Supporting Information

Facile and Regioselective Synthesis of 1-Tetralones via Silver-Catalyzed Ring Expansion

Jiajia Yu,[a] Huijun Zhao,[a] Shuguang Liang,[a] Xiaoguang Bao,*[,c] and Chen Zhu*[,a,b]

[a] Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, 199 Ren-Ai Road, Suzhou, Jiangsu 215123, People's Republic of China

[b] Key Laboratory of Synthetic Chemistry of Natural Substances, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, People's Republic of China

[c] College of Chemistry, Chemical Engineering and Materials Science, Soochow University, 199 Ren-Ai Road, Suzhou, Jiangsu 215123, People's Republic of China

Email: chzhu@suda.edu.cn, xgbao@suda.edu.cn

Table of Contents

1. General experimental details

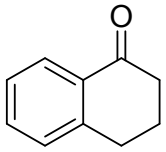
All reactions were maintained under a nitrogen atmosphere unless otherwise stated. Commercially available reagents were used without further purification. Infrared (FT-IR) spectra were recorded on a BRUKER VERTEX 70, ν_{max} in cm^{-1}. ^1H-NMR spectra were recorded on a BRUKER AVANCE III HD (400 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$: δ 7.26). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quadruplet, br = broad, m = multiplet), coupling constants (Hz) and integration. ^{13}C-NMR spectra were recorded on a BRUKER AVANCE III HD (100 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ 77.16). ^{19}F-NMR spectra were recorded on a BRUKER AVANCE III HD (376 MHz) spectrometer. Mass spectra were measured with an Agelent Technologies 6120 Quadrupole LC/MS. High resolution mass spectrometry (HRMS) were measured with a GCT Premier™ and BRUKER micrOTF-Q III. Melting points were measured using INESA WRR and values are uncorrected.

Tertiary cyclobutanols were prepared by the addition of Grignard reagent to the corresponding cyclobutanones according to the reported procedure.[1]

2. General procedure for the synthesis of 1-tetralones

Cyclobutanol **1** (0.3 mmol, 1.0 equiv), $AgNO_3$ (0.06 mmol, 0.2 equiv), and $K_2S_2O_8$ (0.9 mmol, 3.0 equiv) were loaded in a flask which was subjected to evacuation/flushing with nitrogen three times. A mixed solvent DCM/H_2O (0.5/0.5 mL, 0.3 M) was added to the mixture via syringe and the mixture was then stirred at rt until the starting material had been consumed as determined by TLC. The mixture was extracted with CH_2Cl_2 (3×10 mL). The combined organic extracts were washed by brine, dried over Na_2SO_4, filtered, concentrated, and purified by flash chromatography on silica gel (ethyl acetate /PE) to give 1-tetralone product **2**.

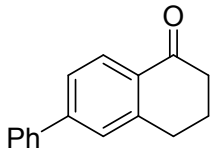
3. Characterization of new compounds



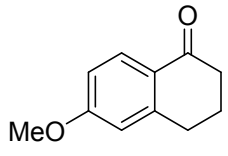
2a: yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.0 Hz, 1H), 7.37 (dt, J = 7.6, 1.2 Hz, 1H), 7.20 (t, J = 7.2 Hz, 1H), 7.15 (d, J = 7.6 Hz, 1H), 2.87 (t, J = 6.0 Hz, 2H), 2.56 (t, J = 6.4 Hz, 2H), 2.08-2.00 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.4, 144.5, 133.4, 132.6, 128.8, 127.1, 126.6, 39.2, 29.7, 23.3. FT-IR: ν (cm^{-1}) 3025, 2943, 1679, 1599, 1454, 1323, 1259, 1183. HRMS [ESI] calcd for $C_{10}H_{10}ONa$ $[M+Na]^+$ 169.0629, found 169.0623. ESI $[M+H]^+$ 147.1.

---

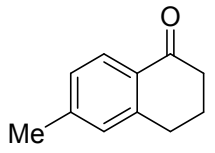
[1] (a) Casey, B. M.; Eakin, C. A.; Flowers, R. A. II, *Tetrahedron Lett.* **2009**, *50*, 1264-1266. (b) Xu, H.-J.; Zhu, F.-F.; Shen, Y.-Y.; Wan, X.; Feng, Y.-S. *Tetrahedron* **2012**, *68*, 4145-4151. (c) Rosa, D.; Chtchemelinine, A.; Orellana, A. *Synthesis* **2012**, *12*, 1885-1891.



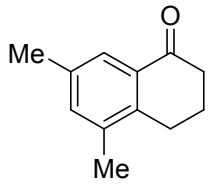
2b: white solid, m.p. 112-114 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.4 Hz, 1H), 7.55-7.50 (m, 2H), 7.44 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.40-7.34 (m, 3H), 7.33-7.27 (m, 1H), 2.93 (t, *J* = 6.0 Hz, 2H), 2.59 (t, *J* = 6.4 Hz, 2H), 2.12-2.04 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (include one overlapping C) δ 198.1, 146.0, 144.9, 140.0, 131.5, 128.9, 128.2, 127.8, 127.3, 125.5, 39.2, 29.9, 23.3. FT-IR: ν (cm^{-1}) 2955, 2938, 1670, 1603, 1503, 1347, 1279. HRMS [ESI] calcd for $C_{16}H_{14}ONa$ $[M+Na]^+$ 245.0942, found 245.0944. ESI $[M+H]^+$ 223.1.



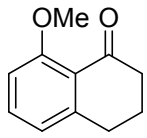
2c: yellow solid, m.p. 73-75 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.8 Hz, 1H), 6.74 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.63 (d, *J* = 2.4 Hz, 1H), 3.78 (s, 3H), 2.85 (t, *J* = 6.0 Hz, 2H), 2.53 (t, *J* = 6.4 Hz, 2H), 2.08-2.00 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 163.5, 146.9, 129.6, 126.3, 113.0, 112.6, 55.4, 38.9, 30.2, 23.4. FT-IR: ν (cm^{-1}) 2947, 2853, 1670, 1589, 1431, 1326, 1162, 1032. HRMS [ESI] calcd for $C_{11}H_{12}O_2Na$ $[M+Na]^+$ 199.0735, found 199.0730. ESI $[M+H]^+$ 177.1.



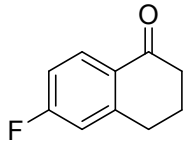
2d: yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.0 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 7.05 (s, 1H), 2.91 (t, *J* = 6.0 Hz, 2H), 2.62 (t, *J* =6.4 Hz, 2H), 2.37 (s, 3H), 2.15-2.07 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.2, 144.6, 144.2, 130.3, 129.2, 127.6, 127.3, 39.1, 29.7, 23.4, 21.7. FT-IR: ν (cm^{-1}) 2943, 2867, 1677, 1606, 1283. HRMS [ESI] calcd for $C_{11}H_{12}ONa$ $[M+Na]^+$ 183.0786, found 183.0783. ESI $[M+H]^+$ 161.1.



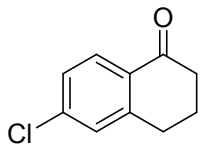
2e: yellow solid, m.p. 47-48 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.18 (s, 1H), 2.81 (t, *J* = 6.0 Hz, 2H), 2.61 (t, *J* = 6.4 Hz, 2H), 2.32 (s, 3H), 2.27 (s, 3H), 2.16-2.09 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.6, 139.4, 135.7, 135.4, 135.1, 132.2, 124.6, 38.3, 25.7, 22.2, 20.3, 18.9. FT-IR: ν (cm^{-1}) 2938, 2866, 1672, 1697, 1476, 1307, 1132, 1094. HRMS [ESI] calcd for $C_{12}H_{14}ONa$ $[M+Na]^+$ 197.0942, found 197.0938. ESI $[M+H]^+$ 175.1.



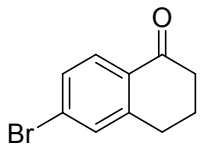
2f: yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, *J* = 8.0 Hz 1H), 6.79-6.73 (m, 2H), 3.84 (s, 3H), 2.85 (t, *J* = 6.0 Hz 2H), 2.56 (t, *J*= 6.4 Hz 2H), 2.03-1.95 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 160.4, 147.2, 133.9, 122.3, 120.7, 109.9, 56.0, 41.0, 30.8, 22.8. FT-IR: ν (cm^{-1}) 2939, 2837, 1671, 1592, 1468, 1304, 1176, 1084. HRMS [ESI] calcd for $C_{11}H_{12}O_2Na$ $[M+Na]^+$ 199.0735, found 199.0733. ESI $[M+H]^+$ 177.1.



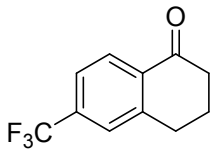
2g: yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 8.8, 6.0 Hz, 1H), 7.02-6.90 (m, 2H), 2.96 (t, *J* = 6.0 Hz, 2H), 2.64 (t, *J* = 6.4 Hz, 2H), 2.19-2.10 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 165.7 (d, $J_{C\text{-}F}$ = 254 Hz), 147.5 (d, $J_{C\text{-}F}$ = 9.0 Hz), 130.3 (d, $J_{C\text{-}F}$ = 9.8 Hz), 129.3 (d, $J_{C\text{-}F}$ = 2.6 Hz), 115.0 (d, $J_{C\text{-}F}$ = 21.2 Hz), 114.3 (d, $J_{C\text{-}F}$ = 21.8 Hz), 38.8, 29.9 (d, $J_{C\text{-}F}$ = 1.4 Hz), 23.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -104.8 (s). FT-IR: ν (cm^{-1}) 2946, 1681, 1488, 1322, 1185, 1026. HRMS [ESI] calcd for $C_{10}H_9FONa$ $[M+Na]^+$ 187.0535, found 187.0526. ESI $[M+H]^+$ 165.1.



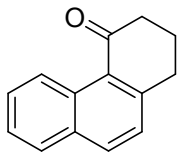
2h: yellow solid, m.p. 23-25 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.4 Hz, 1H), 7.30-7.24 (m, 2H), 2.94 (t, J = 6.0 Hz, 2H), 2.65 (t, J = 6.0 Hz, 2H), 2.18-2.10 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.8, 145.5, 139.2, 130.6, 128.4, 128.1, 126.7, 38.4, 29.1, 22.6. FT-IR: ν (cm^{-1}) 2946, 2882, 1931, 1683, 1429, 1319, 1224, 1056. HRMS [ESI] calcd for $C_{10}H_9ClONa$ $[M+Na]^+$ 203.0239, found 203.0228. ESI $[M+H]^+$ 181.1.



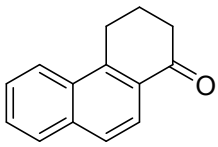
2i: yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J =8.4 Hz, 1H), 7.46-7.42 (m, 2H), 2.94 (t, J = 6.0 Hz, 2H), 2.65 (t, J = 6.4 Hz, 2H), 2.18-2.10 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 145.6, 131.2, 130.9, 129.6, 128.4, 128.1, 38.4, 29.0, 22.6. FT-IR: ν (cm^{-1}) 2943, 2870, 1681, 1585, 1276, 1187, 1023. HRMS [ESI] calcd for $C_{10}H_9BrONa$ $[M+Na]^+$ 246.9734, found 246.9731. ESI $[M+H]^+$ 225.0.



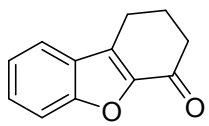
2j: yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 8.0 Hz, 1H), 7.54 (d, J = 8.4 Hz, 1 H), 7.53 (s, 1H), 3.03 (t, J = 6.0 Hz, 2H), 2.70 (t, J = 6.4 Hz, 2H), 2.22-2.14 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 144.9, 135.0, 134.5 (q, $J_{C\text{-}F}$ = 32.2 Hz), 127.9, 125.9 (q, $J_{C\text{-}F}$ = 3.8 Hz), 123.6 (q, $J_{C\text{-}F}$ = 271 Hz), 123.4 (q, $J_{C\text{-}F}$ = 3.7 Hz), 39.0, 29.6, 22.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.3 (s). FT-IR: ν (cm^{-1}) 2950, 2876, 1691, 1424, 1326, 1166, 1025. HRMS [ESI] calcd for $C_{11}H_9F_3ONa$ $[M+Na]^+$ 237.0503, found 237.0501. ESI $[M+H]^+$ 215.1.



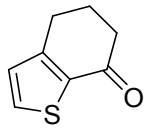
2k: yellow solid, m.p. 62-64 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.32 (d, J = 8.8 Hz, 1H), 7.78 (d, J = 8.4 Hz, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.51 (t, J = 8.0 Hz, 1H), 7.37 (t, J = 8.0 Hz 1H), 7.18 (d, J = 8.4 Hz, 1H), 2.98 (t, J = 6.0 Hz, 2H), 2.66 (t, J = 6.4 Hz, 2H), 2.10-2.02 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.5, 146.8, 134.2, 132.8, 131.4, 128.8, 128.3, 127.3, 127.0, 126.7, 125.8, 41.1, 31.6, 23.0. FT-IR: ν (cm^{-1}) 2942, 2871, 1655, 1594, 1331, 1196, 1016. HRMS [ESI] calcd for $C_{14}H_{12}ONa$ $[M+Na]^+$ 219.0786, found 219.0785. ESI $[M+H]^+$ 197.1.



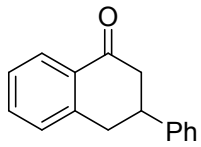
2l: yellow solid, m.p. 90-92 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17-8.13 (m 1H), 8.12 (d, J = 8.8 Hz, 1H), 7.90-7.85 (m, 2H), 7.77 (d, J = 8.8 Hz, 1H), 7.65-7.57 (m, 2H), 3.40 (t, J = 6.0 Hz, 2H), 2.76 (t, J = 6.4 Hz, 2H), 2.36-2.28 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.6, 142.9, 135.7, 131.4, 130.0, 128.8, 128.3, 126.9, 126.7, 124.8, 122.8, 38.4, 25.6, 22.8. FT-IR: ν (cm^{-1}) 3056, 2947, 1671, 1378, 1242, 1012. HRMS [ESI] calcd for $C_{14}H_{12}ONa$ $[M+Na]^+$ 219.0786, found 219.0781. ESI $[M+H]^+$ 197.1.



2m: yellow solid, m.p. 55-57 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 8.0 Hz, 1H), 7.58 (d, J = 8.4 Hz, 1H), 7.50 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.33 (ddd, J = 7.6, 7.6, 1.2 Hz, 1H), 3.01 (t, J = 6.0 Hz, 2H), 2.72 (t, J = 6.4 Hz, 2H), 2.34-2.26 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.0, 155.4, 147.2, 134.2, 128.6, 125.9, 123.2, 121.3, 112.4, 38.1, 23.6, 20.9. FT-IR: ν (cm^{-1}) 2952, 1670, 1591, 1479, 1396, 1194. HRMS [ESI] calcd for $C_{12}H_{10}O_2Na$ $[M+Na]^+$ 209.0578, found 209.0571. ESI $[M+H]^+$ 187.1.

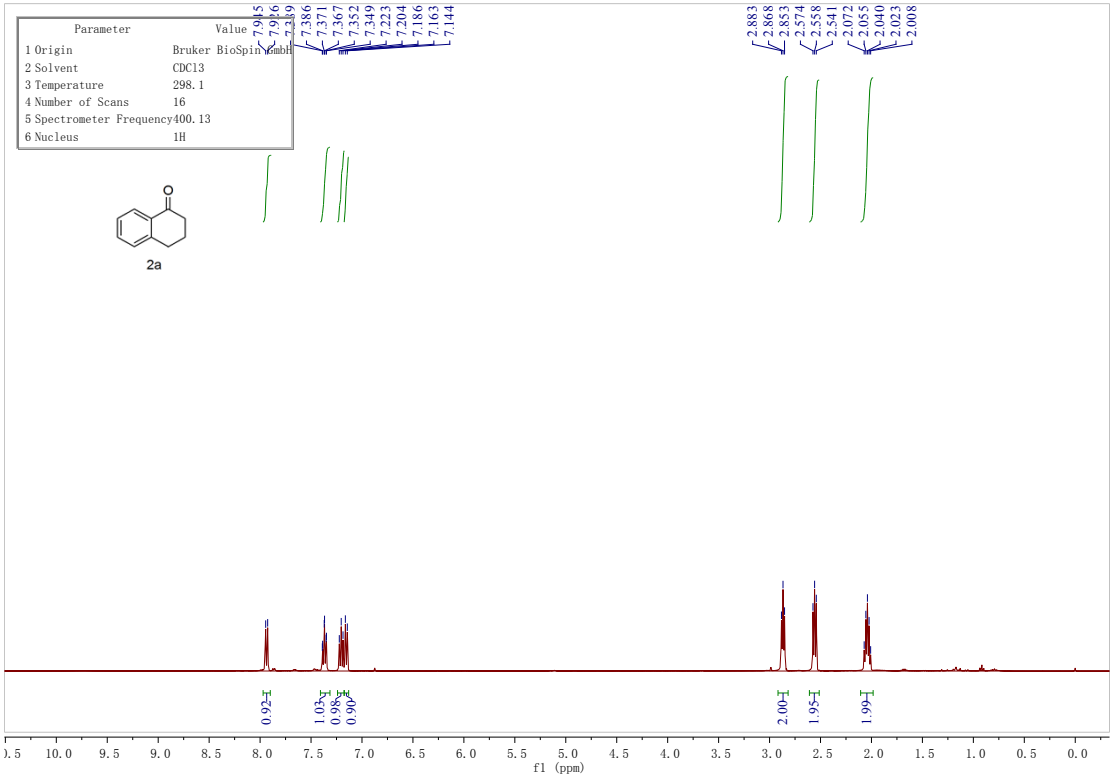


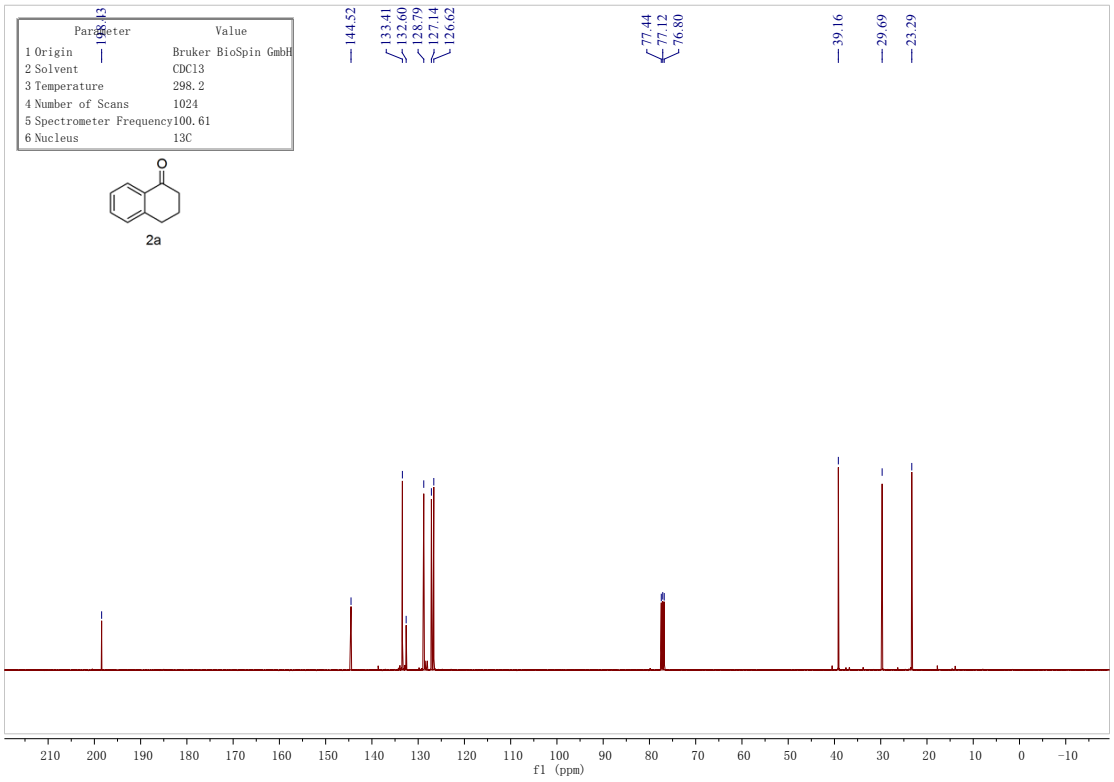
2n: red solid, m.p. 29-31 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 4.8, 0.8 Hz, 1H), 6.97 (d, *J* = 4.4 Hz, 1H), 2.88 (t, *J* = 6.0 Hz, 2H), 2.60 (t, *J* = 6.4 Hz, 2H), 2.22-2.13 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.9, 152.2, 136.0, 133.3, 127.8, 37.7, 25.5, 23.9. FT-IR: ν (cm^{-1}) 3110, 2954, 2883, 1650, 1454, 1344, 1290, 1137, 1025. HRMS [ESI] calcd for C_8H_8OSNa $[M+Na]^+$175.0194, found 175.0188. ESI $[M+H]^+$ 153.1.

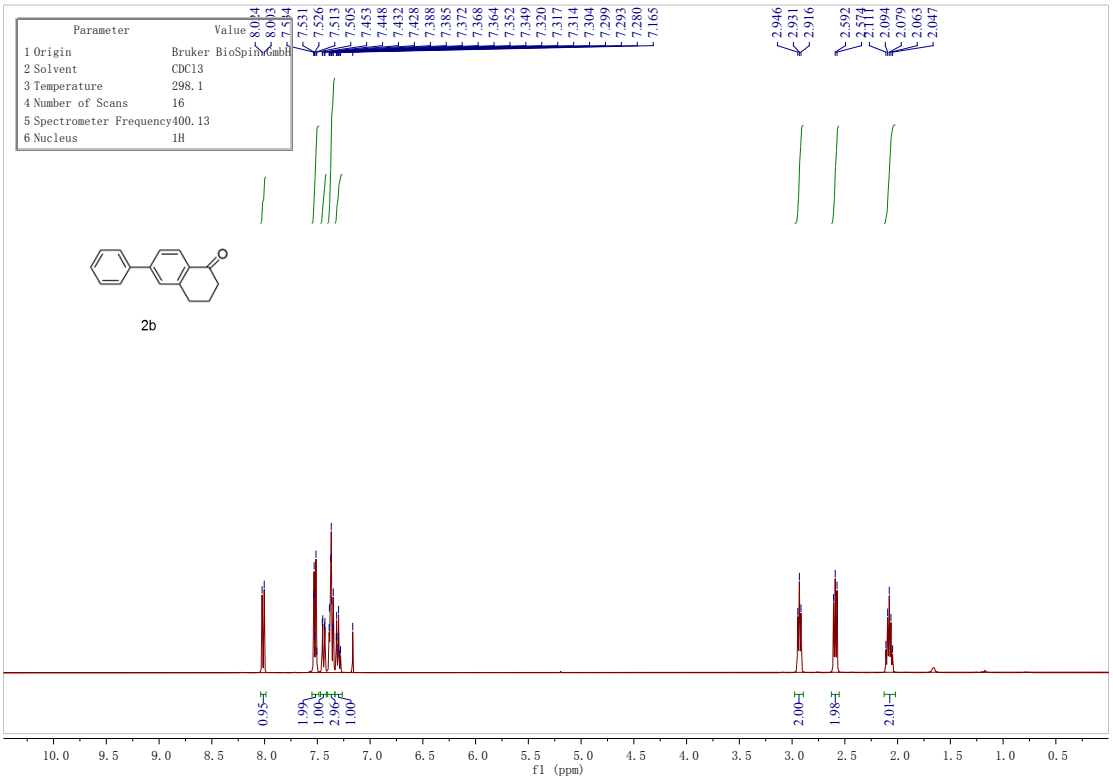


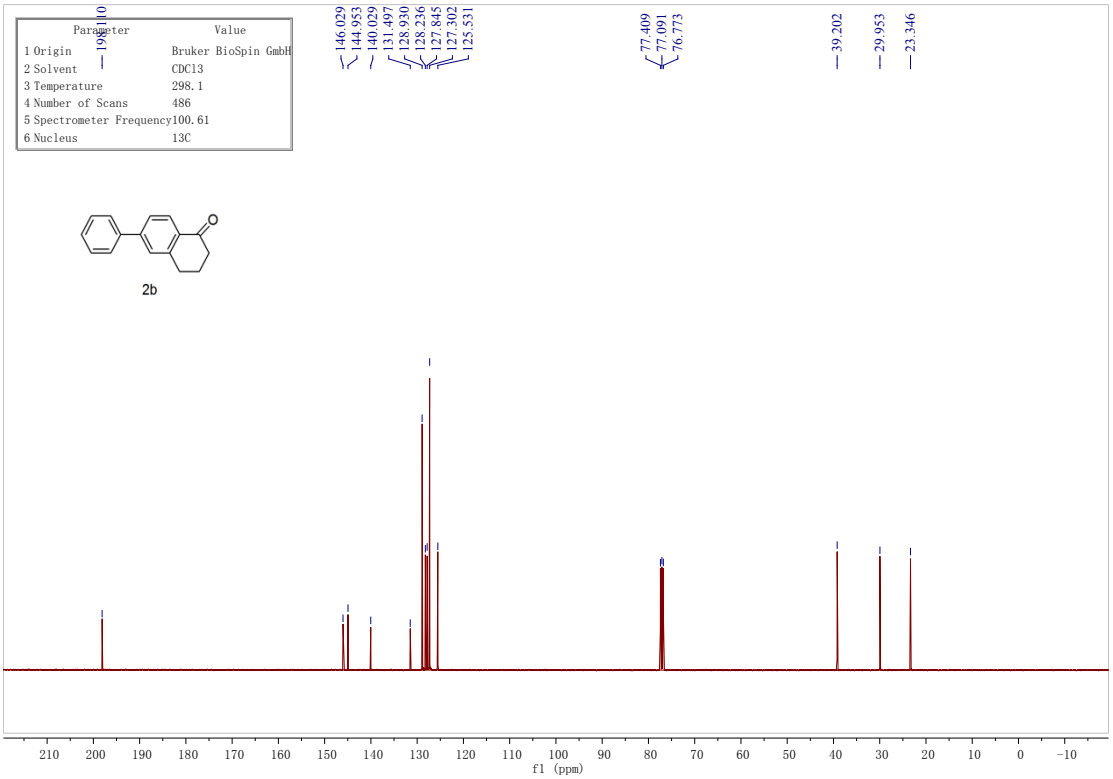
2o: white solid, m.p. 63-65 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.6 Hz, 1H), 7.51 (dt, *J* = 7.6, 1.6 Hz, 1H), 7.39-7.32 (m, 3H), 7.32-7.25 (m, 4H), 3.51-3.41 (m, 1H), 3.26-3.13 (m, 2H), 2.97 (ddd, *J* = 16.8, 4.0, 1.6 Hz, 1H), 2.83 (dd, *J* = 16.8, 12.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 143.0, 142.9, 133.3, 131.7, 128.4, 128.3, 126.8, 126.6, 126.5, 126.2, 45.5, 40.7, 37.2. FT-IR: ν (cm^{-1}) 3032, 2935, 2870, 1673, 1598, 1407, 1262, 1075. HRMS [ESI] calcd for $C_{16}H_{14}ONa$ $[M+Na]^+$ 245.0942, found 245.0954. ESI $[M+H]^+$ 223.1.

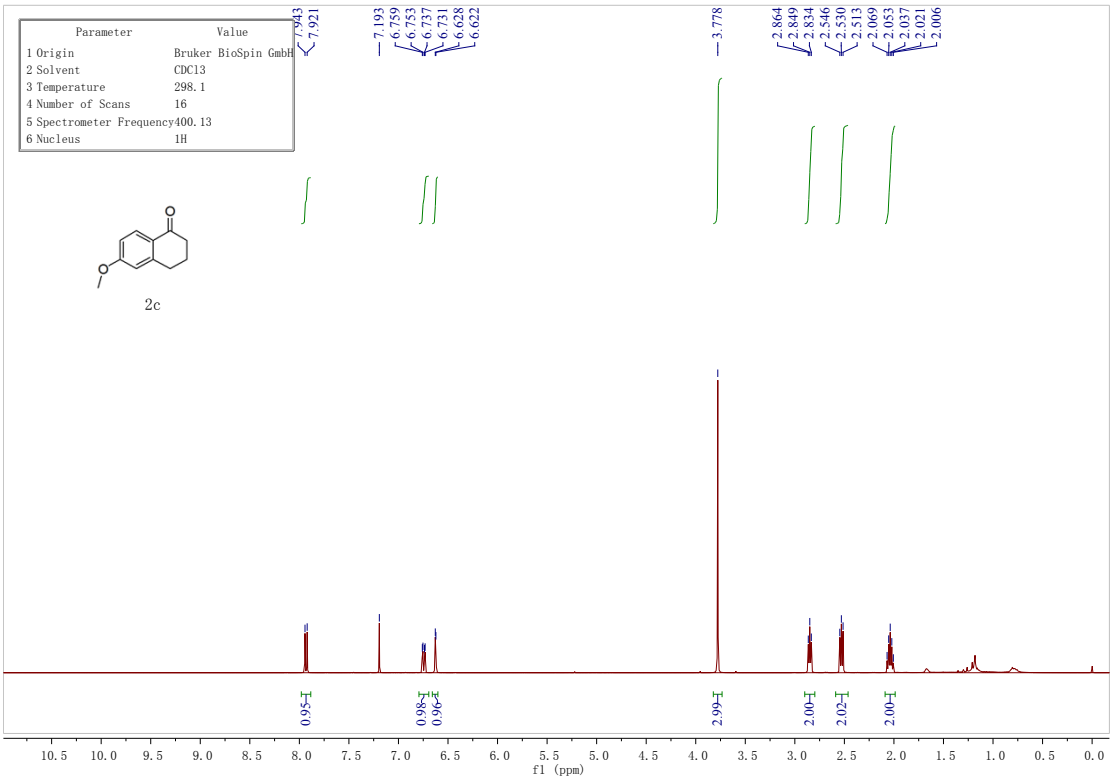
4. ^{1}H, ^{13}C, and ^{19}F NMR spectra of products


Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 16
5 Spectrometer Frequency 400.13
6 Nucleus 1H
7.945
7.916
7.386
7.371
7.367
7.352
7.349
7.223
7.204
7.186
7.163
7.144
2.883
2.868
2.853
2.574
2.558
2.541
2.072
2.055
2.040
2.023
2.008
2a
0.92
1.03
0.98
0.90
2.00
1.95
1.99
f1 (ppm)

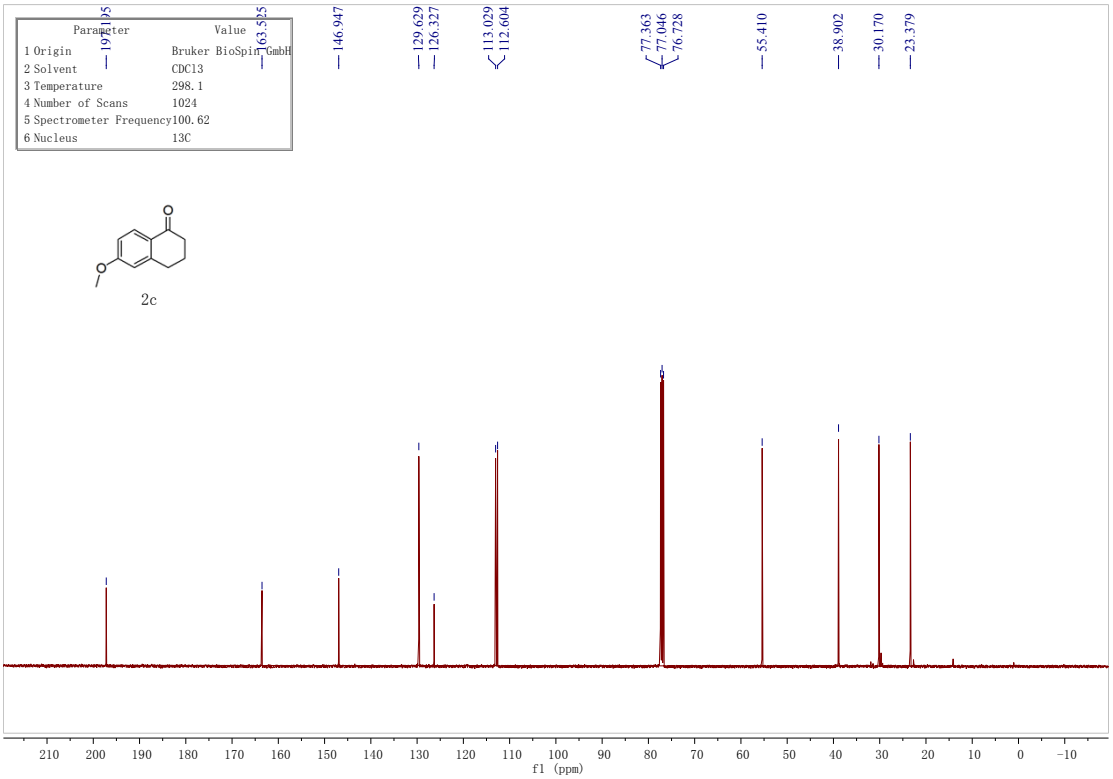

Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 1024
5 Spectrometer Frequency 100.61
6 Nucleus 13C
144.52
133.41
132.60
128.79
127.14
126.62
77.44
77.12
76.80
39.16
29.69
23.29
2a
f1 (ppm)


Parameter Value
1 Origin Bruker BioSpinGmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 16
5 Spectrometer Frequency 400.13
6 Nucleus 1H
8.014
8.003
7.534
7.531
7.526
7.513
7.505
7.453
7.448
7.432
7.428
7.388
7.385
7.372
7.368
7.364
7.352
7.349
7.320
7.317
7.314
7.304
7.299
7.293
7.280
7.165
2.946
2.931
2.916
2.592
2.577
2.571
2.094
2.079
2.063
2.047
2b
0.95
1.99
1.00
2.96
1.00
2.00
1.98
2.01
f1 (ppm)

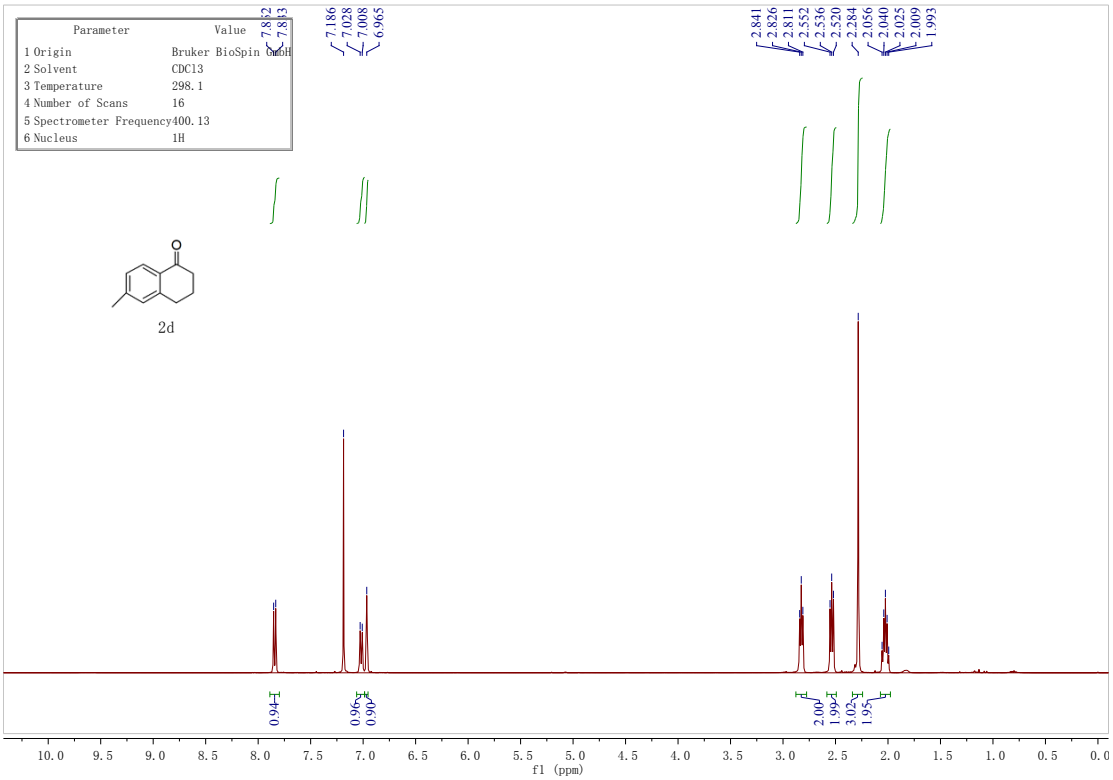

Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 486
5 Spectrometer Frequency 100.61
6 Nucleus 13C
198.410
146.029
144.953
140.029
131.497
128.930
128.236
127.845
127.302
125.531
77.409
77.091
76.773
39.202
29.953
23.346
2b
f1 (ppm)

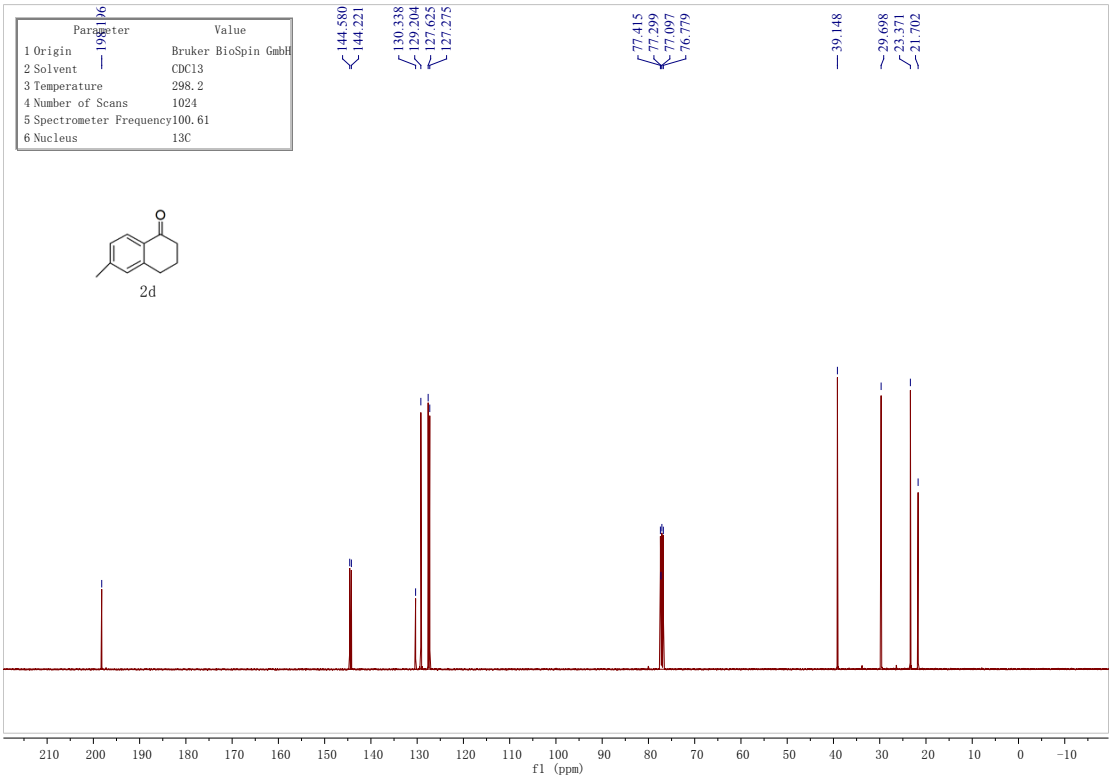

Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 16
5 Spectrometer Frequency 400.13
6 Nucleus 1H
7.943
7.921
7.193
6.759
6.753
6.737
6.731
6.628
6.622
3.778
2.864
2.849
2.834
2.546
2.530
2.513
2.069
2.053
2.037
2.021
2.006
0.95
0.98
0.96
2.99
2.00
2.02
2.00
f1 (ppm)

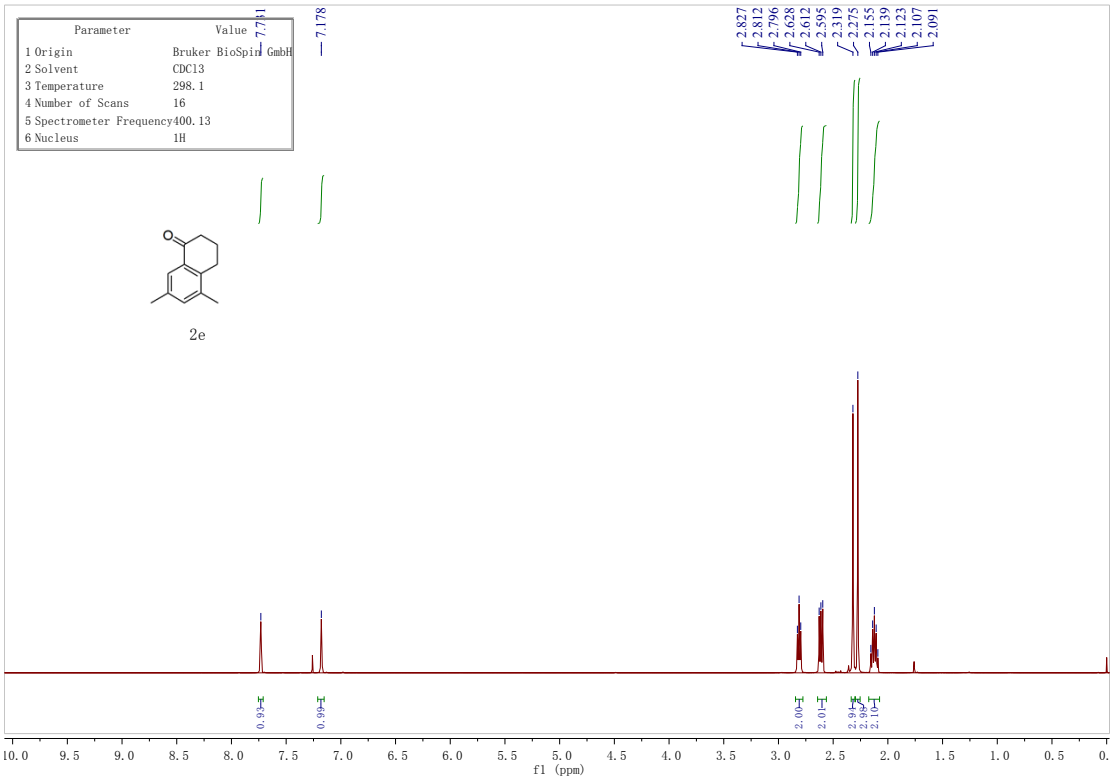
2c


Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 1024
5 Spectrometer Frequency 100.62
6 Nucleus 13C
197.095
163.525
146.947
129.629
126.327
113.029
112.604
77.363
77.046
76.728
55.410
38.902
30.170
23.379
f1 (ppm)

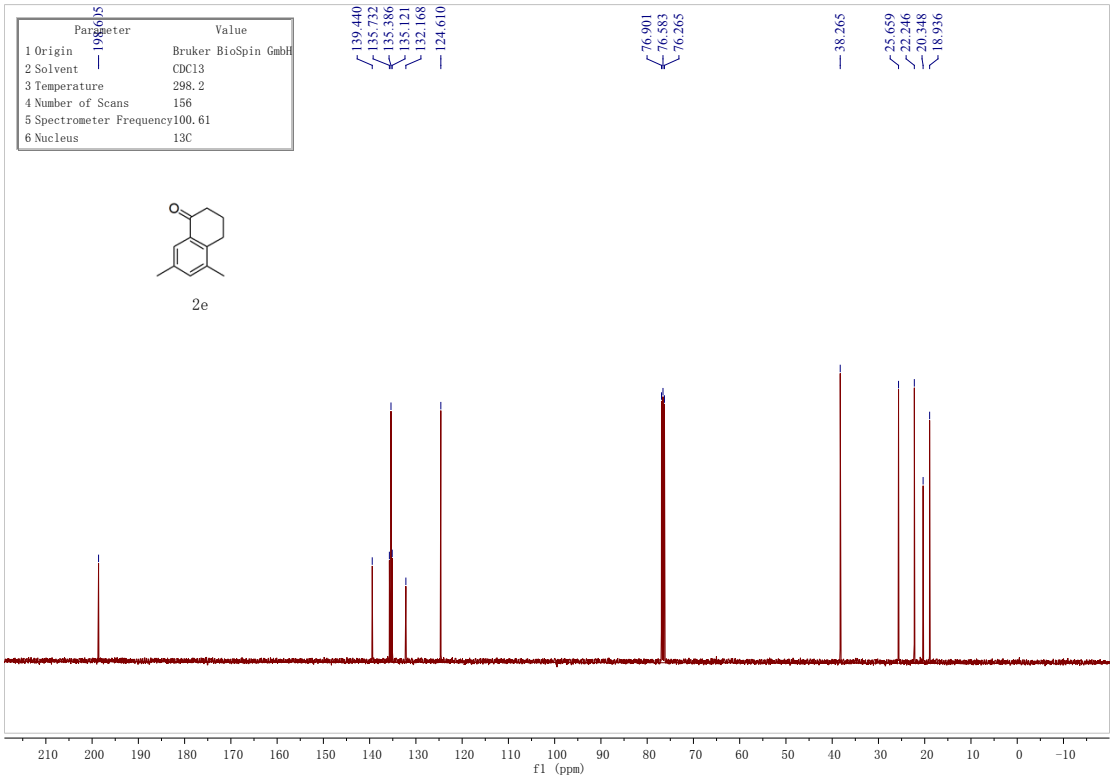
2c


Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 16
5 Spectrometer Frequency 400.13
6 Nucleus 1H
7.852
7.833
7.186
7.028
7.008
6.965
2.841
2.826
2.811
2.552
2.536
2.520
2.284
2.056
2.040
2.025
2.009
1.993
2d
0.94
0.96
0.90
2.00
1.99
3.02
1.95
f1 (ppm)

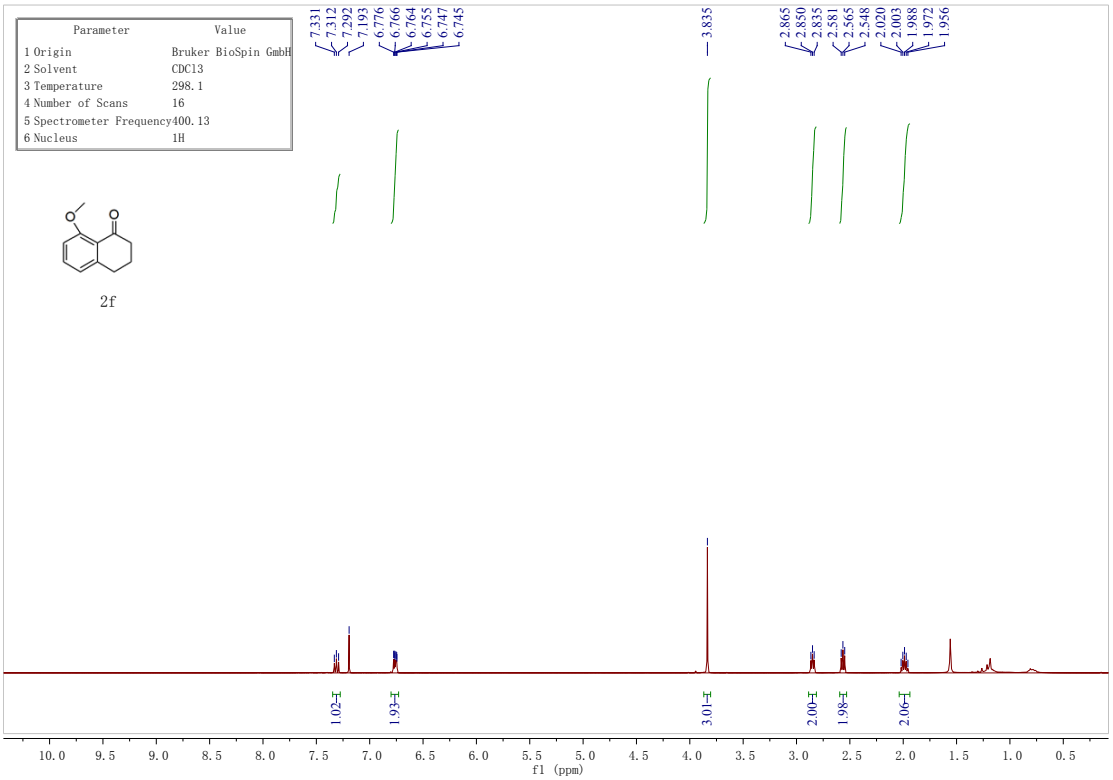

Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 1024
5 Spectrometer Frequency 100.61
6 Nucleus 13C
196.096
144.580
144.221
130.338
129.204
127.625
127.275
77.415
77.299
77.097
76.779
39.148
29.698
23.371
21.702
2d
f1 (ppm)


Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 16
5 Spectrometer Frequency 400.13
6 Nucleus 1H
7.781
7.178
2.827
2.812
2.796
2.628
2.612
2.595
2.319
2.275
2.155
2.139
2.123
2.107
2.091
0.99
0.99
2.00
2.01
2.91
2.91
2.10
f1 (ppm)

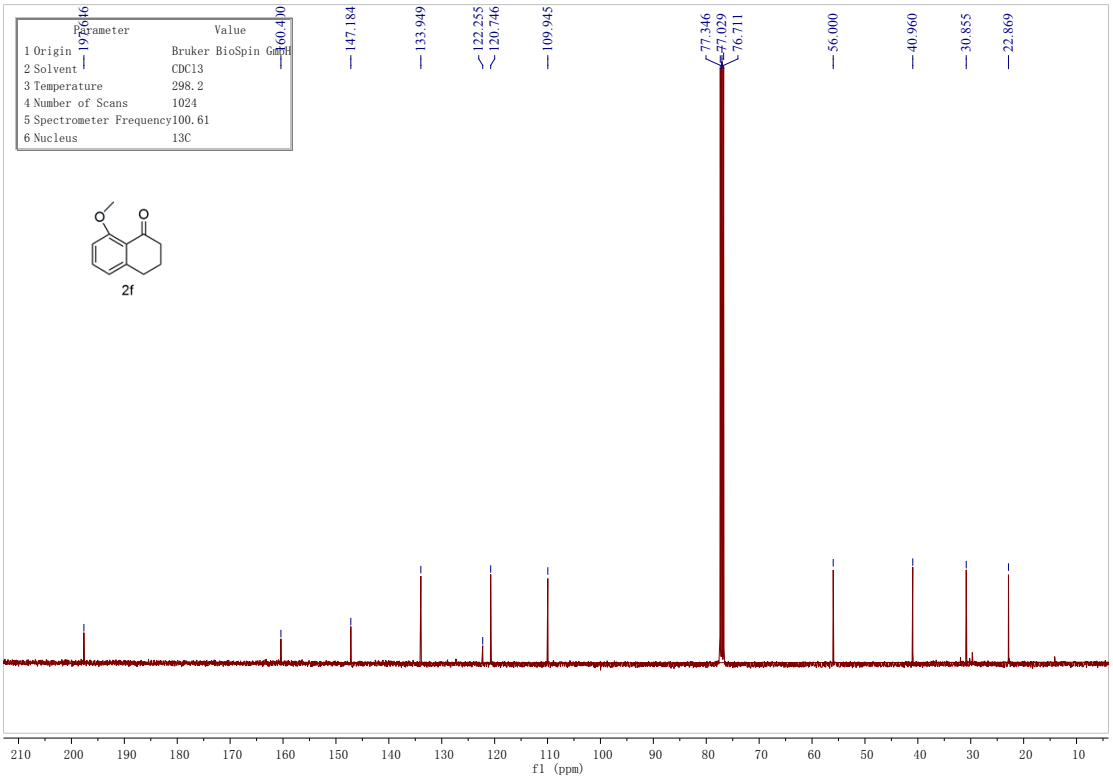
2e


Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 156
5 Spectrometer Frequency 100.61
6 Nucleus 13C
198.605
139.440
135.732
135.386
135.121
132.168
124.610
76.901
76.583
76.265
38.265
25.659
22.246
20.348
18.936
f1 (ppm)

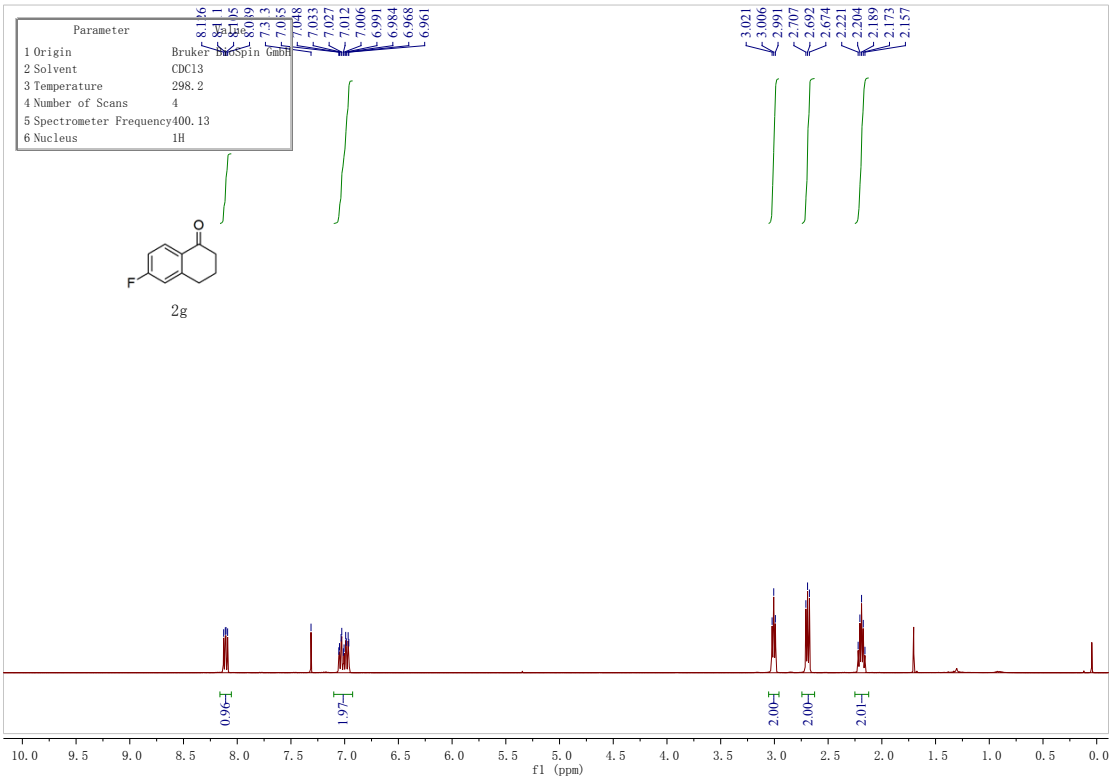
2e


Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 16
5 Spectrometer Frequency 400.13
6 Nucleus 1H
7.331
7.312
7.292
7.193
6.776
6.766
6.764
6.755
6.747
6.745
3.835
2.865
2.850
2.835
2.581
2.565
2.548
2.020
2.003
1.988
1.972
1.956
1.02
1.93
3.01
2.00
1.98
2.06
f1 (ppm)

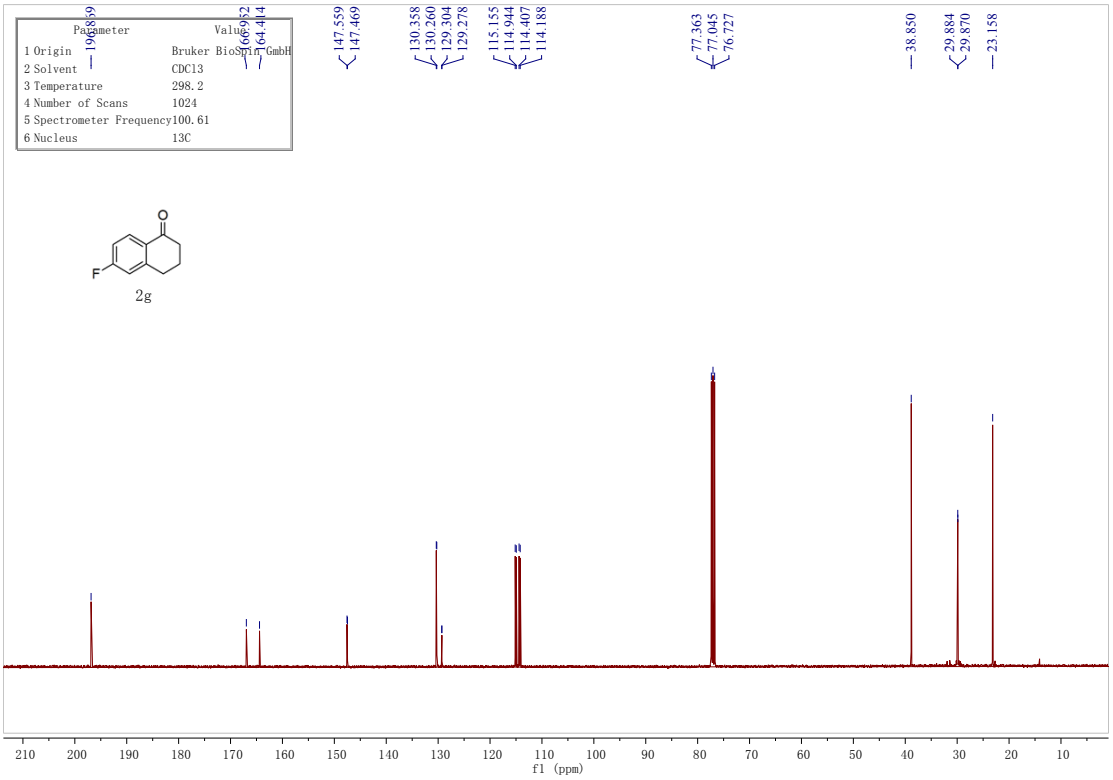
2f


Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 1024
5 Spectrometer Frequency 100.61
6 Nucleus 13C
197.046
160.400
147.184
133.949
122.255
120.746
109.945
77.346
77.029
76.711
56.000
40.960
30.855
22.869
f1 (ppm)

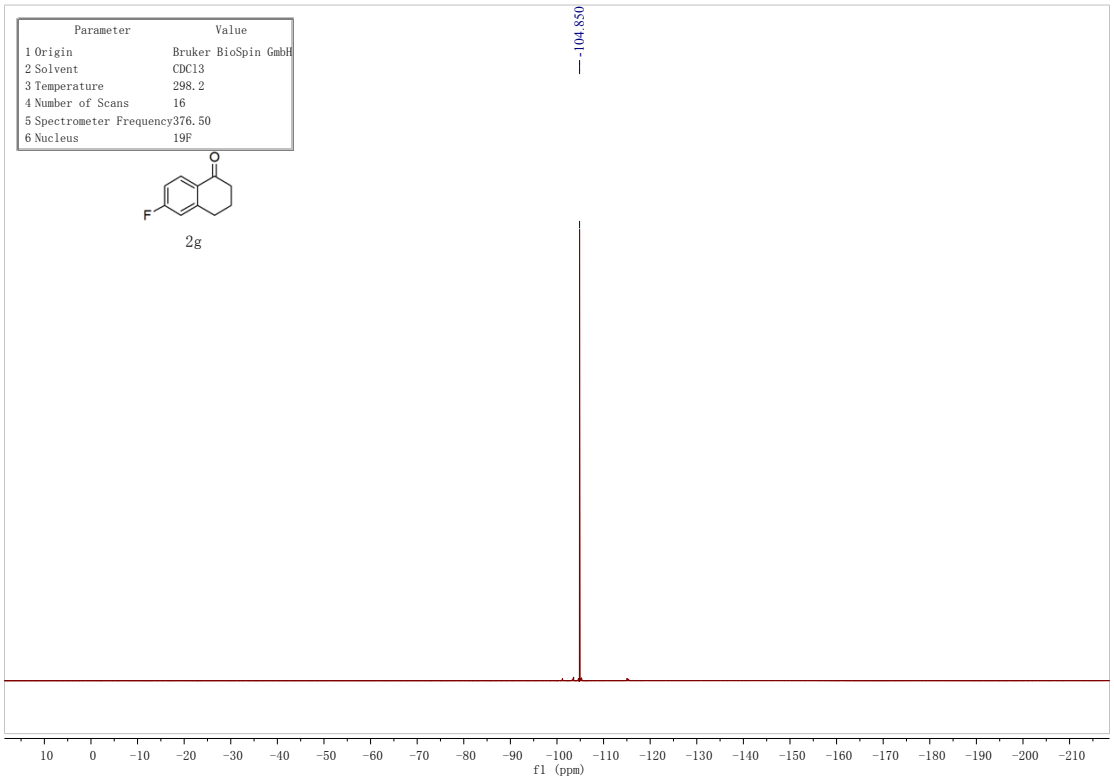
2f

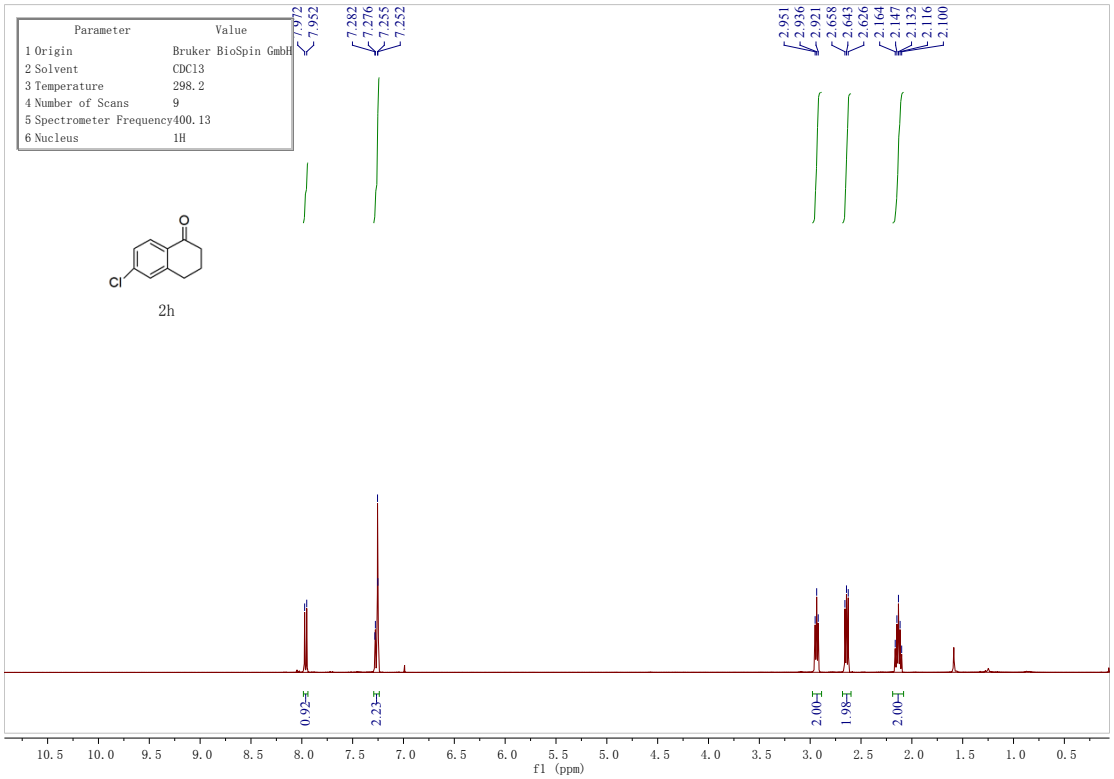

Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 4
5 Spectrometer Frequency 400.13
6 Nucleus 1H
8.126
8.114
8.105
8.089
7.313
7.305
7.048
7.033
7.027
7.012
7.006
6.991
6.984
6.968
6.961
3.021
3.006
2.991
2.707
2.692
2.674
2.221
2.204
2.189
2.173
2.157
0.96
1.97
2.00
2.00
2.01
f1 (ppm)

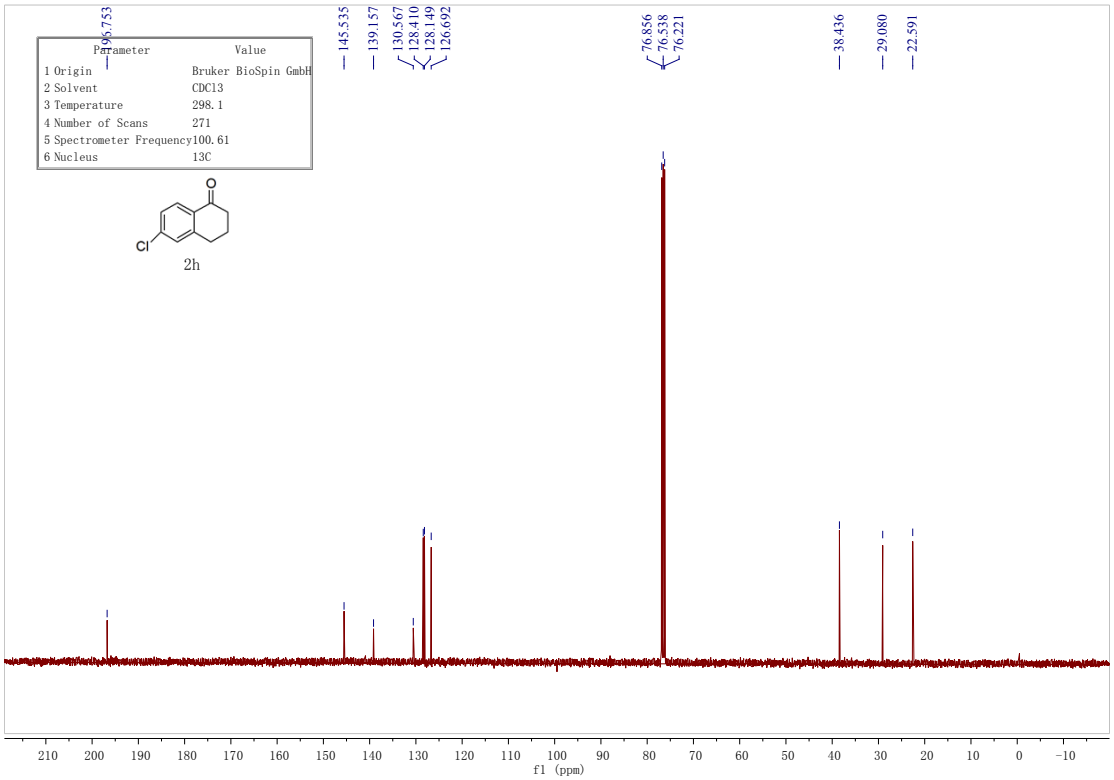
2g

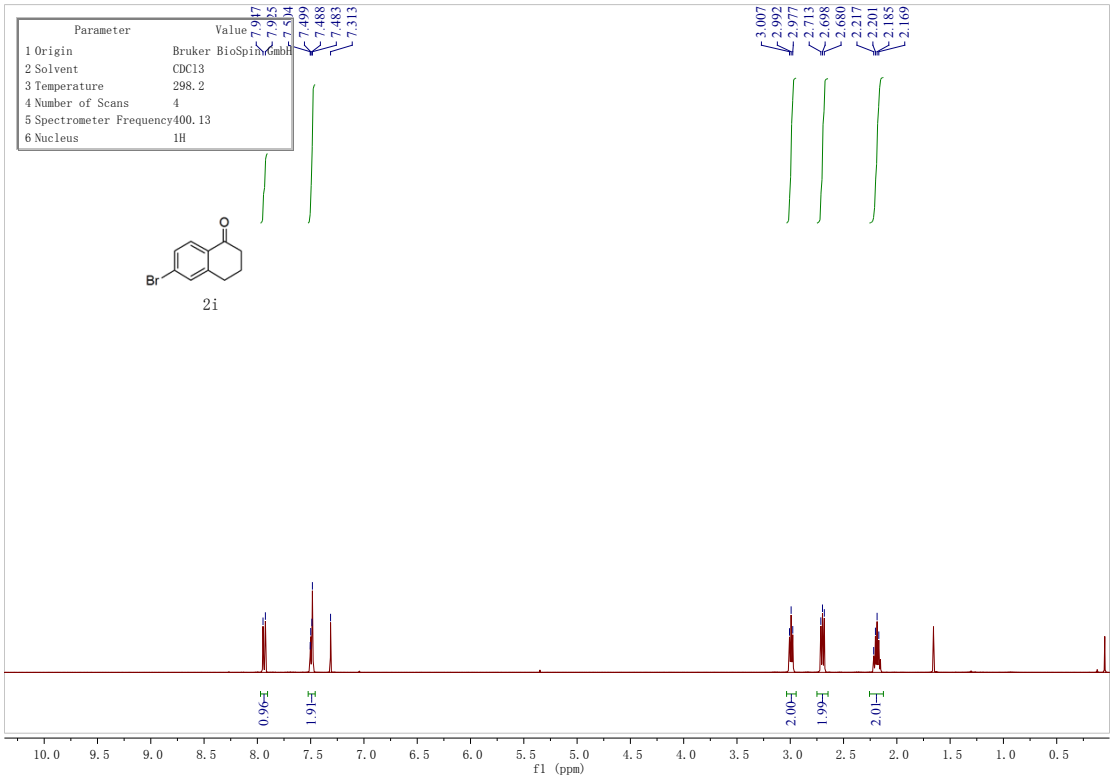

Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 1024
5 Spectrometer Frequency 100.61
6 Nucleus 13C
196.859
166.952
164.414
147.559
147.469
130.358
130.260
129.304
129.278
115.155
114.944
114.407
114.188
77.363
77.045
76.727
38.850
29.884
29.870
23.158
f1 (ppm)

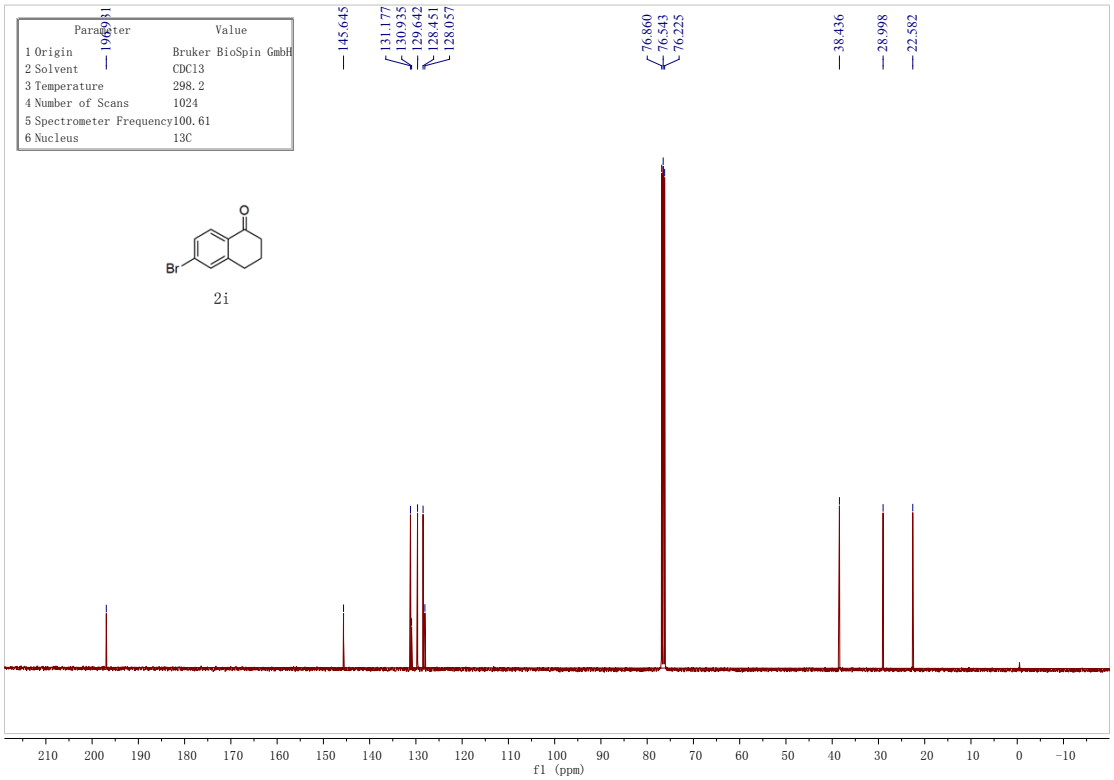
2g

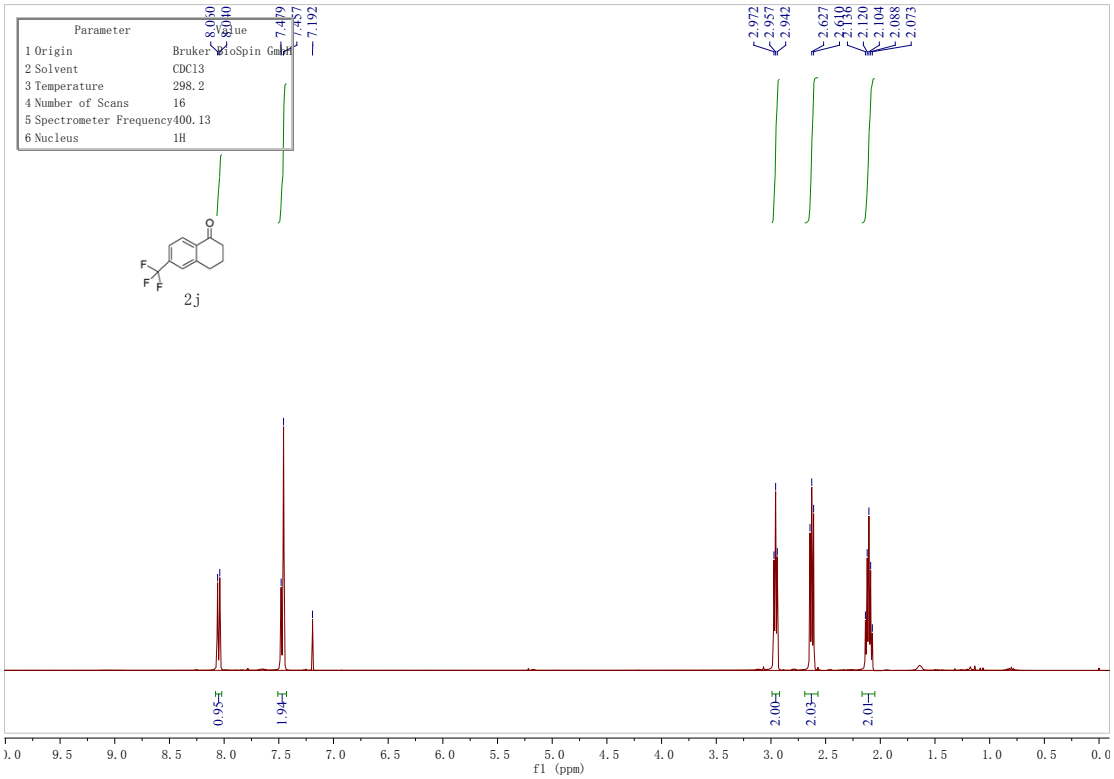

Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 16
5 Spectrometer Frequency 376.50
6 Nucleus 19F
-104.850
O
F
2g
f1 (ppm)

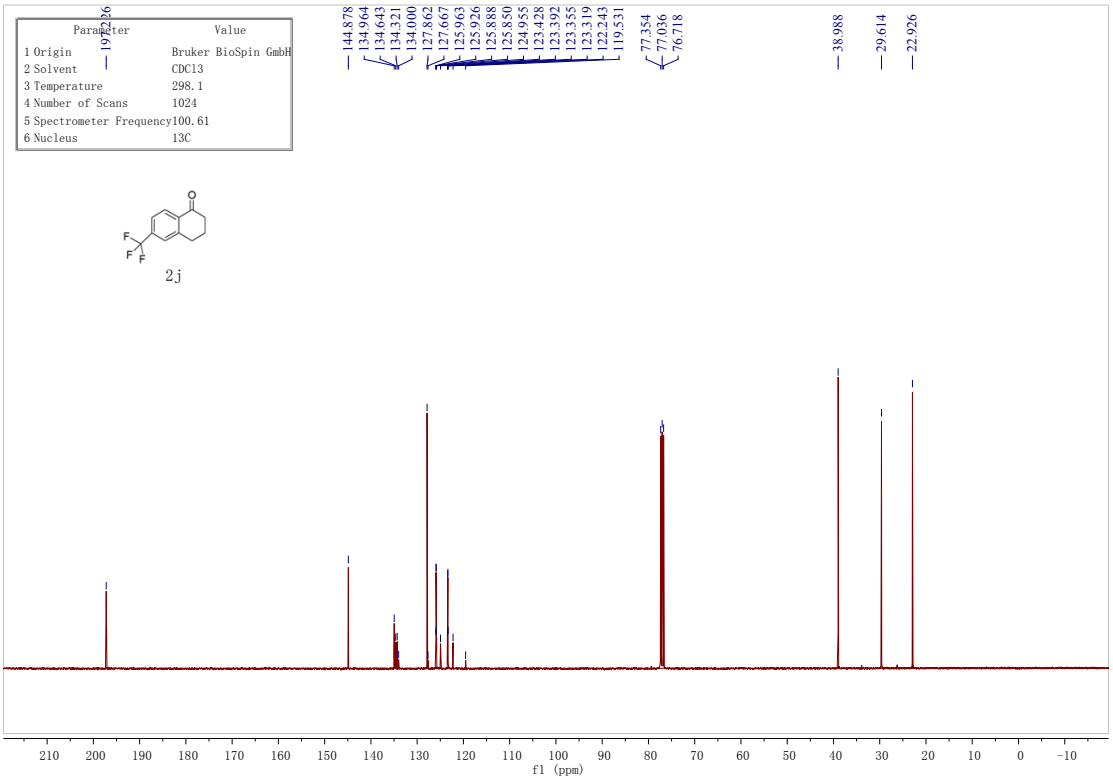

Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 9
5 Spectrometer Frequency 400.13
6 Nucleus 1H
7.972
7.952
7.282
7.276
7.255
7.252
2.951
2.936
2.921
2.658
2.643
2.626
2.164
2.147
2.132
2.116
2.100
O
Cl
2h
0.92
2.23
2.00
1.98
2.00
f1 (ppm)

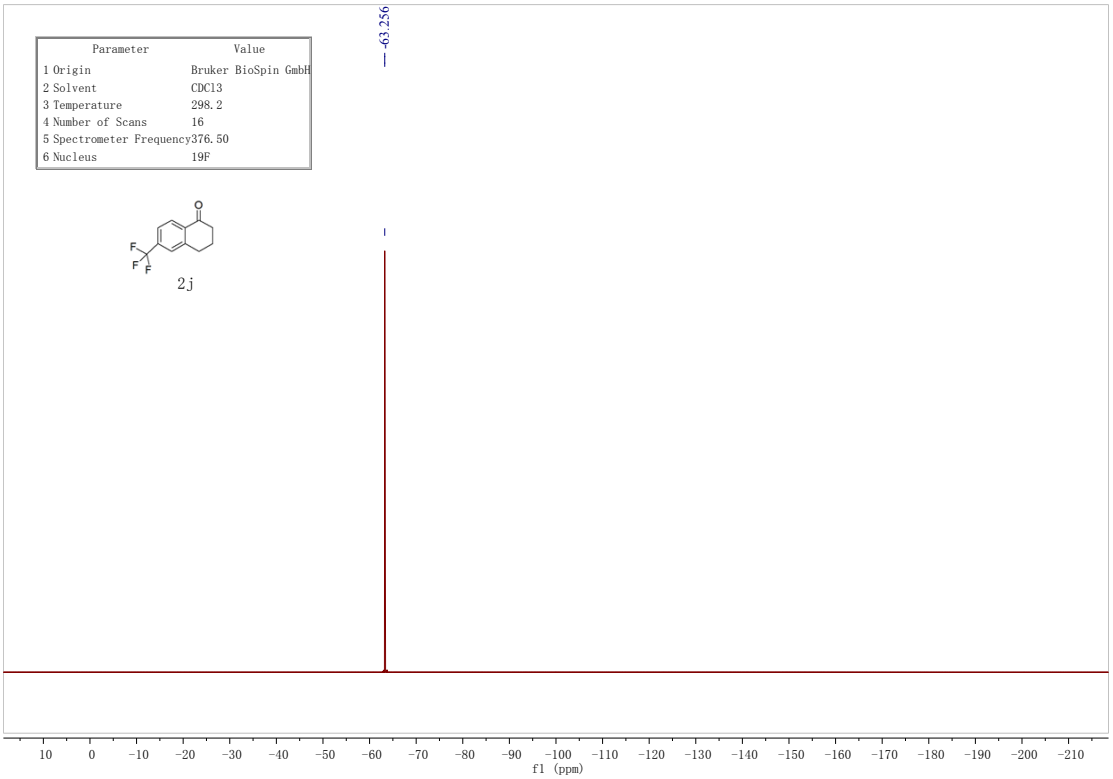

196.753
145.535
139.157
130.567
128.410
128.149
126.692
76.856
76.538
76.221
38.436
29.080
22.591
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 271
5 Spectrometer Frequency 100.61
6 Nucleus 13C
O
Cl
2h
f1 (ppm)

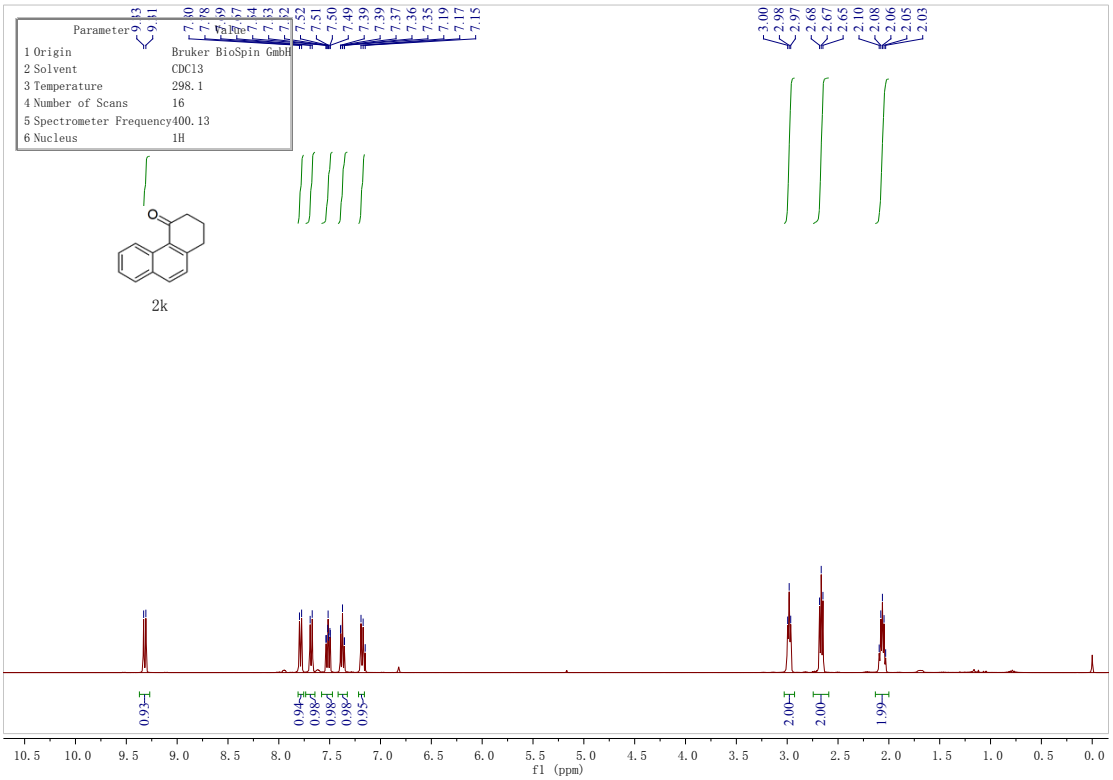

7.947
7.925
7.504
7.499
7.488
7.483
7.313
3.007
2.992
2.977
2.713
2.698
2.680
2.217
2.201
2.185
2.169
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 4
5 Spectrometer Frequency 400.13
6 Nucleus 1H
O
Br
2i
0.96
1.91
2.00
1.99
2.01
f1 (ppm)

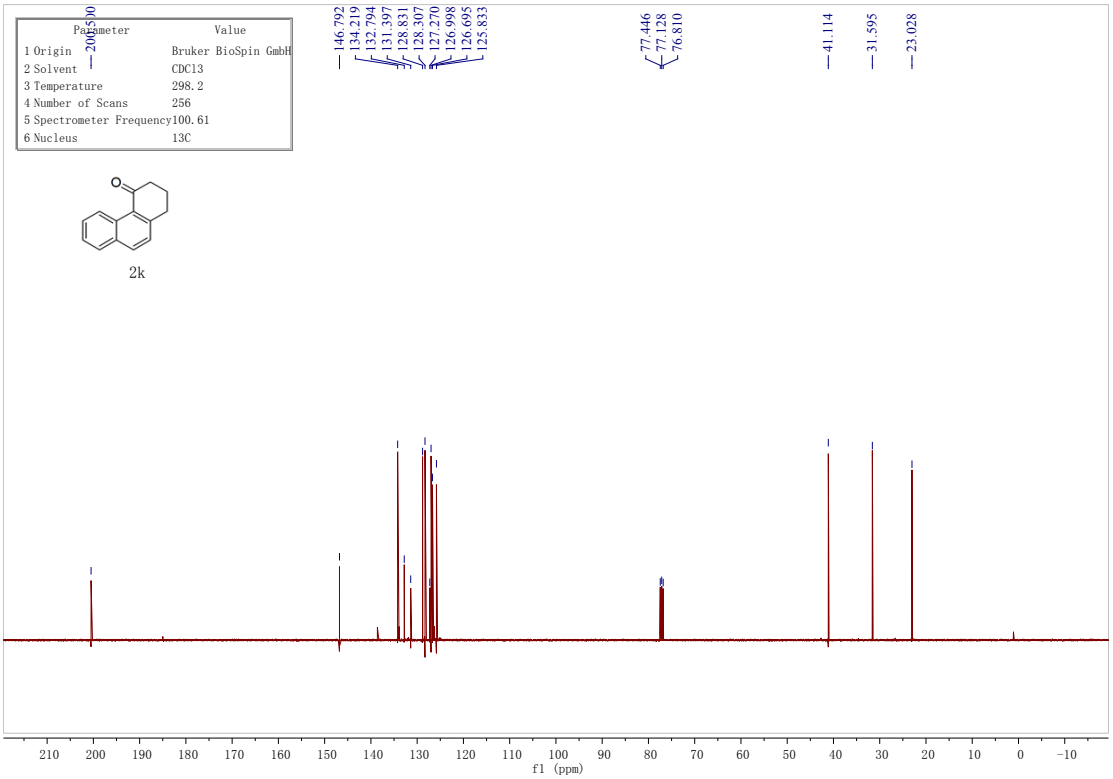

Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 1024
5 Spectrometer Frequency 100.61
6 Nucleus 13C
190.981
145.645
131.177
130.935
129.642
128.451
128.057
76.860
76.543
76.225
38.436
28.998
22.582
Br
2i
f1 (ppm)

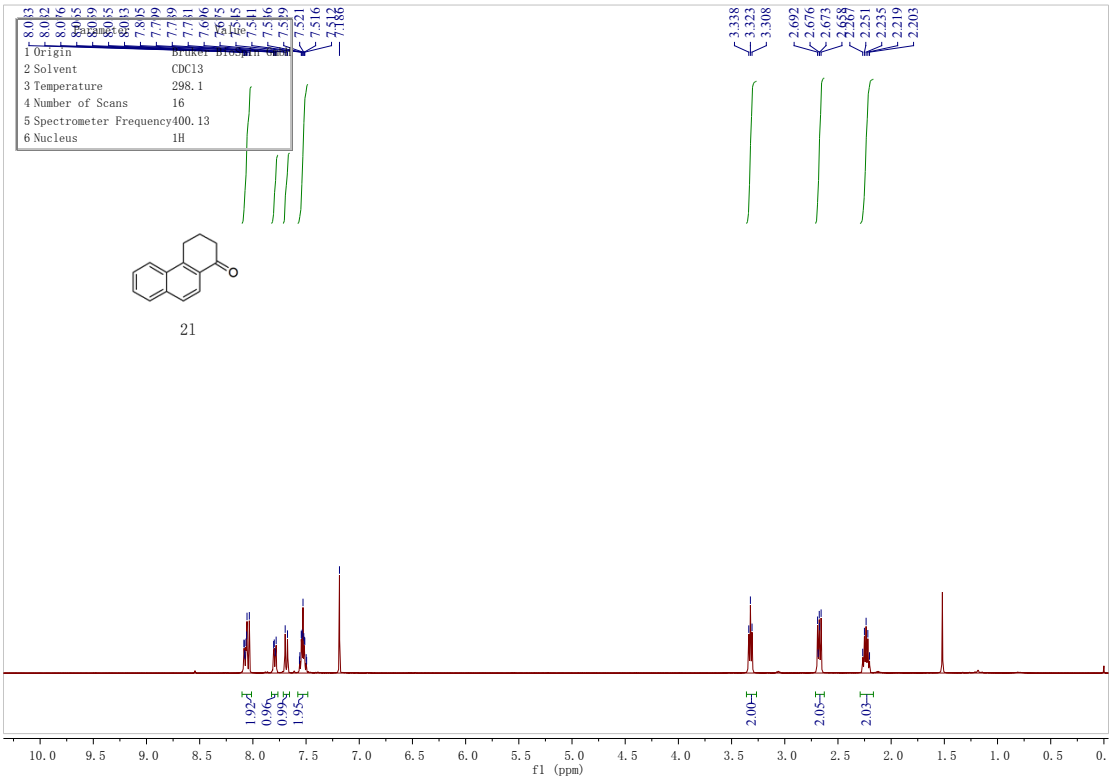

Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 16
5 Spectrometer Frequency 400.13
6 Nucleus 1H
8.050
8.040
7.479
7.457
7.192
2.972
2.957
2.942
2.627
2.610
2.136
2.120
2.104
2.088
2.073
F
F
F
2j
0.95
1.94
2.00
2.03
2.01
f1 (ppm)


Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 1024
5 Spectrometer Frequency 100.61
6 Nucleus 13C
192.226
144.878
134.964
134.643
134.321
134.000
127.862
127.667
125.963
125.926
125.888
125.850
124.955
123.428
123.392
123.355
123.319
122.243
119.531
77.354
77.036
76.718
38.988
29.614
22.926
F
F F
O
2j
f1 (ppm)

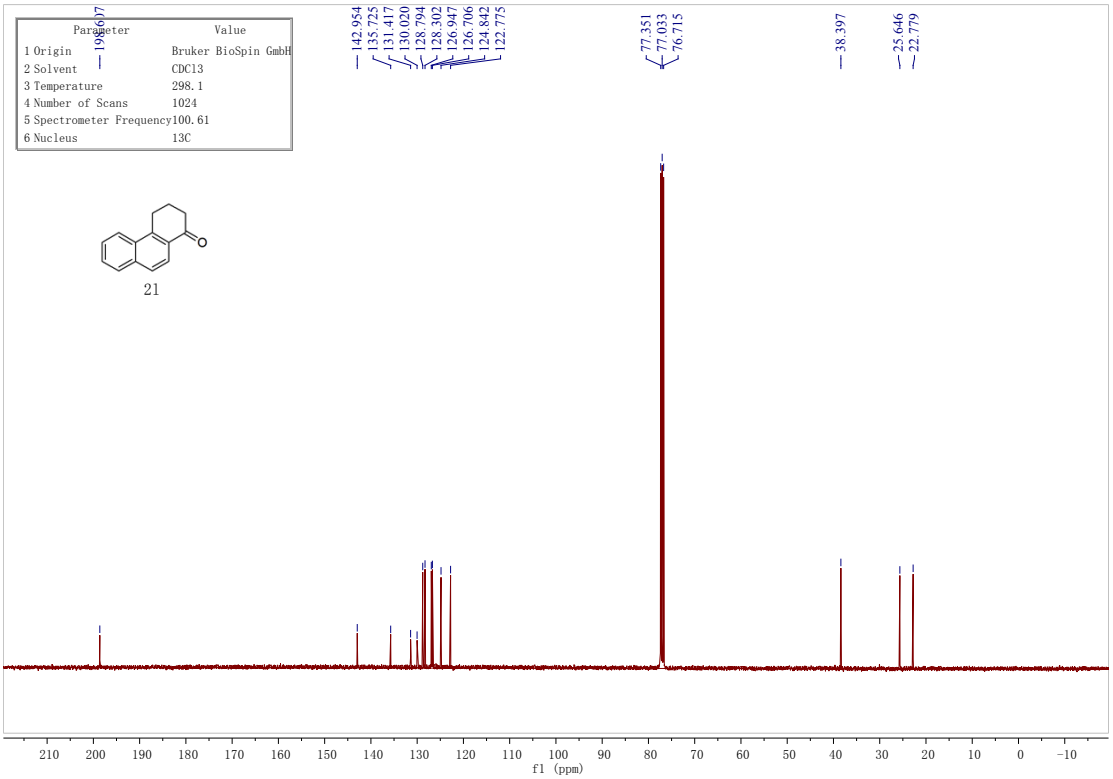

Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 16
5 Spectrometer Frequency 376.50
6 Nucleus 19F
-63.256
F
F F
O
2j
f1 (ppm)


Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 16
5 Spectrometer Frequency 400.13
6 Nucleus 1H
2k
f1 (ppm)

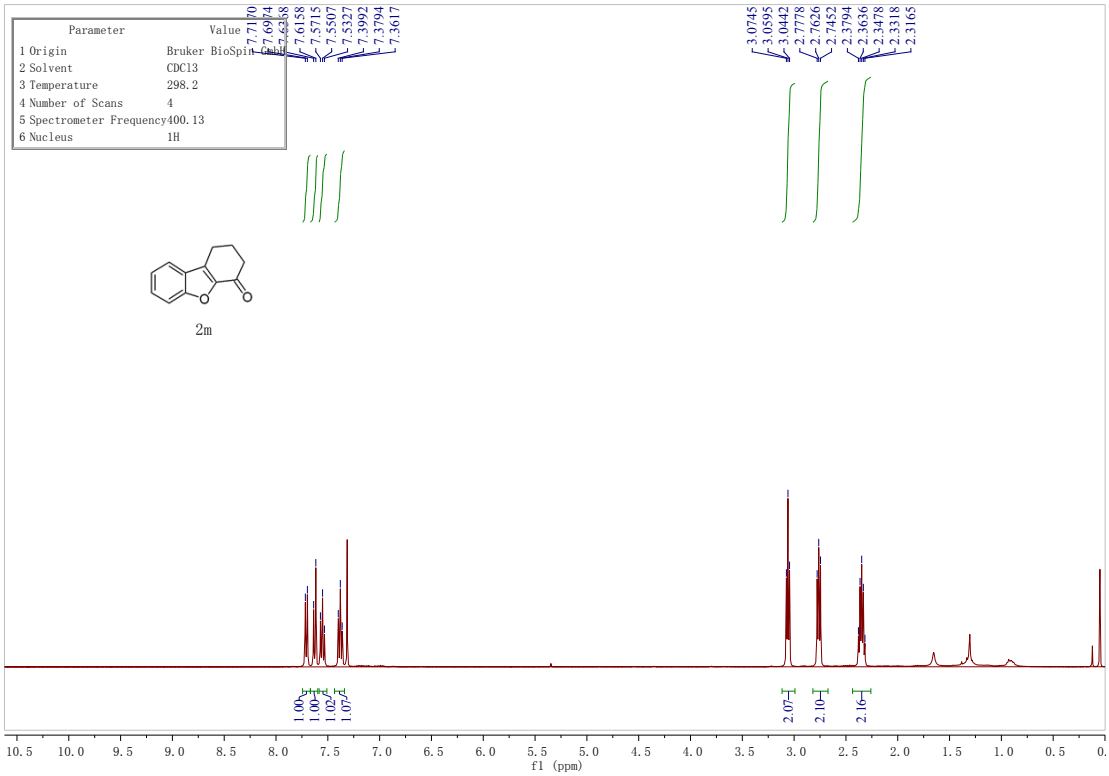

Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 256
5 Spectrometer Frequency 100.61
6 Nucleus 13C
2k
f1 (ppm)

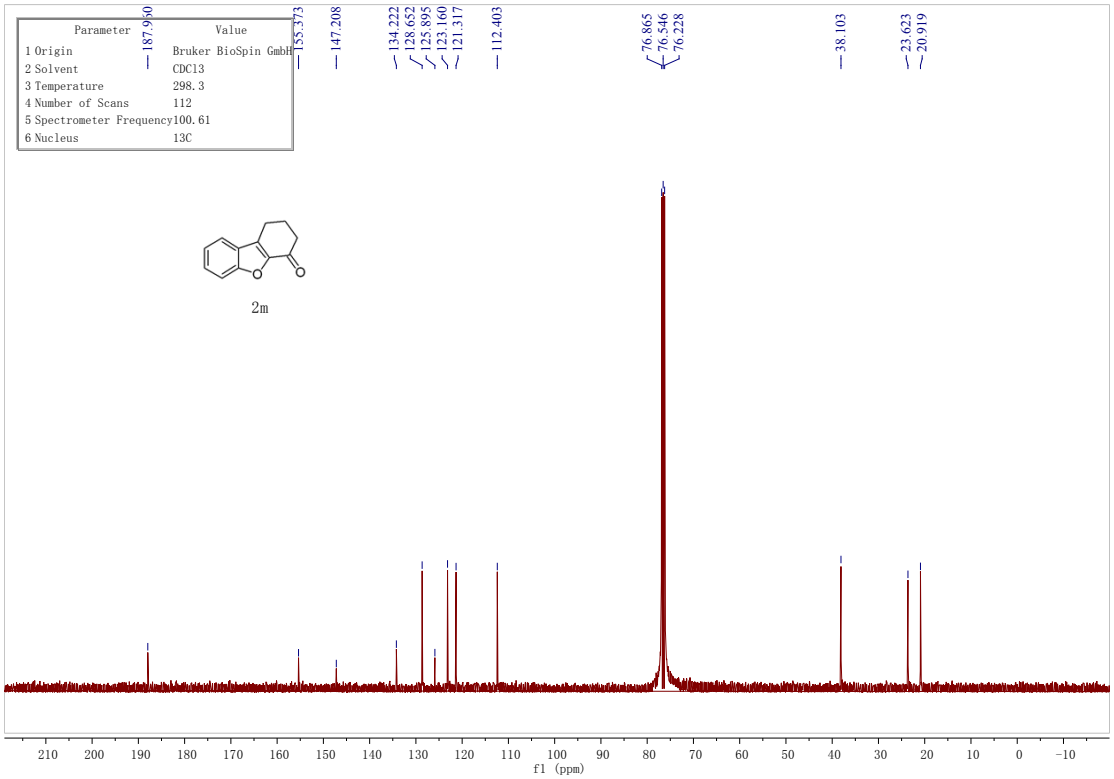

1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 16
5 Spectrometer Frequency 400.13
6 Nucleus 1H
8.003
8.002
8.076
8.065
8.013
7.805
7.799
7.789
7.781
7.606
7.575
7.545
7.541
7.516
7.509
7.521
7.516
7.512
7.186
3.338
3.323
3.308
2.692
2.676
2.673
2.659
2.251
2.235
2.219
2.203
1.92
0.96
0.99
1.95
2.00
2.05
2.03
f1 (ppm)

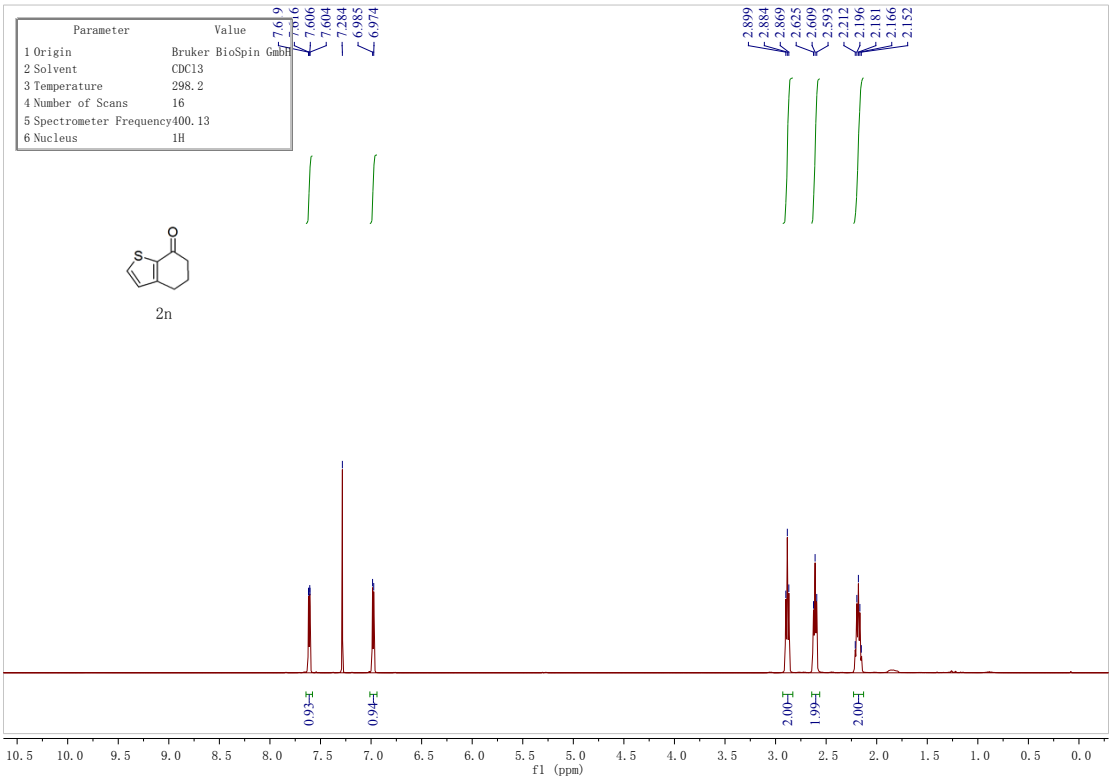
21


Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 1024
5 Spectrometer Frequency 100.61
6 Nucleus 13C
196.017
142.954
135.725
131.417
130.020
128.794
128.302
126.947
126.706
124.842
122.775
77.351
77.033
76.715
38.397
25.646
22.779
f1 (ppm)

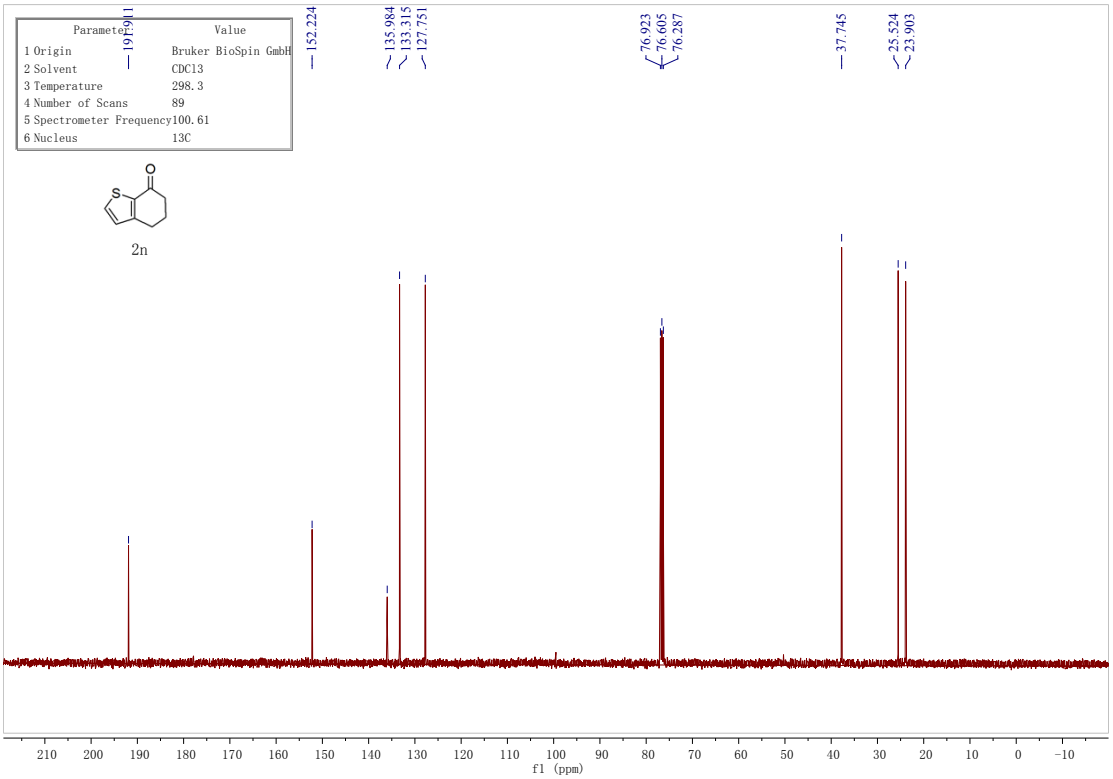
21


Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 4
5 Spectrometer Frequency 400.13
6 Nucleus 1H
7.7170
7.6974
7.6238
7.6158
7.5715
7.5507
7.5327
7.3992
7.3794
7.3617
3.0745
3.0595
3.0442
2.7778
2.7626
2.7452
2.3794
2.3636
2.3478
2.3318
2.3165
2m
1.00
1.00
1.02
1.07
2.07
2.10
2.16
f1 (ppm)

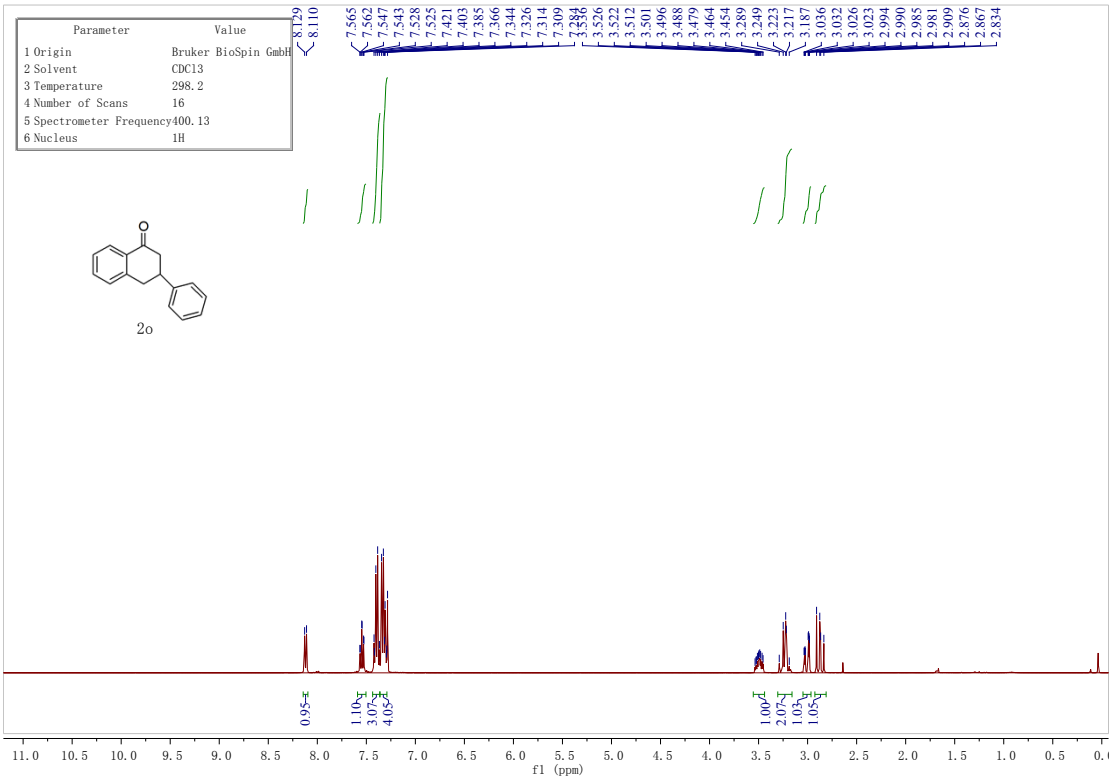

Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.3
4 Number of Scans 112
5 Spectrometer Frequency 100.61
6 Nucleus 13C
187.950
155.373
147.208
134.222
128.652
125.895
123.160
121.317
112.403
76.865
76.546
76.228
38.103
23.623
20.919
2m
f1 (ppm)

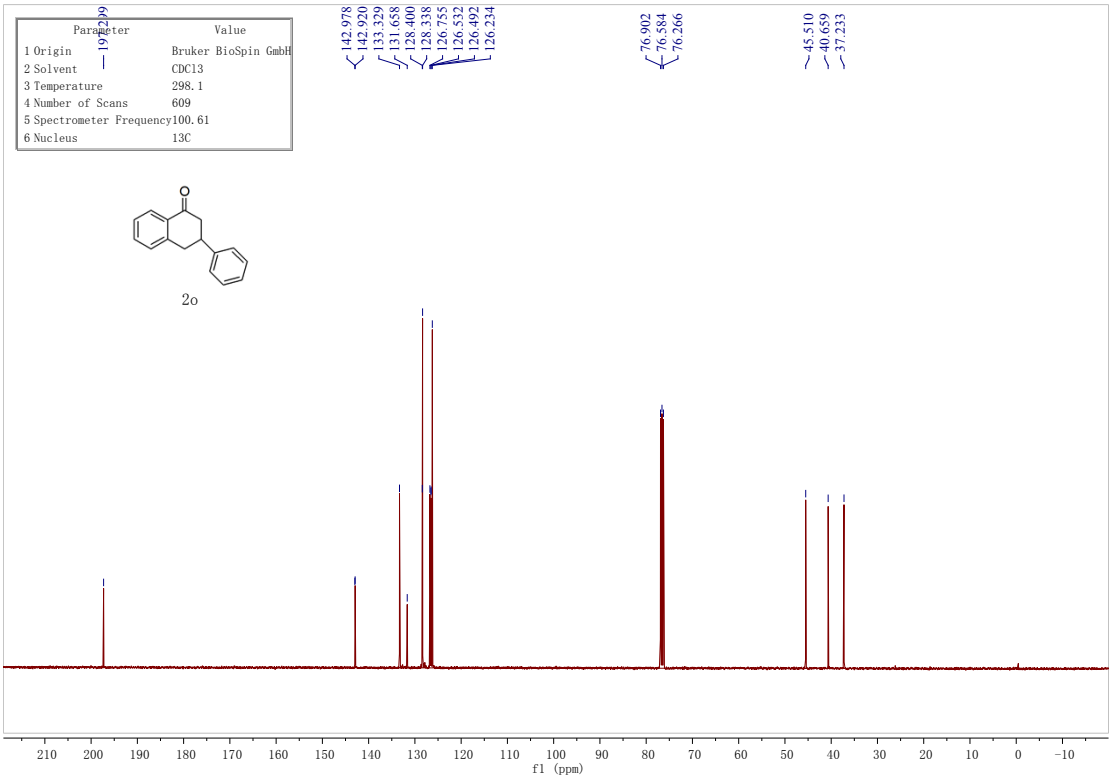

Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 16
5 Spectrometer Frequency 400.13
6 Nucleus 1H
7.616
7.606
7.604
7.284
6.985
6.974
2.899
2.884
2.869
2.625
2.609
2.593
2.212
2.196
2.181
2.166
2.152
0.93
0.94
2.00
1.99
2.00
f1 (ppm)

2n


Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.3
4 Number of Scans 89
5 Spectrometer Frequency 100.61
6 Nucleus 13C
191.911
152.224
135.984
133.315
127.751
76.923
76.605
76.287
37.745
25.524
23.903
f1 (ppm)

2n


Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 16
5 Spectrometer Frequency 400.13
6 Nucleus 1H
2o
f1 (ppm)


Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 609
5 Spectrometer Frequency 100.61
6 Nucleus 13C
2o
f1 (ppm)

5. Computational Studies

Computational Methods

The geometries of all stationary points were optimized using the B3LYP density functional method[2] with the 6-31+G(d,p) basis set[3] for all the atoms. Frequencies were analytically computed at the same level of theory to confirm weather the structures are minima (no imaginary frequency) or transition states and to obtain the thermodynamic energy corrections. Transition states were verified to have one imaginary vibrational frequency and were connected to appropriate reactant and product by optimizations along the reaction coordinate. Larger basis set, 6-311++G(d,p), was utilized for single-point energy calculations on stationary points. The Gibbs free energy was determined by adding the single-point energy and the gas-phase thermal correction to the Gibbs free energy obtained from the vibrational frequencies. Unless otherwise specified, the Gibbs free energy was used in the present discussions. The Gaussian 09 suite of programs[4] was used for all the calculations.

---

[2] (a) Becke, A. D. *J. Chem. Phys*. **1993**, *98*, 5648. (b) Lee., C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

[3] Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

[4] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian 09, Revision C.01, Gaussian, Inc., Wallingford CT, 2010.

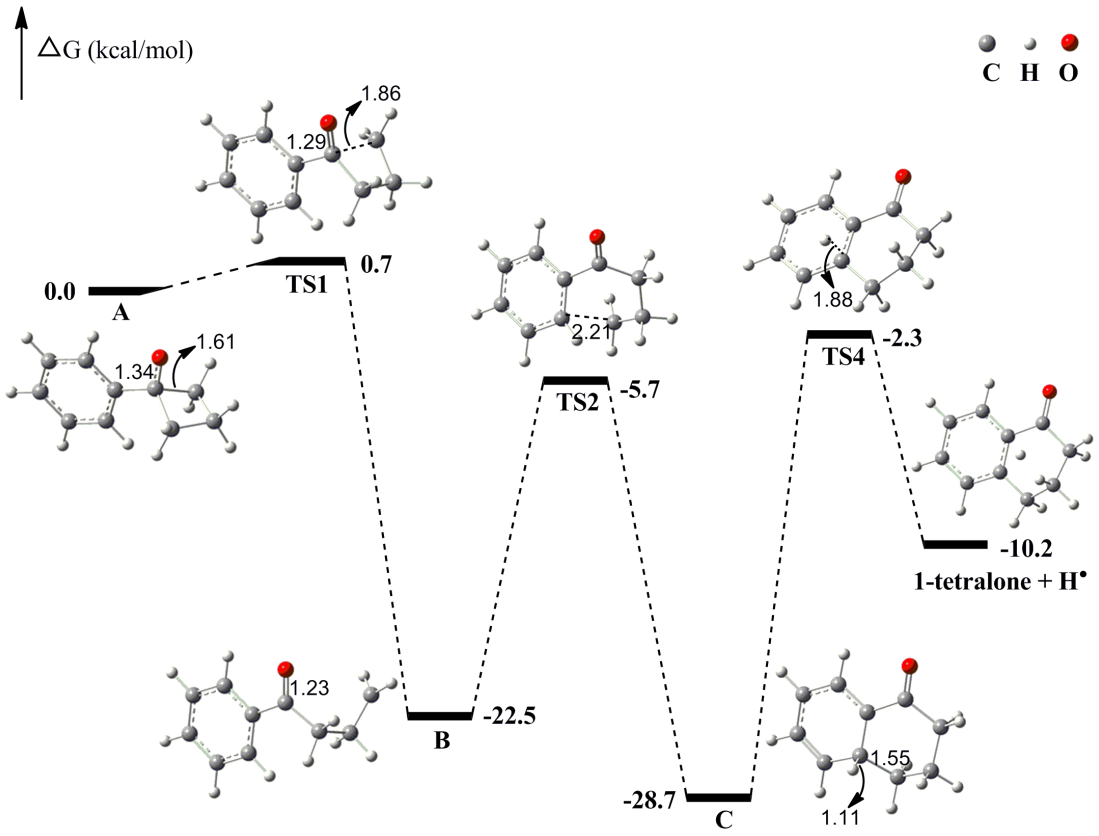


Figure S1. Free energy profile for the transformation from **A** to the desired product (path-b in Scheme 5). Bond lengths are shown in Å.

Cartesian Coordinates and Energies

A

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.082993	-0.650297	0.000044
2	6	0	2.019072	-0.367276	1.078464
3	6	0	1.100928	0.398068	-0.000052
4	6	0	2.019078	-0.367403	-1.078422
5	1	0	3.879039	0.096634	0.000005
6	1	0	3.529155	-1.648027	0.000108
7	1	0	2.285449	0.252287	1.936455
8	1	0	1.498744	-1.268366	1.411764
9	1	0	2.285480	0.252057	-1.936481
10	1	0	1.498790	-1.268547	-1.411640
11	6	0	-0.397607	0.136003	-0.000026
12	6	0	-1.294273	1.213051	-0.000013
13	6	0	-0.916752	-1.168239	-0.000014
14	6	0	-2.673888	0.992373	0.000010
15	1	0	-0.897128	2.222417	-0.000020
16	6	0	-2.295290	-1.391547	0.000011
17	1	0	-0.246865	-2.024501	-0.000022
18	6	0	-3.180350	-0.309805	0.000022
19	1	0	-3.353423	1.840176	0.000018
20	1	0	-2.676576	-2.408861	0.000021
21	1	0	-4.252954	-0.481088	0.000040
22	8	0	1.458353	1.690781	-0.000050

Zero-point correction= 0.181529 (Hartree/Particle)
Thermal correction to Energy= 0.190471
Thermal correction to Enthalpy= 0.191415
Thermal correction to Gibbs Free Energy= 0.146481
Sum of electronic and zero-point Energies= -462.671447
Sum of electronic and thermal Energies= -462.662506
Sum of electronic and thermal Enthalpies= -462.661561
Sum of electronic and thermal Free Energies= -462.706496

TS1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.541196	-1.117352	0.447522
2	6	0	-2.111680	-0.527923	-0.914988
3	6	0	-1.141521	0.549470	-0.330574
4	6	0	-1.985618	0.052732	1.249546
5	1	0	-3.616874	-1.275794	0.567825
6	1	0	-2.026648	-2.052920	0.683661
7	1	0	-2.926049	0.002604	-1.412504
8	1	0	-1.655136	-1.230551	-1.618524
9	1	0	-2.671926	0.863826	1.479461
10	1	0	-1.228125	-0.111436	2.012922
11	6	0	0.329508	0.191310	-0.174234
12	6	0	1.247429	1.221092	0.083564
13	6	0	0.804294	-1.125033	-0.275613
14	6	0	2.605619	0.941511	0.234438
15	1	0	0.877060	2.238550	0.150296
16	6	0	2.165411	-1.405638	-0.124199
17	1	0	0.121150	-1.943794	-0.478540
18	6	0	3.070777	-0.373906	0.132619
19	1	0	3.303511	1.751512	0.427521
20	1	0	2.515858	-2.430316	-0.210715
21	1	0	4.128672	-0.591420	0.248218
22	8	0	-1.434954	1.792771	-0.477264

Zero-point correction= 0.181033 (Hartree/Particle)
Thermal correction to Energy= 0.190264
Thermal correction to Enthalpy= 0.191208
Thermal correction to Gibbs Free Energy= 0.145466
Sum of electronic and zero-point Energies= -462.669818
Sum of electronic and thermal Energies= -462.660587
Sum of electronic and thermal Enthalpies= -462.659643
Sum of electronic and thermal Free Energies= -462.705384

B

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.522027	-1.095217	0.324253
2	6	0	-1.959962	-0.337520	-0.924966

3	6	0	-0.899372	0.692143	-0.564915
4	6	0	-3.237854	-0.219892	1.295768
5	1	0	-3.208791	-1.859869	-0.067151
6	1	0	-1.705246	-1.628691	0.822426
7	1	0	-2.772636	0.205663	-1.414306
8	1	0	-1.566820	-1.073210	-1.635665
9	1	0	-4.178734	0.246996	1.020464
10	1	0	-2.779565	0.084426	2.230395
11	6	0	0.502992	0.246738	-0.256686
12	6	0	1.411129	1.204967	0.227000
13	6	0	0.943961	-1.074792	-0.438621
14	6	0	2.724786	0.850342	0.524582
15	1	0	1.060812	2.223113	0.360022
16	6	0	2.262228	-1.429650	-0.143759
17	1	0	0.268329	-1.834285	-0.817088
18	6	0	3.154052	-0.469026	0.339296
19	1	0	3.415990	1.599375	0.899924
20	1	0	2.591722	-2.453760	-0.292515
21	1	0	4.178948	-0.745869	0.569472
22	8	0	-1.197951	1.878444	-0.495960

Zero-point correction= 0.180035 (Hartree/Particle)
Thermal correction to Energy= 0.190968
Thermal correction to Enthalpy= 0.191912
Thermal correction to Gibbs Free Energy= 0.141153
Sum of electronic and zero-point Energies= -462.703406
Sum of electronic and thermal Energies= -462.692473
Sum of electronic and thermal Enthalpies= -462.691529
Sum of electronic and thermal Free Energies= -462.742288

TS2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.796412	-0.441711	0.027251
2	6	0	1.828037	-1.213965	-0.600956
3	6	0	0.481880	-0.764657	-0.680517
4	6	0	0.178361	0.555895	-0.218276
5	6	0	1.178480	1.330575	0.375282
6	6	0	2.479584	0.837003	0.516538
7	1	0	-0.586047	-2.915708	0.464237

8	1	0	3.813064	-0.815574	0.113343
9	1	0	2.091686	-2.177204	-1.028193
10	6	0	-0.867585	-1.884439	0.666451
11	6	0	-1.218234	1.076565	-0.208938
12	1	0	0.918942	2.320626	0.737514
13	1	0	3.243383	1.445584	0.990652
14	6	0	-2.363545	0.136644	0.191798
15	6	0	-2.166161	-1.388352	0.094903
16	1	0	-2.556272	0.404303	1.241651
17	1	0	-2.253490	-1.711577	-0.951668
18	8	0	-1.457685	2.266486	-0.375373
19	1	0	-3.253717	0.452346	-0.361450
20	1	0	-3.014298	-1.866638	0.612158
21	1	0	-0.552663	-1.510436	1.638412
22	1	0	-0.152477	-1.218967	-1.434891

Zero-point correction= 0.180727 (Hartree/Particle)
Thermal correction to Energy= 0.189922
Thermal correction to Enthalpy= 0.190866
Thermal correction to Gibbs Free Energy= 0.145622
Sum of electronic and zero-point Energies= -462.680529
Sum of electronic and thermal Energies= -462.671334
Sum of electronic and thermal Enthalpies= -462.670390
Sum of electronic and thermal Free Energies= -462.715635

C

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.784913	-0.421942	-0.097014
2	6	0	-1.788543	-1.332380	0.086707
3	6	0	-0.369550	-0.921689	0.367855
4	6	0	-0.118064	0.552433	0.122834
5	6	0	-1.182138	1.432588	-0.028374
6	6	0	-2.504787	0.980255	-0.108559
7	1	0	0.511824	-2.862110	-0.051547
8	1	0	-3.806598	-0.758890	-0.251573
9	1	0	-2.009555	-2.397462	0.096454
10	6	0	0.696389	-1.812479	-0.310482
11	6	0	1.262420	1.068778	0.036579
12	1	0	-0.954151	2.488935	-0.137458

13	1	0	-3.314358	1.690670	-0.242604
14	6	0	2.391757	0.075065	-0.233790
15	6	0	2.096772	-1.384869	0.142645
16	1	0	2.583768	0.143182	-1.315174
17	1	0	2.171471	-1.509165	1.231860
18	8	0	1.511160	2.274404	0.097674
19	1	0	3.293601	0.452752	0.258032
20	1	0	2.858588	-2.039140	-0.296504
21	1	0	0.603859	-1.727646	-1.401432
22	1	0	-0.223788	-1.090918	1.458151

Zero-point correction= 0.183734 (Hartree/Particle)
Thermal correction to Energy= 0.192682
Thermal correction to Enthalpy= 0.193627
Thermal correction to Gibbs Free Energy= 0.148986
Sum of electronic and zero-point Energies= -462.717417
Sum of electronic and thermal Energies= -462.708469
Sum of electronic and thermal Enthalpies= -462.707525
Sum of electronic and thermal Free Energies= -462.752165

$K_2S_2O_8$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-1.928887	0.130455	-0.336924
2	8	0	-2.224943	-1.270380	-0.693837
3	8	0	-2.790348	1.204553	-0.826234
4	16	0	1.928776	-0.130356	-0.336947
5	8	0	1.497052	-0.259893	1.094386
6	8	0	2.790881	-1.203532	-0.827106
7	8	0	-0.477547	0.550041	-1.219526
8	8	0	-1.497369	0.258626	1.094637
9	8	0	0.477670	-0.549628	-1.220055
10	8	0	2.224286	1.270976	-0.692541
11	19	0	-0.308157	-2.304511	0.976325
12	19	0	0.308385	2.304106	0.976525

Zero-point correction= 0.034593 (Hartree/Particle)
Thermal correction to Energy= 0.048011
Thermal correction to Enthalpy= 0.048955

Thermal correction to Gibbs Free Energy= -0.007257

Sum of electronic and zero-point Energies= -2597.956801

Sum of electronic and thermal Energies= -2597.943383

Sum of electronic and thermal Enthalpies= -2597.942439

Sum of electronic and thermal Free Energies= -2597.998651

D

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	5.850845	1.080680	0.868688
2	6	0	5.342118	1.074700	-0.394636
3	6	0	4.026326	0.435765	-0.730970
4	6	0	3.467353	-0.403492	0.396539
5	6	0	4.013794	-0.329428	1.673904
6	6	0	5.171512	0.410020	1.933487
7	1	0	4.374510	0.337104	-2.872501
8	1	0	6.787977	1.590108	1.076599
9	1	0	5.861608	1.591529	-1.198488
10	6	0	4.020341	-0.329143	-2.076884
11	6	0	2.338835	-1.300190	0.141978
12	1	0	3.546357	-0.907603	2.465455
13	1	0	5.586525	0.433320	2.936253
14	6	0	2.067145	-1.749641	-1.285442
15	6	0	2.603253	-0.822943	-2.387319
16	1	0	2.542865	-2.739980	-1.365678
17	1	0	1.935377	0.039963	-2.482836
18	8	0	1.652015	-1.765555	1.071824
19	1	0	0.991278	-1.917791	-1.393972
20	1	0	2.584806	-1.352822	-3.346255
21	1	0	4.724126	-1.170788	-2.022242
22	1	0	3.308113	1.270381	-0.873651
23	16	0	-0.718259	1.522858	-0.266140
24	8	0	-1.520000	2.611703	-0.862870
25	8	0	0.706559	1.440189	-0.593247
26	16	0	-3.486449	-1.170982	-0.290614
27	8	0	-3.527726	-0.571827	1.084994
28	8	0	-4.766675	-1.177217	-0.997630
29	8	0	-1.250299	0.059957	-1.045339
30	8	0	-1.069821	1.298777	1.170970
31	8	0	-2.693005	0.071850	-1.239019
32	8	0	-2.607937	-2.351695	-0.354835

33	19	0	-3.740017	2.079074	0.625615
34	19	0	-0.879047	-1.454382	1.651781

Zero-point correction= 0.219496 (Hartree/Particle)
Thermal correction to Energy= 0.244042
Thermal correction to Enthalpy= 0.244986
Thermal correction to Gibbs Free Energy= 0.159612
Sum of electronic and zero-point Energies= -3060.698488
Sum of electronic and thermal Energies= -3060.673942
Sum of electronic and thermal Enthalpies= -3060.672998
Sum of electronic and thermal Free Energies= -3060.758372

TS3

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.997926	-2.114371	-0.489266
2	6	0	-3.353519	-1.329760	-1.410088
3	6	0	-2.642902	-0.090416	-1.032799
4	6	0	-2.834469	0.316355	0.387565
5	6	0	-3.459064	-0.522633	1.293249
6	6	0	-4.039935	-1.729810	0.871943
7	1	0	-2.466410	0.737884	-3.030547
8	1	0	-4.470711	-3.041716	-0.797779
9	1	0	-3.294824	-1.641865	-2.449615
10	6	0	-2.774977	1.085562	-2.038747
11	6	0	-2.280664	1.615693	0.835102
12	1	0	-3.528108	-0.215567	2.332574
13	1	0	-4.539629	-2.366097	1.595705
14	6	0	-2.250529	2.743291	-0.175219
15	6	0	-1.915939	2.276839	-1.604249
16	1	0	-3.257080	3.192196	-0.156228
17	1	0	-0.856214	2.009578	-1.642237
18	8	0	-1.886504	1.768076	1.998691
19	1	0	-1.546051	3.501271	0.175255
20	1	0	-2.061665	3.113306	-2.296534
21	1	0	-3.832472	1.373708	-2.108037
22	1	0	-1.540744	-0.377073	-1.084289
23	16	0	0.636556	-1.990458	-0.023837
24	8	0	1.578439	-2.764338	-0.867597
25	8	0	-0.733705	-2.517680	0.106170

26	16	0	2.284256	1.519270	-0.482313
27	8	0	2.994179	0.978737	0.733736
28	8	0	3.175941	2.174439	-1.452479
29	8	0	0.328298	-0.551546	-0.808446
30	8	0	1.279882	-1.592936	1.274952
31	8	0	1.845779	0.180132	-1.358817
32	8	0	1.044304	2.233488	-0.093292
33	19	0	3.784799	-1.456511	-0.078322
34	19	0	0.686124	0.850295	2.261050

Zero-point correction= 0.217217 (Hartree/Particle)
Thermal correction to Energy= 0.241235
Thermal correction to Enthalpy= 0.242179
Thermal correction to Gibbs Free Energy= 0.160841
Sum of electronic and zero-point Energies= -3060.675110
Sum of electronic and thermal Energies= -3060.651092
Sum of electronic and thermal Enthalpies= -3060.650148
Sum of electronic and thermal Free Energies= -3060.731486

E

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-6.915225	-1.757171	0.053296
2	6	0	-6.763472	-0.399830	-0.228934
3	6	0	-5.505739	0.215551	-0.168483
4	6	0	-4.387370	-0.574773	0.182824
5	6	0	-4.548097	-1.945015	0.461684
6	6	0	-5.803713	-2.536346	0.401072
7	1	0	-6.116877	2.005926	-1.181247
8	1	0	-7.900402	-2.211525	-0.003138
9	1	0	-7.631323	0.193177	-0.505931
10	6	0	-5.354676	1.693770	-0.458905
11	6	0	-3.029844	0.023441	0.270356
12	1	0	-3.669196	-2.522949	0.727292
13	1	0	-5.922724	-3.593157	0.619223
14	6	0	-2.887573	1.508589	0.007991
15	6	0	-3.949514	2.042483	-0.960603
16	1	0	-2.999332	2.007552	0.984474
17	1	0	-3.793116	1.604054	-1.954689
18	8	0	-2.047857	-0.662649	0.571663

19	1	0	-1.867539	1.712442	-0.330051
20	1	0	-3.840036	3.125964	-1.071710
21	1	0	-5.557745	2.258687	0.464151
22	1	0	2.397756	-2.603518	-2.085115
23	16	0	3.657625	-2.300952	-0.300992
24	8	0	4.723064	-1.519309	-0.984529
25	8	0	3.871305	-3.744406	-0.207111
26	16	0	1.769563	2.475499	0.011256
27	8	0	2.164370	1.598225	1.158528
28	8	0	1.653735	3.949541	0.417943
29	8	0	2.273088	-2.099760	-1.264771
30	8	0	3.178170	-1.601115	0.930525
31	8	0	2.960982	2.646679	-0.934247
32	8	0	0.554010	1.963762	-0.659646
33	19	0	4.650291	0.739034	0.481476
34	19	0	0.628127	-0.667525	0.538729

Zero-point correction=	0.218715 (Hartree/Particle)
Thermal correction to Energy=	0.244804
Thermal correction to Enthalpy=	0.245748
Thermal correction to Gibbs Free Energy=	0.153759
Sum of electronic and zero-point Energies=	-3060.804668
Sum of electronic and thermal Energies=	-3060.778580
Sum of electronic and thermal Enthalpies=	-3060.777635
Sum of electronic and thermal Free Energies=	-3060.869624

TS4

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.771569	-0.463225	-0.054191
2	6	0	-1.703874	-1.349715	-0.085686
3	6	0	-0.366417	-0.885525	0.005965
4	6	0	-0.145237	0.522808	-0.004245
5	6	0	-1.235920	1.402735	0.047587
6	6	0	-2.541256	0.919999	0.031365
7	1	0	0.563384	-2.814489	0.215558
8	1	0	-3.788723	-0.842376	-0.095957
9	1	0	-1.884112	-2.420160	-0.138219
10	6	0	0.794781	-1.838172	-0.222739
11	6	0	1.236065	1.086891	-0.044551

12	1	0	-1.030327	2.467861	0.079440
13	1	0	-3.378494	1.610628	0.062787
14	6	0	2.392300	0.113772	-0.226199
15	6	0	2.110439	-1.286402	0.333846
16	1	0	2.575562	0.049053	-1.310219
17	1	0	2.045516	-1.240396	1.428462
18	8	0	1.435707	2.294268	0.024856
19	1	0	3.283758	0.569315	0.214465
20	1	0	2.938166	-1.961322	0.090111
21	1	0	0.896776	-1.996833	-1.307166
22	1	0	-0.323032	-1.114416	1.874986

Zero-point correction= 0.176532 (Hartree/Particle)
Thermal correction to Energy= 0.185562
Thermal correction to Enthalpy= 0.186506
Thermal correction to Gibbs Free Energy= 0.142051
Sum of electronic and zero-point Energies= -462.675632
Sum of electronic and thermal Energies= -462.666602
Sum of electronic and thermal Enthalpies= -462.665658
Sum of electronic and thermal Free Energies= -462.710113

1-tetralone + H$^{\cdot}$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.788195	-0.498297	0.059583
2	6	0	-1.706548	-1.370248	-0.064573
3	6	0	-0.392376	-0.886679	-0.131904
4	6	0	-0.183507	0.508229	-0.066229
5	6	0	-1.277970	1.381037	0.062918
6	6	0	-2.575387	0.884908	0.122871
7	1	0	0.529789	-2.799147	0.187154
8	1	0	-3.797762	-0.896321	0.112843
9	1	0	-1.880465	-2.442794	-0.104758
10	6	0	0.774709	-1.840359	-0.283539
11	6	0	1.192904	1.088823	-0.132993
12	1	0	-1.078044	2.446601	0.111476
13	1	0	-3.417162	1.563889	0.220819
14	6	0	2.353584	0.119511	-0.301913
15	6	0	2.069962	-1.262707	0.298059
16	1	0	2.530686	0.022906	-1.384580

17	1	0	1.975886	-1.177141	1.388876
18	8	0	1.384519	2.297329	-0.074715
19	1	0	3.245687	0.589041	0.122404
20	1	0	2.909592	-1.939141	0.103414
21	1	0	0.925916	-2.053735	-1.353121
22	1	0	2.176657	-0.438106	3.819521

Zero-point correction=	0.174992 (Hartree/Particle)
Thermal correction to Energy=	0.186013
Thermal correction to Enthalpy=	0.186958
Thermal correction to Gibbs Free Energy=	0.135082
Sum of electronic and zero-point Energies=	-462.682794
Sum of electronic and thermal Energies=	-462.671772
Sum of electronic and thermal Enthalpies=	-462.670828
Sum of electronic and thermal Free Energies=	-462.722704