Supporting Information

Phosphine-Catalyzed β′-Umpolung Addition of Nucleophiles to Activated α-Alkyl Allenes

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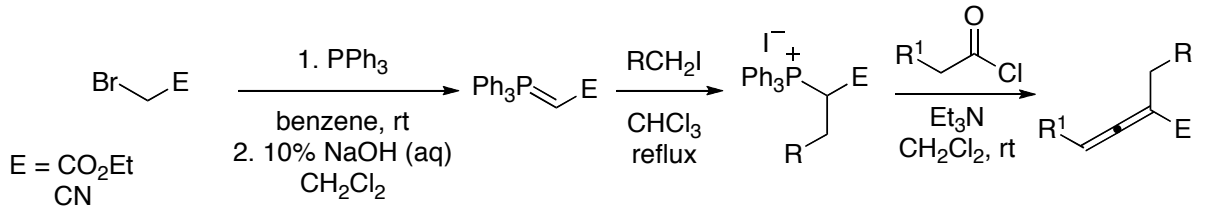
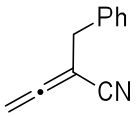
General Information

All reactions were performed under Ar atmospheres with dry solvents and anhydrous conditions, unless otherwise noted. Benzene was distilled from CaH_2. Reactions were monitored using thin layer chromatography (TLC) on 0.25-mm E. Merck silica gel plates (60F-254) and visualized under UV light or through anisaldehyde or permanganate staining. Flash column chromatography was performed using E. Merck silica gel 60 (230–400 mesh) and compressed air. IR spectra were recorded on a Perkin–Elmer pargon 1600 FT-IR spectrometer. NMR spectra were recorded using Bruker Avance-500, ARX-500, or ARX-400 instruments and calibrated using residual $CHCl_3$ as the internal reference (7.26 ppm for ^{1}H NMR; 77.00 ppm for ^{13}C NMR). Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ/ppm), multiplicity, coupling constant (Hz), and integration. Data for ^{13}C NMR spectra are reported in terms of chemical shift, with multiplicities and coupling constants (Hz) in the case of J_{CF} coupling. The following abbreviations are used for the multiplicities: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; br = broad; app = apparent. High-resolution matrix-assisted laser desorption/ionization (MALDI) mass spectra were recorded from a dihydroxybenzoic acid (DHB) matrix using an IonSpec Ultima 7T FT-ICR-MS instrument with internal calibration. Gas chromatography–coupled mass spectra (EI) were recorded using an Agilent 6890-5975 instrument.

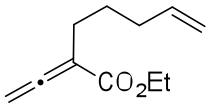
Synthesis of Activated α-Alkyl Allenes



Two new activated α-alkyl allenes were prepared in this study, using slightly modified literature procedures.[1b] The syntheses of the other allenoates have been reported previously.[1] The spectral data of the new allenes are reported below:



Yield: 61%; faint yellow oil; IR (film) ν_{max} 3064, 3030, 2988, 2219, 1967, 1496, 1454 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.38–7.25 (m, 5H), 5.24 (t, J = 2.4 Hz, 2H), 3.51 (t, J = 2.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 215.1, 136.1, 128.8 (2C), 128.7 (2C), 127.4, 115.0, 82.3, 80.9, 37.3; MS (MALDI) calcd for $C_{11}H_9Na$ $[M + Na]^+$ 176.08, found 176.00.



Yield: 78%; faint yellow oil; IR (film) ν_{max} 3076, 2979, 2932, 1967, 1940, 1711, 1261 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.77 (ddt, J = 8.0, 8.0, 4.0 Hz, 1H), 5.10 (d, J = 3.0 Hz, 2H), 4.95 (dd, J = 24.0, 12.0 Hz, 2H), 4.17 (q, J = 6.7 Hz, 2H), 2.24–2.18 (m, 2H), 2.09–2.03 (m, 2H), 1.53 (pentet, J = 6.0 Hz, 2H), 1.25 (t, J = 4.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 213.7, 167.2, 138.3, 114.7, 100.1, 80.0, 79.2, 60.9, 33.1, 27.2, 14.1; MS (MALDI) calcd for $C_{11}H_{16}O_2Na$ $[M + Na]^+$ 203.1, found 202.9.

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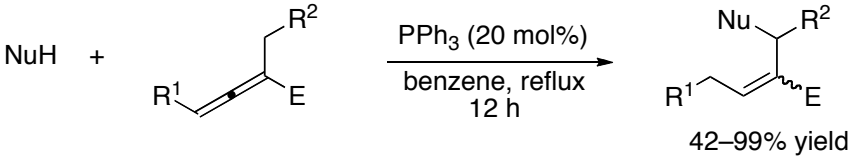
[1] (a) Bestman, H. J.; Hartun, H. *Angew. Chem.* **1963**, *75*, 297. (b) Runge, W.; Kresze, G; Ruch, E. *Justus Liebigs Annalen der Chemie* **1975**, *7–8*, 1361–1378. (c) Bertrand, M.; Zahra, J. P. *Tetrahedron Lett.* **1989**, *30*, 4117–4120. (b) Andrews, S.; Day, A.; Inwood, R. *J. Chem. Soc. (C),* **1969**, 2443–2449. (d) Yang, H.; Xu, B.; Hammond, G. *Org. Lett.* **2008**, *10*, 5589–5591. (e) Zhu, X; Lan, J; Kwon, O. *J. Am. Chem. Soc.* **2003**, *125*, 4716–4717. (f) Xu, S.; Zhou, L.; Ma, R.; Song, H.; He, Z. *Org. Lett.* **2010**, *12*, 544–547.

General Procedure for Phosphine-Catalyzed β′-Umpolung Addition

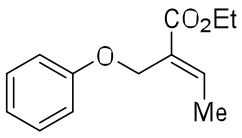


R^1 = H, Ph, 4-pentenyl, CO_2Et
R^2 = H, Me; EWG = CO_2Et, CN
NuH = ArOH, RR'NH, RCO_2H, $CH_2(CN)_2$, $RCH(CN)CO_2Et$, fufuryl alcohol, PhCH=NOH, PhSH

A round-bottom flask equipped with a stirrer bar and a condenser was flame-dried and left to cool under Ar. The pronucleophile (1.0 equiv) and the phosphine (0.2 equiv) were added to the flask. Distilled benzene was added via syringe. Finally, the allene (1.1 equiv) was weighed in a syringe, mixed with distilled benzene and added dropwise to the reaction mixture over 5 h. The reaction was left to proceed until the pronucleophile was consumed, typically 12 h (TLC, 6:1 hexane/EtOAc). The crude reaction mixture was concentrated and loaded onto a silica gel column and separated chromatographically (hexane/EtOAc, 6:1). In all cases, the product stained brightly with a standard permanganate stain.

Assignments of the geometries of the trisubstituted alkenes were made based on the chemical shift of the β-vinyl proton of the enoate,[2] and further confirmed through NOESY-NMR spectroscopic analysis of the selected compounds **1a**, **1c**, **1p**, **1q**, **1r 2f**, **3d**, **3f**, **3g**, **4**, ***E*-5c**, and ***Z*-5c**. See S23, S26, S39, S41, S43, S49, S56, S58, S60, S63, S67, and S69 for NOESY-NMR spectra.

Characterization of β′-Umpolung Addition Products

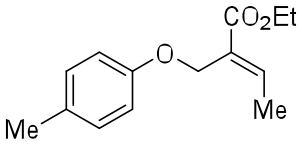


1a

Yield: >99%; clear oil; IR (film) ν_{max} 3062, 3039, 2981, 2905, 1713, 1599, 1284, 1236, 1072,

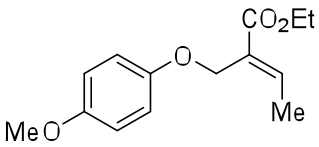
[2] Nair, M. D.; Adams, R. *J. Am. Chem. Soc.* **1960**, *82*, 3786–3787.

1029 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.31–7.27 (m, 2H), 7.22 (q, *J* = 6.7 Hz, 1H), 6.97–6.95 (m, 3H), 4.79 (s, 2H), 4.23 (q, *J* = 7.2 Hz, 2H), 1.96 (d, *J* = 7.0 Hz, 3H), 1.29 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.5, 158.6, 144.2, 129.3 (2C), 128.9, 120.8, 114.7 (2C), 61.5, 60.6, 14.6, 14.1; MS (MALDI) calcd for $C_{13}H_{16}O_3Na$ $[M + Na]^+$ 243.09, found 243.10.



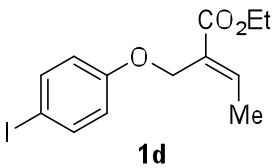
1b

Yield: 97%; clear oil; IR (film) ν_{max} 3029, 2981, 1713, 1510, 1283, 1140, 1015, 1071 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.21 (q, *J* = 6.7 Hz, 1H), 7.09 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 1H), 4.77 (s, 2H), 4.24 (q, *J* = 6.7 Hz, 2H), 2.30 (s, 3H), 1.95 (d, *J* = 8.0 Hz, 3H), 1.29 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.6, 156.6, 144.2, 144.1, 130.2, 129.8, 129.2, 114.8 (2C), 61.9, 60.7, 20.4, 14.7, 14.2; MS (MALDI) calcd for $C_{14}H_{18}O_3Na$ $[M + Na]^+$ 257.11, found 257.18.



1c

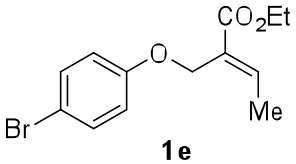
Yield: 92%; clear oil; IR (film) ν_{max} 2882, 2951, 2906, 2834, 1713, 1507, 1284, 1227 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.18 (q, *J* = 8.0 Hz, 1H), 6.86 (dd, *J* = 22.0, 9.0 Hz, 4H), 4.73 (s, 2H), 4.22 (q, *J* = 7.0 Hz, 2H), 3.75 (s, 3H), 1.93 (d, *J* = 8.0 Hz, 3H), 1.28 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 154.1, 152.9, 144.1, 144.0, 129.2, 116.1, 62.6, 60.7, 55.6, 14.7, 14.2; MS (MALDI) calcd for $C_{14}H_{18}O_4Na$ $[M + Na]^+$ 273.11, found 273.13.



1d

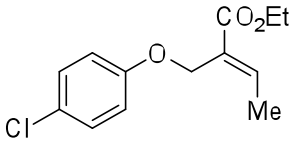
Yield: 69%; clear oil; IR (film) ν_{max} 2978, 1705, 1485, 1279, 1230, 1140 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 9.0 Hz, 2H), 7.20 (q, *J* = 7.0 Hz, 1H), 6.73 (d, *J* = 9.0 Hz, 2H), 4.75

(s, 2H), 4.22 (q, *J* = 7.0 Hz, 2H), 1.94 (d, *J* = 7.0 Hz, 3H), 1.28 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 158.6, 144.5, 138.1, 129.1, 128.7, 117.3 (2C), 83.0, 61.8, 60.8, 14.7, 14.2; MS (MALDI) calcd for $C_{13}H_{15}O_3INa$ $[M + Na]^+$ 368.99, found 369.01.



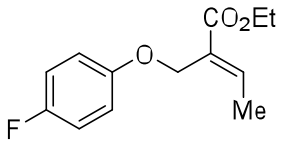
1e

Yield: 72%; clear oil; IR (film) ν_{max} 2919, 2915, 2848, 1708, 1487, 1228 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 9.0 Hz, 2H), 7.21 (q, *J* = 7.0 Hz, 1H), 6.84 (d, *J* = 9.0 Hz, 2H), 4.75 (s, 2H), 4.22 (q, *J* = 7.0 Hz, 2H), 1.94 (d, *J* = 7.0 Hz, 3H), 1.28 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 157.9, 144.5, 132.2 (2C), 128.7, 116.7 (2C), 113.1, 62.0, 60.8, 14.7, 14.2; MS (MALDI) calcd for $C_{13}H_{15}O_3BrNa$ $[M + Na]^+$ 321.01, found 321.04.



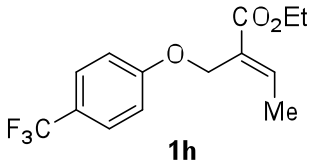
1f

Yield: 62%; clear oil; IR (film) ν_{max} 2980, 2932, 1707, 1491, 1280, 1234, 1141, 1004 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26–7.17 (m, 3H), 6.88 (d, *J* = 9.0 Hz, 2H), 4.75 (s, 2H), 4.22 (q, *J* = 7.0 Hz, 2H), 1.93 (d, *J* = 7.0 Hz, 3H), 1.27 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 157.4, 144.4, 129.2 (2C), 128.7, 125.8, 116.2 (2C), 62.1, 60.8, 14.7, 14.2; MS (MALDI) calcd for $C_{13}H_{15}O_3ClNa$ $[M + Na]^+$ 277.06, found 277.26.



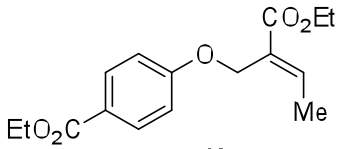
1g

Yield: 78%; clear oil; IR (film) ν_{max} 2982, 1713, 1505, 1283, 1212, 1141, 1012 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (q, *J* = 7.0 Hz, 1H), 6.98–6.87 (m, 4H), 4.74 (s, 2H), 4.22 (q, *J* = 7.0 Hz, 2H), 1.94 (d, *J* = 7.0 Hz, 3H), 1.28 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 158.6, 156.2, 154.9, 144.3, 129.1, 128.9 116.1 (d, J_{FC} = 8.0 Hz), 115.8 (2C), 115.6 (2C), 62.5, 60.8, 14.7, 14.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ –124.27; MS (MALDI) calcd for $C_{13}H_{15}O_3FNa$ $[M + Na]^+$ 261.09, found 261.13.



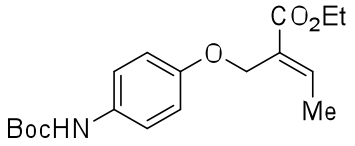
1h

Yield: 73%; clear oil; IR (film) ν_{max} 2983, 2937, 1712, 1327, 1253, 1110, 1068 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 9.0 Hz, 2H), 7.23 (q, *J* = 7.0 Hz, 1H), 7.01 (d, *J* = 9.0 Hz, 2H), 4.83 (s, 2H), 4.23 (q, *J* = 7.0 Hz, 2H), 1.95 (d, *J* = 7.0 Hz, 3H), 1.28 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 161.2, 144.7, 128.4, 126.8 (d, J_{FC} = 4.0 Hz), 123.2, 121.1, 114.7 (2C), 61.8, 60.9, 14.7, 14.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.10; MS (MALDI) calcd for $C_{14}H_{15}O_3F_3Na$ $[M + Na]^+$ 311.08, found 311.19.

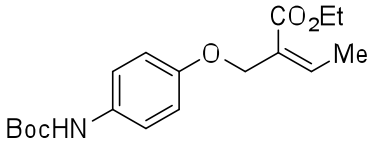


1i

Yield: 90%; clear oil; IR (film) ν_{max} 2981, 2934, 2907, 1717, 1606, 1510, 1276, 1249, 1168, 1103, 1019 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 9.0 Hz, 2H), 7.22 (q, *J* = 7.0 Hz, 1H), 7.95 (d, *J* = 9.0 Hz, 2H), 4.83 (s, 2H), 4.33 (q, *J* = 7.0 Hz, 2H), 4.22 (q, *J* = 7.0 Hz, 2H), 1.95 (d, *J* = 7.0 Hz, 3H), 1.37 (t, *J* = 7.0 Hz, 3H), 1.27 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 162.4, 144.7, 144.6, 131.4 (2C), 129.1, 128.5 (2C), 123.1, 114.3, 61.8, 60.8, 60.6, 14.7, 14.3; MS (MALDI) calcd for $C_{16}H_{20}O_5Na$ $[M + Na]^+$ 315.12, found 315.23.



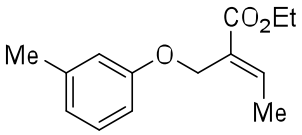
***E*-1j**



***Z*-1j**

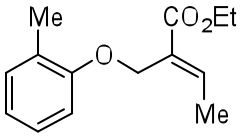
Yield: 89%; 4:1 E:Z selectivity; clear oil; IR (film) ν_{max} 3347, 2979, 2933, 1717, 1703, 1520, 1226, 1160, 1053, 1011 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$), major: δ 7.24 (s, 2H), 7.18 (q, *J* = 8.0 Hz, 1H), 6.88 (d, *J* = 9.0 Hz, 2H), 6.39 (s, 1H), 4.74 (s, 2H), 4.21 (q, *J* = 8.0 Hz, 2H), 1.92 (d, *J* = 7.0 Hz, 3H), 1.50 (s, 9H), 1.27 (t, *J* = 7.0 Hz, 3H); minor: δ 7.24 (s, 2H), 6.84 (d, *J* = 9.0 Hz, 2H), 6.44 (q, *J* = 7.0 Hz, 1H), 4.62 (s, 2H), 4.24 (q, *J* = 7.0 Hz, 2H), 2.08 (d, *J* = 7.0 Hz, 3H), 1.50 (s, 9H), 1.29 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.5, 154.7, 153.0, 144.1, 140.8, 131.6, 128.9, 120.3, 115.3, 80.1, 69.2, 62.1, 60.6, 60.2, 28.2, 15.5, 14.6, 14.1; MS

(MALDI) calcd for $C_{18}H_{25}O_5NNa$ $[M + Na]^+$ 358.16, found 358.22.



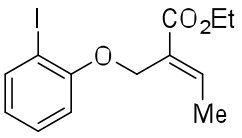
1k

Yield: 95%; clear oil; IR (film) ν_{max} 2980, 1714, 1285, 1260, 1234, 1140, 1038 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.22 (q, *J* = 7.0 Hz, 1H), 7.18 (t, *J* = 6.0 Hz, 1H), 6.79–6.77 (m, 3H), 4.78 (s, 2H), 4.24 (q, *J* = 6.7 Hz, 2H), 2.34 (s, 3H), 1.95 (d, *J* = 8.0 Hz, 3H), 1.30 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.6, 158.8, 144.2, 139.4, 129.1 (2C), 121.7, 115.7, 111.7, 61.6, 60.7, 21.5, 14.7, 14.2; MS (MALDI) calcd for $C_{14}H_{18}O_3Na$ $[M + Na]^+$ 257.11, found 257.38.



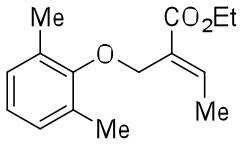
1l

Yield: 96%; clear oil; IR (film) ν_{max} 2980, 2946, 1714, 1495, 1282, 1240, 1120, 1016 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.21 (q, *J* = 7.0 Hz, 1H), 7.18–7.13 (m, 2H), 6.95 (d, *J* = 8.0 Hz, 1H), 6.88 (dt, *J* = 1.0, 8.0 Hz, 1H), 4.80 (s, 2H), 4.24 (q, *J* = 6.7 Hz, 2H), 2.20 (s, 3H), 1.96 (d, *J* = 8.0 Hz, 3H), 1.30 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.7, 156.9, 143.9, 130.6, 129.1, 127.2, 126.7, 120.6, 111.8, 61.9, 60.7, 16.1, 14.7, 14.2; MS (MALDI) calcd for $C_{14}H_{18}O_3Na$ $[M + Na]^+$ 257.11, found 257.31.



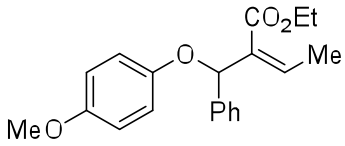
1m

Yield: 91%; clear oil; IR (film) ν_{max} 3060, 2979, 2848, 1713, 1471, 1275, 1230, 1017 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 1.0, 7.0 Hz, 1H), 7.29 (dd, *J* = 1.0, 7.0 Hz, 1H), 7.23 (q, *J* = 7.0 Hz, 1H), 6.96 (dd, *J* = 1.0, 7.0 Hz, 1H), 6.71 (dt, *J* = 1.0, 7.0 Hz, 1H), 4.86 (s, 2H), 4.24 (q, *J* = 7.0 Hz, 2H), 2.00 (d, *J* = 7.0 Hz, 3H), 1.29 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 157.3, 144.9, 139.4, 129.4, 128.5, 122.8, 113.2, 86.9, 63.1, 60.8, 15.1, 14.2; MS (MALDI) calcd for $C_{13}H_{15}O_3INa$ $[M + Na]^+$ 368.99, found 369.12.



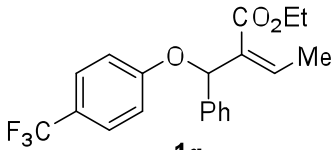
1n

Yield: 66%; clear oil; IR (film) ν_{max} 2980, 2957, 1717, 1280, 1262, 1230, 1195 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.20 (q, *J* = 7.0 Hz, 1H), 7.02–6.90 (m, 3H), 4.60 (s, 2H), 4.26 (q, *J* = 7.0 Hz, 2H), 2.34 (s, 6H), 1.96 (d, *J* = 7.0 Hz, 3H), 1.32 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 155.5, 143.8, 143.7, 131.2, 129.8, 128.8, 123.9, 64.9, 60.7, 16.4, 14.6, 14.2; MS (MALDI) calcd for $C_{15}H_{20}O_3Na$ $[M + Na]^+$ 271.13, found 271.21.



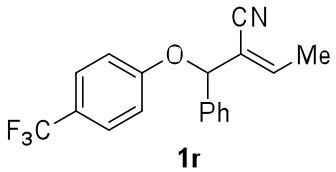
1p

Yield: 89%; clear oil; IR (film) ν_{max} 2916, 2848, 1715, 1506, 1224, 1035 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.40–7.26 (m, 5H), 6.84 (d, *J* = 9.0 Hz, 2H), 6.75 (d, *J* = 9.0 Hz, 2H), 6.20 (dq, *J* = 6.0, 1.0 Hz, 1H), 5.99 (s, 1H), 4.20 (q, *J* = 7.0 Hz, 2H), 3.73 (s, 3H), 2.01 (dd, *J* = 6.0, 1.0 Hz, 3H), 1.23 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.1, 139.5, 138.3, 133.3, 128.4 (2C), 127.8, 127.4 (2C), 117.7, 117.1 (2C), 114.4 (3C), 79.9, 60.4, 55.6, 15.5, 14.1; MS (MALDI) calcd for $C_{20}H_{22}O_4Na$ $[M + Na]^+$ 349.14, found 349.20.



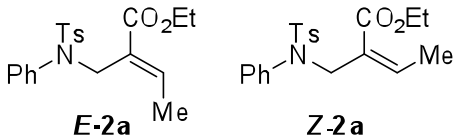
1q

Yield: 97%; clear oil; IR (film) ν_{max} 2979, 2916, 2845, 1716, 1614, 1515, 1324, 1241, 1110, 1067 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 9.0 Hz, 2H), 7.39–7.30 (m, 5H), 6.97 (d, *J* = 9.0 Hz, 2H), 6.17 (q, *J* = 7.0 Hz, 1H), 6.16 (s, 1H), 4.22 (q, *J* = 7.0 Hz, 2H), 2.02 (d, *J* = 7.0 Hz, 3H), 1.23 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 160.1, 139.0, 138.3, 132.5, 128.5 (3C), 128.1, 127.1 (3C), 126.7, 126.6, 115.6 (2C), 79.0, 60.5, 15.5, 14.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.36; MS (MALDI) calcd for $C_{20}H_{19}O_3F_3Na$ $[M + Na]^+$ 387.11, found 387.13.



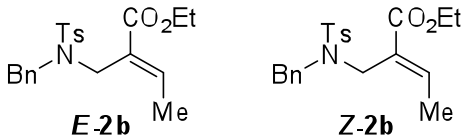
1r

Yield: 88%; clear oil; IR (film) ν_{max} 3068, 3035, 2916, 2222, 1614, 1515, 1328, 1243, 1111, 1068 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 9.0 Hz, 2H), 7.42–7.36 (m, 5H), 6.97 (d, *J* = 9.0 Hz, 2H), 6.53 (dq, *J* = 1.0, 7.0 Hz, 1H), 5.76 (s, 1H), 2.05 (dd, *J* = 1.0, 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 145.0, 136.6, 129.13, 129.10, 127.0, 126.97, 126.94, 126.5 (2C), 117.45, 117.43, 117.0, 116.1 (2C), 115.3, 79.8, 17.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.42; MS (MALDI) calcd for $C_{18}H_{14}OF_3Na$ $[M + Na]^+$ 340.09, found 340.13.



***E*-2a** ***Z*-2a**

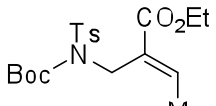
Yield: 94%; 5:2 E:Z selectivity; clear oil; IR (film) ν_{max} 2980, 2933, 1712, 1351, 1258, 1165, 1093 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$), major: δ 7.47 (d, *J* = 6.0 Hz, 2H), 7.25–7.21 (m, 5H), 7.00–6.94 (m, 3H), 4.50 (s, 2H), 4.00 (q, *J* = 7.0 Hz, 2H), 2.42 (s, 3H), 1.88 (d, *J* = 7.0 Hz, 3H), 1.12 (t, *J* = 7.0 Hz, 3H); minor: δ 7.49 (d, *J* = 6.0 Hz, 2H), 7.25–7.21 (m, 5H), 7.00–6.94 (m, 2H), 6.26 (q, *J* = 7.0 Hz, 1H), 4.38 (s, 2H), 4.11 (q, *J* = 7.0 Hz, 2H), 2.41 (s, 3H), 1.92 (d, *J* = 7.0 Hz, 3H), 1.22 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 166.3, 143.9, 143.47, 143.41, 141.3, 139.3, 138.6, 135.5, 134.7, 129.39 (4C), 129.09 (2C), 129.09 (2C), 128.87 (2C), 128.58 (2C), 127.9 (4C), 127.82, 127.73, 127.65, 127.64, 60.63, 60.36, 53.4, 45.3, 30.9, 21.5, 15.6, 14.7, 14.1, 14.0; MS (MALDI) calcd for $C_{20}H_{23}O_4NSNa$ $[M + Na]^+$ 396.12, found 396.68.



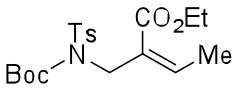
***E*-2b** ***Z*-2b**

Yield: 94%; 5:2 E:Z selectivity; clear oil; IR (film) ν_{max} 3030, 2980, 2929, 1701, 1340, 1159, 1095 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$), major: δ 7.67 (d, *J* = 5.0 Hz, 2H), 7.30–7.19 (m, 7H), 6.77 (q, *J* = 7.0 Hz, 1H), 4.35 (s, 2H), 4.07 (s, 2H), 3.96 (q, *J* = 7.0 Hz, 2H), 2.47 (s, 3H), 1.81 (d, *J* = 7.0 Hz, 3H), 1.15 (t, *J* = 7.0 Hz, 3H); minor: δ 7.69 (d, *J* = 5.0 Hz, 2H), 7.30–7.19 (m,

7H), 6.13 (q, *J* = 7.0 Hz, 1H), 4.38 (s, 2H), 4.02 (q, *J* = 7.0 Hz, 2H), 3.96 (s, 2H), 2.43 (s, 3H), 1.85 (d, *J* = 7.0 Hz, 3H), 1.20 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 166.4, 144.1, 143.13, 143.10, 141.5, 137.3, 136.2, 129.59 (2C), 129.56 (2C), 128.45 (2C), 128.41 (2C), 128.1 (2C), 127.8 (2C), 127.6, 127.5, 127.3, 127.2 (4C), 127.1, 60.5, 60.3, 52.5, 50.1, 43.8, 21.5, 15.6, 14.6, 14.1; MS (MALDI) calcd for $C_{21}H_{25}O_4NSNa$ $[M + Na]^+$ 410.14, found 410.81.

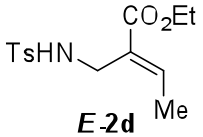


***E*-2c**

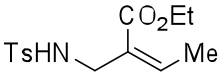


***Z*-2c**

Yield: 83%; 2:1 E:Z selectivity; clear oil; IR (film) ν_{max} 2981, 2930, 1732, 1359, 1282, 1257, 1167, 1150, 1089 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$), major: δ 7.77 (d, *J* = 9.0 Hz, 2H), 7.28 (d, *J* = 9.0 Hz, 2H), 7.26 (q, *J* = 7.0 Hz, 1H), 4.64 (s, 2H), 4.18 (q, *J* = 7.0 Hz, 2H), 2.42 (s, 3H), 2.04 (d, *J* = 7.0 Hz, 3H), 1.32 (s, 9H), 1.26 (t, *J* = 7.0 Hz, 3H); minor: δ 7.72 (d, *J* = 9.0 Hz, 2H), 7.24 (d, *J* = 9.0 Hz, 2H), 7.06 (q, *J* = 7.0 Hz, 1H), 4.76 (s, 2H), 4.07 (q, *J* = 7.0 Hz, 2H), 2.40 (s, 3H), 2.96 (d, *J* = 7.0 Hz, 3H), 1.36 (s, 9H), 1.14 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 150.7, 144.2, 143.8, 142.3, 138.7, 137.4, 137.2, 129.1 (2C), 129.0 (2C), 128.8 (2C), 128.08 (2C), 128.02 (2C), 127.9 (2C), 84.3, 84.2, 60.4, 60.3, 48.4, 41.9, 27.85 (3C), 27.82 (3C), 21.59, 21.55, 15.5, 14.3, 14.1, 14.0; MS (MALDI) calcd for $C_{19}H_{27}O_6NSNa$ $[M + Na]^+$ 420.14, found 420.20.

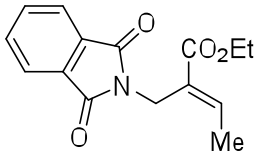


***E*-2d**



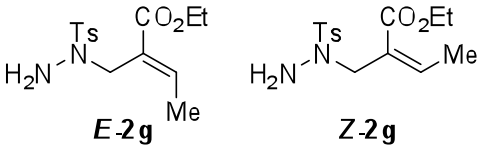
***Z*-2d**

Yield: 53%; 1:1.75 E:Z selectivity; clear oil; IR (film) ν_{max} 3288, 2982, 2917, 1717, 1328, 1287, 1228, 1160, 1093 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$), major: δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 6.24 (q, *J* = 7.0 Hz, 1H), 5.01 (t, *J* = 7.0 Hz, 1H), 4.14 (q, *J* = 7.0 Hz, 2H), 3.73 (d, *J* = 6.0 Hz, 2H), 2.41 (s, 3H), 1.90 (d, *J* = 7.0 Hz, 3H), 1.25 (t, *J* = 6.0 Hz, 3H); minor: δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 6.87 (q, *J* = 7.0 Hz, 1H), 5.14 (t, *J* = 7.0 Hz, 1H), 4.12 (q, *J* = 7.0 Hz, 2H), 3.81 (d, *J* = 6.0 Hz, 2H), 2.41 (s, 3H), 1.83 (d, *J* = 7.0 Hz, 3H), 1.23 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 143.1, 142.8, 141.5, 137.5, 129.5 (4C), 127.3 (2C), 126.9 (2C), 126.9 (4C), 60.6, 60.4, 47.3, 38.9, 21.3, 15.6, 14.2, 14.05, 14.02; MS (MALDI) calcd for $C_{14}H_{19}O_4NSNa$ $[M + Na]^+$ 320.09, found 320.25.



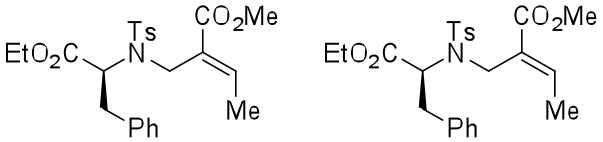
2f

Yield: 71%; clear oil; IR (film) ν_{max} 2981, 2916, 2848, 1771, 1716, 1396, 1256, 1056 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 3.0, 6.0 Hz, 2H), 7.69 (dd, *J* = 3.0. 6.0 Hz, 2H), 7.13 (q, *J* = 7.0 Hz, 1H), 4.56 (s, 2H), 4.15 (q, *J* = 7.0 Hz, 2H), 2.04 (d, *J* = 7.0 Hz, 3H), 1.22 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7 (2C), 166.3, 143.0, 133.8 (2C), 132.1 (2C), 127.2, 123.1 (2C), 60.7, 33.8, 14.6, 14.1; MS (MALDI) calcd for $C_{15}H_{15}O_4NNa$ $[M + Na]^+$ 296.09, found 296.13.



***E*-2g** ***Z*-2g**

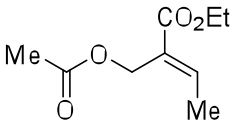
Yield: 57%; 1.5:1 E:Z selectivity; clear oil; IR (film) ν_{max} 2918, 2849, 1716, 1317, 1272, 1177, 1136, 1086 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$), major: δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.22 (q, *J* = 7.0 Hz, 1H), 4.23 (s, 2H), 3.95 (q, *J* = 7.0 Hz, 2H), 2.43 (s, 3H), 1.83 (d, *J* = 7.0 Hz, 3H), 1.13 (t, *J* = 7.0 Hz, 3H); minor: δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 6.28 (q, *J* = 7.0 Hz, 1H), 4.05 (s, 2H), 3.99 (q, *J* = 7.0 Hz, 2H), 2.43 (s, 3H), 2.07 (d, *J* = 7.0 Hz, 3H), 1.17 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 165.1, 147.7, 146.1, 144.6, 144.5, 135.8, 135.8, 135.4, 129.5 (2C), 129.4 (2C), 128.66 (2C), 128.62 (2C), 122.0, 121.2, 60.9, 60.6, 60.2, 53.6, 29.5, 21.5, 16.3, 15.2, 13.9; MS (MALDI) calcd for $C_7H_{15}O_2N_2$ $[M + H – Ts]^+$ 159.11, found 158.98.



***E*-2h** ***Z*-2h**

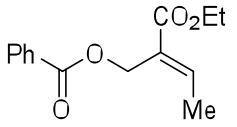
Yield: 92%; 1:1.2 E:Z selectivity; clear oil; IR (film) ν_{max} 3030, 2982, 2952, 1742, 1717, 1346, 1257, 1222, 1156, 1093, 1031 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$), major: δ 7.36 (d, *J* = 8.0 Hz, 2H), 7.27–716 (m, 7H), 6.25 (q, *J* = 7.0 Hz, 1H), 4.76 (dd, *J* = 8.0, 6.0 Hz, 2H), 4.16 (d, *J* = 7.0 Hz, 2H), 4.06 (dq, *J* = 3.0, 7.0 Hz, 2H), 3.43 (s, 3H), 2.99 (dd, *J* = 8.0, 6.0 Hz, 1H), 2.91 (dd, *J* =

8.0, 6.0 Hz, 1H), 2.40 (s, 3H), 1.85 (d, *J* = 7.0 Hz, 3H), 1.27 (t, *J* = 7.0 Hz, 3H); minor: δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.27–716 (m, 7H), 6.94 (q, *J* = 7.0 Hz, 1H), 4.65 (dd, *J* = 8.0, 6.0 Hz, 2H), 4.24 (d, *J* = 7.0 Hz, 2H), 4.16 (q, *J* = 7.0 Hz, 2H), 3.53 (s, 3H), 3.40 (dd, *J* = 8.0, 6.0 Hz, 1H), 3.26 (dd, *J* = 8.0, 6.0 Hz, 1H), 2.40 (s, 3H), 1.91 (d, *J* = 7.0 Hz, 3H), 1.22 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5 (2C), 170.4, 166.6, 166.5, 144.0, 143.4 (2C), 143.2, 141.0, 137.8, 137.5, 137.0, 136.9 (2C), 129.4 (2C), 129.2 (2C), 128.4 (2C), 128.3 (2C), 127.9 (2C), 127.7 (2C) 127.6 (4C), 126.7, 126.5, 117.6, 61.6, 61.0, 60.6, 60.4, 51.9, 47.9, 42.0, 36.5, 36.2, 21.5, 15.6, 14.6, 14.2, 14.1; MS (MALDI) calcd for $C_{24}H_{29}O_6NSNa$ $[M + Na]^+$ 482.16, found 482.47.



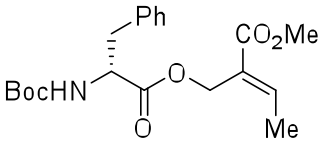
3a

Yield: 97%; clear oil; IR (film) ν_{max} 2982, 1740, 1716, 1248, 1233, 1143, 1073, 1026 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (q, *J* = 7.0 Hz, 1H), 4.86 (s, 2H), 4.22 (q, *J* = 7.0 Hz, 2H), 2.04 (s, 3H), 1.93 (d, *J* = 7.0 Hz, 3H), 1.29 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 166.2, 144.0, 128.2, 60.6, 57.7, 20.7, 14.4, 14.1; MS (MALDI) calcd for $C_9H_{14}O_4Na$ $[M + Na]^+$ 209.07, found 209.05.



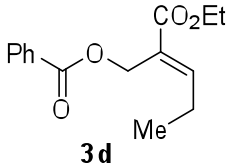
3b

Yield: 95%; clear oil; IR (film) ν_{max} 2981, 2925, 1718, 1270, 1109, 1069 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.0 Hz, 2H), 7.52 (t, *J* = 8.0 Hz, 1H), 7.40 (t, *J* = 8.0 Hz, 2H), 7.19 (q, *J* = 7.0 Hz, 1H), 5.11 (s, 2H), 4.22 (q, *J* = 7.0 Hz, 2H), 1.98 (d, *J* = 7.0 Hz, 3H), 1.27 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 144.2 (2C), 132.8, 130.0, 129.5 (2C), 128.2 (3C), 60.6, 58.1, 14.5, 14.1; MS (MALDI) calcd for $C_{14}H_{16}O_4Na$ $[M + Na]^+$ 271.09, found 271.14.



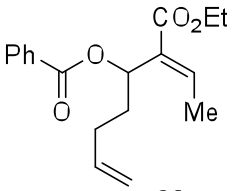
3c

Yield: 96%; clear oil; IR (film) ν_{max} 3368, 2978, 2932, 1712, 1497, 1366, 1284, 1250, 1169, 1072, 1020 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.28–7.20 (m, 3H), 7.16 (q, *J* = 7.0 Hz, 1H), 7.12 (d, *J* = 7.0 Hz, 2H), 4.90 (q, *J* = 10.0 Hz, 2H), 4.76 (dd, *J* = 184.0, 7.0 Hz, 1H), 4.22 (q, *J* = 7.0 Hz, 2H), 3.06 (dd, *J* = 27.0, 6.0 Hz, 2H), 1.89 (d, *J* = 7.0 Hz, 3H), 1.40 (s, 9H), 1.29 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.4, 165.9, 154.9, 144.7, 135.8, 129.2 (3C), 128.3 (2C), 127.6, 126.8, 60.7, 58.4, 54.1, 38.1, 28.1 (3C), 14.5, 14.1; MS (MALDI) calcd for $C_{21}H_{29}O_6NNa$ $[M + Na]^+$ 414.18, found 414.18.



3d

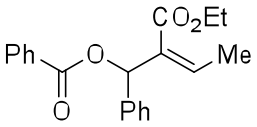
Yield: 90%; clear oil; IR (film) ν_{max} 2975, 2935, 1716, 1267, 1234, 1109, 1069, 1025 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.0 Hz, 2H), 7.56–7.52 (m, 1H), 7.44–7.40 (m, 2H), 7.10 (t, *J* = 7.0 Hz, 1H), 5.10 (s, 2H), 4.24 (q, *J* = 7.0 Hz, 2H), 2.39 (quintet, *J* = 7.0 Hz, 2H), 1.29 (t, *J* = 7.0 Hz, 3H), 1.10 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 166.3, 150.8, 132.2 (2C), 129.6 (3C), 128.3 (2C), 60.8, 58.5, 22.2, 14.2, 13.2; MS (MALDI) calcd for $C_{15}H_{18}O_4Na$ $[M + Na]^+$ 285.11, found 285.29.



3f

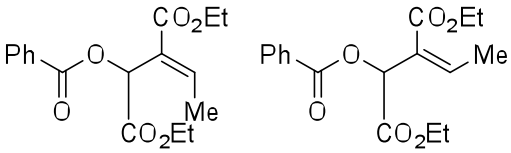
Yield: 85%; clear oil; IR (film) ν_{max} 3072, 2979, 2916, 1720, 1716, 1450, 1262, 1104 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.06–8.03 (m, 2H), 7.57–7.52 (m, 1H), 7.45–7.41 (m, 2H), 7.02 (q, *J* = 7.0 Hz, 1H), 6.00 (dd, *J* = 7.0, 6.0 Hz, 1H), 5.89–5.75 (m, 1H), 5.06–4.98 (m, 2H), 4.25–4.19 (m, 2H), 2.28–2.10 (m, 2H), 2.01 (d, *J* = 7.0 Hz, 3H), 2.05–1.92 (m, 2H), 1.30 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 165.7, 141.5, 137.4, 132.9, 131.7, 130.2, 129.6 (2C), 128.3, 115.3, 115.2, 70.4, 60.5, 32.5, 30.0, 14.6, 14.2; MS (MALDI) calcd for $C_{18}H_{22}O_4Na$ [M +

Na]$^+$ 325.14, found 325.13.



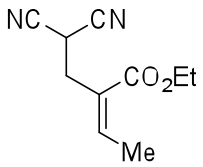
3g

Yield: 95%; clear oil; IR (film) ν_{max} 2982, 2916, 2848, 1721, 1263, 1219, 1095 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.0 Hz, 2H), 7.56 (t, *J* = 7.0 Hz, 1H), 7.46–7.28 (m, 8H), 6.90 (s, 1H), 6.27 (q, *J* = 7.0 Hz, 1H), 4.15 (q, *J* = 7.0 Hz, 2H), 2.07 (d, *J* = 7.0 Hz, 3H), 1.18 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 165.0, 139.0, 138.3, 132.9, 132.4, 130.0, 129.6 (2C), 128.2 (3C), 127.9 (2C), 127.3 (2C), 75.1, 60.2, 15.4, 13.9; MS (MALDI) calcd for $C_{20}H_{20}O_4Na$ [M + Na]$^+$ 347.12, found 347.80.



***E*-3h** ***Z*-3h**

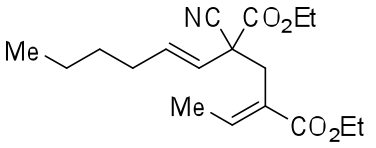
Yield: 96%; 1:1.5 E:Z selectivity; clear oil; IR (film) ν_{max} 2983, 2939, 2907, 1757, 1728, 1451, 1369, 1266, 1215, 1178, 1108, 1070, 1028 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$), major: δ 8.07–8.04 (m, 2H), 7.50 (t, *J* = 6.0 Hz, 1H), 7.41 (t, *J* = 8.0 Hz, 2H), 6.60 (q, *J* = 7.0 Hz, 1H), 6.07 (s, 1H), 4.27–19 (m, 4H), 2.14 (d, *J* = 7.0 Hz, 3H), 1.29 (t, *J* = 7.0 Hz, 3H), 1.24 (t, *J* = 7.0 Hz, 3H); minor: δ 8.07–8.04 (m, 2H), 7.50 (t, *J* = 6.0 Hz, 1H), 7.41 (t, *J* = 8.0 Hz, 2H), 7.24 (q, *J* = 7.0 Hz, 1H), 6.48 (s, 1H), 4.27–4.19 (m, 4H), 2.04 (d, *J* = 7.0 Hz, 3H), 1.29 (t, *J* = 7.0 Hz, 3H), 1.23 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 165.4, 165.2, 165.0, 145.28, 145.22, 133.34 (2C), 133.32 (2C), 129.9 (3C), 129.8 (2C), 129.48, 129.45, 128.39, 128.30 (4C), 127.6 (2C), 73.3, 66.6, 61.7, 61.0, 60.7, 15.9, 14.7, 14.19, 14.16, 14.06; MS (MALDI) calcd for $C_{17}H_{20}O_6Na$ [M + Na]$^+$ 343.11, found 343.13.



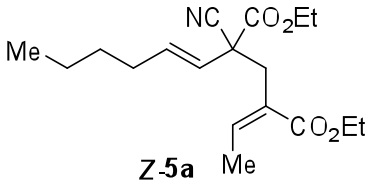
4

Yield: 86%; clear oil; IR (film) ν_{max} 2984, 2916, 2256, 1711, 1245 cm^{-1}; ^{1}H NMR (400 MHz,

$CDCl_3$) δ 6.01 (dt, *J* = 1.0, 7.0 Hz, 1H), 4.23 (q, *J* = 7.0 Hz, 2H), 4.02 (t, *J* = 7.0 Hz, 1H), 3.16 (dt, *J* = 1.0, 7.0 Hz, 2H), 2.00 (d, *J* = 1.0 Hz, 3H), 1.37 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 134.7, 131.6, 112.2 (2C), 60.9, 30.1, 21.6, 20.3, 14.0; MS (MALDI) calcd for $C_{10}H_{12}O_2N_2Na$ $[M + Na]^+$ 215.07, found 214.99.

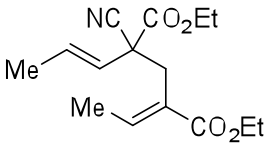


***E*-5a**

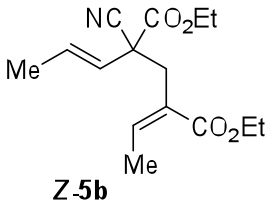


***Z*-5a**

Yield: 57%; 1:5 E:Z selectivity; clear oil; IR (film) ν_{max} 2958, 2932, 2873, 2859, 2244, 1743, 1707, 1235, 1156 cm^{-1}; ^{1}H NMR major (500 MHz, $CDCl_3$) δ 6.24 (q, *J* = 5.7 Hz, 1H), 5.97 (dt, *J* = 12.4, 5.5 Hz, 1H), 5.45 (dt, *J* = 12.0, 1.1 Hz, 1H), 4.24–4.14 (m, 4H), 2.92 (dd, *J* = 36.0, 11.0 Hz, 2H), 2.03 (d, *J* = 4.0 Hz, 3H), 1.90 (d, *J* = 6.0 Hz, 2H), 1.36–1.23 (m, 4H), 1.30 (q, *J* = 5.3 Hz, 6H), 0.88 (t, *J* = 6.0 Hz, 3H); ^{1}H NMR minor (500 MHz, $CDCl_3$) δ 7.11 (q, *J* = 5.7 Hz, 1H), 5.97 (dt, *J* = 12.4, 5.5 Hz, 1H), 5.53 (dt, *J* = 12.0, 1.1 Hz, 1H), 4.24–4.14 (m, 4H), 3.06 (dd, *J* = 36.0, 11.0 Hz, 2H), 2.05 (d, *J* = 4.0 Hz, 3H), 1.78 (d, *J* = 6.0 Hz, 2H), 1.36–1.23 (m, 4H), 1.26 (q, *J* = 5.3 Hz, 6H), 0.88 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.4, 166.6, 143.2 (2C), 135.4 (2C), 126.3, 123.5, 123.2 (2C), 117.0, 77.1, 76.9, 76.6, 62.8, 62.7 (2C), 60.7, 60.4 (2C), 52.5, 41.1, 33.5, 31.6 (2C), 30.6 (2C), 22.48, 22.0, 21.9, 15.9, 15.4 (2C), 14.0, 13.8 (2C), 13.7 (2C); MS (MALDI) calcd for $C_{18}H_{31}O_4NNa$ $[M + Na]^+$ 344.18, found 344.18.



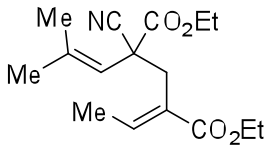
***E*-5b**



***Z*-5b**

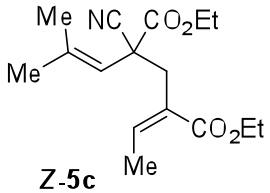
Yield: 42%; 1:5 E:Z selectivity; clear oil; IR (film) ν_{max} 2980.20, 2937.76, 2876.11, 2246.49, 1743.84, 1705.89, 1236.49, 1157.61 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$), major: δ 6.23 (q, *J* = 6.7 Hz, 1H), 6.00 (dt, *J* = 12.4, 5.1 Hz, 1H), 5.43 (d, *J* = 12.0, 1H), 4.26–4.11 (m, 4H), 2.95 (d, *J* = 12.0 Hz, 1H), 2.85 (d, *J* = 12.0 Hz, 1H), 2.10–2.01 (m, 3H), 2.02 (d, *J* = 8.0 Hz, 3H), 1.34–1.23 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.9, 166.6, 143.2, 142.7, 136.7 (2C), 135.9, 126.9, 126.3, 122.7, 122.4 (2C), 117.2, 117.0, 62.8, 62.7 (2C), 60.6, 60.4 (2C), 52.5, 51.6, 41.1 (2C),

36.5, 33.5, 25.0 (2C), 15.9 (2C), 15.3, 14.0; MS (MALDI) calcd for $C_{16}H_{28}O_4NNa$ $[M + Na]^+$ 316.15, found 316.15.



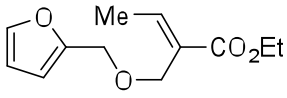
***E*-5c**

Yield: 26%; clear oil; IR (film) ν_{max} 2982, 2939, 2914, 2243, 1740, 1712, 1257, 1143 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.13 (q, *J* = 5.3 Hz, 1H), 5.28 (t, *J* = 1.0 Hz, 1H), 4.27–4.16 (m, 4H), 3.12 (q, *J* = 9.3 Hz, 2H), 1.92 (d, *J* = 6.0 Hz, 3H), 1.82 (d, *J* = 4.0 Hz, 4H), 1.77 (d, *J* = 4.0 Hz, 3H), 1.30 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.3, 167.0, 142.9, 140.8, 127.2, 119.6, 118.2, 62.7, 60.7, 47.3, 34.4, 26.4, 19.0, 15.3, 14.0, 13.7; MS (MALDI) calcd for $C_{16}H_{28}O_4NNa$ $[M + Na]^+$ 316.15, found 316.15.



***Z*-5c**

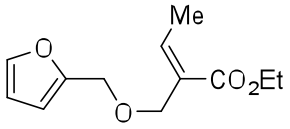
Yield: 53%; clear oil; IR (film) ν_{max} 2982, 2939, 2914, 2243, 1740, 1712, 1257, 1143 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.24 (q, *J* = 5.3 Hz, 1H), 5.15 (t, *J* = 1.0 Hz, 1H), 4.20 (m, 4H), 2.98 (q, *J* = 9.3 Hz, 2H), 2.02 (d, *J* = 6.0 Hz, 3H), 1.81 (d, *J* = 4.0 Hz, 4H), 1.75 (d, *J* = 4.0 Hz, 3H), 1.30 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.1, 166.6, 142.8, 141.0, 126.6, 119.0, 117.9, 62.6, 60.5, 48.1, 41.8, 26.4, 18.9, 15.9, 14.0, 13.8; MS (MALDI) calcd for $C_{16}H_{28}O_4NNa$ $[M + Na]^+$ 316.15, found 316.15.



***E*-6a**

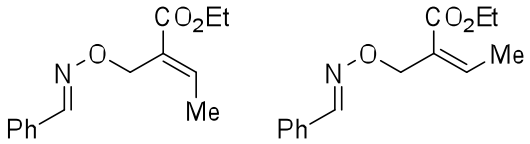
Yield: 44%; clear oil; IR (film) ν_{max} 3122, 2928, 2877, 1711, 1279, 1235, 1151, 1069 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 (t, *J* = 11.0 Hz, 1H), 7.09 (q, *J* = 7.0 Hz, 1H), 6.32 (d, *J* = 11.0 Hz, 2H), 4.46 (s, 2H), 4.26 (s, 2H), 4.18 (q, *J* = 7.0 Hz, 2H), 1.86 (d, *J* = 7.0 Hz, 3H), 1.26 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 151.8, 143.1, 142.7, 129.5, 110.5, 110.2, 109.3, 64.2, 62.8, 14.6, 14.2; MS (MALDI) calcd for $C_{12}H_{16}O_4Na$ $[M + Na]^+$ 247.09, found

247.10.



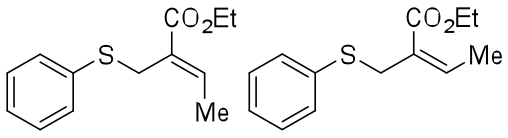
***Z*-6a**

Yield: 44%; clear oil; IR (film) ν_{max} 3122, 2981, 2907, 2862, 1717, 1257, 1235, 1151, 1095, 1067 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 (dd, *J* = 2.0, 1.0 Hz, 1H), 6.34–6.30 (m, 3H), 4.46 (s, 2H), 4.22 (q, *J* = 7.0 Hz, 2H), 4.15 (t, *J* = 1.0 Hz, 2H), 2.04 (d, *J* = 7.0 Hz, 3H), 1.29 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 151.7, 142.7, 140.3, 129.5, 110.2, 109.2, 70.8, 64.1, 60.2, 15.5, 14.2; MS (MALDI) calcd for $C_{12}H_{16}O_4Na$ $[M + Na]^+$ 247.09, found 247.13.



***E*-6b** ***Z*-6b**

Yield: 77%; 4:1 E:Z selectivity; clear oil; IR (film) ν_{max} 2981, 1713, 1652, 1447, 1282, 1245, 1141, 1021 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$), major: δ 8.05 (s, 1H), 7.57–7.53 (m, 2H), 7.38–7.33 (m, 3H), 7.19 (q, *J* = 7.0 Hz, 1H), 4.96 (s, 2H), 4.23 (q, *J* = 7.0 Hz, 2H), 2.02 (d, *J* = 7.0 Hz, 3H), 1.30 (t, *J* = 7.0 Hz, 3H); minor: δ 8.09 (s, 1H), 7.57–7.53 (m, 2H), 7.38–7.33 (m, 3H), 6.41 (q, *J* = 7.0 Hz, 1H), 4.83 (s, 2H), 4.24 (q, *J* = 7.0 Hz, 2H), 2.08 (d, *J* = 7.0 Hz, 3H), 1.31 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9 (2C), 148.8, 148.7, 144.1 (2C), 132.3, 129.7, 129.3, 129.1, 128.6 (4C), 127.06 (4C), 127.00, 117.7, 117.4, 67.1 (2C), 60.6 (2C), 14.8, 14.2; MS (MALDI) calcd for $C_{14}H_{17}O_3NNa$ $[M + Na]^+$ 270.11, found 270.07.

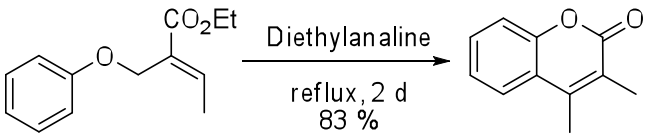


***E*-6c** ***Z*-6c**

Yield: 65%; 5:1 E:Z selectivity; clear oil; IR (film) ν_{max} 2980, 2935, 1711, 1275, 1178, 1052 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) major: δ 7.46–7.41 (m, 2H), 6.34–6.30 (m, 3H), 6.92 (q, *J* = 7.0 Hz, 2H), 4.20 (q, *J* = 7.0 Hz, 2H), 3.80 (s, 2H), 1.57 (d, *J* = 7.0 Hz, 3H), 1.28 (t, *J* = 7.0 Hz, 3H); minor: δ 7.48–7.45 (m, 2H), 6.34–6.30 (m, 3H), 6.81 (q, *J* = 7.0 Hz, 2H), 4.22 (q, *J* = 7.0 Hz,

2H), 3.60 (d, J = 7.0 Hz, 2H), 1.71 (d, J = 3.0 Hz, 3H), 1.32 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 140.1, 135.7, 130.9, 129.4 (2C), 128.9 (2C), 128.8, 126.9, 60.7, 31.2, 14.2 (2); MS (MALDI) calcd for $C_{13}H_{16}O_2SNa$ $[M + Na]^+$ 259.07, found 259.11.

Synthesis of 3,4-Dimethylcoumarin

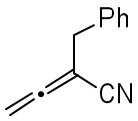


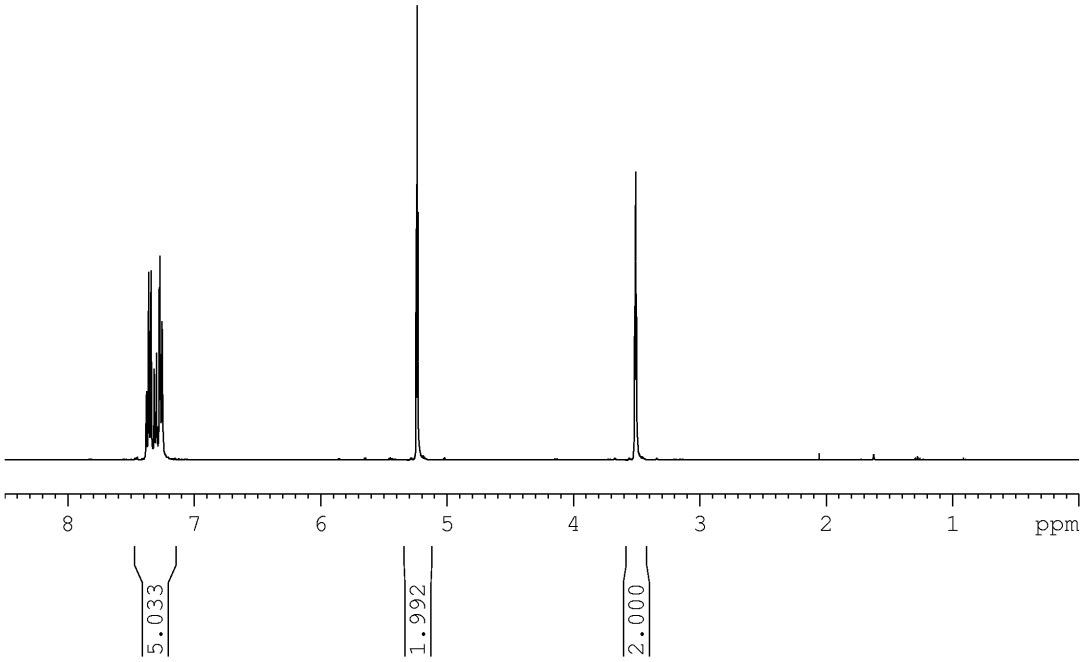
1a **13**

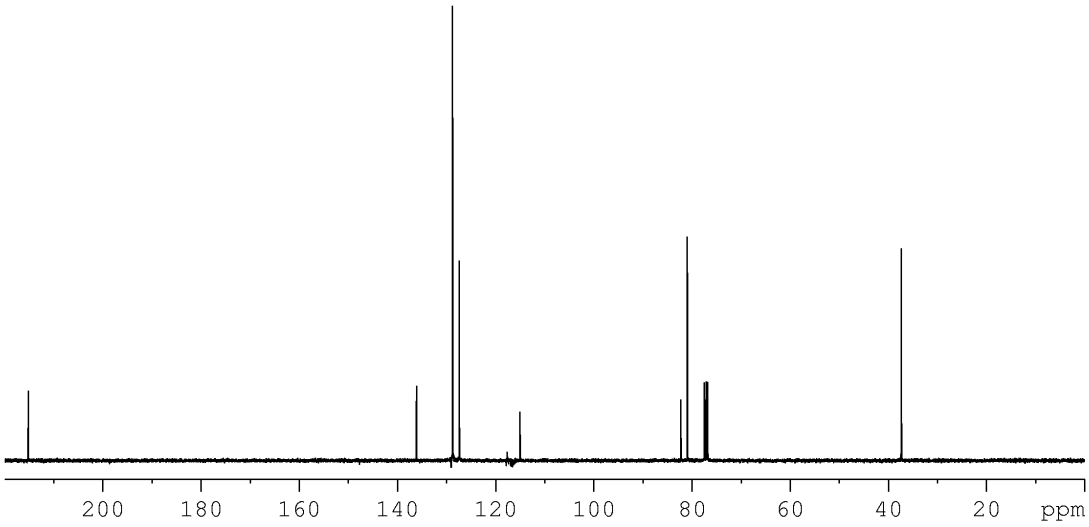
A round-bottom flask equipped with a stirrer bar and condenser was flame-dried and left to cool under Ar. Compound **1a** (0.5 mmol) and diethylaniline (1 mL) were added to the flask. The mixture was heated under reflux and left to react until compound **1a** was consumed, typically 48 h (TLC; hexane/EtOAc, 6:1). The product stained brightly in a standard permanganate stain. The crude reaction mixture was loaded directly onto a silica gel column and separated chromatographically (hexane/EtOAc, 6:1) to provide 3,4-dimethylcoumarin (**12**) in agreement with the literature[3] (164 mg, 83% yield) as a clear oil; IR (film) ν_{max} 2917, 2849, 1715, 1695, 1615, 1604, 1455, 1385, 1288, 1220, 1086 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62–7.60 (m, 1H), 7.46–7.45 (m, 1H), 7.32–7.26 (m, 2H), 2.42 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9, 151.9, 145.8, 130.2, 124.1, 123.9, 122.1, 120.4, 116.6, 14.9, 13.3; MS (MALDI) calcd for $C_{11}H_{10}O_2Na$ $[M + Na]^+$ 197.05, found 197.05.

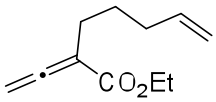
[3] Dittmer, D.; Li, Q; Avilov, D. *J. Org. Chem.* **2005**, *70*, 4882–4686.

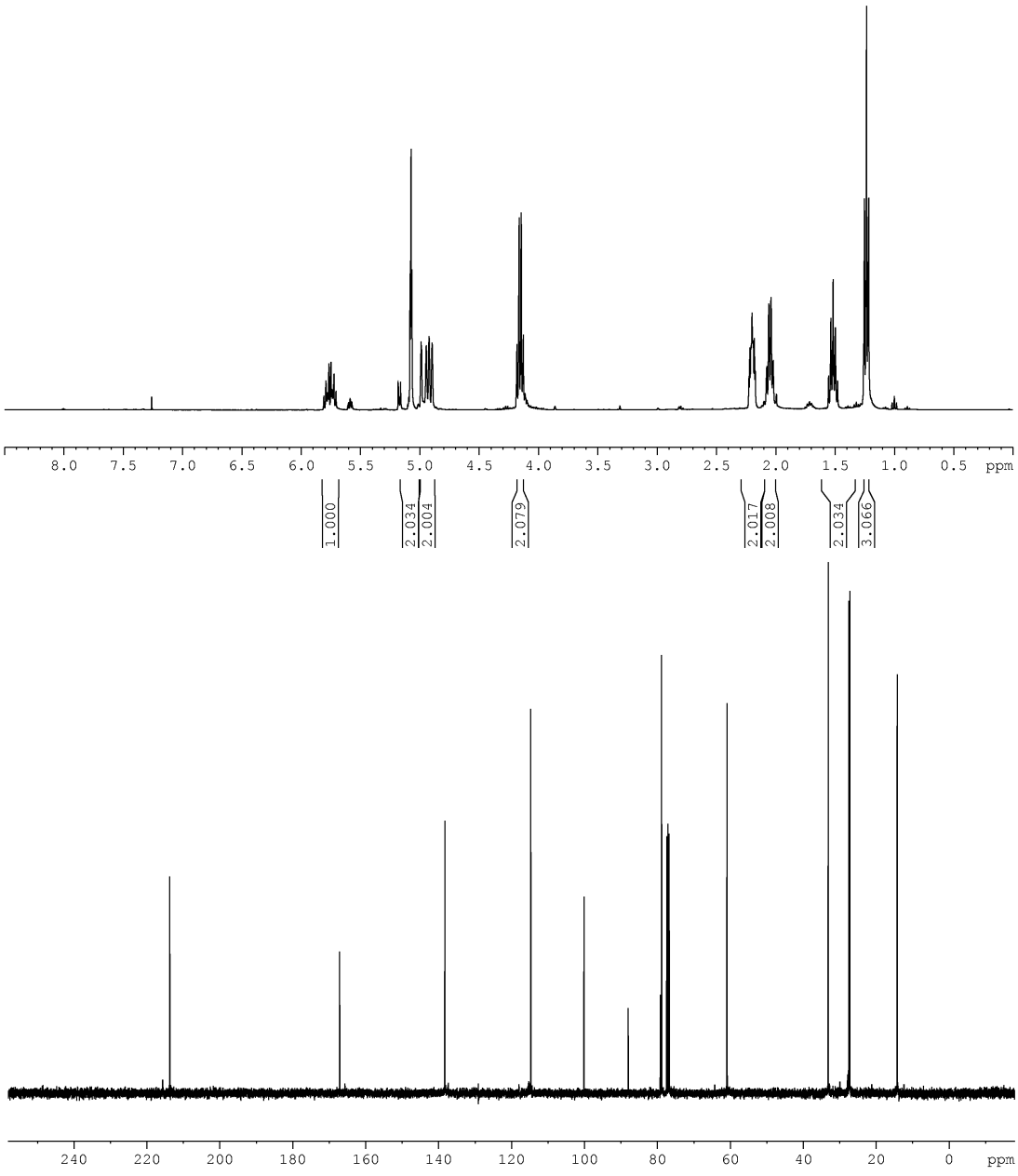
Allennes


Ph
CN

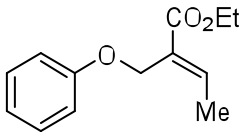

8
7
6
5
4
3
2
1
ppm
5.033
1.992
2.000


200
180
160
140
120
100
80
60
40
20
ppm

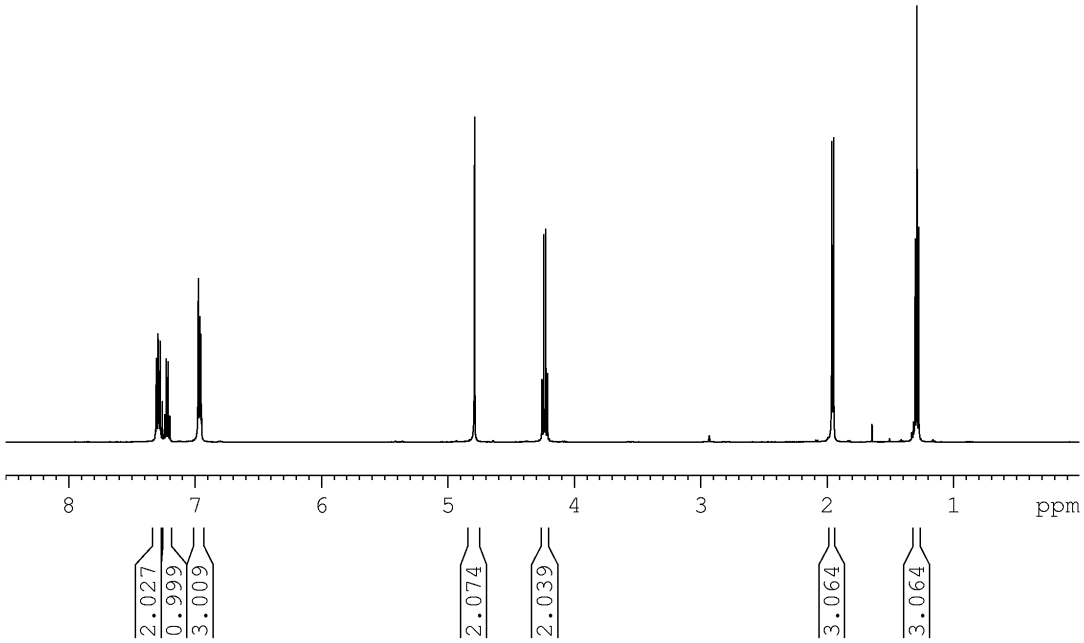

CO2Et

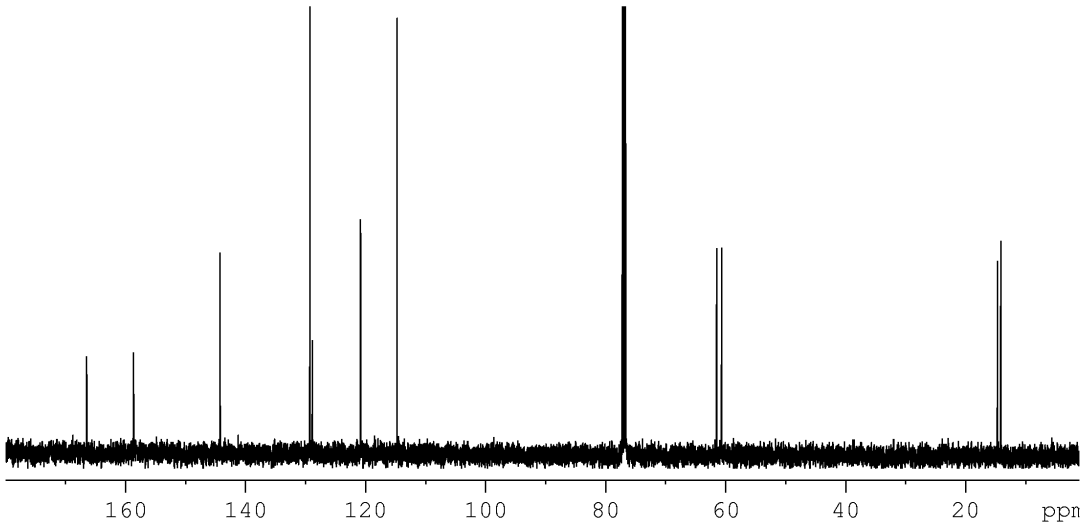

8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.000
2.034
2.004
2.079
2.017
2.008
2.034
3.066
240 220 200 180 160 140 120 100 80 60 40 20 0 ppm

β′-Umpolung Addition Products

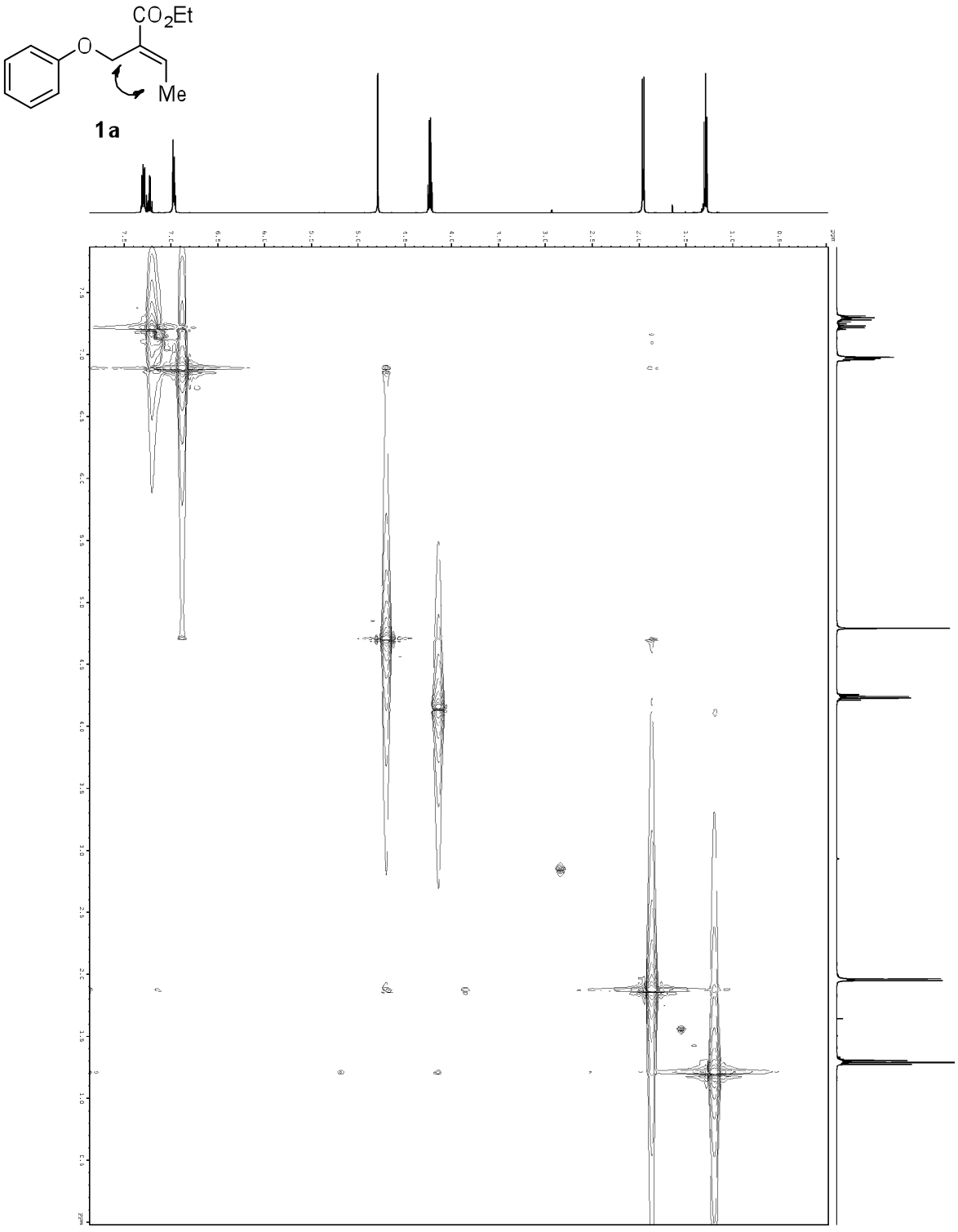


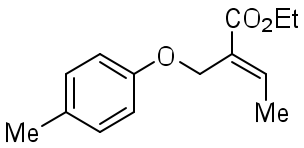
1a



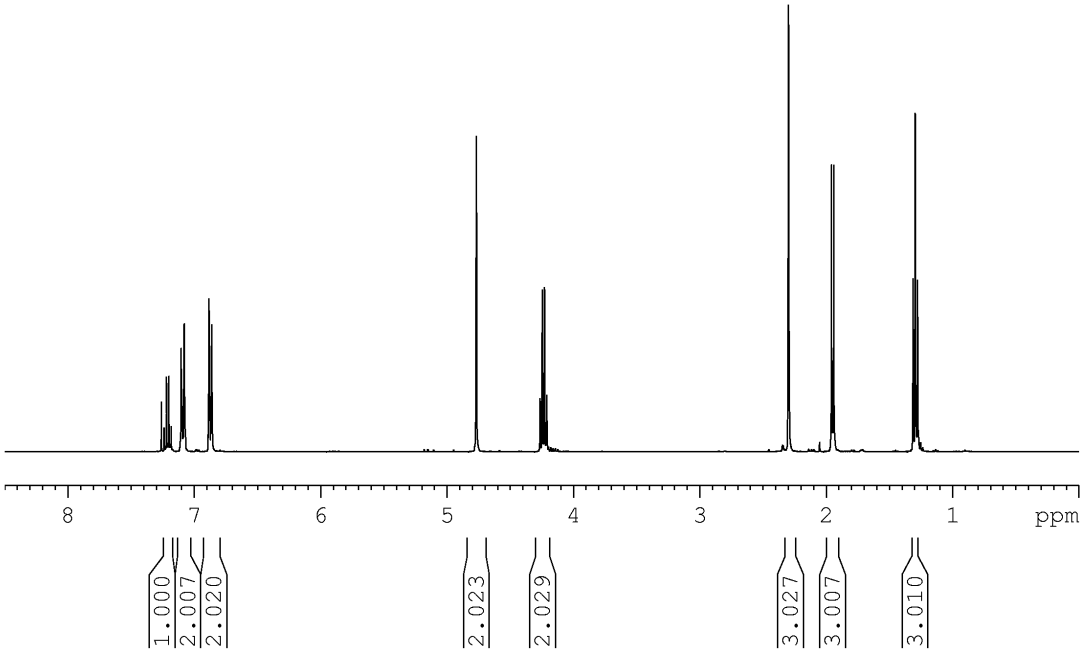


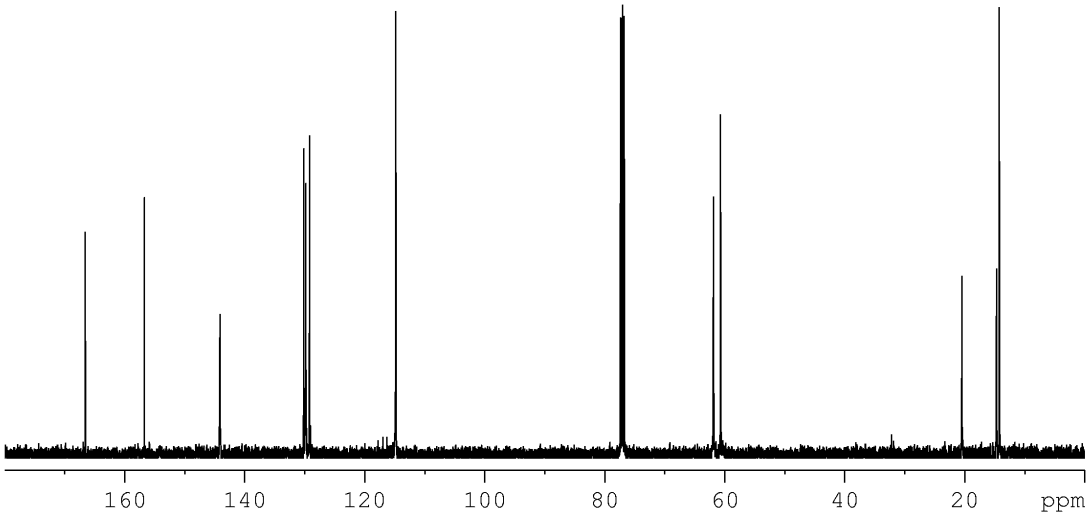
Compound 1a NOESY

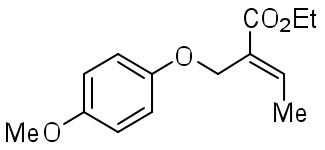



CO2Et
O
Me
Me

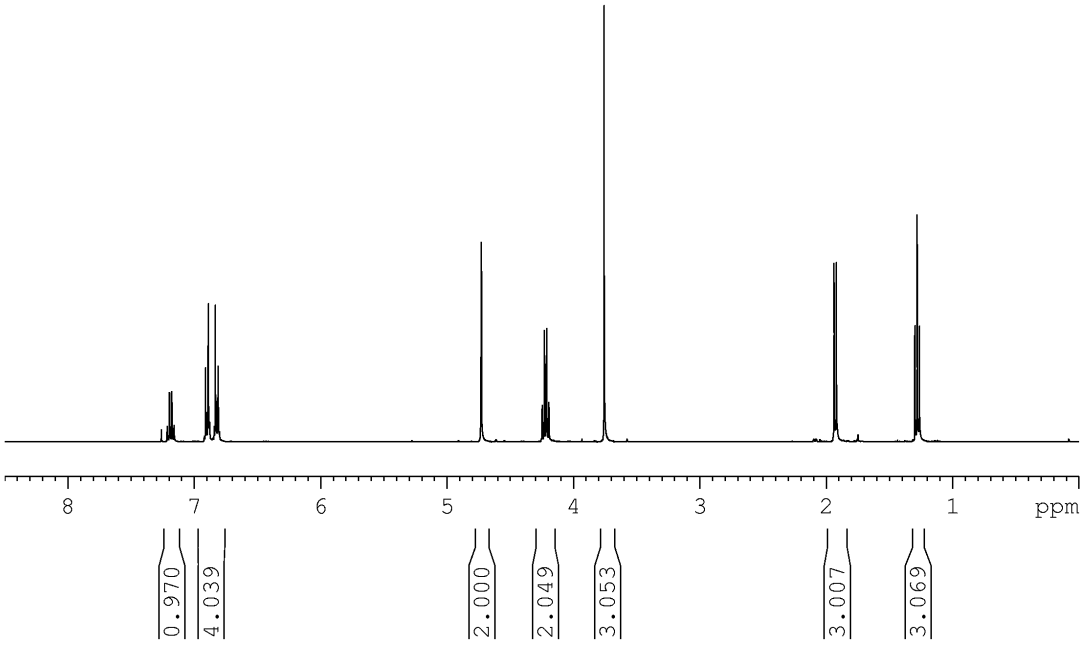
1b

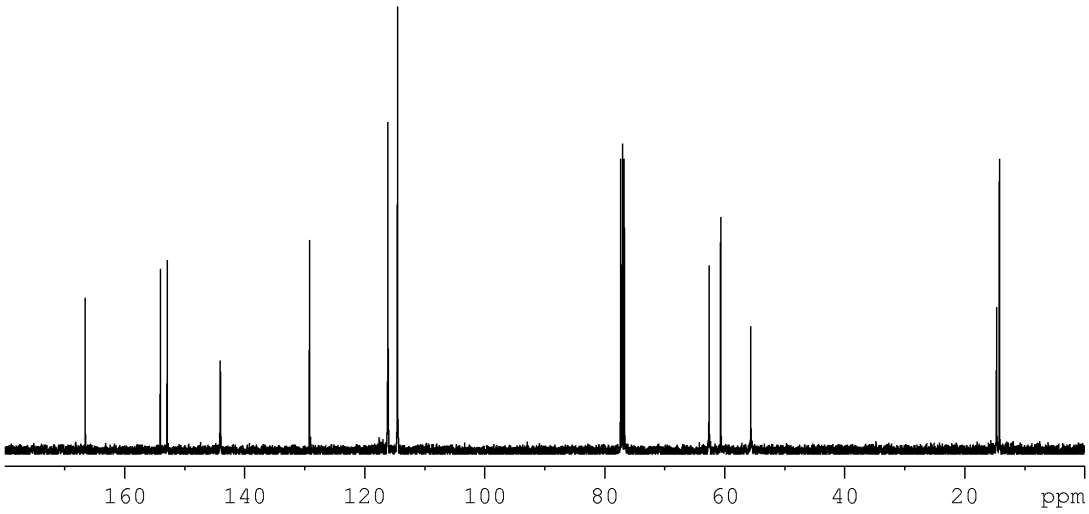

8
7
6
5
4
3
2
1
ppm
1.000
2.007
2.020
2.023
2.029
3.027
3.007
3.010


160
140
120
100
80
60
40
20
ppm

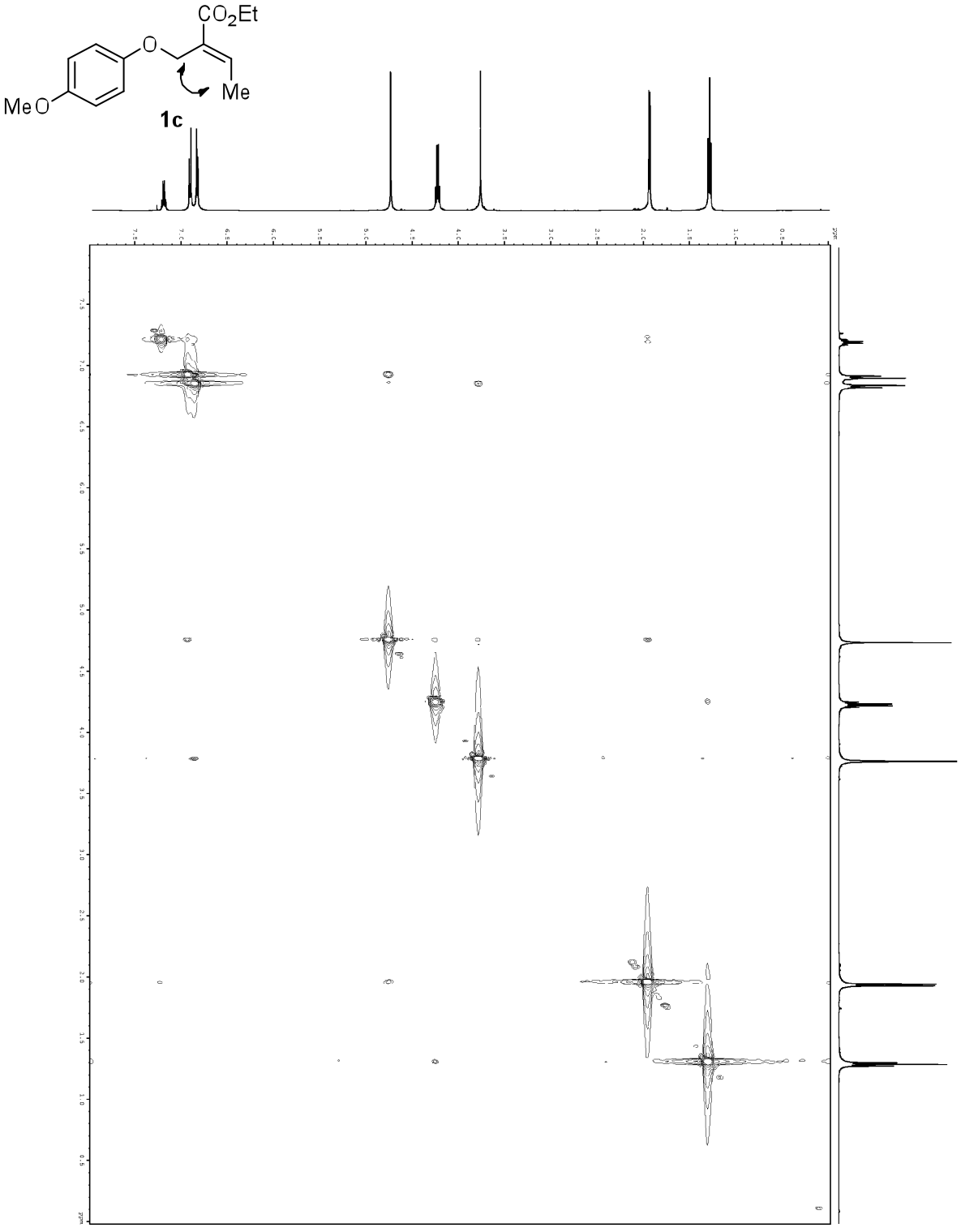

CO2Et
O
Me
MeO

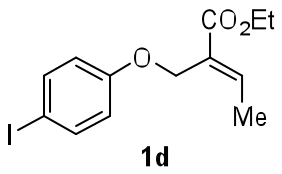
1c


8
7
6
5
4
3
2
1
ppm
0.970
4.039
2.000
2.049
3.053
3.007
3.069

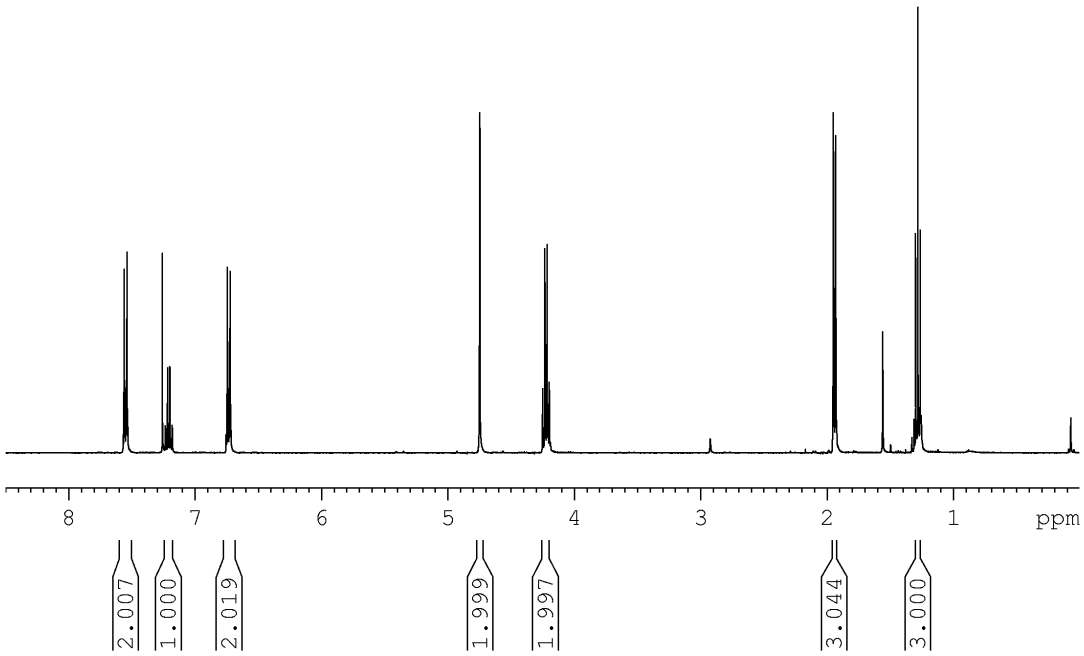

160
140
120
100
80
60
40
20
ppm

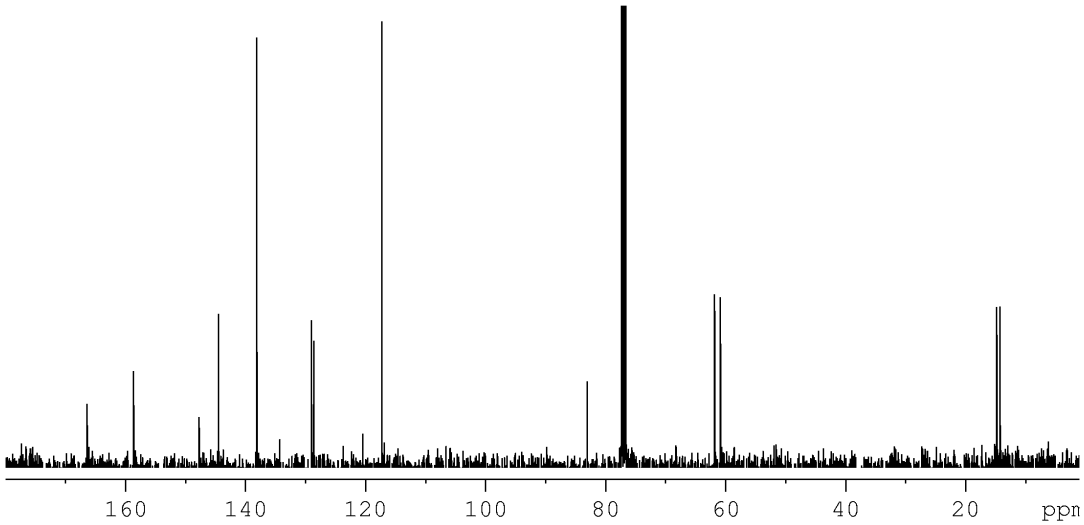
Compound 1c NOESY

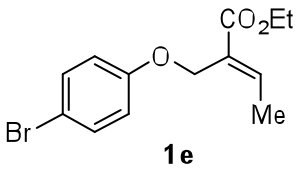



CO2Et
O
Me
I

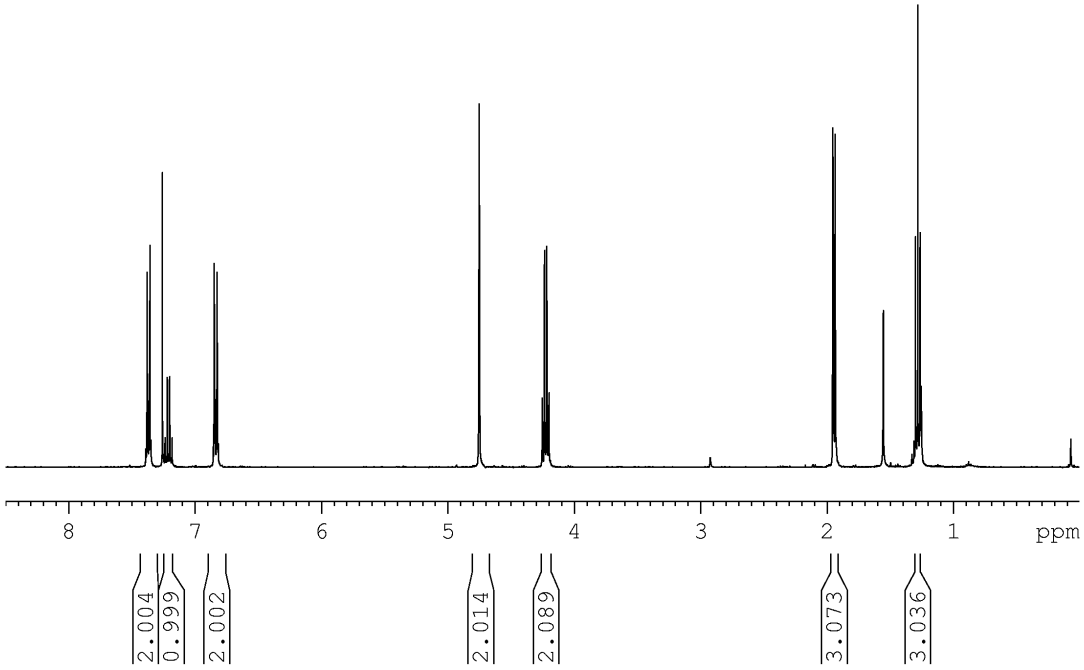
1d

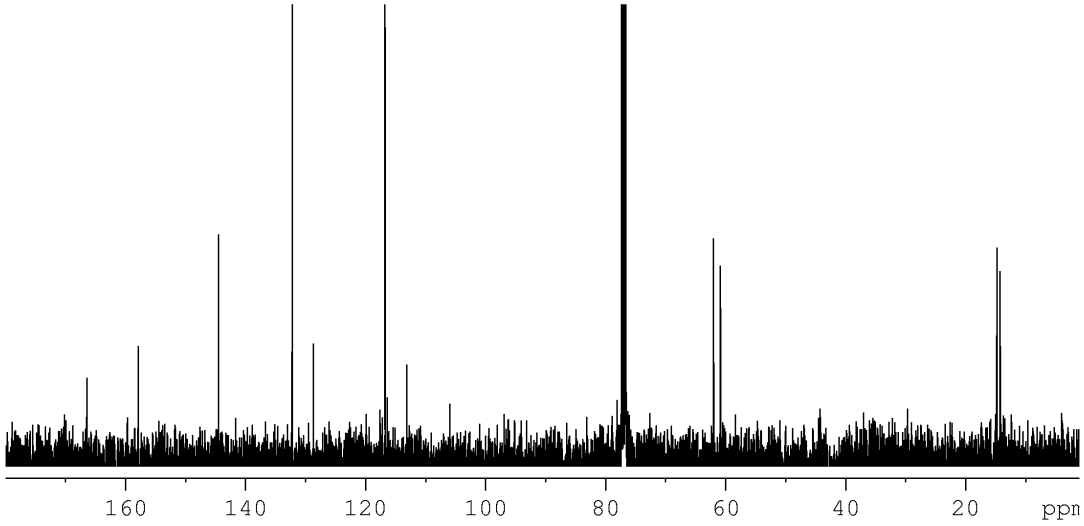

8
7
6
5
4
3
2
1
ppm
2.007
1.000
2.019
1.999
1.997
3.044
3.000

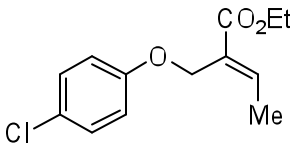

160
140
120
100
80
60
40
20
ppm


CO2Et
O
Me
Br

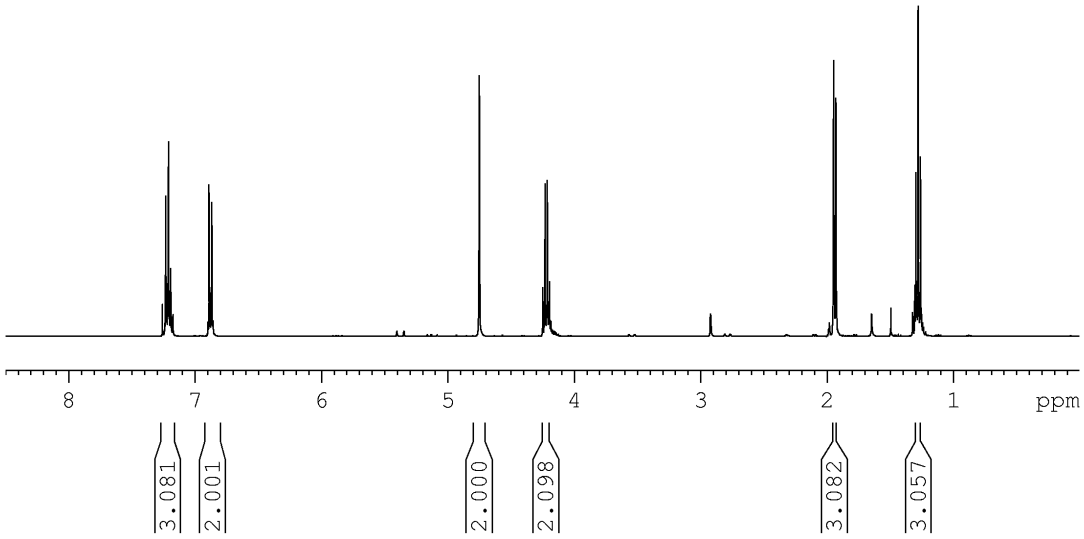
1e

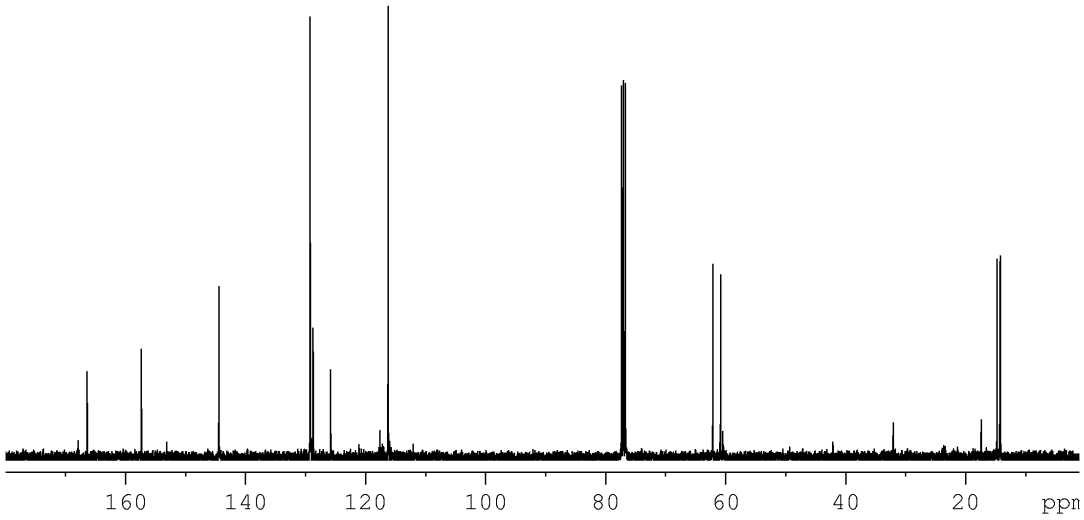

8
7
6
5
4
3
2
1
ppm
2.004
0.999
2.002
2.014
2.089
3.073
3.036

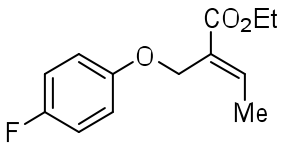

160
140
120
100
80
60
40
20
ppm


CO2Et
O
Me
Cl

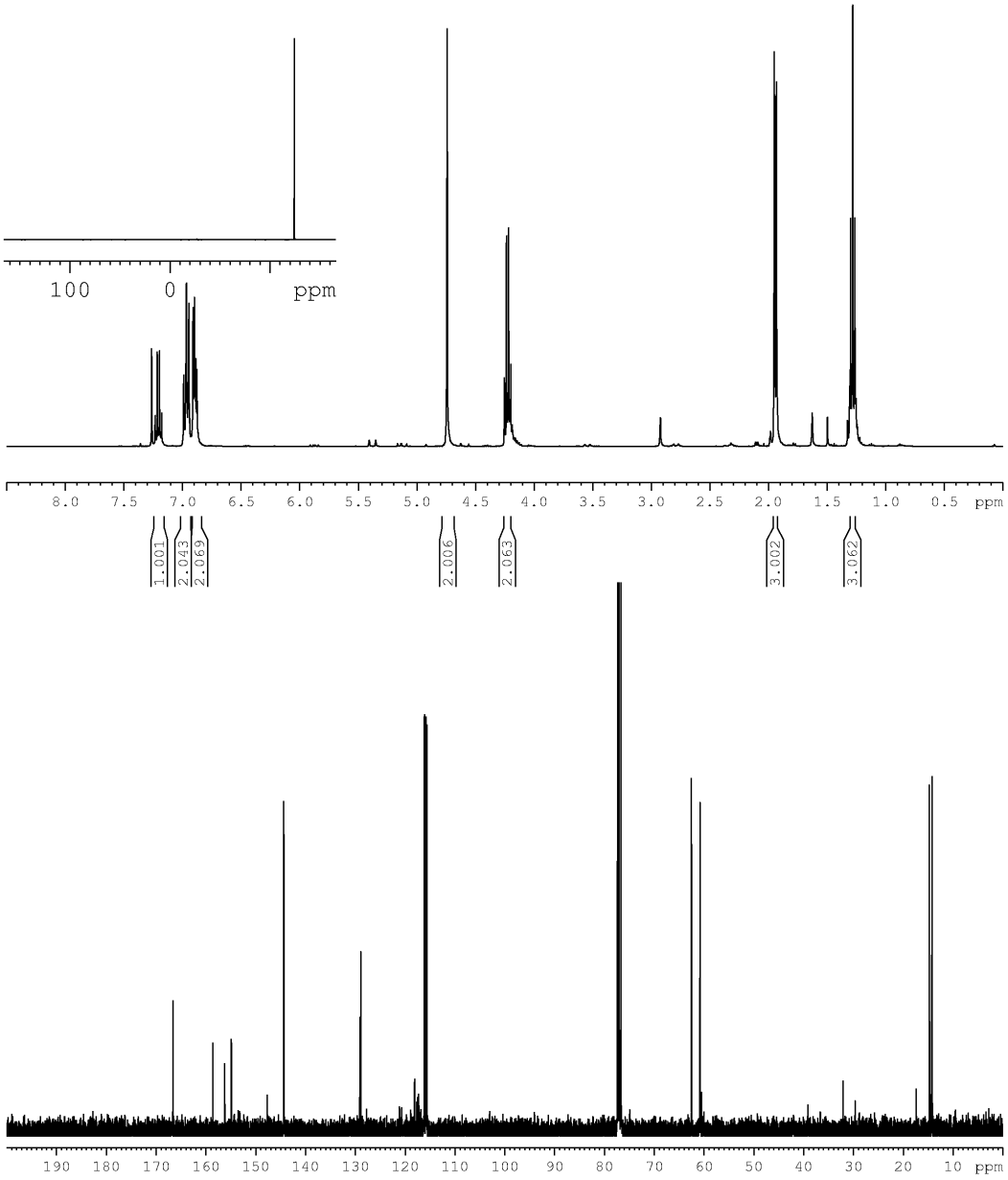
1f

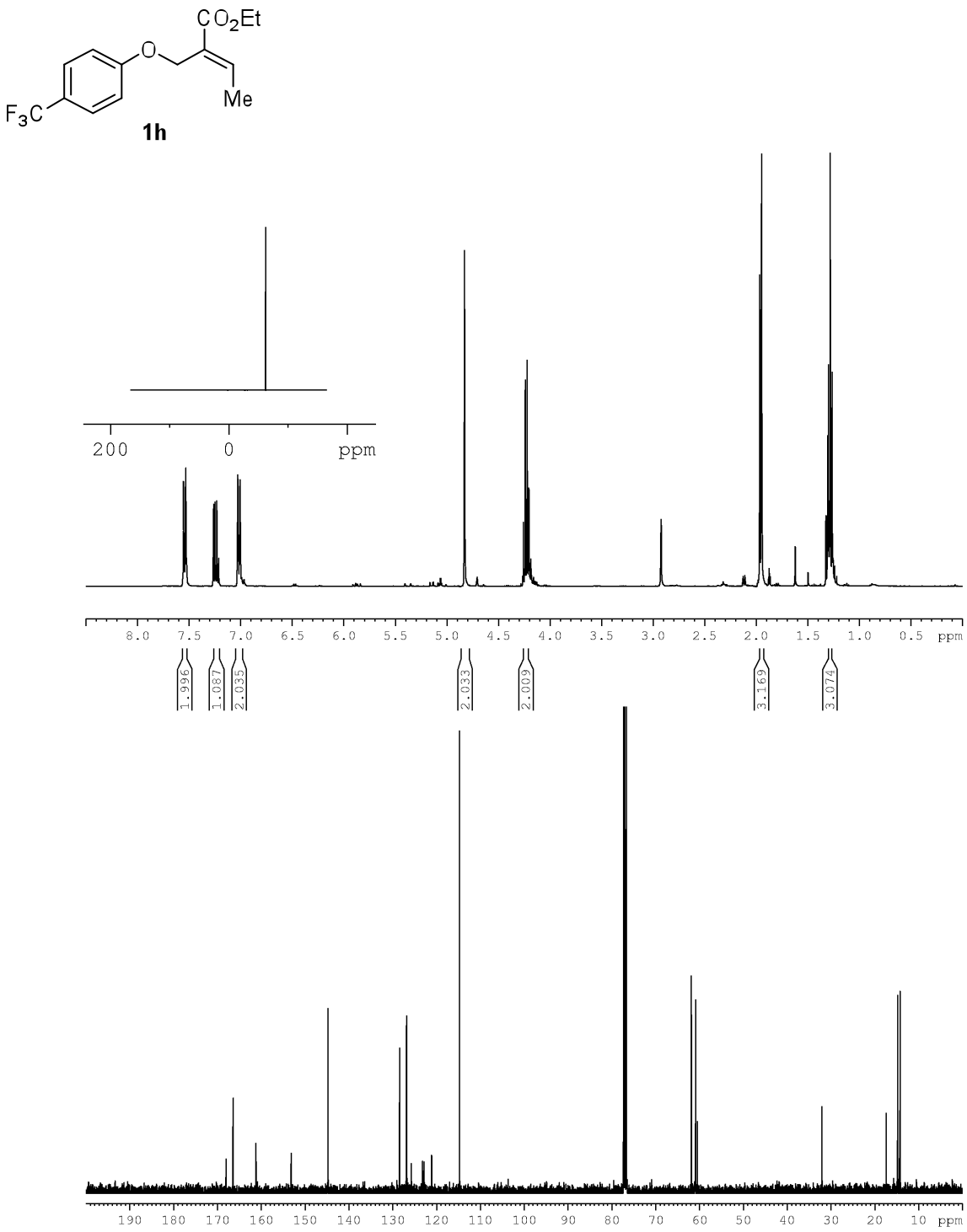

8
7
6
5
4
3
2
1
ppm
3.081
2.001
2.000
2.098
3.082
3.057

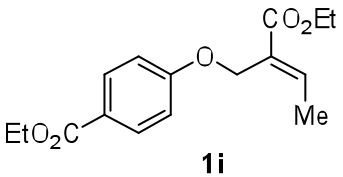

160
140
120
100
80
60
40
20
ppm


CO2Et
O
Me
F

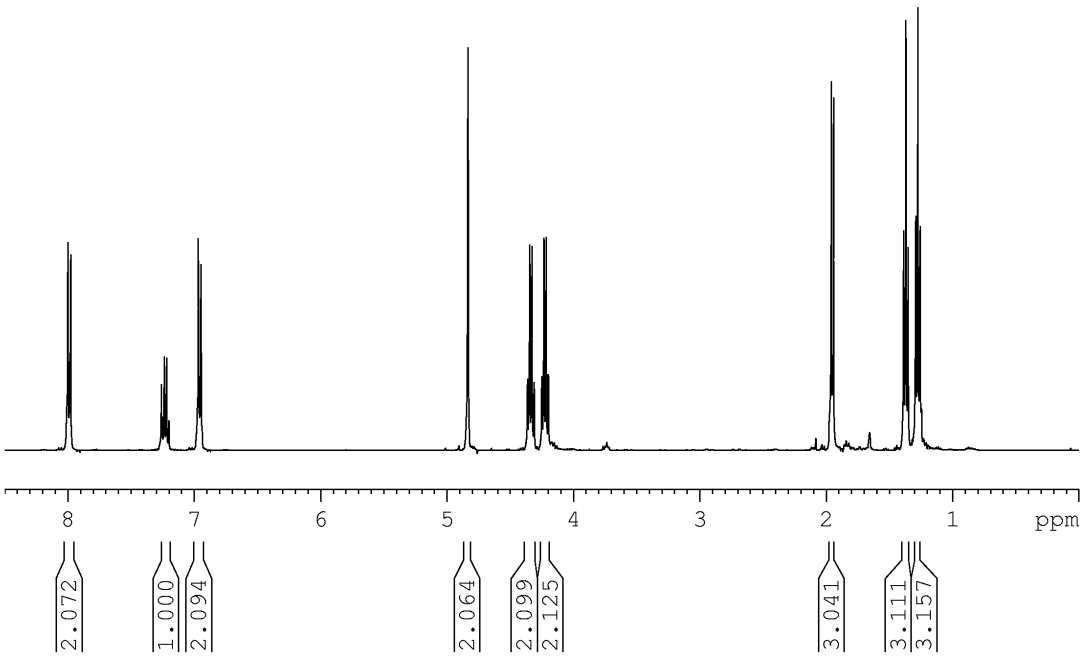
1g

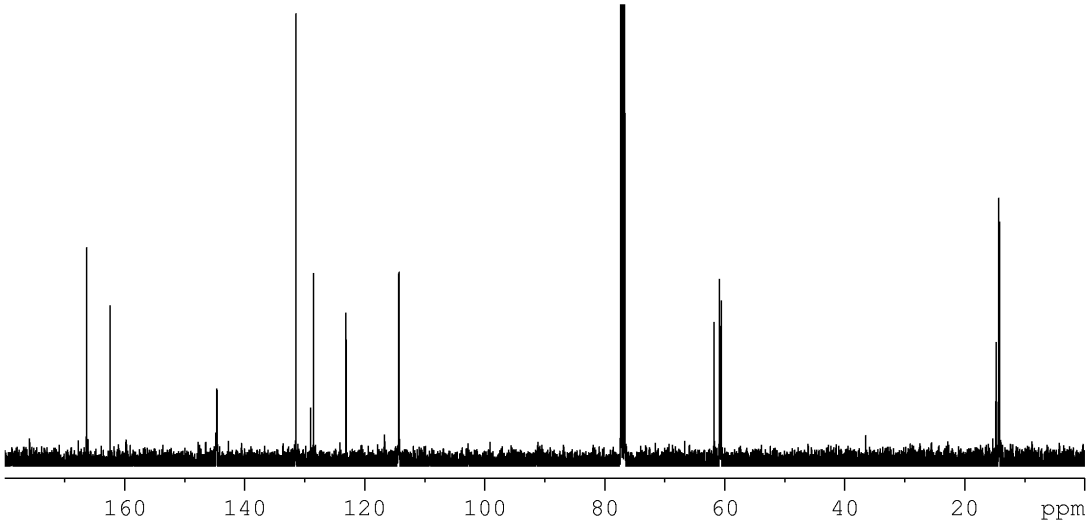

100
0
ppm
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.001
2.043
2.069
2.006
2.063
3.002
3.062
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

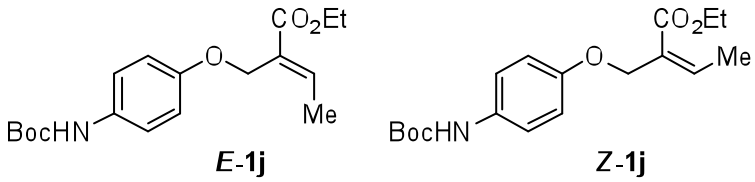

CO2Et
O
Me
F3C
1h
200
0
ppm
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.996
1.087
2.035
2.033
2.009
3.169
3.074
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


CO2Et
O
Me
EtO2C

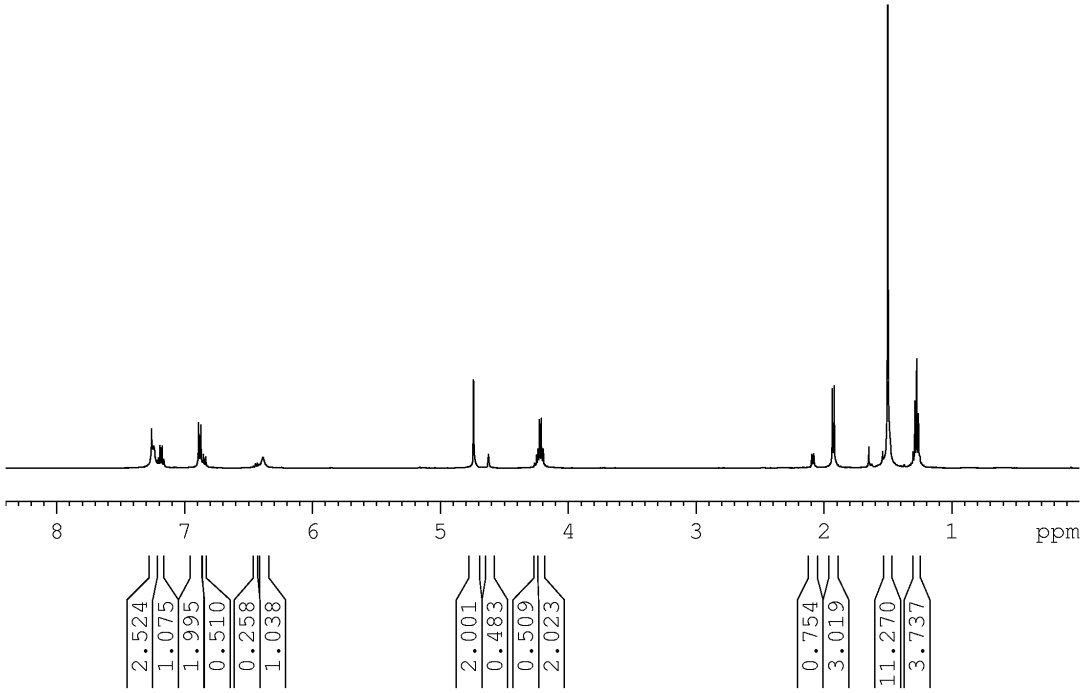
1i

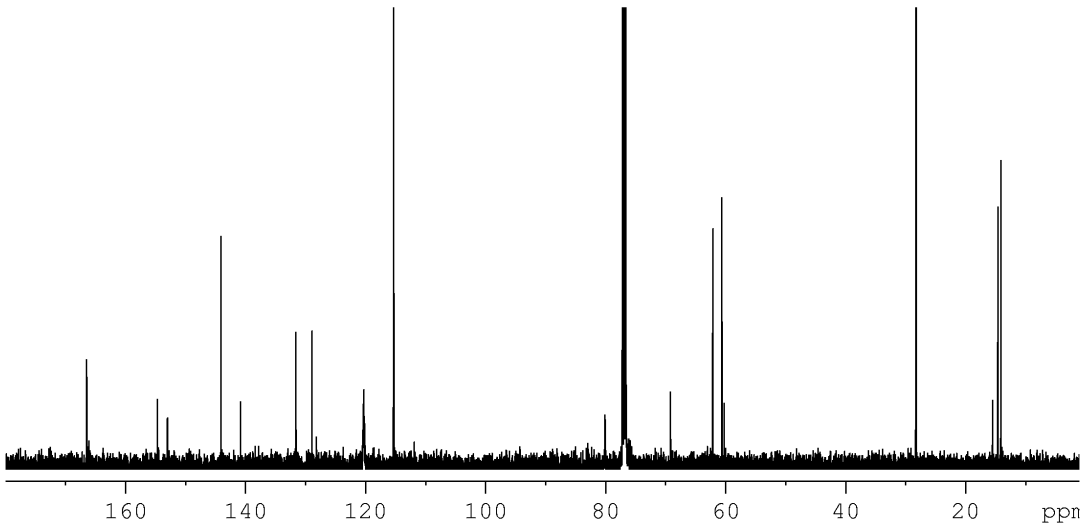

8
7
6
5
4
3
2
1
ppm
2.072
1.000
2.094
2.064
2.099
2.125
3.041
3.111
3.157

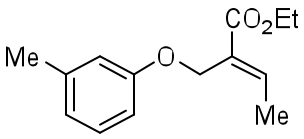

160
140
120
100
80
60
40
20
ppm


CO2Et
O
Me
BocHN
CO2Et
O
Me
BocHN

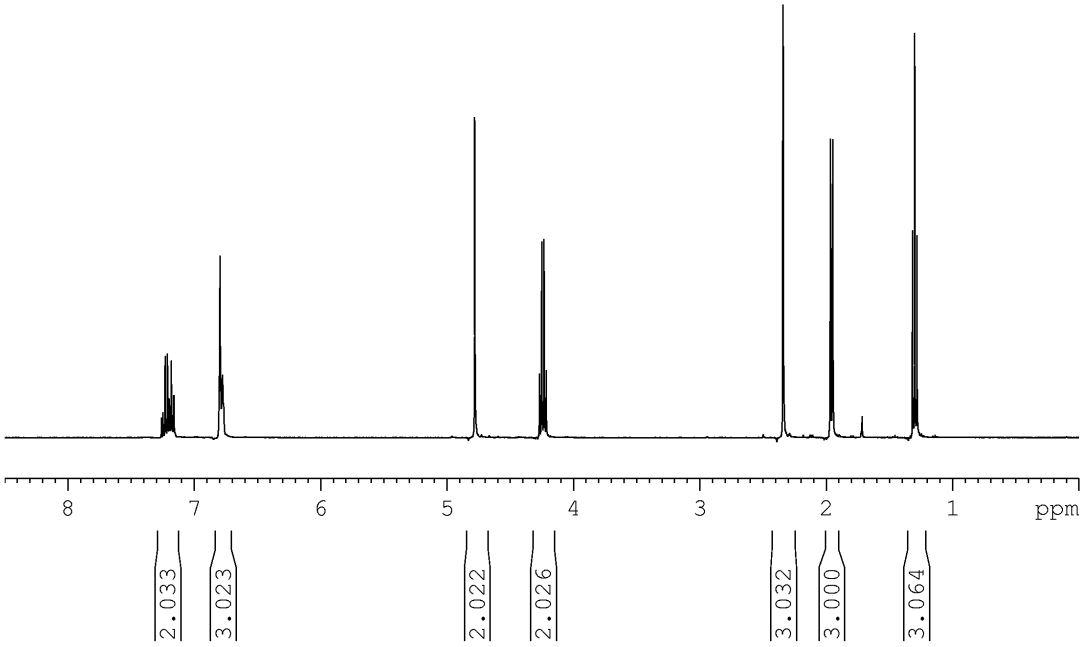
***E*-1j** ***Z*-1j**

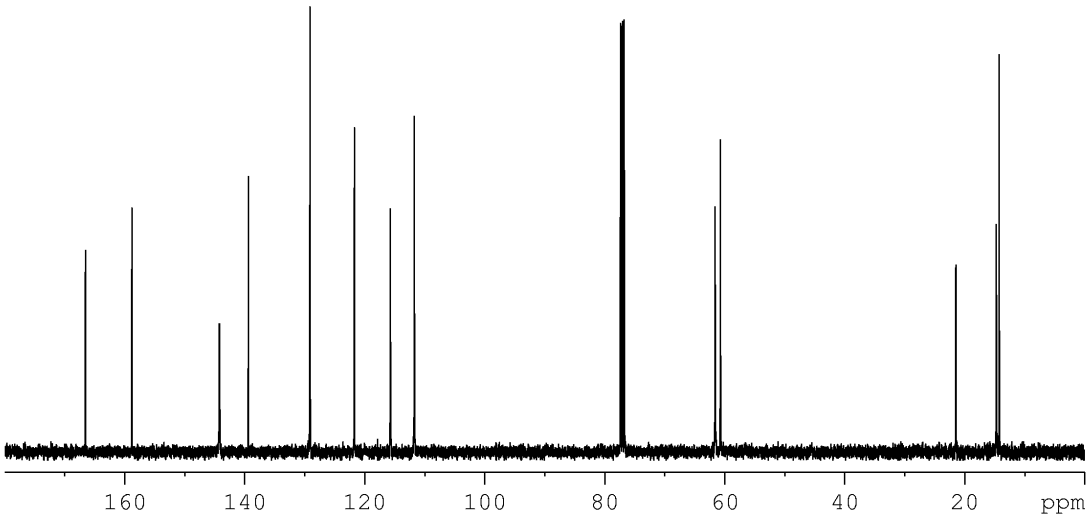

8
7
6
5
4
3
2
1
ppm
2.524
1.075
1.995
0.510
0.258
1.038
2.001
0.483
0.509
2.023
0.754
3.019
11.270
3.737

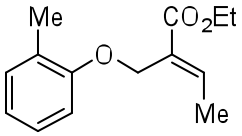

160
140
120
100
80
60
40
20
ppm


CO2Et
Me
O
Me

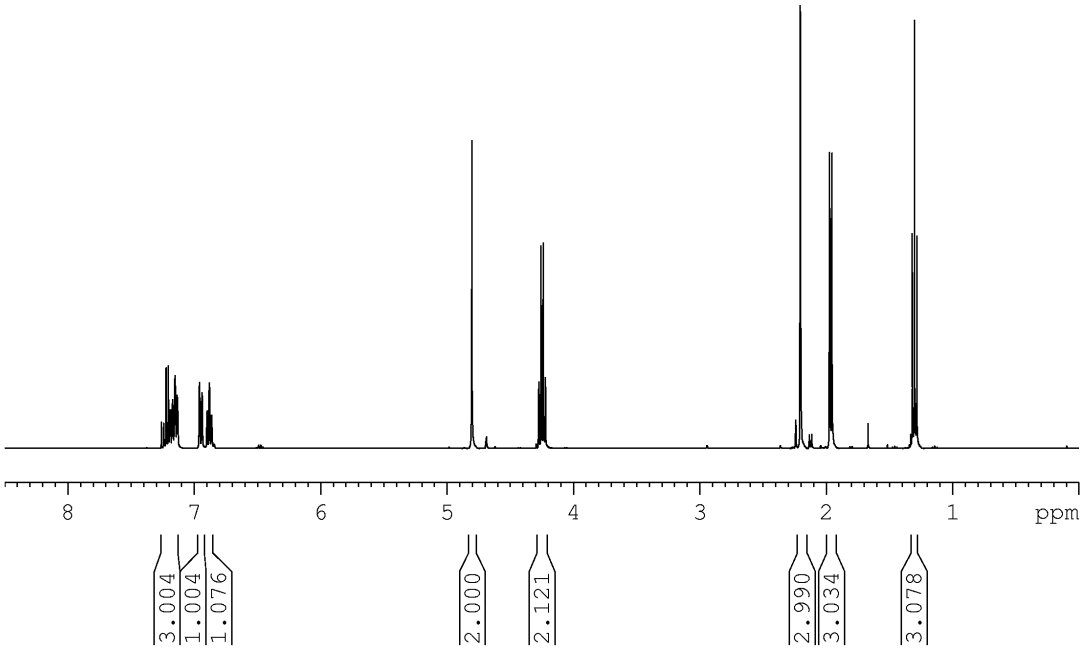
1k

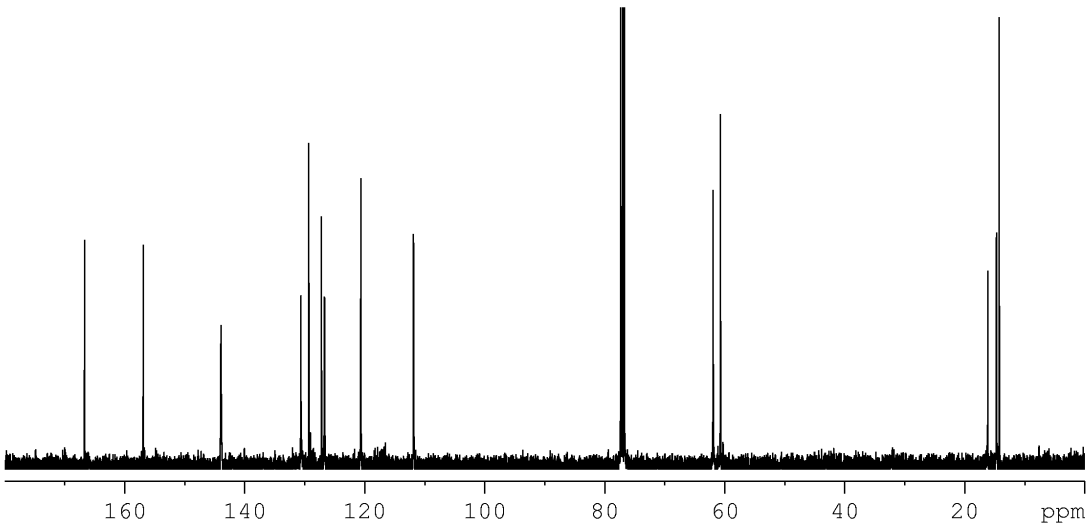

8
7
6
5
4
3
2
1
ppm
2.033
3.023
2.022
2.026
3.032
3.000
3.064

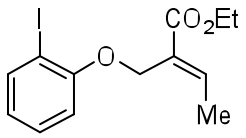

160
140
120
100
80
60
40
20
ppm


Me
CO2Et
O
Me

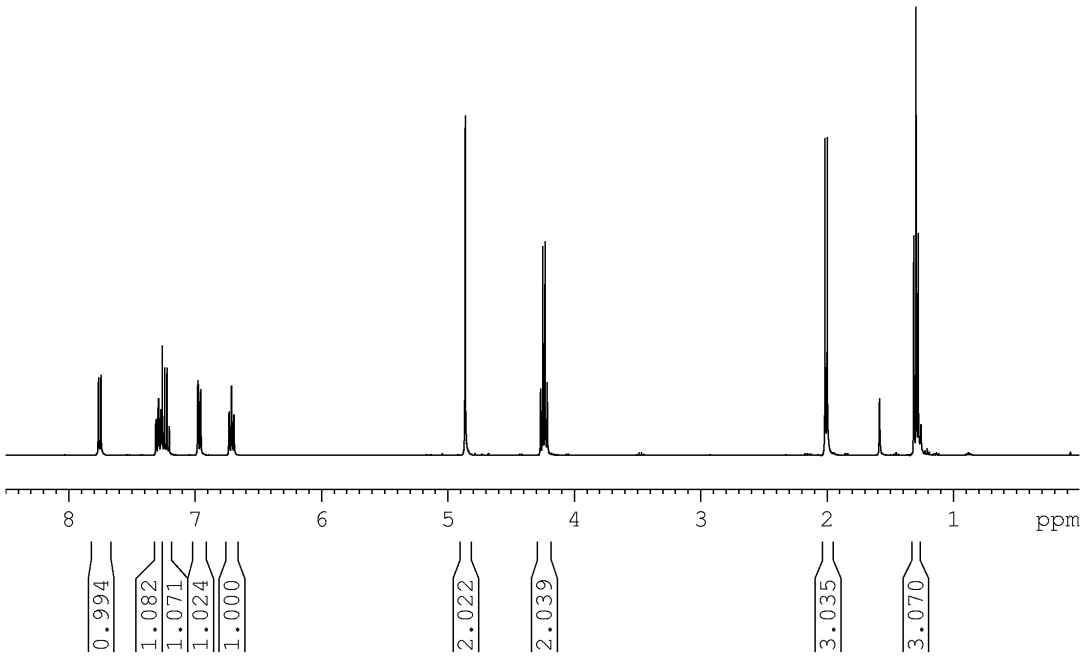
1l

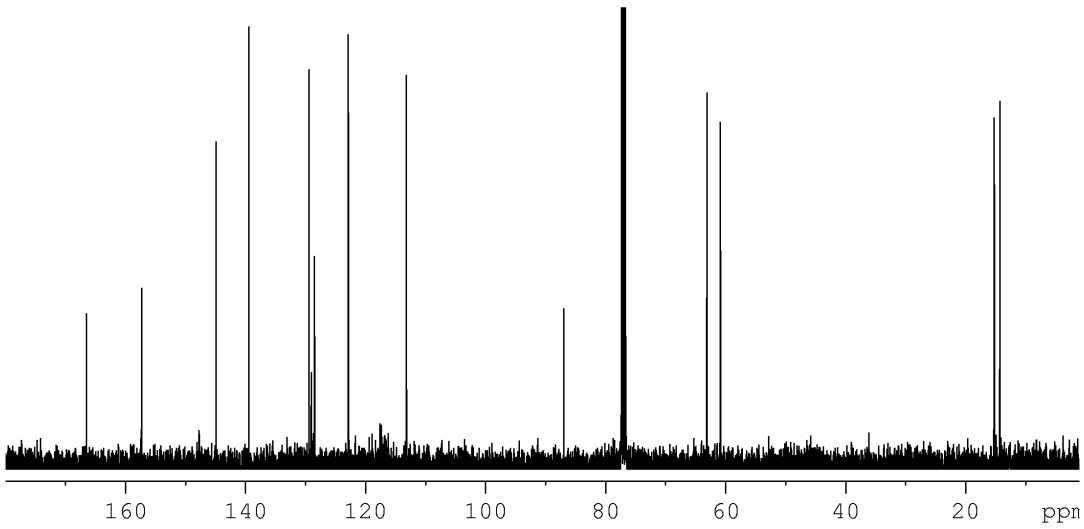

8
7
6
5
4
3
2
1
ppm
3.004
1.004
1.076
2.000
2.121
2.990
3.034
3.078

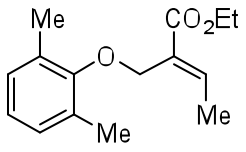

160
140
120
100
80
60
40
20
ppm


I
CO2Et
O
Me

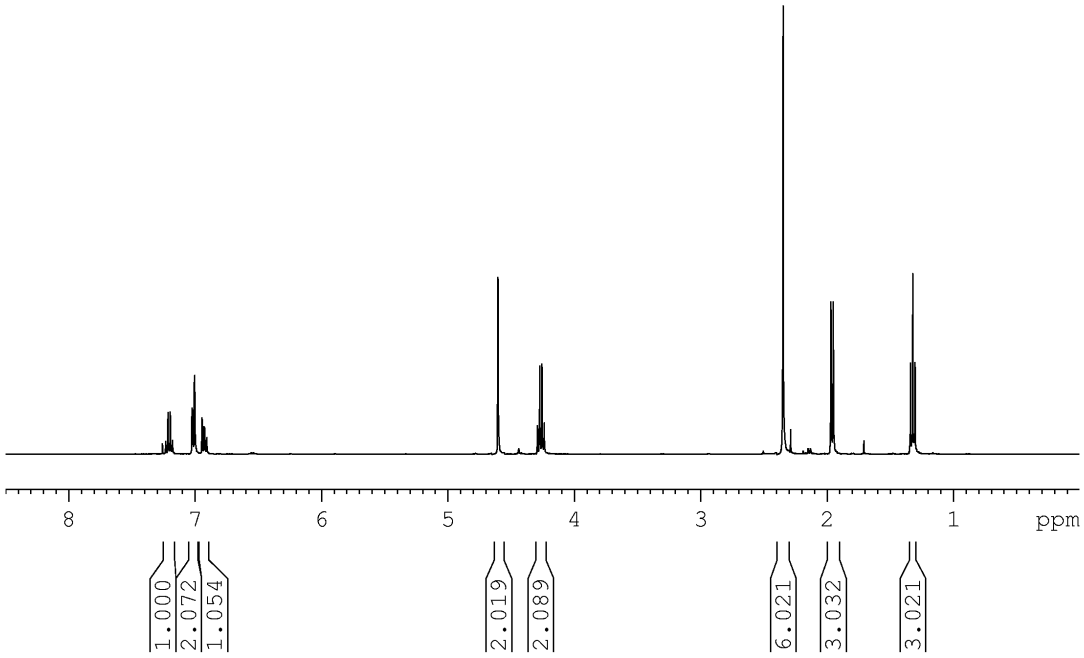
1m

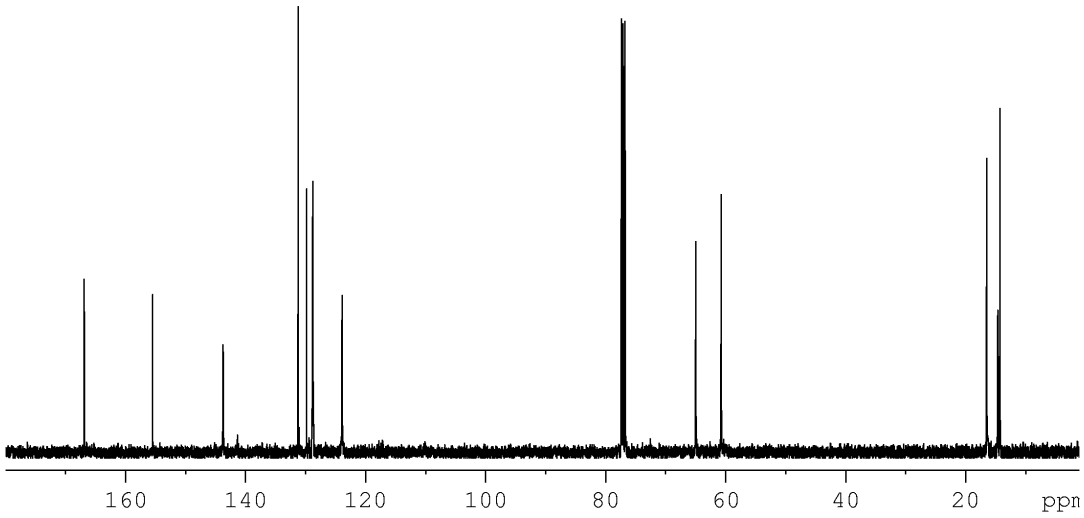

8
7
6
5
4
3
2
1
ppm
0.994
1.082
1.071
1.024
1.000
2.022
2.039
3.035
3.070

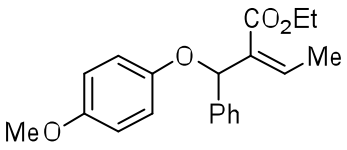

160
140
120
100
80
60
40
20
ppm


Me
CO2Et
O
Me
Me

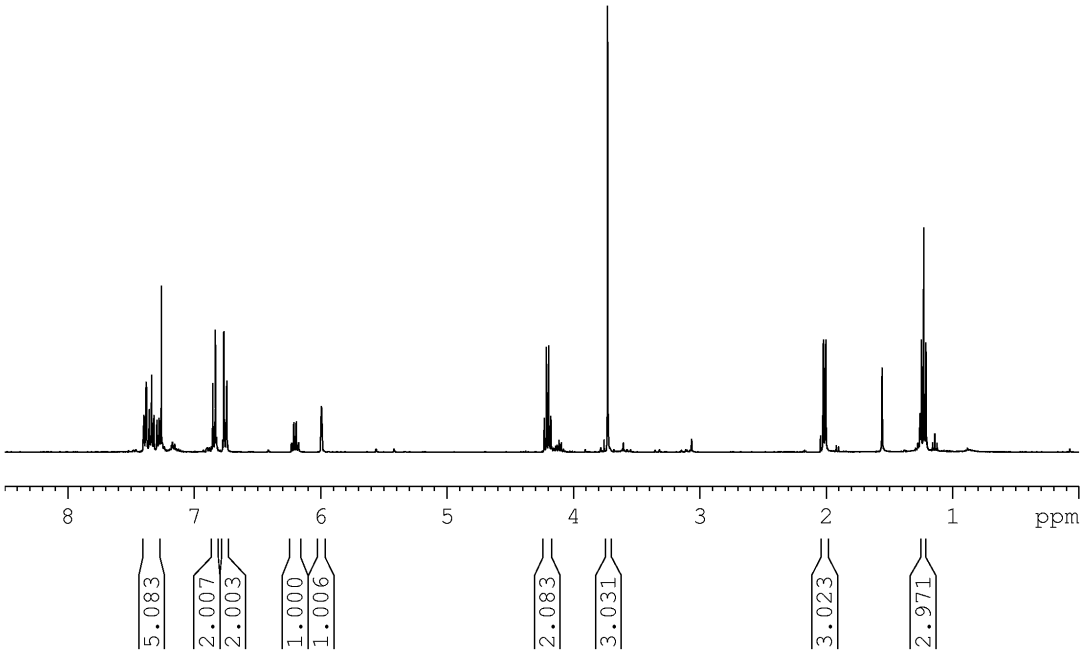
1n

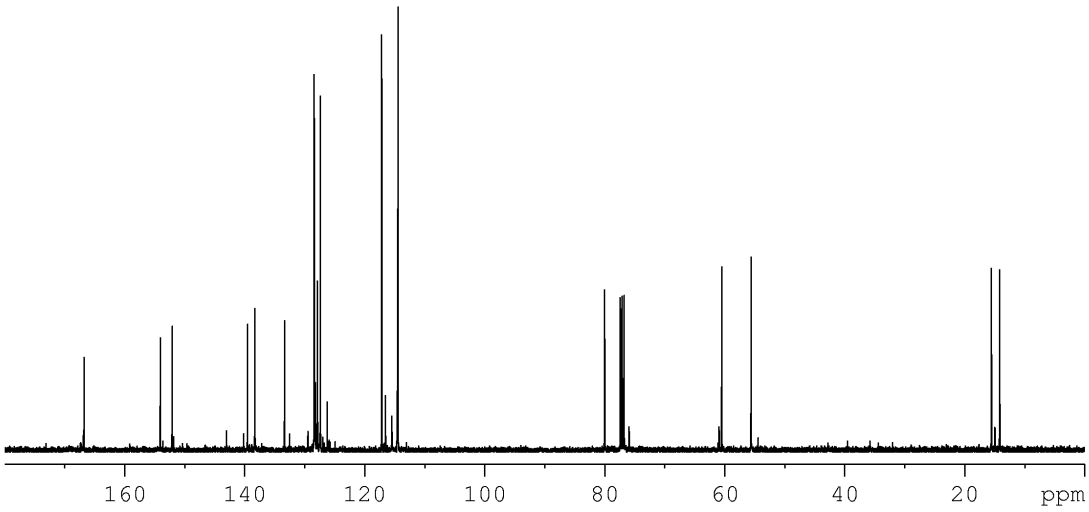

8
7
6
5
4
3
2
1
ppm
1.000
2.072
1.054
2.019
2.089
6.021
3.032
3.021


160
140
120
100
80
60
40
20
ppm

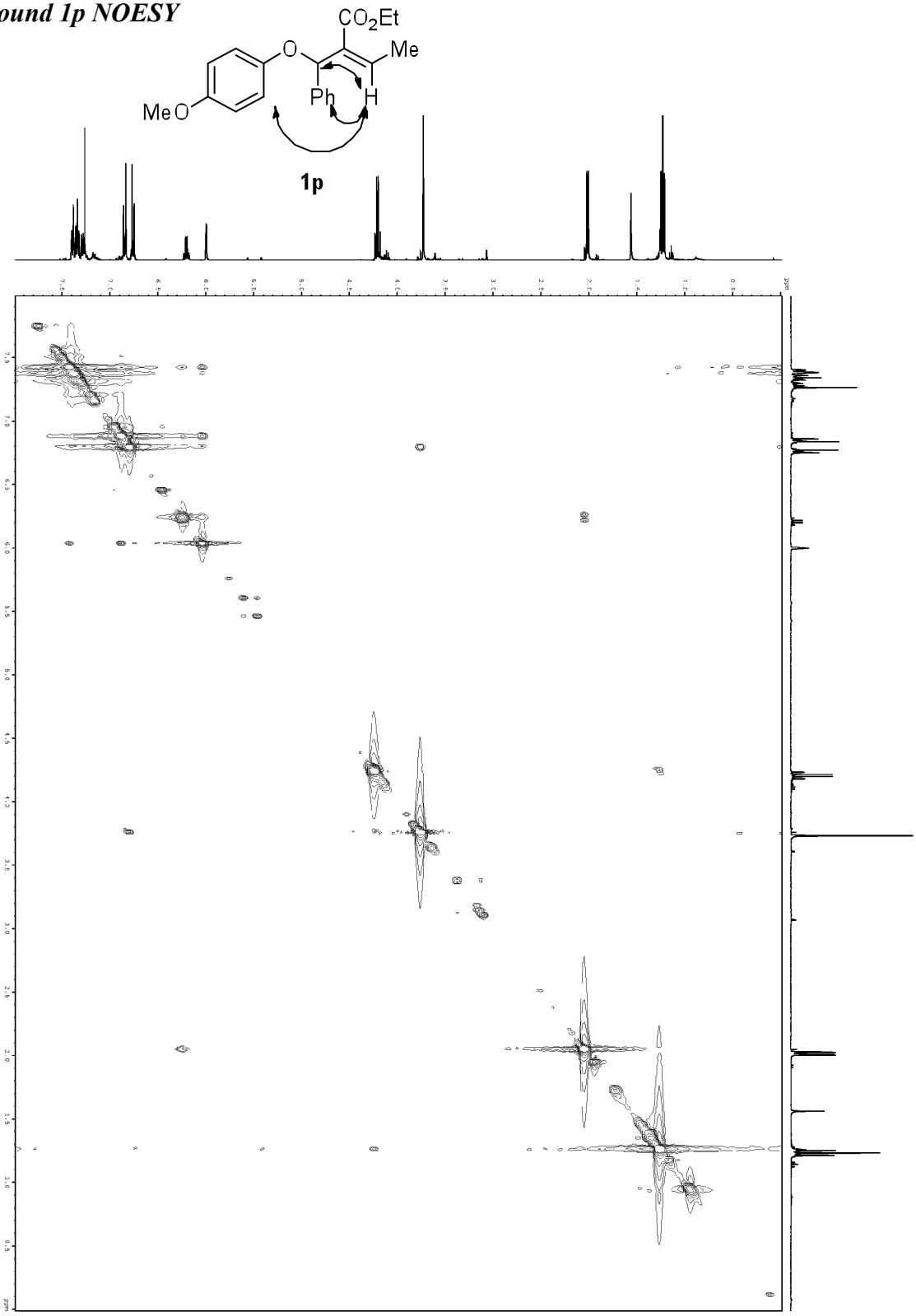

CO2Et
O
Me
Ph
MeO

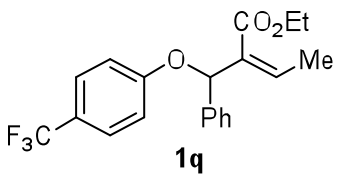
1p


8
7
6
5
4
3
2
1
ppm
5.083
2.007
2.003
1.000
1.006
2.083
3.031
3.023
2.971

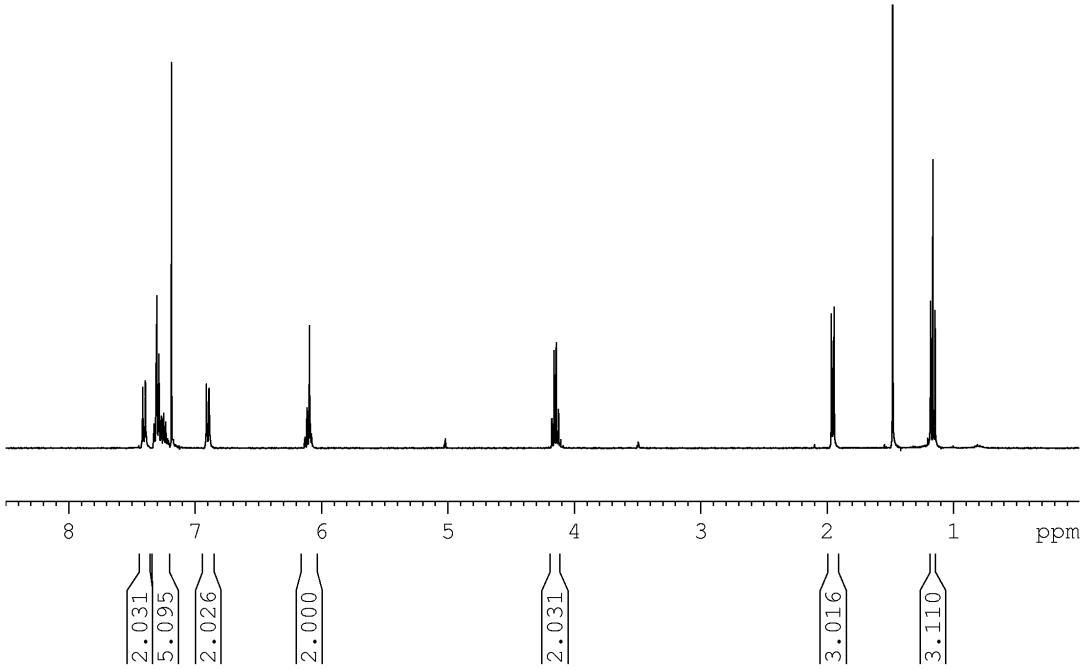

160
140
120
100
80
60
40
20
ppm

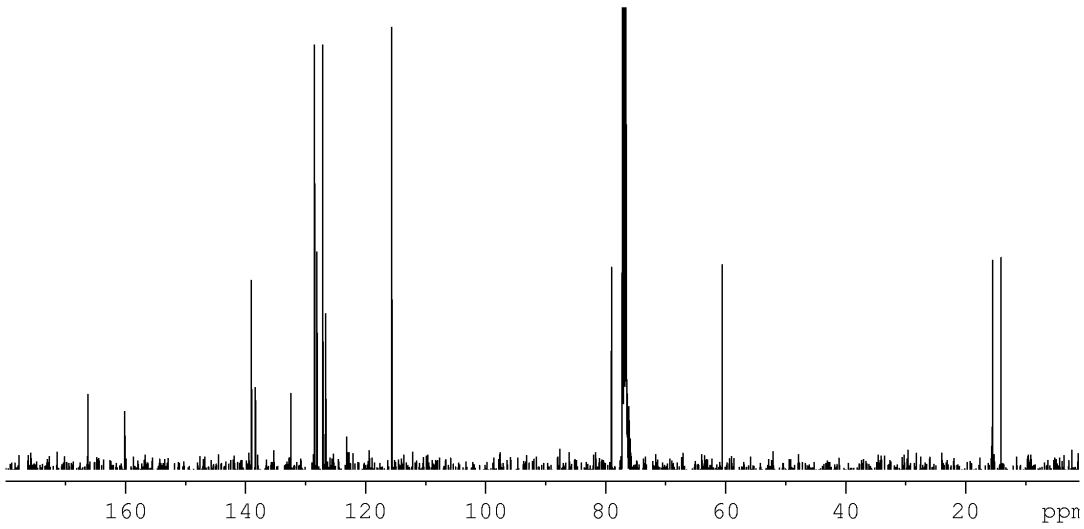
Compound 1p NOESY



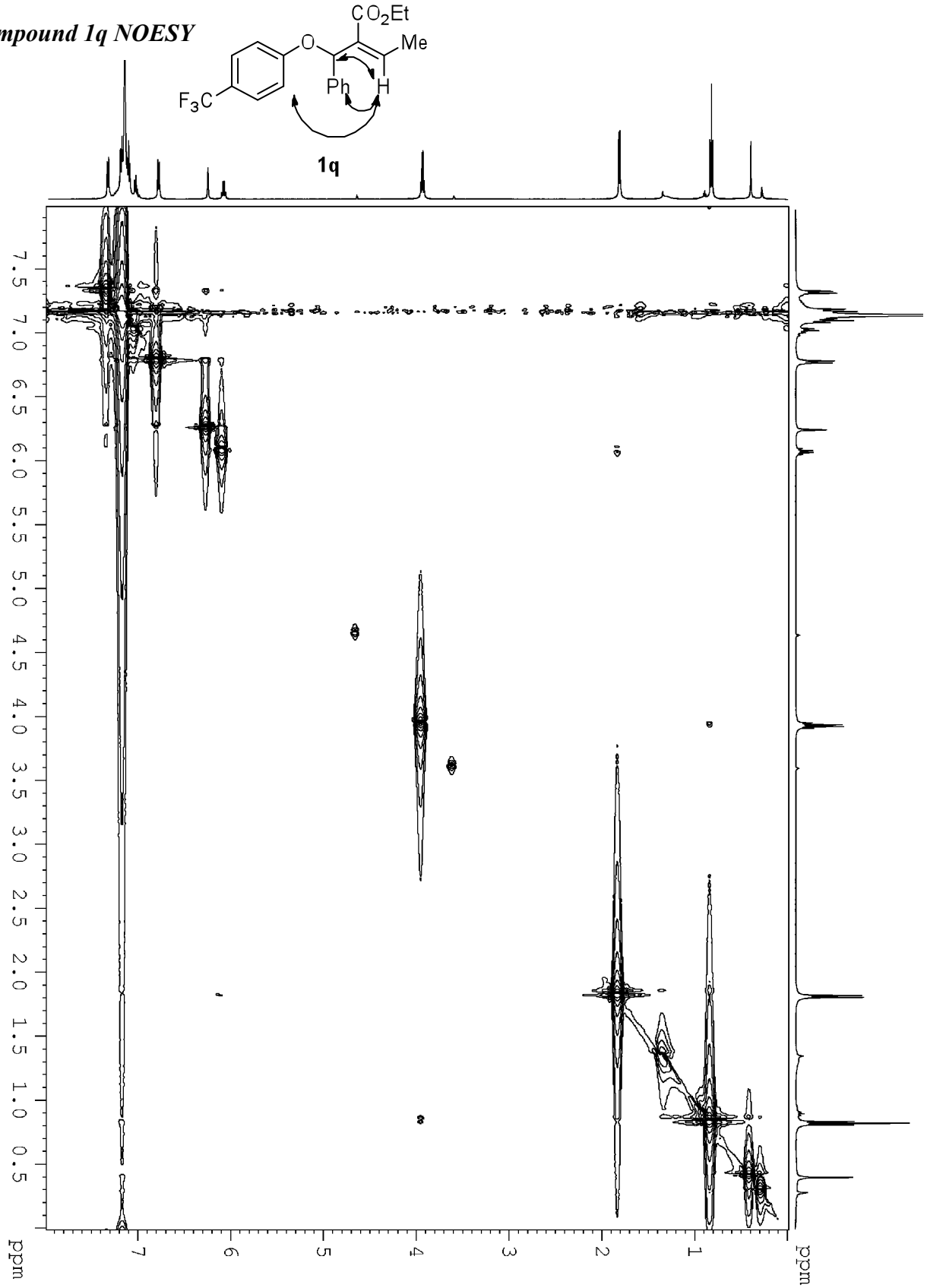

CO2Et
Me
O
Ph
F3C

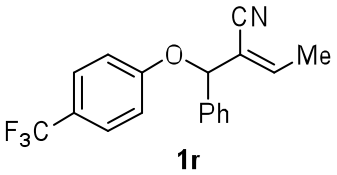
1q


8
7
6
5
4
3
2
1
ppm
2.031
5.095
2.026
2.000
2.031
3.016
3.110

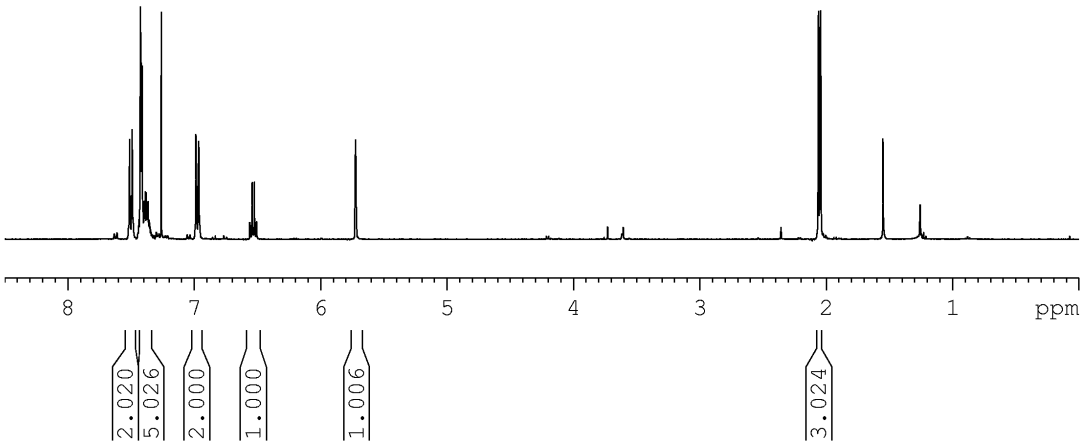

160
140
120
100
80
60
40
20
ppm

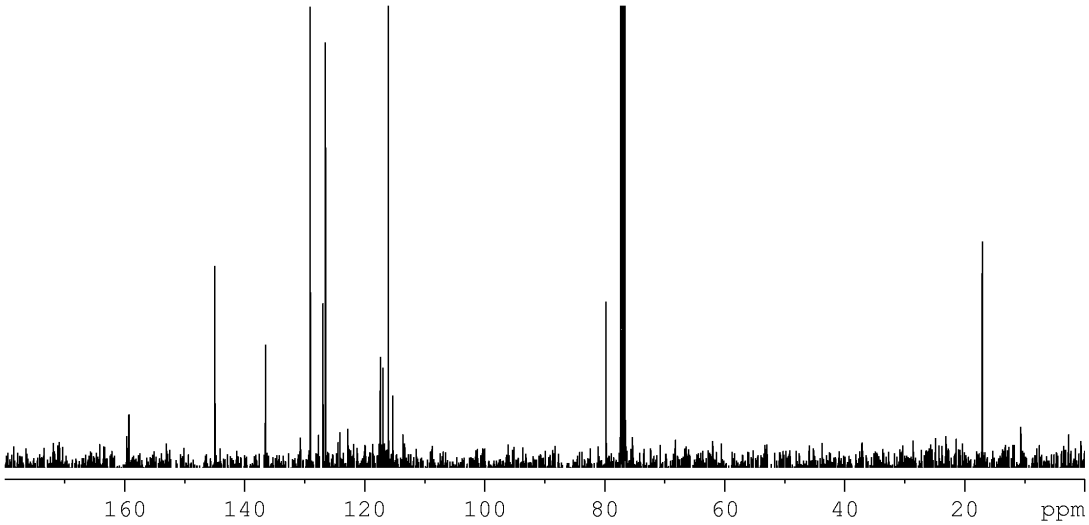
Compound 1q NOESY



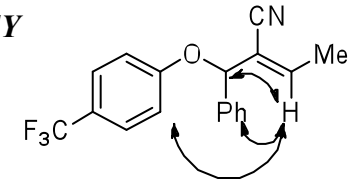

CN
O
Me
Ph
F3C

1r

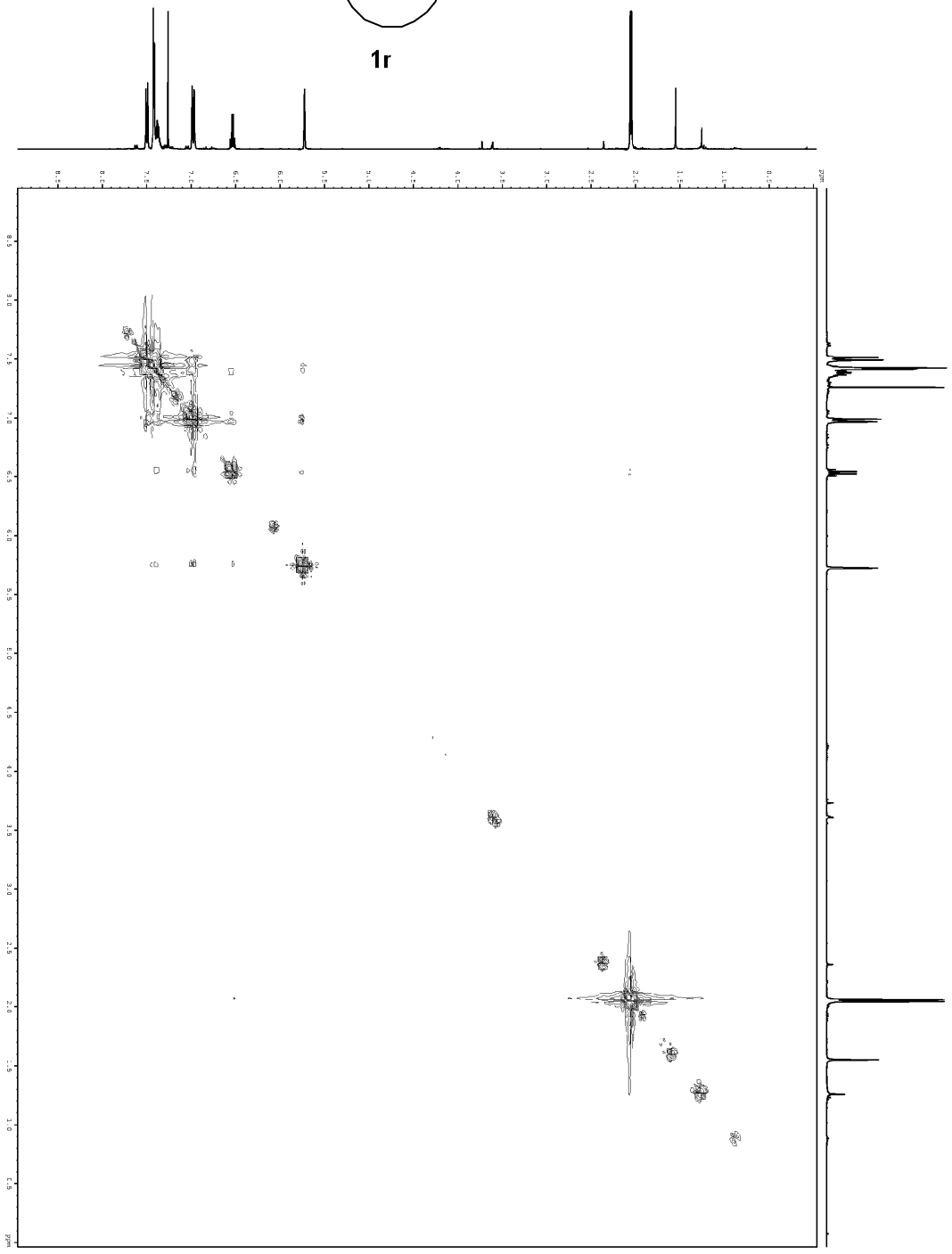

8
7
6
5
4
3
2
1
ppm
2.020
5.026
2.000
1.000
1.006
3.024

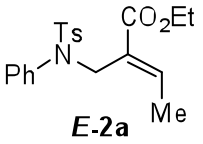

160
140
120
100
80
60
40
20
ppm

Compound 1m NOESY

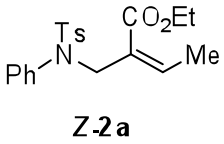


1r

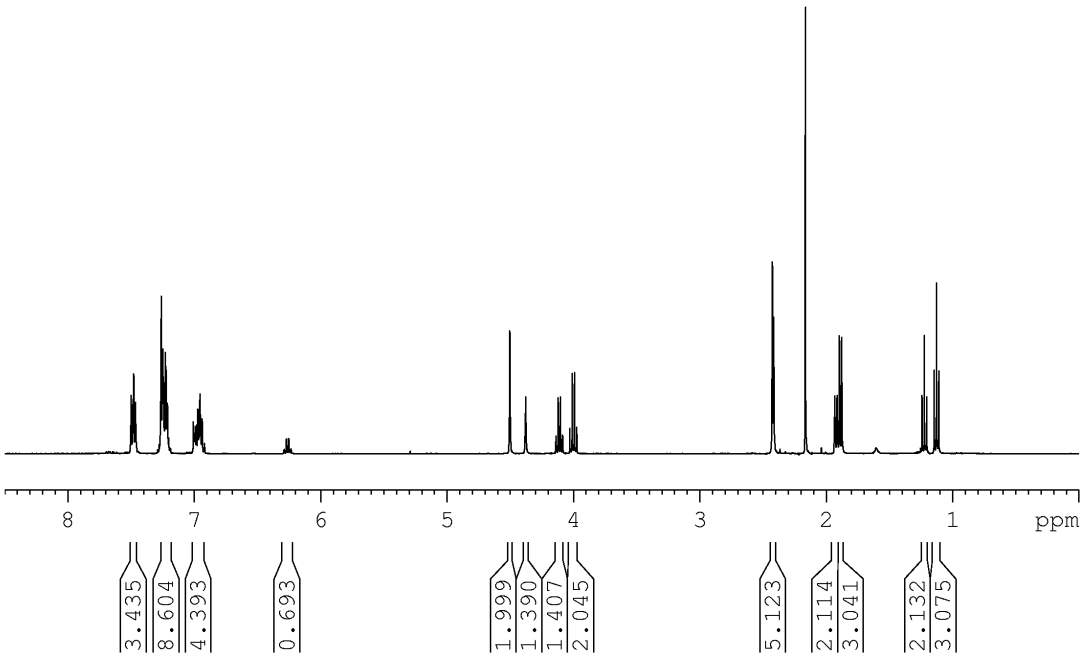


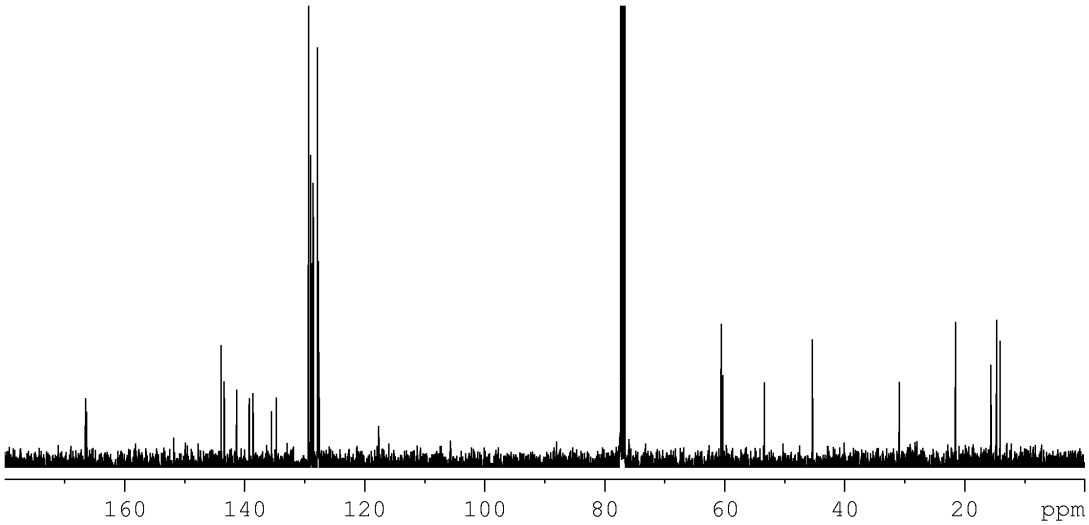

Ts
N
Ph
CO2Et
Me

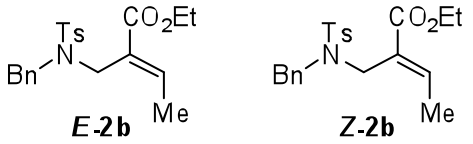
***E*-2a**


Ts
N
Ph
CO2Et
Me

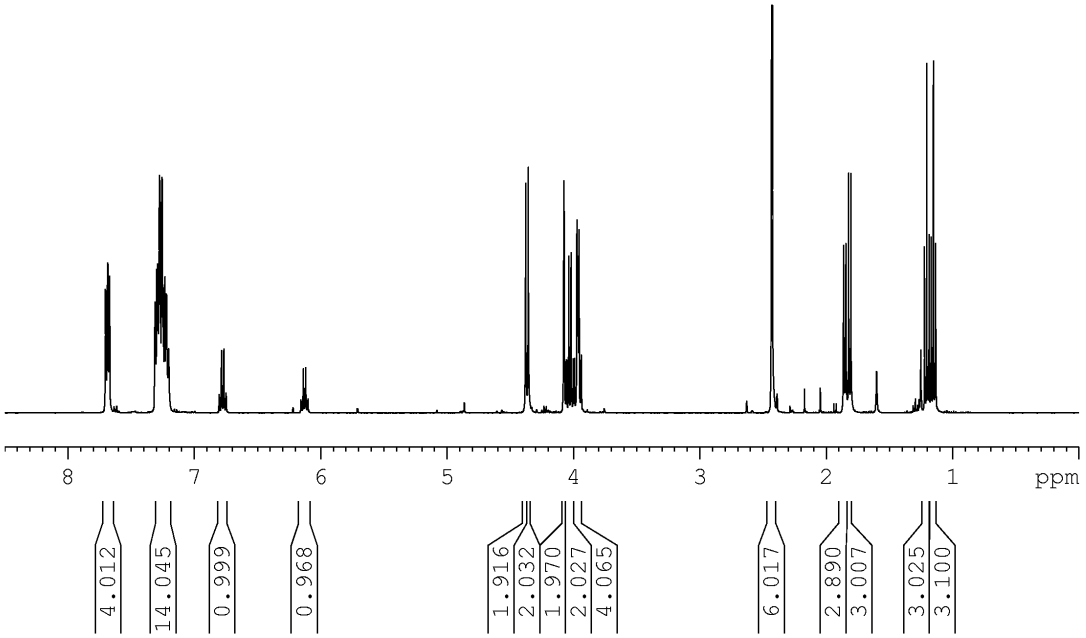
***Z*-2a**

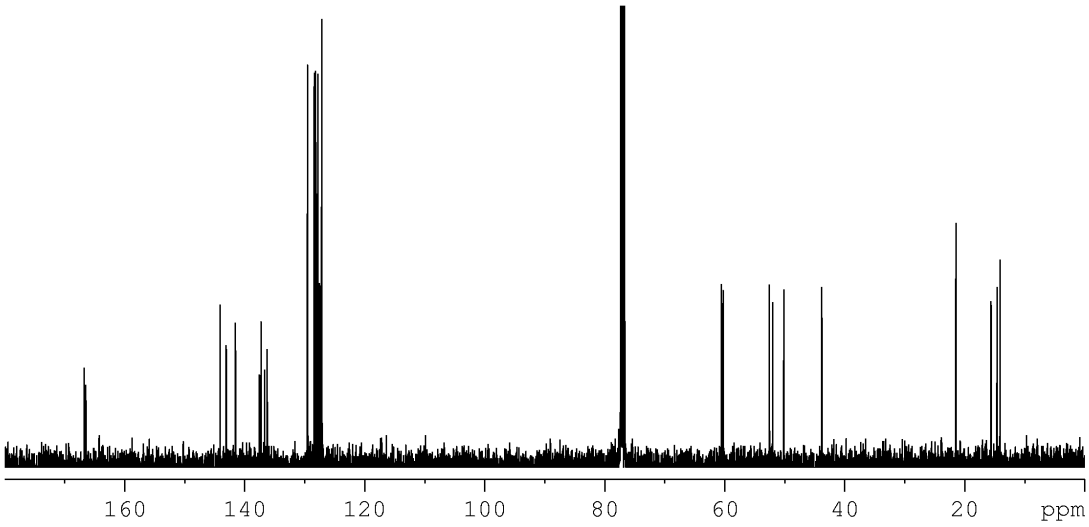

8
7
6
5
4
3
2
1
ppm
3.435
8.604
4.393
0.693
1.999
1.390
1.407
2.045
5.123
2.114
3.041
2.132
3.075

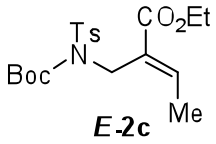

160
140
120
100
80
60
40
20
ppm


Ts
CO2Et
Bn
N
Me
Ts
CO2Et
Bn
N
Me

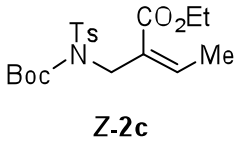
***E*-2b** ***Z*-2b**


8
7
6
5
4
3
2
1
ppm
4.012
14.045
0.999
0.968
1.916
2.032
1.970
2.027
4.065
6.017
2.890
3.007
3.025
3.100

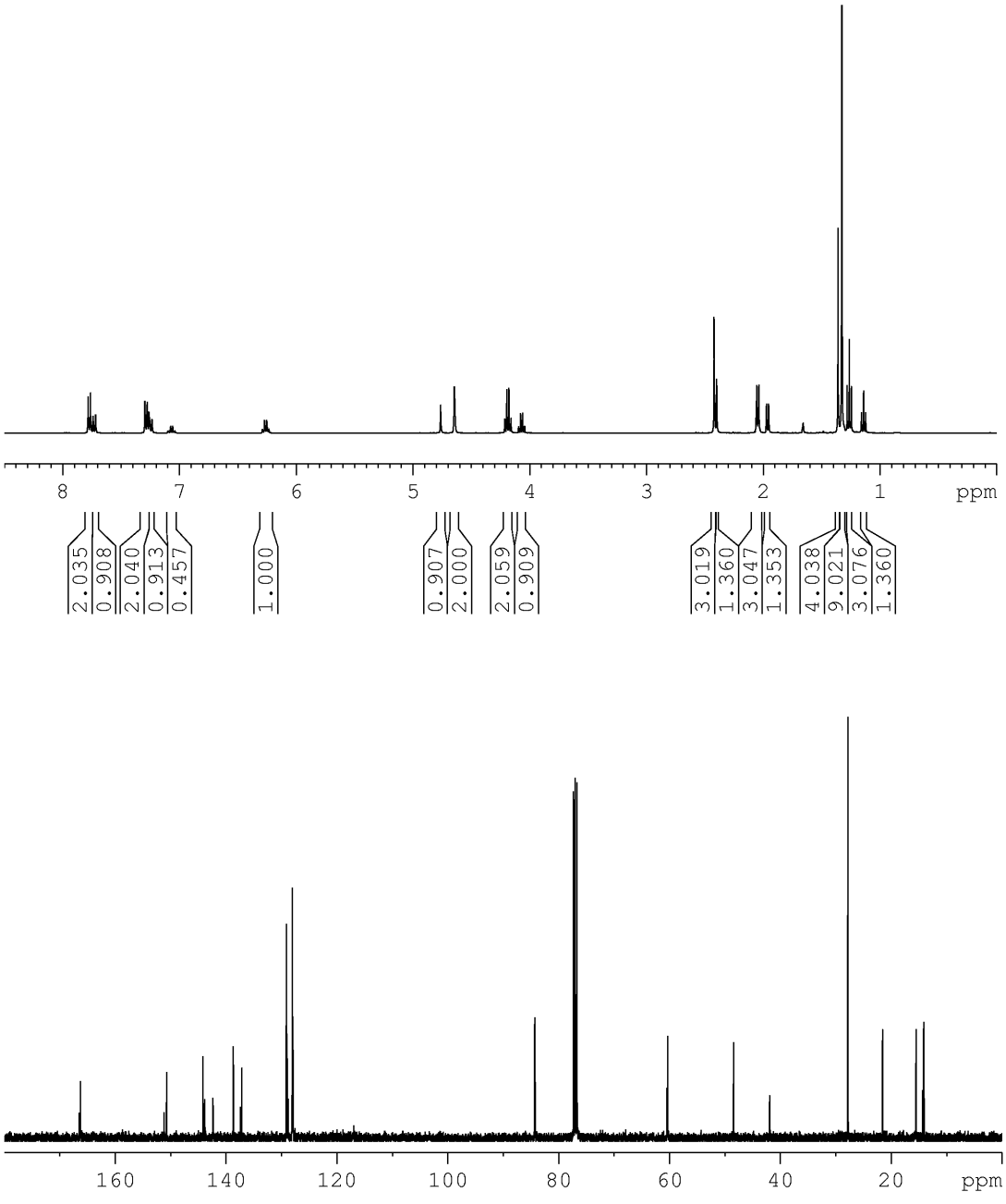

160
140
120
100
80
60
40
20
ppm

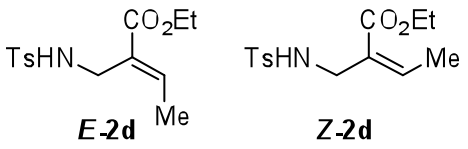

Ts
CO2Et
N
Boc
Me

***E*-2c**

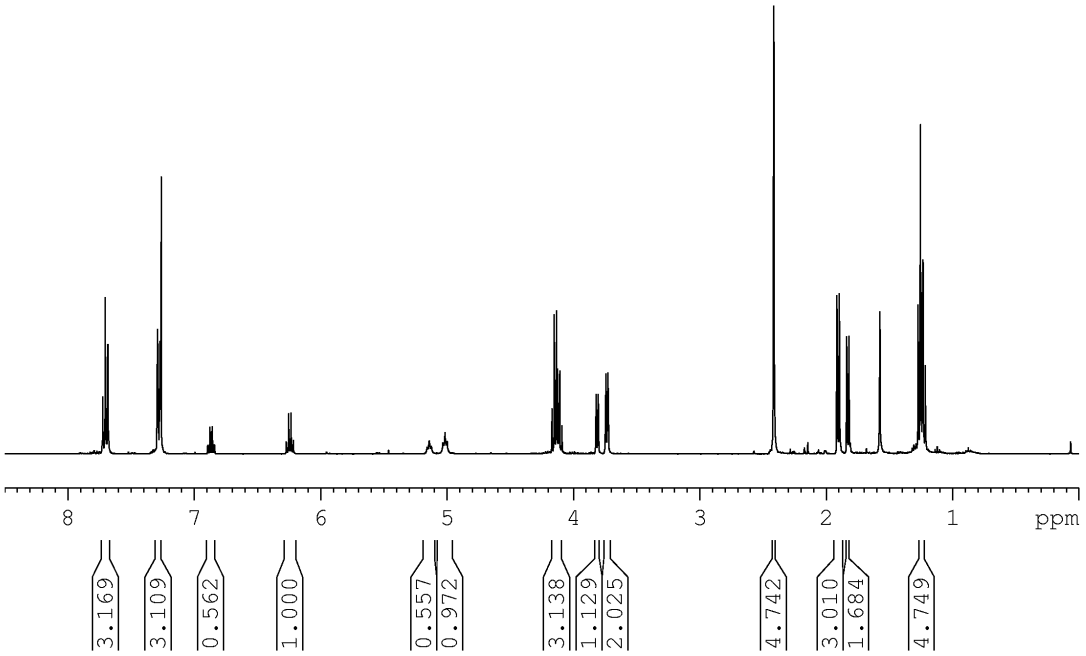

Ts
CO2Et
N
Boc
Me

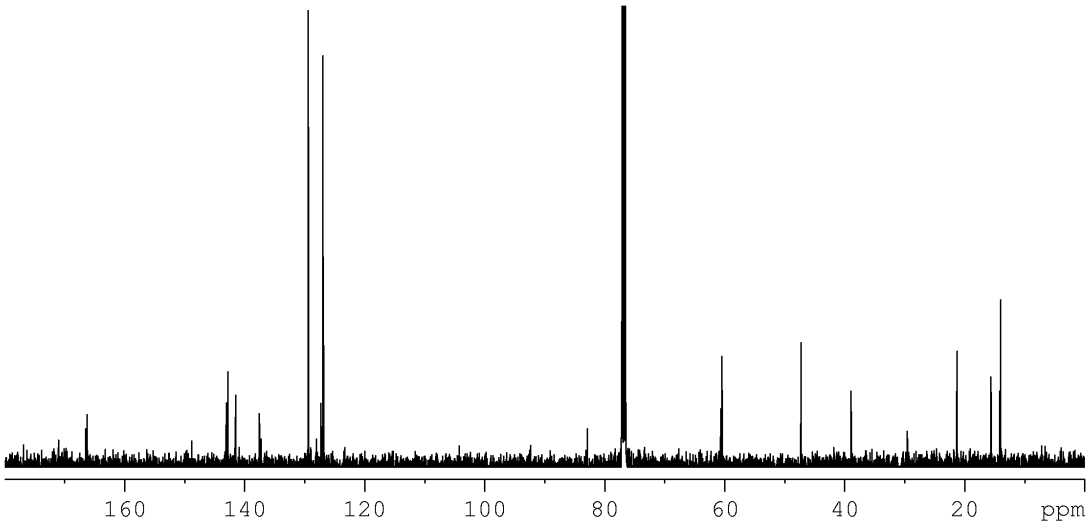
***Z*-2c**

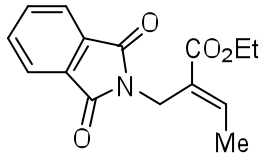

8
7
6
5
4
3
2
1
ppm
2.035
0.908
2.040
0.913
0.457
1.000
0.907
2.000
2.059
0.909
3.019
1.360
3.047
1.353
4.038
9.021
3.076
1.360
160
140
120
100
80
60
40
20
ppm


CO2Et
TsHN
Me
CO2Et
TsHN
Me

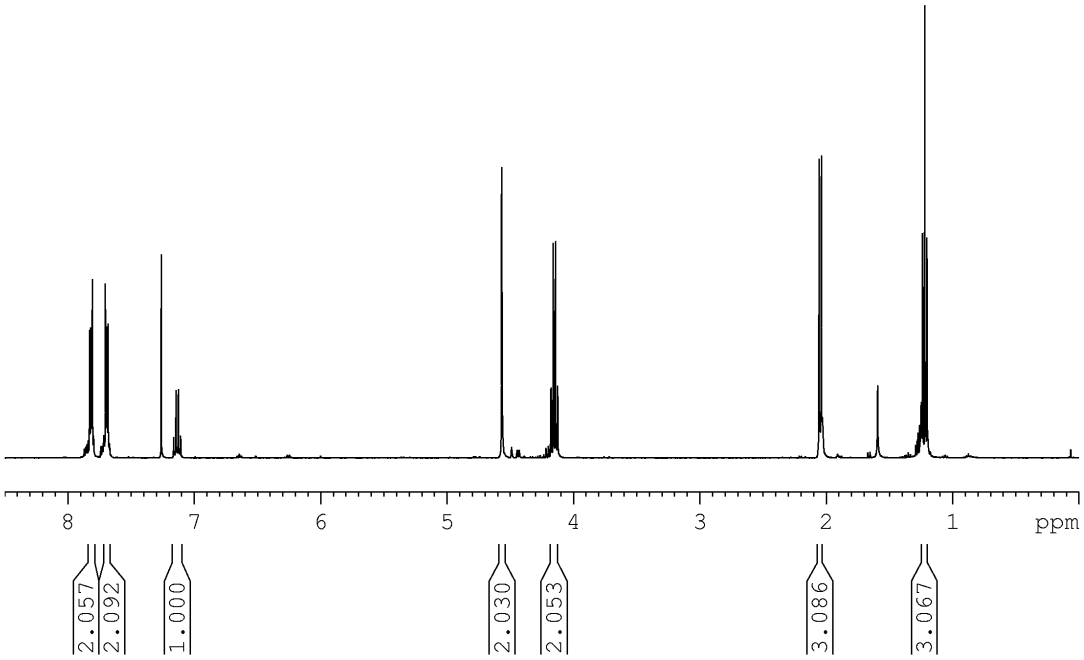
***E*-2d** ***Z*-2d**

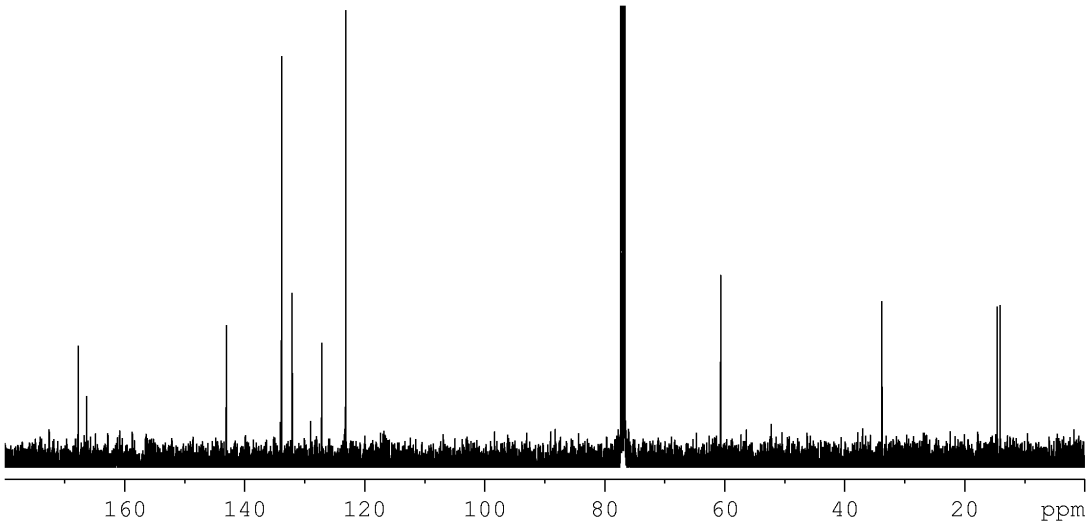

8
7
6
5
4
3
2
1
ppm
3.169
3.109
0.562
1.000
0.557
0.972
3.138
1.129
2.025
4.742
3.010
1.684
4.749


160
140
120
100
80
60
40
20
ppm

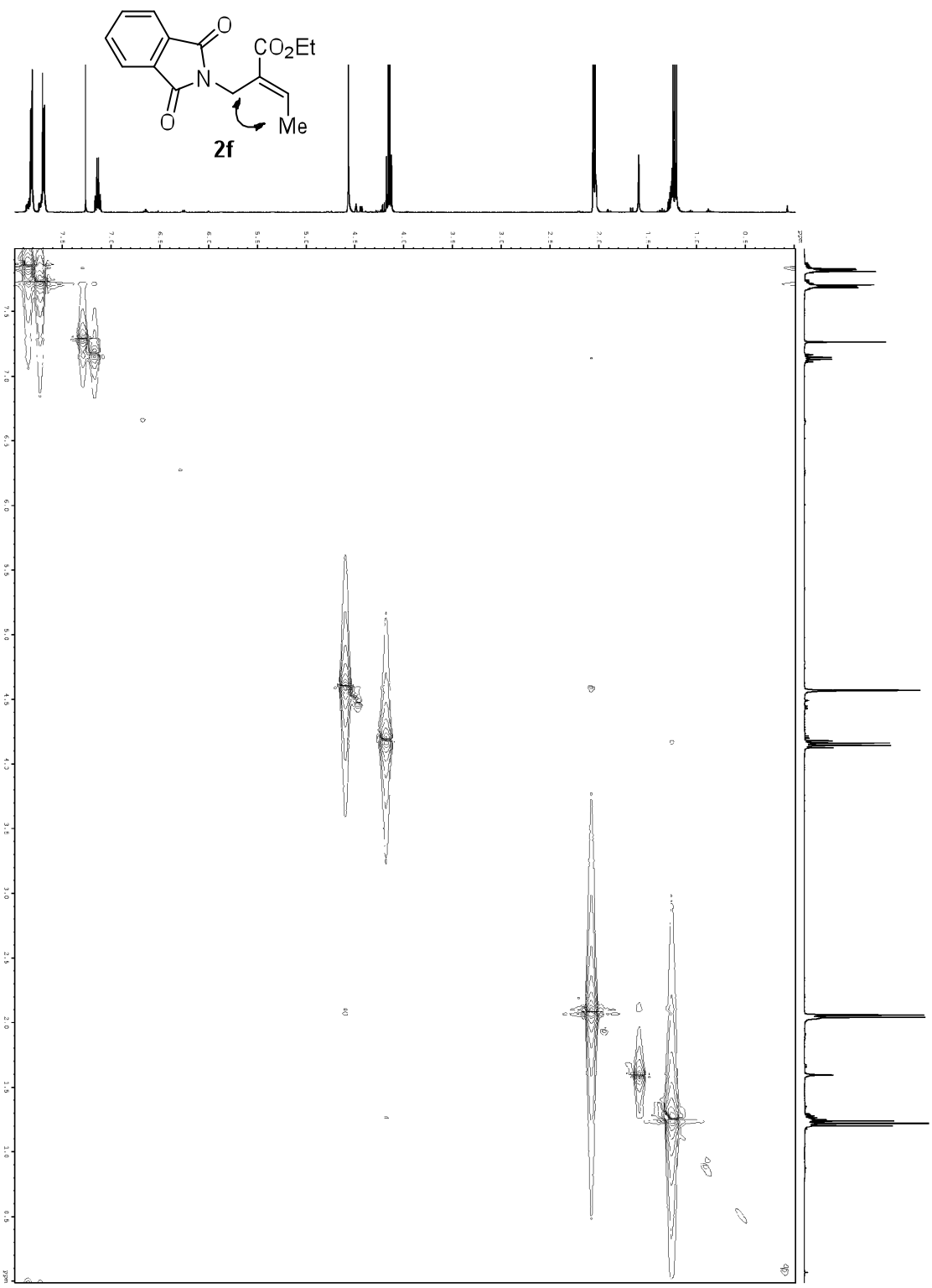

O
CO2Et
N
O
Me

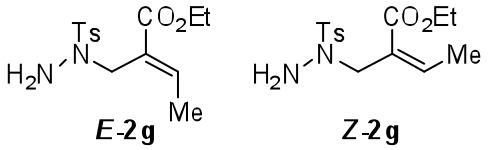
2f


8
7
6
5
4
3
2
1
ppm
2.057
2.092
1.000
2.030
2.053
3.086
3.067

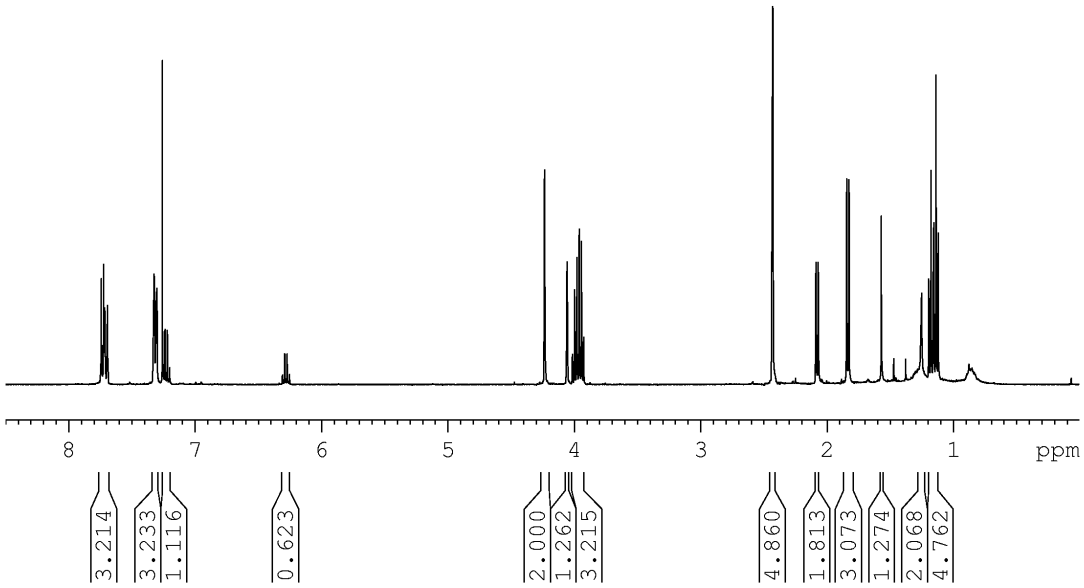

160
140
120
100
80
60
40
20
ppm

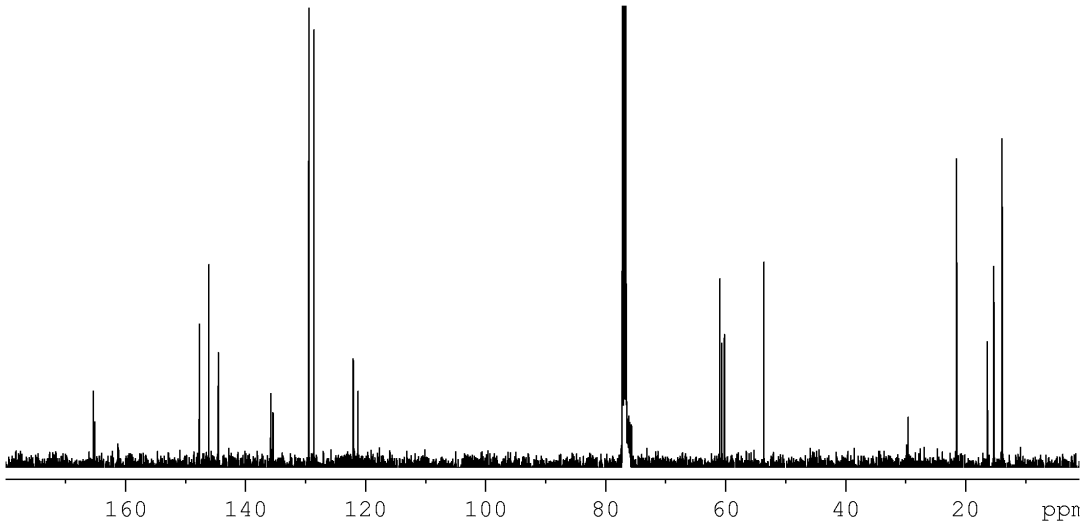
Compound 2f NOESY

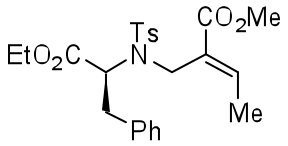



Ts
CO2Et
H2N
N
Me

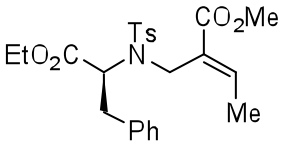
***E*-2g** ***Z*-2g**


8
7
6
5
4
3
2
1
ppm
3.214
3.233
1.116
0.623
2.000
1.262
3.215
4.860
1.813
3.073
1.274
2.068
4.762

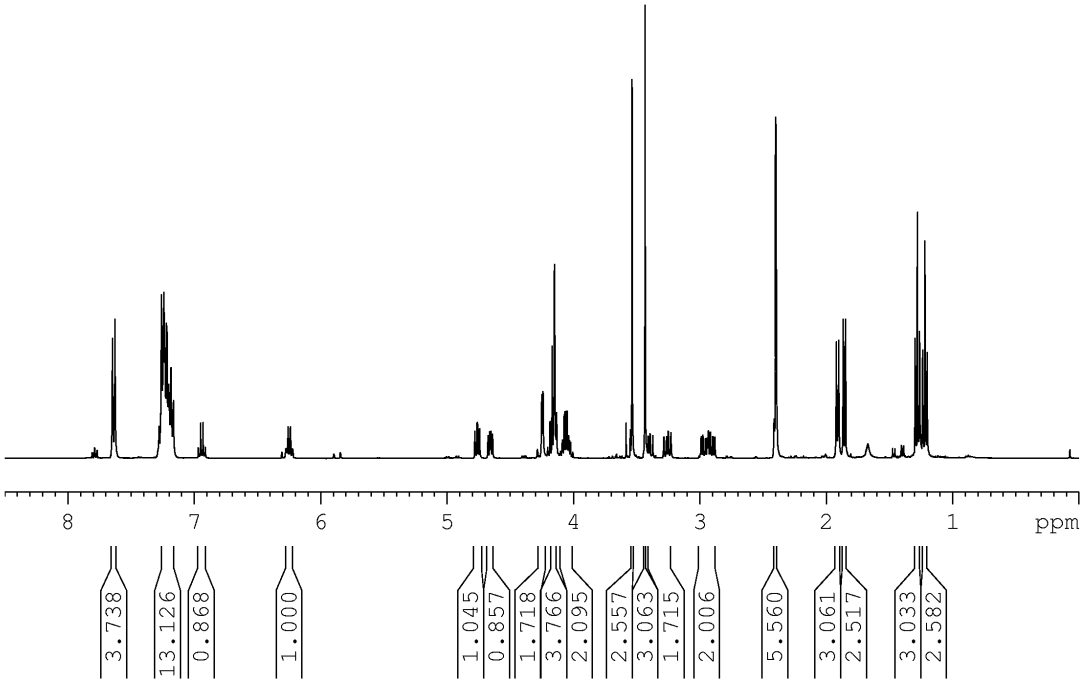

160
140
120
100
80
60
40
20
ppm

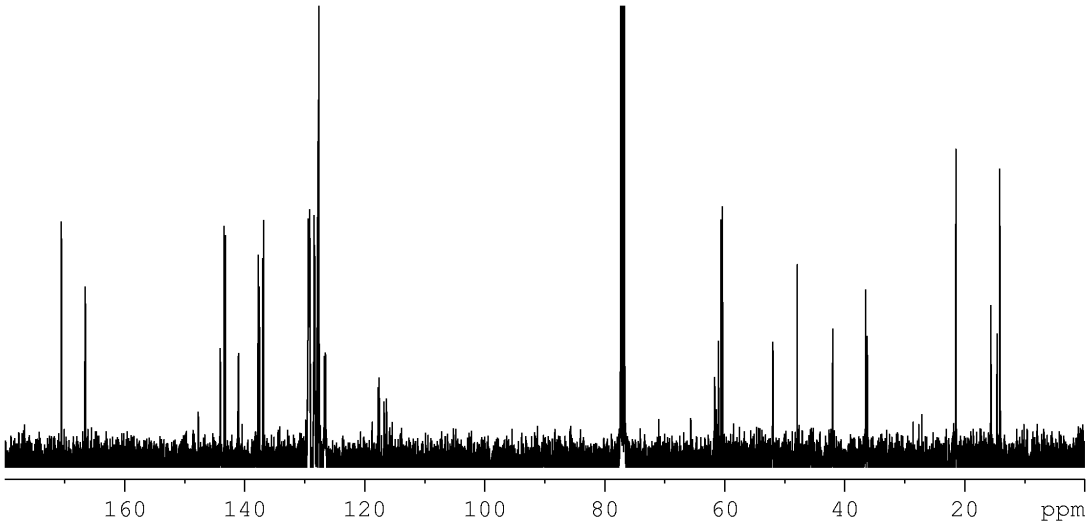

Ts
CO2Me
EtO2C
N
Me
Ph

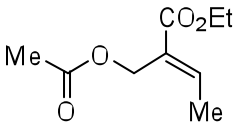
***E*-2h**


Ts
CO2Me
EtO2C
N
Me
Ph

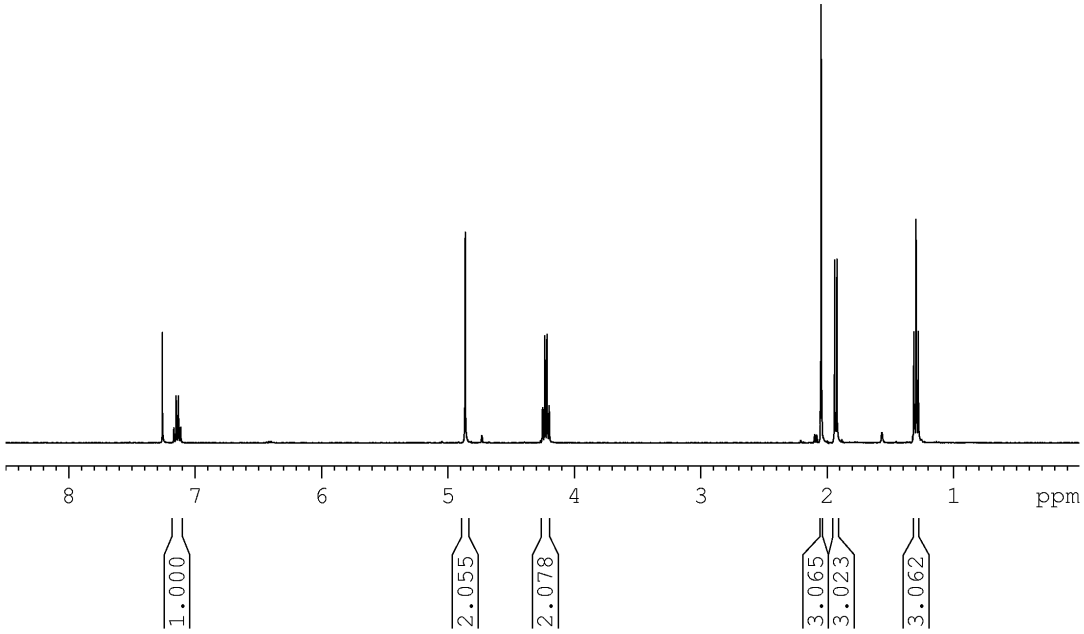
***Z*-2h**

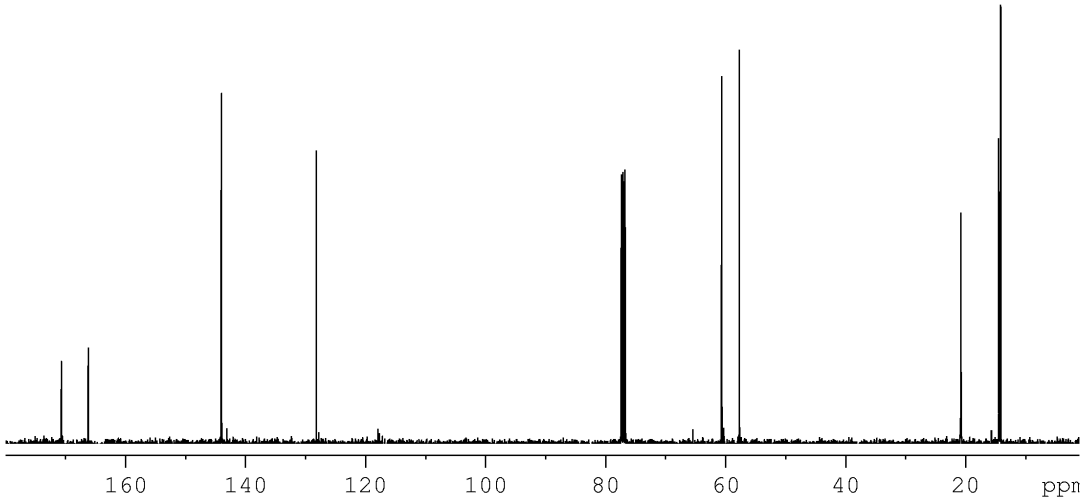

8
7
6
5
4
3
2
1
ppm
3.738
13.126
0.868
1.000
1.045
0.857
1.718
3.766
2.095
2.557
3.063
1.715
2.006
5.560
3.061
2.517
3.033
2.582

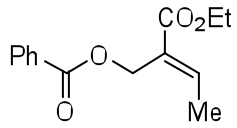

160
140
120
100
80
60
40
20
ppm


CO2Et
Me
O
O
Me

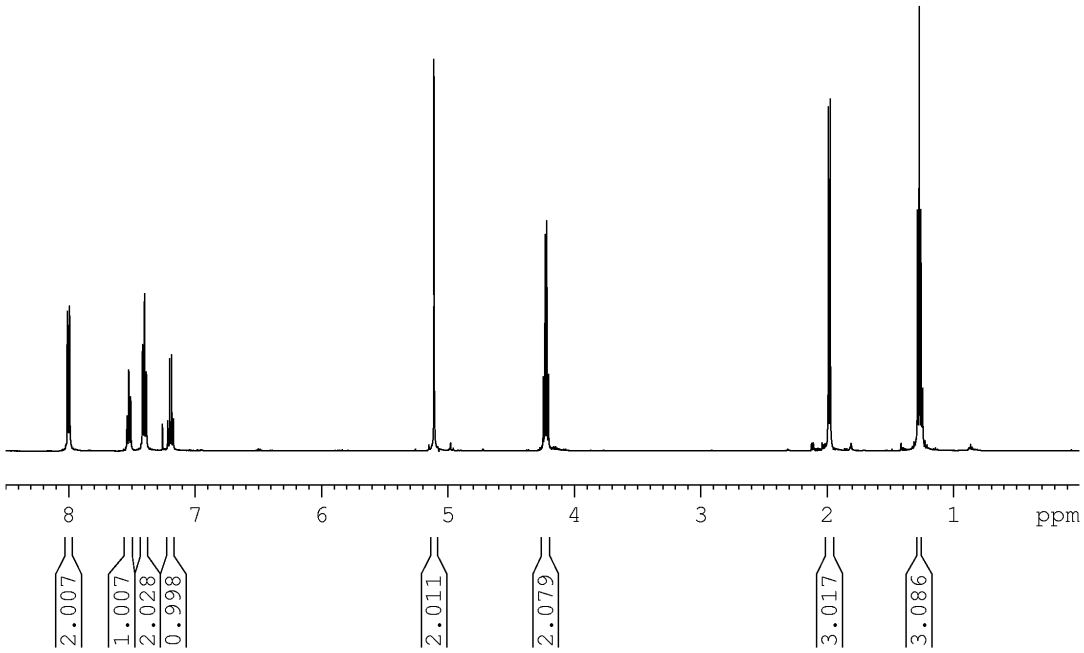
3a

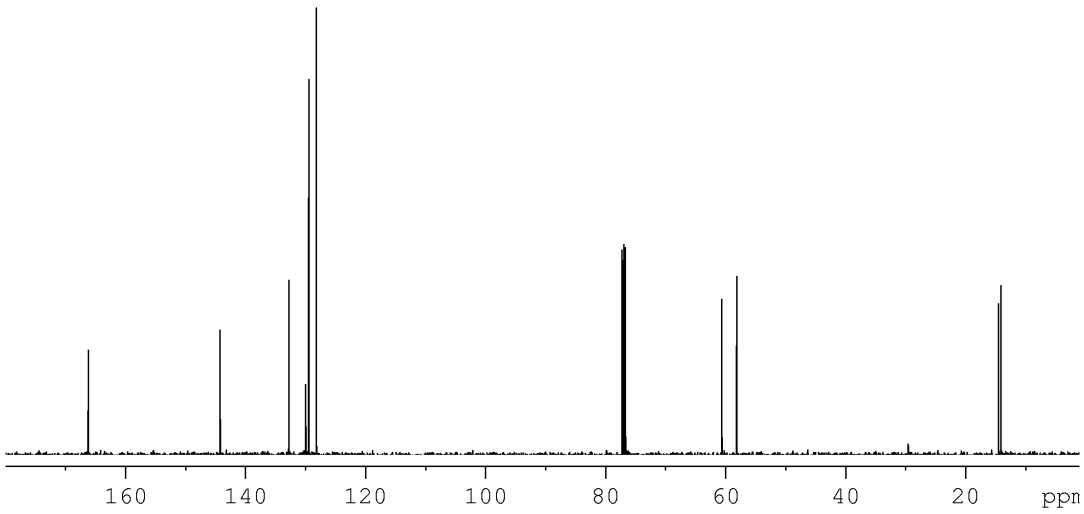

8
7
6
5
4
3
2
1
ppm
1.000
2.055
2.078
3.065
3.023
3.062

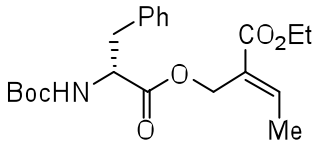

160
140
120
100
80
60
40
20
ppm


CO2Et
Ph
O
O
Me

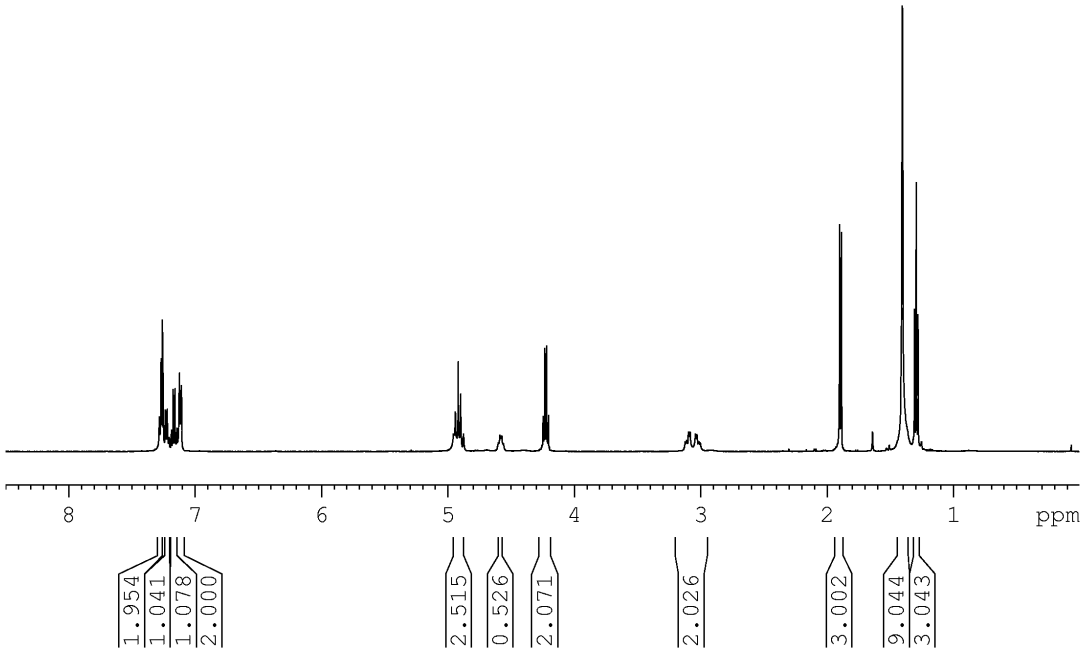
3b

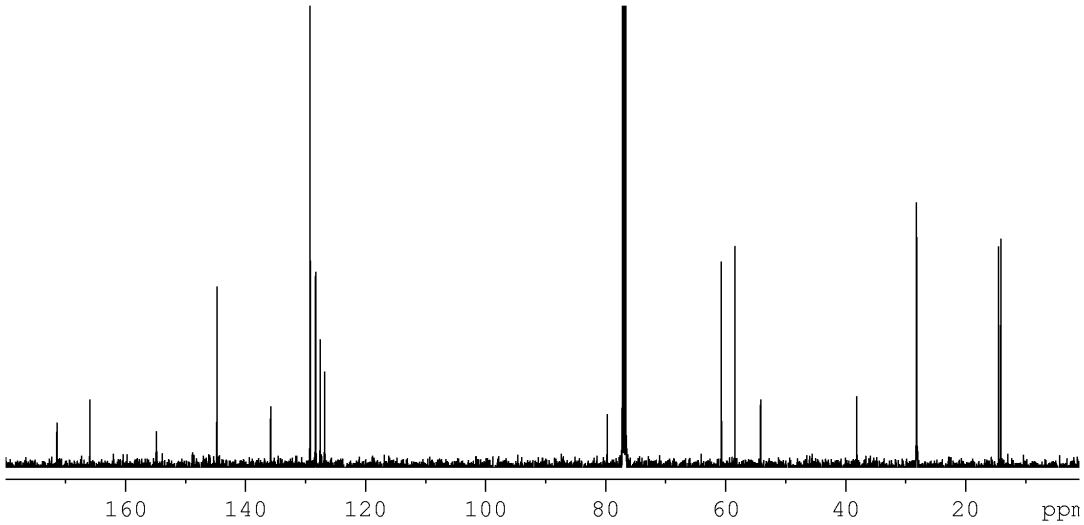

8
7
6
5
4
3
2
1
ppm
2.007
1.007
2.028
0.998
2.011
2.079
3.017
3.086

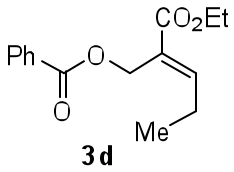

160
140
120
100
80
60
40
20
ppm


Ph
CO2Et
BocHN
O
O
Me

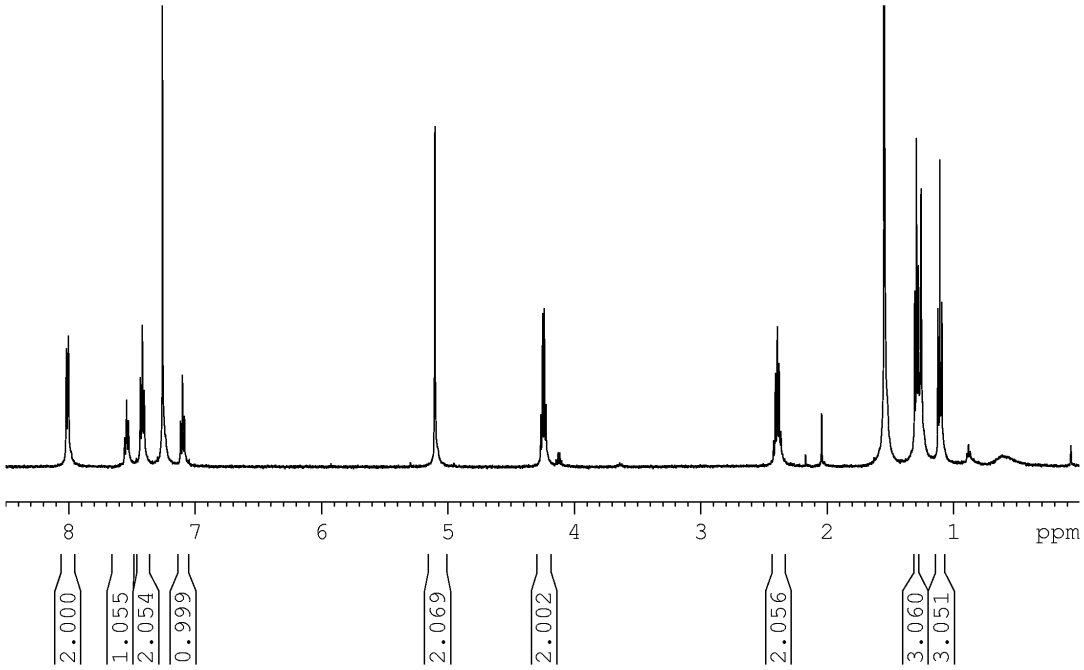
3c

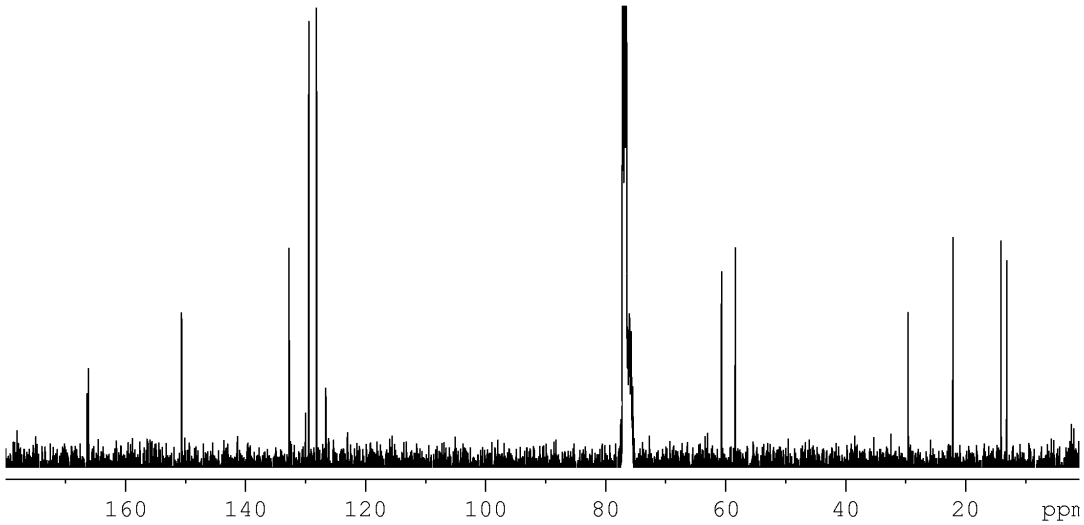

8
7
6
5
4
3
2
1
ppm
1.954
1.041
1.078
2.000
2.515
0.526
2.071
2.026
3.002
9.044
3.043


160
140
120
100
80
60
40
20
ppm

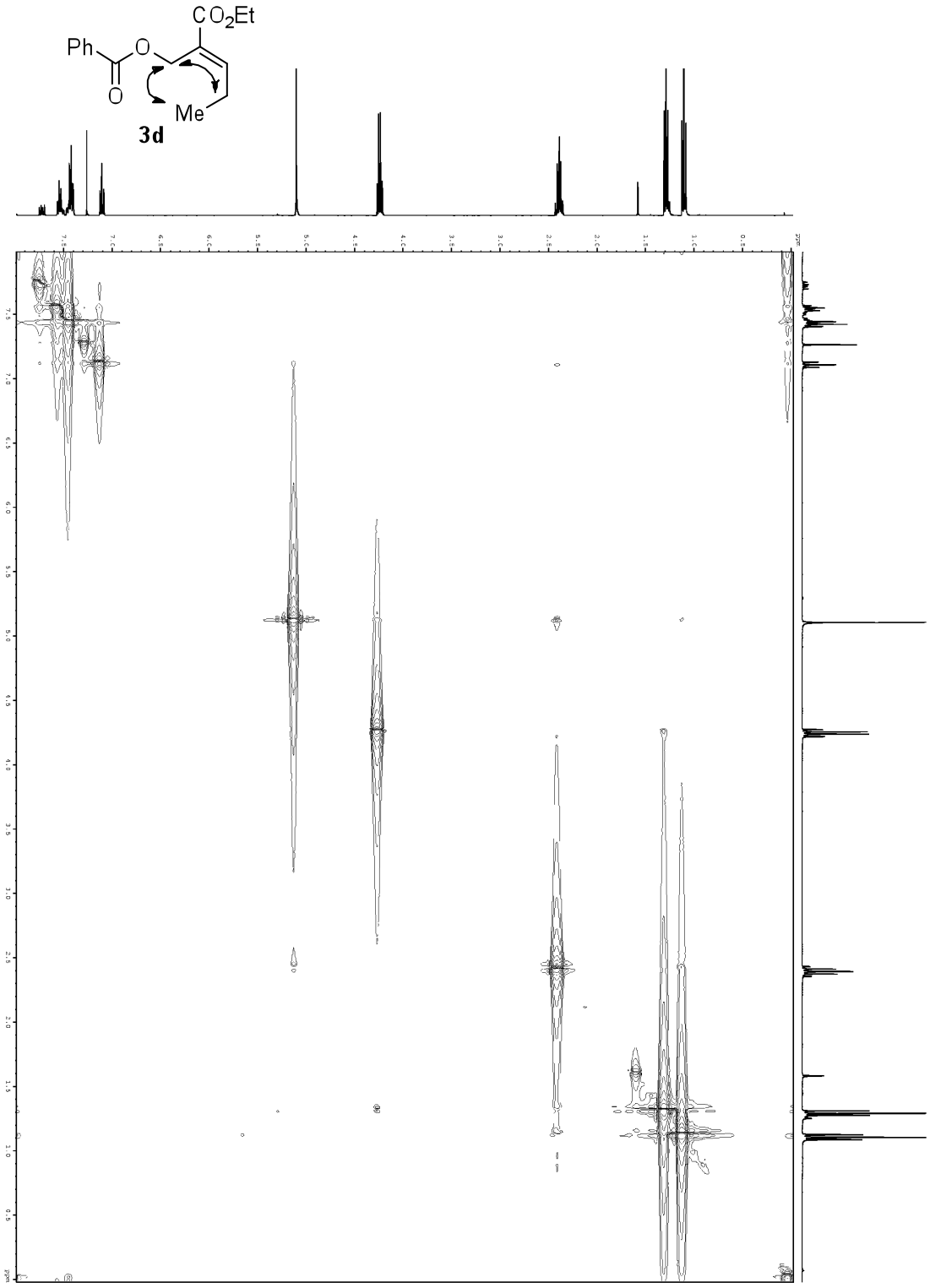


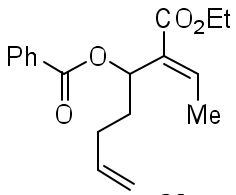
3d



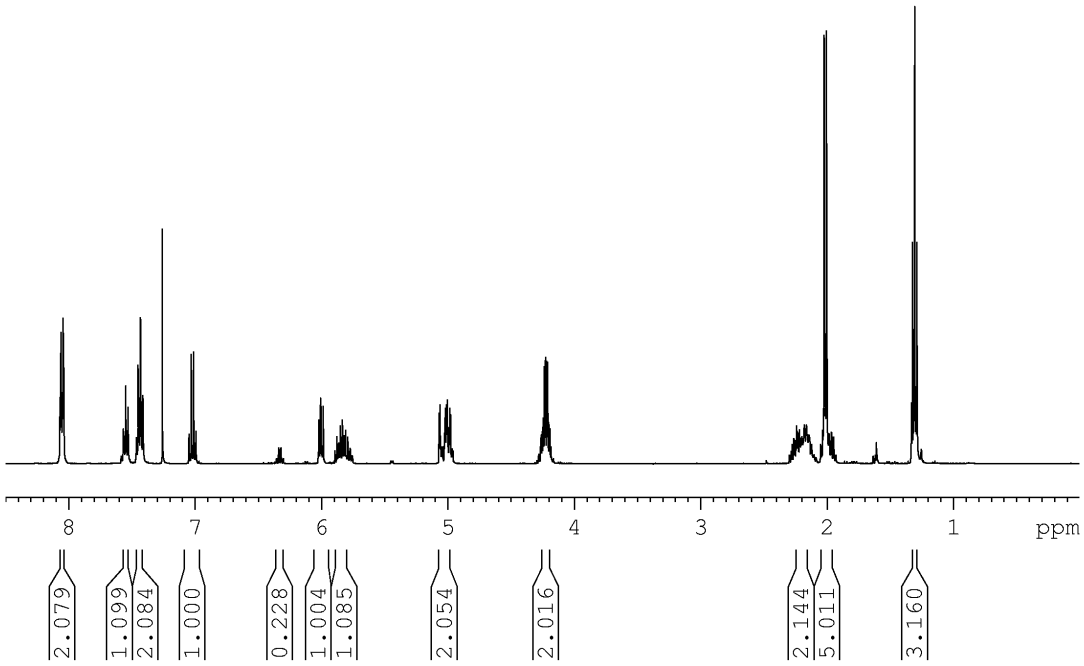


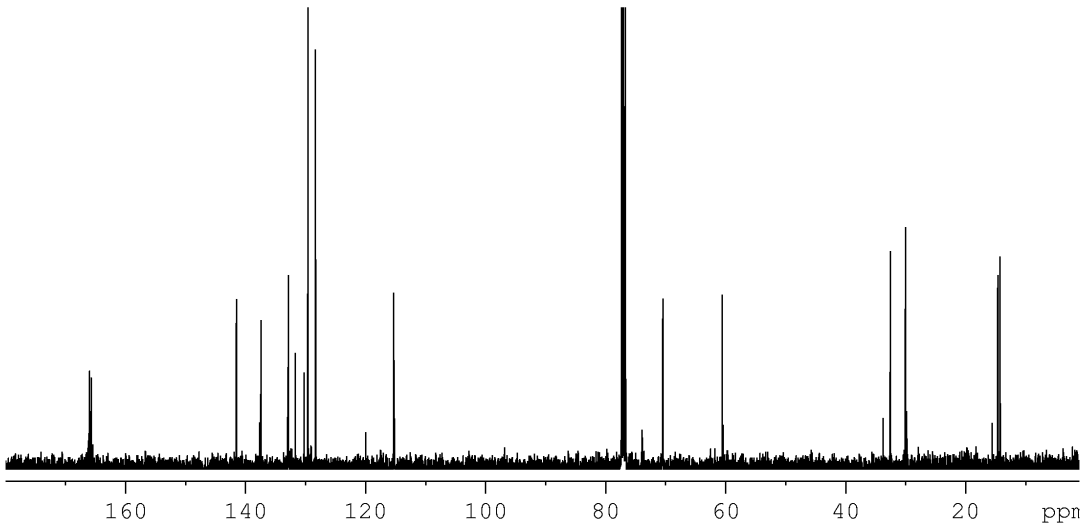
Compound 3d NOESY


CO2Et
Ph
O
O
Me
3d

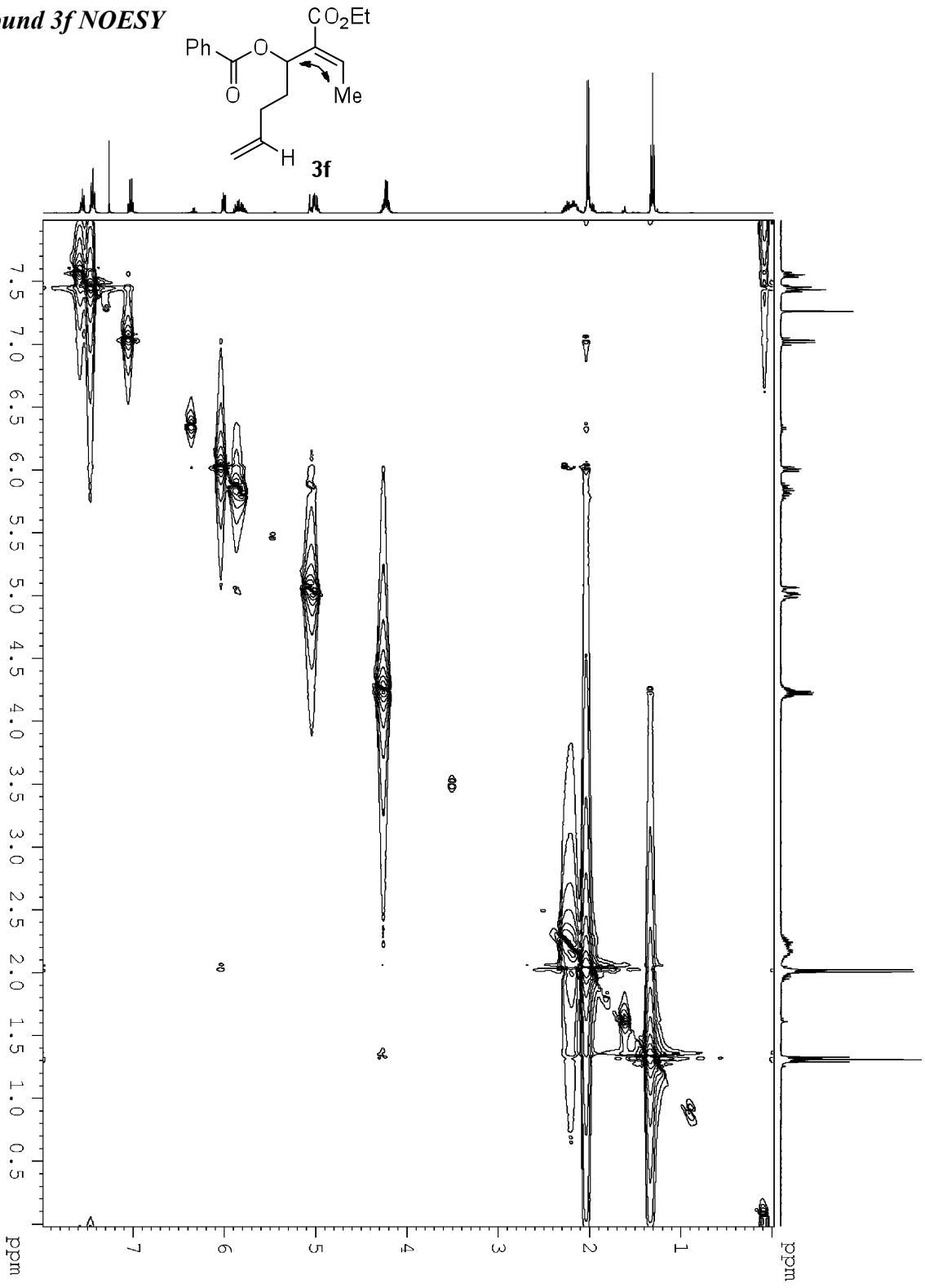

CO2Et
Ph
O
O
Me

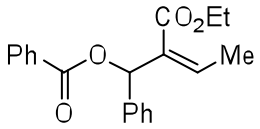
3f


8
7
6
5
4
3
2
1
ppm
2.079
1.099
2.084
1.000
0.228
1.004
1.085
2.054
2.016
2.144
5.011
3.160

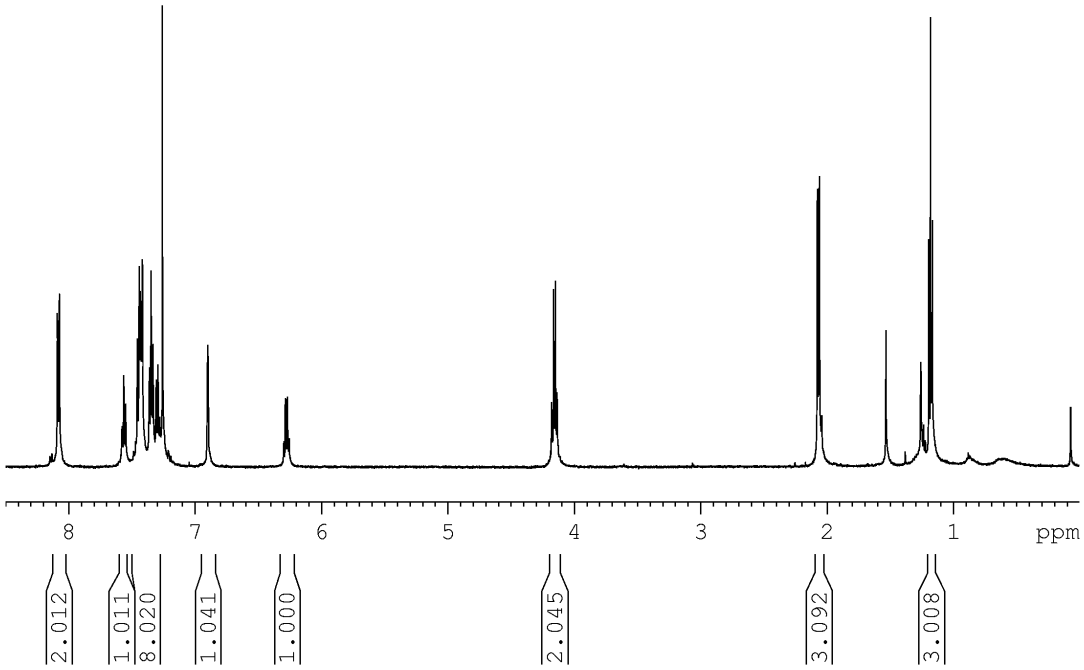

160
140
120
100
80
60
40
20
ppm

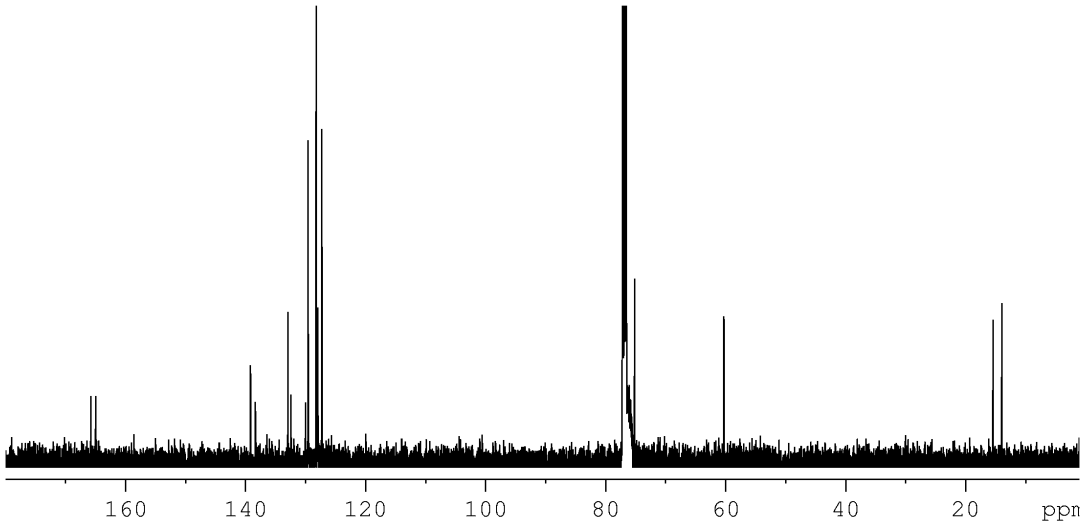
Compound 3f NOESY



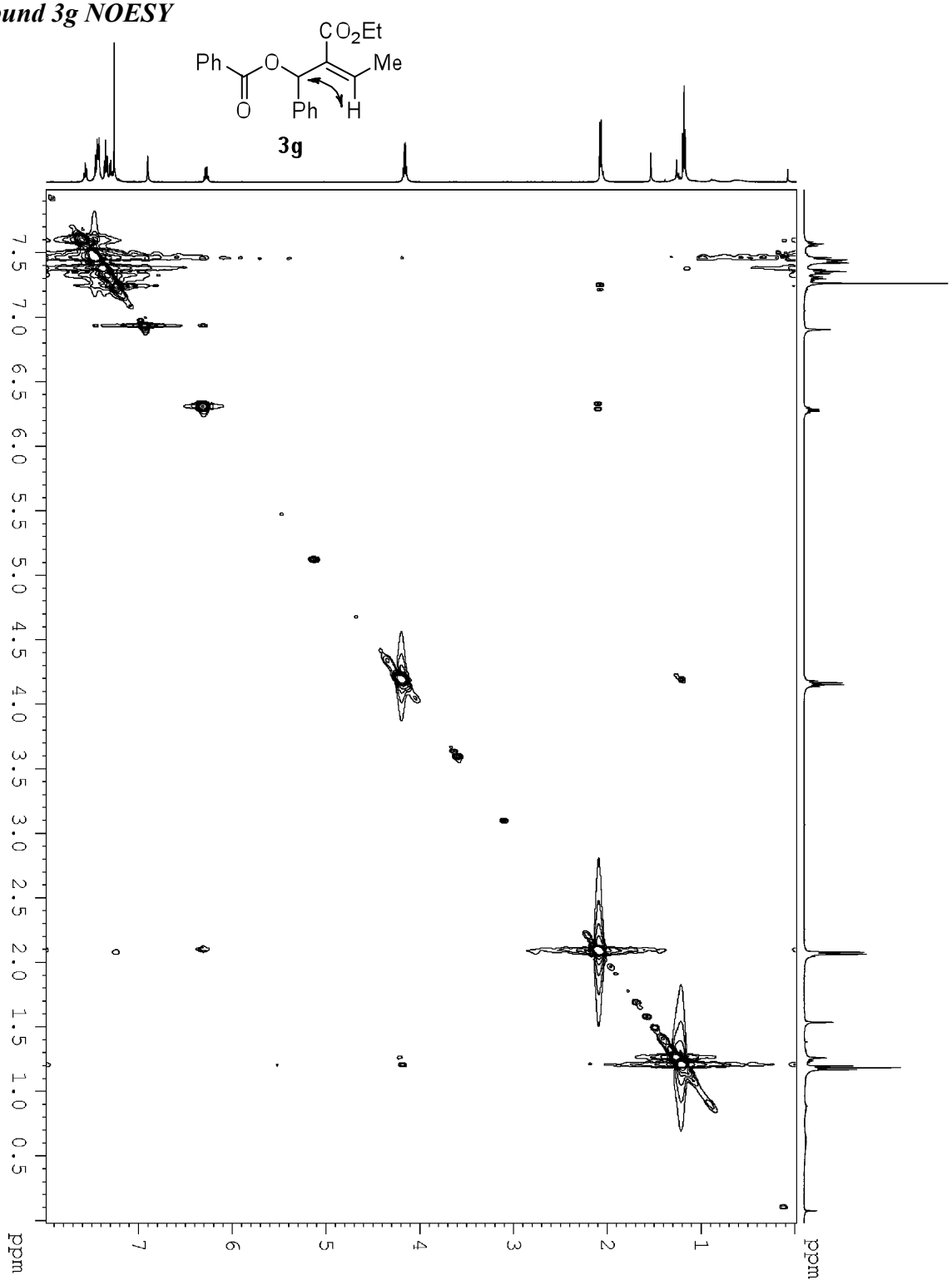

CO2Et
Ph
O
Me
O
Ph

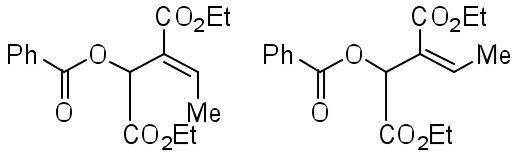
3g


8
7
6
5
4
3
2
1
ppm
2.012
1.011
8.020
1.041
1.000
2.045
3.092
3.008


160
140
120
100
80
60
40
20
ppm

Compound 3g NOESY

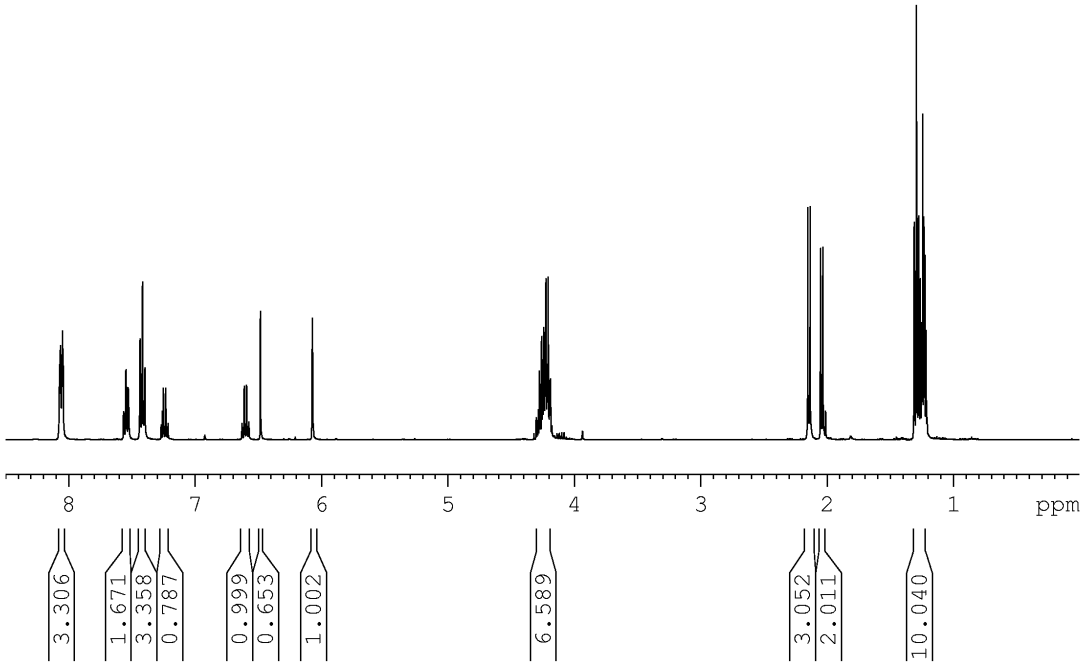


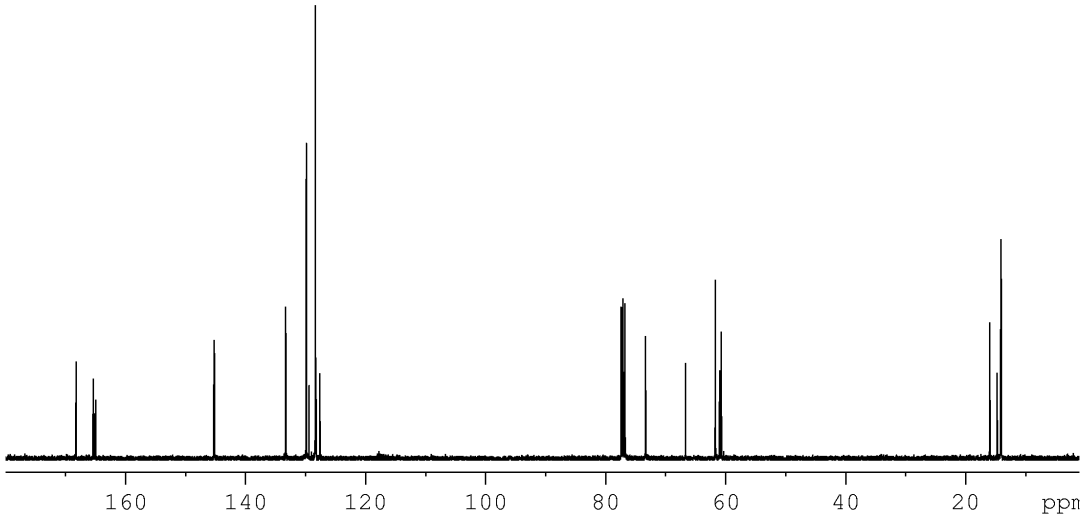

Ph
O
O
CO2Et
Me
CO2Et

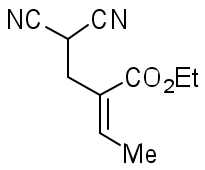
***E*-3h**

Ph
O
O
CO2Et
Me
CO2Et

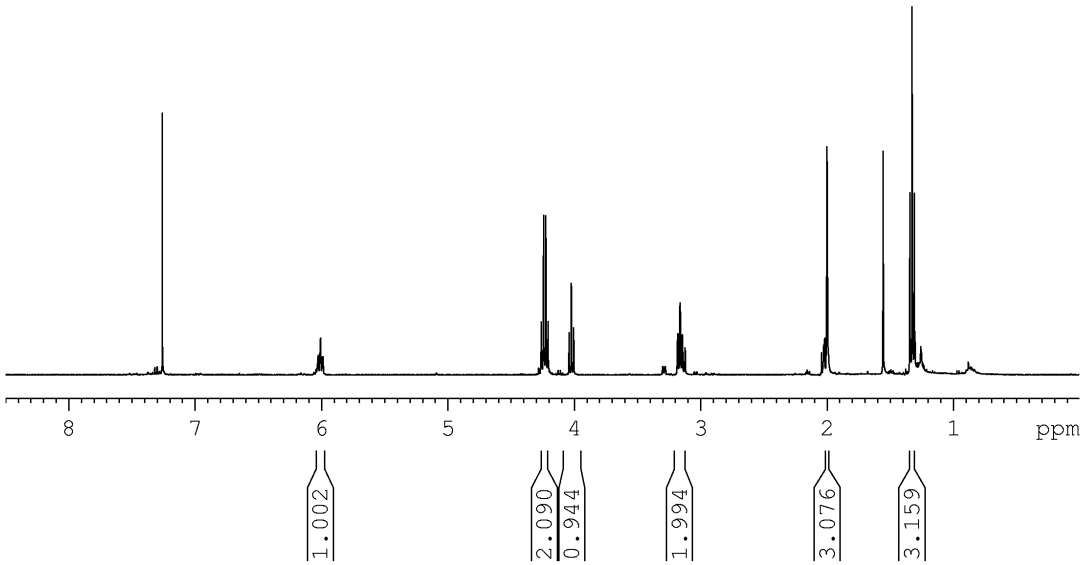
***Z*-3h**

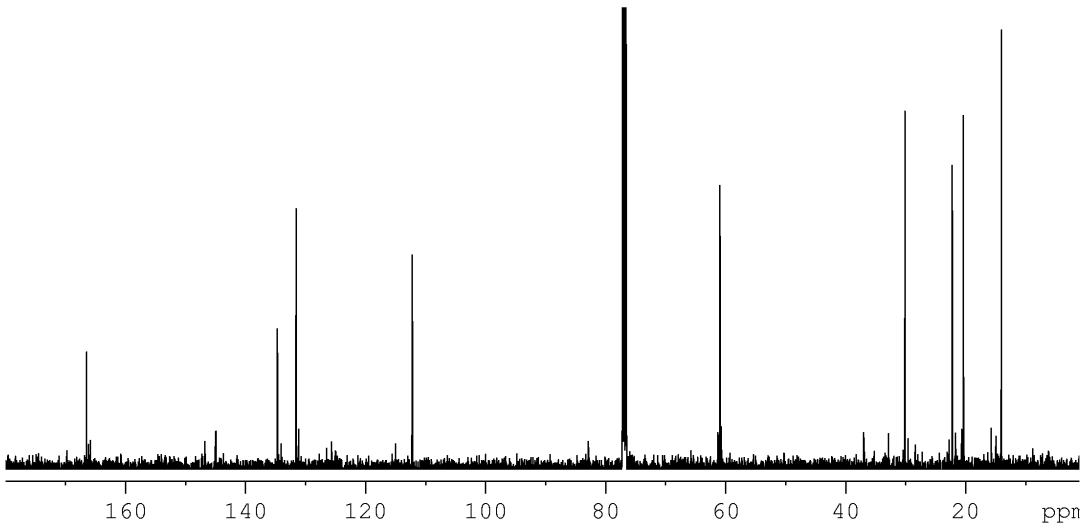

8
7
6
5
4
3
2
1
ppm
3.306
1.671
3.358
0.787
0.999
0.653
1.002
6.589
3.052
2.011
10.040


160
140
120
100
80
60
40
20
ppm

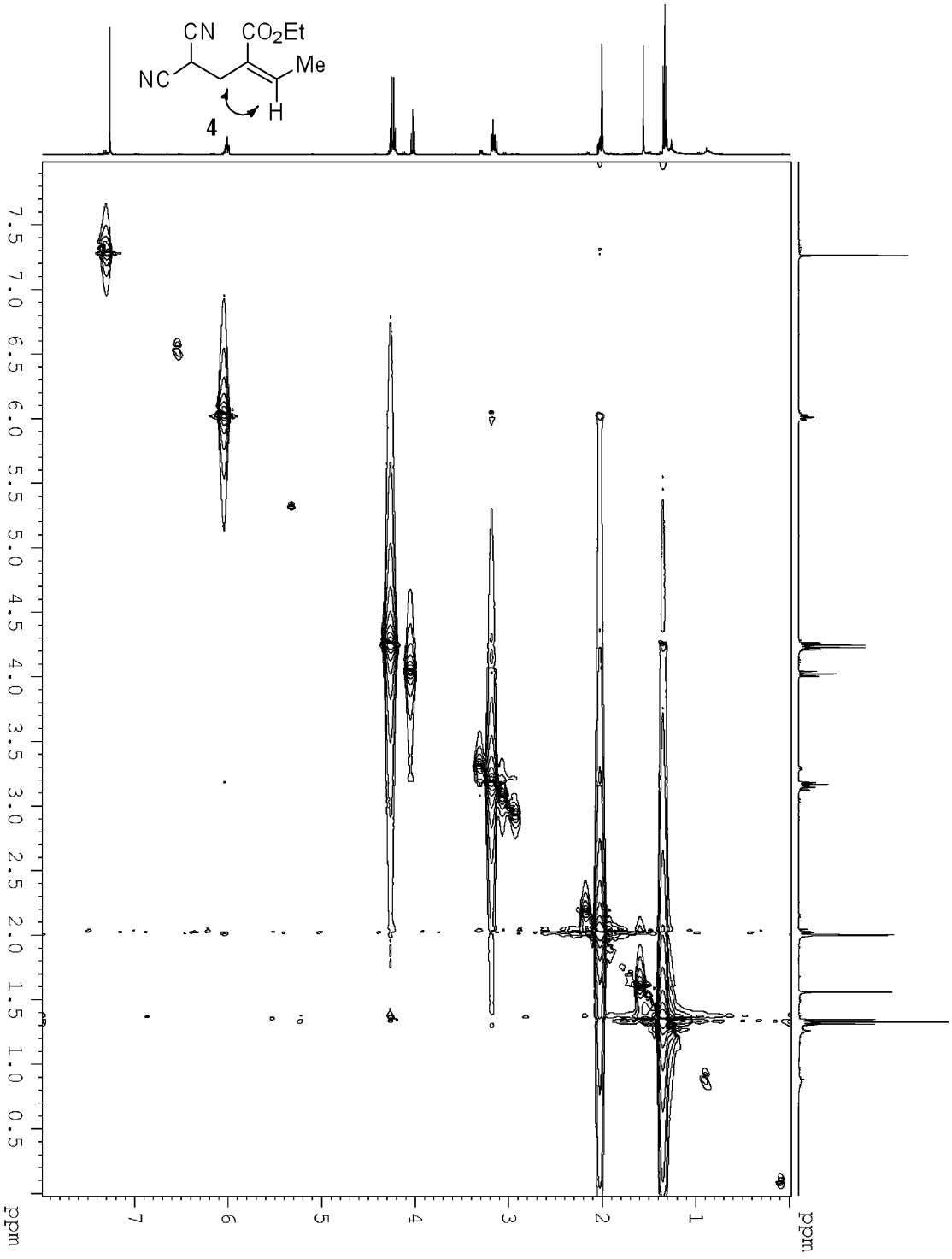

NC
CN
CO2Et
Me

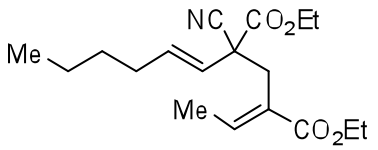
4


8
7
6
5
4
3
2
1
ppm
1.002
2.090
0.944
1.994
3.076
3.159

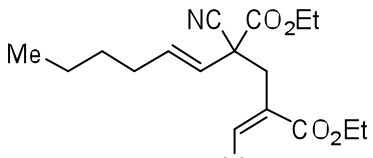

160
140
120
100
80
60
40
20
ppm

Compound 4 NOESY

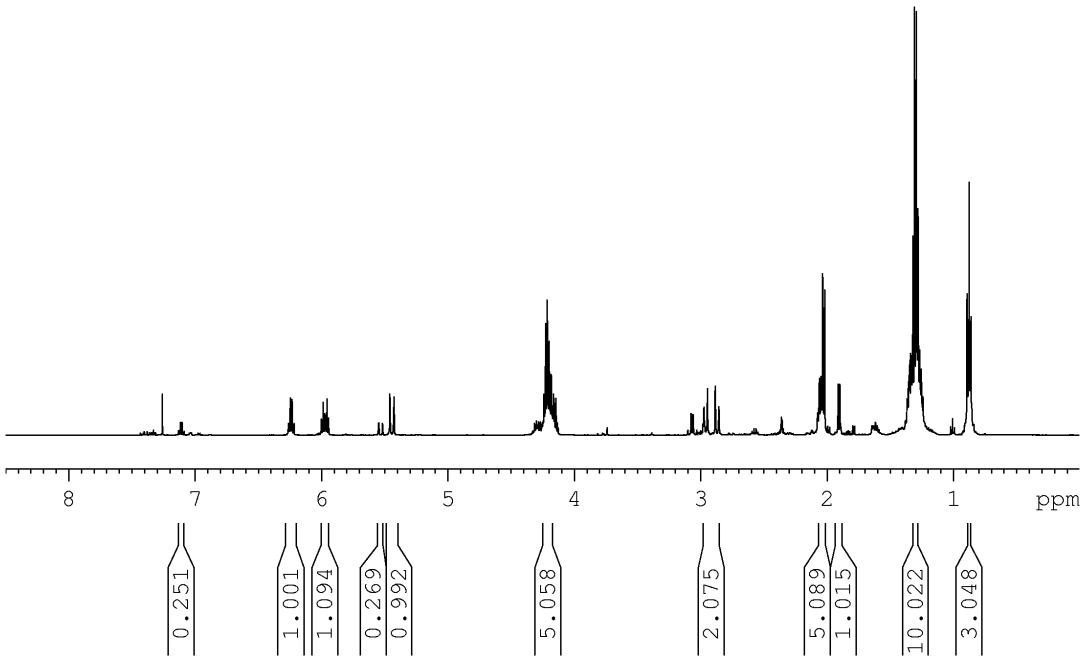


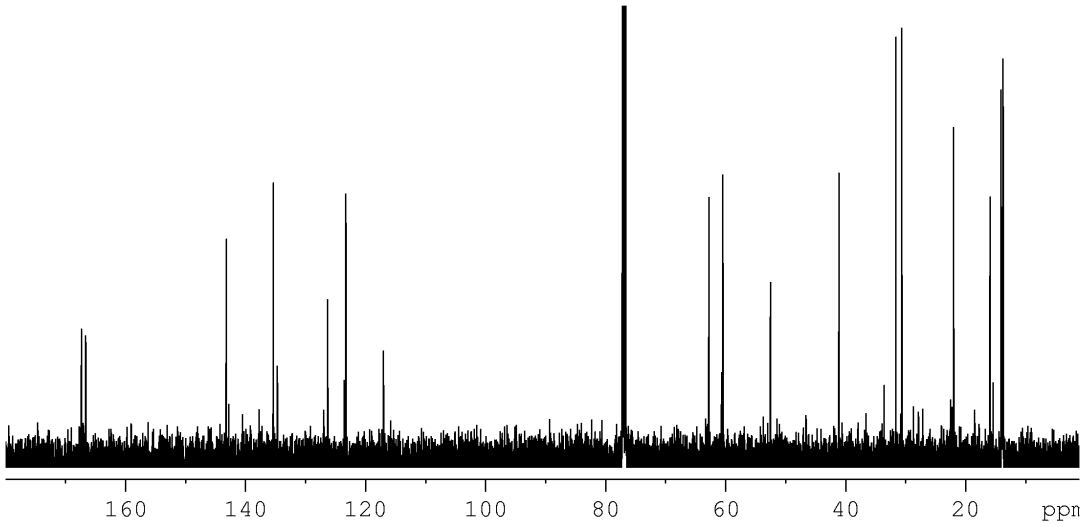

NC
CO2Et
Me
Me
CO2Et

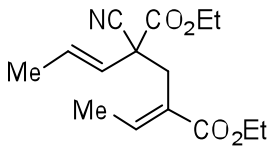
***E*-5a**


NC
CO2Et
Me
CO2Et
Me

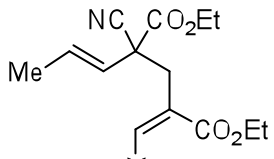
***Z*-5a**


8
7
6
5
4
3
2
1
ppm
0.251
1.001
1.094
0.269
0.992
5.058
2.075
5.089
1.015
10.022
3.048

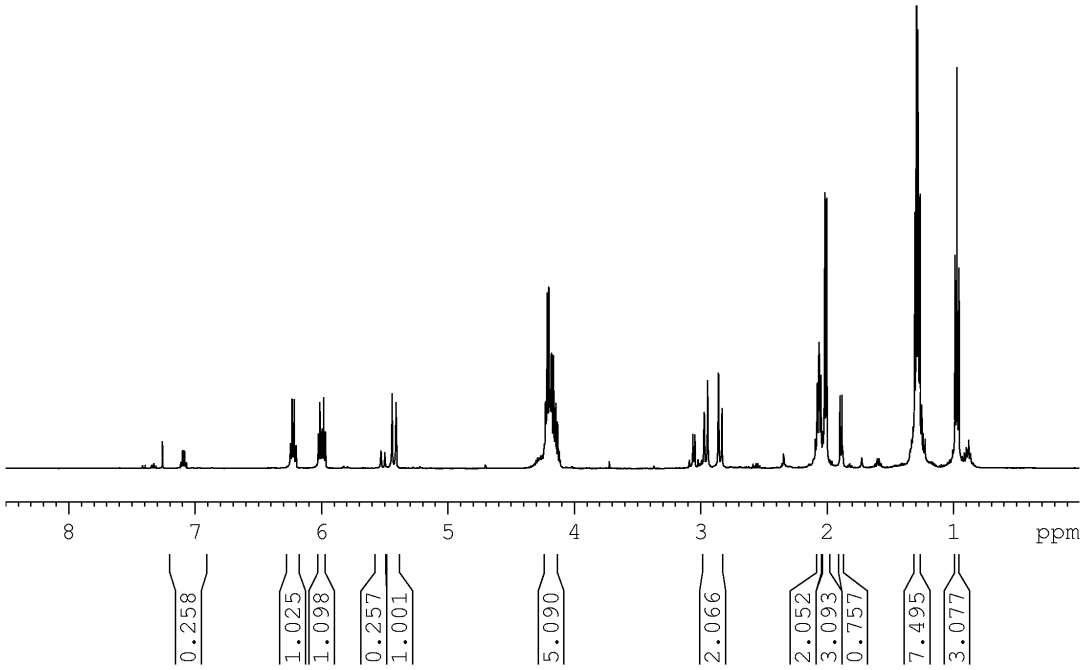

160
140
120
100
80
60
40
20
ppm

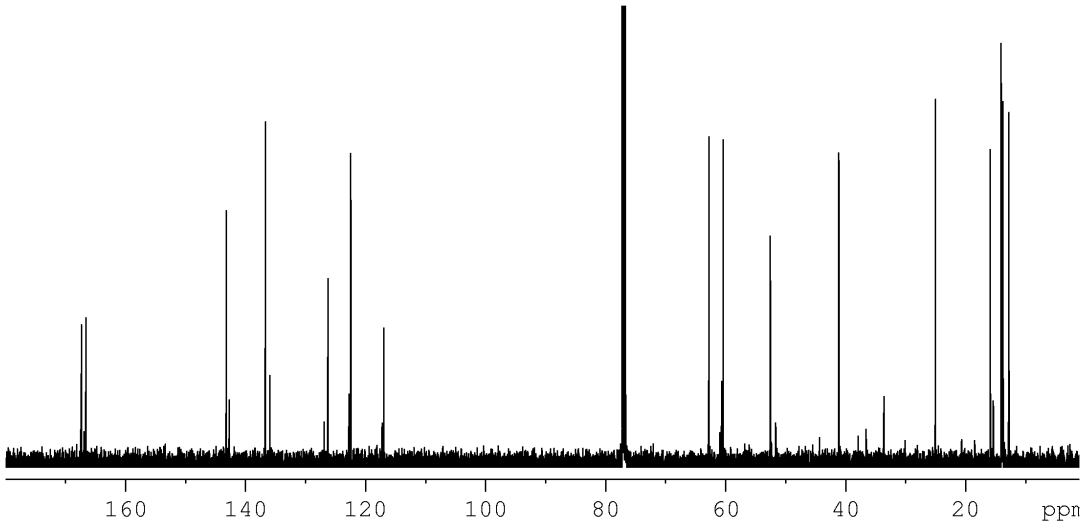

NC
CO2Et
Me
Me
CO2Et

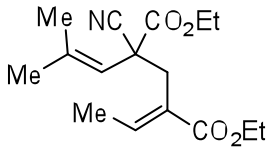
***E*-5b**


NC
CO2Et
Me
CO2Et
Me

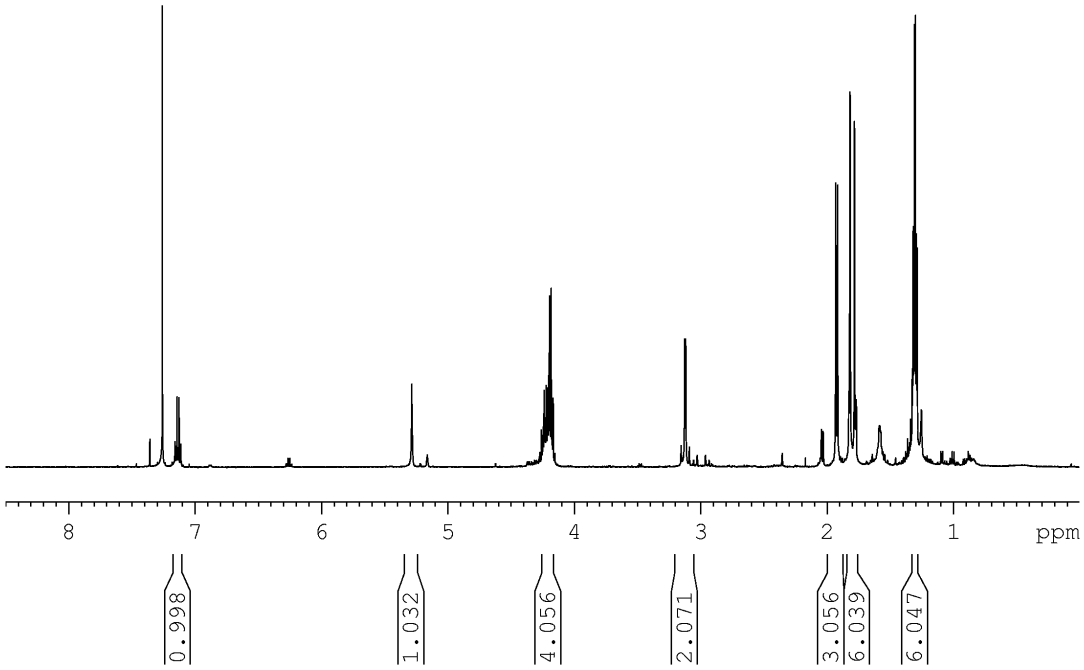
***Z*-5b**

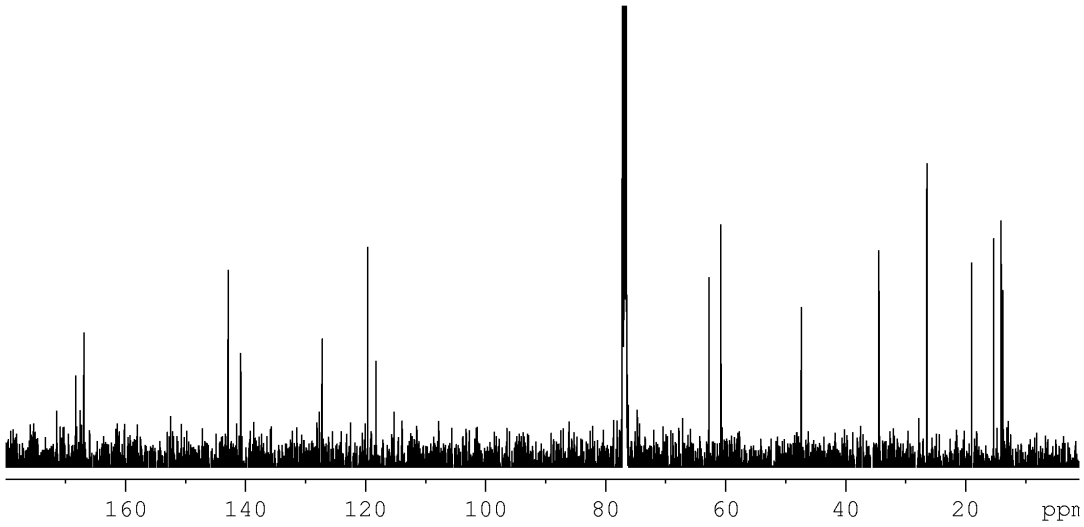

8
7
6
5
4
3
2
1
ppm
0.258
1.025
1.098
0.257
1.001
5.090
2.066
2.052
3.093
0.757
7.495
3.077


160
140
120
100
80
60
40
20
ppm

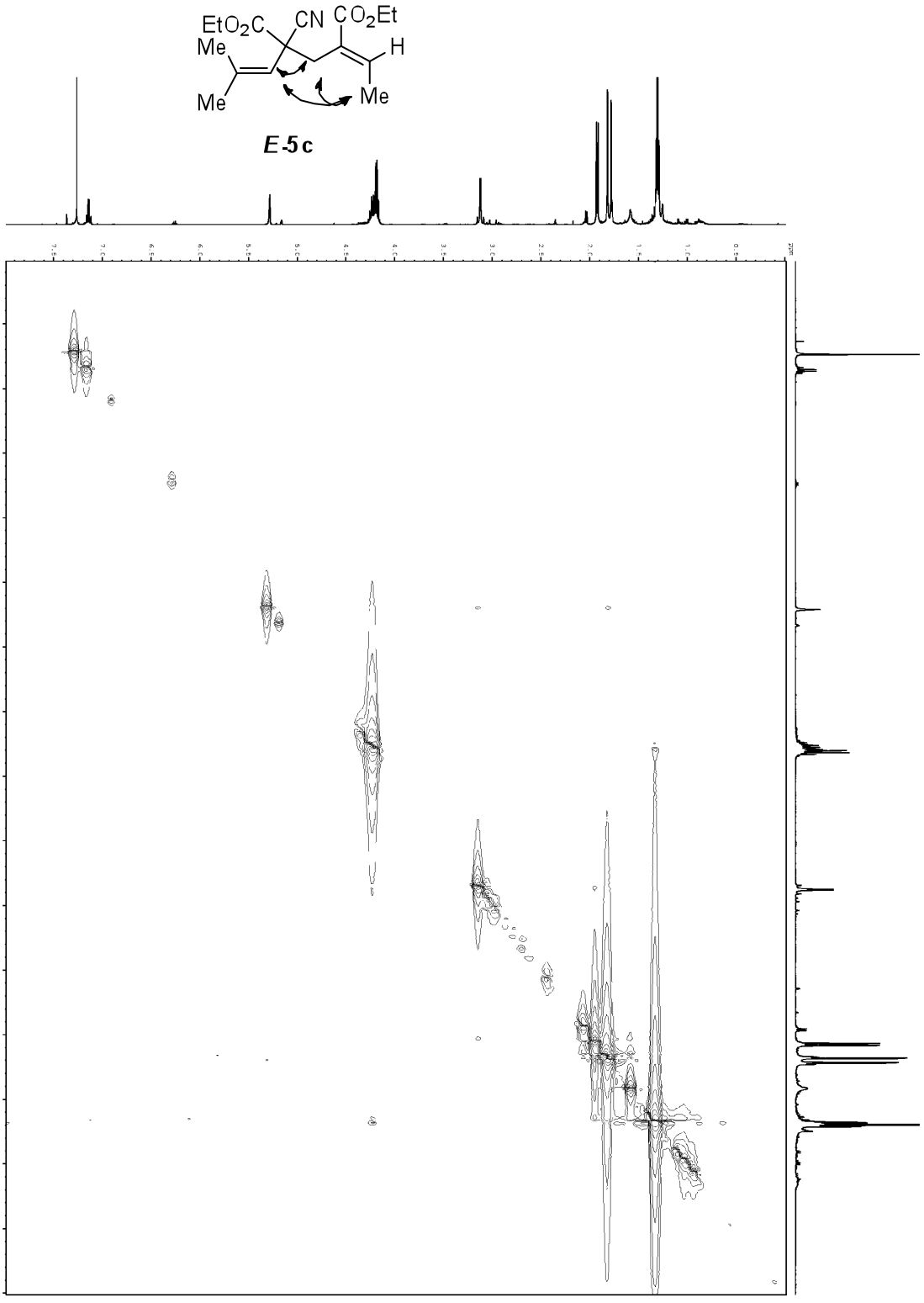

Me
NC
CO2Et
Me
Me
CO2Et

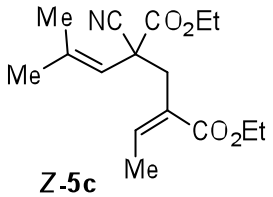
***E*-5c**


8
7
6
5
4
3
2
1
ppm
0.998
1.032
4.056
2.071
3.056
6.039
6.047

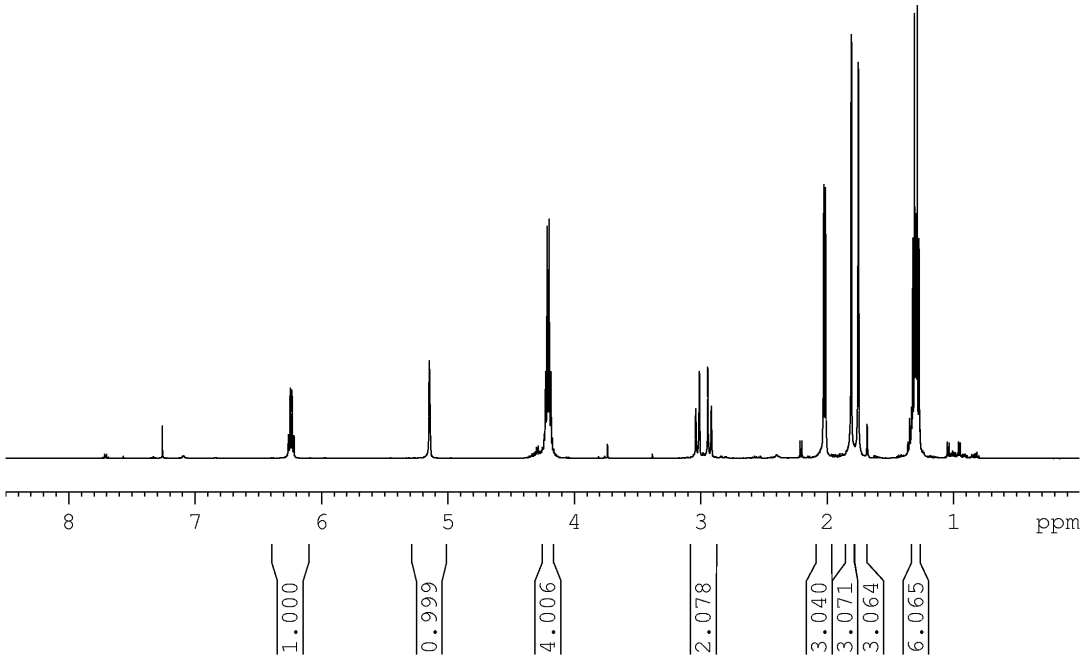

160
140
120
100
80
60
40
20
ppm

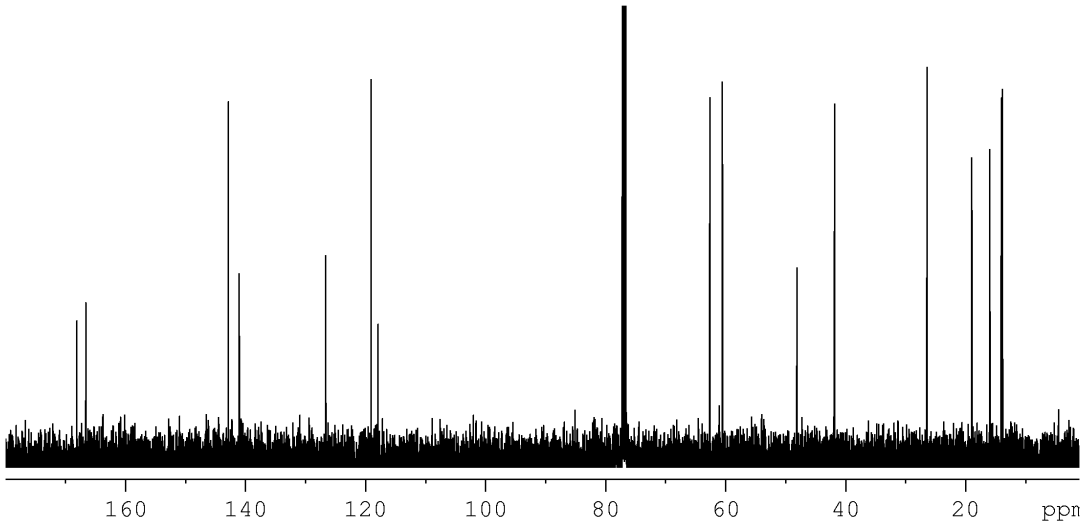
Compound E-5c NOESY



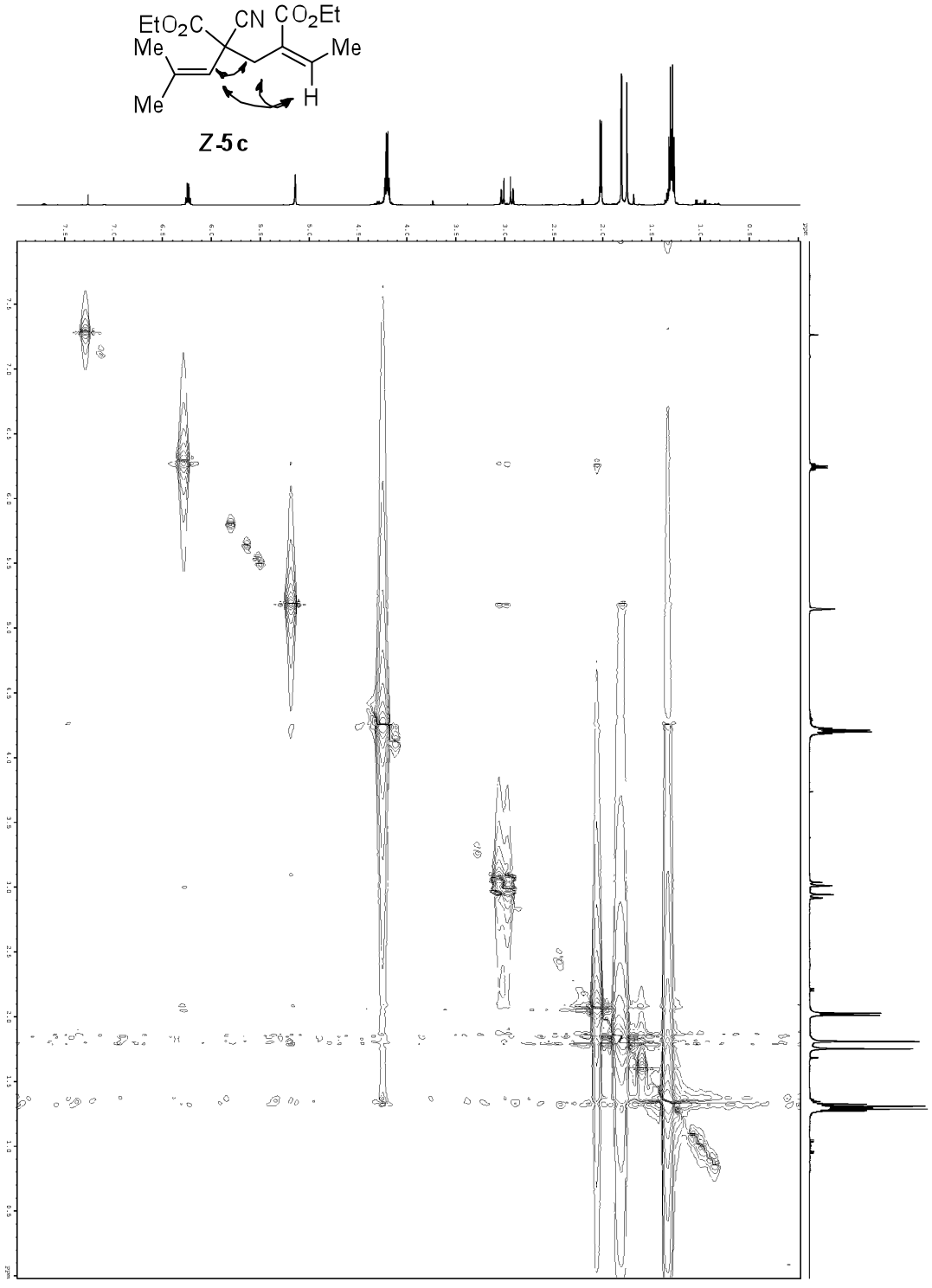

Me
NC
CO2Et
Me
CO2Et
Me

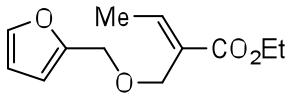
Z-5c


8
7
6
5
4
3
2
1
ppm
1.000
0.999
4.006
2.078
3.040
3.071
3.064
6.065

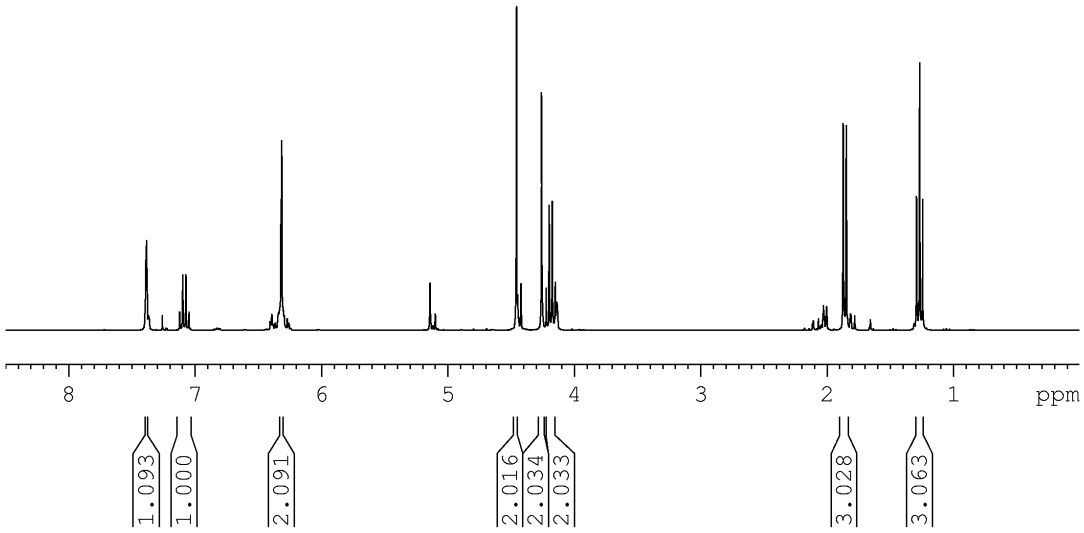

160
140
120
100
80
60
40
20
ppm

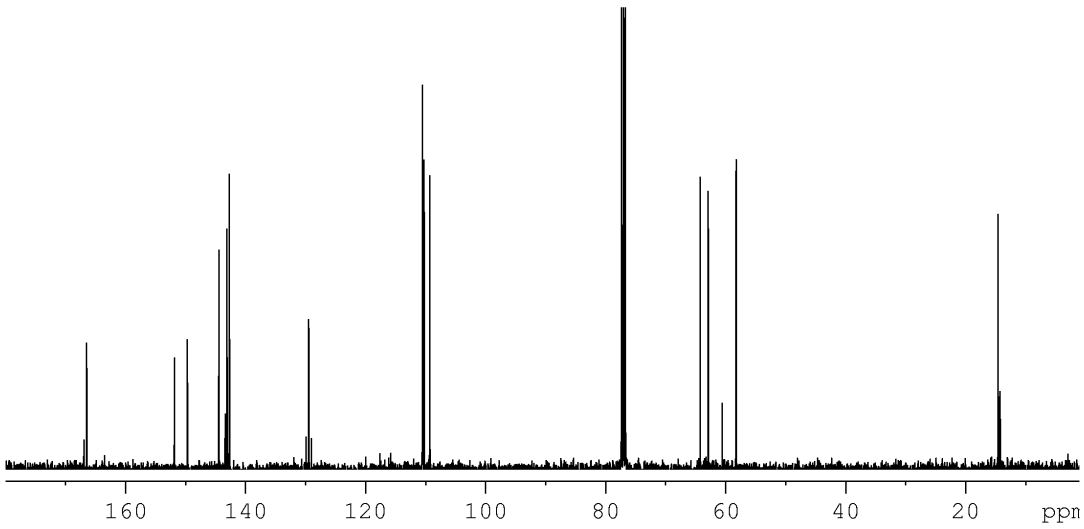
Compound Z-5c NOESY

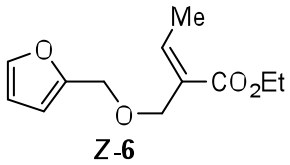



O
Me
CO2Et
O

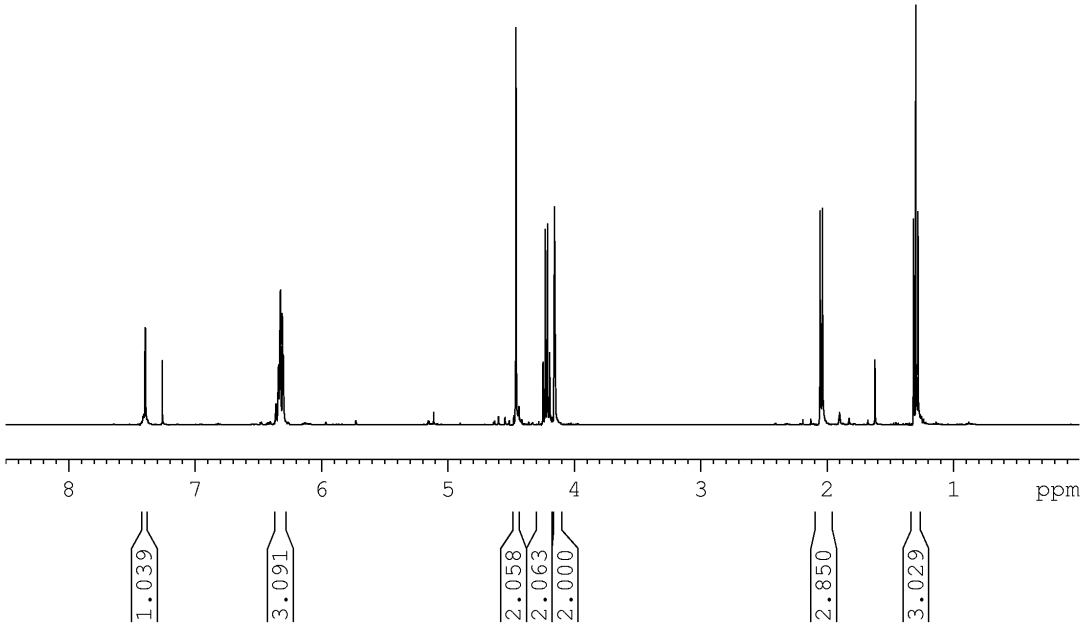
***E*-6**

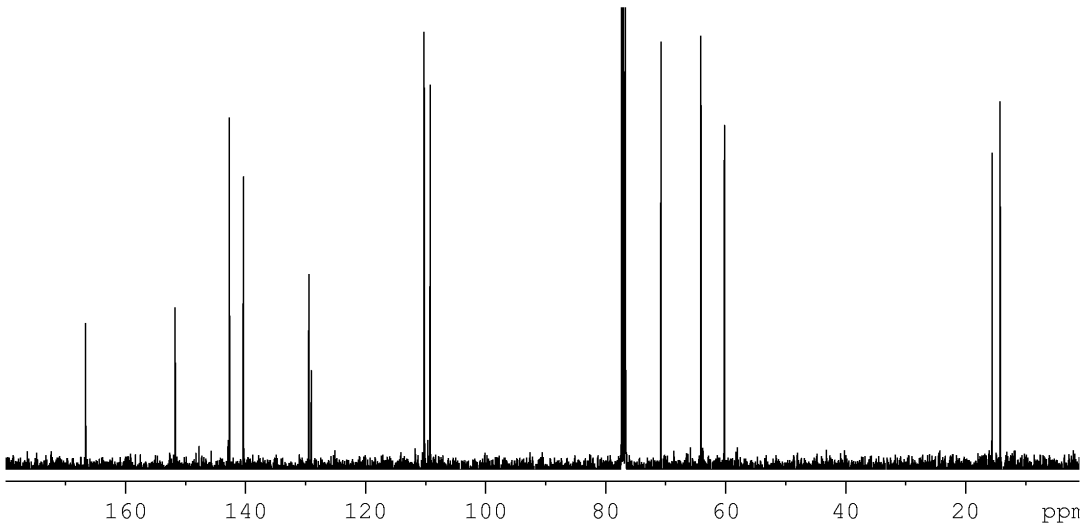

8
7
6
5
4
3
2
1
ppm
1.093
1.000
2.091
2.016
2.034
2.033
3.028
3.063

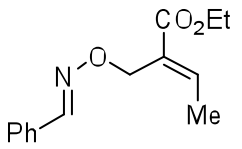

160
140
120
100
80
60
40
20
ppm


Me
O
CO2Et
O

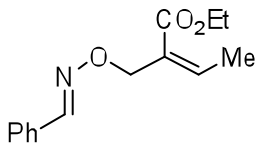
Z-6


8
7
6
5
4
3
2
1
ppm
1.039
3.091
2.058
2.063
2.000
2.850
3.029

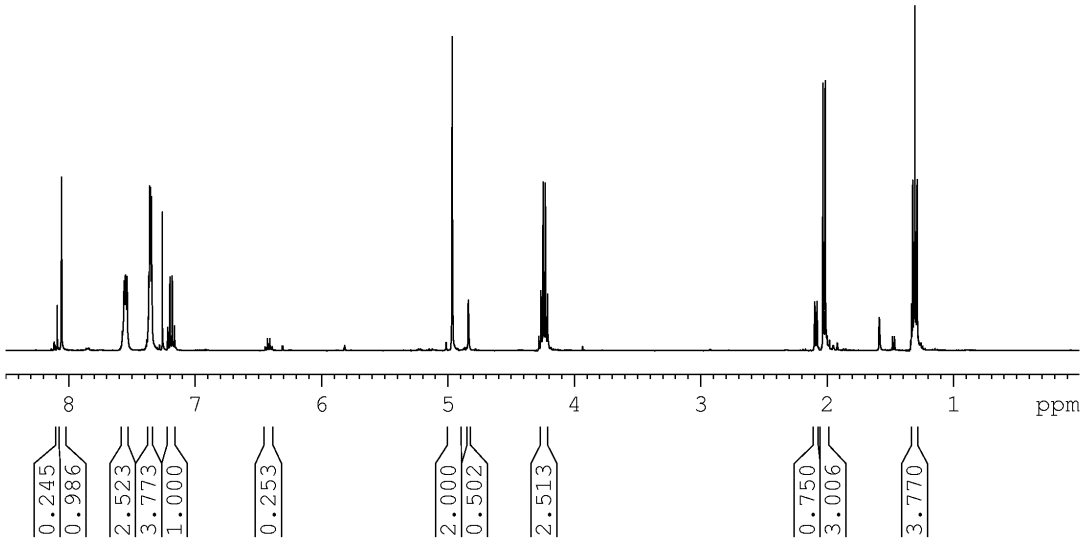

160
140
120
100
80
60
40
20
ppm

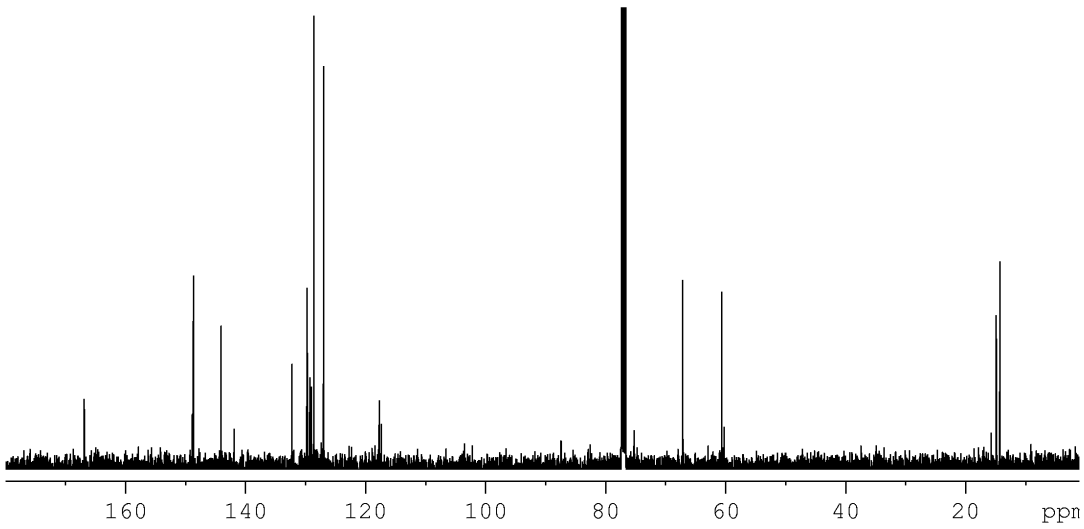

CO2Et
N
O
Me
Ph

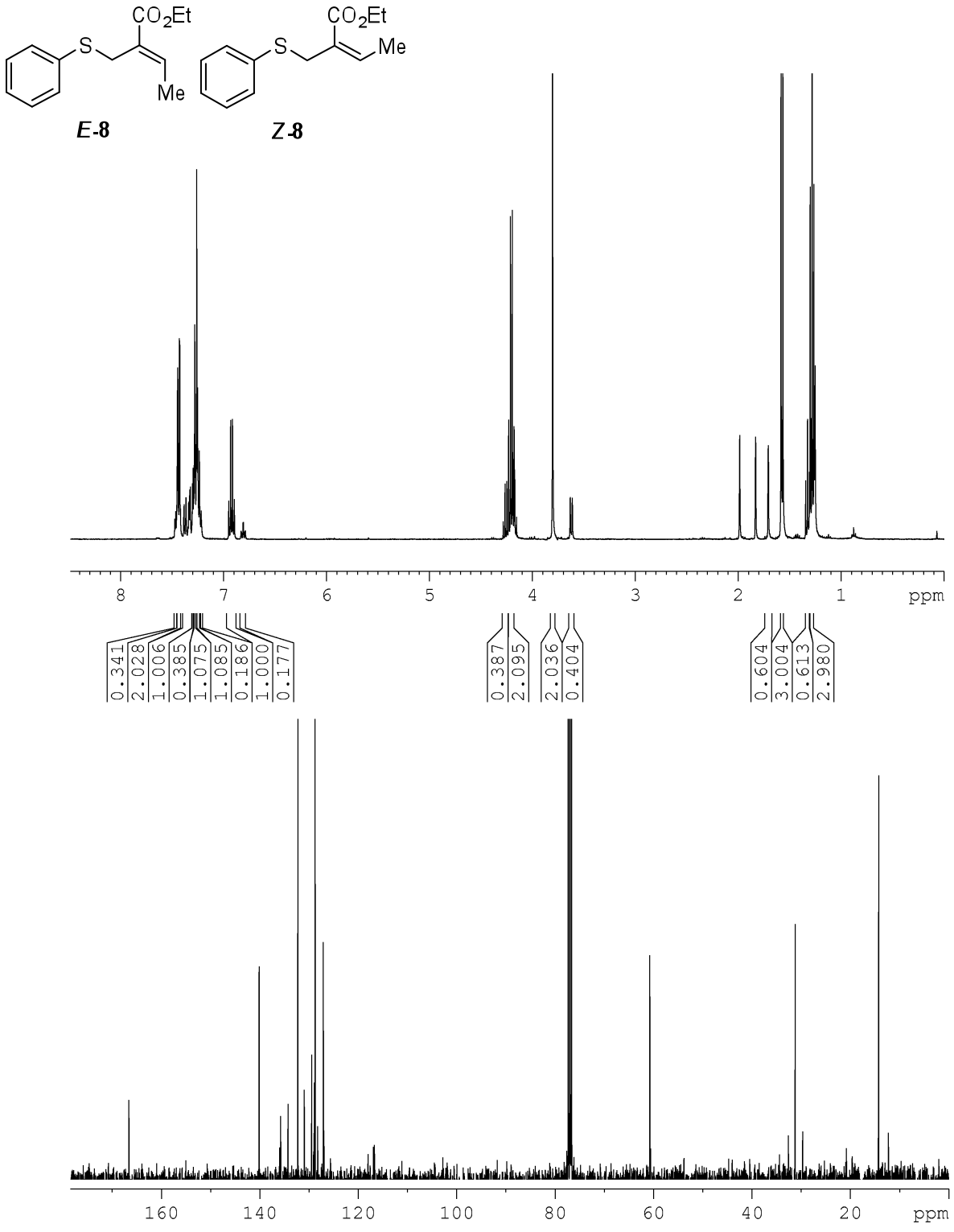
***E*-7**

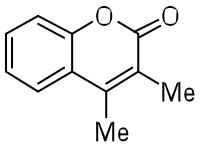

CO2Et
N
O
Me
Ph

***Z*-7**

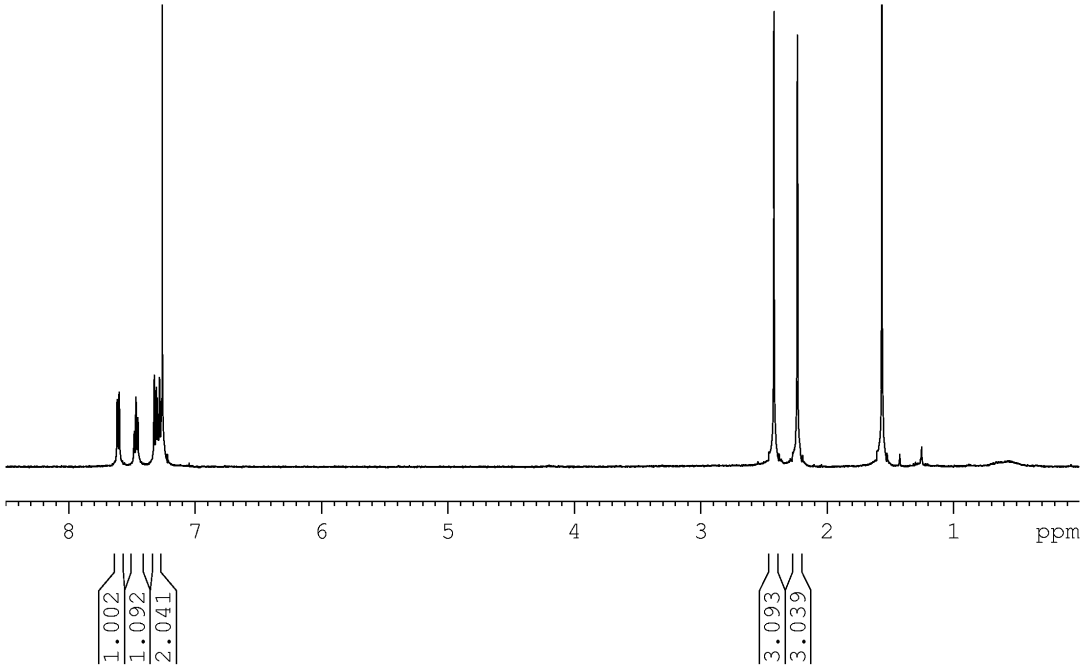

8
7
6
5
4
3
2
1
ppm
0.245
0.986
2.523
3.773
1.000
0.253
2.000
0.502
2.513
0.750
3.006
3.770

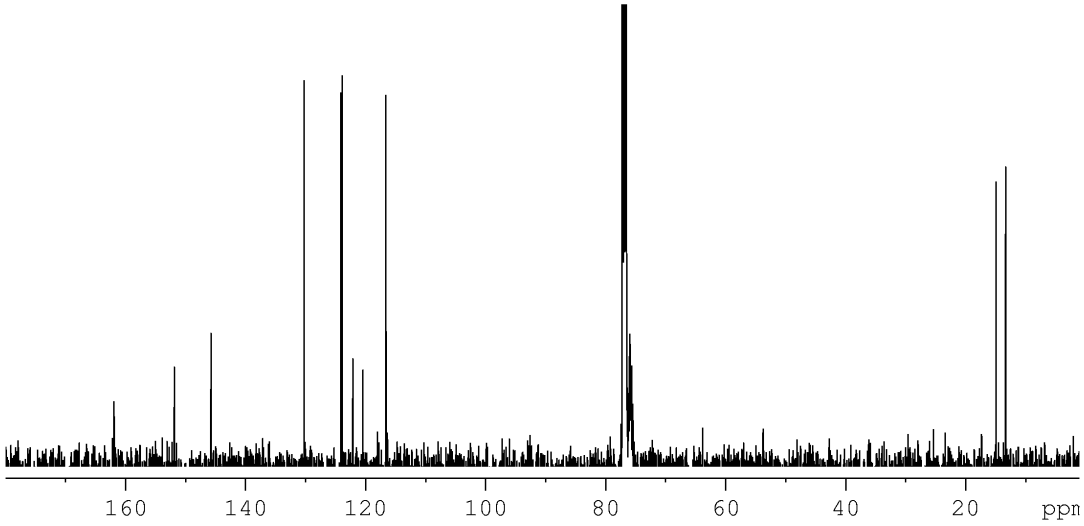

160
140
120
100
80
60
40
20
ppm


CO2Et
S
Me
E-8
CO2Et
S
Me
Z-8
8
7
6
5
4
3
2
1
ppm
0.341
2.028
1.006
0.385
1.075
1.085
0.186
1.000
0.177
0.387
2.095
2.036
0.404
0.604
3.004
0.613
2.980
160
140
120
100
80
60
40
20
ppm


O
O
Me
Me

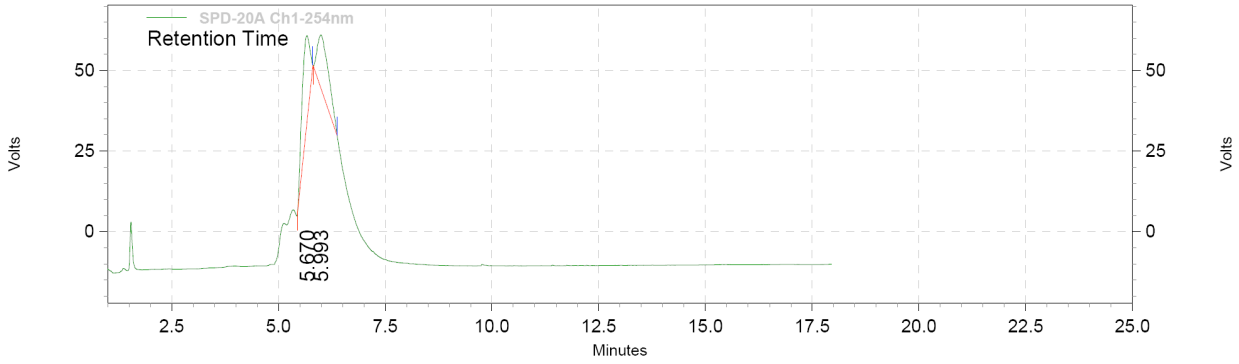
13


8
7
6
5
4
3
2
1
ppm
1.002
1.092
2.041
3.093
3.039


160
140
120
100
80
60
40
20
ppm

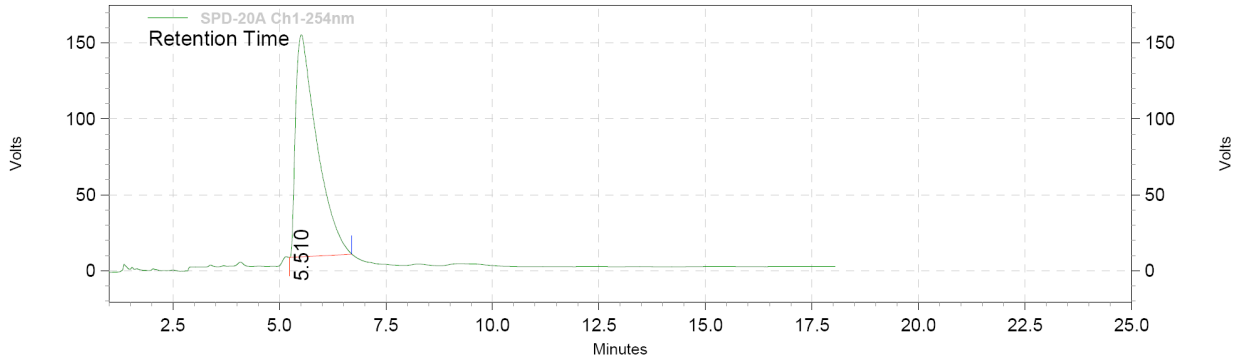
HPLC Trace of Compound 3c

Retention of the amino acid chiral center was evidenced through HPLC analysis against the racemic version of compound **3c** using a REGIS (*R,R*)-DACH DNB chiral column (eluent: 2 mL/min 25% DCM in hexane).



SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
5.670	363142	53.14	26133	61.19
5.993	320260	46.86	16577	38.81
Totals	683402	100.00	42710	100.00



SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
5.510	5090770	100.00	146114	100.00
Totals	5090770	100.00	146114	100.00