Supporting Information

Photocatalytic Generation of Nitrenes for Rapid Diaziridination

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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.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. Reportedmelting pointsare 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) in thin film. HR-MS data were acquired by electron spray ionization technique on a Q-tof-micro quadriple mass spectrophotometer (Bruker). Optical rotation of the chiral compounds was measured in a polarimeter using standard 10 cm quartz cell in sodium-D lamp at amBient temperature.Electronic absorption spectrum were recorded using a Hitachi U-3501 spectrophotometer. XPS analysis with the reaction mixture were performed in a JEOL instrument.

2. **General procedure for the synthesis of diaziridines**

A mixture of amine (**1/3**, 4 mmol), 1,2-diol (**2/4**, 1 mmol) and rose bengal (1 mol %) were taken in a 25 mL RB flask under blue LED light (5 W, λ_{max} = 475 nm), and 5 mL dichloromethane was added under cold condition. After stirring for 5 minutes iodobenzene diacetate (4 mmol) was added portion wise. After addition was complete, the ice bath was removed in order to allow the reaction mixture to achieve room temperature. The progress of the reaction was monitored by performing thin layer chromatography (TLC). After the completion of the reaction, the solvent was removed in rotary evaporator under reduced pressure. Then the reaction mixture was extracted with ethyl acetate (25 mL) and the combined organic layer was washed successively with saturated sodium bicarbonate solution (1 x 10 mL) and brine (1 x 10 mL). It was then dried over anhydrous Na_2SO_4, filtered and evaporated in a rotary evaporator under reduced pressure at room temperature. The crude mass was column chromatographed with ~ 5% ethyl acetate- petroleum ether to get the corresponding product with considerable yield. Thus, the reaction with benzylamine (**1a**, 2.0 mmol, 214 mg), 1,2-ethanediol (**2**, 0.5 mmol, 31 mg) and $PhI(OAc)_2$ (2.0 mmol, 645 mg) afforded 1,2-dibenzyldiaziridine (**6a**) after purification by column chromatography on silica gel (60-120 mesh) with ethyl acetate-petroleum ether (1:25, v/v) as an eluent in an yield of 95% (213 mg, 0.95 mmol). The synthesized diaziridines (**6a-6l**, **7a-7h** and **8a-8i**) were characterized by means of NMR (^{1}H and ^{13}C), FT-IR, melting point (solid compounds only), mass (HR-MS) spectral analyses and X-ray diffractometric analysis of **6d**.

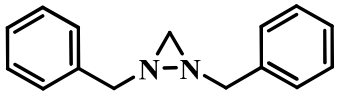
3. **Detailed Synthetic Method for 1,2-Dibenzyldiaziridine (6a):**

A mixture of benzylamine (**1a**, 4.0 mmol, 428 mg), 1,2-ethanediol (**2**, 1.0 mmol, 62 mg) and rose bengal (1 mol %) were taken in a 25 mL RB containing 10 mL dichloromethane. It was then irradiated with blue LED light (5 W, λ_{max} = 475 nm) under cold condition. After stirring for 5 minutes iodobenzene diacetate (4 mmol, 1290 mg) was added portion wise. After addition was complete, the ice bath was removed in order to allow the reaction to achieve room temperature. The progress of the reaction was monitored by performing thin layer chromatography (TLC) and it took only 20 minutes to complete. After the completion of the reaction, the solvent was removed in a rotary evaporator under reduced pressure. The post reaction mixture was extracted with ethyl acetate (2x25 mL) and the combined organic layer was washed successively with saturated aqueous sodium bicarbonate solution (1 x 10 mL) and brine (1 x 10 mL). It was then dried over anhydrous Na_2SO_4, filtered and evaporated in a rotary evaporator under

reduced pressure at room temperature. The crude mass was column chromatographed on silica gel (60-120 mesh) with ethyl acetate-hexane (1:25, v/v) and the desired 1,2-dibenzyldiaziridine (**6a**) was obtained with an yield of 95% (426 mg, 1.90 mmol). The synthesized 1,2-dibenzyldiaziridine (**6a**) was characterized by means of NMR (^{1}H and ^{13}C), FT-IR and mass (HR-MS) spectral analyses.

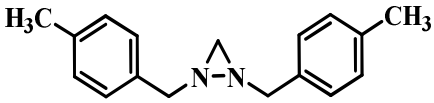
4. **Characterization data of 1,2 di-substituted diaziridine (6a-l)**

4.1. **1,2-Dibenzyldiaziridine (6a)**



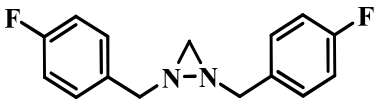
Yield: 95% (213 mg, 0.95 mmol).
Characteristic: Colourless oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.69 (2H, s), 3.49 (2H, d, *J* = 12.9 Hz), 3.66 (2H, d, *J* = 13.2 Hz), 7.23-7.31 (10H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 56.2, 64.8, 127.2, 128.3, 128.6, 137.6.
FT-IR (neat, cm^{-1}): 1224, 1268, 1360, 1445, 1520, 1675, 1714, 2451, 2553.
HR-MS (*m*/*z*) for $C_{15}H_{16}N_2$ (M^+): Calculated 224.1313, found 224.1317.

4.2. **1,2-Bis(4-methylbenzyl)diaziridine (6b)**



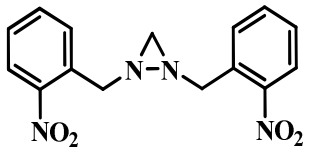
Yield: 92% (232 mg, 0.92 mmol).
Characteristic: Colourless oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.36 (6H, s), 2.68 (2H, s), 3.43 (2H, d, *J* = 12.6 Hz), 3.67 (2H, d, *J* = 12.9 Hz), 7.12 (4H, d, *J* = 8.1 Hz), 7.21 (4H, d, *J* = 7.8 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 21.2, 56.1, 64.6, 128.6, 129.0, 134.5, 136.8.
FT-IR (neat, cm^{-1}): 1227, 1272, 1361, 1447, 1521, 1678, 1715, 2096, 2446, 2552.
HR-MS (m/z) for $C_{17}H_{20}N_2$ (M^+): Calculated 252.1626, found 252.1625.

4.3.**1,2-Bis(4-fluorobenzyl)diaziridine (6c)**



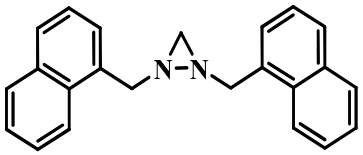
Yield: 90% (235 mg, 0.90 mmol).
Characteristic: Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.59 (2H, s), 3.28 (2H, d, *J* = 13.2 Hz), 3.46 (2H, d, *J* = 12.9 Hz), 6.80-6.85 (4H, m), 7.08-7.16 (4H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 56.1, 64.1, 114.9, 115.1, 130.2, 130.3, 133.4, 160.5, 163.8.
FT-IR (neat, cm^{-1}): 1219, 1268, 1361, 1437, 1523, 1676, 1711, 2093, 2443, 2552.
HR-MS (m/z) for $C_{15}H_{14}F_2N_2$ (M^+): Calculated 260.1125, found260.1127.

4.4. **1,2-Bis(2-nitrobenzyl)diaziridine (6d)**



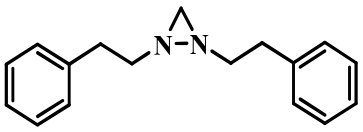
Yield: 92% (289 mg, 0.92 mmol).
Characteristic: Yellow solid.
Melting point: 137 ˚C
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.73 (2H, s), 3.39 (2H, d, *J* = 15.0 Hz), 4.21 (2H, d, *J* = 15.0 Hz), 7.19-7.27 (2H, m), 7.35 (2H, t, *J* = 7.5 Hz), 7.43 (2H, d, *J* = 7.5 Hz), 7.75 (2H, d, *J* = 8.1 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 56.7, 61.0, 124.3, 127.9, 130.9, 132.8, 133.0, 148.5.
FT-IR (KBr, cm^{-1}): 1264, 1354, 1439, 1536, 1611, 1712, 1745, 2279, 2521.
HR-MS (m/z) for $C_{15}H_{14}N_4O_4$ (M^+): Calculated 314.1015, found314.1016.

4.5. **1,2-Bis(naphthalen-1-ylmethyl)diaziridine (6e)**



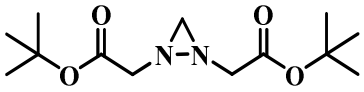
Yield: 95% (308 mg, 0.95 mmol).
Characteristic: Brown oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.73 (2H, s), 3.79 (2H, d, *J* = 13.5 Hz), 4.06 (2H, d, *J* = 13.5 Hz), 7.21-7.26 (2H, m), 7.32 (2H, d, *J* = 6.9 Hz), 7.26-7.43 (4H, m), 7.65 (2H, d, *J* = 8.1 Hz), 7.73-7.76 (2H, m), 8.10-8.13 (2H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 56.9, 62.5, 124.3, 125.2, 125.5, 125.9, 126.8, 128.0, 128.4, 131.9, 133.7.
FT-IR (neat, cm^{-1}): 1132,1170, 1223, 1268, 1354, 1441, 1527, 1676, 2089, 2437, 2548.
HR-MS (m/z) for $C_{23}H_{20}N_2$ (M^+): Calculated 324.1626, found 324.1629.

4.6. **1,2-Diphenethyldiaziridine (6f)**



Yield: 85% (214.5 mg, 0.85 mmol).
Characteristic: Colourless oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.36 (2H, s), 2.41-2.49 (2H, m), 2.66-2.75 (2H, m), 2.87 (4H, t, *J* = 7.5 Hz), 7.10-7.26 (10H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 35.1, 56.8, 62.4, 125.9, 128.2, 128.5, 139.6.
FT-IR (neat, cm^{-1}): 1122,1159, 1224, 1265, 1352, 1434, 1522, 2055, 2089, 2441, 2552.
HR-MS (m/z) for $C_{17}H_{20}N_2$ (M^+): Calculated 252.1626, found 252.1623.

4.7. **Tert-butyl 2,2'-(diaziridine-1,2-diyl)diacetate (6g)**

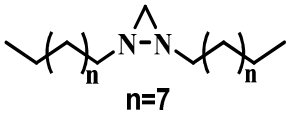


Yield: 80% (218 mg, 0.80 mmol).
Characteristic: Brown oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.35 (18H, s), 2.60 (2H, s), 2.94 (2H, d, *J* = 16.2 Hz), 3.28 (2H, d, *J* = 16.2 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 28.0, 56.4, 61.9, 81.5, 168.6.
FT-IR (neat, cm^{-1}): 1153, 1268, 1366, 1431, 1535, 1739, 2288, 2528.
HR-MS (m/z) for $C_{13}H_{24}N_2O_4$ (M^+): Calculated 272.1736, found 272.1735.

4.8. **1,2-Dibutyldiaziridine (6h)**

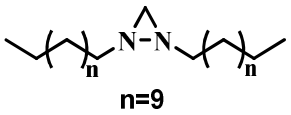
Yield: 95% (148.5 mg, 0.95 mmol).
Characteristic: Colourless oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 0.87 (6H, t, *J* = 7.5 Hz), 1.20-1.41 (4H, m), 1.47-1.57 (4H, m), 2.12-2.14 (2H, m), 2.37-2.46 (4H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 13.8, 20.2, 30.5, 56.5, 60.8.
FT-IR (neat, cm^{-1}): 1268, 1371, 1432, 1463, 1712, 2531.
HR-MS (m/z) for $C_9H_{20}N_2$ (M^+): Calculated 156.1626, found 156.1628.

4.9. **1,2-Didecyldiaziridine (6i)**



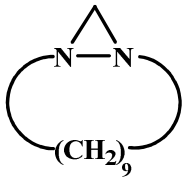
Yield: 82% (266 mg, 0.82 mmol).
Characteristic: Colourless oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 0.77 (6H, t, *J* = 6.6 Hz), 1.16 (28H, s), 1.46 (6H, q, *J* = 7.2 Hz), 2.08-2.17 (2H, m), 2.31-2.39 (4H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 14.0, 22.6, 27.3, 28.6, 29.2, 29.5, 31.8, 56.7, 61.3.
FT-IR (neat, cm^{-1}): 1268, 1369, 1436, 1466, 1715, 2532.
HR-MS (m/z) for $C_{21}H_{44}N_2$ (M^+): Calculated 324.3504, found 324.3507.

4.10. **1,2-Didodecyldiaziridine (6j)**



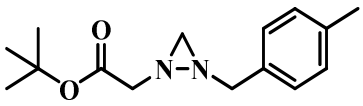
Yield: 80% (304.5 mg, 0.80 mmol).
Characteristic: Colourless oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 0.79-0.83 (6H, m), 1.21 (36H, s), 1.52 (4H, q, *J* = 6.3 Hz), 2.12-2.20 (2H, m), 2.35-2.43 (4H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 14.0, 22.6, 27.3, 28.7, 29.3, 29.5, 31.9, 56.7, 61.3.
FT-IR (neat, cm^{-1}): 1176, 1221, 1263, 1372, 1437, 1470, 1715, 2533.
HR-MS (m/z) for $C_{25}H_{52}N_2$ (M^+): Calculated 380.4130, found 380.4128.

4.11. **1,11-Diazabicyclo[9.1.0]dodecane (6k)**



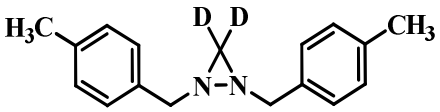
Yield: 65% (109.5 mg, 0.65 mmol).
Characteristic: Colourless oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.18-1.28 (8H, m), 1.54 (6H, b), 1.80 (2H, q, *J* = 6.0 Hz), 2.36 (2H, s), 2.69-2.74 (2H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 27.3, 27.4, 28.6, 29.1, 29.5, 29.7, 29.7, 56.5, 56.6, 61.4.
FT-IR (neat, cm^{-1}): 1175, 1210, 1231, 1258, 1380, 1436, 1447, 1471, 1543, 1717, 2533.
HR-MS (*m*/*z*) for $C_{10}H_{20}N_2$ (M^+): Calculated 168.1626, found 168.1623 (one of the major peaks).

4.12. ***tert*-Butyl-2-(2-(4-methylbenzyl)diaziridin-1-yl)acetate (6l)**



Yield: 28 % (73.5 mg, 0.28 mmol).
Characteristic: Brown oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.36(9H, s), 2.23(3H, s), 2.49 (1H, d, *J* = 4.5 Hz), 2.64 (1H, d, *J* = 4.5 Hz), 2.98 (1H, dd, *J* = 16.2, 0.9 Hz), 3.13 (1H, dd, *J* = 16.2, 0.9 Hz), 3.22 (1H, d, *J* = 13.2 Hz), 3.79 (1H, d, *J* = 12.9 Hz), 7.03 (2H, d, *J* = 7.5 Hz), 7.12-7.16 (2H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 21.1, 28.0, 56.2, 62.3, 64.3, 81.3, 128.6, 129.1, 134.3, 137.0, 168.7.
FT-IR (neat, cm^{-1}): 1156, 1268, 1372, 1538, 1742, 2290, 2528.
HR-MS (m/z) for $C_{15}H_{22}N_2O_2$ (M^+): Calculated 262.1681, found 262.1679.

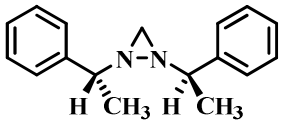
4.13. **3,3-D_2-1,2-Bis(4-methylbenzyl)diaziridine (6b-D_2)**



Yield: 81% (206 mg, 0.81 mmol).
Characteristic: Colourless oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.27 (6H, s), 3.34 (2H, d, *J* = 12.3 Hz), 3.58 (2H, d, *J* = 12.3 Hz), 7.02(4H, d, *J* = 7.8 Hz), 7.12 (4H, d, *J* = 7.8 Hz).
FT-IR (neat, cm^{-1}): 1225, 1274, 1443, 1522, 1681, 1714, 2097, 2448, 2549.
HR-MS (m/z) for $C_{17}H_{18}D_2N_2$ (M^+): Calculated 254.1752, found 254.1756.

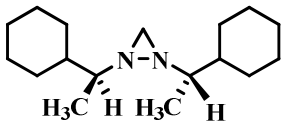
5. Characterization data of optically active diaziridines using chiral amines (7a-h)

5.1. 1,2-bis((R)-1-phenylethyl)diaziridine (7a)



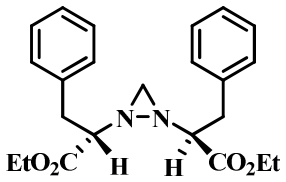
Yield: 78% (197 mg, 0.78 mmol).
Characteristic: Brown oil.
$[\alpha]_D^{25}$ = +36.70° (c 0.5, $CHCl_3$).
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.27 (6H, dd, *J* = 6.6, 0.9 Hz), 2.70 (2H, s), 2.76 (2H, q, *J* = 6.9Hz), 6.92-7.03 (10H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 20.7, 55.5, 69.6, 126.3, 126.7, 127.6, 143.2.
FT-IR (neat, cm^{-1}): 1211, 1267, 1364, 1437, 1522, 1673, 1714, 2441, 2554.
HR-MS (*m*/*z*) for $C_{17}H_{20}N_2$ (M^+): Calculated 252.1626, found 252.1628.

5. 2. 1,2-Bis{(S)-1-cyclohexylethyl}diaziridine (7b)



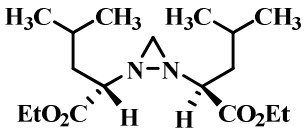
Yield: 74% (196 mg, 0.74 mmol).
Characteristic: Yellow oil.
$[\alpha]_D^{25}$ = +2.30° (c 0.375, $CHCl_3$).
^{1}H NMR (300 MHz, $CDCl_3$): δ 0.83 (6H, d, *J* = 6.0 Hz), 0.89-1.28 (10H, m), 1.36 (2H, d, *J* = 12.6 Hz), 1.45 (2H, d, *J* = 6.6 Hz), 1.61-1.77 (8H, m), 1.97 (2H, d, *J* = 12.3 Hz), 2.34 (2H, s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 12.0, 26.1, 26.5, 26.9, 27.0, 30.7, 41.5, 55.4, 69.8.
FT-IR (neat, cm^{-1}): 1209, 1264, 1377, 1411, 1452, 1717, 2150, 2445, 2552.
HR-MS (m/z) for $C_{17}H_{32}N_2$ (M^+): Calculated 264.2565, found 264.2567.

5.3. **(2S, 2'S)-Diethyl-2,2'-(diaziridine-1,2-diyl)bis(3-phenylpropanoate) (7c)**



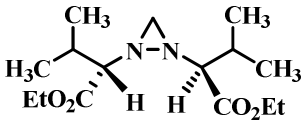
Yield: 72% (285.5 mg, 0.72 mmol).
Characteristic: Colourless oil.
$[\alpha]_D^{25}$ = -39.30° (c 0.285, $CHCl_3$).
^{1}H NMR (300 MHz, $CDCl_3$): δ 0.98 (6H, t, *J* = 7.2 Hz), 2.76-2.82 (4H, m), 3.13 (4H, d, *J* = 7.2 Hz), 3.90-4.00 (4H, m), 7.06-7.19 (10H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 13.9, 38.0, 55.7, 60.9, 73.5, 126.5, 126.7, 128.3, 128.4, 129.1, 129.3, 136.8, 170.3.
FT-IR (neat, cm^{-1}): 1223, 1268, 1369, 1432, 1454, 1725, 1742, 2062, 2443, 2552.
HR-MS (m/z) for $C_{23}H_{28}N_2O_4$ (M^+): Calculated 396.2049, found 396.2053.

5.4. **(2S,2'S)-Diethyl-2,2'-(diaziridine-1,2-diyl)bis(4-methylpentanoate) (7d)**



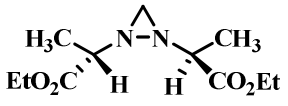
Yield: 74% (243 mg, 0.74 mmol).
Characteristic: Colourless oil.
$[\alpha]_D^{25}$ = -19.50° (c 0.375, $CHCl_3$).
^{1}H NMR (300 MHz, $CDCl_3$): δ 0.88 (12H, dd, *J* = 14.7, 6.0 Hz), 1.23 (6H, t, *J* = 7.2 Hz), 1.56-1.75 (4H, m), 1.82-1.91 (2H, m), 2.58 (2H, dd, *J* = 9.15, 3.9 Hz), 4.15 (4H, q, *J* = 6.9 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 14.1, 21.9, 23.4, 24.9, 40.6, 54.6, 60.7, 70.5, 171.4.
FT-IR (neat, cm^{-1}): 1438, 1452, 1723, 1737, 2053, 2223, 2447, 2550.
HR-MS (*m*/*z*) for $C_{17}H_{32}N_2O_4$ (M^+): Calculated 328.2362, found 328.2363.

5.5. **(2S,2'S)-Diethyl-2,2'-(diaziridine-1,2-diyl)bis(3-methylbutanoate) (7e)**



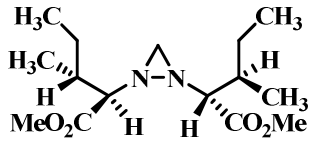
Yield: 75% (225.5 mg, 0.75 mmol).
Characteristic: Light yellow oil.
$[\alpha]_D^{25}$ = -67.00° (c 0.585, $CHCl_3$).
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.01-1.03 (12H, m),1.21-1.26 (6H, m), 2.09-2.12 (2H, m), 2.64 (2H, d, *J* = 4.8 Hz), 2.74 (2H, s), 4.12-4.18 (4H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 14.2, 17.6, 19.6, 30.7, 53.7, 60.4, 76.4, 170.4.
FT-IR (neat, cm^{-1}): 1371,1442, 1461, 1725, 1742, 2053, 2442, 2552.
HR-MS (*m*/*z*) for $C_{15}H_{28}N_2O_4$ (M^+): Calculated 300.2049, found 300.2045(M^++H).

5.6. **(2S,2'S)-Diethyl-2,2'-(diaziridine-1,2-diyl)dipropanoate (7f)**



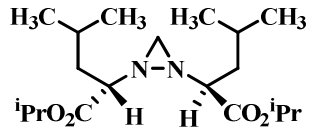
Yield: 76% (186 mg, 0.76 mmol).
Characteristic: Colourless oil.
$[\alpha]_D^{25}$ = -44.9° (c 0.55, $CHCl_3$).
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.27 (6H, t, *J* = 7.2 Hz), 1.46 (6H, d, *J* = 6.9 Hz), 2.53 (2H, q, *J* = 6.9 Hz), 2.86 (2H, s), 4.15-4.22 (4H,m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 14.1, 17.1, 57.5, 60.9, 67.2, 171.5.
FT-IR (neat, cm^{-1}): 1354,1437, 1452, 1721, 1743, 2045, 2445, 2549.
HR-MS (*m*/*z*) for $C_{11}H_{20}N_2O_4$ (M^+): Calculated 244.1423, found 244.1425.

5.7. **(2R,2'R,3R,3'R)-Dimethyl-2,2'-(diaziridine-1,2-diyl)bis(3-methylpentanoate) (7g)**



Yield: 73% (220 mg, 0.73 mmol).
Characteristic: Colourless oil.
$[\alpha]_D^{25}$ = -5.31° (c 0.32, $CHCl_3$).
^{1}H NMR (300 MHz, $CDCl_3$): δ 0.89 (6H, t, *J* = 7.5 Hz), 1.02 (6H, d, *J* = 6.9 Hz), 1.22-1.34 (2H, m), 1.41-1.51 (2H, m), 1.80-1.88 (2H, m), 2.67 (2H, d, *J* = 4.2 Hz), 2.73 (2H, s), 3.67 (6H, s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 11.9, 14.6, 26.7, 37.8, 51.4, 55.0, 75.3, 170.9.
FT-IR (neat, cm^{-1}): 1032, 1248, 1371,1442, 1452, 1723, 1741, 2445, 2554.
HR-MS (*m*/*z*) for $C_{15}H_{28}N_2O_4$ (M^+): Calculated 300.2049, found 300.2054.

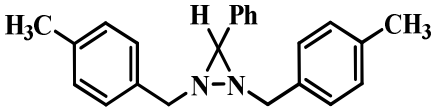
5.8. **(2S,2'S)-Isopropyl-2,2'-(diaziridine-1,2-diyl)bis(4-methylpentanoate) (7h)**



Yield: 78% (278 mg, 0.78 mmol).
Characteristic: Colourless oil.
$[\alpha]_D^{25}$ = -20.70° (c 0.40, $CHCl_3$).
^{1}H NMR (300 MHz, $CDCl_3$): δ 0.82-0.90 (12H, m), 1.17-1.21 (12H, m), 1.55-1.69 (4H, m), 1.79-1.87 (2H, m), 2.53-2.70 (2H, m), 2.71 (2H, s), 4.96-5.02 (2H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 21.6, 21.7, 21.9, 23.4, 24.9, 40.5, 54.2, 68.1, 70.4, 170.9.
FT-IR (neat, cm^{-1}): 1010,1276, 1437, 1452, 1725, 1733, 2053, 2441, 2550.
HR-MS (*m*/*z*) for $C_{19}H_{36}N_2O_4$(M^+): Calculated 356.2675, found 356.2671.

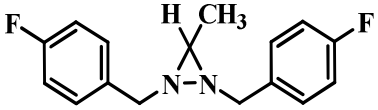
6. **Characterization data of 3-Substituted diaziridine (8a-i)**

6.1. **1,2-Bis(4-methylbenzyl)-3-phenyldiaziridine (8a)**



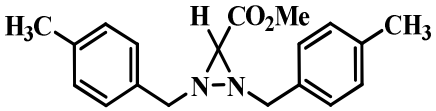
Yield: 65% (214 mg, 0.65 mmol).
Characteristic: Brown oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.24 (6H, d, *J* = 7.5 Hz), 3.17 (1H, d, *J* = 13.5 Hz), 3.34 (1H, d, *J* = 13.5 Hz), 3.54 (1H, d, *J* = 13.2 Hz), 3.84 (1H, d, *J* = 12.3 Hz), 3.86 (1H, s), 6.92 (3H, dd, *J* = 15.4, 8.1 Hz), 7.02 (2H, d, *J* = 7.8 Hz), 7.17 (3H, d, *J* = 8.7 Hz), 7.29 (3H, d, *J* = 0.9 Hz), 7.40 (2H, d, *J* = 3.6 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 21.0, 55.9, 64.6, 65.8, 127.9, 128.5, 128.6, 128.7, 128.9, 129.0, 129.3, 133.3, 134.7, 135.2, 136.3, 136.6.
FT-IR (neat, cm^{-1}): 1229, 1272, 1381, 1407, 1447, 1521, 1679, 1715, 2086, 2446, 2551.
HR-MS (*m*/*z*) for $C_{23}H_{24}N_2$(M^+): Calculated 328.1939, found 328.1943.

6.2. **1,2-Bis(4-fluorobenzyl)-3-methyldiaziridine (8b)**



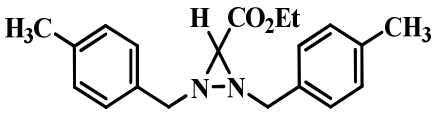
Yield: 63% (173 mg, 0.63 mmol).
Characteristic: Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.36 (3H, d, *J* = 5.4 Hz), 2.82 (1H, q, *J* = 5.4 Hz), 3.29 (1H, d, *J* = 13.2 Hz), 3.42 (1H, d, *J* = 13.8 Hz), 3.51 (1H, d, *J* = 4.2 Hz), 3.55 (1H, d, *J* = 4.2 Hz), 6.78-6.85 (4H, m), 7.05-7.11 (4H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 12.4, 55.4, 60.6, 64.1, 114.8, 115.1, 130.1, 130.2, 130.3, 133.7, 134.3, 163.7, 164.2.
FT-IR (neat, cm^{-1}): 1268, 1372, 1436, 1532, 1666, 1714, 2094, 2446, 2552.
HR-MS (*m*/*z*) for $C_{16}H_{16}F_2N_2$ (M^+): Calculated 274.1282, found 274.1277.

6.3. **Methyl-1,2-bis(4-methylbenzyl)diaziridine-3-carboxylate (8c)**



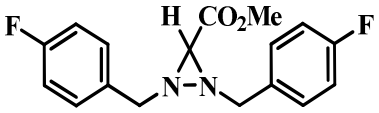
Yield: 70% (218 mg, 0.70 mmol).
Characteristic: Colourless oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.23 (6H, s), 3.21 (1H, s), 3.53 (2H, s), 3.63 (1H, d, *J* = 14.7 Hz), 3.66 (3H, s), 3.77 (1H, d, *J* = 13.2 Hz), 6.97 (4H, d, *J* = 7.5 Hz), 7.02-7.08 (4H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 21.1, 52.4, 57.4, 60.1, 64.2, 128.7, 128.9, 129.5, 133.5, 134.2, 136.8, 137.0, 167.2.
FT-IR (neat, cm^{-1}): 1182, 1212, 1264, 1365, 1443, 1518, 1715, 1753, 2047, 2439, 2532.
HR-MS (*m*/*z*) for $C_{19}H_{22}N_2O_2$ (M^+): Calculated 310.1681, found 310.1677.

6.4. **Ethyl-1,2-bis(4-methylbenzyl)diaziridine-3-carboxylate (8d)**



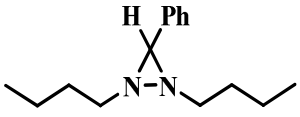
Yield: 68% (221 mg, 0.68 mmol).
Characteristic: Colourless oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.17 (3H, t, *J* = 7.2 Hz), 2.09 (6H, s), 3.21 (1H, s), 3.55 (2H, d, *J* = 5.4 Hz), 3.67 (1H, d, *J* = 13.2 Hz), 3.80 (1H, d, *J* = 13.2 Hz), 4.15 (2H, q, *J* = 7.2 Hz), 6.99 (4H, d, *J* = 7.5 Hz), 7.05-7.19 (4H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 14.0, 20.8, 21.0, 57.3, 60.3, 61.6, 64.2, 126.6, 127.8, 128.7, 128.9, 129.0, 129.2, 129.3, 129.6, 129.9, 133.6, 134.4, 136.7, 136.9, 166.7.
FTHR-MS (*m*/*z*) for $C_{20}H_{24}N_2O_2$ (M^+): Calculated 324.1838, found 324.1841.

6.5. **Methyl-1,2-bis(4-fluorobenzyl)diaziridine-3-carboxylate (8e)**



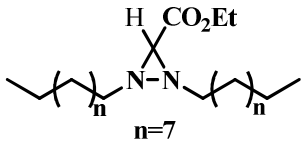
Yield: 62% (198 mg, 0.62 mmol).
Characteristic: Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.24 (1H, s), 3.64-3.70 (7H, m), 6.77-6.83 (4H, m), 7.03-7.10 (4H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 52.4, 56.8, 60.1, 63.6, 114.7, 115.0, 130.2, 130.3, 130.7, 130.8, 132.1, 132.2, 132.8, 132.8, 160.3, 160.4, 163.6, 163.7, 166.8.
FT-IR (neat, cm^{-1}): 1221, 1265, 1371, 1443, 1522, 1723, 1751, 2437, 2530.
HR-MS (*m*/*z*) for $C_{17}H_{16}F_2N_2O_2$ (M^+): Calculated 318.1180, found 318.1182.

6.6. **1,2-Dibutyl-3-phenyldiaziridine (8f)**



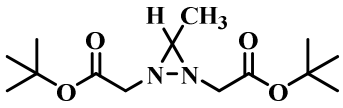
Yield: 71% (165 mg, 0.71 mmol).
Characteristic: Colourless oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 0.76 (3H, t, *J* = 7.5 Hz), 0.90 (3H, t, *J* = 7.5 Hz), 1.15-1.25 (2H, m), 1.32-1.50 (4H, m), 1.54-1.64 (2H, m), 2.10 (2H, t, *J* = 7.5 Hz), 2.53-2.59 (2H, m), 3.62 (1H, s), 7.30 (2H, dd, *J* = 4.9, 1.8 Hz), 7.38-7.41 (2H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 13.9, 14.0, 20.4, 20.5, 30.6, 30.8, 52.0, 61.1, 65.9, 127.8, 128.2, 129.0, 133.7.
FT-IR (neat, cm^{-1}): 1264, 1380, 1406, 1454, 1715, 2152, 2532.
HR-MS (*m*/*z*) for $C_{15}H_{24}N_2$ (M^+): Calculated 232.1939, found 232.1936.

6.7. **Ethyl 1,2-didecyldiaziridine-3-carboxylate (8g)**



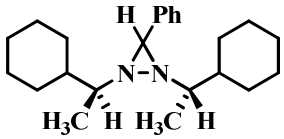
Yield: 65% (258 mg, 0.65 mmol).
Characteristic: Colourless oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 0.80-0.82 (6H, m), 1.18-1.26 (30H, m), 1.46-1.55 (5H, m), 2.17-2.25 (1H, m), 2.49-2.58 (3H, m), 3.01 (1H, s), 4.19 (2H, q, J = 7.2 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 14.1, 14.2, 22.6, 27.1, 28.3, 28.7, 29.3, 29.5, 31.9, 53.9, 61.2, 61.6, 166.9.
FT-IR (neat, cm^{-1}): 1172, 1217, 1263, 1365, 1438, 1520, 1715, 1751, 2439, 2533.
HR-MS (*m*/*z*) for $C_{24}H_{48}N_2O_2$ (M^+): Calculated 396.3716, found 396.3718.

6.8. ***tert*-Butyl-2,2'-(3-methyldiaziridine-1,2-diyl)diacetate (8h)**



Yield: 66% (189 mg, 0.66 mmol).
Characteristic: Brown oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.33 (3H, d, J = 5.4 Hz), 1.40-1.45 (18H, m), 2.81 (1H, q, J = 5.4 Hz), 3.01 (1H, d, J = 16.2 Hz), 3.15 (1H, d, J = 16.8 Hz), 3.39 (2H, d, J = 16.5 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 21.1, 27.6, 27.9, 28.0, 42.1, 54.1, 60.5, 62.2, 81.5, 168.8, 169.2.
FT-IR (neat, cm^{-1}): 1142, 1264, 1368, 1443, 1541, 1729, 2292, 2530.
HR-MS (*m*/*z*) for $C_{14}H_{26}N_2O_4$ (M^+): Calculated 286.1893, found 286.1892.

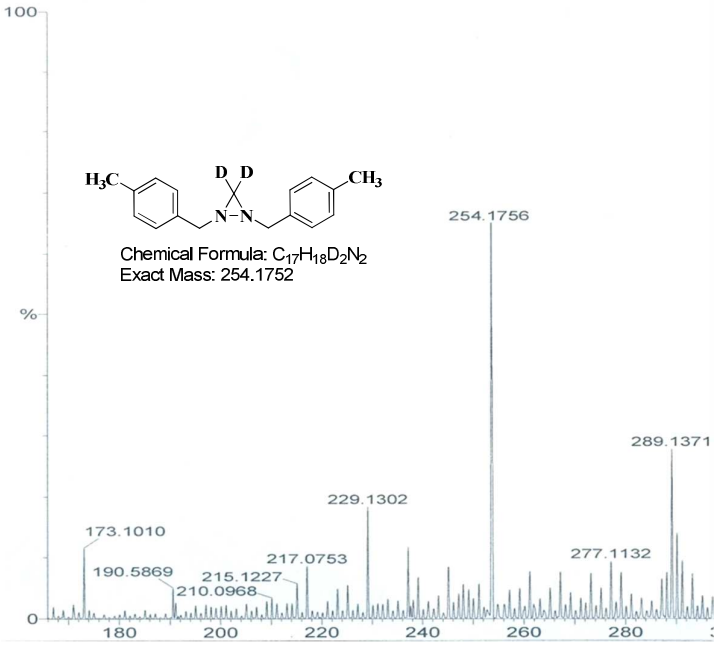
6.9. **1,2-Bis{(S)-1-cyclohexylethyl}-3-phenyldiaziridine (8i)**



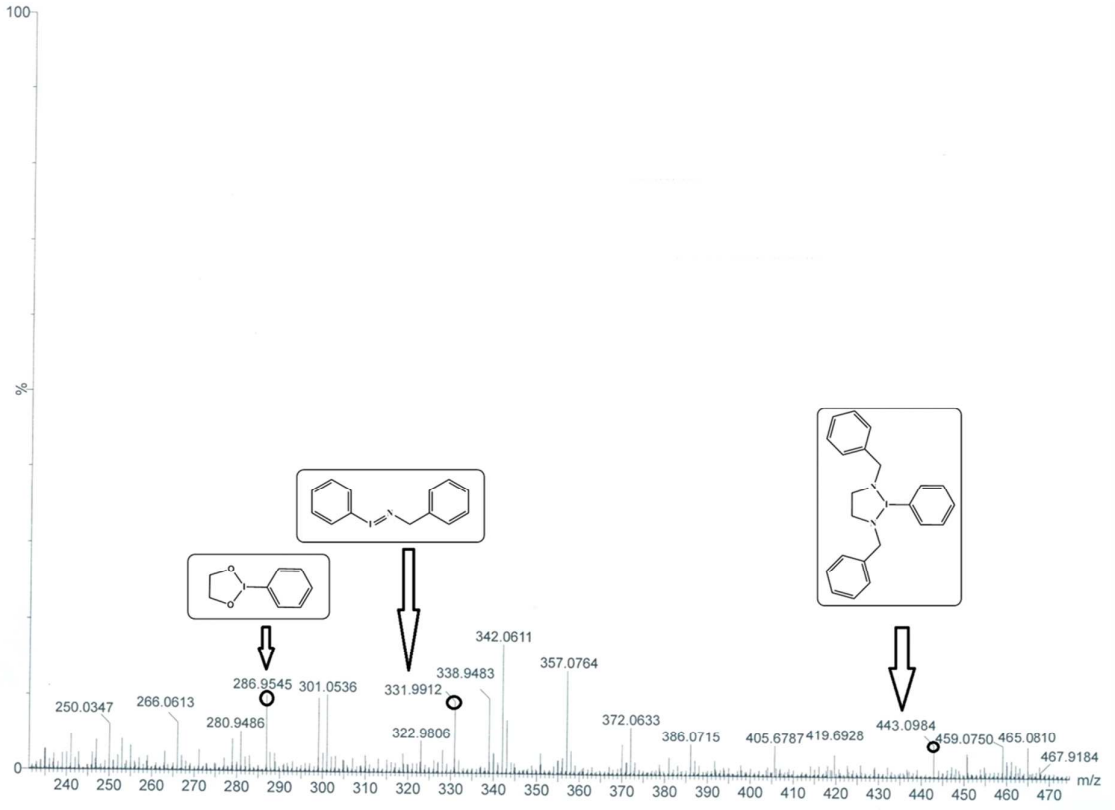
Yield: 62% (211mg, 0.62 mmol).
Characteristic: Colourless oil.
$[\alpha]_D^{25}$ = +2.20° (c 0.280, $CHCl_3$).
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.05-1.19 (9H, m), 1.26-1.31 (8H, m), 1.47-1.52 (2H, m), 1.66-1.89 (9H, m), 2.02 (2H, q, J = 6.6 Hz), 4.54 (1H, s), 7.40 (6H, b).
^{13}C NMR (75 MHz, $CDCl_3$): δ 17.1, 26.1, 26.2, 26.3, 26.6, 28.4, 29.6, 30.0, 41.9, 71.3, 71.6, 82.0, 127.4, 127.5, 128.4, 129.9, 134.9.
FT-IR (neat, cm^{-1}): 1624, 1590, 1573,1499, 1456, 1344, 1127, 1053, 855, 817,760, 711, 698.
HR-MS (*m*/*z*) for $C_{23}H_{36}N_2$ (M^+): Calculated 340.2878, found 340.2874.

7. **Detection of isotope labeled product (6b-D_2), intermediates and by-product (9)**

7. A. HRMS data of **6b-D_2**

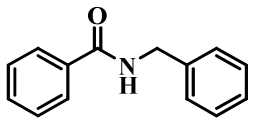


7. B. HRMS data of some intermeditates (HRMS was performed taking aliquat from reaction mixture at 10 min)



7. C. Isolation of by-product **9** (*N*-benzylbenzamide)

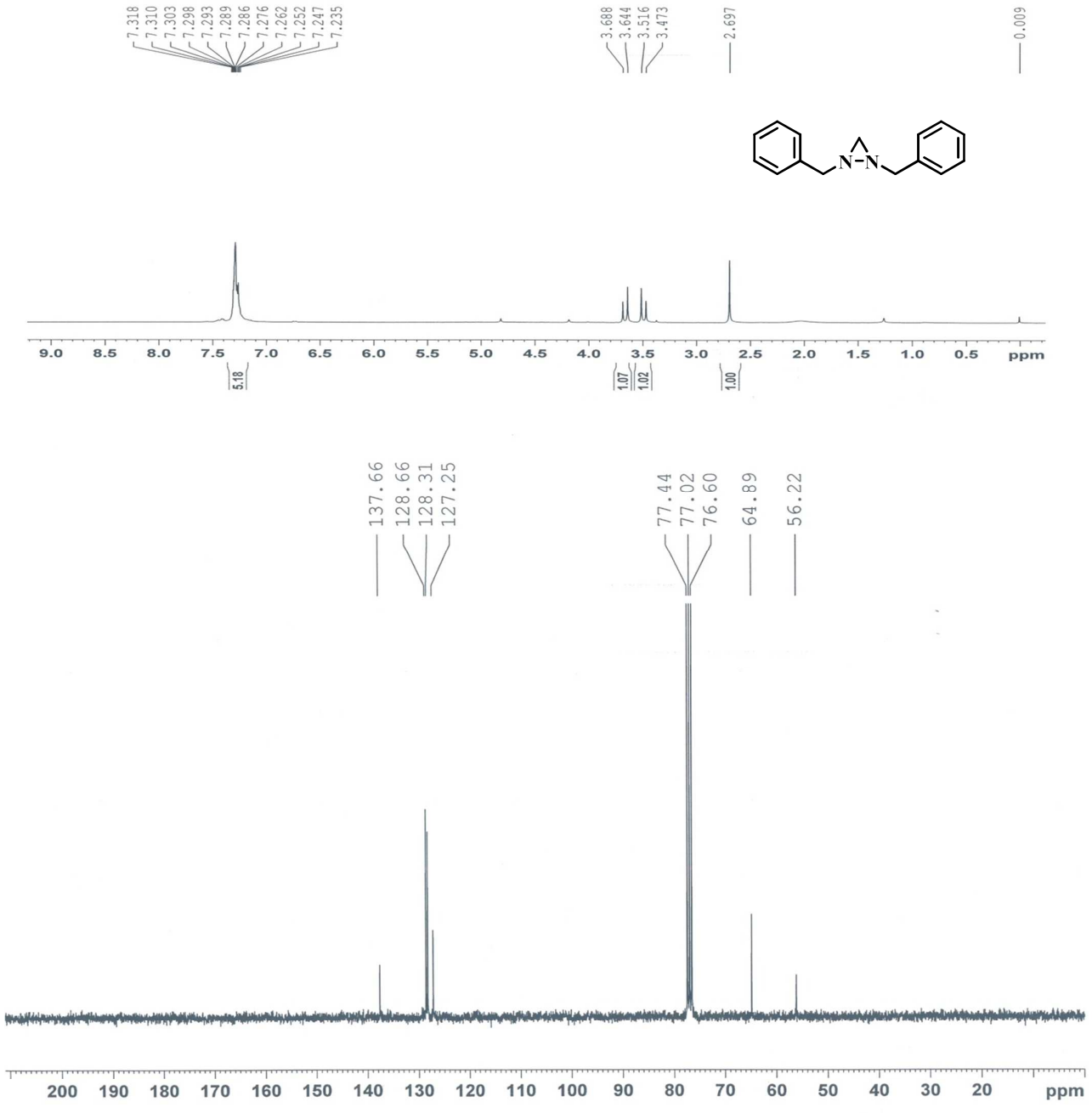
7.C.1. ***N*-Benzylbenzamide (9)**



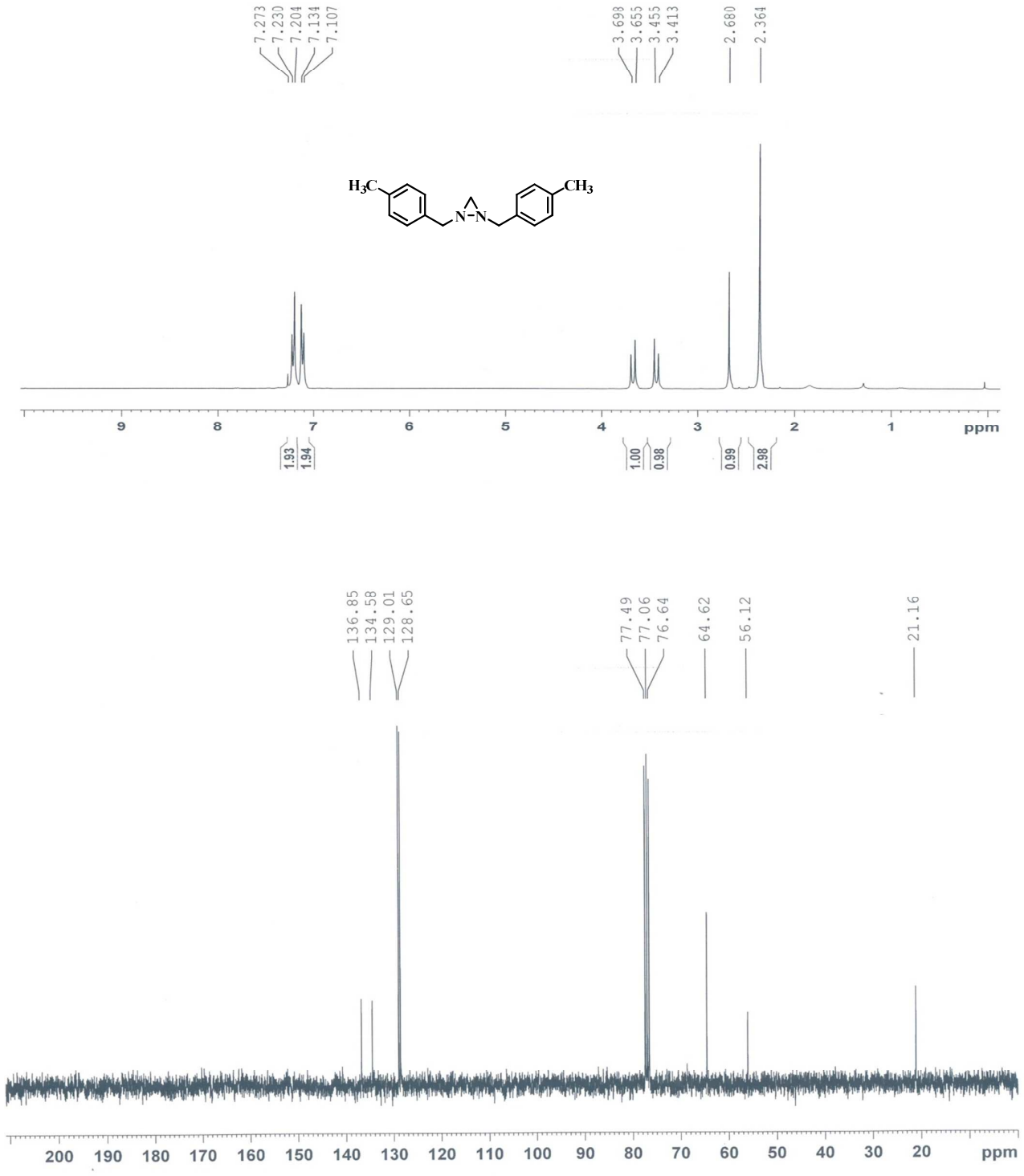
Yield: 4% (9 mg, 0.04 mmol).
Characteristic: Colourless solid.
Melting range: 101-102 °C.
^{1}H NMR (300 MHz, $CDCl_3$): δ 4.65 (2H, d, J = 5.7 Hz), 6.42 (1H, brs), 7.28-7.53 (8H, m), 7.79 (2H, d, J = 6.9 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 44.1, 126.9, 127.6, 127.9, 128.6, 128.8, 131.5, 134.4, 138.1, 167.3.
FT-IR (KBr, cm^{-1}): 1260, 1314, 1454, 1546, 1578, 1604, 1643, 2854, 2930, 3325.
HR-MS (*m*/*z*) for $C_{14}H_{13}NO$ (M^+): Calculated 211.0997, found 211.0998.

8. ^{1}H and ^{13}C-NMR spectra of the compounds (6a-l, 7a-h, 8a-i, 9)

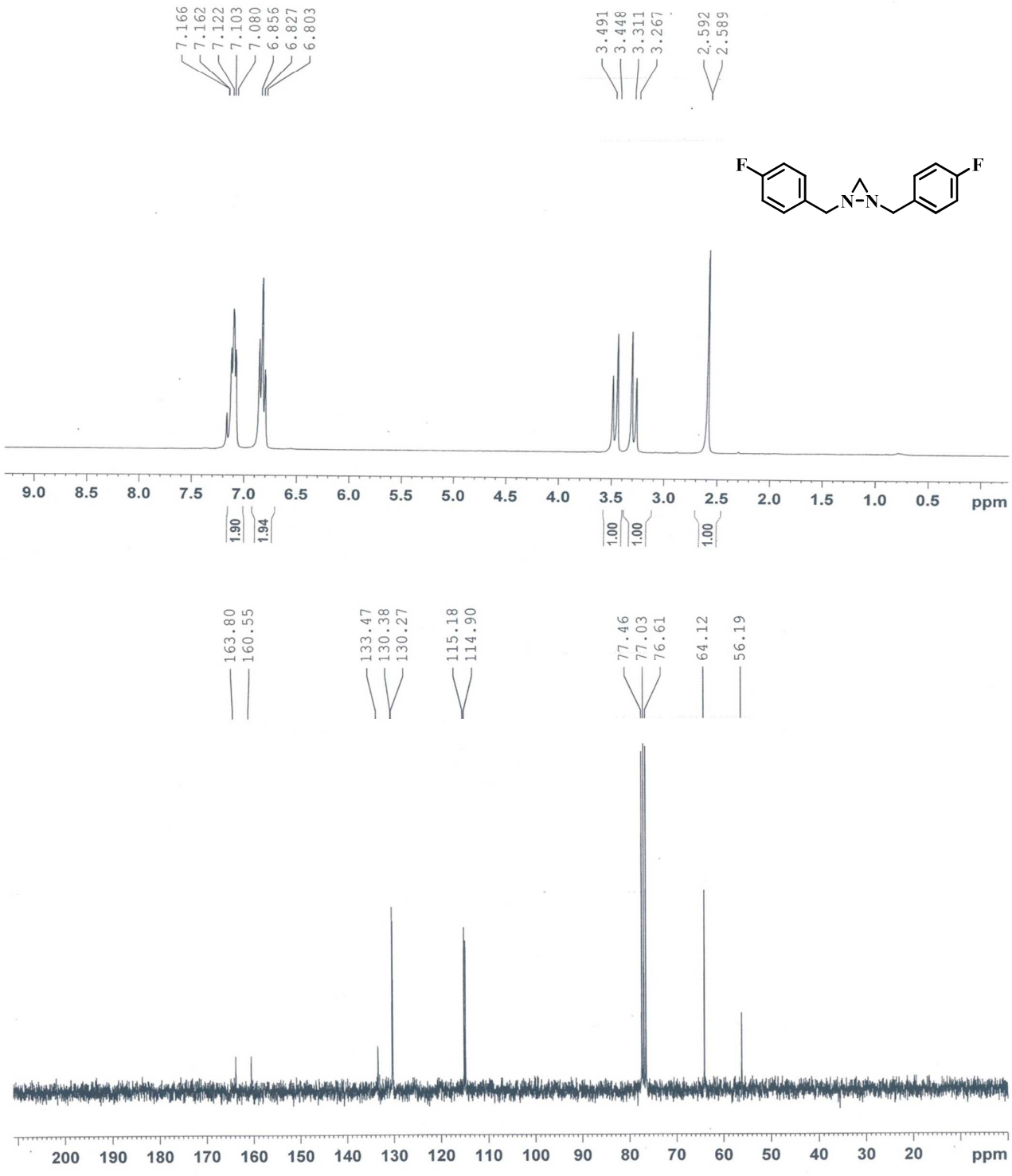
SI Figure 1: ^{1}H and ^{13}C-NMR spectra of compound **6a**



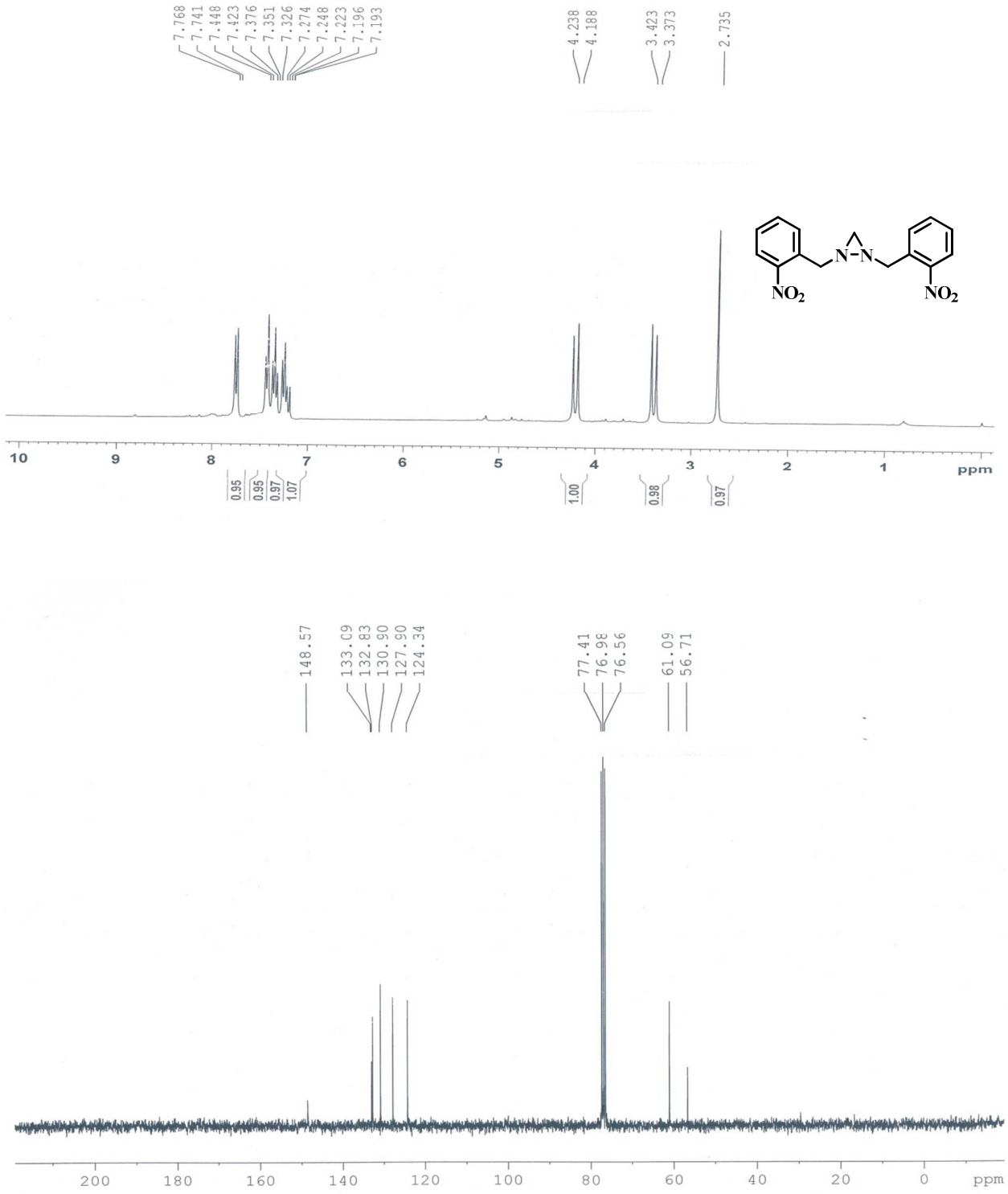
SI Figure 2: ^{1}H and ^{13}C-NMR spectra of compound **6b**



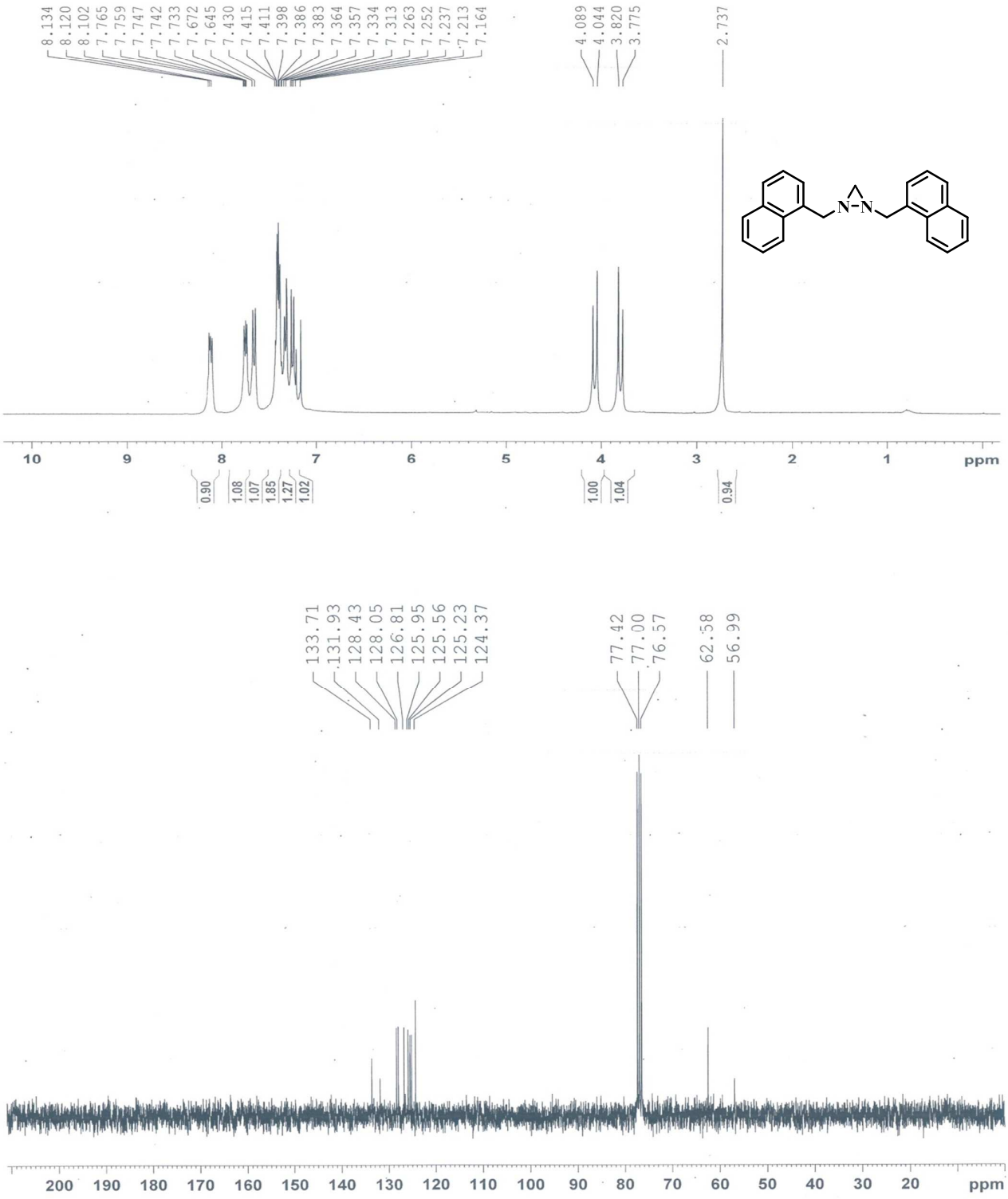
SI Figure 3: ^{1}H and ^{13}C-NMR spectra of compound **6c**



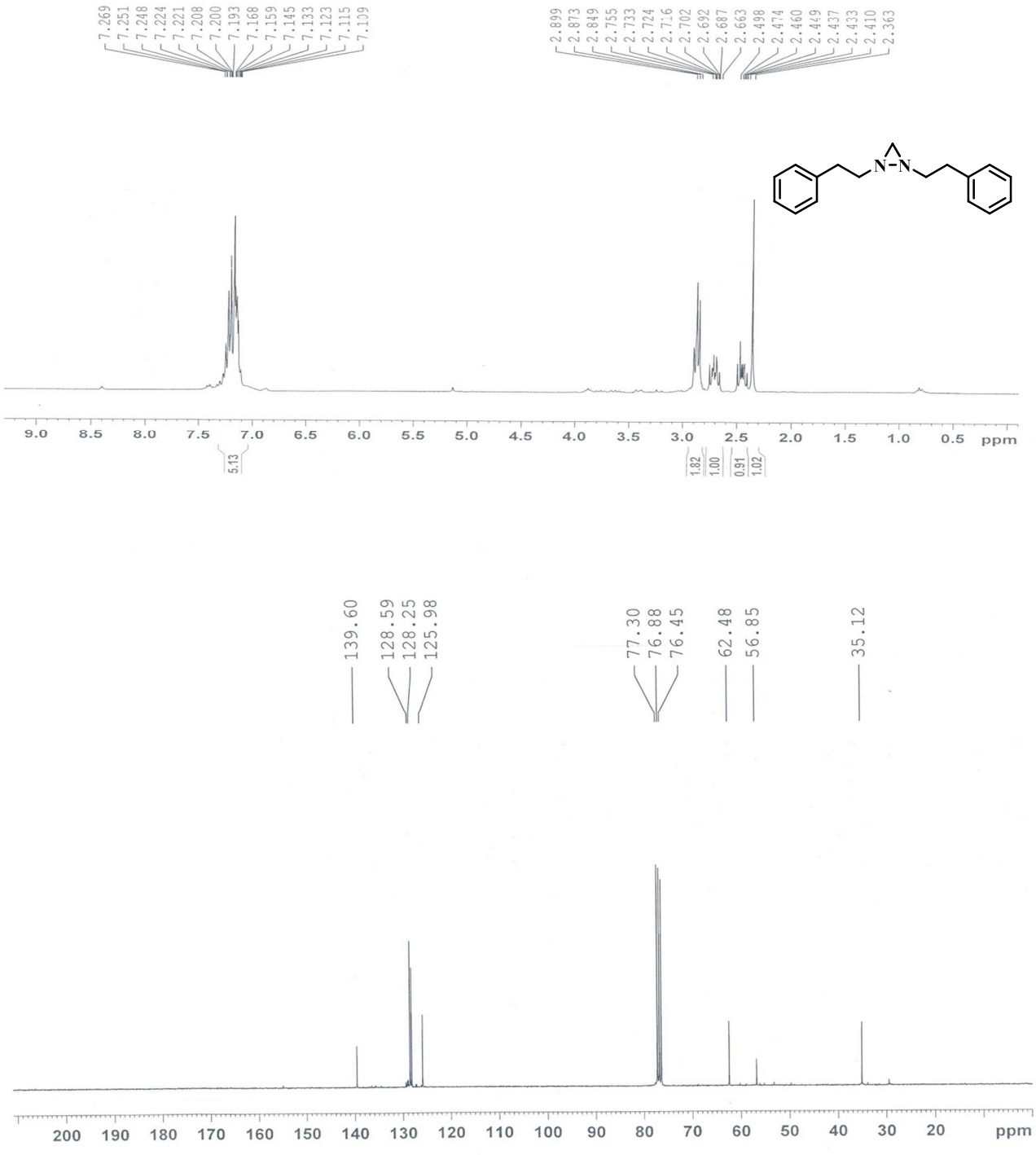
SI Figure 4: ^{1}H and ^{13}C-NMR spectra of compound **6d**



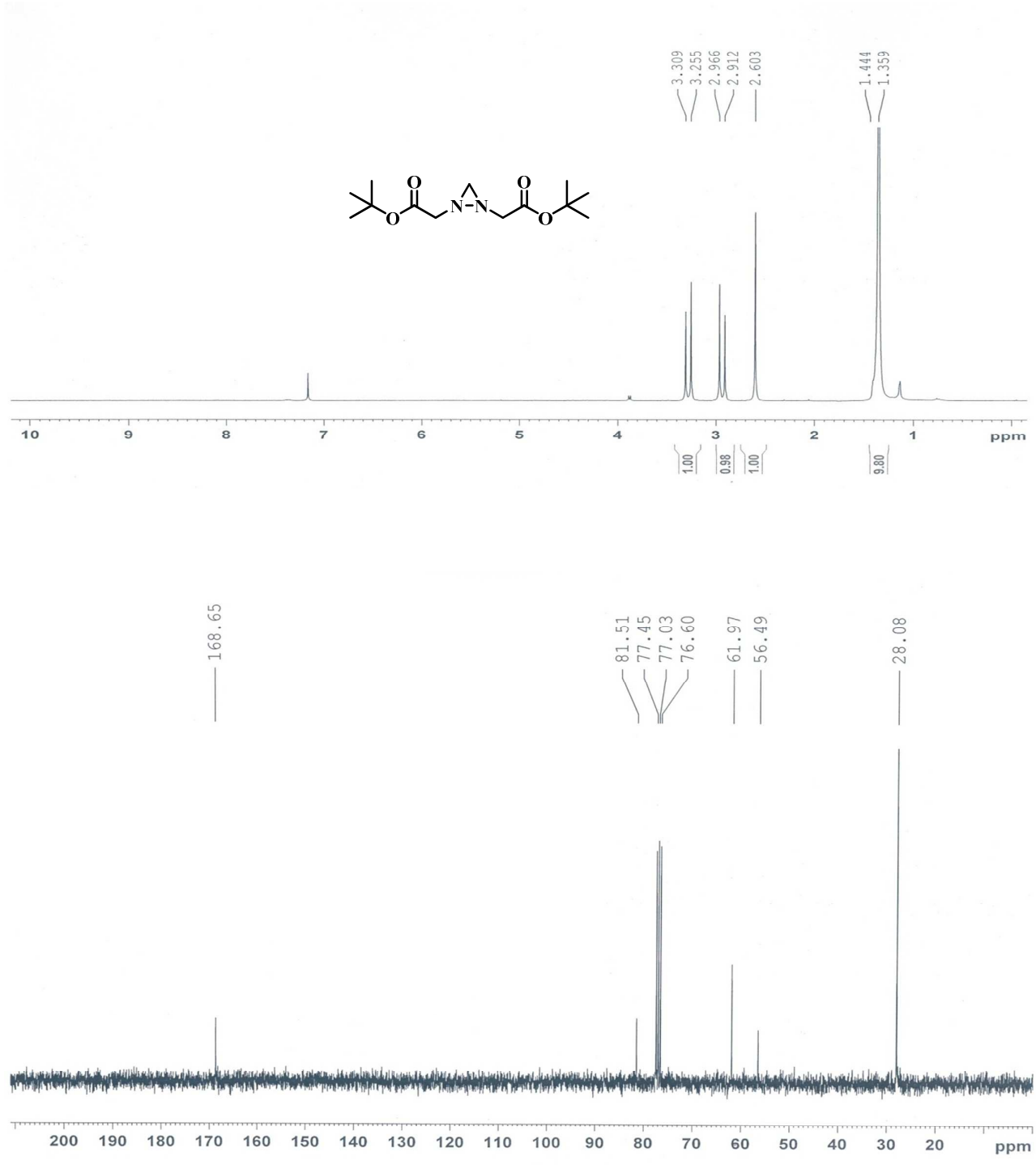
SI Figure 5: ^{1}H and ^{13}C-NMR spectra of compound **6e**



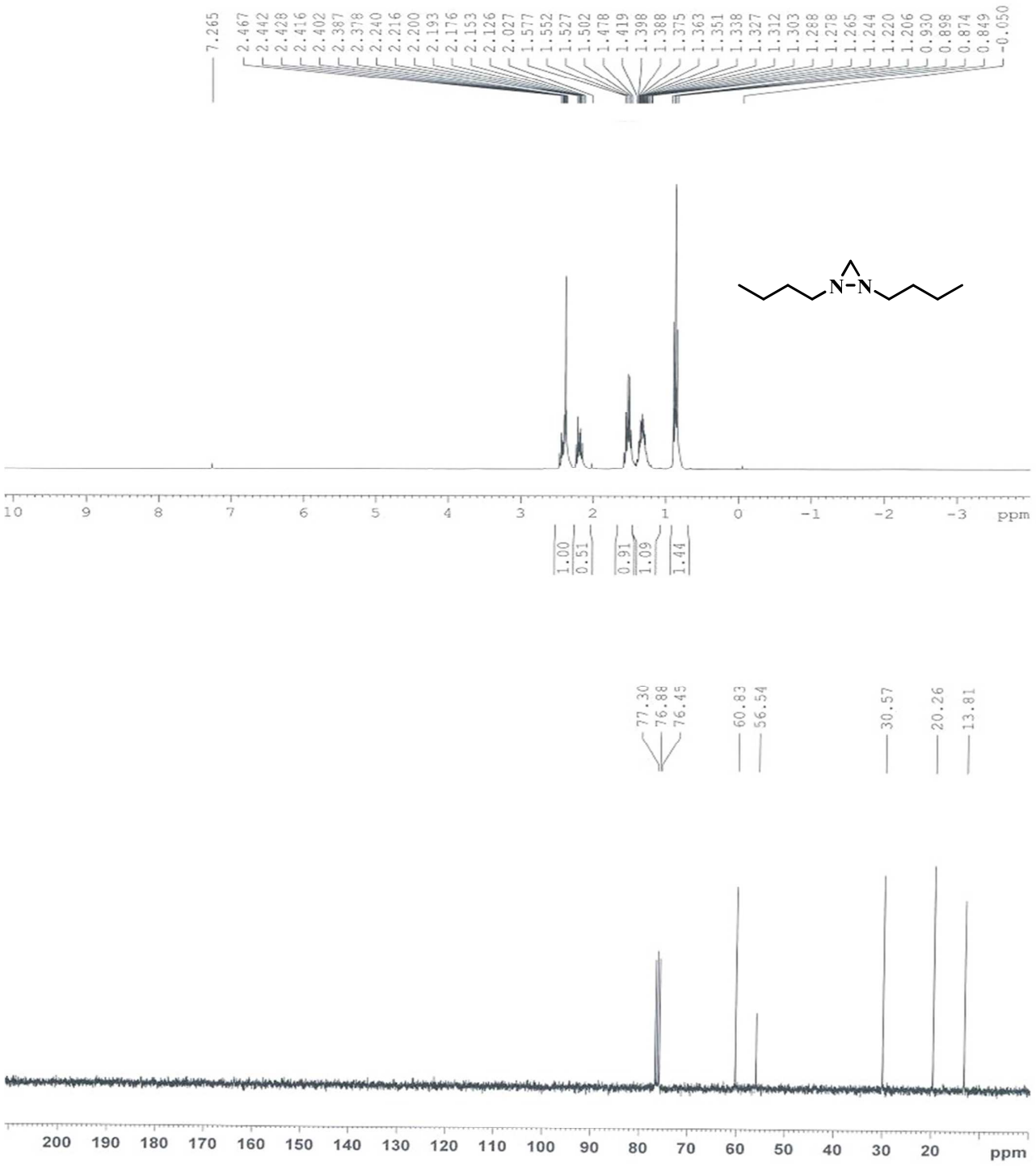
SI Figure 6: ^{1}H and ^{13}C-NMR spectra of compound **6f**



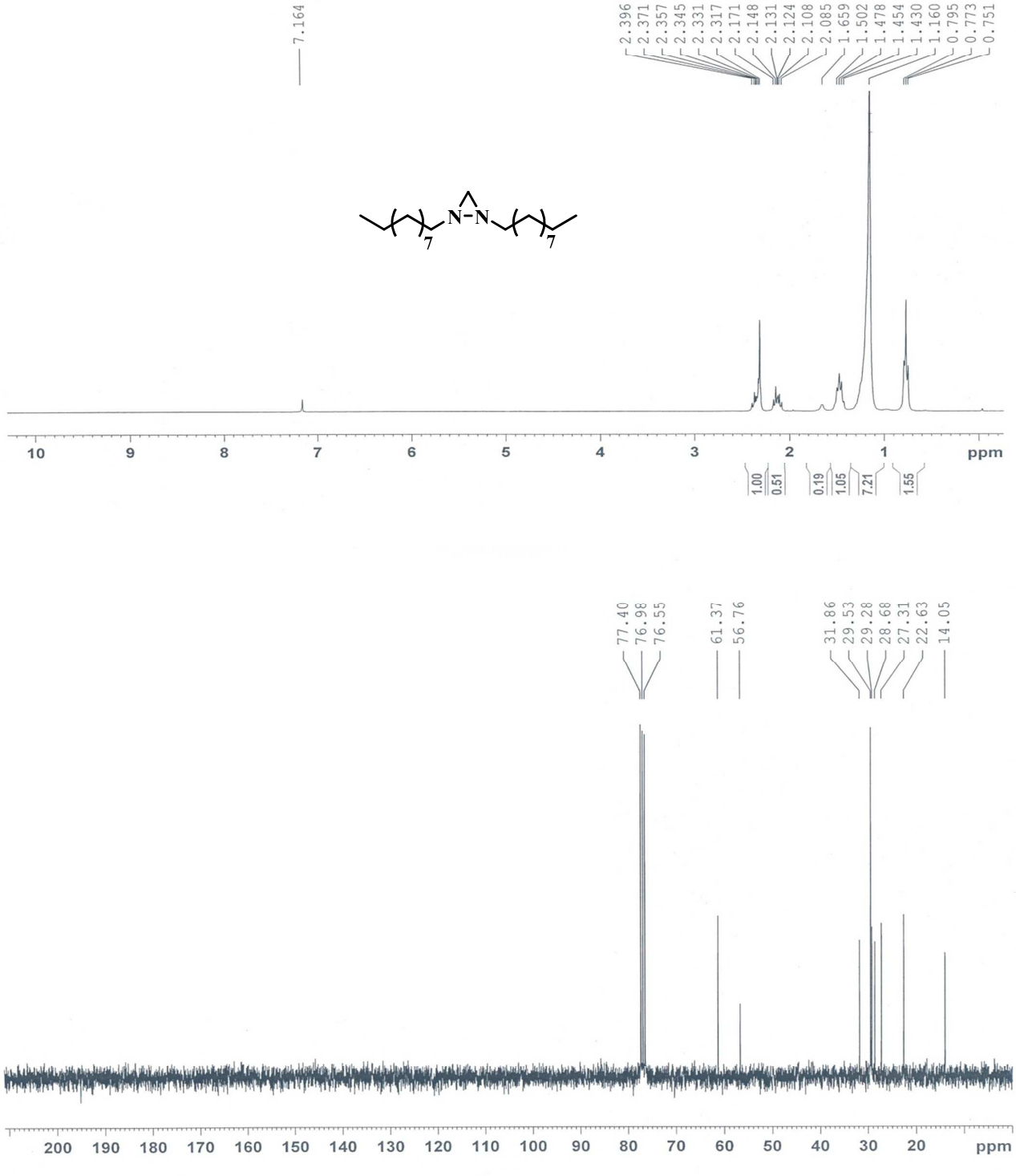
SI Figure 7: ^{1}H and ^{13}C-NMR spectra of compound **6g**



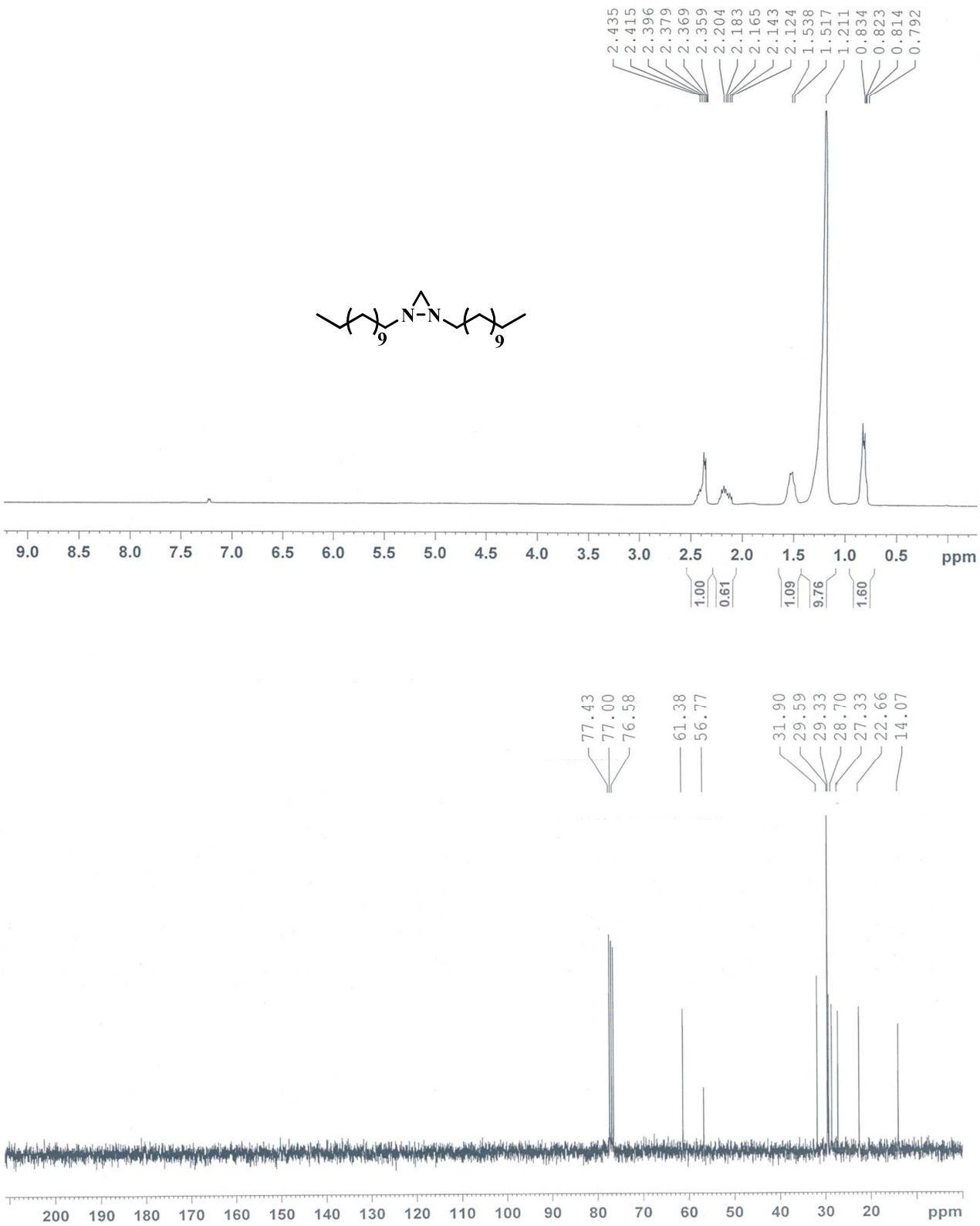
SI Figure 8: ^{1}H and ^{13}C-NMR spectra of compound **6h**



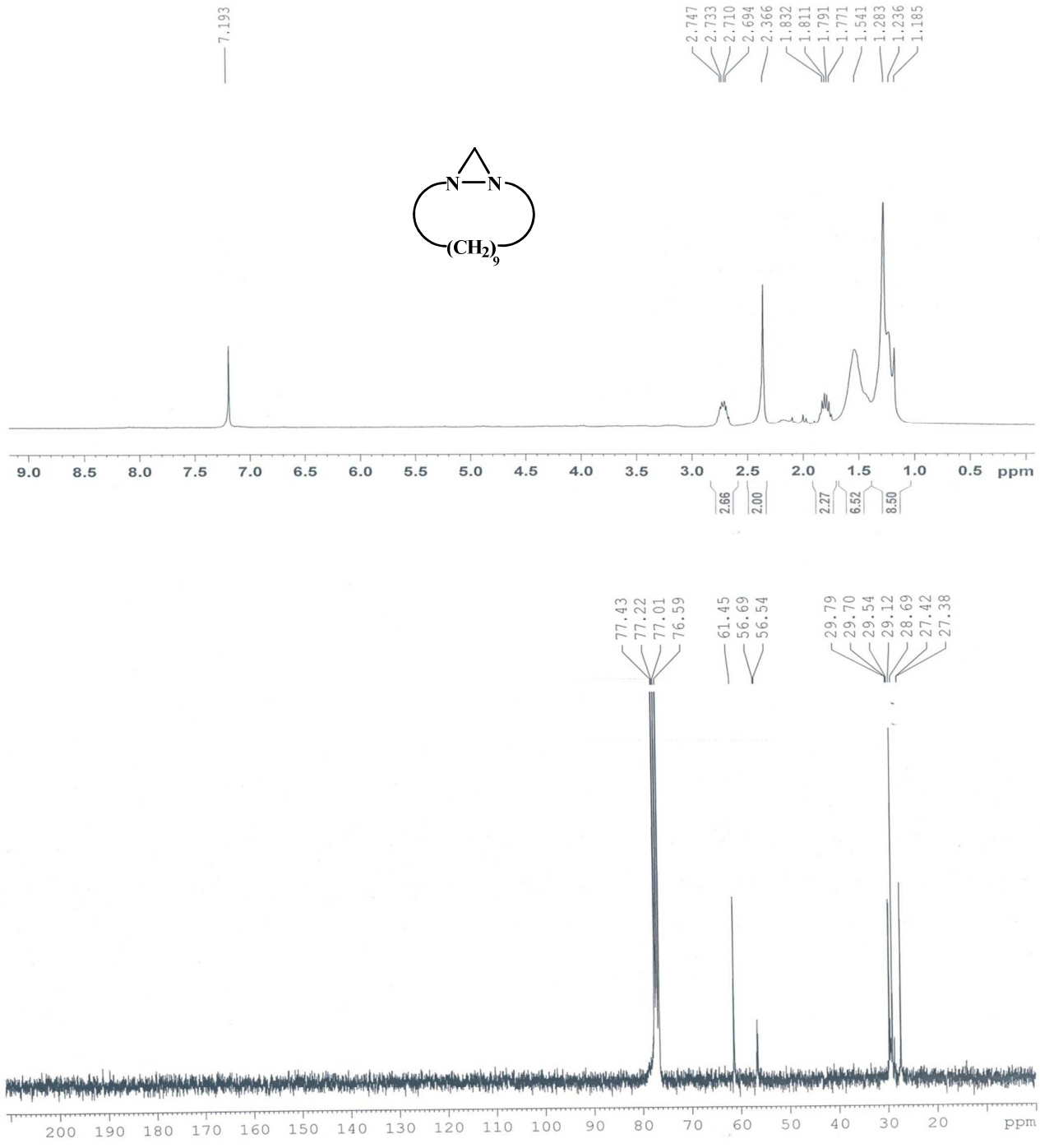
SI Figure 9: ^{1}H and ^{13}C-NMR spectra of compound **6i**



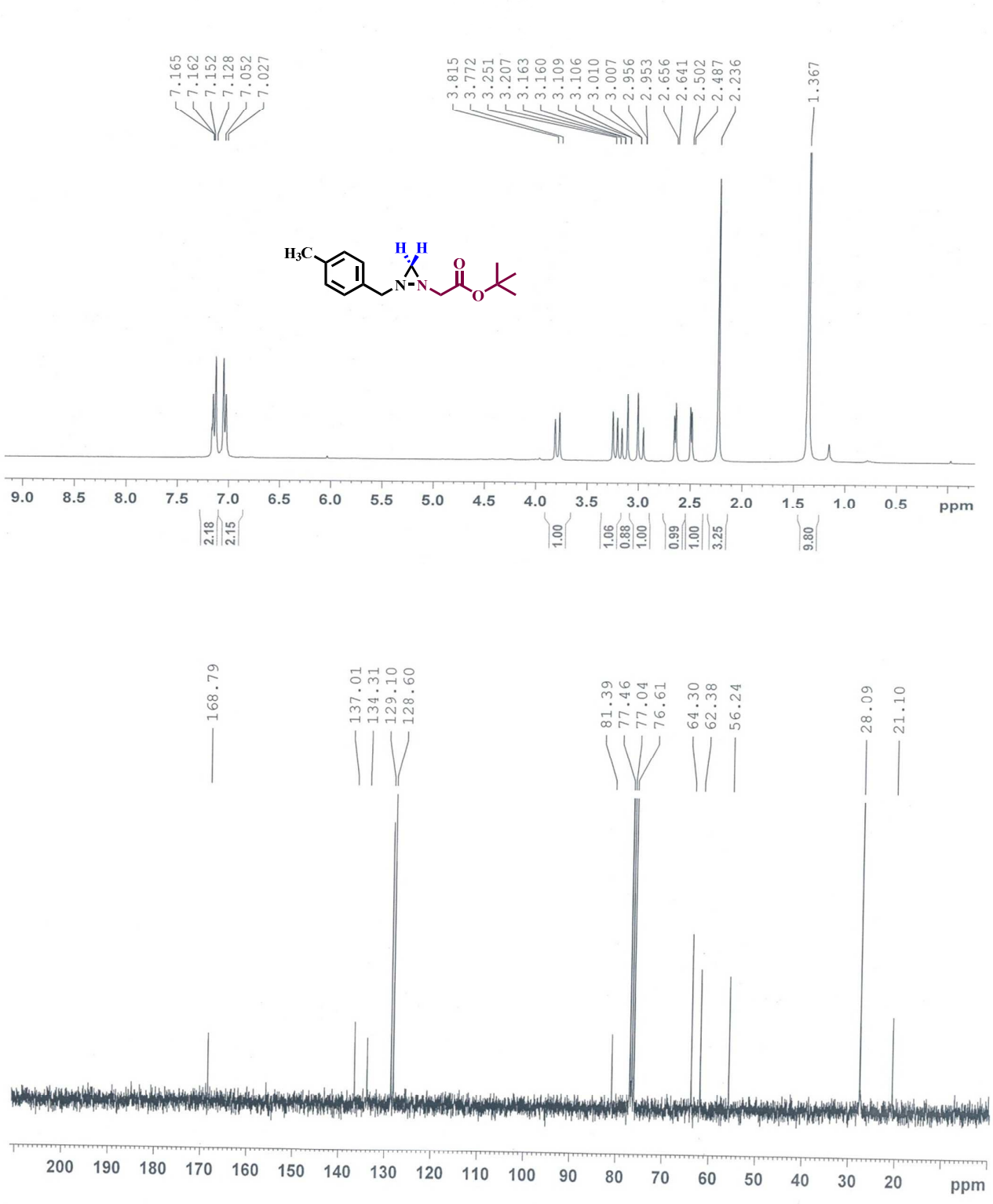
SI Figure 10: ^{1}H and ^{13}C-NMR spectra of compound **6j**



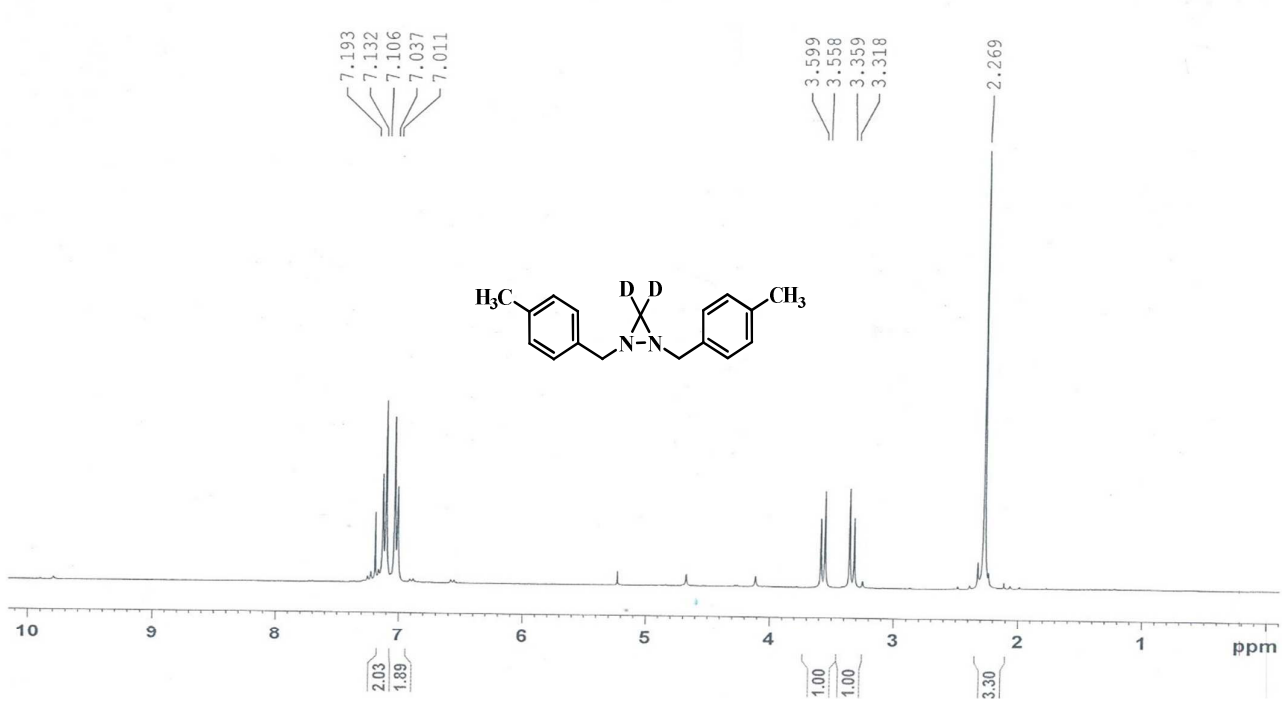
SI Figure 11: ^{1}H and ^{13}C-NMR spectra of compound **6k**



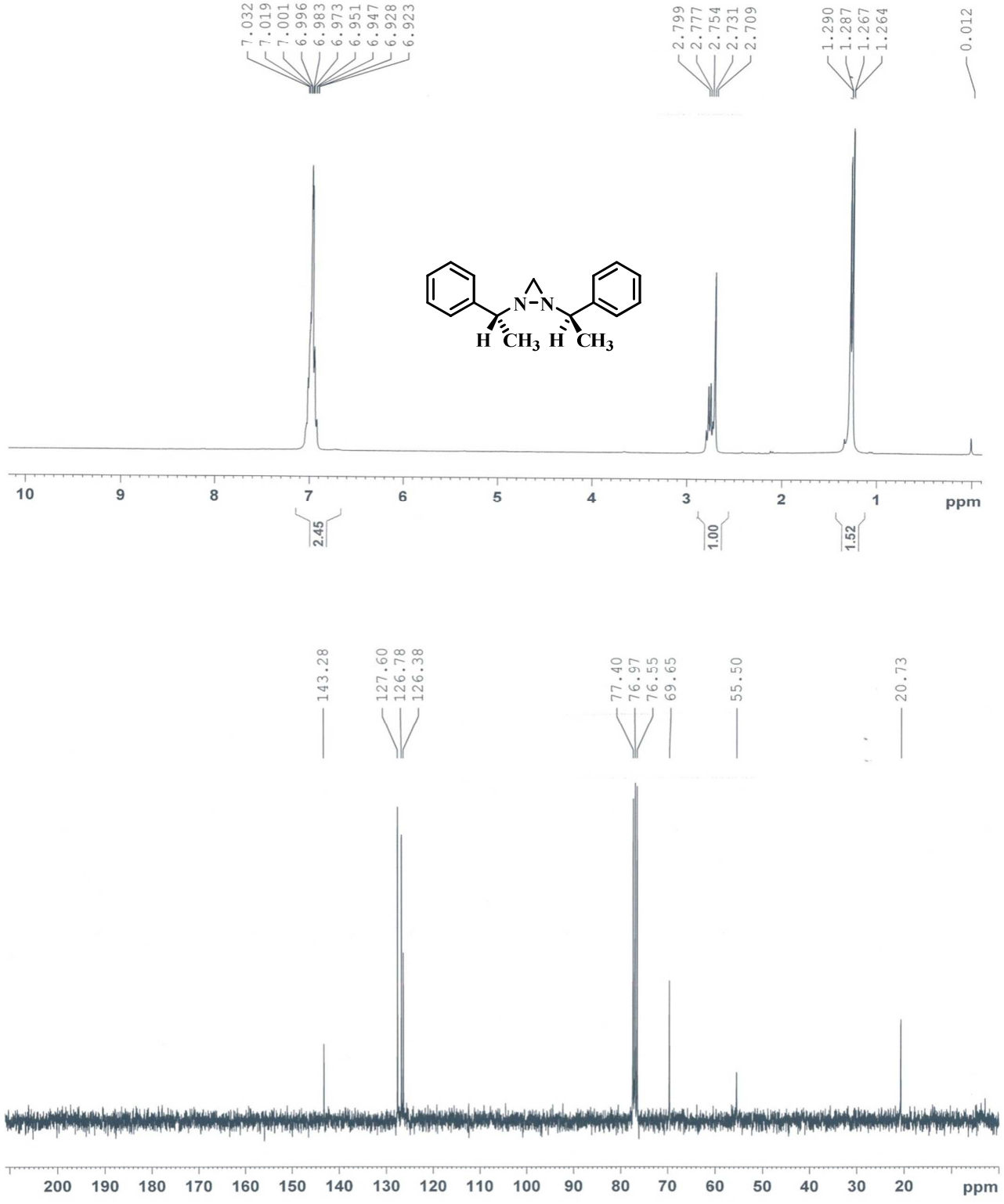
SI Figure 12: ^{1}H and ^{13}C-NMR spectra of compound **6l**



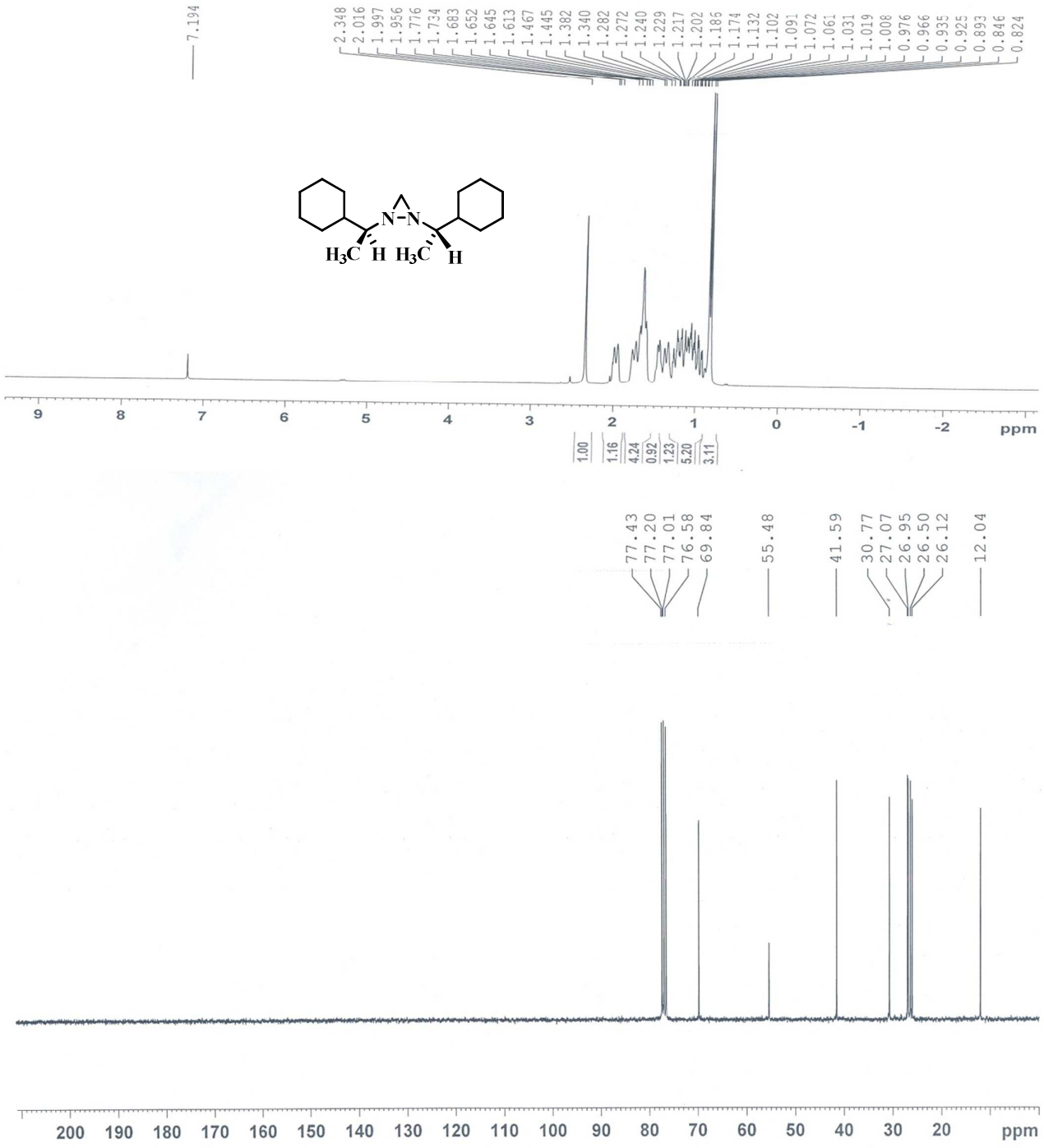
SI Figure 13: ^{1}H spectrum of compound **6b-D_2**



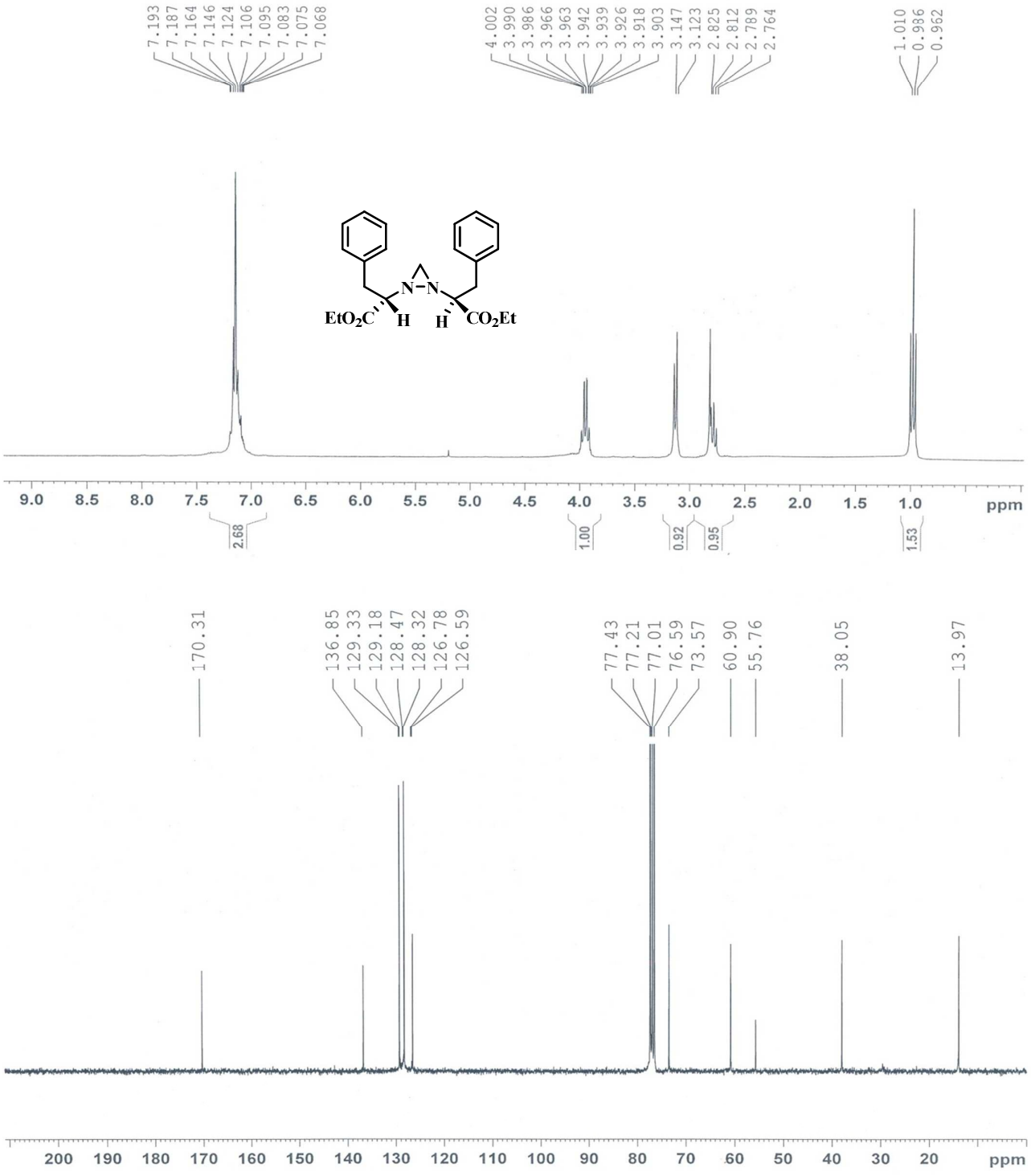
SI Figure 14: ^{1}H and ^{13}C-NMR spectra of compound **7a**



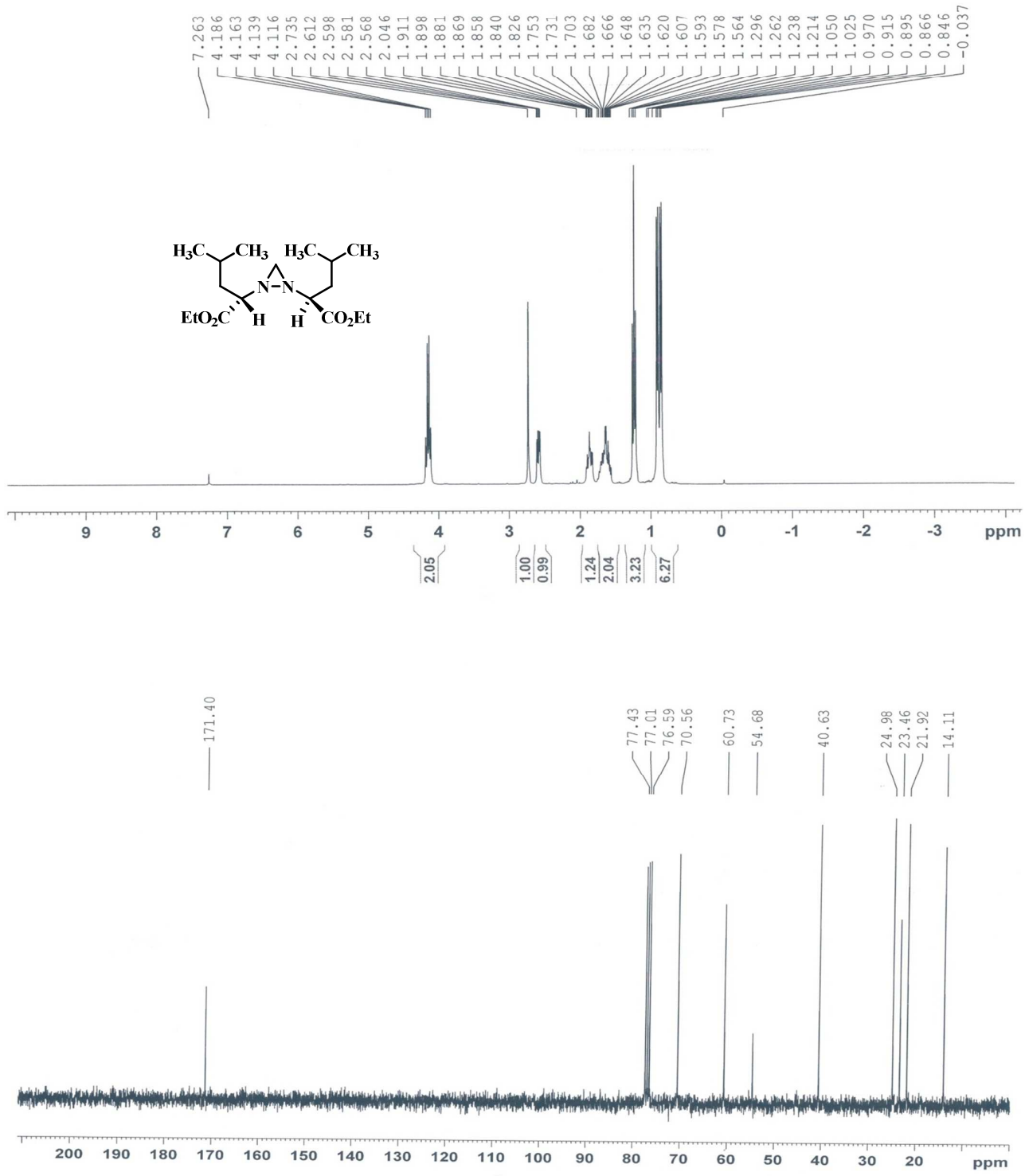
SI Figure 15: ^{1}H and ^{13}C-NMR spectra of compound **7b**



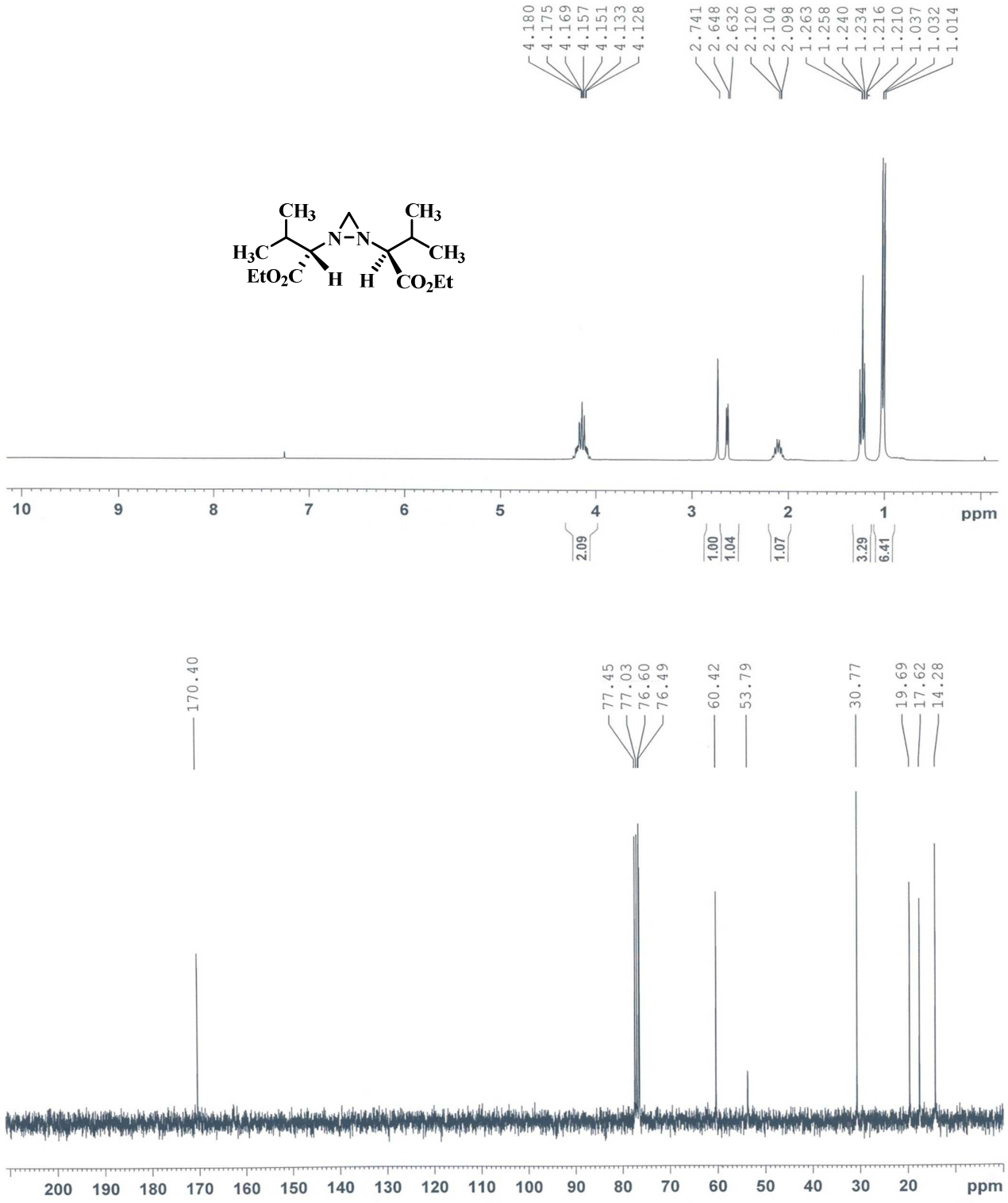
SI Figure 16: ^{1}H and ^{13}C-NMR spectra of compound **7c**



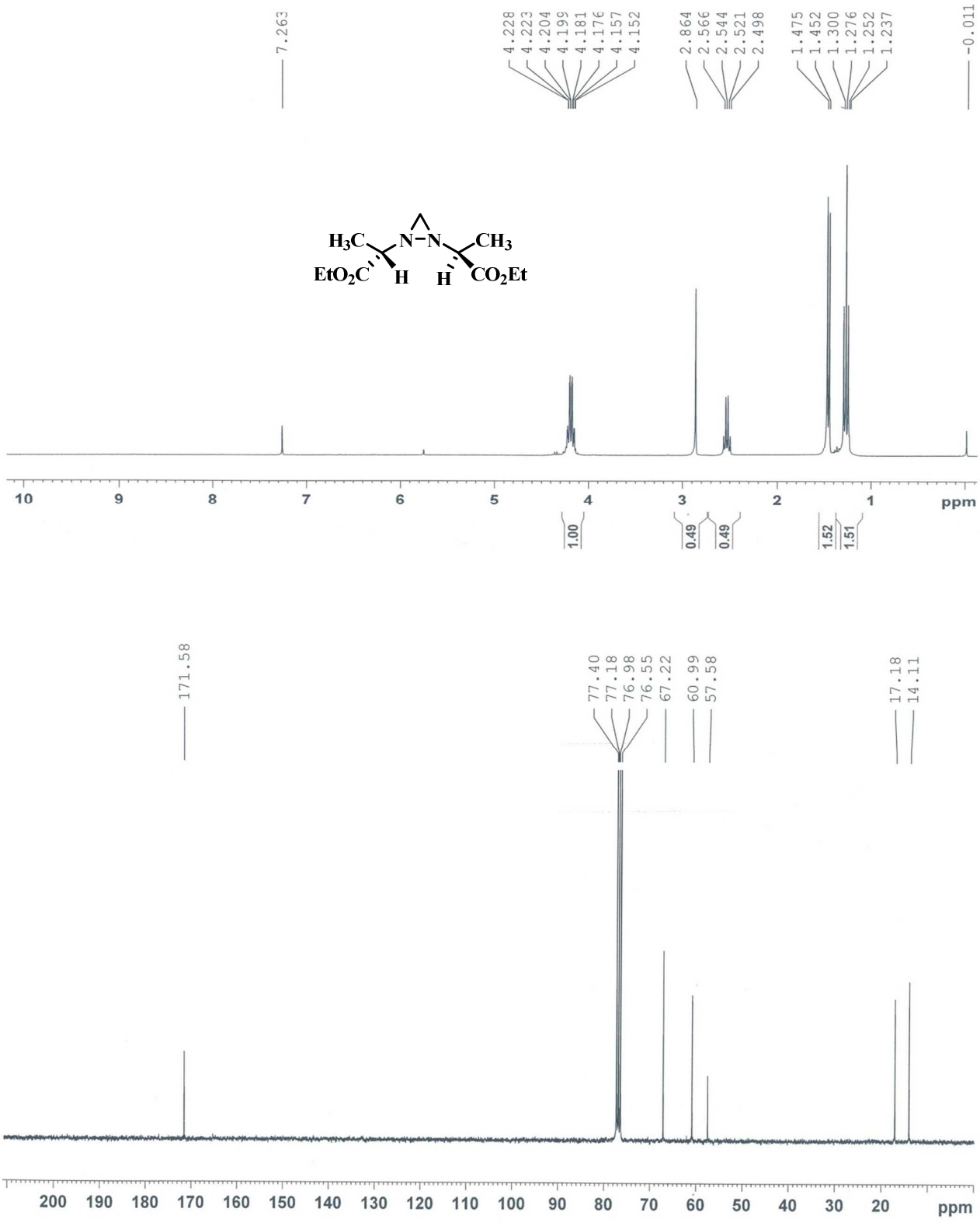
SI Figure 17: ^{1}H and ^{13}C-NMR spectra of compound **7d**



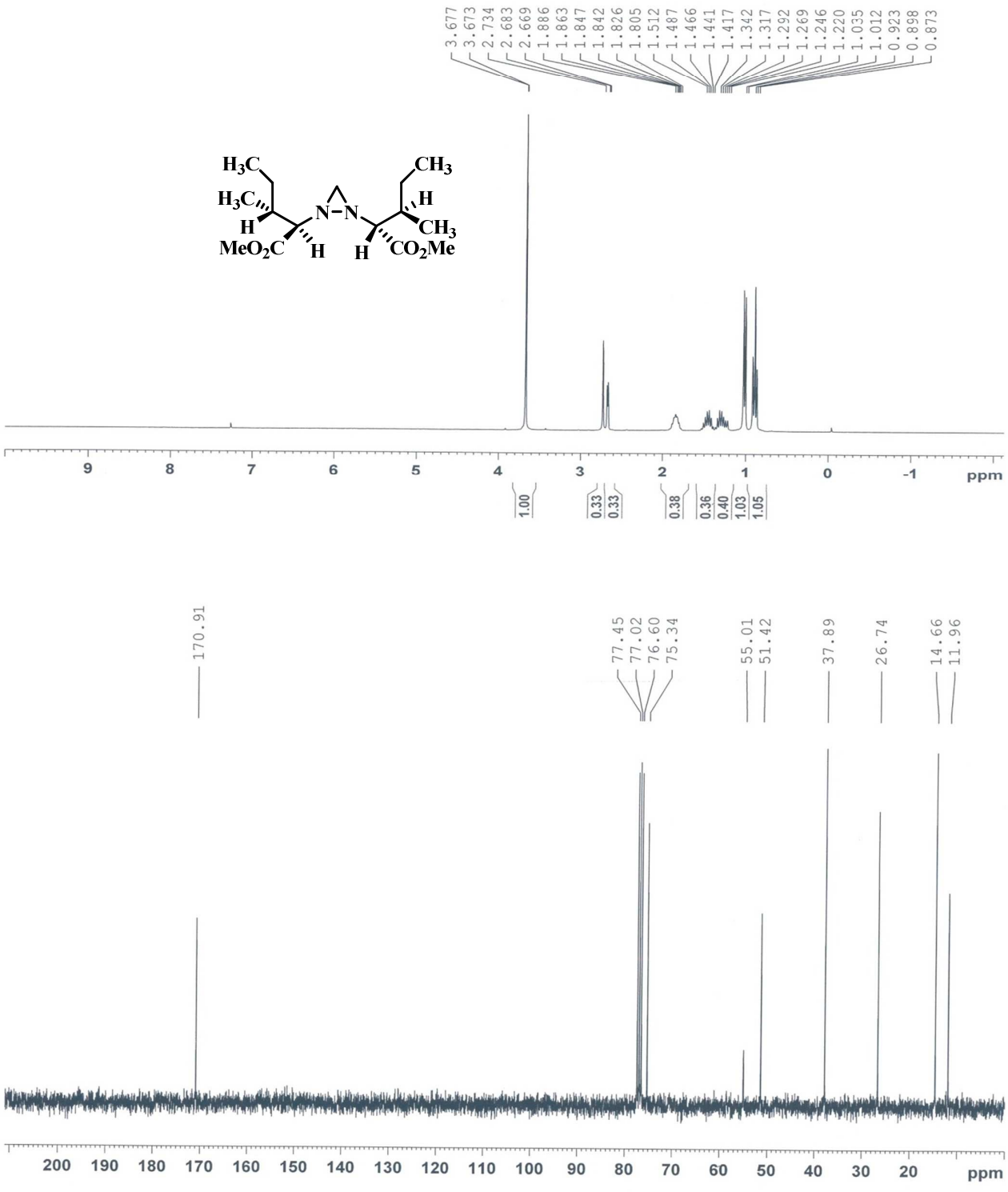
SI Figure 18: ^{1}H and ^{13}C-NMR spectra of compound **7e**



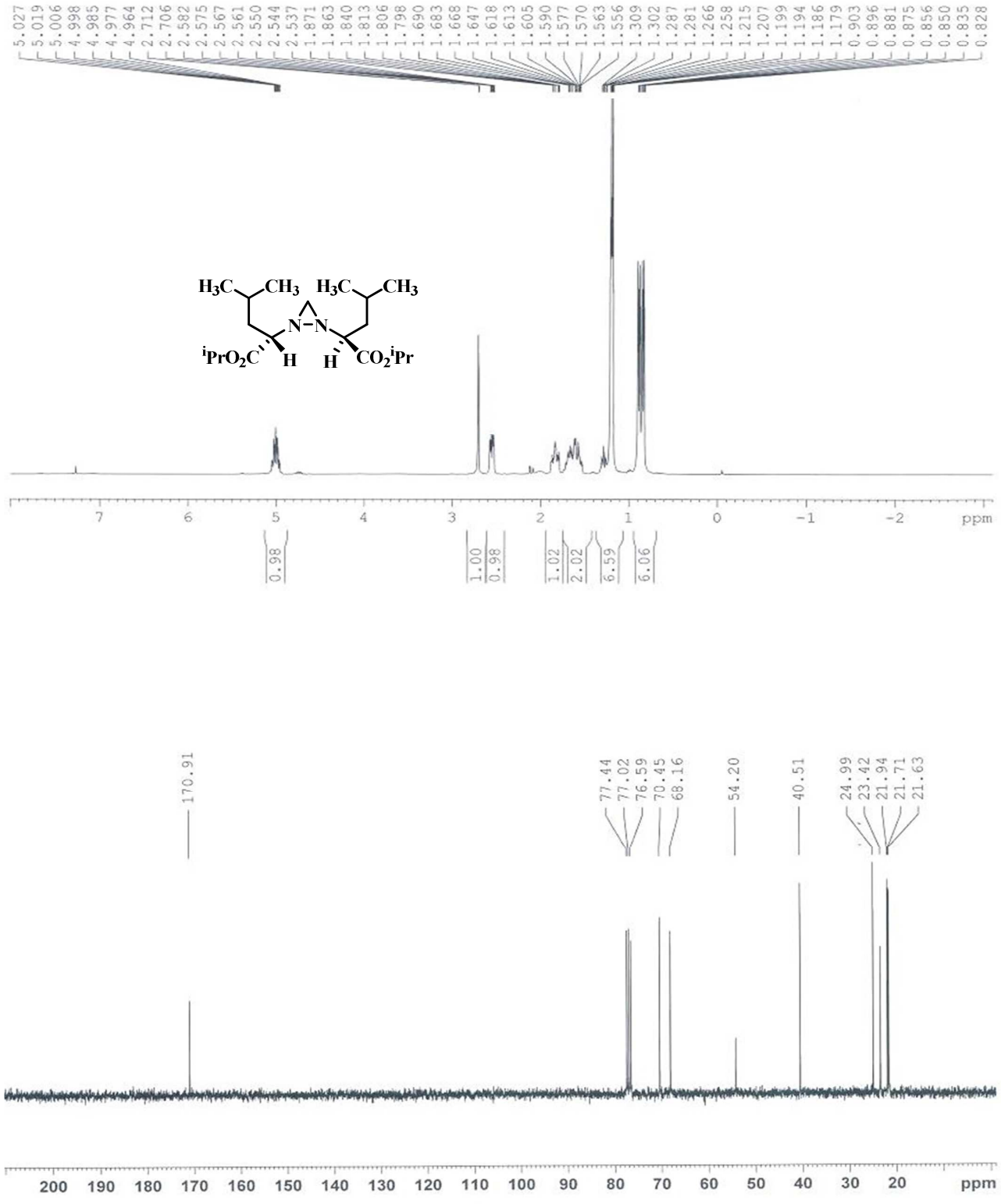
SI Figure 19: ^{1}H and ^{13}C-NMR spectra of compound **7f**



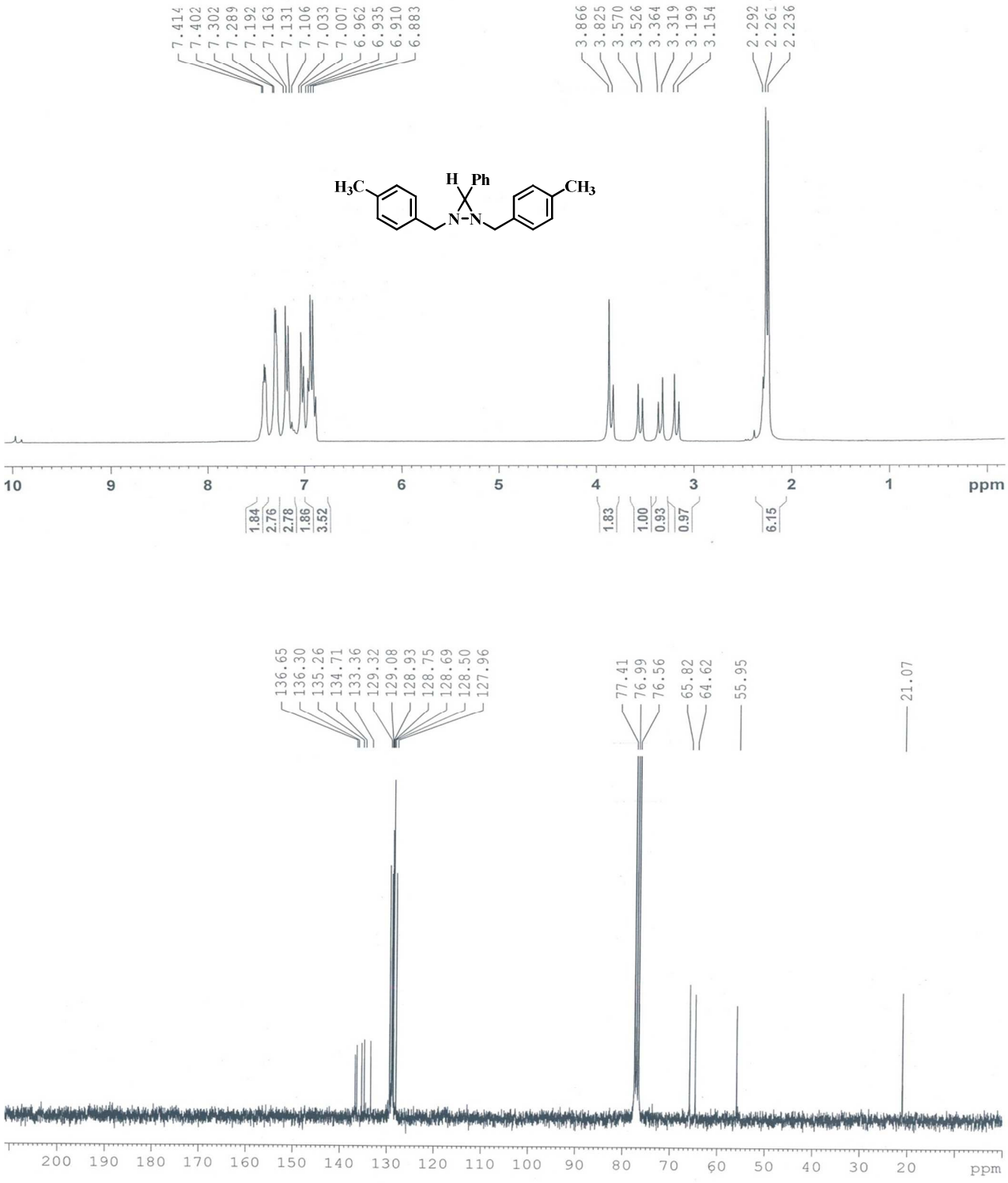
SI Figure 20: ^{1}H and ^{13}C-NMR spectra of compound **7g**



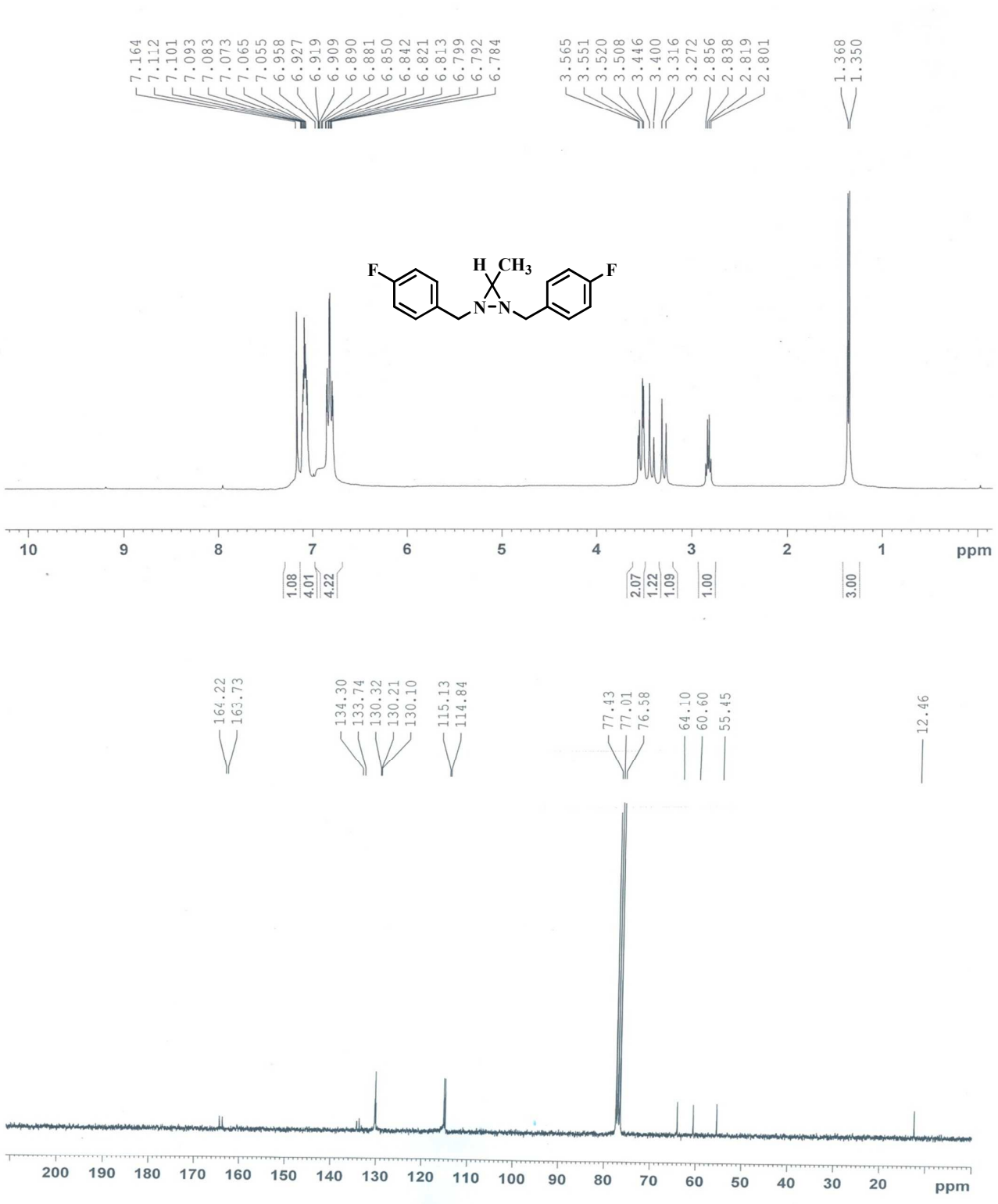
SI Figure 21: ^{1}H and ^{13}C-NMR spectra of compound **7h**



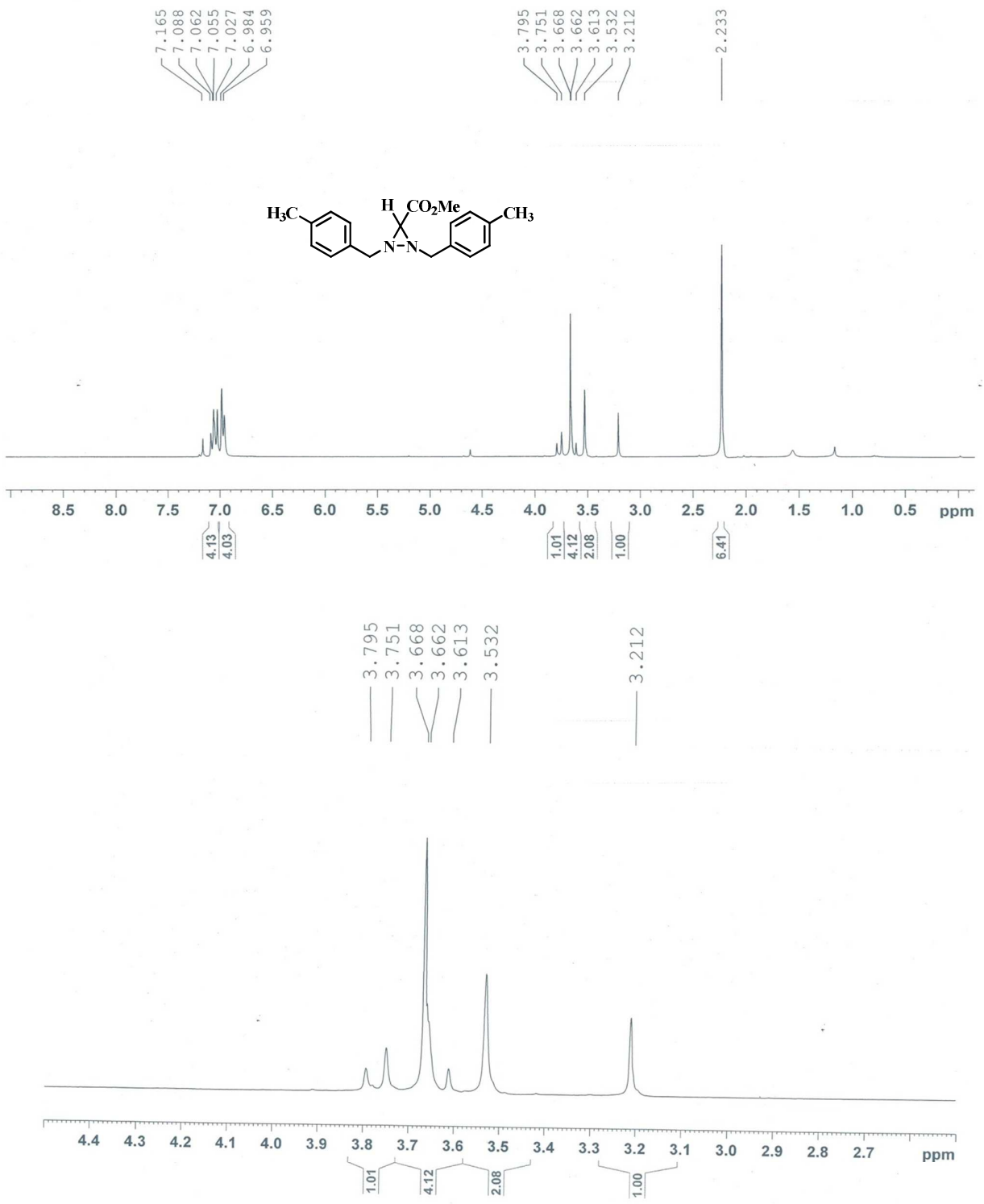
SI Figure 22: ^{1}H and ^{13}C-NMR spectra of compound **8a**

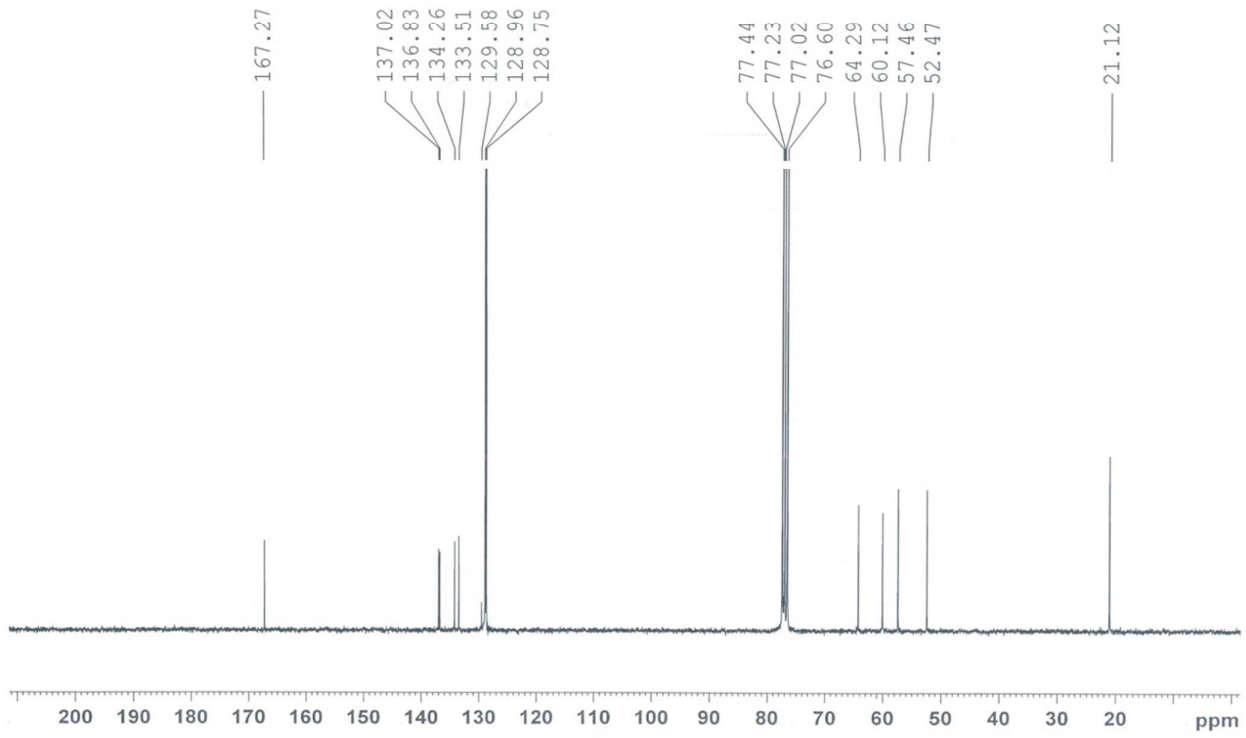


SI Figure 23: ^{1}H and ^{13}C-NMR spectra of compound **8b**

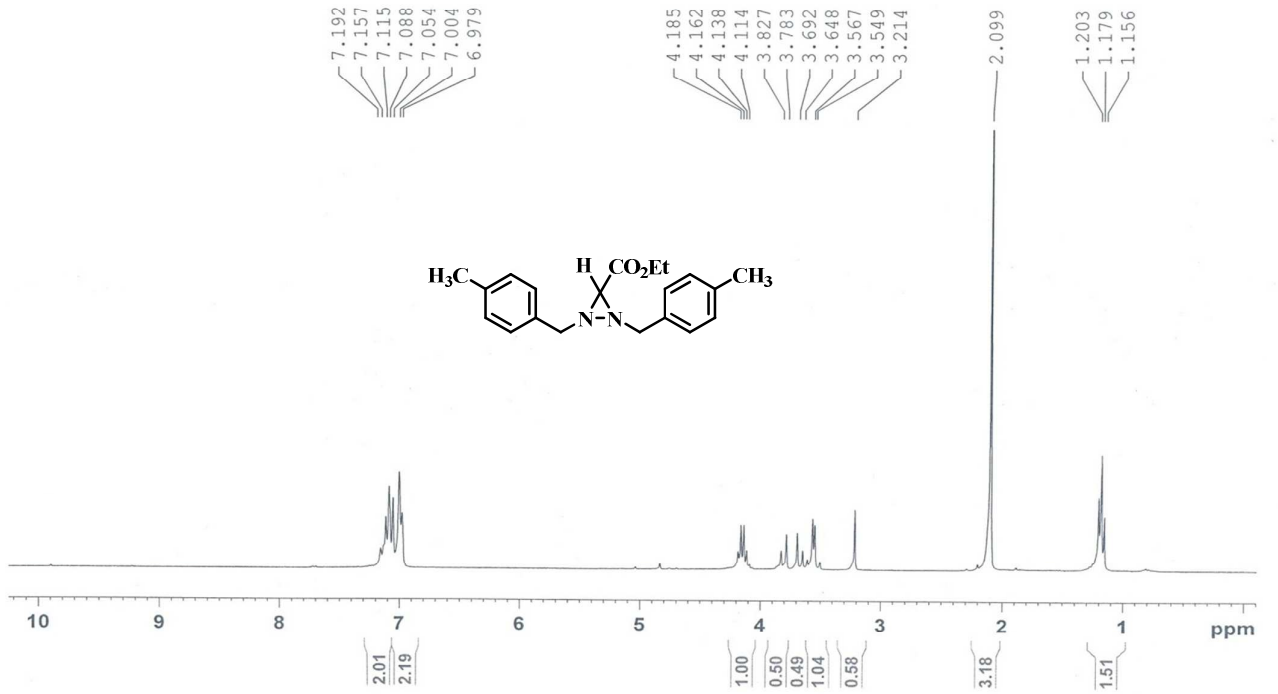


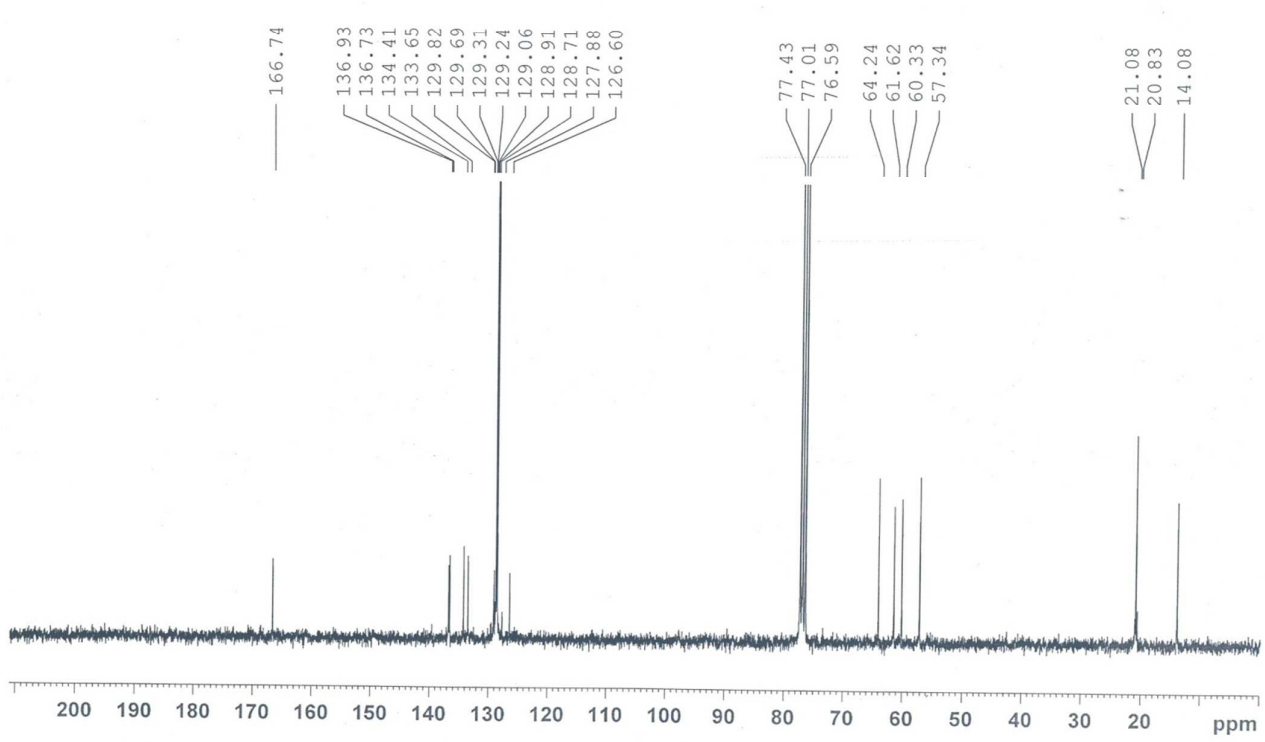
SI Figure 24: ^{1}H and ^{13}C-NMR spectra of compound **8c**



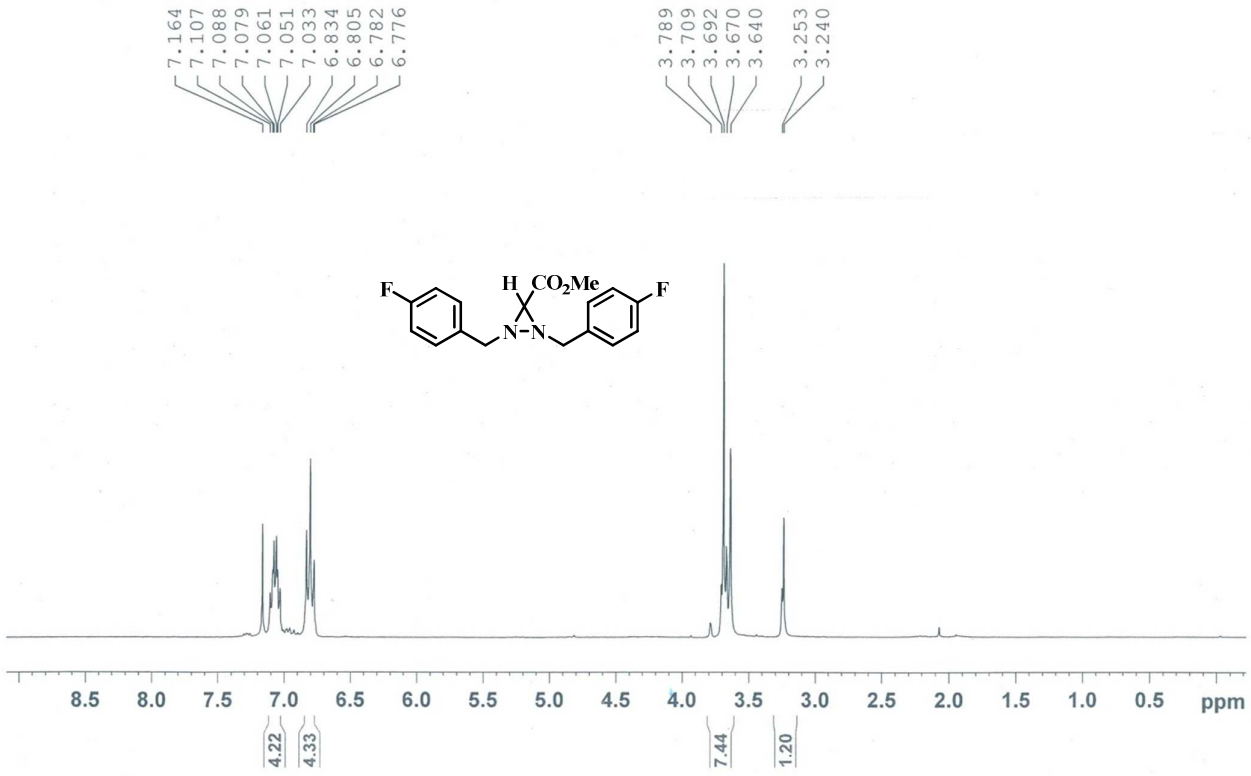


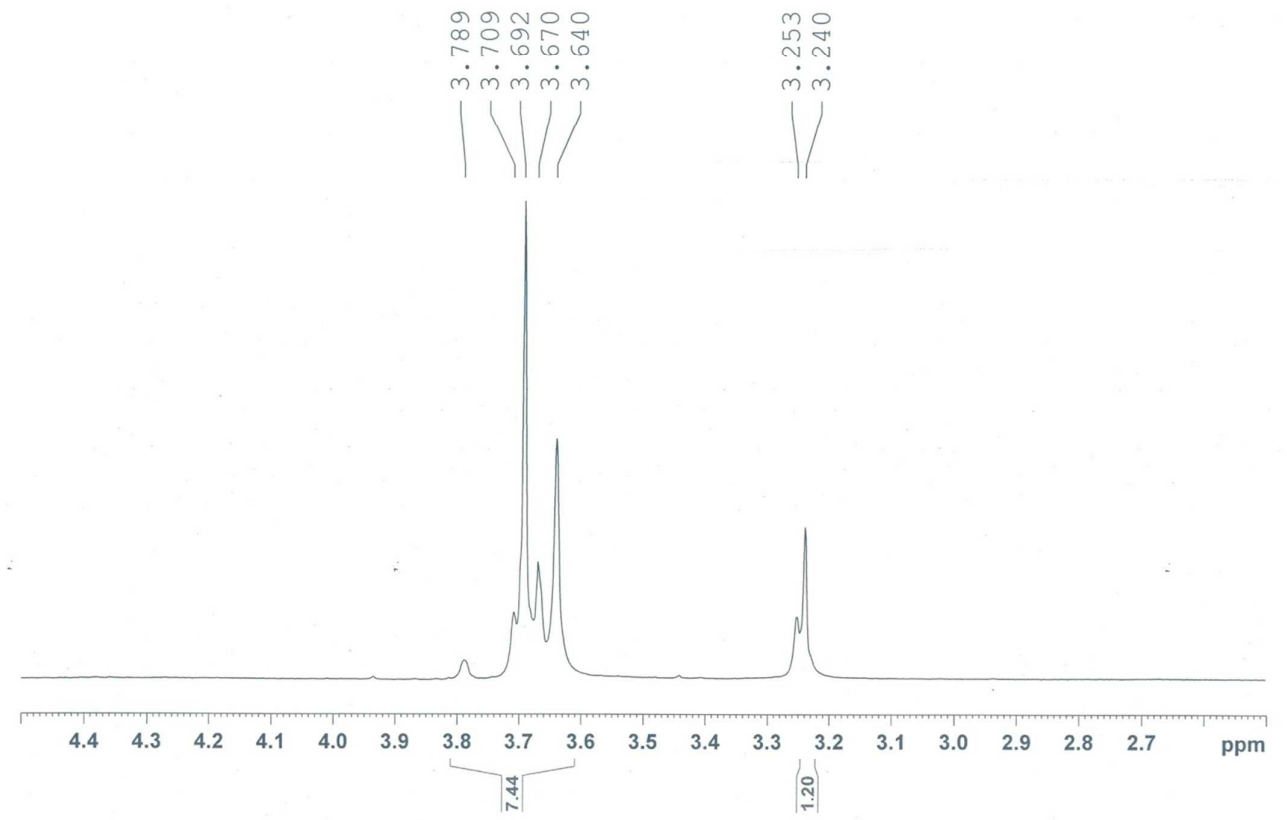
SI Figure 25: ^{1}H and ^{13}C-NMR spectra of compound **8d**

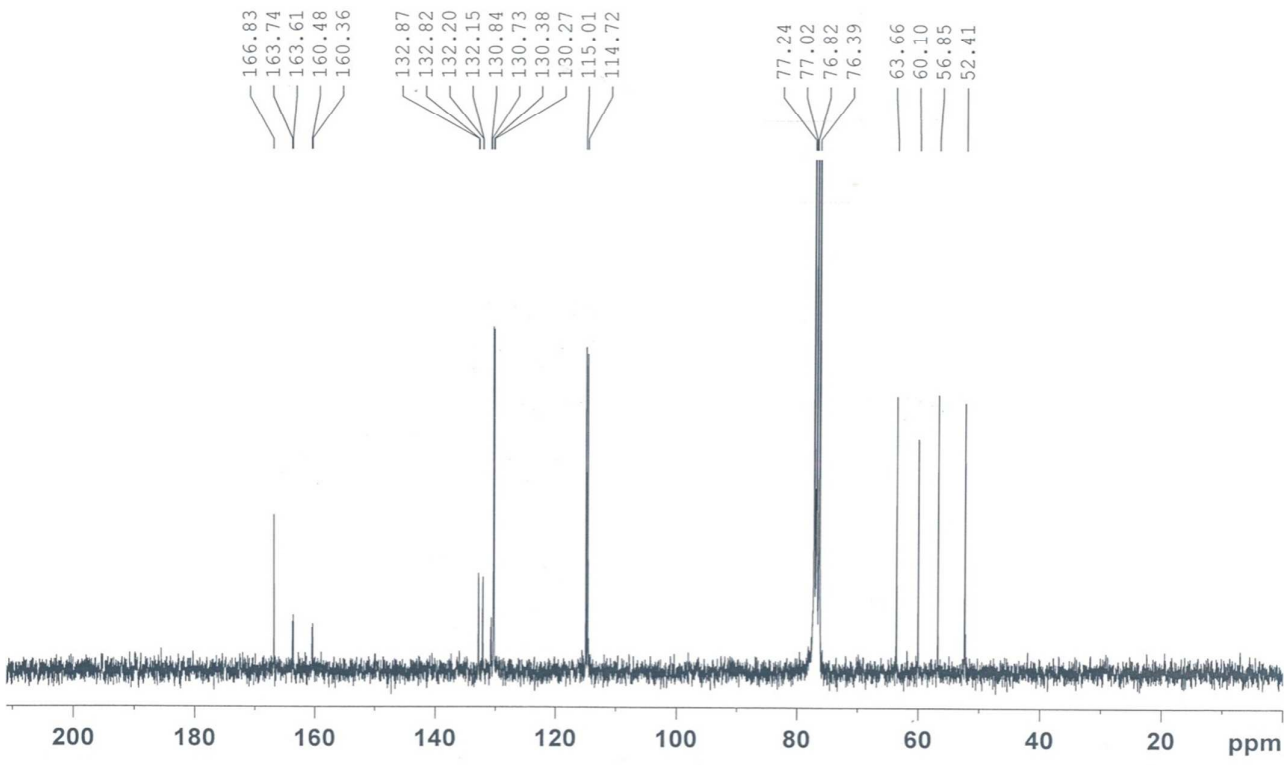




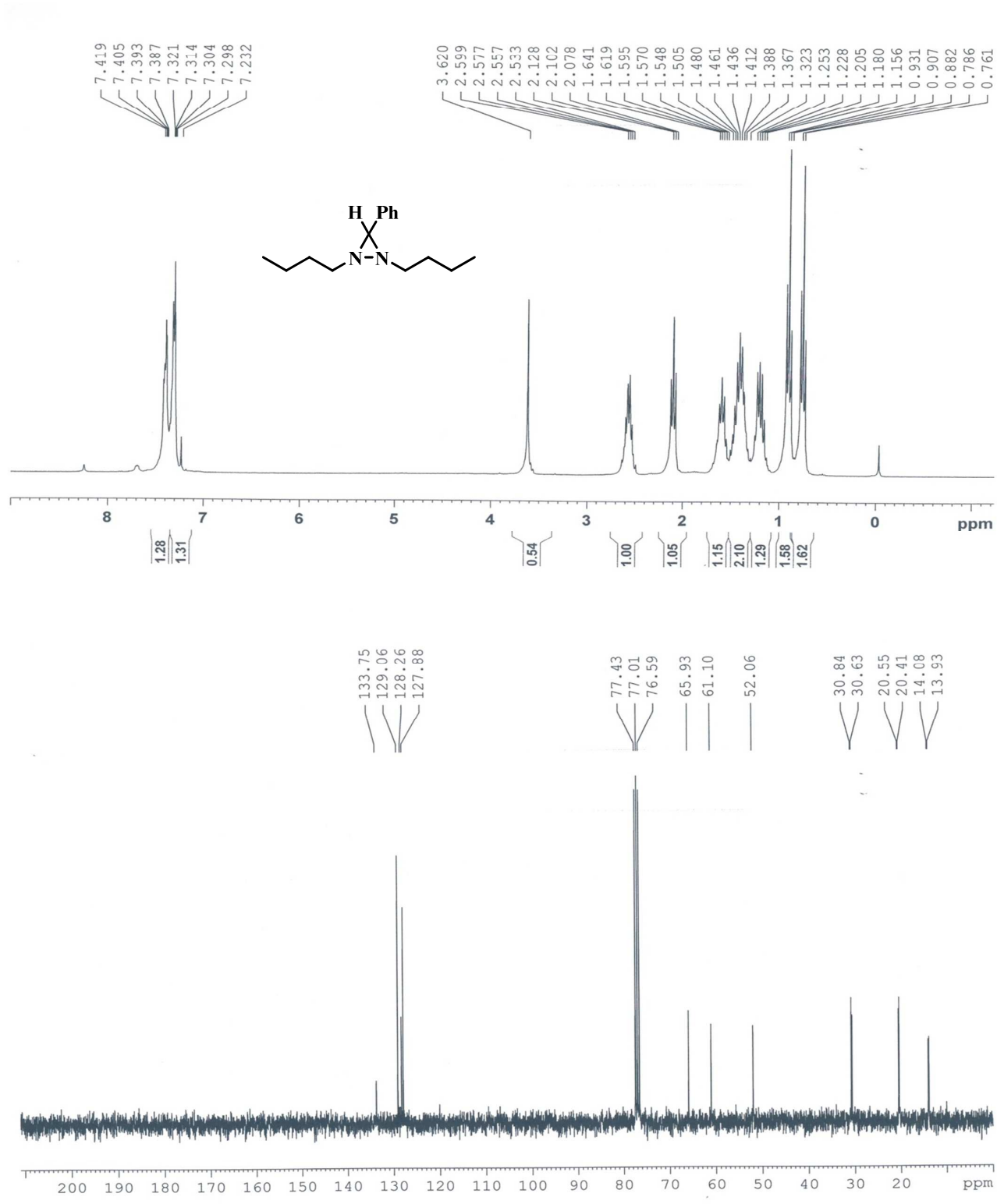
SI Figure 26: ^{1}H and ^{13}C-NMR spectra of compound **8e**



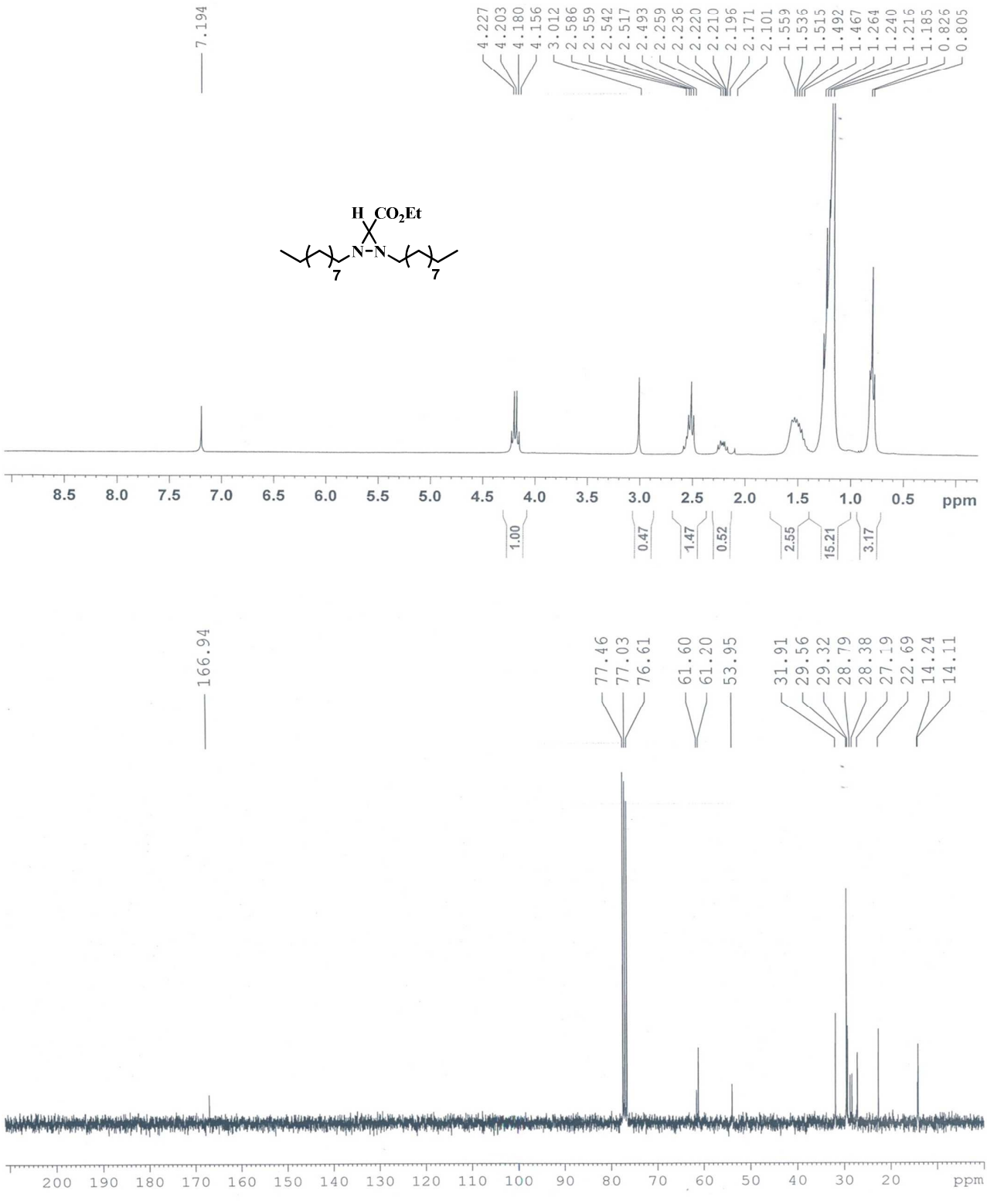

3.789
3.709
3.692
3.670
3.640
3.253
3.240
4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 ppm
7.44
1.20


166.83
163.74
163.61
160.48
160.36
132.87
132.82
132.20
132.15
130.84
130.73
130.38
130.27
115.01
114.72
77.24
77.02
76.82
76.39
63.66
60.10
56.85
52.41
200 180 160 140 120 100 80 60 40 20 ppm

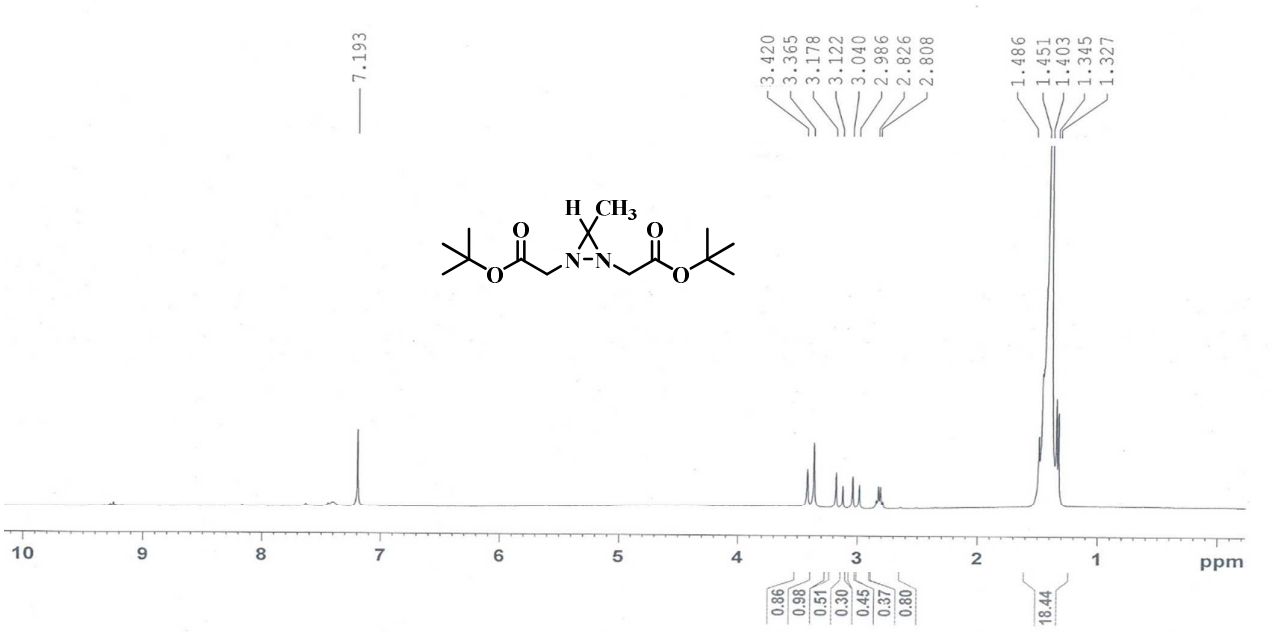
SI Figure 28: ^{1}H and ^{13}C-NMR spectra of compound **8f**

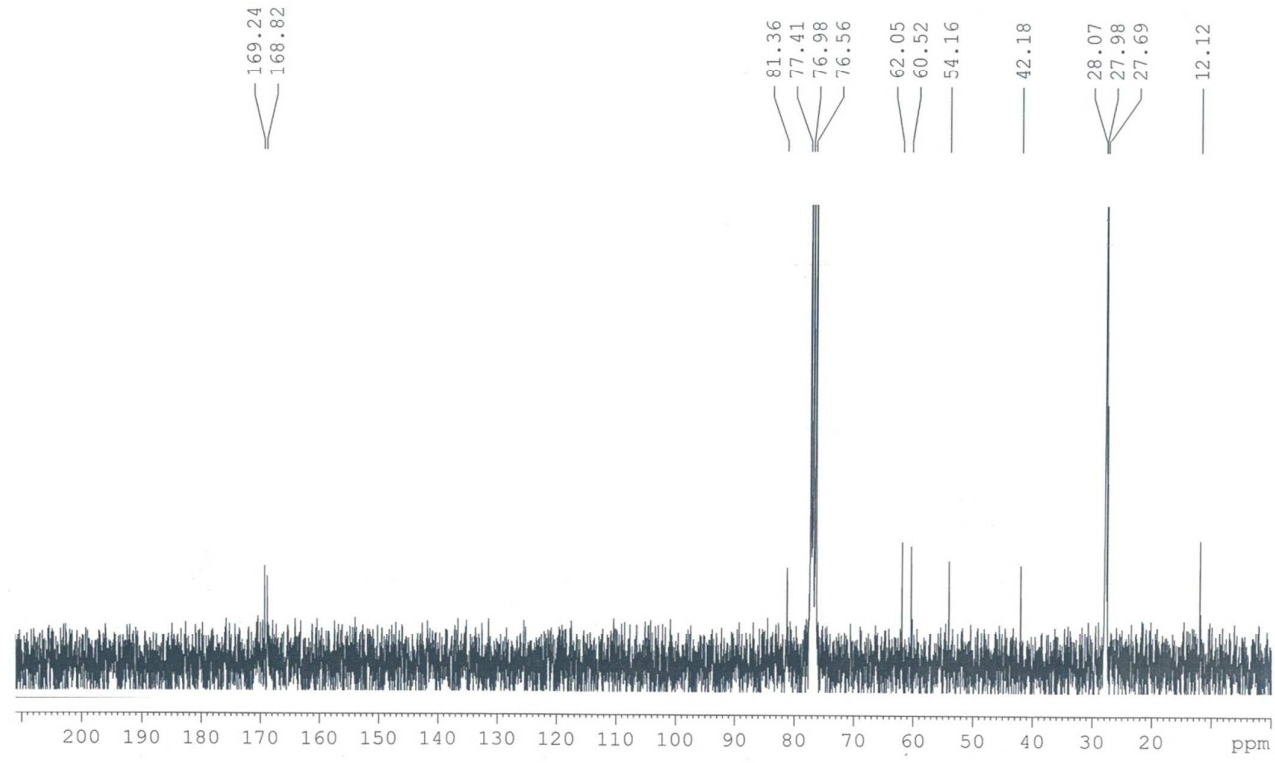


SI Figure 28: ^{1}H and ^{13}C-NMR spectra of compound **8g**

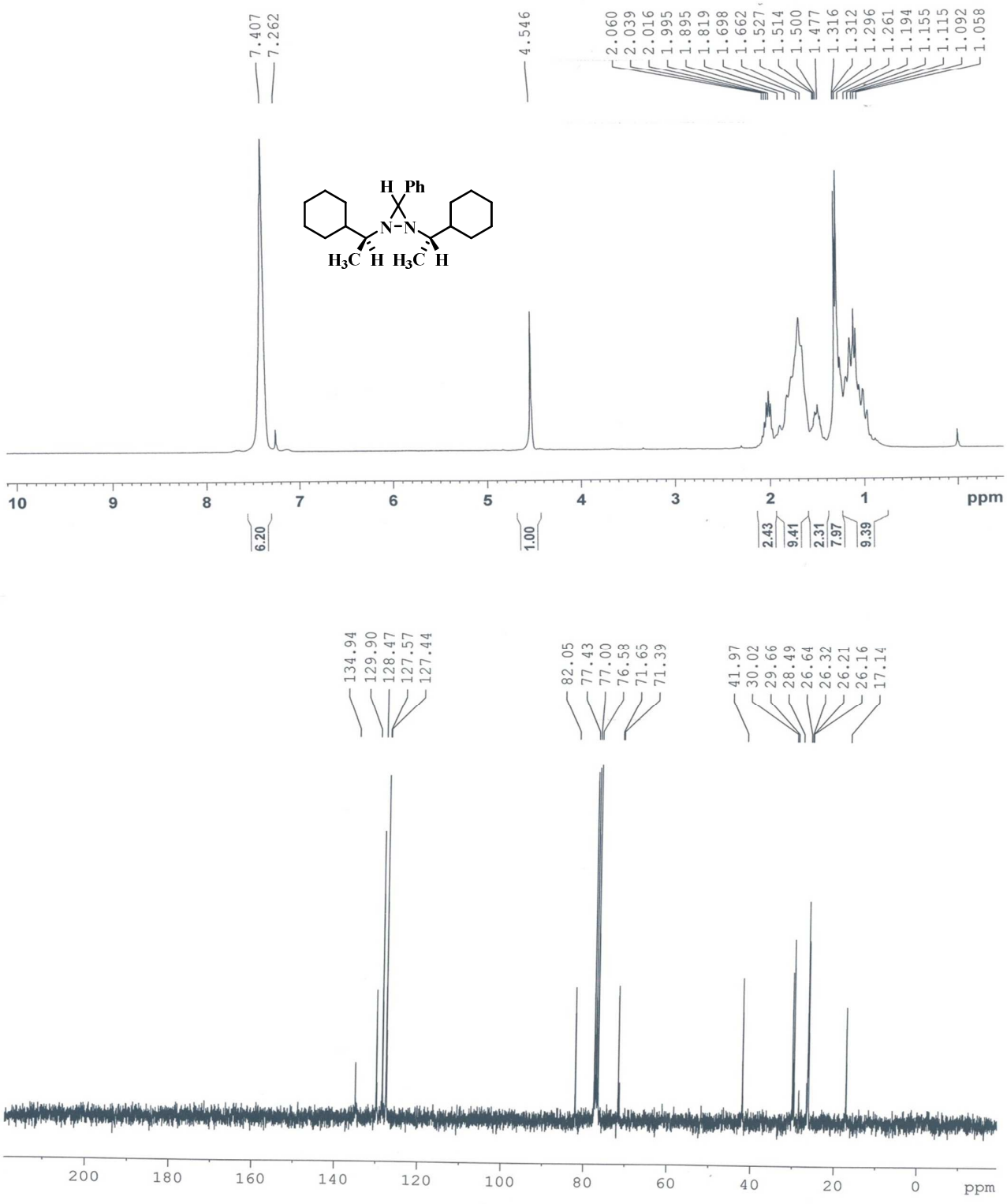


SI Figure 29: ^{1}H and ^{13}C-NMR spectra of compound **8h**

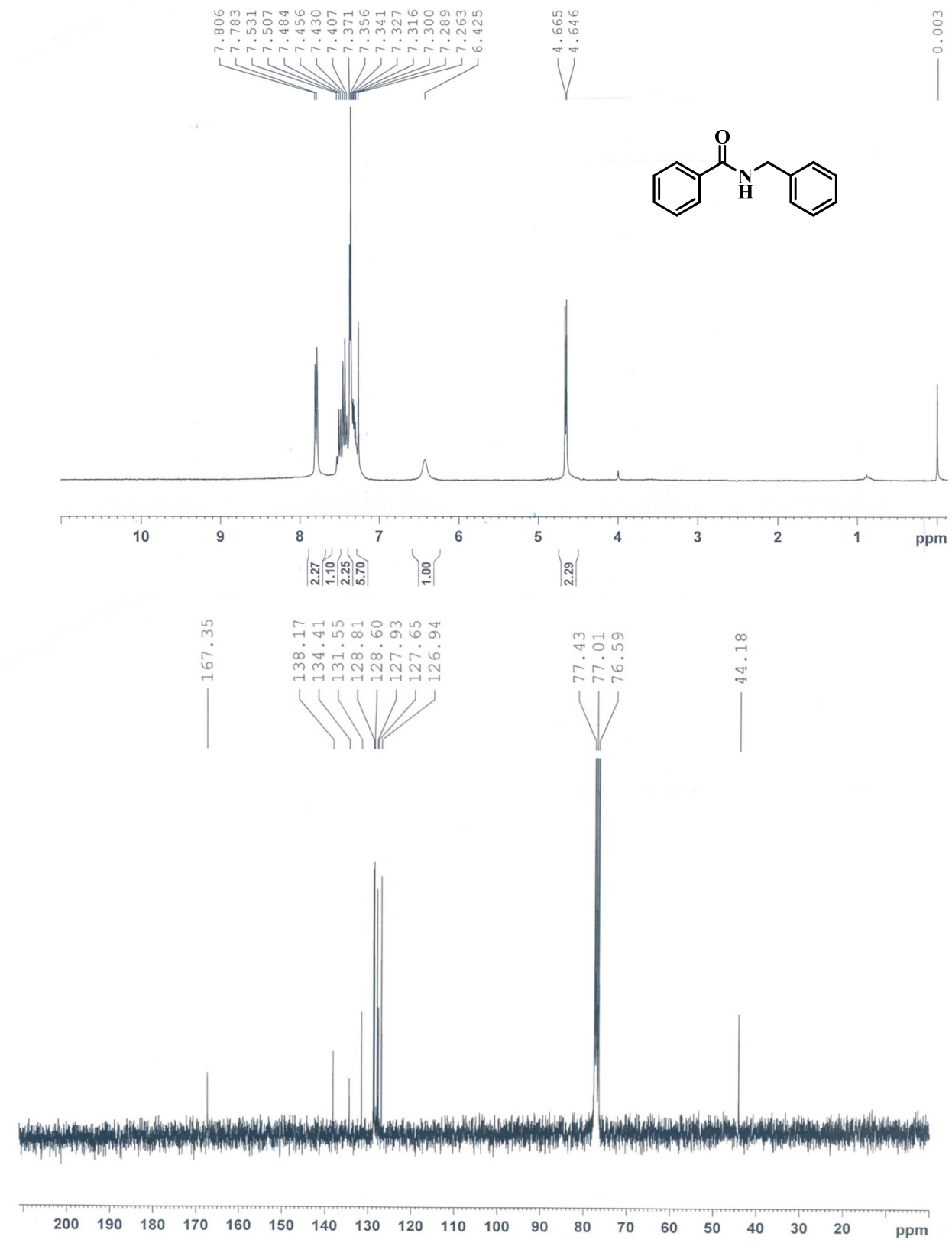




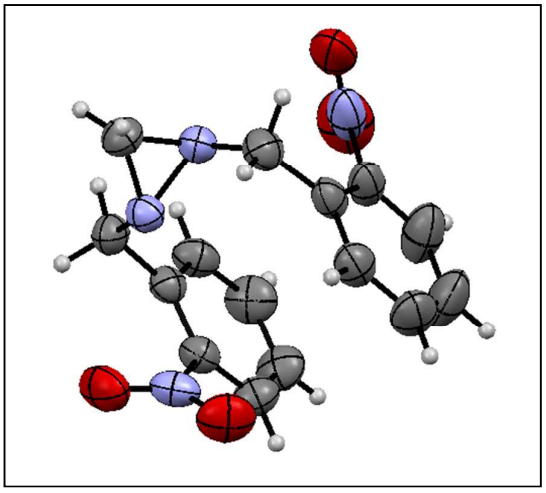
SI Figure 30: ^{1}H and ^{13}C-NMR spectra of compound **8i**



SI Figure 31: ^{1}H and ^{13}C-NMR spectra of compound **9**



9. **Crystal Summary Data of Compound 6d (CCDC 1525569)**



- Chemical formula and formula weight (M): C15 H14 N2 O4and 314.10
- Crystal system: Monoclinic Unit-cell dimensions (angstrom or pm, degrees) and volume, with edges: a 8.006(14) b 12.99(2) c 14.70(2), 90.00, 100.16(2), 90.00, 1504(5)
- Temperature: 296 K
- Space group symbol: P2(1)/n
- No. of formula units in unit cell (Z): 4
- Number of reflections measured and/or number of independent reflections, Rint: 1864
- Final R values (and whether quoted for all or observed data): 0.0506