

Supporting Information
for
Regioselective S_N2' Mitsunobu reaction of
Morita–Baylis–Hillman alcohols: A facile and
stereoselective synthesis of α -alkylidene- β -hydrazino
acid derivatives

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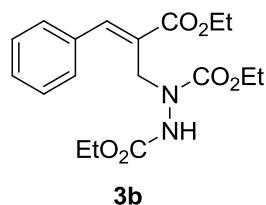
Experimental details on the synthesis of all hydrazines **3 and *1H*-pyrazole **7**, full characterization data and ¹H, ¹³C, DEPT NMR spectra for all compounds **3** and **7**, and a mechanistic rationale for the formation of **7**.**

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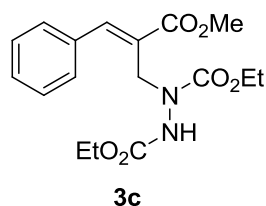
1. Analytical data for compounds 3b–s¹

Table 2, entry 1. Following the general procedure, the reaction of MBH alcohol **1a** (62 mg, 0.3 mmol), PPh₃ (157 mg, 0.6 mmol) and diethyl azodicarboxylate **2b** (94 μL, 0.6 mmol) was performed for 25 minutes.



3b: 107 mg, 98% yield, as slightly yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.89 (s, H), 7.37 (m, 5H), 6.75 (br m, 1H), 4.64 (s, 2H), 4.27 (q, *J* = 7.1 Hz, 2H), 4.11 (m, 4H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.22 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 167.6, 156.0(2C), 143.7, 134.5, 129.3, 128.9, 128.5, 127.3, 62.5, 61.9, 61.1, 46.6, 14.41, 14.37, 14.2; IR (KBr): ν_{max} 3433, 2983, 1638, 1401, 1124 cm⁻¹; HRMS (ESI) calcd for C₁₈H₂₅N₂O₆ [M+H]⁺ requires 365.1713, found 365.1712.

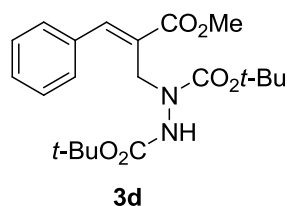
Table 2, entry 2. Following the general procedure, the reaction of MBH alcohol **1b** (58 mg, 0.3 mmol), PPh₃ (157 mg, 0.6 mmol) and diethyl azodicarboxylate **2b** (94 μL, 0.6 mmol) was performed for 25 minutes.



3c: 100 mg, 95% yield, as yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.90 (s, 1H), 7.36 (m, 5H), 6.61 (br m, 1H), 4.65 (s, 2H), 4.18 (m, 4H), 3.83 (s, 3H), 1.29 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 168.0, 155.9(2C), 143.9, 134.3, 129.2, 128.9, 128.4, 127.0, 62.4, 61.7, 52.1, 46.5, 14.3(2C); IR (KBr): ν_{max} 3430, 2980, 1711, 1401, 1125 cm⁻¹; HRMS (ESI) calcd for C₁₇H₂₃N₂O₆ [M+H]⁺ requires 351.1556, found 351.1557.

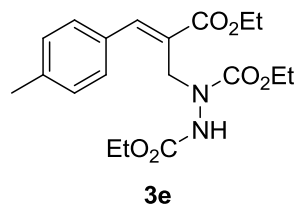
¹ Rotamers were often observed in the ¹H and ¹³C NMR spectra of compounds **3**.

Table 2, entry 3. Following the general procedure, the reaction of MBH alcohol **1b** (58 mg, 0.3 mmol), PPh₃ (157 mg, 0.6 mmol) and di-*tert*-butyl azodicarboxylate **2c** (138 mg, 0.6 mmol) was performed for 50 minutes.



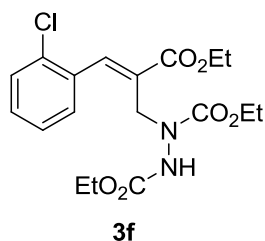
3d: 116 mg, 95% yield, as colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.77 (s, 1H), 7.28 (m, 5H), 6.32 (br m, 1H), 4.53 (s, 2H), 3.72 (s, 3H), 1.35 (m, 18H); ¹³C NMR (100 MHz, CDCl₃) δ 168.0, 155.7, 154.9, 143.5, 134.3, 129.3, 128.8, 128.3, 127.2, 80.9, 80.6, 51.9, 45.1, 27.9(2C); IR (KBr): ν_{max} 3435, 2981, 1639, 1401, 1122 cm⁻¹; HRMS (ESI) calcd for C₂₁H₃₀N₂NaO₆ [M+Na]⁺ requires 429.2002, found 429.1995.

Table 2, entry 4. Following the general procedure, the reaction of MBH alcohol **1c** (66 mg, 0.3 mmol), PPh₃ (157 mg, 0.6 mmol) and diethyl azodicarboxylate **2b** (94 μL, 0.6 mmol) was performed for 35 minutes.



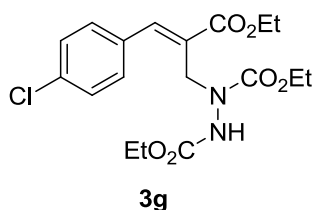
3e: 92 mg, 81% yield, as yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.77 (s, 1H), 7.20 (br s, 2H), 7.08 (d, *J* = 7.9 Hz, 2H), 6.78 (br m, 1H), 4.56 (s, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 4.03 (m, 4H), 2.25 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.11 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 167.5, 155.8(2C), 143.7, 138.9, 131.4, 129.3, 129.0, 126.1, 62.1, 61.5, 60.8, 46.0, 21.0, 14.2, 14.1, 13.9; IR (KBr): ν_{max} 3413, 2981, 1710, 1401, 1124 cm⁻¹; HRMS (ESI) calcd for C₁₉H₂₇N₂O₆ [M+H]⁺ requires 379.1869, found 379.1867.

Table 2, entry 5. Following the general procedure, the reaction of MBH alcohol **1d** (72 mg, 0.3 mmol), PPh₃ (157 mg, 0.6 mmol) and diethyl azodicarboxylate **2b** (94 μL, 0.6 mmol) was performed for 35 minutes.



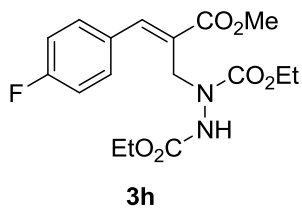
3f: 104 mg, 87 % yield, as slightly yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.94 (s, 1H), 7.33 (m, 4H), 6.61 (br m, 1H), 4.52 (s, 2H), 4.30 (q, $J = 7.1$ Hz, 2H), 4.11 (m, 4H), 1.35 (t, $J = 7.2$ Hz, 3H), 1.23 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.9, 155.9(2C), 140.9, 133.7, 133.2, 130.3, 129.9, 129.4(2C), 126.6, 62.4, 61.8, 61.2, 46.8, 14.3(2C), 14.1; IR (KBr): ν_{max} 3422, 2985, 1717, 1401, 1136 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{24}\text{ClN}_2\text{O}_6$ $[\text{M}+\text{H}]^+$ requires 399.1323, found 399.1324.

Table 2, entry 6. Following the general procedure, the reaction of MBH alcohol **1e** (72 mg, 0.3 mmol), PPh_3 (157 mg, 0.6 mmol) and diethyl azodicarboxylate **2b** (94 μL , 0.6 mmol) was performed for 30 minutes.



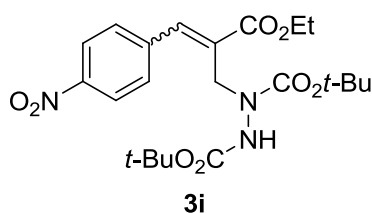
3g: 109 mg, 91% yield, as colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.82 (s, 1H), 7.35 (m, 4H), 6.92 (br m, 1H), 4.61 (s, 2H), 4.27 (q, $J = 7.1$ Hz, 2H), 4.13 (m, 4H), 1.33 (t, $J = 7.1$ Hz, 3H), 1.21 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.1, 155.8(2C), 142.2, 134.8, 132.9, 130.5, 128.6, 127.9, 62.3, 61.7, 61.0, 46.1, 14.3, 14.2, 14.0; IR (KBr): ν_{max} 3448, 2985, 1712, 1401, 1124 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{24}\text{ClN}_2\text{O}_6$ $[\text{M}+\text{H}]^+$ requires 399.1323, found 399.1320.

Table 2, entry 7. Following the general procedure, the reaction of MBH alcohol **1f** (63 mg, 0.3 mmol), PPh_3 (157 mg, 0.6 mmol) and diethyl azodicarboxylate **2b** (94 μL , 0.6 mmol) was performed for 30 minutes.



3h: 87 mg, 79% yield, as yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.76 (s, 1H), 7.33 (br s, 2H), 7.00 (m, 2H), 6.76 (br s, 1H), 4.53 (s, 2H), 4.06 (m, 4H), 3.72 (s, 3H), 1.15 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.8, 162.9 (d, $J_{\text{C-F}} = 250.2$ Hz), 155.9(2C), 142.7, 131.3 (d, $J_{\text{C-F}} = 7.5$ Hz), 130.4, 126.8, 115.5 (d, $J_{\text{C-F}} = 21.7$ Hz), 62.38, 61.73, 52.03, 46.27, 14.25, 14.19; IR (KBr): ν_{max} 3170, 2984, 1718, 1401, 1124 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{22}\text{FN}_2\text{O}_6$ $[\text{M}+\text{H}]^+$ requires 369.1462, found 369.1464.

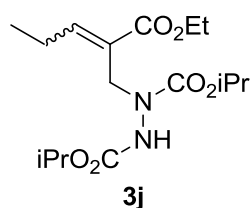
Table 2, entry 8. Following the general procedure, the reaction of MBH alcohol **1g** (75 mg, 0.3 mmol), PPh_3 (157 mg, 0.6 mmol) and di-*tert*-butyl azodicarboxylate **2c** (138 mg, 0.6 mmol) was performed for 40 minutes.



3i: obtained as an inseparable mixture of *E/Z* isomers (*E/Z* 3:1) in 120 mg, 86% yield, as colorless oil; NMR data for *E*-**3i**: ^1H NMR (400 MHz, CDCl_3) δ 8.23 (d, $J = 8.2$ Hz, 2H), 7.85 (s, 1H), 7.61 (m, 2H), 6.39 (br m, 1H), 4.56 (s, 2H), 4.30 (q, $J = 7.1$ Hz, 2H), 1.46 (m, 18H), 1.36 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.8, 154.8(2C), 147.4, 141.1, 140.3, 130.0, 129.0, 123.4, 81.3, 81.0, 61.2, 45.3, 27.9(2C), 14.0; selected NMR data for *Z*-**3i**: ^1H NMR (400 MHz, CDCl_3) δ 8.18 (d, $J = 8.3$ Hz, 2H), 7.46 (d, $J = 8.3$ Hz, 2H), 6.94 (s, 1H), 4.48 (s, 2H), 4.16 (q, $J = 7.1$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.0, 142.1, 131.1, 123.1, 61.1, 13.6; IR (KBr): ν_{max} 3433, 2986, 1521, 1710, 1401, 1369, 1122 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{31}\text{N}_3\text{NaO}_8$ $[\text{M}+\text{Na}]^+$ requires 488.2009, found 488.2003.

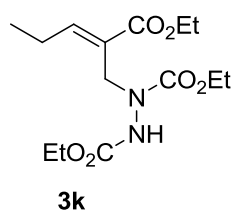
Table 2, entry 9. Following the general procedure, the reaction of MBH alcohol **1h**

(47 mg, 0.3 mmol), PPh₃ (157 mg, 0.6 mmol) and diisopropyl azodicarboxylate **2a** (118 μL, 0.6 mmol) was performed for 30 minutes.



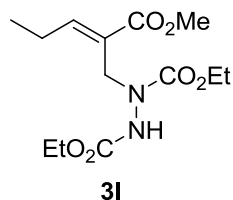
3j: obtained as an inseparable mixture of *E/Z* isomers (*E/Z* 9:1) in 83 mg, 80 % yield, as slightly yellow oil; NMR data for *E*-**3j**: ¹H NMR (400 MHz, CDCl₃) δ 6.98 (t, *J* = 7.0 Hz, 1H), 6.56 (br m, 1H), 5.00 (m, 2H), 4.35 (m, 2H), 4.19 (q, *J* = 7.1 Hz, 2H), 2.31 (br s, 2H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.25 (m, 12H), 1.06 (t, *J* = 7.6 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 167.0, 155.4(2C), 149.8, 126.3, 69.7, 69.3, 60.5, 44.9, 21.9, 21.81, 21.76, 14.1, 13.1; selected NMR data for *Z*-**3j**: ¹H NMR (400 MHz, CDCl₃) δ 6.10 (br s, 1H), 4.29 (s, 2H), 2.51 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 149.5, 126.2, 70.3, 60.3, 44.5, 21.6, 13.5; IR (KBr): ν_{max} 3437, 2982, 1715, 1401, 1135 cm⁻¹; HRMS (ESI) calcd for C₁₆H₂₉N₂O₆ [M+H]⁺ requires 345.2026, found 345.2020.

Table 2, entry 10. Following the general procedure, the reaction of MBH alcohol **1h** (47 mg, 0.3 mmol), PPh₃ (157 mg, 0.6 mmol) and diethyl azodicarboxylate **2b** (94 μL, 0.6 mmol) was performed for 20 minutes.



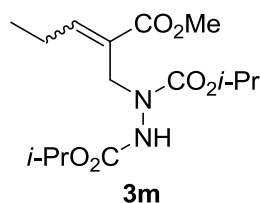
3k: 78 mg, 82% yield, as colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 6.99 (m, 2H), 4.43 (s, 2H), 4.18 (m, 6H), 2.32 (br s, 2H), 1.28 (m, 9H), 1.06 (t, *J* = 7.5 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.9, 155.7(2C), 149.7, 126.0, 62.1, 61.6, 60.5, 45.0, 21.6, 14.3, 14.2, 13.9, 12.9; IR (KBr): ν_{max} 3434, 2983, 1712, 1401, 1124 cm⁻¹; HRMS (ESI) calcd for C₁₄H₂₅N₂O₆ [M+H]⁺ requires 317.1713, found 317.1712.

Table 2, entry 11. Following the general procedure, the reaction of MBH alcohol **1i** (43 mg, 0.3 mmol), PPh₃ (157 mg, 0.6 mmol) and diethyl azodicarboxylate **2b** (94 μL, 0.6 mmol) was performed for 25 minutes.



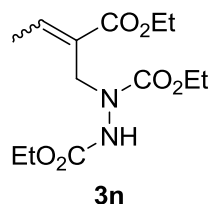
3l: 72 mg, 80% yield, as slightly yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 6.94 (m, 2H), 4.37 (s, 2H), 4.13 (m, 4H), 3.69 (s, 3H), 2.28 (m, 2H), 1.22 (t, *J* = 7.1 Hz, 6H), 1.02 (t, *J* = 7.5 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 167.4, 156.0(2C), 150.3, 125.8, 62.2, 61.6, 51.7, 45.2, 21.7, 14.33, 14.28, 13.0; IR (KBr): ν_{max} 3448, 2981, 1718, 1401, 1122 cm⁻¹; HRMS (ESI) calcd for C₁₃H₂₃N₂O₆ [M+H]⁺ requires 303.1556, found 303.1554.

Table 2, entry 12. Following the general procedure, the reaction of MBH alcohol **1i** (43 mg, 0.3 mmol), PPh₃ (157 mg, 0.6 mmol) and diisopropyl azodicarboxylate **2a** (118 μL, 0.6 mmol) was performed for 30 minutes.



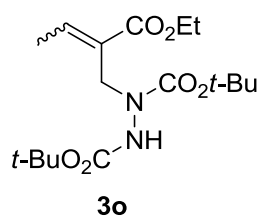
3m: obtained as an inseparable mixture of *E/Z* isomers (*E/Z* 13:1) in 80 mg, 81% yield, as slightly yellow oil; NMR data for *E*-**3m**: ¹H NMR (400 MHz, CDCl₃) δ 6.98 (br s, 1H), 6.54 (br m, 1H), 4.95 (m, 2H), 4.41 (s, 2H), 3.74 (s, 3H), 2.31 (m, 2H), 1.26 (m, 12H), 1.06 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 167.4, 155.6(2C), 150.2, 126.0, 69.8, 69.3, 51.7, 45.0, 21.9, 21.8, 21.5, 13.0; selected NMR data for *Z*-**3m**: ¹H NMR (400 MHz, CDCl₃) δ 6.12 (br s, 1H), 4.19 (s, 2H), 2.51 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 149.8, 125.8, 51.3, 44.5, 13.4; IR (KBr): ν_{max} 3427, 2981, 1718, 1401, 1144 cm⁻¹; HRMS (ESI) calcd for C₁₅H₂₇N₂O₆ [M+H]⁺ requires 331.1869, found 331.1864.

Table 2, entry 13. Following the general procedure, the reaction of MBH alcohol **1j** (43 mg, 0.3 mmol), PPh₃ (157 mg, 0.6 mmol) and diethyl azodicarboxylate **2b** (94 μ L, 0.6 mmol) was performed for 21 minutes.



3n: obtained as an inseparable mixture of *E/Z* isomers (*E/Z* 13:1) in 75 mg, 83% yield, as colorless oil; NMR data for *E*-**3n**: ¹H NMR (400 MHz, CDCl₃) δ 7.11 (q, *J* = 6.9 Hz, 1H), 6.70 (br m, 1H), 4.34 (s, 2H), 4.19 (m, 6H), 1.92 (m, 3H), 1.28 (m, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 166.9, 155.8(2C), 143.5, 127.8, 62.4, 61.8, 60.6, 45.2, 14.43, 14.38, 14.3, 14.1; selected NMR data for *Z*-**3n**: ¹H NMR (400 MHz, CDCl₃) δ 6.26 (br m, 1H), 2.05 (d, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 64.0, 60.4, 15.6; IR (KBr): ν_{\max} 3427, 2985, 1712, 1401, 1137 cm⁻¹; HRMS (ESI) calcd for C₁₃H₂₃N₂O₆ [M+H]⁺ requires 303.1556, found 303.1555.

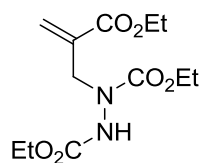
Table 2, entry 14. Following the general procedure, the reaction of MBH alcohol **1j** (43 mg, 0.3 mmol), PPh₃ (157 mg, 0.6 mmol) and di-*tert*-butyl azodicarboxylate **2c** (138 mg, 0.6 mmol) was performed for 40 minutes.



3o: obtained as an inseparable mixture of *E/Z* isomers (*E/Z* 5:1) in 59 mg, 55% yield, as colorless oil; NMR data for *E*-**3o**: ¹H NMR (400 MHz, CDCl₃) δ 7.09 (q, *J* = 6.9 Hz, 1H), 6.24 (br m, 1H), 4.41 (s, 2H), 4.19 (q, *J* = 7.1 Hz, 2H), 1.90 (d, *J* = 6.9 Hz, 3H), 1.46 (m, 18H), 1.30 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.9, 155.0(2C), 143.1, 128.3, 80.8(2C), 60.5, 44.2, 28.1(2C), 14.2, 14.1; selected NMR data for *Z*-**3o**: ¹H NMR (400 MHz, CDCl₃) δ 6.07 (br s, 1H), 2.04 (d, *J* = 7.2 Hz, 3H), 1.14 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 142.6, 128.1, 60.2, 29.6, 15.6;

IR (KBr): ν_{\max} 3432, 2980, 1711, 1400, 1152 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{31}\text{N}_2\text{O}_6$ $[\text{M}+\text{H}]^+$ requires 359.2182, found 359.2177.

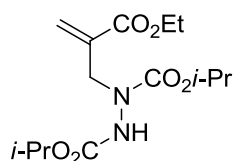
Table 2, entry 15. Following the general procedure, the reaction of MBH alcohol **1k** (39 mg, 0.3 mmol), PPh_3 (157 mg, 0.6 mmol) and diethyl azodicarboxylate **2b** (94 μL , 0.6 mmol) was performed for 10 minutes.



3p

3p: 78 mg, 90% yield, as colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.12 (br m, 1H), 6.33 (s, 1H), 5.78 (s, 1H), 4.37 (s, 2H), 4.20 (m, 6H), 1.28 (m, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.9, 156.0(2C), 135.3, 128.0, 62.4, 61.8, 60.8, 51.3, 14.28, 14.24, 13.9; IR (KBr): ν_{\max} 3417, 2983, 1718, 1401, 1138 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{21}\text{N}_2\text{O}_6$ $[\text{M}+\text{H}]^+$ requires 289.1400, found 289.1398.

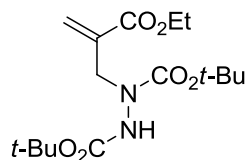
Table 2, entry 16. Following the general procedure, the reaction of MBH alcohol **1k** (39 mg, 0.3 mmol), PPh_3 (157 mg, 0.6 mmol) and diisopropyl azodicarboxylate **2a** (118 μL , 0.6 mmol) was performed for 20 minutes.



3q

3q: 84 mg, 89% yield, as colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.10 (br m, 1H), 6.24 (s, 1H), 5.69 (s, 1H), 4.86 (m, 2H), 4.27 (s, 2H), 4.13 (q, $J = 7.1$ Hz, 2H), 1.22 (t, $J = 7.1$ Hz, 3H), 1.16 (d, $J = 6.3$ Hz, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.8, 155.6(2C), 135.4, 127.6, 69.8, 69.3, 60.6, 50.9, 21.73, 21.67, 13.9; IR (KBr): ν_{\max} 3448, 2983, 1718, 1401, 1108 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{25}\text{N}_2\text{O}_6$ $[\text{M}+\text{H}]^+$ requires 317.1713, found 317.1713.

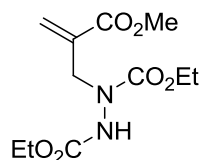
Table 2, entry 17. Following the general procedure, the reaction of MBH alcohol **1k** (39 mg, 0.3 mmol), PPh₃ (157 mg, 0.6 mmol) and di-*tert*-butyl azodicarboxylate **2c** (138 mg, 0.6 mmol) was performed for 25 minutes.



3r

3r: 93 mg, 90% yield, as colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 6.50 (br m, 1H), 6.31 (s, 1H), 5.73 (s, 1H), 4.32 (s, 2H), 4.22 (q, *J* = 7.1 Hz, 2H), 1.47 (s, 18H), 1.30 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.0, 155.0(2C), 135.9, 127.3, 81.2(2C), 60.7, 50.9, 28.1(2C), 14.1; IR (KBr): ν_{max} 3344, 2981, 1713, 1400, 1152 cm⁻¹; HRMS (ESI) calcd for C₁₆H₂₈N₂NaO₆ [M+Na]⁺ requires 367.1845, found 367.1840.

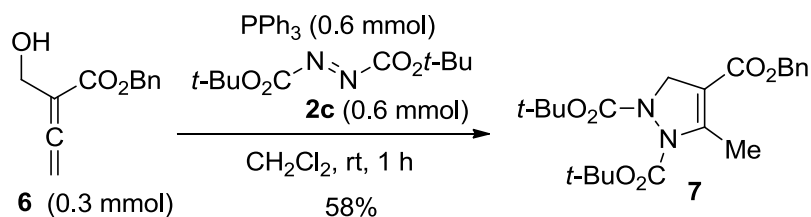
Table 2, entry 18. Following the general procedure, the reaction of MBH alcohol **1l** (35 mg, 0.3 mmol), PPh₃ (157 mg, 0.6 mmol) and diethyl azodicarboxylate **2b** (94 μL, 0.6 mmol) was performed for 13 minutes.



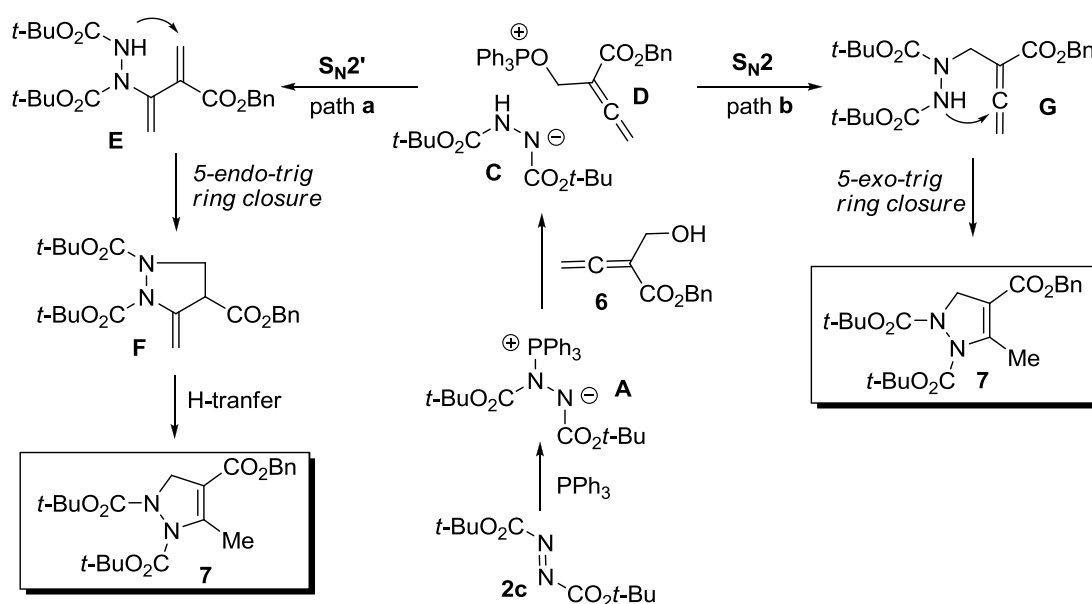
3s

3s: 72 mg, 87% yield, as slightly yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 6.84 (br m, 1H), 6.34 (s, 1H), 5.79 (m, 1H), 4.37 (s, 2H), 4.19 (m, 4H), 3.77 (s, 3H), 1.27 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 166.4, 156.1(2C), 135.1, 128.6, 62.6, 61.9, 51.9, 51.6, 14.4, 14.3; IR (KBr): ν_{max} 3449, 2981, 1719, 1401, 1139 cm⁻¹; HRMS (ESI) calcd for C₁₁H₁₉N₂O₆ [M+H]⁺ requires 275.1243, found 275.1243..

2. Analytical data for 1*H*-pyrazole **7** and mechanistic rationale



7: ¹H NMR (400 MHz, CDCl₃) δ 7.36 (m, 5H), 5.20 (s, 2H), 4.49 (s, 2H), 2.59 (s, 3H), 1.51 (s, 9H), 1.49 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 163.7, 156.4, 151.5, 151.2, 136.0, 128.6, 128.2, 128.1, 107.4, 83.2, 82.4, 65.9, 52.4, 28.1, 28.0, 14.6; IR (KBr): ν_{max} 2981, 1716, 1637, 1401, 1144 cm⁻¹; HRMS (ESI) calcd for C₂₂H₃₀N₂NaO₆ [M+Na]⁺ requires 441.2002, found 441.2005.

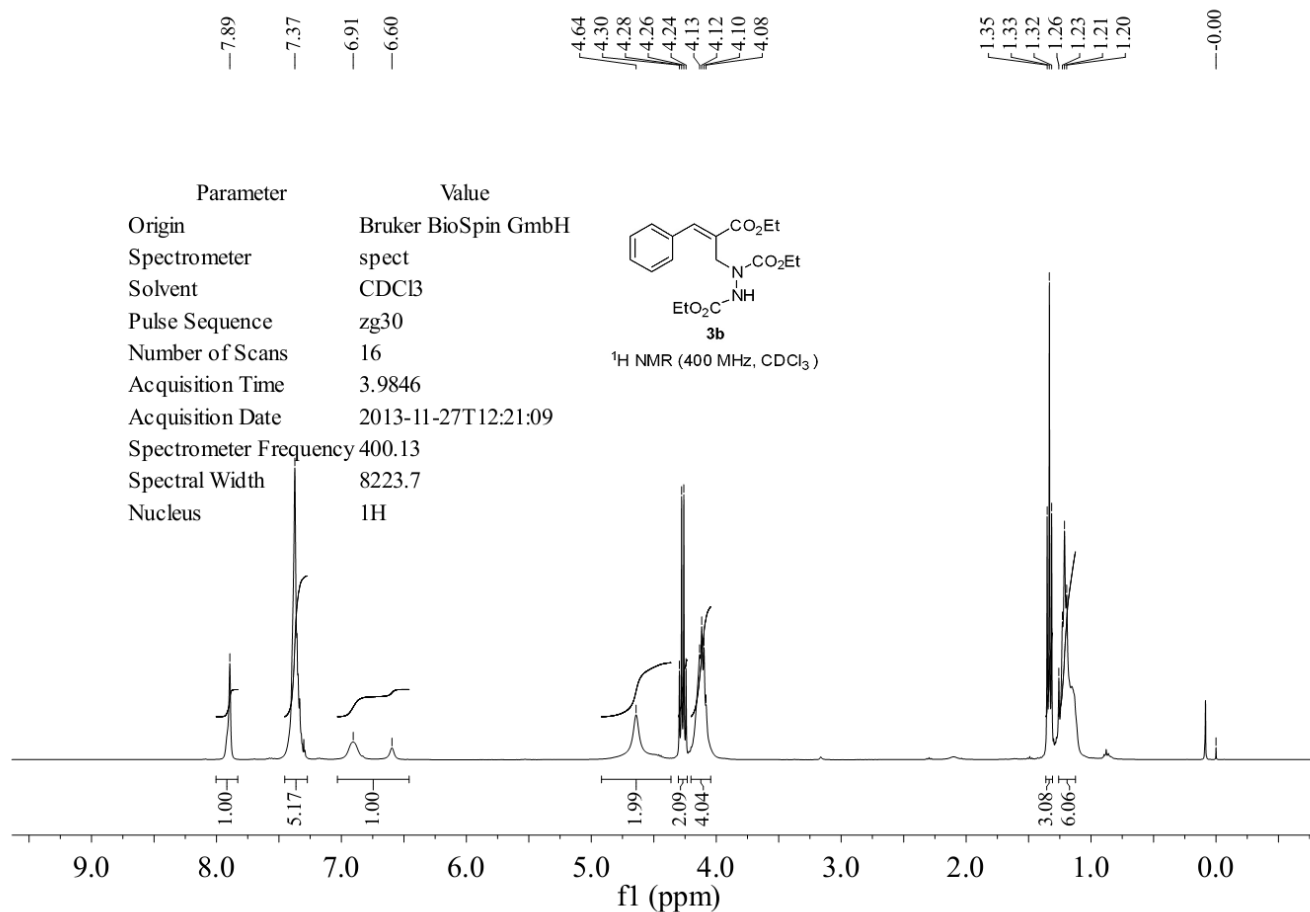


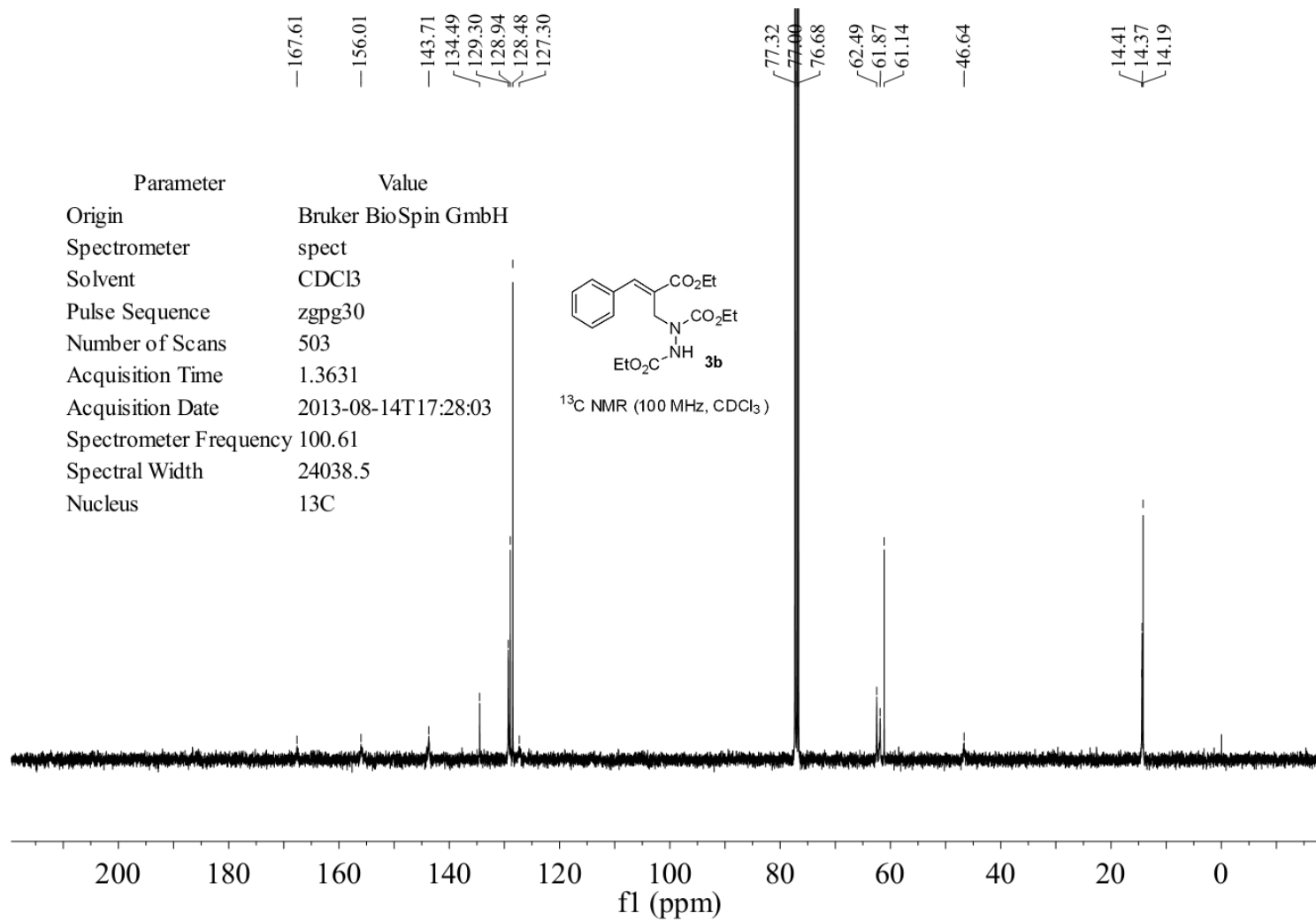
Scheme S1: Plausible mechanism for the formation of compound **7**.

The formation of compound **7** from the reaction between azodicarboxylate **2c**, allenic MBH alcohol **6**, and PPh₃ can be tentatively rationalized in Scheme S1. Initially, addition of PPh₃ to **2c** forms the Huisgen zwitterion **A**, which deprotonates the OH of **6** followed by the migration of the phosphonium to produce the anionic species **C** and the oxophosphonium intermediate **D**. In one of the possible pathways (**path a**), S_N2' attack of intermediate **C** on **D** brings about the hydrazine **E**, which undergoes a 5-*endo-trig* cyclization to furnish **F**. A final 1,3-proton transfer of **F** results in the

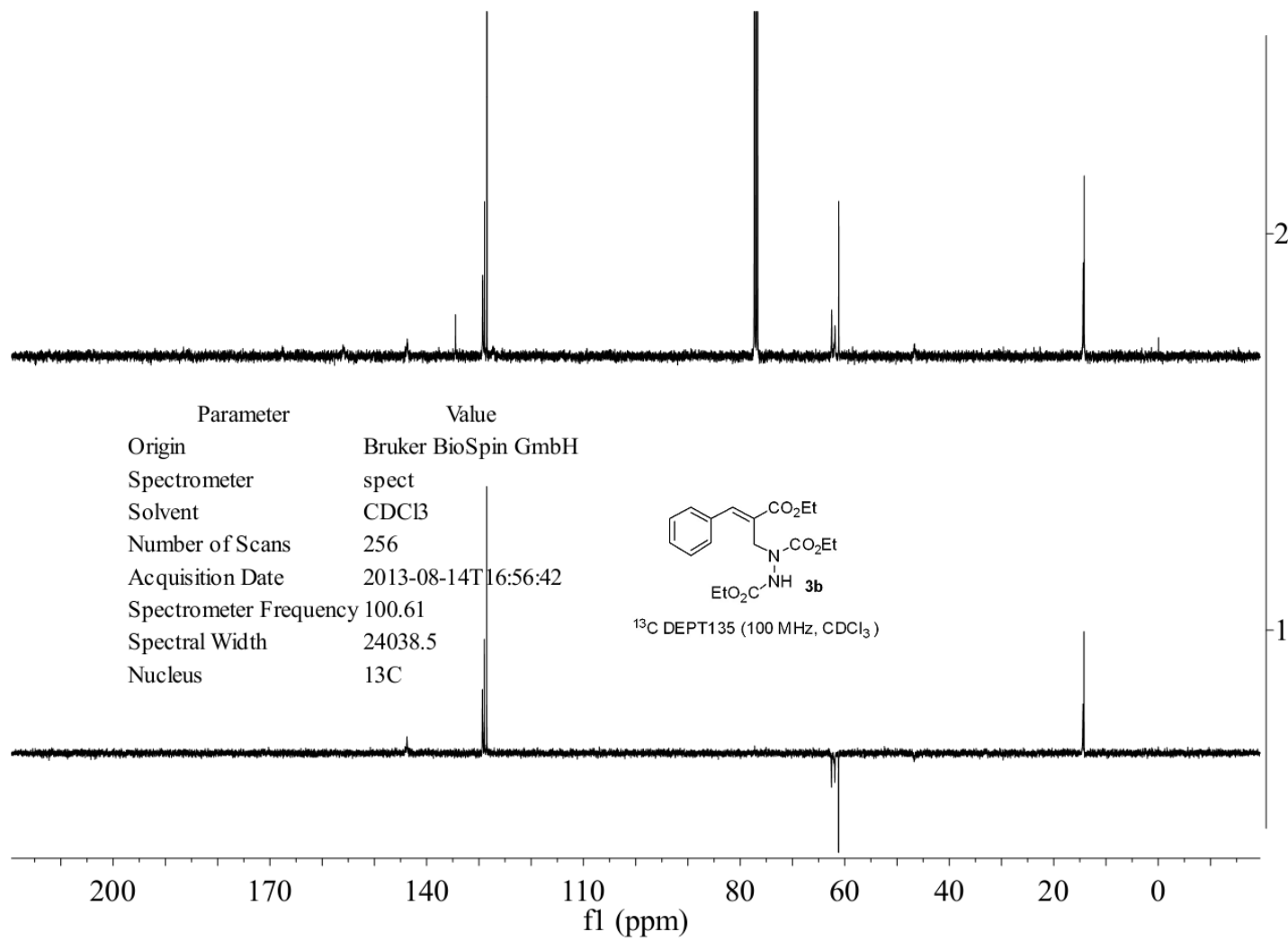
formation of 1*H*-pyrazole **7**. Another possible pathway for the formation of **7** (path **b**) involves the S_N2 displacement of **D** with the species **C** generating the allenic hydrazine **G**, which undertakes a favorable 5-*exo-trig* ring closure to furnish the 1*H*-pyrazole **7**.

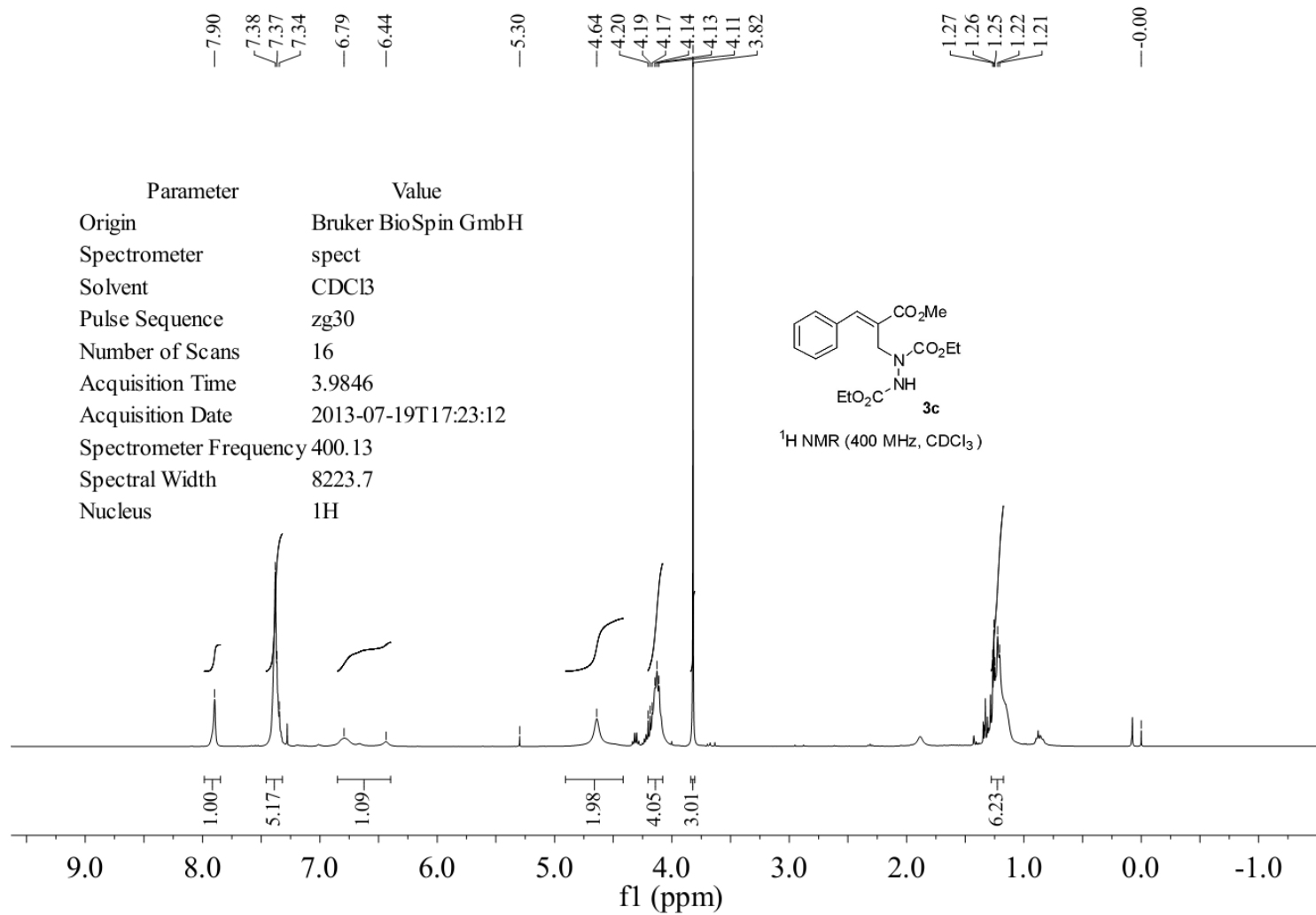
3. Copies of ^1H , ^{13}C , DEPT, and NOESY NMR spectra





Parameter	Value
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl ₃
Pulse Sequence	zgpg30
Number of Scans	503
Acquisition Time	1.3631
Acquisition Date	2013-08-14T17:28:03
Spectrometer Frequency	100.61
Spectral Width	24038.5
Nucleus	13C





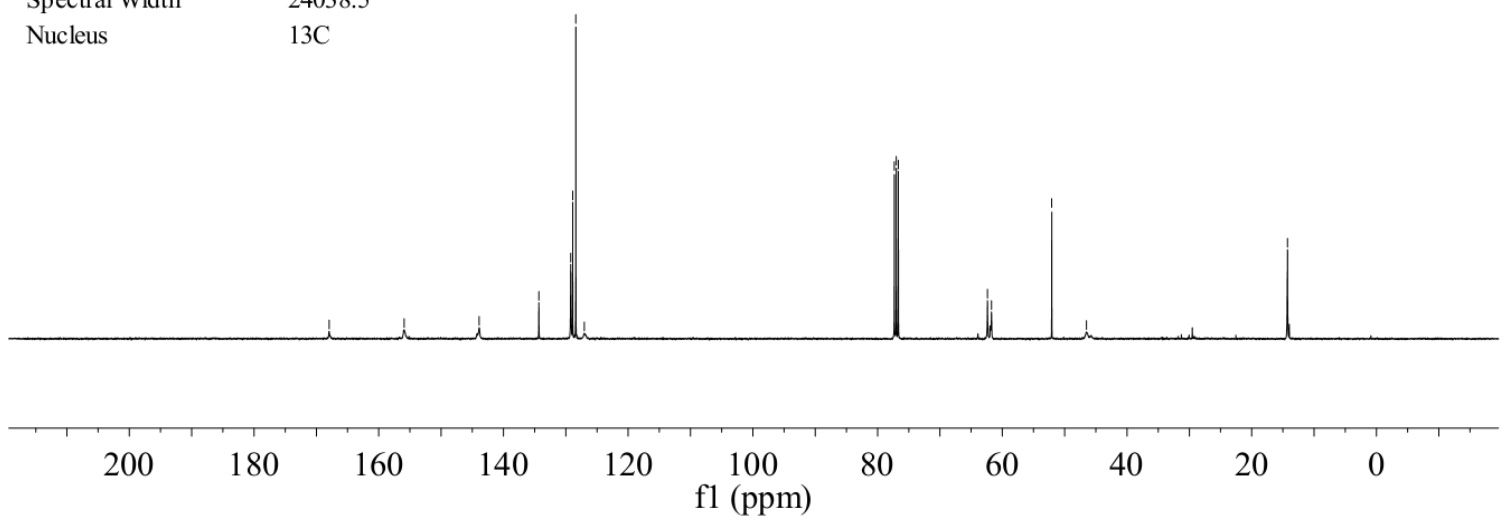
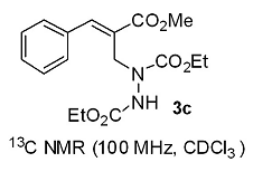
— 167.95
 — 155.92
 — 143.89
 { 134.32
 { 129.22
 { 128.90
 { 128.39
 { 127.04

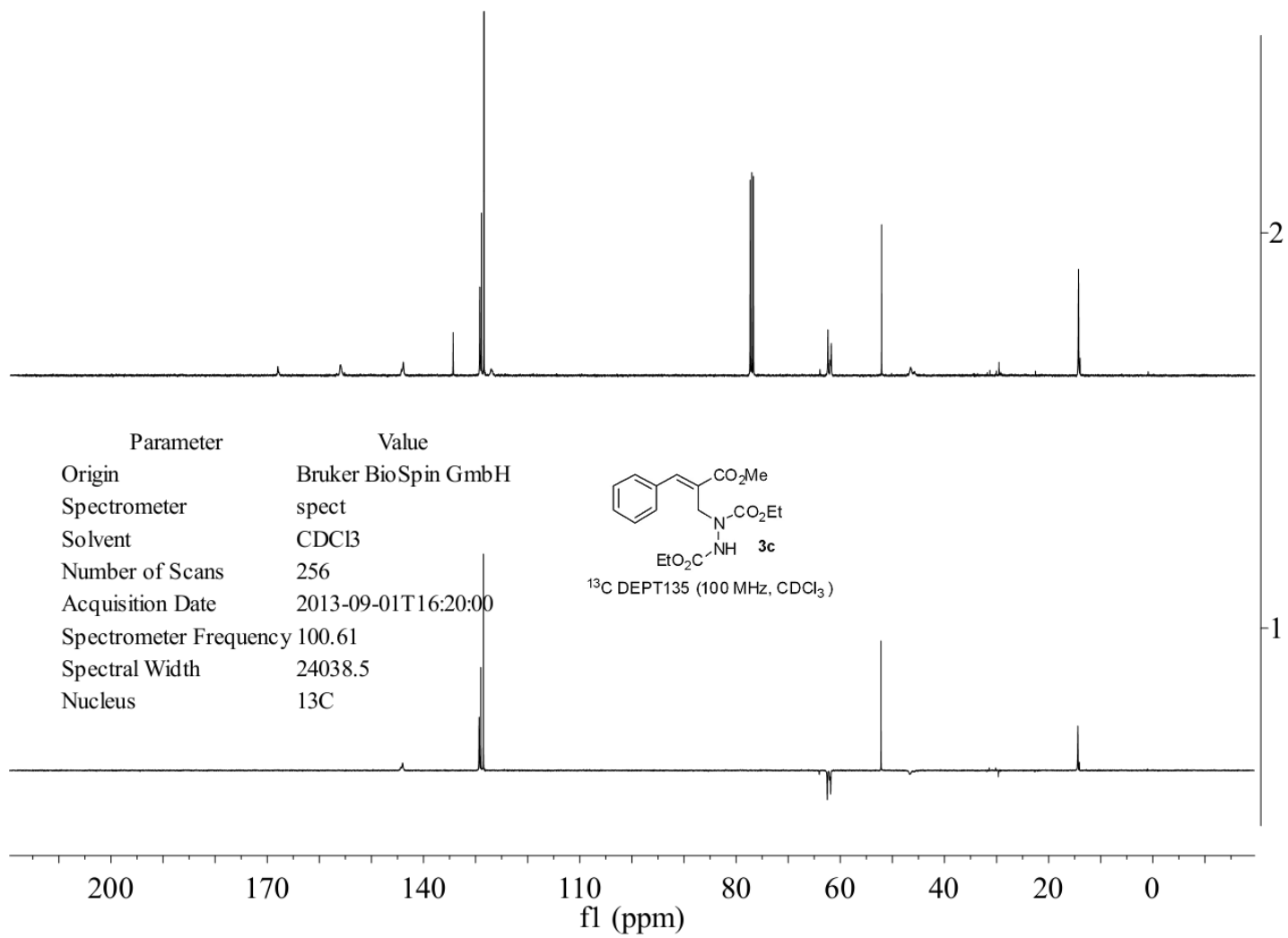
 { 77.32
 { 77.00
 { 76.68

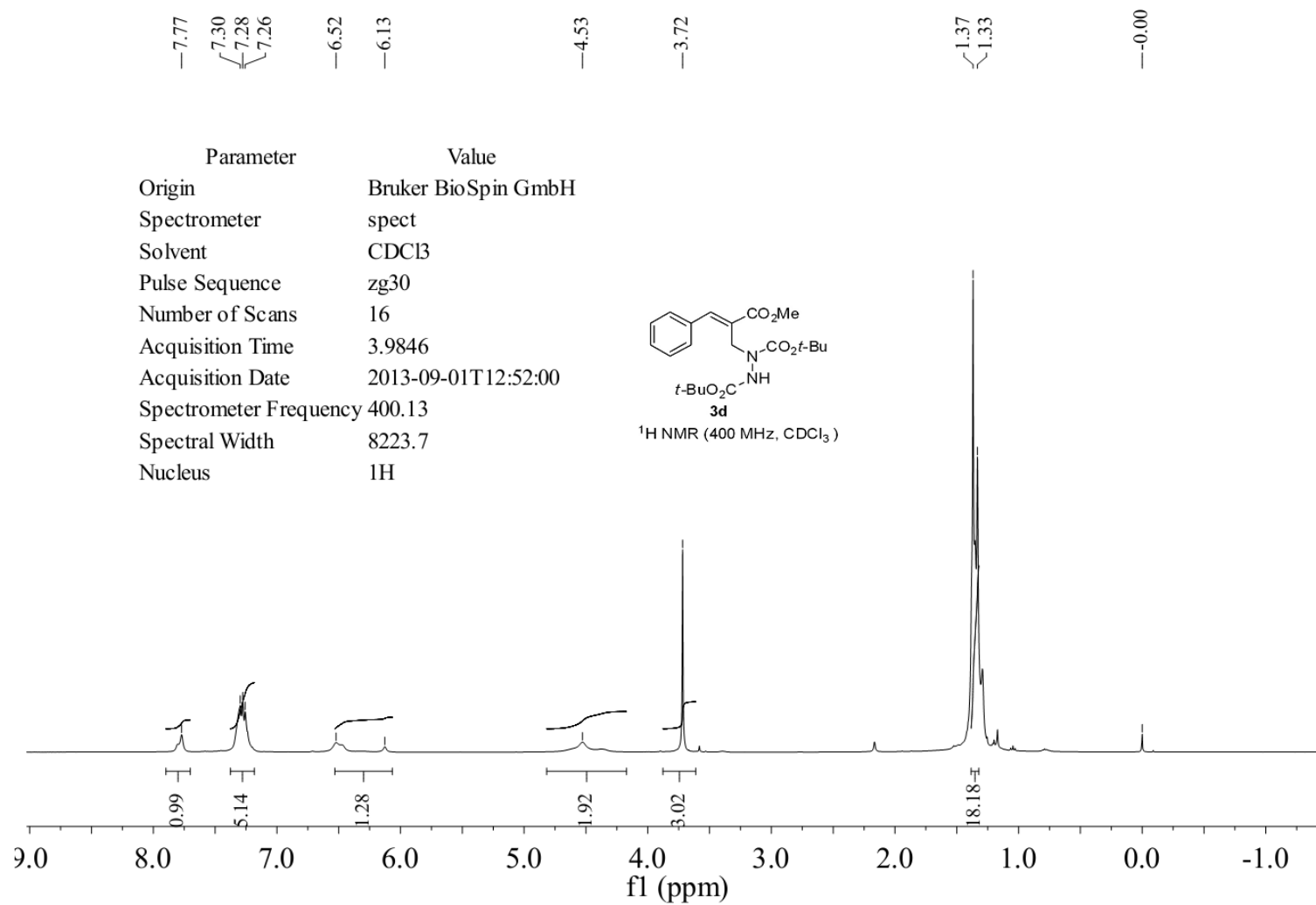
 { 62.38
 { 61.73
 — 52.07
 — 46.50

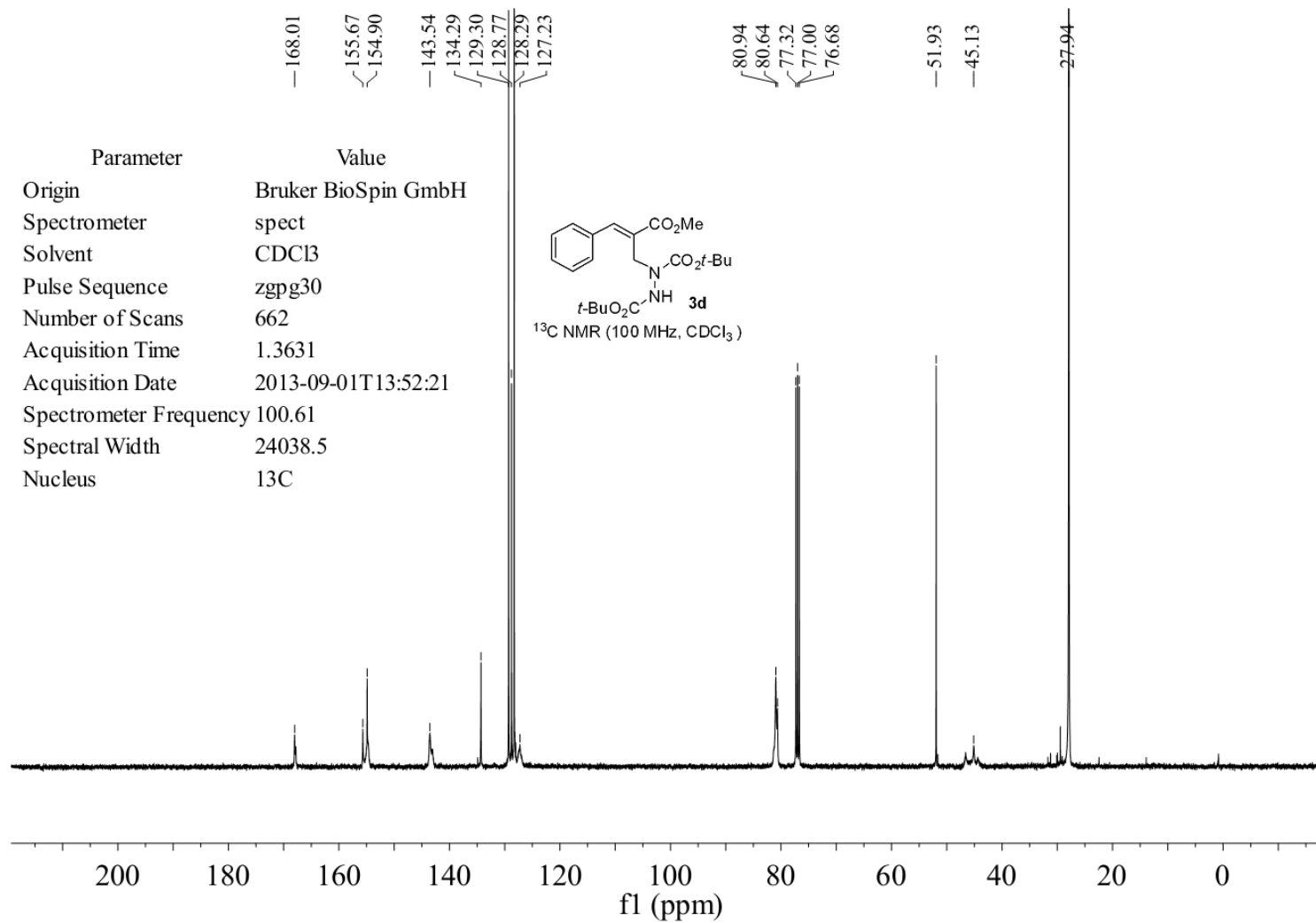
 — 14.27

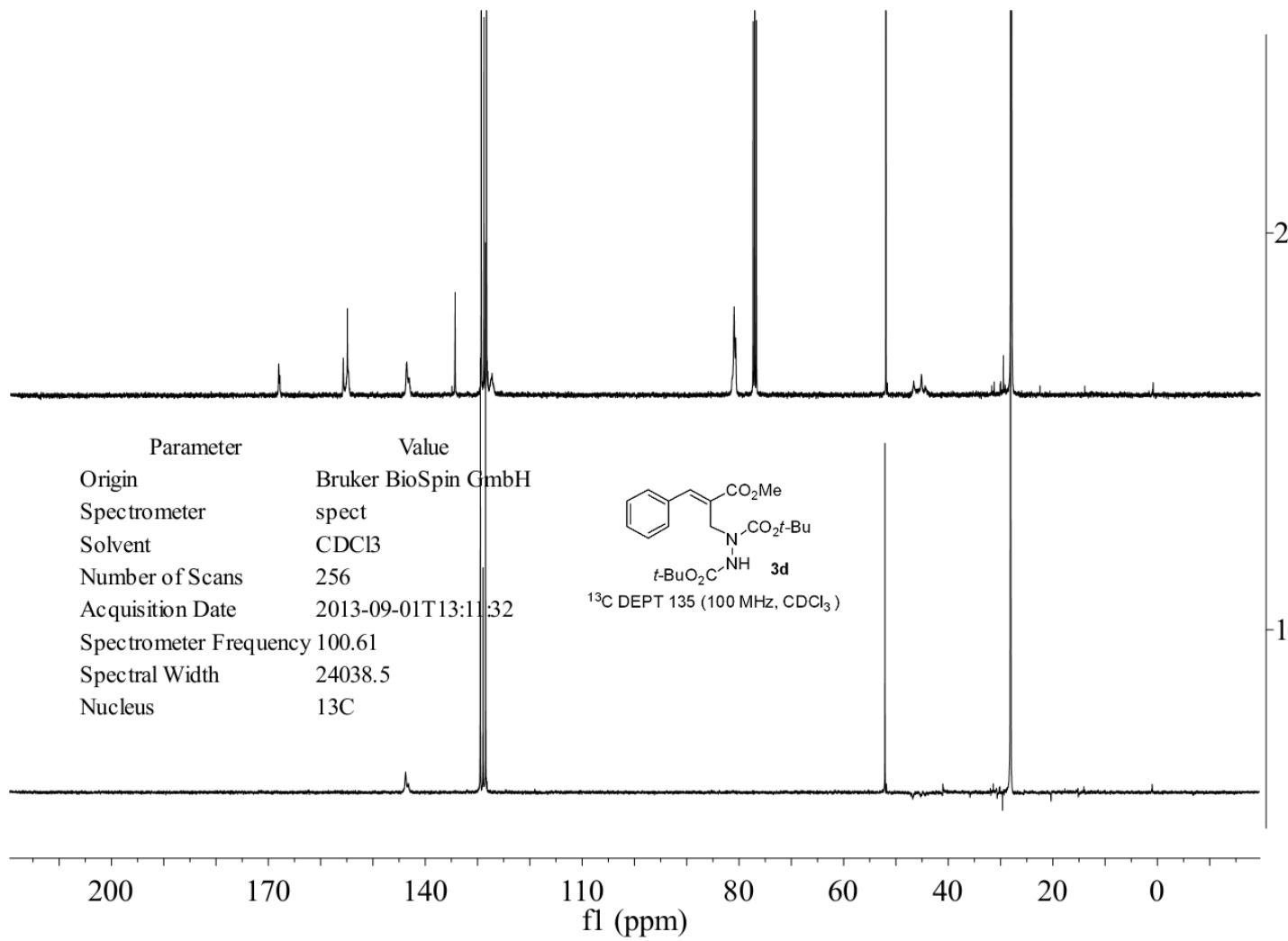
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Spectrometer	spect
Solvent	CDCl ₃
Pulse Sequence	zgpg30
Number of Scans	677
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Acquisition Date	2013-09-01T16:02:08
Spectrometer Frequency	100.61
Spectral Width	24038.5
Nucleus	¹³ C

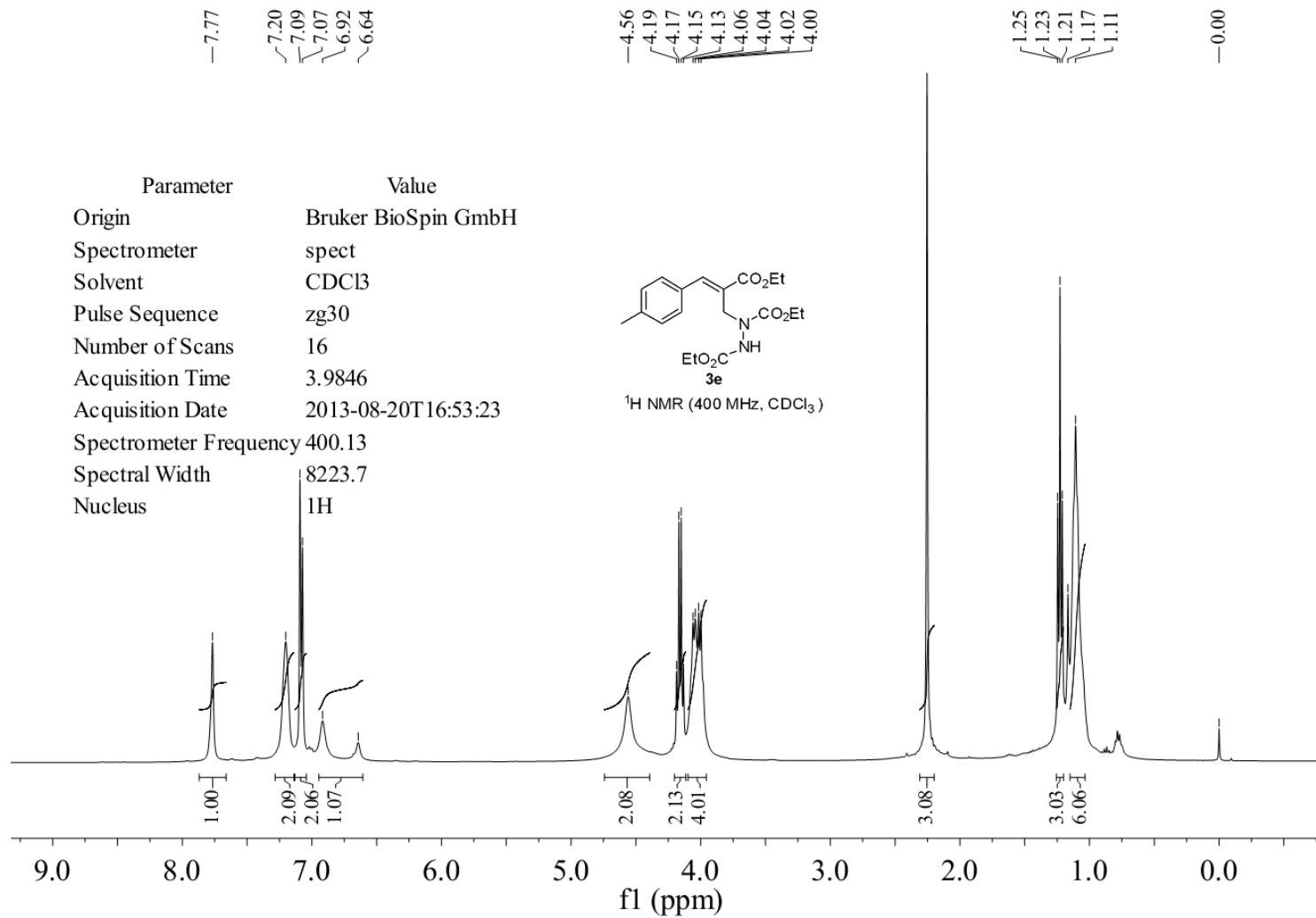










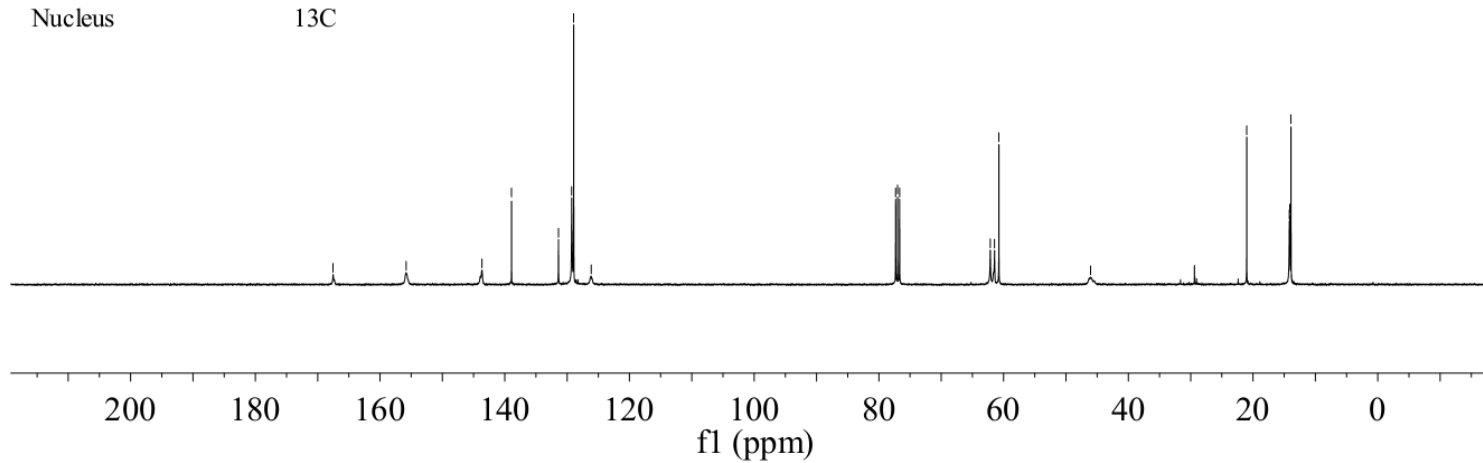
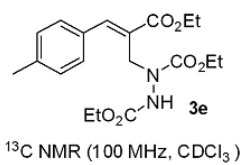


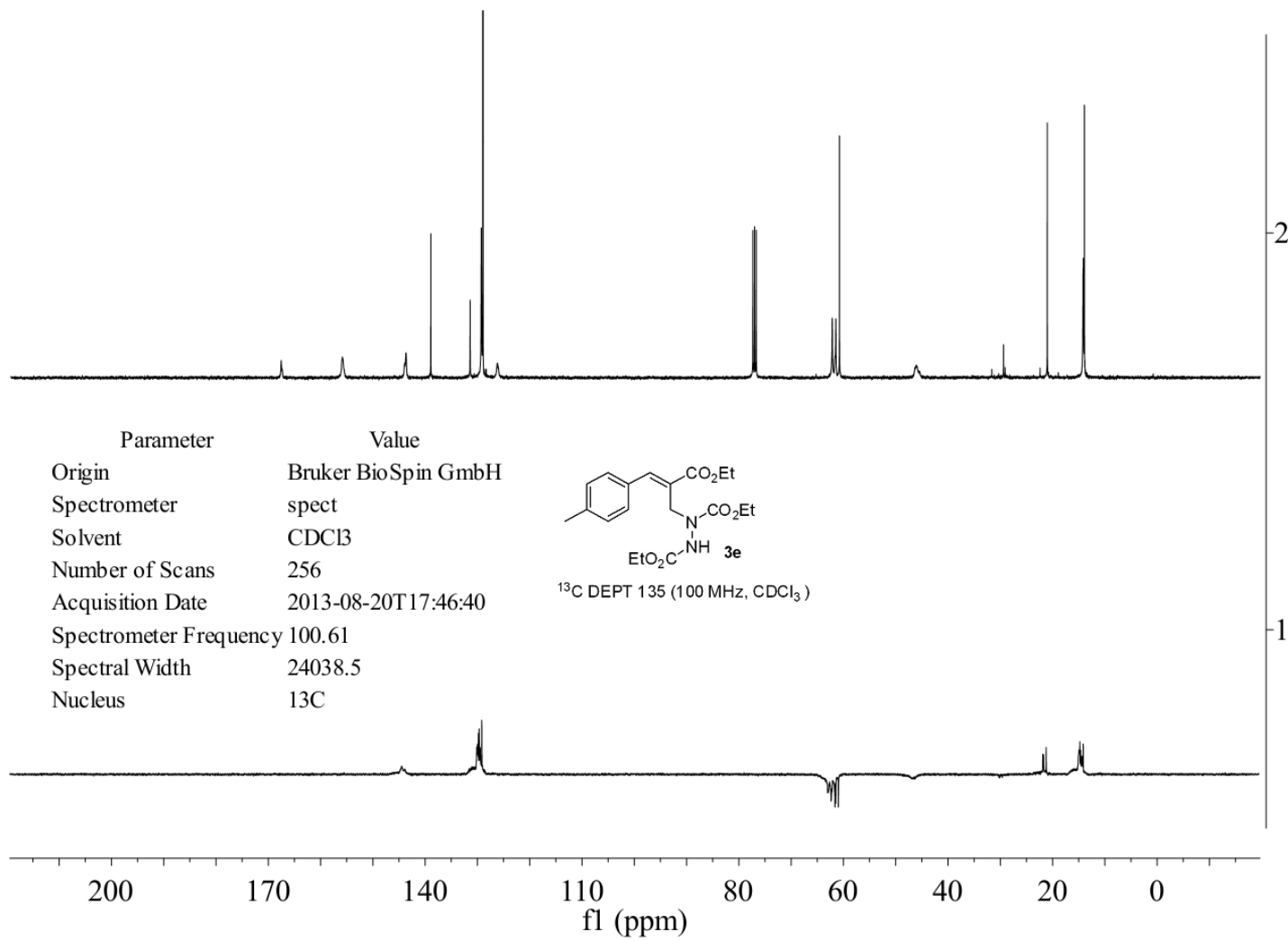
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 — 155.82
 / 143.66
 / 138.91
 / 131.39
 / 129.27
 / 128.95
 / 126.14

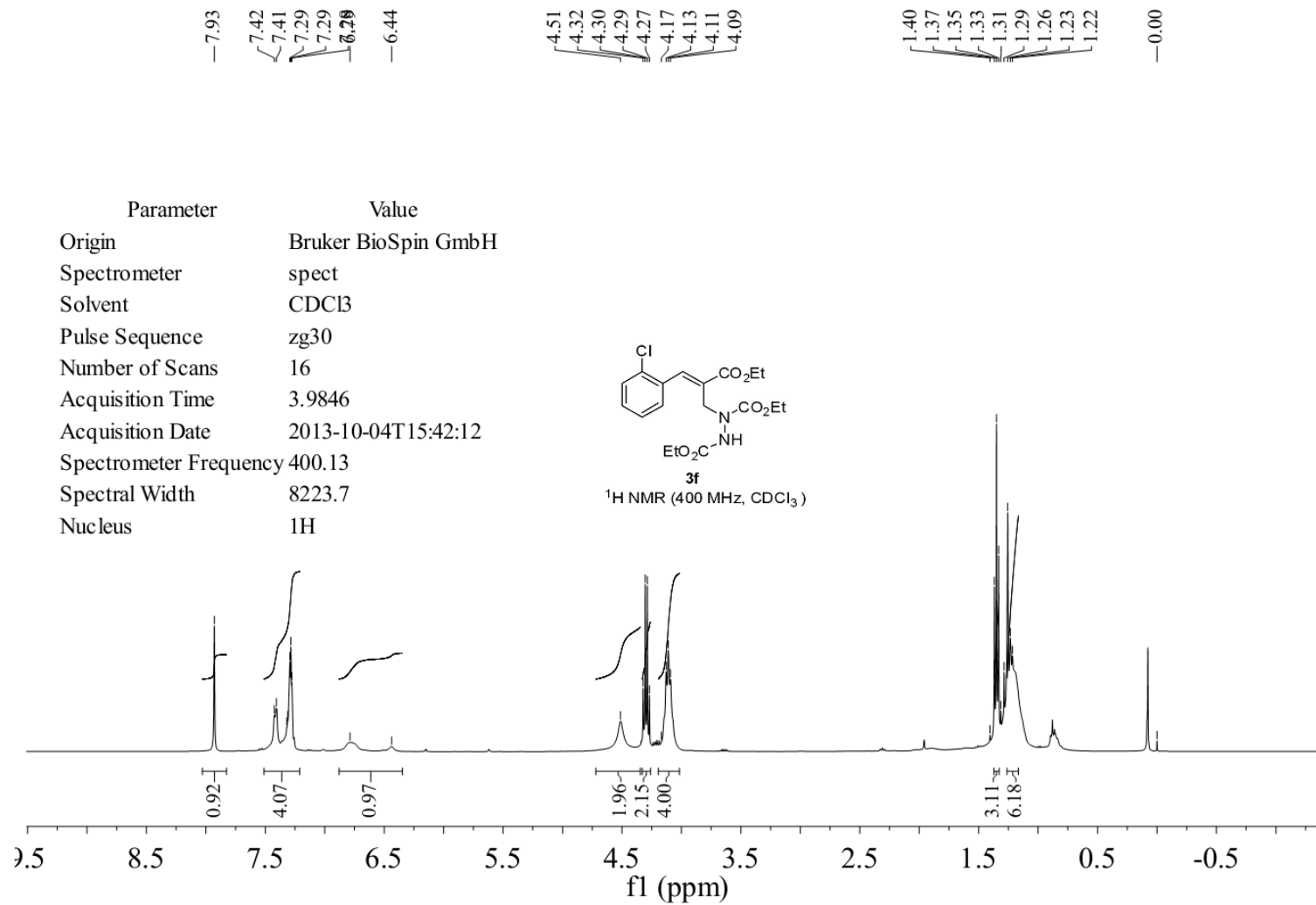
 / 77.32
 / 77.00
 / 76.68
 / 62.14
 / 61.46
 / 60.76
 — 46.04

 / 21.02
 / 14.17
 / 14.11
 / 13.92

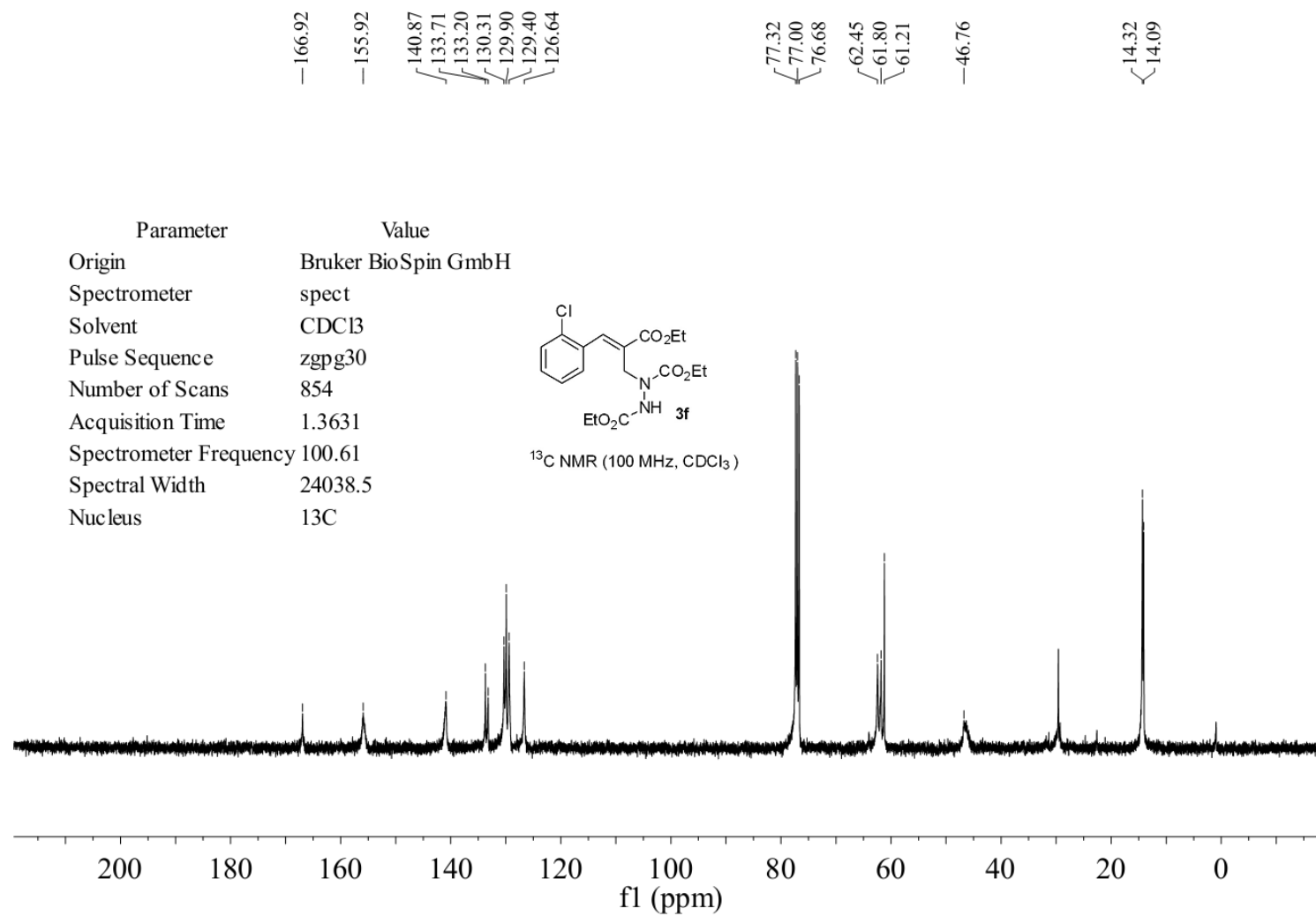
Parameter	Value
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl ₃
Pulse Sequence	zgpg30
Number of Scans	532
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Acquisition Date	2013-08-20T17:27:26
Spectrometer Frequency	100.61
Spectral Width	24038.5
Nucleus	¹³ C

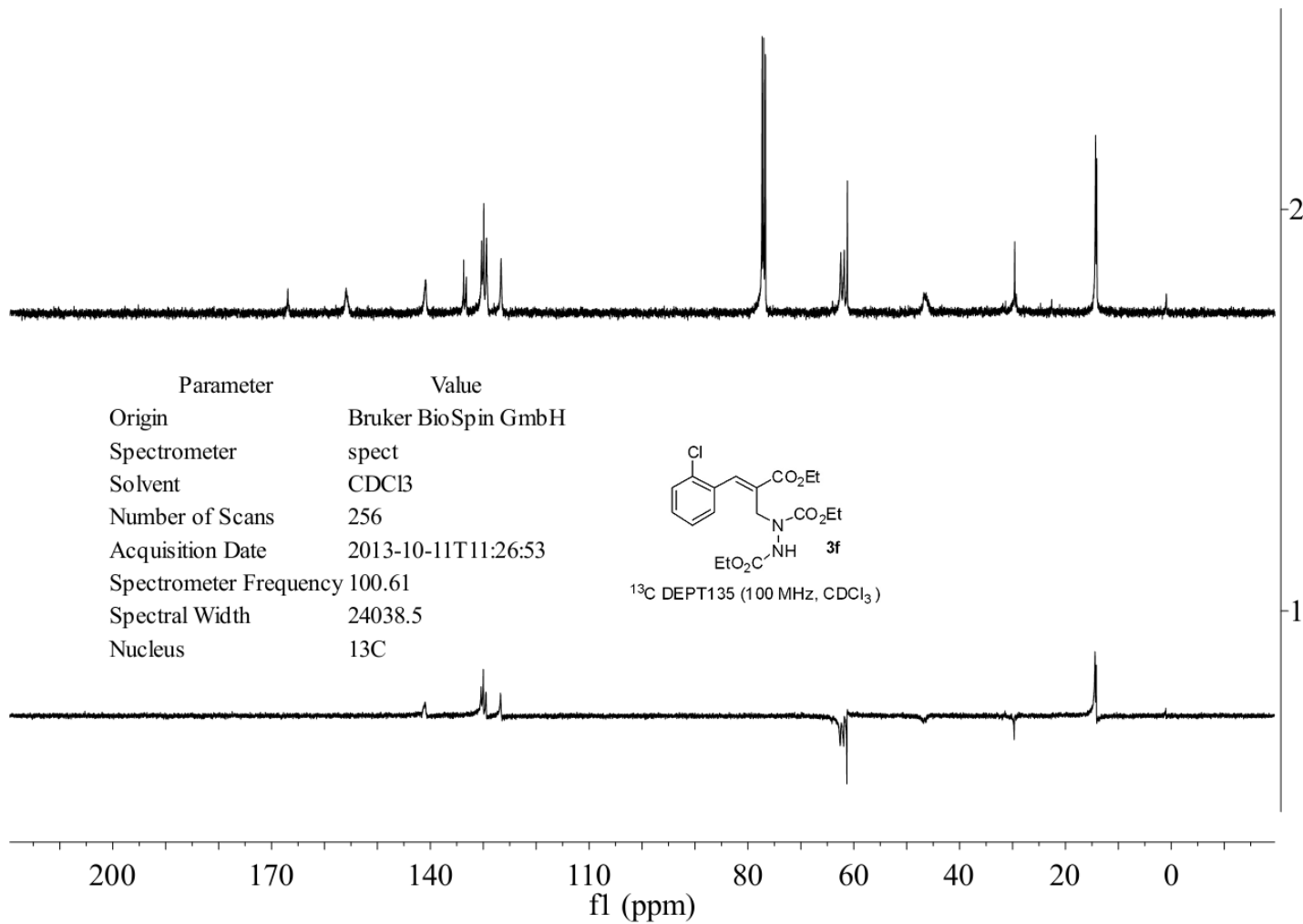


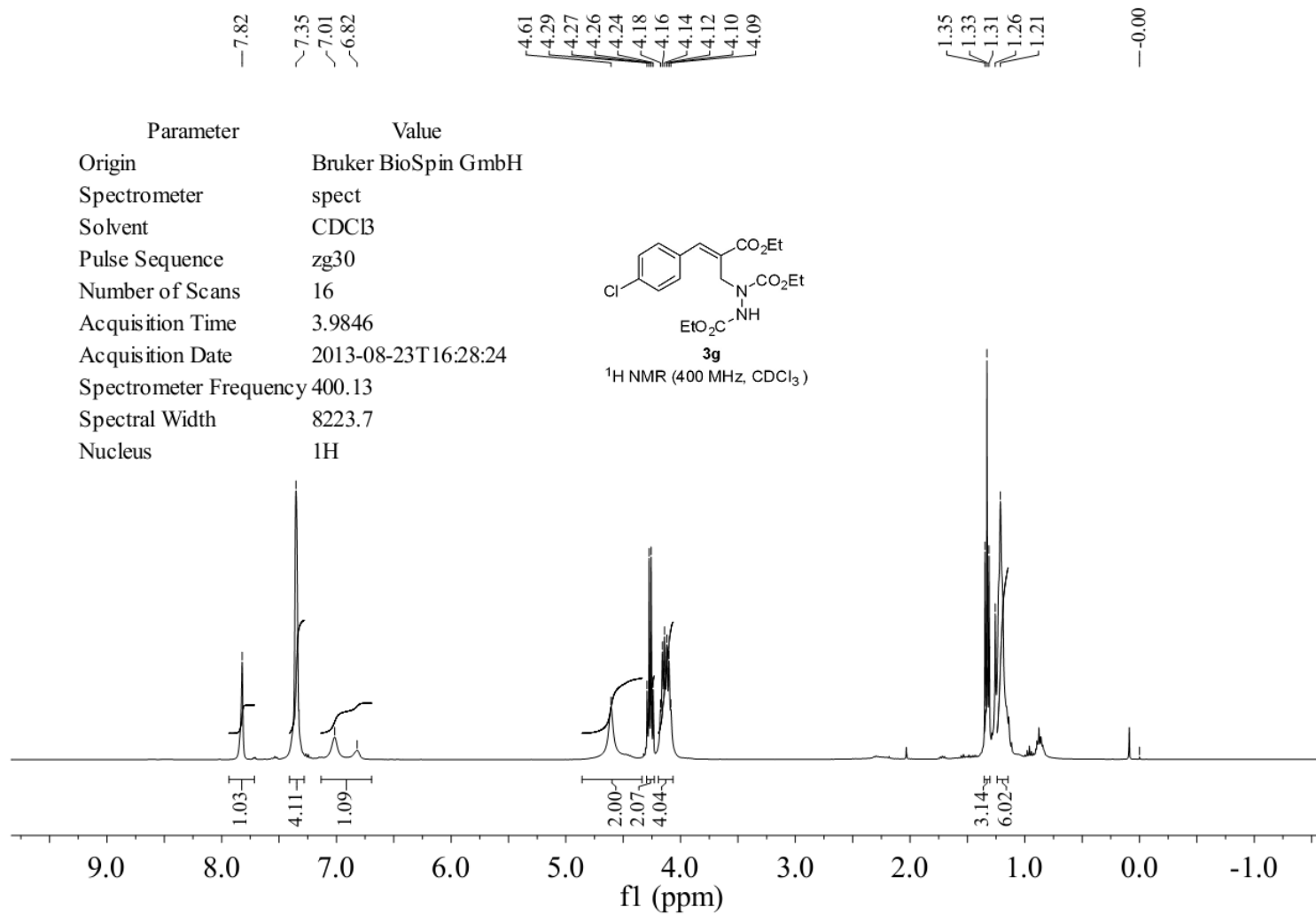


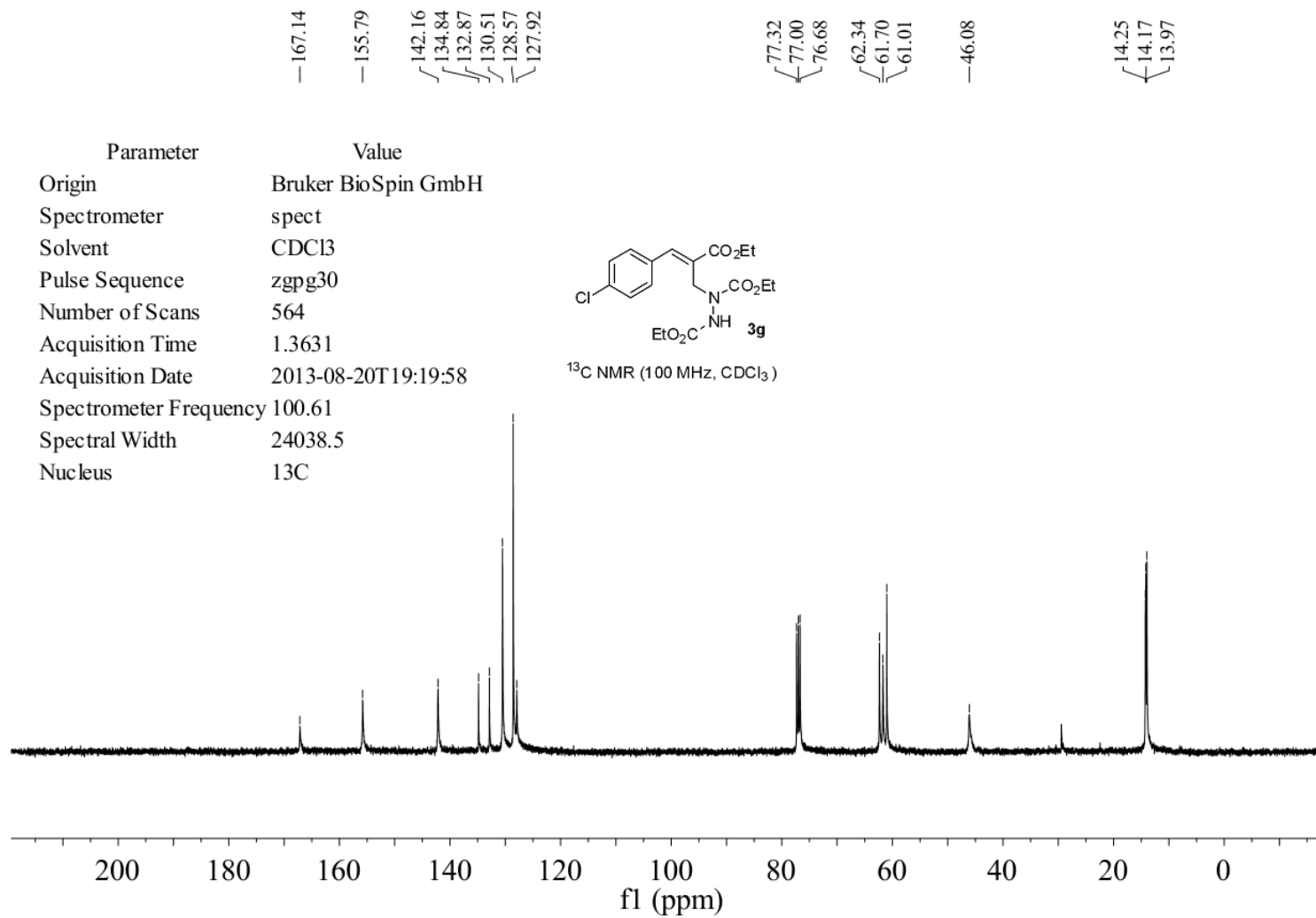


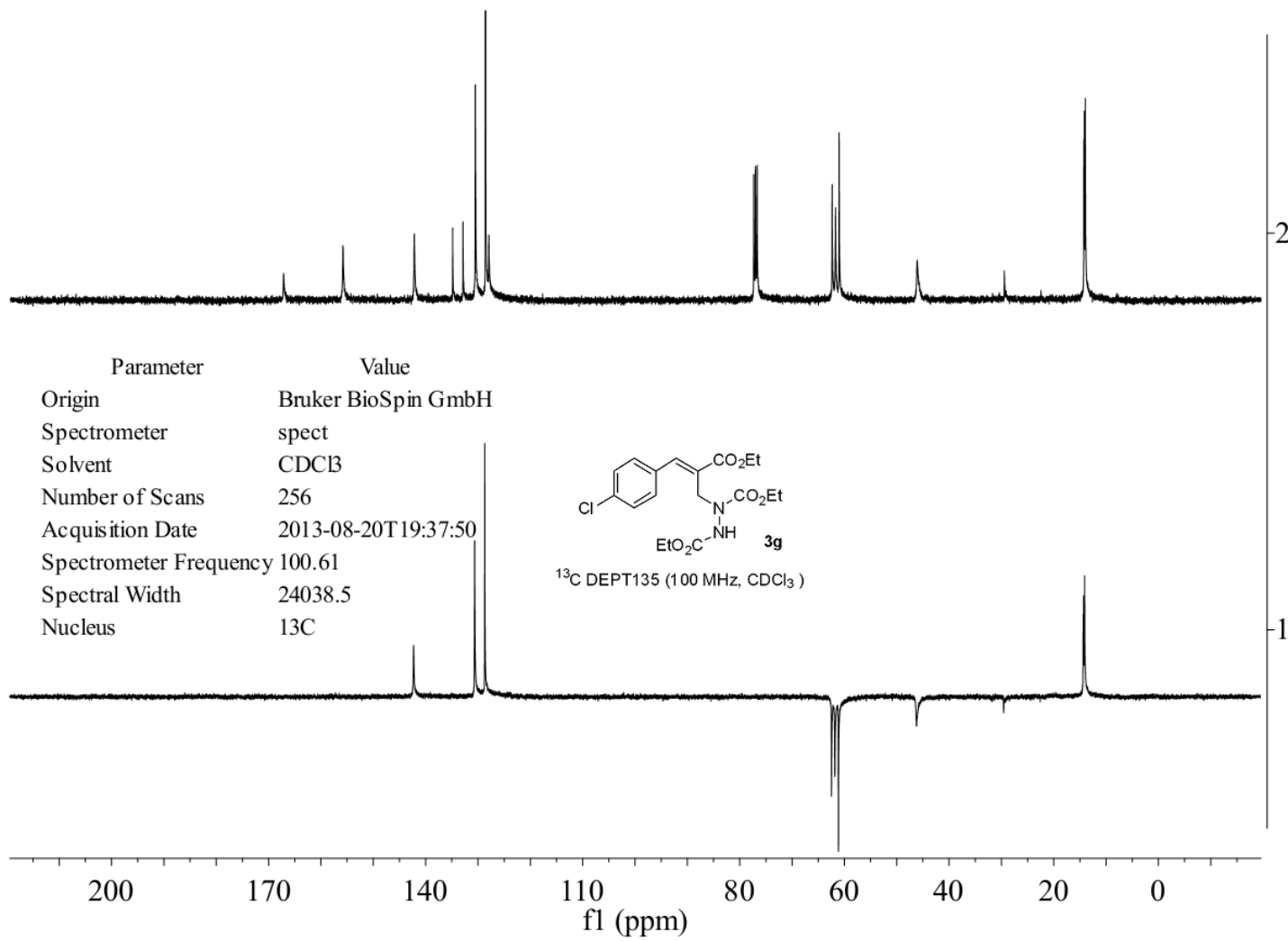
Parameter	Value
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl ₃
Pulse Sequence	zg30
Number of Scans	16
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Acquisition Date	2013-10-04T15:42:12
Spectrometer Frequency	400.13
Spectral Width	8223.7
Nucleus	¹ H









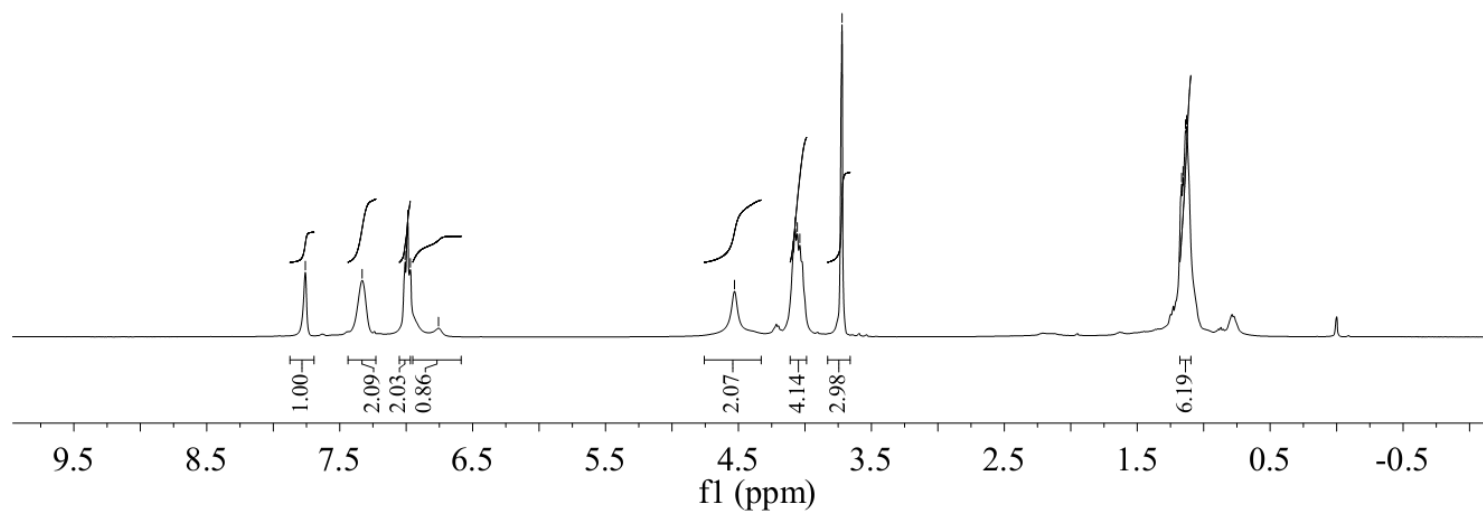
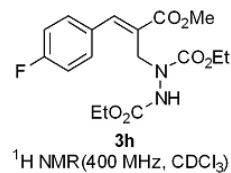


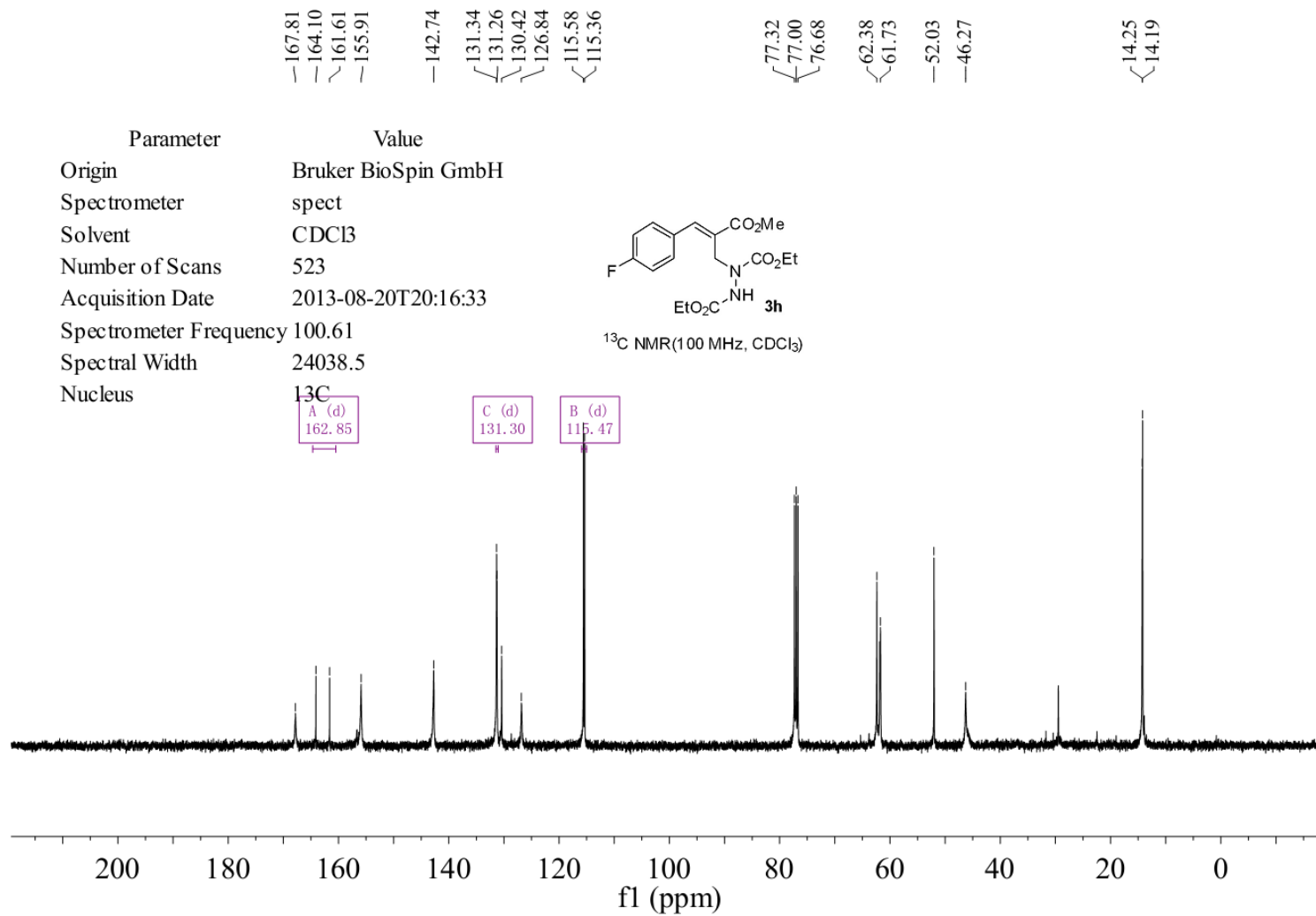
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7.01
6.99
6.97
6.76

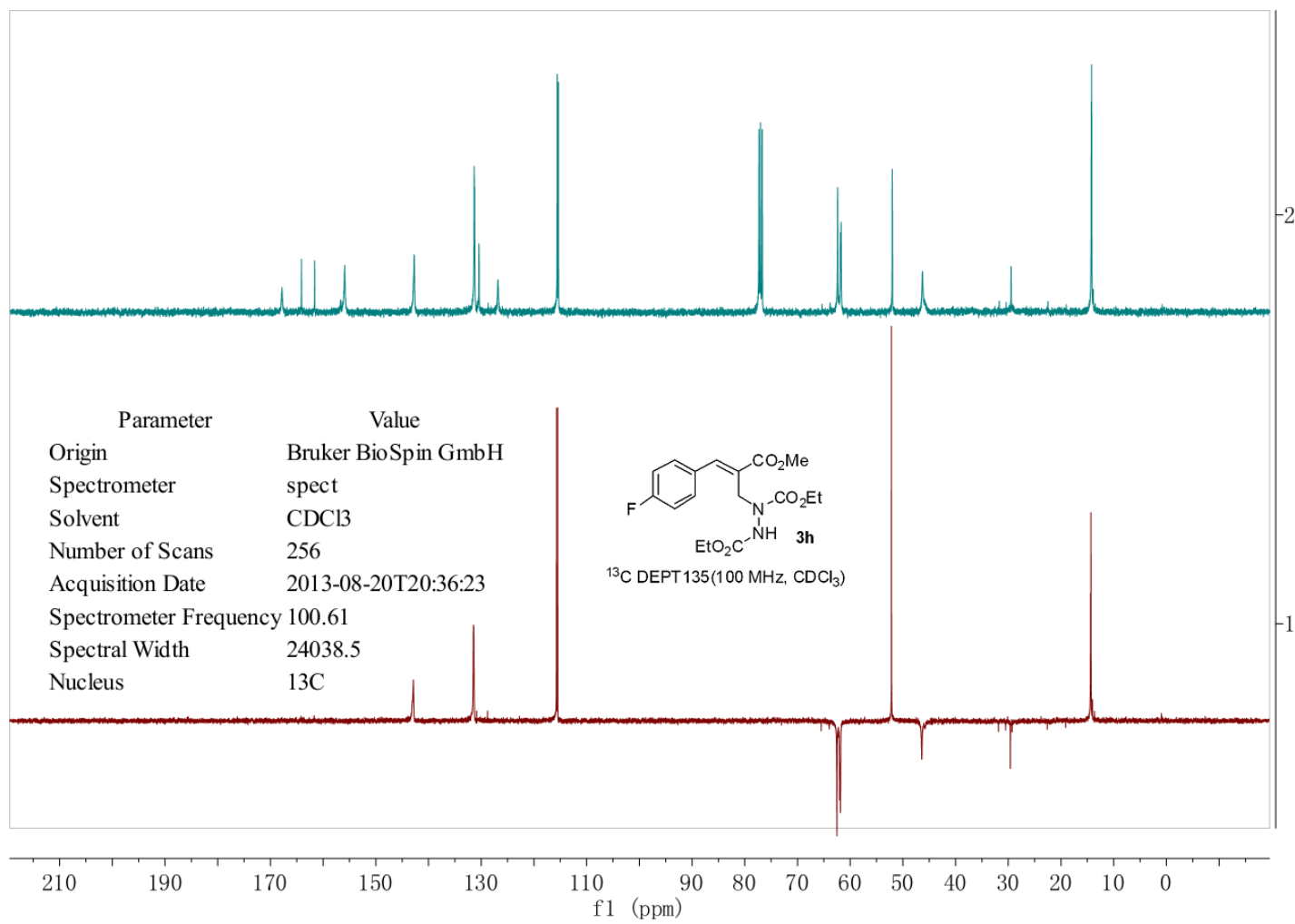
4.53
4.09
4.07
4.06
4.04
3.72

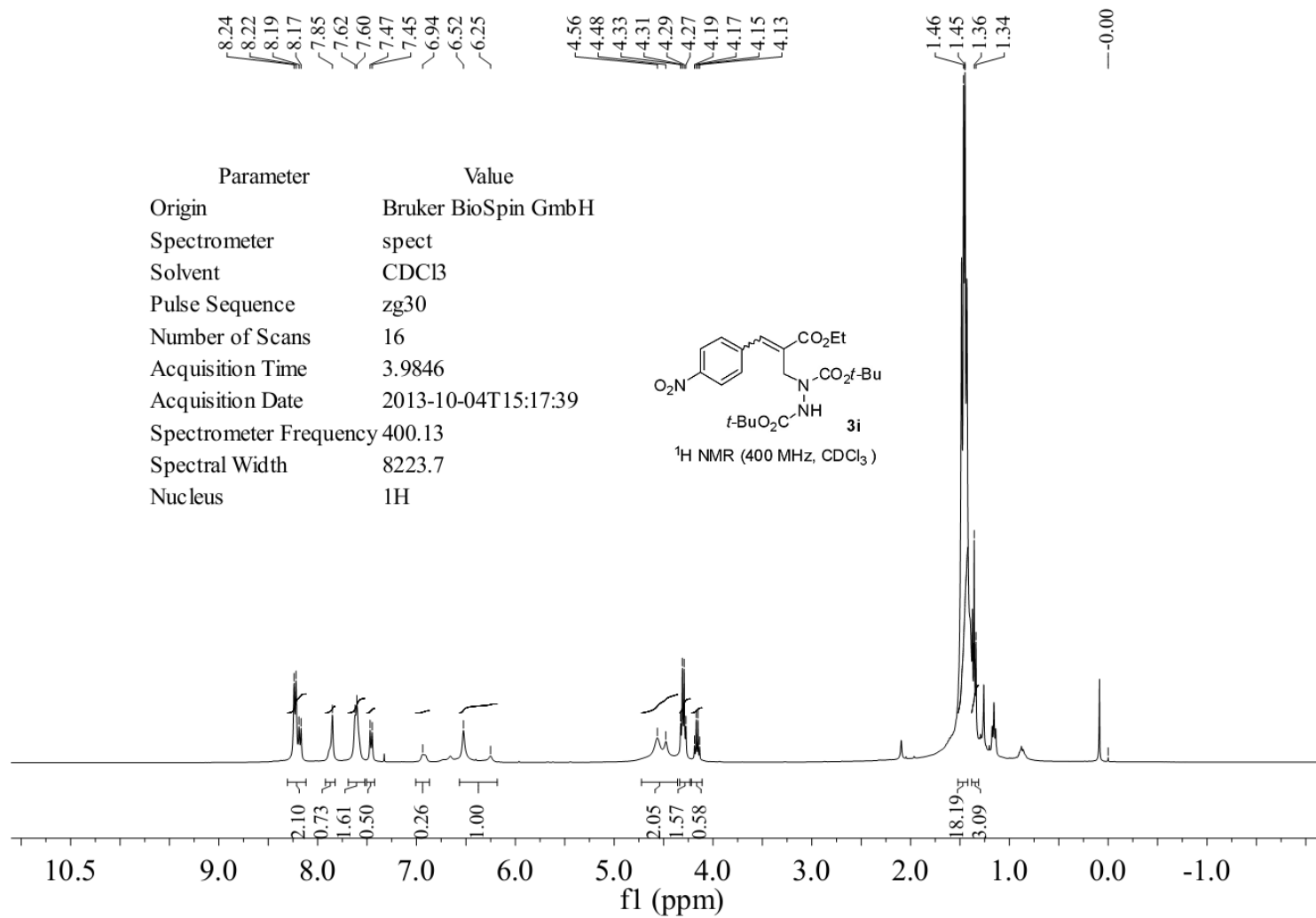
1.17
1.16
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1.13

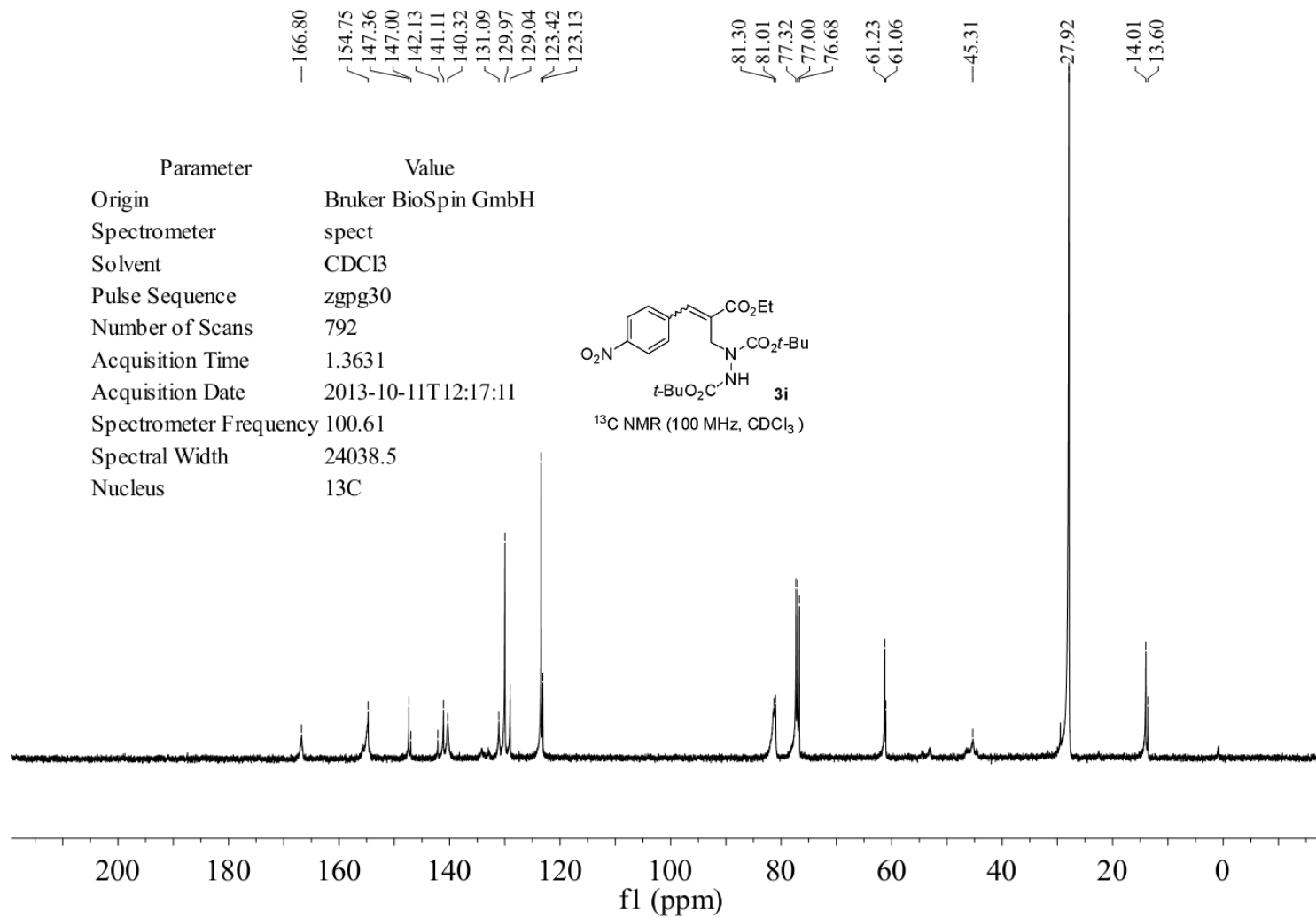
Parameter	Value
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl ₃
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Spectrometer	400.13
Frequency	
Spectral Width	8223.7
Nucleus	¹ H

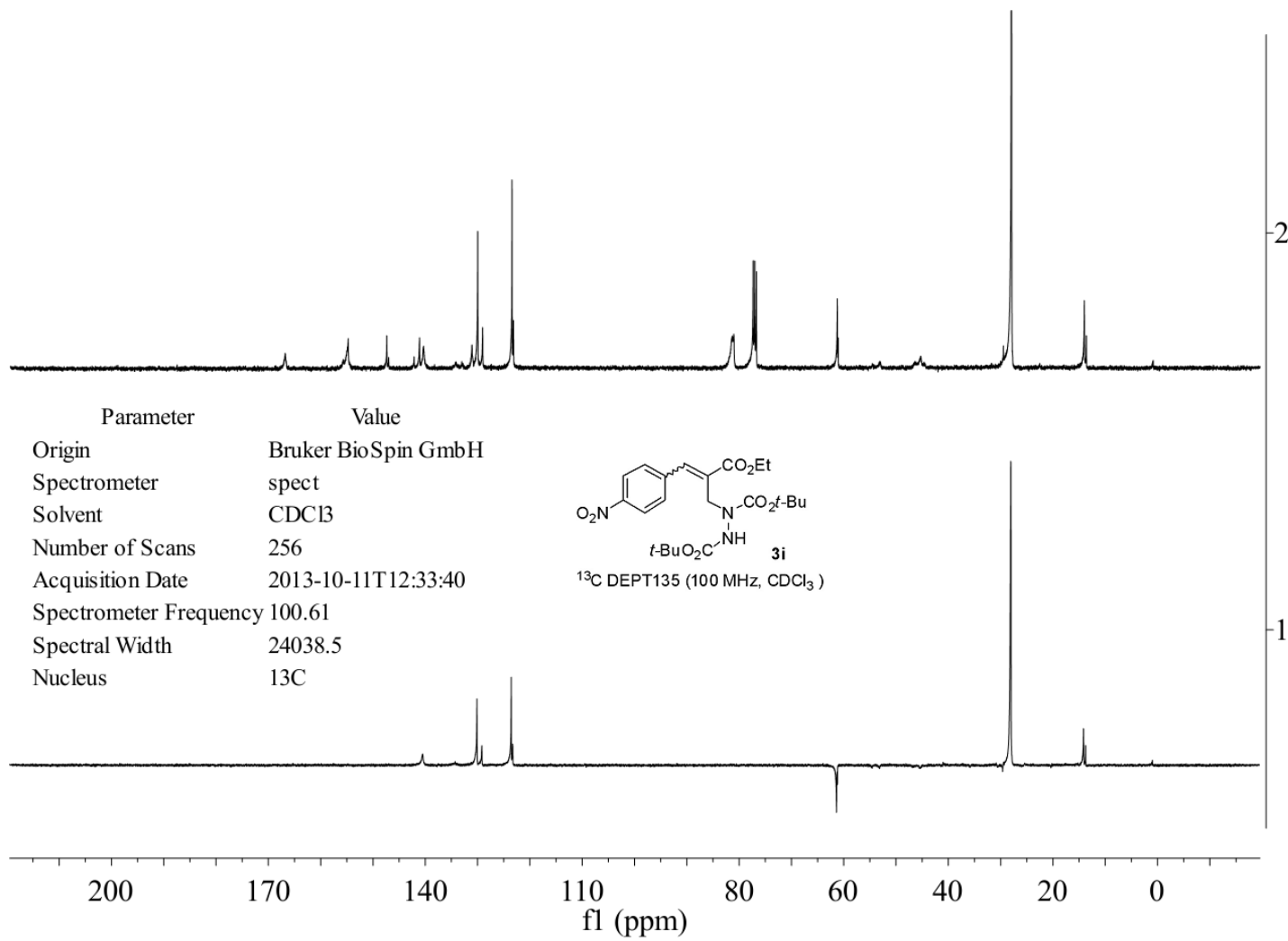


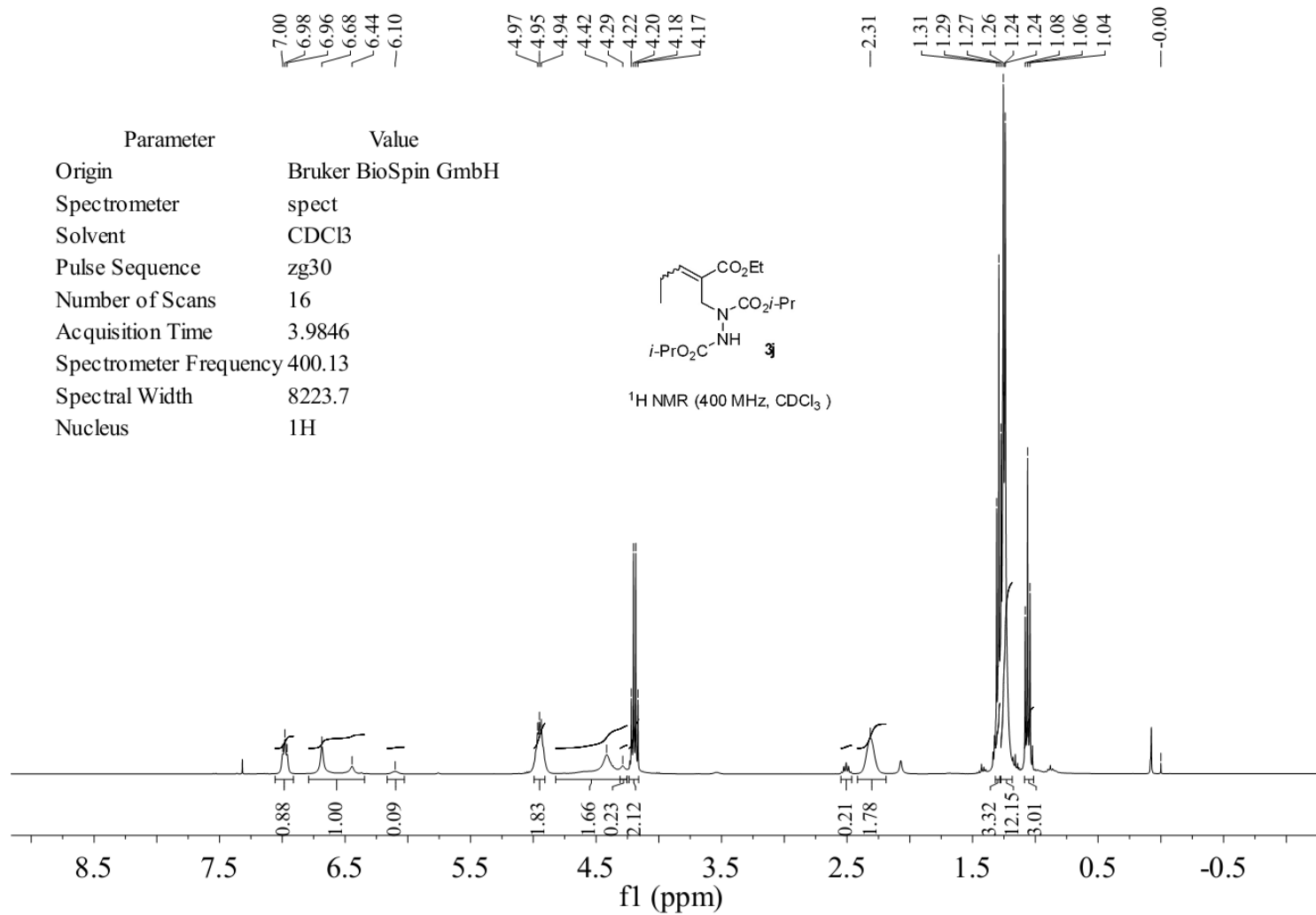


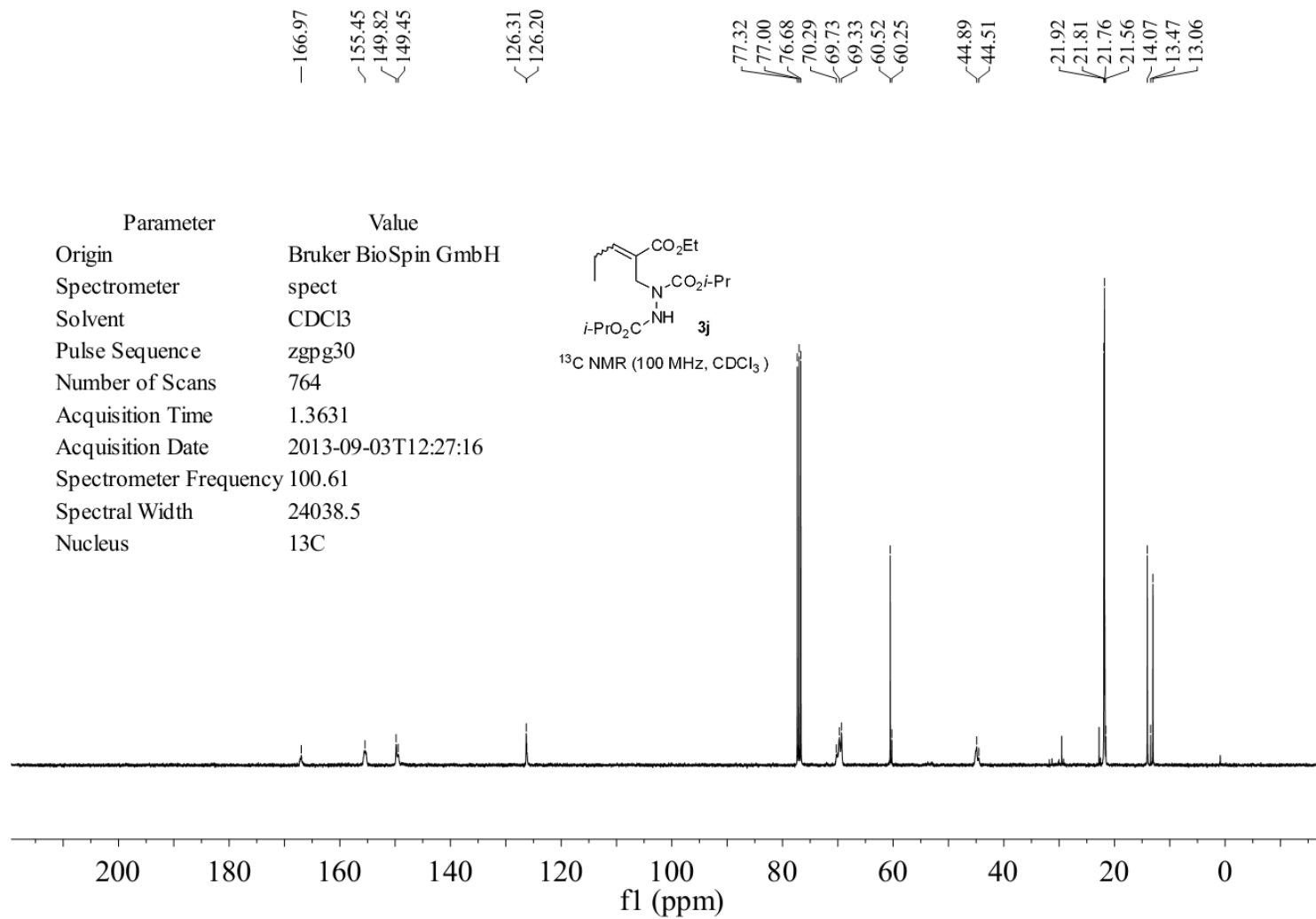




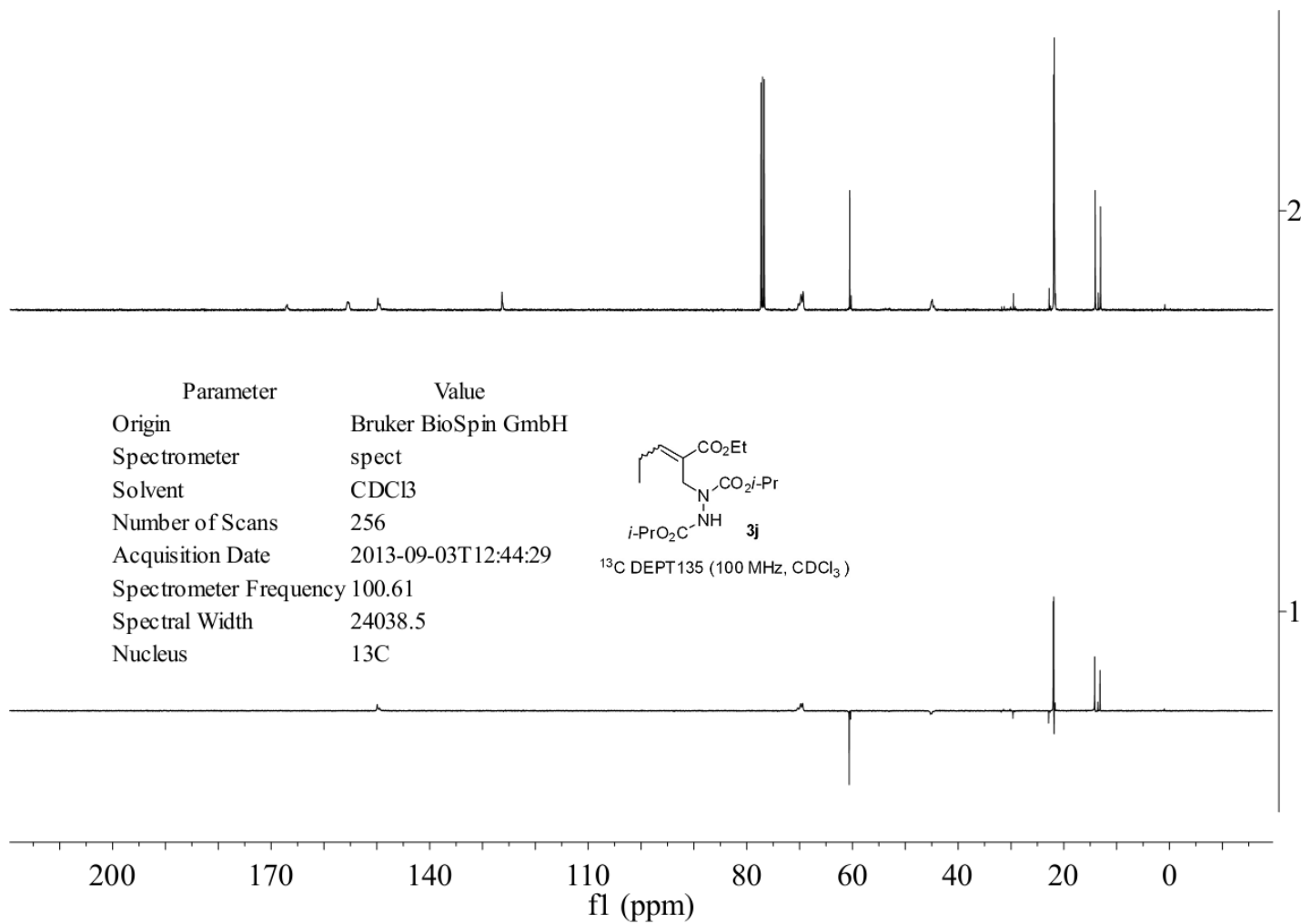


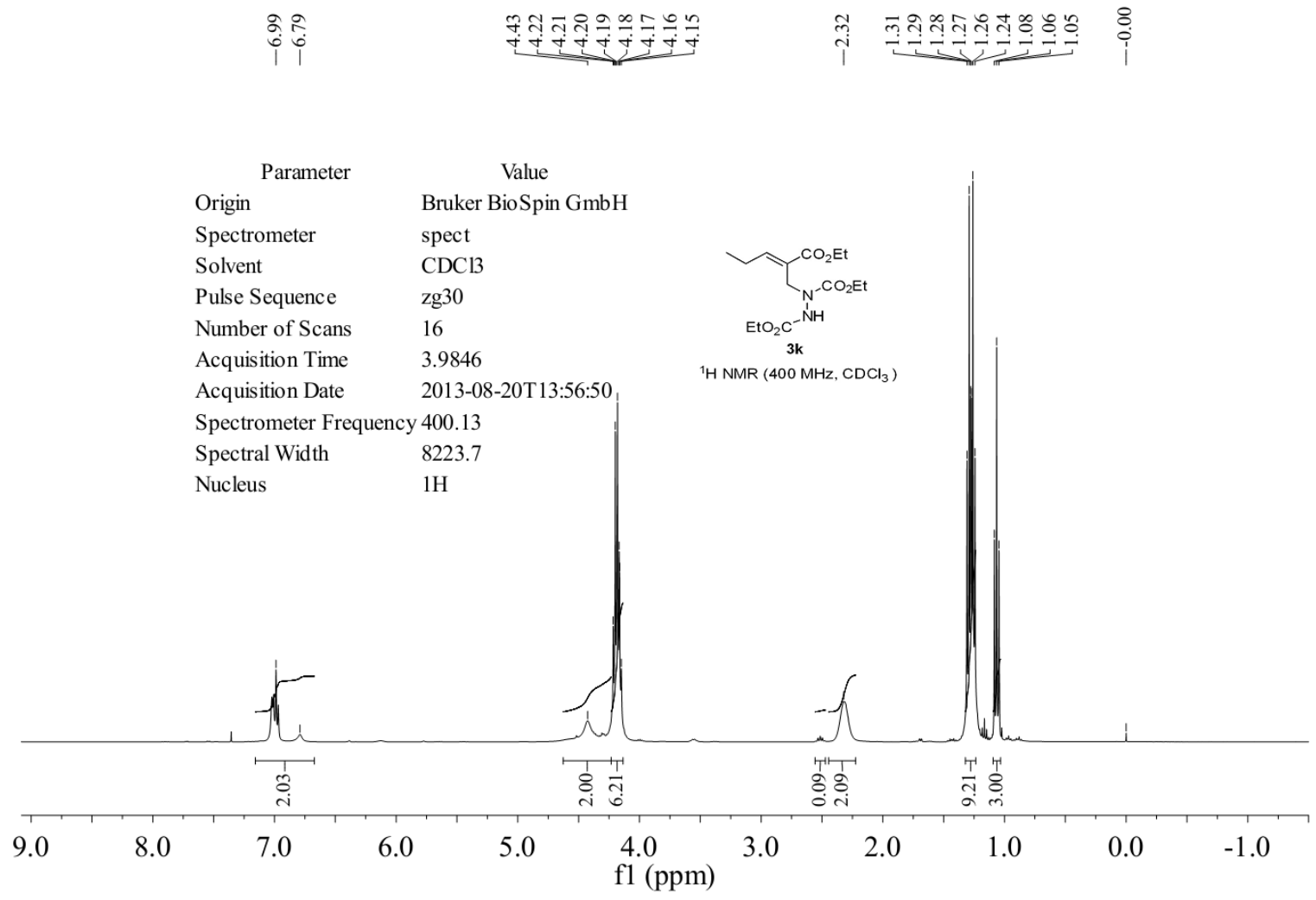


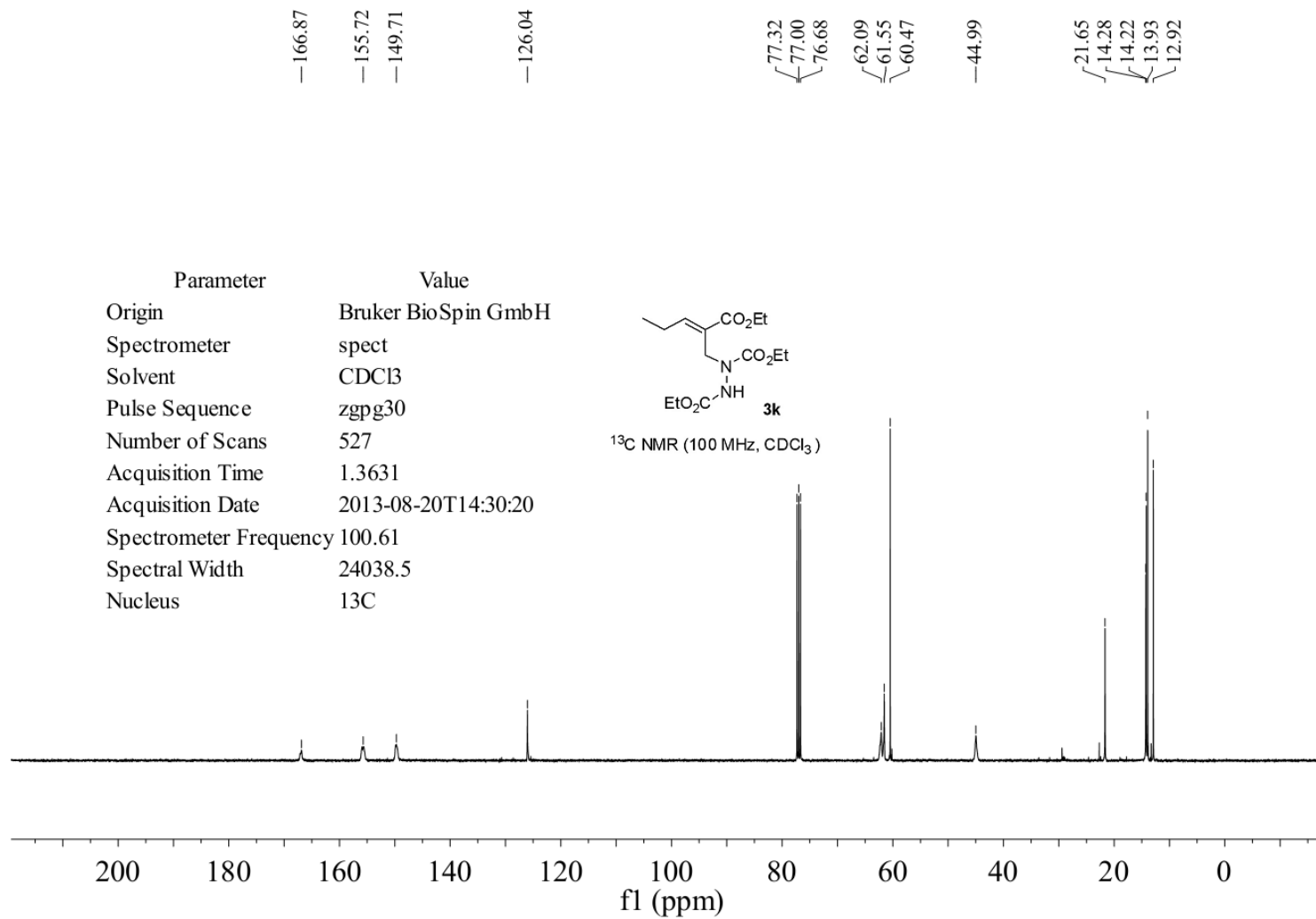


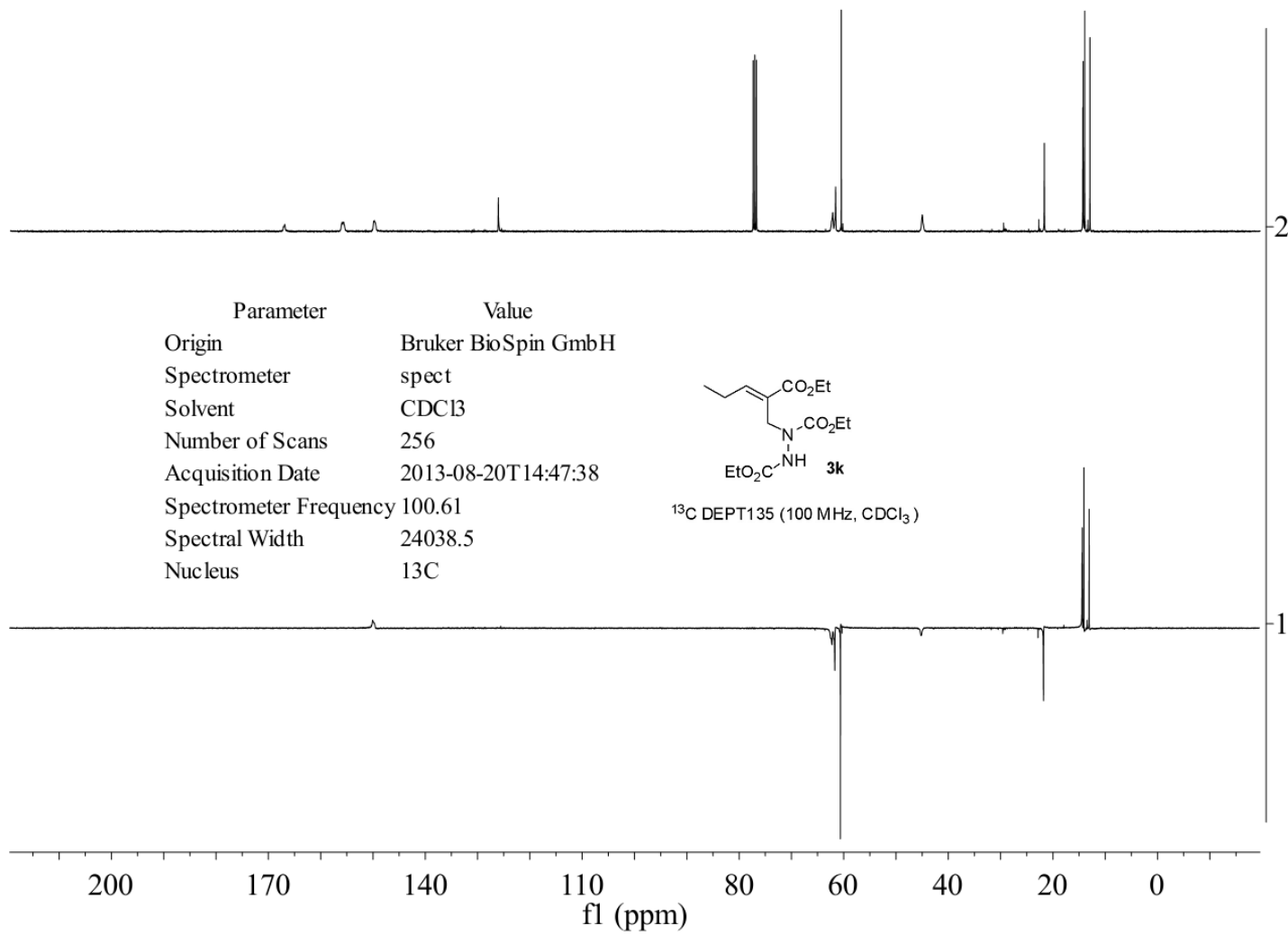


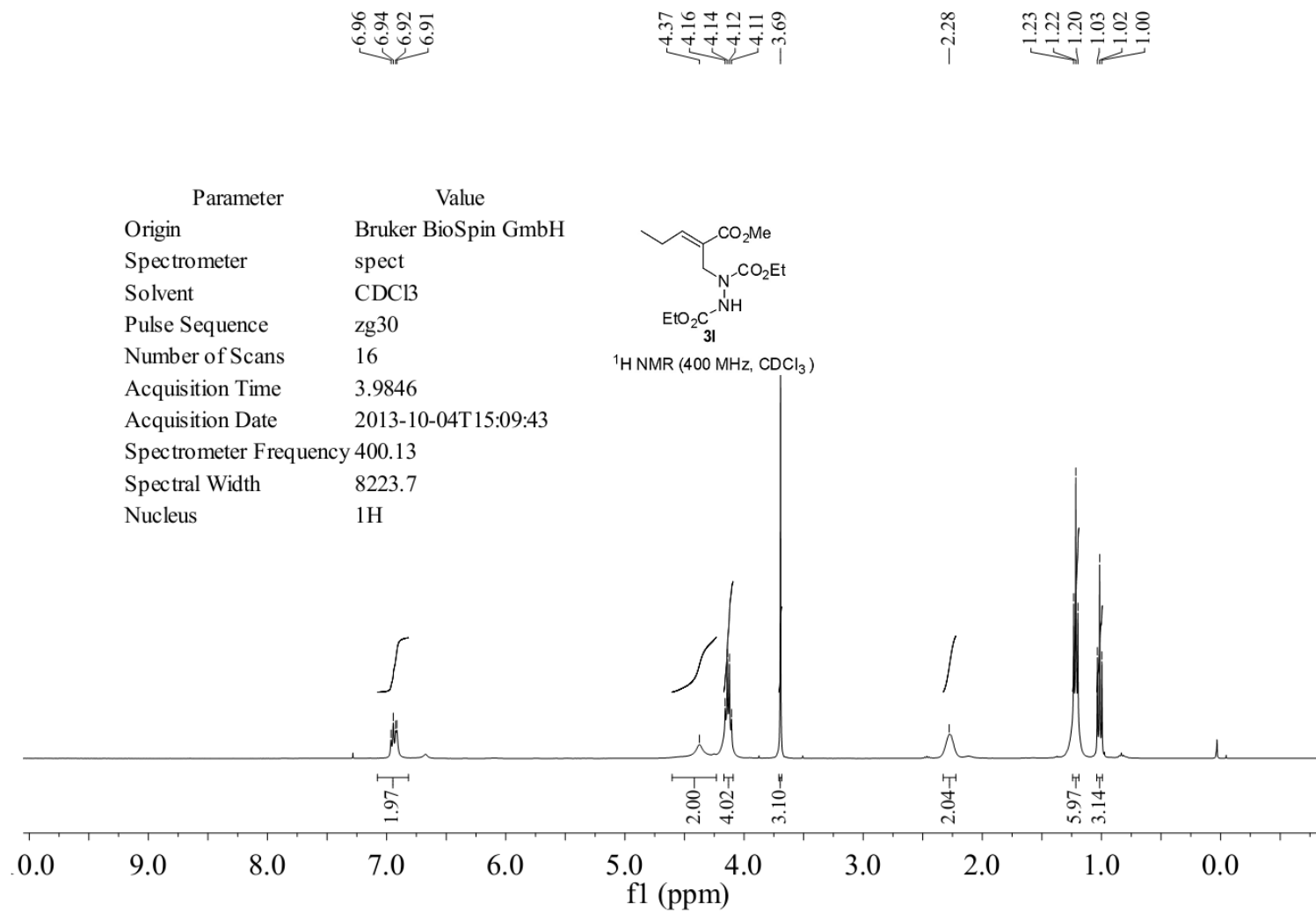
Parameter	Value
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl ₃
Pulse Sequence	zgpg30
Number of Scans	764
Acquisition Time	1.3631
Acquisition Date	2013-09-03T12:27:16
Spectrometer Frequency	100.61
Spectral Width	24038.5
Nucleus	¹³ C





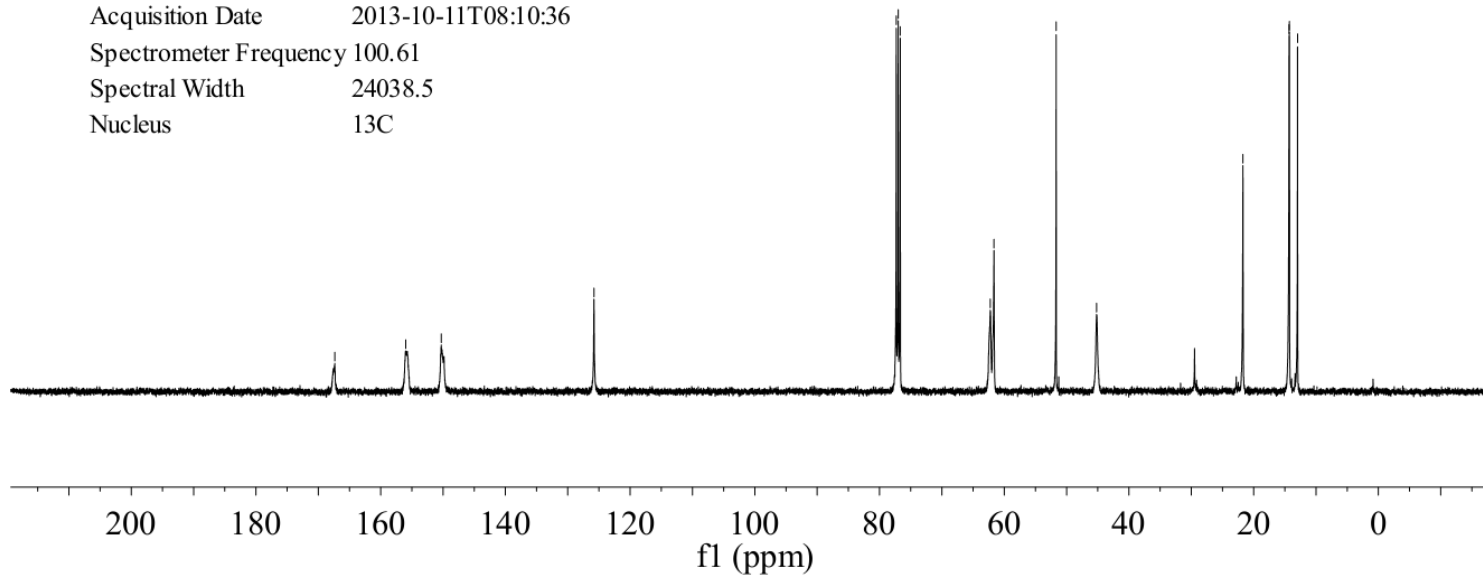
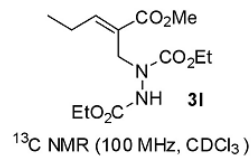


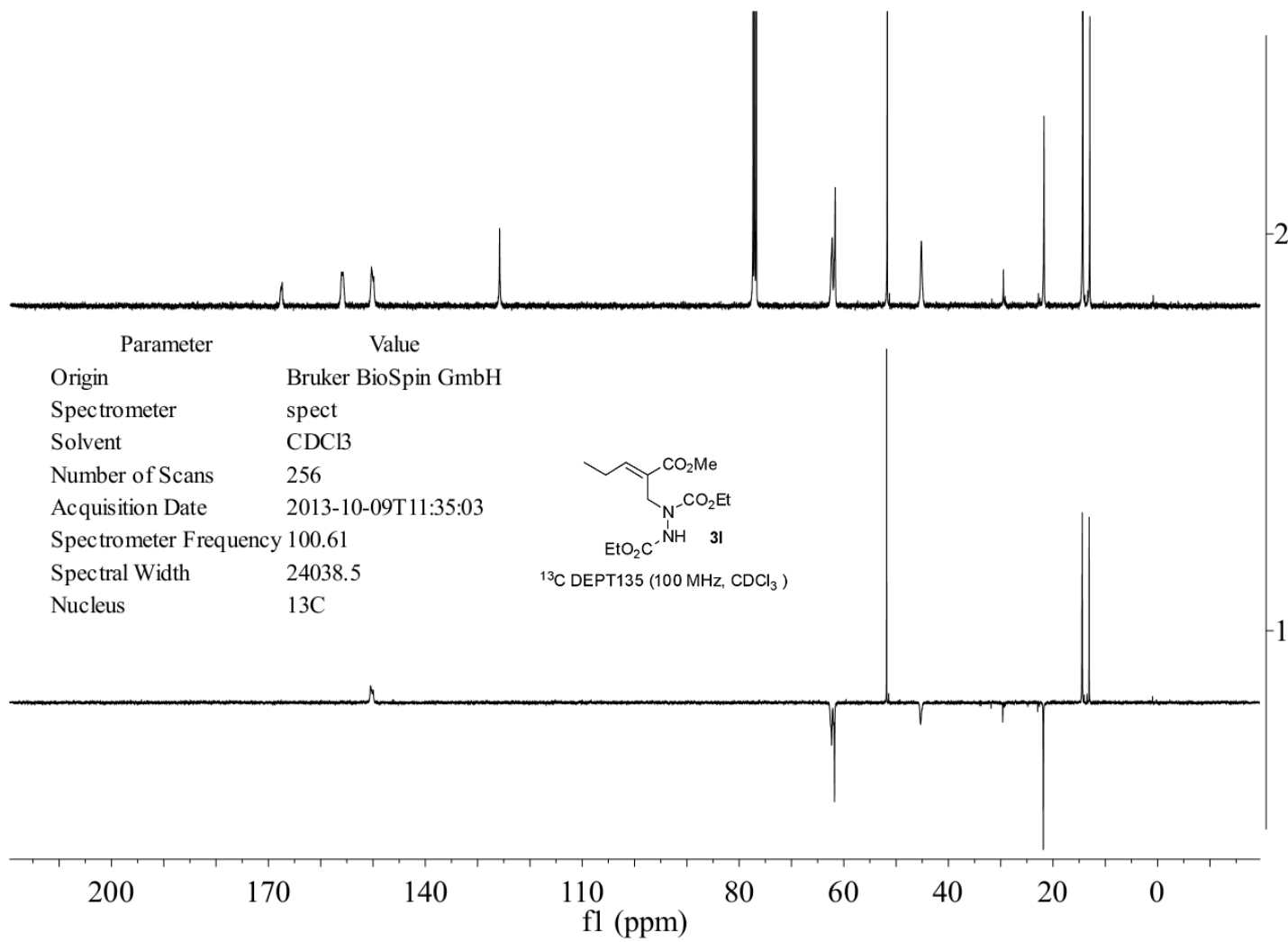


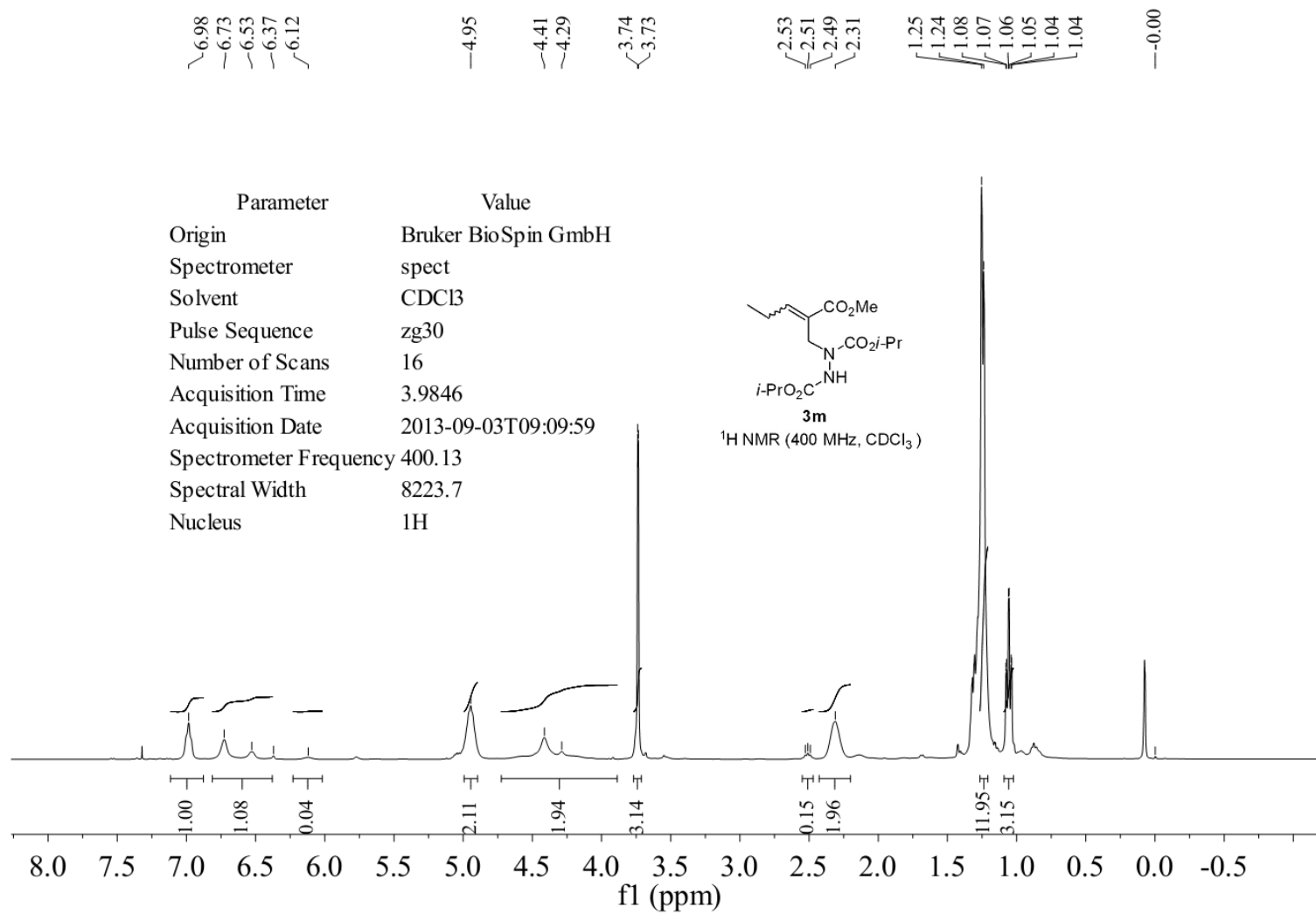


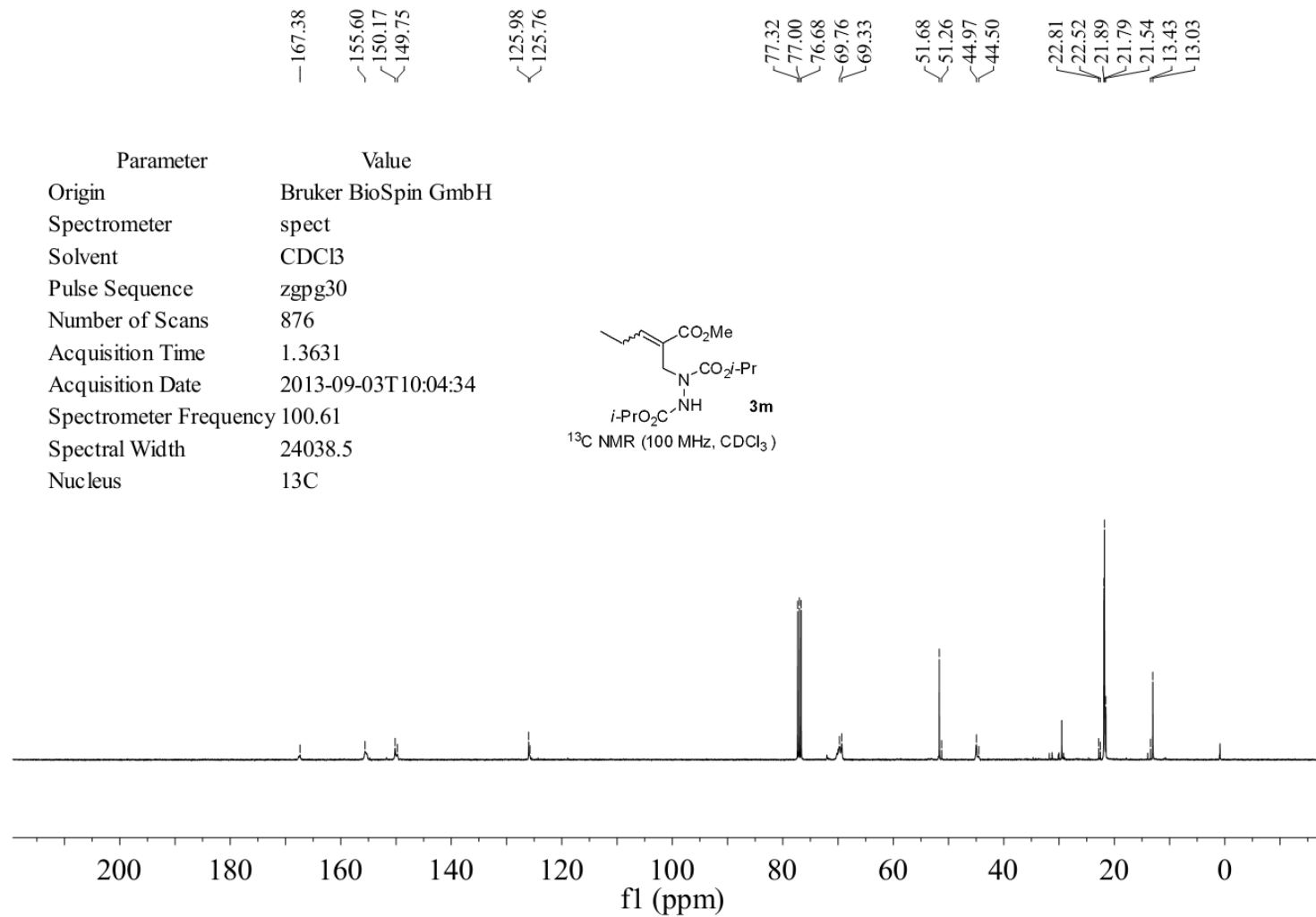
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 14.28
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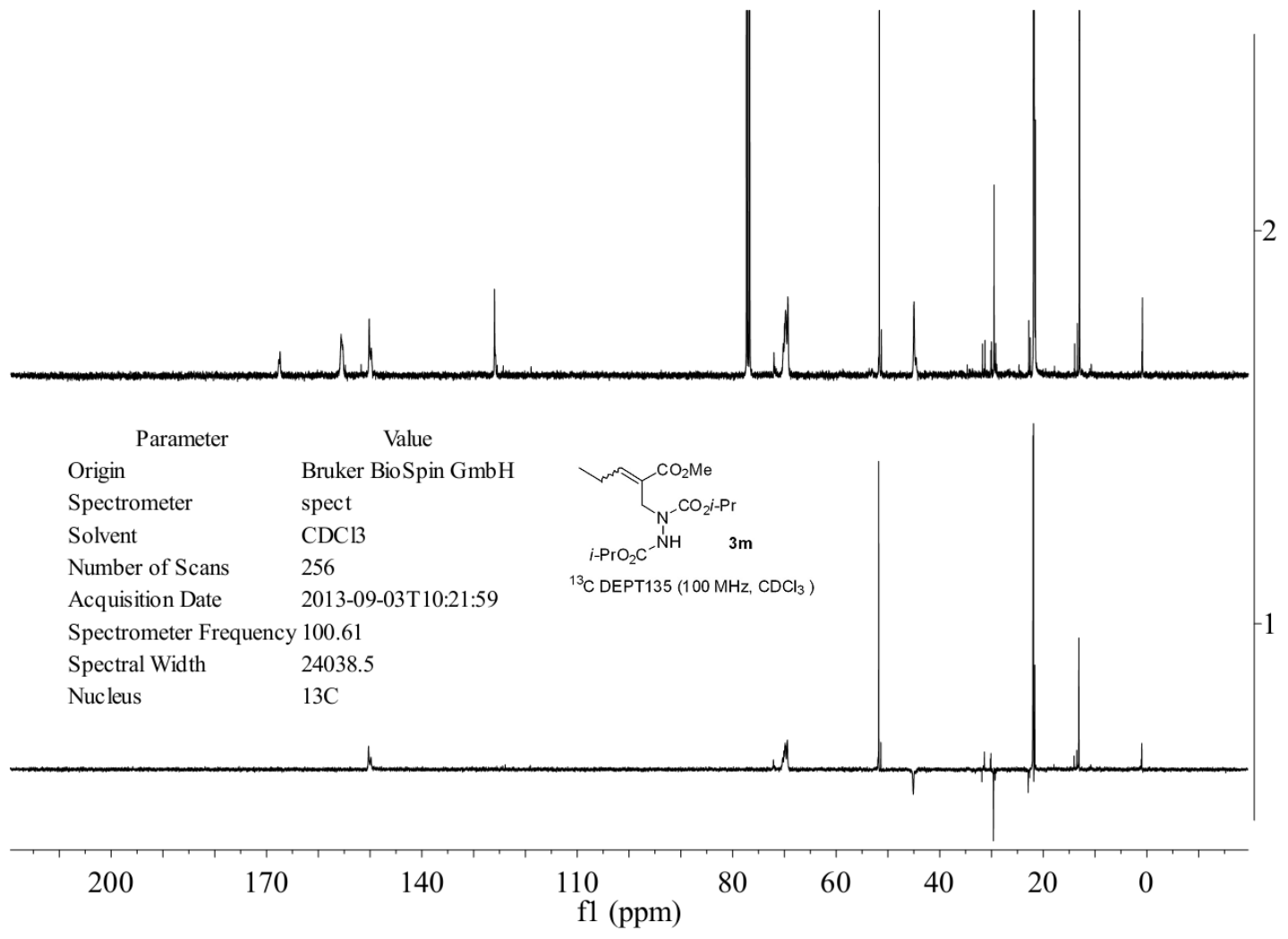
Parameter	Value
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl ₃
Pulse Sequence	zgpg30
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Acquisition Date	2013-10-11T08:10:36
Spectrometer Frequency	100.61
Spectral Width	24038.5
Nucleus	¹³ C

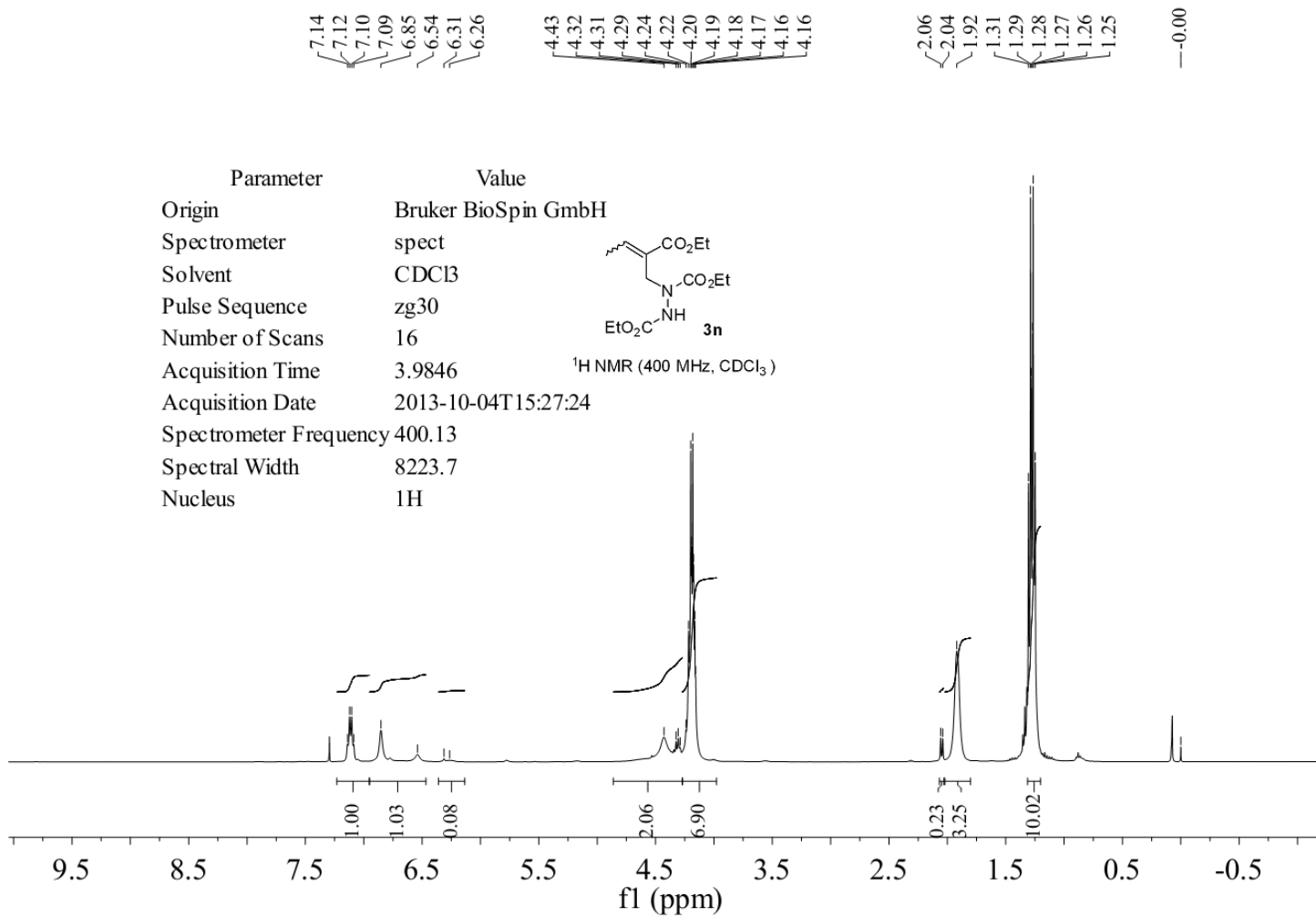


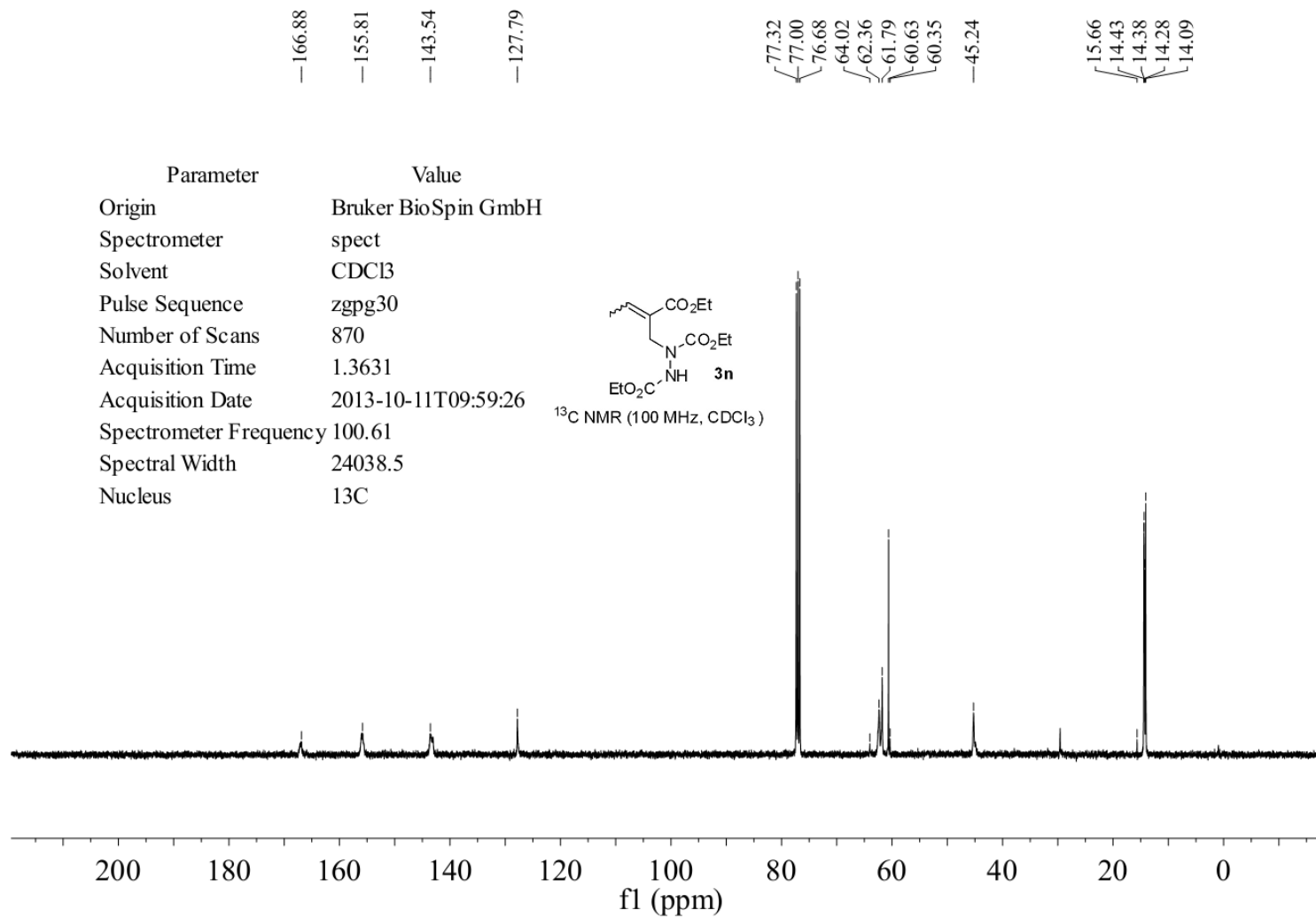


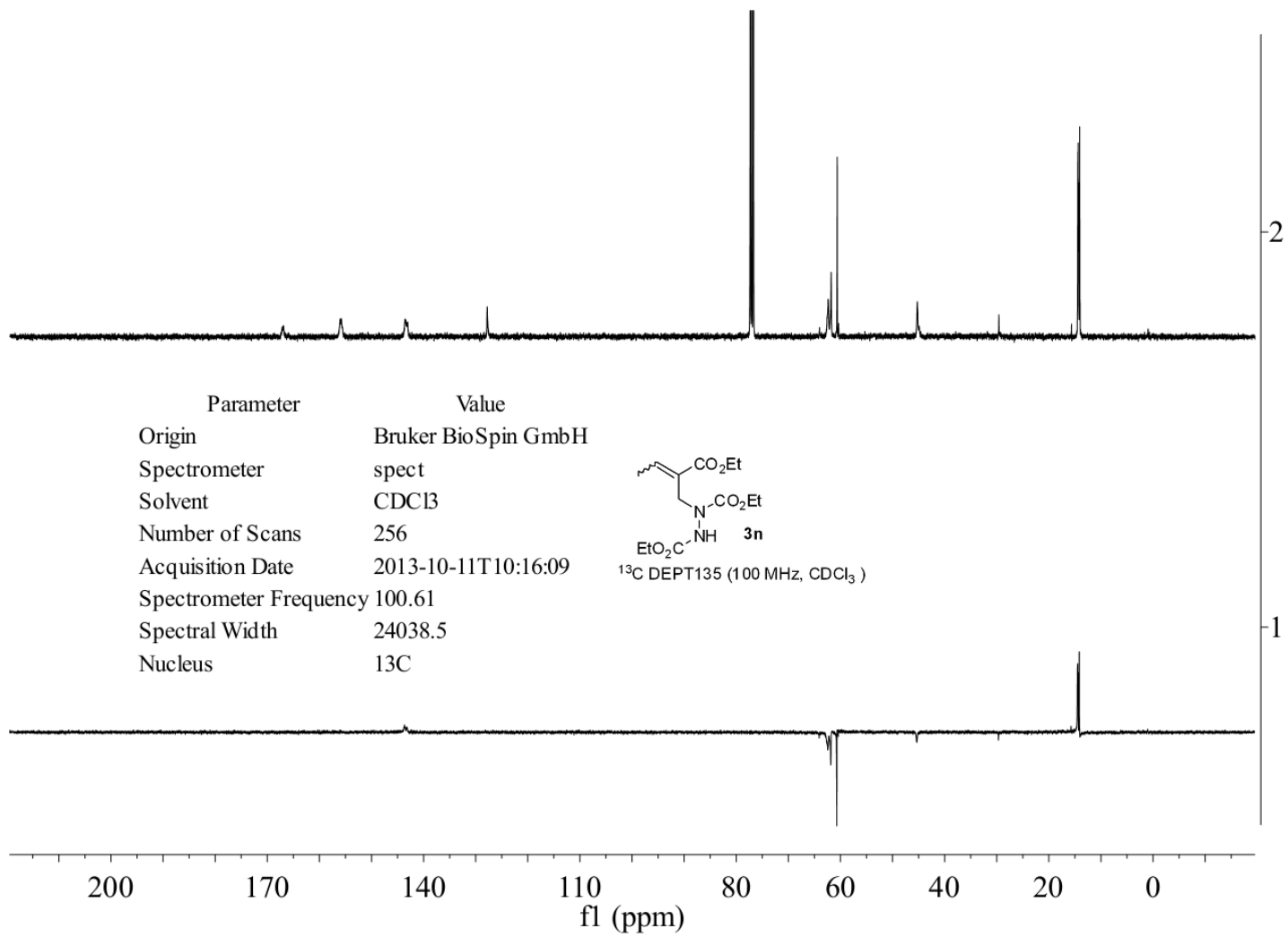


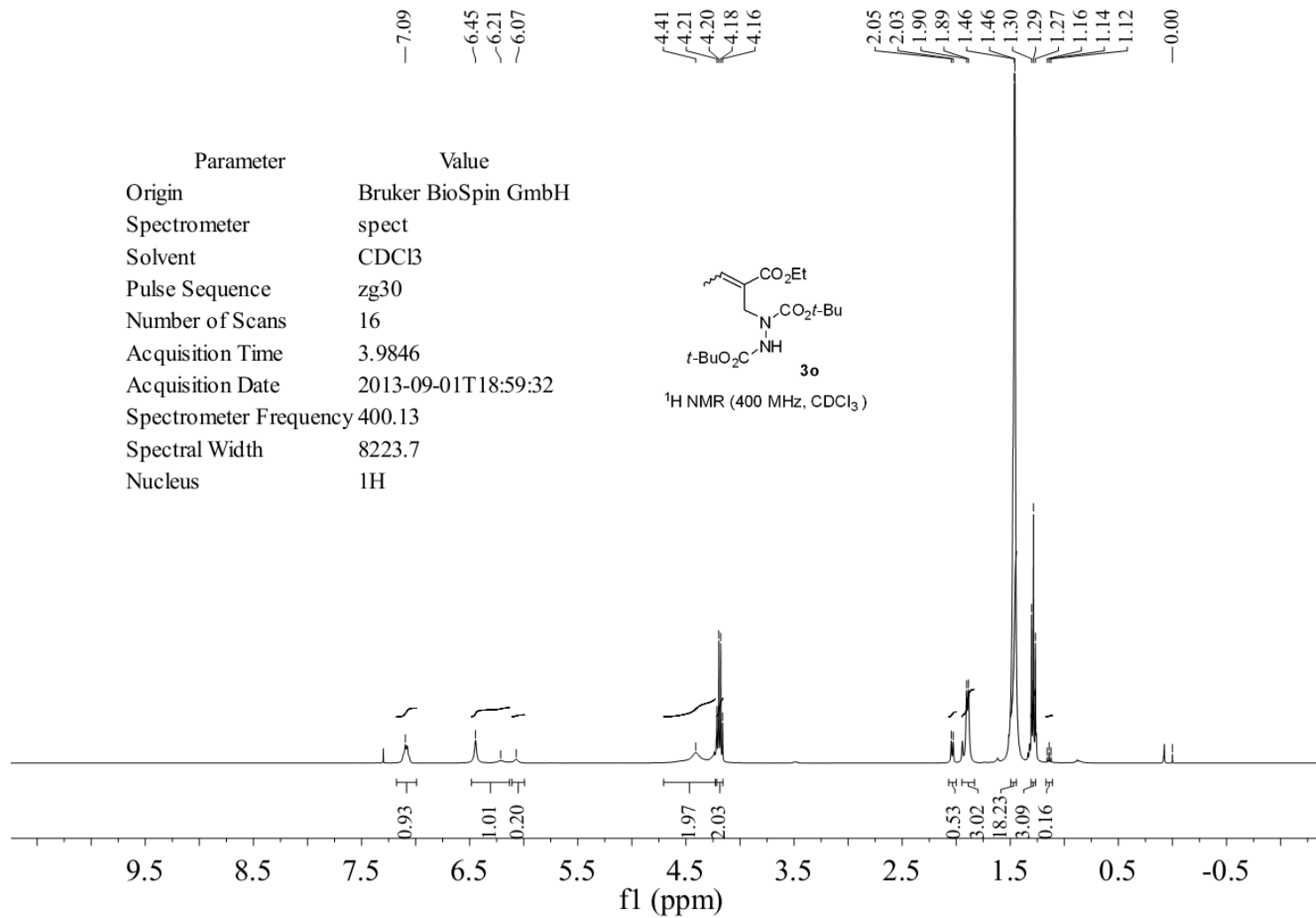


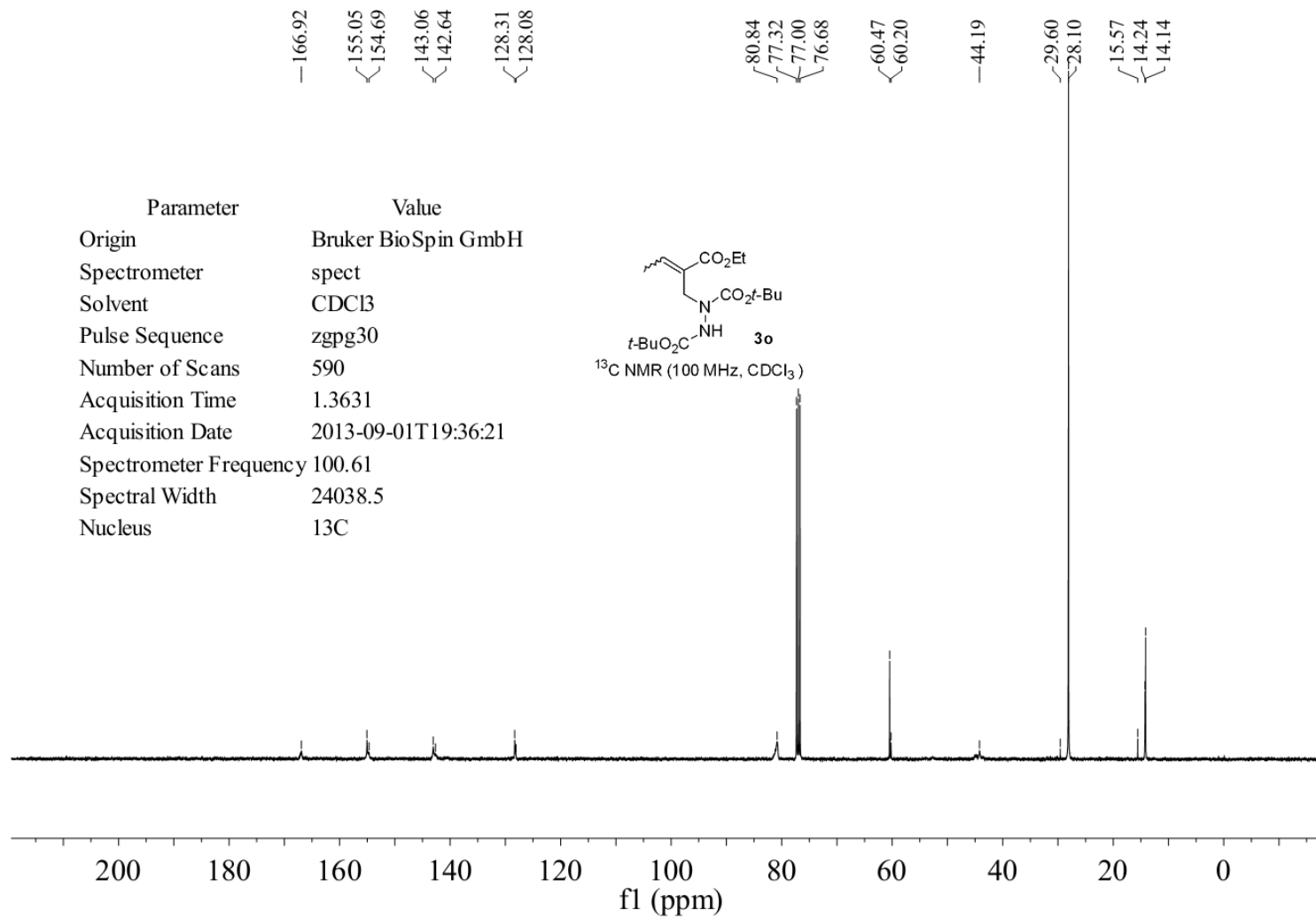




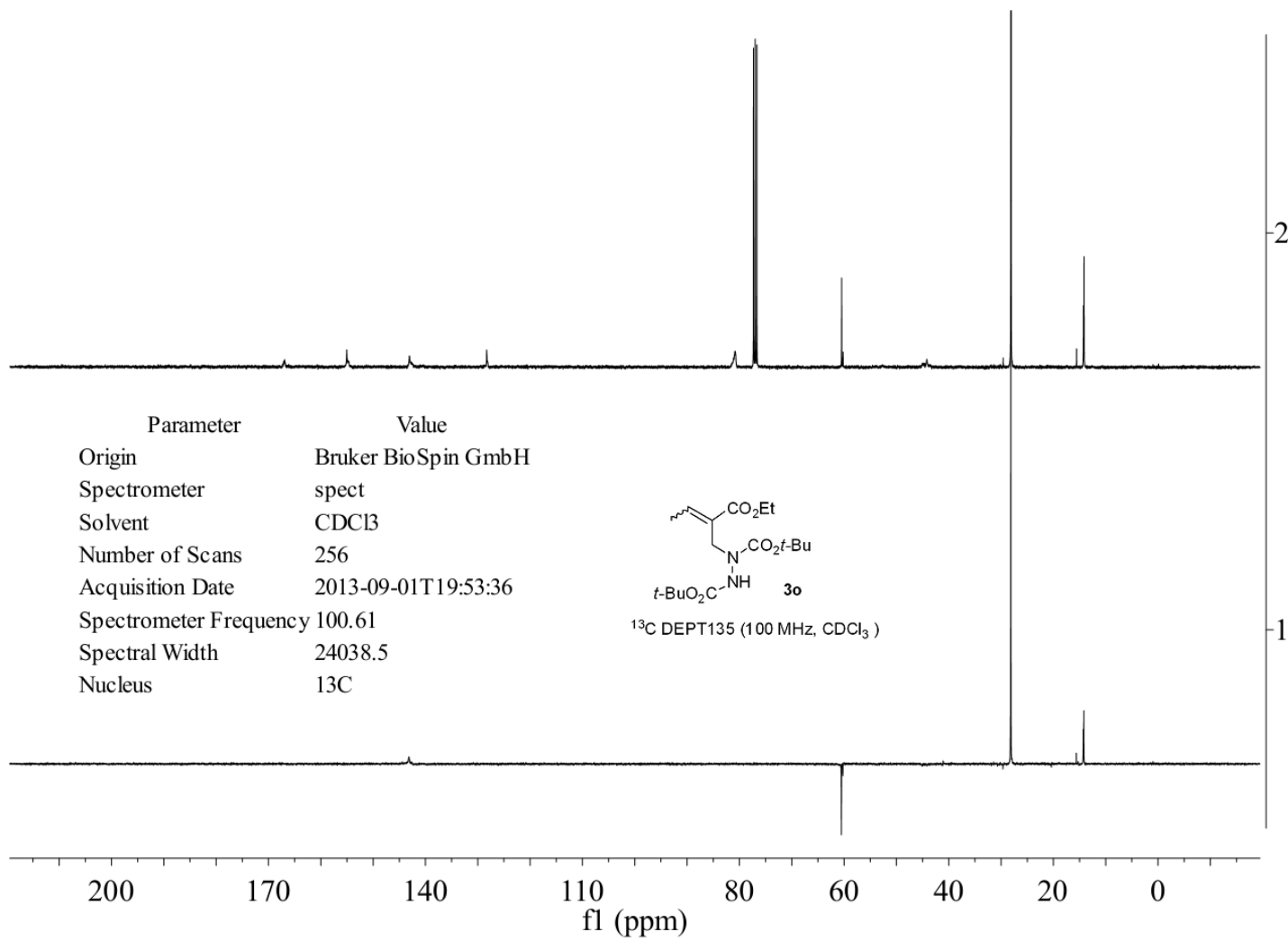


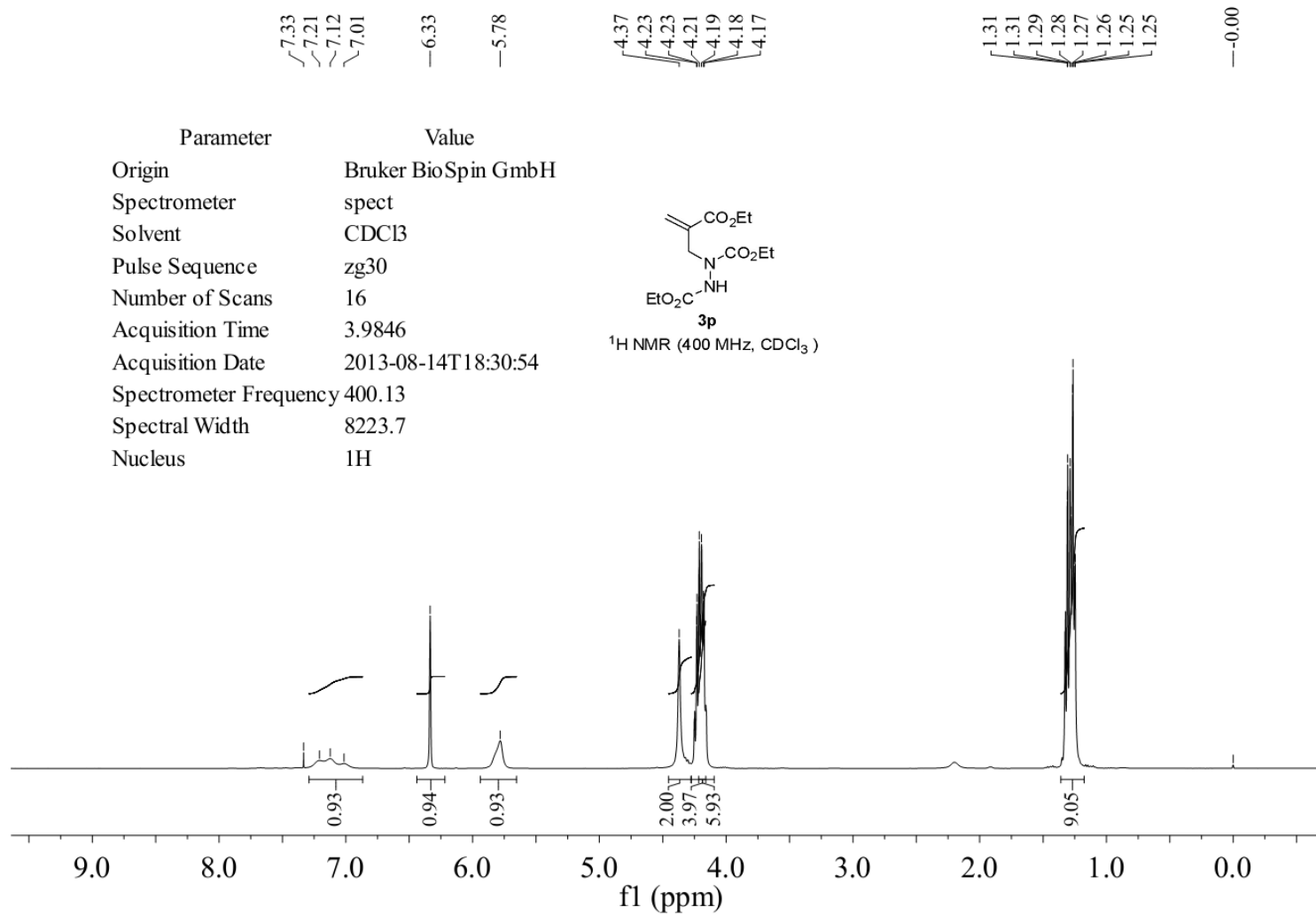


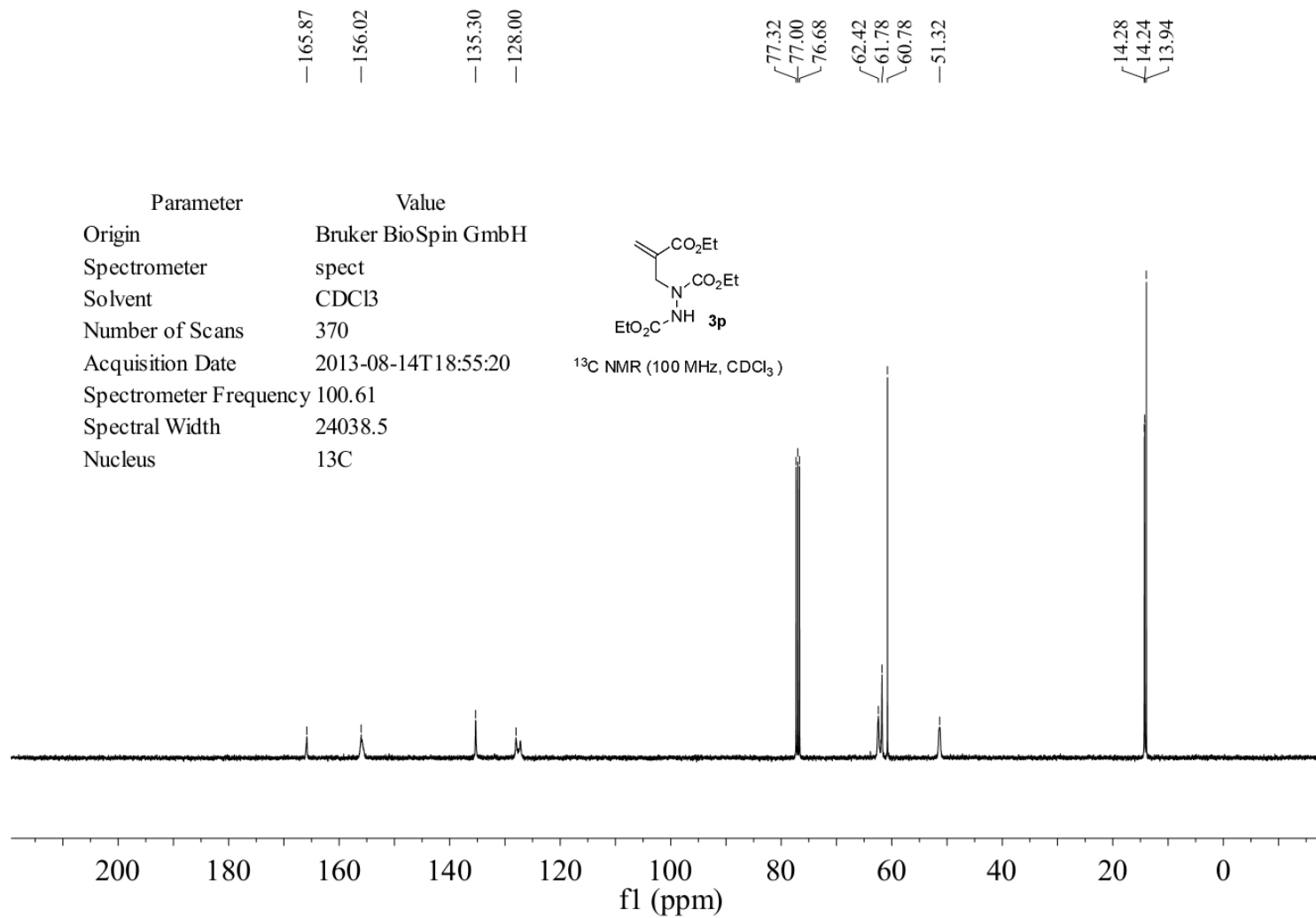


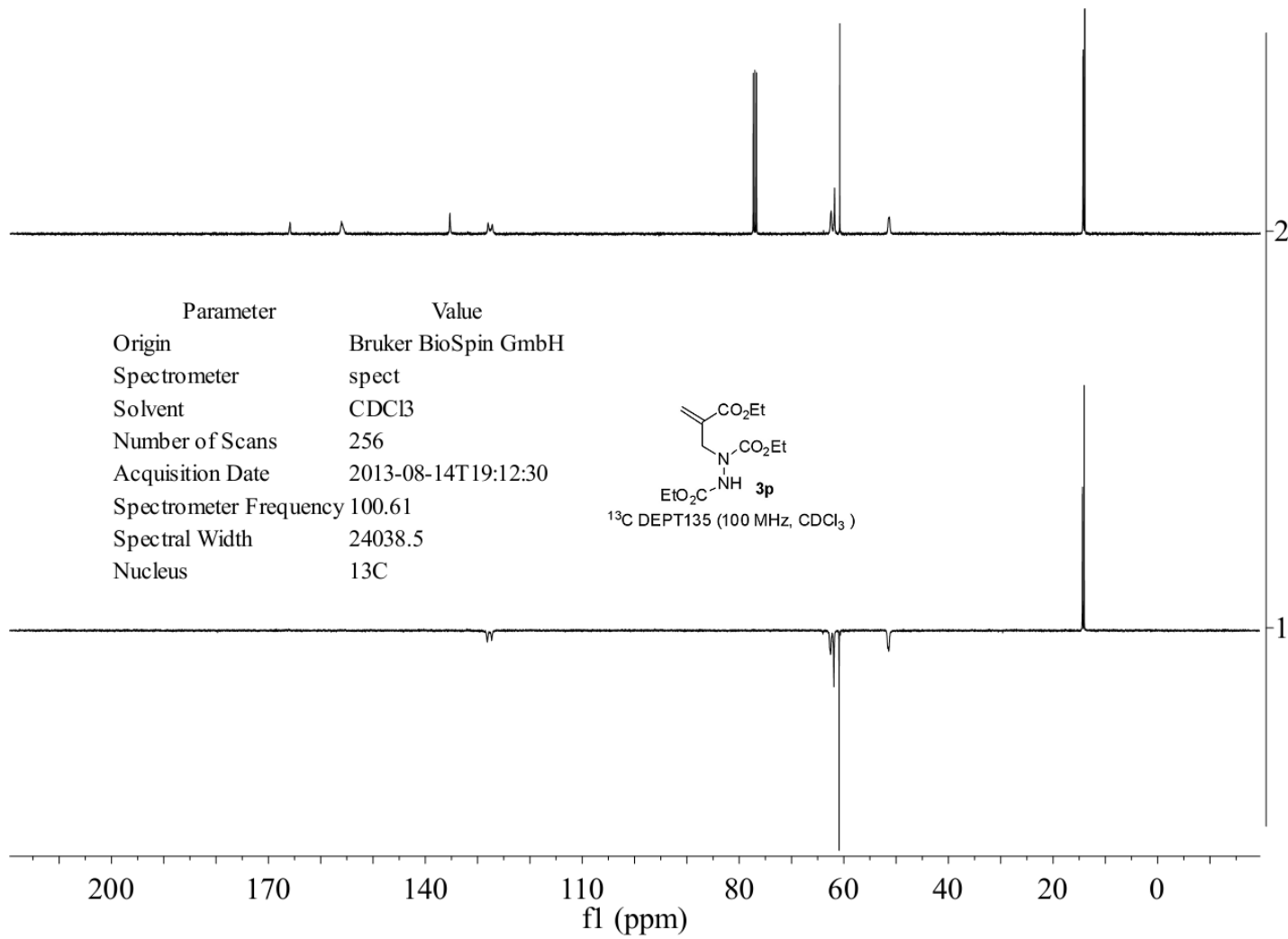


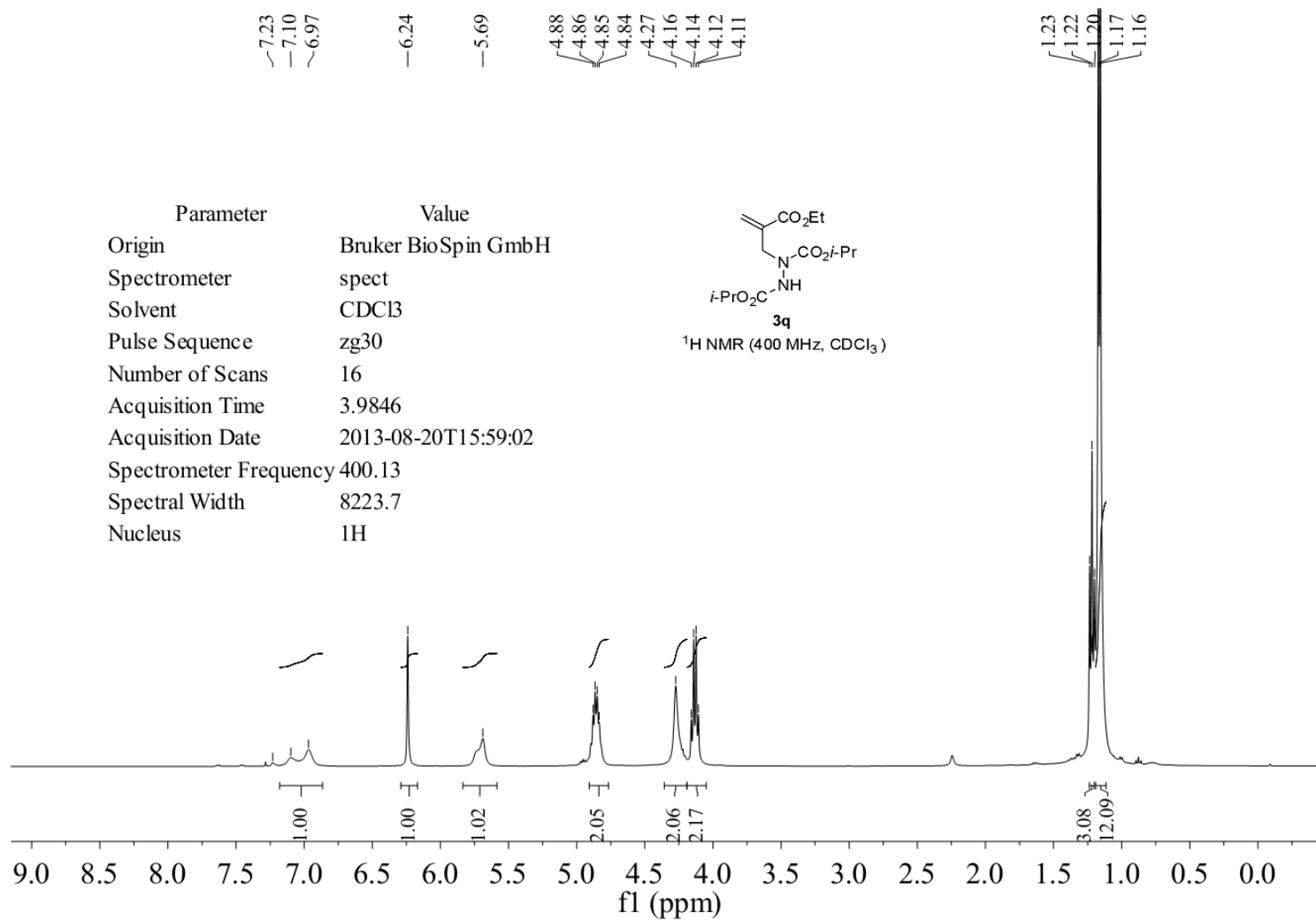
Parameter	Value
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl ₃
Pulse Sequence	zgpg30
Number of Scans	590
Acquisition Time	1.3631
Acquisition Date	2013-09-01T19:36:21
Spectrometer Frequency	100.61
Spectral Width	24038.5
Nucleus	¹³ C



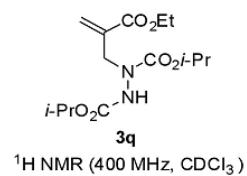


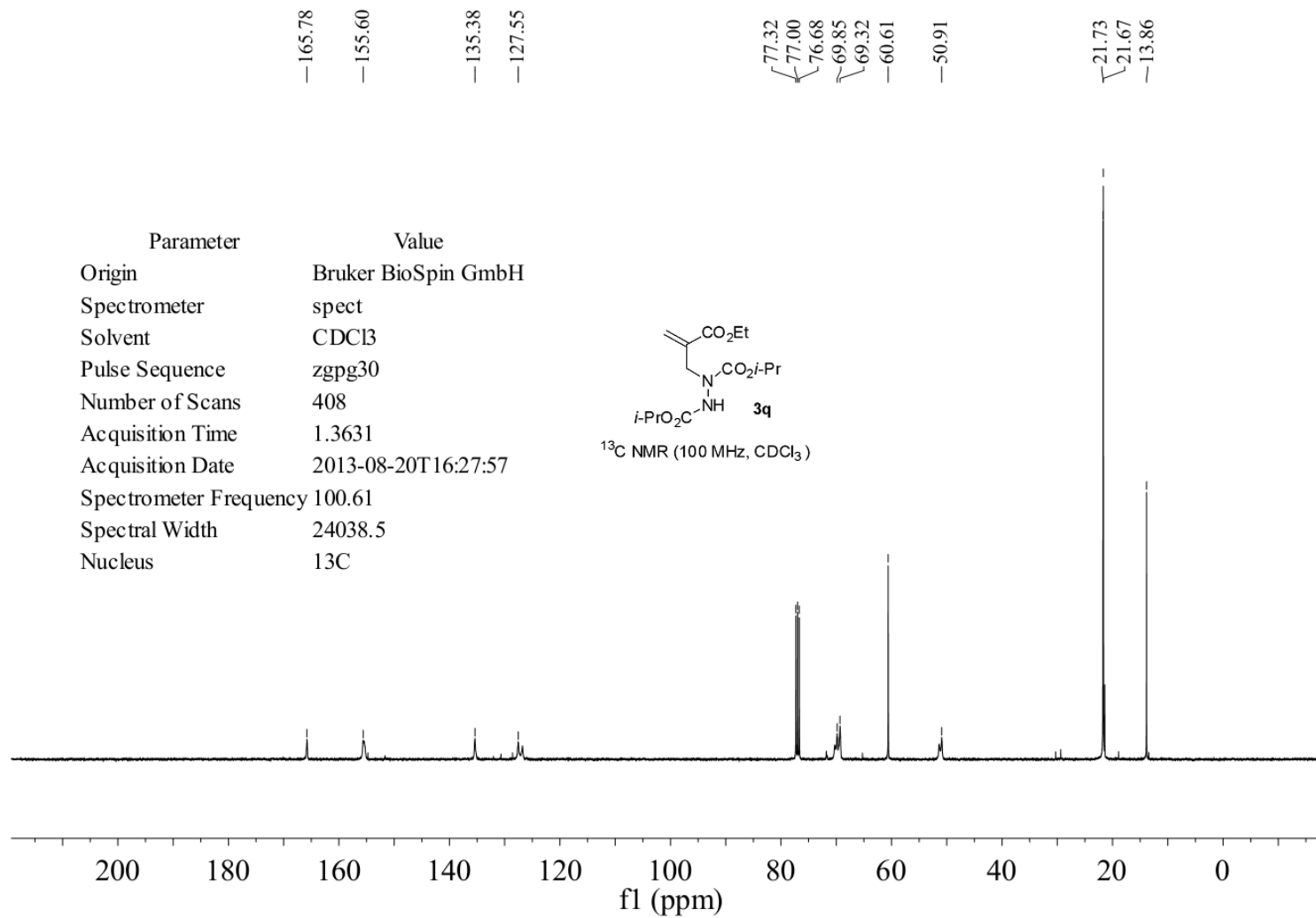


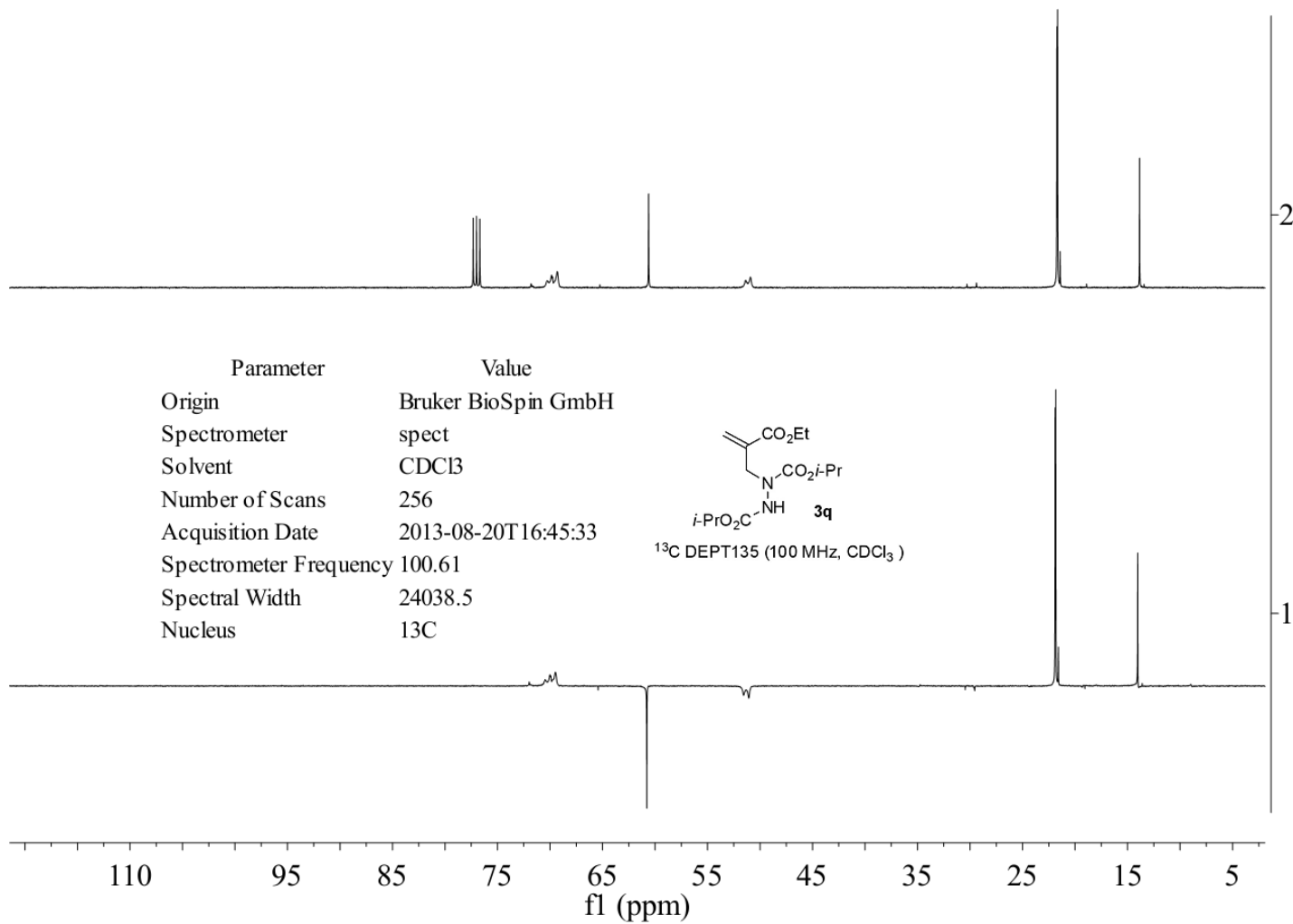


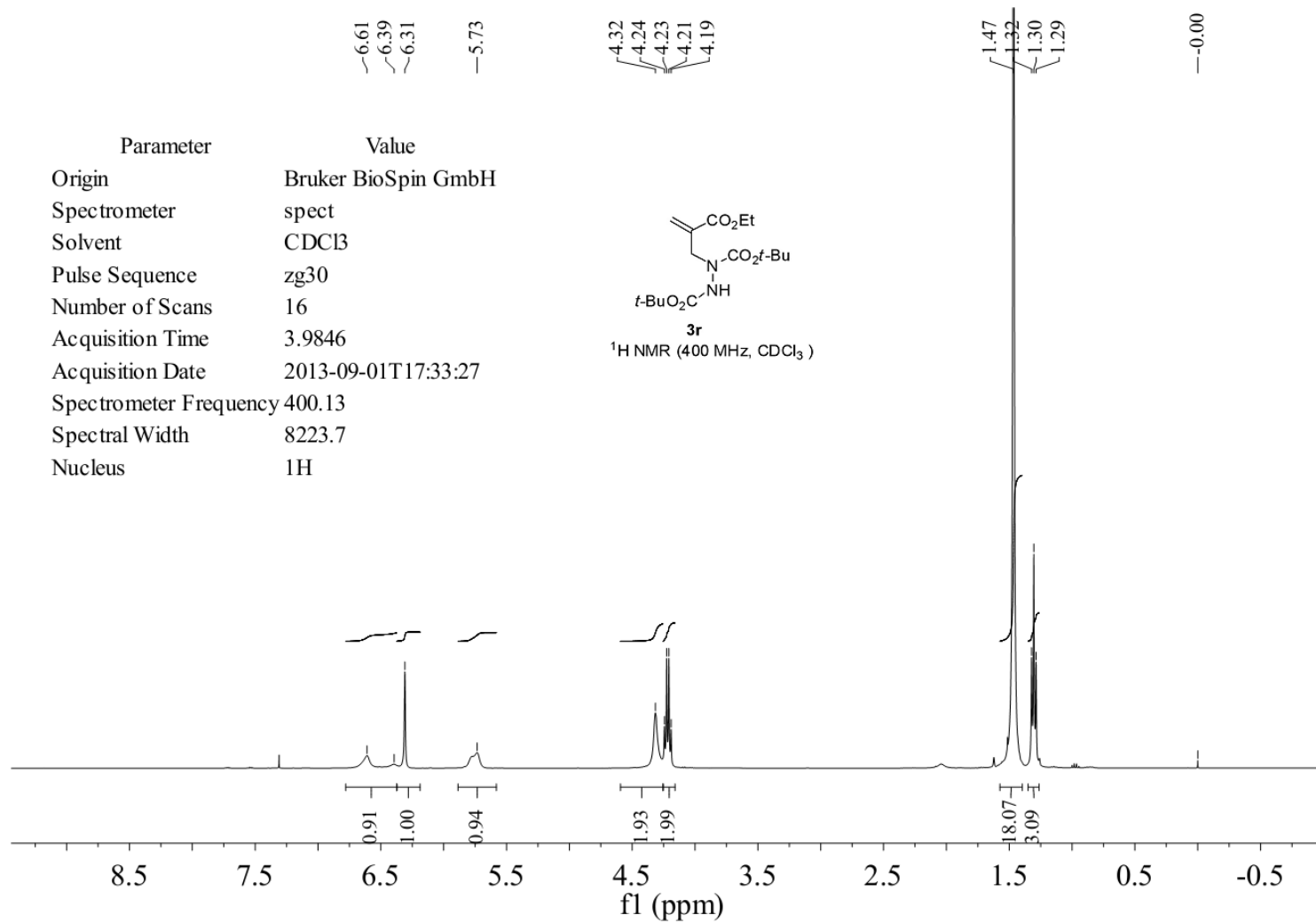


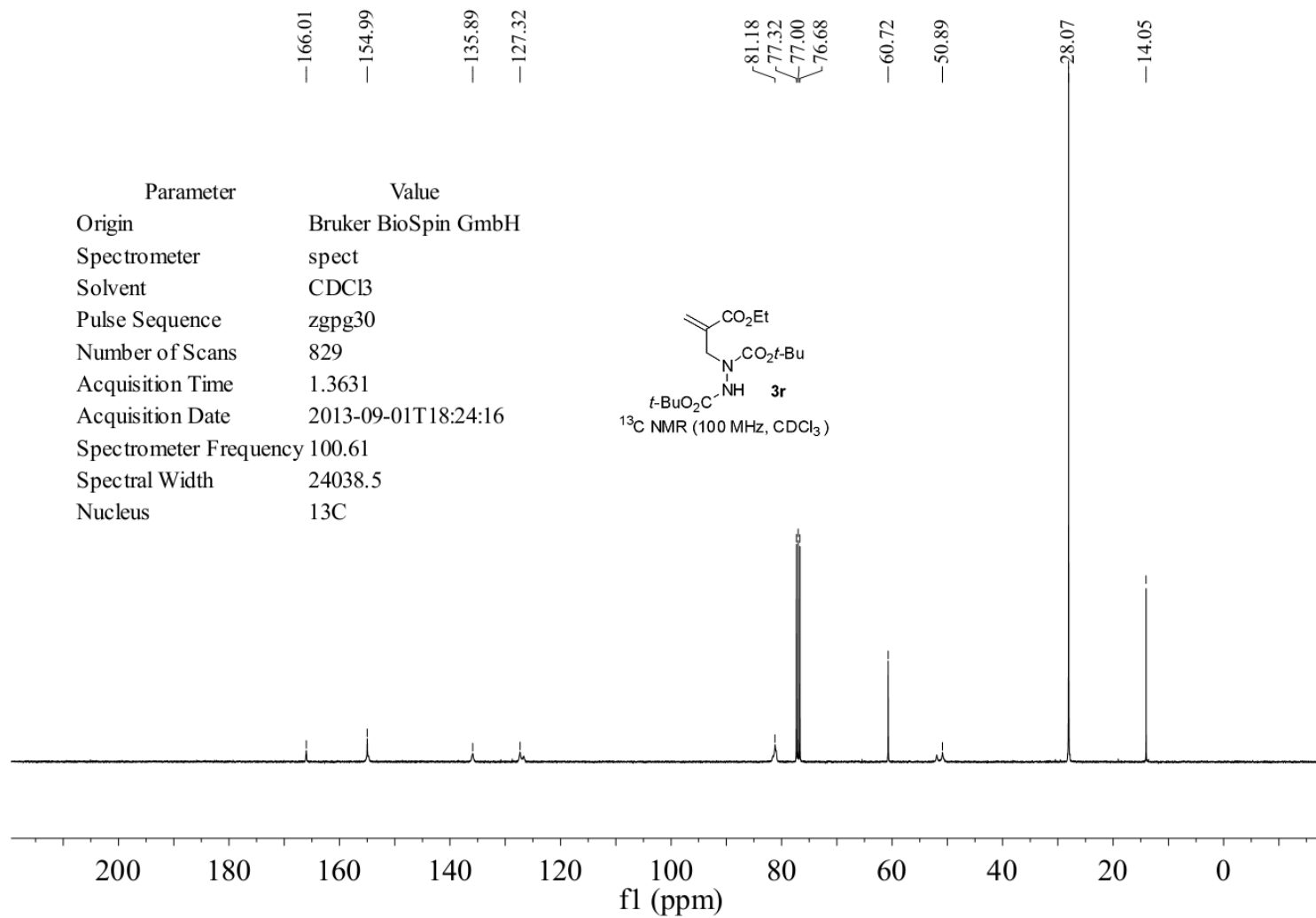
Parameter	Value
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl ₃
Pulse Sequence	zg30
Number of Scans	16
Acquisition Time	3.9846
Acquisition Date	2013-08-20T15:59:02
Spectrometer Frequency	400.13
Spectral Width	8223.7
Nucleus	¹ H

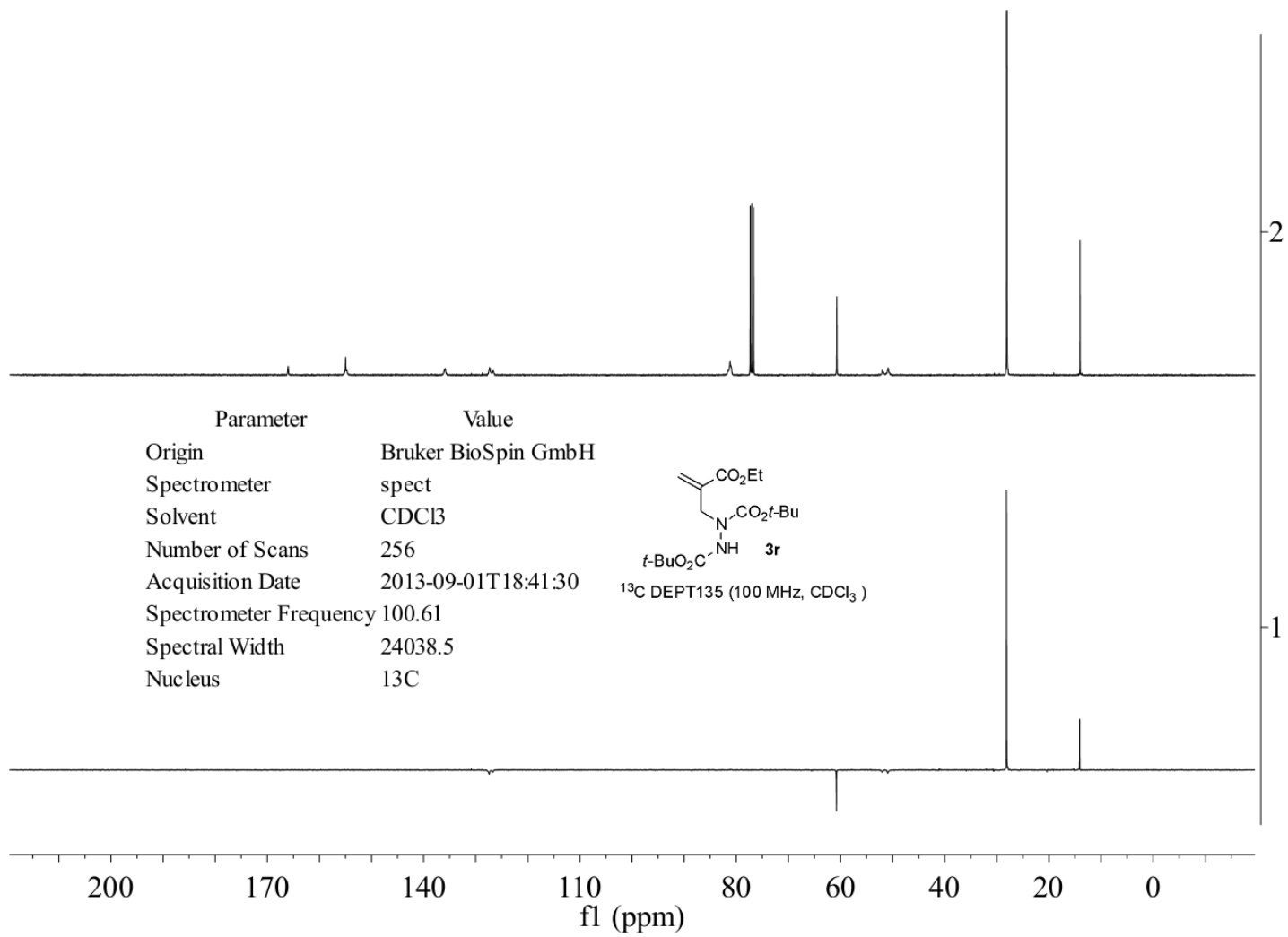


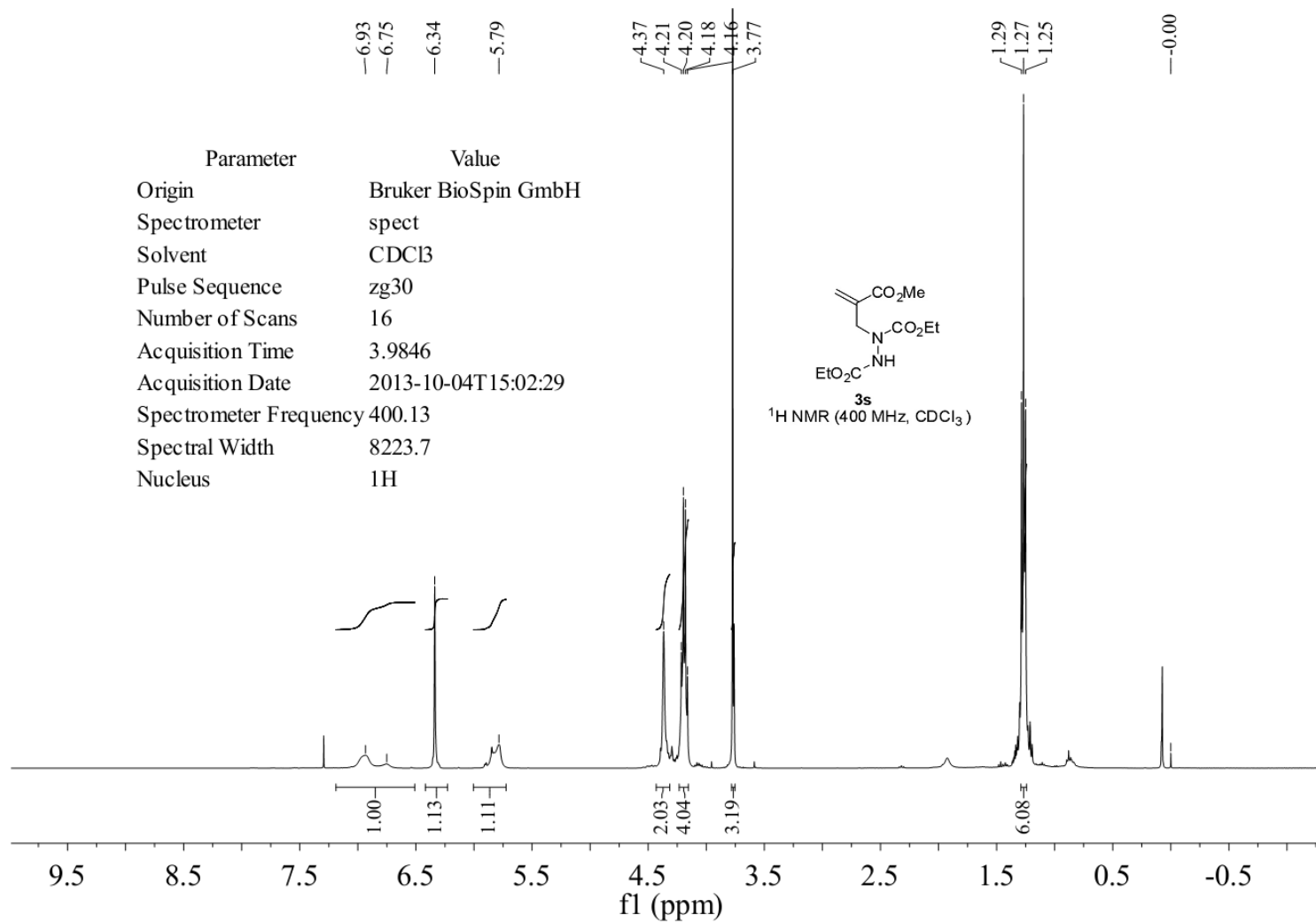


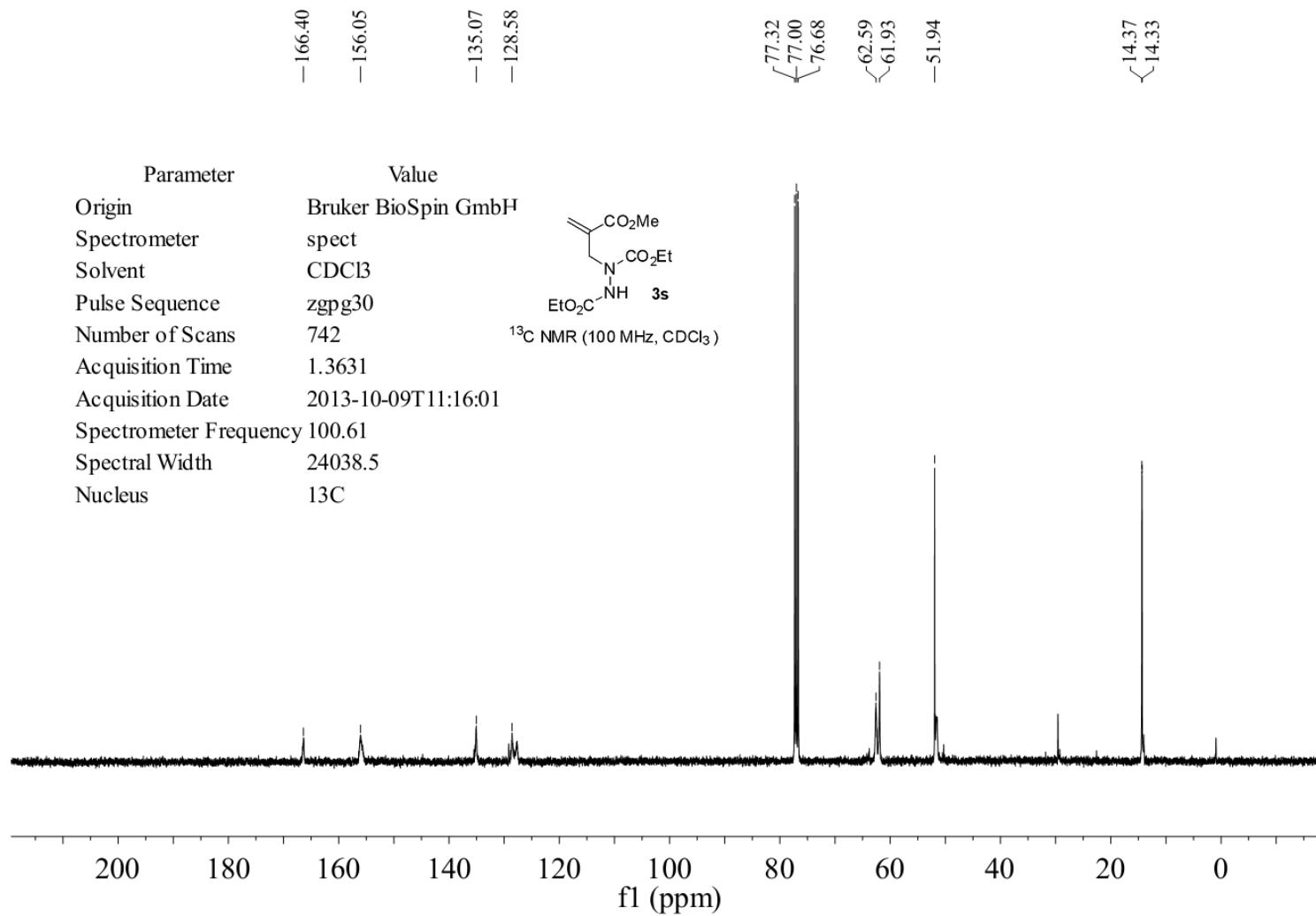












Parameter	Value
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl ₃
Pulse Sequence	zgpg30
Number of Scans	742
Acquisition Time	1.3631
Acquisition Date	2013-10-09T11:16:01
Spectrometer Frequency	100.61
Spectral Width	24038.5
Nucleus	¹³ C

