Ring Expansion of Alkynyl Cyclopropanes to Highly substituted Cyclobutenes via a *N*-Sulfonyl-1,2,3-Triazole Intermediate

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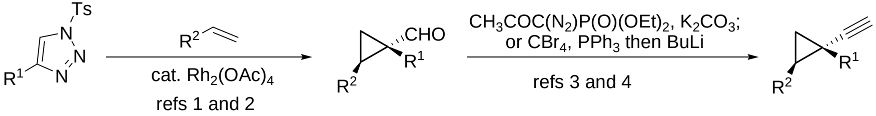
General remarks

All reactions in non-aqueous media were conducted under a positive pressure of dry argon in glassware that had been oven dried prior to use unless noted otherwise. Anhydrous solutions of reaction mixtures were transferred via an oven dried syringe or cannula. All solvents were dried prior to use unless noted otherwise. Reagents were purchased from Aldrich, Acros, TCI, or VWR unless otherwise noted. Thin layer chromatography was performed using precoated silica gel plates (EMD Chemical Inc. 60,F254). Flash column chromatography was performed with silica gel (Sillicycle, 40-63μm). Infrared spectra (IR) were obtained as neat oils on a Bruker Equinox 55 spectrophotometer. ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were obtained on a Varian Unity-Inova 400 MHz or 500 MHz recorded in ppm (δ) downfield of TMS (δ = 0) in $CDCl_3$, CD_3OD. Signal splitting patterns were described as singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint), or multiplet (m), with coupling constants (*J*) in hertz. High resolution mass spectra (HRMS) were performed by Analytical Instrument Center at the School of Pharmacy or Department of Chemistry on an Electron Spray Injection (ESI) mass spectrometer. Enantiomeric excess was determined by chiral HPLC analysis. The optical rotation was determined by Perkin–Elmer 241 Polarimeter.

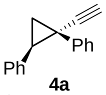
Characterization data for alkynyl cyclopropane substrates:

Unless noted otherwise, alkynyl cyclopropanes were prepared by cyclopropanation of alkenes followed by alkyne formation as shown below following literature procedures.



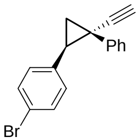
References:

1) S. Chuprakov, S. W. Kwok, L. Zhang, L. Lercher and V. V. Fokin, *J. Am. Chem. Soc.*, 2009, **131**, 18034.
2) N. Grimster, L. Zhang and V. V. Fokin, *J. Am. Chem. Soc.*, 2010, **132**, 2510.
3) S. Muller, B. Liepold, G. J. Roth and H. J. Bestmann, *Synlett*, 1996, 521.
4) E. J. Corey and P. L. Fuchs, *Tetrahedron Lett.*, 1972, **13,** 3769.



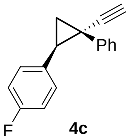
4a

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.89 (dd, *J* = 8.97, 5.65 Hz, 1H), 1.97 (dd, *J* = 7.21, 5.46 Hz, 1H), 2.13 (s, 1H), 2.95 (dd, *J* = 9.1, 7.21 Hz, 1H), 6.91 (m, 2H), 7.05-7.21 (m, 8H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 19.94, 24.21, 34.44, 64.77, 89.77, 126.24, 126.63, 127.71, 127.92, 128.42, 129.26, 136.12, 136.63. IR ($CHCl_3$) ν 3289, 3028, 2113, 1712, 1498, 762, 695cm^{-1}. HRMS (ESI) m/z calcd for $C_{17}H_{14}$ $(M+Na)^+$ 241.0988, found 241.0989.



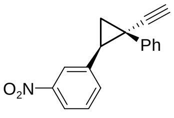
4b

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.89 (m, 2H), 2.11 (s, 1H), 2.85 (d, *J*=8.1Hz, 1H), 6.74 (d, *J*=8.2Hz, 2H), 7.09-7.17(m, 5H), 7.36 (d, *J*=8.5Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 20.04, 24.42, 33.79, 65.03, 89.37, 120.15, 126.92, 128.14, 129.24, 130.01, 130.82, 135.37, 136.24. IR ($CHCl_3$) ν 3294, 3027, 2925, 2114, 1712, 1489, 1009, 697cm^{-1}. HRMS (ESI) m/z calcd for $C_{17}H_{13}Br$ $(M+Na)^+$ 319.0093, found 319.0094.



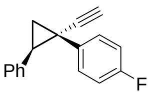
4c

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.89 (m, 2H), 2.11 (s, 1H), 2.89 (d, *J*=8.2Hz, 1H), 6.78 (t, *J*=8.77Hz, 2H), 6.85 (m, 2H), 7.08-7.17(m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 19.99, 24.05, 33.72, 64.91, 89.52, 114.63 (d, ^2J=21.5 Hz), 126.74, 128.00, 129.13, 129.88 (d, ^3J=8.5 Hz), 131.86 (d, ^4J=3.1 Hz), 136.42, 161.42 (d, ^1J=244.9 Hz). IR ($CHCl_3$) ν 3295, 3058, 2114, 1510, 1218, 836, 697cm^{-1}. HRMS (ESI) m/z calcd for $C_{17}H_{13}F$ $(M+Na)^+$ 259.0894, found 259.0892.



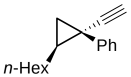
4d

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.95 (dd, *J*=8.85, 5.97Hz, 1H), 2.04 (t, *J*=6Hz, 1H), 2.12 (s, 1H), 2.96 (t, *J*=7.4Hz, 1H), 7.05-7.25 (m, 7H), 7.73 (s, 1H), 7.85 (d, *J*=7.8Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 19.83, 25.04, 33.57, 65.48, 88.67, 121.29, 123.02, 127.18, 128.26, 128.52, 129.19, 134.36, 135.57, 138.63, 147.72. IR ($CHCl_3$) ν 3294, 3027, 2356, 2116, 1527, 1347, 693cm^{-1}. HRMS (ESI) m/z calcd for $C_{17}H_{13}NO_2$ $(M+Na)^+$ 286.0839, found 286.0837.



4e

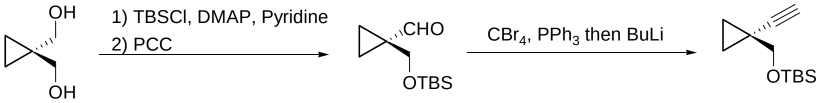
^{1}H NMR (500 MHz, $CDCl_3$): δ 1.94-2.00 (m, 2H), 2.20 (s, 1H), 3.02 (dd, *J*=9.0, 7.5Hz, 1H), 6.89-6.92 (m, 2H), 6.98 (d, *J*=12.0Hz, 2H), 7.16-7.23 (m, 5H); ^{13}C NMR ($CDCl_3$, 125 MHz): 20.21, 23.76, 34.50, 65.23, 89.67, 115.02 (^{2}J = 21.4 Hz), 126.60, 128.04, 128.55, 131.09 (^{3}J = 8.1Hz), 132.76 (^{4}J = 3.1Hz), 136.07, 161.71 (^{1}J=244 Hz); IR ($CHCl_3$) ν 3300, 2114, 1509, 1221, 907, 731 cm^{-1}. HRMS (ESI) m/z calcd for $C_{17}H_{13}F$ $(M+Na)^+$ 259.0894, found 259.0898.



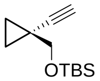
4f

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.70 (m, 1H), 0.82 (t, *J*=7.4Hz, 3H), 1.10-1.33 (m, 10H), 1.38 (dd, *J*=8.8, 4.9Hz, 1H), 1.53 (m, 1H), 1.96 (s, 1H), 7.23 (m, 1H), 7.30 (m, 2H), 7.37 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.01, 19.90, 20.69, 22.49, 28.72, 28.92, 29.14, 29.99, 31.63, 63.69, 90.67, 126.67, 128.13, 129.10, 137.95. IR ($CHCl_3$) ν 3310, 2927, 2856, 2114, 1448, 909, 733, 698cm^{-1}. HRMS (ESI) m/z calcd for $C_{17}H_{22}$ $(M+H)^+$ 227.1794, found 227.1792.

Alkynyl cyclopropane **4h** was prepared in three steps following literature procedures.

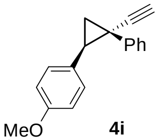


1) S. Zhou, M. N. Prichard, J. Zemlicka, *Tetrahedron*, 2007, **63**, 9406.
2) E. J. Corey and P. L. Fuchs, Tetrahedron *Lett.*, 1972, **13**, 3769.



4h

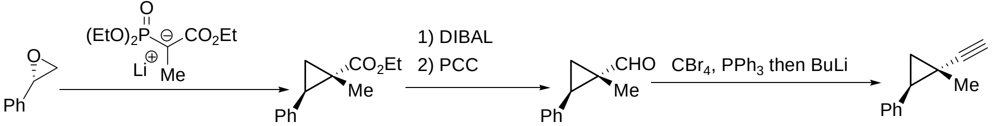
^{1}H NMR (400 MHz, $CDCl_3$): δ 0.07 (s, 6H), 0.81 (m, 2H), 0.85 (m, 2H), 0.90 (s, 9H), 1.88 (s, 1H), 3.64 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ -5.31, 11.91, 13.58, 18.38, 25.88, 65.09, 66.10, 87.92. IR ($CHCl_3$) ν 3316, 2930, 2896, 2115, 1102, 835 cm^{-1}. HRMS (ESI) m/z calcd for $C_{12}H_{22}OSi$ $(M+Na)^+$ 233.1332, found 233.1325.



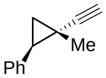
4i

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.83 (m, 2H), 2.08 (s, 1H), 2.85 (t, *J*=8Hz, 1H), 3.68 (s, 3H), 6.61 (d, *J*=8.7Hz, 2H), 6.80 (d, *J*=8.6Hz, 2H), 7.04-7.16 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 20.08, 23.83, 33.96, 55.07, 64.65, 89.94, 113.22, 126.54, 127.92, 128.15, 129.16, 129.49, 136.81, 158.03. IR ($CHCl_3$) ν 3286, 3006, 2935, 2112, 1712, 1513, 697cm^{-1}. HRMS (ESI) m/z calcd for $C_{17}H_{16}O$ $(M+Na)^+$ 271.1093, found 271.1094.

Alkynyl cyclopropane **4j** was prepared in four steps following literature procedures.



1) C. D. Bray, F. Minicone , *Chem. Commun.*, 2010, **46**, 5867.
2) E. J. Corey and P. L. Fuchs, Tetrahedron *Lett.*, 1972, **13**, 3769.

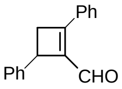


4j

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.97 (s, 3H), 1.09 (dd, *J*=6.82, 5.07Hz, 1H), 1.39 (dd, *J*=8.77, 4.87Hz, 1H), 1.94 (s, 1H), 2.53 (t, *J*=8.5 Hz, 1H), 7.18-7.31 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 13.00, 18.82, 19.91, 31.23, 63.51, 91.17, 126.51, 128.13, 129.15, 136.98. IR ($CHCl_3$) ν 2923, 2854, 2341, 1460, 1166, 736cm^{-1}. HRMS (ESI) m/z calcd for $C_{12}H_{12}(M+H)^+$ 157.1017, found 157.1011.

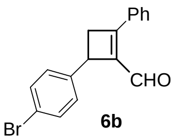
General procedure for the ring expansion of alkynyl cyclopropanes to cyclobutene aldehydes:

To a 4 mL vial equipped with a stirring bar, azide 13c (0.2 mmol), and alkyne (0.2 mmol) was added CuTc (0.02 mmol), AgOTf (0.02 mmol) and toluene (2 mL). The reaction mixture was stirred in the capped vial at room temperature for 4-8 h until starting material was completely consumed as determined by TLC analysis. Several drops of water and 20 mg alumina oxide were added to the reaction mixture. The resulting suspension was stirred for 1 h until hydrolysis of imine was completed. Solvents were removed under vacuum. The residue was purified by flash column chromatography with ethyl acetate/hexane (1/10 to 1/4) as eluent to give the corresponding cyclobutene aldehyde.



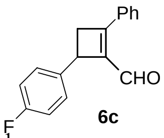
6a

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.77 (dd, *J*=15.6, 2.8Hz, 1H), 3.38 (dd, *J*=15.6, 5.1Hz, 1H), 4.27 (d, *J*=5.1Hz, 1H), 7.24 (m, 3H), 7.31 (m, 2H), 7.46 (m, 5H), 10.04 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ.37.79, 41.84, 109.76, 126.73, 126.80, 128.44, 128.51, 128.58, 128.87, 131.09, 185.83. IR ($CHCl_3$) ν 3029, 2918, 1658, 907, 728cm^{-1}. HRMS (ESI) m/z calcd for $C_{17}H_{14}O$ $(M+Na)^+$ 257.0937, found 257.0935.

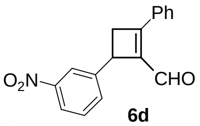


6b

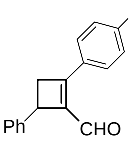
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.74 (dd, *J*=15.6, 2.0Hz, 1H), 3.38 (dd, *J*=15.6, 5.1Hz, 1H), 4.22 (d, *J*=5.0Hz, 1H), 7.18 (d, *J*=8.6Hz, 2H), 7.41-7.52(m, 5H), 7.75 (m, 2H), 10.05 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 37.84, 41.46, 120.72, 128.75, 128.81, 129.19, 131.50, 131.88, 133.07, 139.29, 140.79, 159.45, 185.23. IR ($CHCl_3$) ν 2921, 1656, 1402, 907, 728cm^{-1}. HRMS (ESI) m/z calcd for $C_{17}H_{13}BrO$ $(M+Na)^+$ 335.0042, found 335.0038.


6c

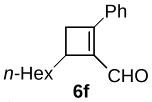
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.72 (dd, *J*=15.6, 2.1Hz, 1H), 3.37 (dd, *J*=15.6, 5.2Hz, 1H), 4.21 (dd, *J*=5.1, 2.0Hz, 1H), 6.99 (m, 2H), 7.25 (m, 2H), 7.47 (m, 3H), 7.74 (m, 2H), 10.04 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 37.87, 41.07, 115.35 (d, ^2J=20.7Hz), 128.26 (d, ^3J=8.5Hz), 128.51, 128.93, 131.21, 132.9, 136.95 (d, ^4J=3.1Hz), 139.34, 159.01, 161.71 (d, ^1J=224.9Hz) 185.69. IR ($CHCl_3$) ν 2918, 2849, 1709, 1508, 1220, 692cm^{-1}. HRMS (ESI) m/z calcd for $C_{17}H_{13}FO$ $(M+Na)^+$ 275.0843, found 275.0839.


6d

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.81 (dd, *J*=15.6, 1.6Hz, 1H), 3.46 (dd, *J*=15.6, 5.6Hz, 1H), 4.36 (dd, *J*=5.1, 1.8Hz, 1H), 7.44-7.55 (m, 4H), 7.65 (d, *J*=8.0Hz, 1H), 7.74 (m, 2H), 8.10 (d, *J*=8.0Hz, 1H), 8.14 (m, 1H),10.14 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 37.40, 41.15, 121.69, 121.85, 128.57, 129.04, 129.46, 131.53, 132.53, 133.29, 138.47, 143.43, 148.51, 159.18, 185.10. IR ($CHCl_3$) ν 3017, 2116, 1627, 1327, 693cm^{-1}. HRMS (ESI) m/z calcd for $C_{17}H_{13}NO_3$ $(M+Na)^+$ 302.0788, found 302.0783.

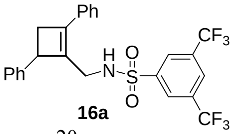

6e

^{1}H NMR (500 MHz, $CDCl_3$): 2.73 (dd, *J*=15.0, 1.5Hz, 1H), 3.34 (dd, *J*=16.0, 5.5Hz, 1H), 4.26(dd, *J*=5.0, 1.5Hz, 1H), 7.12-7.16(m, 2H), 7.22-7.25 (m, 1H), 7.28-7.33(m, 4H), 7.82-7.85(m, 2H), 9.86(s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 38.06, 42.07, 116.23 (^2J =21.8Hz), 127.00, 127.05, 128.85, 129.67 (^4J =3.1Hz), 131.00 (^3J=8.6Hz), 138.68, 141.43, 157.47, 164.54 (^1J=251.9Hz), 186.2; IR ($CHCl_3$) ν 1598, 1231, 1158, 906 cm^{-1}. HRMS (ESI) m/z calcd for $C_{17}H_{13}FO$ $(M+Na)^+$ 275.0843, found 275.0834.

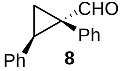

6f

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86 (t, *J*=6.6Hz, 3H), 1.18-1.56 (m, 10H), 2.43 (d, *J*=15.4Hz, 1H), 2.99 (dd, *J*=15.4, 4.7Hz, 1H), 3.06 (m, 1H), 7.42 (m, 3H), 7.64 (m, 2H), 10.05 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.08, 22.64, 27.46, 29.42, 31.83, 33.21, 34.21, 38.11, 128.21, 128.78, 130.58, 133.57, 141.83, 157.85, 186.06. IR($CHCl_3$) ν 2926, 2136, 1656, 1279, 758cm^{-1}. HRMS (ESI) m/z calcd for $C_{17}H_{22}O$ $(M+Na)^+$ 265.1563, found 265.1559.

General procedure for the ring expansion of alkynyl cyclopropanes to cyclobutene sulfonamides:
To a 4 mL vial equipped with a stirring bar, azide **13c** (0.2 mmol), and alkyne (0.2 mmol) was added CuTc (0.02 mmol), AgOTf (0.02 mmol) and toluene (2 mL). The reaction mixture was stirred in the capped vial at room temperature for 1-8 h until starting material was completely consumed as determined by TLC analysis. The reaction mixture was cooled to -78°C and a solution of $LiAlH_4$ in THF (2 mL, 0.2M, 0.4 mmol) was added slowly. The mixture was stirred at the same temperature for 1 h and warmed up to 0 °C. The reaction was quenched by careful addition of methanol followed by water. The solid was removed by filtration through a thin silica gel pad. The resulting solution was concentrated under reduced pressure to afford an oily residue which was purified by column chromatography to give the corresponding cyclobutene sulfonamide.


16a

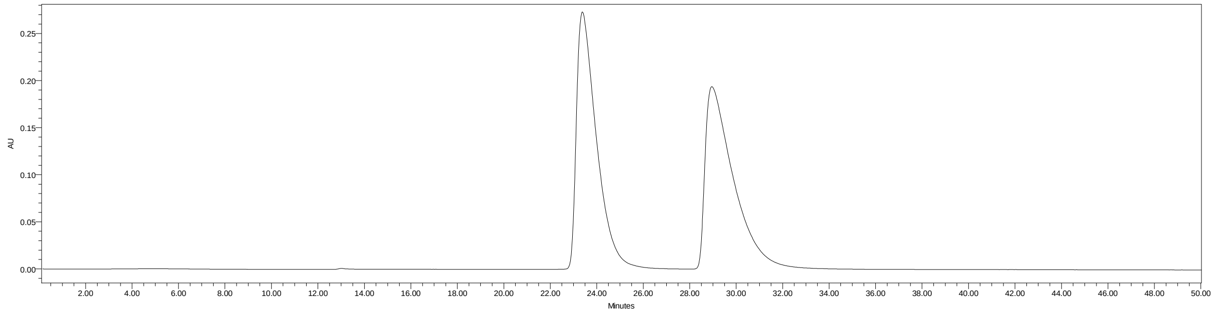
$[\alpha]_D^{20}$ =-23 (c=0.5, MeOH). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.50 (d, *J*=13.1Hz, 1H), 2.98 (dd, *J*=13.1, 4.9Hz, 1H), 3.57 (d, *J*=4.3Hz, 1H), 3.82 (dd, *J*=17.2, 5.3Hz, 1H), 4.20 (dd, *J*=15.2, 5.5Hz, 1H), 4.67 (t, *J*=5.5Hz, 1H), 7.08 (m, 2H), 7.17-7.39 (m, 8H), 8.00 (s, 1H), 8.18 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 36.75, 40.62, 43.99, 122.36 (d, ^1J=272.6Hz), 126.17, 126.28, 126.55, 127.06, 127.29, 128.48, 128.69, 128.88, 132.77 (d, ^2J=34.6Hz), 133.52, 136.01, 140.97, 142.88, 143.39. IR ($CHCl_3$) ν 3378, 2256, 1279, 908, 733cm^{-1}. HRMS (ESI) m/z calcd for $C_{25}H_{19}F_6NO_2S$ $(M+Na)^+$ 534.0933, found 534.0928.


8

Racemic and chiral cyclopropanes **8** are known compounds and were prepared according to the following reference.

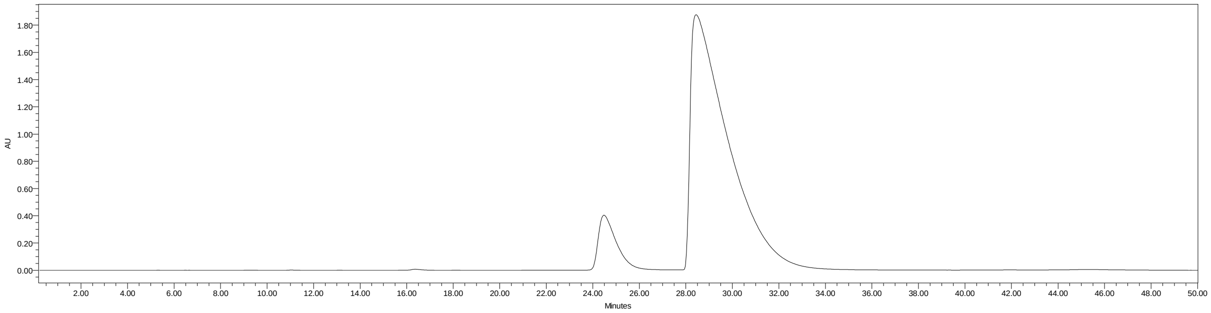
S. Chuprakov, S. W. Kwok, L. Zhang, L. Lercher and V. V. Fokin, *J. Am. Chem. Soc.*, 2009, **131**, 18034.

Racemic **8**:



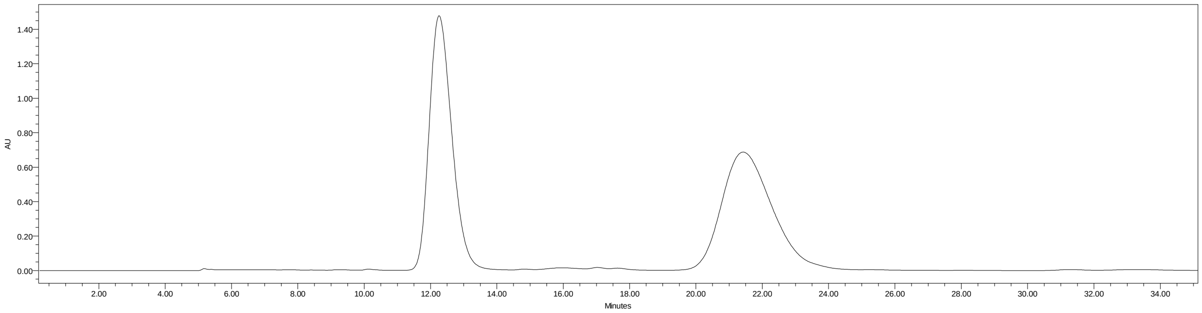
	Retention Time	Area	% Area	Height
1	23.382	16286193	49.97	272843
2	28.957	16304775	50.03	193596

Chiral **8** $[\alpha]_D^{20}$ =+130, (c=1, MeOH):



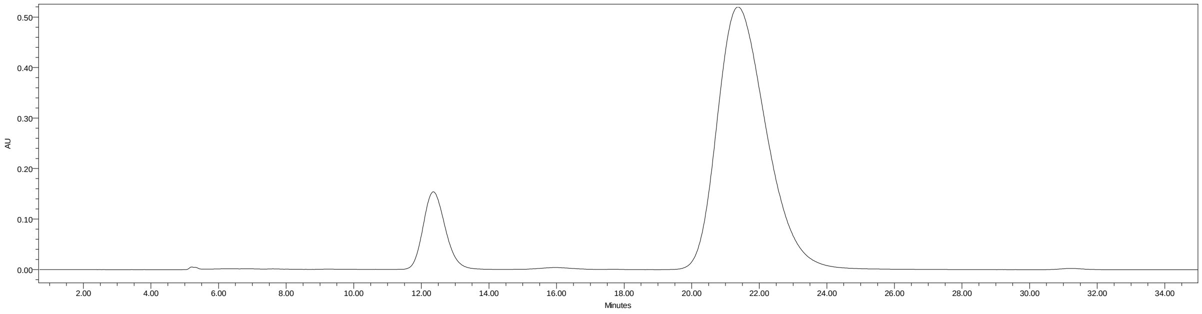
	Retention Time	Area	% Area	Height
1	24.479	21520024	9.49	402980
2	28.442	205127815	90.51	1863761

Racemic **16a**:

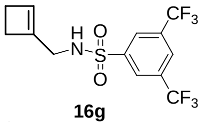


	Retention Time	Area	% Area	Height
1	12.257	69966637	49.77	1476051
2	21.423	70602059	50.23	680665

Chiral **16a**:

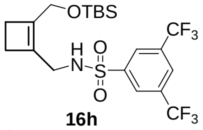


	Retention Time	Area	% Area	Height
1	12.354	5939471	10.21	143624
2	21.370	52255960	89.79	519707



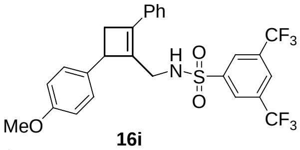
16g

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.28 (m, 4H), 3.69 (m, 2H), 4.80 (t, *J*=5.5Hz, 1H), 5.79 (m, 1H), 8.08 (s, 1H), 8.33 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 26.77, 29.74, 43.30, 122.44 (d, ^{1}*J*=273.3Hz), 126.14, 127.42, 131.67, 132.92 (d, ^{2}*J*=34.6Hz), 142.72, 143.27 . IR ($CHCl_3$) ν 3303, 2929, 2258, 1278, 1142, 905, 730cm^{-1}. HRMS (ESI) m/z calcd for $C_{13}H_{11}F_6NO_2S$ (M+Na)$^+$ 382.0307, found 382.0308.



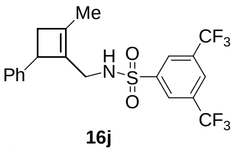
16h

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.15 (s, 6H), 0.92 (s, 9H), 2.09 (d, *J*=19Hz, 4H), 3.68 (br s, 2H), 4.01 (br s, 2H), 6.74 (m, 1H), 8.04 (s, 1H), 8.36 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ -5.57, 18.56, 25.91, 26.49, 27.53, 42.12, 62.00, 125.73, 127.29, 132.49, 132.83, 134.79, 141.00, 143.73. IR ($CHCl_3$) ν 2367, 2331, 1724, 1280, 908, 734cm^{-1}.



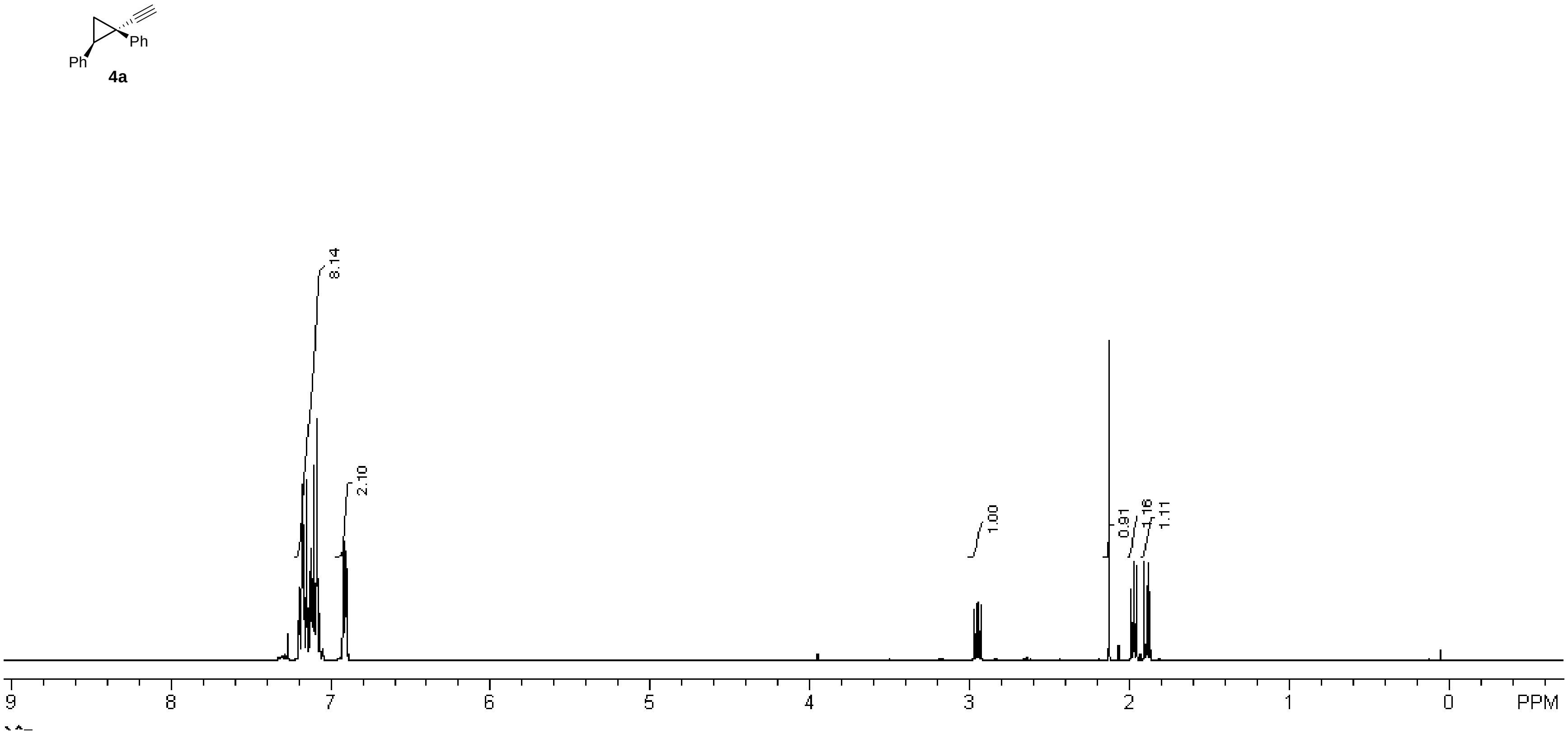
16i

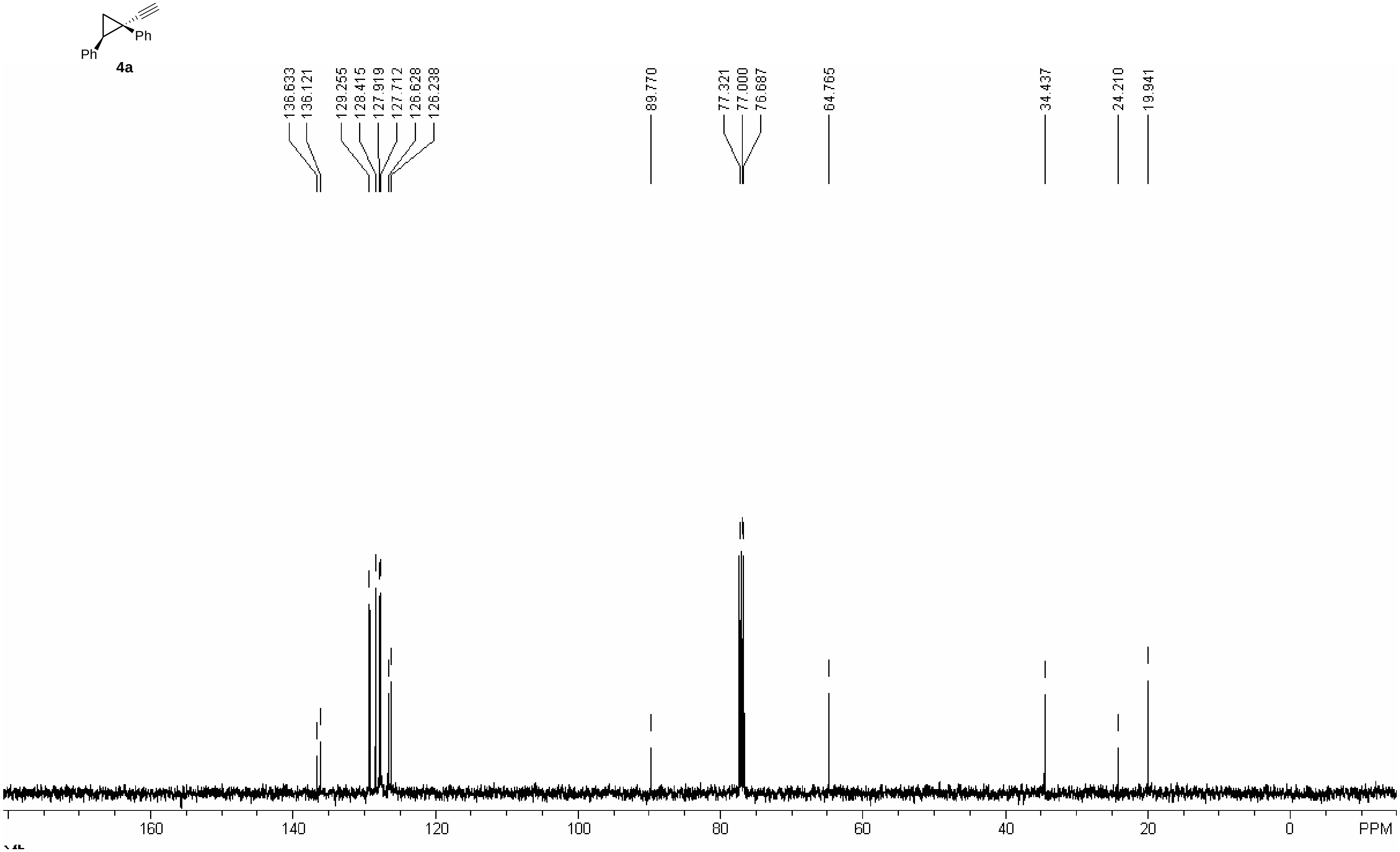
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.43 (d, *J*=13.1Hz, 1H), 2.94 (dd, *J*=13.1, 4.9Hz, 1H), 3.50 (d, *J*=4.1Hz, 1H), 3.77 (s, 3H), 3.82 (m, 1H), 4.20 (dd, *J*=15.2, 5.5Hz, 1H), 4.88 (t, *J*=5.5Hz, 1H), 6.78 (d, *J*=8.6Hz, 2H), 7.00 (d, *J*=8.7Hz, 2H), 7.24-7.37 (m, 5H), 8.00 (s, 1H), 8.20 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 37.02, 40.47, 43.20, 55.16, 114.23, 126.15, 126.25, 127.29, 127.35 (d, ^{1}*J*=240.3Hz), 127.56, 128.38, 132.54, 132.82, 132.88, 136.18, 133.57, 142.89, 143.09, 158.57. IR ($CHCl_3$) ν 3278, 2839, 2256, 1358, 729cm^{-1}. HRMS (ESI) m/z calcd for $C_{26}H_{21}F_6NO_3S$ (M+Na)$^+$ 564.1039, found 564.1041.



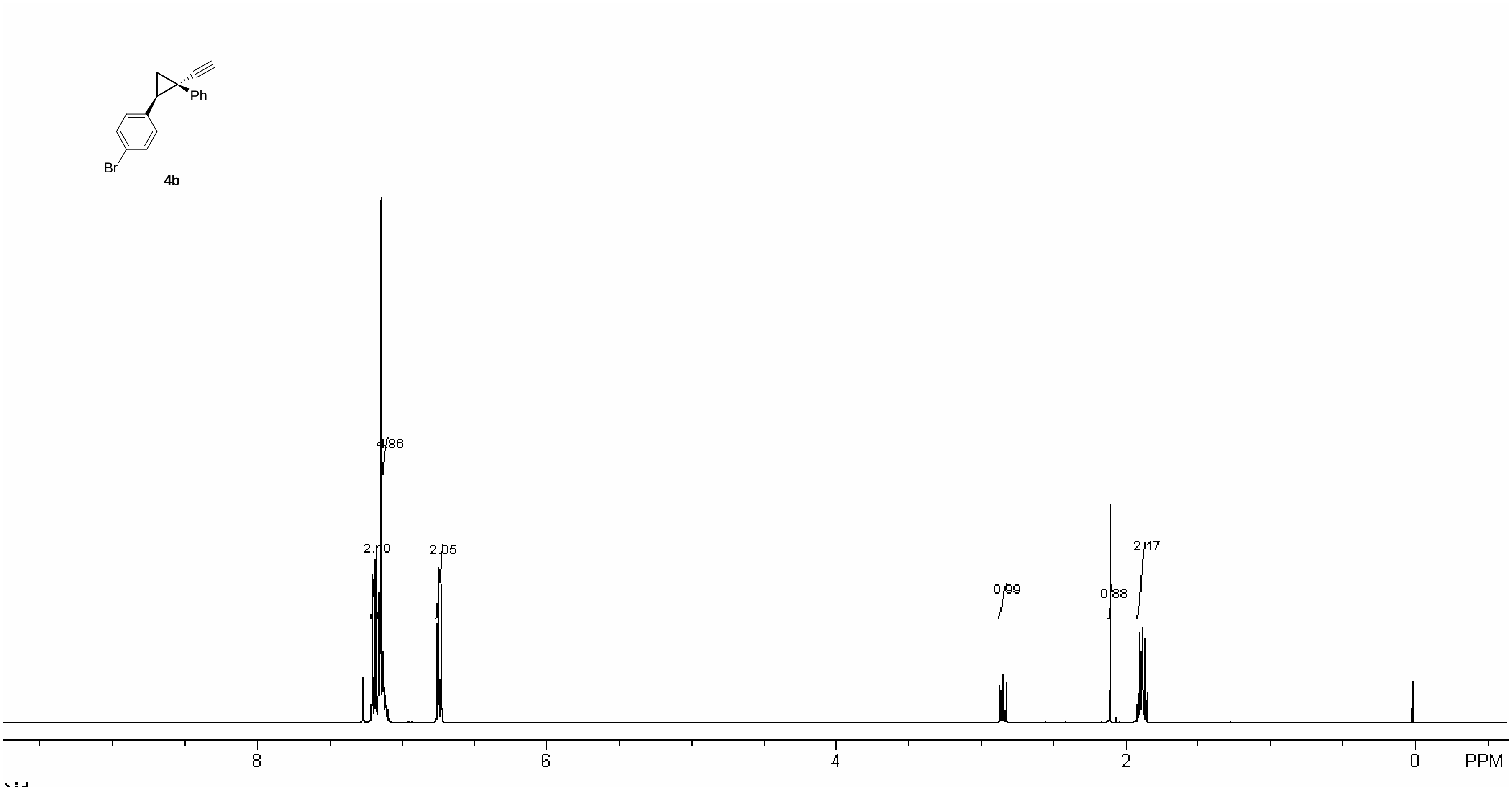
16j

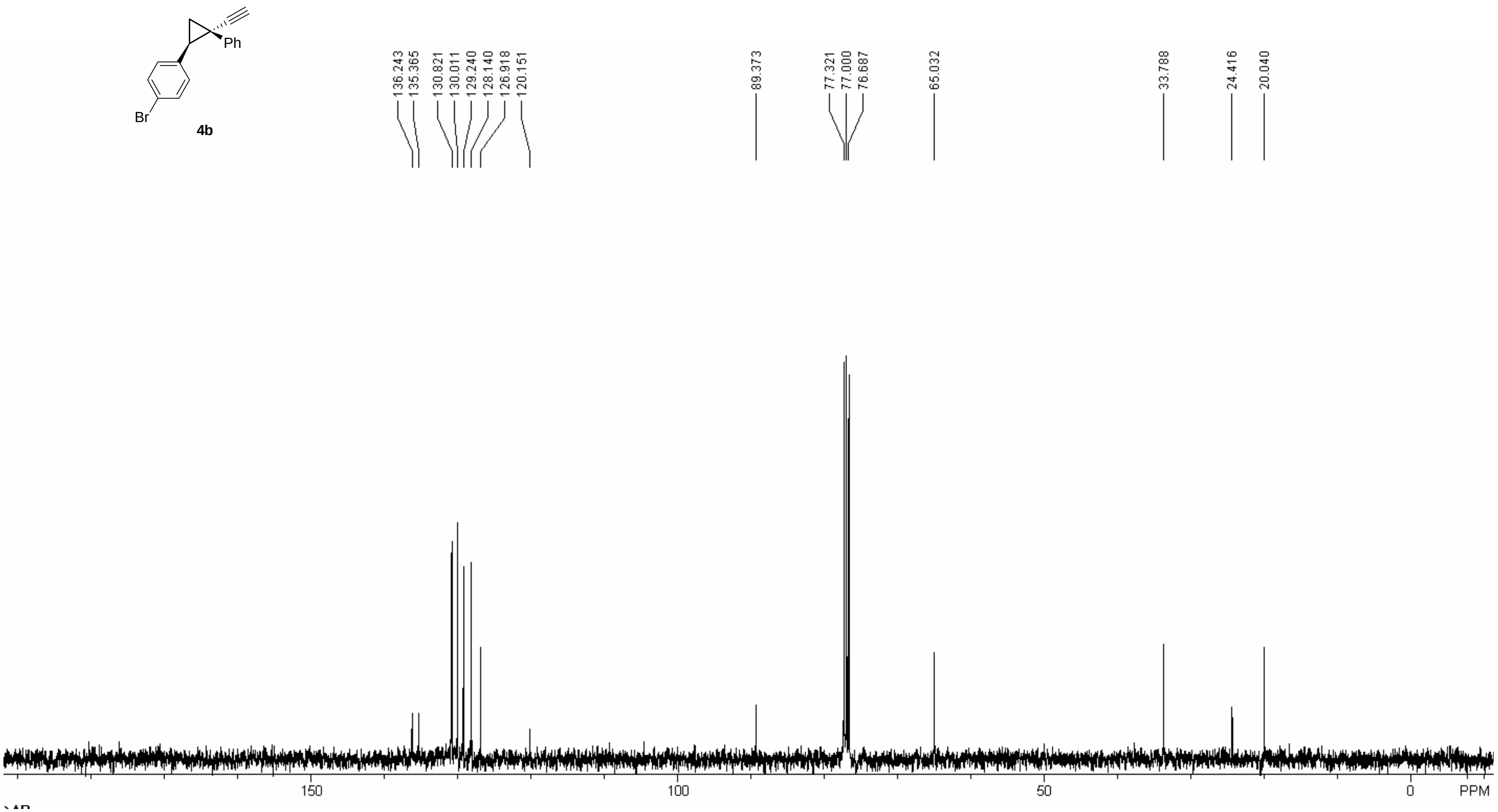
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.74 (s, 3H), 2.12 (d, *J*=13.5Hz, 1H), 2.58 (dd, *J*=17.7, 4.5Hz, 1H), 3.35 (s, 1H), 3.53 (dd, *J*=20.5, 5.5Hz, 1H), 3.79 (dd, *J*=14.8, 5.3Hz, 1H), 4.52 (t, *J*=5.6Hz, 1H), 6.99 (m, 2H), 7.14-7.26 (m, 3H), 8.04 (s, 1H), 8.21 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 13.92, 39.98, 40.41, 44.48, 122.44 (d, ^{1}*J*=274.1Hz), 126.06, 126.31, 126.74, 127.24, 128.71, 132.75 (d, ^{2}*J*=34.6Hz), 136.23, 141.43, 143.22, 144.10. IR ($CHCl_3$) ν 3296, 2916, 1359, 1278, 1141, 906, 712cm^{-1}. HRMS (ESI) m/z calcd for $C_{20}H_{17}F_6NO_2S$ (M+Na)$^+$472.0776, found 472.0761.


4a


4a

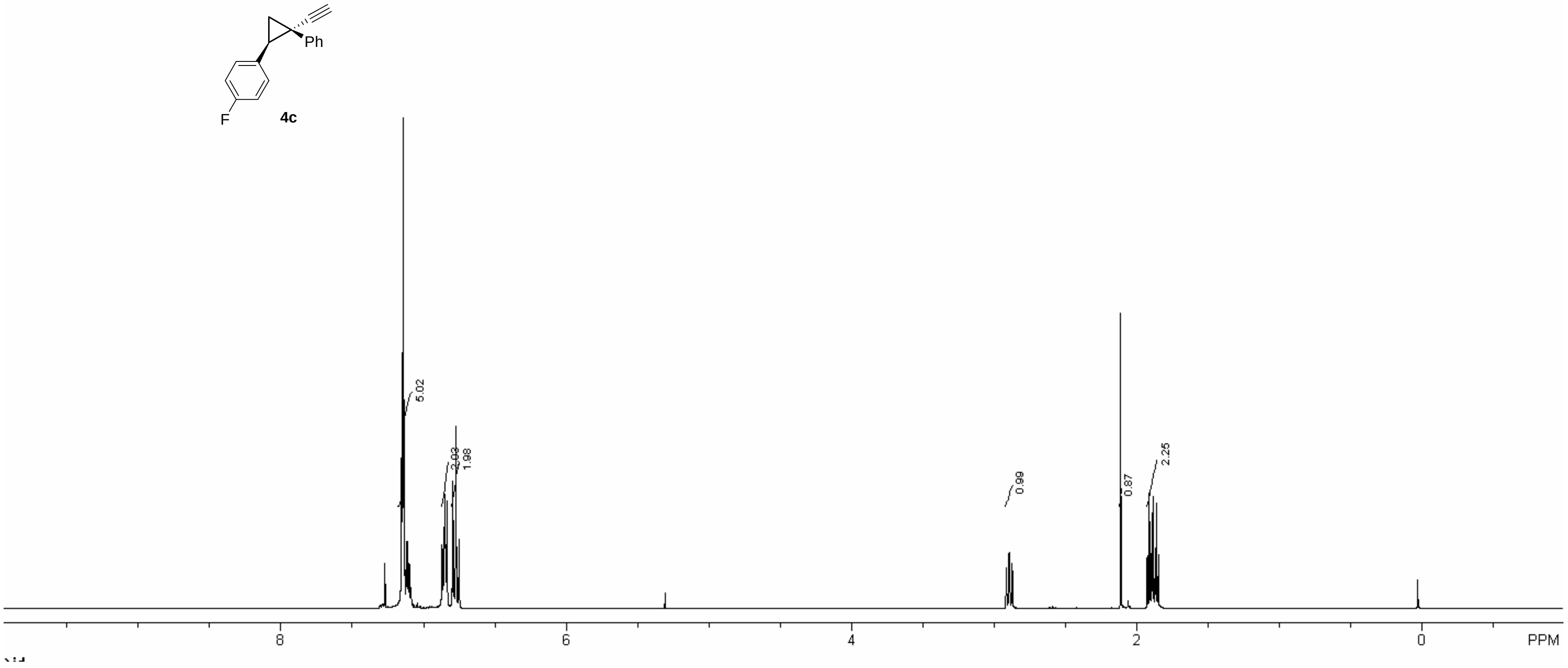
Ph
Ph
136.633
136.121
129.255
128.415
127.919
127.712
126.628
126.238
89.770
77.321
77.000
76.687
64.765
34.437
24.210
19.941
160
140
120
100
80
60
40
20
0
PPM


Ph
Br
4b
4.86
2.10
2.05
0.99
0.88
2.17
8
6
4
2
0
PPM



Br
Ph
136.243
135.365
130.821
130.011
129.240
128.140
126.918
120.151
89.373
77.321
77.000
76.687
65.032
33.788
24.416
20.040
150
100
50
0
PPM

4b



Ph
F
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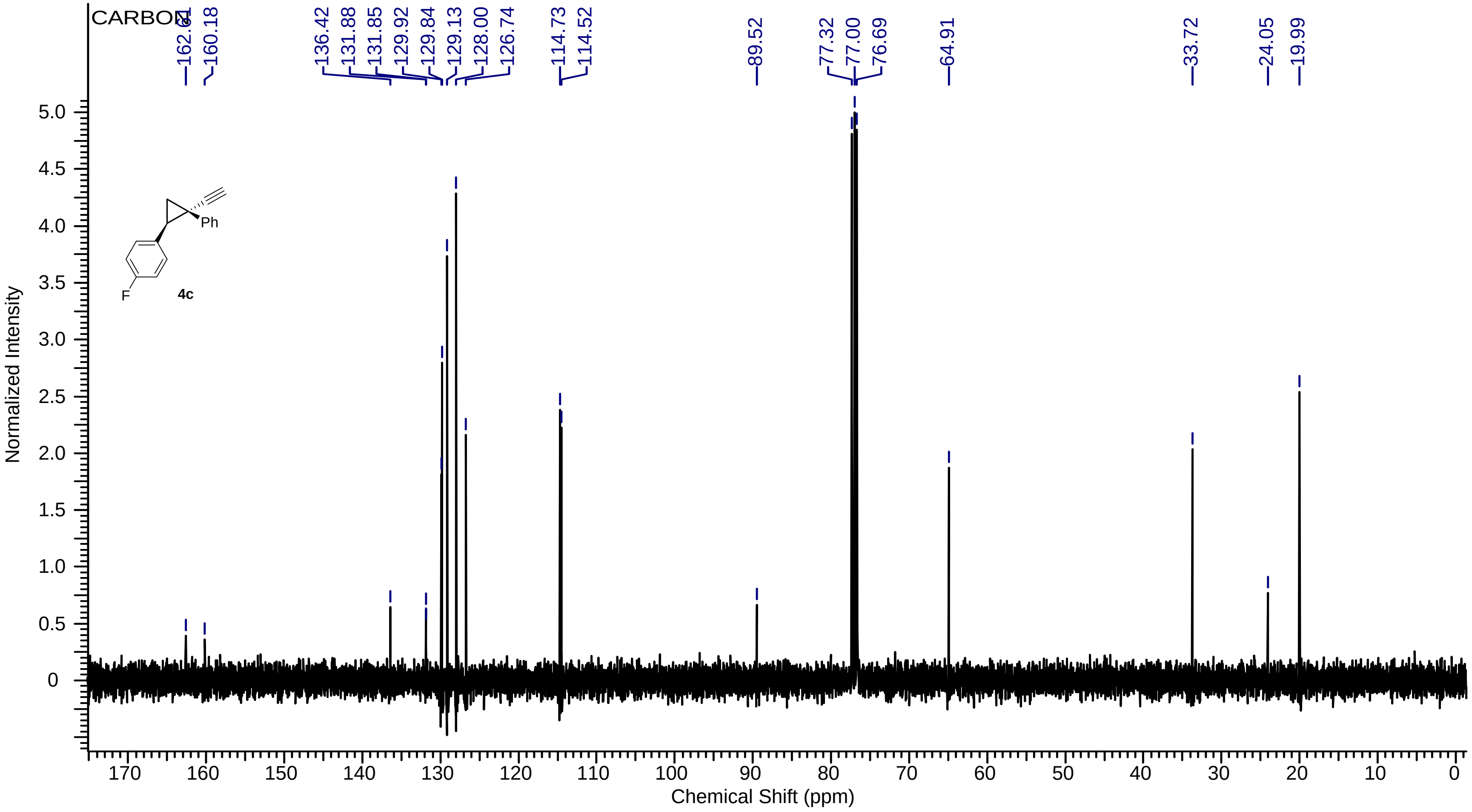
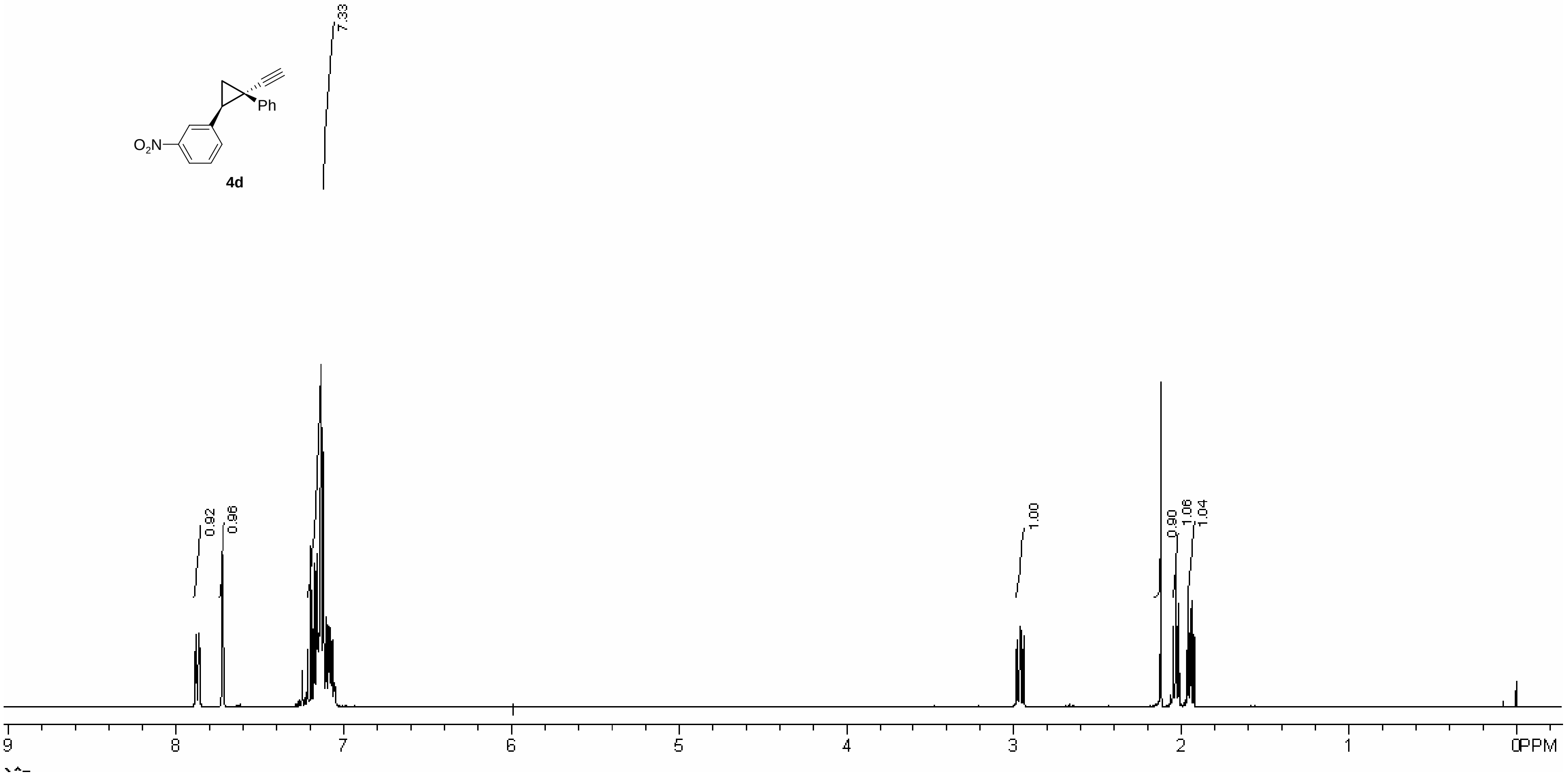
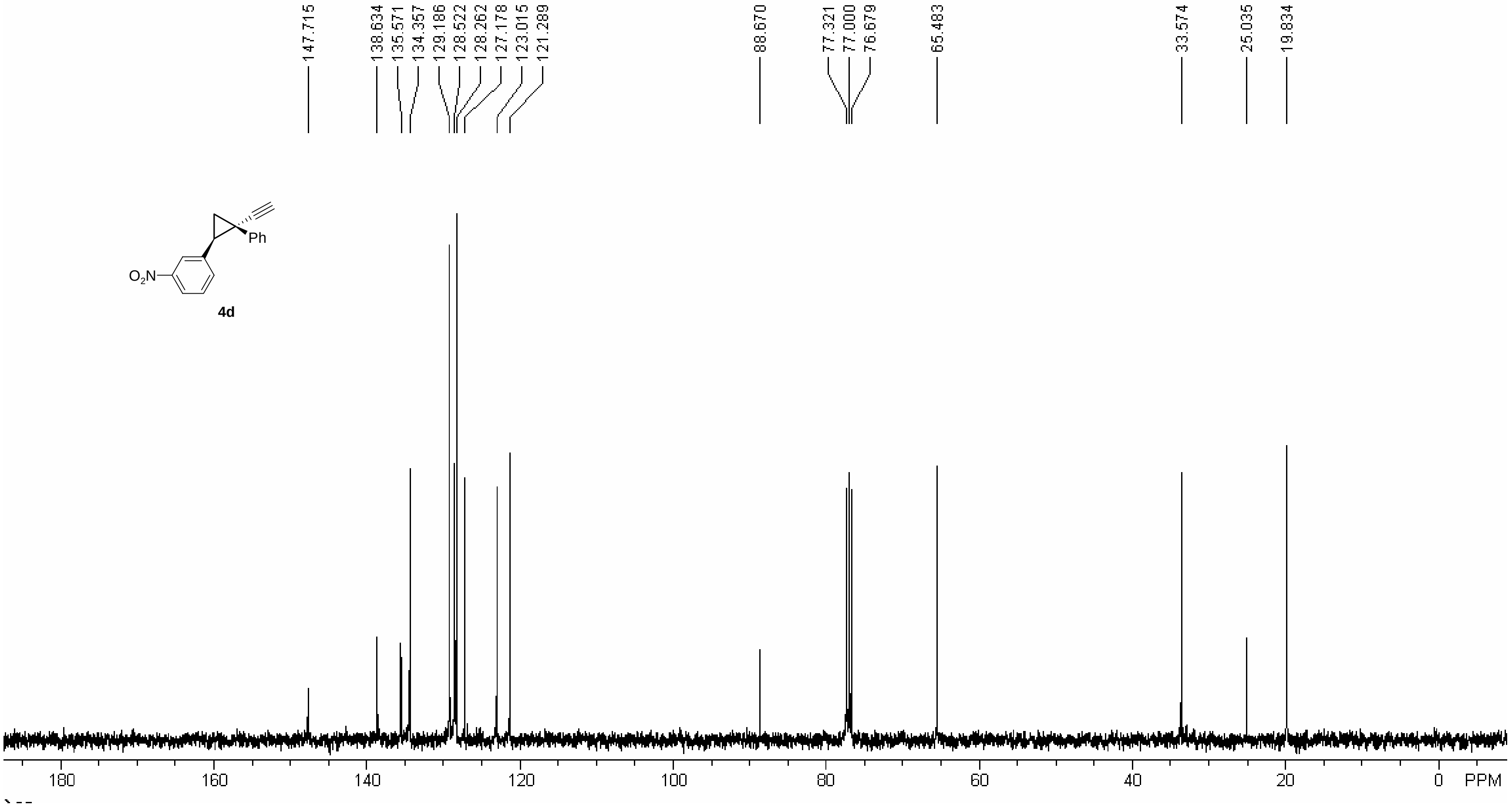
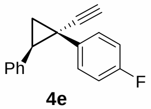
5.02
2.03
1.98
0.99
0.87
2.25
8
6
4
2
0
PPM

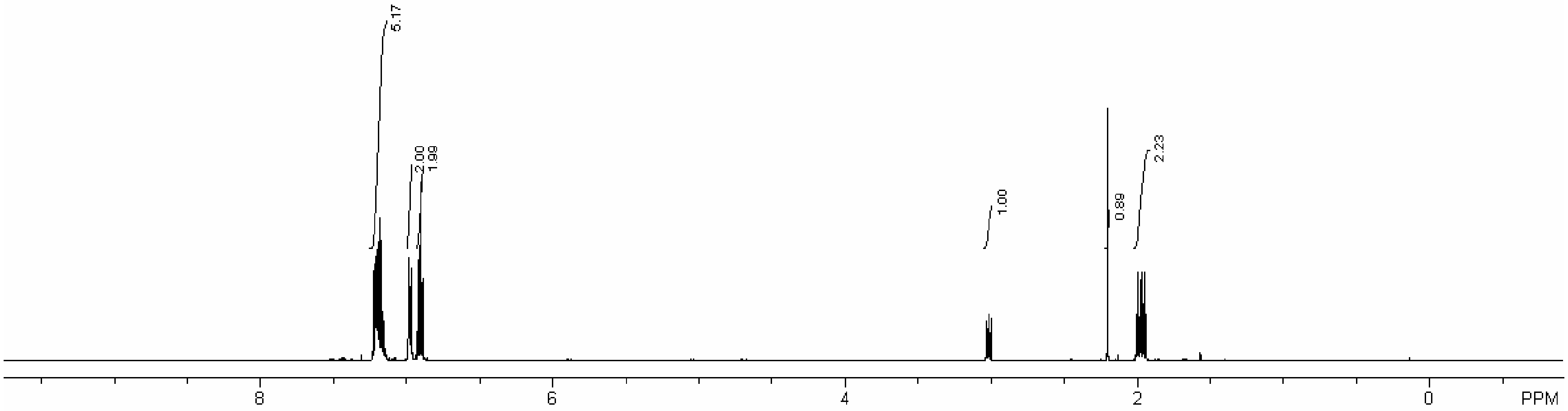

CARBON
162.61
160.18
136.42
131.88
131.85
129.92
129.84
129.13
128.00
126.74
114.73
114.52
89.52
77.32
77.00
76.69
64.91
33.72
24.05
19.99
Ph
F
4c
Normalized Intensity
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)


O$_2$N
Ph
4d
7.33
0.92
0.96
1.00
0.90
1.06
1.04
9
8
7
6
5
4
3
2
1
0PPM

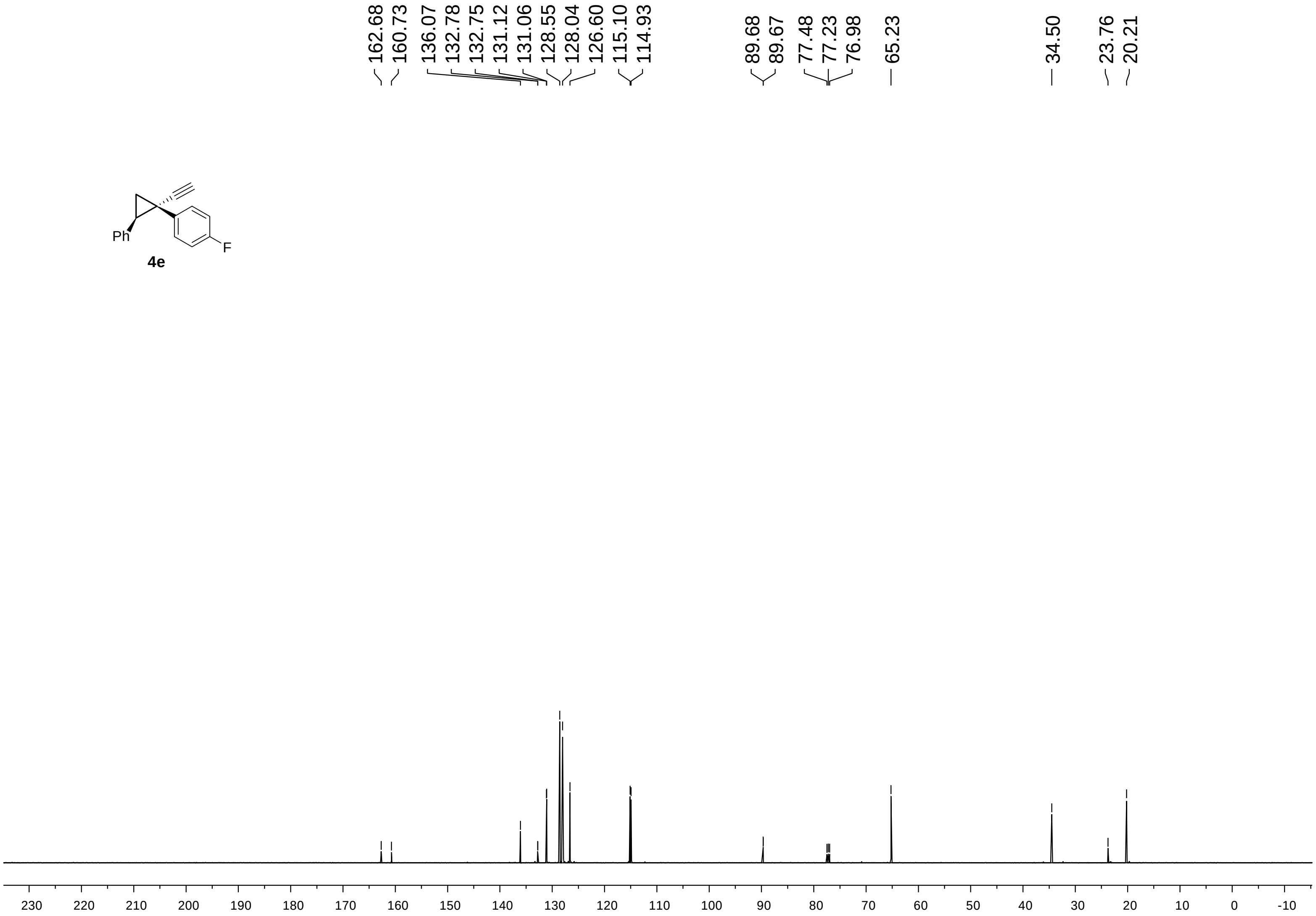

147.715
138.634
135.571
134.357
129.186
128.522
128.262
127.178
123.015
121.289
88.670
77.321
77.000
76.679
65.483
33.574
25.035
19.834
Ph
O2N
4d
180
160
140
120
100
80
60
40
20
0
PPM



4e



4e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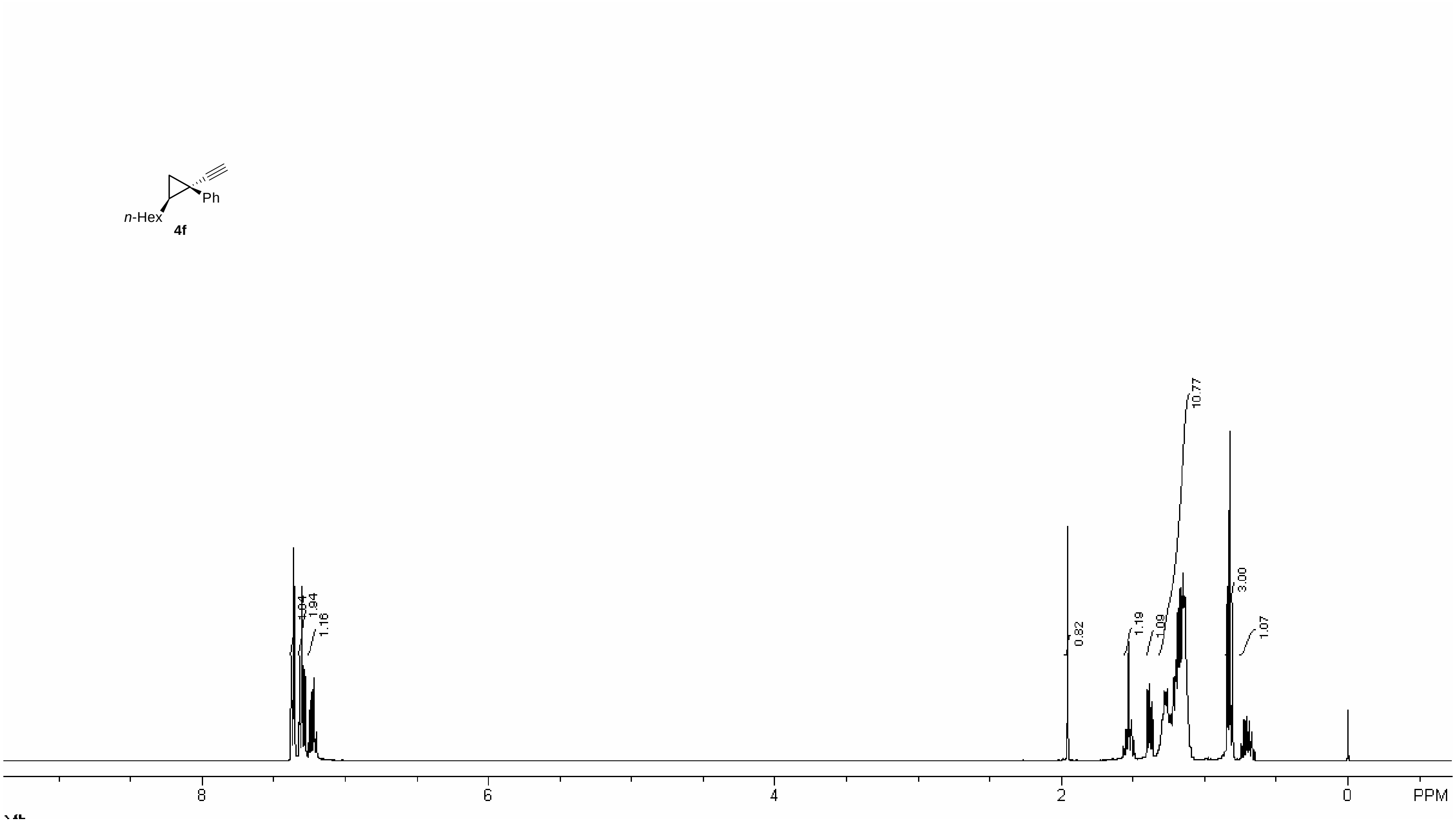
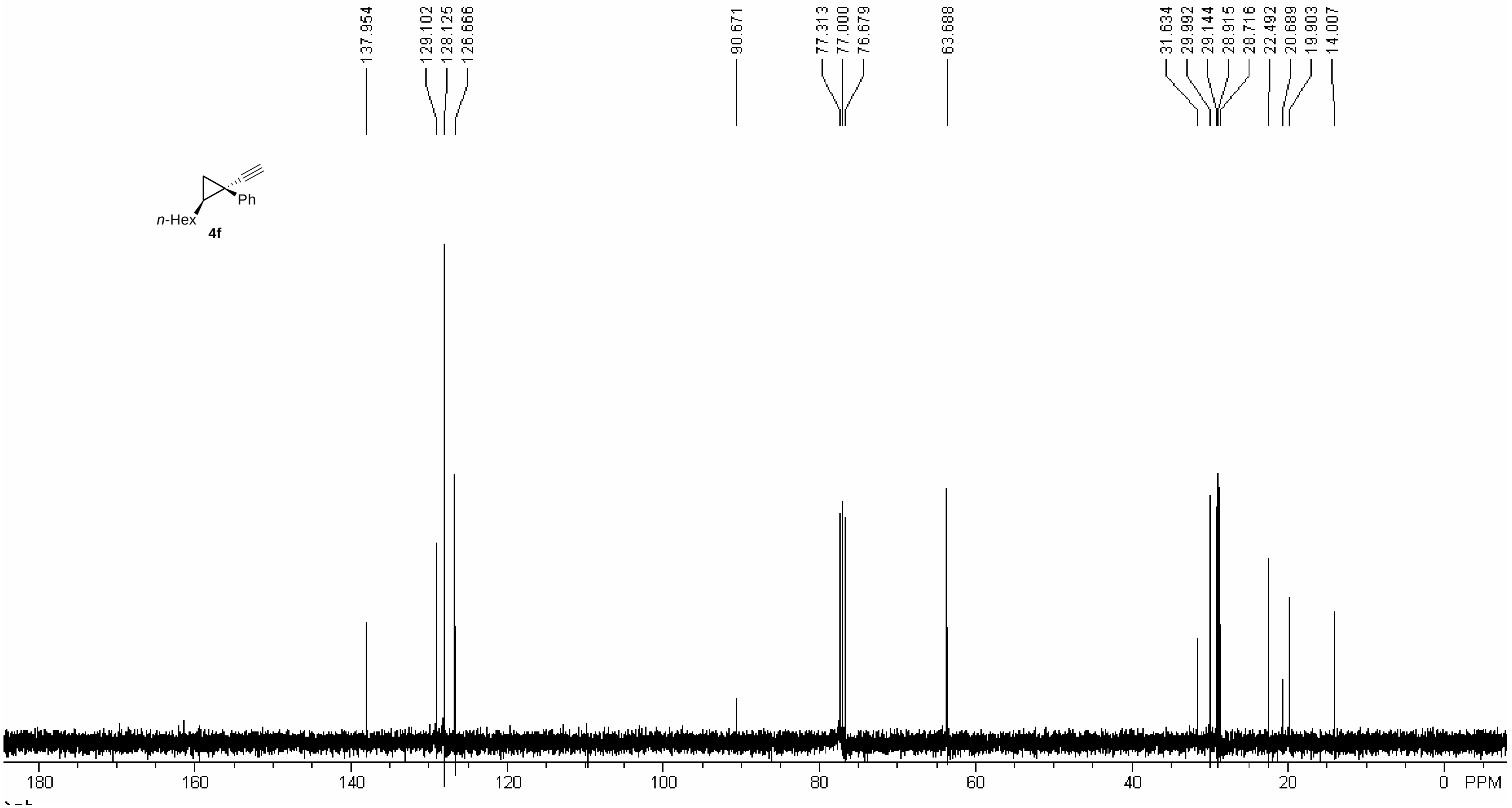
160.73
136.07
132.78
132.75
131.12
131.06
128.55
128.04
126.60
115.10
114.93
89.68
89.67
77.48
77.23
76.98
65.23
34.50
23.76
20.21
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


Ph
n-Hex
4f
1.04
1.94
1.16
0.82
1.19
1.09
10.77
3.00
1.07
8
6
4
2
0
PPM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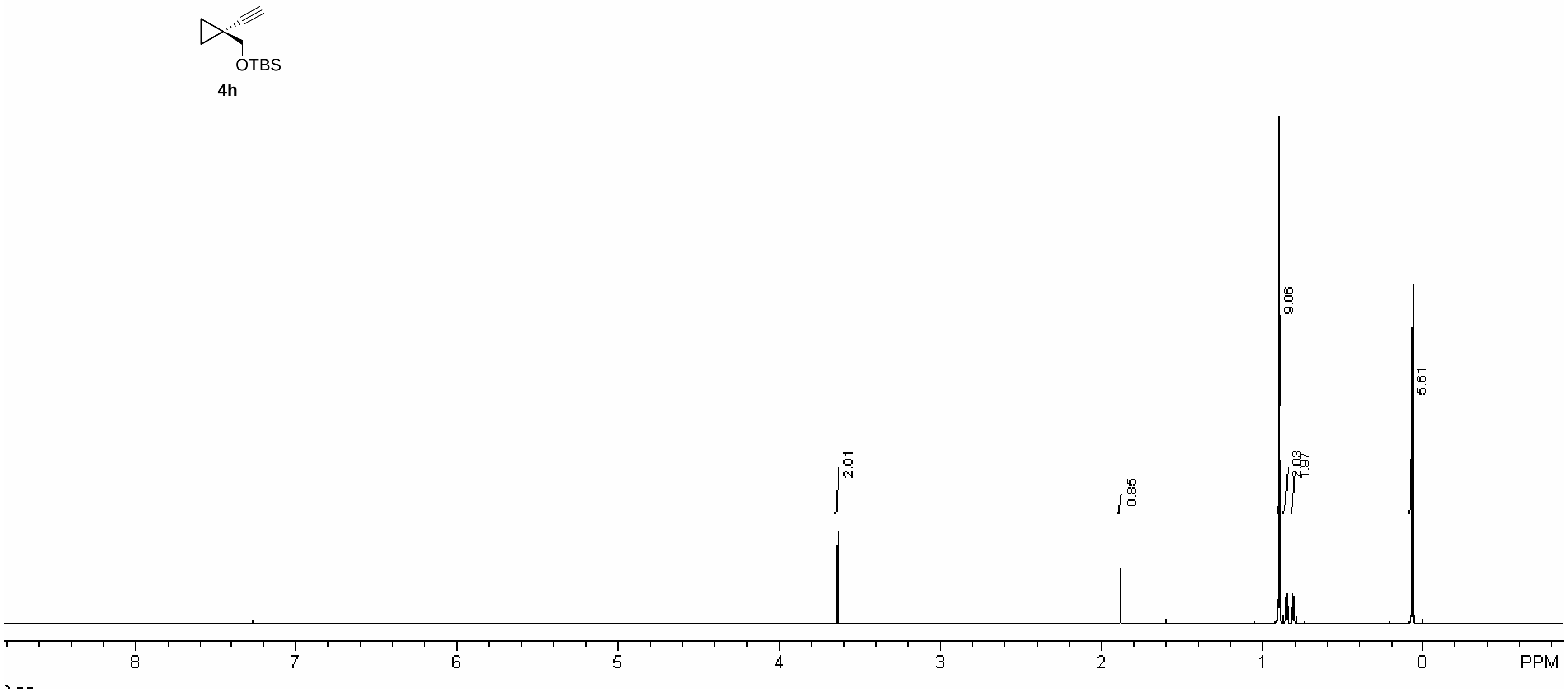
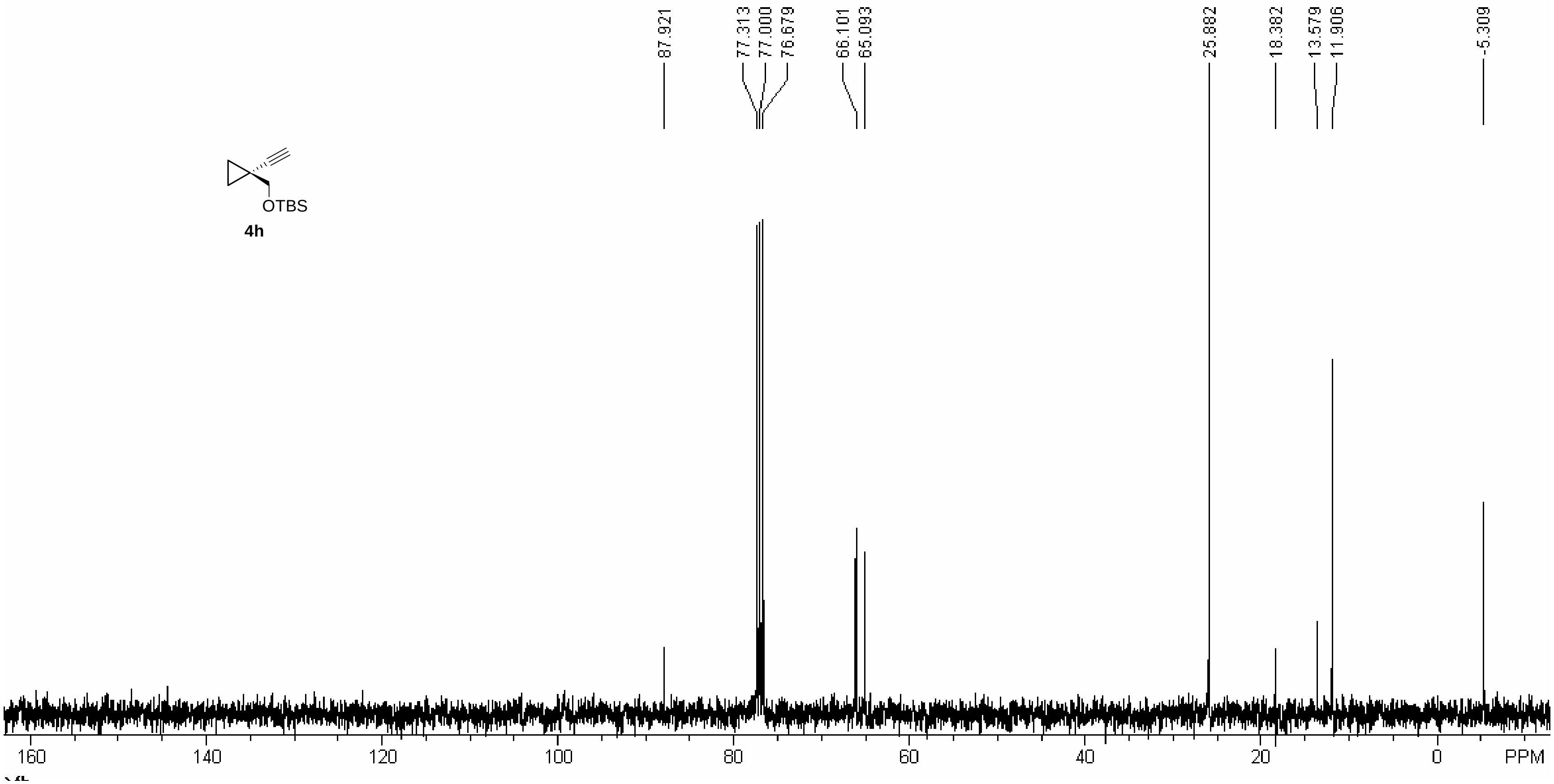
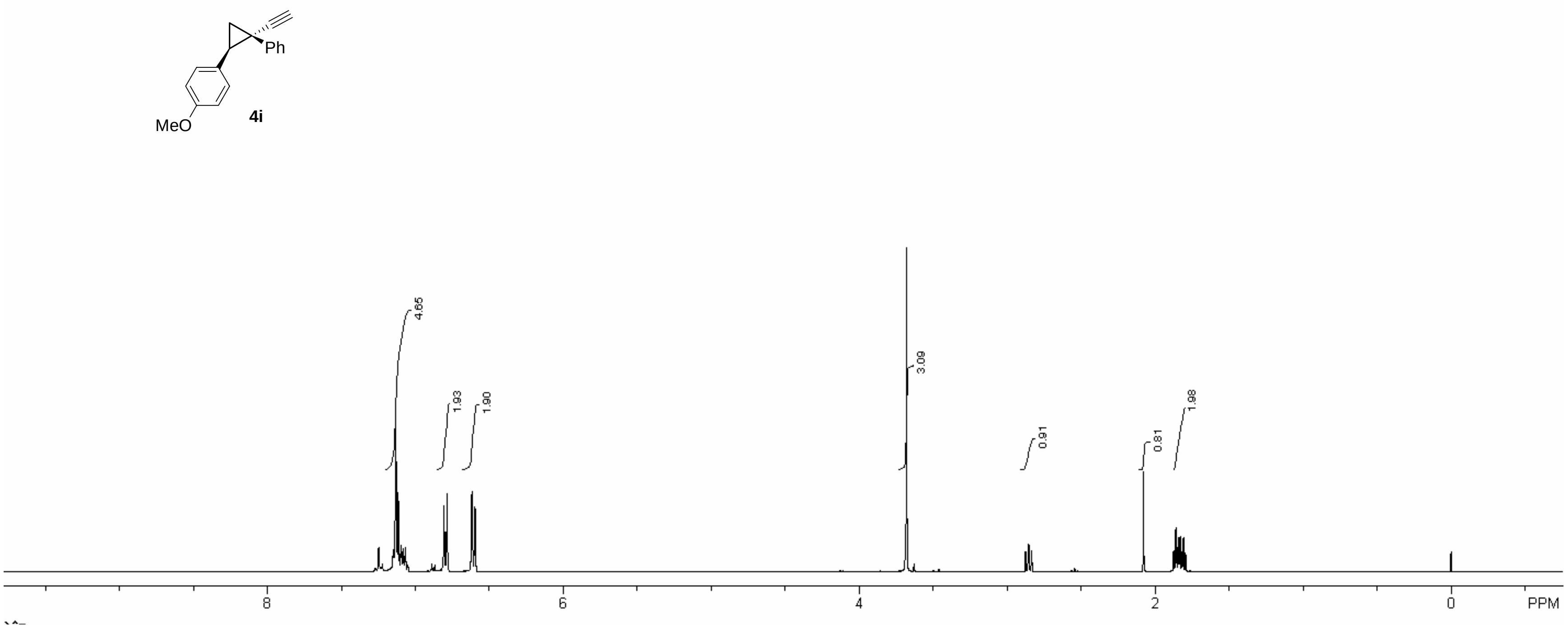
126.666
90.671
77.313
77.000
76.679
63.688
31.634
29.992
29.144
28.915
28.716
22.492
20.689
19.903
14.007
Ph
n-Hex
4f
180
160
140
120
100
80
60
40
20
0
PPM


4h


87.921
77.313
77.000
76.679
66.101
65.093
25.882
18.382
13.579
11.906
-5.309
OTBS
4h
160
140
120
100
80
60
40
20
0
PPM


Ph
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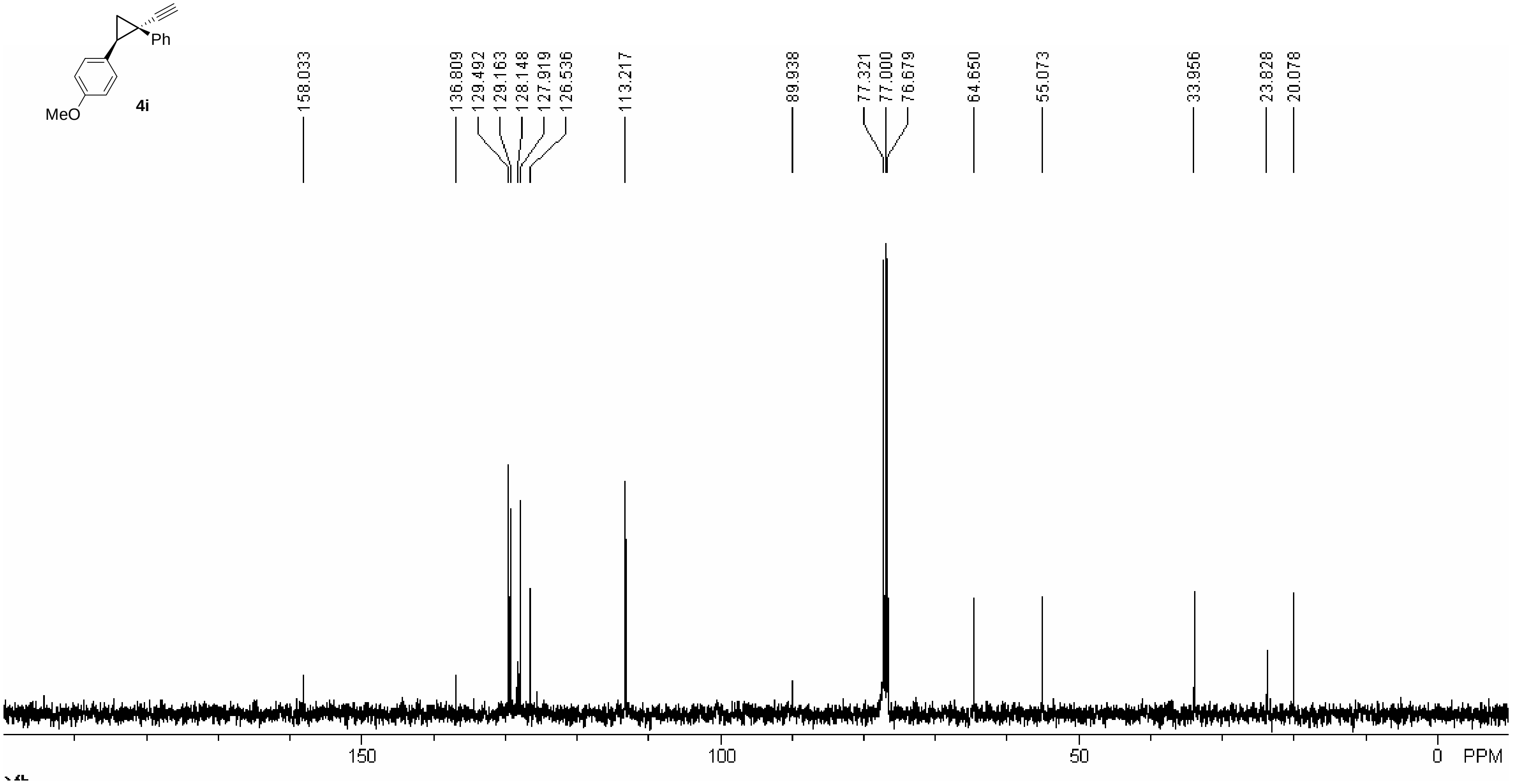
3.09
0.91
0.81
1.98
8
6
4
2
0
PPM



4i

MeO
Ph
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136.809
129.492
129.163
128.148
127.919
126.536
113.217
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76.679
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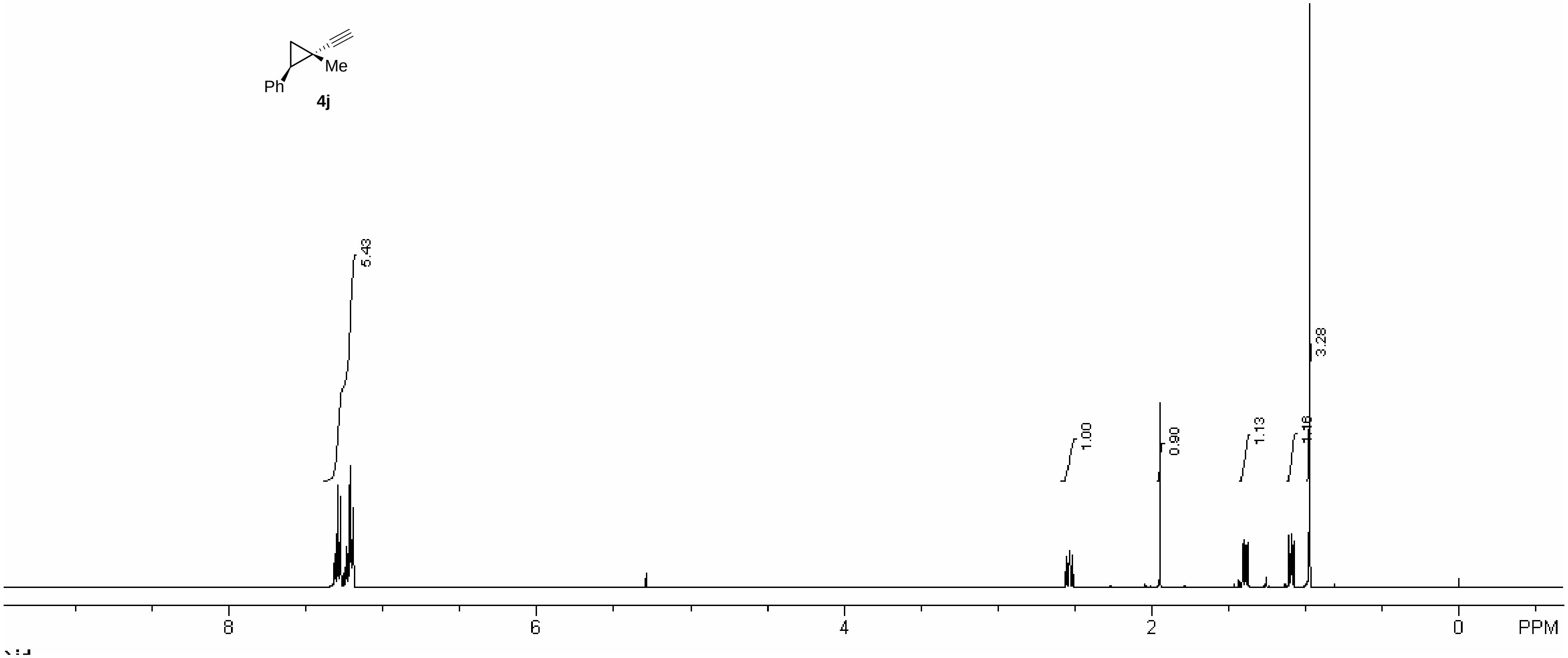
PPM



Ph
Me
4j
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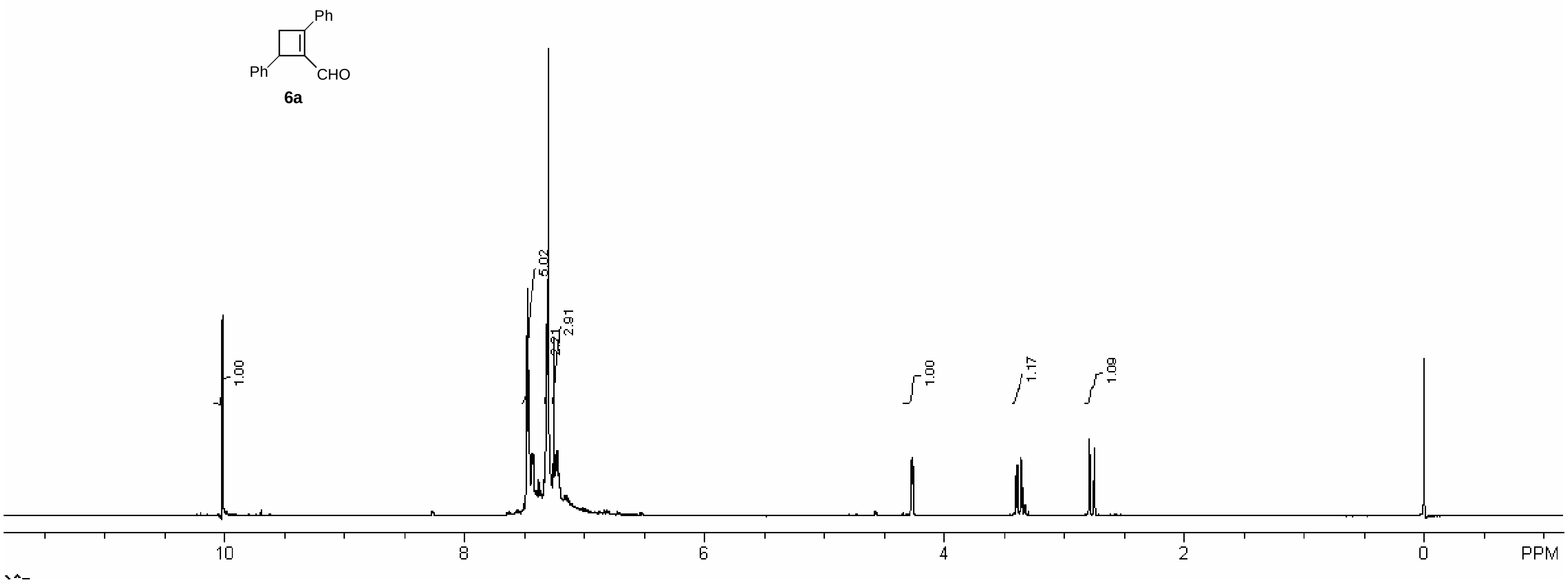
1.13
1.16
3.28
8
6
4
2
0
PPM


Ph
Ph
CHO
6a
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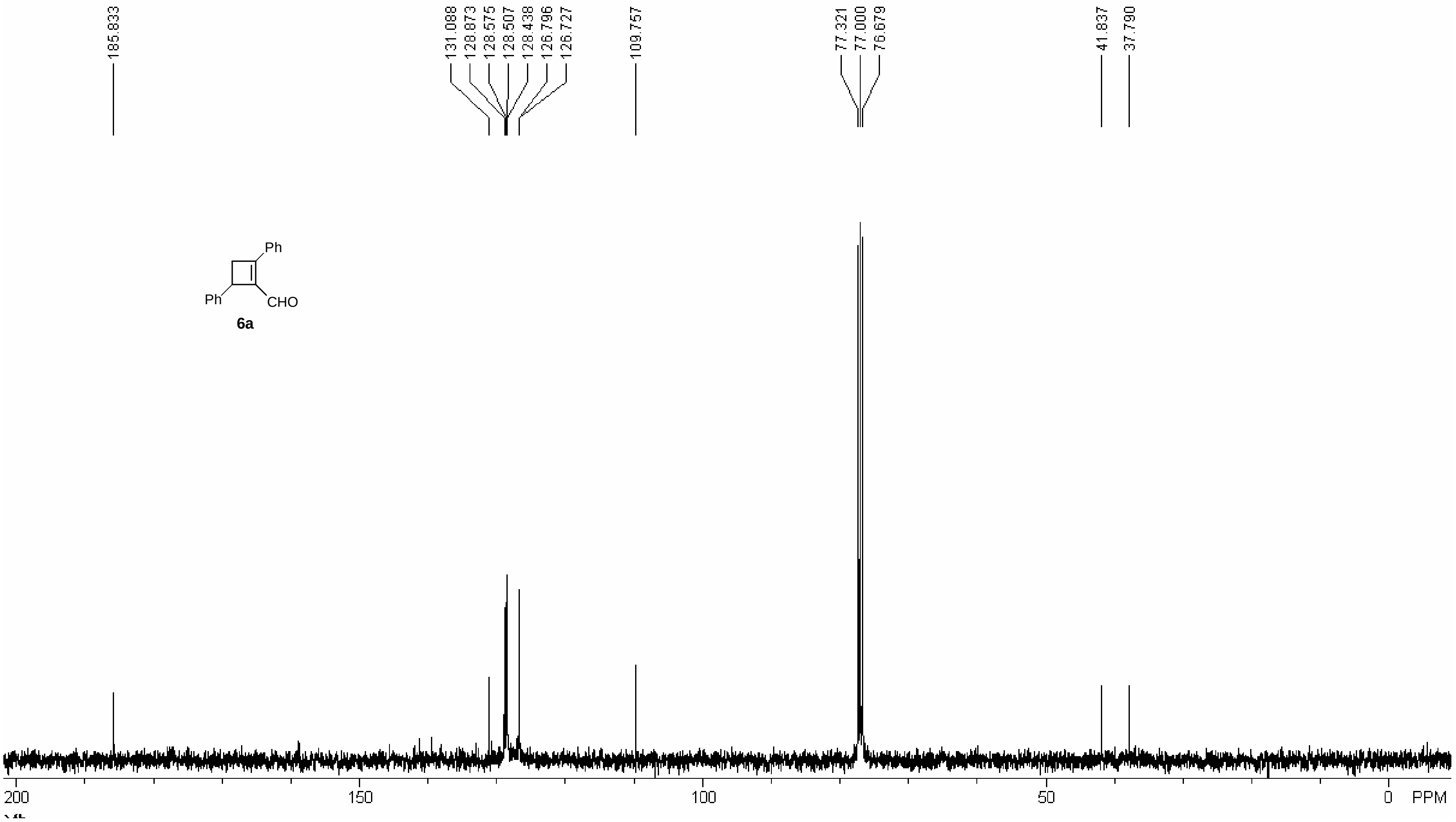
2.21
2.91
1.00
1.17
1.09
10
8
6
4
2
0
PPM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128.507
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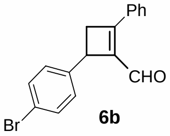
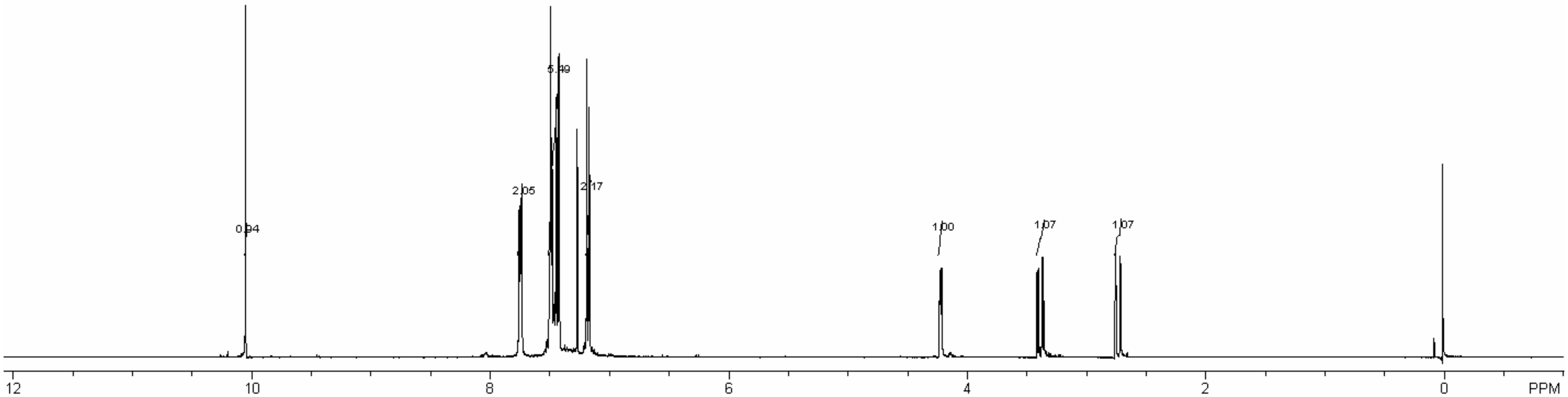
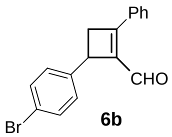
76.679
41.837
37.790
Ph
Ph
CHO
6a
200
150
100
50
0
PPM

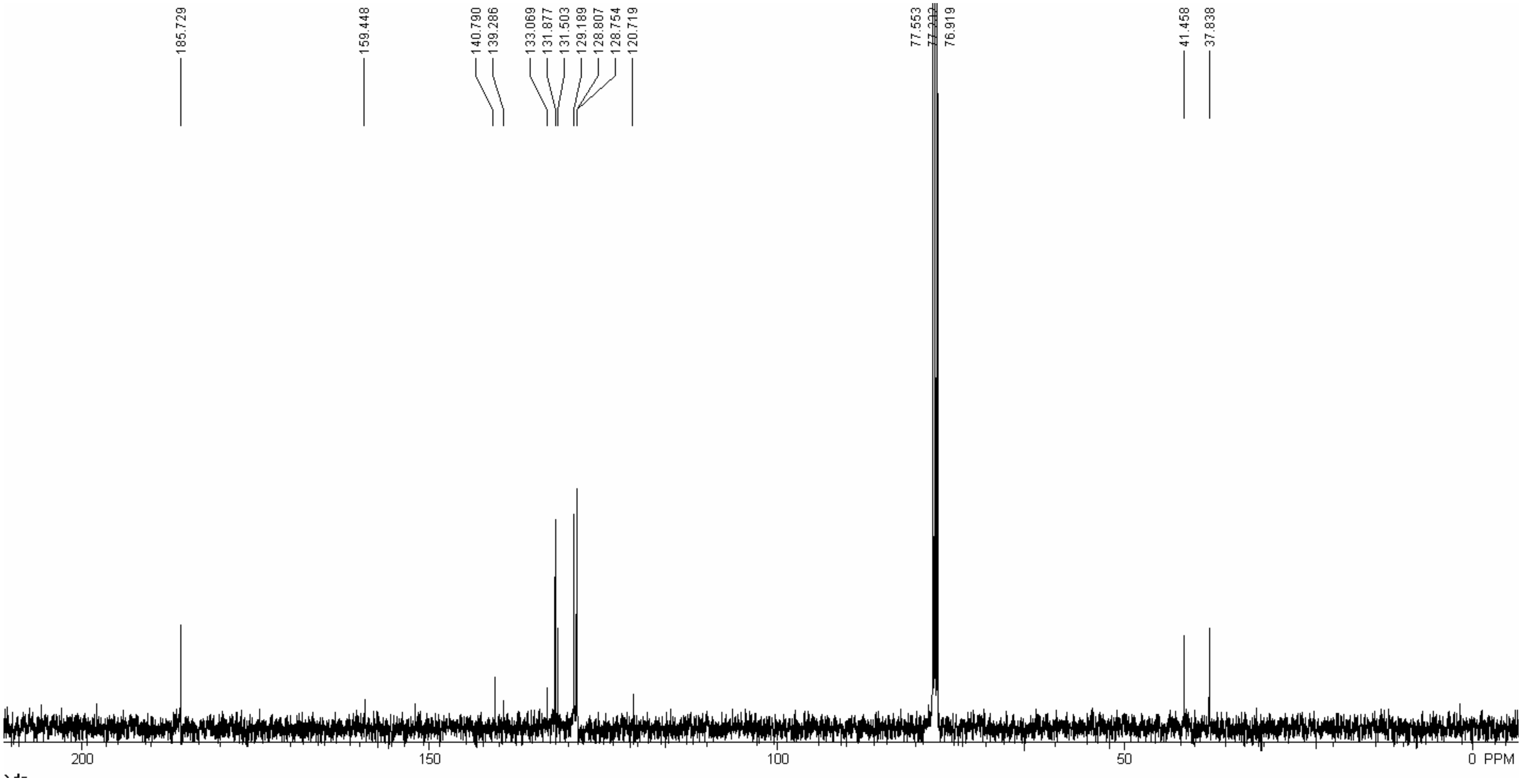


6b




Ph
CHO
Br

6b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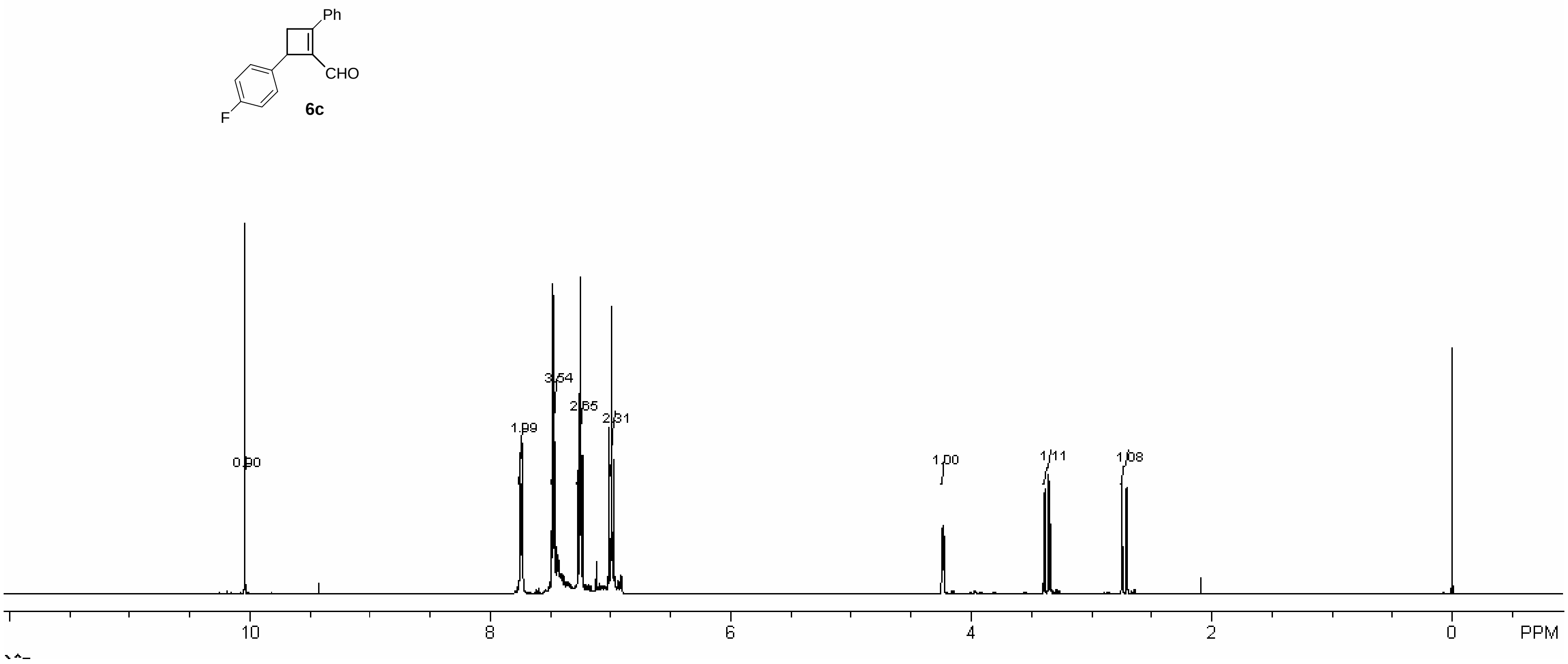
200
150
100
50
0 PPM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10
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6
4
2
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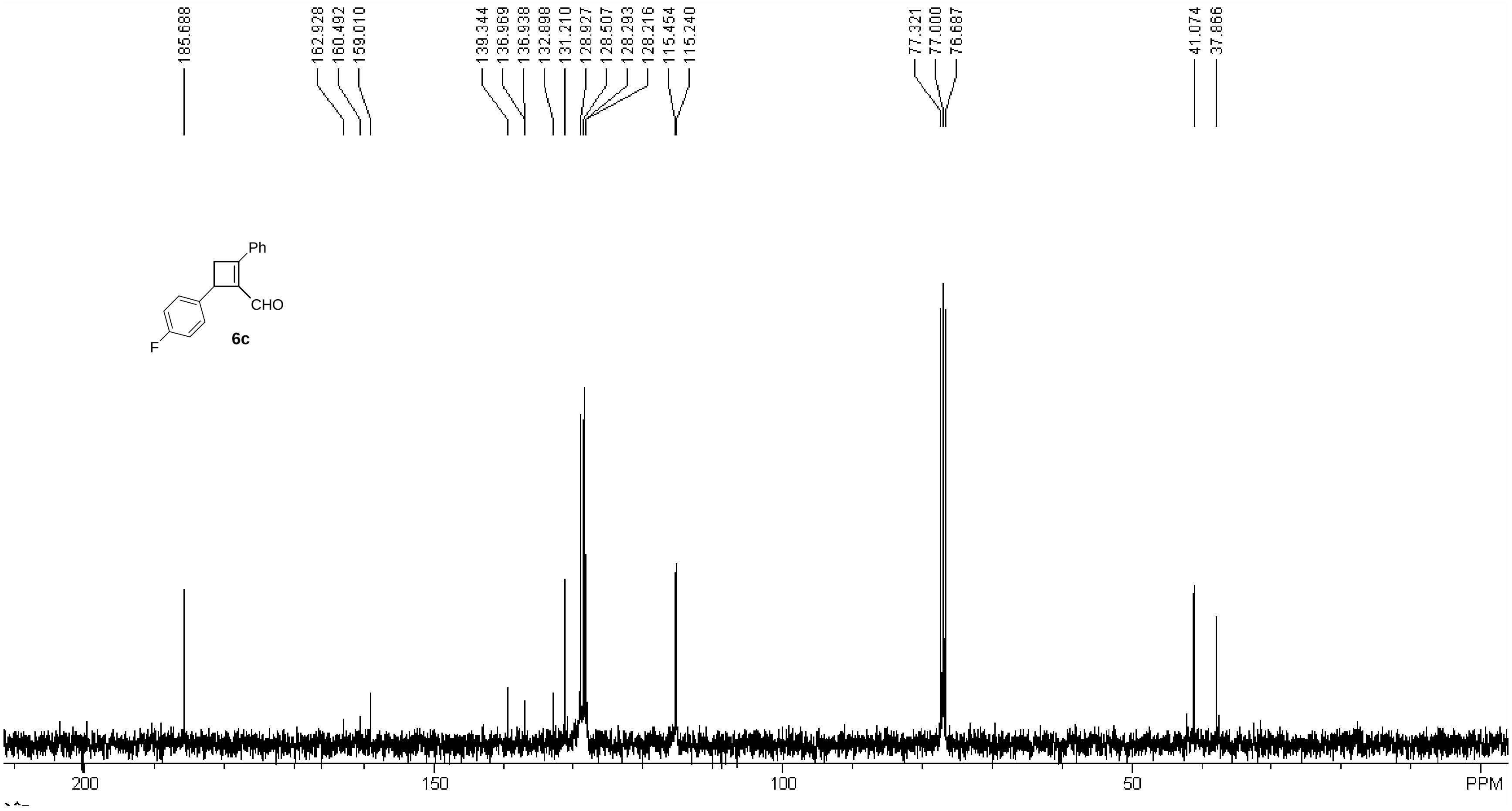
PPM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128.507
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6c
200
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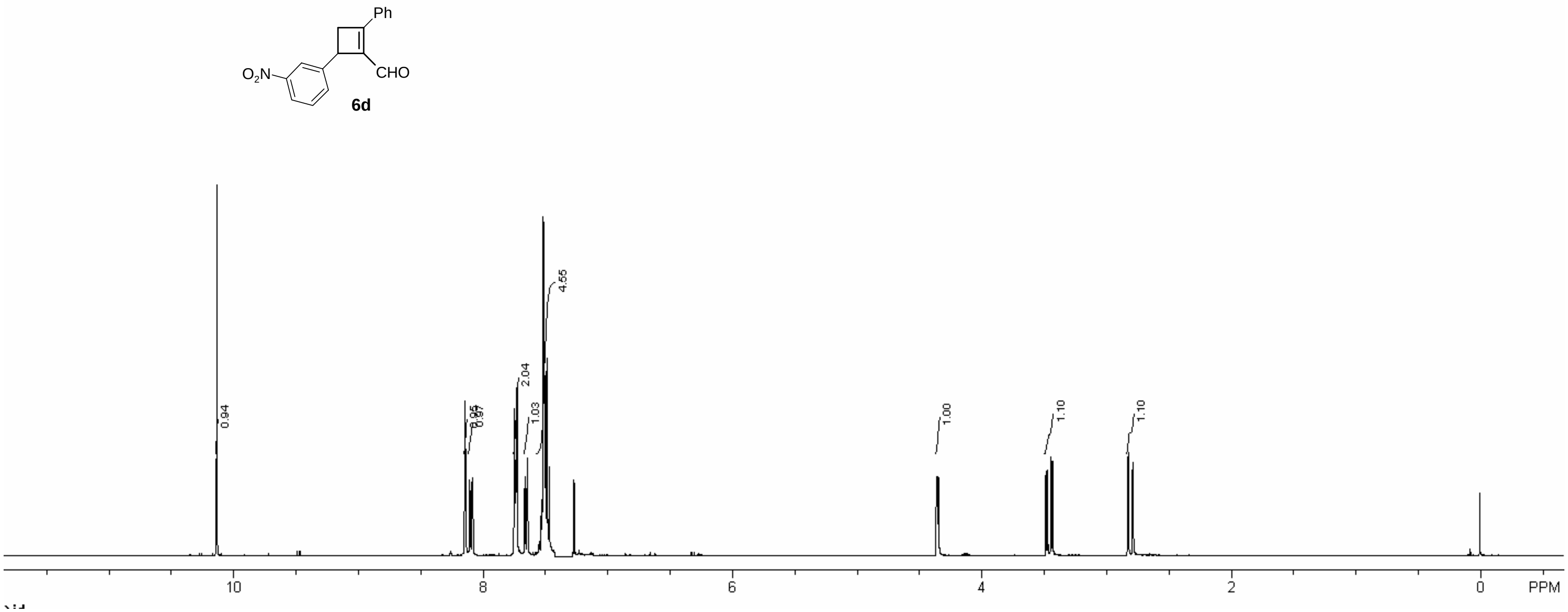
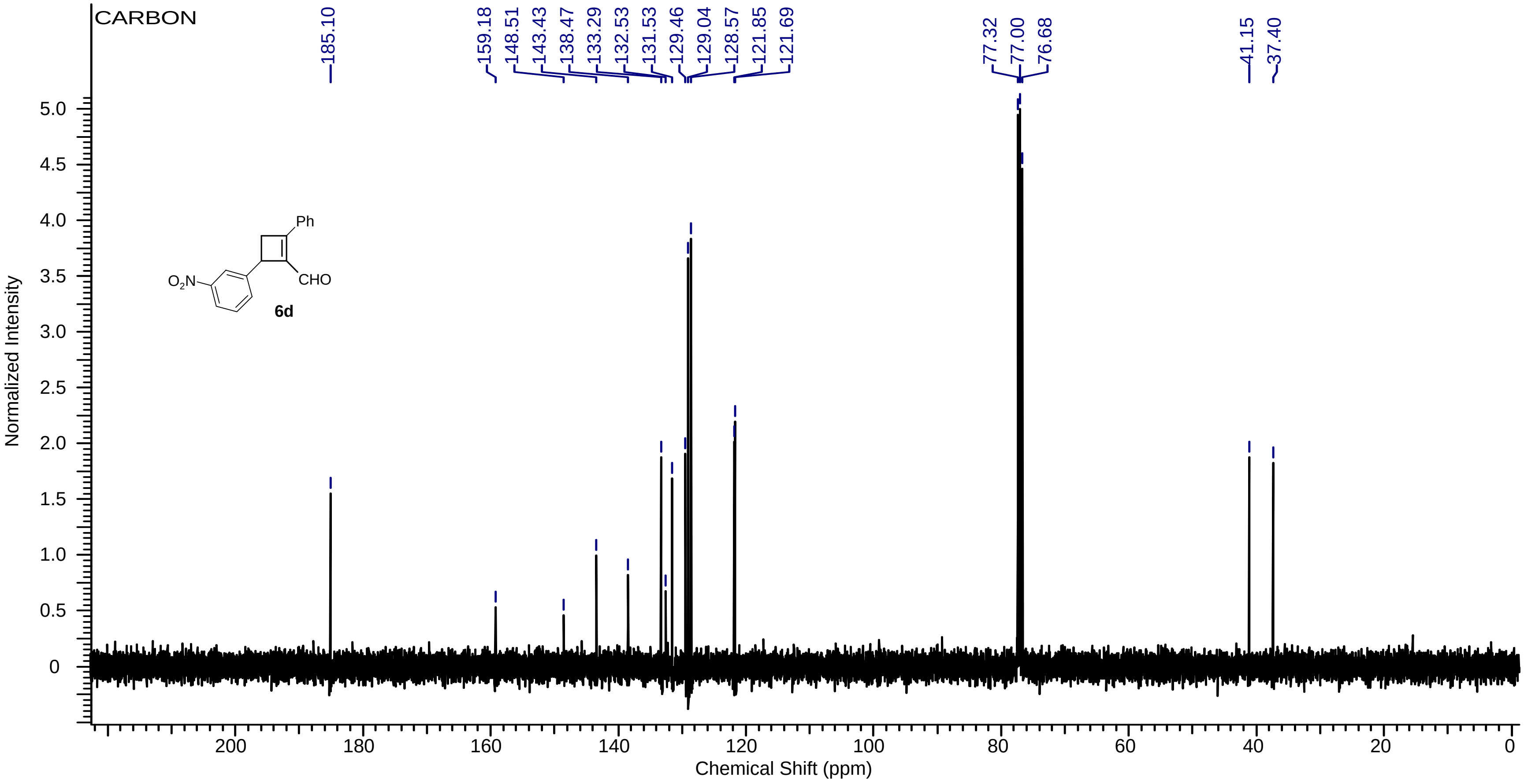
PPM



6d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132.53
131.53
129.46
129.04
128.57
121.85
121.69
77.32
77.00
76.68
41.15
37.40
Ph
O_2N
CHO
6d
Normalized Intensity
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
200
180
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140
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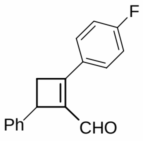
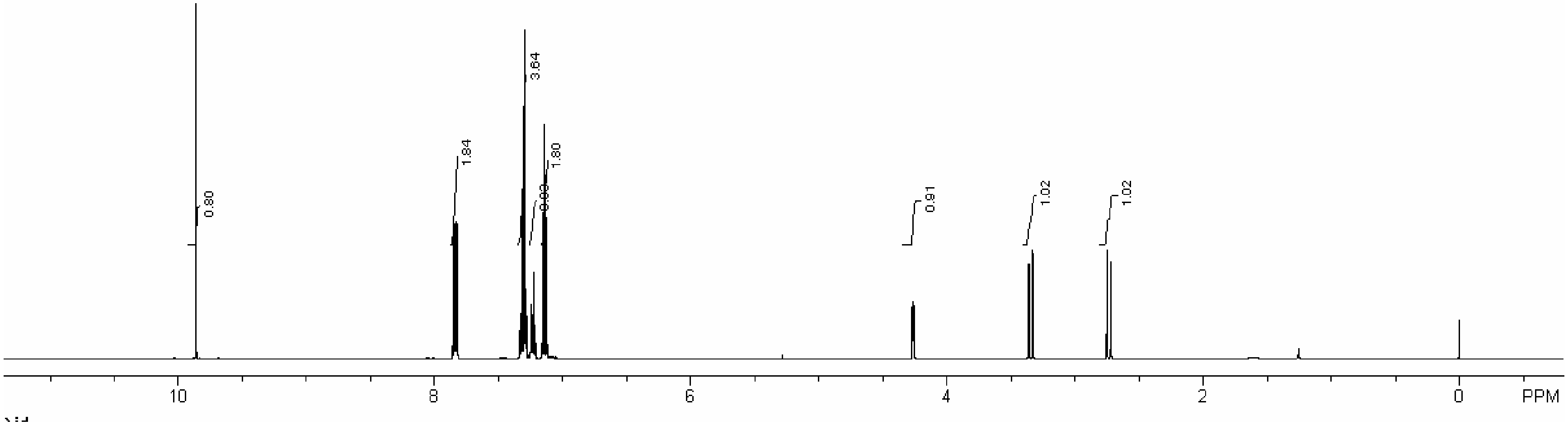
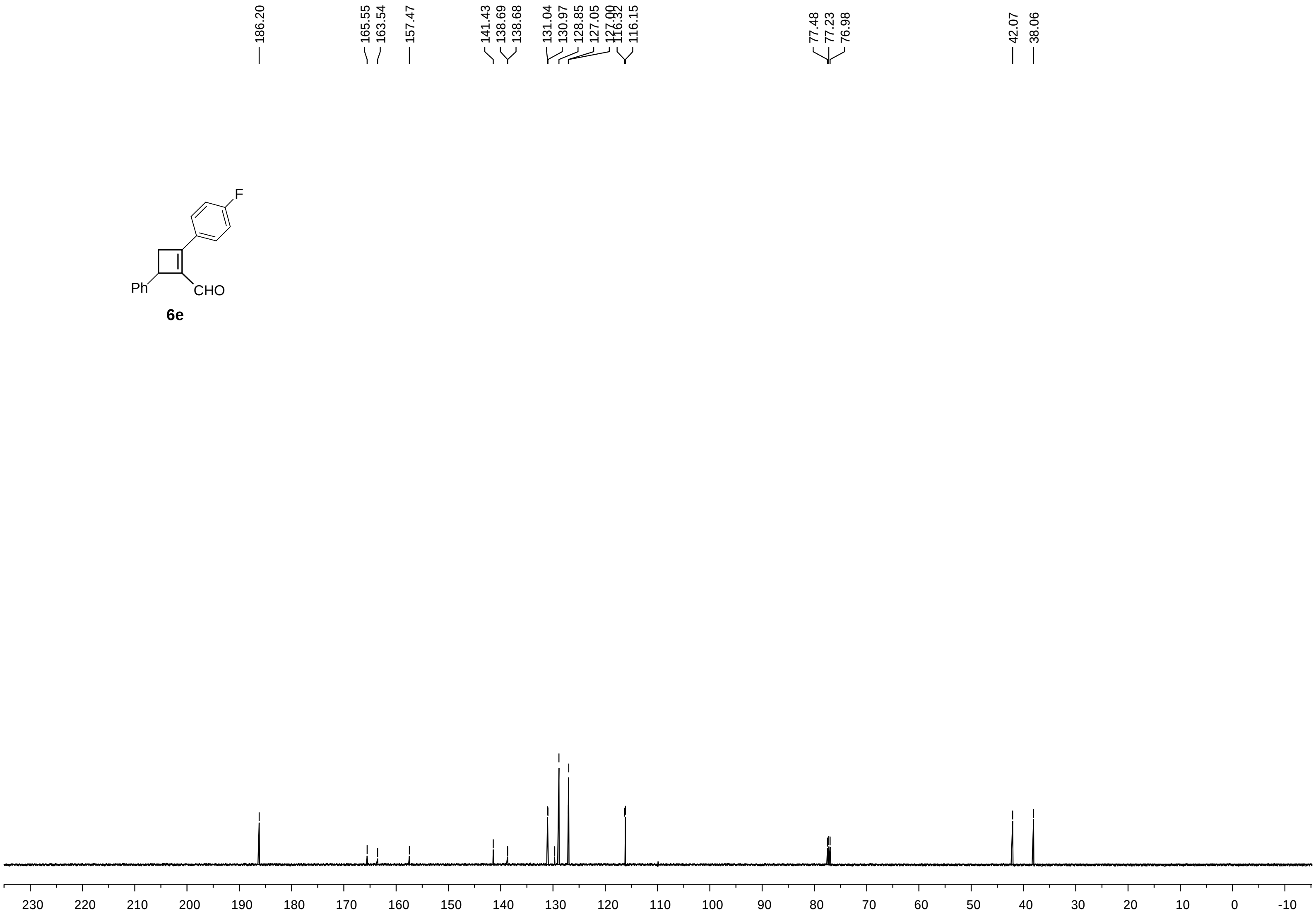
80
60
40
20
0
Chemical Shift (ppm)



6e

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138.69
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127.05
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116.32
116.15
77.48
77.23
76.98
42.07
38.06
F
Ph
CHO
6e
230
220
210
200
190
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100
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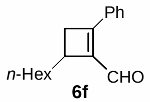
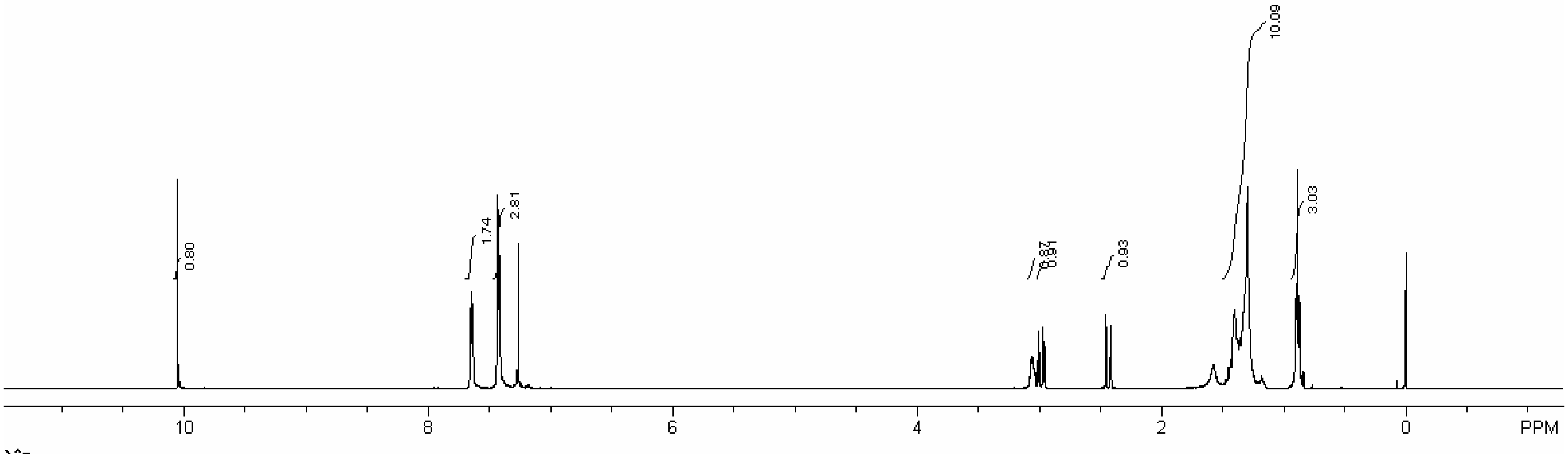
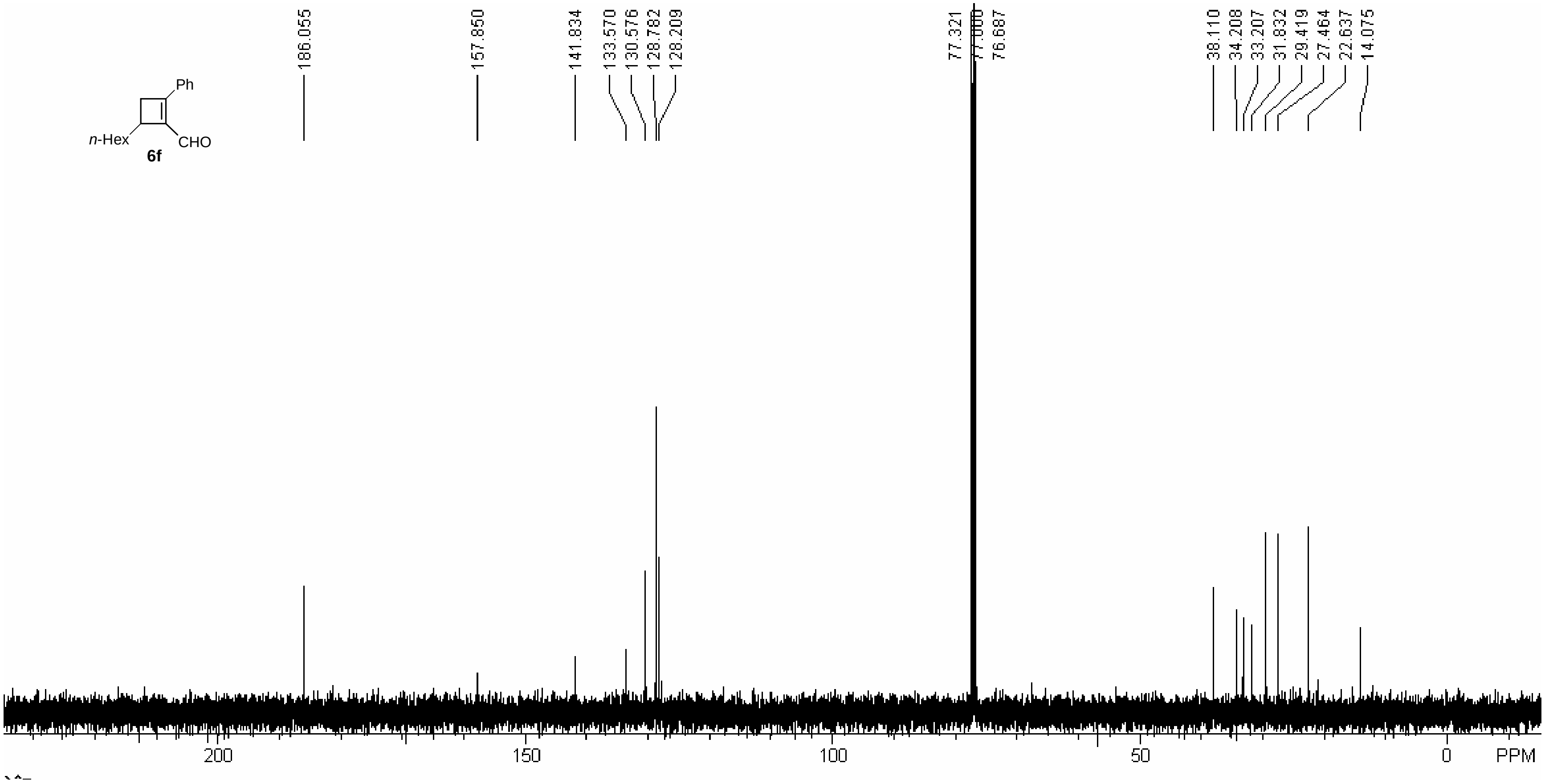
-10



6f





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128.782
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77.000
76.687
38.110
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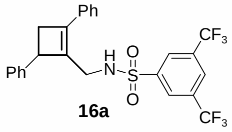
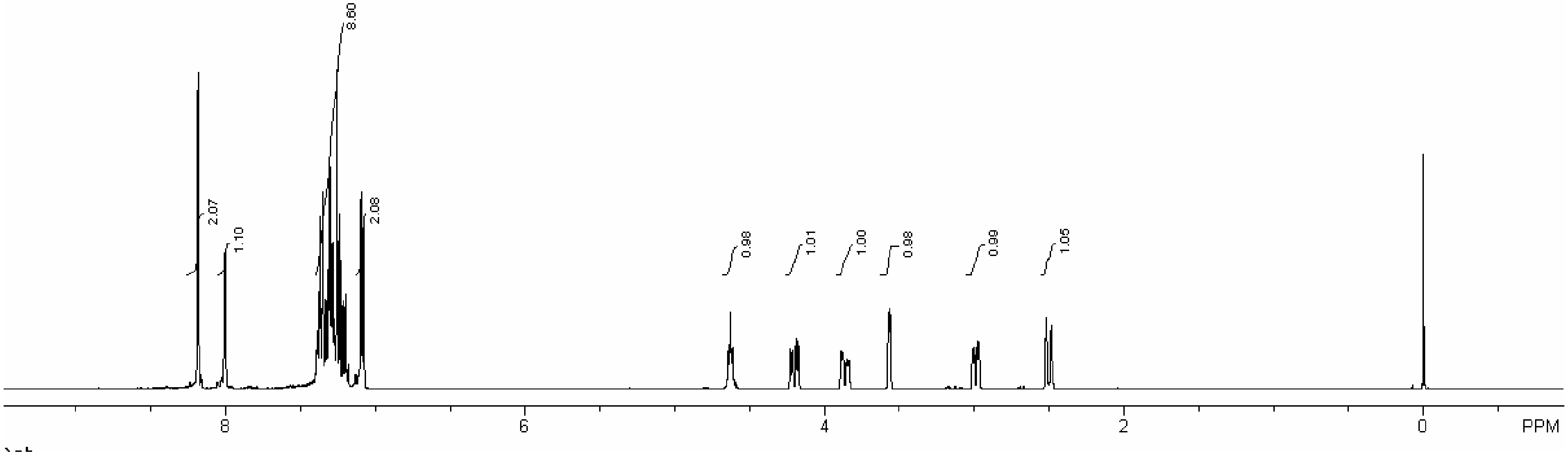
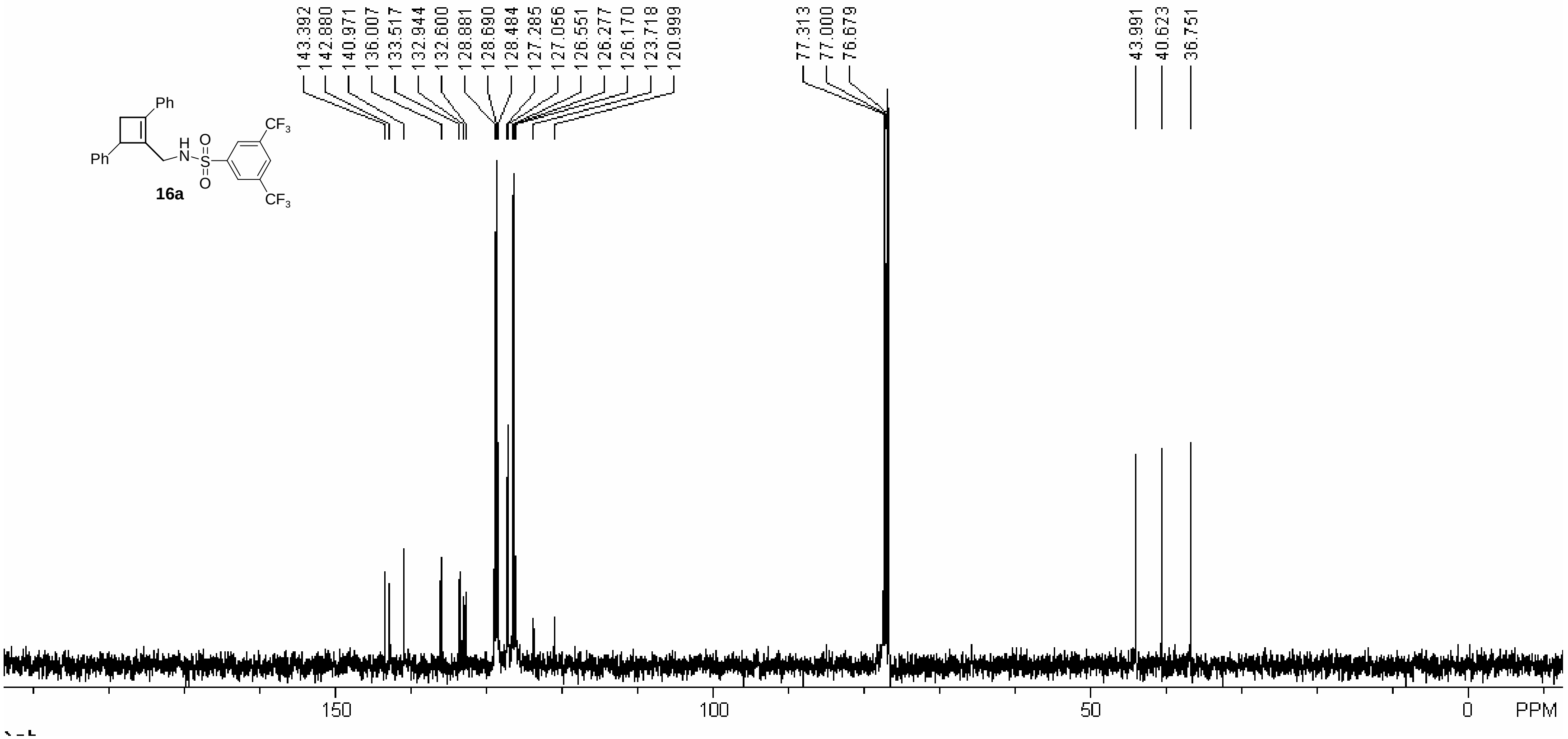
33.207
31.832
29.419
27.464
22.637
14.075
Ph
n-Hex
CHO
6f
200
150
100
50
0
PPM

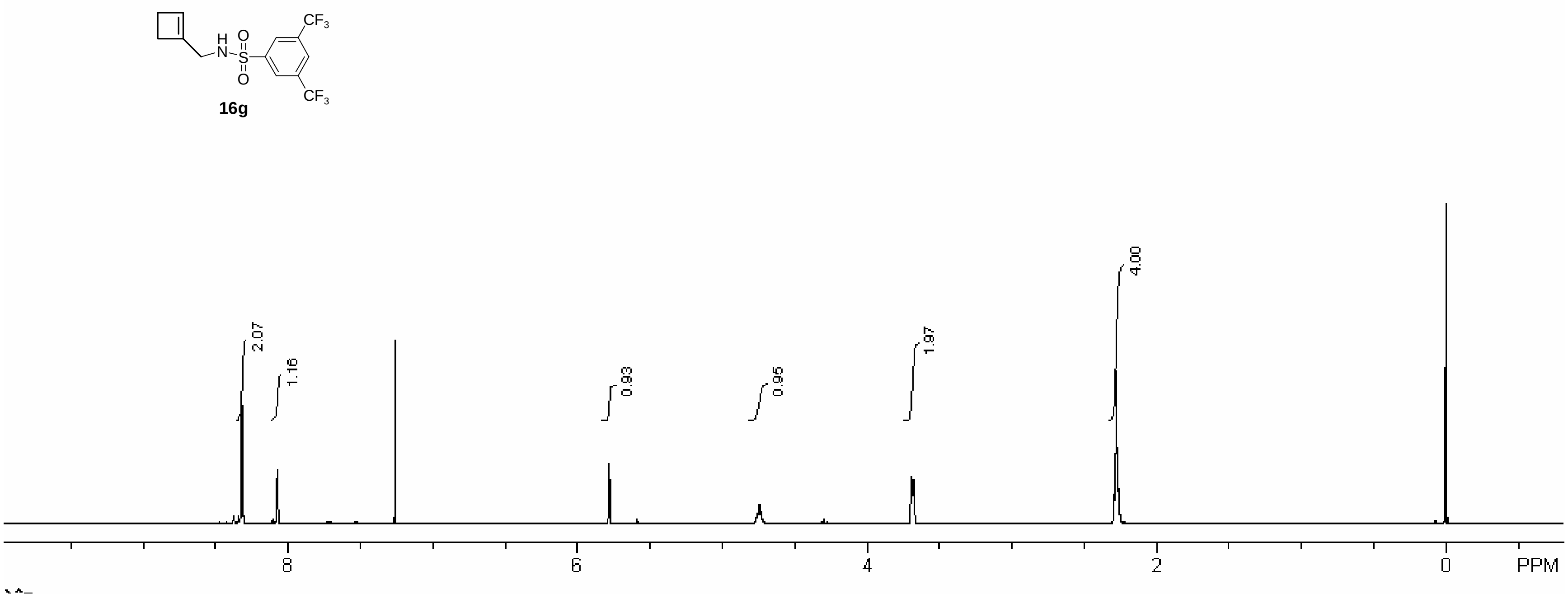

Ph
Ph
H
N
S
O
O
CF$_3$
CF$_3$

16a

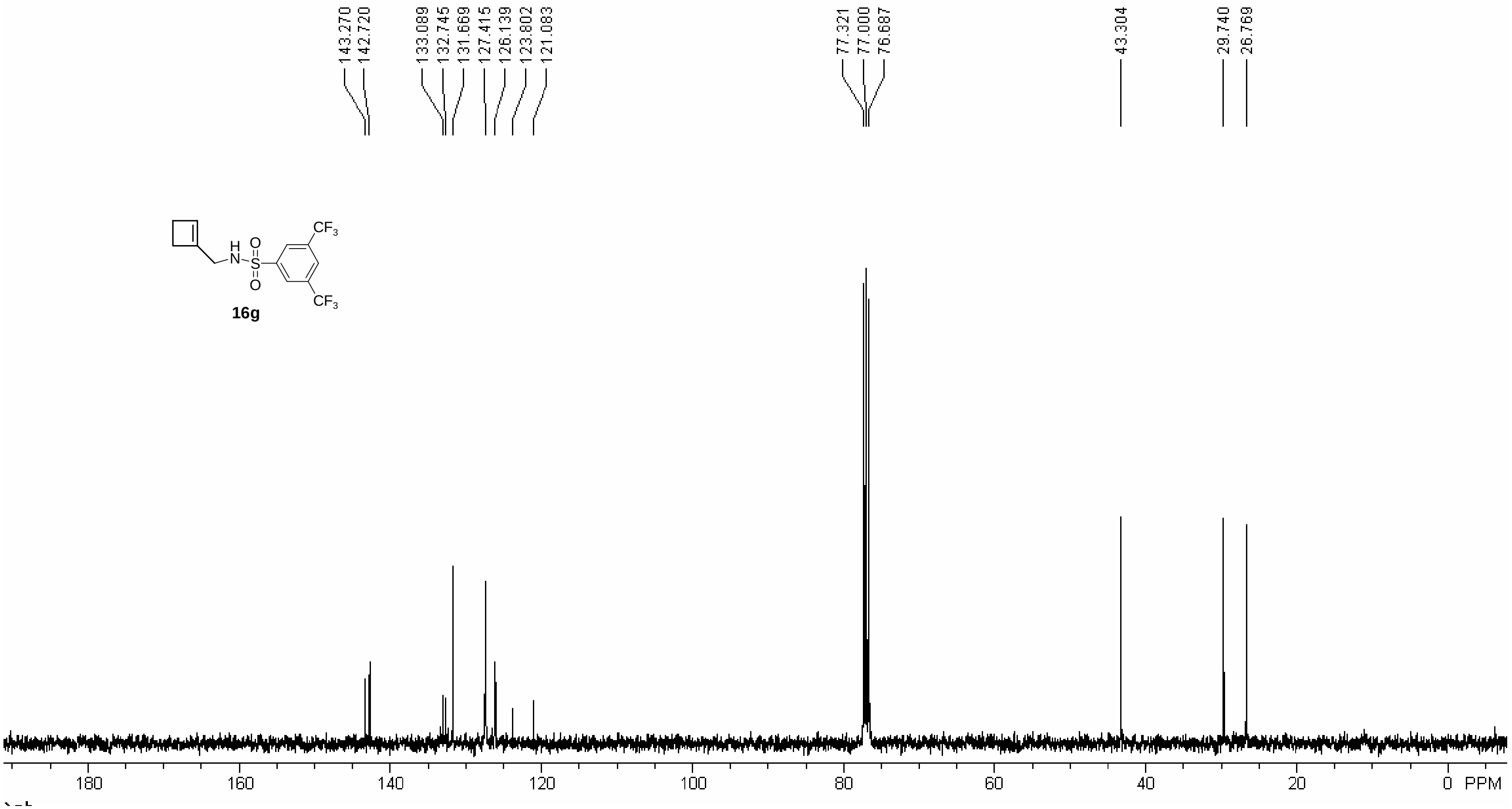

2.07
1.10
8.60
2.08
0.98
1.01
1.00
0.98
0.99
1.05
8
6
4
2
0
PPM

143.392
142.880
140.971
136.007
133.517
132.944
132.600
128.881
128.690
128.484
127.285
127.056
126.551
126.277
126.170
123.718
120.999
77.313
77.000
76.679
43.991
40.623
36.751
Ph
Ph
H
N
S
O
O
CF_3
CF_3
150
100
50
0
PPM

16a

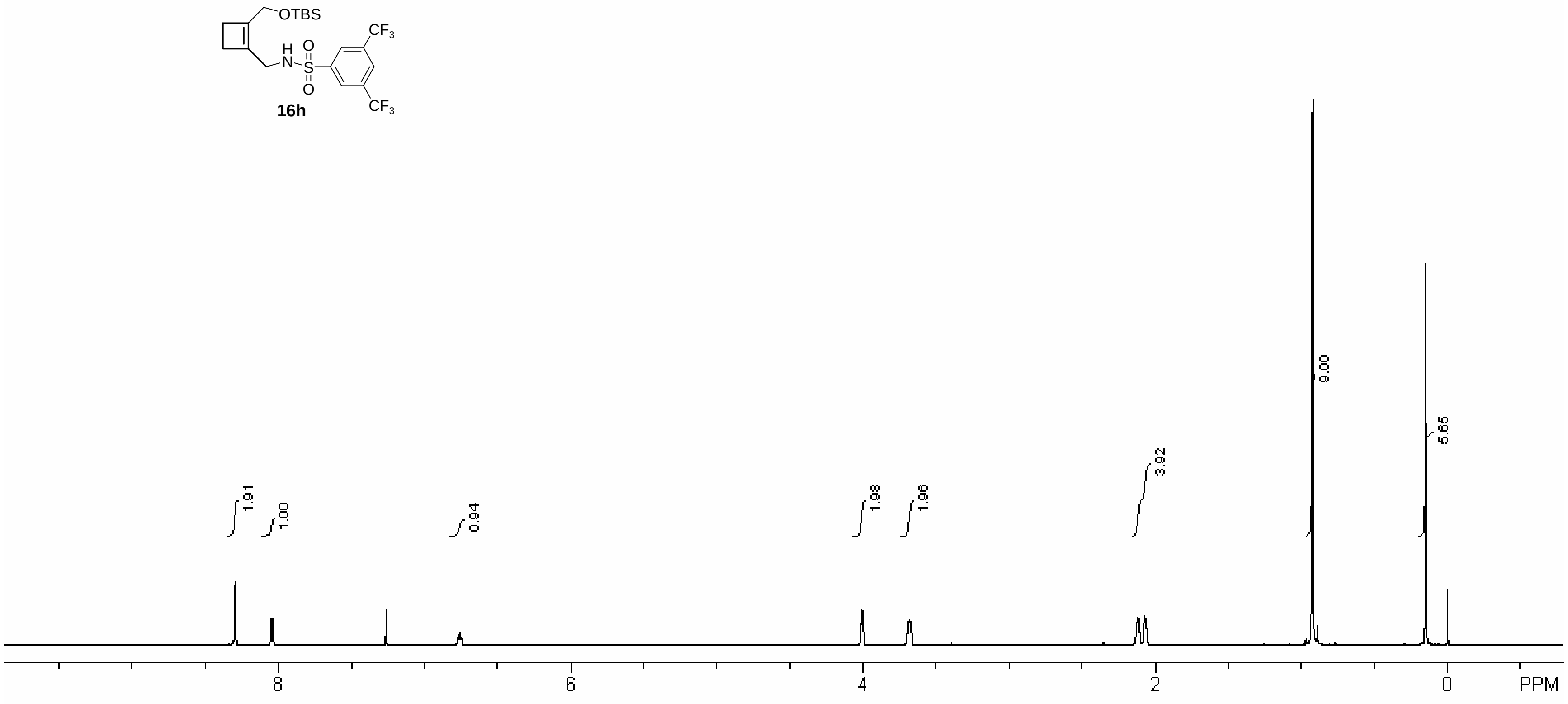


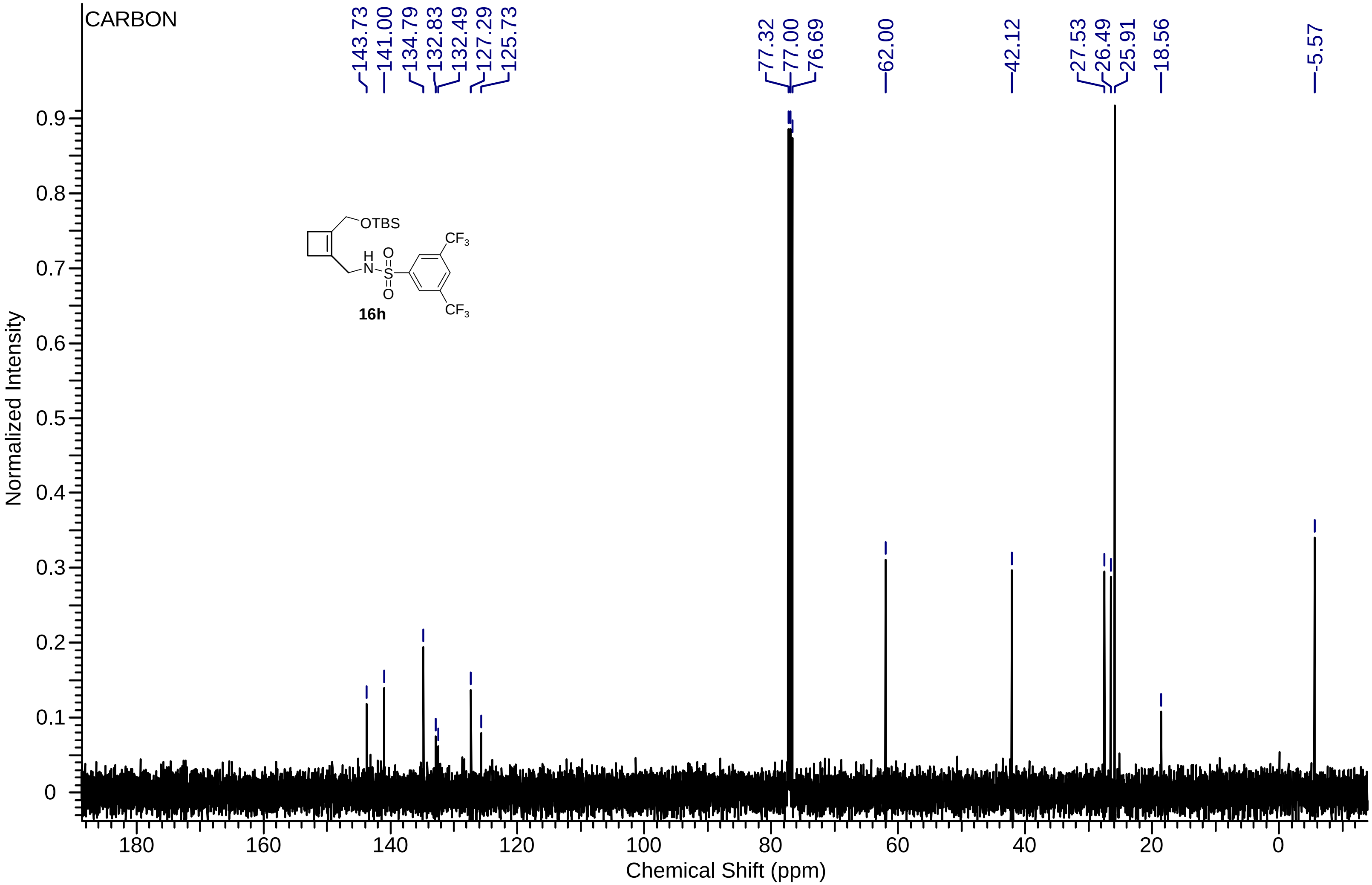
16g

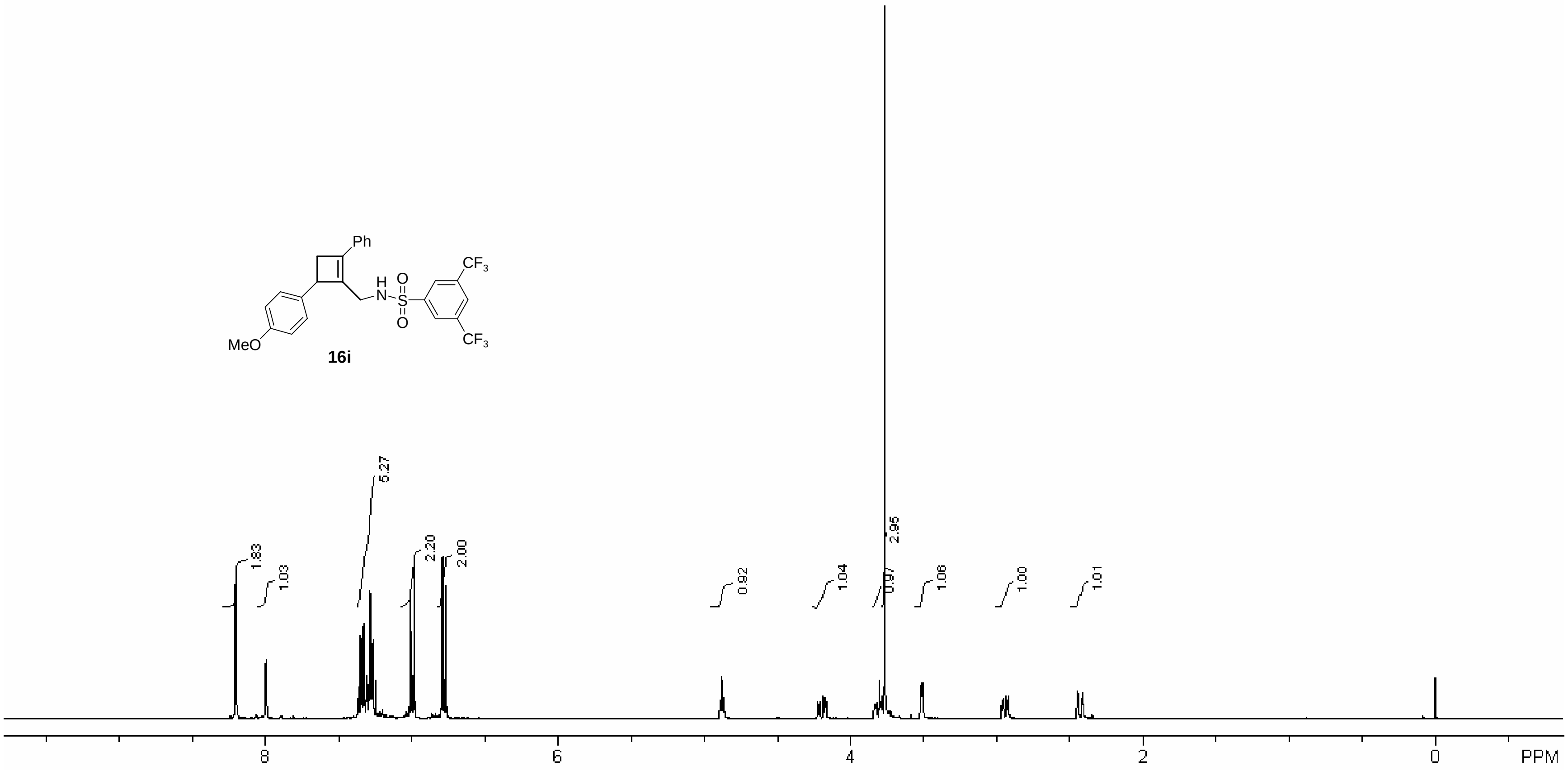


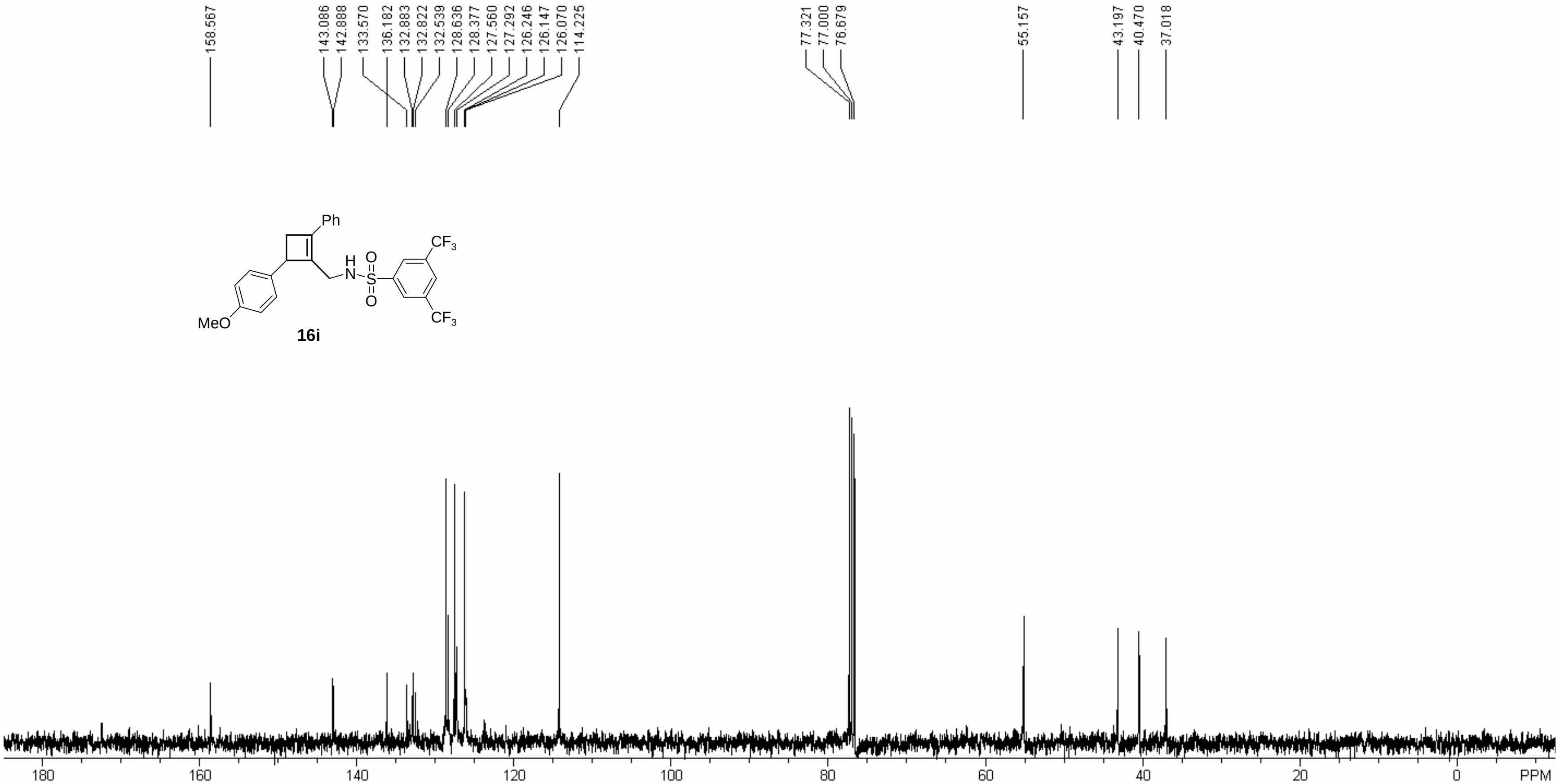
16g

143.270
142.720
133.089
132.745
131.669
127.415
126.139
123.802
121.083
77.321
77.000
76.687
43.304
29.740
26.769
CF3
CF3
H
N
S
O
O
180
160
140
120
100
80
60
40
20
0 PPM

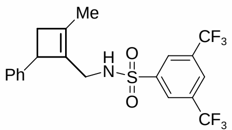

OTBS
H
N
S
O
O
CF3
CF3
16h
1.91
1.00
0.94
1.98
1.96
3.92
9.00
5.65
8
6
4
2
0
PPM


CARBON
143.73
141.00
134.79
132.83
132.49
127.29
125.73
77.32
77.00
76.69
62.00
42.12
27.53
26.49
25.91
18.56
-5.57
OTBS
H
N
S
O
O
CF3
CF3
16h
Normalized Intensity
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

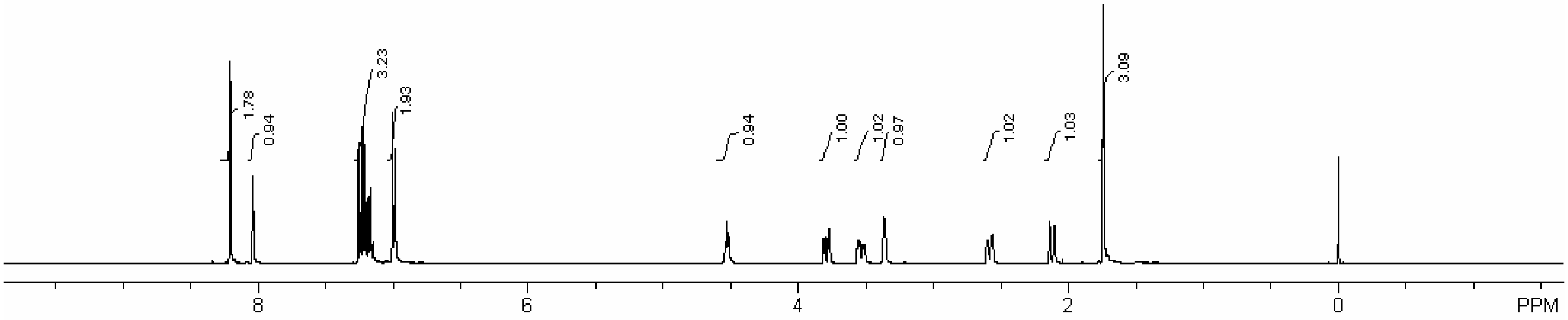

Ph
CF3
H
N
S
O
O
CF3
MeO
16i
1.83
1.03
5.27
2.20
2.00
0.92
1.04
0.97
2.95
1.06
1.00
1.01
8
6
4
2
0
PPM

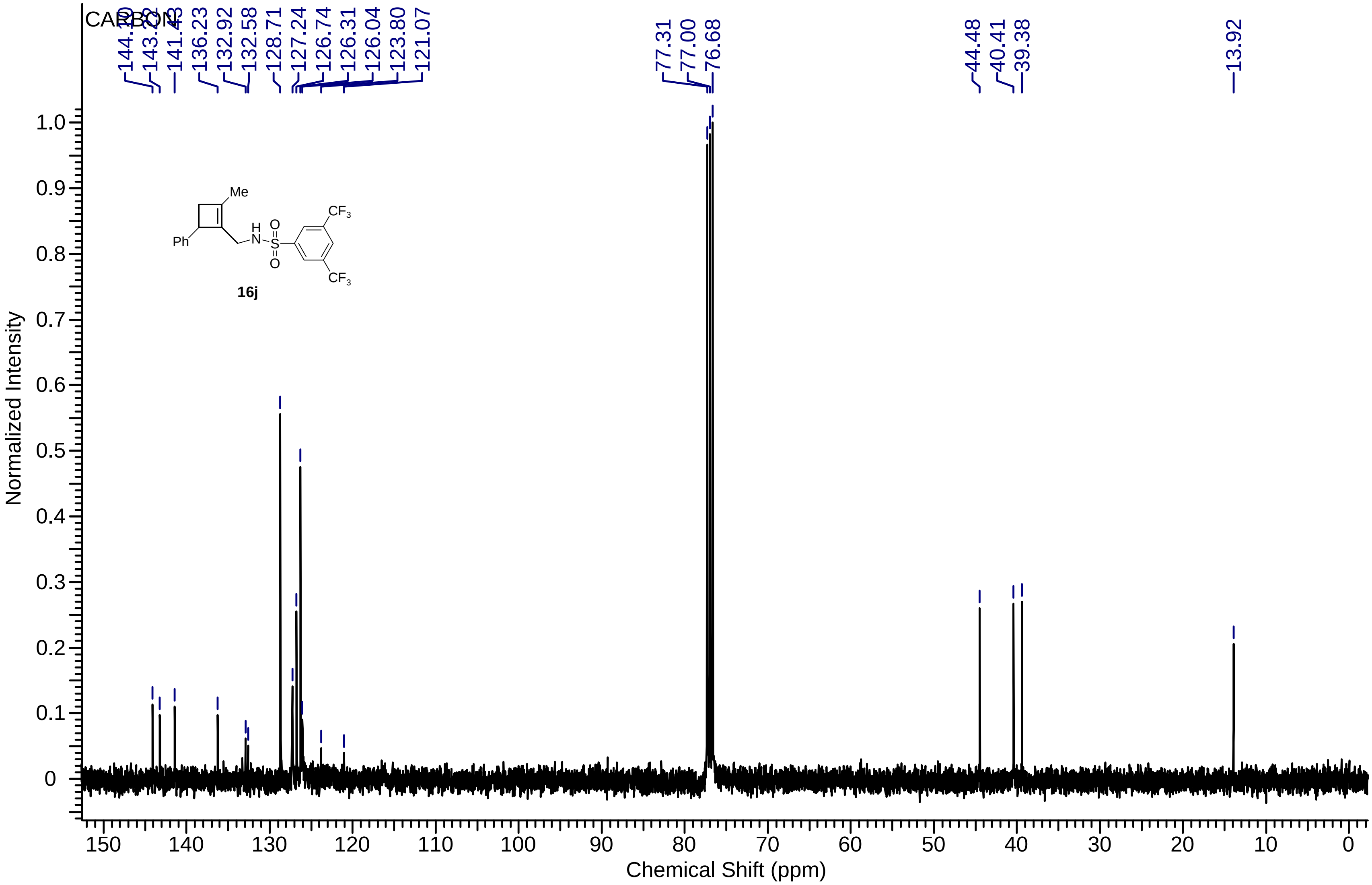

158.567
143.086
142.888
133.570
136.182
132.883
132.822
132.539
128.636
128.377
127.560
127.292
126.246
126.147
126.070
114.225
77.321
77.000
76.679
55.157
43.197
40.470
37.018
Ph
H
N
S
O
O
CF_3
CF_3
MeO
180
160
140
120
100
80
60
40
20
0
PPM

16i


Me
CF3
H
O
N
S
O
Ph
CF3

16j


1.78
0.94
3.23
1.93
0.94
1.00
1.02
0.97
1.02
1.03
3.09
8
6
4
2
0
PPM


CARBON
144.10
143.22
141.43
136.23
132.92
132.58
128.71
127.24
126.74
126.31
126.04
123.80
121.07
77.31
77.00
76.68
44.48
40.41
39.38
13.92
Me
CF3
Ph
H
N
S
O
O
CF3
16j
Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)