Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Electronic Supplementary Information

Regioselective prenylation of bromocarbazoles by palladium(0)-catalysed cross-coupling – synthesis of *O*-methylsiamenol, *O*-methylmicromeline and carquinostatin A

Claudia Thomas, Olga Kataeva, Arndt W. Schmidt and Hans-Joachim Knölker*

Department Chemie, Technische Universität Dresden, Bergstrasse 66, 01069 Dresden, Germany.

E-mail: hans-joachim.knoelker@tu-dresden.de

Materials and methods

All reactions were carried out in oven-dried glassware using dry solvents under an argon atmosphere unless stated otherwise. Tetrahydrofuran was dried using a solvent purification system (MBraun-SPS). Other chemicals were used as received from commercial sources. All reactions were carried out in a MBraun MB 150B-G-II glove box under an argon atmosphere. Flash chromatography was performed on a Büchi Sepacore system equipped with an UV monitor using silica gel from Acros Organics (0.035–0.070 mm). Thin layer chromatography was performed with TLC plates from Merck (60 F254) using UV-light for visualisation. Melting points were measured on a Gallenkamp MPD 350 melting point apparatus. Ultraviolet spectra were recorded on a Perkin Elmer 25 UV/VIS spectrometer. Infrared spectra were recorded on a Thermo Nicolet Avatar 360 FT-IR spectrometer using the ATR method (Attenuated Total Reflectance). NMR spectra were recorded on Bruker Avance II 300 and DRX 500 spectrometers. Chemical shifts d are reported in parts per million with the non-deuterated solvent as internal standard. The following abbreviations have been used: s: singlet, d: doublet, t: triplet, quint: quintet, m: multiplet and br: broad. Mass spectra were recorded on a Finnigan MAT-95 spectrometer (electron impact, 70 eV) or by GC/MS-coupling using an Agilent Technologies 6890 N GC System equipped with a 5973 Mass Selective Detector (electron impact, 70 eV). Elemental analyses were measured on an EuroVector EuroEA3000 elemental analyser.

3-Prenylcarbazole (3-(3-methyl-but-2-enyl)carbazole) (6)

The *tert*-prenylstannane **9** (90.0 mg, 251 µmol) and caesium fluoride (50.0 mg, 329 µmol) were added at room temperature to a solution of 3-bromocarbazole (**5**) (51.1 mg, 208 µmol), $Pd(dba)_2$ (12 mg, 21 µmol) and $P(t\text{-}Bu)_3$ (9.0 mg, 49 µmol) in dry DMF (3 mL) under an argon atmosphere. The mixture was stirred under an argon atmosphere for 24 h (TLC control showed complete conversion). The mixture was diluted with diethyl ether and washed with a saturated aqueous solution of potassium fluoride, water (2 ×) and brine. The water washings were extracted with diethyl ether and the

combined organic layers were dried over sodium sulfate. The solvent was evaporated and the crude product was further purified by column chromatography on silica gel (petroleum ether–dichloromethane 50:1) provide 3-prenylcarbazole (**6**) (40.0 mg, 82%) as a colourless solid; mp 128–129 °C. UV (MeOH): λ = 230, 237, 248 (sh), 260, 284 (sh), 290 (sh), 296, 328, 341 nm. Fluorescence (MeOH): λ_{ex} = 296 nm, λ_{em} = 352, 364 nm. IR (ATR): ν = 3411, 3078, 3054, 2960, 2923, 2869, 2030, 1817, 1631, 1603, 1575, 1458, 1411, 1360, 1333, 1287, 1239, 1136, 1113, 1083, 1040, 1002, 904, 886, 812, 770, 751, 734, 701, 684, 630 cm^{-1}. ^1H NMR (500 MHz, acetone-d_6): δ = 1.75 (d, J = 1.0 Hz, 3 H), 1.78 (s, 3 H), 3.50 (d, J = 7.4 Hz, 2 H), 5.42 (tquint, J = 7.4, 1.4 Hz, 1 H), 7.14 (br t, J = 7.5 Hz, 1 H), 7.22 (dd, J = 8.3, 1.6 Hz, 1 H), 7.35 (br t, J = 7.6, 1 H), 7.41 (d, J = 8.2 Hz, 1 H), 7.47 (d, J = 8.3 Hz, 1 H), 7.91 (d, J = 0.7 Hz, 1 H), 8.07 (d, J = 7.8 Hz, 1 H), 10.21 (br. s, 1 H). ^{13}C NMR and DEPT (75 MHz, acetone-d_6): δ = 17.90 (CH_3), 25.92 (CH_3), 35.01 (CH_2), 111.49 (CH), 111.61 (CH), 119.41 (CH), 120.11 (CH), 120.79 (CH), 123.87 (C), 124.11 (C), 125.52 (CH), 126.22 (CH), 127.18 (CH), 131.92 (C), 133.02 (C), 139.35 (C), 141.20 (C). MS (EI): m/z (%) = 235 (67) [M^+], 220 (100), 205 (26), 204 (21), 180 (21), 167 (19).

3-*tert*-Prenylcarbazole (3-(2-methyl-but-3-en-2-yl)carbazole) (7)

A solution of 3-bromocarbazole (**5**) (88.9 mg, 361 µmol), $Pd(dba)_2$ (33.1 mg, 57.6 µmol) and P(*t*-Bu)$_3$ (22.4 mg, 111 µmol) in a mixture of dry DMF (3 mL) and dry THF (3 mL) was stirred at room temperature under an argon atmosphere for 5 min (the colour had then changed from purple to olive). The prenylboronate **10** (106 mg, 541 µmol) and caesium fluoride (220 mg, 1.45 mmol) were added and the mixture was stirred under an argon atmosphere for 5 days (TLC control showed complete conversion). The mixture was diluted with diethyl ether, poured into water and the layers were separated. The aqueous layer was extracted twice with diethyl ether. The combined organic layers were washed with water and brine and dried over sodium sulfate. The solvent was evaporated and the crude product was further purified by column chromatography on silica gel (petroleum ether–dichloromethane 10:1) to provide 3-*tert*-prenylcarbazole (**7**) (75.9 mg, 89%) as a colourless solid; mp 110–113 °C. UV (MeOH): λ = 229 (sh), 236, 246 (sh), 259, 284 (sh), 288 (sh), 295, 325, 338 nm. Fluorescence (MeOH): λ_{ex} = 295 nm, λ_{em} = 354, 364 nm. IR (ATR): ν = 3417, 3080, 3052, 2961, 2924, 2869, 1635, 1604, 1493, 1478, 1459, 1410, 1389, 1377, 1359, 1287, 1245, 1137, 1113, 1041, 1004, 996, 907, 815, 750, 735, 631 cm^{-1}. ^1H NMR (500 MHz, acetone-d_6): δ = 1.50 (s, 6 H), 5.04 (dd, J = 10.6, 1.4 Hz, 1 H), 5.10 (dd, J = 17.5, 1.4 Hz, 1 H), 6.15 (dd, J = 17.5, 10.6 Hz, 1 H), 7.15 (br t, J = 7.5 Hz, 1 H), 7.35 (br t, J = 7.6 Hz, 1 H), 7.415 (d, J = 1.7 Hz, 1 H), 7.424 (s, 1 H), 7.48 (d, J = 8.1 Hz, 1 H), 8.11 (d, J = 7.5 Hz, 1 H), 8.12 (s, 1 H), 10.23 (br s, 1 H). ^{13}C NMR and DEPT (125 MHz, acetone-d_6): δ = 29.21 (2 CH_3), 41.75 (C), 110.49 (CH_2), 111.25 (CH), 111.69 (CH), 117.83 (CH), 119.45 (CH), 120.75 (CH), 123.75 (C), 124.18 (C), 125.33 (CH), 126.18 (CH), 139.34 (C), 139.83 (C), 141.40 (C), 149.97 (CH). MS (EI): m/z (%) = 235 (53) [M^+], 220 (100), 205 (28), 204 (235), 180 (13), 167 (11).

(*R*)-2′-*O*-Acetyl-4-*O*-methylneocarazostatin B [(*R*)-1-(2-acetoxypropyl)-3,4-dimethoxy-2-methyl-6-(3-methylbut-2-enyl)carbazole] (13)

Method A:

The *tert*-prenylstannane **9** (56.0 mg, 156 µmol) and caesium fluoride (22.0 mg, 145 µmol) were added at room temperature to a solution of (*R*)-6-bromo-1-(2-acetoxypropyl)-3,4-dimethoxy-2-methylcarbazole (**12**) (51.0 mg, 121 µmol), $Pd(dba)_2$ (11 mg, 19 µmol) and P(*t*-Bu)$_3$ (9.0 mg, 44 µmol) in dry DMF (2.5 mL) under an argon atmosphere. The mixture was stirred under an argon atmosphere for 24 h (TLC control showed complete conversion). The mixture was diluted with diethyl ether and washed with a saturated aqueous solution of potassium fluoride, water (2 ×) and brine. The water washings were extracted with diethyl ether and the combined organic layers were dried over sodium sulfate. The solvent was evaporated and the crude product was further purified by column chromatography on silica gel (petroleum ether–acetone 100:1) to provide (*R*)-2′-O-acetyl-4-O-methylneocarazostatin B (**13**) (38.5 mg, 78%) as beige crystals. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.29 (d, *J* = 6.3 Hz, 3 H), 1.78 (s, 3 H), 1.80 (s, 3 H), 2.16 (s, 3 H), 2.41 (s, 3 H), 3.02 (dd, *J* = 13.7, 10.0 Hz, 1 H), 3.25 (dd, *J* = 13.7, 3.1 Hz, 1 H), 3.51 (d, *J* = 7.3 Hz, 2 H), 3.89 (s, 3 H), 4.11 (s, 3 H), 5.04 (m, 1 H), 5.45 (m, 1 H), 7.21 (dd, *J* = 8.3, 1.6 Hz, 1 H), 7.40 (d, *J* = 8.3 Hz, 1 H), 8.01 (s, 1 H), 9.47 (br s, 1 H). MS (EI): *m*/*z* (%) = 410 (28), 409 (100) [M^+], 394 (33), 349 (23), 335 (18), 334 (71), 323 (18), 322 (79), 306 (8), 278 (10), 174 (10), 167 (9), 159 (7), 69 (16). For further spectroscopic data, see: W. Fröhner, K. R. Reddy, H.-J. Knölker, *Heterocycles*, 2007, **74**, 895.

Method B:

A solution of (*R*)-6-bromo-1-(2-acetoxypropyl)-3,4-dimethoxy-2-methylcarbazole (**12**) (40.0 mg, 95.2 µmol), $Pd(dba)_2$ (11.3 mg, 19.7 µmol) and P(*t*-Bu)$_3$ (8.0 mg, 40 µmol) in dry DMF (2 mL) was stirred at room temperature under an argon atmosphere for 5 min (the colour had then changed from purple to olive). The *tert*-prenylboronate **11** (44.4 mg, 226 µmol) and caesium fluoride (16.2 mg, 107 µmol) were added and the mixture was stirred under an argon atmosphere for 5 days (TLC control showed complete conversion). The mixture was diluted with diethyl ether, poured into water and the layers were separated. The aqueous layer was extracted twice with diethyl ether. The combined organic layers were washed with water and brine and dried over sodium sulfate. The solvent was evaporated and the crude product was further purified by column chromatography on silica gel (petroleum ether–ethyl acetate 8:1) to provide (*R*)-2′-O-acetyl-4-O-methylneocarazostatin B (**13**) (33.0 mg, 85%) as beige crystals.

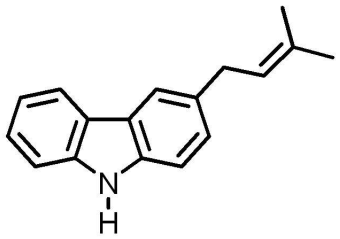
O-Methylsiamenol (7-methoxy-3-methyl-6-(3-methyl-2-butenyl)carbazole) (15)

A solution of 6-bromo-7-methoxy-3-methylcarbazole (**14**) (31.4 mg, 108 µmol), $Pd(dba)_2$ (13.8 mg, 24.0 µmol) and P(*t*-Bu)$_3$ (9.2 mg, 45 µmol) in a mixture of dry DMF (1.5 mL) and dry THF (0.75 mL) was stirred at room temperature under an argon atmosphere for 5 min (the colour had then changed from purple to olive). The *tert*-prenylboronate **11** (50.0 mg, 255 µmol) and caesium fluoride (40.2 mg, 265 µmol) were added and the mixture was stirred under an argon atmosphere for 4 days (TLC control showed complete conversion). The mixture was diluted with diethyl ether, poured into

water and the layers were separated. The aqueous layer was extracted with diethyl ether an the combined organic layers were washed with water and brine and dried over sodium sulfate. The solvent was evaporated and the crude product was further purified by column chromatography on silica gel (petroleum ether–dichloromethane, 1:2) to provide *O*-methylsiamenol (**15**) (17.2 mg, 57%) as beige crystals; mp 141.5 –142.5 °C. IR (ATR): ν = 3413, 3028, 2924, 2850, 2055, 1873, 1727, 1612, 1582, 1485, 1460, 1437, 1374, 1321, 1299, 1219, 1199, 1165, 1134, 1114, 1038, 1003, 891, 876, 847, 822, 804, 782, 585 cm^{-1}. ^1H NMR (500 MHz, acetone-d_6): δ = 1.74 (s, 3 H), 1.76 (s, 3H), 2.45 (s, 3 H), 3.41 (d, J = 7.3 Hz, 2 H), 3.89 (s, 3 H), 5.40 (m, 1 H), 7.00 (s, 1 H), 7.08 (dd, J = 8.2, 1.2 Hz, 1 H), 7.30 (d, J = 8.2 Hz, 1 H), 7.74 (br s, 1H), 7.76 (s, 1 H), 9.97 (br. s, 1 H). ^{13}C NMR and DEPT (125 MHz, acetone-d_6): δ = 17.83 (CH_3), 21.49 (CH_3), 25.99 (CH_3), 29.60 (CH_2), 55.82 (CH_3), 93.66 (CH), 111.04 (CH), 116.81 (C), 119.83 (CH), 120.88 (CH), 122.60 (C), 124.47 (C), 124.71 (CH), 125.94 (CH), 128.36 (C), 131.78 (C), 139.08 (C), 141.05 (C), 157.79 (C). MS (EI): m/z (%) = 279 [M^+] (100), 264 (91), 248 (12), 211 (31), 194 (39), 180 (46), 167 (17), 152 (20), 139 (12), 97 (25).

_O_-Methylmicromeline (6-Methoxy-5-(3-methyl-but-2-enyl)carbazole-3-carbaldehyde) (17)

A solution of 5-bromo-6-methoxy-9*H*-carbazole-3-carbaldehyde (**16**) (20.4 mg, 67.1 µmol), $Pd(dba)_2$ (8.6 mg, 15 µmol) and P(*t*-Bu)$_3$ (5.5 mg, 27 µmol) in dry DMF (2 mL) was stirred at room temperature under an argon atmosphere for 1 min (the colour had then changed from purple to olive). The *tert*-prenylboronate **11** (23.0 mg, 117 µmol), caesium fluoride (22.2 mg, 146 µmol) and dry THF (1 mL) were added and the mixture was stirred under an argon atmosphere for 4 days (TLC control showed complete conversion). The mixture was diluted with dichloromethane, poured into water and the layers were separated. The organic layer was washed with water and brine and dried over sodium sulfate. The solvent was evaporated and the crude product was further purified by column chromatography on silica gel (petroleum ether–dichloromethane, 1:2) to provide *O*-methyl-micromeline (**17**) (16.3 mg, 83%) as colourless crystals; mp 200.5–202 °C. UV (MeOH): λ = 232, 248 (sh), 276, 296, 337 cm^{-1}. IR (ATR): ν = 3311, 3163, 3035, 2955, 2922, 2852, 2730, 2116, 1808, 1735, 1696, 1666, 1623, 1579, 1567, 1542, 1500, 1465, 1374, 1352, 1307, 1292, 1273, 1230, 1213, 1168, 1122, 1085, 1029, 944, 900, 850, 803, 780, 716, 651, 575 cm^{-1}. ^1H NMR (500 MHz, acetone-d_6): δ = 1.68 (d, J = 1.1 Hz, 3 H), 1.98 (s, 3 H), 3.90 (s, 3 H), 4.02 (d, J = 6.3 Hz, 2 H), 5.28 (m, 1 H), 7.24 (d, J = 8.7 Hz, 1 H), 7.42 (d, J = 8.7 Hz, 1 H), 7.62 (d, J = 8.4 Hz, 1 H), 7.94 (dd, J = 8.4, 1.2 Hz, 1 H), 8.66 (d, J = 1.2 Hz, 1 H), 10.06 (s, 1 H), 10.75 (br. s, 1 H). ^{13}C NMR and DEPT (125 MHz, acetone-d_6): δ = 18.41 (CH_3), 25.84 (CH_3), 26.17 (CH_2), 57.73 (CH_3), 110.10 (CH), 111.93 (CH), 113.59 (CH), 123.03 (CH), 123.22 (C), 123.98 (C). 125.61 (C), 127.06 (CH), 127.42 (CH), 129.60 (C), 133.07 (C), 136.90 (C), 145.72 (C), 152.41 (C), 191.88 (CHO). MS (EI): m/z (%) = 294 (21), 293 (100) [M^+], 262 (10), 250 (17), 234 (19), 217 (12), 208 (31), 131 (10), 180 (29), 167 (12), 139 (10). HRMS: m/z calcd for $C_{19}H_{19}NO_2$ [M^+]: 293.1416; found: 293.1423. Elemental analysis calcd for $C_{19}H_{19}NO_2$: C 77.79, H 6.53, N 4.77; found: C 72.71, H 4.32, N 4.13.

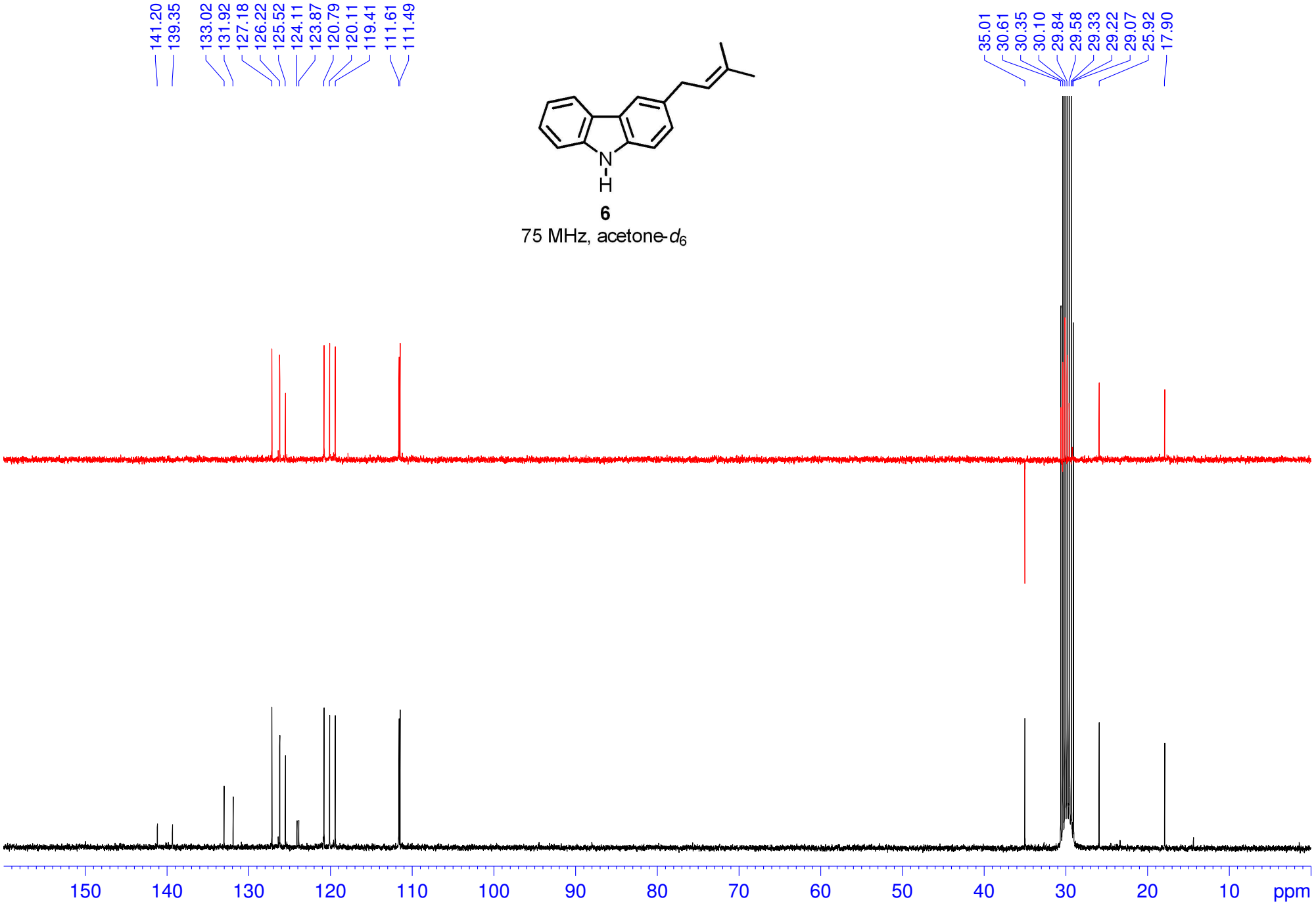


6

500 MHz, acetone-d_6

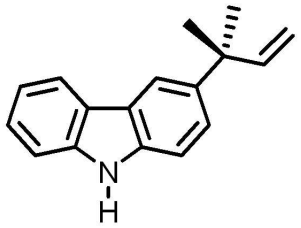
Sep 9, 2013 (10:25:42 AM) CT247 10 1 D:\NMR ClaudiaThomas... Page 1/1

Peak	ν(F1) [ppm]	ν(F1) [Hz]	Intensity [abs]	Annotation
1	10.2133	5108.0044	202329.62	
2	8.0815	4041.8217	2032043.88	
3	8.0659	4034.0196	2002831.38	
4	7.9095	3955.7989	2737983.88	
5	7.9081	3955.0987	2993551.38	
6	7.4803	3741.1420	1806851.75	
7	7.4640	3732.9898	2426218.25	
8	7.4167	3709.3335	2495892.25	
9	7.4002	3701.0813	2822706.38	
10	7.3668	3684.3769	1140661.75	
11	7.3646	3683.2766	1315691.88	
12	7.3526	3677.2750	1581755.88	
13	7.3505	3676.2248	2091968.50	
14	7.3364	3669.1729	1156432.38	
15	7.3341	3668.0226	1014214.25	
16	7.2299	3615.9088	1809782.62	
17	7.2267	3614.3083	1834037.12	
18	7.2134	3607.6566	1523338.25	
19	7.2102	3606.0561	1513401.12	
20	7.1587	3580.2993	1445011.75	
21	7.1569	3579.3991	1246358.38	
22	7.1429	3572.3972	2500091.25	
23	7.1289	3565.3954	1196095.50	
24	7.1271	3564.4951	1215044.88	
25	5.4421	2721.7717	240813.25	
26	5.4394	2720.4213	512757.62	
27	5.4365	2718.9709	709866.50	
28	5.4337	2717.5706	537875.75	
29	5.4308	2716.1202	368763.12	
30	5.4275	2714.4697	540859.50	
31	5.4246	2713.0194	895810.75	
32	5.4218	2711.6190	1393580.88	
33	5.4189	2710.1686	1142381.75	
34	5.4161	2708.7682	559459.50	
35	5.4129	2707.1678	361534.25	
36	5.4099	2705.6674	578503.38	
37	5.4070	2704.2170	615523.12	
38	5.4042	2702.8167	552886.25	
39	5.4014	2701.4163	245987.75	
40	3.5068	1753.8650	2855850.50	
41	3.4921	1746.5131	2796692.12	
42	2.0500	1025.2719	41208663.62	
43	1.7833	891.8865	9971001.62	
44	1.7494	874.9320	9017905.12	
45	1.7475	873.9817	9073567.38	



6

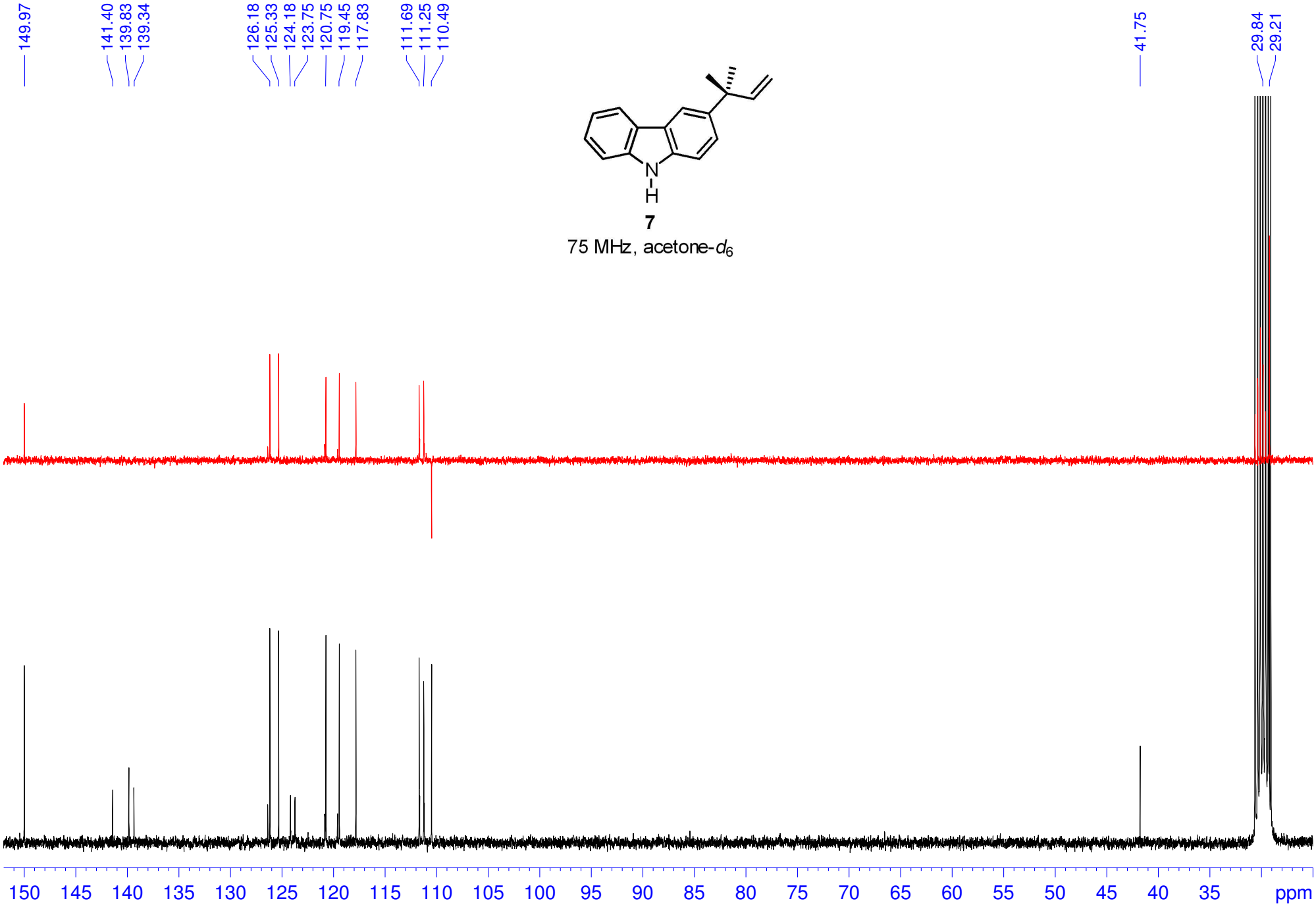
75 MHz, acetone-d_6

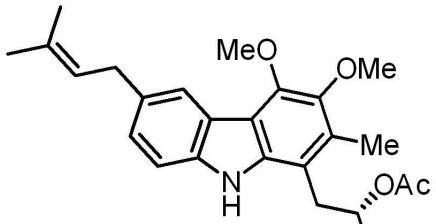


7

500 MHz, acetone-d_6

Peak	ν(F1) [ppm]	ν(F1) [Hz]	Intensity [abs]	Annotation
1	10.2286	5115.6300	234837.00	
2	8.1179	4060.0056	4792691.88	
3	8.1030	4052.5536	2301321.75	
4	7.4886	3745.2737	1814202.62	
5	7.4724	3737.1716	2377887.88	
6	7.4406	3721.2675	837788.00	
7	7.4237	3712.8153	4109640.62	
8	7.4168	3709.3644	3125610.25	
9	7.4134	3707.6640	3195394.38	
10	7.3996	3700.7622	637428.25	
11	7.3963	3699.1117	899506.88	
12	7.3704	3686.1584	1051847.38	
13	7.3686	3685.2581	1207476.75	
14	7.3543	3678.1063	1972838.50	
15	7.3400	3670.9544	949069.38	
16	7.3382	3670.0542	1026535.25	
17	7.1656	3583.7317	1367256.88	
18	7.1511	3576.4799	2243191.75	
19	7.1358	3568.8279	1113162.62	
20	6.1783	3089.9534	1572898.75	
21	6.1571	3079.3506	1685246.12	
22	6.1434	3072.4988	1635650.25	
23	6.1222	3061.8961	1748513.88	
24	5.1143	2557.8150	1819015.12	
25	5.1114	2556.3646	1956435.88	
26	5.0793	2540.3105	1632929.38	
27	5.0765	2538.9101	1992095.25	
28	5.0497	2525.5066	1944221.12	
29	5.0469	2524.1062	2038373.88	
30	5.0285	2514.9039	1947183.38	
31	5.0257	2513.5035	1836523.88	
32	2.0500	1025.2666	28766067.88	
33	1.5024	751.3954	40624675.75	



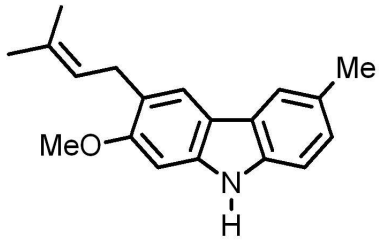


13

300 MHz, $CDCl_3$

Peak	ν(F1) [ppm]	ν(F1) [Hz]	Intensity [abs]	Annotation
1	9.4690	2841.9311	696475.45	
2	8.0107	2404.2515	1191947.08	
3	7.4159	2225.7341	1007841.84	
4	7.3883	2217.4505	1297533.91	
5	7.2600	2178.9439	2738787.70	
6	7.2283	2169.4297	783817.05	
7	7.2231	2167.8691	741739.98	
8	7.2007	2161.1462	593449.34	
9	7.1955	2159.5855	559508.45	
10	5.4776	1643.9921	203059.75	
11	5.4734	1642.7316	254789.09	
12	5.4690	1641.4110	215904.64	
13	5.4635	1639.7603	163376.09	
14	5.4534	1636.7290	428753.61	
15	5.4490	1635.4084	522591.03	
16	5.4446	1634.0878	416866.30	
17	5.4290	1629.4058	227938.77	
18	5.4247	1628.1153	259293.25	
19	5.4204	1626.8247	203285.23	
20	5.0932	1528.6222	61484.34	
21	5.0826	1525.4408	90198.38	
22	5.0725	1522.4095	197241.11	
23	5.0614	1519.0780	277350.47	
24	5.0512	1516.0167	265547.05	
25	5.0400	1512.6552	415837.23	
26	5.0288	1509.2938	268062.39	
27	5.0187	1506.2625	284079.75	
28	5.0075	1502.9010	200312.34	
29	4.9979	1500.0198	83635.22	
30	4.9870	1496.7484	60491.55	
31	4.1139	1234.7048	8626706.36	
32	3.8874	1166.7254	8485450.23	
33	3.5269	1058.5285	1134794.70	
34	3.5027	1051.2654	1110541.28	
35	3.2813	984.8166	338515.92	
36	3.2710	981.7253	344204.88	
37	3.2356	971.1007	500676.28	
38	3.2253	968.0093	471776.70	
39	3.0553	916.9872	611419.62	
40	3.0221	907.0229	612792.84	
41	3.0097	903.3013	445243.86	
42	2.9765	893.3370	414230.36	
43	2.4074	722.5330	6940333.59	
44	2.1621	648.9111	8135037.16	
45	1.7955	538.8834	4251849.52	

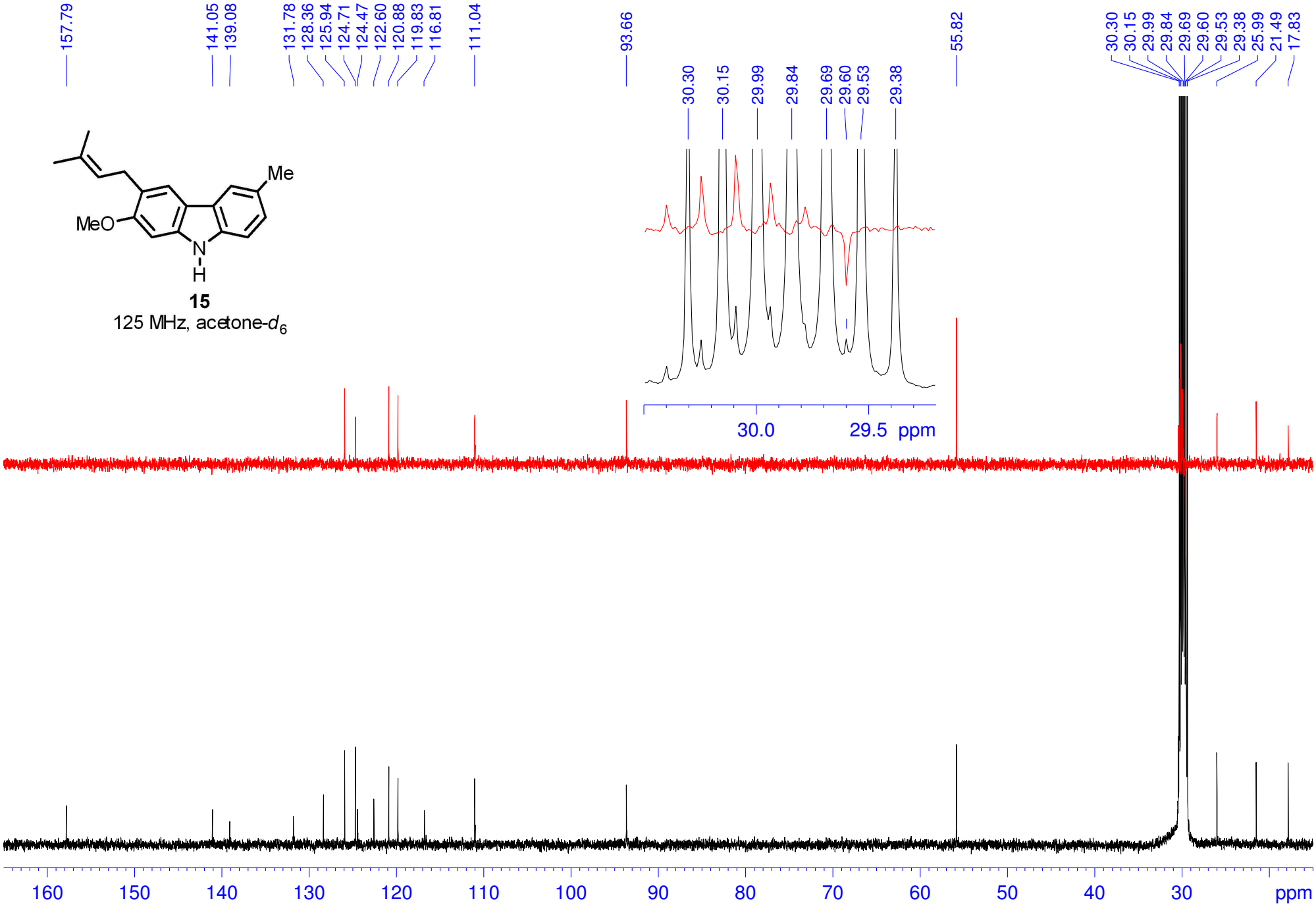
Peak	ν(F1) [ppm]	ν(F1) [Hz]	Intensity [abs]	Annotation
46	1.7756	532.9108	3783730.11	
47	1.3045	391.5196	2948334.91	
48	1.2835	385.2169	3113920.86	
49	1.2617	378.6740	2209727.97	

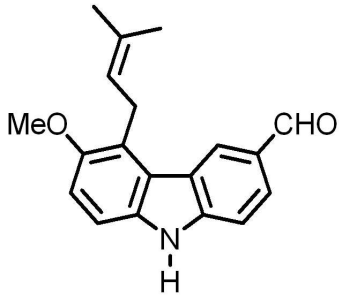


15

500 MHz, acetone-d_6

Peak	ν(F1) [ppm]	ν(F1) [Hz]	Intensity [abs]	Annotation
1	9.9654	4983.9958	358425.81	
2	7.7631	3882.5594	2603365.44	
3	7.7447	3873.3570	1788742.62	
4	7.3062	3654.0500	1438400.56	
5	7.2899	3645.8979	1690311.69	
6	7.0915	3546.6721	979805.44	
7	7.0891	3545.4718	1009818.50	
8	7.0752	3538.5200	865020.31	
9	7.0729	3537.3697	873402.25	
10	7.0029	3502.3606	2974328.50	
11	5.4128	2707.1038	291131.12	
12	5.4102	2705.8035	375267.12	
13	5.4074	2704.4031	343048.50	
14	5.4045	2702.9527	231266.06	
15	5.3982	2699.8019	561773.56	
16	5.3954	2698.4016	810100.31	
17	5.3927	2697.0512	647793.69	
18	5.3867	2694.0504	258290.31	
19	5.3835	2692.4500	355001.69	
20	5.3807	2691.0497	408077.19	
21	5.3780	2689.6993	349656.94	
22	3.8925	1946.7561	11979984.12	
23	3.4209	1710.8948	1816200.81	
24	3.4063	1703.5929	1765150.31	
25	2.4490	1224.8184	9140394.00	
26	2.0587	1029.6177	10300503.31	
27	2.0543	1027.4171	20236548.25	
28	2.0500	1025.2666	29413406.44	
29	2.0456	1023.0660	20878677.19	
30	2.0412	1020.8654	11052389.00	
31	1.7583	879.3786	6330299.56	
32	1.7366	868.5258	5600288.81	





17

500 MHz, acetone-d_6

Peak	ν(F1) [ppm]	ν(F1) [Hz]	Intensity [abs]	Annotation
1	10.7492	5375.9977	20273.08	
2	10.0597	5031.1581	512877.61	
3	8.6563	4329.2756	278958.94	
4	8.6545	4328.3753	280328.78	
5	7.9486	3975.3336	152417.95	
6	7.9458	3973.9332	146173.88	
7	7.9317	3966.8814	155028.16	
8	7.9289	3965.4810	161120.80	
9	7.6280	3814.9919	226968.53	
10	7.6112	3806.5897	206475.61	
11	7.4300	3715.9661	209436.09	
12	7.4127	3707.3139	265057.92	
13	7.2502	3626.0427	237666.91	
14	7.2327	3617.2905	207274.56	
15	5.2905	2645.9379	55258.61	
16	5.2801	2640.7366	94937.09	
17	5.2775	2639.4362	111129.39	
18	5.2748	2638.0859	88896.45	
19	5.2645	2632.9345	59392.89	
20	4.0251	2013.0734	230375.59	
21	4.0126	2006.8218	222416.72	
22	3.8979	1949.4568	1754431.17	
23	2.0587	1029.6177	2246457.33	
24	2.0544	1027.4671	4185907.16	
25	2.0501	1025.3166	5837982.14	
26	2.0457	1023.1160	4145289.53	
27	2.0413	1020.9154	2173322.33	
28	1.9826	991.5578	836087.17	
29	1.6819	841.1687	731083.12	
30	1.6798	840.1184	704121.44