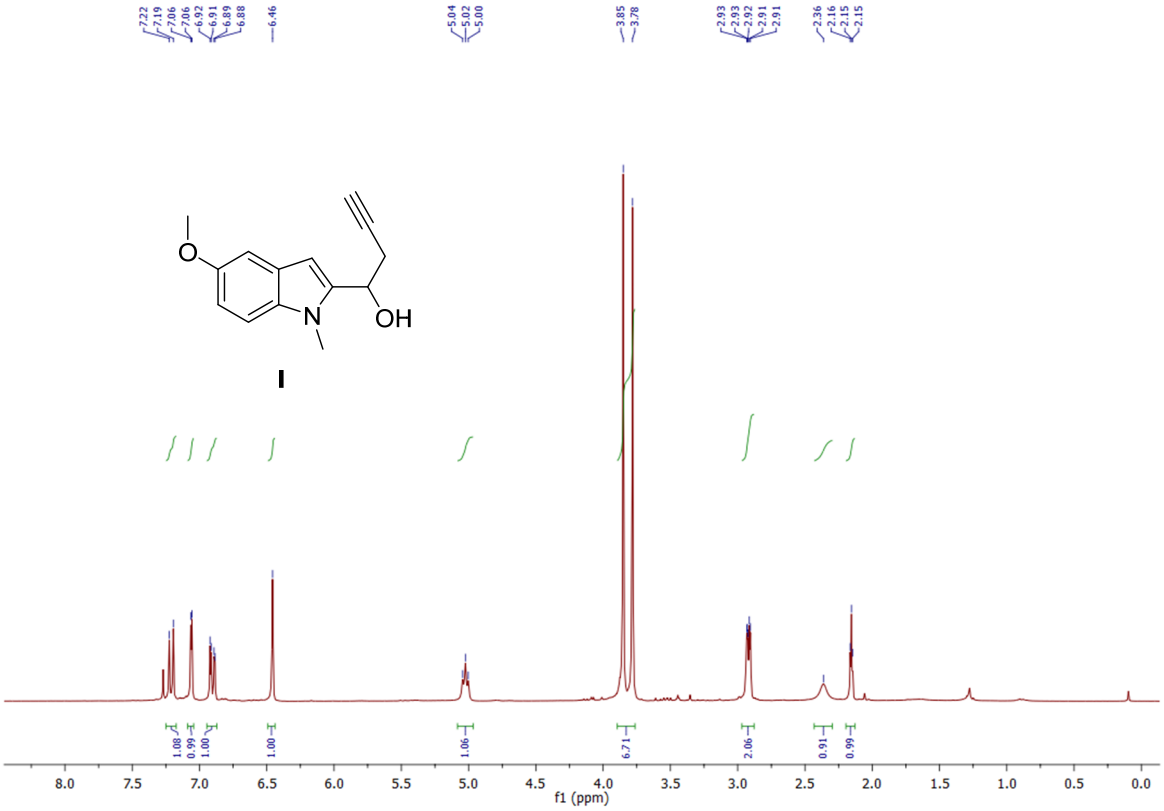
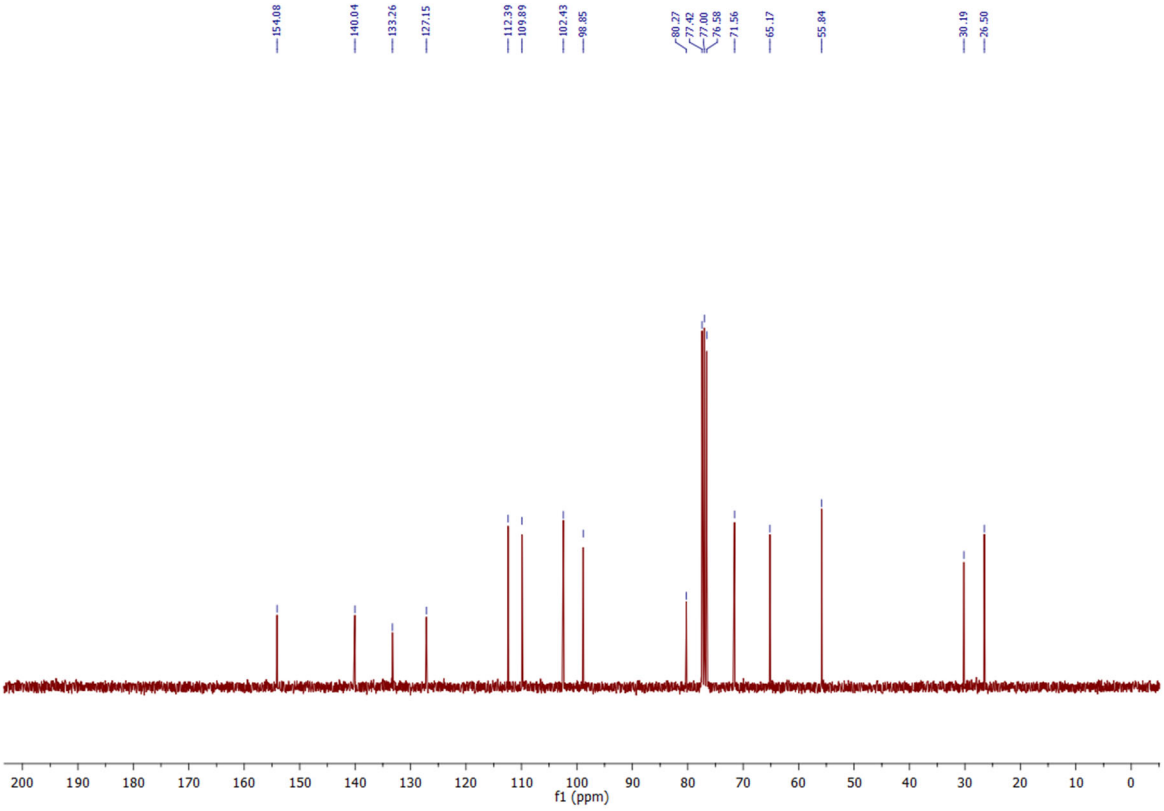


I

^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC)



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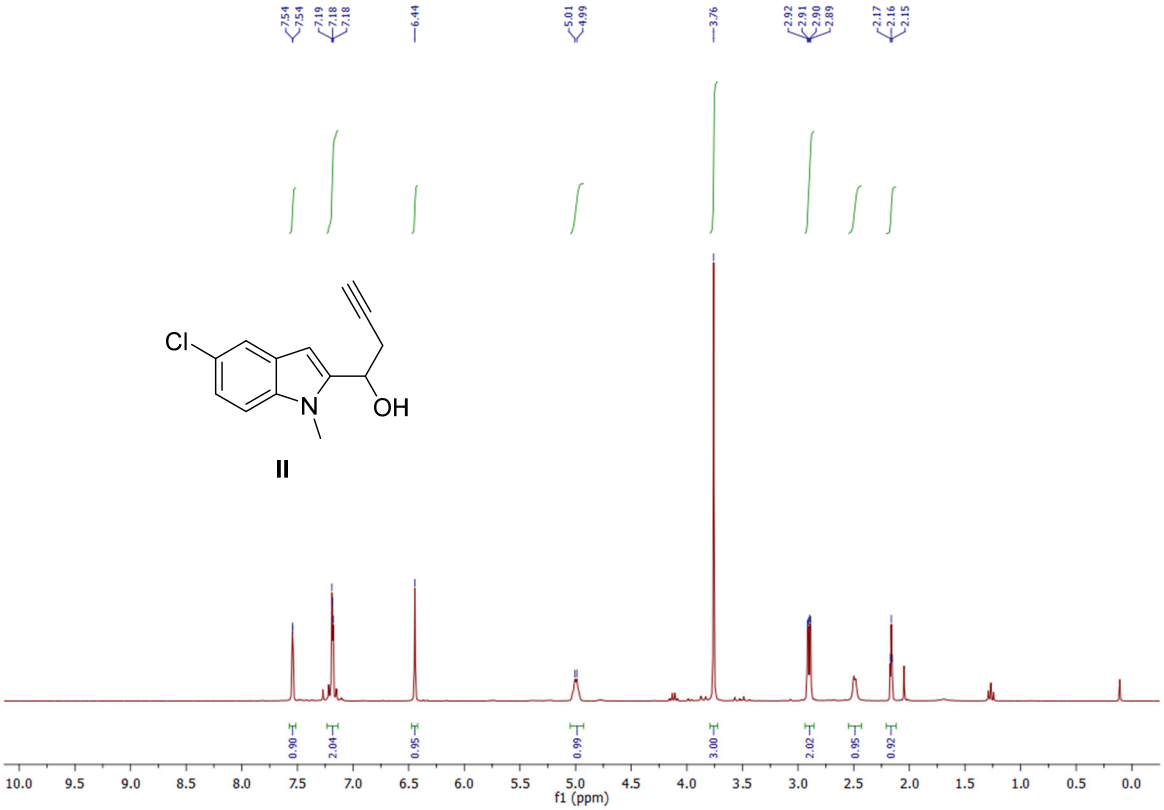

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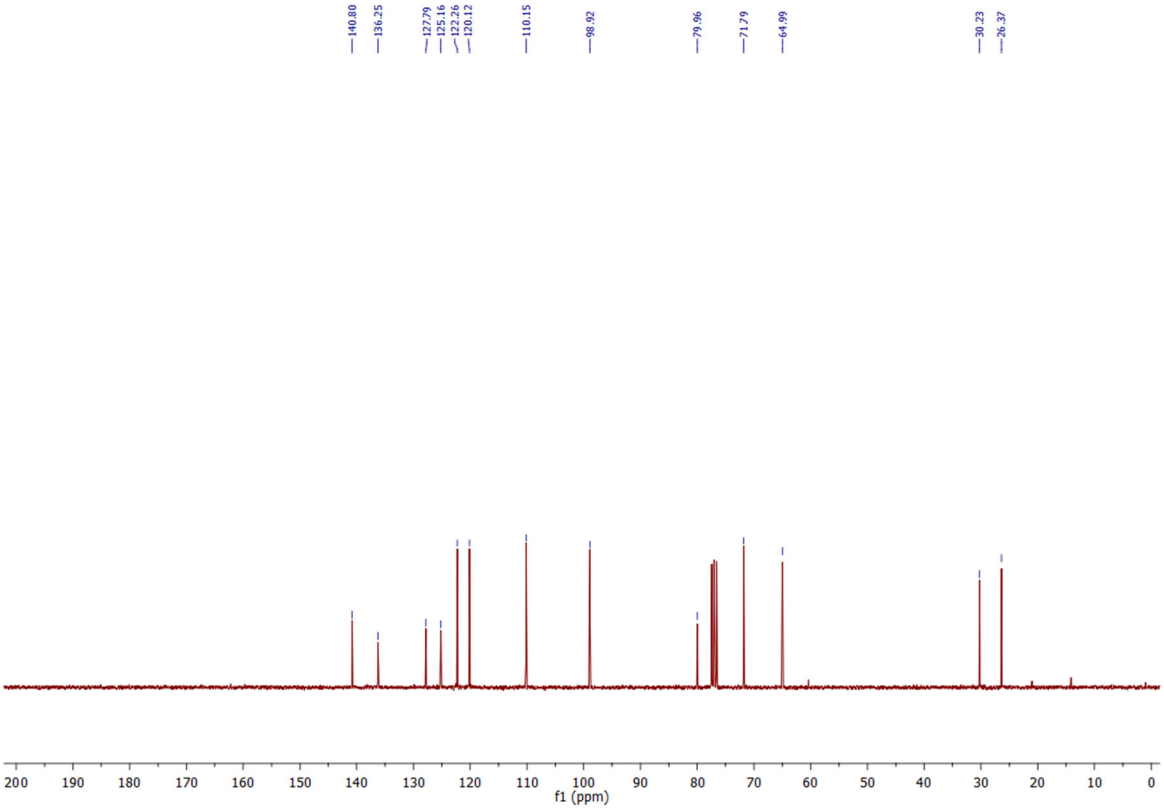

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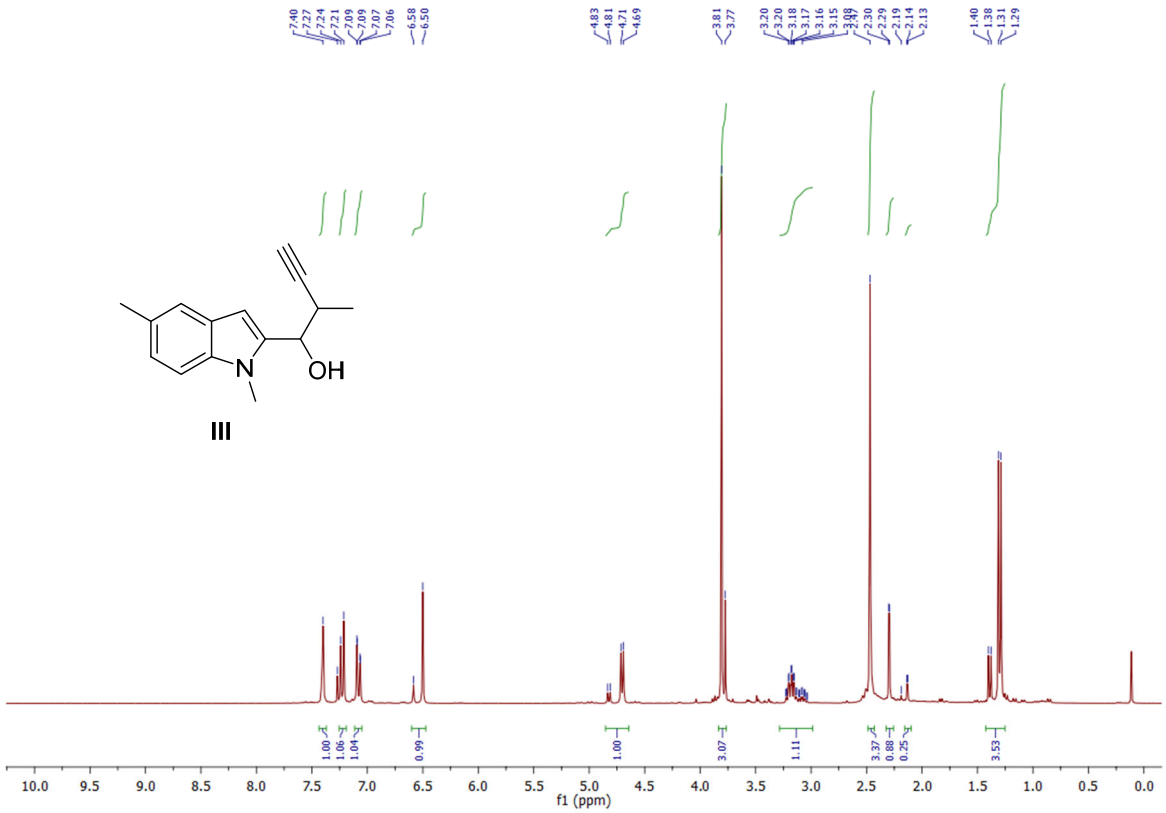
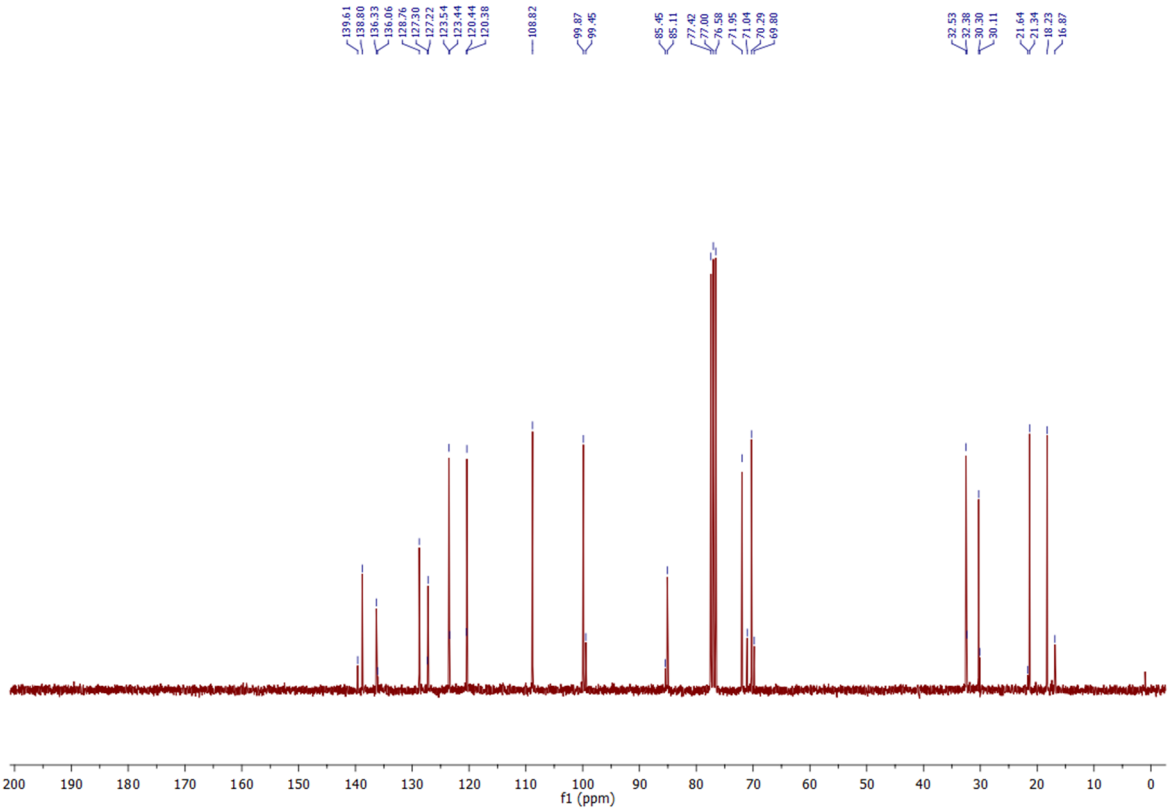
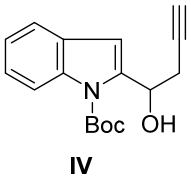


III

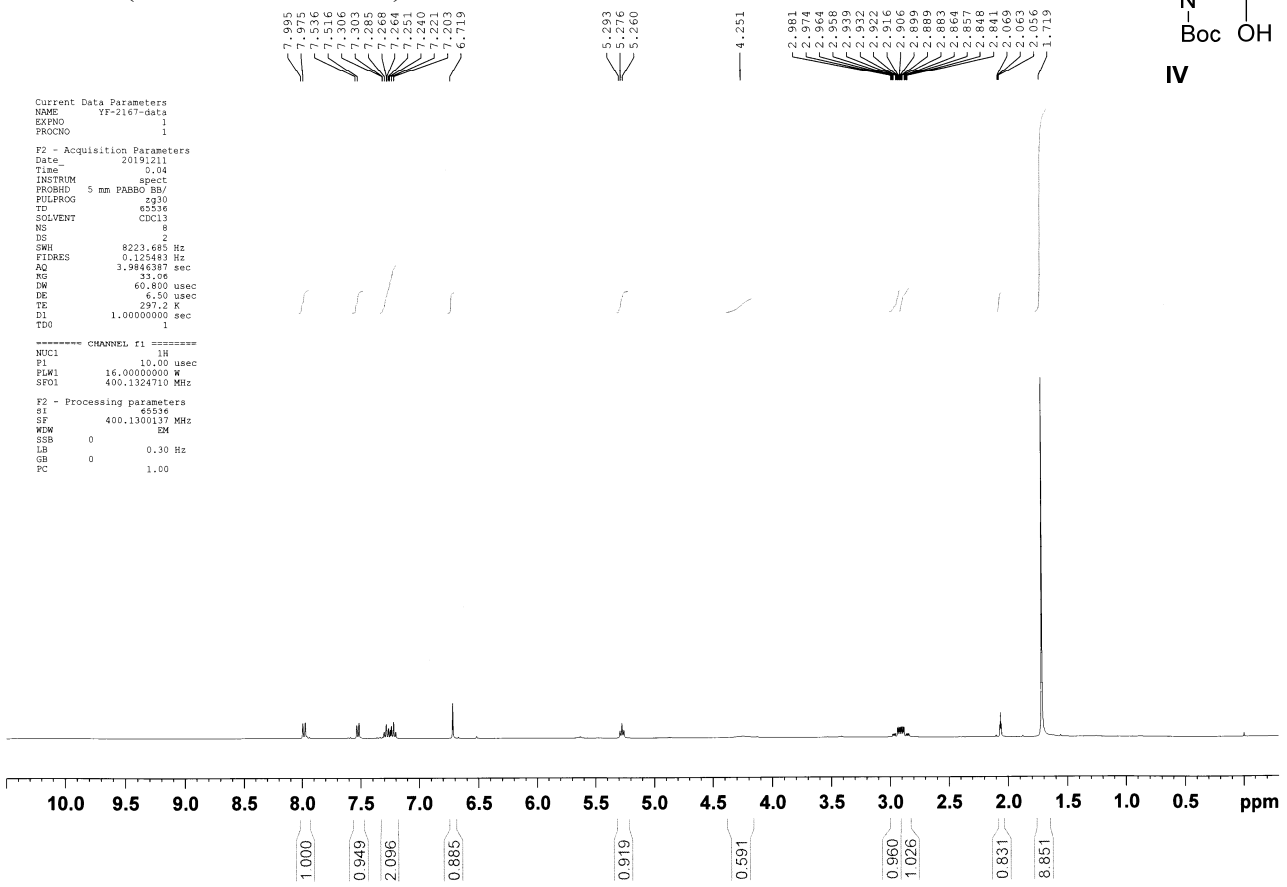
^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC)



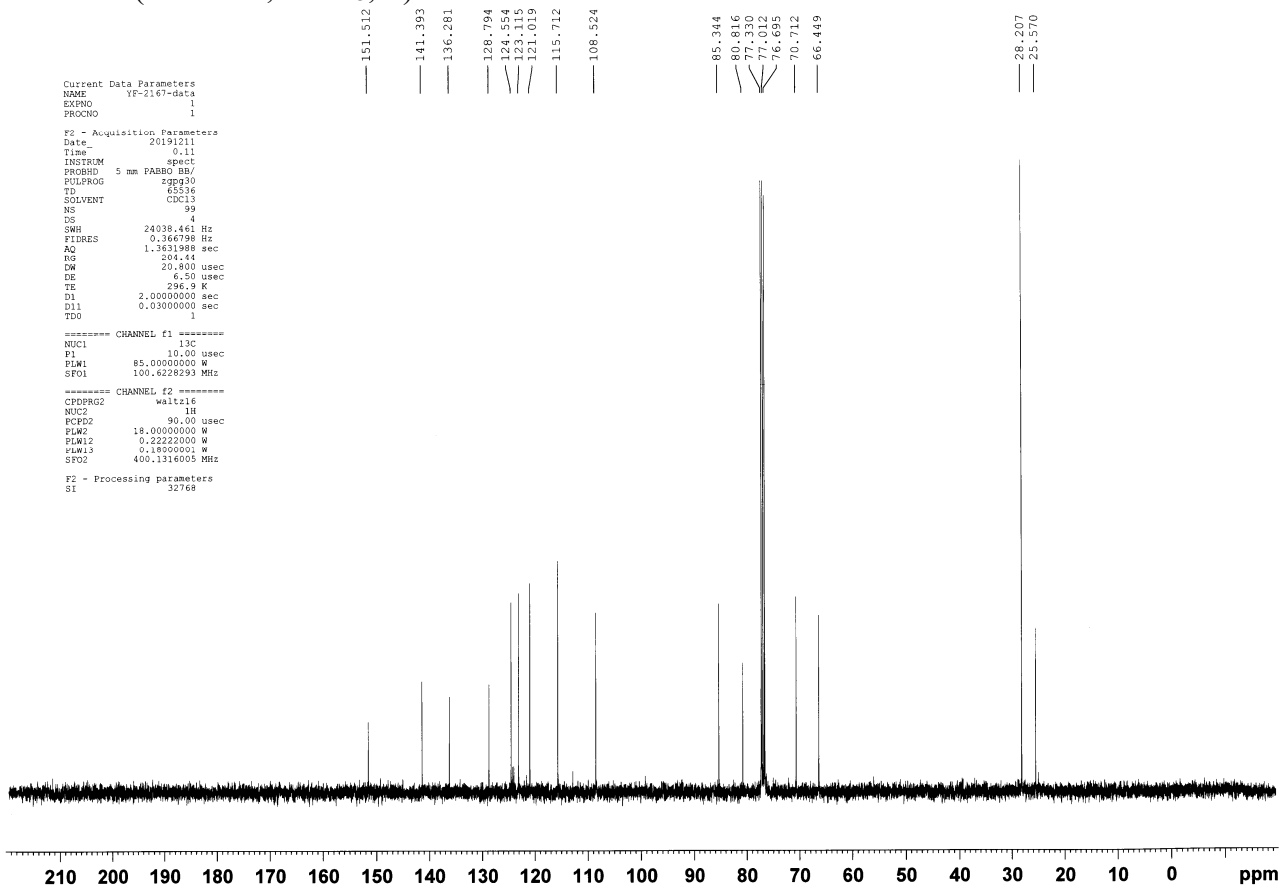
^{1}H NMR (400 MHz, $CDCl_3$, rt)



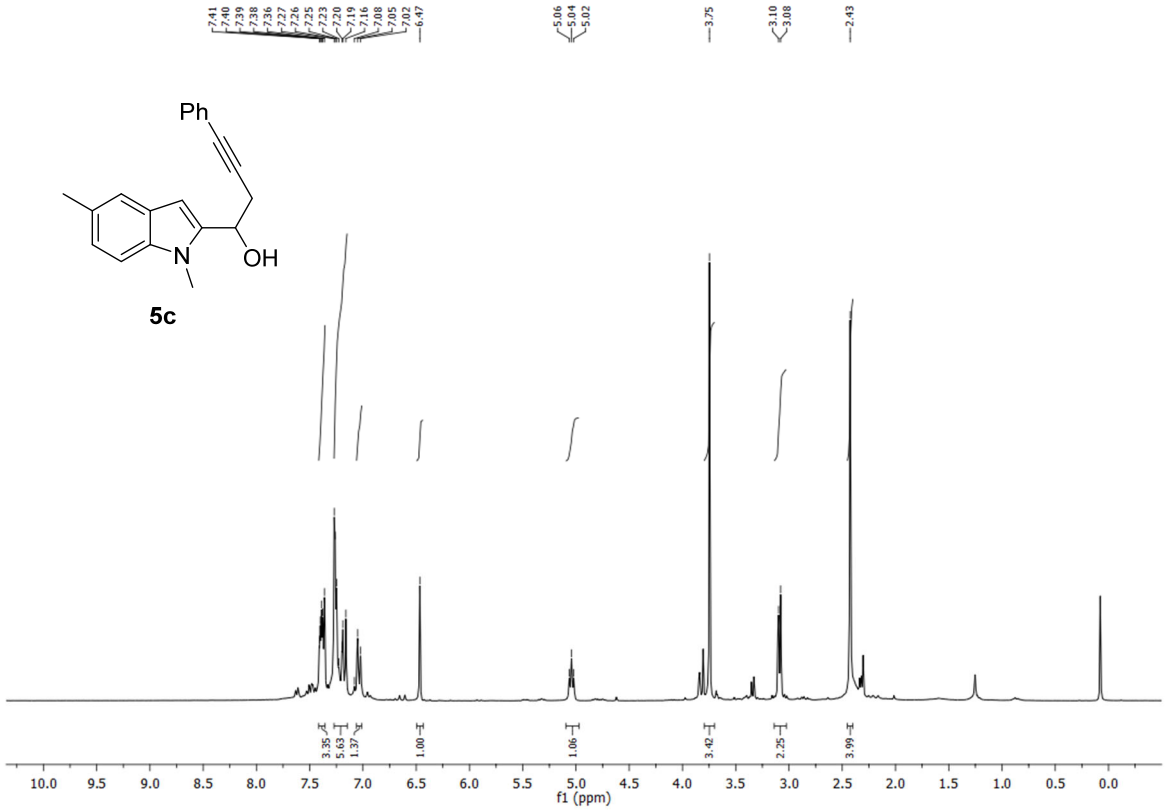
IV



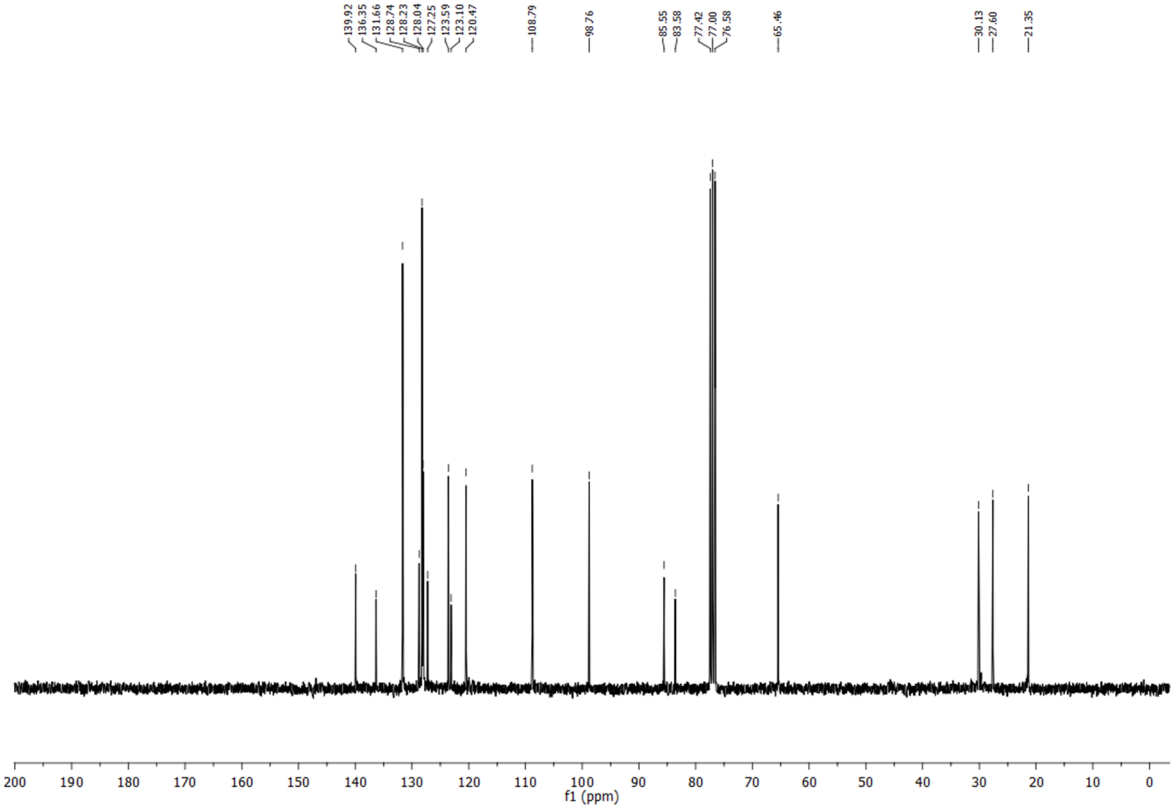
^{13}C NMR (100 MHz, $CDCl_3$, rt)



^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC)



^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC)



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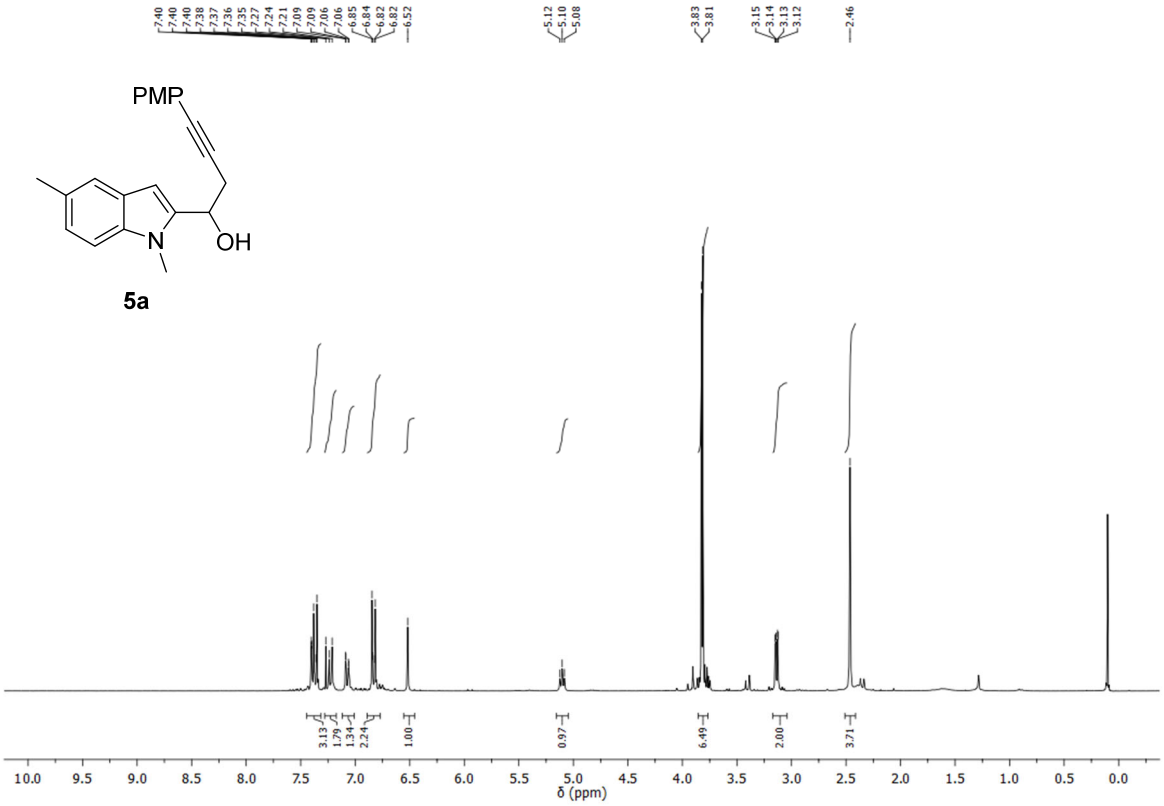
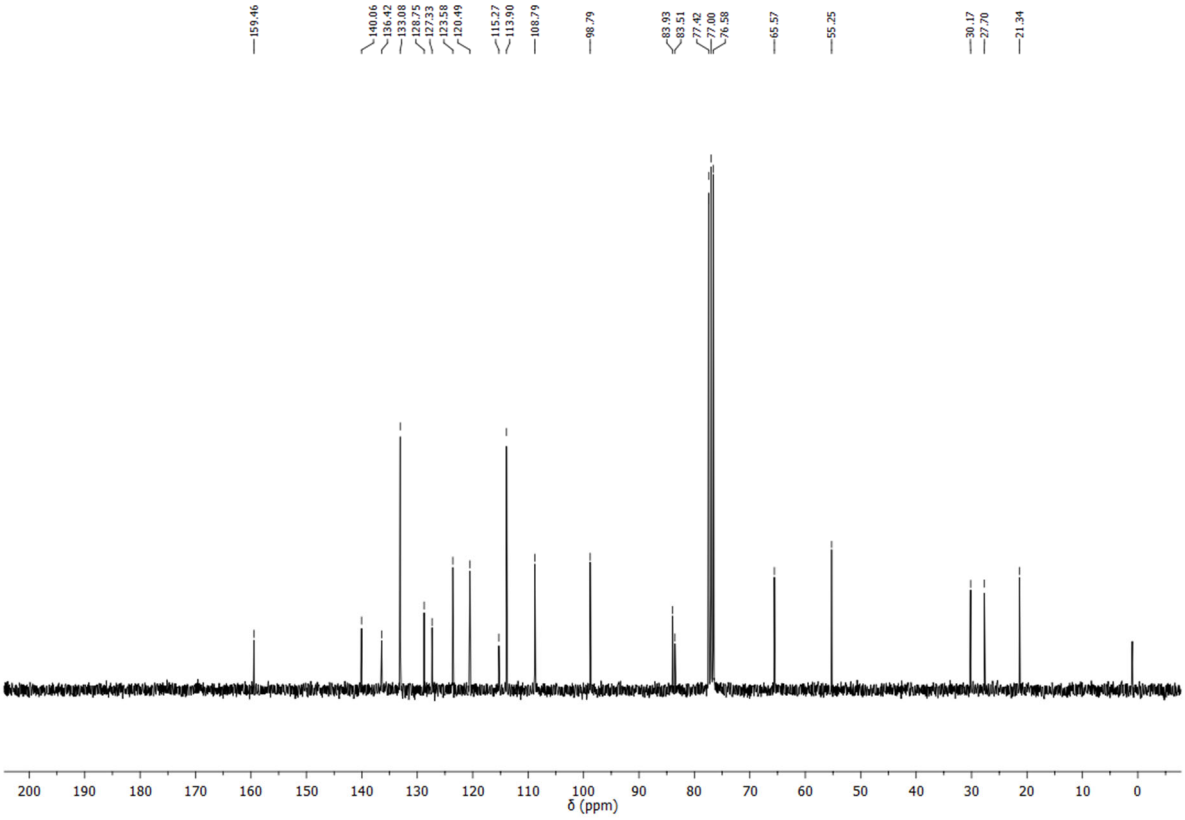


^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC)



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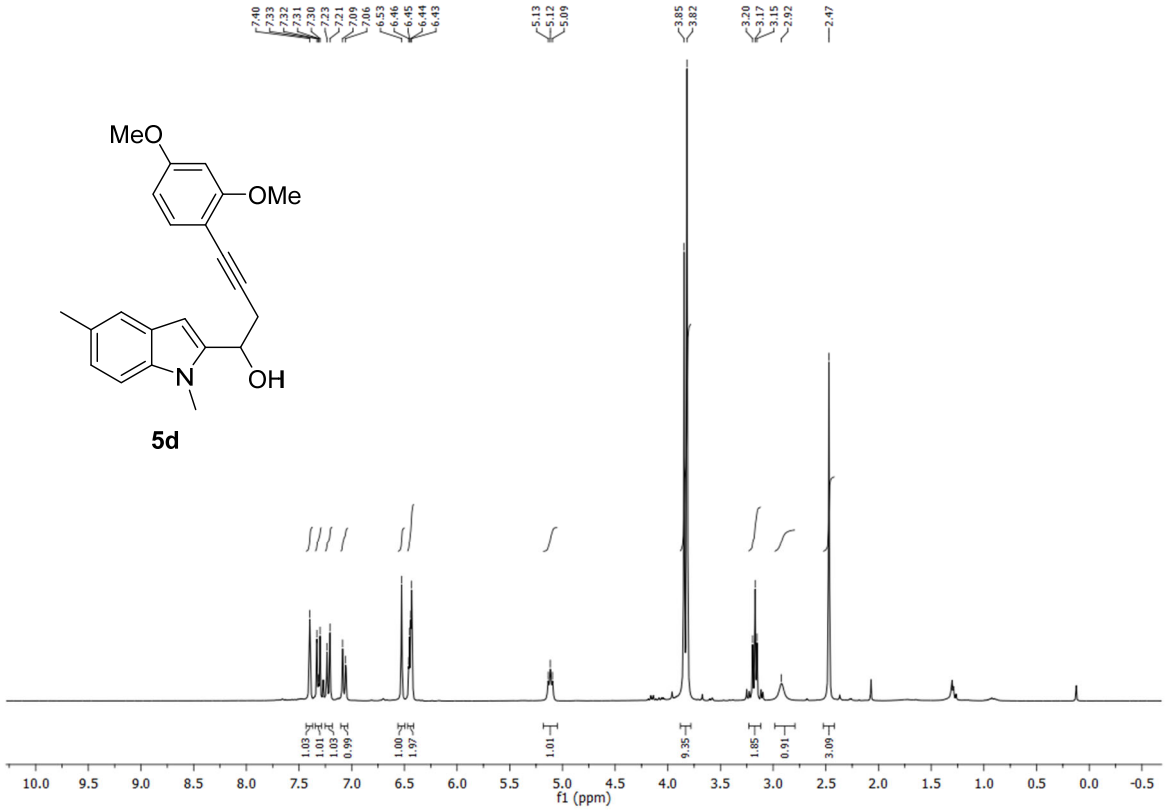

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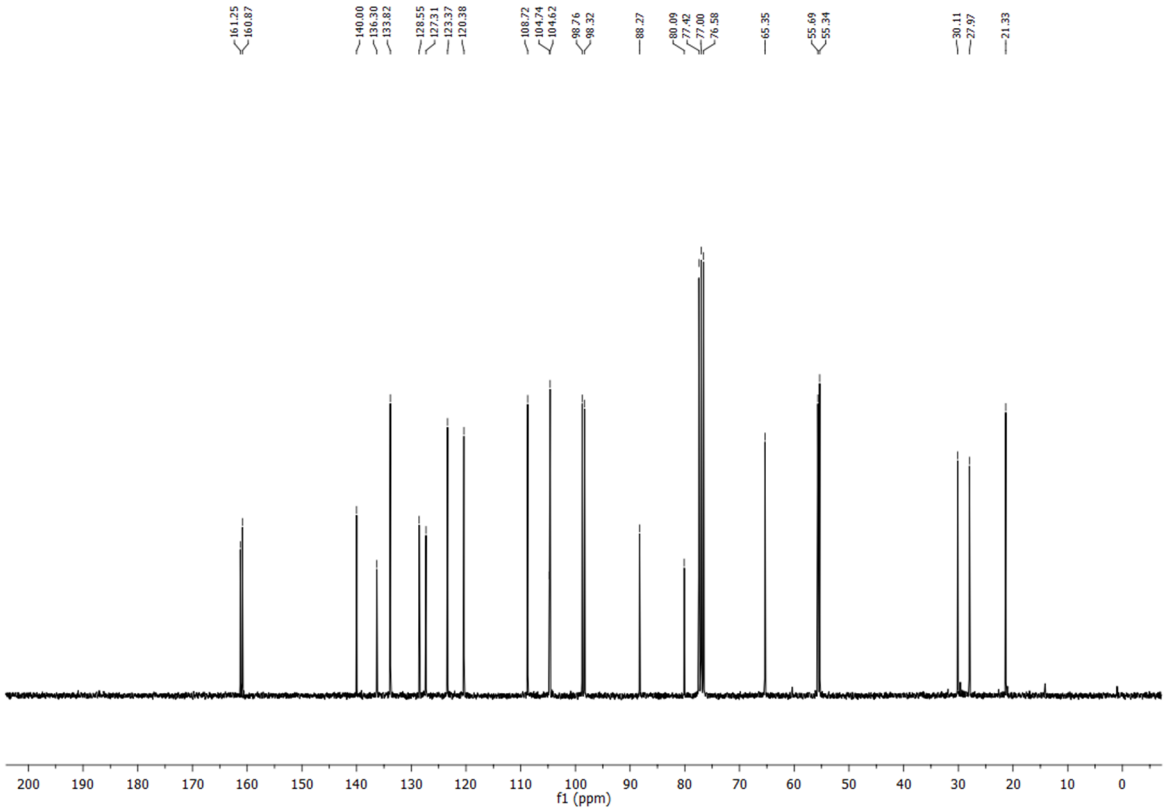
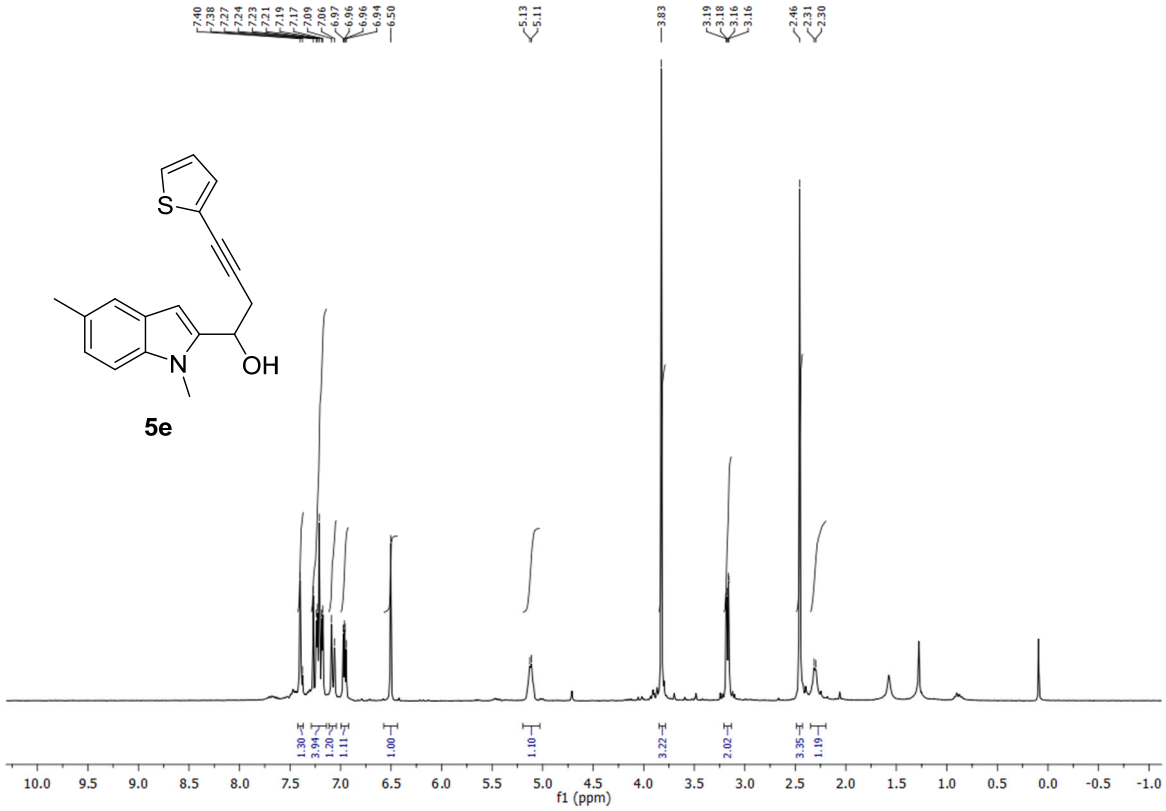


^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC)



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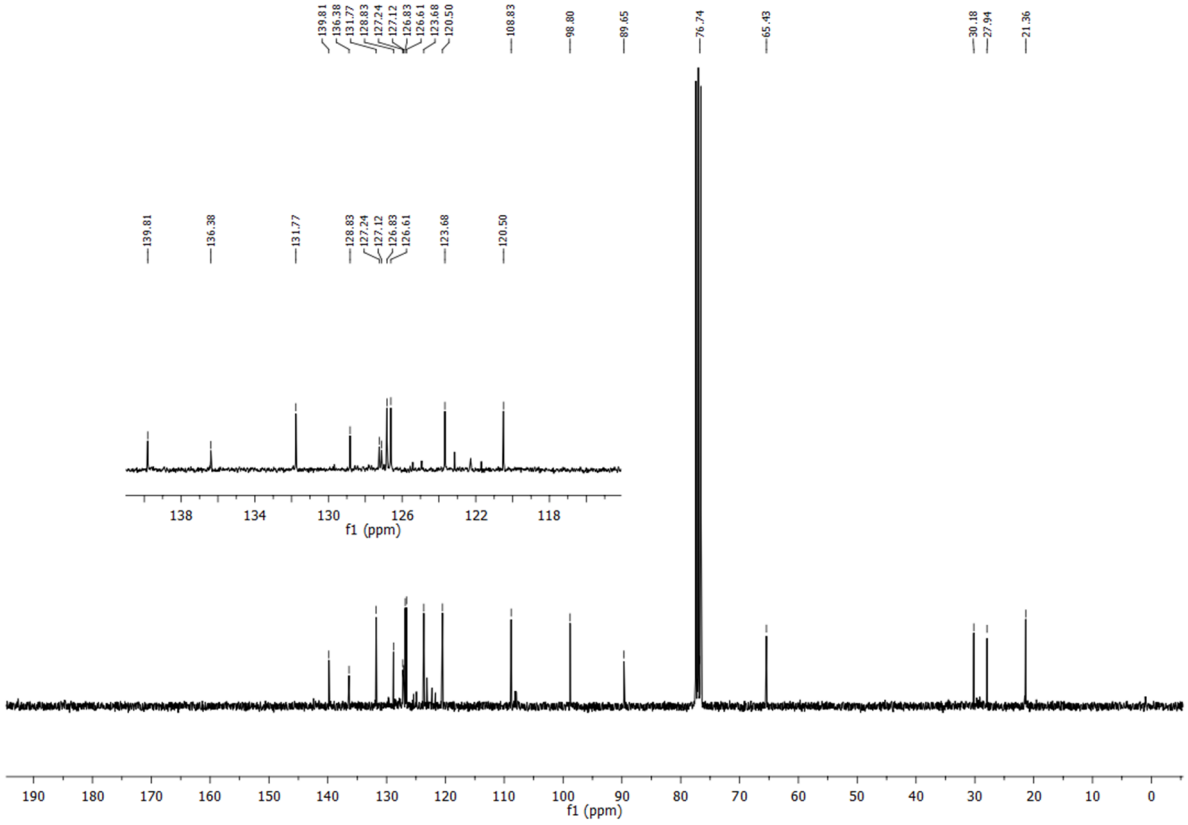

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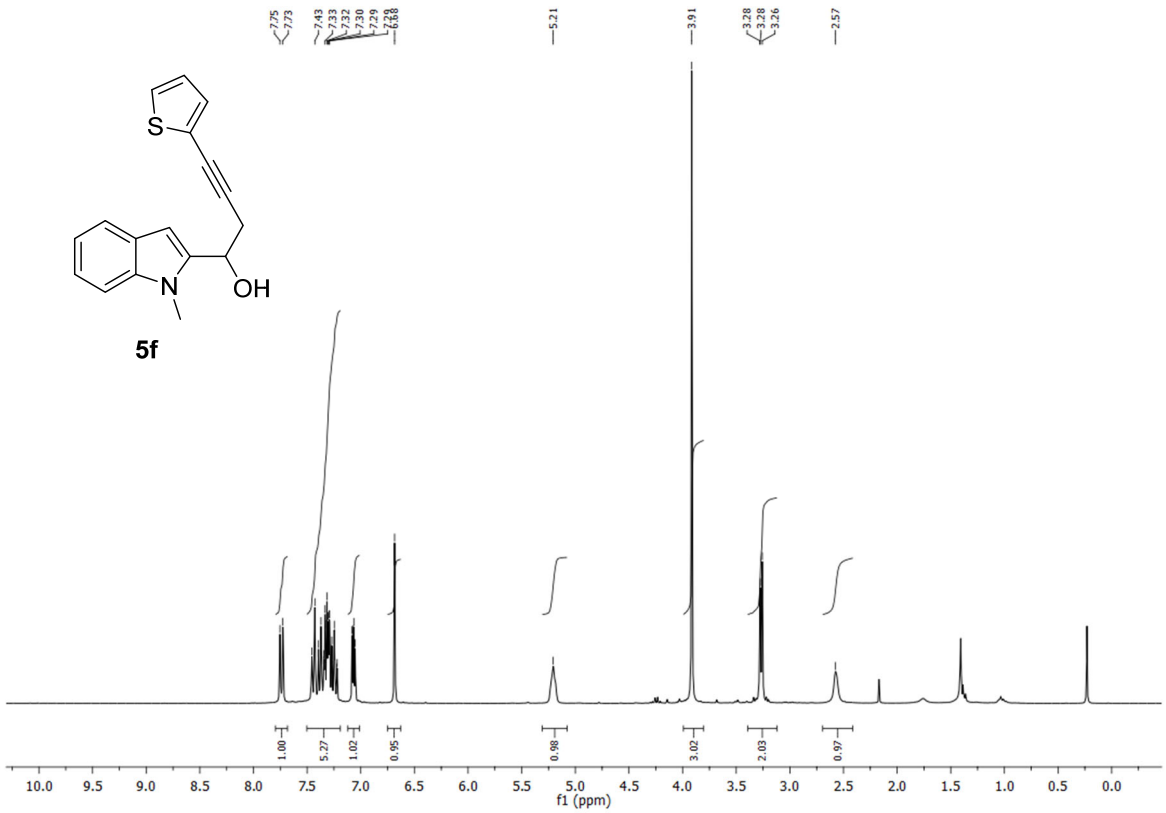

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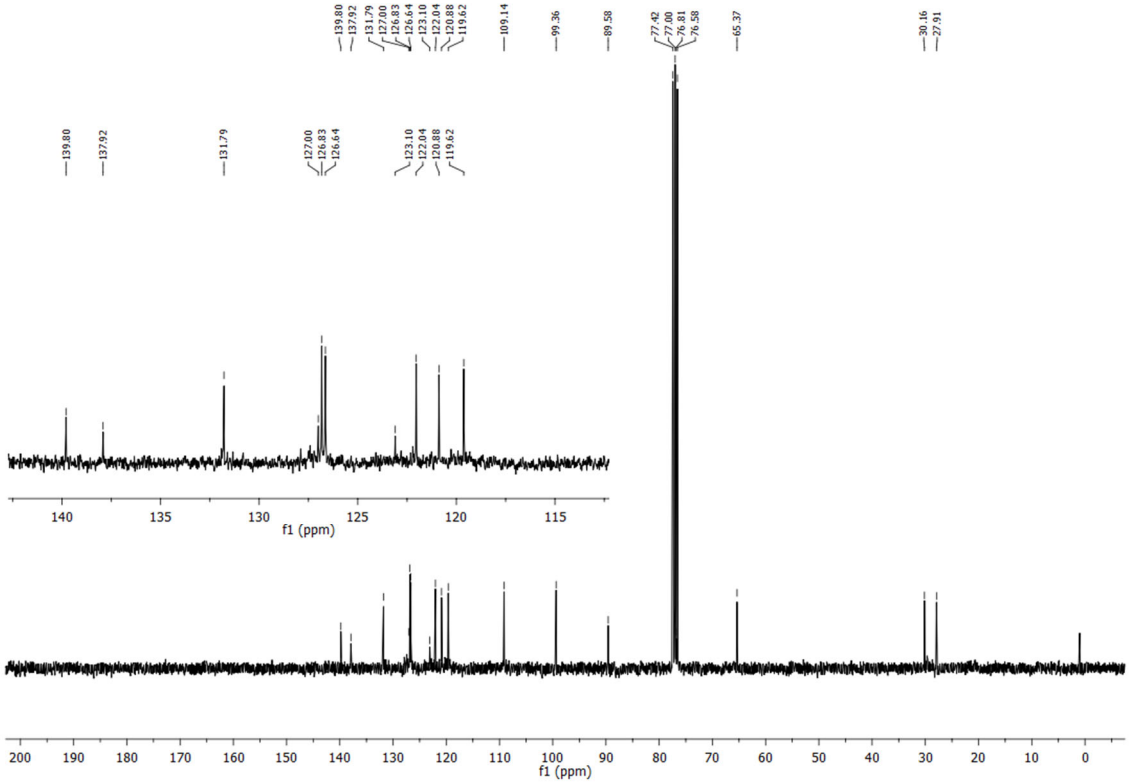

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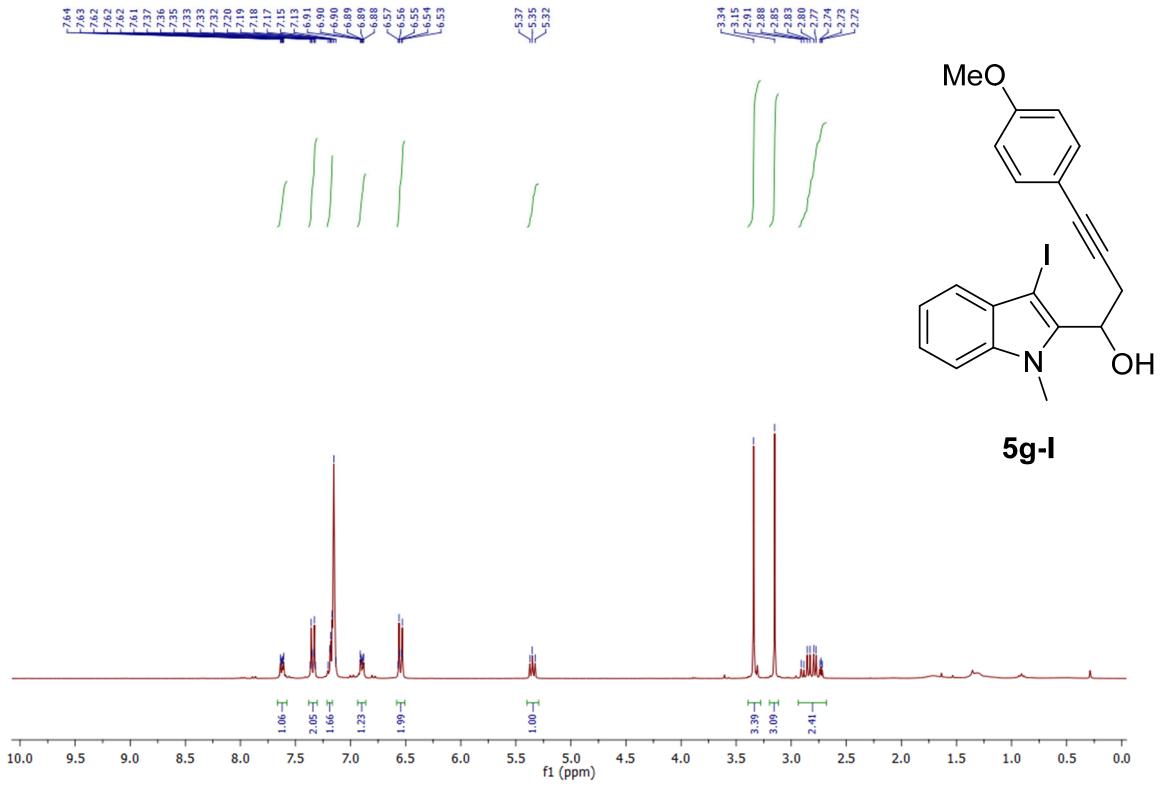

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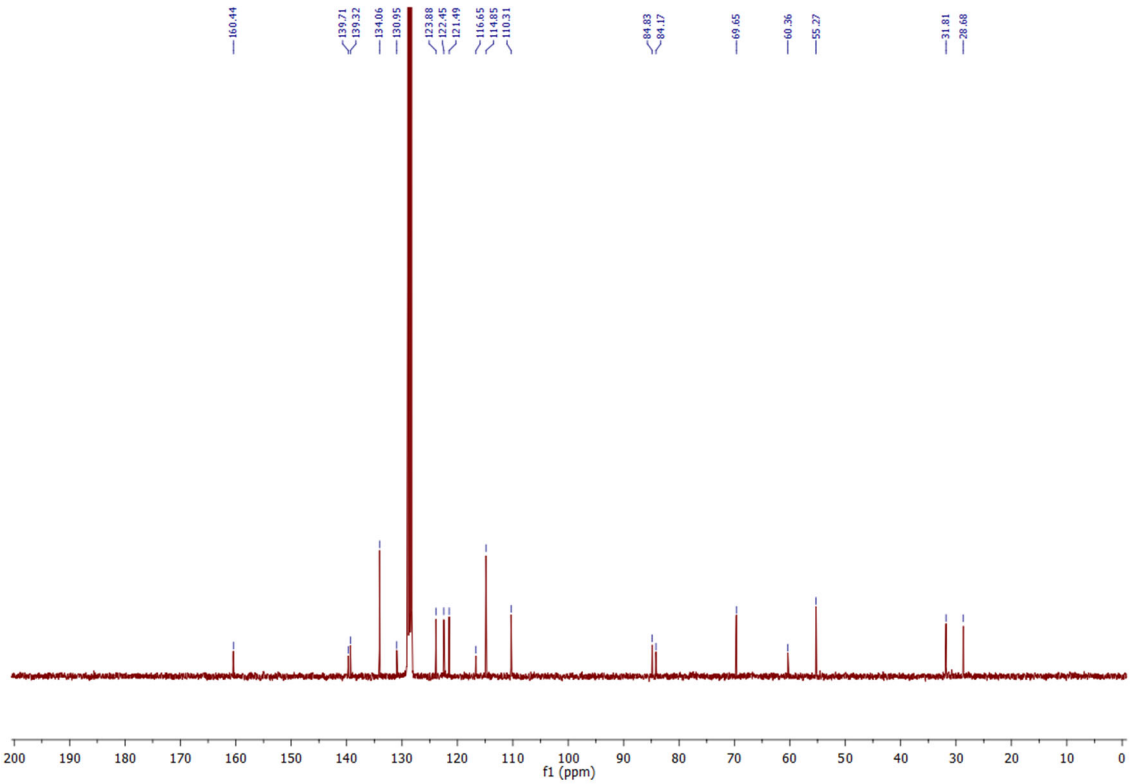

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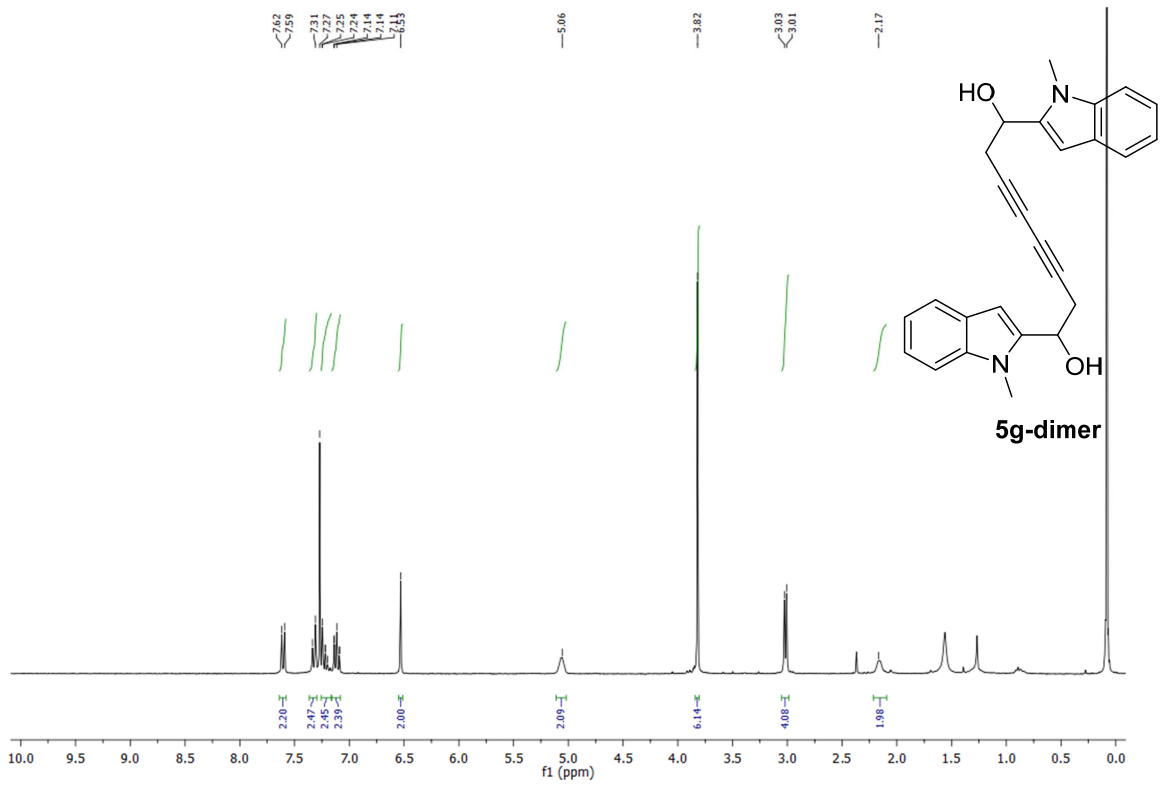

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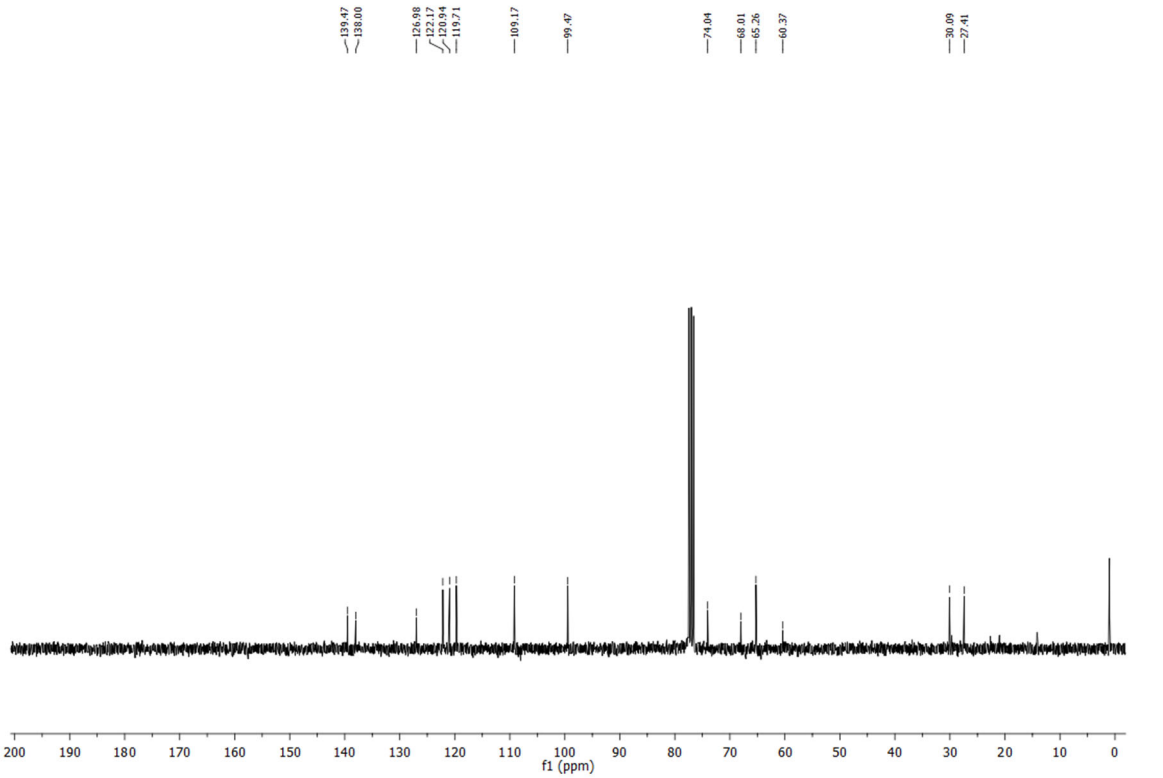

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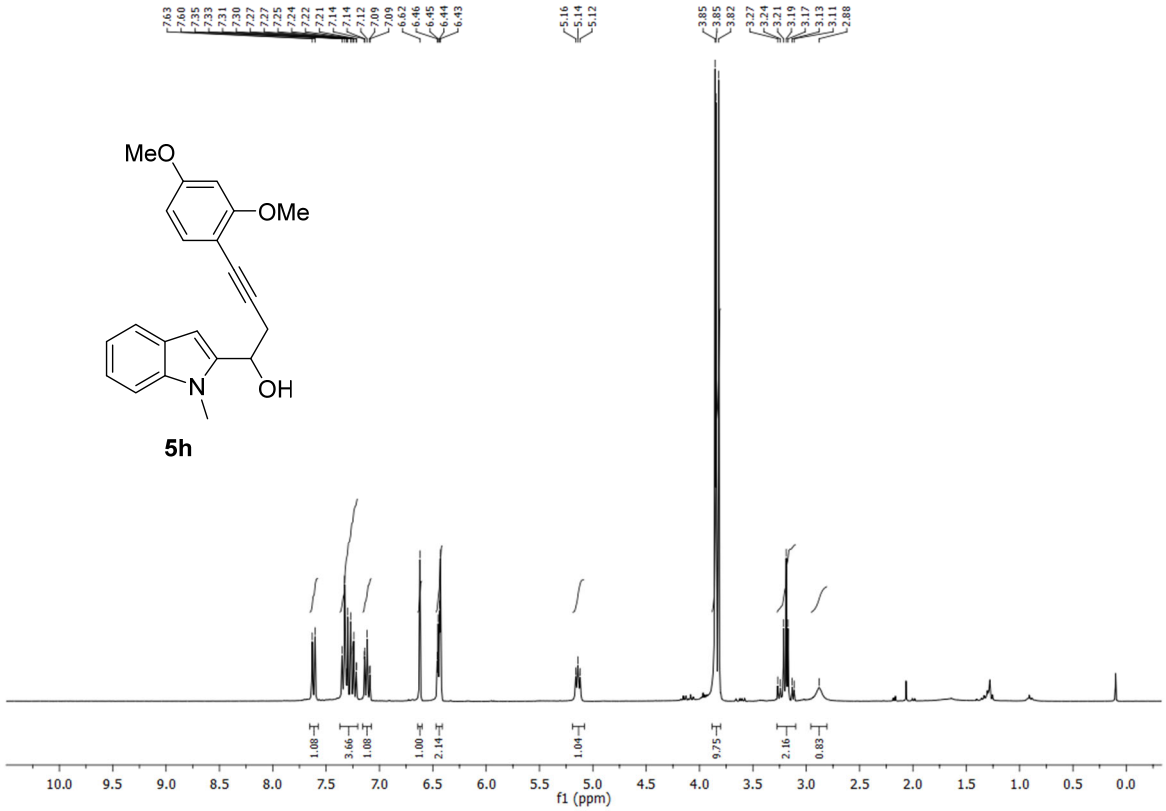

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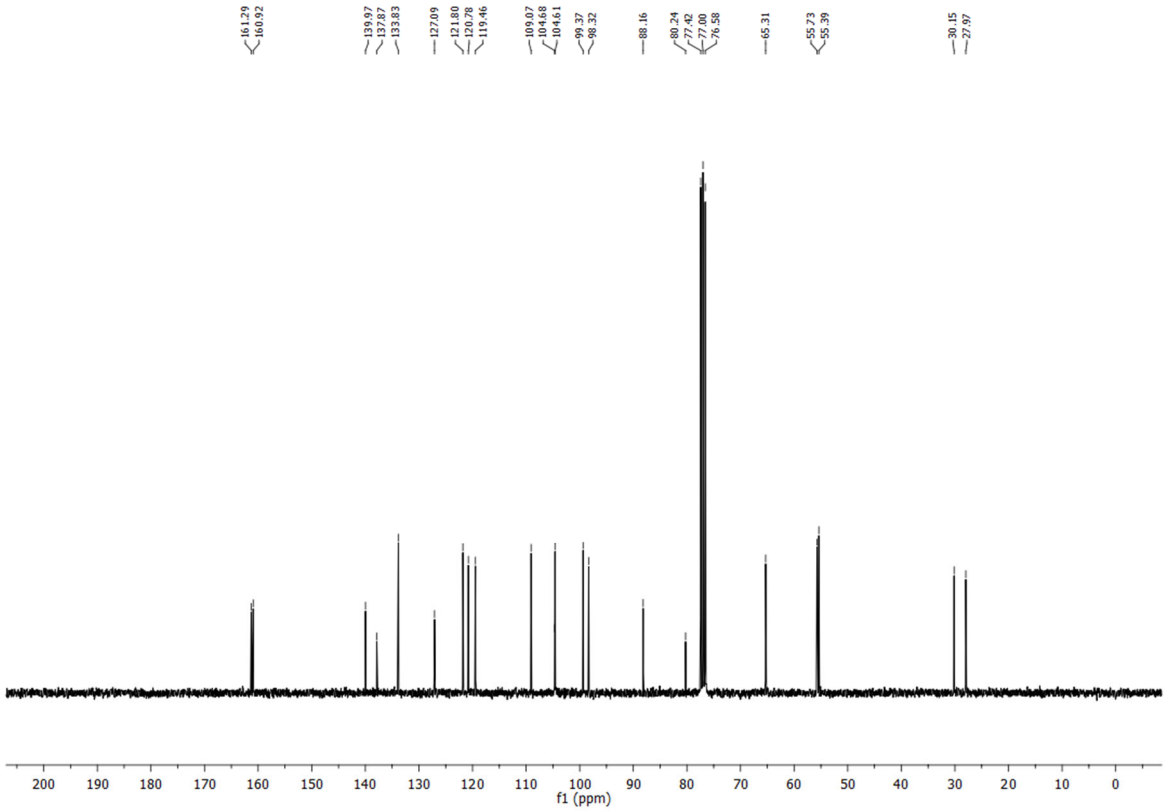

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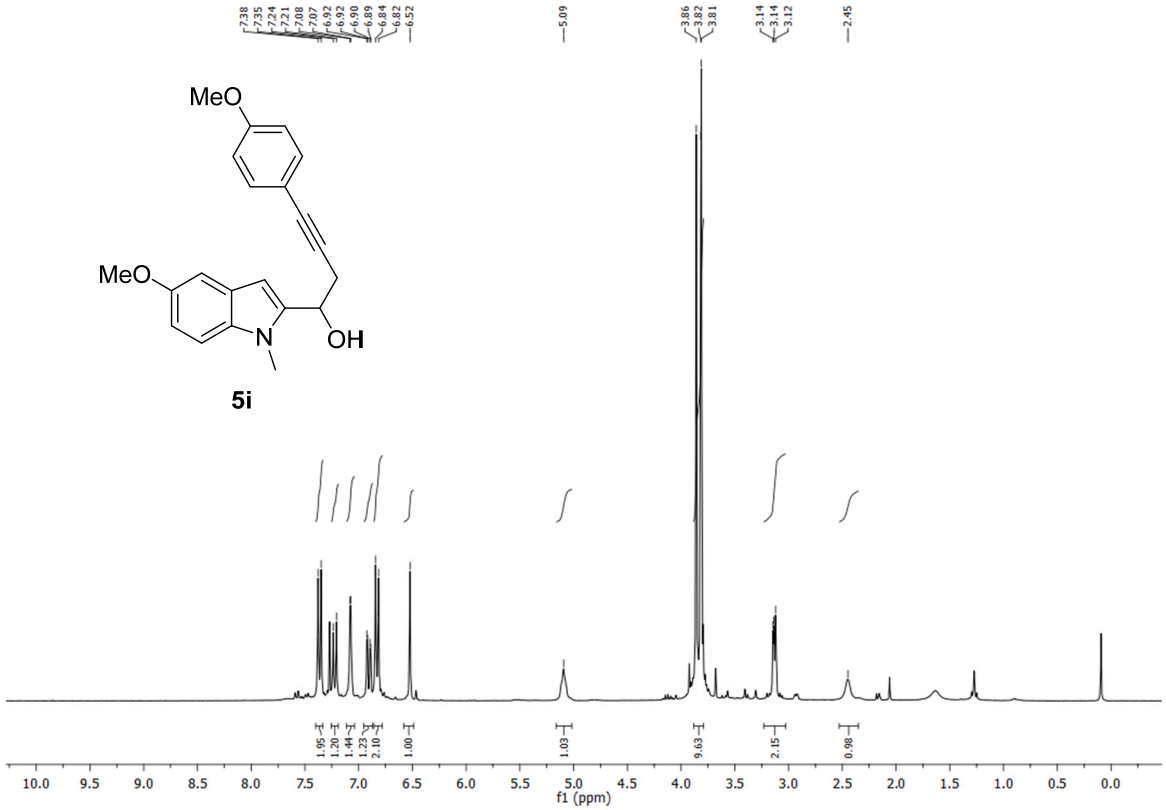

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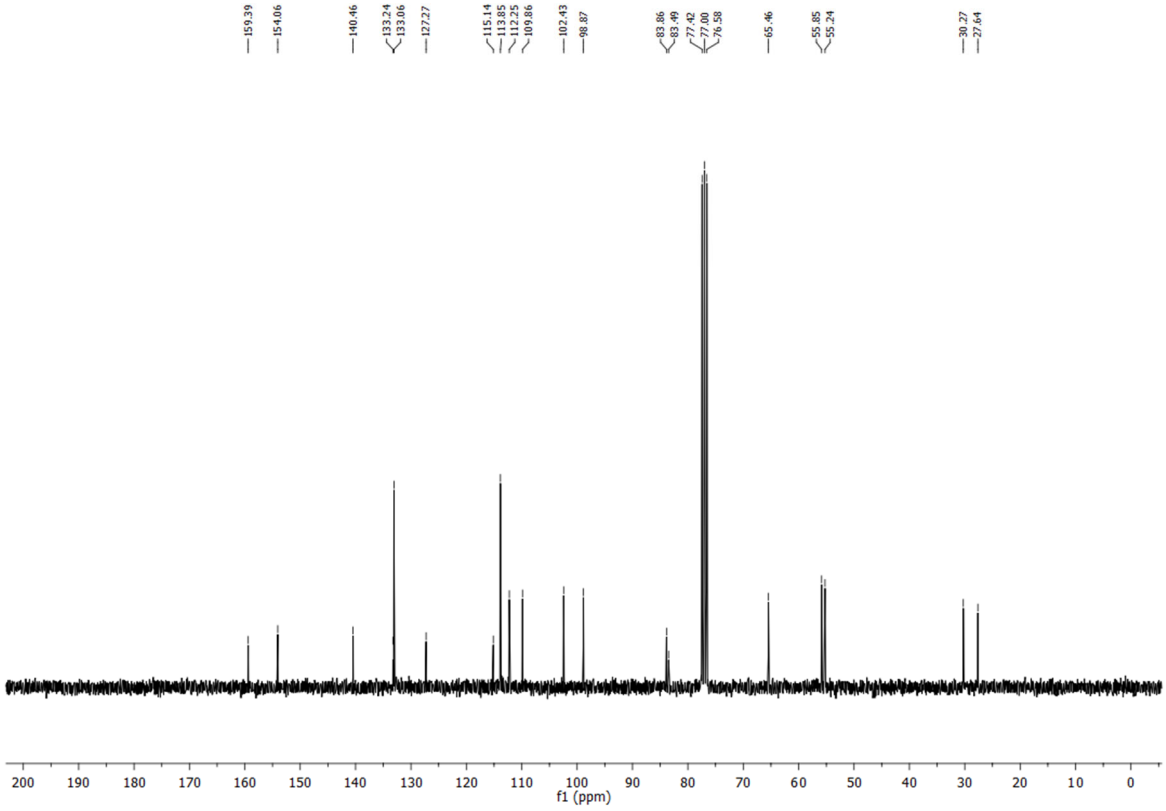

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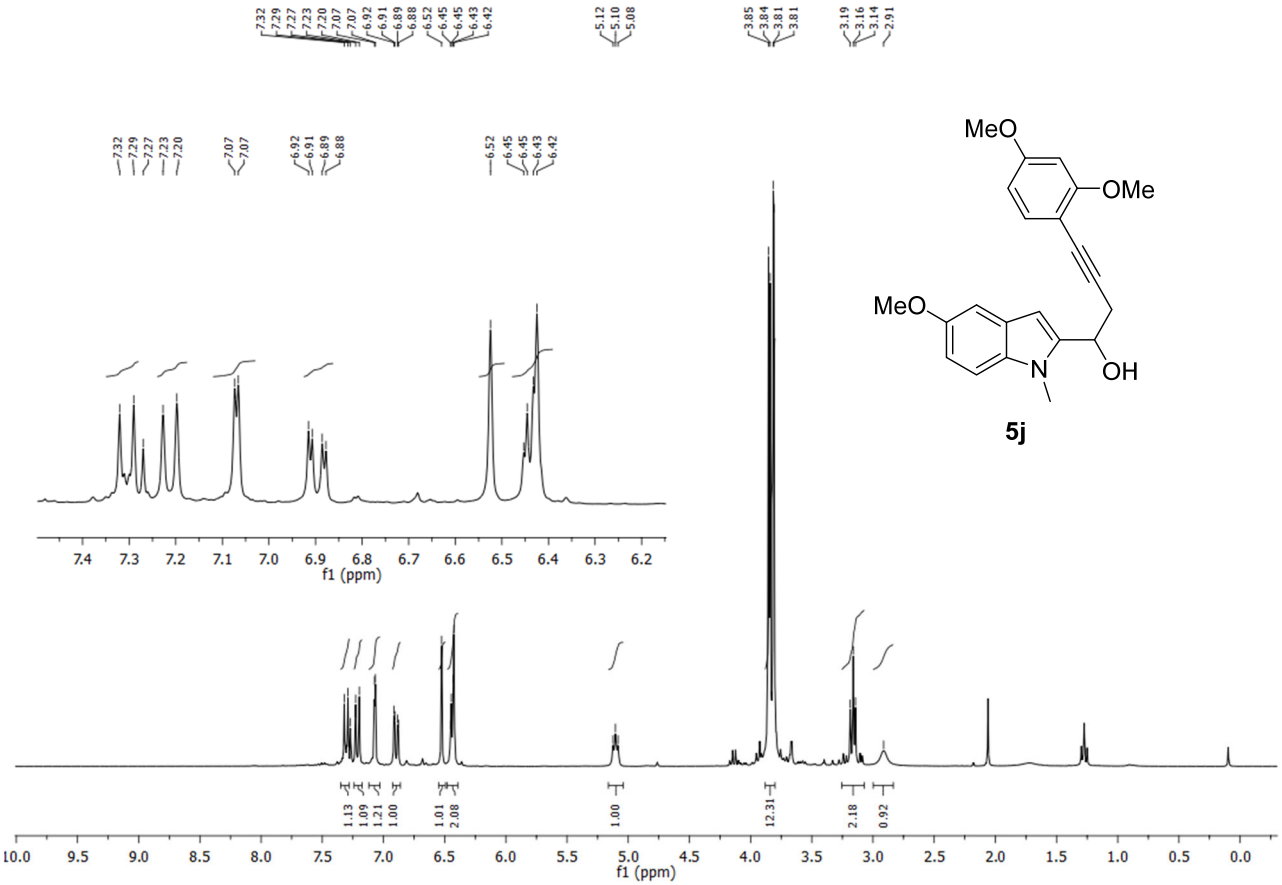

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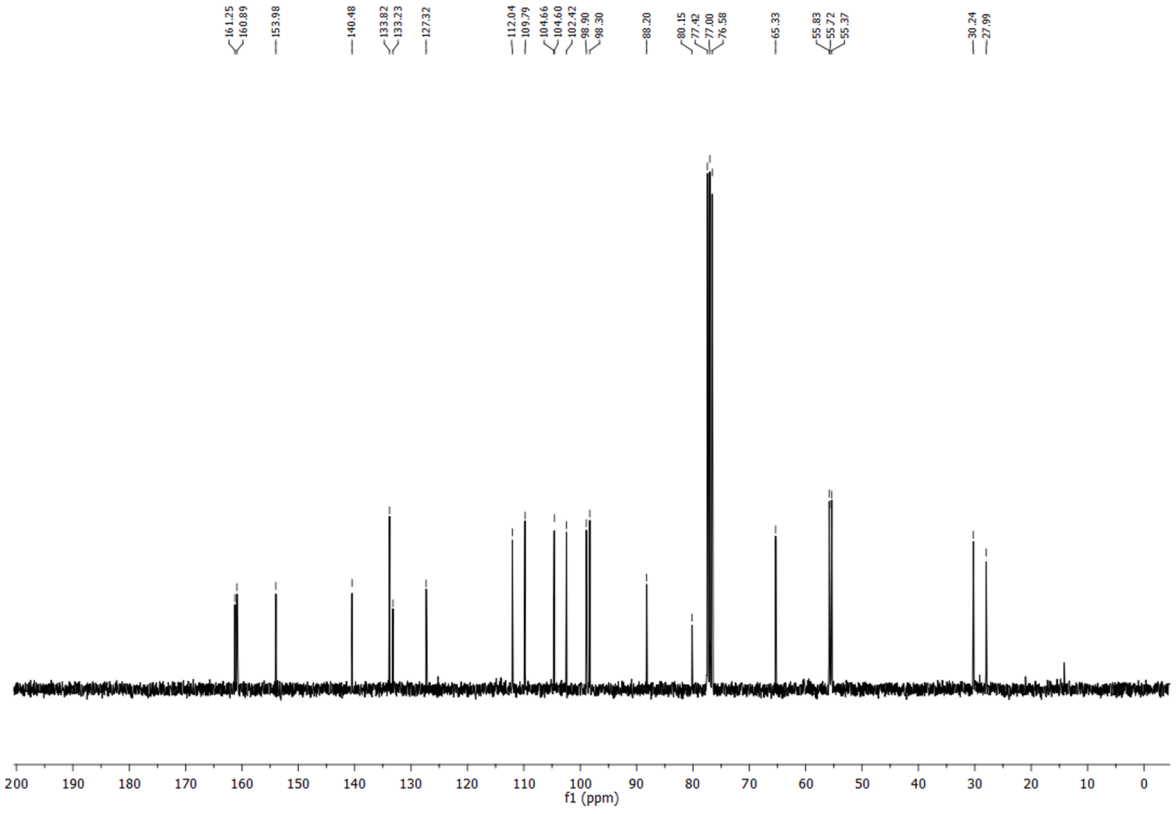

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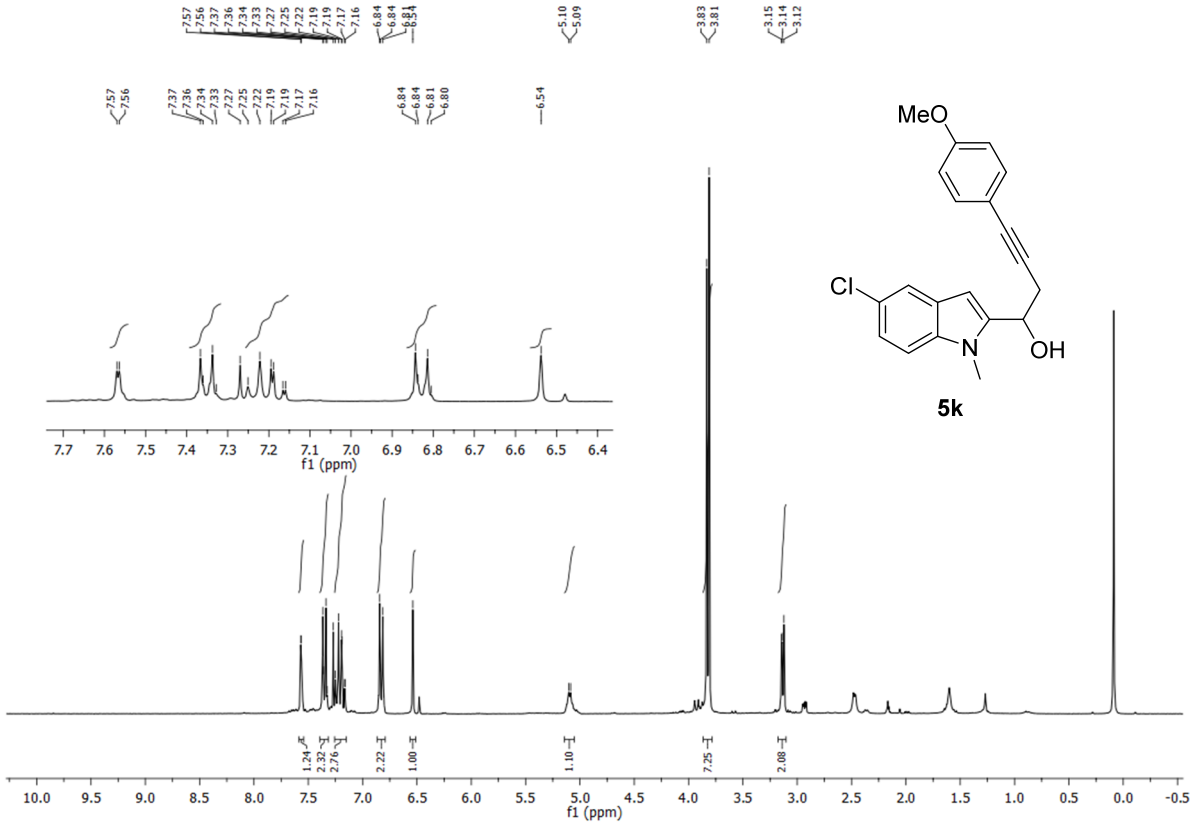

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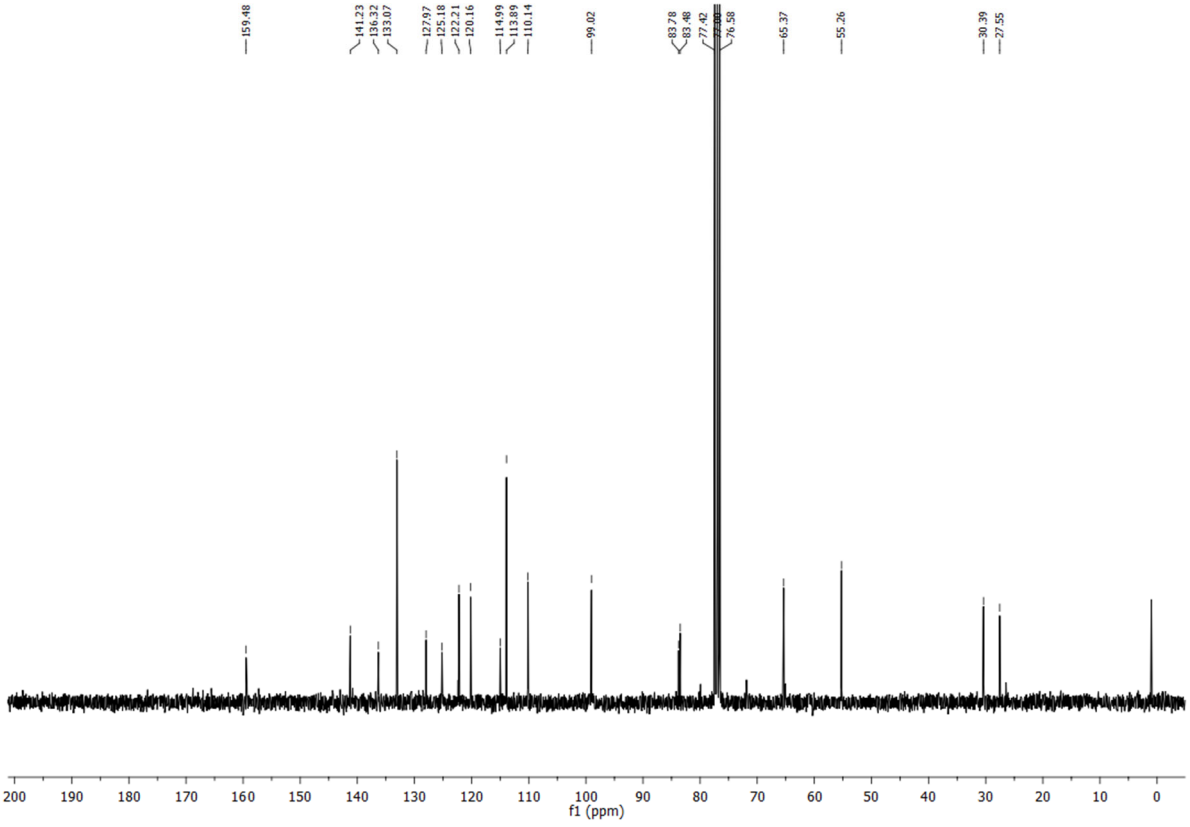

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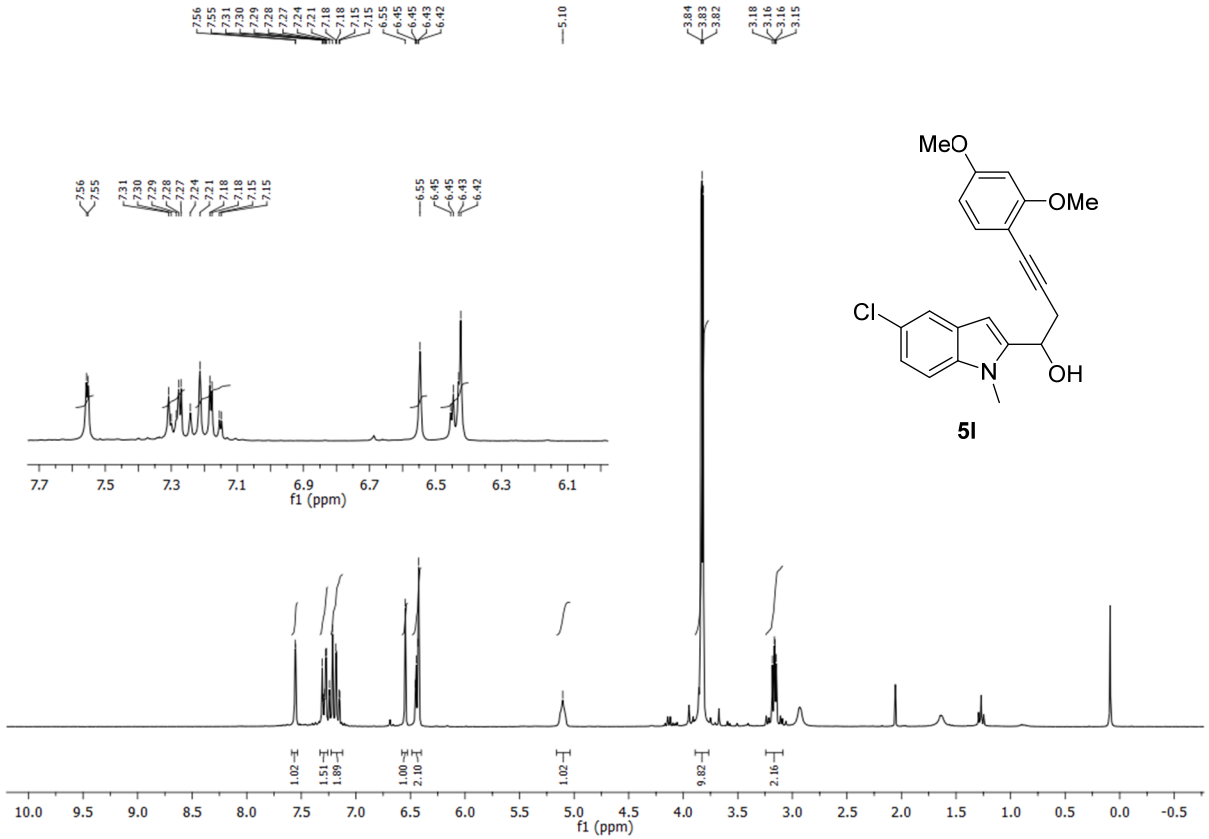

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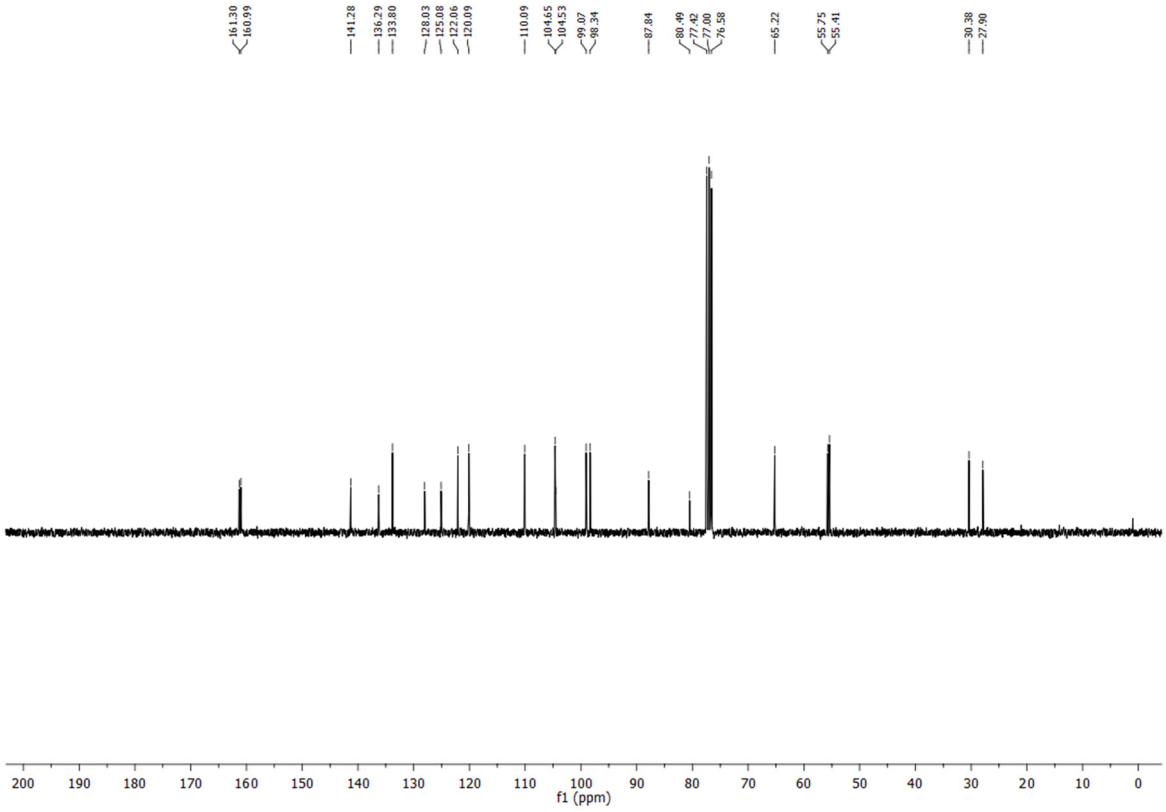
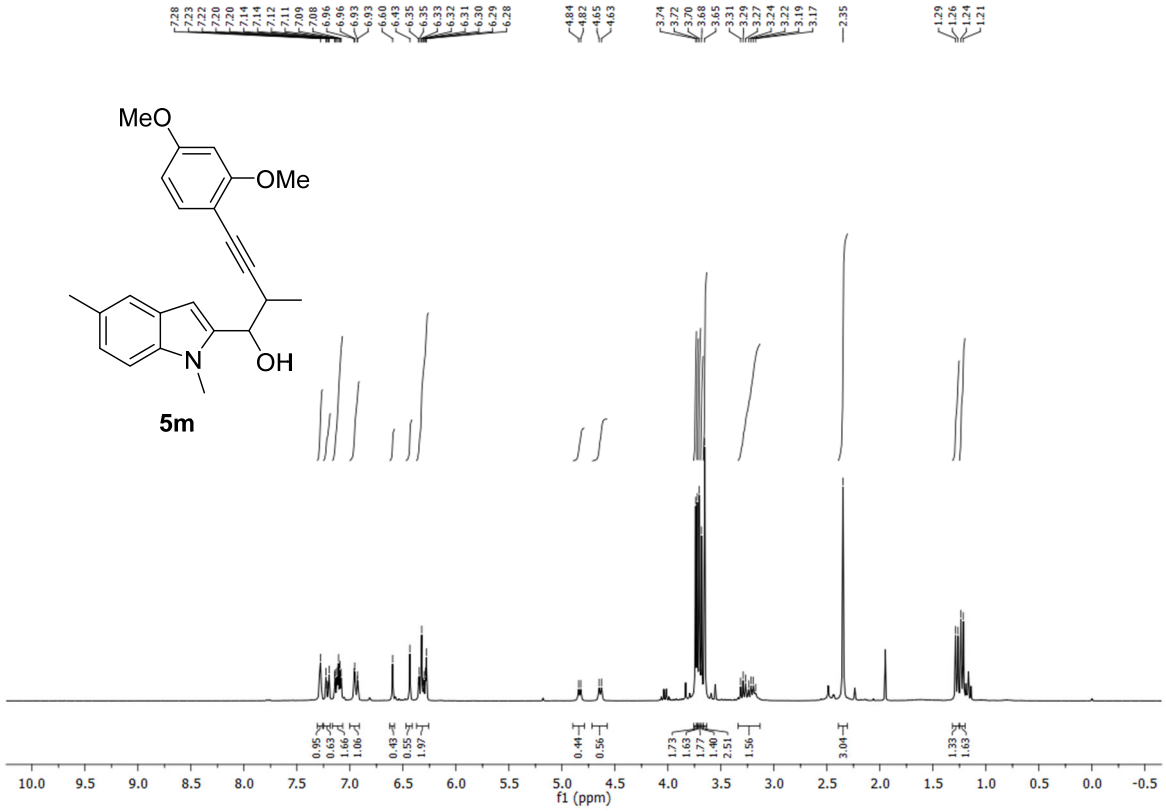
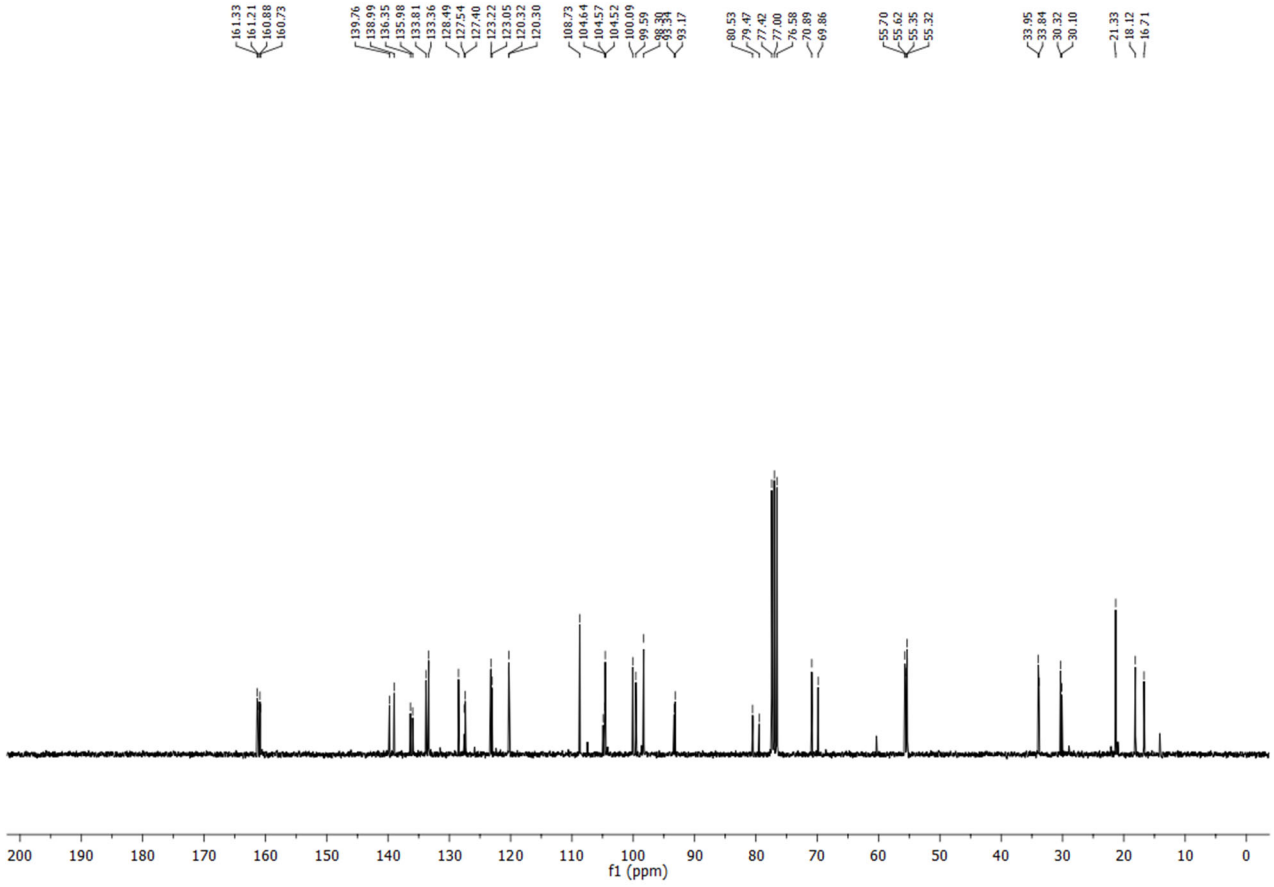


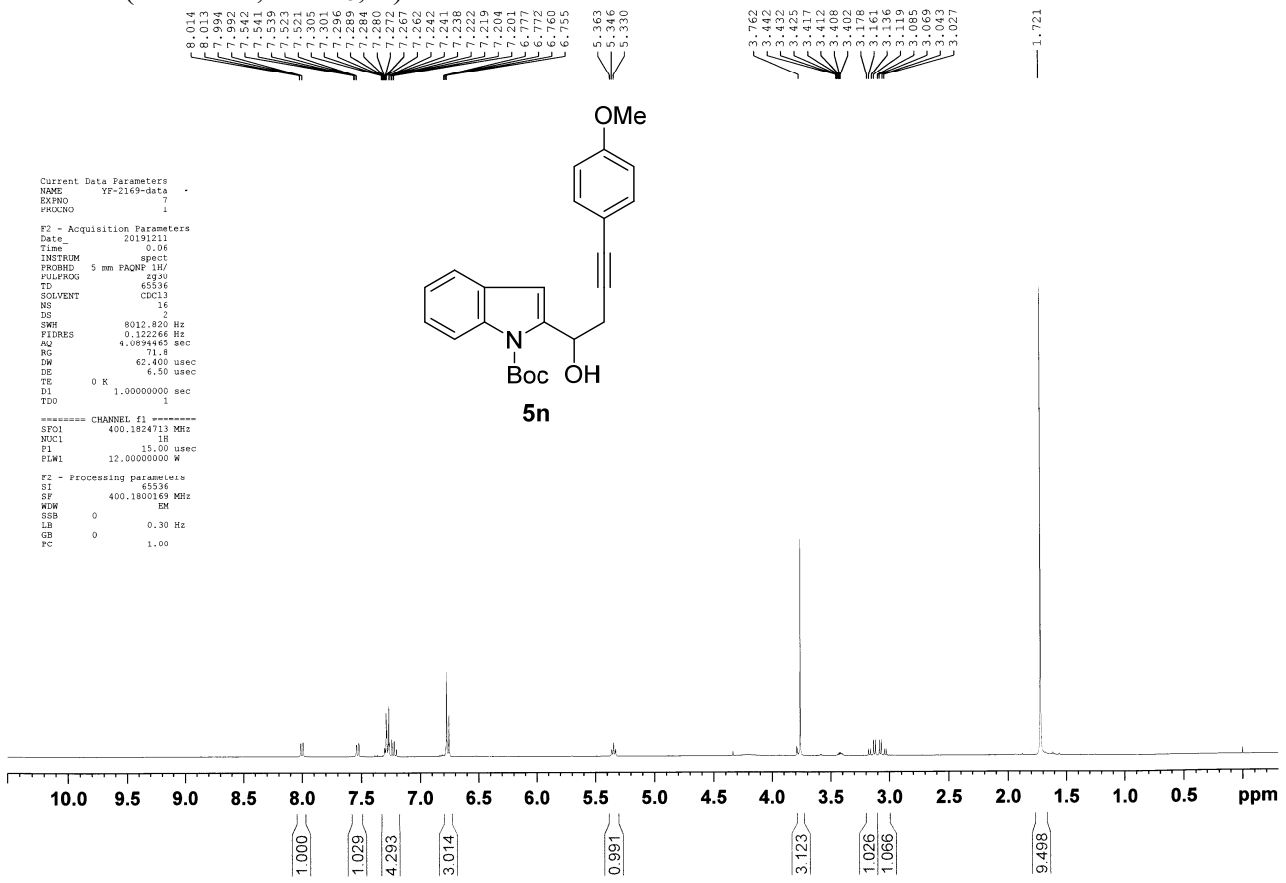
^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC)



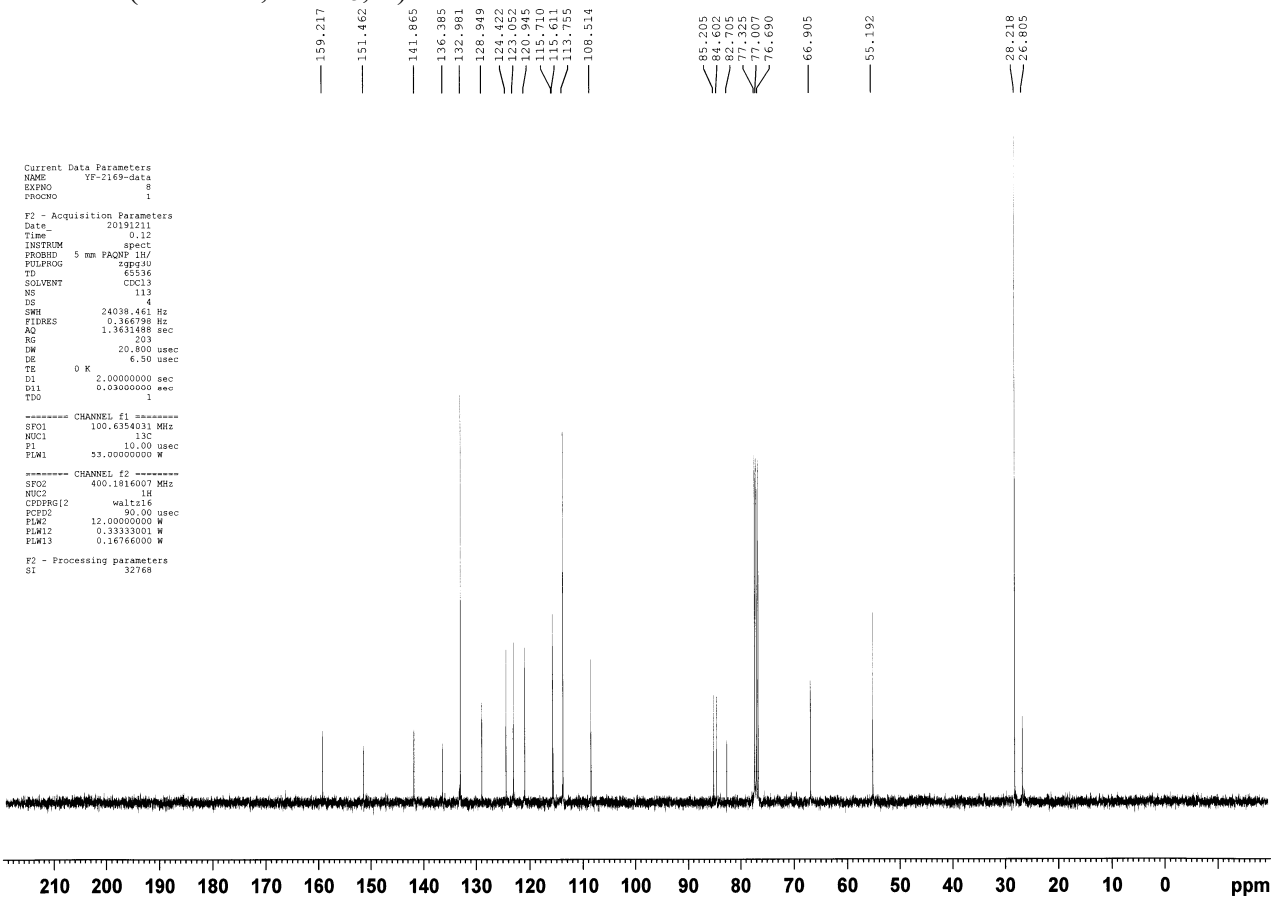
^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC)



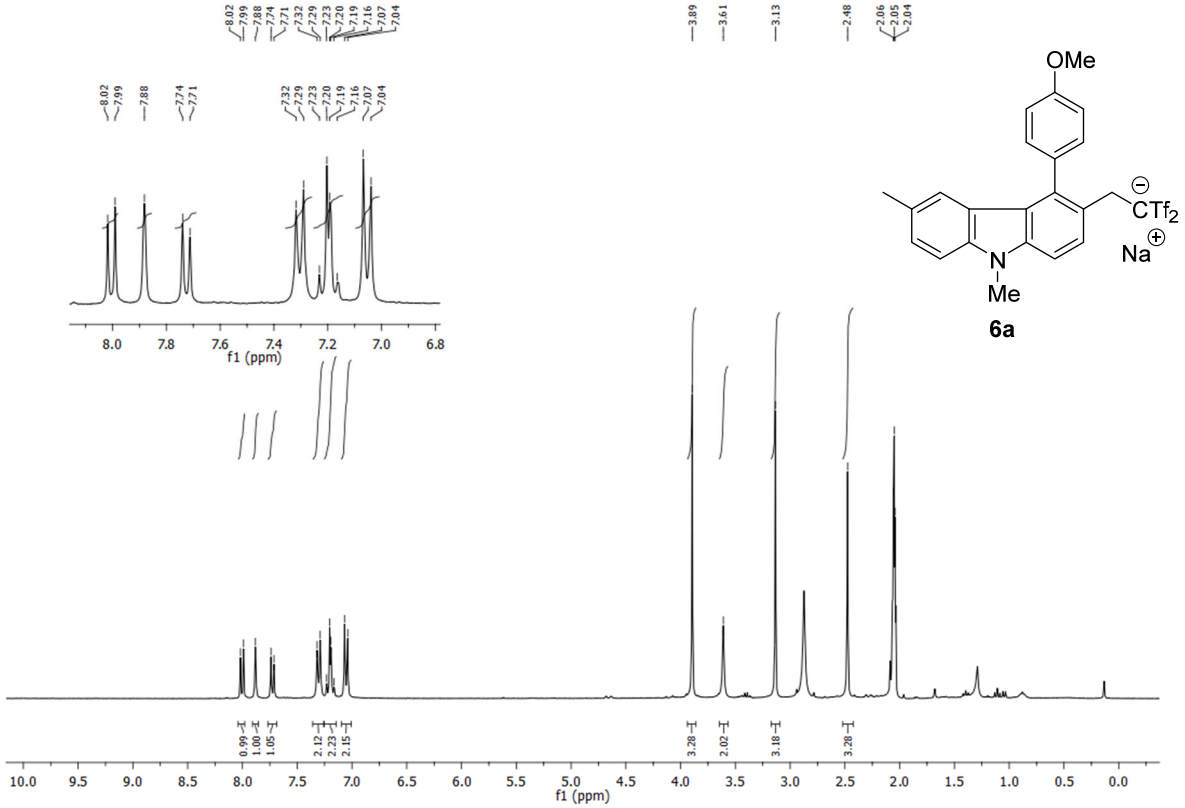
^{1}H NMR (400 MHz, $CDCl_3$, rt)



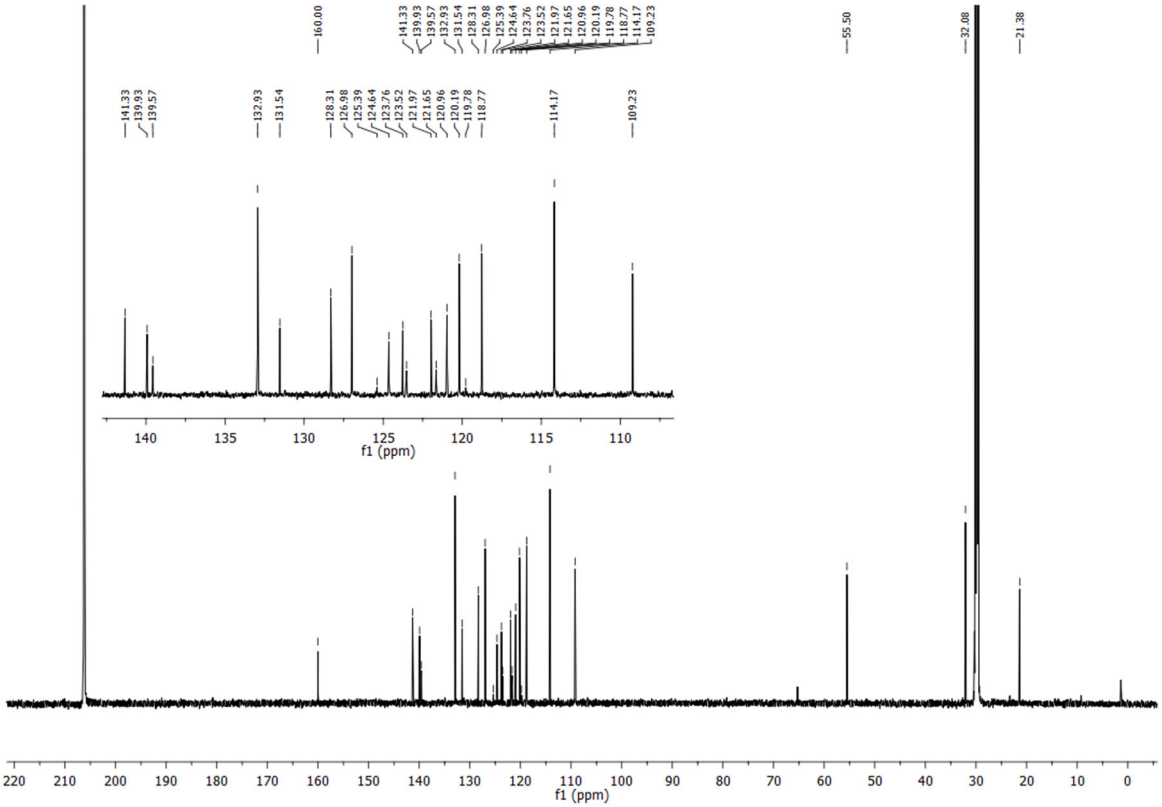
^{13}C NMR (100 MHz, $CDCl_3$, rt)



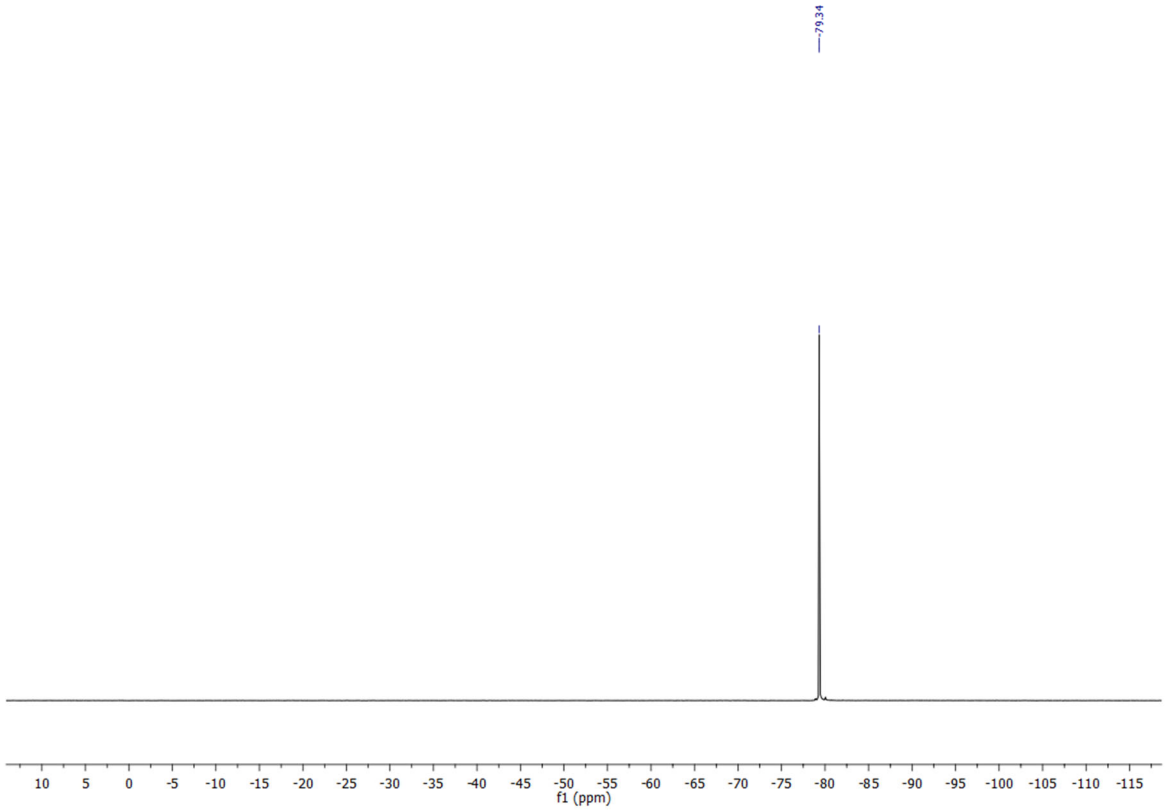
^{1}H NMR (300 MHz, CD_3COCD_3, 25 ºC)



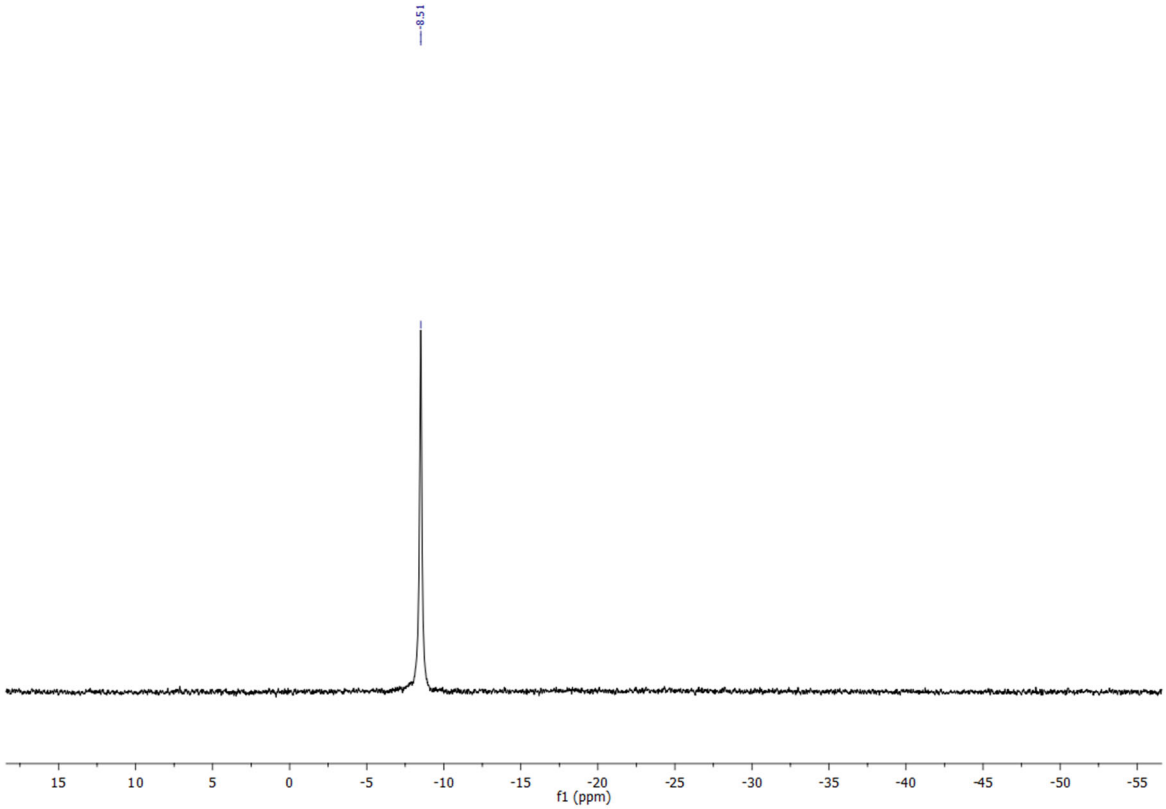
^{13}C NMR (175 MHz, CD_3COCD_3, 25 ºC)



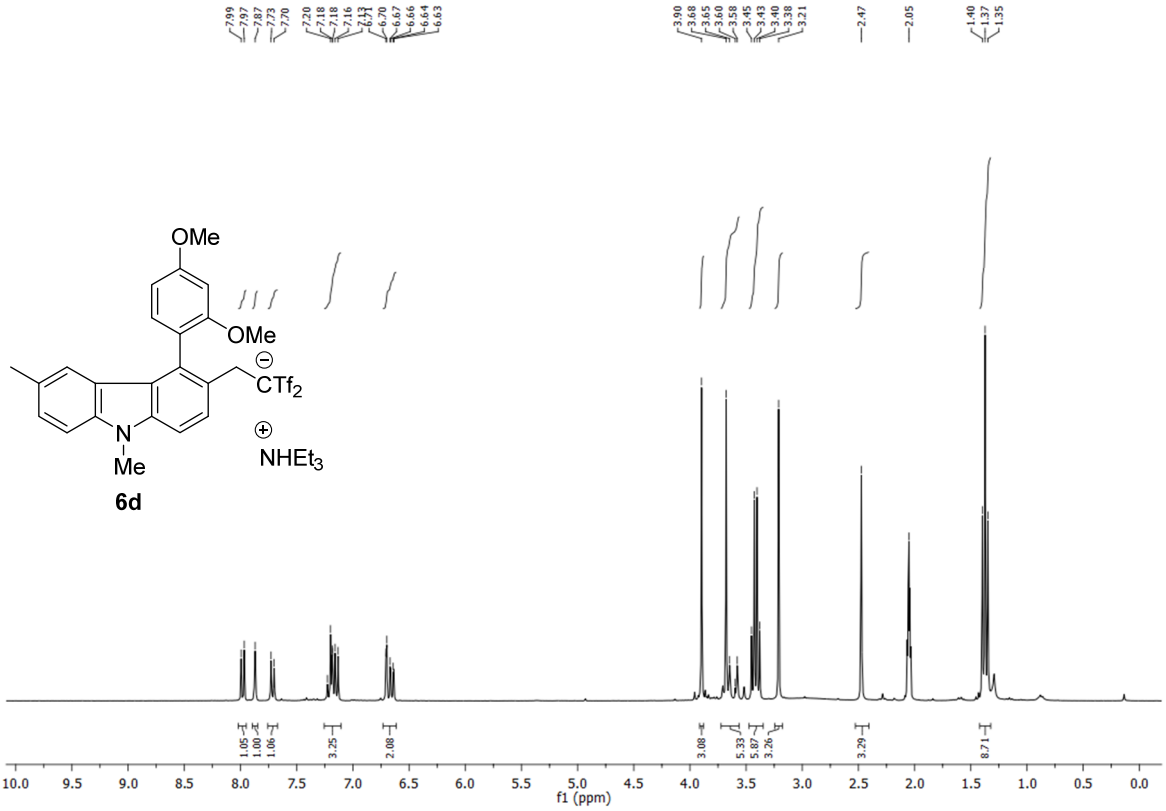
^{19}F NMR (282 MHz, CD_3COCD_3, 25 °C)



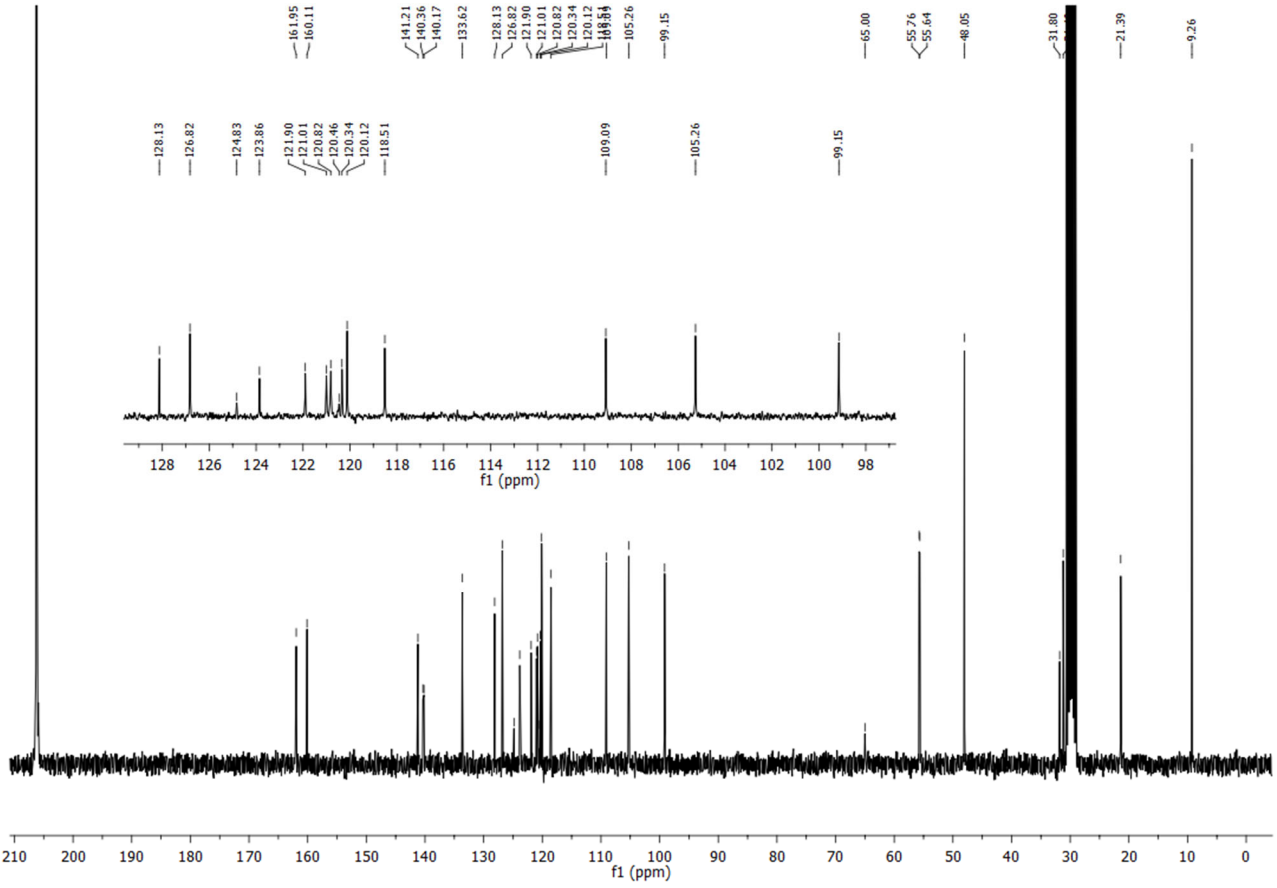
^{23}Na NMR (132 MHz, CD_3COCD_3, 25 °C)



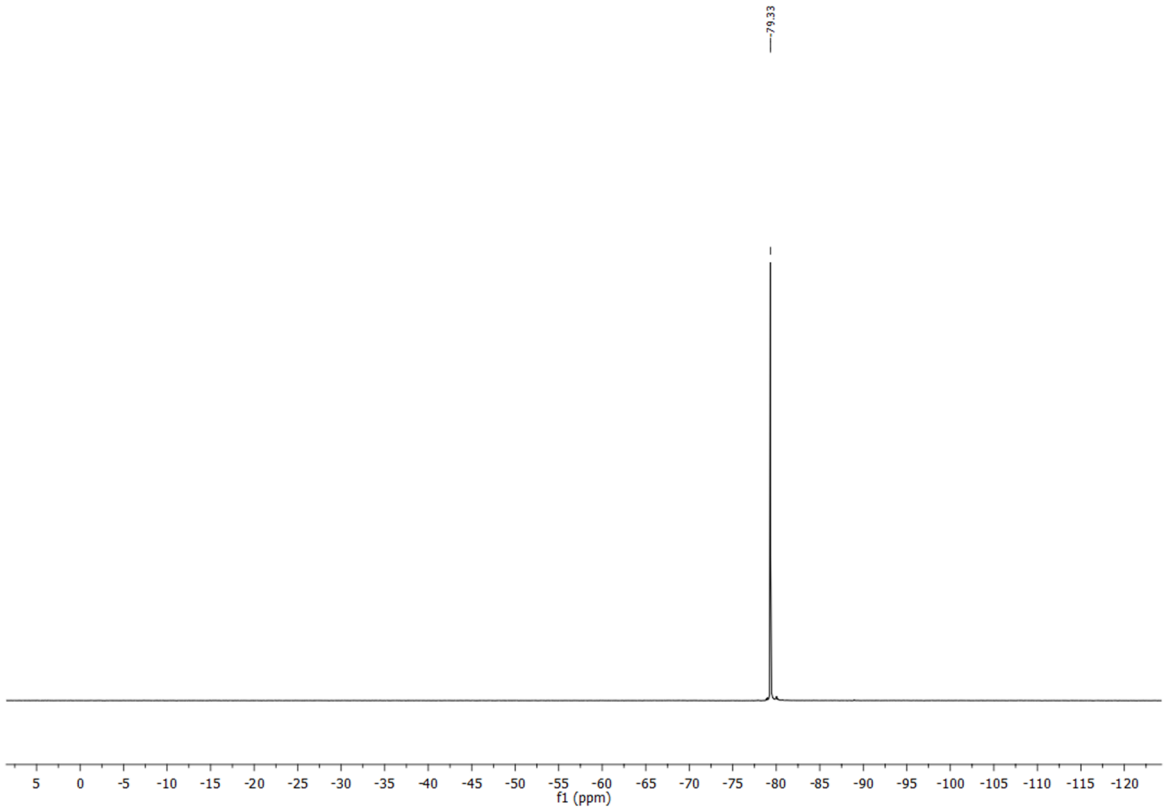
^{1}H NMR (300 MHz, CD_3COCD_3, 25 °C)



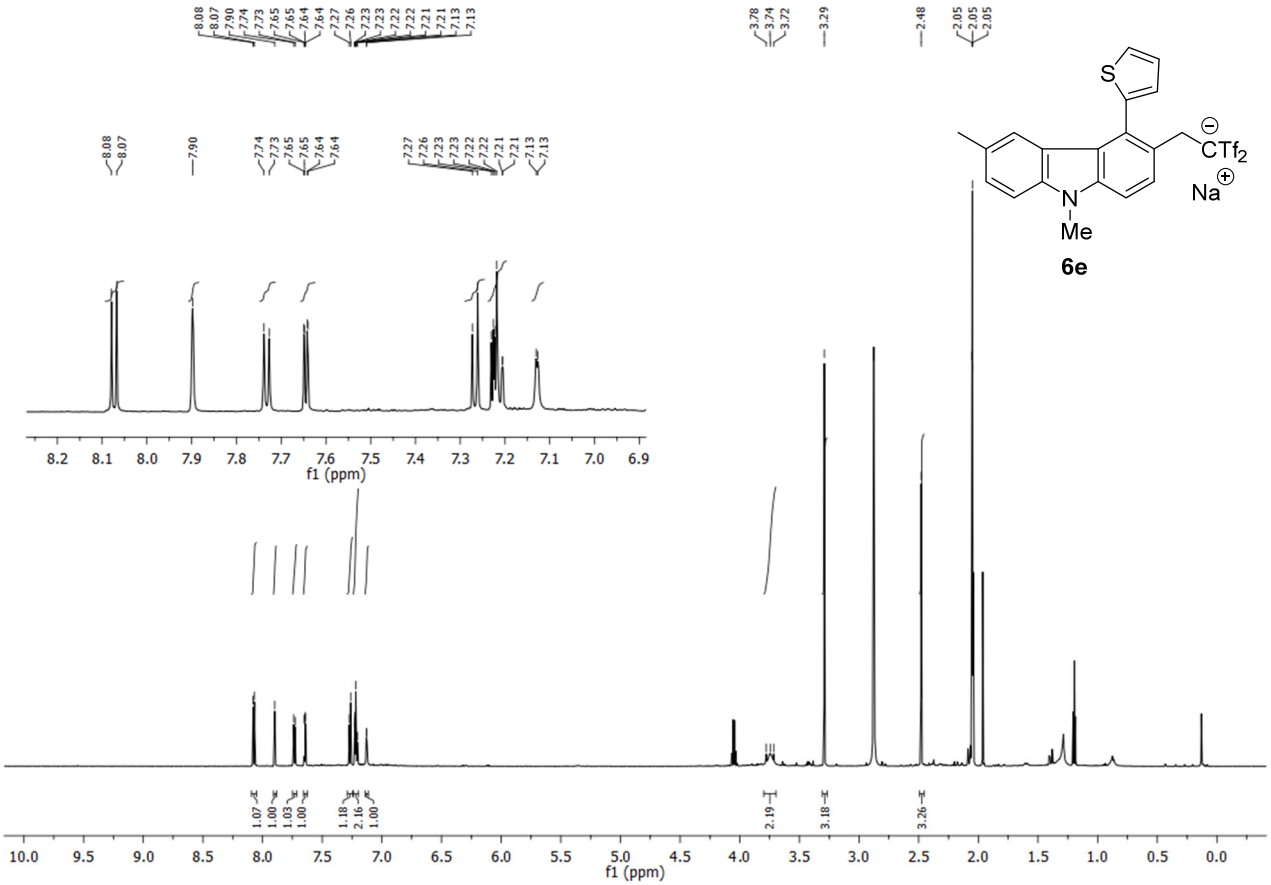
^{13}C NMR (175 MHz, CD_3COCD_3, 25 °C)



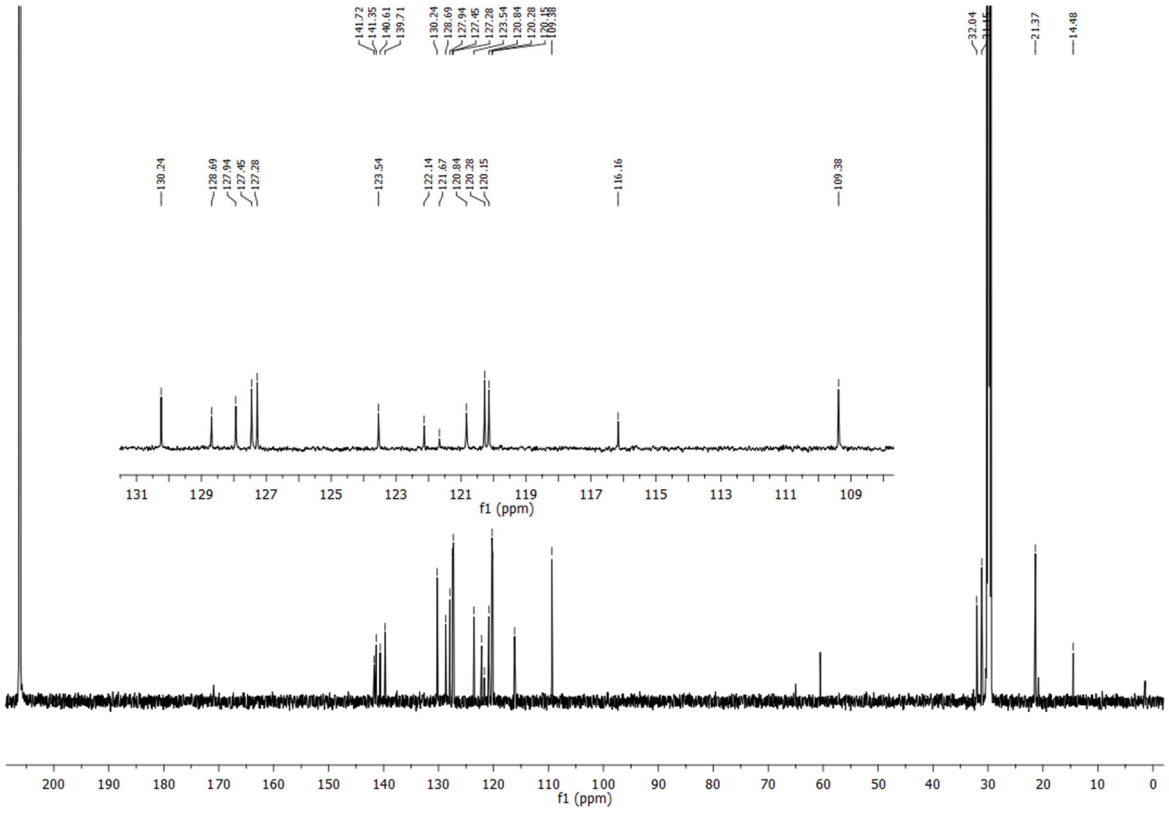
^{19}F NMR (282 MHz, CD_3COCD_3, 25 °C)



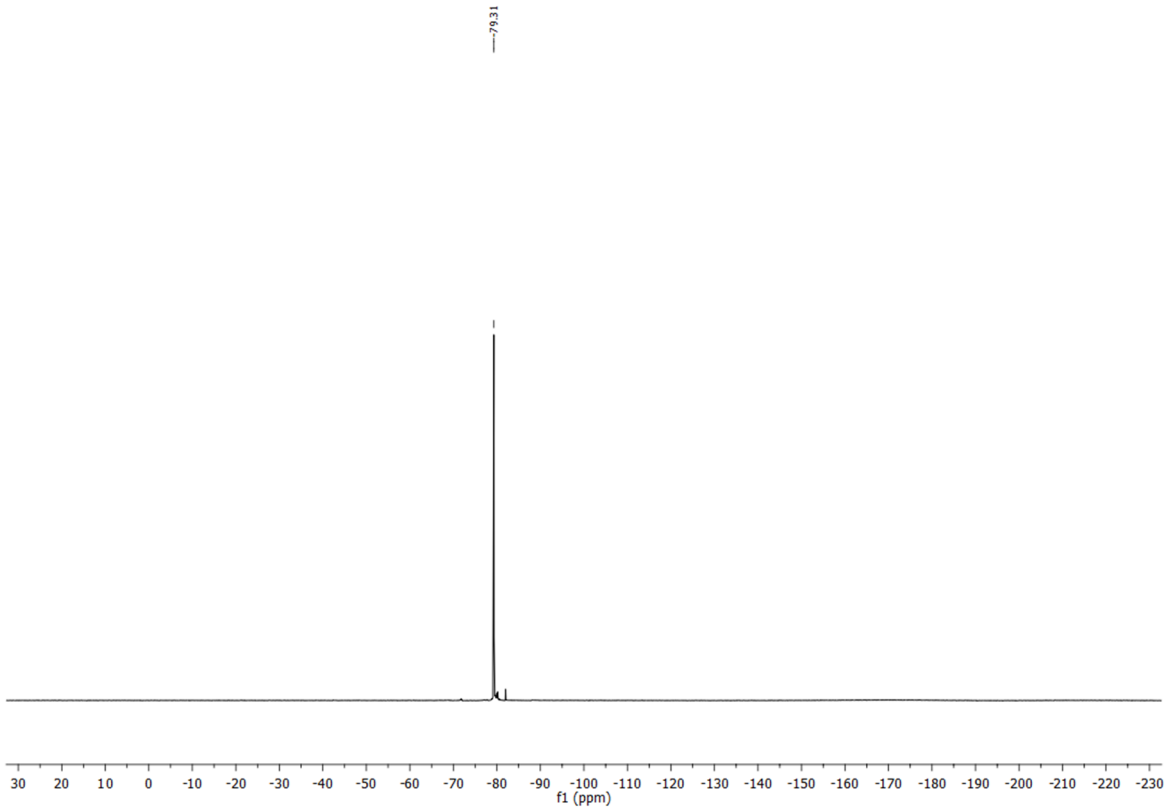
^{1}H NMR (300 MHz, CD_3COCD_3, 25 ºC)



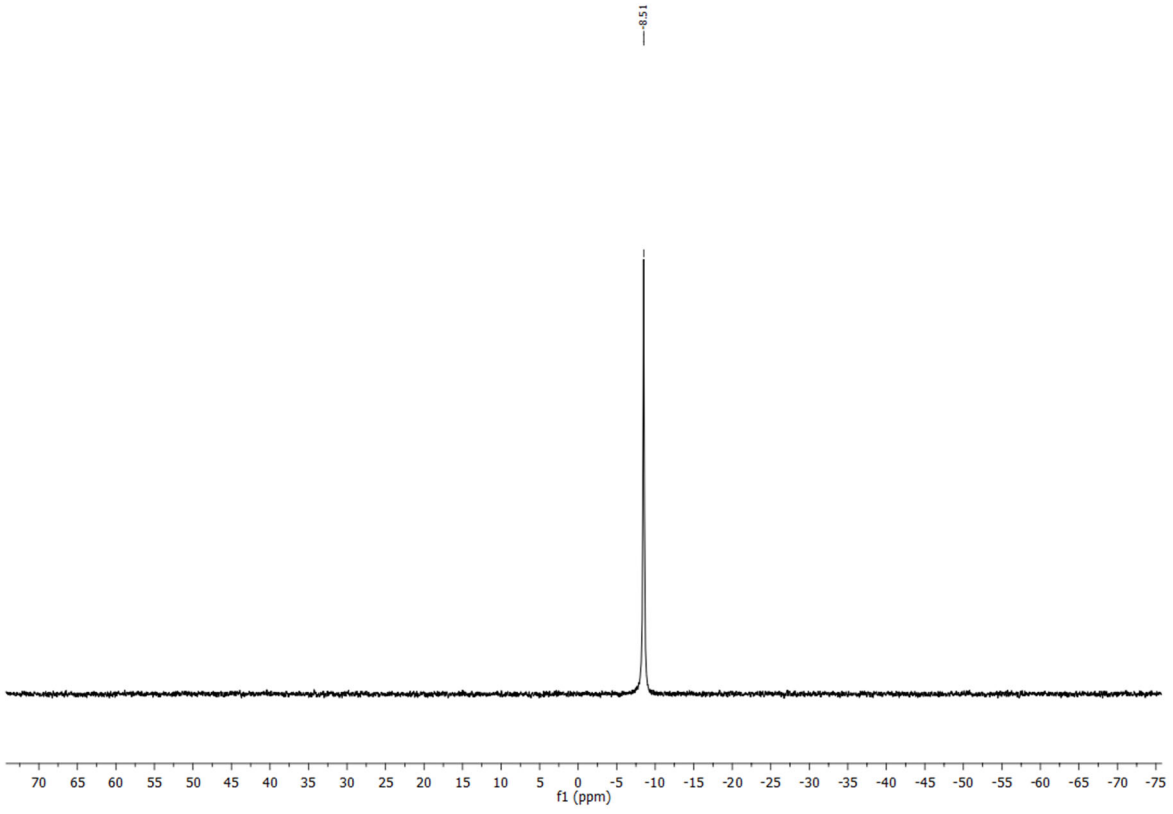
^{13}C NMR (175 MHz, CD_3COCD_3, 25 ºC)



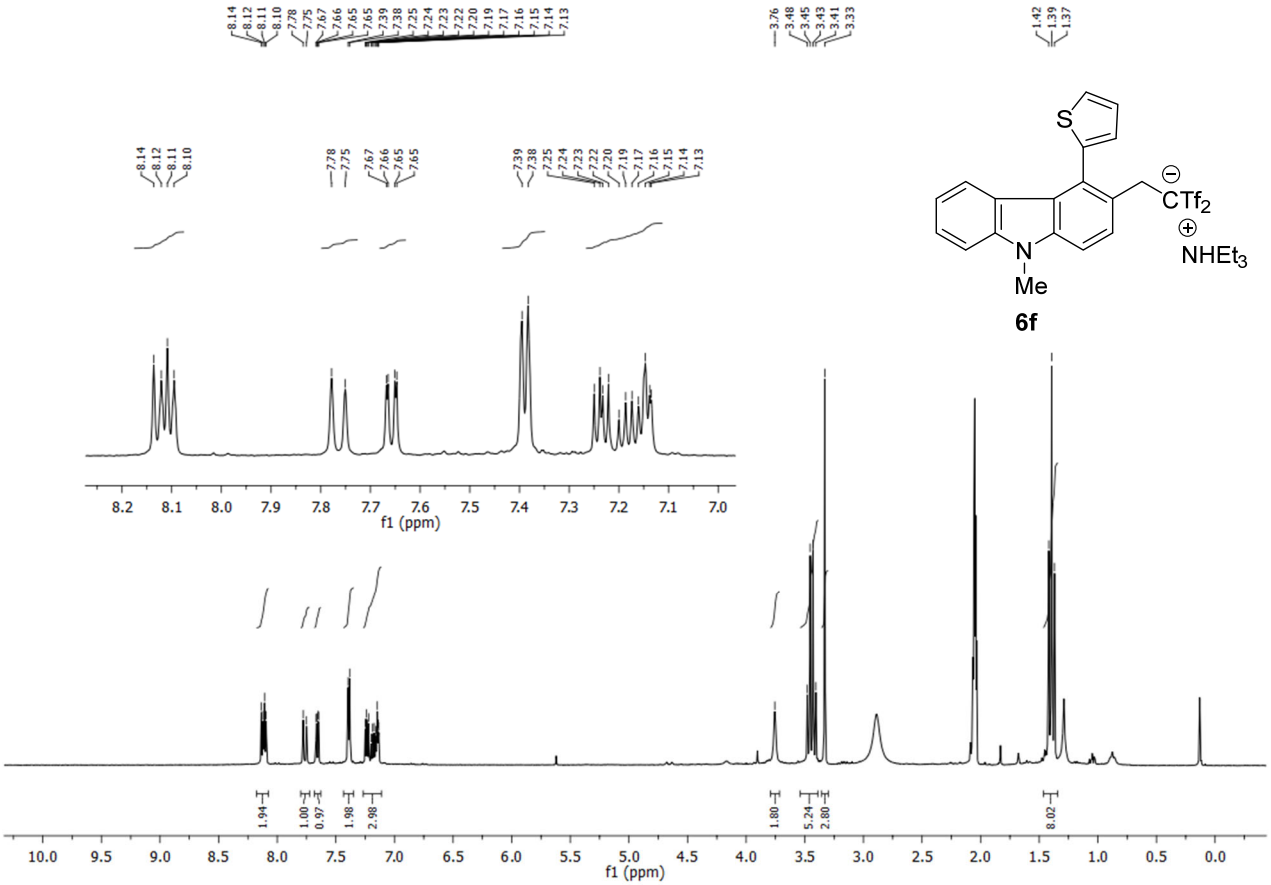
^{19}F NMR (282 MHz, CD_3COCD_3, 25 °C)



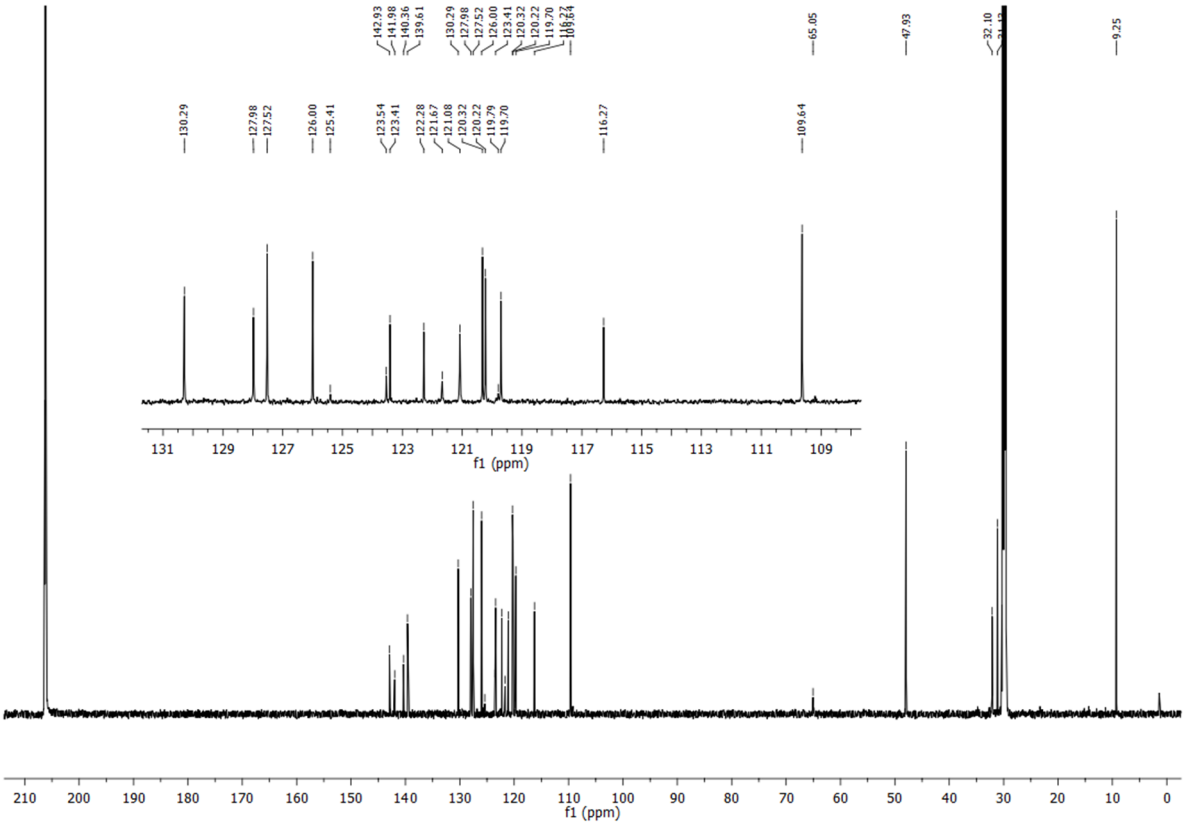
^{23}Na NMR (132 MHz, CD_3COCD_3, 25 °C)



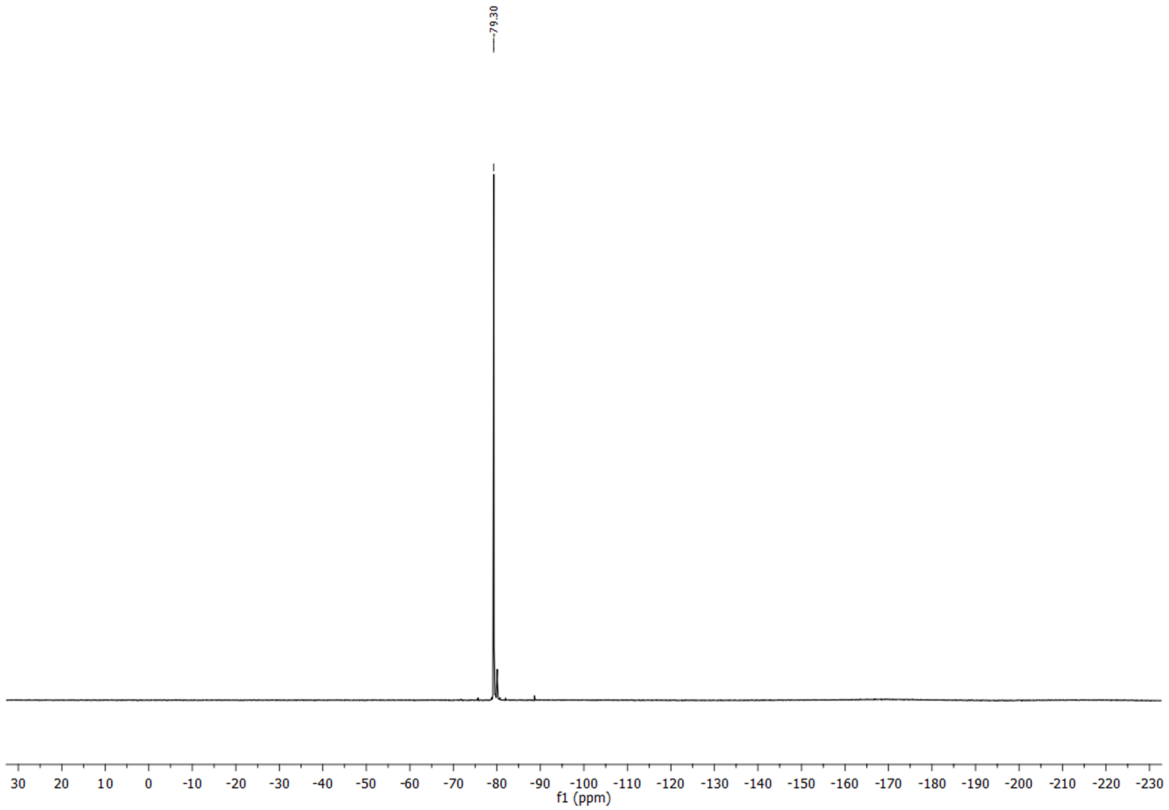
^{1}H NMR (300 MHz, CD_3COCD_3, 25 ºC)



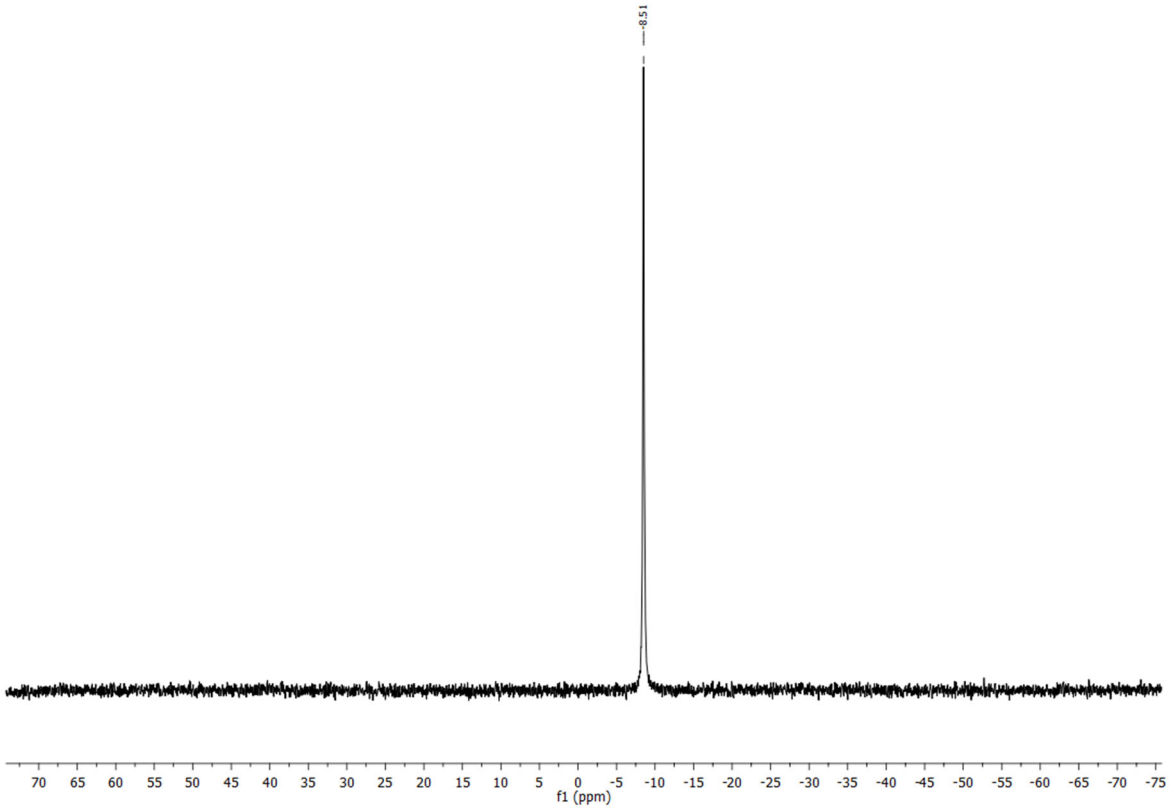
^{13}C NMR (175 MHz, CD_3COCD_3, 25 ºC)



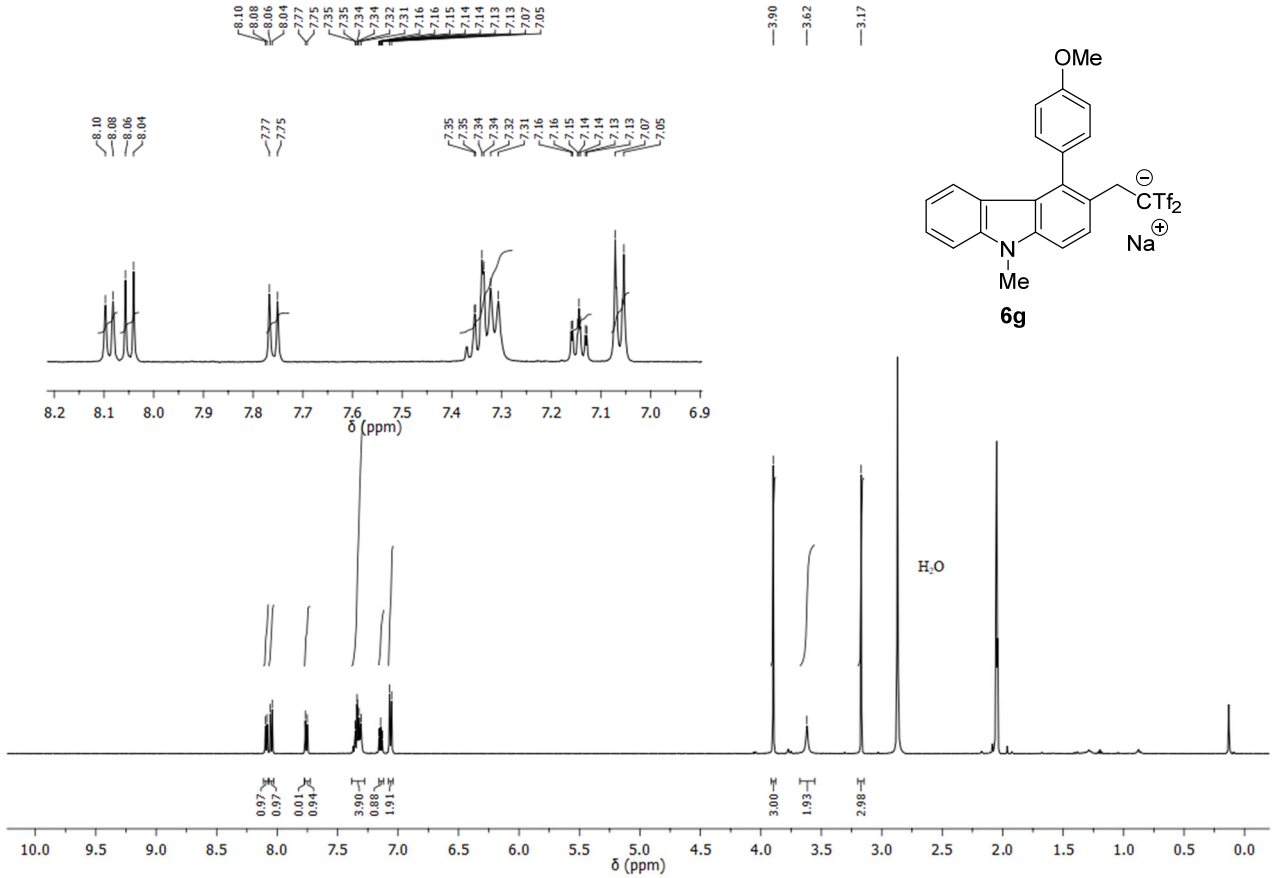
^{19}F NMR (282 MHz, CD_3COCD_3, 25 °C)



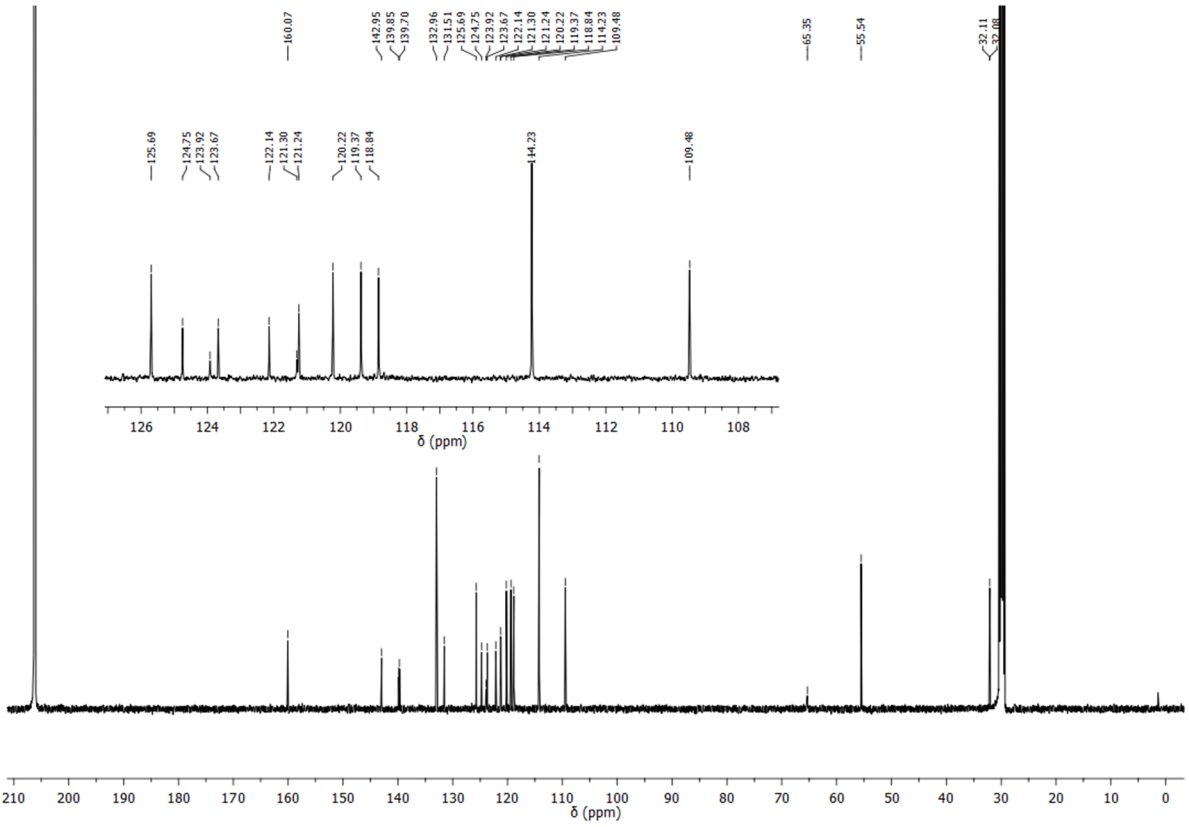
^{23}Na NMR (132 MHz, CD_3COCD_3, 25 °C)



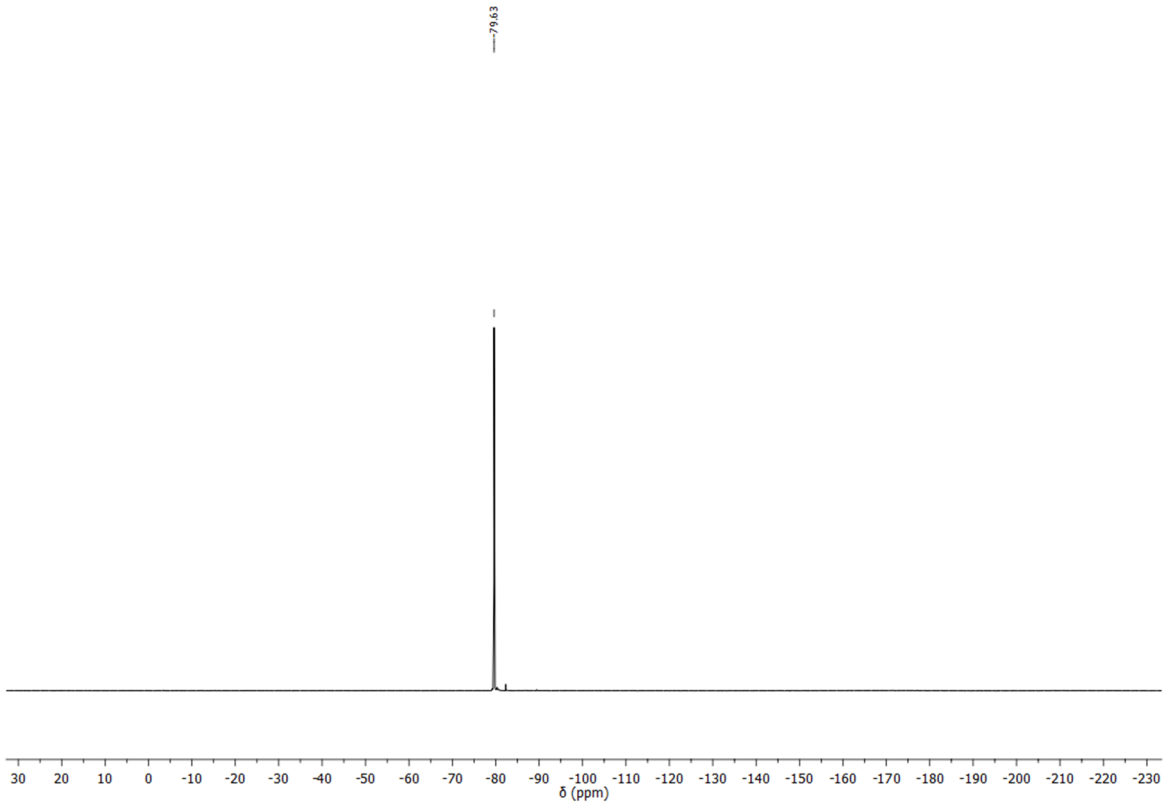
^{1}H NMR (300 MHz, CD_3COCD_3, 25 ºC)



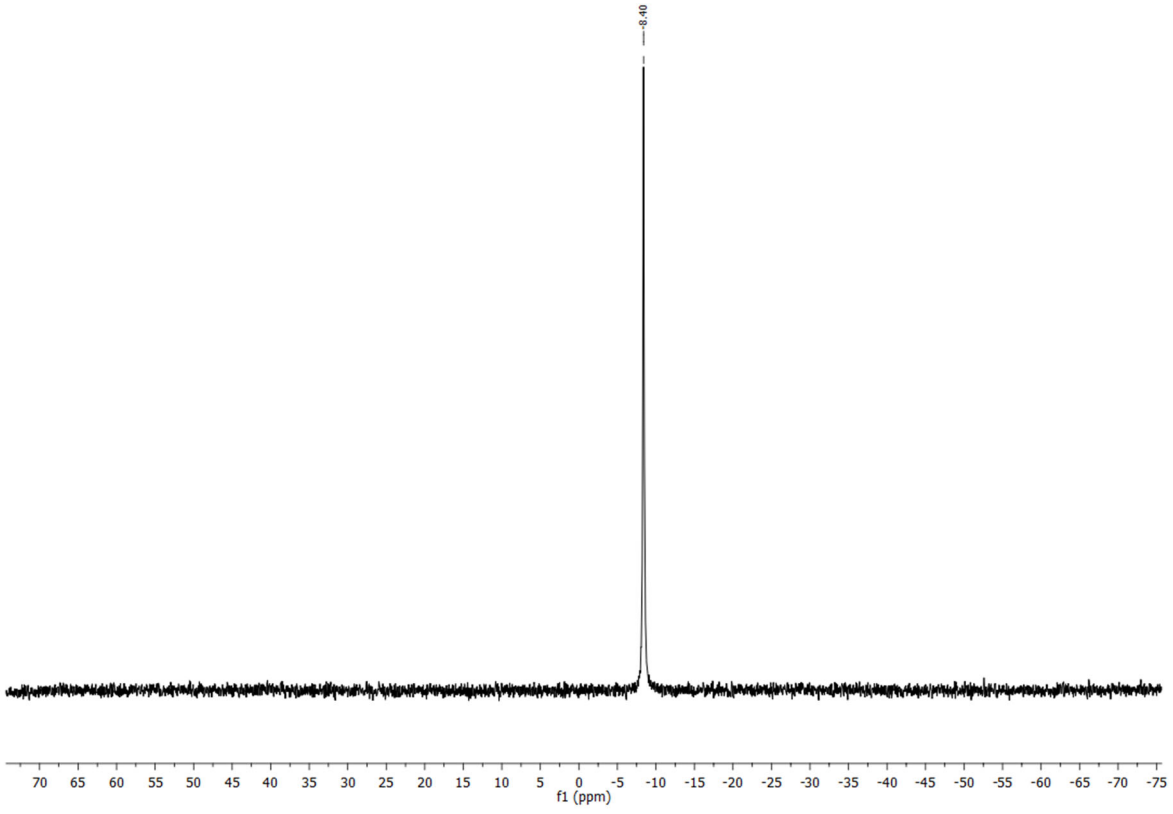
^{13}C NMR (175 MHz, CD_3COCD_3, 25 ºC)



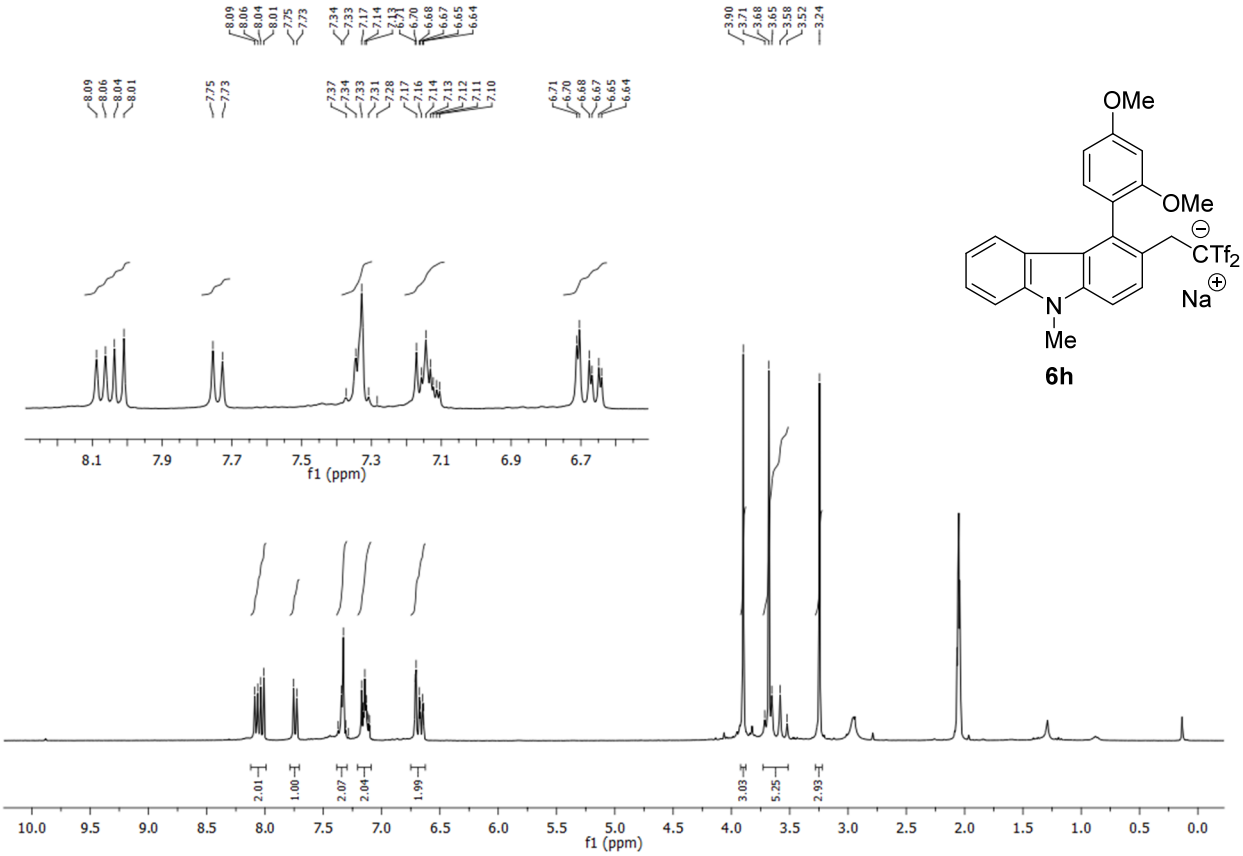
^{19}F NMR (282 MHz, CD_3COCD_3, 25 °C)



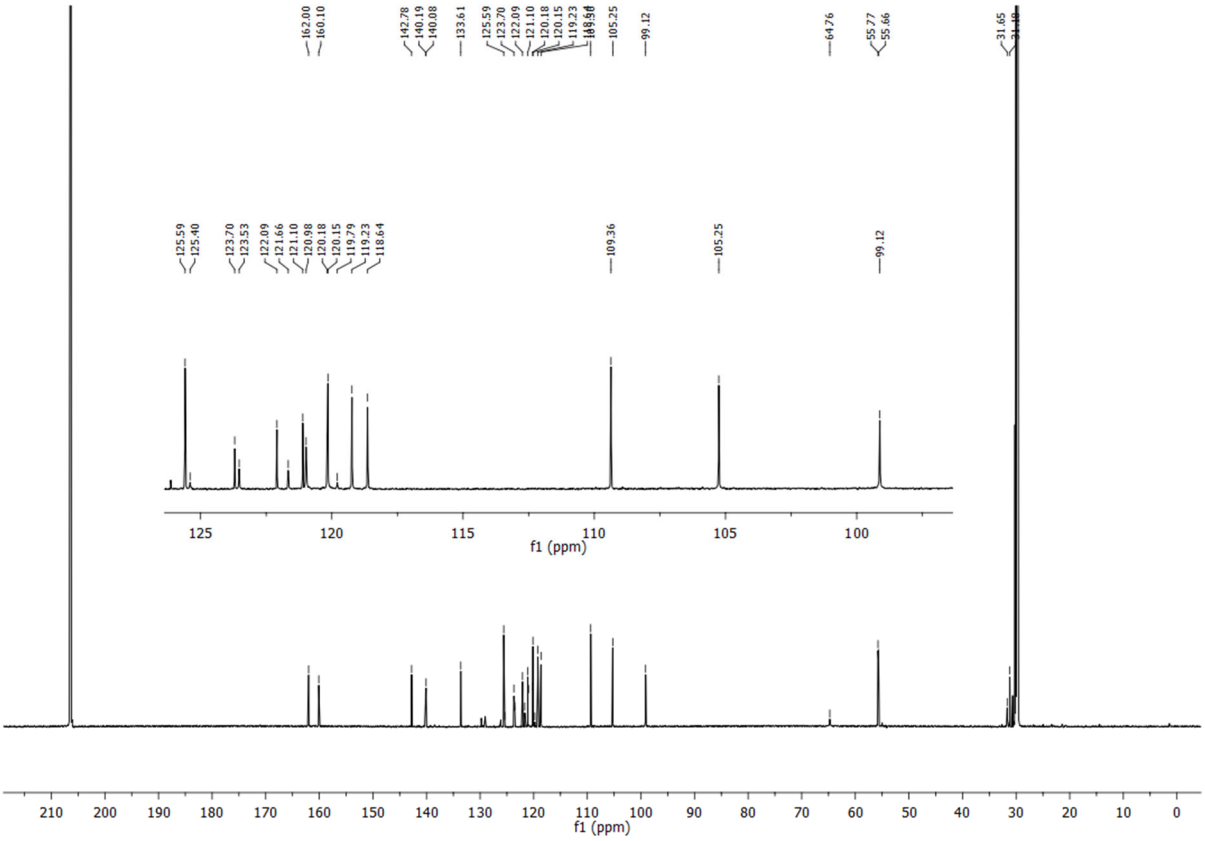
^{23}Na NMR (132 MHz, CD_3COCD_3, 25 °C)



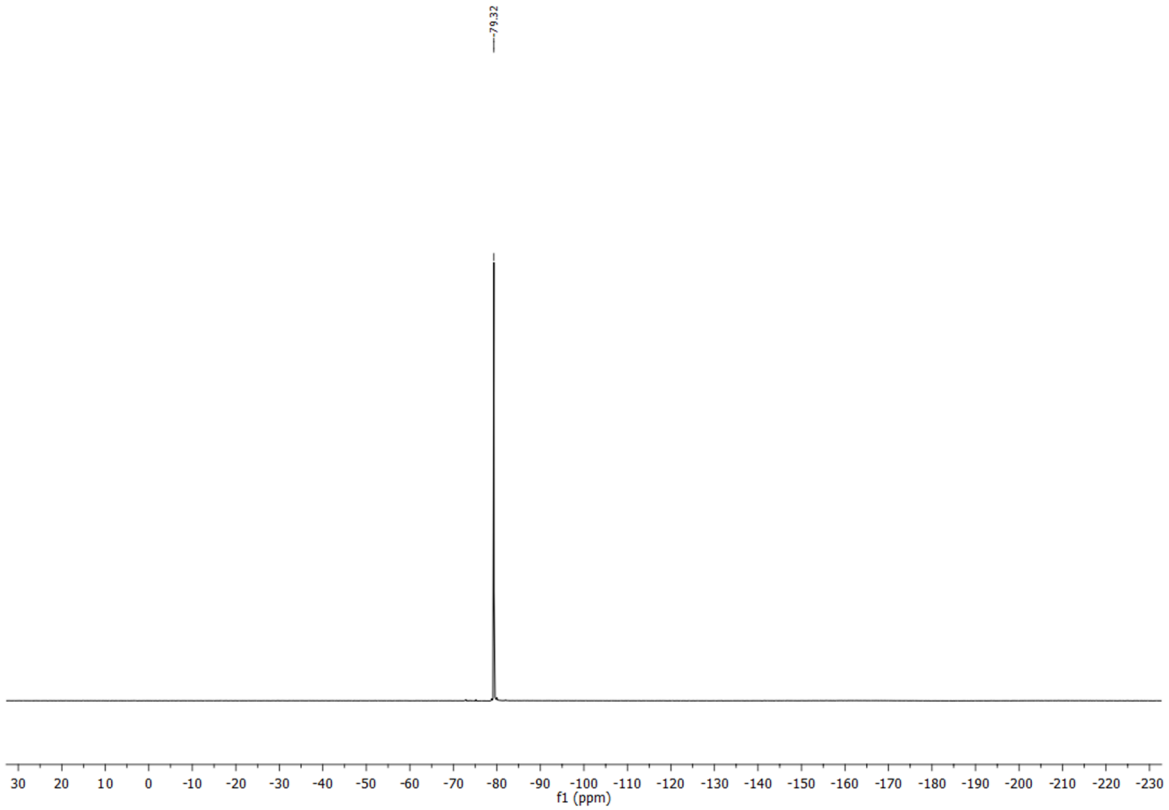
^{1}H NMR (300 MHz, CD_3COCD_3, 25 ºC)



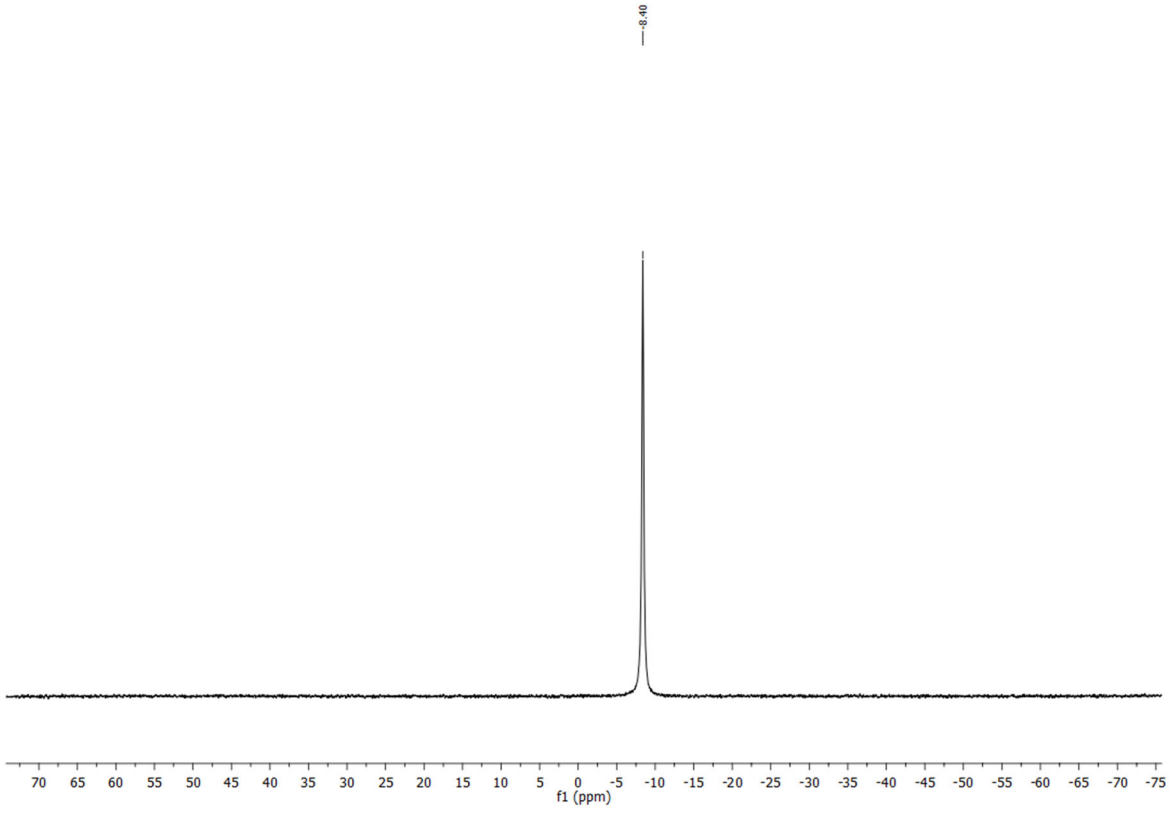
^{13}C NMR (175 MHz, CD_3COCD_3, 25 ºC)



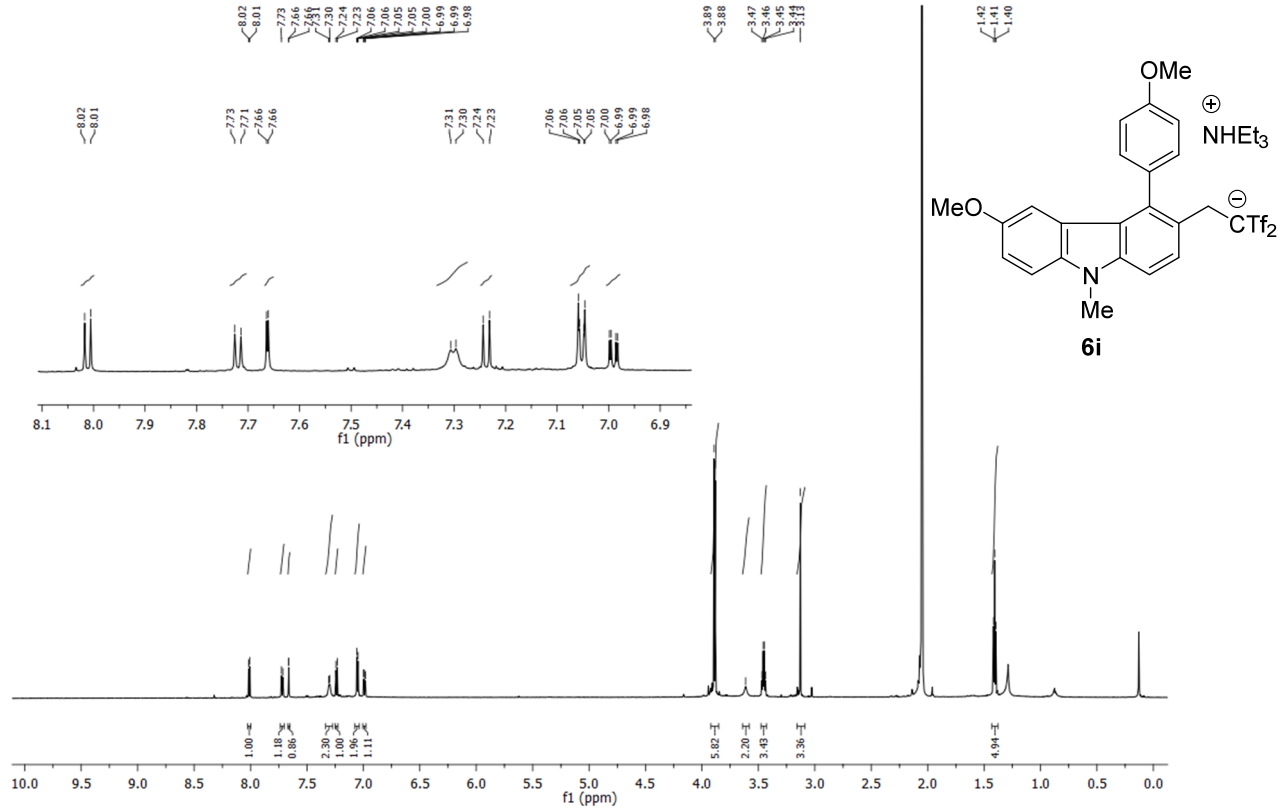
^{19}F NMR (282 MHz, CD_3COCD_3, 25 °C)



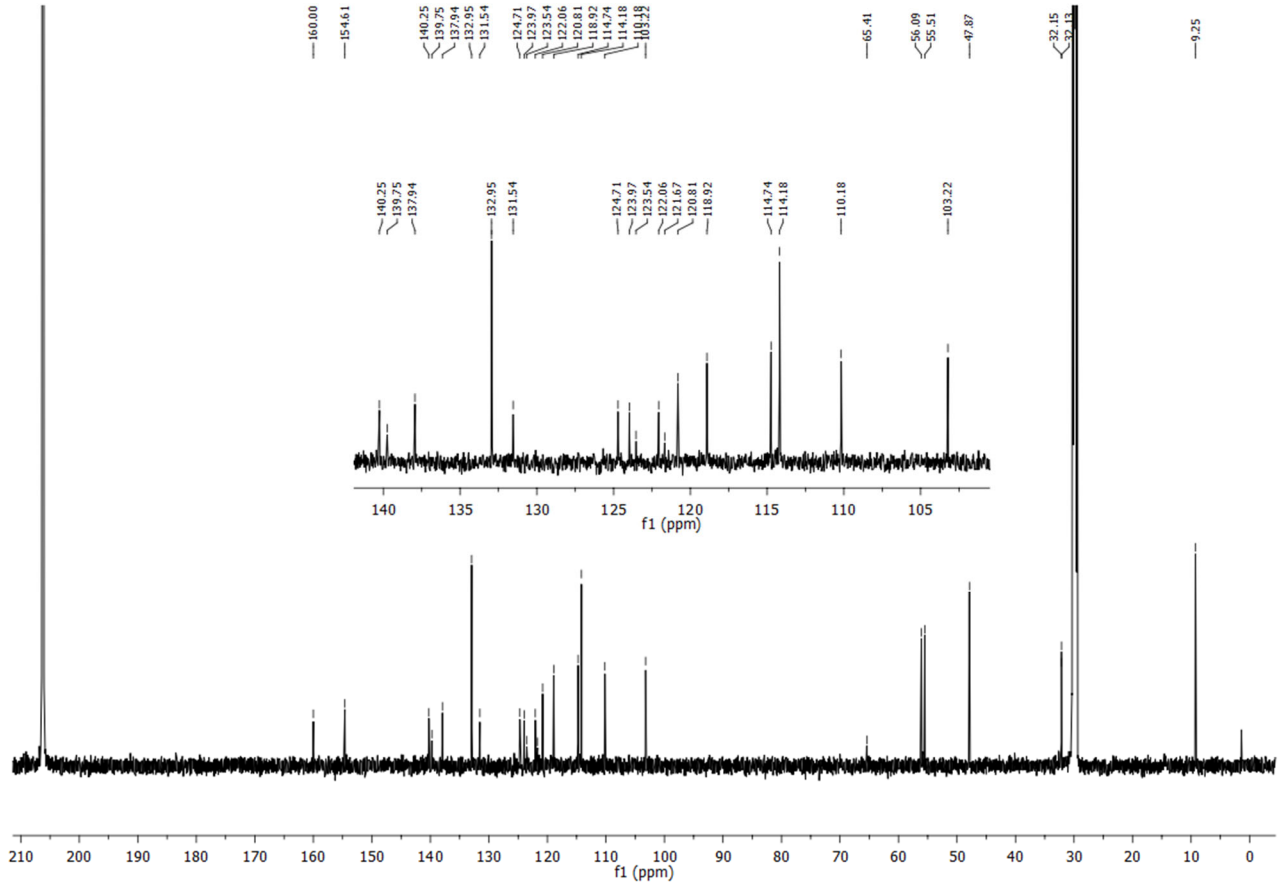
^{23}Na NMR (132 MHz, CD_3COCD_3, 25 °C)



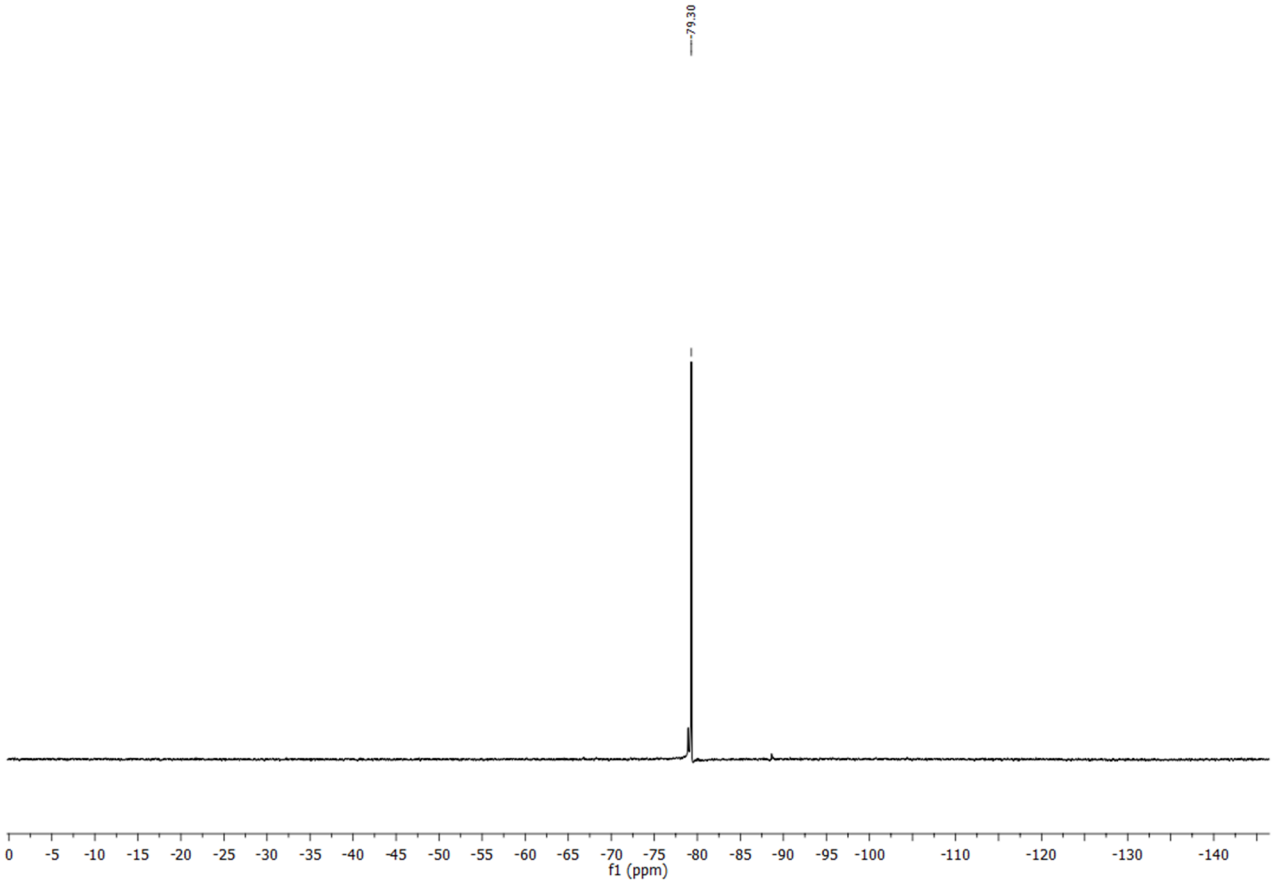
^{1}H NMR (300 MHz, CD_3COCD_3, 25 °C)



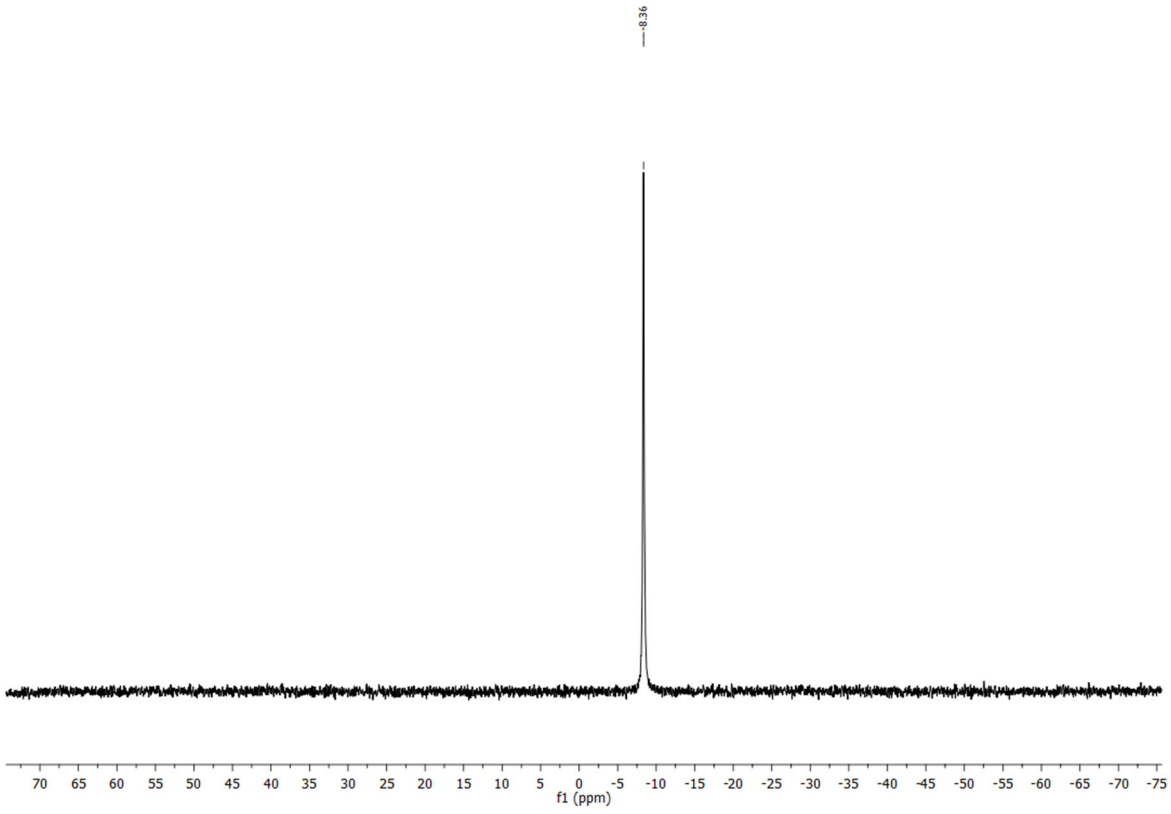
^{13}C NMR (175 MHz, CD_3COCD_3, 25 °C)



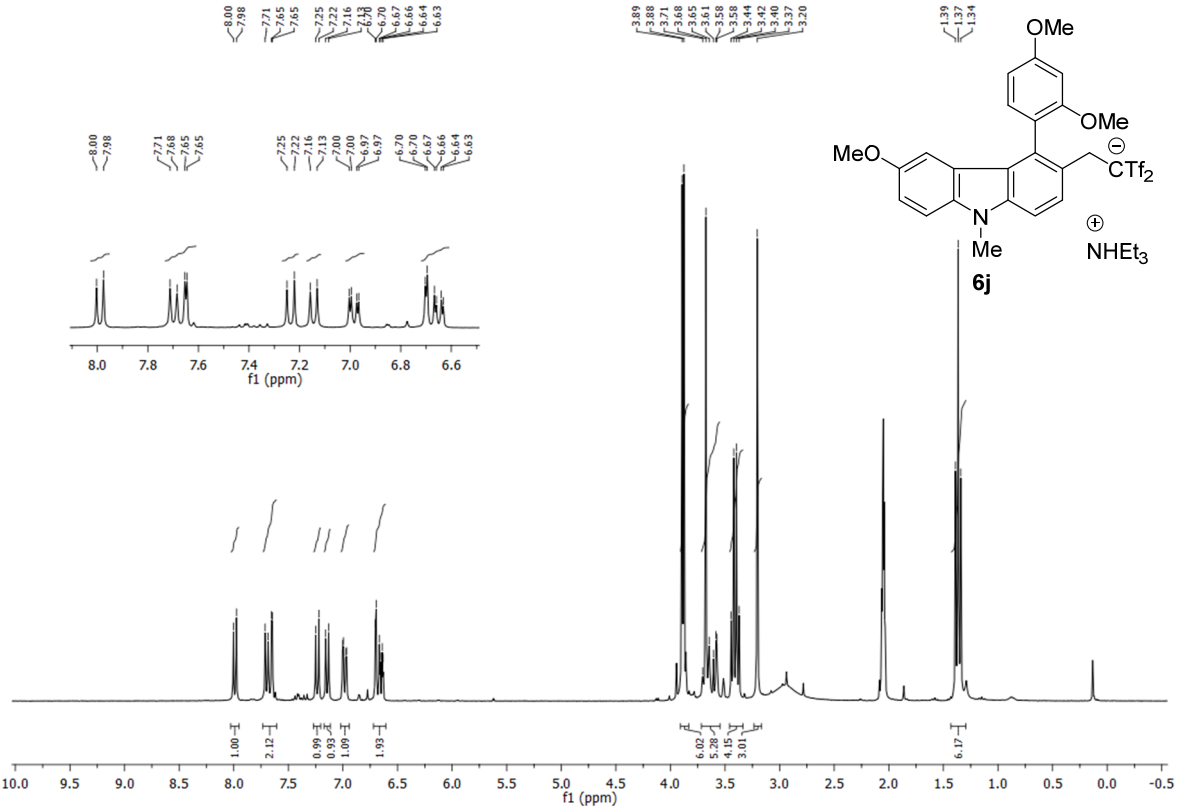
^{19}F NMR (282 MHz, CD_3COCD_3, 25 ºC)



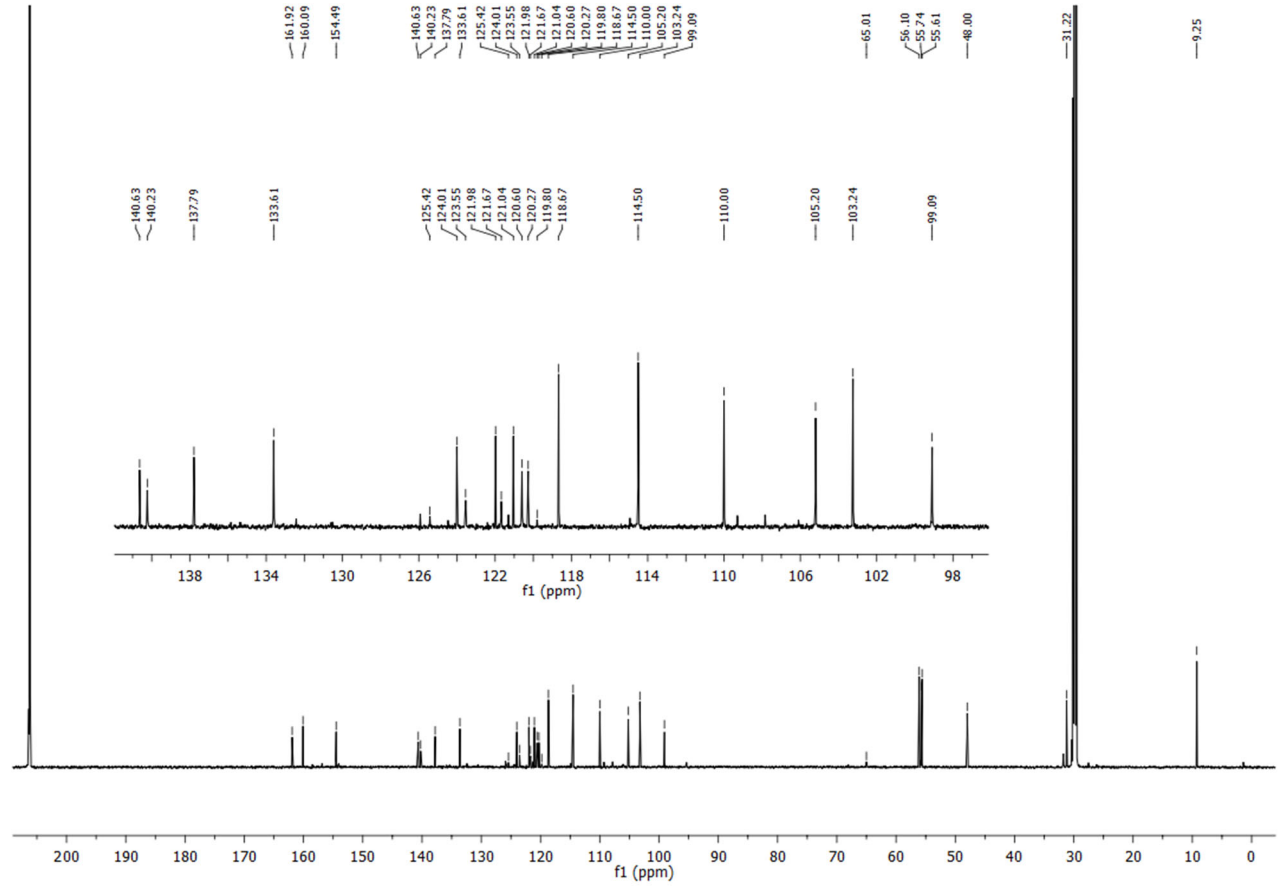
^{23}Na NMR (132 MHz, CD_3COCD_3, 25 ºC)



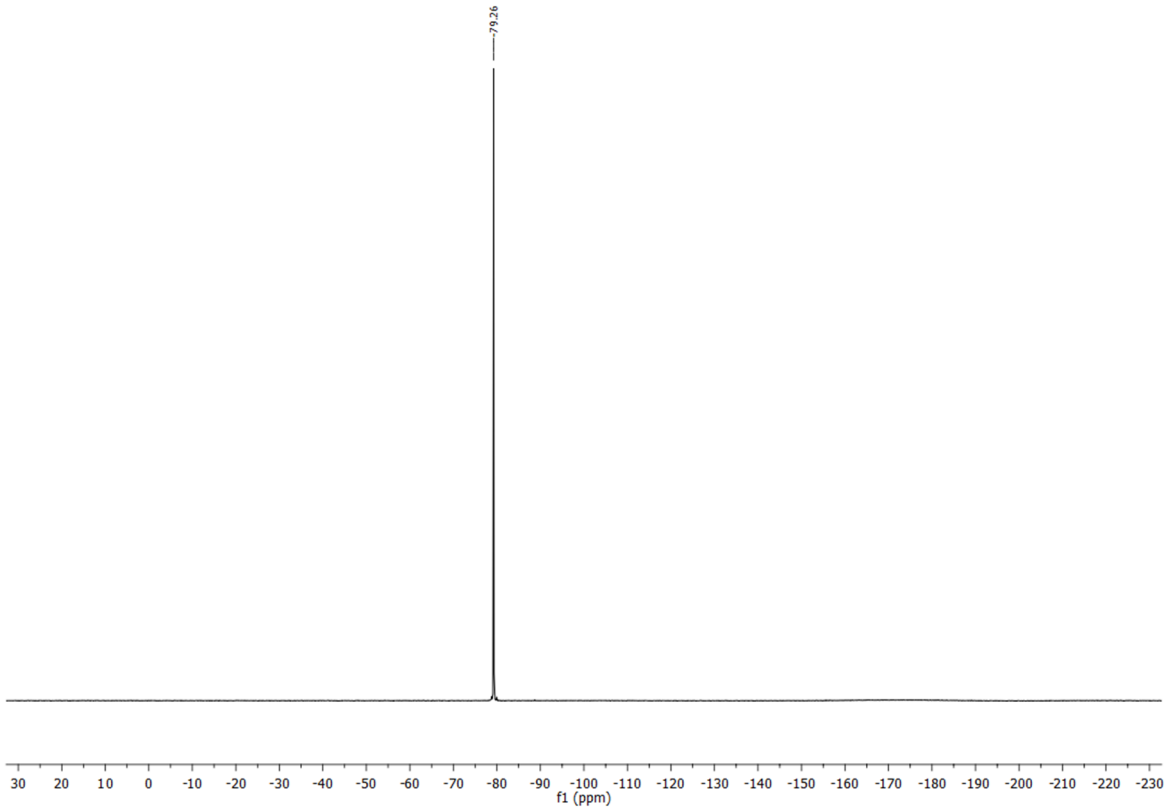
^{1}H NMR (300 MHz, CD_3COCD_3, 25 °C)



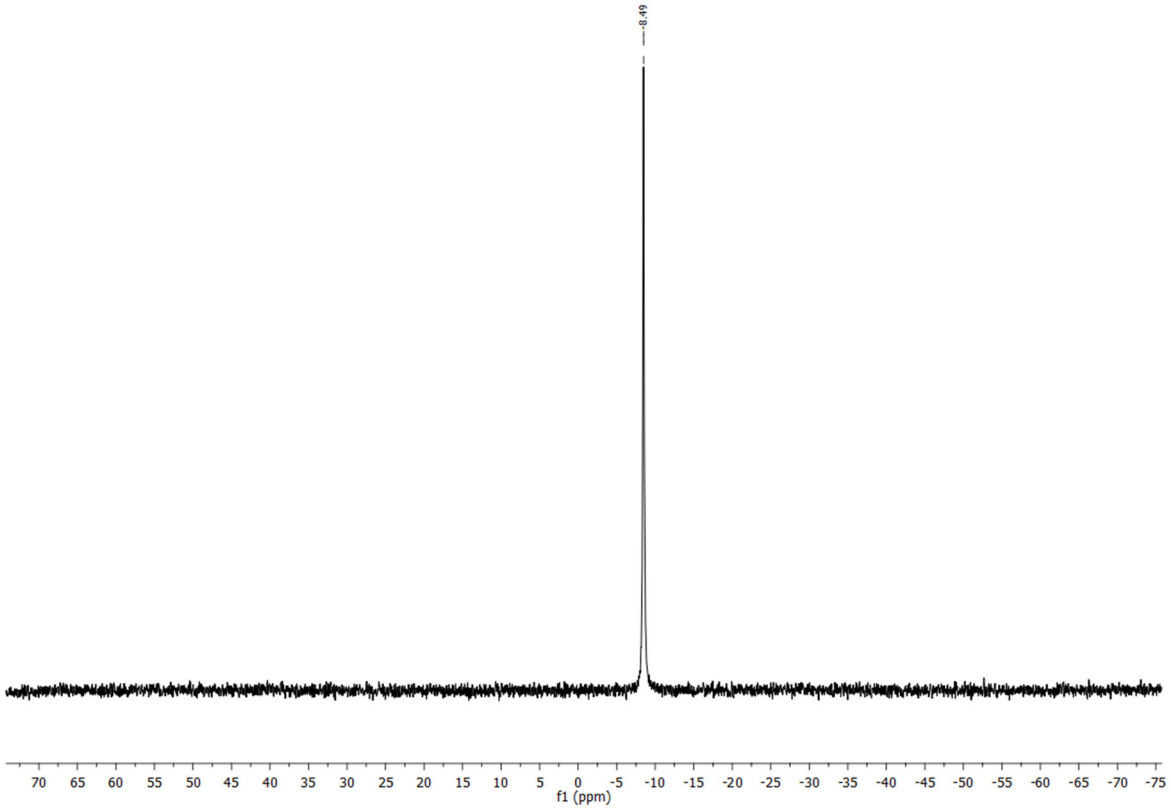
^{13}C NMR (175 MHz, CD_3COCD_3, 25 °C)



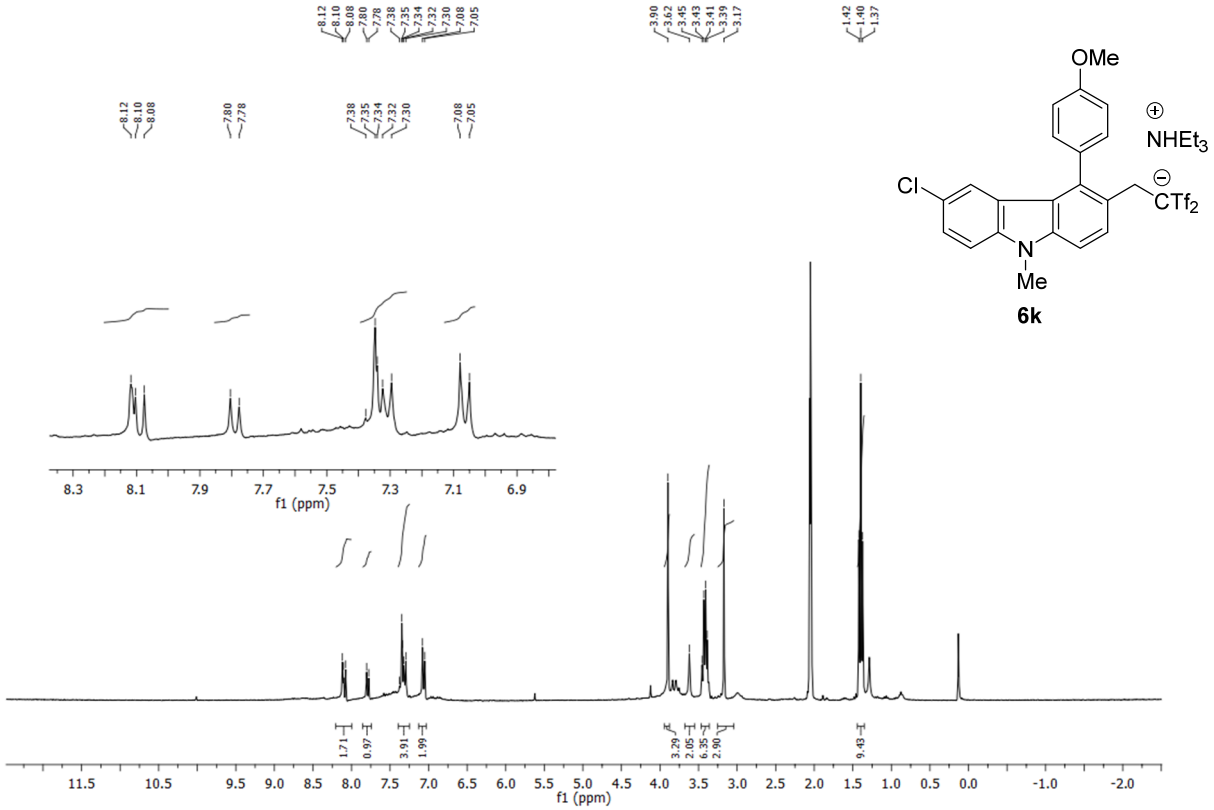
^{19}F NMR (282 MHz, CD_3COCD_3, 25 °C)



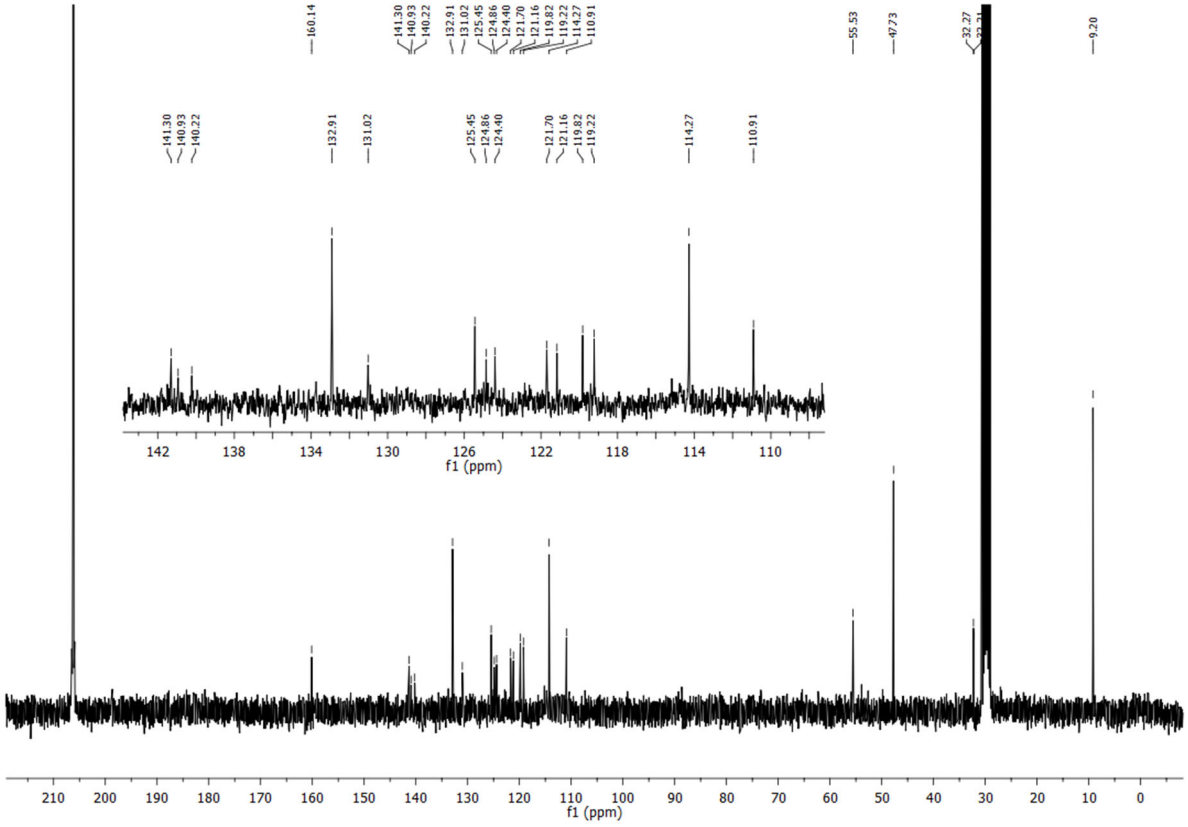
^{23}Na NMR (132 MHz, CD_3COCD_3, 25 °C)



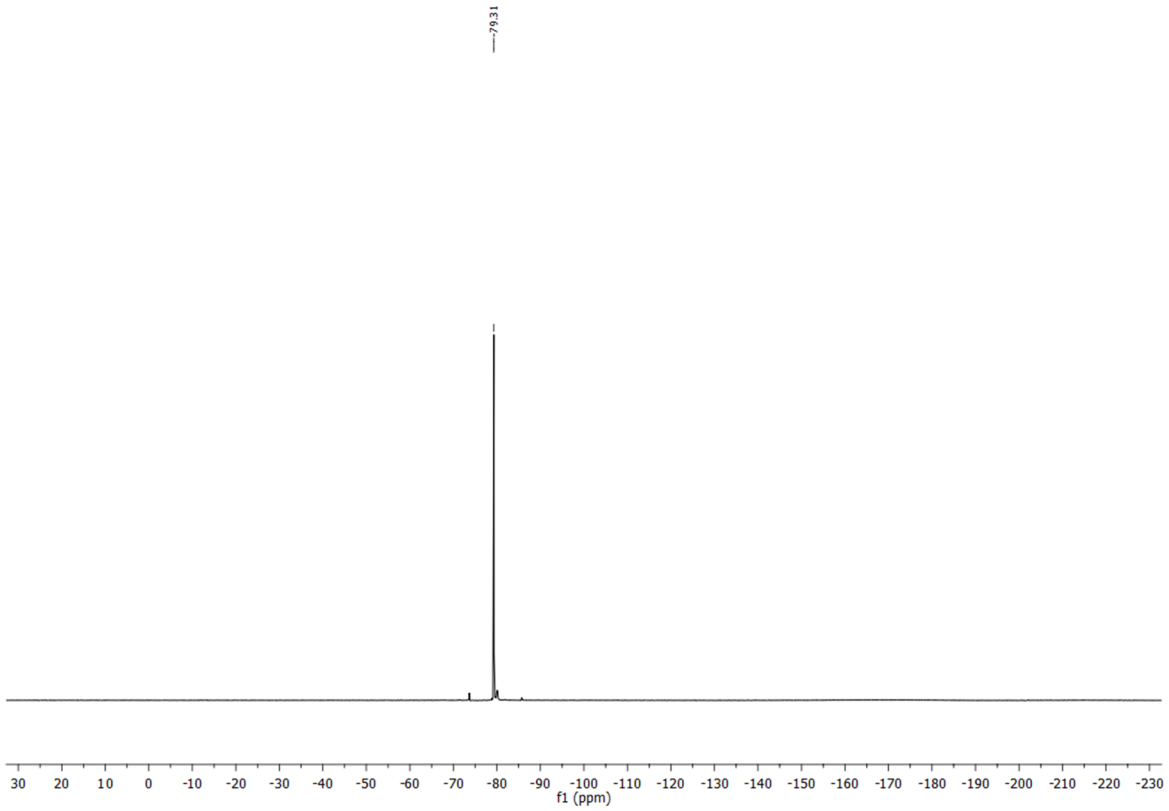
^{1}H NMR (300 MHz, CD_3COCD_3, 25 °C)



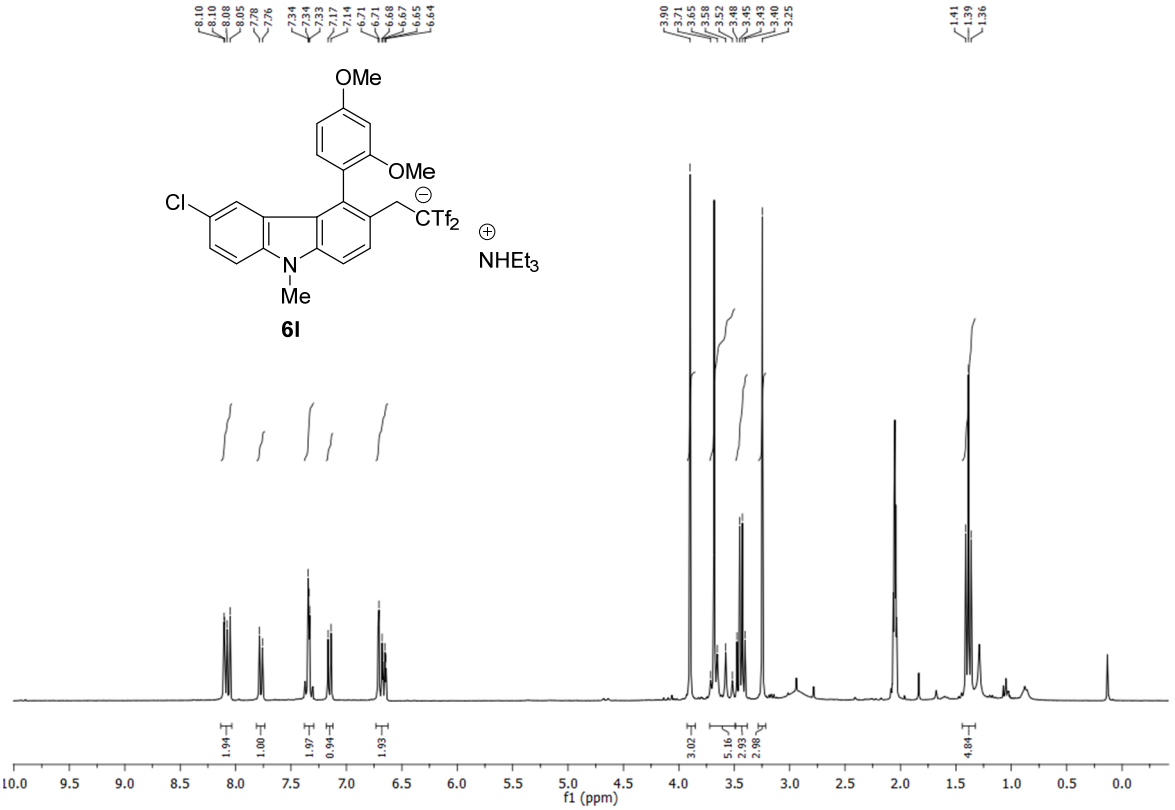
^{13}C NMR (175 MHz, CD_3COCD_3, 25 °C)



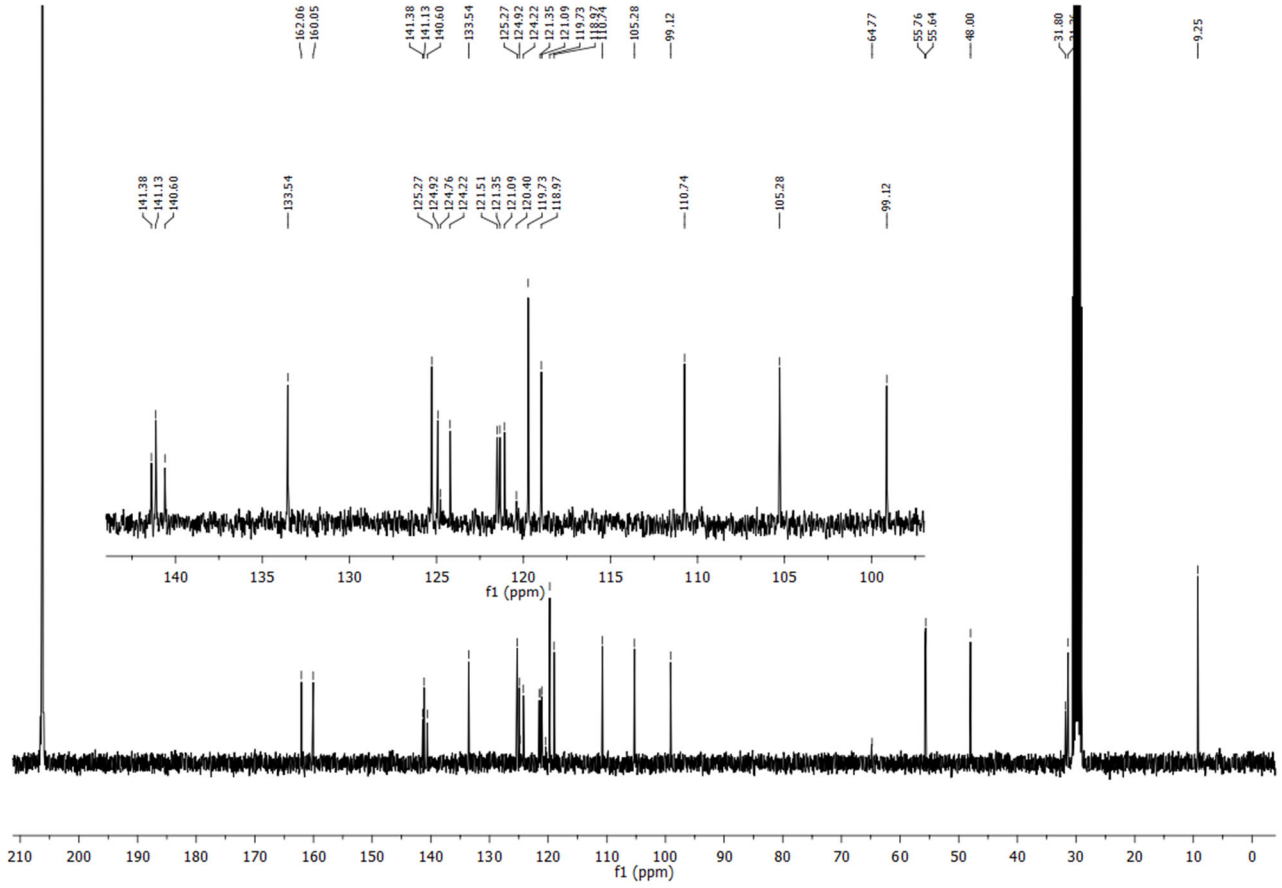
^{19}F NMR (282 MHz, CD_3COCD_3, 25 °C)



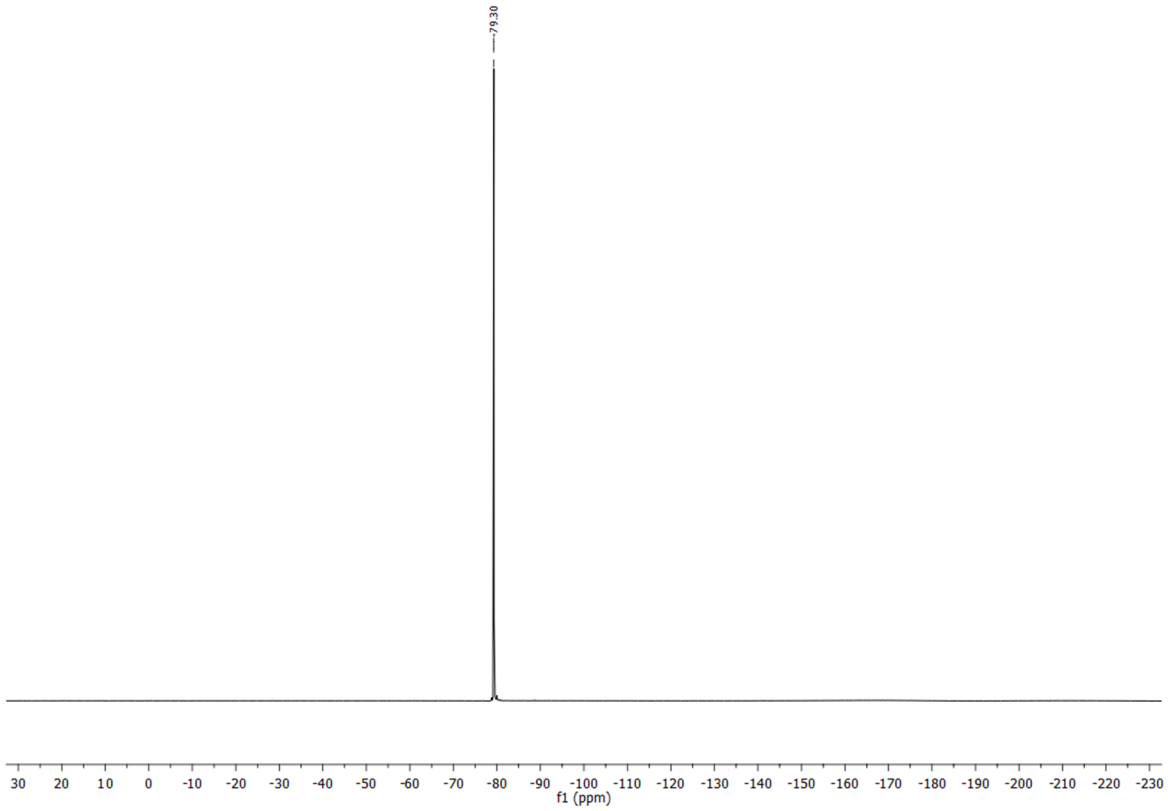
^{1}H NMR (300 MHz, CD_3COCD_3, 25 °C)



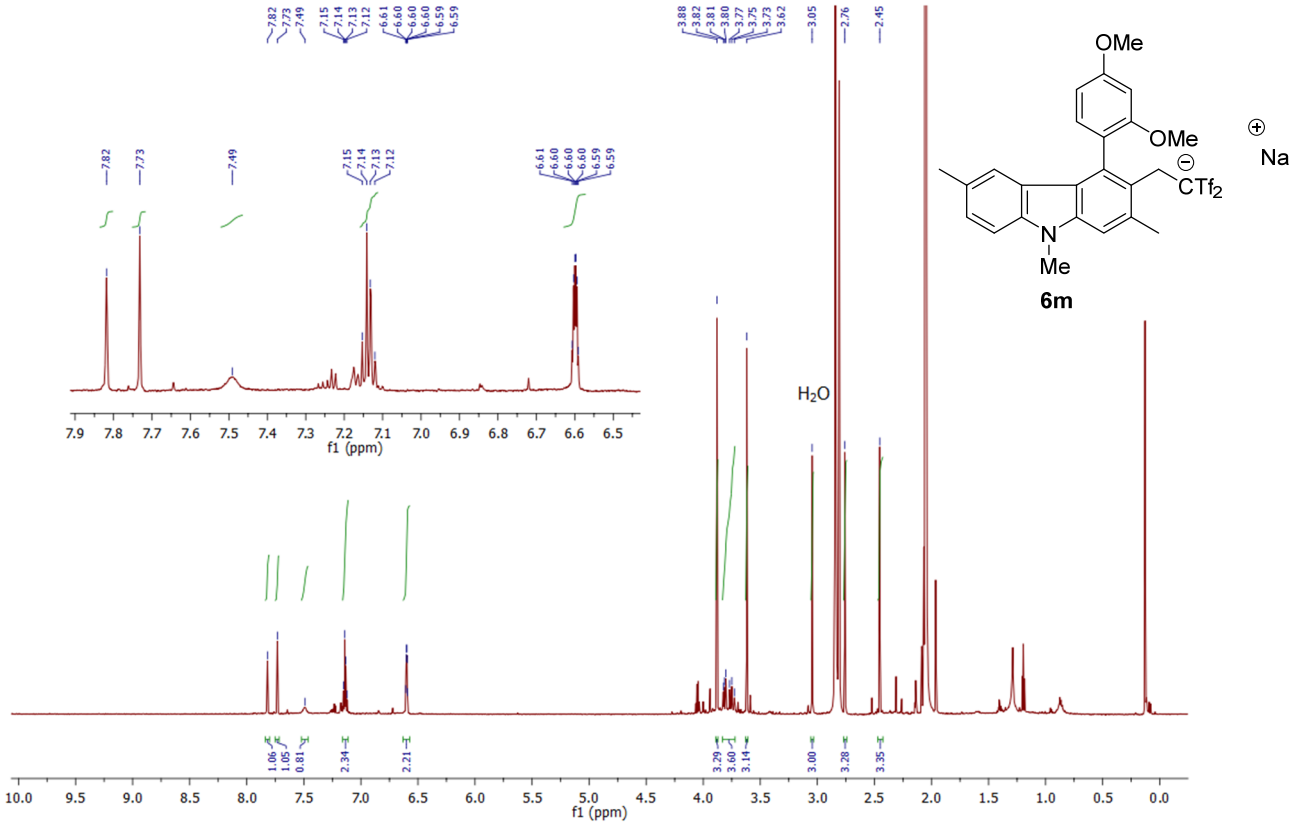
^{13}C NMR (175 MHz, CD_3COCD_3, 25 °C)



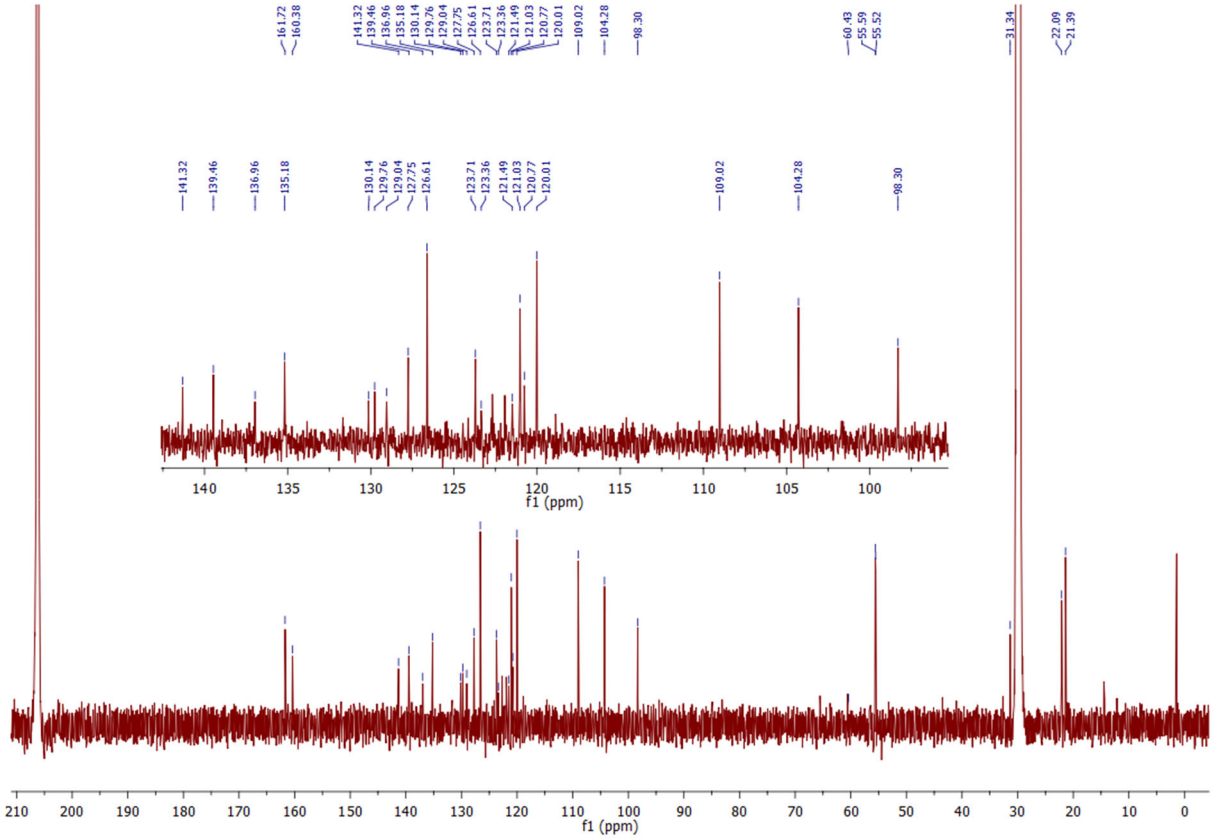
^{19}F NMR (282 MHz, CD_3COCD_3, 25 °C)



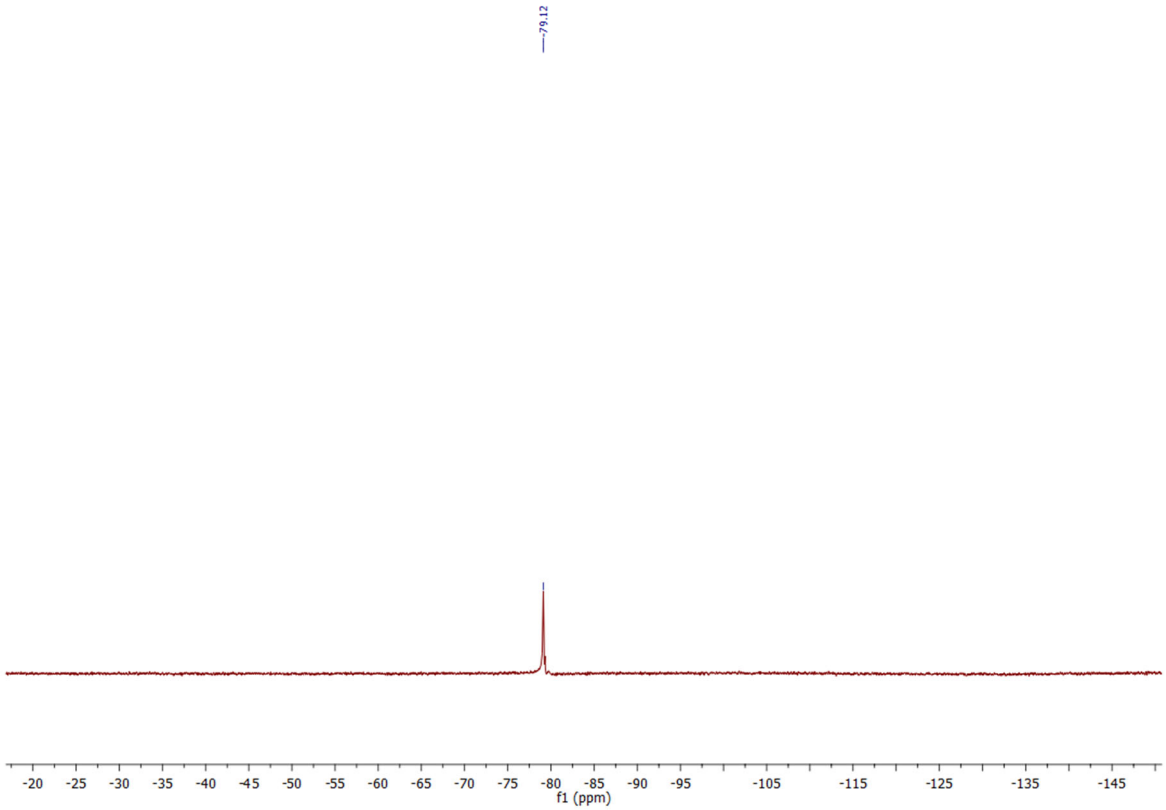
^{1}H NMR (300 MHz, CD_3COCD_3, 25 °C)



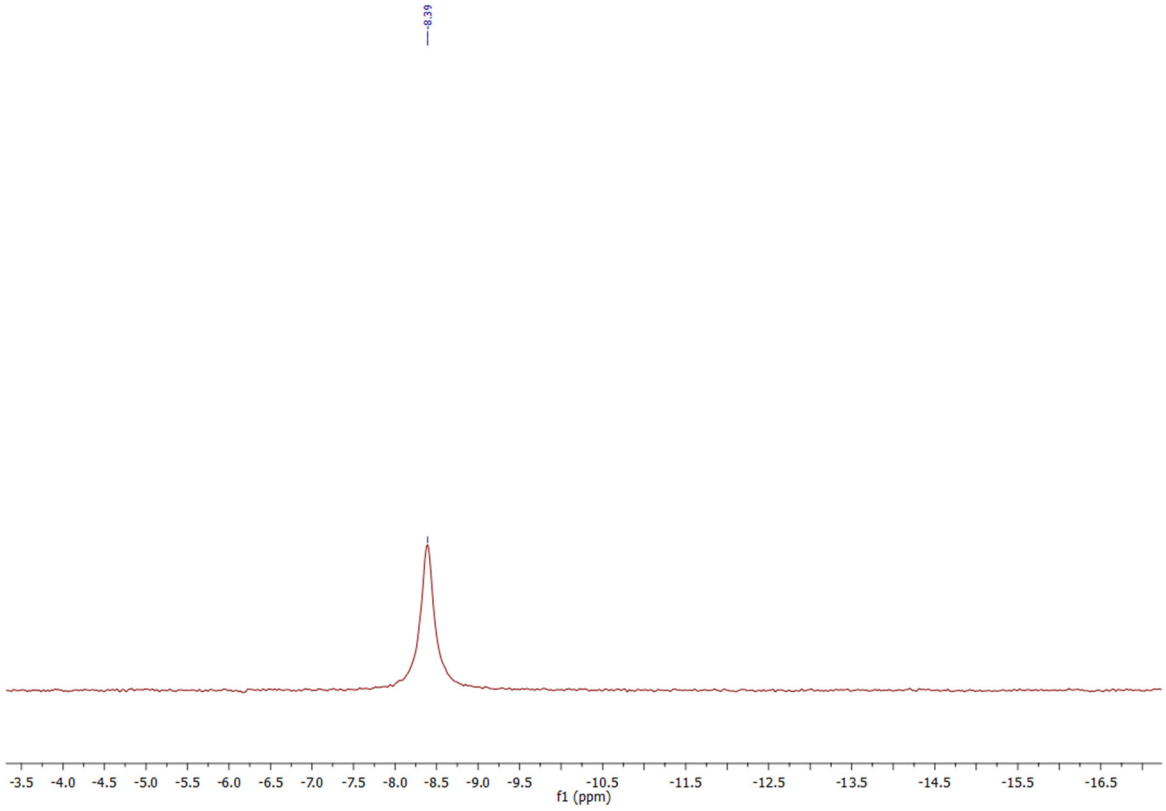
^{13}C NMR (175 MHz, CD_3COCD_3, 25 °C)



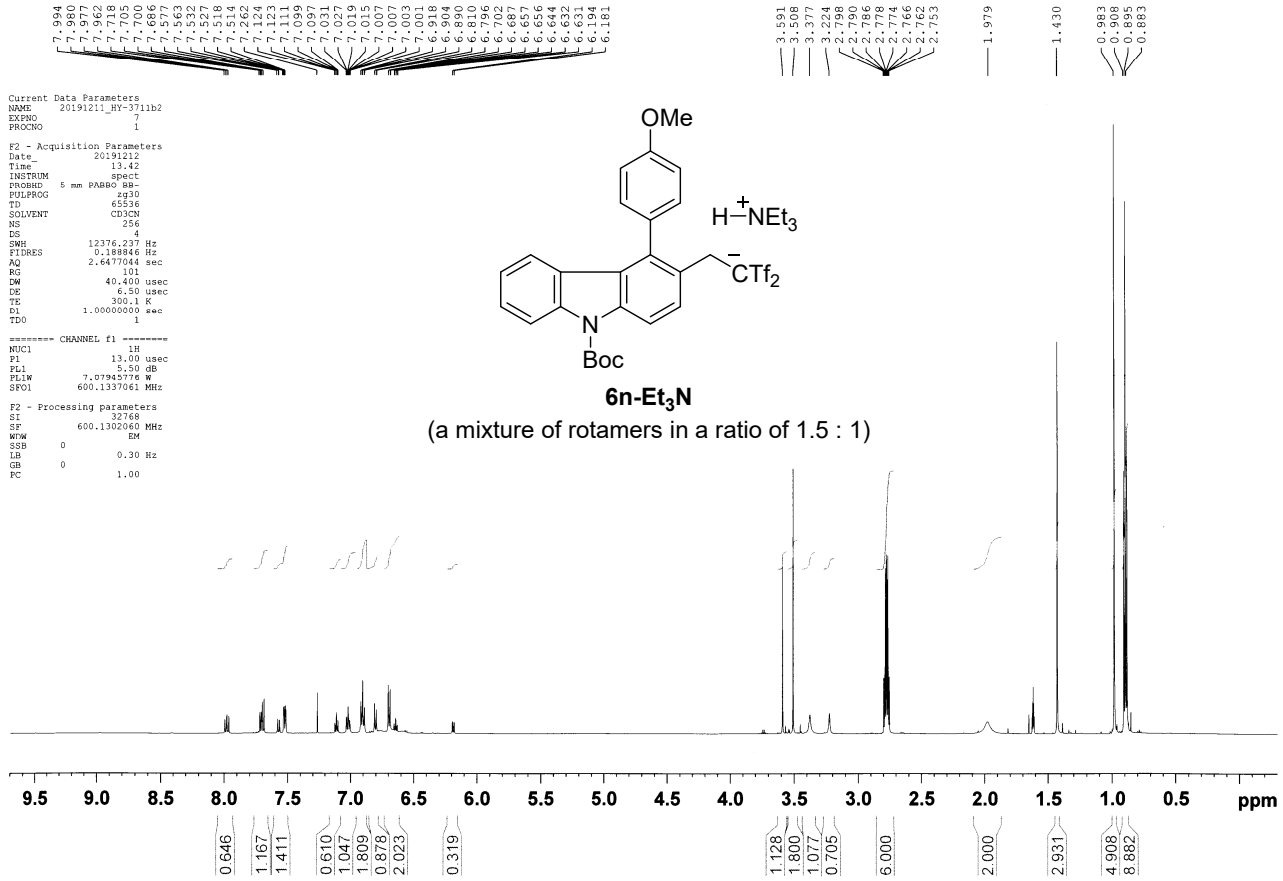
^{19}F NMR (282 MHz, CD_3COCD_3, 25 °C)



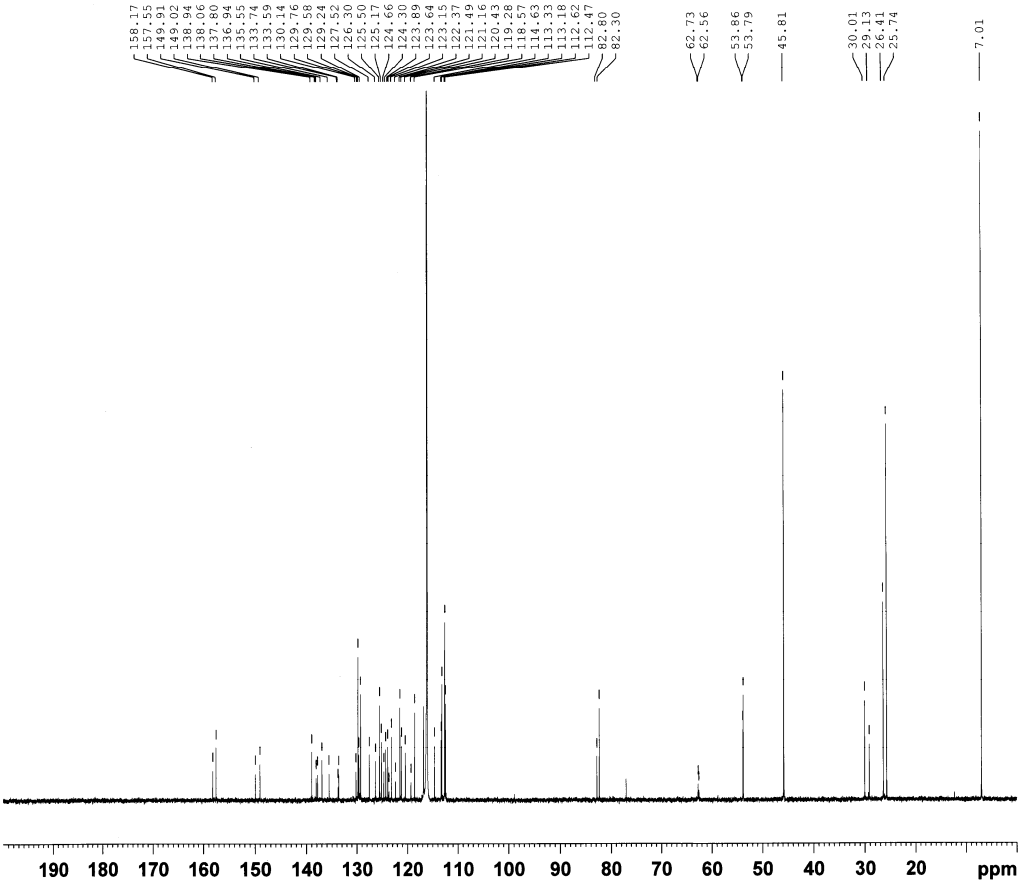
^{23}Na NMR (132 MHz, CD_3COCD_3, 25 °C)



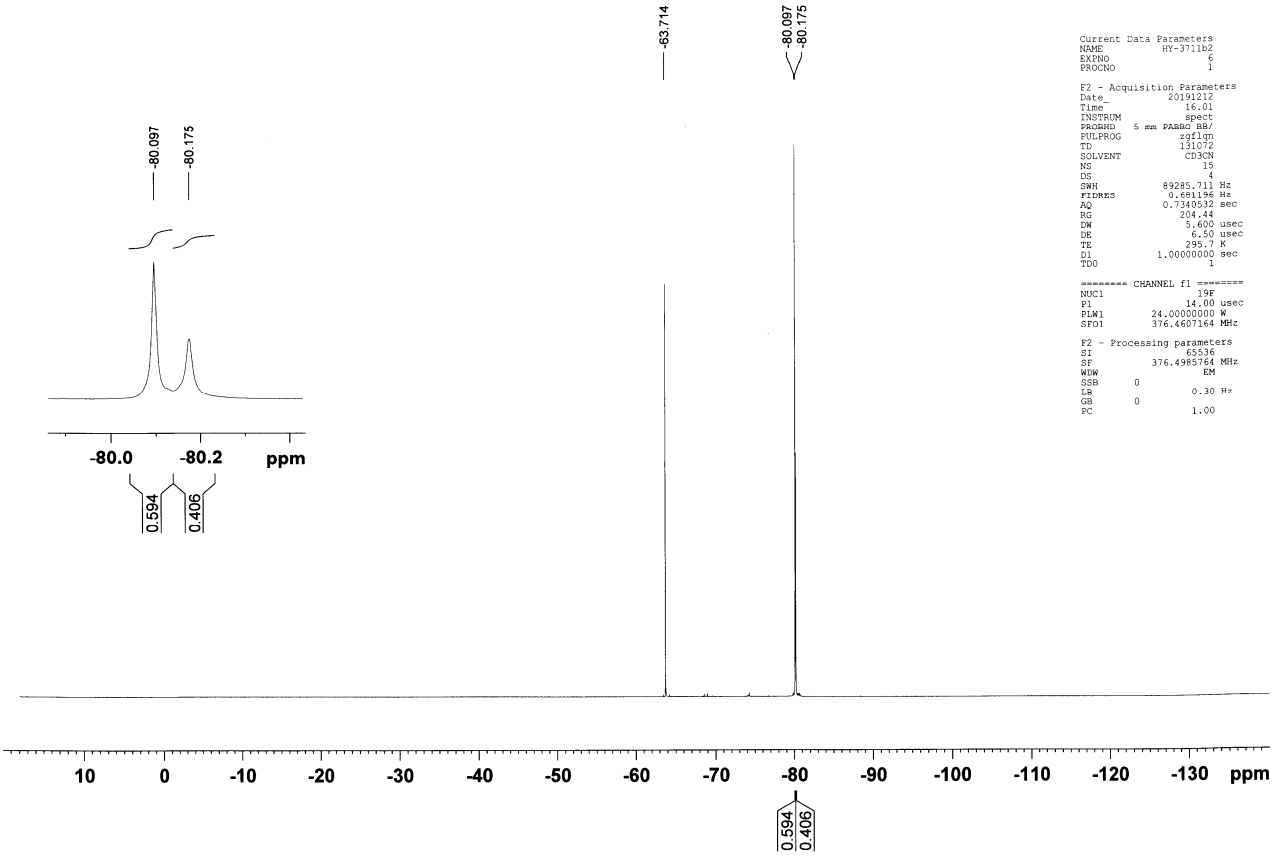
^{1}H NMR (600 MHz, CD_3CN, rt)



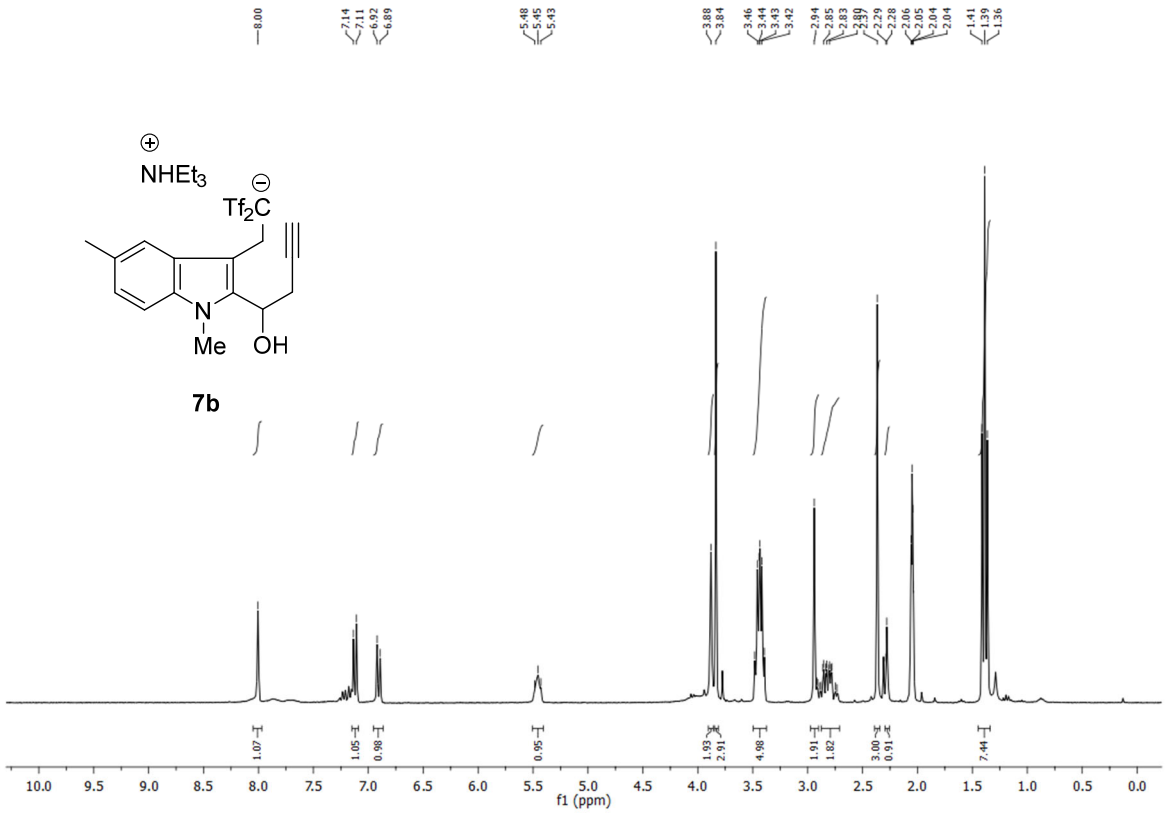
^{13}C NMR (150 MHz, CD_3CN, rt)



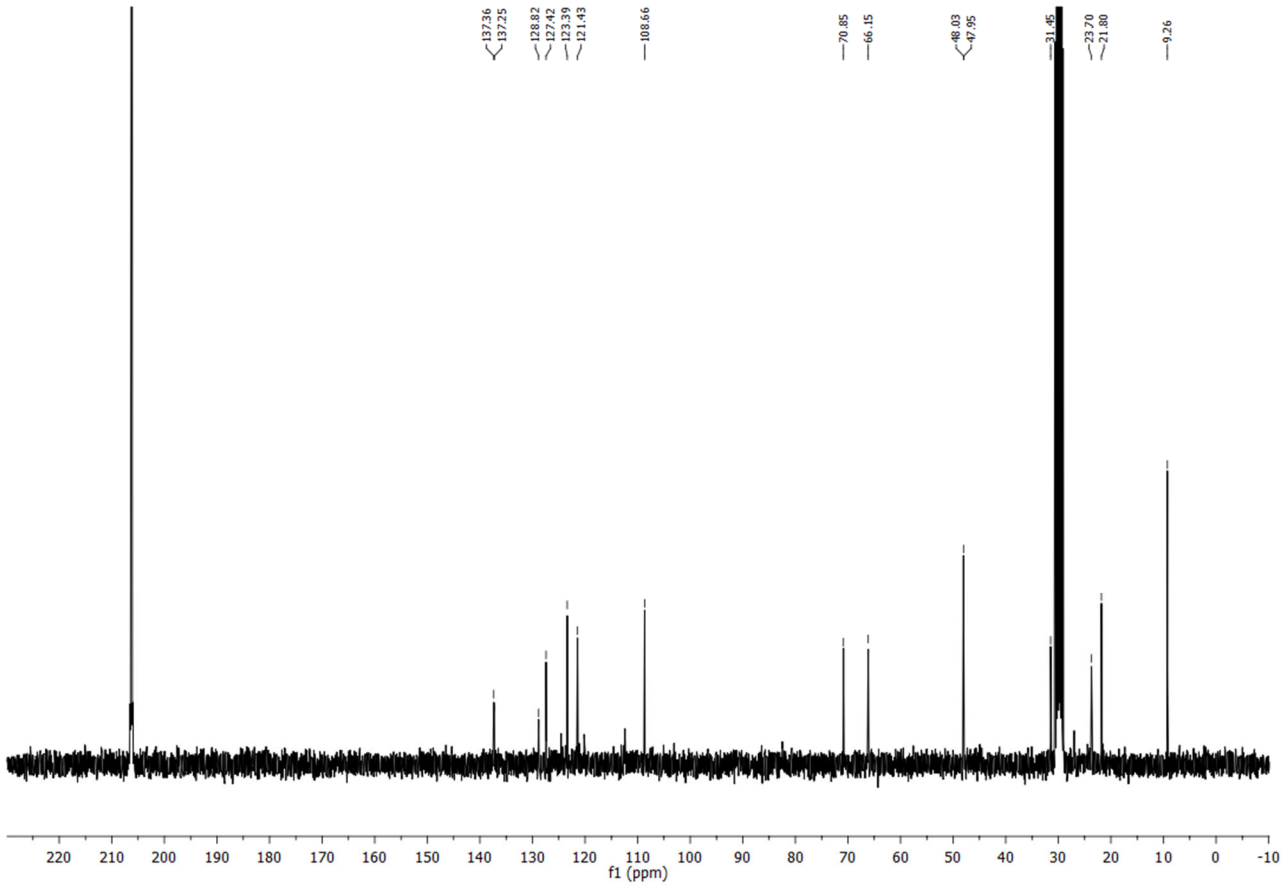
^{19}F NMR with $PhCF_3$ (376 MHz, CD_3CN, rt)



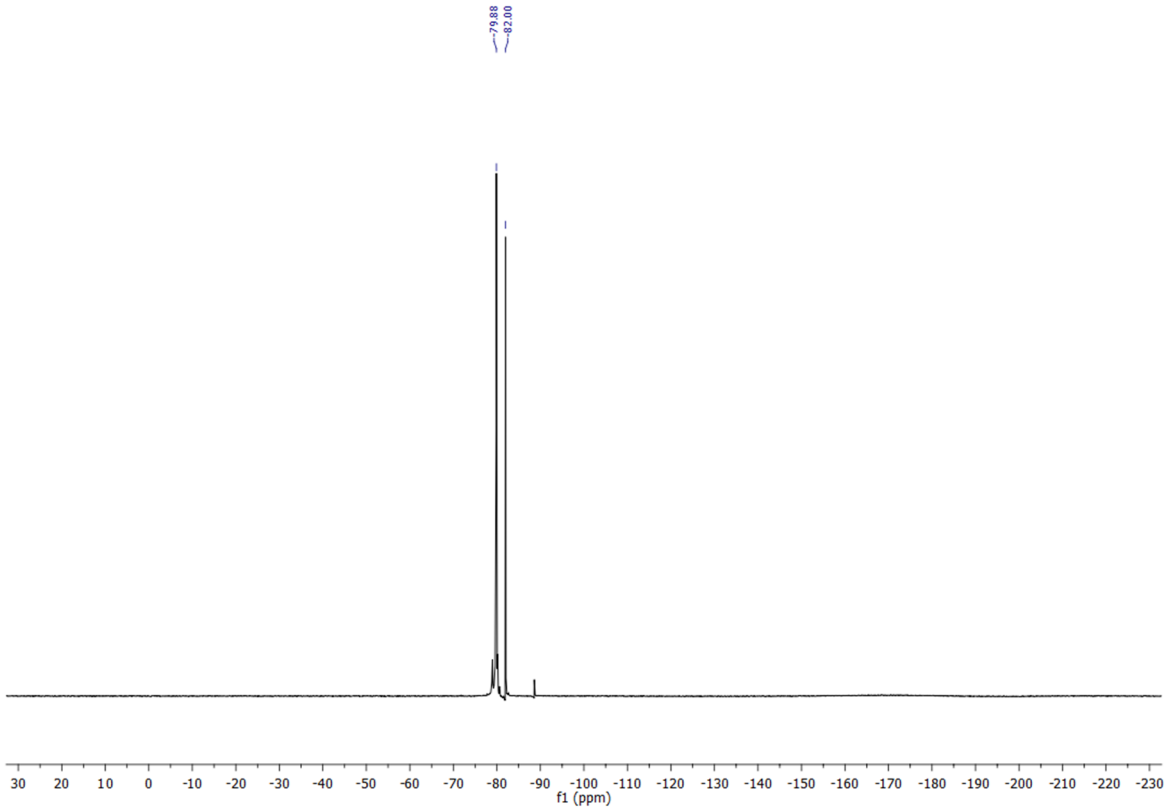
^{1}H NMR (300 MHz, CD_3COCD_3, 25 ºC)



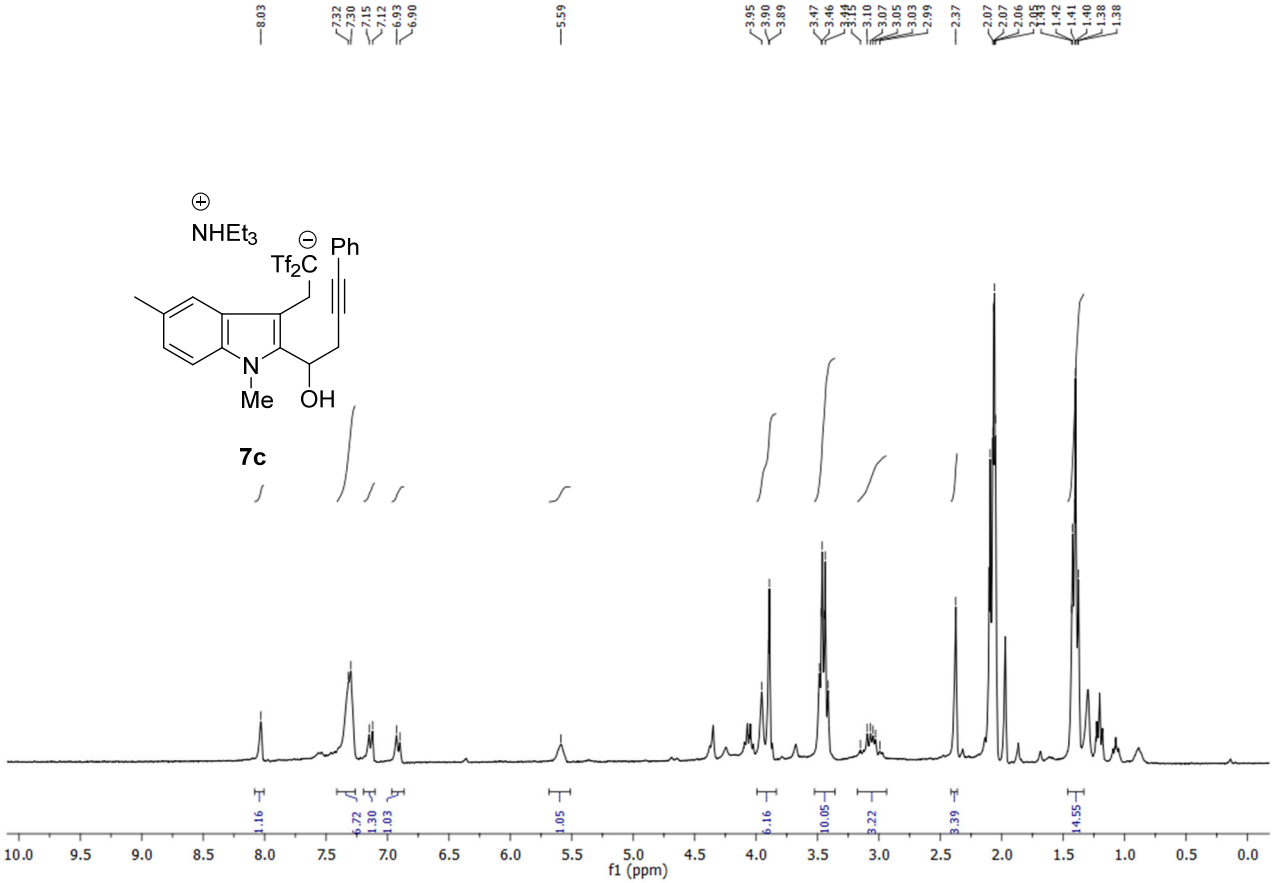
^{13}C NMR (175 MHz, CD_3COCD_3, 25 ºC)



^{19}F NMR (282 MHz, CD_3COCD_3, 25 °C)

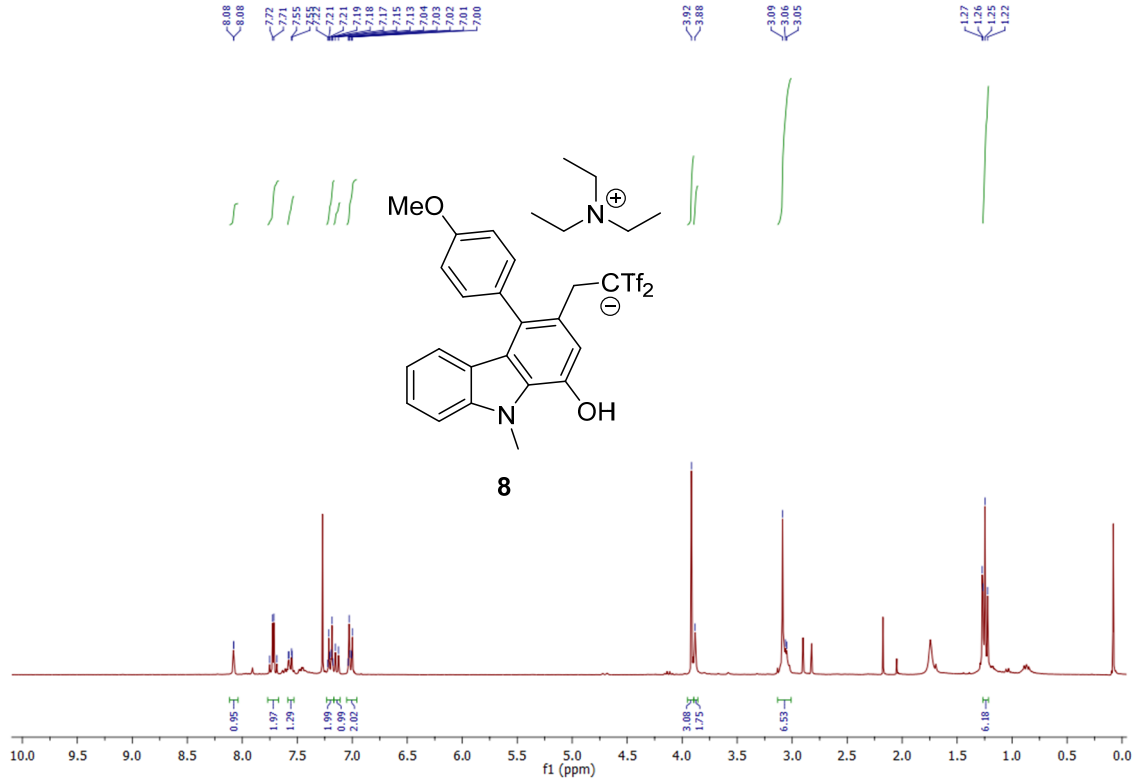


^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC)



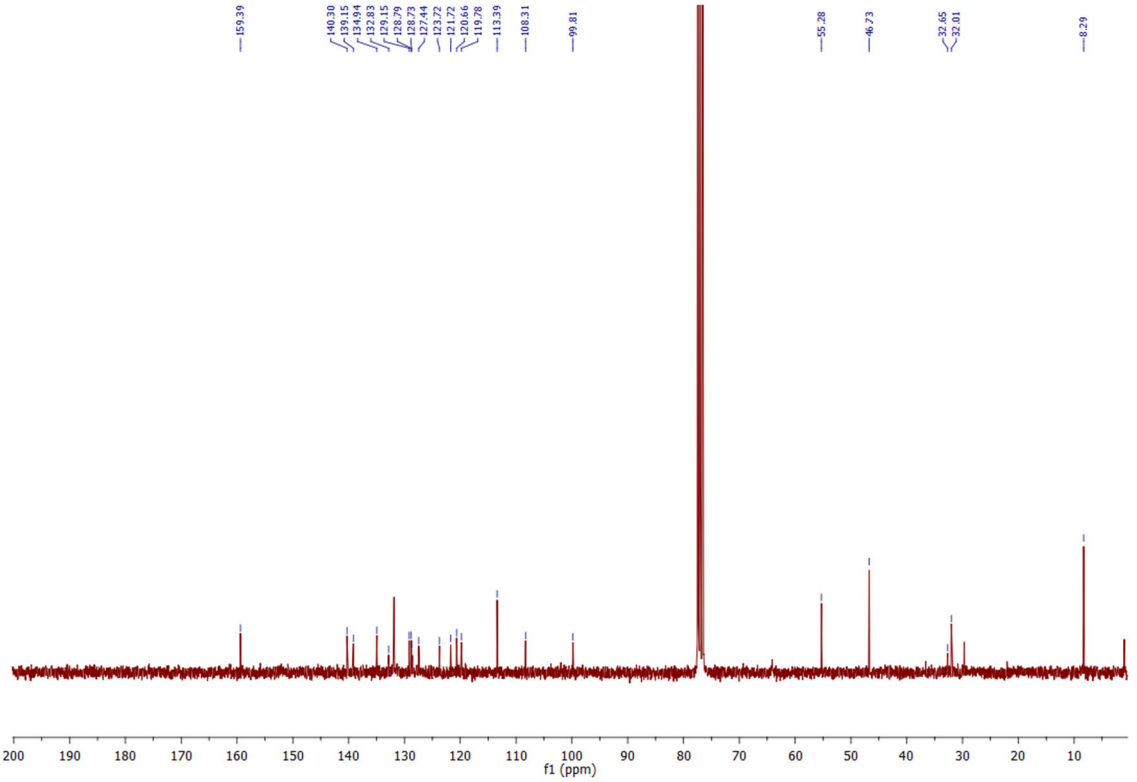
Compound **7c** is unstable in solution and a good quality ^{13}C NMR spectrum cannot be recorded.

^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC)

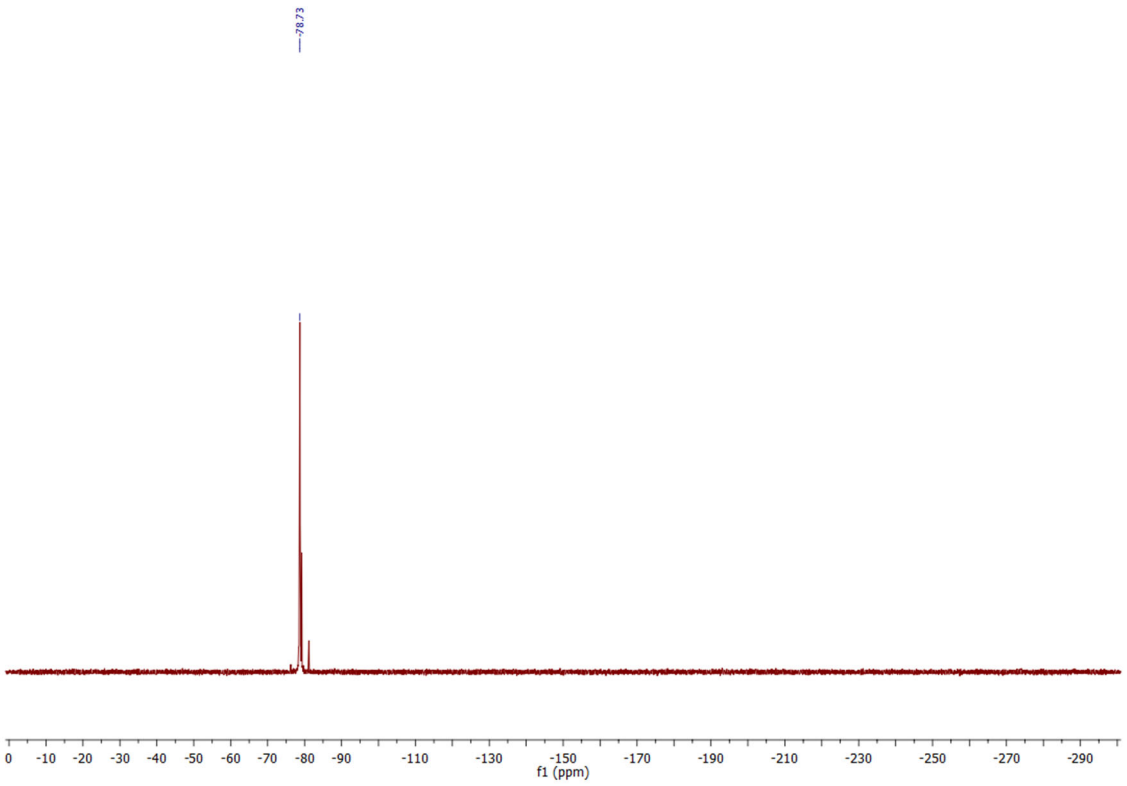


8

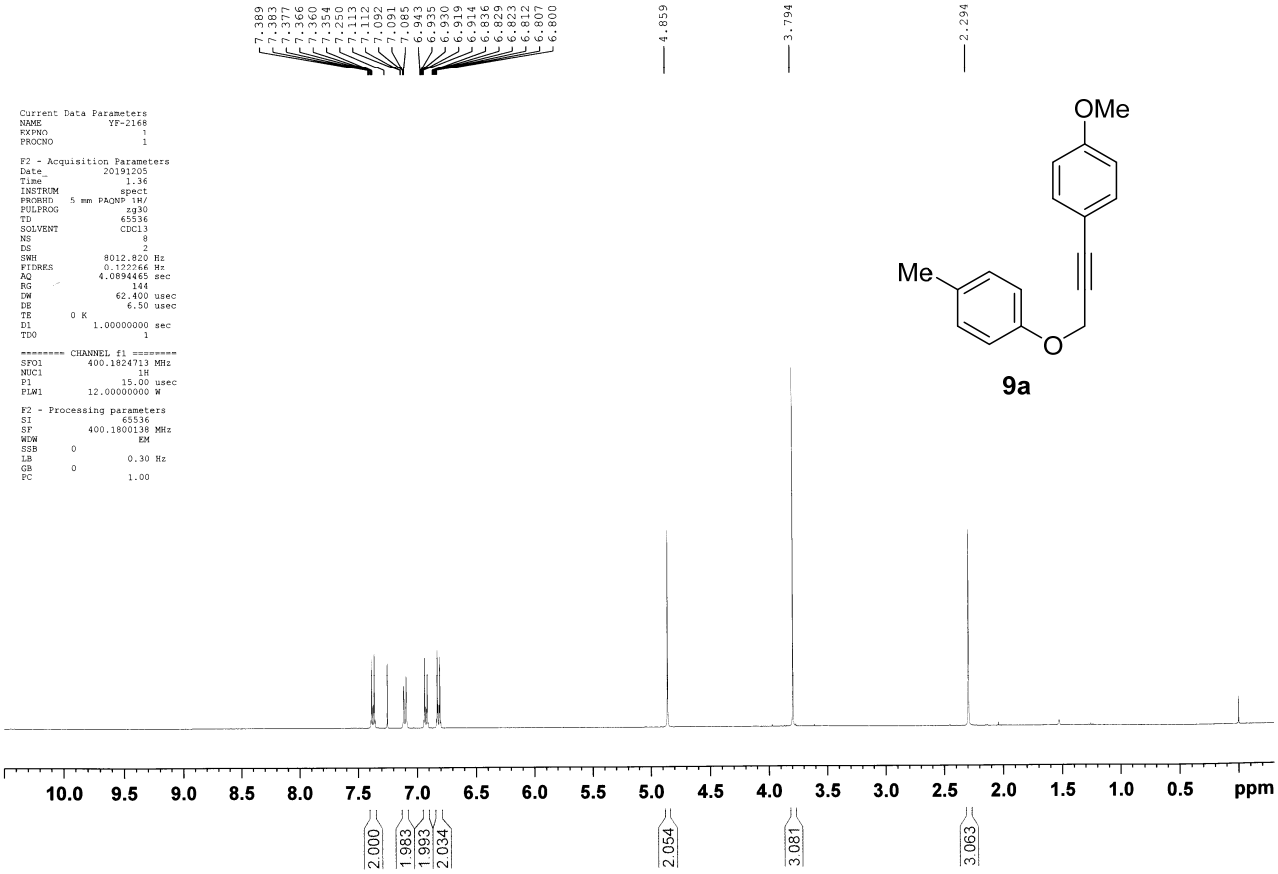
^{13}C NMR (75 MHz, $CDCl_3$, rt)



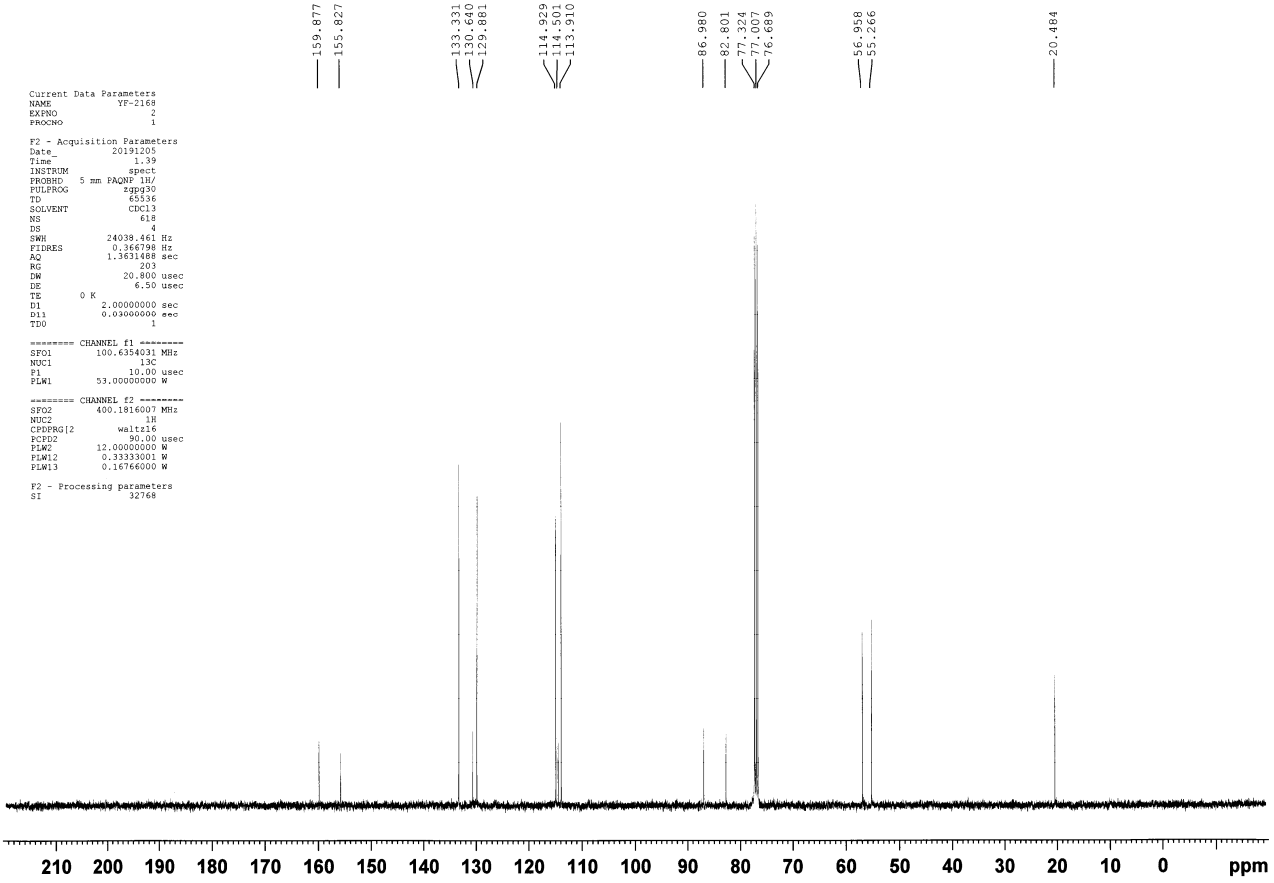
^{19}F NMR (282 MHz, $CDCl_3$, 25 °C)



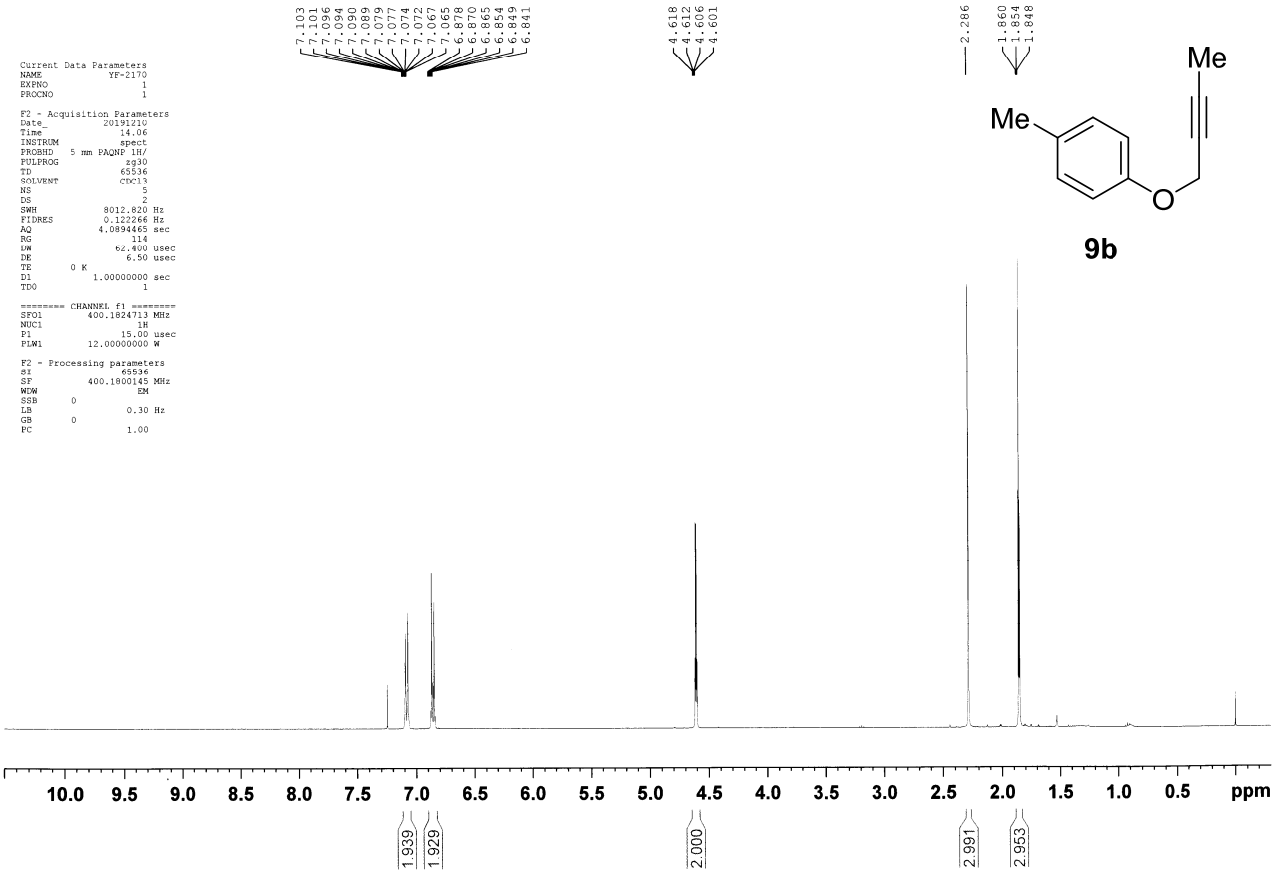
^{1}H NMR (400 MHz, $CDCl_3$, rt)



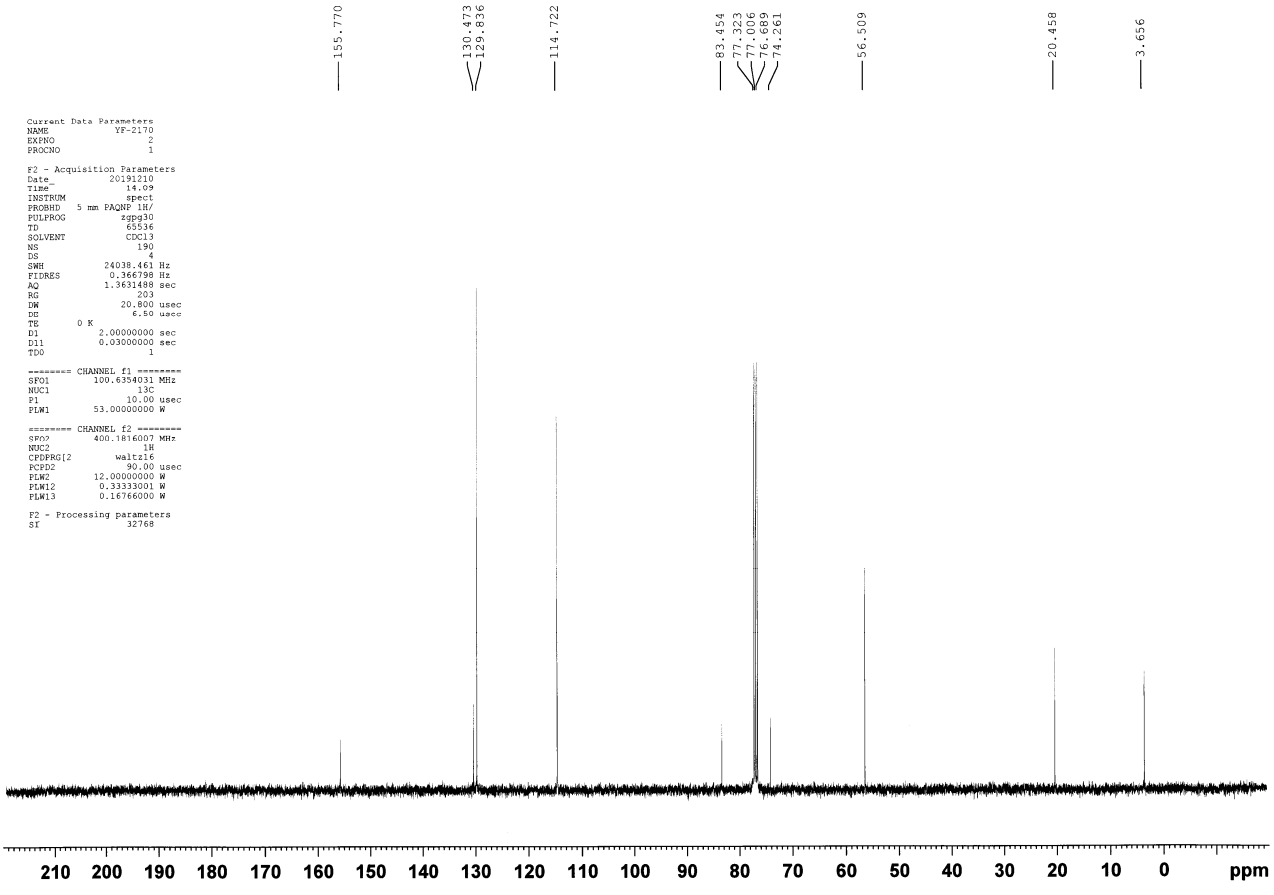
^{13}C NMR (100 MHz, $CDCl_3$, rt)



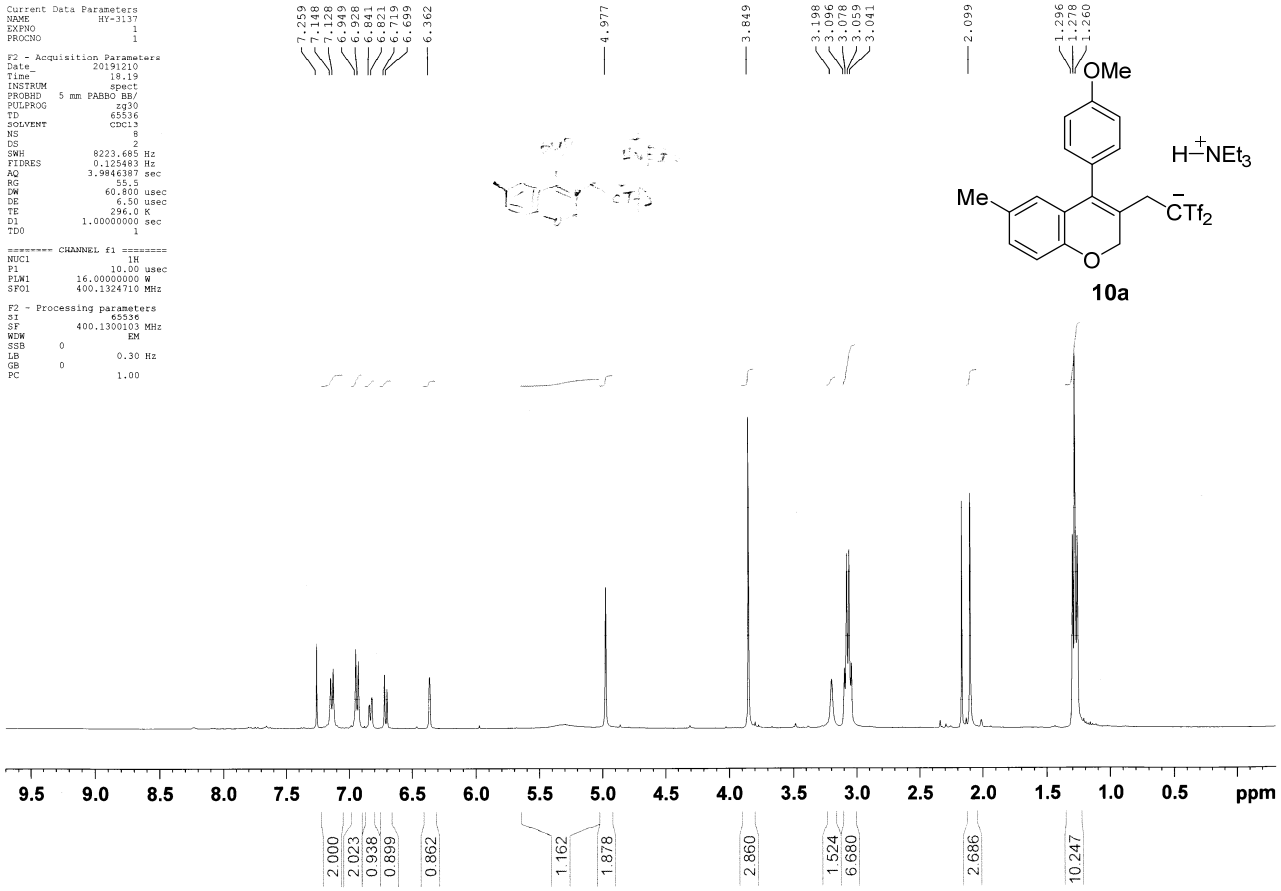
^{1}H NMR (400 MHz, $CDCl_3$, rt)



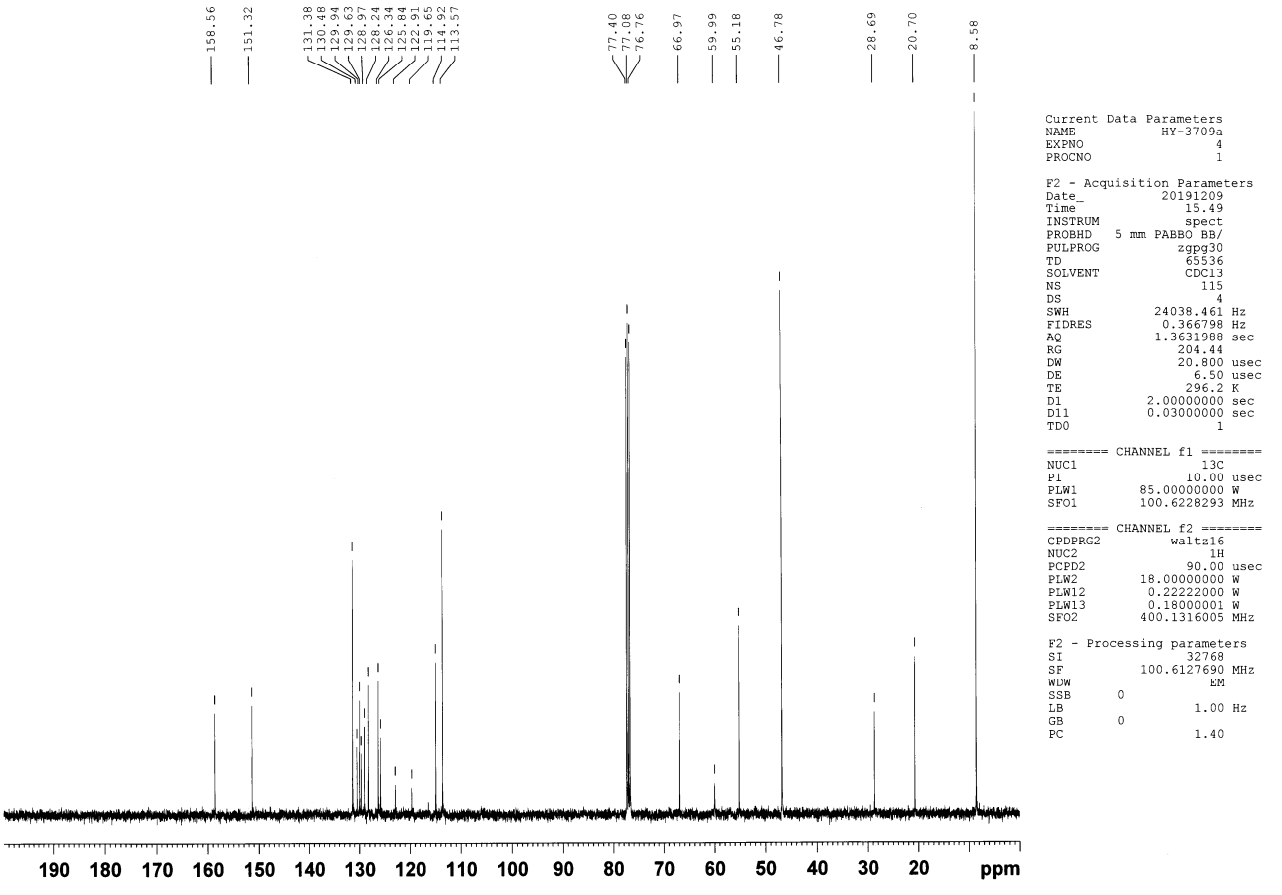
^{13}C NMR (100 MHz, $CDCl_3$, rt)



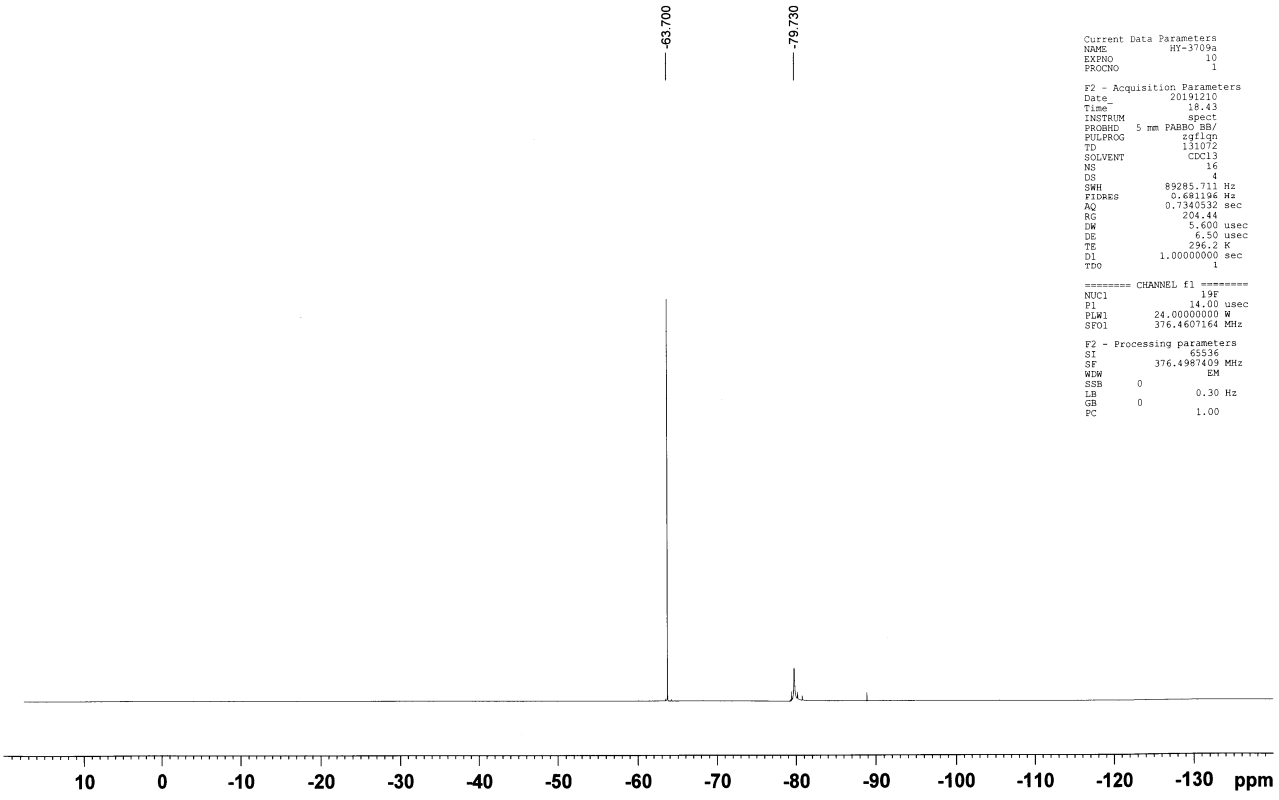
^{1}H NMR (400 MHz, $CDCl_3$, rt)



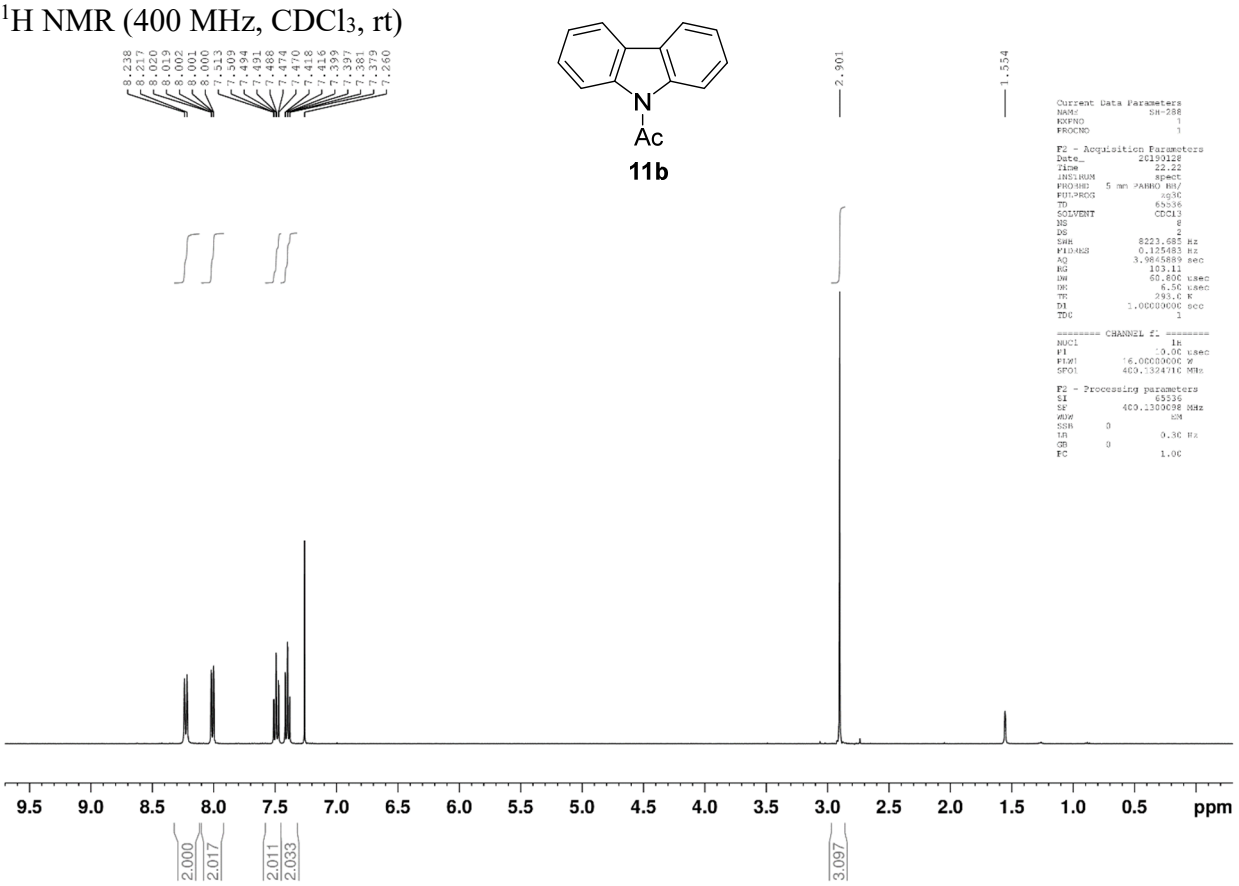
^{13}C NMR (100 MHz, $CDCl_3$, rt)



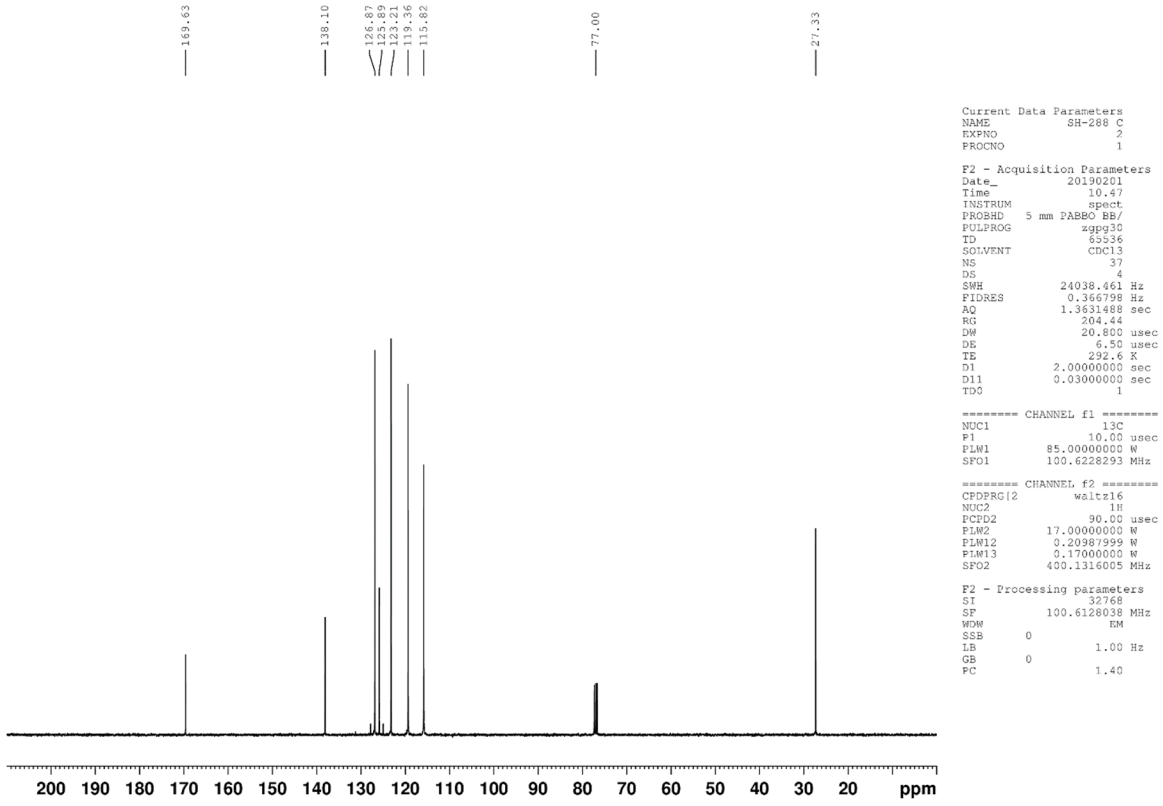
^{19}F NMR with $PhCF_3$ (376 MHz, $CDCl_3$, rt)



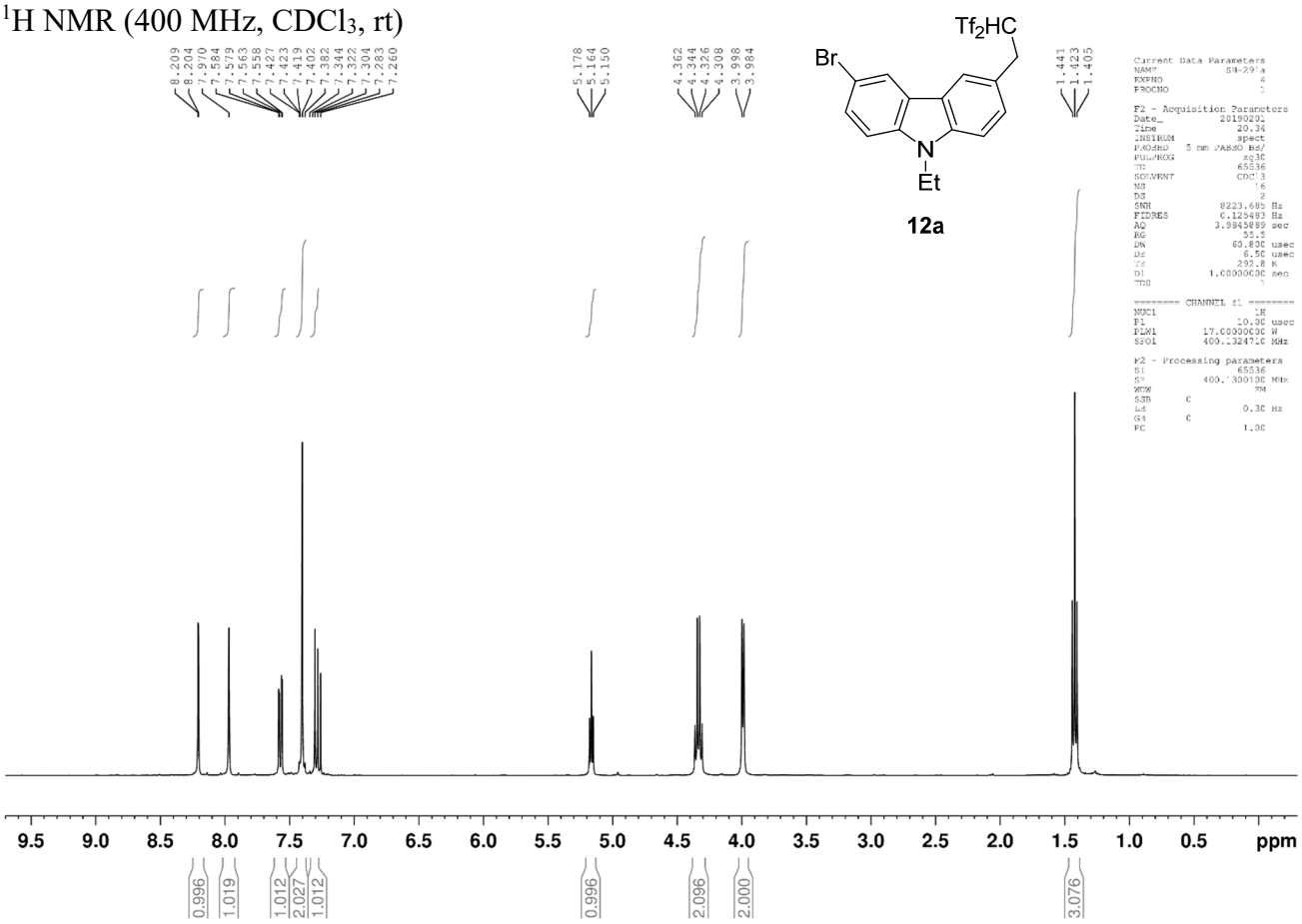
^{1}H NMR (400 MHz, $CDCl_3$, rt)



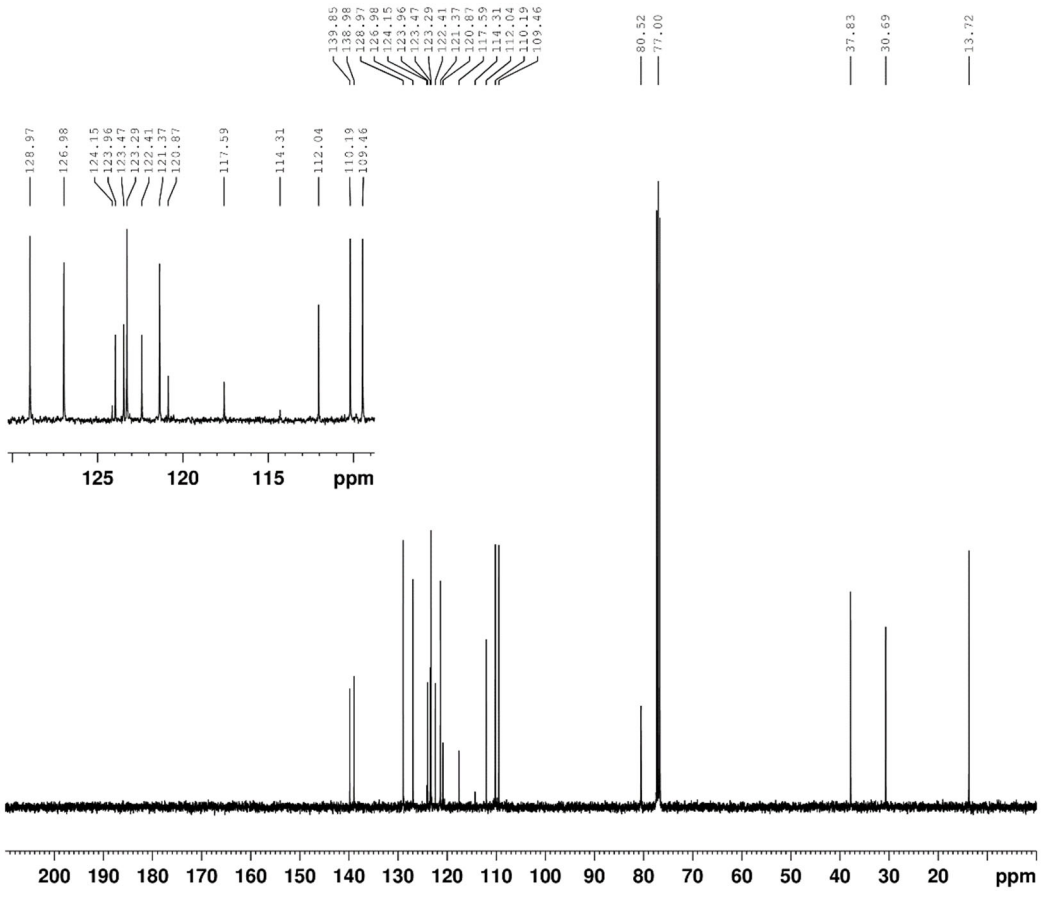
^{13}C NMR (100 MHz, $CDCl_3$, rt)



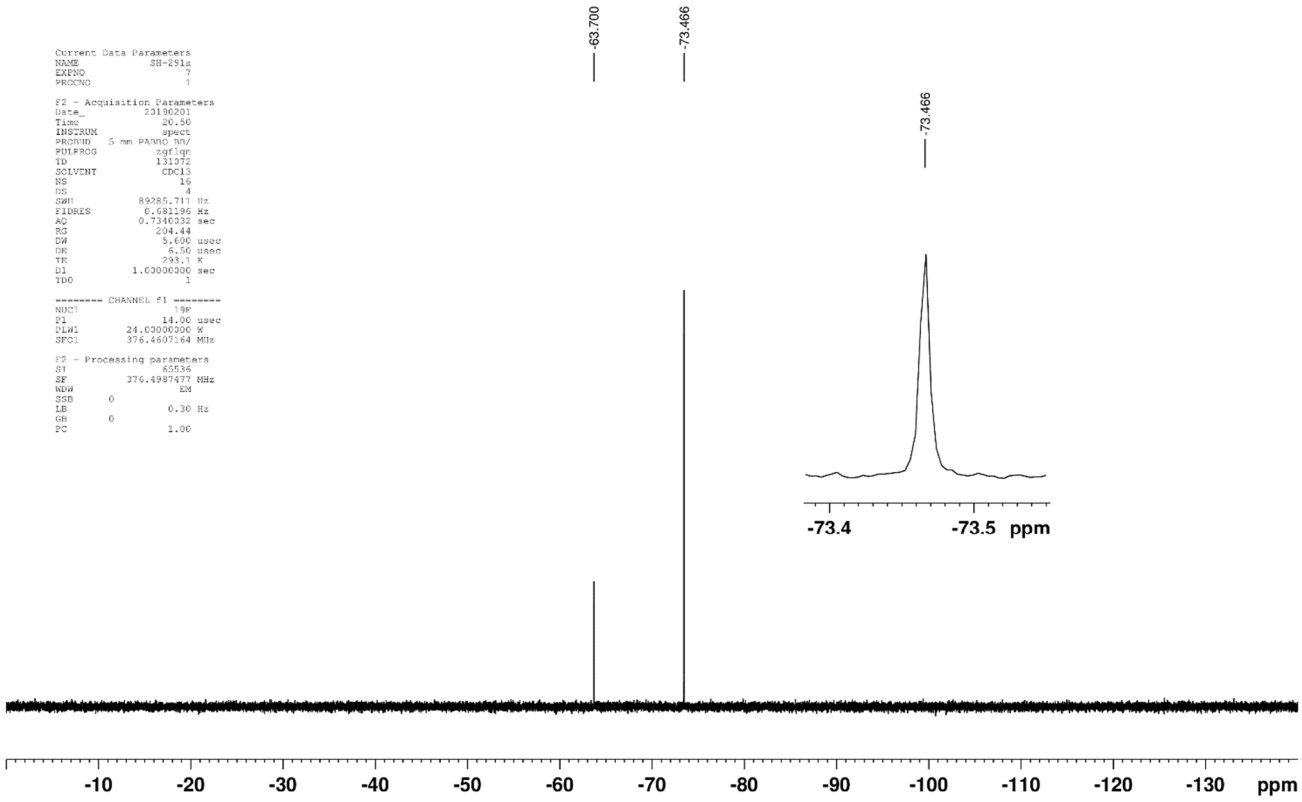
^{1}H NMR (400 MHz, $CDCl_3$, rt)



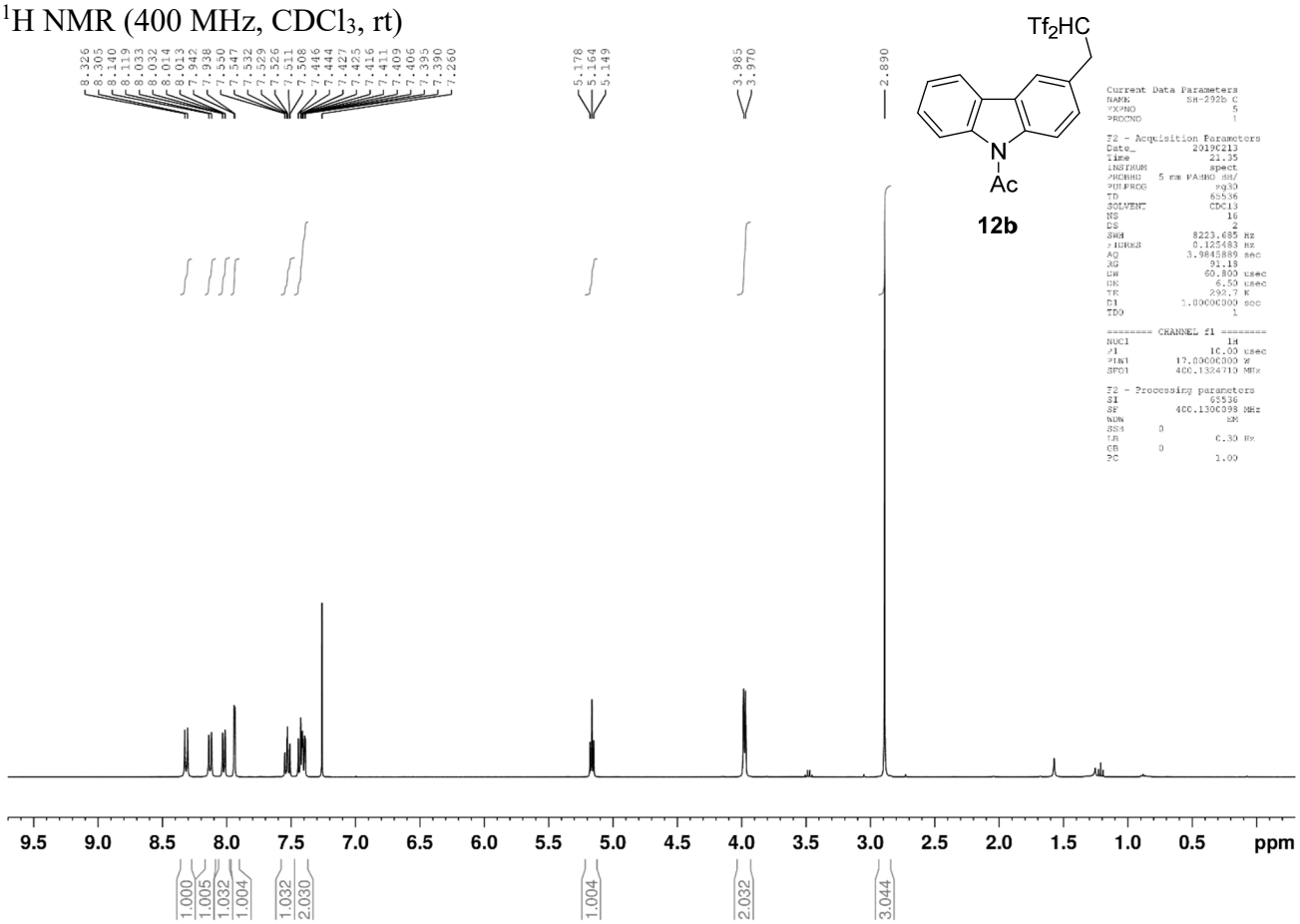
^{13}C NMR (100 MHz, $CDCl_3$, rt)



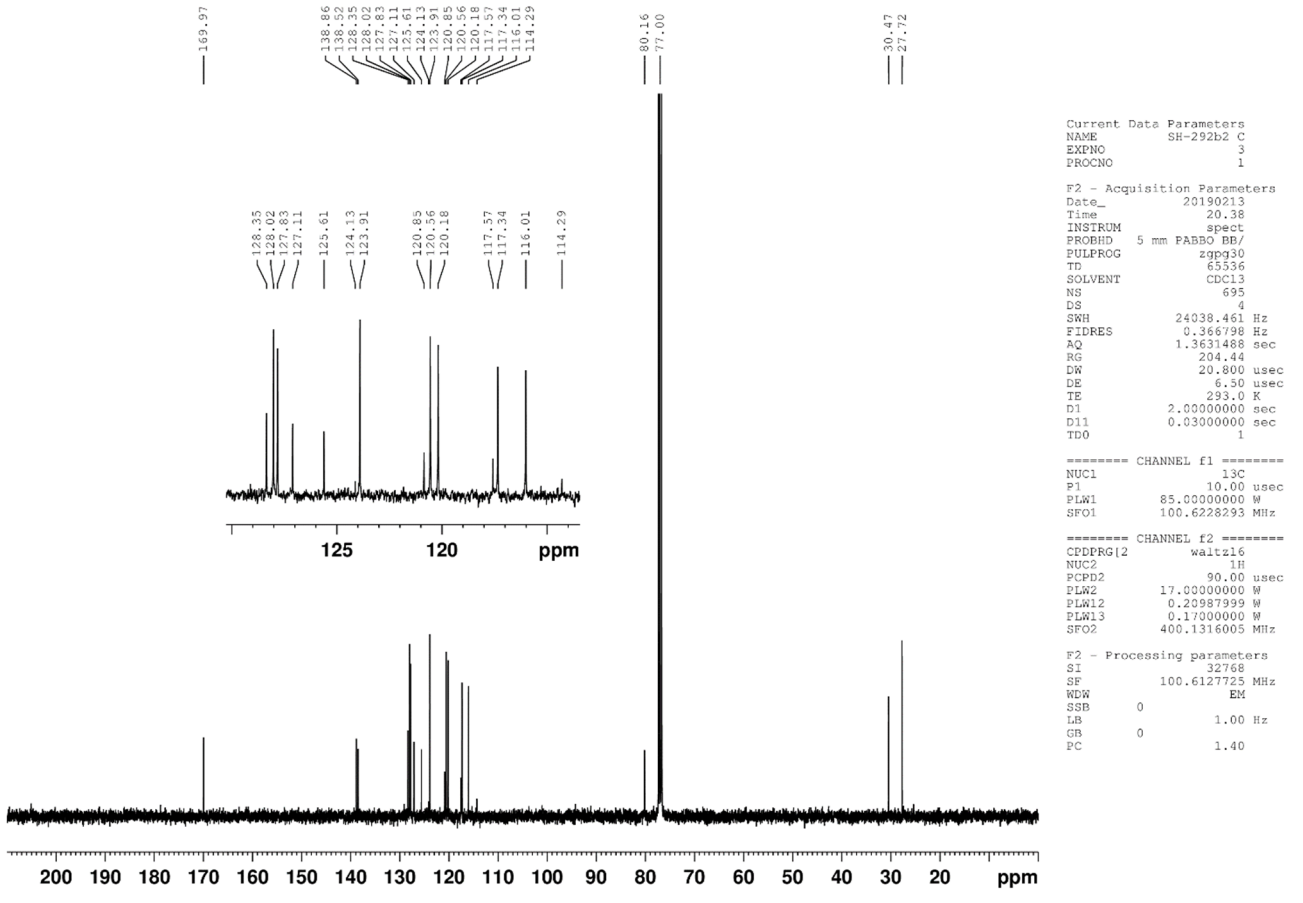
^{19}F NMR with $PhCF_3$ (376 MHz, $CDCl_3$, rt)



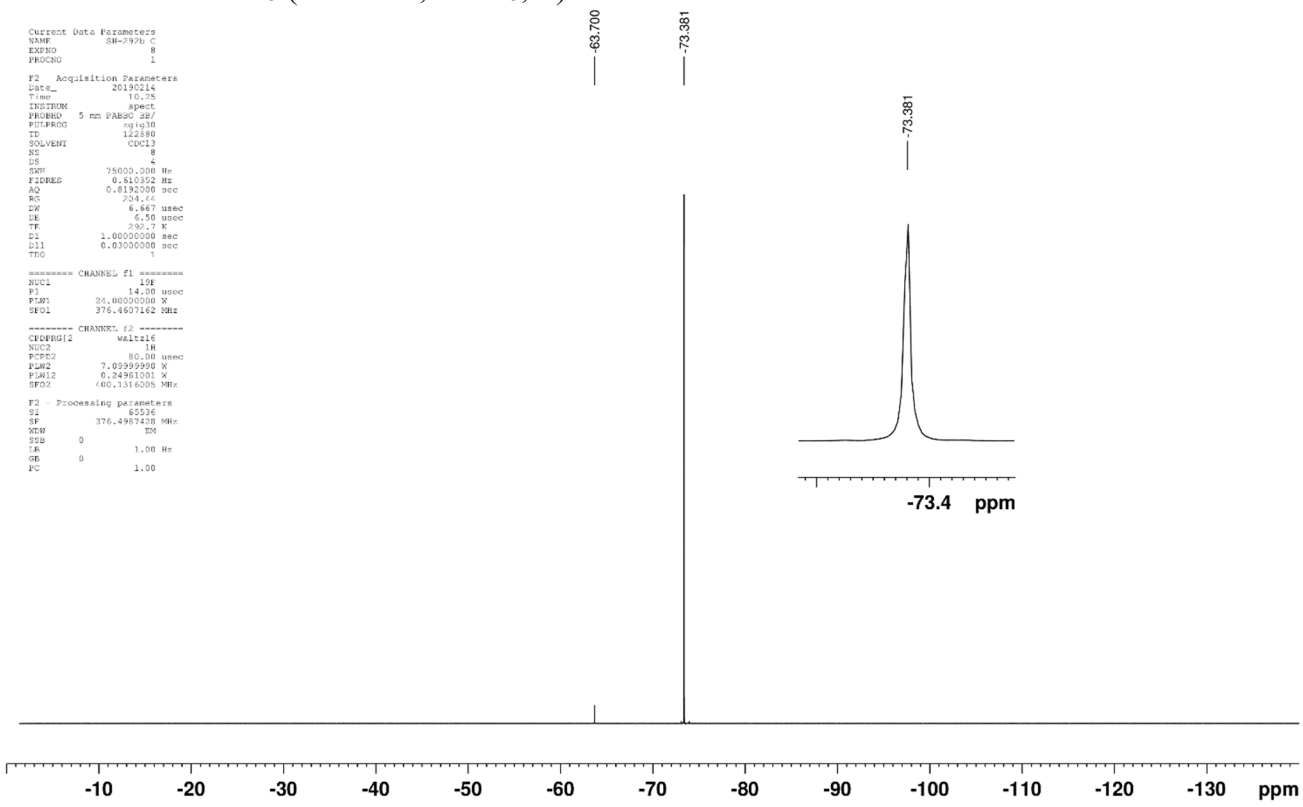
^{1}H NMR (400 MHz, $CDCl_3$, rt)



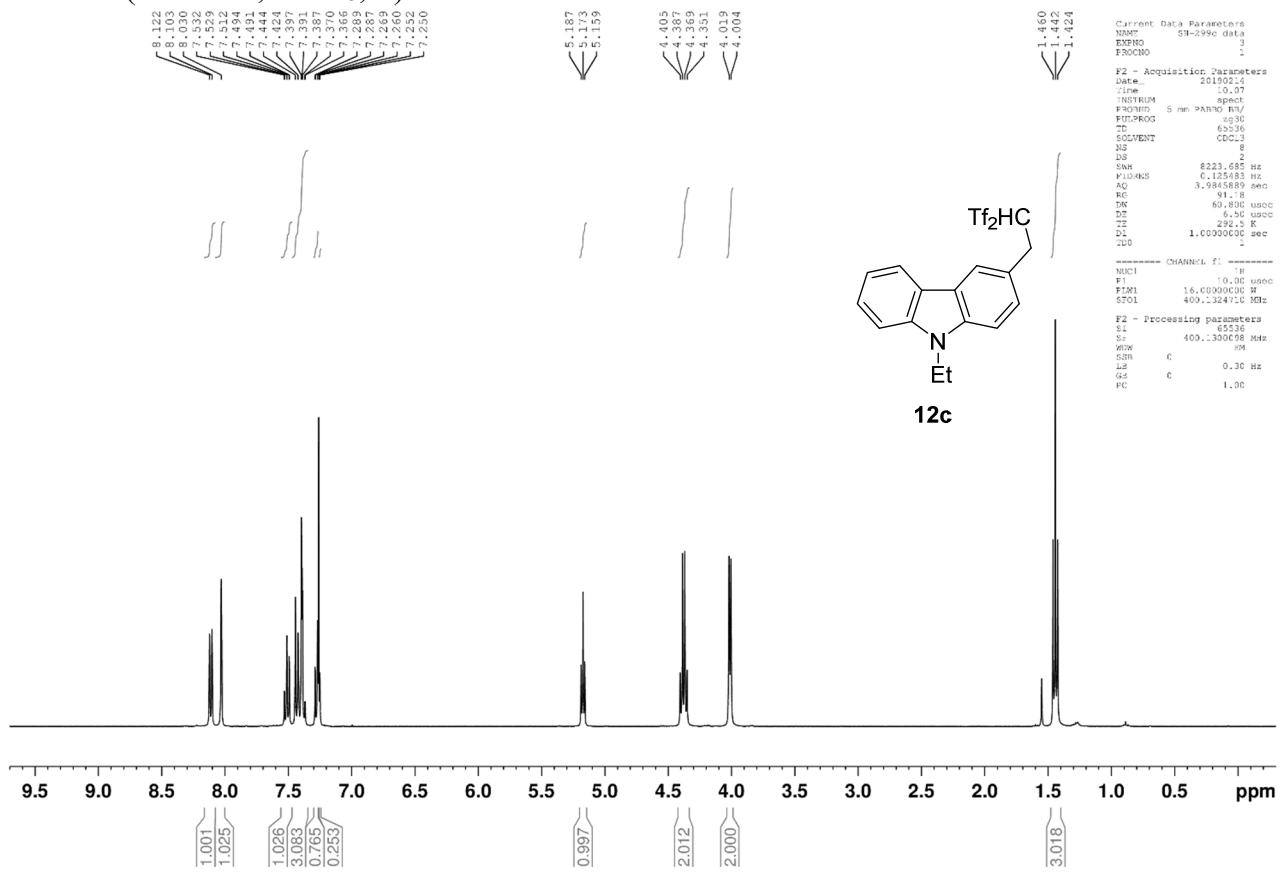
^{13}C NMR (100 MHz, $CDCl_3$, rt)



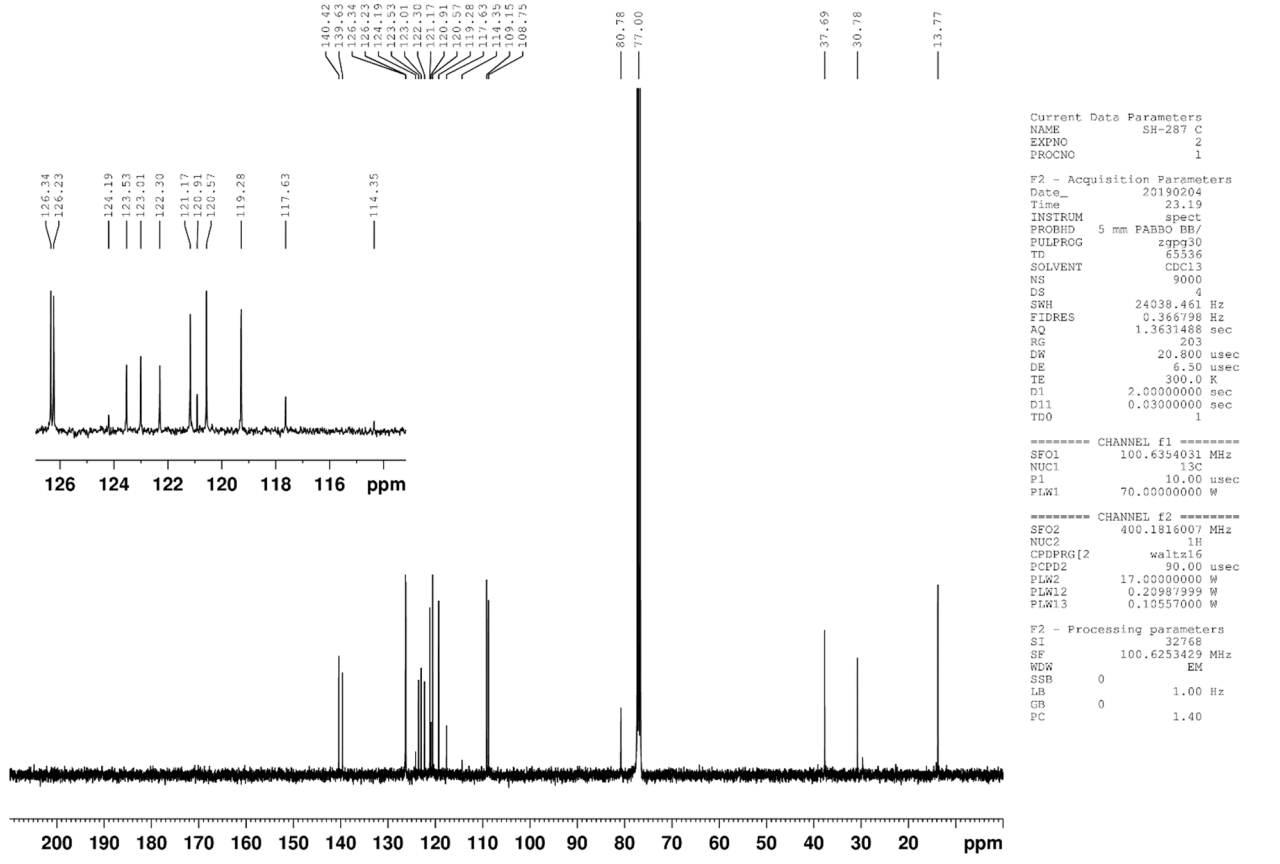
^{19}F NMR with $PhCF_3$ (376 MHz, $CDCl_3$, rt)



^{1}H NMR (400 MHz, $CDCl_3$, rt)



^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC)



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PROCNO 1

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FIDRES 0.366798 Hz
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DE 6.50 usec
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D11 0.03000000 sec
TD0 1

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P1 10.00 usec
PLW1 70.00000000 W

======== CHANNEL f2 ========
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NUC2 1H
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F2 - Processing parameters
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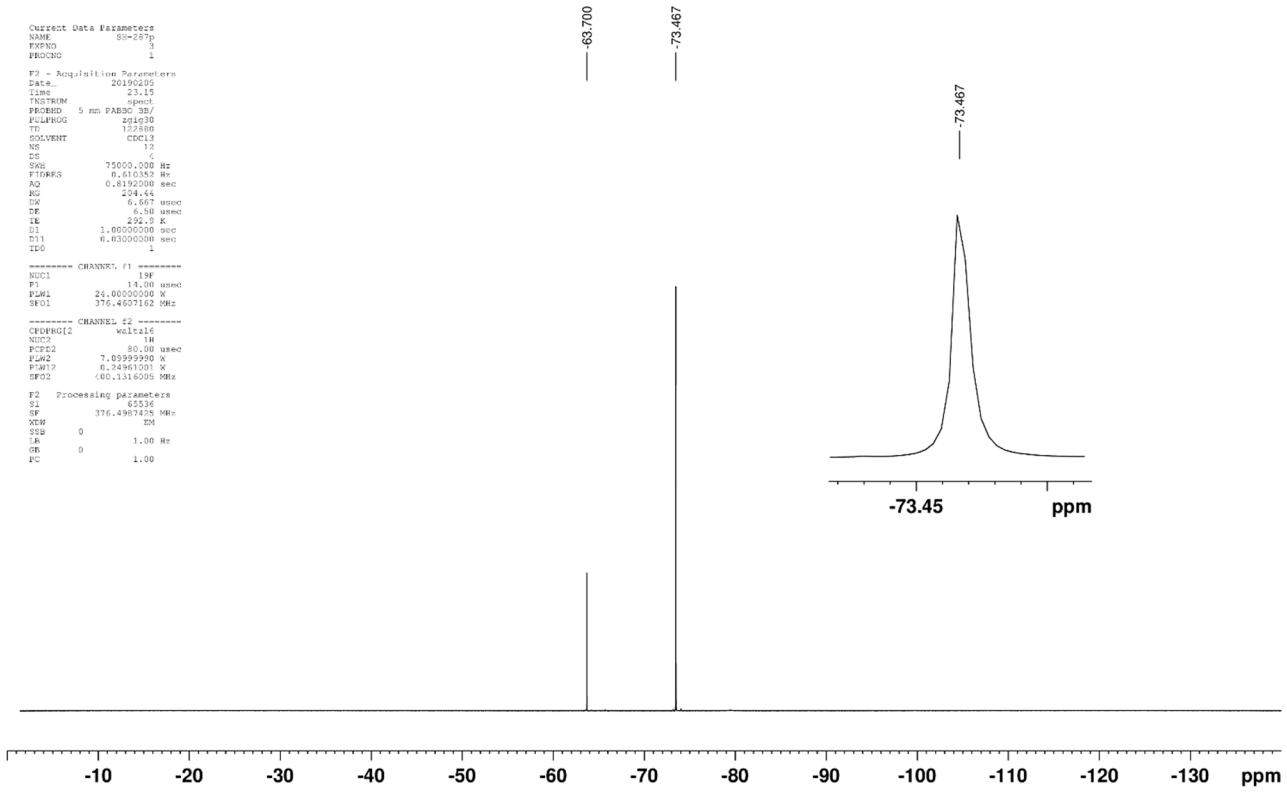
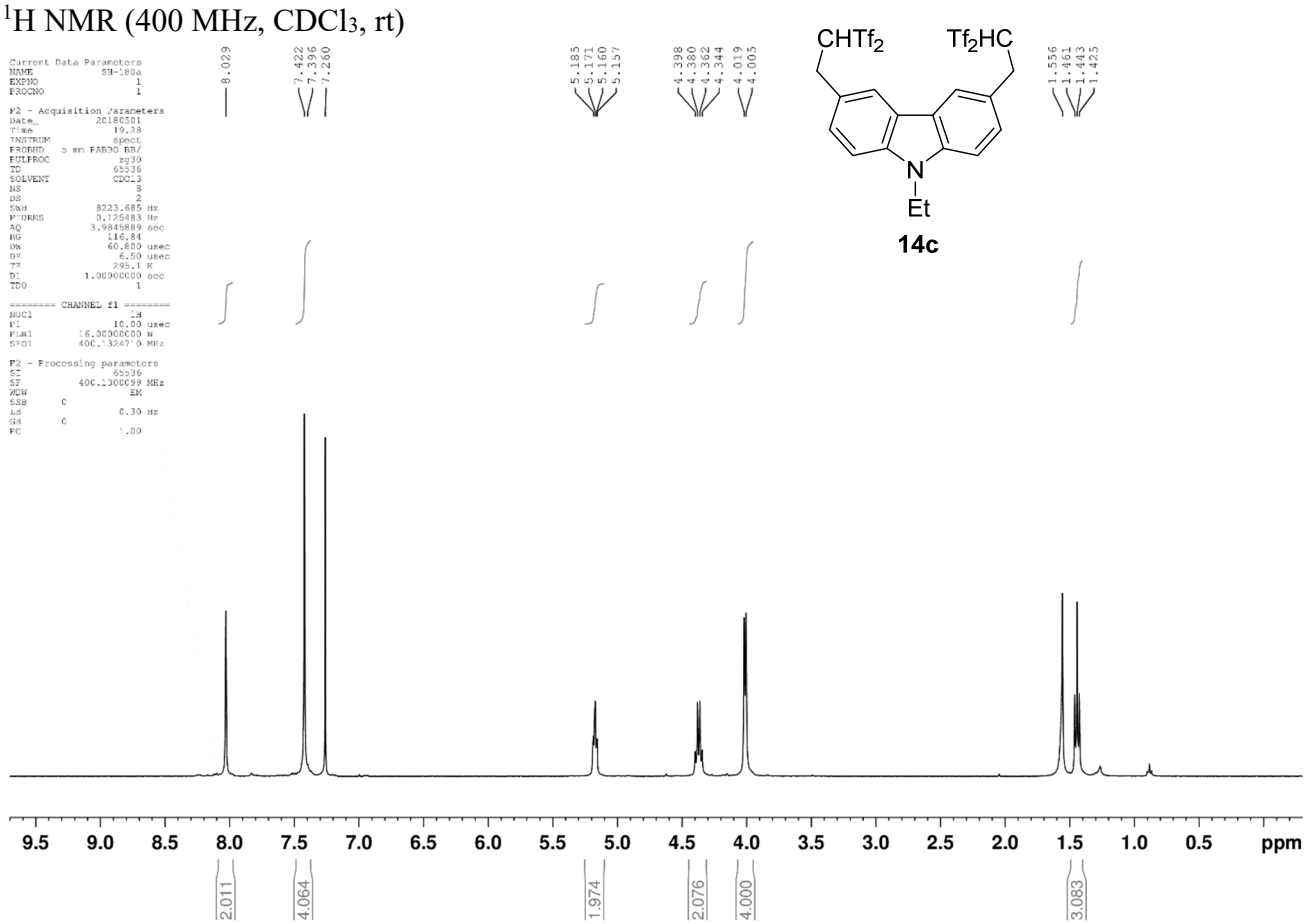
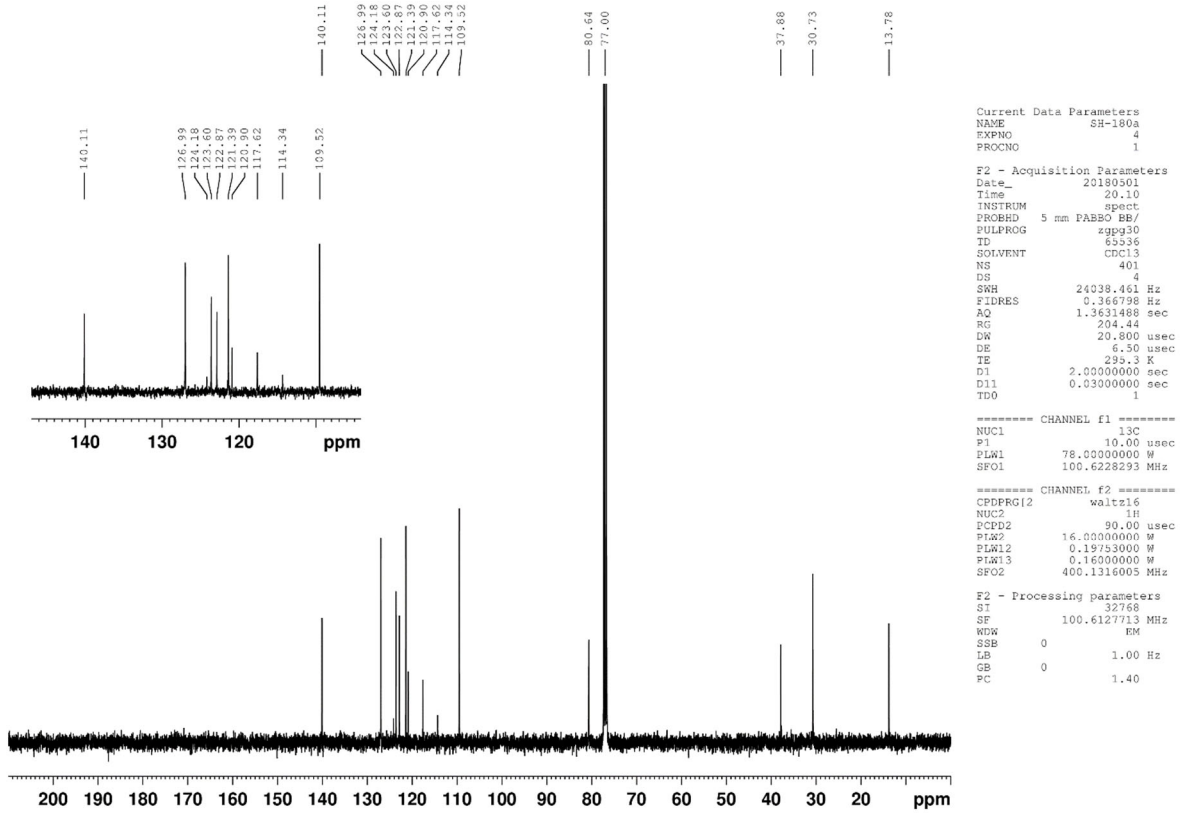
^{19}F NMR with $PhCF_3$ (376 MHz, $CDCl_3$, rt)



^{1}H NMR (400 MHz, $CDCl_3$, rt)



^{13}C NMR (100 MHz, $CDCl_3$, rt)

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PROCNO                      1

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RG                     204.44
DW                     20.800 usec
DE                      6.50 usec
TE                     295.3 K
D1                  2.00000000 sec
D11                 0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
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SFO1               100.6228293 MHz

======== CHANNEL f2 ========
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F2 - Processing parameters
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^{19}F NMR with $PhCF_3$ (376 MHz, $CDCl_3$, rt)