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New selective cyclizations of alk-4-ynals with primary amines and azoles: one-pot synthesis of 2-azolylpyrrolidines and 3-iminocyclopentenes

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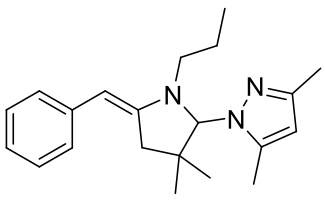
Experimental

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-200p spectrometer in solutions in DMSO-d_6 (for aminals **4a-g**) or in $CDCl_3$ (for imines **7a-f**). Signals of the solvents were used as references. High resolution mass spectra were recorded on a Bruker micrOTOF II instrument with electrospray ionization (ESI). The measurements were performed on the positive ions (capillary voltage 4500 V). Masses were scanned in the range of m/z from 50 to 3000 Da, using an external or an internal calibration (Electrospray Calibrant Solution, Fluka). Solutions of compounds in acetonitrile were injected using a syringe, the flow rate 3 dm min^{-1}. Nebulizer gas was nitrogen (4 dm min^{-1}), the interface temperature was 180 °C.

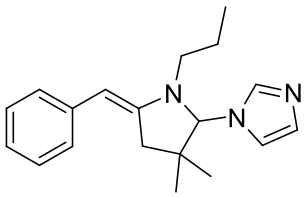
DMSO was distilled in vacuum over CaH_2 prior use. THF was dried over $LiAlH_4$ at room temperature followed by distillation in argon atmosphere. Starting aldehydes **1a-c** were prepared from corresponding propargylic chlorides (1-chloro-3-phenylprop-2-yne, 1-chloro-3-(2-thienyl) prop-2-yne) and aldehydes (isobutyraldehyde and cyclohexanecarboxaldehyde) according to the procedure described in our previous work[1].

Characterization data for compounds **4b-g** *and* **7b-f.**

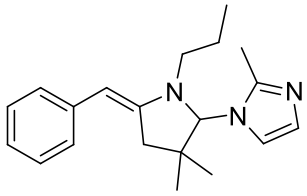


1-[(5E)-5-Benzylidene-3,3-dimethyl-1-propylpyrrolidin-2-yl]-3,5-dimethyl-1H-pyrazole **4b** was prepared from aldehyde **1a,** *n*-propylamine and 2,5-dimethylpyrazole in 75% yield. ^{1}H NMR, δ: 0.63 (s, 3H, CH_3), 0.84 (t, 3H, CH_3, J 7.4 Hz), 1.11 (s, 3H, CH_3), 1.26-1.63 (m, 2H, $NCH_2CH_2CH_3$), 2.07 (s, 3H, CH_3 at pyrazole ring), 2.28 (s, 3H, CH_3 at pyrazole ring), 2.50 (d, 1H, =CC*H*H, J 14.8 Hz), 2.75 (ddd, 1H, NC*H*HCH_2CH_3, ^{2}J 14.1 Hz, ^{3}J 8.6 Hz, ^{3}J 5.9 Hz), 3.06 (br.d, 1H, =CC*H*H, J 14.8 Hz), 3.10 (ddd, 1H, NC*H*HCH_2CH_3, ^{2}J 14.1 Hz, ^{3}J 8.6 Hz, ^{3}J 6.4 Hz), 4.99 (s, 1H, NCHN), 5.17 (br. s, 1H, PhC*H*=), 5.81 (s, 1H, $C^{4}H$, pyrazole), 6.84-6.96 (m, 1H, Ph), 7.05-7.25 (m, 4H, Ph). ^{13}C NMR, δ: 10.8 (CH_3 at pyrazole ring), 11.6 ($NCH_2CH_2CH_3$), 13.8 (CH_3 at

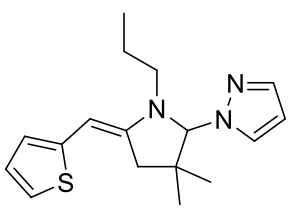
pyrazole ring), 19.6 ($NCH_2CH_2CH_3$), 21.4 (CH_3), 28.0 (CH_3), 40.7 ($C(CH_3)_2$), 43.0, 45.6 ($NCH_2CH_2CH_3$, $=CCH_2$-), 81.1 (NCHN), 91.2 (PhCH=), 104.8 (C^4, pyrazole), 122.1 (C^4, Ph), 125.8, 128.1 (C^2, C^3, C^5, C^6, Ph), 139.5, 140.3 (C^5, pyrazole; C^1, Ph), 146.6, 148.9 (C^3, pyrazole; PhCH=*C*). Found (%): C, 78.15; H, 8.78; N, 12.74. Calc. for $C_{21}H_{29}N_3$ (%): C, 77.97; H, 9.04; N, 12.99.



1-[(5E)-5-Benzylidene-3,3-dimethyl-1-propylpyrrolidin-2-yl]-1H-imidazole **4c** was prepared from aldehyde **1a**, *n*-propylamine and imidazole in 59% yield. ^{1}H NMR, δ: 0.65 (s, 3H, CH_3), 0.86 (t, 3H, CH_3, *J* 7.4 Hz), 1.10 (s, 3H, CH_3), 1.33-1.65 (m, 2H, $NCH_2CH_2CH_3$), 2.59 (d, 1H, =CC*H*H, *J* 14.9 Hz), 2.81 (ddd, 1H, C*H*HCH$_2$CH$_3$, ^2J 14.1 Hz, ^3J 8.5 Hz, ^3J 5.9 Hz), 2.87 (br.d, 1H, =CC*H*H, *J* 14.8 Hz), 3.17 (ddd, 1H, NC*H*HCH$_2$CH$_3$, ^2J 14.1 Hz, ^3J 8.5 Hz, ^3J 6.3 Hz), 5.26 (s, 1H, NCHN), 5.30 (br. s, 1H, PhC*H*=), 6.90-7.01 (m, 1H, Ph), 6.94 (br. s, 1H, C^4H, imidazole), 7.03 (br. s, 1H, C^5H, imidazole), 7.12-7.27 (m, 4H, Ph), 6.94 (s, 1H, C^2H, imidazole). ^{13}C NMR, δ: 11.4 ($NCH_2CH_2CH_3$), 19.4 ($NCH_2CH_2CH_3$), 21.6 (CH_3), 27.3 (CH_3), 40.1 ($C(CH_3)_2$), 41.9, 45.5 ($NCH_2CH_2CH_3$, $=CCH_2$-), 81.9 (NCHN), 92.6 (PhCH=), 117.5 (C^5,imidazole), 122.7 (C^4, Ph), 126.3, 128.1 (C^2, C^3, C^5, C^6, Ph), 128.7 (C^4, imidazole), 136.4 (C^2, imidazole), 139.6 (C^1, Ph), 146.6 (PhCH=*C*). Found (%): C, 77.38; H, 8.39; N, 14.30. Calc. for $C_{19}H_{25}N_3$ (%): C, 77.25; H, 8.53; N, 14.22.

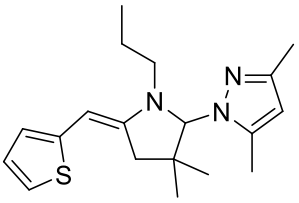


1-[(5E)-5-Benzylidene-3,3-dimethyl-1-propylpyrrolidin-2-yl]-2-methyl-1H-imidazole **4d** was prepared from aldehyde **1a** , *n*-propylamine and 2-methylimidazole in 64% yield. ^{1}H NMR, δ: 0.64 (s, 3H, CH_3), 0.86 (t, 3H, CH_3, *J* 7.4 Hz), 1.13 (s, 3H, CH_3), 1.36-1.64 (m, 2H, $NCH_2CH_2CH_3$), 2.36 (s, 3H, CH_3 at imidazole ring), 2.57 (d, 1H, =CC*H*H, *J* 14.9 Hz), 2.82 (ddd, 1H, C*H*HCH$_2$CH$_3$, ^2J 14.1 Hz, ^3J 8.5 Hz, ^3J 5.9 Hz), 2.84 (br.d, 1H, =CC*H*H, *J* 14.8 Hz), 3.15 (ddd, 1H, NC*H*HCH$_2$CH$_3$, ^2J 14.1 Hz, ^3J 8.5 Hz, ^3J 6.3 Hz), 5.10 (s, 1H, NCHN), 5.28 (br. s, 1H, PhC*H*=), 6.72 (d, 1H, C^4H, imidazole, *J* 1.3 Hz), 6.79 (d, 1H, C^5H, imidazole, *J* 1.3 Hz), 6.88-7.00 (m, 1H, Ph), 7.11-7.26 (m, 4H, Ph).). ^{13}C NMR, δ: 11.4 ($NCH_2CH_2CH_3$), 13.3 (CH_3 at imidazole ring), 19.4 ($NCH_2CH_2CH_3$), 21.7 (CH_3), 27.7 (CH_3), 40.4 ($C(CH_3)_2$), 42.1, 45.7 ($NCH_2CH_2CH_3$, $=CCH_2$-), 80.7 (NCHN), 92.5 (PhCH=), 115.7 (C^5,imidazole), 122.7 (C^4, Ph), 126.2, 128.1 (C^2, C^3, C^5, C^6, Ph), 128.0 (C^4, imidazole), 139.6 (C^1, Ph), 146.6 (PhCH=*C*), 148.1 (C^2, imidazole). Found (%): C, 77.44; H, 8.58; N, 13.71. Calc. for $C_{20}H_{27}N_3$ (%): C, 77.63; H, 8.79; N, 13.58.

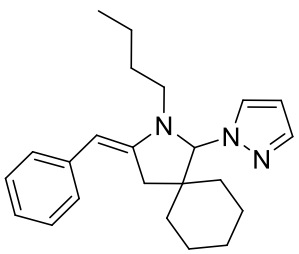


1-[(5E)-3,3-Dimethyl-1-propyl-5-(2-thienylmethylidene)pyrrolidin-2-yl]-1H-pyrazole **4e** was prepared from aldehyde **1b,** *n*-propylamine and pyrazole in

68% yield. ^{1}H NMR, δ: 0.61 (s, 3H, CH_3), 0.83 (t, 3H, CH_3, J 7.4 Hz), 1.16 (s, 3H, CH_3), 1.25-1.61 (m, 2H, $NCH_2CH_2CH_3$), 2.64 (d, 1H, =CC*H*H, J 14.8 Hz), 2.70 (ddd, 1H, NC*H*HCH_2CH_3, ^{2}J 14.1 Hz, ^{3}J 8.7 Hz, ^{3}J 5.9 Hz), 2.79 (br.d, 1H, =CC*H*H, J 14.8 Hz), 3.08 (ddd, 1H, NC*H*HCH_2CH_3, ^{2}J 14.1 Hz, ^{3}J 8.6 Hz, ^{3}J 6.4 Hz), 5.31 (s, 1H, NCHN), 5.53 (br. s, 1H, ThiC*H*=), 6.27 (dd, 1H, C^{4}H, pyrazole, J 2.2 Hz, J 1.7 Hz), 6.67 (dd, 1H, C^{3}H, thienyl, ^{3}J 3.6 Hz, ^{4}J 1.0 Hz), 6.91 (dd, 1H, C^{4}H, thienyl, ^{3}J 5.2 Hz, ^{3}J 3.6 Hz), 7.08 (dd, 1H, C^{5}H, thienyl, ^{3}J 5.2 Hz, ^{4}J 1.0 Hz), 7.48 (d, 1H, C^{3}H, pyrazole, J 1.7 Hz), 7.72 (d, 1H, C^{5}H, pyrazole, J 2.2 Hz). ^{13}C NMR, δ: 11.4 ($NCH_2CH_2CH_3$), 19.5 ($NCH_2CH_2CH_3$), 21.4 (CH_3), 28.1 (CH_3), 40.6 ($C(CH_3)_2$), 42.8, 45.5 ($NCH_2CH_2CH_3$, =CCH_2-), 85.7 (NCHN), 88.7 (ThiCH=), 105.0 (C^{4}, pyrazole), 119.4, 120.2, 127.1 (C^{2}, C^{3}, C^{4}, C^{5}, Thi), 129.4 (C^{5}, pyrazole), 139.2 (C^{3}, pyrazole), 143.9 (C^{2}, Thi), 147.5 (ThiCH=*C*). Found (%): C, 67.52; H, 7.84; N, 13.81. Calc. for $C_{17}H_{23}N_3S$ (%): C, 67.73; H, 7.69; N, 13.94.

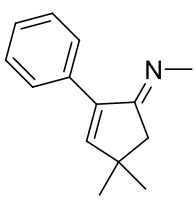


1-[(5E)-3,3-Dimethyl-1-propyl-5-(2-thienylmethylidene)pyrrolidin-2-yl]-3,5-dimethyl-1H-pyrazole **4f** was prepared from aldehyde **1b,** *n*-propylamine and 2,5-dimethylpyrazole in 74% yield. ^{1}H NMR, δ: 0.63 (s, 3H, CH_3), 0.84 (t, 3H, CH_3, J 7.4 Hz), 1.17 (s, 3H, CH_3), 1.23-1.61 (m, 2H, $NCH_2CH_2CH_3$), 2.05 (s, 3H, CH_3 at pyrazole ring), 2.27 (s, 3H, CH_3 at pyrazole ring), 2.58 (d, 1H, =CC*H*H, J 14.8 Hz), 2.70 (ddd, 1H, NC*H*HCH_2CH_3, ^{2}J 14.1 Hz, ^{3}J 8.7 Hz, ^{3}J 5.9 Hz), 2.85 (br.d, 1H, =CC*H*H, J 14.8 Hz), 3.05 (ddd, 1H, NC*H*HCH_2CH_3, ^{2}J 14.1 Hz, ^{3}J 8.6 Hz, ^{3}J 6.4 Hz), 5.03 (s, 1H, NCHN), 5.46 (br. s, 1H, ThiC*H*=), 5.80 (s, 1H, C^{4}H, pyrazole), 6.63 (dd, 1H, C^{3}H, thienyl, ^{3}J 3.6 Hz, ^{4}J 1.0 Hz), 6.90 (dd, 1H, C^{4}H, thienyl, ^{3}J 5.2 Hz, ^{3}J 3.6 Hz), 7.04 (dd, 1H, C^{5}H, thienyl, ^{3}J 5.2 Hz, ^{4}J 1.0 Hz). ^{13}C NMR, δ: 10.8 (CH_3 at pyrazole ring), 11.5 ($NCH_2CH_2CH_3$), 13.7 (CH_3 at pyrazole ring), 19.6 ($NCH_2CH_2CH_3$), 21.4 (CH_3), 28.3 (CH_3), 40.7 ($C(CH_3)_2$), 43.2, 45.5 ($NCH_2CH_2CH_3$, =CCH_2-), 81.4 (NCHN), 86.0 (ThiCH=), 104.8 (C^{4}, pyrazole), 118.9, 119.6, 127.1 (C^{2}, C^{3}, C^{4}, C^{5}, Thi), 139.5 (C^{5}, pyrazole), 144.3 (C^{2}, Thi), 146.7 (C^{3}, pyrazole), 148.3 (ThiCH=*C*). Found (%): C, 69.43; H, 8.05; N, 12.92. Calc. for $C_{19}H_{27}N_3S$ (%): C, 69.26; H, 8.26; N, 12.75.

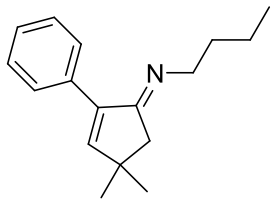


(3E)-3-Benzylidene-2-butyl-1-(1H-pyrazol-1-yl)-2-azaspiro[4.5]decane **4g** was prepared from aldehyde **1c,** *n*-butylamine and pyrazole in 73% yield. ^{1}H NMR, δ: 0.85 (t, 3H, CH_3, J 7.4 Hz), 1.05-1.70 (m, 14H, $NCH_2CH_2CH_2CH_3$; 5CH_2, *cyclo*-C6), 2.72 (d, 1H, =CC*H*H, J 15.3 Hz), 2.76 (ddd, 1H, NC*H*HCH_2CH_3, ^{2}J 14.1 Hz, ^{3}J 8.7 Hz, ^{3}J 5.9 Hz), 2.85 (br.d, 1H, =CC*H*H, J 15.3 Hz), 3.14 (ddd, 1H, NC*H*HCH_2CH_3, ^{2}J 14.1 Hz, ^{3}J 8.5 Hz, ^{3}J 5.9 Hz), 5.21 (br. s, 1H, PhC*H*=), 5.39 (s, 1H, NCHN), 6.26 (dd, 1H, C^{4}H, pyrazole, J 2.3 Hz, J 1.8 Hz), 6.87-6.99 (m, 1H, Ph), 7.11-7.27 (m, 4H, Ph), 7.48 (d, 1H, C^{3}H, pyrazole, J 1.8 Hz), 7.75 (d, 1H, C^{5}H, pyrazole, J 2.3 Hz). ^{13}C NMR, δ: 13.7 ($NCH_2CH_2CH_2CH_3$), 19.7, 22.0, 22.6, 25.4, 28.2, 30.9,

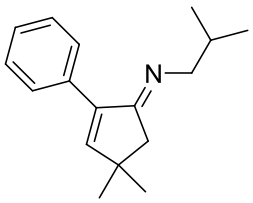
35.1 ($NCH_2CH_2CH_2CH_3$; $5CH_2$, *cyclo*-C_6), 39.7, 43.3 ($NCH_2CH_2CH_2CH_3$, $=CCH_2$-), 43.8 (quaternary C), 84.5 (NCHN), 92.0 (Ph*C*H=), 104.8 (C^4, pyrazole), 122.4 (C^4, Ph), 126.0, 128.1 (C^2, C^3, C^5, C^6, Ph), 129.5 (C^5, pyrazole), 138.9 (C^3, pyrazole), 139.9 (C^1, Ph), 147.3 (PhCH=*C*). Found (%): C, 79.11; H, 8.82; N, 11.88. Calc. for $C_{23}H_{31}N_3$ (%): C, 79.04; H, 8.94; N, 12.02.



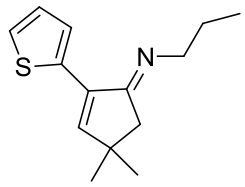
N-[(1E)-4,4-Dimethyl-2-phenylcyclopent-2-en-1-ylidene]-N-methylamine **7b** was prepared from aldehyde **1a** and methylamine and isolated in 42% yield by vacuum microdistillation (1 Torr, bath temperature 90-100 °C). ^{1}H NMR, δ: 1.26 (s, 6H, $2CH_3$), 2.51 (q, 2H, CH_2C=N, ^4J 1.3 Hz), 3.30 (t, 3H, NCH_3, ^4J 1.3 Hz), 6.78 (s, 1H, =CH-), 7.24-7.43 (m, 3H, C^3H, C^4H, C^5H, Ph), 7.69-7.79 (m, 2H, C^2H, C^6H, Ph). ^{13}C NMR, δ: 28.7 ($2CH_3$), 40.3 ($C(CH_3)_2$), 40.8 (NCH_3), 43.3 (CH_2C=N), 127.4, 127.8, 128.2 (Ph), 133.7 (C^1, Ph), 141.2 (*C*=CH), 155.5 (C=*C*H); 176.5 (C=N). HRMS, *m/z* 200.1431, calculated for $C_{14}H_{18}N$, $[M+H]^+$: *m/z* 200.1434.



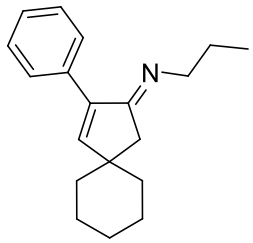
N-[(1E)-4,4-Dimethyl-2-phenylcyclopent-2-en-1-ylidene]-N-butylamine **7c** was prepared from aldehyde **1a** and *n*-butylamine and isolated in 40% yield by vacuum microdistillation (1 Torr, bath temperature 130-140 °C). ^{1}H NMR, δ: 1.00 (t, 3H, $NCH_2CH_2CH_2CH_3$, *J* 7.2 Hz), 1.25 (s, 6H, $2CH_3$), 1.37–1.59 (m, 2H, $NCH_2CH_2CH_2CH_3$), 1.62 – 1.81 (m, 2H, $NCH_2CH_2CH_2CH_3$), 2.49 (t, 2H, CH_2C=N, ^4J 1.2 Hz), 3.38 (tt, 2H, $NCH_2CH_2CH_2CH_3$, ^3J 7.1 Hz, ^4J 1.2 Hz), 6.77 (s, 1H, =CH-), 7.27-7.43 (m, 3H, C^3H, C^4H, C^5H, Ph), 7.71-7.80 (m, 2H, C^2H, C^6H, Ph). ^{13}C NMR, δ: 14.2 ($NCH_2CH_2CH_2CH_3$), 21.0 ($NCH_2CH_2CH_2CH_3$), 29.1 ($2CH_3$), 33.2 ($NCH_2CH_2CH_2CH_3$), 40.6 ($C(CH_3)_2$), 43.8 (CH_2C=N), 53.9 ($NCH_2CH_2CH_2CH_3$), 127.7, 128.1, 128.4 (Ph), 134.1 (C^1, Ph), 141.2 (*C*=CH), 155.5 (C=*C*H); 174.4 (C=N). HRMS, *m/z* 242.1899, calculated for $C_{17}H_{23}N$, $[M+H]^+$: *m/z* 242.1903.



N-[(1E)-4,4-Dimethyl-2-phenylcyclopent-2-en-1-ylidene]-N-isobutylamine **7d** was prepared from aldehyde **1a** and isobutylamine and isolated in 26% yield by vacuum microdistillation (1 Torr, bath temperature 130-140 °C). ^{1}H NMR, δ: 1.05 (d, 6H, $NCH_2CH(CH_3)_2$, *J* 6.7 Hz), 1.26 (s, 6H, $2CH_3$), 1.96-2.21 (m, 1H, $NCH_2CH(CH_3)_2$), 2.49 (s, 2H, CH_2C=N), 3.21 (d, 2H, $NCH_2CH(CH_3)_2$, *J* 6.7 Hz), 6.80 (s, 1H, =CH-), 7.24-7.48 (m, 3H, C^3H, C^4H, C^5H, Ph), 7.77-7.85 (m, 2H, C^2H, C^6H, Ph). ^{13}C NMR, δ: 21.0 ($NCH_2CH(CH_3)_2$), 29.0 ($2CH_3$), 30.0 ($NCH_2CH(CH_3)_2$), 40.5 ($C(CH_3)_2$), 43.9 (CH_2C=N), 62.0 ($NCH_2CH(CH_3)_2$), 127.6, 128.0, 128.3 (Ph), 134.0 (C^1, Ph), 141.0 (*C*=CH), 155.2 (C=*C*H); 174.2 (C=N). HRMS, *m/z* 242.1906, calculated for $C_{17}H_{23}N$, $[M+H]^+$: *m/z* 242.1903.



N-[(1E)-4,4-Dimethyl-2-(2-thienyl)cyclopent-2-en-1-ylidene]-N-propylamine **7e** was prepared from aldehyde **1b** and *n*-propylamine and isolated in 40% yield by vacuum microdistillation (1 Torr, bath temperature 130-140 °C). ^{1}H NMR, δ: 1.06 (t, 3H, NCH$_2$CH$_2$C*H*$_3$, *J* 7.2 Hz), 1.23 (s, 6H, 2CH$_3$), 1.68 – 1.88 (m, 2H, NCH$_2$C*H*$_2$CH$_3$), 2.44 (t, 2H, CH$_2$C=N, ^{4}J 1.2 Hz), 3.35 (tt, 2H, NC*H*$_2$CH$_2$CH$_3$, ^{3}J 7.0 Hz, ^{4}J 1.2 Hz), 6.83 (s, 1H, =CH-), 7.03 (dd, 1H, C^{4}H, thienyl, ^{3}J 5.2 Hz, ^{3}J 3.6 Hz), 7.26 (dd, 1H, C^{5}H, thienyl, ^{3}J 5.2 Hz, ^{4}J 1.0 Hz), 7.69 (dd, 1H, C^{3}H, thienyl, ^{3}J 3.6 Hz, ^{4}J 1.0 Hz). ^{13}C NMR, δ: 12.3 (NCH$_2$CH$_2$*C*H$_3$), 24.2 (NCH$_2$*C*H$_2$CH$_3$), 28.9 (2CH$_3$), 41.1 (*C*(CH$_3$)$_2$), 43.3 (*C*H$_2$C=N), 55.4 (NCH$_2$CH$_2$CH$_3$), 125.6, 125.7, 126.5 (C^{3}, C^{4}, C^{5}, Thi), 134.8, 135.1 (C^{1}, Thi; *C*=CH), 152.2 (C=*C*H); 173.3 (C=N). HRMS, *m/z* 234.1308, calculated for C$_{14}$H$_{20}$NS, [M+H]$^{+}$: *m/z* 234.1311.

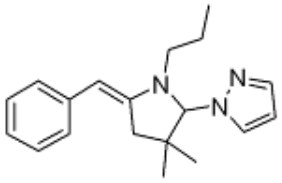


N-[(2E)-3-Phenylspiro[4.5]dec-3-en-2-ylidene]-N-propylamine **7f** was prepared from aldehyde **1c** and *n*-propylamine and isolated in 48% yield by column chromatography on basic Al$_2$O$_3$ [hexane–Et$_2$O (20:1→10:1) as eluent]. ^{1}H NMR, δ: 1.05 (t, 3H, NCH$_2$CH$_2$C*H*$_3$, *J* 7.2 Hz), 1.10 – 1.65 (m, 12H, NCH$_2$C*H*$_2$CH$_3$; 5CH$_2$, *cyclo*-C$_6$), 2.48 (t, 2H, CH$_2$C=N, ^{4}J 1.2 Hz), 3.39 (tt, 2H, NC*H*$_2$CH$_2$CH$_3$, ^{3}J 7.0 Hz, ^{4}J 1.2 Hz), 6.79 (s, 1H, =CH-), 7.22-7.44 (m, 3H, C^{3}H, C^{4}H, C^{5}H, Ph), 7.75-7.82 (m, 2H, C^{2}H, C^{6}H, Ph). ^{13}C NMR, δ: 12.4 (NCH$_2$CH$_2$*C*H$_3$), 21.6 (double intensity, 2CH$_2$, *cyclo*-C$_6$), 24.0 (NCH$_2$*C*H$_2$CH$_3$), 27.9 (CH$_2$, *cyclo*-C$_6$), 36.4 (double intensity, 2CH$_2$, *cyclo*-C$_6$), 43.8 (*C*H$_2$C=N), 44.2 (quaternary C), 55.6 (NCH$_2$CH$_2$CH$_3$), 127.6, 128.0, 128.3 (Ph), 134.4 (C^{1}, Ph), 144.2 (*C*=CH), 155.8 (C=*C*H); 174.1 (C=N). HRMS, *m/z* 268.4155, calculated for C$_{19}$H$_{26}$N, [M+H]$^{+}$: *m/z* 268.4159.

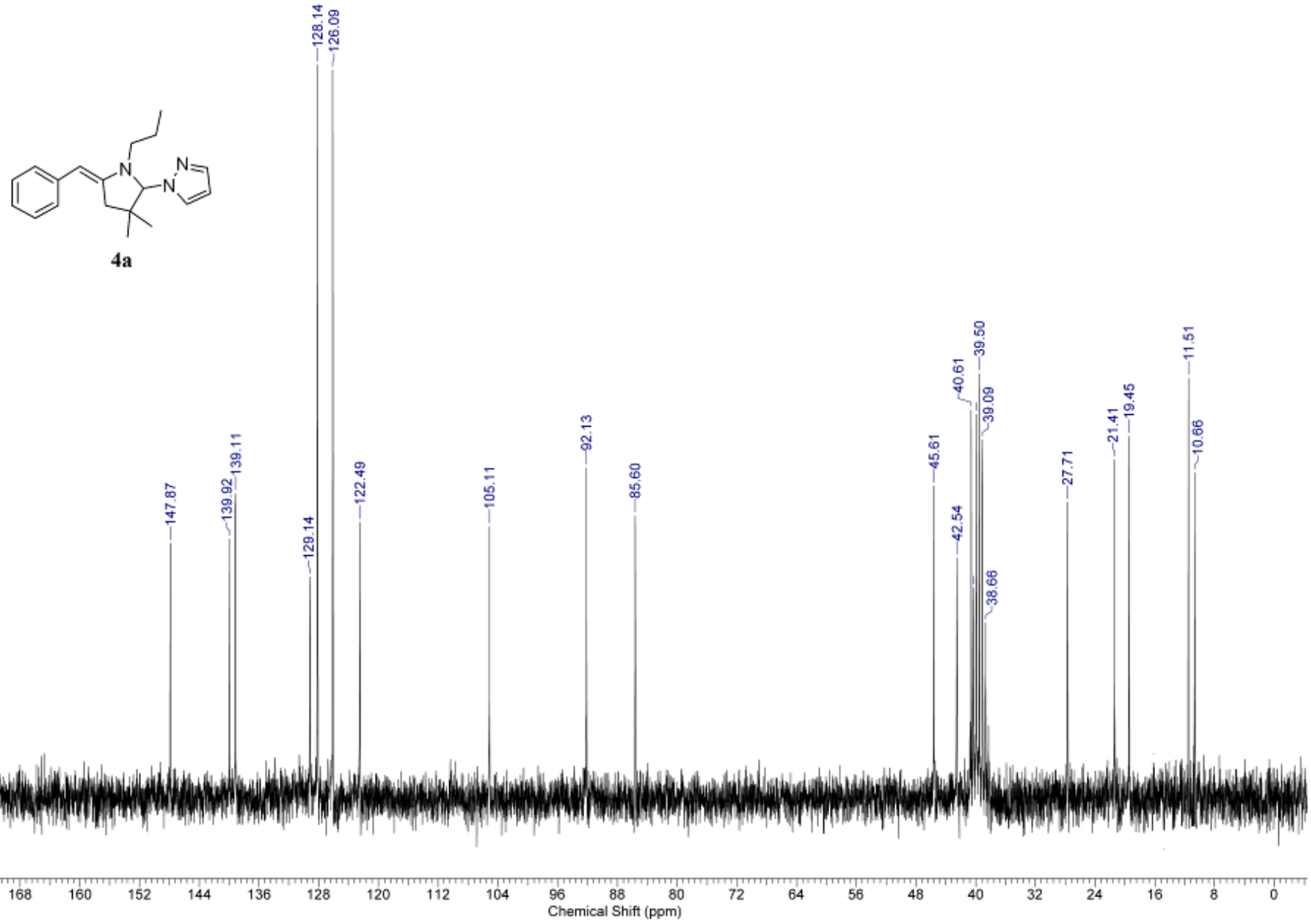
References

1 V. D. Gvozdev, K. N. Shavrin and O. M. Nefedov, *Russ. Chem. Bull., Int. Ed.*, 2013, **62**, 2430 (*Izv. Akad. Nauk, Ser. Khim.*, 2013, 2430).

Copies of NMR-spectra for compounds **4a-g** *and* **7a-f**



4a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11.51
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160
152
144
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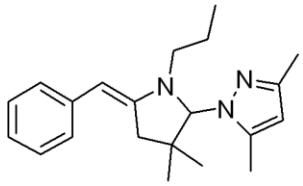
Chemical Shift (ppm)



4b

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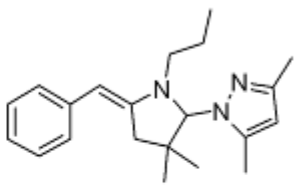
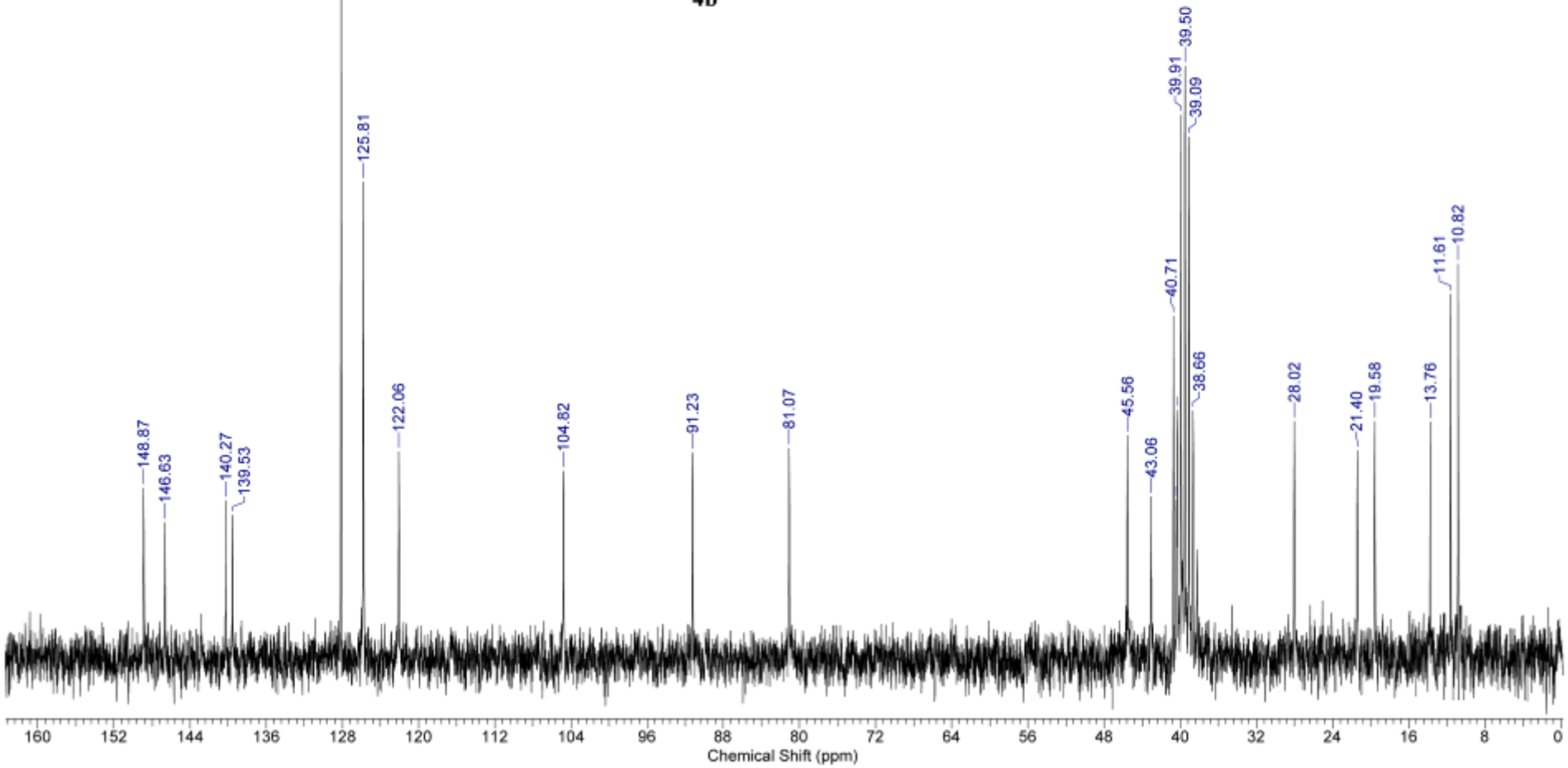


4b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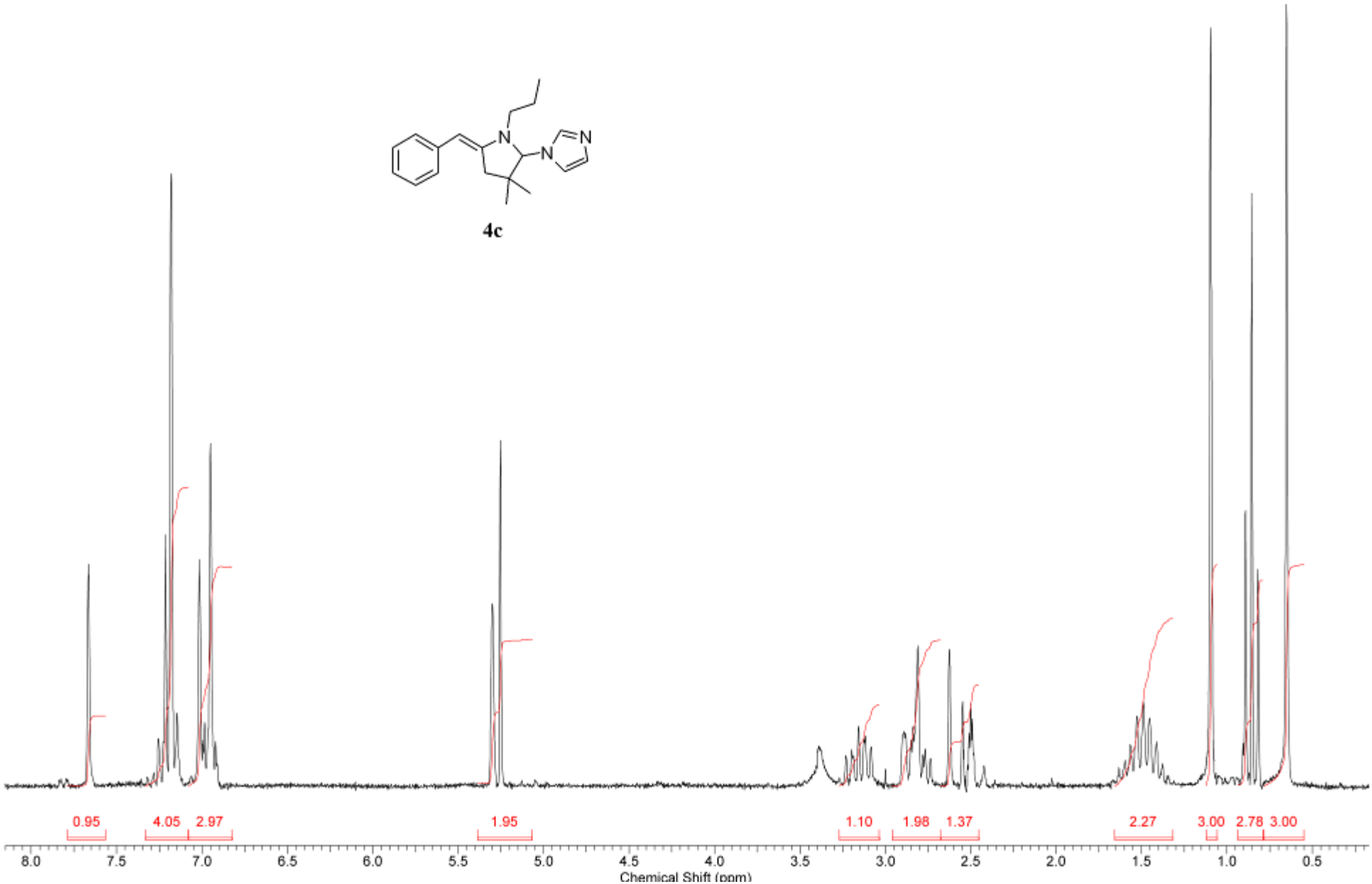
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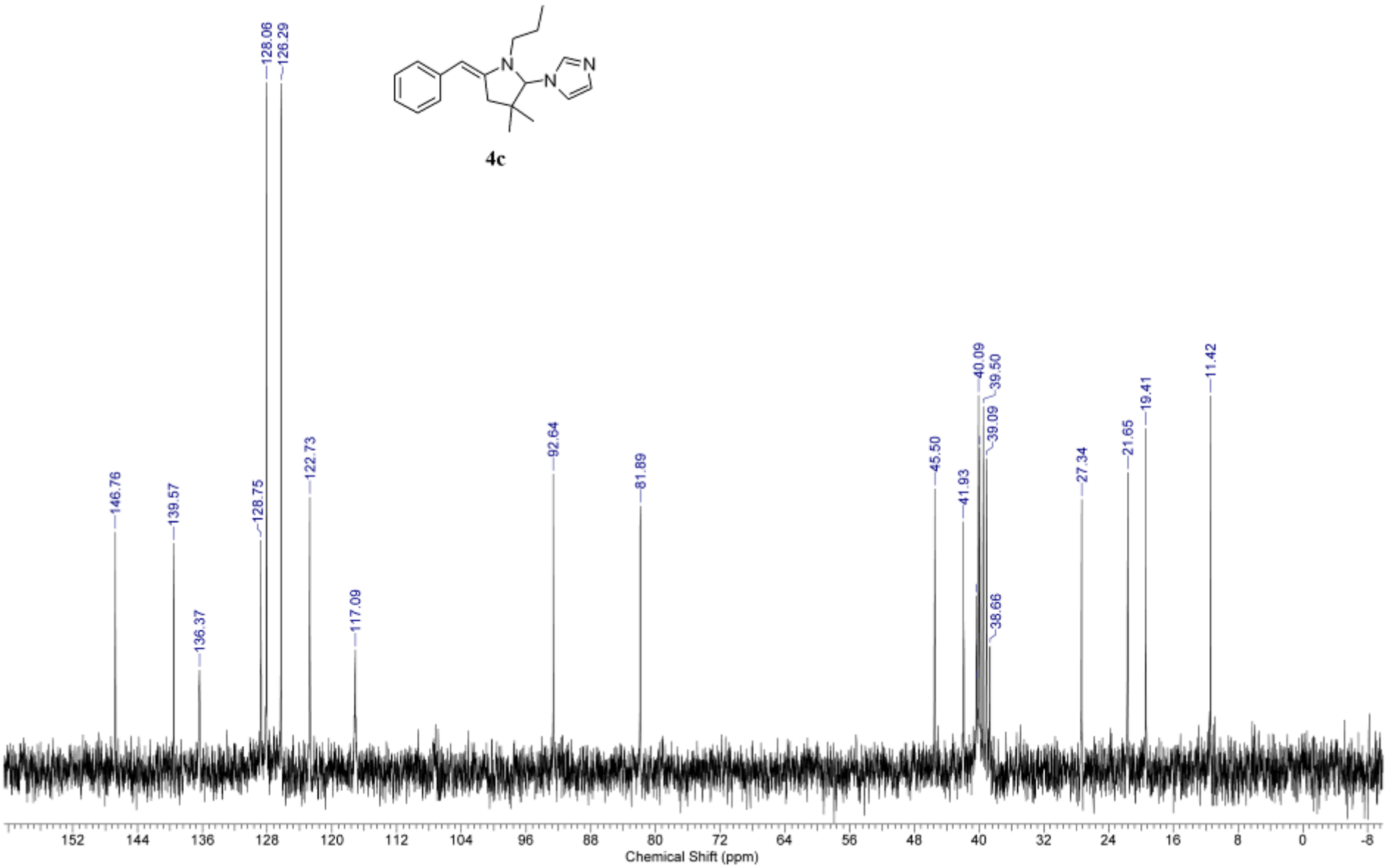
Chemical Shift (ppm)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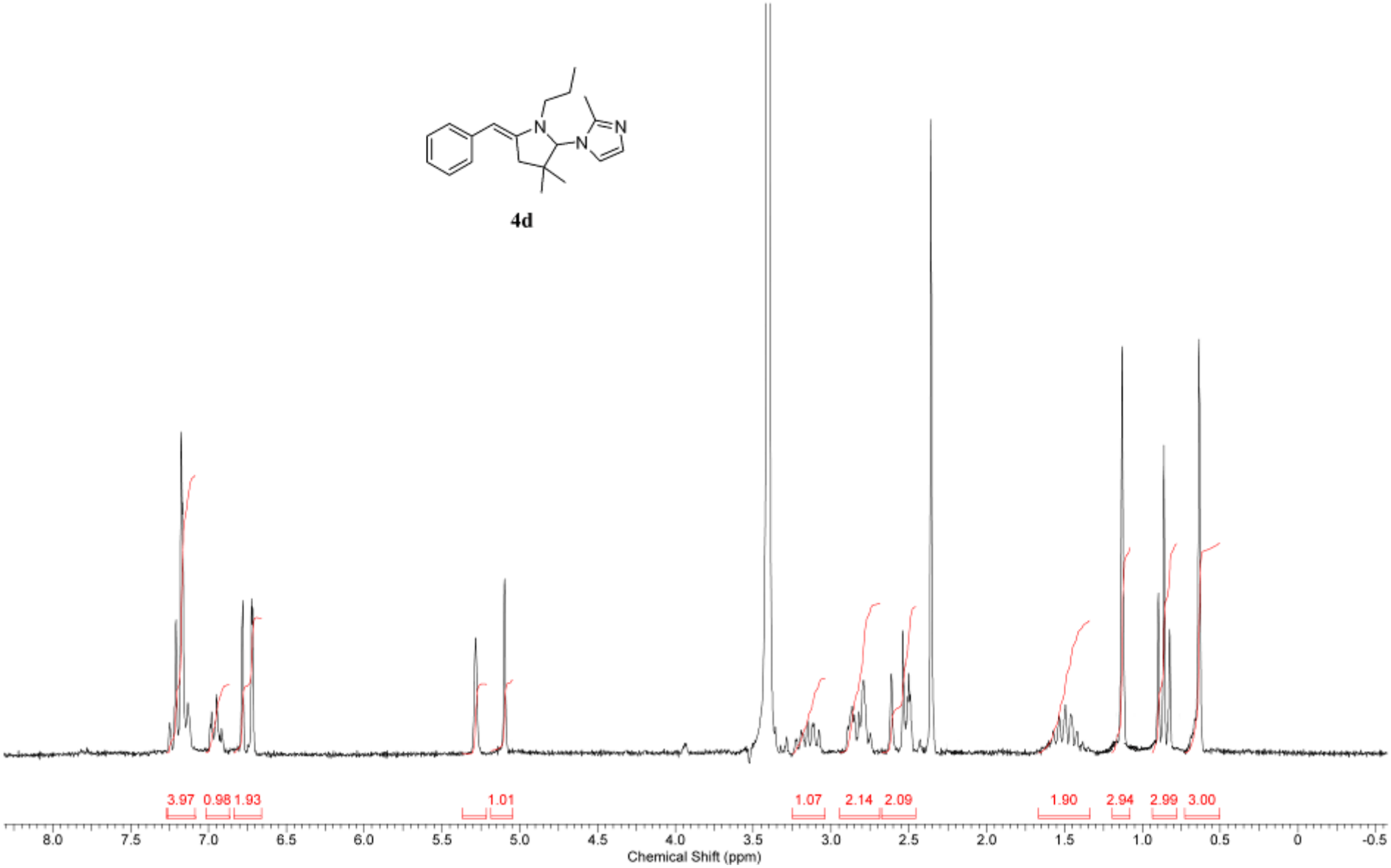
Chemical Shift (ppm)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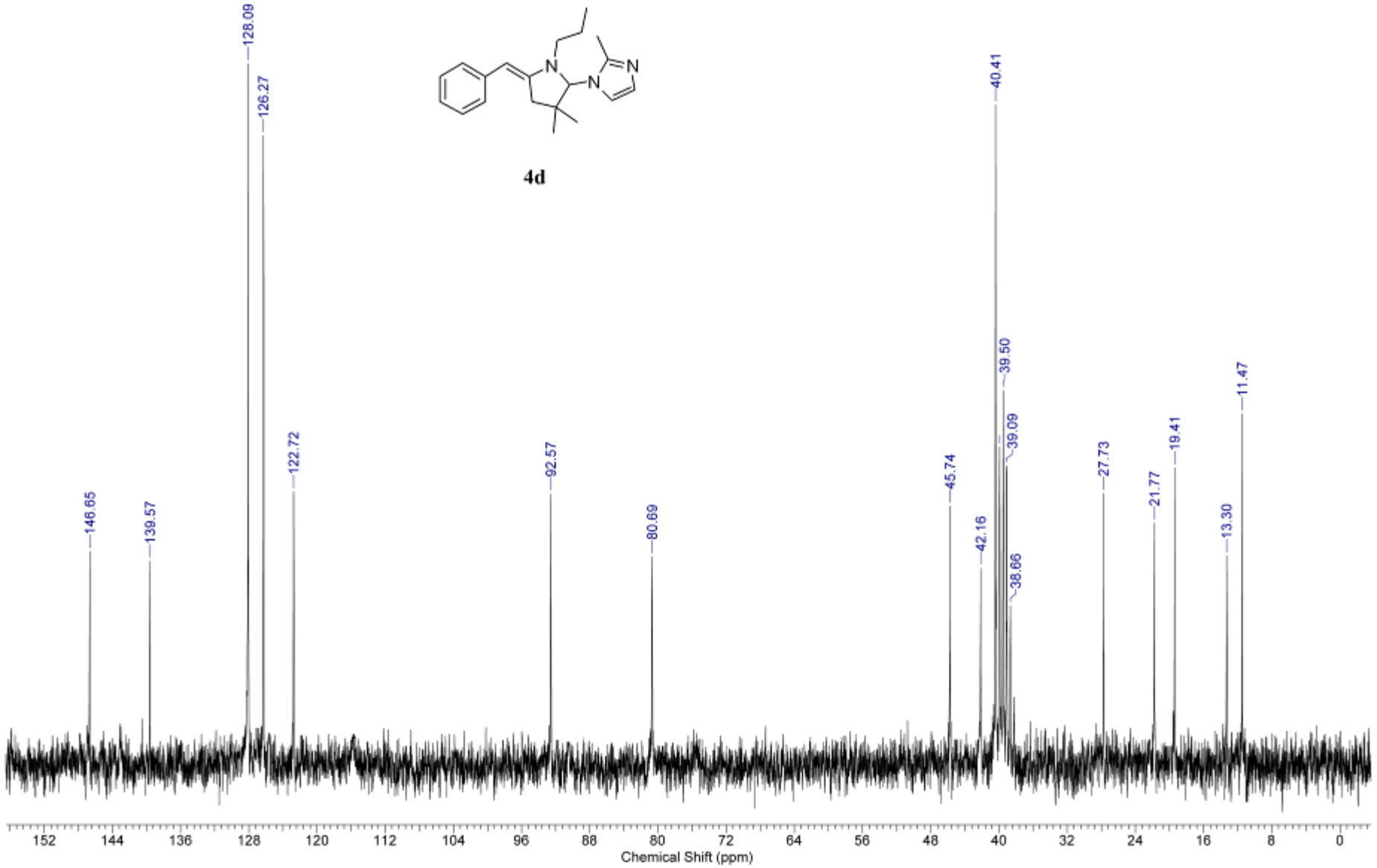
Chemical Shift (ppm)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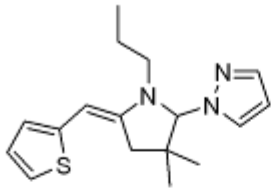
Chemical Shift (ppm)

4d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S

4e

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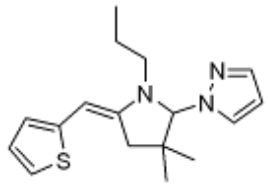
Chemical Shift (ppm)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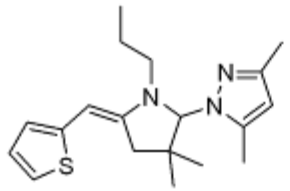
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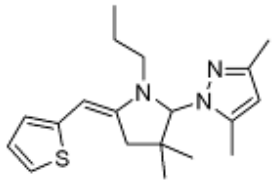
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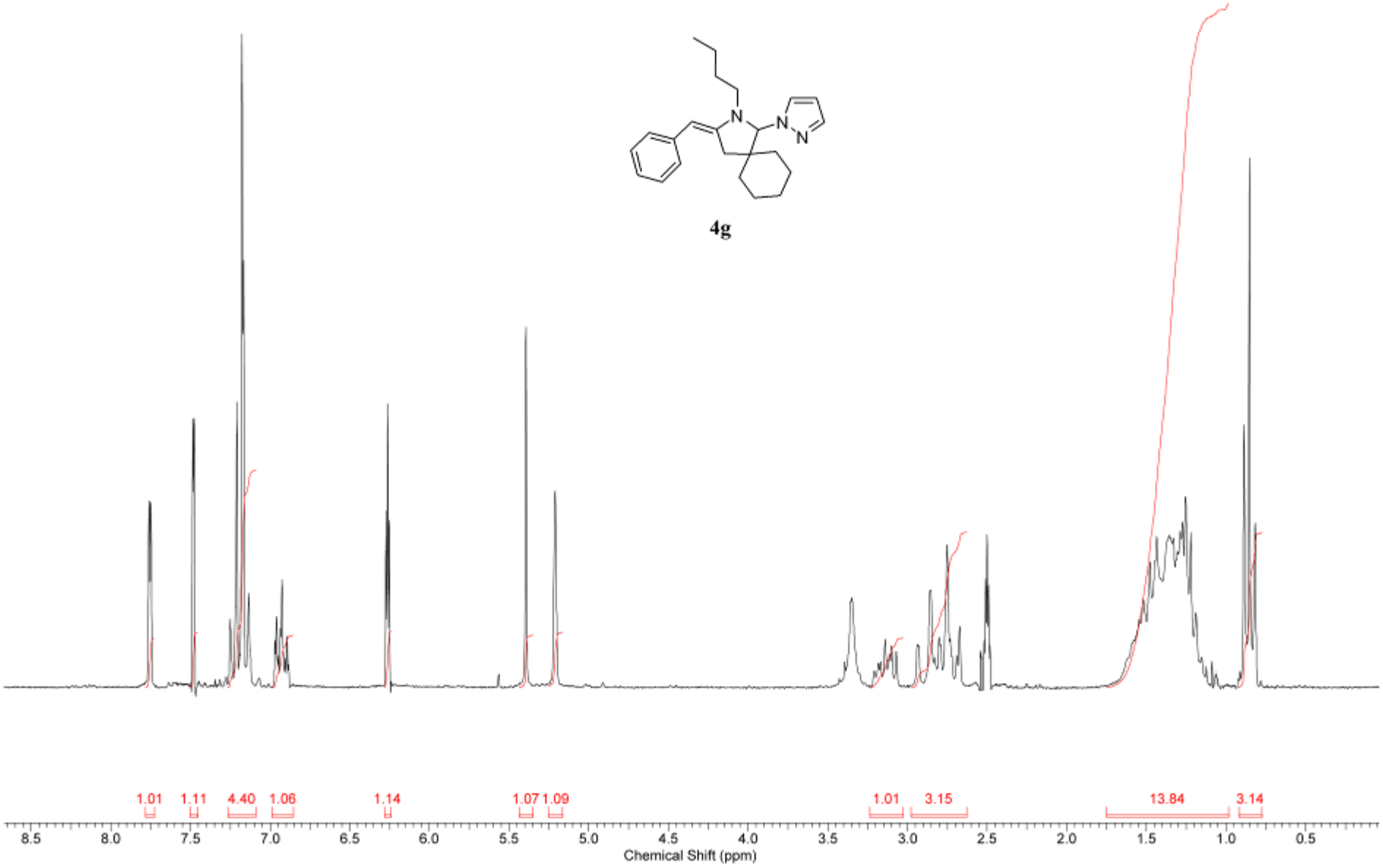
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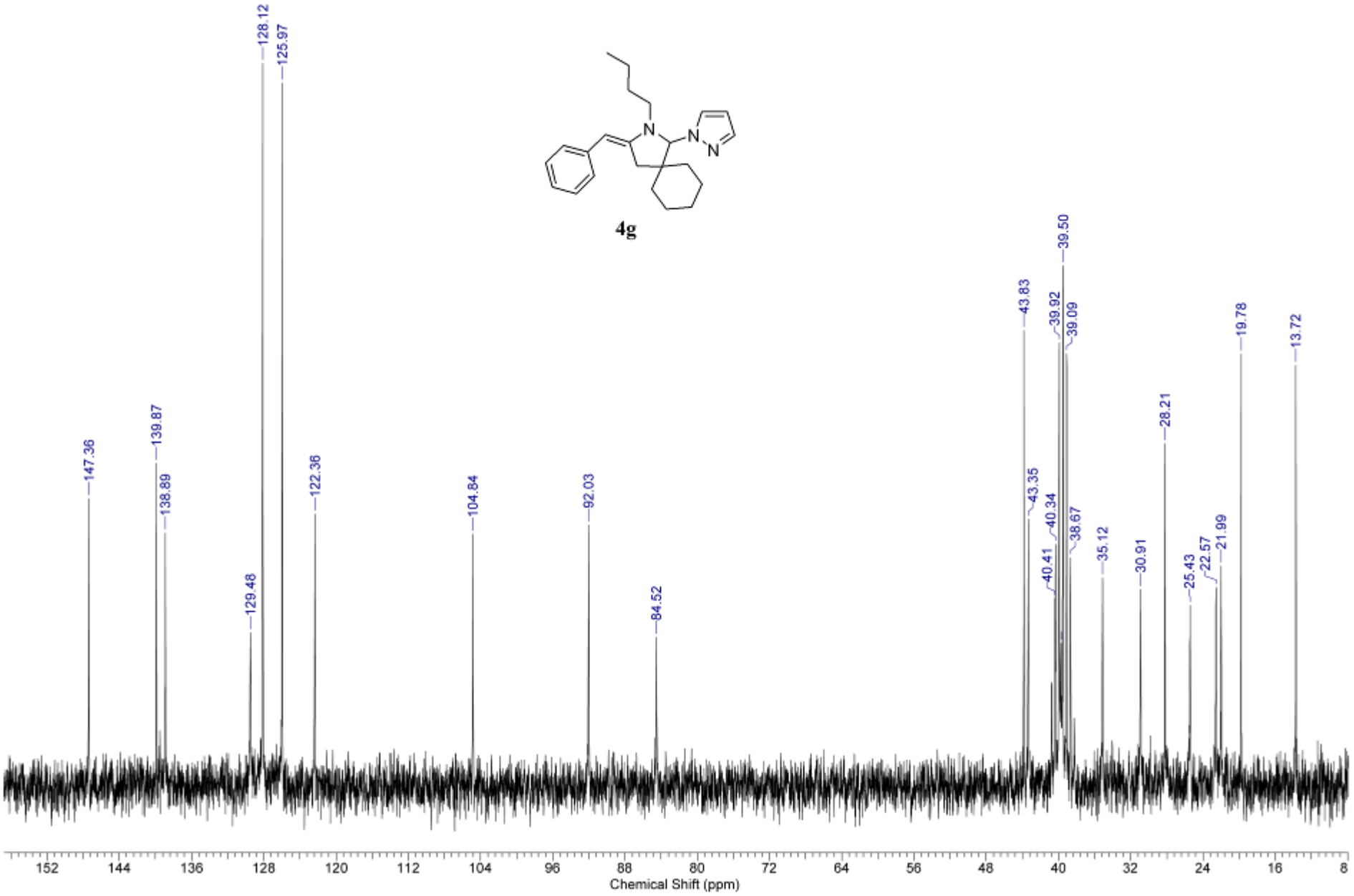
Chemical Shift (ppm)

4g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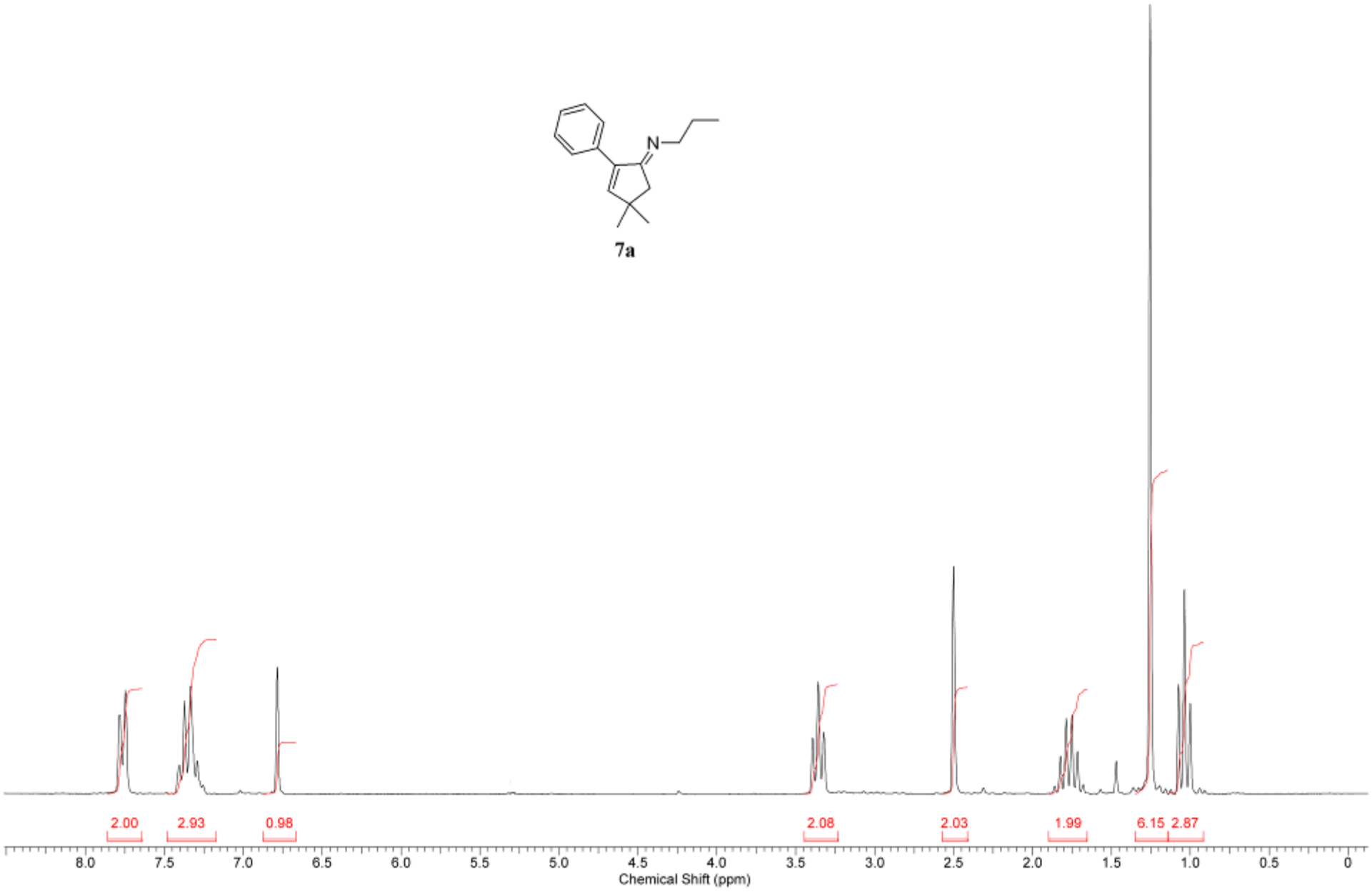
Chemical Shift (ppm)

4g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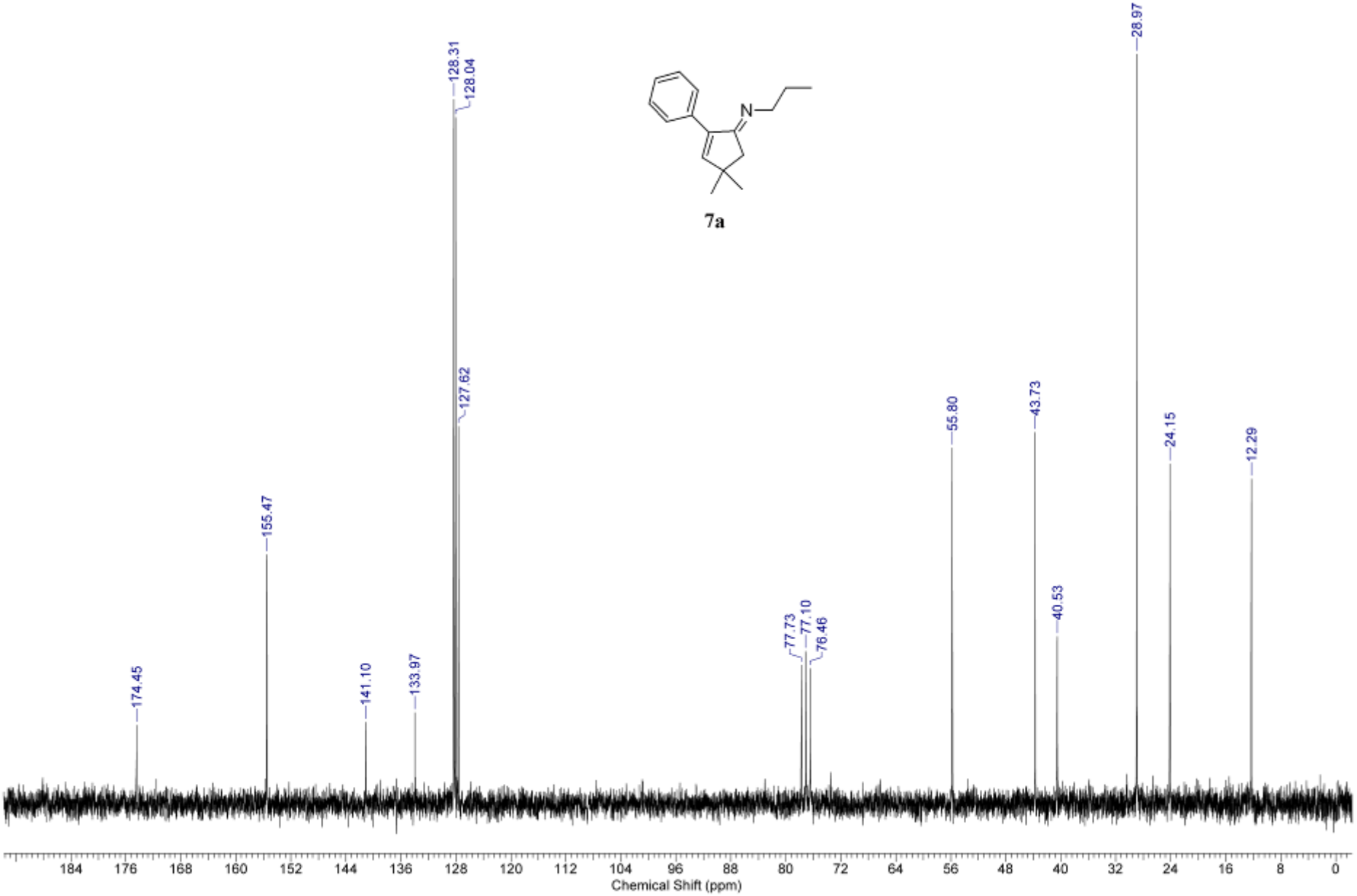
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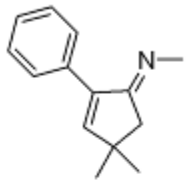
Chemical Shift (ppm)


N—

7b

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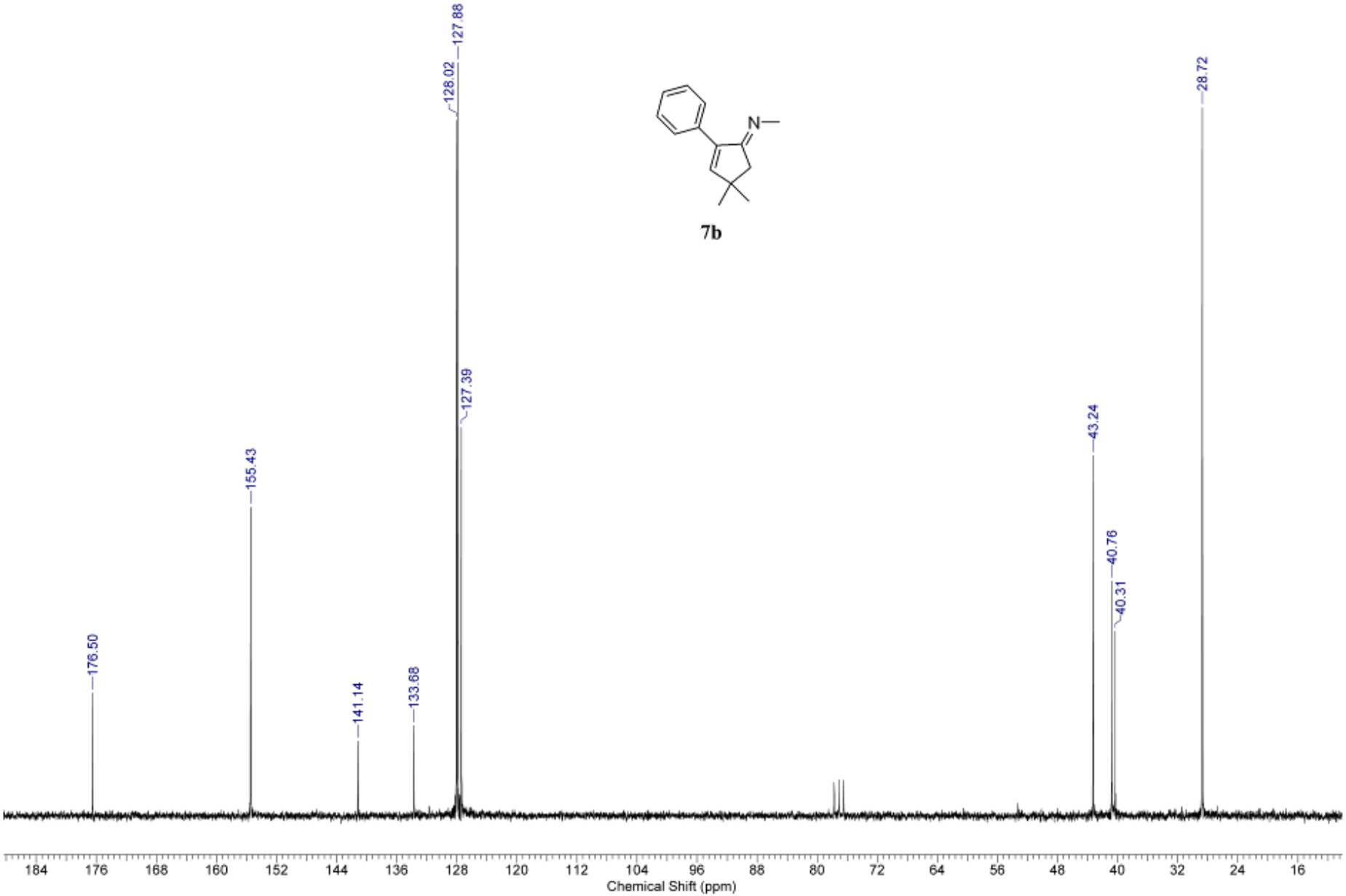
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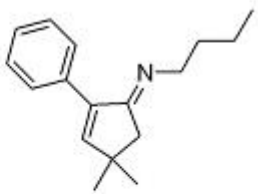
16
Chemical Shift (ppm)

7b


N

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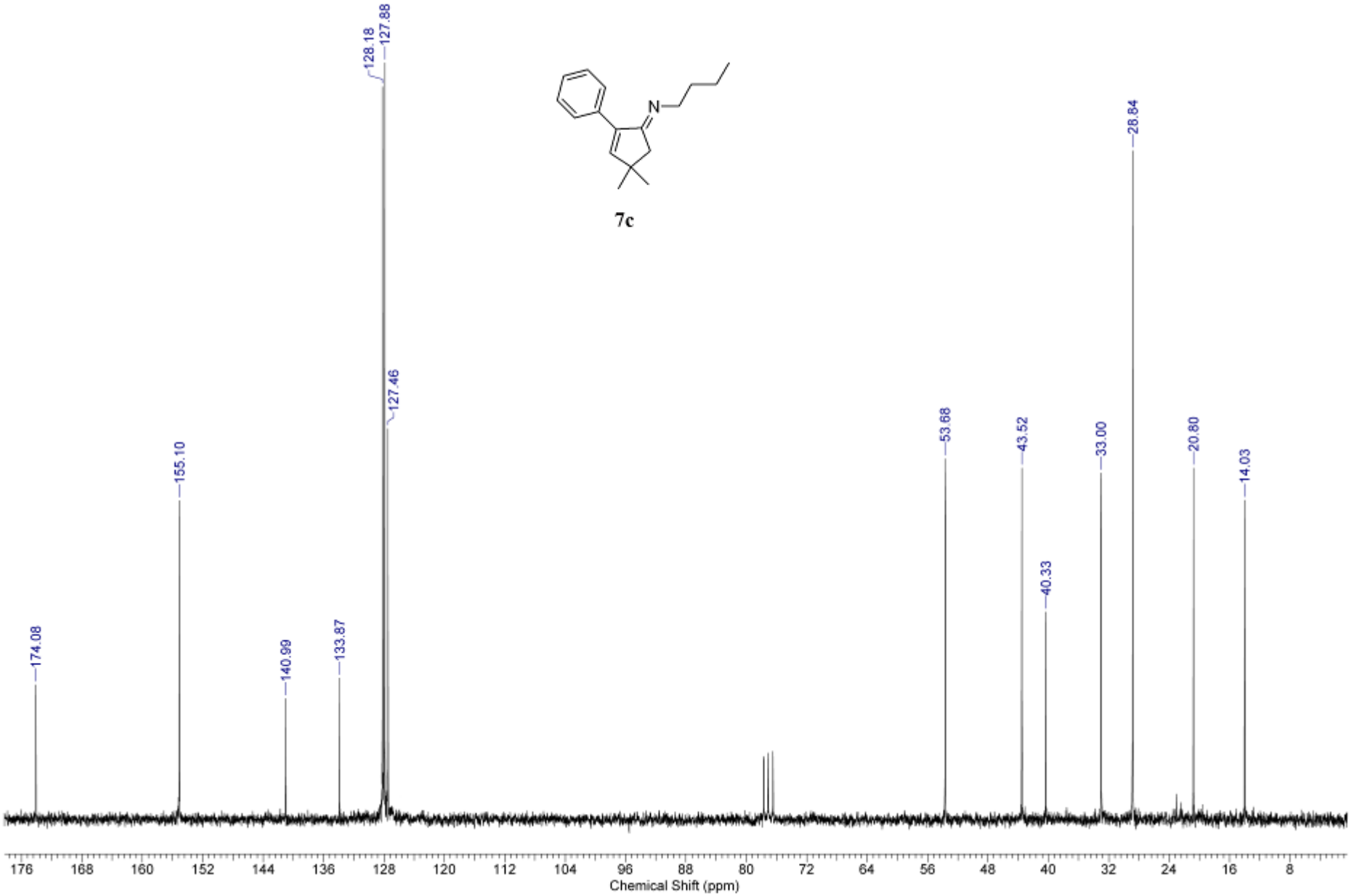
Chemical Shift (ppm)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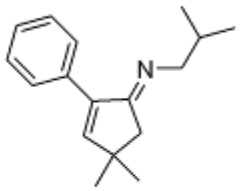
8
Chemical Shift (ppm)


N

7d

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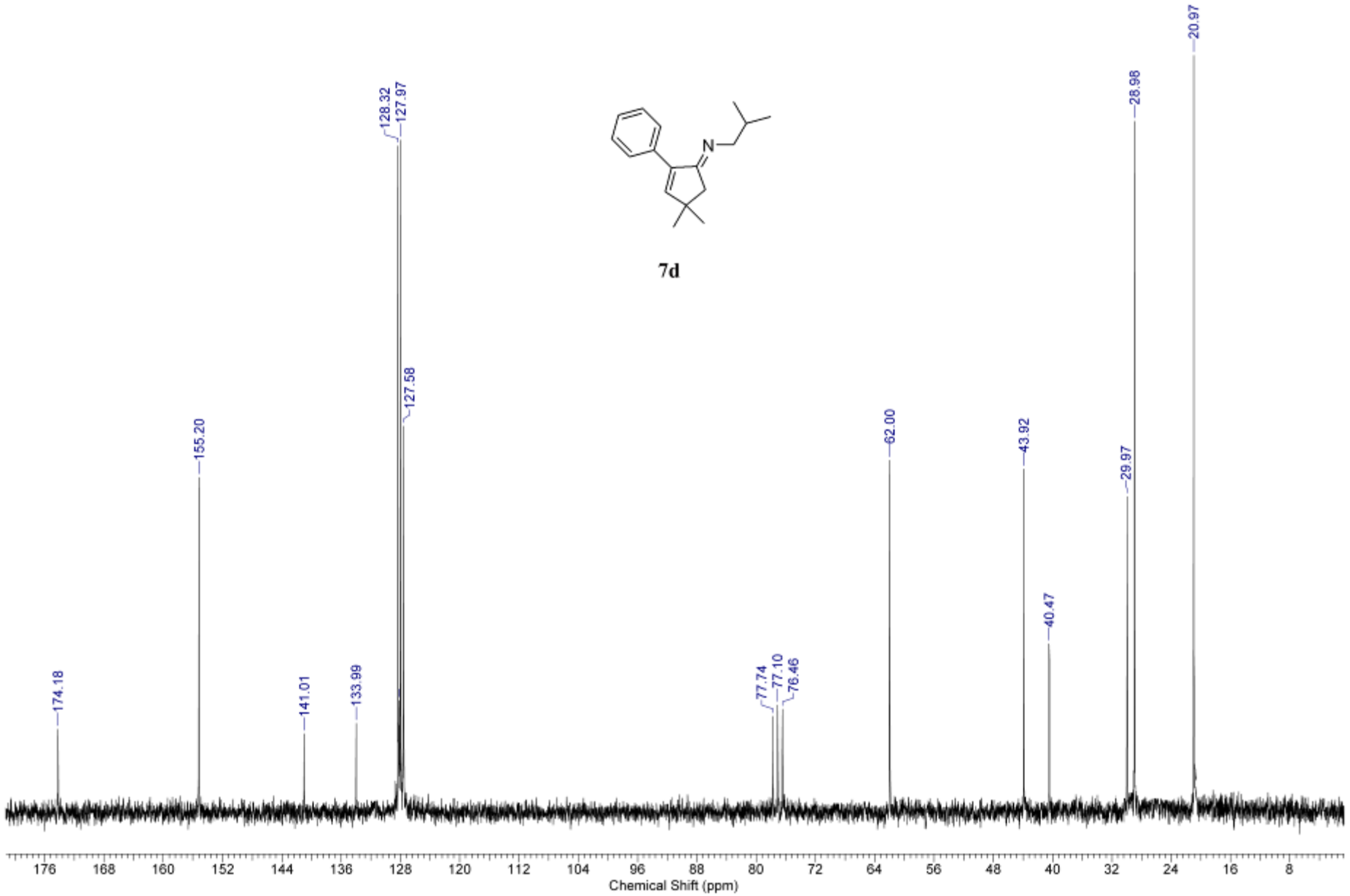
Chemical Shift (ppm)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7d
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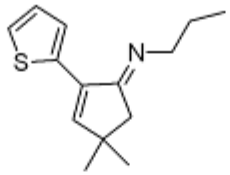
Chemical Shift (ppm)


S
N

7e

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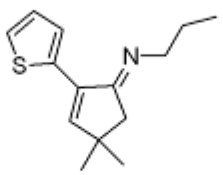
S
N

7e

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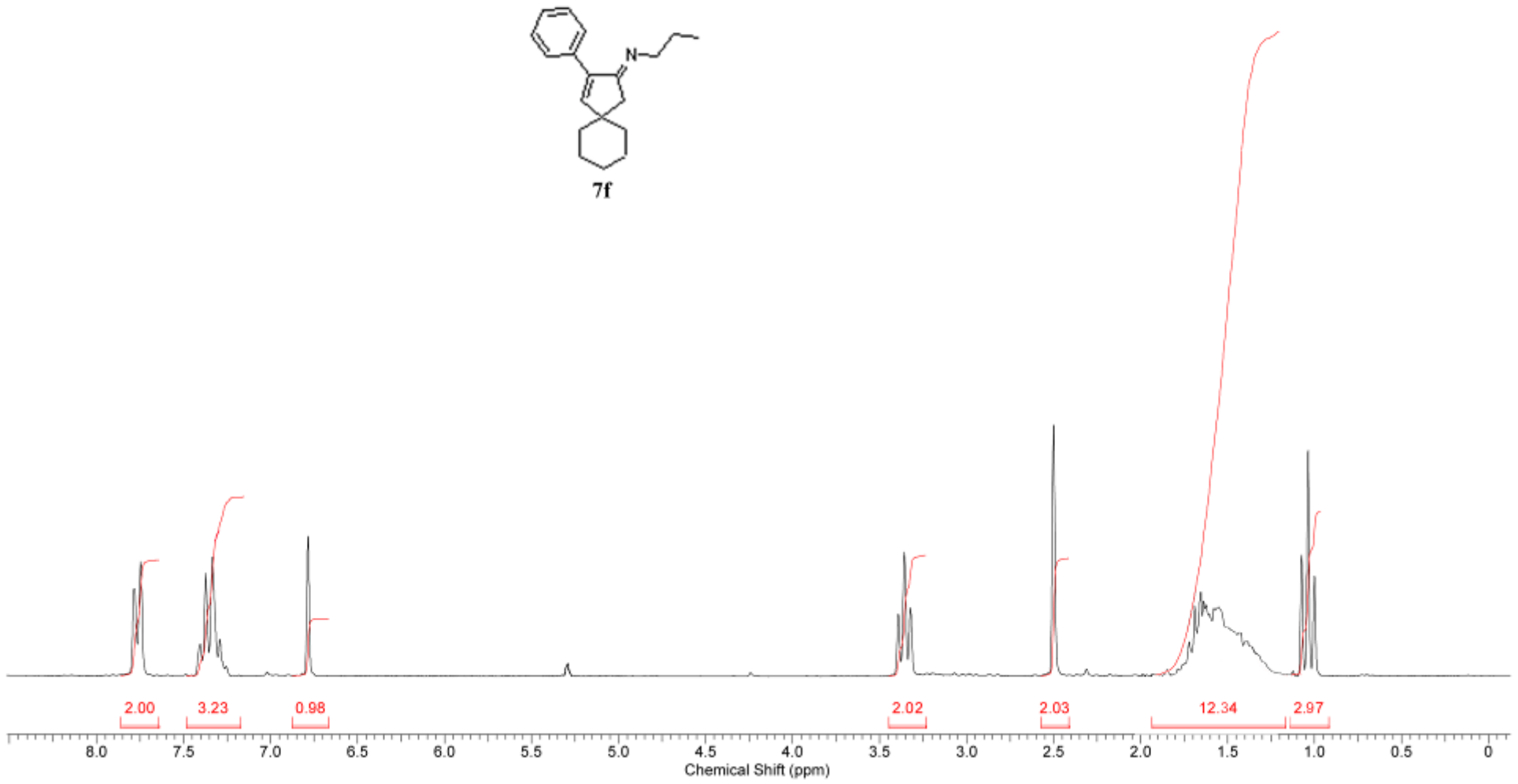
135.12
134.76
77.74
77.10
76.46
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)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3.23
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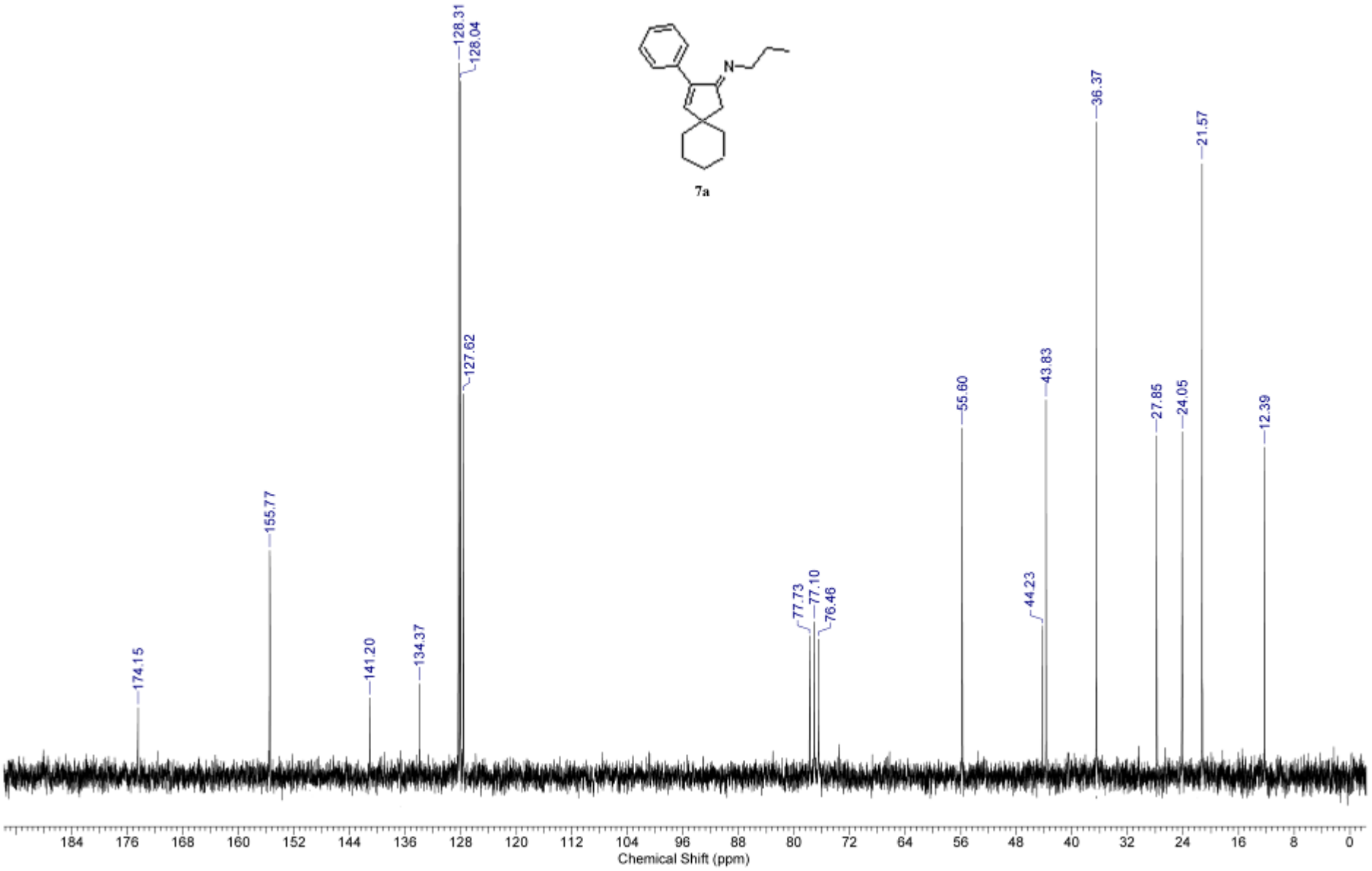
2.02
2.03
12.34
2.97
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)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128.04
127.62
155.77
174.15
141.20
134.37
77.73
77.10
76.46
55.60
44.23
43.83
36.37
27.85
24.05
21.57
12.39
N
7a
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)