Nickel(II)-Catalyzed Borylation of Alkenyl Methyl Ethers via C-O Bond Cleavage

(Supporting Information)

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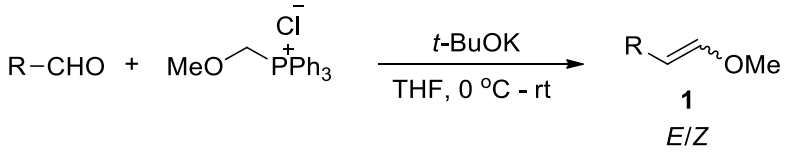
CONTENTS

1. General Information.

Unless otherwise noted, all reactions were performed under an nitrogen atmosphere using flame-dried glassware. Toluene and THF were distilled over Na, DCE and acetonitrile were distilled over CaH_2. Cyclohexane was purchased as anhydrous solvent and used directly. All new compounds were fully characterized. NMR-spectra were recorded on Bruker AV-300, ARX-400 MHz or a ARX-600 Associated. ^{1}H NMR spectra data were reported as δ values in ppm relative to chloroform (δ 7.26), methanol (δ 3.30), or DMSO (δ 2.50) if collected in $CDCl_3$, CD_3OD, or DMSO-d^6. ^{13}C NMR spectra data were reported as δ values in ppm relative to chloroform (δ 77.0) methanol (δ 49.0) or DMSO (δ 39.5) if collected in $CDCl_3$ (the carbon attached to B was not observed), CD_3OD, DMSO-d^6. ^{1}H NMR coupling constants were reported in Hz, and multiplicity was indicated as follows: s (singlet); d (doublet); t (triplet); q (quartet); quint (quintet); m (multiplet); dd (doubletof doublets); ddd (doublet of doublet of doublets); dddd (doublet of doublet of doublet of doublets); dt (doublet of triplets); td (triplet of doublets); ddt (doublet of doublet of triplets); dq (doubletof quartets); app (apparent); br (broad). Mass spectra were conducted at Micromass Q-Tof instrument (ESI) and Agilent Technologies 5973N (EI). All reactions were carried out in flame-dried 25 mL Schlenk tubes with Teflon screw caps under nitrogen. B_2Pin_2 was vacuumized under room temperature for 12 h before use. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Compounds **1a**,[S1] **1b**,[S2] **1d**,[S3] **1f**,[S1] **1g**,[S1] **1j**,[S2] **1l**,[S4] **1m**,[S5] **1p**,[S5] **1r**,[S1] **1s**[S6] were prepared according to litriture reports.

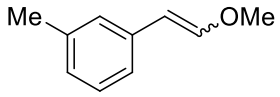
2. General Procedure for Synthesis of Enol Ethers



To a flame dried flask was added (methoxymethyl)triphenylphosphonium chloride (7.5 mmol, 2.57 g) and *t*-BuOK (9.0 mmol, 1.01 g), the flask was vacuumed and refilled with nitrogen three times and put under the ice bath. 15 mL anhydrous THF was added and the mixture was stirred for 30 min. After that, the solution of aldehyde (5.0 mmol) in THF (5 mL) was added dropwise into the reaction mixturre, then the reaction was stirred under room temperature overnight. The reaction was monitored by TLC. After the aldehyde was dispeared, 30 mL water was added and stirred for another 5 min. The aqueous phase

was extracted by ethyl acetate and the combined organic phase was dried over anhydrous sodium sulfate. The mixture was then filtered and the solvent was removed under reduced pressure. Further purification through flash chromatography (PE : EA = 50 : 1) would prodive the product **1** as a mixture with both *E* and *Z* isomers.

1-(2-Methoxyvinyl)-3-methylbenzene (1c)

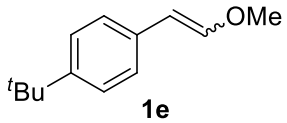


1c

E/Z

Compound **1c** was prepared from 3-methylbenzaldehyde in 92% yield as a colorless oil (680 mg). The spectral data were given for the mixture of both (*E*)-**1c** and (*Z*)-**1c** (*E*:*Z* = 51:49). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 6.4 Hz, 2H), 7.23 – 7.13 (m,, 2H), 7.09 – 7.01 (m, 3H), 7.00 – 6.94 (m, 2H), 6.13 (d, *J* = 7.0 Hz, 1H), 5.79 (d, *J* = 12.9 Hz, 1H), 5.20 (d, *J* = 7.0 Hz, 1H), 3.79 (s, 3H), 3.69 (s, 3H), 2.34 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.7, 147.8, 138.1, 137.6, 136.2, 135.7, 128.8, 128.5, 128.1, 126.5, 126.4, 125.9, 125.3, 122.2, 105.7, 105.0, 60.6, 56.5, 21.5, 21.4. ATR-FTIR (cm^{-1}): 1421, 1262, 896, 733, 703. HRMS m/z (ESI) calcd for $C_{10}H_{13}O$ $(M + H)^+$ 149.0961, found 149.0960.

1-(*tert*-Butyl)-4-(2-methoxyvinyl)benzene (1e)

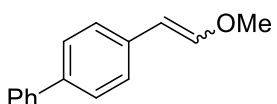


1e

E/Z

Compound **1e** was prepared from 4-(*tert*-butyl)benzaldehyde in 95% yield as a colorless oil (906 mg). The spectral data were given for the mixture of both (*E*)-**1e** and (*Z*)-**1e** (*E*:*Z* = 39:61). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.45 (m, 2H), 7.36 – 7.24 (m, 3.28H), 7.21 – 7.13 (m, 1.49H), 7.01 (d, *J* = 13.0 Hz, 0.63H), 6.08 (d, *J* = 6.9 Hz, 1H), 5.79 (d, *J* = 13.0 Hz, 0.63H), 5.20 (d, *J* = 7.0 Hz, 1H), 3.73 (s, 3H), 3.65 (s, 2H), 1.30 (s, 15.75H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.53, 148.52, 148.3, 147.3, 133.4, 133.0, 127.8, 125.5, 125.0, 124.8, 105.4, 104.7, 60.5, 56.4, 34.4, 34.3, 31.29, 31.28. ATR-FTIR (cm^{-1}): 1642, 1264, 1097, 895, 841, 733, 702. HRMS m/z (ESI) calcd for $C_{13}H_{19}O$ $(M + H)^+$ 191.1430, found 191.1429.

4-(2-Methoxyvinyl)-1,1'-biphenyl (1h)



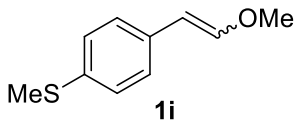
1h

E/Z

Compound **1h** was prepared from [1,1'-biphenyl]-4-carbaldehyde in 94% yield as a white solid (985 mg). The spectral data were given for the mixture of both (*E*)-**1h** and (*Z*)-**1h** (*E*:*Z* = 87:13). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.57 (m, 2.50H), 7.56 – 7.49 (m, 2.26H), 7.56 – 7.49 (m, 2.26H), 7.47 – 7.37 (m, 2.23H), 7.36 – 7.28

(m, 3.13H), 7.11 (d, J = 13.0 Hz, 1H), 6.18 (d, J = 7.0 Hz, 0.15H), 5.86 (d, J = 13.0 Hz, 1H), 5.28 (d, J = 7.0 Hz, 0.15H), 3.81 (s, 0.40H), 3.72 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.0, 148.2, 141.1, 140.8, 138.4, 138.3, 135.4, 135.0, 128.72, 128.68, 128.5, 127.3, 126.99, 126.95, 126.9, 126.83, 126.76, 125.4, 105.2, 104.6, 60.7, 56.6. ATR-FTIR (cm^{-1}): 3030, 2930, 1635, 1482, 1243, 1149, 1087, 95, 843, 760, 693. HRMS m/z (ESI) calcd for $C_{15}H_{15}O$ $(M + H)^+$ 211.1117, found 211.1116.

(4-(2-Methoxyvinyl)phenyl)(methyl)sulfane (1i)

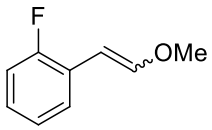


1i

E/*Z*

Compound **1i** was prepared from 4-(methylthio)benzaldehyde in 90% yield as a colorless oil (813 mg). The spectral data were given for the mixture of both (*E*)-**1i** and (*Z*)-1i (*E*:*Z* = 58:42). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 8.5 Hz, 1.44H), 7.23 – 7.11 (m, 5.42H), 7.03 (d, J = 13.0 Hz, 1H), 6.12 (d, J = 6.9 Hz, 0.71H), 5.77 (d, J = 13.0 Hz, 1H), 5.19 (d, J = 7.0 Hz, 0.71H), 3.78 (s, 2.13H), 3.68 (s, 3H), 2.474 (s, 2.17H), 2.471 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.6, 147.7, 135.1, 135.0, 133.5, 133.0, 128.6, 127.4, 126.7, 125.5, 105.1, 104.5, 60.7, 56.5, 16.4, 16.2. ATR-FTIR (cm^{-1}): 1423, 1265, 898, 734, 701. HRMS m/z (ESI) calcd for $C_{10}H_{13}OS$ $(M + H)^+$ 181.0682, found 181.0681.

1-Fluoro-2-(2-methoxyvinyl)benzene (1k)

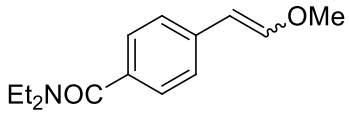


1k

E/*Z*

Compound **1k** was prepared from 2-fluorobenzaldehyde in 87% yield as a colorless oil (662 mg). The spectral data were given for the mixture of both (*E*)-**1k** and (*Z*)-**1k** (*E*:*Z* = 60:40). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (td, J = 7.7, 2.5 Hz, 0.66H), 7.33 – 7.23 (m, 1H), 7.18 (d, J = 13.0 Hz, 1H), 7.15 – 6.96 (m, 4.95H), 6.24 (d, J = 7.1 Hz, 0.67H), 5.88 (d, J = 13.1 Hz, 1H), 5.50 (d, J = 7.0 Hz, 0.67H), 3.80 (s, 2.09H), 3.72 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4 (d, J = 39.6 Hz), 158.0 (d, J = 40.7 Hz), 150.7 (d, J = 6.6 Hz), 149.1 (d, J = 2.2 Hz), 130.0 (d, J = 3.3 Hz), 126.9 (d, J = 8.3 Hz), 126.6 (d, J = 8.2 Hz), 126.5 (d, J = 4.4 Hz), 124.1, 124.0 (d, J = 3.4 Hz), 124.0, 123.7 (d, J = 3.6 Hz), 123.6 (d, J = 11.9 Hz), 115.5 (d, J = 22.2 Hz), 114.7 (d, J = 22.2 Hz), 98.2 (d, J = 2.8 Hz), 96.4 (d, J = 7.6 Hz), 60.7, 56.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -118.8, -117.5. ATR-FTIR (cm^{-1}): 1420, 1262, 894, 732, 702. HRMS m/z (ESI) calcd for $C_9H_{10}FO$ $(M + H)^+$ 153.0710, found 153.0713.

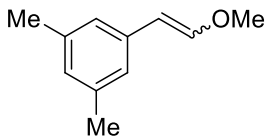
***N*,*N*-diethyl-4-(2-methoxyvinyl)benzamide (1n)**



1n
E/Z

Compound **1n** was prepared from *N*,*N*-diethyl-4-formylbenzamide in 85% yield as a colorless oil (995 mg). The spectral data were given for the mixture of both (*E*)-**1n** and (*Z*)-**1n** (*E*:*Z* = 36:64). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.52 (m, 2H), 7.35 – 7.26 (m, 3.61H), 7.26 – 7.21 (m, 1.14H), 7.09 (d, *J* = 13.0 Hz, 0.58H), 6.18 (d, *J* = 7.0 Hz, 1H), 5.80 (d, *J* = 13.0 Hz, 0.56H), 5.23 (d, *J* = 7.0 Hz, 1H), 3.80 (s, 3H), 3.70 (s, 1.69H), 3.65 – 3.10 (m, 6.45H), 1.35 – 0.97 (m, 9.98H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 171.2, 149.6, 148.7, 137.4, 136.8, 134.2, 134.1, 127.9, 126.8, 126.3, 124.8, 104.9, 104.3, 60.8, 56.5, 43.2, 39.2, 14.2, 12.9. ATR-FTIR (cm^{-1}): 1624, 1424, 1263, 1095, 895, 731, 702. HRMS m/z (ESI) calcd for $C_{14}H_{20}NO_2$ $(M + H)^+$ 234.1489, found 234.1488.

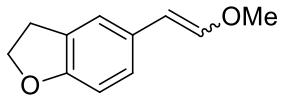
1-(2-Methoxyvinyl)-3,5-dimethylbenzene (1o)



1o
E/Z

Compound **1o** was prepared from 3,5-dimethylbenzaldehyde in 95% yield as a colorless oil (770 mg). The spectral data were given for the mixture of both (*E*)-**1o** and (*Z*)-**1o** (*E*:*Z* = 50:50). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (s, 2H), 7.05 (d, *J* = 13.0 Hz, 1H), 6.93 – 6.75 (m, 4H), 6.11 (d, *J* = 7.0 Hz, 1H), 5.78 (d, *J* = 13.0 Hz, 1H), 5.18 (d, *J* = 7.0 Hz, 1H), 3.79 (s, 3H), 3.69 (s, 3H), 2.36 – 2.22 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.6, 147.6, 138.0, 137.5, 136.1, 135.6, 127.5, 127.4, 126.0, 123.0, 105.7, 105.0, 60.6, 56.4, 21.3, 21.3. ATR-FTIR (cm^{-1}): 1421, 1264, 1100, 895, 731, 702. HRMS m/z (ESI) calcd for $C_{11}H_{15}O$ $(M + H)^+$ 163.1117, found 163.1117.

5-(2-Methoxyvinyl)-2,3-dihydrobenzofuran (1q)

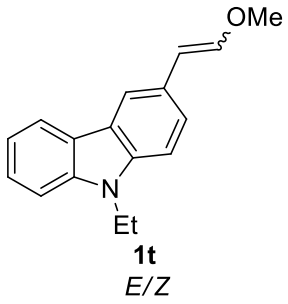


1q
E/Z

Compound **1q** was prepared from 2,3-dihydrobenzofuran-5-carbaldehyde in 94% yield as a colorless oil (825 mg). The spectral data were given for the mixture of both (*E*)-**1q** and (*Z*)-**1q** (*E*:*Z* = 45:55). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (s, 1H), 7.29 (d, *J* = 8.2 Hz, 1H), 7.11 (s, 0.81H), 6.99 (d, *J* = 8.2 Hz, 0.80H), 6.93 (d, *J* = 13.0 Hz, 0.81H), 6.78 – 6.68 (m, 1.77H), 6.04 (d, *J* = 7.0 Hz, 1H), 5.80 (d, *J* = 13.0 Hz, 0.81H), 5.19 (d, *J* = 7.0 Hz, 1H), 4.63 – 4.50 (m, 3.74H), 3.76 (s, 3H), 3.67 (s, 2.43H), 3.24 – 3.13 (m, 3.78H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.3, 158.0, 147.0, 145.7, 128.6, 128.5, 128.0, 127.3, 126.7 , 125.0, 124.7, 121.3, 109.1, 108.7, 105.5, 104.9, 71.1, 71.1, 60.3, 56.3, 29.6, 29.6. ATR-FTIR (cm^{-1}): 1646, 1490, 1264, 1106, 984, 735, 702. HRMS m/z (ESI) calcd for $C_{11}H_{13}O_2$

$(M + H)^+$ 177.0910, found 177.0909.

9-Ethyl-3-(2-methoxyvinyl)-9*H*-carbazole (1t)

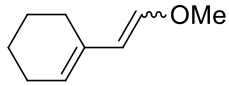


1t

E/Z

Compound **1t** was prepared from 9-ethyl-9*H*-carbazole-3-carbaldehyde in 86% yield as a pale yellow solid (1.08 g). The spectral data were given for the mixture of both (*E*)-**1t** and (*Z*)-**1t** (*E*:*Z* = 50:50). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 – 8.27 (m, 1H), 8.15 – 7.96 (m, 2H), 7.95 – 7.85 (m, 1H), 7.74 – 7.63 (m, 1H), 7.43 – 7.32 (m, 2H), 7.31 – 7.10 (m, 7H), 7.09 – 6.99 (m, 1H), 6.08 – 5.91 (m, 2H), 5.43 – 5.30 (m, 1H), 4.22 – 4.04 (m, 4H), 3.71 (s, 3H), 3.63 (s, 3H), 1.34 – 1.14 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.2, 145.9, 140.2, 138.5, 138.3, 127.1, 127.0, 126.5, 125.6, 125.4, 123.3, 123.2, 123.1, 122.9, 122.8 , 120.5, 120.4, 120.0, 118.61, 118.55, 116.9, 108.6, 108.43, 108.35, 108.0, 106.4, 105.9, 60.5, 56.5, 37.5, 37.5, 13.8. ATR-FTIR (cm^{-1}): 1421, 1267, 894, 734, 703. HRMS m/z (ESI) calcd for $C_{17}H_{18}NO_2$ $(M + H)^+$ 252.1383, found 252.1383.

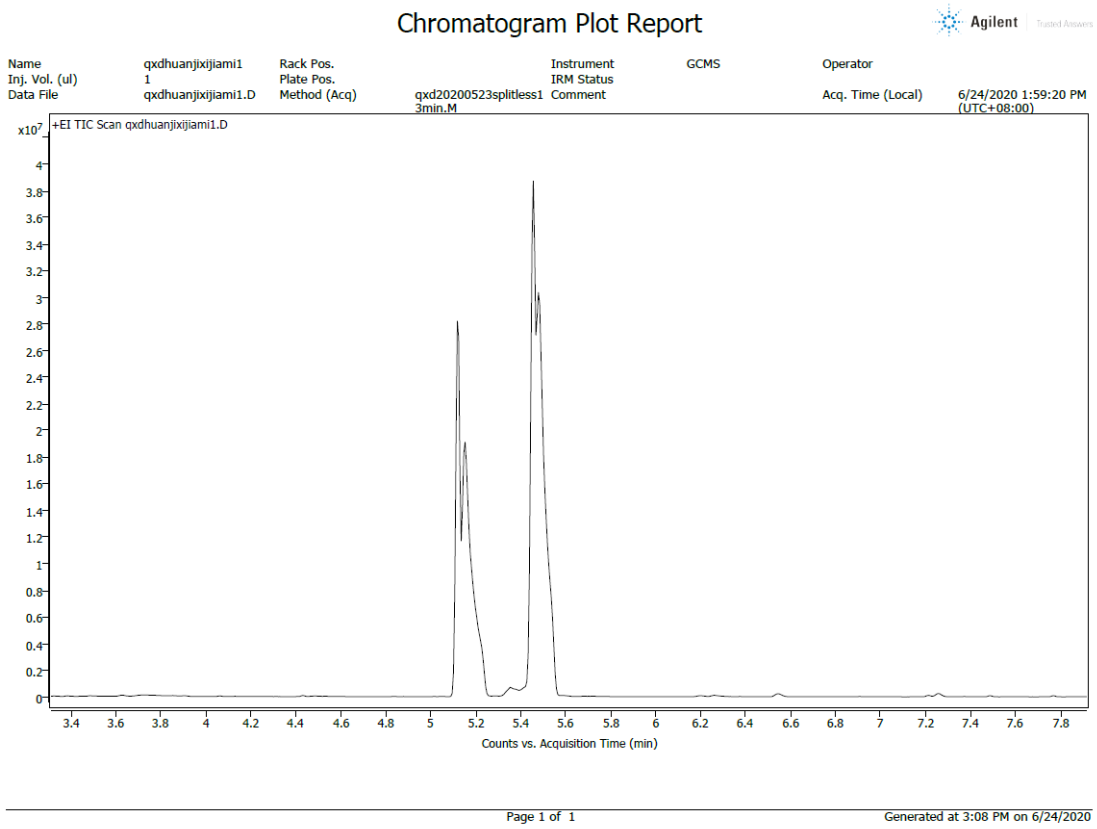
1-(2-Methoxyvinyl)cyclohex-1-ene (1v)



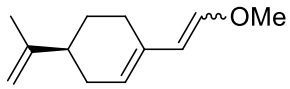
1v

E/Z

Compound **1v** was prepared from cyclohex-1-enecarbaldehyde in 68% yield as a colorless oil (469 mg). Due to the instability of **1v** under room temperature, it was put into the borylation reaction immediately after purification by column chromatography on silica gel. The NMR spectral data of **1v** were deficient but it could be easily judged from GC-MS that **1v** was the mixture of *E*/*Z* isomers (42:58). EI-MS (m/z, relative intensity, rt = 5.118 min): 138 (M^+, 100), 123 (36), 109 (52), 106 (20), 95 (45), 91 (42), 79 (56), 67 (31), 53(14). EI-MS (m/z, relative intensity, rt = 5.158 min): 138 (M^+, 100), 123 (35), 109 (50), 106 (19), 95 (43), 91 (41), 79 (54), 67 (30), 53(13). EI-MS (m/z, relative intensity, rt = 5.456 min): 138 (M^+, 100), 123 (40), 109 (54), 106 (21), 95 (49), 91 (46), 79 (59), 67 (33), 53(14). EI-MS (m/z, relative intensity, rt = 5.479 min): 138 (M^+, 100), 123 (39), 109 (52), 106 (20), 95 (47), 91 (44), 79 (58), 67 (32), 53(14). ATR-FTIR (cm^{-1}): 1266, 1091, 894, 734, 704. HRMS m/z (ESI) calcd for $C_9H_{15}O$ $(M + H)^+$ 139.1117, found 139.1117.



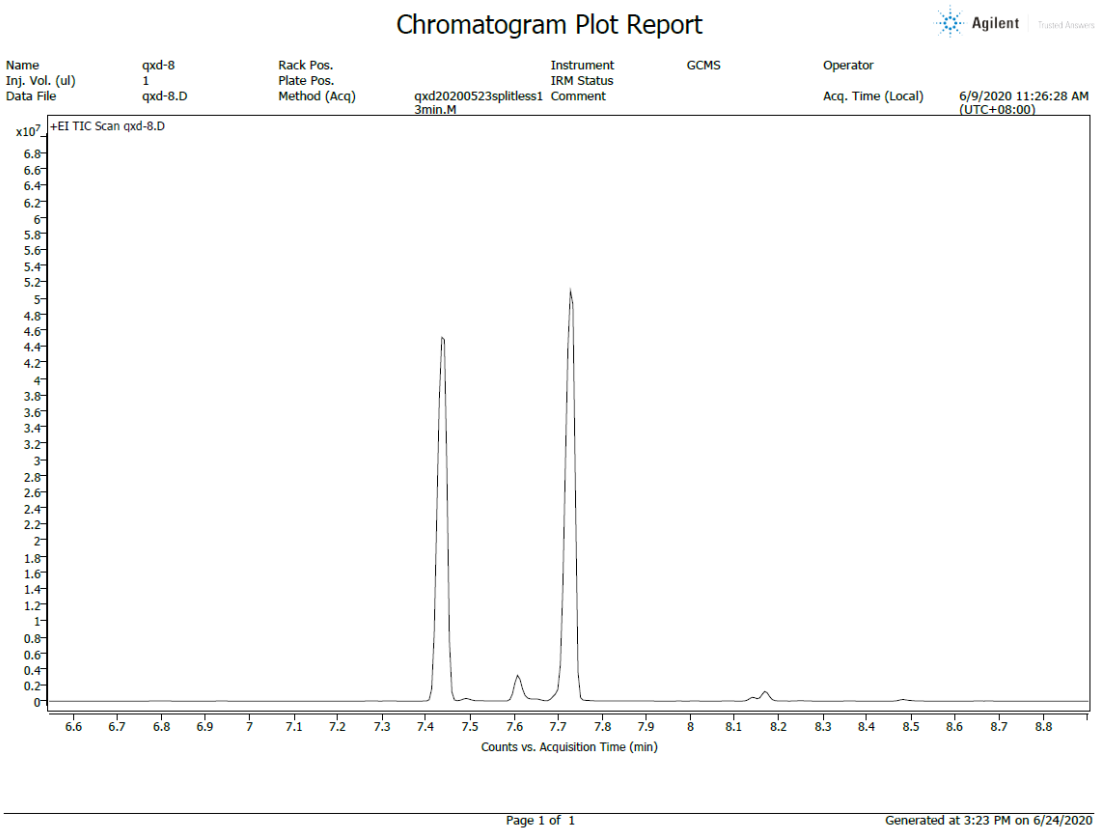
(*S*)-1-(2-methoxyvinyl)-4-(prop-1-en-2-yl)cyclohex-1-ene (1w)



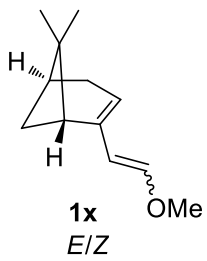
1w

E/*Z*

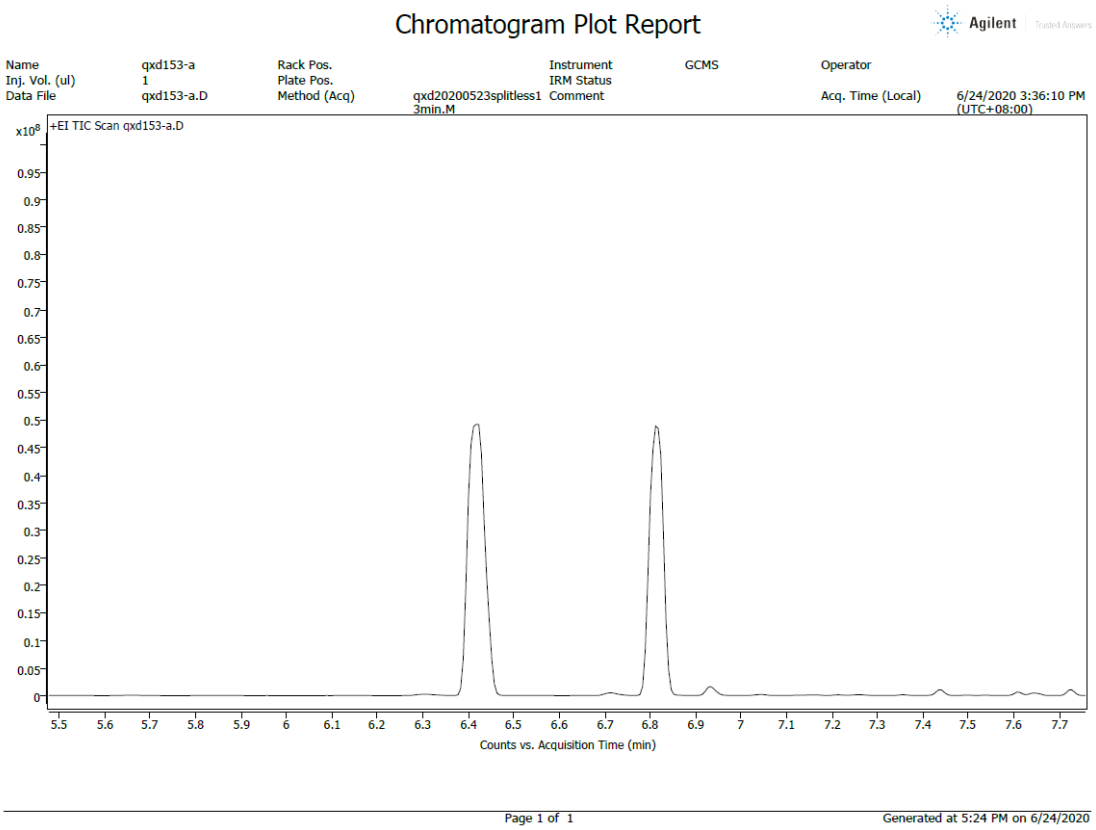
Compound **1w** was prepared from (-)-perillaldehyde in 60% yield as a colorless oil (535 mg). Due to the instability of **1w** under room temperature, it was put into the borylation reaction immediately after purification by column chromatography on silica gel. The NMR spectral data of **1w** were deficient but it could be easily judged from GC-MS that two isomers existed (47:53). EI-MS (m/z, relative intensity, rt = 7.436 min): 178 (M^+, 36), 137 (91), 110 (100), 95 (85), 91 (28), 79 (47), 67 (35), 53(13). EI-MS (m/z, relative intensity, rt = 7.728 min): 178 (M^+, 37), 137 (91), 110 (100), 95 (87), 91 (29), 79 (49), 67 (37), 53(14). ATR-FTIR (cm^{-1}): 1649, 1623, 1267, 1091, 893, 733, 704. HRMS m/z (ESI) calcd for $C_{12}H_{19}O$ $(M + H)^+$ 179.1430, found 179.1429.



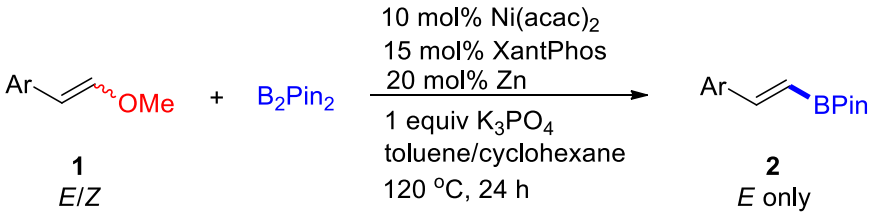
(1*R*,5*S*)-2-(2-methoxyvinyl)-6,6-dimethylbicyclo[3.1.1]hept-2-ene (1x)



Compound **1x** was prepared from (-)-myrtenal in 53% yield as a colorless oil (474 mg). Due to the instability of **1x** under room temperature, it was put into the borylation reaction immediately after purification by column chromatography on silica gel. The NMR spectral data of **1x** were deficient but it could be easily judged from GC-MS that two isomers existed (45:55). EI-MS (m/z, relative intensity, rt = 6.417 min): 178 (M^+, 72), 163 (62), 135(95), 131(65), 122 (32), 110 (21), 105 (80), 103(84), 91 (100), 86 (38), 77(55), 65 (24), 53(21). EI-MS (m/z, relative intensity, rt = 6.812 min): 178 (M^+, 77), 163 (56), 135(84), 131(64), 117 (30), 110 (22), 105 (79), 103(83), 91 (100), 86 (61), 77(54), 73 (20), 65 (24), 53(20). ATR-FTIR (cm^{-1}): 1422, 1263, 896, 735, 703. HRMS m/z (ESI) calcd for $C_{12}H_{19}O$ $(M + H)^+$ 179.1430, found 179.1429.



3. General Procedure for Borylation of Alkenyl Methyl Ethers

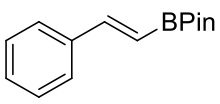


1
E/*Z*

2
E only

To a flame dried 25 mL Schlenk tube was added $Ni(acac)_2$ (0.05 mmol, 12.8 mg), XantPhos (0.075 mol, 43.4 mg) and Zn (0.1 mmol, 6.5 mg), then B_2Pin_2 (1.0 mmol, 254.0 mg) and K_3PO_4 (0.5 mmol, 106.1 mg) were added. The tube was vacuumed and refilled with nitrogen three times followed by the addition of anhydrous toluene (1.25 mL) and cyclohexane (3.75 mL). Substrates **1** (0.5 mmol) was also added with a syringe under nitrogen atmosphere and the plug is screwed. After that, The reaction was stirred under 120 °C in the heating module for 24 h. Then the mixture was cooled to room temperature, the solvents were removed under reduced pressure and the crude product was purified through flash chromatography with petroleum ether and ethyl actate as the eluent to afford the pure product **2**.

(*E*)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (2a)

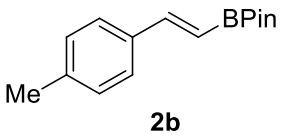


2a

Eluent: petroleum ether/ethyl acetate (100:1). Colorless oil (93.1 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.46 (m, 2H), 7.40 (d, *J* = 18.4 Hz, 1H), 7.37 – 7.26 (m, 3H), 6.18 (d, *J* = 18.4 Hz, 1H), 1.32 (s, 12H). ^{13}C NMR (101

MHz, $CDCl_3$) δ 149.5, 137.4, 128.9, 128.5, 127.0, 83.3, 24.8. The spectra data are consistent with those in literature report.[S7]

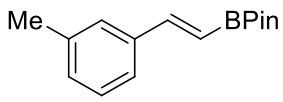
(*E*)-4,4,5,5-tetramethyl-2-(4-methylstyryl)-1,3,2-dioxaborolane (2b)



2b

Eluent: petroleum ether/ethyl acetate (100:1). Colorless oil (97.6 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.31 (m, 3H), 7.14 (d, *J* = 7.9 Hz, 2H), 6.11 (d, *J* = 18.4 Hz, 1H), 2.35 (s, 3H), 1.31 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.4, 139.0, 134.8, 129.3, 127.0, 83.3, 24.8, 21.3. The spectra data are consistent with those in literature report.[S7]

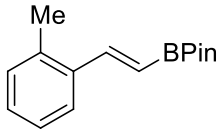
(*E*)-4,4,5,5-tetramethyl-2-(3-methylstyryl)-1,3,2-dioxaborolane (2c)



2c

Eluent: petroleum ether/ethyl acetate (100:1). Colorless oil (93.8 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 18.4 Hz, 1H), 7.33 – 7.27 (m, 2H), 7.23 (t, J = 7.8 Hz, 1H), 7.11 (d, J = 7.5 Hz, 1H), 6.15 (d, J = 18.4 Hz, 1H), 2.35 (s, 3H), 1.31 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.6, 138.1, 137.4, 129.7, 128.4, 127.8, 124.2, 83.3, 24.8, 21.4. The spectra data are consistent with those in literature report.[S8]

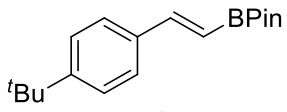
(*E*)-4,4,5,5-tetramethyl-2-(2-methylstyryl)-1,3,2-dioxaborolane (2d)



2d

Eluent: petroleum ether/ethyl acetate (100:1). Colorless oil (70.7 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 18.3 Hz, 1H), 7.61 – 7.51 (m, 1H), 7.23 – 7.09 (m, 3H), 6.10 (d, *J* = 18.3 Hz, 1H), 2.43 (s, 3H), 1.32 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.1, 136.6, 136.2, 130.3, 128.5, 126.0, 125.7, 83.2, 24.8, 19.8. The spectra data are consistent with those in literature report.[S7]

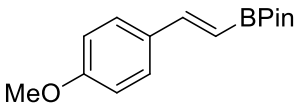
(*E*)-2-(4-(tert-butyl)styryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2e)



2e

Eluent: petroleum ether/ethyl acetate (100:1). White solid (107.1 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.31 (m, 5H), 6.13 (d, *J* = 18.4 Hz, 1H), 1.32 (s, 21H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.1, 149.4, 134.7, 126.8, 125.5, 83.2, 34.7, 31.2, 24.8. The spectra data are consistent with those in literature report.[S7]

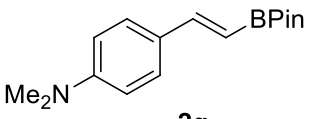
(*E*)-2-(4-methoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2f)



2f

Eluent: petroleum ether/ethyl acetate (80:1). Colorless oil (106.7 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.39 (m, 2H), 7.35 (d, *J* = 18.4 Hz, 1H), 6.92 – 6.80 (m, 2H), 6.01 (d, *J* = 18.4 Hz, 1H), 3.81 (s, 3H), 1.31 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3, 149.0, 130.4, 128.4, 113.9, 83.2, 55.3, 24.8. The spectra data are consistent with those in literature report.[S8]

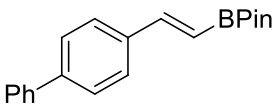
(*E*)-*N*,*N*-dimethyl-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)aniline (2g)



2g

Eluent: petroleum ether/ethyl acetate (80:1). White solid (120.2 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.37 (m, 2H), 7.34 (d, *J* = 18.3 Hz, 1H), 6.67 (d, *J* = 8.8 Hz, 2H), 5.92 (d, *J* = 18.3 Hz, 1H), 2.98 (s, 6H), 1.31 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.9, 149.8, 128.4, 125.9, 111.9, 83.0, 40.3, 24.8. The spectra data are consistent with those in literature report.[S7]

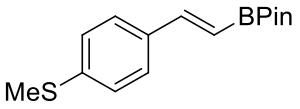
(*E*)-2-(2-([1,1'-biphenyl]-4-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2h)



2h

Eluent: petroleum ether/ethyl acetate (100:1). White solid (116.2 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.52 (m, 6H), 7.49 – 7.38 (m, 3H), 7.38 – 7.31 (m, 1H), 6.21 (d, *J* = 18.4 Hz, 1H), 1.33 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.0, 141.6, 140.5, 136.4, 128.8, 127.5, 127.4, 127.2, 127.0, 83.4, 24.8. The spectra data are consistent with those in literature report.[S8]

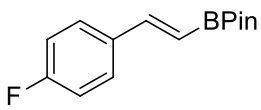
(*E*)-4,4,5,5-tetramethyl-2-(4-(methylthio)styryl)-1,3,2-dioxaborolane (2i)



2i

Eluent: petroleum ether/ethyl acetate (80:1). Colorless oil (117.3 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.37 (m, 2H), 7.34 (d, *J* = 18.4 Hz, 1H), 7.24 – 7.17 (m, 2H), 6.11 (d, *J* = 18.4 Hz, 1H), 2.48 (s, 3H), 1.31 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.8, 139.6, 134.3, 127.4, 126.1, 83.3, 24.8, 15.4. The spectra data are consistent with those in literature report.[S9]

(*E*)-2-(4-fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2j)

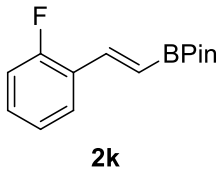


2j

Eluent: petroleum ether/ethyl acetate (100:1). Colorless oil (91.6 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.39 (m, 2H), 7.35 (d, *J* = 18.4 Hz, 1H), 7.02 (t, *J* = 8.7 Hz, 2H), 6.07 (d, *J* = 18.4 Hz, 1H), 1.31 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1 (d, *J* = 248.6 Hz), 148.1, 133.7 (d, *J* = 3.2 Hz), 128.7 (d, *J* = 8.2 Hz), 115.5

(d, J = 21.7 Hz), 83.4, 24.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.4. The spectra data are consistent with those in literature report.[S8]

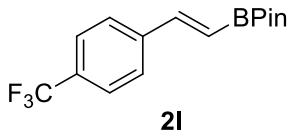
(*E*)-2-(2-fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolanee (2k)



2k

Eluent: petroleum ether/ethyl acetate (100:1). Colorless oil (74.5 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.51 (m, 2H), 7.36 – 7.19 (m, 1H), 7.16 – 7.07 (m, 1H), 7.03 (ddd, J = 10.8, 8.2, 1.2 Hz, 1H), 6.24 (d, J = 18.6 Hz, 1H), 1.31 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7 (d, J = 251.6 Hz), 141.3 (d, J = 4.1 Hz), 130.2 (d, J = 8.6 Hz), 127.4 (d, J = 3.3 Hz), 125.4 (d, J = 11.6 Hz), 124.1 (d, J = 3.6 Hz), 115.8 (d, J = 22.1 Hz), 83.4, 24.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.7. The spectra data are consistent with those in literature report.[S7]

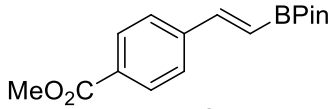
(*E*)-4,4,5,5-tetramethyl-2-(4-(trifluoromethyl)styryl)-1,3,2-dioxaborolane (2l)



2l

Eluent: petroleum ether/ethyl acetate (100:1). Colorless oil (104.4 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.52 (m, 4H), 7.40 (d, J = 18.4 Hz, 1H), 6.26 (d, J = 18.4 Hz, 1H), 1.32 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.7, 140.7, 130.4 (q, J = 32.4 Hz), 128.3, 127.1, 125.5 (q, J = 3.9 Hz), 124.1 (q, J = 272.0 Hz), 83.6, 24.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.6. The spectra data are consistent with those in literature report.[S8]

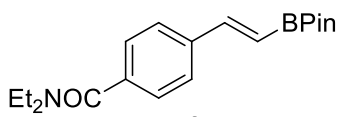
(*E*)-methyl 4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzoate (2m)[6]



2m

Eluent: petroleum ether/ethyl acetate (60:1). White solid (97.8 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.4 Hz, 2H), 7.58 – 7.46 (m, 2H), 7.40 (d, J = 18.4 Hz, 1H), 6.26 (d, J = 18.4 Hz, 1H), 3.90 (s, 3H), 1.30 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 148.1, 141.6 ,130.1, 129.9, 126.8, 83.5, 52.1, 24.8. The spectra data are consistent with those in literature report.[S10]

(*E*)-*N*,*N*-diethyl-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzamide (2n)

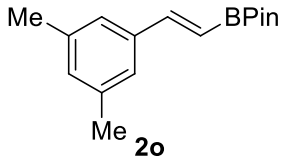


2n

Eluent: petroleum ether/ethyl acetate (10:1). White solid (125.0 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.45 (m, 2H), 7.43 – 7.29 (m, 3H), 6.19 (d, J = 18.5 Hz, 1H), 3.73 – 3.70 (m, 4H), 1.31 (s, 12H), 1.30 – 1.00 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 148.5, 138.2, 137.5, 127.0, 126.7, 83.4, 43.2,

39.2, 24.8, 14.2, 12.9. ATR-FTIR (cm^{-1}): 1421, 1268, 892, 734, 702. HRMS m/z (ESI) calcd for $C_{19}H_{29}BNO_3$ $(M + H)^+$ 330.2235, found 330.2233.

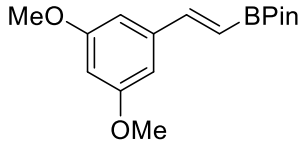
(*E*)-2-(3,5-dimethylstyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2o)



2o

Eluent: petroleum ether/ethyl acetate (100:1). Colorless oil (81.3 mg, 63%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 18.4 Hz, 1H), 7.11 (brs, 2H), 6.94 (brs, 1H), 6.13 (d, *J* = 18.4 Hz, 1H), 2.31 (s, 6H), 1.31 (s, 12H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 149.8, 137.9, 137.4, 130.6, 124.9, 83.2, 24.8, 21.2. ATR-FTIR (cm^{-1}): 1264, 907, 729, 706, 650. HRMS m/z (ESI) calcd for $C_{16}H_{24}BO_2$ $(M + H)^+$ 259.1864, found 259.1864.

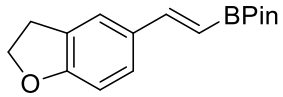
(*E*)-2-(3,5-dimethoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2p)



2p

Eluent: petroleum ether/ethyl acetate (50:1). White solid (92.6 mg, 64%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 18.4 Hz, 1H), 6.65 (d, *J* = 2.2 Hz, 2H), 6.42 (t, *J* = 2.3 Hz, 1H), 6.14 (d, *J* = 18.4 Hz, 1H), 3.79 (s, 6H), 1.31 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.8, 149.3, 139.5, 104.9, 101.3, 83.4, 55.3, 24.8. The spectra data are consistent with those in literature report.[S11]

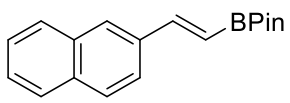
(*E*)-2-(2-(2,3-dihydrobenzofuran-5-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2q)



2q

Eluent: petroleum ether/ethyl acetate (50:1). Colorless oil (89.6 mg, 66%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.28 (m, 2H), 7.24 (dd, *J* = 8.3, 1.8 Hz, 1H), 6.74 (d, *J* = 8.3 Hz, 1H), 5.96 (d, *J* = 18.3 Hz, 1H), 4.58 (t, *J* = 8.7 Hz, 2H), 3.20 (t, *J* = 8.7 Hz, 2H), 1.30 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0, 149.5, 130.5, 128.1, 127.5, 123.2, 109.2, 83.2, 71.6, 29.4, 24.8. ATR-FTIR (cm^{-1}): 1423, 1261, 895, 733, 705. HRMS m/z (ESI) calcd for $C_{16}H_{22}BO_3$ $(M + H)^+$ 273.1657, found 273.1653.

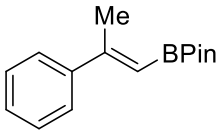
(*E*)-4,4,5,5-tetramethyl-2-(2-(naphthalen-2-yl)vinyl)-1,3,2-dioxaborolane (2r)



2r

Eluent: petroleum ether/ethyl acetate (100:1). Yellowish solid (110.8 mg, 79%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.76 (m, 4H), 7.70 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.57 (d, *J* = 18.4 Hz, 1H), 7.51 – 7.42 (m, 2H), 6.29 (d, *J* = 18.4 Hz, 1H), 1.34 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.5, 134.9, 133.7, 133.4, 128.4, 128.2, 128.0, 127.7, 126.4, 126.3, 123.4, 83.4, 24.8. The spectra data are consistent with those in literature report.[S7]

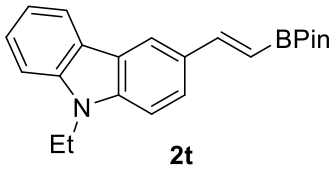
(*E*)-4,4,5,5-tetramethyl-2-(2-phenylprop-1-en-1-yl)-1,3,2-dioxaborolane (2s)



2s

Eluent: petroleum ether/ethyl acetate (100:1). Colorless oil (57.0 mg, 47%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.46 (m, 2H), 7.37 – 7.26 (m, 3H), 5.75 (s, 1H), 2.41 (s, 3H), 1.32 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8, 143.8, 128.1, 127.9, 125.8, 82.9, 24.9, 20.1. The spectra data are consistent with those in literature report.[S7]

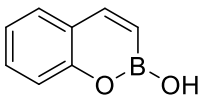
(*E*)-9-ethyl-3-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-2-yl)-9*H*-carbazole (2t)



2t

Eluent: petroleum ether/ethyl acetate (80:1). Yellowish solid (140.3 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 1.7 Hz, 1H), 8.09 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.73 – 7.58 (m, 2H), 7.48 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.43 – 7.32 (m, 2H), 7.29 – 7.20 (m, 1H), 6.20 (d, *J* = 18.4 Hz, 1H), 4.35 (q, *J* = 7.2 Hz, 2H), 1.43 (t, *J* = 7.2 Hz, 3H), 1.35 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.6, 140.5, 140.3, 128.8, 125.8, 124.8, 123.0, 123.0, 120.4, 119.8, 119.1, 108.6, 108.5, 83.1, 37.6, 24.8, 13.8. ATR-FTIR (cm^{-1}): 2977, 1472, 1455, 1332, 1233, 1146, 1124, 745, 728, 670, 630. HRMS m/z (ESI) calcd for $C_{22}H_{27}BNO_2$ $(M + H)^+$ 348.2129, found 348.2122.

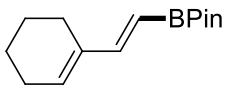
2*H*-benzo[e][1,2]oxaborinin-2-ol (2u)



2u

Eluent: petroleum ether/ethyl acetate (40:1). White solid (44.7 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 11.9 Hz, 1H), 7.47 – 7.31 (m, 2H), 7.28 – 7.23 (m, 1H), 7.15 (td, *J* = 7.4, 1.2 Hz, 1H), 6.22 (d, *J* = 11.8 Hz, 1H), 4.54 (brs, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.3, 149.4, 129.4, 128.7, 124.4, 122.3, 118.4. The spectra data was consistent with literature report.[S12]

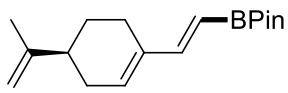
(*E*)-2-(2-(cyclohex-1-en-1-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2v)



2v

Eluent: petroleum ether/ethyl acetate (80:1). Colorless oil (65.6 mg, 56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (d, *J* = 18.2 Hz, 1H), 5.96 (t, *J* = 3.9 Hz, 1H), 5.42 (d, *J* = 18.2 Hz, 1H), 2.22 – 2.07 (m, 4H), 1.76 – 1.47 (m, 4H), 1.27 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.2, 137.1, 134.3, 83.0, 26.2, 24.8, 23.7, 22.4, 22.3. The spectra data was consistent with literature report.[S13] ATR-FTIR (cm^{-1}): 1424, 1264, 893, 735, 703. HRMS m/z (ESI) calcd for $C_{14}H_{24}BO_2$ $(M + H)^+$ 235.1864, found 235.1859.

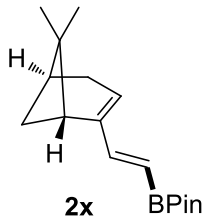
(*S*,*E*)-4,4,5,5-tetramethyl-2-(2-(4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)vinyl)-1,3,2-dioxaborolane (2w)



2w

Eluent: petroleum ether/ethyl acetate (80:1). Colorless oil (69.7 mg, 51%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (d, *J* = 18.3 Hz, 1H), 6.01 – 5.95 (m, 1H), 5.43 (d, *J* = 18.3 Hz, 1H), 4.76 – 4.68 (m, 2H), 2.40 – 2.22 (m, 2H), 2.22 – 2.01 (m, 3H), 1.74 (s, 3H), 1.66 – 1.55 (m, 2H), 1.28 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.6, 149.5, 136.8, 133.5, 108.8, 83.1, 41.0, 31.5, 27.3, 24.8, 24.1, 20.8. The spectra data was consistent with literature report.[S13] HRMS m/z (ESI) calcd for $C_{17}H_{28}BO_2$ $(M + H)^+$ 275.2177, found 275.2174.

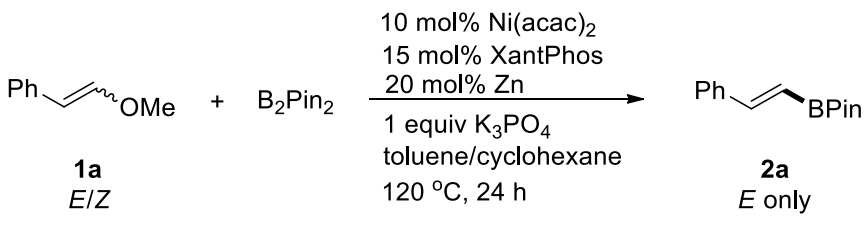
2-((*E*)-2-((1*R*,5*S*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2x)



2x

Eluent: petroleum ether/ethyl acetate (80:1). Colorless oil (57.6 mg, 42%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (d, J = 18.2 Hz, 1H), 5.82 – 5.75 (m, 1H), 5.41 (d, J = 18.2 Hz, 1H), 2.63 (td, J = 5.7, 1.5 Hz, 1H), 2.46 – 2.27 (m, 3H), 2.15 – 2.07 (m, 1H), 1.30 (s, 3H), 1.27 (s, 12H), 1.09 (d, J = 8.8 Hz, 1H), 0.75 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.4, 147.9, 129.2, 83.0, 40.9, 40.2, 37.7, 32.2, 31.2, 26.3, 24.8, 24.7, 20.8. ATR-FTIR (cm^{-1}): 1424, 1264, 892, 732, 701. HRMS m/z (ESI) calcd for $C_{17}H_{28}BO_2$ $(M + H)^+$ 275.2177, found 275.2172.

4. Experimental Procedure for Gram-Scale Borylation of 1a

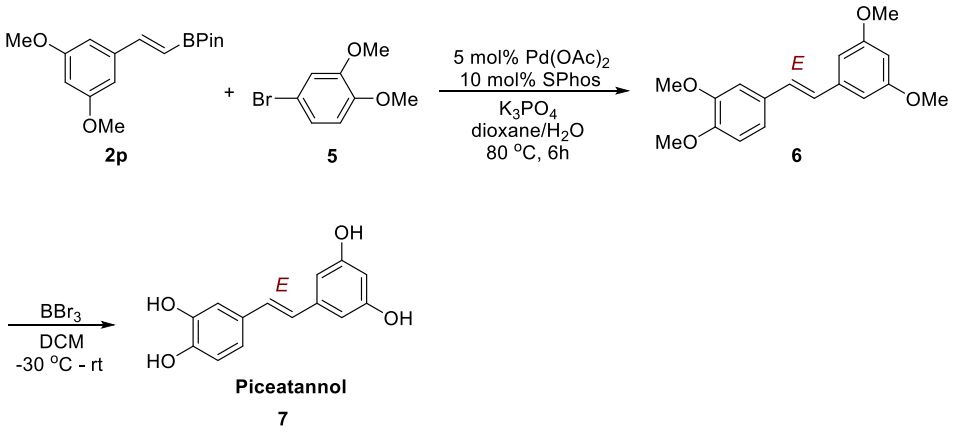


1a
E/*Z*

2a
E only

To a flame dried 100 mL Schlenk tube was added $Ni(acac)_2$ (0.6 mmol, 154.2 mg), XantPhos (0.9 mmol, 520.7 mg) and Zn (1.2 mmol, 78 mg), then B_2Pin_2 (12 mmol, 3.048 g) and K_3PO_4 (6 mmol, 1.272 g) were added. The tube was vacuumed and refilled with nitrogen three times followed by the addition of anhydrous toluene (15 mL) and cyclohexane (45 mL). Substrates **1a** (6 mmol, 804 mg) was also added with a syringe under nitrogen atmosphere and the plug is screwed. After that, The reaction was stirred under 120 ℃ in the heating module for 24 h. Then the mixture was cooled to room temperature, the solvents were removed under reduced pressure and the crude product was purified through flash chromatography with petroleum ether and ethyl actate as the eluent to afford the pure product **2a** as a colorless oil in 80% yield (1.10g).

5. Experimental Procedure for the Synthesis of Piceatannol (7)



To a flame dried 25 mL Schlenk tube was added **2p** (0.3 mmol, 87.1 mg), $Pd(OAc)_2$ (0.015 mmol, 3.4 mg), SPhos (0.03 mmol, 12.3 mg) and K_3PO_4 (0.9 mmol, 190.8 mg). The tube was vacuumed and refilled with nitrogen three times followed by the addition of 1,4-dioxane (3.0 mL) and H_2O (30 μL). Aryl bromide **5** (0.36 mmol, 78.1 mg) was also added with a syringe under nitrogen atmosphere and the plug was screwed. After that, the reaction was stirred under 80 °C in the heating module for 6 h. Then the mixture was cooled to room temperature, the solvents were removed under reduced pressure and the crude product was purified by flash chromatography with petroleum ether and ethyl actate as the eluent to afford the pure product **6** (white solid, 75.4 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 – 6.98 (m, 3H), 6.95 – 6.80 (m, 2H), 6.66 (d, *J* = 2.3 Hz, 2H), 6.39 (t, *J* = 2.3 Hz, 1H), 3.94 (s, 3H), 3.90 (s, 3H), 3.83 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.9, 149.0, 148.9, 139.5, 130.1, 128.9, 126.7, 119.9, 111.1, 108.7, 104.2, 99.6, 55.8, 55.8, 55.3. The spectra data was consistent with literature report.[S14]

To the above compound **6** (0.1 mmol, 30.0 mg) in 25 mL flame dried Schlenk tube was added anhydrous CH_2Cl_2 (1.0 mL). The solution was stirred under -30°C and BBr_3 (1.0 M in DCM, 1.0 mmol, 1mL) was added dropwise to the mixture. Then the reaction was slowly warmed to room temperature and stirred for another 4 h. When the reaction was finished, 5 mL of water was added and stirred for another 5 min. The aqueous phase was extracted by DCM and the combined organic phase was dried over anhydrous sodium sulfate. The mixture was then filtered and the solvent was removed under reduced pressure. Further purification by flash chromatography would afford the complete *E*-isomer of Piceatannol (**7**) as a light brown solid (26.9 mg) in 90% yield. ^{1}H NMR (400 MHz, CD_3OD) δ 6.97 (d, *J* = 2.0 Hz, 1H), 6.89 (d, *J* = 16.3 Hz, 1H), 6.83 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.78 – 6.70 (m, 2H), 6.44 (d, *J* = 2.2 Hz, 2H), 6.16 (t, *J* = 2.1 Hz, 1H). ^{13}C NMR (101 MHz, CD_3OD) δ 159.6, 146.5, 146.5, 141.3, 131.1,

129.7, 127.0, 120.2, 116.4, 113.8, 105.8, 102.6. The spectra data was consistent with literature report.[S15]

HRMS m/z (ESI) calcd for $C_{14}H_{12}NaO_4$ $(M + Na)^+$ 267.0628, found 267.0624.

6. References

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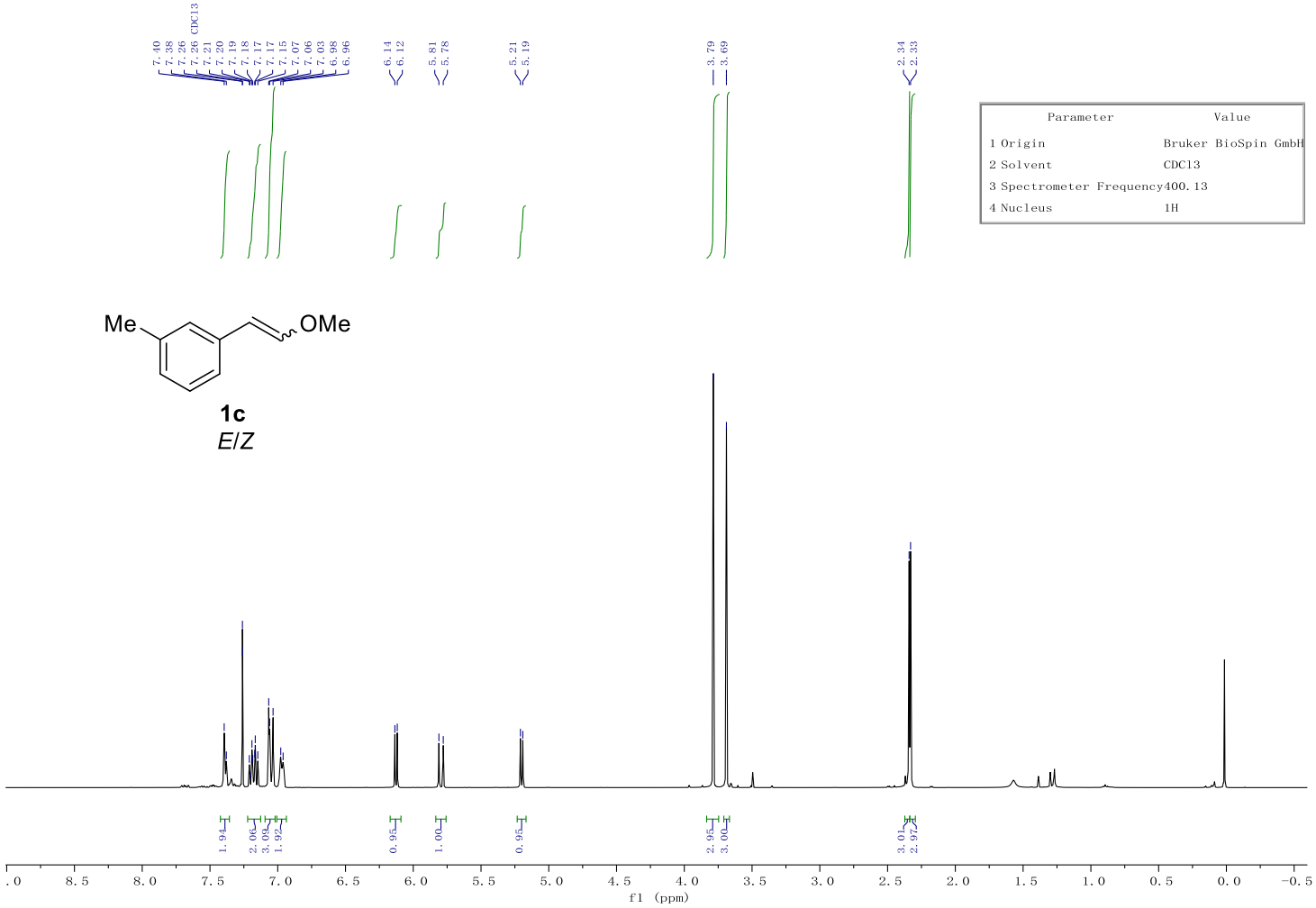
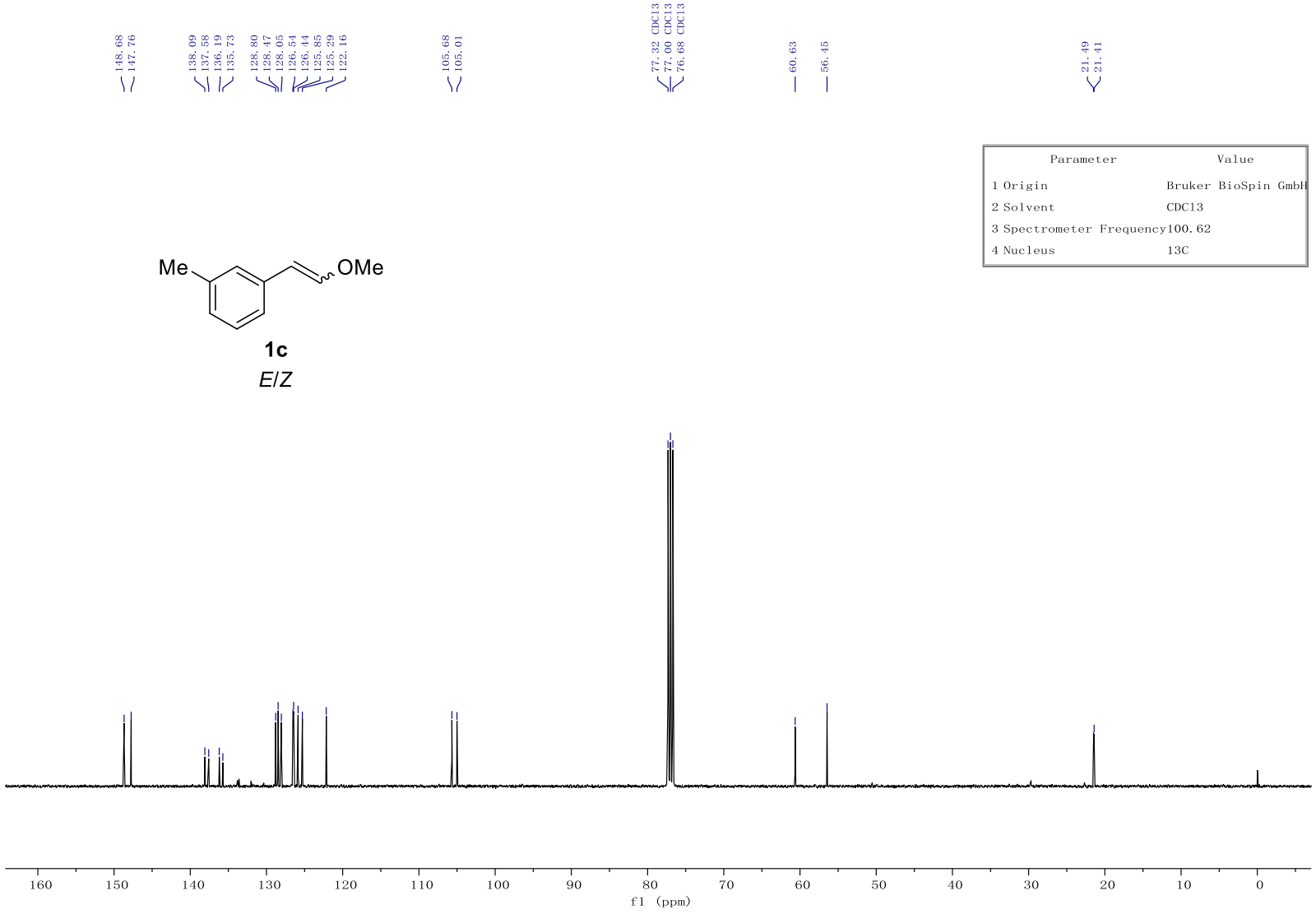
7. Spectroscopic Data

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122.16
105.68
105.01
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77.00 CDCl3
76.68 CDCl3
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21.49
21.41
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OMe
1c
E/Z
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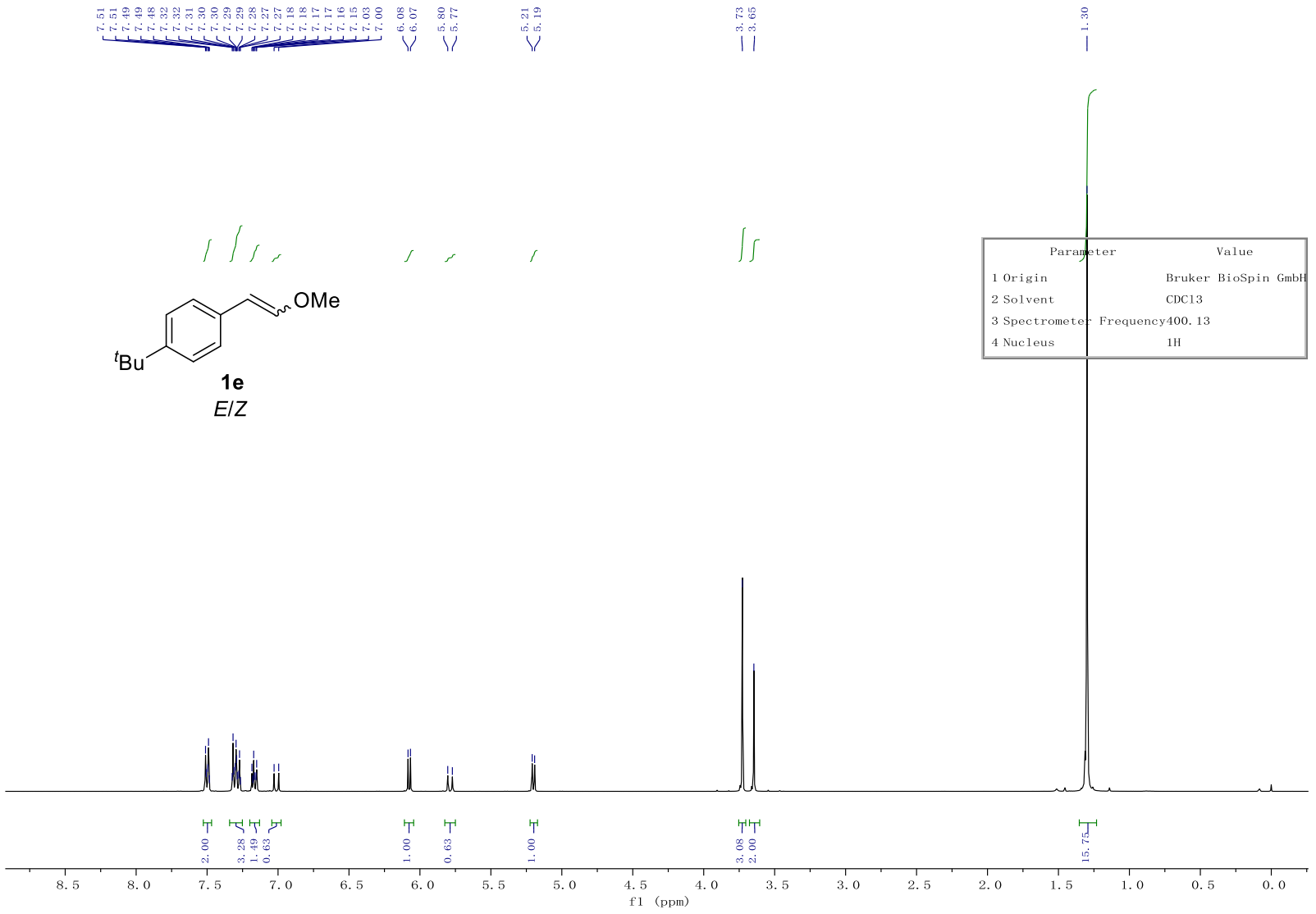
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6.07
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5.21
5.19
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tBu
1e
E/Z
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2.00
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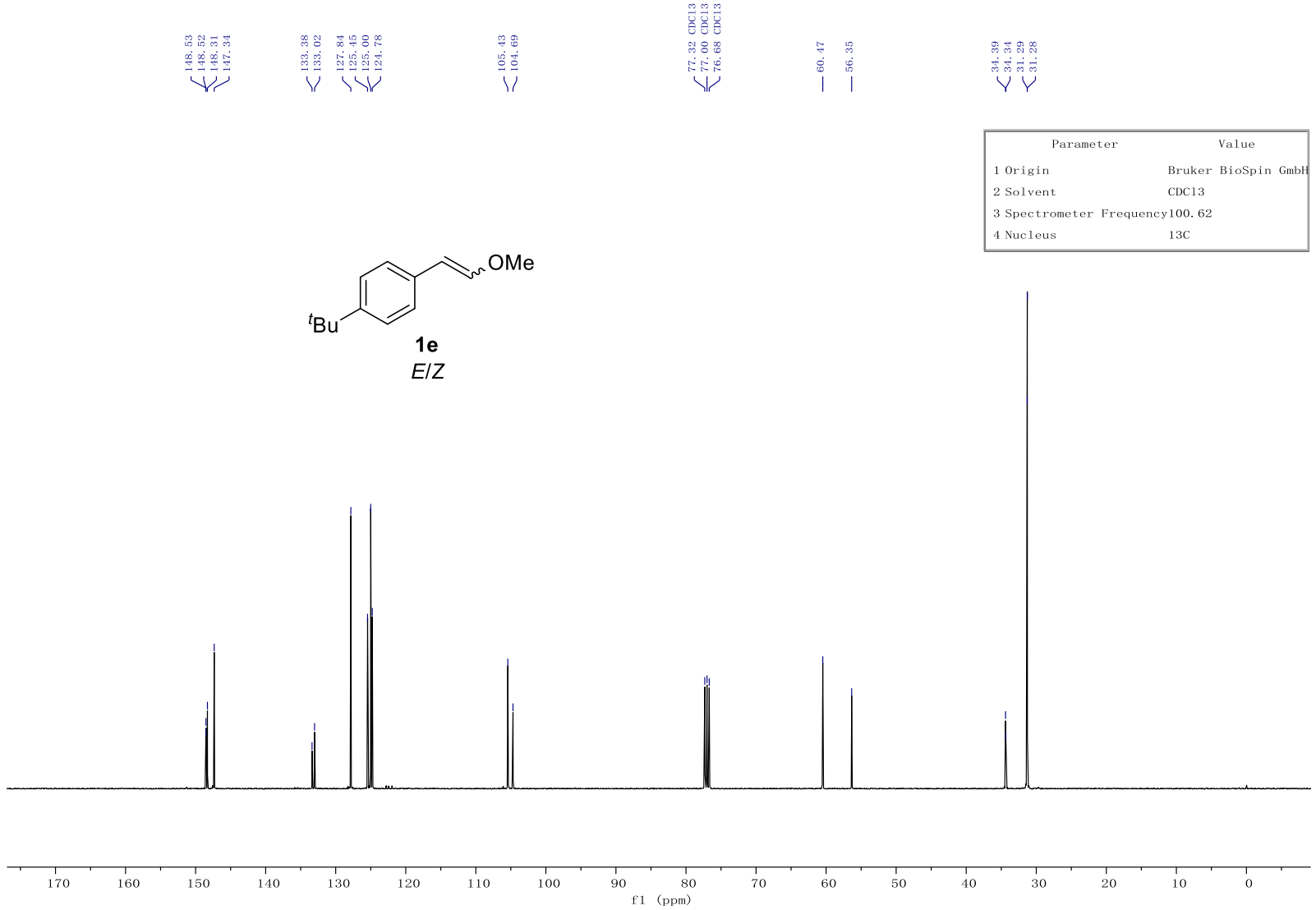
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E/Z
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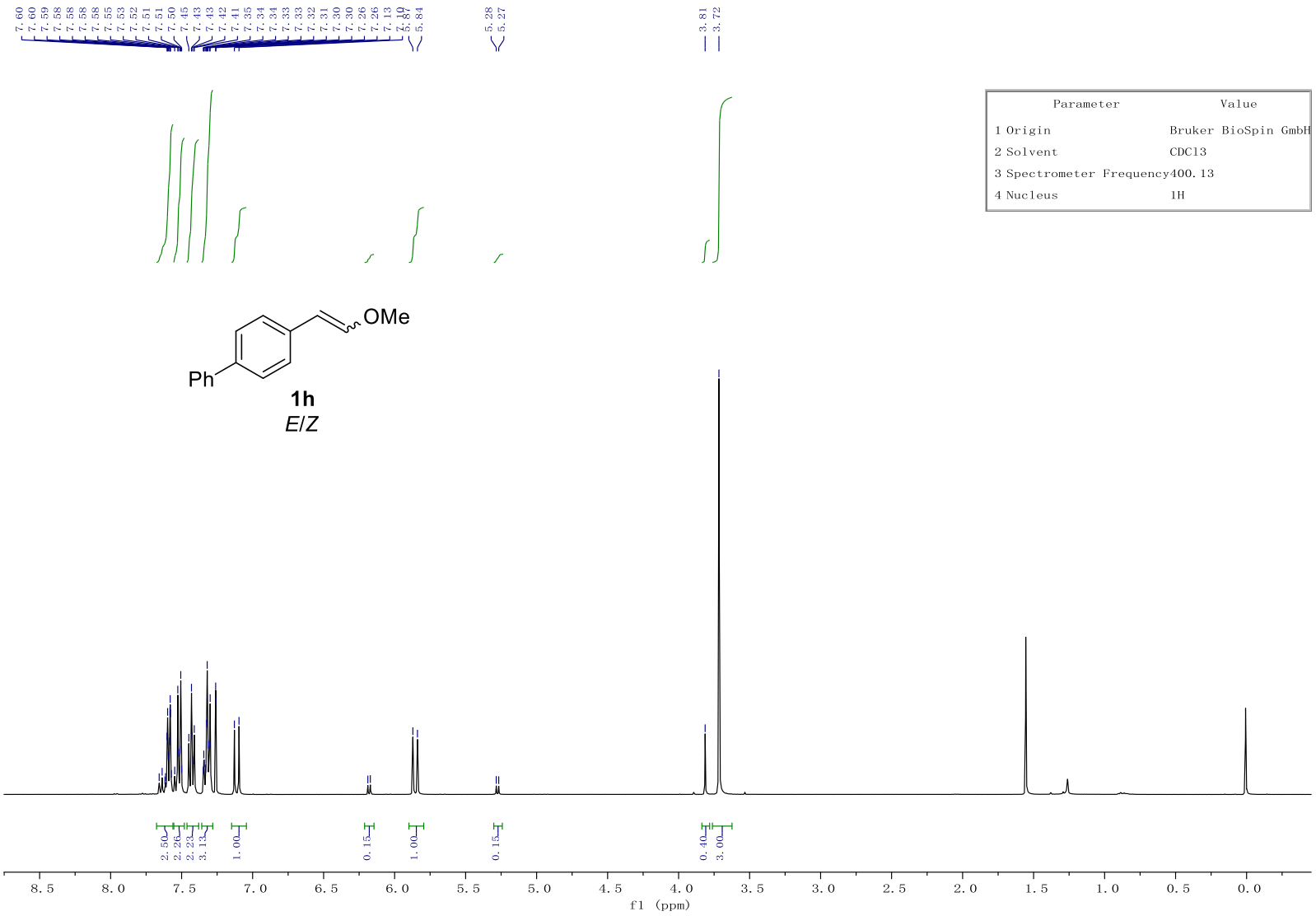
f1 (ppm)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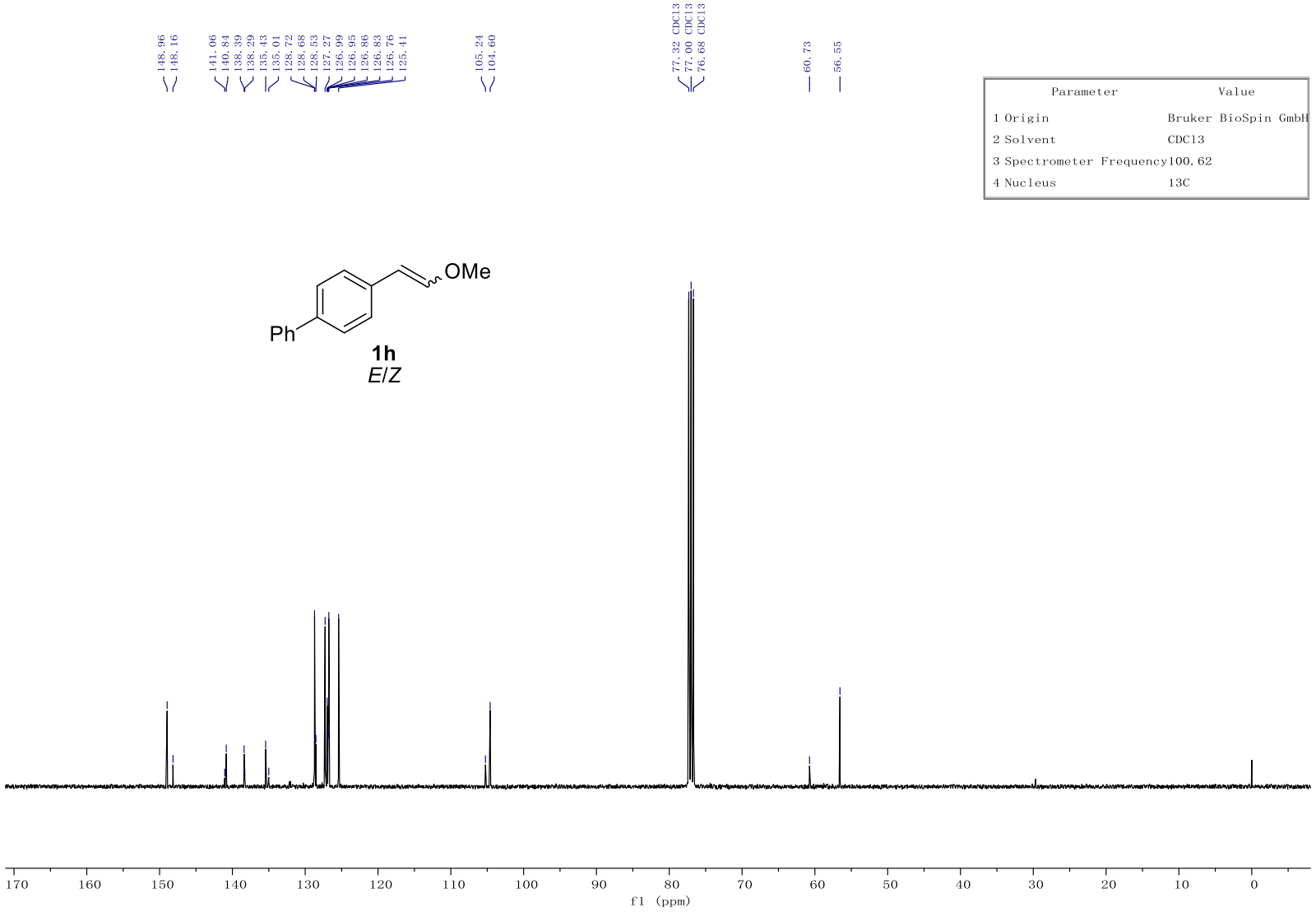
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77.00 CDCl3
76.68 CDCl3
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Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
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4 Nucleus 13C
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Ph
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E/Z
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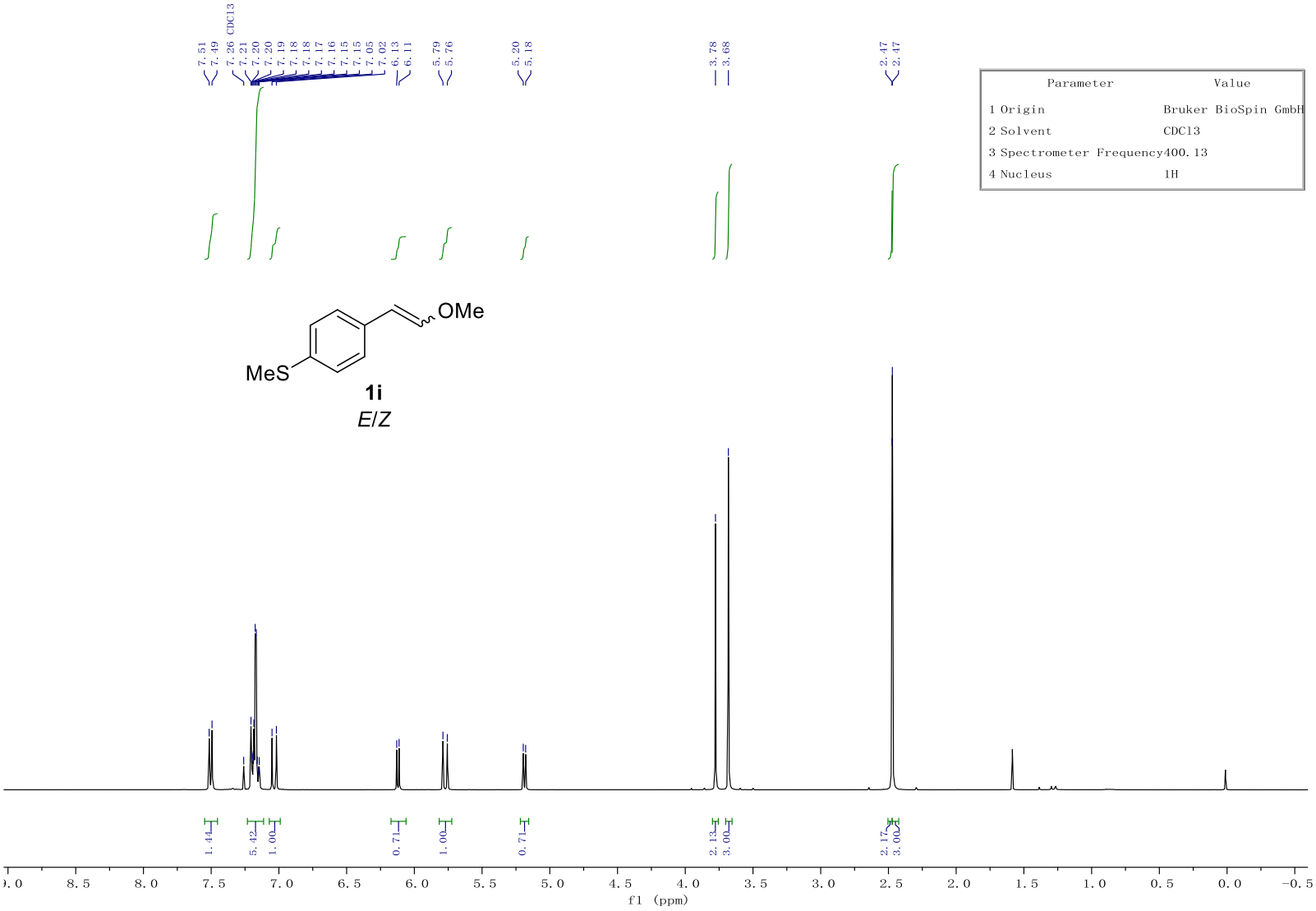
f1 (ppm)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2.47
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Parameter Value
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3 Spectrometer Frequency 400.13
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OMe
MeS
1i
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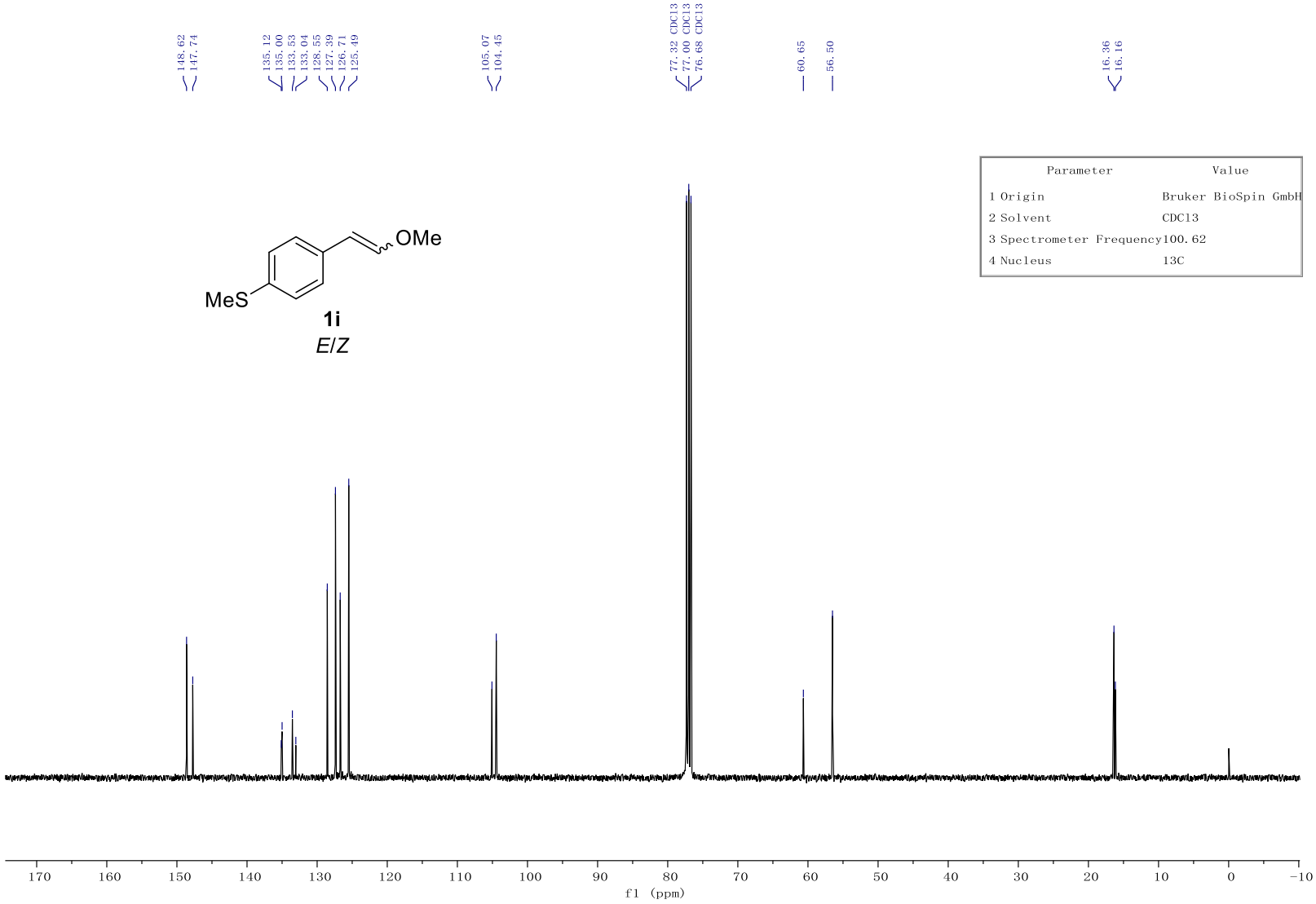
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1i
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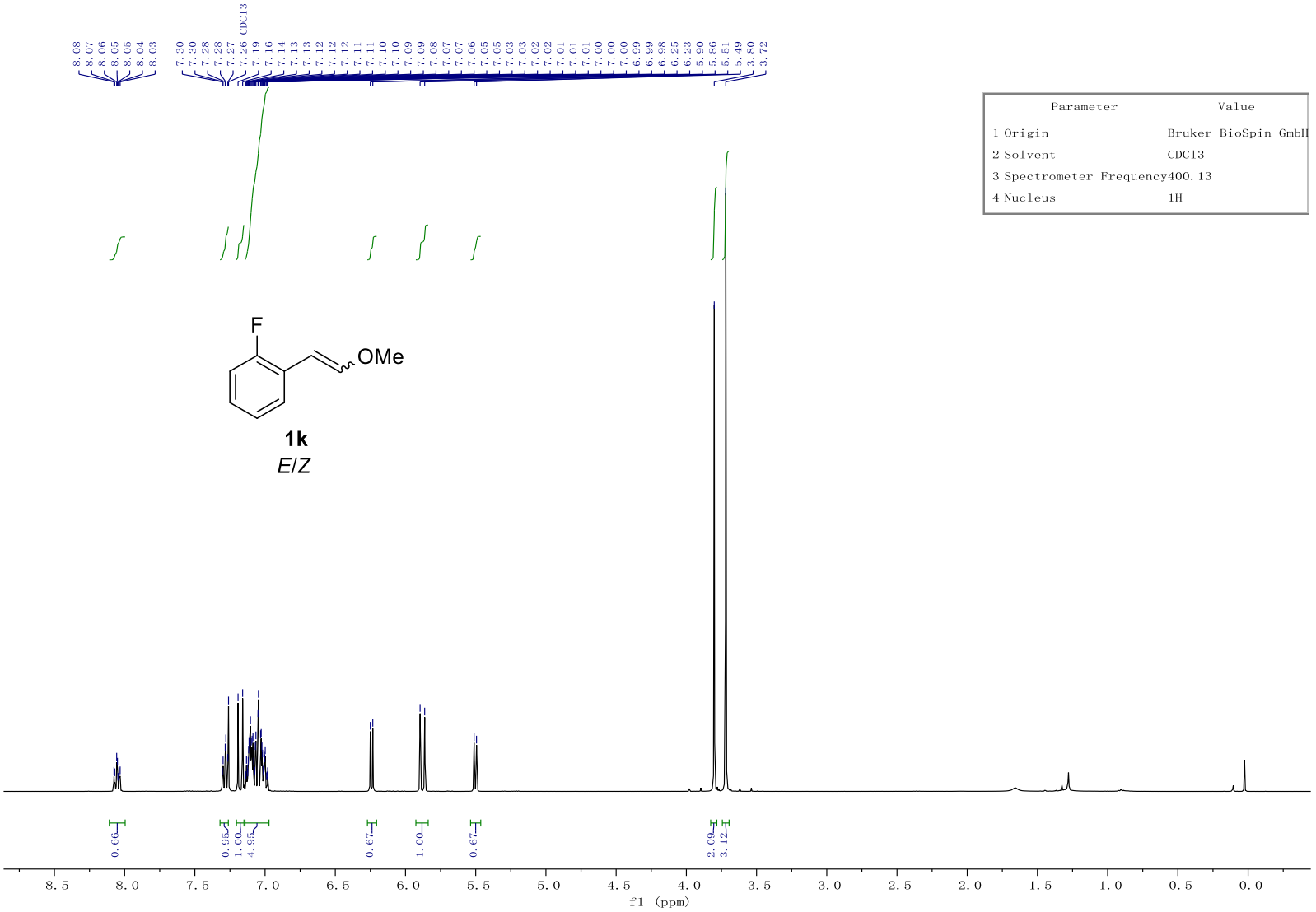
f1 (ppm)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E/Z
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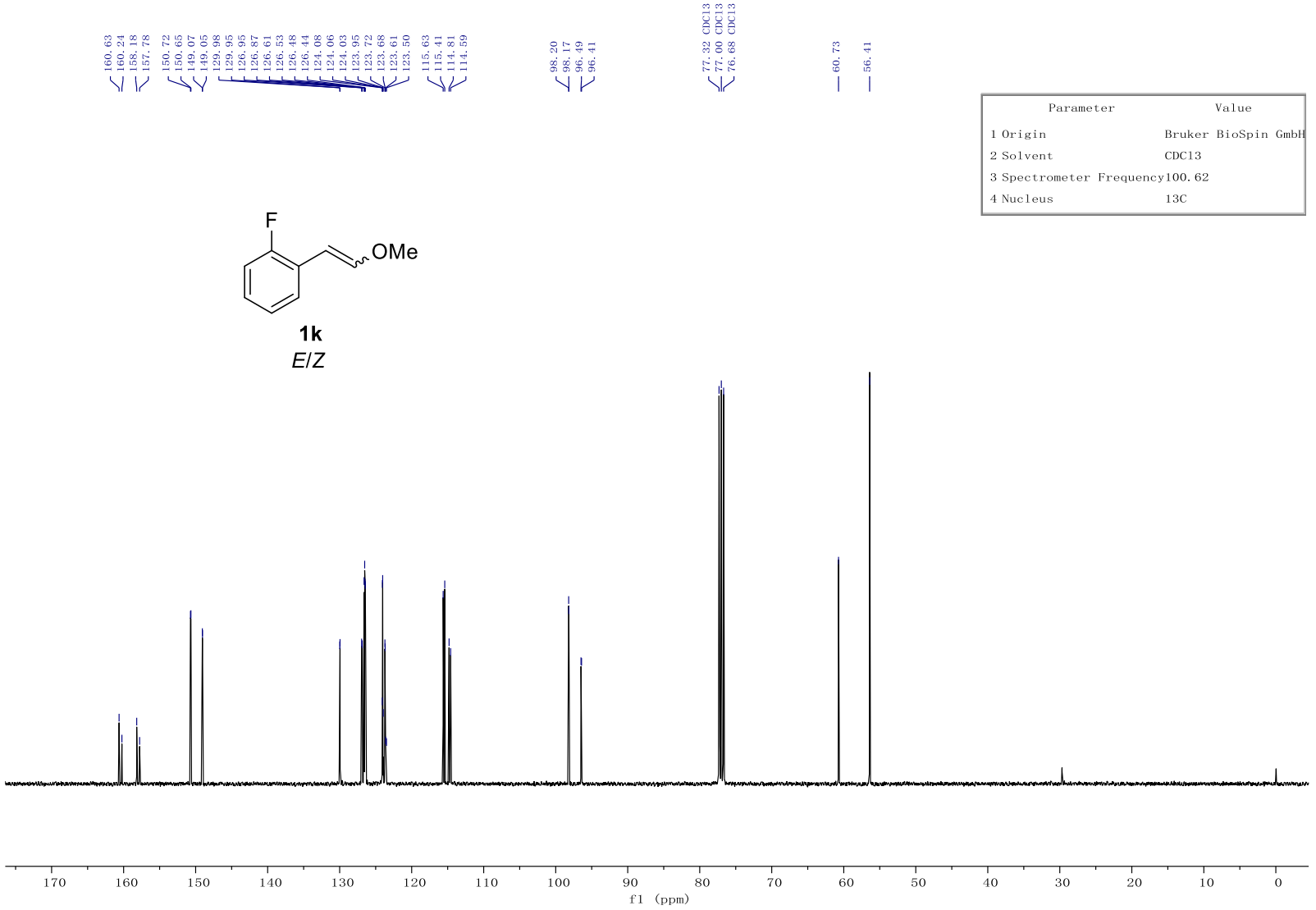
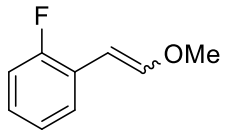
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


160.63
160.24
158.18
157.78
150.72
150.65
149.07
149.05
129.98
129.95
126.95
126.87
126.61
126.53
126.48
126.44
124.08
124.06
124.03
123.95
123.72
123.68
123.61
123.50
115.63
115.41
114.81
114.59
98.20
98.17
96.49
96.41
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
60.73
56.41
Parameter
Value
1 Origin
Bruker BioSpin GmbH
2 Solvent
CDCl3
3 Spectrometer Frequency
100.62
4 Nucleus
13C
F
OMe
1k
E/Z
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

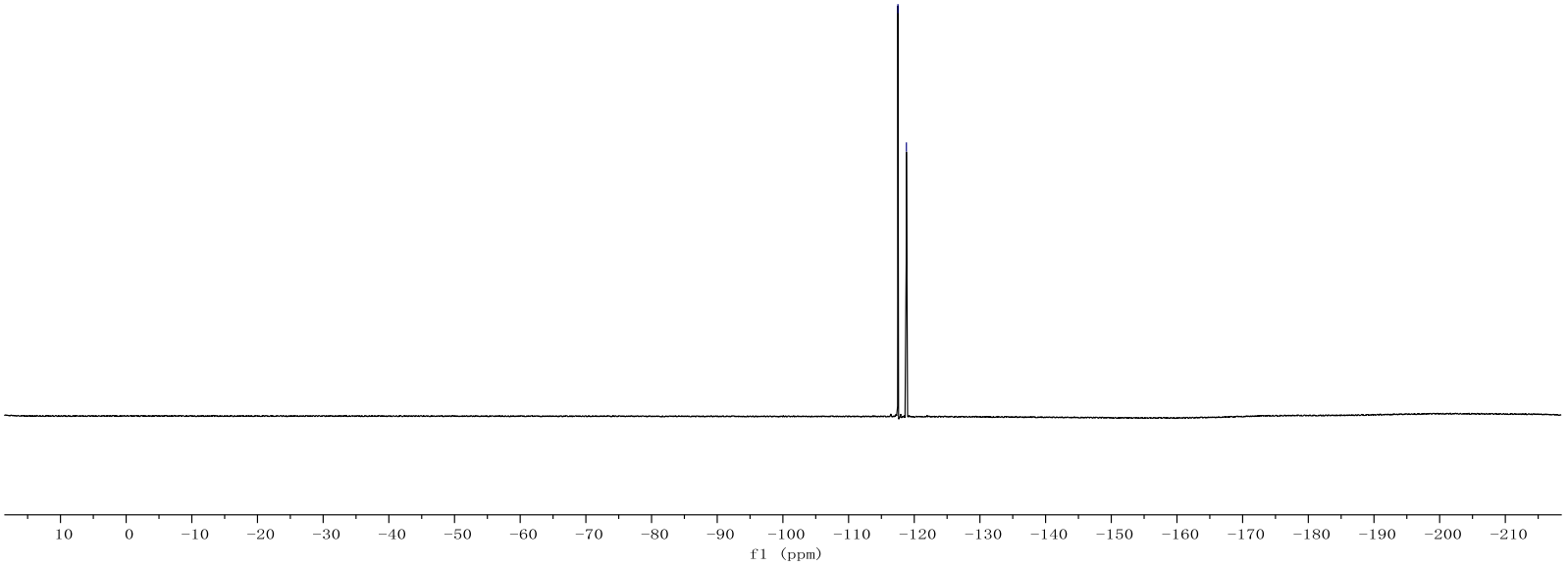


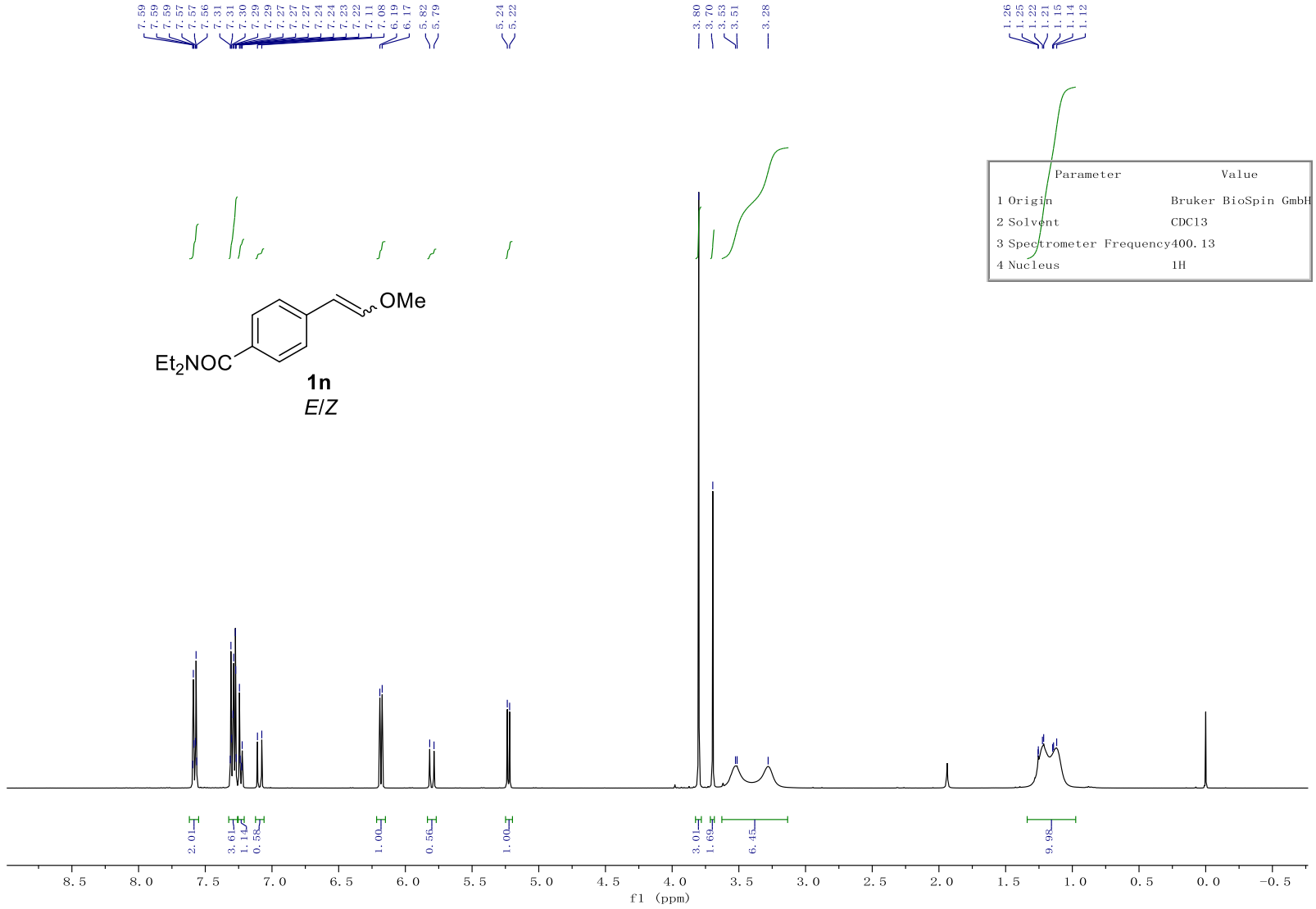
1k

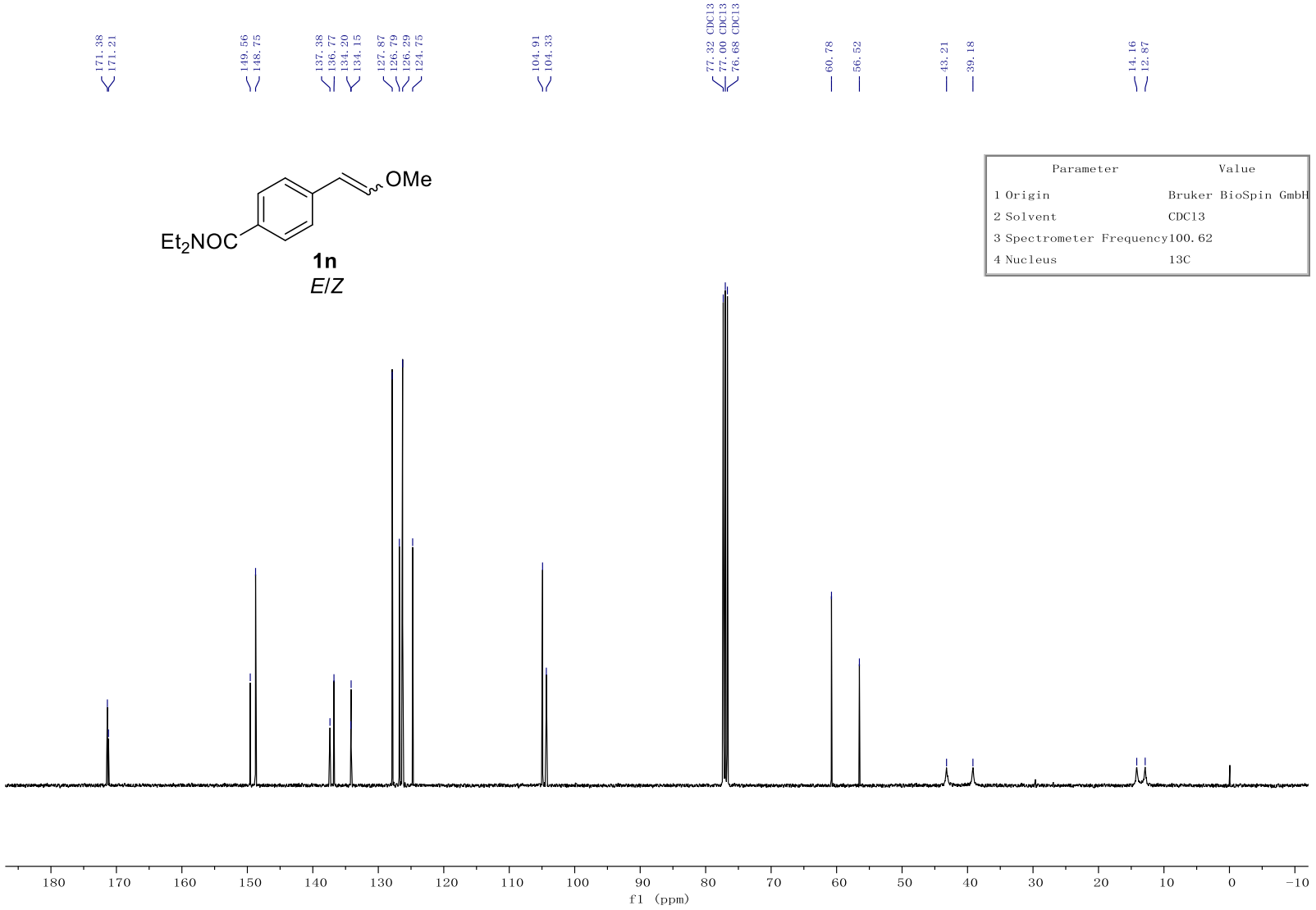
E/*Z*

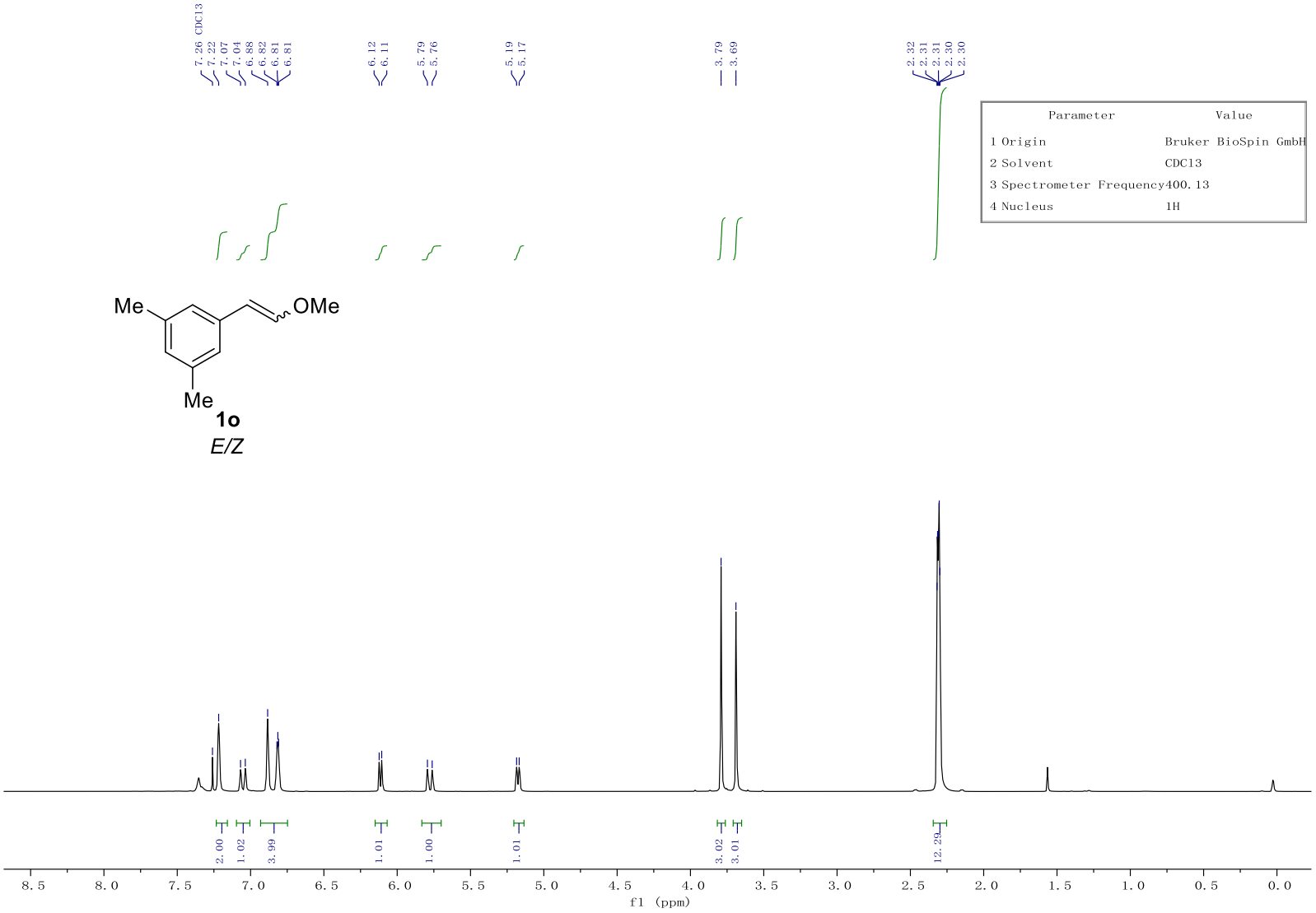
−117.62
−118.81

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Spectrometer Frequency	376.46
4 Nucleus	19F



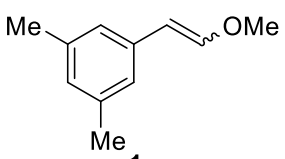

7.59 7.59 7.59 7.57 7.57 7.56 7.31 7.31 7.30 7.29 7.29 7.27 7.27 7.27 7.24 7.24 7.23 7.22 7.11 7.08 6.19 6.17 5.82 5.79
5.24 5.22
3.80 3.70 3.53 3.51 3.28
1.26 1.25 1.22 1.21 1.15 1.14 1.12
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Spectrometer Frequency 400.13
4 Nucleus 1H
OMe
Et2NOC
1n
E/Z
2.01 3.61 1.14 0.58 1.00 0.56 1.00 3.01 1.69 6.45 9.98
8.5 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 0.0 -0.5
f1 (ppm)


171.38
171.21
149.56
148.75
137.38
136.77
134.20
134.15
127.87
126.79
126.29
124.75
104.91
104.33
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
60.78
56.52
43.21
39.18
14.16
12.87
OMe
Et2NOC
1n
E/Z
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Spectrometer Frequency 100.62
4 Nucleus 13C
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


7.26 CDCl3
7.22
7.07
7.04
6.88
6.82
6.81
6.81
6.12
6.11
5.79
5.76
5.19
5.17
3.79
3.69
2.32
2.31
2.31
2.30
2.30
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Spectrometer Frequency 400.13
4 Nucleus 1H
Me
OMe
Me
1o
E/Z
2.00
1.02
3.99
1.01
1.00
1.01
3.02
3.01
12.29
8.5
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
0.0
f1 (ppm)

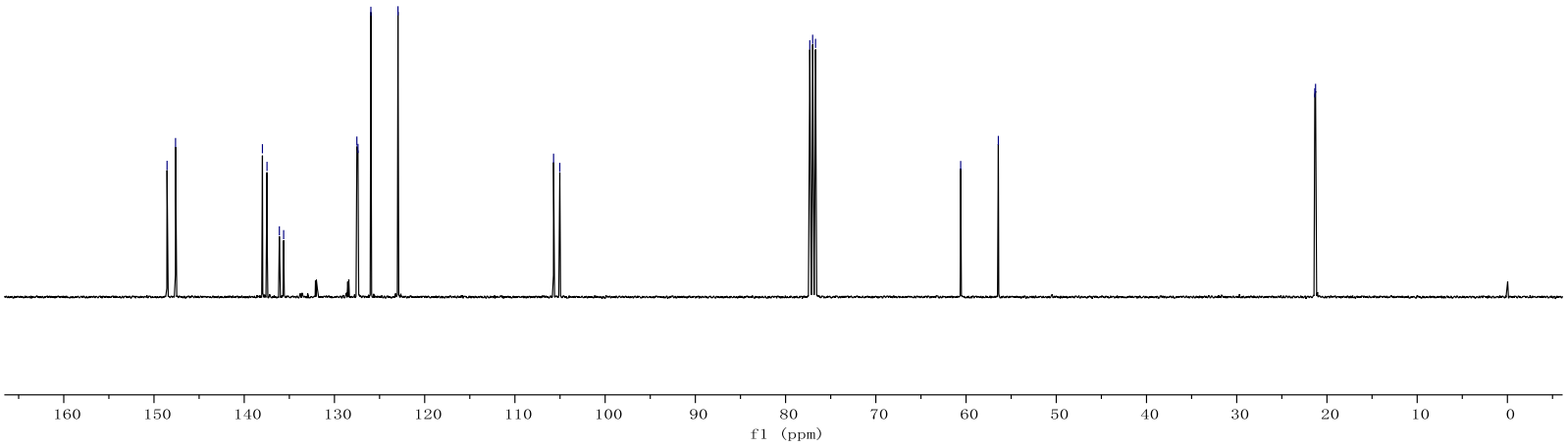
148.55
147.61
137.98
137.47
136.11
135.63
127.52
127.39
125.96
122.96
105.71
105.02
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
60.59
56.42
21.35
21.26

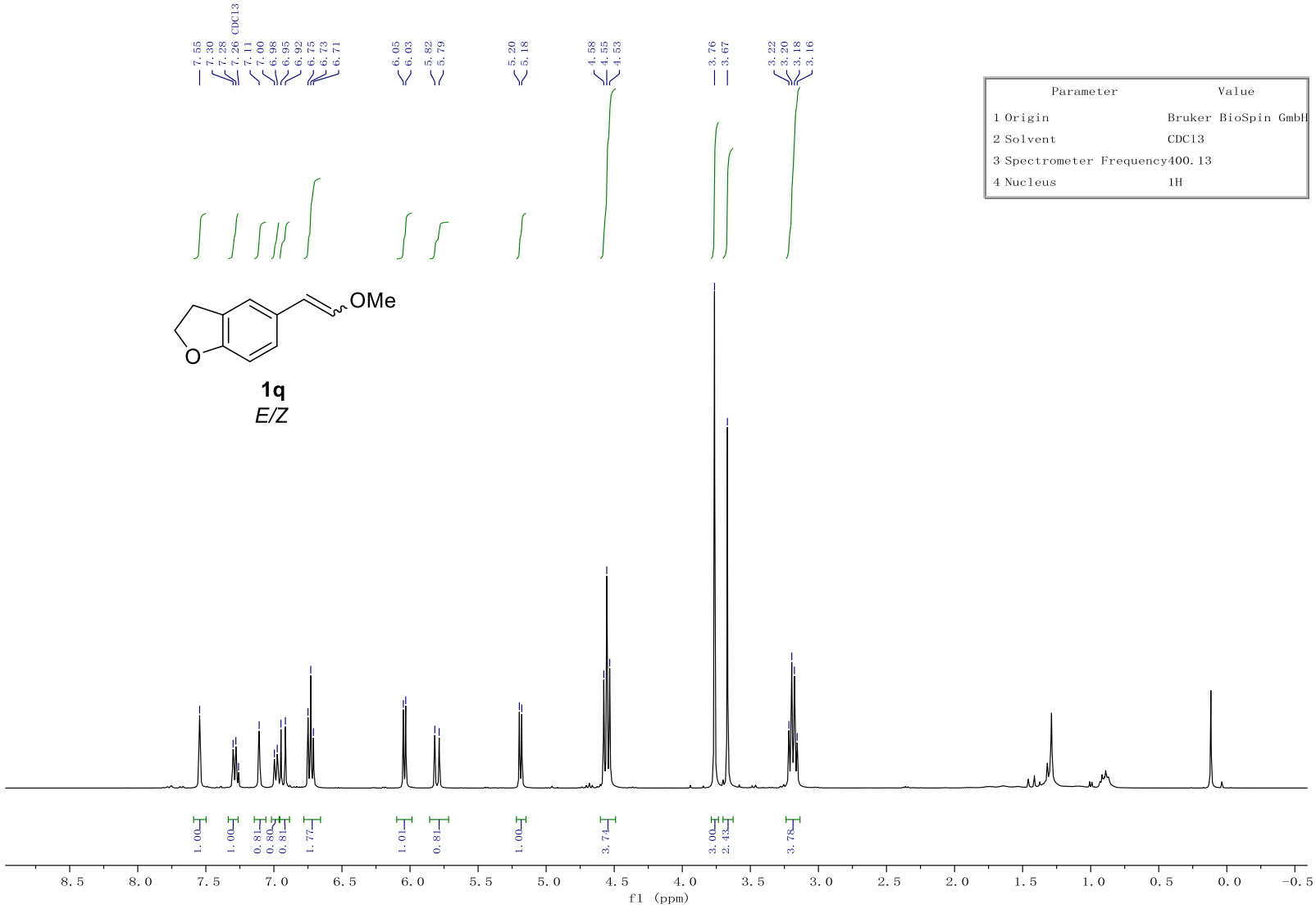
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Spectrometer Frequency	100.62
4 Nucleus	13C



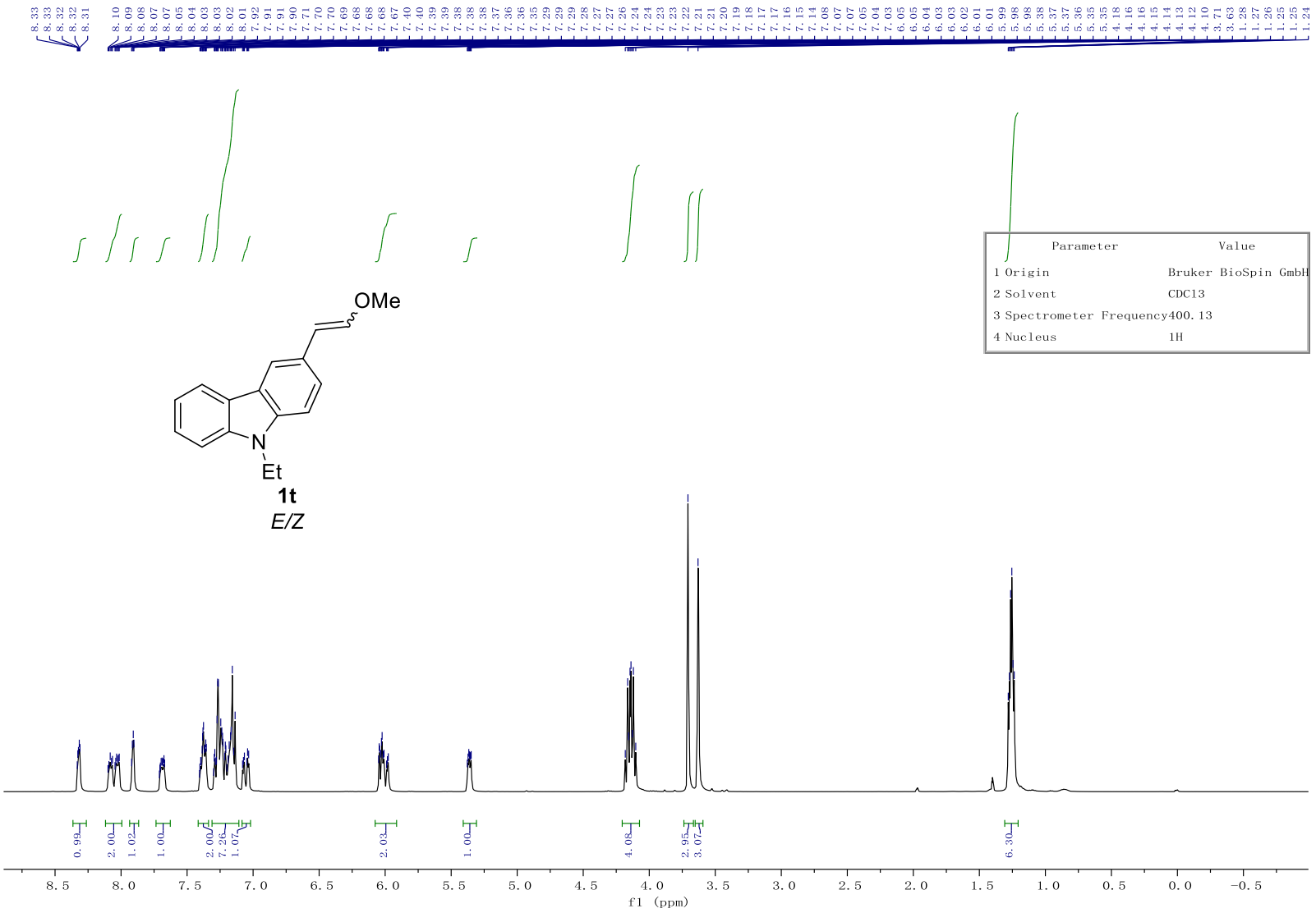
1o

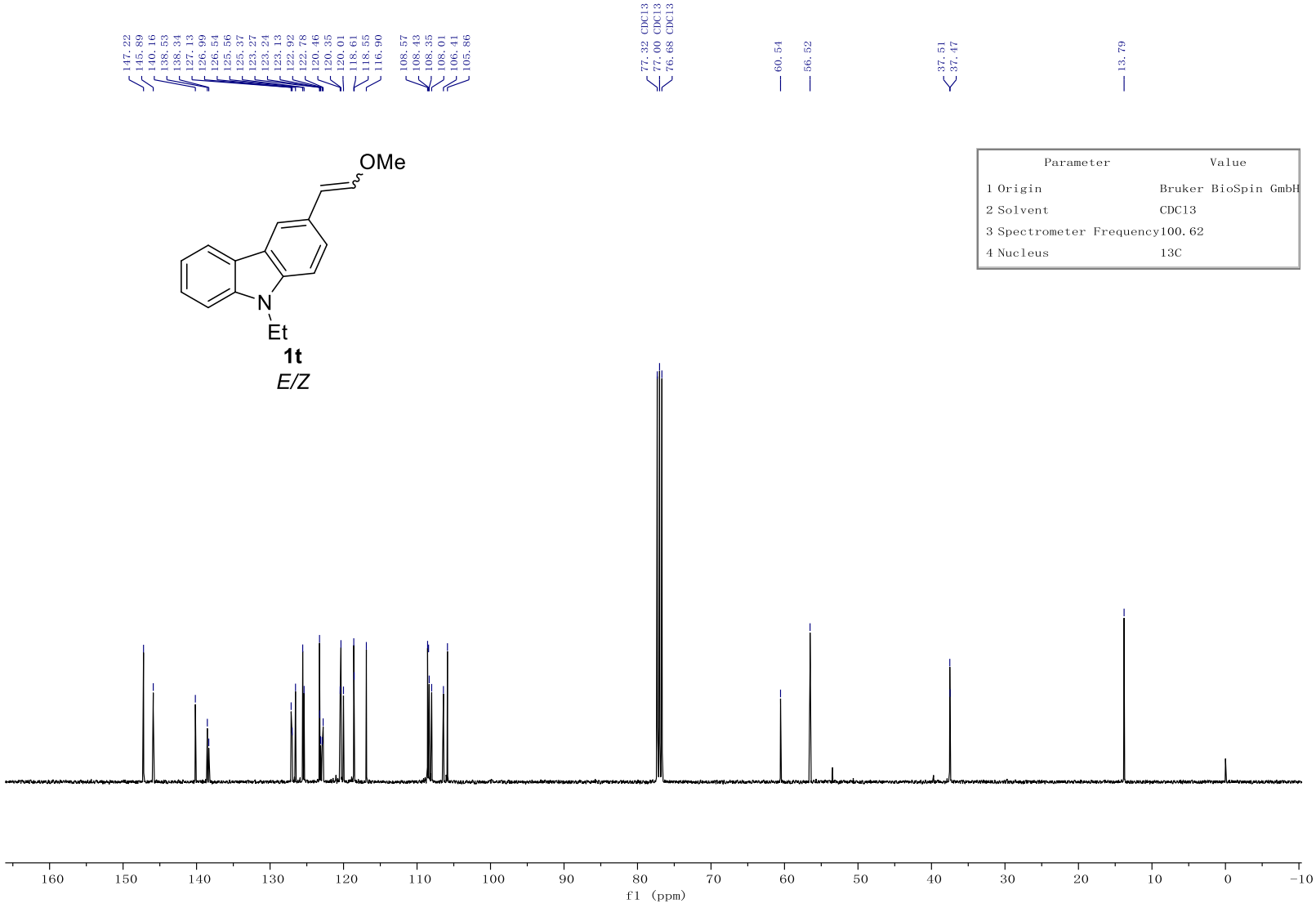
E/Z

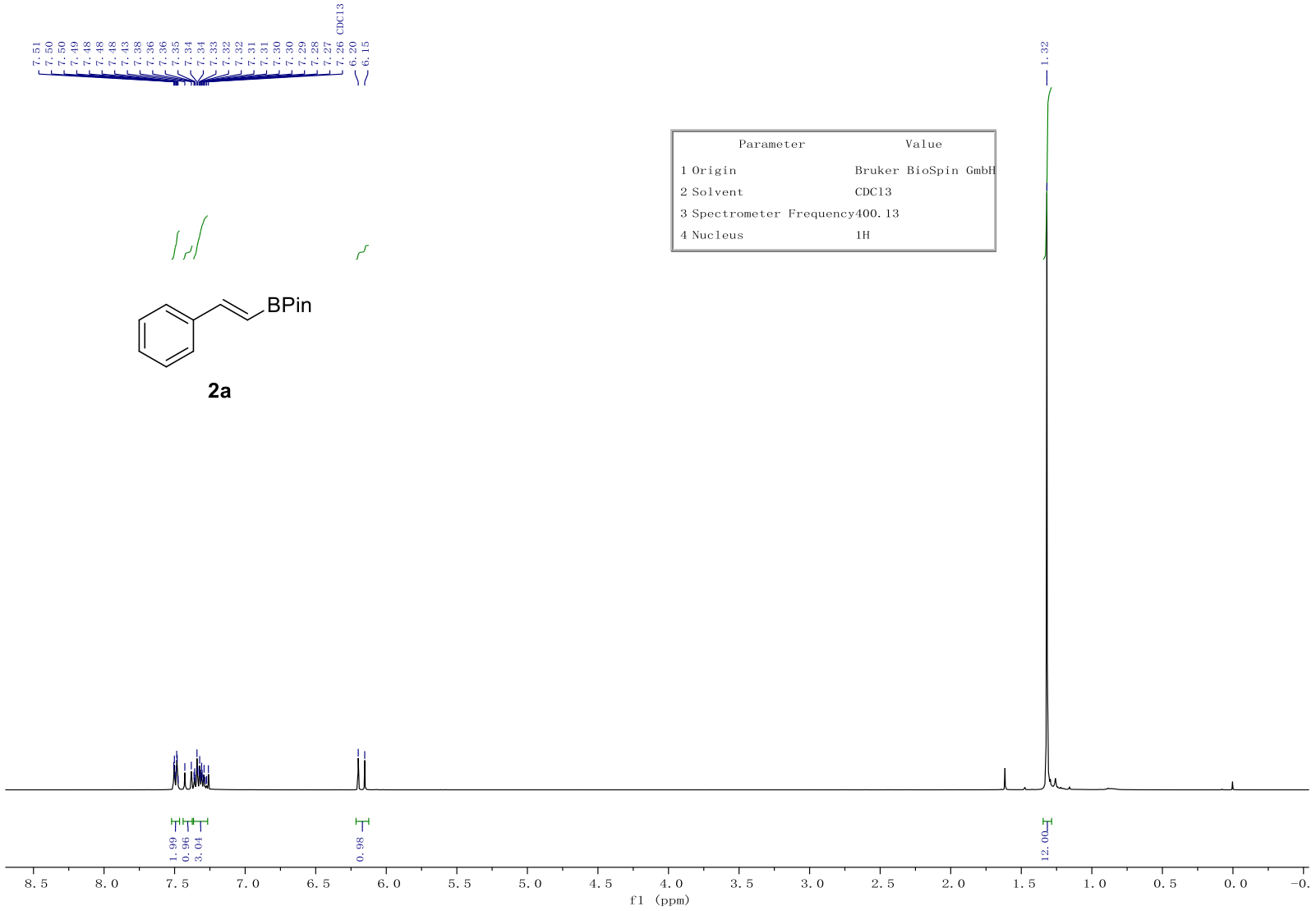


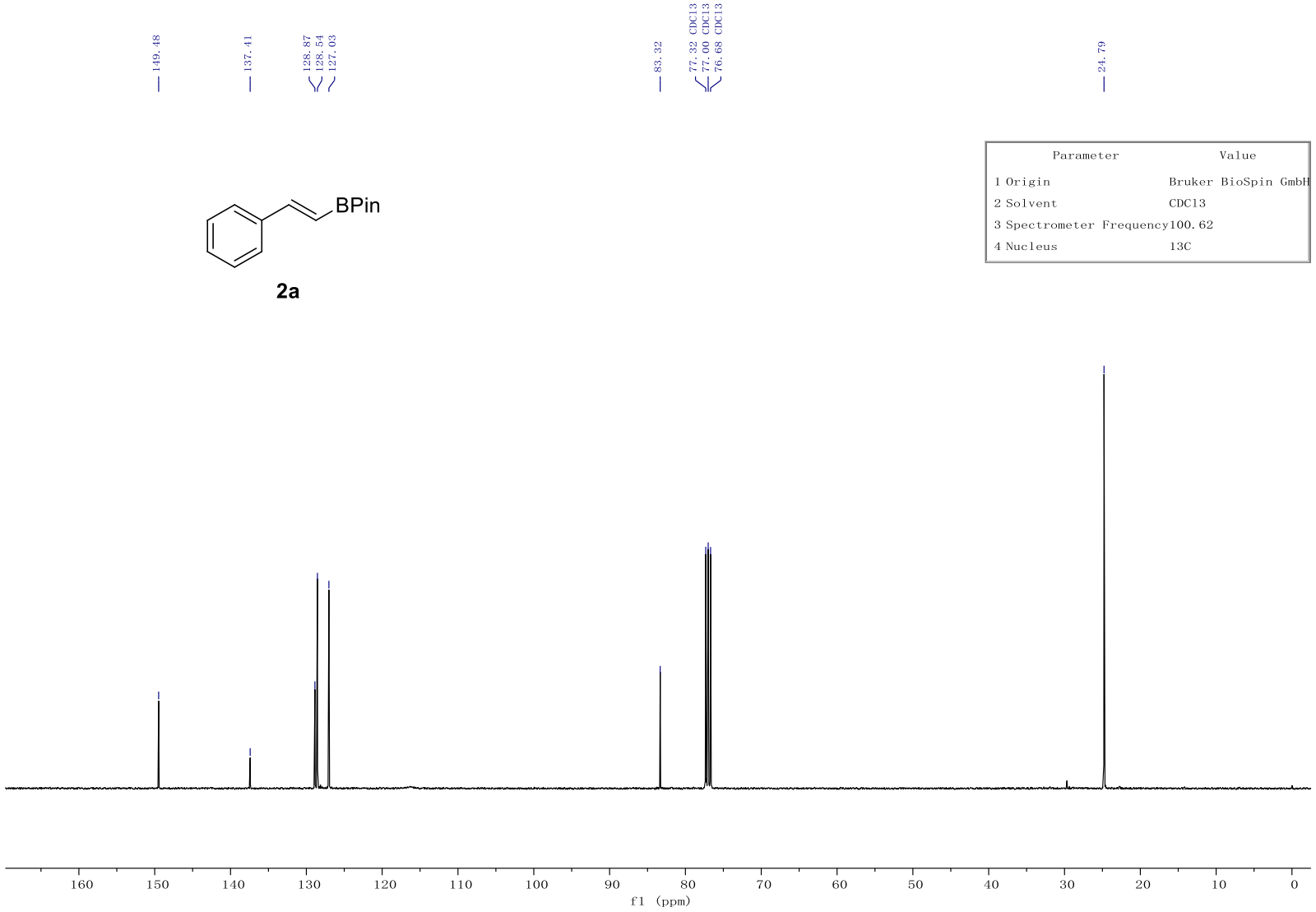

7.55
7.30
7.28
7.26 CDCl3
7.11
7.00
6.98
6.95
6.92
6.75
6.73
6.71
6.05
6.03
5.82
5.79
5.20
5.18
4.58
4.55
4.53
3.76
3.67
3.22
3.20
3.18
3.16
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Spectrometer Frequency 400.13
4 Nucleus 1H
OMe
O
1q
E/Z
1.00
1.00
0.81
0.80
0.81
1.77
1.01
0.81
1.00
3.74
3.00
2.43
3.78
8.5
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
0.0
-0.5
f1 (ppm)

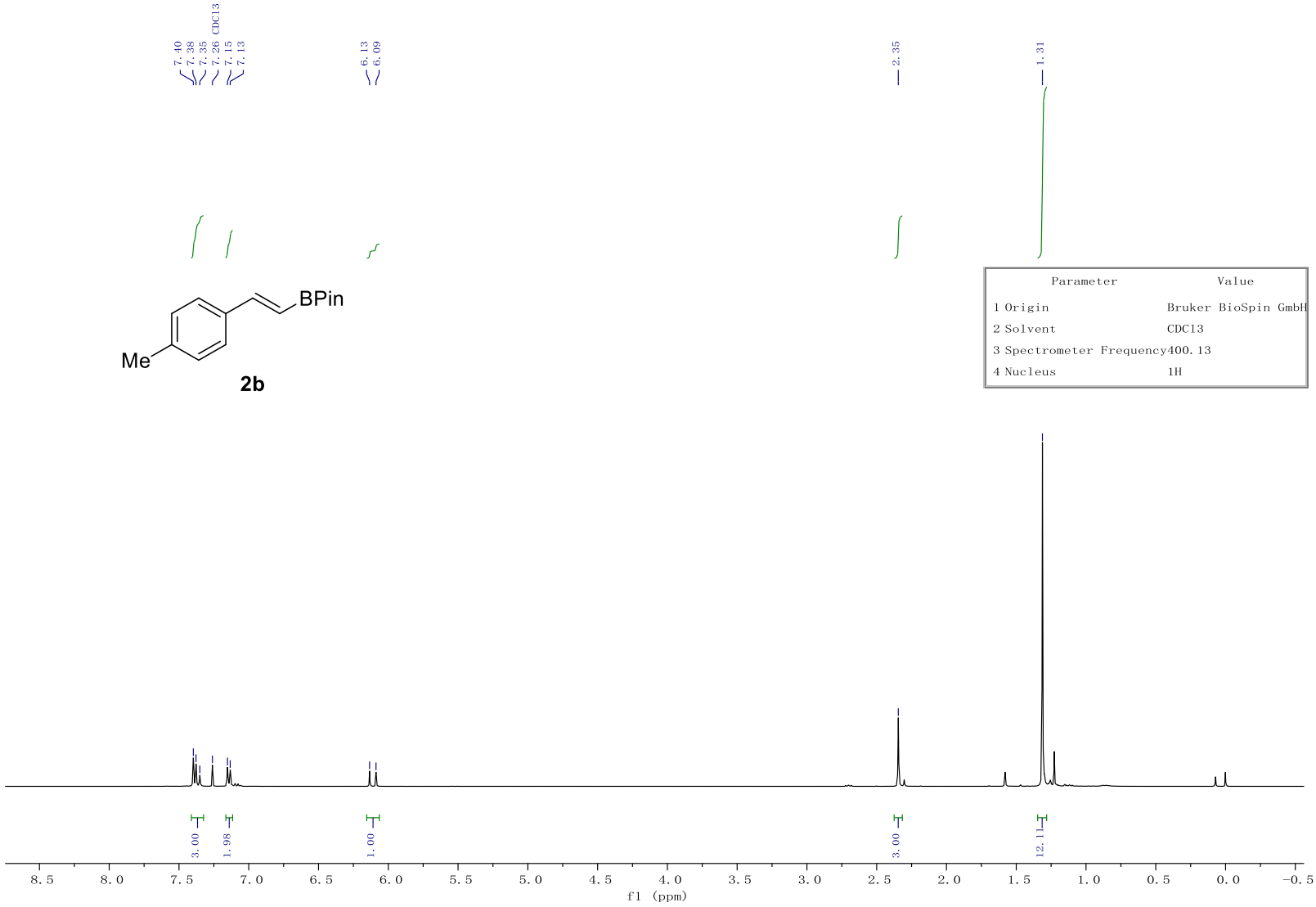

158.28
158.00
147.00
145.72
128.64
128.54
128.05
127.30
126.71
125.00
124.67
121.34
109.13
108.73
105.51
104.93
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
71.10
71.07
60.32
56.31
29.65
29.62
OMe
O
1q
E/Z
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Spectrometer Frequency 100.62
4 Nucleus 13C
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

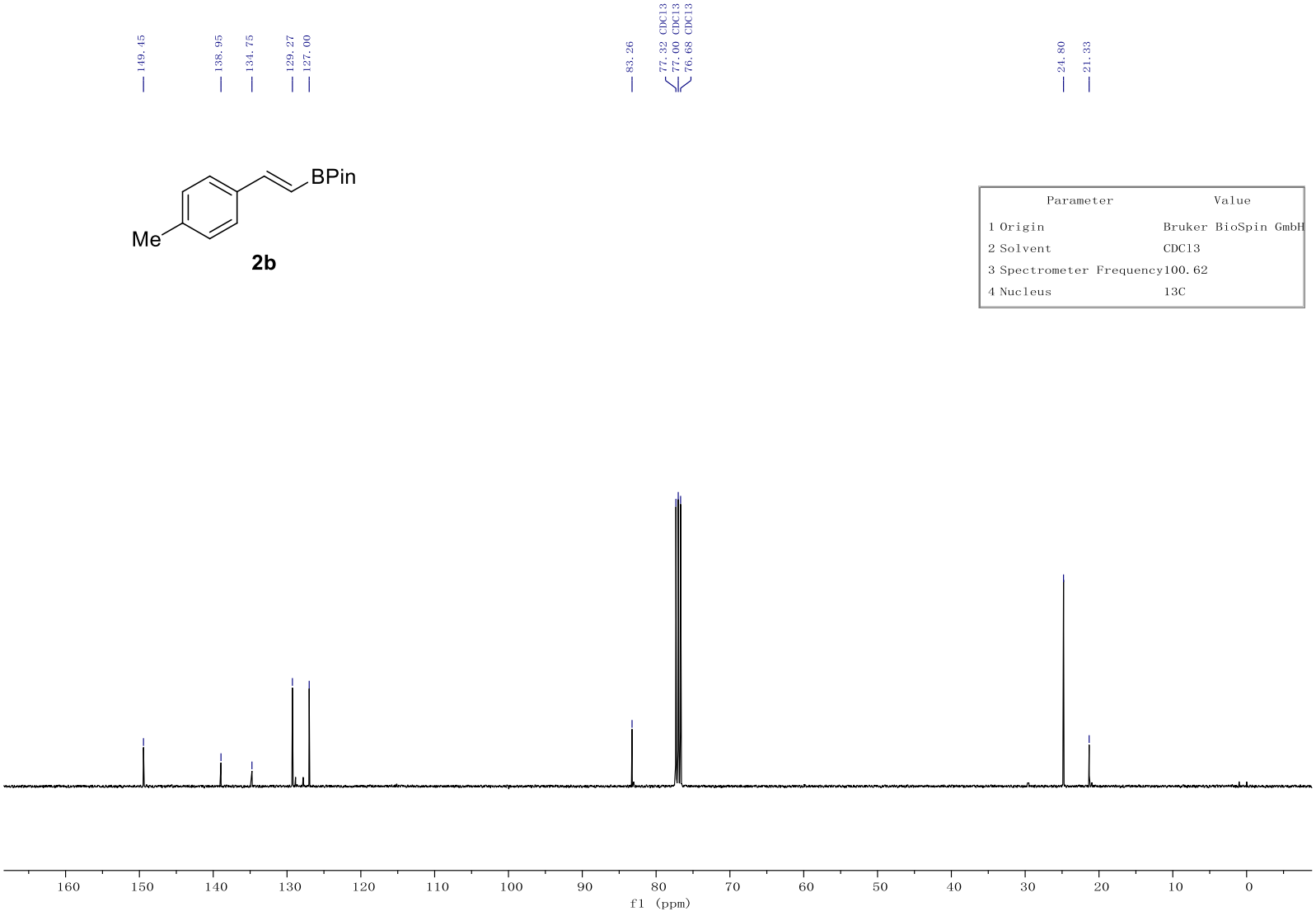

OMe
N
Et
1t
E/Z
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Spectrometer Frequency 400.13
4 Nucleus 1H
f1 (ppm)

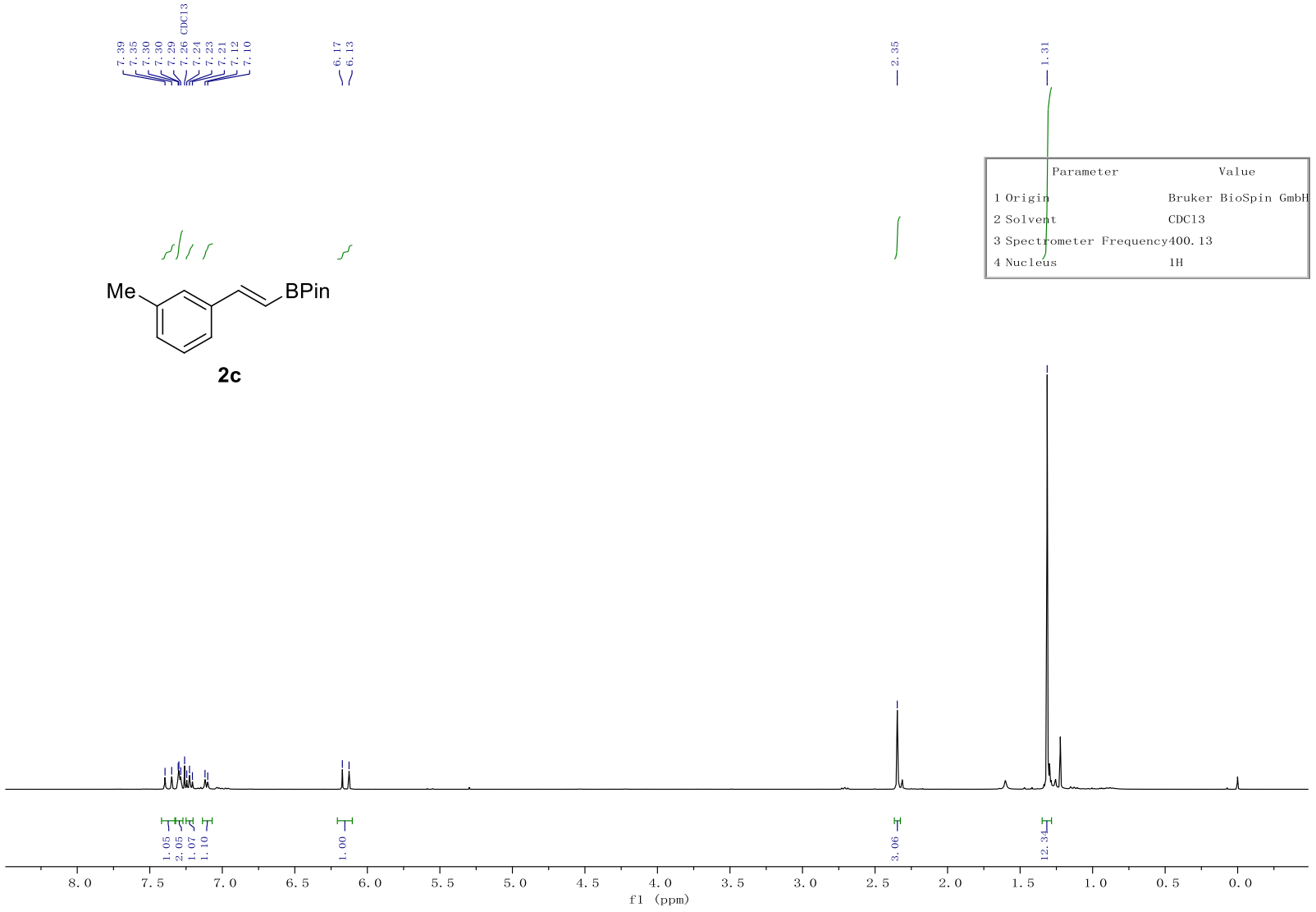

147.22
145.89
140.16
138.53
138.34
127.13
126.99
126.54
125.56
125.37
123.27
123.24
123.13
122.92
122.78
120.46
120.35
120.01
118.61
118.55
116.90
108.57
108.43
108.35
108.01
106.41
105.86
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
60.54
56.52
37.51
37.47
13.79
OMe
N
Et
1t
E/Z
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Spectrometer Frequency 100.62
4 Nucleus 13C
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

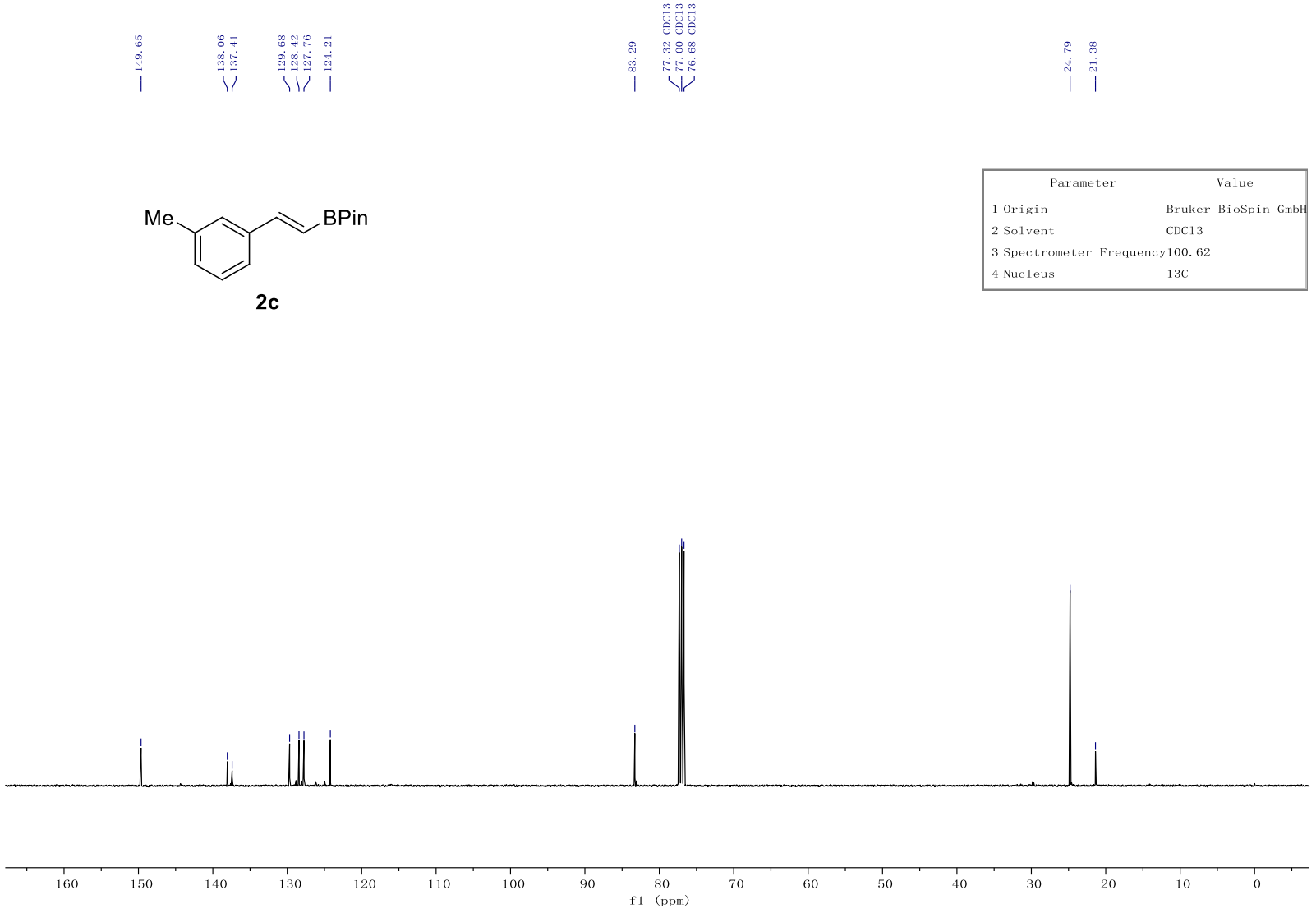

7.51
7.50
7.50
7.49
7.48
7.48
7.48
7.43
7.38
7.36
7.36
7.35
7.34
7.34
7.33
7.32
7.32
7.31
7.31
7.30
7.30
7.29
7.28
7.27
CDCl3
7.26
6.20
6.15
1.32
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Spectrometer Frequency 400.13
4 Nucleus 1H
BPin
2a
1.99
0.96
3.04
0.98
12.00
8.5
8.0
7.5
7.0
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
0.0
f1 (ppm)

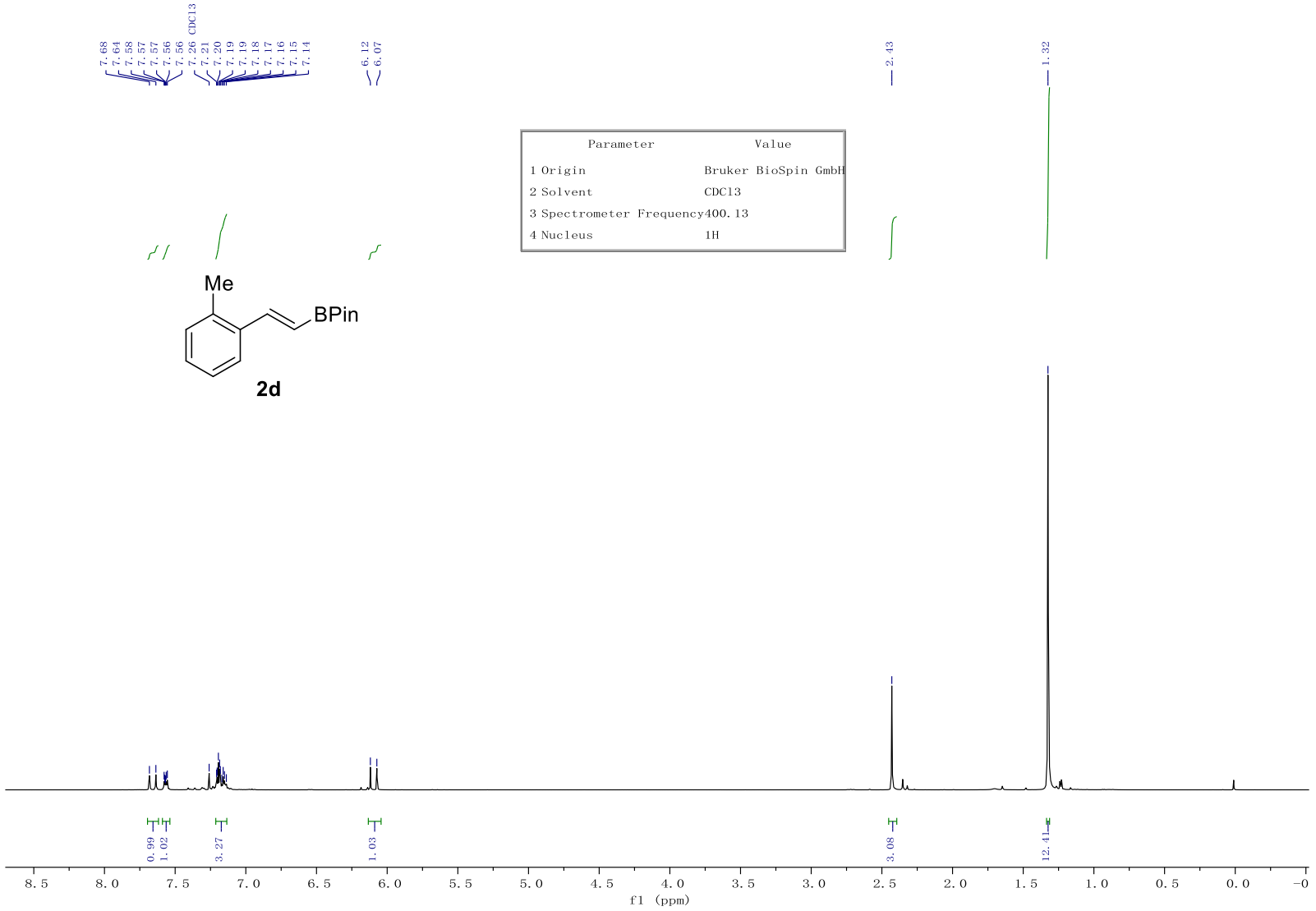

149.48
137.41
128.87
128.54
127.03
83.32
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
24.79
BPin
2a
Parameter
Value
1 Origin
Bruker BioSpin GmbH
2 Solvent
CDCl3
3 Spectrometer Frequency
100.62
4 Nucleus
13C
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

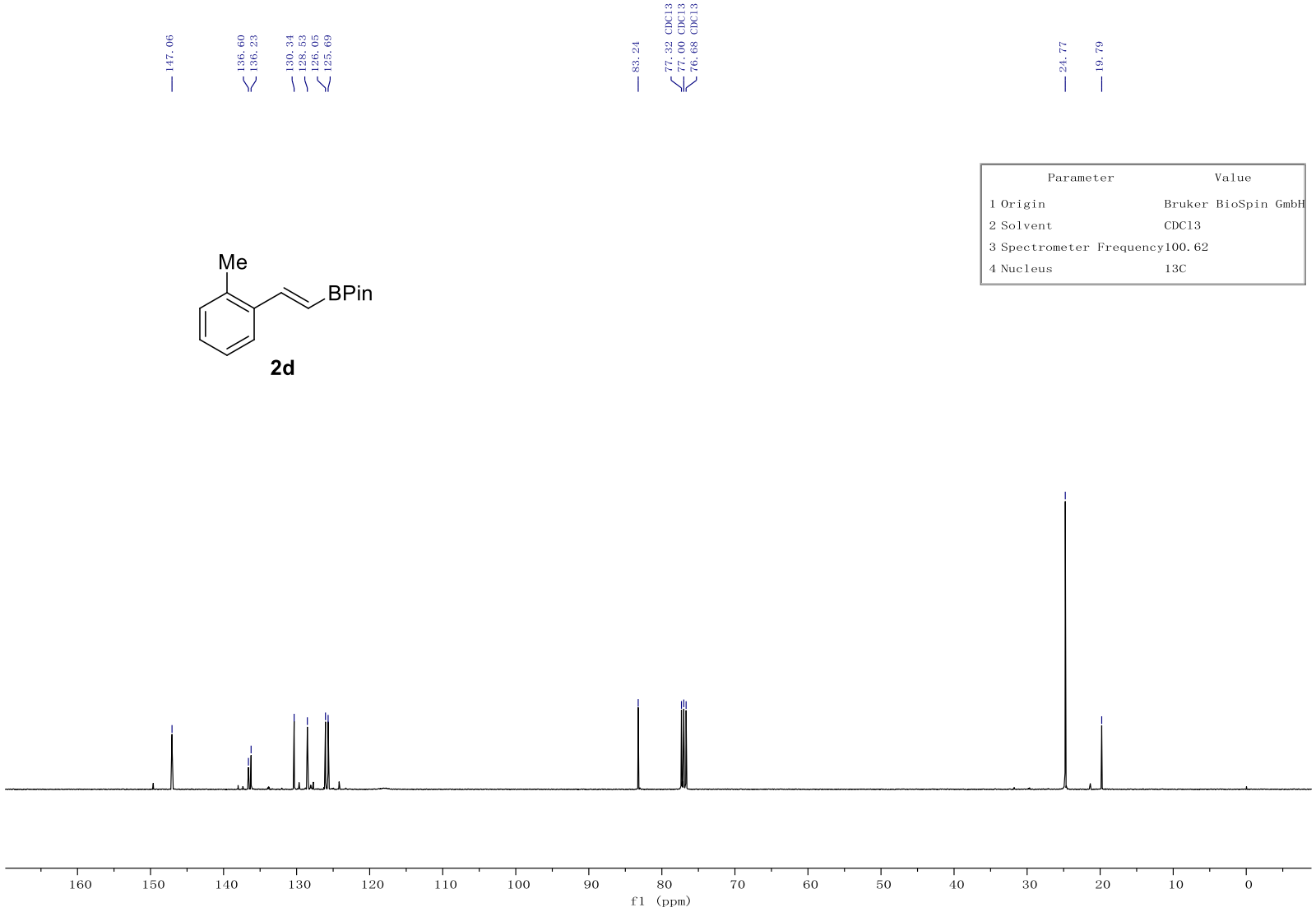

7.40
7.38
7.35
7.26 CDCl3
7.15
7.13
6.13
6.09
2.35
1.31
BPin
Me
2b
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Spectrometer Frequency 400.13
4 Nucleus 1H
3.00
1.98
1.00
3.00
12.11
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

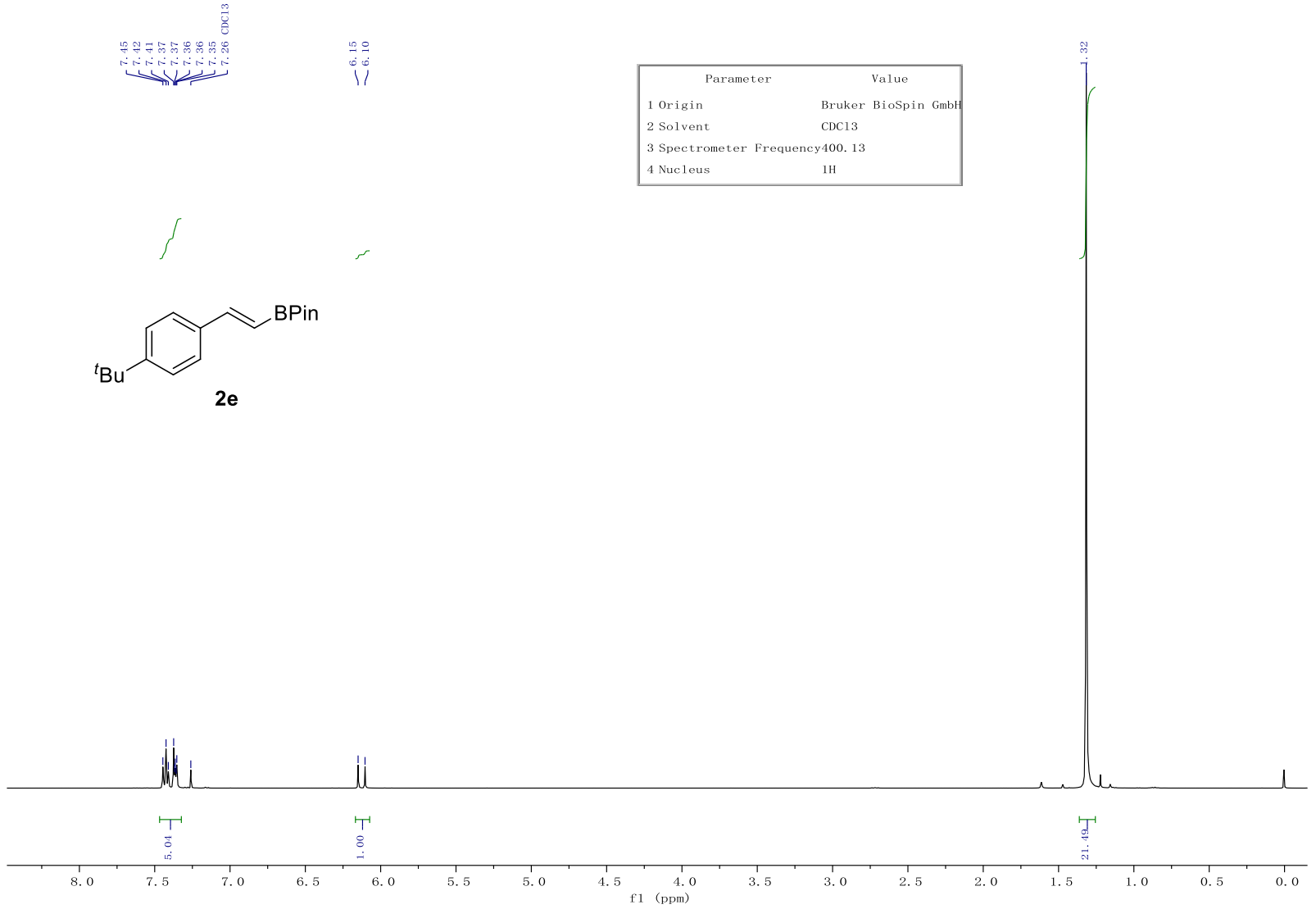

149.45
138.95
134.75
129.27
127.00
83.26
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
24.80
21.33
BPin
Me
2b
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Spectrometer Frequency 100.62
4 Nucleus 13C
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

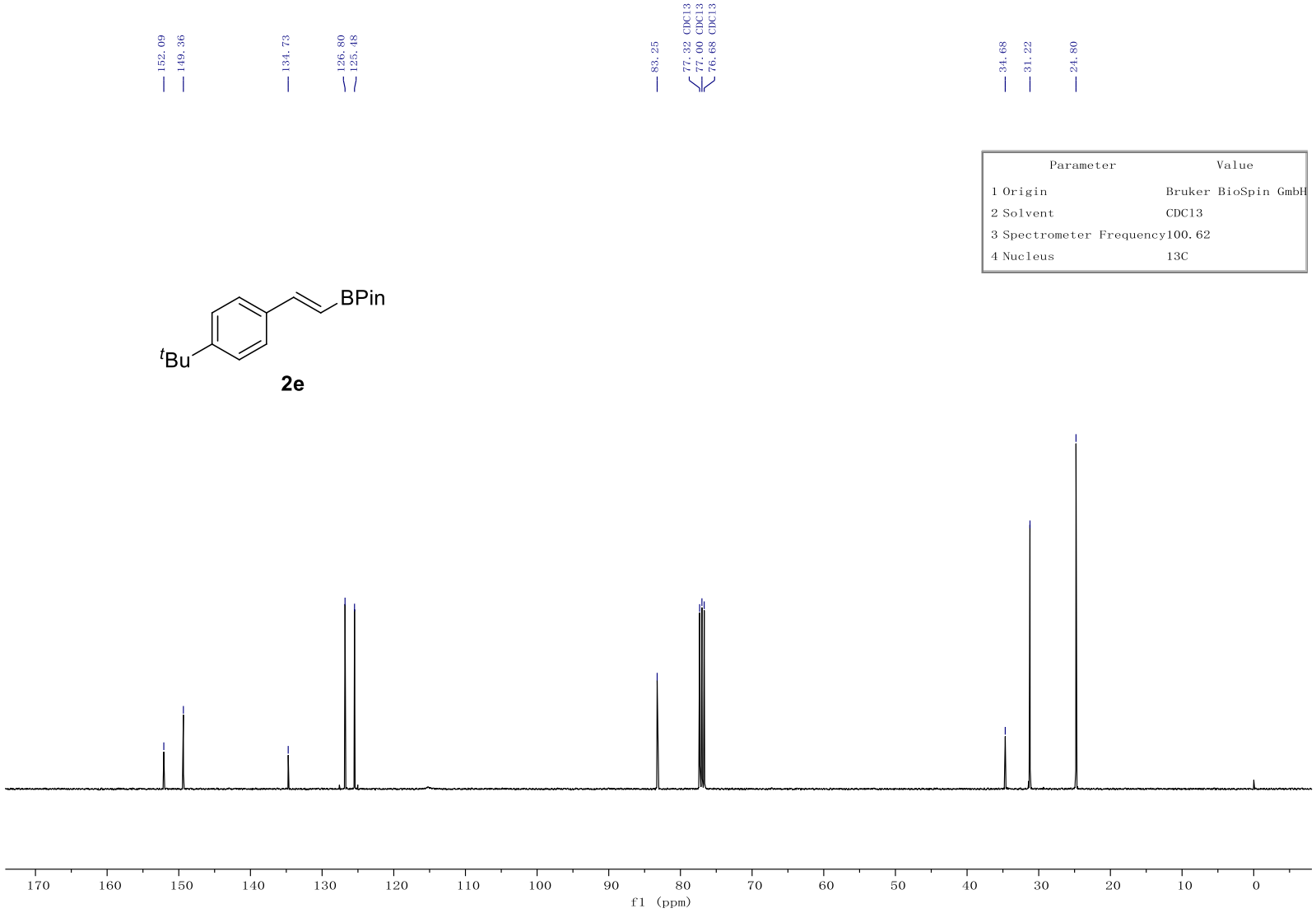

7.39
7.35
7.30
7.30
7.29
CDCl3
7.26
7.24
7.23
7.21
7.12
7.10
6.17
6.13
2.35
1.31
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Spectrometer Frequency 400.13
4 Nucleus 1H
Me
BPin
2c
1.05
2.05
1.07
1.10
1.00
3.06
12.34
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


149.65
138.06
137.41
129.68
128.42
127.76
124.21
83.29
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
24.79
21.38
Me
BPin
2c
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Spectrometer Frequency 100.62
4 Nucleus 13C
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

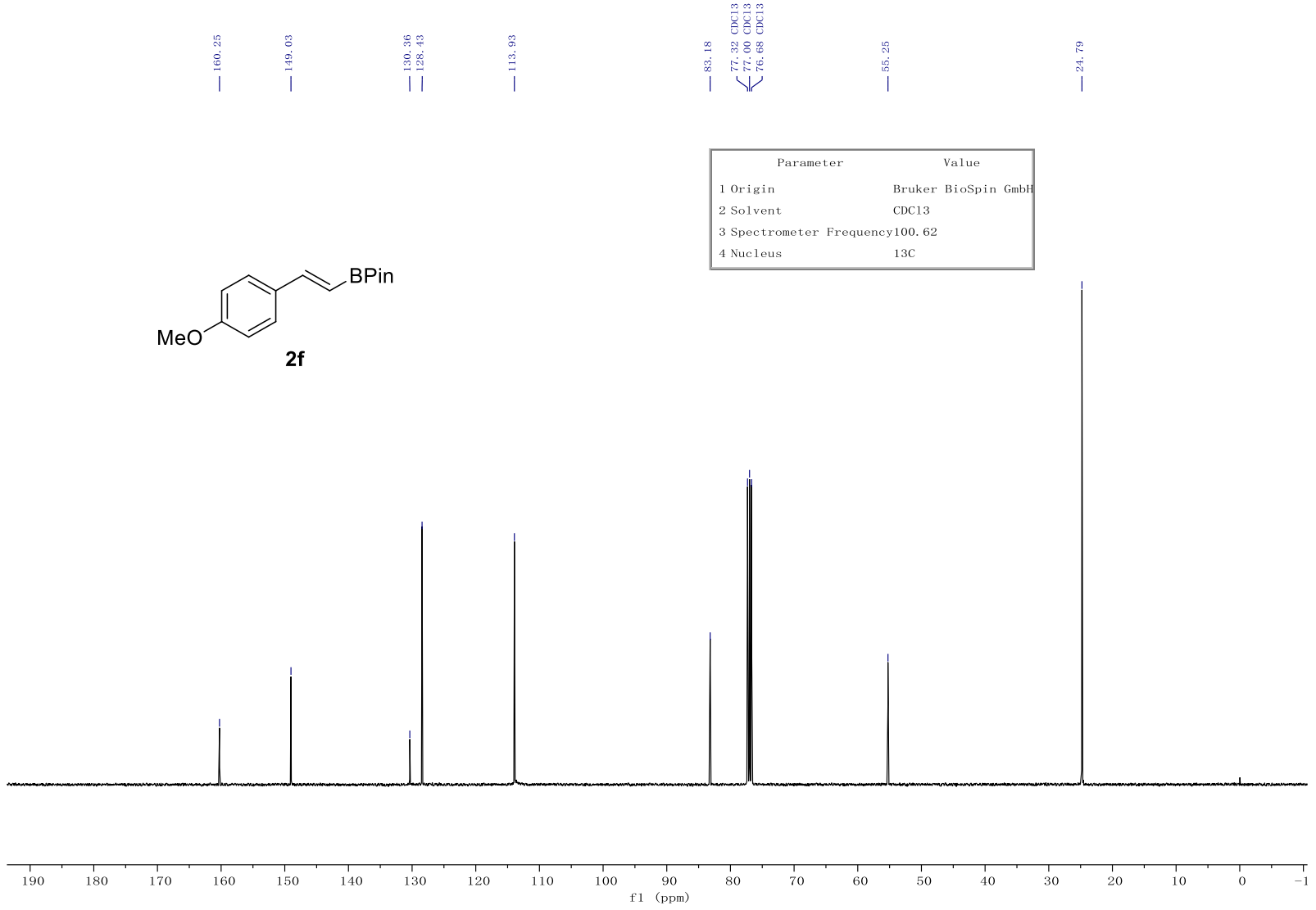

7.68
7.64
7.58
7.57
7.57
7.56
7.56
CDCl3
7.26
7.21
7.20
7.19
7.19
7.18
7.17
7.16
7.15
7.14
6.12
6.07
2.43
1.32
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Spectrometer Frequency 400.13
4 Nucleus 1H
Me
BPin
2d
0.99
1.02
3.27
1.03
3.08
12.41
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0
f1 (ppm)

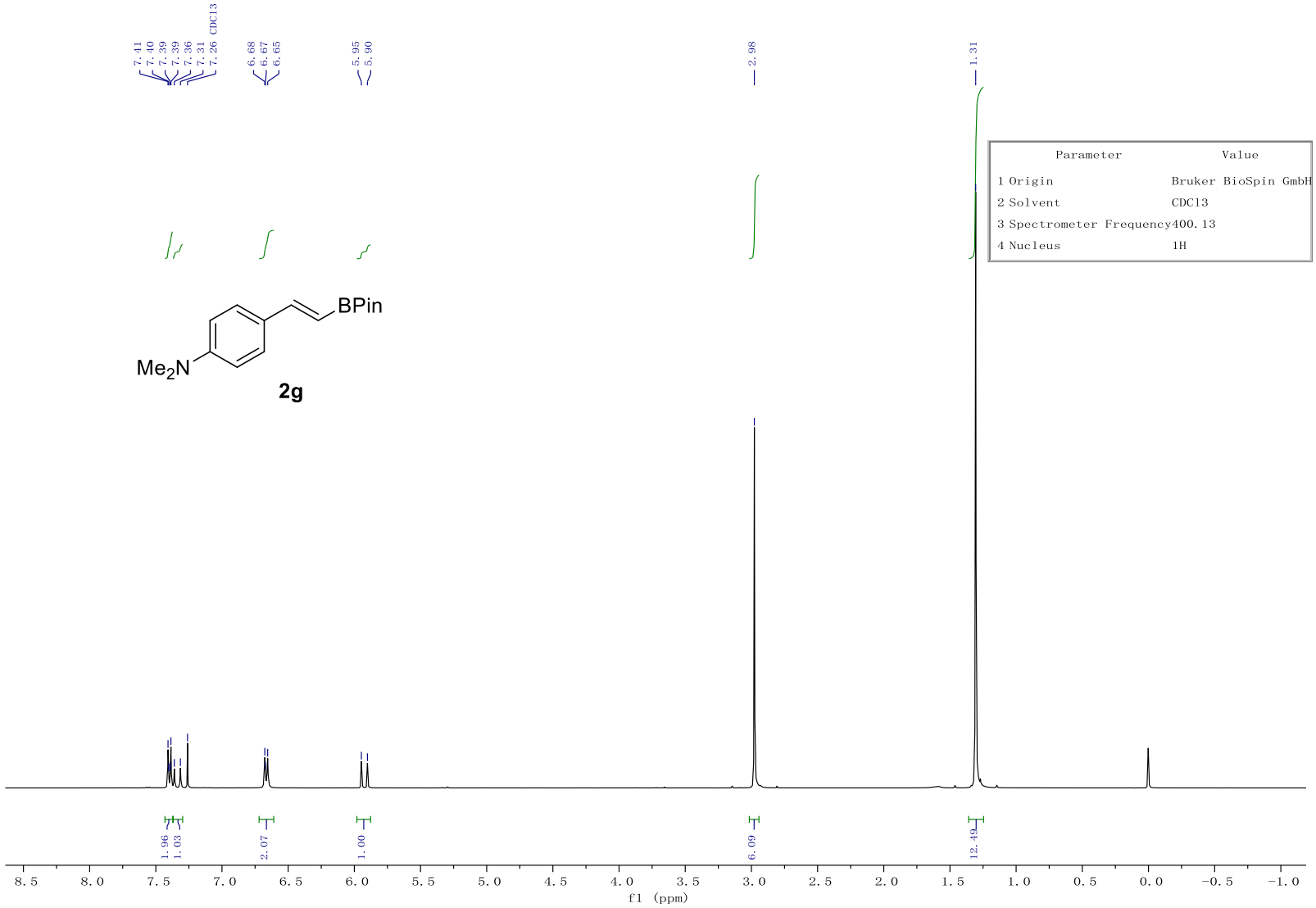

147.06
136.60
136.23
130.34
128.53
126.05
125.69
83.24
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
24.77
19.79
Me
BPin
2d
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Spectrometer Frequency 100.62
4 Nucleus 13C
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

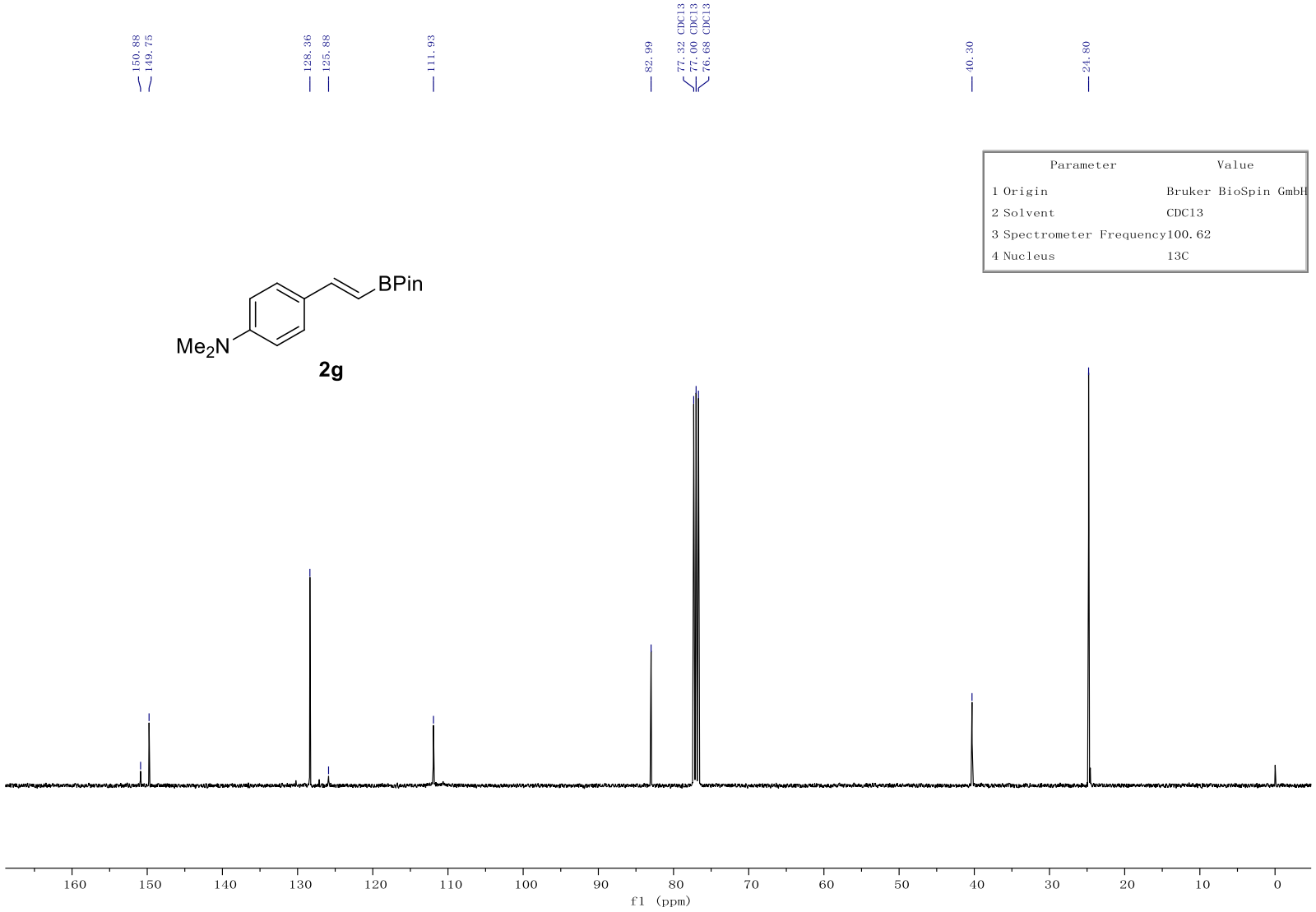

7.45
7.42
7.41
7.37
7.37
7.36
7.36
7.35
7.26 CDCl3
6.15
6.10
1.32
BPin
tBu
2e
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Spectrometer Frequency 400.13
4 Nucleus 1H
5.04
1.00
21.49
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

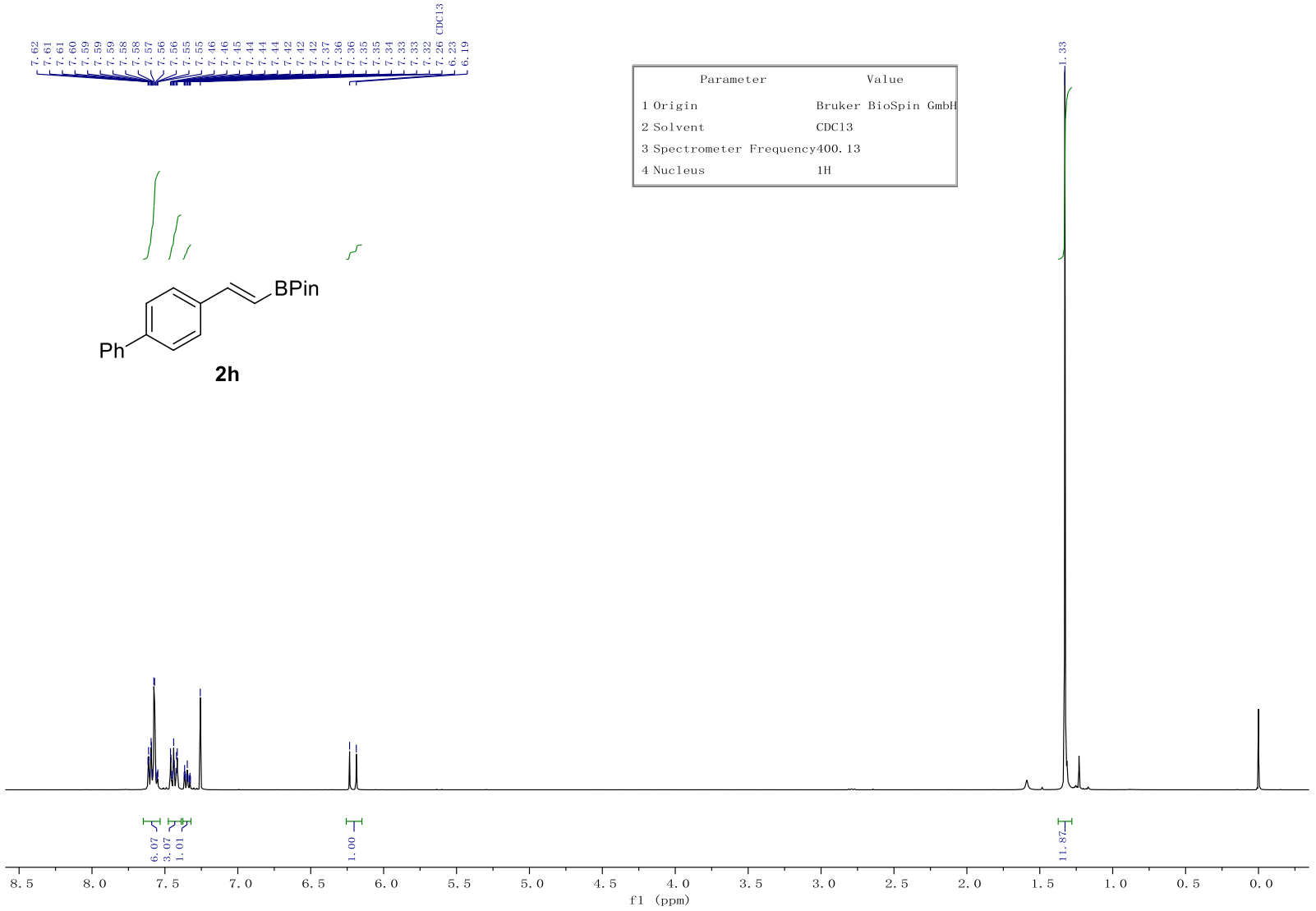

152.09
149.36
134.73
126.80
125.48
83.25
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
34.68
31.22
24.80
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Spectrometer Frequency 100.62
4 Nucleus 13C
BPin
tBu
2e
f1 (ppm)

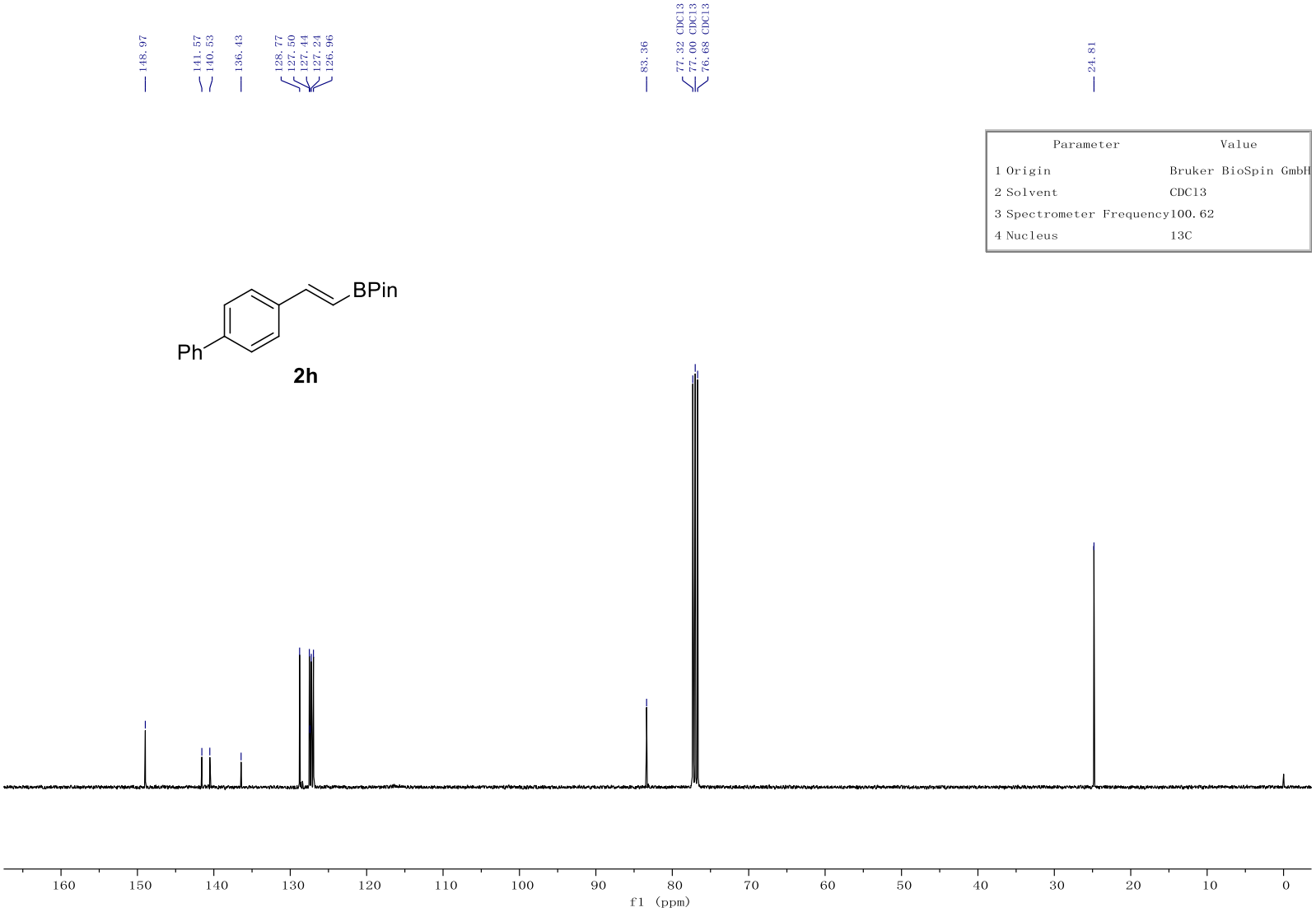

7.45
7.44
7.43
7.42
7.37
7.33
CDCl3
7.26
6.87
6.87
6.86
6.85
6.03
5.99
3.81
1.31
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Spectrometer Frequency 400.13
4 Nucleus 1H
BPin
MeO
2f
2.01
1.01
2.01
1.00
3.05
12.20
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)

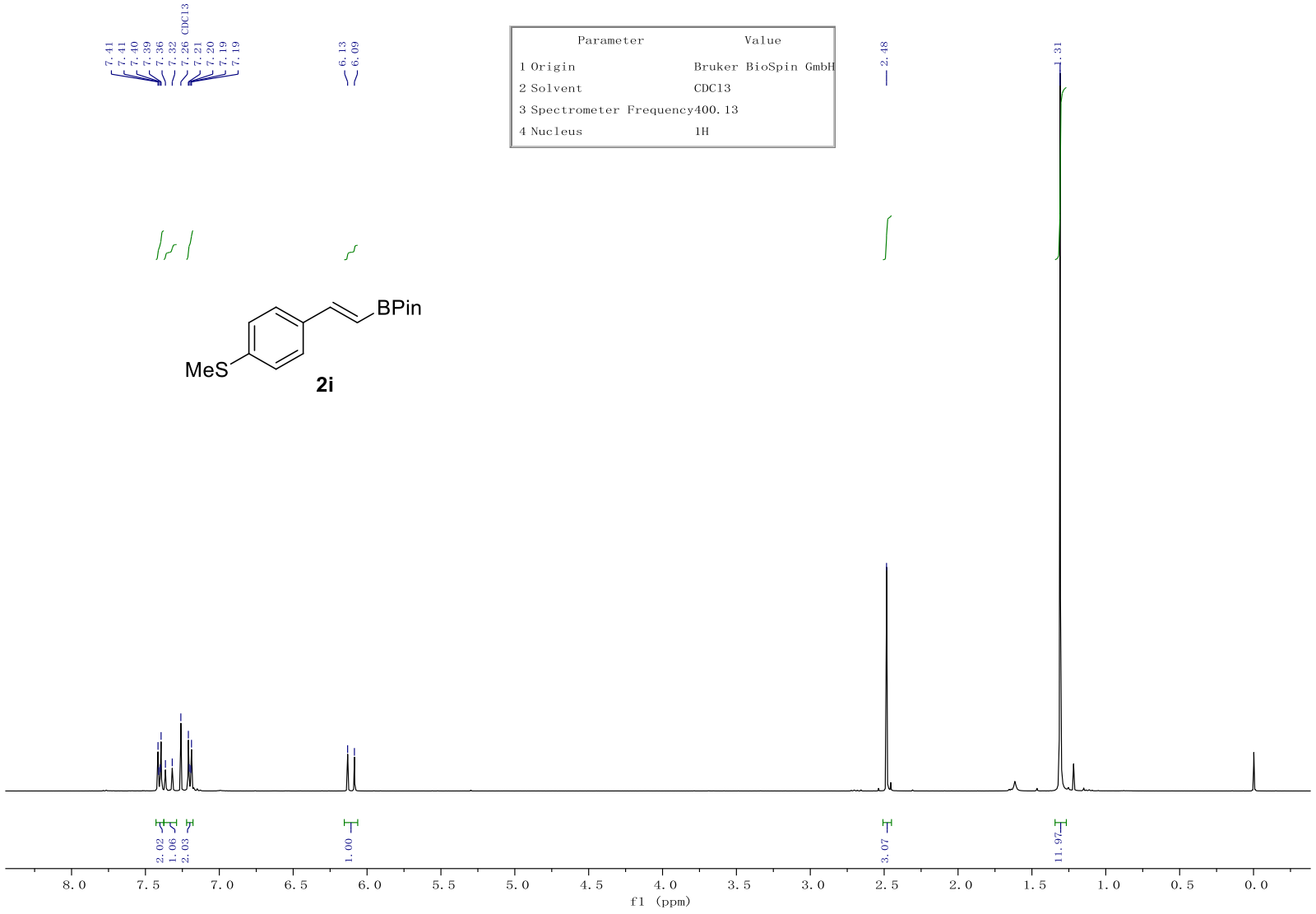

160.25
149.03
130.36
128.43
113.93
83.18
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
55.25
24.79
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Spectrometer Frequency 100.62
4 Nucleus 13C
BPin
MeO
2f
f1 (ppm)


7.41
7.40
7.39
7.39
7.36
7.31
7.26 CDCl3
6.68
6.67
6.65
5.95
5.90
2.98
1.31
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Spectrometer Frequency 400.13
4 Nucleus 1H
BPin
Me2N
2g
1.96
1.03
2.07
1.00
6.09
12.49
8.5 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 0.0 -0.5 -1.0
f1 (ppm)


150.88
149.75
128.36
125.88
111.93
82.99
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
40.30
24.80
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Spectrometer Frequency 100.62
4 Nucleus 13C
BPin
Me2N
2g
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.62
7.61
7.61
7.60
7.59
7.59
7.59
7.58
7.58
7.57
7.56
7.56
7.55
7.55
7.46
7.46
7.45
7.44
7.44
7.44
7.42
7.42
7.42
7.37
7.36
7.36
7.35
7.35
7.34
7.33
7.33
7.32
7.26
CDCl3
6.23
6.19
1.33
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Spectrometer Frequency 400.13
4 Nucleus 1H
BPin
Ph
2h
6.07
3.07
1.01
1.00
11.87
8.5
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
0.0
f1 (ppm)


148.97
141.57
140.53
136.43
128.77
127.50
127.44
127.24
126.96
83.36
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
24.81
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Spectrometer Frequency 100.62
4 Nucleus 13C
BPin
Ph
2h
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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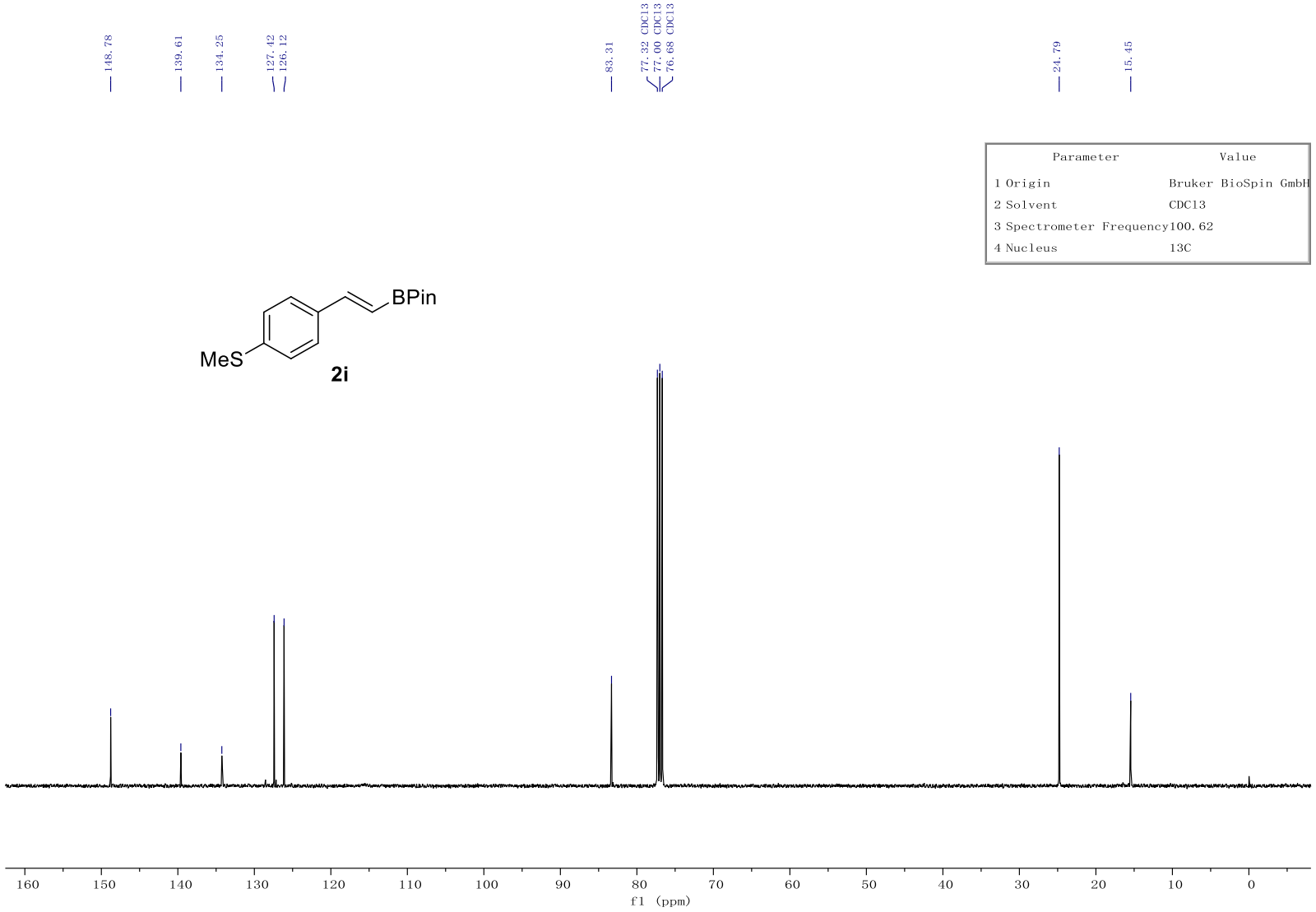
7.41
7.40
7.39
7.36
7.32
7.26 CDCl3
7.21
7.20
7.19
7.19
6.13
6.09
2.48
1.31
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Spectrometer Frequency 400.13
4 Nucleus 1H
BPin
MeS
2i
2.02
1.06
2.03
1.00
3.07
11.97
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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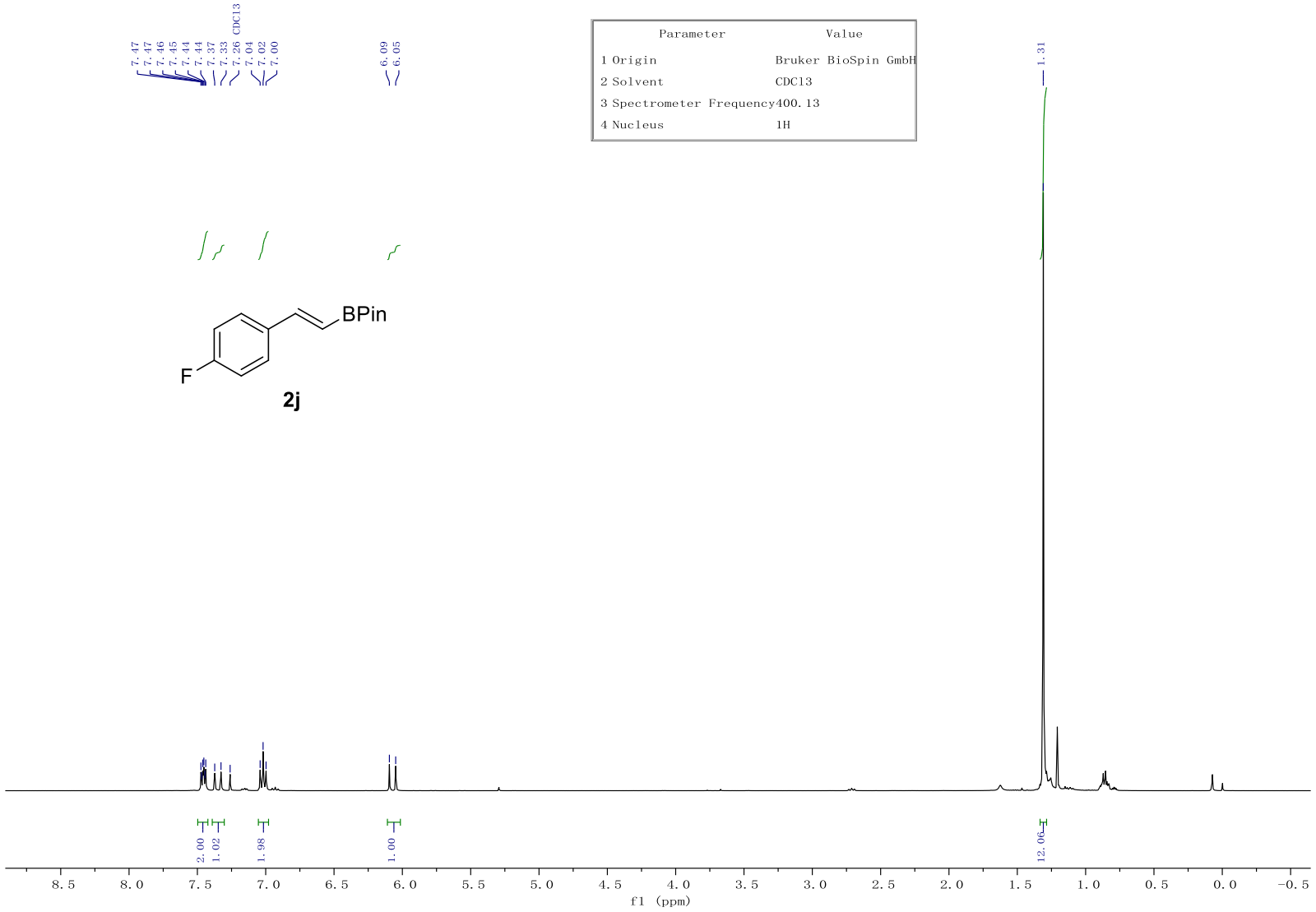
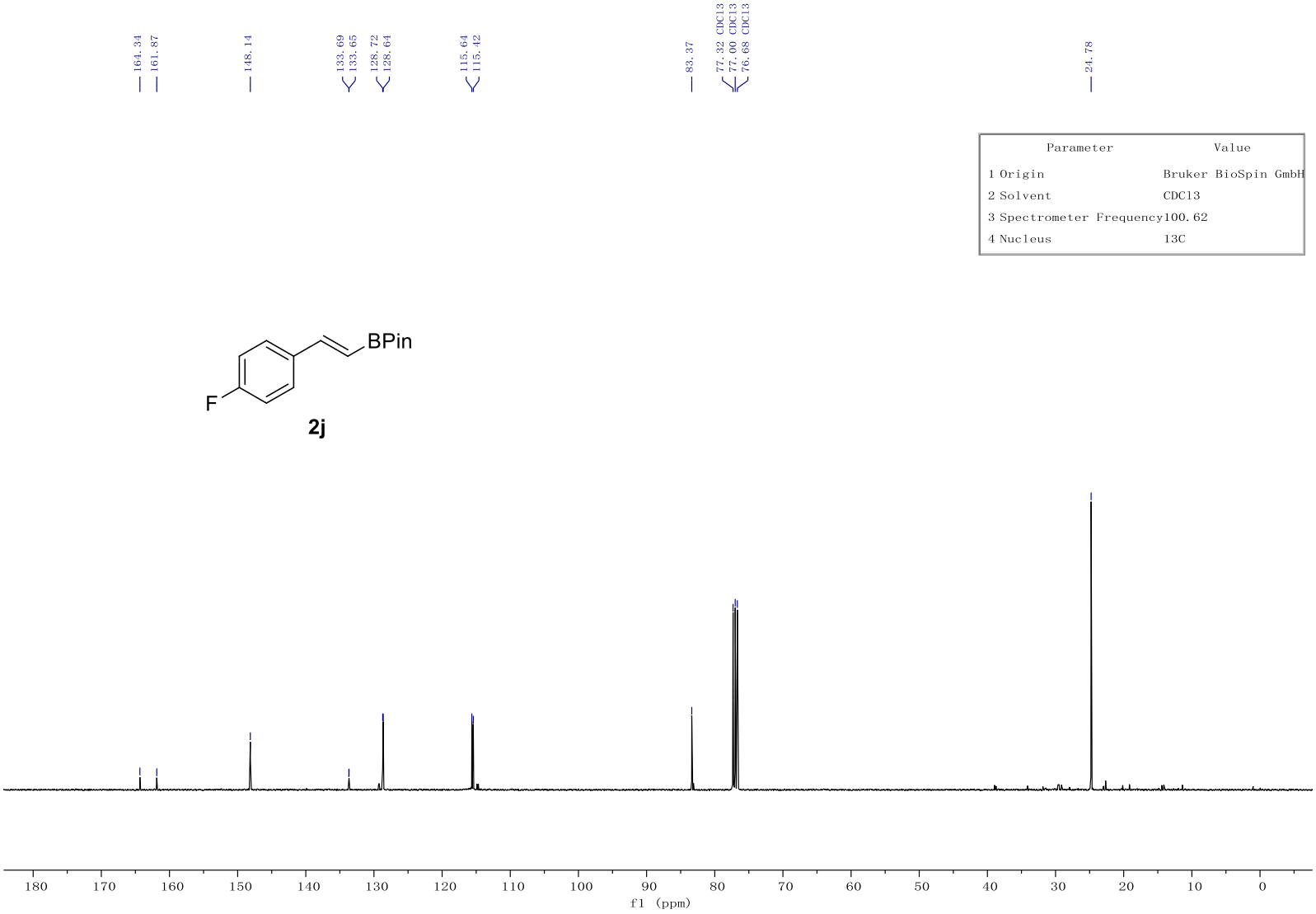
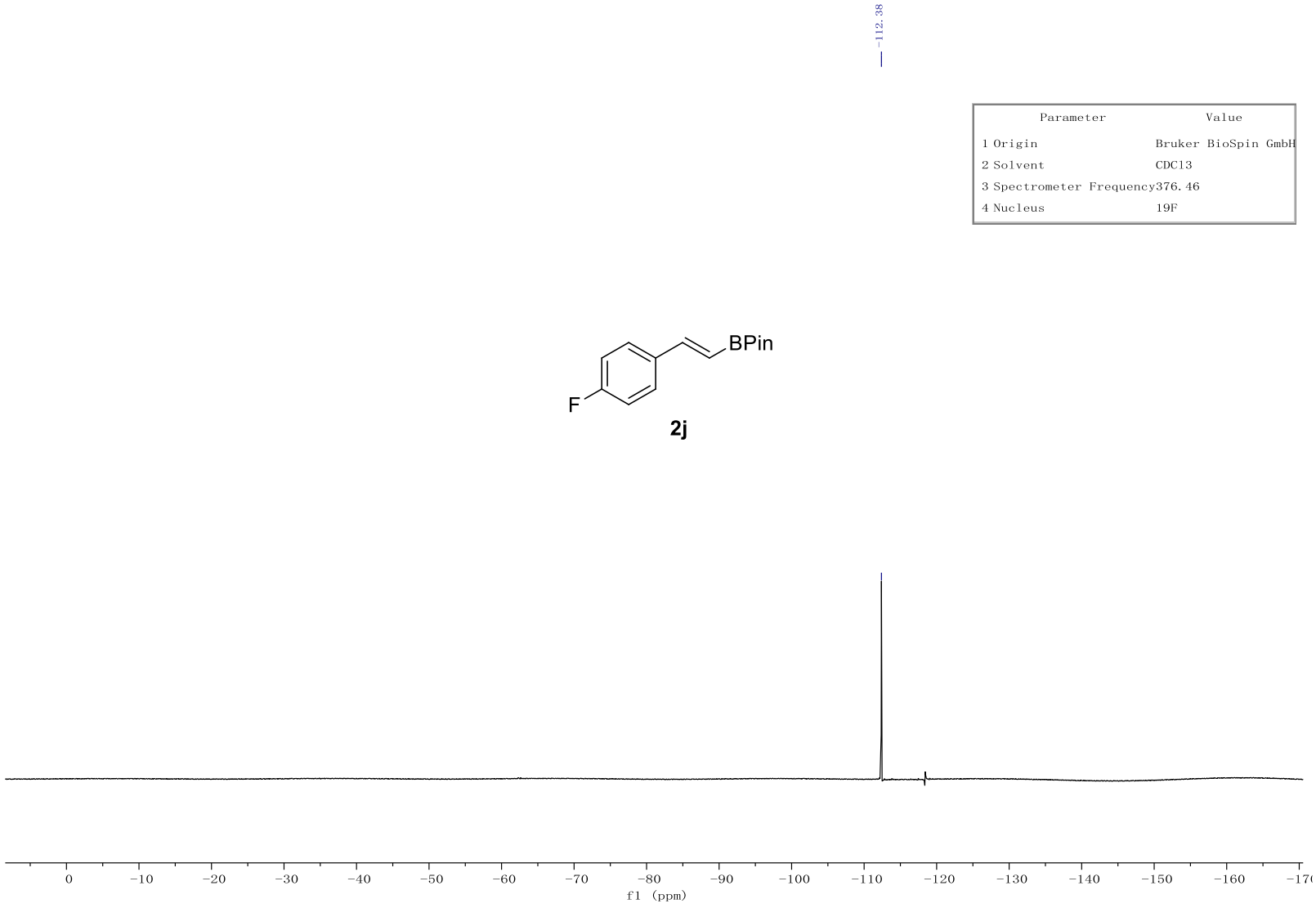
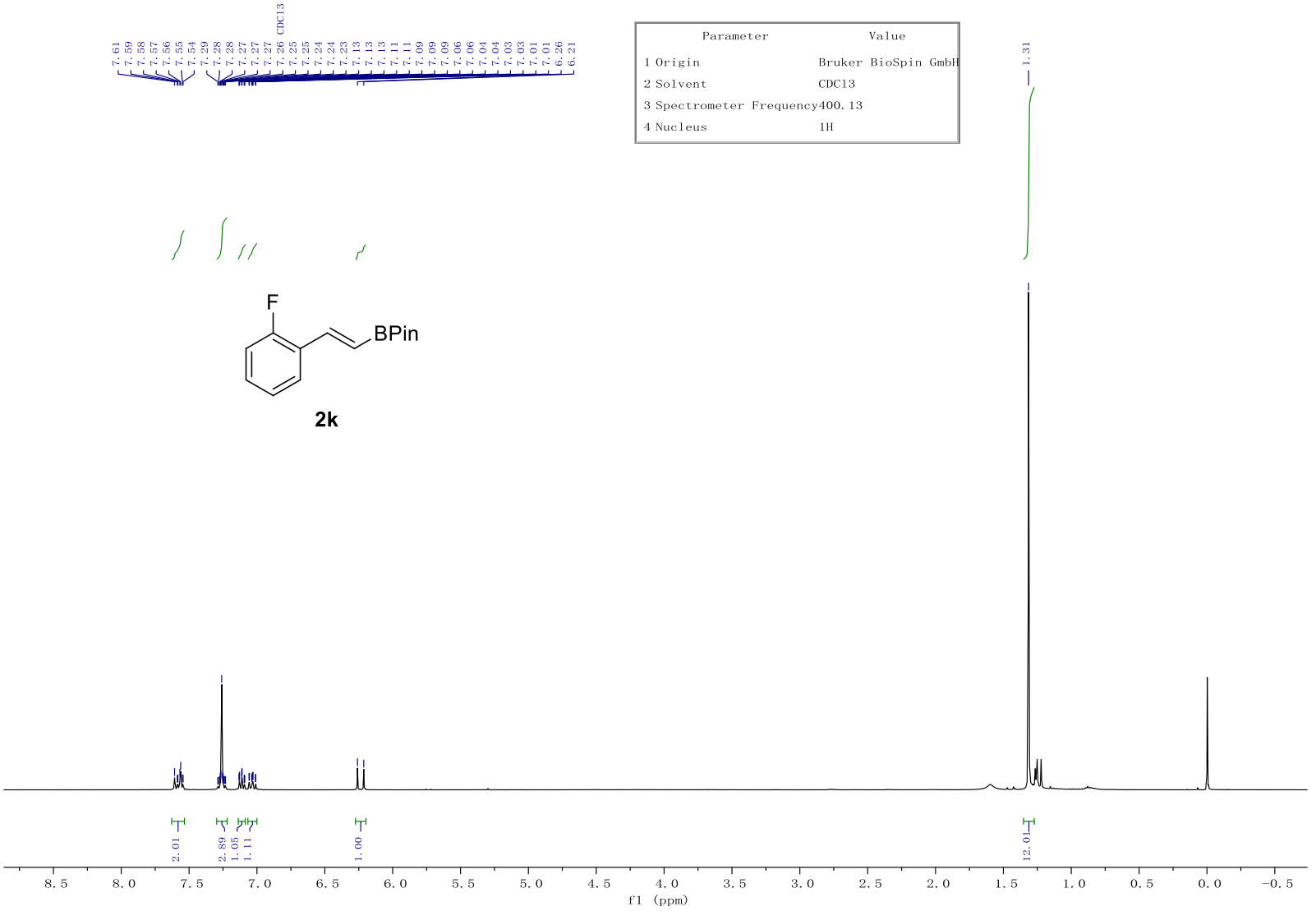
139.61
134.25
127.42
126.12
83.31
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
24.79
15.45
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Spectrometer Frequency 100.62
4 Nucleus 13C
BPin
MeS
2i
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Spectrometer Frequency	400.13
4 Nucleus	1H


164.34
161.87
148.14
133.69
133.65
128.72
128.64
115.64
115.42
83.37
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
24.78
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Spectrometer Frequency 100.62
4 Nucleus 13C
BPin
F
2j
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-112.38
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Spectrometer Frequency 376.46
4 Nucleus 19F
BPin
F
2j
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160
f1 (ppm)


7.61
7.59
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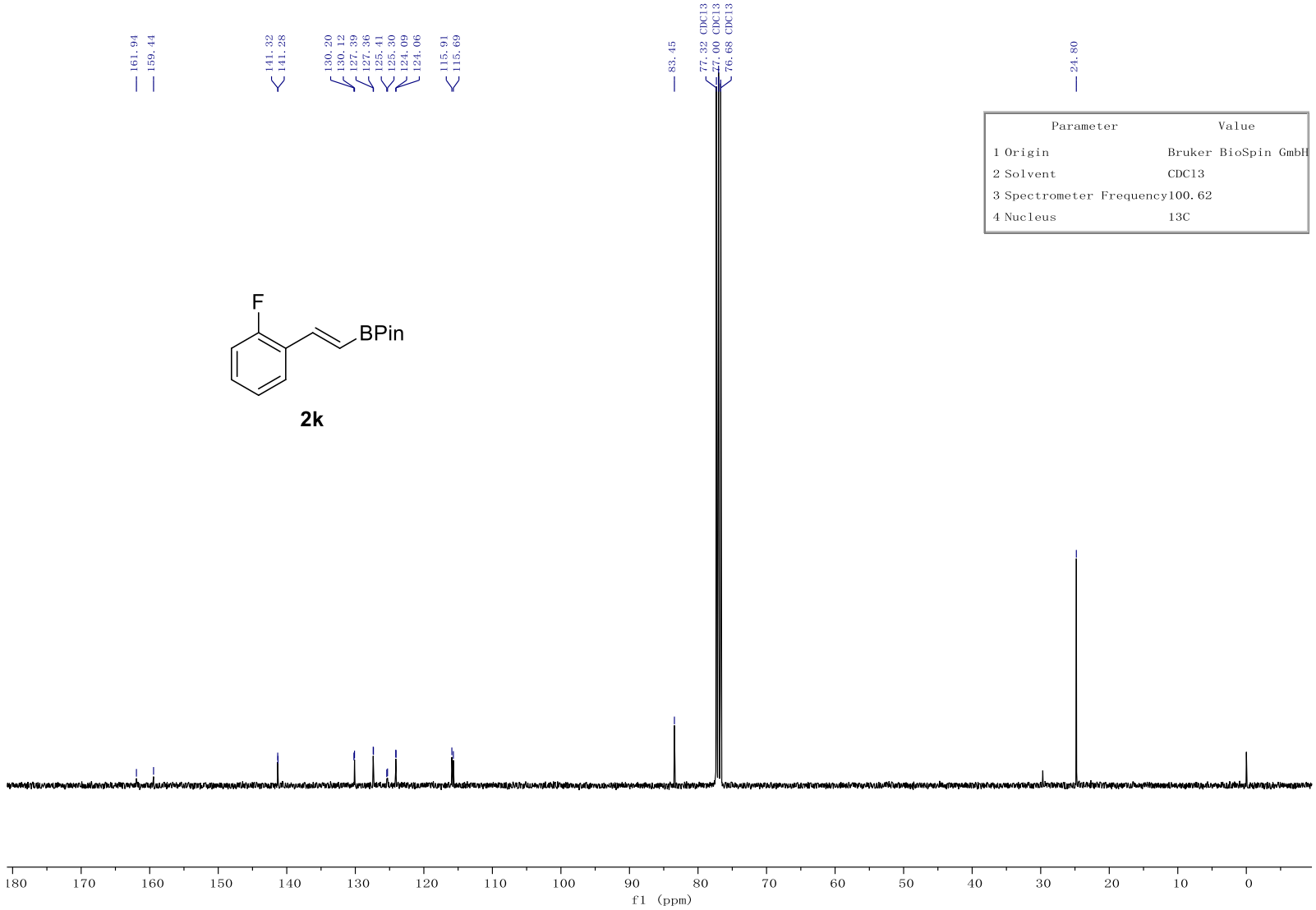
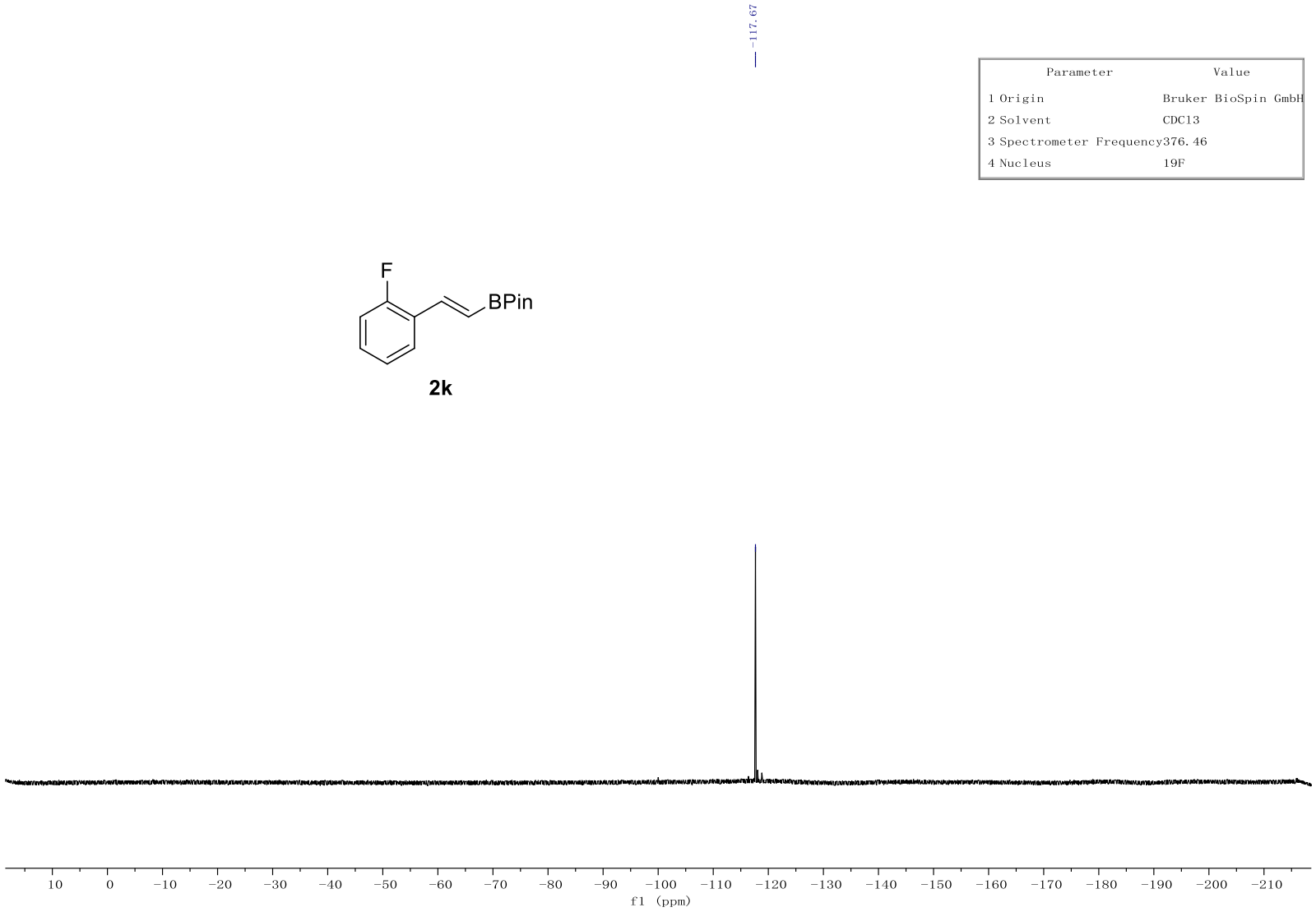
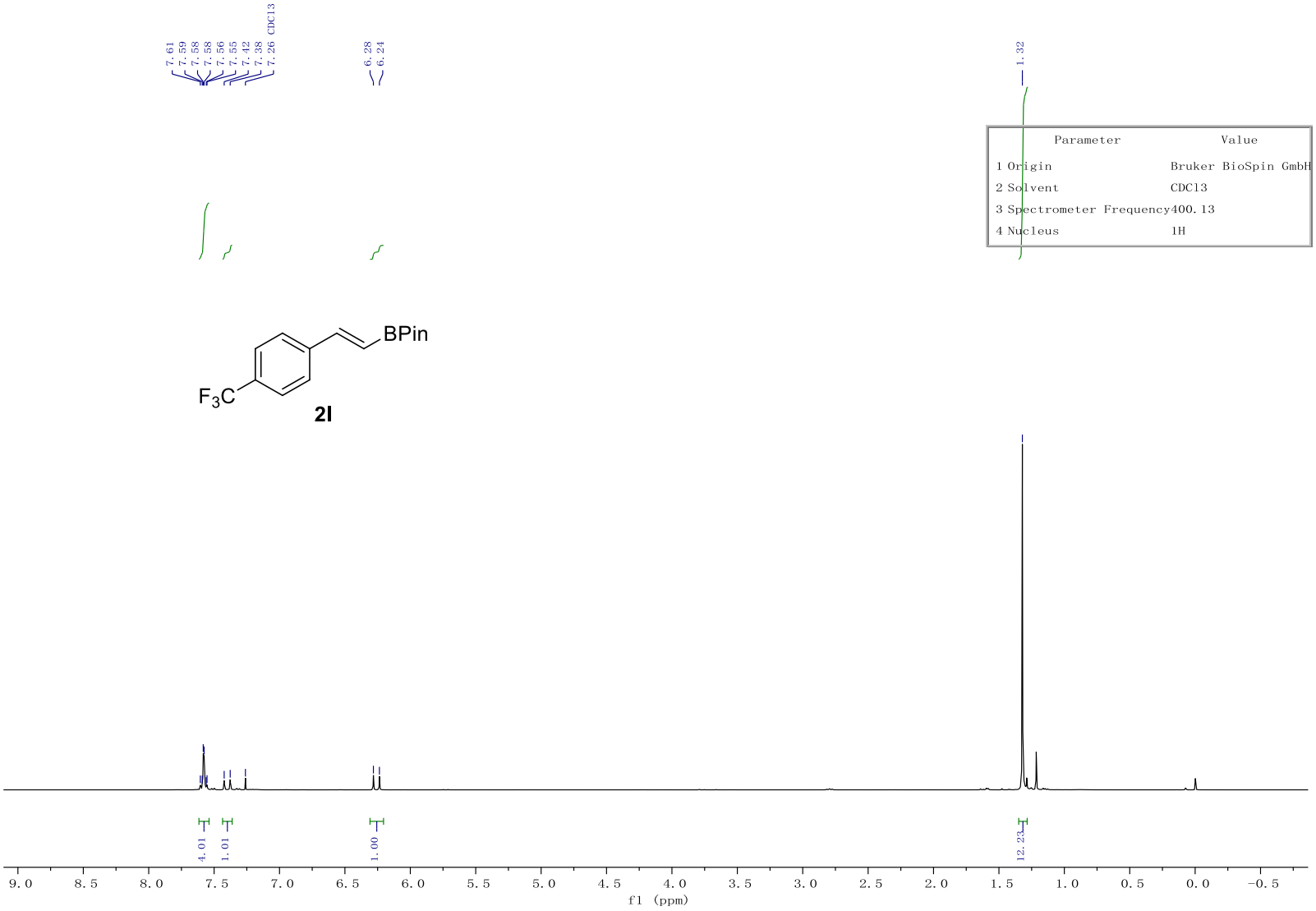
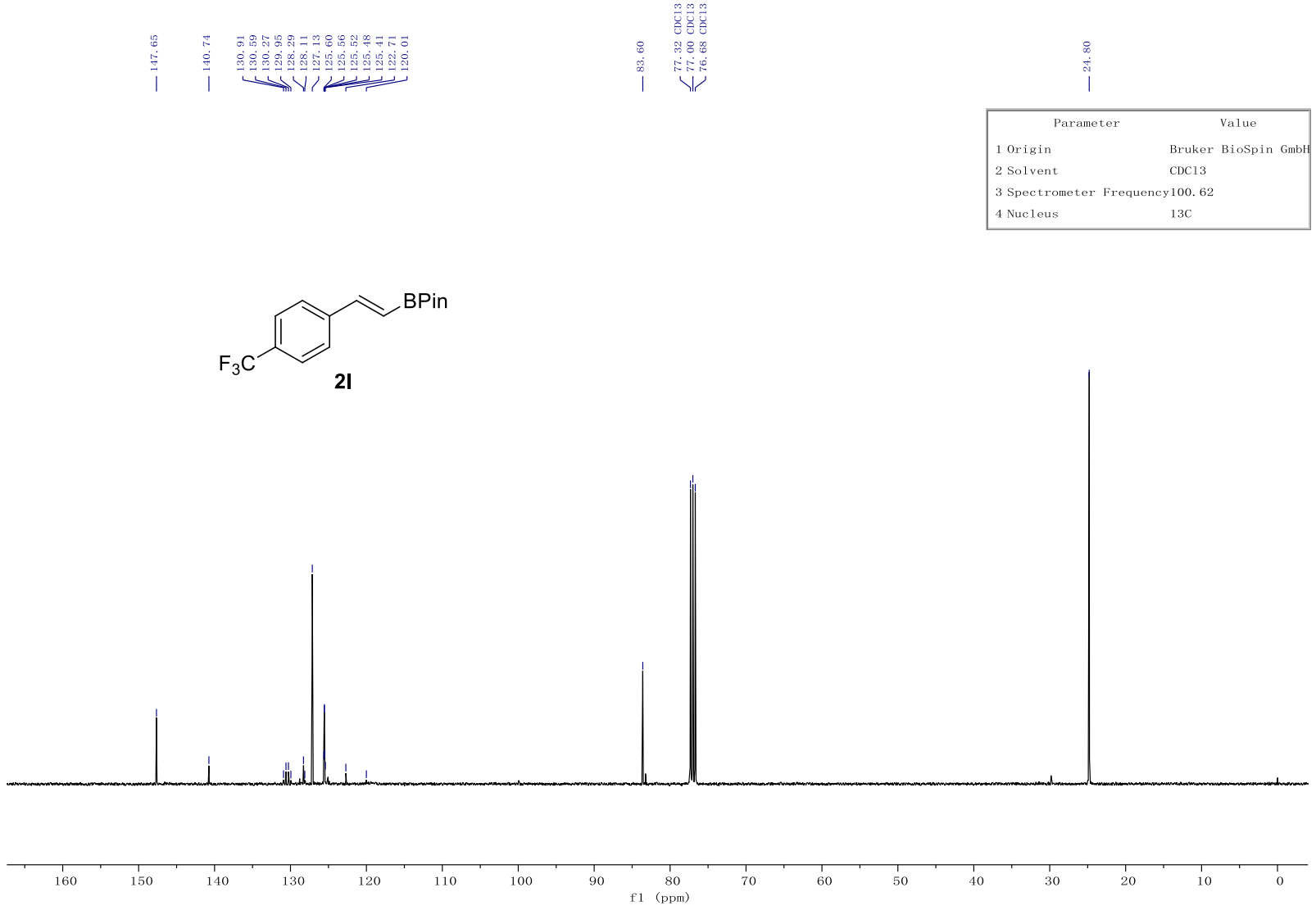
7.57
7.56
7.55
7.54
7.29
7.28
7.28
7.27
7.27
7.27
CDCl3
7.26
7.25
7.25
7.24
7.24
7.23
7.13
7.13
7.11
7.11
7.09
7.09
7.09
7.06
7.06
7.04
7.04
7.03
7.01
7.01
6.26
6.21
Parameter
Value
1 Origin
Bruker BioSpin GmbH
2 Solvent
CDCl3
3 Spectrometer Frequency
400.13
4 Nucleus
1H
1.31
F
BPin
2k
2.01
2.89
1.05
1.11
1.00
12.01
8.5
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
0.0
-0.5
f1 (ppm)

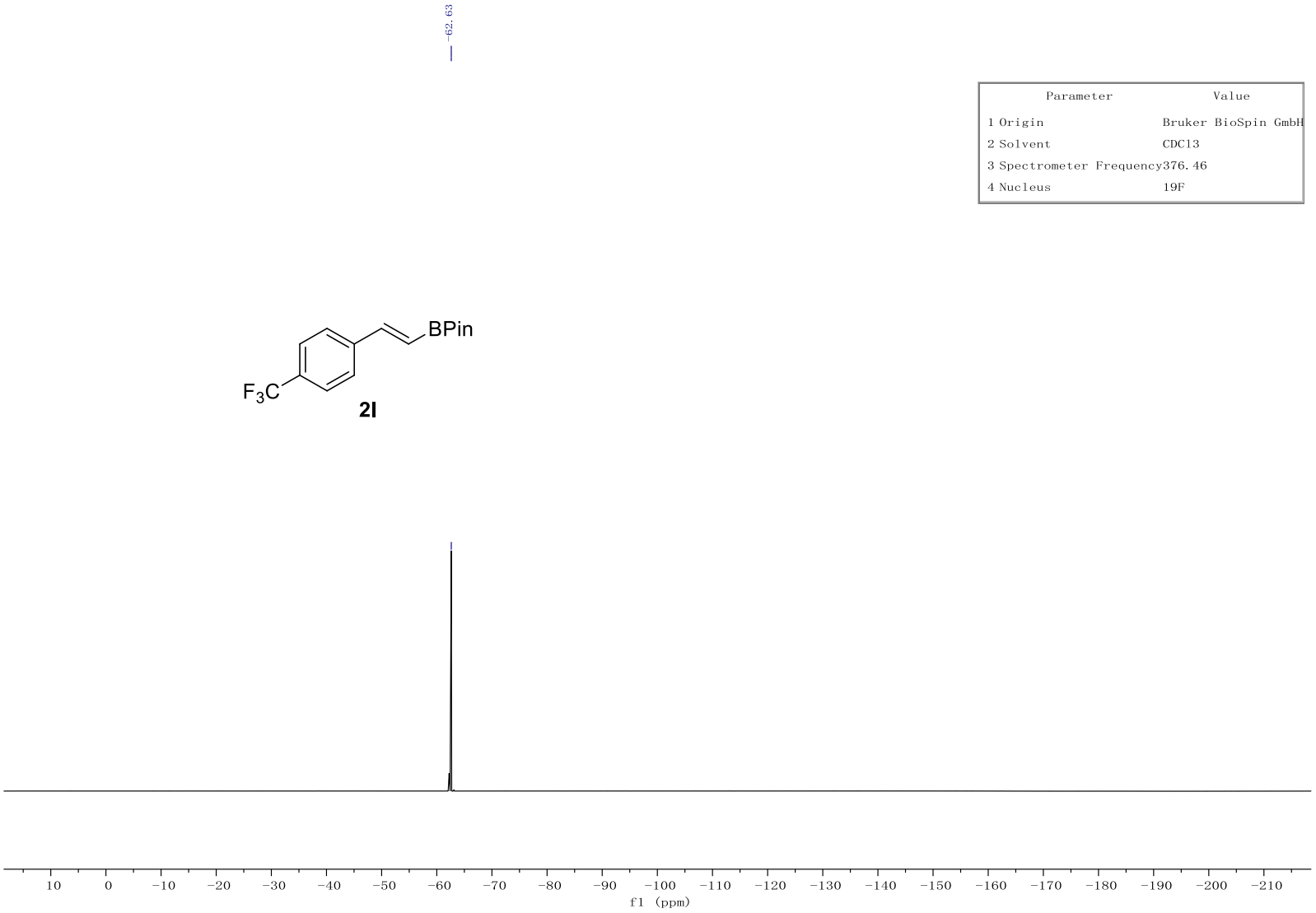

161.94
159.44
141.32
141.28
130.20
130.12
127.39
127.36
125.41
125.30
124.09
124.06
115.91
115.69
83.45
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
24.80
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Spectrometer Frequency 100.62
4 Nucleus 13C
F
BPin
2k
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-117.67
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Spectrometer Frequency376.46
4 Nucleus 19F
F
BPin
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

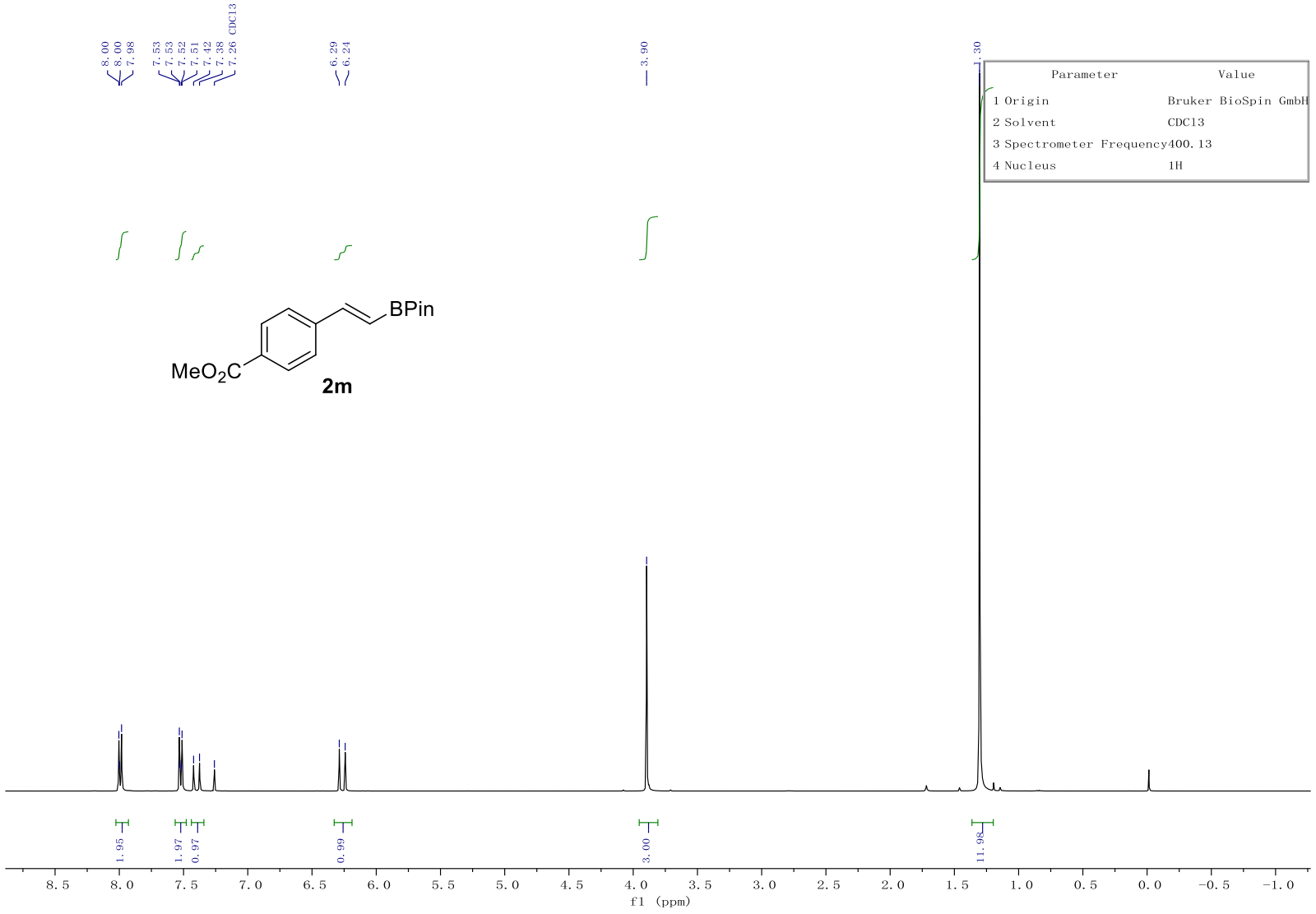
2k

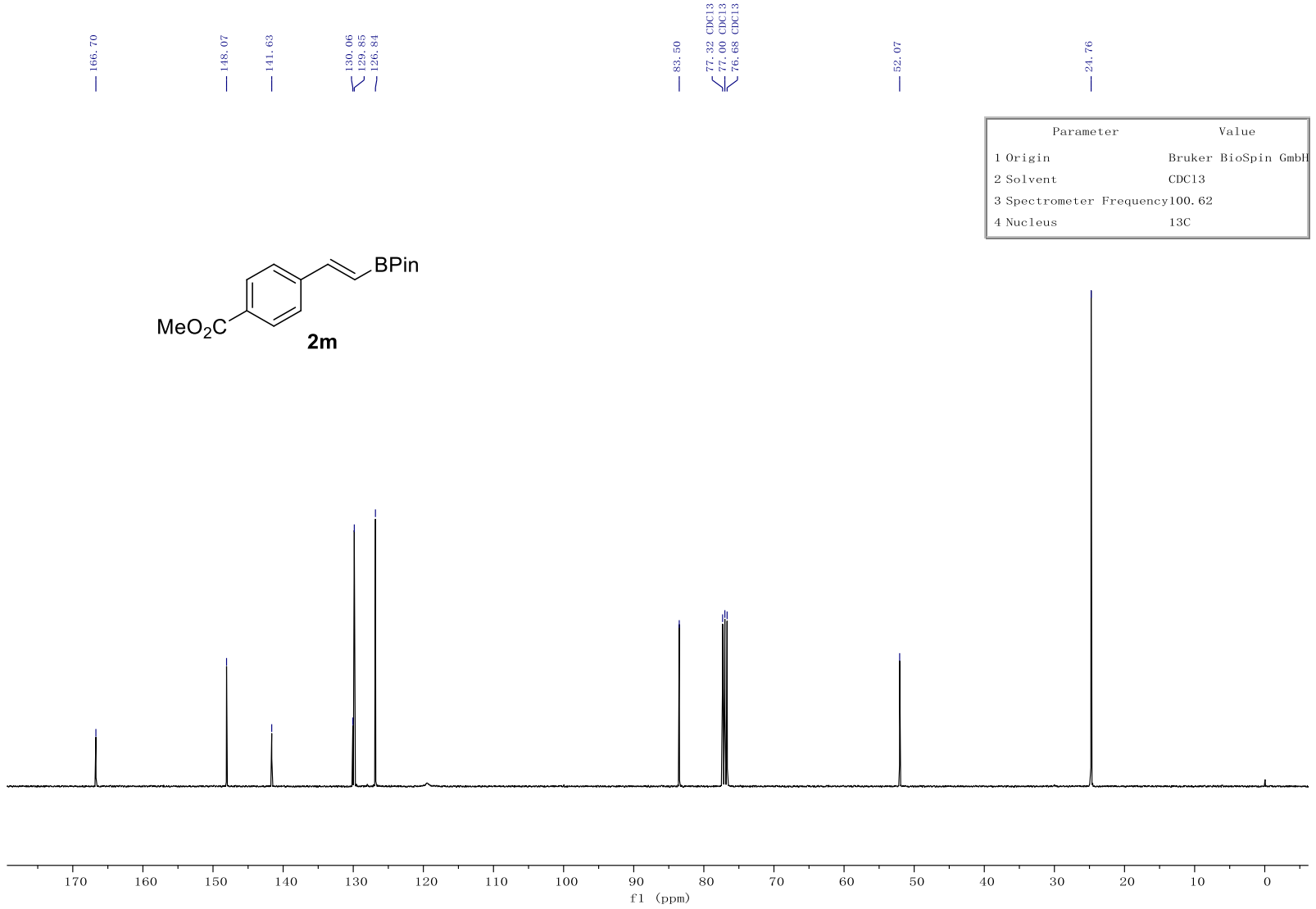

7.61
7.59
7.58
7.58
7.56
7.55
7.42
7.38
7.26 CDCl3
6.28
6.24
1.32
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Spectrometer Frequency 400.13
4 Nucleus 1H
BPin
F3C
2l
4.01
1.01
1.00
12.23
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

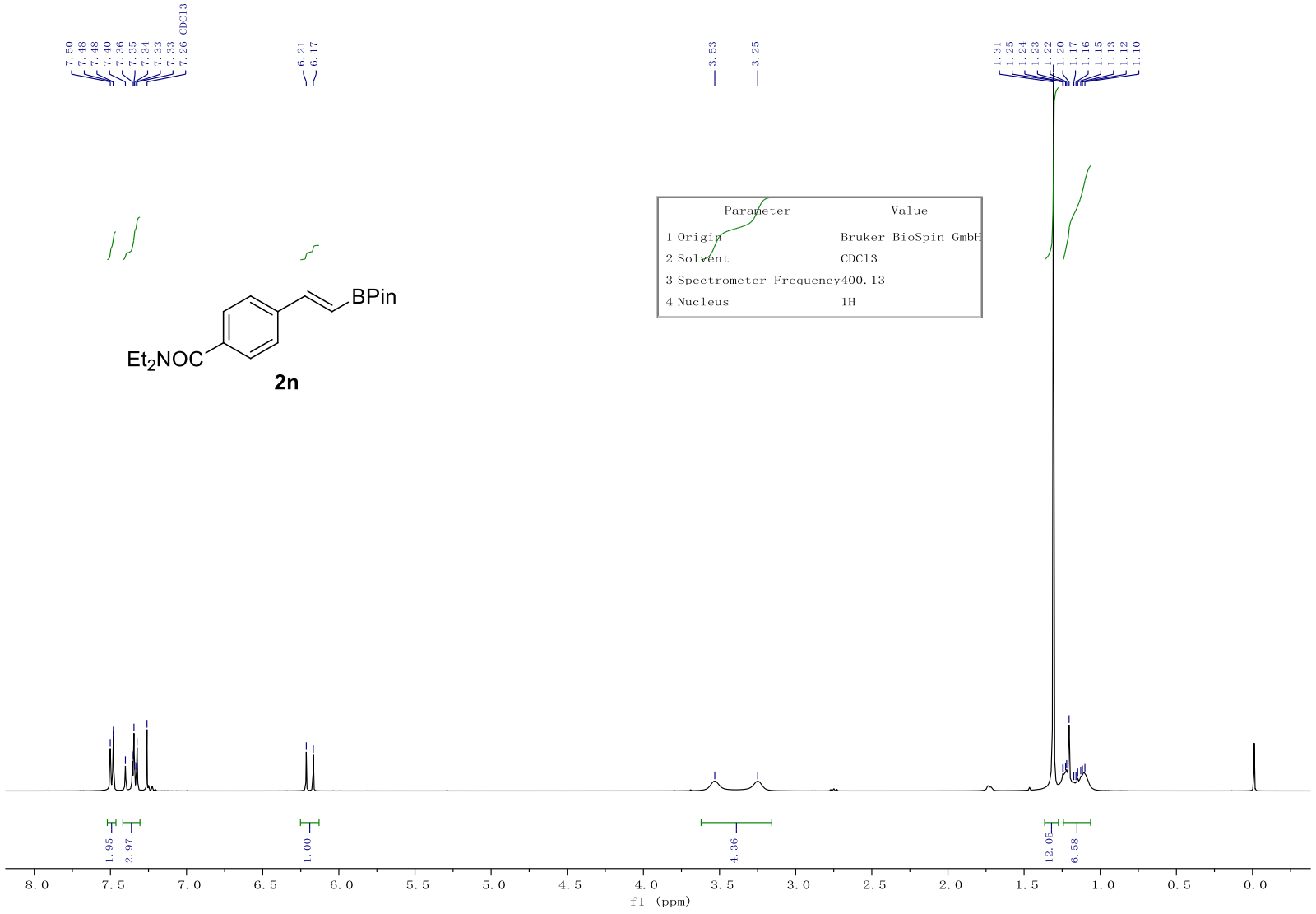

147.65
140.74
130.91
130.59
130.27
129.95
128.29
128.11
127.13
125.60
125.56
125.52
125.48
125.41
122.71
120.01
83.60
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
24.80
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Spectrometer Frequency 100.62
4 Nucleus 13C
BPin
F3C
2l
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

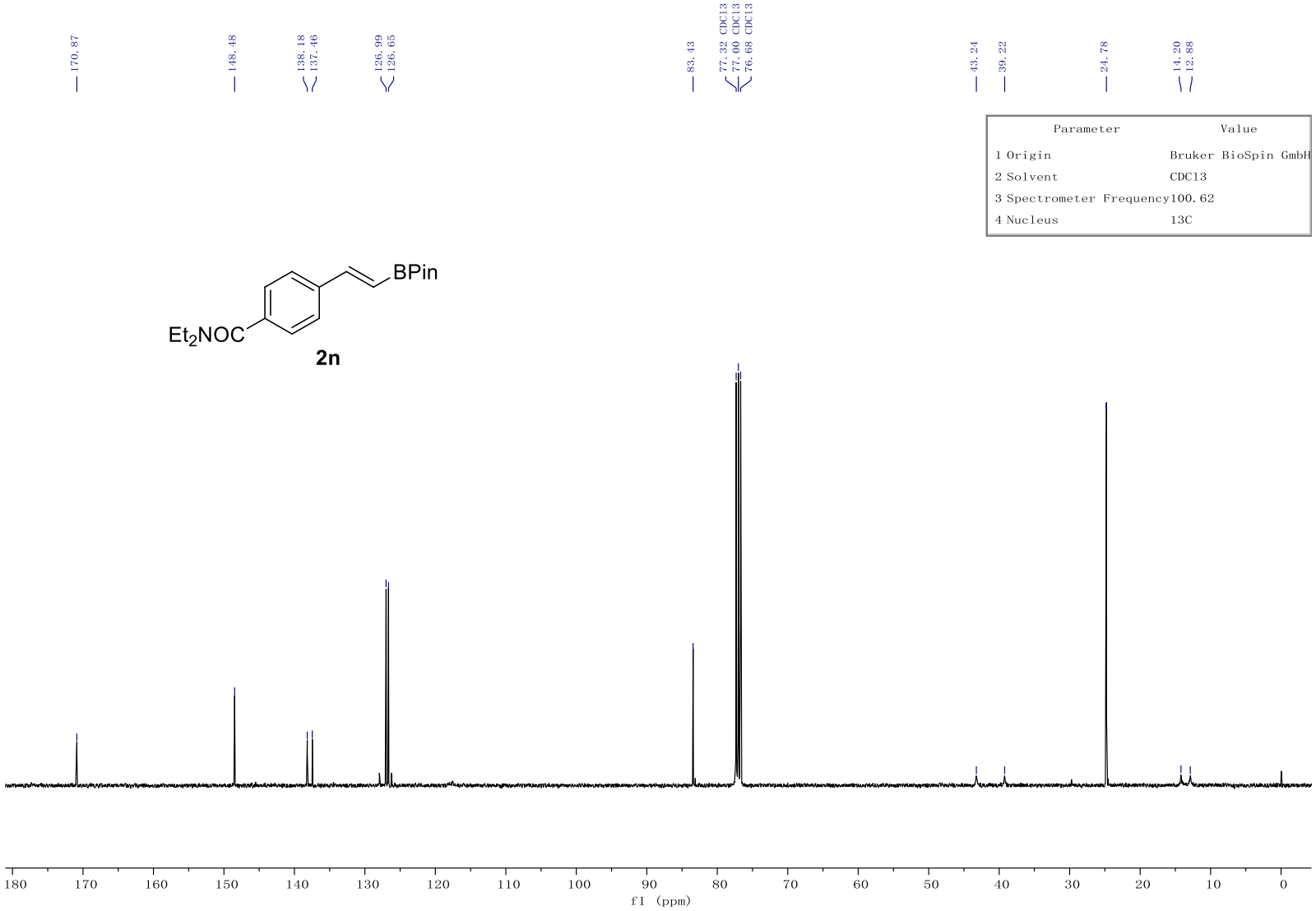


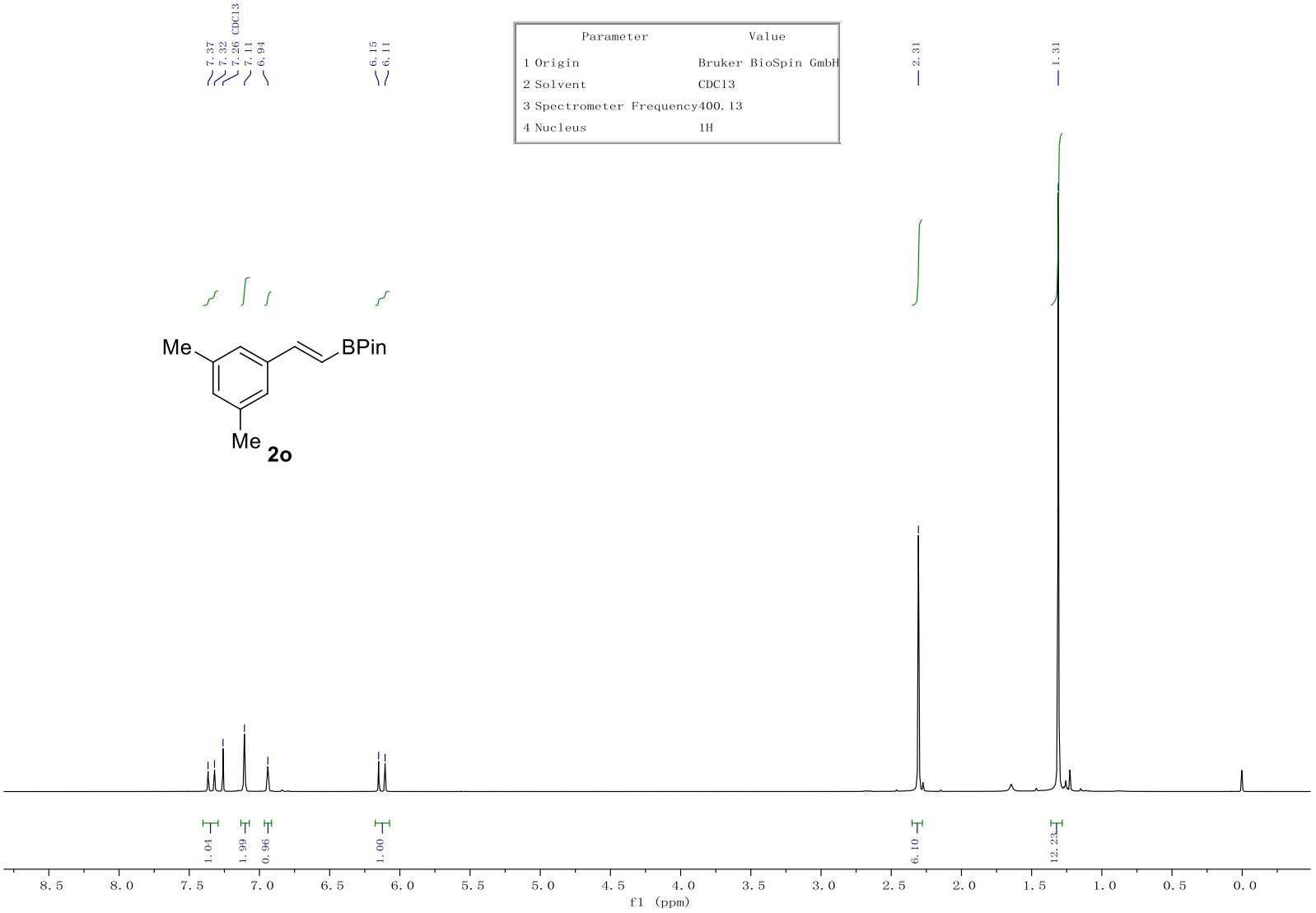
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Spectrometer Frequency	376.46
4 Nucleus	19F

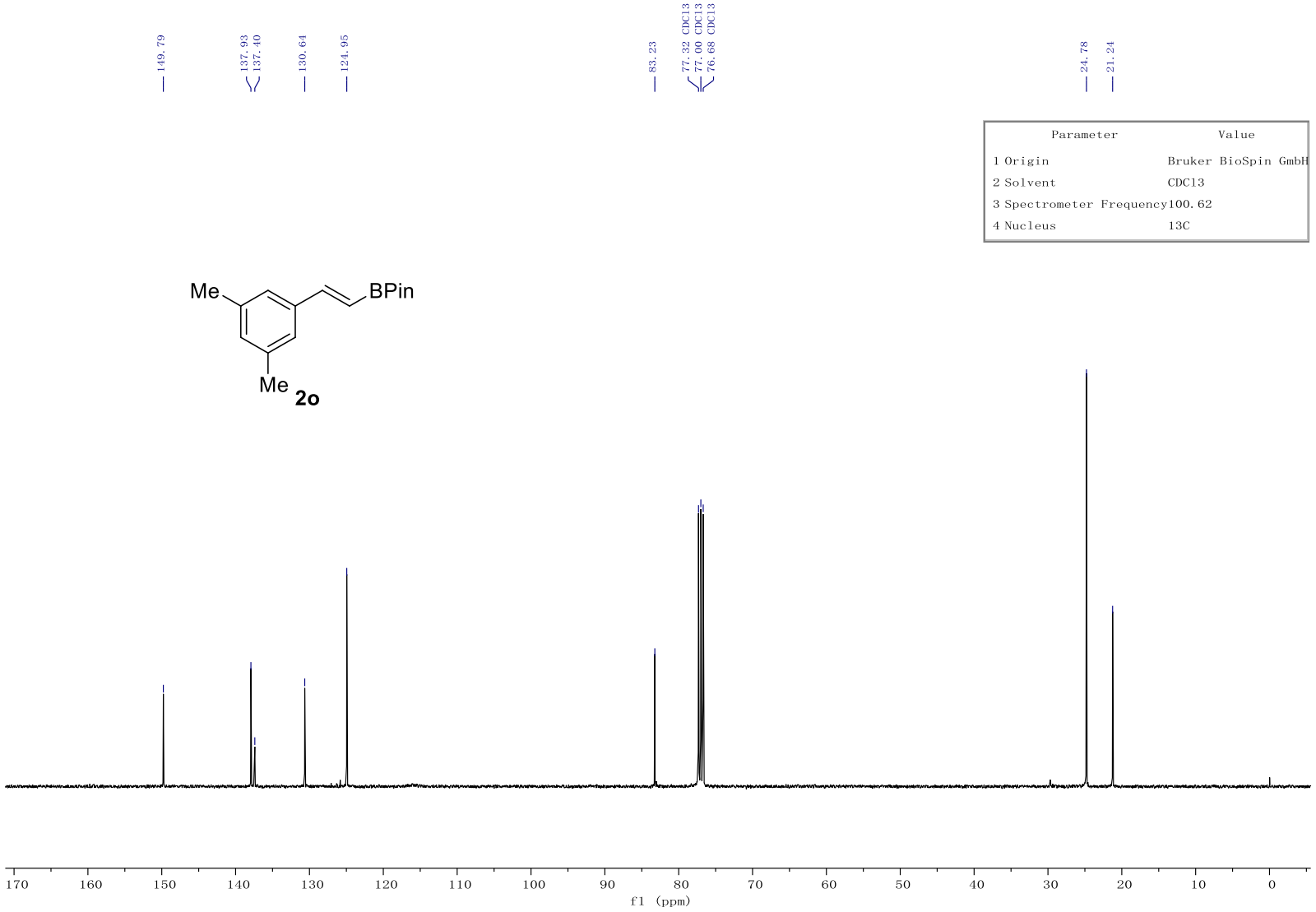

8.00
8.00
7.98
7.53
7.53
7.52
7.51
7.42
7.38
7.26
CDCl3
6.29
6.24
3.90
1.30
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Spectrometer Frequency 400.13
4 Nucleus 1H
BPin
MeO2C
2m
1.95
1.97
0.97
0.99
3.00
11.98
f1 (ppm)

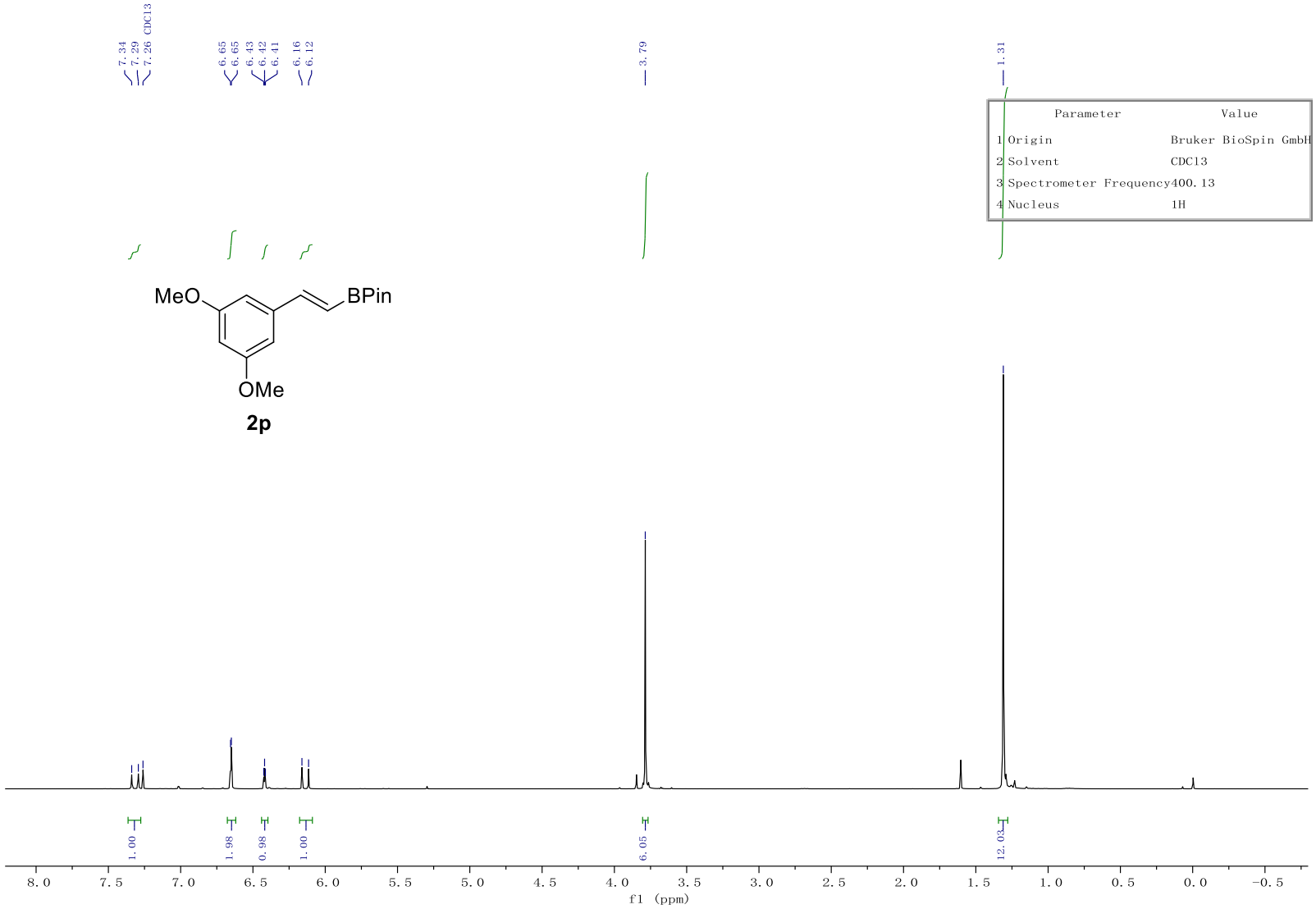

166.70
148.07
141.63
130.06
129.85
126.84
83.50
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
52.07
24.76
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Spectrometer Frequency 100.62
4 Nucleus 13C
BPin
MeO2C
2m
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

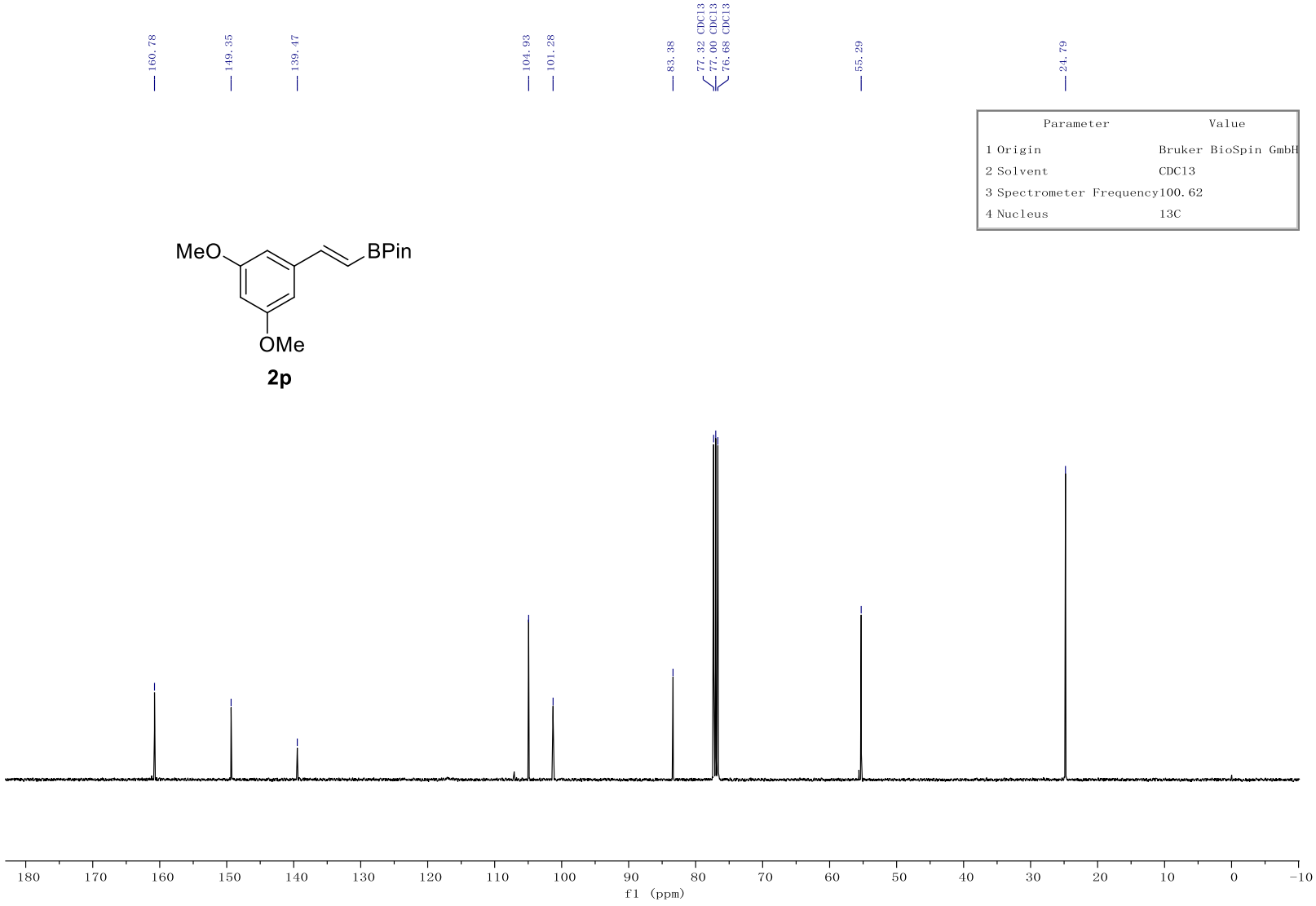

7.50
7.48
7.48
7.40
7.36
7.35
7.34
7.33
7.33
7.26 CDCl3
6.21
6.17
3.53
3.25
1.31
1.25
1.24
1.23
1.22
1.20
1.17
1.16
1.15
1.13
1.12
1.10
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Spectrometer Frequency 400.13
4 Nucleus 1H
BPin
Et2NOC
2n
1.95
2.97
1.00
4.36
12.05
6.58
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

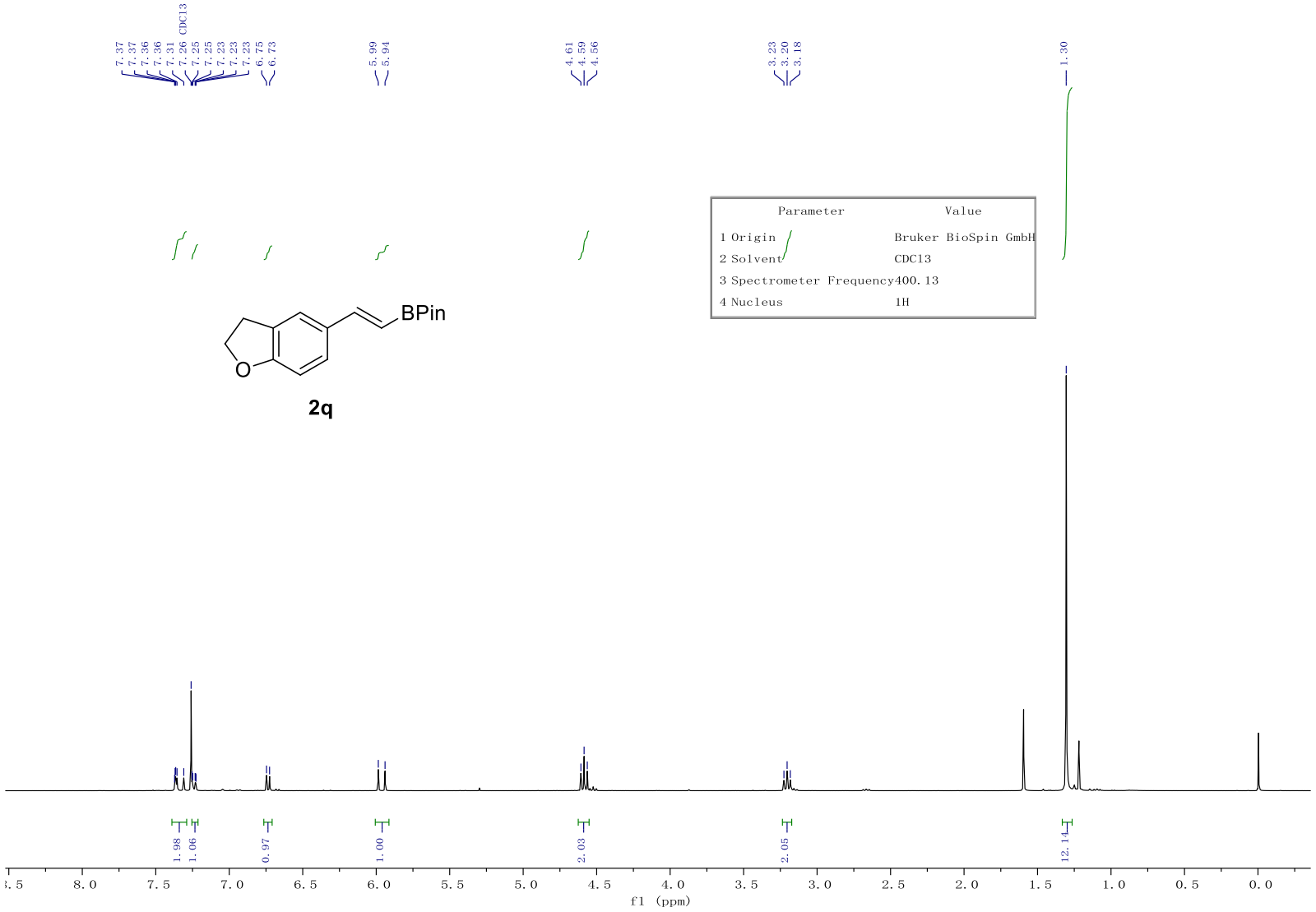

170.87
148.48
138.18
137.46
126.99
126.65
83.43
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
43.24
39.22
24.78
14.20
12.88
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Spectrometer Frequency 100.62
4 Nucleus 13C
BPin
Et2NOC
2n
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

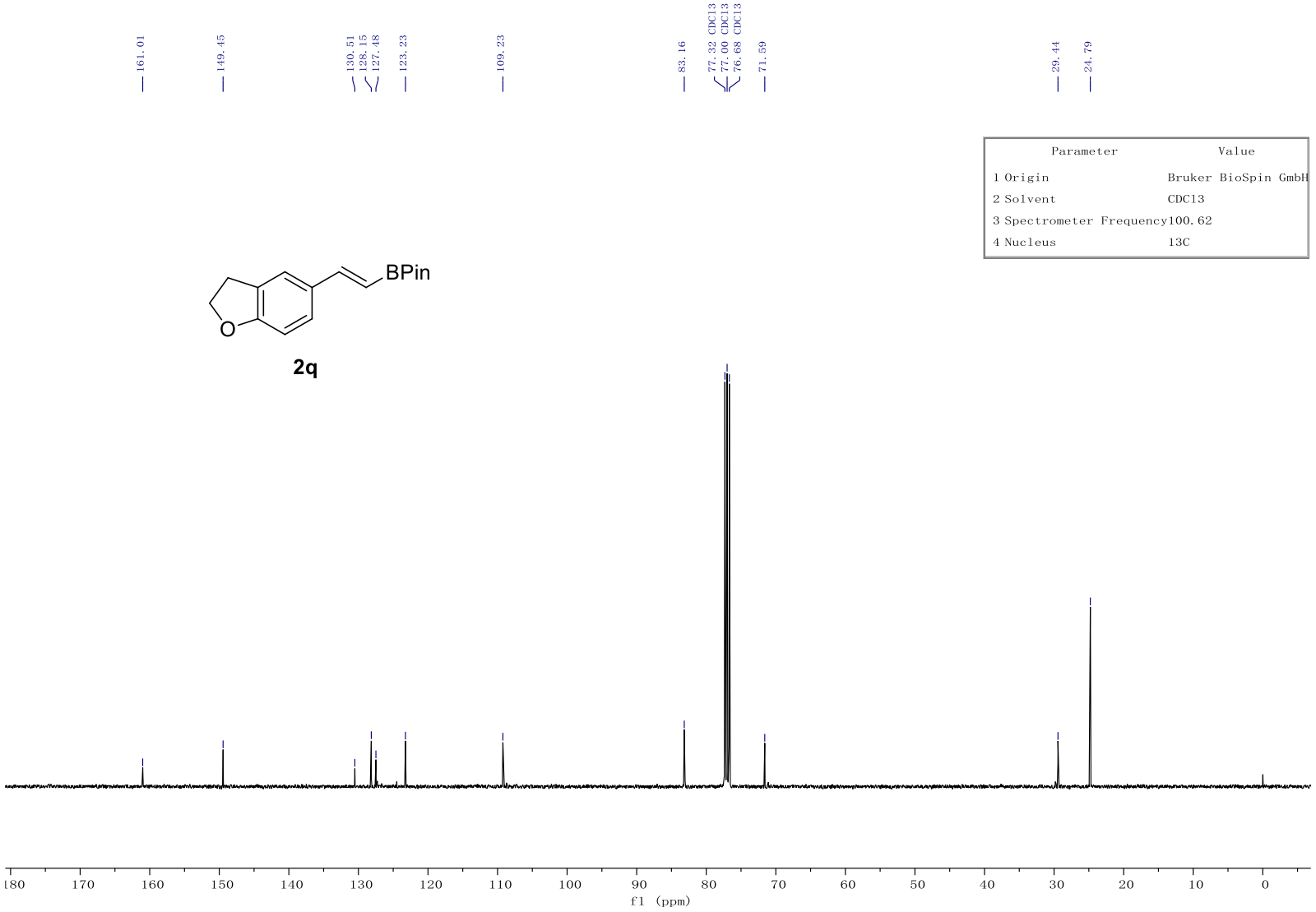

7.37
7.32
7.26 CDCl3
7.11
6.94
6.15
6.11
2.31
1.31
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Spectrometer Frequency 400.13
4 Nucleus 1H
Me
BPin
Me
2o
1.04
1.99
0.96
1.00
6.10
12.23
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


149.79
137.93
137.40
130.64
124.95
83.23
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
24.78
21.24
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Spectrometer Frequency 100.62
4 Nucleus 13C
Me
BPin
Me
2o
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.34
7.29
7.26 CDCl3
6.65
6.65
6.43
6.42
6.41
6.16
6.12
3.79
1.31
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Spectrometer Frequency 400.13
4 Nucleus 1H
MeO
BPin
OMe
2p
1.00
1.98
0.98
1.00
6.05
12.03
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 0.0 -0.5
f1 (ppm)


160.78
149.35
139.47
104.93
101.28
83.38
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
55.29
24.79
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Spectrometer Frequency 100.62
4 Nucleus 13C
MeO
BPin
OMe
2p
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


7.37
7.37
7.36
7.36
7.31
CDCl3
7.26
7.25
7.25
7.23
7.23
7.23
6.75
6.73
5.99
5.94
4.61
4.59
4.56
3.23
3.20
3.18
1.30
Parameter
Value
1 Origin
Bruker BioSpin GmbH
2 Solvent
CDCl3
3 Spectrometer Frequency
400.13
4 Nucleus
1H
BPin
O
2q
1.98
1.06
0.97
1.00
2.03
2.05
12.14
f1 (ppm)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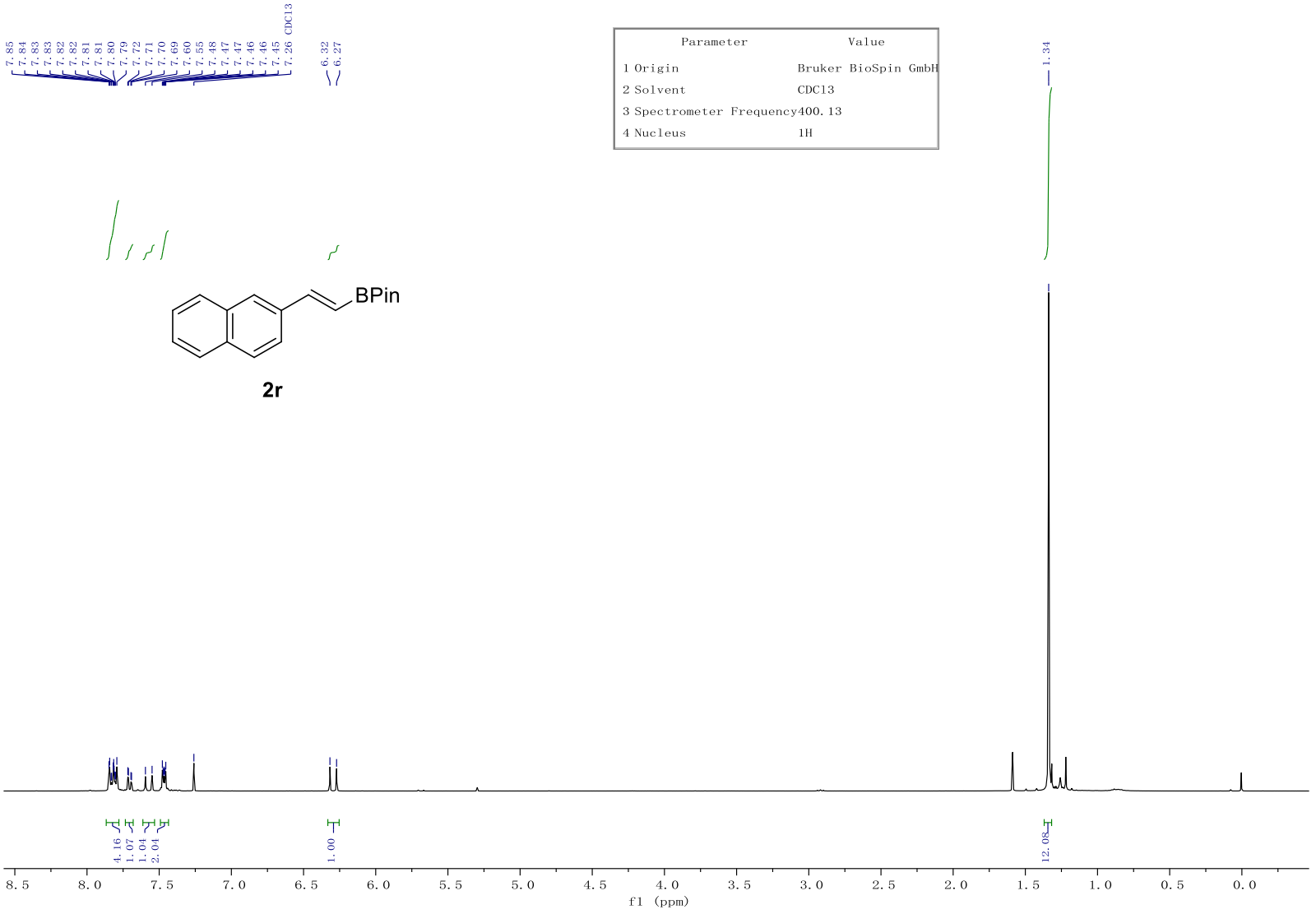
149.45
130.51
128.15
127.48
123.23
109.23
83.16
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
71.59
29.44
24.79
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Spectrometer Frequency 100.62
4 Nucleus 13C
BPin
O
2q
f1 (ppm)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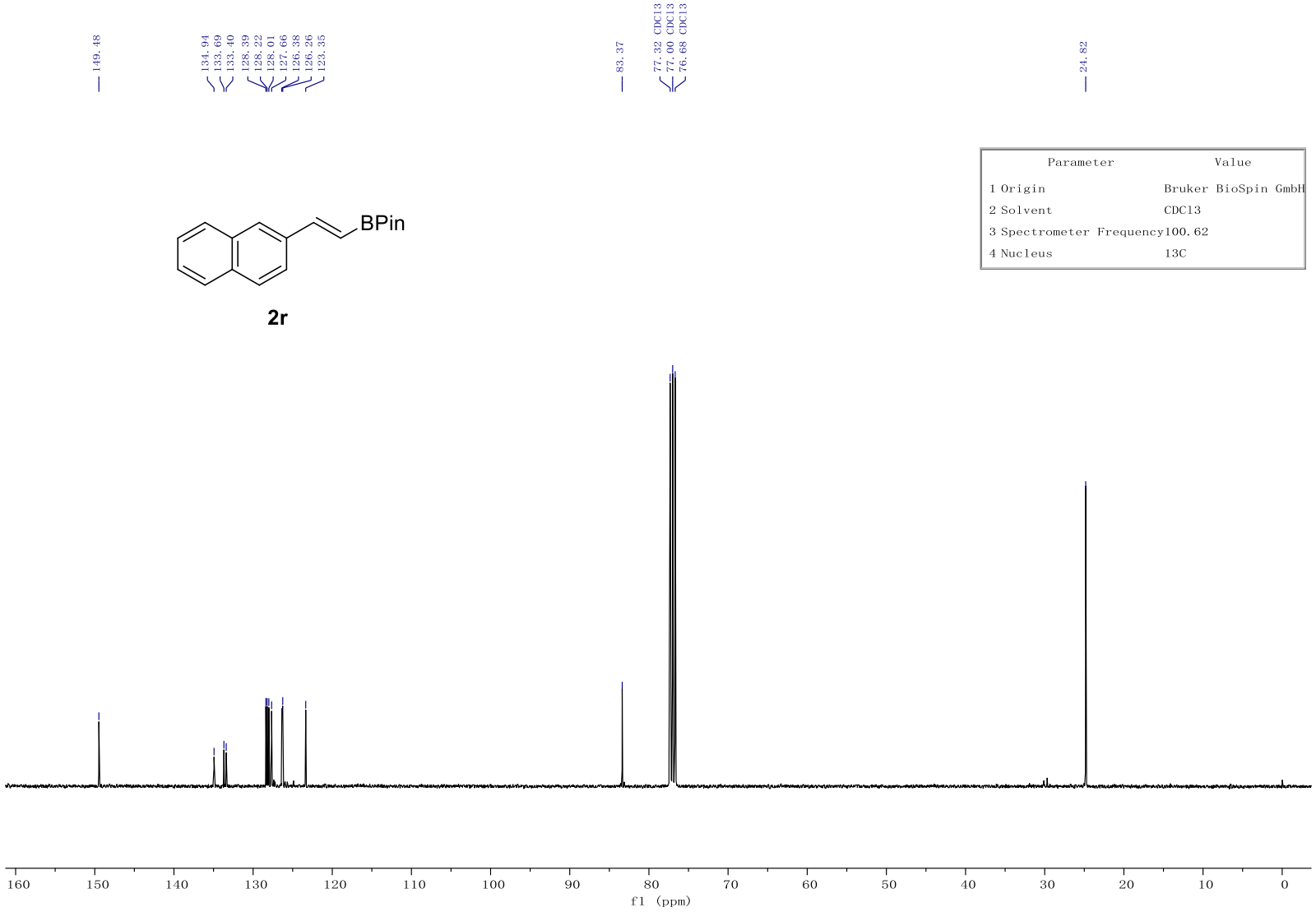
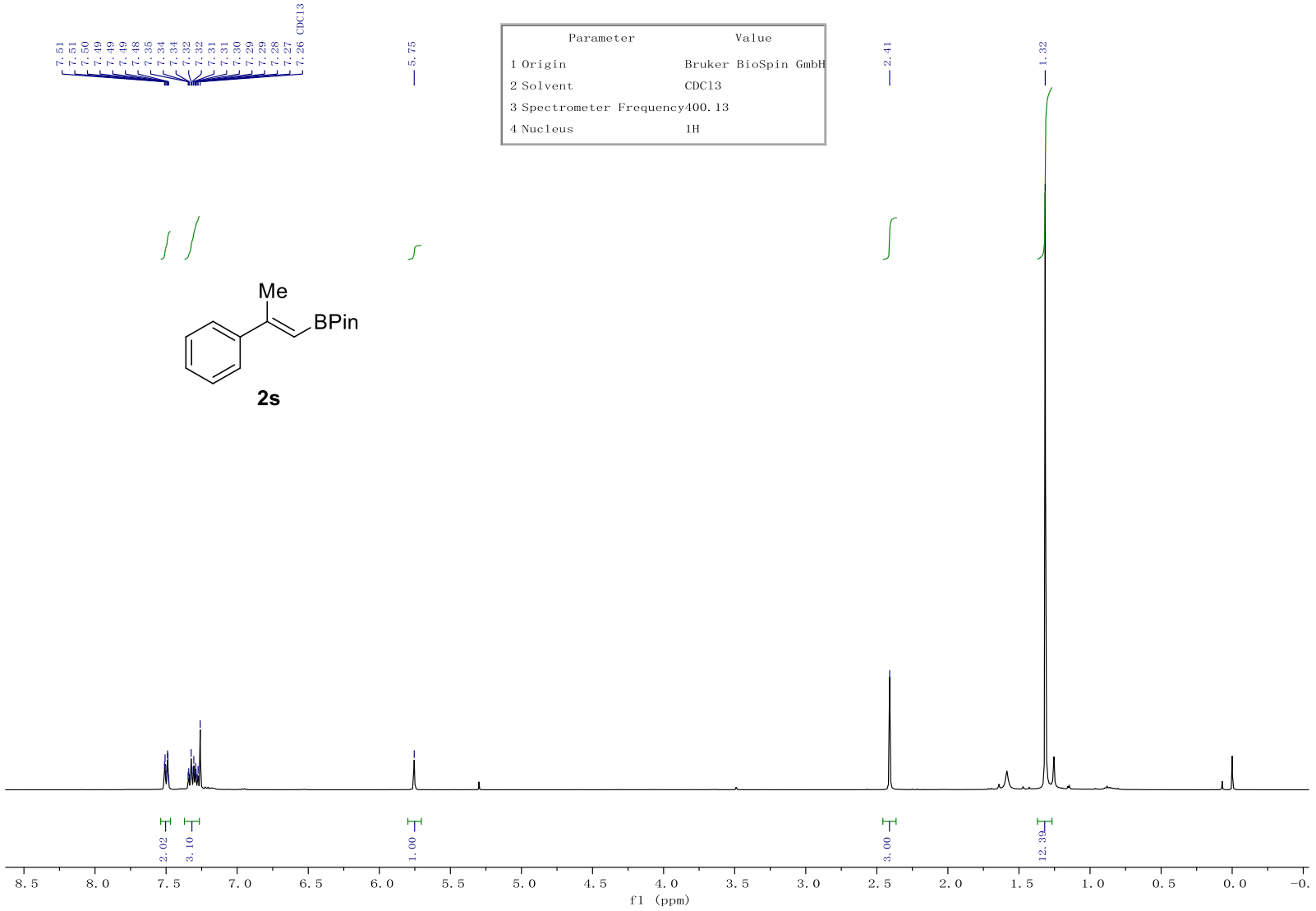
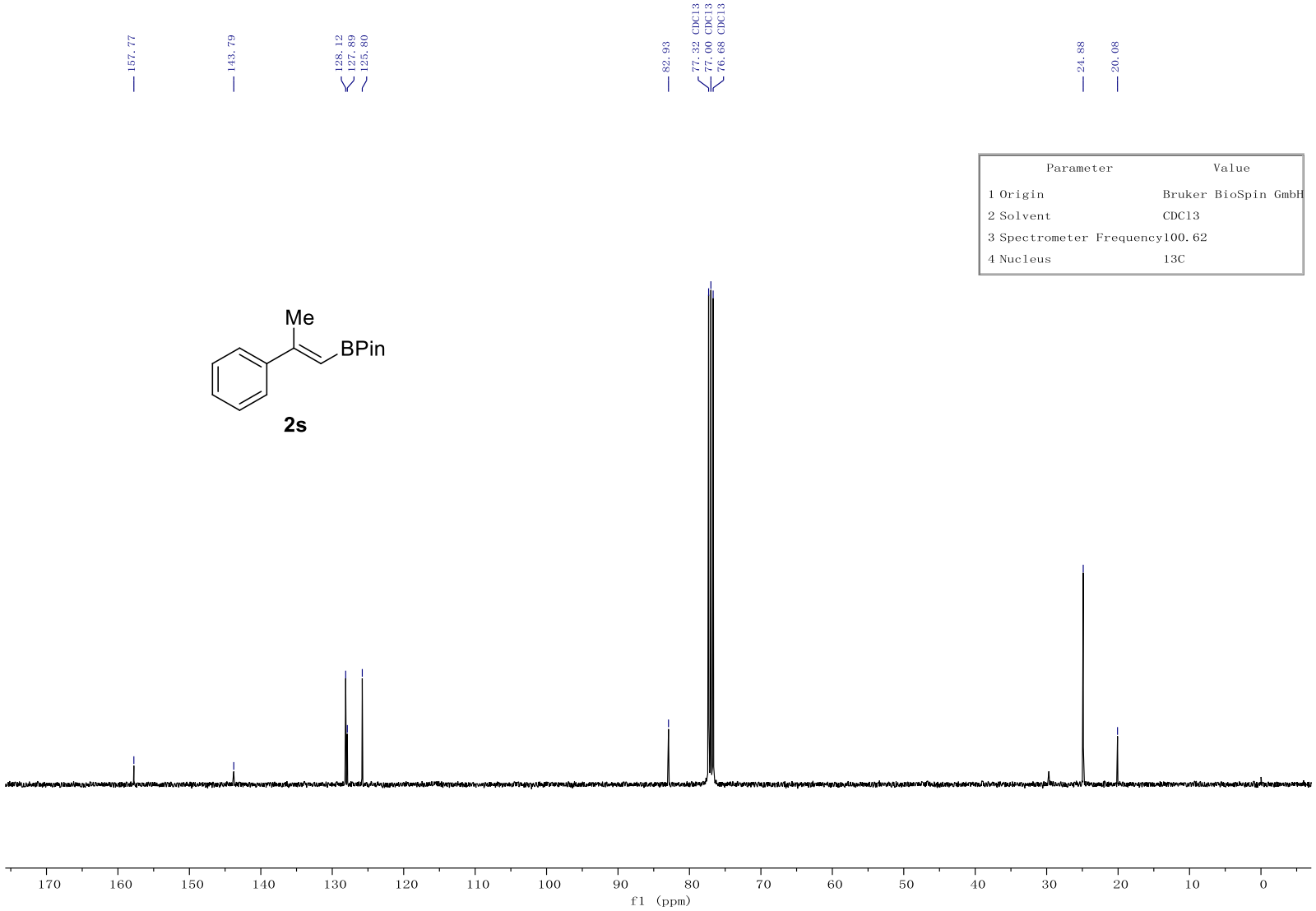
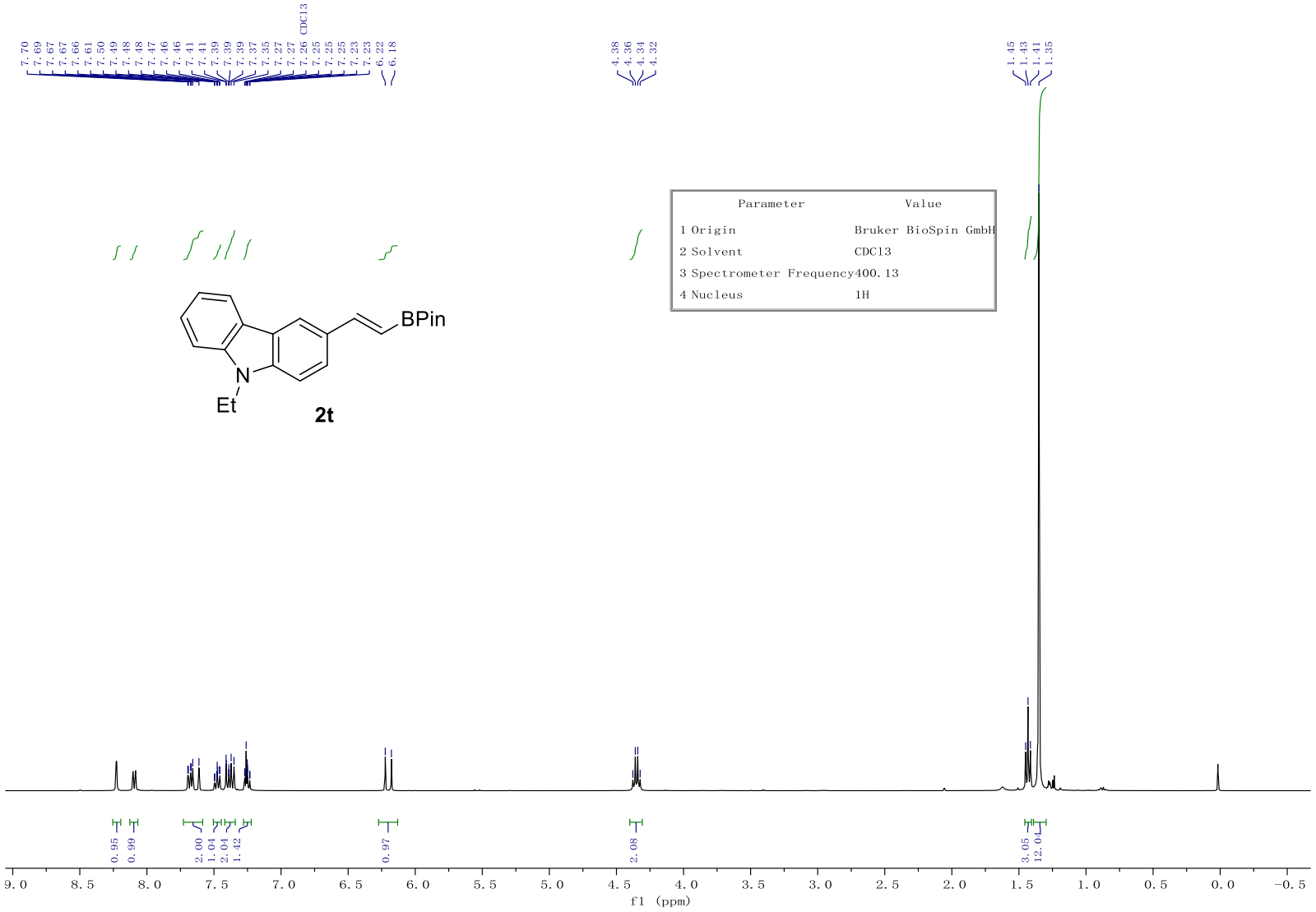
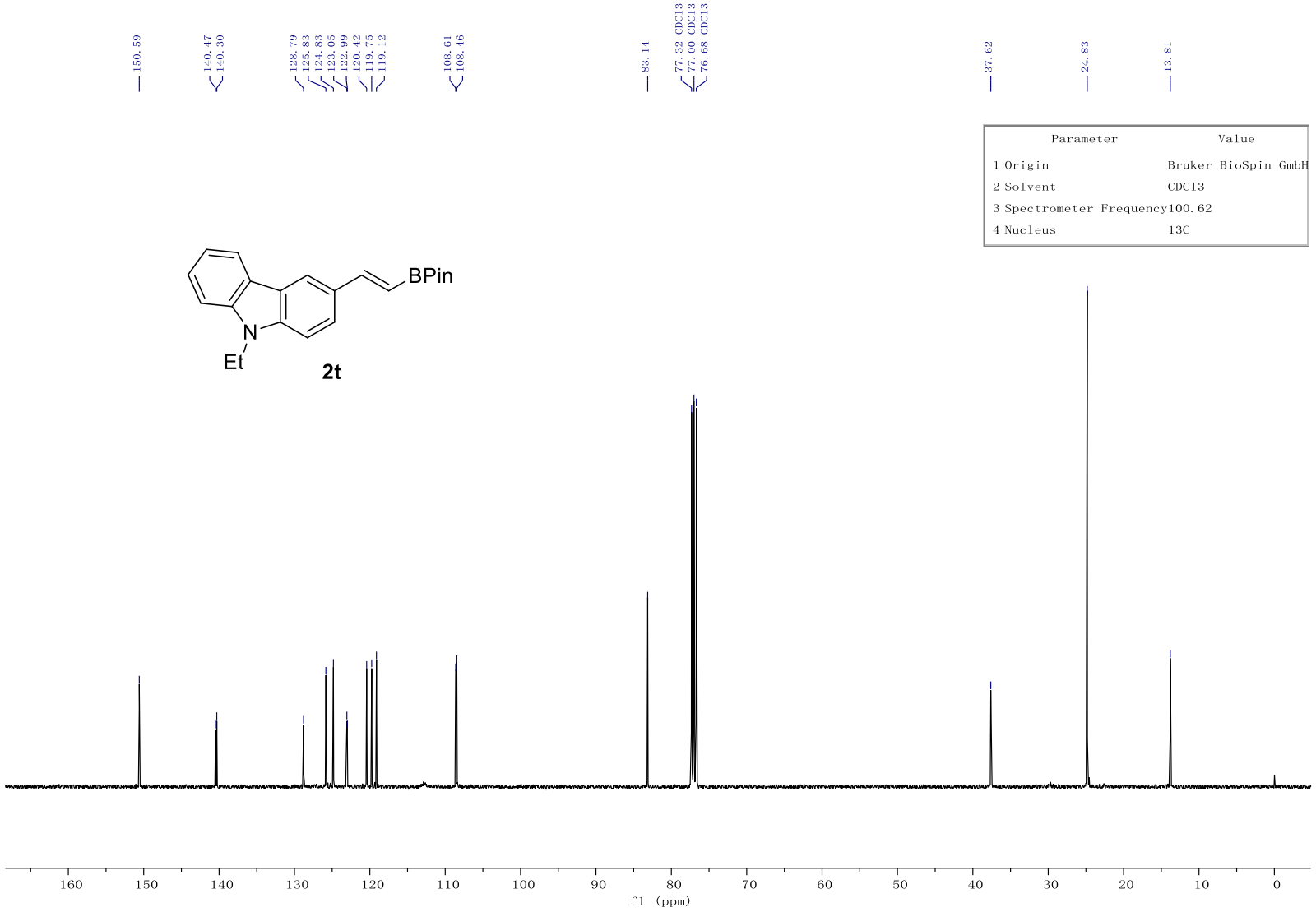
7.84
7.83
7.83
7.82
7.82
7.81
7.81
7.80
7.79
7.72
7.71
7.70
7.69
7.60
7.55
7.48
7.47
7.47
7.46
7.46
7.45
7.26 CDCl3
6.32
6.27
1.34
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Spectrometer Frequency 400.13
4 Nucleus 1H
BPin
2r
4.16
1.07
1.04
2.04
1.00
12.08
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

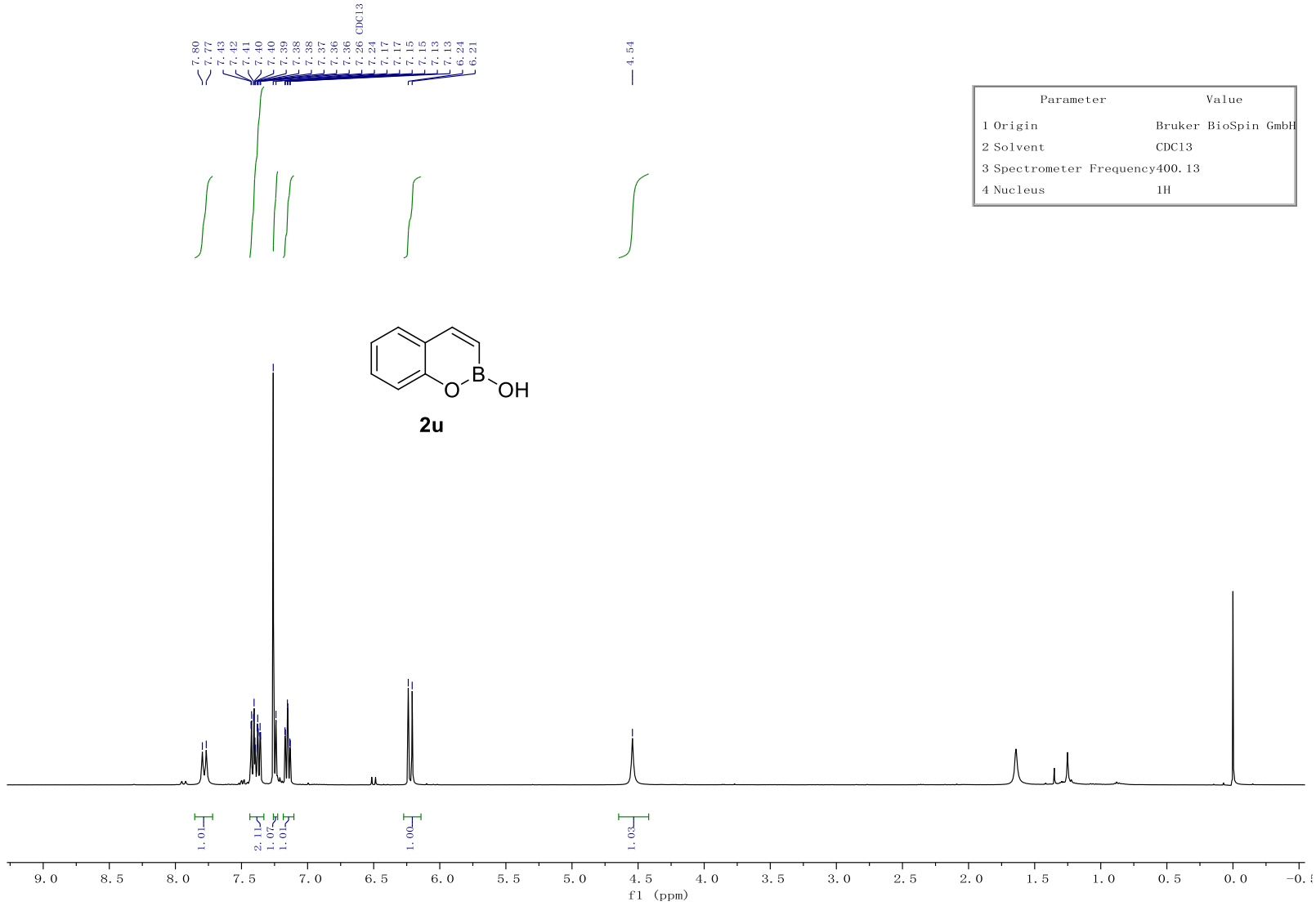

149.48
134.94
133.69
133.40
128.39
128.22
128.01
127.66
126.38
126.26
123.35
83.37
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
24.82
BPin
2r
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Spectrometer Frequency 100.62
4 Nucleus 13C
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

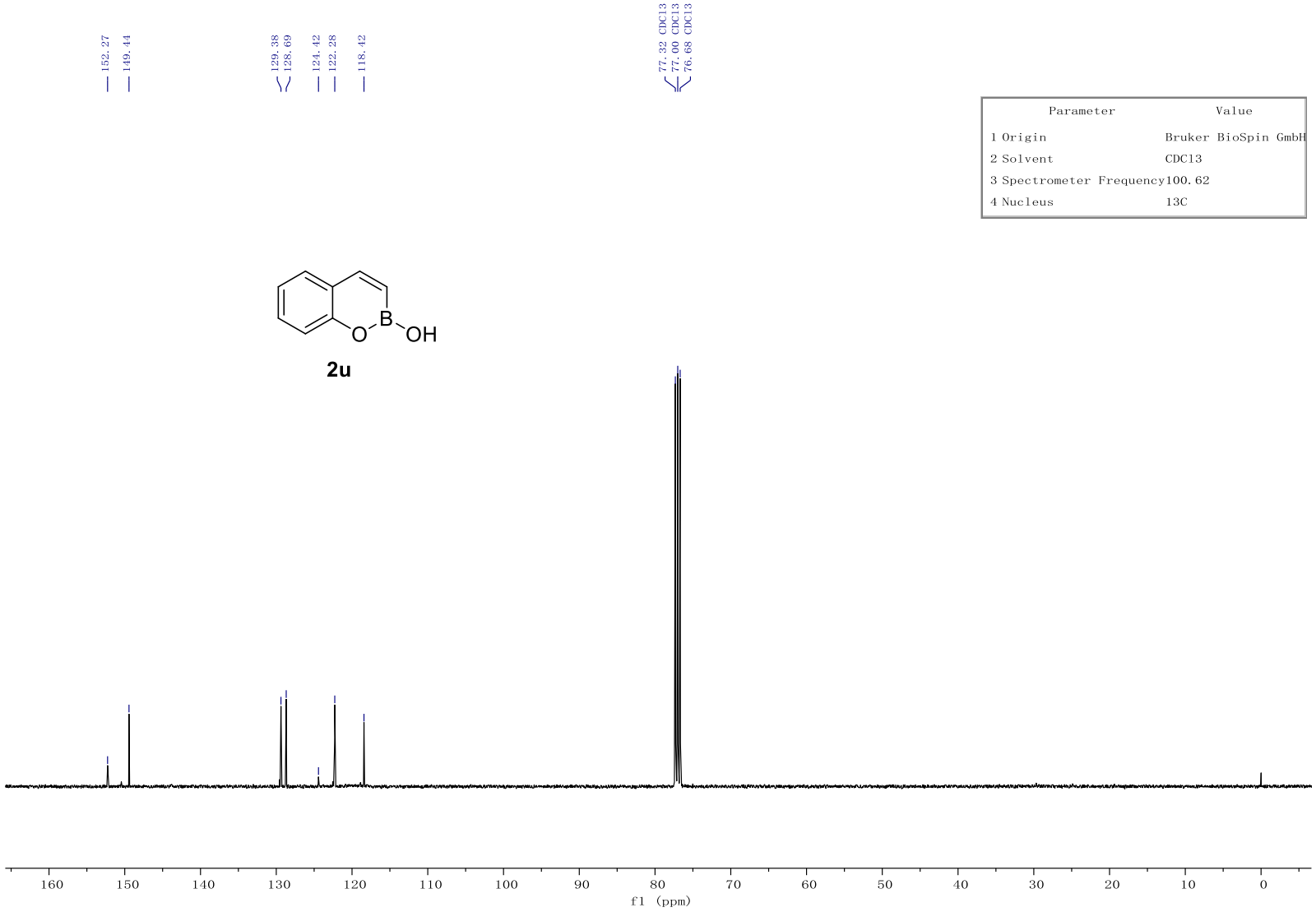

7.51
7.51
7.50
7.49
7.49
7.49
7.48
7.35
7.34
7.34
7.32
7.32
7.31
7.31
7.30
7.29
7.29
7.28
7.27
7.26 CDCl3
5.75
2.41
1.32
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Spectrometer Frequency 400.13
4 Nucleus 1H
Me
BPin
2s
2.02
3.10
1.00
3.00
12.39
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

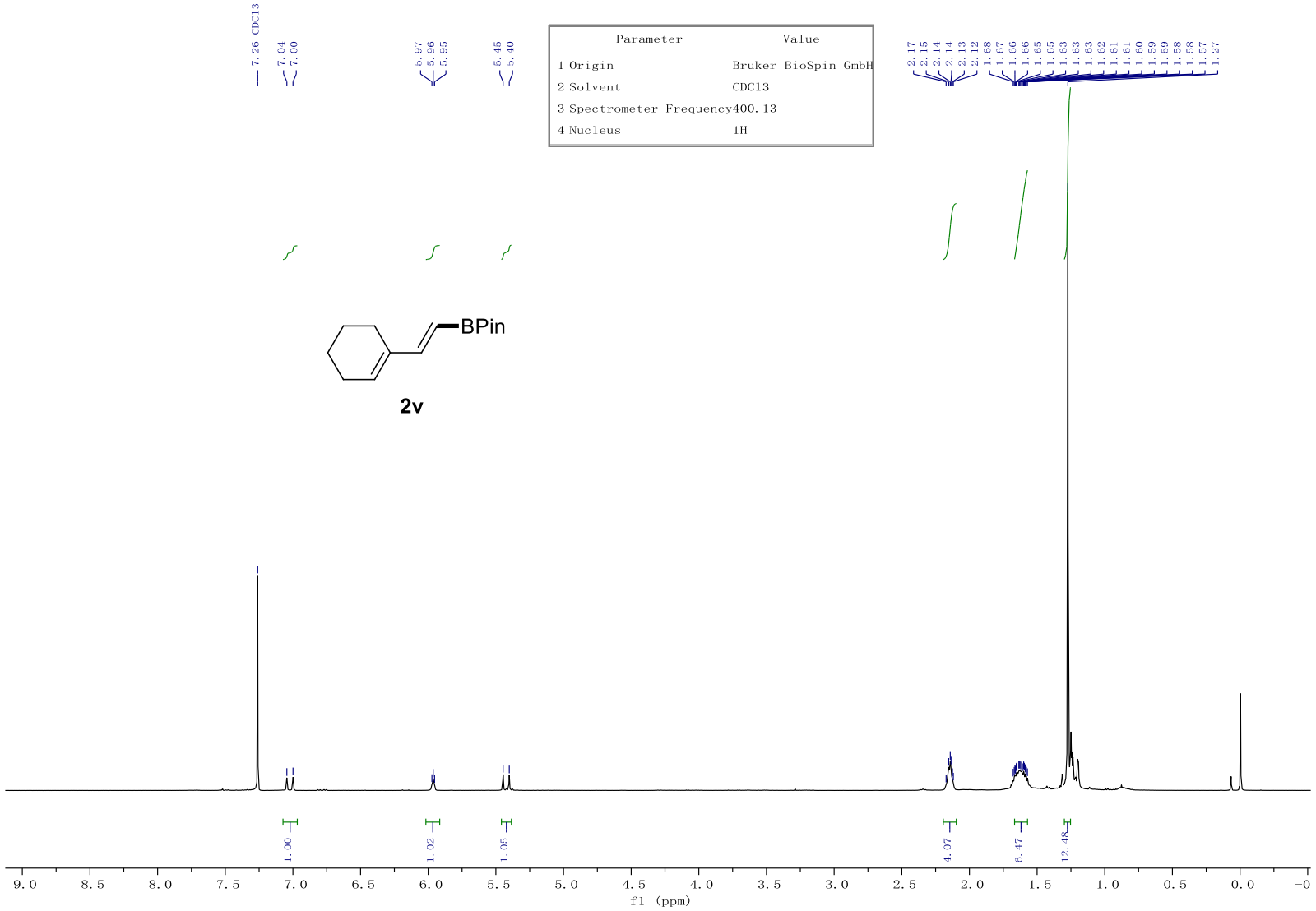

157.77
143.79
128.12
127.89
125.80
82.93
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
24.88
20.08
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Spectrometer Frequency 100.62
4 Nucleus 13C
Me
BPin
2s
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

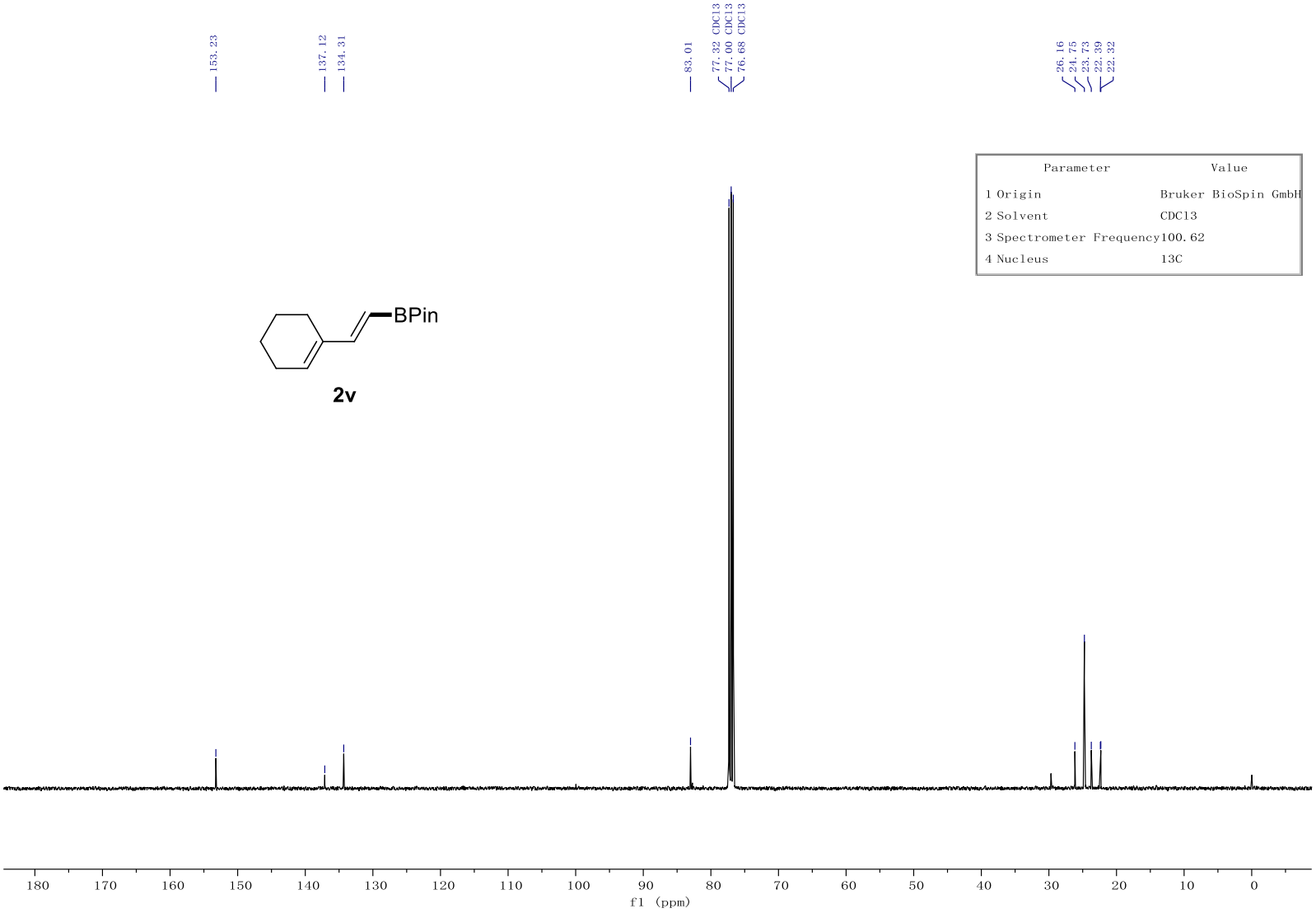

7.70
7.69
7.67
7.67
7.66
7.61
7.50
7.49
7.48
7.48
7.47
7.46
7.46
7.41
7.41
7.39
7.39
7.39
7.37
7.35
7.27
7.27
CDCl3
7.26
7.25
7.25
7.25
7.23
7.23
6.22
6.18
4.38
4.36
4.34
4.32
1.45
1.43
1.41
1.35
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Spectrometer Frequency 400.13
4 Nucleus 1H
BPin
N
Et
2t
0.95
0.99
2.00
1.04
2.04
1.42
0.97
2.08
3.05
12.04
9.0
8.5
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
0.0
-0.5
f1 (ppm)

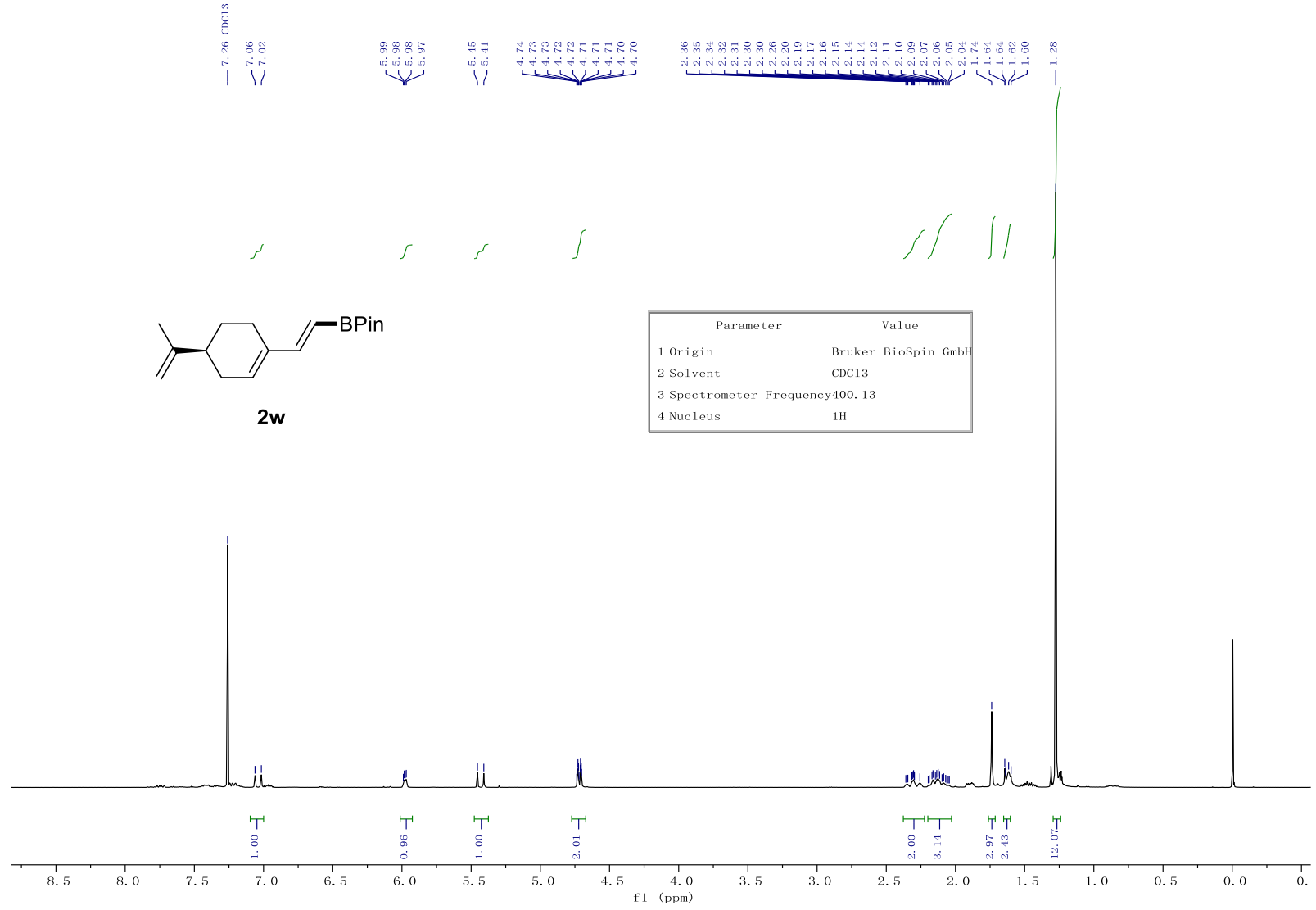

150.59
140.47
140.30
128.79
125.83
124.83
123.05
122.99
120.42
119.75
119.12
108.61
108.46
83.14
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
37.62
24.83
13.81
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Spectrometer Frequency 100.62
4 Nucleus 13C
BPin
N
Et
2t
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

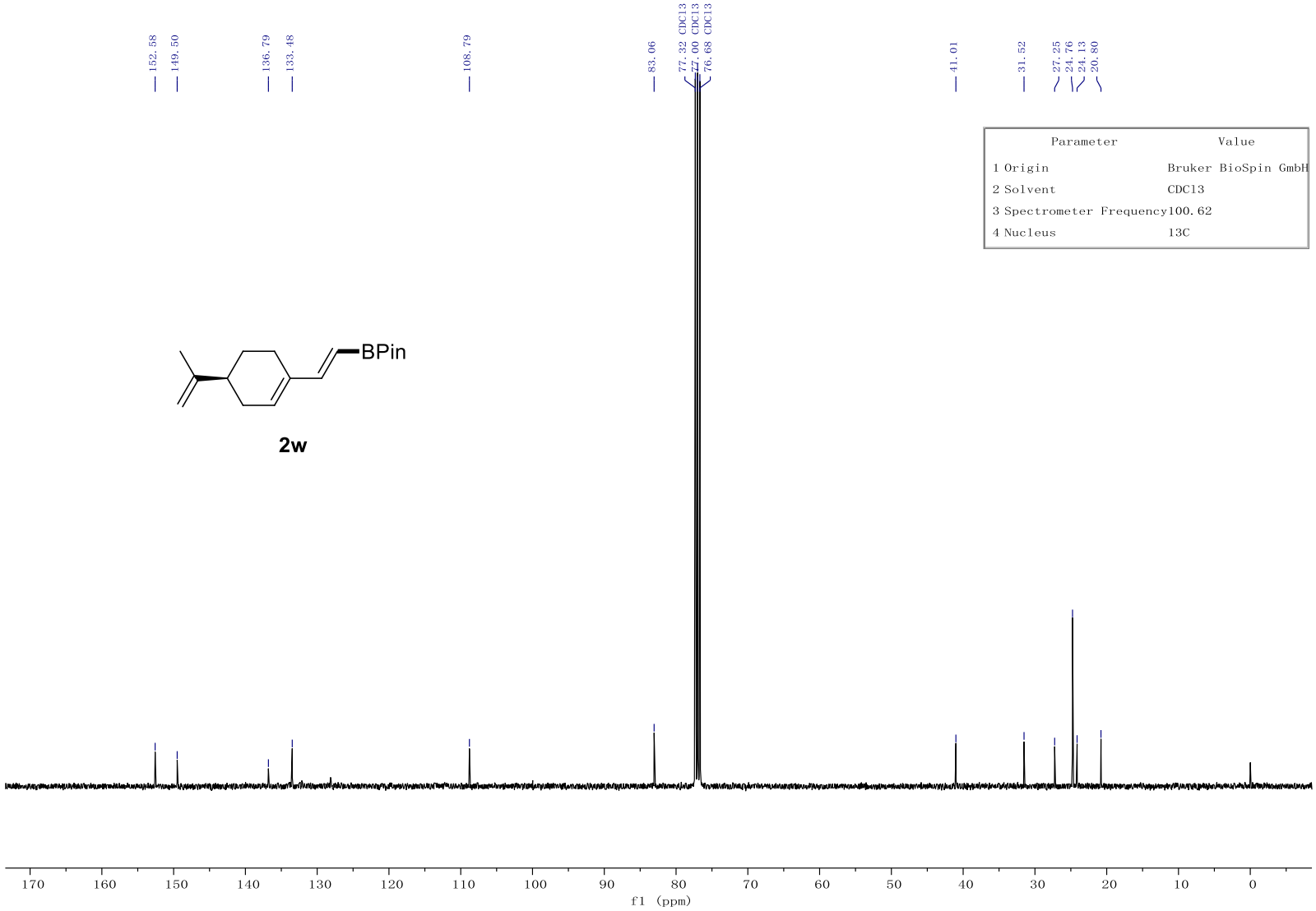

7.80
7.77
7.43
7.42
7.41
7.40
7.40
7.39
7.38
7.38
7.37
7.36
7.36
CDCl3
7.26
7.24
7.17
7.17
7.15
7.13
7.13
6.24
6.21
4.54
Parameter
Value
1 Origin
Bruker BioSpin GmbH
2 Solvent
CDCl3
3 Spectrometer Frequency
400.13
4 Nucleus
1H
O
B
OH
2u
1.01
2.11
1.07
1.01
1.00
1.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

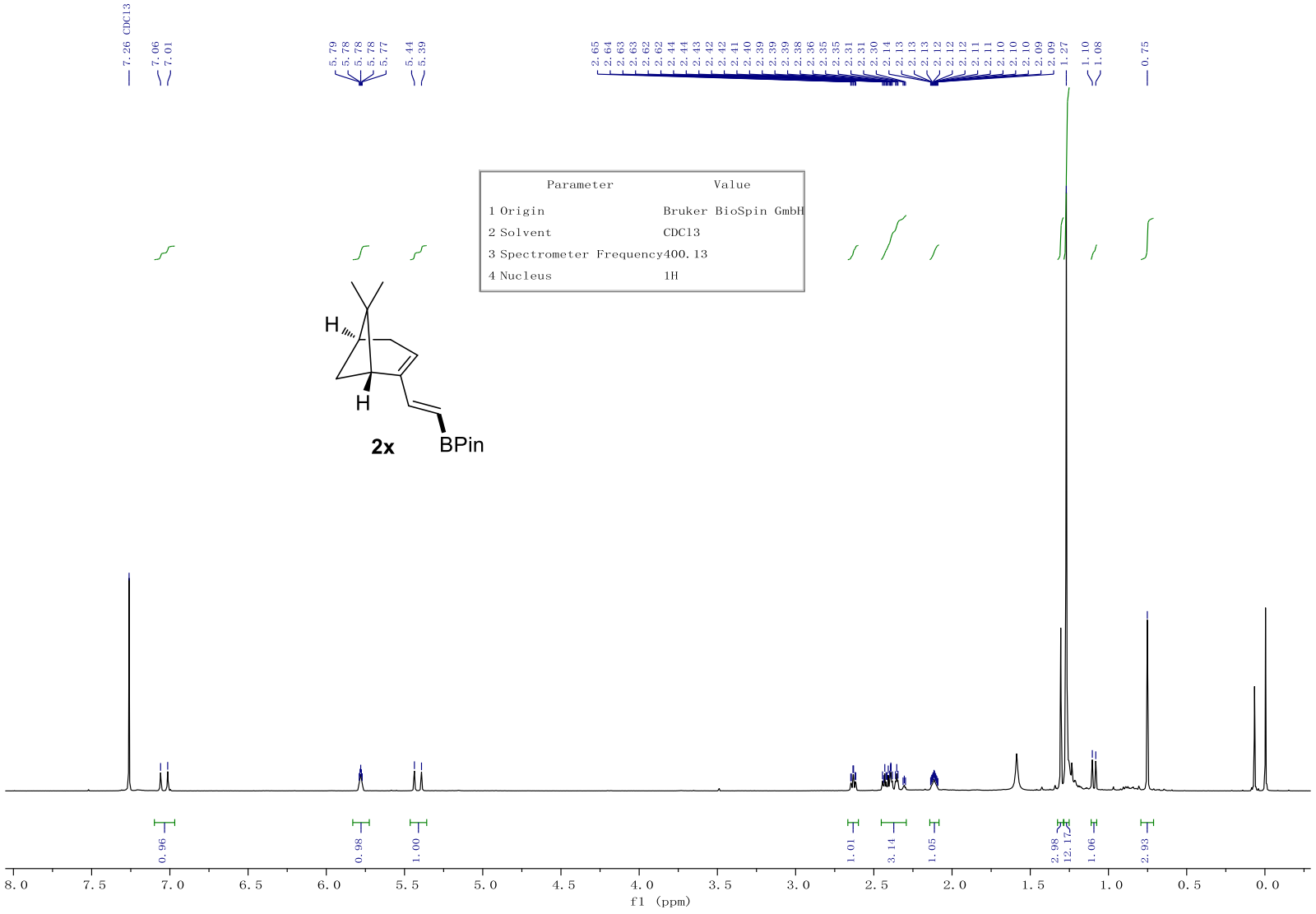

152.27
149.44
129.38
128.69
124.42
122.28
118.42
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Spectrometer Frequency 100.62
4 Nucleus 13C
B
O
OH
2u
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

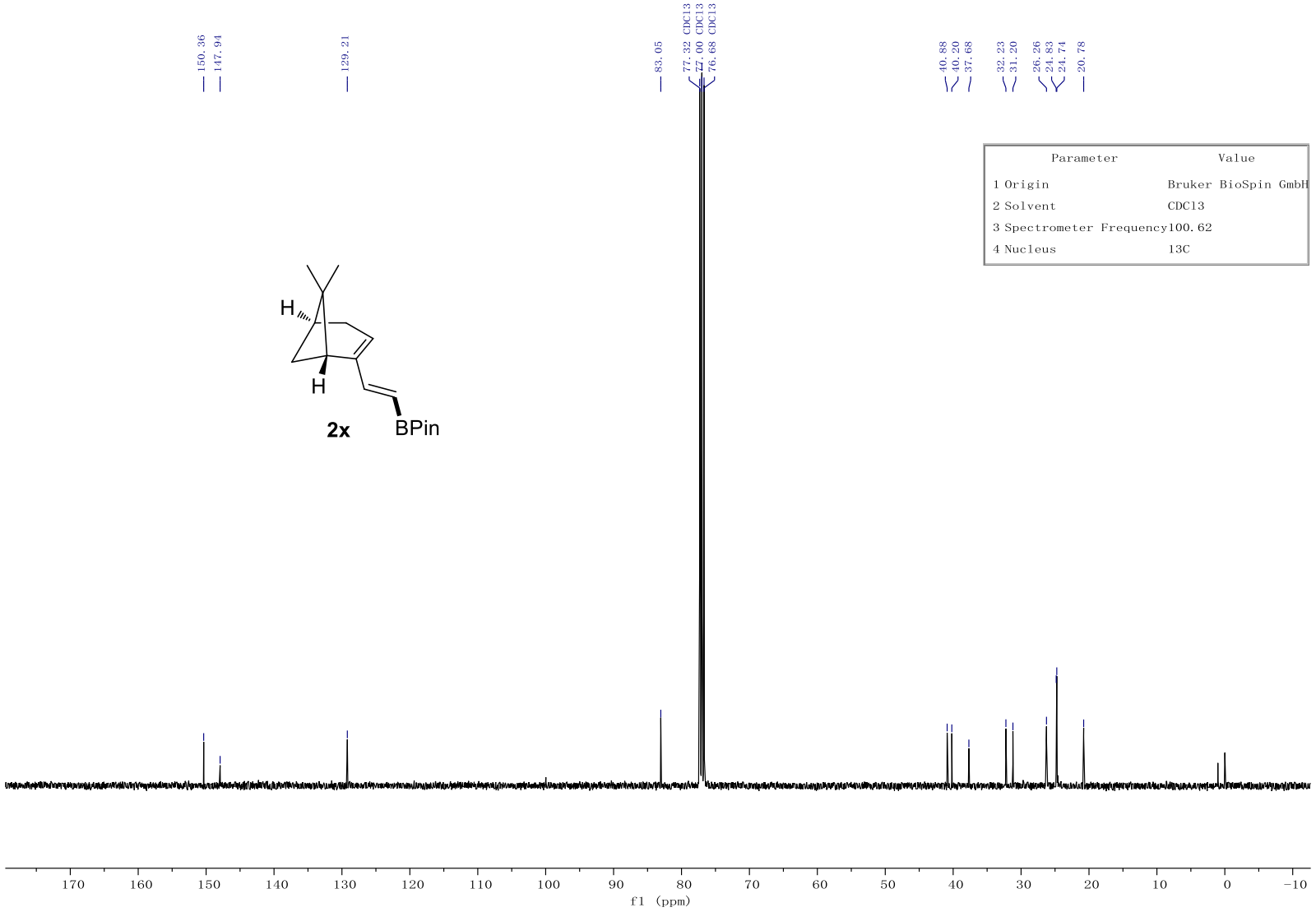

7.26 CDCl3
7.04
7.00
5.97
5.96
5.95
5.45
5.40
2.17
2.15
2.14
2.14
2.13
2.12
1.68
1.67
1.66
1.66
1.65
1.65
1.63
1.63
1.63
1.62
1.61
1.61
1.60
1.59
1.59
1.58
1.58
1.57
1.27
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Spectrometer Frequency 400.13
4 Nucleus 1H
BPin
2v
1.00
1.02
1.05
4.07
6.47
12.48
9.0 8.5 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 0.0 −0
f1 (ppm)

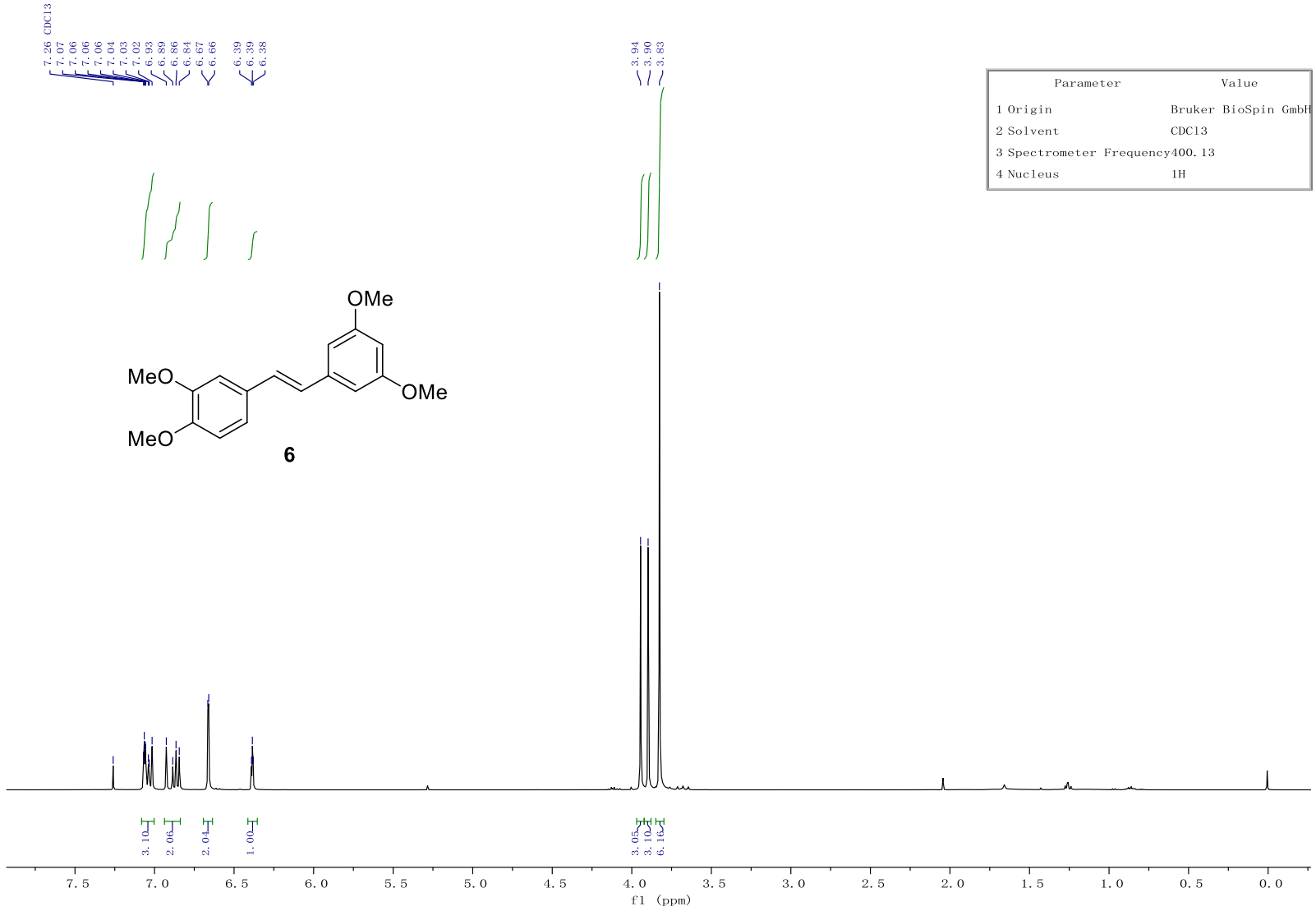

153.23
137.12
134.31
83.01
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
26.16
24.75
23.73
22.39
22.32
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Spectrometer Frequency 100.62
4 Nucleus 13C
BPin
2v
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.26 CDCl3
7.06
7.02
5.99
5.98
5.98
5.97
5.45
5.41
4.74
4.73
4.73
4.72
4.72
4.71
4.71
4.71
4.70
4.70
2.36
2.35
2.34
2.32
2.31
2.30
2.30
2.26
2.20
2.19
2.17
2.16
2.15
2.14
2.14
2.12
2.11
2.10
2.09
2.07
2.06
2.05
2.04
1.74
1.64
1.64
1.62
1.60
1.28
BPin
2w
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Spectrometer Frequency 400.13
4 Nucleus 1H
1.00
0.96
1.00
2.01
2.00
3.14
2.97
2.43
12.07
f1 (ppm)

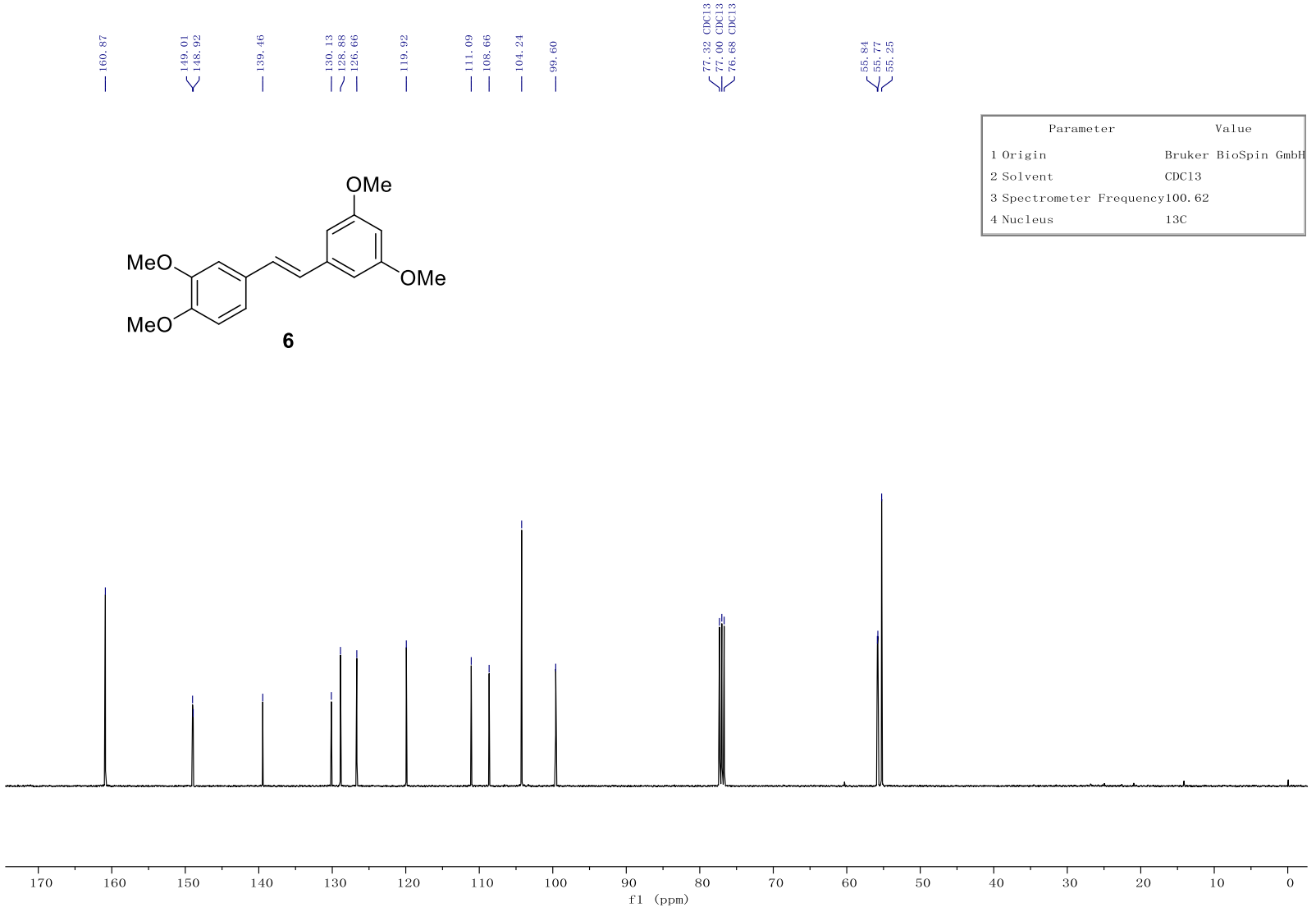

152.58
149.50
136.79
133.48
108.79
83.06
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
41.01
31.52
27.25
24.76
24.13
20.80
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Spectrometer Frequency 100.62
4 Nucleus 13C
BPin
2w
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

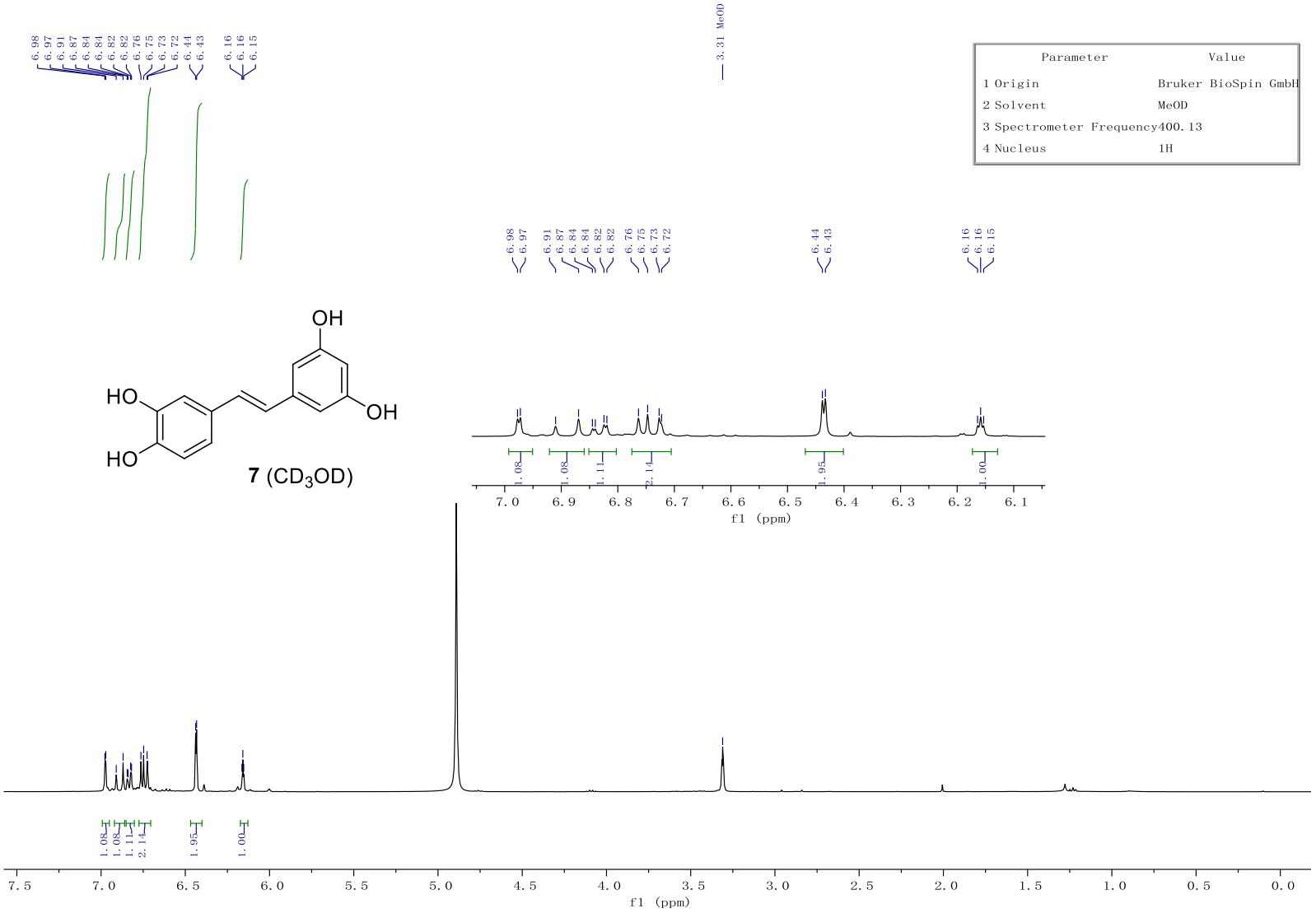

7.26 CDCl3
7.06
7.01
5.79
5.78
5.78
5.78
5.77
5.44
5.39
2.65
2.64
2.63
2.63
2.62
2.44
2.44
2.43
2.42
2.42
2.41
2.40
2.39
2.39
2.39
2.38
2.36
2.35
2.35
2.31
2.31
2.30
2.14
2.13
2.13
2.13
2.12
2.12
2.12
2.11
2.11
2.10
2.10
2.10
2.09
2.09
1.27
1.10
1.08
0.75
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Spectrometer Frequency 400.13
4 Nucleus 1H
H
H
2x
BPin
0.96
0.98
1.00
1.01
3.14
1.05
2.98
12.17
1.06
2.93
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
0.0
f1 (ppm)

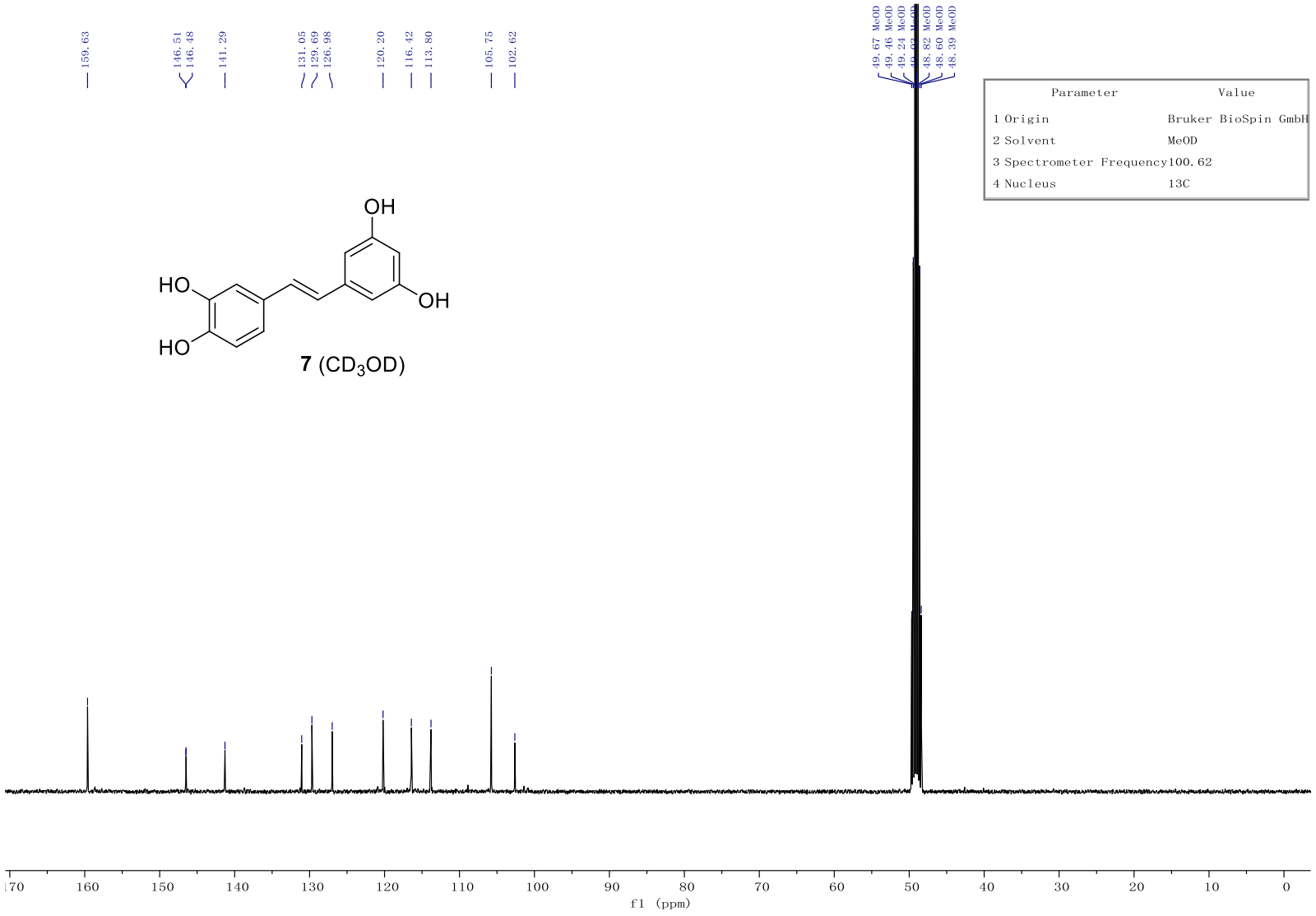

150.36
147.94
129.21
83.05
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
40.88
40.20
37.68
32.23
31.20
26.26
24.83
24.74
20.78
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Spectrometer Frequency 100.62
4 Nucleus 13C
H
H
2x
BPin
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Spectrometer Frequency	400.13
4 Nucleus	1H


160.87
149.01
148.92
139.46
130.13
128.88
126.66
119.92
111.09
108.66
104.24
99.60
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
55.84
55.77
55.25
OMe
MeO
MeO
OMe
6
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Spectrometer Frequency 100.62
4 Nucleus 13C
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


6.98
6.97
6.91
6.87
6.84
6.84
6.82
6.82
6.76
6.75
6.73
6.72
6.44
6.43
6.16
6.16
6.15
3.31 MeOD
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent MeOD
3 Spectrometer Frequency 400.13
4 Nucleus 1H
OH
HO
OH
HO
7 (CD3OD)
1.08
1.08
1.11
2.14
1.95
1.00
f1 (ppm)


159.63
146.51
146.48
141.29
131.05
129.69
126.98
120.20
116.42
113.80
105.75
102.62
49.67 MeOD
49.46 MeOD
49.24 MeOD
48.82 MeOD
48.60 MeOD
48.39 MeOD
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent MeOD
3 Spectrometer Frequency 100.62
4 Nucleus 13C
OH
HO
HO
OH
7 (CD3OD)
f1 (ppm)