Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Synthesis of Imidazo[1,2-*a*]benzoazepines by Alkyne-Carbonyl-Metathesis

Maryam Sobhani [a], Rúben Manuel Figueira de Abreu [a],Alexander Villinger [a], Peter Ehlers [a]*, Peter Langer [a,b]*

[a] Universität Rostock, Institut für Chemie, A.-Einstein-Str.3a, 18059 Rostock,Germany
Tel.: +49 381 498 6410, Fax: +49 381 498 6412
[b] Leibniz Institut für Katalyse an der Universität Rostock, A.-Einstein-Str.29a, 18059 Rostock,Germany

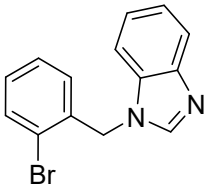
*Corresponding authors: peter.ehlers@uni-rostock.de, peter.langer@uni-rostock.de

Contents

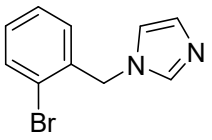
Experimental procedures

Table S1: *N*-alkylation of imidazole and benzimidazoles.

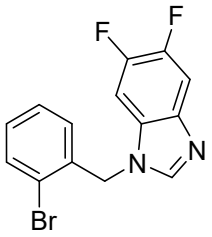
1a-d **2** **3a-d**



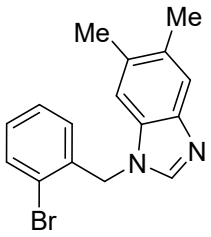
3a, 87%



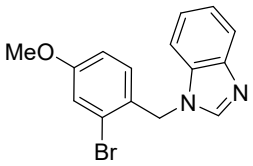
3b, 66%



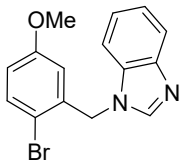
3c, 77%



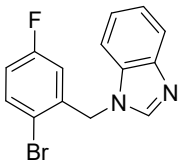
3d, 93%



3e, 93%



3f, 84%



3g, 78%

Single-crystal X-ray diffraction data

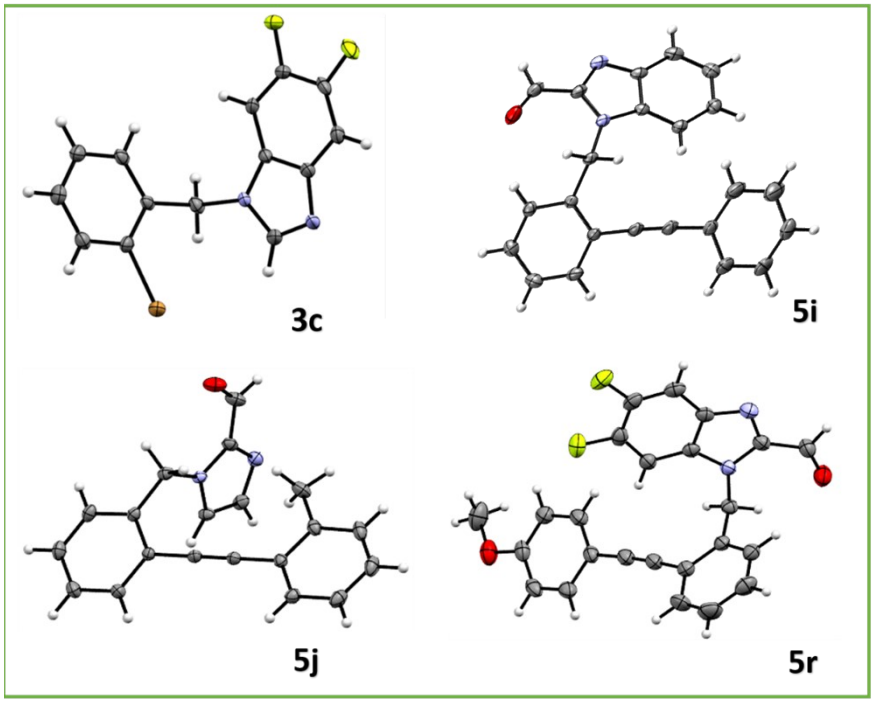


Figure S1: ORTEP diagrams of **3c**, **5i**, **5j** and **5r** (determined from X-ray structural analysis at 123 K). The thermal ellipsoids are drawn at the 50 % probability level.

Table S2: Crystallographic details of products, **3c**, **5i**, **5j,** and **5r**.

	3c	**5i**	**5j**	**5r**
Chem. Formula	$C_{14}H_9BrF_2N_2$	$C_{23}H_{16}N_2O$	$C_{20}H_{16}N_2O$	$C_{24}H_{16}F_2N_2O_2$
Form. Weight [g mol^{-1}]	323.14	336.38	300.35	402.39
Cryst. system	monoclinic	monoclinic	triclinic	triclinic
Cryt. descript.	needle	needle	block	block
Space group (Hall group)	P 21/c (-P 2ybc)	P 21/n (-P 2yn)	P -1 (-P 1)	P -1 (-P 1)
Color	colourless	Colourless	colourless	colourless
a [Å]	4.46200	4.4491 (2)	7.6764(15)	9.225(2)
b [Å]	19.53900	19.9827 (11)	10.420(2)	10.669(2)
c [Å]	27.23300	19.1892(11)	10.633(2)	20.170(4)
α [°]	90	90	96.896(6)	91.526(6)
β [°]	93.3500	95.304(2)	102.772(5	102.762(6)
γ [°]	90	90	106.607(5)	90.111(6)
V [Å^3]	2370	1698.71(16)	779.4(3)	1935.3(7)
Z	8	4	2	4
N_{ref}	6269	4958	5636	9333
θ [°]	28.998	29.999	32.499	27.999
h,k,l_{max}	6,26,37	6,28,26	11,15,16	12,14,26
Dx [g cm^{-3}]	1.811	1.315	1.280	1.381
μ [mm^{-1}]	3.480	0.082	0.080	0.102
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073	0.71073
T [K]	123	123	123	173
F(000)	1280.0	704.0	316.0	832.0
Npar	343	235	209	543
R	0.0458(4316	0.0435(3856)	0.0419(4989)	0.0474(5159)
w*R*	0.0891(6269)	0.1168(4949)	0.1235(5636)	0.1445(9333)
S	1.018	1.043	1.026	1.024

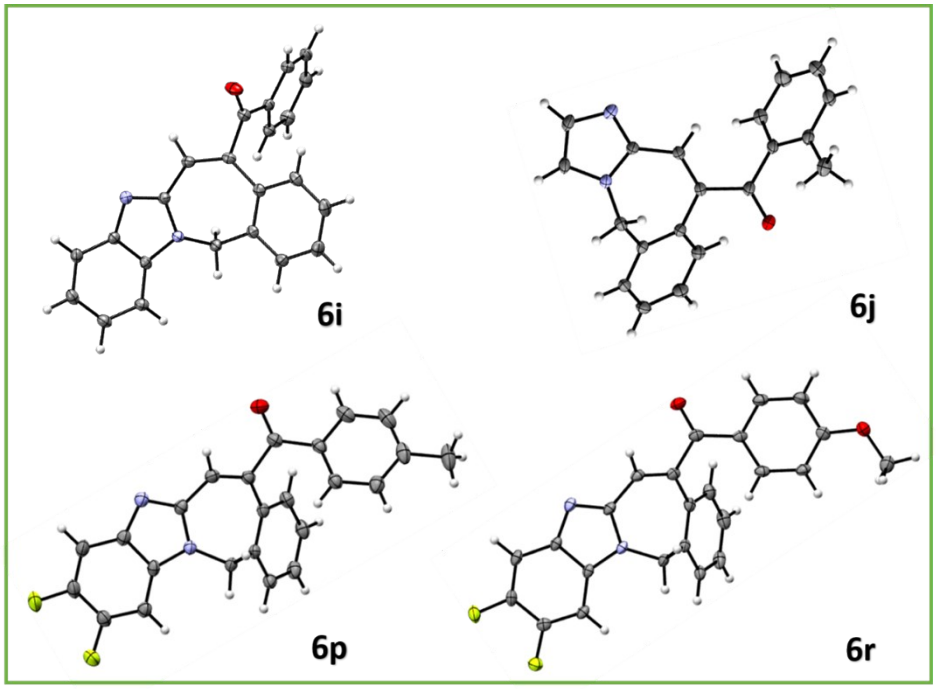


Figure S2: ORTEP diagrams of **6i**, **6j**, **6r** (determined from X-ray structural analysis at 123 K) and **6p** (determined from X-ray structural analysis at 173 K). The thermal ellipsoids are drawn at the 50 % probability level.

Table S3: Crystallographic details of products, **6i**, **6j**, **6p** and **6r**.

	6i	**6j**	**6p**	**6r**
Chem. Formula	$C_{23}H_{16}N_2O$	$C_{20}H_{16}N_2O$	$C_{24}H_{16}F_2N_2O$	$C_{24}H_{16}F_2N_2O_2$
Form. Weight [g mol^{-1}]	336.38	300.35	386.39	402.39
Cryst. system	monoclinic	monoclinic	monoclinic	triclinic
Cryt. descript.	Block	Block	block	needle
Space group (Hall group)	P 21/n (-P 2yn)	P 21/n (-P 2yn)	C 2 (C 2y)	P -1 (-P 1)
Color	colourless	colourless	colourless	colourless
a [Å]	11.034(2)	8.2236(4)	23.3551(19)	6.6890(13)
b [Å]	14.502(3)	13.2218(7)	6.4154(5)	11.222(2)
c [Å]	11.291(2)	14.5288(7)	14.5468(12)	13.775(3)
α [°]	90	90	90	109.827(7)
β [°]	117.137(5)	102.306(2)	124.943(2)	97.404(7)
γ [°]	90	90	90	104.970(7)
V [Å^3]	1607.9(5)	1543.43(13	1786.6(3)	912.6(3)
Z	4	4	4	2
N_{ref}	3800	4085	5188	4376
θ [°]	27.995	28.999	29.999	27.996
h,k,l_{max}	13,19,14	11,18,19	32,9,20	0,0,0
Dx [g cm^{-3}]	1.390	1.293	1.436	1.464
μ [mm^{-1}]	0.086	0.081	0.103	0.108
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073	0.71073
T [K]	123	123	173	123
F(000)	704.0	632.0	800.0	416.0
Npar	235	209	264	272
R	0.0476(2905)	0.0500(2898)	0.0395(4600)	0.0667(3432)
w*R*	0.1281(3800)	0.1266(4085)	0.0998(5188)	0.2042(4376)
S	1.029	1.018	1.022	1.074

6j crystallizes in monoclinic space group P 21/n (-P 2yn) including four molecules in each unit cell. The dihedral angle between imidazole and fused benzene plane is 57.6 (0) °, whereas the imidazole ring displays a torsion angle of 7.0 (7°) (C(12)−C(11)−N(2)−C(8)), while the fused benzene ring shows a torsion angle of -0.8 (9)° (C(1)−C(2)−C(7)−C(8)) (Figure S5, a). However, **6j** crystalized in a complex packing motif the shortest distance between two adjacent molecules ranges from 2.79-2.81 Å. Moreover, the main hydrogen bonds observed are formed by imidazole nitrogen and the benzoyl moiety (2.55 Å, Figure S5, b). In comparison to analogous benzoimidazole based product **6g**, **6a** has a slightly increased dihedral angle by 13°. Benzimidazole derived product **6i** exhibits a smaller dihedral angle between the benzimidazole and benzene planes (44.7°) rather than **6j**. Hence, respective torsion angles are 7.7 (5)° (C(1)−C(2)−N(2)−C(10)) and fused benzene has a torsion angle of 9.1 (4)° (C(3)−C(4)−C(9)−C(10)) (Figure S4, a). This results in a face to face *π*-*π* interaction of 3.54 Å among phenyl ring of benzimidazoles moieties, and a face to edge C–H/*π* interaction between the fused benzene ring of the imidazoazepines motif (2.87 Å). Additional hydrogen bonding interactions of the type C-H···N (2.67 Å) are located between two adjacent imidazole molecules along the a-axis (Figure S4, b).

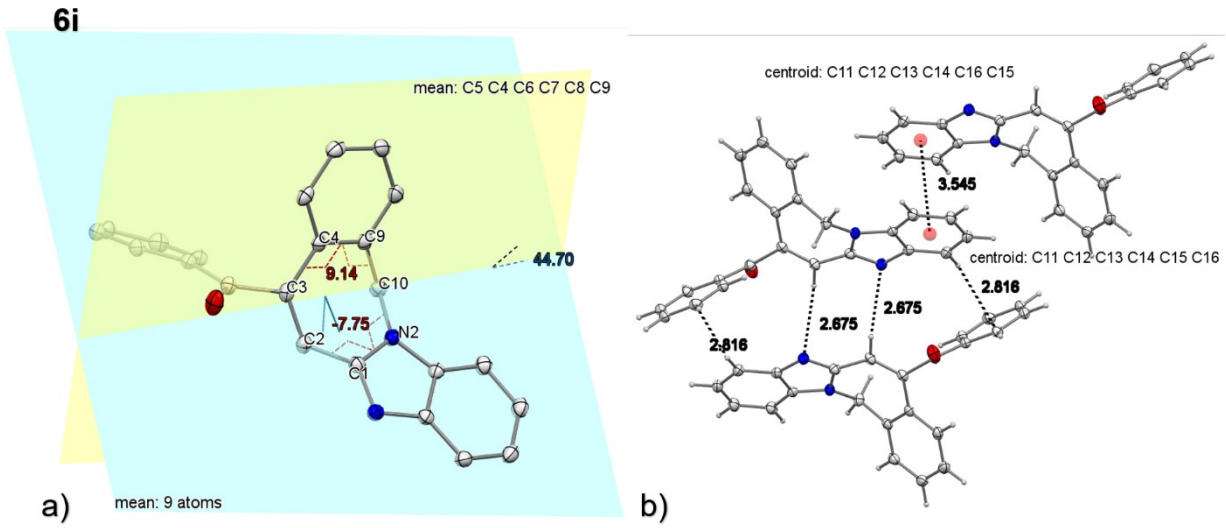


Figure S4: Crystal structure of **6i** a) with crystallographic labelling number. The dihedral angle formed between the plane of the imidazole ring (blue) and benzene ring (yellow) and all hydrogens are omitted for clarity. b) The 3D framework of the title compound is connected by hydrogen bonding, C-H···π and π···π stacking interactions and their distances.

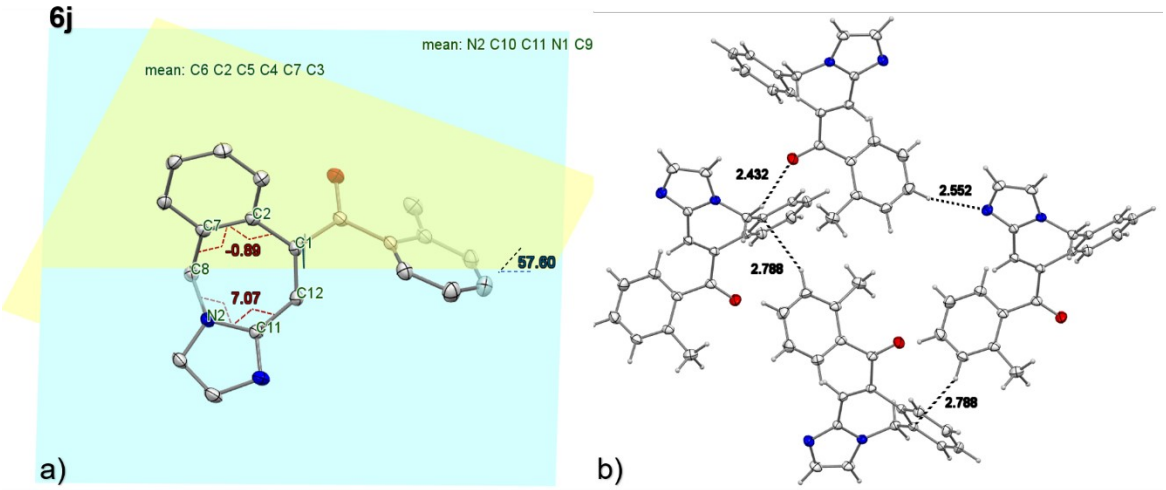


Figure S5: Crystal structure of **6j** a) with crystallographic labelling number. The dihedral angle formed between the plane of the imidazole ring (blue) and benzene ring (yellow) and all hydrogens are omitted for clarity. b) The 3D framework of the title compound is connected by hydrogen bonding interactions and their distances.

Experimental data

1-(2-Bromobenzyl)-1*H*-benzo[*d*]imidazole (3a)

According to general procedure A, compound **3a** was obtained as a white solid in 87 % yield (2.13 g, 7.41 mmol, R_f = 0.15 ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.89 (s, 1H), 7.82 – 7.75 (m, 1H), 7.59 – 7.52 (m, 1H), 7.26 – 7.17 (m, 3H), 7.17 – 7.07 (m, 2H), 6.77 – 6.70 (m, 1H), 5.35 (d, *J* = 0.7 Hz, 2H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$): δ = 43.9, 143.5, 134.8, 133.9, 133.3, 129.9, 128.6, 128.1, 123.3, 122.9, 122.5, 120.6, 110.0, 48.9. HRMS (ESI-TOF) m/z = calcd. for $C_{14}H_{12}BrN_2$ $[M + H]^+$ 287.0184, found: 287.0187.[1]

1-(2-Bromobenzyl)-1*H*-imidazole (3b)

According to general procedure A, compound **3b** was obtained as a white solid in 66 % yield (2.45 g, 10.4 mmol, R_f = 0.10 ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.58 – 7.52 (m, 2H), 7.27 – 7.12 (m, 2H), 7.07 (m, 1H), 6.92 – 6.84 (m, 2H), 5.17 (s, 2H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$): δ = 137.7, 135.7, 133.1, 129.9, 129.8, 129.0, 128.1, 123.0, 119.4, 50.7. HRMS (ESI-TOF) m/z = calcd. for $C_{10}H_{10}BrN_2$ $[M + H]^+$ 237.0027, found: 237.0032.[1]

1-(2-Bromobenzyl)-5,6-difluoro-1*H*-benzo[*d*]imidazole (3c)

According to general procedure A, compound **3c** was obtained as a white solid in 77 % yield (2.55 g, 8.87 mmol, R_f = 0.2 heptane/ethyl acetate, 1:2); mp = 111 – 113 °C. IR (ATR):

[1] J. K. Laha, N. Dayal, S. Singh, R. Bhimpuria, *European J. Org. Chem.* **2014**, *2014*, 5469–5475.

$\tilde{\nu}$ [cm^{-1}] = 1496 (m), 1479 (vs), 1467 (vs), 1436 (m), 1294 (m), 1215 (s), 1170 (s), 1123 (s), 1024 (m), 937 (w), 853 (vs), 760 (s). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.91 (s, 1H), 7.60 – 7.48 (m, 2H), 7.22 – 7.11 (m, 2H), 7.01 (dd, *J* = 9.7, *J* = 6.9 Hz, 1H), 6.81 – 6.75 (m, 1H), 5.32 (s, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -140.27 (d, *J* = 20.8 Hz), -142.99 (d, *J* = 20.6 Hz). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$): δ = 148.7 (dd, *J* = 244.3, *J* = 15.7 Hz), 148.2 (dd, *J* = 241.1, *J* = 15.0 Hz), 144.8, 139.0 (d, *J* = 9.2 Hz), 134.0, 133.6, 130.3, 128.8, 128.3, 123.2, 107.9 (dd, *J* = 19.8, 1.3 Hz), 98.2 (d, *J* = 23.2 Hz), 49.4 (signal of one carbon is absent, which may relate to signal overlap). MS (EI, 70 eV): m/z (%) = 324 (M^+, 67), 244 (8), 234 (49), 242 (14), 241 (19), 172 (7), 171 (98), 169 (100), 121 (14), 90 (24). HRMS (EI) m/z = calcd. for $C_{14}H_9{}^{79}BrF_2N_2$ $[M]^+$ 321.99117, found: 321.99133; calcd. for $C_{14}H_9{}^{81}BrF_2N_2$ $[M]^+$ 323.98912, found: 323.98950.

1-(2-Bromobenzyl)-5,6-dimethyl-1*H*-benzo[*d*]imidazole (3d)

According to general procedure A, compound **3d** was obtained as a pale-yellow solid in 93 % yield (1.6 g, 4.5 mmol, R_f = 0.2 heptane/ethyl acetate, 1:2); mp = 130 °C. IR (ATR):$\tilde{\nu}$ [cm^{-1}] = 1496 (vs),1463 (vs), 1432 (s), 1350 (m), 1325 (m), 1224 (m), 1181 (m), 1022 (s), 837 (s), 752 (s). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.78 (s, 1H), 7.57 – 7.54 (m, 1H), 7.53 (d, *J* = 1.2 Hz, 1H), 7.15 – 7.06 (m, 2H), 6.98 (s, 1H), 6.70 – 6.63 (m, 1H), 5.30 (s, 2H), 2.30 (s, 3H), 2.26 (s, 3H). ^{13}C {^{1}H} NMR (63 MHz, $CDCl_3$): δ = 142.6, 142.2, 135.0, 133.1, 132.6, 132.4, 131.5, 129.7, 128.3, 128.0, 122.6, 120.4, 110.0, 48.7, 20.6, 20.3. MS (EI, 70 eV): m/z (%) = 316 (M^+, 98), 315 (25), 314 (99), 236 (18), 235 (100), 233 (14), 220 (24), 171 (76), 169 (77). HRMS (EI): calcd. for $C_{16}H_{15}{}^{79}BrN_2$ $[M]^+$ 314.0413 found: 314.0408; calcd for $C_{16}H_{15}{}^{81}BrN_2$ $[M]^+$ 316.0392, found: 316.0392.

1-(2-Bromo-4-methoxybenzyl)-1*H*-benzo[*d*]imidazole (3e)

According to general procedure A, compound 3e was obtained as a white solid in 93 % yield (945 mg, 3.32 mmol, R_f = 0.25 , ethyl acetate); m.p.= 94 – 95 °C. IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 1603 (m), 1572 (m), 1487 (s), 1289 (s), 1228 (s), 1180 (s), 1036 (s), 1022 (s), 851 (s), 768 (s). ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 7.94 (s, 1H), 7.89 – 7.76 (m, 1H), 7.35 – 7.31 (m, 1H), 7.31 – 7.28 (m, 1H), 7.28 – 7.25 (m, 1H), 7.17 (d, *J* = 2.5 Hz, 1H), 6.88 – 6.83 (m, 1H), 6.76 (dd, *J* = 8.6, 2.5 Hz, 1H), 5.37 (s, 2H), 3.78 (s, 3H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$): δ [ppm] = 160.2, 143.9, 143.4, 134.0, 129.9, 126.5, 123.7, 123.3, 122.5, 120.6, 118.7, 114.0, 110.1, 55.7, 48.5. MS (EI, 70 eV): m/z (%) = 316 (38), 202 (8), 201 (99), 199 (100), 118 (9). HRMS (EI) m/z = calcd. for $C_{15}H_{13}{}^{79}BrN_2O$ $[M]^+$ 316.02058, found 316.02064; calcd. for $C_{15}H_{13}{}^{81}BrN_2O$ $[M]^+$ 318.01853, found 318.01878.

1-(2-Bromo-5-methoxybenzyl)-1*H*-benzo[*d*]imidazole (3f)

According to general procedure A, compound 3f was obtained as a white solid in 84 % yield (2.27 g, 7.18 mmol, R_f = 0.27, ethyl acetate); m.p.= 76 – 78 °C. IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 1596 (m), 1570 (m), 1467 (s), 1456 (s), 1285 (s), 1240 (s), 1228 (s), 840 (s), 820 (s), 739 (vs). ^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.87 (s, 1H), 7.77 – 7.73 (m, 1H), 7.43 (d, *J* = 8.8 Hz, 1H), 7.26 – 7.17 (m, 3H), 6.66 (dd, *J* = 8.8, 3.0 Hz, 1H), 6.29 (d, *J* = 3.0 Hz, 1H), 5.30 (s, 2H), 3.53 (s, 3H). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): δ [ppm] = 159.5, 143.8, 143.4, 135.7, 133.9, 123.4, 122.6, 120.6, 115.1, 114.9, 113.1, 110.1, 55.5, 49.0 (signal of one carbon is absent, which may relate to signal overlap). MS (EI, 70 eV): m/z (%) = 316 (30), 238 (22), 237 (100), 222 (19), 201 (37), 199 (38), 119 (14). HRMS (EI) m/z = calcd. for $C_{15}H_{13}{}^{79}BrN_2O$ $[M]^+$ 316.02058, found 316.02058; calcd. for $C_{15}H_{13}{}^{81}BrN_2O$ $[M]^+$ 318.01853, found 318.01867.

1-(2-Bromo-5-fluorobenzyl)-1*H*-benzo[*d*]imidazole (3g)

According to general procedure A, compound 3g was obtained as a white solid in 78 % yield (2.03 g, 6.64 mmol, R_f = 0.40, ethyl acetate); m.p.= 92 – 95 °C. IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 1469 (s), 1458 (s), 1413 (m), 1267 (s), 1203 (s), 1178 (m), 1030 (m), 853 (m), 832 (m), 739 (vs), 591 (s), 420 (s). ^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.83 (s, 1H), 7.76 – 7.71 (m, 1H), 7.46 (dd, *J* = 8.8, 5.1 Hz, 1H), 7.24 – 7.10 (m, 3H), 6.79 (td, *J* = 8.3, 3.0 Hz, 1H), 6.36 (dd, *J* = 8.9, 3.0 Hz, 1H), 5.26 (s, 2H). ^{19}F NMR (471 MHz, CDCl3): δ = -112.6. ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): δ [ppm] = 162.2 (d, *J* = 248.7 Hz), 143.7, 143.3, 137.0 (d, *J* = 7.0 Hz), 134.5 (d, *J* = 7.9 Hz), 133.6, 123.5, 122.7, 120.6, 117.0 (d, *J* = 22.5 Hz), 116.6 (d, *J* = 3.4 Hz), 115.6 (d, *J* = 24.2 Hz), 109.8, 48.6. MS (EI, 70 eV): m/z (%) = 305 (6), 304 (35), 225 (100), 224 (18), 223 (14), 189 (50), 187 (53), 112 (14), 108 (28), 107 (20). HRMS (ESI-TOF) m/z = calcd. for $C_{14}H_{11}BrN_2F$ $[M+H]^+$ 305.0089, found 305.0082.

1-(2-Bromobenzyl)-1*H*-benzo[*d*]imidazole-2-carbaldehyde (4a)

According to general procedure B, compound **4a** was obtained as a yellow solid in 77 % yield (3.87 g, 12.3 mmol, R_f = 0.19 heptane/ethyl acetate, 4:1); mp = 160-162 °C. IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 1690 (s), 1588 (m), 1490 (s), 1465 (s), 1434 (s), 1408 (m), 1283 (s), 1240 (s), 1149 (m), 1028 (s), 896 (s), 863 (s), 754 (vs). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 10.08 (s, 1H), 7.90 – 7.93 (m, 1H), 7.55 (dd, *J* = 1.5 Hz, *J* = 7.7 Hz, 1H), 7.33 – 7.37 (m, 2H), 7.24 – 7.28 (m, 1H), 7.00 – 7.08 (m, 3H), 5.87 (s, 2H).^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): δ = 184.8, 146.2, 143.0, 136.5, 135.1, 133.1, 129.3, 128.0, 127.4, 126.8, 124.6, 122.7, 122.2, 111.3, 48.3. MS (EI, 70 eV): *m*/*z* (%) = 314 (M^+, 26), 286 (112), 285 (79), 236 (20), 235 (93), 207(75), 206 (48), 205 (42), 171 (58), 169 (60). HRMS (EI) m/z = calcd. for $C_{15}H_{11}{}^{79}BrN_2O$ $[M]^+$ 314.0049, found: 314.0047, for $C_{15}H_{11}{}^{81}BrN_2O$ $[M]^+$ 316.0028, found: 316.0028.

1-(2-Bromobenzyl)-1*H*-imidazole-2-carbaldehyde (4b)

According to general procedure B, compound **4b** was obtained as a white solid in 53 % yield (1.40 g, 5.28 mmol), R_f = 0.12 heptane/ethyl acetate, 1:1). **1**H NMR (300 MHz, $CDCl_3$): δ = 9.82 (d, *J* = 1.0 Hz, 1H), 7.60 – 7.54 (m, 1H), 7.28 (d, *J* = 1.0 Hz, 1H), 7.25 – 7.19 (m, 1H), 7.19 – 7.15 (m, 1H), 7.14 – 7.09 (m, 1H), 6.90 – 6.85 (m, 1H), 5.69 (s, 2H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$): δ = 182.2, 143.5, 135.3, 133.2, 132.0, 130.0, 129.2, 128.1, 126.3, 123.3, 50.9. HRMS (ESI) m/z = calcd. for $C_{11}H_{10}BrN_2O$ $[M + H]^+$ 364.9977, found: 364.9978.[2]

1-(2-Bromobenzyl)-5,6-difluoro-1*H*-benzo[*d*]imidazole-2-carbaldehyde (4c)

According to general procedure B, compound **4c** was obtained as a yellow solid in 35 % yield (3.87 g, 12.3 mmol, R_f = 0.21 heptane/ethyl acetate, 4:1); mp = 168 – 173 °C. IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 1693 (s), 1590 (m), 1491 (s), 1463 (s), 1438 (s), 1411 (m), 1283 (s), 1240 (s), 1149 (m), 1028 (s), 896 (s), 863 (s), 754 (vs). **1**H NMR (300 MHz, $CDCl_3$): δ = 10.09 (s, 1H), 7.74 (dd, *J* = 9.8, *J* = 7.3 Hz, 1H), 7.67 – 7.61 (m, 1H), 7.21 – 7.06 (m, 3H), 6.46 – 6.40 (m, 1H), 5.91 (s, 2H). **19**F NMR (282 MHz, $CDCl_3$): δ = -132.21 (d, *J* = 20.3 Hz), -138.40 (d, *J* = 20.4 Hz). ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ = 184.0, 151.2 (dd, *J* = 251.6, *J* = 16.3 Hz), 149.7 (dd, *J* = 246.7, *J* = 15.7 Hz), 147.5 (d, *J* = 3.3 Hz), 138.3 (d, *J* = 10.6 Hz), 134.5, 133.4, 132.3 (d, *J* = 10.8 Hz), 129.8, 128.2, 127.0, 122.4, 109.5 (dd, *J* = 19.4, *J* = 1.7 Hz), 99.2 (d, *J* = 23.3 Hz), 48.7. MS (EI, 70 eV): m/z (%) = 350 (M^+, 26), 323 (62), 321 (59), 272 (19), 271 (100), 244 (11), 243 (79), 242 (50), 241 (42), 215 (12), 171 (72). HRMS (EI) m/z = calcd. for $C_{15}H_9BrF_2N_2O$ $[M]^+$ 349.98608, found: 349.98545.

1-(2-Bromobenzyl)-5,6-dimethyl-1*H*-benzo[*d*]imidazole-2-carbaldehyde (4d)

According to general procedure B, compound **4d** was obtained as a white solid in 43 % yield. (600 mg, 1.8 mmol, R_f = 0.20, heptane/ethyl acetate, 3:1); mp: 155 -157 °C. IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 1688 (vs),1484 (s), 1463 (m), 1434 (s), 1409 (s), 1245 (s), 1020 (s), 892 (s), 837 (m), 775 (vs). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 10.01 (s, 1H), 7.64 (s, 1H), 7.57 – 7.53 (m, 1H), 7.09 – 6.98 (m, 3H), 6.28 – 6.23 (m, 1H), 5.81 (s, 2H), 2.33 (s, 3H), 2.28 (s, 3H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$): δ = 184.4, 145.6, 141.8, 137.9, 135.3, 135.2, 134.3, 132.9, 129.1, 127.9, 126.6, 122.1, 121.9, 110.7, 48.2, 21.0, 20.4. MS (EI, 70 eV): m/z (%) =344 (M^+, 41), 343 (11), 342 (41), 342 (43), 314 (19), 313 (18), 264 (17), 263 (93), 235 (69), 234 (21), 171 (40), 169 (40). HRMS (EI): calcd. for $C_{17}H_{15}{}^{79}BrN_2O$ $[M]^+$ 342.0362 found: 342.0361; calcd for $C_{17}H_{15}{}^{81}BrN_2O$ $[M]^+$344.0341, found: 344.0344.

1-(2-Bromo-4-methoxybenzyl)-1*H*-benzo[*d*]imidazole-2-carbaldehyde (4e)

[2] S. Mitra, H. Darira, P. Chattopadhyay, *Synth.* **2013**, *45*, 85–92.

According to general procedure B, compound 4e was obtained as a yellow solid in 16 % yield (88.3 mg, 0.256 mmol, R_f = 0.27, heptane/ethyl acetate, 7:3); m.p.= 117 – 119 °C. IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 1681 (s), 1599 (m), 1463 (s), 1285 (m), 1240 (s), 1226 (s), 1026 (s), 848 (s), 741 (vs), 438 (m). ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 10.16 (s, 1H), 8.00 – 7.93 (m, 1H), 7.45 – 7.37 (m, 2H), 7.37 – 7.31 (m, 1H), 7.17 (d, *J* = 2.6 Hz, 1H), 6.65 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.41 – 6.35 (m, 1H), 5.90 (d, *J* = 0.6 Hz, 2H), 3.75 (s, 3H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$): δ [ppm] = 184.9, 159.7, 146.2, 143.1, 136.6, 127.9, 127.4, 127.0, 124.6, 122.7, 122.6, 118.5, 114.0, 111.6, 55.7, 47.8. MS (EI, 70 eV): m/z (%) = 346 (44), 344 (43), 317 (35), 315 (36), 266 (14), 265 (98), 201 (97), 199 (100). HRMS (EI) m/z = calcd. for $C_{16}H_{13}{}^{79}BrN_2O_2$ $[M]^+$ 344.01549, found 344.01386; calcd. for $C_{16}H_{13}{}^{81}BrN_2O_2$ $[M]^+$ 346.01345, found 346.01358.

1-(2-Bromo-5-methoxybenzyl)-1*H*-benzo[*d*]imidazole-2-carbaldehyde (4f)

According to general procedure B, compound 4f was obtained as a white solid in 52 % yield (561 mg, 1.63 mmol, R_f = 0.29, heptane/ethyl acetate, 7:3); m.p.= 122 – 125 °C. IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 1681 (s), 1570 (m), 1458 (s), 11294 (s), 1164 (m), 1057 (m), 1015 (m), 863 (s), 741 (s), 733 (s). ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 10.15 (s, 1H), 8.02 – 7.92 (m, 1H), 7.51 (d, *J* = 8.8 Hz, 1H), 7.46 – 7.38 (m, 2H), 7.37 – 7.31 (m, 1H), 6.68 (dd, *J* = 8.8, 3.0 Hz, 1H), 5.99 – 5.94 (m, 1H), 5.89 (t, *J* = 0.7 Hz, 2H), 3.55 (s, 3H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$): δ [ppm] = 184.9, 159.5, 146.1, 143.0, 136.5, 136.2, 133.8, 127.5, 124.6, 122.7, 114.2, 113.6, 112.5, 111.4, 55.4, 48.4. MS (EI, 70 eV): m/z (%) = 346 (11), 344 (10), 317 (14), 315 (14), 266 (17), 265 (100), 237 (17), 222 (14), 201 (10), 199 (11). HRMS (EI) m/z = calcd. for $C_{16}H_{13}{}^{79}BrN_2O_2$ $[M]^+$ 344.01549, found 344.01463; calcd. for $C_{16}H_{13}{}^{81}BrN_2O_2$ $[M]^+$ 346.01345, found 346.01390.

1-(2-Bromo-5-fluorobenzyl)-1*H*-benzo[*d*]imidazole-2-carbaldehyde (4g)

According to general procedure B, compound 4g was obtained as a white solid in 46 % yield (504 mg, 1.51 mmol, R_f = 0.37, heptane/ethyl acetate, 7:3); m.p.= 84 – 87 °C. IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 1693 (s), 1578 (m), 1460 (s), 1405 (m), 1273 (m), 1166 (m), 1026 (m), 1017 (m), 748 (vs), 585 (s). ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 10.15 (s, 1H), 8.06 – 7.97 (m, 1H), 7.59 (dd, *J* = 8.8, 5.2 Hz, 1H), 7.51 – 7.39 (m, 2H), 7.38 – 7.30 (m, 1H), 6.93 – 6.82 (m, 1H), 6.13 – 6.04 (m, 1H), 5.89 (d, *J* = 0.8 Hz, 2H). ^{19}F NMR (282 MHz, CDCl3): δ = -113.0. ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$): δ [ppm] = 184.9, 162.5 (d, *J* = 248.2 Hz), 146.0, 143.1, 137.5 (d, *J* = 7.1 Hz), 136.4, 134.5 (d, *J* = 8.0 Hz), 127.7, 124.8, 122.9, 116.6 (d, *J* = 22.6 Hz), 116.2 (d, *J* = 3.3 Hz), 114.3 (d, *J* = 24.5 Hz), 111.1, 48.3. MS (EI, 70 eV): m/z (%) = 333 (6), 306 (12), 305 (92), 304 (14), 303 (94), 254 (14), 253 (100), 225 (71), 224 (28), 223 (15), 189 (32),

187 (33). HRMS (EI) m/z = calcd. for $C_{15}H_{10}{}^{79}BrFN_2O_1$ $[M]^+$ 331.99551, found 331.99413; calcd. for $C_{19}H_{13}{}^{81}BrFN_2O_1$ $[M]^+$ 333.99346, found 333.99358.

1-(2-(*p*-Tolylethynyl)benzyl)-1*H*-benzo[*d*]imidazole-2-carbaldehyde (5a)

According to general procedure C, compound **5a** was obtained as a white solid in 77 % yield (170 mg, 0.48 mmol, R_f = 0.19 heptane/ethyl acetate, 2:1); mp: 163 – 165 °C. IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 1686 (m), 1508 (m), 1465 (m), 1329 (w), 1228 (m), 1010 (m), 847 (m), 742 (vs), 814 (m). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 10.18 (s, 1H), 7.99 – 7.94 (m, 1H), 7.61 – 7.58 (m, 1H), 7.50 – 7.41 (m, 3H), 7.40 – 7.37 (m, 2H), 7.29 – 7.22 (m, 1H), 7.21 – 7.17 (m, 2H), 7.14 (dd, *J* = 7.6 Hz, *J* = 1.4 Hz, 1H), 6.64 (dd, *J* = 7.8 Hz, *J* = 1.4 Hz, 1H), 6.16 (s, 2H), 2.39 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 184.9, 146.1, 142.9, 139.0, 137.2, 136.6, 132.4, 131.5, 129.3, 128.8, 127.7, 127.2, 125.9, 124.3, 122.4, 121.9, 119.7, 111.7, 95.7, 85.9, 46.7, 21.6. MS (EI, 70 eV): m/z (%) = 350 (M^+, 2), 323 (3), 322 (26), 321 (100), 319 (4), 306 (5), 305 (4), 205 (6), 203 (8), 202 (9), 189 (15). HRMS (EI): calcd. for $C_{24}H_{18}N_2O$ $[M]^+$ 350.1413 found: 350.1407.

1-(2-((4-Methoxyphenyl)ethynyl)benzyl)-1H-benzo[d]imidazole-2-carbaldehyde (5b)

According to general procedure C, compound **5b** was obtained as a yellow solid in 73 % yield (126 mg, 0.37 mmol, R_f = 0.2 heptane/ethyl acetate, 2:1); mp: 145 – 148°. IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 1686 (s), 1599 (m), 1506 (m), 1228 (s), 1247 (s), 744 (vs), 1173 (m), 1010 (m), 828 (s), 1463 (s). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 10.10 (s, 1H), 7.90 – 7.87 (m, 1H), 7.51 (dd, *J* = 7.7 Hz, *J* = 1.3 Hz, 1H), 7.46 – 7.42 (m, 2H), 7.38 – 7.35 (m, 1H), 7.33 – 7.30 (m, 2H), 7.19 - 715 (m, 1H), 7.07 (m, 1H), 6.83 (d, *J* = 8.6 Hz, 2H), 6.57 (d, *J* = 7.8 Hz, 1H), 6.08 (s, 2H), 3.76 (s, 3H). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): δ = 184.9, 160.0, 146.1, 142.9, 137.1, 136.6, 133.1, 132.4, 128.6, 127.7, 127.2, 125.9, 124.3, 122.4, 122.1, 114.8, 114.2, 111.7, 95.5, 85.3, 55.4, 46.7. MS (EI, 70 eV): m/z (%) = 366 (M^+, 6), 365 (4), 339 (3), 338 (25), 337 (100), 323 (8), 321 (5), 294 (7), 293 (9), 206 (5). HRMS (EI): calcd. for $C_{24}H_{18}N_2O_2$ $[M]^+$ 366.1447 found: 366.1450.

1-(2-((4-(*tert*-Butyl)phenyl)ethynyl)benzyl)-1*H*-benzo[*d*]imidazole-2-carbaldehyde (5c)

According to general procedure C, compound **5c** was obtained as a yellow solid in 88 % yield (165 mg, 0.42 mmol, R_f = 0.25, heptane/ethyl acetate, 2:1); mp: 185 – 188 °C. IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 1688 (vs), 1482 (m), 1461 (s), 1409 (m), 1241 (m), 1018 (m), 849 (m), 746 (vs), 762 (s), 832 (s). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.10 (s, 1H), 7.90 – 7.87 (m, 1H), 7.52 (dd, *J* = 7.7 Hz, *J* = 1.3 Hz, 1H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.39 – 7.35 (m, 1H), 7.34 – 7.29 (m, 4H), 7.18 – 7.15 (m, 1H), 7.07 (ptd, *J* = 7.6 Hz, *J* = 1.4 Hz, 1H), 6.57 (d, *J* = 7.8 Hz, 1H), 6.09 (s,

2H), 1.26 (s, 9H). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): δ = 184.9, 152.2, 146.1, 142.9, 137.2, 136.6, 132.5, 131.4, 128.8, 127.7, 127.2, 125.9, 125.5, 124.3, 122.4, 121.9, 119.7, 111.7, 95.6, 85.9, 46.6, 34.9, 31.2. MS (EI, 70 eV): m/z (%) = 392 (M^+, 6), 365 (4), 364 (29), 363 (100), 349 (4), 348 (6), 347 (13), 307 (7), 306 (5), 213 (6), 215 (11). HRMS (EI): calcd. for $C_{27}H_{24}N_2O$ $[M]^+$ 392.1967 found 392.1968.

1-(2-((4-Fluorophenyl)ethynyl)benzyl)-1H-benzo[d]imidazole-2-carbaldehyde (5d)

According to general procedure C, compound **5d** was obtained as a white solid in 71 % yield (118 mg, 0.33 mmol, R_f = 0.26, heptane/ethyl acetate, 2:1); mp: 130 – 132 °C. IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 1692 (s), 1504 (m), 1484 (m), 1463 (s), 1409 (m), 752 (vs), 1156 (m), 781 (m), 837 (vs), 1220 (s). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 10.07 (s, 1H), 7.90 – 7.84 (m, 1H), 7.51 – 7.47 (m, 2H), 7.47 – 7.42 (m, 1H), 7.34 – 7.27 (m, 3H), 7.19 – 7.13 (m, 1H), 7.07 (m, 1H), 7.02 – 6.93 (m, 2H), 6.55 (dd, *J* = 7.7 Hz, *J* = 1.4 Hz, 1H), 6.05 (s, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -109.98. ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$): δ = 184.9, 162.8 (d, *J* = 250.4 Hz), 146.2, 143.0, 137.3, 136.6, 133.5 (d, *J* = 8.5 Hz), 132.5, 129.0, 127.7, 127.2, 125.9, 124.3, 122.5, 121.5, 118.8 (d, *J* = 3.6 Hz), 115.9 (d, *J* = 22.2 Hz), 111.5, 94.3, 86.2 (d, *J* = 1.6 Hz), 46.7. MS (EI, 70 eV): m/z (%) = 354 (M^+, 3), 327 (4), 326 (35), 325 (100), 323 (9), 209 (12), 208 (9), 207 (24), 183 (14), 162 (10). HRMS (ESI-TOF): calcd. for $C_{23}H_{16}FN_2O$ $[M + H]^+$ 355.1248 found: 355.1250.

1-(2-(*o*-Tolylethynyl)benzyl)-1*H*-benzo[*d*]imidazole-2-carbaldehyde (5e)

According to general procedure C, compound **5e** was obtained as a grey solid in 73 % yield (414 mg, 1.18 mmol, R_f = 0.29 heptane/ethyl acetate, 4:1); mp = 124 – 127 °C. IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 1695 (s), 1460 (s), 1411 (m), 1329 (m), 1221 (m), 1158 (m), 1007 (m), 844 (m), 743 (vs), 712 (s). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.17 (s, 1H), 7.99 – 7.94 (m, 1H), 7.62 (dd, *J* = 7.7, *J* = 1.3 Hz, 1H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.46 – 7.41 (m, 1H), 7.41 – 7.36 (m, 2H), 7.29 – 7.23 (m, 3H), 7.22 – 7.18 (m, 1H), 7.14 (ptd, *J* = 7.7, *J* = 1.4 Hz, 1H), 6.61 (d, *J* = 7.9 Hz, 1H), 6.17 (s, 2H), 2.56 (s, 3H). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): δ = 185.0, 146.2, 143.1, 140.2, 137.2, 136.7, 132.6, 132.1, 129.8, 129.0, 128.9, 127.8, 127.3, 125.9, 125.8, 124.5, 122.7, 122.6, 122.0, 111.7, 94.6, 90.5, 46.7, 21.2. MS (EI, 70 eV): m/z (%) = 350 (M^+, 4), 332 (16), 321 (53), 308 (23), 307 (100), 306 (13), 204 (17), 203 (38), 202 (32). HRMS (ESI-TOF) m/z = calcd. for $C_{24}H_{19}N_2O$ $[M + H]^+$ 351.1497, found: 351.1501.

1-(2-((2-Fluorophenyl)ethynyl)benzyl)-1*H*-benzo[*d*]imidazole-2-carbaldehyde (5f)

According to general procedure C, compound **5f** was obtained as a brown solid in 46 % yield (265 mg, 0.747 mmol, R_f = 0.23 heptane/ethyl acetate, 4:1); mp = 151 – 153 °C. IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3060 (w), 3029 (w), 2845 (w), 1689 (s), 1479 (s), 1460 (s), 1413 (m), 1221

(s), 1160 (m), 1090 (m), 1007 (m), 846 (s), 745 (vs), 710 (m), 500 (s). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.19 (s, 1H), 8.00 – 7.93 (m, 1H), 7.63 (ddd, *J* = 7.7, *J* = 1.5, *J* = 0.5 Hz, 1H), 7.57 (m, 1H), 7.50 – 7.31 (m, 4H), 7.27 (m, 1H), 7.21 – 7.09 (m, 3H), 6.64 (m, 1H), 6.18 (s, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -109.4 (s). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$): δ = 185.0, 164.6, 161.2, 146.2, 143.1, 137.7, 136.7, 133.4, 132.6, 130.6 (d, *J* = 8.0 Hz), 129.4, 127.8, 127.4, 124.5, 124.3 (d, *J* = 3.8 Hz), 122.5, 121.4, 115.8 (d, *J* = 20.8 Hz), 111.8, 111.5, 91.8 (d, *J* = 3.3 Hz), 88.9, 46.6. MS (EI, 70 eV): m/z (%) = 354 (M^+, 3), 326 (20), 325 (72), 308 (24), 307 (100), 306 (23), 305 (17), 209 (18), 207 (28). HRMS (ESI-TOF) m/z = calcd. for $C_{23}H_{16}FN_2O$ $[M + H]^+$ 355.1247, found: 355.1248.

1-(2-((2-Methoxyphenyl)ethynyl)benzyl)-1*H*-benzo[*d*]imidazole-2-carbaldehyde (5g)

According to general procedure C, compound **5g** was obtained as a beige solid in 73 % yield (254 mg, 0.693 mmol, R_f = 0.18 heptane/ethyl acetate, 4:1); mp = 119 – 121 °C. IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 1693 (m), 1594 (w), 1465 (m), 1343 (w), 1279 (m), 1242 (m), 1156 (w), 1046 (w), 1007 (m), 846 (m), 758 (s), 745 (vs). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.21 (s, 1H), 7.99 – 7.92 (m, 1H), 7.64 – 7.59 (m, 1H), 7.58 – 7.51 (m, 2H), 7.44 – 7.31 (m, 3H), 7.28 – 7.21 (m, 1H), 7.14 (dd, *J* = 7.6, *J* = 1.4 Hz, 1H), 6.98 (dd, *J* = 7.5, *J* = 1.0 Hz, 1H), 6.92 (dd, *J* = 8.4, *J* = 1.0 Hz, 1H), 6.70 – 6.63 (m, 1H), 6.24 (s, 2H), 3.85 (s, 3H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$): δ = 185.1, 160.3, 146.2, 143.1, 137.6, 136.8, 133.3, 132.2, 130.3, 128.9, 127.7, 127.3, 126.0, 124.4, 122.4, 122.3, 120.7, 112.2, 112.0, 110.8, 92.1, 90.9, 55.9, 46.5. MS (EI, 70 eV): m/z (%) = 366 (M^+, 2), 337 (11), 308 (24), 307 (100), 306 (17), 219 (8), 206 (8), 205 (12). HRMS (ESI-TOF) m/z = calcd. for $C_{24}H_{19}N_2O_2$ $[M + H]^+$ 367.1447, found: 367.1442.

1-(2-((3-Methoxyphenyl)ethynyl)benzyl)-1*H*-benzo[*d*]imidazole-2-carbaldehyde (5h)

According to general procedure C, compound **5h** was obtained as a beige solid in 76 % yield (264 mg, 0.721 mmol, R_f = 0.23 heptane/ethyl acetate, 4:1); mp = 105 – 108 °C. IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 1694 (m), 1594 (w), 1496 (m), 1465 (m), 1415 (m), 1279 (m), 1242 (m), 1228 (m), 1007 (m), 846 (m), 758 (s), 745 (vs). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.16 (s, 1H), 7.98 – 7.93 (m, 1H), 7.61 – 7.58 (m, 1H), 7.44 – 7.36 (m, 3H), 7.29 – 7.24 (m, 2H), 7.18 – 7.13 (m, 2H), 7.10 – 7.08 (m, 1H), 6.92 (dd, *J* = 8.4, *J* = 2.6 Hz, 1H), 6.63 (d, *J* = 7.8 Hz, 1H), 6.15 (s, 2H), 3.82 (s, 3H). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): δ = 185.0, 159.6, 146.3, 143.1, 137.5, 136.7, 132.7, 129.7, 129.1, 127.8, 127.3, 126.0, 124.5, 124.3, 123.8, 122.5, 121.7, 116.5, 115.4, 111.7, 95.4, 86.4, 55.5, 46.8. MS (EI, 70 eV): m/z (%) = 366 (M^+, 3), 338 (25), 337 (100), 323 (6), 332 (7), 295 (6), 294 (11), 293 (10). HRMS (ESI-TOF) m/z = calcd. for $C_{24}H_{19}N_2O_2$ $[M + H]^+$ 367.1447, found: 367.1445.

1-(2-(Phenylethynyl)benzyl)-1*H*-benzo[*d*]imidazole-2-carbaldehyde (5i)

According to general procedure C, compound **5i** was obtained as a grey solid in 63 % yield (206 mg, 0.613 mmol, R_f = 0.25 heptane/ethyl acetate, 4:1); mp = 132 °C. IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 1693 (s), 1460 (m), 1413 (m), 1324 (m), 1221 (m), 1158 (m), 1092 (w), 1007 (m), 844 (m), 743 (vs). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.18 (s, 1H), 8.00 – 7.93 (m, 1H), 7.63 – 7.54 (m, 3H), 7.47 – 7.35 (m, 6H), 7.30 – 7.23 (m, 1H), 7.16 (dd, *J* = 7.6, *J* = 1.5 Hz, 1H), 6.68 – 6.62 (m, 1H), 6.17 (s, 2H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$): δ = 185.1, 146.3, 143.1, 137.4, 136.7, 132.6, 131.7, 129.1, 128.9, 128.6, 127.8, 127.3, 126.0, 124.5, 122.9, 122.6, 121.8, 111.7, 95.6, 86.6, 46.8 .MS (EI, 70 eV): m/z (%) = 336 (M^+, 2), 308 (25), 307 (100), 306 (16), 190 (9), 189 (21). HRMS (ESI-TOF) m/z = calcd. for $C_{23}H_{17}N_2O$ $[M + H]^+$ 337.1341, found: 337.1340.

1-(2-(*o*-Tolylethynyl)benzyl)-1*H*-imidazole-2-carbaldehyde (5j)

According to general procedure C, compound **5j** was obtained as a beige solid in 38 % yield (129 mg, 0.429 mmol, R_f = 0.16 heptane/ethyl acetate, 1:1); mp = 78 – 81 °C. IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 1687 (s),1479 (m), 1405 (s), 1397 (m), 1343 (m), 1250 (m), 1151 (m), 925 (m), 793 (m), 754 (vs). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.80 (s, 1H), 7.54 (dd, *J* = 7.6, *J* = 1.6 Hz, 1H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.29 – 7.08 (m, 7H), 7.05 – 7.01 (m, 1H), 5.82 (s, 2H), 2.39 (s, 3H). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): δ = 182.4, 140.2, 137.1, 132.8, 132.1, 132.0, 129.8, 129.1, 129.0, 128.6, 128.3, 126.4, 125.9, 123.1, 122.5, 94.0, 90.5, 49.6, 21.0 (signal of one carbon is absent, which may relate to signal overlap). MS (EI, 70 eV): m/z (%) = 300 (M^+, 3), 272 (21), 271 (86), 258 (45), 257 (100), 256 (25), 204 (29), 203 (75), 202 (71), 201 (11). HRMS (ESI-TOF) m/z = calcd. for $C_{20}H_{17}N_2O$ $[M + H]^+$ 301.1341, found: 301.1347.

1-(2-(*p*-Tolylethynyl)benzyl)-1*H*-imidazole-2-carbaldehyde (5k)

According to general procedure C, compound **5k** was obtained as a white solid in 98 % yield (340 mg, 1.13 mmol, R_f = 0.14 heptane/ethyl acetate, 1:1); mp = 107 – 108 °C. IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 1677 (vs), 1510 (m), 1469 (m), 1407 (s), 1335 (s), 1279 (m), 1153 (m), 818 (m), 799 (s), 766 (vs), 752 (vs). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.78 (d, *J* = 0.9 Hz, 1H), 7.55 – 7.46 (m, 1H), 7.32 – 7.27 (m, 2H), 7.25 – 7.15 (m, 4H), 7.12 – 7.02 (m, 3H), 5.79 (s, 2H), 2.29 (s, 3H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$): δ = 182.4, 143.5, 139.2, 137.3, 132.7, 132.0, 131.6, 129.4, 129.0, 128.5, 128.4, 126.4, 123.0, 119.5, 95.2, 86.0, 49.4, 21. MS (EI, 70 eV): m/z (%) = 300 (M^+, 1), 272 (23), 271 (100), 203 (7), 202 (11), 190 (5), 189 (13). HRMS (ESI-TOF) m/z = calcd. for $C_{20}H_{17}N_2O$ $[M + H]^+$ 301.1341, found: 301.1339.

1-(2-((2-Fluorophenyl)ethynyl)benzyl)-1*H*-imidazole-2-carbaldehyde (5l)

According to general procedure C, compound **5l** was obtained as a yellow solid in 85 % yield (299 mg, 0.983 mmol, R_f = 0.12 heptane/ethyl acetate, 1:1); mp = 83 – 85 °C. IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 1683 (s), 1570 (w), 1496 (m), 1475 (m), 1339 (m), 1271 (m), 1213 (m), 1158 (m), 916 (w), 772 (s), 754 (vs), 700 (s). ^{1}H NMR (300 MHz, $CDCl_3$): δ= 9.87 (d, *J* = 1.0 Hz, 1H), 7.66 – 7.56 (m, 1H), 7.50 (ptd, *J* = 7.3, *J* = 1.8 Hz, 1H), 7.38 – 7.27 (m, 5H), 7.19 – 7.08 (m, 3H), 5.90 (s, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ =-109.54 (s). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$): δ = 182.3, 162.7 (d, *J* = 251.7 Hz), 143.4, 137.6, 133.2, 132.6, 132.0, 130.6 (d, *J* = 8.0 Hz), 129.4, 128.4, 128.4, 126.5, 124.2 (d, *J* = 3.6 Hz), 122.3, 115.7 (d, *J* = 20.8 Hz), 111.3 (d, *J* = 15.6 Hz), 91.7 (d, *J* = 3.3 Hz), 88.1, 49.1. MS (EI, 70 eV): m/z (%) = 276 (25), 275 (81), 274 (14), 258 (27), 257 (100), 256 (26), 255 (13), 209 (23), 208 (12), 207 (43), 189 (24), 183 (26) (no molecular peak was observed). HRMS (ESI-TOF) m/z = calcd. for Formular: $C_{19}H_{14}FN_2O$ $[M + H]^+$ 305.1090 , found: 305.1090.

1-(2-((4-Fluorophenyl)ethynyl)benzyl)-1*H*-imidazole-2-carbaldehyde (5m)

According to general procedure C, compound **5m** was obtained as a white solid in 89 % yield (314 mg, 1.03 mmol, R_f = 0.14 heptane/ethyl acetate, 1:1); mp = 103 – 104 °C. IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 1679 (s), 1594 (w), 1506 (s), 1471 (m), 1413 (s), 1335 (m), 1300 (m), 1215 (s), 1158 (m), 834 (s), 768 (vs), 754 (vs). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.93 (d, *J* = 1.0 Hz, 1H), 7.68 – 7.61 (m, 1H), 7.57 – 7.47 (m, 2H), 7.45 – 7.32 (m, 3H), 7.28 – 7.25 (m, 1H), 7.22 – 7.07 (m, 3H), 5.94 (s, 2H); ^{19}F NMR (282 MHz, $CDCl_3$): δ = -109.9 (s). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$): δ = 182.3, 162.8 (d, *J* = 250.6 Hz), 143.5, 137.2, 133.5 (d, *J* = 8.4 Hz), 132.7, 131.9, 129.1, 128.5, 128.3, 126.2, 122.6, 118.6 (d, *J* = 3.6 Hz), 115.9 (d, *J* = 22.2 Hz), 93.7, 86.1 (d, *J* = 1.5 Hz), 49.4. MS (EI, 70 eV): m/z (%) = 276 (23), 275 (100), 274 (16), 209 (9), 207 (18), 183 (10) (no molecular peak was observed). HRMS (ESI-TOF) m/z = calcd. for Formular: $C_{19}H_{14}FN_2O$ $[M + H]^+$ 305.1090 , found: 305.1093.

1-(2-((4-Methoxyphenyl)ethynyl)benzyl)-1*H*-imidazole-2-carbaldehyde (5n)

According to general procedure C, compound **5n** was obtained as a white solid in 95 % yield (345 mg, 1.09 mmol, R_f = 0.10 heptane/ethyl acetate, 1:1); mp = 83 °C. IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 1681 (s), 1607 (m), 1512 (s), 1409 (s), 1333 (m), 1287 (m), 1250 (vs), 1182 (m), 1026 (s), 830 (s), 770 (vs), 756 (vs). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.90 (d, *J* = 1.0 Hz, 1H), 7.62 – 7.55 (m, 1H), 7.47 – 7.41 (m, 2H), 7.39 – 7.26 (m, 4H), 7.18 – 7.14 (m, 1H), 6.94 – 6.88 (m, 2H), 5.90 (s, 2H), 3.86 (s, 3H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$): δ = 182.4, 160.2, 143.5, 137.2, 133.2, 132.6, 132.0, 128.9, 128.6, 128.5, 126.4, 123.3, 114.7, 114.3, 95.1, 85.4, 55.5, 49.5

MS (EI, 70 eV): m/z (%) =316 (M^+, 7), 288 (23), 287 (100), 272 (11), 244 (10), 178 (17), 152 (6). HRMS (EI) m/z = calcd. for $C_{20}H_{16}N_2O_2$ $[M]^+$ 316.12063, found: 316.12061.

1-(2-((4-(*tert*-Butyl)phenyl)ethynyl)benzyl)-1*H*-imidazole-2-carbaldehyde (5o)

According to general procedure C, compound **5o** was obtained as a beige solid in 99 % yield (395 mg, 1.15 mmol, R_f = 0.22 heptane/ethyl acetate, 1:1); mp = 106 – 109 °C. IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 1689 (s), 1506 (w), 1469 (m), 1411 (s), 1337 (m), 1296 (w), 1162 (w), 834 (s), 776 (vs), 768 (vs). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.86 (d, *J* = 0.9 Hz, 1H), 7.60 – 7.54 (m, 1H), 7.45 – 7.33 (m, 4H), 7.32 – 7.22 (m, 4H), 7.17 – 7.11 (m, 1H), 5.87 (s, 2H), 1.32 (s, 9H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$): δ = 182.4, 152.3, 143.5, 137.3, 132.7, 132.0, 131.4, 129.0, 128.5, 126.4, 125.7, 123.1, 119.6, 95.2, 86.0, 49.4, 35.0, 31.3 (signal of one carbon is absent, which may relate to signal overlap). MS (EI, 70 eV): m/z (%) = 342 (M^+, 2), 314 (27), 313 (100), 298 (7), 297 (12), 231 (6), 216 (6), 215 (14), 202 (7). HRMS (ESI-TOF) m/z = calcd. for Formular: $C_{23}H_{23}N_2O$ $[M + H]^+$ 343.1810 , found: 343.1806.

5,6-Difluoro-1-(2-(*p*-tolylethynyl)benzyl)-1*H*-benzo[*d*]imidazole-2-carb-aldehyde (5p)

According to general procedure C, compound **5p** was obtained as a beige solid in 42 % yield (140 mg, 0.362 mmol, R_f = 0.32 heptane/ethyl acetate, 4:1); mp = 170 – 172 °C. IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 1697 (vs), 1588 (m), 1487 (s), 1465 (s), 1421 (m), 1273 (m), 1224 (s), 1116 (m), 1085 (m), 984 (m), 892 (s), 760 (vs). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.10 (s, 1H), 7.70 (dd, *J* = 9.9, *J* = 7.3 Hz, 1H), 7.63 – 7.58 (m, 1H), 7.48 – 7.42 (m, 2H), 7.32 – 7.27 (m, 1H), 7.25 – 7.17 (m, 4H), 6.76 – 6.71 (m, 1H), 6.11 (s, 2H), 2.39 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -132.56 (d, *J* = 20.3 Hz), -138.78 (d, *J* = 20.3 Hz). ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): 184.3, 151.1 (dd, *J* = 250.8, *J* = 16.2 Hz), 149.6 (dd, *J* = 246.2, *J* = 15.8 Hz), 147.5 (d, *J* = 3.3 Hz), 139.4, 136.5, 132.9, 132.5 (d, *J* = 10.8 Hz), 131.6, 129.5, 129.1, 128.3, 126.4, 122.3, 119.5, 109.3 (d, *J* = 19.5 Hz), 99.6 (d, *J* = 23.2 Hz), 96.0, 85.8, 47.1, 21.7. (Signal of one carbon is absent, which may relate to signal overlap). MS (EI, 70 eV): m/z (%) = 386 (M^+, 4), 358 (26), 357 (100), 205 (7), 203 (7), 202 (9), 190 (7), 189 (13), 178 (7), 171 (7). HRMS (ESI-TOF) m/z = calcd. for $C_{24}H_{16}F_2N_2O$ $[M + H]^+$ 387.1309, found: 387.1311.

5,6-Difluoro-1-(2-((4-fluorophenyl)ethynyl)benzyl)-1*H*-benzo[*d*]imidazole-2-carbaldehyde (5q)

According to general procedure C, compound **5q** was obtained as a beige solid in 39 % yield (130 mg, 0.330 mmol, 39 R_f = 0.30 heptane/ethyl acetate, 4:1); mp = 143 – 146 °C. IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 1697 (vs), 1594 (m), 1508 (s), 1487 (s), 1463 (s), 1339 (m), 1275 (m),

1224 (vs), 1149 (m), 987 (m), 838 (s), 760 (s). **1**H NMR (300 MHz, $CDCl_3$): δ = 10.09 (s, 1H), 7.71 (dd, *J* = 9.9, *J* = 7.3 Hz, 1H), 7.63 – 7.59 (m, 1H), 7.58 – 7.50 (m, 2H), 7.30 (m, 1H), 7.25 – 7.18 (m, 2H), 7.13 – 7.03 (m, 2H), 6.77 – 6.71 (m, 1H), 6.10 (s, 2H). **19**F NMR (282 MHz, $CDCl_3$): δ = -109.74, -132.52 (d, *J* = 20.3 Hz), -138.69 (d, *J* = 20.3 Hz). ^{13}C {^1H} NMR (125 MHz, $CDCl_3$): δ = 184.3, 163.0 (d, *J* = 250.6 Hz), 151.1 (dd, *J* = 251.0 Hz, *J* = 16.2 Hz), 149.6 (dd, *J* = 246.4, *J* = 15.7 Hz), 147.6 (d, *J* = 2.1 Hz), 138.4 (d, *J* = 10.8 Hz), 136.5, 133.7 (d, *J* = 8.4 Hz), 133.0, 132.5 (d, *J* = 10.9 Hz), 129.3, 128.3, 126.4, 121.9, 118.7 (d, *J* = 3.4 Hz), 116.1 (d, *J* = 22.4 Hz), 109.3 (d, *J* = 19.7 Hz), 99.5 (d, *J* = 23.3 Hz), 94.6, 86.1, 47.2. MS (EI, 70 eV): m/z (%) = 390 (M^+, 3), 362 (26), 361 (100), 360 (11), 209 (14), 208 (7), 207 (20). HRMS (ESI-TOF) m/z = calcd. for $C_{23}H_{14}F_3N_2O$ $[M + H]^+$ 391.1058, found: 391.1056.

5,6-Difluoro-1-(2-((4-methoxyphenyl)ethynyl)benzyl)-1*H*-benzo[*d*]imidazole-2-carbaldehyde (5r)

According to general procedure C, compound **5r** was obtained as a beige solid in 48 % yield (167 mg, 0.415 mmol, R_f = 0.23 heptane/ethyl acetate, 4:1); mp = 147 – 149 °C. IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 1697 (vs), 1605 (m), 1512 (m), 1487 (s), 1465 (s), 1250 (s), 1224 (s), 1174 (s), 1026 (s), 890 (s), 832 (s), 760 (vs). **1**H NMR (300 MHz, $CDCl_3$): δ = 10.10 (s, 1H), 7.70 (dd, *J* = 9.9, *J* = 7.3 Hz, 1H), 7.61 – 7.55 (m, 1H), 7.53 – 7.46 (m, 2H), 7.32 – 7.26 (m, 1H), 7.24 (d, *J* = 6.9 Hz, 1H), 7.19 (dd, *J* = 7.6, *J* = 1.5 Hz, 1H), 6.94 – 6.88 (m, 2H), 6.77 – 6.72 (m, 1H), 6.10 (s, 2H), 3.84 (s, 3H). **19**F NMR (282 MHz, $CDCl_3$): δ = -132.59 (d, *J* = 20.3 Hz), -138.80 (d, *J* = 20.3 Hz). ^{13}C {^1H} NMR (125 MHz, $CDCl_3$): δ = 184.2, 160.1, 150.9 (dd, *J* = 250.7, *J* = 16.3 Hz), 149.5 (dd, *J* = 246.2, *J* = 15.7 Hz), 147.4 (d, *J* = 3.4 Hz), 138.2 (d, *J* = 11.0 Hz), 136.2, 133.1, 132.7, 132.4 (d, *J* = 11.0 Hz), 128.8, 128.1, 126.3, 122.3, 114.5, 114.2, 109.1 (d, *J* = 19.4 Hz), 99.4 (d, *J* = 23.2 Hz), 95.7, 85.1, 55.4, 47.0. MS (EI, 70 eV): m/z (%) = 402 (M^+, 9), 374 (27), 373 (100), 358 (7), 330 (8), 329 (9), 221 (9), 206 (7). HRMS (ESI-TOF) m/z = calcd. for $C_{24}H_{17}F_2N_2O_2$ $[M + H]^+$ 403.1258 found: 403.1260.

1-(2-((4-Fluorophenyl)ethynyl)benzyl)-5,6-dimethyl-1*H*-benzo[*d*]imidazole-2-carbaldehyde (5s)

According to general procedure C, compound **5s** was obtained as an orange solid in 73 % yield (162 mg, 0.43 mmol, R_f = 0.25, heptane/ethyl acetate, 2:1); mp = 202 – 204 °C. IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 1686 (vs),1504 (vs), 1484 (vs), 1465 (s), 1407 (vs), 1236 (s), 1218 (s), 1156 (s), 837 (s), 775 (s), 750 (vs). ^1H NMR (300 MHz, $CDCl_3$): δ = 10.03 (s, 1H), 7.62 (s, 1H), 7.53 – 7.45 (m, 3H), 7.20 – 7.14 (m, 1H), 7.12 – 7.05 (m, 2H), 7.03 – 6.96 (m, 2H), 6.53 (dd, *J* = 7.7 Hz, *J* = 1.4 Hz, 1H), 6.01 (s, 2H), 2.30 (s, 3H), 2.24 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -110.1.^{13}C {^1H} NMR (75 MHz, $CDCl_3$): δ = 184.6, 162.8 (d, *J* = 250.3 Hz), 141.8, 137.6, 134.1, 133.5 (d, *J* = 8.5 Hz), 132.5, 129.0,127.9, 127.6, 125.8, 121.9, 121.4, 118.9, 115.8 (d,

J = 22.1 Hz), 111.1, 94.2, 86.3 (d, *J* = 1.5 Hz), 46.6, 21.0, 20.4. 0 (signal of two carbons are absent, which may relate to signal overlap). MS (EI, 70 eV): m/z (%) = 382 (M^+, 4), 355 (4), 354 (27), 353 (100), 352 (10), 209 (8), 208 (6), 207 (14), 189 (5), 183 (10). HRMS (EI): calcd. for $C_{25}H_{19}FN_2O$ $[M]^+$ 382.1475, found: 382.1470.

1-(2-((4-Methoxyphenyl)ethynyl)benzyl)-5,6-dimethyl-1*H*-benzo[*d*]imidazole-2-carbaldehyde (5t)

According to general procedure C, compound **5t** was obtained as a dark yellow solid in 78 % yield (112 mg, 0.29 mmol, R_f = 0.22 heptane/ethyl acetate, 2:1); mp = 193 – 195 °C. IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 1686 (m),1508 (m), 1465 (m), 1329 (w), 1228 (m), 1010 (m), 847 (m), 742 (vs), 814 (m) .^{1}H NMR (250 MHz, $CDCl_3$): δ = 10.0 (s, 1H), 7.6 (s, 1H), 7.5 (dd, *J* = 7.6 Hz, *J* = 1.4 Hz, 1H), 7.5 – 7.4 (m, 2H), 7.2 – 7.1 (m, 2H), 7.1 (dd, *J* = 7.6 Hz, *J* = 1.5 Hz, 1H), 6.9 – 6.8 (m, 2H), 6.5 (d, *J* = 7.7 Hz, 1H), 6.0 (s, 2H), 3.8 (s, 3H), 2.3 (s, 3H), 2.2 (s, 3H). ^{13}C{^{1}H} NMR (63 MHz, $CDCl_3$): δ = 184.6, 160.0, 137.6, 137.4, 134.0, 133.1, 132.3, 128.6, 127.5, 125.8, 121.9, 121.8, 114.9, 114.1, 111.2, 95.4, 85.4, 55.3, 46.3, 21.0, 20.4 (signal of tree carbons are absent, which may relate to signal overlap).MS (EI, 70 eV): m/z (%) = 394 (M^+, 7), 393 (4), 366 (28), 365 (100), 351 (5), 350 (6), 322 (4), 321 (5), 221 (5), 206 (4), 178 (14). HRMS (EI): calcd for $C_{26}H_{22}N_2O_2$ $[M]^+$ 394.1675, found: 394.1669.

1-(2-((4-(*tert*-Butyl)phenyl)ethynyl)benzyl)-5,6-dimethyl-1*H*-benzo[*d*]imidazole-2-carbaldehyde (5u)

According to general procedure C, compound **5u** was obtained as a yellow solid in 72 % yield (120 mg, 0.29 mmol, R_f = 0.22 heptane/ethyl acetate, 2:1); mp = 160 – 163° C. IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 1681 (s),1484 (vs), 1463 (vs), 1455 (s), 1405 (s), 1234 (s), 1006 (s), 835 (s), 779 (s), 756 (m), 750 (vs). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 10.0 (s, 1H), 7.6 (s, 1H), 7.5 – 7.5 (m, 1H), 7.5 – 7.4 (m, 1H), 7.4 – 7.4 (m, 1H), 7.3 (d, *J* = 2.0 Hz, 1H), 7.3 – 7.3 (m, 1H), 7.2 – 7.2 (m, 1H), 7.1 (s, 1H), 7.1 – 7.0 (m, 1H), 6.5 (dd, *J* = 7.8 Hz, *J* = 2.1 Hz, 1H), 6.0 (s, 2H), 2.3 (s, 3H), 2.2 (s, 3H), 1.3 (s, 9H).^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$): δ = 184.6, 152.1, 145.7, 141.8, 137.6,137.7, 135.4, 134.0, 132.4, 131.4, 128.7, 127.5, 125.8, 125.5, 121.9,121.8, 119.8, 111.2, 95.6, 86.0, 46.6, 34.9, 31.2, 21.0, 20.4. MS (EI, 70 eV): m/z (%) = 420 (M^+, 8), 393 (5), 392 (31), 391 (100), 377 (3), 376 (5), 375 (11), 361 (3), 335 (5), 217 (6), 215 (8). HRMS (EI): calcd. for $C_{29}H_{28}N_2O$ $[M]^+$ 420.2196, found: 420.2184

1-(4-Methoxy-2-(*p*-tolylethynyl)benzyl)-1*H*-benzo[*d*]imidazole-2-carbaldehyde (5v)

According to general procedure C, compound 5v was obtained as a brown in 99 % yield (48.3 mg, 0.127 mmol, R_f = 0.20, heptane/ethyl acetate, 7:3); m.p.= 112 – 115 °C. IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2921 (m), 2851 (m), 1683 (s), 1607 (m), 1463 (s), 1413 (m), 1304 (s), 1226 (s), 1092

(s), 1032 (s), 848 (s), 739 (vs), 492 (m). ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 10.17 (s, 1H), 7.99 – 7.90 (m, 1H), 7.51 – 7.44 (m, 3H), 7.41 – 7.33 (m, 2H), 7.22 – 7.15 (m, 2H), 7.10 (d, *J* = 2.5 Hz, 1H), 6.75 – 6.64 (m, 2H), 6.10 (s, 2H), 3.78 (s, 3H), 2.39 (s, 3H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$): δ [ppm] = 185.1, 158.9, 146.2, 143.1, 139.2, 136.8, 131.7, 129.6, 129.4, 127.8, 127.2, 124.4, 123.2, 122.5, 119.7, 117.0, 115.6, 112.0, 95.4, 86.2, 55.5, 46.3, 21.7 (signal of two carbons are absent, which may relate to signal overlap). MS (EI, 70 eV): m/z (%) = 380 (7), 352 (30), 351 (100), 235 (41), 192 (27), 191 (22), 189 (12). HRMS (ESI-TOF) m/z = calcd. for $NaC_{25}H_{20}N_2O_2$ $[M+Na]^+$ 403.1422, found 403.1427.

1-(5-Methoxy-2-(*p*-tolylethynyl)benzyl)-1*H*-benzo[*d*]imidazole-2-carbaldehyde (5w)

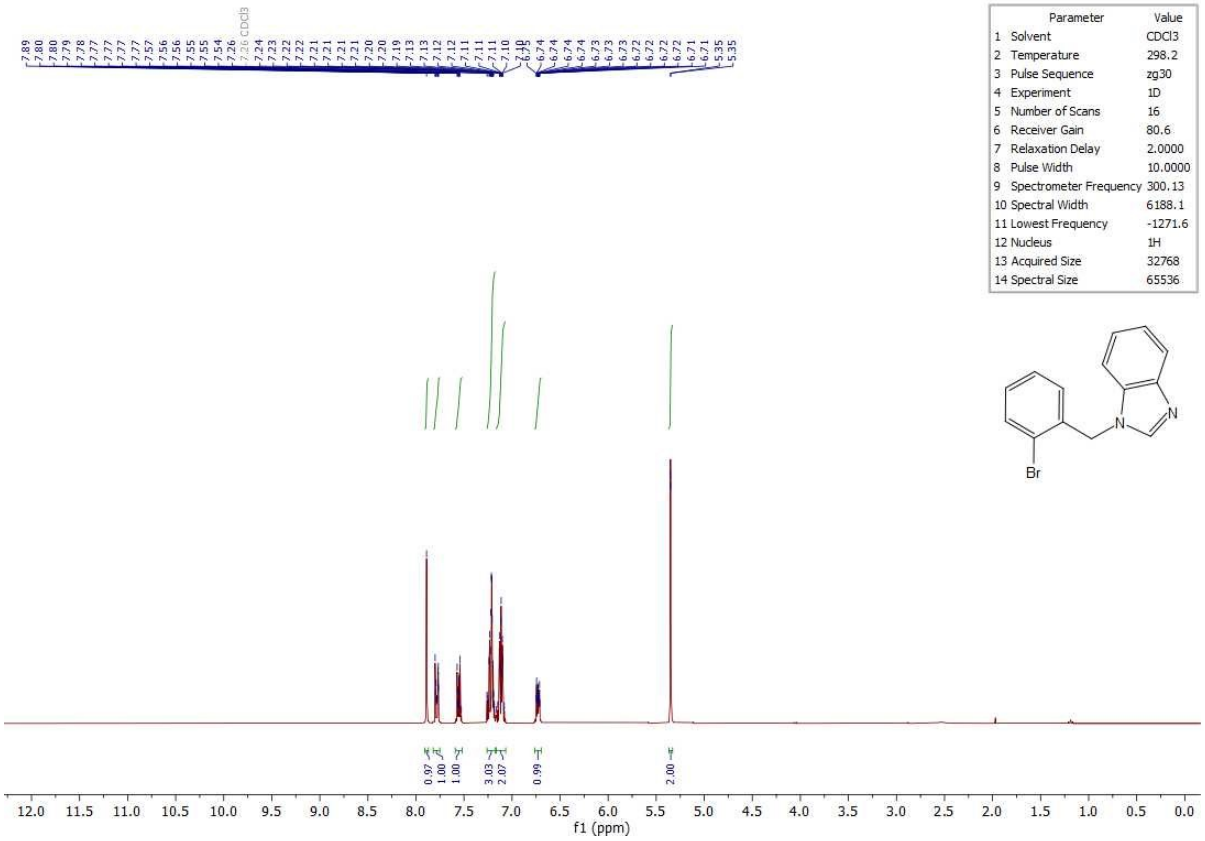
According to general procedure C, compound 5w was obtained as a yellow in 80 % yield (132 mg, 0.347 mmol, R_f = 0.21, heptane/ethyl acetate, 7:3); m.p.= 116 – 119 °C. IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2921 (m), 1693 (s), 1687 (s), 1603 (s), 1460 (s), 1324 (m), 1240 (s), 1032 (m), 853 (s), 811 (s), 739 (vs), 498 (s). ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 10.18 (s, 1H), 8.02 – 7.93 (m, 1H), 7.56 – 7.35 (m, 6H), 7.22 – 7.13 (m, 2H), 6.78 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.20 (d, *J* = 2.6 Hz, 1H), 6.12 (s, 2H), 3.63 (s, 3H), 2.38 (s, 3H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$): δ [ppm] = 185.1, 160.1, 146.2, 143.0, 139.1, 138.8, 136.7, 134.0, 131.5, 129.4, 127.4, 124.5, 122.5, 120.1, 114.2, 112.9, 112.5, 111.8, 94.3, 86.1, 55.3, 46.8, 21.7 (signal of two carbons are absent, which may relate to signal overlap). MS (EI, 70 eV): m/z (%) = 380 (19), 352 (32), 351 (100), 350 (10), 336 (12), 307 (12), 192 (18), 191 (16), 189 (11). HRMS (ESI-TOF) m/z = calcd. for $C_{25}H_{21}N_2O_2$ $[M+H]^+$ 381.1603, found 381.1612.

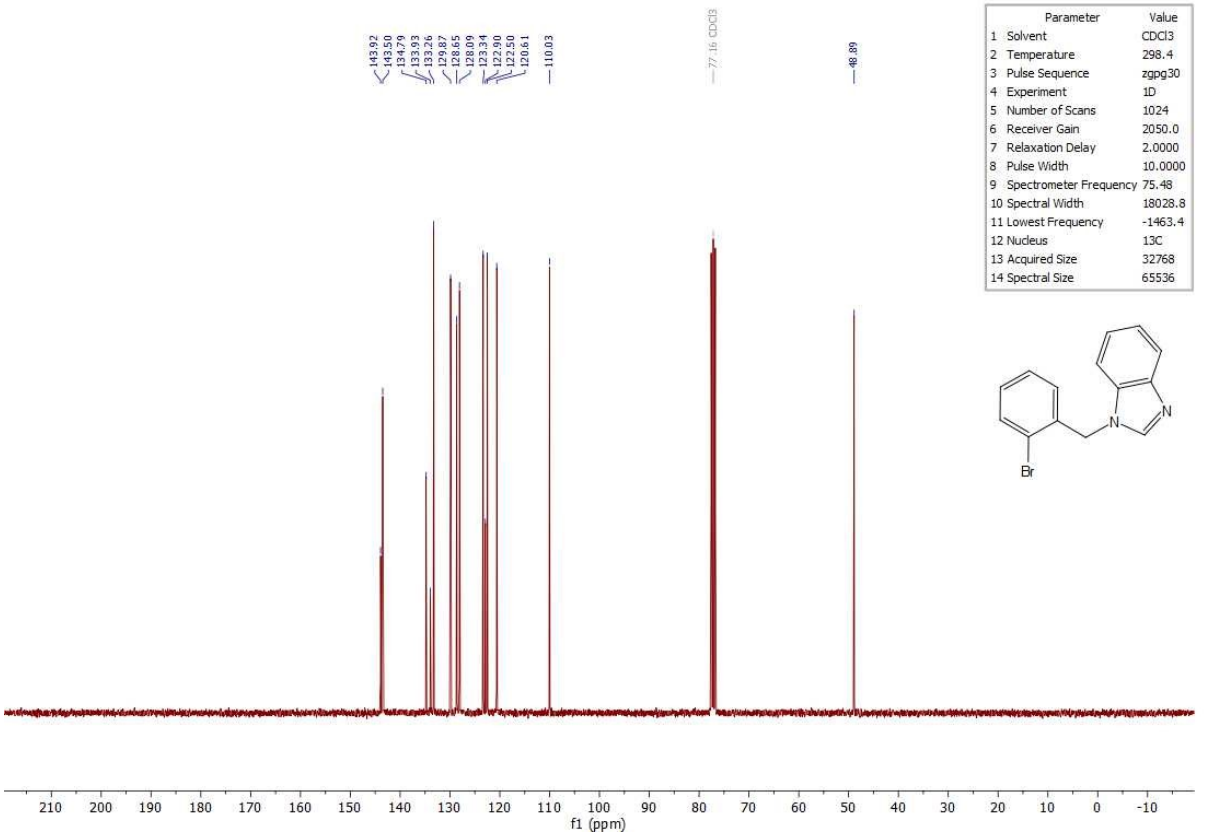
1-(5-Fluoro-2-(*p*-tolylethynyl)benzyl)-1*H*-benzo[*d*]imidazole-2-carbaldehyde (5x)

According to general procedure C, compound 5y was obtained as a white in 82 % yield (92.1 mg, 0.250 mmol, R_f = 0.29, heptane/ethyl acetate, 7:3); m.p.= 150 – 153 °C. IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2921 (m), 2851 (m), 1685 (s), 1603 (m), 1460 (s), 1277 (m), 1230 (s), 1158 (m), 958 (m), 853 (s), 813 (s), 735 (vs), 498 (s). ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 10.18 (s, 1H), 8.04 – 7.92 (m, 1H), 7.58 (dd, *J* = 8.6, 5.6 Hz, 1H), 7.51 – 7.36 (m, 5H), 7.23 – 7.14 (m, 2H), 7.02 – 6.90 (m, 1H), 6.32 (dd, *J* = 9.3, 2.7 Hz, 1H), 6.12 (s, 2H), 2.39 (s, 3H). ^{19}F NMR (282 MHz, CDCl3): δ = -109.4. ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$): δ [ppm] = 185.08, 162.83 (d, *J* = 250.9 Hz), 146.08, 143.07, 140.11 (d, *J* = 7.5 Hz), 139.27, 136.56, 134.42 (d, *J* = 8.4 Hz), 131.61, 129.45, 127.56, 124.67, 122.73, 119.61, 118.04 (d, *J* = 3.4 Hz), 115.25 (d, *J* = 22.1 Hz), 113.42 (d, *J* = 23.6 Hz), 111.46, 95.55, 85.00, 46.60, 21.70 (signal of two carbons are absent, which may relate to signal overlap). MS (EI, 70 eV): m/z (%) = 340 (25), 339 (100), 220 (10), 207 (13) (no molecular peak was observed). HRMS (ESI-TOF) m/z = calcd. for $C_{24}H_{28}N_2O$ $[M+H]^+$ 369.1403, found 369.1412.

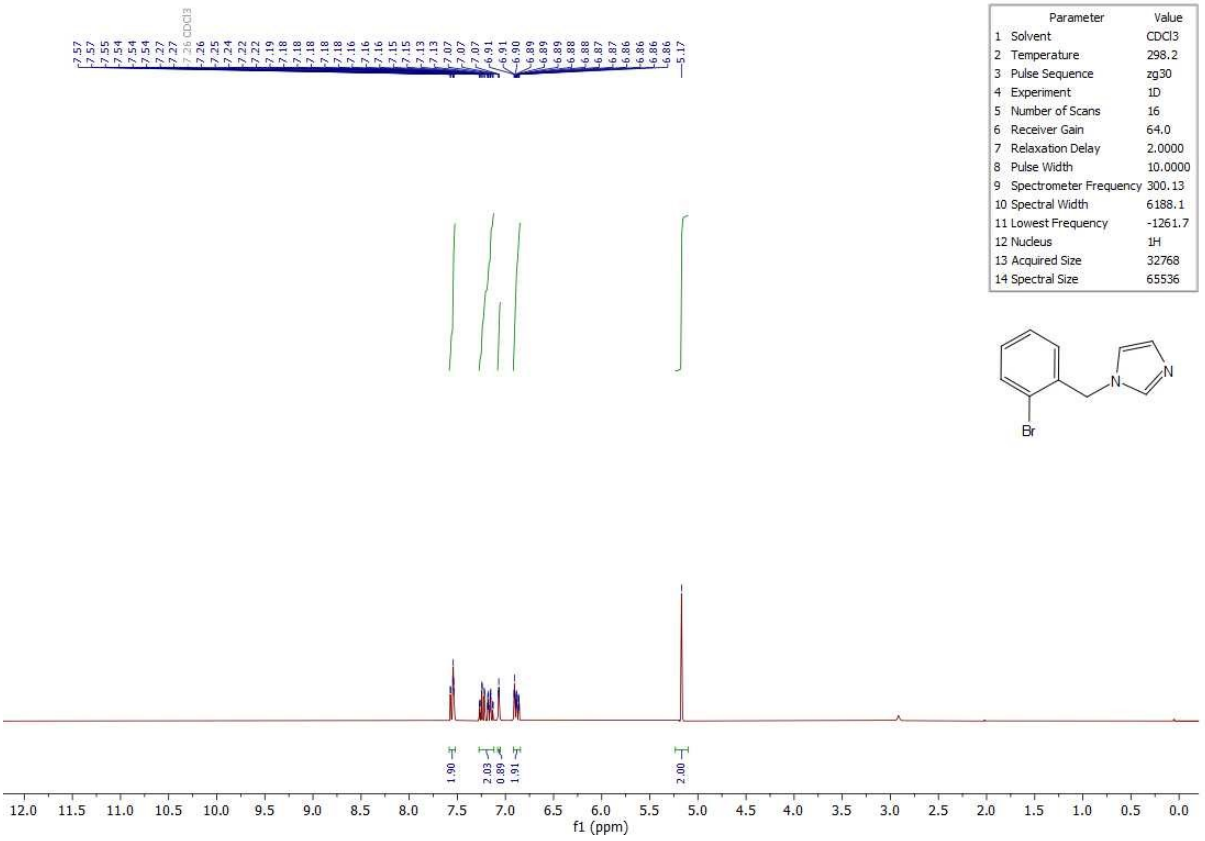
1-(2-bromobenzyl)-1H-benzo[d]imidazole (3a)

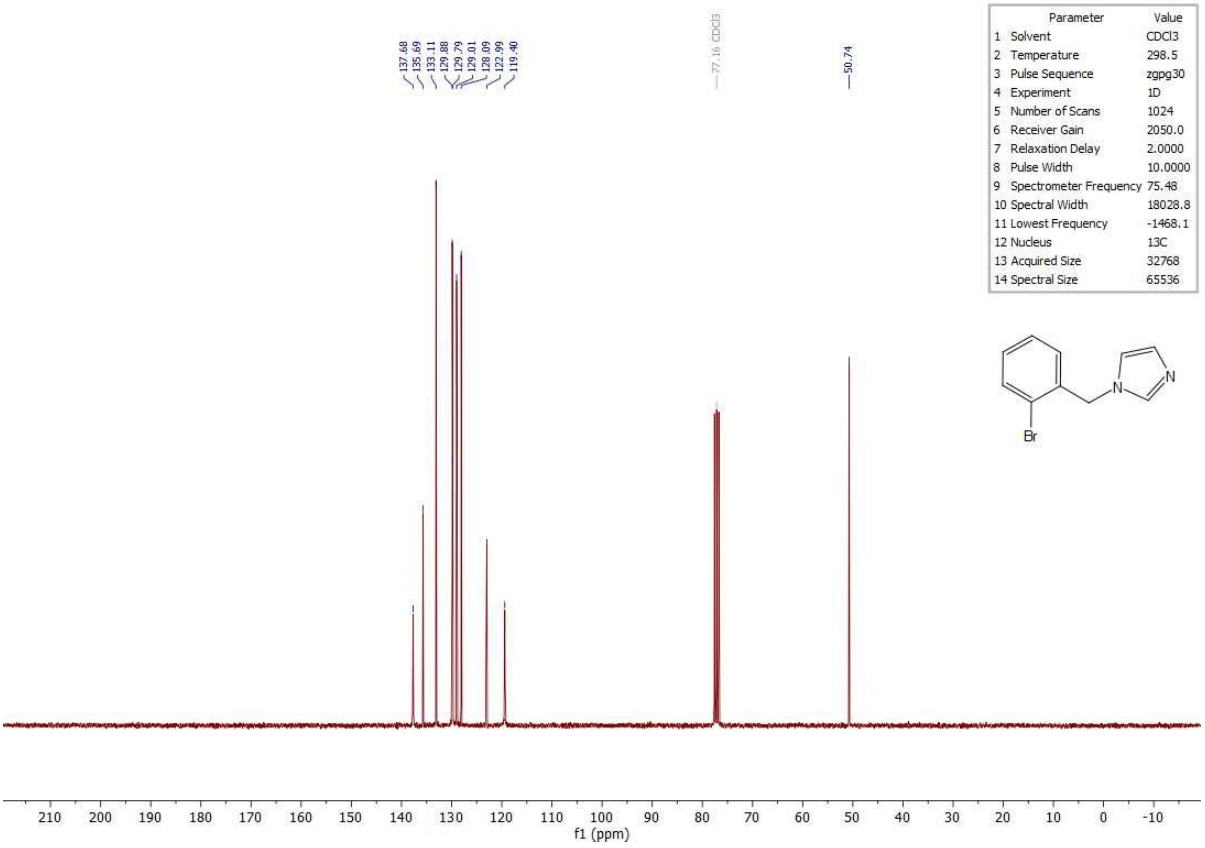
^{1}H, ^{13}C and ^{19}F NMR spectra



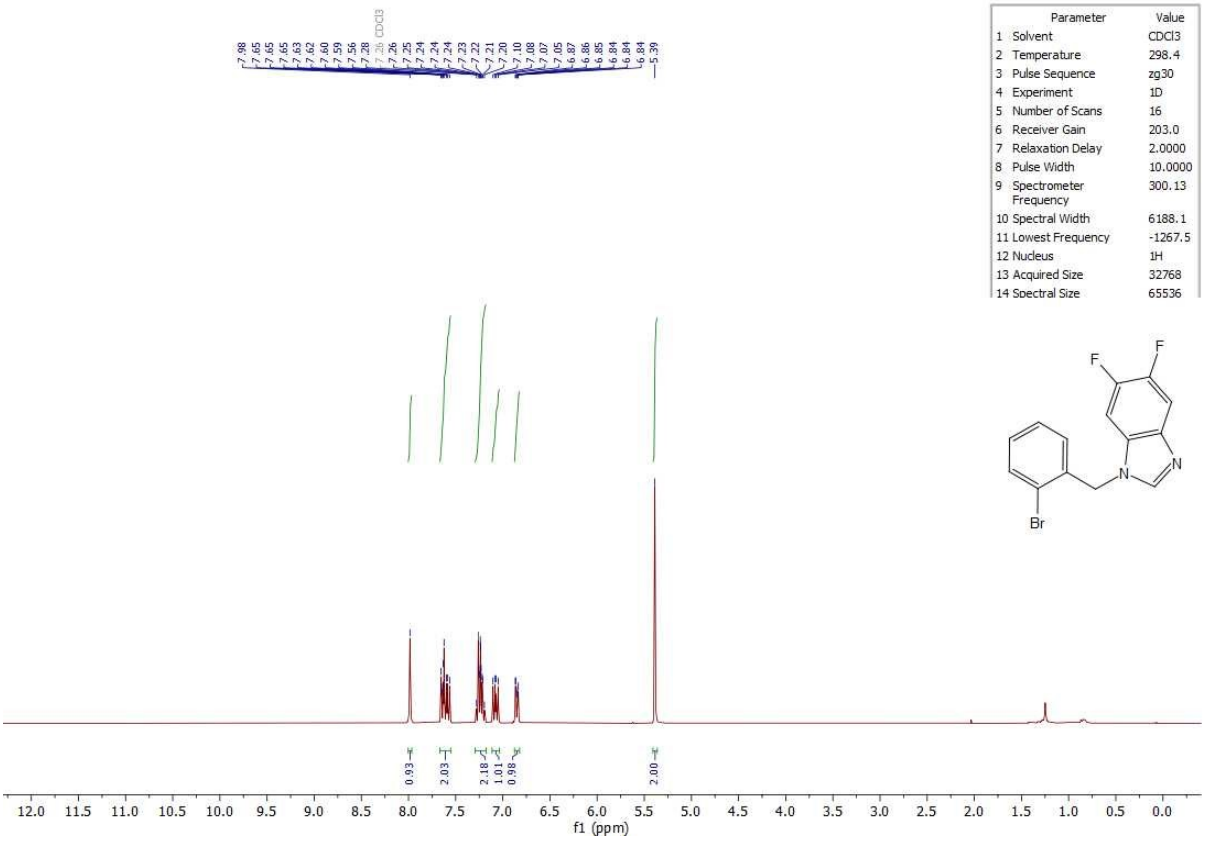


1-(2-Bromobenzyl)-1*H*-imidazole (3b)

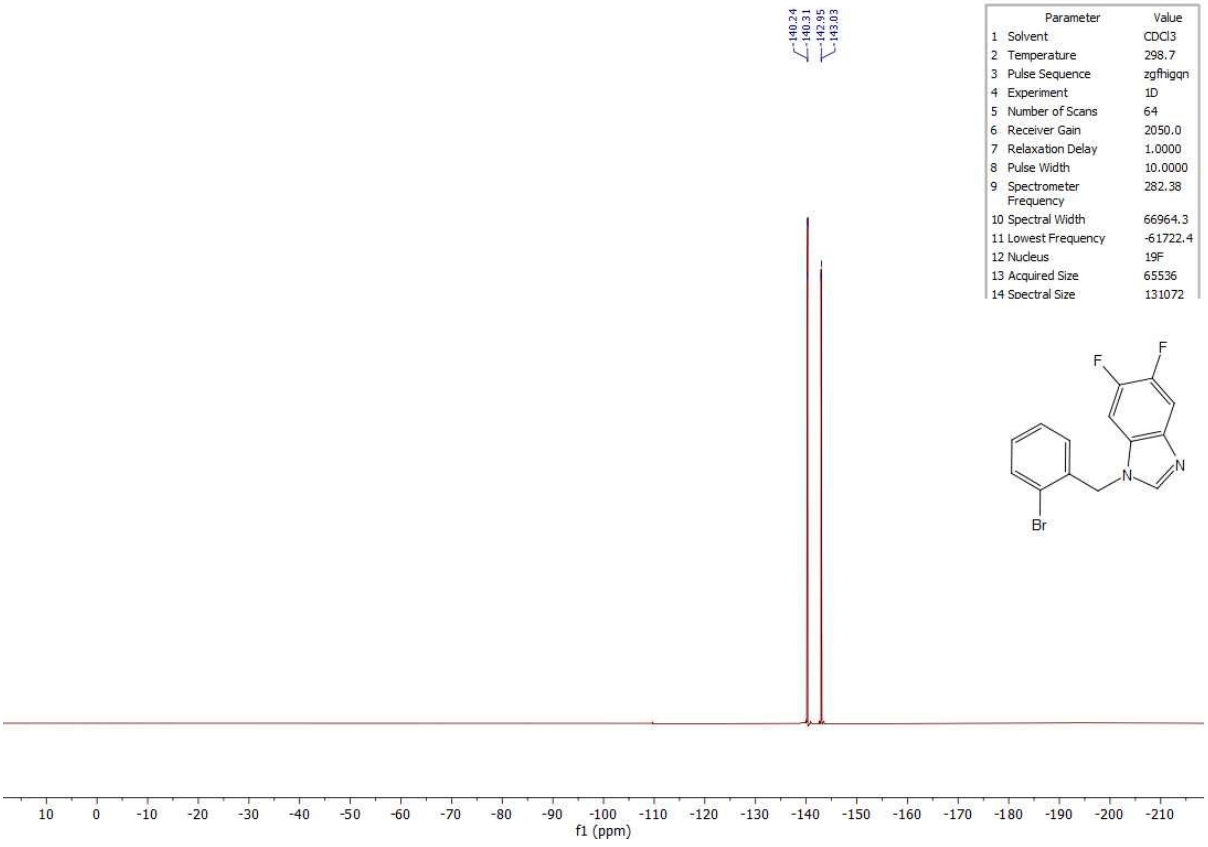




1-(2-Bromobenzyl)-5,6-difluoro-1*H*-benzo[*d*]imidazole (3c)

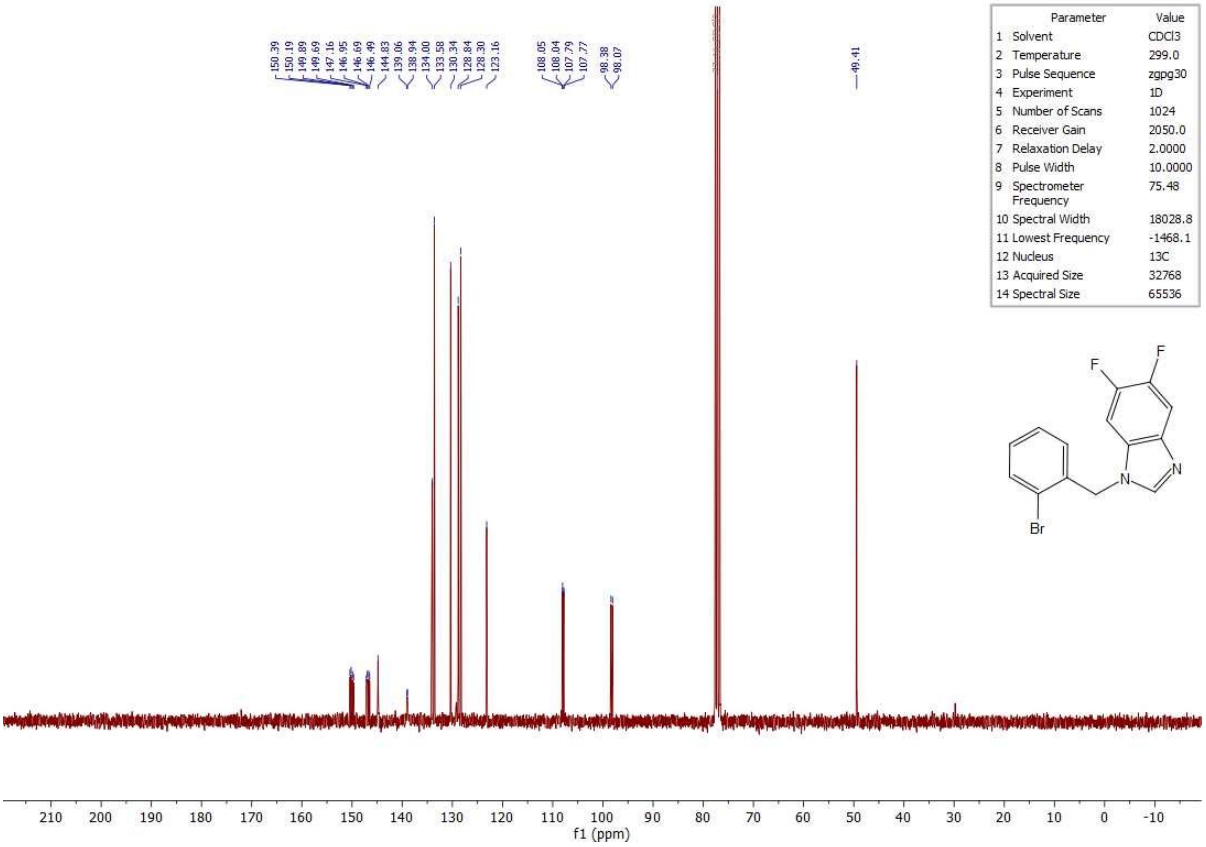


	Parameter	Value
1	Solvent	CDCl3
2	Temperature	298.4
3	Pulse Sequence	zg30
4	Experiment	1D
5	Number of Scans	16
6	Receiver Gain	203.0
7	Relaxation Delay	2.0000
8	Pulse Width	10.0000
9	Spectrometer Frequency	300.13
10	Spectral Width	6188.1
11	Lowest Frequency	-1267.5
12	Nucleus	1H
13	Acquired Size	32768
14	Spectral Size	65536

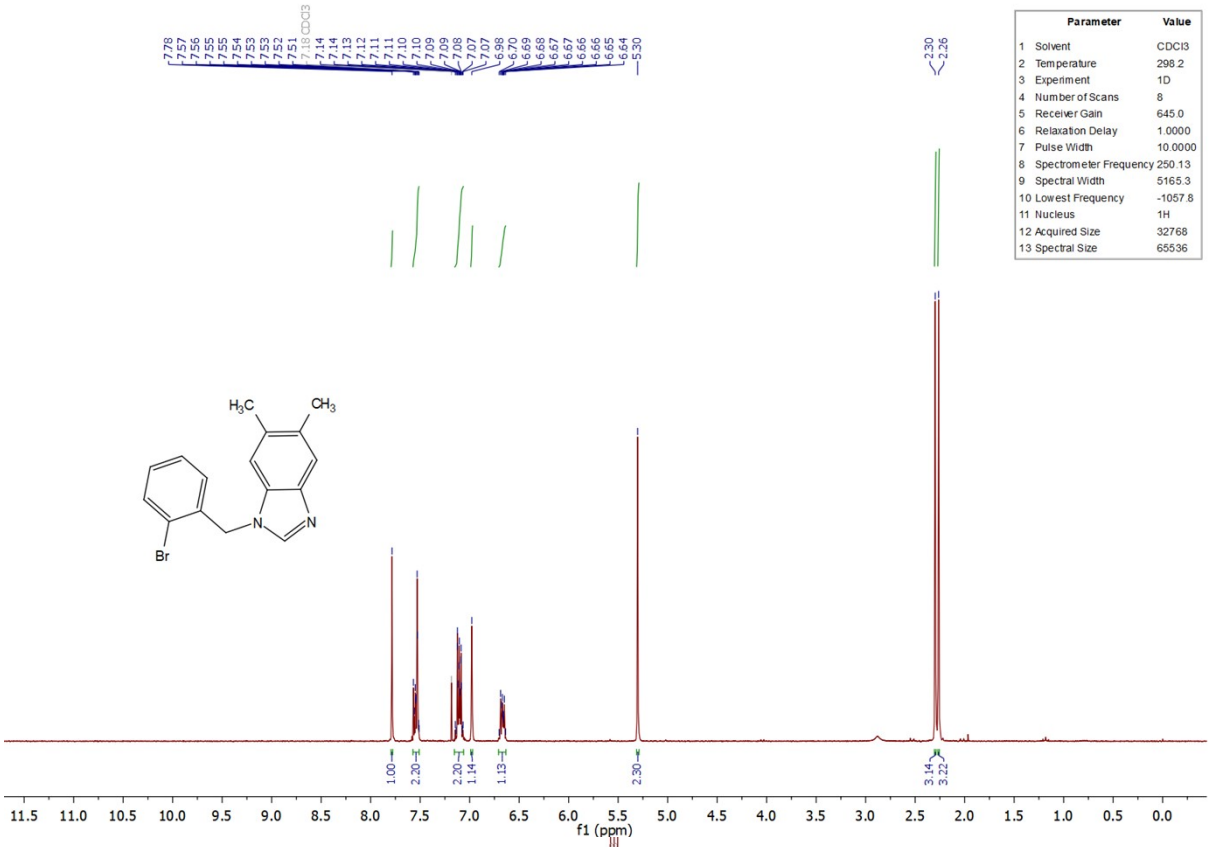


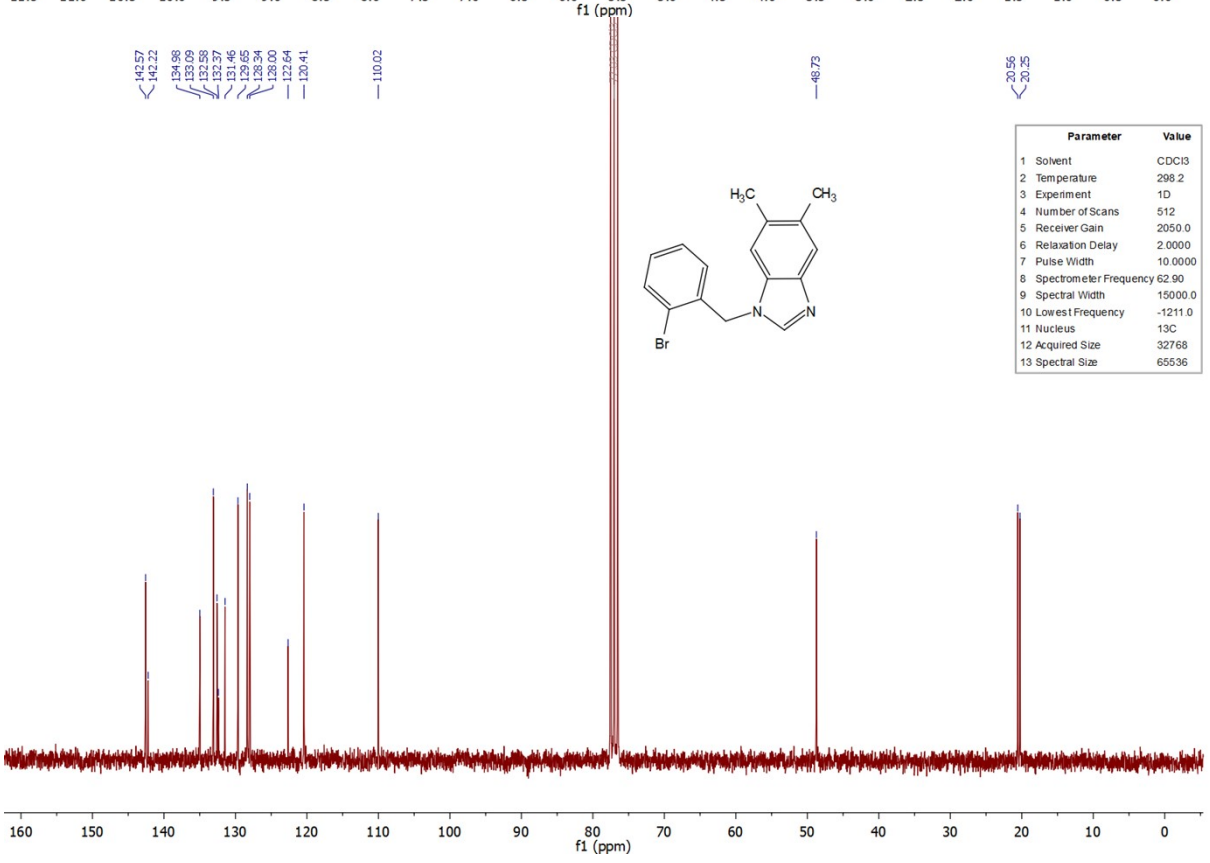
	Parameter	Value
1	Solvent	CDCl3
2	Temperature	298.7
3	Pulse Sequence	zgfhigqn
4	Experiment	1D
5	Number of Scans	64
6	Receiver Gain	2050.0
7	Relaxation Delay	1.0000
8	Pulse Width	10.0000
9	Spectrometer Frequency	282.38
10	Spectral Width	66964.3
11	Lowest Frequency	-61722.4
12	Nucleus	19F
13	Acquired Size	65536
14	Spectral Size	131072

1-(2-Bromobenzyl)-5,6-difluoro-1*H*-benzo[*d*]imidazole (3c)

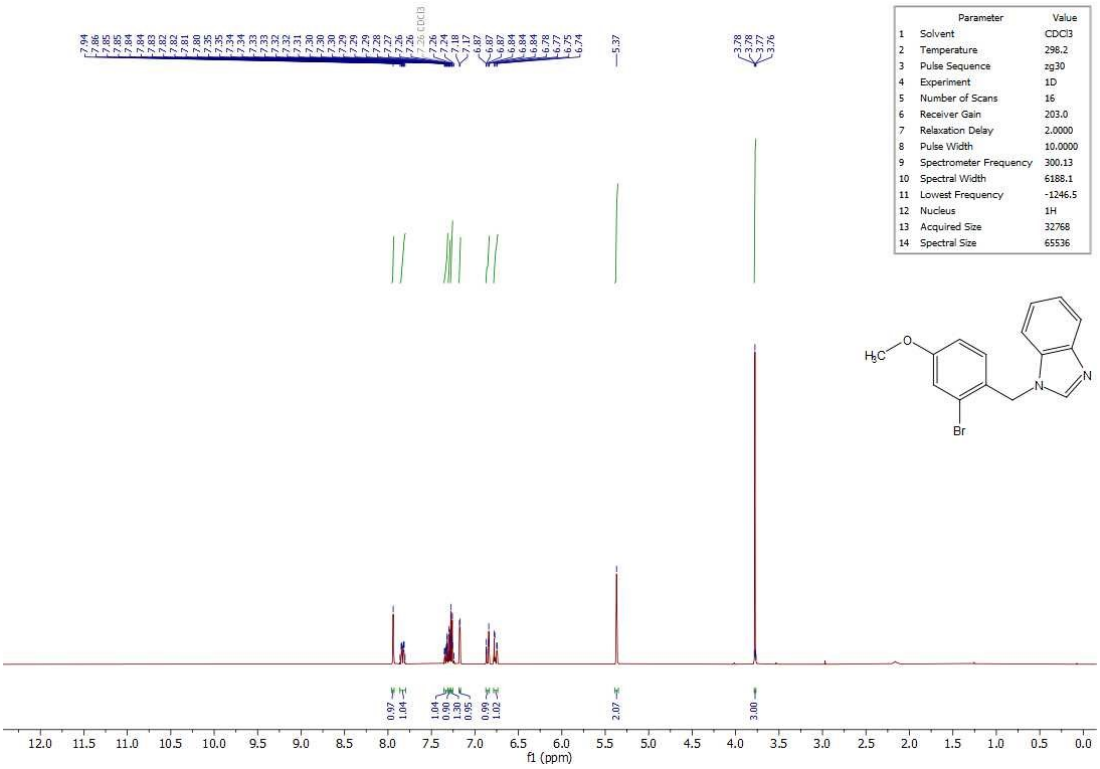


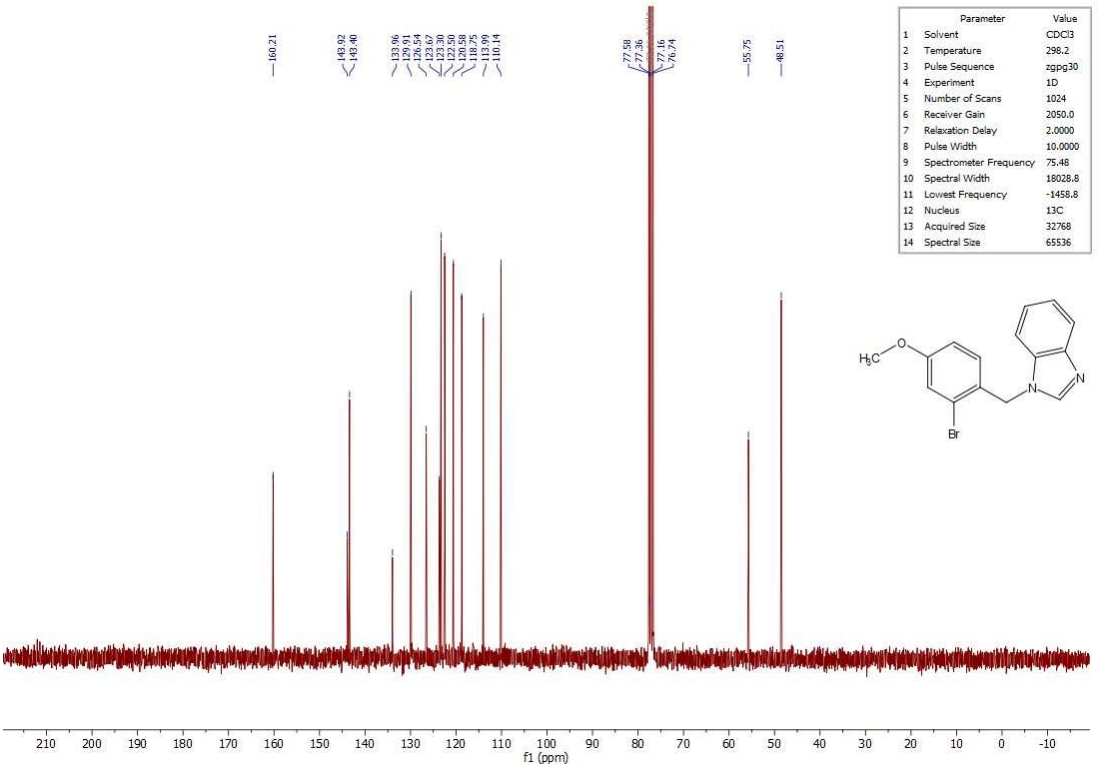
1-(2-Bromobenzyl)-5,6-dimethyl-1*H*-benzo[*d*]imidazole (3d)



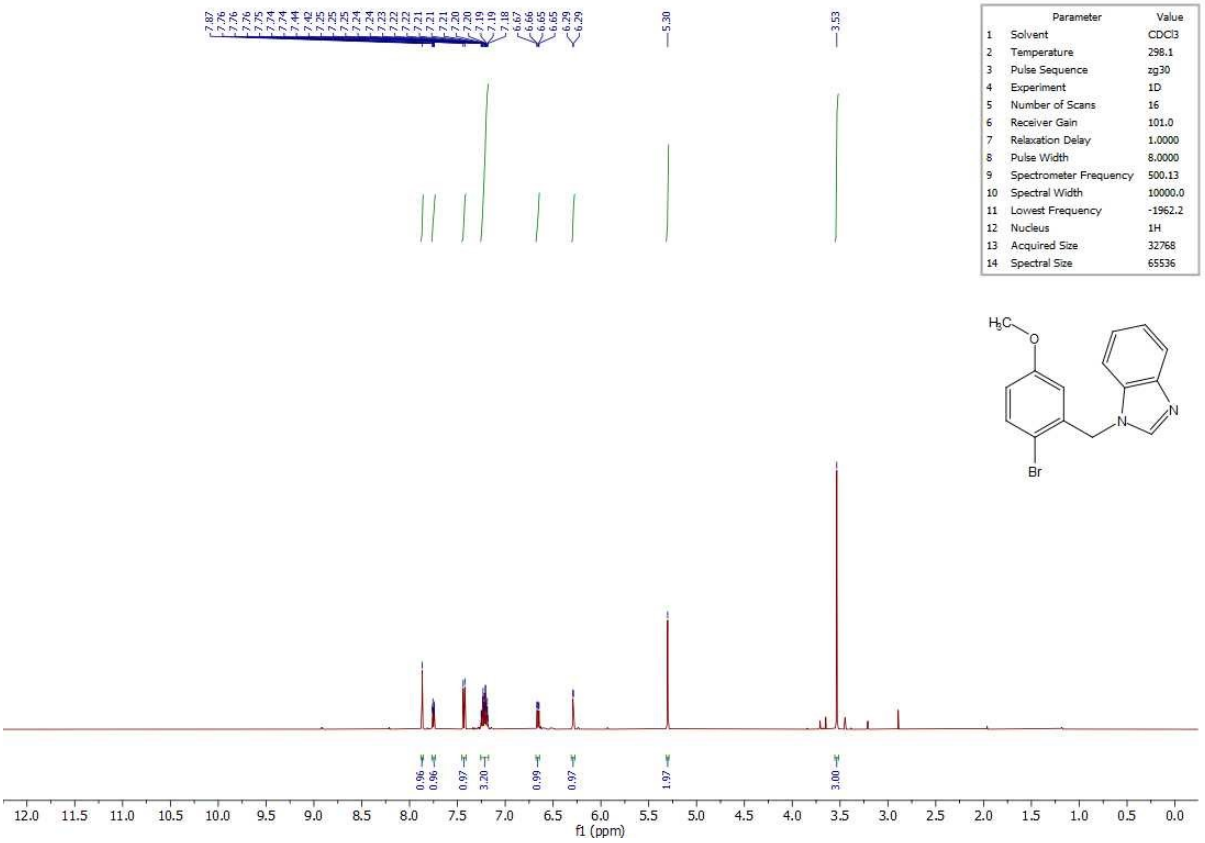


1-(2-Bromo-4-methoxybenzyl)-1*H*-benzo[*d*]imidazole (3e)

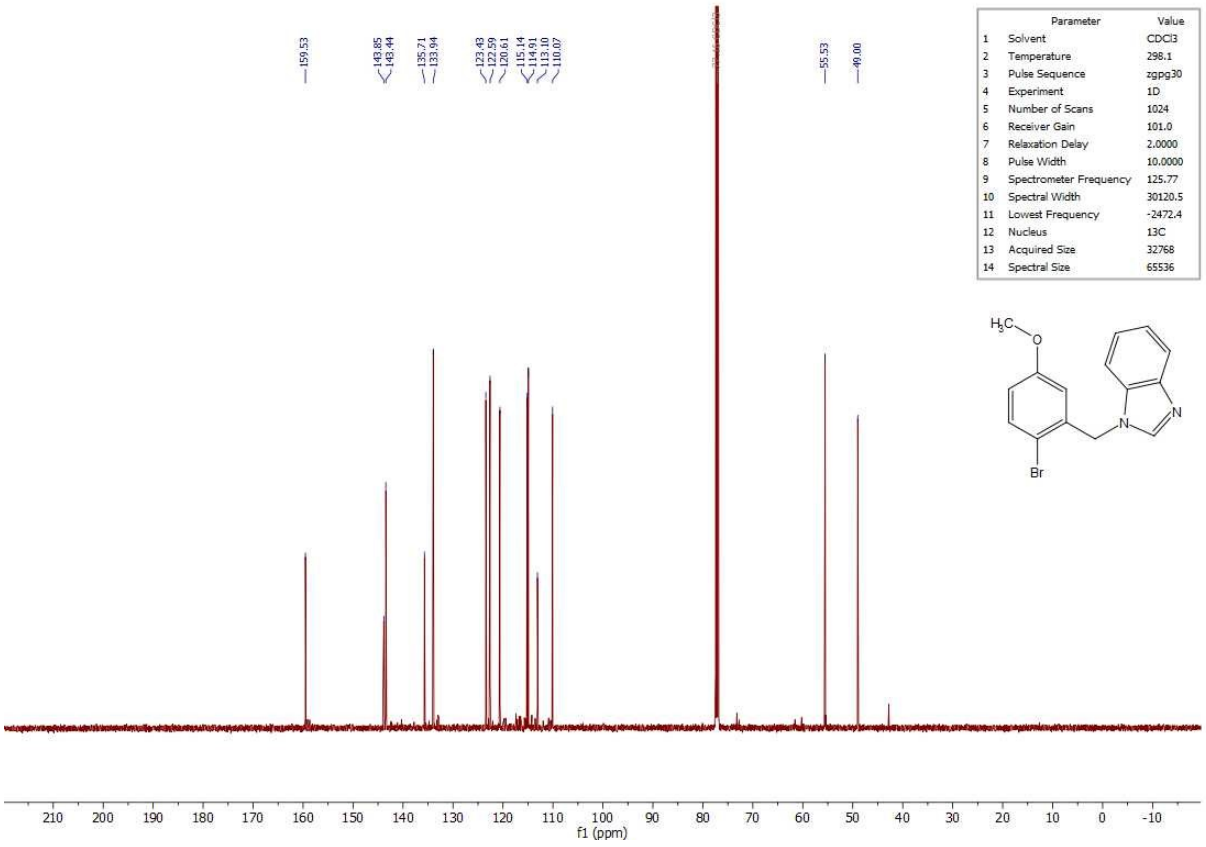




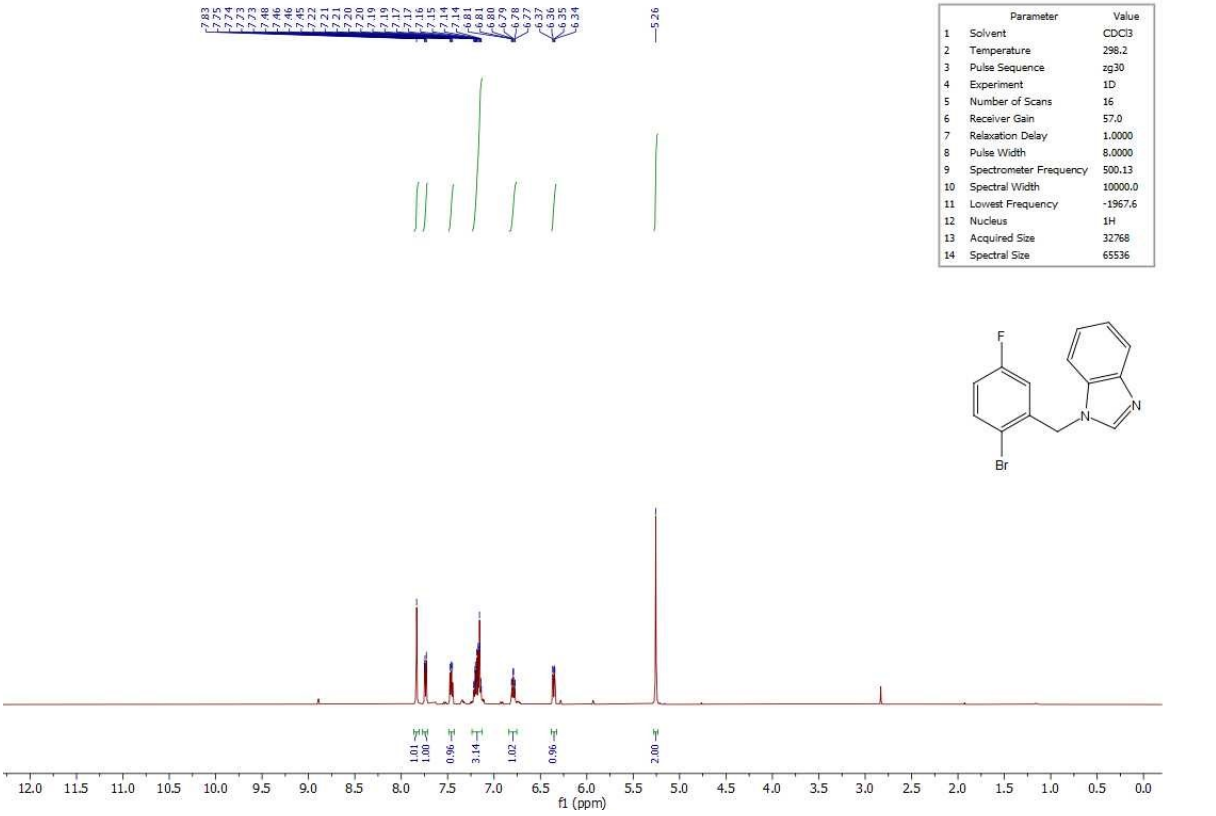
1-(2-Bromo-5-methoxybenzyl)-1*H*-benzo[*d*]imidazole (3f)



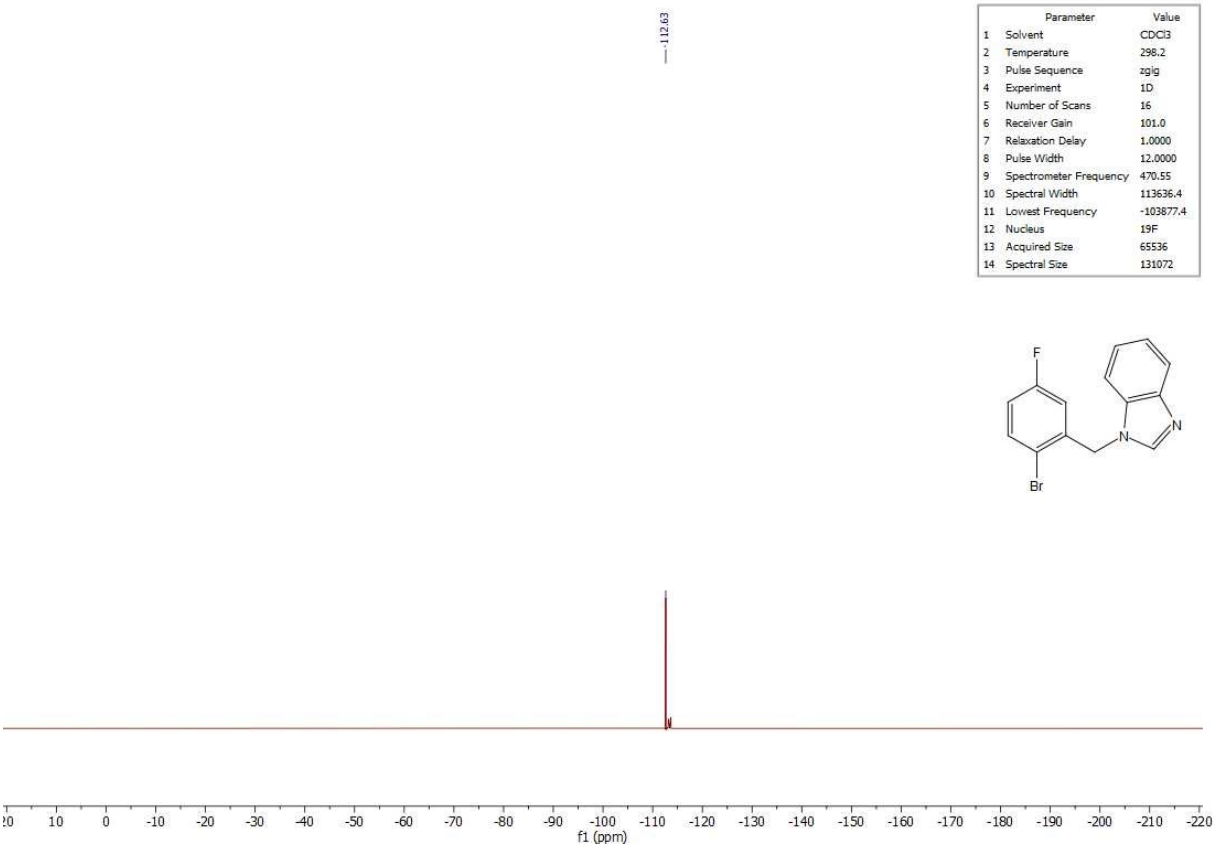
1-(2-Bromo-5-methoxybenzyl)-1*H*-benzo[*d*]imidazole (3f)



1-(2-Bromo-5-fluorobenzyl)-1*H*-benzo[*d*]imidazole (3g)

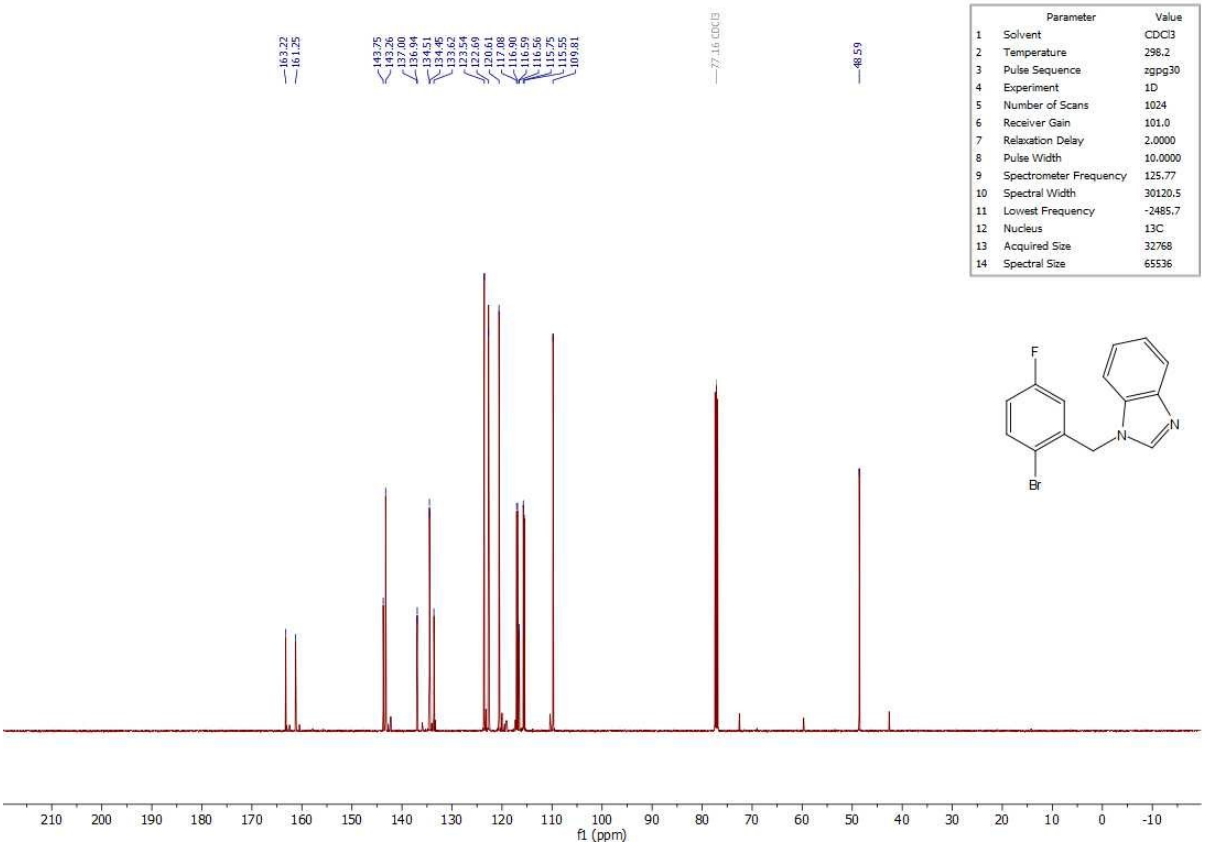


	Parameter	Value
1	Solvent	CDCl3
2	Temperature	298.2
3	Pulse Sequence	zg30
4	Experiment	1D
5	Number of Scans	16
6	Receiver Gain	57.0
7	Relaxation Delay	1.0000
8	Pulse Width	8.0000
9	Spectrometer Frequency	500.13
10	Spectral Width	10000.0
11	Lowest Frequency	-1967.6
12	Nucleus	1H
13	Acquired Size	32768
14	Spectral Size	65536

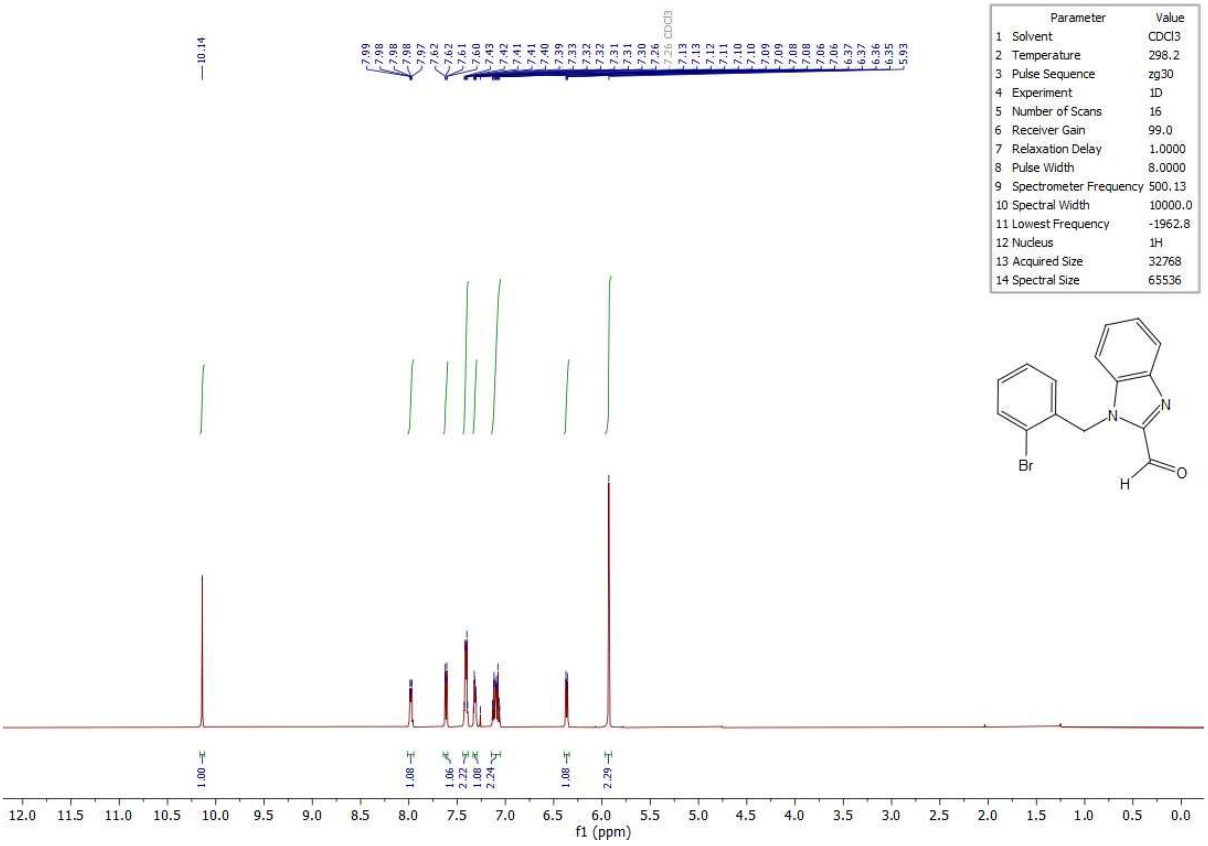


	Parameter	Value
1	Solvent	CDCl3
2	Temperature	298.2
3	Pulse Sequence	zgig
4	Experiment	1D
5	Number of Scans	16
6	Receiver Gain	101.0
7	Relaxation Delay	1.0000
8	Pulse Width	12.0000
9	Spectrometer Frequency	470.55
10	Spectral Width	113636.4
11	Lowest Frequency	-103877.4
12	Nucleus	19F
13	Acquired Size	65536
14	Spectral Size	131072

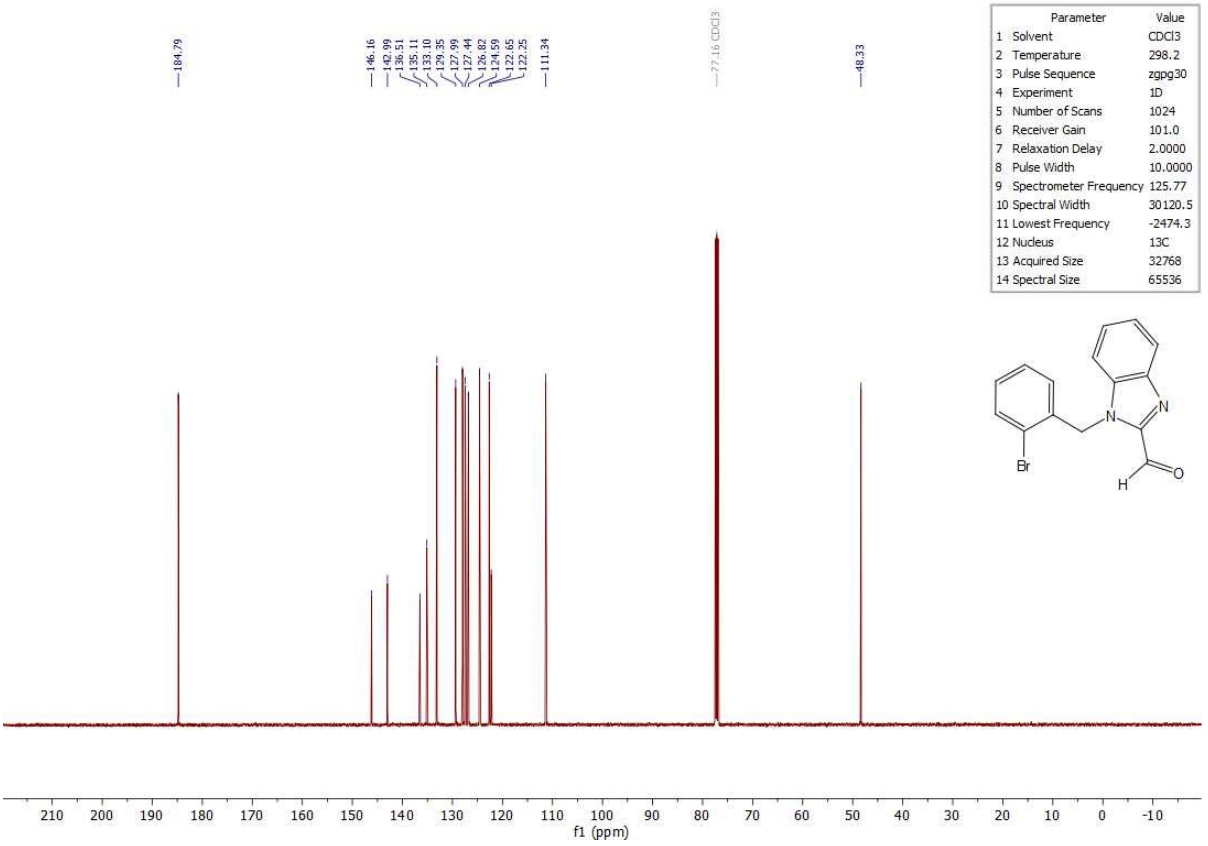
1-(2-Bromo-5-fluorobenzyl)-1*H*-benzo[*d*]imidazole (3g)



1-(2-Bromobenzyl)-1H-benzo[d]imidazole-2-carbaldehyde (4a)

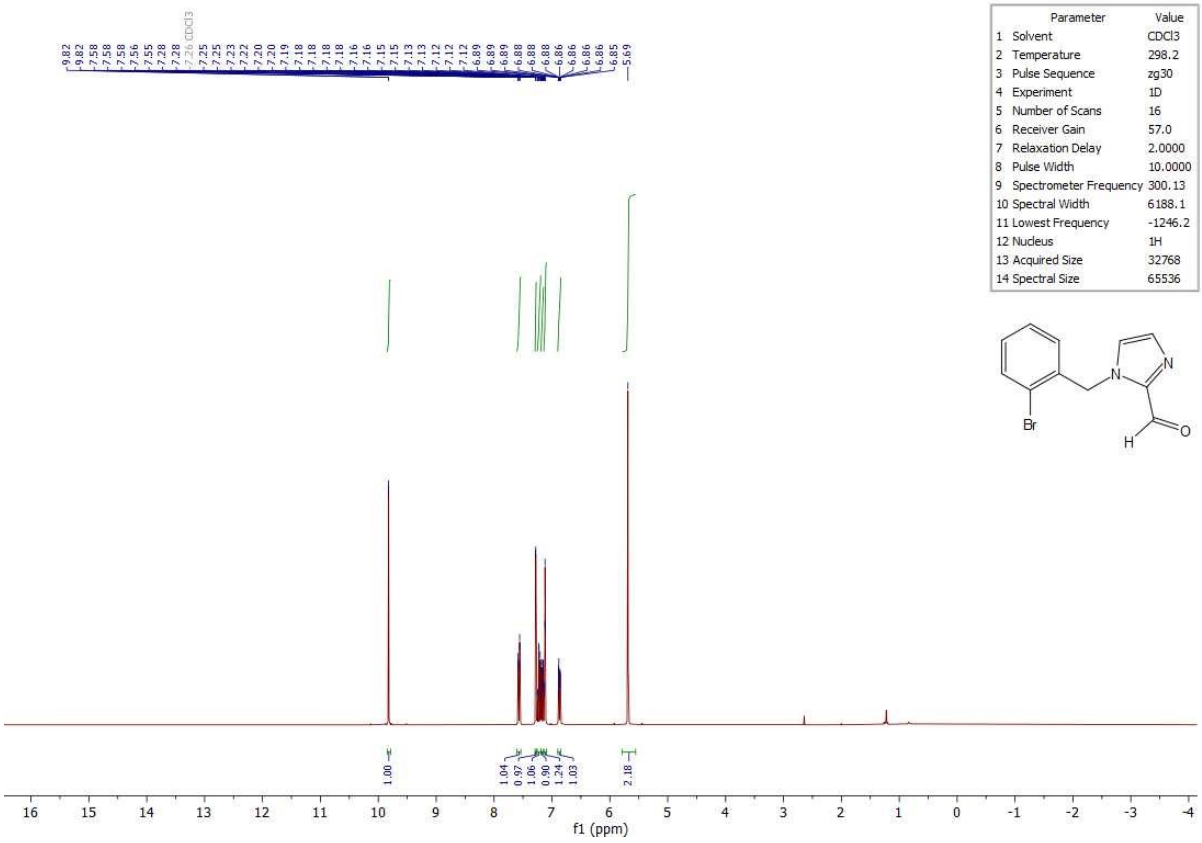


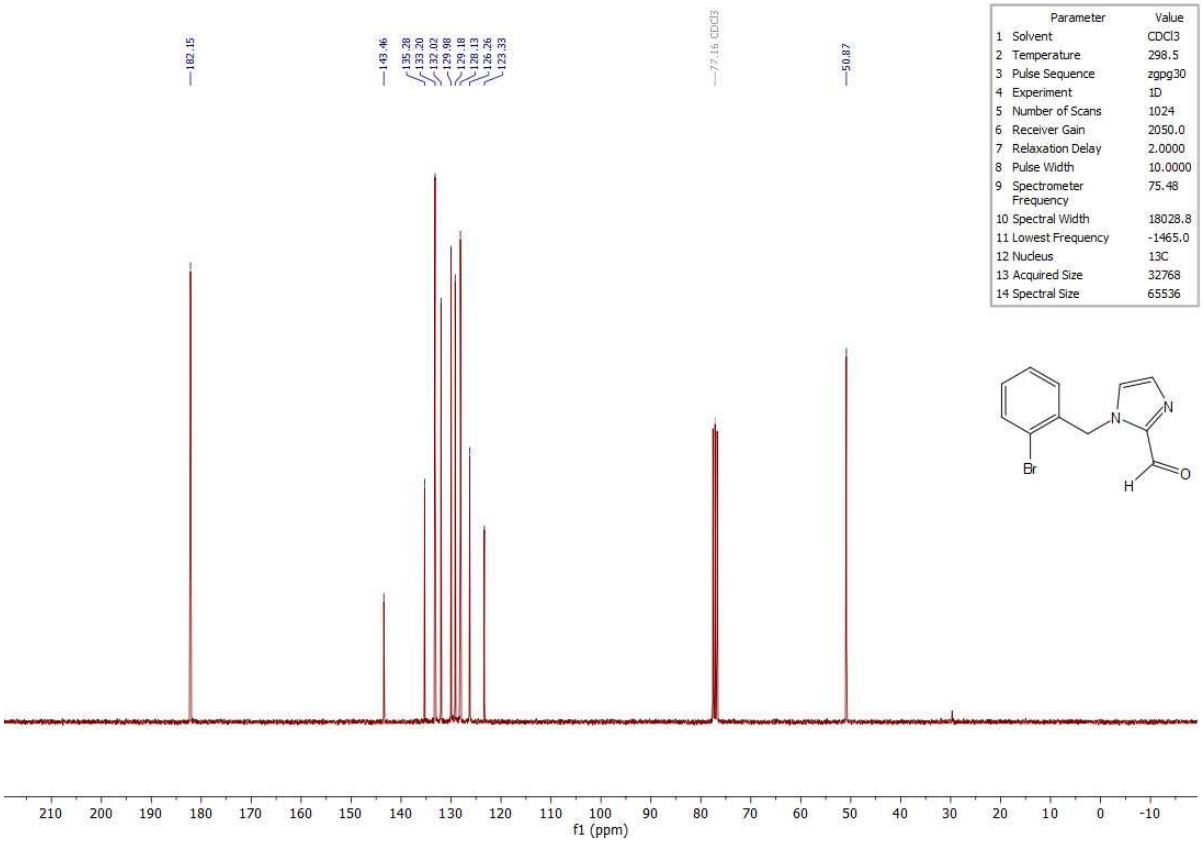
	Parameter	Value
1	Solvent	CDCl3
2	Temperature	298.2
3	Pulse Sequence	zg30
4	Experiment	1D
5	Number of Scans	16
6	Receiver Gain	99.0
7	Relaxation Delay	1.0000
8	Pulse Width	8.0000
9	Spectrometer Frequency	500.13
10	Spectral Width	10000.0
11	Lowest Frequency	-1962.8
12	Nucleus	1H
13	Acquired Size	32768
14	Spectral Size	65536



	Parameter	Value
1	Solvent	CDCl3
2	Temperature	298.2
3	Pulse Sequence	zgpg30
4	Experiment	1D
5	Number of Scans	1024
6	Receiver Gain	101.0
7	Relaxation Delay	2.0000
8	Pulse Width	10.0000
9	Spectrometer Frequency	125.77
10	Spectral Width	30120.5
11	Lowest Frequency	-2474.3
12	Nucleus	13C
13	Acquired Size	32768
14	Spectral Size	65536

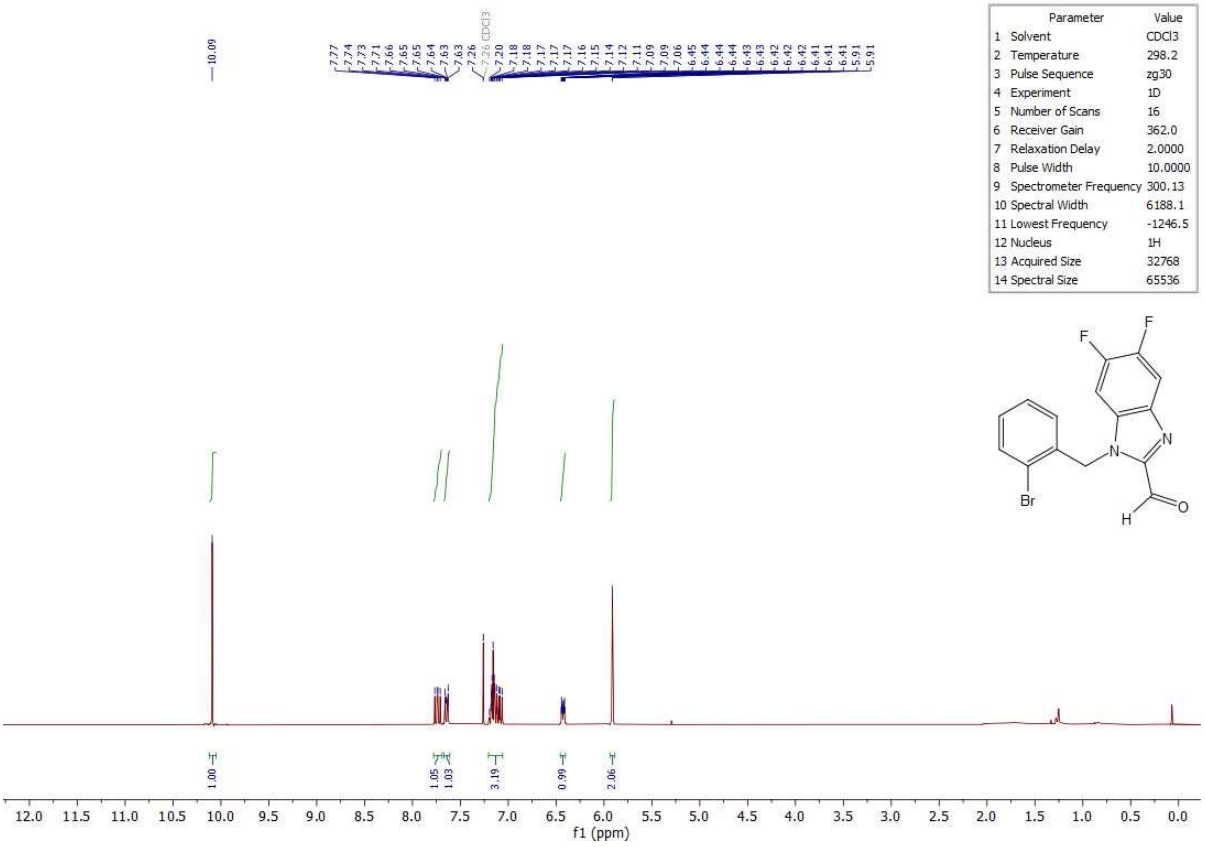
1-(2-Bromobenzyl)-1H-imidazole-2-carbaldehyde (4b)

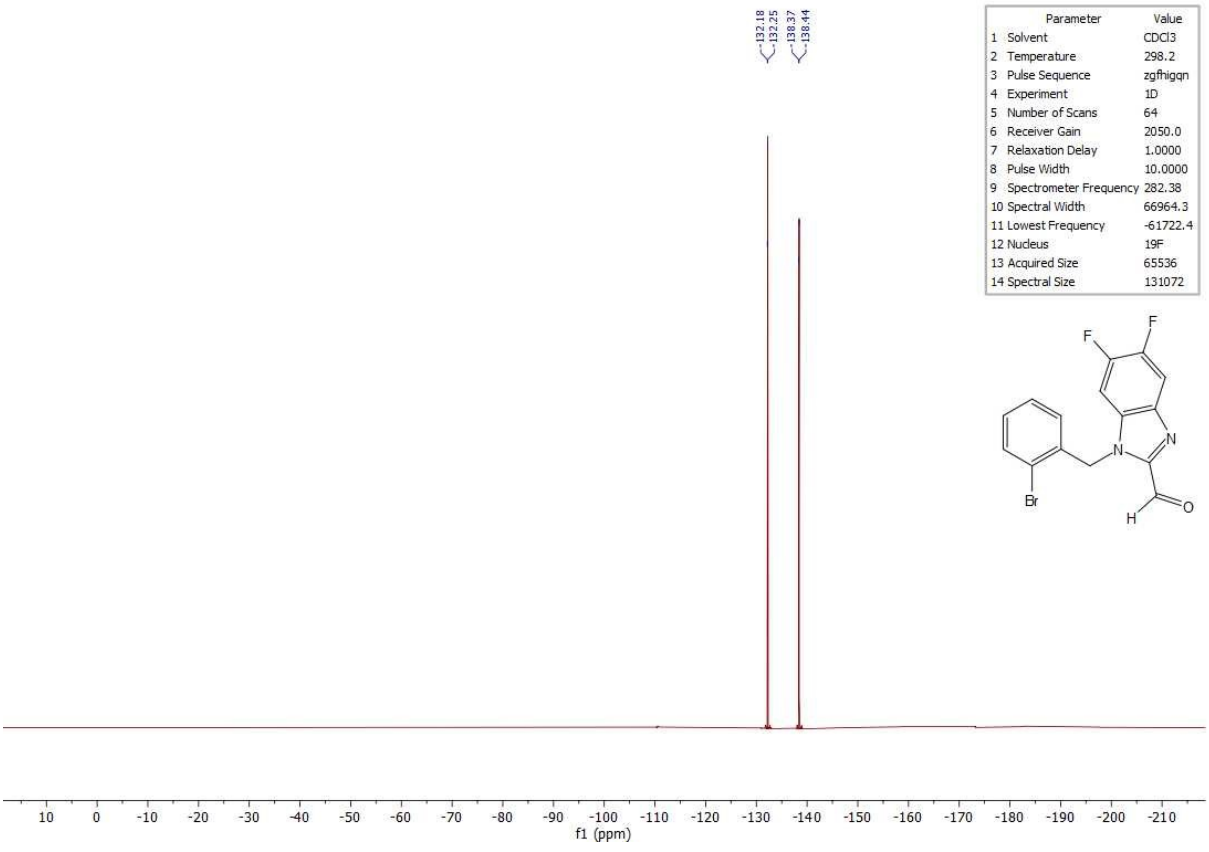




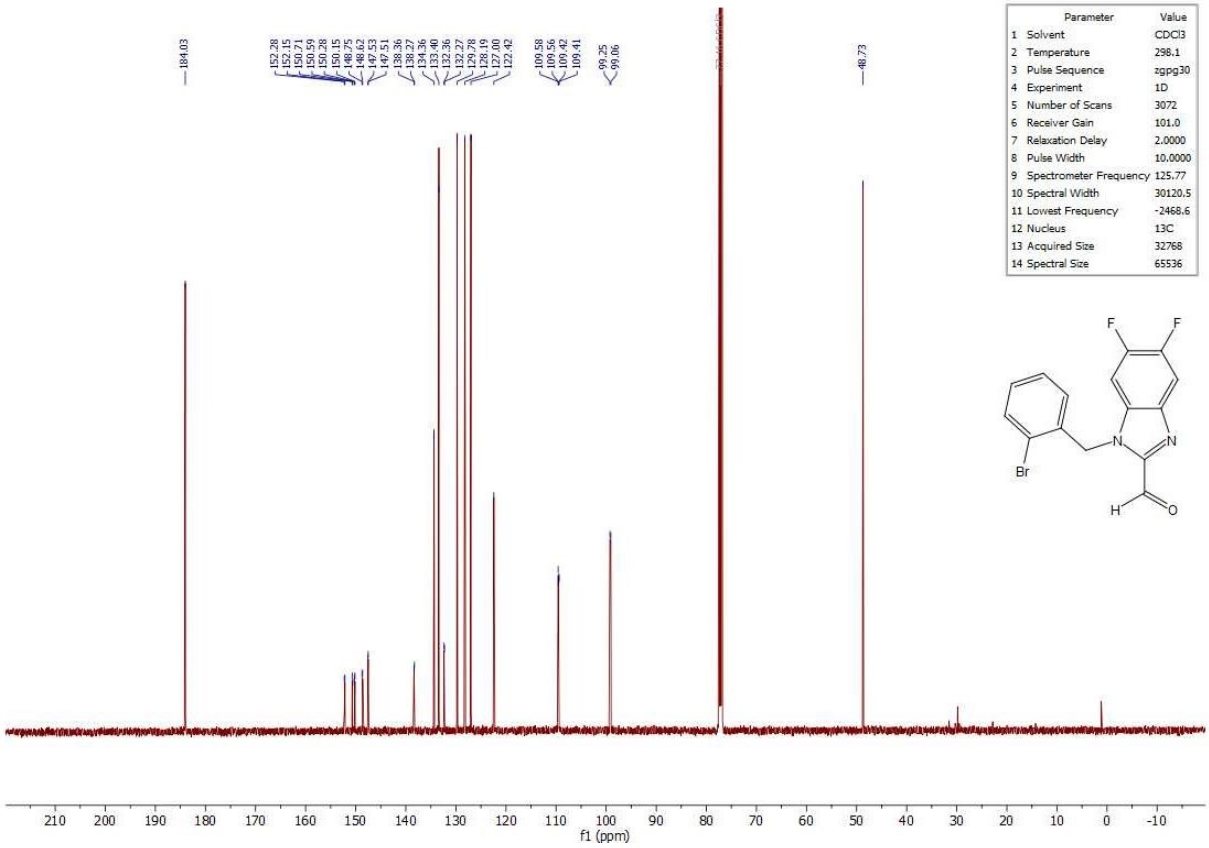
1-(2-Bromobenzyl)-5,6-difluoro-1*H*-benzo[*d*]imidazole-2-carbaldehyde (4c)

-

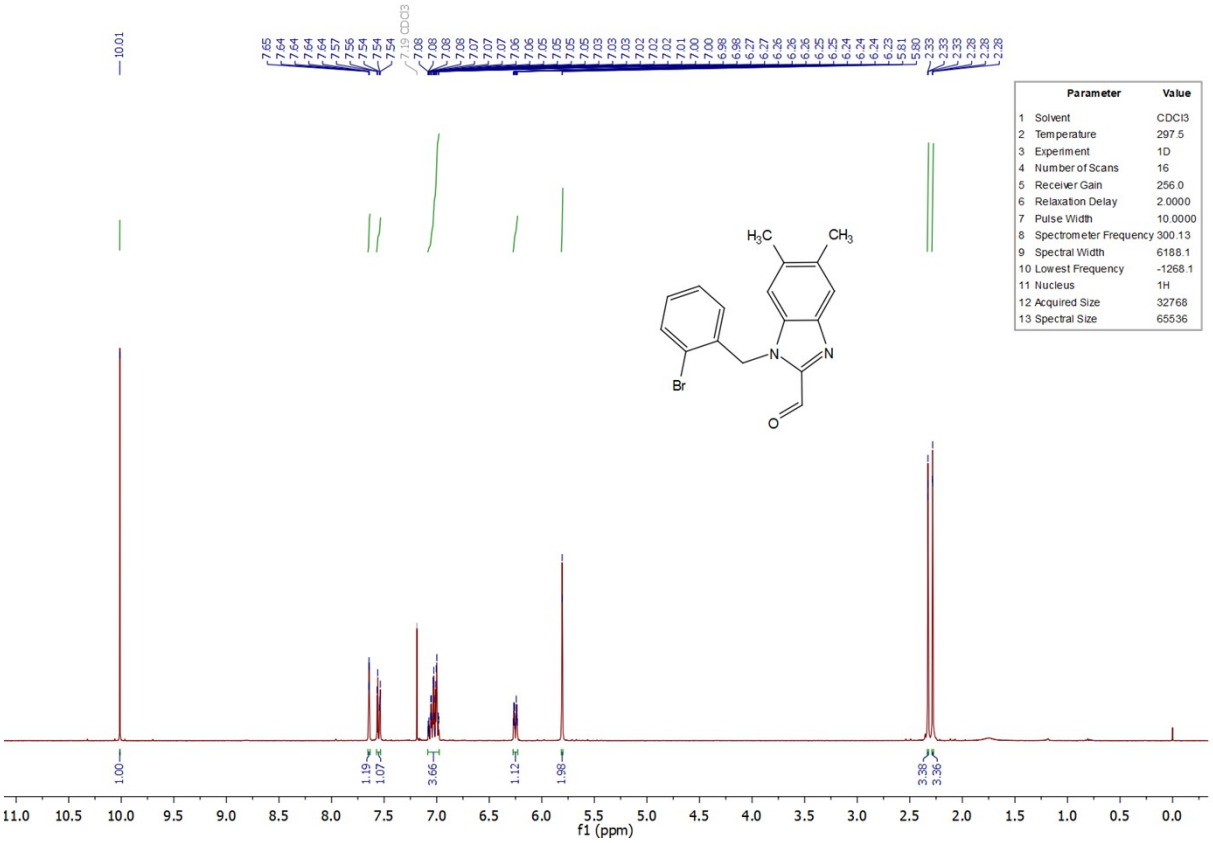


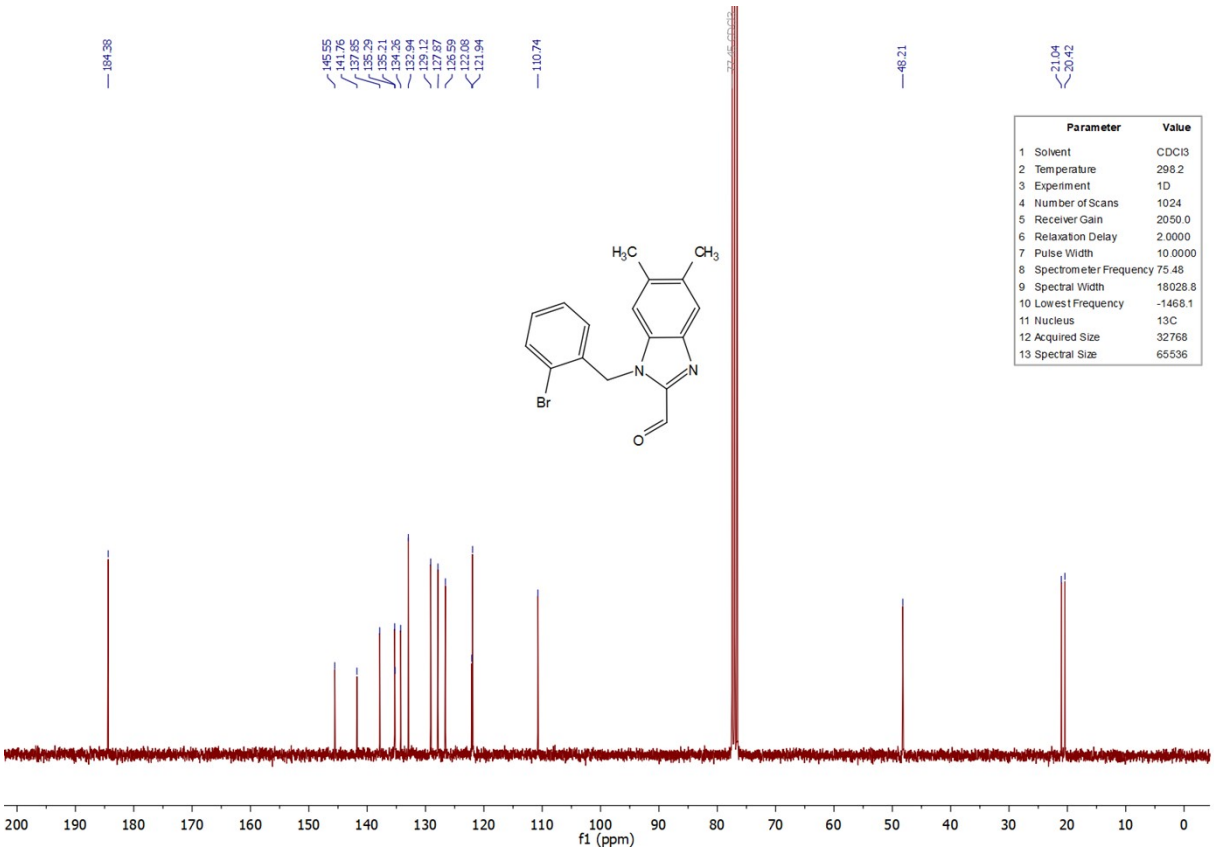


1-(2-Bromobenzyl)-5,6-difluoro-1*H*-benzo[*d*]imidazole-2-carbaldehyde (4c)

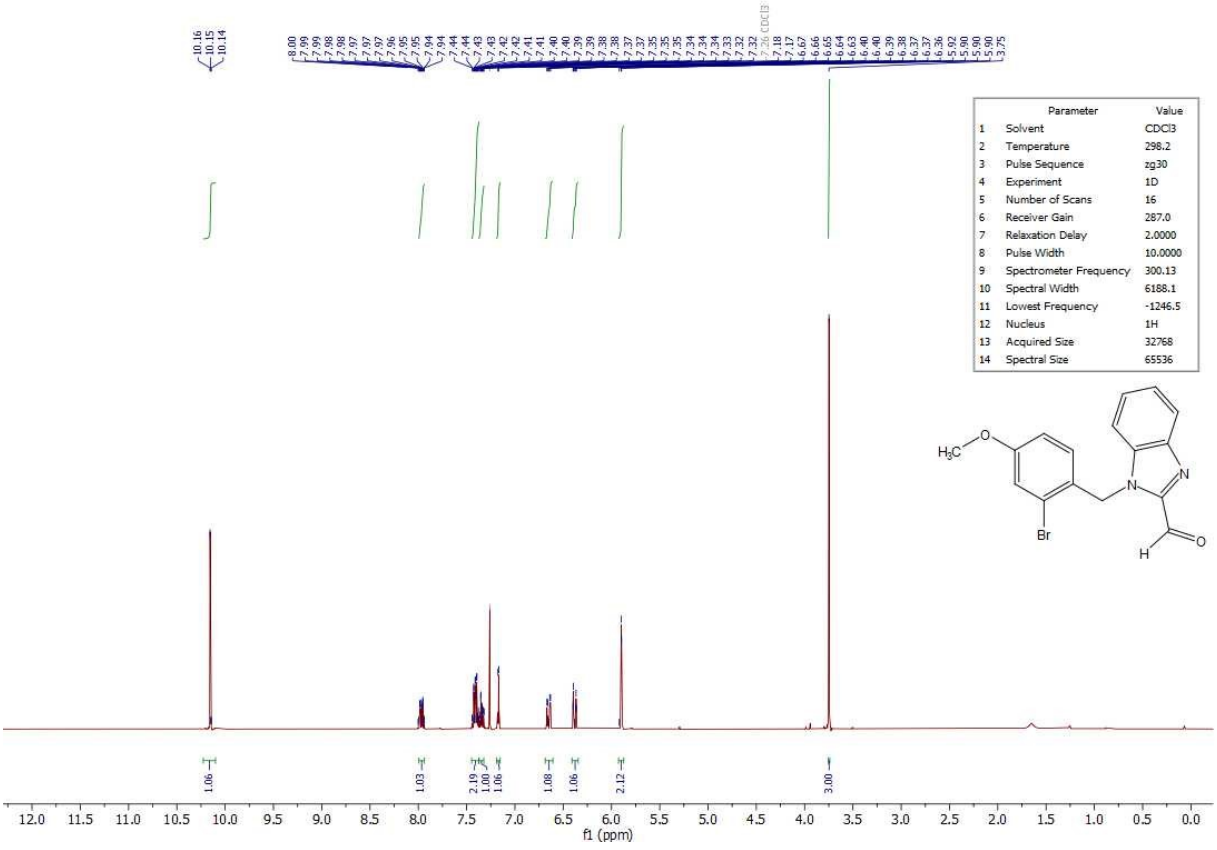


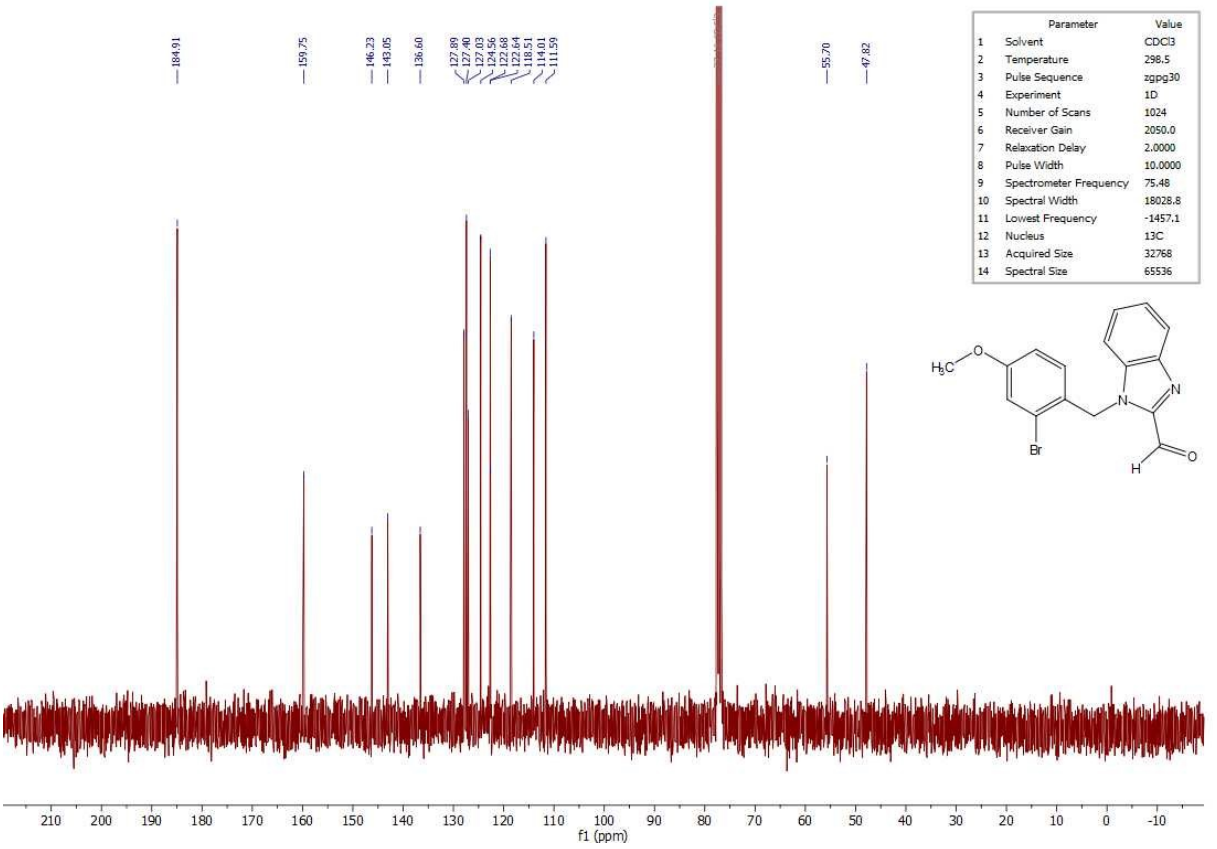
1-(2-Bromobenzyl)-5,6-dimethyl-1*H*-benzo[*d*]imidazole-2-carbaldehyde (4d)



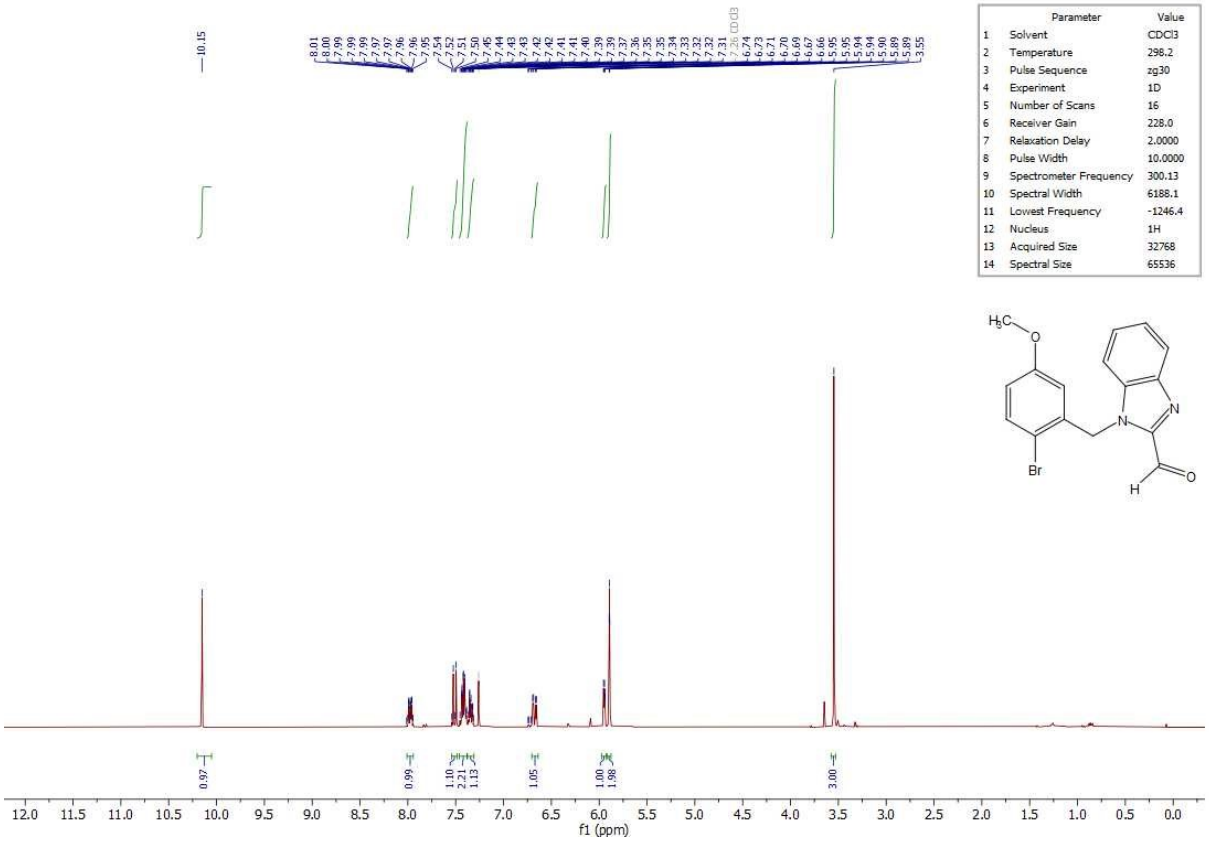


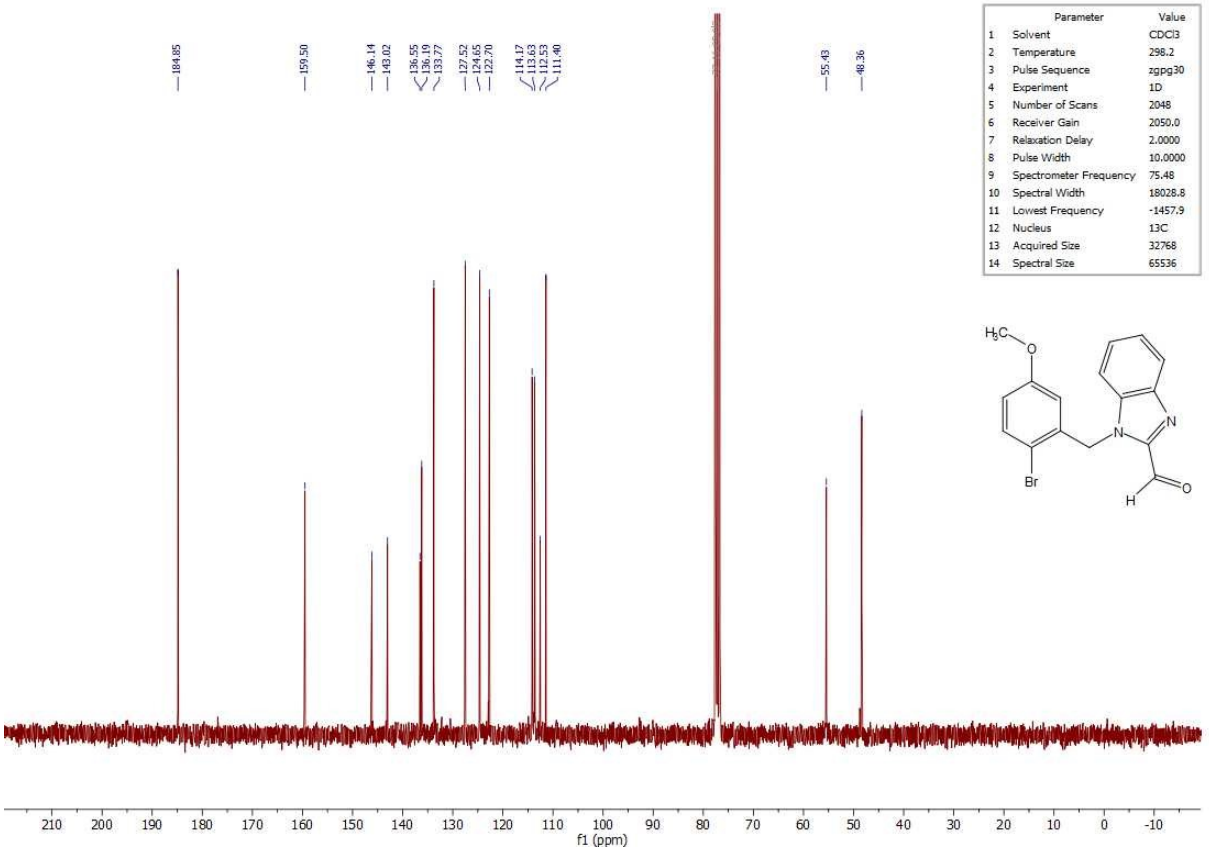
1-(2-Bromo-4-methoxybenzyl)-1*H*-benzo[*d*]imidazole-2-carbaldehyde (4e)



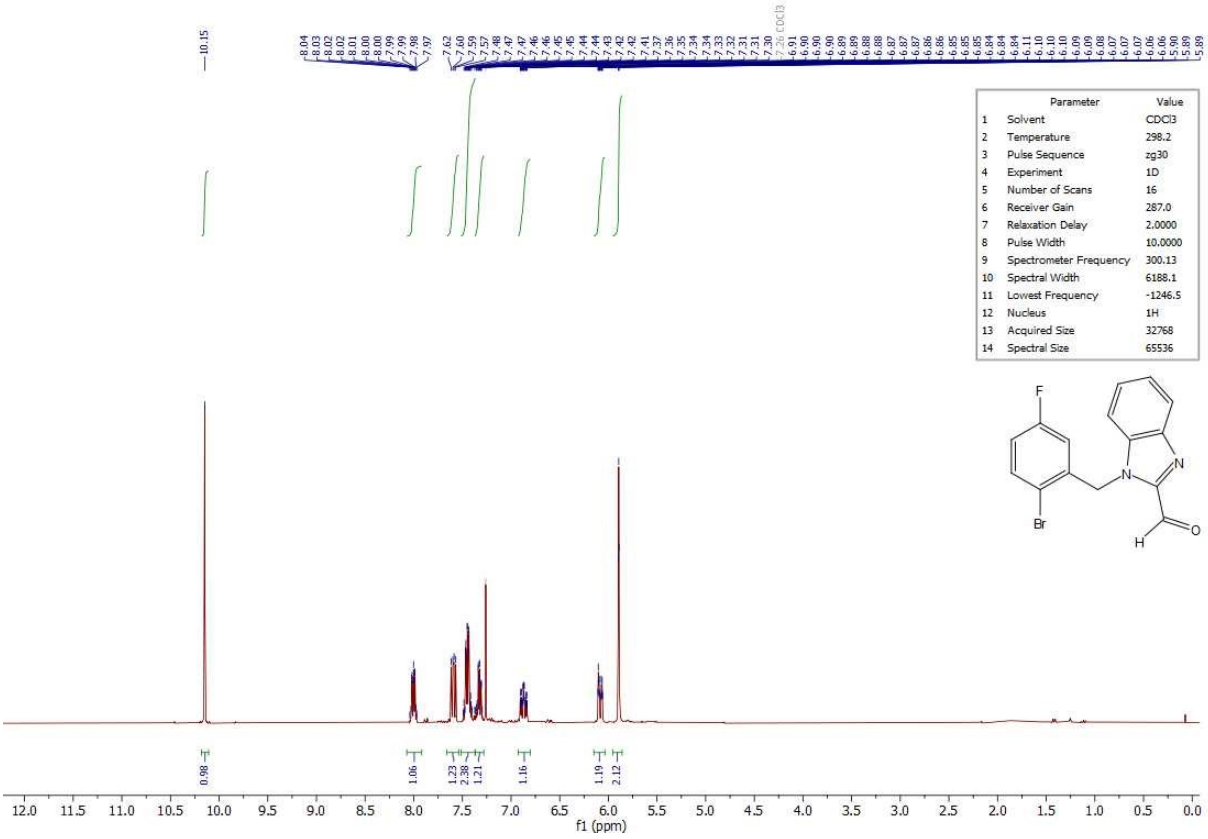


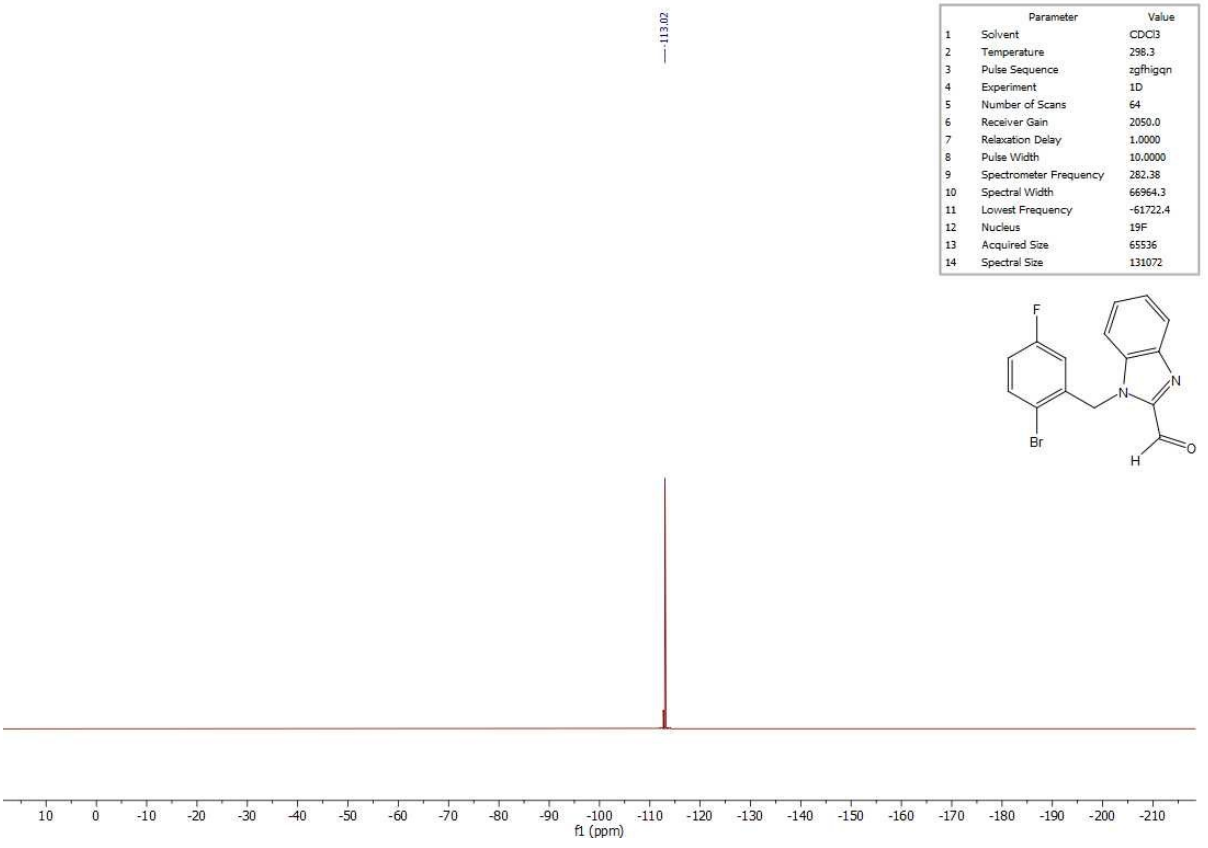
1-(2-Bromo-5-methoxybenzyl)-1*H*-benzo[*d*]imidazole-2-carbaldehyde (4f)



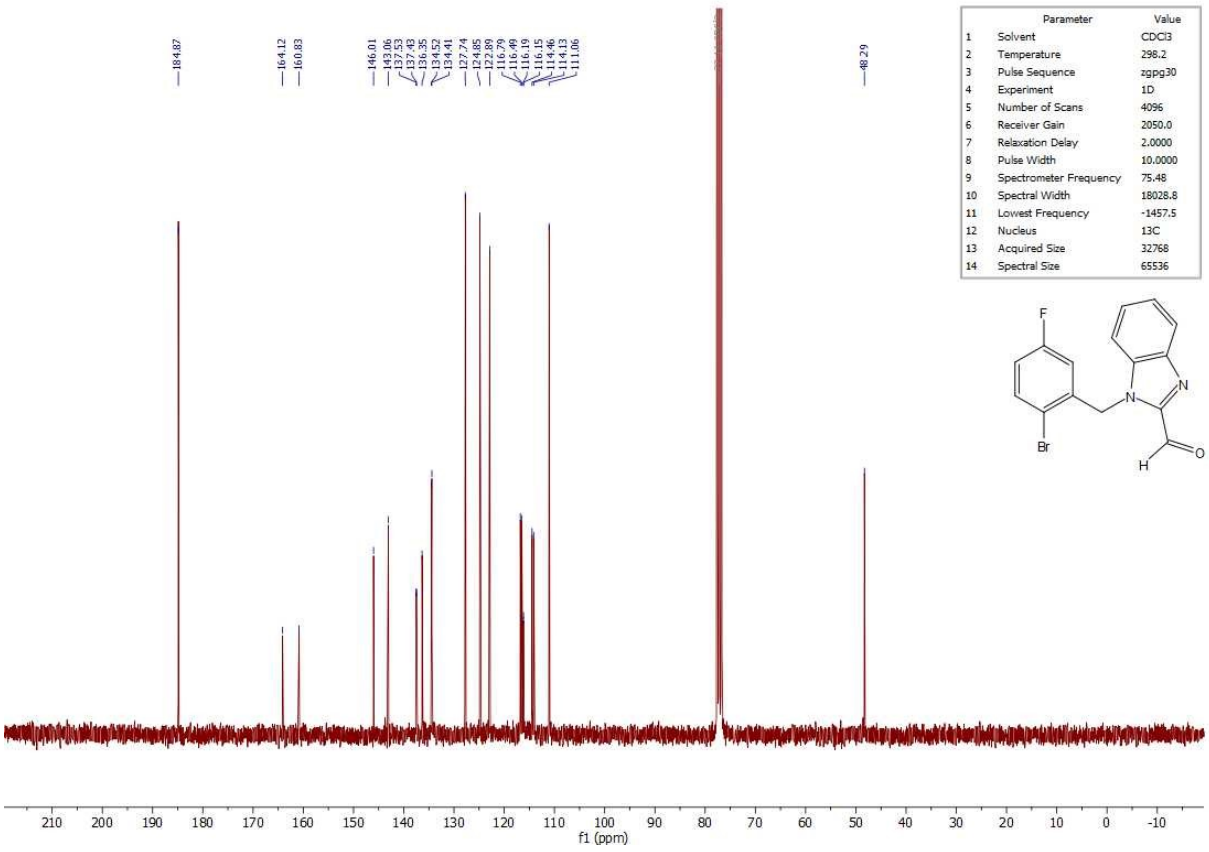


(2-Bromo-5-fluorobenzyl)-1*H*-benzo[*d*]imidazole-2-carbaldehyde (4g)

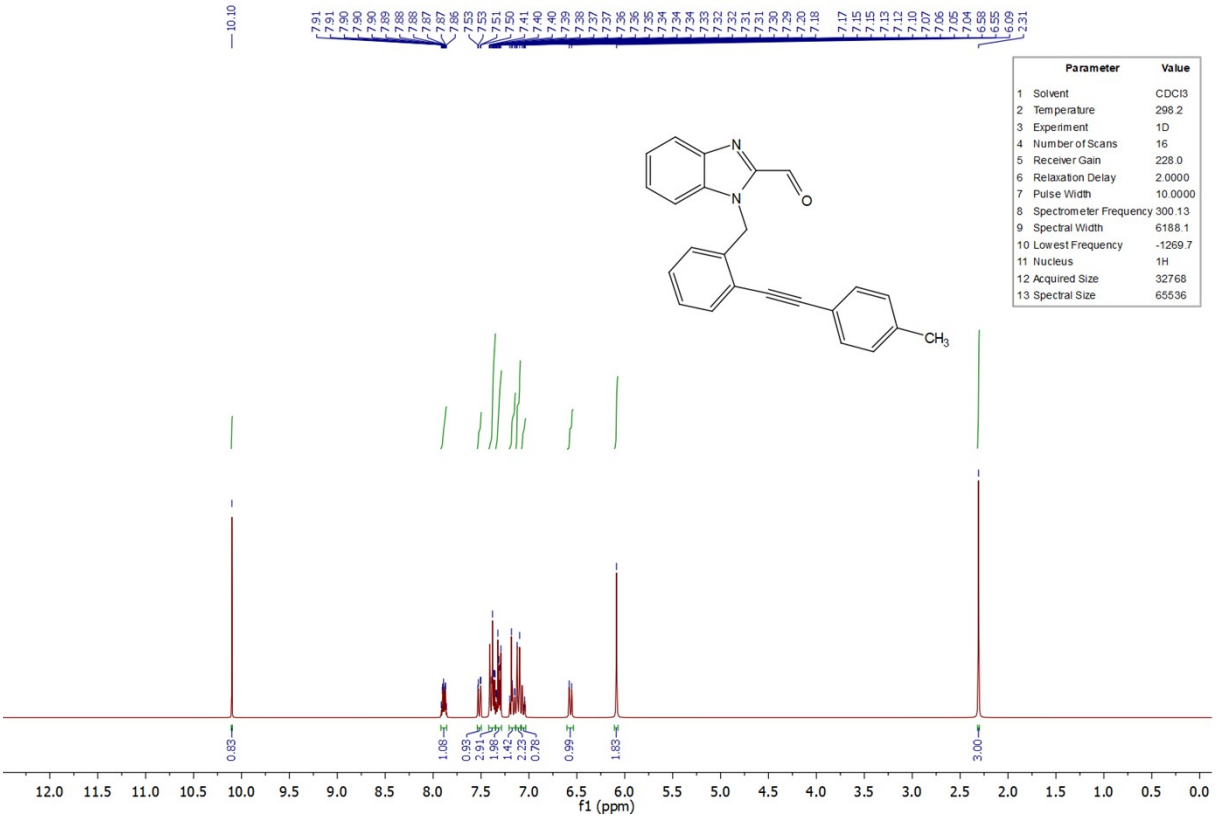


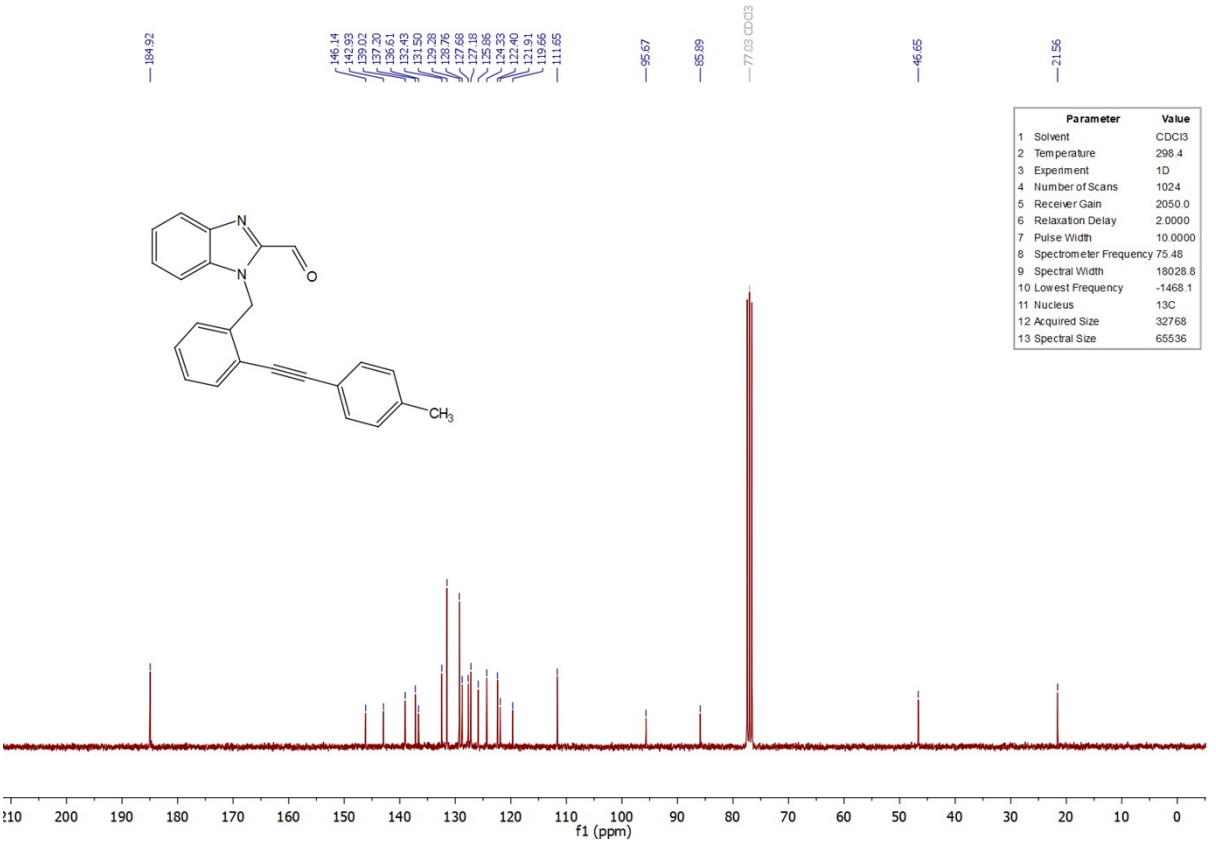


(2-Bromo-5-fluorobenzyl)-1*H*-benzo[*d*]imidazole-2-carbaldehyde (4g)

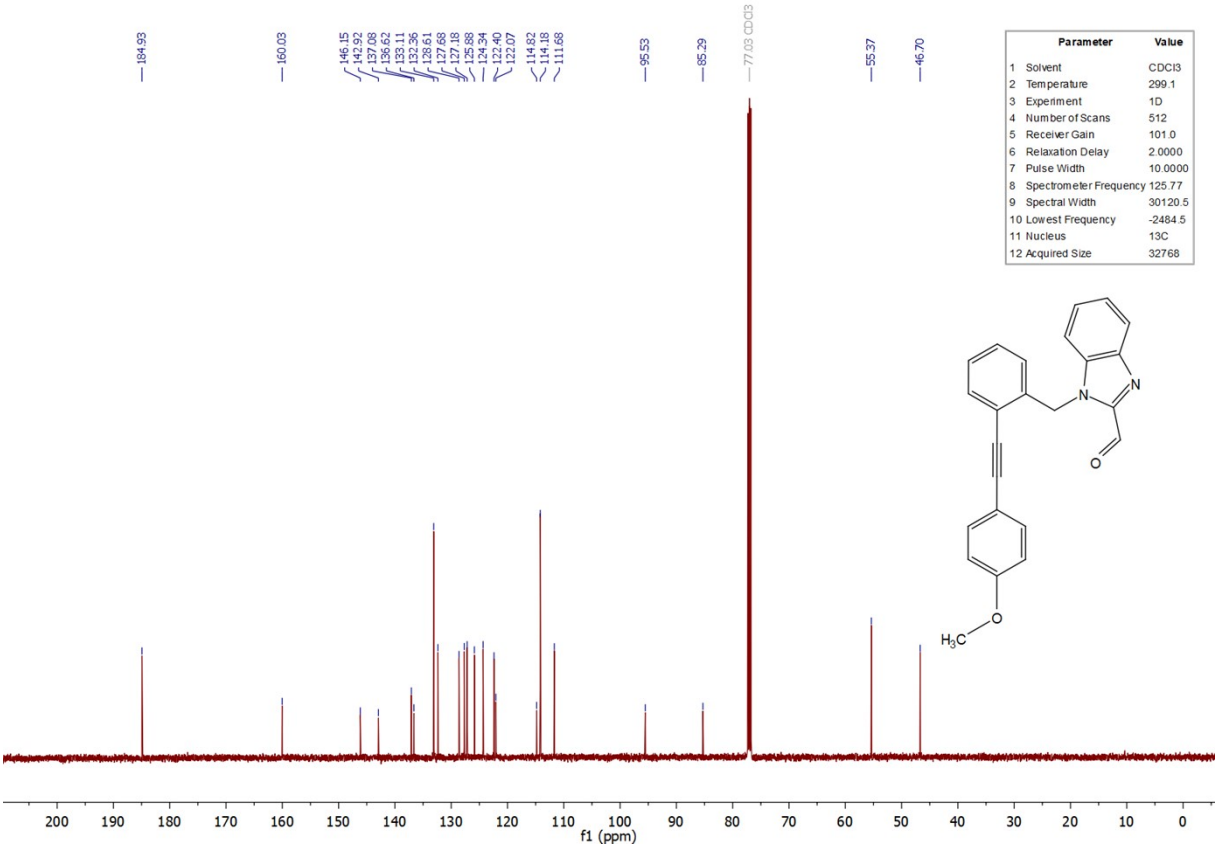


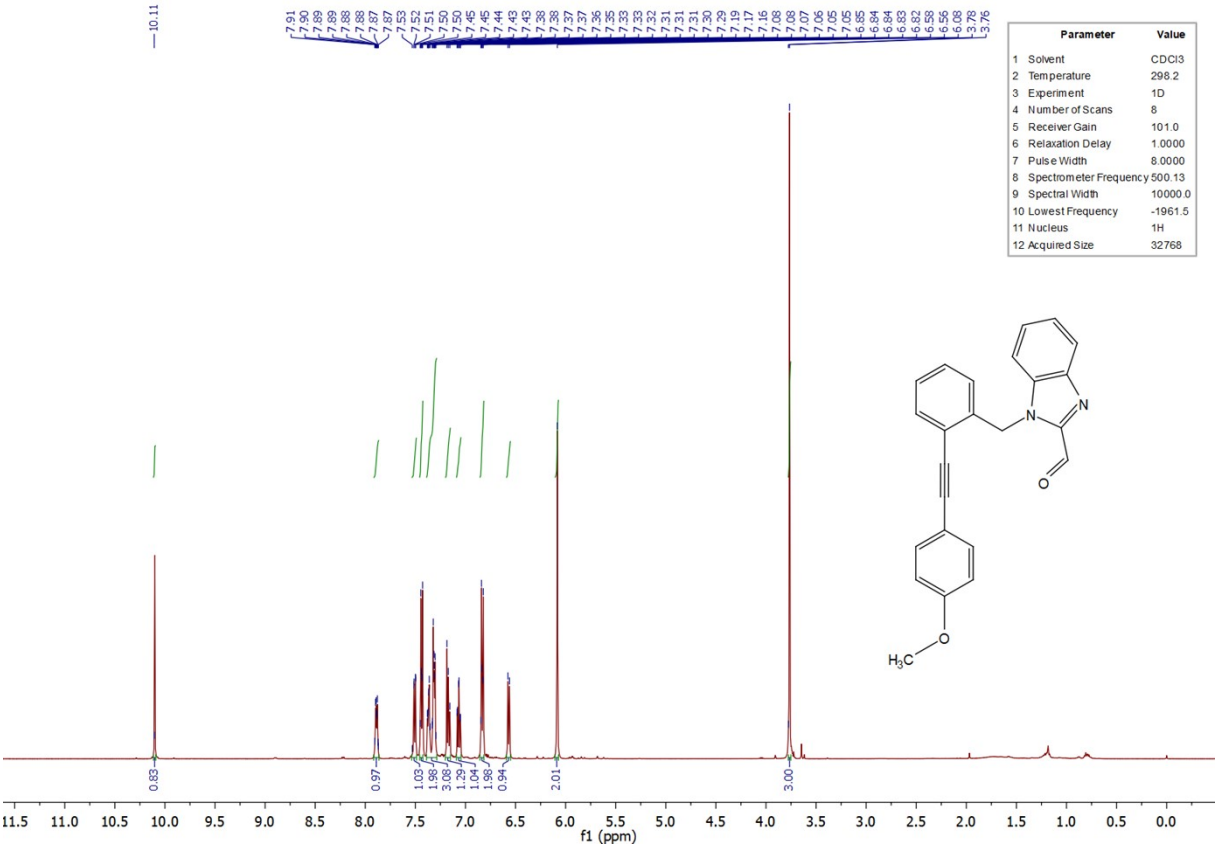
1-(2-(p-tolylethynyl)benzyl)-1H-benzo[d]imidazole-2-carbaldehyde (5a)



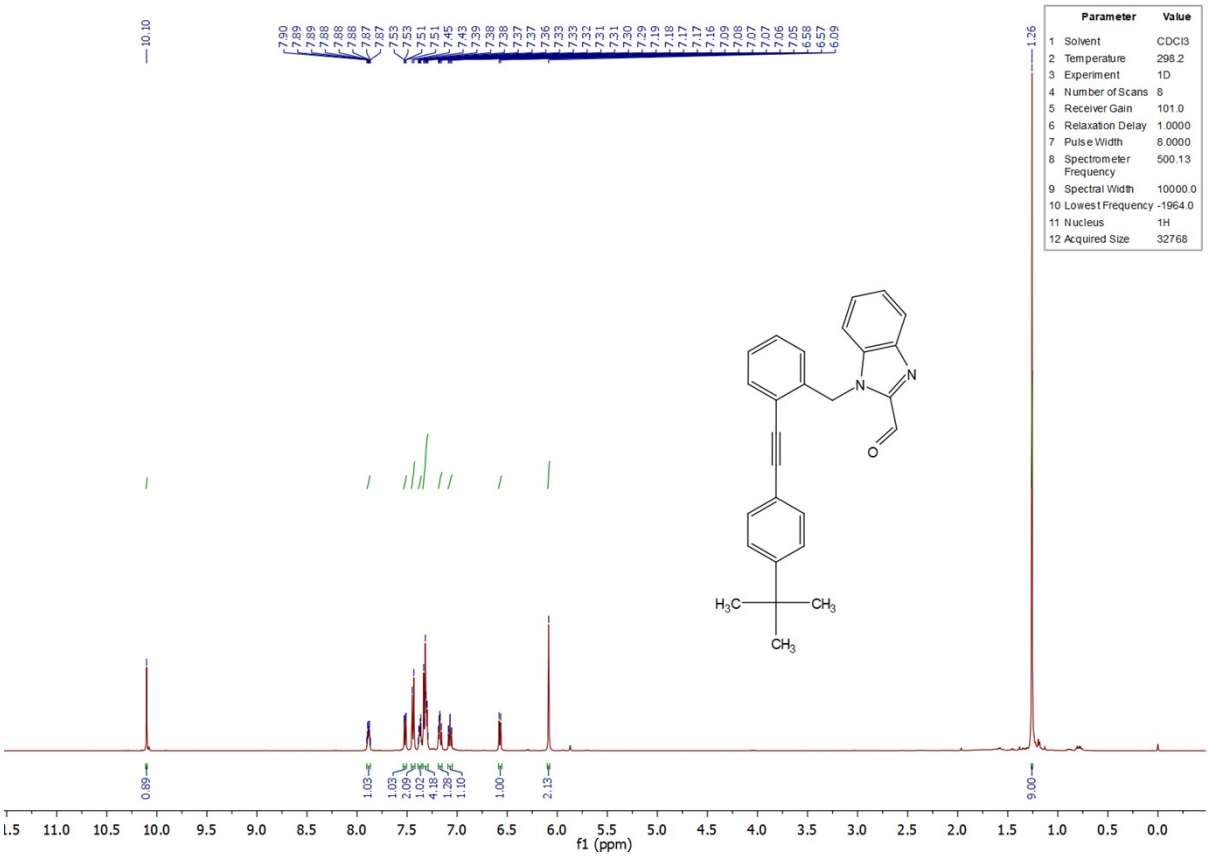


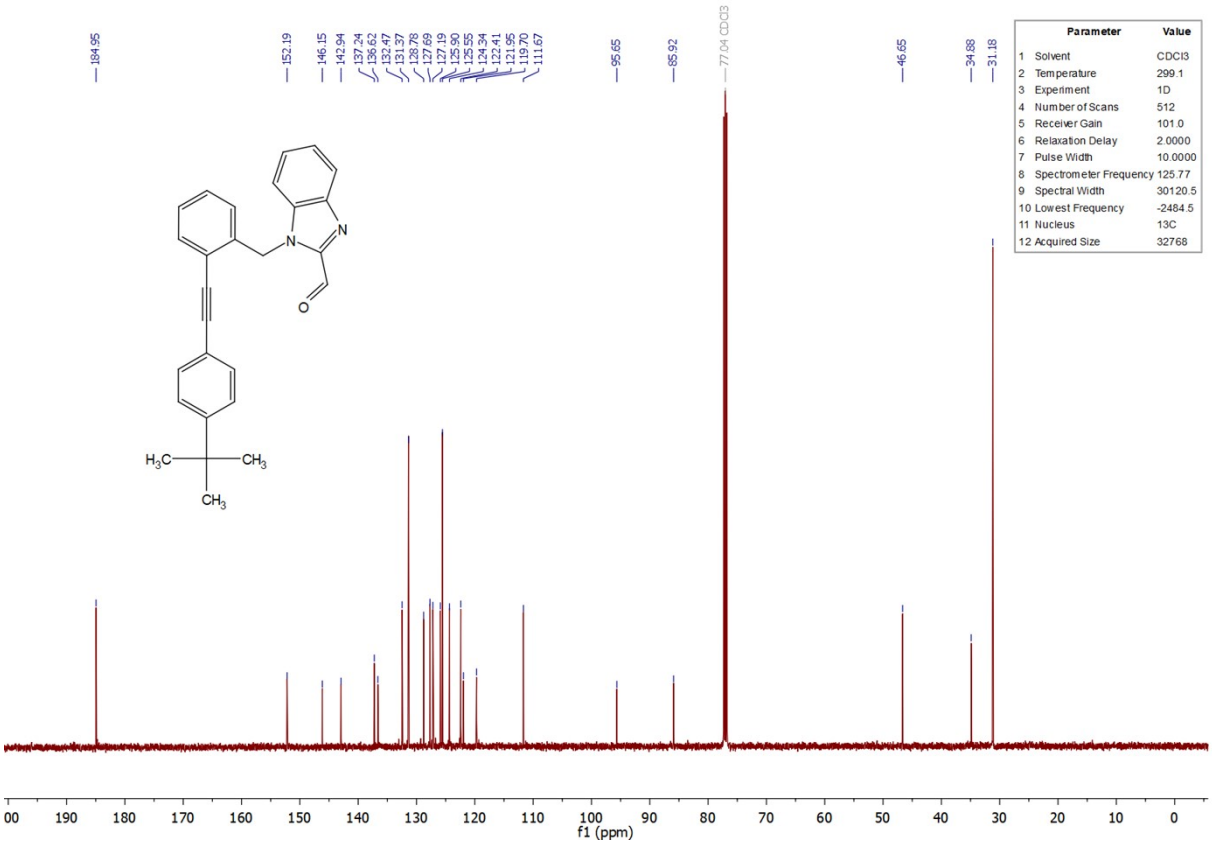
1-(2-((4-methoxyphenyl)ethynyl)benzyl)-1H-benzo[d]imidazole-2-carbaldehyde (5b)



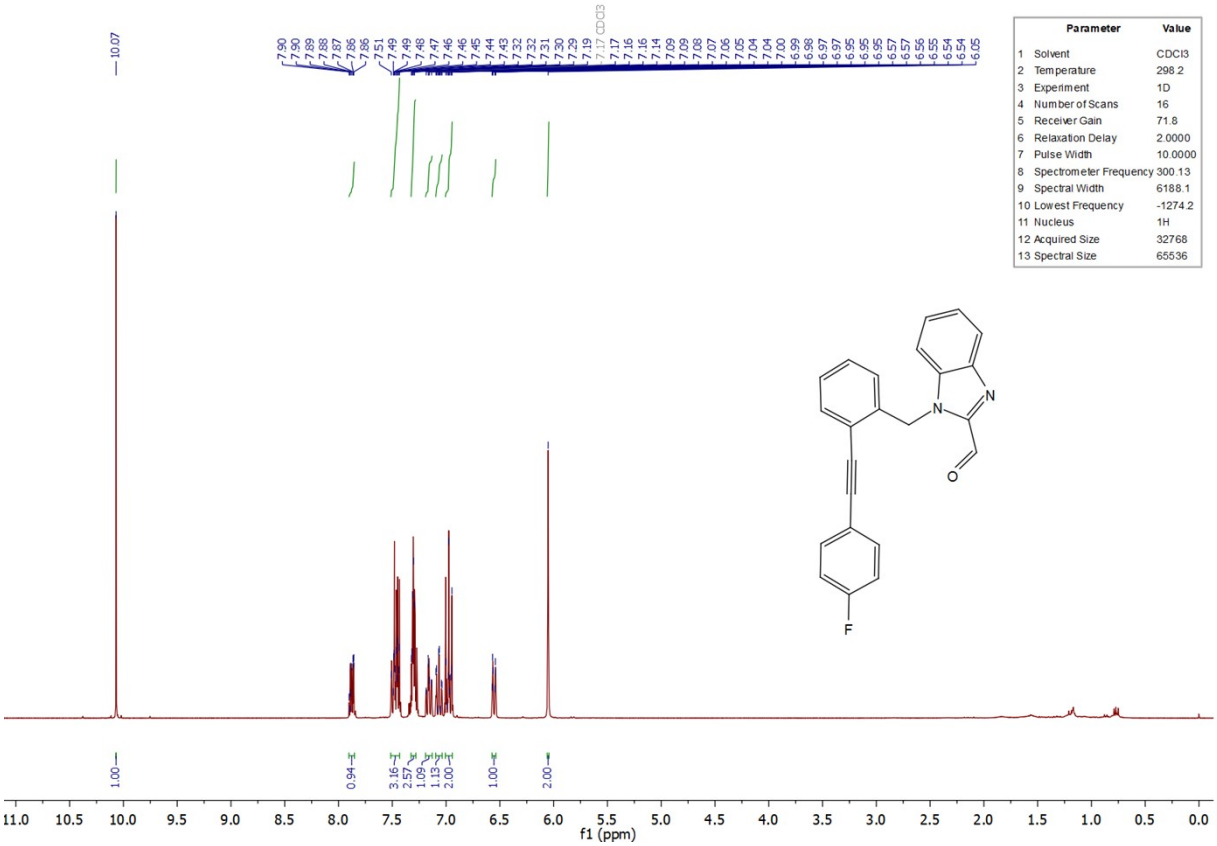


1-(2-((4-(tert-butyl)phenyl)ethynyl)benzyl)-1H-benzo[d]imidazole-2-carbaldehyde (5c)

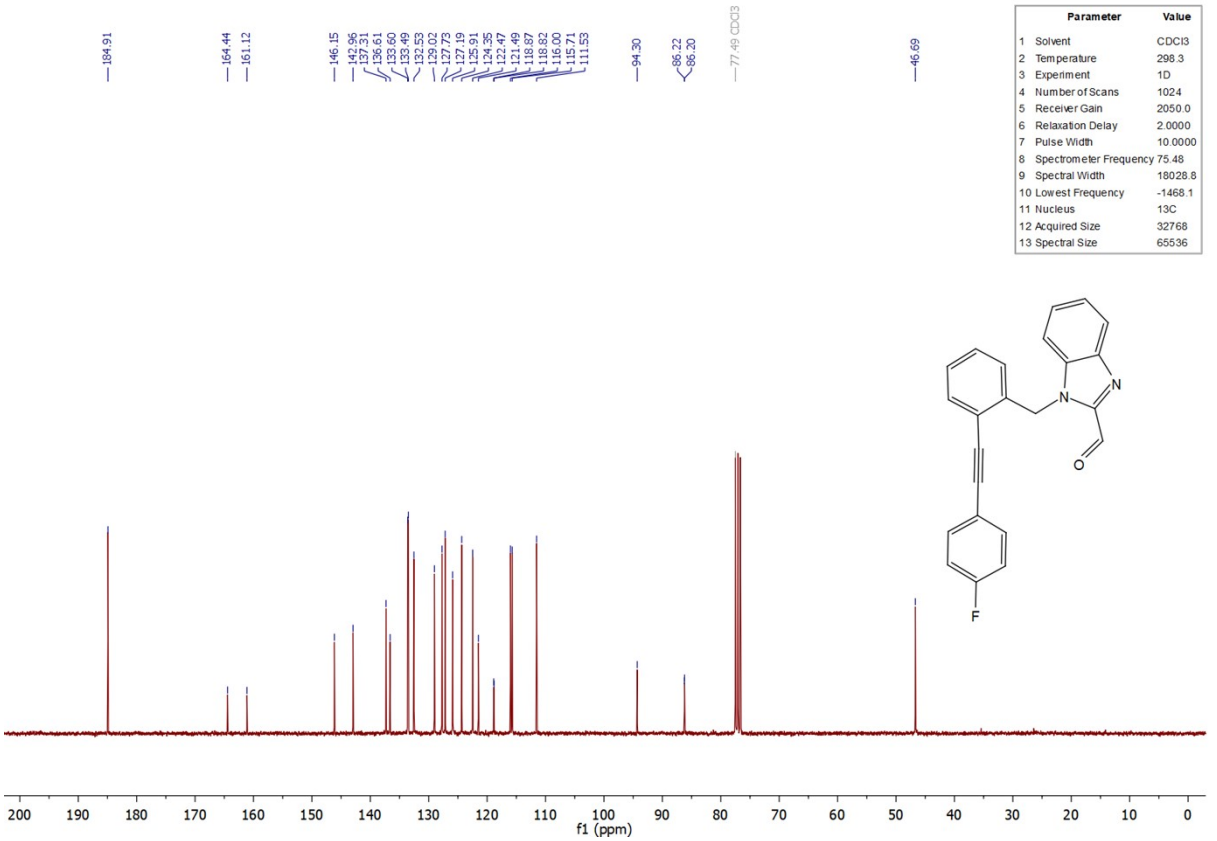




1-(2-((4-fluorophenyl)ethynyl)benzyl)-1H-benzo[d]imidazole-2-carbaldehyde (5d)

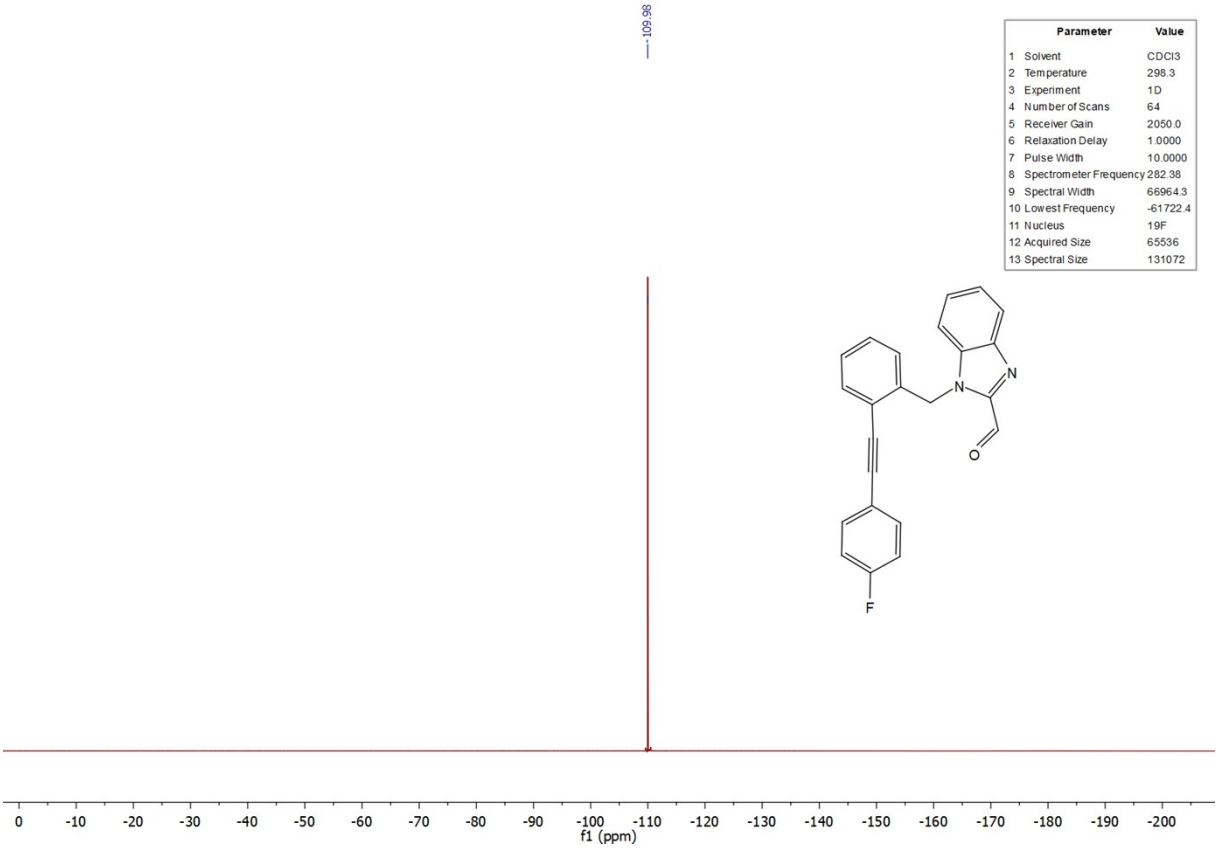


	Parameter	Value
1	Solvent	CDCl3
2	Temperature	298.2
3	Experiment	1D
4	Number of Scans	16
5	Receiver Gain	71.8
6	Relaxation Delay	2.0000
7	Pulse Width	10.0000
8	Spectrometer Frequency	300.13
9	Spectral Width	6188.1
10	Lowest Frequency	-1274.2
11	Nucleus	1H
12	Acquired Size	32768
13	Spectral Size	65536

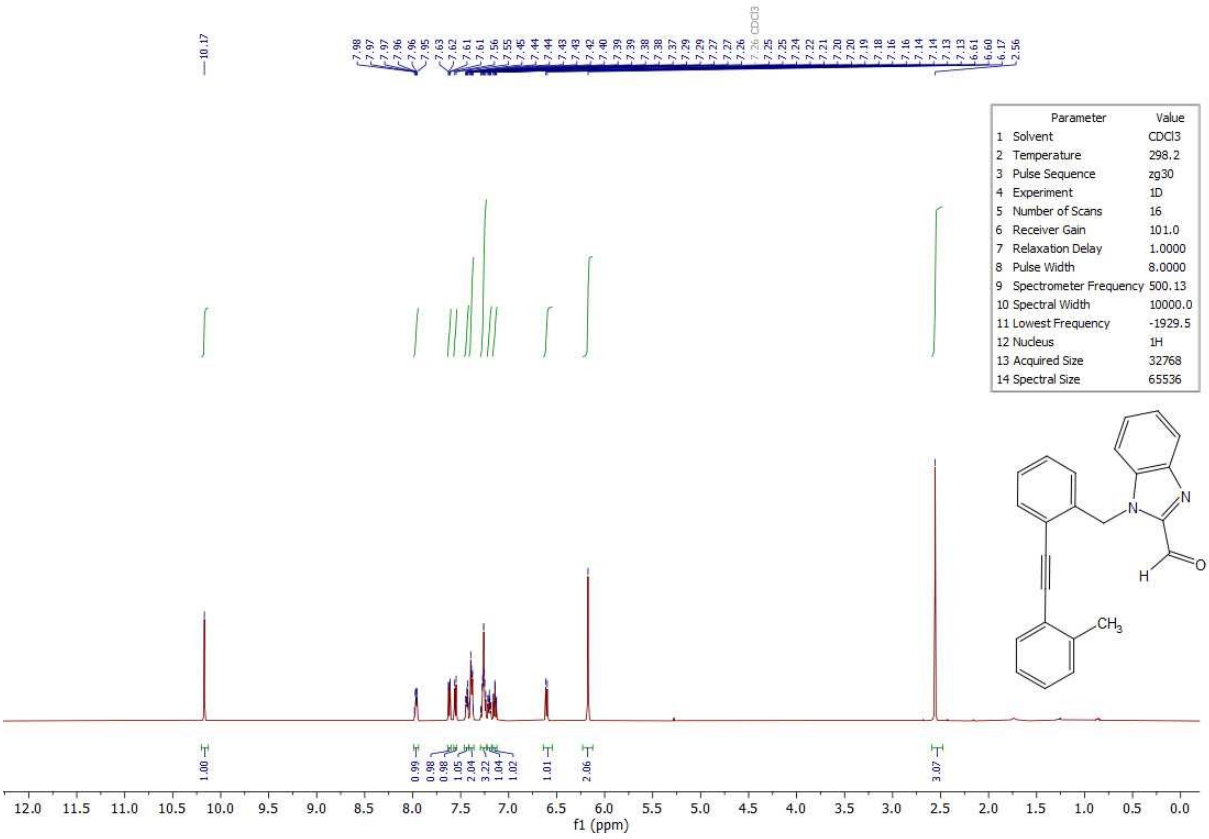


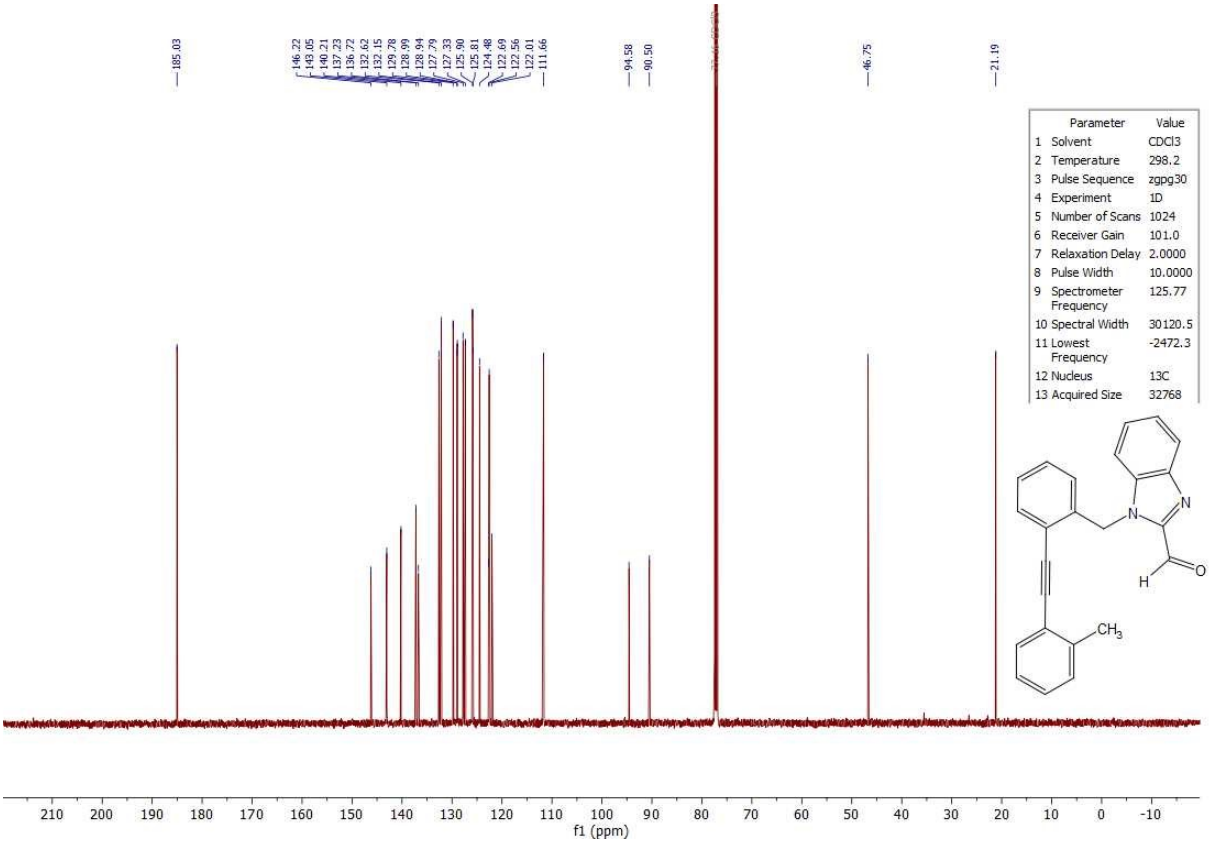
	Parameter	Value
1	Solvent	CDCl3
2	Temperature	298.3
3	Experiment	1D
4	Number of Scans	1024
5	Receiver Gain	2050.0
6	Relaxation Delay	2.0000
7	Pulse Width	10.0000
8	Spectrometer Frequency	75.48
9	Spectral Width	18028.8
10	Lowest Frequency	-1468.1
11	Nucleus	13C
12	Acquired Size	32768
13	Spectral Size	65536

1-(2-((4-fluorophenyl)ethynyl)benzyl)-1H-benzo[d]imidazole-2-carbaldehyde (5d)

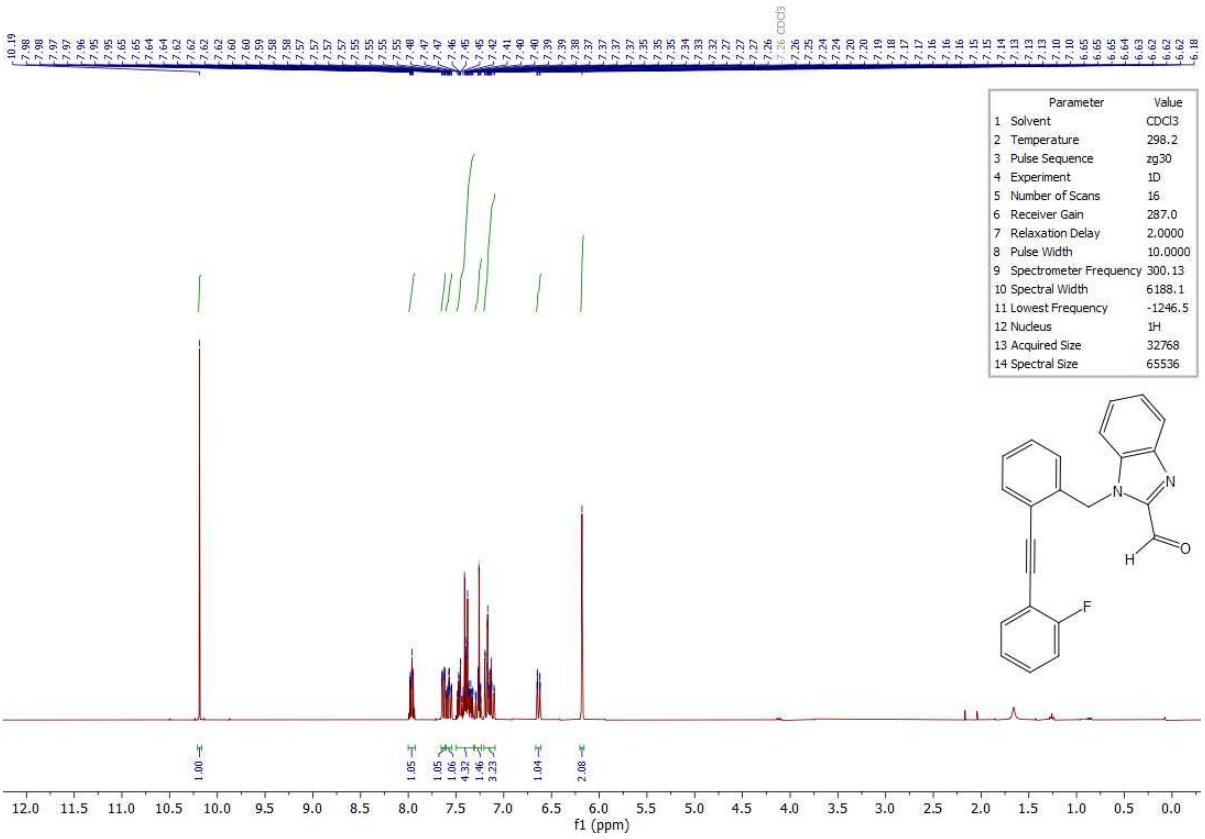


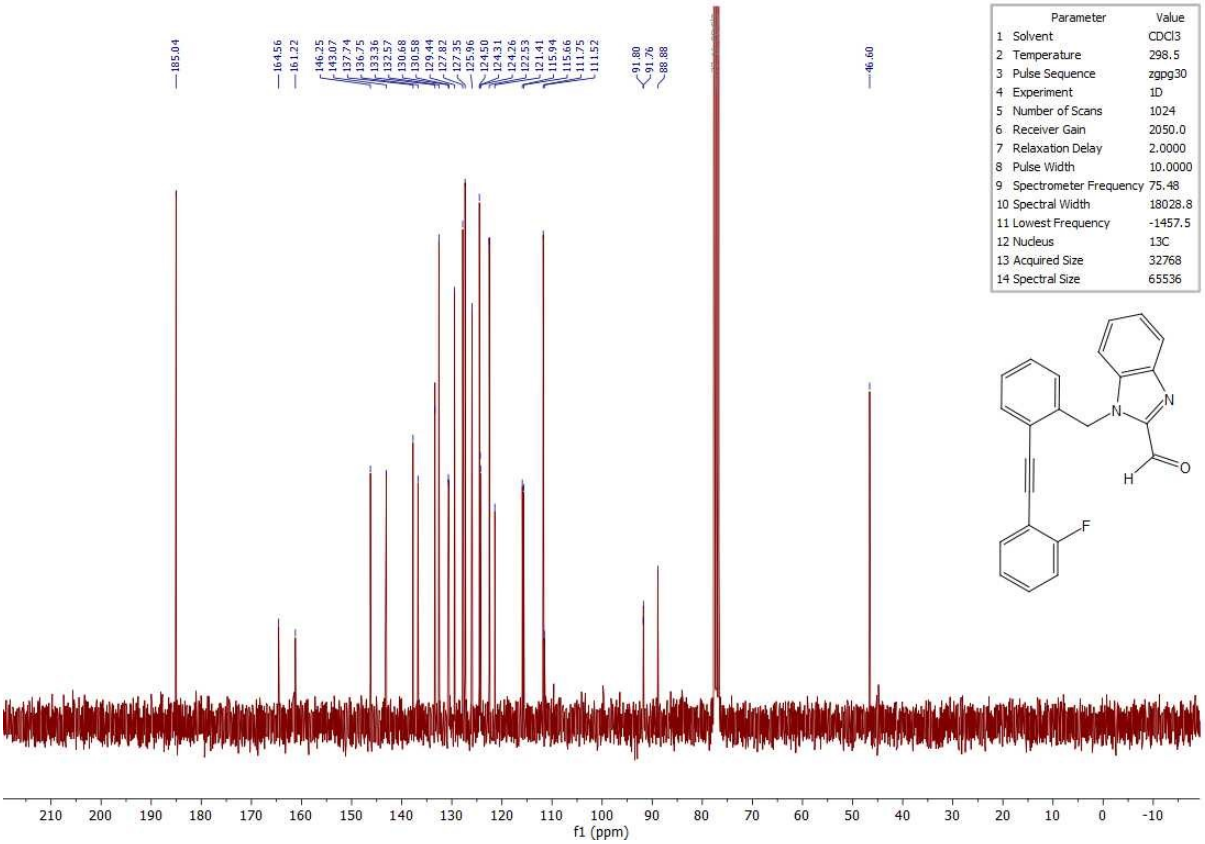
1-(2-(*o*-Tolylethynyl)benzyl)-1*H*-benzo[*d*]imidazole-2-carbaldehyde (5e)



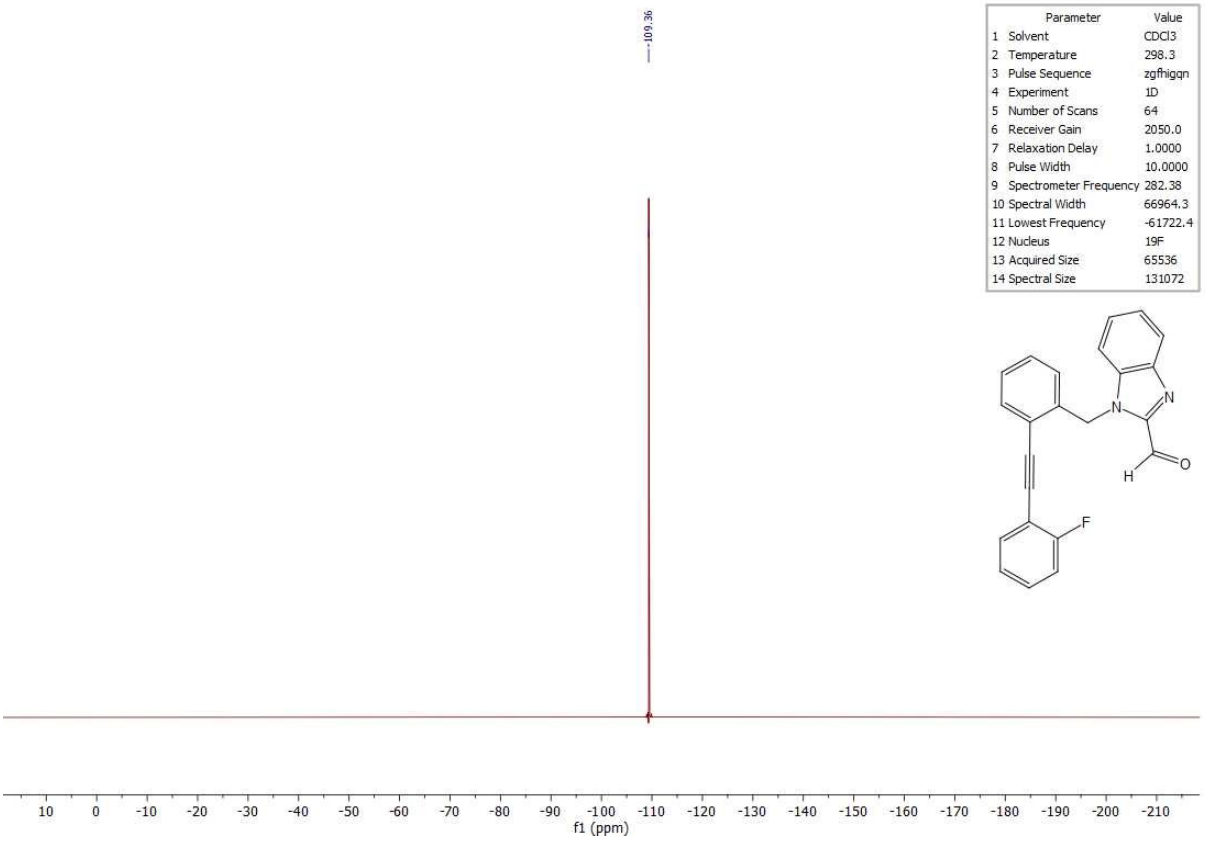


1-(2-((2-Fluorophenyl)ethynyl)benzyl)-1*H*-benzo[*d*]imidazole-2-carbaldehyde (5f)



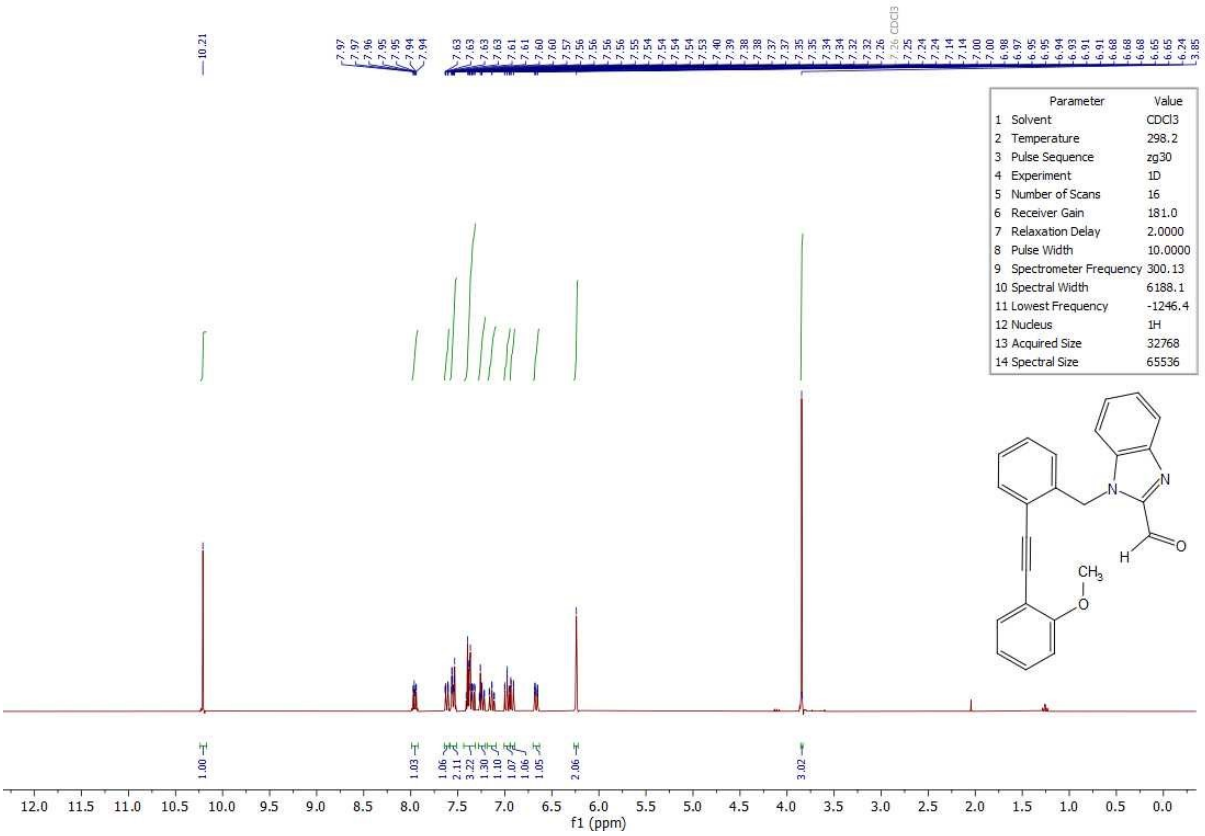


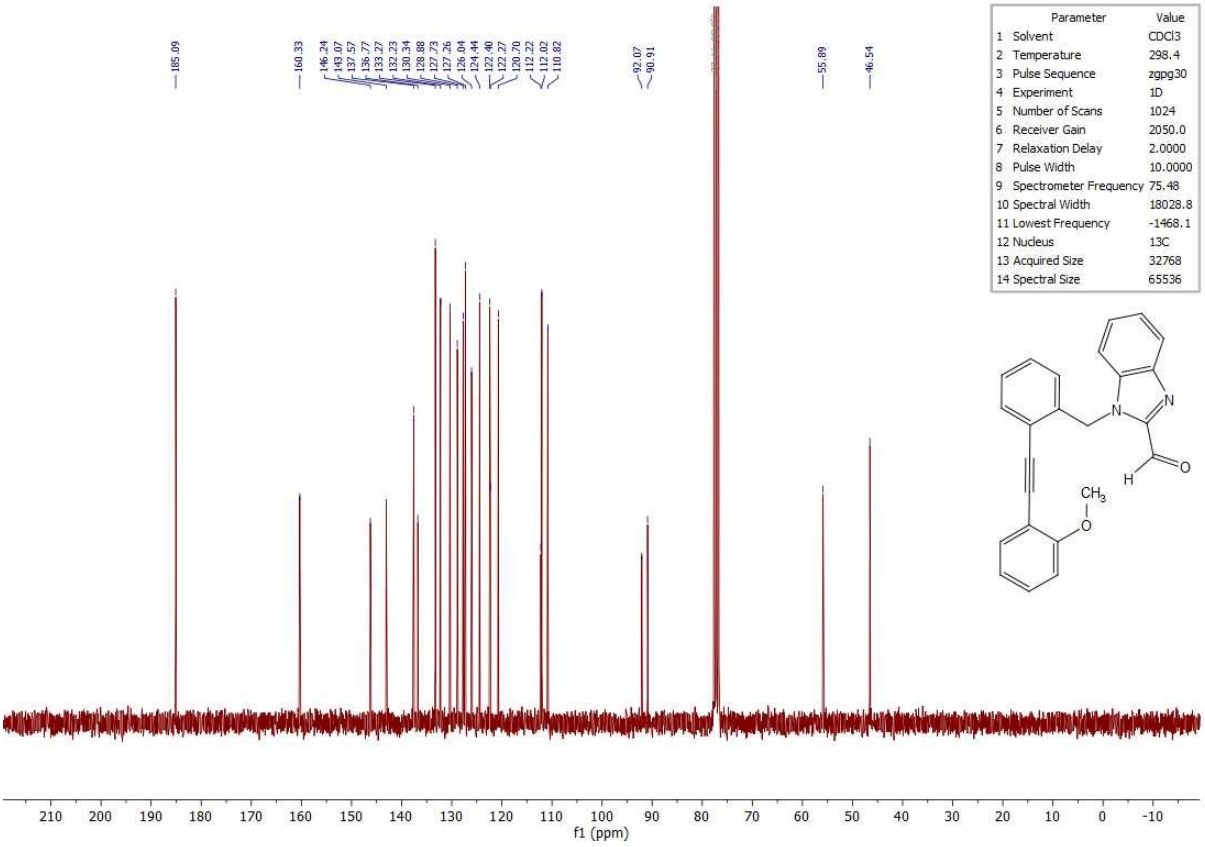
1-(2-((2-Fluorophenyl)ethynyl)benzyl)-1*H*-benzo[*d*]imidazole-2-carbaldehyde (5f)



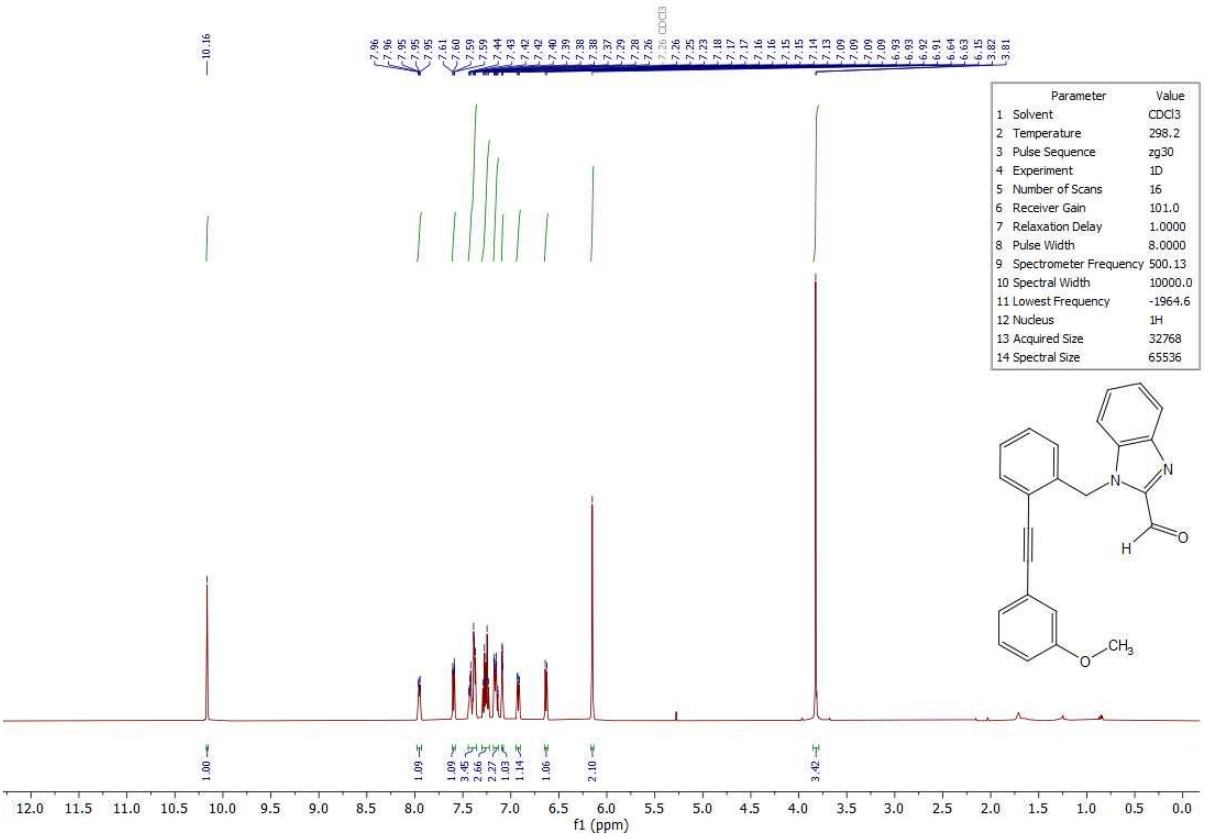
	Parameter	Value
1	Solvent	CDCl3
2	Temperature	298.3
3	Pulse Sequence	zgfhigqn
4	Experiment	1D
5	Number of Scans	64
6	Receiver Gain	2050.0
7	Relaxation Delay	1.0000
8	Pulse Width	10.0000
9	Spectrometer Frequency	282.38
10	Spectral Width	66964.3
11	Lowest Frequency	-61722.4
12	Nucleus	19F
13	Acquired Size	65536
14	Spectral Size	131072

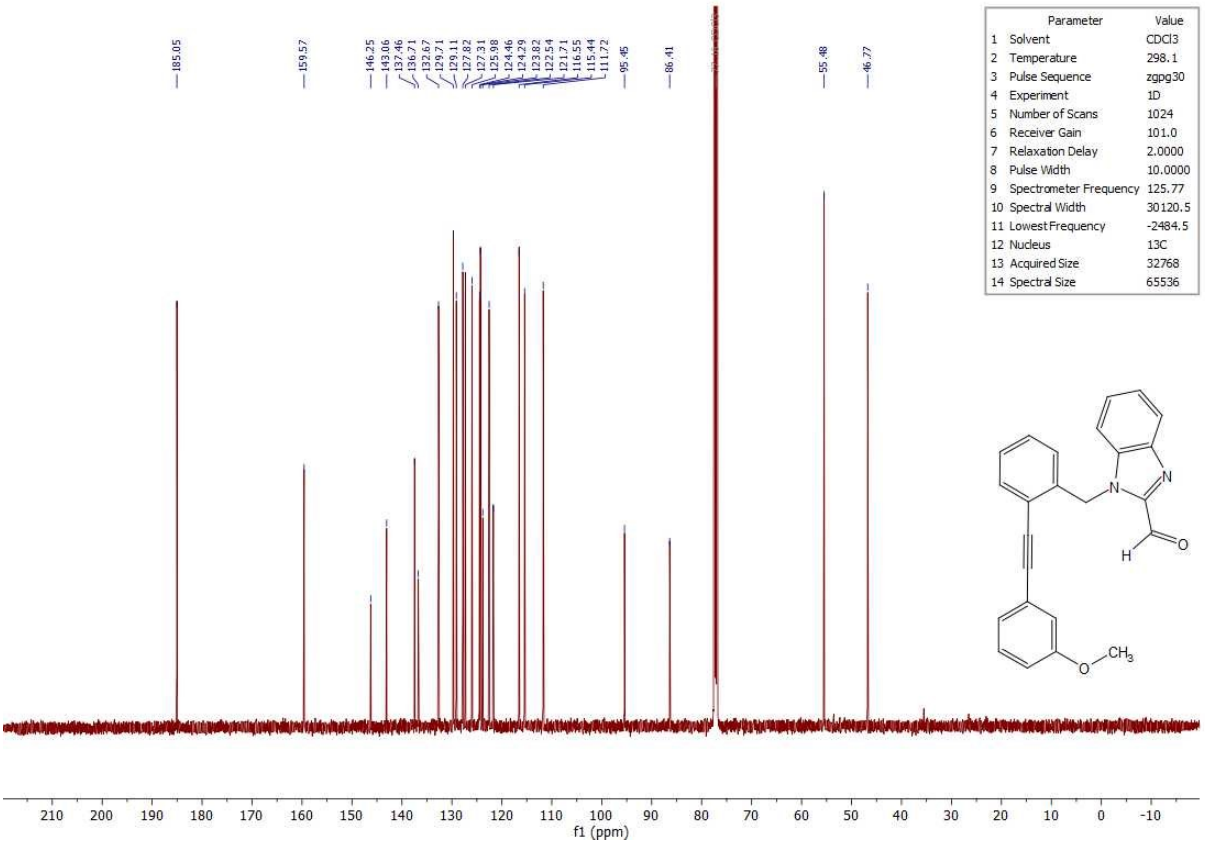
1-(2-((2-Methoxyphenyl)ethynyl)benzyl)-1*H*-benzo[*d*]imidazole-2-carbaldehyde (5g)



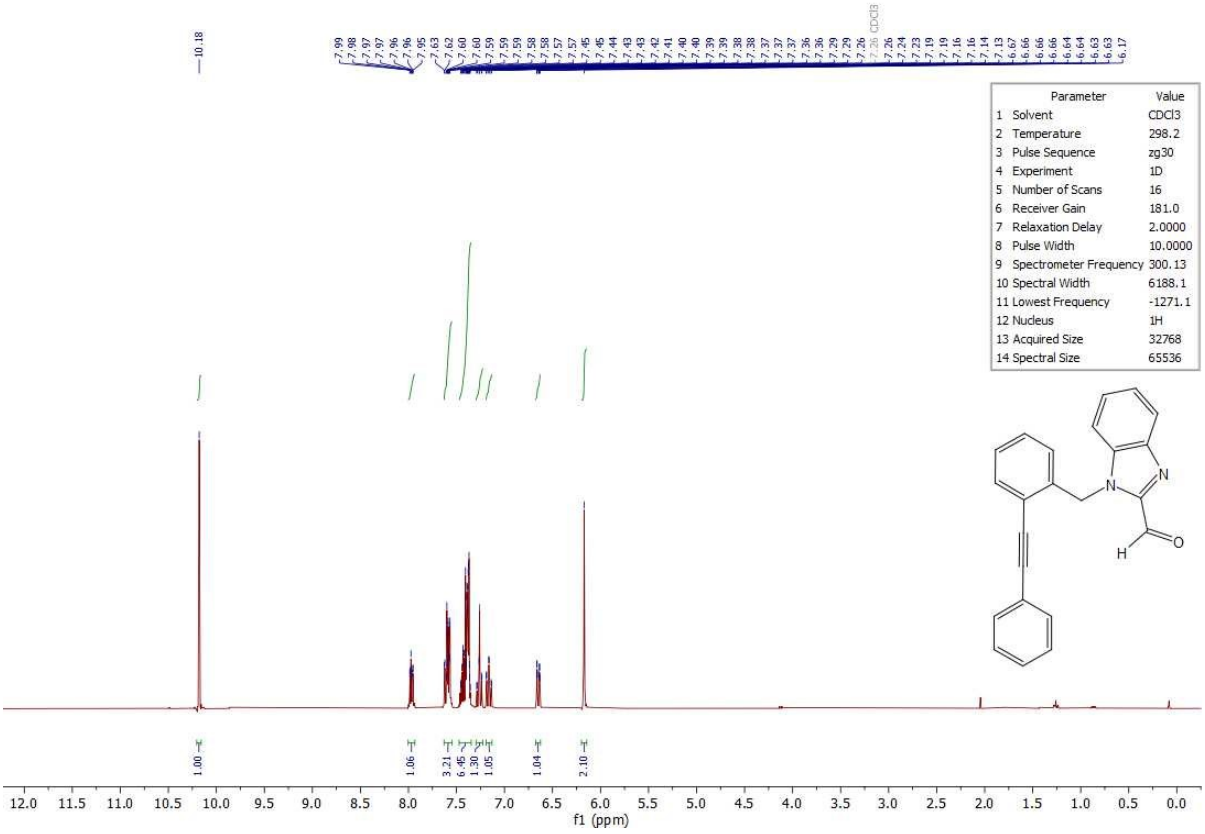


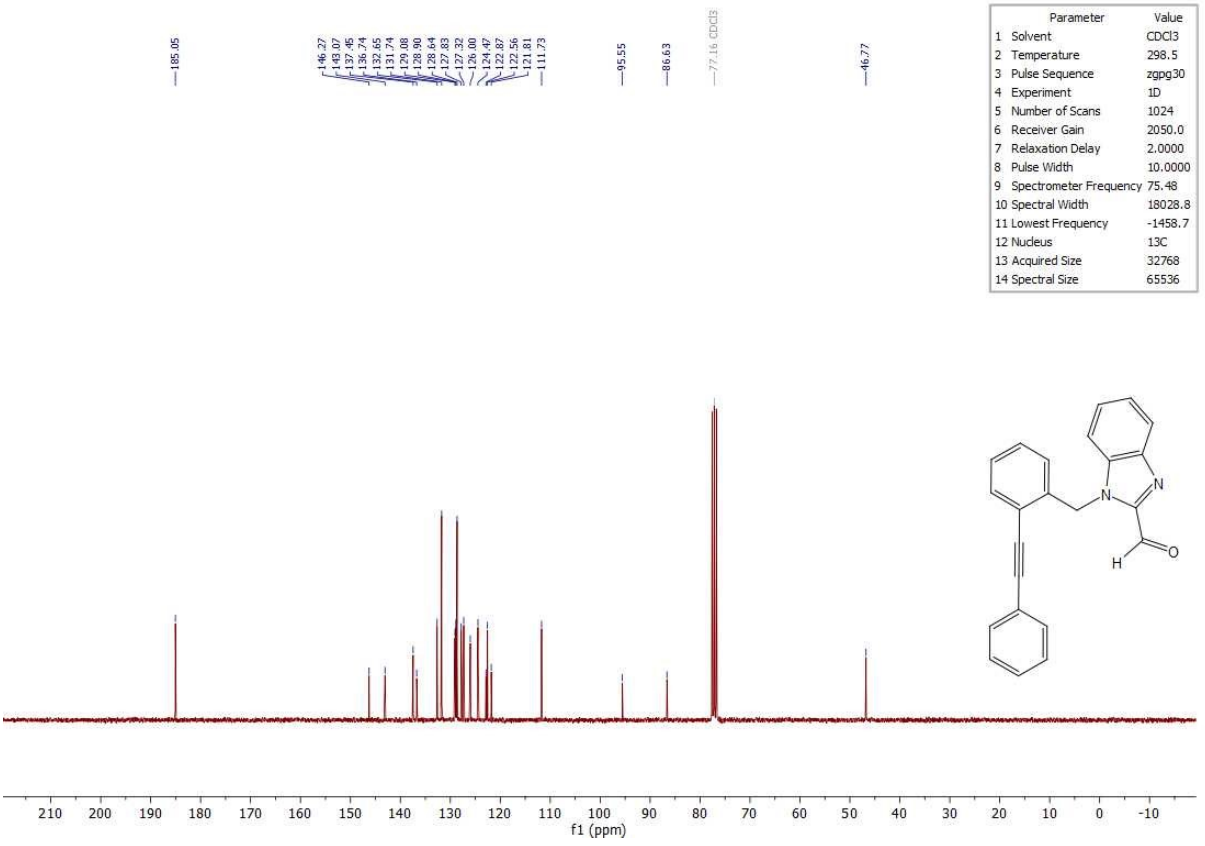
1-(2-((3-Methoxyphenyl)ethynyl)benzyl)-1*H*-benzo[*d*]imidazole-2-carbaldehyde (5h)



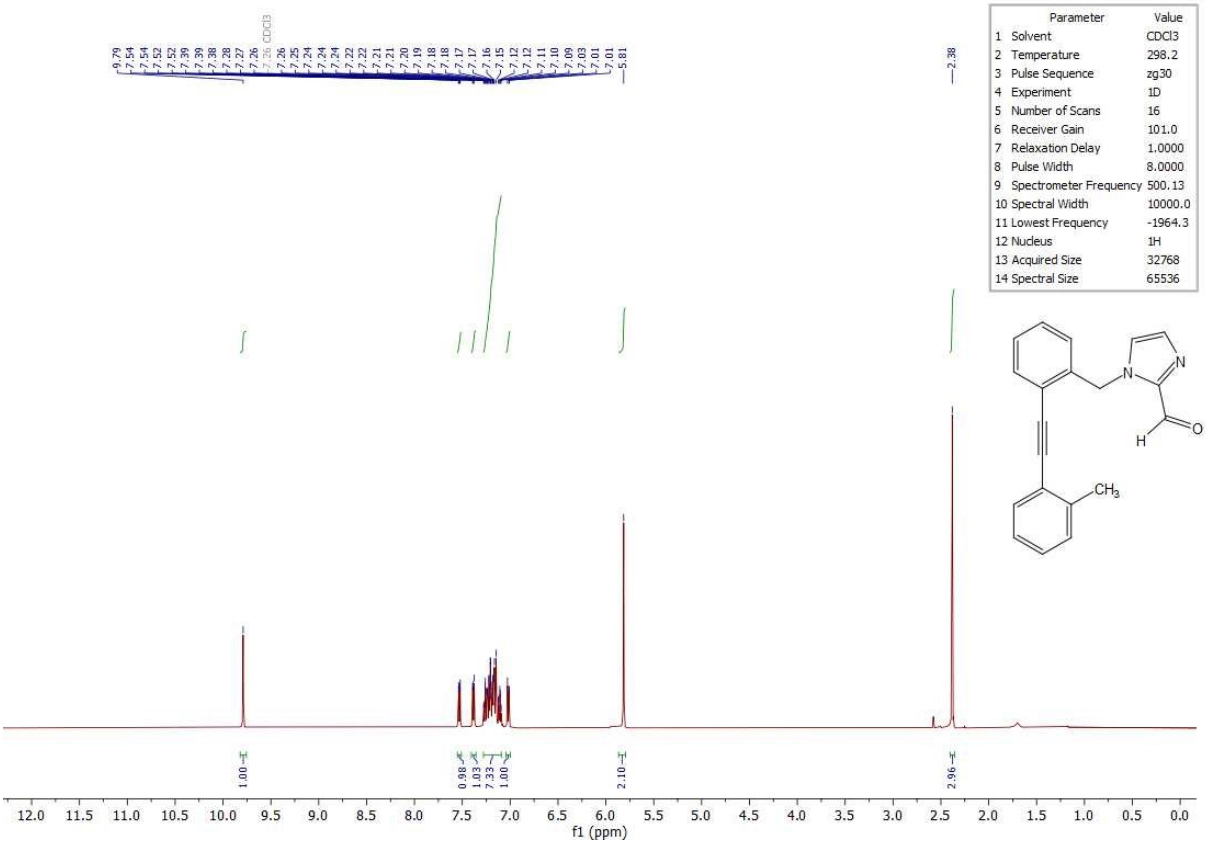


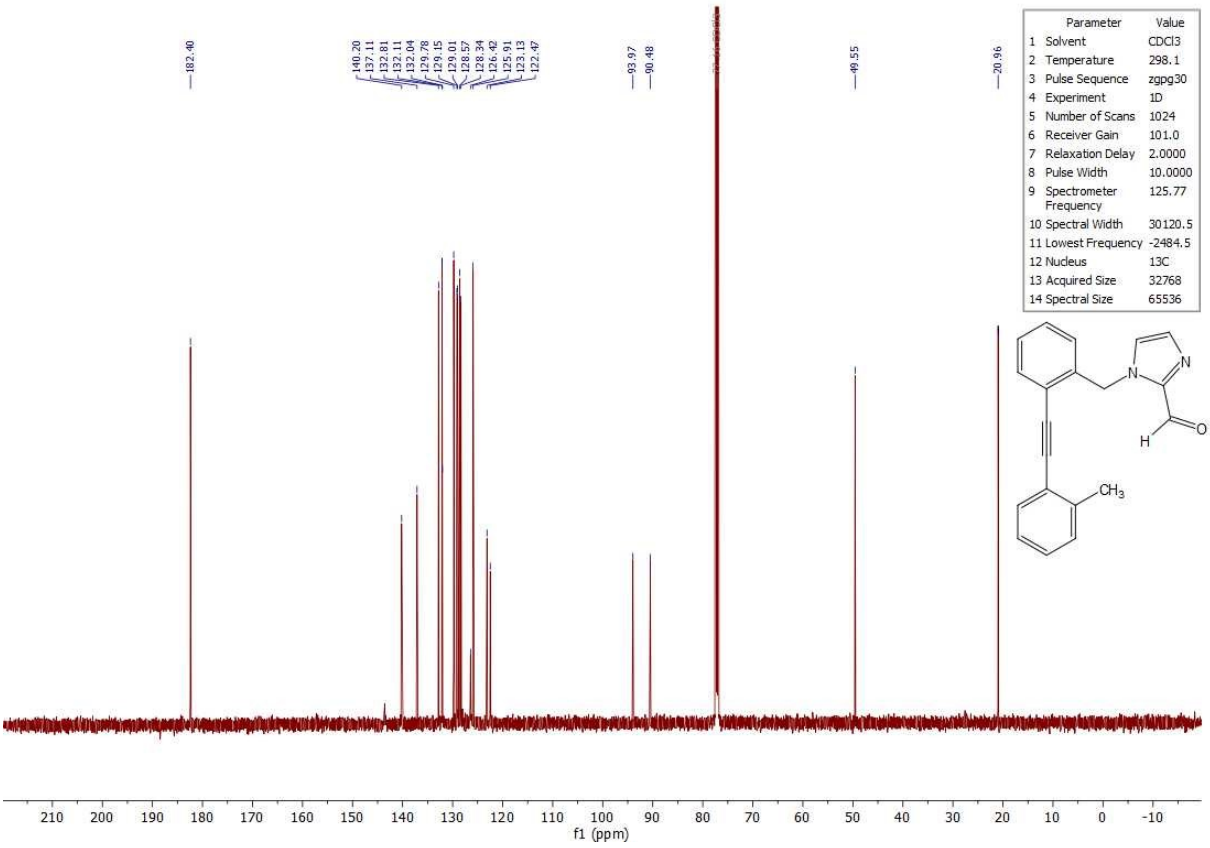
1-(2-(Phenylethynyl)benzyl)-1*H*-benzo[*d*]imidazole-2-carbaldehyde (5i)



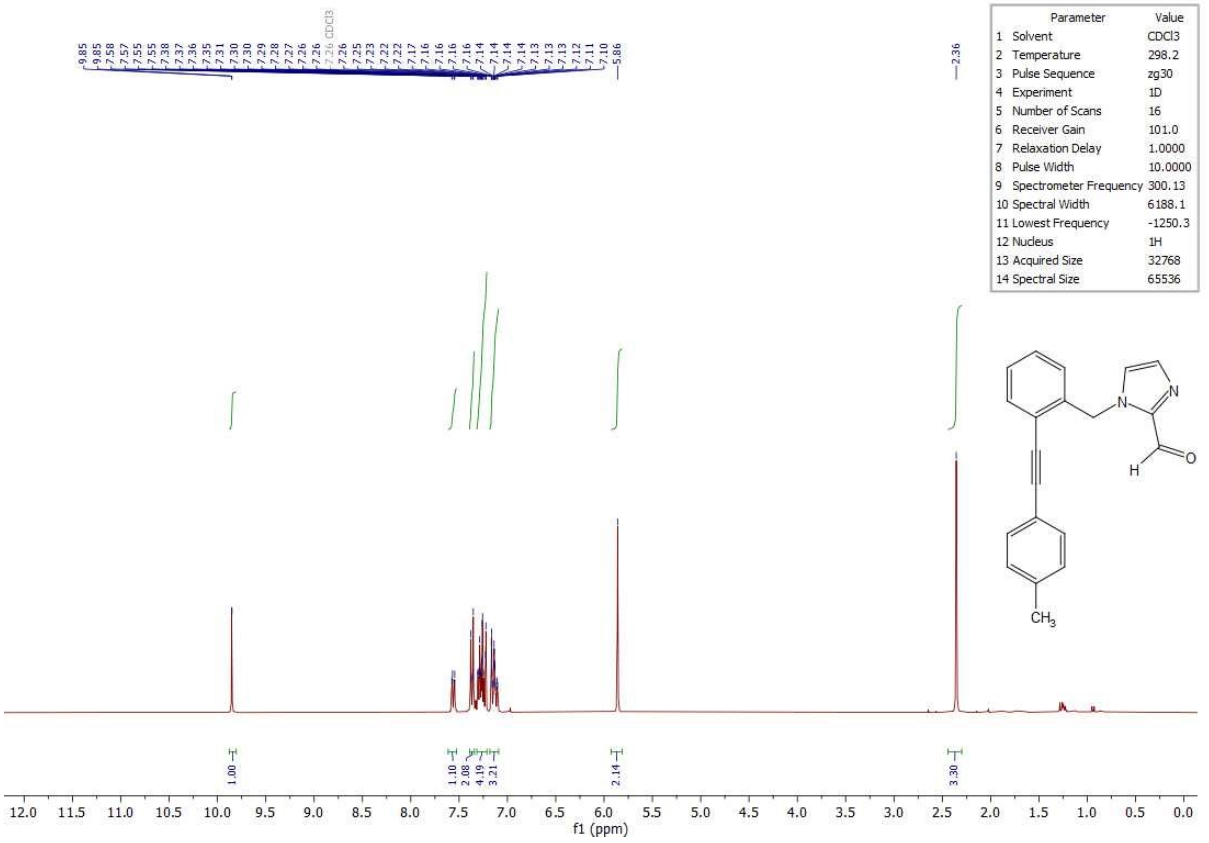


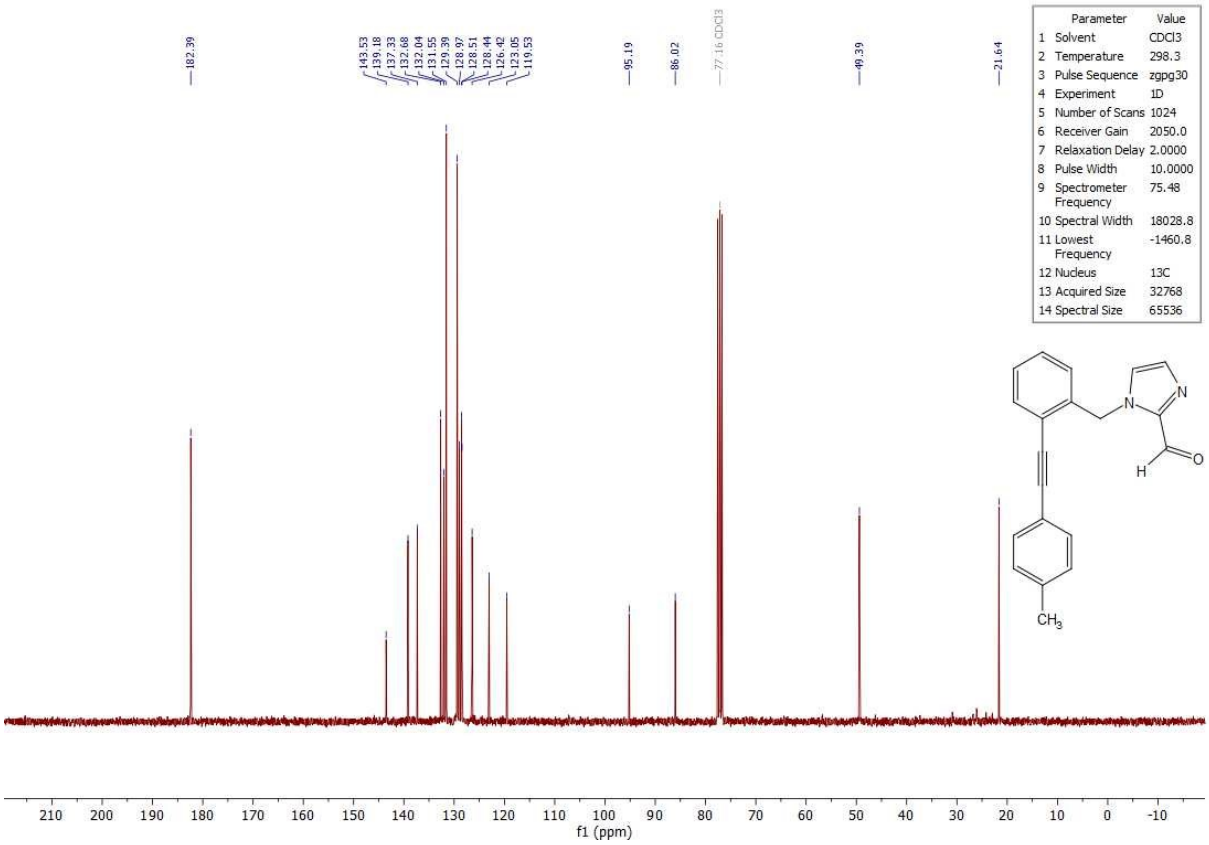
1-(2-(*o*-Tolylethynyl)benzyl)-1*H*-imidazole-2-carbaldehyde (5j)



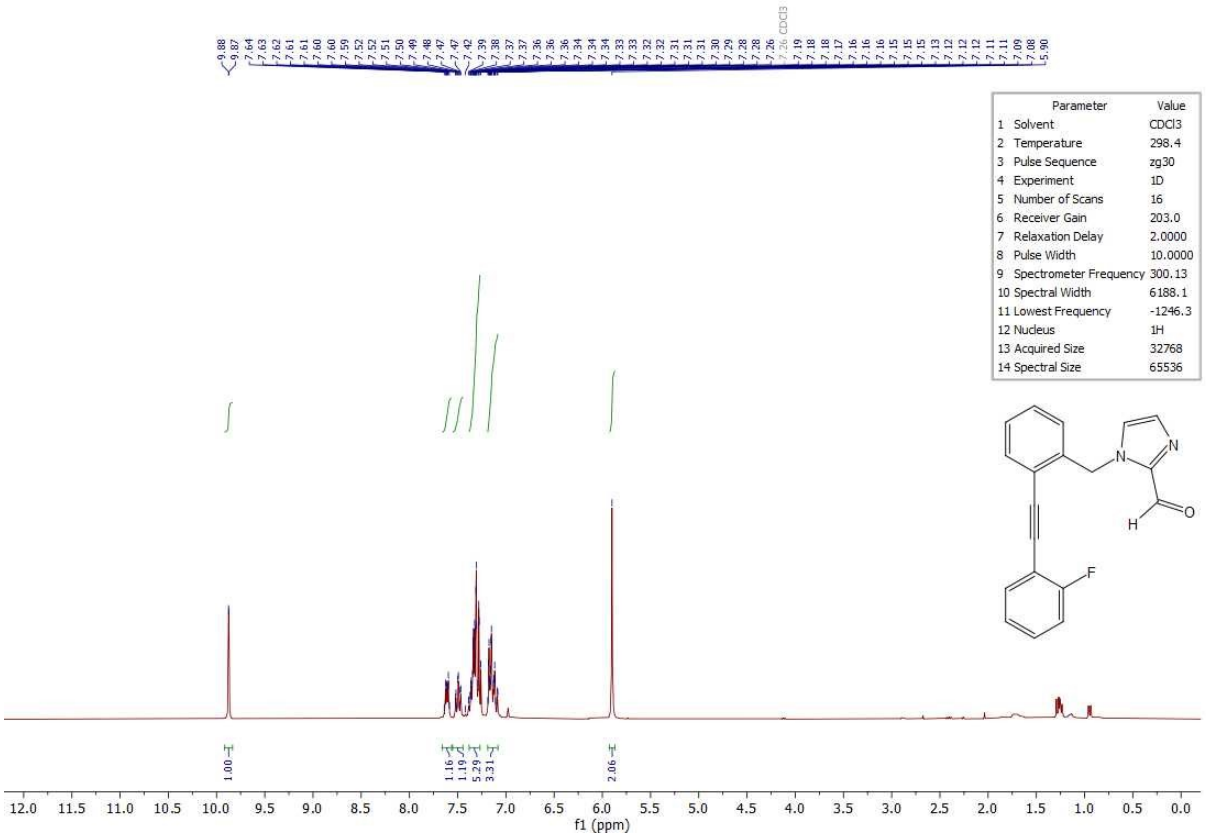


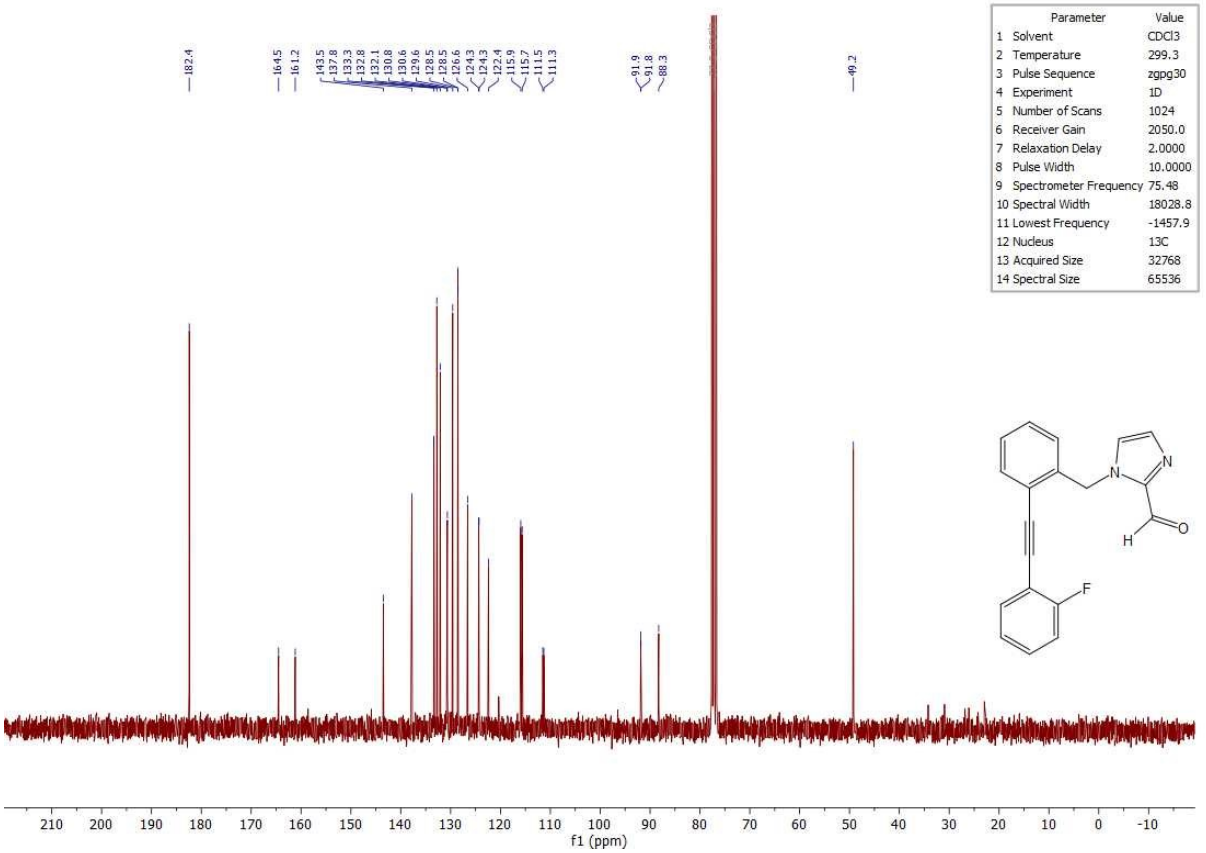
1-(2-(*p*-Tolylethynyl)benzyl)-1*H*-imidazole-2-carbaldehyde (5k)



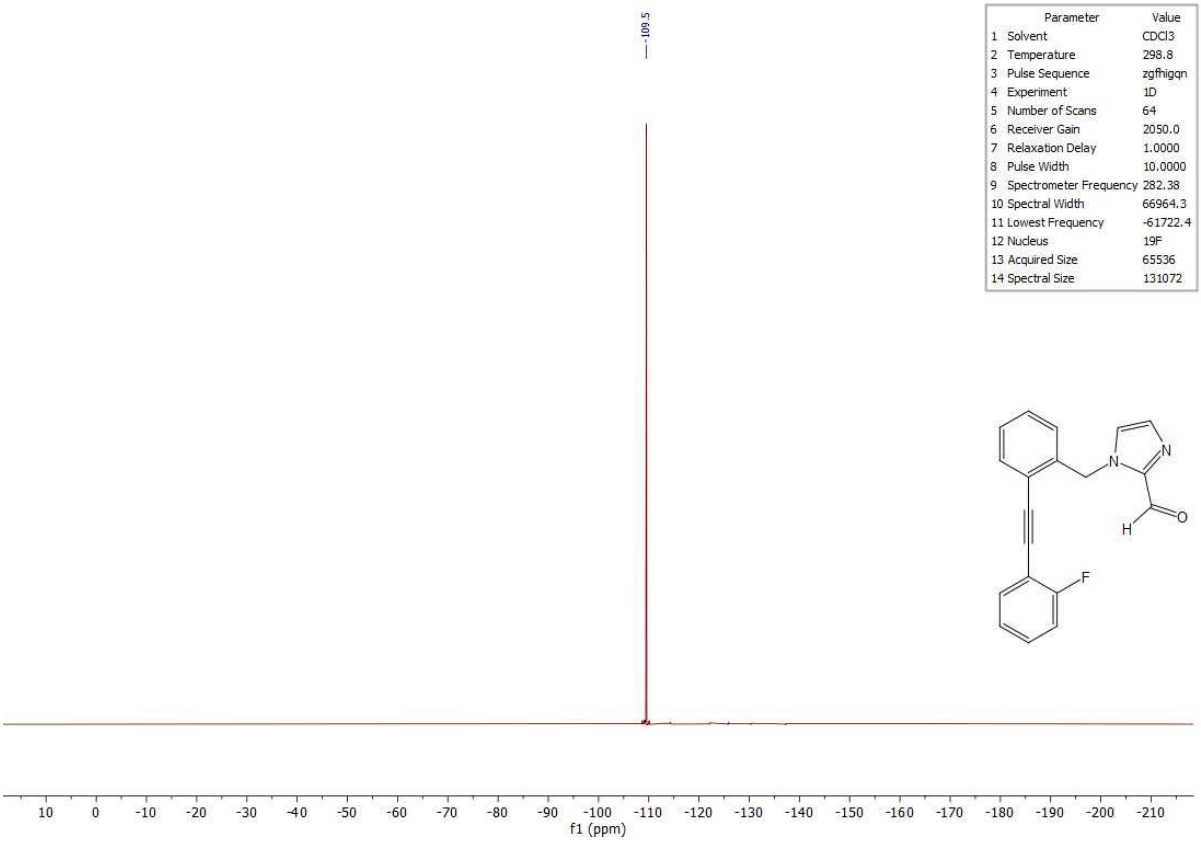


1-(2-((2-Fluorophenyl)ethynyl)benzyl)-1*H*-imidazole-2-carbaldehyde (5l)

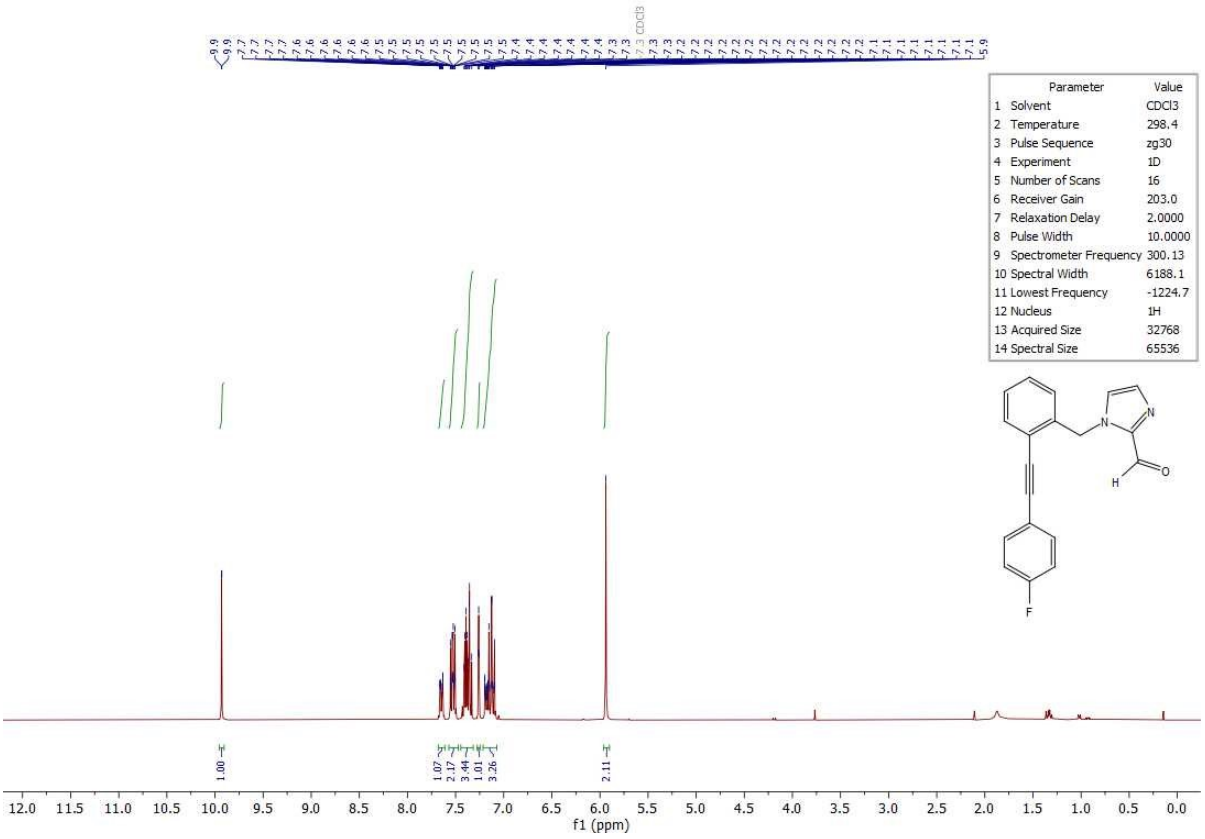


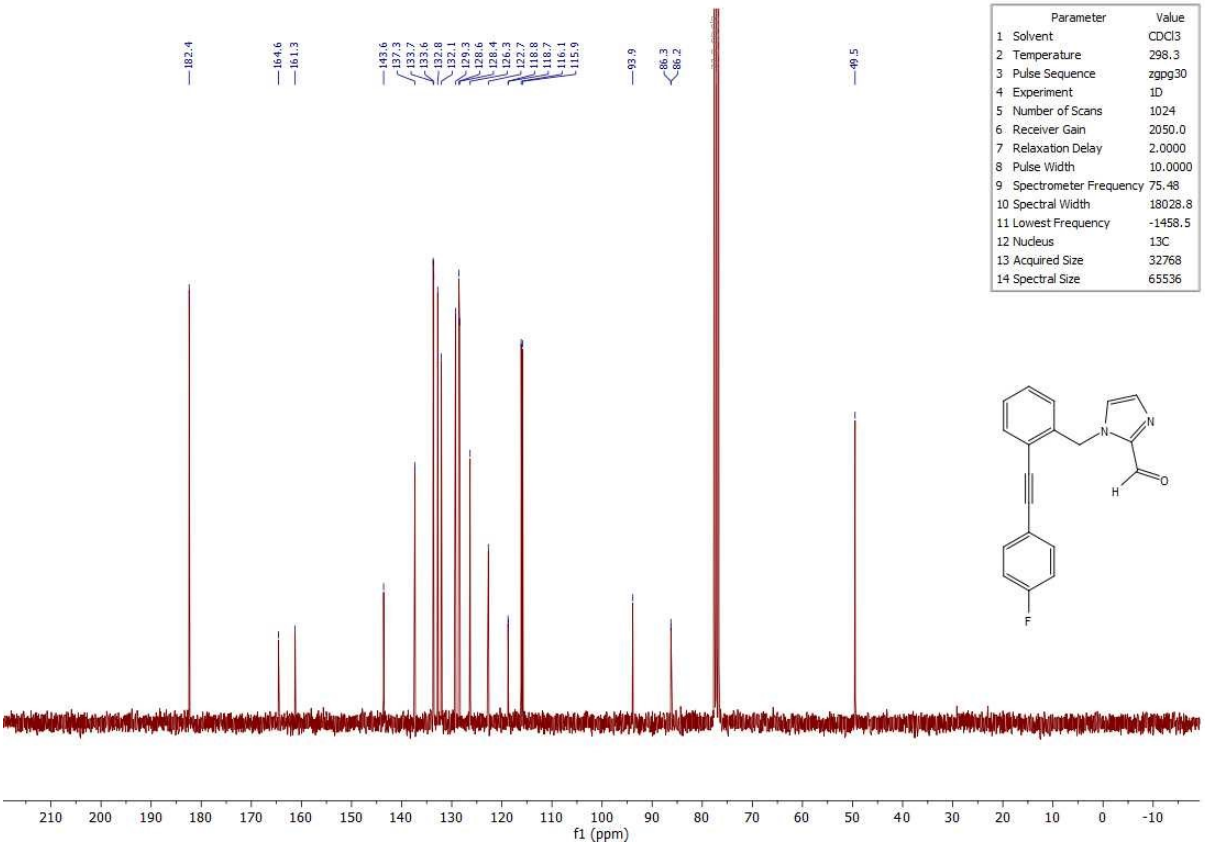


1-(2-((2-Fluorophenyl)ethynyl)benzyl)-1*H*-imidazole-2-carbaldehyde (5l)

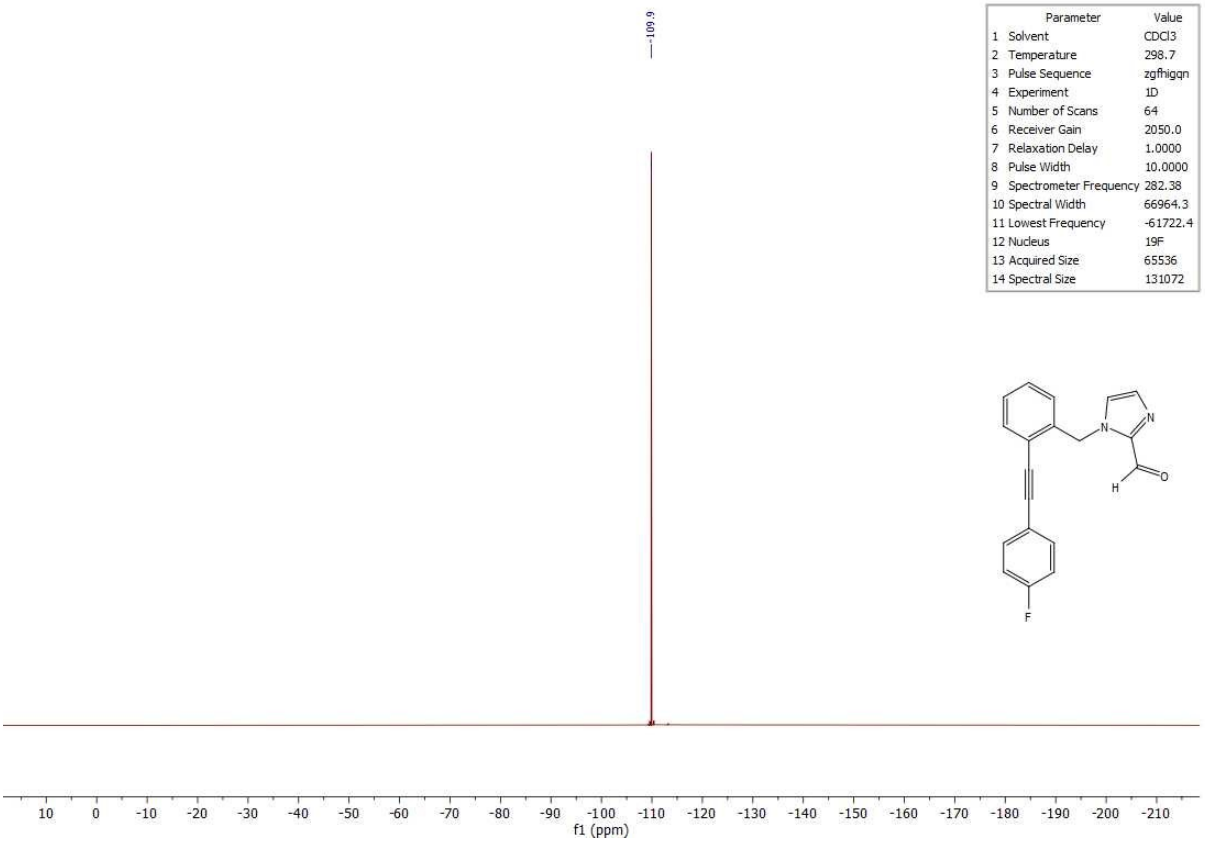


1-(2-((4-Fluorophenyl)ethynyl)benzyl)-1*H*-imidazole-2-carbaldehyde (5m)

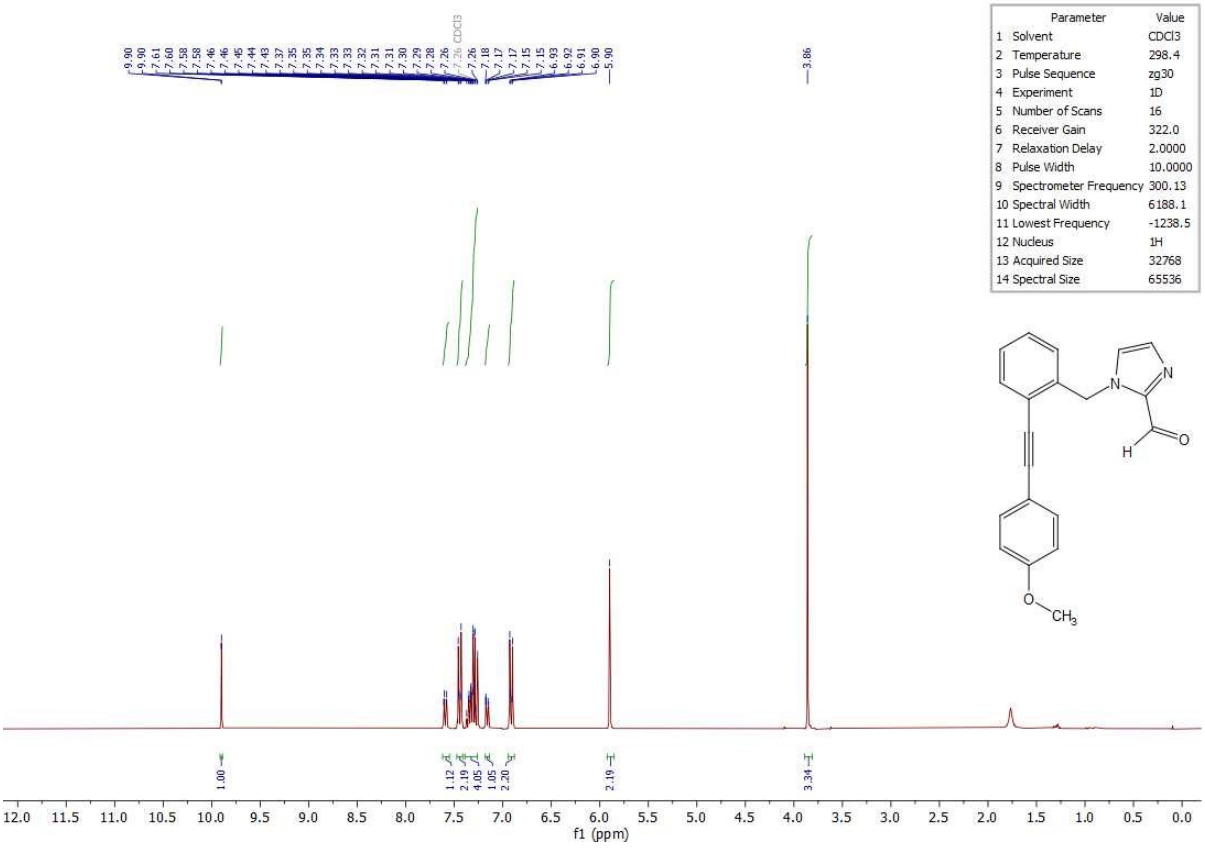


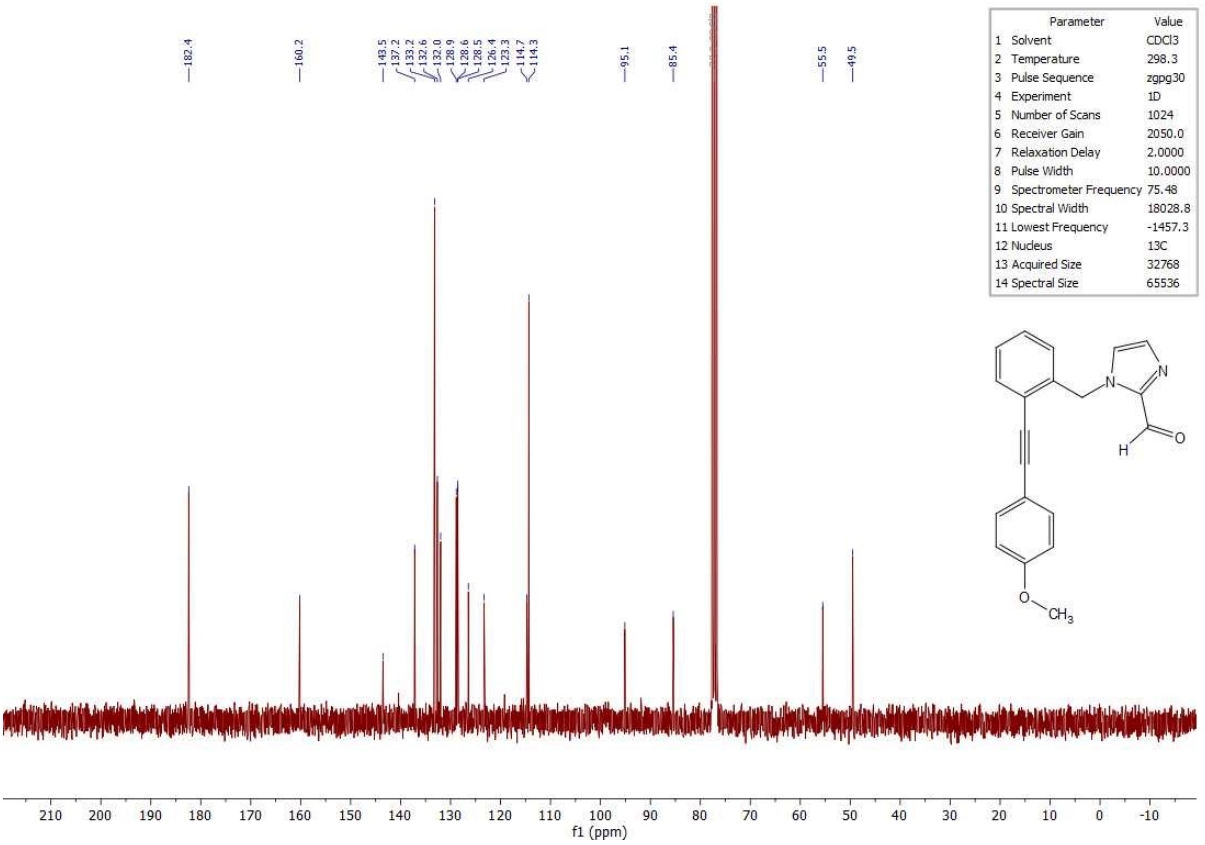


1-(2-((4-Fluorophenyl)ethynyl)benzyl)-1*H*-imidazole-2-carbaldehyde (5m)

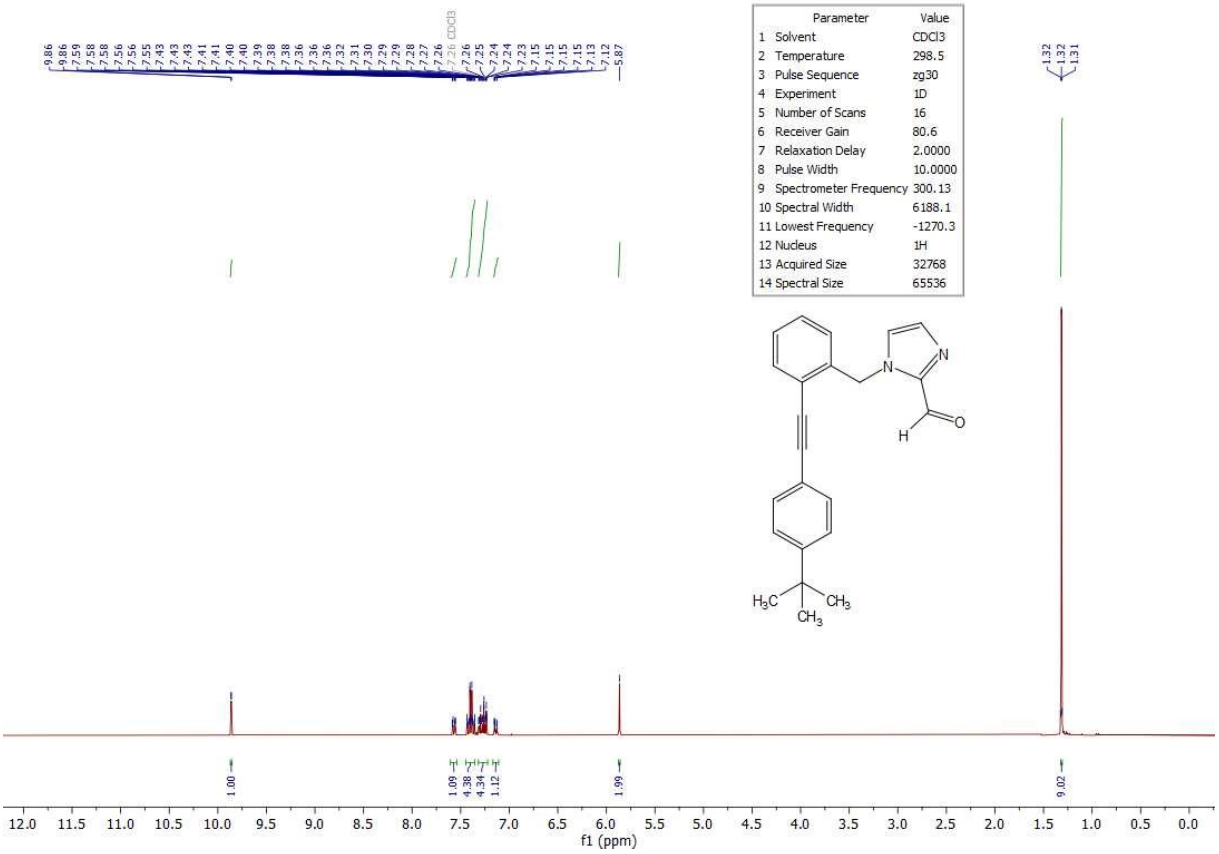


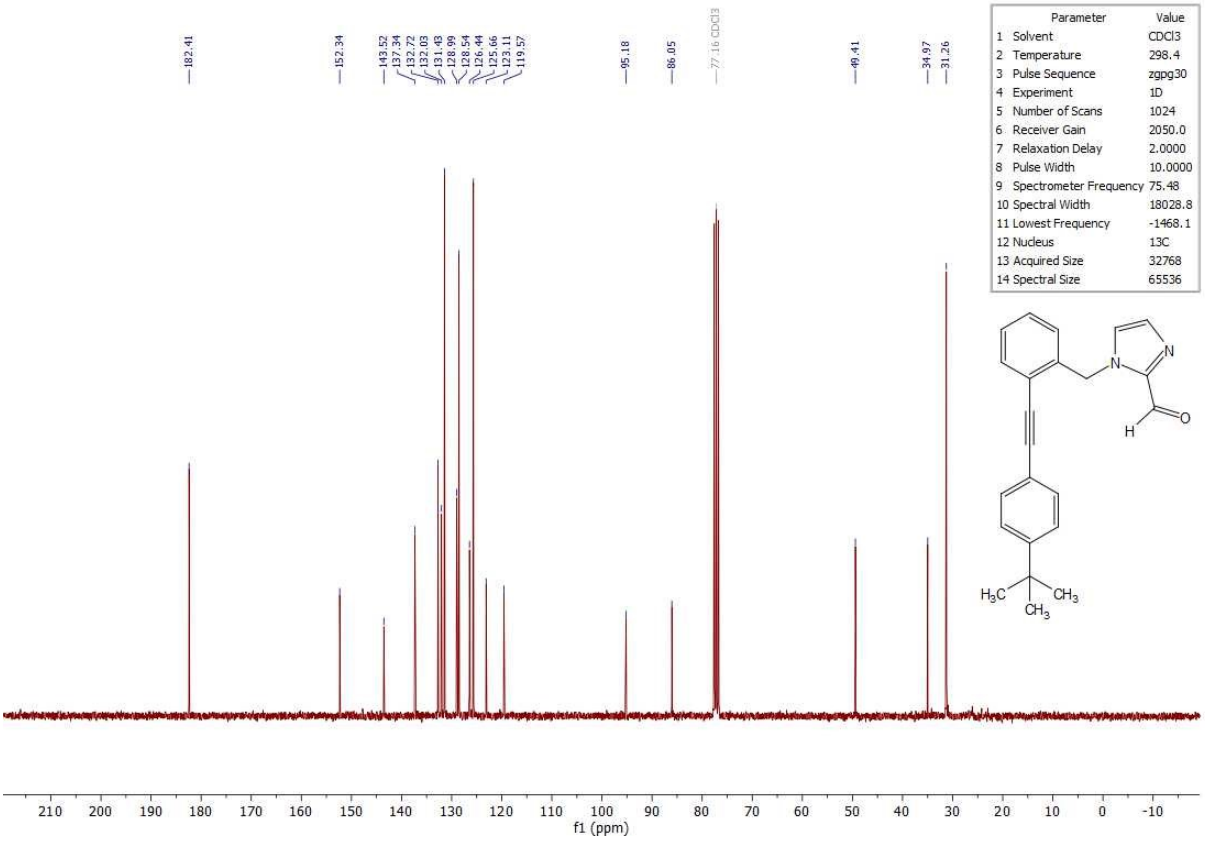
1-(2-((4-Methoxyphenyl)ethynyl)benzyl)-1*H*-imidazole-2-carbaldehyde (5n)



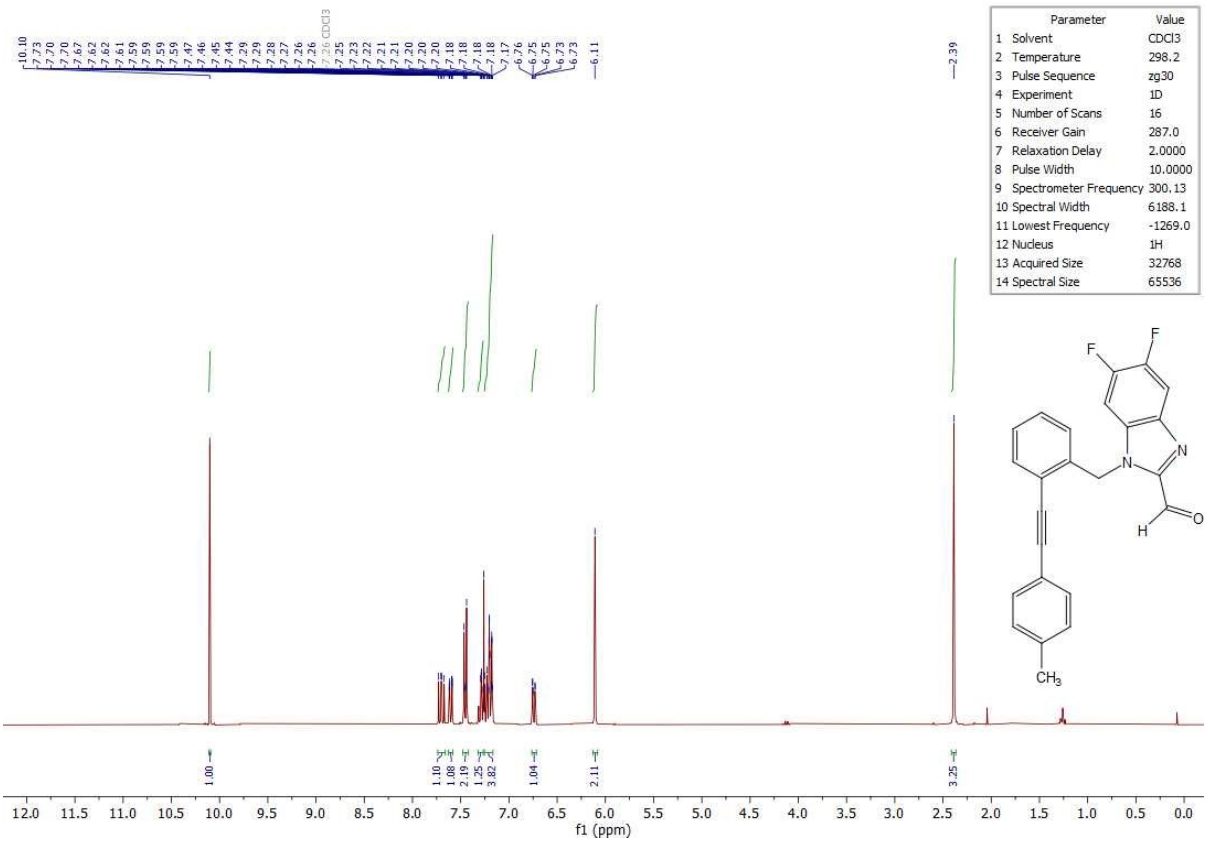


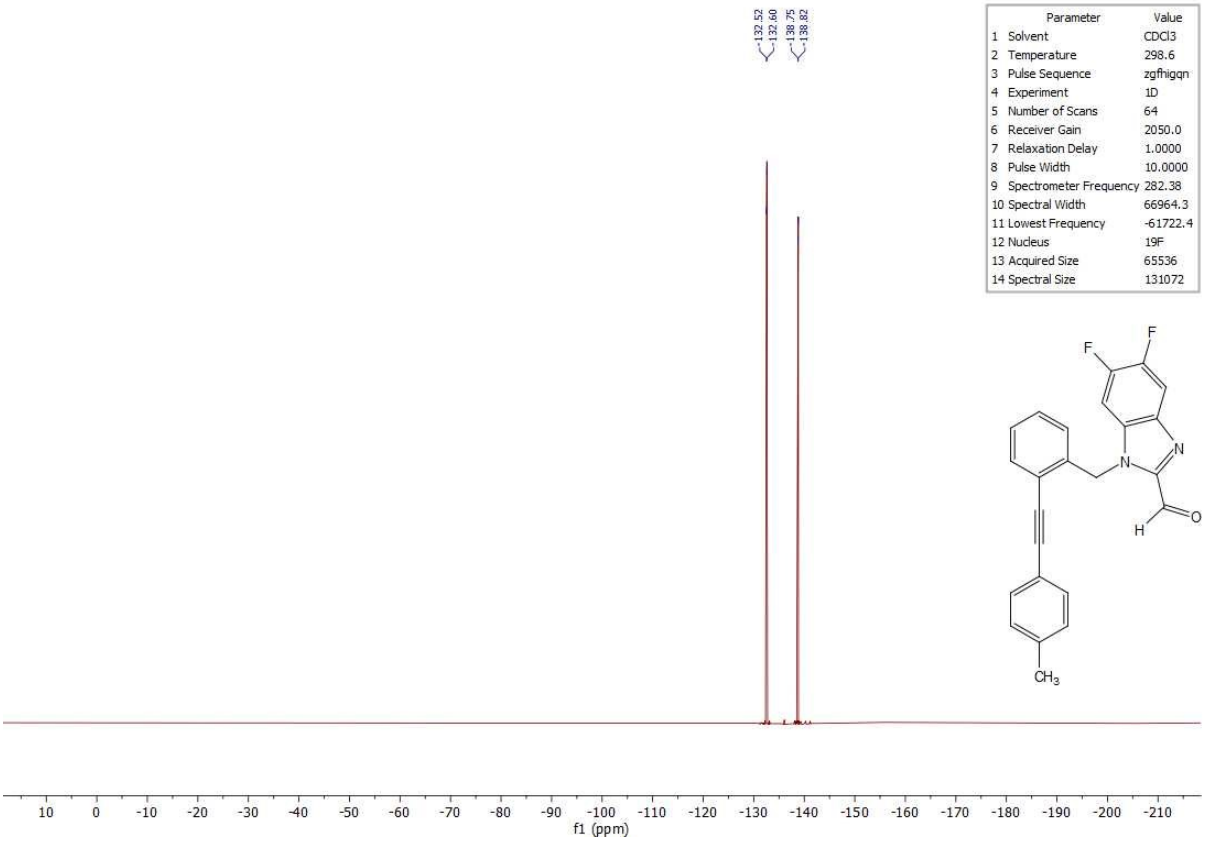
1-(2-((4-(tert-Butyl)phenyl)ethynyl)benzyl)-1H-imidazole-2-carbaldehyde (5o)



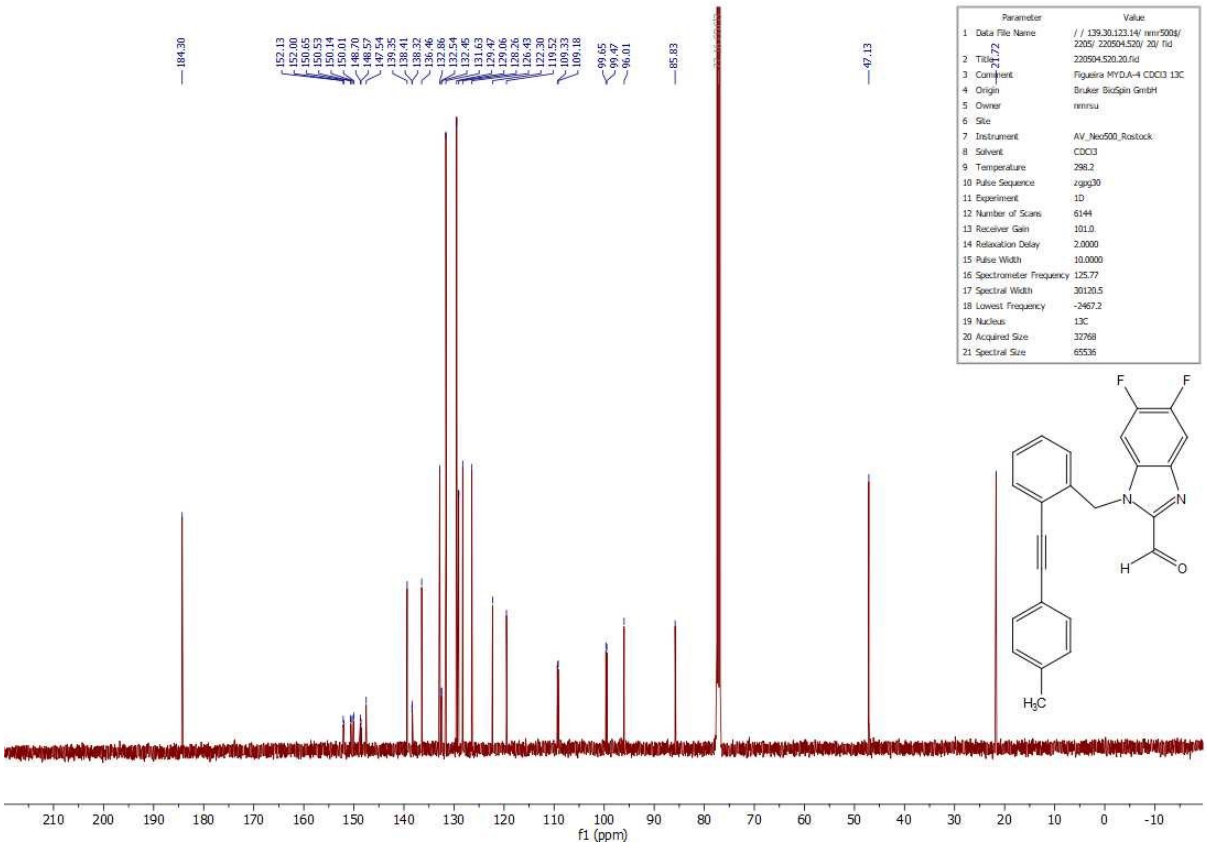


5,6-Difluoro-1-(2-(*p*-tolylethynyl)benzyl)-1*H*-benzo[*d*]imidazole-2-carbaldehyde (5p)

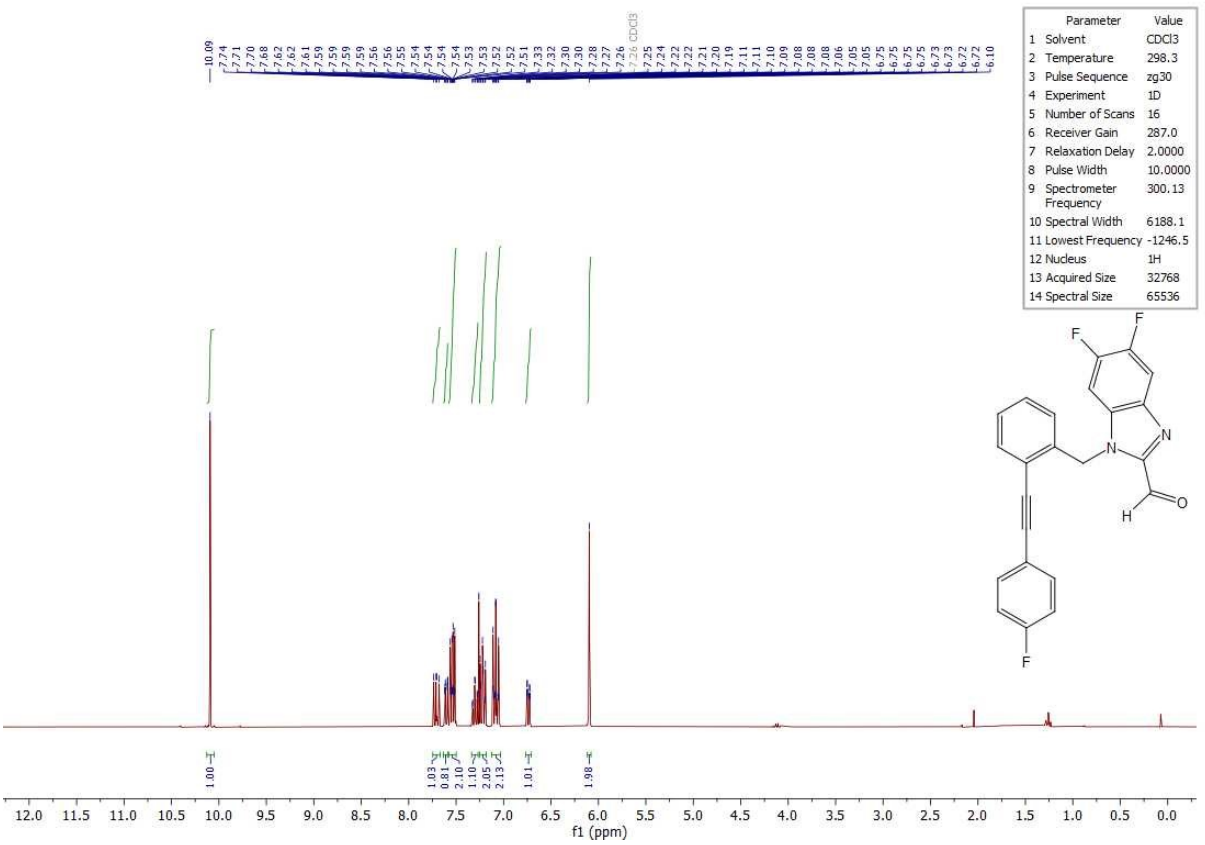


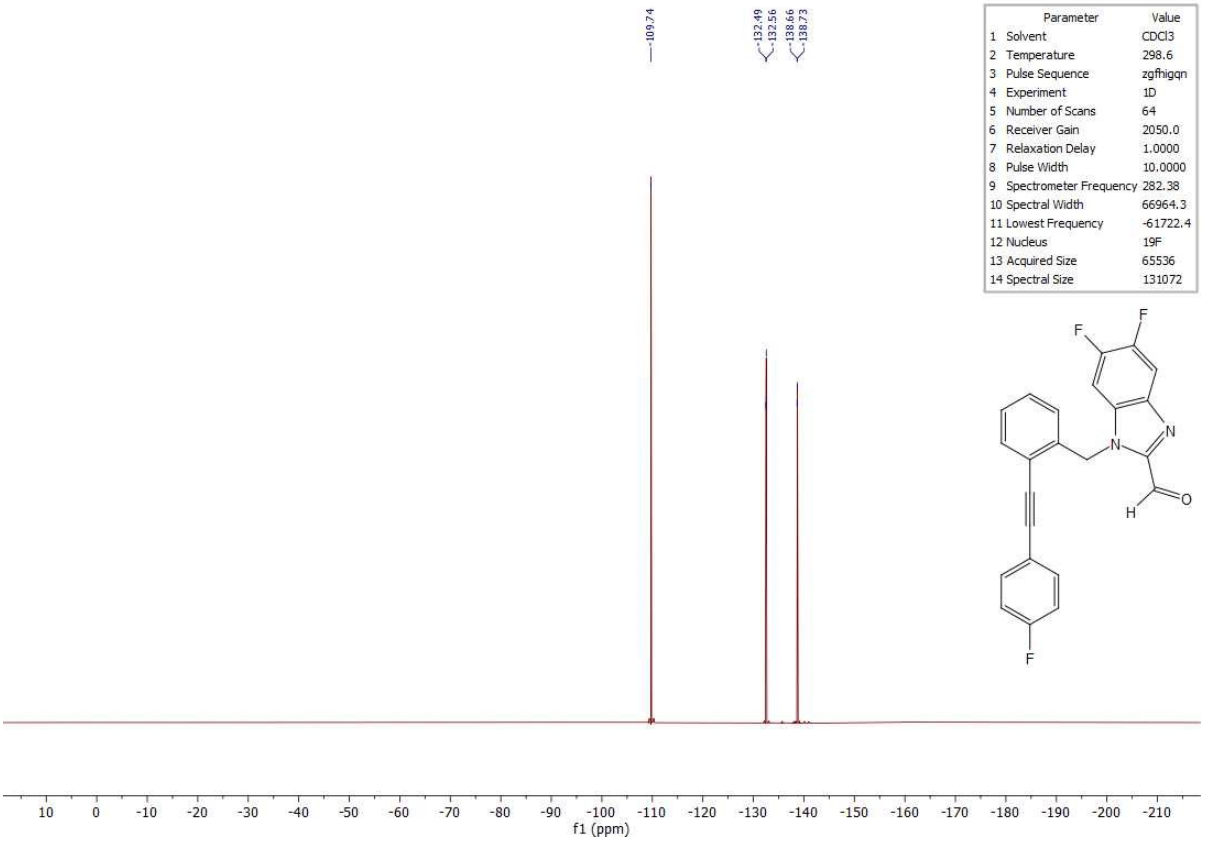


5,6-Difluoro-1-(2-(*p*-tolylethynyl)benzyl)-1*H*-benzo[*d*]imidazole-2-carbaldehyde (5p)

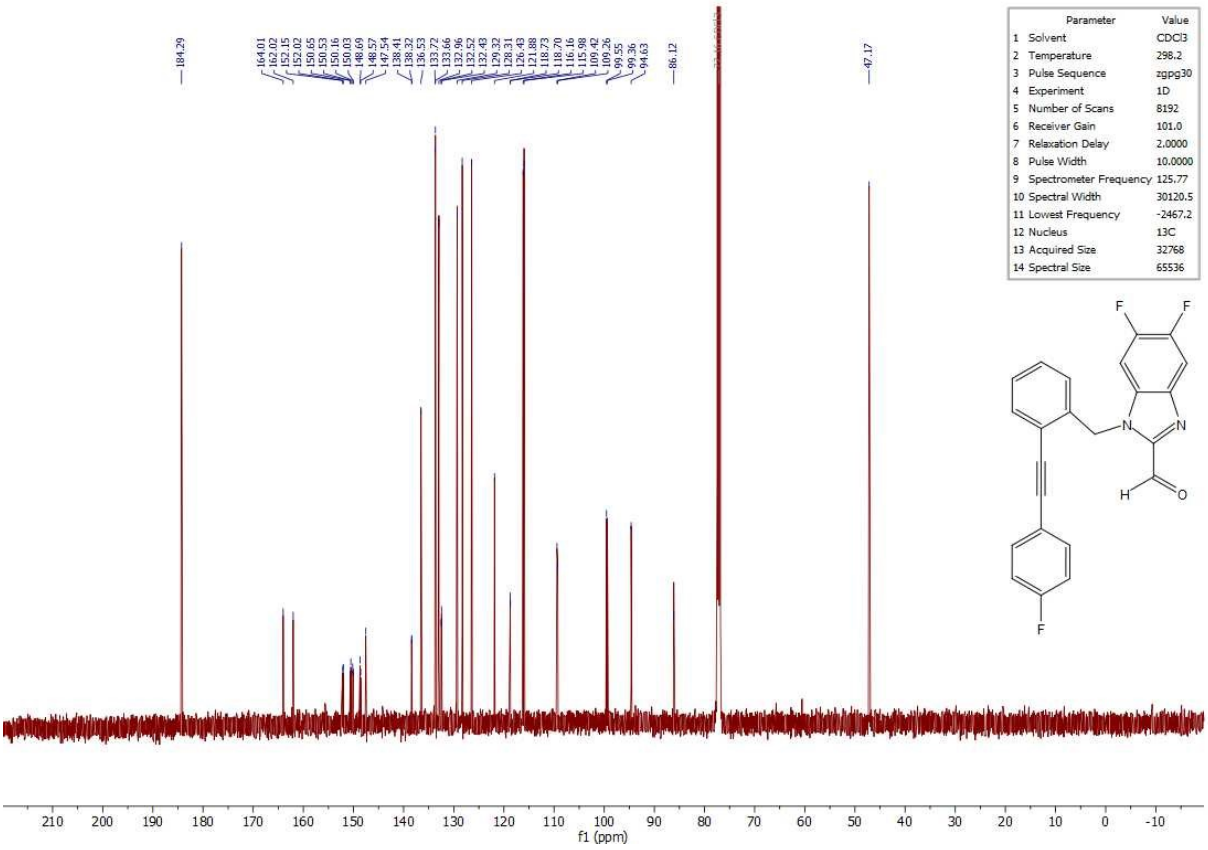


5,6-Difluoro-1-(2-((4-fluorophenyl)ethynyl)benzyl)-1*H*-benzo[*d*]imidazole-2-carbaldehyde (5q)

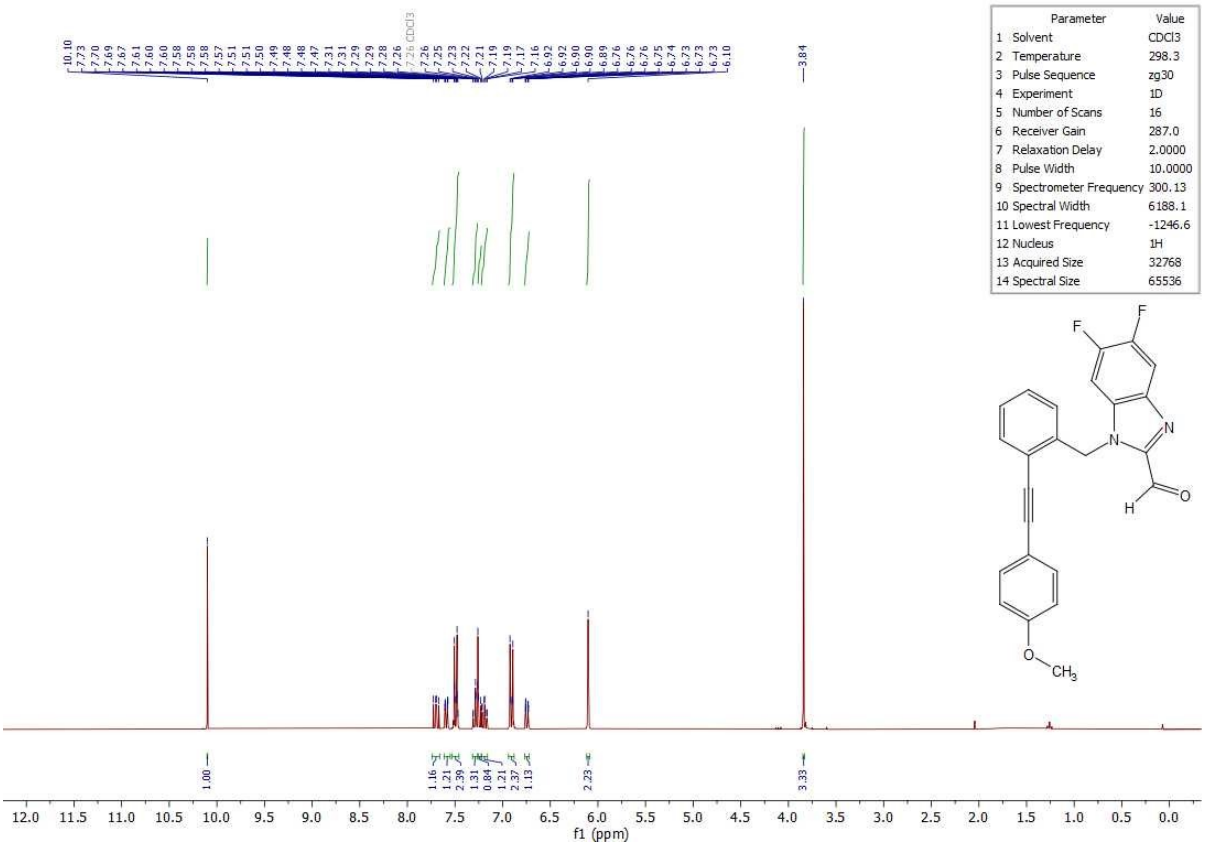


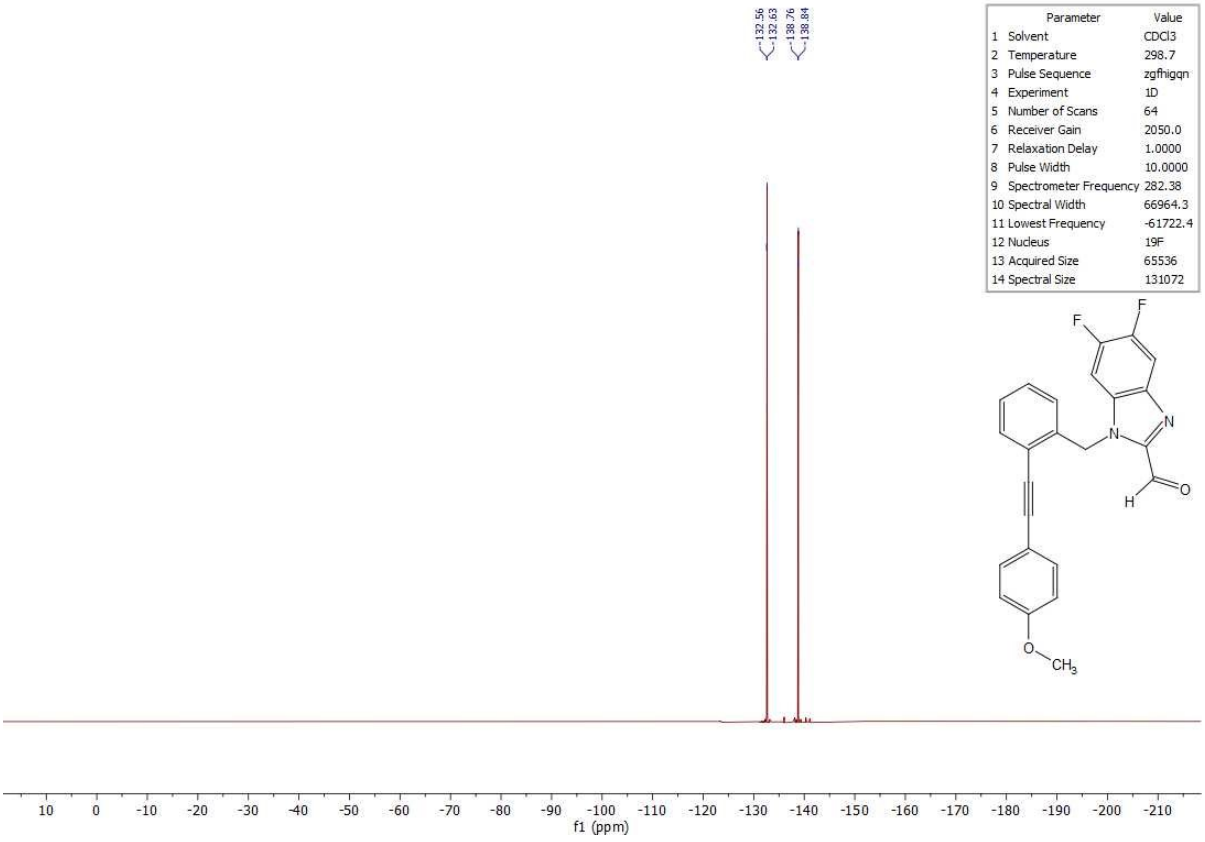


5,6-Difluoro-1-(2-((4-fluorophenyl)ethynyl)benzyl)-1*H*-benzo[*d*]imidazole-2-carbaldehyde (5q)

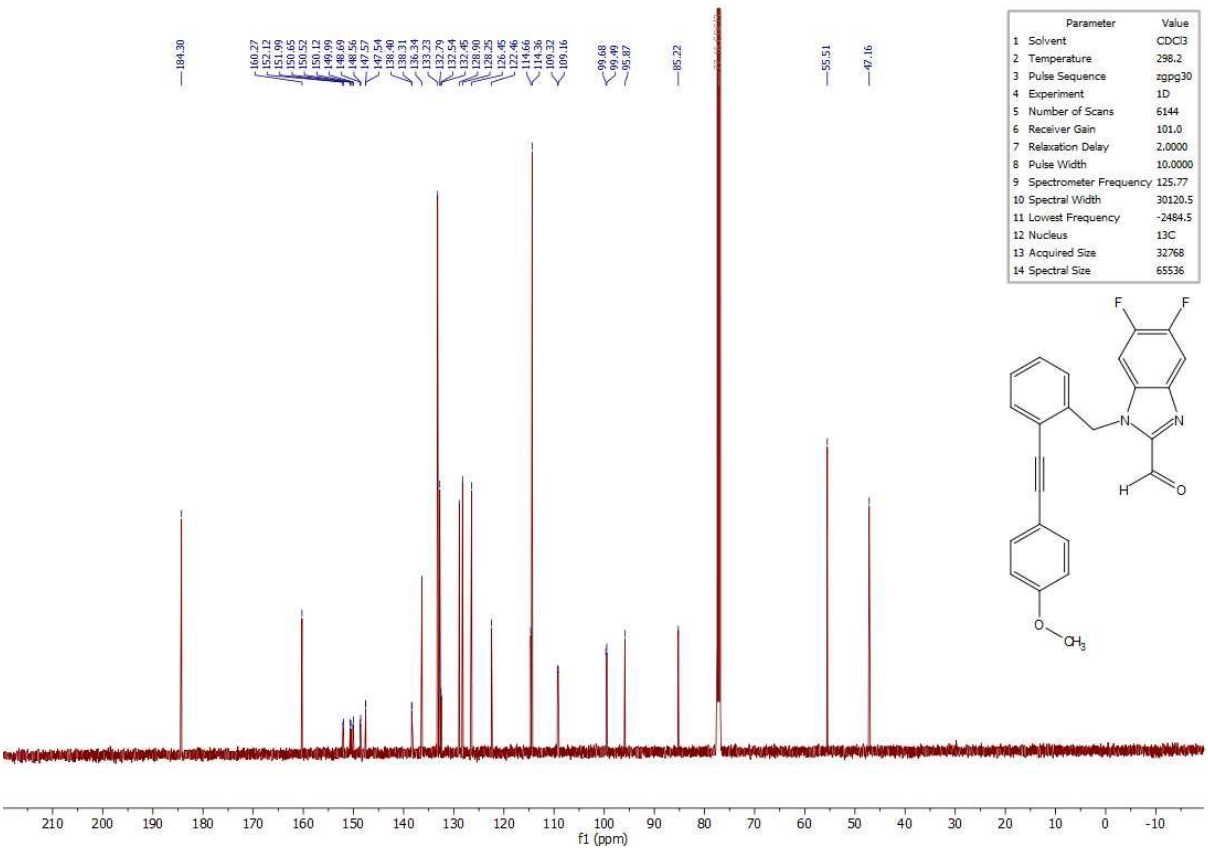


5,6-Difluoro-1-(2-((4-methoxyphenyl)ethynyl)benzyl)-1*H*-benzo[*d*]imidazole-2 carbaldehyde (5r)

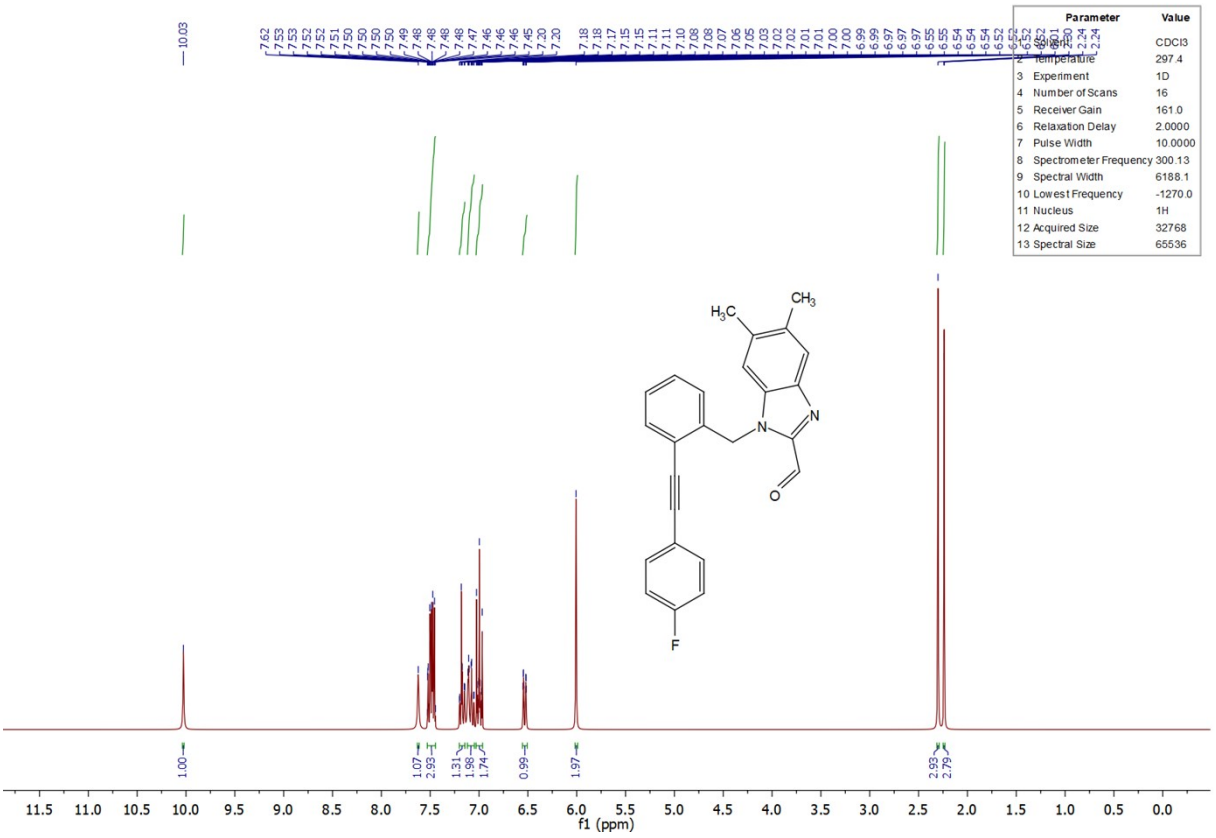


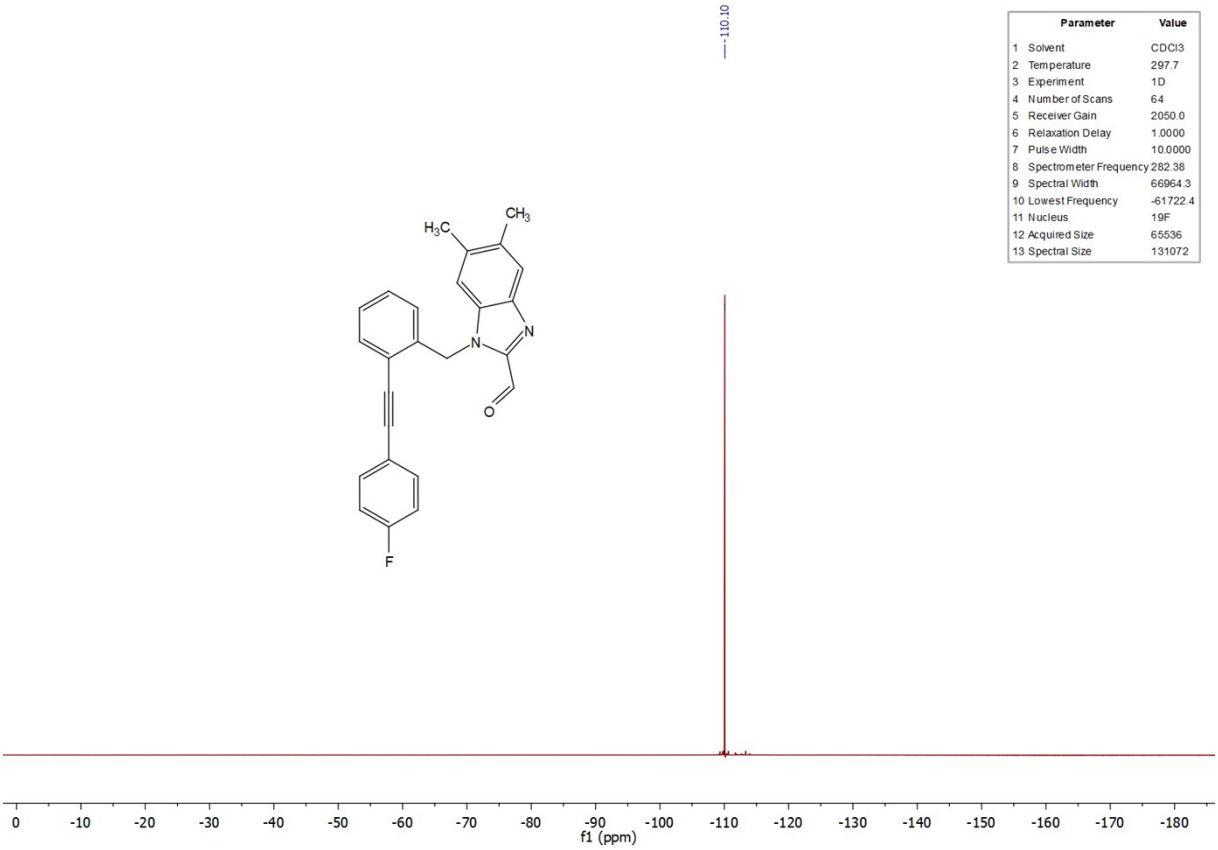


5,6-Difluoro-1-(2-((4-methoxyphenyl)ethynyl)benzyl)-1*H*-benzo[*d*]imidazole-2 carbaldehyde (5r)

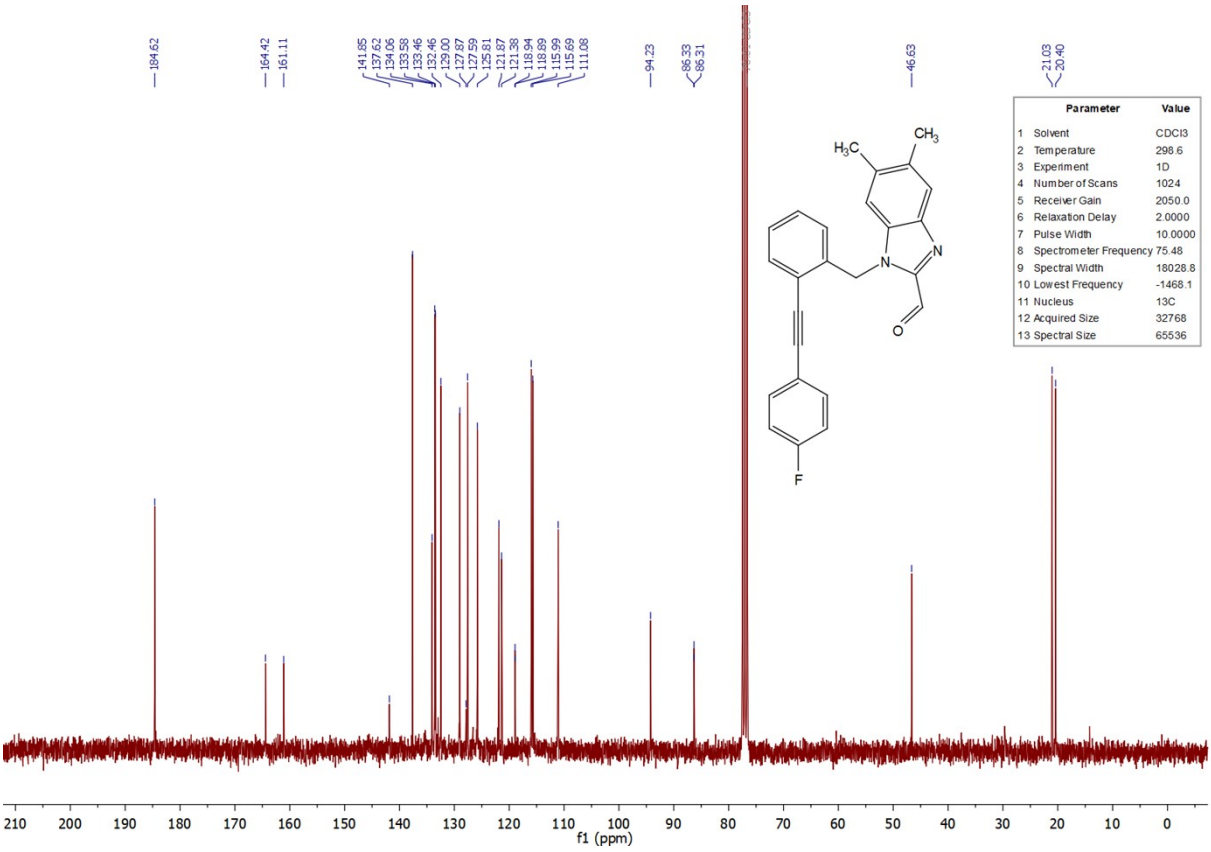


1-(2-((4-Fluorophenyl)ethynyl)benzyl)-5,6-dimethyl-1*H*-benzo[*d*]imidazole-2-carbaldehyde (5s)

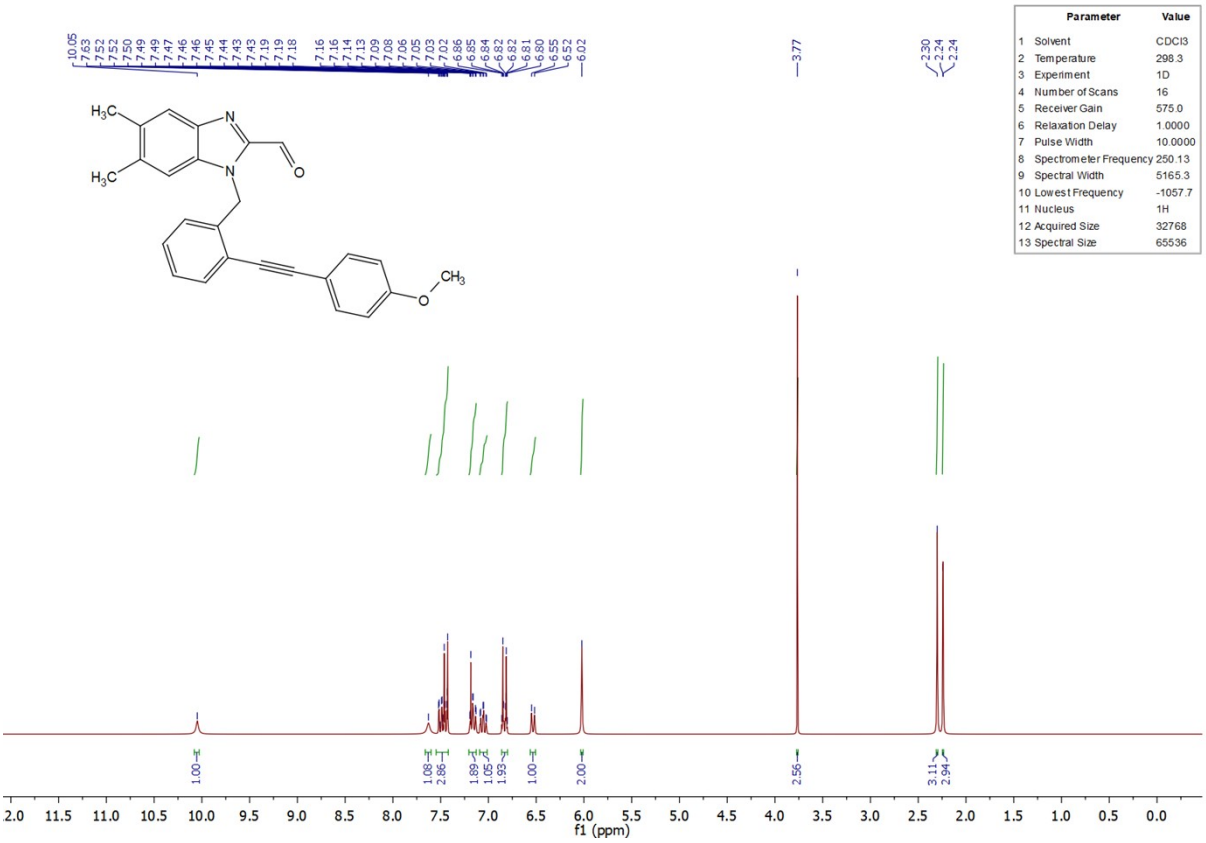


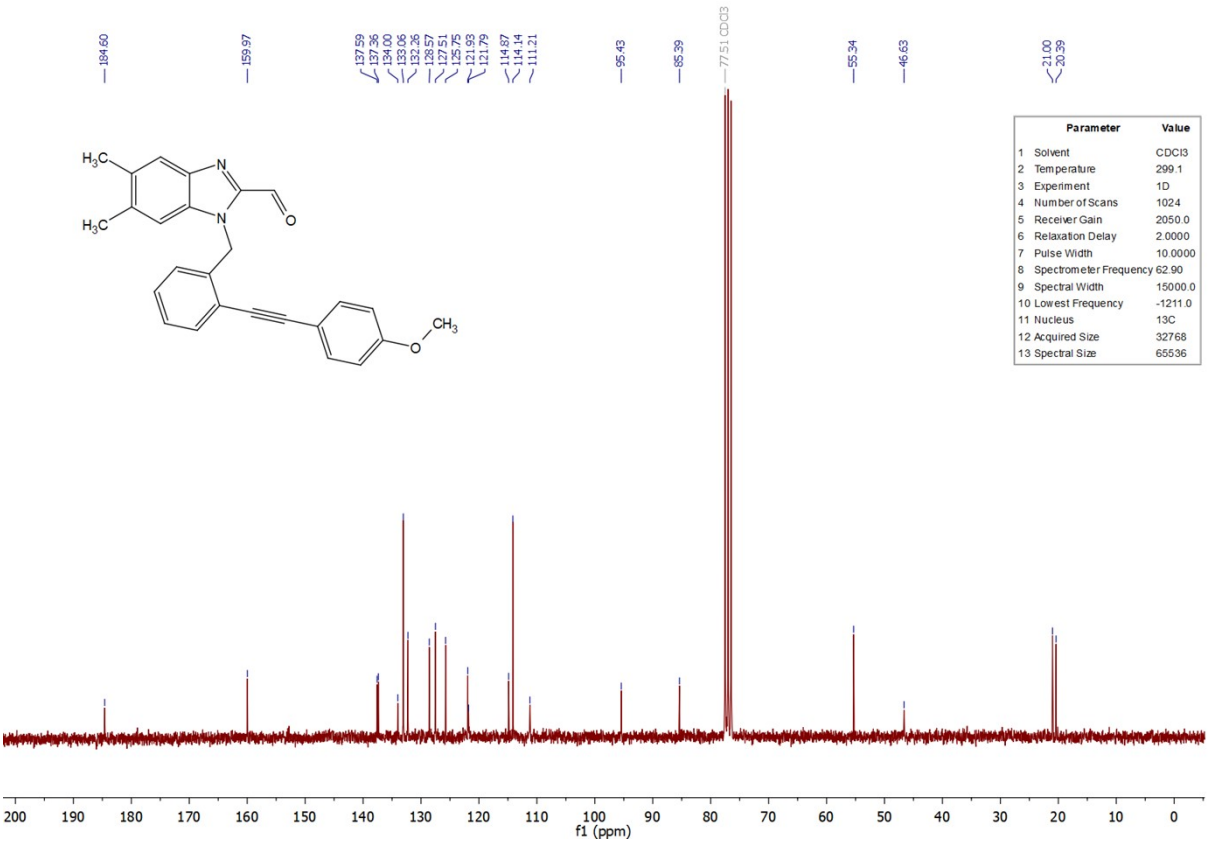


1-(2-((4-Fluorophenyl)ethynyl)benzyl)-5,6-dimethyl-1*H*-benzo[*d*]imidazole-2-carbaldehyde (5s)

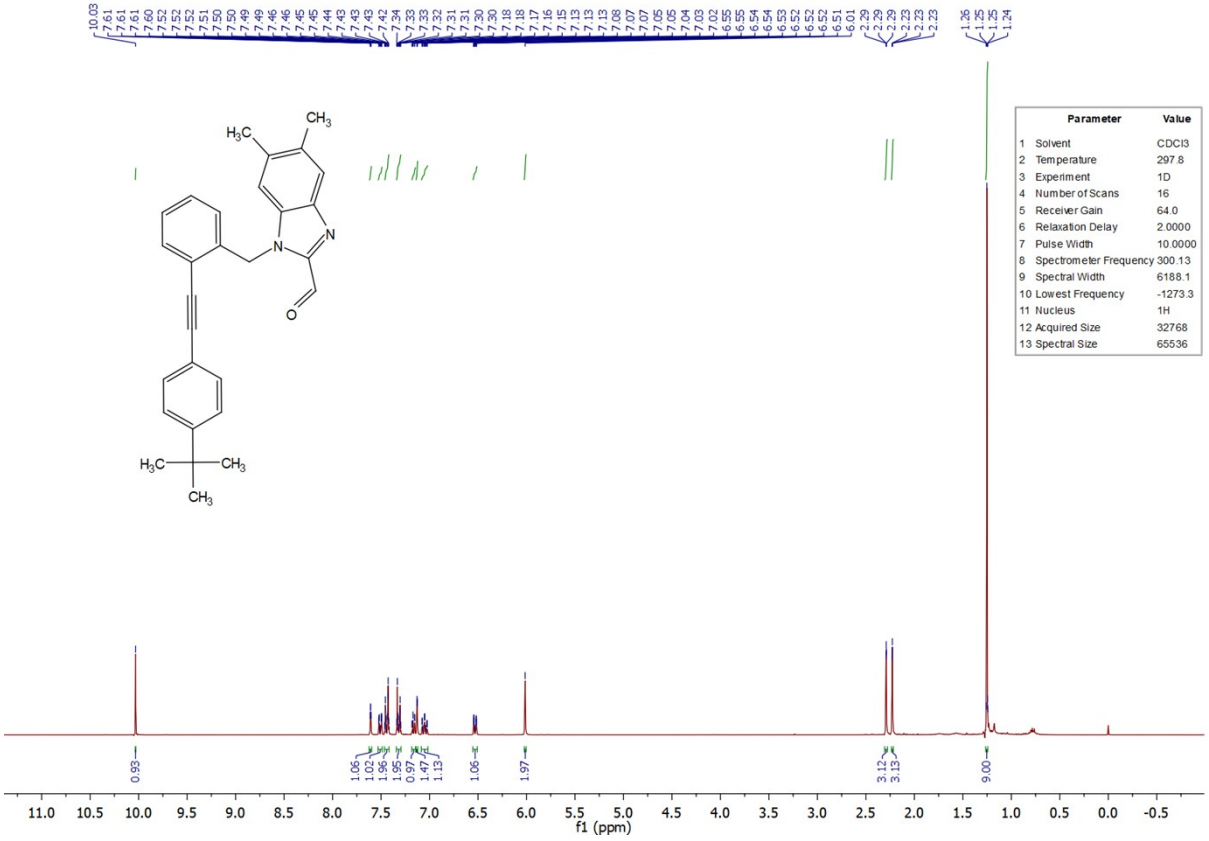


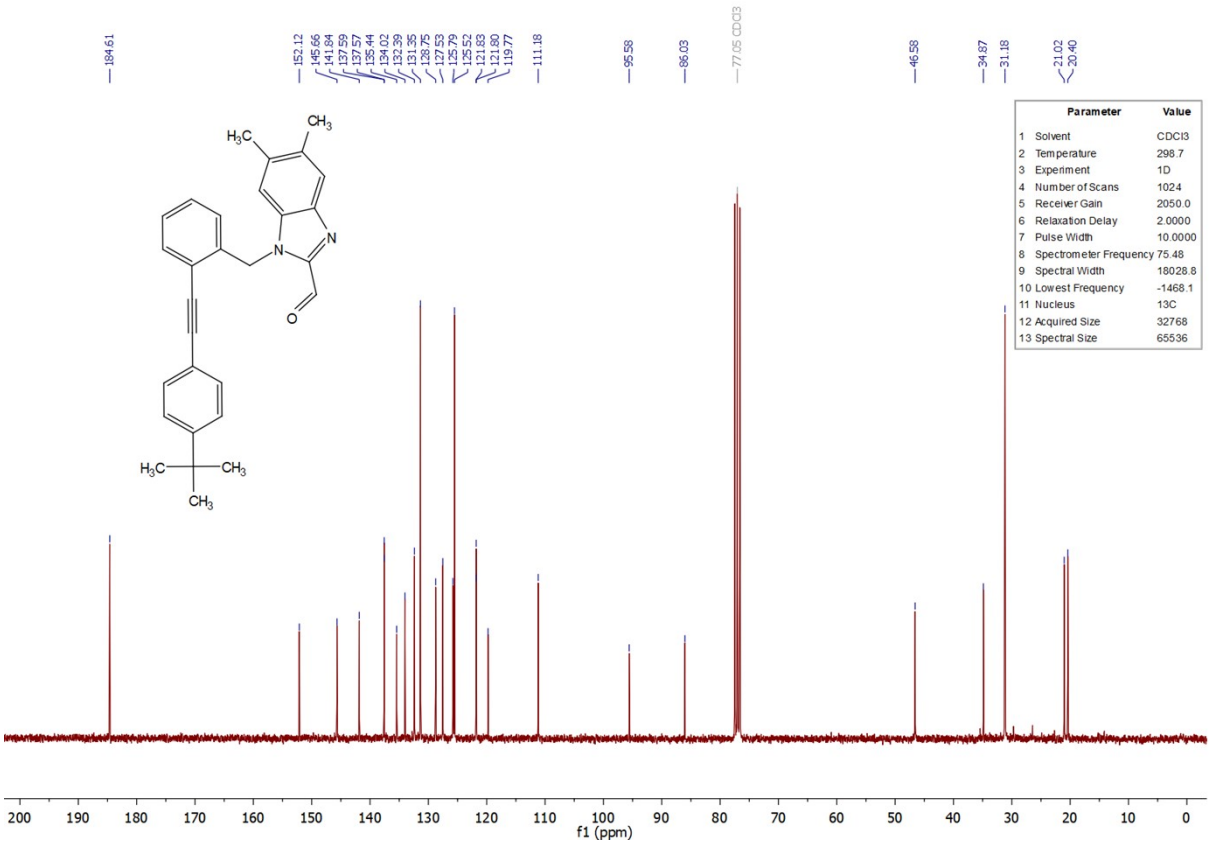
1-(2-((4-Methoxyphenyl)ethynyl)benzyl)-5,6-dimethyl-1*H*-benzo[*d*]imidazole-2-carbaldehyde (5t)



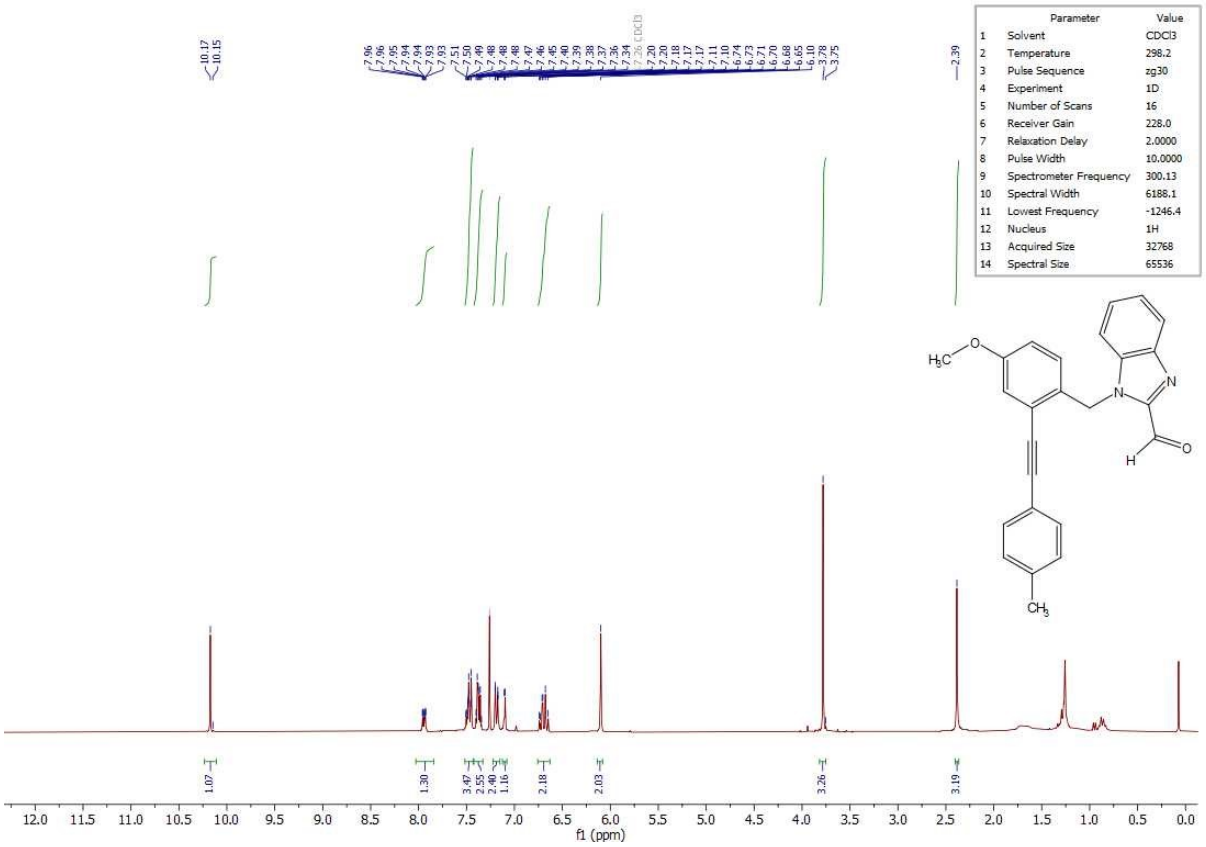


1-(2-((4-(*tert*-Butyl)phenyl)ethynyl)benzyl)-5,6-dimethyl-1*H*-benzo[*d*]imidazole-2-carbaldehyde (5u)

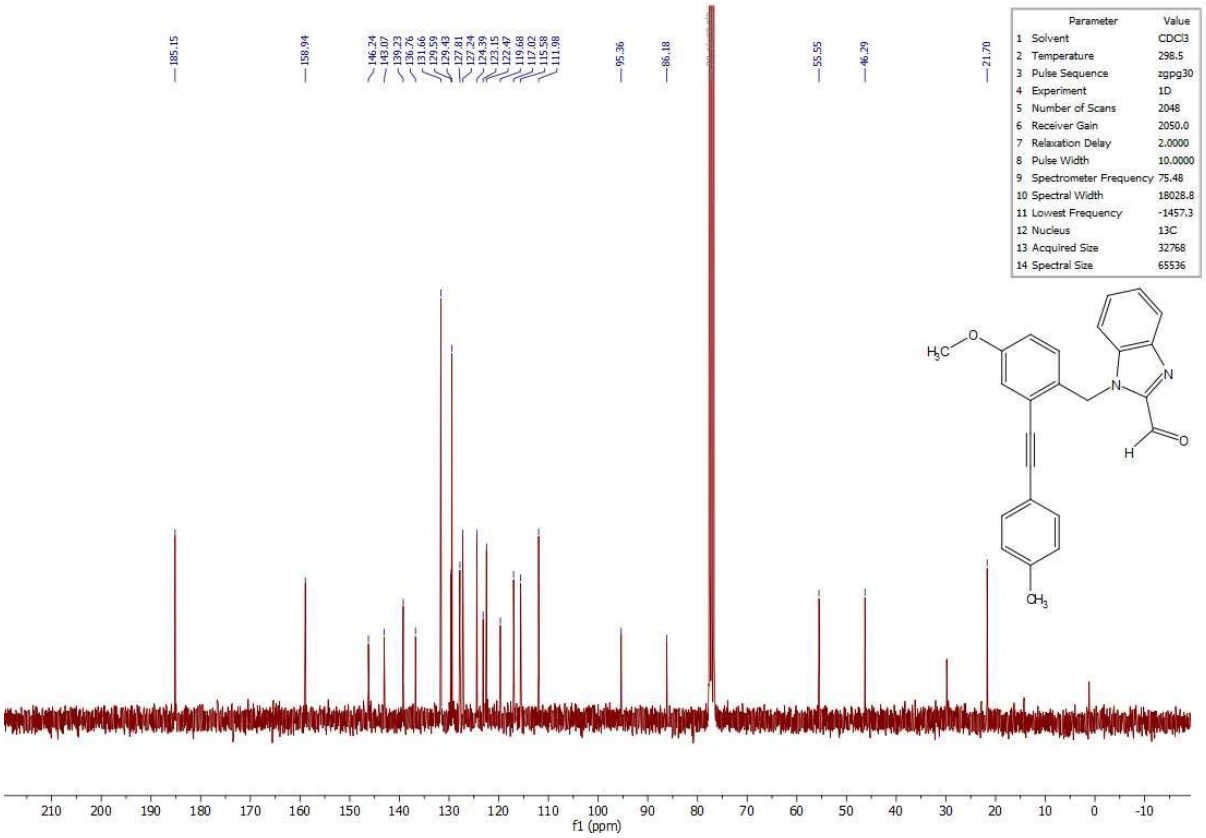




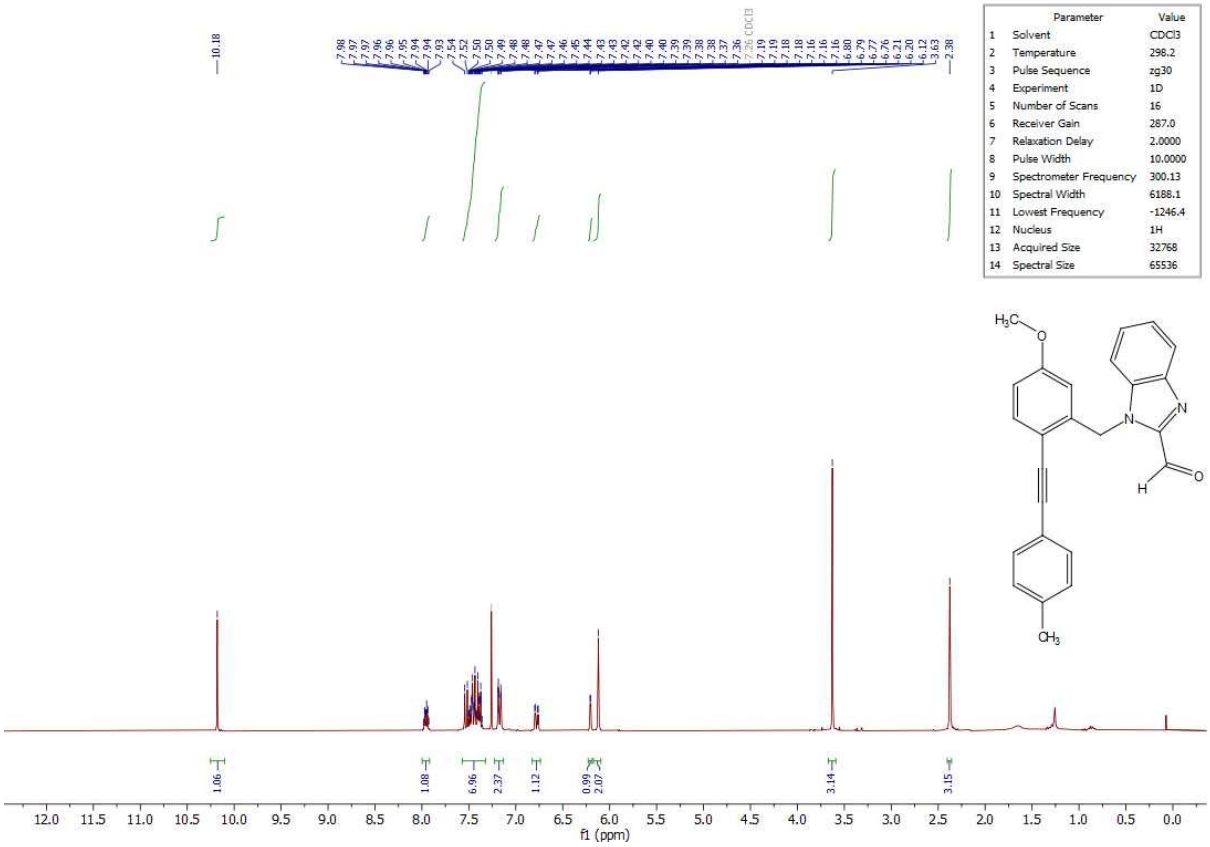
1-(4-Methoxy-2-(4-tolylethynyl)benzyl)-1*H*-benzo[*d*]imidazole-2-carbaldehyde (5v)

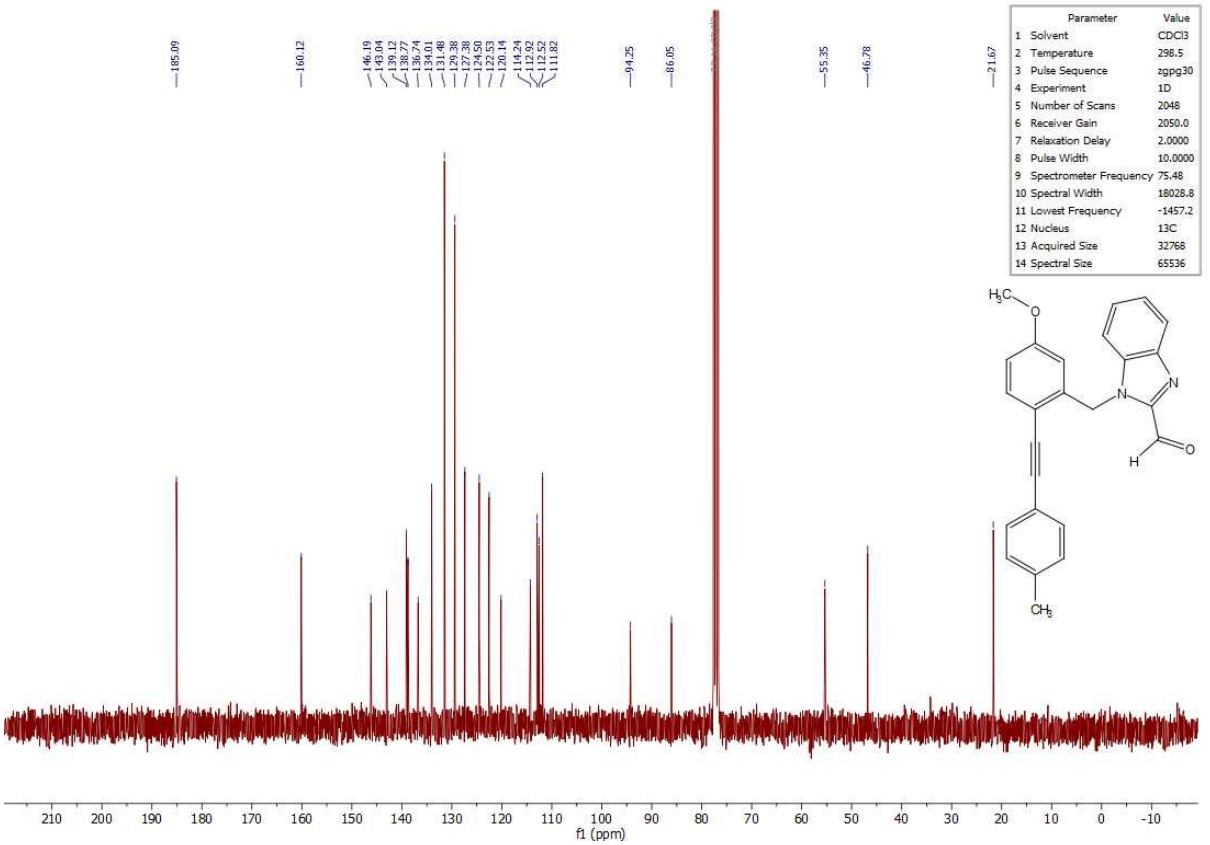


1-(4-Methoxy-2-(4-tolylethynyl)benzyl)-1*H*-benzo[*d*]imidazole-2-carbaldehyde (5v)

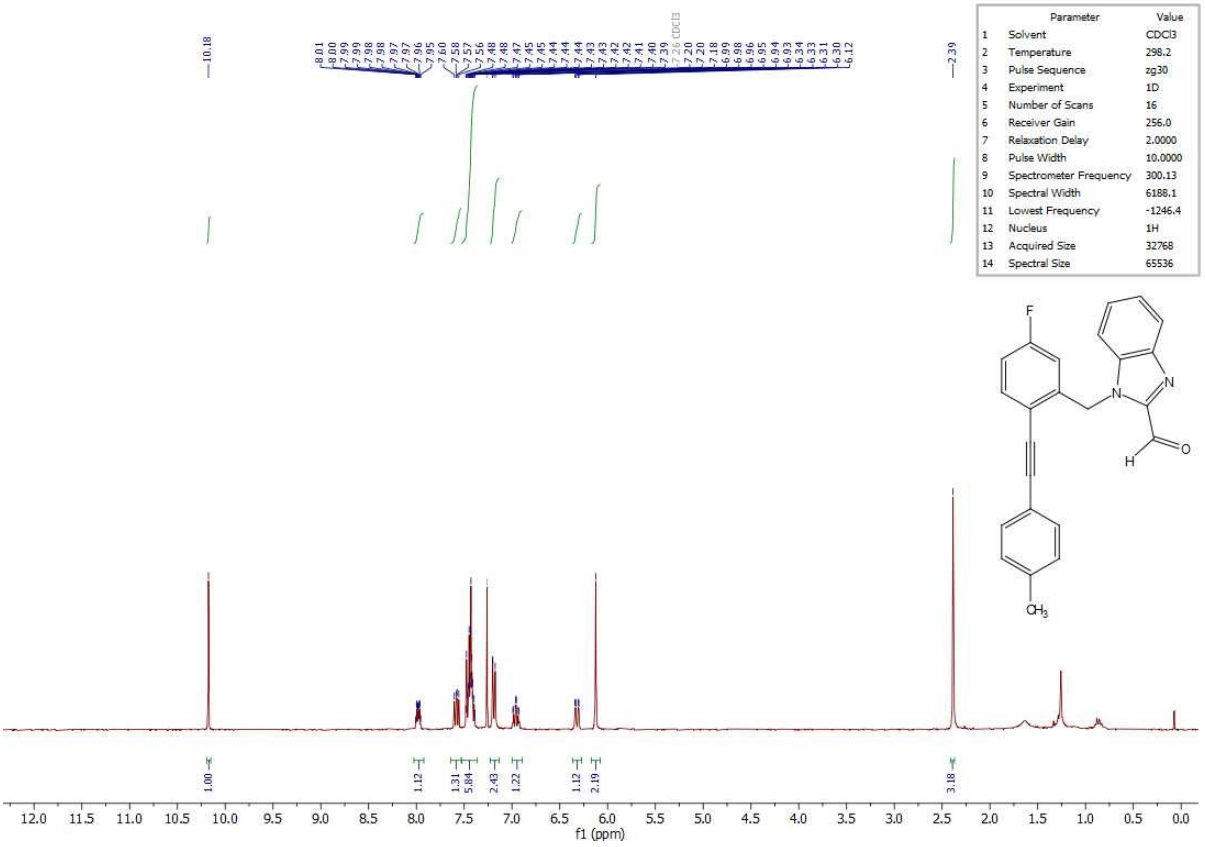


1-(5-Methoxy-2-(4-tolylethynyl)benzyl)-1*H*-benzo[*d*]imidazole-2-carbaldehyde (5w)

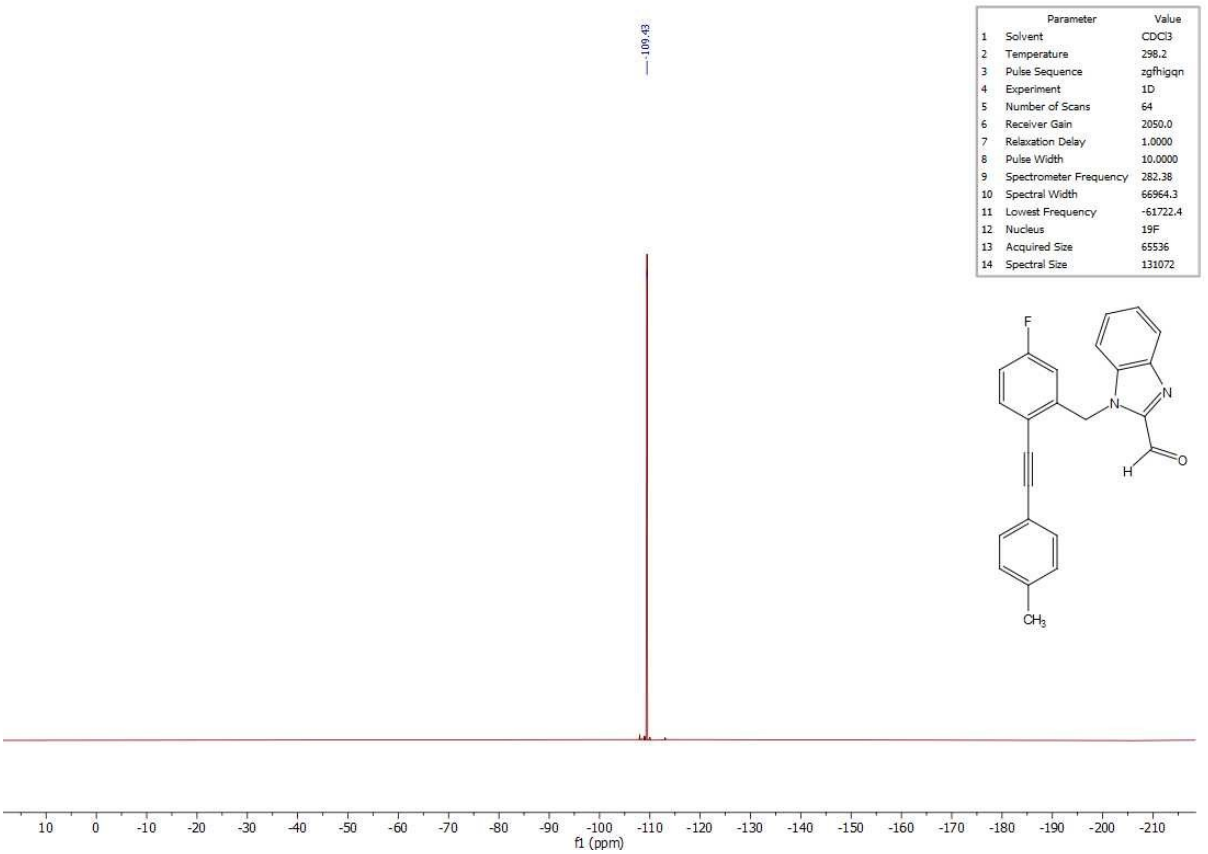


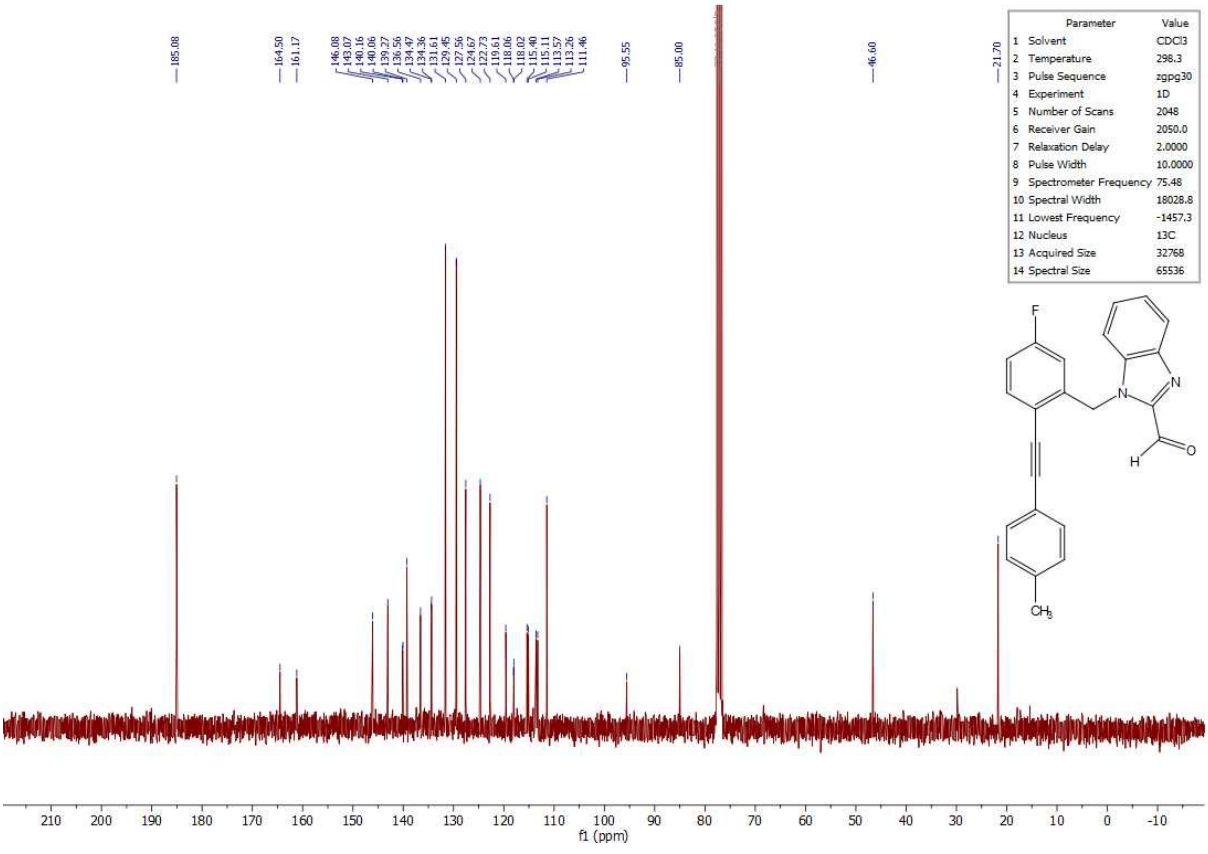


1-(5-Fluoro-2-(4-tolylethynyl)benzyl)-1*H*-benzo[*d*]imidazole-2-carbaldehyde (5x)

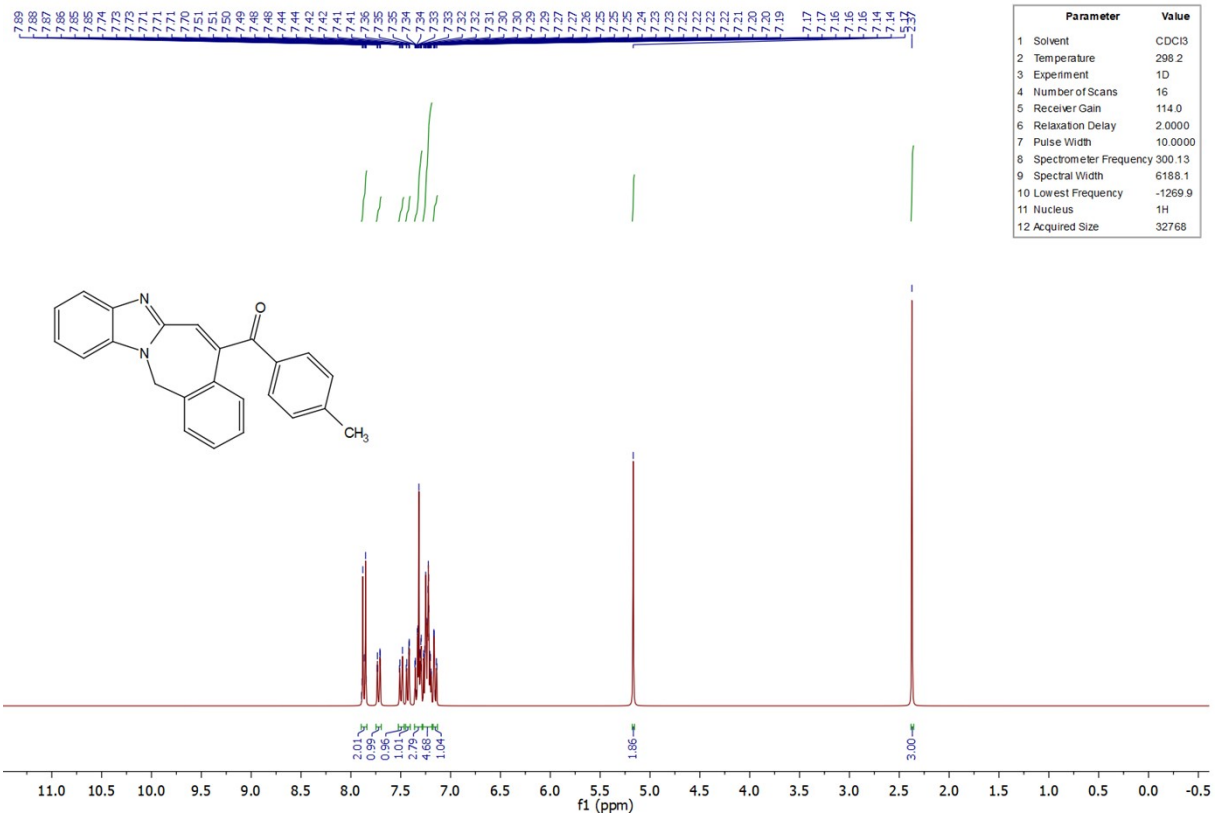


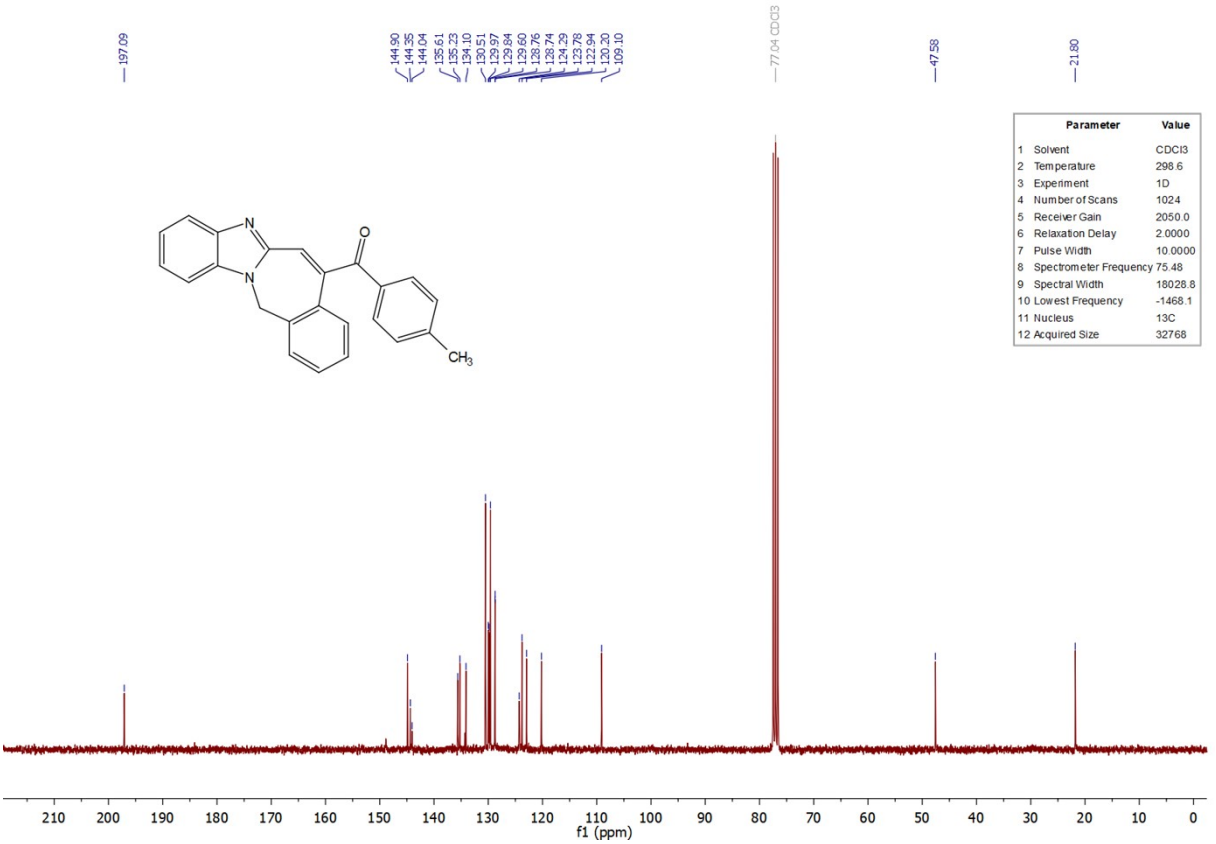
1-(5-Fluoro-2-(4-tolylethynyl)benzyl)-1*H*-benzo[*d*]imidazole-2-carbaldehyde (5x)



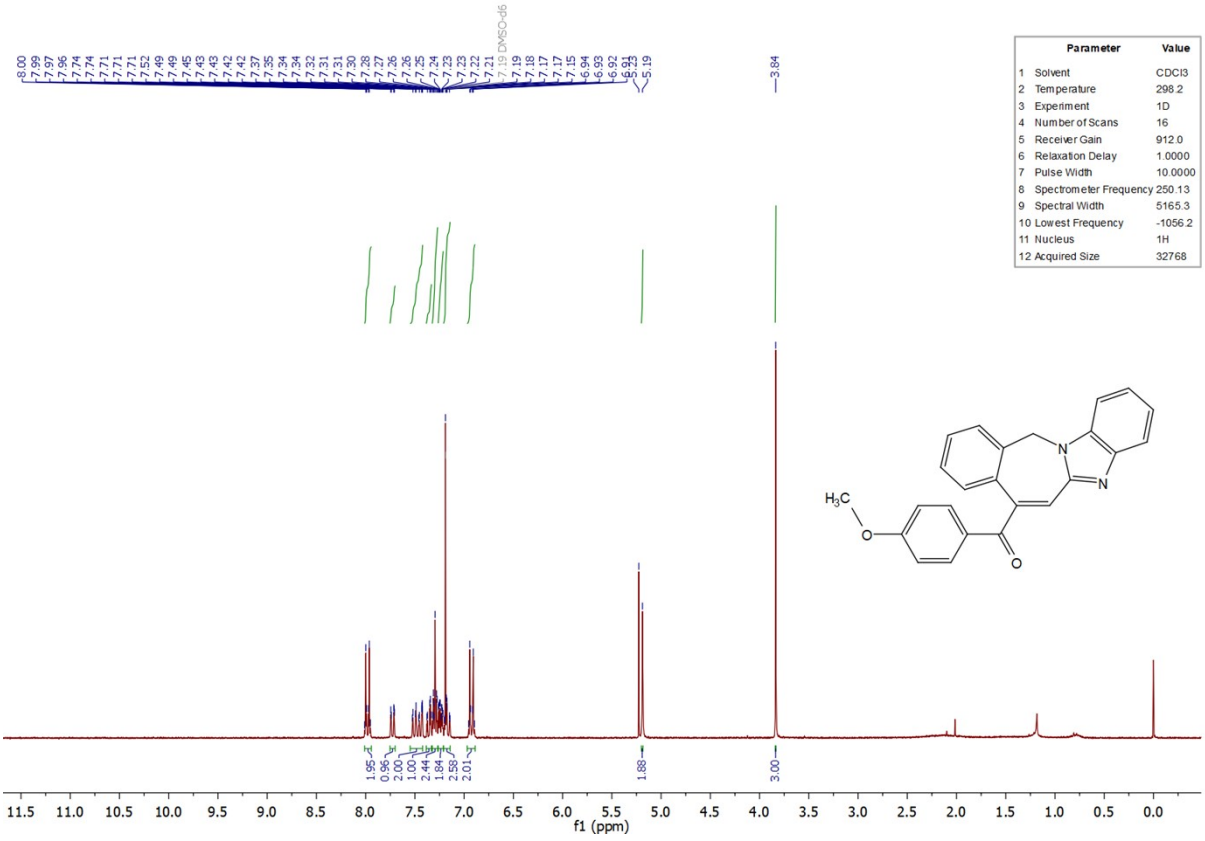


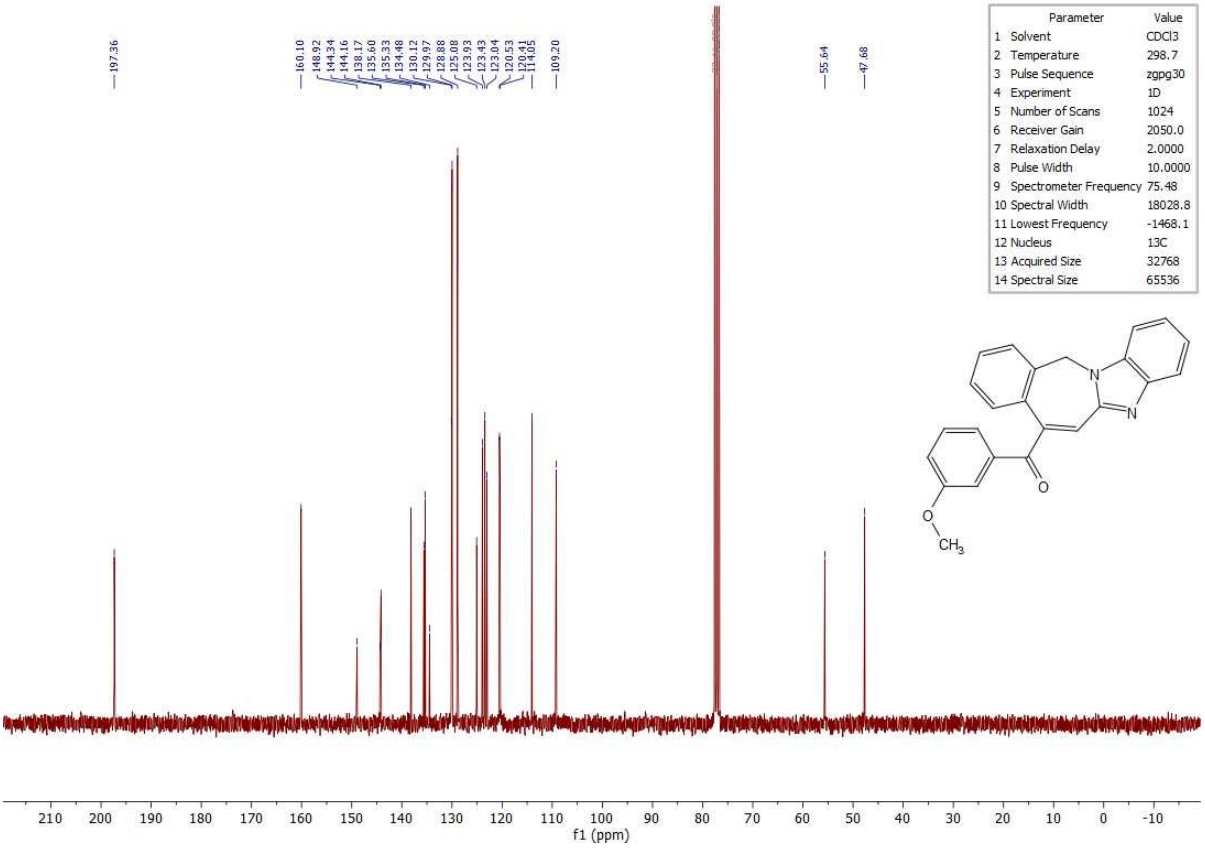
(12H-benzo[e]benzo[4,5]imidazo[1,2-a]azepin-7-yl)(p-tolyl)methanone (6a)



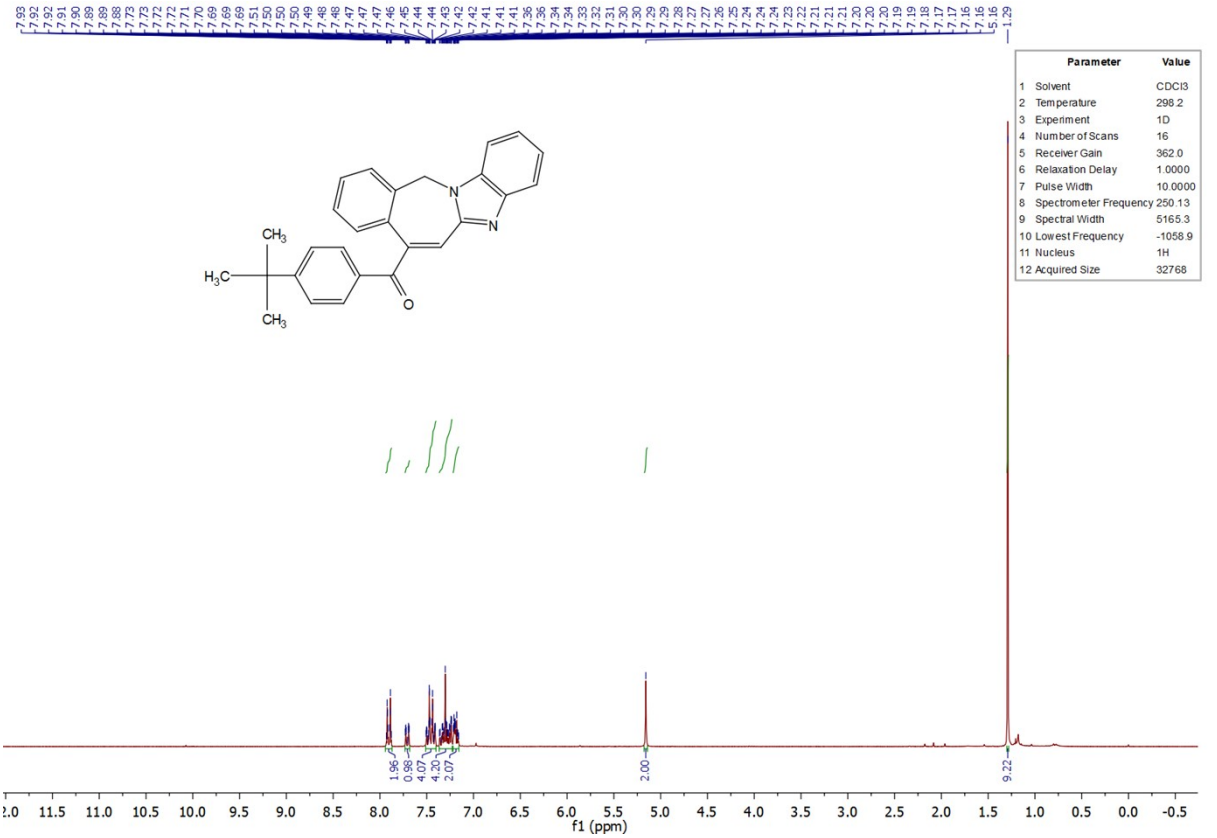


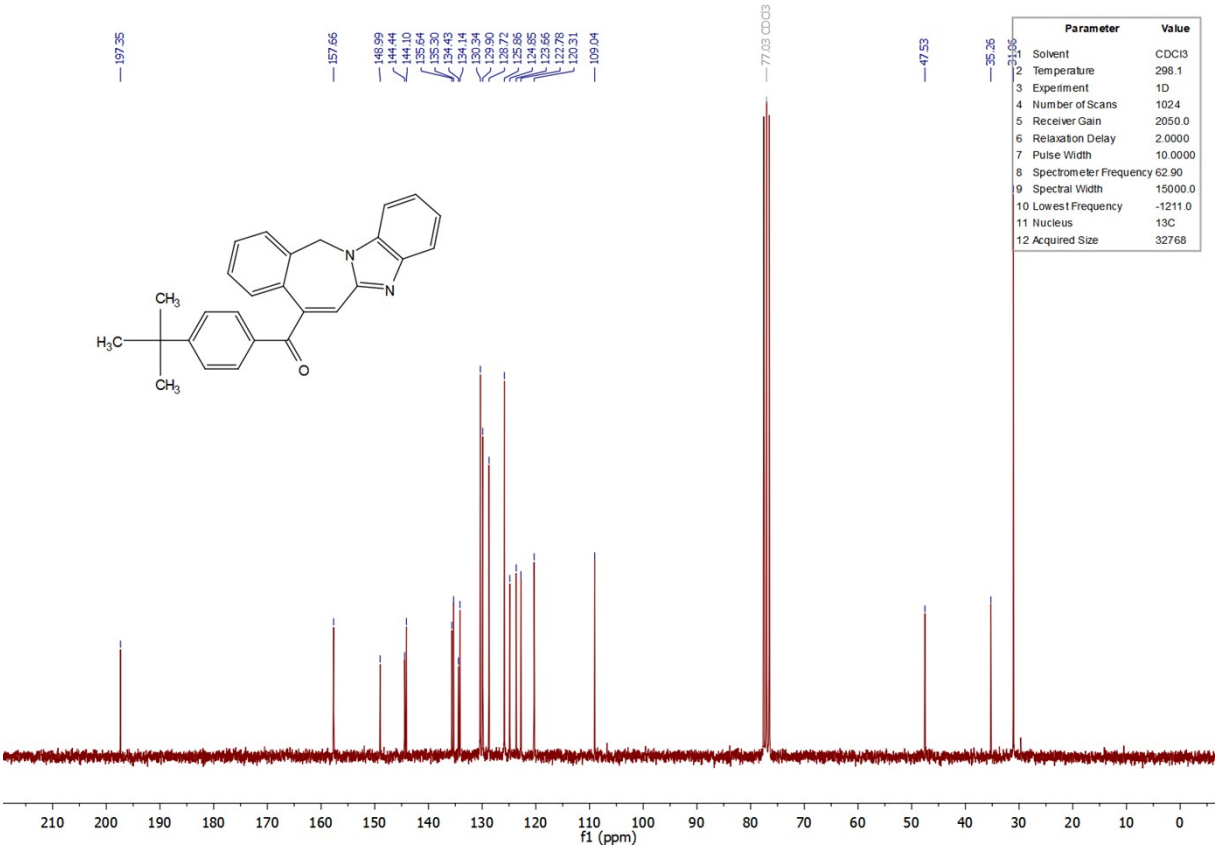
(12H-benzo[e]benzo[4,5]imidazo[1,2-a]azepin-7-yl)(4-methoxyphenyl)methanone (6b)



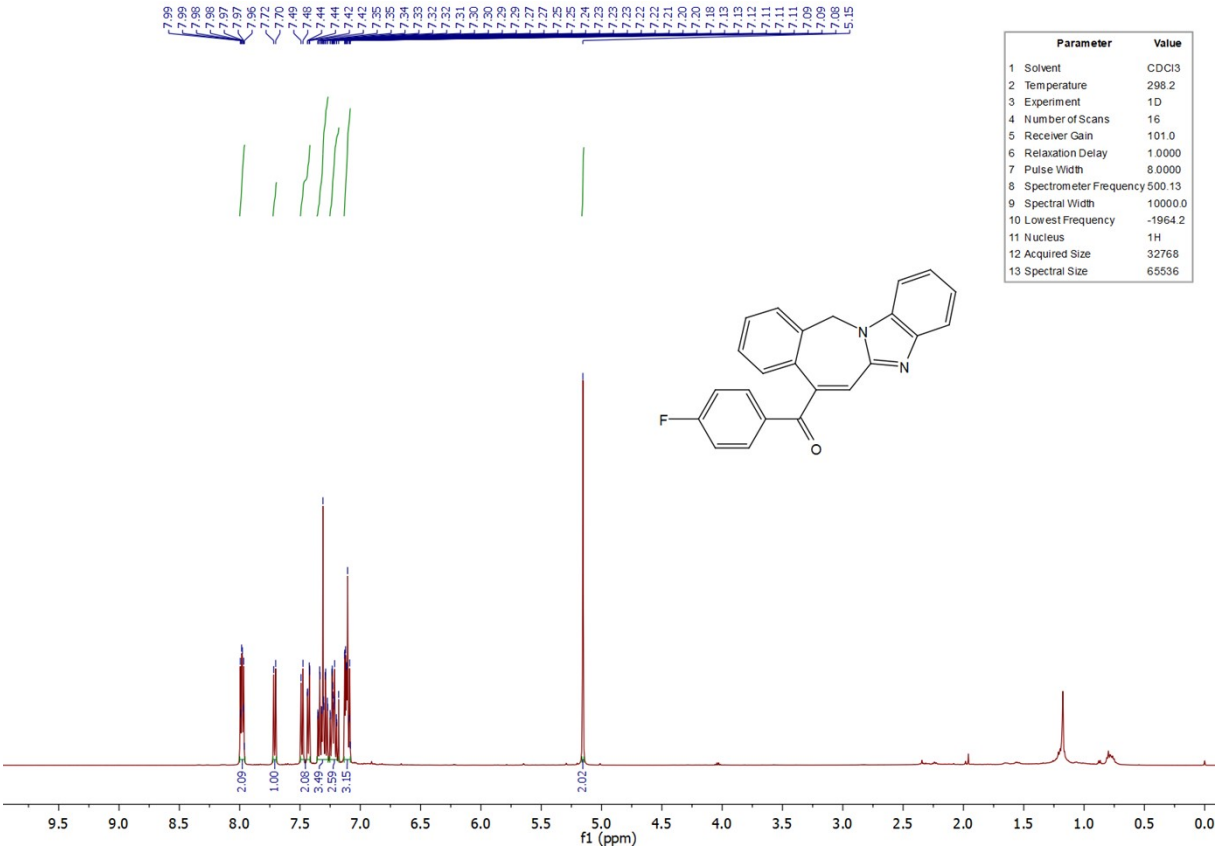


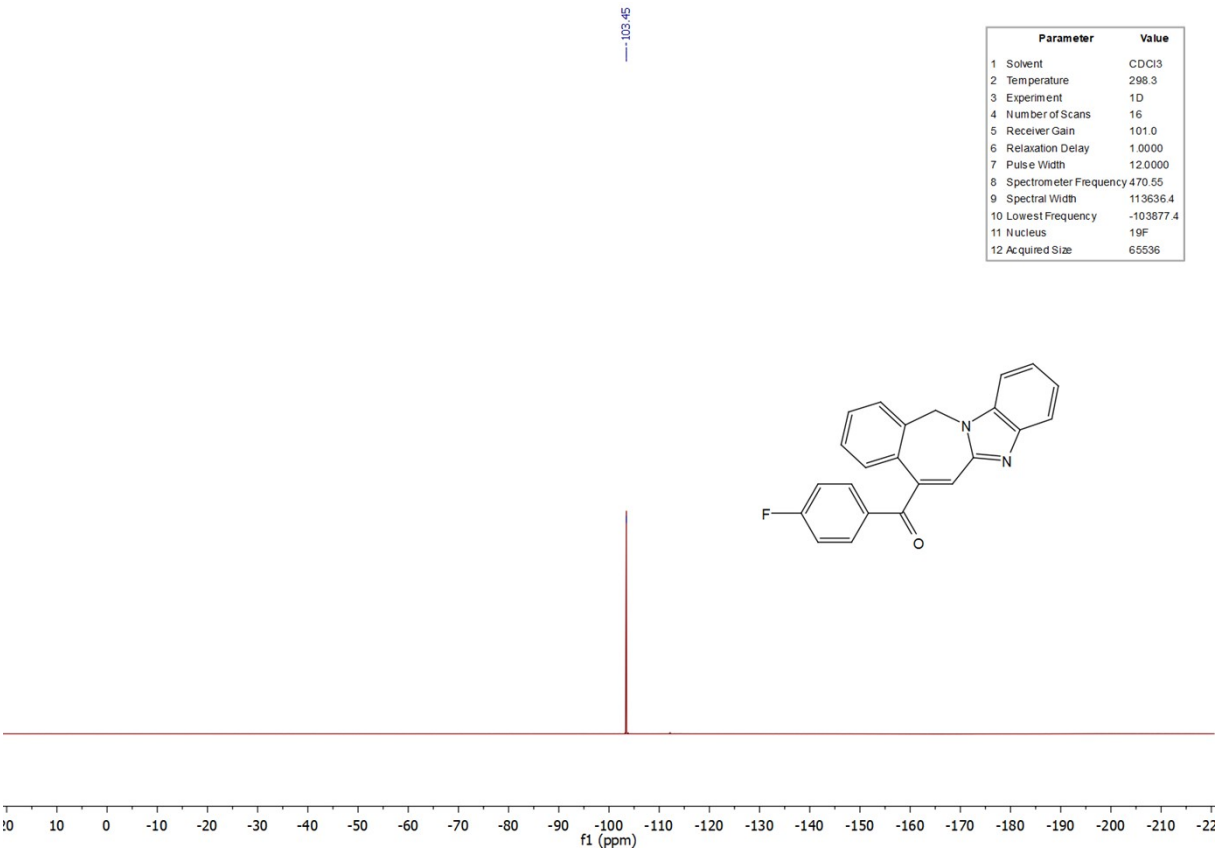
(12H-benzo[e]benzo[4,5]imidazo[1,2-a]azepin-7-yl)(4-(tert-butyl)phenyl)methanone (6c)



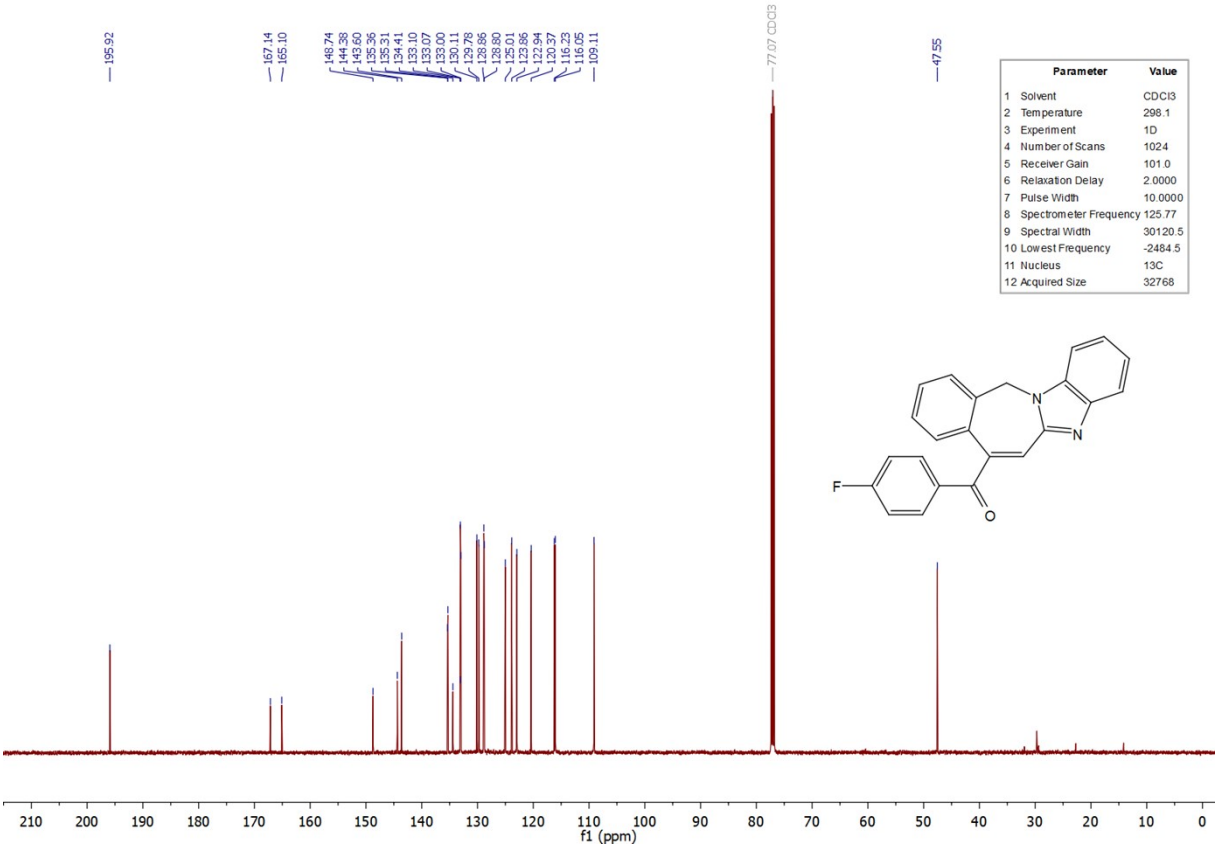


(12H-benzo[e]benzo[4,5]imidazo[1,2-a]azepin-7-yl)(4-fluorophenyl)methanone (6d)

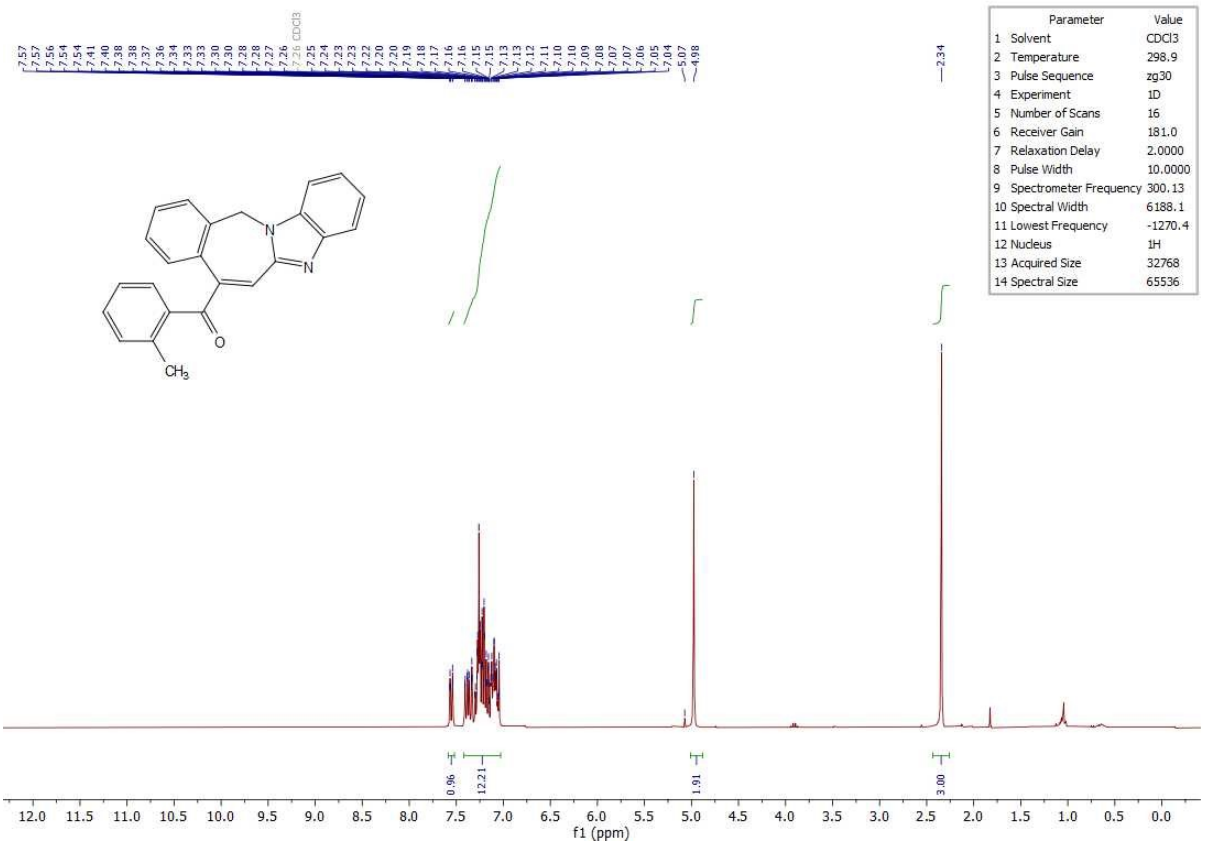


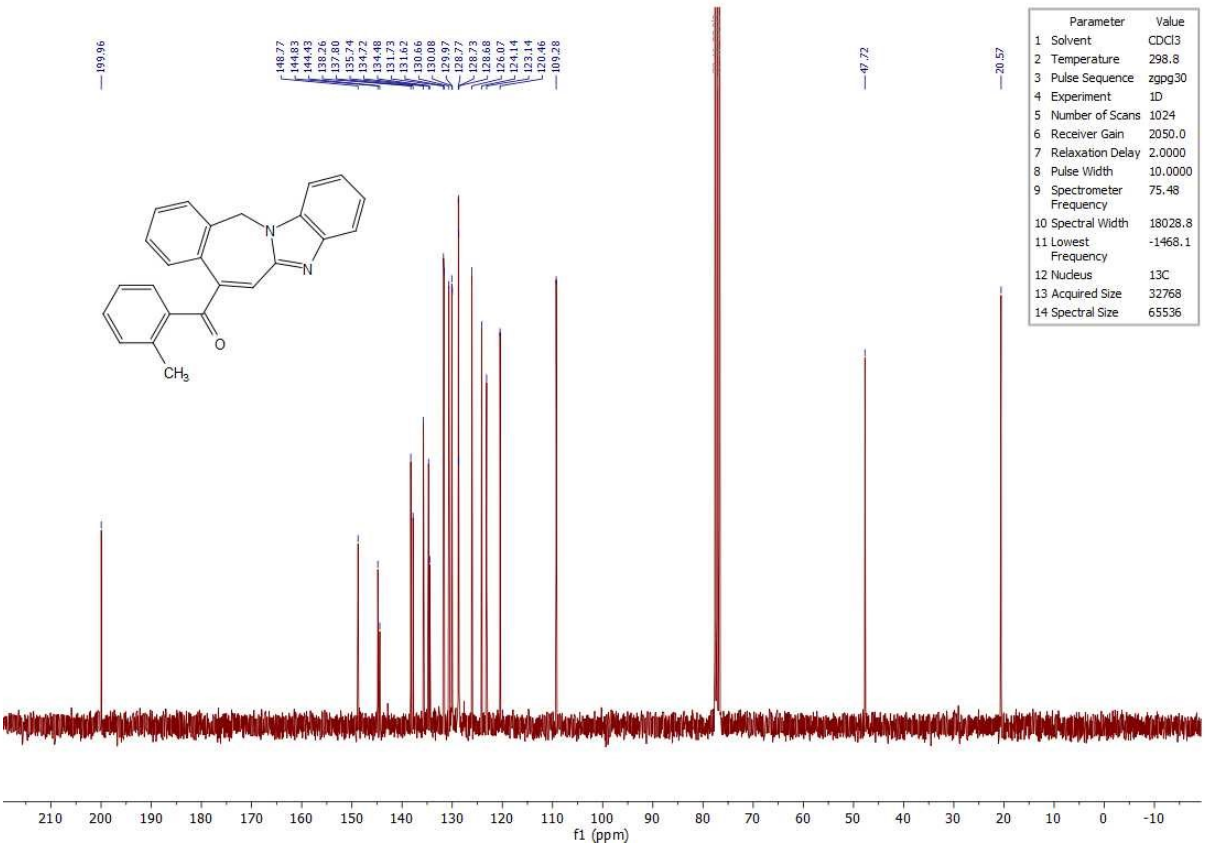


(12H-benzo[e]benzo[4,5]imidazo[1,2-a]azepin-7-yl)(4-fluorophenyl)methanone (6d)

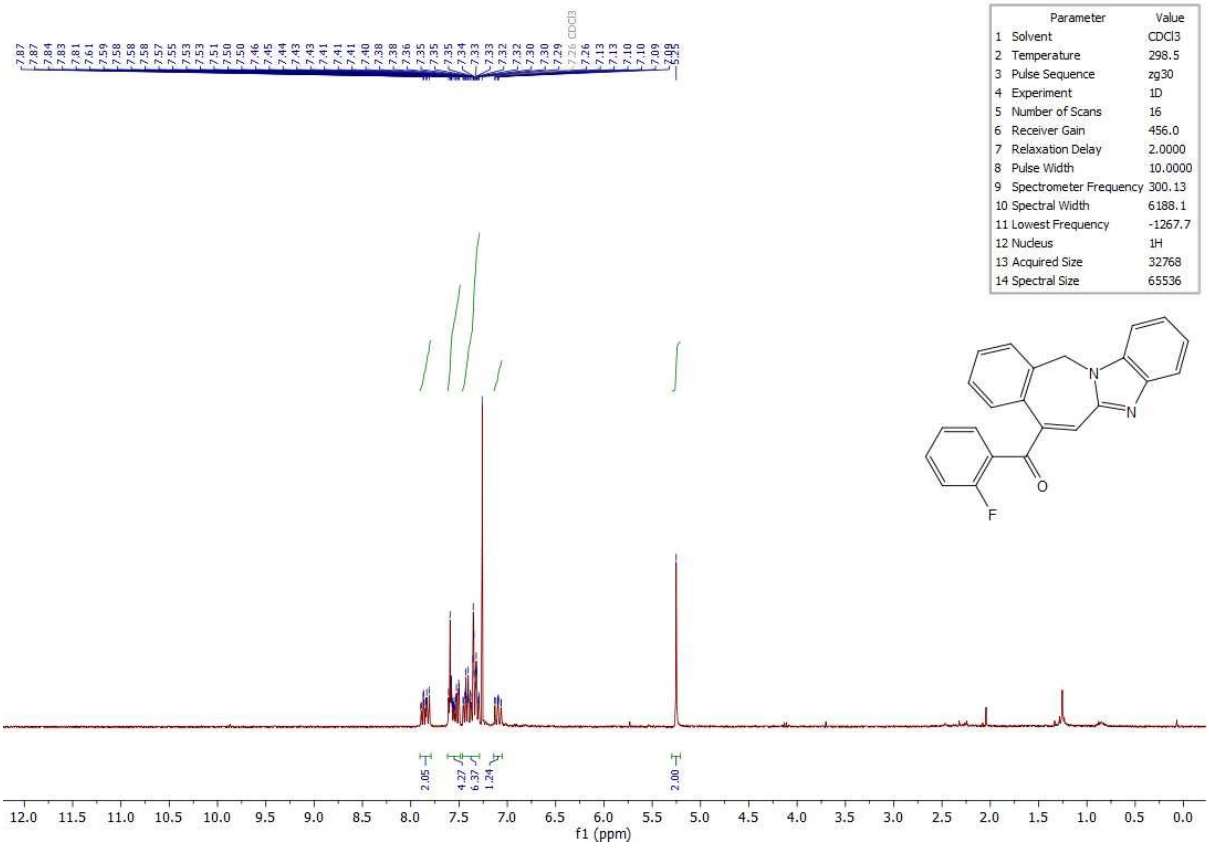


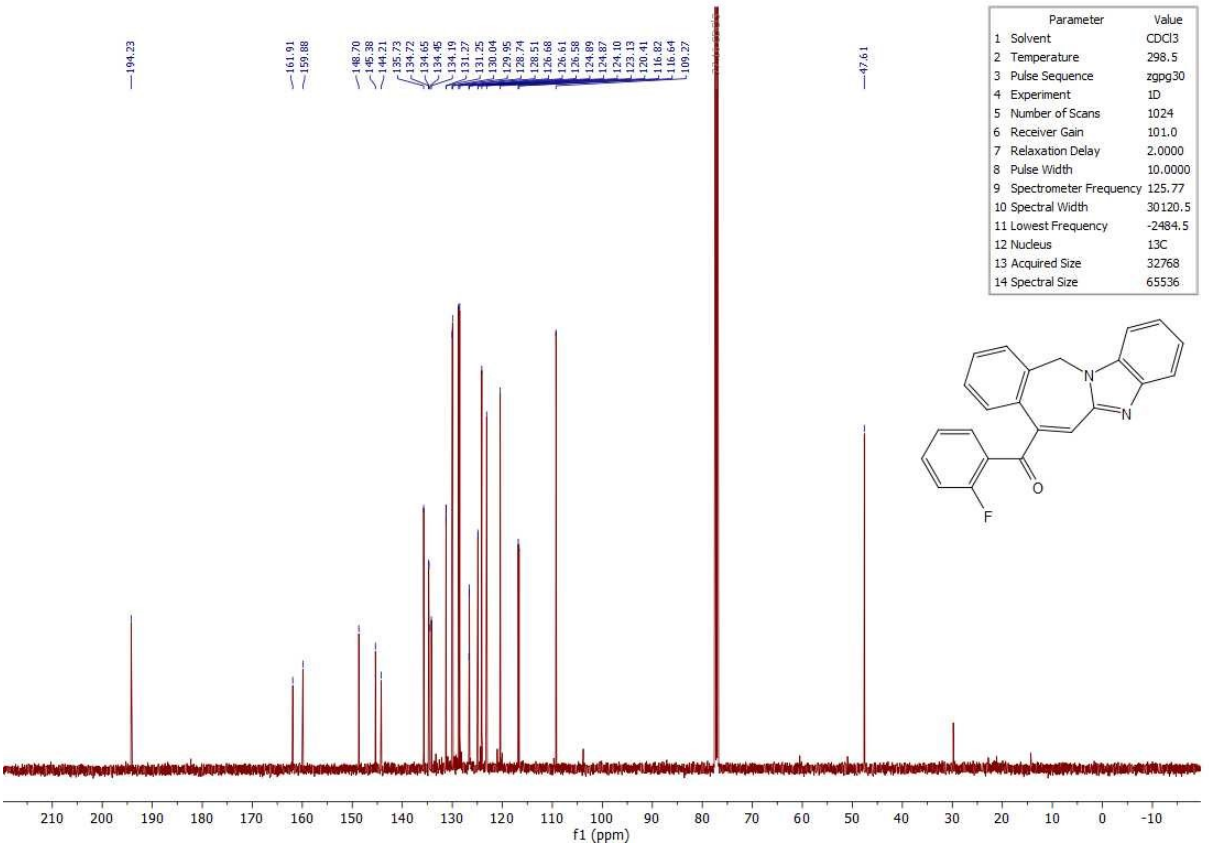
(12H-Benzo[e]benzo[4,5]imidazo[1,2-a]azepin-7-yl)(o-tolyl)methanone (6f)



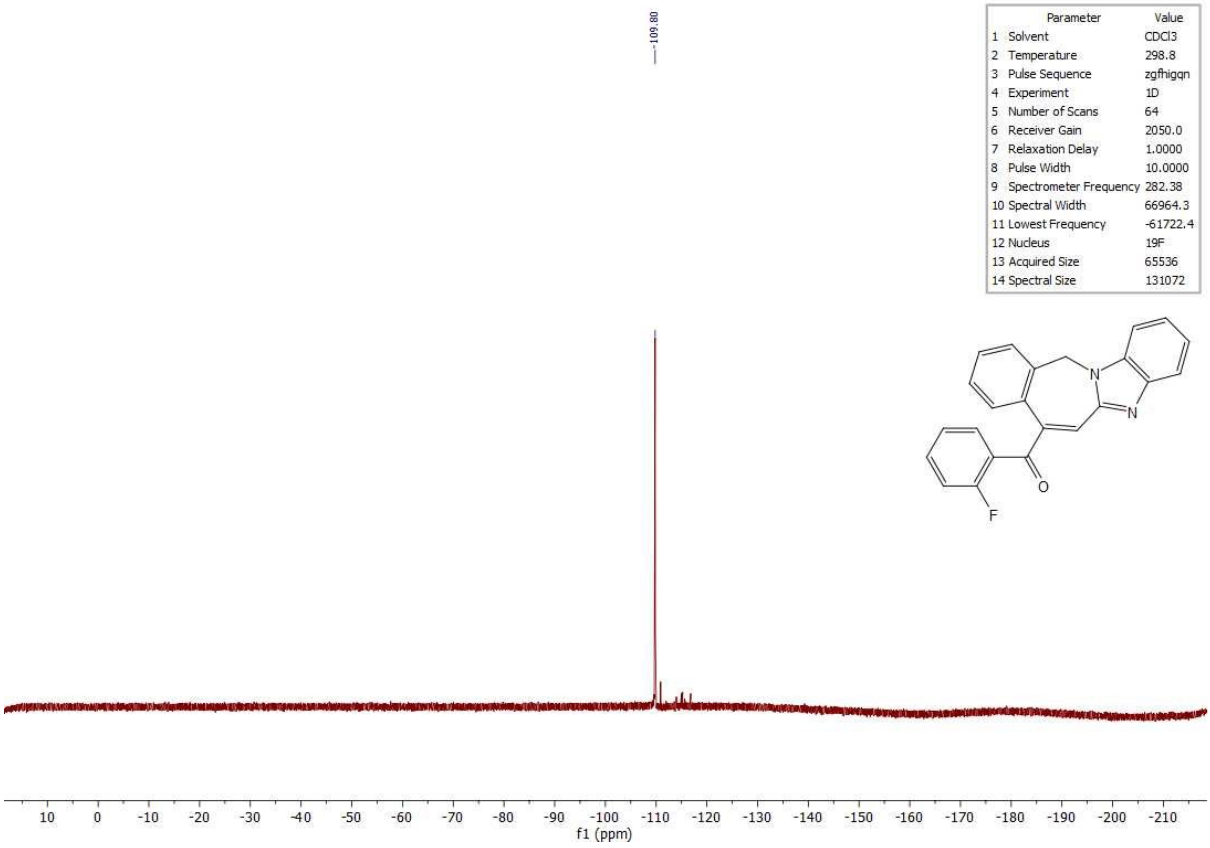


(12H-Benzo[e]benzo[4,5]imidazo[1,2-a]azepin-7-yl)(o-tolyl)methanone (6f)

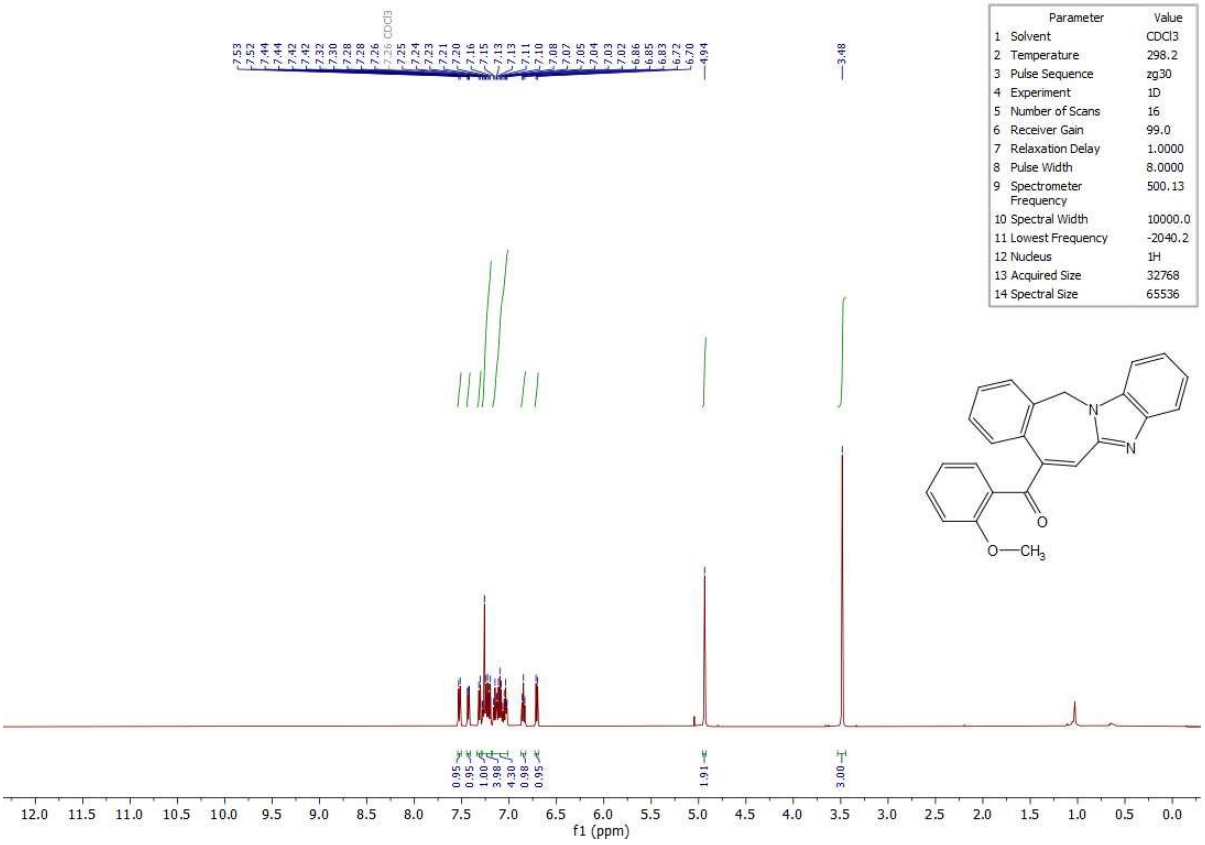


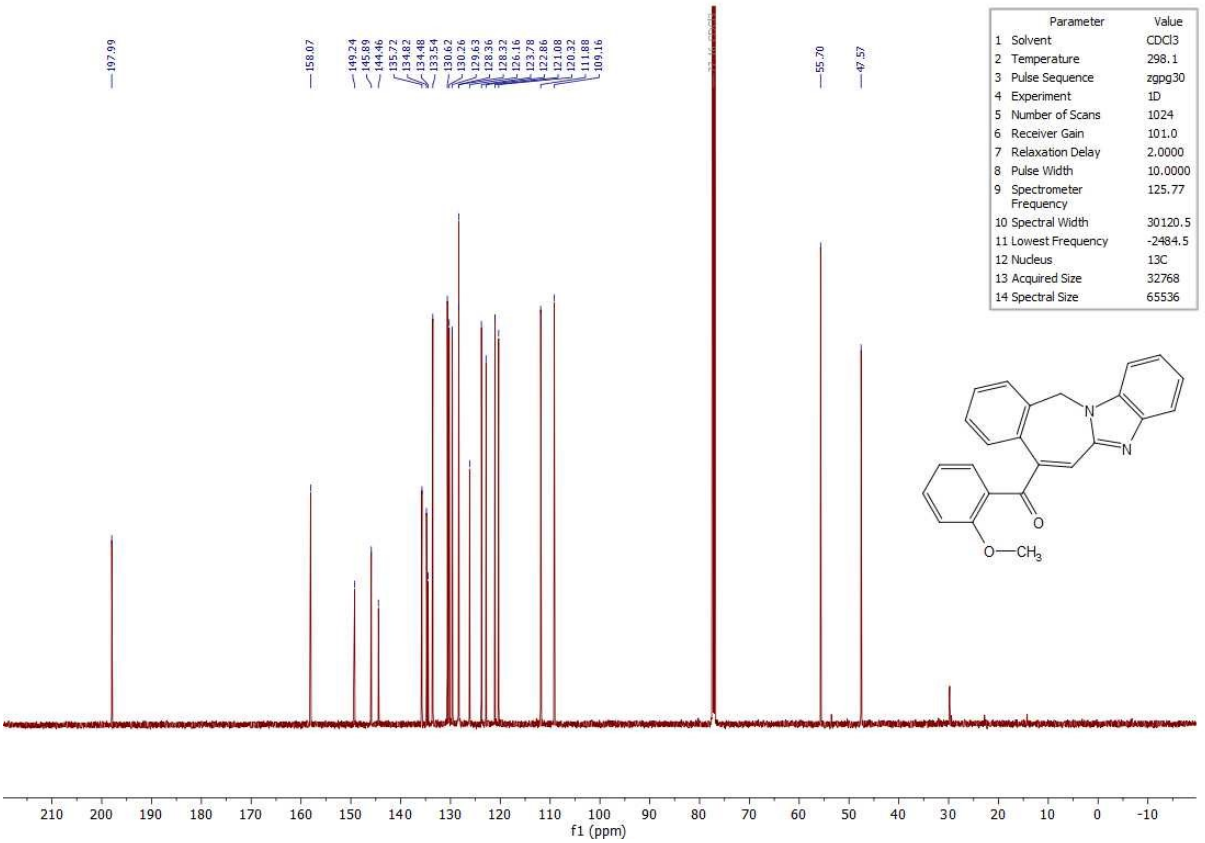


(12H-Benzo[e]benzo[4,5]imidazo[1,2-a]azepin-7-yl)(o-tolyl)methanone (6f)

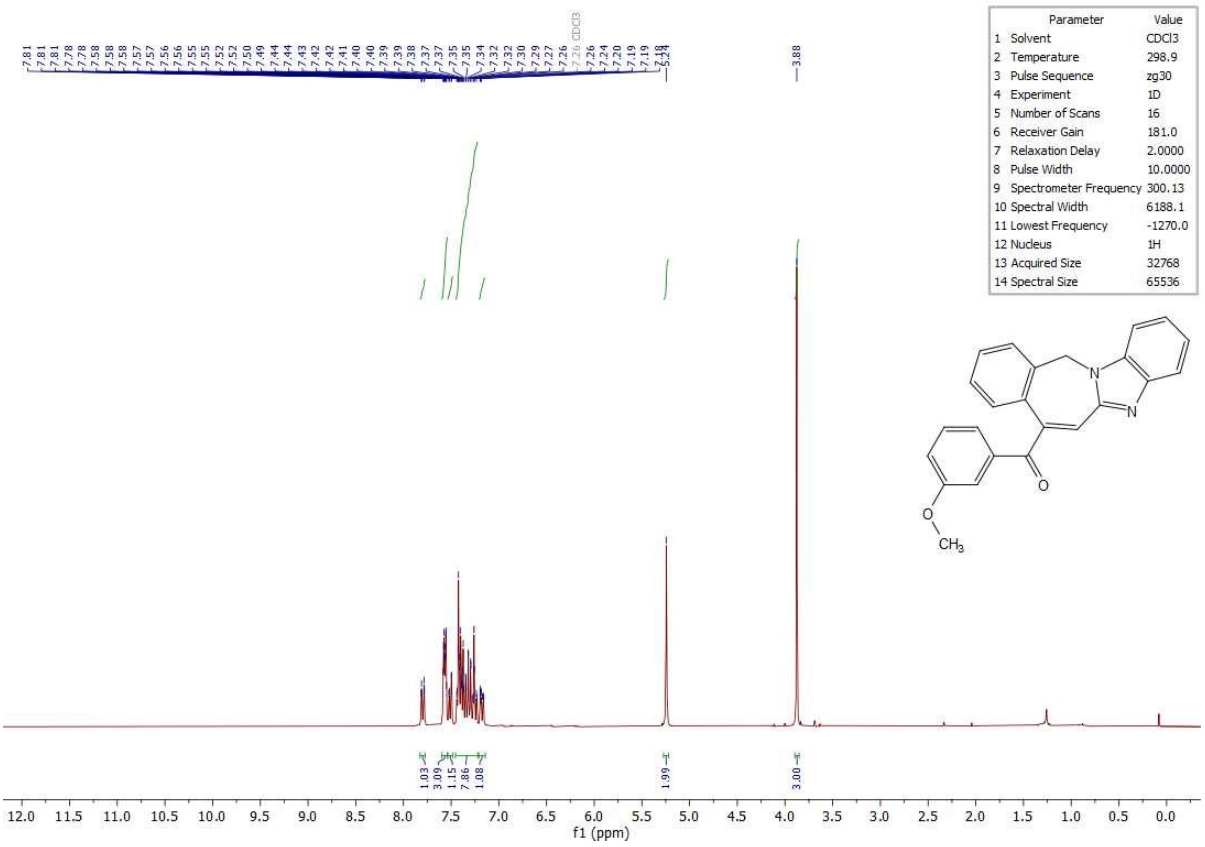


(12H-Benzo[e]benzo[4,5]imidazo[1,2-a]azepin-7-yl)(2-methoxyphenyl)methanone (6g)

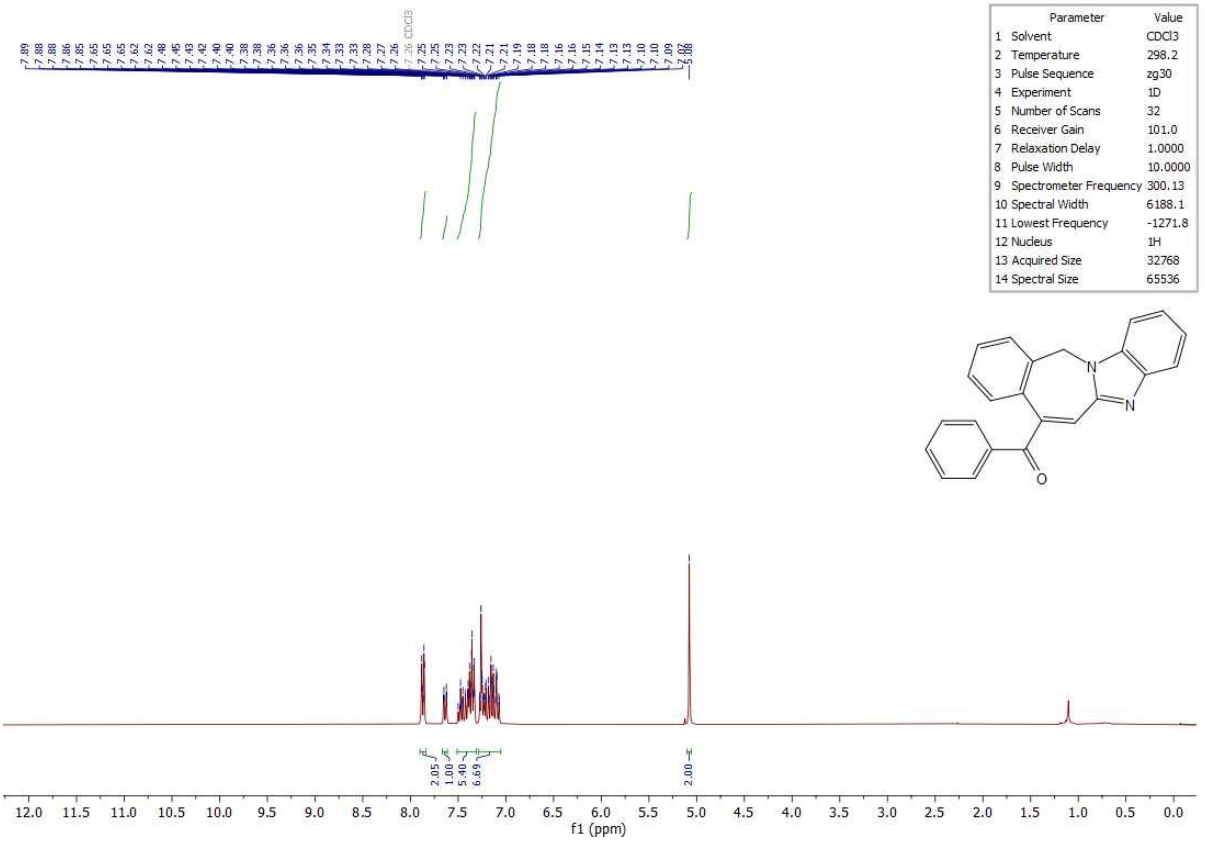


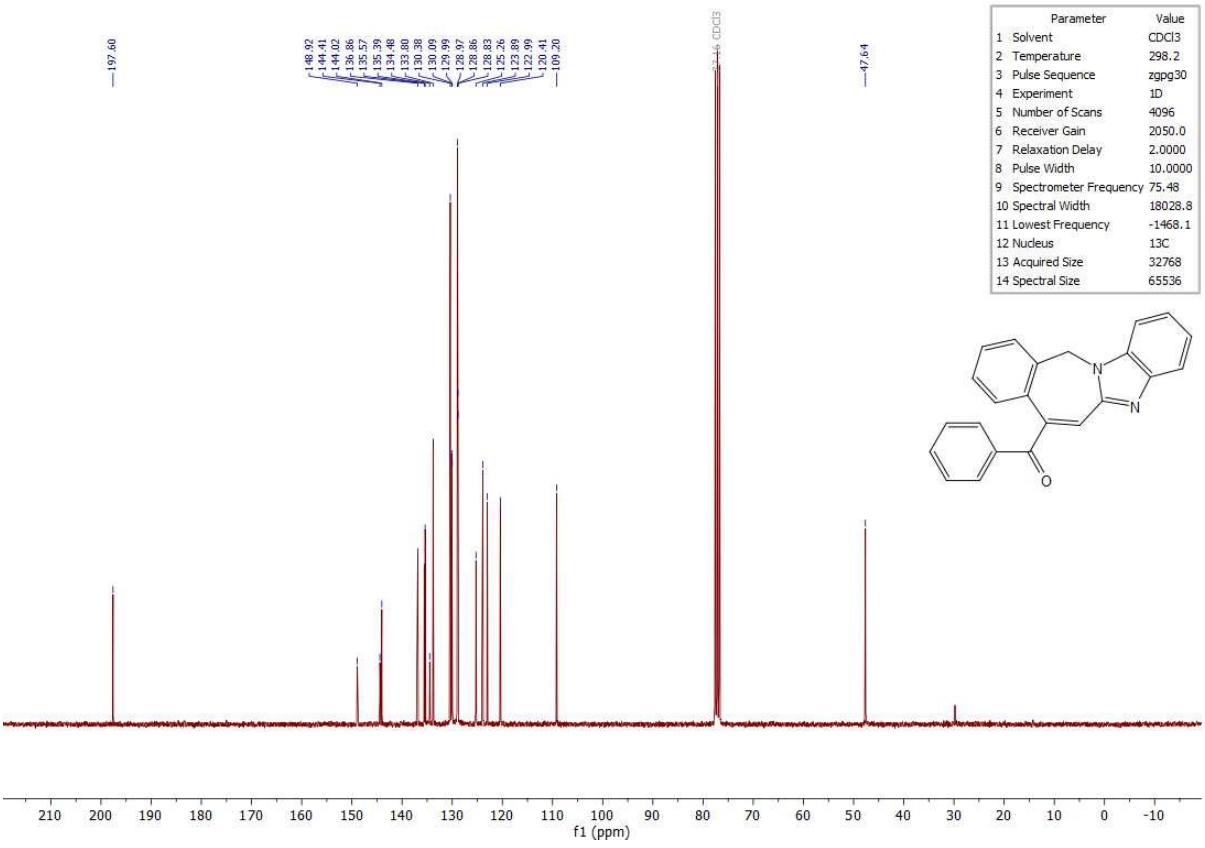


(12H-Benzo[e]benzo[4,5]imidazo[1,2-a]azepin-7-yl)(3-methoxyphenyl)methanone (6h)

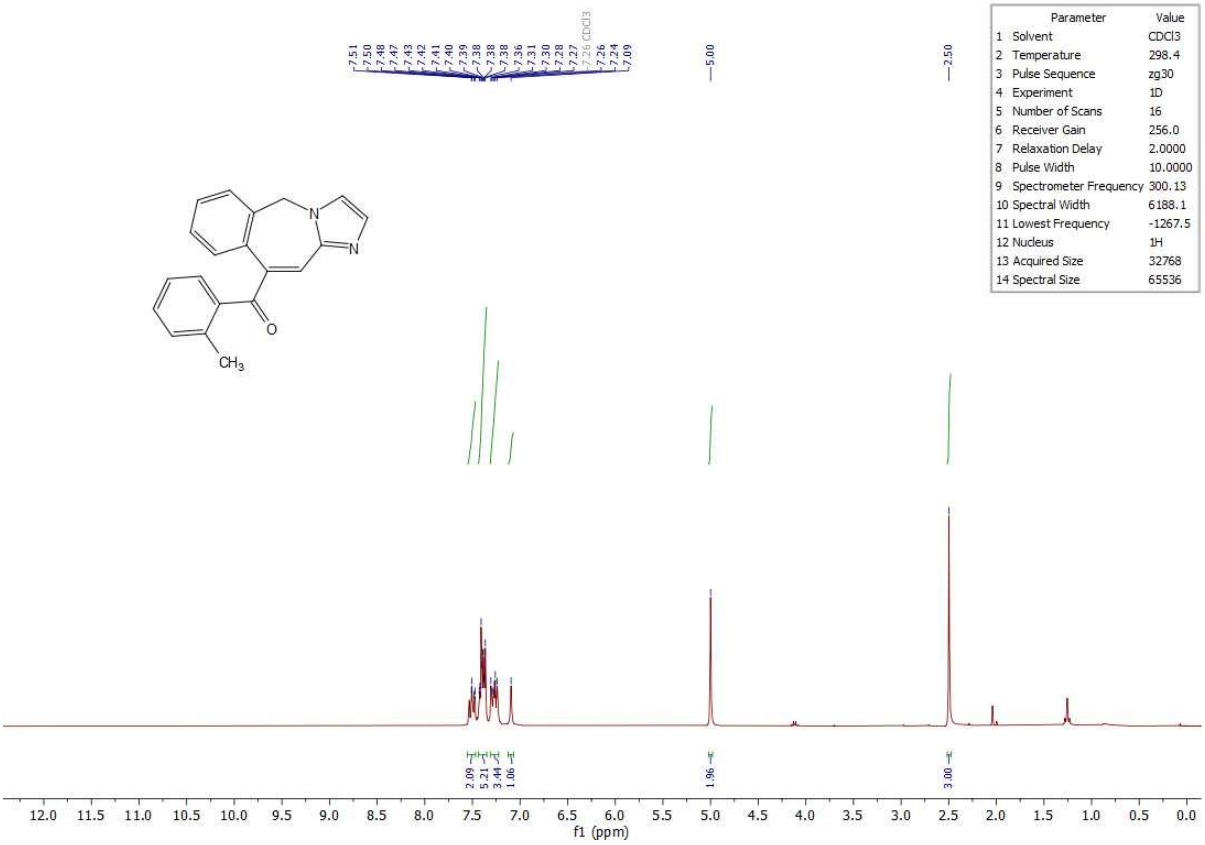


12-Dihydro-5H-benzo[e]benzo[4,5]imidazo[1,2-a]azepin-7-yl)(phenyl)-methanone (6i)

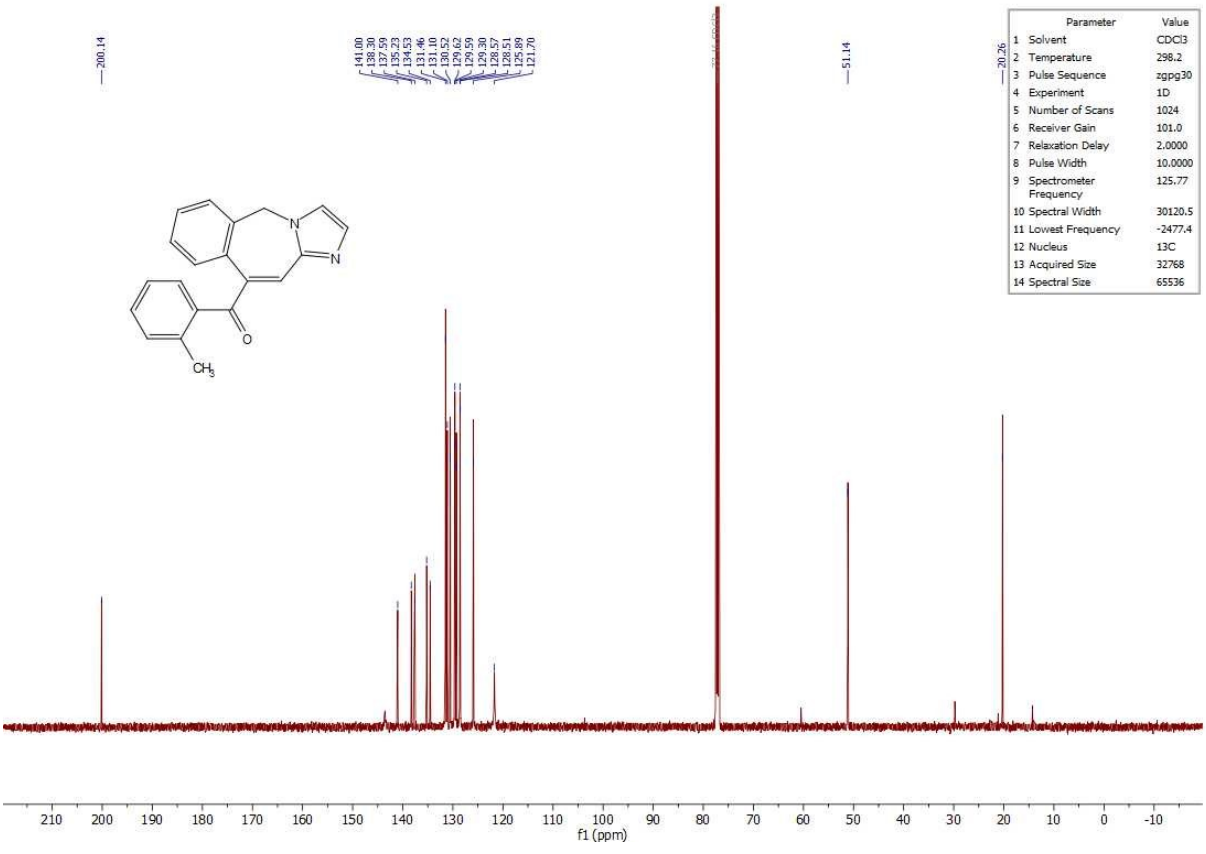




(5H-benzo[e]imidazo[1,2-a]azepin-10-yl)(o-tolyl)methanone (6j)

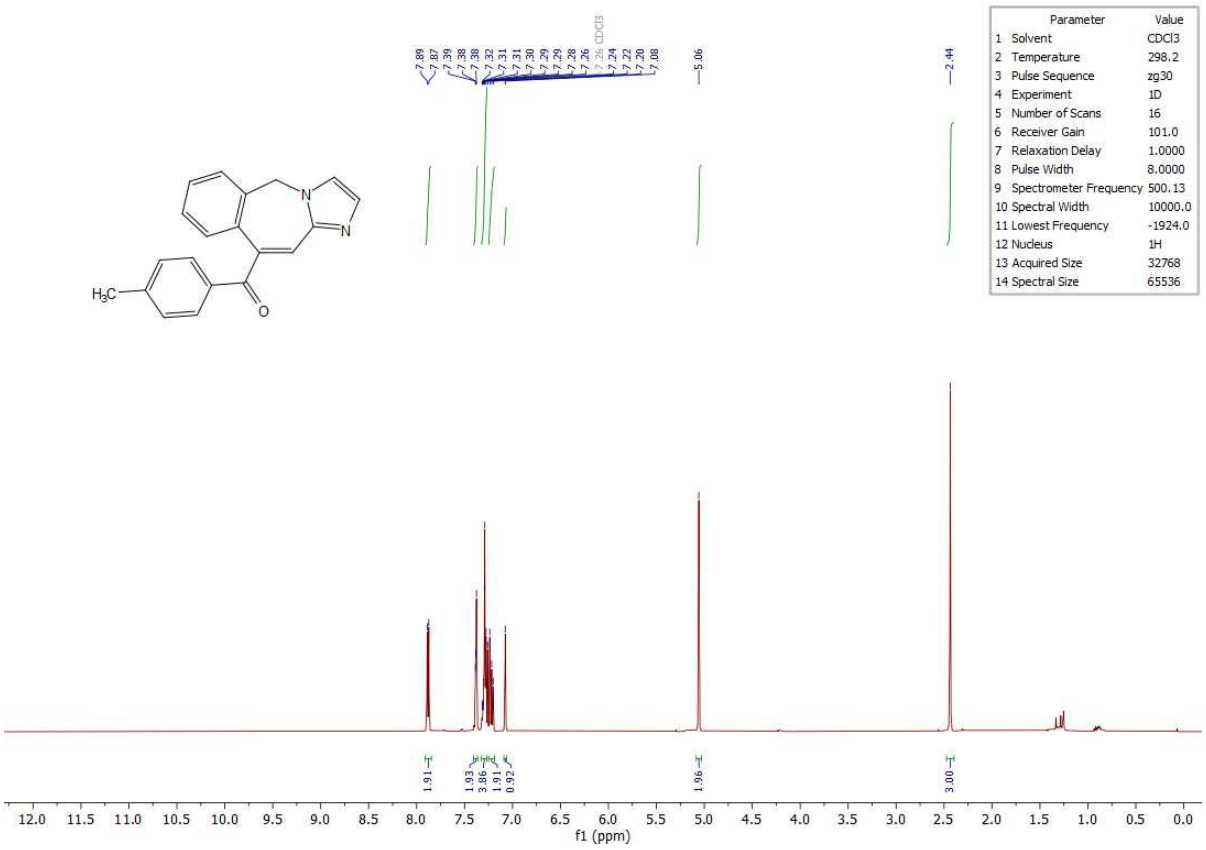


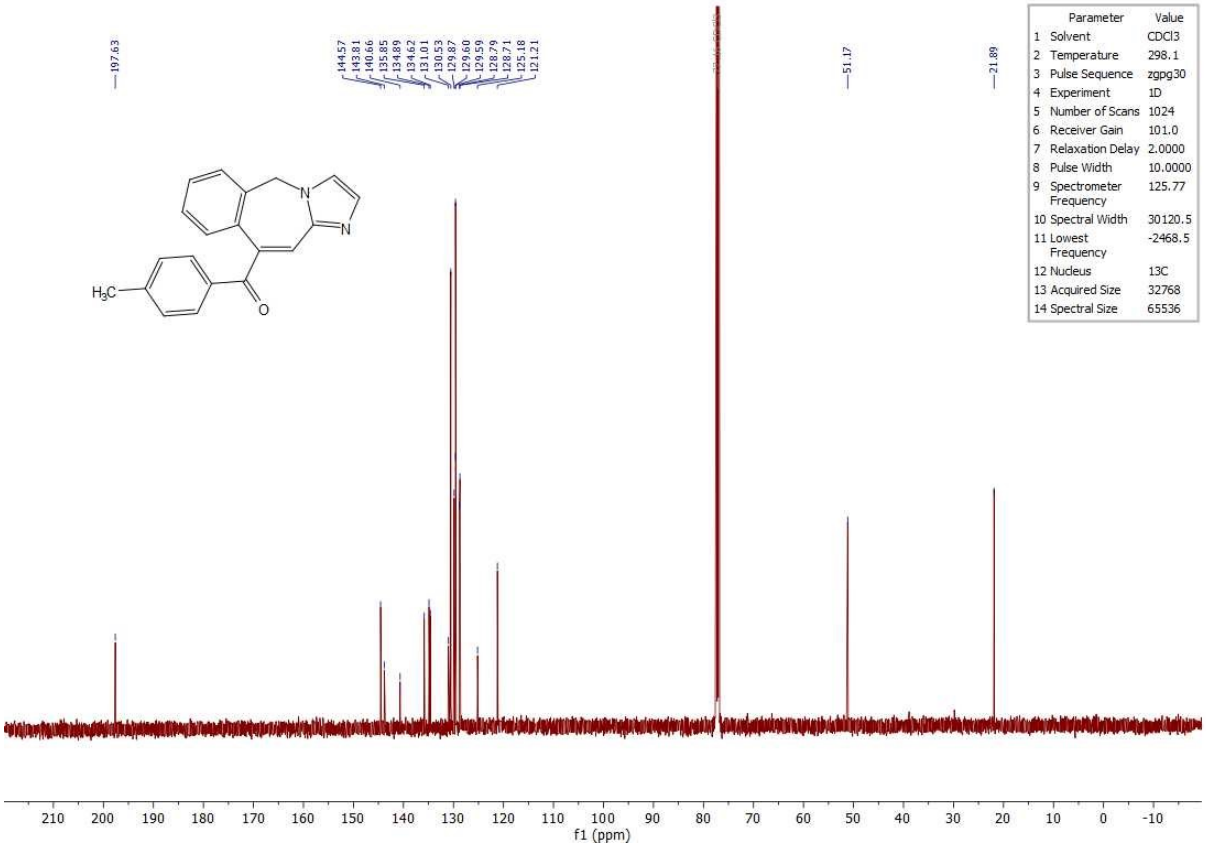
Parameter	Value
1 Solvent	CDCl3
2 Temperature	298.4
3 Pulse Sequence	zg30
4 Experiment	1D
5 Number of Scans	16
6 Receiver Gain	256.0
7 Relaxation Delay	2.0000
8 Pulse Width	10.0000
9 Spectrometer Frequency	300.13
10 Spectral Width	6188.1
11 Lowest Frequency	-1267.5
12 Nucleus	1H
13 Acquired Size	32768
14 Spectral Size	65536



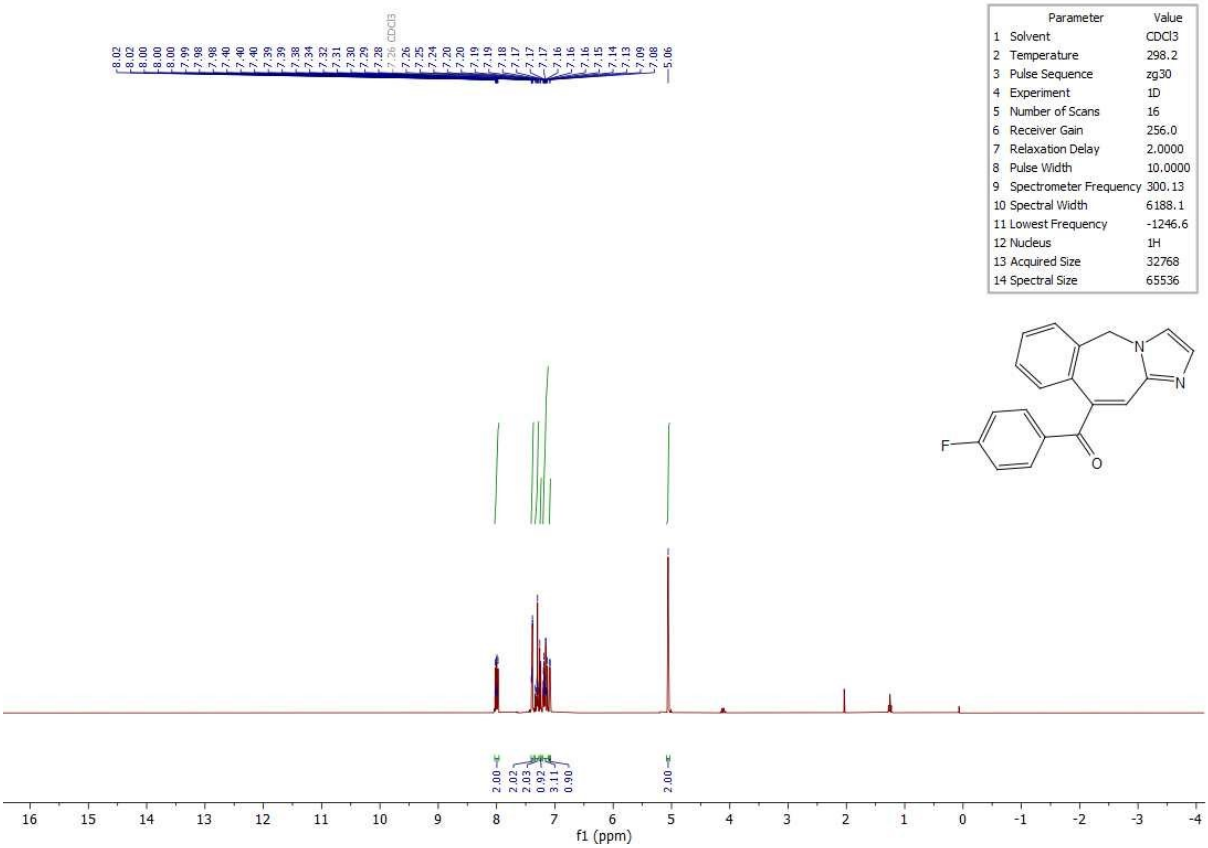
Parameter	Value
1 Solvent	CDCl3
2 Temperature	298.2
3 Pulse Sequence	zgpg30
4 Experiment	1D
5 Number of Scans	1024
6 Receiver Gain	101.0
7 Relaxation Delay	2.0000
8 Pulse Width	10.0000
9 Spectrometer Frequency	125.77
10 Spectral Width	30120.5
11 Lowest Frequency	-2477.4
12 Nucleus	13C
13 Acquired Size	32768
14 Spectral Size	65536

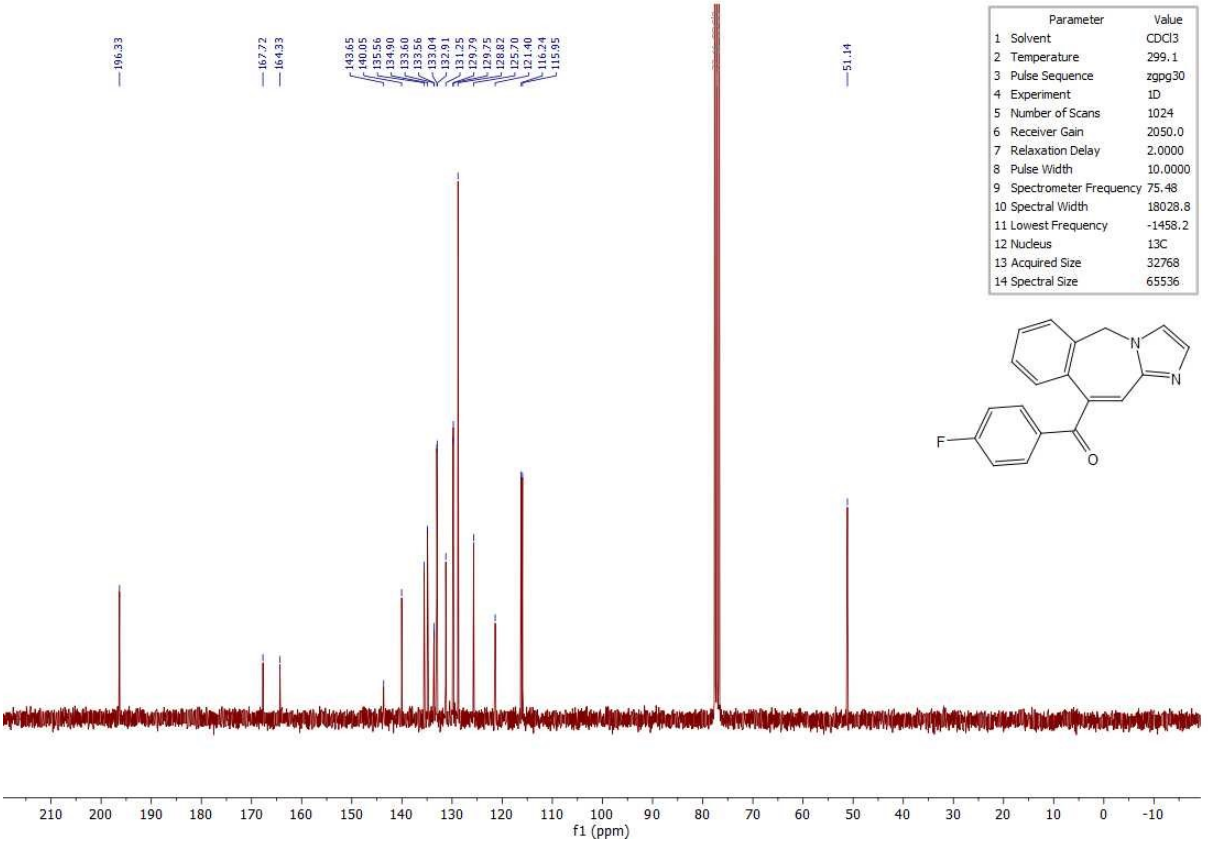
(5H-Benzo[e]imidazo[1,2-a]azepin-10-yl)(p-tolyl)methanone (6k)



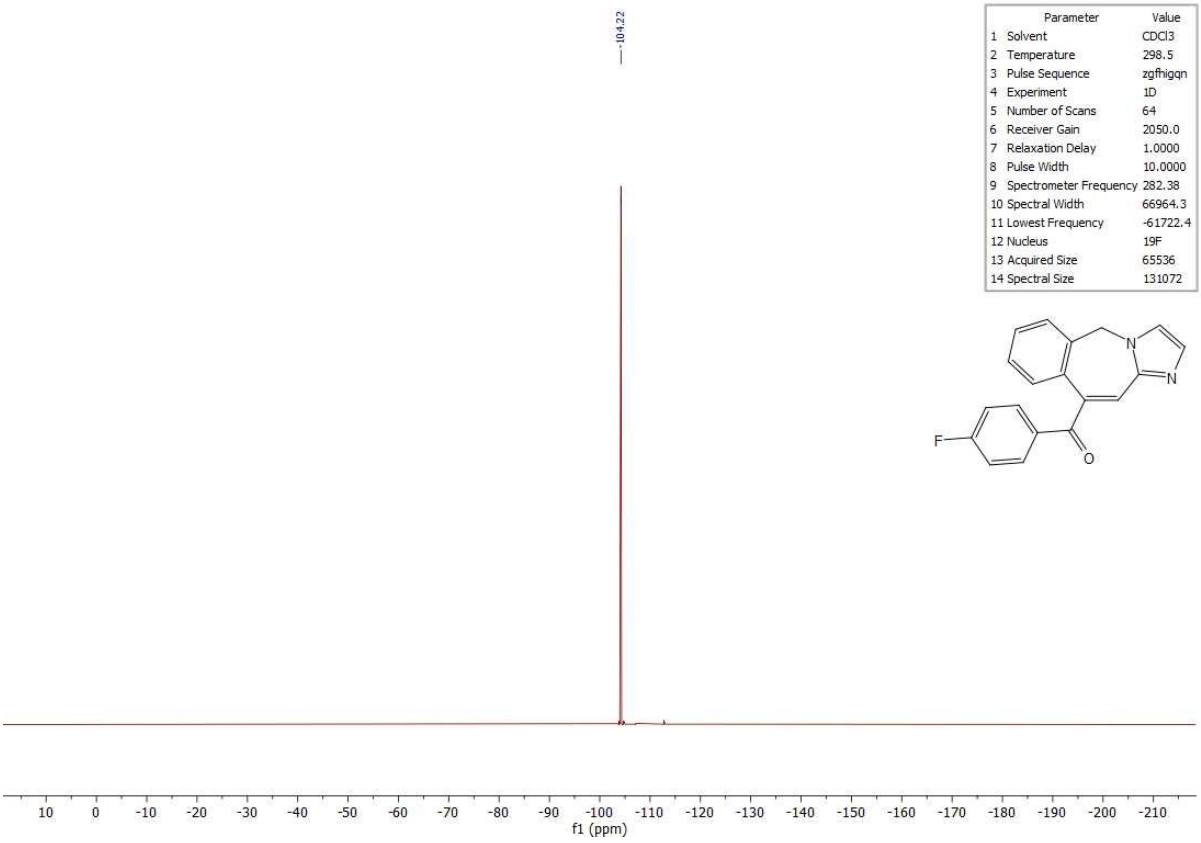


(5*H*-Benzo[*e*]imidazo[1,2-*a*]azepin-10-yl)(4-fluorophenyl)methanone (6m)

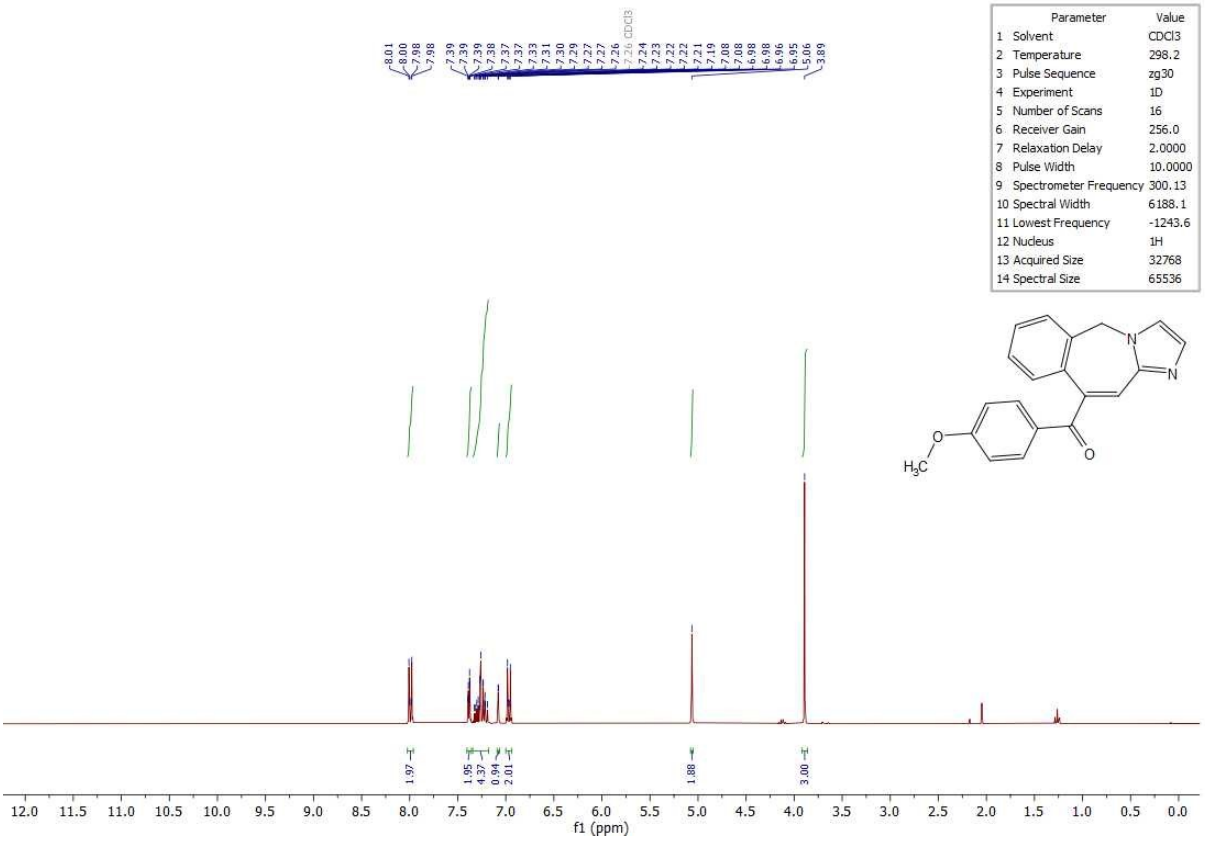


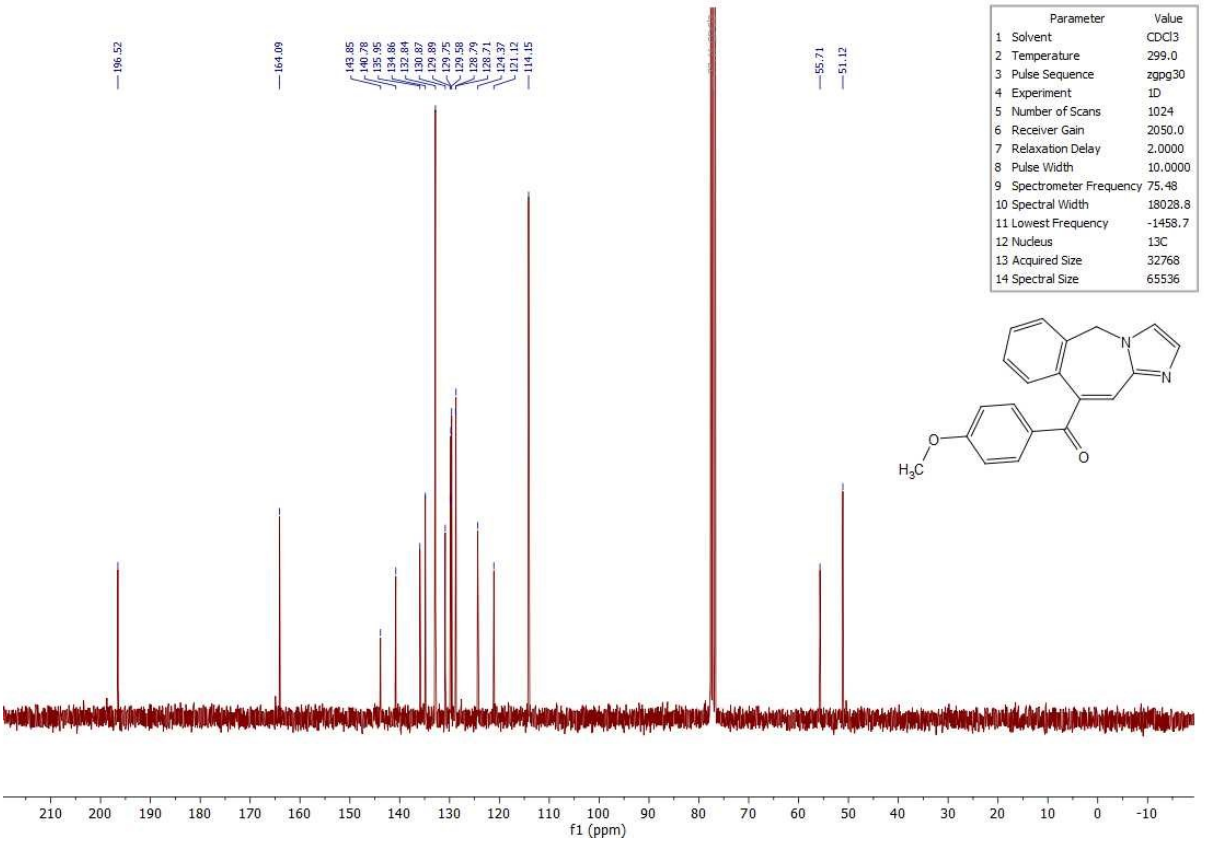


(5*H*-Benzo[*e*]imidazo[1,2-*a*]azepin-10-yl)(4-fluorophenyl)methanone (6m)

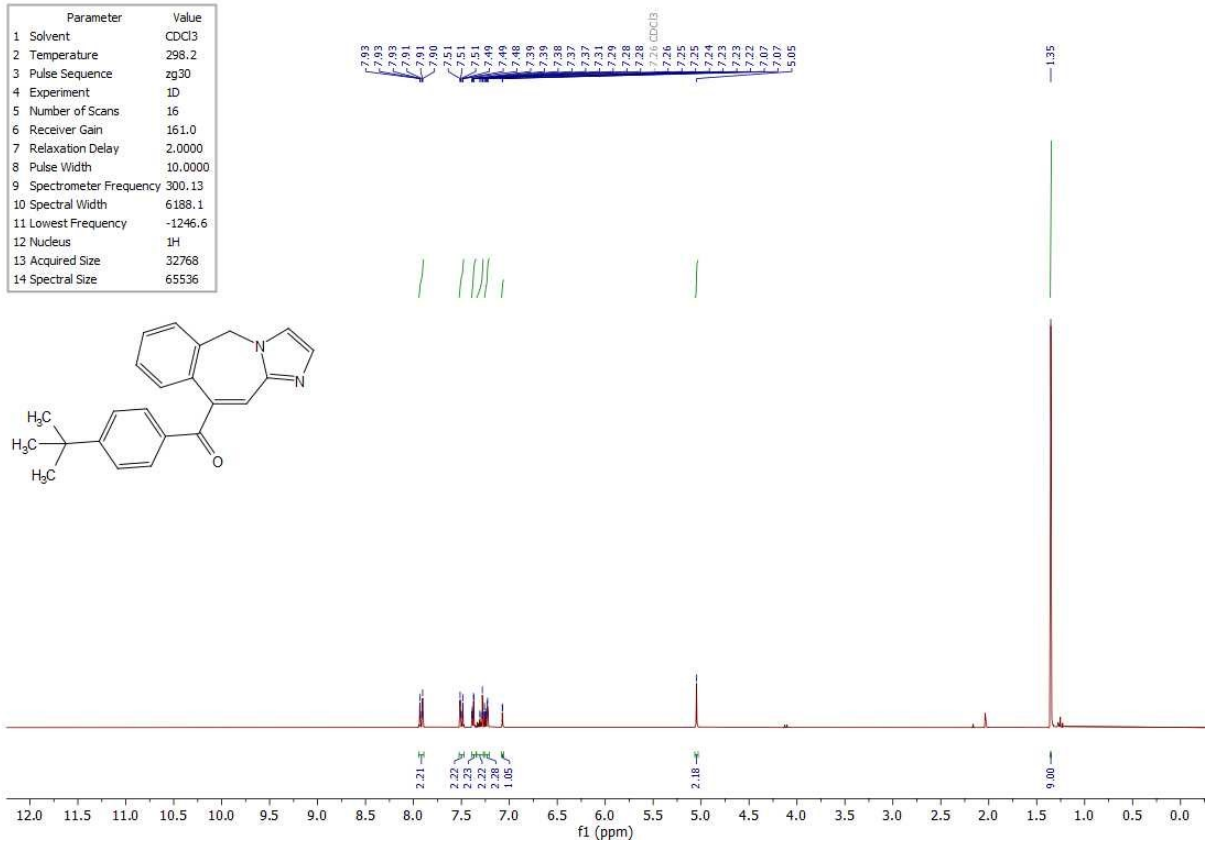


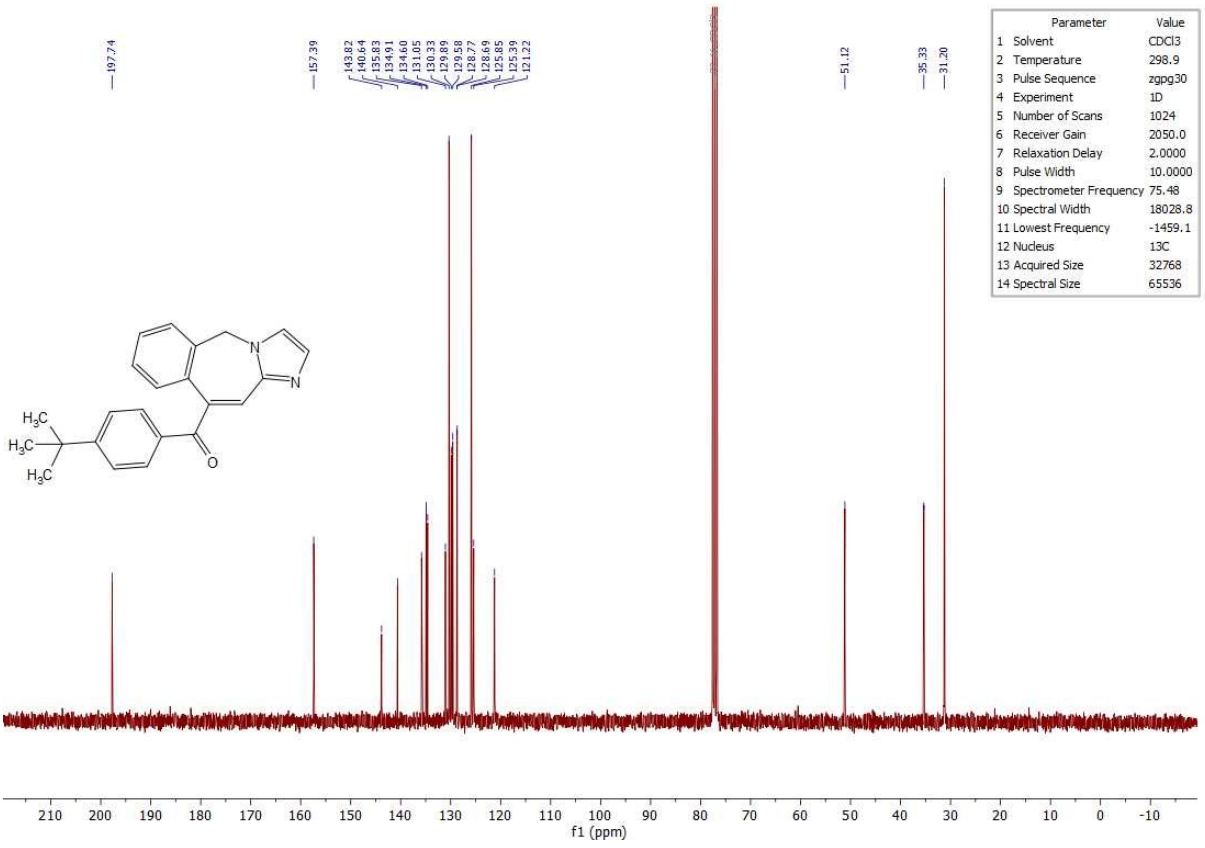
(5*H*-Benzo[*e*]imidazo[1,2-*a*]azepin-10-yl)(4-methoxyphenyl)methanone (6n)



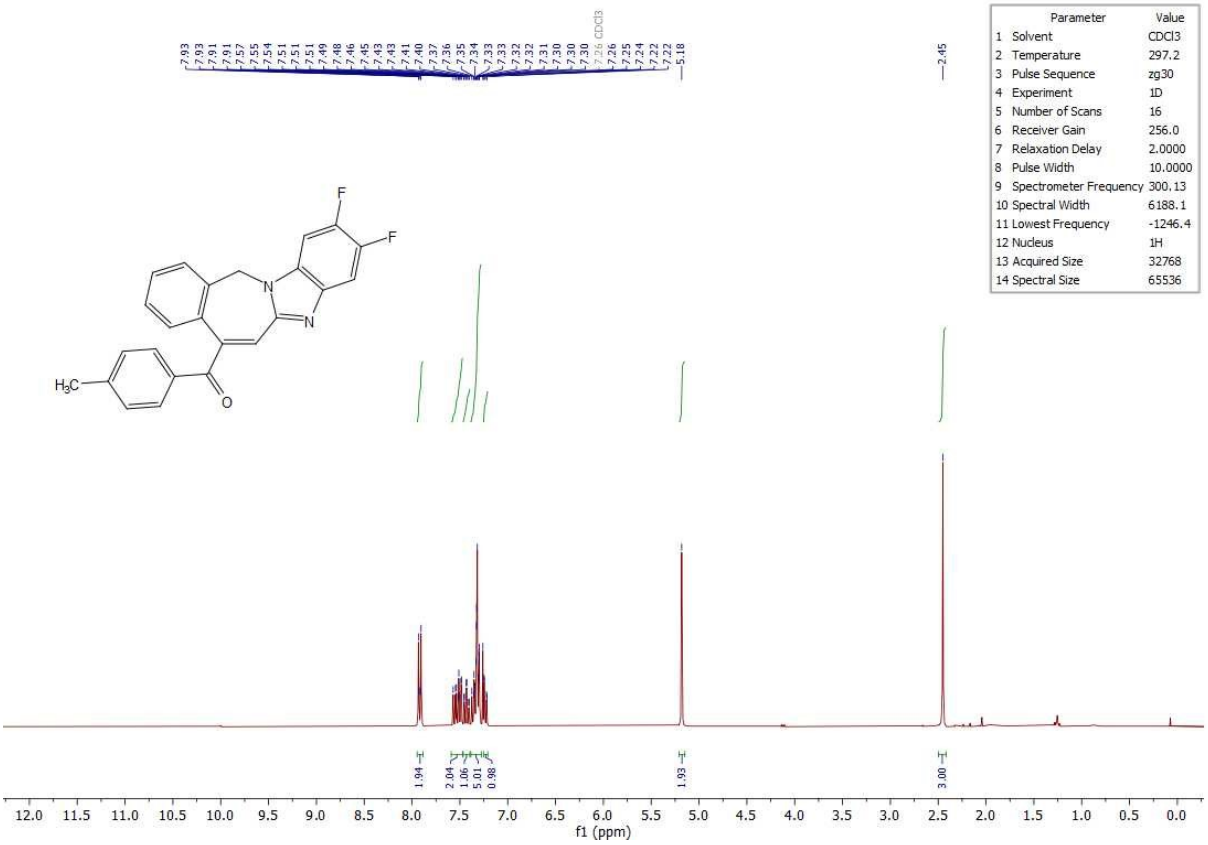


(5*H*-Benzo[*e*]imidazo[1,2-*a*]azepin-10-yl)(4-(*tert*-butyl)phenyl)methanone (6o)

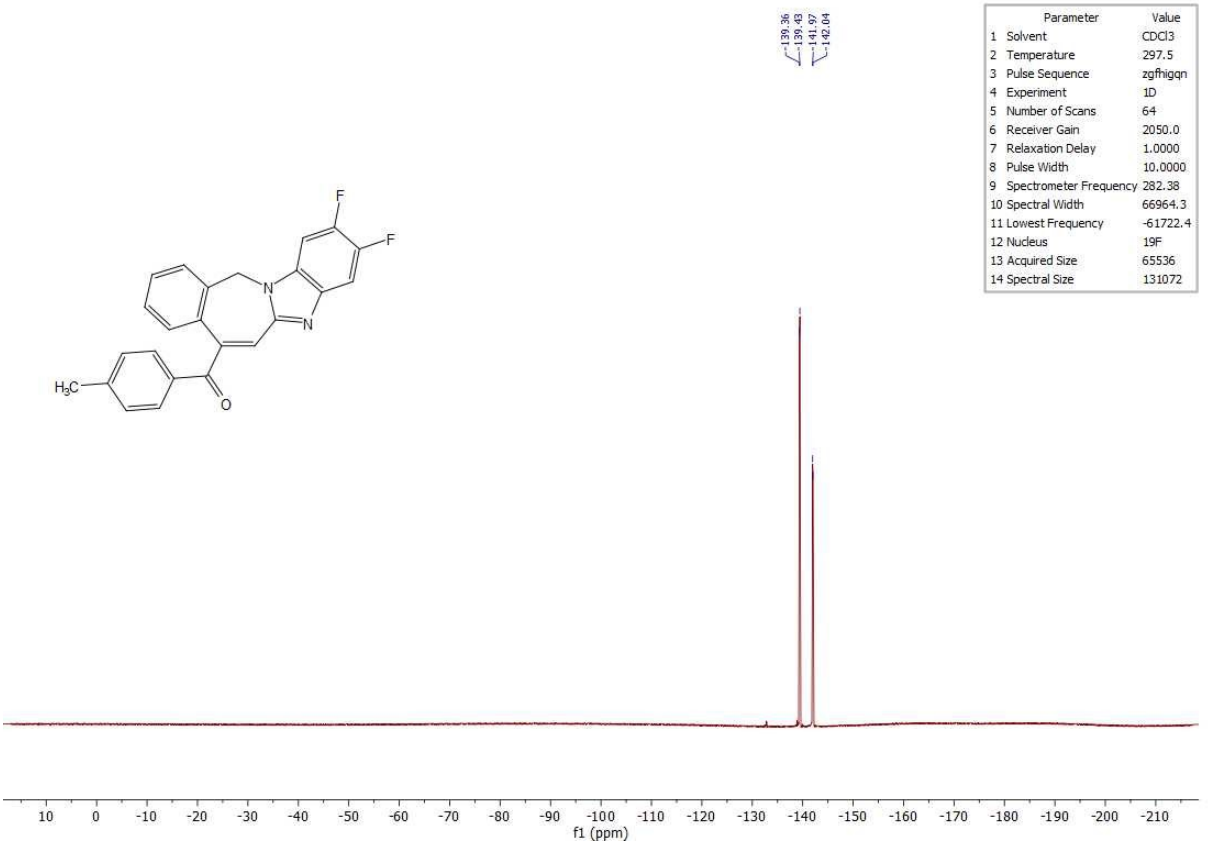




(2,3-Difluoro-12*H*-benzo[*e*]benzo[4,5]imidazo[1,2-*a*]azepin-7-yl)(*p*-tolyl)-methanone (6p)

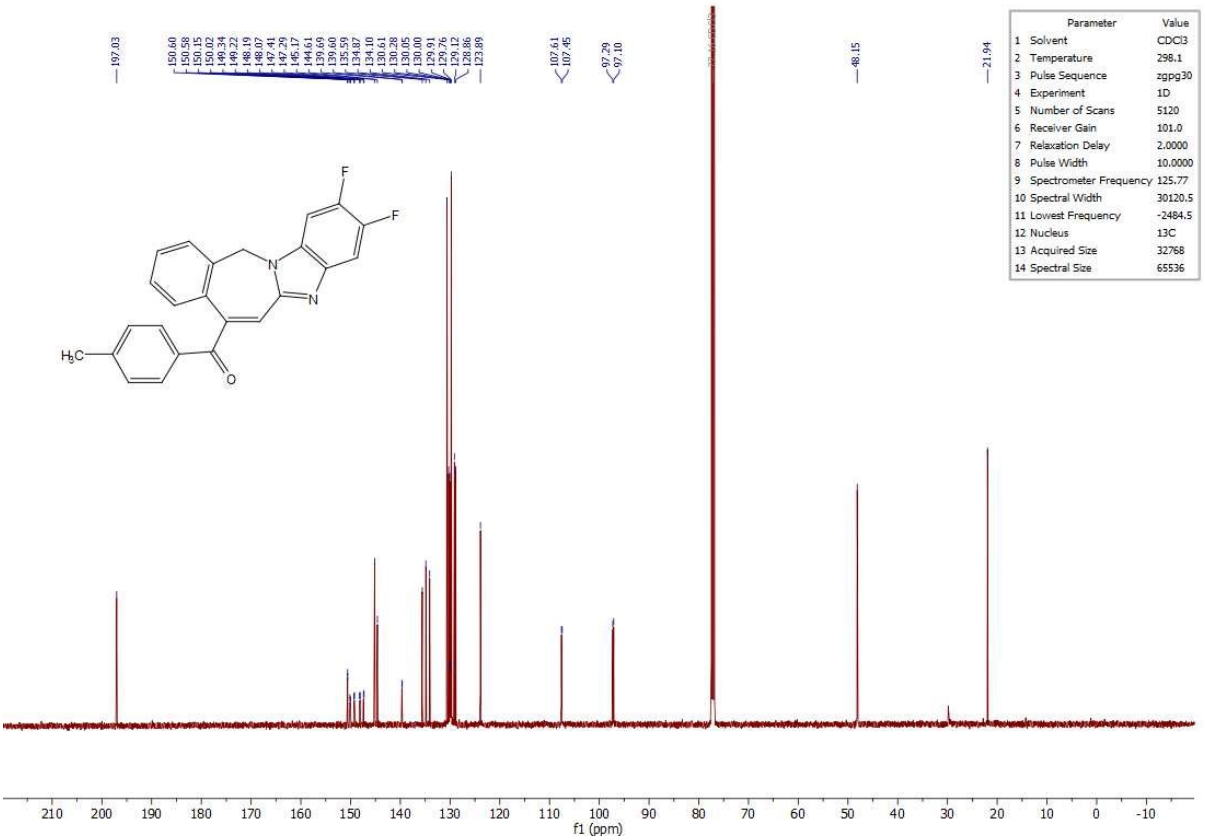


Parameter	Value
1 Solvent	CDCl3
2 Temperature	297.2
3 Pulse Sequence	zg30
4 Experiment	1D
5 Number of Scans	16
6 Receiver Gain	256.0
7 Relaxation Delay	2.0000
8 Pulse Width	10.0000
9 Spectrometer Frequency	300.13
10 Spectral Width	6188.1
11 Lowest Frequency	-1246.4
12 Nucleus	1H
13 Acquired Size	32768
14 Spectral Size	65536

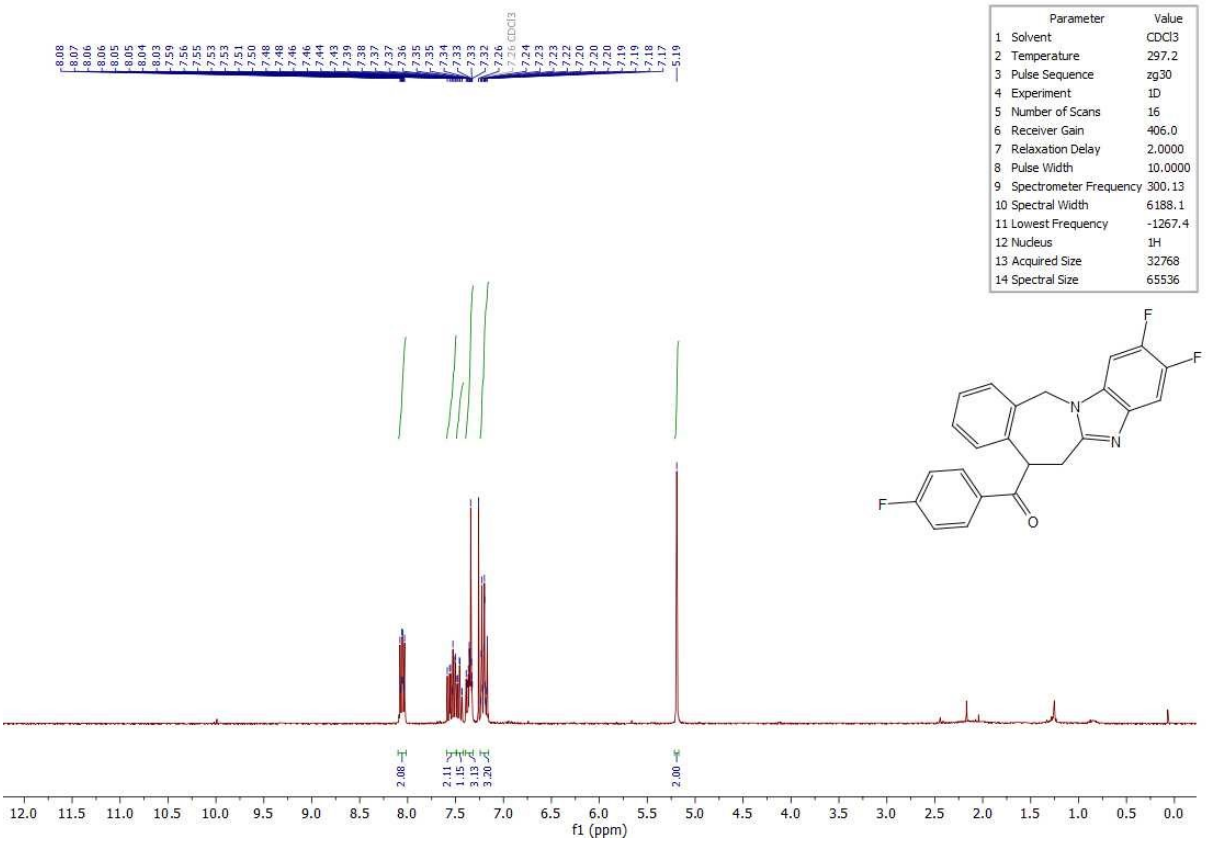


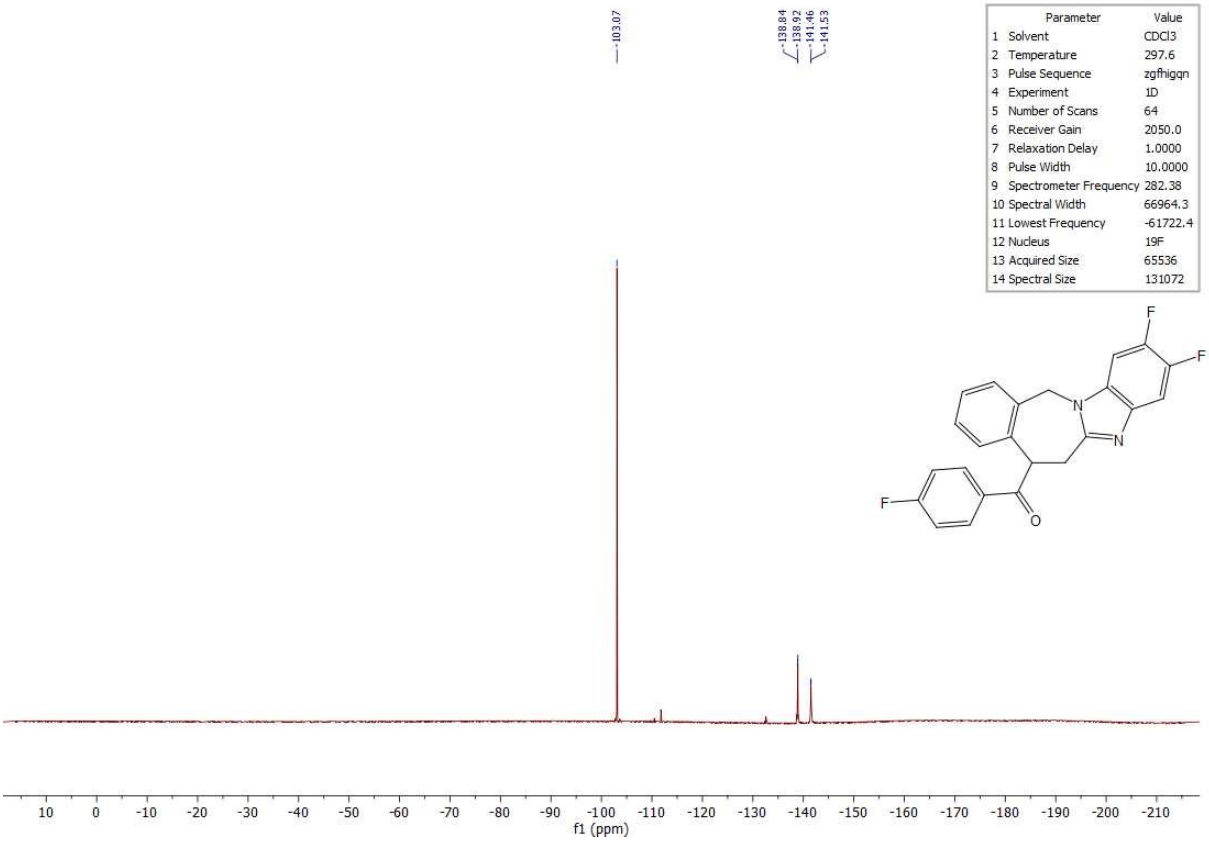
Parameter	Value
1 Solvent	CDCl3
2 Temperature	297.5
3 Pulse Sequence	zgfhigqn
4 Experiment	1D
5 Number of Scans	64
6 Receiver Gain	2050.0
7 Relaxation Delay	1.0000
8 Pulse Width	10.0000
9 Spectrometer Frequency	282.38
10 Spectral Width	66964.3
11 Lowest Frequency	-61722.4
12 Nucleus	19F
13 Acquired Size	65536
14 Spectral Size	131072

(2,3-Difluoro-12*H*-benzo[*e*]benzo[4,5]imidazo[1,2-*a*]azepin-7-yl)(*p*-tolyl)-methanone (6p)

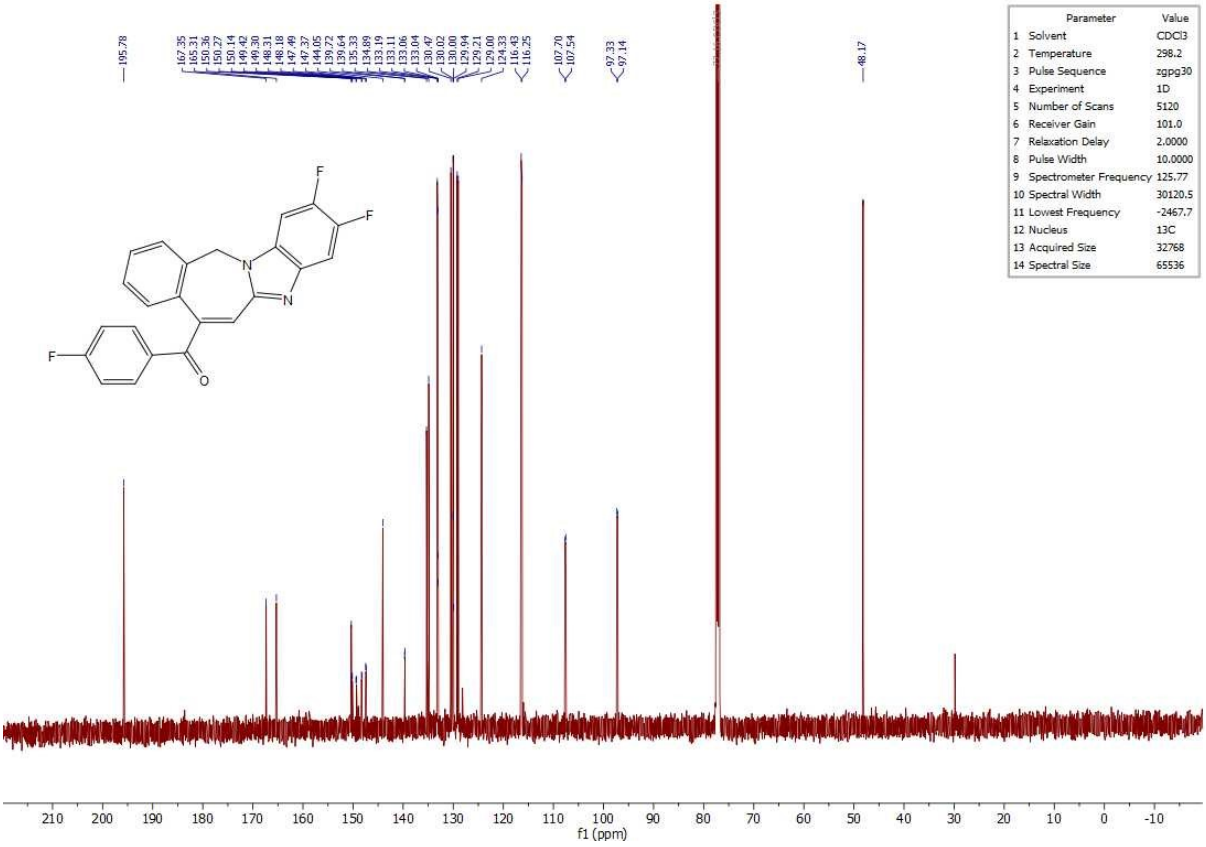


(2,3-Difluoro-12*H*-benzo[*e*]benzo[4,5]imidazo[1,2-*a*]azepin-7-yl)(4-fluoro-phenyl)-methanone (6q)

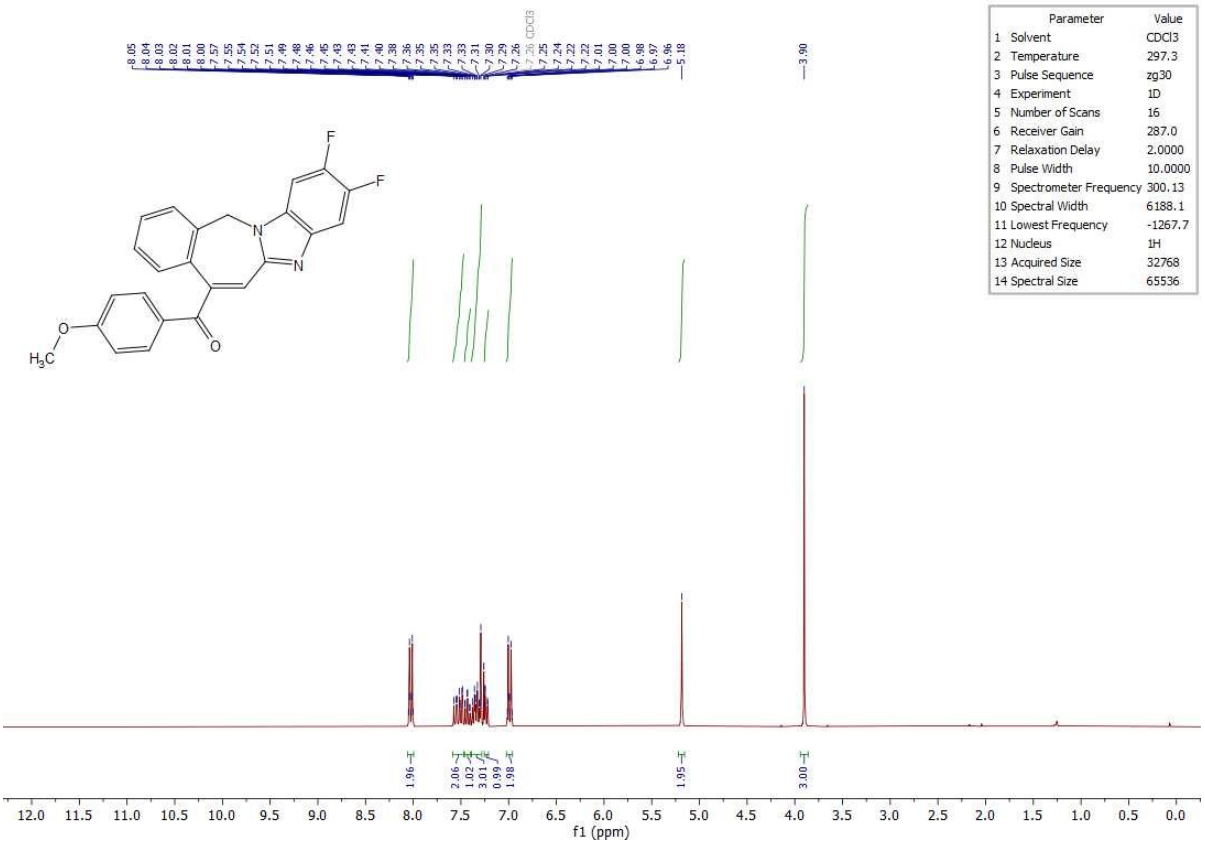


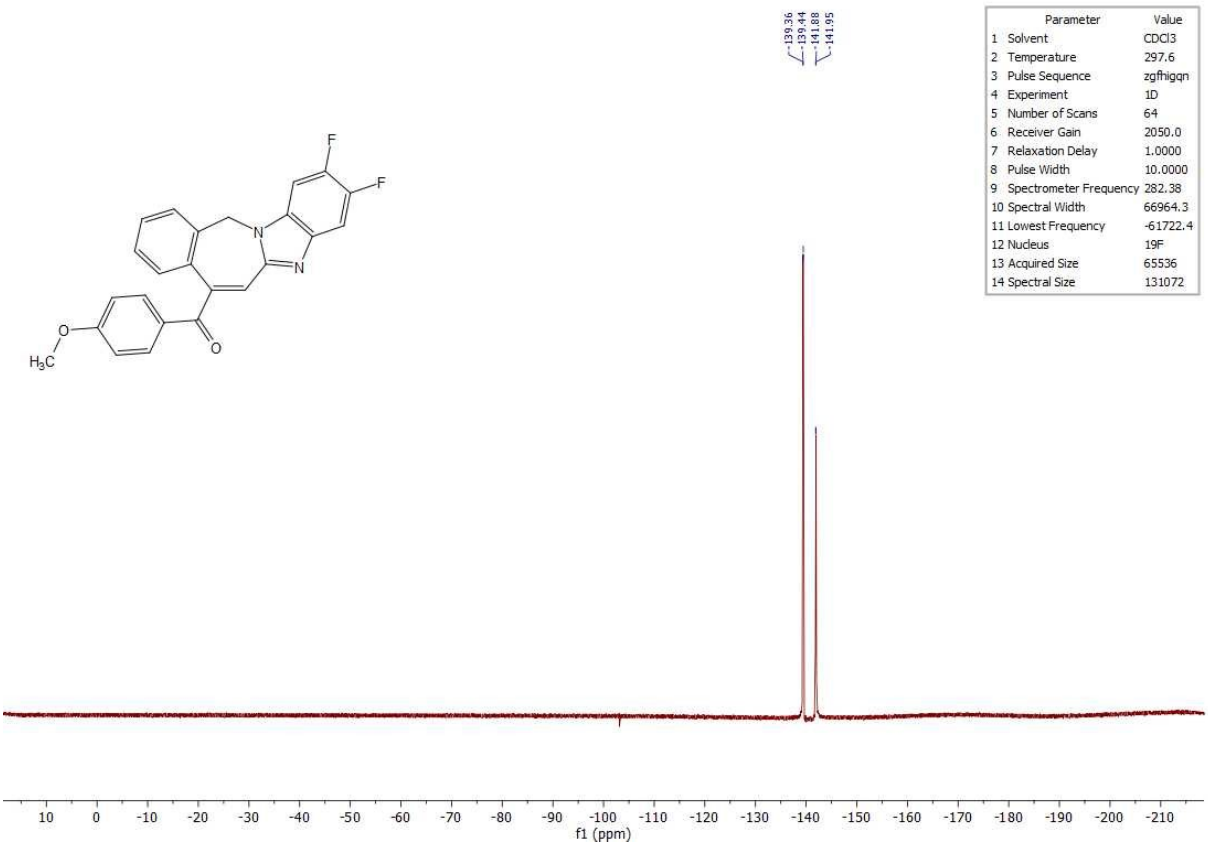


(2,3-Difluoro-12*H*-benzo[*e*]benzo[4,5]imidazo[1,2-*a*]azepin-7-yl)(4-fluoro-phenyl)-methanone (6q)

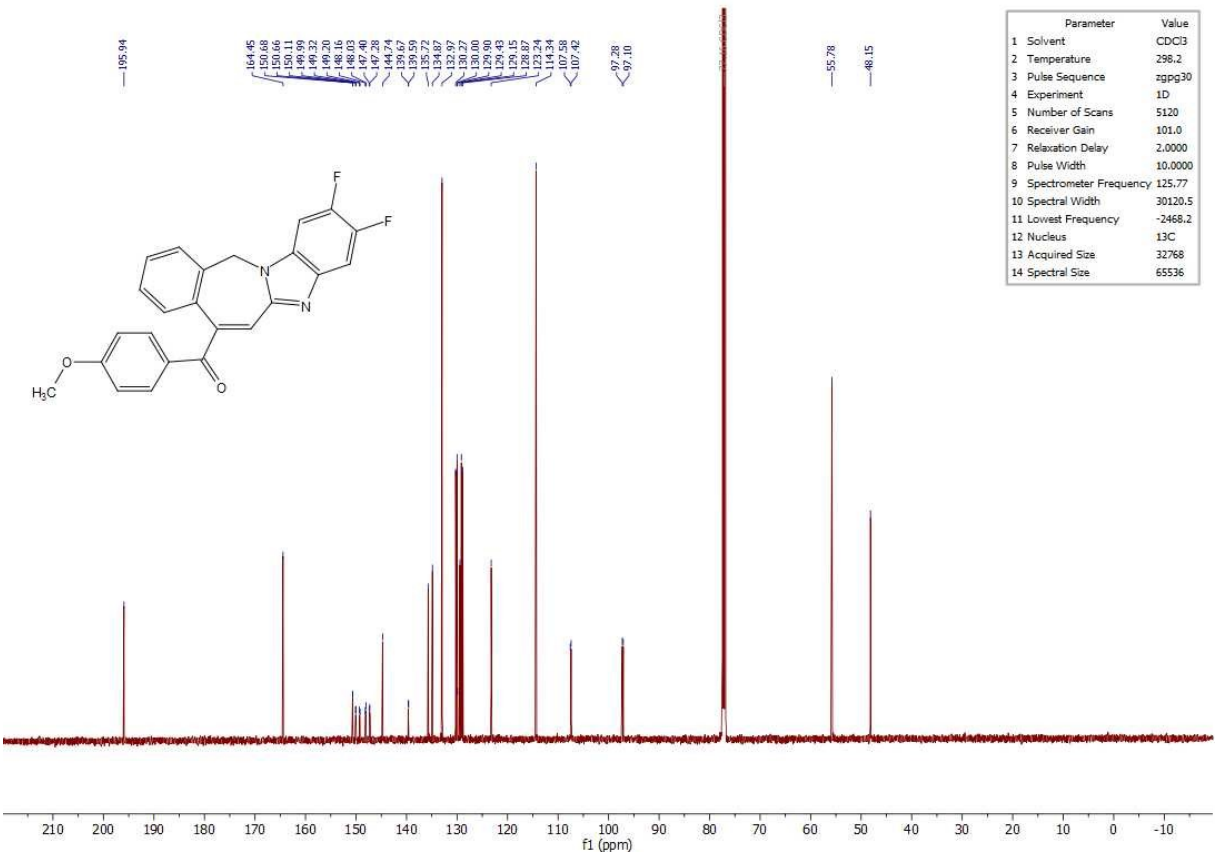


(2,3-Difluoro-12*H*-benzo[*e*]benzo[4,5]imidazo[1,2-*a*]azepin-7-yl)(4-methoxyphenyl)-methanone (6r)

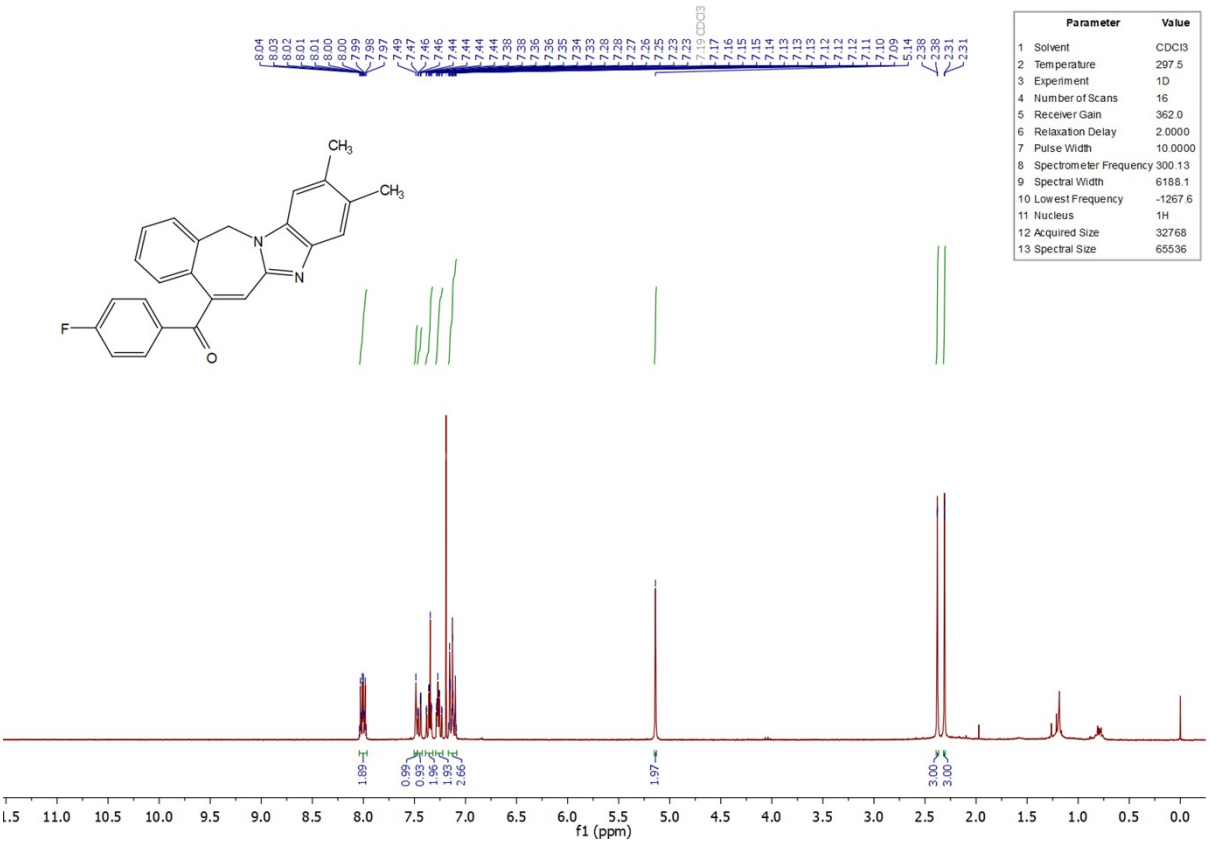


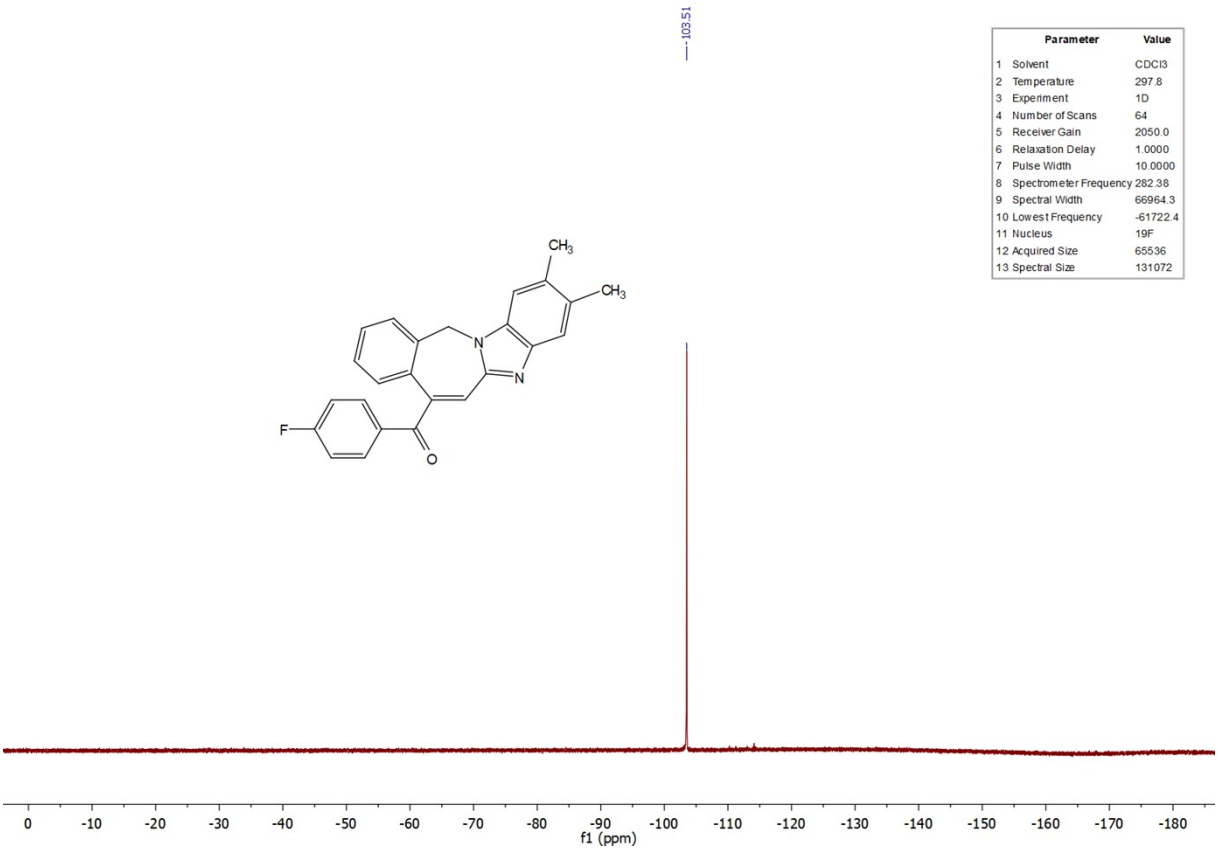


(2,3-Difluoro-12*H*-benzo[*e*]benzo[4,5]imidazo[1,2-*a*]azepin-7-yl)(4-methoxyphenyl)-methanone (6r)

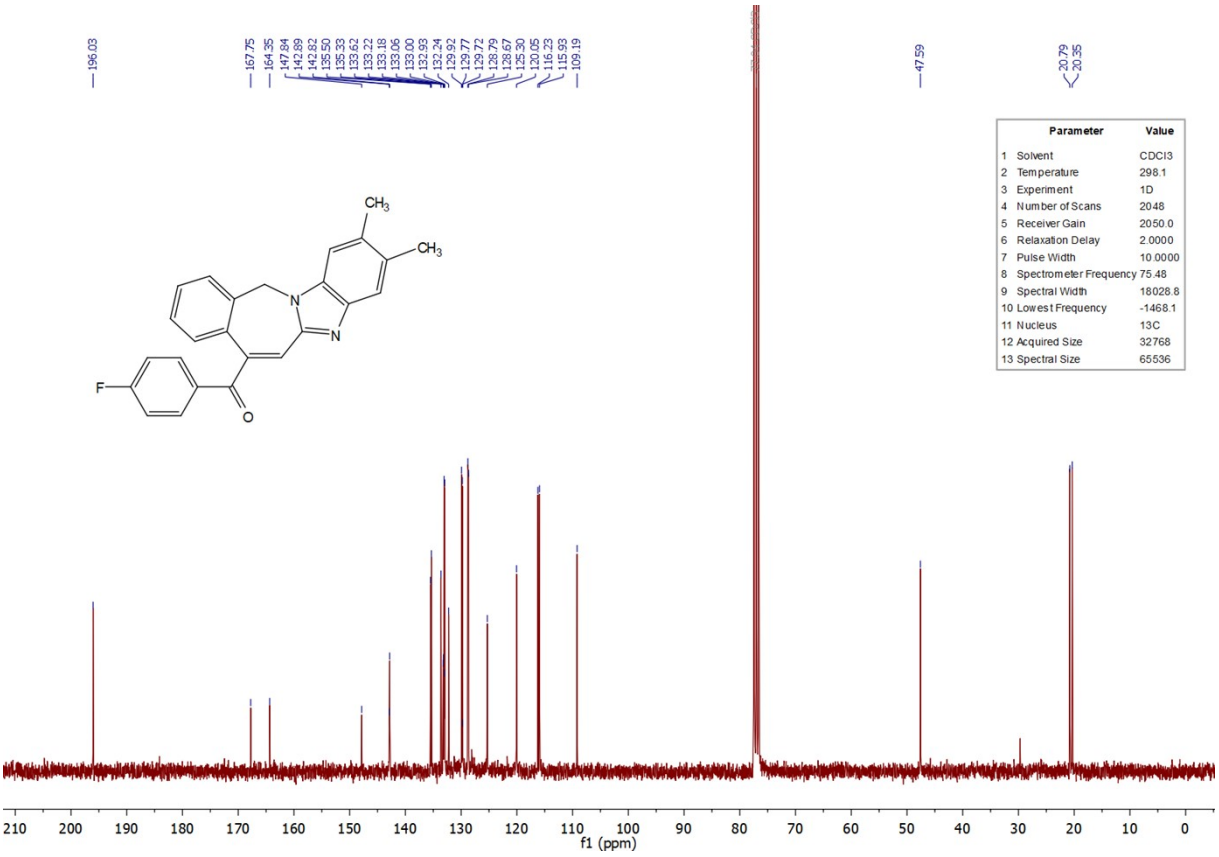


(2,3-Dimethyl-12*H*-benzo[*e*]benzo[4,5]imidazo[1,2-*a*]azepin-7-yl)(4-fluorophenyl)methanone (6s)

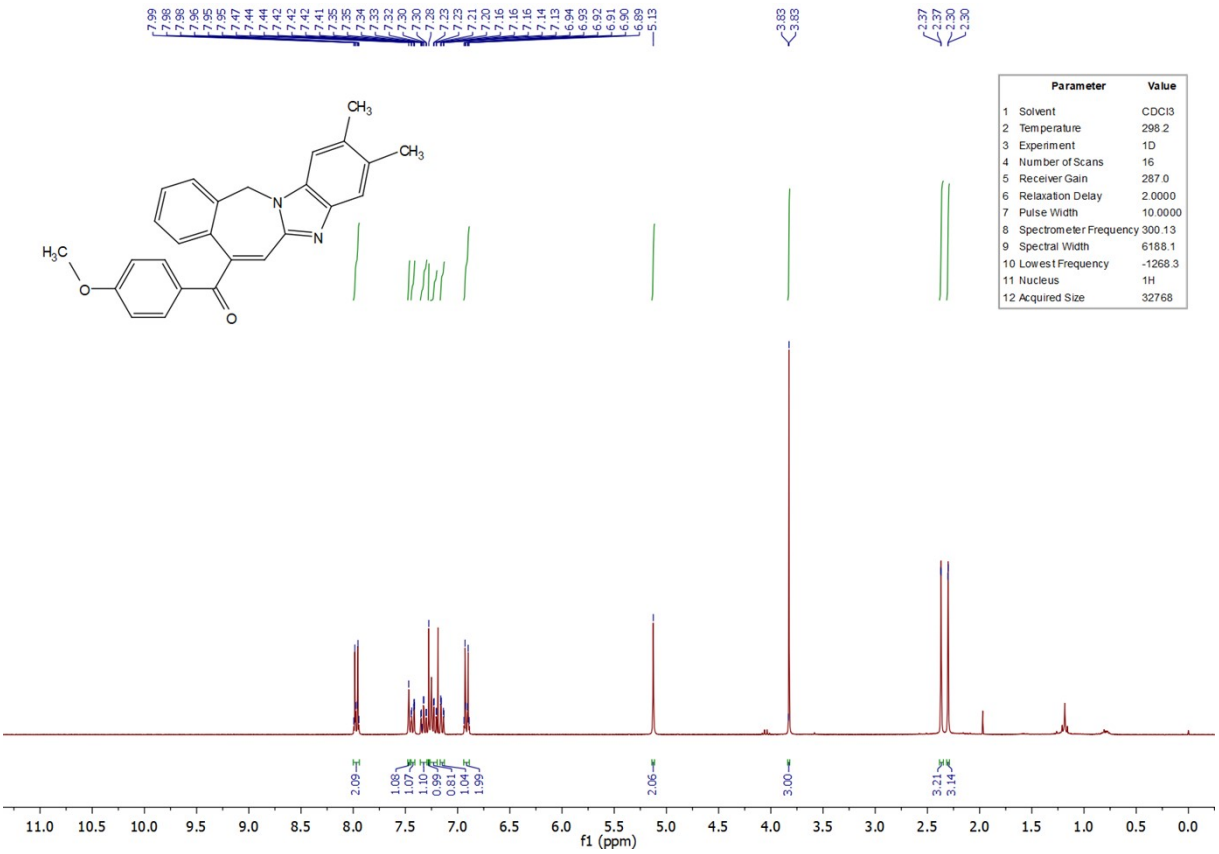


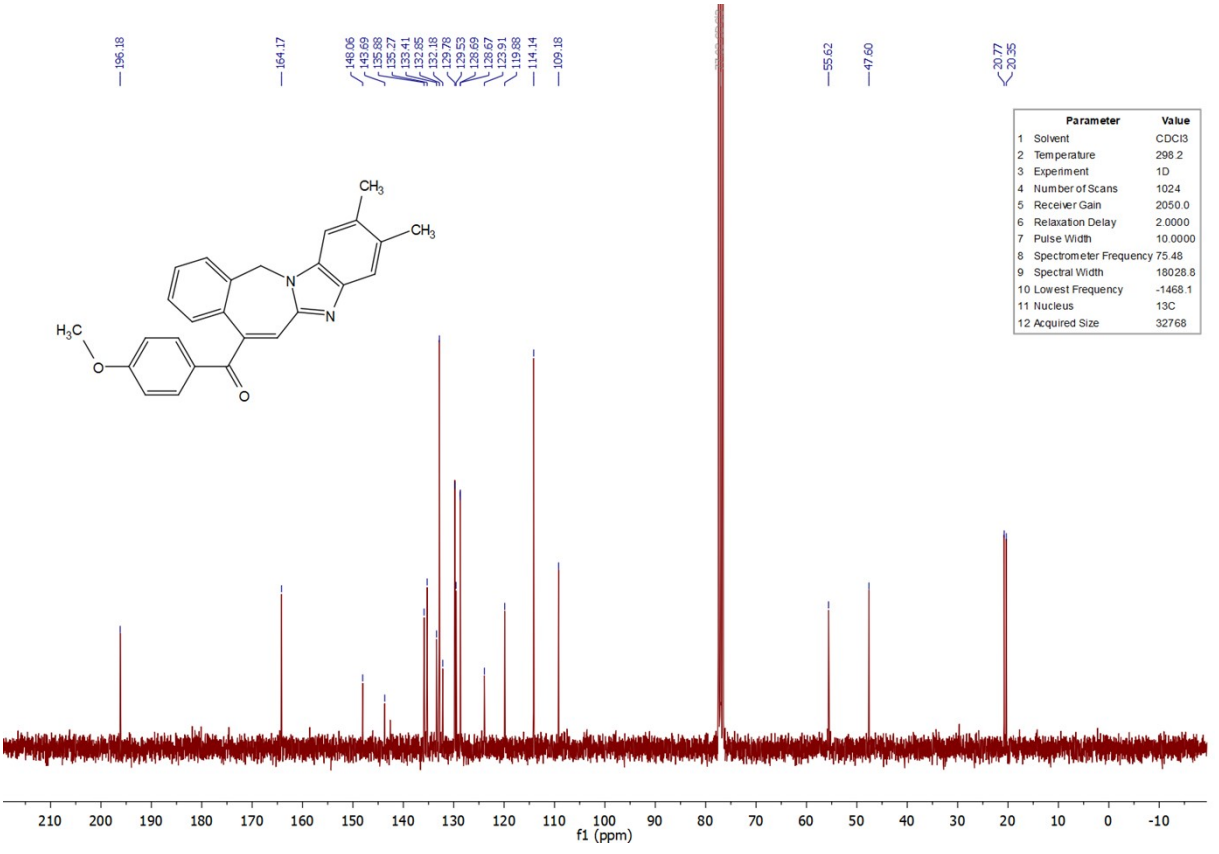


(2,3-Dimethyl-12*H*-benzo[*e*]benzo[4,5]imidazo[1,2-*a*]azepin-7-yl)(4-fluorophenyl)methanone (6s)

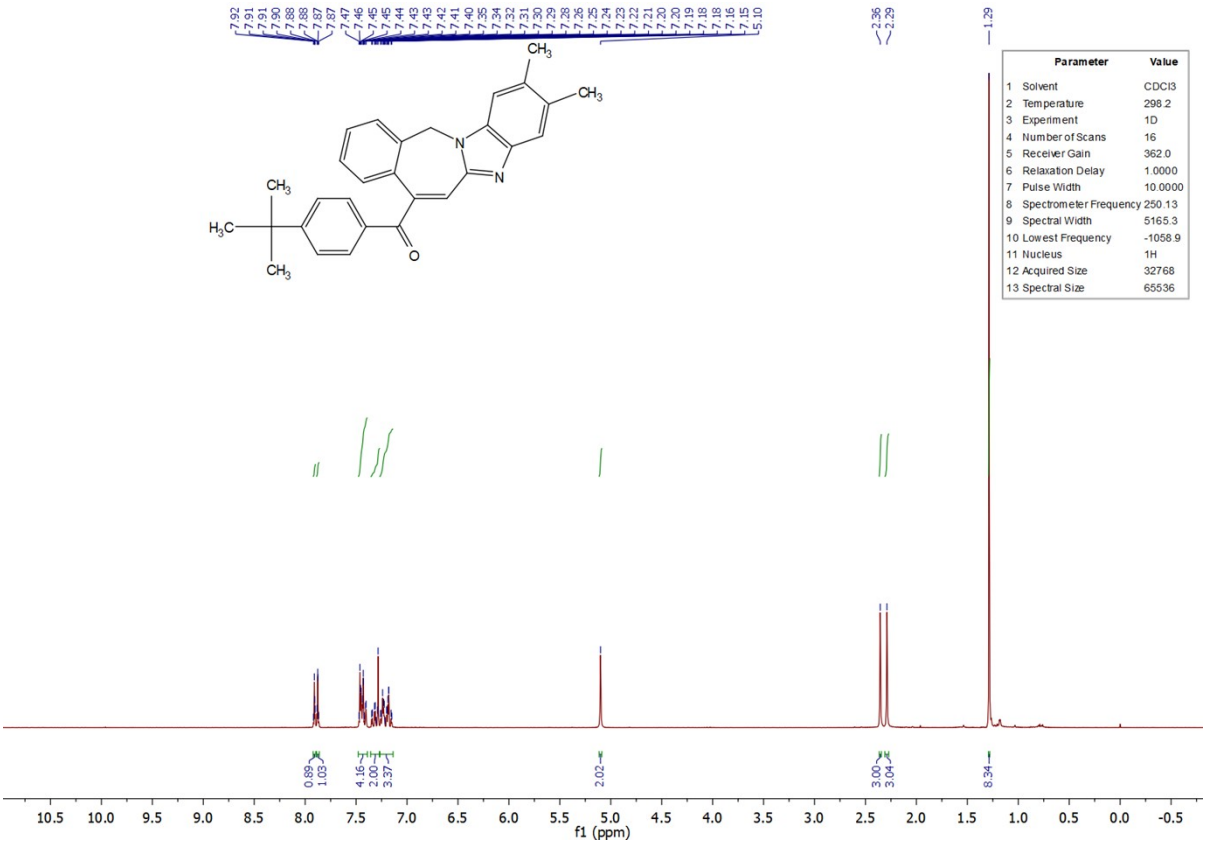


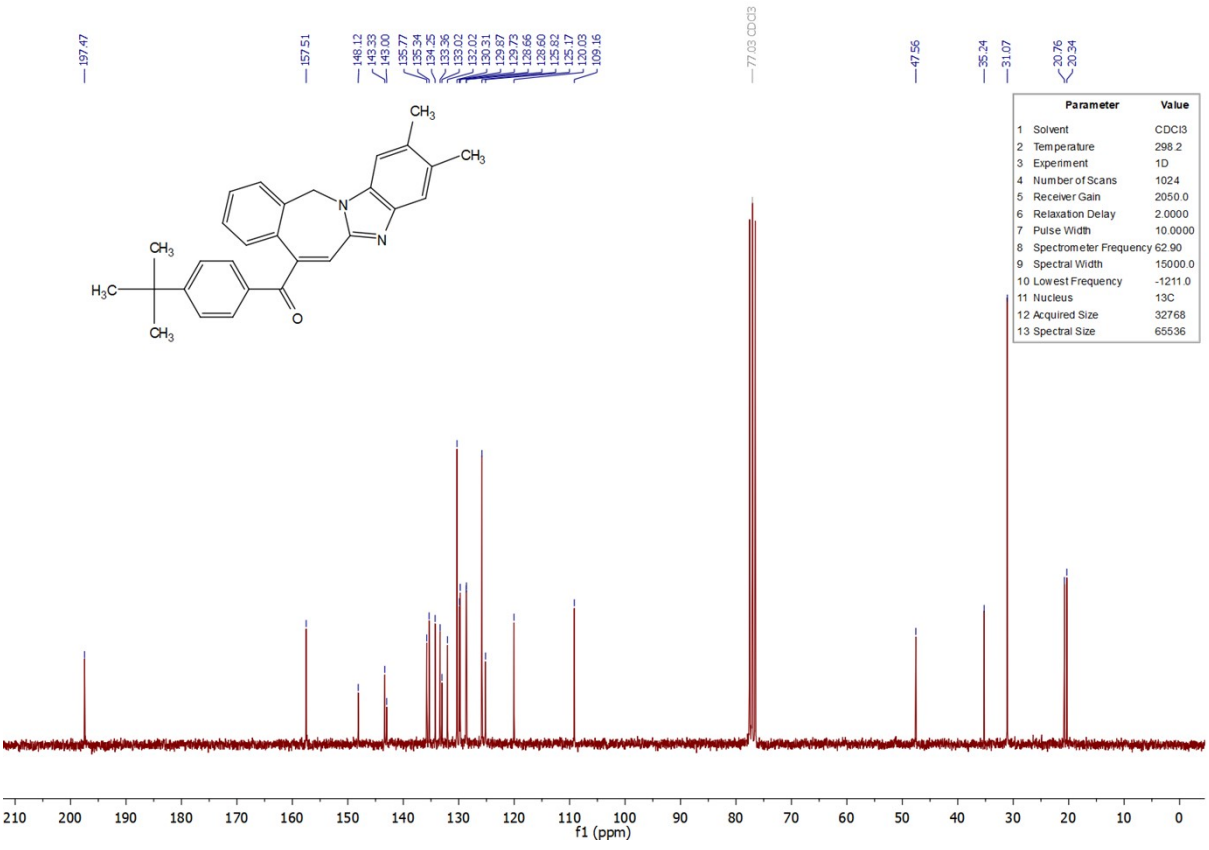
(2,3-Dimethyl-12*H*-benzo[*e*]benzo[4,5]imidazo[1,2-*a*]azepin-7-yl)(4-methoxyphenyl)methanone (6t)



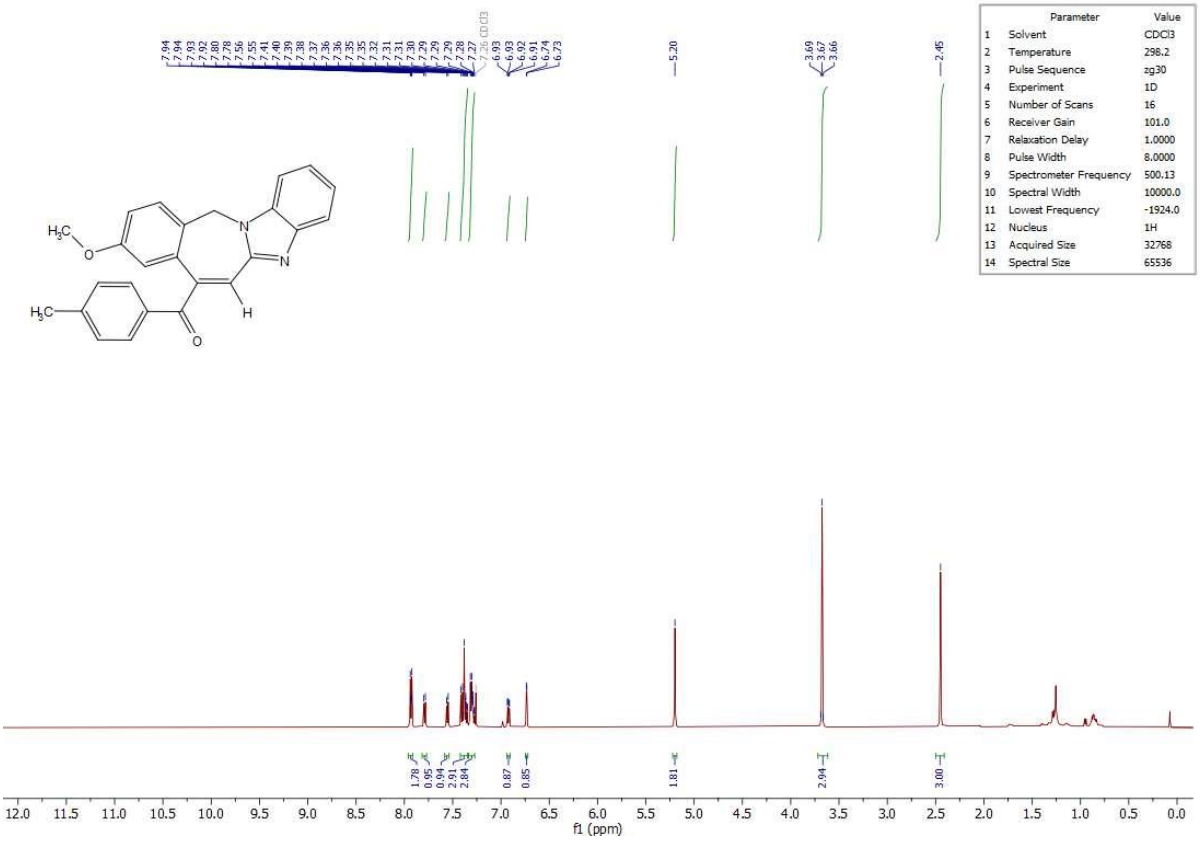


(4-(*tert*-Butyl)phenyl)(2,3-dimethyl-12*H*-benzo[*e*]benzo[4,5]imidazo[1,2-*a*]azepin-7-yl)methanone (6u)

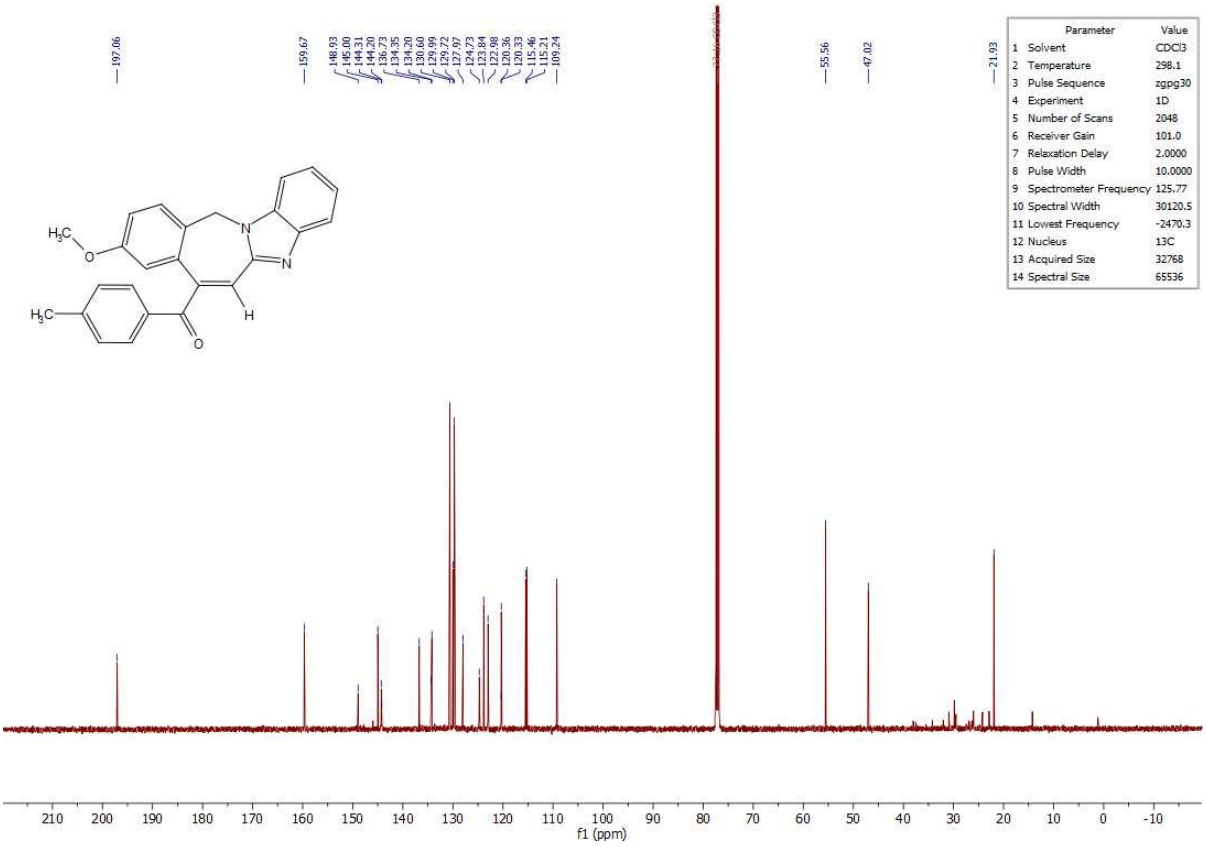




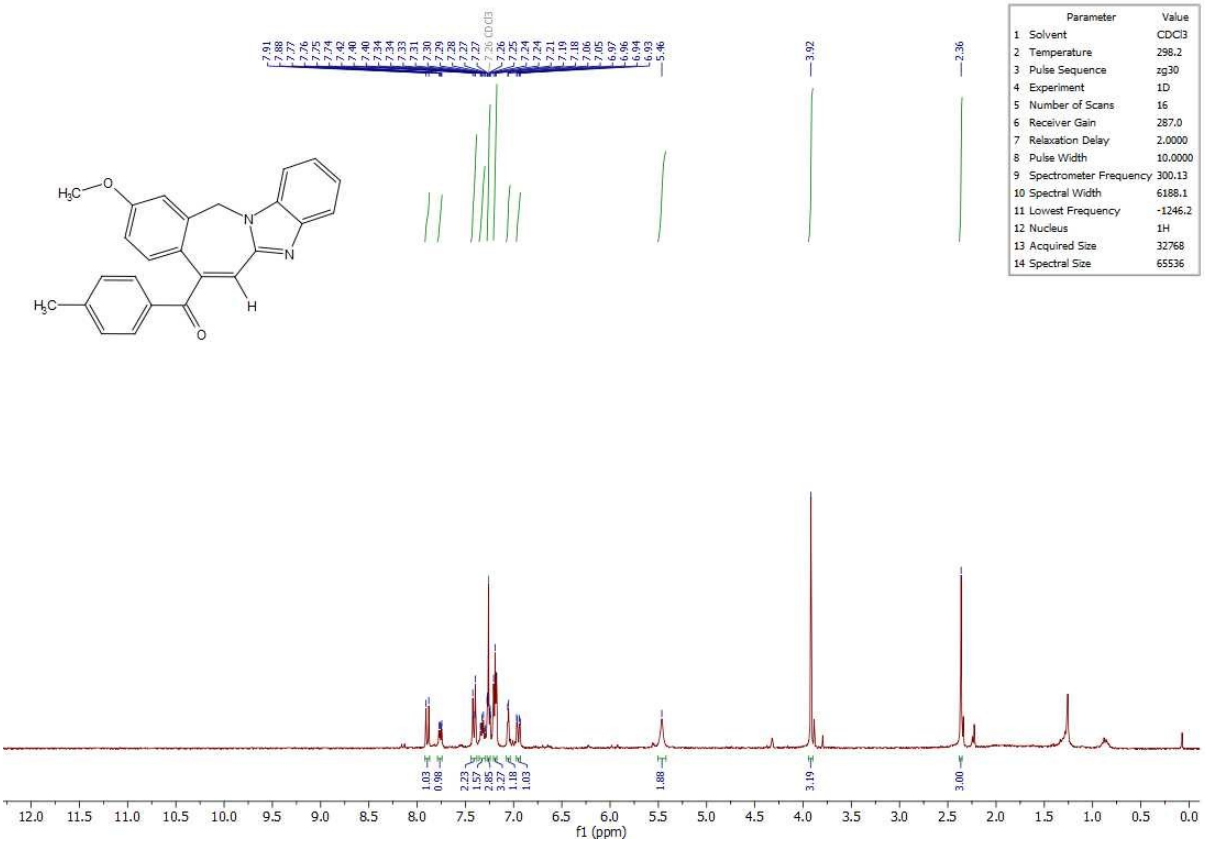
(9-Methoxy-12*H*-benzo[*e*]benzo[4,5]imidazo[1,2-*a*]azepin-7-yl)(*p*-tolyl)methanone (6v)

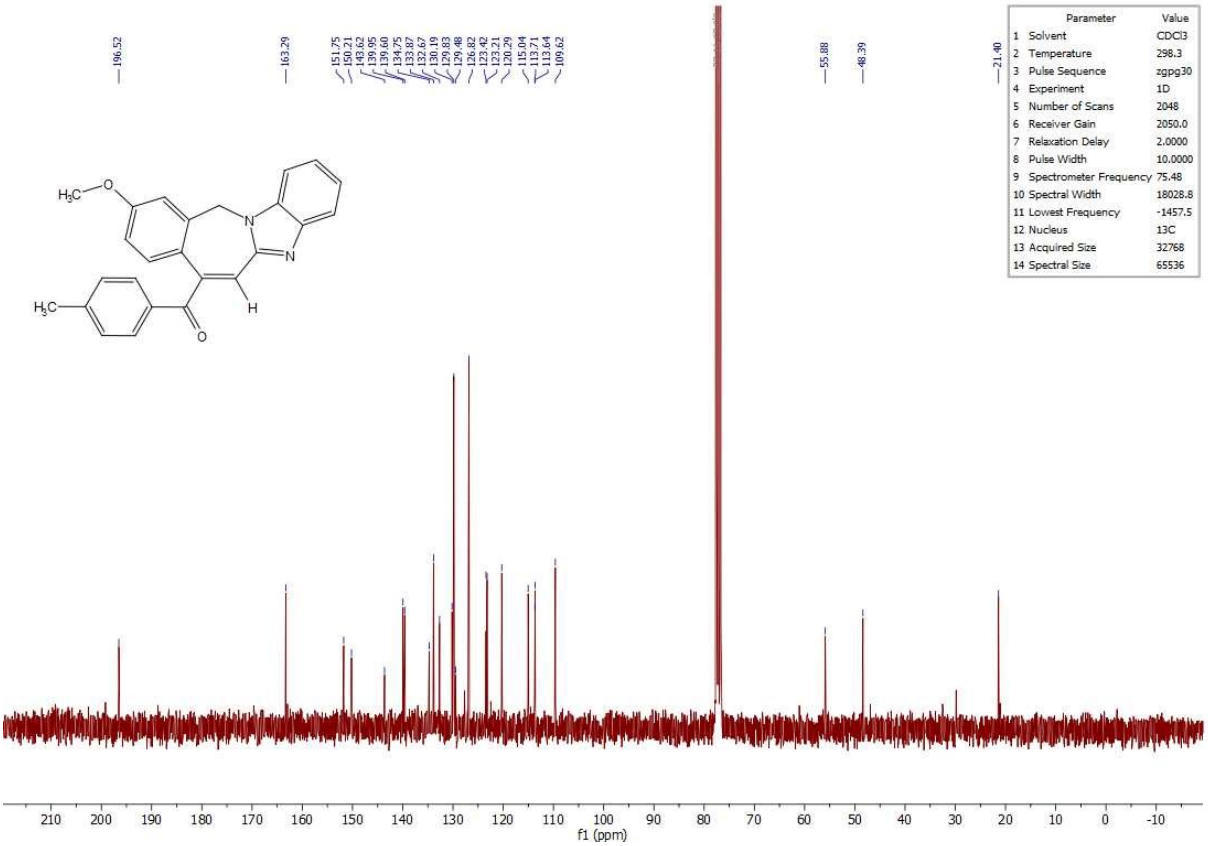


(9-Methoxy-12*H*-benzo[*e*]benzo[4,5]imidazo[1,2-*a*]azepin-7-yl)(*p*-tolyl)methanone (6v)

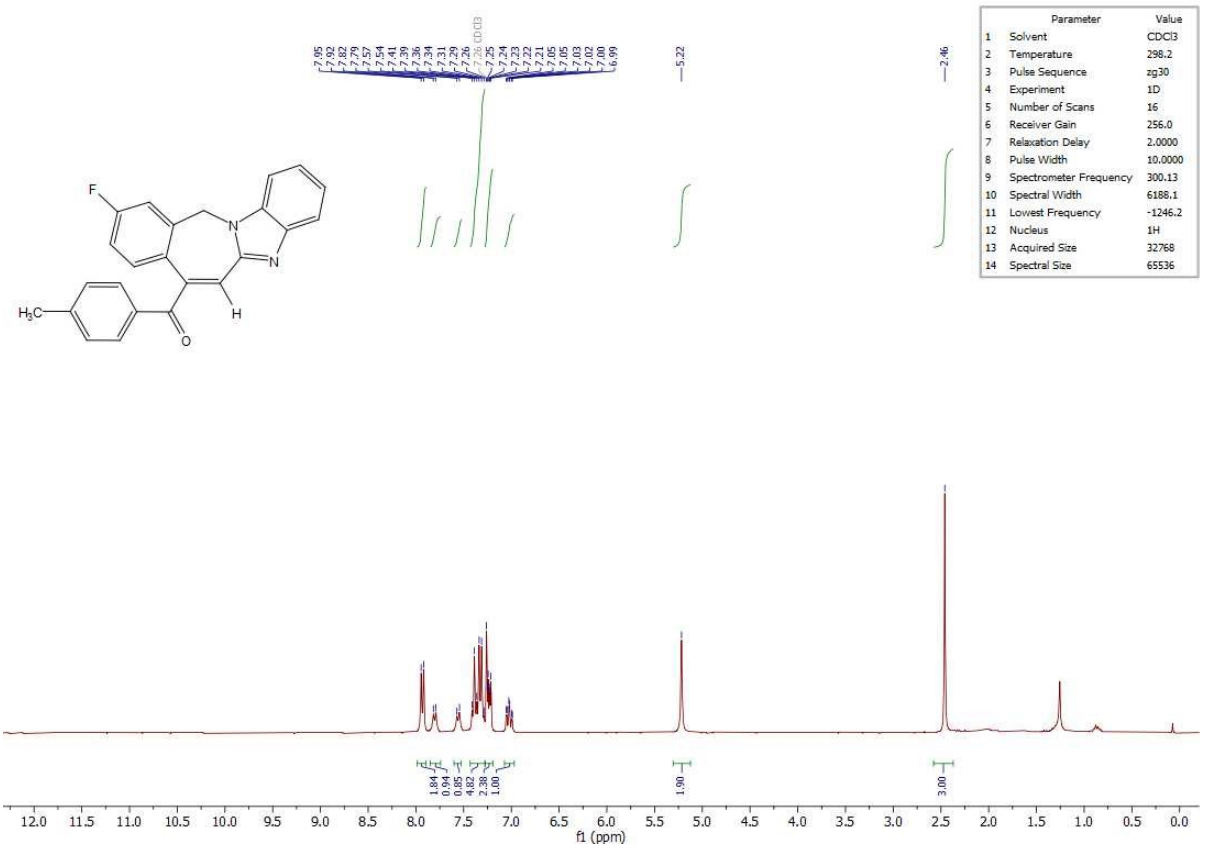


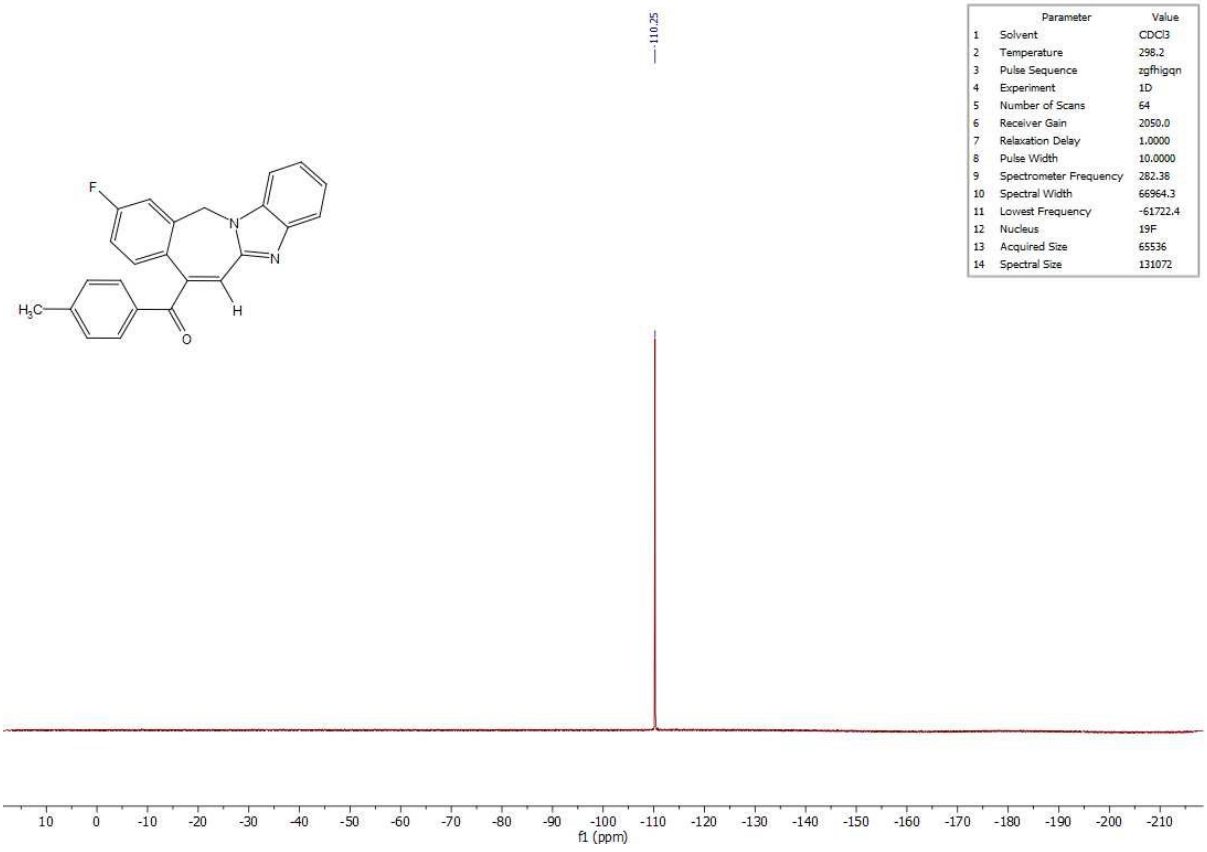
(10-Methoxy-12*H*-benzo[*e*]benzo[4,5]imidazo[1,2-*a*]azepin-7-yl)(*p*-tolyl)methanone (6w)





(10-Fluoro-12*H*-benzo[*e*]benzo[4,5]imidazo[1,2-*a*]azepin-7-yl)(*p*-tolyl)methanone (6x)





(10-Fluoro-12*H*-benzo[*e*]benzo[4,5]imidazo[1,2-*a*]azepin-7-yl)(*p*-tolyl)methanone (6x)