

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

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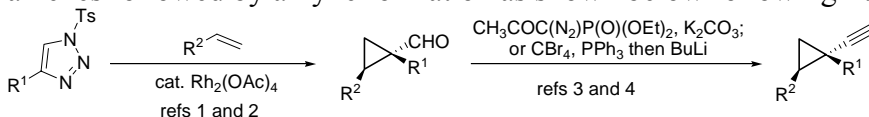
wtang@pharmacy.wisc.edu

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 (Silicycle, 40-63 μ m). Infrared spectra (IR) were obtained as neat oils on a Bruker Equinox 55 spectrophotometer. ^1H 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 ($\delta = 0$) 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.

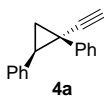
Characterization data for alkynyl cyclopropane substrates:

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

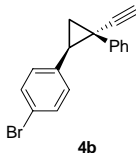


References:

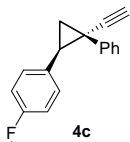
- 1) S. Chuprakov, S. W. Kwok, L. Zhang, L. Lercher and V. V. Fokin, *J. Am. Chem. Soc.*, 2009, **131**, 18034.
- 2) N. Grimster, L. Zhang and V. V. Fokin, *J. Am. Chem. Soc.*, 2010, **132**, 2510.
- 3) S. Muller, B. Liepold, G. J. Roth and H. J. Bestmann, *Synlett*, 1996, 521.
- 4) E. J. Corey and P.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



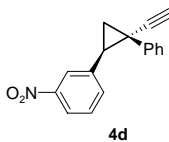
1H NMR (400 MHz, $CDCl_3$): δ 1.89 (dd, $J = 8.97, 5.65$ Hz, 1H), 1.97 (dd, $J = 7.21, 5.46$ Hz, 1H), 2.13 (s, 1H), 2.95 (dd, $J = 9.1, 7.21$ Hz, 1H), 6.91 (m, 2H), 7.05-7.21 (m, 8H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 19.94, 24.21, 34.44, 64.77, 89.77, 126.24, 126.63, 127.71, 127.92, 128.42, 129.26, 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.



1H NMR (400 MHz, $CDCl_3$): δ 1.89 (m, 2H), 2.11 (s, 1H), 2.85 (d, $J=8.1$ Hz, 1H), 6.74 (d, $J=8.2$ Hz, 2H), 7.09-7.17 (m, 5H), 7.36 (d, $J=8.5$ Hz, 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.

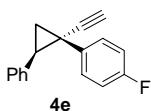


1H NMR (400 MHz, $CDCl_3$): δ 1.89 (m, 2H), 2.11 (s, 1H), 2.89 (d, $J=8.2$ Hz, 1H), 6.78 (t, $J=8.77$ Hz, 2H), 6.85 (m, 2H), 7.08-7.17 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 19.99, 24.05, 33.72, 64.91, 89.52, 114.63 (d, $^2J=21.5$ Hz), 126.74, 128.00, 129.13, 129.88 (d, $^3J=8.5$ Hz), 131.86 (d, $^4J=3.1$ 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.

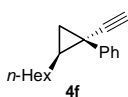


1H NMR (400 MHz, $CDCl_3$): δ 1.95 (dd, $J=8.85, 5.97$ Hz, 1H), 2.04 (t, $J=6$ Hz, 1H), 2.12 (s, 1H), 2.96 (t, $J=7.4$ Hz, 1H), 7.05-7.25 (m, 7H), 7.73 (s, 1H), 7.85 (d, $J=7.8$ Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 19.83, 25.04, 33.57, 65.48, 88.67, 121.29, 123.02, 127.18,

128.26, 128.52, 129.19, 134.36, 135.57, 138.63, 147.72. IR (CHCl₃) ν 3294, 3027, 2356, 2116, 1527, 1347, 693 cm⁻¹. HRMS (ESI) m/z calcd for C₁₇H₁₃NO₂ (M+Na)⁺ 286.0839, found 286.0837.

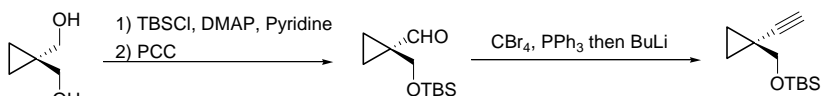


¹H NMR (500 MHz, CDCl₃): δ 1.94-2.00 (m, 2H), 2.20 (s, 1H), 3.02 (dd, $J=9.0, 7.5$ Hz, 1H), 6.89-6.92 (m, 2H), 6.98 (d, $J=12.0$ Hz, 2H), 7.16-7.23 (m, 5H); ¹³C NMR (CDCl₃, 125 MHz): 20.21, 23.76, 34.50, 65.23, 89.67, 115.02 (² $J=21.4$ Hz), 126.60, 128.04, 128.55, 131.09 (³ $J=8.1$ Hz), 132.76 (⁴ $J=3.1$ Hz), 136.07, 161.71 (¹ $J=244$ Hz); IR (CHCl₃) ν 3300, 2114, 1509, 1221, 907, 731 cm⁻¹. HRMS (ESI) m/z calcd for C₁₇H₁₃F (M+Na)⁺ 259.0894, found 259.0898.

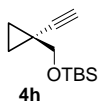


¹H NMR (400 MHz, CDCl₃): δ 0.70 (m, 1H), 0.82 (t, $J=7.4$ Hz, 3H), 1.10-1.33 (m, 10H), 1.38 (dd, $J=8.8, 4.9$ Hz, 1H), 1.53 (m, 1H), 1.96 (s, 1H), 7.23 (m, 1H), 7.30 (m, 2H), 7.37 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ 14.01, 19.90, 20.69, 22.49, 28.72, 28.92, 29.14, 29.99, 31.63, 63.69, 90.67, 126.67, 128.13, 129.10, 137.95. IR (CHCl₃) ν 3310, 2927, 2856, 2114, 1448, 909, 733, 698 cm⁻¹. HRMS (ESI) m/z calcd for C₁₇H₂₂ (M+H)⁺ 227.1794, found 227.1792.

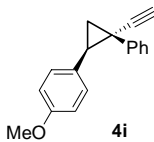
Alkynyl cyclopropane **4h** was prepared in three steps following literature procedures.



- 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.

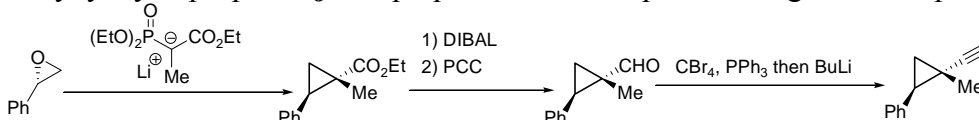


¹H NMR (400 MHz, CDCl₃): δ 0.07 (s, 6H), 0.81 (m, 2H), 0.85 (m, 2H), 0.90 (s, 9H), 1.88 (s, 1H), 3.64 (s, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ -5.31, 11.91, 13.58, 18.38, 25.88, 65.09, 66.10, 87.92. IR (CHCl₃) ν 3316, 2930, 2896, 2115, 1102, 835 cm⁻¹. HRMS (ESI) m/z calcd for C₁₂H₂₂OSi (M+Na)⁺ 233.1332, found 233.1325.

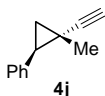


¹H NMR (400 MHz, CDCl₃): δ 1.83 (m, 2H), 2.08 (s, 1H), 2.85 (t, $J=8$ Hz, 1H), 3.68 (s, 3H), 6.61 (d, $J=8.7$ Hz, 2H), 6.80 (d, $J=8.6$ Hz, 2H), 7.04-7.16 (m, 5H); ¹³C NMR (CDCl₃, 100 MHz): δ 20.08, 23.83, 33.96, 55.07, 64.65, 89.94, 113.22, 126.54, 127.92, 128.15, 129.16, 129.49, 136.81, 158.03. IR (CHCl₃) ν 3286, 3006, 2935, 2112, 1712, 1513, 697 cm⁻¹. HRMS (ESI) m/z calcd for C₁₇H₁₆O (M+Na)⁺ 271.1093, found 271.1094.

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



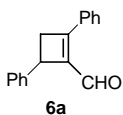
- 1) C. D. Bray, F. Minicone, *Chem. Commun.*, 2010, **46**, 5867.
- 2) E. J. Corey and P. L. Fuchs, *Tetrahedron Lett.*, 1972, **13**, 3769.



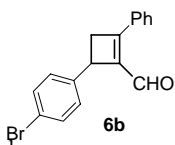
¹H NMR (400 MHz, CDCl₃): δ 0.97 (s, 3H), 1.09 (dd, *J*=6.82, 5.07Hz, 1H), 1.39 (dd, *J*=8.77, 4.87Hz, 1H), 1.94 (s, 1H), 2.53 (t, *J*=8.5 Hz, 1H), 7.18-7.31 (m, 5H); ¹³C NMR (CDCl₃, 100 MHz): δ 13.00, 18.82, 19.91, 31.23, 63.51, 91.17, 126.51, 128.13, 129.15, 136.98. IR (CHCl₃) ν 2923, 2854, 2341, 1460, 1166, 736cm⁻¹. HRMS (ESI) *m/z* calcd for C₁₂H₁₂(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.

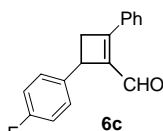


¹H NMR (400 MHz, CDCl₃): δ 2.77 (dd, *J*=15.6, 2.8Hz, 1H), 3.38 (dd, *J*=15.6, 5.1Hz, 1H), 4.27 (d, *J*=5.1Hz, 1H), 7.24 (m, 3H), 7.31 (m, 2H), 7.46 (m, 5H), 10.04 (s, 1H); ¹³C NMR (CDCl₃, 100 MHz): δ 37.79, 41.84, 109.76, 126.73, 126.80, 128.44, 128.51, 128.58, 128.87, 131.09, 185.83. IR (CHCl₃) ν 3029, 2918, 1658, 907, 728cm⁻¹. HRMS (ESI) *m/z* calcd for C₁₇H₁₄O (M+Na)⁺ 257.0937, found 257.0935.

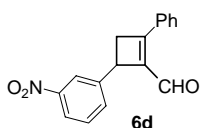


¹H NMR (400 MHz, CDCl₃): δ 2.74 (dd, *J*=15.6, 2.0Hz, 1H), 3.38 (dd, *J*=15.6, 5.1Hz, 1H), 4.22 (d, *J*=5.0Hz, 1H), 7.18 (d, *J*=8.6Hz, 2H), 7.41-7.52(m, 5H), 7.75 (m, 2H), 10.05 (s, 1H); ¹³C NMR (CDCl₃, 100 MHz): δ 37.84, 41.46, 120.72, 128.75, 128.81, 129.19, 131.50, 131.88, 133.07, 139.29, 140.79, 159.45, 185.23. IR (CHCl₃) ν 2921,

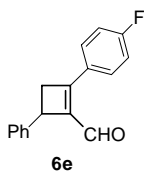
1656, 1402, 907, 728 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{13}\text{BrO}$ ($\text{M}+\text{Na}$) $^{+}$ 335.0042, found 335.0038.



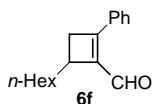
^1H NMR (400 MHz, CDCl_3): δ 2.72 (dd, $J=15.6, 2.1\text{Hz}$, 1H), 3.37 (dd, $J=15.6, 5.2\text{Hz}$, 1H), 4.21 (dd, $J=5.1, 2.0\text{Hz}$, 1H), 6.99 (m, 2H), 7.25 (m, 2H), 7.47 (m, 3H), 7.74 (m, 2H), 10.04 (s, 1H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 37.87, 41.07, 115.35 (d, $^2J=20.7\text{Hz}$), 128.26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



^1H NMR (400 MHz, CDCl_3): δ 2.81 (dd, $J=15.6, 1.6\text{Hz}$, 1H), 3.46 (dd, $J=15.6, 5.6\text{Hz}$, 1H), 4.36 (dd, $J=5.1, 1.8\text{Hz}$, 1H), 7.44-7.55 (m, 4H), 7.65 (d, $J=8.0\text{Hz}$, 1H), 7.74 (m, 2H), 8.10 (d, $J=8.0\text{Hz}$, 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, 693 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{13}\text{NO}_3$ ($\text{M}+\text{Na}$) $^{+}$ 302.0788, found 302.0783.



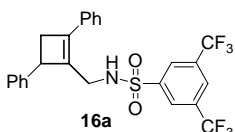
^1H NMR (500 MHz, CDCl_3): 2.73 (dd, $J=15.0, 1.5\text{Hz}$, 1H), 3.34 (dd, $J=16.0, 5.5\text{Hz}$, 1H), 4.26 (dd, $J=5.0, 1.5\text{Hz}$, 1H), 7.12-7.16 (m, 2H), 7.22-7.25 (m, 1H), 7.28-7.33 (m, 4H), 7.82-7.85 (m, 2H), 9.86 (s, 1H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 38.06, 42.07, 116.23 ($^2J=21.8\text{Hz}$),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



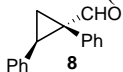
^1H NMR (400 MHz, CDCl_3): δ 0.86 (t, $J=6.6\text{Hz}$, 3H), 1.18-1.56 (m, 10H), 2.43 (d, $J=15.4\text{Hz}$, 1H), 2.99 (dd, $J=15.4, 4.7\text{Hz}$, 1H), 3.06 (m, 1H), 7.42 (m, 3H), 7.64 (m, 2H), 10.05 (s, 1H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 14.08, 22.64, 27.46, 29.42, 31.83, 33.21, 34.21, 38.11, 128.21, 128.78, 130.58, 133.57, 141.83, 157.85, 186.06. IR (CHCl_3) ν 2926, 2136, 1656, 1279, 758 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{22}\text{O}$ ($\text{M}+\text{Na}$) $^{+}$ 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 LiAlH₄ 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.



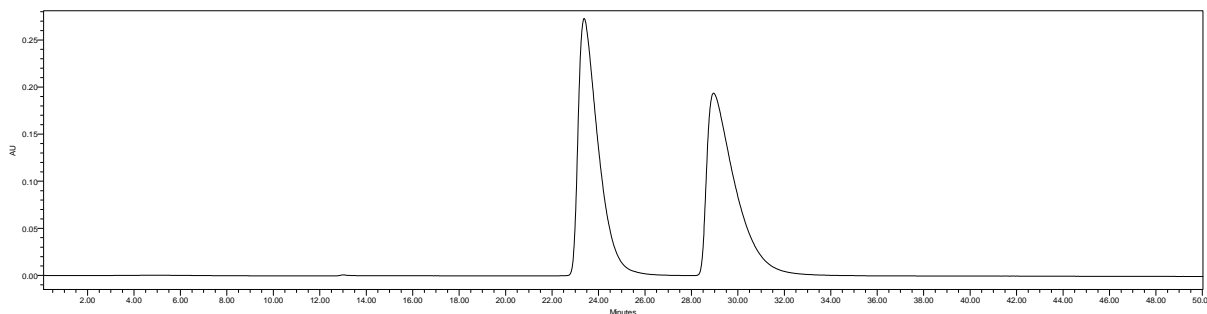
$[\alpha]_D^{20} = -23$ (c=0.5, MeOH). ¹H NMR (400 MHz, CDCl₃): δ 2.50 (d, *J*=13.1Hz, 1H), 2.98 (dd, *J*=13.1, 4.9Hz, 1H), 3.57 (d, *J*=4.3Hz, 1H), 3.82 (dd, *J*=17.2, 5.3Hz, 1H), 4.20 (dd, *J*=15.2, 5.5Hz, 1H), 4.67 (t, *J*=5.5Hz, 1H), 7.08 (m, 2H), 7.17-7.39 (m, 8H), 8.00 (s, 1H), 8.18 (s, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ 36.75, 40.62, 43.99, 122.36 (d, ¹*J*=272.6Hz), 126.17, 126.28, 126.55, 127.06, 127.29, 128.48, 128.69, 128.88, 132.77 (d, ²*J*=34.6Hz), 133.52, 136.01, 140.97, 142.88, 143.39. IR (CHCl₃) ν 3378, 2256, 1279, 908, 733cm⁻¹. HRMS (ESI) *m/z* calcd for C₂₅H₁₉F₆NO₂S (M+Na)⁺ 534.0933, found 534.0928.



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

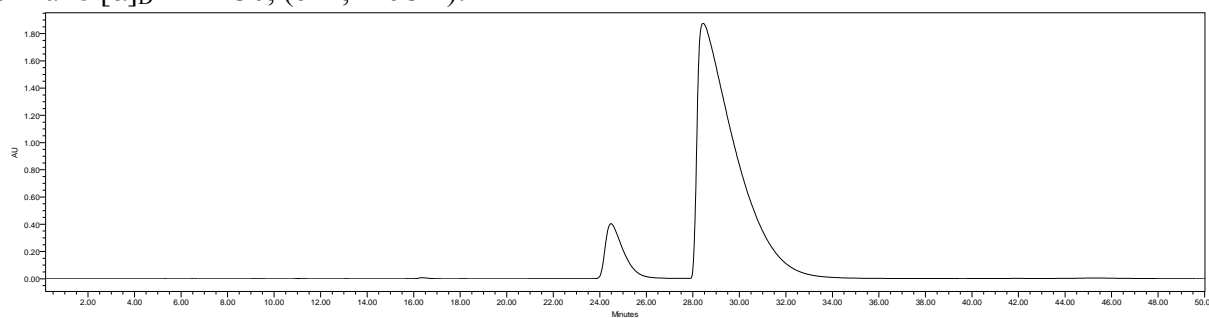
S. Chuprakov, S. W. Kwok, L. Zhang, L. Lercher and V. V. Fokin, *J. Am. Chem. Soc.*, 2009, **131**, 18034.

Racemic **8**:



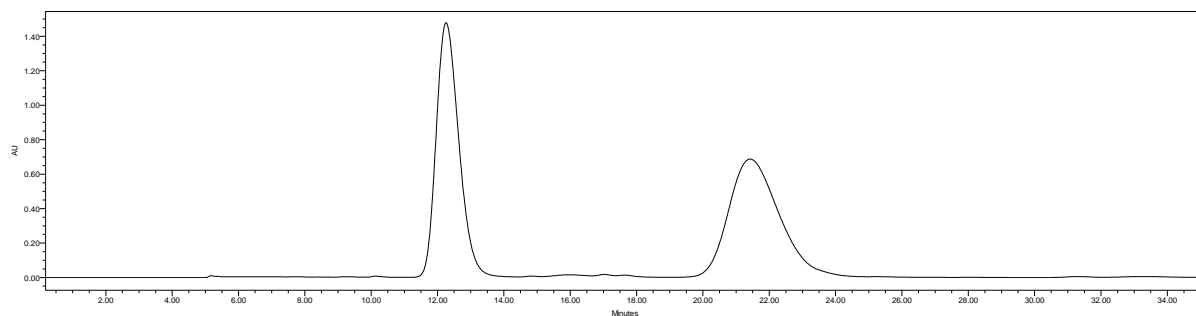
	Retention Time	Area	% Area	Height
1	23.382	16286193	49.97	272843
2	28.957	16304775	50.03	193596

Chiral **8** [α]_D²⁰ = +130, (c=1, MeOH):



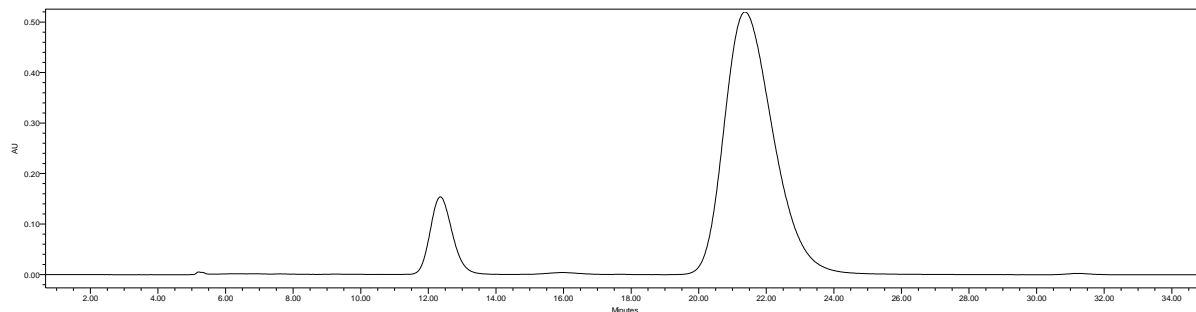
	Retention Time	Area	% Area	Height
1	24.479	21520024	9.49	402980
2	28.442	205127815	90.51	1863761

Racemic **16a**:

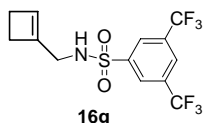


	Retention Time	Area	% Area	Height
1	12.257	69966637	49.77	1476051
2	21.423	70602059	50.23	680665

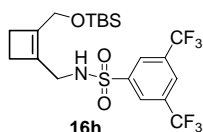
Chiral **16a**:



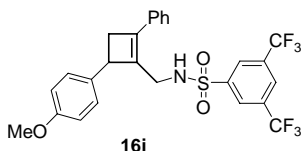
	Retention Time	Area	% Area	Height
1	12.354	5939471	10.21	143624
2	21.370	52255960	89.79	519707



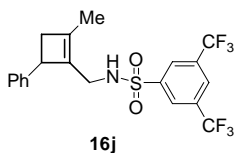
$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 2.28 (m, 4H), 3.69 (m, 2H), 4.80 (t, $J=5.5\text{Hz}$, 1H), 5.79 (m, 1H), 8.08 (s, 1H), 8.33 (s, 2H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 26.77, 29.74, 43.30, 122.44 (d, $^1J=273.3\text{Hz}$), 126.14, 127.42, 131.67, 132.92 (d, $^2J=34.6\text{Hz}$), 142.72, 143.27. IR (CHCl_3) ν 3303, 2929, 2258, 1278, 1142, 905, 730cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{11}\text{F}_6\text{NO}_2\text{S}$ ($\text{M}+\text{Na}$) $^+$ 382.0307, found 382.0308.



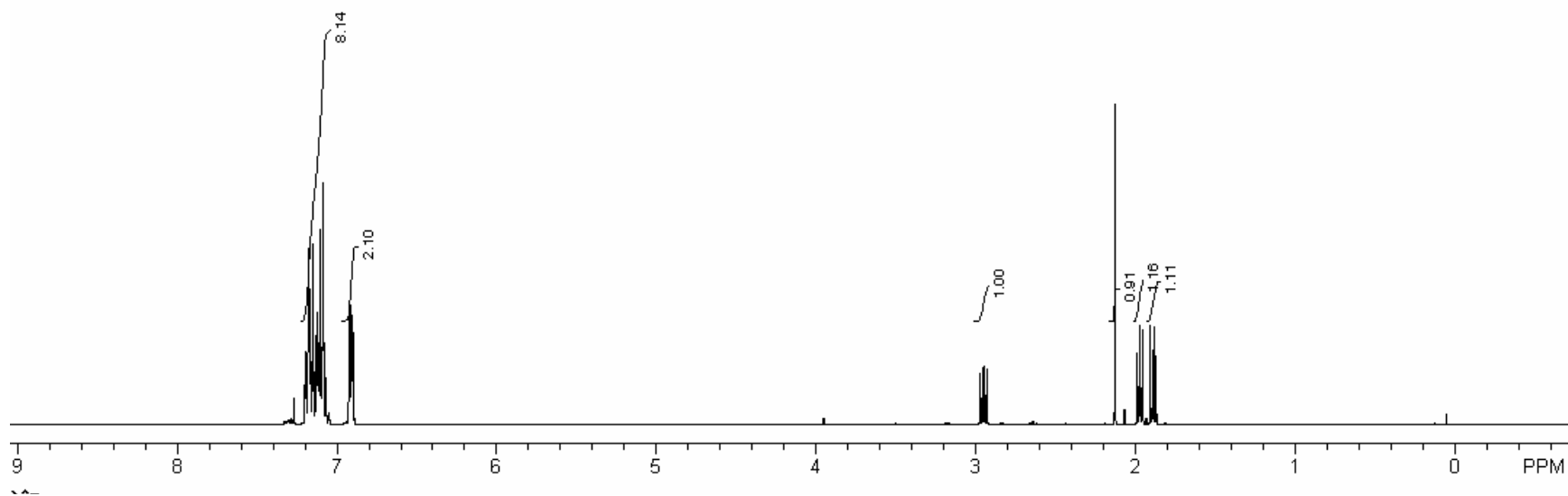
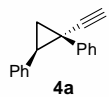
$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 0.15 (s, 6H), 0.92 (s, 9H), 2.09 (d, $J=19\text{Hz}$, 4H), 3.68 (br s, 2H), 4.01 (br s, 2H), 6.74 (m, 1H), 8.04 (s, 1H), 8.36 (s, 2H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ -5.57, 18.56, 25.91, 26.49, 27.53, 42.12, 62.00, 125.73, 127.29, 132.49, 132.83, 134.79,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

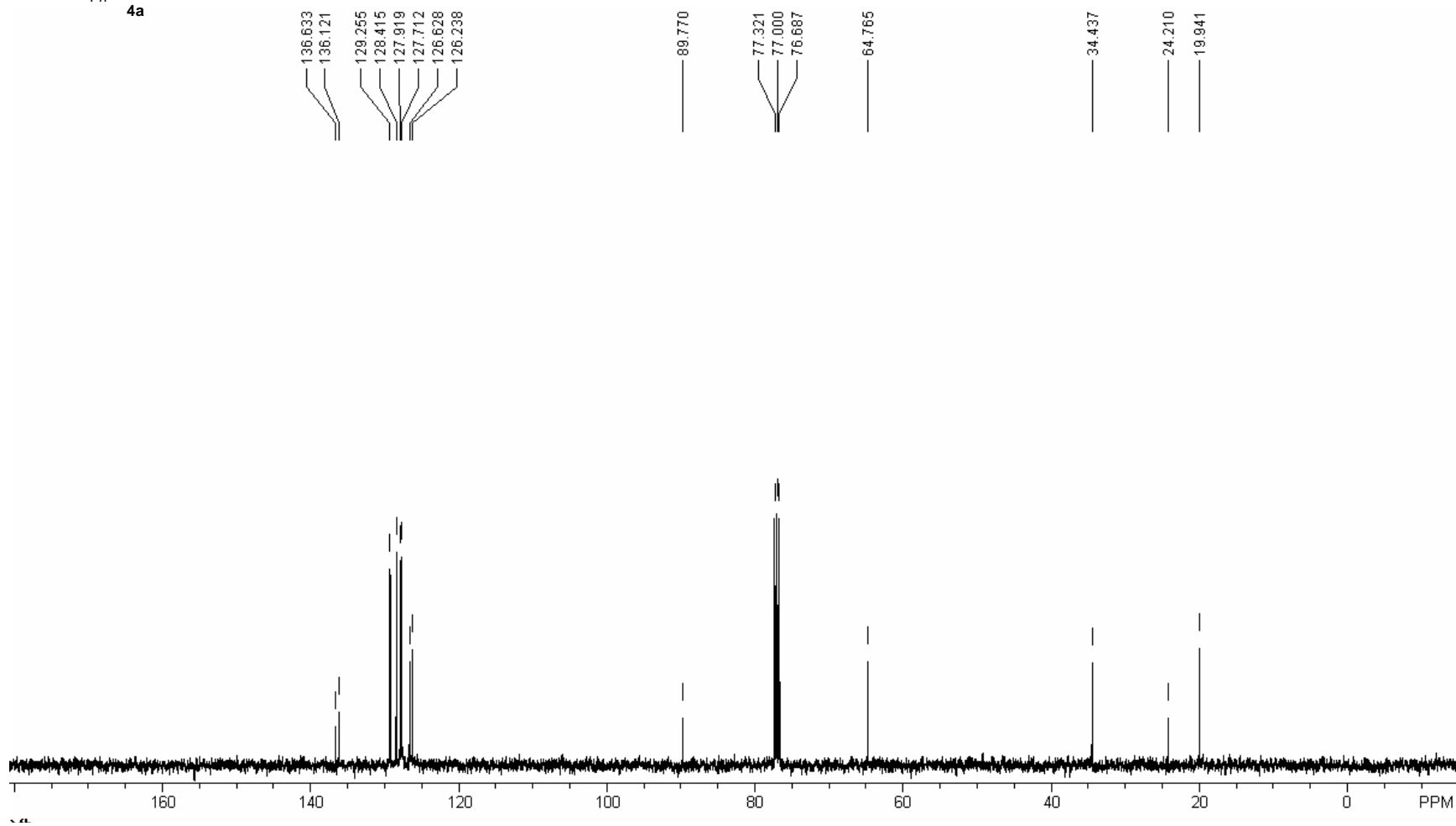
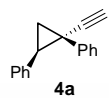


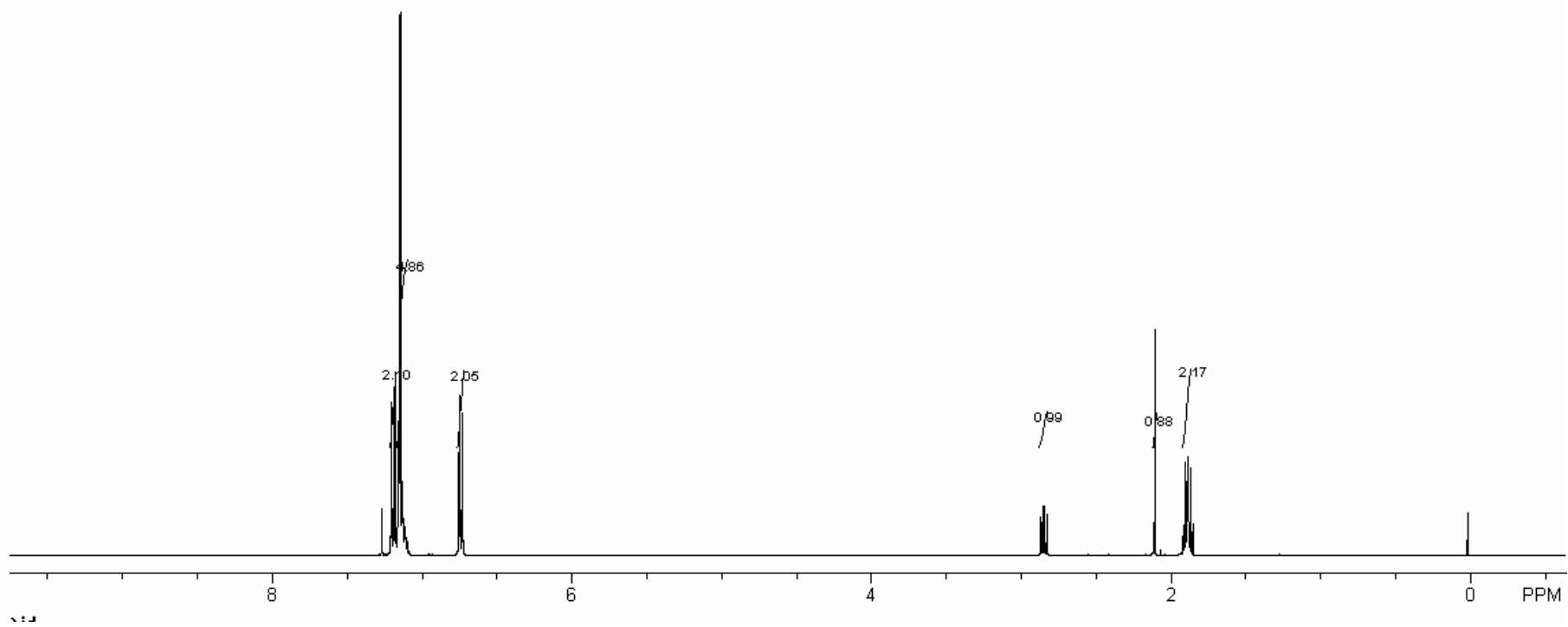
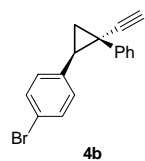
$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 2.43 (d, $J=13.1\text{Hz}$, 1H), 2.94 (dd, $J=13.1, 4.9\text{Hz}$, 1H), 3.50 (d, $J=4.1\text{Hz}$, 1H), 3.77 (s, 3H), 3.82 (m, 1H), 4.20 (dd, $J=15.2, 5.5\text{Hz}$, 1H), 4.88 (t, $J=5.5\text{Hz}$, 1H), 6.78 (d, $J=8.6\text{Hz}$, 2H), 7.00 (d, $J=8.7\text{Hz}$, 2H), 7.24-7.37 (m, 5H), 8.00 (s, 1H), 8.20 (s, 2H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 37.02, 40.47, 43.20, 55.16, 114.23, 126.15, 126.25, 127.29, 127.35 (d, $^1J=240.3\text{Hz}$), 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 $\text{C}_{26}\text{H}_{21}\text{F}_6\text{NO}_3\text{S}$ ($\text{M}+\text{Na}$) $^+$ 564.1039, found 564.1041.

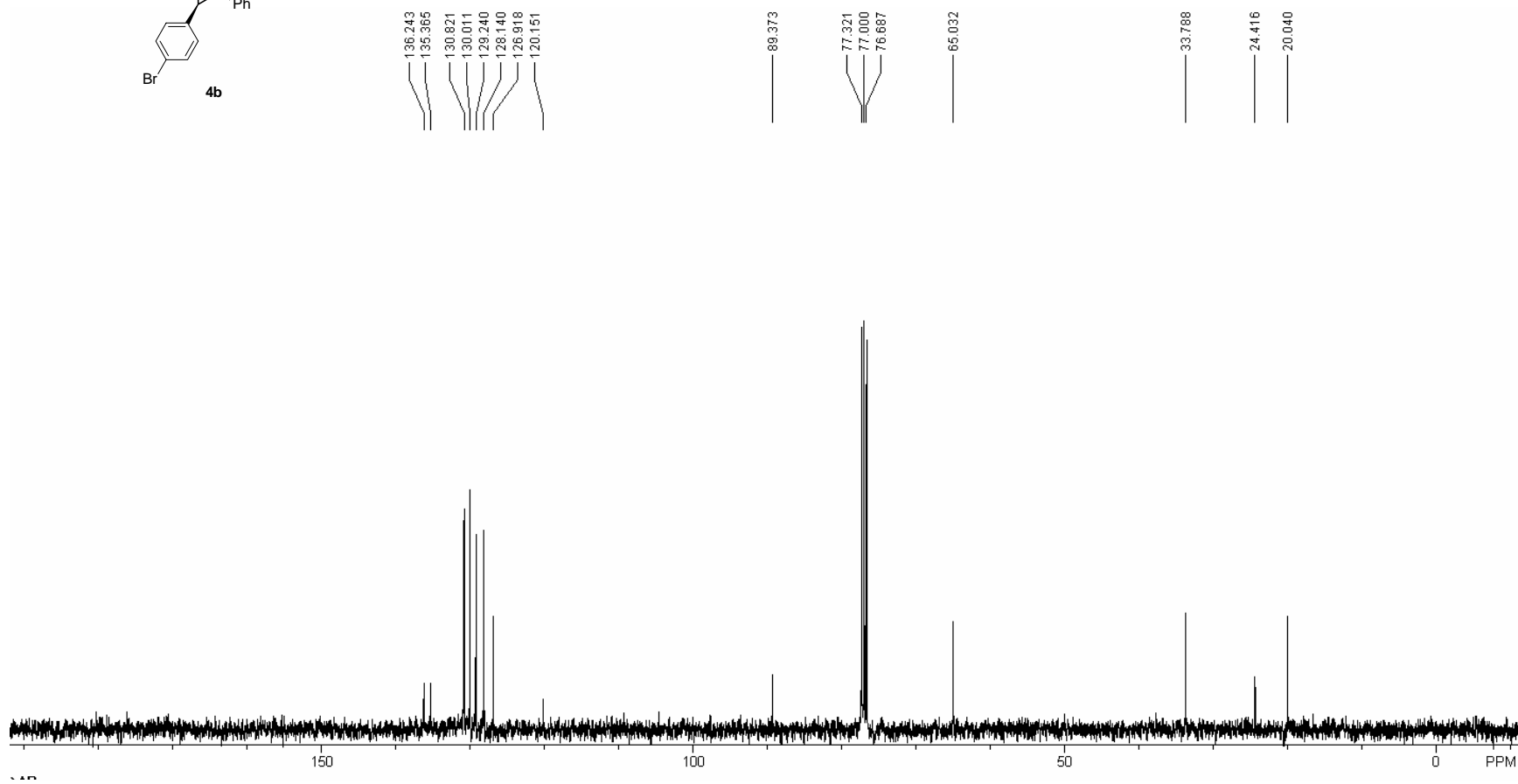
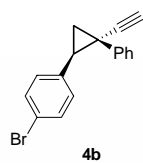


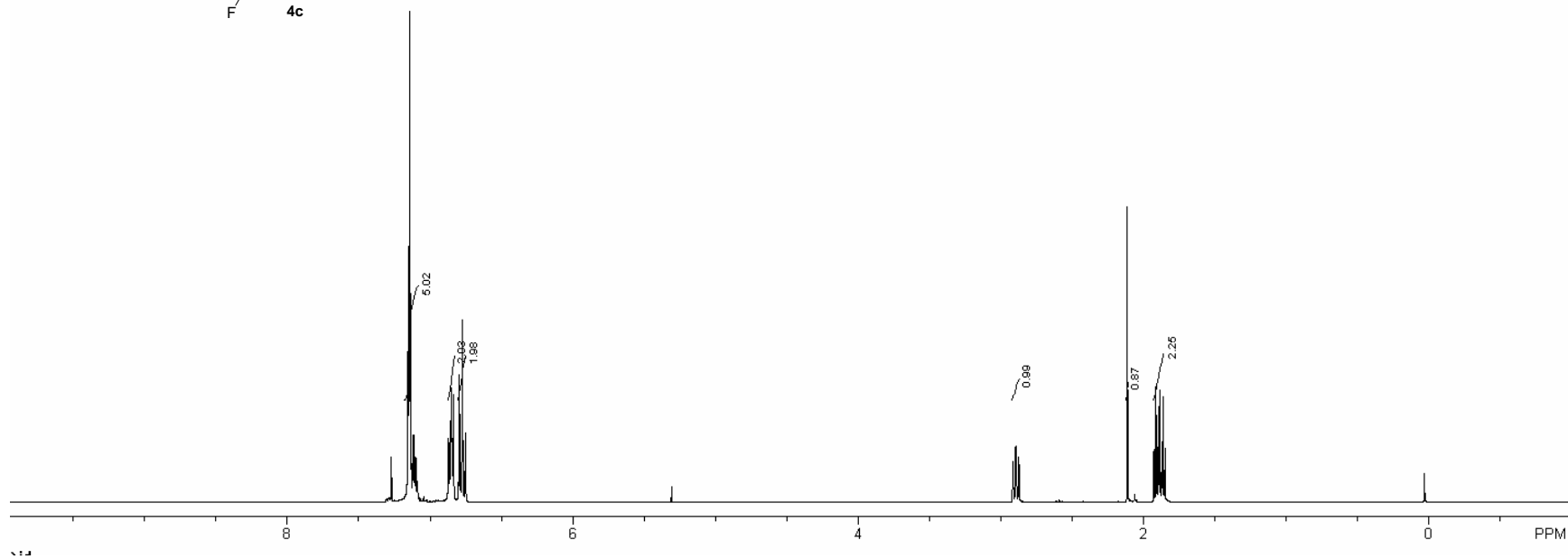
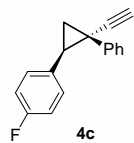
$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 1.74 (s, 3H), 2.12 (d, $J=13.5\text{Hz}$, 1H), 2.58 (dd, $J=17.7, 4.5\text{Hz}$, 1H), 3.35 (s, 1H), 3.53 (dd, $J=20.5, 5.5\text{Hz}$, 1H), 3.79 (dd, $J=14.8, 5.3\text{Hz}$, 1H), 4.52 (t, $J=5.6\text{Hz}$, 1H), 6.99 (m, 2H), 7.14-7.26 (m, 3H), 8.04 (s, 1H), 8.21 (s, 2H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 13.92, 39.98, 40.41, 44.48, 122.44 (d, $^1J=274.1\text{Hz}$), 126.06, 126.31, 126.74, 127.24, 128.71, 132.75 (d, $^2J=34.6\text{Hz}$), 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 $\text{C}_{20}\text{H}_{17}\text{F}_6\text{NO}_2\text{S}$ ($\text{M}+\text{Na}$) $^+$ 472.0776, found 472.0761.

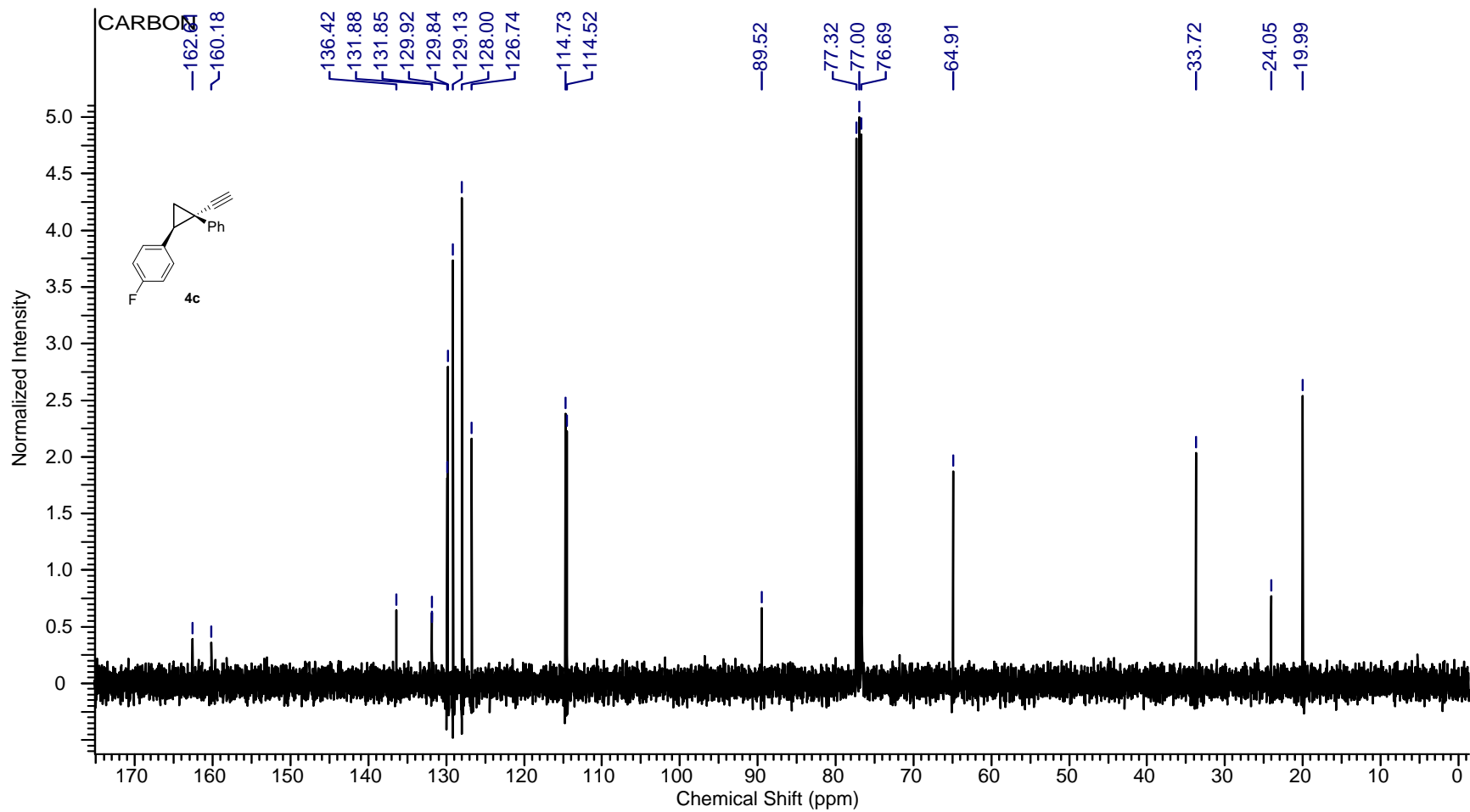


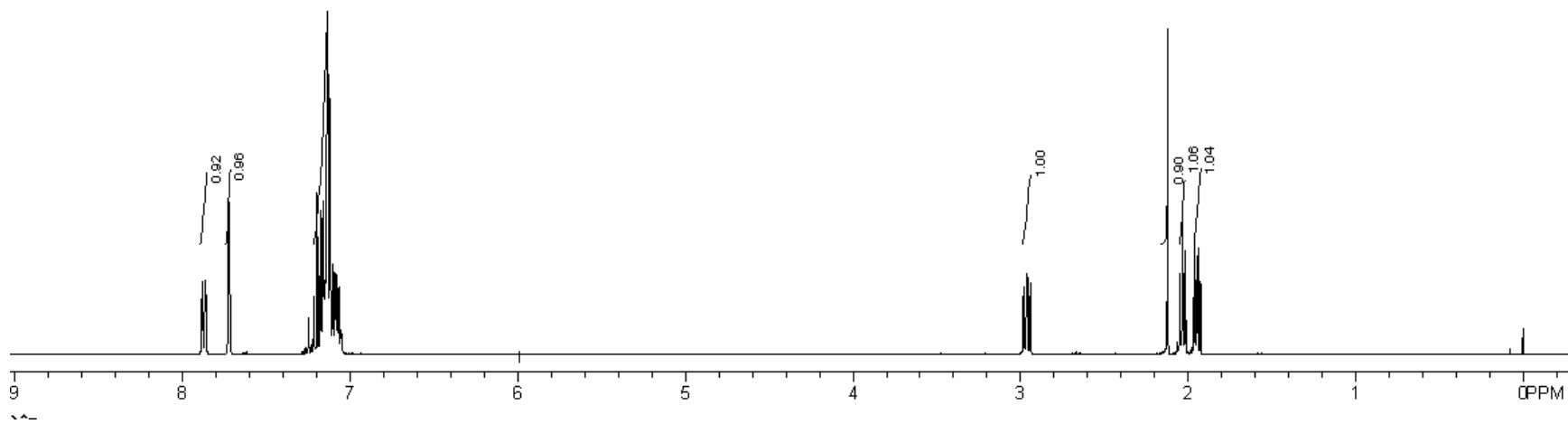
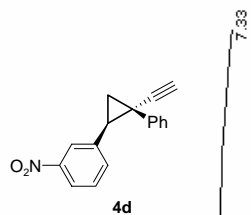


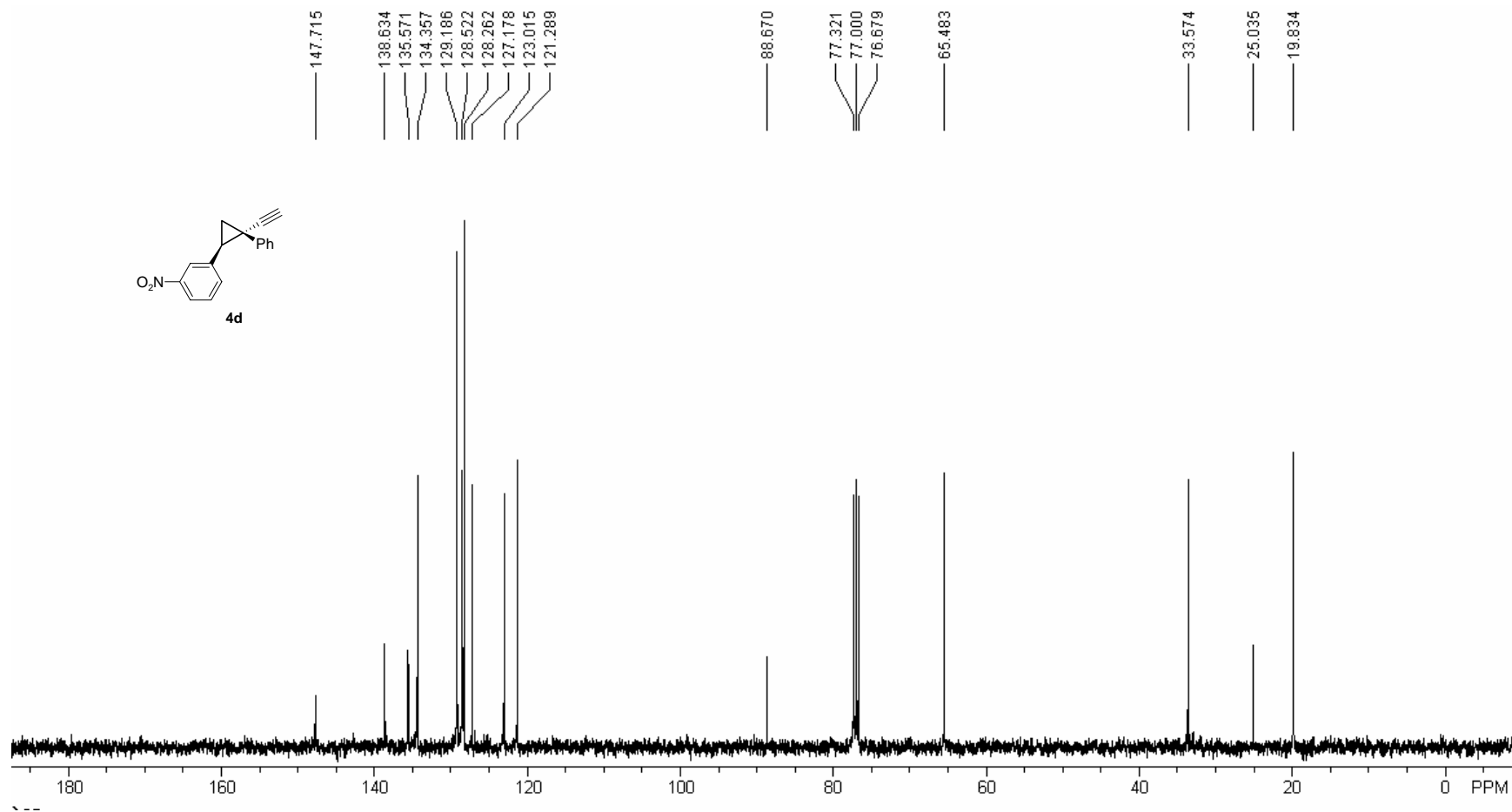


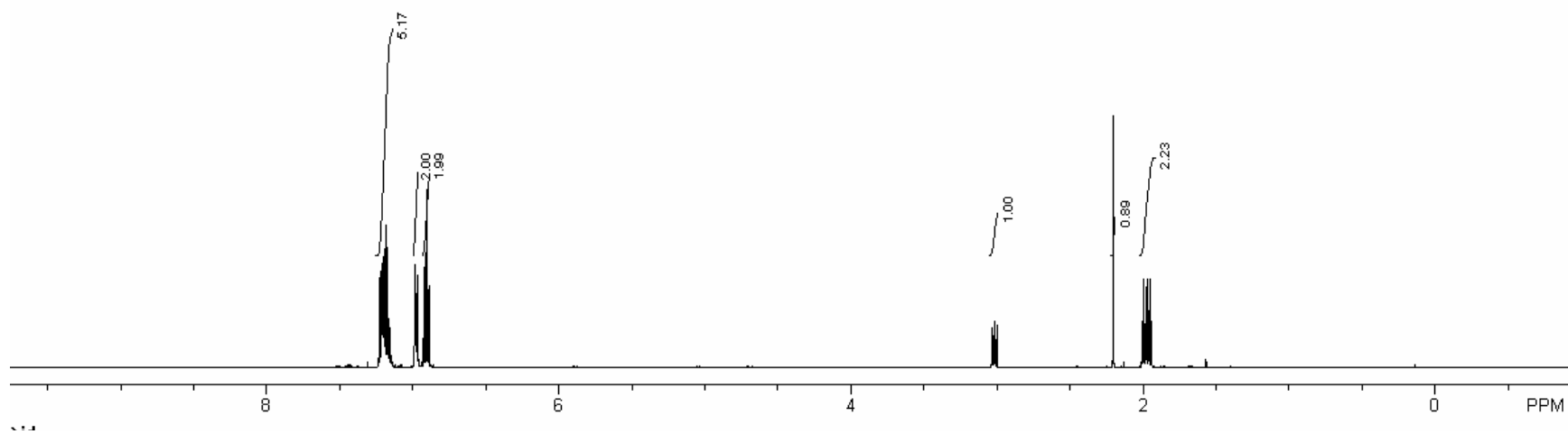
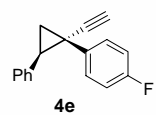


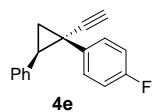












162.68
160.73
136.07
132.78
132.75
131.12
131.06
128.55
128.04
126.60
115.10
114.93

89.68
89.67
77.48
77.23
76.98
65.23

34.50
23.76
20.21

