Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

First synthesis of fused-Δ^1-pyrrolines *via* intramolecular 1,3-dipolar cycloaddition of ketoimine: A complete diastereoselective approach

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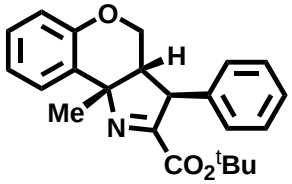
1. **Materials and methods**

All reagents were purchased from commercial suppliers and used without further purification, unless otherwise specified. Commercially supplied ethyl acetate and petroleum ether were distilled before use. CH_2Cl_2 was dried by distillation over P_2O_5. THF was dried over sodium and distilled out prior to use. Petroleum ether used in our experiments was in the boiling range of 60°-80° C. Column chromatography was performed on silica gel (60-120 mesh, 0.120 mm-0.250 mm). Analytical thin layer chromatography was performed on 0.25 mm extra hard silica gel plates with UV254 fluorescent indicator. Melting points are reported uncorrected. ^{1}H NMR and ^{13}C NMR spectra (Bruker Advance 300) were recorded at ambient temperature using 300 MHz spectrometers (300 MHz for ^{1}H and 75 MHz for ^{13}C). Chemical shift is reported in ppm from internal reference tetramethylsilane and coupling constant in Hz. Proton multiplicities are represented as s (singlet), d (doublet), dd (double doublet), t (triplet), q (quartet), and m (multiplet). Infrared spectra were recorded on FT-IR spectrometer (Perkin Elmer Spectrum 100) as KBr pellets (solid sample) and in thin film on NaCl window (liquid sample). Optical rotation of the chiral compounds was measured in a polarimeter (Perkin Elmer 343) using standard 10 cm quartz cell in sodium-D lamp at ambient temperature. EI-MS analysis was performed in GC-MS machine (Perkin Elmer Clarus 600) using column Elite 5 MS (30 m x 0.25 mm x 0.25 um) with maximum temperature 300º C. HR-MS data were acquired by electron spray ionization technique on a Q-tof-micro quadriple mass spectrophotometer (Bruker). Single crystal X-ray diffraction studies of the crystalline heterocyclic compound were done in X-ray diffractometer (Bruker Smart Apex-II, CCD).

2. **Synthesis and characterization data of fused-Δ^1-pyrrolines (4a-g)**

***General procedure*:** A solution of ketoimine **1** (1.0 mmol), anhydrous $MgSO_4$ (0.5 g), dichloromethane (10 mL) were taken together in a round-bottom flask (25 mL) and the content was cooled to 0° C. PhIO (277 mg, 1.25 mm) was added under vigorous stirring and the content of the reaction mixture was allowed to attain room temperature. Progress of the reaction was monitored by TLC and the reaction was complete after 2-5 h depending on the ketoimine used. The post reaction mixture was filtered and concentrated in a rotary evaporator under reduced pressure at room temperature. Thus, the reaction with **1a** (364 mg, 1.0 mmol) afforded **4a** after purification by column chromatography on silica gel (60-120 mesh) with ethyl acetate-petroleum ether (1:8, v/v) as an eluent in an isolated yield of 67% (243 mg, 0.67 mmol). The fused pyrrolines (**4a**-**g**) were characterized by NMR, FT-IR and Mass (EI-MS and HR-MS) spectral analysis.

2.1. **Characterization data of compound 4a**:

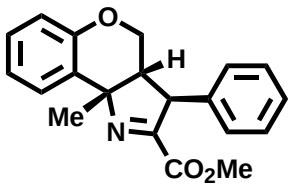


(±)-4a

Colorless crystalline solid.
Melting point: 83° C.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.06 (9H, s), 1.82 (3H, s), 2.26-2.31 (1H, m), 4.10-4.12 (2H, m), 4.23 (1H, d, *J* = 10.2 Hz), 6.81 (1H, dd, *J* = 1.2, 8.1 Hz), 6.89-6.94 (1H, m), 7.10-7.31 (6H, m), 7.55 (1H, dd, *J* = 1.8, 7.8 Hz).

^{13}C NMR (75 MHz, $CDCl_3$): δ 27.4, 30.2, 55.1, 56.8, 63.2, 71.9, 82.9, 118.6, 126.6, 127.3, 127.8, 128.2, 128.5, 128.9, 129.2, 139.5, 151.8, 161.4, 168.1.
EI-MS (m/z): 364 (M+1), 348, 297, 277, 220, 202, 135, 105, 77, 56.
IR (KBr, cm^{-1}): 1154, 1229, 1262, 1302, 1482, 1736, 2920, 2972.
HR-MS (*m*/*z*) for $C_{23}H_{26}NO_3$ (M+H): Calculated 364.1913, found 364.1953.

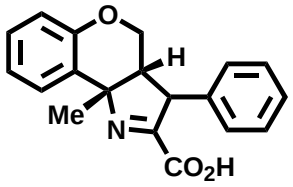
2.2. **Compound 4b**



(±)-4b

Yield: 70% (224 mg, 0.70 mmol).
Characteristic: yellow semi-solid.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.90 (3H, s), 2.36-2.41 (1H, m), 3.66 (3H, s), 4.21-4.22 (2H, m), 4.44 (1H, d, *J* = 9.6 Hz), 6.87 (1H, dd, *J* = 0.9, 8.1 Hz), 6.95-7.01 (1H, m), 7.13-7.21 (1H, m), 7.25-7.39 (5H, m), 7.60 (1H, dd, *J* = 1.8, 7.8 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 30.2, 52.5, 55.4, 56.6, 63.1, 72.6, 117.4, 121.9, 126.4, 127.3, 127.6, 128.5, 129.0, 129.3, 139.4, 153.3, 163.0, 166.2.
EI-MS (m/z): 321 (M^+), 252, 237, 219, 147, 145, 131, 105, 91, 77.
IR (neat, cm^{-1}): 1221, 1298, 1447, 1492, 1708, 2957, 3061, 3407.
HR-MS (*m*/*z*) for $C_{20}H_{20}NO_3$ (M+H): Calculated 322.1443, found 322.1461.

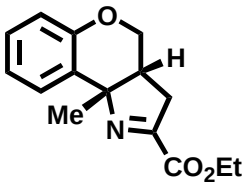
2.3. **Compound 4c**



(±)-4c

Yield: 80% (245 mg, 0.80 mmol).
Characteristic: Pale yellow semisolid.
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.60 (3H, s), 3.36-3.38 (1H, m), 3.86 (1H, d, *J* = 2.1 Hz), 4.15 (1H, dd, *J* = 5.7, 11.1 Hz), 4.39 (1H, dd, *J* = 3.0, 11.1 Hz), 6.90-7.00 (5H, m), 7.10-7.42 (3H, m), 7.67 (1H, dd, *J* = 1.8, 7.5 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 31.8, 56.3, 59.8, 68.7, 112.7, 121.3, 125.6, 128.4, 128.5, 128.6, 128.8, 128.9, 130.5, 133.5, 136.1, 157.5, 199.6.
EI-MS (m/z): 307 (M^+), 263, 248, 221, 145, 131, 121, 91.
IR (neat, cm^{-1}): 1240, 1293, 1449, 1482, 1596, 1675, 1730, 2927, 2999, 3070.
HR-MS (*m*/*z*) for $C_{19}H_{18}NO_3$ (M+H): Calculated 308.1287, found 308.1275.

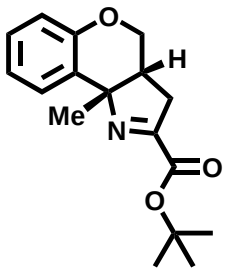
2.4. **Compound 4d**



(±)-4d

Yield: 62% (161 mg, 0.62 mmol).
Characteristic: Yellow semi-solid.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.27 (3H, t, *J* = 2.4 Hz), 1.61 (3H, s), 2.50-2.53 (1H, m), 2.76 (1H, dd, *J* = 6.3, 18.3 Hz), 3.07 (1H, dd, *J* = 8.7, 18.3 Hz), 3.75 (1H, dd, *J* = 7.2, 11.4 Hz), 4.07 (1H, dd, *J* = 3.9, 11.4 Hz), 4.21-4.28 (2H, m), 6.76 (1H, dd, *J* = 1.5, 8.4 Hz), 6.88-6.94 (1H, m), 7.03-7.19 (1H, m), 7.60 (1H, dd, *J* = 1.5, 7.8 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 14.0, 29.3, 38.0, 43.1, 61.9, 65.6, 74.0, 117.1, 121.8, 126.7, 128.2, 129.3, 154.2, 162.8, 164.9.
EI-MS (m/z): 259 (M^+), 244, 187, 186, 146, 145, 144, 131, 115, 91.
IR (neat, cm^{-1}): 1095, 1155, 1226, 1379, 1451, 1478, 1622, 1727, 2870, 2931, 2974, 3342.
HR-MS (*m*/*z*) for $C_{15}H_{18}NO_3$ (M+H): Calculated 260.1287, found 260.1297.

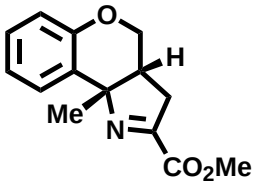
2.5. **Compound 4e**



(±)-4e

Yield: 71% (204 mg, 0.71 mmol).
Characteristic: Yellow semi-solid.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.56 (9H, s), 1.65 (3H, s), 2.56-2.59 (1H, m), 2.74 (1H, dd, *J* = 6, 18 Hz), 3.08 (1H, dd, *J* = 8.7, 18 Hz), 3.78 (1H, dd, *J* = 7.2, 11.4 Hz), 4.12 (1H, dd, *J* = 3.9, 11.4 Hz), 6.83 (1H, dd, *J* = 1.5, 8.1 Hz), 6.96-7.01 (1H, m), 7.10-7.16 (1H, m), 7.68 (1H, dd, *J* = 1.5, 7.8 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 27.9, 29.4, 38.1, 43.1, 65.8, 73.7, 82.9, 117.0, 121.8, 127.1, 128.1, 129.4, 154.3, 161.9, 165.8.
EI-MS (m/z): 288 (M+1), 287, 231, 187, 186, 146, 145, 131, 71, 56.
IR (neat, cm^{-1}): 1102, 1153, 1258, 1319, 1367, 1451, 1480, 1622, 1722, 2869, 2930, 2975, 3068, 3448.
HR-MS (*m*/*z*) for $C_{17}H_{22}NO_3$ (M+H): Calculated 288.1600, found 288.1611.

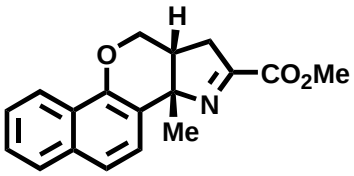
2.6. **Compound 4f**



(±)-4f

Yield: 60% (147 mg, 0.60 mmol).
Characteristic: yellow semi-solid.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.62 (3H, s), 2.48-2.57 (1H, m), 2.77 (1H, dd, *J* = 6, 18 Hz), 3.09 (1H, dd, *J* = 8.7, 18 Hz), 3.71-3.83 (4H, m), 4.13 (1H, dd, *J* = 3.9, 11.4 Hz), 6.77 (1H, dd, *J* = 1.5, 8.1 Hz), 6.89-6.94 (1H, m), 7.04-7.19 (1H, m), 7.59 (1H, dd, *J* = 1.5, 7.8 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 29.3, 37.9, 43.1, 52.7, 65.6, 74.1, 117.2, 121.9, 126.6, 128.3, 129.2, 154.2, 163.2, 164.6
EI-MS (m/z): 246 (M+1), 245 (M^+), 230, 187, 186, 146, 145, 144, 131, 115, 91.
IR (neat, cm^{-1}): 1098, 1228, 1445, 1622, 1732, 2961.
HR-MS (*m*/*z*) for $C_{14}H_{16}NO_3$ (M+H): Calculated 246.1130, found 246.1116.

2.7. **Compound 4g**



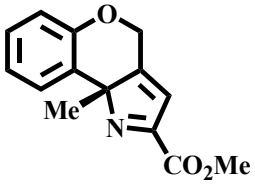
(±)-4g

Yield: 61% (179 mg, 0.61 mmol).
Characteristic**:** Orange semi-solid.
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.42 (3H, s), 2.57-2.76 (3H, m), 3.76 (3H, s), 4.99-5.16 (1H, m), 5.32-5.46 (1H, m), 7.43-7.51 (2H, m), 7.60-7.79 (3H, m), 7.36 (1H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 28.3, 46.4, 63.5, 64.1, 71.7, 77.4, 121.1, 126.4, 127.1, 128.3, 128.7, 130.3, 135.0, 152.7, 189.9.
EI-MS (m/z): 295 (M^+), 290, 233, 148, 104, 76, 74.
IR (neat, cm^{-1}): 1010, 1250, 1600, 1680, 1725, 2855, 2921.
HR-MS (*m*/*z*) for $C_{18}H_{18}NO_3$ (M+H): Calculated 296.1287, found 296.1290.

3. **Synthesis and characterization data of fused-2*H*-pyrroles (6a-c)**

Synthesis of fused-2*H*-pyrroles were performed under the similar reaction conditions as described in section 2 (page S-2). Characterization data of the compounds were given below.

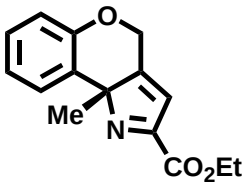
3.1. **characterization data Compound 6a:**



(±)-6a

Yield: 70% (170 mg, 0.70 mmol).
Characteristic: Semi-solid.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.54 (3H, s), 3.89 (3H, m), 5.06 (2H, dd, *J* = 1.5, 3 Hz), 6.60 (1H, s), 6.79-6.90 (2H, m), 7.06-7.18 (1H, m), 7.66 (1H, dd, *J* = 1.8, 7.8 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 25.9, 52.9, 63.5, 79.6, 116.5, 121.5, 125.5, 127.6, 128.9, 152.2, 162.5, 162.7, 164.7, 168.5.
EI-MS (m/z): 243 (M^+), 228, 207, 168, 108, 96, 74, 69.
IR (neat, cm^{-1}): 1218, 1411, 1439, 1638, 2918, 3414.
HR-MS (*m*/*z*) for $C_{14}H_{14}NO_3$ (M+H): Calculated 244.0974, found 244.0979.

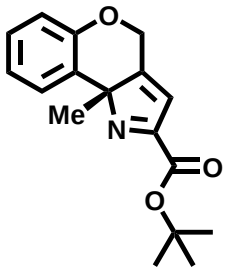
3.2. **Compound 6b**



(±)-6b

Yield: 72% (185 mg, 0.72 mmol).
Characteristic: Semi-solid.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.35 (3H, t, *J* = 4.2 Hz), 1.55 (3H, s), 4.32-4.42 (2H, m), 5.07 (2H, dd, *J* = 2.1, 2.4 Hz), 6.59 (1H, s), 6.79-6.91 (2H, m), 7.06-7.12 (1H, m), 7.68 (1H, dd, *J* = 1.8, 7.8 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 14.2, 25.8, 62.1, 63.5, 79.8, 116.4, 119.8, 121.4, 125.6, 127.7, 128.8, 152.2, 162.3, 165.0, 168.2.
EI-MS (m/z): 257 (M^+), 207, 145, 96, 71, 55.
IR (neat, cm^{-1}): 1226, 1450, 1588, 1639, 1738, 2857, 2919.
HR-MS (*m*/*z*) for $C_{15}H_{16}NO_3$ (M+H): Calculated 258.1130, found 258.1115.

3.3. **Compound 6c**



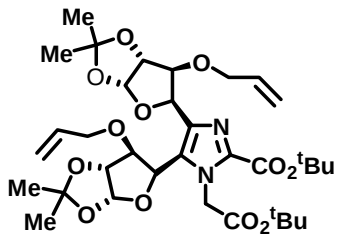
(±)-6c

Yield: 62% (176 mg, 0.62 mmol).
Characteristic: Semi-solid.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.52 (9H, s), 1.54 (3H, s), 5.05-5.11 (2H, m), 6.51 (1H, s), 6.80 (1H, dd, *J* = 0.9, 8.1 Hz), 6.86-6.91 (1H, m), 7.06-7.15 (1H, m), 7.71 (1H, dd, *J* = 6, 7.8 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 25.8, 28.0, 63.6, 79.4, 83.11, 116.4, 120.0, 121.4, 125.9, 127.8, 128.8, 152.2, 161.3, 167.7.
EI-MS (m/z): 285 (M^+), 207, 115, 81, 57.
IR (neat, cm^{-1}): 1157, 1402, 1487, 1667, 2255, 2931, 2986.
HR-MS (*m*/*z*) for $C_{17}H_{20}NO_3$ (M+H): Calculated 286.1443, found 286.1448.

4. **Synthesis and characterization data of sugar-based chiral imidazoles (7a-e)**

General procedure: The sugar-based chiral aldimine **3** (1.0 mmol), anhydrous $MgSO_4$ (0.5 g), PhIO (500 mg, 2.25 mmol) and dichloromethane (10 mL) were taken together in a round-bottom flask (25 mL) and the mixture was stirred at 0° C. The content of the reaction mixture was allowed to attain room temperature. Progress of the reaction was monitored by TLC and the reaction was complete after 3.5 -5.0 h depending on the aldimine used. The post reaction mixture was filtered and washed well with dichloromethane. The combined organic portion was washed with aqueous sodium bicarbonate solution (1 x 10 mL) and brine (3 x 10 mL) solution, dried on activated sodium sulfate, and concentrated in a rotary evaporator under reduced pressure at room temperature. The crude product was chromatographed on silica gel (60-120 mesh) and eluted with ethyl acetate-petroleum ether (1:2, v/v). Thus, the reaction with [(6-allyloxy-2,2-dimethyl-tetrahydro-furo[2,3-*d*][1,3]dioxol-5-ylmmethylene)-amino]-acetic acid *tert*-butyl ester (**3a**, 341 mg, 1.0 mmol) afforded 4,5-bis-(6-allyloxy-2,2-dimethyl-tetrahydro-furo[2,3-*d*][1,3]dioxol-5-yl)-1-*tert*-butoxycarbonylmethyl-1*H*-imidazole-2-carboxylic acid *tert*-butyl ester (**7a**) after processing in an isolated yield of 82% (556 mg, 0.82 mmol). The compound **7a** and others (**7b**-**7e**) were characterized by ^{1}H and ^{13}C NMR (NDC & DEPT), FT-IR, Mass spectra (EI-MS) and HR-MS analysis.

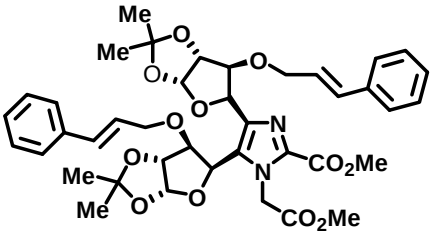
4.1. **Characterization data of compound 7a**



(-)-7a

Yield: 82% (556 mg, 0.82 mmol).
Characteristic: Yellow semisolid.
$[\alpha]_D^{20}$ -35.07° (*c* 0.75, $CHCl_3$).
^1H NMR (300 MHz, $CDCl_3$): δ 1.30 (6H, s), 1.45 (18H, s), 1.47 (6H, s) 3.10-3.15 (2H, m), 3.34-3.48 (2H, m), 3.49-3.61 (2H, m) 4.03-4.17 (4H, m), 4.58 (2H, d, *J* = 3.3 Hz), 5.15-5.29 (4H, m), 5.81-5.90 (2H, m), 5.95 (2H, d, *J* = 3.3 Hz).
^{13}C NMR (75 MHz,$CDCl_3$): δ 26.3, 26.9, 28.0, 55.2, 60.6, 61.5, 71.1, 76.5, 81.3, 82.9, 83.1, 105.7, 11.9, 117.3, 133.9, 168.7, 168.9.
EI-MS (m/z): 678 (M^+), 627, 594, 565, 327, 297, 257, 256, 194, 110.
IR (neat, cm^{-1}): 1157, 1223, 1370, 1654, 1739, 2933, 2980.
HR-MS (*m*/*z*) for $C_{34}H_{51}N_2O_{12}$ (M+H): Calculated 679.3442, found 679.3444.

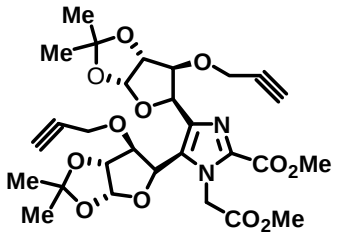
4.2. **Compound 7b**



(-)-7b

Yield: 82% (612 mg, 0.82 mmol).
Characteristic: Yellow liquid.
$[\alpha]_D^{20}$ -12.90° (*c* 1.00, $CHCl_3$).
^1H NMR (300 MHz, $CDCl_3$): δ 1.31 (6H, s), 1.43 (6H, s), 3.22-3.56 (4H, m), 3.68 (3H, s), 3.75 (3H, s) 4.07-4.11 (2H, m), 4.16-4.23 (4H, m), 4.30-4.33 (2H, m), 4.64 (1H, d, *J* = 3.6 Hz), 5.98 (1H, d, *J* = 3.6 Hz), 6.19-6.24 (2H, m), 6.56-6.61 (2H, m), 7.22-7.38 (10 H, m).
^{13}C NMR (75 MHz,$CDCl_3$): δ 26.2, 26.9, 51.9, 54.4, 60.8, 70.7, 71.7, 82.1, 83.1, 105.7, 121.0, 118.1, 124.8, 125.0, 126.5, 126.6, 127.8, 127.9, 128.5, 128.6, 132.8, 132.9, 162.3, 169.7, 170.1.
EI-MS (m/z): 746 (M^+), 645, 476, 299, 147, 108, 107.
IR (neat, cm^{-1}): 1022, 1075, 1213, 1374, 1438, 1672, 1745, 2930.
HR-MS (*m*/*z*) for $C_{40}H_{47}N_2O_{12}$ (M+H): Calculated 747.3129, found 747.3121.

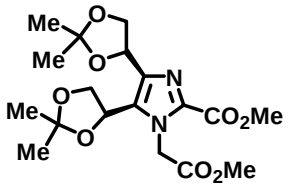
4.3. **Compound 7c**



(-)-7c

Yield: 80% (472 mg, 0.80 mmol).
Characteristic: Yellow liquid.
$[\alpha]_D^{20}$ -19.80° (*c* 0.50, $CHCl_3$).
^1H NMR (300 MHz, $CDCl_3$): δ 1.33 (6H, s), 1.50 (6H, s), 2.54-2.57 (2H, m), 3.82 (3H, s), 3.93 (3H, s), 4.16-4.48 (8H, m), 4.66-4.77 (4H, m), 5.97-6.00 (2H, m).
^{13}C NMR (75 MHz,$CDCl_3$): δ 26.3, 26.9, 51.9, 54.3, 57.8, 60.3, 76.4, 81.8, 83.2, 84.4, 105.6, 112.1, 112.6, 162.3, 169.8, 170.0.
EI-MS (m/z): 590 (M^+), 567, 538, 519, 476, 429, 305, 252, 211, 197, 106.
IR (neat, cm^{-1}): 1032, 1079, 1218, 1377, 1660, 1664, 2850, 2921.
HR-MS (*m*/*z*) for $C_{28}H_{34}N_2O_{12}$ (M+): Calculated 590.2112, found 590.2122.

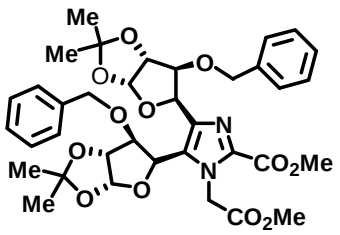
4.4. **Compound 7d**



(-)-7d

Yield: 72% (287 mg, 0.72 mmol).
Characteristic: Yellow liquid.
$[\alpha]_D^{20}$ -2.00° (*c* 0.80, $CHCl_3$).
^1H NMR (300 MHz, $CDCl_3$): δ 1.38 (6H, s), 1.48 (6H, s), 2.88 (1H, d, *J* = 8.4 Hz), 3.09 (1H, d, *J* = 16.2 Hz), 3.40 (1H, d, *J* = 23 Hz), 3.66 (1H, s), 3.72 (3H, s), 3.75 (3H, s), 3.84 (1H, s), 4.00-4.04 (1H, m), 4.04-4.30 (2H, m).
^{13}C NMR (75 MHz,$CDCl_3$): δ 25.2, 26.8, 51.8, 51.9, 54.2, 60.6, 65.1, 67.4, 72.6, 110.3, 118.1, 169.5, 170.2.
EI-MS (m/z): 398 (M^+), 366, 352, 281, 252, 236, 207, 156, 122, 108, 101.
IR (neat, cm^{-1}): 1067, 1208, 1373, 1438, 1747, 1754, 2955, 2988.
HR-MS (*m*/*z*) for $C_{18}H_{26}N_2O_8$ (M+): Calculated 398.1689, found 398.1685.

4.5. **Compound 7e**

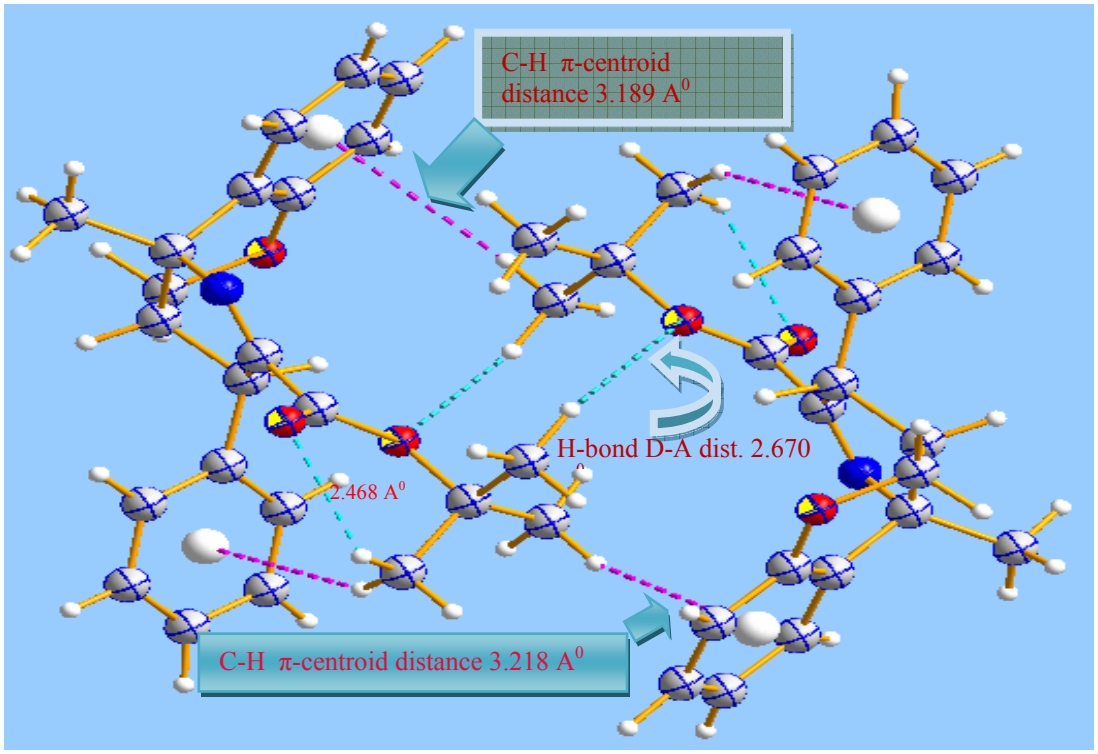


(-)-7e

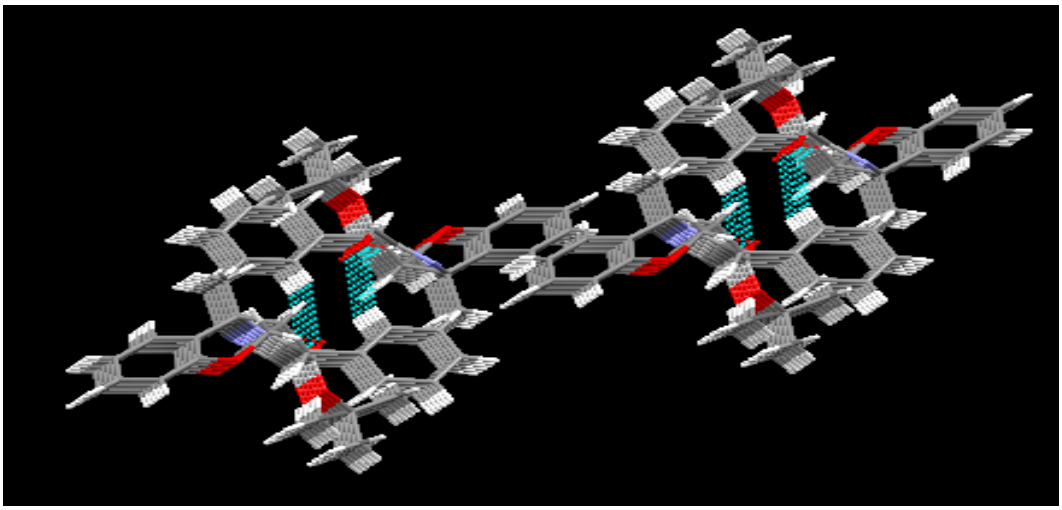
Yield: 78% (541 mg, 0.78 mmol).
Characteristic: Yellow liquid.
$[\alpha]_D^{20}$ -17.88° (*c* 0.90, $CHCl_3$).
^1H NMR (300 MHz, $CDCl_3$): δ 1.31 (6H, s), 1.43 (6H, s), 314-3.24 (2H, m), 3.36-3.50 (3H, m), 3.65 (3H, s), 3.75 (3H, s), 4.04-4.12 (2H, m), 4.20 (2H, d, J = 3 Hz), 4.53-4.71 (4H, m), 5.97 (1H, d, J = 3.6 Hz), 7.26-7.36 (10H, m).
^{13}C NMR (75 MHz,$CDCl_3$): δ 26.2, 26.9, 51.7, 51.9, 54.3, 60.7, 72.0, 76.3, 81.9, 83.2, 105.5, 112.1, 127.5, 127.8, 128.5, 137.3, 169.7, 170.1.
EI-MS (m/z): 694 (M^+), 630, 508, 439, 347, 170, 107.
IR (neat, cm^{-1}): 1027, 1075, 1211, 1374, 1442, 1671, 1747, 2929.
HR-MS (*m*/*z*) for $C_{36}H_{43}N_2O_{12}$ (M+H): Calculated 695.2816, found 695.2812.

5. **Studies of weak binding interactions present in the heterocyclic scaffold**

The crystal engineering projection of the crystal lattice of compound **4a** reveals that it possess intermolecular weak binding forces like hydrogen bonding (C*H*···*O*) and π-stacking (C*H*···π_m) interactions (SI Figure 1) where π_m represents the ring midpoint (π-cloud). The measured distance of hydrogen binding (C*H*···*O* distance: 2.670 and 2.468 Å) and π-stacking (C*H*···π_m distance: 3.189 and 3.218 Å) indicates that the corresponding binding forces are quite strong. These weak noncovalent interactions are extremely useful in understanding of chemical, biological and material phenomena.[1,2] As for example, these weak interactions can operate as gluing interaction between the organic building blocks to fabricate interesting nanostructured materials.[1] These preliminary observations have prompted us to start fabrication of low molecular mass organic nanostructured materials in our laboratory with these novel heterocyclic scaffolds.



SI Figure 1: Weak binding interactions found in the crystal lattice of compound **4a**



SI Figure 2: Top view of the crystal packing diagram showing H-bonding and π-stacking interactions

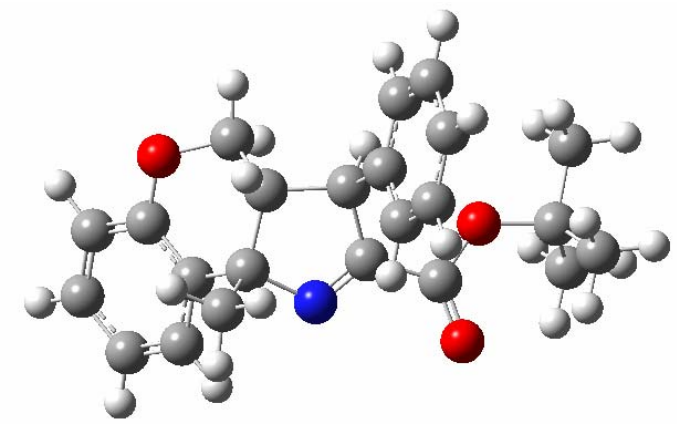
Reference

1 (a) P. Pandit, N. Chatterjee, S. Halder, S. K. Hota, A. Patra, D. K. Maiti, *J. Org. Chem.* **2009**, *74*, 2581-2584; b) D. K. Maiti, S. Halder, P. Pandit, N. Chatterjee, D. D. Joarder, N. Pramanik, Y. Saima, A. Patra, P. K. Maiti, *J. Org. Chem.* **2009**, *74*, 8086-8097.

[2] a**)** Y. Umezawa, M. Nishio, *Nucleic Acids Res.* **2002**, *30*, 2183–2192; (b) Y. Ferrand, E. Klein, N. P. Barwell, M. P. Crump, J. Jiménez-Barbero, C. Vicent, G.-J. Boons, S. Ingale, A. P. Davis, *Angew. Chem. Int. Ed.* **2009**, *48*, 1775-1779.

6. **Z-matrix of the Geometry Optimized Structures of 4a, 5a, TS-III and TS-IV**

6.1. **Z-matrix of compound 4a using basis set 6-31G of HF**



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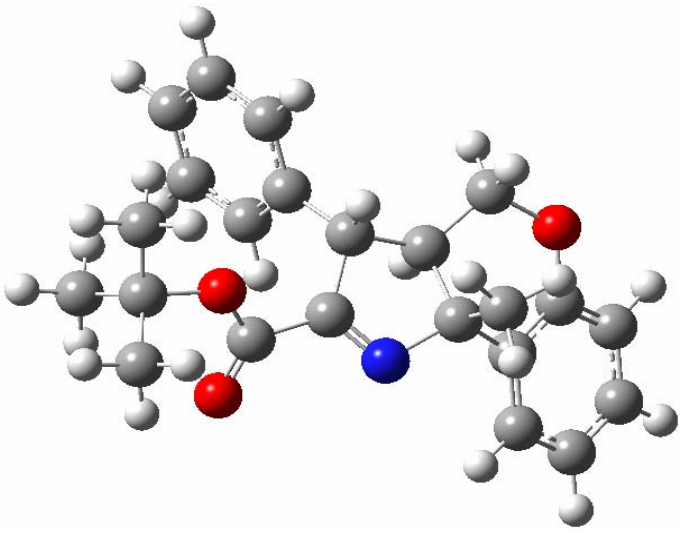
6.2. **Z-matrix of compound 5a using basis set 6-31G of HF**



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H	20	B41	17	A40	16	D39	0
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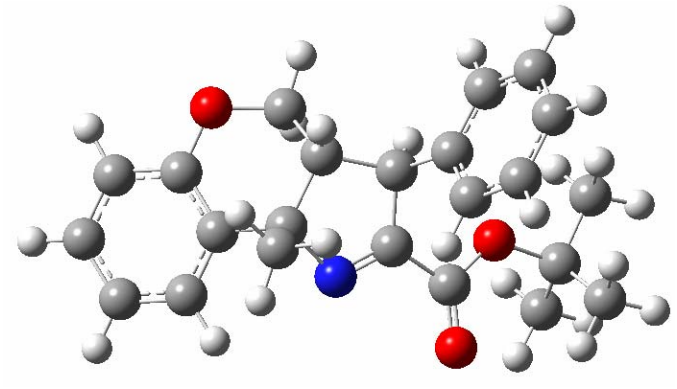
6.3. **Z-matrix of compound 4a using basis set 6-31G of DFT**



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C	19	B21	18	A20	16	D19	0
C	15	B22	13	A21	12	D20	0
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C	24	B24	23	A23	15	D22	0
C	25	B25	24	A24	23	D23	0
C	26	B26	25	A25	24	D24	0
H	1	B27	6	A26	5	D25	0
H	2	B28	1	A27	6	D26	0
H	3	B29	2	A28	1	D27	0
H	6	B30	1	A29	2	D28	0
H	8	B31	7	A30	4	D29	0
H	9	B32	8	A31	7	D30	0
H	9	B33	8	A32	7	D31	0
H	13	B34	12	A33	11	D32	0

H	14	B35	7	A34	4	D33	0
H	14	B36	7	A35	4	D34	0
H	14	B37	7	A36	4	D35	0
H	20	B38	19	A37	18	D36	0
H	20	B39	19	A38	18	D37	0
H	20	B40	19	A39	18	D38	0
H	21	B41	19	A40	18	D39	0
H	21	B42	19	A41	18	D40	0
H	21	B43	19	A42	18	D41	0
H	22	B44	19	A43	18	D42	0
H	22	B45	19	A44	18	D43	0
H	22	B46	19	A45	18	D44	0
H	23	B47	15	A46	13	D45	0
H	24	B48	23	A47	15	D46	0
H	25	B49	24	A48	23	D47	0
H	26	B50	25	A49	24	D48	0
H	27	B51	26	A50	25	D49	0

Variables:

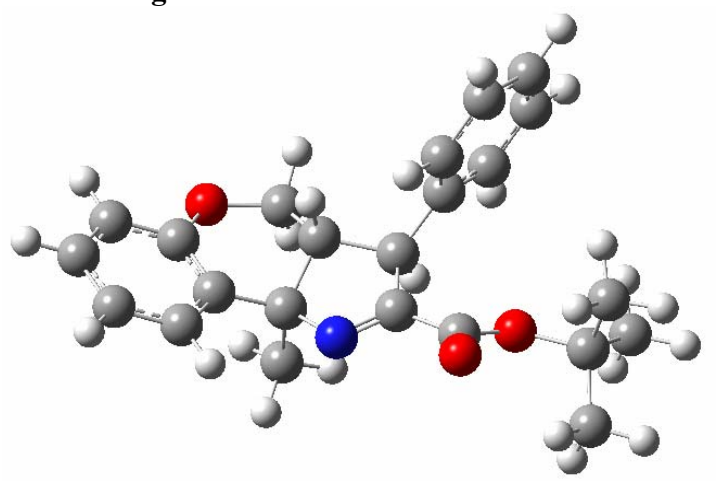
B1	1.4027
B2	1.39705
B3	1.40453
B4	1.40391
B5	1.39571
B6	1.52616
B7	1.57777
B8	1.53029
B9	1.40222
B10	1.50201
B11	1.287
B12	1.52566
B13	1.54827
B14	1.52544
B15	1.49569
B16	1.23525
B17	1.3695
B18	1.5163
B19	1.53387
B20	1.53421
B21	1.53093
B22	1.40569
B23	1.39969
B24	1.39923
B25	1.39997
B26	1.39852
B27	1.08529
B28	1.08494
B29	1.08445
B30	1.08379
B31	1.0932
B32	1.09947
B33	1.09145

B34	1.09751
B35	1.0949
B36	1.0949
B37	1.09318
B38	1.09613
B39	1.095
B40	1.09141
B41	1.09608
B42	1.09146
B43	1.0948
B44	1.09552
B45	1.09403
B46	1.09429
B47	1.08587
B48	1.08555
B49	1.08527
B50	1.08562
B51	1.08673
A1	119.9248
A2	120.85295
A3	118.18996
A4	120.08007
A5	121.01331
A6	113.78043
A7	111.96567
A8	120.76577
A9	109.45973
A10	110.03368
A11	116.99068
A12	109.39286
A13	114.17475
A14	120.27763
A15	125.15767
A16	109.54614
A17	122.6128
A18	109.02657
A19	108.92925
A20	101.86409
A21	121.90221
A22	120.70168
A23	120.26719
A24	119.51993
A25	120.10889
A26	119.71798
A27	120.16873
A28	120.49732
A29	121.93897
A30	109.58997
A31	110.45365
A32	111.78392
A33	108.82337

A34	110.67156
A35	109.71938
A36	110.27088
A37	109.37685
A38	110.37218
A39	111.08254
A40	109.29634
A41	111.12746
A42	110.31001
A43	109.91441
A44	110.42638
A45	110.54646
A46	119.89687
A47	119.63453
A48	120.24185
A49	120.10587
A50	119.69108
D1	-0.32119
D2	-1.75286
D3	1.67786
D4	173.39917
D5	166.42388
D6	-10.16624
D7	-176.78733
D8	48.45593
D9	129.82124
D10	-0.40236
D11	-68.72899
D12	118.08043
D13	179.38858
D14	-19.0706
D15	160.75852
D16	177.61813
D17	63.06831
D18	-60.45708
D19	-178.57191
D20	-32.65936
D21	-178.3456
D22	0.08305
D23	-0.31218
D24	0.07156
D25	-179.79681
D26	-178.49204
D27	-179.78757
D28	178.16844
D29	110.59191
D30	-71.60658
D31	166.55811
D32	-122.22297
D33	-177.96335
D34	-58.00446

D35	61.70688
D36	173.99749
D37	55.12043
D38	-65.92925
D39	-173.47282
D40	66.58047
D41	-54.53215
D42	179.2971
D43	59.29742
D44	-60.83308
D45	2.378
D46	-179.78345
D47	179.95369
D48	-179.6333
D49	-179.39721

6.4. **Z-matrix of compound 5a using basis set 6-31G of DFT**



Charge = 0 Multiplicity = 1

C							
C	1	B1					
C	2	B2	1	A1			
C	3	B3	2	A2	1	D1	0
C	4	B4	3	A3	2	D2	0
C	1	B5	2	A4	3	D3	0
C	4	B6	3	A5	2	D4	0
C	7	B7	4	A6	3	D5	0
C	8	B8	7	A7	4	D6	0
O	5	B9	4	A8	3	D7	0
N	7	B10	4	A9	3	D8	0
C	11	B11	7	A10	4	D9	0
C	12	B12	11	A11	7	D10	0
C	12	B13	11	A12	7	D11	0
O	14	B14	12	A13	11	D12	0
O	14	B15	12	A14	11	D13	0
C	16	B16	14	A15	12	D14	0
C	17	B17	16	A16	14	D15	0

C	17	B18	16	A17	14	D16	0
C	17	B19	16	A18	14	D17	0
C	7	B20	4	A19	3	D18	0
C	13	B21	12	A20	11	D19	0
C	22	B22	13	A21	12	D20	0
C	23	B23	22	A22	13	D21	0
C	24	B24	23	A23	22	D22	0
C	25	B25	24	A24	23	D23	0
C	26	B26	25	A25	24	D24	0
H	1	B27	6	A26	5	D25	0
H	2	B28	1	A27	6	D26	0
H	3	B29	2	A28	1	D27	0
H	6	B30	1	A29	2	D28	0
H	8	B31	7	A30	4	D29	0
H	9	B32	8	A31	7	D30	0
H	9	B33	8	A32	7	D31	0
H	13	B34	12	A33	11	D32	0
H	18	B35	17	A34	16	D33	0
H	18	B36	17	A35	16	D34	0
H	18	B37	17	A36	16	D35	0
H	19	B38	17	A37	16	D36	0
H	19	B39	17	A38	16	D37	0
H	19	B40	17	A39	16	D38	0
H	20	B41	17	A40	16	D39	0
H	20	B42	17	A41	16	D40	0
H	20	B43	17	A42	16	D41	0
H	21	B44	7	A43	4	D42	0
H	21	B45	7	A44	4	D43	0
H	21	B46	7	A45	4	D44	0
H	23	B47	22	A46	13	D45	0
H	24	B48	23	A47	22	D46	0
H	25	B49	24	A48	23	D47	0
H	26	B50	25	A49	24	D48	0
H	27	B51	26	A50	25	D49	0

Variables:

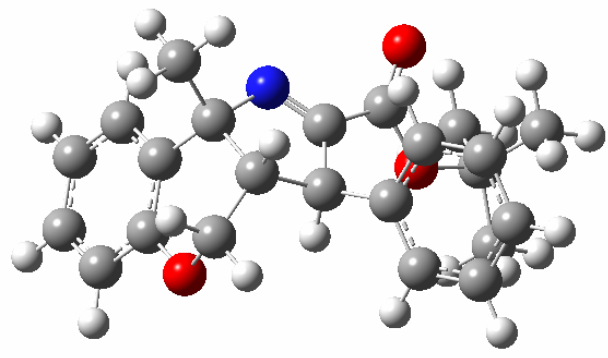
B1	1.40136
B2	1.39967
B3	1.39787
B4	1.41181
B5	1.39808
B6	1.50606
B7	1.55407
B8	1.51293
B9	1.40551
B10	1.50096
B11	1.29249
B12	1.54916
B13	1.49402
B14	1.23518
B15	1.36758
B16	1.51808

B17	1.53372
B18	1.53396
B19	1.53082
B20	1.55188
B21	1.51757
B22	1.40648
B23	1.3988
B24	1.40033
B25	1.39961
B26	1.3993
B27	1.08543
B28	1.08483
B29	1.08479
B30	1.08367
B31	1.09939
B32	1.09502
B33	1.09263
B34	1.09929
B35	1.09616
B36	1.09498
B37	1.09143
B38	1.09616
B39	1.09149
B40	1.09467
B41	1.09556
B42	1.09388
B43	1.09432
B44	1.09573
B45	1.0937
B46	1.09373
B47	1.08666
B48	1.08544
B49	1.08527
B50	1.08559
B51	1.08655
A1	119.75054
A2	120.3669
A3	119.39814
A4	120.54838
A5	125.36928
A6	106.80627
A7	110.36751
A8	123.2917
A9	117.16096
A10	107.51539
A11	116.2719
A12	120.38878
A13	125.02713
A14	109.32362
A15	122.61571
A16	109.00134

A17	108.84555
A18	101.90279
A19	109.97868
A20	115.70395
A21	121.01177
A22	120.65287
A23	120.219
A24	119.57992
A25	120.09138
A26	119.38452
A27	120.24598
A28	121.01593
A29	121.73422
A30	105.65027
A31	112.61824
A32	112.76524
A33	108.55066
A34	109.3331
A35	110.37855
A36	111.08941
A37	109.25899
A38	111.11797
A39	110.35046
A40	109.8493
A41	110.41978
A42	110.54049
A43	111.6469
A44	110.85608
A45	108.73742
A46	119.85679
A47	119.69248
A48	120.19129
A49	120.11614
A50	119.77368
D1	-0.06408
D2	0.83639
D3	-0.65888
D4	-178.48018
D5	-140.79959
D6	-66.74848
D7	-179.83529
D8	-26.40919
D9	-142.07406
D10	4.97716
D11	-174.02461
D12	-32.63604
D13	146.94379
D14	177.41623
D15	63.03389
D16	-60.47379
D17	-178.60726

D18	94.68046
D19	139.49929
D20	-47.20249
D21	-178.94447
D22	0.2208
D23	-0.15021
D24	-0.07959
D25	-179.90936
D26	179.25705
D27	179.40409
D28	-179.2271
D29	48.64018
D30	-68.10541
D31	168.1432
D32	-98.23868
D33	173.98256
D34	55.12028
D35	-65.94314
D36	-173.33872
D37	66.77565
D38	-54.33995
D39	179.44218
D40	59.43583
D41	-60.72793
D42	171.22466
D43	49.36568
D44	-69.42066
D45	1.52602
D46	-179.77133
D47	179.86726
D48	179.98836
D49	-179.48361

6.5. **Z-matrix of compound 4a using basis set 6-311G of DFT**



Charge = 0 Multiplicity = 1

N							
O	1	B1					
O	1	B2	2	A1			
O	3	B3	1	A2	2	D1	0
C	2	B4	1	A3	3	D2	0

C	5	B5	2	A4	1	D3	0
C	6	B6	5	A5	2	D4	0
C	7	B7	6	A6	5	D5	0
C	8	B8	7	A7	6	D6	0
C	2	B9	1	A8	5	D7	0
C	2	B10	1	A9	5	D8	0
C	11	B11	2	A10	1	D9	0
C	1	B12	12	A11	11	D10	0
C	12	B13	11	A12	2	D11	0
C	1	B14	13	A13	5	D12	0
C	3	B15	1	A14	15	D13	0
C	14	B16	12	A15	11	D14	0
C	17	B17	14	A16	12	D15	0
C	18	B18	17	A17	14	D16	0
C	19	B19	18	A18	17	D17	0
C	20	B20	19	A19	18	D18	0
C	21	B21	20	A20	19	D19	0
C	13	B22	1	A21	15	D20	0
C	4	B23	3	A22	1	D21	0
C	24	B24	4	A23	3	D22	0
C	24	B25	4	A24	3	D23	0
C	24	B26	4	A25	3	D24	0
H	19	B27	18	A26	17	D25	0
H	20	B28	19	A27	18	D26	0
H	21	B29	20	A28	19	D27	0
H	22	B30	21	A29	20	D28	0
H	17	B31	14	A30	12	D29	0
H	9	B32	8	A31	7	D30	0
H	8	B33	7	A32	6	D31	0
H	7	B34	6	A33	5	D32	0
H	6	B35	5	A34	2	D33	0
H	27	B36	24	A35	4	D34	0
H	27	B37	24	A36	4	D35	0
H	27	B38	24	A37	4	D36	0
H	25	B39	24	A38	4	D37	0
H	25	B40	24	A39	4	D38	0
H	26	B41	24	A40	4	D39	0
H	26	B42	24	A41	4	D40	0
H	23	B43	13	A42	1	D41	0
H	23	B44	13	A43	1	D42	0
H	23	B45	13	A44	1	D43	0
H	11	B46	2	A45	1	D44	0
H	11	B47	2	A46	1	D45	0
H	14	B48	12	A47	11	D46	0
H	12	B49	11	A48	2	D47	0
H	25	B50	24	A49	4	D48	0
H	26	B51	24	A50	4	D49	0

Variables:

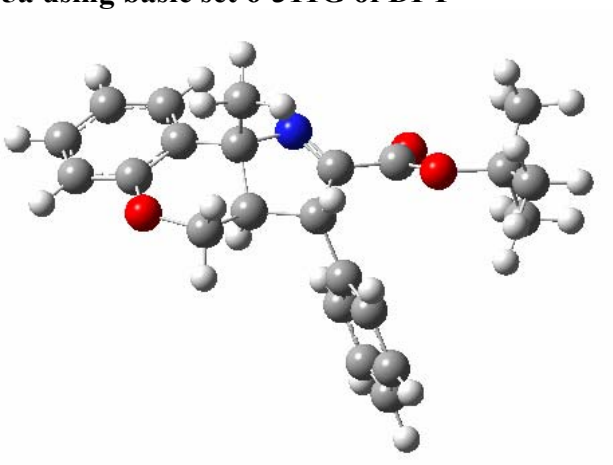
B1	3.99765
B2	2.93885
B3	2.25552

B4	2.42051
B5	1.39835
B6	1.38361
B7	1.36744
B8	1.3648
B9	1.36706
B10	1.4305
B11	1.51036
B12	1.50047
B13	1.53103
B14	1.26744
B15	1.2009
B16	2.52106
B17	1.38518
B18	1.37334
B19	1.38361
B20	1.37439
B21	1.36067
B22	1.52672
B23	1.48957
B24	1.51513
B25	1.50782
B26	1.50596
B27	0.95716
B28	1.02143
B29	0.99091
B30	0.96028
B31	0.97154
B32	0.91287
B33	1.06614
B34	0.90433
B35	1.02377
B36	1.06012
B37	0.96529
B38	0.97491
B39	0.96876
B40	1.00176
B41	0.98699
B42	0.94814
B43	1.01219
B44	0.95663
B45	1.01823
B46	0.98313
B47	1.07752
B48	1.06194
B49	1.00902
B50	1.06499
B51	0.96323
A1	131.29877
A2	80.34069
A3	35.10674

A4	145.73769
A5	121.54836
A6	119.85788
A7	120.20683
A8	60.41002
A9	68.13586
A10	111.59989
A11	38.28456
A12	114.91496
A13	107.64962
A14	53.18012
A15	103.12428
A16	31.12822
A17	118.36902
A18	121.04667
A19	119.75281
A20	119.97766
A21	108.77658
A22	97.53612
A23	108.4654
A24	102.1833
A25	109.68161
A26	116.19489
A27	121.66604
A28	114.51422
A29	119.98068
A30	89.04922
A31	126.7219
A32	117.99116
A33	118.15559
A34	116.78611
A35	105.826
A36	107.25333
A37	106.89012
A38	109.98578
A39	107.41575
A40	109.48461
A41	110.7265
A42	110.14065
A43	113.28577
A44	109.49634
A45	105.10631
A46	111.01439
A47	108.82941
A48	107.22553
A49	113.13362
A50	105.2519
D1	20.01344
D2	-147.63088
D3	146.37463
D4	-0.96111

D5	-0.94275
D6	1.37729
D7	18.01781
D8	-119.76268
D9	-11.90882
D10	47.21153
D11	-58.27862
D12	-100.90297
D13	22.75188
D14	-115.26813
D15	122.80538
D16	178.00797
D17	-1.35513
D18	0.94658
D19	-0.72935
D20	137.27504
D21	168.78284
D22	-66.05733
D23	177.68568
D24	59.06652
D25	-178.28879
D26	175.73255
D27	-175.90675
D28	177.83117
D29	-53.36344
D30	-179.95261
D31	176.77599
D32	178.83129
D33	178.68534
D34	51.9319
D35	-74.31277
D36	173.86786
D37	73.41253
D38	-176.37635
D39	-177.41097
D40	57.17937
D41	-50.93321
D42	69.0948
D43	-171.92439
D44	-132.98511
D45	107.08461
D46	31.5448
D47	177.43767
D48	-55.72629
D49	-68.20741

6.6. **Z-matrix of compound 5a using basic set 6-311G of DFT**



Charge = 0 Multiplicity = 1

N							
O	1	B1					
O	1	B2	2	A1			
O	3	B3	1	A2	2	D1	0
C	1	B4	3	A3	4	D2	0
C	5	B5	1	A4	3	D3	0
C	6	B6	5	A5	1	D4	0
C	7	B7	6	A6	5	D5	0
C	8	B8	7	A7	6	D6	0
C	9	B9	8	A8	7	D7	0
C	2	B10	1	A9	5	D8	0
C	11	B11	2	A10	1	D9	0
C	1	B12	12	A11	11	D10	0
C	12	B13	11	A12	2	D11	0
C	1	B14	13	A13	5	D12	0
C	3	B15	1	A14	15	D13	0
C	14	B16	12	A15	11	D14	0
C	17	B17	14	A16	12	D15	0
C	18	B18	17	A17	14	D16	0
C	19	B19	18	A18	17	D17	0
C	20	B20	19	A19	18	D18	0
C	17	B21	14	A20	12	D19	0
C	13	B22	1	A21	15	D20	0
C	4	B23	3	A22	1	D21	0
C	24	B24	4	A23	3	D22	0
C	24	B25	4	A24	3	D23	0
C	24	B26	4	A25	3	D24	0
H	19	B27	18	A26	17	D25	0
H	20	B28	19	A27	18	D26	0
H	21	B29	20	A28	19	D27	0
H	22	B30	17	A29	14	D28	0
H	17	B31	14	A30	12	D29	0
H	9	B32	8	A31	7	D30	0
H	8	B33	7	A32	6	D31	0
H	7	B34	6	A33	5	D32	0

H	6	B35	5	A34	1	D33	0
H	27	B36	24	A35	4	D34	0
H	27	B37	24	A36	4	D35	0
H	27	B38	24	A37	4	D36	0
H	25	B39	24	A38	4	D37	0
H	25	B40	24	A39	4	D38	0
H	26	B41	24	A40	4	D39	0
H	26	B42	24	A41	4	D40	0
H	23	B43	13	A42	1	D41	0
H	23	B44	13	A43	1	D42	0
H	23	B45	13	A44	1	D43	0
H	11	B46	2	A45	1	D44	0
H	11	B47	2	A46	1	D45	0
H	14	B48	12	A47	11	D46	0
H	12	B49	11	A48	2	D47	0
H	25	B50	24	A49	4	D48	0
H	26	B51	24	A50	4	D49	0

Variables:

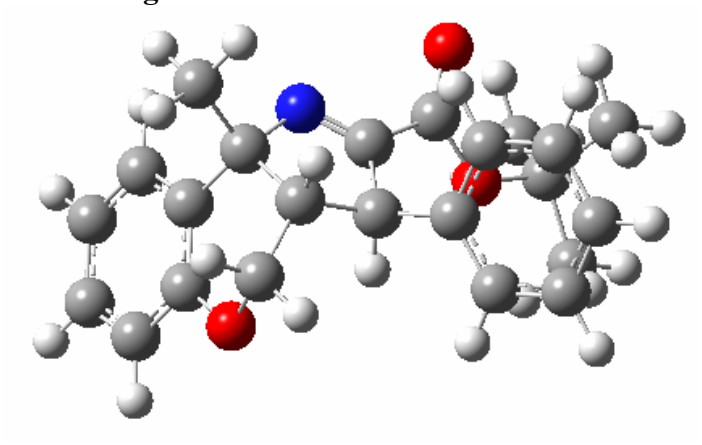
B1	4.01504
B2	2.92408
B3	2.31299
B4	2.44562
B5	1.40444
B6	1.39345
B7	1.40038
B8	1.39159
B9	1.39797
B10	1.46293
B11	1.5197
B12	1.51428
B13	1.5601
B14	1.28607
B15	1.23244
B16	2.5433
B17	1.40483
B18	1.40228
B19	1.39761
B20	1.39701
B21	1.39645
B22	1.5341
B23	1.52055
B24	1.53152
B25	1.5286
B26	1.53169
B27	1.0828
B28	1.08213
B29	1.08181
B30	1.08204
B31	1.08332
B32	1.08042
B33	1.08178

B34	1.08132
B35	1.08085
B36	1.09027
B37	1.08691
B38	1.09222
B39	1.08685
B40	1.09214
B41	1.09151
B42	1.08964
B43	1.09123
B44	1.08849
B45	1.09175
B46	1.0871
B47	1.09447
B48	1.09405
B49	1.09332
B50	1.09052
B51	1.08946
A1	133.31898
A2	81.53852
A3	152.65341
A4	97.81573
A5	121.42621
A6	119.70261
A7	119.94966
A8	119.7863
A9	68.72345
A10	111.50864
A11	38.61337
A12	115.18727
A13	109.26007
A14	53.7425
A15	102.52618
A16	30.74795
A17	118.53217
A18	120.83504
A19	120.12837
A20	151.47233
A21	108.70366
A22	96.94855
A23	108.83098
A24	101.88588
A25	108.81104
A26	119.32253
A27	119.78908
A28	120.23292
A29	119.74043
A30	89.03419
A31	121.94467
A32	120.30249
A33	119.98662

A34	118.61465
A35	110.25037
A36	111.18963
A37	109.3327
A38	111.15418
A39	109.42246
A40	109.90807
A41	110.44254
A42	109.94721
A43	110.89637
A44	110.42156
A45	104.99886
A46	108.61914
A47	109.71301
A48	107.90584
A49	110.28907
A50	110.43175
D1	8.78819
D2	-42.86337
D3	-79.04407
D4	147.68939
D5	-0.08507
D6	-0.04248
D7	-0.02901
D8	-121.02388
D9	-9.94981
D10	50.70192
D11	-63.69048
D12	-102.69559
D13	19.49802
D14	-117.31311
D15	117.96298
D16	-178.55959
D17	0.28822
D18	-0.35911
D19	115.47008
D20	135.80714
D21	166.70408
D22	-61.71578
D23	-179.9794
D24	61.82676
D25	-179.28406
D26	179.88253
D27	-179.77503
D28	-178.95683
D29	-63.79798
D30	-179.90873
D31	179.95139
D32	-179.62616
D33	-30.04749
D34	53.94505

D35	-67.12692
D36	172.88179
D37	66.49965
D38	-173.38904
D39	179.59968
D40	59.68304
D41	-56.39049
D42	63.21117
D43	-176.59343
D44	-131.48247
D45	112.13795
D46	31.94344
D47	175.38323
D48	-54.47249
D49	-60.40985

6.7. **Z-matrix of compound 4a using basis set 6-311G** of DFT**



Charge = 0 Multiplicity = 1

N							
O	1	B1					
O	1	B2	2	A1			
O	3	B3	1	A2	2	D1	0
C	1	B4	3	A3	4	D2	0
C	5	B5	1	A4	3	D3	0
C	6	B6	5	A5	1	D4	0
C	7	B7	6	A6	5	D5	0
C	8	B8	7	A7	6	D6	0
C	9	B9	8	A8	7	D7	0
C	2	B10	1	A9	5	D8	0
C	11	B11	2	A10	1	D9	0
C	1	B12	12	A11	11	D10	0
C	12	B13	11	A12	2	D11	0
C	1	B14	13	A13	5	D12	0
C	3	B15	1	A14	15	D13	0
C	14	B16	12	A15	11	D14	0
C	17	B17	14	A16	12	D15	0
C	18	B18	17	A17	14	D16	0
C	19	B19	18	A18	17	D17	0

C	20	B20	19	A19	18	D18	0
C	17	B21	14	A20	12	D19	0
C	13	B22	1	A21	15	D20	0
C	4	B23	3	A22	1	D21	0
C	24	B24	4	A23	3	D22	0
C	24	B25	4	A24	3	D23	0
C	24	B26	4	A25	3	D24	0
H	19	B27	18	A26	17	D25	0
H	20	B28	19	A27	18	D26	0
H	21	B29	20	A28	19	D27	0
H	22	B30	17	A29	14	D28	0
H	17	B31	14	A30	12	D29	0
H	9	B32	8	A31	7	D30	0
H	8	B33	7	A32	6	D31	0
H	7	B34	6	A33	5	D32	0
H	6	B35	5	A34	1	D33	0
H	27	B36	24	A35	4	D34	0
H	27	B37	24	A36	4	D35	0
H	27	B38	24	A37	4	D36	0
H	25	B39	24	A38	4	D37	0
H	25	B40	24	A39	4	D38	0
H	26	B41	24	A40	4	D39	0
H	26	B42	24	A41	4	D40	0
H	23	B43	13	A42	1	D41	0
H	23	B44	13	A43	1	D42	0
H	23	B45	13	A44	1	D43	0
H	11	B46	2	A45	1	D44	0
H	11	B47	2	A46	1	D45	0
H	14	B48	12	A47	11	D46	0
H	12	B49	11	A48	2	D47	0
H	25	B50	24	A49	4	D48	0
H	26	B51	24	A50	4	D49	0

Variables:

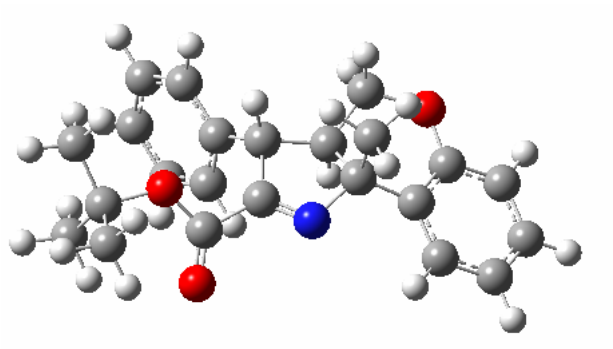
B1	4.01504
B2	2.92408
B3	2.31299
B4	2.44562
B5	1.40444
B6	1.39345
B7	1.40038
B8	1.39159
B9	1.39797
B10	1.46293
B11	1.5197
B12	1.51428
B13	1.5601
B14	1.28607
B15	1.23244
B16	2.5433
B17	1.40483
B18	1.40228

B19	1.39761
B20	1.39701
B21	1.39645
B22	1.5341
B23	1.52055
B24	1.53152
B25	1.5286
B26	1.53169
B27	1.0828
B28	1.08213
B29	1.08181
B30	1.08204
B31	1.08332
B32	1.08042
B33	1.08178
B34	1.08132
B35	1.08085
B36	1.09027
B37	1.08691
B38	1.09222
B39	1.08685
B40	1.09214
B41	1.09151
B42	1.08964
B43	1.09123
B44	1.08849
B45	1.09175
B46	1.0871
B47	1.09447
B48	1.09405
B49	1.09332
B50	1.09052
B51	1.08946
A1	133.31898
A2	81.53852
A3	152.65341
A4	97.81573
A5	121.42621
A6	119.70261
A7	119.94966
A8	119.7863
A9	68.72345
A10	111.50864
A11	38.61337
A12	115.18727
A13	109.26007
A14	53.7425
A15	102.52618
A16	30.74795
A17	118.53217
A18	120.83504

A19	120.12837
A20	151.47233
A21	108.70366
A22	96.94855
A23	108.83098
A24	101.88588
A25	108.81104
A26	119.32253
A27	119.78908
A28	120.23292
A29	119.74043
A30	89.03419
A31	121.94467
A32	120.30249
A33	119.98662
A34	118.61465
A35	110.25037
A36	111.18963
A37	109.3327
A38	111.15418
A39	109.42246
A40	109.90807
A41	110.44254
A42	109.94721
A43	110.89637
A44	110.42156
A45	104.99886
A46	108.61914
A47	109.71301
A48	107.90584
A49	110.28907
A50	110.43175
D1	8.78819
D2	-42.86337
D3	-79.04407
D4	147.68939
D5	-0.08507
D6	-0.04248
D7	-0.02901
D8	-121.02388
D9	-9.94981
D10	50.70192
D11	-63.69048
D12	-102.69559
D13	19.49802
D14	-117.31311
D15	117.96298
D16	-178.55959
D17	0.28822
D18	-0.35911
D19	115.47008

D20	135.80714
D21	166.70408
D22	-61.71578
D23	-179.9794
D24	61.82676
D25	-179.28406
D26	179.88253
D27	-179.77503
D28	-178.95683
D29	-63.79798
D30	-179.90873
D31	179.95139
D32	-179.62616
D33	-30.04749
D34	53.94505
D35	-67.12692
D36	172.88179
D37	66.49965
D38	-173.38904
D39	179.59968
D40	59.68304
D41	-56.39049
D42	63.21117
D43	-176.59343
D44	-131.48247
D45	112.13795
D46	31.94344
D47	175.38323
D48	-54.47249
D49	-60.40985

6.8. **Z-matrix of compound 5a using basis set 6-311G** of DFT**



Charge = 0 Multiplicity = 1

C							
C	1	B1					
C	2	B2	1	A1			
C	3	B3	2	A2	1	D1	0
C	4	B4	3	A3	2	D2	0
C	1	B5	2	A4	3	D3	0
C	4	B6	3	A5	2	D4	0

C	7	B7	4	A6	3	D5	0
C	8	B8	7	A7	4	D6	0
O	5	B9	4	A8	3	D7	0
N	7	B10	4	A9	3	D8	0
C	11	B11	7	A10	4	D9	0
C	8	B12	7	A11	4	D10	0
C	13	B13	8	A12	7	D11	0
C	7	B14	4	A13	3	D12	0
C	12	B15	11	A14	7	D13	0
O	16	B16	12	A15	11	D14	0
O	16	B17	12	A16	11	D15	0
C	18	B18	16	A17	12	D16	0
C	19	B19	18	A18	16	D17	0
C	19	B20	18	A19	16	D18	0
C	19	B21	18	A20	16	D19	0
C	14	B22	13	A21	8	D20	0
C	23	B23	14	A22	13	D21	0
C	24	B24	23	A23	14	D22	0
C	25	B25	24	A24	23	D23	0
C	26	B26	25	A25	24	D24	0
H	1	B27	6	A26	5	D25	0
H	2	B28	1	A27	6	D26	0
H	3	B29	2	A28	1	D27	0
H	6	B30	1	A29	2	D28	0
H	8	B31	7	A30	4	D29	0
H	9	B32	8	A31	7	D30	0
H	9	B33	8	A32	7	D31	0
H	13	B34	8	A33	7	D32	0
H	15	B35	7	A34	4	D33	0
H	15	B36	7	A35	4	D34	0
H	15	B37	7	A36	4	D35	0
H	20	B38	19	A37	18	D36	0
H	20	B39	19	A38	18	D37	0
H	20	B40	19	A39	18	D38	0
H	21	B41	19	A40	18	D39	0
H	21	B42	19	A41	18	D40	0
H	21	B43	19	A42	18	D41	0
H	22	B44	19	A43	18	D42	0
H	22	B45	19	A44	18	D43	0
H	22	B46	19	A45	18	D44	0
H	23	B47	14	A46	13	D45	0
H	24	B48	23	A47	14	D46	0
H	25	B49	24	A48	23	D47	0
H	26	B50	25	A49	24	D48	0
H	27	B51	26	A50	25	D49	0

Variables:

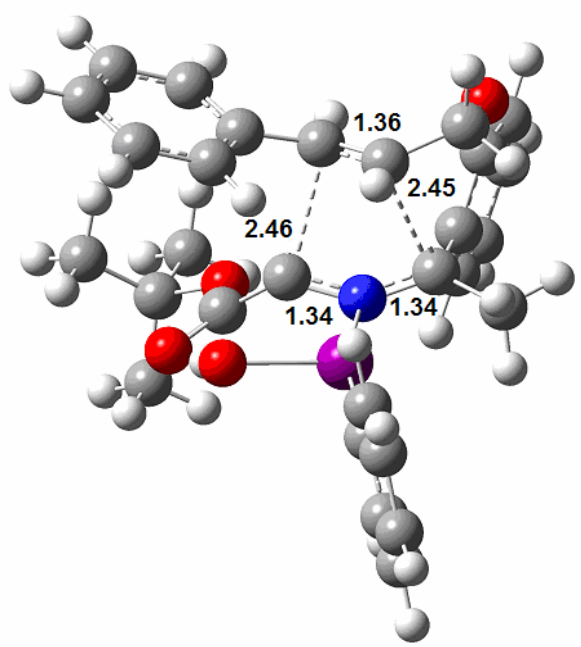
B1	1.39422
B2	1.39297
B3	1.39237
B4	1.40789
B5	1.39136

B6	1.5065
B7	1.54348
B8	1.50859
B9	1.37434
B10	1.4799
B11	1.27295
B12	1.53951
B13	1.51398
B14	1.54734
B15	1.51314
B16	1.20174
B17	1.34045
B18	1.48483
B19	1.52949
B20	1.52976
B21	1.52851
B22	1.40033
B23	1.3925
B24	1.39367
B25	1.39282
B26	1.39327
B27	1.08452
B28	1.08376
B29	1.08399
B30	1.08342
B31	1.09644
B32	1.09498
B33	1.09222
B34	1.0965
B35	1.09353
B36	1.09131
B37	1.09141
B38	1.09339
B39	1.0929
B40	1.08898
B41	1.09355
B42	1.08886
B43	1.09251
B44	1.09279
B45	1.09195
B46	1.09233
B47	1.0855
B48	1.08435
B49	1.08419
B50	1.08451
B51	1.08541
A1	119.54244
A2	120.62639
A3	119.5254
A4	120.57342
A5	125.34955

A6	106.09498
A7	110.43436
A8	123.67107
A9	117.43036
A10	107.46963
A11	102.81893
A12	115.30807
A13	109.33977
A14	120.13797
A15	124.12491
A16	108.8301
A17	121.94536
A18	109.43515
A19	109.68962
A20	102.59344
A21	120.99773
A22	120.7368
A23	120.22782
A24	119.5497
A25	120.08966
A26	119.32739
A27	120.35083
A28	120.92875
A29	121.5499
A30	105.48154
A31	112.19216
A32	112.23001
A33	111.59658
A34	111.81588
A35	111.28804
A36	108.59122
A37	109.2874
A38	110.38162
A39	111.3692
A40	109.15386
A41	111.42206
A42	110.41805
A43	110.06932
A44	110.56387
A45	110.62013
A46	119.88598
A47	119.67602
A48	120.21058
A49	120.11611
A50	119.69547
D1	-0.07761
D2	0.96297
D3	-0.74897
D4	-178.638
D5	-141.12441
D6	-65.63172

D7	-179.92452
D8	-26.5362
D9	-141.51045
D10	160.05027
D11	-154.06202
D12	94.82254
D13	-174.14386
D14	-42.66151
D15	138.96053
D16	178.30792
D17	58.70529
D18	-65.15055
D19	176.77874
D20	66.54422
D21	-178.71665
D22	0.18846
D23	-0.25359
D24	0.
D25	-179.94146
D26	179.19734
D27	179.38427
D28	-179.13903
D29	49.4809
D30	-68.96324
D31	168.91072
D32	81.55964
D33	171.04043
D34	48.89568
D35	-69.81638
D36	173.09214
D37	54.34002
D38	-66.77429
D39	-172.91424
D40	67.13367
D41	-54.12194
D42	-179.82009
D43	60.26405
D44	-59.98104
D45	1.75124
D46	-179.7645
D47	179.8531
D48	-179.90634
D49	-179.58516

6.9. **Z-matrix of TS-III using basis set LANL2DZ of DFT**



Optimized Energy: -935123.72 kcal/mol
Charge = 0 Multiplicity = 2

N						
O	1	B1				
O	1	B2	2	A1		
O	3	B3	1	A2	2	D1
C	1	B4	4	A3	3	D2
C	5	B5	1	A4	4	D3
C	6	B6	5	A5	1	D4
C	7	B7	6	A6	5	D5
C	8	B8	7	A7	6	D6
C	2	B9	1	A8	5	D7
C	2	B10	1	A9	5	D8
C	11	B11	2	A10	1	D9
C	1	B12	5	A11	10	D10
C	12	B13	11	A12	2	D11
C	1	B14	13	A13	5	D12
C	3	B15	1	A14	13	D13
C	14	B16	12	A15	11	D14
C	17	B17	14	A16	12	D15
C	18	B18	17	A17	14	D16
C	19	B19	18	A18	17	D17
C	20	B20	19	A19	18	D18
C	17	B21	14	A20	12	D19
C	13	B22	1	A21	15	D20
C	4	B23	3	A22	1	D21
C	24	B24	4	A23	3	D22
C	24	B25	4	A24	3	D23
C	24	B26	4	A25	3	D24
H	19	B27	18	A26	17	D25
H	20	B28	19	A27	18	D26
H	21	B29	20	A28	19	D27
H	22	B30	17	A29	14	D28

H	17	B31	14	A30	12	D29
H	9	B32	8	A31	7	D30
H	8	B33	7	A32	6	D31
H	7	B34	6	A33	5	D32
H	6	B35	5	A34	1	D33
H	27	B36	24	A35	4	D34
H	27	B37	24	A36	4	D35
H	27	B38	24	A37	4	D36
H	25	B39	24	A38	4	D37
H	25	B40	24	A39	4	D38
H	26	B41	24	A40	4	D39
H	26	B42	24	A41	4	D40
H	23	B43	13	A42	1	D41
H	23	B44	13	A43	1	D42
H	23	B45	13	A44	1	D43
H	11	B46	2	A45	1	D44
H	11	B47	2	A46	1	D45
H	14	B48	12	A47	11	D46
H	12	B49	11	A48	2	D47
H	25	B50	24	A49	4	D48
H	26	B51	24	A50	4	D49
I	1	B52	13	A51	5	D50
C	23	B53	13	A52	1	D51
C	54	B54	23	A53	13	D52
C	54	B55	23	A54	13	D53
C	55	B56	54	A55	23	D54
H	55	B57	54	A56	23	D55
C	56	B58	54	A57	23	D56
H	56	B59	54	A58	23	D57
C	59	B60	56	A59	54	D58
H	57	B61	55	A60	54	D59
H	59	B62	56	A61	54	D60
H	61	B63	59	A62	56	D61
O	3	B64	1	A63	13	D62
H	65	B65	3	A64	1	D63

B1	4.02100747
B2	3.46267985
B3	2.33100309
B4	2.39331300
B5	1.41790144
B6	1.40150955
B7	1.41068143
B8	1.39992373
B9	1.39415213
B10	1.46450678
B11	1.52171419
B12	1.34700018
B13	1.36699939
B14	1.34700309
B15	1.25718574
B16	2.56523283
B17	1.41645591
B18	1.41515693
B19	1.40747244
B20	1.40646678
B21	1.40210279
B22	1.51842191
B23	1.53081069
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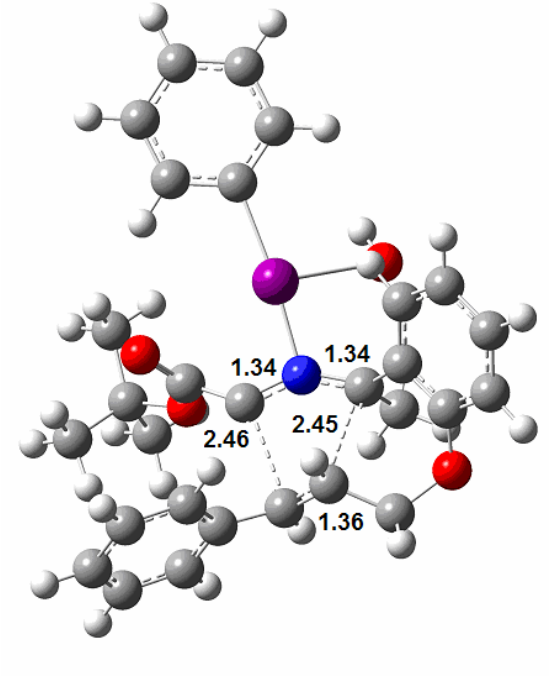
6.10. Z-matrix of TS-IV using basis set LANL2DZ of DFT



Optimized Energy: -935114.21 kcal/mol
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C	9	B9	8	A8	7	D7
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C	17	B17	14	A16	12	D15
C	18	B18	17	A17	14	D16
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C	24	B24	4	A23	3	D22
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H	17	B31	14	A30	12	D29
H	9	B32	8	A31	7	D30

H	8	B33	7	A32	6	D31
H	7	B34	6	A33	5	D32
H	6	B35	5	A34	2	D33
H	27	B36	24	A35	4	D34
H	27	B37	24	A36	4	D35
H	27	B38	24	A37	4	D36
H	25	B39	24	A38	4	D37
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H	26	B41	24	A40	4	D39
H	26	B42	24	A41	4	D40
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B60	1.40983254
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B62	1.08851150
B63	1.08845266
B64	3.35854018
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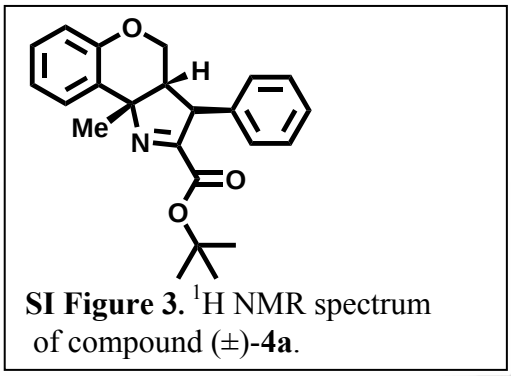
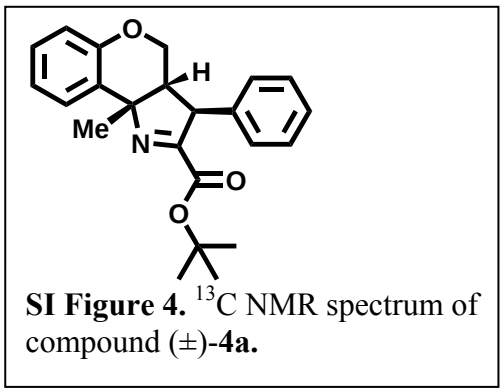
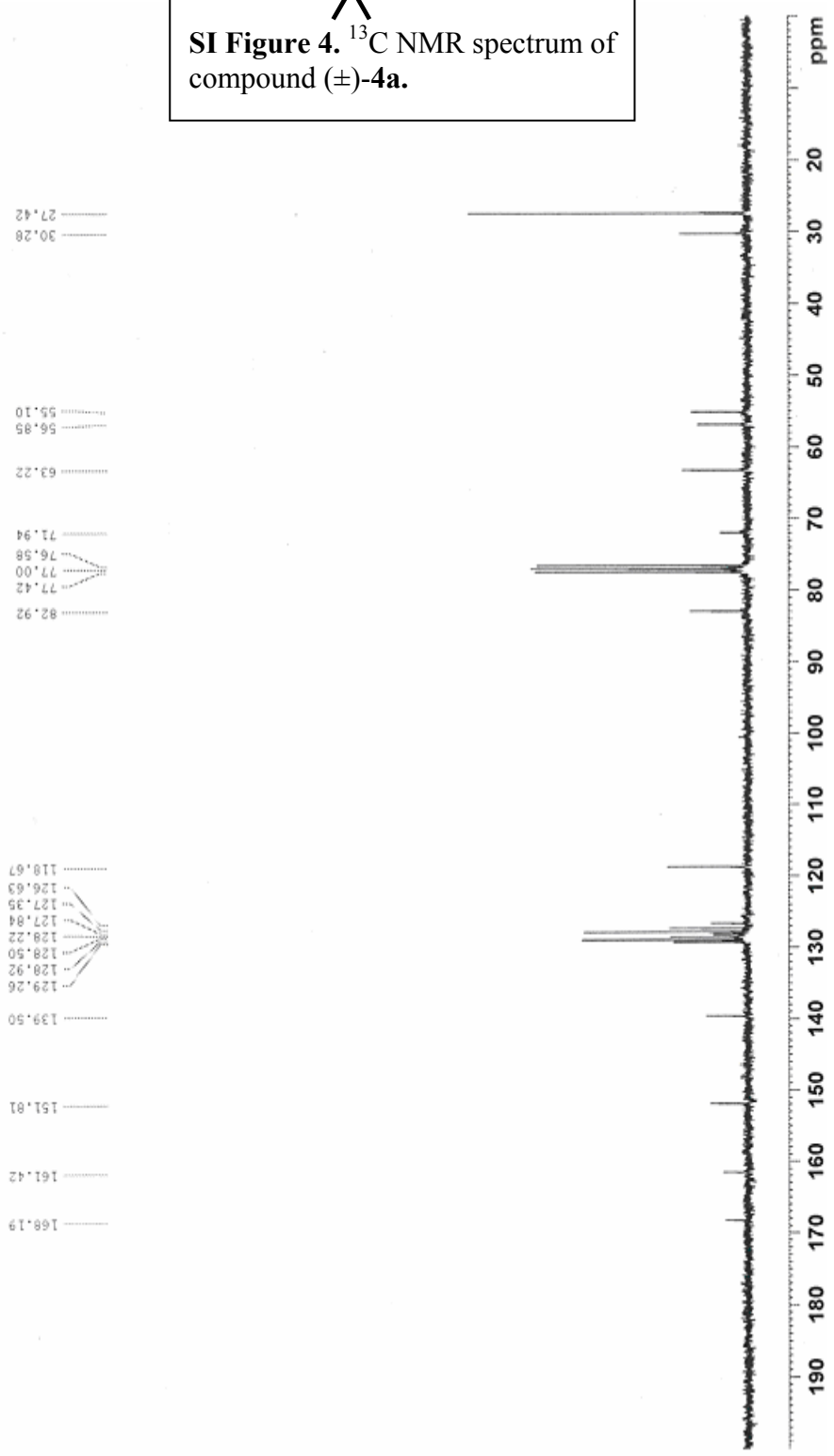
7. ^{1}H and ^{13}C spectra of the compounds (4a-g, 6a-c and 7a-7e)

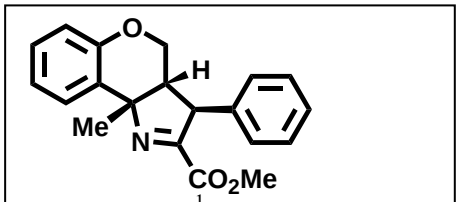


SI Figure 3. ^{1}H NMR spectrum of compound (±)-**4a**.

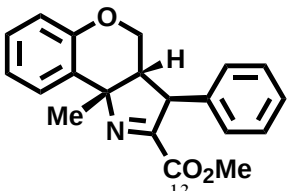


SI Figure 4. ^{13}C NMR spectrum of compound (±)-**4a.**

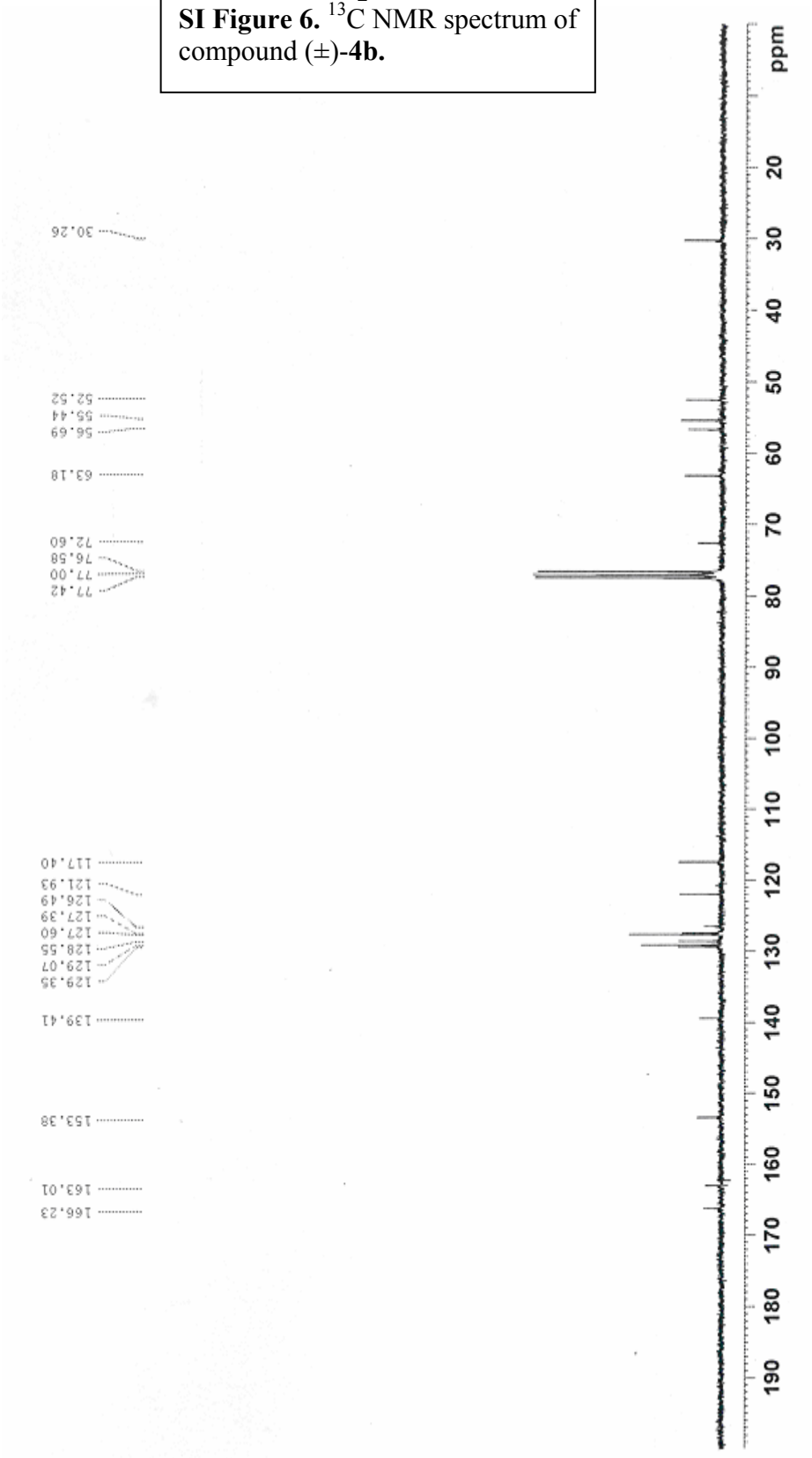


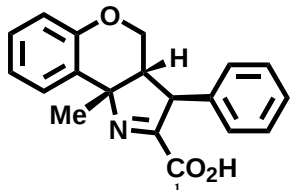


SI Figure 5. ^{1}H NMR spectrum of compound (±)-**4b**.

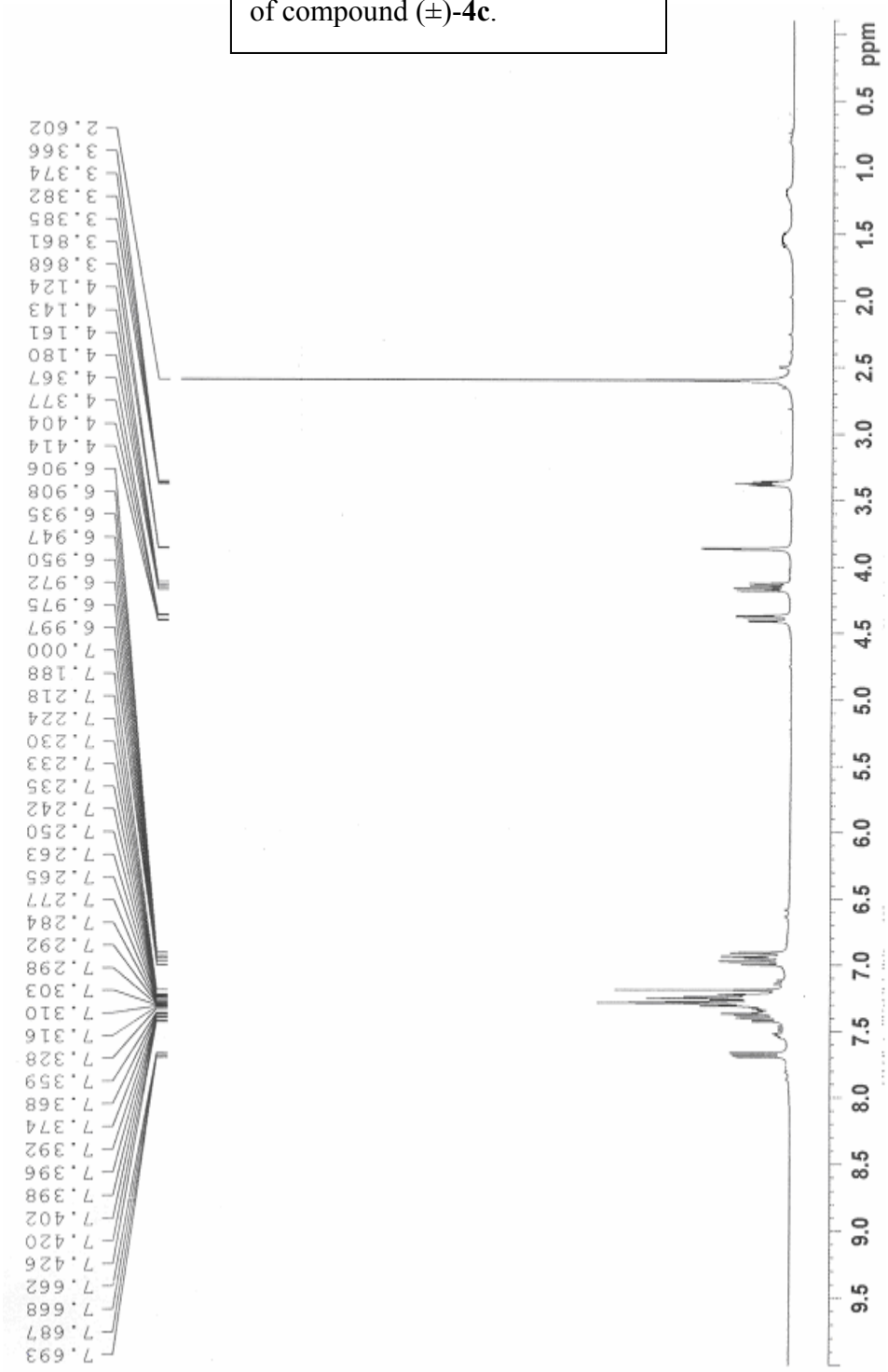


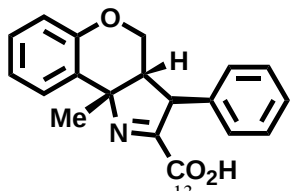
SI Figure 6. ^{13}C NMR spectrum of compound (±)-**4b.**



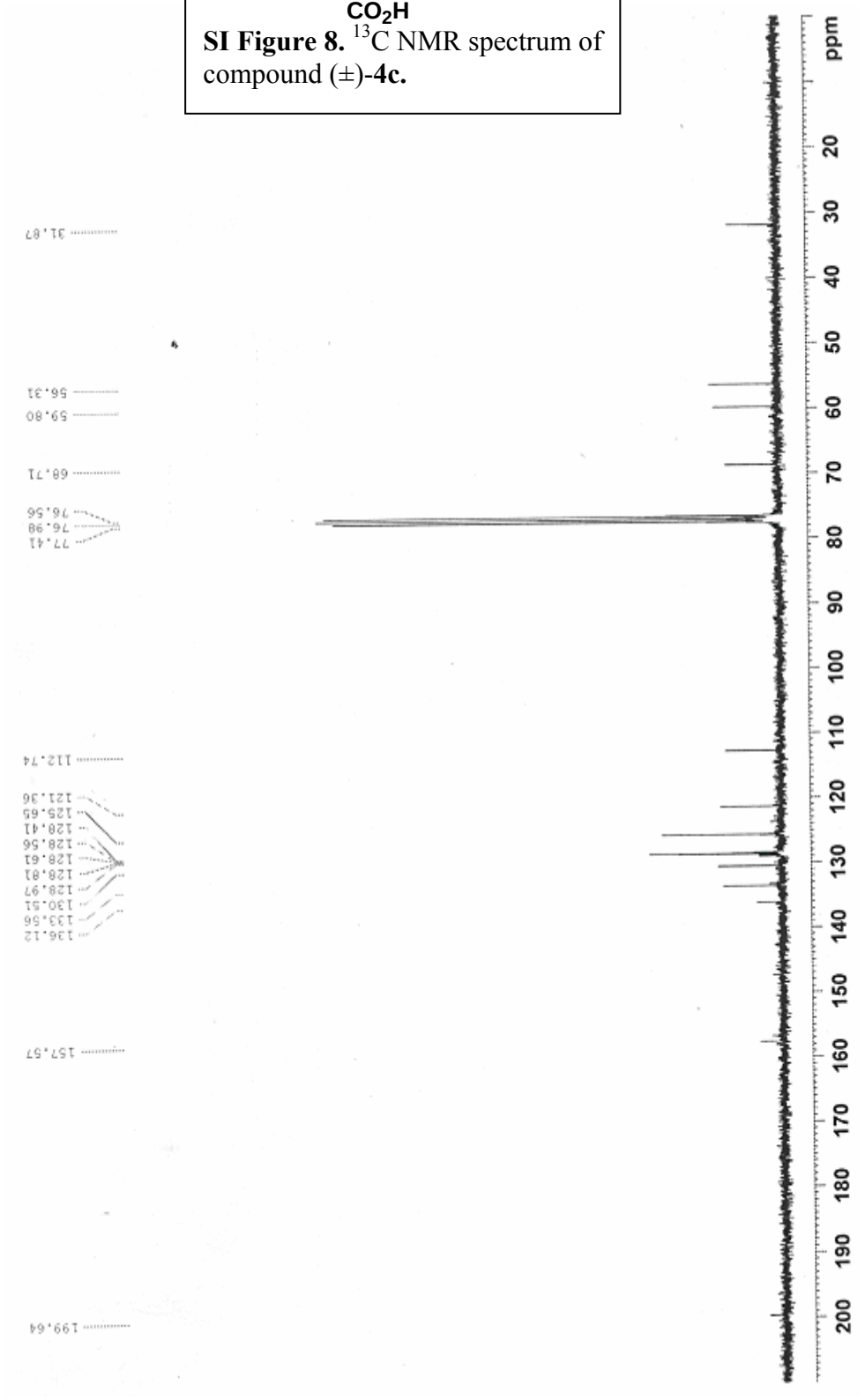


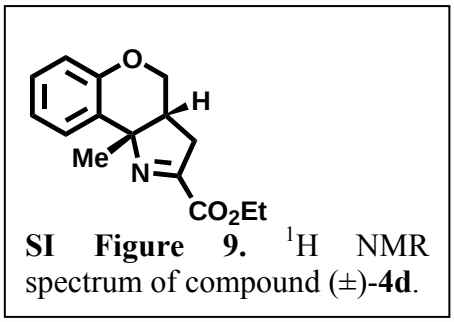
SI Figure 7. ^{1}H NMR spectrum of compound (±)-**4c**.



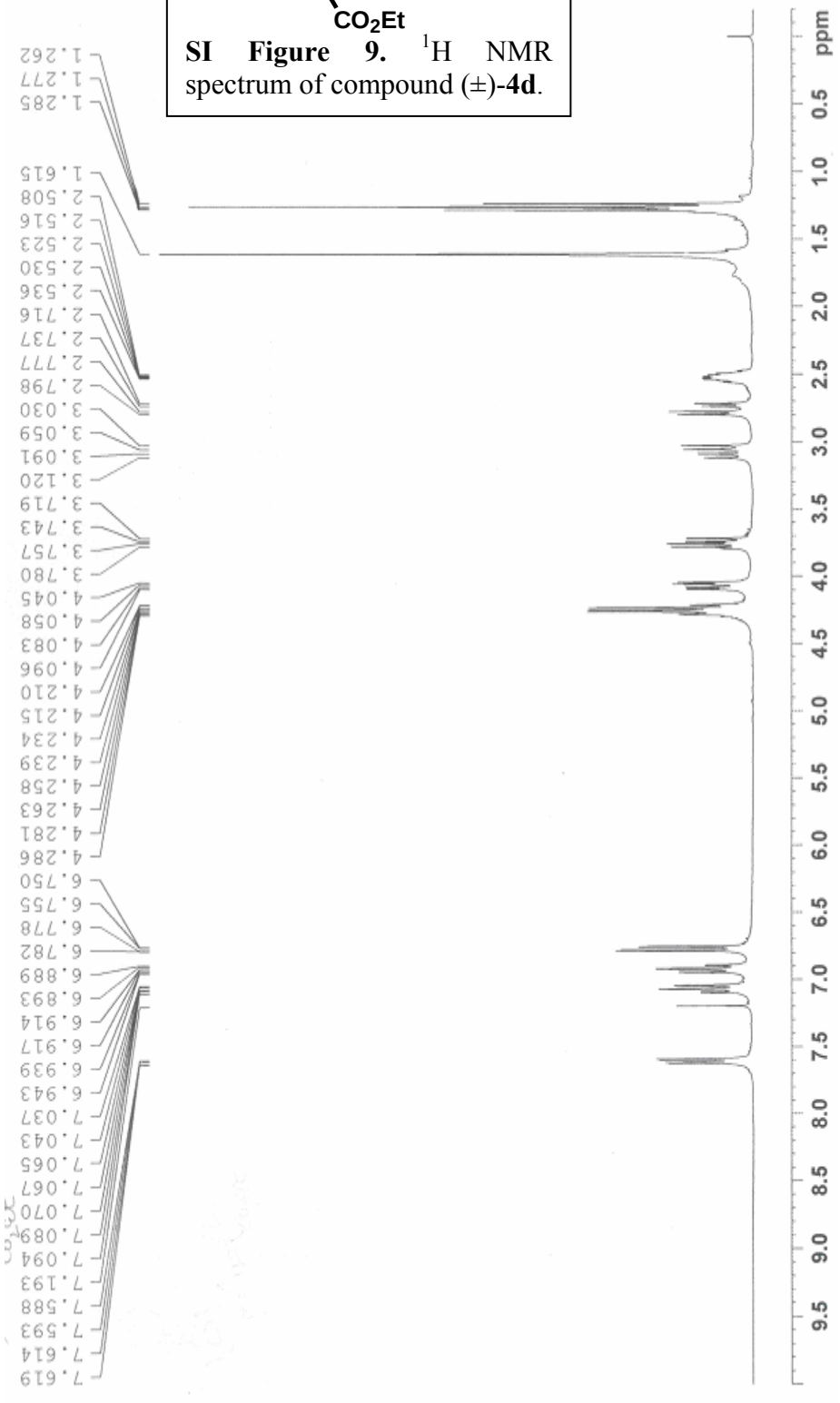


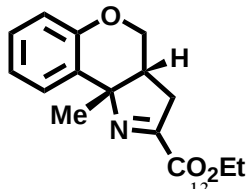
SI Figure 8. ^{13}C NMR spectrum of compound (±)-**4c.**



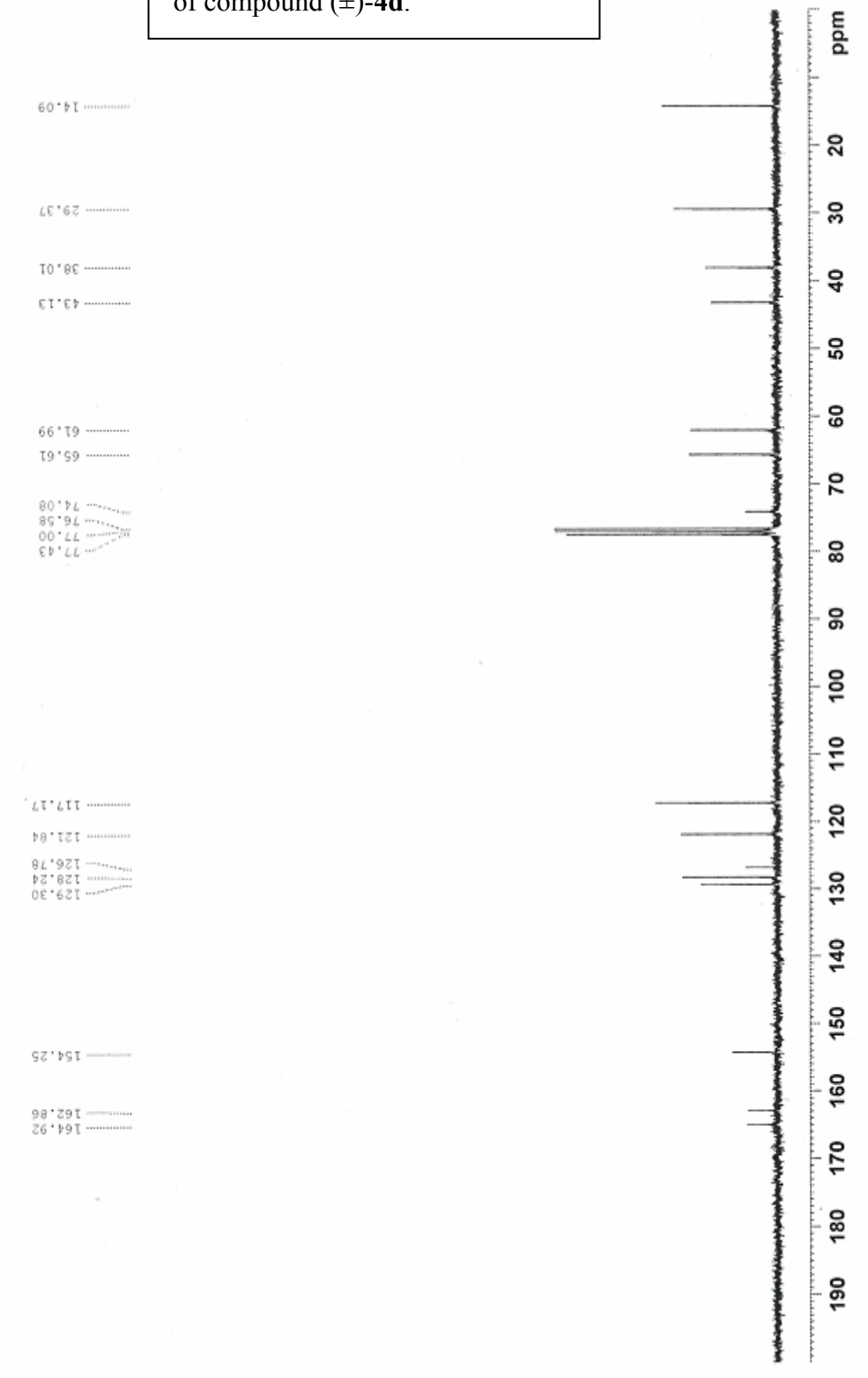


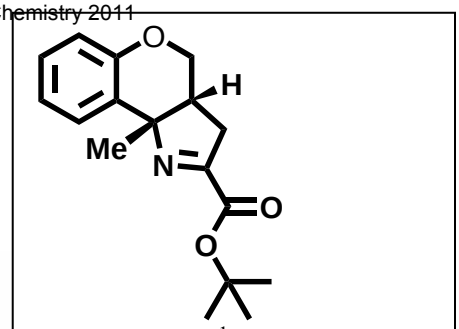
SI Figure 9. ^{1}H NMR spectrum of compound (±)-**4d**.



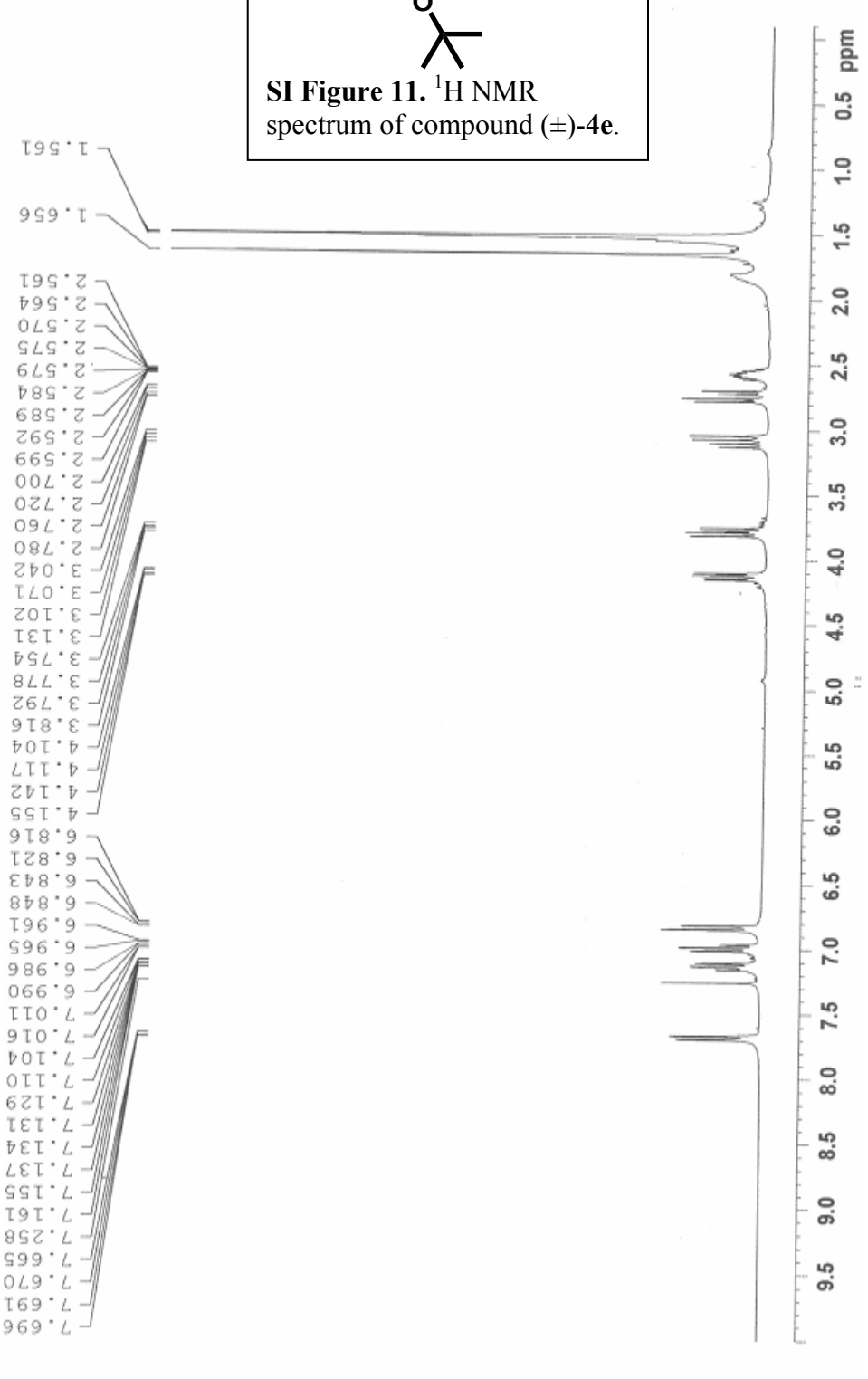


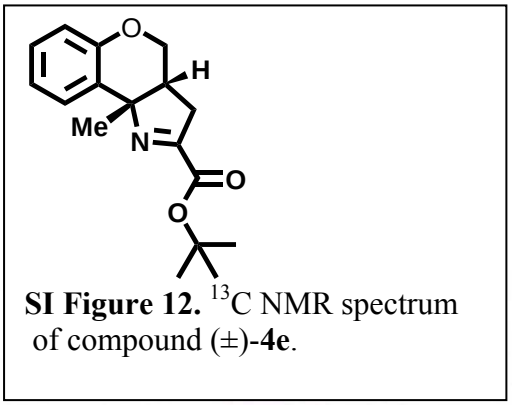
SI Figure 10. ^{13}C NMR spectrum of compound (±)-**4d**.



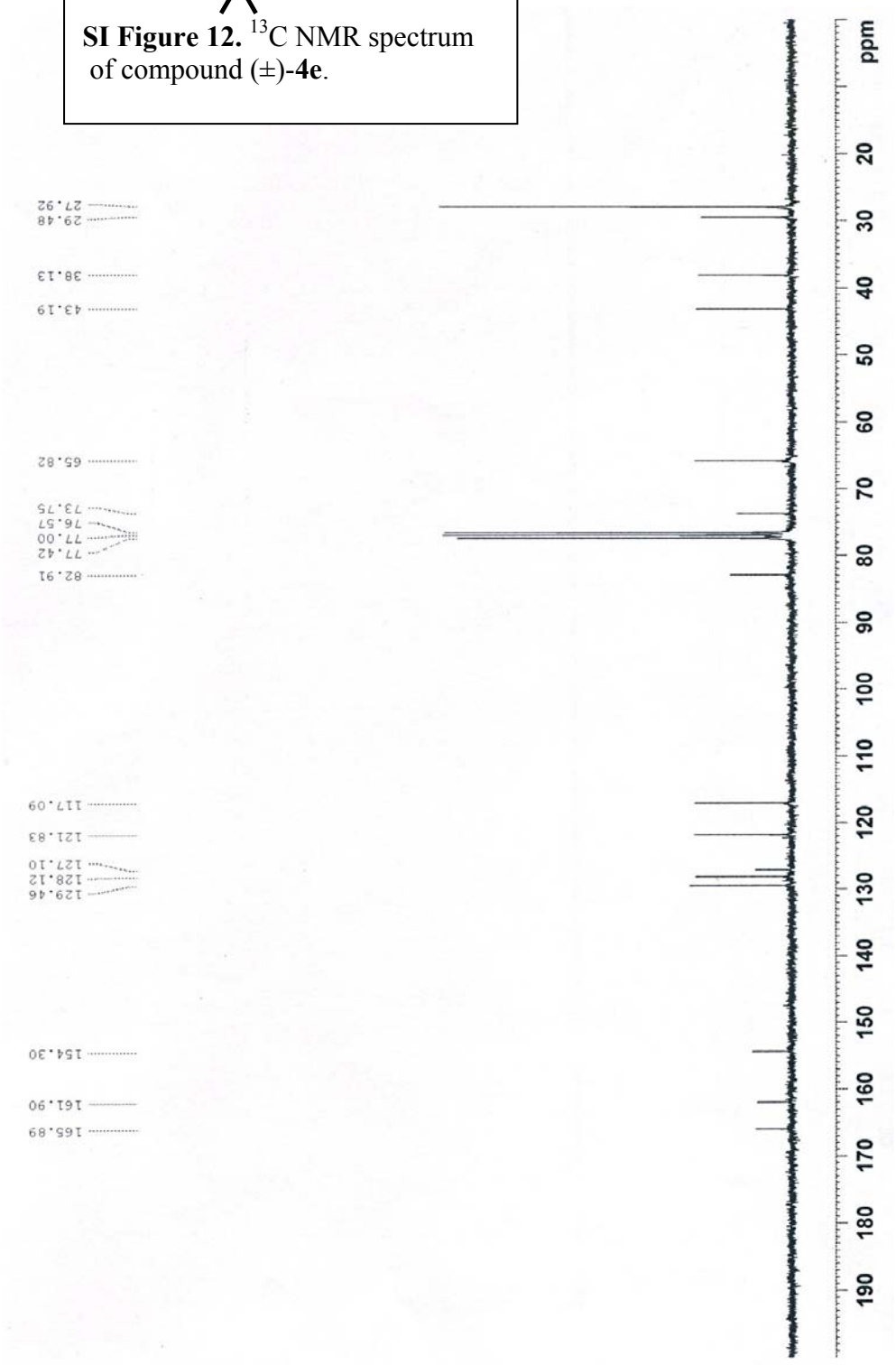


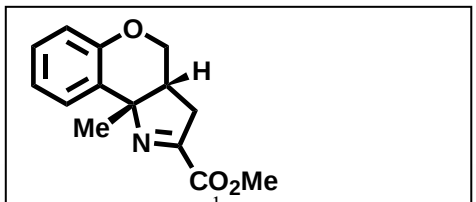
SI Figure 11. ^{1}H NMR spectrum of compound (±)-**4e**.



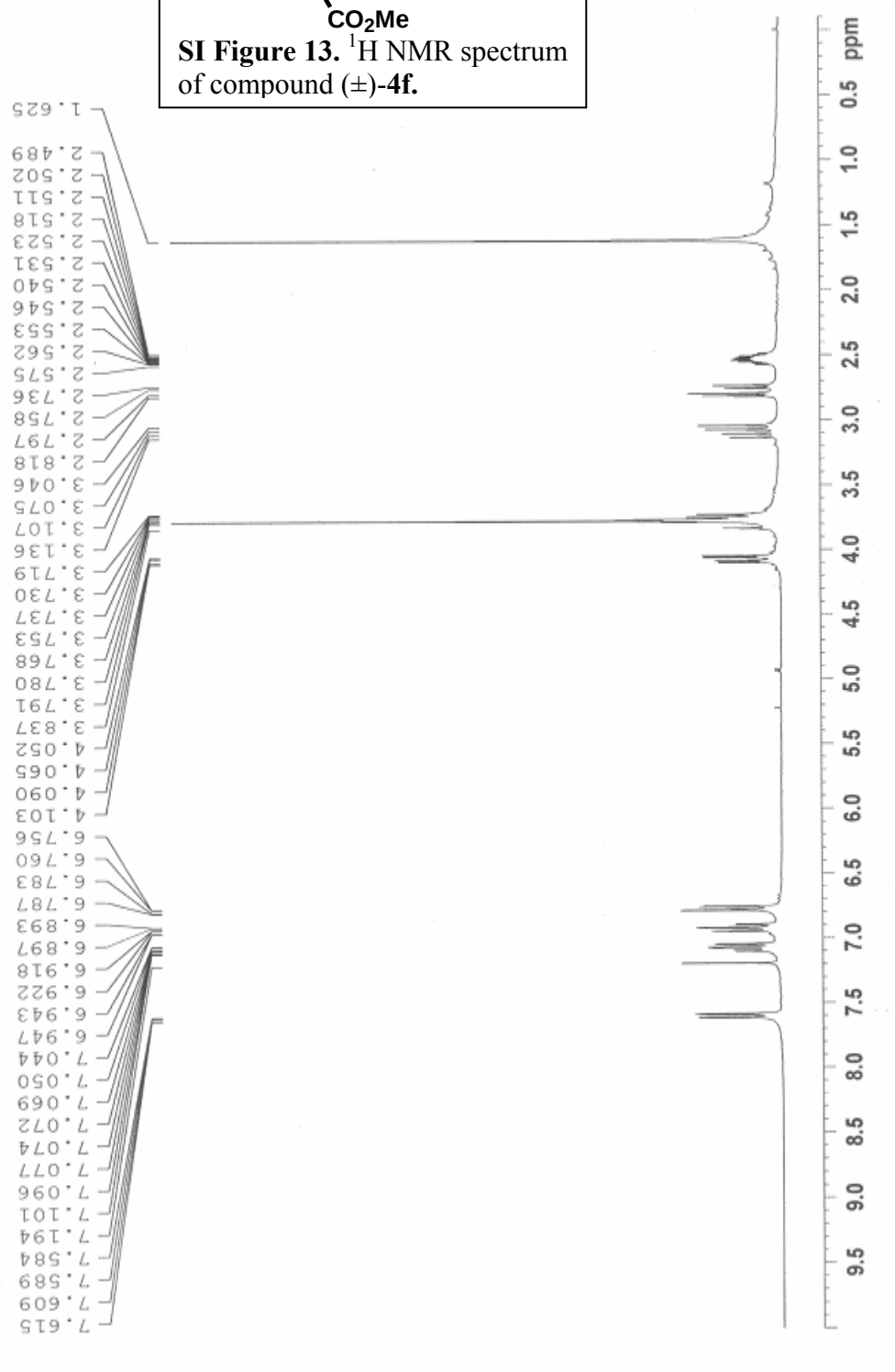


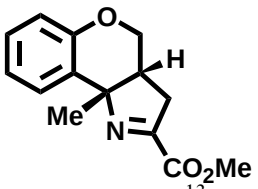
SI Figure 12. ^{13}C NMR spectrum of compound (±)-**4e**.



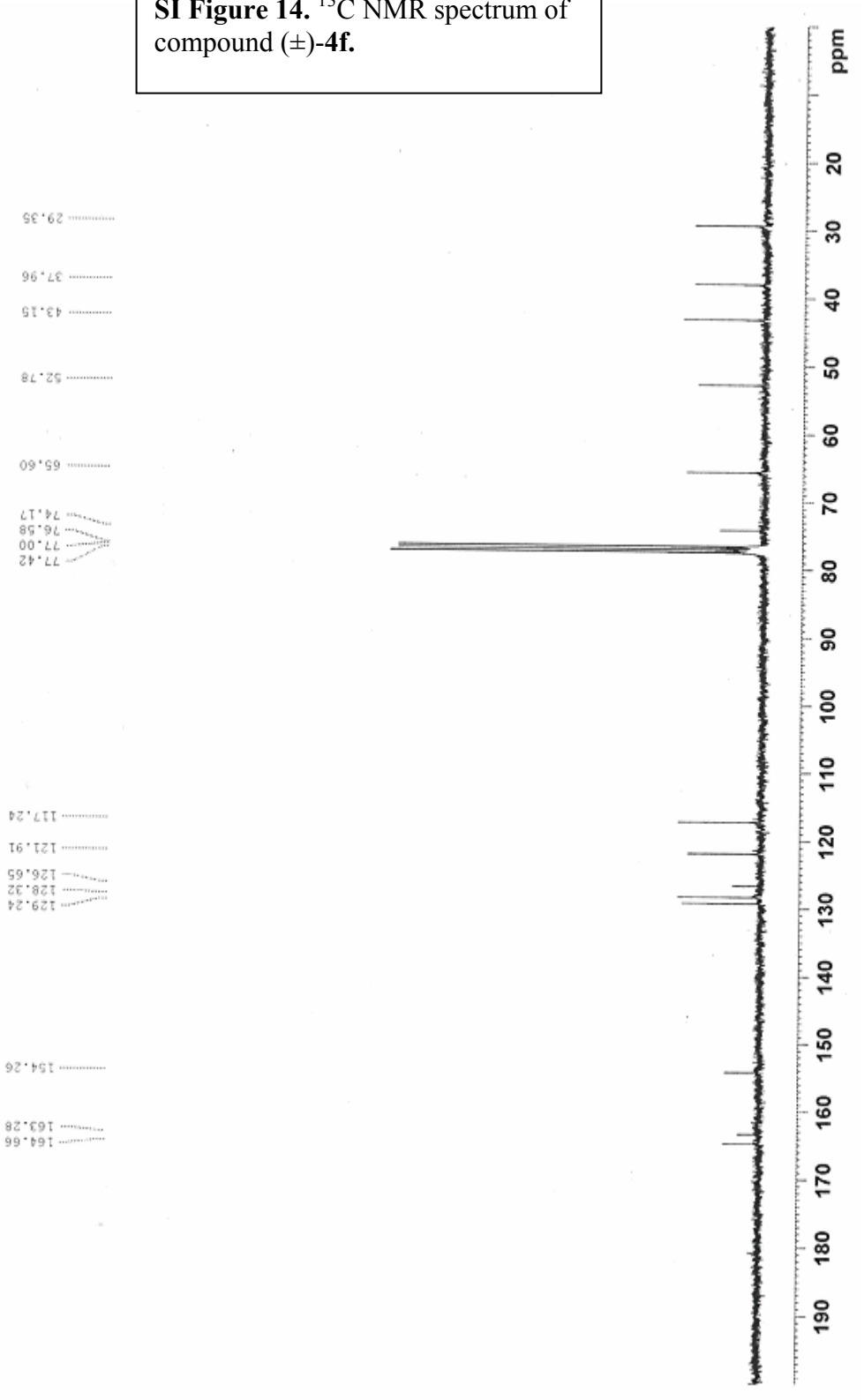


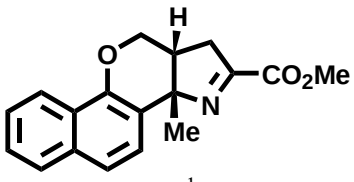
SI Figure 13. ^{1}H NMR spectrum of compound (±)-**4f.**



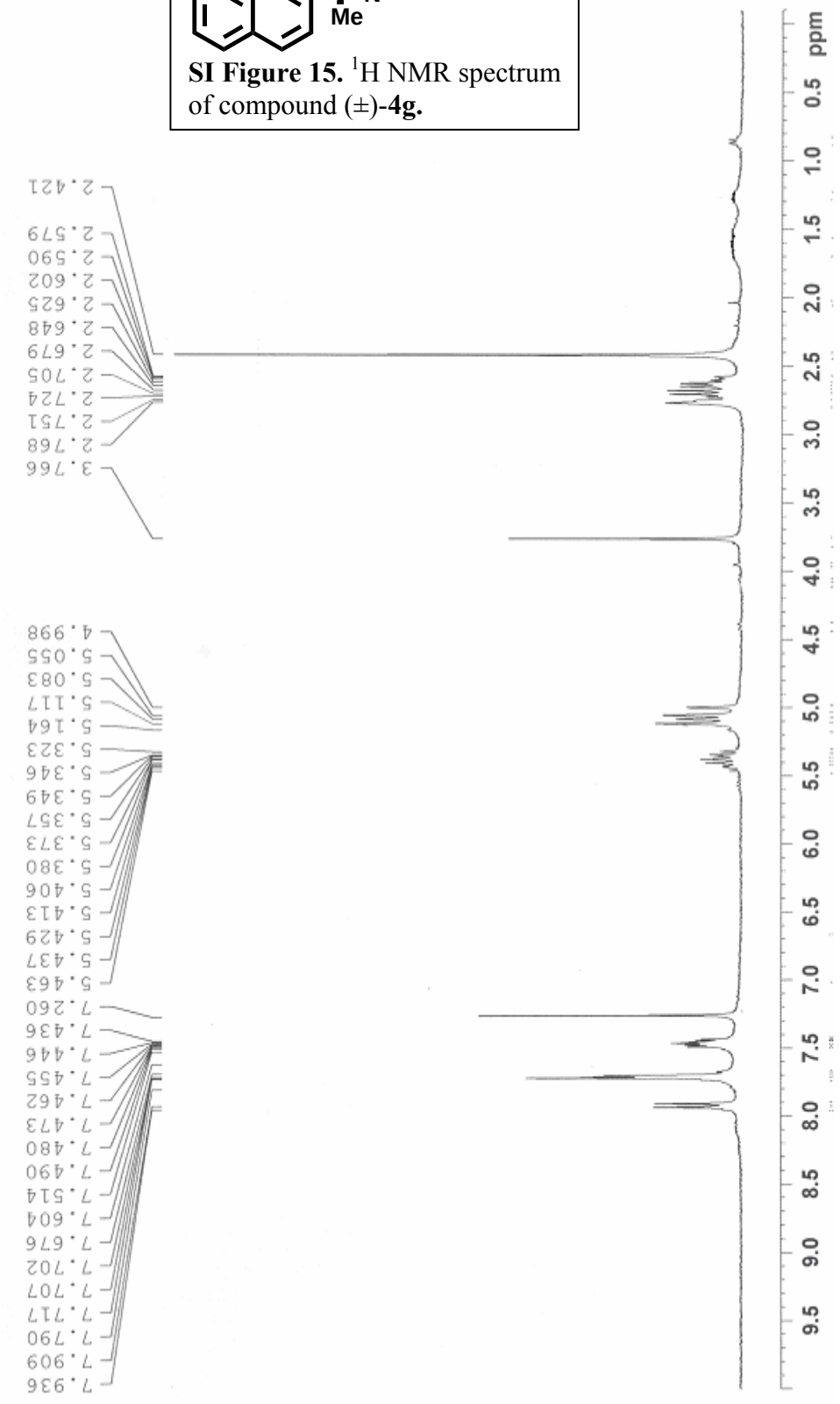


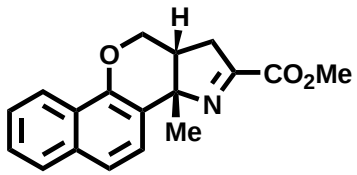
SI Figure 14. ^{13}C NMR spectrum of compound (±)-**4f.**



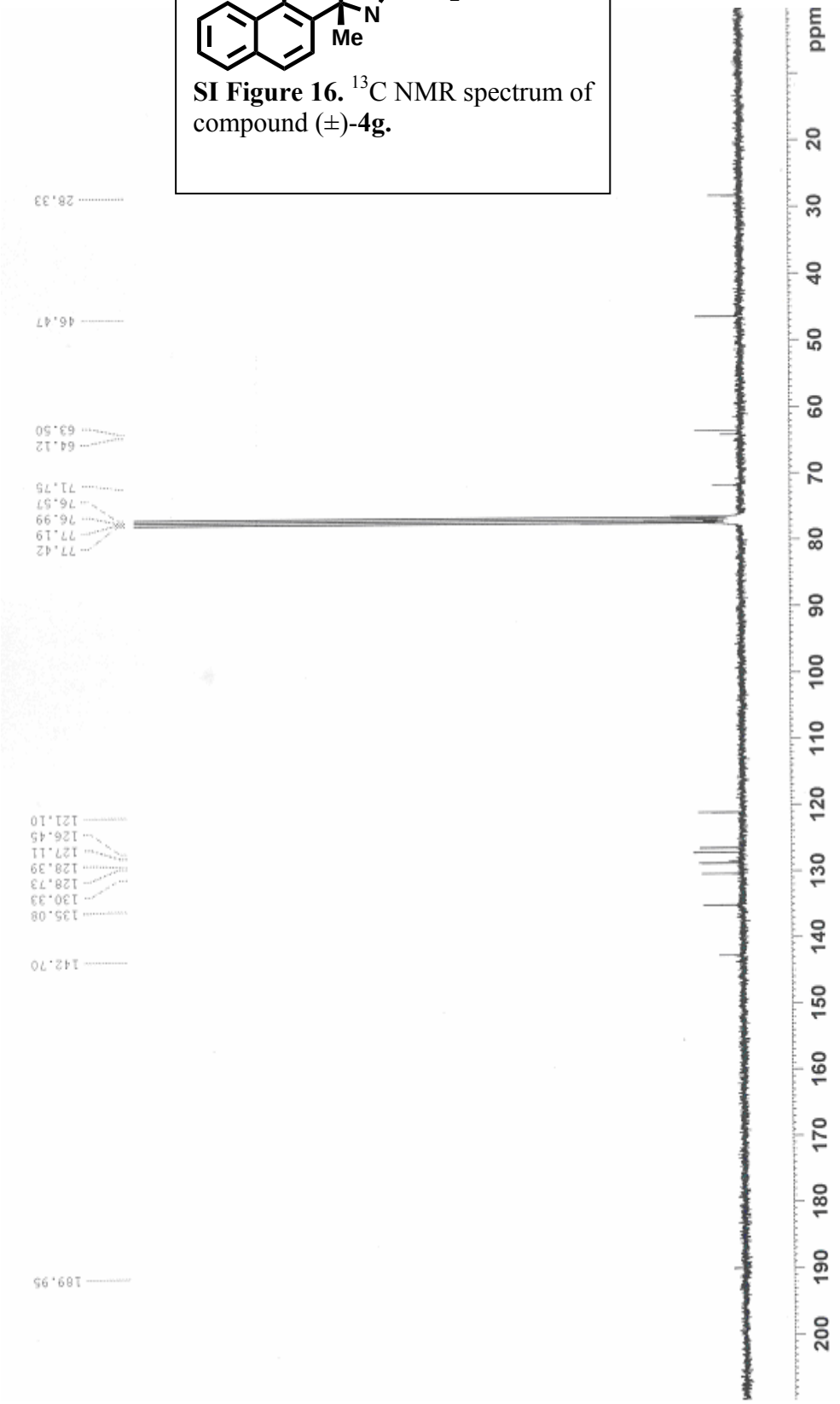


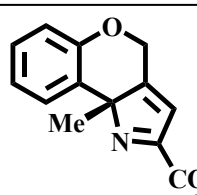
SI Figure 15. ^{1}H NMR spectrum of compound (±)-**4g.**



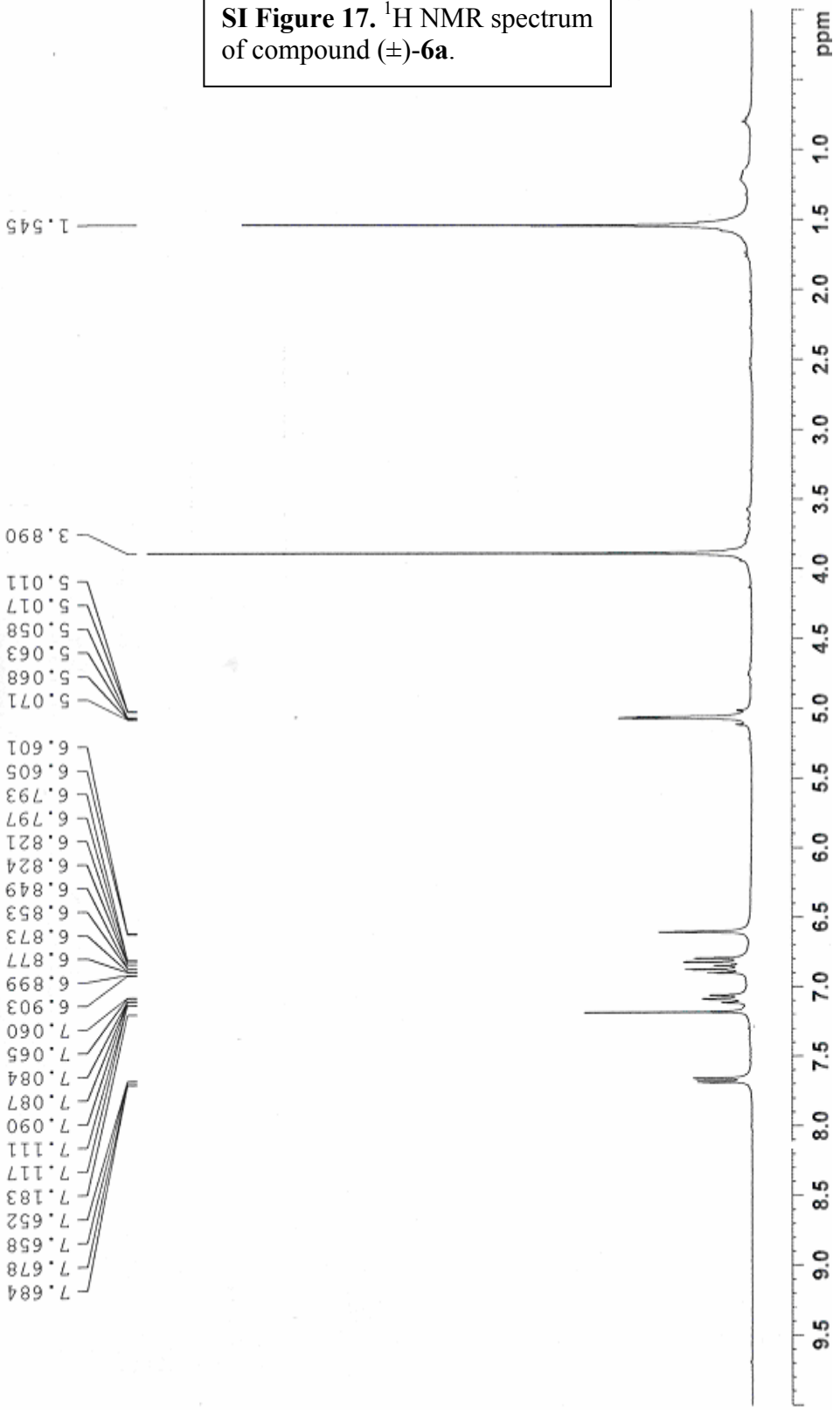


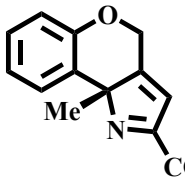
SI Figure 16. ^{13}C NMR spectrum of compound (±)-**4g.**



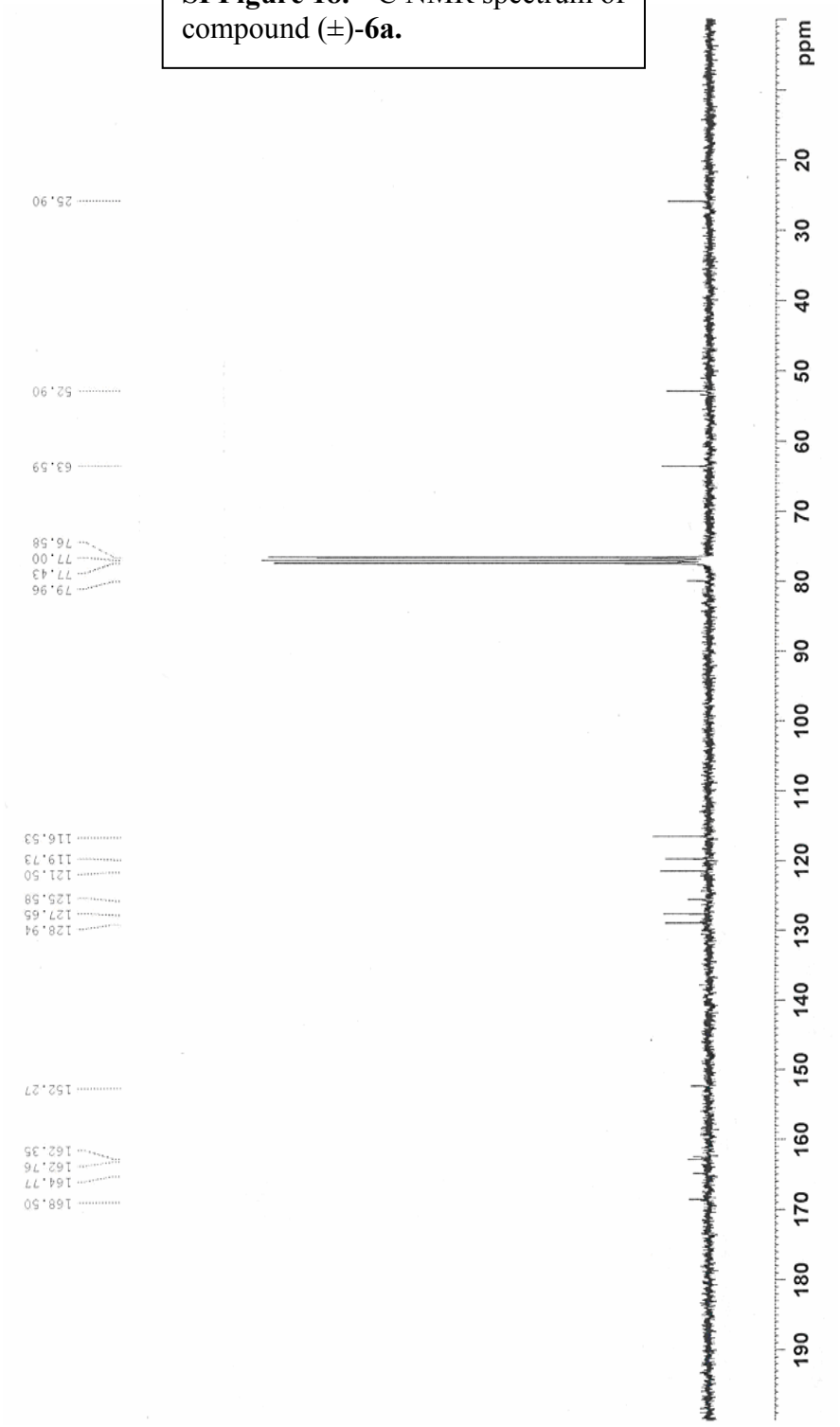


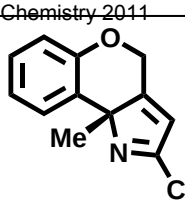
SI Figure 17. ^{1}H NMR spectrum of compound (±)-**6a**.



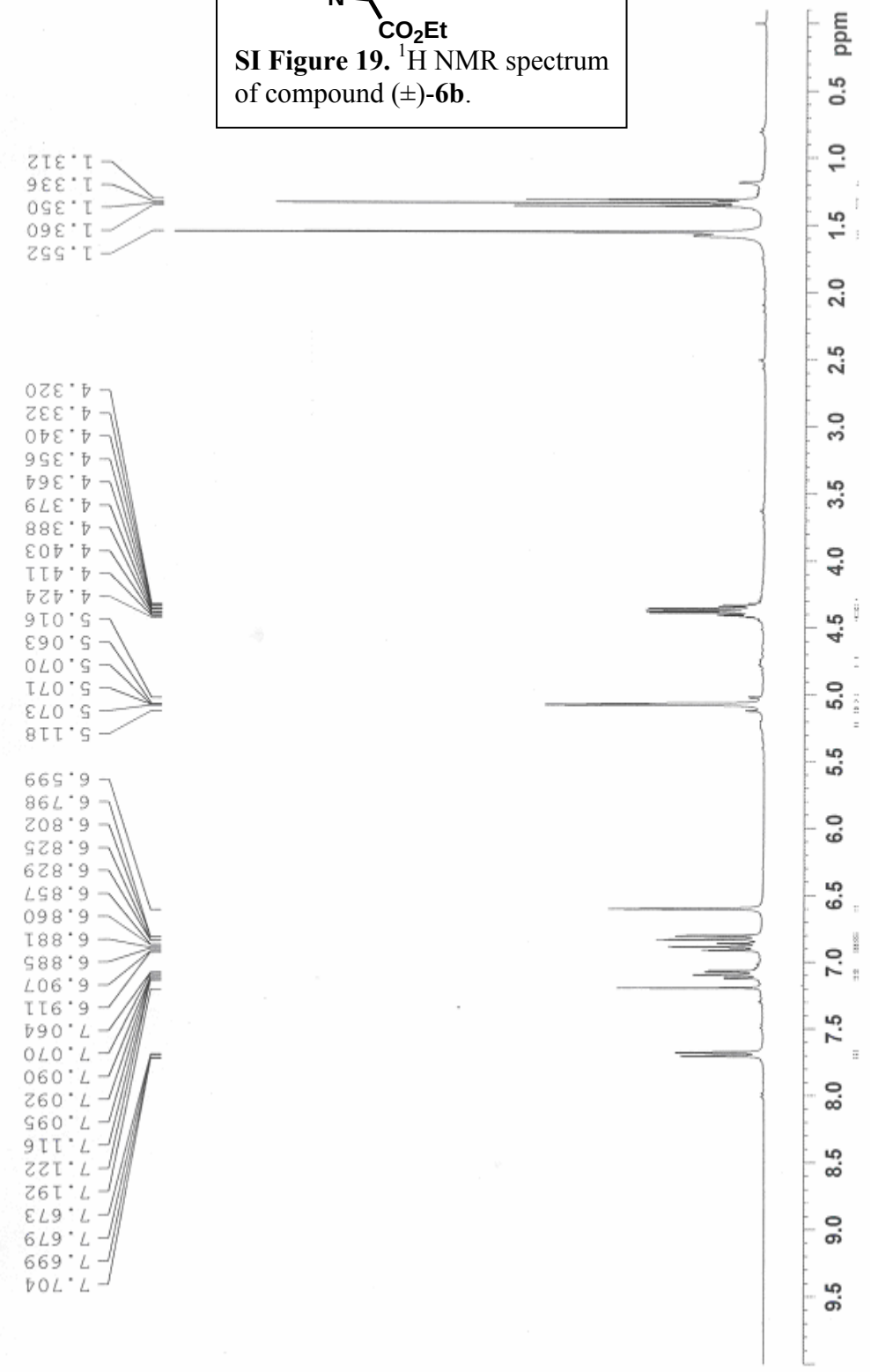


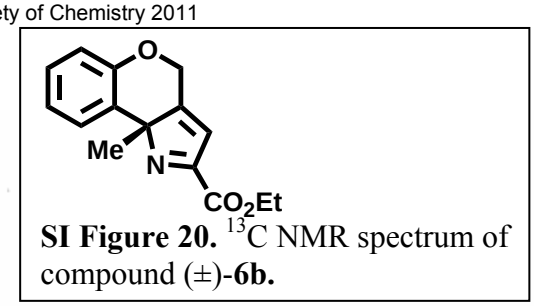
SI Figure 18. ^{13}C NMR spectrum of compound (±)-**6a.**



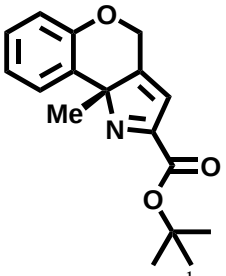


SI Figure 19. ^{1}H NMR spectrum of compound (±)-**6b**.

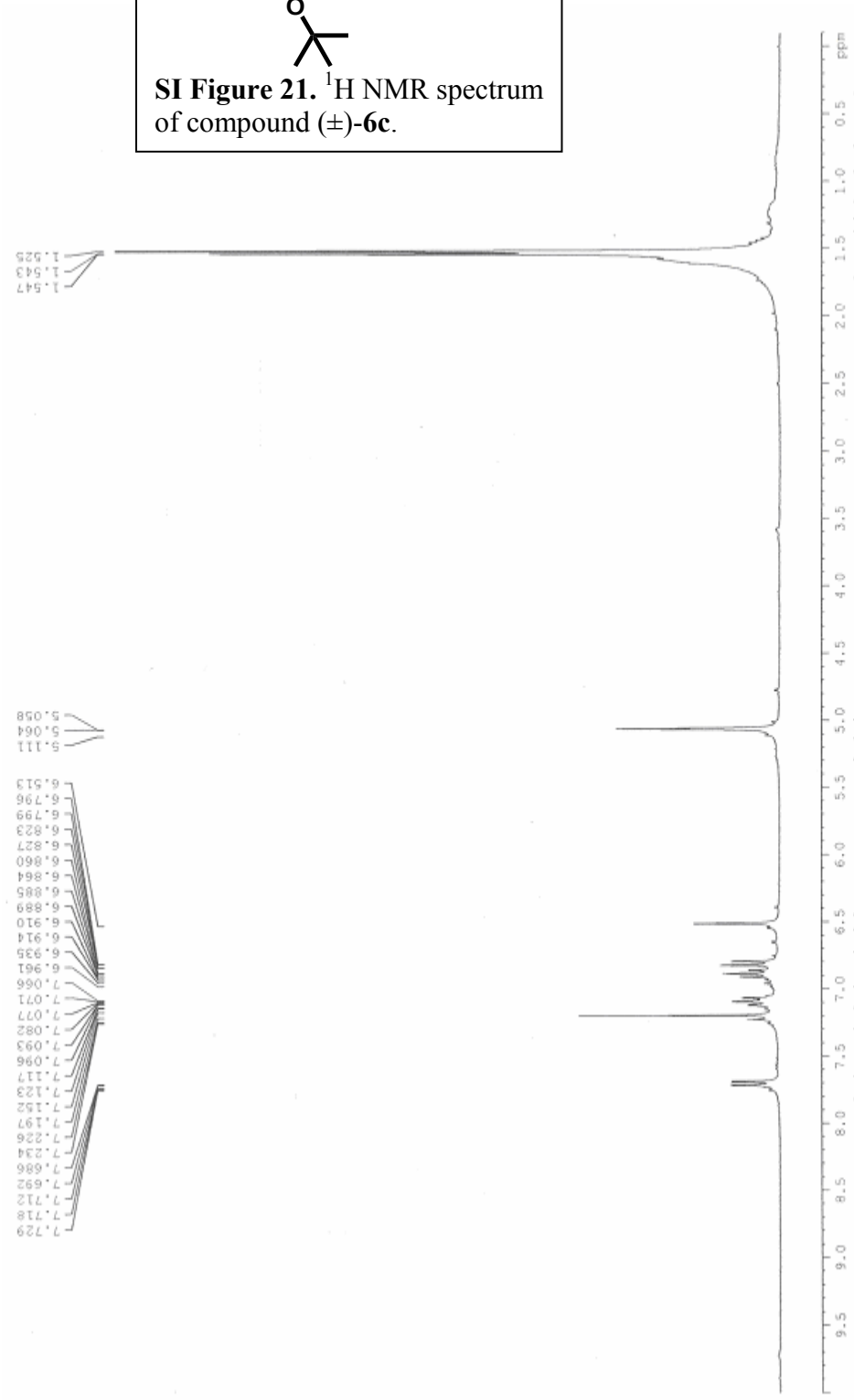


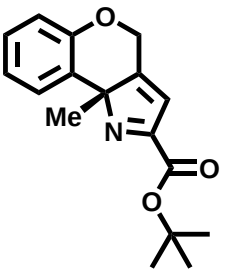


SI Figure 20. ^{13}C NMR spectrum of compound (±)-**6b.**

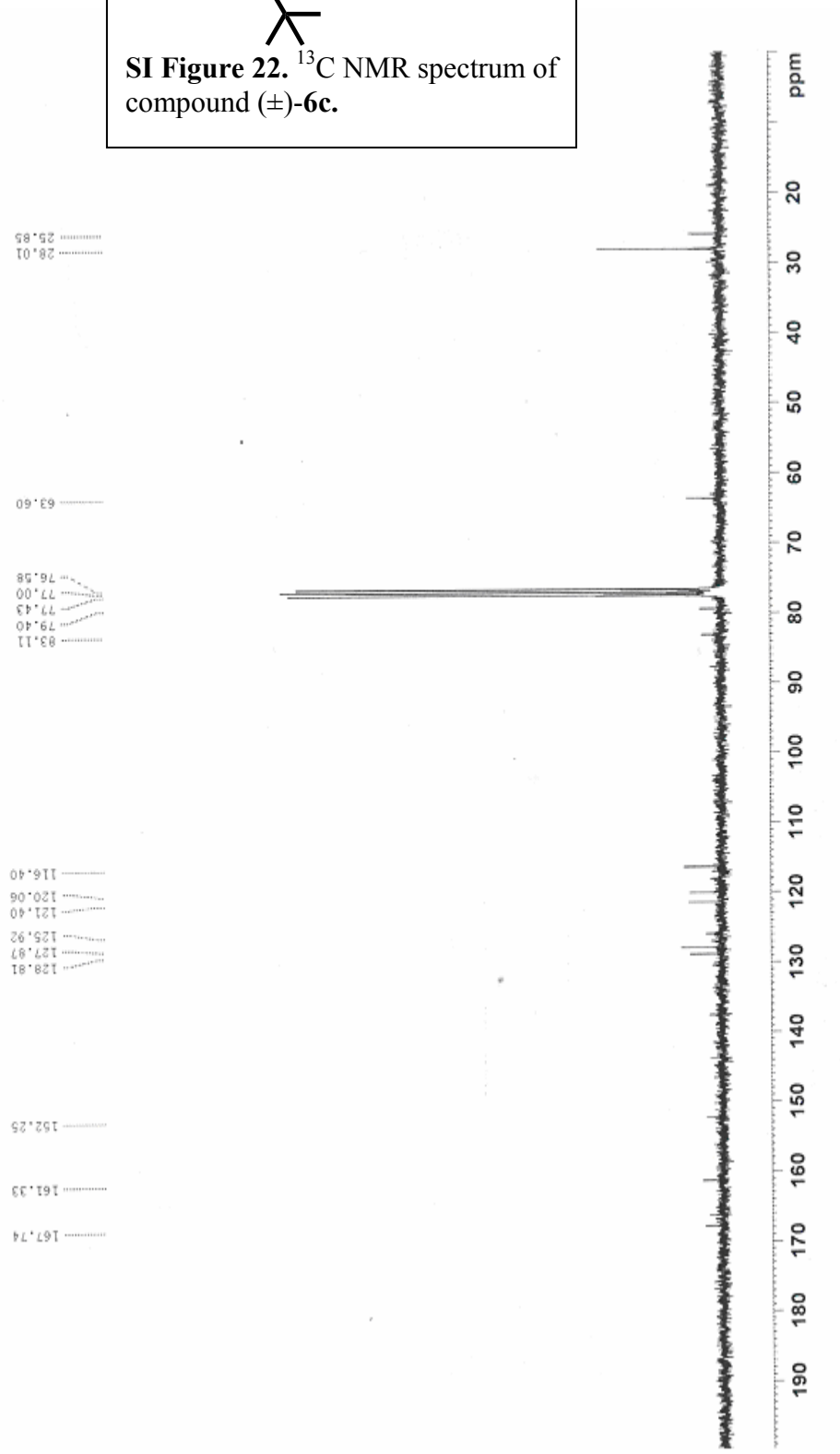


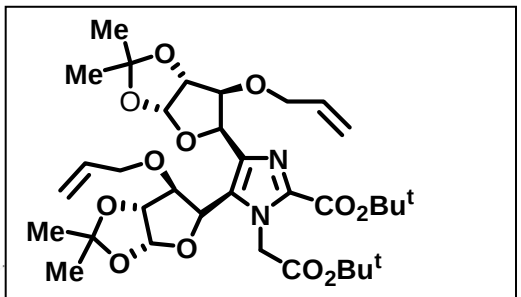
SI Figure 21. ^{1}H NMR spectrum of compound (±)-**6c**.



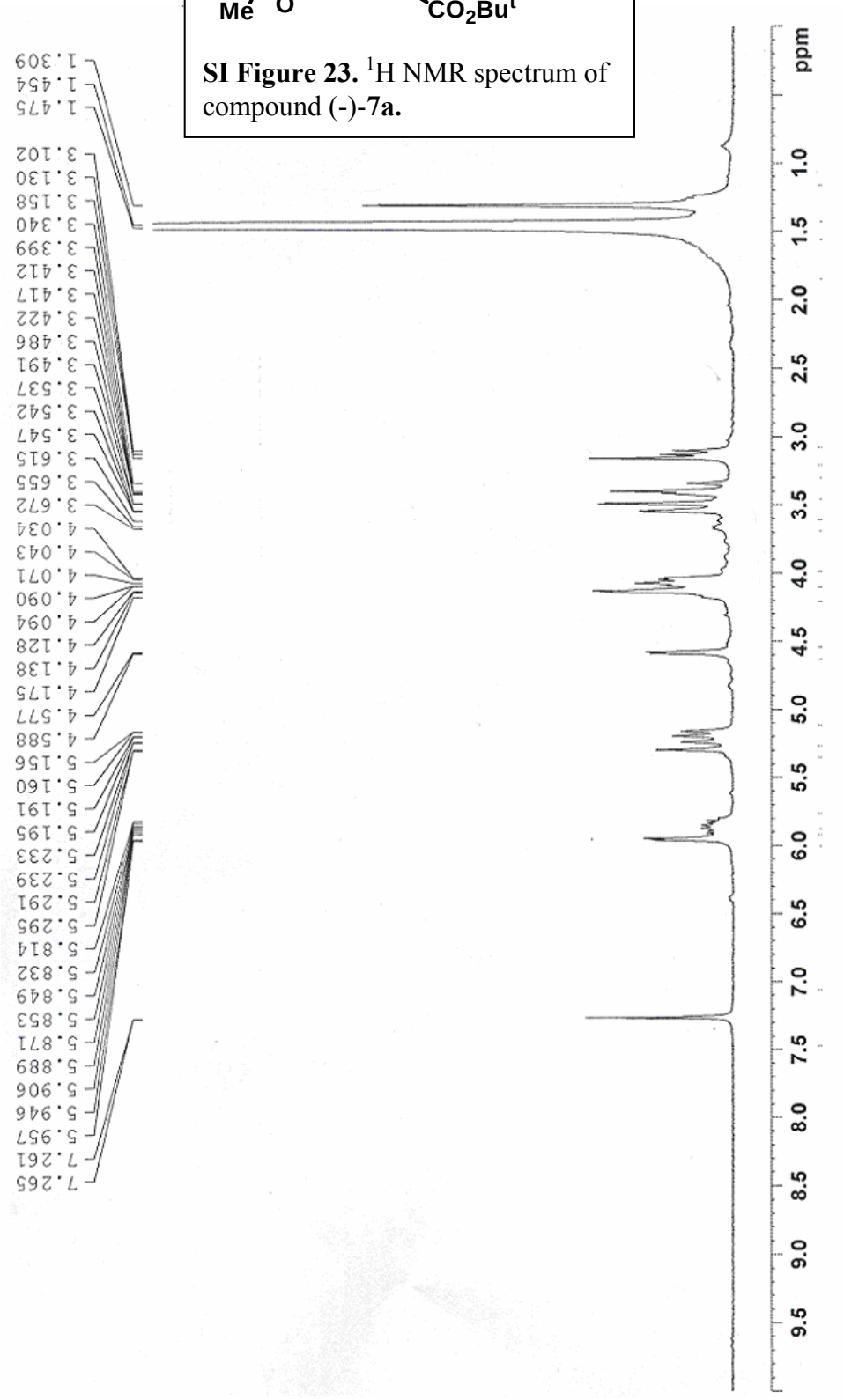


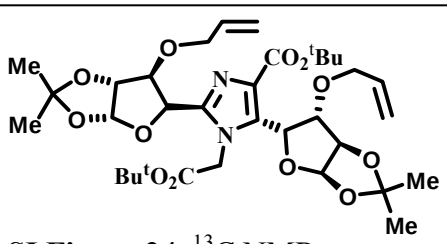
SI Figure 22. ^{13}C NMR spectrum of compound (±)-**6c.**



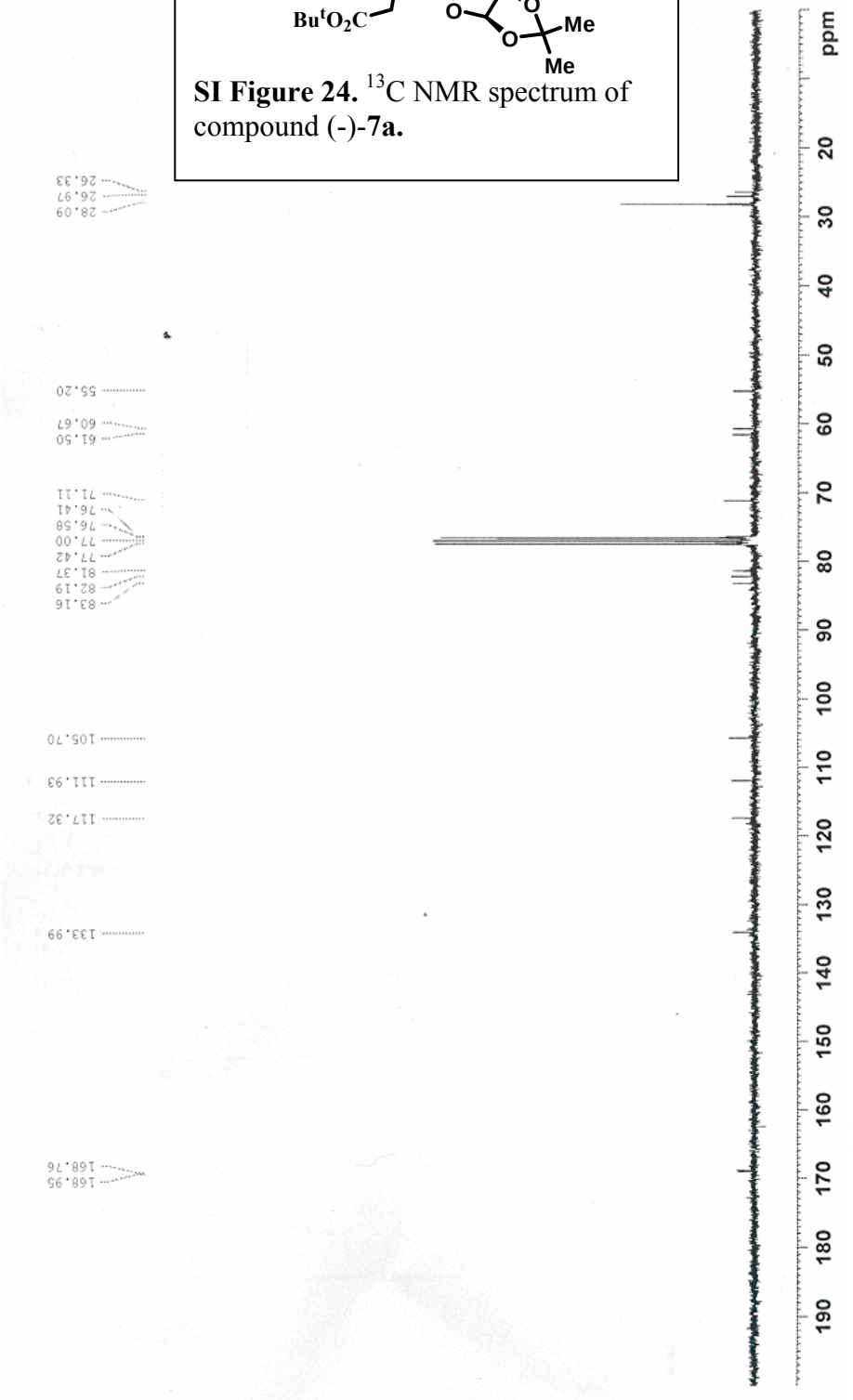


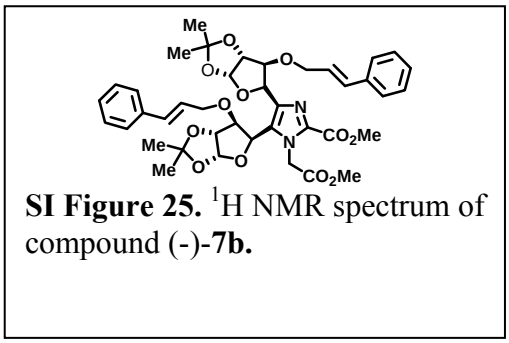
SI Figure 23. ^{1}H NMR spectrum of compound (-)-**7a.**



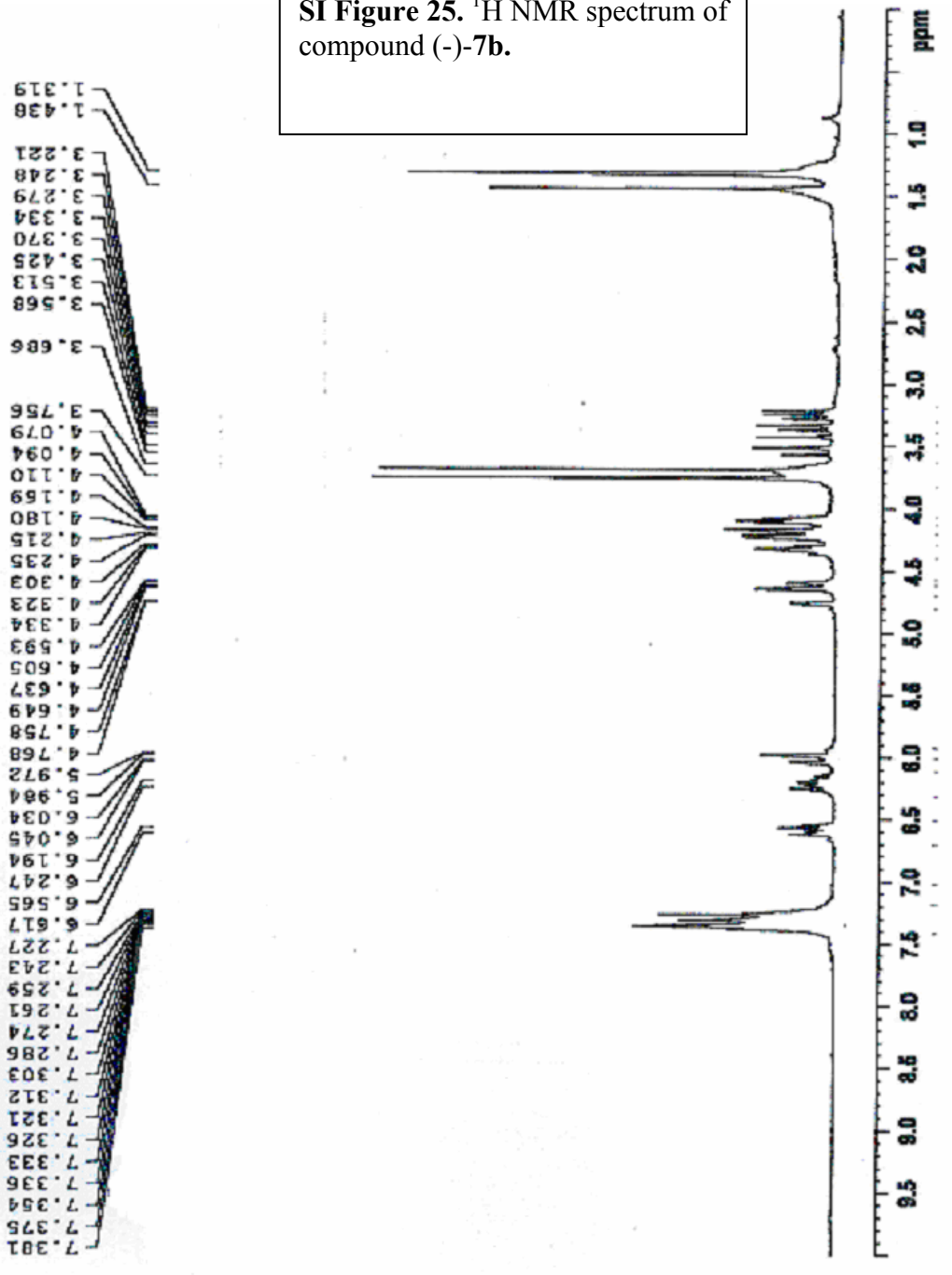


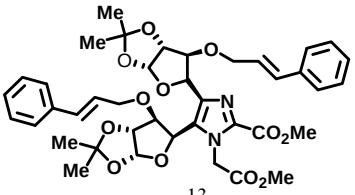
SI Figure 24. ^{13}C NMR spectrum of compound (-)-**7a.**



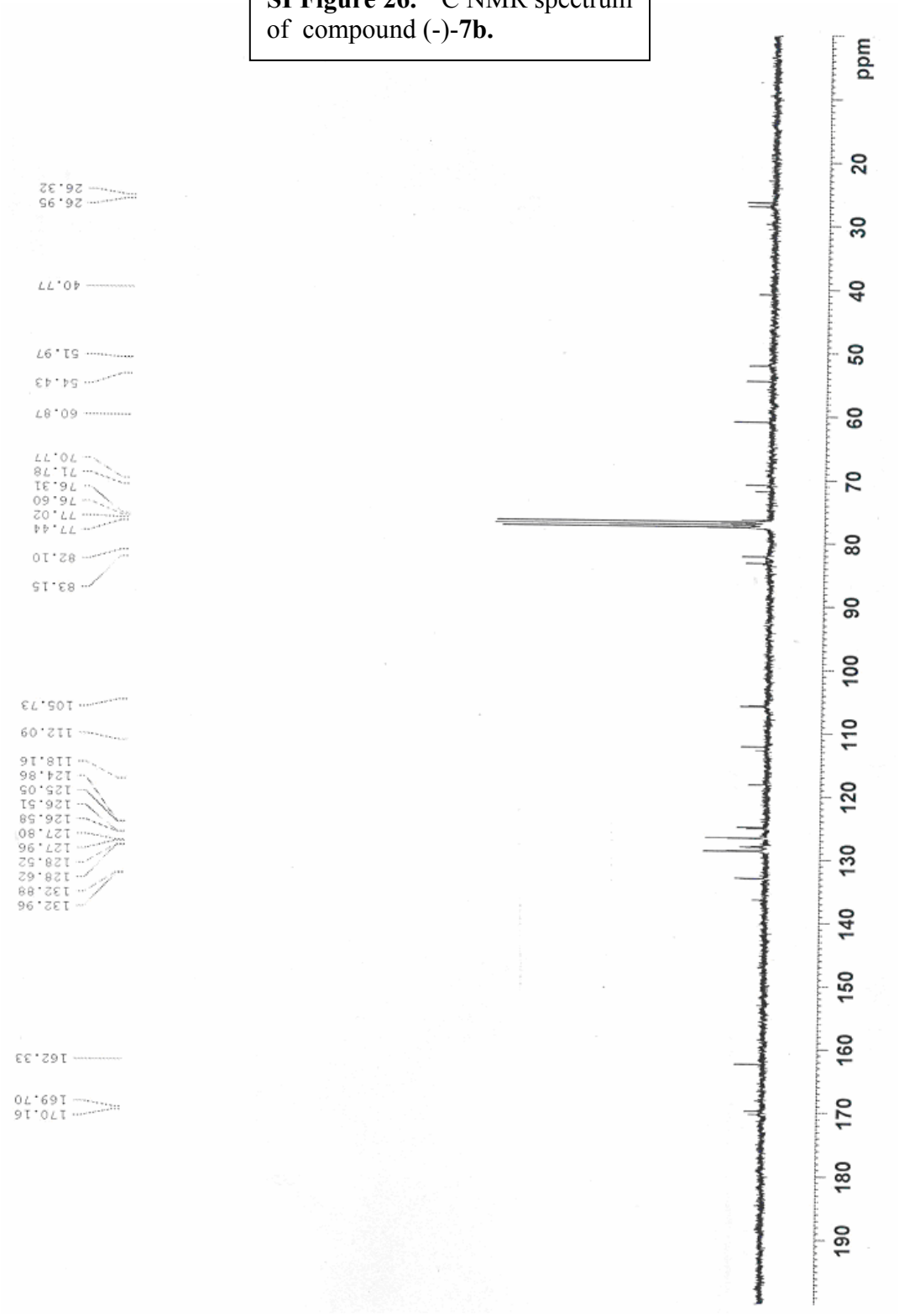


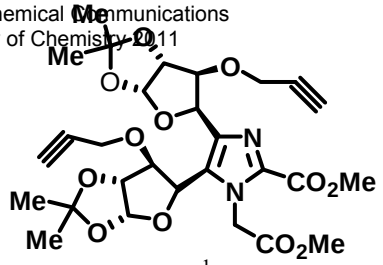
SI Figure 25. ^{1}H NMR spectrum of compound (-)-**7b.**



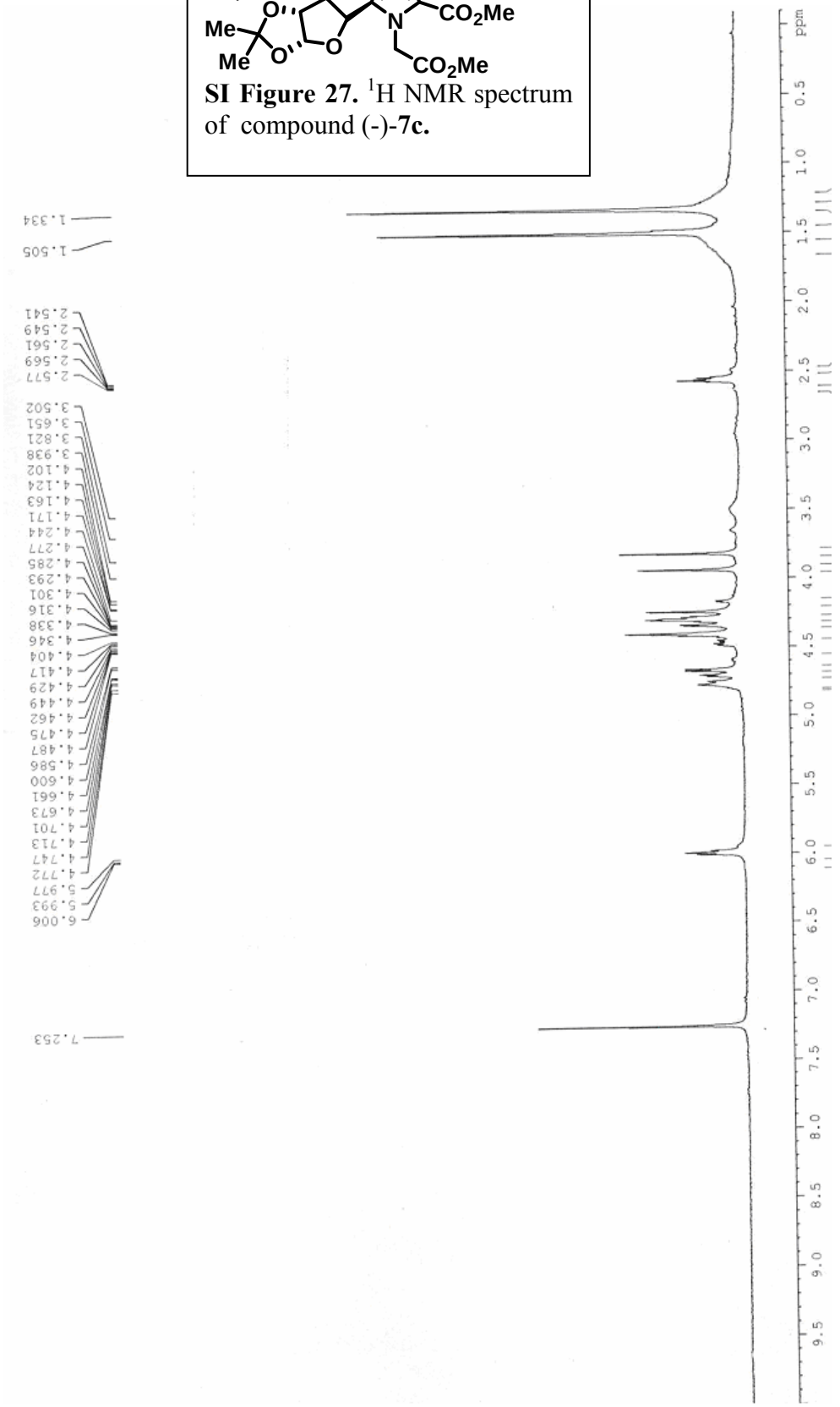


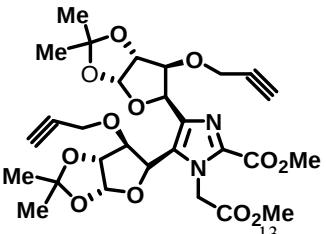
SI Figure 26. ^{13}C NMR spectrum of compound (-)-**7b.**



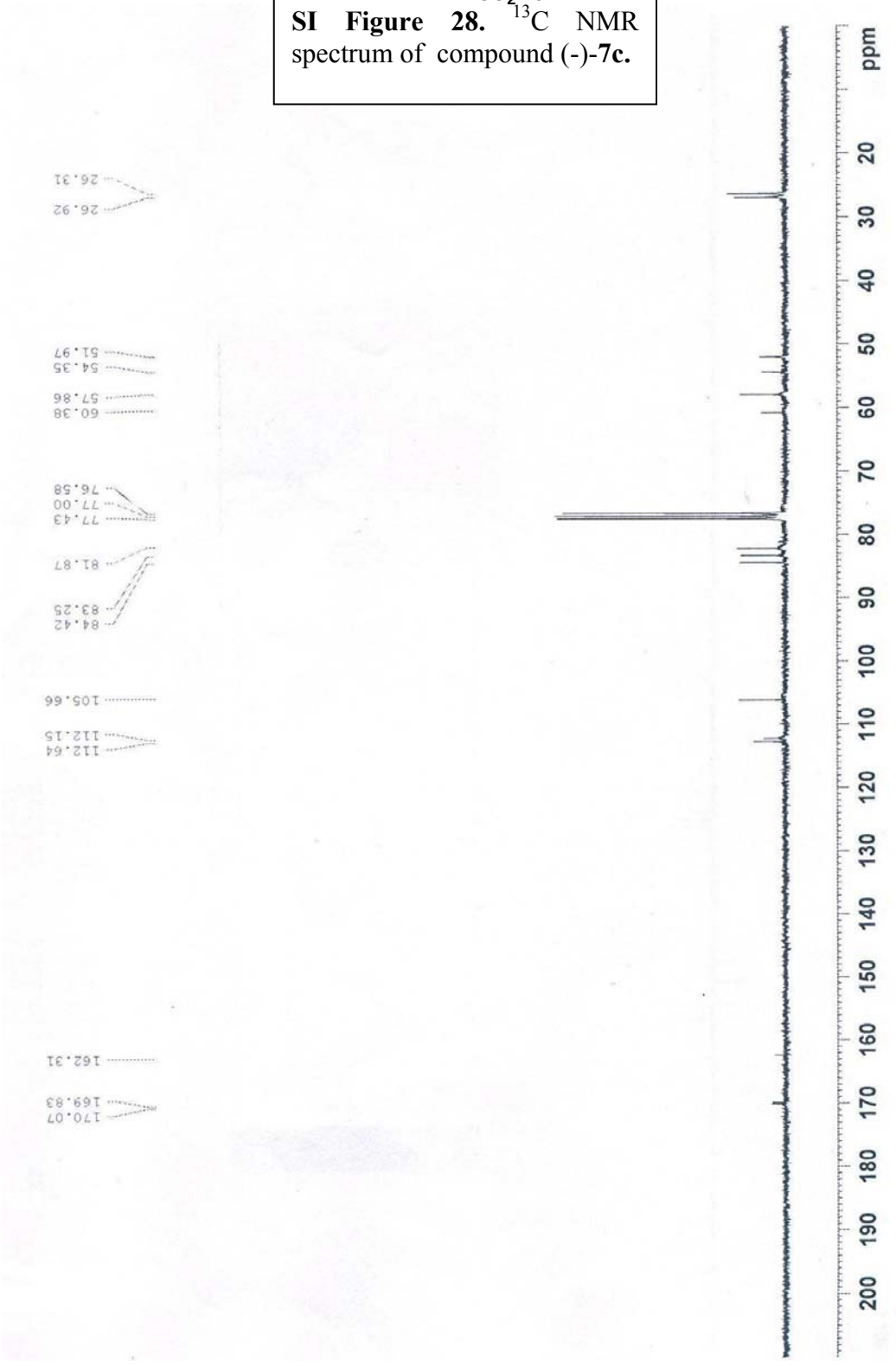


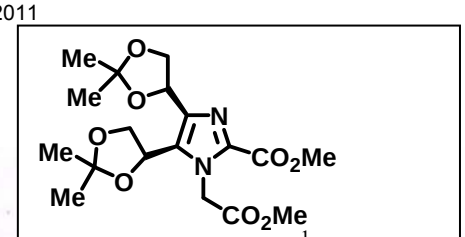
SI Figure 27. ^{1}H NMR spectrum of compound (-)-**7c.**



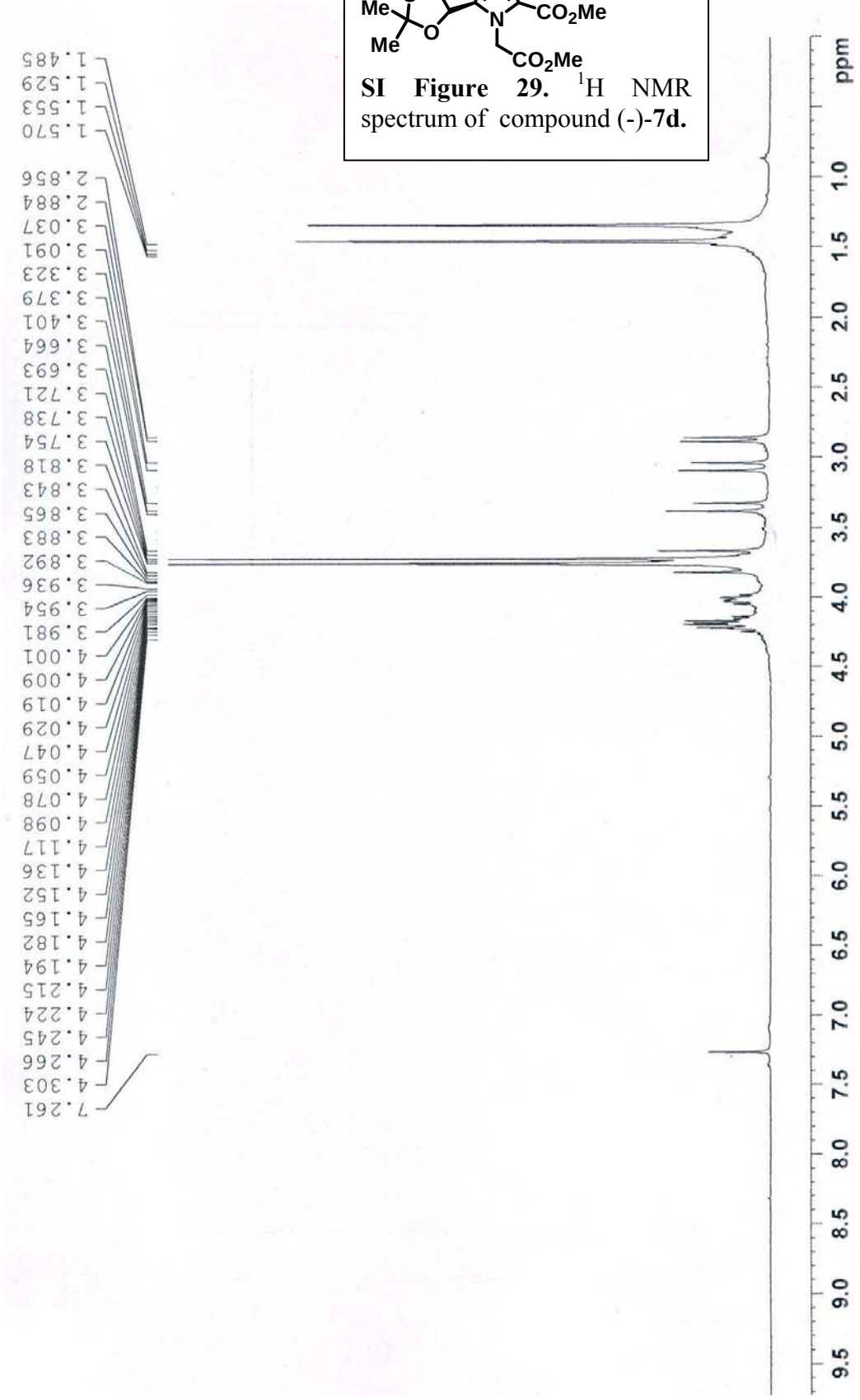


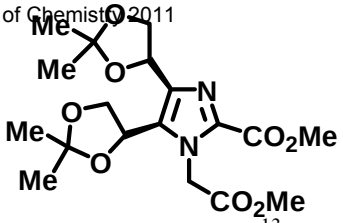
SI Figure 28. ^{13}C NMR spectrum of compound (-)-**7c.**



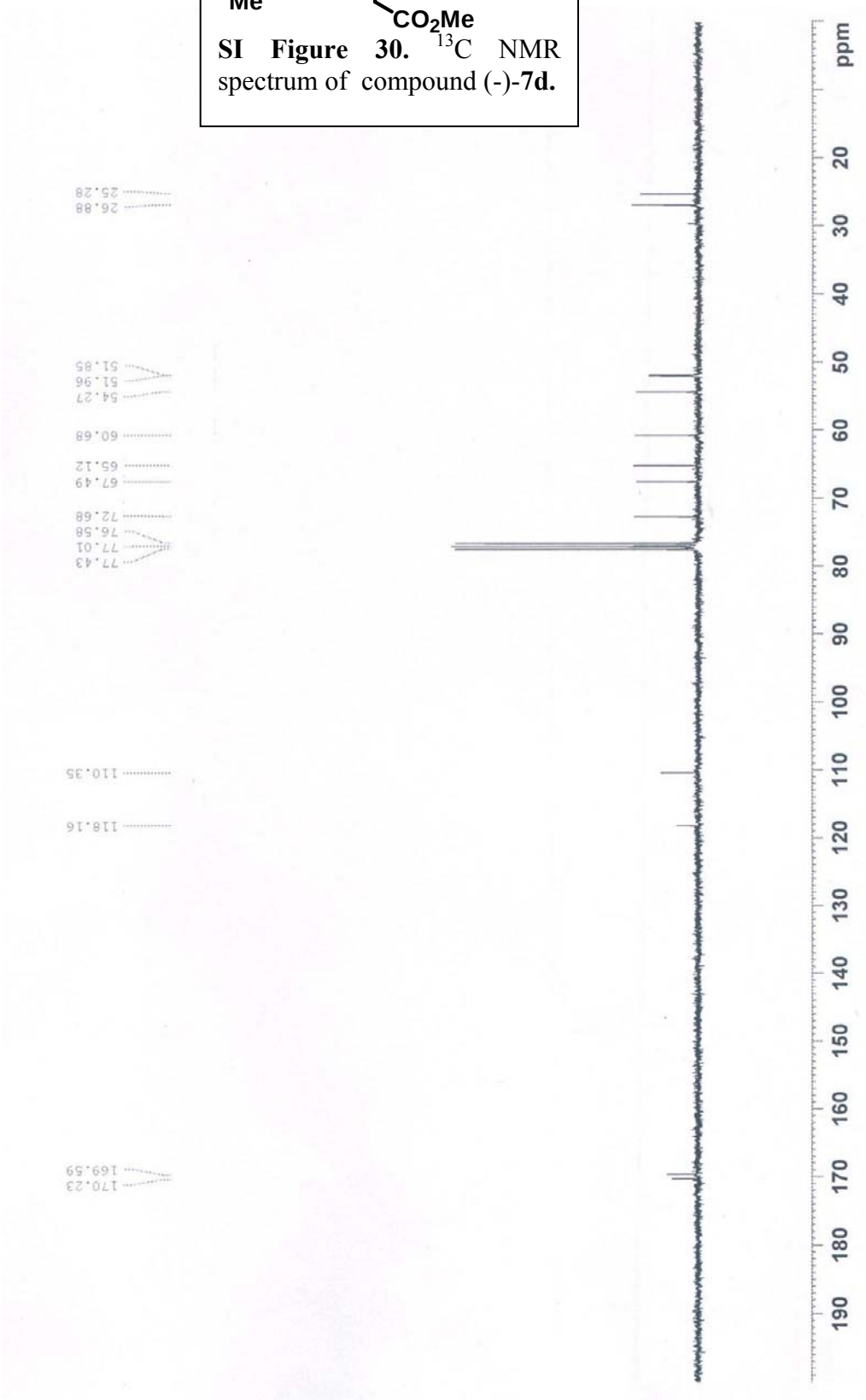


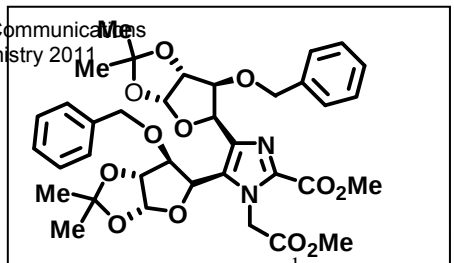
SI Figure 29. ^{1}H NMR spectrum of compound (-)-**7d.**



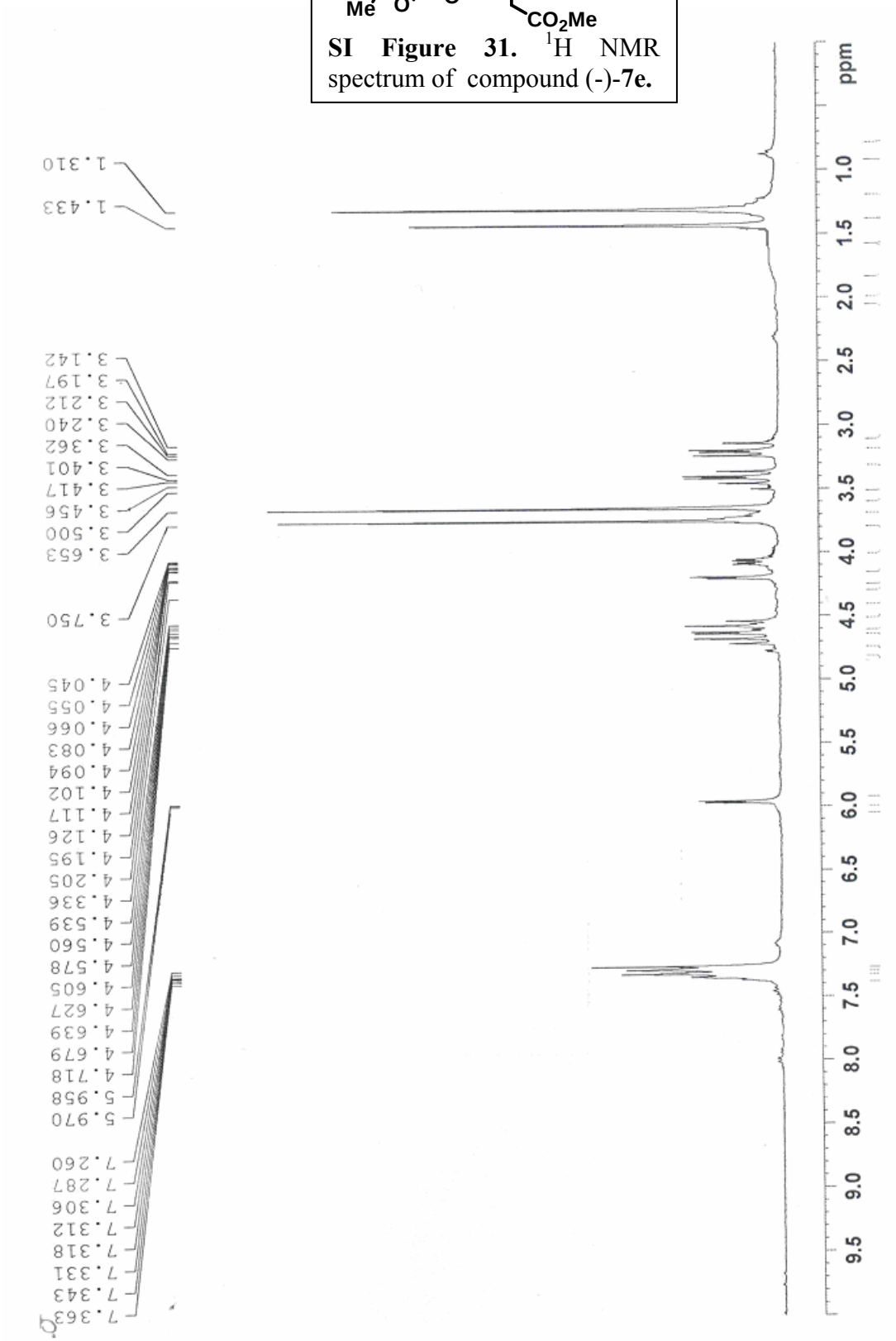


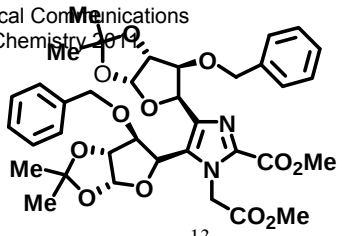
SI Figure 30. ^{13}C NMR spectrum of compound (-)-**7d.**



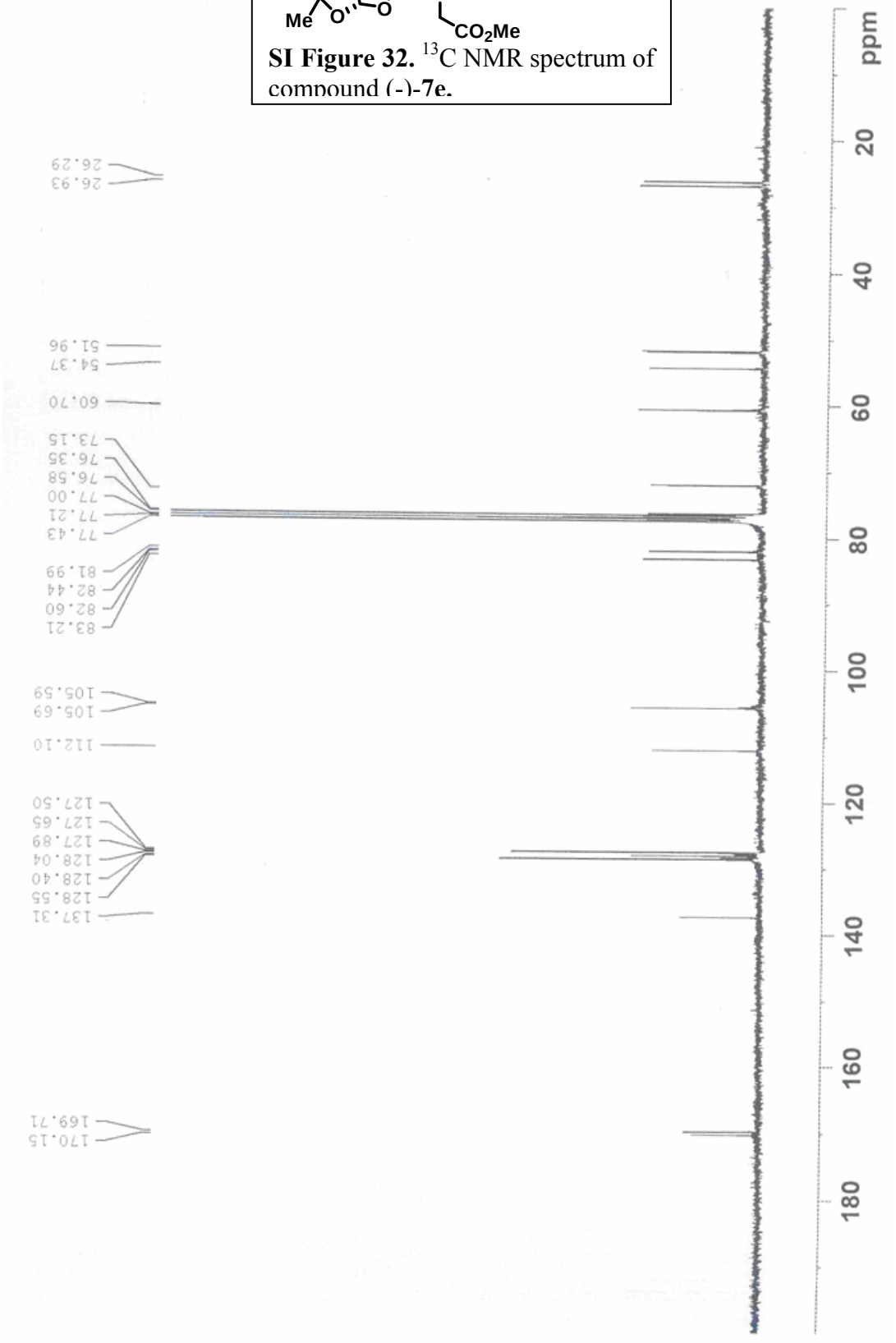


SI Figure 31. ^{1}H NMR spectrum of compound (-)-**7e.**





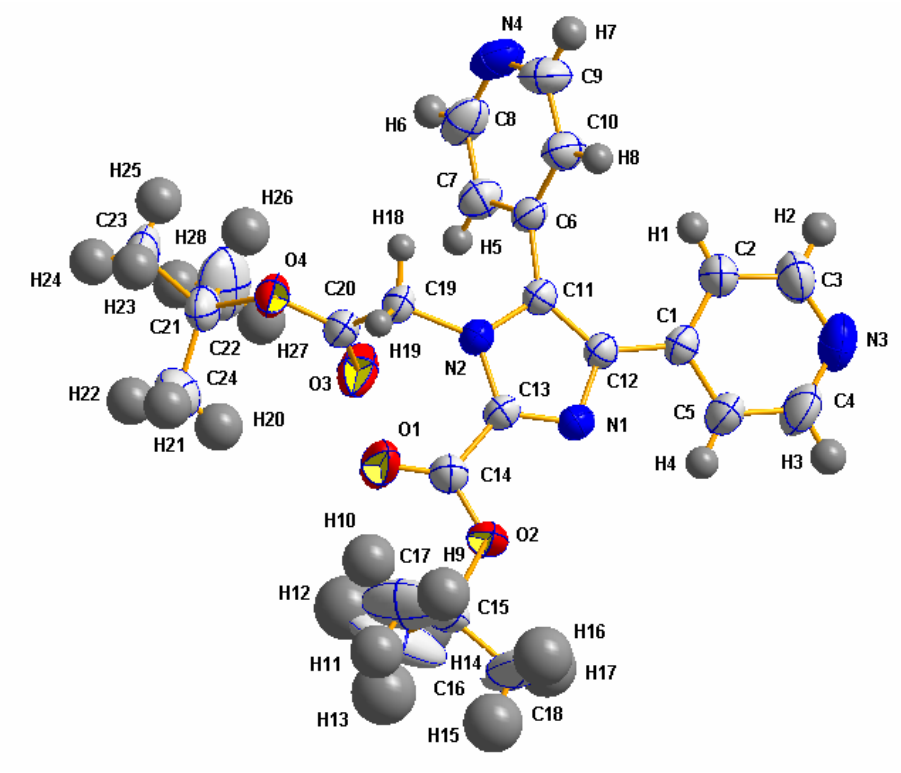
SI Figure 32. ^{13}C NMR spectrum of compound (-)-**7e**.



8. **Summary of data CCDC 773893 (compound 4a)**

. Chemical formula and formula weight (M):	C23 H25 N O3 and 363.44
. Crystal system:	Triclinic
. Unit-cell dimensions (angstrom or pm, degrees) and volume, with esds:	a 8.752(6), b 10.838(8), c 11.416(8), 69.727(9), 85.757(9), 85.893(8), 1011.8(13)
. Temperature:	293 (2)
. Space group symbol:	P-1
. No. of formula units in unit cell (Z):	2
. Number of reflections measured and/or number of independent reflections, Rint:	2537
. Final R values (and whether quoted for all or observed data):	0.0469

9. Single crystal structure of imidazole and summary of data CCDC 790083



. Chemical formula and formula weight (M): C24 H28 N4 O4 and 436.50
. Crystal system: monoclinic
. Unit-cell dimensions (angstrom or pm, degrees) and volume, with esds: a 14.9775(10), b 16.1633(12), c 10.1797(7), 90.00, 105.199(2), 90.00, 2378.2(3)
. Temperature: 296(2)
. Space group symbol: P21/c
. No. of formula units in unit cell (Z): 4
. Number of reflections measured and/or number of independent reflections, Rint: 4990
. Final R values (and whether quoted for all or observed data): 0.064