Supplementary Information

Practical, Metal-Free Remote Heteroarylation of Amides via Unactivated C(sp^3)-H Bond Functionalization

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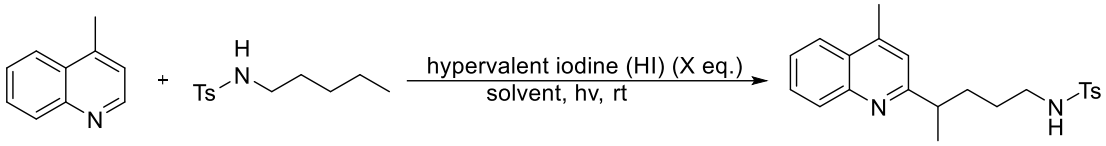
1. General experimental details

Commercially available reagents were used without further purification. Infrared (FT-IR) spectra were recorded on a BRUKER VERTEX 70, ν_{max} in cm^{-1}. ^{1}H-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 Agilent 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.

2. Reaction conditions optimization

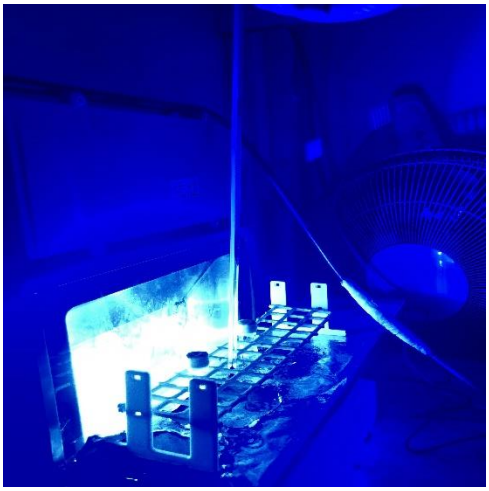


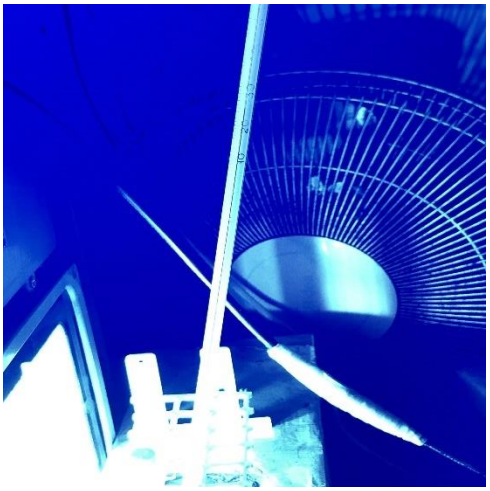
entry	HI(X equiv.)	*hv*	Amide(equiv.)	Solvent	Yield(%)
1	PIFA(2.3)	2 X 50 W blue LEDs	3.0	DCM	84%
2	**PIFA(2.3)**	**2 X 50 W blue LEDs**	**3.0**	**DCE**	**85%**
3	PIFA(2.3)	2 X 50 W blue LEDs	3.0	CH_3CN	57%
4	PIFA(2.3)	2 X 50 W blue LEDs	3.0	$PhCF_3$	75%
5	PIFA(2.3)	2 X 50 W blue LEDs	3.0	MeOH	51%
6	PIFA(2.3)	2 X 50 W blue LEDs	3.0	$CHCl_3$	41%
7	PIFA(2.3)	2 X 50 W blue LEDs	3.0	DMF	34%
8	PIFA(2.3)	2 X 50 W blue LEDs	3.0	DMSO	<5%
9	PIDA(2.3)	2 X 50 W blue LEDs	3.0	DCE	<5%
10	BI-OH(2.3)	2 X 50 W blue LEDs	3.0	DCE	ND
11	BI-OAc(2.3)	2 X 50 W blue LEDs	3.0	DCE	ND

12	PIFA(2.3)	In dark	3.0	DCE	ND
13	PIFA(2.3)	30 W white LEDs	3.0	DCE	79%
14	PIFA(2.3)	30 W green LEDs	3.0	DCE	ND
15	PIFA(2.3)	30 W blue LEDs	3.0	DCE	77%
16	PIFA(2.3)	In dark, 80 ^{o}C	3.0	DCE	<10%
17	PIFA(1.9)	2 X 50 W blue LEDs	3.0	DCE	68%
18	PIFA(2.1)	2 X 50 W blue LEDs	3.0	DCE	72%
19	PIFA(2.5)	2 X 50 W blue LEDs	3.0	DCE	84%
20	PIFA(2.3)	2 X 50 W blue LEDs	2.0	DCE	77%
21	PIFA(2.3)	2 X 50 W blue LEDs	2.5	DCE	80%
22	PIFA(2.3)	2 X 50 W blue LEDs	3.5	DCE	84%

3. General procedure for the C(sp^3)-H heteroarylation of amides

Heteroarene **2** (0.2 mmol) and amide **1** (0.6 mmol) were loaded in a reaction vial without N_2 atmosphere. Then DCE (2.0 mL) followed by PIFA (0.46 mmol) was added to the mixture. The reaction was irradiated with 2 x 50 W blue LEDs from 5 cm away and kept at 25 ^{o}C under fan cooling. After the reaction completion monitored by TLC, the mixture was neutralized by aq. KOH until pH > 8 and then extracted with ethyl acetate (3 x 10 mL). The combined organic extracts were washed by brine, dried over Na_2SO_4, filtered, concentrated, and purified by flash column chromatography on silica gel (eluent: ethyl acetate/ petroleum ether) to give the desired products **3**-**5**.





Lamp parameters: blue light, rated voltage: AC220V, rated frequency: 50/60Hz, executive standard: GB700.1-2007, GB700.202-2008, quality inspection number: QC-H02, production date: 2017.13.

4. Synthesis of starting materials

Starting materials and the references for known compounds:

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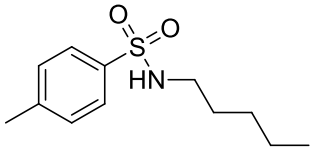
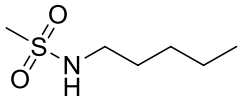
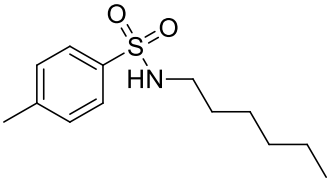
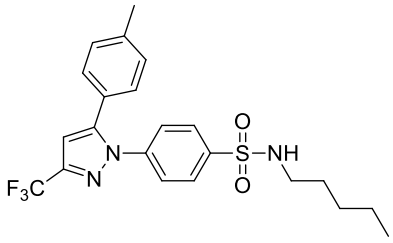
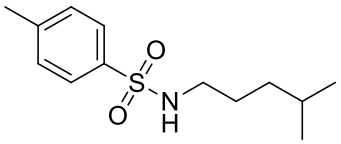
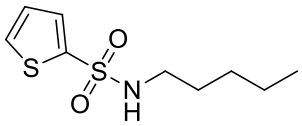
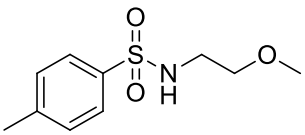
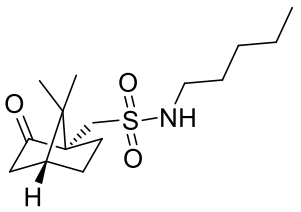
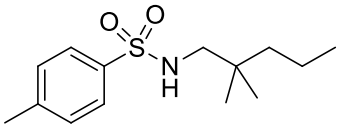
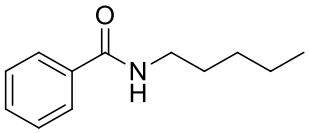
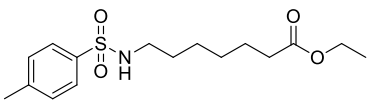
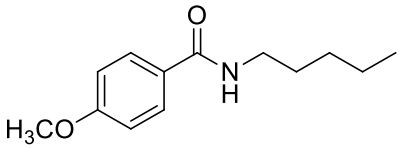
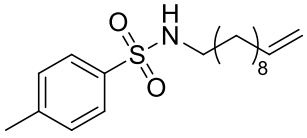
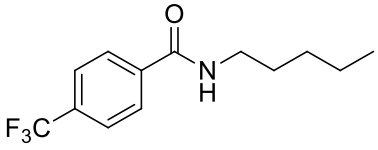
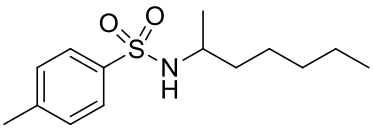
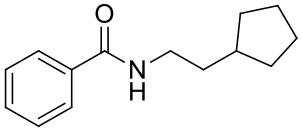
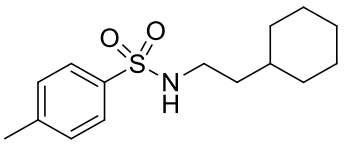
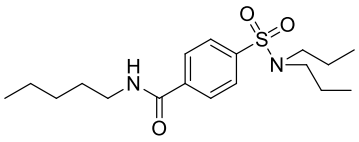
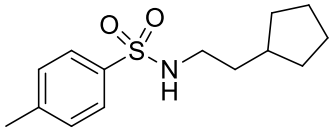
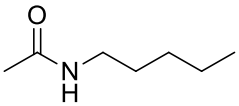
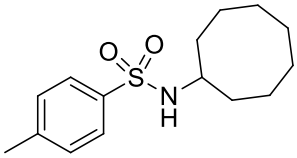
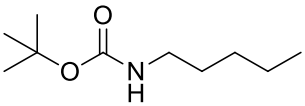
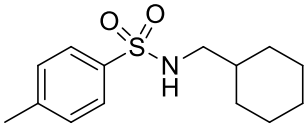
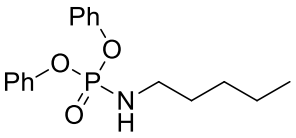
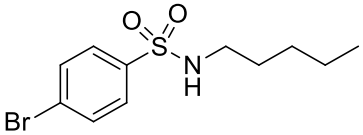
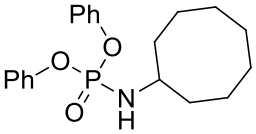
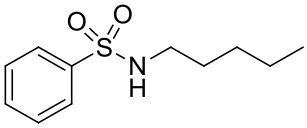
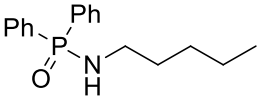
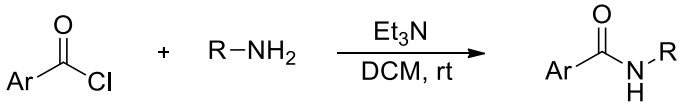
1a[6]		**1ah**[6]	
1u[7]		**1ai**	
1v[19]		**1aj**	
1w[20]		**1ak**[6]	
1x[8]		**7a**[14]	
1y		**7b**[15]	
1z		**7c**	

1aa		**7d**	
1ab[9]		**7f**	
1ac[10]		**7g**[16]	
1ad[11]		**7h**[17]	
1ae[12]		**8a**	
1af		**8e**[18]	
1ag[13]		**8f**	

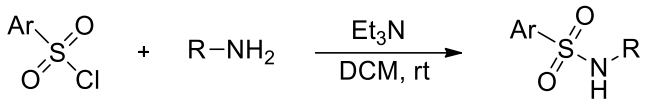
4.1 General procedure for carboxamides synthesis



A flame-dried round-bottomed flask was charged with aroyl chloride (11 mmol, 1.1 equiv.), DCM (20 mL), Et_3N (2.9 mL, 21 mmol, 2.1 equiv.) and amine/ amine hydrochloride (10 mmol, 1 equiv.). The reaction mixture was stirred at RT for 3 h. The reaction mixture was then diluted with DCM (20 mL), washed with 1 M HCl (20 mL), water (20 mL), and brine (20 mL), and then dried over Na_2SO_4 and concentrated. The crude product was purified by flash column chromatography on silica gel (gradient 100% petroleum ether to 25% ethyl acetate/ petroleum ether) to afford the desired product **7c**, **7d**, **7f**.[1]

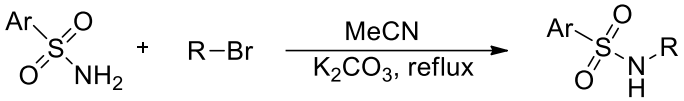
4.2 General procedure for sulfonamides synthesis

Method A:



A flame-dried round-bottomed flask was charged with arylsulfony chloride (11 mmol, 1.1 equiv.), DCM (20 mL), Et_3N (2.9 mL, 21 mmol, 2.1 equiv.) and amine/ amine hydrochloride (10 mmol, 1equiv.). The reaction mixture was stirred at RT for 3 h. The reaction mixture was then diluted with DCM (20 mL), washed with 1 M HCl (20 mL), water (20 mL), and brine (20 mL), and then dried over Na_2SO_4 and concentrated. The crude product was purified by flash column chromatography on silica gel (gradient 100% petroleum ether to 25% ethyl acetate/ petroleum ether) to afford the desired product **1af, 1aj**.[2]

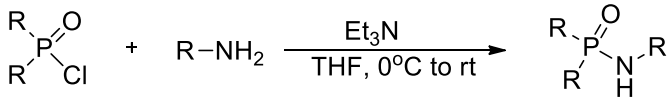
Method B:



To a solution of alkyl bromide (5 mmol, 1 equiv.) in MeCN (20 mL) were added K_2CO_3 (1.38 g, 10 mmol, 2 equiv.) and $TsNH_2$ (1.171 g, 10 mmol, 2 equiv.), and the reaction was heated to reflux. After 5 h, the reaction mixture was filtrated through Celite® and concentrated in vacuo. The desired product was afforded after purification by flash column chromatography on silica gel (petroleum ether/ ethyl acetate = 90/ 10).

1y, 1z, **1ai** are new compounds which were prepared according to the known procedures.[3]

4.3 General procedure for phosphoramides synthesis



To a stirred solution of amines (10 mmol) in THF (25 mL) was added triethylamine (21 mmol) at RT. Diphenylphosphinic chloride (12 mmol) or diphenyl chlorophosphate (12 mmol) in 25 mL of THF was added to the solution at 0 °C. After being stirred for 15 min at 0 °C, the reaction solution was allowed back to RT and stirred for overnight. The resulting mixture was cooled in ice bath, and diluted with $CHCl_3$ and water. The product was extracted with $CHCl_3$ and combined organic layer was washed by brine, 1 N HCl, sat. $NaHCO_3$ and brine. The combined organic phases were dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel (CH_2Cl_2/ MeOH = 95:5) to give the corresponding phosphinic amides or phosphoramidates.

8a, **8f** are new compounds which were prepared according to the known procedures.[4]

References:

[1] T. Aubineau, J. Cossy, *Chem. Commun.*, **2013**, 49, 3303-330.

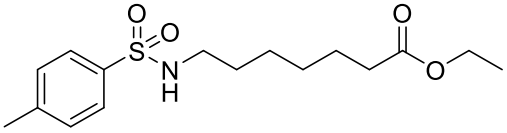
[2] T. Cochet, V. Bellosta, D. Roche, J.-Y. Ortholand, A. Greiner, J. Cossy, *Chem. Commun.*, **2012**, 48, 10745-10747.

[3] C. Bakkali-Hassani, E. Rieger, J. Vignolle, F. R. Wurm, S. Carlotti, D. Taton, *Chem. Commun.*, **2016**,52, 9719-9722.

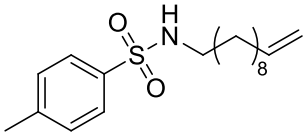
[4] B.-J. Li, R. D. Simard, A. M. Beauchemin, *Chem. Commun.*, **2017**,53, 8667-8670.

[5] X. Xiao, C. Hou, Z. Zhang, Z. Ke, J. Lan, H. Jiang, W. Zeng, *Angew. Chem. Int. Ed.*, **2016**, *19*, 11897-11901.
[6] D. Chang, R. Zhao,C. Wei, Y. Yao,Y. Liu, L. Shi, *J. Org. Chem.*, **2018**, *83*, 3305-3315.
[7] C. Bakkali-Hassani, E. Rieger, J. Vignolle, F. R. Wurm, S. Carlotti, D. Taton, *Chem. Commun.*, **2016**, *52*, 9719-9722.
[8] D. Meng, Y. Tang, J. Wei, X. Shi, M. Yang, *Chem. Commun.*, **2017**, *53*, 5744-5747.
[9] M. Lecomte, G. Evano, *Angew. Chem. Int. Ed.*, **2016**, *24*, 4547-4551.
[10] A. Martínez-Asencio, D. J. Ramón, M. Yus, *Tetrahedron Lett.*, **2010**, *51*, 325-327.
[11] D. C. Rosenfeld, S. Shekhar, A. Takemiya, M. Utsonomiya, J. F. Hartwig, *Org. Lett.*, **2006**, *8*, 4179-4182.
[12] R. Cano, D. J. Ramón, M. Yus, *J. Org. Chem.*, **2011**, *76*, 5547-5557.
[13] W. Wei, C. Liu, D. Yang, J. Wen, J. You, H. Wang, *Adv.Synth.Cata.*, **2015**, *23*, 987-992.
[14] T. Aubineau, J. Cossy, *Chem. Commun.*, **2013**, *49*, 3303-3305.
[15] G. J. Choi, Q. Zhu, D. C. Miller, C. Gu, R. R. Knowles, *Nature*, **2016**, *539*, 268-271.
[16] M. Milan, G. Carboni, M. Salamone, M. Costas, M. Bietti, *ACS Cat.* **2017**, *7*, 5903-5911.
[17] S. Chowdhury, R. F. Standaert, *J. Org. Chem.* **201**6, *81*, 9957-9963.
[18] A. K. Gupta, D. K .Dubey, M. Sharma, M. P. Kaushik, *Organic Preparations and Procedures International*, **2007**, *39*, 297-305.
[19] M. Zhu, K. Fujita, R. Yamaguchi, *Org. Lett.*, **2010**, *12*, 1336-1339.
[20] M. Zhu, W. Wei, D. Yang, H. Cui, L. Wang, G. Menga and H. Wang. *Org. Biomol. Chem.*, **2017**, *15*, 4789-4793.

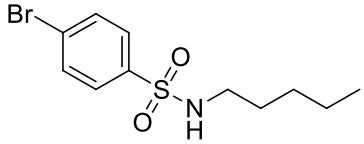
5. Characterization of new starting materials



1y: colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74-7.70 (m, 2H), 7.29-7.24 (m, 2H), 5.03 (t, *J* = 6.0 Hz, 1H), 4.07 (q, *J* = 7.2 Hz, 2H), 2.90-2.83 (m, 2H), 2.39 (s, 3H), 2.20 (t, *J* = 7.6 Hz, 2H), 1.56-1.46 (m, 2H), 1.46-1.37 (m, 2H), 1.28-1.14 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 143.2, 137.0, 129.6, 127.0, 60.2, 43.0, 34.1, 29.2, 28.5, 26.1, 24.7, 21.4, 14.2. FT-IR: ν (cm^{-1}) 2936, 2862, 1732, 1652, 1599, 1420, 1398, 1327. HRMS [ESI] calcd for $C_{16}H_{26}NO_4S$ $[M+H]^+$ 328.1577, found 328.1585.

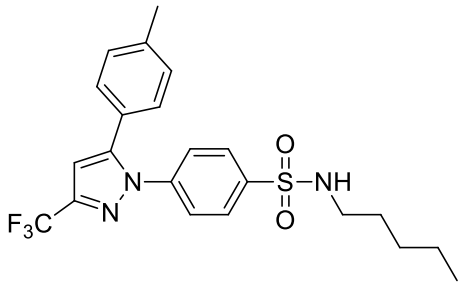


1z: white solid, m.p. 53-54 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77-7.74 (m, 2H), 7.31-7 .27(m, 2H), 5.84-5.73 (m, 1H), 5.00-4.87 (m, 3H), 2.89 (q, *J* = 6.8 Hz, 2H), 2.41 (s, 3H), 2.04-1.97 (m, 2H), 1.47-1.29 (m, 4H), 1.26-1.15 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 139.1, 137.0, 129.6, 127.1, 114.1, 43.2, 33.8, 29.5, 29.4, 29.3, 29.1, 29.0, 28.9, 26.5, 21.5. FT-IR: ν (cm^{-1}) 3293, 2917, 2850, 2340, 1643, 1596, 1467, 1384, 1290. HRMS [ESI] calcd for $C_{18}H_{29}NNaO_2S$ $[M+Na]^+$ 346.1811, found 346.1803.

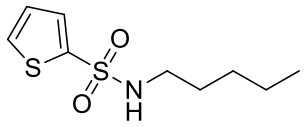


1af: yellow solid, m.p. 59-60 °C.. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75-7.71 (m, 2H), 7.67-7.62 (m, 2H), 4.85 (t, *J* = 6.0 Hz, 1H), 2.92 (q, *J* = 6.8 Hz, 2H), 1.49-1.40 (m, 2H), 1.28-1.18 (m, 4H),

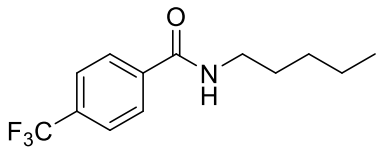
0.83 (t, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.1, 132.4, 128.6, 127.5, 43.3, 29.2, 28.6, 22.1, 13.9. FT-IR: ν (cm-1) 3247, 3083, 2954, 2860, 1574, 1437, 1391, 1298. HRMS [ESI] calcd for $C_{11}H_{16}BrNNaO_2S$ $[M+Na]^+$ 327.9977, found 327.9963.



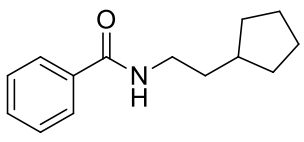
1ai: white solid, m.p. 167-168 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88-7.82 (m, 2H), 7.49-7.43 (m, 2H), 7.19-7.17 (m, 4H), 6.74 (s, 1H), 5.10 (br, 1H), 2.96-2.88 (m, 2H), 2.36 (s, 3H), 1.50-1.40 (m, 2H), 1.28-1.20 (m, 4H), 0.84 (t, J = 6.0 Hz, 3H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.3, 144.0 (q, $J_{C\text{-}F}$ = 38.2 Hz), 142.4, 139.8, 139.6, 129.7, 128.7, 128.1, 125.7, 125.6, 121.1 (q, $J_{C\text{-}F}$ = 267.5 Hz), 106.2, 43.3, 29.2, 28.6, 22.1, 21.3, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.4 (s). FT-IR: ν (cm-1) 3290, 3066, 2962, 2918, 2849, 1601, 1561, 1471, 1374, 1269. HRMS [ESI] calcd for $C_{22}H_{24}F_3N_3NaO_2S$ $[M+Na]^+$ 474.1434, found 474.1429.



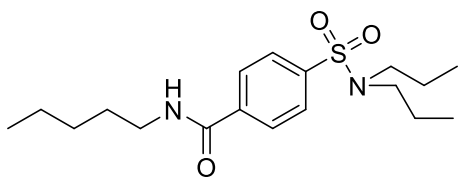
1aj: yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.53 (m, 1H), 7.52-7.50 (m, 1H), 6.99 (dd, J = 4.8, 3.6 Hz, 1H), 5.45 (t, J = 6.0 Hz, 1H), 2.91 (q, J = 6.8 Hz, 2H), 1.45-1.35 (m, 2H), 1.21-1.09 (m, 4H), 0.77-0.71 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 131.9, 131.8, 127.5, 43.4, 28.9, 28.6, 22.1, 13.9. FT-IR: ν (cm^{-1}) 3283, 3107, 2957, 2870, 1508, 1465, 1379, 1226. HRMS [ESI] calcd for $C_9H_{16}NO_2S_2$ $[M+Na]^+$ 234.0617, found 234.0617.



7c: white solid, m.p. 84-85 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88-7.83 (m, 2H), 7.67-7.62 (m, 2H), 6.52 (br, 1H), 3.46-3.39 (m, 2H), 1.65-1.56 (m, 2H), 1.38-1.28 (m, 4H), 0.89 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 138.1, 133.0 (q, $J_{C\text{-}F}$ = 32.6 Hz), 127.4, 125.4 (q, $J_{C\text{-}F}$ = 3.1 Hz), 123.7 (q, $J_{C\text{-}F}$ = 270.9 Hz), 40.3, 29.2, 29.1, 22.3, 13.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.0 (s). FT-IR: ν (cm^{-1}) 3306, 2953, 2934, 2872, 1631, 1579, 1477, 1374, 1289. HRMS [ESI] calcd for $C_{13}H_{16}F_3NNaO$ $[M+Na]^+$ 282.1076, found 282.1082.

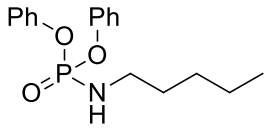


7d: white solid, m.p. 57-58 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80-7.75 (m, 2H), 7.50-7.43 (m, 1H), 7.42-7.35 (m, 2H), 6.56 (br, 1H), 3.48-3.40 (m, 2H), 1.88-1.74 (m, 3H), 1.66-1.45 (m, 6H), 1.18-1.06 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 134.8, 131.2, 128.5, 126.9, 39.6, 37.9, 35.9, 32.6, 25.1. FT-IR: ν (cm^{-1}) 3301, 3062, 2944, 2854, 1702, 1633, 1577, 1488, 1359, 1293. HRMS [ESI] calcd for $C_{14}H_{19}NNaO$ $[M+H]^+$ 240.1359, found 240.1354.

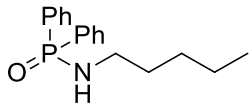


7f: yellow solid, m.p. 100-101 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.82 (m, 2H), 7.80-7.74 (m, 2H), 6.58-6.45 (br, 1H), 3.47-3.39 (m, 2H), 3.08-3.02 (m, 4H), 1.67-1.57 (m, 2H), 1.57-1.46 (m, 4H), 1.38-1.31

(m, 4H), 0.93-0.87 (m, 3H), 0.85 (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 142.2, 138.6, 127.8, 126.9, 50.0, 40.3, 29.1, 22.3, 21.9, 13.9, 11.1. FT-IR: ν (cm^{-1}) 3306, 2964, 2928, 2874, 1633, 1552, 1467, 1372, 1296. HRMS [ESI] calcd for $C_{18}H_{31}N_2O_3P$ $[M+Na]^+$ 355.2050, found 355.2053.

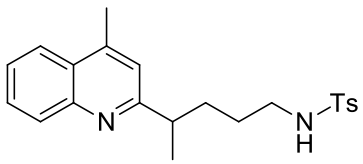


8a: colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.25 (m, 8H), 7.16-7.09 (m, 2H), 4.50-4.35 (m, 1H), 3.04-2.94 (m, 2H), 1.45-1.36 (m, 2H), 1.26-1.15 (m, 4H), 0.82 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0 (d, J_{C-P} = 6.5 Hz), 129.6, 124.7, 120.2 (d, J_{C-P} = 5.0Hz), 41.7, 31.0 (d, J_{C-P} = 6.2 Hz), 28.7, 22.3, 14.0; ^{31}P NMR (161 MHz, $CDCl_3$) δ 0.11 (s). FT-IR: ν (cm^{-1}) 3223, 3069, 2956, 2871, 1590, 1455, 1378, 1220. HRMS [ESI] calcd for $C_{17}H_{22}NNaO_3P$ $[M+Na]^+$ 342.1230, found 342.1224.

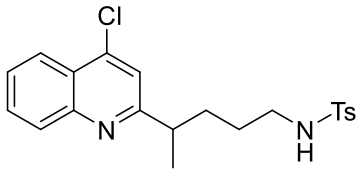


8f: colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89-7.82 (m, 4H), 7.46-7.34 (m, 6H), 2.98-2.85 (m, 3H), 1.57-1.48 (m, 2H), 1.28-1.18 (m, 4H), 0.82 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.6 (d, J_{C-P} = 128.2 Hz), 132.1 (d, J_{C-P} = 9.3 Hz), 131.7 (d, J_{C-P} = 2.7 Hz), 128.5 (d, J_{C-P} = 12.5 Hz), 40.8 (d, J_{C-P} = 1.7 Hz), 31.8 (d, J_{C-P} = 7.1 Hz), 28.9, 22.3, 14.0; ^{31}P NMR (161 MHz, $CDCl_3$) δ 23.5 (s). FT-IR: ν (cm^{-1}) 3224, 3123, 3026, 2954, 2867, 1456, 1438, 1377, 1186. HRMS [ESI] calcd for $C_{17}H_{23}NOP$ $[M+Na]^+$ 288.1512, found 288.1520.

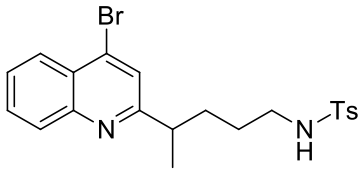
6. Characterization of products



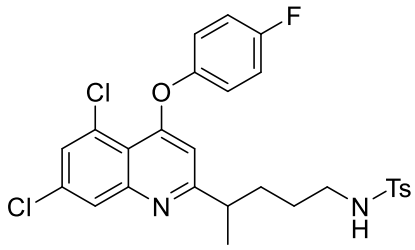
3a: yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12-8.08 (m, 1H), 7.94 (dd, J = 8.4, 0.8 Hz, 1H), 7.71-7.65 (m, 3H), 7.52 (ddd, J = 8.0, 6.8, 0.8 Hz, 1H), 7.20-7.17 (m, 2H), 7.08 (s, 1H), 5.63-5.55 (m, 1H), 3.02-2.82 (m, 3H), 2.67 (s, 3H), 2.36 (s, 3H), 1.88-1.77 (m, 1H), 1.68-1.57 (m, 1H), 1.50-1.32 (m, 2H), 1.28 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 146.8, 144.4, 142.5, 136.6, 129.1, 128.8, 128.7, 126.6, 125.2, 123.1, 119.8, 42.6, 41.3, 33.2, 26.7, 21.0, 20.5, 18.4. FT-IR: ν (cm^{-1}) 3069, 2961, 2928, 2869, 2855, 1604, 1509, 1455, 1381, 1264. HRMS [ESI] calcd for $C_{22}H_{27}N_2O_2S$ $[M+H]^+$ 383.1788, found 383.1803.



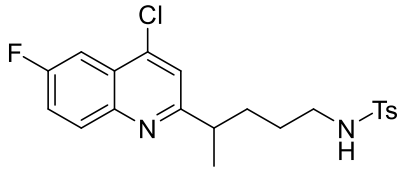
3b: yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18-8.13(m, 1H), 8.10-8.05 (m, 1H), 7.76-7.70 (m, 1H), 7.70-7.65 (m, 2H), 7.61-7.55 (m, 1H), 7.32 (s, 1H), 7.21 - 7.17 (m, 2H), 5.51-5.40 (m, 1H), 3.03-2.83 (m, 3H), 2.34 (s, 3H), 1.86-1.74 (m, 1H), 1.68-1.57 (m, 1H), 1.51-1.31 (m, 2H), 1.27 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 148.3, 143.2, 143.1, 137.0, 130.5, 129.6, 129.2, 127.0, 127.0, 125.1, 123.9, 119.8, 43.1, 41.8, 33.5, 27.2, 21.5, 20.9. FT-IR: ν (cm^{-1})3282, 3067, 2964, 2927, 2870, 1615, 1553, 1455, 1378, 1219. HRMS [ESI] calcd for $C_{21}H_{24}ClN_2O_2S$ $[M+H]^+$ 403.1242, found 403.1247.



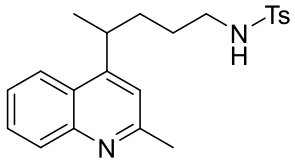
3c: yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11-8.07 (m, 1H), 8.04-8.00 (m, 1H), 7.72-7.65 (m, 3H), 7.55 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 7.51 (s, 1H), 7.19-7.15 (m, 2H), 5.54 (t, *J* = 5.6 Hz, 1H), 2.99-2.83 (m, 3H), 2.32 (s, 3H), 1.84-1.73 (m, 1H), 1.66-1.56 (m, 1H), 1.51-1.28 (m, 2H), 1.26 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 148.2, 143.1, 137.0, 134.5, 130.4, 129.6, 129.3, 127.1, 127.0, 126.6, 126.5, 123.7, 43.1, 41.7, 33.5, 27.2, 21.5, 20.8. FT-IR: ν (cm^{-1}) 3279, 3064, 2962, 2850, 1614, 1551, 1454, 1378, 1214. HRMS [ESI] calcd for $C_{21}H_{24}BrN_2O_2S$ $[M+H]^+$ 447.0736, found 447.0744.



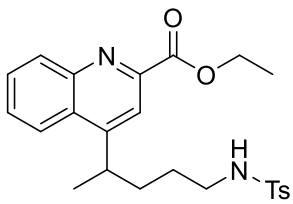
3d: white solid, m.p. 122-123 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98-7.95 (m, 1H), 7.69-7.64 (m, 2H), 7.53-7.51 (m, 1H), 7.25-7.21 (m, 2H), 7.19-7.12 (m, 2H), 7.12-7.07 (m, 2H), 6.44 (s, 1H), 5.07-4.99 (m, 1H), 2.93-2.74 (m, 3H), 2.39 (s, 3H), 1.76-1.64 (m, 1H), 1.58-1.46 (m, 1H), 1.46-1.27 (m, 2H), 1.15 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 162.7, 160.0 (d, $J_{C\text{-}F}$ = 243.1 Hz), 151.2, 150.1 (d, $J_{C\text{-}F}$ = 2.7 Hz), 143.3, 137.0, 135.0, 130.0, 129.6, 128.9, 127.4, 127.0, 122.0 (d, $J_{C\text{-}F}$ = 8.3 Hz), 117.1 (d, $J_{C\text{-}F}$ = 23.3 Hz), 117.0, 105.6, 43.0, 41.8, 33.1, 27.3, 21.5, 20.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.0 (s). FT-IR: ν (cm^{-1}) 3282, 3074, 2961, 1598, 1551, 1455, 1364, 1211. HRMS [ESI] calcd for $C_{27}H_{26}Cl_2FN_2O_3S$ $[M+Na]^+$ 547.1020, found 547.1015.



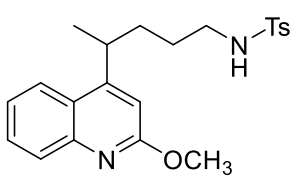
3e: yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08-8.03 (m, 1H), 7.78-7.73 (m, 1H), 7.71-7.65 (m, 2H), 7.51-7.45 (m, 1H), 7.33 (s, 1H), 7.24-7.19 (m, 2H), 5.36 (t, *J* = 6.0 Hz, 1H), 3.00-2.84 (m, 3H), 2.36 (s, 3H), 1.85-1.74 (m, 1H), 1.68-1.56 (m, 1H), 1.51-1.30 (m, 2H), 1.27 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3 (d, $J_{C\text{-}F}$ = 2.8 Hz), 160.9 (d, $J_{C\text{-}F}$ = 247.2 Hz), 145.4, 143.2, 142.2 (d, $J_{C\text{-}F}$ = 5.5 Hz), 137.0, 131.9 (d, $J_{C\text{-}F}$ = 9.1 Hz), 129.6, 127.1, 126.0 (d, $J_{C\text{-}F}$ = 10.1 Hz), 120.6, 120.6 (d, $J_{C\text{-}F}$ = 25.4 Hz), 107.7 (d, $J_{C\text{-}F}$ = 24.4 Hz), 43.1, 41.7, 33.5, 27.2, 21.5, 20.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ - 112.0 (s). FT-IR: ν (cm^{-1}) 3281, 2931, 2870, 1626, 1559, 1456, 1373, 1228. HRMS [ESI] calcd for $C_{21}H_{23}ClFN_2O_2S$ $[M+Na]^+$ 421.1147, found 421.11150.



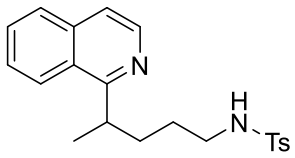
3f: yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04-7.99 (m, 1H), 7.98-7.93 (m, 1H), 7.70-7.61(m, 3H), 7.50-7.44 (m, 1H), 7.25-7.20 (m, 2H), 7.09 (s, 1H), 4.80-4.60 (m, 1H), 3.54-3.43 (m, 1H), 2.95-2.86 (m, 2H), 2.69 (s, 3H), 2.38 (s, 3H), 1.81-1.62 (m, 2H), 1.54-1.35 (m, 2H), 1.30 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 152.9, 148.0, 143.3, 136.9, 129.6, 129.3, 128.9, 127.0, 125.5, 125.3, 122.7, 118.4, 43.1, 33.9, 32.8, 27.5, 25.3, 21.5, 21.2. FT-IR: ν (cm^{-1}) 3281, 3062, 2965, 2870, 1598, 1510, 1455, 1379, 1184. HRMS [ESI] calcd for $C_{22}H_{27}N_2O_2S$ $[M+H]^+$ 383.1788, found 383.1795.



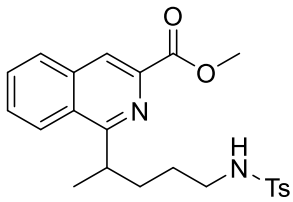
3g: yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30-8.25 (m, 1H), 8.06-8.01 (m, 1H), 7.90-7.96 (m, 1H), 7.75-7.68 (m, 1H), 7.68-7.63 (m, 2H), 7.63-7.57 (m, 1H), 7.22-7.15 (m, 2H), 5.08-4.92 (m, 1H), 4.56-4.47 (m, 2H), 3.58-3.50 (m, 1H), 2.93-2.84 (m, 2H), 2.34 (s, 3H), 1.83-1.64 (m, 2H), 1.54-1.35 (m, 5H), 1.34-1.28 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 154.1, 147.5, 147.4, 142.9, 136.3, 131.2, 129.2, 129.1, 127.9, 127.6, 126.5, 122.3, 116.9, 76.9, 42.6, 33.4, 32.7, 27.0, 21.0, 20.6, 13.9. FT-IR: ν (cm^{-1}) 3283, 2965, 2929, 2869, 1718, 1590, 1459, 1395, 1262. HRMS [ESI] calcd for $C_{24}H_{29}N_2O_4S$ $[M+H]^+$ 441.1843, found 441.1852.



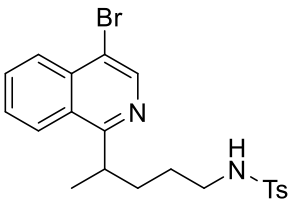
3h: yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89-7.84 (m, 2H), 7.71-7.66 (m, 2H), 7.62-7.56 (m, 1H), 7.39-7.33 (m, 1H), 7.24-7.22 (m, 2H), 6.70 (s, 1H), 5.00-4.74 (m, 1H), 4.05 (s, 3H), 3.45-3.34 (m 1H), 2.93-2.85 (m, 2H), 2.38 (s, 3H), 1.76-1.55 (m, 2H), 1.52-1.34 (m, 2H), 1.28-1.24 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 155.5, 147.2, 143.4, 136.9, 129.7, 129.1, 128.2, 127.0, 124.1, 123.9, 122.9, 109.1, 53.2, 43.2, 33.7, 32.9, 27.4, 21.5, 21.0. FT-IR: ν (cm^{-1}) 3283, 2968, 2934, 2874, 1697, 1552, 1420, 1388, 1249. HRMS [ESI] calcd for $C_{22}H_{26}N_2NaO_3S$ $[M+Na]^+$ 421.1556, found 421.1556.



3i: yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48-8.45 (m, 1H), 8.17-8.13 (m, 1H), 7.84-7.80 (m, 1H), 7.71 - 7.64 (m, 3H), 7.59 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 7.52-7.48 (m, 1H), 7.25-7.21 (m, 2H), 5.08 (t, *J* = 5.2 Hz, 1H), 3.78-3.68 (m, 1H), 2.93-2.85(m, 2H), 2.38 (s, 3H), 2.10-1.99 (m, 1H), 1.76-1.65 (m, 1H), 1.58-1.45 (m, 1H),1.39-1.27(m, 1H), 1.32 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 142.7, 140.9, 136.5, 136.0, 129.5, 129.1, 127.2, 126.8, 126.6, 126.2, 124.2, 118.9, 42.7, 35.3, 31.9, 27.0, 21.0, 20.9. FT-IR: ν (cm^{-1}) 3280, 3053, 2958, 2919, 2850, 1622, 1560, 1455, 1378, 1260. HRMS [ESI] calcd for $C_{21}H_{25}N_2O_2S$ $[M+H]^+$ 369.1631, found 369.1656.

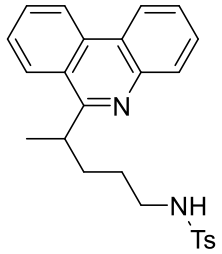


3j: yellow solid, m.p. 134-135 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 8.20-8.14 (m, 1H), 7.93-7.87(m, 1H), 7.73-7.64 (m, 4H), 7.20-7.14 (m, 2H), 5.43 (s, 1H), 4.02 (s, 3H), 3.73-3.62 (m, 1H), 2.98-2.88 (m, 1H), 2.83-2.73 (m, 1H), 2.33 (s, 3H), 2.29-2.19 (m, 1H), 1.72-1.51 (m, 2H), 1.41-1.32 (m, 1H), 1.29 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 165.3, 142.9, 140.2, 137.3, 136.0, 130.4, 129.5, 129.4, 129.1, 128.0, 127.0, 124.8, 122.6, 52.8, 43.0, 36.5, 31.3, 27.7, 21.6, 21.5. FT-IR: ν (cm^{-1}) 3242, 3080, 2975, 2868, 2849, 1711, 1500, 1424, 1318, 1264. HRMS [ESI] calcd for $C_{23}H_{26}N_2NaO_4S$ $[M+Na]^+$ 449.1505, found 449.1499.

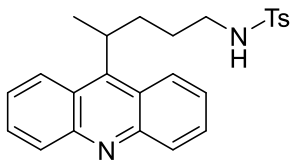


3k: yellow solid, m.p. 126-127 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.17 (dd, *J* = 15.2, 8.4 Hz, 2H), 7.78 (t, *J* = 7.7 Hz, 1H), 7.70-7.62 (m, 3H), 7.25-7.20 (m, 2H), 4.92-4.82 (m, 1H), 3.74-3.64 (m, 1H), 2.89 (q, *J* = 6.6 Hz, 2H), 2.38 (s, 3H), 2.07-1.96 (m, 1H), 1.74-1 .63 (m, 1H), 1.55-1.42 (m, 1H),

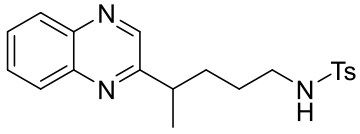
1.40-1.32 (m, 1H) 1.30 (d, *J* = 6.8Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 143.3, 143.2, 136.9, 134.9, 131.1, 129.6, 128.1, 128.0, 127.0, 126.9, 125.0, 117.8, 43.2, 35.7, 32.5, 27.5, 21.5, 21.2. FT-IR: ν (cm^{-1}) 3275, 3069, 3046, 2961, 2924, 2852, 1615, 1566, 1450, 1388, 1241. HRMS [ESI] calcd for $C_{21}H_{24}Br_3N_2O_2S$ $[M+H]^+$ 447.0736, found 447.0760.



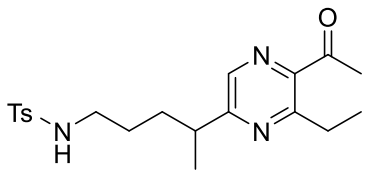
3l: yellow solid, m.p. 47-48 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65-8.61 (m, 1H), 8.55-8.10 (m, 1H), 8.25-8.17 (m, 2H), 7.83-7.77 (m, 1H), 7.76-7.70 (m, 1H), 7.70-7.59 (m, 4H), 7.15-7.09 (m, 2H), 5.30 (t, *J* = 5.6 Hz, 1H), 3.80-3.69 (m, 1H), 3.00-2.82 (m, 2H), 2.30 (s, 3H), 2.29-2.19 (m, 1H), 1.77-1.66 (m, 1H), 1.64-1.51 (m, 1H), 1.47-1.38 (m, 1H), 1.36 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 143.1, 142.6, 136.5, 132.6, 129.8, 129.3, 129.0, 128.2, 126.9, 126.5, 126.0, 125.1, 124.5, 122.9, 122.1, 121.4, 42.7, 35.8, 31.1, 27.0, 21.0, 20.9. FT-IR: ν (cm^{-1}) 3268, 3069, 2966, 2866, 2225, 1911, 1610, 1573, 1486, 1380, 1265. HRMS [ESI] calcd for $C_{25}H_{27}N_2O_2S$ $[M+H]^+$ 419.1788, found 419.1792.



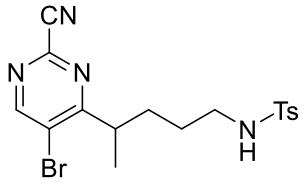
3m: yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40-8.22 (m, 2H), 8.21-8.15 (m, 2H), 7.72-7.64 (m, 2H), 7.62-7.58 (m, 2H), 7.50-7.40 (m, 2H), 7.15-7.11 (m, 2H), 5.18-5.08 (m, 1H), 4.26-4.15 (m, 1H), 2.88-2.78 (m, 2H), 2.33 (s, 3H), 2.22-2.06 (m, 2H), 1.62 (d, *J* = 7.2 Hz, 3H), 1.53-1.41 (m, 1H), 1.22-1.09 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2, 148.6, 143.3, 136.9, 130.9, 130.4, 129.6, 126.9, 125.9, 124.7, 123.5, 43.0, 34.0, 33.7, 28.7, 21.5, 21.2. FT-IR: ν (cm^{-1}) 3283, 3066, 3048, 2960, 2960, 2851, 1599, 1457, 1379, 1289. HRMS [ESI] calcd for $C_{25}H_{27}N_2O_2S$ $[M+H]^+$ 419.1788, found 419.1777.



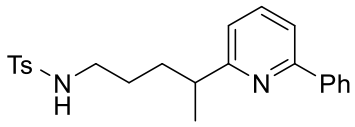
3n: yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (s, 1H), 8.08-8.03 (m, 2H), 7.77-7.65 (m, 4H), 7.23-7.18 (m, 2H), 5.09-4.99 (m, 1H), 3.12-3.02 (m, 1H), 2.98-2.88 (m, 2H), 2.36 (s, 3H), 1.94-1.83 (m, 1H), 1.75-1.64 (m, 1H), 1.57-1.44 (m, 1H), 1.41-1.30 (m, 4H), 1.34 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 145.0, 143.3, 142.0, 141.4, 136.9, 130.1, 129.6, 129.2, 129.1, 129.0, 127.0, 43.1, 39.7, 32.9, 27.4, 21.5, 20.6. FT-IR: ν (cm^{-1}) 3358, 3287, 3182, 3066, 2958, 2919, 2850, 1658, 1598, 1469, 1368, 1323, 1156. HRMS [ESI] calcd for $C_{20}H_{24}N_3O_2S$ $[M+H]^+$ 370.1584, found 370.1593.



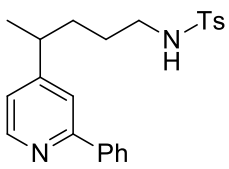
3o: yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.73-7.69 (m, 2H), 7.29-7.24 (m, 2H), 4.94-4.79 (br, 1H), 3.10 (q, *J* = 7.6 Hz, 2H), 2.94-2.83 (m, 3H), 2.66 (s, 3H), 2.40 (s, 3H), 1.81-1.70 (m, 1H), 1.66-1.55 (m, 1H), 1.51-1.38 (m, 1H), 1.38-1.27 (m, 1H), 1.26-1.20 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.3, 162.5, 158.0, 144.5, 143.4, 139.1, 136.9, 129.7, 127.1, 43.1, 39.0, 33.1, 28.8, 28.1, 27.4, 21.5, 20.3, 13.1. FT-IR: ν (cm^{-1}) 3280, 3182, 3064, 2850, 2850, 1647, 1573, 1494, 1378, 1243. HRMS [ESI] calcd for $C_{20}H_{28}N3O3S$ $[M+H]^+$390.1846, found 390.1857.



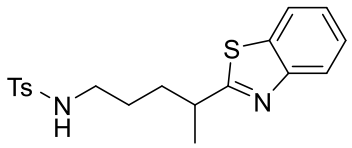
3p: white solid, m.p. 84-85 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (s, 1H), 7.73-7.69 (m, 2H), 7.31-7.27 (m, 2H), 4.88-4.80 (m, 1H), 3.37-3.25 (m, 1H), 2.90 (q, *J* = 6.8 Hz, 2H), 2.42 (s, 3H), 1.84-1.72 (m, 1H), 1.63-1.52 (m, 1H), 1.52-1.39 (m, 1H), 1.38-1.27 (m, 1H), 1.19 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 159.6, 143.5, 143.1, 136.9, 129.8, 127.1, 124.4, 115.3, 43.0, 38.8, 31.7, 27.4, 21.5, 18.9. FT-IR: ν (cm^{-1}) 3282, 2933, 2870, 2358, 2254, 1598, 1495, 1378, 1257. HRMS [ESI] calcd for $C_{17}H_{20}BrN_4O_2S$ $[M+H]^+$ 423.0485, found 423.0478.



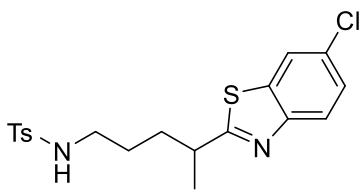
3q-1: yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03-7.98 (m, 2H), 7.69-7.65 (m, 2H), 7.65-7.61 (m, 1H), 7.55-7.51 (m, 1H), 7.49-7.43 (m, 2H), 7.43-7.37 (m, 1H), 7.25-7.21 (m, 2H), 7.03-6.99 (m, 1H), 4.83-4.77 (m, 1H), 2.96-2.87 (m, 3H), 2.38 (s, 3H), 1.86-1.75 (m, 1H), 1.66-1.55 (m, 1H), 1.52-1.32 (m, 2H), 1.27 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (10 MHz, $CDCl_3$) δ 165.5, 156.4, 143.2, 139.6, 137.1, 137.0, 129.6, 128.8, 128.7, 127.1, 127.0, 119.9, 117.9, 43.3, 41.3, 33.9, 27.5, 21.5, 21.0. FT-IR: ν (cm^{-1}) 3277, 3062, 2962, 2868, 1597, 1509, 1435, 1379, 1261. HRMS [ESI] calcd for $C_{23}H_{27}N_2O_2S$ $[M+H]^+$ 395.1786, found 395.1788.



3q-2: yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57-8.34 (m, 1H), 7.96-7.10 (m, 2H), 7.72-7.66 (m, 2H), 7.48-7.36 (m, 4H), 7.25-7.20 (m, 2H), 6.99-6.95 (m, 1H), 4.96-4.92 (m, 1H), 2.92-2.85 (m, 1H), 2.71-2.61 (m, 1H), 2.37 (s, 3H), 1.62-1.54 (m, 2H), 1.47-1.27 (m, 2H), 1.22 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 156.9, 149.5, 143.4, 139.2, 136.9, 129.7, 129.0, 128.7, 127.0, 127.0, 120.9, 119.6, 43.1, 39.3, 34.3, 27.6, 21.5. FT-IR: ν (cm^{-1}) 3356, 3181, 3061, 2958, 2850, 1658, 1598, 1470, 1378, 1156. HRMS [ESI] calcd for $C_{23}H_{27}N_2O_2S$ $[M+H]^+$ 395.1788, found 395.1787.

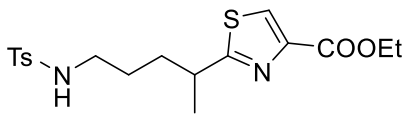


3r: yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.93 (m, 1H), 7.84-7.81 (m, 1H), 7.72-7.67 (m, 2H), 7.47-7.41 (m, 1H), 7.37-7.31 (m, 1H), 7.24-7.19 (m, 2H), 5.20-5.14 (m, 1H), 3.26-3.16 (m, 1H), 2.98-2.89 (m, 2H), 2.36 (s, 3H), 1.89-1.78 (m, 1H), 1.77-1.67 (m, 1H), 1.60-1.40 (m, 2H), 1.38 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.2, 152.7, 143.3, 136.9, 134.5, 129.6, 127.0, 126.0, 124.8, 122.6, 121.6, 43.0, 38.8, 34.0, 27.1, 21.5, 21.4. FT-IR: ν (cm^{-1}) 3276, 3063, 2964, 2927, 2869, 1597, 1495, 1739, 1242. HRMS [ESI] calcd for $C_{19}H_{22}N_2NaO_2S_2$ $[M+Na]^+$ 397.1015, found 397.1020.

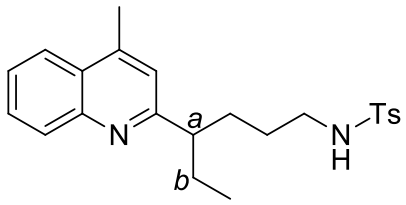


3s: yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.75-7.67 (m, 3H), 7.34-7.30 (m, 1H), 7.25-7.21 (m, 2H), 5.04-4.92 (m, 1H), 3.25-3.15 (m, 1H), 2.99-2.89 (m, 2H), 2.38 (s, 3H), 1.89-1.78 (m, 1H), 1.78-1.67 (m, 1H), 1.60-1.41 (m, 2H), 1.38 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.2, 153.7, 143.3, 136.9, 132.8, 132.0, 129.7, 127.0, 125.3, 122.5, 122.3, 42.9, 38.9, 34.0, 27.1, 21.5, 21.2. FT-IR: ν (cm^{-1}) 3280, 3061, 2959, 2852, 1590,

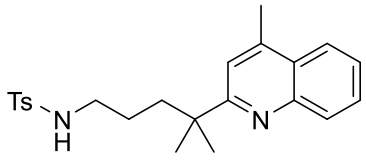
1495, 1378, 1323. HRMS [ESI] calcd for $C_{19}H_{21}ClN_2NaO_2S_2$ $[M+Na]^+$ 431.0625, found 431.0632.



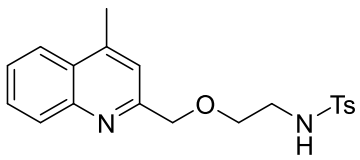
3t: yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.74-7.70 (m, 2H), 7.30-7.26 (m, 2H), 4.80-4.69 (m, 1H), 4.40 (q, *J* = 7.2 Hz, 2H), 3.27-3.17 (m, 1H), 2.97-2.87 (m, 2H), 2.41 (s, 3H), 1.83-1.61 (m, 2H), 1.59-1.41 (m, 2H), 1.39 (t, *J* = 7.2 Hz, 3H), 1.34 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.4, 161.4, 146.5, 143.3, 137.0, 129.7, 127.1, 126.6, 61.4, 42.9, 38.2, 34.4, 27.2, 21.5, 21.4, 14.4. FT-IR: ν (cm^{-1}) 3280, 3121, 2963, 2871, 2854, 1717, 1598, 1453, 1369, 1212. HRMS [ESI] calcd for $C_{18}H_{24}N_2NaO_4S_2$ $[M+Na]^+$ 419.1070, found 419.1064.



3u (4.6:1): yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08-8.02(m, 1H, two isomers), 7.93-7.89 (m, 1H, two isomers), 7.71-7.59 (m, 3H, two isomers), 7.51-7.42 (m, 1H, two isomers), 7.22-7.17 (m, 0.36H, one isomer), 7.17-7.12 (m, 1.64H, one isomer), 7.07 (s, 0.18H, one isomer), 7.03 (s, 0.82H, one isomer), 6.00-5.91 (m, 0.82H, one isomer), 5.40-5.25 (m, 0.18H, one isomer), 2.97-2.78 (m, 2H, two isomers), 2.74-2.65 (m, 1H, two isomers), 2.64 (s, 0.54H, one isomer), 2.63 (s, 2.36H, one isomer), 2.33 (s, 0.54H, one isomer), 2.32 (s, 2.36H, one isomer), 1.79-1.58 (m, 3H, two isomers), 1.47-1.19 (m, 3.54H, two isomers), 0.74 (t, *J* = 7.6 Hz, 2.46H, one isomer); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3 & 164.7 (two isomers), 147.4 & 147.3 (two isomers), 144.7 (overlap, two isomers), 143.1 & 143.0 (two isomers), 137.1 (overlap, two isomers), 129.6 & 129.5 (two isomers), 129.4 (overlap, two isomers), 129.2 & 129.0 (two isomers), 127.1 (overlap, two isomers), 125.7 & 125.5 (two isomers), 123.7 (overlap, two isomers), 120.7 & 120.2 (two isomers), 49.2 & 43.0 (two isomers), 43.2 & 42.52 (two isomers), 36.2 & 32.3 (two isomers), 29.5 & 28.7 (two isomers), 27.0 & 24.5 (two isomers), 21.5 & 20.8 (two isomers), 18.9 (overlap, two isomers), 12.1 (overlap, two isomers). FT-IR: ν (cm^{-1}) 3065, 2964, 2927, 2850, 1635, 1556, 1456, 1379, 1246. HRMS [ESI] calcd for $C_{23}H_{29}N_2O_2S$ $[M+H]^+$ 397.1944, found 397.1966.

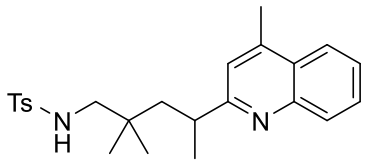


3v: yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23-8.19 (m, 1H), 7.97-7.93 (m, 1H), 7.71 (ddd, *J* = 8.4, 6.8, 1.6 Hz, 1H), 7.69-7.65 (m, 2H), 7.53 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 7.26 (s, 1H), 7.22-7.17 (m, 2H), 5.49-5.44 (m, 1H), 2.91-2.85 (m, 2H), 2.37 (s, 3H), 1.81-1.75 (m, 2H), 1.38-1.30 (m, 2H), 1.33 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 147.1, 144.3, 143.0, 137.0, 129.7, 129.5, 129.2, 127.1, 126.5, 125.8, 123.4, 119.4, 43.4, 40.7, 38.0, 28.5, 24.6, 21.5, 19.0. FT-IR: ν (cm^{-1}) 3273, 3068, 2960, 2920, 2851, 1600, 1508, 1448, 1387, 1263. HRMS [ESI] calcd for $C_{23}H_{29}N_2O_2S$ $[M+H]^+$ 397.1944, found 397.1968.

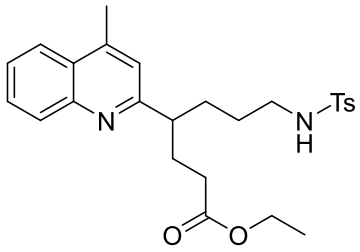


3w: yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23-8.18 (m, 1H),

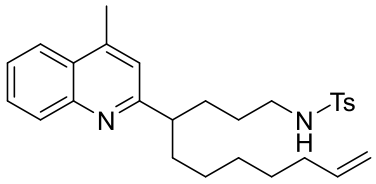
7.99-7.94 (m, 1H), 7.76-7.68 (m, 3H), 7.58-7.52 (m, 1H), 7.22-7.18 (m, 3H), 6.50 (br, 1H), 4.68 (s, 2H), 3.63 (t, *J* = 4.8 Hz, 2H), 3.23-3.17 (m, 2H), 2.68 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 147.3, 145.4, 143.1, 137.1, 129.7, 129.6, 129.6, 127.5, 127.1, 126.4, 123.7, 119.9, 73.6, 69.2, 43.2, 21.5, 18.8. FT-IR: ν (cm^{-1}) 3551, 3477, 3414, 2924, 2866, 1638, 1566, 1447, 1384, 1326. HRMS [ESI] calcd for $C_{20}H_{23}N_2O_3S$ $[M+H]^+$ 371.1424, found 371.1432.



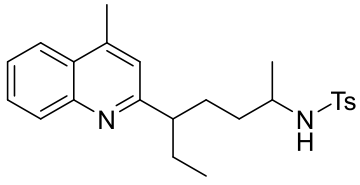
3x: white solid, m.p. 113-114 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26-8.22 (m, 1H), 7.97-7.93 (m, 1H), 7.78-7.72 (m, 1H), 7.59-7.54 (m, 1H), 7.18-7.14 (m, 2H), 7.08 (s, 1H), 6.95-6.91 (m, 2H), 6.66-6.60 (m, 1H), 3.05-2.95 (m, 1H), 2.63 (s, 3H), 2.57-2.50 (m, 1H), 2.47-2.39 (m, 1H), 2.28 (s, 3H), 2.16-2.10 (m, 1H), 1.32-1.28 (m, 1H), 1.27 (d, *J* = 6.8 Hz, 3H), 0.98 (s, 3H), 0.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 147.2, 145.2, 142.2, 137.3, 129.8, 129.5, 129.1, 127.0, 126.6, 125.9, 123.6, 121.1, 51.3, 44.3, 37.7, 34.5, 27.7, 25.5, 24.4, 21.4, 18.8. FT-IR: ν (cm^{-1}) 3064, 2965, 2928, 2874, 1599, 1510, 1457, 1375, 1286, 1183. HRMS [ESI] calcd for $C_{24}H_{31}N_2NaO_2S$ $[M+Na]^+$ 411.2101, found 411.2098.



3y: yellow oil.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08-8.03 (m, 1H), 7.96-7.91 (m, 1H), 7.70-7.62 (m, 3H), 7.54-7.46 (m, 1H), 7.20-7.15 (m, 2H), 7.04 (s, 1H), 5.61-5.47 (m, 1H), 4.07-3.97(m, 2H), 2.96-2.76 (m, 3H), 2.65 (s, 3H), 2.35 (s, 3H), 2.23-1.91 (m, 4H), 1.87-1.74 (m, 1H), 1.72-1.61 (m, 1H), 1.45-1.21 (m, 2H), 1.17 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 163.4, 147.5, 144.9, 143.1, 137.0, 129.6, 129.3, 127.1, 127.0, 125.9, 123.6, 120.9, 60.3, 46.9, 43.1, 32.2, 30.6, 27.0, 21.5, 18.9, 14.2. FT-IR: ν (cm^{-1}) 3282, 2938, 2869, 1733, 1653, 1559, 1456, 1375, 1158. HRMS [ESI] calcd for $C_{26}H_{33}N_2O_4S$ $[M+H]^+$ 469.2156, found 469.2166.

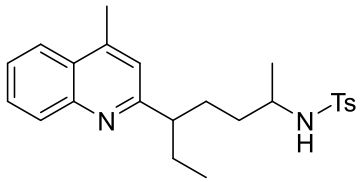


3z: yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16-8.10 (m, 1H), 7.98-7.94 (m, 1H), 7.73-7.64 (m, 3H), 7.53 (ddd, *J* = 8.4, 6.8, 1.2 Hz, 1H), 7.22-7.17 (m, 2H), 7.05 (s, 1H), 5.80-5.69 (m, 1H), 5.59-5.52 (m, 1H), 4.97-4.86 (m, 2H), 2.99-2.898 (m, 1H), 2.88-2.76 (m, 2H), 2.68 (s, 3H), 2.37 (s, 3H), 2.00-1.92 (m, 3H), 1.82-1.56 (m, 5H), 1.38-1.16 (m, 5H), 1.12-1.01 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 143.0, 139.0, 137.1, 129.5, 129.4, 129.3, 127.1, 127.0, 125.8, 123.6, 120.6, 114.2, 47.5, 43.2, 35.8, 33.7, 32.7, 29.2, 28.7, 27.4, 26.9, 21.5, 18.9. FT-IR: ν (cm^{-1}) 3282, 3065, 2927, 2854, 1639, 1561, 1447, 1379, 1157. HRMS [ESI] calcd for $C_{28}H_{37}N_2O_2S$ $[M+H]^+$ 465.2570, found 465.2563.

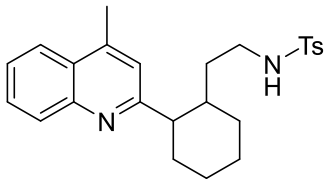


3aa-1 (*d.r.* =1/1.15, one isomer)**:** yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27-8.22 (m, 1H), 7.98-7.93 (m, 1H), 7.80-7.75 (m, 2H), 7.74-7.68 (m, 1H), 7.55-7.50 (m, 1H), 7.23-7.19 (m, 2H), 7.04 (s, 1H), 5.71-5.64 (m, 1H), 3.28-3.16 (m, 1H), 2.76-2.68 (m, 1H), 2.67 (s, 3H), 2.36 (s, 3H),

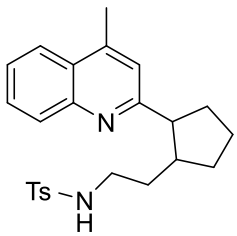
1.72-1.44 (m, 4H), 1.41-1.31 (m, 1H), 1.13-1.03 (m, 1H), 1.01 (d, *J* = 6.4 Hz, 3H), 0.72 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 147.5, 144.5, 142.9, 138.1, 129.6, 129.5, 129.3, 127.2, 127.0, 125.7, 123.6, 121.6, 50.3, 48.9, 34.5, 29.2, 29.1, 22.3, 21.5, 18.9, 11.6. FT-IR: ν (cm^{-1}) 3278, 3064, 2962, 2872, 1601, 1508, 1448, 1379, 1158. HRMS [ESI] calcd for $C_{24}H_{31}N_2O_2S$ $[M+H]^+$ 411.2101, found 411.2098.



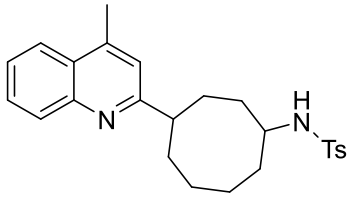
3aa-2 (*d.r.* =1/1.15, one isomer)**:** yellow oil ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14-8.10 (m, 1H), 7.98-7.40 (m, 1H), 7.72-7.65 (m, 3H), 7.55-7.50 (m, 1H), 7.18-7.13 (m, 2H), 7.03 (s, 1H), 5.37-5.26 (m, 1H), 3.29-3.18 (m, 1H), 2.73-2.59 (m, 1H), 2.68 (s, 3H) 2.34 (s, 3H), 1.77-1.56 (m, 4H), 1.38-1.21 (m, 1H), 1.18-1.08 (m, 1H), 1.01 (d, *J* = 6.4 Hz, 3H), 0.76 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 147.4, 144.6, 142.9, 138.3, 129.5, 129.5, 129.2, 127.0, 127.0, 125.7, 123.6, 120.7, , 50.5, 49.2, 34.8, 31.1, 28.5, 22.2, 21.4, 18.9, 12.0. FT-IR: ν (cm^{-1}) 3278, 3062, 2963, 2929, 2872, 1601, 1508, 1448, 1379, 1158. HRMS [ESI] calcd for $C_{24}H_{31}N_2O_2S$ $[M+H]^+$ 411.2101, found 411.2098.



3ab (*d.r.* >19:1): yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28-8.24 (m, 1H), 7.95-7.91 (m, 1H), 7.71 (ddd, *J* = 8.4, 6.8, 1.6 Hz, 1H), 7.68-7.64 (m, 2H), 7.51 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 7.17-7.12 (m, 2H), 7.08-7.59 (m, 1H), 6.42 (t, *J* = 4.4 Hz, 1H), 2.90-2.83 (m, 2H), 2.64 (s, 3H), 2.56-2.48 (m, 1H), 2.34 (s, 3H), 1.90-1.65 (m, 5H), 1.39-1.22 (m, 3H), 1.17-1.07 (m, 2H), 1.06-0.94 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 147.2, 145.0, 142.8, 136.9, 129.5, 129.4, 129.3, 127.1, 127.0, 125.8, 123.6, 121.8, 51.7, 40.7, 37.2, 34.9, 33.3, 32.3, 26.4, 26.1, 21.5, 18.8. FT-IR: ν (cm^{-1}) 3272, 3063, 2924, 2853, 1602, 1508, 1446, 1326, 1289.HRMS [ESI] calcd for $C_{25}H_{31}N_2O_2S$ $[M+H]^+$ 423.2101, found 423.2114.

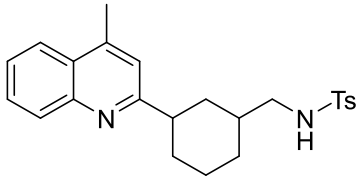


3ac (*d.r.* >19:1): yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.76-7.70 (m, 1H), 7.58-7.52 (m, 1H), 7.49-7.45 (m, 2H), 7.10 (s, 1H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.50 (t, *J* = 6.0 Hz, 1H), 3.00-2.84 (m, 2H), 2.74-2.65 (m, 1H), 2.66 (s, 3H), 2.58-2.47 (m, 1H), 2.32 (s, 3H), 2.22-2.14 (m, 1H), 1.97-1.88 (m, 1H), 1.79-1.64 (m, 4H), 1.52-1.42 (m, 1H), 1.37-1.28 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 147.0, 144.9, 142.6, 137.3, 129.6, 129.3, 127.0, 126.9, 125.9, 123.6, 121.2, 53.1, 41.6, 41.3, 34.9, 34.5, 33.3, 24.7, 21.4, 18.8. FT-IR: ν (cm^{-1}) 3280, 3062, 2925, 2867, 1601, 1508, 1495, 1412, 1325, 1155. HRMS [ESI] calcd for $C_{24}H_{29}N_2O_2S$ $[M+H]^+$ 409.1944, found 409.1944.

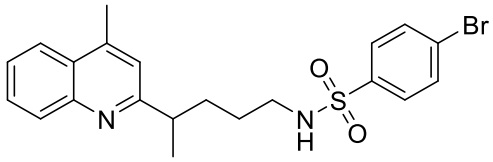


3ad (*d.r.* = 1:1.5): yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04-8.00 (m, 0.4H, one isomer), 8.00-7.96 (m, 0.6H, one isomer), 7.93-7.88 (m, 1H, two isomers), 7.82-7.76 (m, 2H), 7.67-7.60 (m, 1H, two isomers), 7.50-7.44 (m, 1H, two isomers), 7.28-7.22 (m, 2H, two isomers), 7.06-7.03 (m, 1H, two isomers),

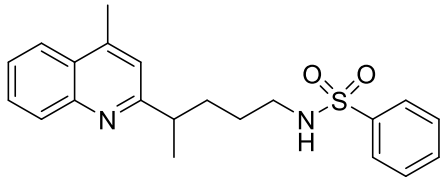
5.48-5.36 (m, 0.4H, one isomer), 5.33-5.17 (m, 0.6H, one isomer), 3.58-3.43 (m, 1H), 3.06-2.92 (m, 1H, two isomers), 2.63 (s, 3H, two isomers), 2.37 (s, 3H, two isomers), 2.05-1.35 (m, 12H, two isomers); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4 & 167.2 (two isomers), 147.3 & 147.3 (two isomers), 144.6 (overlap, two isomers), 143.1 (overlap, two isomers), 138.4 & 138.3 (two isomers), 129.6 & 129.6 (two isomers), 129.4 & 129.3 (two isomers), 129.0 & 129.0 (two isomers), 127.0 (overlap, two isomers), 126.9 & 126.9 (two isomers), 125.5 (two isomers), 123.6 (two isomers), 120.6 (two isomers), 53.9 & 53.5 (overlap, two isomers), 47.9 & 47.4 (overlap, two isomers), 32.3 & 32.03 (overlap, two isomers), 31.5 & 31.5 (overlap, two isomers), 30.1 & 28.5 (overlap, two isomers), 27.0 & 26.1 (overlap, two isomers), 23.3 & 23.3 (overlap, two isomers), 21.5 (overlap, two isomers), 18.8 (overlap, two isomers). FT-IR: ν (cm^{-1}) 3280, 3062, 3031, 2922, 2856, 1601, 1508, 1446, 1379, 1156. HRMS [ESI] calcd for $C_{25}H_{31}N_2O_2S$ $[M+H]^+$ 423.2101, found 423.2105.



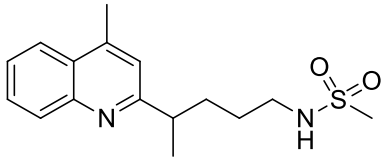
3ae (*dr* >19:1): yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 - 7.99 (m, 1H), 7.96-7.92 (m, 1H), 7.75-7.71 (m, 2H), 7.69-7.63 (m, 1H), 7.53-7.47 (m, 1H), 7.30-7.25 (m, 2H), 7.01 (s, 1H), 4.74 (t, *J* = 6.4 Hz, 1H), 2.90-2.79 (m, 3H), 2.67 (s, 3H), 2.38 (s, 3H), 2.03-1.95 (m, 2H), 1.95-1.87 (m, 1H), 1.84-1.75 (m, 1H), 1.73-1.61 (m, 1H), 1.59-1.36 (m, 2H), 1.34-1.23 (m, 1H), 1.05-0.93 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 147.5, 144.6, 143.3, 137.0, 129.6, 129.3, 129.1, 127.1, 125.5, 123.6, 120.3, 49.4, 46.6, 37.9, 36.3, 32.4, 30.0, 25.7, 21.5, 18.8. FT-IR: ν (cm^{-1}) 3280, 3061, 2923, 2852, 1683, 1560, 1446, 1378, 1323, 1156. HRMS [ESI] calcd for $C_{24}H_{29}N_2O_2S$ $[M+H]^+$ 409.1944, found 409.1949.



3af: yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12-8.08 (m, 1H), 7.97-7.93 (m, 1H), 7.72-7.66 (m, 1H), 7.66-7.59 (m, 2H), 7.55-7.48 (m, 3H), 7.08 (s, 1H), 6.17 (br, 1H), 3.03-2.91 (m, 2H), 2.91-2.82 (m, 1H), 2.67 (s, 3H), 1.90 - 1.78 (m, 1H), 1.69 - 1.57 (m, 1H), 1.50 - 1.32 (m, 2H), 1.28 (d, *J* = 7.2 Hz, 3H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 147.1, 145.1, 139.2, 132.1, 129.4, 129.2, 128.6, 127.1, 127.0, 125.8, 123.7, 120.3, 43.1, 41.5, 33.7, 26.9, 21.2, 18.9. FT-IR: ν (cm^{-1}) 3281, 3063, 2961, 2868, 1603, 1561, 1470, 1388, 1274. HRMS [ESI] calcd for $C_{21}H_{24}BrN_2O_2S$ $[M+H]^+$ 447.0736, found 447.0726.

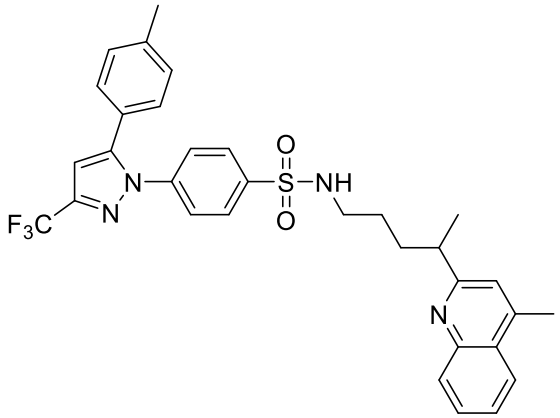


3ag: yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.4 Hz, 1H), 7.96-7.92 (d, *J* = 8.0 Hz, 1H), 7.83-7.77 (m, 2H), 7.71-7.65 (m, 1H), 7.55-7.44 (m, 2H), 7.42-7.36 (m, 2H), 7.08 (s, 1H), 5.87-5.81 (t, *J* = 1.3 Hz, 1H), 3.03-2.84 (m, 3H), 2.66 (s, 3H), 1.87-1.75 (m, 1H), 1.68-1.57 (m, 1H), 1.50-1.32 (m, 2H), 1.28 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 147.0, 145.2, 140.1, 132.3, 129.4, 129.2, 128.9, 127.0, 127.0, 125.8, 123.6, 120.2, 43.1, 41.5, 33.8, 27.1, 21.0, 18.9. FT-IR: ν (cm^{-1}) 3282, 3064, 2959, 2868, 2853, 1603, 1508, 1446, 1380, 1156. HRMS [ESI] calcd for $C_{21}H_{25}N_2O_2S$ $[M+H]^+$ 369.1631, found 369.1632.

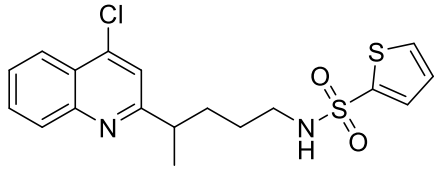


3ah: yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06-8.01 (m, 1H), 7.93-7.88 (m, 1H), 7.67-7.60 (m, 1H), 7.50-7.44 (m, 1H),

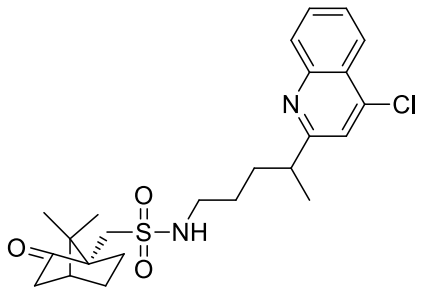
7.11 (s, 1H), 5.60-5.53 (m, 1H), 3.12-2.98 (m, 3H), 2.82 (s, 3H), 2.65 (s, 3H), 1.96-1.84 (m, 1H), 1.77-1.65 (m, 1H), 1.60-1.40 (m, 2H), 1.33 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 147.3, 144.9, 129.2, 129.2, 127.1, 125.7, 123.7, 120.3, 43.2, 41.9, 39.7, 33.7, 27.7, 21.1, 18.9. FT-IR: ν (cm^{-1}) 3286, 2958, 2918, 2850, 1602, 1508, 1448, 1379, 1147. HRMS [ESI] calcd for $C_{16}H_{23}N_2O_2S$ $[M+H]^+$ 307.1475, found 307.1481.



3ai: yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11-8.07 (m, 1H), 7.94-7.90 (m, 1H), 7.78-7.73 (m, 2H), 7.68-7.61 (m, 1H), 7.52-7.46 (m, 1H), 7.34-7.29 (m, 2H), 7.17-7.12 (m, 2H), 7.11-7.04 (m, 3H), 6.73 (s, 1H), 6.42-6.36 (m, 1H), 3.04-2.93 (m, 2H), 2.93-2.83 (m, 1H), 2.65 (s, 3H), 2.35 (s, 3H), 1.91-1.79 (m, 1H), 1.70-1.59 (m, 1H), 1.49-1.33 (m, 2H), 1.29 (d, J = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 147.1, 145.2 (q, J_{C-F} = 4.7 Hz), 143.9 (q, J_{C-F} = 38.2 Hz), 142.1, 139.8 (q, J_{C-F} = 7.3 Hz), 129.7, 129.4, 129.2, 128.7, 128.0, 127.0, 125.8, 125.7, 125.4, 123.7, 121.2 (q, J_{C-F} = 267.4 Hz), 120.3, 106.2, 43.1, 41.5, 33.8, 26.9, 21.3, 21.3, 18.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.4 (s). FT-IR: ν (cm^{-1}) 3290, 3066, 2962, 2849, 1601, 1561, 1471, 1374, 1269. HRMS [ESI] calcd for $C_{32}H_{32}F_3N_4O_2S$ $[M+H]^+$ 593.2193, found 593.2190.

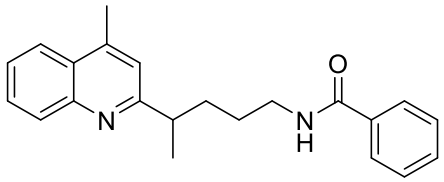


3aj: yellow oil ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19-8.15 (m, 1H), 8.12-8.07 (m, 1H), 7.77-7.71 (m, 1H), 7.62-7.56 (m, 1H), 7.53-7.50 (m, 1H), 7.47-7.43 (m, 1H), 7.35-7.33 (m, 1H), 6.99-6.95 (m, 1H), 5.79-5.71 (m, 1H), 3.1-2.95 (m, 3H), 1.89-1.77 (m, 1H), 1.73-1.62 (m, 1H), 1.54-1.33 (m, 2H), 1.32-1.28 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 148.3, 143.0, 141.1, 131.9, 131.5, 130.5, 129.2, 127.3, 127.0, 125.1, 123.9, 119.9, 43.4, 41.8, 33.6, 27.0, 20.9. FT-IR: ν (cm^{-1}) 3283, 3095, 2963, 2869, 1615, 1553, 1454, 1371, 1225. HRMS [ESI] calcd for $C_{18}H_{20}ClN_2O_2S$ $[M+H]^+$ 395.0649, found 395.0641.

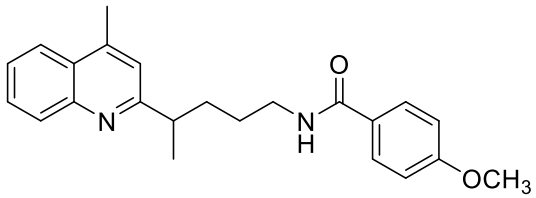


3ak (*d.r.* =1:1.2): yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16-8.12 (m, 1H, two isomers), 8.06-8.01 (m, 1H, two isomers), 7.73-7.67 (m, 1H, two isomers), 7.58-7.51 (m, 1H, two isomers), 7.37 (s, 1H, two isomers), 5.44-5.38 (br, 1H, two isomers), 3.36-3.34 (m, 0.46H, one isomer), 3.32-3.30 (m, 0.54H, one isomer), 3.21-3.00 (m, 3H), 2.87-2.84 (m, 0.54H, one isomer), 2.83-2.80 (m, 0.46H, one isomer), 2.35-2.25 (m, 1H, two isomers), 2.25-2.16 (m, 1H, two isomers), 2.07-2.03 (m, 1H, two isomers), 2.02-1.80 (m, 4H, two isomers), 1.80-1.69 (m, 1H, two isomers), 1.67-1.55 (m, 1H, two isomers), 1.54-1.43 (m, 1H, two isomers), 1.42-1.31 (m, 1H, two isomers), 1.34 (d, J = 6.8 Hz, 3H, two isomers); ^{13}C NMR (100 MHz, $CDCl_3$) δ 216.8 (overlap, two isomers), 166.2 (overlap, two isomers), 148.5 (overlap, two isomers), 142.8 (overlap,

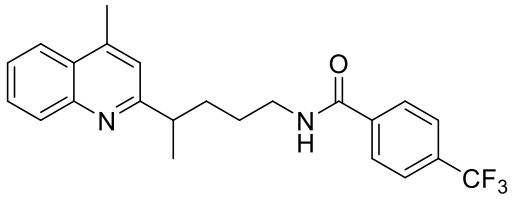
two isomers), 130.3 (overlap, two isomers), 129.3 (overlap, two isomers), 126.8 (overlap, two isomers), 125.1 (overlap, two isomers), 123.9 (overlap, two isomers), 119.9 (overlap, two isomers), 59.1 (overlap, two isomers), 49.1 & 49.1 (two isomers), 48.7 & 48.7 (two isomers), 43.6 & 43.6 (two isomers), 42.9 & 42.7 (two isomers), 42.2 & 42.2 (two isomers), 33.6 (overlap, two isomers), 28.0 & 28.0 (two isomers), 27.0 (overlap, two isomers), 26.4 & 26.4 (two isomers), 20.8 & 20.7 (two isomers), 19.8 & 19.5(two isomers). FT-IR: ν (cm^{-1}) 3290, 3062, 2960, 1739, 1615, 1553, 1454, 1374, 1277. HRMS [ESI] calcd for $C_{24}H_{31}ClN_2NaO_3S$ $[M+Na]^+$ 485.1636, found 485.1636.



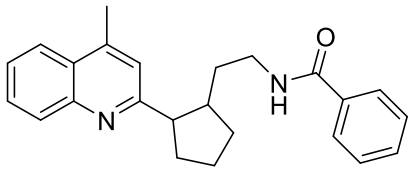
4a: yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99-7.91 (m, 2H), 7.81-7.76 (m, 2H), 7.62 (ddd, *J* = 8.4, 6.8, 1.2 Hz, 1H), 7.52-7.41 (m, 2H), 7.41-7.34 (m, 2H), 7.14 (s, 1H), 6.86 (t, *J* = 7.2 Hz, 1H), 3.50-3.32 (m, 2H), 3.17-3.06 (m, 1H), 2.67 (s, 3H), 1.99-1.87 (m, 1H), 1.81-1.70 (m, 1H), 1.68-1.56 (m, 1H), 1.56-1.43 (m, 1H), 1.36 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 166.0, 147.3, 144.9, 134.8, 131.2, 129.2, 129.1, 128.4, 127.1, 127.0, 125.6, 123.7, 120.2, 42.1, 40.2, 34.5, 27.3, 21.0, 18.9. FT-IR: ν (cm^{-1}) 3321, 3062, 2961, 2929, 2869, 1637, 1578, 1489, 1373, 1158. HRMS [ESI] calcd for $C_{22}H_{24}N_2ONa$ $[M+Na]^+$ 355.1781, found 355.1792.



4b: yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.79-7.73 (m, 2H), 7.67-7.61 (m, 1H), 7.52-7.46 (m, 1H), 7.14 (s, 1H), 6.90-6.85 (m, 2H), 6.65-6.54 (m, 1H), 3.82 (s, 3H), 3.49-3.32 (m, 2H), 3.17-3.06 (m, 1H), 2.67 (s, 3H), 1.99-1.88 (m, 1H), 1.81-1.71 (m, 1H), 1.68-1.55 (m, 1H), 1.55-1.43 (m, 1H), 1.37 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 166.1, 162.0, 147.4, 144.8, 129.3, 129.1, 128.8, 127.2, 127.1, 125.6, 123.7, 120.3, 113.6, 55.4, 42.2, 40.2, 34.6, 27.4, 21.0, 18.9. FT-IR: ν (cm^{-1}) 3318, 3063, 2929, 2856, 1631, 1574, 1442, 1272, 1298. HRMS [ESI] calcd for $C_{23}H_{26}N_2NaO_2$ $[M+Na]^+$ 385.1886, found 385.1887.

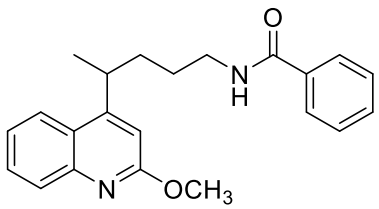


4c: yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-7.85 (m, 4H), 7.61-7.56 (m, 3H), 7.50-7.40 (m, 2H), 7.13 (s, 1H), 3.50-3.31 (m, 2H), 3.16-3.05 (m, 1H), 2.65 (s, 3H), 1.98-1.85 (m, 1H), 1.80-1.68 (m, 1H), 1.66-1.44 (m, 2H), 1.34 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 165.9, 147.1, 145.2, 138.2, 132.9 (q, $J_{C\text{-}F}$ = 32.4 Hz,), 129.3, 128.9, 127.6, 127.1, 125.8, 125.4 (q, $J_{C\text{-}F}$ = 3.7 Hz), 123.8 (q, $J_{C\text{-}F}$ = 270.8 Hz), 123.7, 120.2, 41.9, 40.5, 34.7, 26.9, 21.0, 18.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.9 (s). FT-IR: ν (cm^{-1}) 3301, 3070, 2963, 2871, 1642, 1549, 1376, 1262. HRMS [ESI] calcd for $C_{23}H_{24}F_3N_2O$ $[M+H]^+$ 401.1835, found 401.1848.

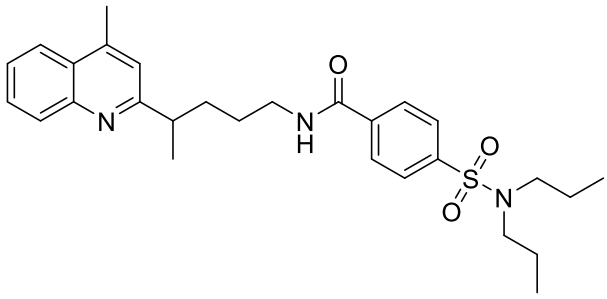


4d: yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96-7.87 (m, 2H), 7.76-7.71 (m, 2H), 7.62-7.56 (m, 1H), 7.51-7.42 (m,

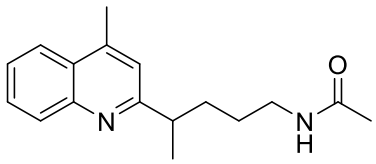
2H), 7.40-7.34 (m, 2H), 7.18 (s, 1H), 7.01 (br, 1H), 3.47-3.37 (m, 1H), 3.29-3.19 (m, 1H), 3.07-2.98 (m, 1H), 2.67 (s, 3H), 2.59-2.47 (m, 1H), 2.26-2.17 (m, 1H), 2.17-2.07 (m, 1H), 1.92-1.76 (m, 4H), 1.69-1.60 (m, 1H), 1.52-1.41 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 165.3, 147.4, 144.7, 135.1, 131.1, 129.2, 129.1, 128.4, 127.1, 127.1, 125.6, 123.7, 121.2, 54.4, 43.7, 38.6, 35.0, 34.8, 33.3, 24.8, 18.8. FT-IR: ν (cm^{-1}) 3317, 3062, 2947, 2868, 1640, 1578, 1488, 1345, 1177. HRMS [ESI] calcd for $C_{24}H_{27}N_2O$ $[M+H]^+$ 359.2118, found 359.2111.



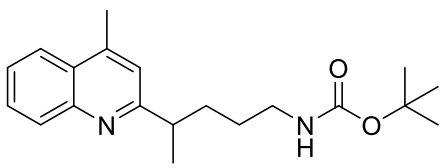
4e: yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.0 Hz, 1H), 7.90-7.85 (m, 1H), 7.72-7.68 (m, 2H), 7.60 (ddd, *J* = 8.4, 6.8, 1.2 Hz, 1H), 7.50-7.44 (m, 1H), 7.42-7.33 (m, 3H), 6.79 (s, 1H), 6.20-6.12 (m, 1H), 4.06 (s, 3H), 3.58-3.48 (m, 1H), 3.47-3.35 (m, 2H), 1.91-1.51 (m, 4H), 1.35 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 162.5, 155.6, 147.2, 134.6, 131.4, 129.2, 128.5, 128.2, 126.8, 124.2, 123.9, 122.9, 109.2, 53.2, 39.9, 34.3, 33.1, 27.7, 21.1. FT-IR: ν (cm^{-1}) 3317, 3064, 2930, 2857, 1635, 1574, 1489, 1387, 1235. HRMS [ESI] calcd for $C_{22}H_{25}N_2O_2$ $[M+H]^+$ 349.1911, found 349.1916.



4f: yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.92 (m, 3H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.84-7.80 (m, 2H), 7.65-7.59 (m, 1H), 7.53-7.48 (m, 1H), 7.22-7.15 (m, 1H), 7.16 (s, 1H), 3.55-3.45 (m, 1H), 3.45-3.34 (m, 1H), 3.22-3.10 (m, 1H), 3.10-3.03 (m, 4H), 2.69 (s, 3H), 2.01-1.90 (m, 1H), 1.84-1.74 (m, 1H), 1.68-1.47 (m, 6H), 1.38 (d, *J* = 6.8 Hz, 3H), 0.85 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 165.9, 147.2, 145.0, 142.5, 138.5, 129.2, 129.0, 127.9, 127.1, 127.1, 125.7, 123.8, 120.2, 50.0, 42.0, 40.6, 34.8, 26.8, 21.9, 21.0, 18.9, 11.2. FT-IR: ν (cm^{-1}) 3320, 2926, 2934, 2875, 1736, 1645, 1539, 1487, 1372, 1241. HRMS [ESI] calcd for $C_{28}H_{37}N_3NaO_3S$ $[M+Na]^+$ 518.2448, found 518.2446.

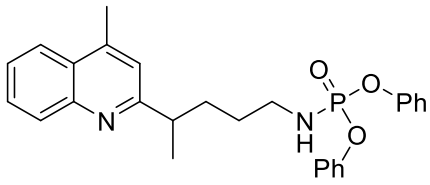


4g: yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04-7.99 (m, 1H), 7.96-7.91 (m, 1H), 7.68-7.62 (m, 1H), 7.52-7.46 (m, 1H), 7.12 (s, 1H), 6.12 (br, 1H), 3.28-3.11 (m, 2H), 3.10-3.00 (m, 1H), 2.67 (s, 3H), 1.93 (s, 3H), 1.90-1.80 (m, 1H), 1.74-1.63 (m, 1H), 1.55-1.44 (m, 1H), 1.44-1.36 (m, 1H), 1.34 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 166.1, 147.4, 144.8, 129.2, 129.1, 127.1, 125.6, 123.7, 120.3, 42.2, 39.7, 34.4, 27.3, 23.3, 21.0, 18.9. FT-IR: ν (cm^{-1}) 3284, 3063, 2958, 2850, 1649, 1558, 1447, 1367, 1294. HRMS [ESI] calcd for $C_{17}H_{23}N_2O$ $[M+H]^+$ 271.1805, found 271.1811.

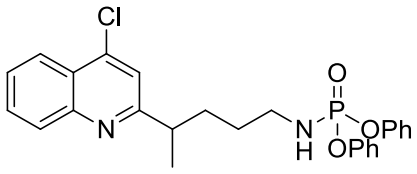


4h: yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03-7.99 (m, 1H), 7.97-7.31 (m, 1H), 7.67 (ddd, *J* = 8.4, 7.2, 1.6 Hz, 1H), 7.51 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 7.16-7.15

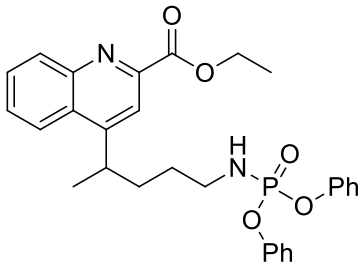
(m, 1H), 5.86 (s, 1H), 3.15-3.05 (m, 1H), 2.68 (s, 3H), 2.13-1.92 (m, 5H), 1.38 (d, J = 6.8 Hz, 3H), 1.35-1.30 (m, 1H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 165.7, 147.3, 144.9, 129.3, 129.1, 127.1, 125.7, 123.7, 119.9, 51.0, 41.7, 35.7, 33.3, 28.8, 20.8, 18.9. FT-IR: ν (cm^{-1}) 3312, 3300, 3065, 2964, 2871, 2851, 1648, 1545, 1391, 1269. HRMS [ESI] calcd for $C_{20}H_{29}N_2O_2$ $[M+H]^+$ 329.2224, found 329.2219.



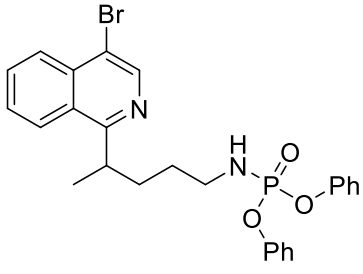
5a: yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.4 Hz, 1H), 7.97-7.92 (m, 1H), 7.67 (ddd, J = 8.4, 7.2, 1.6 Hz, 1H), 7.51 (ddd, J = 8.4, 7.2, 1.2 Hz, 1H), 7.29-7.16 (m, 8H), 7.13-7.06 (m, 2H), 7.08 (s, 1H), 3.49-3.37 (m, 1H), 3.12-2.95 (m, 3H), 2.66 (s, 3H), 1.89-1.78 (m, 1H), 1.70-1.58 (m, 1H), 1.56-1.44 (m, 1H), 1.43-1.33 (m, 1H), 1.30 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 150.9 (d, J_{C-P} = 2.3 Hz), 150.8 (d, J_{C-P} = 2.4 Hz), 150.9, 150.8, 150.8, 147.4, 144.7, 129.6, 129.4, 129.2, 127.1, 125.7, 124.8, 123.6, 120.2, 42.2, 41.8, 33.6, 29.4 (d, J_{C-P} = 6.4 Hz), 21.0, 18.9; ^{31}P NMR (161 MHz, $CDCl_3$) δ -0.6 (s). FT-IR: ν (cm^{-1}) 3227, 3063, 2959, 2871, 1591, 1488, 1379, 1254. HRMS [ESI] calcd for $C_{27}H_{30}N_2O_3P$ $[M+H]^+$ 461.1989, found 461.1996.



5b: yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20-8.16 (m, 1H), 8.06 (d, J = 8.4 Hz, 1H), 7.76-7.70 (m, 1H), 7.61-7.56 (m, 1H), 7.32 (s, 1H), 7.29-7.17 (m, 8H), 7.13-7.06 (m, 2H), 3.60-3.42 (m, 1H), 3.13-2.94 (m, 3H), 1.86-1.75 (m, 1H), 1.68-1.57 (m, 1H), 1.55-1.31 (m, 2H), 1.29 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 150.8 (d, J_{C-P} = 2.0 Hz), 150.8 (d, J_{C-P} = 2.0 Hz), 148.5, 142.9, 130.4, 129.6, 129.3, 126.9, 125.2, 124.8, 123.3, 120.2 (d, J_{C-P} = 1.8 Hz), 120.2 (d, J_{C-P} = 1.8 Hz), 119.8, 42.2, 41.7, 33.50, 29.3 (d, J_{C-P} = 6.2 Hz), 20.8. ^{31}P NMR (161 MHz, $CDCl_3$) δ -0.6 (s). FT-IR: ν (cm^{-1}) 3229, 3068, 2963, 2873, 1589, 1489, 1376, 1220. HRMS [ESI] calcd for $C_{26}H_{27}ClN_2O_3P$ $[M+H]^+$ 481.1442, found 481.1449.

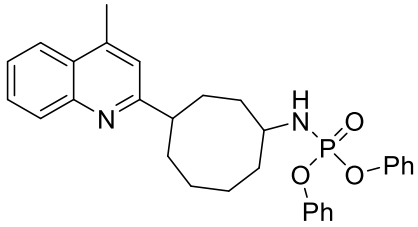


5c: yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J = 8.4 Hz, 1H), 8.03 (d, J = 8.8 Hz, 1H), 8.00 (s, 1H), 7.76-7.71 (m, 1H), 7.63-7.57 (m, 1H), 7.28-7.21 (m, 4H), 7.20-7.15 (m, 4H), 7.12-7.15 (m, 2H), 4.54 (q, J = 7.2 Hz, 2H), 3.58-3.37 (m, 2H), 3.08-2.97 (m, 2H), 1.80-1.61 (m, 2H), 1.53-1.42 (m, 4H), 1.42-1.34 (m, 1H), 1.33-1.29 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 154.7, 150.8 (d, J_{C-P} = 6.6 Hz), 148.1, 147.9, 131.8, 129.7, 129.6, 128.3, 128.1, 124.7, 122.8, 120.1 (d, J_{C-P} = 3.7 Hz), 120.1 (d, J_{C-P} = 3.8 Hz), 117.5, 62.3, 41.7, 34.0, 33.3, 29.5 (d, J_{C-P} = 5.9 Hz), 21.1, 14.4; ^{31}P NMR (161 MHz, $CDCl_3$) δ -0.6 (s). FT-IR: ν (cm-1) 3227, 3069, 2965, 2874, 1716, 1559, 1488, 1369, 1243. HRMS [ESI] calcd for $C_{29}H_{32}N_2O_5P$ $[M+H]^+$ 519.2043, found 519.2033.

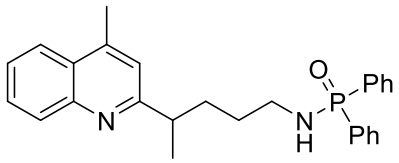


5d: yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 8.20 (d, J = 8.4 Hz, 1H), 8.14 (d, J = 8.4 Hz, 1H), 7.80-7.75 (m, 1H), 7.66-7.60 (m, 1H), 7.31-7.23 (m, 4H), 7.22-7.17 (m, 4H),

7.15-7.08 (m, 2H), 3.74-3.63 (m, 1H), 3.29-3.21 (m, 1H), 3.09-2.96 (m, 2H), 2.08-1.97 (m, 1H), 1.74-1.63 (m, 1H), 1.53-1.42 (m, 1H), 1.41-1.32 (m, 1H), 1.32 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 150.8 (d, $J_{C\text{-}P}$ = 6.5 Hz), 143.6, 134.9, 131.0, 129.6, 128.1, 128.0, 126.9, 124.9, 124.8 (d, $J_{C\text{-}P}$ = 2.6 Hz), 120.2 (t, $J_{C\text{-}P}$ = 4.4 Hz), 120.2 ($J_{C\text{-}P}$ = 4.5 Hz), 117.7, 41.9, 35.8, 32.8, 29.6 ($J_{C\text{-}P}$ = 5.9 Hz), 21.1. ^{31}P NMR (161 MHz, $CDCl_3$) δ -0.7 (s). FT-IR: ν (cm^{-1}) 3228, 3070, 2961, 2871, 2852, 1615, 1565, 1448, 1338, 1256. HRMS [ESI] calcd for $C_{26}H_{27}BrN_2O_3P$ $[M+H]^+$ 525.0937, found 525.0936.

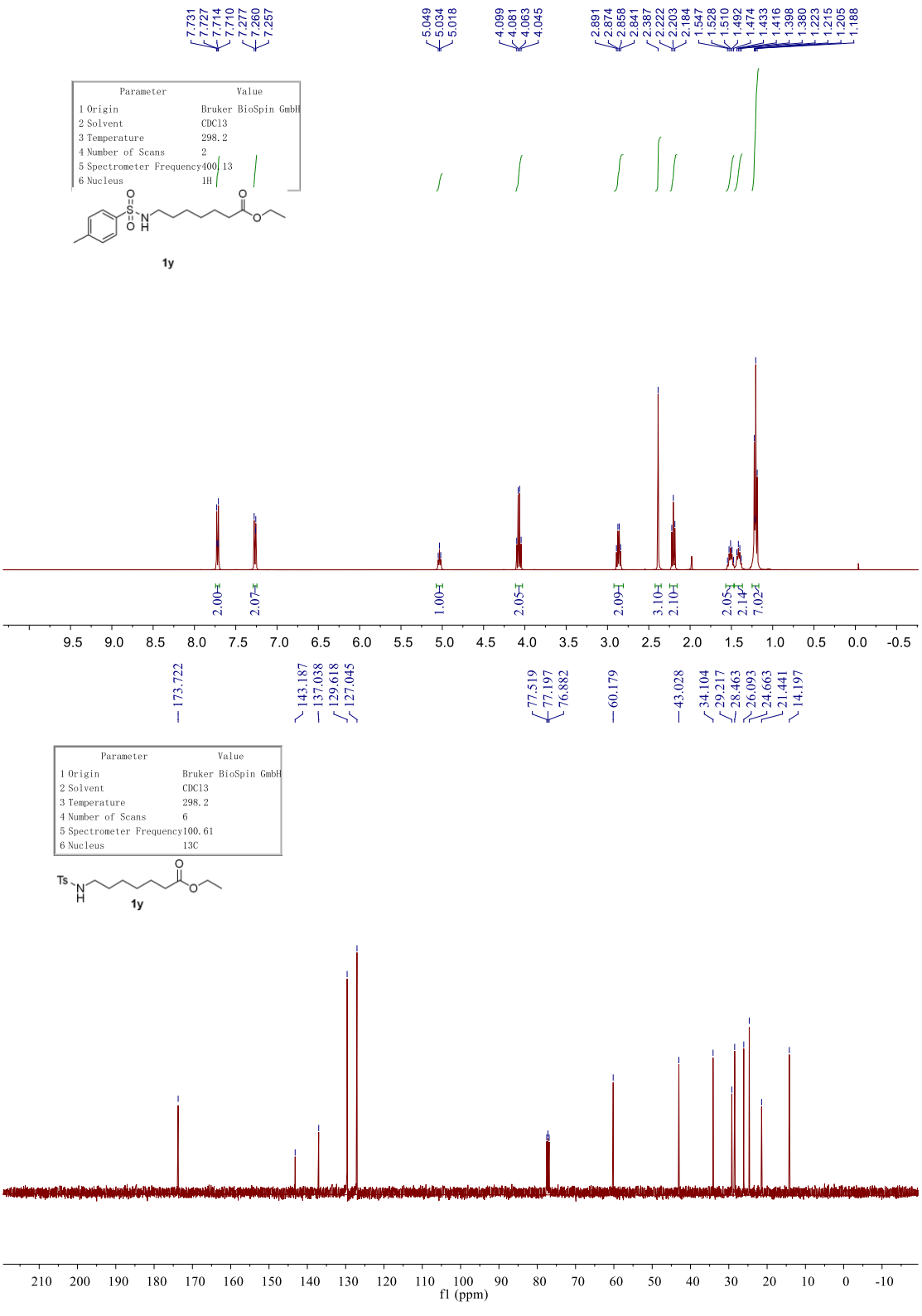


5e (dr = 1/1.4): yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03-7.97 (m, 1H, two isomers), 7.87-7.82 (m, 1H, two isomers), 7.62-7.55 (m, 1H, two isomers), 7.44-7.38 (m, 1H, two isomers), 7.28-7.20 (m, 8H, two isomers), 7.10-7.00 (m, 3H, two isomers), 4.20-3.85 (m, 1H, two isomers), 3.67-3.50 (m, 1H, two isomers), 3.05-2.95 (m, 1H, two isomers), 2.56 (s, 3H, two isomers), 2.10-1.67 (m, 8H, two isomers), 1.64-1.36 (m, 4H, two isomers); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6 & 167.5 (overlap, two isomers), 151.1 (overlap, two isomers, d, $J_{C\text{-}P}$ = 6.5 Hz), 147.4 (overlap, two isomers), 144.5 (overlap, two isomers), 129.7 (overlap, two isomers), 129.5 (overlap, two isomers), 129.0 (overlap, two isomers), 126.9 (overlap, two isomers), 125.5 (overlap, two isomers), 124.7 (overlap, two isomers), 123.6 (overlap, two isomers), 120.6 (overlap, two isomers, $J_{C\text{-}P}$ = 9.8 Hz), 120.3 &120.2 (two isomers), 52.5 & 52.0 (two isomers), 48.1 & 47.6 (two isomers), 33.7 (single isomer, d, $J_{C\text{-}P}$ = 5.2 Hz) , 33.6 (single isomer, d, $J_{C\text{-}P}$ = 5.2 Hz), 33.1 (single isomer, d, $J_{C\text{-}P}$ = 4.7 Hz), 33.0 (single isomer, d, $J_{C\text{-}P}$ = 5.2 Hz), 31.8 & 31.6 (two isomers), 30.3 & 28.9 (two isomers), 27.0 & 26.4 (two isomers), 23.6 & 23.3 (two isomers), 18.8 (overlap, two isomers). ^{31}P NMR (161 MHz, $CDCl_3$) δ -1.4 (s) & -1.5 (s). FT-IR: ν (cm^{-1}) 3210, 3064, 3042, 2922, 2852, 1698, 1560, 1447, 1252. HRMS [ESI] calcd for $C_{30}H_{34}N_2O_3P$ $[M+H]^+$ 501.2302, found 501.2315.



5f: yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95-7.91 (m, 2H), 7.87-7.79 (m, 4H), 7.65-7.09 (m, 1H), 7.51-7.34 (m, 7H), 7.08 (s, 1H), 3.07-2.08 (m, 2H), 2.97-2.88 (m, 2H), 2.65 (s, 3H), 1.95-1.84 (m, 1H), 1.73-1.53 (m, 2H), 1.50-1.38 (m, 1H), 1.33 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 147.5, 144.5, 133.2 (d, $J_{C\text{-}P}$ = 4.2 Hz), 132.1 (d, $J_{C\text{-}P}$ = 9.3 Hz), 132.1 (d, $J_{C\text{-}P}$ = 9.3 Hz), 131.9 (d, $J_{C\text{-}P}$ = 4.4 Hz), 131.7 (d, $J_{C\text{-}P}$ = 2.4 Hz), 129.2 (d, $J_{C\text{-}P}$ = 44.1 Hz), 128.5 (d, $J_{C\text{-}P}$ = 12.5 Hz), 127.0, 125.5, 123.6, 120.4, 42.4, 40.7 (d, $J_{C\text{-}P}$ = 1.1 Hz), 33.8, 30.2 (d, $J_{C\text{-}P}$ = 7.0 Hz), 21.0, 18.8; ^{31}P NMR (161 MHz, $CDCl_3$) δ 23.5 (s). FT-IR: ν (cm^{-1}) 3356, 3196, 3059, 2959, 2854, 1719, 1661, 1561, 1438, 1379, 1263. HRMS [ESI] calcd for $C_{27}H_{30}N_2OP$ $[M+H]^+$ 429.2090, found 429.2101.

7. ^{1}H, ^{13}C, ^{19}F, ^{31}P NMR spectra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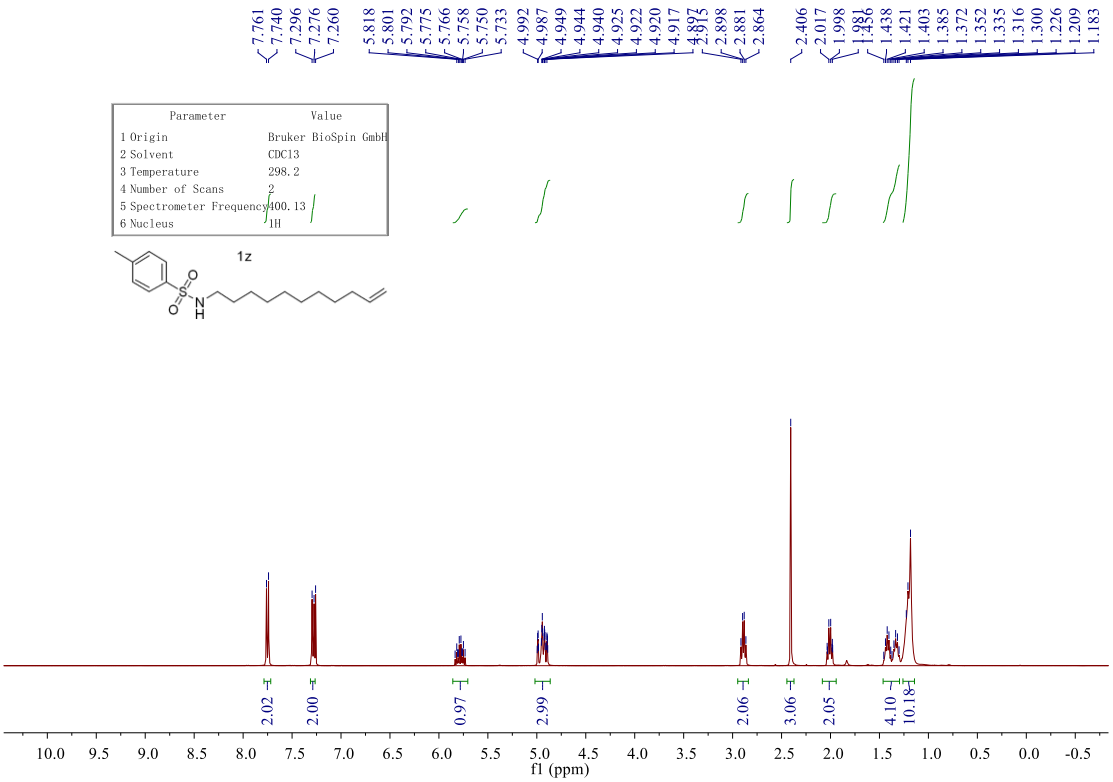
7.710
7.277
7.260
7.257
5.049
5.034
5.018
4.099
4.081
4.063
4.045
2.891
2.874
2.858
2.841
2.387
2.222
2.203
2.184
1.547
1.528
1.510
1.492
1.474
1.433
1.416
1.398
1.380
1.223
1.215
1.205
1.188
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 2
5 Spectrometer Frequency 400.13
6 Nucleus 1H
1y
2.00
2.07
1.00
2.05
2.09
3.10
2.10
2.05
2.14
7.02
9.5 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
173.722
143.187
137.038
129.618
127.045
77.519
77.197
76.882
60.179
43.028
34.104
29.217
28.463
26.093
24.663
21.441
14.197
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 6
5 Spectrometer Frequency 100.61
6 Nucleus 13C
1y
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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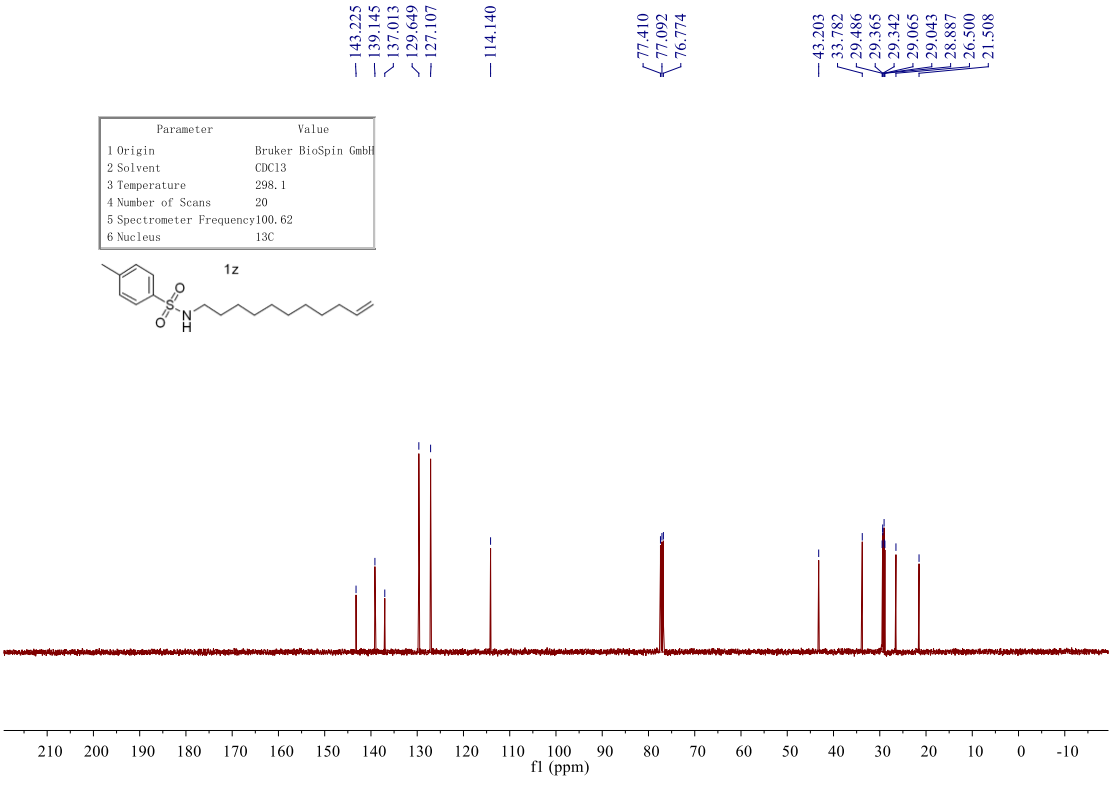
7.740
7.296
7.276
7.260
5.818
5.801
5.792
5.775
5.766
5.758
5.750
5.733
4.992
4.987
4.949
4.944
4.940
4.925
4.922
4.920
4.917
2.898
2.881
2.864
2.406
2.017
1.998
1.438
1.421
1.403
1.385
1.372
1.352
1.335
1.316
1.300
1.226
1.209
1.183
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 2
5 Spectrometer Frequency 400.13
6 Nucleus 1H
1z
2.02
2.00
0.97
2.99
2.06
3.06
2.05
4.10
10.18
f1 (ppm)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114.140
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77.092
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43.203
33.782
29.486
29.365
29.342
29.065
29.043
28.887
26.500
21.508
Parameter Value
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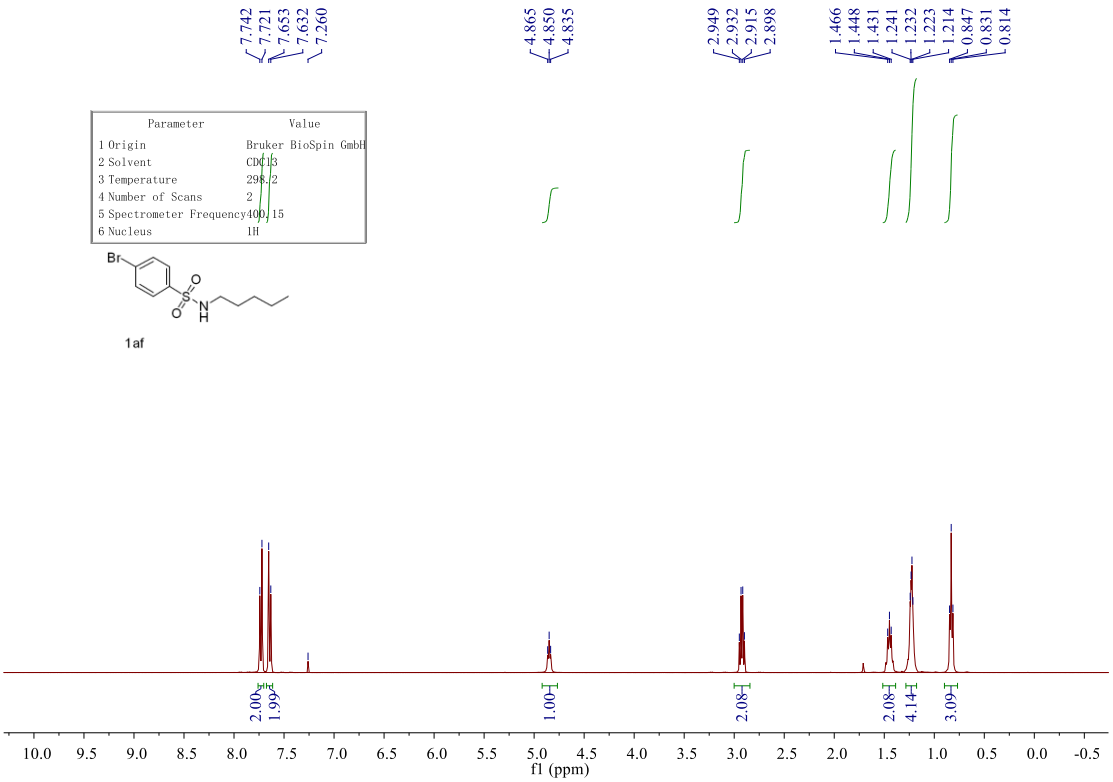
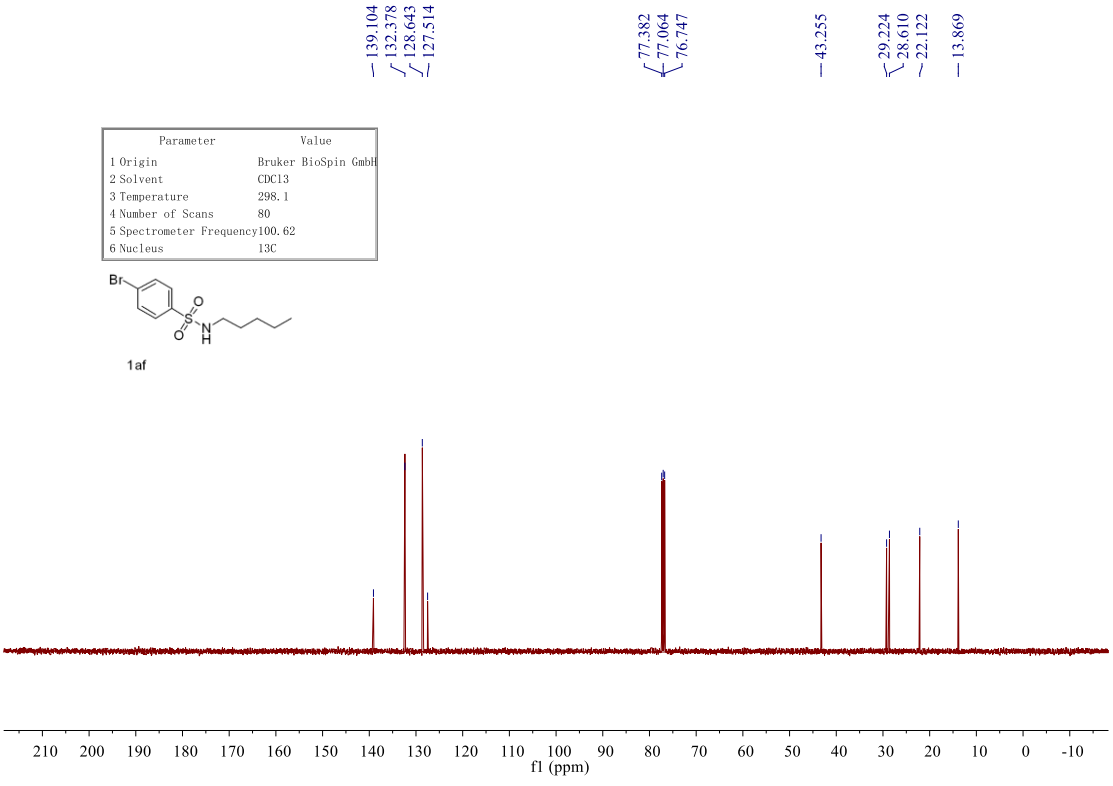
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 20
5 Spectrometer Frequency 100.62
6 Nucleus 13C
1z
f1 (ppm)


7.742
7.721
7.653
7.632
7.260
4.865
4.850
4.835
2.949
2.932
2.915
2.898
1.466
1.448
1.431
1.241
1.232
1.223
1.214
0.847
0.831
0.814
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 2
5 Spectrometer Frequency 400.15
6 Nucleus 1H
Br
O
S
O
N
H
1af
2.00
1.99
1.00
2.08
2.08
4.14
3.09
10.0 9.5 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)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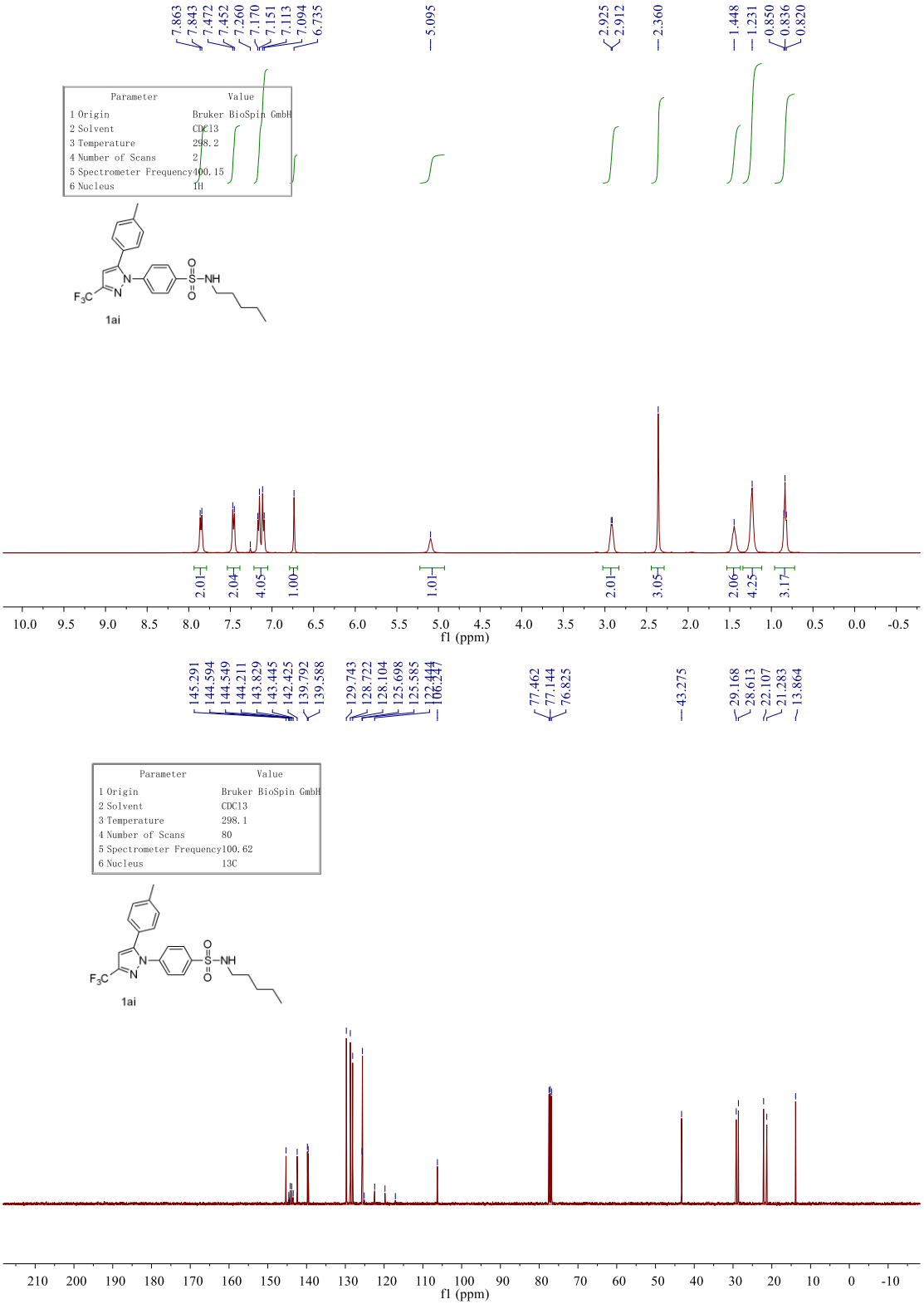
132.378
128.643
127.514
77.382
77.064
76.747
43.255
29.224
28.610
22.122
13.869
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 80
5 Spectrometer Frequency 100.62
6 Nucleus 13C
Br
O
S
O
N
H
1af
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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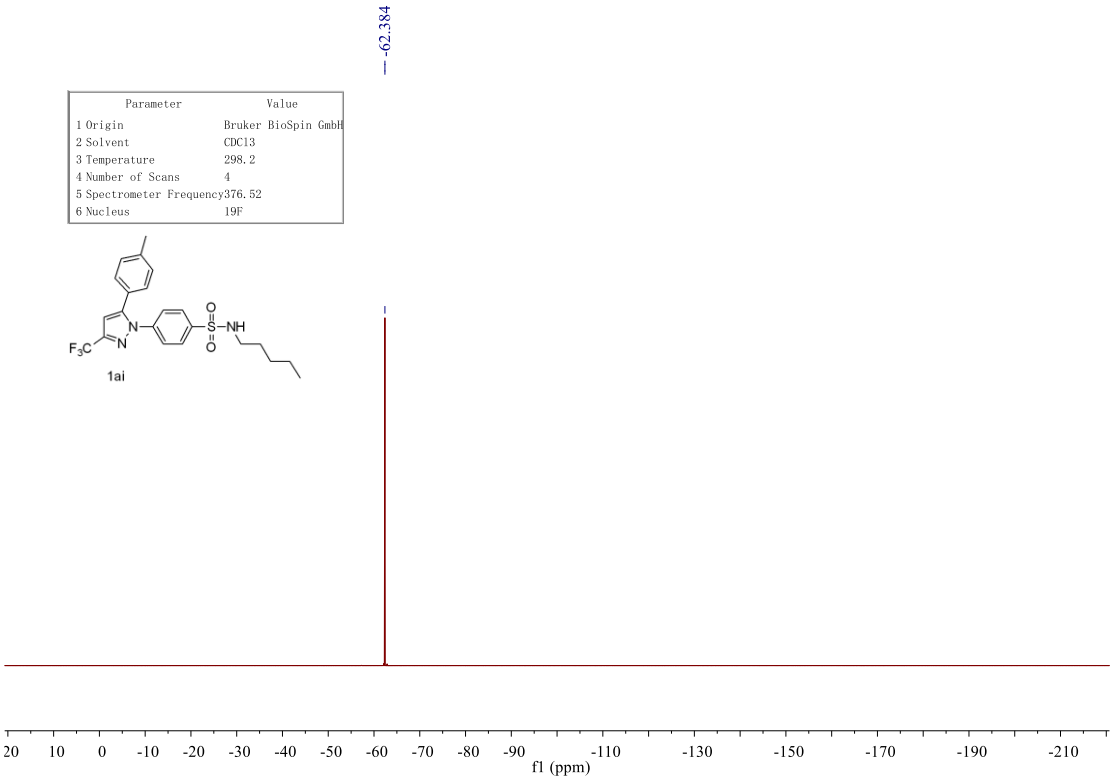
7.170
7.151
7.113
7.094
6.735
5.095
2.925
2.912
2.360
1.448
1.231
0.850
0.836
0.820
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 2
5 Spectrometer Frequency 400.15
6 Nucleus 1H
1ai
2.01
2.04
4.05
1.00
1.01
2.01
3.05
2.06
4.25
3.17
f1 (ppm)
145.291
144.594
144.549
144.211
143.829
143.445
142.425
139.792
139.588
129.743
128.722
128.104
125.698
125.585
77.462
77.144
76.825
43.275
29.168
28.613
22.107
21.283
13.864
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 80
5 Spectrometer Frequency 100.62
6 Nucleus 13C
1ai
f1 (ppm)


-62.384
Parameter Value
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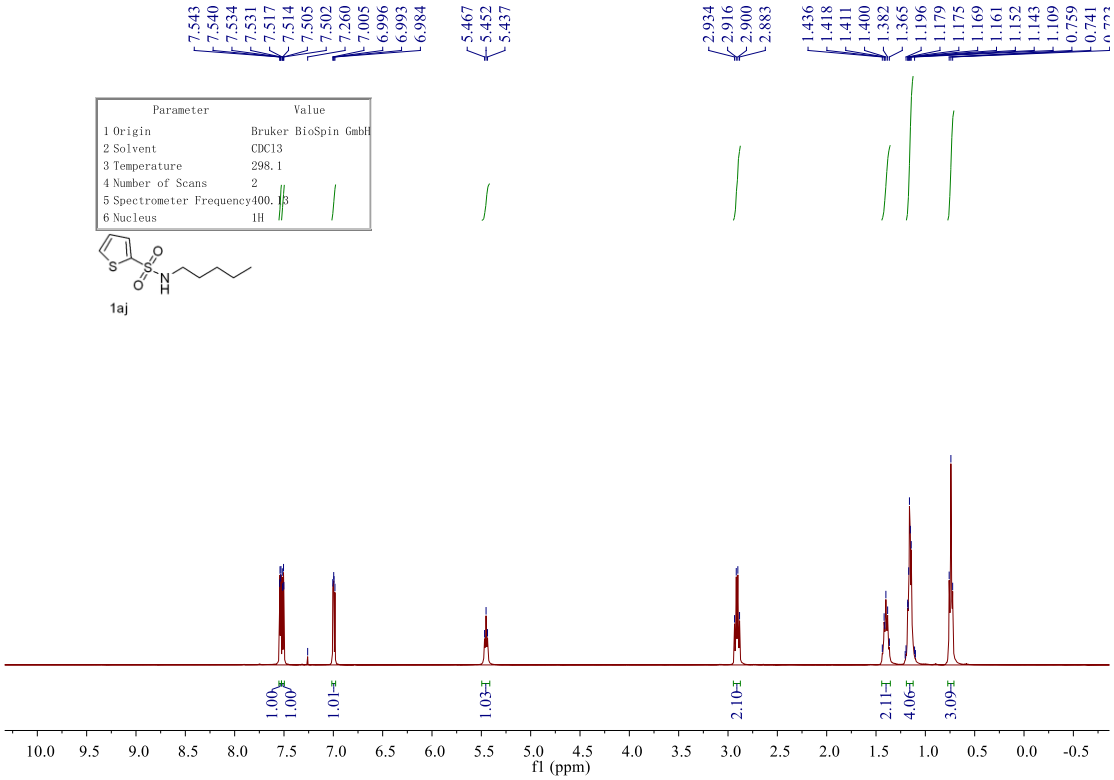
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 4
5 Spectrometer Frequency 376.52
6 Nucleus 19F
1ai
f1 (ppm)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7.540
7.534
7.531
7.517
7.514
7.505
7.502
7.260
7.005
6.996
6.993
6.984
5.467
5.452
5.437
2.934
2.916
2.900
2.883
1.436
1.418
1.411
1.400
1.382
1.365
1.196
1.179
1.175
1.169
1.161
1.152
1.143
1.109
0.759
0.741
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 2
5 Spectrometer Frequency 400.13
6 Nucleus 1H
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1.00
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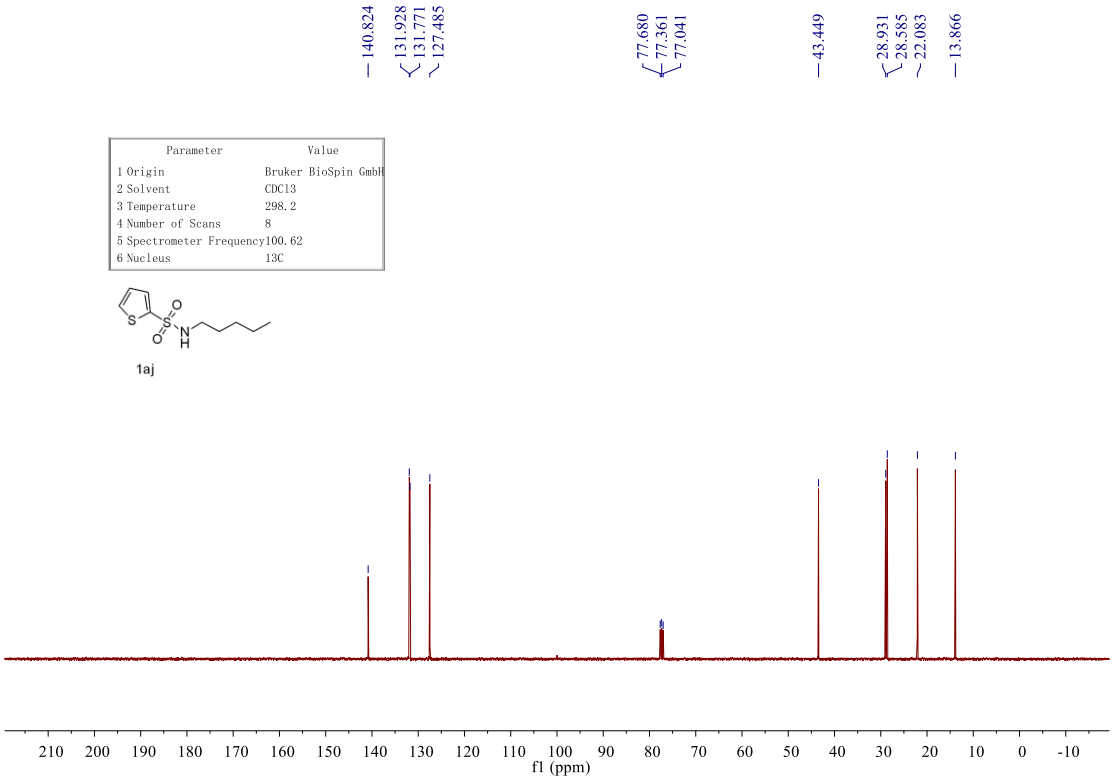
2.11
4.06
3.09
f1 (ppm)


140.824
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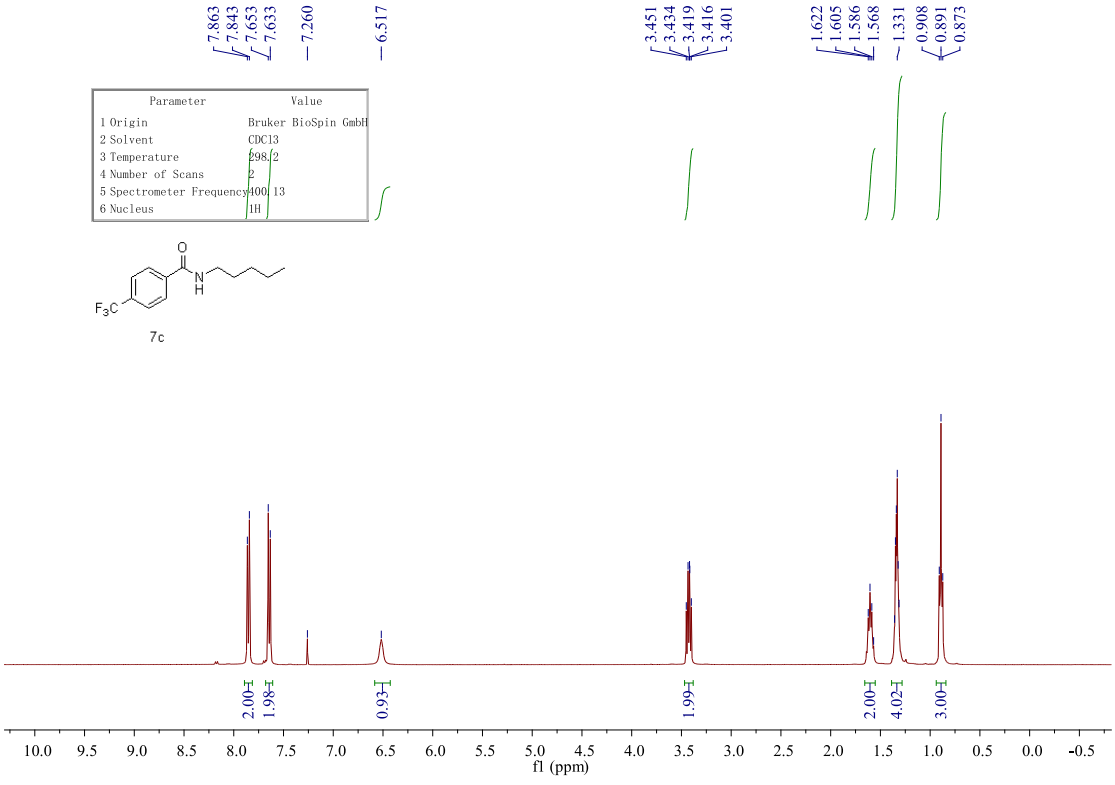
131.771
127.485
77.680
77.361
77.041
43.449
28.931
28.585
22.083
13.866
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 8
5 Spectrometer Frequency 100.62
6 Nucleus 13C
1aj
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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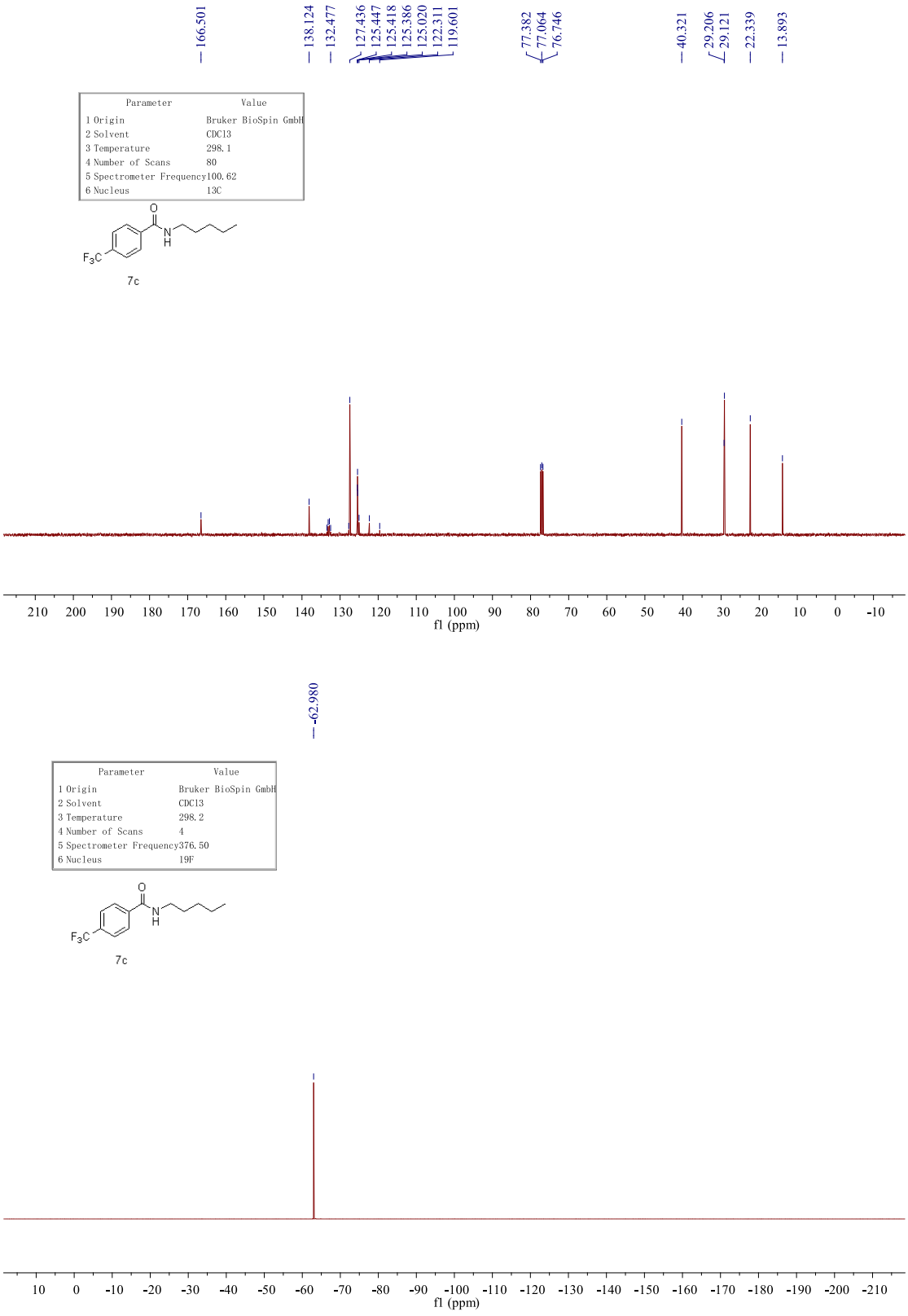
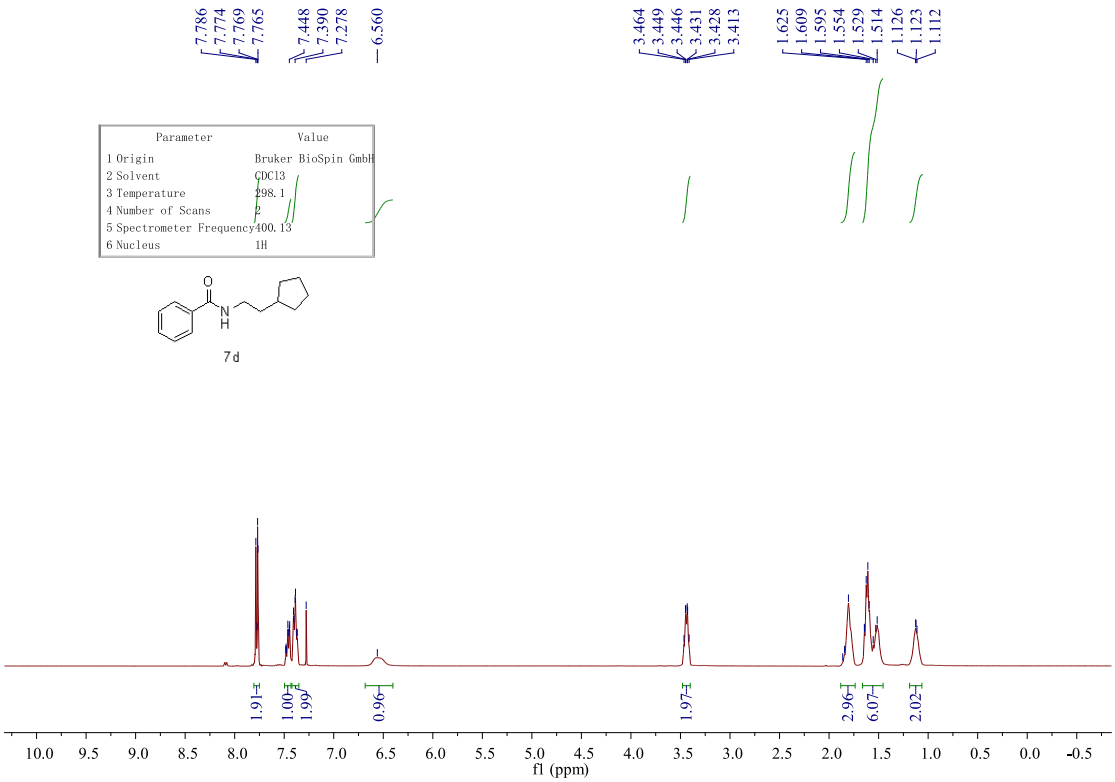
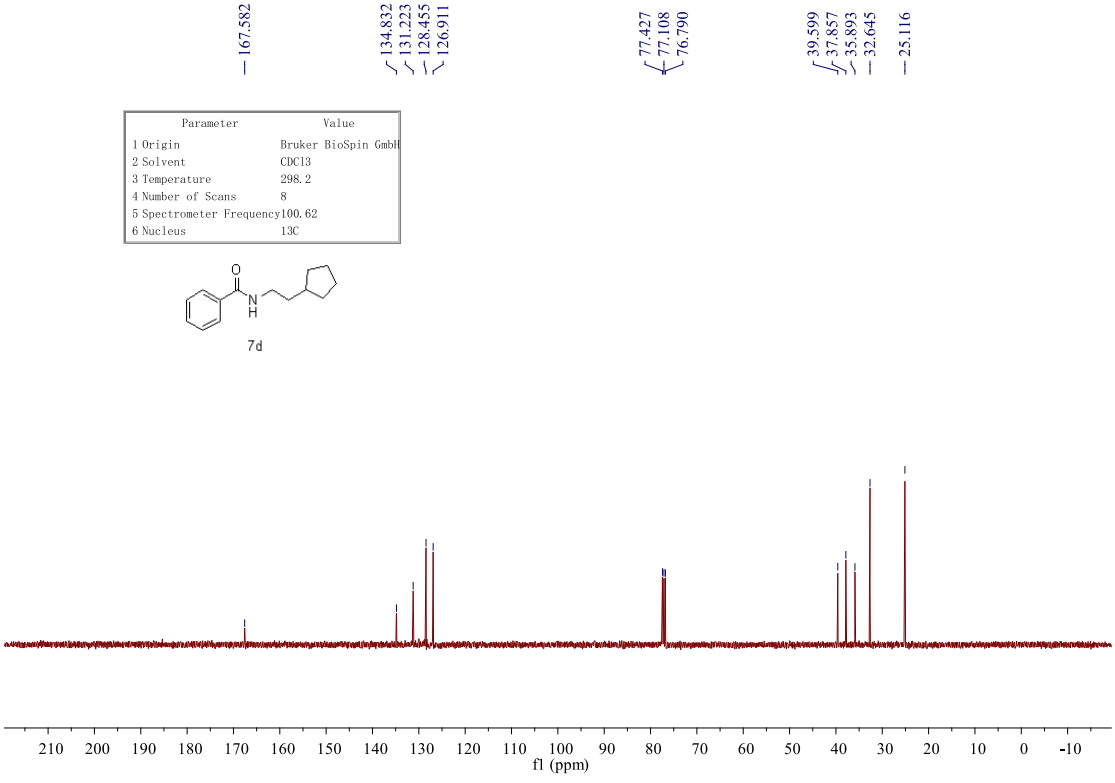
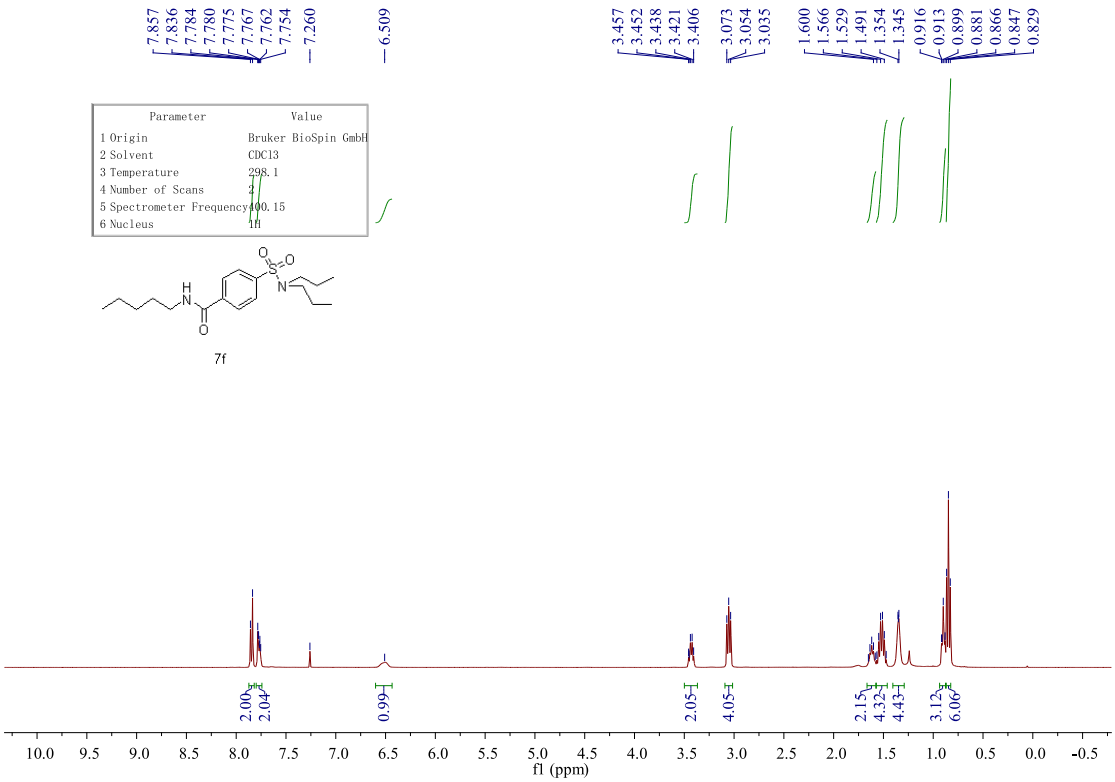
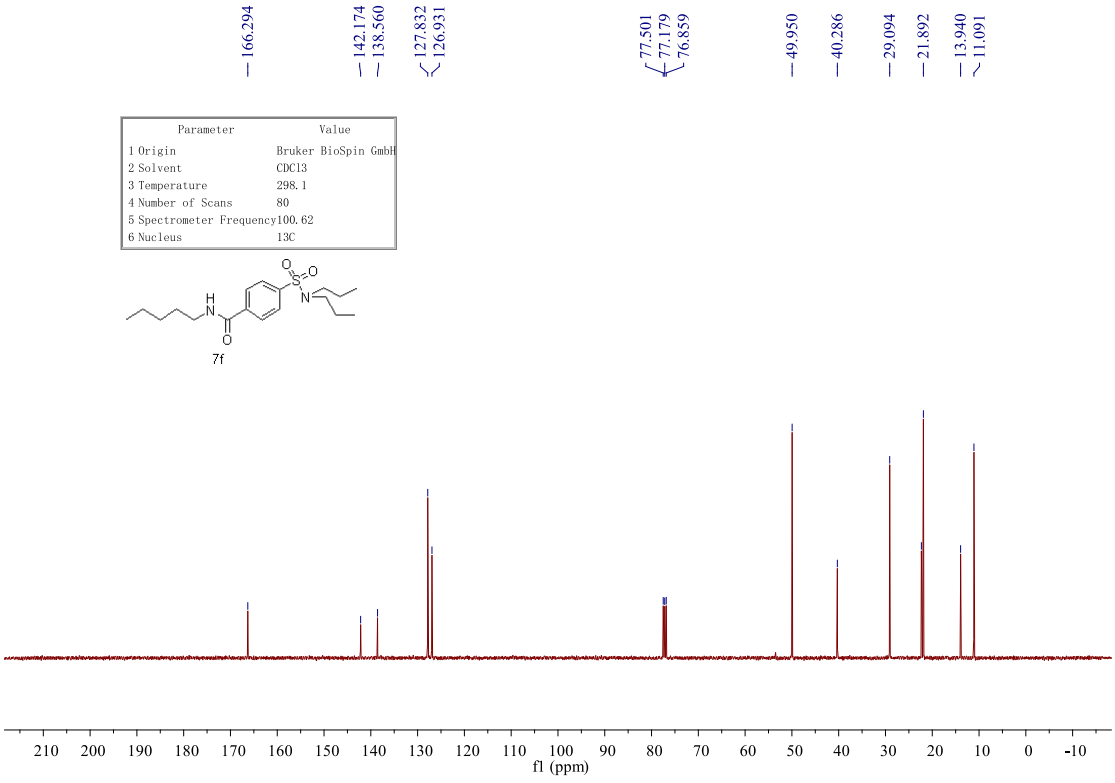
7.653
7.633
7.260
6.517
3.451
3.434
3.419
3.416
3.401
1.622
1.605
1.586
1.568
1.331
0.908
0.891
0.873
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 2
5 Spectrometer Frequency 400.13
6 Nucleus 1H
7c
2.00
1.98
0.93
1.99
2.00
4.02
3.00
10.0 9.5 9.0 8.5 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)

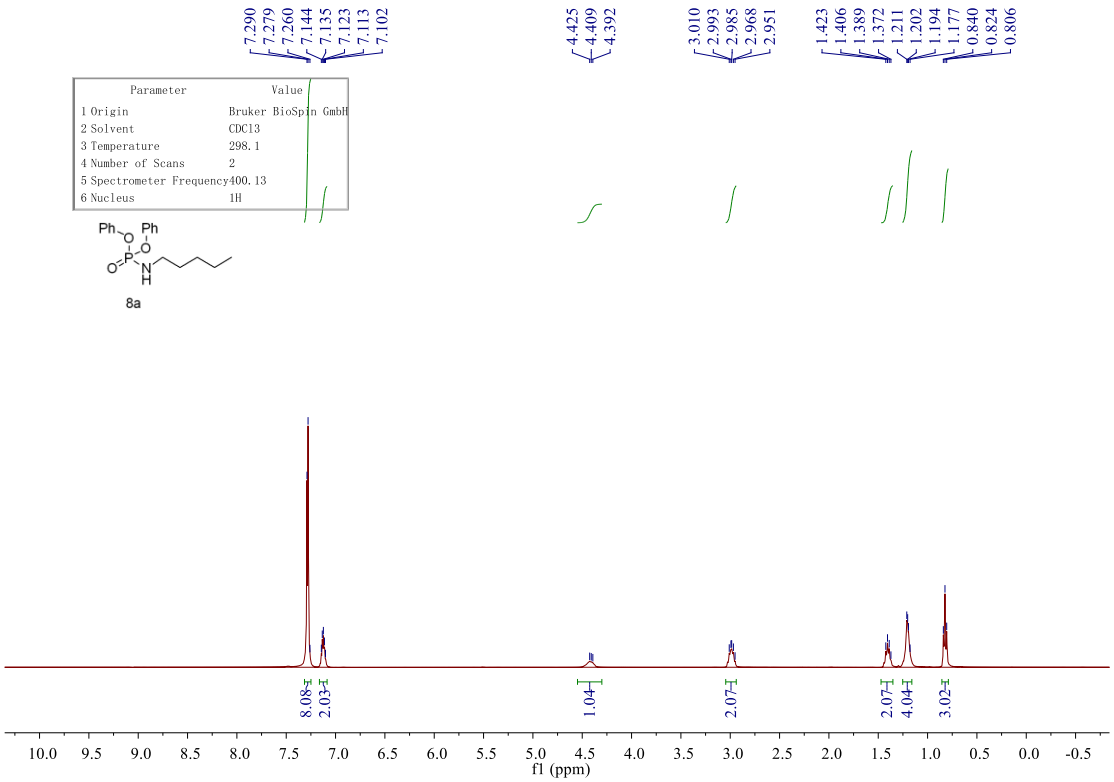

166.501
138.124
132.477
127.436
125.447
125.418
125.386
125.020
122.311
119.601
77.382
77.064
76.746
40.321
29.206
29.121
22.339
13.893
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 80
5 Spectrometer Frequency 100.62
6 Nucleus 13C
O
N
H
F3C
7c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
-62.980
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 4
5 Spectrometer Frequency 376.50
6 Nucleus 19F
O
N
H
F3C
7c
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)

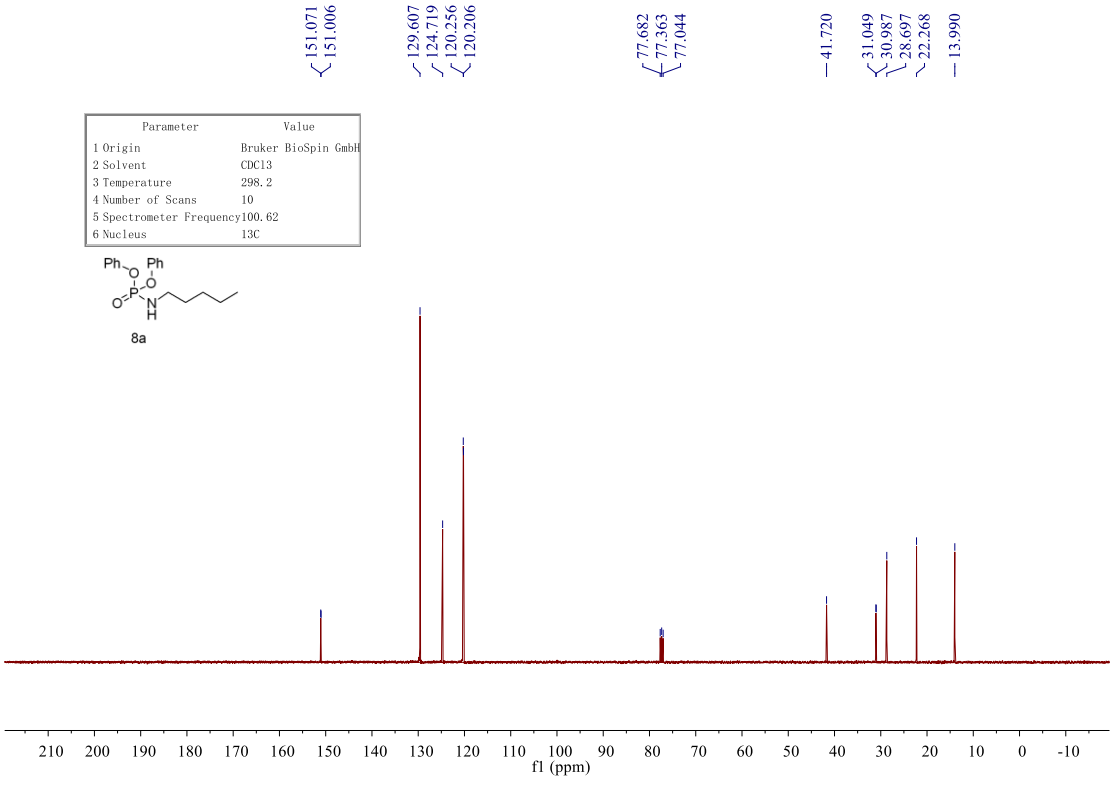

7.786
7.774
7.769
7.765
7.448
7.390
7.278
6.560
3.464
3.449
3.446
3.431
3.428
3.413
1.625
1.609
1.595
1.554
1.529
1.514
1.126
1.123
1.112
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 2
5 Spectrometer Frequency 400.13
6 Nucleus 1H
7d
1.91
1.00
1.99
0.96
1.97
2.96
6.07
2.02
10.0 9.5 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)

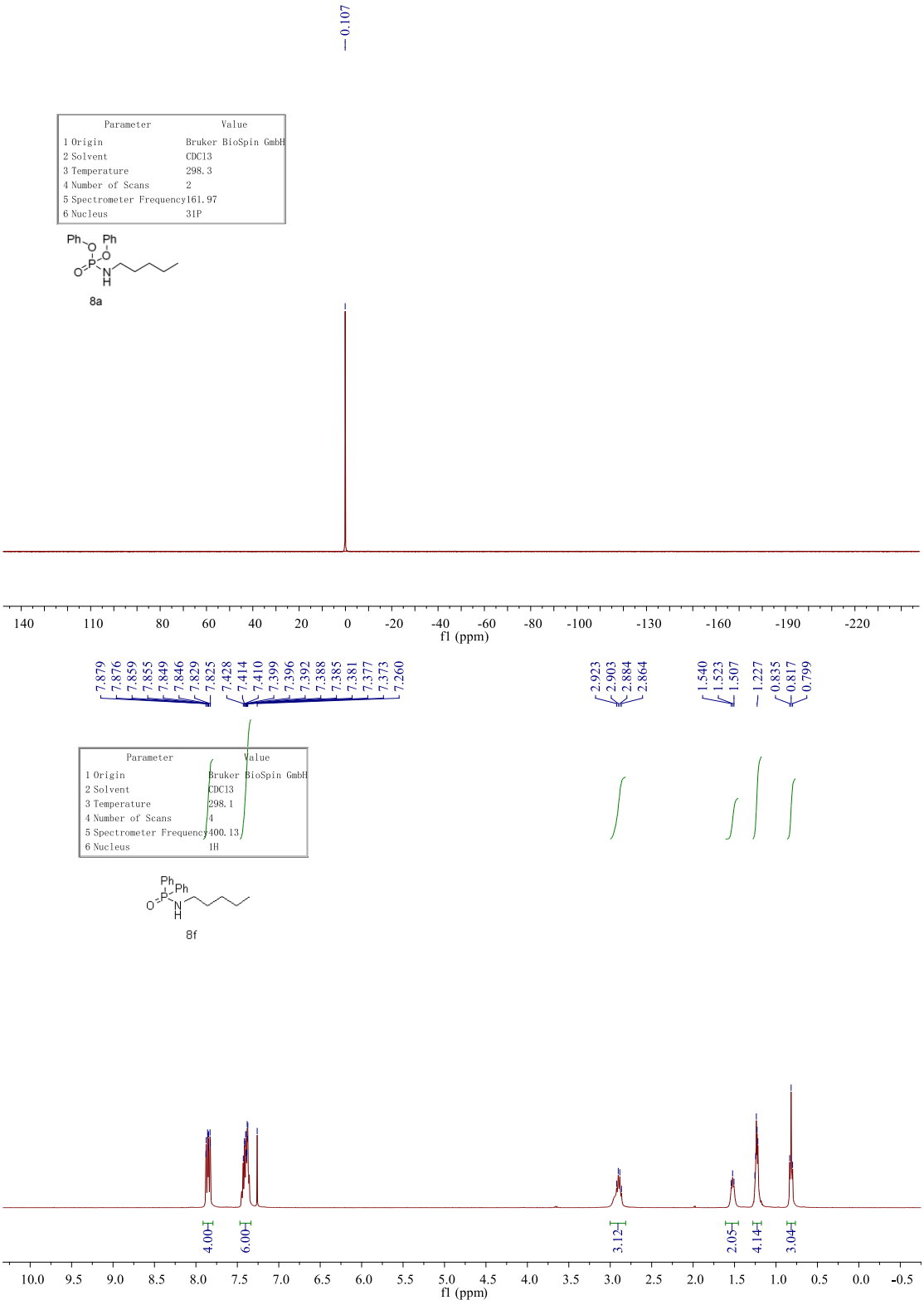

167.582
134.832
131.223
128.455
126.911
77.427
77.108
76.790
39.599
37.857
35.893
32.645
25.116
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 8
5 Spectrometer Frequency 100.62
6 Nucleus 13C
7d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

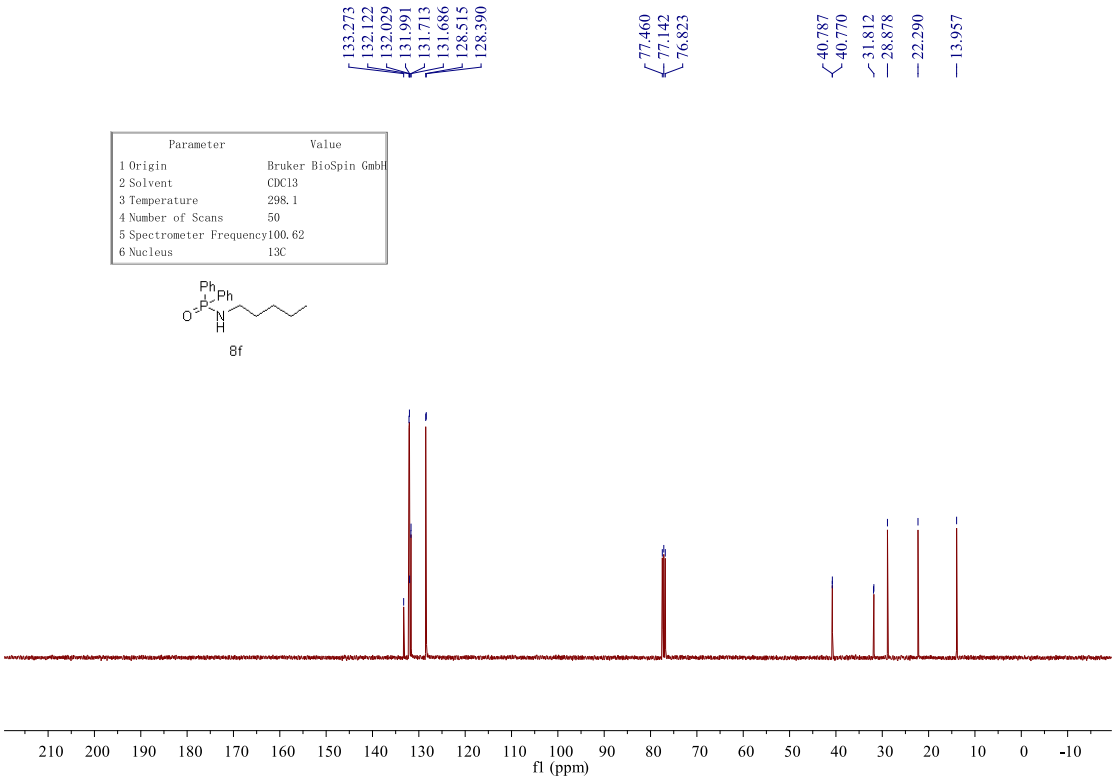

7.857
7.836
7.784
7.780
7.775
7.767
7.762
7.754
7.260
6.509
3.457
3.452
3.438
3.421
3.406
3.073
3.054
3.035
1.600
1.566
1.529
1.491
1.354
1.345
0.916
0.913
0.899
0.881
0.866
0.847
0.829
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 2
5 Spectrometer Frequency 400.15
6 Nucleus 1H
7f
2.00
2.04
0.99
2.05
4.05
2.15
4.32
4.43
3.12
6.06
fl (ppm)

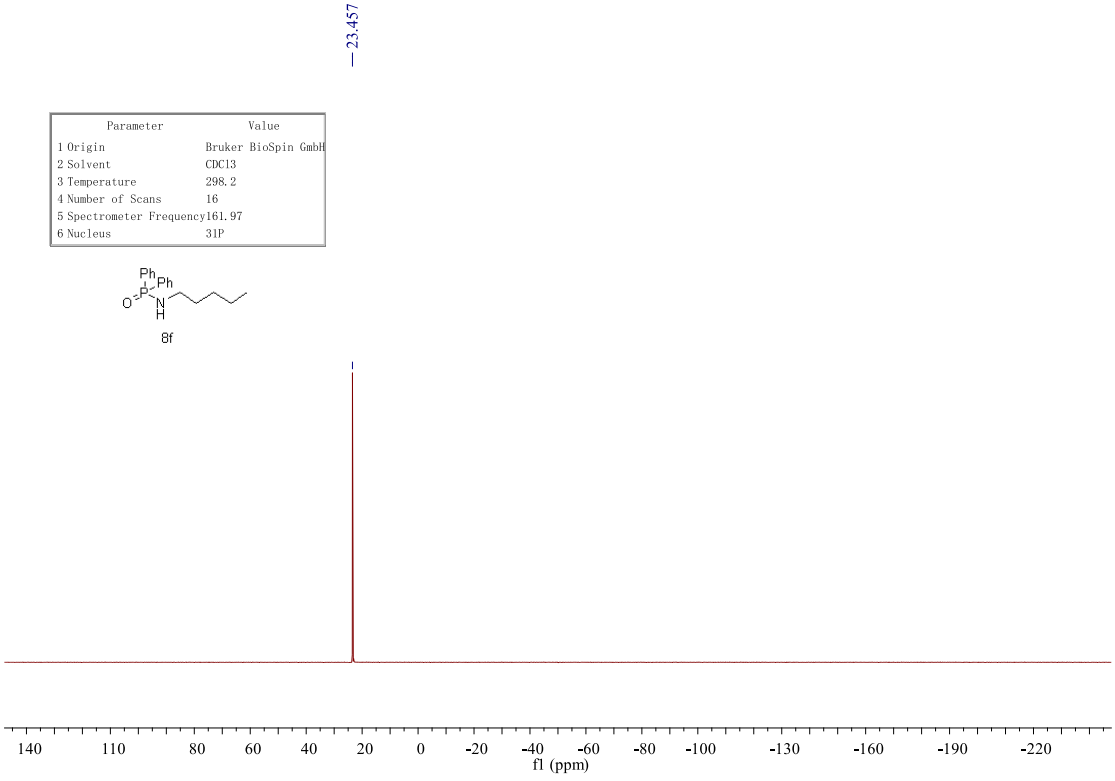

166.294
142.174
138.560
127.832
126.931
77.501
77.179
76.859
49.950
40.286
29.094
21.892
13.940
11.091
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 80
5 Spectrometer Frequency 100.62
6 Nucleus 13C
7f
fl (ppm)

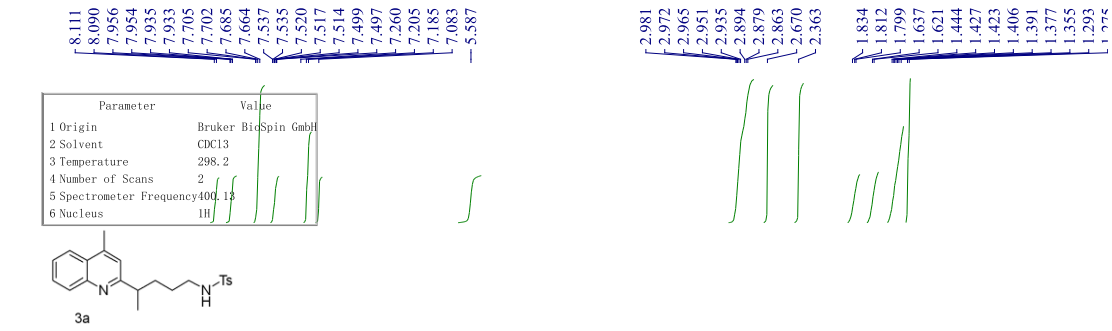

7.290
7.279
7.260
7.144
7.135
7.123
7.113
7.102
4.425
4.409
4.392
3.010
2.993
2.985
2.968
2.951
1.423
1.406
1.389
1.372
1.211
1.202
1.194
1.177
0.840
0.824
0.806
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 2
5 Spectrometer Frequency 400.13
6 Nucleus 1H
Ph
Ph
O
O
P
O
N
H
8a
8.08
2.03
1.04
2.07
2.07
4.04
3.02
10.0 9.5 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)

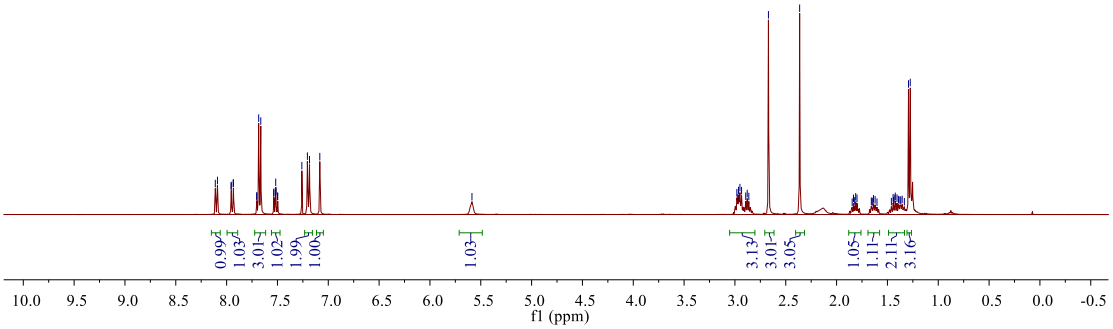

151.071
151.006
129.607
124.719
120.256
120.206
77.682
77.363
77.044
41.720
31.049
30.987
28.697
22.268
13.990
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 10
5 Spectrometer Frequency 100.62
6 Nucleus 13C
Ph
Ph
O
O
P
O
N
H
8a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


— 0.107
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.3
4 Number of Scans 2
5 Spectrometer Frequency 161.97
6 Nucleus 31P
Ph
Ph
O
O
P
O
N
H
8a
f1 (ppm)
7.879
7.876
7.859
7.855
7.849
7.846
7.829
7.825
7.428
7.414
7.410
7.399
7.396
7.392
7.388
7.385
7.381
7.377
7.373
7.260
2.923
2.903
2.884
2.864
1.540
1.523
1.507
1.227
0.835
0.817
0.799
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 4
5 Spectrometer Frequency 400.13
6 Nucleus 1H
Ph
Ph
O
P
N
H
8f
4.00
6.00
3.12
2.05
4.14
3.04
f1 (ppm)

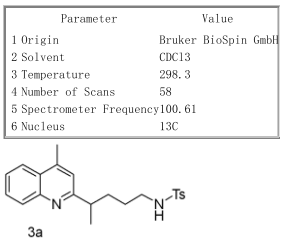

133.273
132.122
132.029
131.991
131.713
131.686
128.515
128.390
77.460
77.142
76.823
40.787
40.770
31.812
28.878
22.290
13.957
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 50
5 Spectrometer Frequency 100.62
6 Nucleus 13C
Ph
Ph
O
P
N
H
8f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

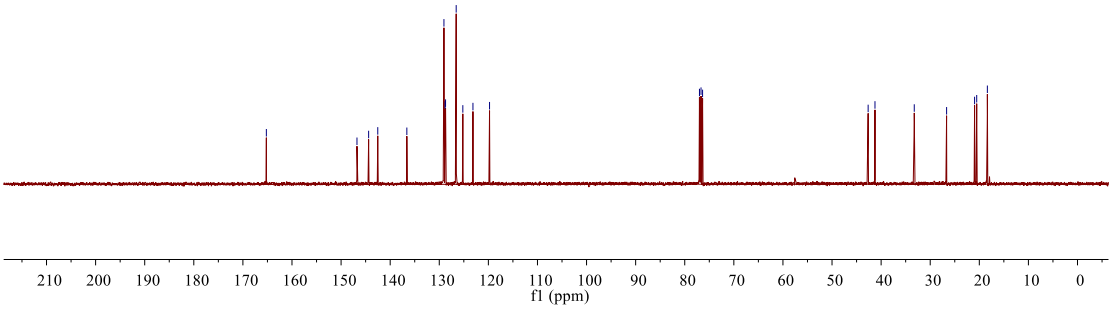

23.457
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 16
5 Spectrometer Frequency 161.97
6 Nucleus 31P
Ph
Ph
O
P
N
H
8f
140 110 80 60 40 20 0 -20 -40 -60 -80 -100 -130 -160 -190 -220
f1 (ppm)

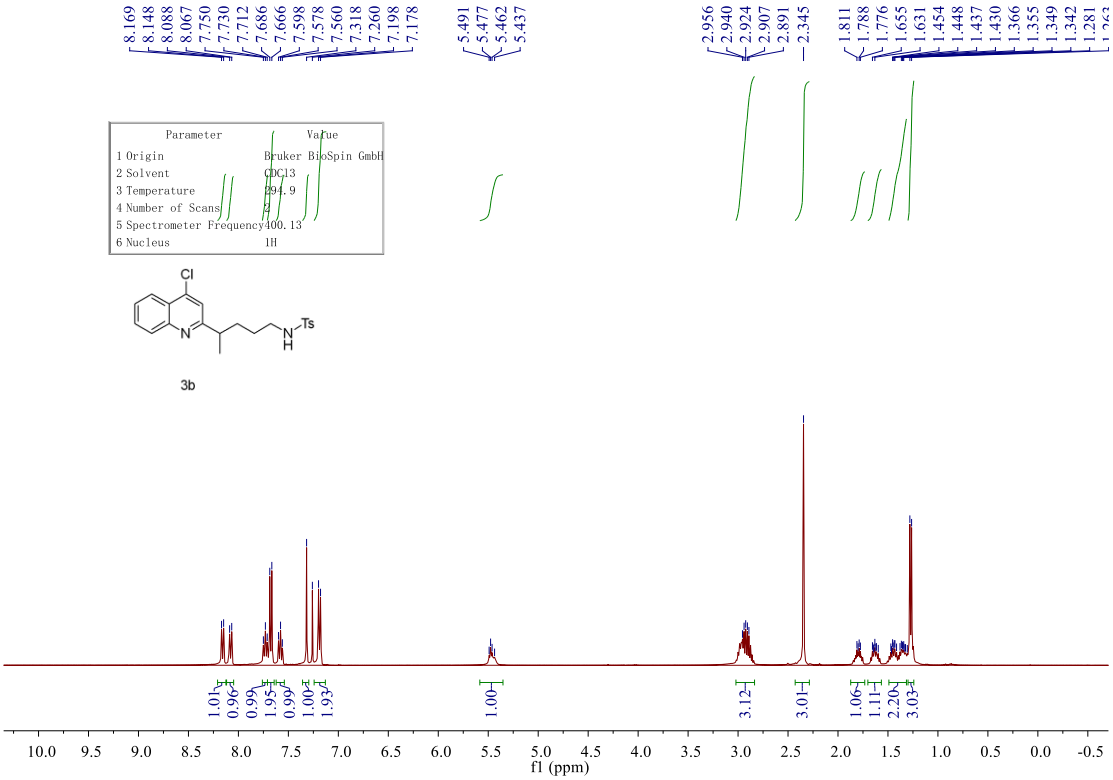

8.111
8.090
7.956
7.954
7.935
7.933
7.705
7.702
7.685
7.664
7.537
7.535
7.520
7.517
7.514
7.499
7.497
7.260
7.205
7.185
7.083
5.587
2.981
2.972
2.965
2.951
2.935
2.894
2.879
2.863
2.670
2.363
1.834
1.812
1.799
1.637
1.621
1.444
1.427
1.423
1.406
1.391
1.377
1.355
1.293
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 2
5 Spectrometer Frequency 400.13
6 Nucleus 1H
Ts
N
H
3a

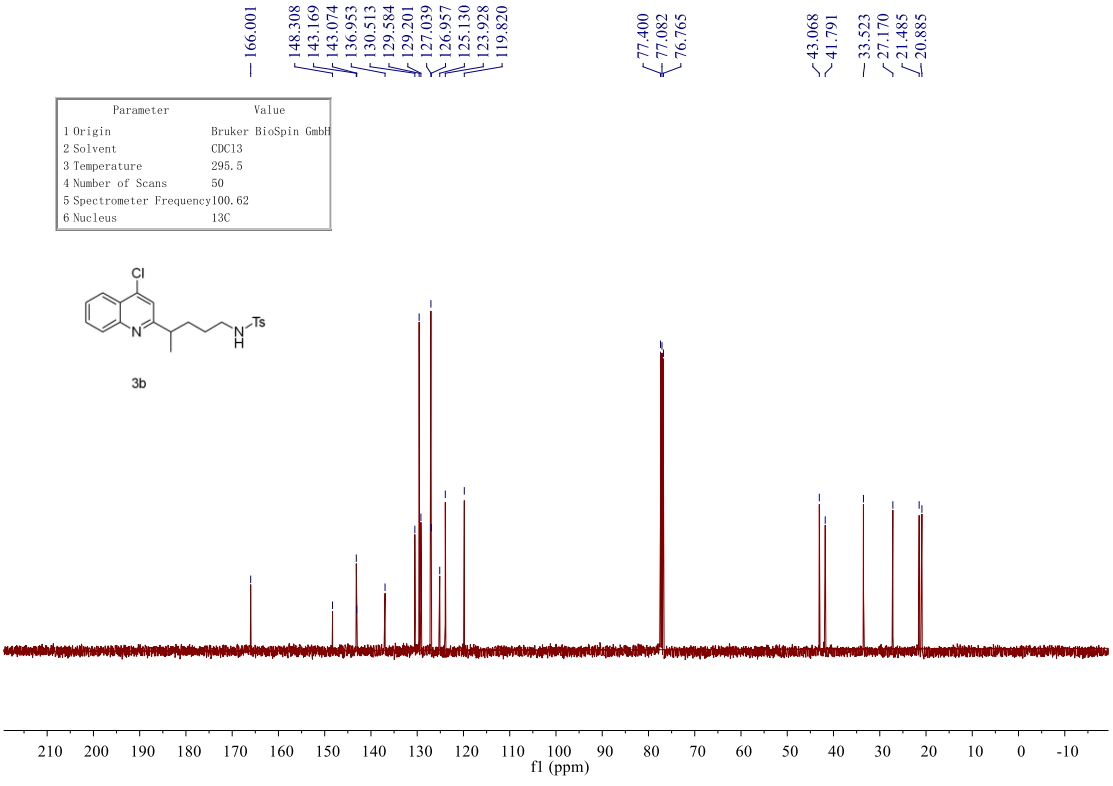

0.99
1.03
3.01
1.02
1.99
1.00
1.03
3.13
3.01
3.05
1.05
1.11
2.11
3.16
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

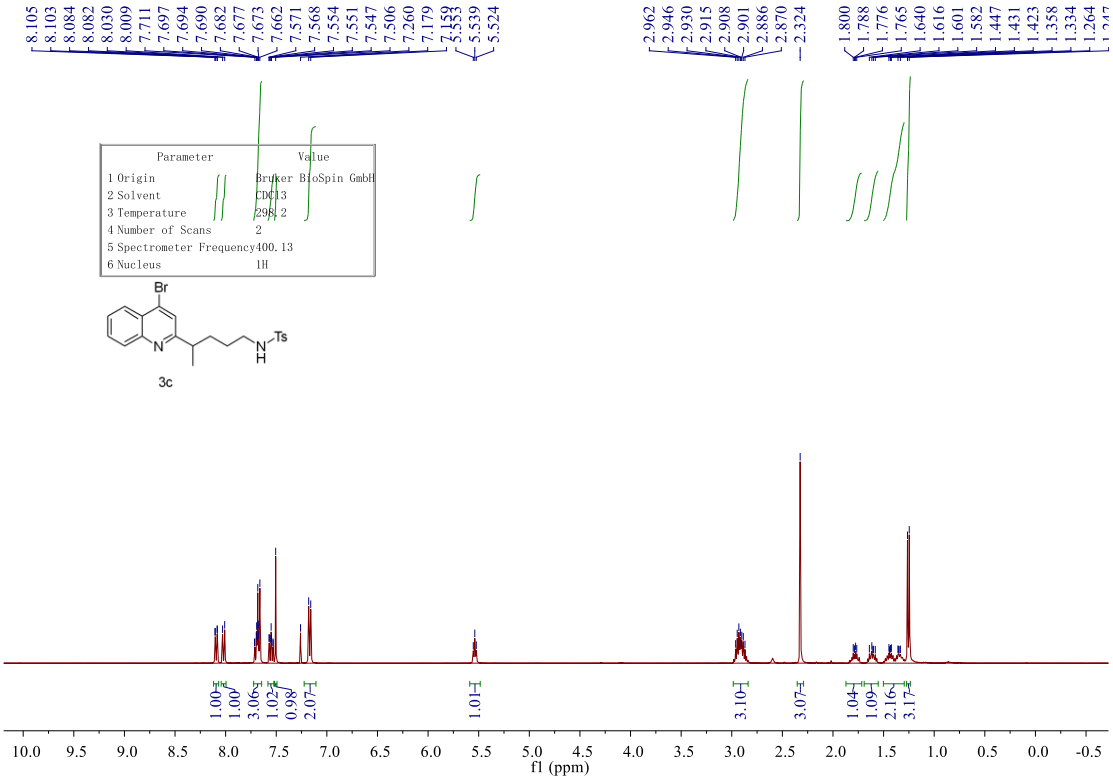

165.222
146.763
144.388
142.527
136.606
129.050
128.809
128.718
126.554
125.199
123.141
119.761
77.002
76.684
76.365
42.644
41.252
33.248
26.663
20.964
20.529
18.360

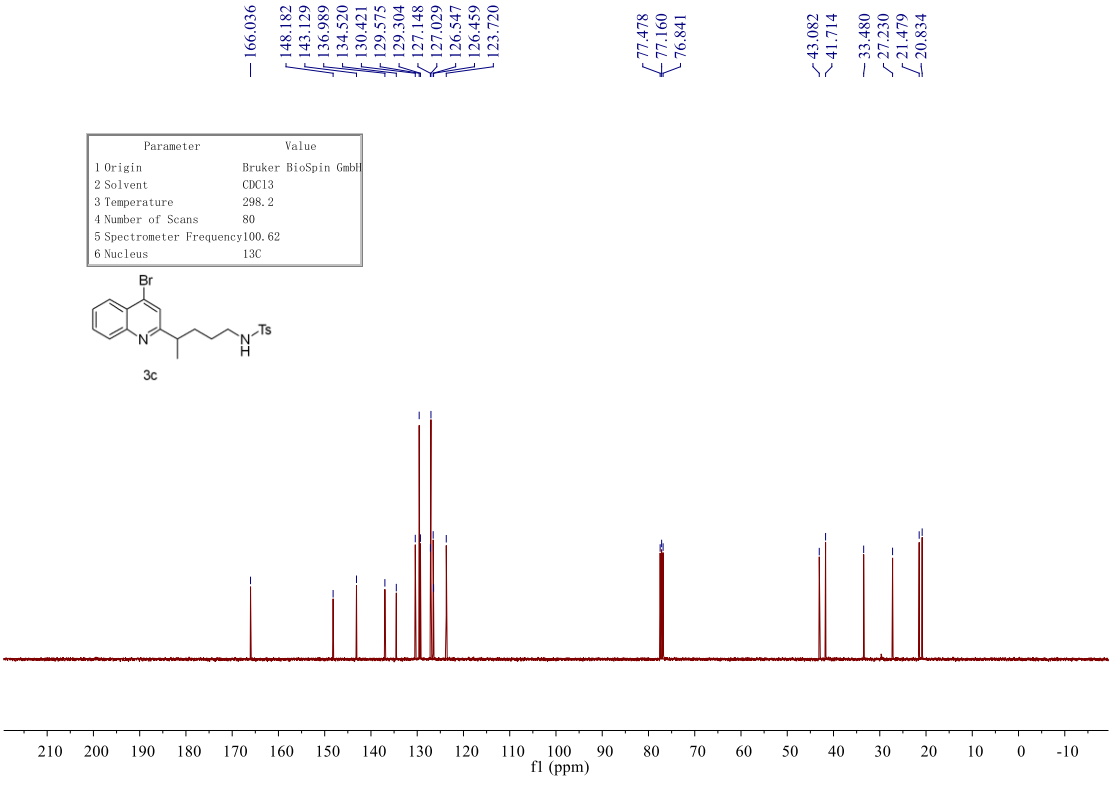

Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.3
4 Number of Scans 58
5 Spectrometer Frequency 100.61
6 Nucleus 13C
Ts
N
H
3a

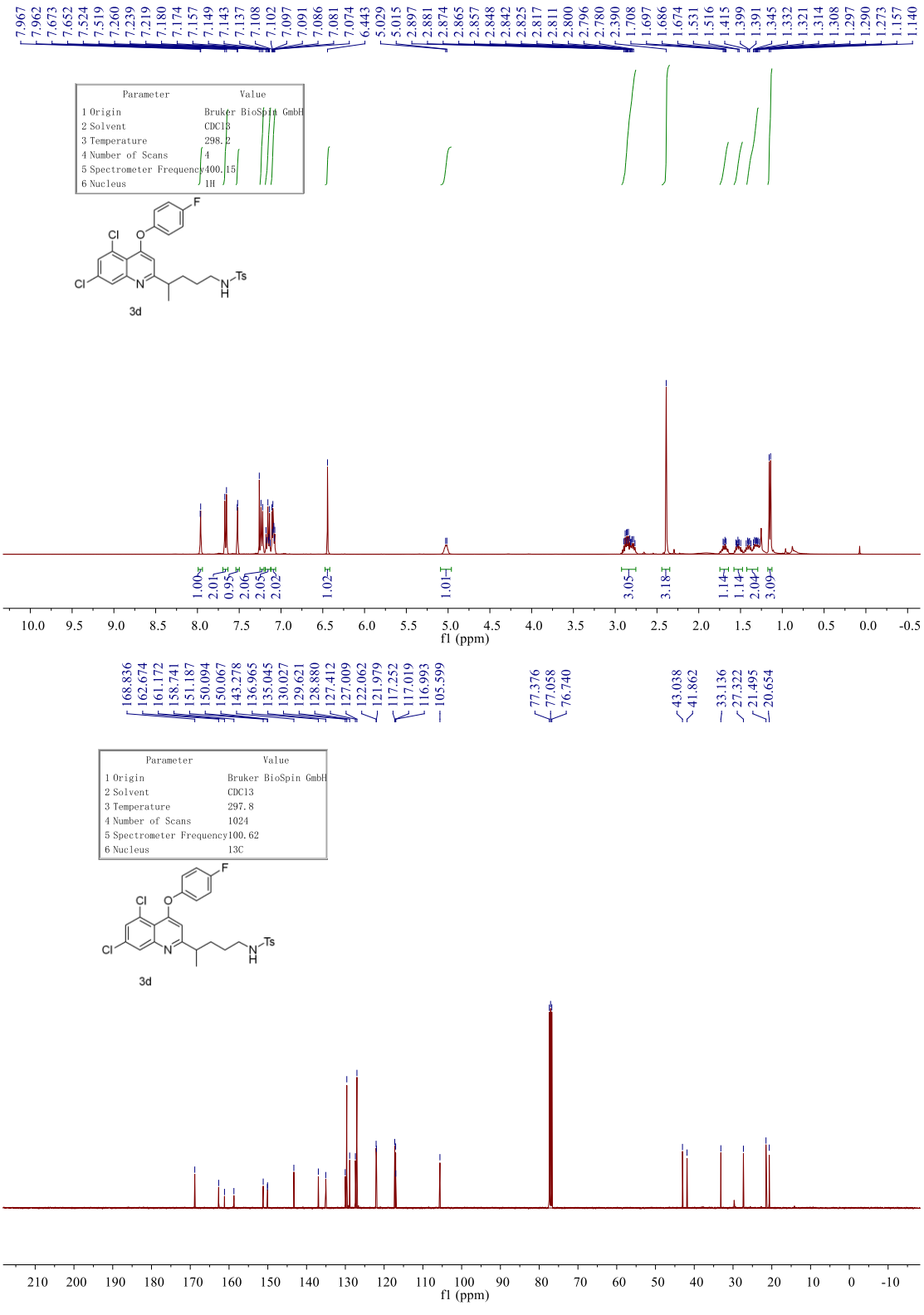

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.169
8.148
8.088
8.067
7.750
7.730
7.712
7.686
7.666
7.598
7.578
7.560
7.318
7.260
7.198
7.178
5.491
5.477
5.462
5.437
2.956
2.940
2.924
2.907
2.891
2.345
1.811
1.788
1.776
1.655
1.631
1.454
1.448
1.437
1.430
1.366
1.355
1.349
1.342
1.281
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 294.9
4 Number of Scans 8
5 Spectrometer Frequency 400.13
6 Nucleus 1H
Cl
N
Ts
N
H
3b
1.01
0.96
0.99
1.95
0.99
1.00
1.93
1.00
3.12
3.01
1.06
1.11
2.26
3.03
10.0 9.5 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)

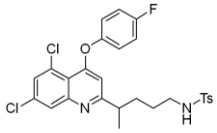

166.001
148.308
143.169
143.074
136.953
130.513
129.584
129.201
127.039
126.957
125.130
123.928
119.820
77.400
77.082
76.765
43.068
41.791
33.523
27.170
21.485
20.885
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 295.5
4 Number of Scans 50
5 Spectrometer Frequency 100.62
6 Nucleus 13C
Cl
N
Ts
N
H
3b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.105
8.103
8.084
8.082
8.030
8.009
7.711
7.697
7.694
7.690
7.682
7.677
7.673
7.662
7.571
7.568
7.554
7.551
7.547
7.506
7.260
7.179
5.553
5.539
5.524
2.962
2.946
2.930
2.915
2.908
2.901
2.886
2.870
2.324
1.800
1.788
1.776
1.765
1.640
1.616
1.601
1.582
1.447
1.431
1.423
1.358
1.334
1.264
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 2
5 Spectrometer Frequency 400.13
6 Nucleus 1H
Br
N
N
H
Ts
3c
1.00
1.00
3.06
1.02
0.98
2.07
1.01
3.10
3.07
1.04
1.09
2.16
3.17
10.0 9.5 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)

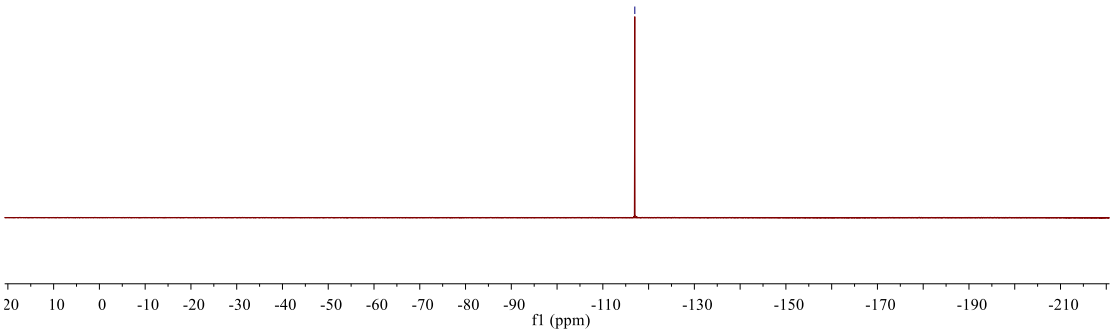

166.036
148.182
143.129
136.989
134.520
130.421
129.575
129.304
127.148
127.029
126.547
126.459
123.720
77.478
77.160
76.841
43.082
41.714
33.480
27.230
21.479
20.834
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 80
5 Spectrometer Frequency 100.62
6 Nucleus 13C
Br
N
N
H
Ts
3c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

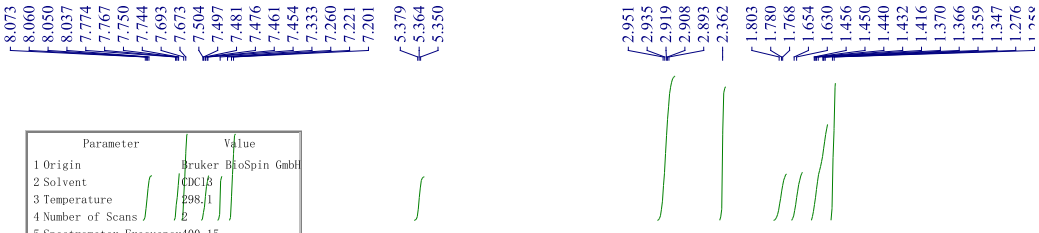

7.967 7.962 7.673 7.652 7.524 7.519 7.260 7.239 7.219 7.180 7.174 7.157 7.149 7.143 7.137 7.108 7.102 7.097 7.091 7.086 7.081 7.074 6.443 5.029 5.015 2.897 2.881 2.874 2.865 2.857 2.848 2.842 2.825 2.817 2.811 2.800 2.796 2.780 2.390 1.708 1.697 1.686 1.674 1.531 1.516 1.415 1.399 1.391 1.345 1.332 1.321 1.314 1.308 1.297 1.290 1.273 1.157 1.140
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 4
5 Spectrometer Frequency 400.15
6 Nucleus 1H
F
Cl
O
Cl
N
Ts
N
H
3d
1.00 2.01 0.95 2.06 2.05 2.02 1.02 1.01 3.05 3.18 1.14 1.14 2.04 3.09
10.0 9.5 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)
168.836 162.674 161.172 158.741 151.187 150.094 150.067 143.278 136.965 135.045 130.027 129.621 128.880 127.412 127.009 122.062 121.979 117.252 117.019 116.993 105.599
77.376 77.058 76.740
43.038 41.862 33.136 27.322 21.495 20.654
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 297.8
4 Number of Scans 1024
5 Spectrometer Frequency 100.62
6 Nucleus 13C
F
Cl
O
Cl
N
Ts
N
H
3d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Number of Scans	4
5 Spectrometer Frequency	376.52
6 Nucleus	19F

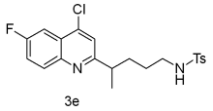


3d

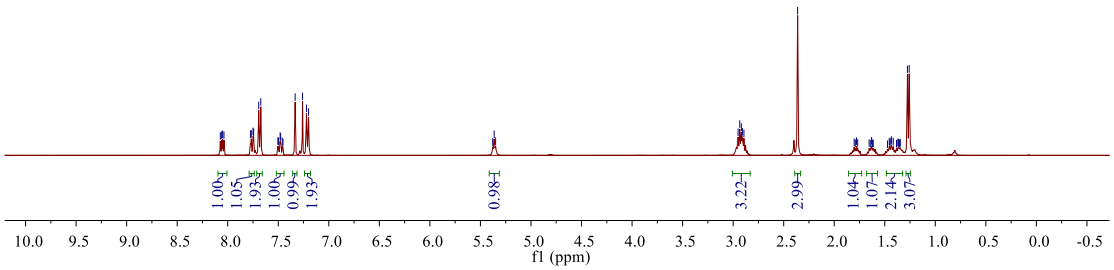


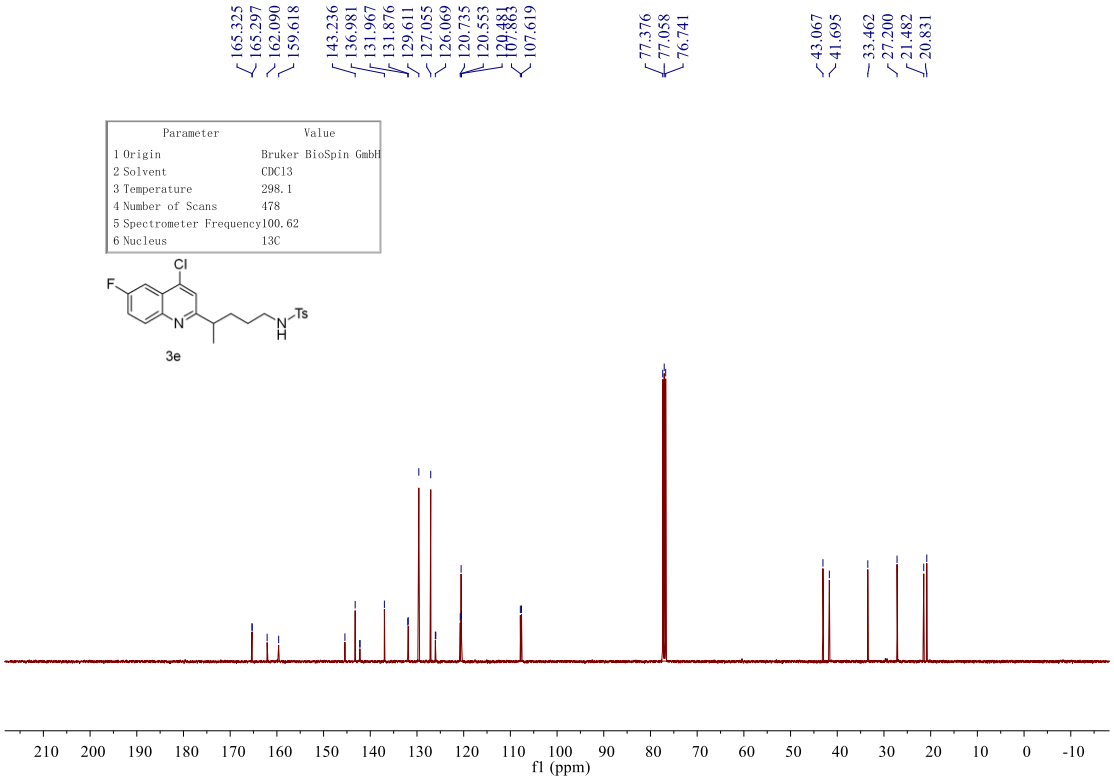


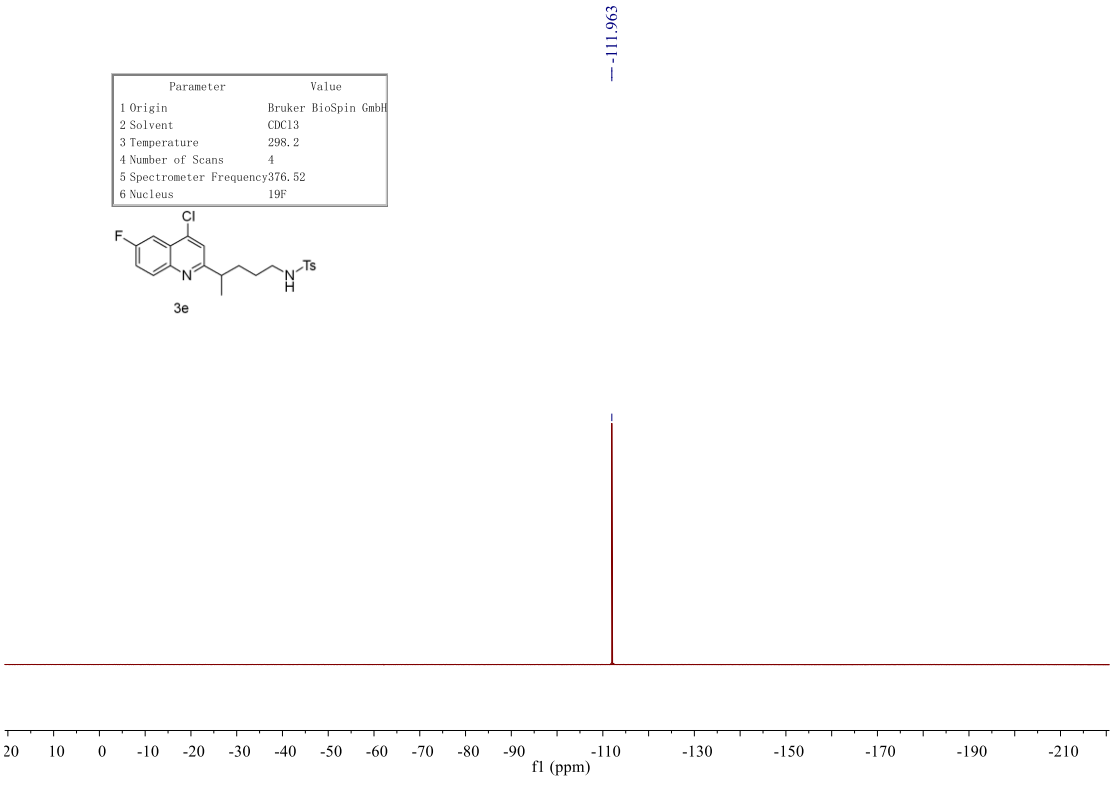
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.1
4 Number of Scans	2
5 Spectrometer Frequency	400.15
6 Nucleus	1H

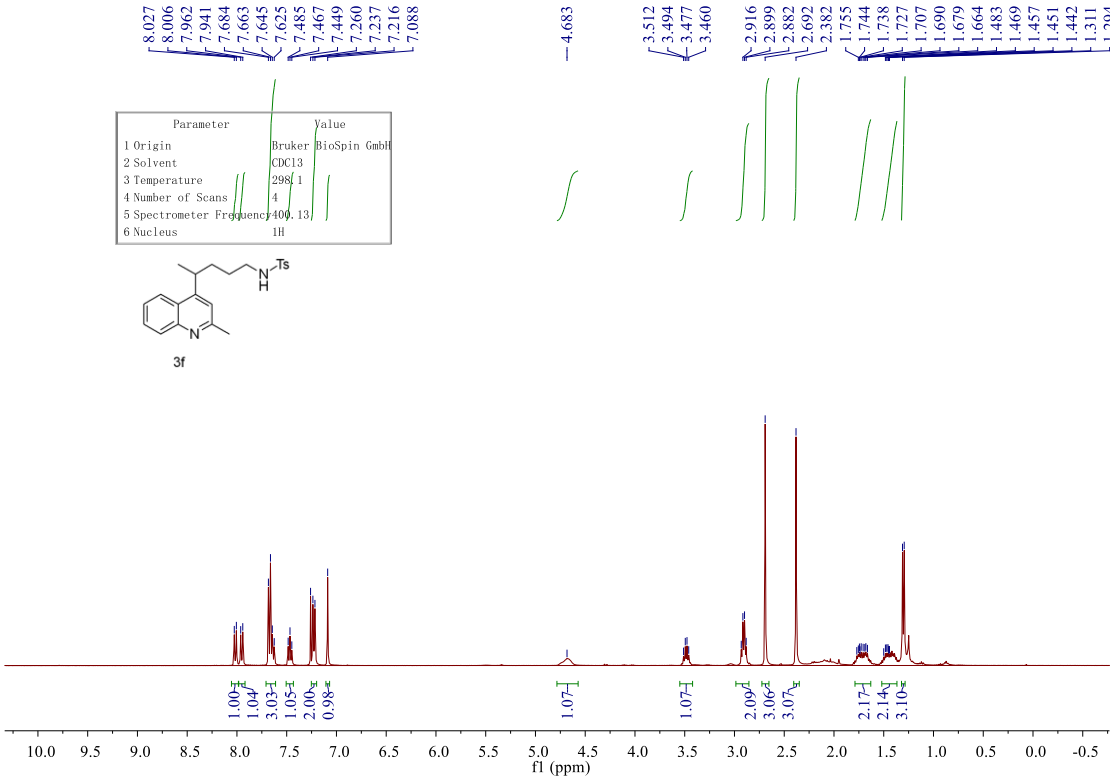


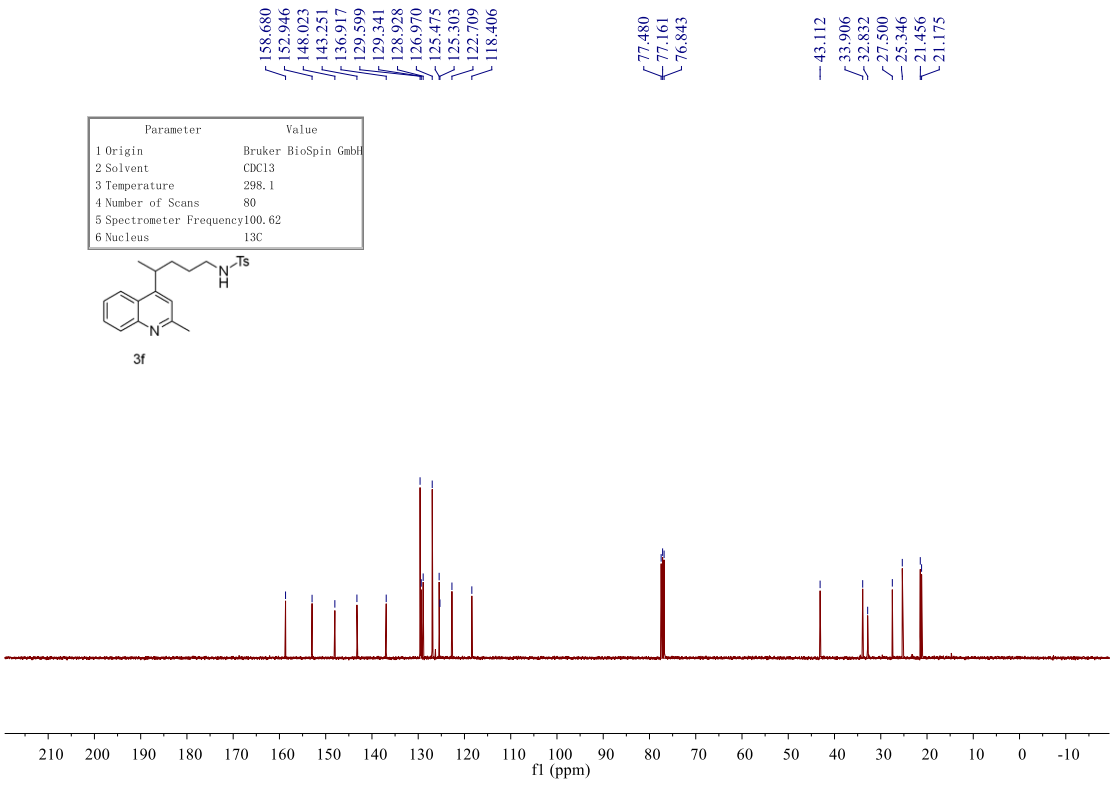
3e

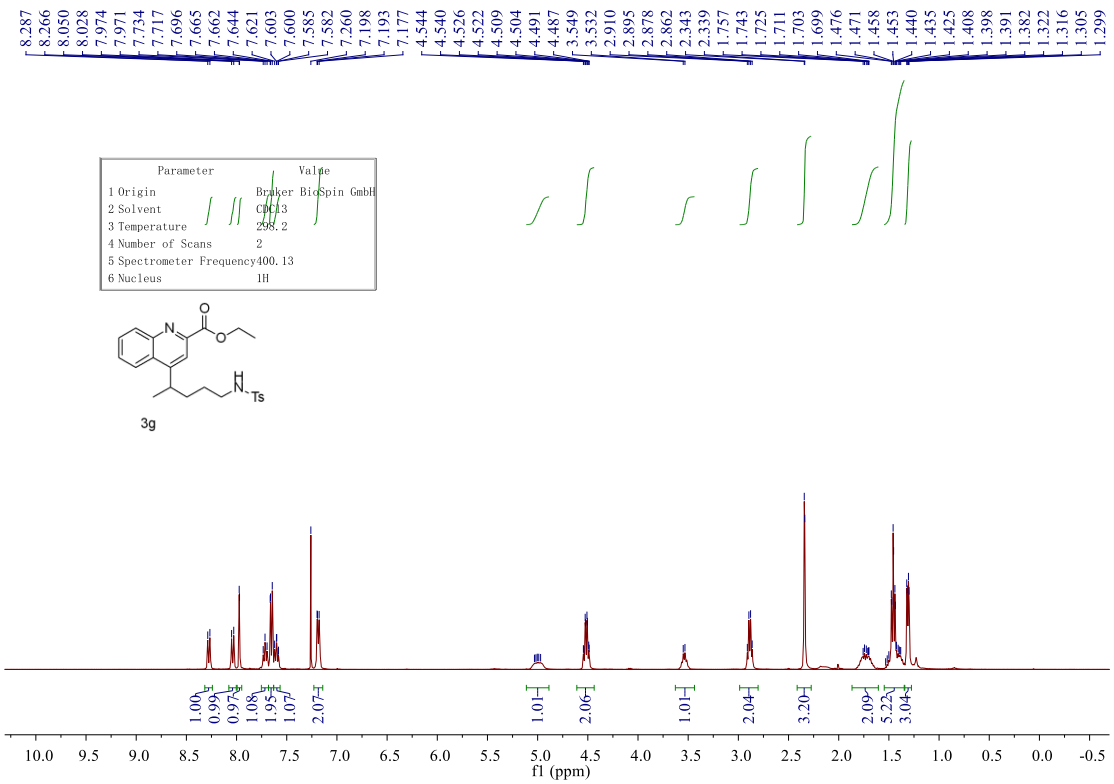



165.325
165.297
162.090
159.618
143.236
136.981
131.967
131.876
129.611
127.055
126.069
120.735
120.553
120.481
107.883
107.619
77.376
77.058
76.741
43.067
41.695
33.462
27.200
21.482
20.831
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 478
5 Spectrometer Frequency 100.62
6 Nucleus 13C
Cl
F
N
Ts
N
H
3e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-111.963
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 4
5 Spectrometer Frequency 376.52
6 Nucleus 19F
Cl
F
N
Ts
N
H
3e
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190 -210
f1 (ppm)


8.027
8.006
7.962
7.941
7.684
7.663
7.645
7.625
7.485
7.467
7.449
7.260
7.237
7.216
7.088
4.683
3.512
3.494
3.477
3.460
2.916
2.899
2.882
2.692
2.382
1.755
1.744
1.738
1.727
1.707
1.690
1.679
1.664
1.483
1.469
1.457
1.451
1.442
1.311
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 4
5 Spectrometer Frequency 400.13
6 Nucleus 1H
Ts
N
H
N
3f
1.00
1.04
3.03
1.05
2.00
0.98
1.07
1.07
2.09
3.06
3.07
2.17
2.14
3.10
10.0 9.5 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)


158.680
152.946
148.023
143.251
136.917
129.599
129.341
128.928
126.970
125.475
125.303
122.709
118.406
77.480
77.161
76.843
43.112
33.906
32.832
27.500
25.346
21.456
21.175
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 80
5 Spectrometer Frequency 100.62
6 Nucleus 13C
Ts
N
H
N
3f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.287
8.266
8.050
8.028
7.974
7.971
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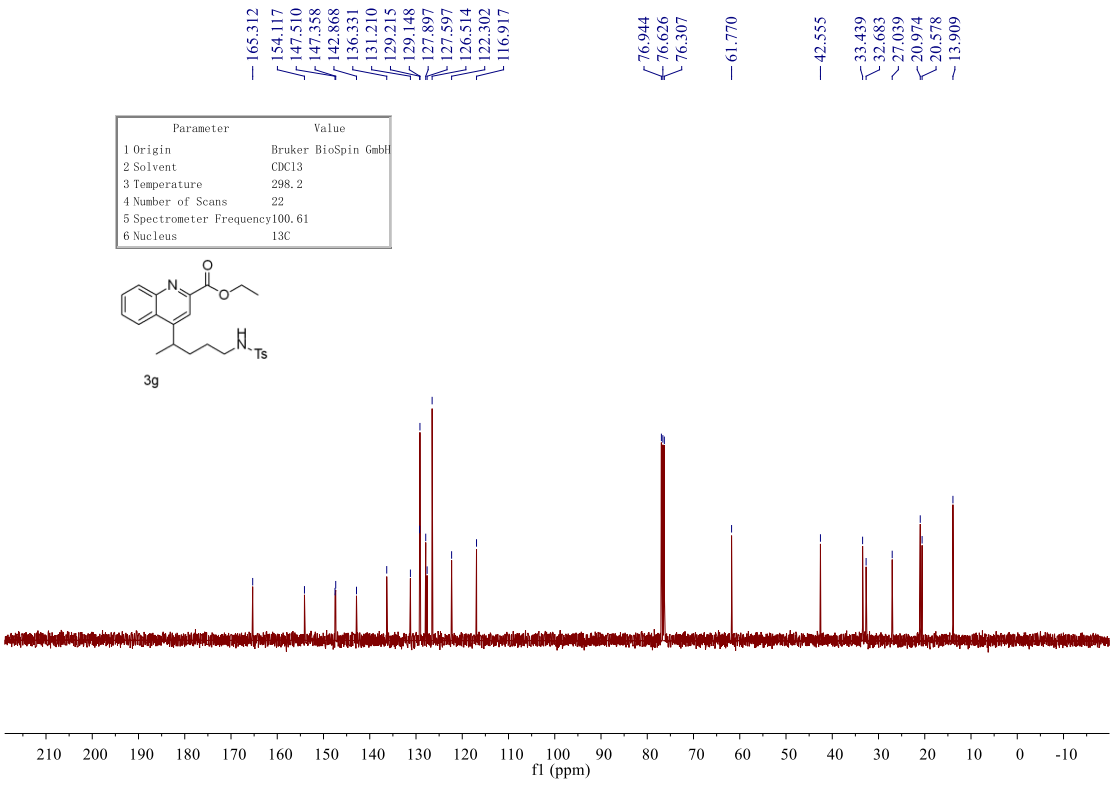
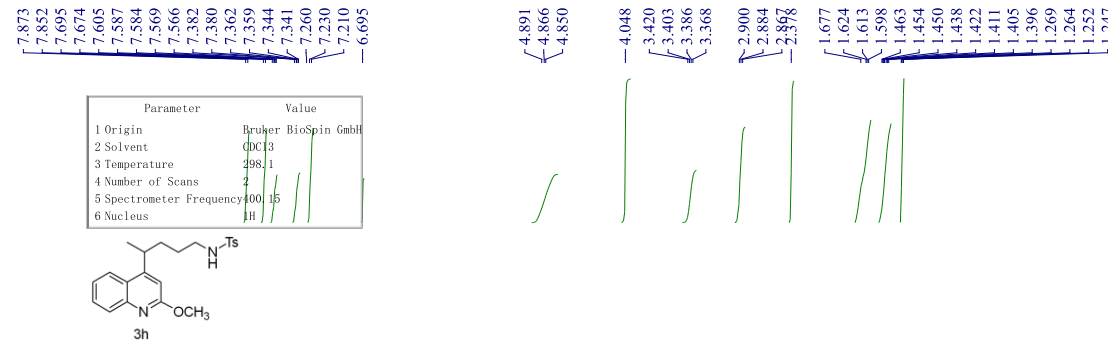
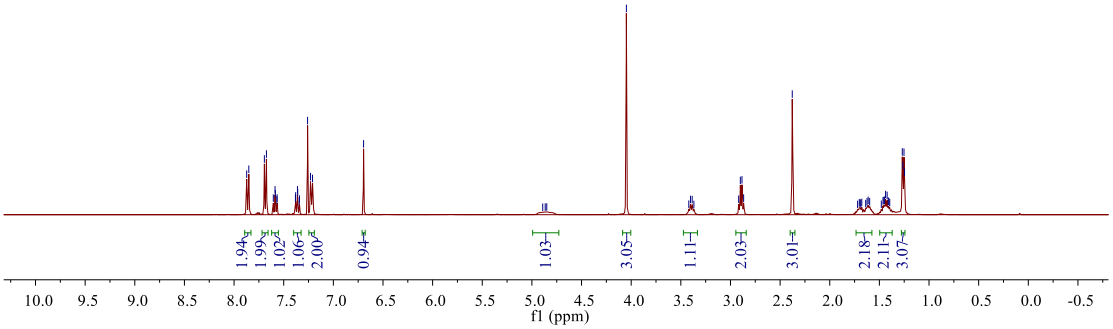
7.717
7.696
7.665
7.662
7.644
7.621
7.603
7.600
7.585
7.582
7.260
7.198
7.193
7.177
4.544
4.540
4.526
4.522
4.509
4.504
4.491
4.487
3.549
3.532
2.910
2.895
2.878
2.862
2.343
2.339
1.757
1.743
1.725
1.711
1.703
1.699
1.476
1.471
1.458
1.453
1.440
1.435
1.425
1.408
1.398
1.391
1.382
1.322
1.316
1.305
1.299
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 2
5 Spectrometer Frequency 400.13
6 Nucleus 1H
3g
1.00
0.99
0.97
1.08
1.95
1.07
2.07
1.01
2.06
1.01
2.04
3.20
2.09
5.22
3.04
f1 (ppm)


165.312
154.117
147.510
147.358
142.868
136.331
131.210
129.215
129.148
127.897
127.597
126.514
122.302
116.917
76.944
76.626
76.307
61.770
42.555
33.439
32.683
27.039
20.974
20.578
13.909
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 22
5 Spectrometer Frequency 100.61
6 Nucleus 13C
3g
f1 (ppm)

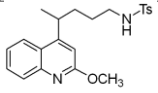


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.1
4 Number of Scans	2
5 Spectrometer Frequency	400.15
6 Nucleus	1H

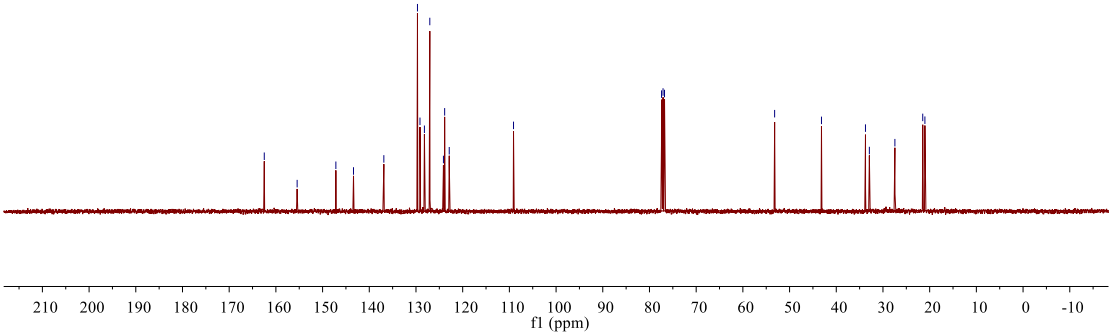
3h

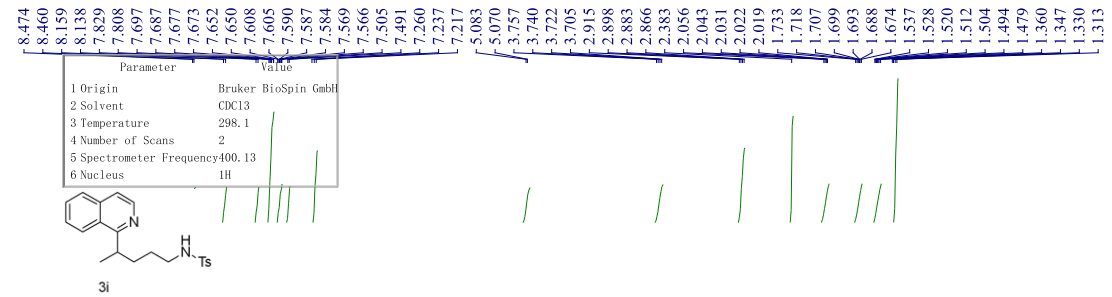


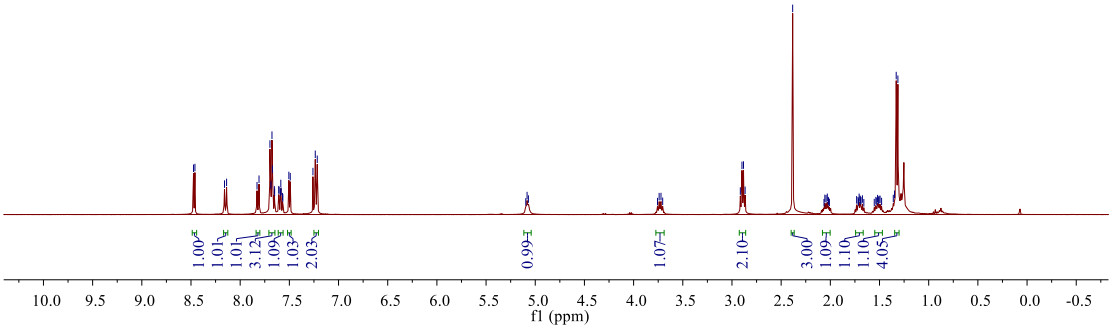
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.1
4 Number of Scans	80
5 Spectrometer Frequency	100.62
6 Nucleus	13C

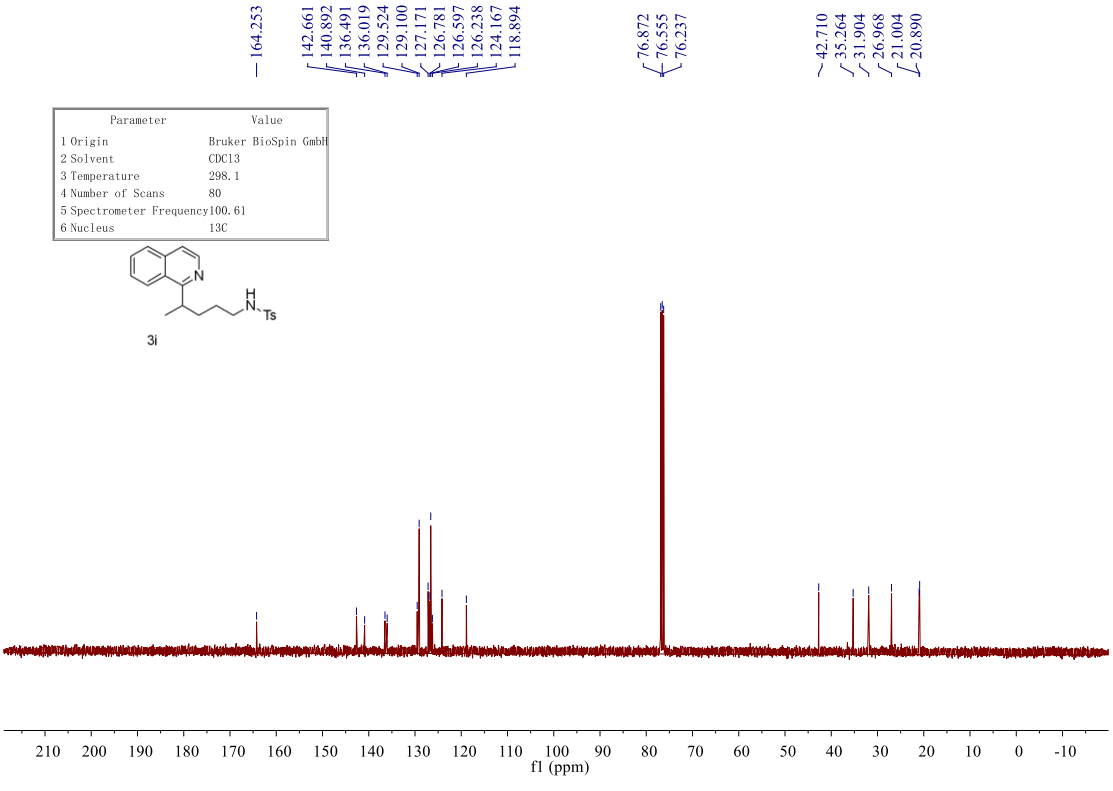


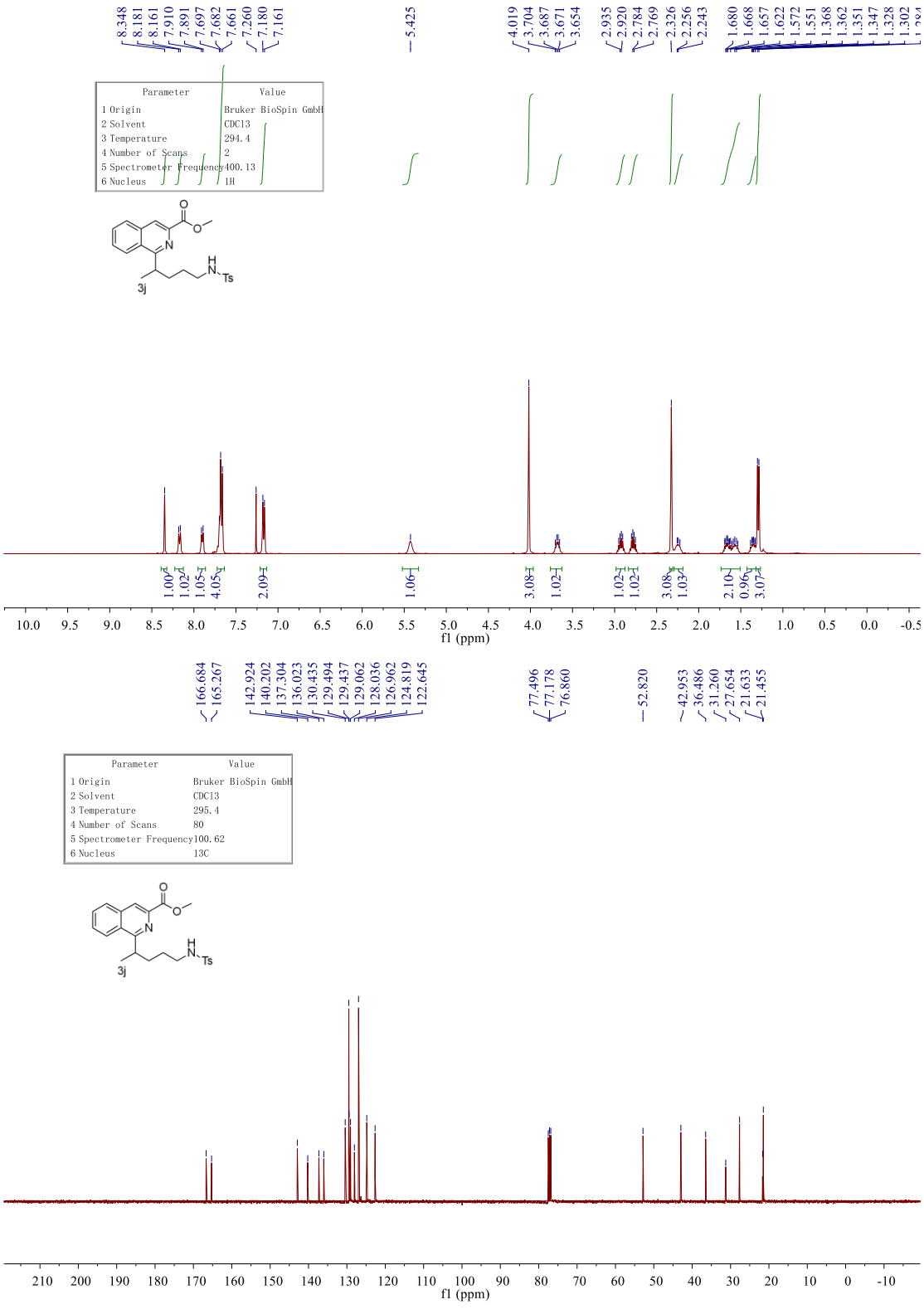
3h

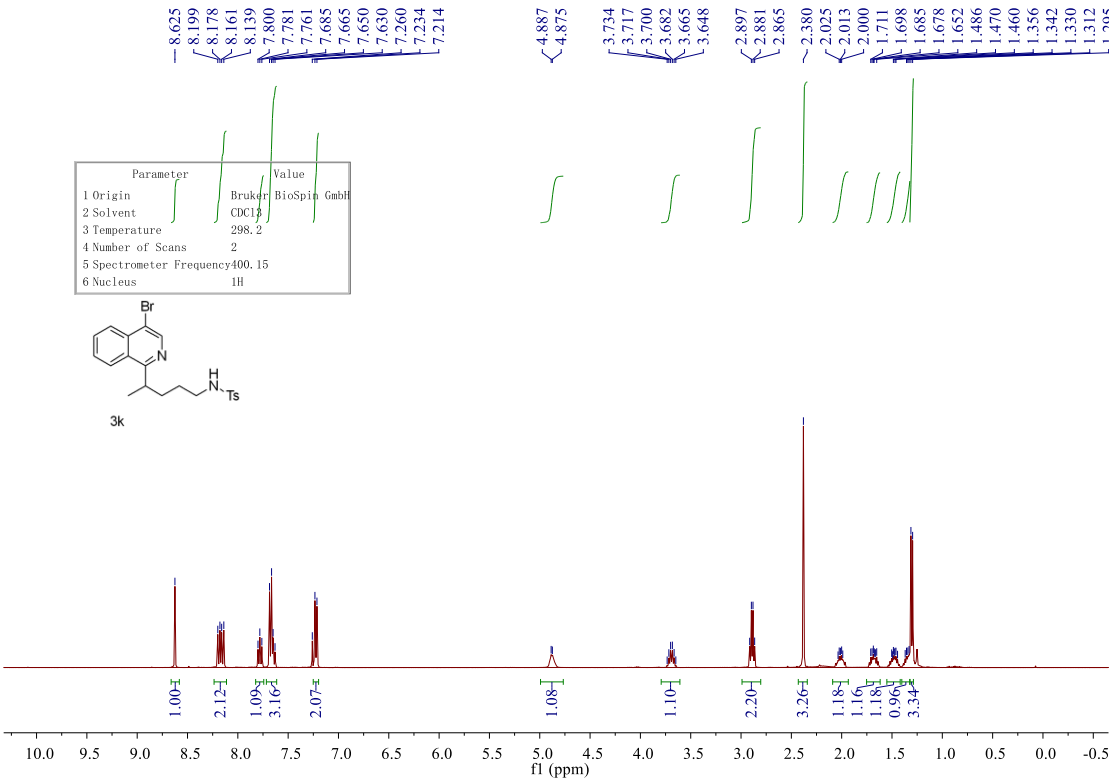


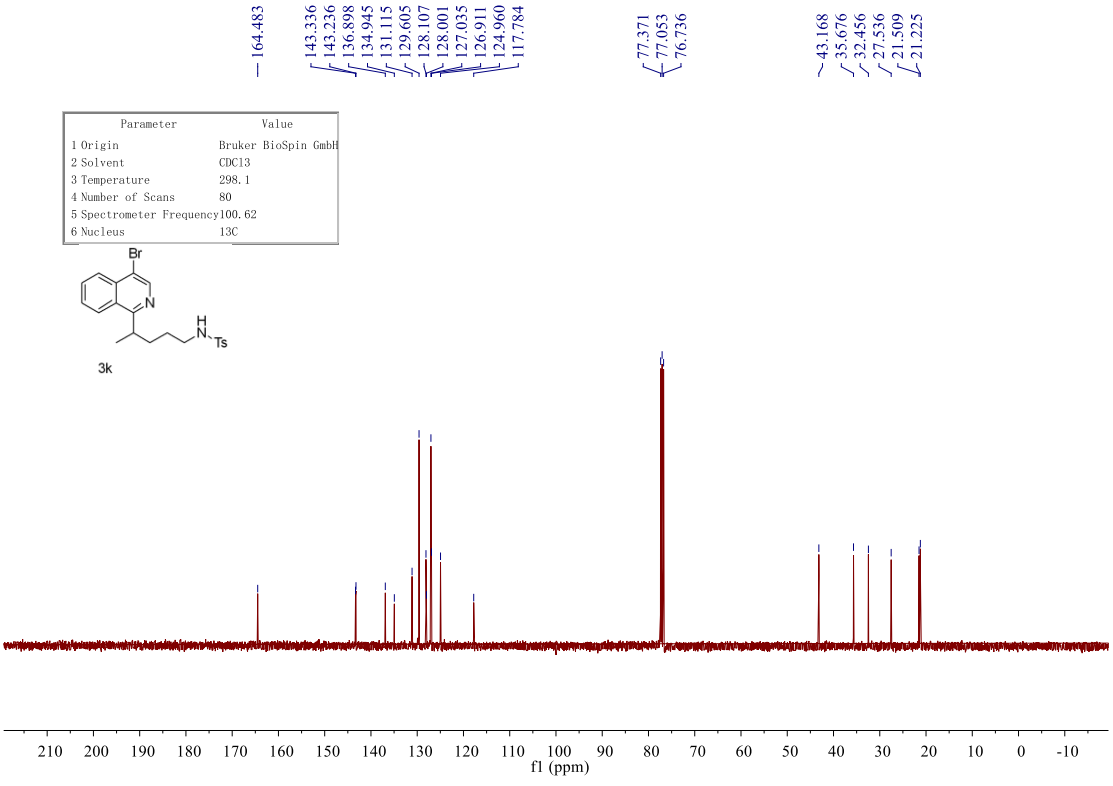

8.474 8.460 8.159 8.138 7.829 7.808 7.697 7.687 7.677 7.673 7.652 7.650 7.608 7.605 7.590 7.587 7.584 7.569 7.566 7.505 7.491 7.260 7.237 7.217
5.083 5.070 3.757 3.740 3.722 3.705 2.915 2.898 2.883 2.866 2.383 2.056 2.043 2.031 2.022 2.019 1.733 1.718 1.707 1.699 1.693 1.688 1.674 1.537 1.528 1.520 1.512 1.504 1.494 1.479 1.360 1.347 1.330 1.313
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 2
5 Spectrometer Frequency 400.13
6 Nucleus 1H
N
H
N
Ts
3i

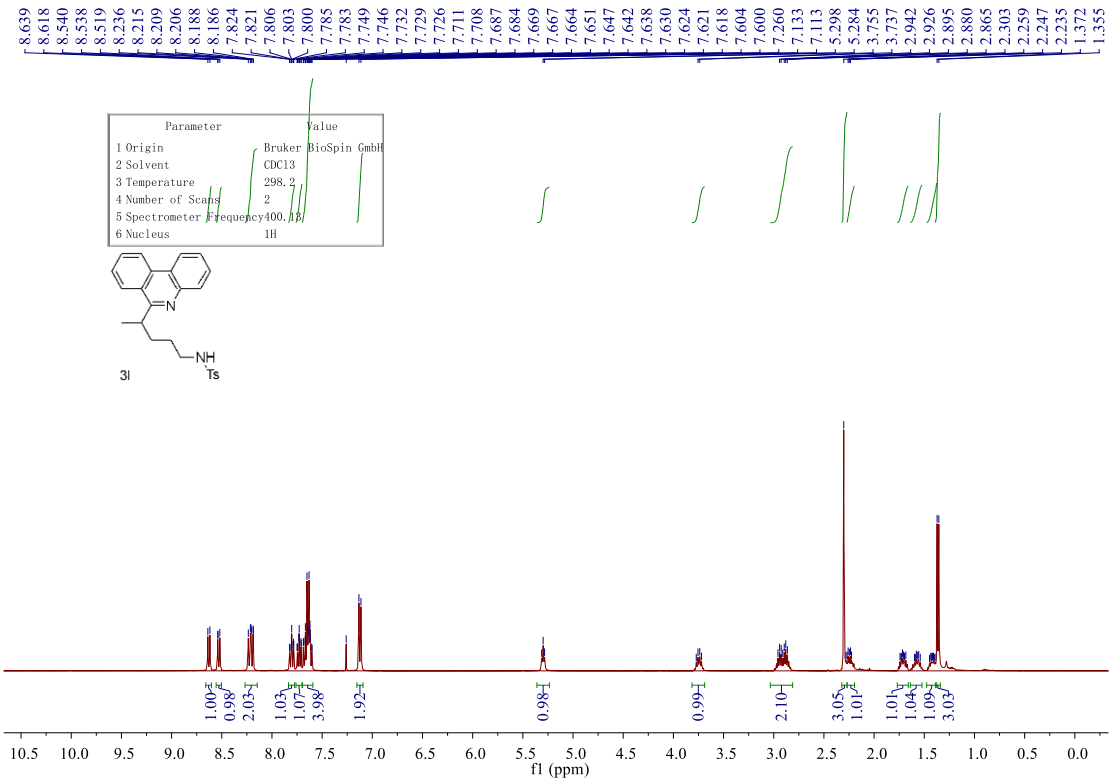

1.00 1.01 1.01 3.12 1.09 1.03 2.03 0.99 1.07 2.10 3.00 1.09 1.10 1.10 4.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

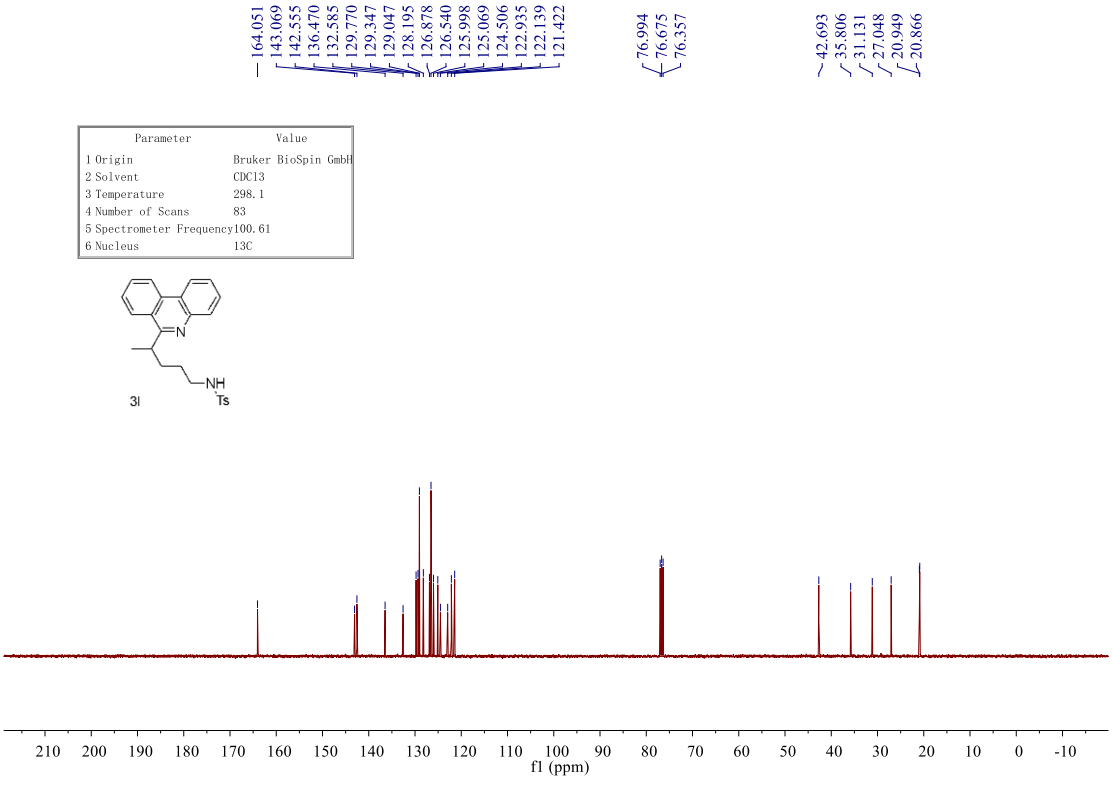

164.253
142.661 140.892 136.491 136.019 129.524 129.100 127.171 126.781 126.597 126.238 124.167 118.894
76.872 76.555 76.237
42.710 35.264 31.904 26.968 21.004 20.890
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 80
5 Spectrometer Frequency 100.61
6 Nucleus 13C
N
H
N
Ts
3i
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

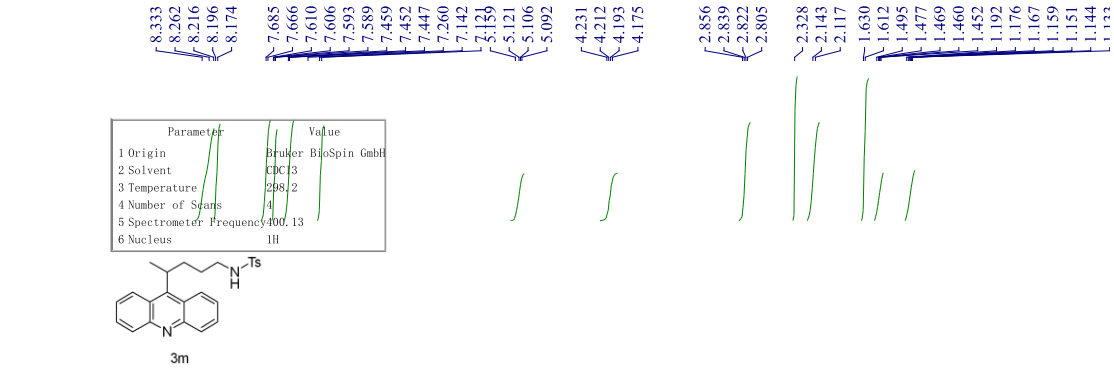

8.348
8.181
8.161
7.910
7.891
7.697
7.682
7.661
7.260
7.180
7.161
5.425
4.019
3.704
3.687
3.671
3.654
2.935
2.920
2.784
2.769
2.326
2.256
2.243
1.680
1.668
1.657
1.622
1.572
1.551
1.368
1.362
1.351
1.347
1.328
1.302
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 294.4
4 Number of Scans 2
5 Spectrometer Frequency 400.13
6 Nucleus 1H
O
O
N
H
N
Ts
3j
1.00
1.02
1.05
4.05
2.09
1.06
3.08
1.02
1.02
1.02
3.08
1.03
2.10
0.96
3.07
10.0 9.5 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)
166.684
165.267
142.924
140.202
137.304
136.023
130.435
129.494
129.437
129.062
128.036
126.962
124.819
122.645
77.496
77.178
76.860
52.820
42.953
36.486
31.260
27.654
21.633
21.455
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 295.4
4 Number of Scans 80
5 Spectrometer Frequency 100.62
6 Nucleus 13C
O
O
N
H
N
Ts
3j
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.625
8.199
8.178
8.161
8.139
7.800
7.781
7.761
7.685
7.665
7.650
7.630
7.260
7.234
7.214
4.887
4.875
3.734
3.717
3.700
3.682
3.665
3.648
2.897
2.881
2.865
2.380
2.025
2.013
2.000
1.711
1.698
1.685
1.678
1.652
1.486
1.470
1.460
1.356
1.342
1.330
1.312
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 2
5 Spectrometer Frequency 400.15
6 Nucleus 1H
Br
N
H
N
Ts
3k
1.00
2.12
1.09
3.16
2.07
1.08
1.10
2.20
3.26
1.18
1.16
1.18
0.96
3.34
10.0 9.5 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)


164.483
143.336
143.236
136.898
134.945
131.115
129.605
128.107
128.001
127.035
126.911
124.960
117.784
77.371
77.053
76.736
43.168
35.676
32.456
27.536
21.509
21.225
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 80
5 Spectrometer Frequency 100.62
6 Nucleus 13C
Br
N
H
N
Ts
3k
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.639 8.618 8.540 8.538 8.519 8.236 8.215 8.209 8.206 8.188 8.186 7.824 7.821 7.806 7.803 7.800 7.785 7.783 7.749 7.746 7.732 7.729 7.726 7.711 7.708 7.687 7.684 7.669 7.667 7.664 7.651 7.647 7.642 7.638 7.630 7.624 7.621 7.618 7.604 7.600 7.260 7.133 7.113 5.298 5.284 3.755 3.737 2.942 2.926 2.895 2.880 2.865 2.303 2.259 2.247 2.235 1.372 1.355
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 2
5 Spectrometer Frequency 400.13
6 Nucleus 1H
NH
Ts
3l
1.00 0.98 2.03 1.03 1.07 3.98 1.92 0.98 0.99 2.10 3.05 1.01 1.04 1.09 3.03
10.5 10.0 9.5 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)


164.051 143.069 142.555 136.470 132.585 129.770 129.347 129.047 128.195 126.878 126.540 125.998 125.069 124.506 122.935 122.139 121.422
76.994 76.675 76.357
42.693 35.806 31.131 27.048 20.949 20.866
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 83
5 Spectrometer Frequency 100.61
6 Nucleus 13C
NH
Ts
3l
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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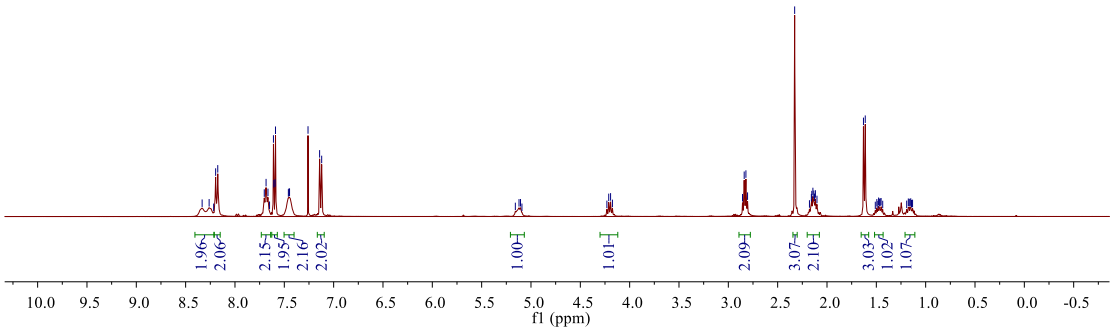
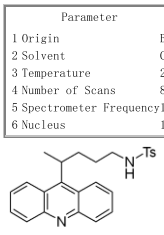
8.262
8.216
8.196
8.174
7.685
7.666
7.610
7.606
7.593
7.589
7.459
7.452
7.447
7.260
7.142
5.121
5.106
5.092
4.231
4.212
4.193
4.175
2.856
2.839
2.822
2.805
2.328
2.143
2.117
1.630
1.612
1.495
1.477
1.469
1.460
1.452
1.192
1.176
1.167
1.159
1.151
1.144
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 4
5 Spectrometer Frequency 400.13
6 Nucleus 1H
Ts
N
H
N

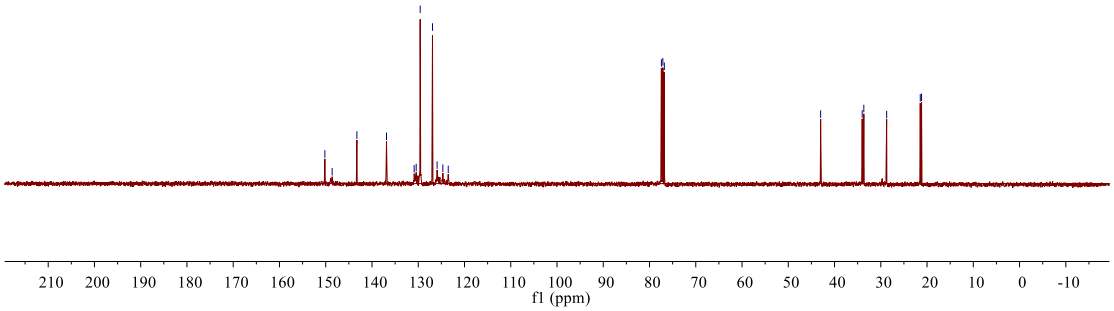
3m

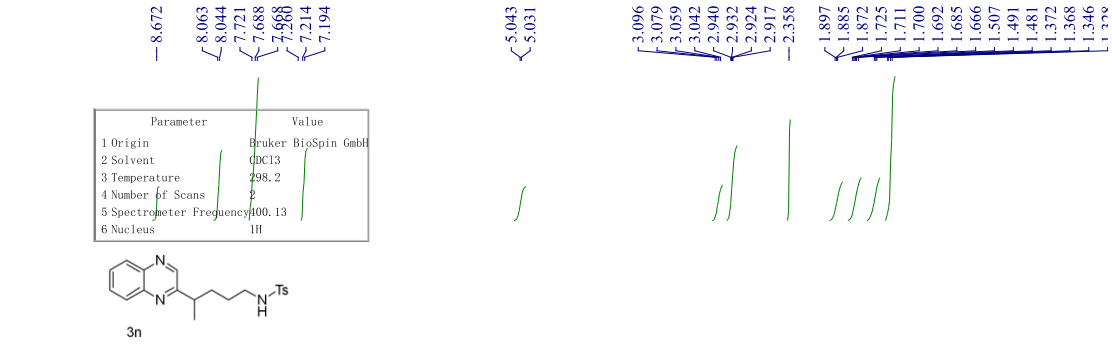

1.96
2.06
2.15
1.95
2.16
2.02
1.00
1.01
2.09
3.07
2.10
3.03
1.02
1.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

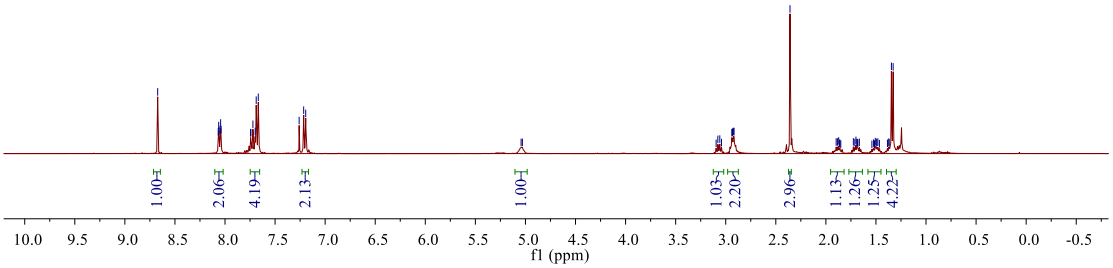

150.186
148.611
143.265
136.861
130.882
130.440
129.582
126.918
125.922
124.677
123.514
77.430
77.112
76.794
43.005
34.023
33.669
28.730
21.468
21.188

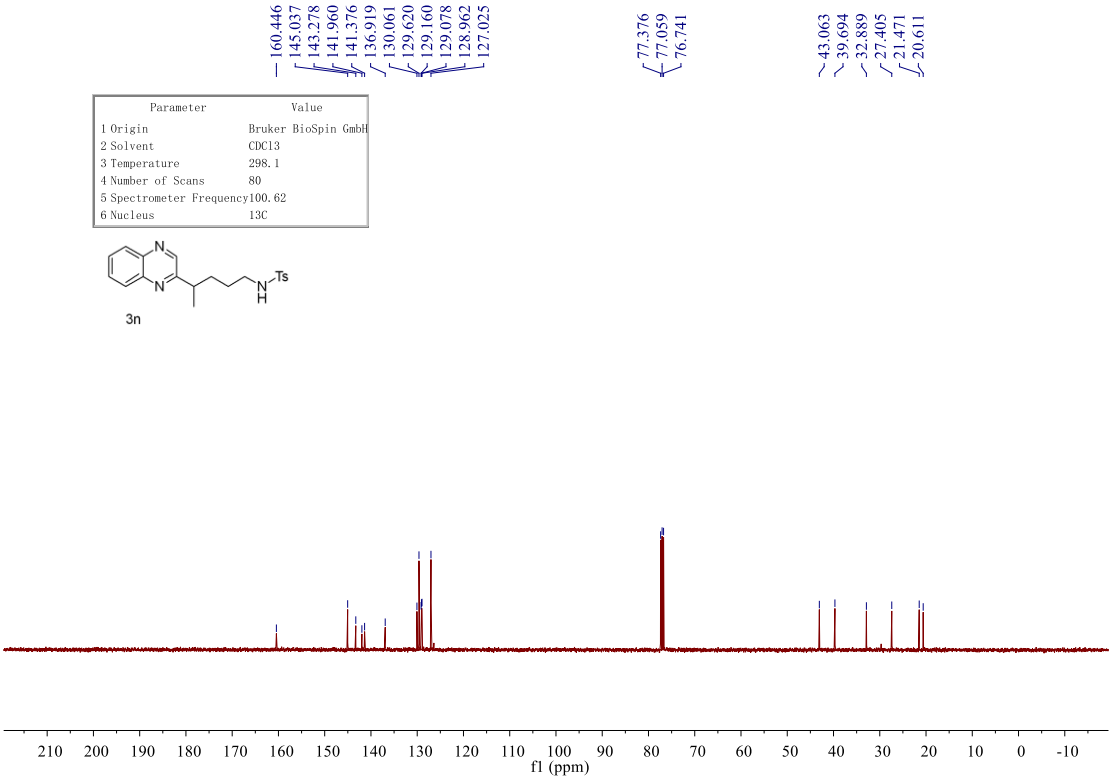

Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 80
5 Spectrometer Frequency 100.62
6 Nucleus 13C
Ts
N
H
N

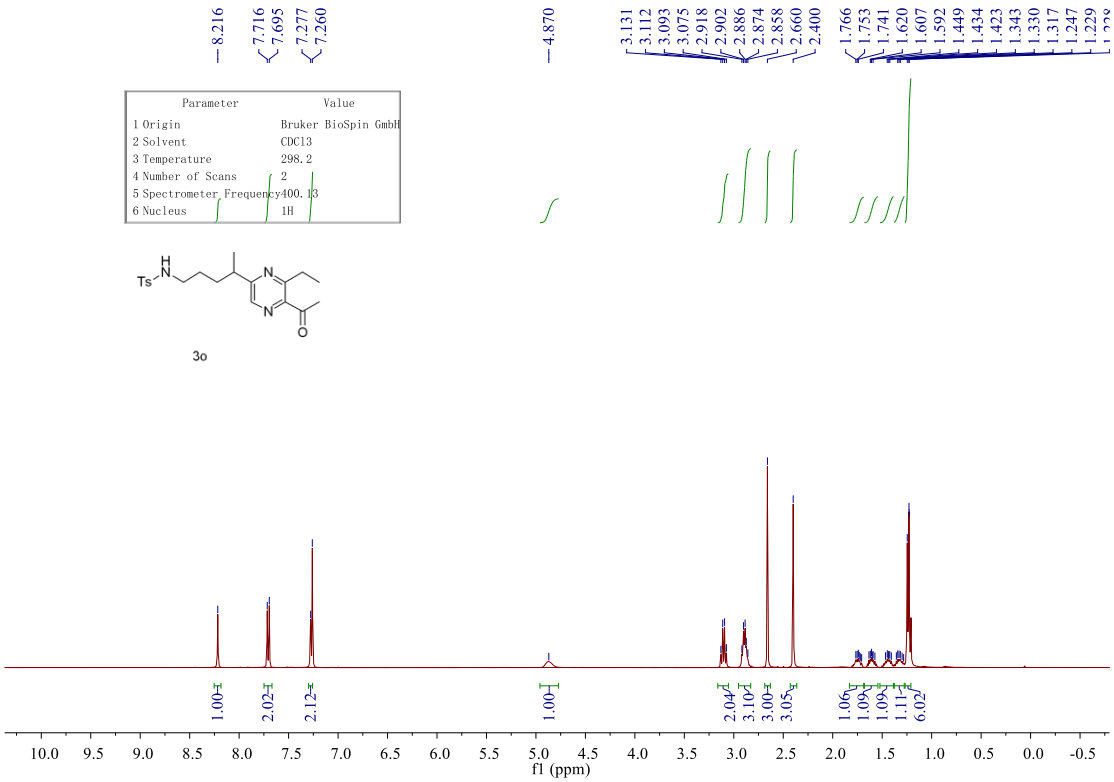
3m

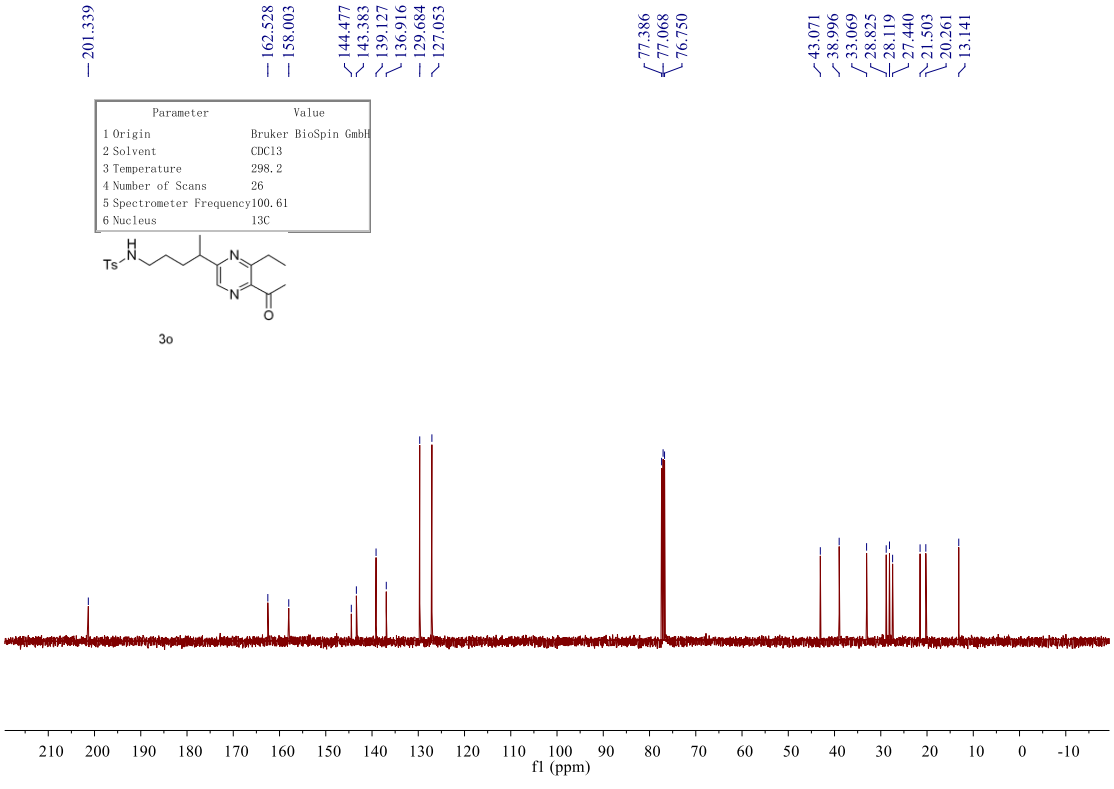

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

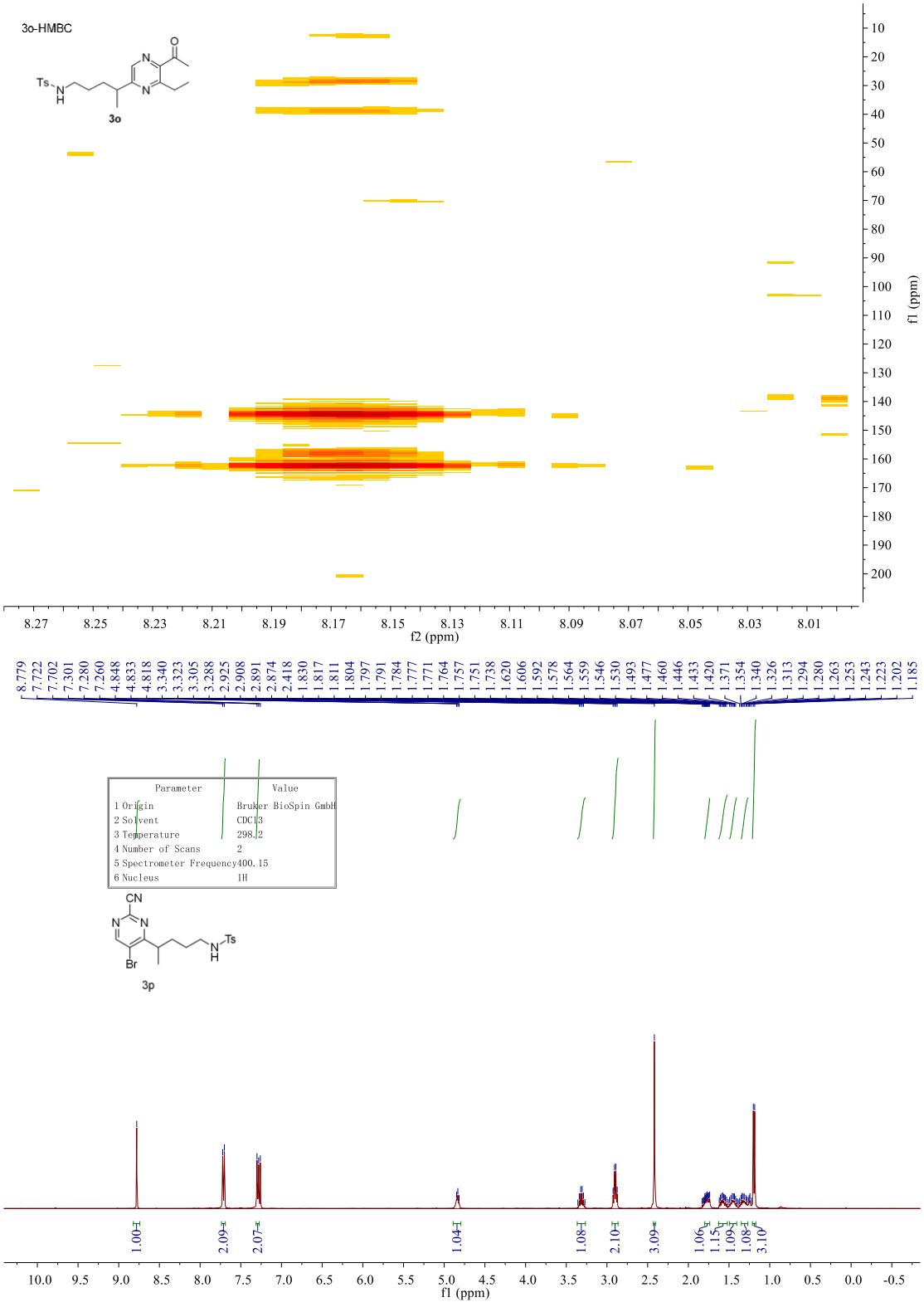

8.672
8.063
8.044
7.721
7.688
7.668
7.260
7.214
7.194
5.043
5.031
3.096
3.079
3.059
3.042
2.940
2.932
2.924
2.917
2.358
1.897
1.885
1.872
1.725
1.711
1.700
1.692
1.685
1.666
1.507
1.491
1.481
1.372
1.368
1.346
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 2
5 Spectrometer Frequency 400.13
6 Nucleus 1H
Ts
3n

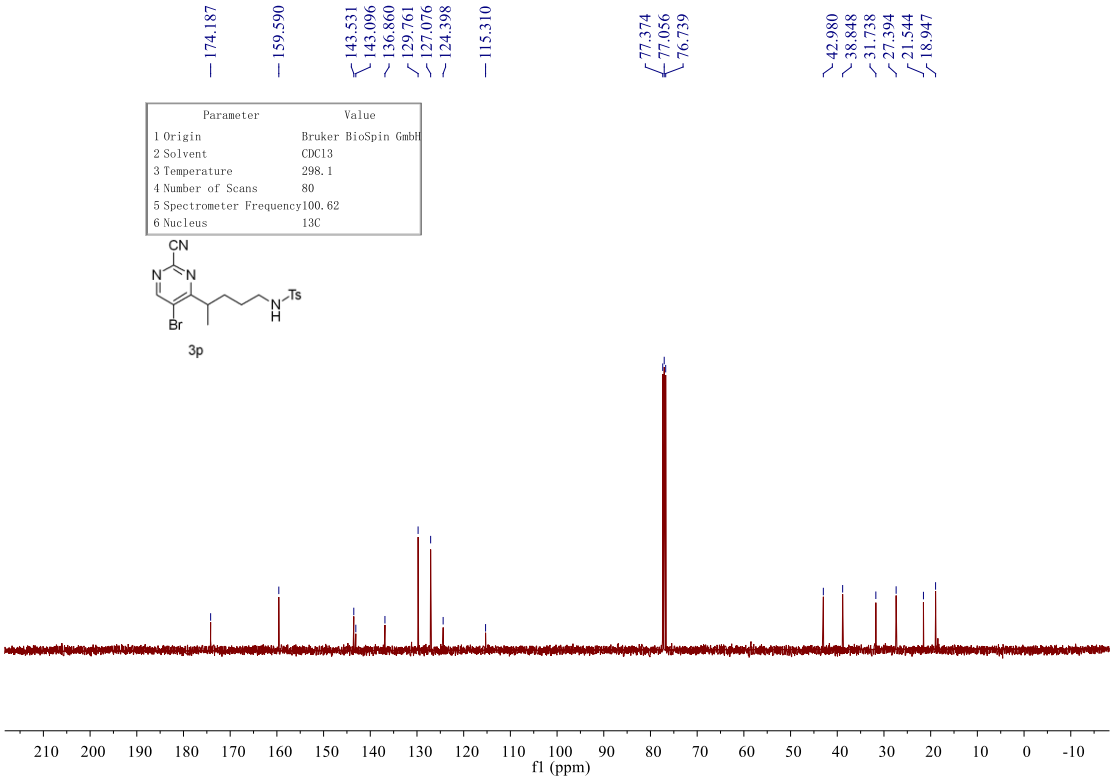

1.00
2.06
4.19
2.13
1.00
1.03
2.20
2.96
1.13
1.26
1.25
4.22
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


160.446
145.037
143.278
141.960
141.376
136.919
130.061
129.620
129.160
129.078
128.962
127.025
77.376
77.059
76.741
43.063
39.694
32.889
27.405
21.471
20.611
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 80
5 Spectrometer Frequency 100.62
6 Nucleus 13C
Ts
3n
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.216
7.716
7.695
7.277
7.260
4.870
3.131
3.112
3.093
3.075
2.918
2.902
2.886
2.874
2.858
2.660
2.400
1.766
1.753
1.741
1.620
1.607
1.592
1.449
1.434
1.423
1.343
1.330
1.317
1.247
1.229
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 2
5 Spectrometer Frequency 400.13
6 Nucleus 1H
Ts
H
N
N
N
O
3o
1.00
2.02
2.12
1.00
2.04
3.10
3.00
3.05
1.06
1.09
1.09
1.11
6.02
f1 (ppm)


201.339
162.528
158.003
144.477
143.383
139.127
136.916
129.684
127.053
77.386
77.068
76.750
43.071
38.996
33.069
28.825
28.119
27.440
21.503
20.261
13.141
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 26
5 Spectrometer Frequency 100.61
6 Nucleus 13C
Ts
H
N
N
N
O
3o
f1 (ppm)


3o-HMBC
Ts
N
H
O
N
N
3o
f2 (ppm)
f1 (ppm)
8.27 8.25 8.23 8.21 8.19 8.17 8.15 8.13 8.11 8.09 8.07 8.05 8.03 8.01
10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200
8.779 7.722 7.702 7.301 7.280 7.260 4.848 4.833 4.818 3.340 3.323 3.305 3.288 2.925 2.908 2.891 2.874 2.418 1.830 1.817 1.811 1.804 1.797 1.791 1.784 1.777 1.771 1.764 1.757 1.751 1.738 1.620 1.606 1.592 1.578 1.564 1.559 1.546 1.530 1.493 1.477 1.460 1.446 1.433 1.420 1.371 1.354 1.340 1.326 1.313 1.294 1.280 1.263 1.253 1.243 1.223 1.202 1.185
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 2
5 Spectrometer Frequency 400.15
6 Nucleus 1H
CN
N
N
Br
Ts
N
H
3p
1.00 2.09 2.07 1.04 1.08 2.10 3.09 1.06 1.15 1.09 1.08 3.10
f1 (ppm)
10.0 9.5 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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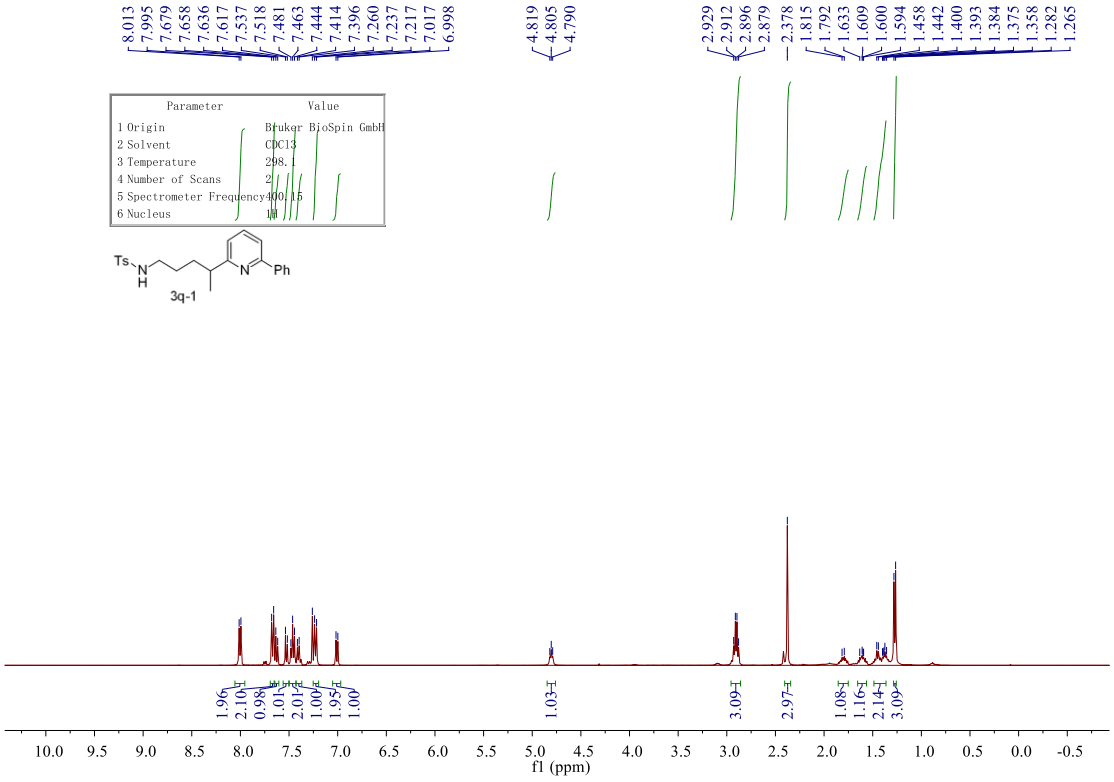
159.590
143.531
143.096
136.860
129.761
127.076
124.398
115.310
77.374
77.056
76.739
42.980
38.848
31.738
27.394
21.544
18.947
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 80
5 Spectrometer Frequency 100.62
6 Nucleus 13C
CN
N
N
Ts
N
H
Br
3p
f1 (ppm)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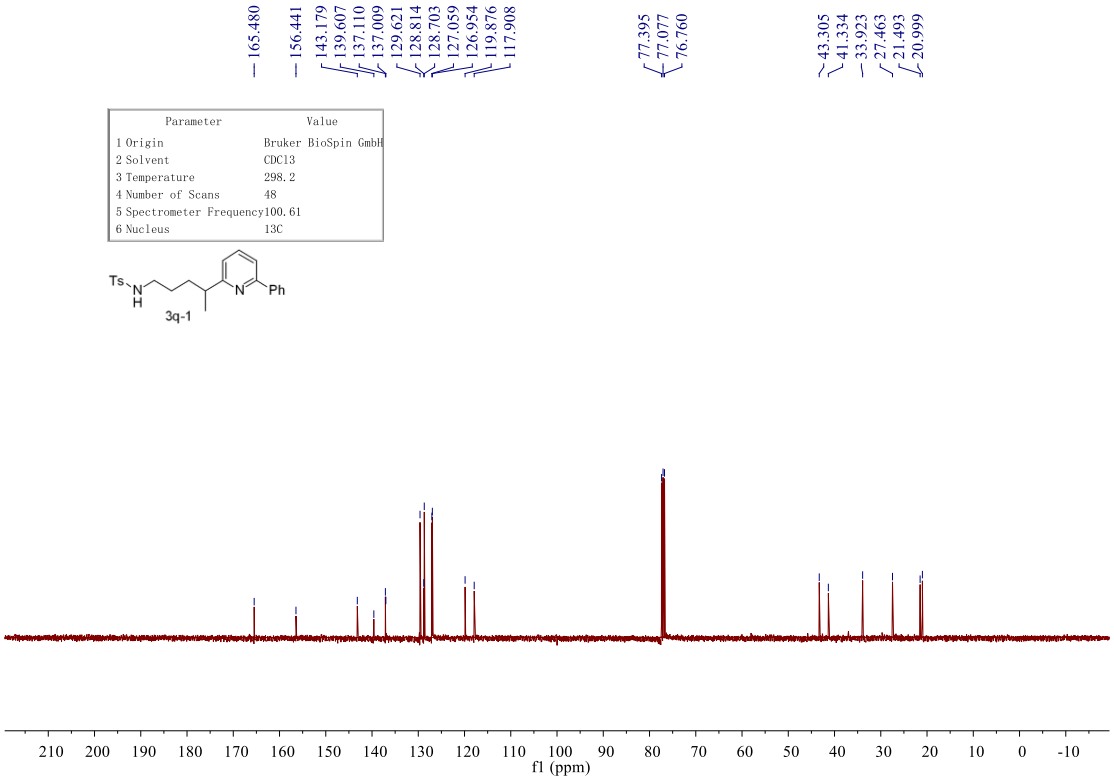
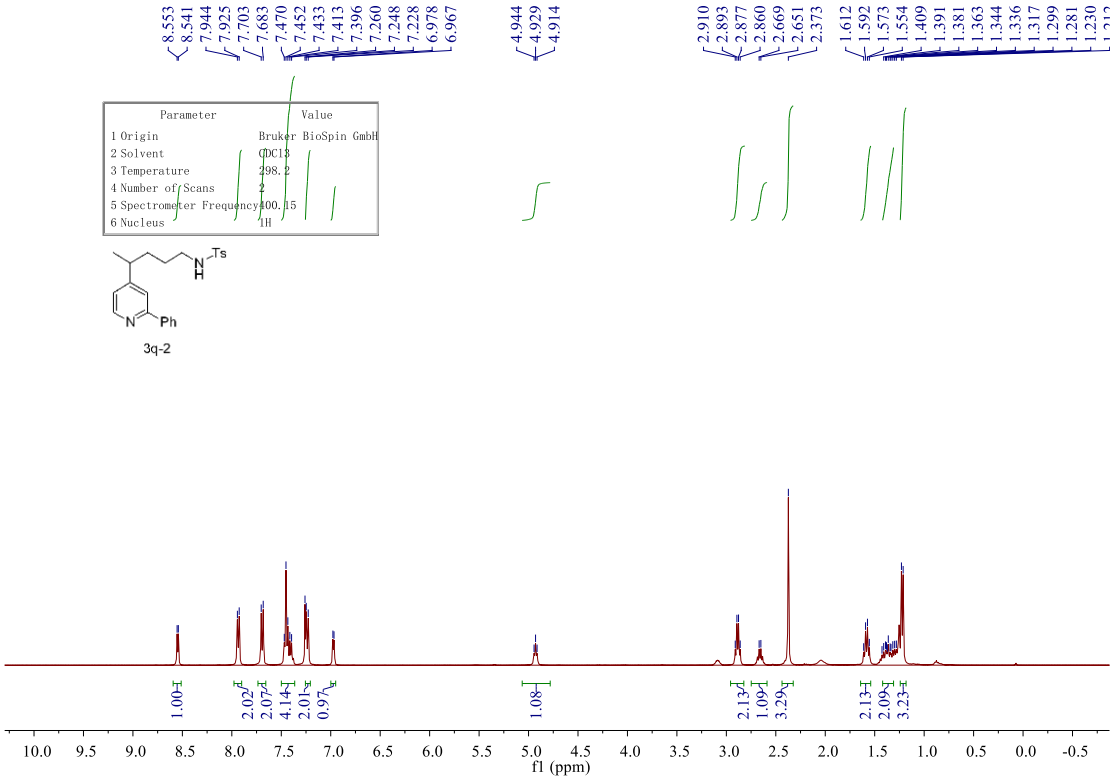
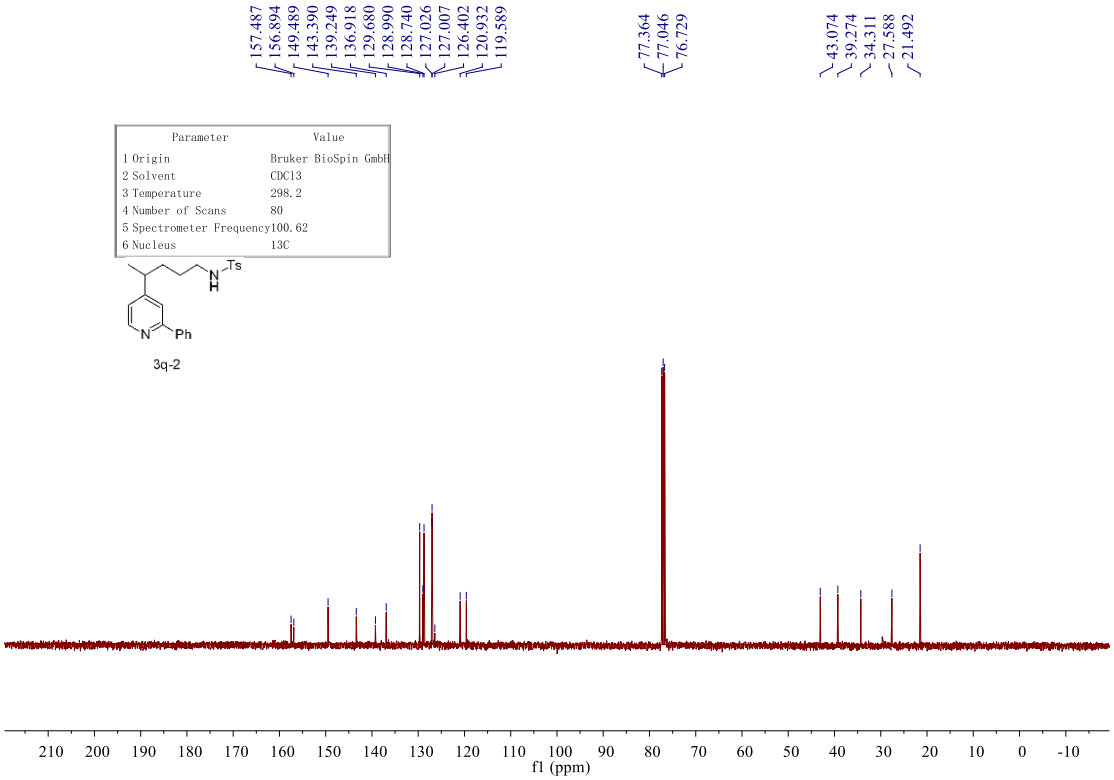
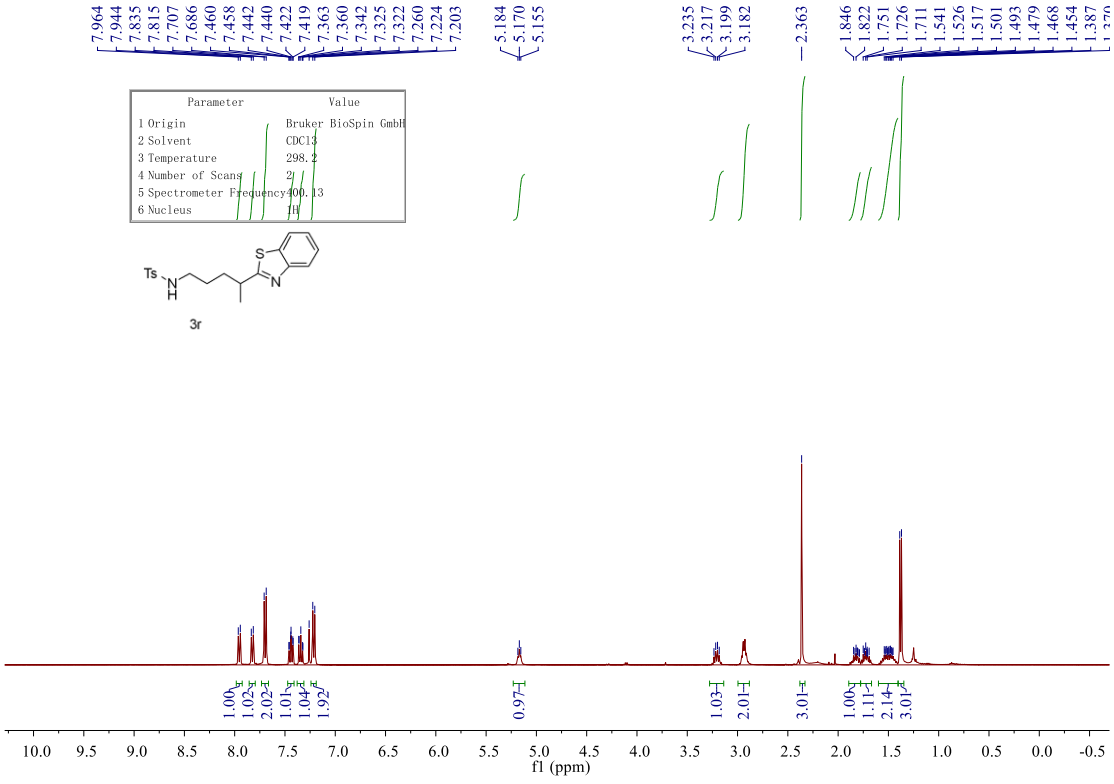
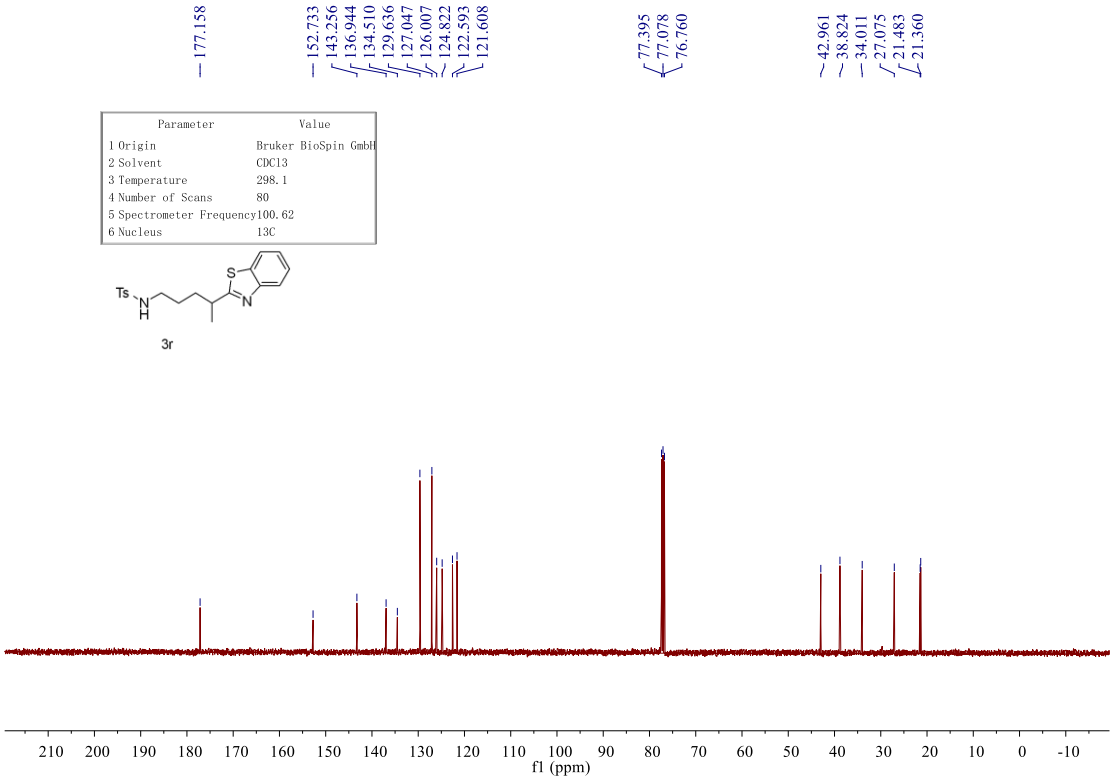
7.995
7.679
7.658
7.636
7.617
7.537
7.518
7.481
7.463
7.444
7.414
7.396
7.260
7.237
7.217
7.017
6.998
4.819
4.805
4.790
2.929
2.912
2.896
2.879
2.378
1.815
1.792
1.633
1.609
1.600
1.594
1.458
1.442
1.400
1.393
1.384
1.375
1.358
1.282
1.265
Parameter Value
1 Origin Brukqr BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 2
5 Spectrometer Frequency 400.15
6 Nucleus 1H
Ts
N
H
N
Ph
3q-1
1.96
2.10
0.98
1.01
2.01
1.00
1.95
1.00
1.03
3.09
2.97
1.08
1.16
2.14
3.09
f1 (ppm)

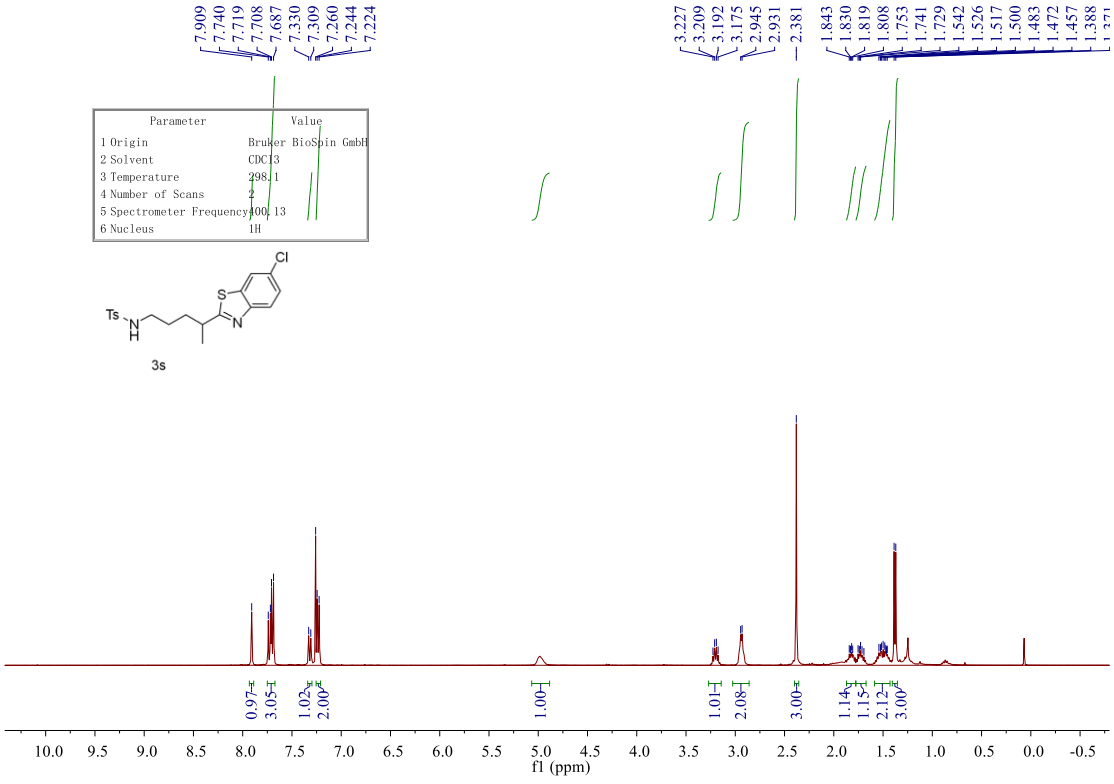

165.480
156.441
143.179
139.607
137.110
137.009
129.621
128.814
128.703
127.059
126.954
119.876
117.908
77.395
77.077
76.760
43.305
41.334
33.923
27.463
21.493
20.999
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 48
5 Spectrometer Frequency 100.61
6 Nucleus 13C
Ts
N
H
N
Ph
3q-1
f1 (ppm)

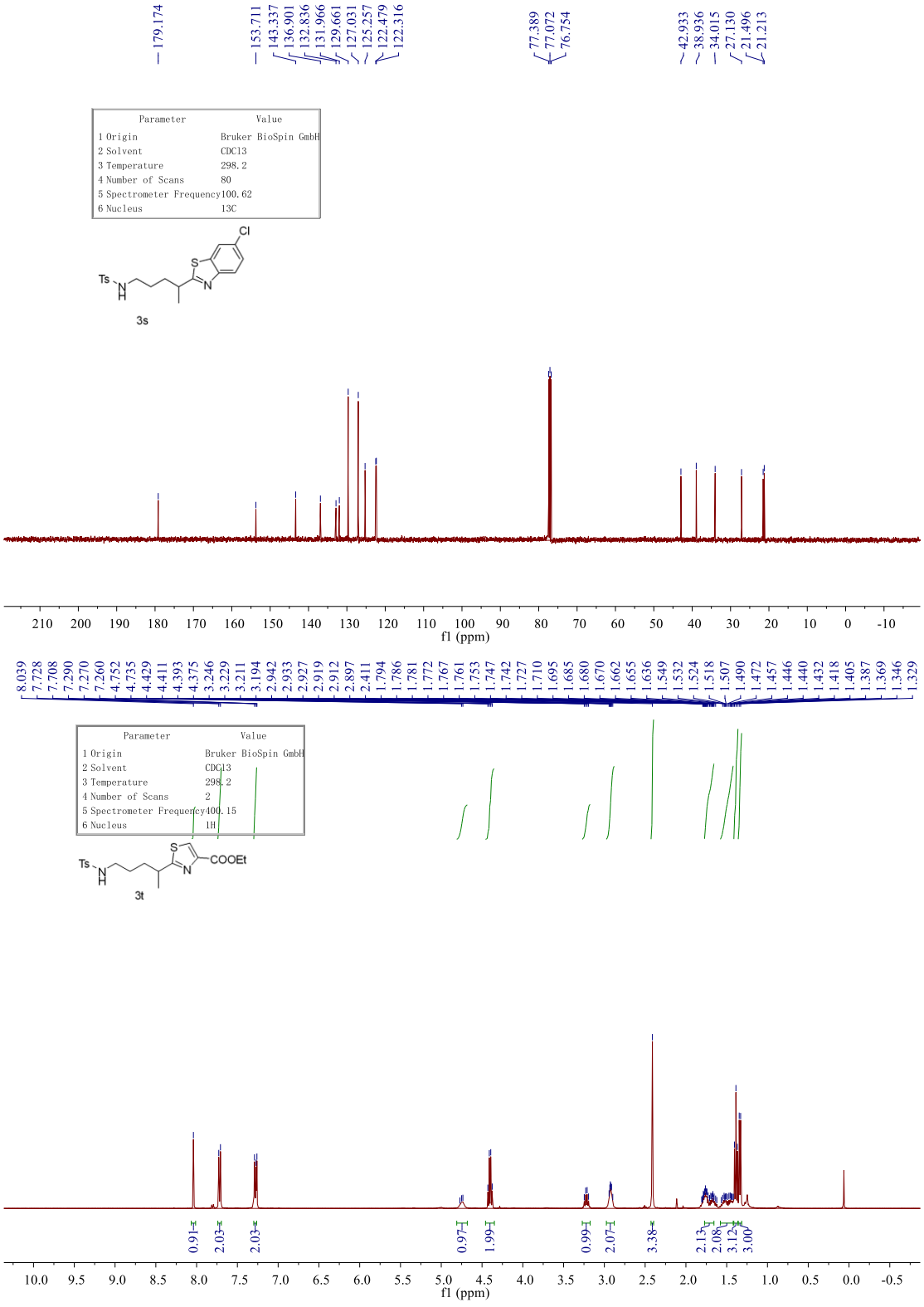

8.553
8.541
7.944
7.925
7.703
7.683
7.470
7.452
7.433
7.413
7.396
7.260
7.248
7.228
6.978
6.967
4.944
4.929
4.914
2.910
2.893
2.877
2.860
2.669
2.651
2.373
1.612
1.592
1.573
1.554
1.409
1.391
1.381
1.363
1.344
1.336
1.317
1.299
1.281
1.230
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 2
5 Spectrometer Frequency 400.15
6 Nucleus 1H
N
H
Ts
N
Ph
3q-2
1.00
2.02
2.07
4.14
2.01
0.97
1.08
2.13
1.09
3.29
2.13
2.09
3.23
f1 (ppm)


157.487
156.894
149.489
143.390
139.249
136.918
129.680
128.990
128.740
127.026
127.007
126.402
120.932
119.589
77.364
77.046
76.729
43.074
39.274
34.311
27.588
21.492
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 80
5 Spectrometer Frequency 100.62
6 Nucleus 13C
Ts
N
H
N
Ph
3q-2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.964
7.944
7.835
7.815
7.707
7.686
7.460
7.458
7.442
7.440
7.422
7.419
7.363
7.360
7.342
7.325
7.322
7.260
7.224
7.203
5.184
5.170
5.155
3.235
3.217
3.199
3.182
2.363
1.846
1.822
1.751
1.726
1.711
1.541
1.526
1.517
1.501
1.493
1.479
1.468
1.454
1.387
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 2
5 Spectrometer Frequency 400.13
6 Nucleus 1H
Ts
N
H
S
N
3r
1.00
1.02
2.02
1.01
1.04
1.92
0.97
1.03
2.01
3.01
1.00
1.11
2.14
3.01
10.0 9.5 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)


177.158
152.733
143.256
136.944
134.510
129.636
127.047
126.007
124.822
122.593
121.608
77.395
77.078
76.760
42.961
38.824
34.011
27.075
21.483
21.360
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 80
5 Spectrometer Frequency 100.62
6 Nucleus 13C
Ts
N
H
S
N
3r
f1 (ppm)


7.909
7.740
7.719
7.708
7.687
7.330
7.309
7.260
7.244
7.224
3.227
3.209
3.192
3.175
2.945
2.931
2.381
1.843
1.830
1.819
1.808
1.753
1.741
1.729
1.542
1.526
1.517
1.500
1.483
1.472
1.457
1.388
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 2
5 Spectrometer Frequency 400.13
6 Nucleus 1H
Cl
Ts
N
H
S
N
3s
0.97
3.05
1.02
2.00
1.00
1.01
2.08
3.00
1.14
1.15
2.12
3.00
f1 (ppm)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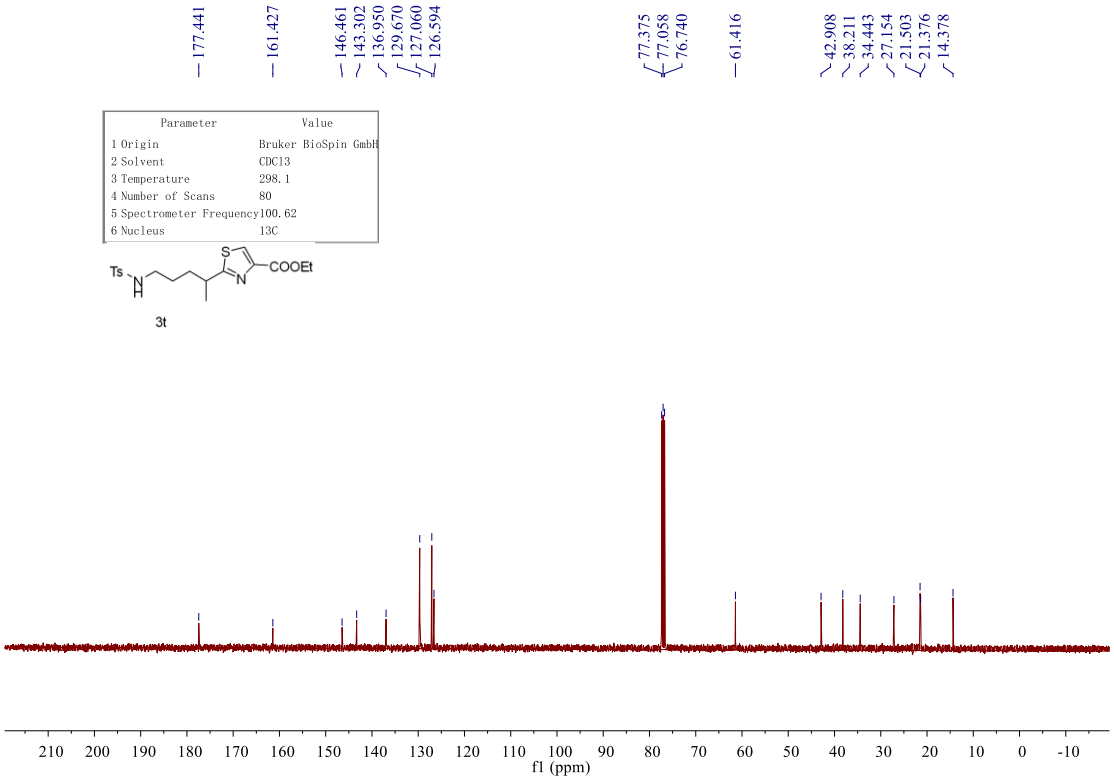
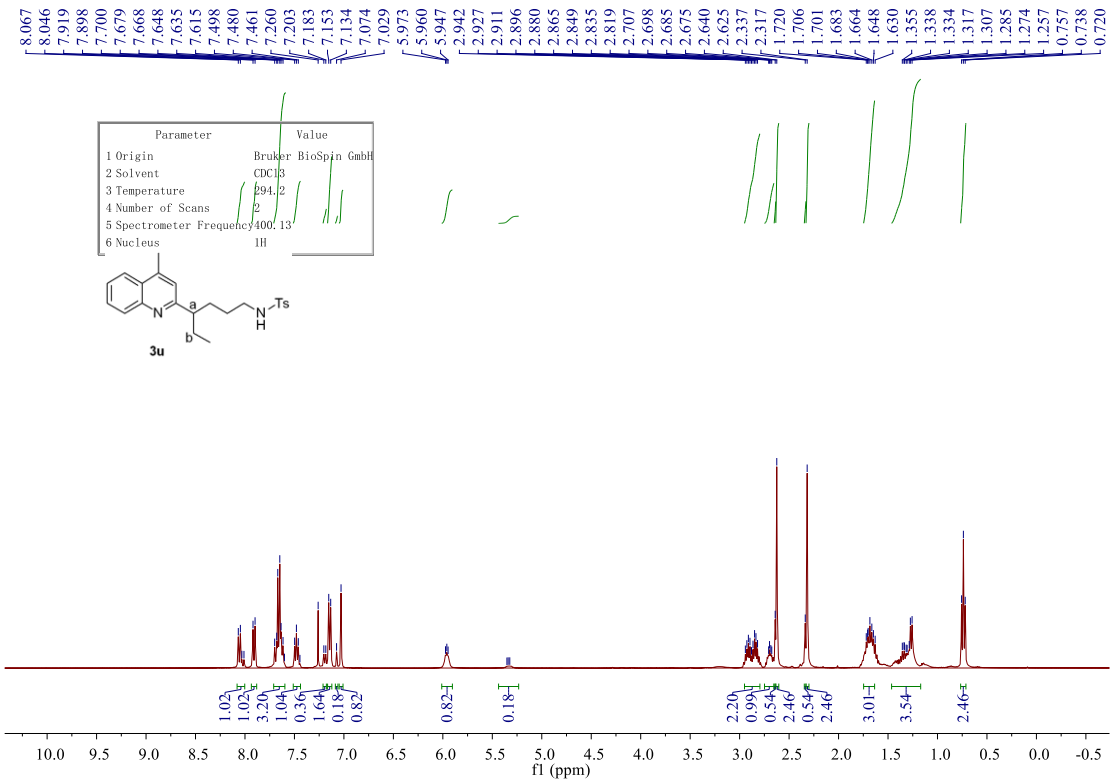
131.966
129.661
127.031
125.257
122.479
122.316
77.389
77.072
76.754
42.933
38.936
34.015
27.130
21.496
21.213
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 80
5 Spectrometer Frequency 100.62
6 Nucleus 13C
Cl
S
N
Ts
N
H
3s
f1 (ppm)
8.039
7.728
7.708
7.290
7.270
7.260
4.752
4.735
4.429
4.411
4.393
4.375
3.246
3.229
3.211
3.194
2.942
2.933
2.927
2.919
2.912
2.897
2.411
1.794
1.786
1.781
1.772
1.767
1.761
1.753
1.747
1.742
1.727
1.710
1.695
1.685
1.680
1.670
1.662
1.655
1.636
1.549
1.532
1.524
1.518
1.507
1.490
1.472
1.457
1.446
1.440
1.432
1.418
1.405
1.387
1.369
1.346
1.329
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 2
5 Spectrometer Frequency 400.15
6 Nucleus 1H
S
N
COOEt
Ts
N
H
3t
0.91
2.03
2.03
0.97
1.99
0.99
2.07
3.38
2.13
2.08
3.12
3.00
f1 (ppm)


177.441
161.427
146.461
143.302
136.950
129.670
127.060
126.594
77.375
77.058
76.740
61.416
42.908
38.211
34.443
27.154
21.503
21.376
14.378
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 80
5 Spectrometer Frequency 100.62
6 Nucleus 13C
Ts
N
H
S
N
COOEt
3t
f1 (ppm)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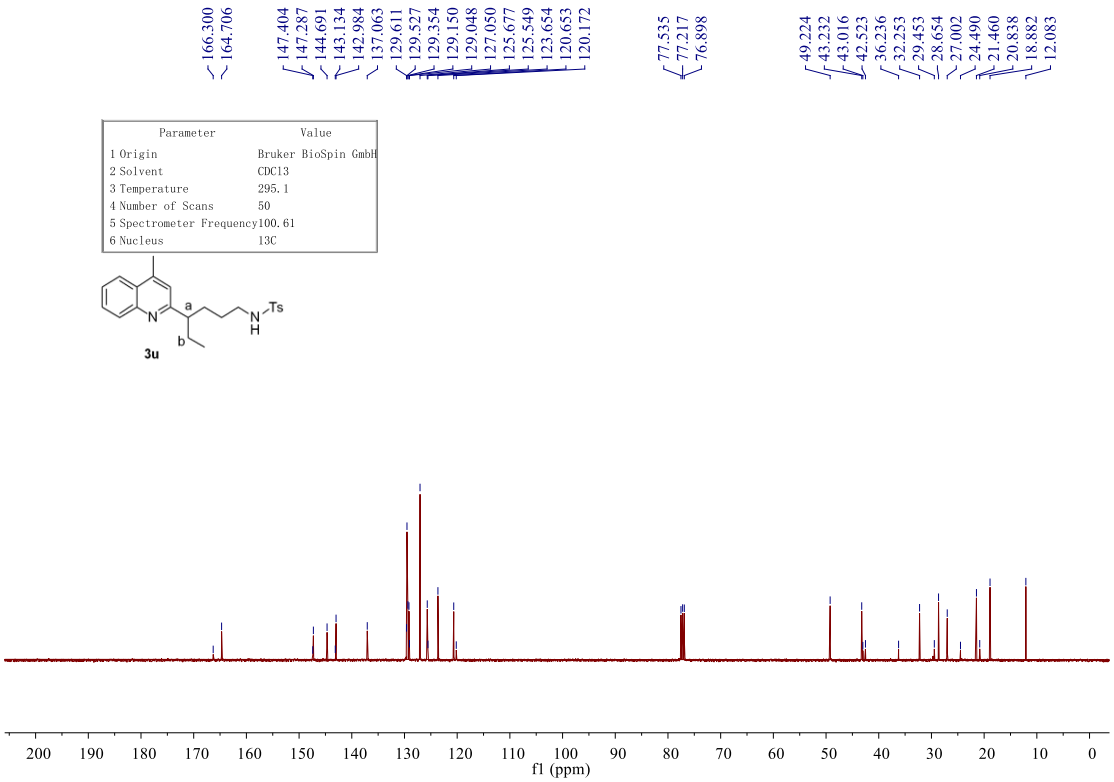
7.898
7.700
7.679
7.668
7.648
7.635
7.615
7.498
7.480
7.461
7.260
7.203
7.183
7.153
7.134
7.074
7.029
5.973
5.960
5.947
2.942
2.927
2.911
2.896
2.880
2.865
2.849
2.835
2.819
2.707
2.698
2.685
2.675
2.640
2.625
2.337
2.317
1.720
1.706
1.701
1.683
1.664
1.648
1.630
1.355
1.338
1.334
1.317
1.307
1.285
1.274
1.257
0.757
0.738
0.720
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 294.2
4 Number of Scans 2
5 Spectrometer Frequency 400.13
6 Nucleus 1H
N
a
b
N
H
Ts
3u
1.02
1.02
3.20
1.04
0.36
1.64
0.18
0.82
0.82
0.18
2.20
0.99
0.54
2.46
0.54
2.46
3.01
3.54
2.46
f1 (ppm)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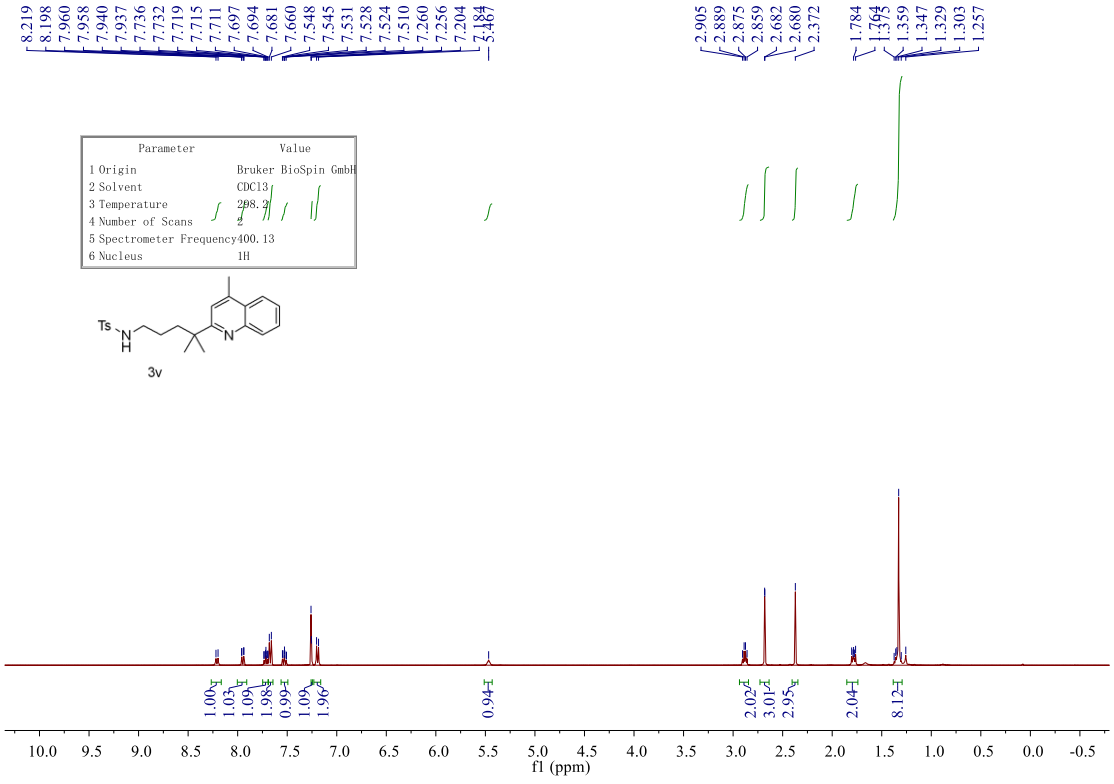
147.404
147.287
144.691
143.134
142.984
137.063
129.611
129.527
129.354
129.150
129.048
127.050
125.677
125.549
123.654
120.653
120.172
77.535
77.217
76.898
49.224
43.232
43.016
42.523
36.236
32.253
29.453
28.654
27.002
24.490
21.460
20.838
18.882
12.083
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 295.1
4 Number of Scans 50
5 Spectrometer Frequency 100.61
6 Nucleus 13C
a
b
Ts
N
H
3u
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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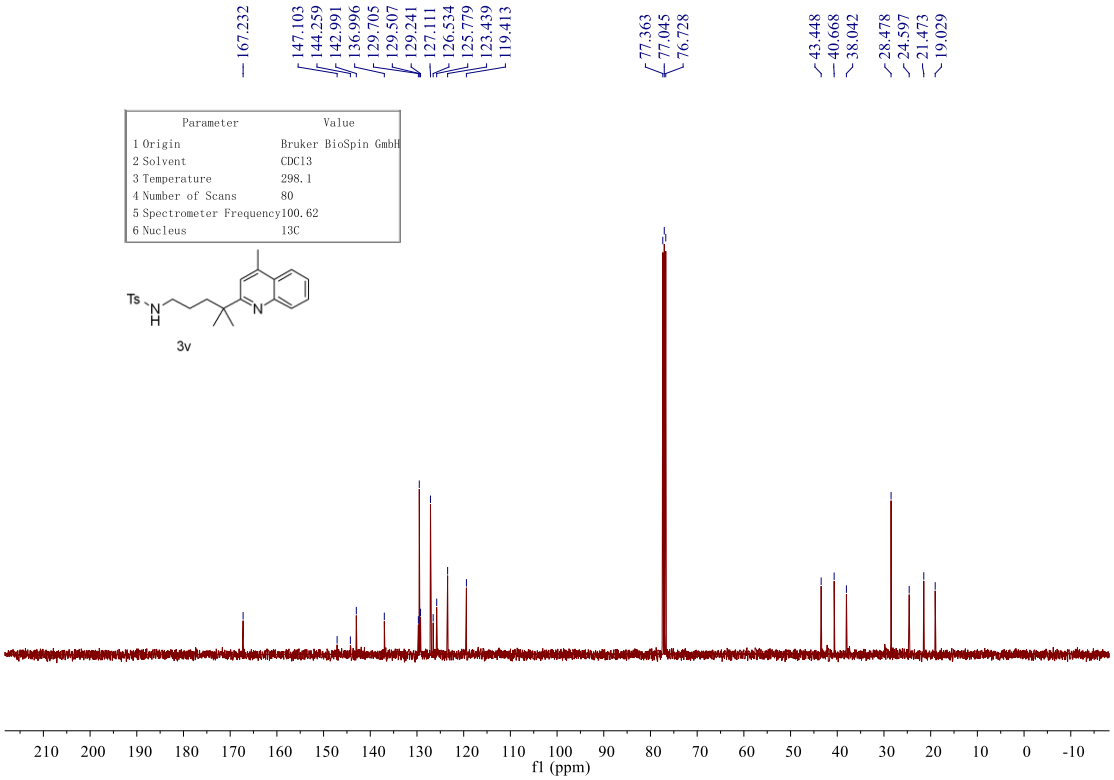
7.958
7.940
7.937
7.736
7.732
7.719
7.715
7.711
7.697
7.694
7.681
7.660
7.548
7.545
7.531
7.528
7.524
7.510
7.260
7.256
7.204
7.184
5.487
2.905
2.889
2.875
2.859
2.682
2.680
2.372
1.784
1.375
1.359
1.347
1.329
1.303
1.257
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 2
5 Spectrometer Frequency 400.13
6 Nucleus 1H
Ts
N
H
3v
1.00
1.03
1.09
1.98
0.99
1.09
1.96
0.94
2.02
3.01
2.95
2.04
8.12
10.0 9.5 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)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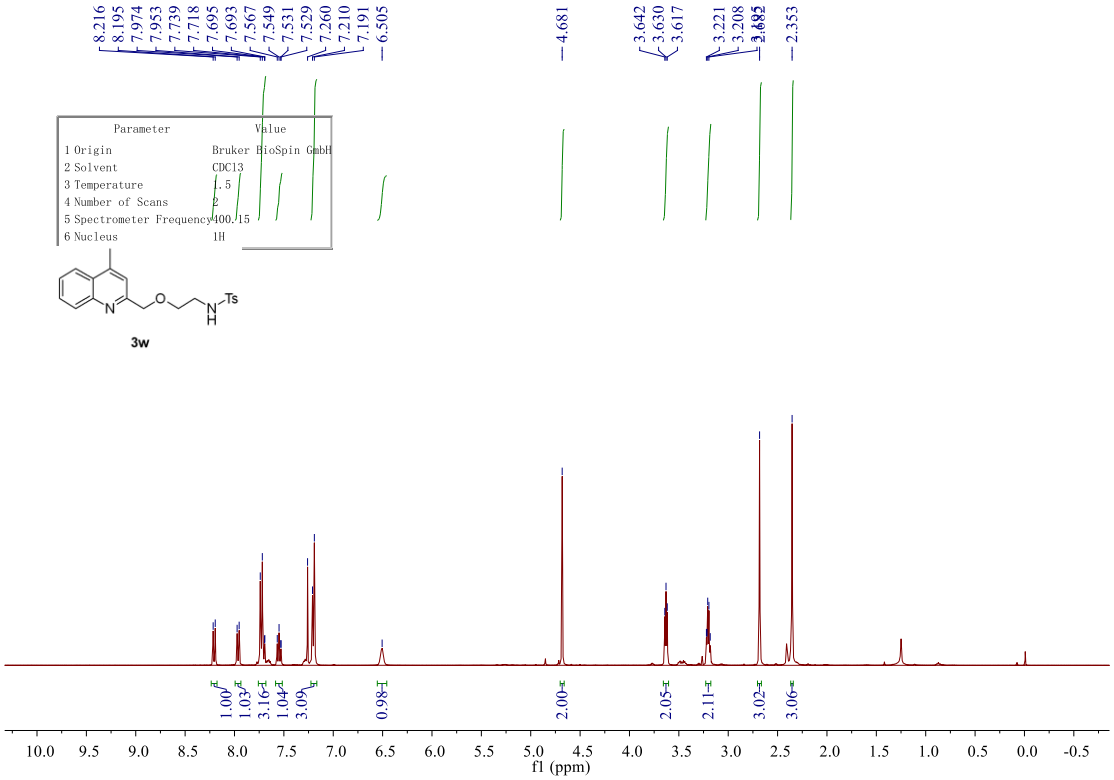
144.259
142.991
136.996
129.705
129.507
129.241
127.111
126.534
125.779
123.439
119.413
77.363
77.045
76.728
43.448
40.668
38.042
28.478
24.597
21.473
19.029
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 80
5 Spectrometer Frequency 100.62
6 Nucleus 13C
Ts
N
H
N
3v
f1 (ppm)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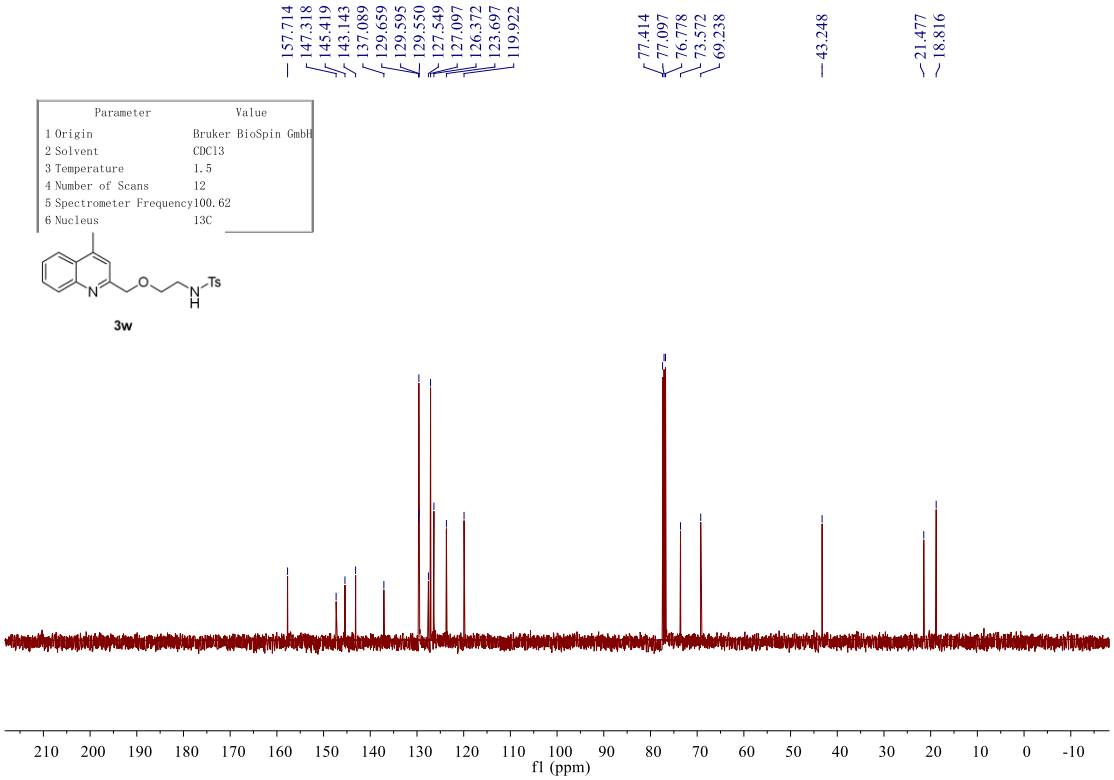
7.974
7.953
7.739
7.718
7.695
7.693
7.567
7.549
7.531
7.529
7.260
7.210
7.191
6.505
4.681
3.642
3.630
3.617
3.221
3.208
2.353
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 1.5
4 Number of Scans 2
5 Spectrometer Frequency 400.15
6 Nucleus 1H
N
O
N
H
Ts
3w
1.00
1.03
3.16
1.04
3.09
0.98
2.00
2.05
2.11
3.02
3.06
f1 (ppm)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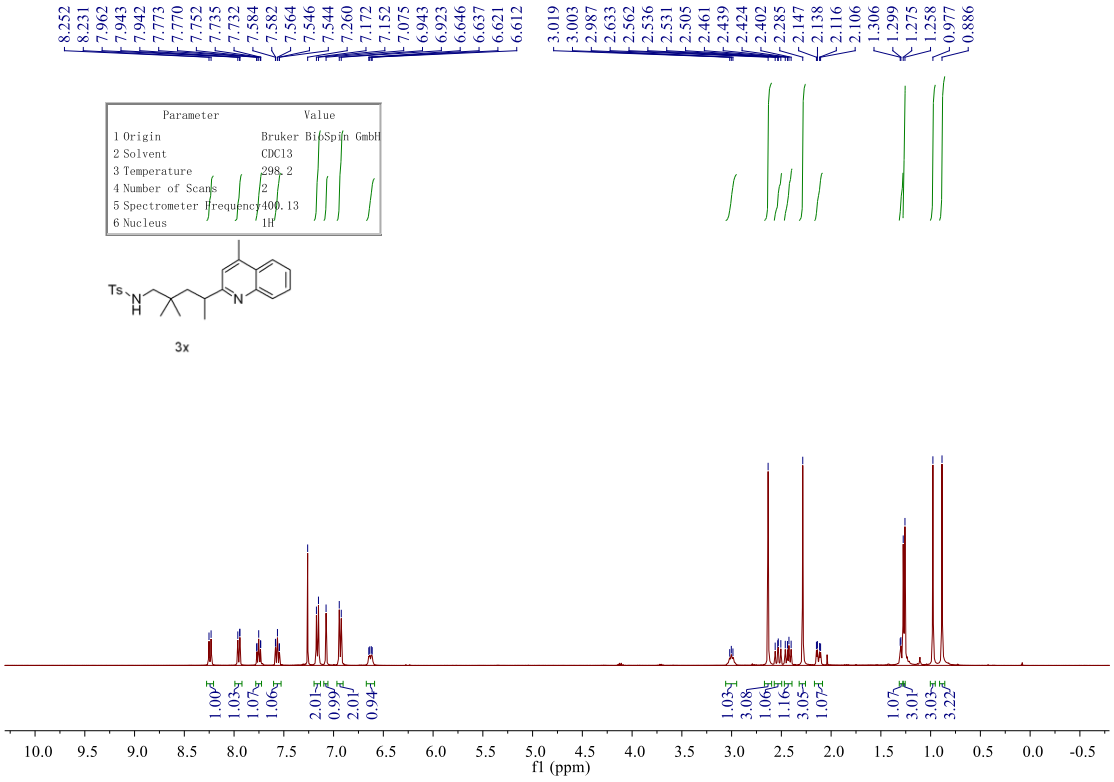
147.318
145.419
143.143
137.089
129.659
129.595
129.550
127.549
127.097
126.372
123.697
119.922
77.414
77.097
76.778
73.572
69.238
43.248
21.477
18.816
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 1.5
4 Number of Scans 12
5 Spectrometer Frequency 100.62
6 Nucleus 13C
Ts
3w
f1 (ppm)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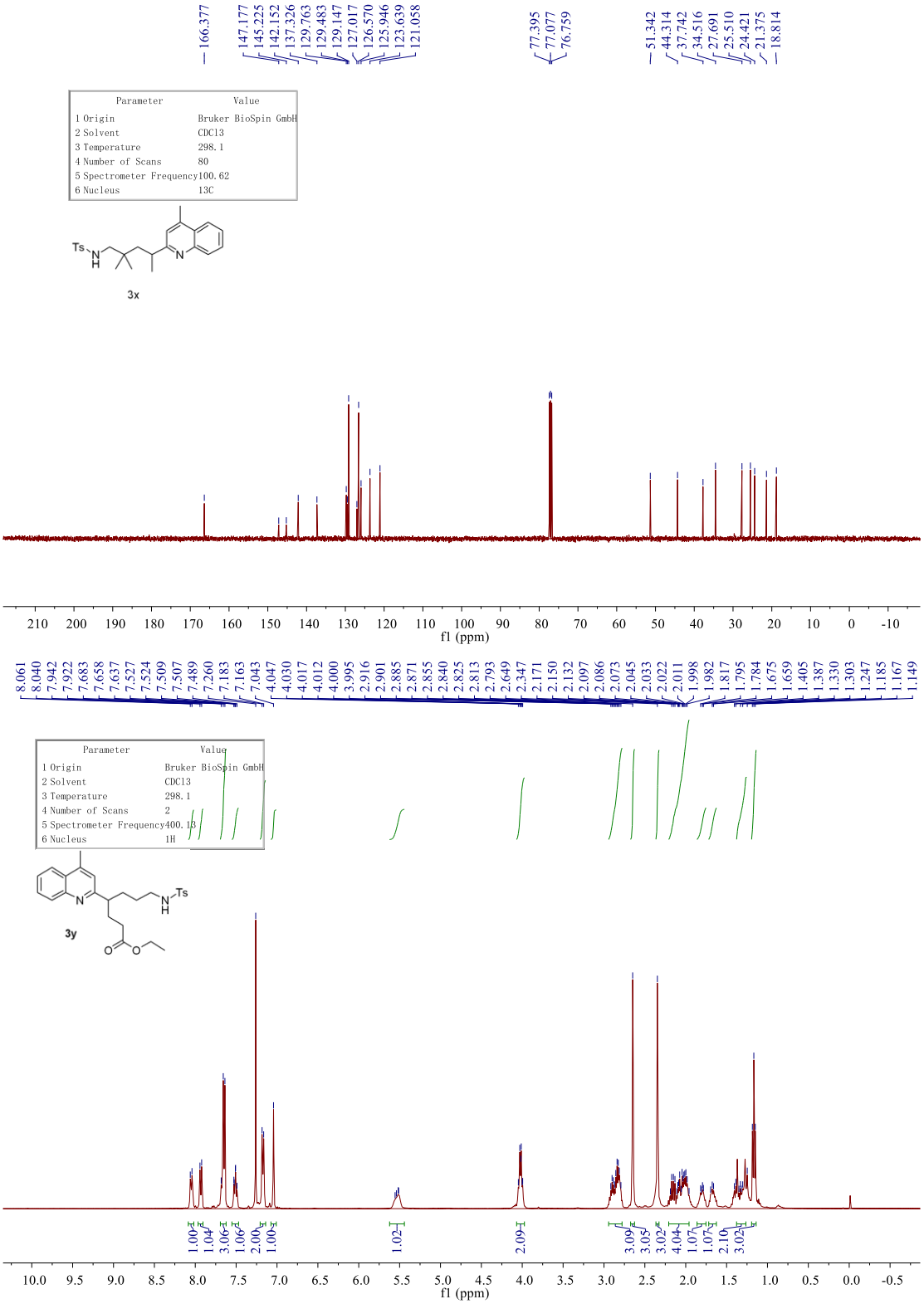
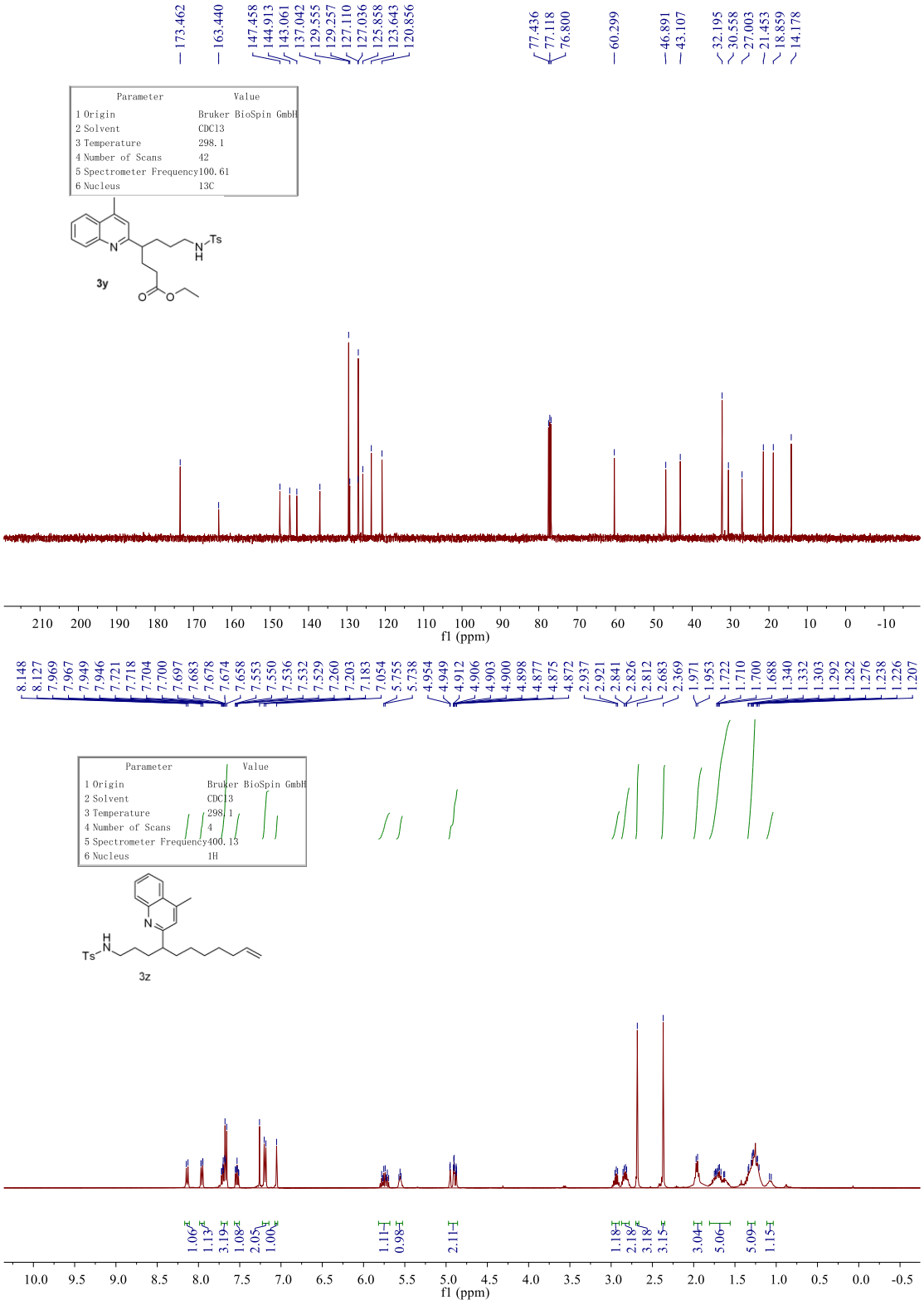
8.231
7.962
7.943
7.942
7.773
7.770
7.752
7.735
7.732
7.584
7.582
7.564
7.546
7.544
7.260
7.172
7.152
7.075
6.943
6.923
6.646
6.637
6.621
6.612
3.019
3.003
2.987
2.633
2.562
2.536
2.531
2.505
2.461
2.439
2.424
2.402
2.285
2.147
2.138
2.116
2.106
1.306
1.299
1.275
1.258
0.977
0.886
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 2
5 Spectrometer Frequency 400.13
6 Nucleus 1H
Ts
3x
1.00
1.03
1.07
1.06
2.01
0.99
2.01
0.94
1.03
3.08
1.06
1.16
3.05
1.07
1.07
3.01
3.03
3.22
f1 (ppm)


166.377
147.177
145.225
142.152
137.326
129.763
129.483
129.147
127.017
126.570
125.946
123.639
121.058
77.395
77.077
76.759
51.342
44.314
37.742
34.516
27.691
25.510
24.421
21.375
18.814
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 80
5 Spectrometer Frequency 100.62
6 Nucleus 13C
Ts
N
H
3x
f1 (ppm)
8.061
8.040
7.942
7.922
7.683
7.658
7.637
7.527
7.524
7.509
7.507
7.489
7.260
7.183
7.163
7.043
4.047
4.030
4.017
4.012
4.000
3.995
2.916
2.901
2.885
2.871
2.855
2.840
2.825
2.813
2.793
2.649
2.347
2.171
2.150
2.132
2.097
2.086
2.073
2.045
2.033
2.022
2.011
1.998
1.982
1.817
1.795
1.784
1.675
1.659
1.405
1.387
1.330
1.303
1.247
1.185
1.167
1.149
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 2
5 Spectrometer Frequency 400.13
6 Nucleus 1H
N
Ts
N
H
O
O
3y
1.00
1.04
3.06
1.06
2.00
1.00
1.02
2.09
3.09
3.05
3.02
4.04
1.07
1.07
2.10
3.02
f1 (ppm)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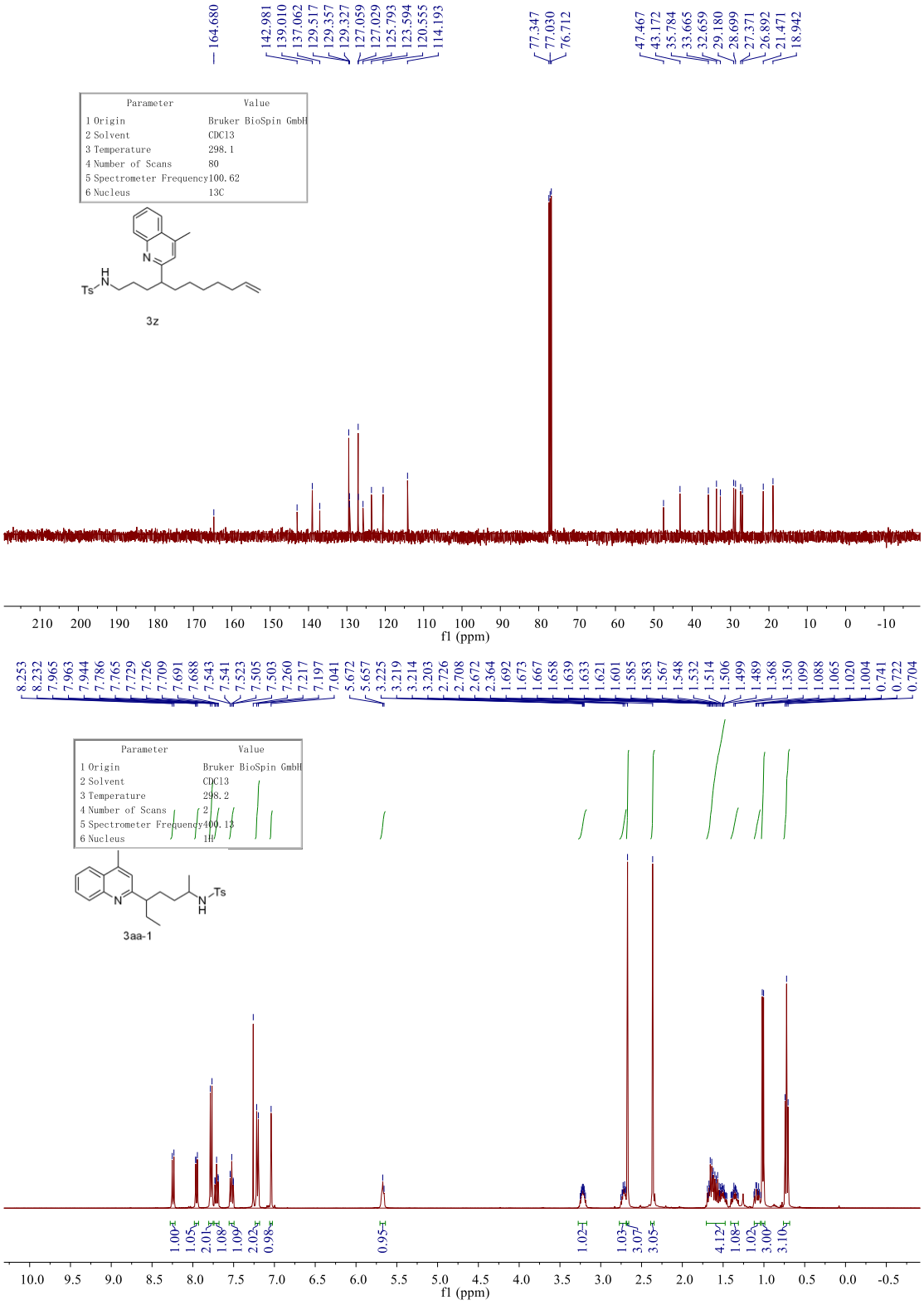
163.440
147.458
144.913
143.061
137.042
129.555
129.257
127.110
127.036
125.858
123.643
120.856
77.436
77.118
76.800
60.299
46.891
43.107
32.195
30.558
27.003
21.453
18.859
14.178
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 42
5 Spectrometer Frequency 100.61
6 Nucleus 13C
Ts
N
H
O
3y
f1 (ppm)
8.148
8.127
7.969
7.967
7.949
7.946
7.721
7.718
7.704
7.700
7.697
7.683
7.678
7.674
7.658
7.553
7.550
7.536
7.532
7.529
7.260
7.203
7.183
7.054
5.755
5.738
4.954
4.949
4.912
4.906
4.903
4.900
4.898
4.877
4.875
4.872
2.937
2.921
2.841
2.826
2.812
2.683
2.369
1.971
1.953
1.722
1.710
1.700
1.688
1.340
1.332
1.303
1.292
1.282
1.276
1.238
1.226
1.207
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 4
5 Spectrometer Frequency 400.13
6 Nucleus 1H
N
H
Ts
3z
1.06
1.13
3.19
1.08
2.05
1.00
1.11
0.98
2.11
1.18
2.18
3.18
3.15
3.04
5.06
5.09
1.15
f1 (ppm)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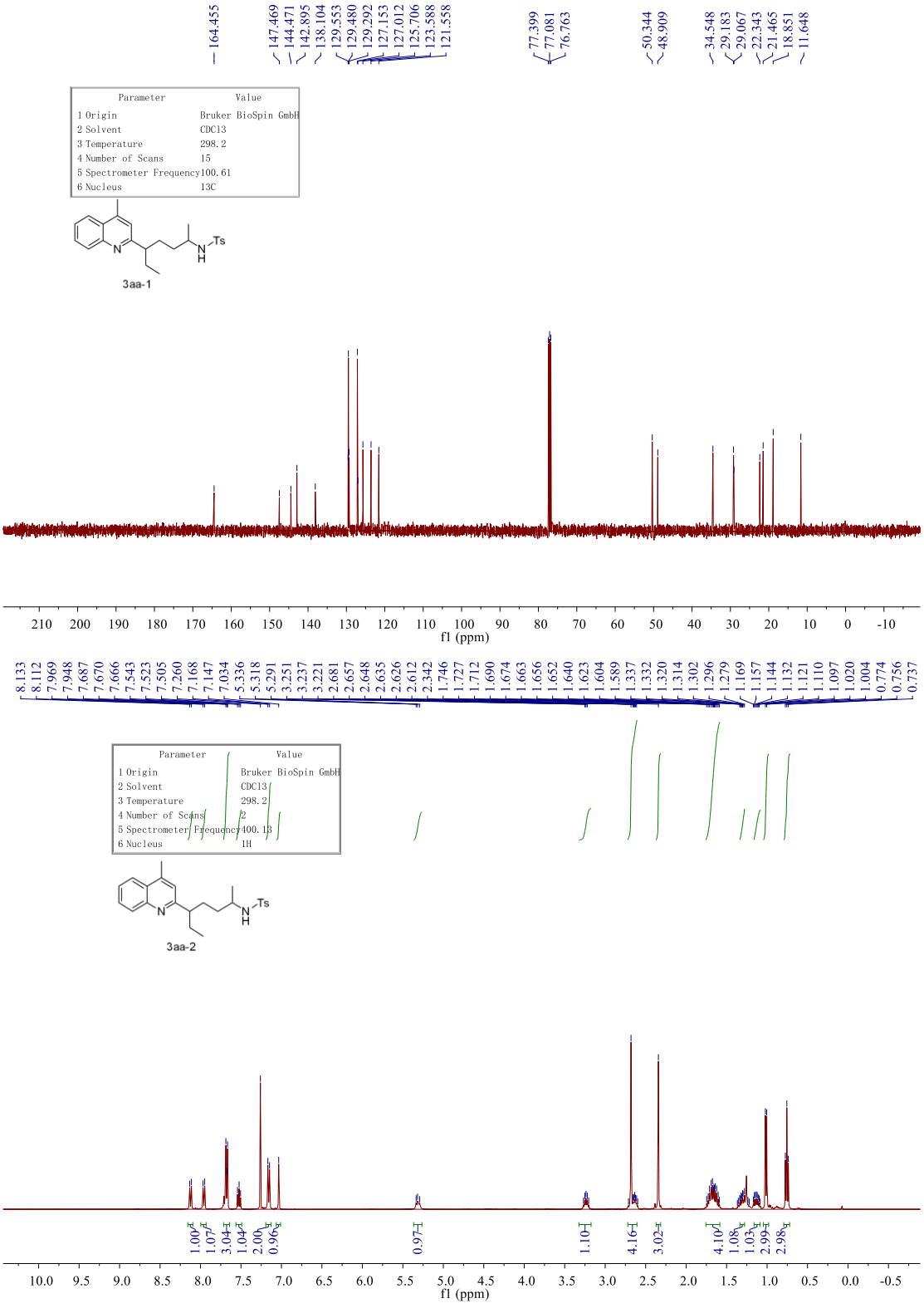
142.981
139.010
137.062
129.517
129.357
129.327
127.059
127.029
125.793
123.594
120.555
114.193
77.347
77.030
76.712
47.467
43.172
35.784
33.665
32.659
29.180
28.699
27.371
26.892
21.471
18.942
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 80
5 Spectrometer Frequency 100.62
6 Nucleus 13C
3z
f1 (ppm)
8.253
8.232
7.965
7.963
7.944
7.786
7.765
7.729
7.726
7.709
7.691
7.688
7.543
7.541
7.523
7.505
7.503
7.260
7.217
7.197
7.041
5.672
5.657
3.225
3.219
3.214
3.203
2.726
2.708
2.672
2.364
1.692
1.673
1.667
1.658
1.639
1.633
1.621
1.601
1.585
1.583
1.567
1.548
1.532
1.514
1.506
1.499
1.489
1.368
1.350
1.099
1.088
1.065
1.020
1.004
0.741
0.722
0.704
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 2
5 Spectrometer Frequency 400.13
6 Nucleus 1H
3aa-1
1.00
1.05
2.01
1.08
1.09
2.02
0.98
0.95
1.02
1.03
3.07
3.05
4.12
1.08
1.02
3.00
3.10
f1 (ppm)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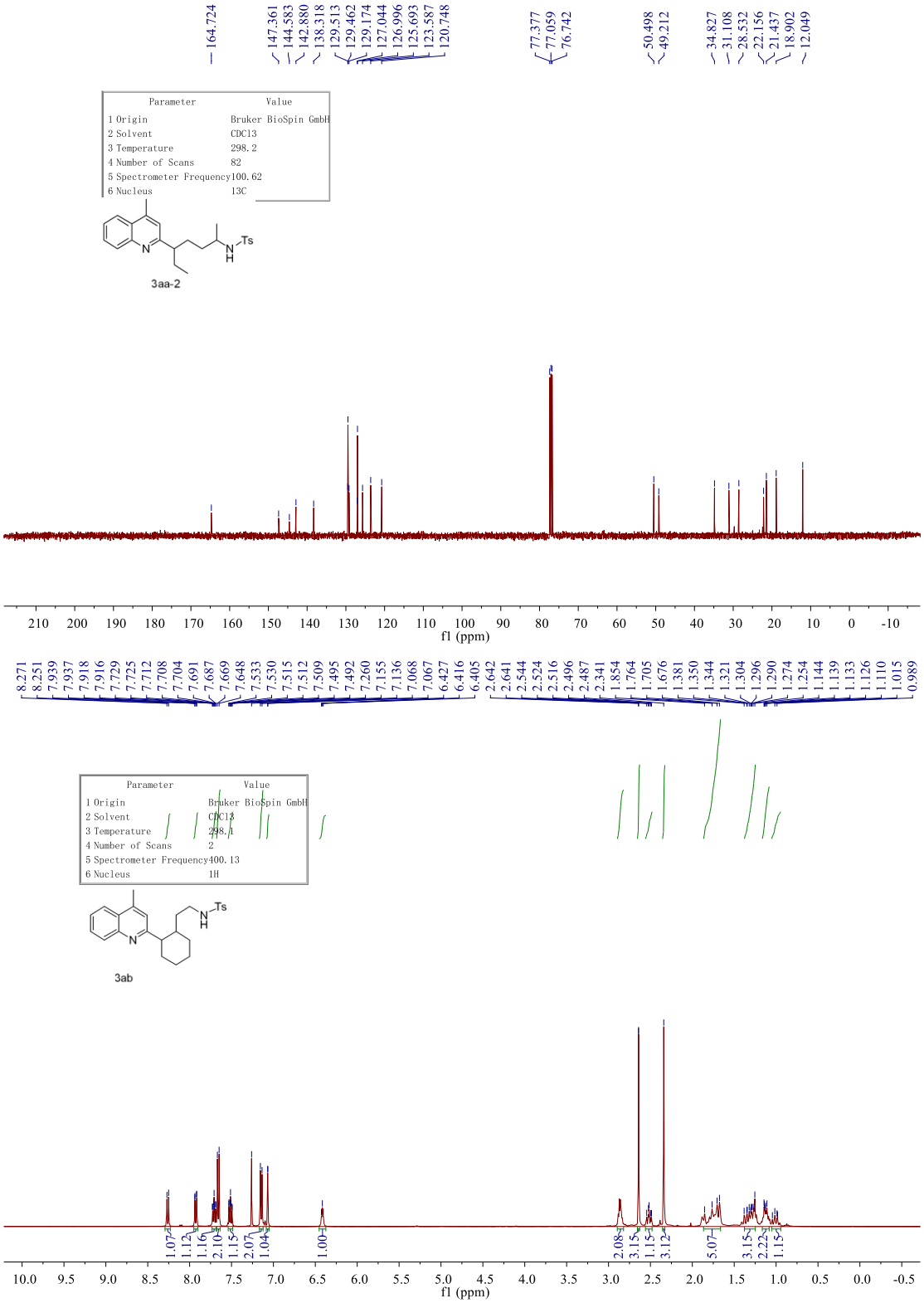
144.471
142.895
138.104
129.553
129.480
129.292
127.153
127.012
125.706
123.588
121.558
77.399
77.081
76.763
50.344
48.909
34.548
29.183
29.067
22.343
21.465
18.851
11.648
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 15
5 Spectrometer Frequency 100.61
6 Nucleus 13C
Ts
3aa-1
f1 (ppm)
8.133
8.112
7.969
7.948
7.687
7.670
7.666
7.543
7.523
7.505
7.260
7.168
7.147
7.034
5.336
5.318
5.291
3.251
3.237
3.221
2.681
2.657
2.648
2.635
2.626
2.612
2.342
1.746
1.727
1.712
1.690
1.674
1.663
1.656
1.652
1.640
1.623
1.604
1.589
1.337
1.332
1.320
1.314
1.302
1.296
1.279
1.169
1.157
1.144
1.132
1.121
1.110
1.097
1.020
1.004
0.774
0.756
0.737
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 2
5 Spectrometer Frequency 400.13
6 Nucleus 1H
Ts
3aa-2
1.00
1.07
3.04
1.04
2.00
0.96
0.97
1.10
4.16
3.02
4.10
1.08
1.03
2.99
2.98
f1 (ppm)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144.583
142.880
138.318
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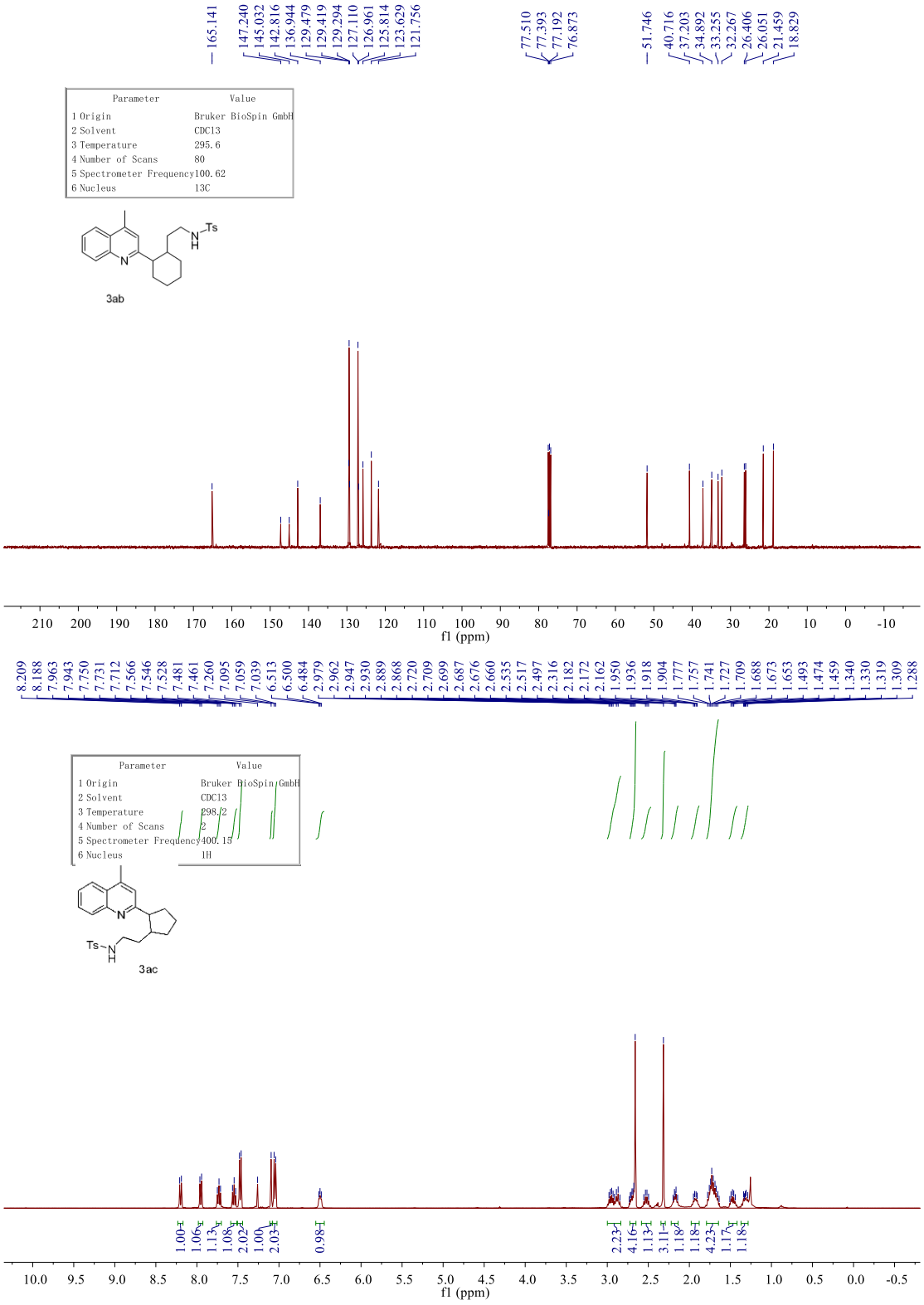
129.462
129.174
127.044
126.996
125.693
123.587
120.748
77.377
77.059
76.742
50.498
49.212
34.827
31.108
28.532
22.156
21.437
18.902
12.049
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 82
5 Spectrometer Frequency 100.62
6 Nucleus 13C
Ts
3aa-2
f1 (ppm)
8.271
8.251
7.939
7.937
7.918
7.916
7.729
7.725
7.712
7.708
7.704
7.691
7.687
7.669
7.648
7.533
7.530
7.515
7.512
7.509
7.495
7.492
7.260
7.155
7.136
7.068
7.067
6.427
6.416
6.405
2.642
2.641
2.544
2.524
2.516
2.496
2.487
2.341
1.854
1.764
1.705
1.676
1.381
1.350
1.344
1.321
1.304
1.296
1.290
1.274
1.254
1.144
1.139
1.133
1.126
1.110
1.015
0.989
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 2
5 Spectrometer Frequency 400.13
6 Nucleus 1H
Ts
3ab
1.07
1.12
1.16
2.10
1.15
2.07
1.04
1.00
2.08
3.15
1.15
3.12
5.07
3.15
2.22
1.15
f1 (ppm)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142.816
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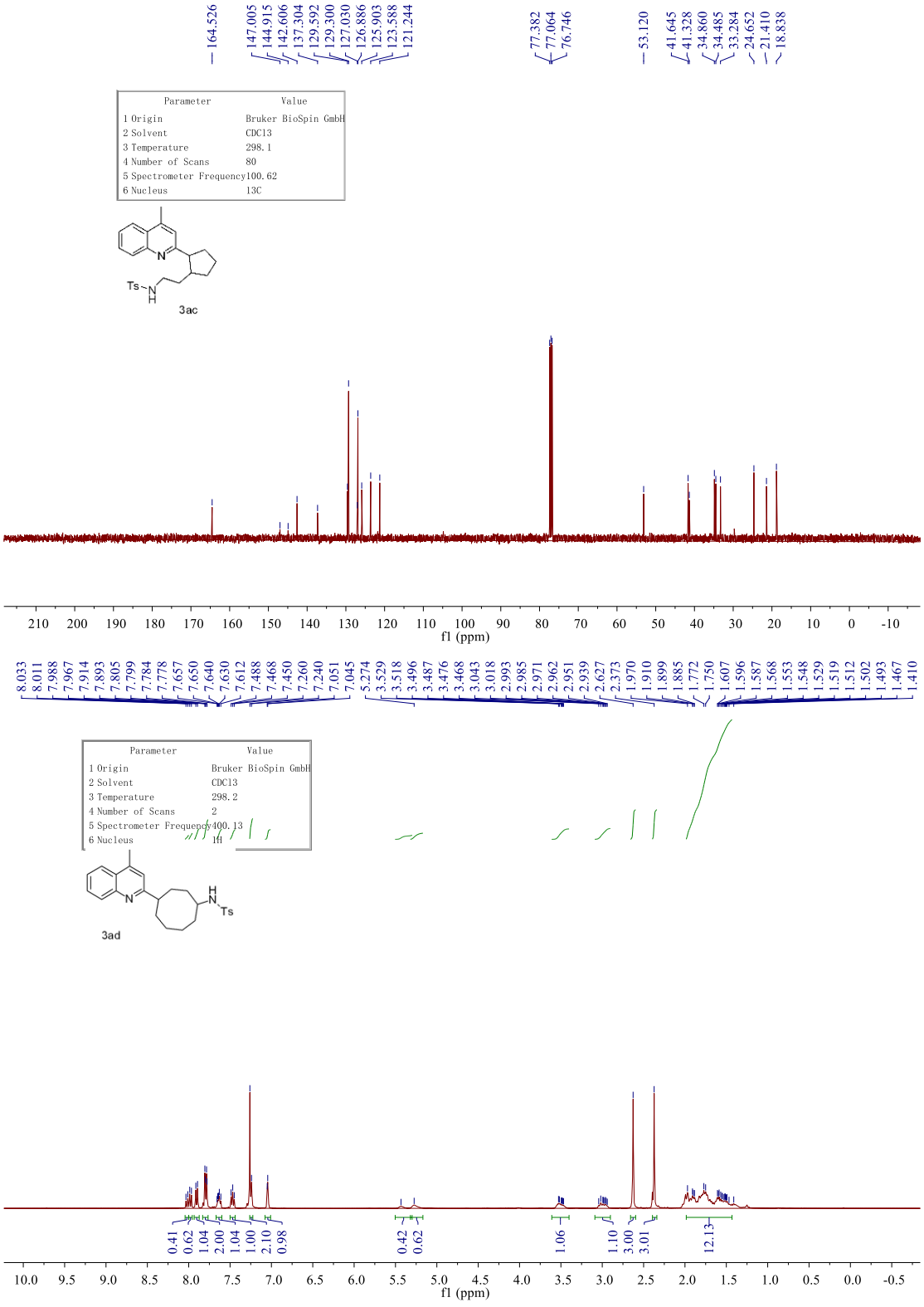
129.479
129.419
129.294
127.110
126.961
125.814
123.629
121.756
77.510
77.393
77.192
76.873
51.746
40.716
37.203
34.892
33.255
32.267
26.406
26.051
21.459
18.829
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDC13
3 Temperature 295.6
4 Number of Scans 80
5 Spectrometer Frequency 100.62
6 Nucleus 13C
Ts
N
H
3ab
f1 (ppm)
8.209
8.188
7.963
7.943
7.750
7.731
7.712
7.566
7.546
7.528
7.481
7.461
7.260
7.095
7.059
7.039
6.513
6.500
6.484
2.979
2.962
2.947
2.930
2.889
2.868
2.720
2.709
2.699
2.687
2.676
2.660
2.535
2.517
2.497
2.316
2.182
2.172
2.162
1.950
1.936
1.918
1.904
1.777
1.757
1.741
1.727
1.709
1.688
1.673
1.653
1.493
1.474
1.459
1.340
1.330
1.319
1.309
1.288
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDC13
3 Temperature 298.2
4 Number of Scans 2
5 Spectrometer Frequency 400.13
6 Nucleus 1H
Ts
N
H
3ac
1.00
1.06
1.13
1.08
2.02
1.00
2.03
0.98
2.23
4.16
1.13
3.11
1.18
1.18
4.23
1.17
1.18
f1 (ppm)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129.592
129.300
127.030
126.886
125.903
123.588
121.244
77.382
77.064
76.746
53.120
41.645
41.328
34.860
34.485
33.284
24.652
21.410
18.838
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 80
5 Spectrometer Frequency 100.62
6 Nucleus 13C
Ts
N
H
3ac
f1 (ppm)
8.033
8.011
7.988
7.967
7.914
7.893
7.805
7.799
7.784
7.778
7.657
7.650
7.640
7.630
7.612
7.488
7.468
7.450
7.260
7.240
7.051
7.045
5.274
3.529
3.518
3.496
3.487
3.476
3.468
3.043
3.018
2.993
2.985
2.971
2.962
2.951
2.939
2.627
2.373
1.970
1.910
1.899
1.885
1.772
1.750
1.607
1.596
1.587
1.568
1.553
1.548
1.529
1.519
1.512
1.502
1.493
1.467
1.410
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 2
5 Spectrometer Frequency 400.13
6 Nucleus 1H
N
H
Ts
3ad
0.41
0.62
1.04
2.00
1.04
1.00
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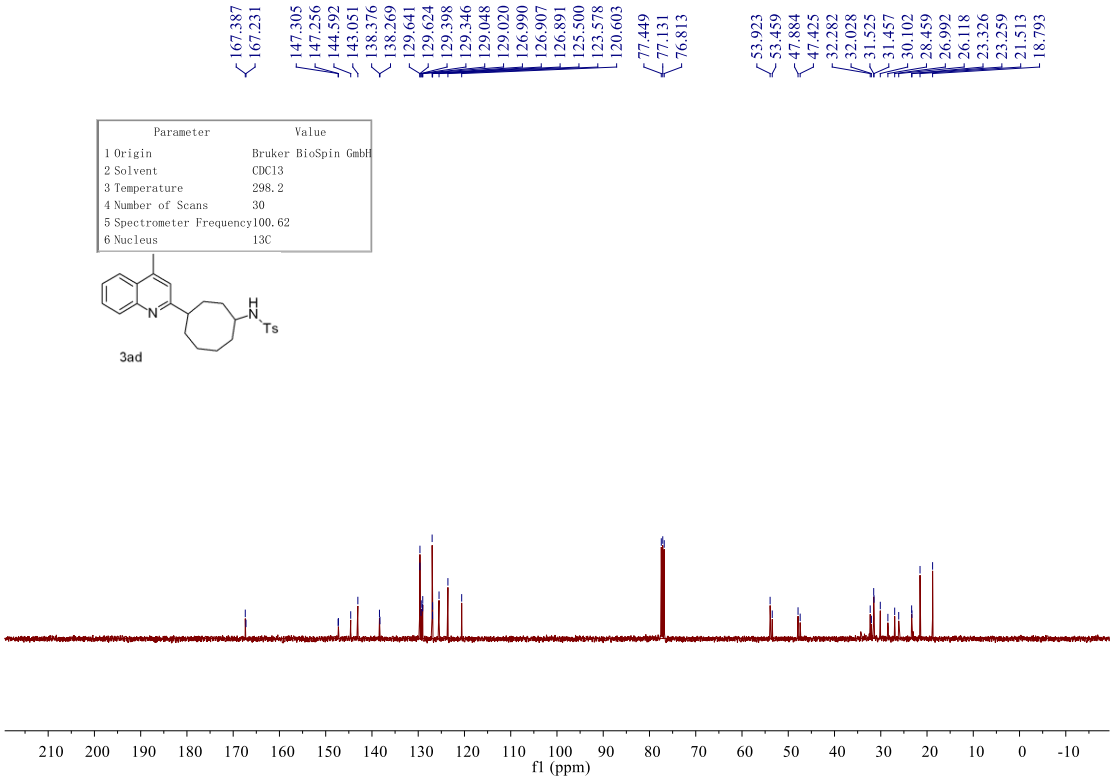
0.98
0.42
0.62
1.06
1.10
3.00
3.01
12.13
f1 (ppm)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143.051
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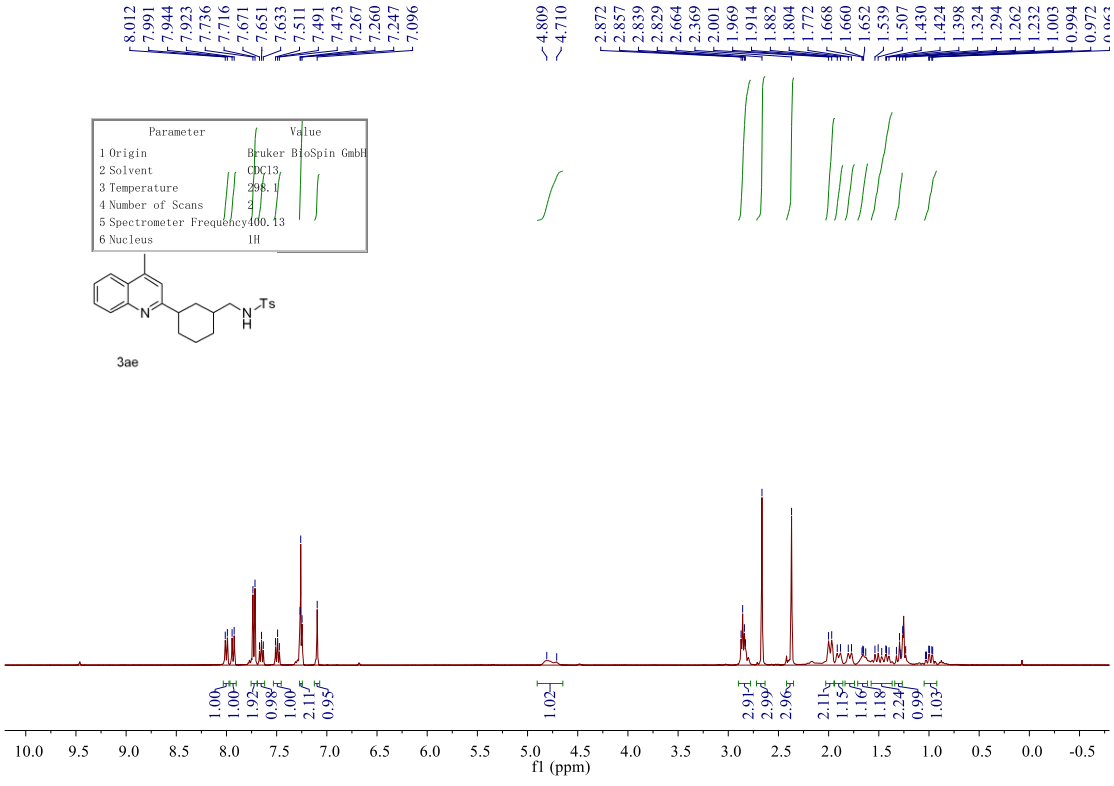
138.269
129.641
129.624
129.398
129.346
129.048
129.020
126.990
126.907
126.891
125.500
123.578
120.603
77.449
77.131
76.813
53.923
53.459
47.884
47.425
32.282
32.028
31.525
31.457
30.102
28.459
26.992
26.118
23.326
23.259
21.513
18.793
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 30
5 Spectrometer Frequency 100.62
6 Nucleus 13C
3ad
f1 (ppm)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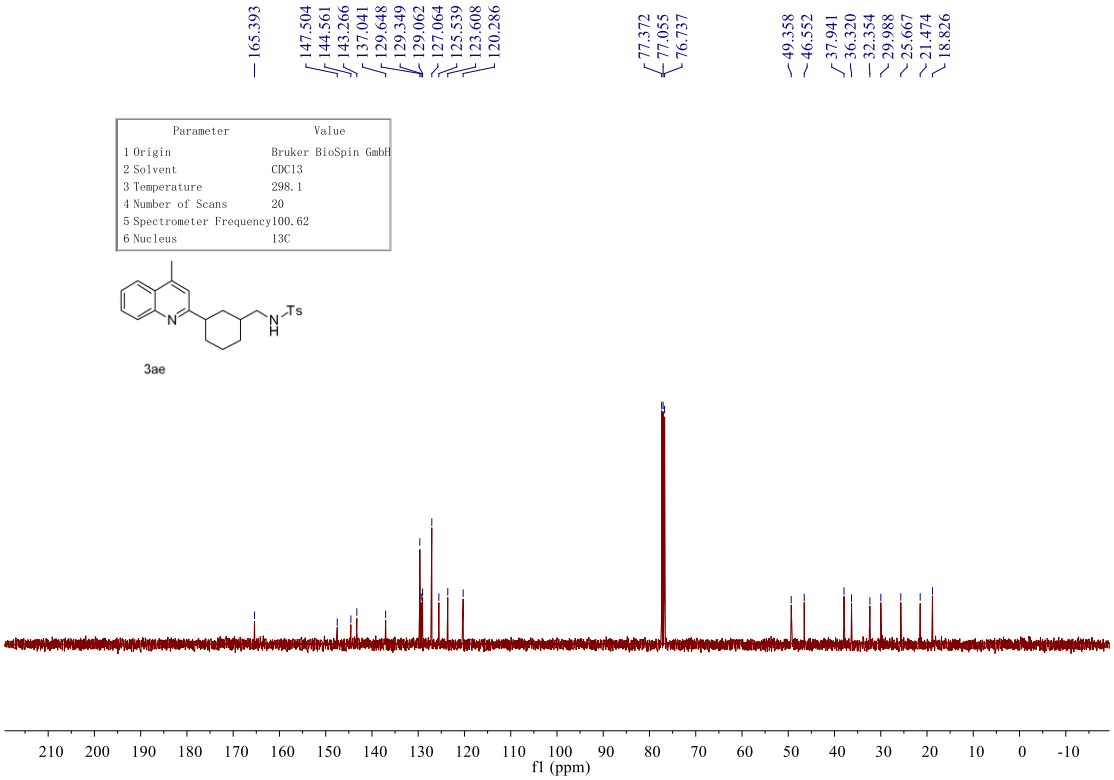
7.923
7.736
7.716
7.671
7.651
7.633
7.511
7.491
7.473
7.267
7.260
7.247
7.096
4.809
4.710
2.872
2.857
2.839
2.829
2.664
2.369
2.001
1.969
1.914
1.882
1.804
1.772
1.668
1.660
1.652
1.539
1.507
1.430
1.424
1.398
1.324
1.294
1.262
1.232
1.003
0.994
0.972
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 2
5 Spectrometer Frequency 400.13
6 Nucleus 1H
3ae
1.00
1.00
1.92
0.98
1.00
2.11
0.95
1.02
2.91
2.99
2.96
2.11
1.15
1.16
1.18
2.24
0.99
1.03
f1 (ppm)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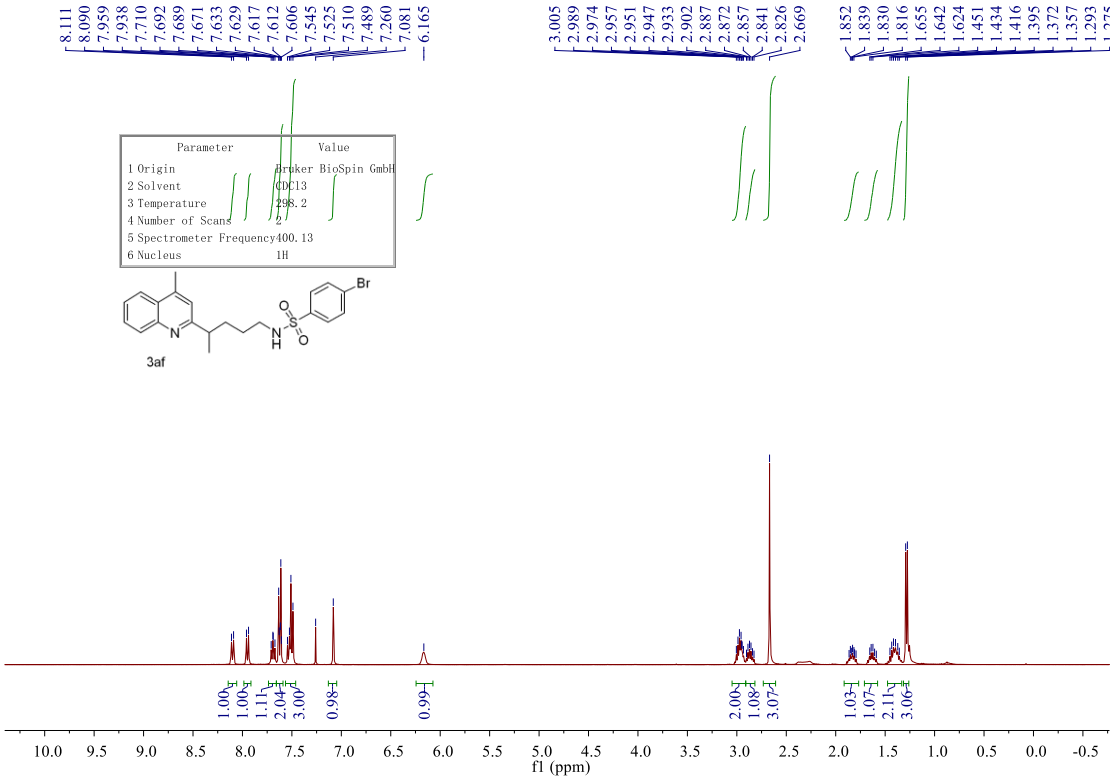
129.062
127.064
125.539
123.608
120.286
77.372
77.055
76.737
49.358
46.552
37.941
36.320
32.354
29.988
25.667
21.474
18.826
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 20
5 Spectrometer Frequency 100.62
6 Nucleus 13C
Ts
N
H
3ae
f1 (ppm)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8.090
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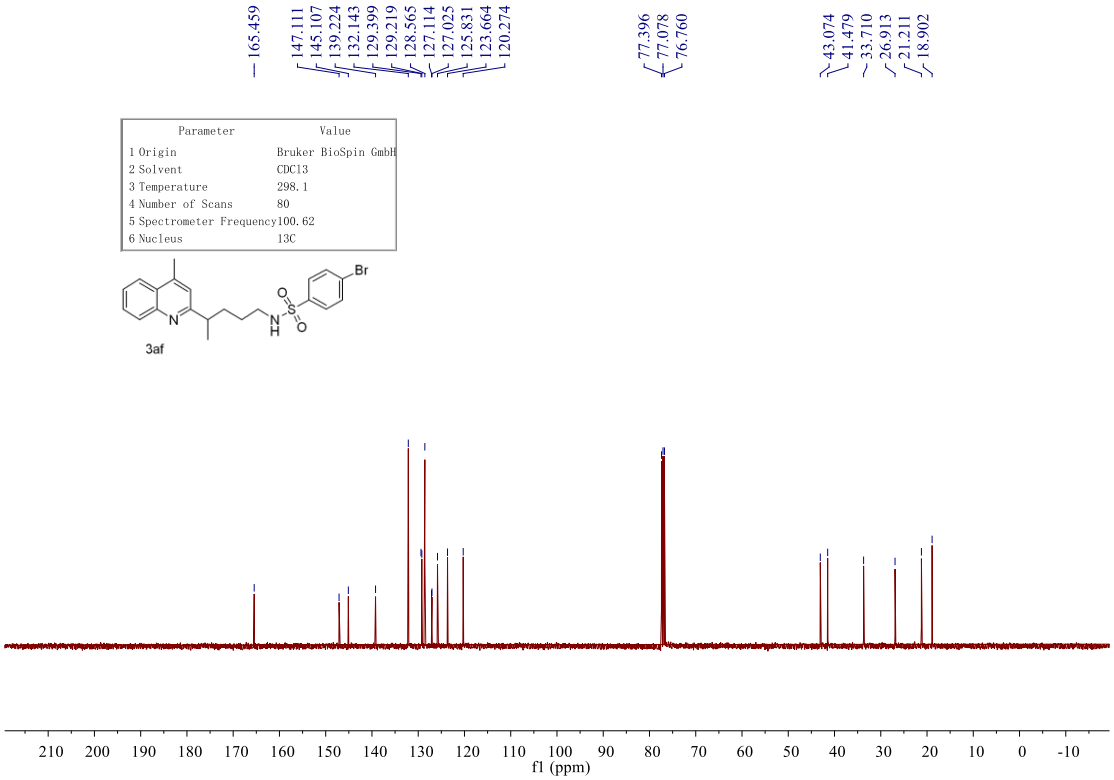
7.938
7.710
7.692
7.689
7.671
7.633
7.629
7.617
7.612
7.606
7.545
7.525
7.510
7.489
7.260
7.081
6.165
3.005
2.989
2.974
2.957
2.951
2.947
2.933
2.902
2.887
2.872
2.857
2.841
2.826
2.669
1.852
1.839
1.830
1.816
1.655
1.642
1.624
1.451
1.434
1.416
1.395
1.372
1.357
1.293
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 2
5 Spectrometer Frequency 400.13
6 Nucleus 1H
Br
O
S
O
N
H
3af
1.00
1.00
1.11
2.04
3.00
0.98
0.99
2.00
1.08
3.07
1.03
1.07
2.11
3.06
f1 (ppm)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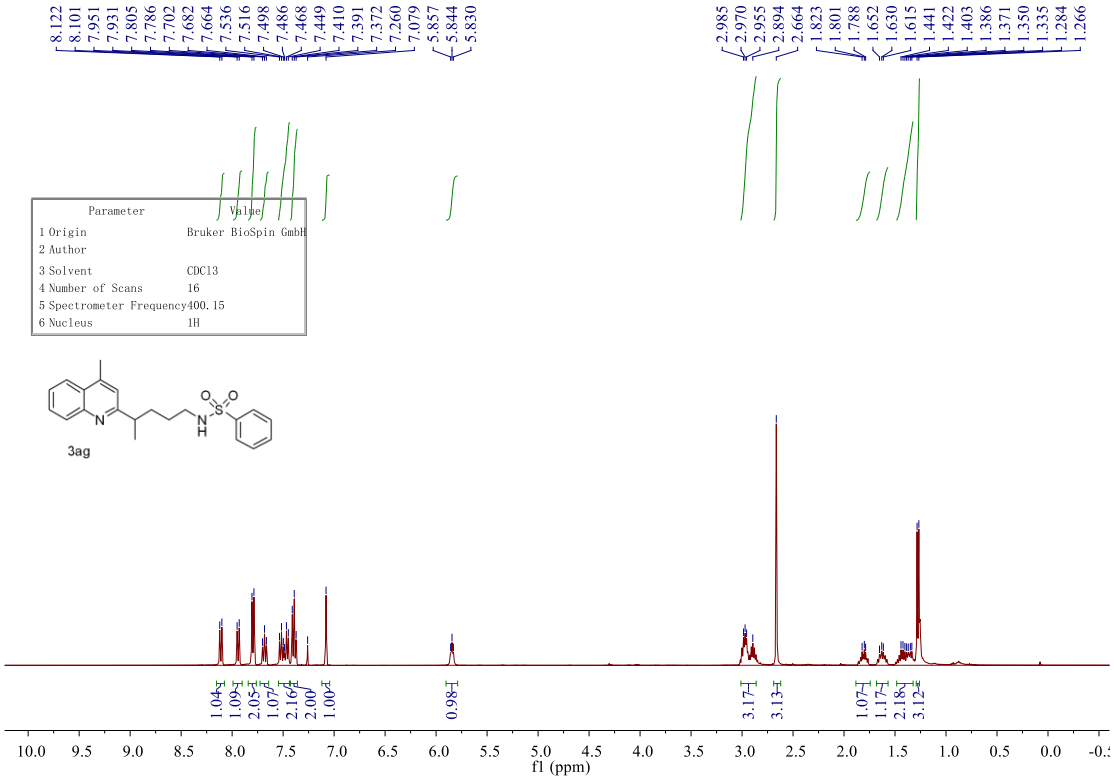
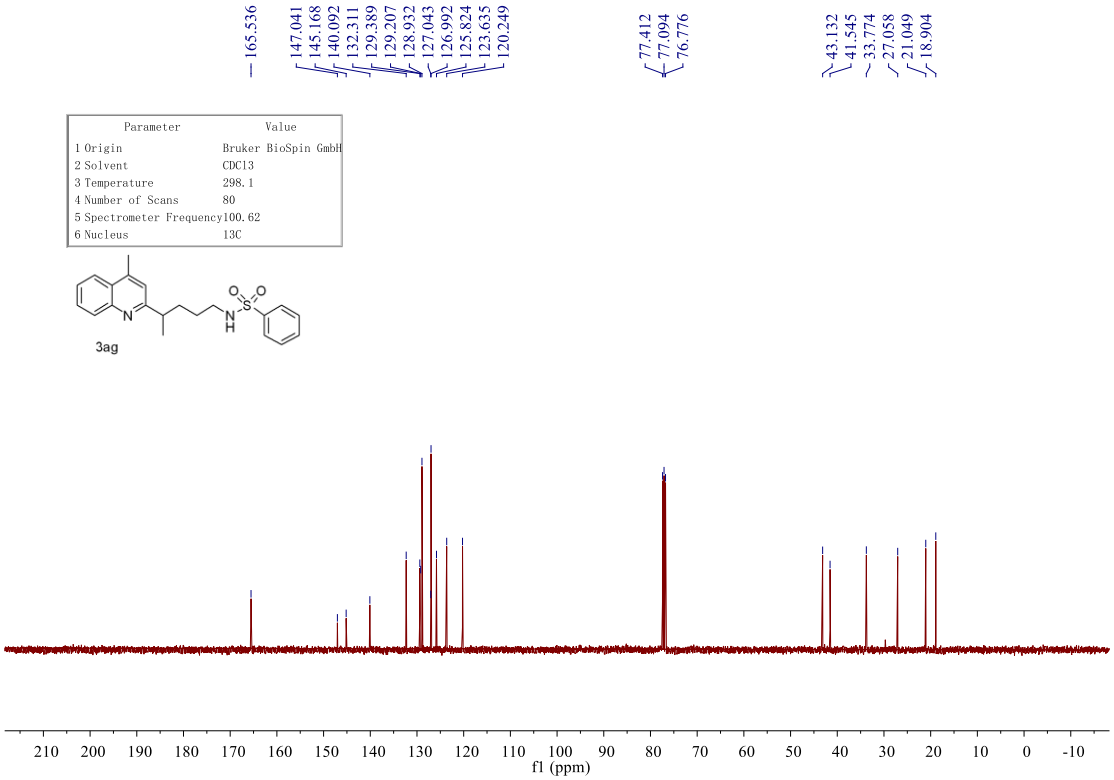
147.111
145.107
139.224
132.143
129.399
129.219
128.565
127.114
127.025
125.831
123.664
120.274
77.396
77.078
76.760
43.074
41.479
33.710
26.913
21.211
18.902
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 80
5 Spectrometer Frequency 100.62
6 Nucleus 13C
Br
N
O
S
O
N
H
3af
f1 (ppm)


8.122
8.101
7.951
7.931
7.805
7.786
7.702
7.682
7.664
7.536
7.516
7.498
7.486
7.468
7.449
7.410
7.391
7.372
7.260
7.079
5.857
5.844
5.830
2.985
2.970
2.955
2.894
2.664
1.823
1.801
1.788
1.652
1.630
1.615
1.441
1.422
1.403
1.386
1.371
1.350
1.335
1.284
1.266
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Author
3 Solvent CDCl3
4 Number of Scans 16
5 Spectrometer Frequency 400.15
6 Nucleus 1H
N
O
S
O
N
H
3ag
1.04
1.09
2.05
1.07
2.16
2.00
1.00
0.98
3.17
3.13
1.07
1.17
2.18
3.12
f1 (ppm)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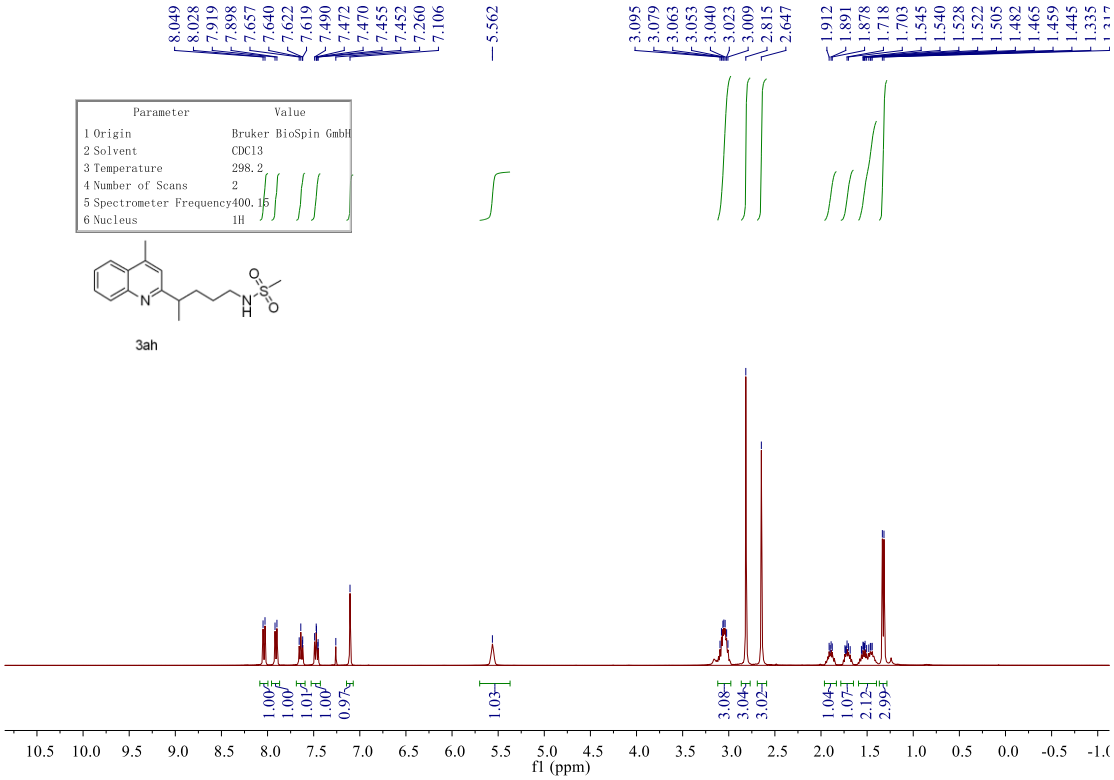
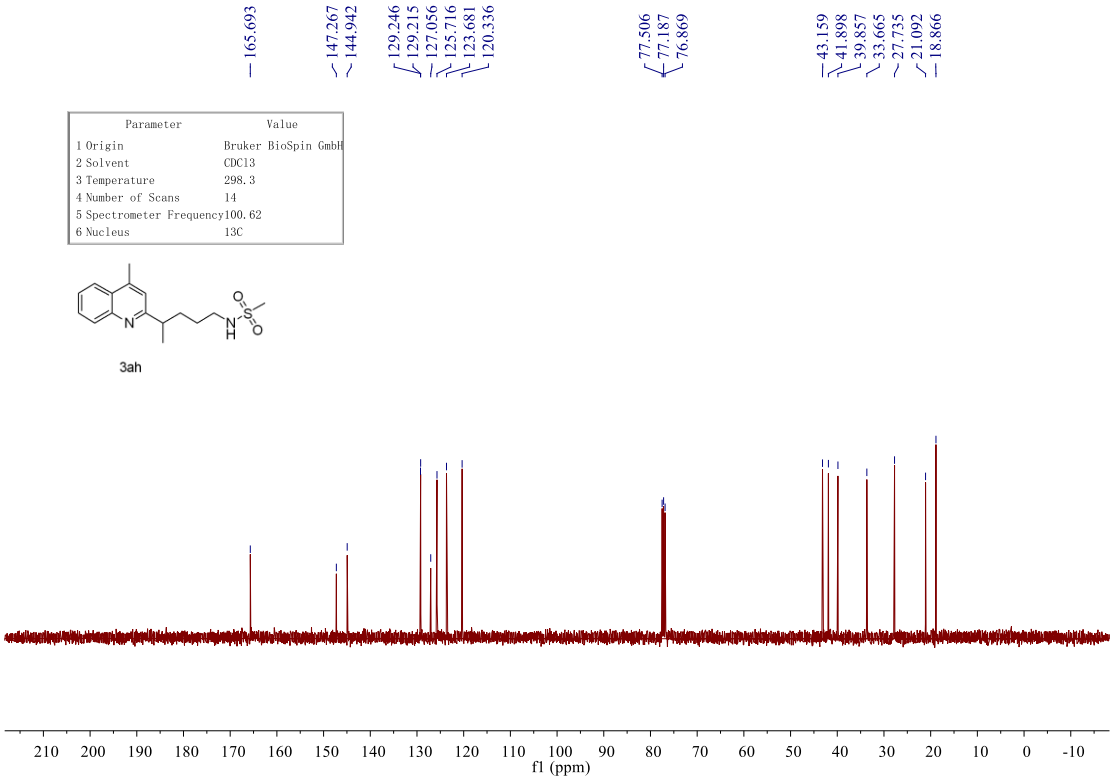
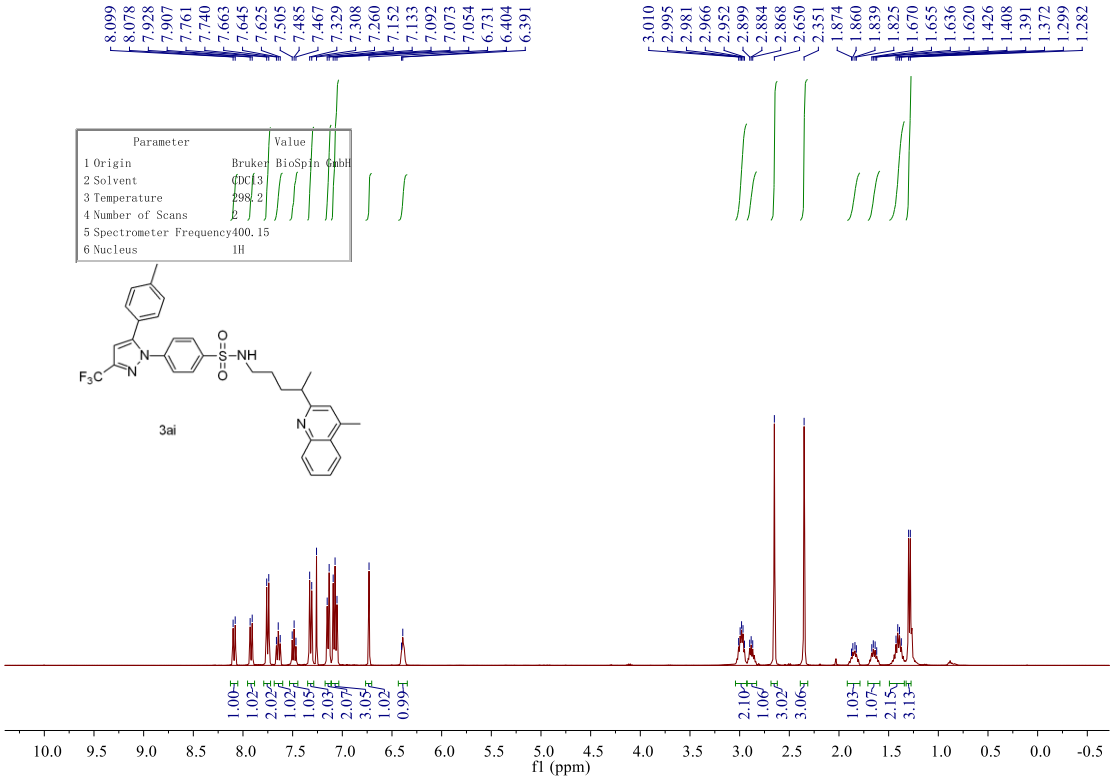
147.041
145.168
140.092
132.311
129.389
129.207
128.932
127.043
126.992
125.824
123.635
120.249
77.412
77.094
76.776
43.132
41.545
33.774
27.058
21.049
18.904
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 80
5 Spectrometer Frequency 100.62
6 Nucleus 13C
3ag
f1 (ppm)


8.049
8.028
7.919
7.898
7.657
7.640
7.622
7.619
7.490
7.472
7.470
7.455
7.452
7.260
7.106
5.562
3.095
3.079
3.063
3.053
3.040
3.023
3.009
2.815
2.647
1.912
1.891
1.878
1.718
1.703
1.545
1.540
1.528
1.522
1.505
1.482
1.465
1.459
1.445
1.335
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 2
5 Spectrometer Frequency 400.15
6 Nucleus 1H
3ah
1.00
1.00
1.01
1.00
0.97
1.03
3.08
3.04
3.02
1.04
1.07
2.12
2.99
f1 (ppm)


165.693
147.267
144.942
129.246
129.215
127.056
125.716
123.681
120.336
77.506
77.187
76.869
43.159
41.898
39.857
33.665
27.735
21.092
18.866
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.3
4 Number of Scans 14
5 Spectrometer Frequency 100.62
6 Nucleus 13C
3ah
f1 (ppm)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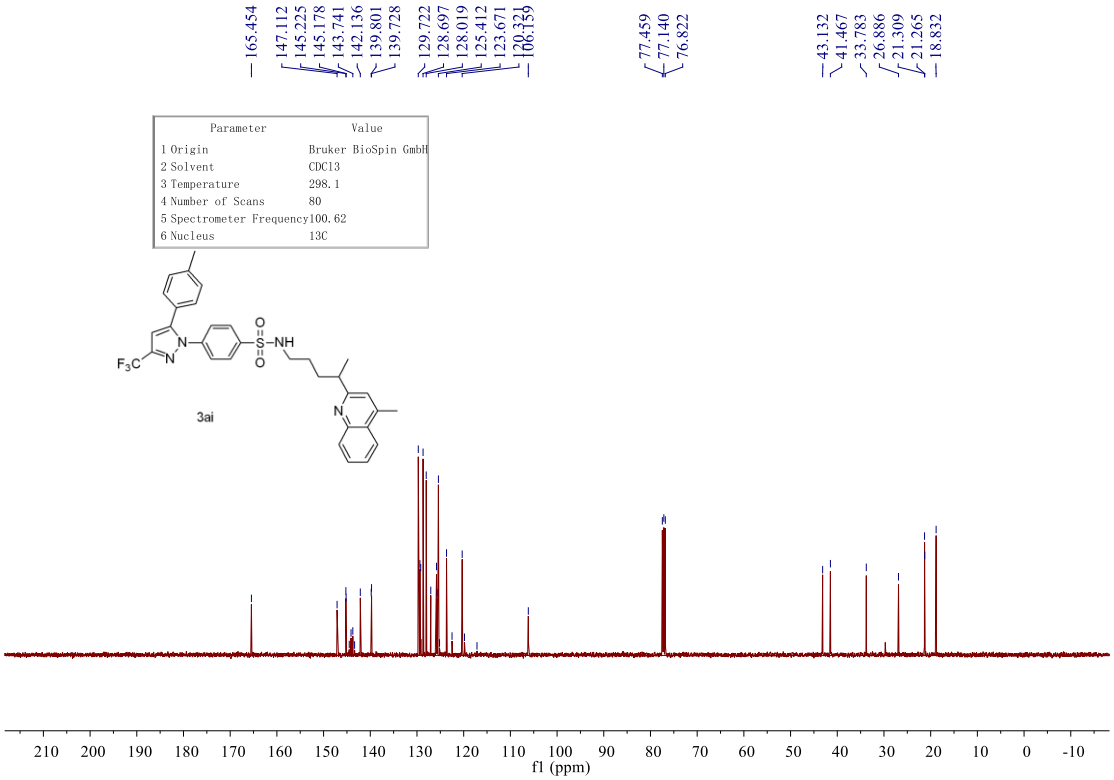
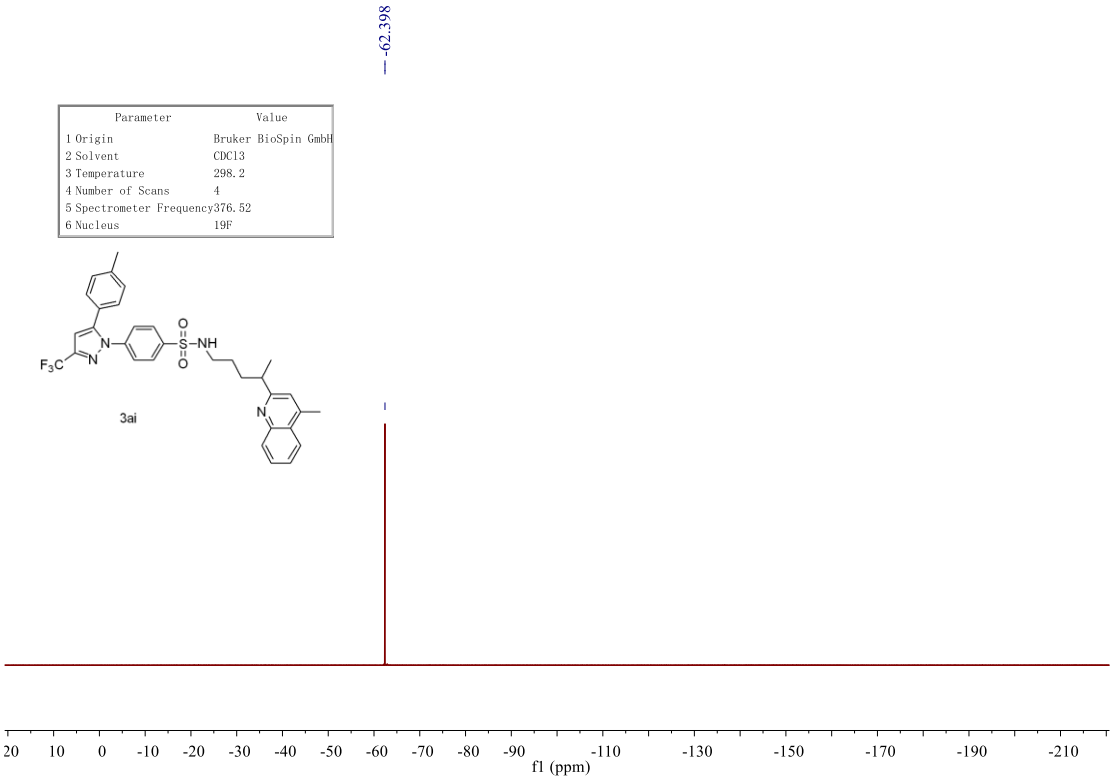
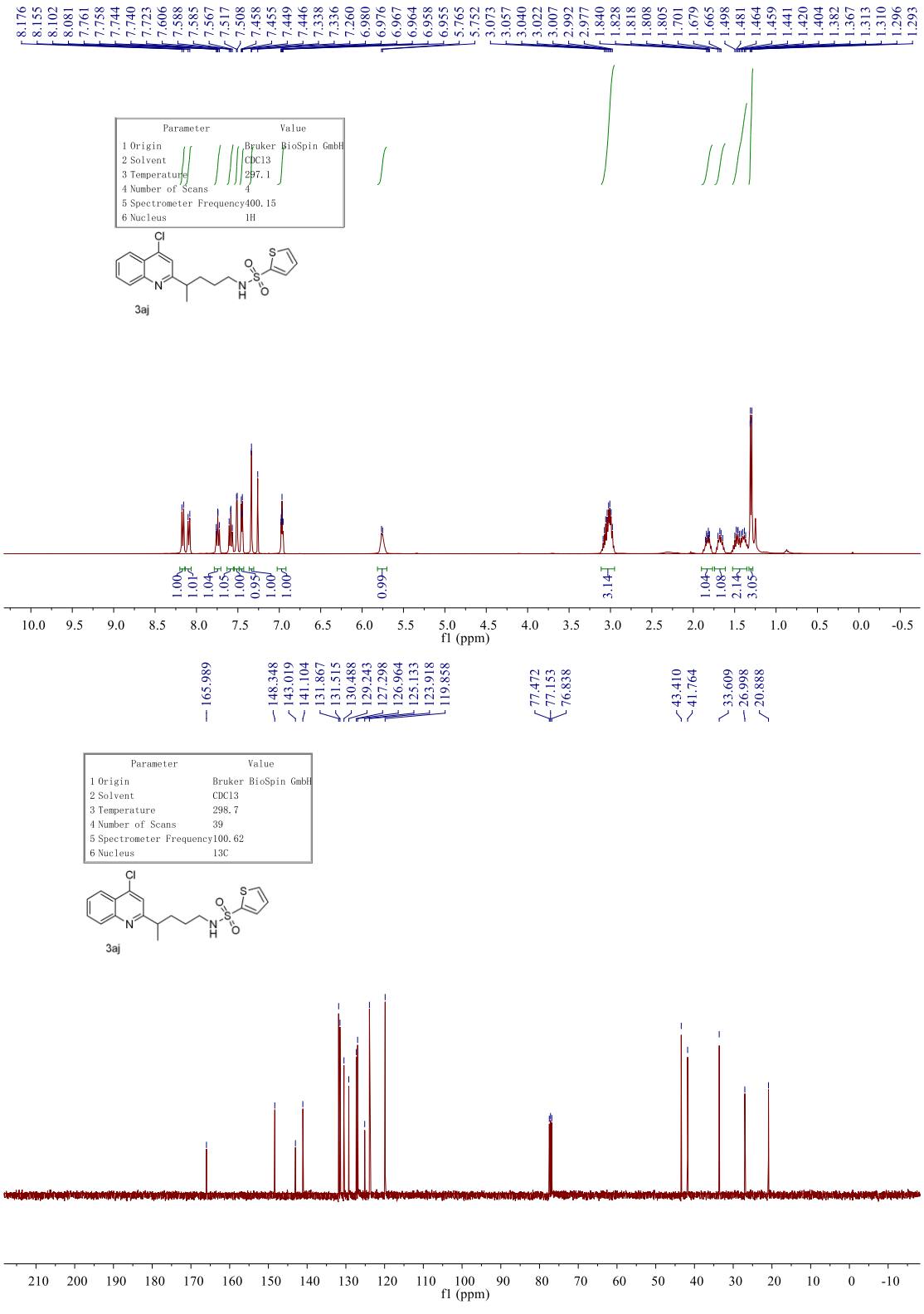
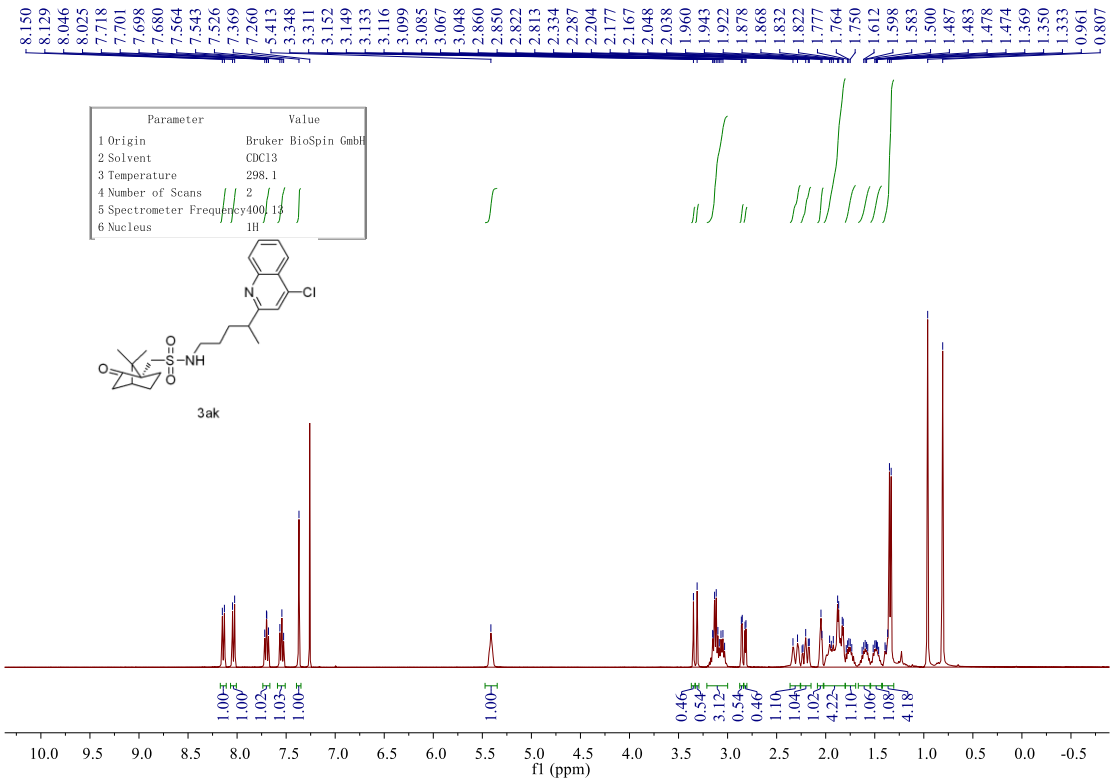
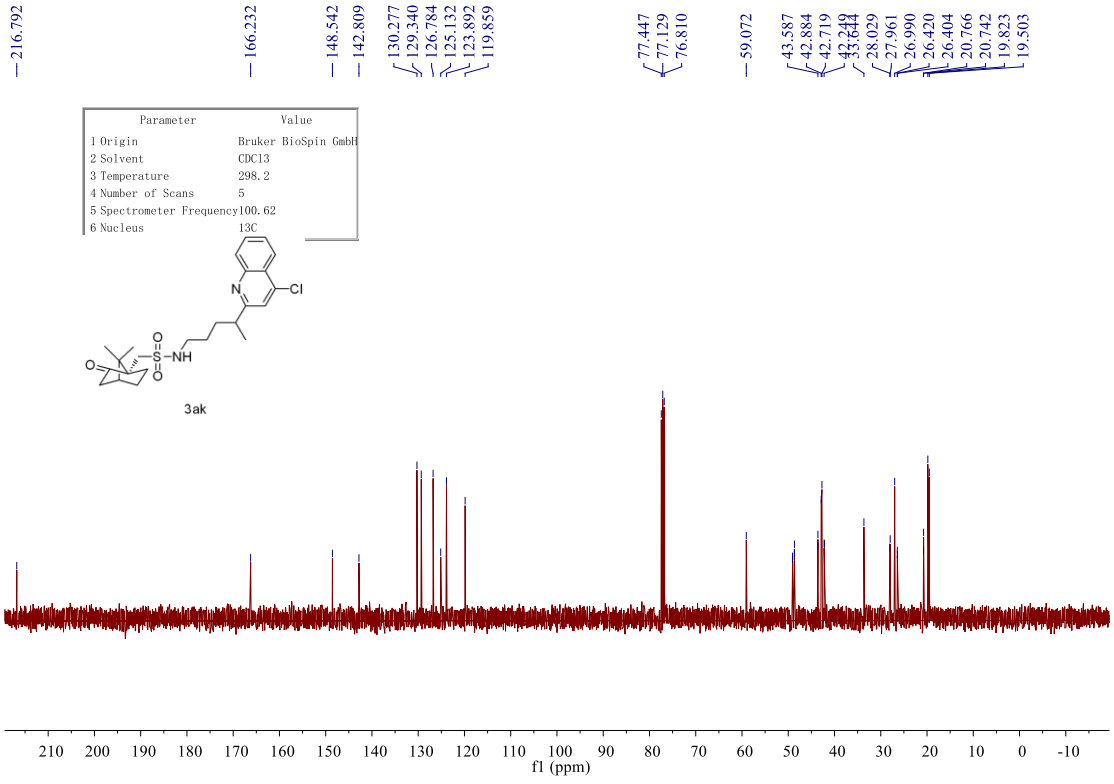
8.078
7.928
7.907
7.761
7.740
7.663
7.645
7.625
7.505
7.485
7.467
7.329
7.308
7.260
7.152
7.133
7.092
7.073
7.054
6.731
6.404
6.391
3.010
2.995
2.981
2.966
2.952
2.899
2.884
2.868
2.650
2.351
1.874
1.860
1.839
1.825
1.670
1.655
1.636
1.620
1.426
1.408
1.391
1.372
1.299
1.282
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 2
5 Spectrometer Frequency 400.15
6 Nucleus 1H
3ai
1.00
1.02
2.02
1.02
1.05
2.03
2.07
3.05
1.02
0.99
2.10
1.06
3.02
3.06
1.03
1.07
2.15
3.13
f1 (ppm)

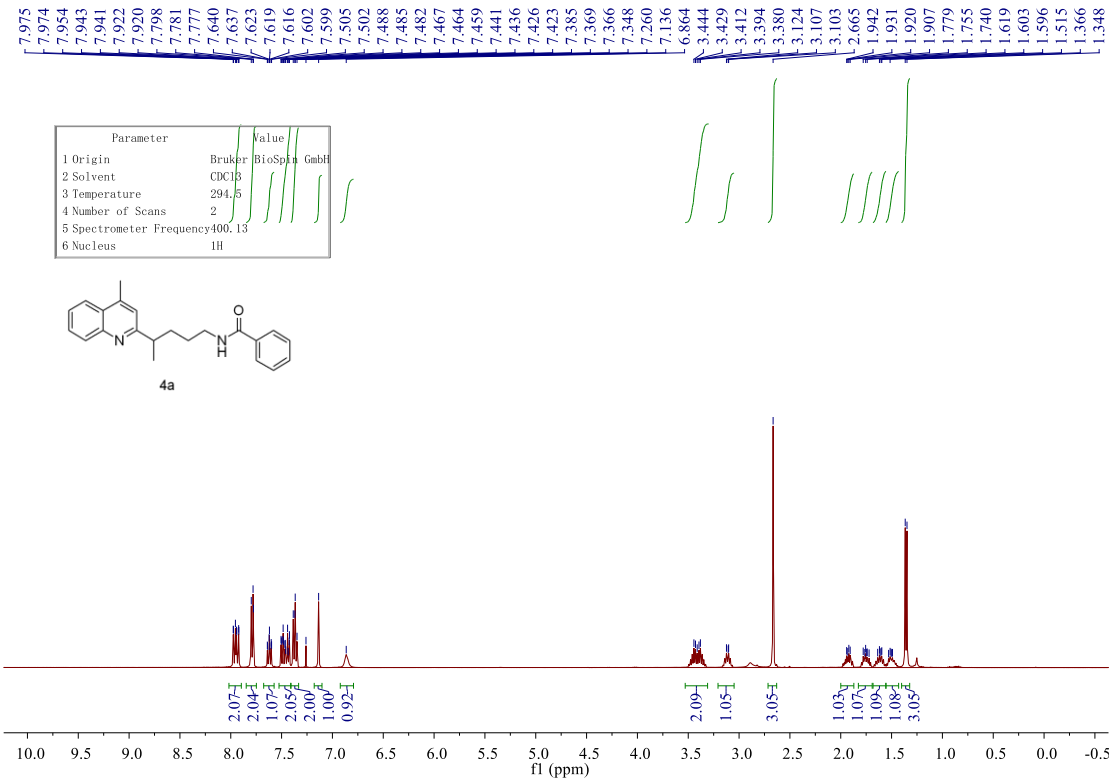

165.454
147.112
145.225
145.178
143.741
142.136
139.801
139.728
129.722
128.697
128.019
125.412
123.671
120.321
116.159
77.459
77.140
76.822
43.132
41.467
33.783
26.886
21.309
21.265
18.832
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 80
5 Spectrometer Frequency 100.62
6 Nucleus 13C
3ai
f1 (ppm)

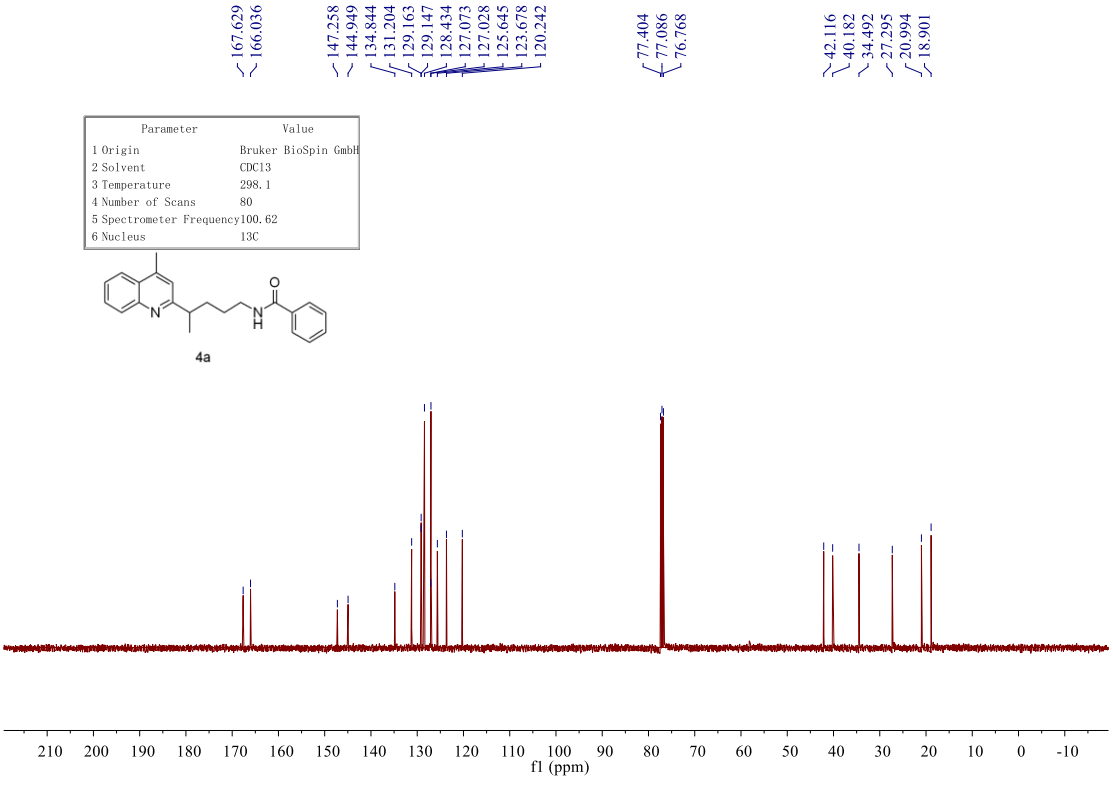

-62.398
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 4
5 Spectrometer Frequency 376.52
6 Nucleus 19F
3ai
f1 (ppm)

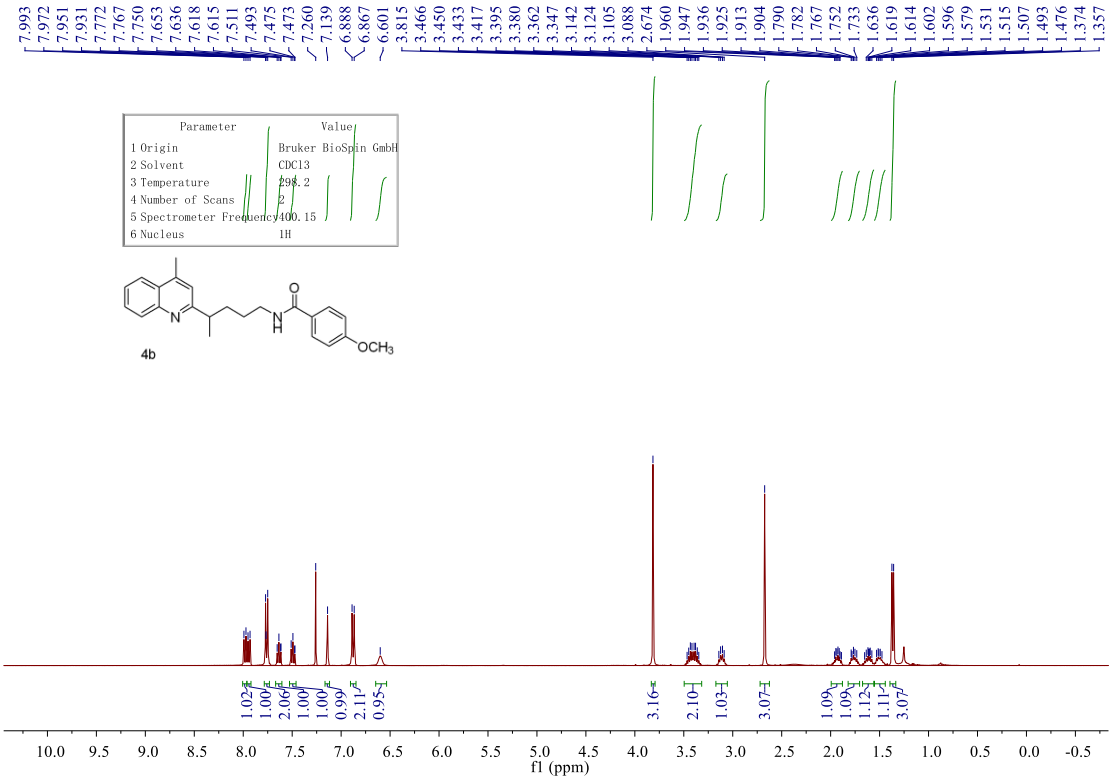

8.176 8.155 8.102 8.081 7.761 7.758 7.744 7.740 7.723 7.606 7.588 7.585 7.567 7.517 7.508 7.458 7.455 7.449 7.446 7.338 7.336 7.260 6.980 6.976 6.967 6.964 6.958 6.955 5.765 5.752 3.073 3.057 3.040 3.022 3.007 2.992 2.977 1.840 1.828 1.818 1.808 1.805 1.701 1.679 1.665 1.498 1.481 1.464 1.459 1.441 1.420 1.404 1.382 1.367 1.313 1.310 1.296 1.293
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 297.1
4 Number of Scans 4
5 Spectrometer Frequency 400.15
6 Nucleus 1H
Cl
S
O
N
H
3aj
1.00 1.01 1.04 1.05 1.00 0.95 1.00 1.00 0.99 3.14 1.04 1.08 2.14 3.05
f1 (ppm)
165.989 148.348 143.019 141.104 131.867 131.515 130.488 129.243 127.298 126.964 125.133 123.918 119.858 77.472 77.153 76.838 43.410 41.764 33.609 26.998 20.888
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.7
4 Number of Scans 39
5 Spectrometer Frequency 100.62
6 Nucleus 13C
Cl
S
O
N
H
3aj
f1 (ppm)


8.150 8.129 8.046 8.025 7.718 7.701 7.698 7.680 7.564 7.543 7.526 7.369 7.260 5.413 3.348 3.311 3.152 3.149 3.133 3.116 3.099 3.085 3.067 3.048 2.860 2.850 2.822 2.813 2.334 2.287 2.204 2.177 2.167 2.048 2.038 1.960 1.943 1.922 1.878 1.868 1.832 1.822 1.777 1.764 1.750 1.612 1.598 1.583 1.500 1.487 1.483 1.478 1.474 1.369 1.350 1.333 0.961 0.807
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 2
5 Spectrometer Frequency 400.13
6 Nucleus 1H
Cl
N
NH
O
S
3ak
1.00 1.00 1.02 1.03 1.00 1.00 0.46 0.54 3.12 0.54 0.46 1.10 1.04 1.02 4.22 1.10 1.06 1.08 4.18
10.0 9.5 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)


216.792 166.232 148.542 142.809 130.277 129.340 126.784 125.132 123.892 119.859 77.447 77.129 76.810 59.072 43.587 42.884 42.719 33.644 28.029 27.961 26.990 26.420 26.404 20.766 20.742 19.823 19.503
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 5
5 Spectrometer Frequency 100.62
6 Nucleus 13C
Cl
N
NH
O
S
3ak
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.975
7.974
7.954
7.943
7.941
7.922
7.920
7.798
7.781
7.777
7.640
7.637
7.623
7.619
7.616
7.602
7.599
7.505
7.502
7.488
7.485
7.482
7.467
7.464
7.459
7.441
7.436
7.426
7.423
7.385
7.369
7.366
7.348
7.260
7.136
6.864
3.444
3.429
3.412
3.394
3.380
3.124
3.107
3.103
2.665
1.942
1.931
1.920
1.907
1.779
1.755
1.740
1.619
1.603
1.596
1.515
1.366
1.348
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 294.5
4 Number of Scans 2
5 Spectrometer Frequency 400.13
6 Nucleus 1H
4a
2.07
2.04
1.07
2.05
2.00
1.00
0.92
2.09
1.05
3.05
1.03
1.07
1.09
1.08
3.05
10.0 9.5 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)


167.629
166.036
147.258
144.949
134.844
131.204
129.163
129.147
128.434
127.073
127.028
125.645
123.678
120.242
77.404
77.086
76.768
42.116
40.182
34.492
27.295
20.994
18.901
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 80
5 Spectrometer Frequency 100.62
6 Nucleus 13C
4a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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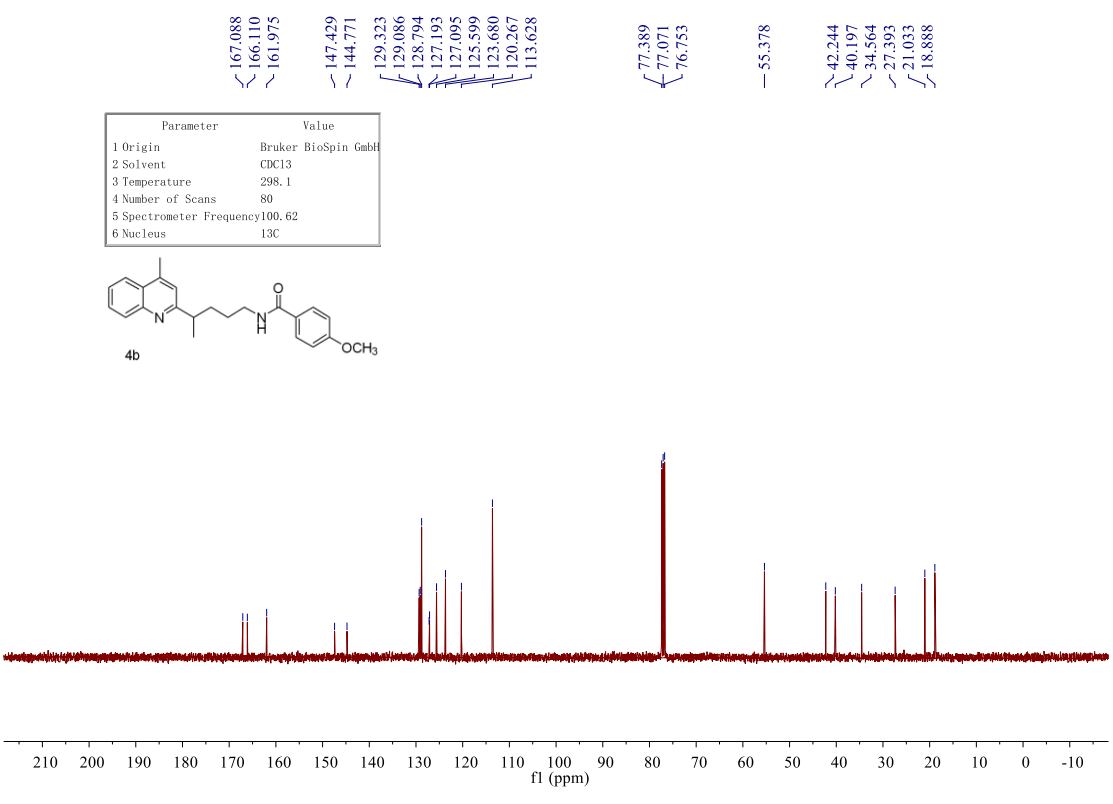
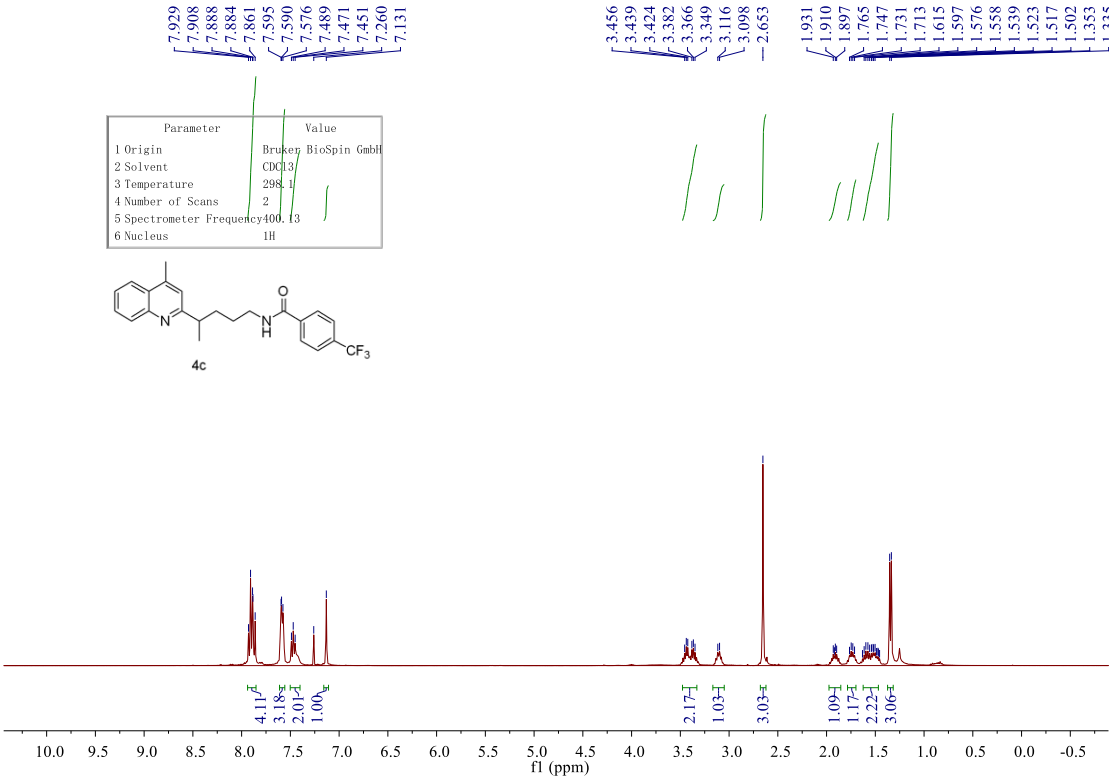
7.931
7.772
7.767
7.750
7.653
7.636
7.618
7.615
7.511
7.493
7.475
7.473
7.260
7.139
6.888
6.867
6.601
3.815
3.466
3.450
3.433
3.417
3.395
3.380
3.362
3.347
3.142
3.124
3.105
3.088
2.674
1.960
1.947
1.936
1.925
1.913
1.904
1.790
1.782
1.767
1.752
1.733
1.636
1.619
1.614
1.602
1.596
1.579
1.531
1.515
1.507
1.493
1.476
1.374
1.357
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 2
5 Spectrometer Frequency 400.15
6 Nucleus 1H
4b
1.02
1.00
2.06
1.00
1.00
0.99
2.11
0.95
3.16
2.10
1.03
3.07
1.09
1.09
1.12
1.11
3.07
f1 (ppm)


167.088
166.110
161.975
147.429
144.771
129.323
129.086
128.794
127.193
127.095
125.599
123.680
120.267
113.628
77.389
77.071
76.753
55.378
42.244
40.197
34.564
27.393
21.033
18.888
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 80
5 Spectrometer Frequency 100.62
6 Nucleus 13C
4b
f1 (ppm)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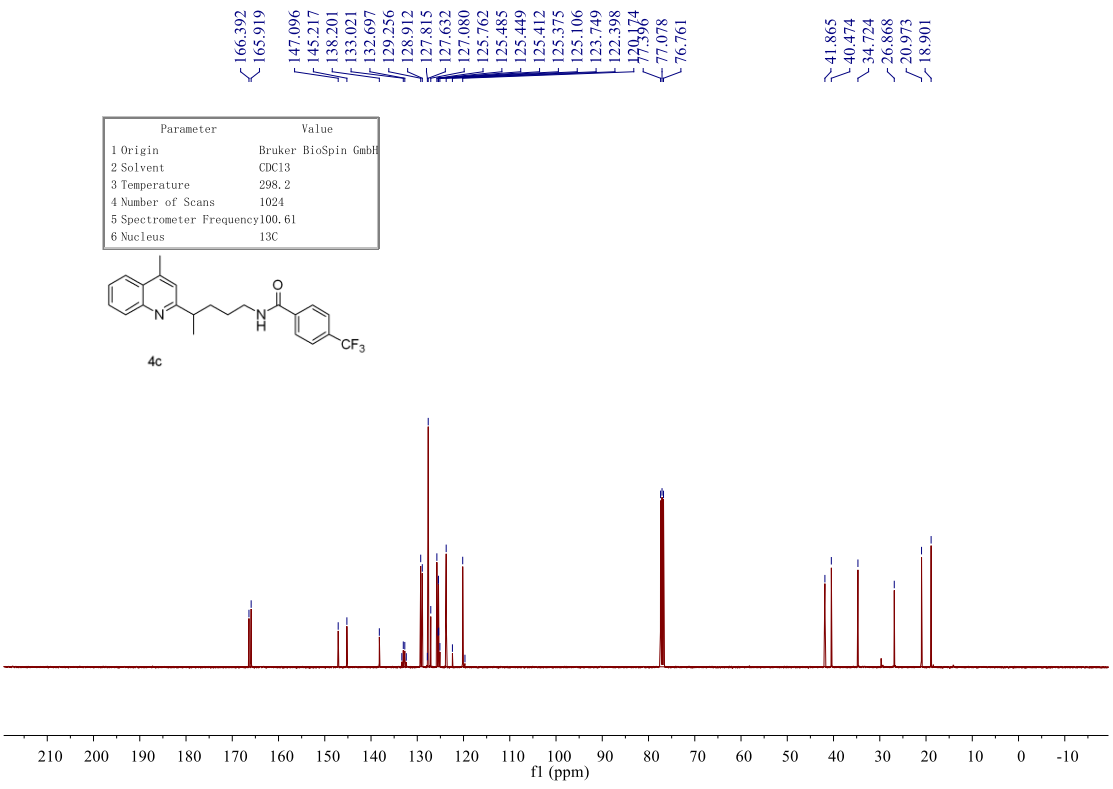
7.861
7.595
7.590
7.576
7.489
7.471
7.451
7.260
7.131
3.456
3.439
3.424
3.382
3.366
3.349
3.116
3.098
2.653
1.931
1.910
1.897
1.765
1.747
1.731
1.713
1.615
1.597
1.576
1.558
1.539
1.523
1.517
1.502
1.353
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 2
5 Spectrometer Frequency 400.13
6 Nucleus 1H
4c
4.11
3.18
2.01
1.00
2.17
1.03
3.03
1.09
1.17
2.22
3.06
f1 (ppm)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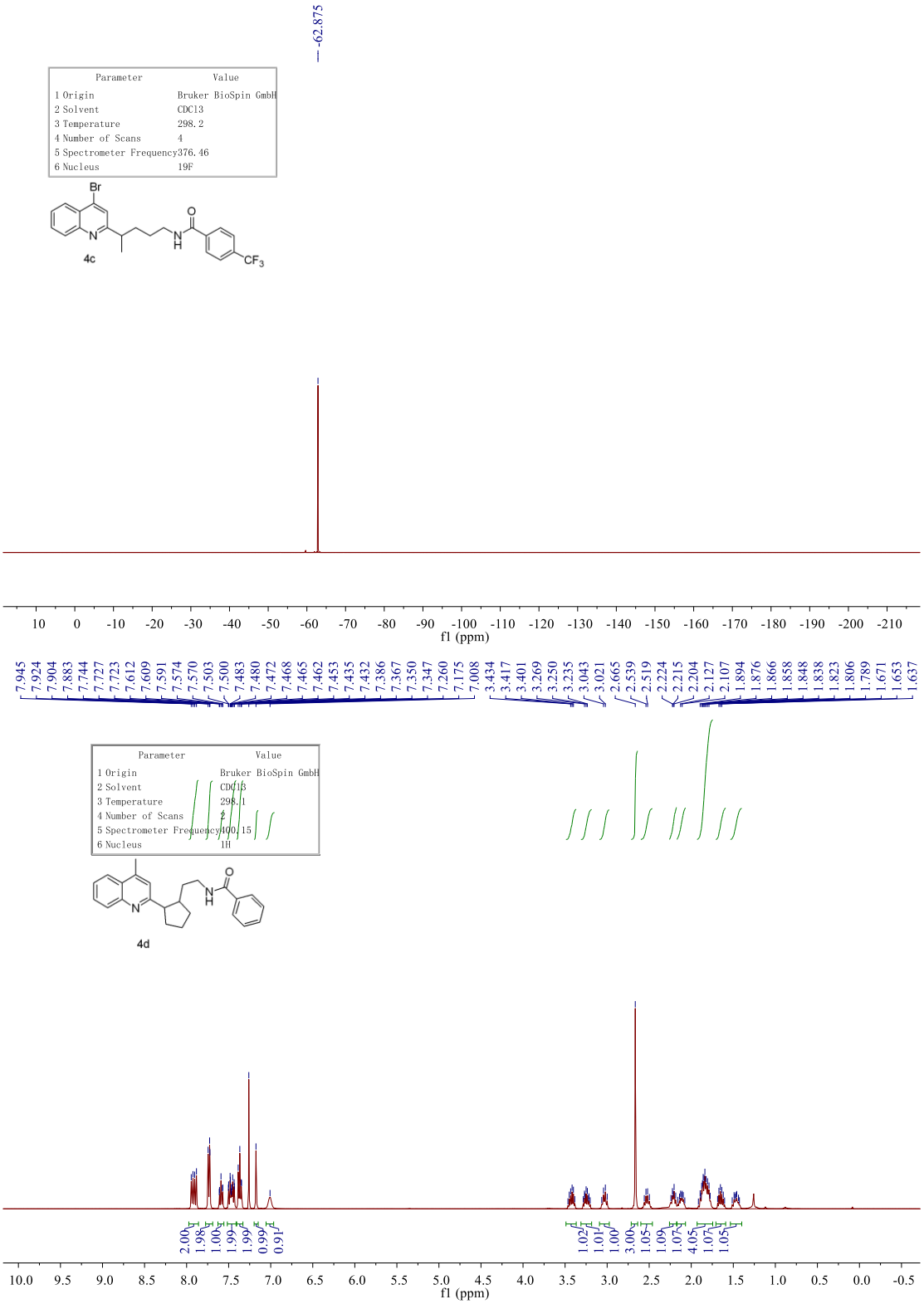
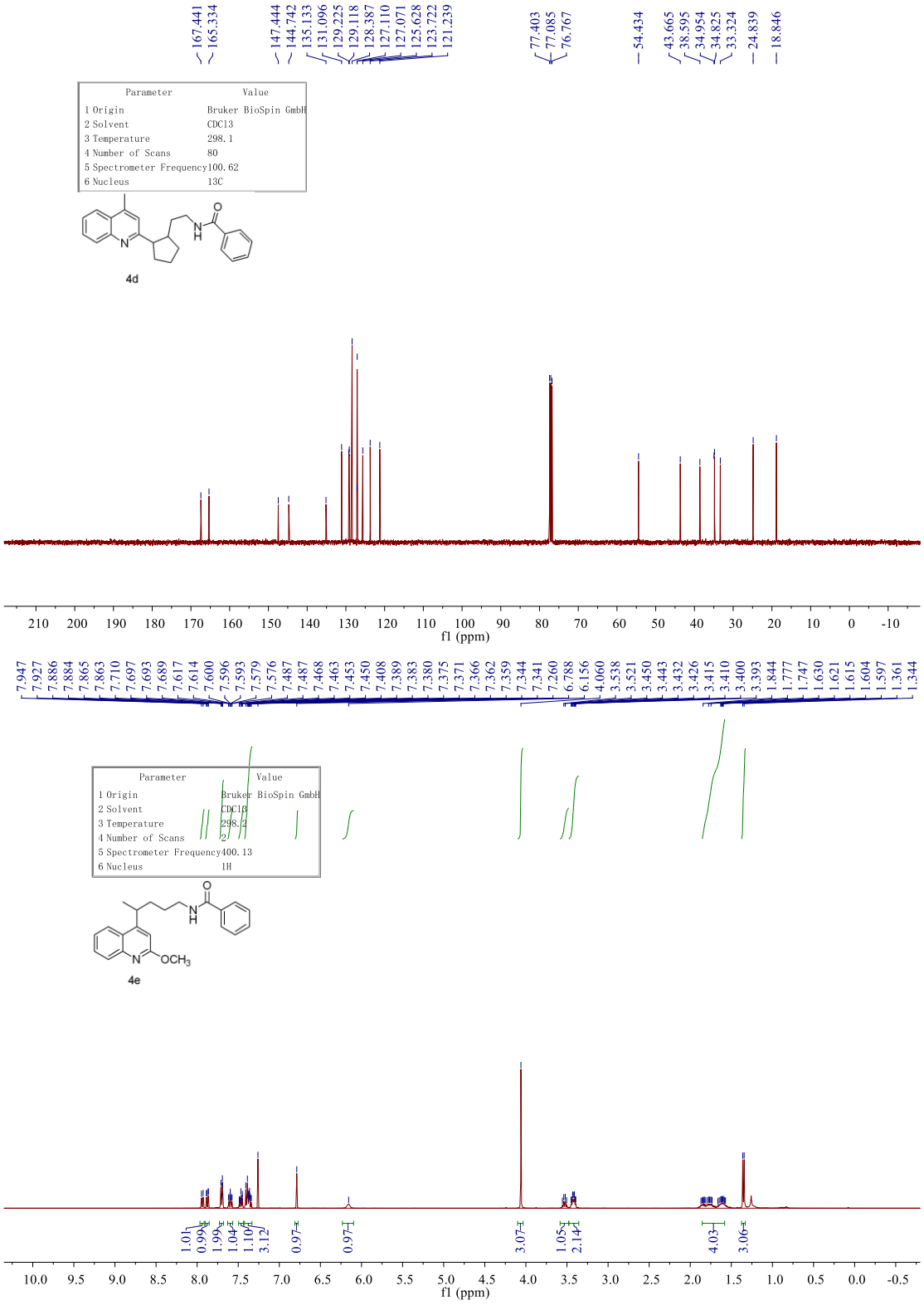
147.096
145.217
138.201
133.021
132.697
129.256
128.912
127.815
127.632
127.080
125.762
125.485
125.449
125.412
125.375
125.106
123.749
122.398
120.174
77.396
77.078
76.761
41.865
40.474
34.724
26.868
20.973
18.901
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 1024
5 Spectrometer Frequency 100.61
6 Nucleus 13C
4c
f1 (ppm)


-62.875
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 4
5 Spectrometer Frequency376.46
6 Nucleus 19F
Br
N
O
N
H
CF3
4c
f1 (ppm)
7.945 7.924 7.904 7.883 7.744 7.727 7.723 7.612 7.609 7.591 7.574 7.570 7.503 7.500 7.483 7.480 7.472 7.468 7.465 7.462 7.453 7.435 7.432 7.386 7.367 7.350 7.347 7.260 7.175 7.008
3.434 3.417 3.401 3.269 3.250 3.235 3.043 3.021 2.665 2.539 2.519 2.224 2.215 2.204 2.127 2.107 1.894 1.876 1.866 1.858 1.848 1.838 1.823 1.806 1.789 1.671 1.653 1.637
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 2
5 Spectrometer Frequency400.15
6 Nucleus 1H
N
H
O
4d
2.00 1.98 1.00 1.99 1.99 0.99 0.91
1.02 1.01 1.00 3.00 1.05 1.09 1.07 4.05 1.07 1.05
f1 (ppm)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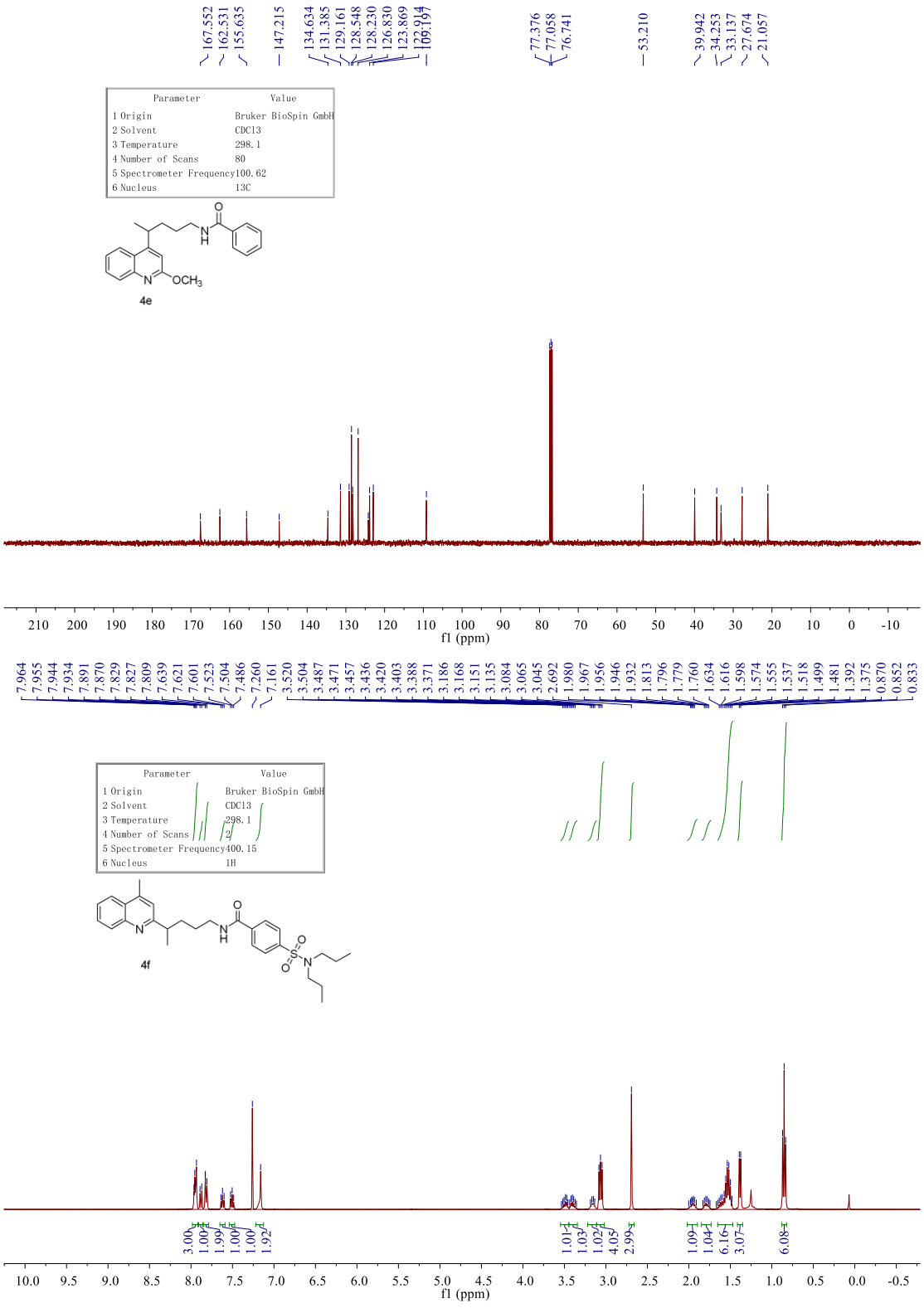
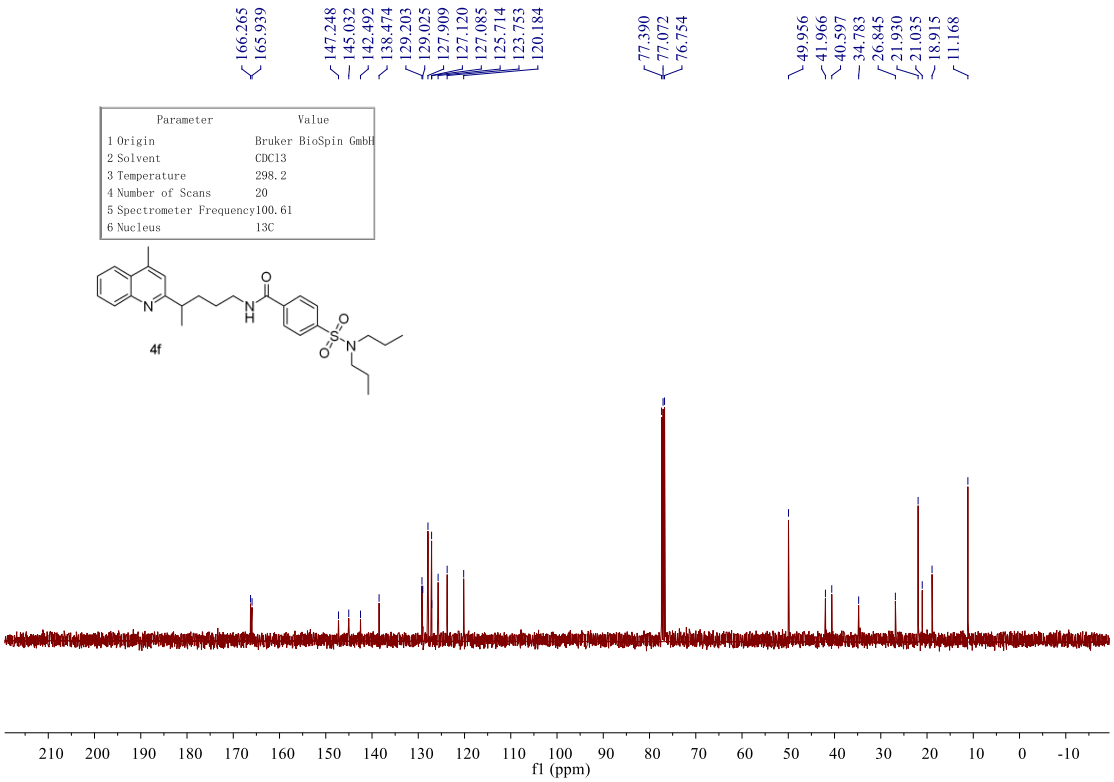
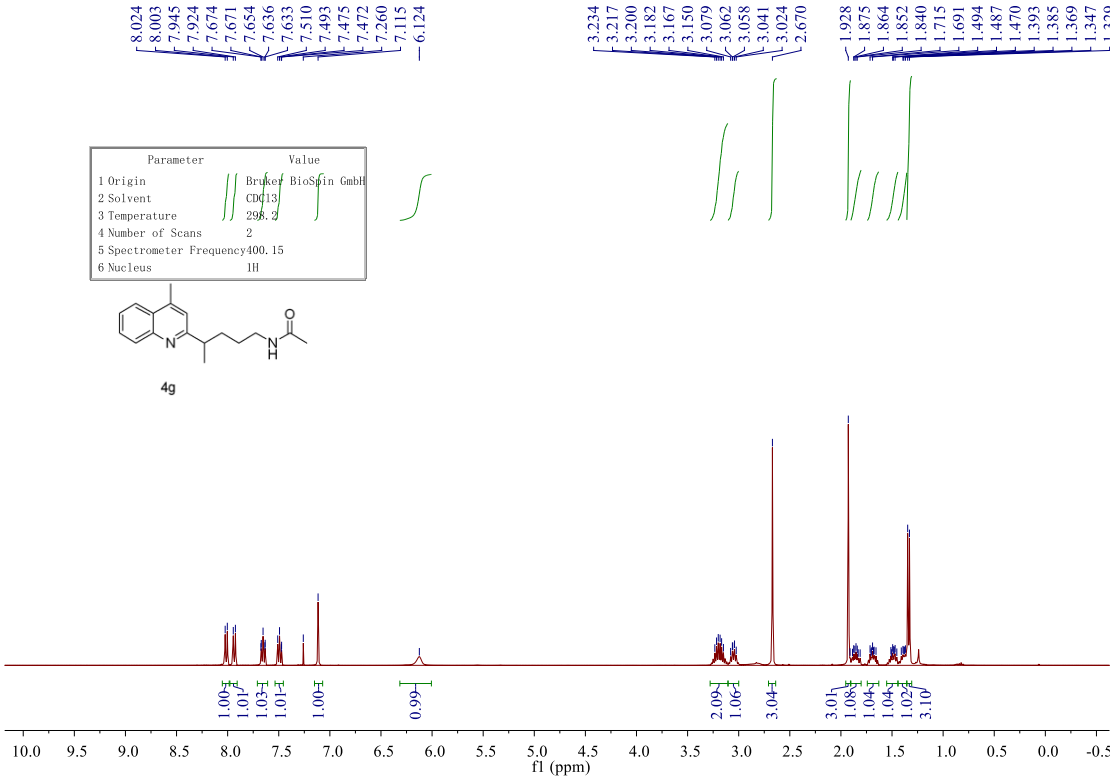
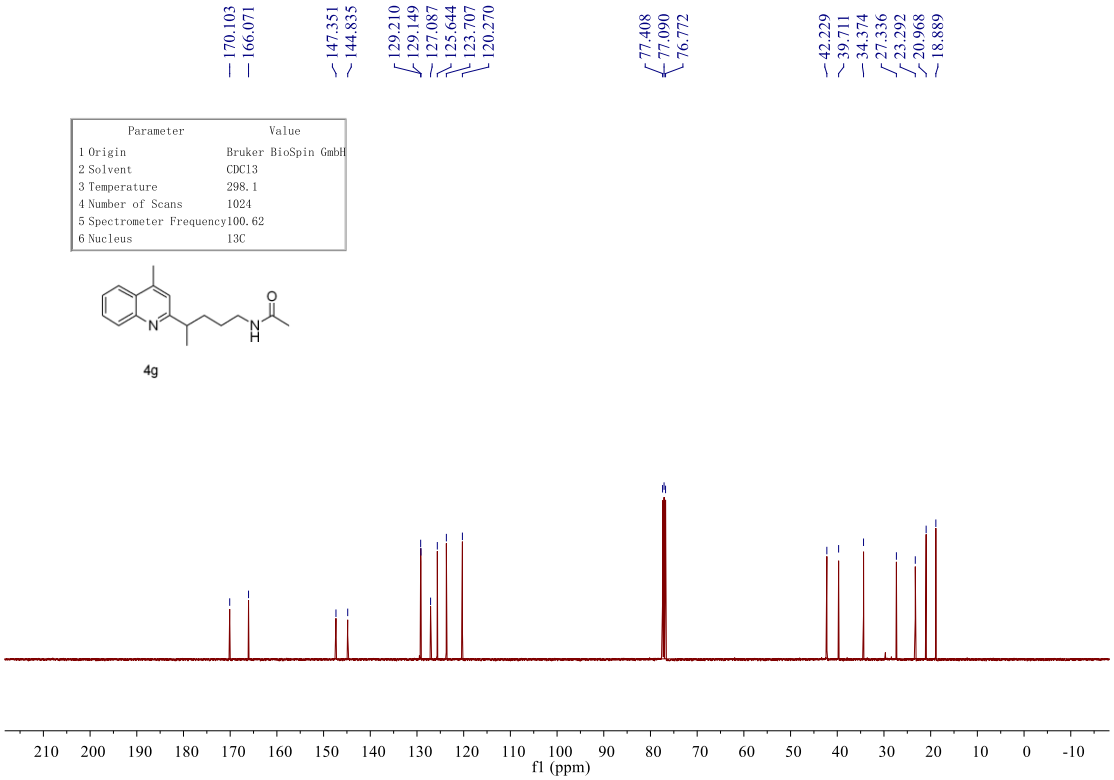
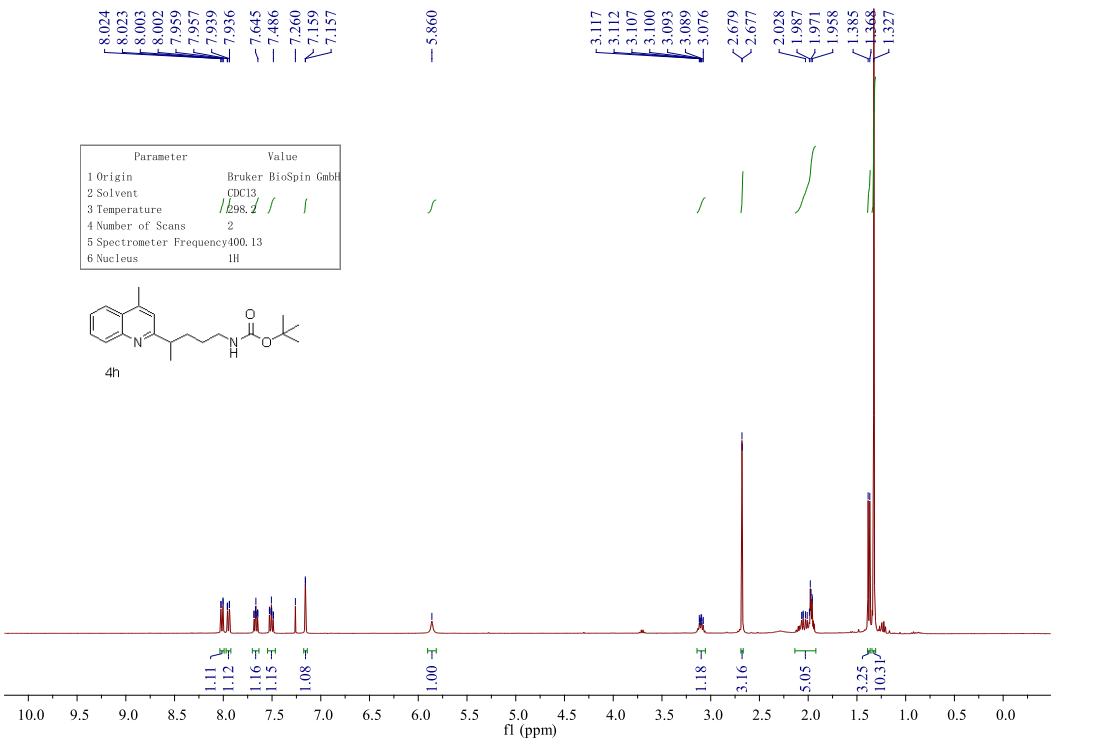
147.444
144.742
135.133
131.096
129.225
129.118
128.387
127.110
127.071
125.628
123.722
121.239
77.403
77.085
76.767
54.434
43.665
38.595
34.954
34.825
33.324
24.839
18.846
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 80
5 Spectrometer Frequency 100.62
6 Nucleus 13C
4d
f1 (ppm)
7.947
7.927
7.886
7.884
7.865
7.863
7.710
7.697
7.693
7.689
7.617
7.614
7.600
7.596
7.593
7.579
7.576
7.487
7.487
7.468
7.463
7.453
7.450
7.408
7.389
7.383
7.380
7.375
7.371
7.366
7.362
7.359
7.344
7.341
7.260
6.788
6.156
4.060
3.538
3.521
3.450
3.443
3.432
3.426
3.415
3.410
3.400
3.393
1.844
1.777
1.747
1.630
1.621
1.615
1.604
1.597
1.361
1.344
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 2
5 Spectrometer Frequency 400.13
6 Nucleus 1H
4e
1.01
0.99
1.99
1.04
1.10
3.12
0.97
0.97
3.07
1.05
2.14
4.03
3.06
f1 (ppm)

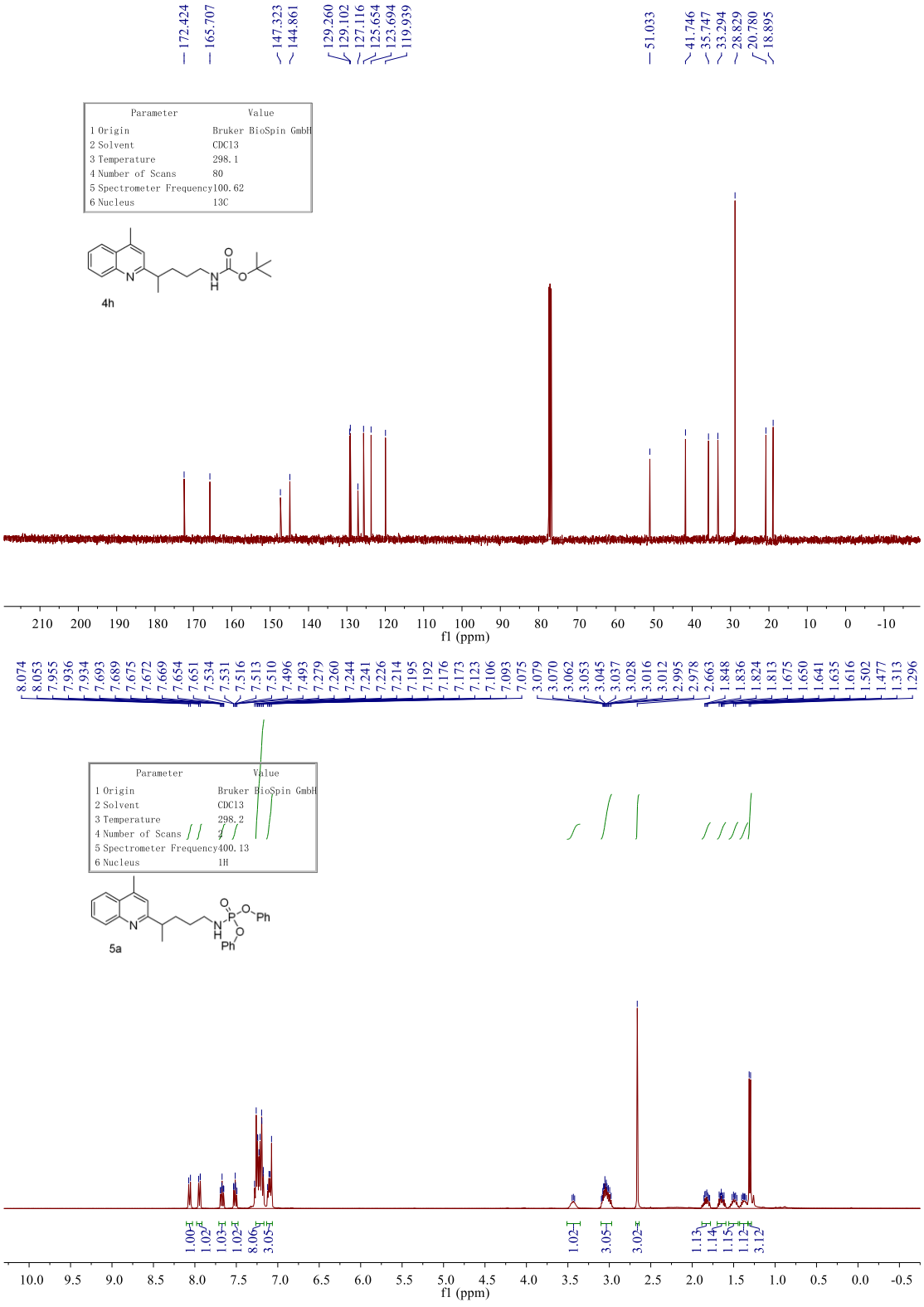

167.552
162.531
155.635
147.215
134.634
131.385
129.161
128.548
128.230
126.830
123.869
122.914
109.197
77.376
77.058
76.741
53.210
39.942
34.253
33.137
27.674
21.057
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 80
5 Spectrometer Frequency 100.62
6 Nucleus 13C
4e
f1 (ppm)
7.964
7.955
7.944
7.934
7.891
7.870
7.829
7.827
7.809
7.639
7.621
7.601
7.523
7.504
7.486
7.260
7.161
3.520
3.504
3.487
3.471
3.457
3.436
3.420
3.403
3.388
3.371
3.186
3.168
3.151
3.135
3.084
3.065
3.045
2.692
1.980
1.967
1.956
1.946
1.932
1.813
1.796
1.779
1.760
1.634
1.616
1.598
1.574
1.555
1.537
1.518
1.499
1.481
1.392
1.375
0.870
0.852
0.833
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 2
5 Spectrometer Frequency 400.15
6 Nucleus 1H
4f
3.00
1.00
1.99
1.00
1.00
1.92
1.01
1.03
1.02
4.05
2.99
1.09
1.04
6.16
3.07
6.08
f1 (ppm)

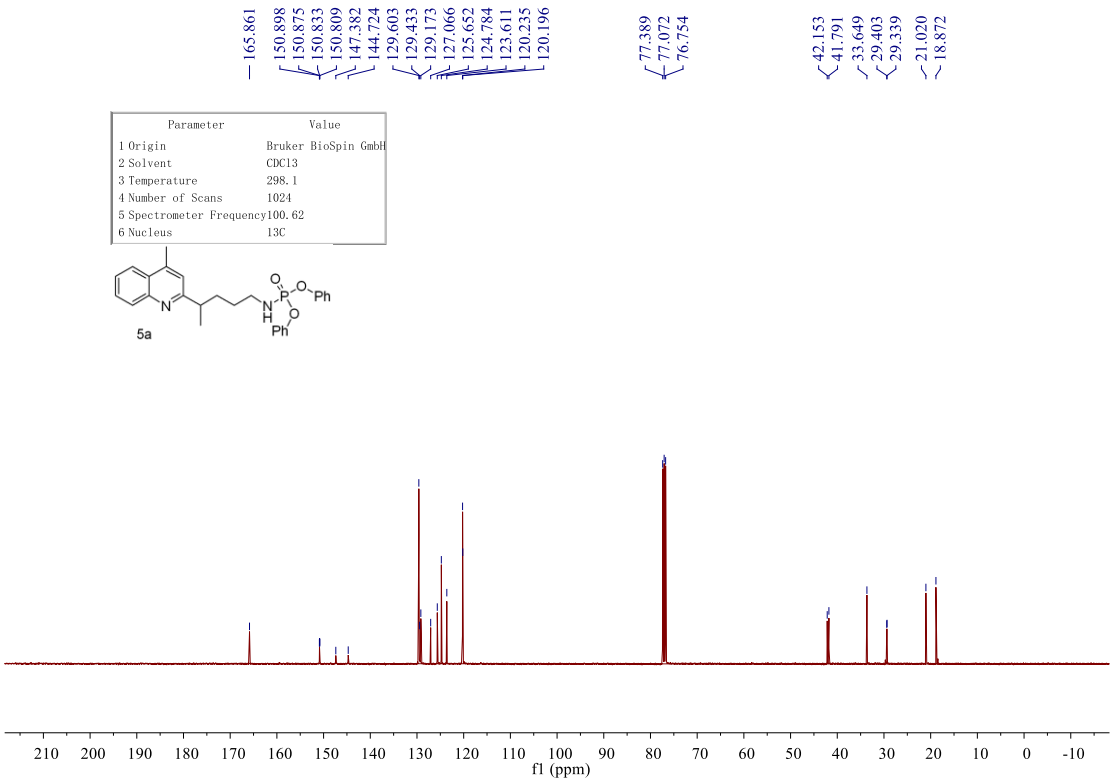

166.265
165.939
147.248
145.032
142.492
138.474
129.203
129.025
127.909
127.120
127.085
125.714
123.753
120.184
77.390
77.072
76.754
49.956
41.966
40.597
34.783
26.845
21.930
21.035
18.915
11.168
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 20
5 Spectrometer Frequency 100.61
6 Nucleus 13C
4f
f1 (ppm)

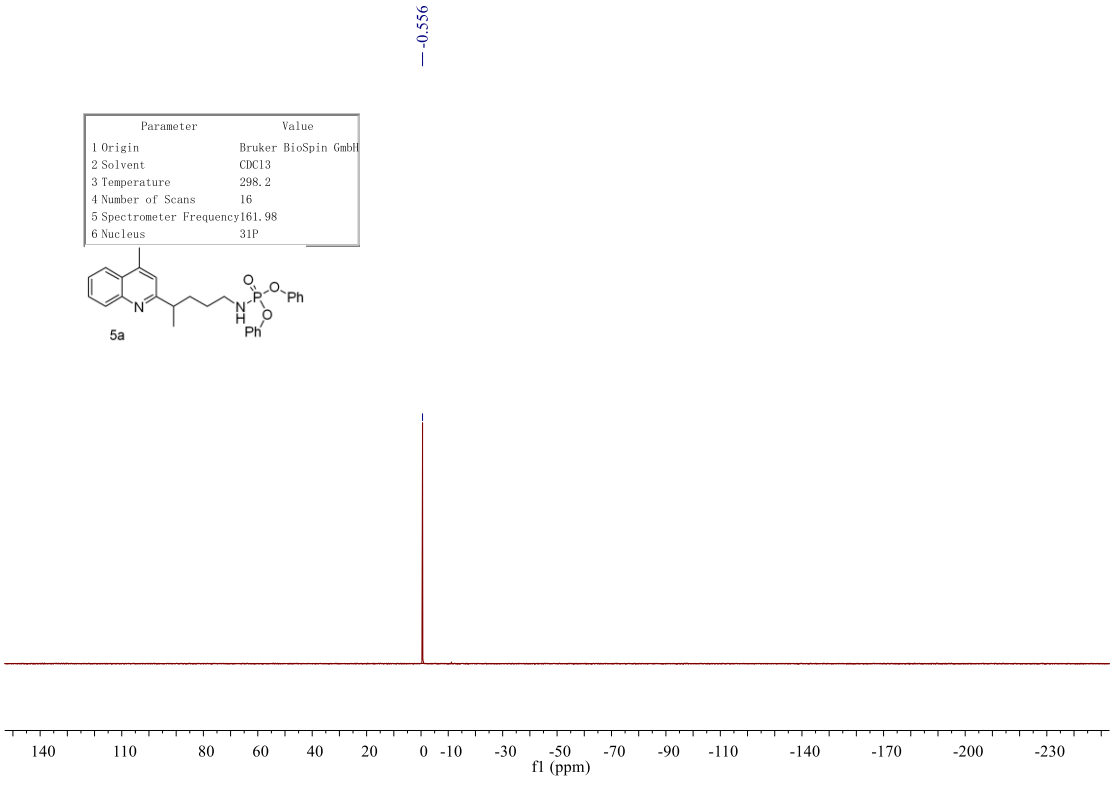

8.024
8.003
7.945
7.924
7.674
7.671
7.654
7.636
7.633
7.510
7.493
7.475
7.472
7.260
7.115
6.124
3.234
3.217
3.200
3.182
3.167
3.150
3.079
3.062
3.058
3.041
3.024
2.670
1.928
1.875
1.864
1.852
1.840
1.715
1.691
1.494
1.487
1.470
1.393
1.385
1.369
1.347
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 2
5 Spectrometer Frequency 400.15
6 Nucleus 1H
4g
1.00
1.01
1.03
1.01
1.00
0.99
2.09
1.06
3.04
3.01
1.08
1.04
1.04
1.02
3.10
f1 (ppm)

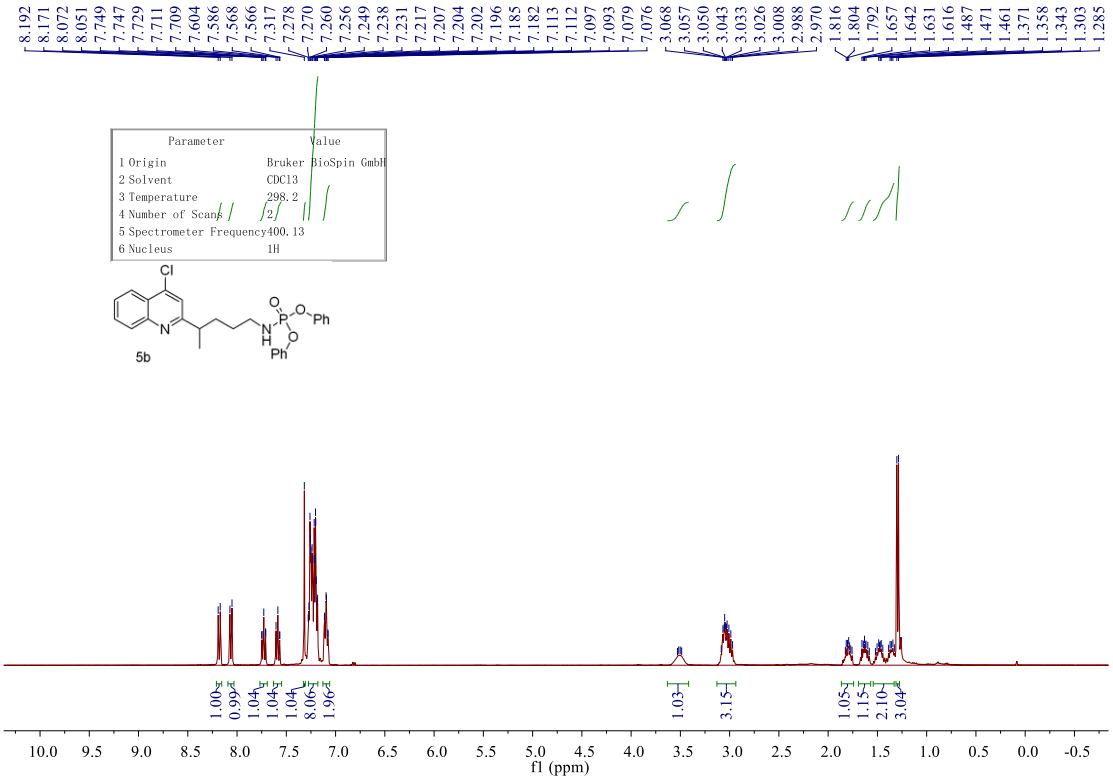

170.103
166.071
147.351
144.835
129.210
129.149
127.087
125.644
123.707
120.270
77.408
77.090
76.772
42.229
39.711
34.374
27.336
23.292
20.968
18.889
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 1024
5 Spectrometer Frequency 100.62
6 Nucleus 13C
O
N
H
4g
f1 (ppm)

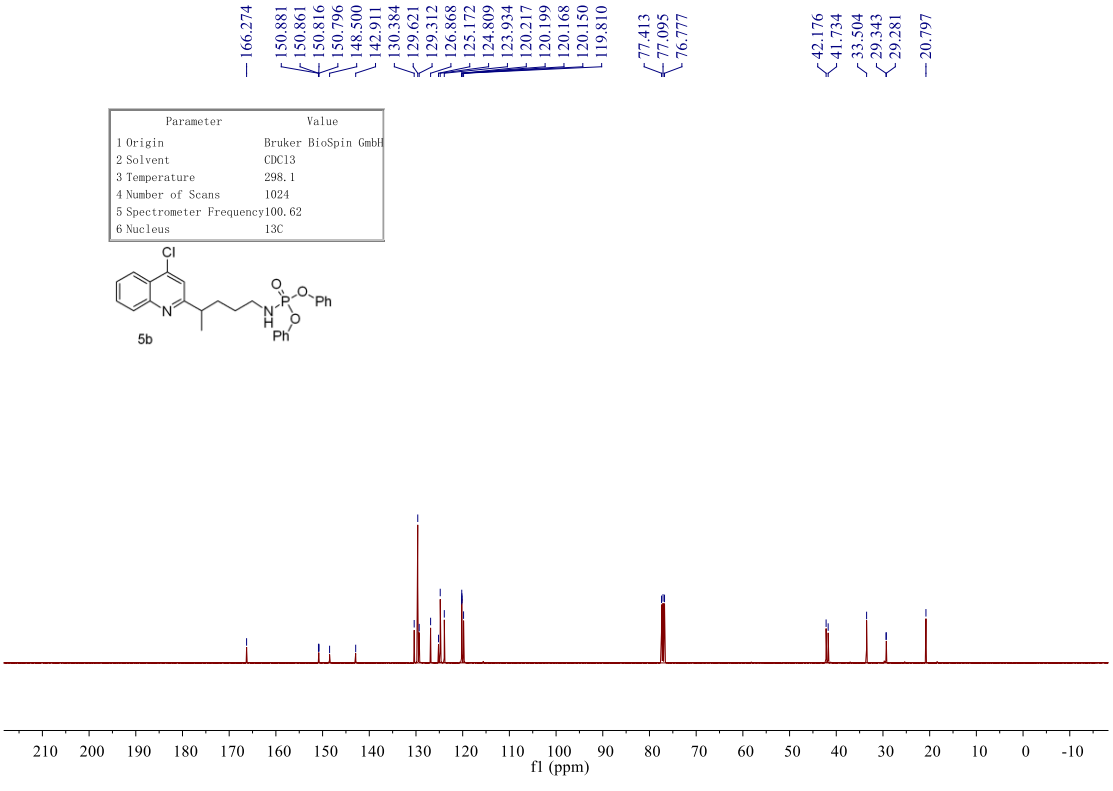

8.024
8.023
8.003
8.002
7.959
7.957
7.939
7.936
7.645
7.486
7.260
7.159
7.157
5.860
3.117
3.112
3.107
3.100
3.093
3.089
3.076
2.679
2.677
2.028
1.987
1.971
1.958
1.385
1.368
1.327
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 2
5 Spectrometer Frequency 400.13
6 Nucleus 1H
O
N
H
O
4h
1.11
1.12
1.16
1.15
1.08
1.00
1.18
3.16
5.05
3.25
10.31
f1 (ppm)

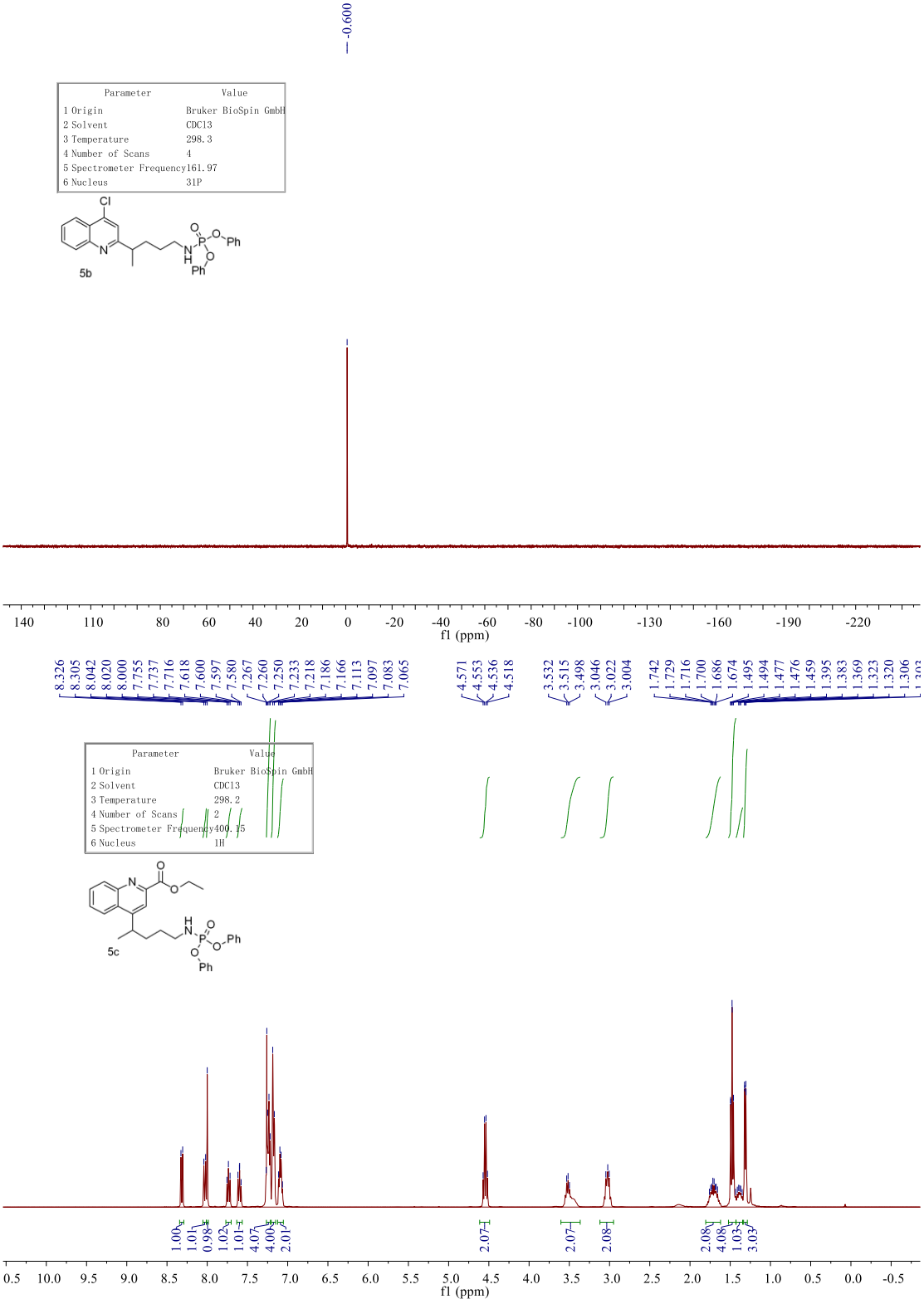

172.424
165.707
147.323
144.861
129.260
129.102
127.116
125.654
123.694
119.939
51.033
41.746
35.747
33.294
28.829
20.780
18.895
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 80
5 Spectrometer Frequency 100.62
6 Nucleus 13C
4h
f1 (ppm)
8.074
8.053
7.955
7.936
7.934
7.693
7.689
7.675
7.672
7.669
7.654
7.651
7.534
7.531
7.516
7.513
7.510
7.496
7.493
7.279
7.260
7.244
7.241
7.226
7.214
7.195
7.192
7.176
7.173
7.123
7.106
7.093
7.075
3.079
3.070
3.062
3.053
3.045
3.037
3.028
3.016
3.012
2.995
2.978
2.663
1.848
1.836
1.824
1.813
1.675
1.650
1.641
1.635
1.616
1.502
1.477
1.313
1.296
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 2
5 Spectrometer Frequency 400.13
6 Nucleus 1H
5a
Ph
Ph
1.00
1.02
1.03
1.02
8.06
3.05
1.02
3.05
3.02
1.13
1.14
1.15
1.12
3.12
f1 (ppm)

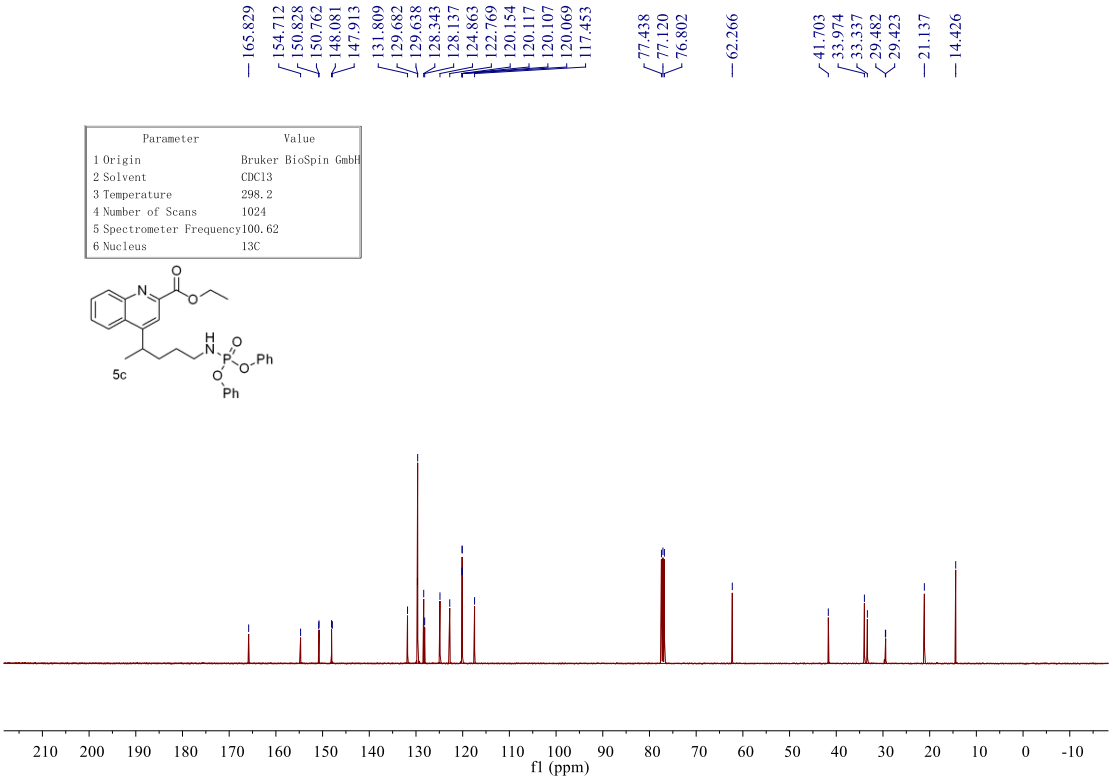

165.861
150.898
150.875
150.833
150.809
147.382
144.724
129.603
129.433
129.173
127.066
125.652
124.784
123.611
120.235
120.196
77.389
77.072
76.754
42.153
41.791
33.649
29.403
29.339
21.020
18.872
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 1024
5 Spectrometer Frequency 100.62
6 Nucleus 13C
5a
f1 (ppm)

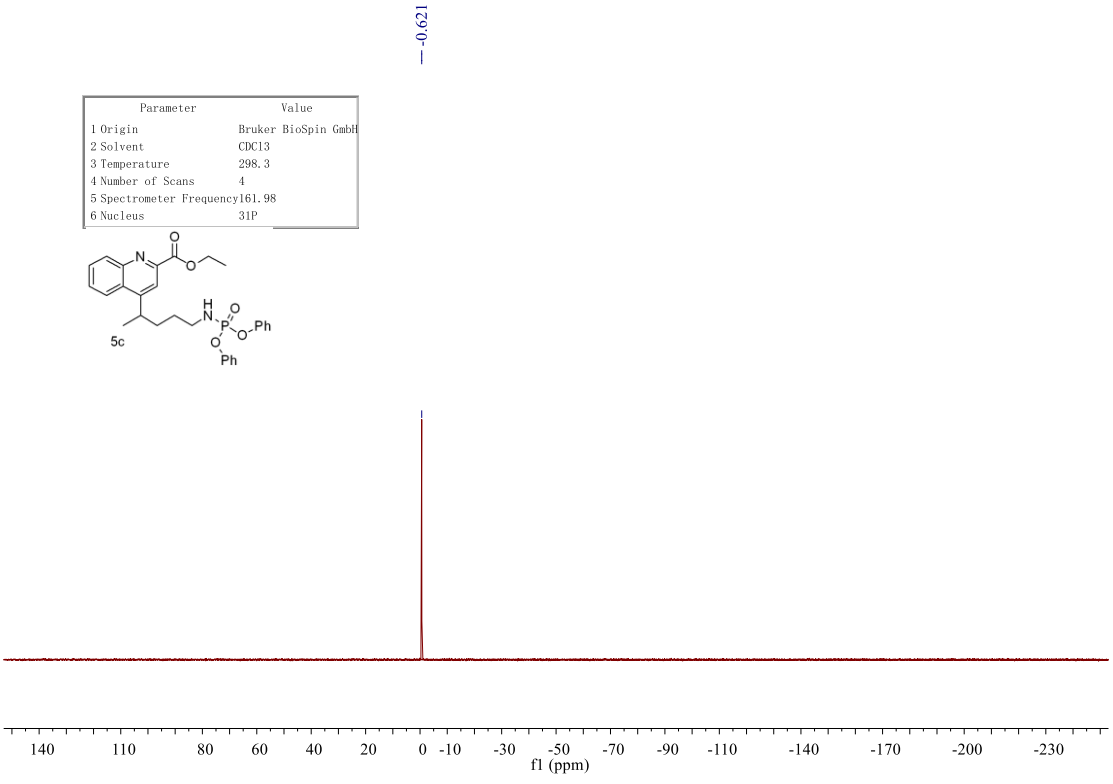

-0.556
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 16
5 Spectrometer Frequency 161.98
6 Nucleus 31P
5a
f1 (ppm)

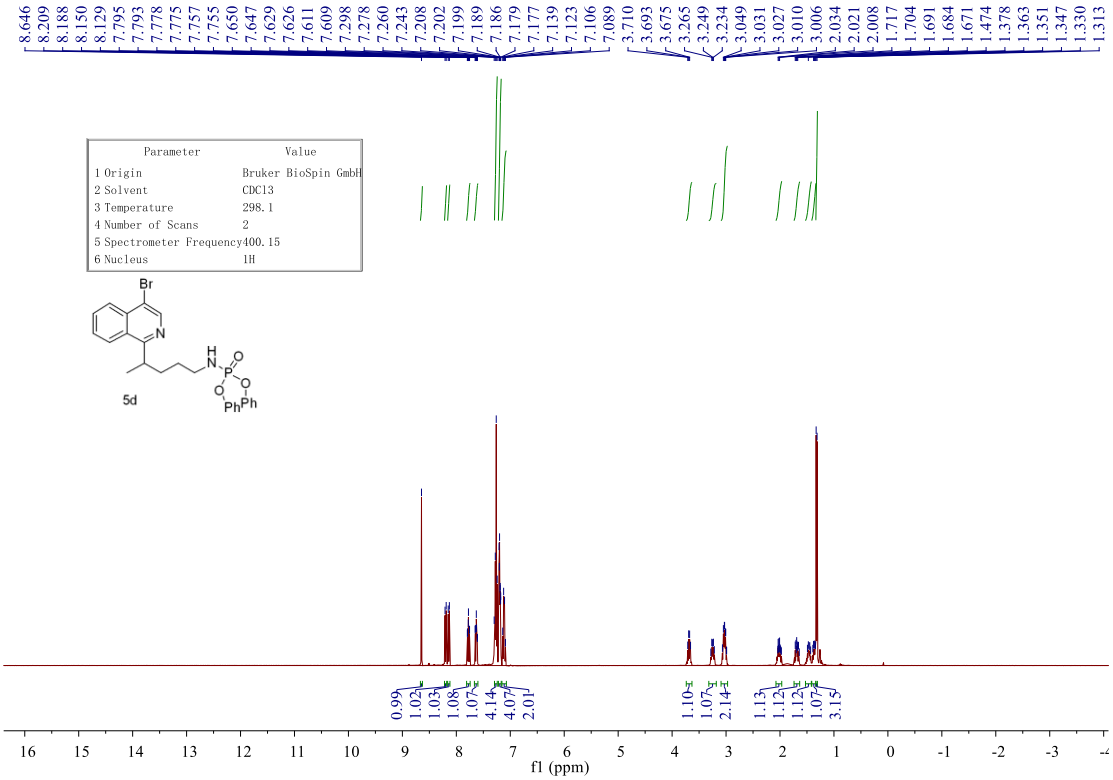

8.192
8.171
8.072
8.051
7.749
7.747
7.729
7.711
7.709
7.604
7.586
7.568
7.566
7.317
7.278
7.270
7.260
7.256
7.249
7.238
7.231
7.217
7.207
7.204
7.202
7.196
7.185
7.182
7.113
7.112
7.097
7.093
7.079
7.076
3.068
3.057
3.050
3.043
3.033
3.026
3.008
2.988
2.970
1.816
1.804
1.792
1.657
1.642
1.631
1.616
1.487
1.471
1.461
1.371
1.358
1.343
1.303
1.285
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 2
5 Spectrometer Frequency 400.13
6 Nucleus 1H
Cl
N
O
P
O
Ph
N
H
O
Ph
5b
1.00
0.99
1.04
1.04
1.04
8.06
1.96
1.03
3.15
1.05
1.15
2.10
3.04
10.0 9.5 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)


166.274
150.881
150.861
150.816
150.796
148.500
142.911
130.384
129.621
129.312
126.868
125.172
124.809
123.934
120.217
120.199
120.168
120.150
119.810
77.413
77.095
76.777
42.176
41.734
33.504
29.343
29.281
20.797
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
Cl
N
O
P
O
Ph
N
H
O
Ph
5b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-0.600
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.3
4 Number of Scans 4
5 Spectrometer Frequency 161.97
6 Nucleus 31P
Cl
N
O
P
O
Ph
H
N
O
Ph
5b
140 110 80 60 40 20 0 -20 -40 -60 -80 -100 -130 -160 -190 -220
f1 (ppm)
8.326 8.305 8.042 8.020 8.000 7.755 7.737 7.716 7.618 7.600 7.597 7.580 7.267 7.260 7.250 7.233 7.218 7.186 7.166 7.113 7.097 7.083 7.065
4.571 4.553 4.536 4.518
3.532 3.515 3.498 3.046 3.022 3.004
1.742 1.729 1.716 1.700 1.686 1.674 1.495 1.494 1.477 1.476 1.459 1.395 1.383 1.369 1.323 1.320 1.306
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 2
5 Spectrometer Frequency 400.15
6 Nucleus 1H
N
O
O
H
N
O
P
O
Ph
O
Ph
5c
1.00 1.01 0.98 1.02 1.01 4.07 4.00 2.01 2.07 2.07 2.08 2.08 4.08 1.03 3.03
0.5 10.0 9.5 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)


165.829
154.712
150.828
150.762
148.081
147.913
131.809
129.682
129.638
128.343
128.137
124.863
122.769
120.154
120.117
120.107
120.069
117.453
77.438
77.120
76.802
62.266
41.703
33.974
33.337
29.482
29.423
21.137
14.426
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 1024
5 Spectrometer Frequency 100.62
6 Nucleus 13C
5c
f1 (ppm)


-0.621
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.3
4 Number of Scans 4
5 Spectrometer Frequency 161.98
6 Nucleus 31P
5c
f1 (ppm)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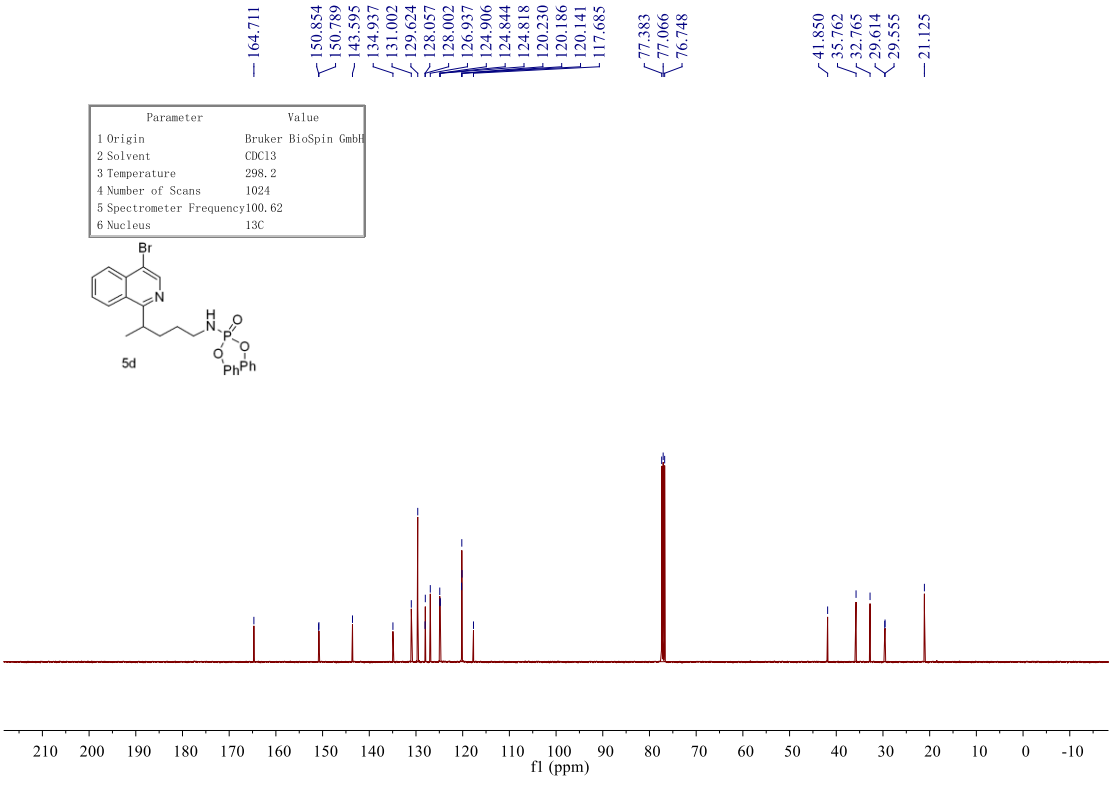
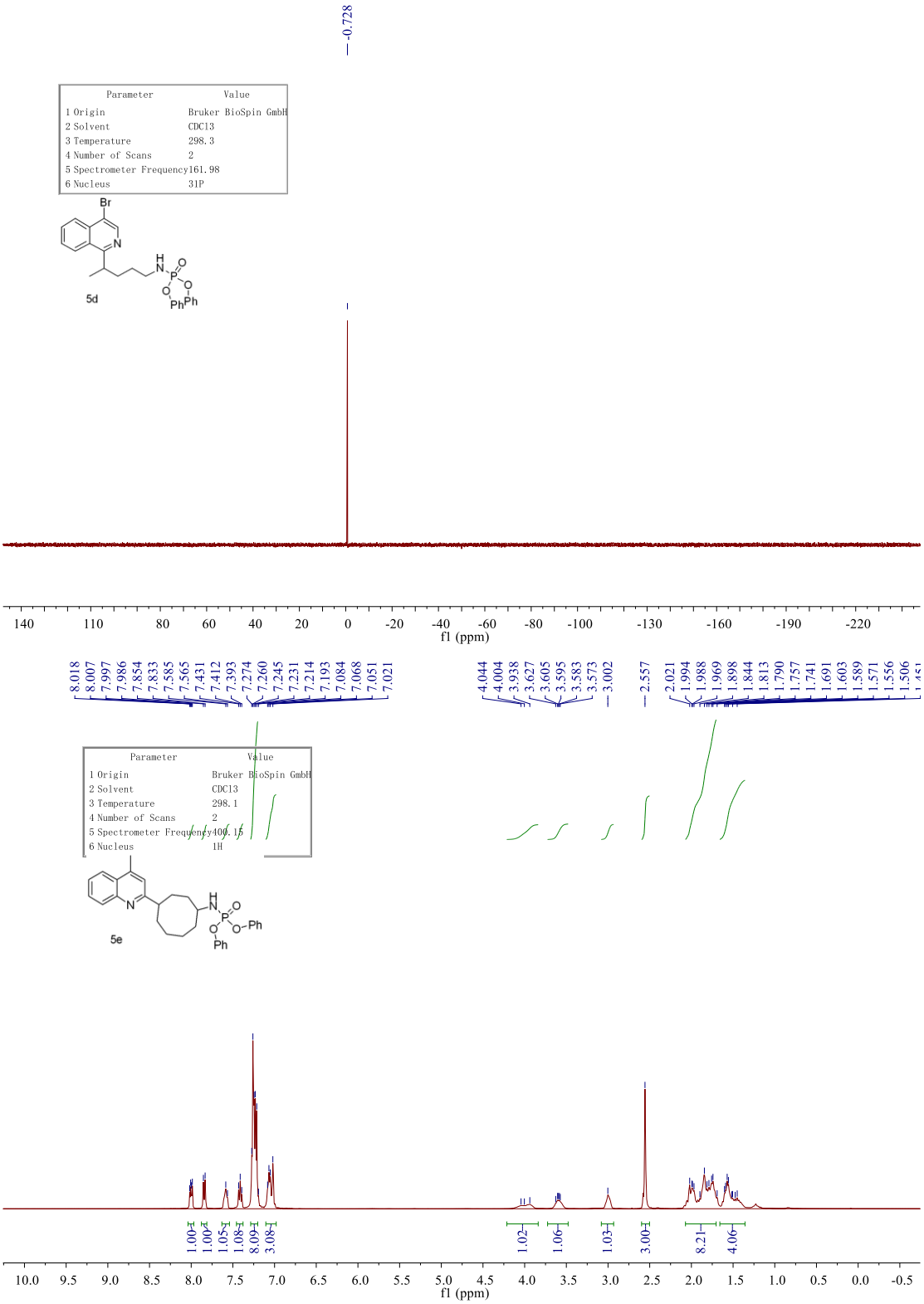
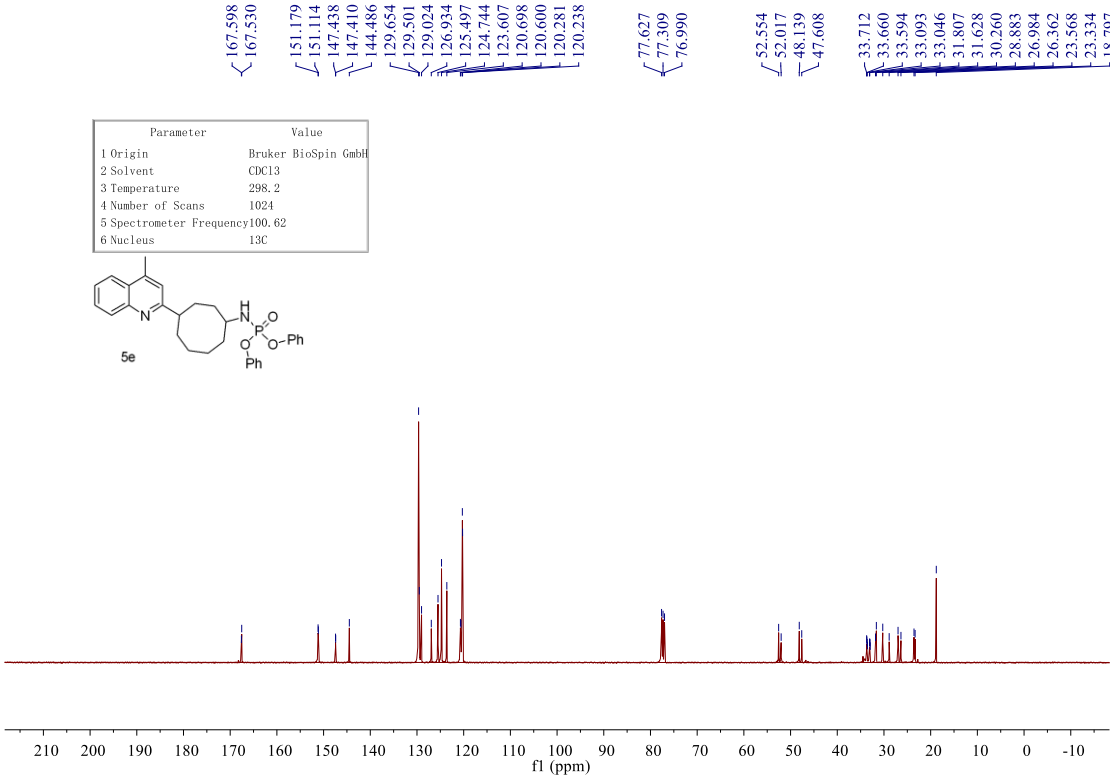
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 2
5 Spectrometer Frequency 400.15
6 Nucleus 1H
Br
N
H
N
P
O
O
O
Ph
Ph
5d
0.99 1.02 1.03 1.08 1.07 4.14 4.07 2.01 1.10 1.07 2.14 1.13 1.12 1.12 1.07 3.15
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


164.711 150.854 150.789 143.595 134.937 131.002 129.624 128.057 128.002 126.937 124.906 124.844 124.818 120.230 120.186 120.141 117.685 77.383 77.066 76.748 41.850 35.762 32.765 29.614 29.555 21.125
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 1024
5 Spectrometer Frequency 100.62
6 Nucleus 13C
Br
N
H
N
P
O
O
O
Ph
Ph
5d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-0.728
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.3
4 Number of Scans 2
5 Spectrometer Frequency 161.98
6 Nucleus 31P
Br
N
H
N
P
O
O
O
Ph
Ph
5d
f1 (ppm)
8.018
8.007
7.997
7.986
7.854
7.833
7.585
7.565
7.431
7.412
7.393
7.274
7.260
7.245
7.231
7.214
7.193
7.084
7.068
7.051
7.021
4.044
4.004
3.938
3.627
3.605
3.595
3.583
3.573
3.002
2.557
2.021
1.994
1.988
1.969
1.898
1.844
1.813
1.790
1.757
1.741
1.691
1.603
1.589
1.571
1.556
1.506
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 2
5 Spectrometer Frequency 400.13
6 Nucleus 1H
N
H
N
P
O
O
O-Ph
Ph
5e
1.00
1.00
1.05
1.08
8.09
3.08
1.02
1.06
1.03
3.00
8.21
4.06
f1 (ppm)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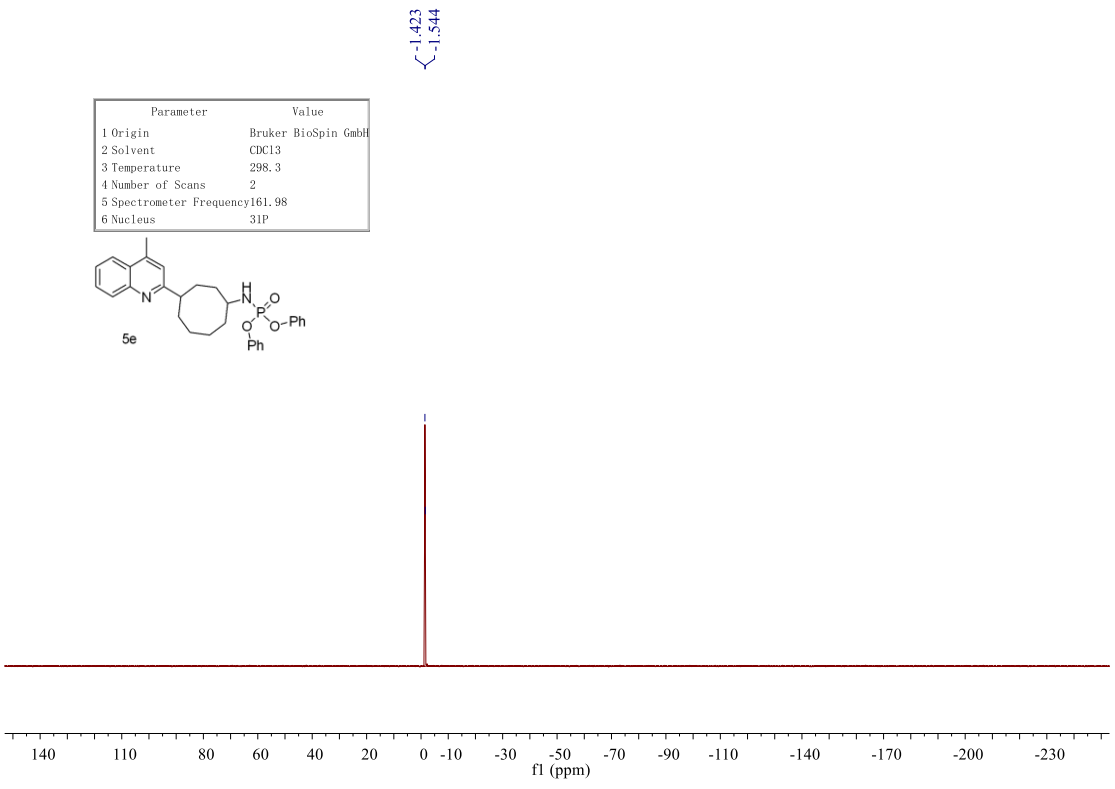
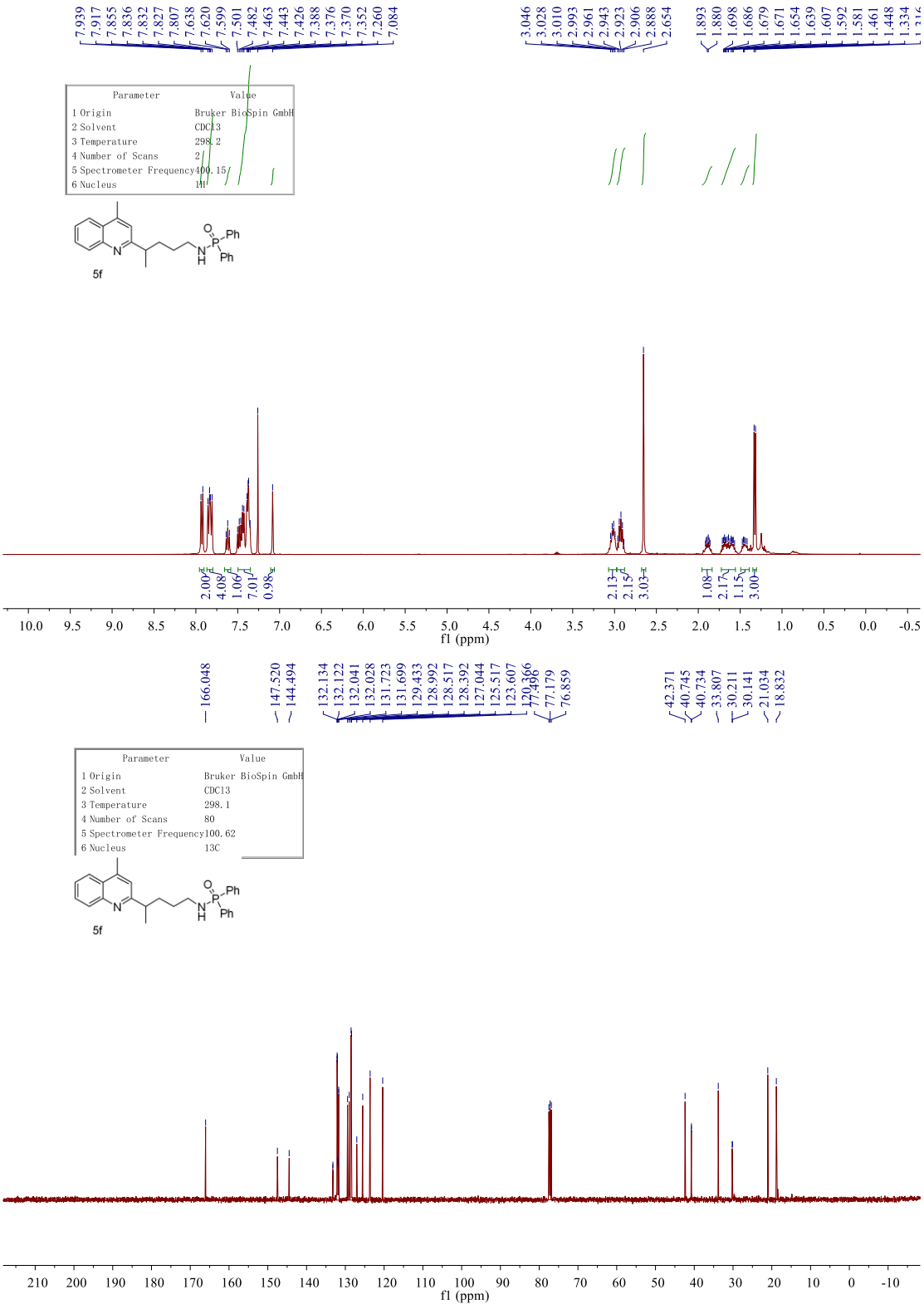
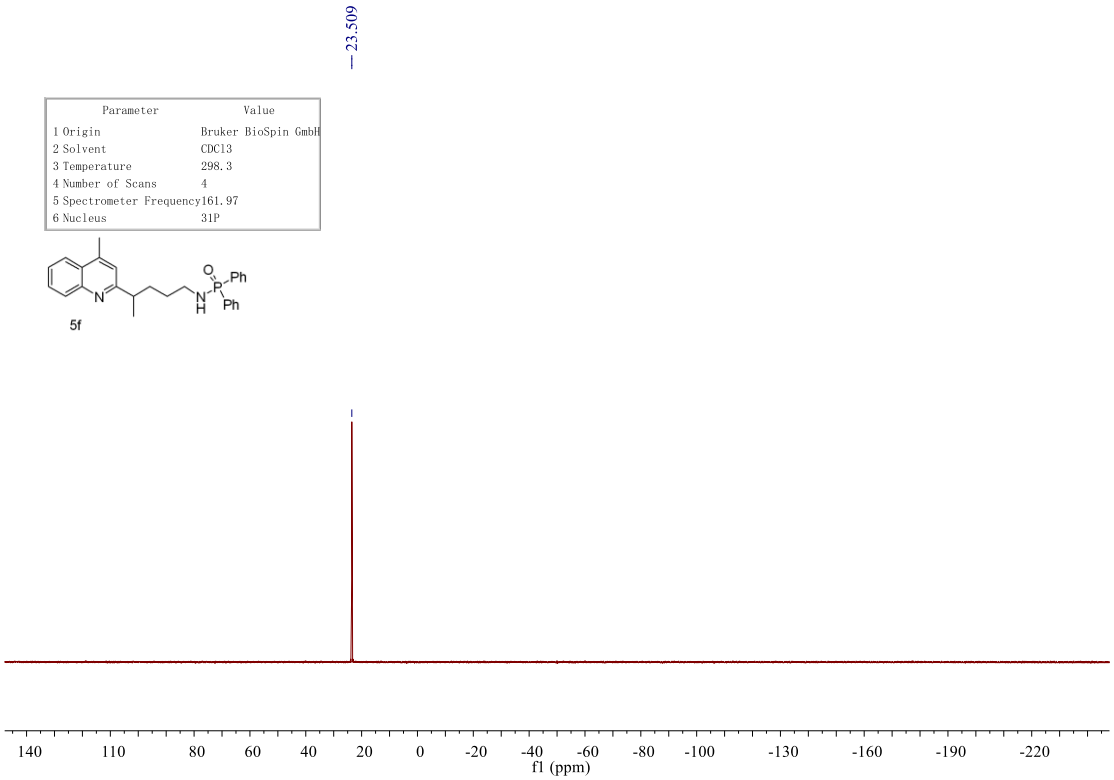
167.530
151.179
151.114
147.438
147.410
144.486
129.654
129.501
129.024
126.934
125.497
124.744
123.607
120.698
120.600
120.281
120.238
77.627
77.309
76.990
52.554
52.017
48.139
47.608
33.712
33.660
33.594
33.093
33.046
31.807
31.628
30.260
28.883
26.984
26.362
23.568
23.334
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 1024
5 Spectrometer Frequency 100.62
6 Nucleus 13C
5e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-1.423
-1.544
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.3
4 Number of Scans 2
5 Spectrometer Frequency 161.98
6 Nucleus 31P
5e
140 110 80 60 40 20 0 -10 -30 -50 -70 -90 -110 -140 -170 -200 -230
f1 (ppm)


7.939
7.917
7.855
7.836
7.832
7.827
7.807
7.638
7.620
7.599
7.501
7.482
7.463
7.443
7.426
7.388
7.376
7.370
7.352
7.260
7.084
3.046
3.028
3.010
2.993
2.961
2.943
2.923
2.906
2.888
2.654
1.893
1.880
1.698
1.686
1.679
1.671
1.654
1.639
1.607
1.592
1.581
1.461
1.448
1.334
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 2
5 Spectrometer Frequency 400.15
6 Nucleus 1H
O
P
Ph
Ph
N
H
5f
2.00
4.08
1.06
7.01
0.98
2.13
2.15
3.03
1.08
2.17
1.15
3.00
10.0 9.5 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)
166.048
147.520
144.494
132.134
132.122
132.041
132.028
131.723
131.699
129.433
128.992
128.517
128.392
127.044
125.517
123.607
120.366
77.418
77.179
76.859
42.371
40.745
40.734
33.807
30.211
30.141
21.034
18.832
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 80
5 Spectrometer Frequency 100.62
6 Nucleus 13C
O
P
Ph
Ph
N
H
5f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

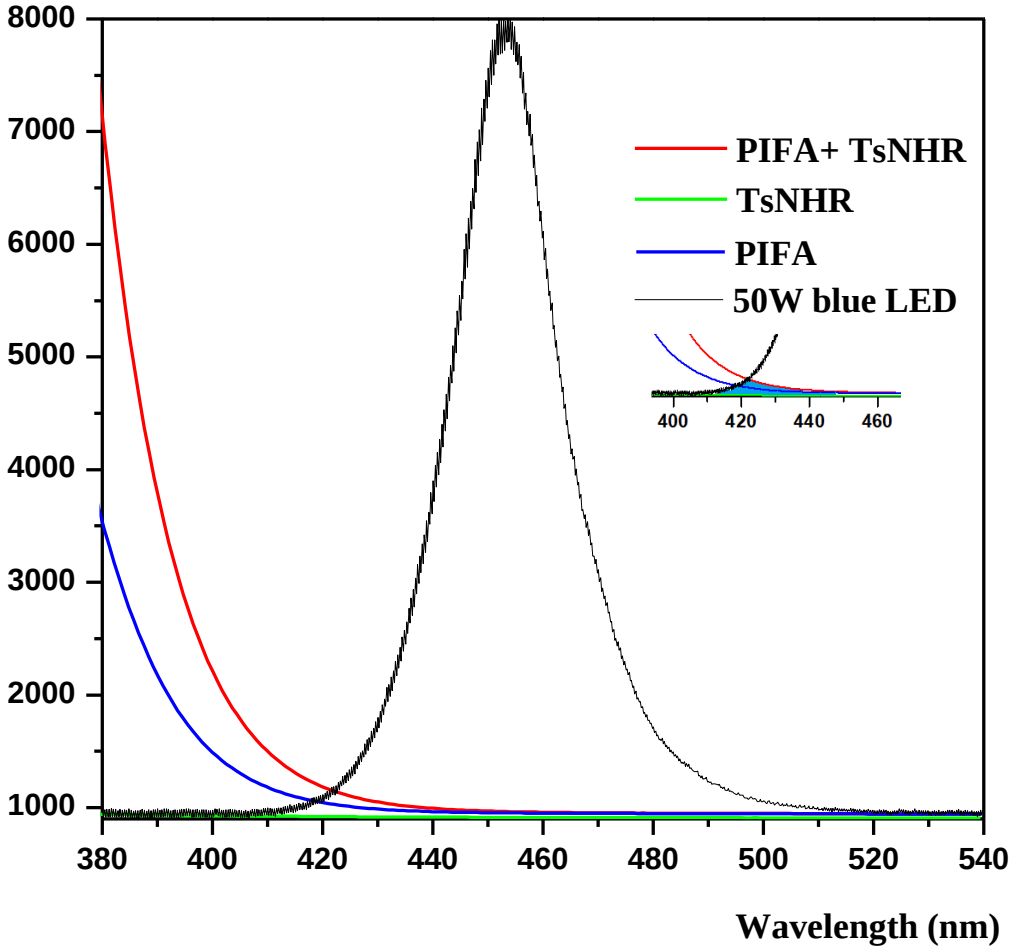

23.509
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.3
4 Number of Scans 4
5 Spectrometer Frequency 161.97
6 Nucleus 31P
O
Ph
P
N
H
Ph
5f
140 110 80 60 40 20 0 -20 -40 -60 -80 -100 -130 -160 -190 -220
f1 (ppm)

8. Absorption and emission studies

Solutions of different complexes were introduced to a 1 cm path length quartz cuvette equipped with a Teflon® septum and analyzed using an Agilent Cary 5000 spectrophotometer.

For the solutions of benzenesulfonamide **1a** and PIFA in DCE: **1a** (0.3 mmol) and PIFA (0.23 mmol) were dissolved in DCE (2 mL). The mixtures were stirred for 5 min, then transformed to 1 cm path length quartz cuvettes, sealed with Teflon® septa and degassed with a stream of argon for 10 minutes.

For the solutions of PIFA in DCE: PIFA (0.23 mmol) were dissolved in DCE (2 mL). The mixtures were stirred for 5 min, then transformed to 1 cm path length quartz cuvettes, sealed with



Teflon® septa and degassed with a stream of argon for 10 minutes.

Fig. 1 Absorption spectra of **1a**, PIFA, and the mixture of **1a** and PIFA, and emission spectrum of blue LEDs.

9. Determination of quantum yield

The quantum yield (Φ) was determined by the known ferrioxalate actinometry method, according to the reported procedures: W. Xu, J. Ma, X. Yuan, J. Dai, J. Xie, C. Zhu, *Angew. Chem. Int. Ed.*, **2018**, *57*, 10357-10361.

A ferrioxalate actinometry solution was prepared by following the Hammond variation of the Hatchard and Parker procedure outlined in Handbook of Photochemistry. The actinometry solutions (1mL) were irradiated with 50 W blue LEDs (400±5 nm) for specified time intervals (0 sec, 20 sec, 40 sec, 60 sec, 80 sec and 100 sec). The UV-Vis spectra was shown in **Fig 2a**.

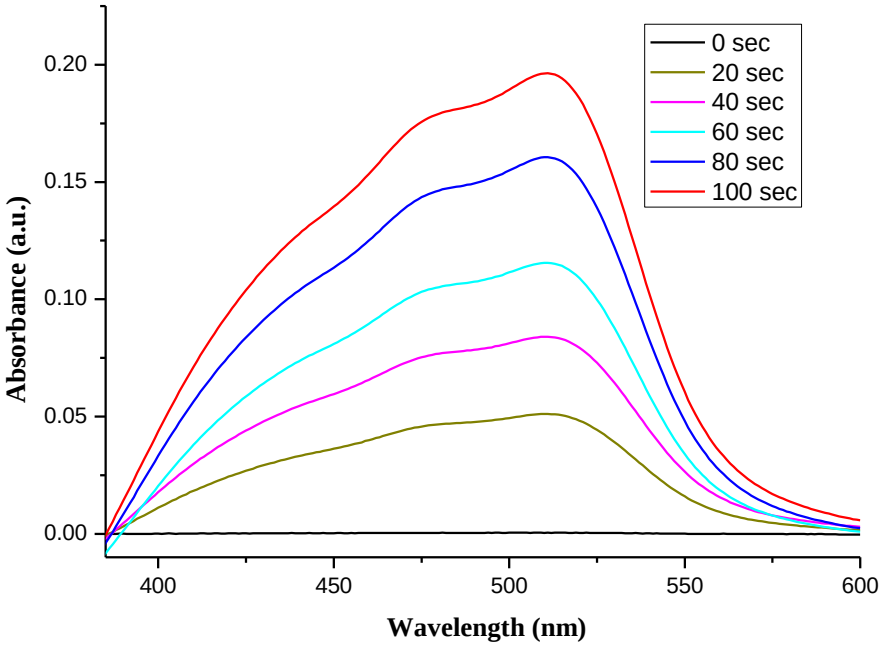


Fig 2a.

Based on the data, we got the graph (**Fig 2b**) between the number of moles of products (y axis) and time (x axis). Then, photon flux was estimated to 3.78 x 10^{-8} einstein S^{-1} by using $K_3[Fe(C_2O_4)_3]$ as an actinometer.

Photon flux may be determined by:

$$\text{Photon flux} = \frac{\text{moles } Fe^{2+}}{\Phi_{510nm} * t * F}$$

A plot of moles Fe^{2+} as a function of time yields a linear equation with an intercept at zero. Division of the slope by the documented quantum yield of the actinometer (Φ = 1.14 at 405 nm) and the mean fraction of light absorbed by the ferrioxalate solution (F ~ 1 at 402 nm) provides the photon flux in einsteins s^{-1}.

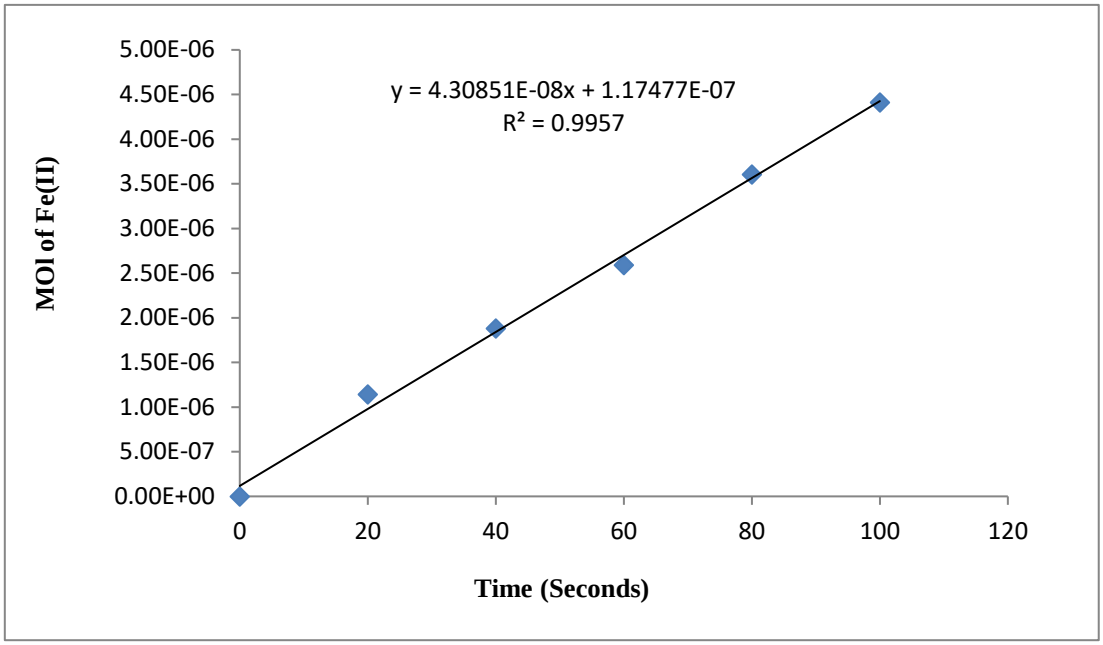


Fig 2b

$$\text{Photon flux} = \frac{\text{moles } Fe^{2+}}{\Phi_{510nm} * t * F} = 3.78 * 10^{-8} \text{ einsteins } s^{-1}$$

The slope collected is $4.31 * 10^{-8}$; division by the known quantum yield $\Phi = 1.14$ yields a photon flux of $3.78 * 10^{-8}$ einsteins s^{-1}.

The quantum yield is defined as:

$$\Phi = \frac{\text{Moles of Product Formed}}{\text{Photons Absorbed by Sample}}$$

If the transmittance of photons at the blue LEDs wavelength (400±5 nm) is sufficiently small, it can be assumed that all of the photons which pass through the cell are absorbed. The above equation may be then written as:

$$\Phi = \frac{\text{Moles of Product Formed}}{\text{Photon Flux} * \text{Time}} = \frac{\text{Moles of Product Formed}}{\text{Photons}}$$

According to this relationship, the experiment procedure is as follows:

For six clean tubes, according to the general procedure, the 0.1 mmol scale model reaction solution was irradiated with 50 W blue LEDs (400±5 nm) for specified time intervals (0 h, 1 h, 2 h, 3 h, 4 h and 5 h). The moles of products formed were determined by H-NMR yield with 1,3,5-trimethoxybenzene as reference standard.

Mol/ products	Mol of photons (Photon Flux*Time)	Time（s）
0.0000E+00	0.0000E+00	0
4.0000E-06	1.3606E-04	3600
1.1000E-05	2.7212E-04	7200
2.0000E-05	4.0817E-04	10800
2.4000E-05	5.4423E-04	14400
3.2000E-05	6.8029E-04	18000

Based on the data, we got the graph (**Fig.2c)**. The number of moles of products (y axis) per unit time is related to the number of photons (x axis, calculated from Photon Flux*Time). The slope gave the quantum yield (Φ) of the photoreaction, 0.048 (4.8%).

$$\Phi = \frac{\text{Moles of Product Formed}}{\text{Photon Flux} * \text{Time}} = \frac{\text{Moles of Product Formed}}{\text{Photons}} = \frac{y}{x} = 0.048$$

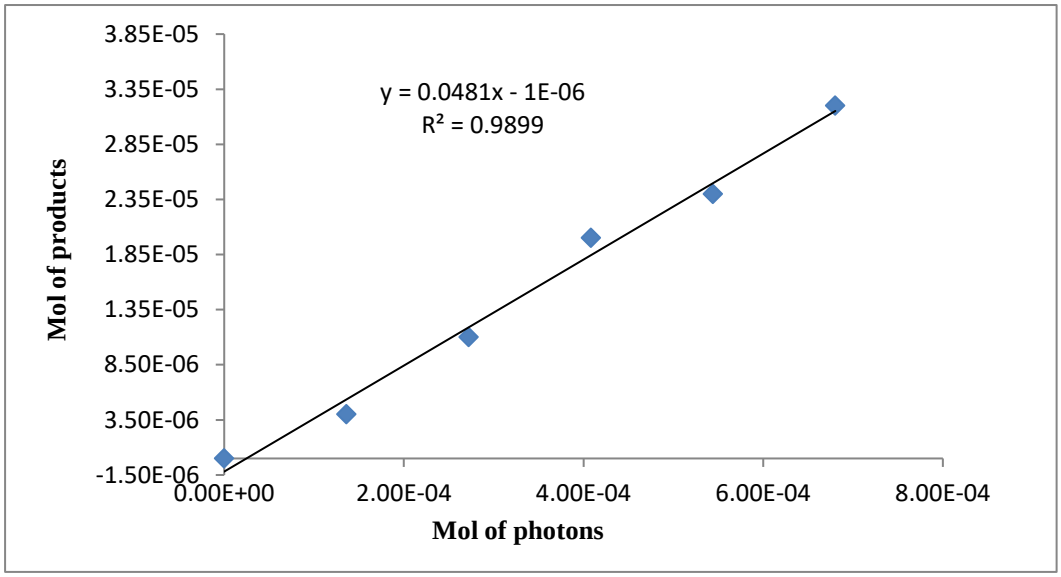


Fig 2c