Supporting Information

Copper-Catalyzed Decarboxylative Cross-Coupling of Alkynyl Carboxylic Acids with Aryl Halides

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I. General remarks

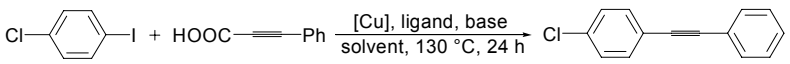
The ^{1}H NMR (400 MHz or 600 MHz) chemical shifts were measured relative to tetramethylsilane or solvent (i.e. $CDCl_3$, DMSO-d_6) as the internal reference. The ^{13}C NMR (100 MHz or 150 MHz) chemical shifts were given using $CDCl_3$ as the internal standard ($CDCl_3$: δ = 77.16 ppm). Low-resolution mass spectra (MS) were obtained by GC-MS. High-resolution mass spectra (HR-MS) were recorded by ESI-TOF.

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Aromatic alkynyl carboxylic acids were prepared according to the literature procedure.[1] Solvents were dried by refluxing for at least 24 h over CaH_2 (DMF or DMSO), or sodium (dioxane or *m*-xylene), and freshly distilled prior to use. All syntheses and manipulations were carried out under N_2 atmosphere.

II. Optimization of the decarboxylative coupling of phenylpropiolic acid with *p*-chloroiodobenzene

A Schlenk test tube with a magnetic stirring bar was charged with copper source (0.0125-0.025 mmol), ligand (0.0125-0.025 mmol), base (0.375 mmol), 1-chloro-4-iodobenzene (59.5 mg, 0.25 mmol), phenylpropiolic acid (51 mg, 0.35 mmol), and solvent (1 mL) under N_2. A rubber septum was replaced with a glass stopper, and the system was then evacuated twice and back filled with N_2. The reaction mixture was stirred for 10 min at room temperature, and then heated at 130 ºC for 12-24 h. The reaction mixture was then cooled to ambient temperature, diluted with 5-6 mL of CH_2Cl_2, filtered through a plug of silica gel, and washed with 10-20 mL of CH_2Cl_2. The combined organic extracts were concentrated and the resulting residue was purified by column chromatography on silica gel to provide the desired product.

Table S1 Optimization of the decarboxylative coupling of phenylpropiolic acid with *p*-chloroiodobenzene[a]



Entry	Ligand	Solvent	Base	[Cu]	Yield[b]
1	-	DME	Cs_2CO_3	CuI	23%
2	phen	DME	Cs_2CO_3	CuI	96%
3	L-Pro	DME	Cs_2CO_3	CuI	28%
4	bipy	DME	Cs_2CO_3	CuI	21%
5	dmeda	DME	Cs_2CO_3	CuI	trace
6	phen	DME	K_2CO_3	CuI	55%
7	phen	DME	K_3PO_4	CuI	74%
8	phen	DME	*t*BuOLi	CuI	trace
9	phen	DMSO	Cs_2CO_3	CuI	84%
10	phen	DMF	Cs_2CO_3	CuI	98%
11	phen	*m*-xylene	Cs_2CO_3	CuI	76%
12	phen	DME	Cs_2CO_3	CuCl	92%
13	phen	DME	Cs_2CO_3	$Cu(OAc)_2$	92%
14[c]	phen	DME	Cs_2CO_3	CuI	68%
15[d]	phen	DME	Cs_2CO_3	CuI	95%

[a] Conditions: 1-chloro-4-iodobenzene (0.25 mmol), phenylpropiolic acid (0.35 mmol), CuI (10 mol%), phen (10 mol%), solvent (1 mL), 24 h, 130 °C. [b] Yield of isolated product. [c] 12 h. [d] phen (5 mol%), CuI (5 mol%). L-Pro = L-proline, bipy = 2,2'-bipyridine, dmeda = *N*,*N*'-dimethylethanediamine, DMF = *N*,*N*-dimethylformamide, DMSO = dimethyl sulfoxide.

III. General Procedure for Tables 1-2

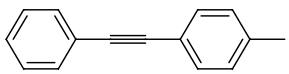
A Schlenk test tube with a magnetic stirring bar was charged with CuI (4.8 mg, 0.025 mmol), 1,10-phenanthroline (4.5 mg, 0.025 mmol), Cs_2CO_3 (122 mg, 0.375 mmol),

aryl halide (0.25 mmol), alkynyl carboxylic acid (0. 35 mmol) and DMF (1 mL) under N_2. A rubber septum was replaced with a glass stopper, and the system was then evacuated twice and back filled with N_2. The reaction mixture was stirred for 10 min at room temperature, and then heated at 130 ºC for 24 h. The reaction mixture was then cooled to ambient temperature, diluted with 5-6 mL of CH_2Cl_2, filtered through a plug of silica gel, and washed with 10-20 mL of CH_2Cl_2. The combined organic extracts were concentrated and the resulting residue was purified by column chromatography on silica gel to provide the desired product.

IV. General procedure for the synthesis of benzofurans from 2-iodophenol

A Schlenk test tube with a magnetic stirring bar was charged with CuI (4.8 mg, 0.025 mmol), 1,10-phenanthroline (4.5 mg, 0.025 mmol), Cs_2CO_3 (122 mg, 0.375 mmol), 2-iodophenol (55 mg, 0.25 mmol), alkynyl carboxylic acid (0. 35 mmol) and DMF (1 mL) under N_2. A rubber septum was replaced with a glass stopper, and the system was then evacuated twice and back filled with N_2. The reaction mixture was stirred for 10 min at room temperature, and then heated at 130 ºC for 24 h. The reaction mixture was then cooled to ambient temperature, diluted with 5-6 mL of CH_2Cl_2, filtered through a plug of silica gel, and washed with 10-20 mL of CH_2Cl_2. The combined organic extracts were concentrated and the resulting residue was purified by column chromatography on silica gel to provide the desired product.

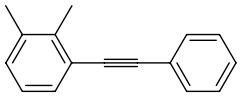
VI. Experimental data for the described substances



4-Methyldiphenylacetylene (3a)[2]

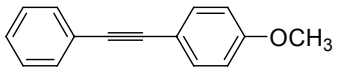
1-Iodo-4-methylbenzene (54.5 mg, 0.25 mmol), phenylpropiolic acid (51 mg, 0.35 mmol), CuI (4.8 mg, 0.025 mmol), 1,10-phenanthroline (4.5 mg, 0.025 mmol), Cs_2CO_3 (122 mg, 0.375 mmol) and DMF (1 mL) at 130 ºC for 24 h. Purification via silica gel column chromatography using petroleum ether afforded a pale yellow solid

(98 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.38 (s, 3H), 7.16 (d, J = 8.0 Hz, 2H), 7.31-7.36 (m, 3H), 7.44 (d, J = 8.0 Hz, 2H), 7.53-7.55 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.5, 88.8, 89.6, 120.3, 123.5, 128.1, 128.3, 129.1, 131.5, 131.6 138.4 ppm. GC-MS (EI, m/z): 192 [M^+].



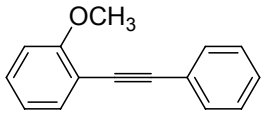
2,3-Dimethyldiphenylacetylene (3b)

1-Iodo-2,3-dimethylbenzene (58 mg, 0.25 mmol), phenylpropiolic acid (51 mg, 0.35 mmol), CuI (4.8 mg, 0.025 mmol), 1,10-phenanthroline (4.5 mg, 0.025 mmol), Cs_2CO_3 (122 mg, 0.375 mmol) and DMF (1 mL) at 130 ºC for 24 h. Purification via silica gel column chromatography using petroleum ether afforded colorless oil (95 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.33 (s, 3H), 2.51 (s, 3H), 7.09 (t, J = 7.6 Hz, 1H), 7.15 (d, J = 6.8 Hz, 1H), 7.35-7.38 (m, 3H), 7.40 (d, J = 8.0 Hz, 1H), 7.56-7.59 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.0, 19.8, 88.5, 92.2, 122.6, 123.2, 124.8, 127.6, 127.8, 129.3, 129.4, 131.0, 136.3, 138.0. HR-MS (ESI) calcd for $C_{16}H_{15}$ $[M+H]^+$ 207.1174, found: 207.1173.



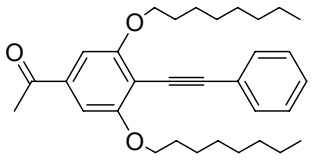
4-Methoxydiphenylacetylene (3c)[2]

1-Iodo-4-methoxybenzene (58.5 mg, 0.25 mmol), phenylpropiolic acid (51 mg, 0.35 mmol), CuI (4.8 mg, 0.025 mmol), 1,10-phenanthroline (4.5 mg, 0.025 mmol), Cs_2CO_3 (122 mg, 0.375 mmol) and DMF (1 mL) at 130 ºC for 24 h. Purification via silica gel column chromatography using 10% CH_2Cl_2 in petroleum ether afforded a white solid (85 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.83 (s, 3H), 6.88 (d, J = 8.8 Hz, 2H), 7.32-7.37 (m, 3H), 7.48 (d, J = 8.4 Hz, 2H), 7.52-7.54 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.3, 88.1, 89.4, 114.0, 115.4, 123.6, 128.0, 128.3, 131.5, 133.1, 159.7 ppm. GC-MS (EI, m/z): 208 [M^+].



2-Methoxydiphenylacetylene (3d)[3]

1-Iodo-2-methoxybenzene (58.5 mg, 0.25 mmol), phenylpropiolic acid (51 mg, 0.35 mmol), CuI (4.8 mg, 0.025 mmol), 1,10-phenanthroline (4.5 mg, 0.025 mmol), Cs_2CO_3 (122 mg, 0.375 mmol) and DMF (1 mL) at 130 ºC for 24 h. Purification via silica gel column chromatography using 10% CH_2Cl_2 in petroleum ether afforded colorless oil (80 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.92 (s, 3H), 6.90 (d, J = 8.4 Hz, 1H), 6.93 (t, J = 7.6 Hz, 1H), 7.30-7.37 (m, 4H), 7.51 (d, J = 7.6 Hz, 1H), 7.57 (d, J = 7.6 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 54.8, 84.7, 92.4, 109.7, 111.4, 119.5, 122.5, 127.1, 127.2, 128.7, 130.6, 132.5, 158.9 ppm. GC-MS (EI, m/z): 208 [M^+].

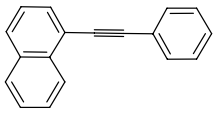


1-(3,5-Bis(octyloxy)-4-(2-phenylethynyl)phenyl)ethanone (3e)

1-(4-Iodo-3,5-bis(octyloxy)phenyl)ethanone (125.5 mg, 0.25 mmol), phenylpropiolic acid (51 mg, 0.35 mmol), CuI (4.8 mg, 0.025 mmol), 1,10-phenanthroline (4.5 mg, 0.25 mmol), Cs_2CO_3 (122 mg, 0.375 mmol) and DMF (1 mL) at 130 ºC for 24 h. Purification via silica gel column chromatography using petroleum ether afforded a yellow solid (93 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.85 (t, J = 6.8 Hz, 3H), 1.28-1.37 (m, 16H), 1.53-1.61 (m, 4H), 1.84-1.91 (m, 4H), 2.60 (s, 3H), 4.10 (t, J = 6.0 Hz, 4H), 7.10 (s, 2H), 7.33-7.39 (m, 3H), 7.54-7.59 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 22.7, 26.1, 26.7, 29.2, 29.3, 29.4, 31.8, 69.2, 82.0, 100.6, 104.6, 107.7, 123.9, 128.19, 128.23, 131.6, 137.5, 160.8, 197.3 ppm. HR-MS (ESI) calcd for $C_{32}H_{45}O_3$ $[M+H]^+$ 477.3369, found: 477.3359.

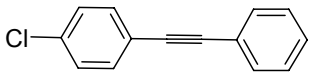
Diphenylacetylene (3f) [2]

Iodobenzene (51 mg, 0.25 mmol), phenylpropiolic acid (51 mg, 0.35 mmol), CuI (4.8 mg, 0.025 mmol), 1,10-phenanthroline (4.5 mg, 0.025 mmol), Cs_2CO_3 (122 mg, 0.375 mmol) and DMF (1 mL) at 130 ºC for 24 h. Purification via silica gel column chromatography using petroleum ether afforded a white solid (99 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33-7.39 (m, 6H), 7.54-7.57 (m, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 89.4, 123.3, 128.3, 128.4, 131.6. GC-MS (EI, m/z): 178 [M^+].



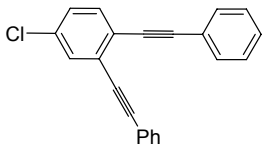
1-(Phenylethynyl)naphthalene (3g) [3]

1-Iodonaphthalene (63.5 mg, 0.25 mmol), phenylpropiolic acid (51 mg, 0.35 mmol), CuI (4.8 mg, 0.025 mmol), 1,10-phenanthroline (4.5 mg, 0.025 mmol), Cs_2CO_3 (122 mg, 0.375 mmol) and DMF (1 mL) at 130 ºC for 24 h. Purification via silica gel column chromatography using petroleum ether afforded colorless oil (86 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38-7.45 (m, 3H), 7.47 (t, J = 8.0 Hz, 1H), 7.55 (t, J = 8.0 Hz, 1H), 7.61 (t, J = 8.0 Hz, 1H), 7.68 (d, J = 1.6 Hz, 1H), 7.70 (d, J = 2.0 Hz, 1H), 7.80 (d, J = 7.2 Hz, 1H), 7.86 (t, J = 9.2 Hz, 2H), 8.48 (d, J = 8.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 86.5, 93.3, 119.9, 122.4, 124.3, 125.2, 125.4, 125.8, 127.3, 127.4, 127.4, 127.8, 129.4, 130.7, 132.2, 132.3.



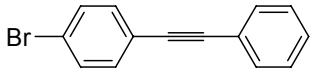
4-Chlorodiphenylacetylene (3h)[4]

1-Chloro-4-iodobenzene (59.5 mg, 0.25 mmol), phenylpropiolic acid (51 mg, 0.35 mmol), CuI (4.8 mg, 0.025 mmol), 1,10-phenanthroline (4.5 mg, 0.025 mmol), Cs_2CO_3 (122 mg, 0.375 mmol) and DMF (1 mL) at 130 ºC for 24 h. Purification via silica gel column chromatography using petroleum ether afforded a white solid (96 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32-7.36 (m, 5H), 7.46 (d, J = 8.4 Hz, 2H), 7.52-7.54 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 88.3, 90.3, 121.8, 122.9, 128.4, 128.5, 128.7, 131.6, 132.8, 134.3. GC-MS (EI, m/z): 212 [M^+].



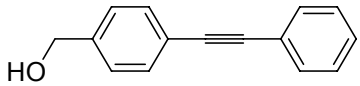
1-(2-(4-Chloro-2-(2-phenylethynyl)phenyl)ethynyl)benzene (3i)[5]

4-Chloro-1-iodo-2-(2-phenylethynyl)benzene (85 mg, 0.25 mmol), phenylpropiolic acid (51 mg, 0.35 mmol), CuI (4.8 mg, 0.025 mmol), 1,10-phenanthroline (4.5 mg, 0.025 mmol), Cs_2CO_3 (122 mg, 0.375 mmol) and DMF (1 mL) at 130 ºC for 24 h. Purification via silica gel column chromatography using petroleum ether afforded a white solid (86 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28 (d, J = 8.0 Hz,, 1H), 7.36-7.42 (m, 6H), 7.48 (d, J = 8.4 Hz,, 1H), 7.56-7.63 (m, 5H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 87.1, 87.4, 94.5, 94.8, 122.8, 123.0, 124.4, 127.4, 128.4, 128.5, 128.5, 128.7, 128.8, 131.6, 131.7, 131.8, 132.8, 133.8 ppm. HR-MS (ESI) calcd for $C_{22}H_{14}Cl$ $[M+H]^+$ 313.0784, found: 313.0792.



4-Bromodiphenylacetylene (3j)[4]

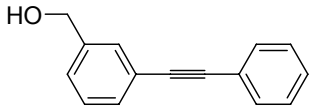
1-Bromo-4-iodobenzene (71 mg, 0.25 mmol), phenylpropiolic acid (51 mg, 0.35 mmol), CuI (4.8 mg, 0.025 mmol), 1,10-phenanthroline (4.5 mg, 0.025 mmol), Cs_2CO_3 (122 mg, 0.375 mmol) and DMF (1 mL) at 130 ºC for 24 h. Purification via silica gel column chromatography using petroleum ether afforded a white solid (83% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35-7.36 (m, 3H), 7.38 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 8.4 Hz, 2H), 7.52-7.54 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 87.8, 90.0, 121.8, 122.0, 122.4, 127.9, 128.0, 131.11, 131.13, 132.5 ppm. GC-MS (EI, m/z): 257 $[M^+]$.



(4-(2-Phenylethynyl)phenyl)methanol (3k)[6]

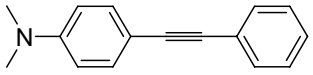
(4-Iodophenyl)methanol (58.5 mg, 0.25 mmol), phenylpropiolic acid (51 mg, 0.35 mmol), CuI (9.6 mg, 0.05 mmol), 1,10-phenanthroline (9.0 mg, 0.05 mmol),

Cs_2CO_3 (122 mg, 0.375 mmol) and DMF (1 mL) at 130 ºC for 24 h. Purification via silica gel column chromatography using 30 % EtOAc in petroleum ether afforded a white solid (84 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.85 (s, 1H), 4.70 (s, 2H), 7.34-7.38 (m, 5H), 7.52-7.55 (m, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 64.4, 88.7, 89.0, 122.0, 122.7, 126.3, 127.8, 127.9, 131.1, 131.3, 140.6 ppm. GC-MS (EI, m/z): 208 [M^+].



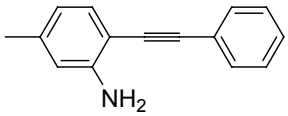
(3-(2-Phenylethynyl)phenyl)methanol (3l)[7]

(3-Iodophenyl)methanol (58.5 mg, 0.25 mmol), phenylpropiolic acid (51 mg, 0.35 mmol), CuI (4.8 mg, 0.025 mmol), 1,10-phenanthroline (4.8 mg, 0.025 mmol), Cs_2CO_3 (122 mg, 0.375 mmol) and DMF (1 mL) at 130 ºC for 24 h. Purification via silica gel column chromatography using 35 % EtOAc in petroleum ether afforded a white solid (93% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.98 (s, 1H), 4.69 (s, 2H), 7.34-7.39 (m, 5H), 7.46 (d, J = 6.4 Hz, 1H), 7.54-7.61 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 63.8, 88.2, 88.5, 122.1, 122.4, 125.8, 127.28, 127.33, 127.6, 129.0, 129.7, 130.6, 140.0 ppm. HR-MS (ESI) calcd for $C_{15}H_{13}O$ $[M+H]^+$ 209.0966, found: 209.1005.



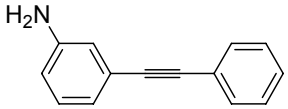
***4-N,N*-dimethyldiphenylacetylene (3m)** [8]

4-Iodo-*N*,*N*-dimethylbenzenamine (61.8 mg, 0.25 mmol), phenylpropiolic acid (51 mg, 0.35 mmol), CuI (9.6 mg, 0.05 mmol), 1,10-phenanthroline (9.0 mg, 0.05 mmol), Cs_2CO_3 (122 mg, 0.375 mmol) and DMF (1 mL) at 130 ºC for 24 h. Purification via silica gel column chromatography using 24 % EtOAc in petroleum ether afforded a white solid (95 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.00 (s, 6H), 6.66 (d, J = 8.4 Hz, 2H), 7.28-7.33 (m, 3H), 7.41 (d, J = 8.8 Hz, 2H), 7.50 (d, J = 6.8 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 40.2, 87.4, 90.6, 110.1, 111.9, 124.2, 127.5, 128.3, 131.3, 132.7, 150.1 ppm. GC-MS (EI, m/z): 221 [M^+].



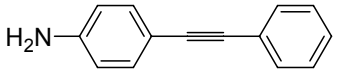
2-Amino-4-methyldiphenylacetylene (3n)[9]

2-Iodo-5-methylbenzenamine (58.3 mg, 0.25 mmol), phenylpropiolic acid (51 mg, 0.35 mmol), CuI (4.8 mg, 0.025 mmol), 1,10-phenanthroline (4.5 mg, 0.025 mmol), Cs_2CO_3 (122 mg, 0.375 mmol) and DMF (1 mL) at 130 ºC for 24 h. Purification via silica gel column chromatography using 30% EtOAc in petroleum ether afforded a yellow solid (91 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.25 (s, 3H), 5.25 (br, 2H), 6.75 (d, J = 8.0 Hz, 1H), 6.94 (d, J = 8.0 Hz, 1H), 7.22 (s, 1H), 7.30-7.32 (m, 3H), 7.53-7.55 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.3, 85.9, 94.6, 108.6, 115.1, 123.3, 127.9, 128.2, 128.3, 130.6, 131.5, 132.3, 144.5.



3-Aminodiphenylacetylene (3o)[10]

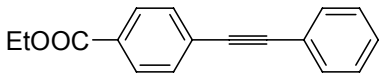
3-Iodobenzenamine (54.8 mg, 0.25 mmol), phenylpropiolic acid (51 mg, 0.35 mmol), CuI (4.8 mg, 0.025 mmol), 1,10-phenanthroline (4.5 mg, 0.025 mmol), Cs_2CO_3 (122 mg, 0.375 mmol) and DMF (1 mL) at 130 ºC for 24 h. Purification via silica gel column chromatography using 30% EtOAc in petroleum ether afforded a yellow solid (90 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.49 (br, 2H), 6.66 (dd, J = 8.0, 2.0 Hz, 1H), 6.87 (s, 1H), 6.96 (d, J = 7.6 Hz, 1H), 7.13 (t, J = 7.6 Hz, 1H), 7.32-7.36 (m, 3H), 7.53-7.55 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 87.8, 88.6, 114.3, 116.8, 121.0, 122.3, 122.9, 127.1, 127.3, 128.3, 130.6, 145.2. GC-MS (EI, m/z): 193 [M^+].



4-Aminodiphenylacetylene (3p)[10]

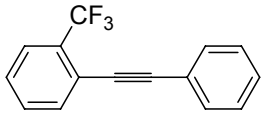
4-Iodobenzenamine (54.8 mg, 0.25 mmol), phenylpropiolic acid (51 mg, 0.35 mmol), CuI (4.8 mg, 0.025 mmol), 1,10-phenanthroline (4.5 mg, 0.025 mmol), Cs_2CO_3 (122 mg, 0.375 mmol) and DMF (1 mL) at 130 ºC for 24 h. Purification via silica gel column chromatography using 30 % EtOAc in petroleum ether afforded a yellow solid (88% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.81 (br, 2H), 6.63 (d, J = 8.4 Hz, 2H), 7.29-7.36 (m, 5H), 7.49 (d, J = 6.8 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$):

δ = 87.3, 90.1, 112.6, 114.8, 123.9, 127.7, 128.3, 131.4, 133.0, 146.7 ppm. GC-MS (EI, m/z): 193 [M^+].



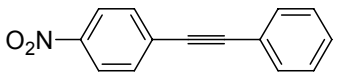
Ethyl 4-(2-phenylethynyl)benzoate (3q)[11]

Ethyl 4-iodobenzoate (69 mg, 0.25 mmol), phenylpropiolic acid (51 mg, 0.35 mmol), CuI (4.8 mg, 0.025 mmol), 1,10-phenanthroline (4.5 mg, 0.025 mmol), Cs_2CO_3 (122 mg, 0.375 mmol) and DMF (1 mL) at 130 ºC for 24 h. Purification via silica gel column chromatography using 20 % CH_2Cl_2 in petroleum ether afforded a white solid (82 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.39 (t, J = 7.2 Hz, 3H), 4.37 (q, J = 7.2 Hz, 2H), 7.36-7.38 (m, 3H), 7.54-7.56 (m, 2H), 7.57 (d, J = 8.4 Hz, 2H), 8.02 (d, J = 8.4 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.3, 61.1, 88.7, 92.3, 122.7, 127.9, 128.4, 128.8, 129.5, 129.8, 131.5, 131.7, 166.1.



2-Trifluoromethyldiphenylacetylene (3r)[8]

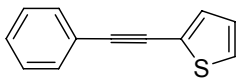
1-Iodo-2-(trifluoromethyl)benzene (68 mg, 0.25 mmol), phenylpropiolic acid (51 mg, 0.35 mmol), CuI (4.8 mg, 0.025 mmol), 1,10-phenanthroline (4.5 mg, 0.025 mmol), Cs_2CO_3 (122 mg, 0.375 mmol) and DMF (1 mL) at 130 ºC for 24 h. Purification via silica gel column chromatography using petroleum ether afforded colorless oil (80 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35-7.38 (m, 3H), 7.42 (d, J = 7.6 Hz, 1H), 7.51 (t, J = 7.6 Hz, 1H), 7.54-7.57 (m, 2H), 7.67 (t, J = 7.2 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 85.4, 95.0, 121.6, 122.8, 125.83, 125.88, 125.93, 125.99, 127.9, 128.4, 128.5, 128.8, 131.4, 131.7, 132.5, 133.7.



4-Nitrodiphenylacetylene (3s)[3]

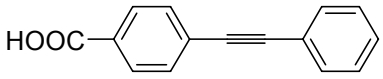
p-Nitro-1-iodobenzene (63 mg, 0.25 mmol), phenylpropiolic acid (51 mg, 0.35 mmol), CuI (4.8 mg, 0.025 mmol), 1,10-phenanthroline (4.5 mg, 0.025 mmol), Cs_2CO_3 (122

mg, 0.375 mmol) and DMF (1 mL) at 130 ºC for 24 h. Purification via silica gel column chromatography using 25% EtOAc in petroleum ether afforded a yellow solid (98 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39-7.40 (m, 3H), 7.55-7.57 (m, 2H), 7.66 (d, J = 8.4 Hz, 2H), 8.21 (d, J = 8.8 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 87.6, 94.7, 122.1, 123.6, 128.5, 129.3, 130.3, 131.8, 132.3, 147.0 ppm. HR-MS (ESI) calcd for $C_{14}H_9NO_2Na$ $[M+Na]^+$ 246.0531, found: 246.0533.



2-(Phenylethynyl)thiophene (3t)[3]

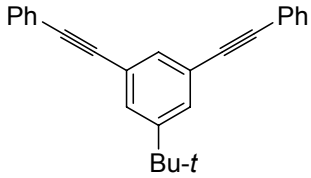
2-Iodothiophene (52.5 mg, 0.25 mmol), phenylpropiolic acid (51 mg, 0.35 mmol), CuI (4.8 mg, 0.025 mmol), 1,10-phenanthroline (4.5 mg, 0.025 mmol), Cs_2CO_3 (122 mg, 0.375 mmol) and DMF (1 mL) at 130 ºC for 24 h. Purification via silica gel column chromatography using petroleum ether afforded a white solid (95% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.01 (t, J = 4.4 Hz, 1H), 7.29 (d, J = 4.4 Hz, 2H), 7.35-7.39 (m, 3H), 7.52-7.55 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 82.6, 93.1, 123.0, 123.4, 127.1, 127.3, 128.39, 128.44, 131.4, 131.9 ppm. GC-MS (EI, m/z): 184 $[M^+]$.



4-Carboxyl diphenylacetylene (3u)[12]

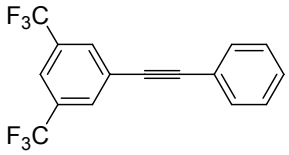
4-Iodobenzoic acid (62 mg, 0.25 mmol), phenylpropiolic acid (51 mg, 0.35 mmol), CuI (9.6 mg, 0.05 mmol), 1,10-phenanthroline (9.0 mg, 0.05 mmol), Cs_2CO_3 (196 mg, 0.60 mmol) and DMF (1 mL) at 130 ºC for 24 h. The reaction mixture was then allowed to cool to ambient temperature, carefully acidified with dilute aqueous HCl, diluted with 4-5 mL of ethyl acetate, filtered through a plug of silica gel, and washed with 10-20 mL of ethyl acetate. The combined organic extracts were concentrated and the resulting residue was purified by column chromatography on silica gel to provide a white solid (85 % yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.43-7.45 (m, 3H), 7.56-7.59 (m, 4H), 7.97 (d, J = 7.2 Hz, 2H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 89.1, 92.4, 122.3, 126.9, 129.3, 129.7, 130.1, 131.3, 131.96, 132.00, 167.3. HR-MS

(ESI) calcd for $C_{15}H_{11}O_2$ $[M+H]^+$ 223.0759, found:223.0764.



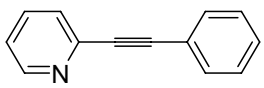
1-*t*-Butyl-3,5-bis(2-phenylethynyl)benzene (3v)

1-t-Butyl-3,5-diiodobenzene (96.5 mg, 0.25 mmol), phenylpropiolic acid (102 mg, 0.70 mmol), CuI (9.6 mg, 0.05 mmol), 1,10-phenanthroline (9.0 mg, 0.05 mmol), Cs_2CO_3 (244 mg, 0.75 mmol) and DMF (1 mL) at 130 ºC for 24 h. Purification via silica gel column chromatography using petroleum ether afforded a white solid (92 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.37 (s, 9H), 7.36-7.40 (m, 6H), 7.55-7.57 (m, 7H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.2, 34.8, 89.1, 89.4, 123.1, 123.2, 128.38, 128.39, 128.7, 131.7, 131.8, 151.6 ppm. HR-MS (ESI) calcd for $C_{26}H_{23}$ $[M+H]^+$ 335.1800, found:335.1806.



3, 5-Ditrifluoromethyldiphenylacetylene (3w)[2]

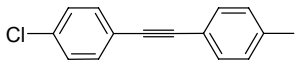
1-Bromo-3,5-bis(trifluoromethyl)benzene (73.3 mg, 0.25 mmol), phenylpropiolic acid (51 mg, 0.35 mmol), CuI (4.8 mg, 0.025 mmol), 1,10-phenanthroline (4.5 mg, 0.025 mmol), Cs_2CO_3 (122 mg, 0.375 mmol) and DMF (1 mL) at 130 ºC for 24 h. Purification via silica gel column chromatography using petroleum ether afforded a yellow solid (78 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37-7.40 (m, 3H), 7.55-7.57 (m, 2H), 7.82 (s, 1H), 7.96 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 86.4, 92.9, 121.6 (m), 122.0, 122.2, 124.0, 125.8, 128.7, 129.4, 131.6 (m), 132.0 (m) ppm. HR-MS (ESI) calcd for $C_{16}H_9F_6$ $[M+H]^+$ 315.0608, found: 315.0651.



2-(2-phenylethynyl)pyridine (3x) [4]

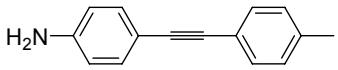
2-Bromopyridine (40 mg, 0.25 mmol), phenylpropiolic acid (51 mg, 0.35 mmol), CuI (9.6 mg, 0.05 mmol), 1,10-phenanthroline (9.0 mg, 0.05 mmol), Cs_2CO_3 (122 mg,

0.375 mmol) and DMF (1 mL) at 130 ºC for 24 h. Purification via silica gel column chromatography using 10 % CH_2Cl_2 in petroleum ether afforded colorless oil (94 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.20-7.24 (m, 1H), 7.34-7.36 (m, 3H), 7.50 (d, J = 7.6 Hz, 1H), 7.58-7.61 (m, 2H), 7.64 (td, J = 7.6, 1.6 Hz, 1H), 8.60 (d, J = 4.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 88.1, 88.9, 121.7, 122.3, 126.7, 127.9, 128.5, 131.6, 135.8, 142.9, 149.5 ppm. GC-MS (EI, m/z): 179 [M^+].



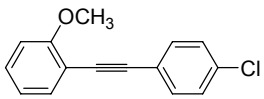
1-(2-(4-Chlorophenyl)ethynyl)-4-methylbenzene (4a) [13]

1-Iodo-4-methylbenzene (54.5 mg, 0.25 mmol), 3-(4-chlorophenyl)propiolic acid (63.2 mg, 0.35 mmol), CuI (4.8 mg, 0.025 mmol), 1,10-phenanthroline (4.5 mg, 0.025 mmol), Cs_2CO_3 (122 mg, 0.375 mmol) and DMF (1 mL) at 130 ºC for 24 h. Purification via silica gel column chromatography using petroleum ether afforded a white solid (91 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.37 (s, 3H), 7.15 (d, J = 8.0 Hz, 2H), 7.30-7.33 (m, 2H), 7.41-7.46 (m, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.0, 87.1, 90.0, 119.4, 121.5, 128.2, 128.7, 131.0, 132.3, 133.6, 138.2 ppm. GC-MS (EI, m/z): 226 [M^+].



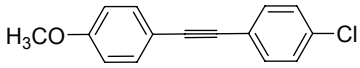
4-(2-*p*-Tolylethynyl)benzenamine (4b)[13]

4-Iodobenzenamine (54.8 mg, 0.25 mmol), 3-*p*-tolylpropiolic acid (56 mg, 0.35 mmol), CuI (4.8 mg, 0.025 mmol), 1,10-phenanthroline (4.5 mg, 0.025 mmol), Cs_2CO_3 (122 mg, 0.375 mmol) and DMF (1 mL) at 130 ºC for 24 h. Purification via silica gel column chromatography using 30% EtOAc in petroleum ether afforded a white solid (82 % yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.36 (s, 3H), 3.80 (br, 2H), 6.62 (d, J = 8.4 Hz, 2H), 7.13 (d, J = 7.8 Hz, 2H), 7.32 (d, J = 7.8 Hz, 2H), 7.38 (d, J = 7.8 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.5, 87.4, 89.4, 112.9, 114.8, 120.8, 129.0, 131.3, 132.9, 137.7, 146.5 ppm. GC-MS (EI, m/z): 207 [M^+].



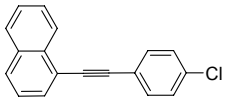
1-Chloro-4-(2-(2-methoxyphenyl)ethynyl)benzene (4c)

1-Chloro-4-iodobenzene (59.5 mg, 0.25 mmol), 3-(2-methoxyphenyl)propiolic acid (61.6 mg, 0.375 mmol), CuI (9.6 mg, 0.05 mmol), 1,10-phenanthroline (9.0 mg, 0.05 mmol), Cs_2CO_3 (122 mg, 0.375 mmol) and DMF (1 mL) at 130 ºC for 24 h. Purification via silica gel column chromatography using 10% CH_2Cl_2 in petroleum ether afforded a white solid (90% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.92 (s, 3H), 6.90 (d, J = 5.6 Hz, 1H), 6.94 (t, J = 5.2 Hz, 1H), 7.31-7.34 (m, 3H), 7.48 (d, J = 5.6 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.8, 86.8, 92.3, 110.7, 112.1, 120.5, 122.1, 128.6, 130.0, 132.9, 133.6, 134.1, 160.0 ppm. HR-MS (ESI) calcd for $C_{15}H_{12}ClO$ $[M+H]^+$ 243.0577, found: 243.0570.



1-Chloro-4-(2-(4-methoxyphenyl)ethynyl)benzene (4d)[13]

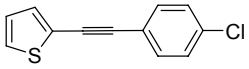
1-Chloro-4-iodobenzene (59.5 mg, 0.25 mmol), 3-(4-methoxyphenyl)propiolic acid (61.6 mg, 0.375 mmol), CuI (4.8 mg, 0.025 mmol), 1,10-phenanthroline (4.5 mg, 0.025 mmol), Cs_2CO_3 (122 mg, 0.375 mmol) and DMF (1 mL) at 130 ºC for 24 h. Purification via silica gel column chromatography using 10% CH_2Cl_2 in petroleum ether afforded a yellow solid (92% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.83 (s, 3H), 6.87 (d, J = 8.8 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.42-7.47 (m, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.3, 87.0, 90.4, 114.1, 115.0, 122.1, 128.7, 132.6, 133.1, 133.9, 159.8 ppm. GC-MS (EI, m/z): 242 $[M^+]$.



1-(2-(4-Chlorophenyl)ethynyl)naphthalene (4e)[14]

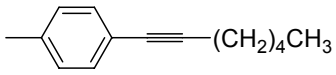
1-Chloro-4-iodobenzene (59.5 mg, 0.25 mmol), 3-(naphthalen-1-yl)propiolic acid (68.6 mg, 0.35 mmol), CuI (4.8 mg, 0.025 mmol), 1,10-phenanthroline (4.5 mg, 0.025 mmol), Cs_2CO_3 (122 mg, 0.375 mmol) and DMF (1 mL) at 130 ºC for 24 h. Purification via silica gel column chromatography using petroleum ether afforded a yellow solid (90 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37 (d, J = 8.0 Hz, 2H), 7.45 (t, J = 7.6 Hz, 1H), 7.53-7.63 (m, 4H), 7.75 (d, J = 7.2 Hz, 1H), 7.85 (t, J = 7.2 Hz, 2H), 8.40 (d, J = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 88.5, 93.2,

120.6, 121.9, 125.3, 126.1, 126.5, 126.9, 128.4, 128.8, 129.0, 130.5, 132.9, 133.2, 134.4 ppm. GC-MS (EI, m/z): 262 [M^+].



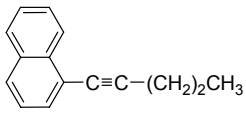
2-(2-(4-Chlorophenyl)ethynyl)thiophene (4f)[14]

1-Chloro-4-iodobenzene (59.5 mg, 0.25 mmol), 3-(thiophen-2-yl)propiolic acid (53.2 mg, 0.35 mmol), CuI (4.8 mg, 0.025 mmol), 1,10-phenanthroline (4.5 mg, 0.025 mmol), Cs_2CO_3 (122 mg, 0.375 mmol) and DMF (1 mL) at 130 ºC for 24 h. Purification via silica gel column chromatography using petroleum ether afforded a white solid (87 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.01 (t, J = 4.0 Hz, 1H), 7.28-7.33 (m, 4H), 7.43 (d, J = 8.0 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 83.6, 91.9, 121.4, 122.9, 127.2, 127.6, 128.7, 132.1, 132.6, 134.4 ppm. GC-MS (EI, m/z): 218 [M^+].



1-(Hept-1-ynyl)-4-methylbenzene (4g)[15]

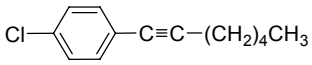
1-Iodo-4-methylbenzene (54.5 mg, 0.25 mmol), oct-2-ynoic acid (49 mg, 0.35 mmol), CuI (4.8 mg, 0.025 mmol), 1,10-phenanthroline (4.5 mg, 0.25 mmol), Cs_2CO_3 (122 mg, 0.375 mmol) and DMF (1 mL) at 130 ºC for 24 h. Purification via silica gel column chromatography using petroleum ether afforded colorless oil (85% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91 (t, J = 6.8 Hz, 3H), 1.31-1.44 (m, 4H), 1.57-1.64 (m, 2H), 2.33 (s, 3H), 2.37 (t, J = 7.2 Hz, 2H), 7.08 (d, J = 7.6 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.5, 18.9, 20.9, 21.8, 28.1, 30.7, 80.1, 89.2, 120.5, 128.4, 130.9, 136.9 ppm. GC-MS (EI, m/z): 186 [M^+].



1-(Pent-1-ynyl)naphthalene (4h)

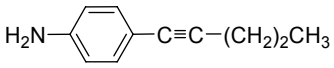
1-Iodonaphthalene (63.5 mg, 0.25 mmol), hex-2-ynoic acid (39.2 mg, 0.35 mmol), CuI (9.6 mg, 0.05 mmol), 1,10-phenanthroline (9.0 mg, 0.05 mmol), Cs_2CO_3 (122 mg, 0.375 mmol) and DMF (1 mL) at 130 ºC for 24 h. Purification via silica gel column chromatography using petroleum ether afforded colorless oil (88 % yield). ^{1}H NMR

(400 MHz, $CDCl_3$): δ = 1.15 (t, J = 7.6 Hz, 3H), 1.73-1.80 (m, 2H), 2.57 (t, J = 6.8 Hz, 1H), 7.40 (t, J = 8.0 Hz, 1H), 7.51 (t, J = 7.2 Hz, 1H), 7.57 (t, J = 8.0 Hz, 1H), 7.65 (d, J = 7.2 Hz, 1H), 7.79 (d, J = 8.4 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.7, 21.8, 22.4, 78.8, 95.4, 121.9, 125.3, 126.2, 126.3, 126.5, 127.9, 128.2, 130.0, 133.3, 133.6 ppm. GC-MS (EI, m/z): 194 [M^+].



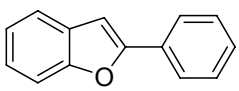
1-Chloro-4-(hept-1-ynyl)benzene (4i)[15]

1-Chloro-4-iodobenzene (59.5 mg, 0.25 mmol), oct-2-ynoic acid (49 mg, 0.35 mmol), CuI (4.8 mg, 0.025 mmol), 1,10-phenanthroline (4.5 mg, 0.025 mmol), Cs_2CO_3 (122 mg, 0.375 mmol) and DMF (1 mL) at 130 ºC for 24 h. Purification via silica gel column chromatography using petroleum ether afforded colorless oil (87 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91 (t, J = 6.8 Hz, 3H), 1.31-1.44 (m, 4H), 1.57-1.64 (m, 2H), 2.37 (t, J = 6.8 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0, 19.4, 22.2, 28.4, 31.1, 79.5, 91.6, 122.6, 128.5, 132.8, 133.4 ppm. GC-MS (EI, m/z): 206 [M^+].



4-(Pent-1-ynyl)benzenamine (4j)

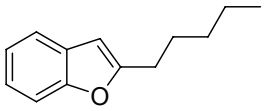
4-Iodobenzenamine (54.8 mg, 0.25 mmol), hex-2-ynoic acid (39.2 mg, 0.35 mmol), CuI (9.6 mg, 0.05 mmol), 1,10-phenanthroline (9.0 mg, 0.05 mmol), Cs_2CO_3 (122 mg, 0.375 mmol) and DMF (1 mL) at 130 ºC for 24 h. Purification via silica gel column chromatography using 30 % EtOAc in petroleum ether afforded colorless oil (84 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.01 (t, J = 7.2 Hz, 3H), 1.56-1.65 (m, 2H), 2.34 (t, J = 7.2 Hz, 2H), 3.48 (br, 2H), 6.58 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 8.4 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.6, 21.4, 22.4, 80.9, 87.7, 113.7, 114.8, 132.7, 145.9 ppm. GC-MS (EI, m/z): 159 [M^+].



2-Phenylbenzofuran (5a)[16]

2-Iodophenol (55 mg, 0.25 mmol), phenylpropiolic acid (51 mg, 0.35 mmol), CuI (4.8

mg, 0.025 mmol), 1,10-phenanthroline (4.5 mg, 0.025 mmol), Cs_2CO_3 (122 mg, 0.375 mmol) and DMF (1 mL) at 130 ºC for 24 h. Purification via silica gel column chromatography using petroleum ether afforded a white solid (86 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.04 (s, 1H), 7.22 (t, J = 7.2 Hz, 1H), 7.28 (t, J = 7.6 Hz, 1H), 7.34 (t, J = 7.2 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 7.53 (d, J = 8.0 Hz, 1H), 7.59 (d, J = 7.6 Hz, 1H), 7.87 (d, J = 7.6 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 100.8., 110.7, 120.4, 122.4, 123.8, 124.4, 128.1, 128.3, 128.7, 130.0, 154.41, 155.44 ppm.



2-Pentylbenzofuran (5b)[17]

2-Iodophenol (55 mg, 0.25 mmol), oct-2-ynoic acid (49 mg, 0.35 mmol), CuI (4.8 mg, 0.025 mmol), 1,10-phenanthroline (4.5 mg, 0.025 mmol), Cs_2CO_3 (122 mg, 0.375 mmol) and DMF (1 mL) at 130 ºC for 24 h. Purification via silica gel column chromatography using petroleum ether afforded colorless oil (83 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, J = 4.4 Hz, 3H), 1.37-1.40 (m, 4H), 1.73-1.78 (m, 2H), 2.75 (t, J = 5.2 Hz, 2H), 6.38 (s, 1H), 7.16-7.22 (m, 2H), 7.40 (d, J = 5.2 Hz, 1H), 7.47 (d, J = 4.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0, 22.4, 27.4, 28.4, 31.4, 101.8, 110.7, 120.2, 122.4, 123.0, 129.1, 154.6, 159.8 ppm. GC-MS (EI, m/z): 188 [M^+].

VI. DFT simulation on the copper-catalyzed decarboxylative cross-coupling of alkynyl carboxylic acid with aryl halide

(i) Computational details

The geometry optimizations for all stationary points, including reactant complex (RC), product complex (PC), transition state (TS), and intermediate (INT), were performed in the gas phase using the density functional theory with the Beck's three-parameter exchange function and the gradient-corrected function of Lee, Yang, and Parr (B3LYP).[18, 19] The standard 6-31G(d) basis set[20] was applied for C, H, N, O, and Cu atoms, while the Stuttgart RSC 1997 ECP (ECP10MDF)[21] was used to describe I and Cs atoms. Each stationary point was confirmed by the harmonic

frequency analysis at the same calculational level as a true minimum with no imaginary frequency or a transition state with only one imaginary frequency. The frequency calculations without scaling also provided the thermodynamic quantities such as the zero-point vibrational energy, thermal correction, enthalpies, Gibbs free energies, and entropies at temperature of 298.15 K and pressure of 101325 Pa. Transition state structures were verified with intrinsic reaction coordinate (IRC)[22,23] calculations at the same level of theory indeed to connect two relevant minima. All calculations were carried out using Gaussian 03 program.[24]

(ii) Free energy profiles of two plausible mechanisms

Two plausible mechanisms illustrated in Figure S1 were proposed. We herein addressed the competition between oxidative addition and decarboxylation with the DFT calculations of the corresponding reaction mechanisms. In pathway A, the oxidative addition of PhI (Re3) with the copper(I)-phen complex Re1 occurred initially with the activation free energy of +13.1 kcal.mol^{-1}. The resulting copper(III) species INTa1 reacted with alkynyl carboxylate (Re2) to form the intermediate INTa2, which subsequently encountered the decarboxylation via the transition state TSa2. The free energy barrier for the decarboxylation of INTa2 to TSa2 was calculated to be +18.8 kcal.mol^{-1}, which was higher than that of the oxidative addition. It suggested that pathway A involved a rate-determining decarboxylation process. After the decarboxylation, reductive elimination proceeded to yield the corresponding product PC.

In an alternative route, the Cu(I)-phen complex (Re1) and alkynyl carboxylate (Re2) first formed the complex RCb, which subsequently underwent the decarboxylation through the transition state TSb1 ($\Delta G^{\neq}$ = +7.1 kcal.mol^{-1}). After the decarboxylation, a high-energy step was identified for the oxidative addition of PhI from INTb to TSb2 ($\Delta G^{\neq}$ = +34.7 kcal.mol^{-1}). Therefore, the oxidative addition constituted the rate-limiting step in pathway B.

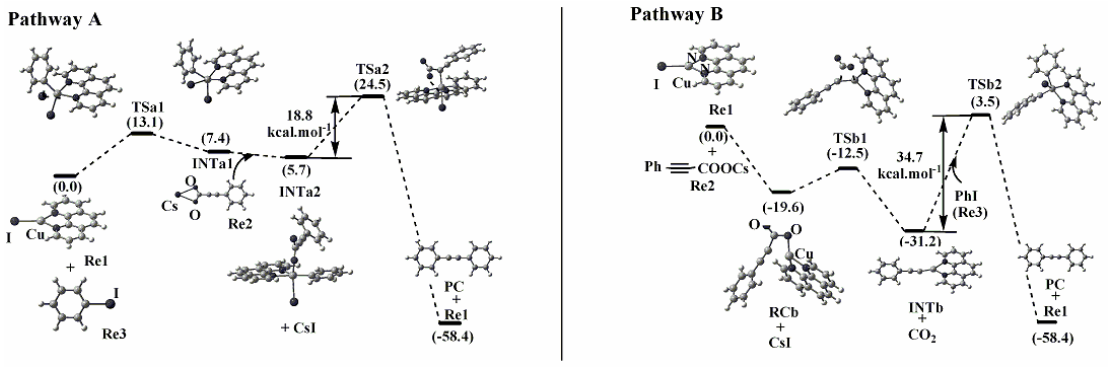
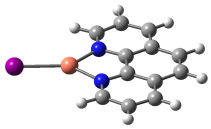


Figure S1. Free energy profiles of two plausible mechanisms for the copper-catalyzed decarboxylative cross-coupling of alkynyl carboxylic acid with aryl iodide calculated at the B3LYP level with SDD basis set for I and Cs as well as 6-31G(d) for C, H, O, N, and Cu. All energies (in parentheses) are given in kcal.mol^{-1}.

Since $\Delta G^{\neq}$ in the rate-limiting step in pathway A is 15.9 kcal.mol^{-1} lower than that of pathway B, we concluded that pathway A should be substantially more favorable and the decarboxylation likely occurred on the copper(III) species after the oxidative addition.

(iii) Cartesian coordinates and electronic energies in the gas phase for all speices

Re1



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6	0.568235	2.665914	0.000353
6	4.266730	0.682314	-0.000373
6	4.266786	-0.682058	-0.000340
6	3.037664	-1.425243	-0.000122
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1	-0.416862	3.122288	0.000577
1	1.644397	4.535381	0.000130
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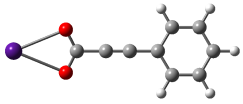
$C_6H_5C{\equiv}CCOOCs$ (Re2)



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6	6.408355	0.000309	-0.002528
6	-0.527349	-0.000482	0.001259
8	-1.088134	1.085124	0.323414
8	-1.088022	-1.086036	-0.321245
1	3.763930	-2.136590	0.224215
1	6.246761	-2.139084	0.226156
1	7.495260	0.000388	-0.004506
1	6.245592	2.139808	-0.229463
1	3.762772	2.136716	-0.220008
6	0.949561	-0.000474	0.001593
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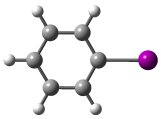
PhI (Re3)



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CsI

E = -31.6568362401 A.U.

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CO_2

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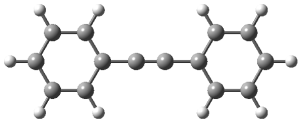
PC



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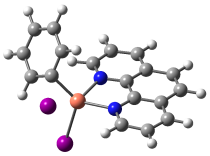
Pathway A

TSa1



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6	-1.023521	-2.552084	-1.067266
6	-4.793346	-0.727570	-0.908775
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1	2.863091	3.767510	0.833484
1	1.899110	4.923637	-1.153097
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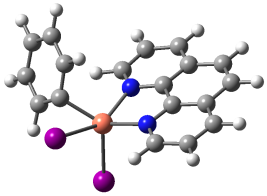
INTa1



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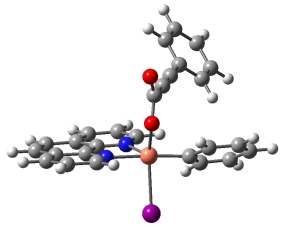
INTa2



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6	4.077344	0.808555	0.671691
6	4.567298	-0.056832	-0.328322
6	5.721221	0.271540	-1.036858
6	6.400781	1.462636	-0.767131
6	5.922553	2.325876	0.222538
6	4.773374	2.003974	0.940848
7	-0.087008	1.029189	-0.799887
6	-0.978242	2.043389	-0.672247
6	-0.835511	3.288477	-1.334397
6	0.301150	3.454401	-2.156495
6	1.215541	2.426089	-2.262609
6	0.981675	1.228096	-1.559417
6	-1.820271	4.313312	-1.130136
6	-2.874710	4.118669	-0.288516
6	-3.038453	2.879260	0.417028
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6	-4.150199	1.418786	1.986124
6	-4.086945	2.633074	1.330343
6	0.726160	-0.170730	2.828484
8	-0.313930	-0.698121	2.227816
8	0.775021	0.019741	4.035693
1	-4.934820	1.204533	2.703458
1	-3.191690	-0.523490	2.205053
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1	-1.700648	5.257774	-1.653957
1	0.091272	-3.105536	1.999727
1	0.792358	-1.597899	-1.975081
1	1.797530	-4.853021	1.628887
1	2.553088	-3.288304	-2.309824
1	3.059731	-4.942799	-0.515998
53	-2.502139	-1.948253	-1.227724
1	4.402541	2.667363	1.716077
1	6.450591	3.250523	0.439842
1	7.300743	1.714553	-1.321594
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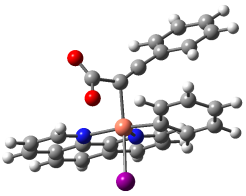
TSa2



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6	1.208252	-1.855135	-0.357674
6	1.762393	-1.620835	-1.613600
6	2.967358	-2.244496	-1.960315
29	-0.237486	-0.764882	0.281563
6	3.060546	1.509688	0.979845
6	4.216001	0.827573	0.530899

6	5.327008	1.546865	0.103276
6	5.308666	2.945547	0.119374
6	4.172100	3.630898	0.562600
6	3.053513	2.923417	0.988752
7	-0.316661	1.196295	-1.119134
6	-1.456463	1.868300	-0.830469
6	-1.837272	3.059194	-1.505047
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6	-3.066107	3.712111	-1.158019
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6	-2.302827	1.347804	0.218816
7	-1.910410	0.226901	0.879846
6	-2.679147	-0.257953	1.854214
6	-3.891763	0.345400	2.228471
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6	1.932952	0.778989	1.412915
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6	0.229544	-0.635698	2.970173
8	0.226645	0.042878	3.985126
1	-4.474949	-0.091842	3.031423
1	-2.296270	-1.139198	2.359325
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1	1.249441	-1.006507	-2.344723
1	3.463370	-4.064191	0.870936
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1	2.168181	3.442187	1.342448
1	4.163683	4.717127	0.578225
1	6.181444	3.502239	-0.211115
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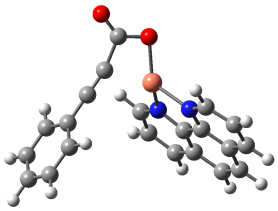
1	4.215805	-0.257631	0.521828

Pathway B

RCb



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6	1.830611	-2.886273	-1.949673
6	0.665528	-2.442041	-2.551190
6	0.120129	-1.207264	-2.168337
6	2.333574	-0.052420	0.437181
6	3.541319	-0.423797	1.076032
6	4.182361	-1.650235	0.691302
6	3.643192	-2.457502	-0.265978
6	4.039174	0.441735	2.072770
6	3.334985	1.592359	2.382529
6	2.132309	1.864142	1.710696
7	1.627690	1.066357	0.768550
29	0.089435	1.325145	-0.522433
8	-0.306035	3.113191	-1.167650
6	-1.594448	3.069093	-1.022872
8	-2.437282	3.913707	-1.257044
6	-1.979313	1.713012	-0.461296
6	-2.565000	0.755684	0.044348
6	-3.230483	-0.377087	0.587364
6	-3.200229	-0.639850	1.973796
6	-3.864269	-1.745477	2.495909
6	-4.569222	-2.610023	1.653775
6	-4.607986	-2.358585	0.279769
6	-3.947456	-1.255632	-0.253304
1	0.177403	-3.022634	-3.327169
1	-0.778841	-0.822914	-2.640340
1	2.287582	-3.828017	-2.241473
1	4.131875	-3.388562	-0.540307
1	1.551323	2.751781	1.943303
1	-3.984879	-1.052770	-1.319278
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1	-3.833906	-1.933217	3.565932

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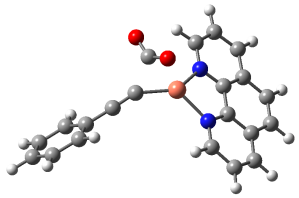
TSb1



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6	4.216643	-1.988092	1.219741
6	3.238966	-2.927119	0.947093
6	2.019100	-2.511814	0.381308
6	2.418036	1.053831	-0.004148
6	3.367099	2.073079	0.244830
6	4.626725	1.720734	0.839123
6	4.920401	0.427592	1.158303
6	3.011387	3.390524	-0.117973
6	1.775867	3.624475	-0.692713
6	0.898952	2.546641	-0.903229
7	1.201585	1.291858	-0.573479
29	0.121144	-0.382316	-0.697535
6	-1.049895	-1.992896	-1.397105
8	-1.162188	-3.075525	-0.855940
8	-0.591345	-1.532498	-2.460278
6	-1.755069	-0.678327	-0.449687
6	-2.869053	-0.289972	-0.091647
6	-4.159368	0.115713	0.342616
6	-4.628271	-0.230415	1.628036
6	-5.893836	0.166373	2.049273
6	-6.718618	0.909283	1.199937
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6	-5.001836	0.868534	-0.503109
1	3.394169	-3.978441	1.165983
1	1.218675	-3.213054	0.158682
1	5.164829	-2.282071	1.662347
1	5.879096	0.175640	1.603718
1	-0.078382	2.699240	-1.350394

1	-4.646778	1.134603	-1.494056
1	-6.908411	1.830680	-0.741756
1	-7.707713	1.214663	1.530924
1	-6.241635	-0.107868	3.041815
1	-3.985779	-0.814065	2.279933
1	5.348269	2.511256	1.026828
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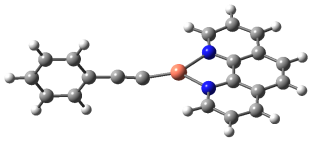
INTb



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6	-3.781208	2.837078	0.062479
6	-2.547575	3.450177	-0.056439
6	-1.389859	2.658154	-0.162359
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6	-3.853590	-1.425036	0.072003
6	-5.076858	-0.681121	0.188947
6	-5.076405	0.683126	0.189179
6	-3.783083	-2.835894	0.061718
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7	-1.420632	-1.327191	-0.153253
29	0.078172	-0.000735	-0.078781
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6	3.102246	-0.000940	0.105219
6	4.524467	-0.000496	0.068975
6	5.226559	0.001005	-1.156359
6	6.618716	0.001493	-1.185050
6	7.353193	0.000506	0.003566
6	6.674238	-0.000991	1.225150
6	5.282649	-0.001502	1.261245
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1	-0.408628	-3.110226	-0.254437

1	4.757403	-0.002672	2.211782
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1	8.439870	0.000895	-0.021476
1	7.134711	0.002659	-2.142612
1	4.659481	0.001775	-2.082788
1	-6.010336	-1.230245	0.278953
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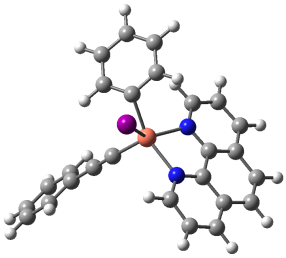
TSb2



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6	4.067239	-1.189464	0.071571
6	4.567834	-1.684458	1.295161
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29	-0.217441	0.380292	-0.072134
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6	-2.639855	-3.013713	-1.149391
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6	-1.767514	-2.264996	-3.270038
6	-1.173267	-1.180068	-2.601143
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6	-1.490597	-0.383383	2.670331
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1	6.821555	-1.828890	-1.854352
1	4.538757	-0.873309	-2.007248

VII. References

1. J. P. Das, U. K. Roy and S. Roy, *Organometallics* 2005**, 24***,* 6136.

2. J.-C. Hierso, J. Boudon, M. Picquet and P. Meunier, *Eur. J. Org. Chem.,* 2007, 583.

3. A. D. Finke, E. C. Elleby, M. J. Boyd, H. Weissman and J. S. Moore, *J. Org. Chem.,* 2009, **74**, 8897.

4. G. Fabrizi, A. Goggiamani, A. Sferrazza and S. Cacchi, *Angew. Chem. Int. Ed.,* 2010, **49**, 4067.

5. J. Blum, W. Baidossi, Y. Badrieh and R. E. Hoffman, *J. Org. Chem.,* 1996, **60**, 4738.

6. S. Raghavan and A. Rajender, *Chem. Commun.,* 2002, 1572.

7. N. Matsunaga, T. Kaku, F. Itoh, T. Tanaka, T. Hara, H. Miki, M. Iwasaki, T. Aono, M. Yamaok, M. Kusakab and A. Tasakaa, *Bioorg. & Med. Chem.,* 2004, **12**, 2251.

8. C. A. Fleckenstein and H. Plenio, *Chem. Eur. J.* 2007, **13**, 2701.

9. J. S. Kim, J. H. Han, J. J. Lee, Y. M. Jun, B. M. Lee and B. H. Kim, *Tetrahedron Lett.,* 2008, **49**, 3733.

10. M. S. M. Ahmed and A. Mori, *Tetrahedron* 2004, **60**, 9977.

11. H. Kima and P. H. Lee, *Adv. Synth. Catal.* 2009, **351**, 2827.

12. L. R. Moore, E. C. Western, R. Craciun, J. M. Spruell, D. A. Dixon, K. P. O'Halloran and K. H. Shaughnessy, *Organometallics* 2008, **27**, 576.

13. C. Pan, F. Luo, W. Wang, Z. Ye and J. Cheng, *Tetrahedron Lett.,* 2009, **50**, 5044.

14. M. J. Mio, L. C. Kopel, J. B. Braun, T. L. Gadzikwa, K. L. Hull, R. G. Brisbois, C. J. Markworth and Paul A. Grieco, *Org. Lett.,* 2002, **4**, 3199.

15. C. Yi and R. Hua, *J. Org. Chem.,* 2006, **71**, 2535.

16. J. -M. Becht, A. Gissot, A.Wagner and C. Miokowski, *Chem. Eur. J.,* 2003, **9**, 3209.

17. X. Guinchard, X. Bugaut, C. Cook and E. Roulland, *Chem. Eur. J.,* 2009, **15**, 5793.

18. A. D. Beck, *J. Chem. Phys.* 1993, ***98***, 5648.

[19] R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules*; Oxford University Press: Oxford, U.K., 1989.

[20] R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys.* 1980, ***72***, 650.

[21] M. Dolg, U. Wedig, H. Stoll and H. Preuss, *J. Chem. Phys.*1987, ***86***, 866.

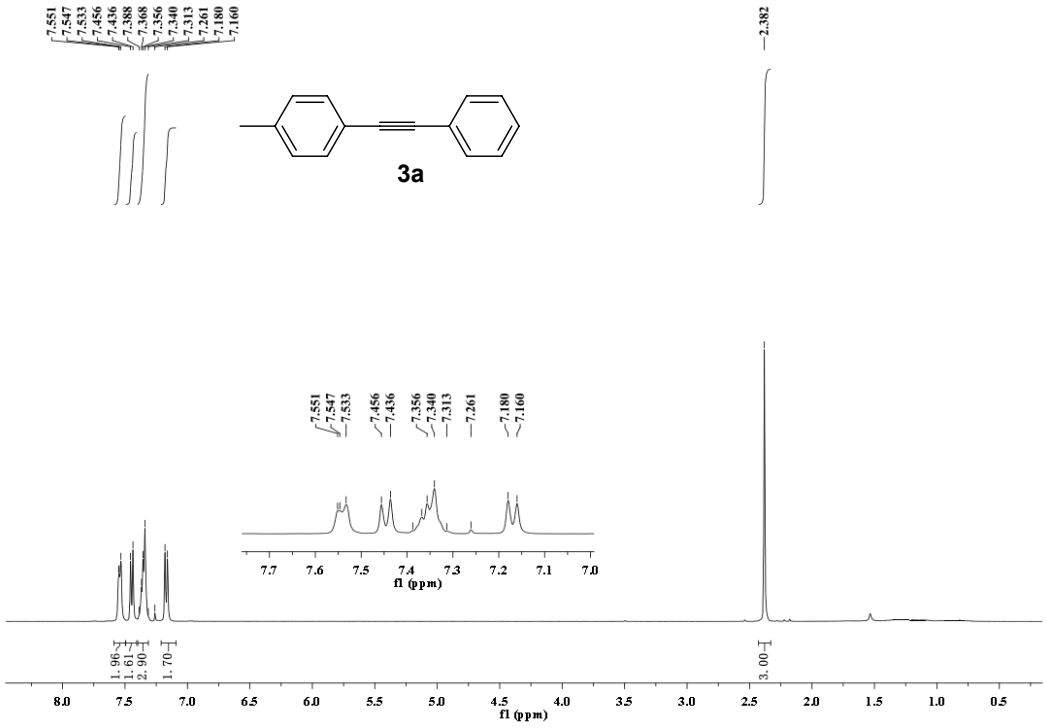
[22] K. Fukui, *J. Phys. Chem.* 1970, ***74***, 4161.

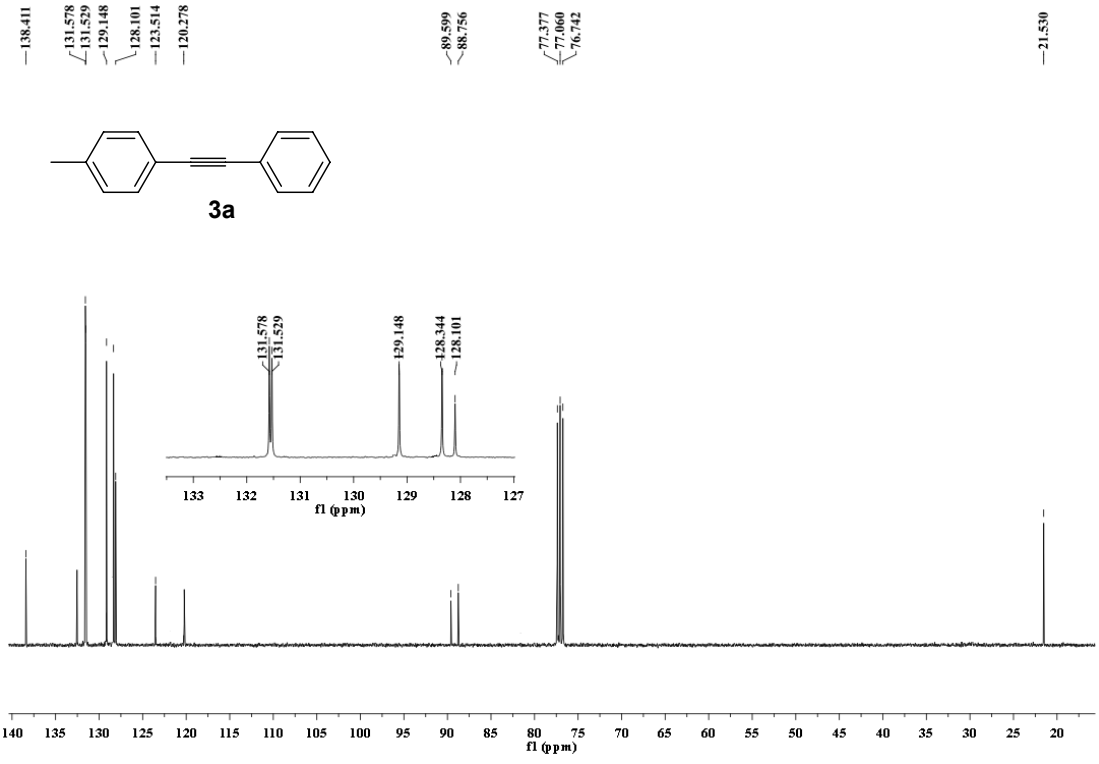
[23] K. Fukui, *Acc. Chem. Res.* 1981, ***14***, 363.

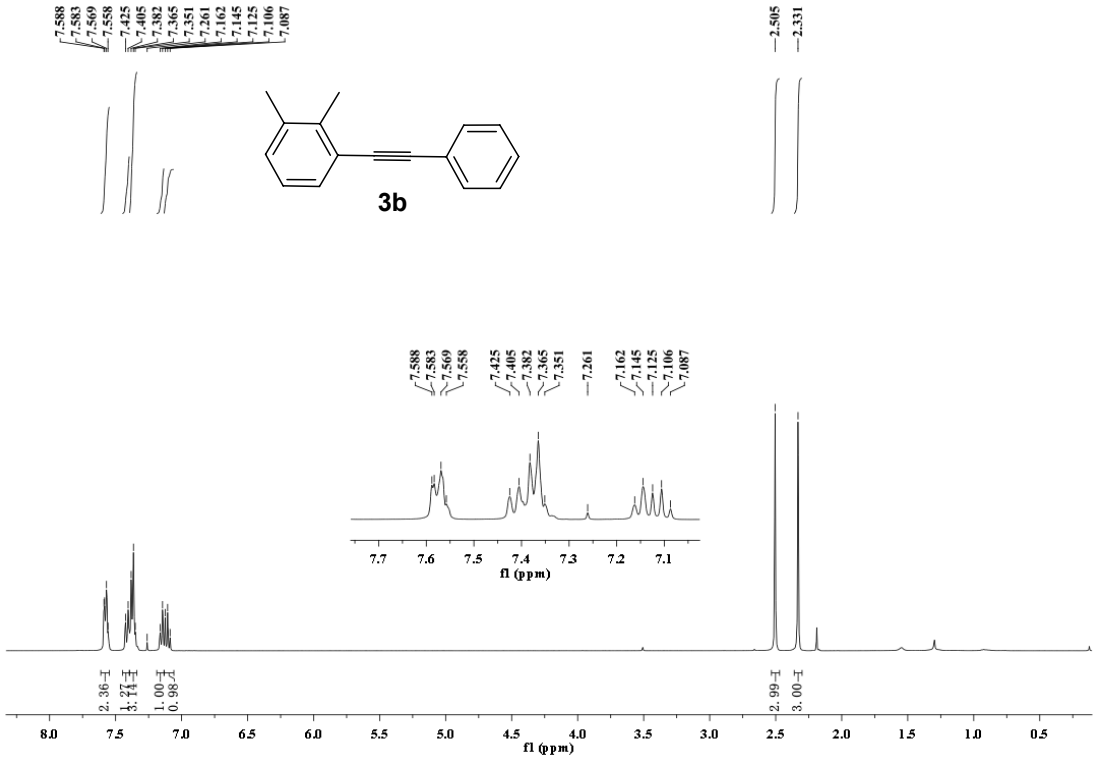
[24] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Jr. Montgomery, R. E. Stratmann, J. C. Burant, S.Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A.Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L.Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle and J. A. Pople, *Gaussian*

03, revision D.01; Gaussian, Inc.: Pittsburgh, PA, 2005.

VIII. Copies of ^{1}H NMR and ^{13}C NMR spectra



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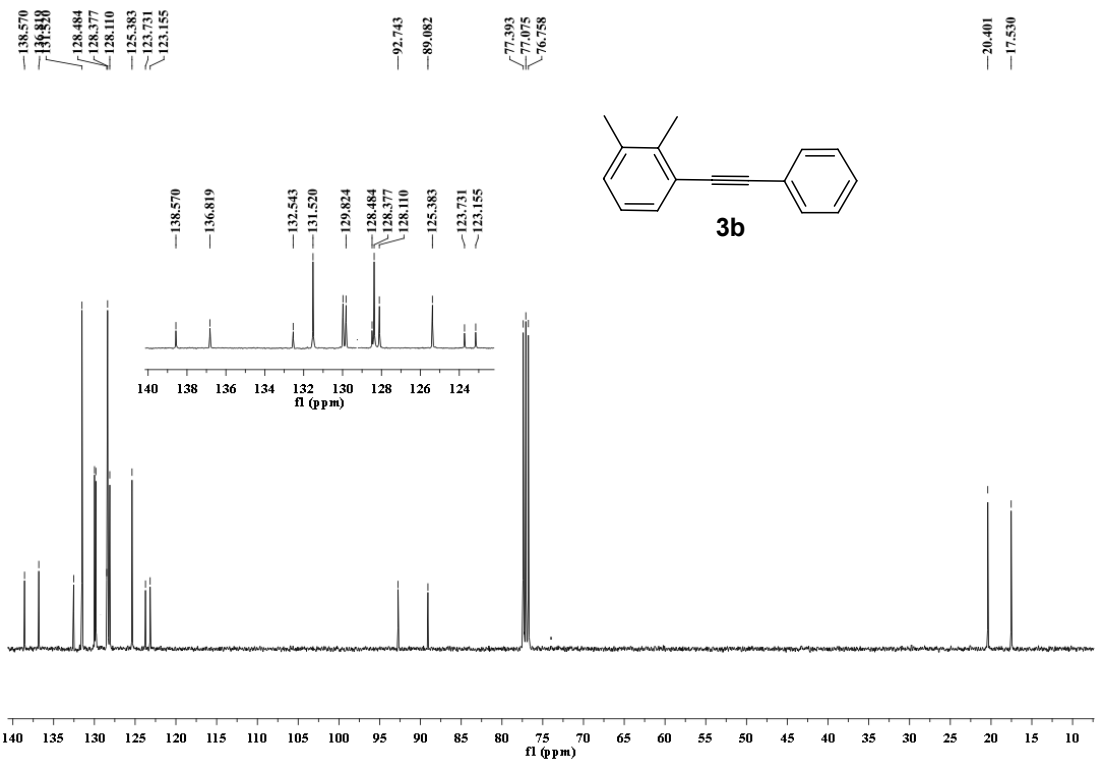
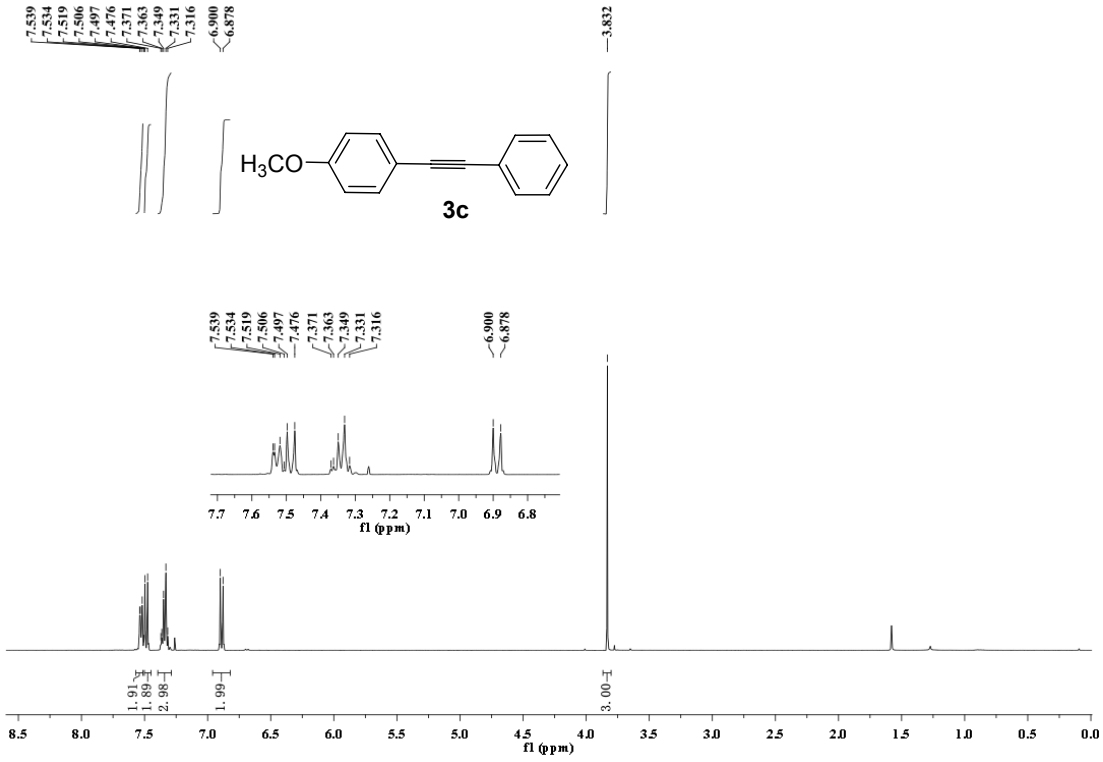
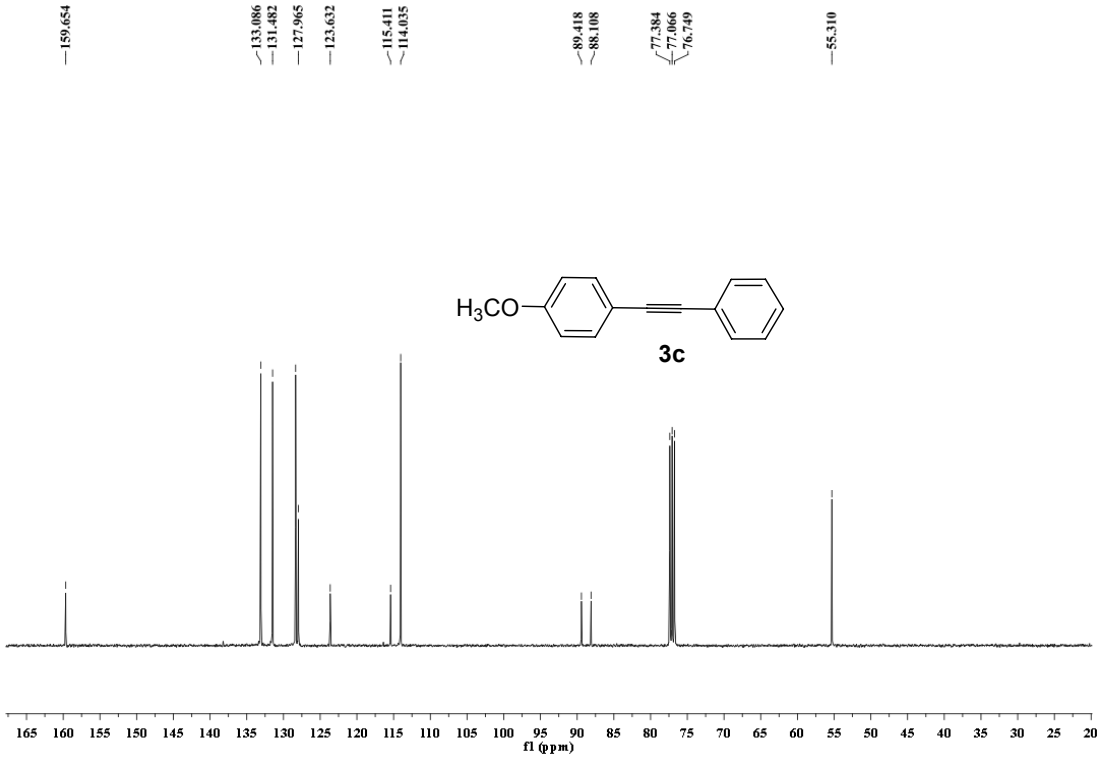
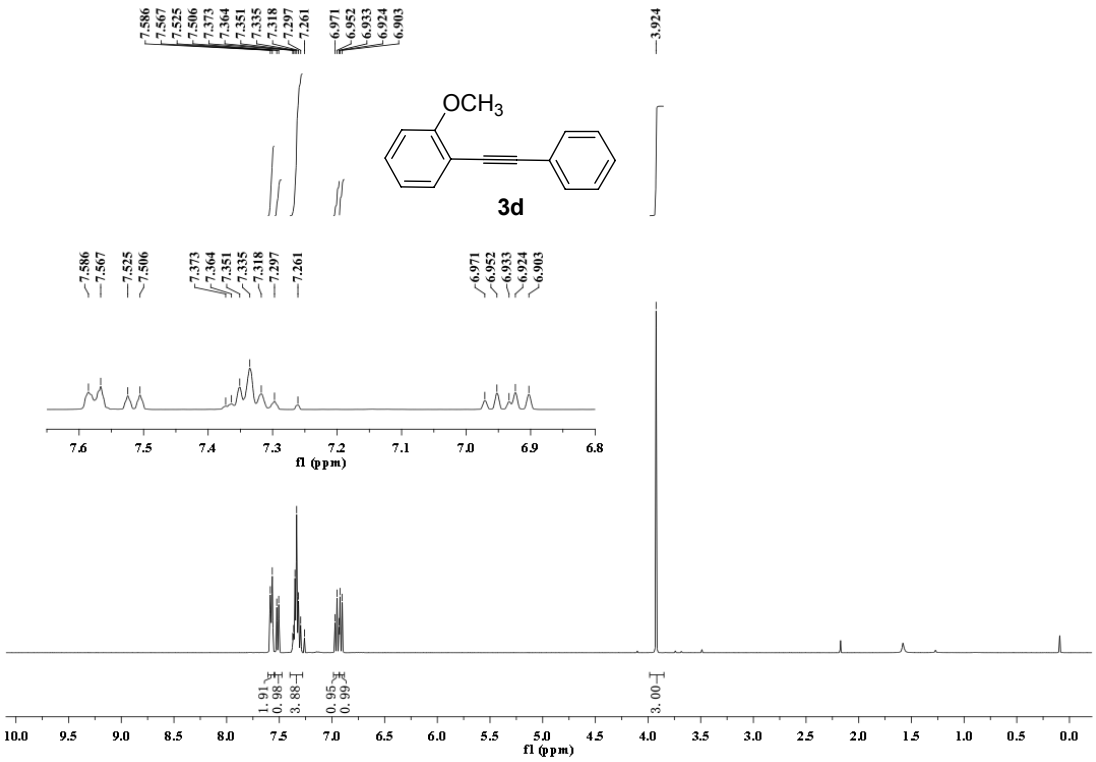
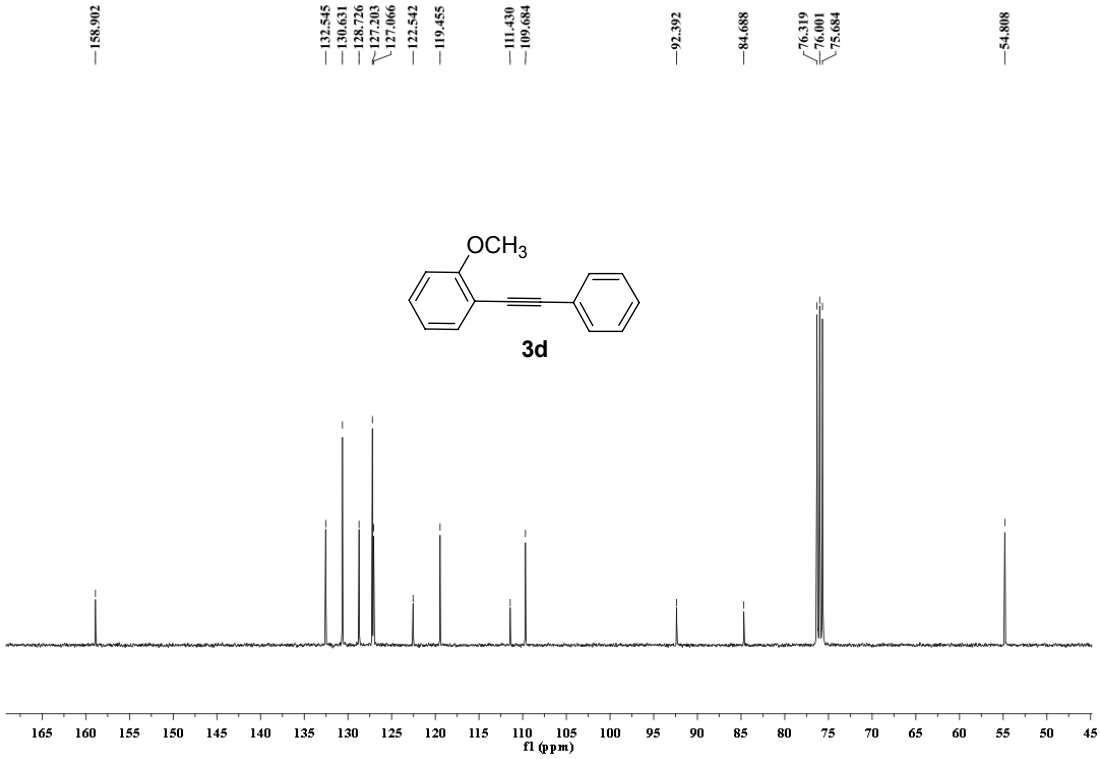
3b
f1 (ppm)

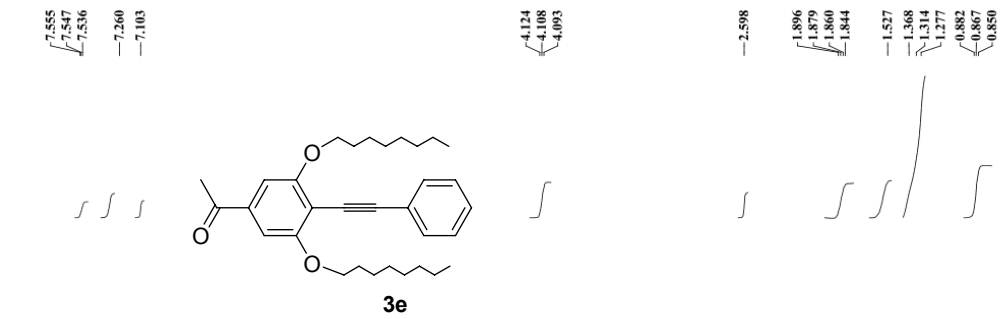

138.570
136.819
132.543
131.520
129.824
128.484
128.377
128.110
125.383
123.731
123.155
92.743
89.082
77.393
77.075
76.758
20.401
17.530
3b
f1 (ppm)


7.539
7.534
7.519
7.506
7.497
7.476
7.371
7.363
7.349
7.331
7.316
6.900
6.878
3.832
H3CO
3c
f1 (ppm)
1.91
1.89
2.98
1.99
3.00

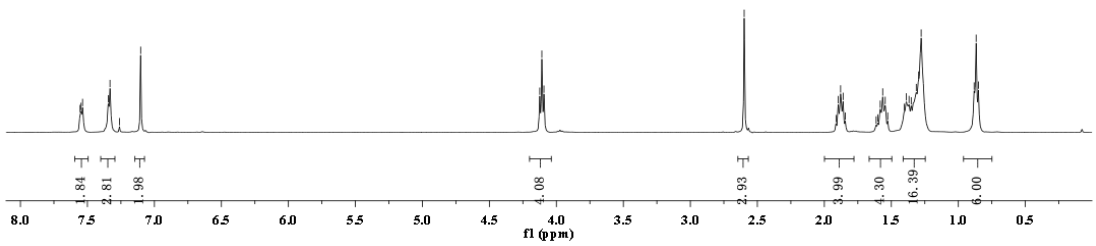

159.654
133.086
131.482
127.965
123.632
115.411
114.035
89.418
88.108
77.384
77.066
76.749
55.310
H3CO
3c
f1 (ppm)

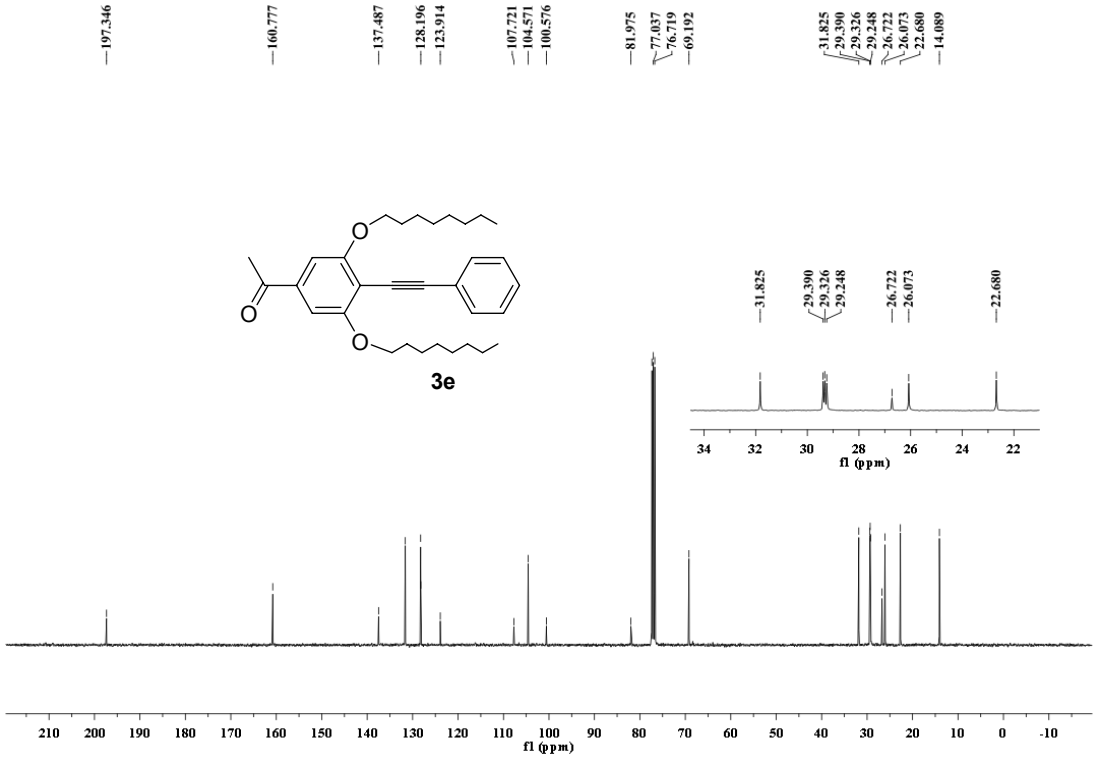

7.586
7.567
7.525
7.506
7.373
7.364
7.351
7.335
7.318
7.297
7.261
6.971
6.952
6.933
6.924
6.903
3.924
OCH3
3d
f1 (ppm)
1.91
0.98
3.88
0.95
0.99
3.00


158.902
132.545
130.631
128.726
127.203
127.066
122.542
119.455
111.430
109.684
92.392
84.688
76.319
76.001
75.684
54.808
OCH3
3d
f1 (ppm)

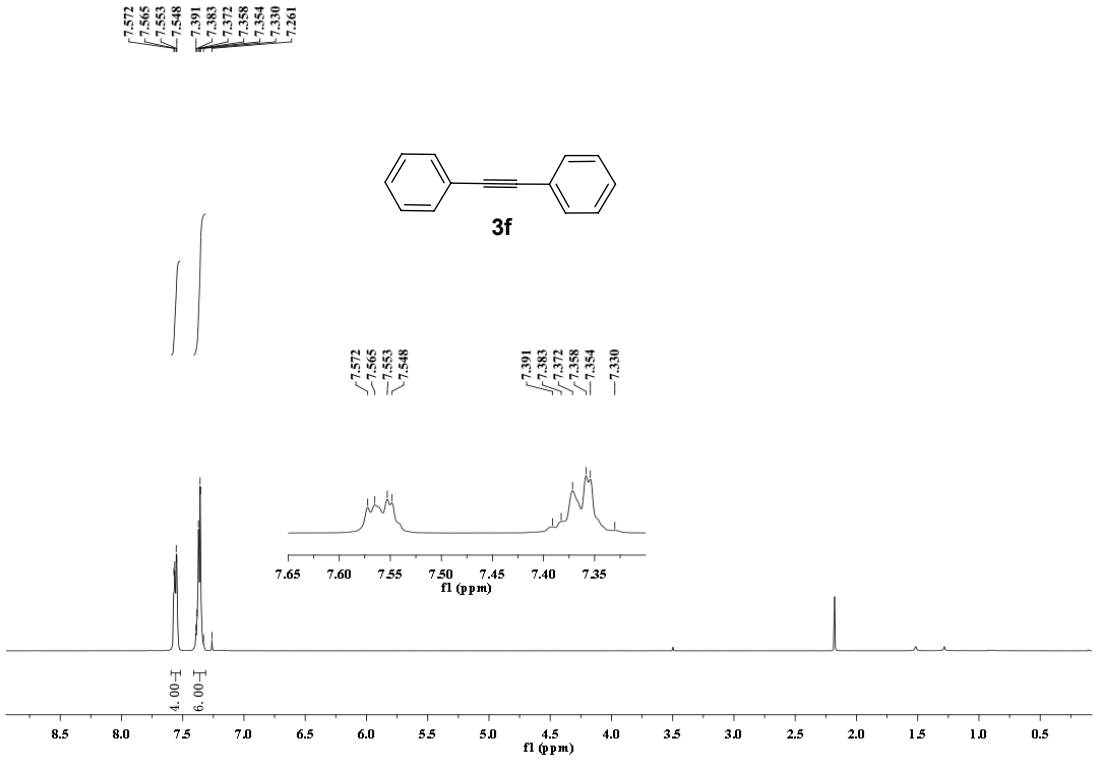

7.555
7.547
7.536
7.260
7.103
4.124
4.108
4.093
2.598
1.896
1.879
1.860
1.844
1.527
1.368
1.314
1.277
0.882
0.867
0.850
O
O
O

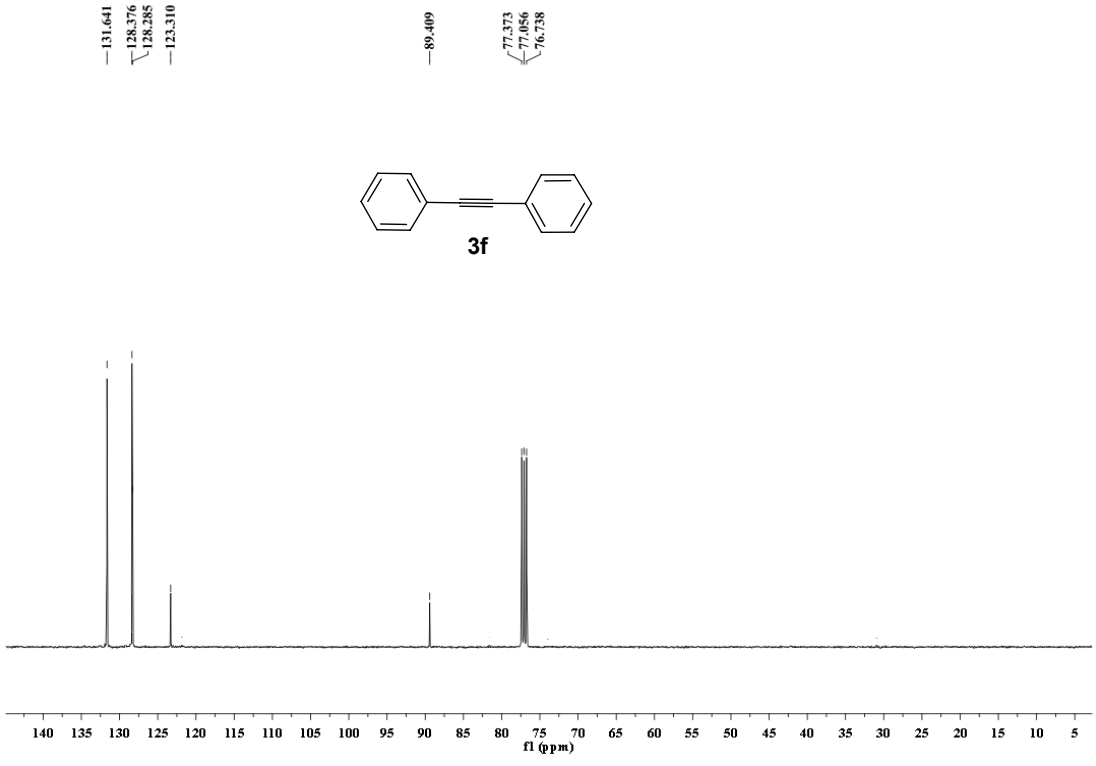
3e

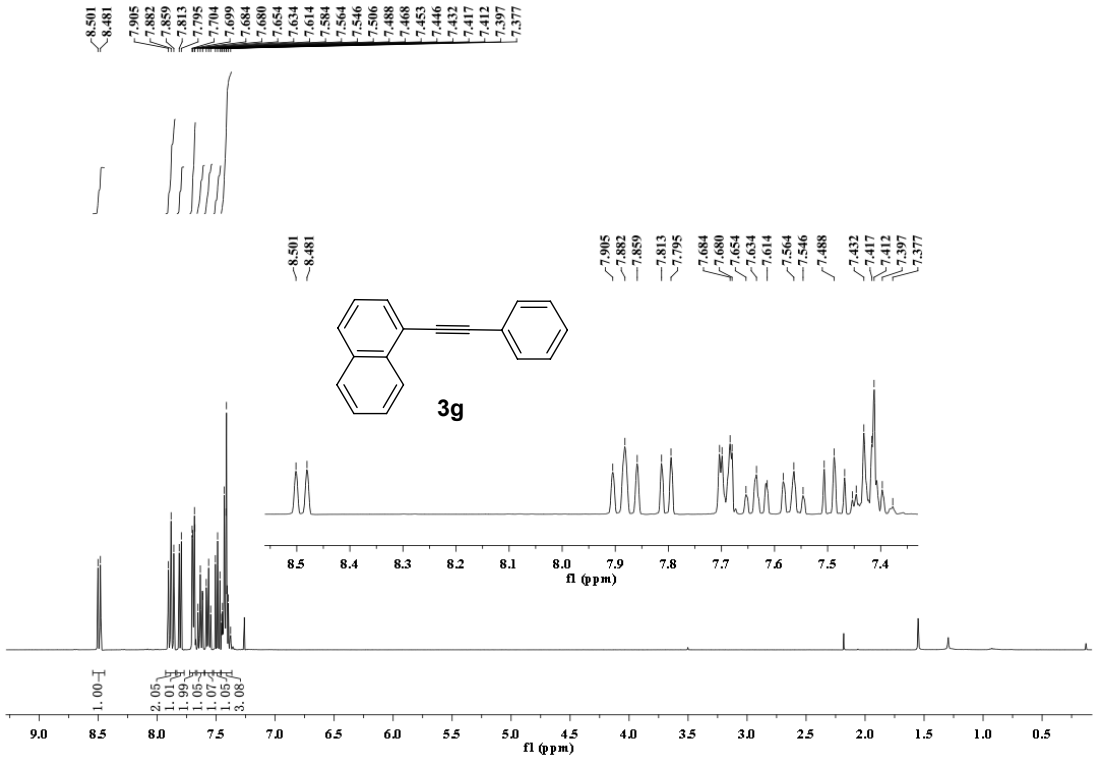

1.84
2.81
1.98
4.08
2.93
3.99
4.30
16.39
6.00
f1 (ppm)

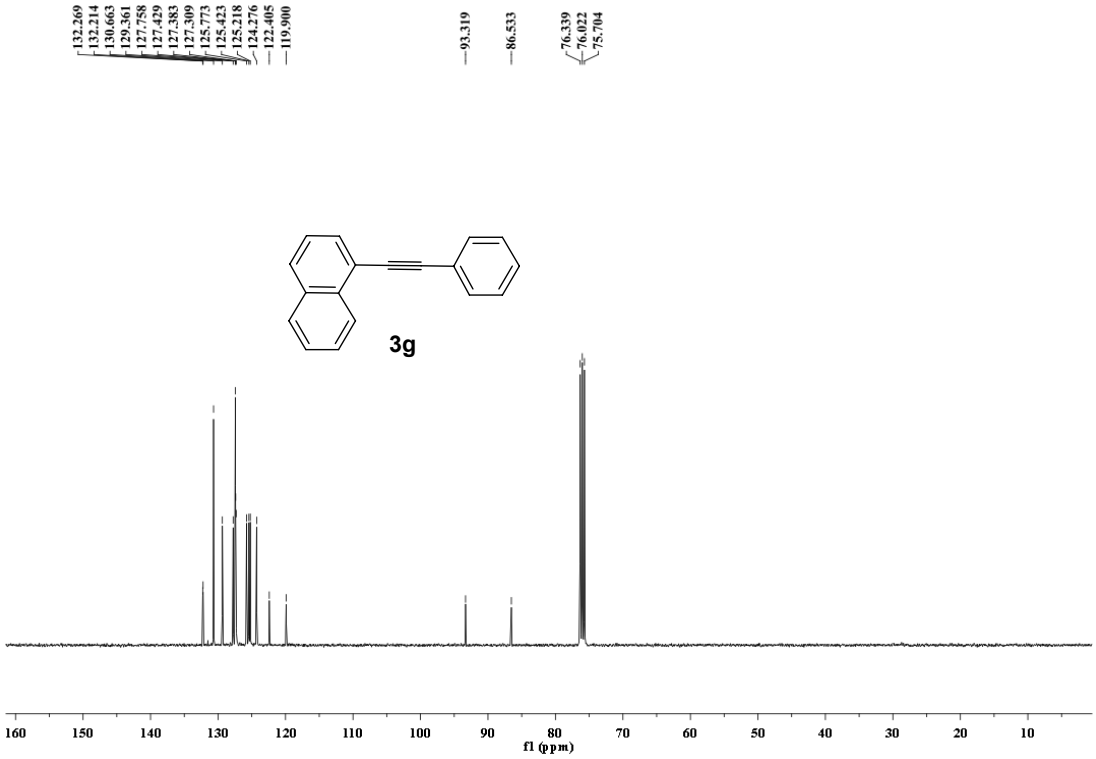

197.346
160.777
137.487
128.196
123.914
107.721
104.571
100.576
81.975
77.037
76.719
69.192
31.825
29.390
29.326
29.248
26.722
26.073
22.680
14.089
O
O
O
f1 (ppm)

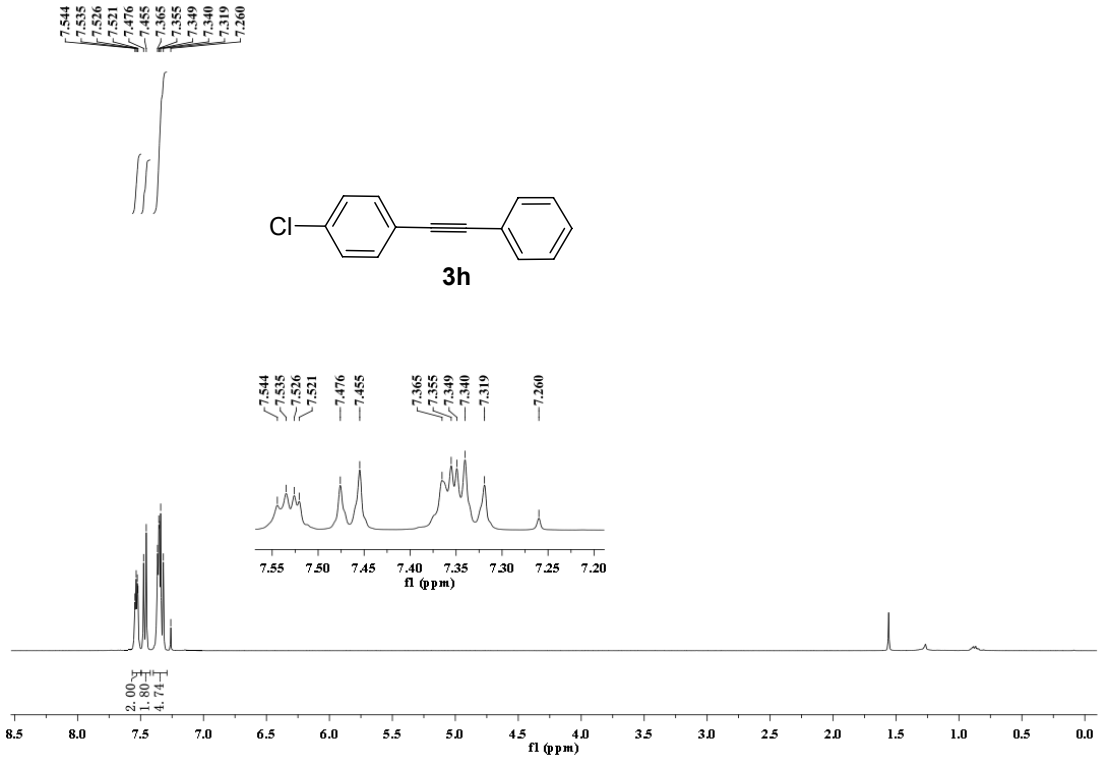
3e

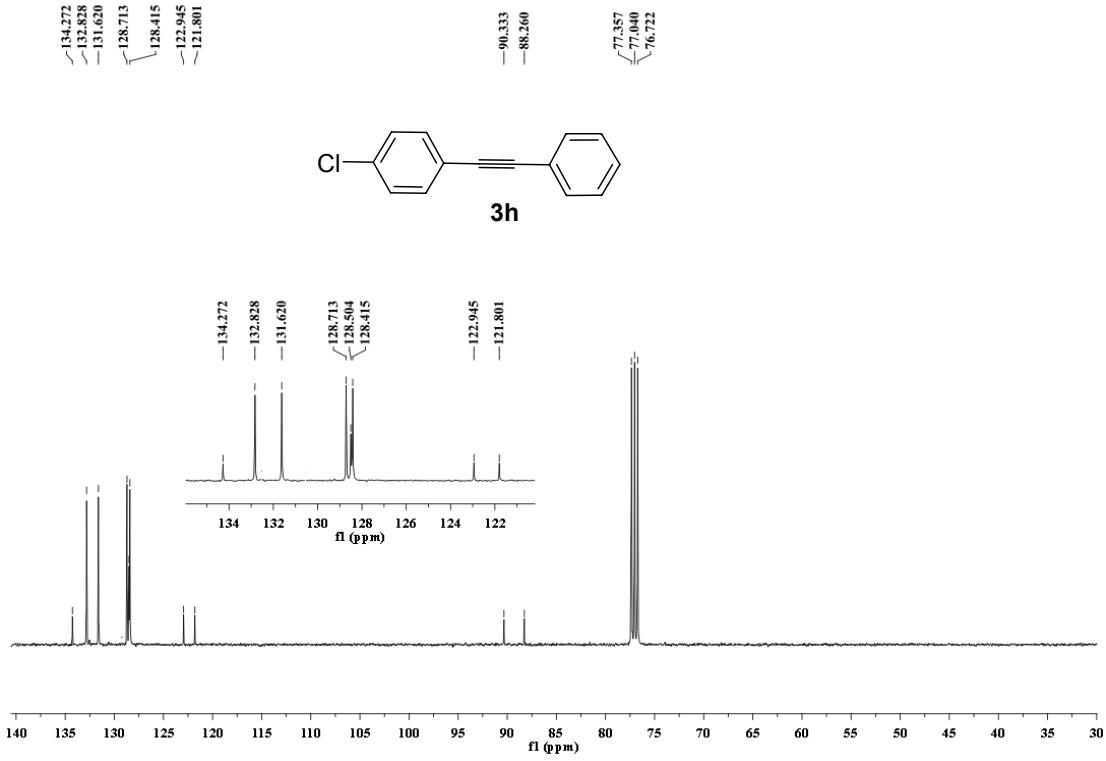

7.572
7.565
7.553
7.548
7.391
7.383
7.372
7.358
7.354
7.330
7.261
3f
4.00
6.00
f1 (ppm)

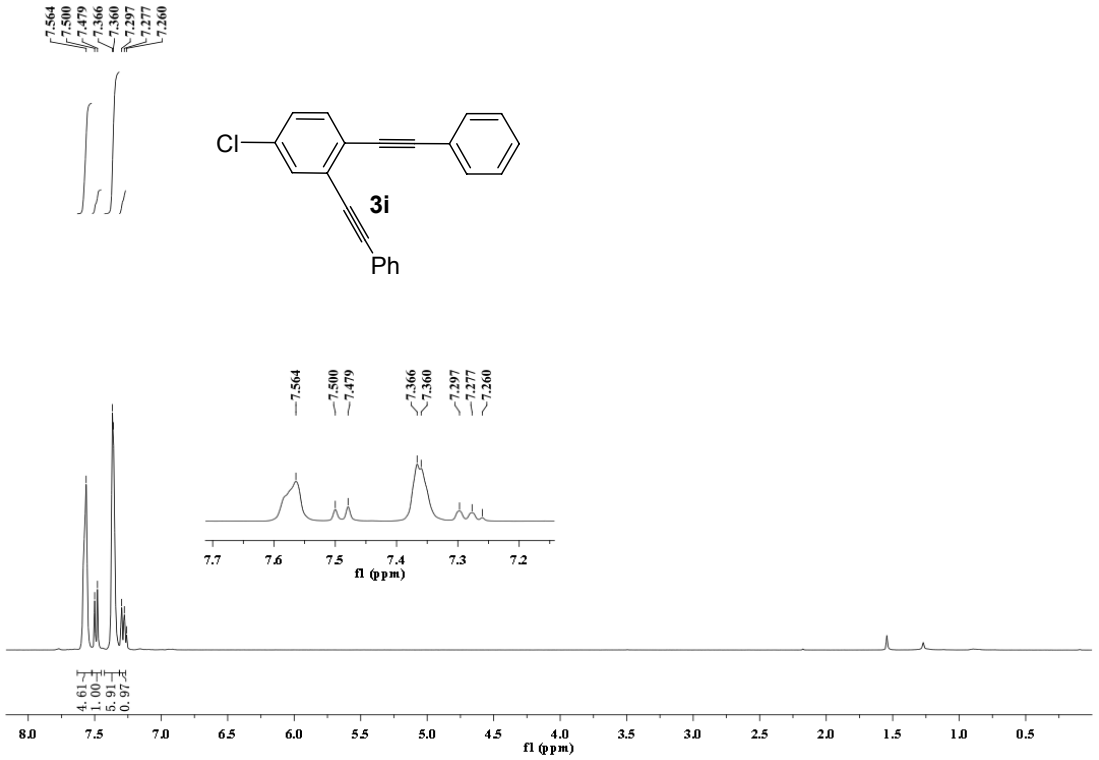

131.641
128.376
128.285
123.310
89.409
77.373
77.056
76.738
3f
f1 (ppm)

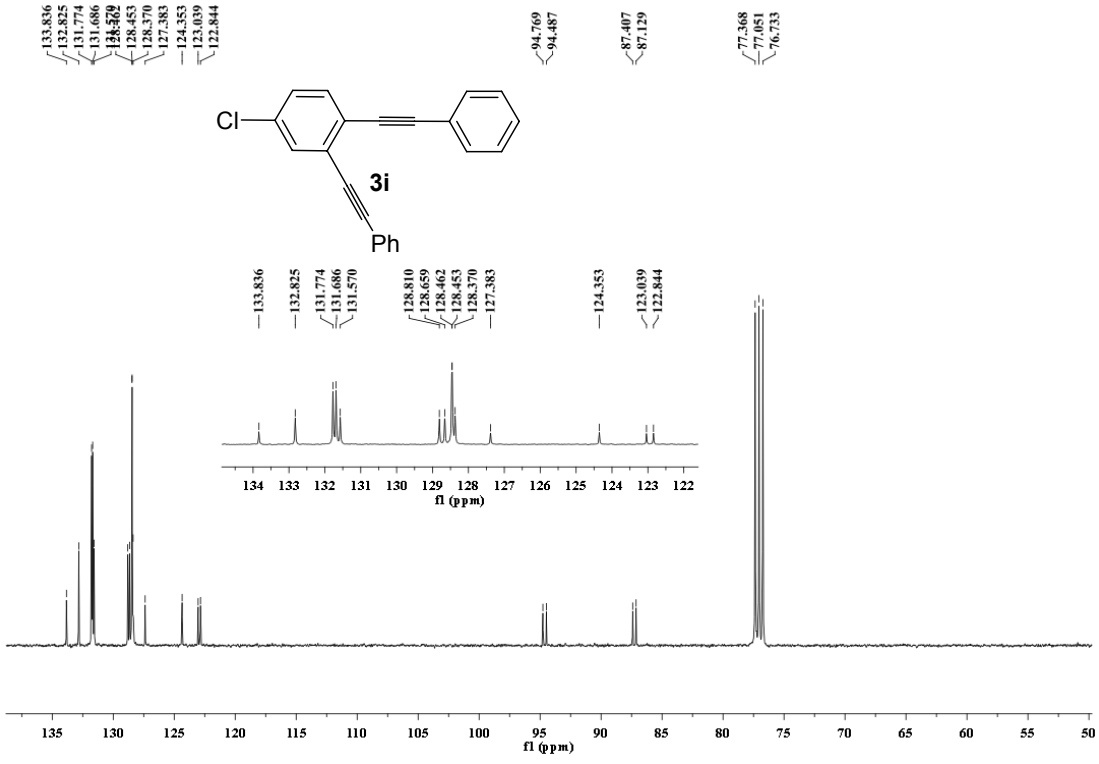

8.501
8.481
7.905
7.882
7.859
7.813
7.795
7.704
7.699
7.684
7.680
7.654
7.634
7.614
7.584
7.564
7.546
7.506
7.488
7.468
7.453
7.446
7.432
7.417
7.412
7.397
7.377
3g
1.00
2.05
1.01
1.99
1.05
1.07
1.05
3.08
f1 (ppm)

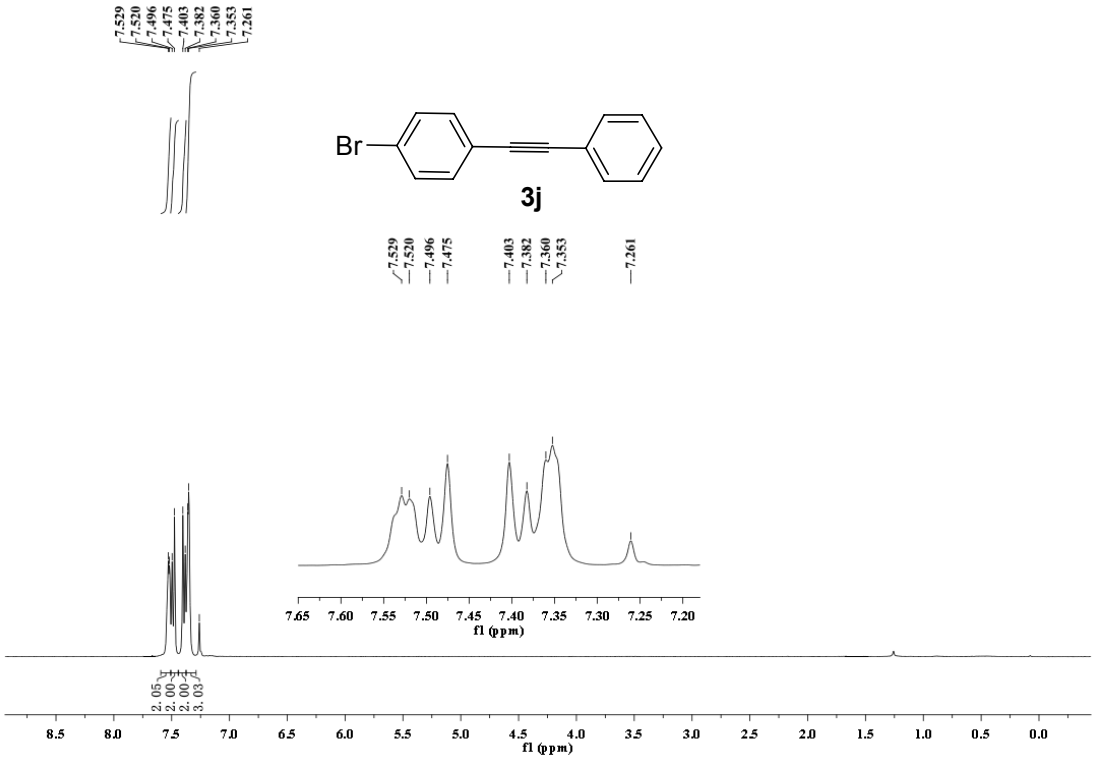

132.269
132.214
130.663
129.361
127.758
127.429
127.383
127.309
125.773
125.423
125.218
124.276
122.405
119.900
93.319
86.533
76.339
76.022
75.704
3g
f1 (ppm)

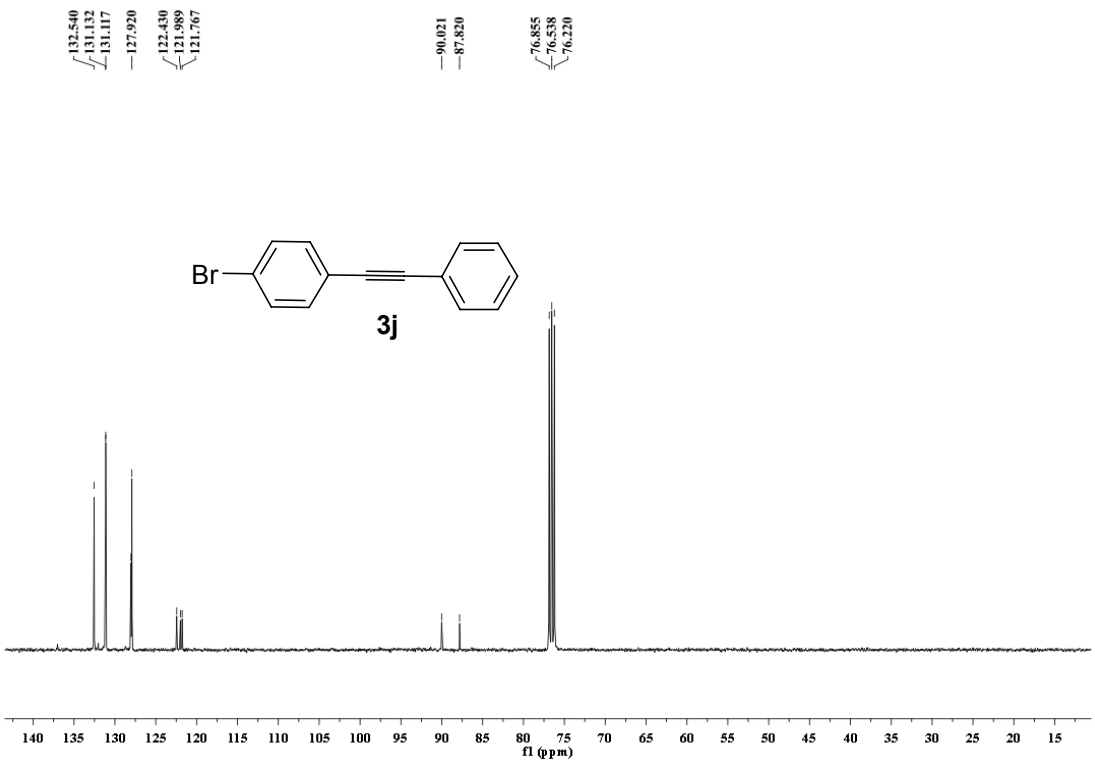

7.544
7.535
7.526
7.521
7.476
7.455
7.365
7.355
7.349
7.340
7.319
7.260
Cl
3h
2.00
1.80
4.74
f1 (ppm)

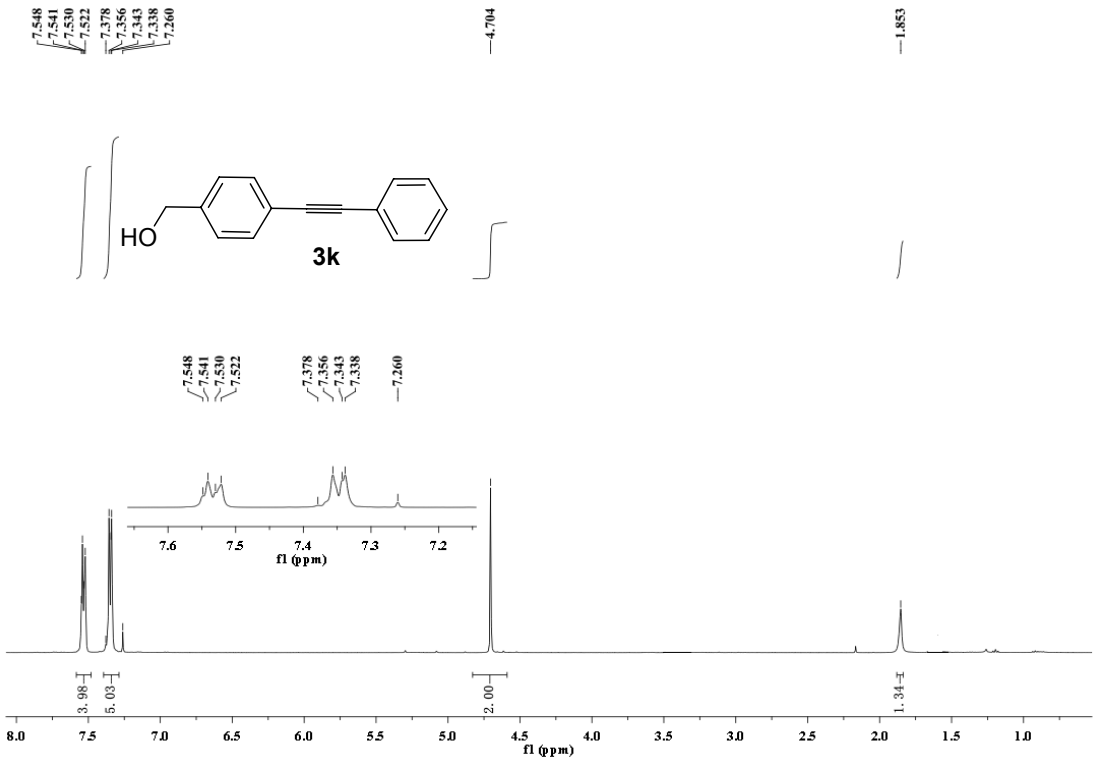

134.272
132.828
131.620
128.713
128.415
122.945
121.801
90.333
88.260
77.357
77.040
76.722
Cl
3h
f1 (ppm)

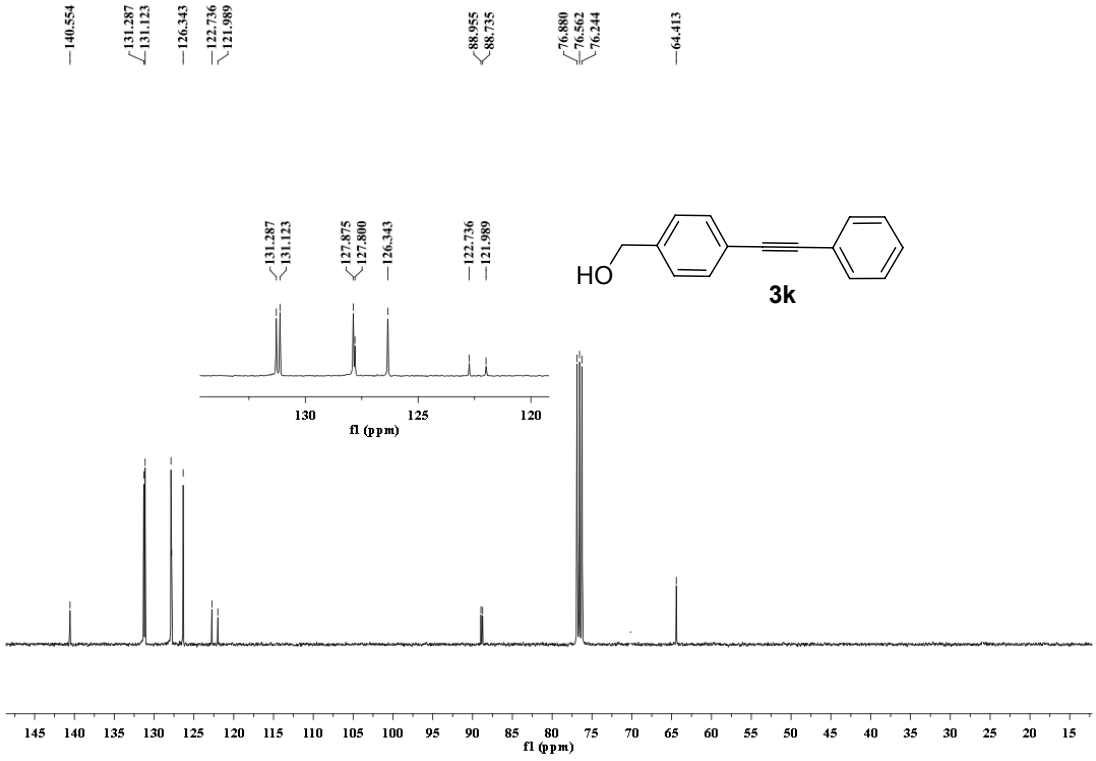

7.564
7.500
7.479
7.366
7.360
7.297
7.277
7.260
Cl
3i
Ph
4.61
1.00
5.91
0.97
f1 (ppm)

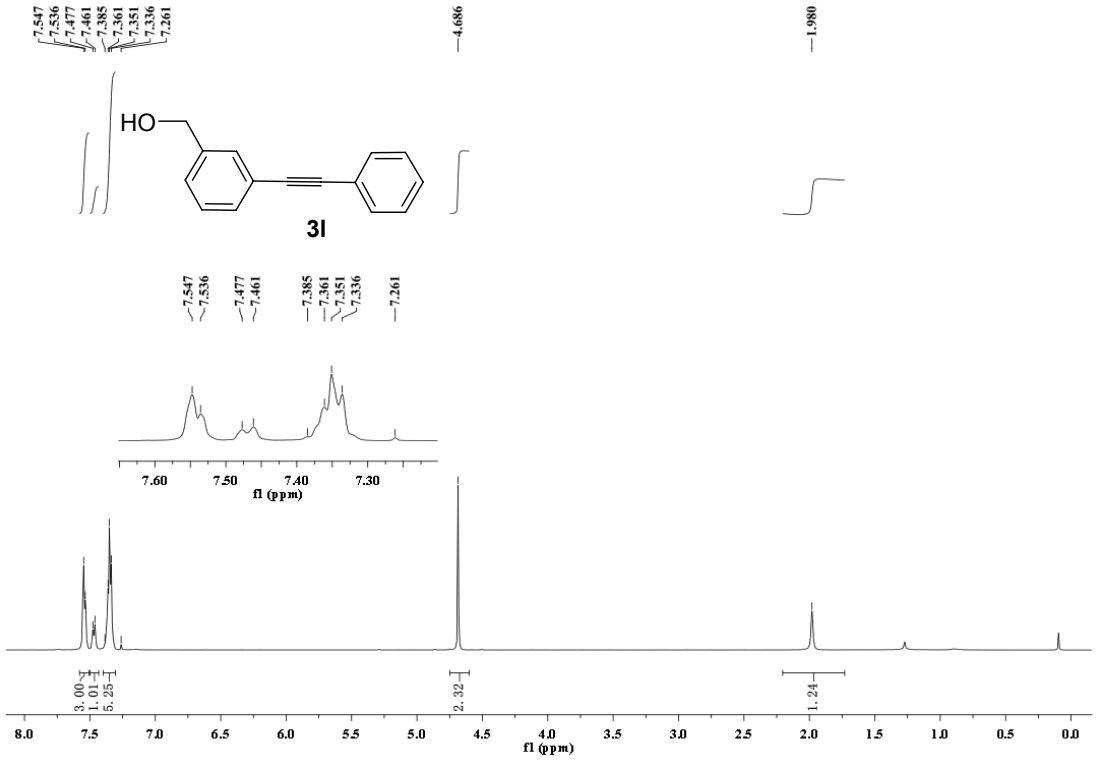

133.836
132.825
131.774
131.686
128.453
128.370
127.383
124.353
123.039
122.844
94.769
94.487
87.407
87.129
77.368
77.051
76.733
Cl
3i
Ph
f1 (ppm)

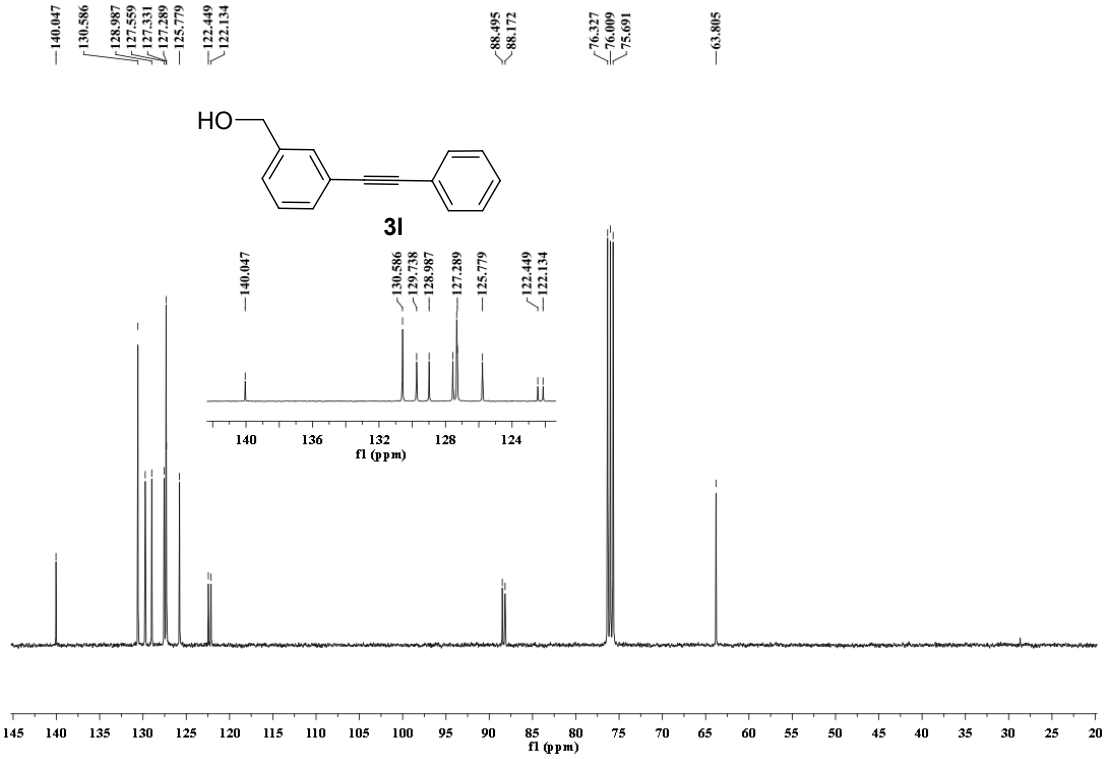

7.529
7.520
7.496
7.475
7.403
7.382
7.360
7.353
7.261
Br
3j
f1 (ppm)


132.540
131.132
131.117
127.920
122.430
121.989
121.767
90.021
87.820
76.855
76.538
76.220
Br
3j
f1 (ppm)


7.548
7.541
7.530
7.522
7.378
7.356
7.343
7.338
7.260
4.704
1.853
HO
3k
f1 (ppm)
3.98
5.03
2.00
1.34


140.554
131.287
131.123
126.343
122.736
121.989
88.955
88.735
76.880
76.562
76.244
64.413
127.875
127.800
HO
3k
f1 (ppm)


7.547
7.536
7.477
7.461
7.385
7.361
7.351
7.336
7.261
4.686
1.980
HO
3l
7.60
7.50
7.40
7.30
f1 (ppm)
3.00
1.01
5.25
2.32
1.24
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


140.047
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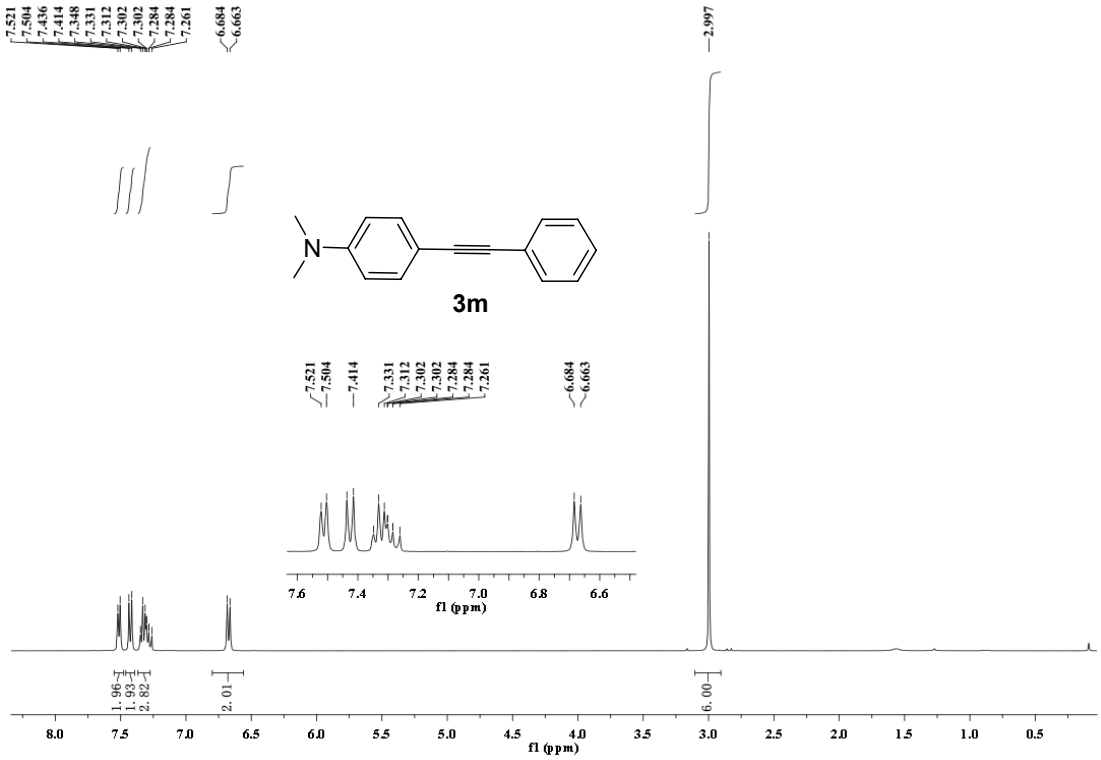
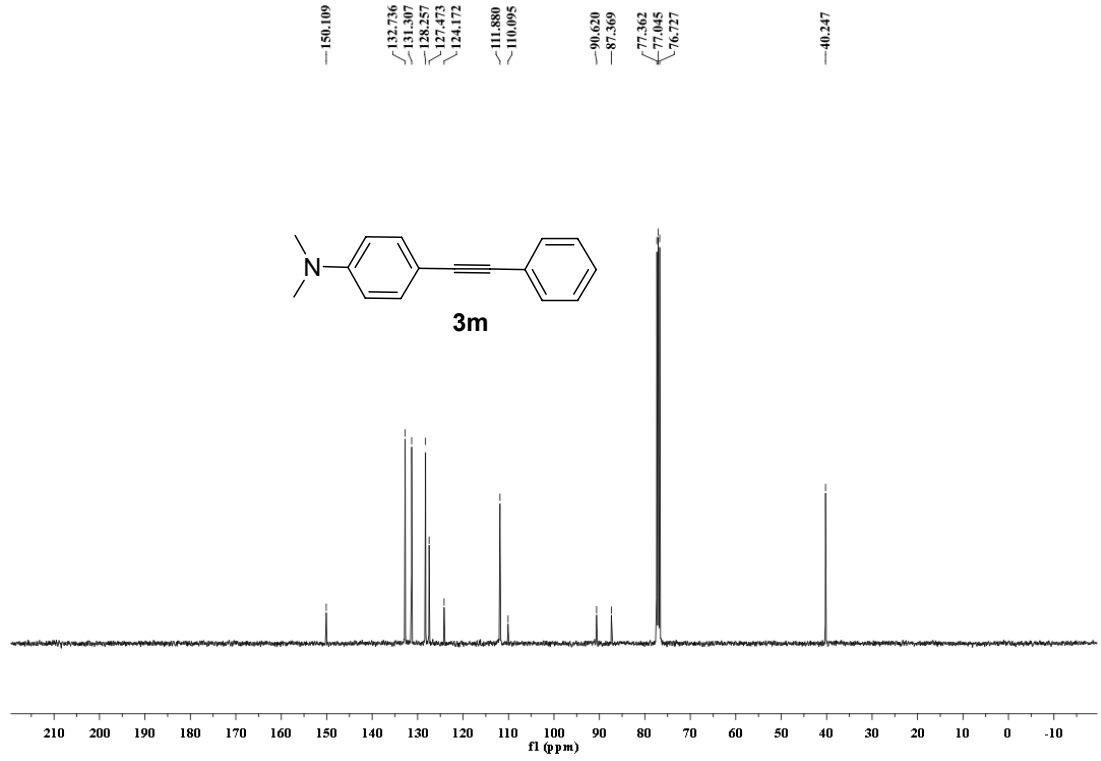
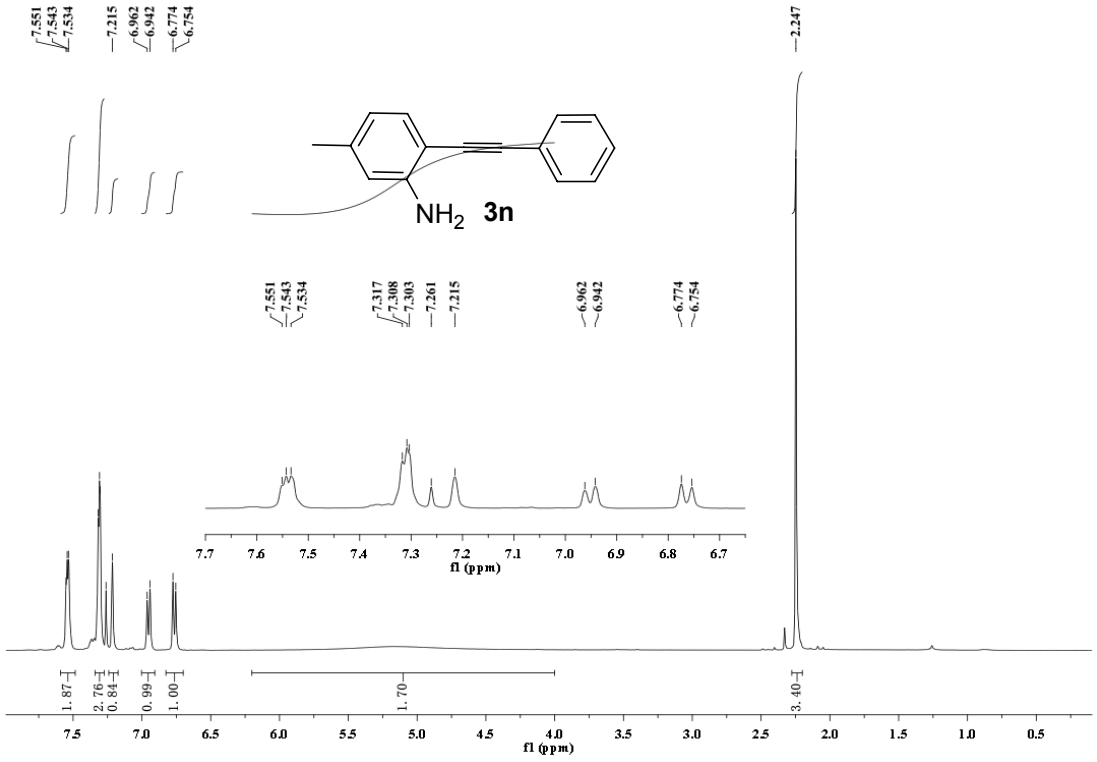
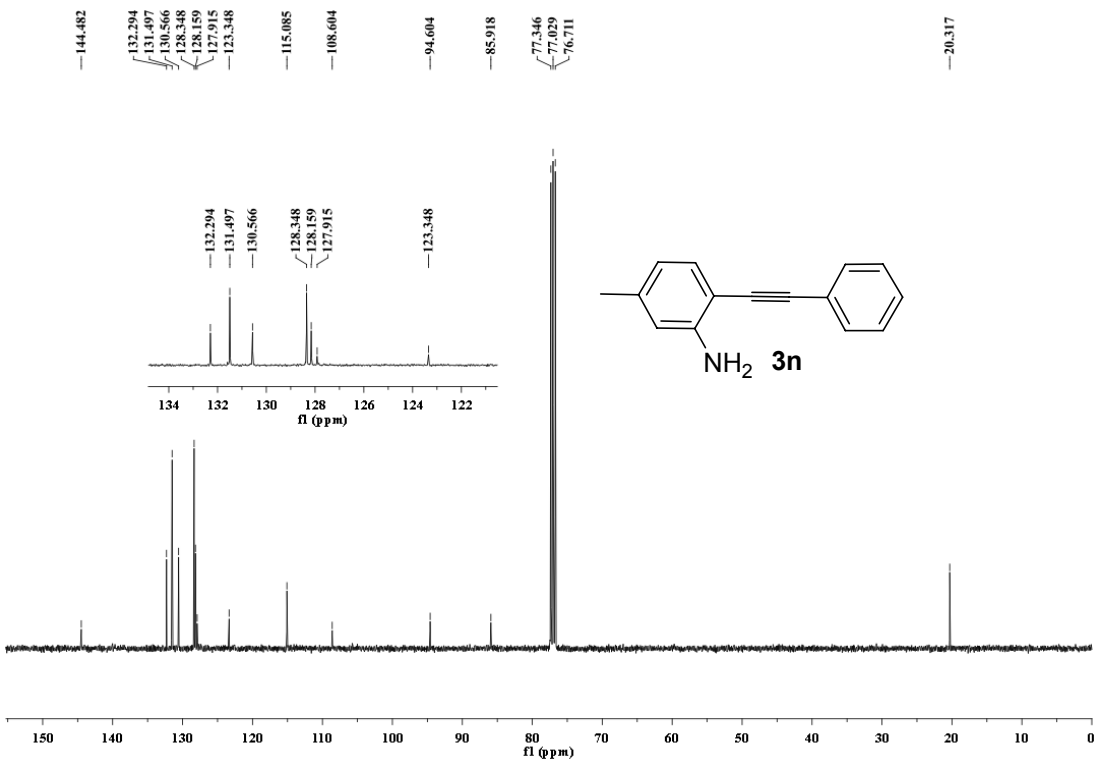
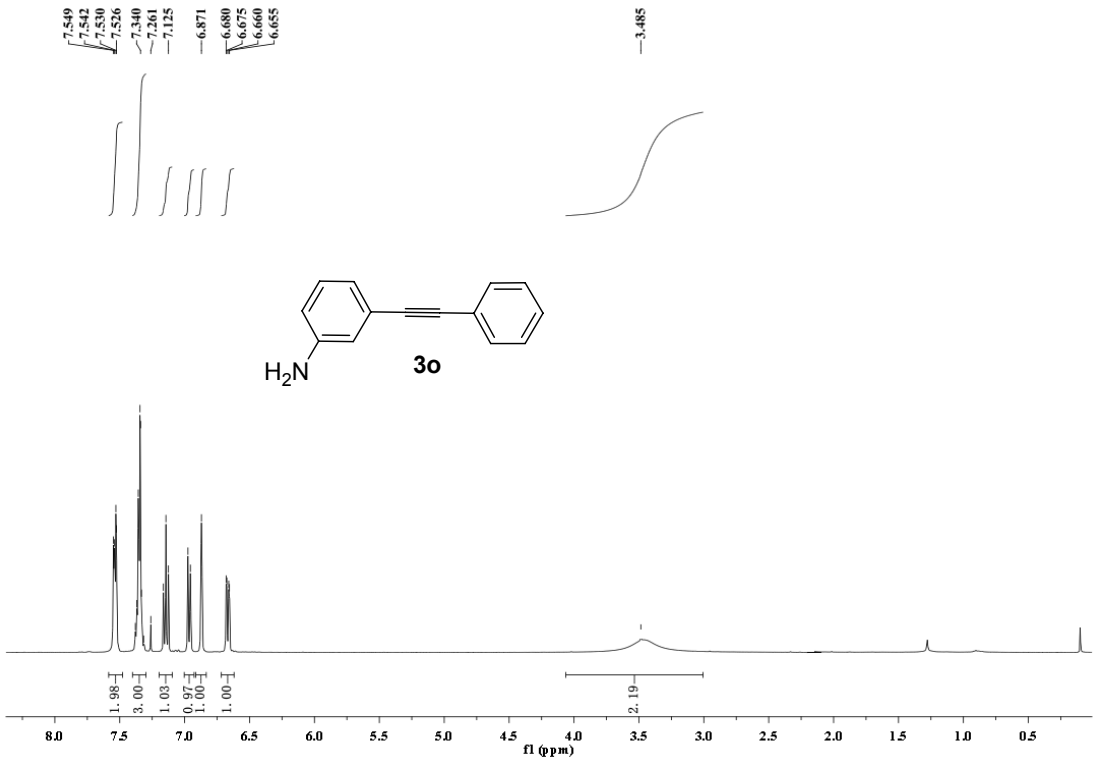
128.987
127.559
127.331
127.289
125.779
122.449
122.134
88.495
88.172
76.327
76.009
75.691
63.805
HO
3l
140.047
130.586
129.738
128.987
127.289
125.779
122.449
122.134
140
136
132
128
124
f1 (ppm)
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
f1 (ppm)

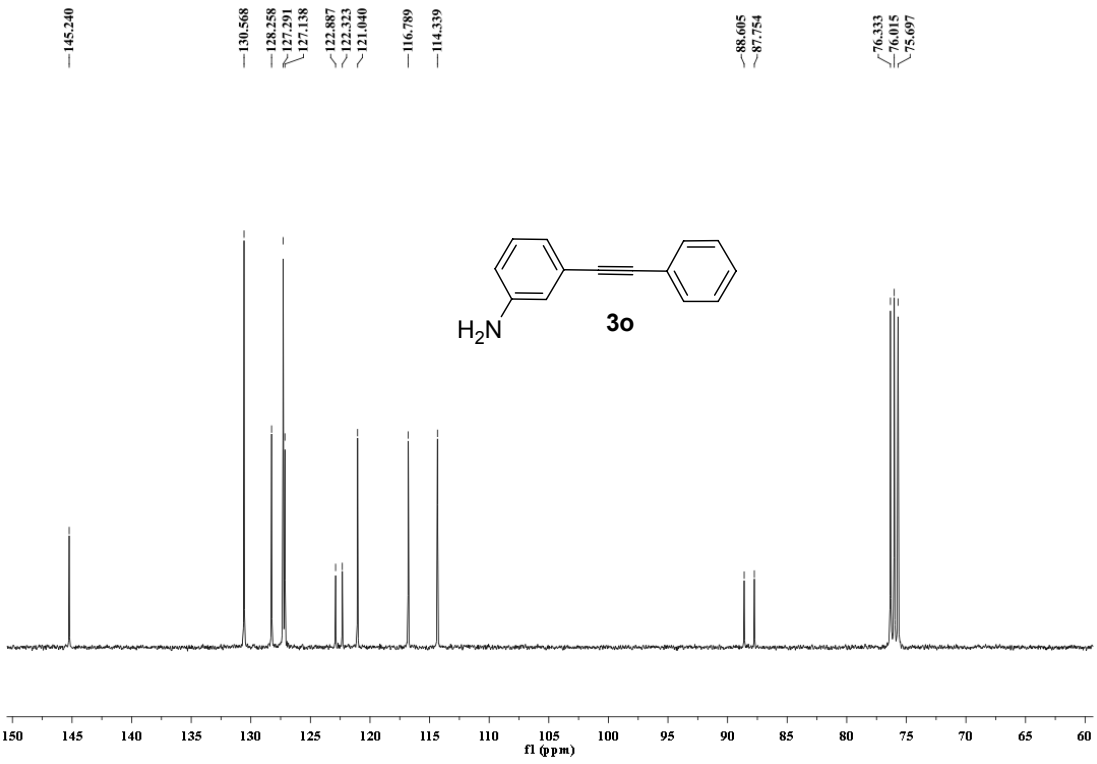

7.521
7.504
7.436
7.414
7.348
7.331
7.312
7.302
7.302
7.284
7.284
7.261
6.684
6.663
2.997
N
3m
f1 (ppm)
1.96
1.93
2.82
2.01
6.00

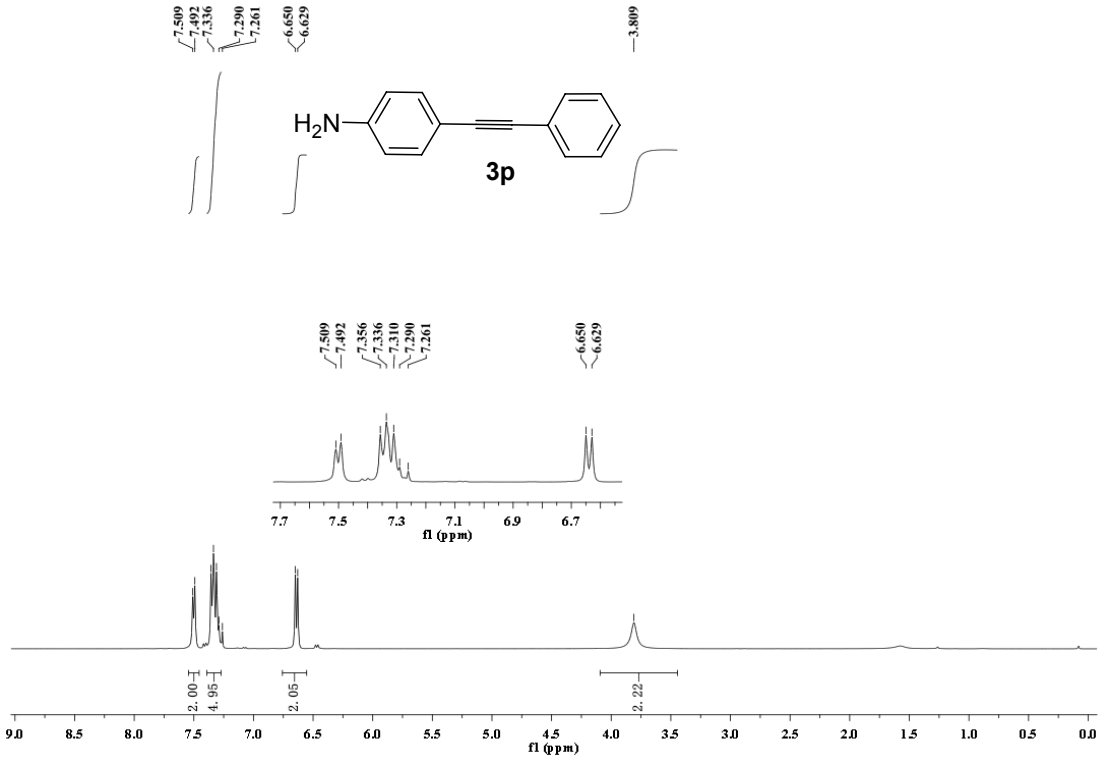

150.109
132.736
131.307
128.257
127.473
124.172
111.880
110.095
90.620
87.369
77.362
77.045
76.727
40.247
N
3m
f1 (ppm)

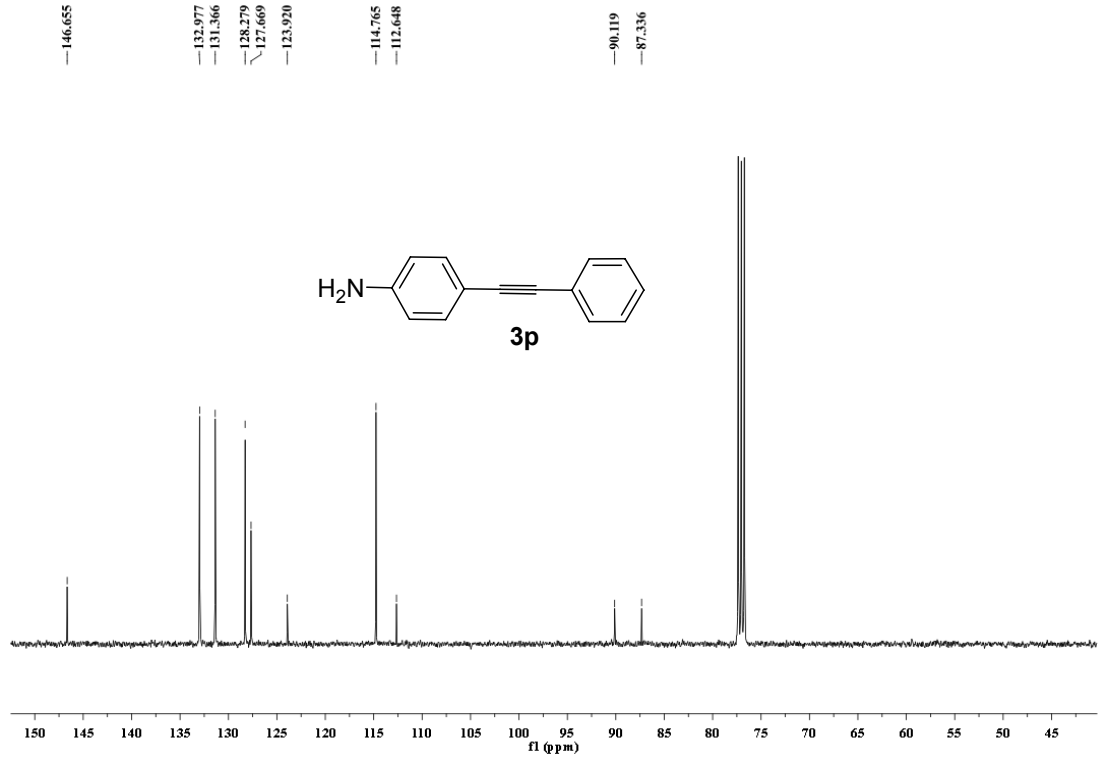

7.551
7.543
7.534
7.215
6.962
6.942
6.774
6.754
2.247
NH2
3n
7.317
7.308
7.303
7.261
1.87
2.76
0.84
0.99
1.00
1.70
3.40
f1 (ppm)

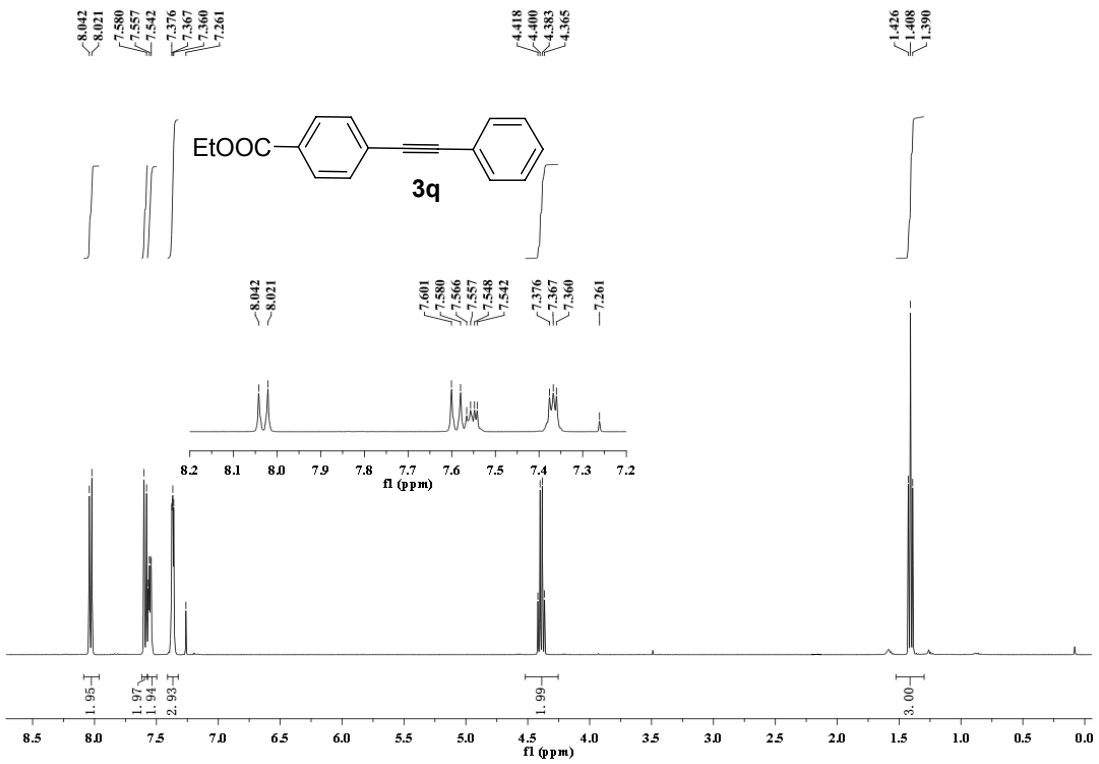

144.482
132.294
131.497
130.566
128.348
128.159
127.915
123.348
115.085
108.604
94.604
85.918
77.346
77.029
76.711
20.317
NH2
3n
f1 (ppm)

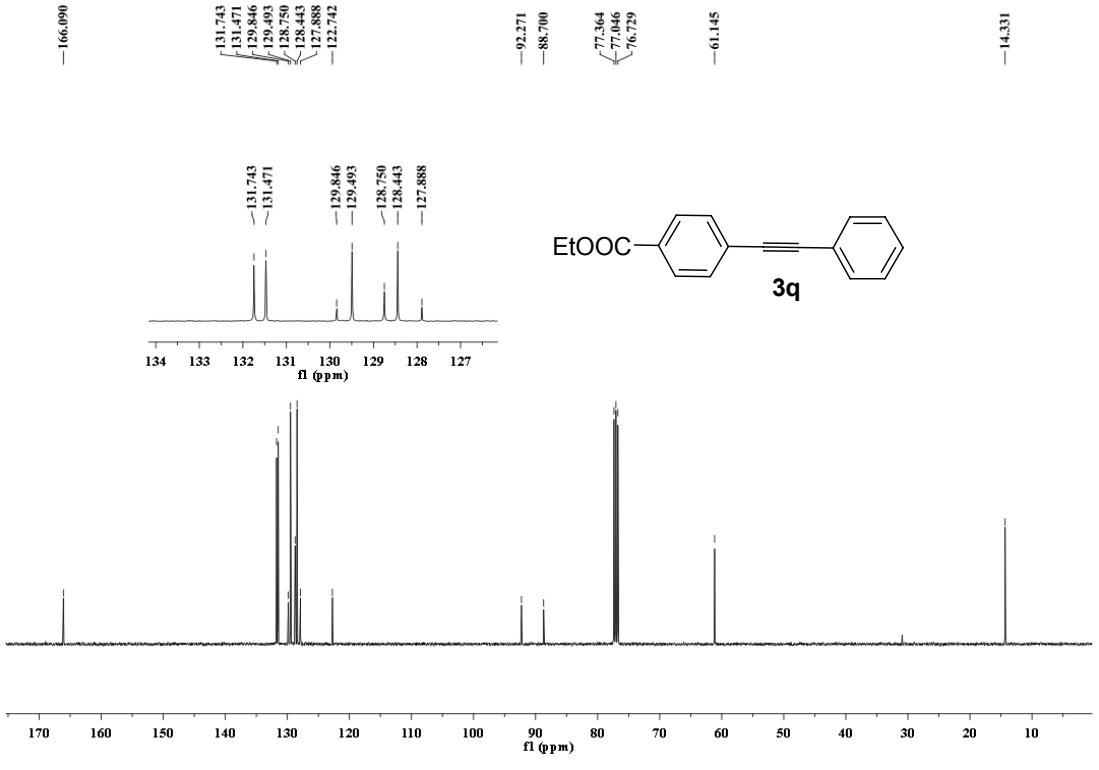

7.549
7.542
7.530
7.526
7.340
7.261
7.125
6.871
6.680
6.675
6.660
6.655
3.485
H2N
3o
1.98
3.00
1.03
0.97
1.00
1.00
2.19
f1 (ppm)

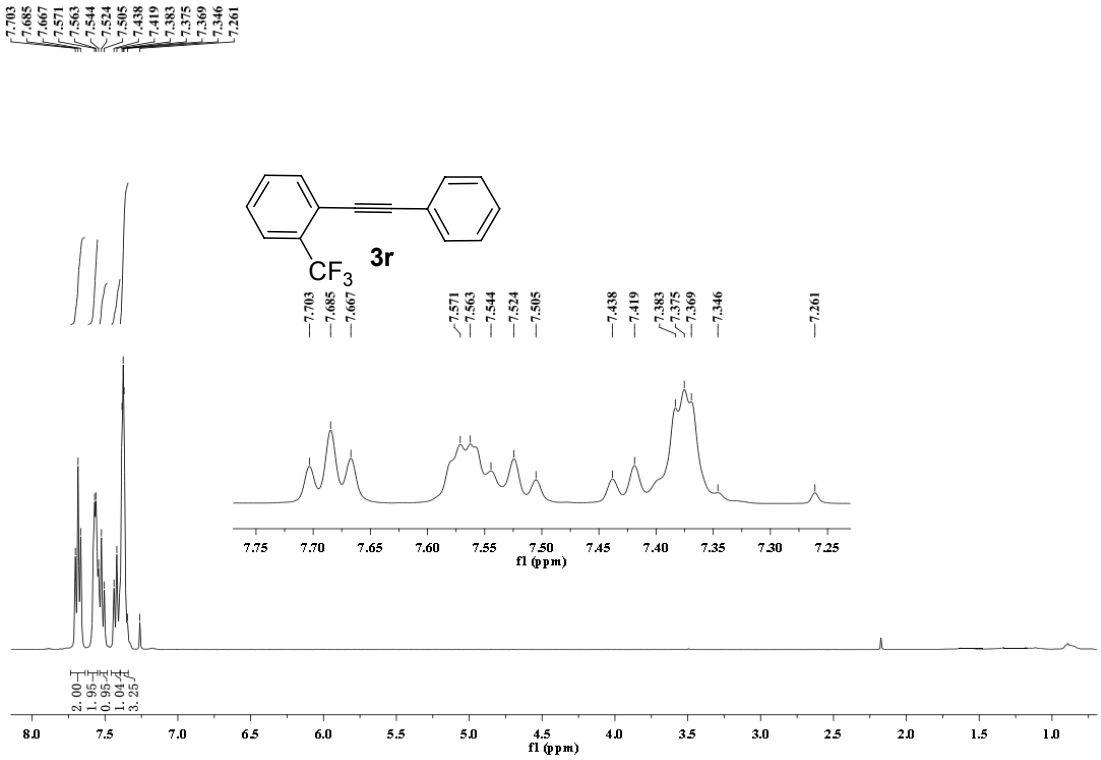

145.240
130.568
128.258
127.291
127.138
122.887
122.323
121.040
116.789
114.339
88.605
87.754
76.333
76.015
75.697
H2N
3o
f1 (ppm)

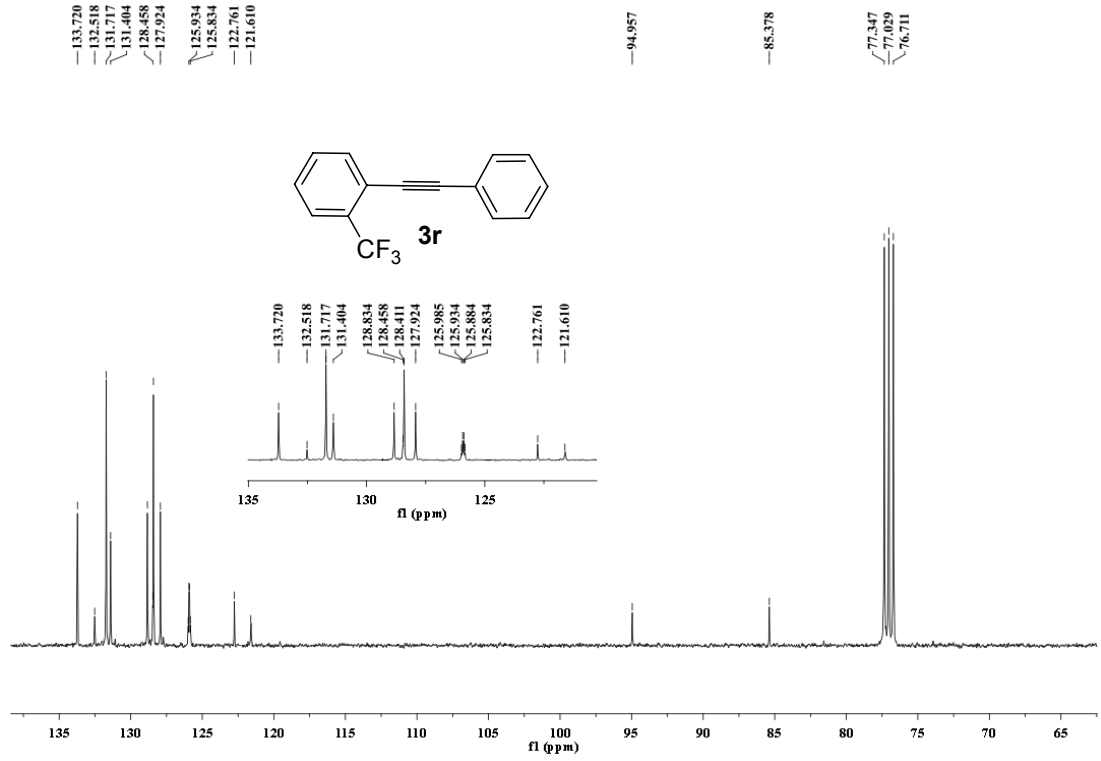

7.509
7.492
7.336
7.290
7.261
6.650
6.629
3.809
H2N
3p
7.509
7.492
7.356
7.336
7.310
7.290
7.261
6.650
6.629
7.7
7.5
7.3
7.1
6.9
6.7
f1 (ppm)
2.00
4.95
2.05
2.22
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

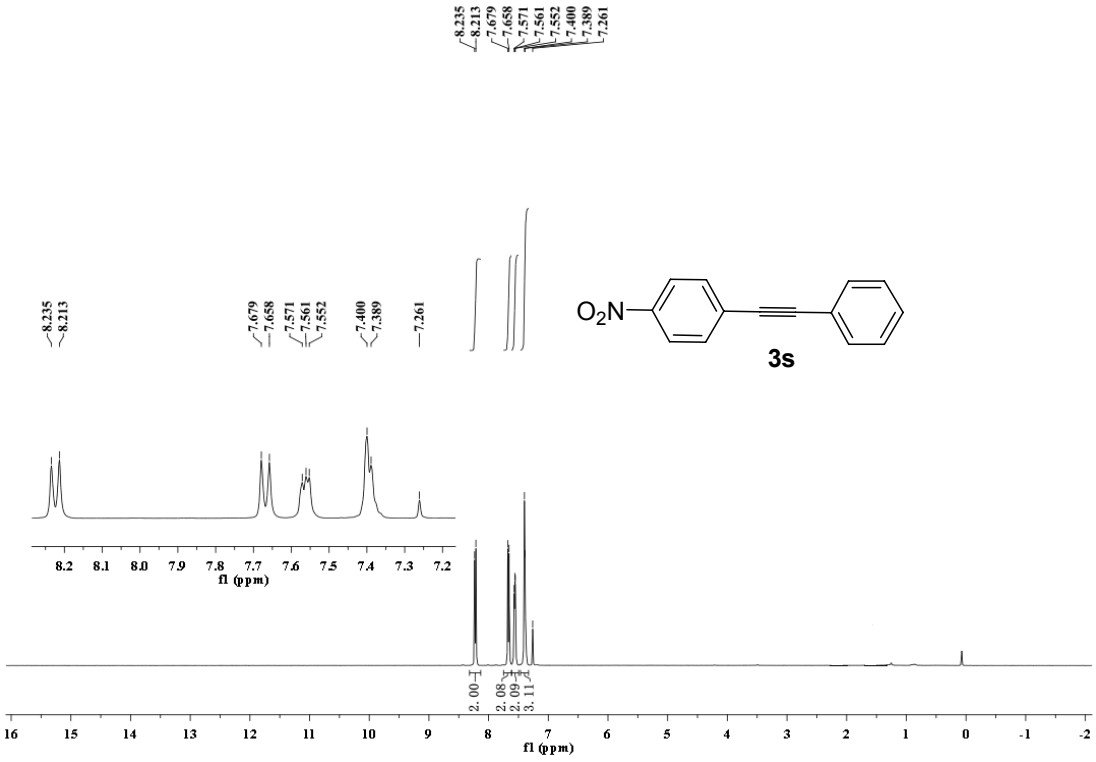

146.655
132.977
131.366
128.279
127.669
123.920
114.765
112.648
90.119
87.336
H2N
3p
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
f1 (ppm)

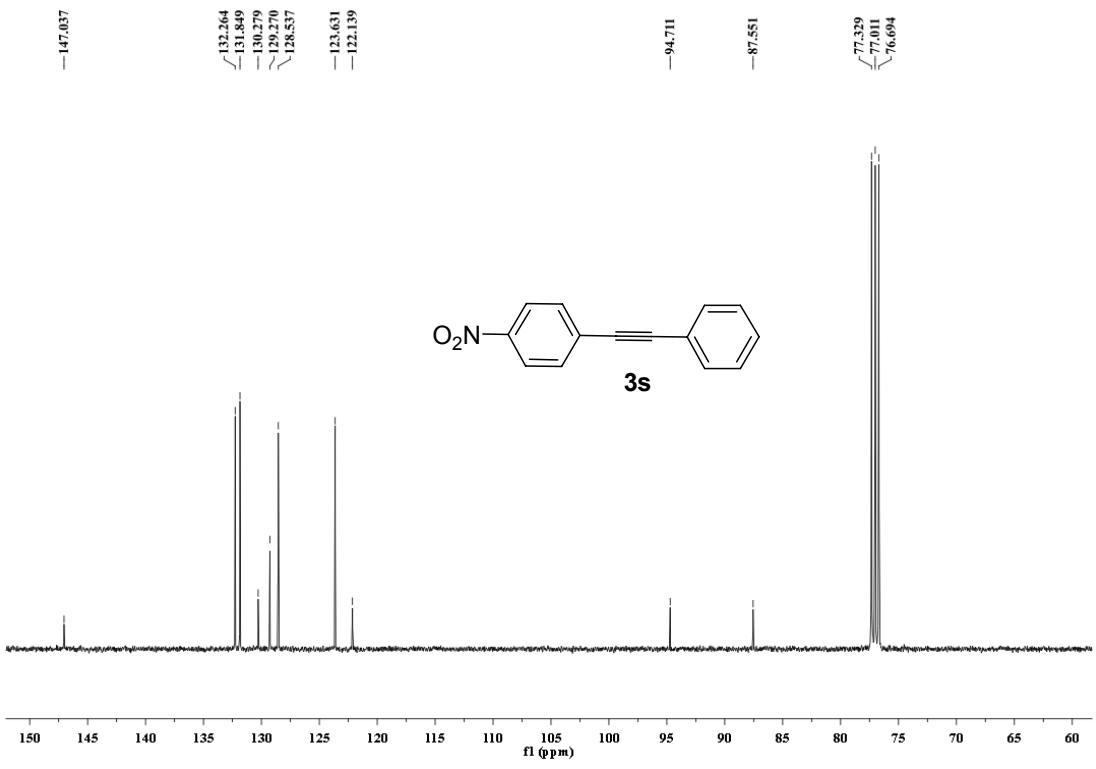

8.042
8.021
7.580
7.557
7.542
7.376
7.367
7.360
7.261
4.418
4.400
4.383
4.365
1.426
1.408
1.390
EtOOC
3q
7.601
7.580
7.566
7.557
7.548
7.542
f1 (ppm)
1.95
1.97
1.94
2.93
1.99
3.00

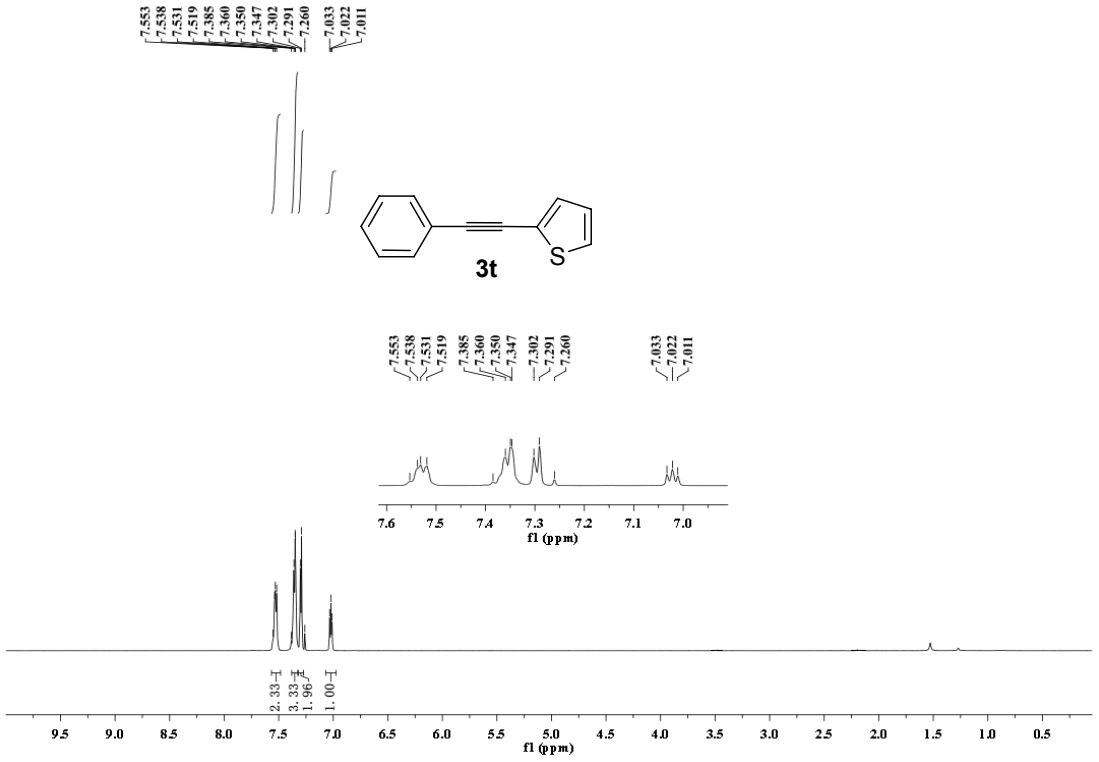

166.090
131.743
131.471
129.846
129.493
128.750
128.443
127.888
122.742
92.271
88.700
77.364
77.046
76.729
61.145
14.331
EtOOC
3q
f1 (ppm)

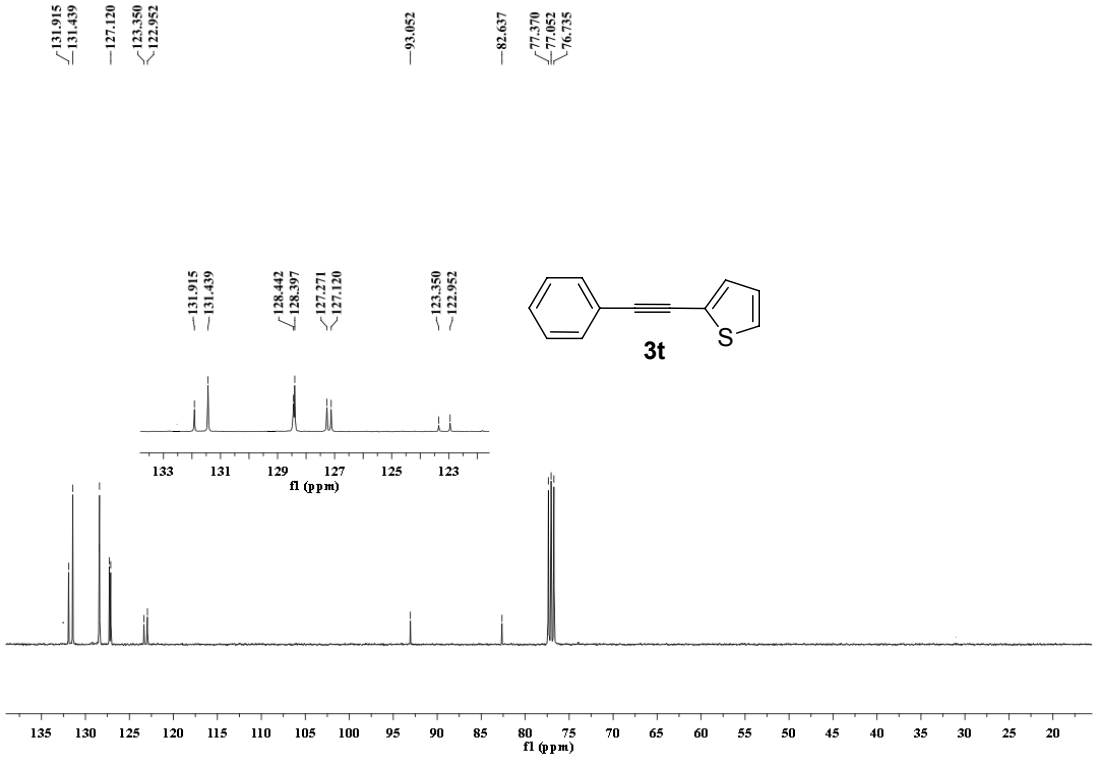

7.703
7.685
7.667
7.571
7.563
7.544
7.524
7.505
7.438
7.419
7.383
7.375
7.369
7.346
7.261
3r
CF3
f1 (ppm)

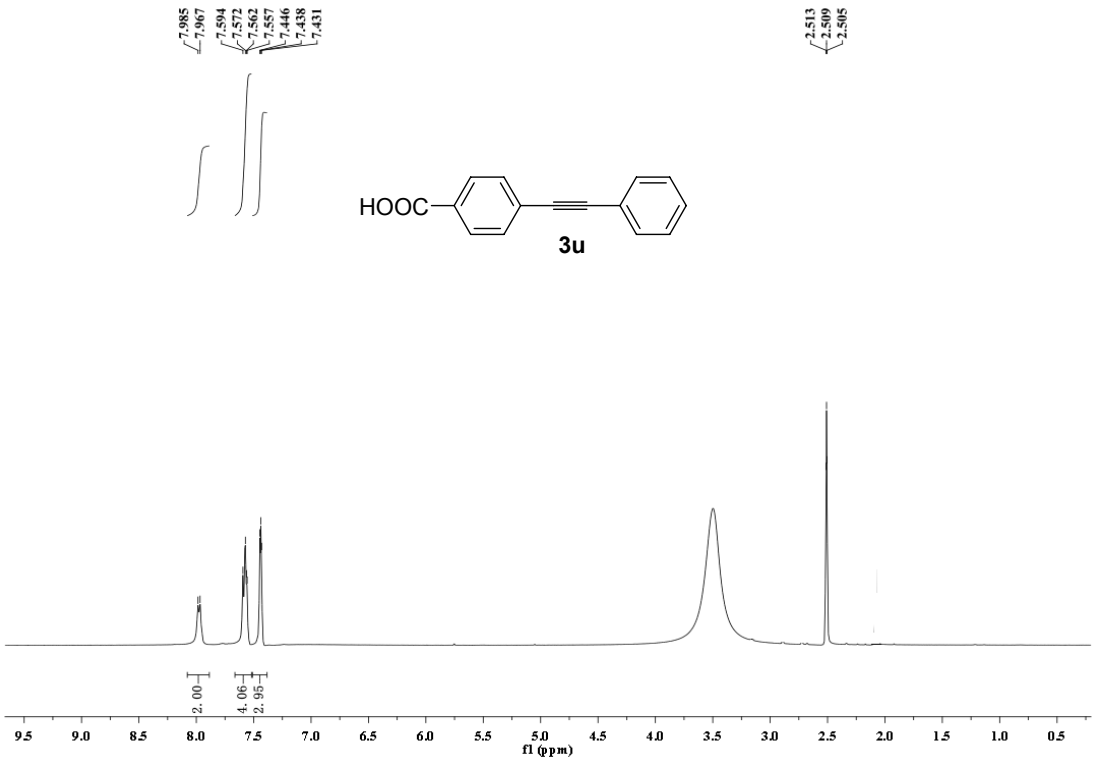

133.720
132.518
131.717
131.404
128.458
127.924
125.934
125.834
122.761
121.610
94.957
85.378
77.347
77.029
76.711
3r
CF3
f1 (ppm)

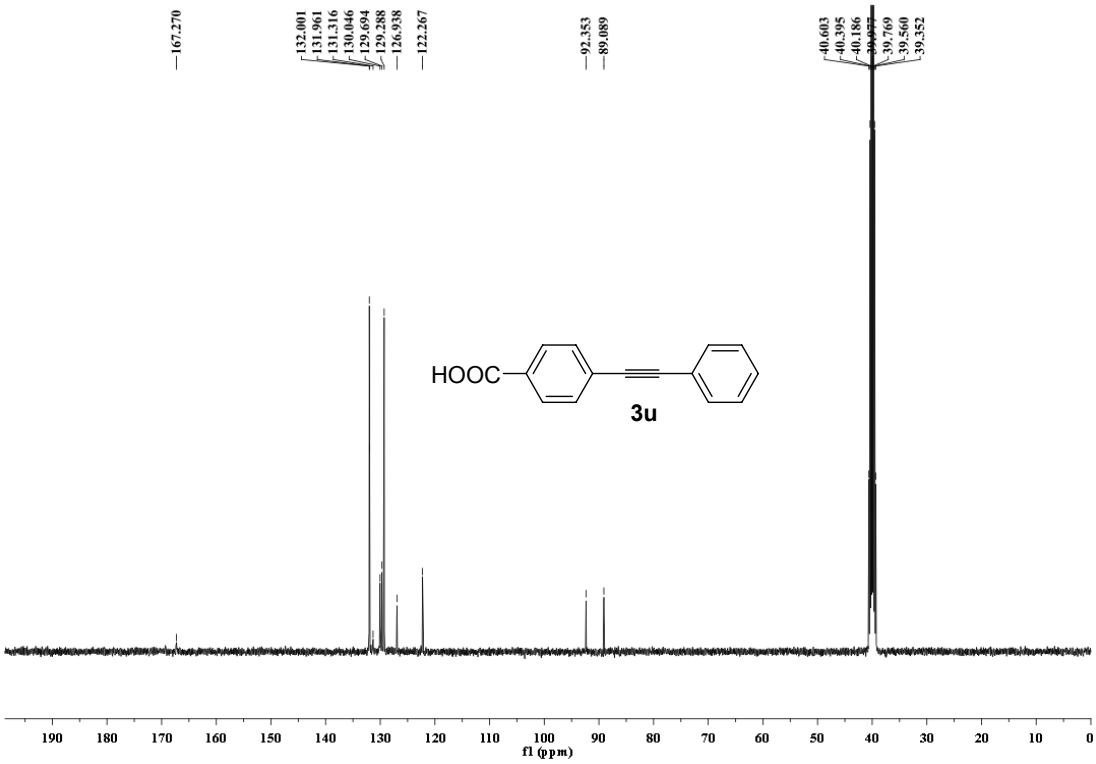

8.235
8.213
7.679
7.658
7.571
7.561
7.552
7.400
7.389
7.261
O2N
3s
fl (ppm)
2.00
2.08
2.09
3.11

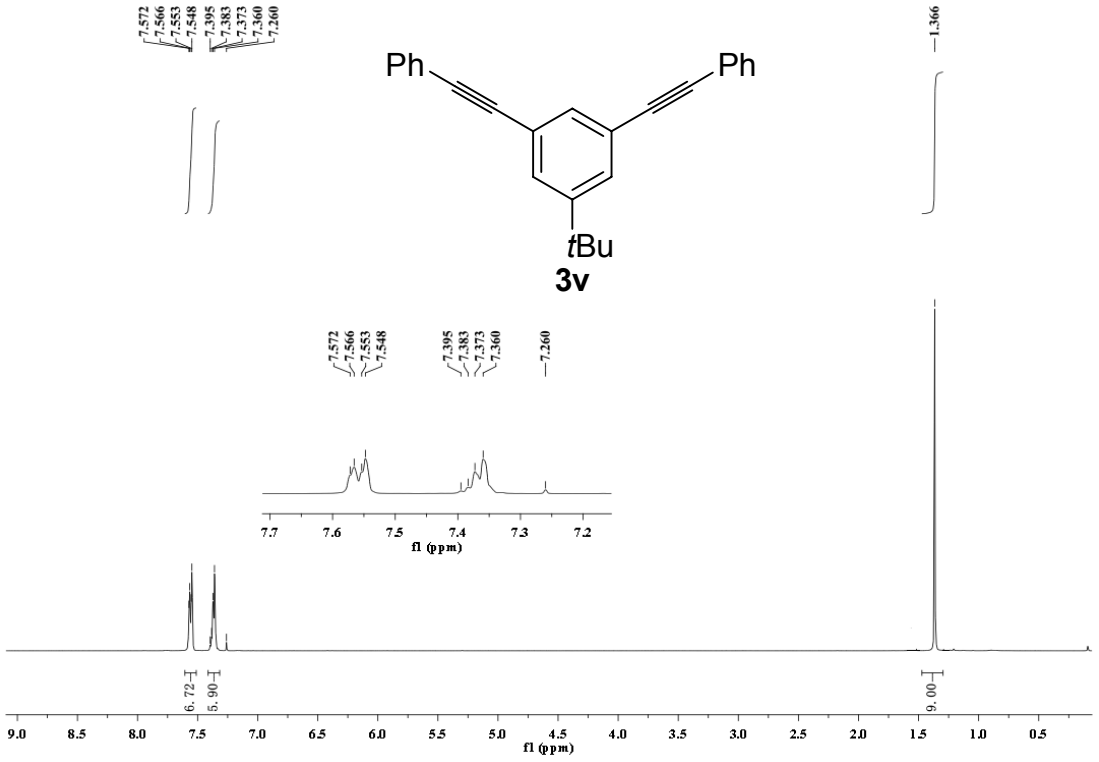

147.037
132.264
131.849
130.279
129.270
128.537
123.631
122.139
94.711
87.551
77.329
77.011
76.694
O2N
3s
fl (ppm)

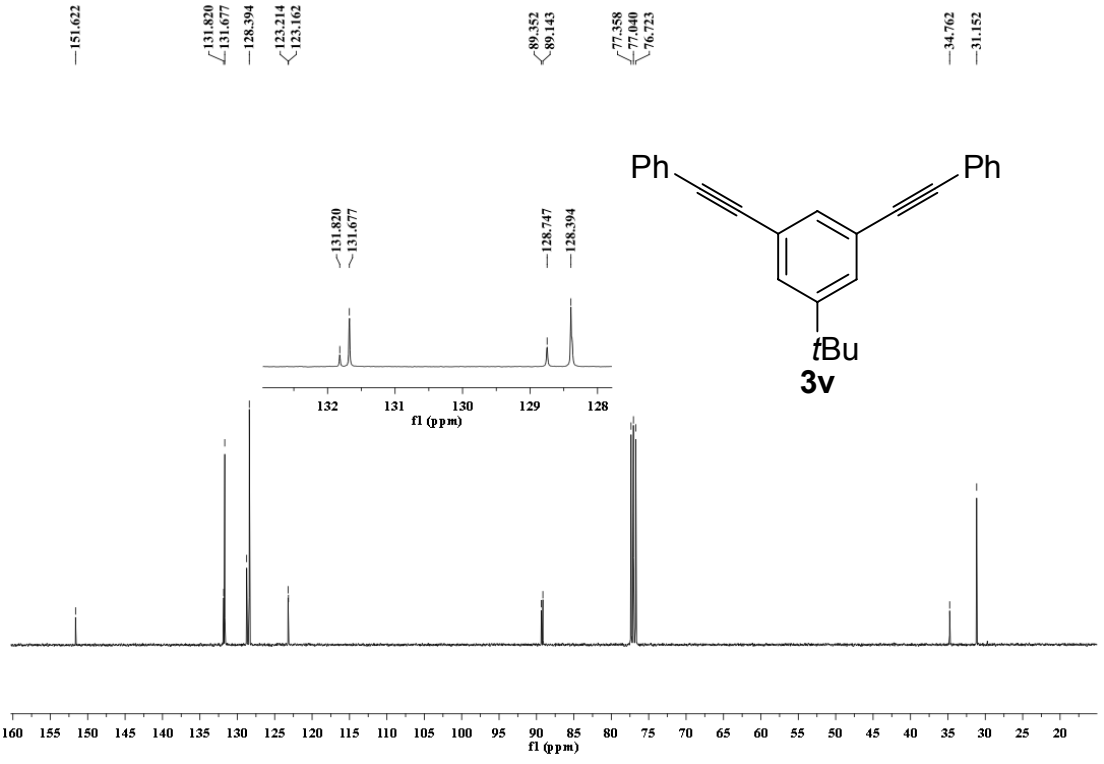

7.553
7.538
7.531
7.519
7.385
7.360
7.350
7.347
7.302
7.291
7.260
7.033
7.022
7.011
S
3t
f1 (ppm)
2.33
3.33
1.96
1.00

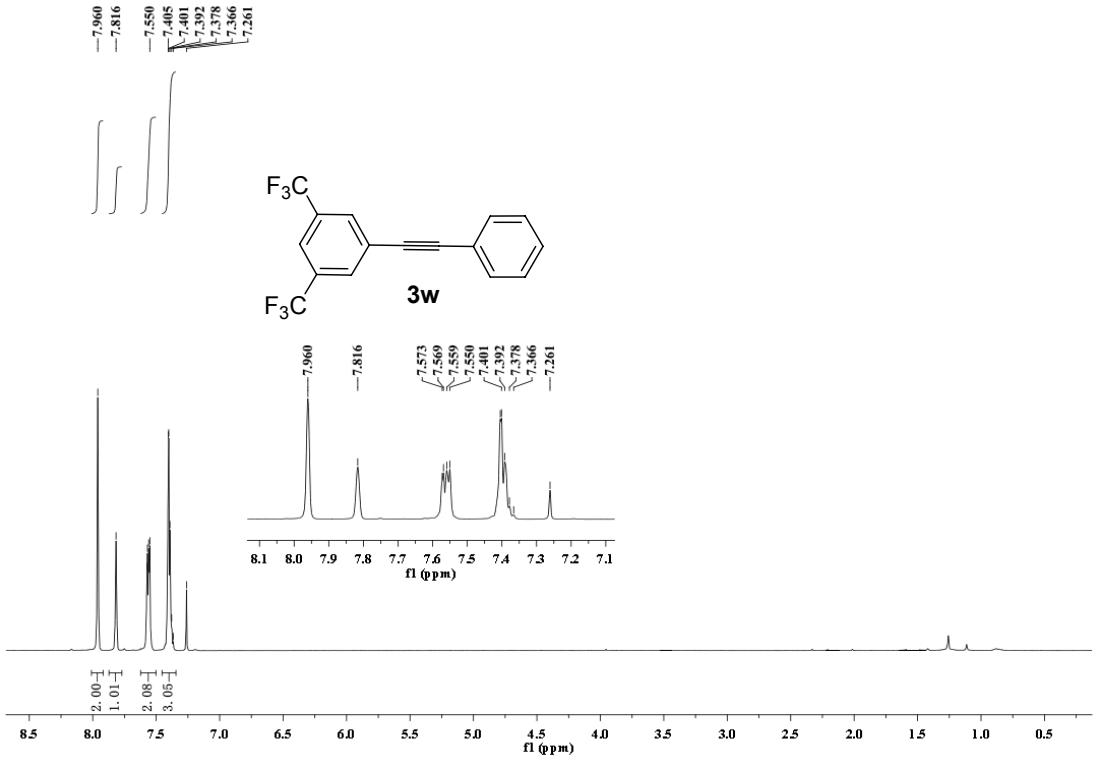

131.915
131.439
127.120
123.350
122.952
93.052
82.637
77.370
77.052
76.735
128.442
128.397
127.271
127.120
S
3t
f1 (ppm)

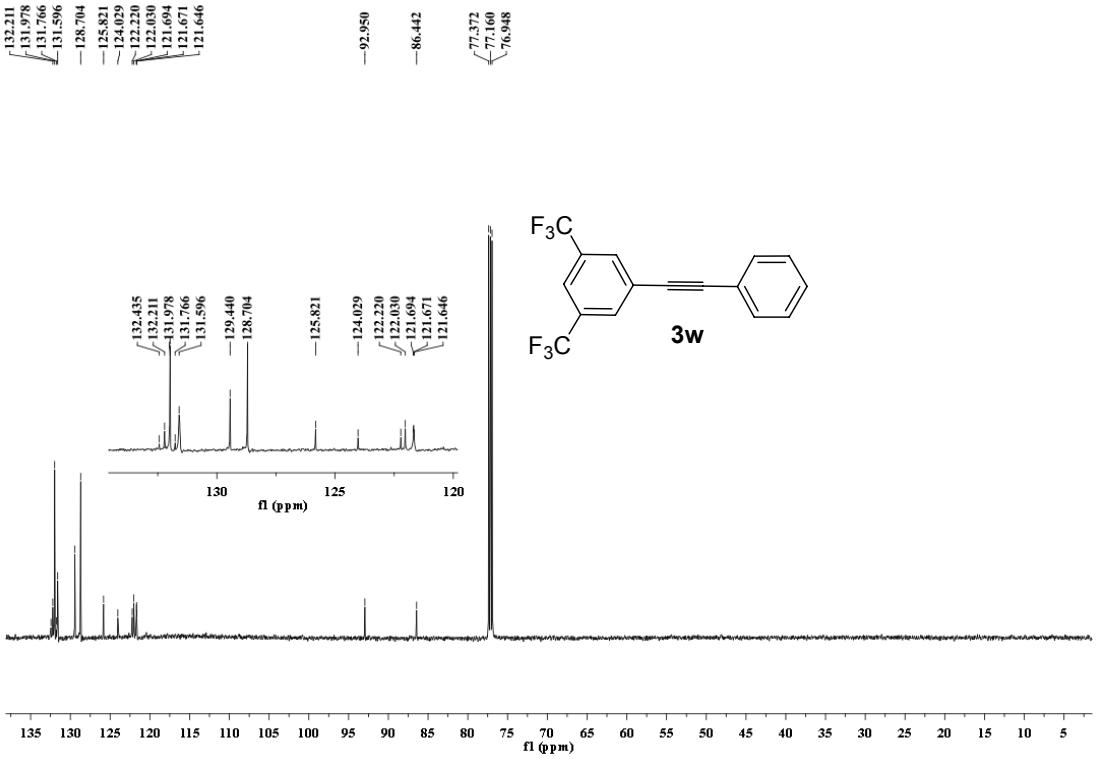

7.985
7.967
7.594
7.572
7.562
7.557
7.446
7.438
7.431
2.513
2.509
2.505
HOOC
3u
2.00
4.06
2.95
f1 (ppm)

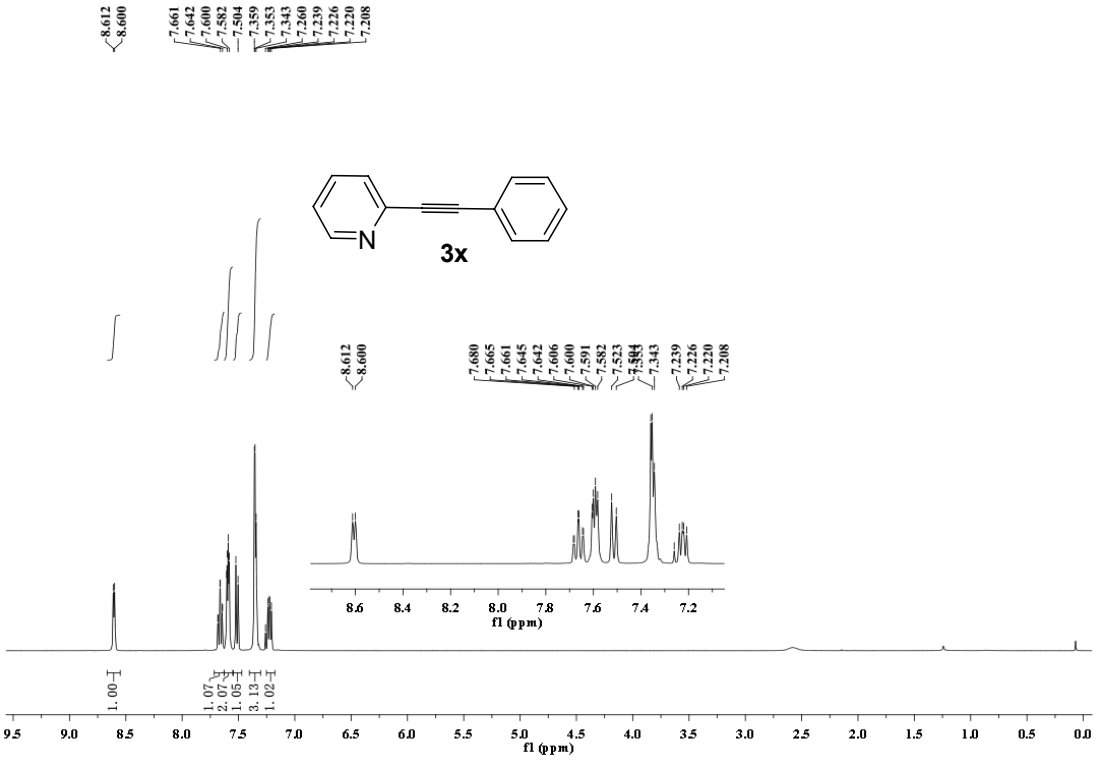

167.270
132.001
131.961
131.316
130.046
129.694
129.288
126.938
122.267
92.353
89.089
40.603
40.395
40.186
39.769
39.560
39.352
HOOC
3u
f1 (ppm)

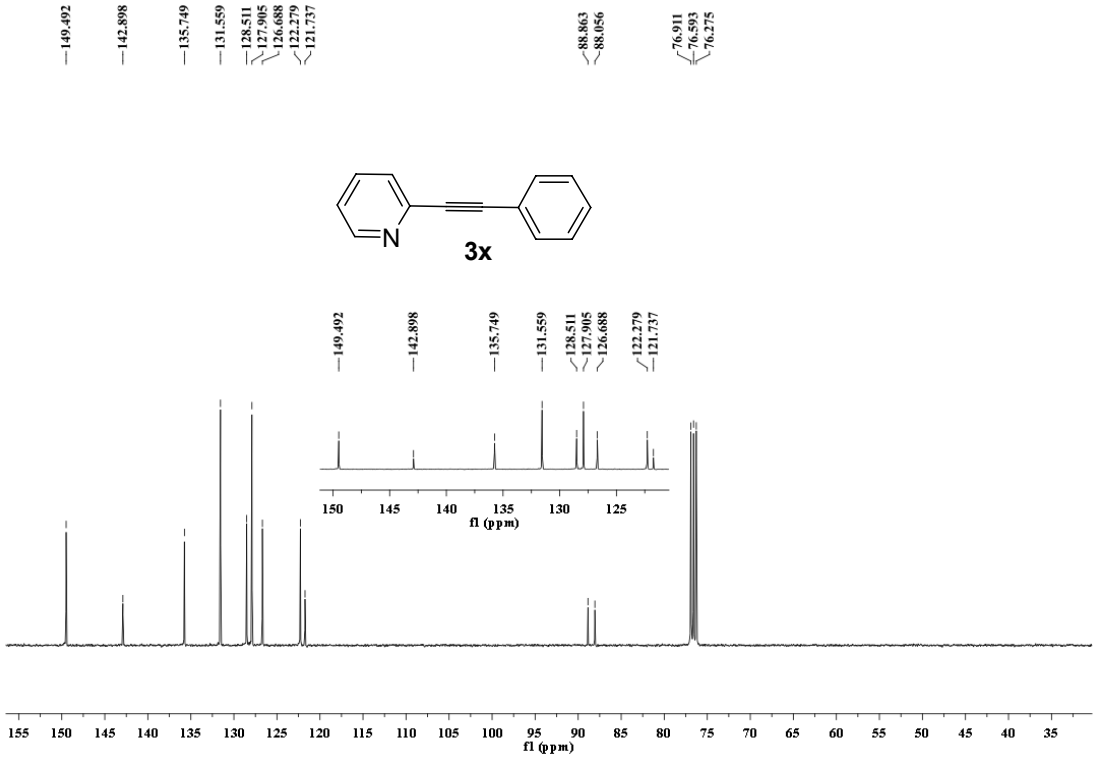

7.572
7.566
7.553
7.548
7.395
7.383
7.373
7.360
7.260
1.366
Ph
Ph
tBu
3v
6.72
5.90
9.00
f1 (ppm)

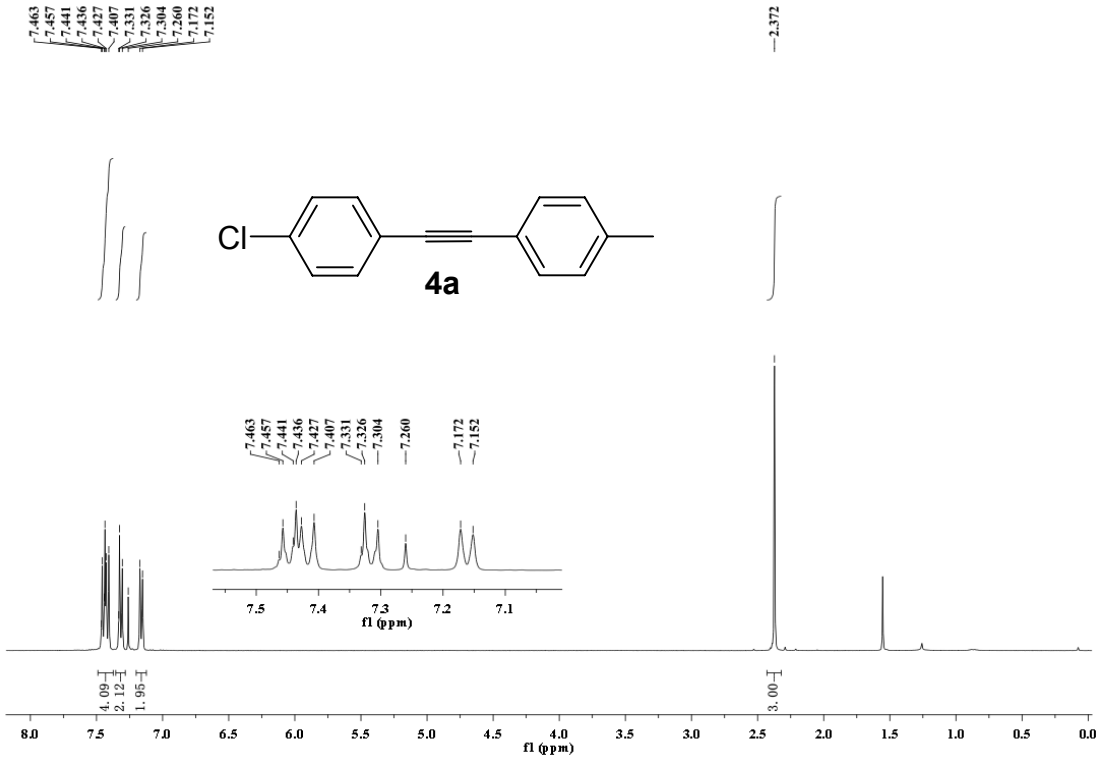

151.622
131.820
131.677
128.394
123.214
123.162
89.352
89.143
77.358
77.040
76.723
34.762
31.152
128.747
Ph
Ph
tBu
3v
f1 (ppm)

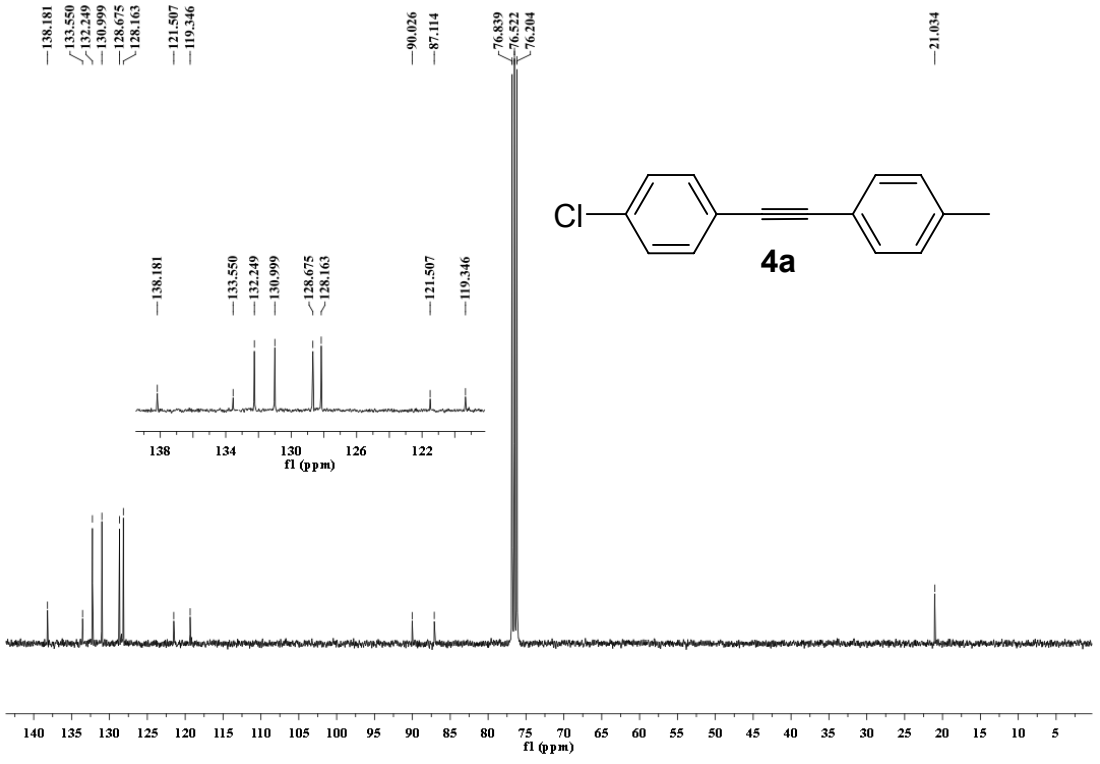

7.960
7.816
7.550
7.405
7.401
7.392
7.378
7.366
7.261
F3C
F3C
3w
7.573
7.569
7.559
2.00
1.01
2.08
3.05
f1 (ppm)

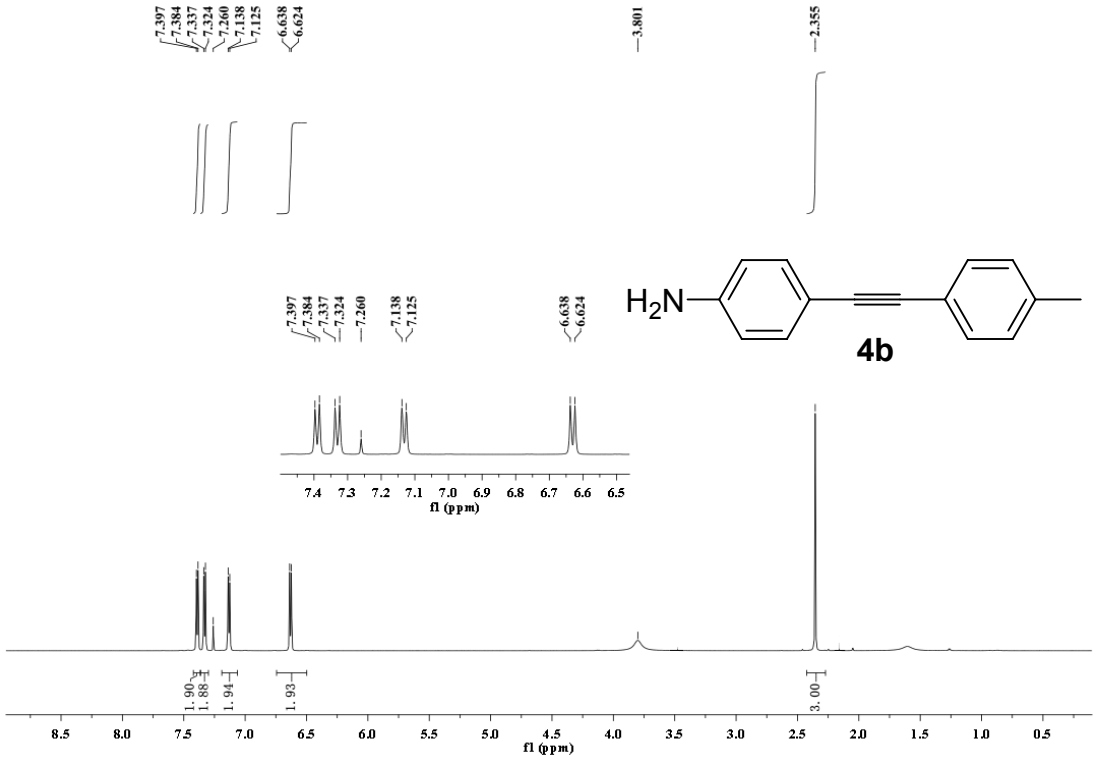

132.211
131.978
131.766
131.596
128.704
125.821
124.029
122.220
122.030
121.694
121.671
121.646
92.950
86.442
77.372
77.160
76.948
132.435
129.440
F3C
F3C
3w
f1 (ppm)

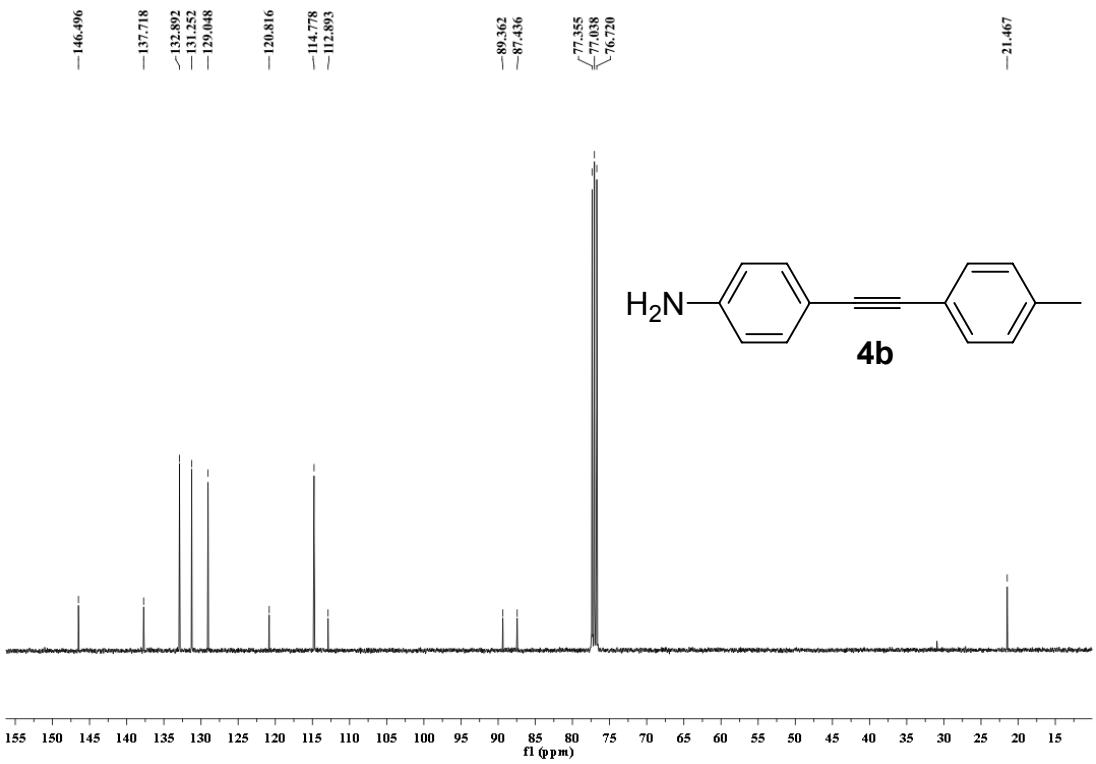

8.612
8.600
7.661
7.642
7.600
7.582
7.504
7.359
7.353
7.343
7.260
7.239
7.226
7.220
7.208
N
3x
8.612
8.600
7.680
7.665
7.661
7.645
7.642
7.606
7.600
7.591
7.582
7.523
7.343
7.239
7.226
7.220
7.208
1.00
1.07
2.07
1.05
3.13
1.02
f1 (ppm)

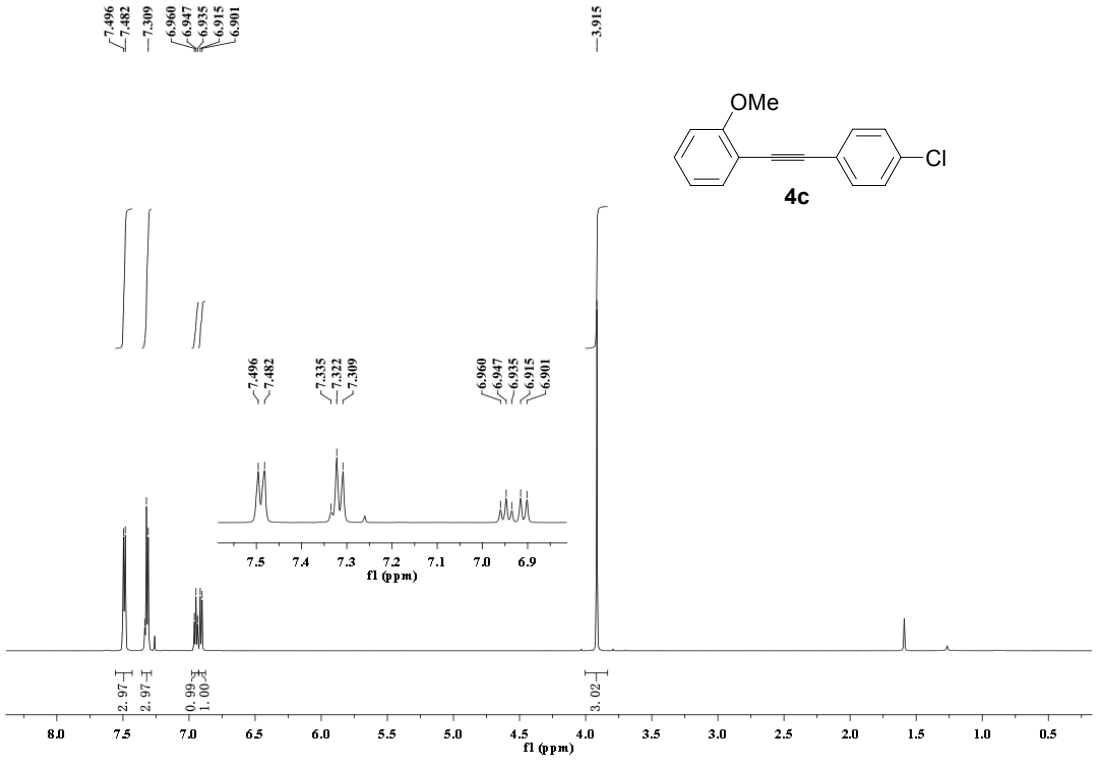

149.492
142.898
135.749
131.559
128.511
127.905
126.688
122.279
121.737
88.863
88.056
76.911
76.593
76.275
N
3x
f1 (ppm)

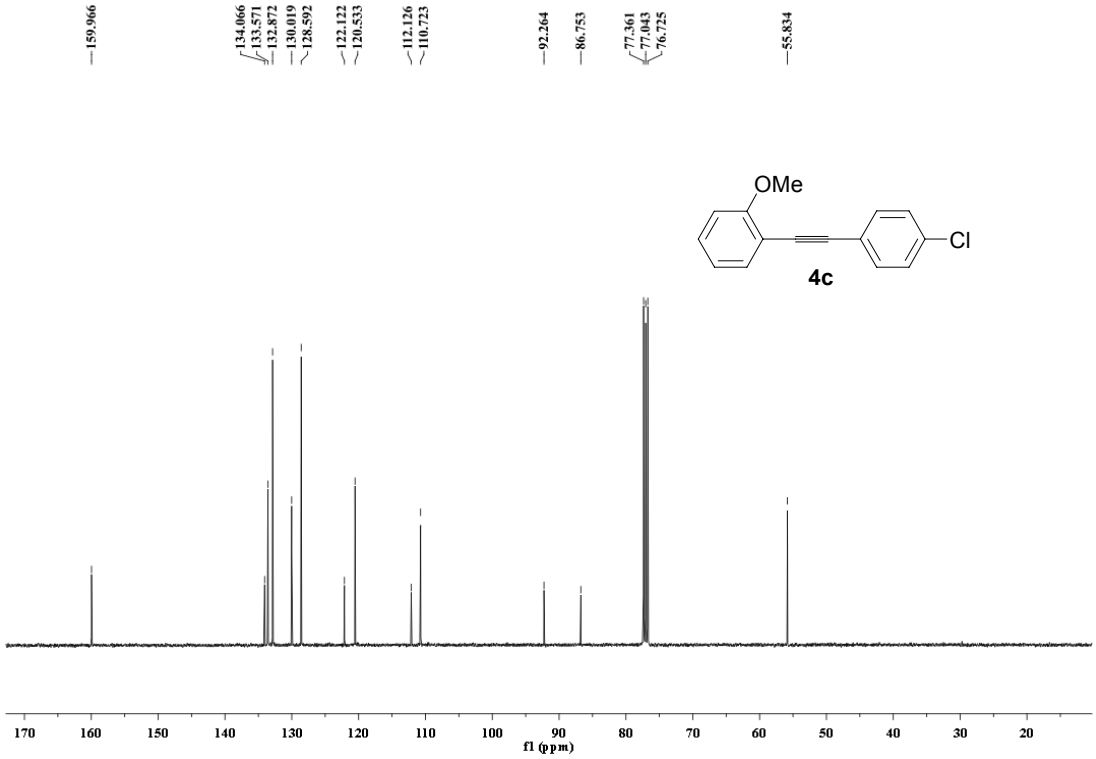

7.463
7.457
7.441
7.436
7.427
7.407
7.331
7.326
7.304
7.260
7.172
7.152
2.372
Cl
4a
4.09
2.12
1.95
3.00
f1 (ppm)

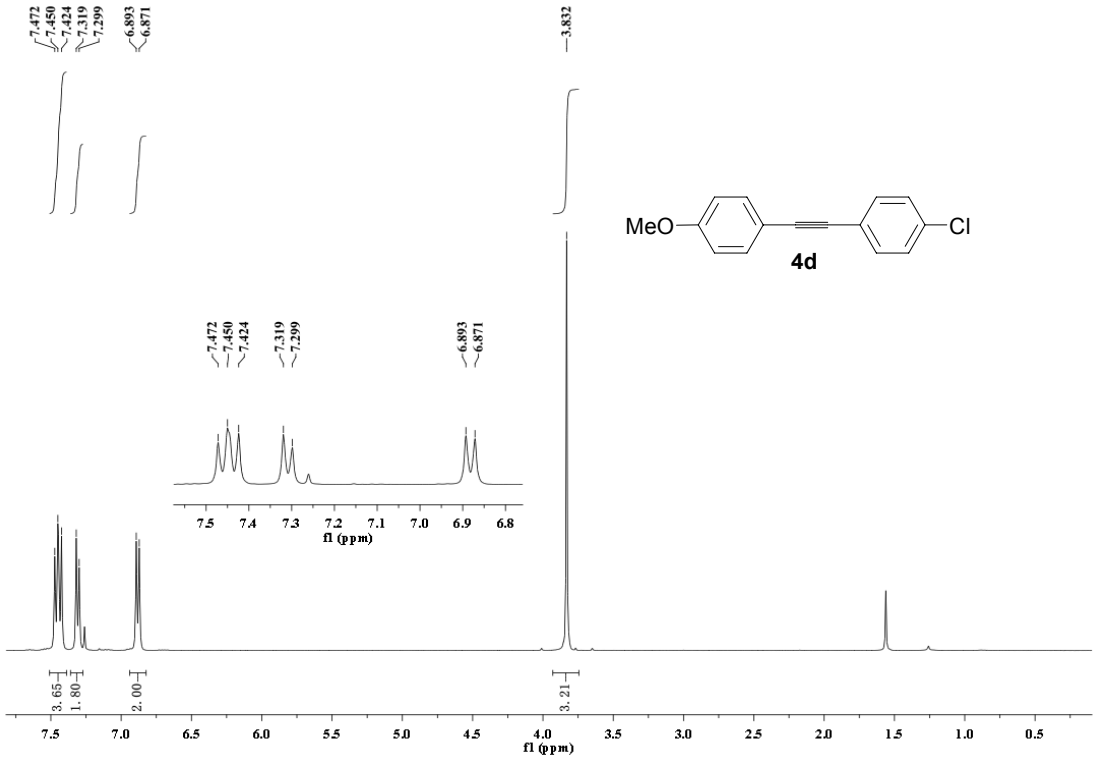

138.181
133.550
132.249
130.999
128.675
128.163
121.507
119.346
90.026
87.114
76.839
76.522
76.204
21.034
Cl
4a
f1 (ppm)

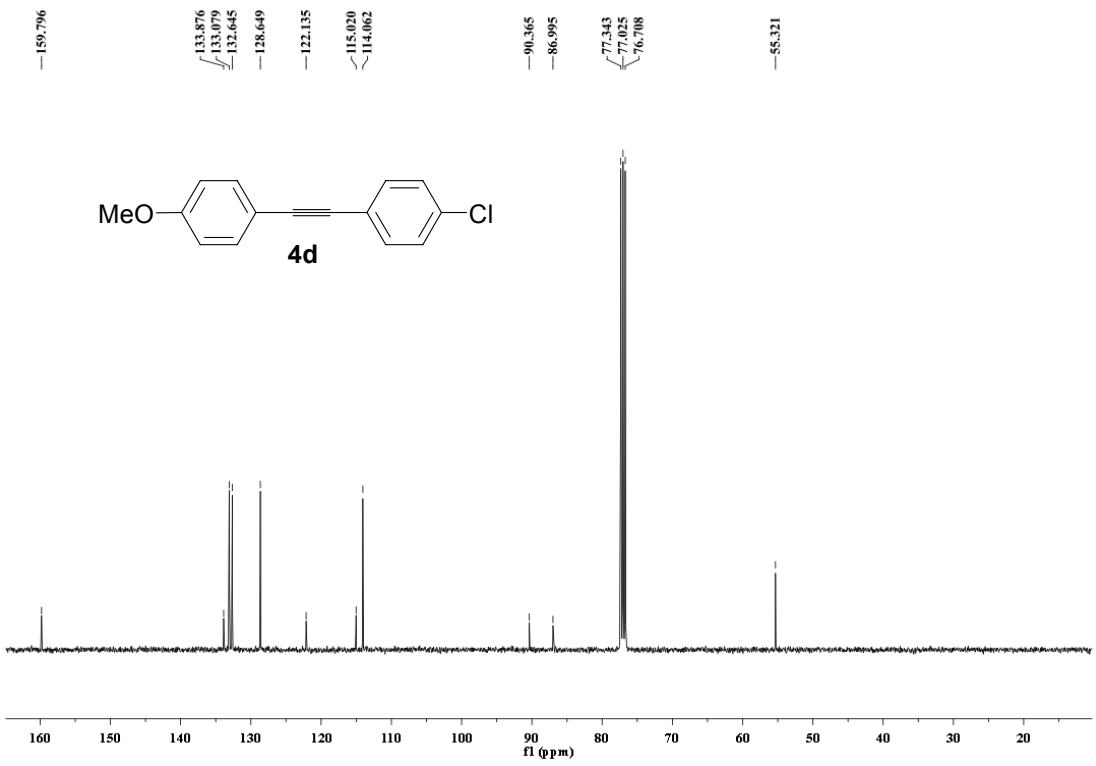

7.397
7.384
7.337
7.324
7.260
7.138
7.125
6.638
6.624
3.801
2.355
H2N
4b
f1 (ppm)
1.90
1.88
1.94
1.93
3.00

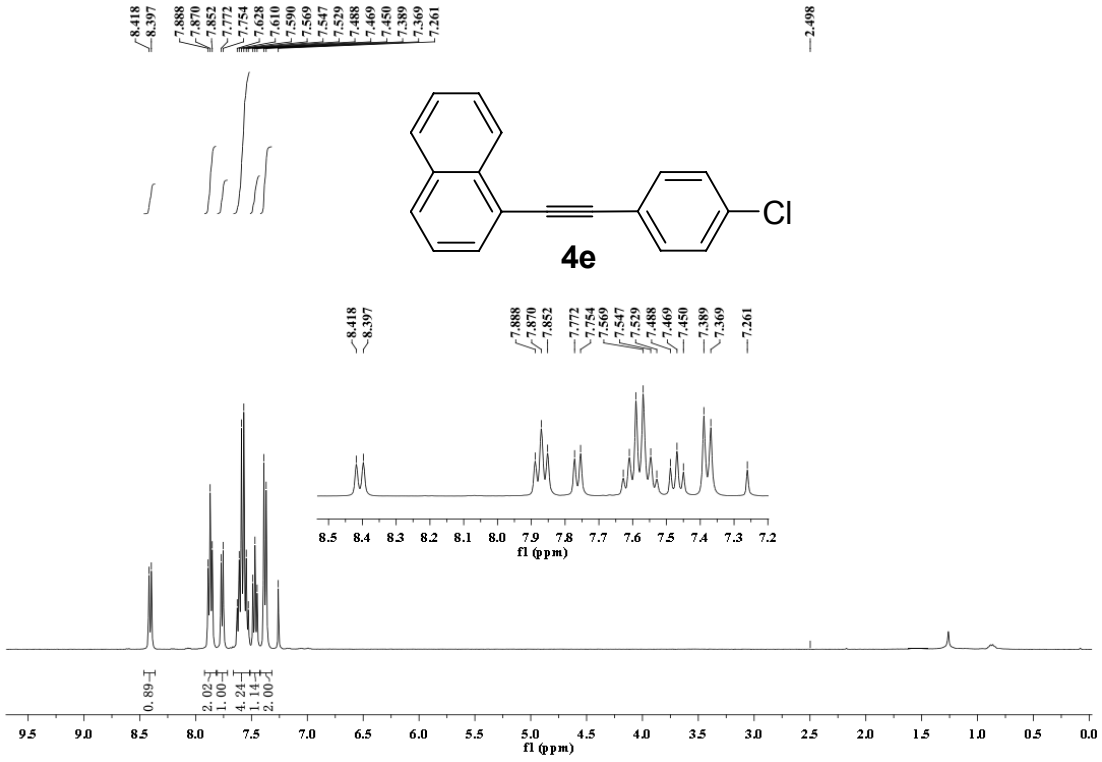

146.496
137.718
132.892
131.252
129.048
120.816
114.778
112.893
89.362
87.436
77.355
77.038
76.720
21.467
H2N
4b
f1 (ppm)

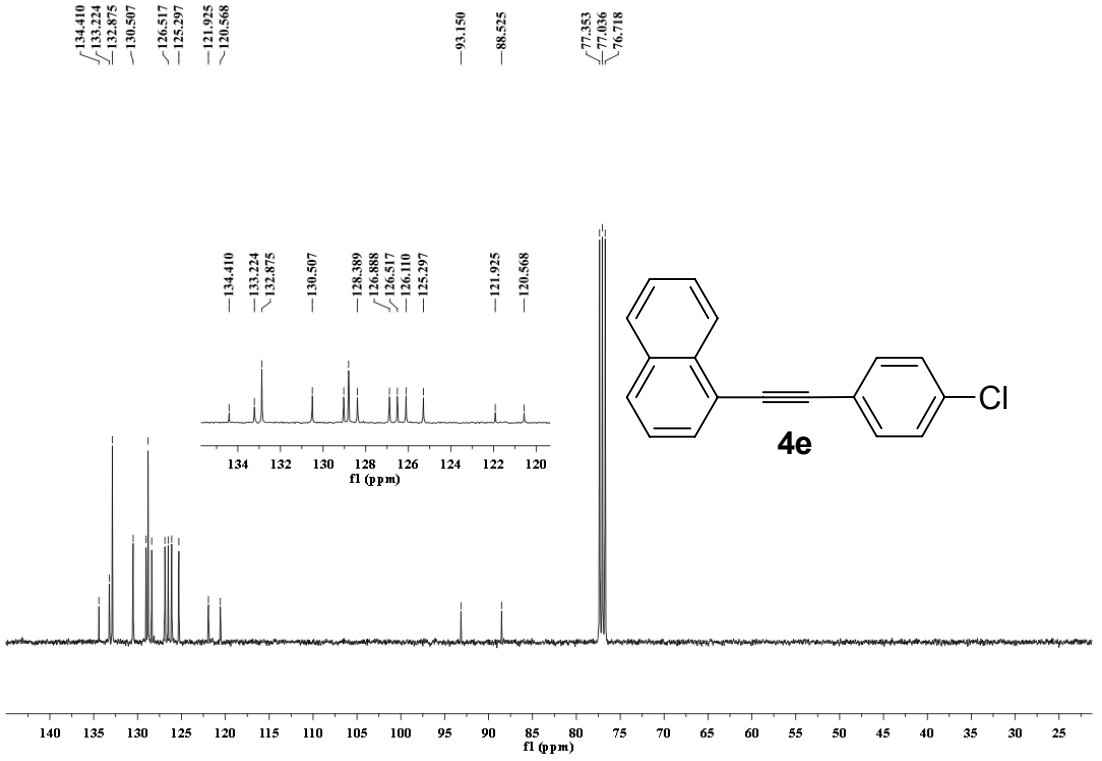

7.496
7.482
7.309
6.960
6.947
6.935
6.915
6.901
3.915
OMe
Cl
4c
7.335
7.322
f1 (ppm)
2.97
2.97
0.99
1.00
3.02

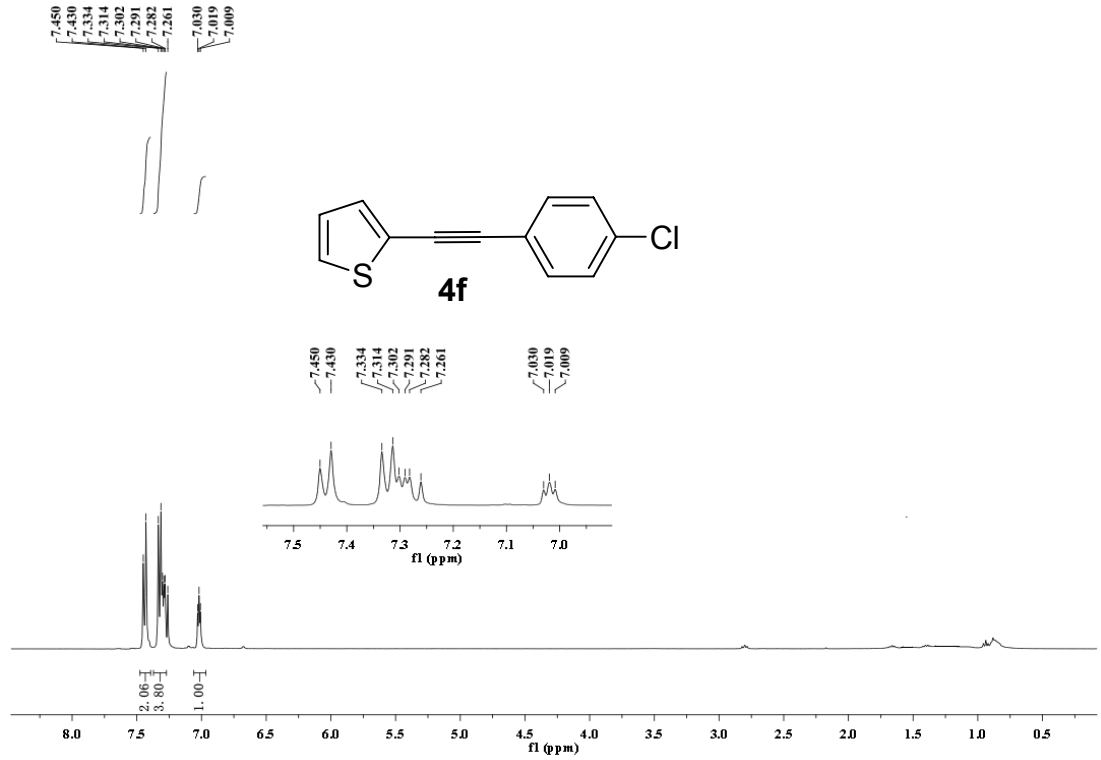

159.966
134.066
133.571
132.872
130.019
128.592
122.122
120.533
112.126
110.723
92.264
86.753
77.361
77.043
76.725
55.834
OMe
Cl
4c
f1 (ppm)

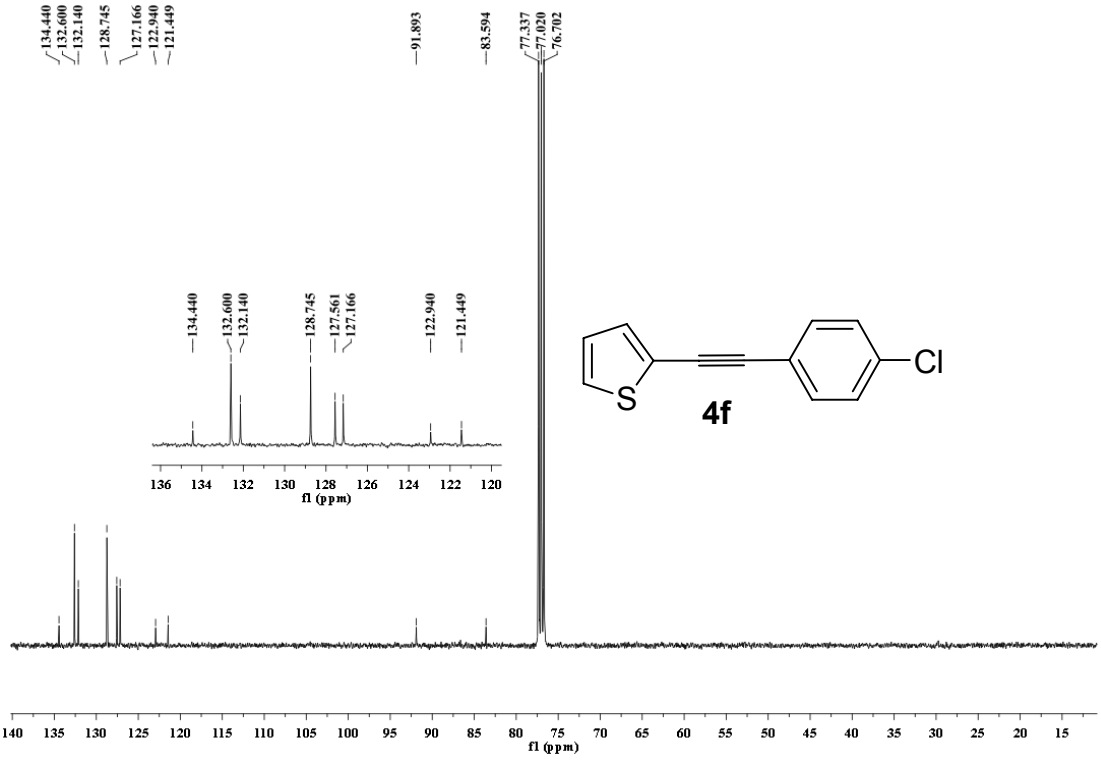

7.472
7.450
7.424
7.319
7.299
6.893
6.871
3.832
MeO
Cl
4d
3.65
1.80
2.00
3.21
f1 (ppm)


159.796
133.876
133.079
132.645
128.649
122.135
115.020
114.062
90.365
86.995
77.343
77.025
76.708
55.321
MeO
Cl
4d
f1 (ppm)


8.418
8.397
7.888
7.870
7.852
7.772
7.754
7.628
7.610
7.590
7.569
7.547
7.529
7.488
7.469
7.450
7.389
7.369
7.261
2.498
Cl
4e
0.89
2.02
1.00
4.24
1.14
2.00
f1 (ppm)


134.410
133.224
132.875
130.507
126.517
125.297
121.925
120.568
93.150
88.525
77.353
77.036
76.718
Cl
4e
f1 (ppm)


7.450
7.430
7.334
7.314
7.302
7.291
7.282
7.261
7.030
7.019
7.009
Cl
S
4f
2.06
3.80
1.00
f1 (ppm)


134.440
132.600
132.140
128.745
127.166
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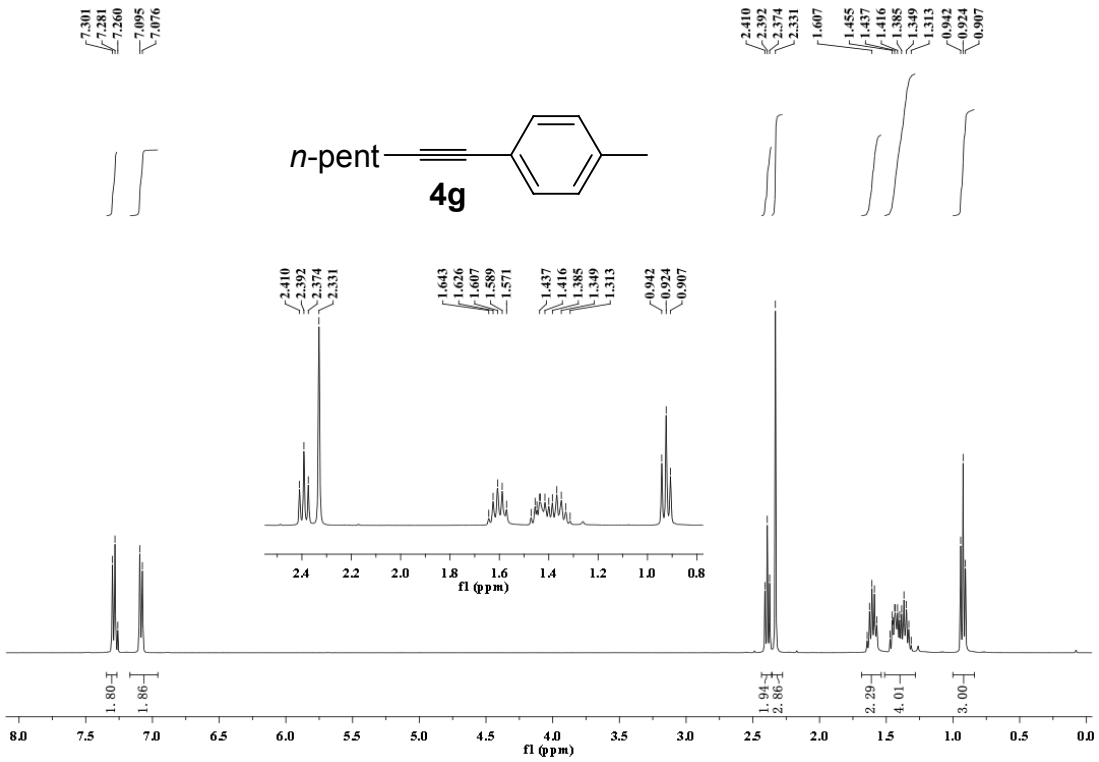
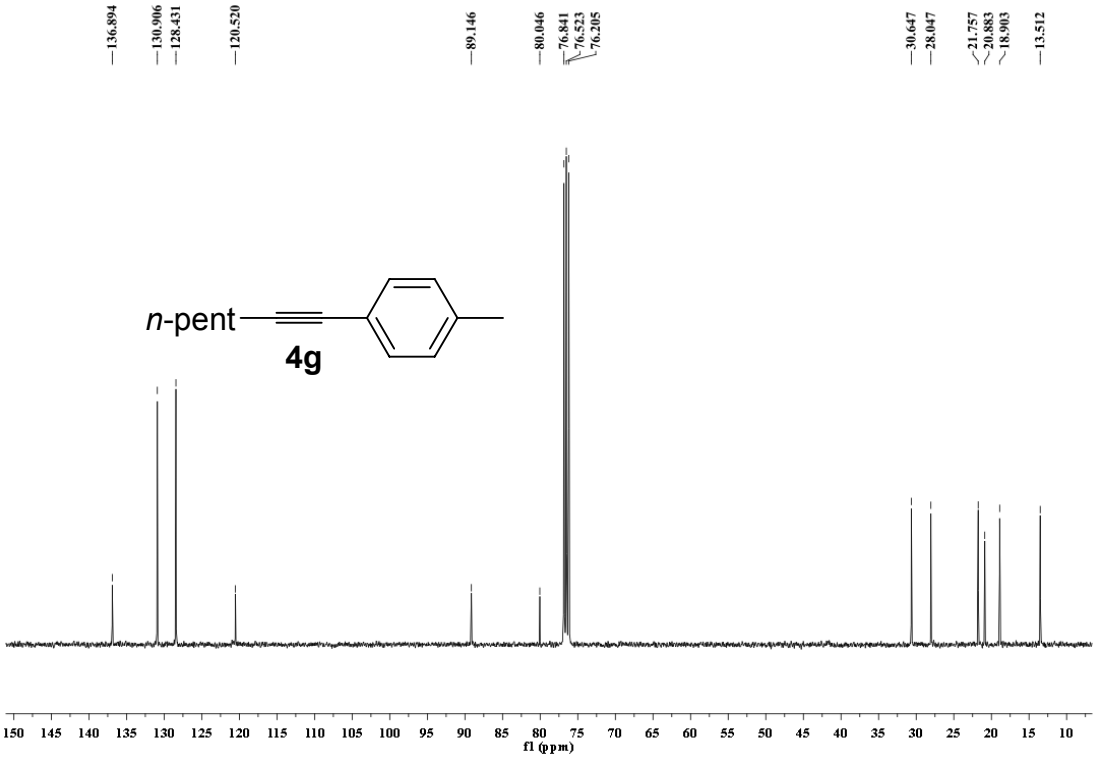
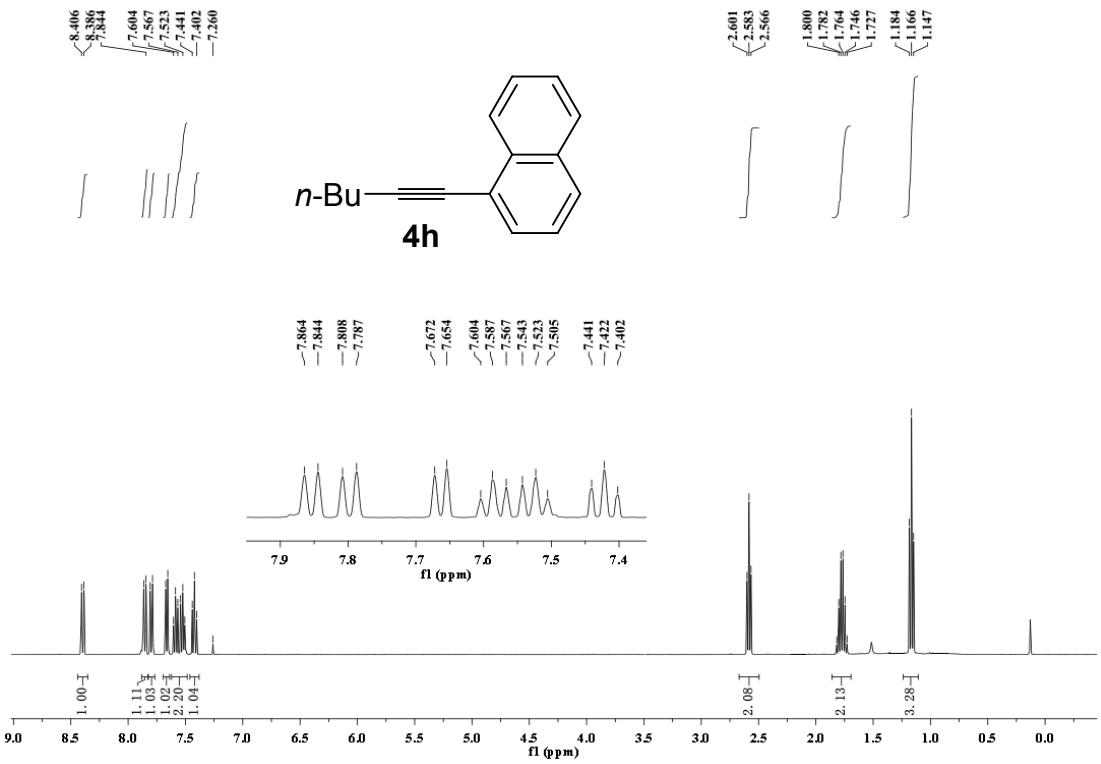
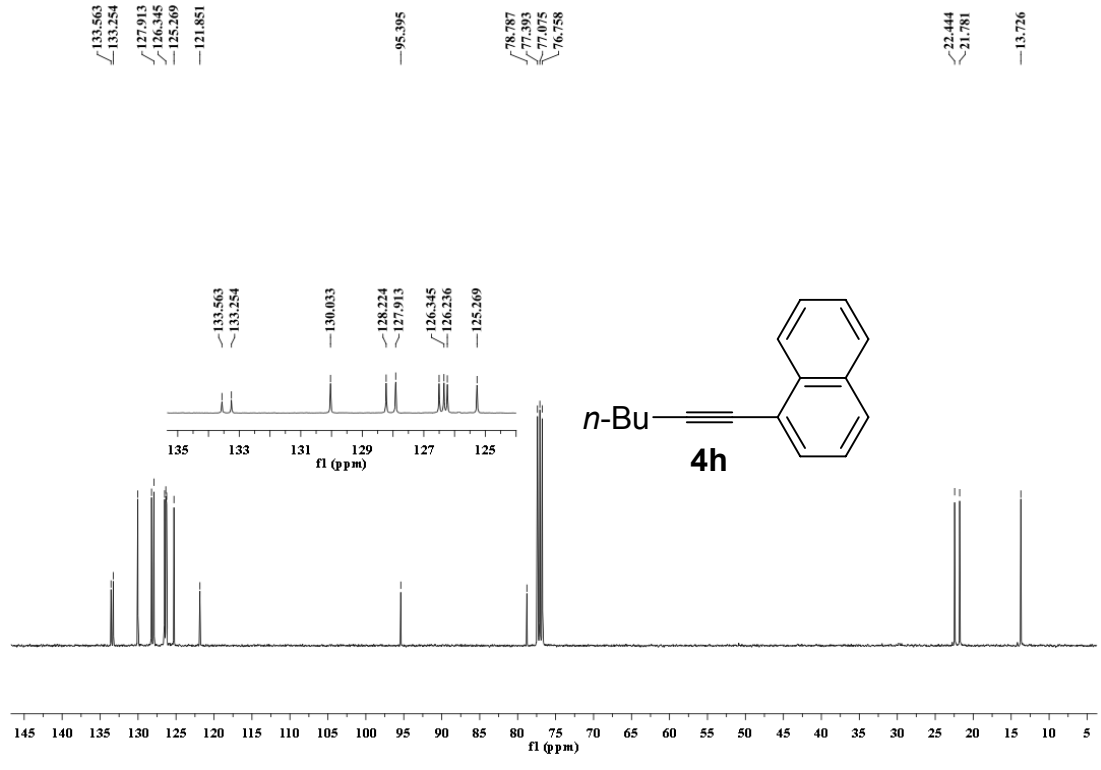
121.449
91.893
83.594
77.337
77.020
76.702
Cl
S
4f
f1 (ppm)


7.301
7.281
7.260
7.095
7.076
2.410
2.392
2.374
2.331
1.607
1.455
1.437
1.416
1.385
1.349
1.313
0.942
0.924
0.907
n-pent
4g
1.643
1.626
1.607
1.589
1.571
1.437
1.416
1.385
1.349
1.313
f1 (ppm)
1.80
1.86
1.94
2.86
2.29
4.01
3.00
f1 (ppm)


136.894
130.906
128.431
120.520
89.146
80.046
76.841
76.523
76.205
30.647
28.047
21.757
20.883
18.903
13.512
n-pent
4g
f1 (ppm)


8.406
8.386
7.844
7.604
7.567
7.523
7.441
7.402
7.260
2.601
2.583
2.566
1.800
1.782
1.764
1.746
1.727
1.184
1.166
1.147
n-Bu
4h
7.864
7.844
7.808
7.787
7.672
7.654
7.604
7.587
7.567
7.543
7.523
7.505
7.441
7.422
7.402
f1 (ppm)
1.00
1.11
1.03
1.02
2.20
1.04
2.08
2.13
3.28
f1 (ppm)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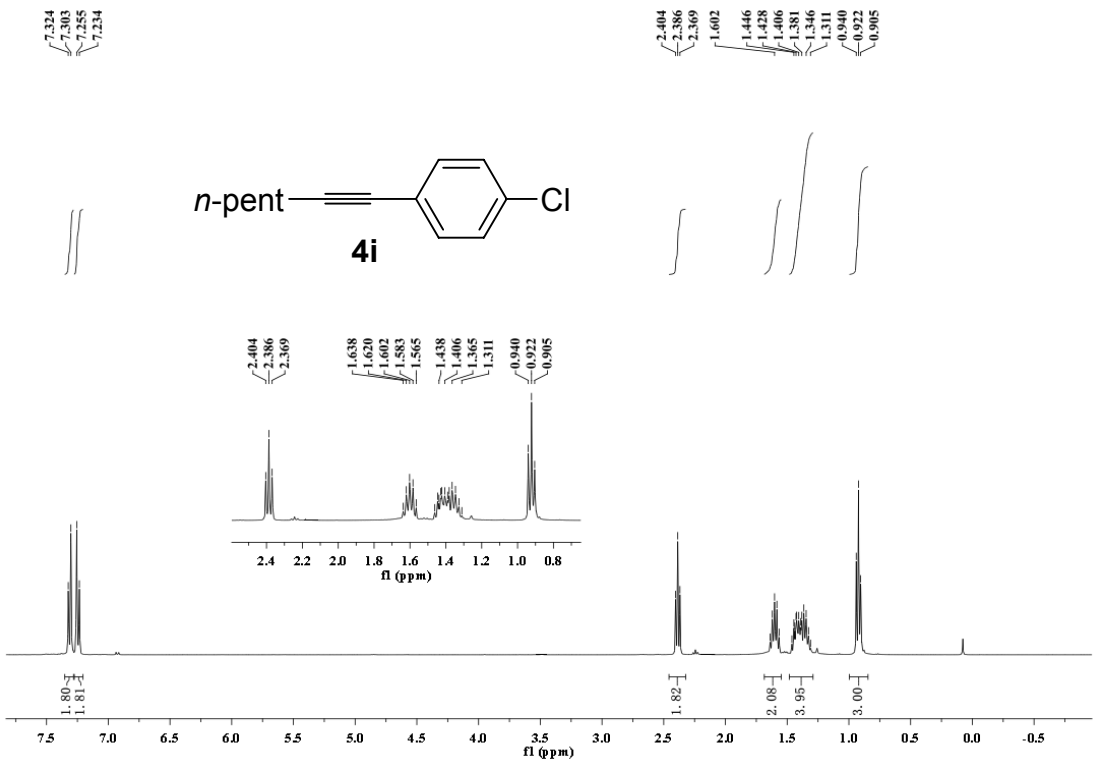
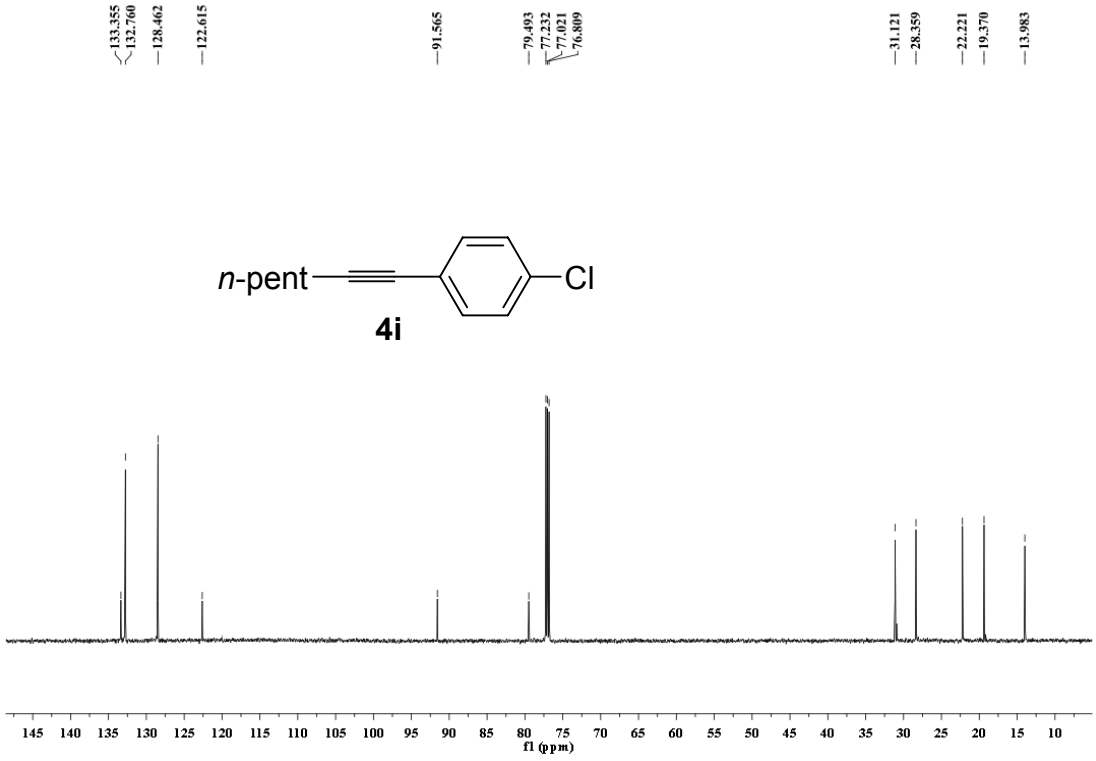
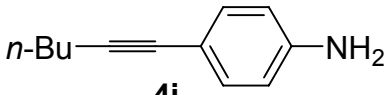
133.254
127.913
126.345
125.269
121.851
95.395
78.787
77.393
77.075
76.758
22.444
21.781
13.726
130.033
128.224
127.913
126.345
126.236
125.269
f1 (ppm)
n-Bu
4h
f1 (ppm)

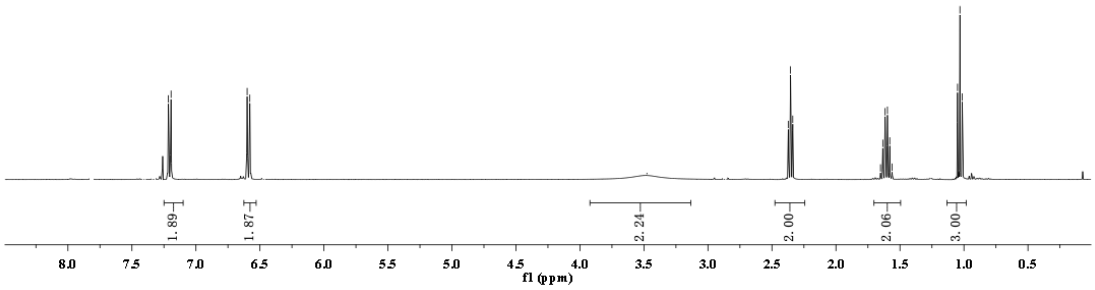

7.324
7.303
7.255
7.234
2.404
2.386
2.369
1.602
1.446
1.428
1.406
1.381
1.346
1.311
0.940
0.922
0.905
n-pent
Cl
4i
1.638
1.620
1.602
1.583
1.565
1.438
1.406
1.365
1.311
f1 (ppm)
1.80
1.81
1.82
2.08
3.95
3.00
f1 (ppm)

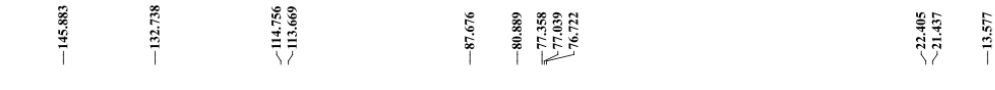

133.355
132.760
128.462
122.615
91.565
79.493
77.232
77.021
76.809
31.121
28.359
22.221
19.370
13.983
n-pent
Cl
4i
f1 (ppm)


7.215
7.194
6.600
6.579
3.477
2.373
2.355
2.337
1.652
1.634
1.616
1.598
1.580
1.562
1.050
1.031
1.013


n-Bu
NH2

4j


1.89
1.87
2.24
2.00
2.06
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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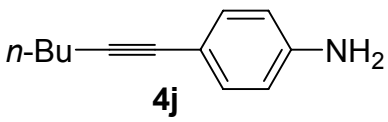
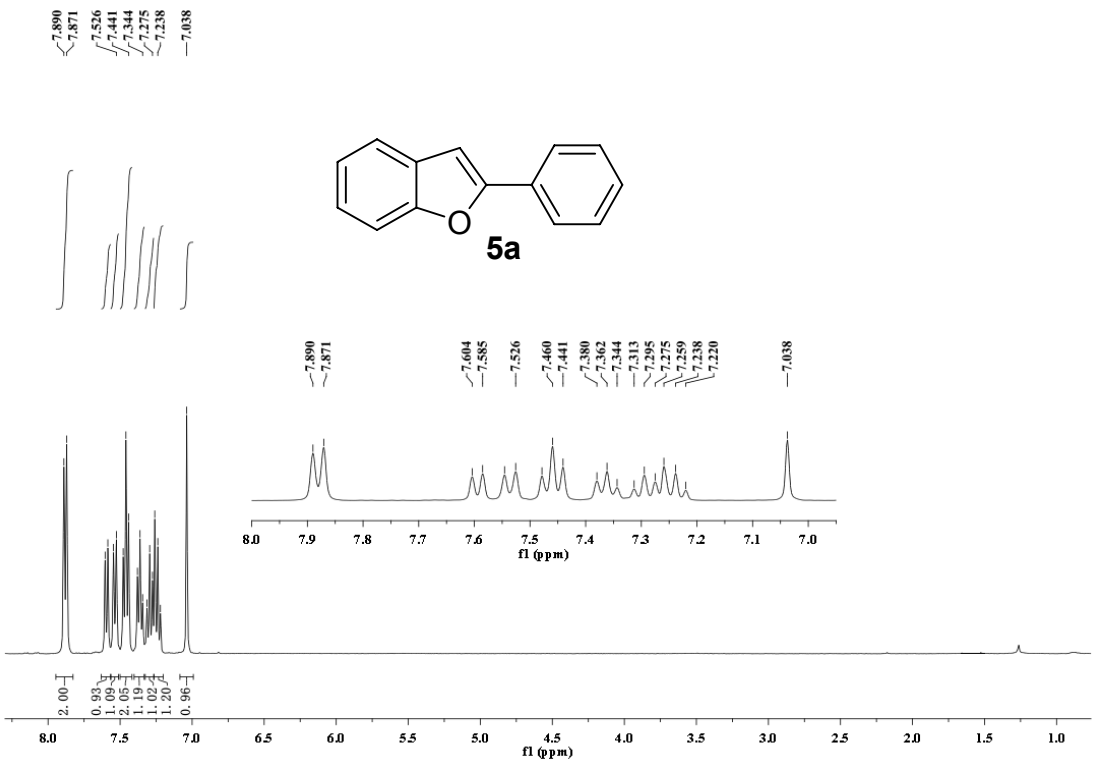
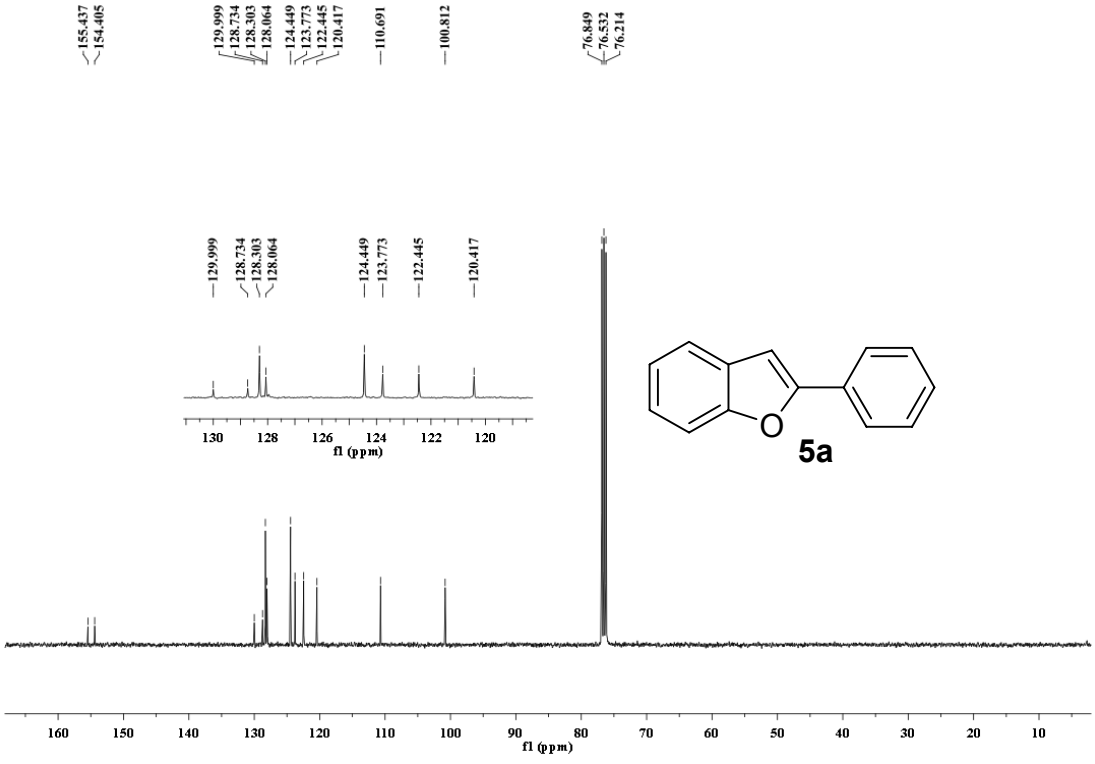
113.669
87.676
80.889
77.358
77.039
76.722
22.405
21.437
13.577

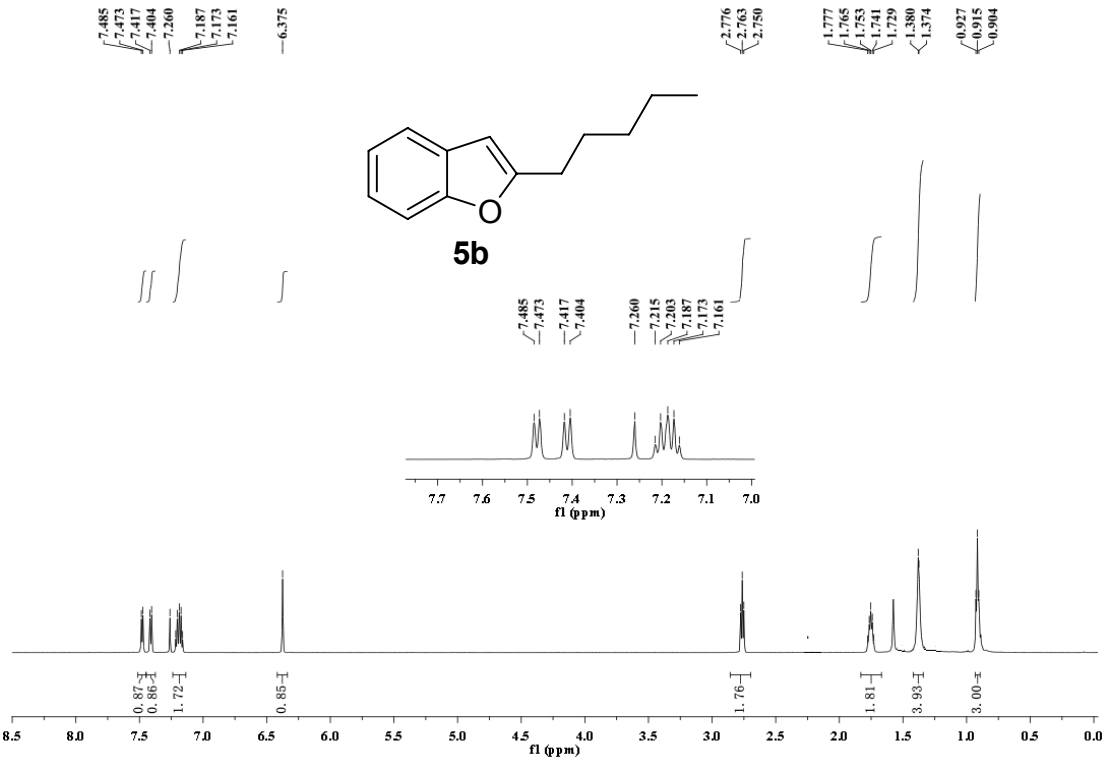

n-Bu
NH2

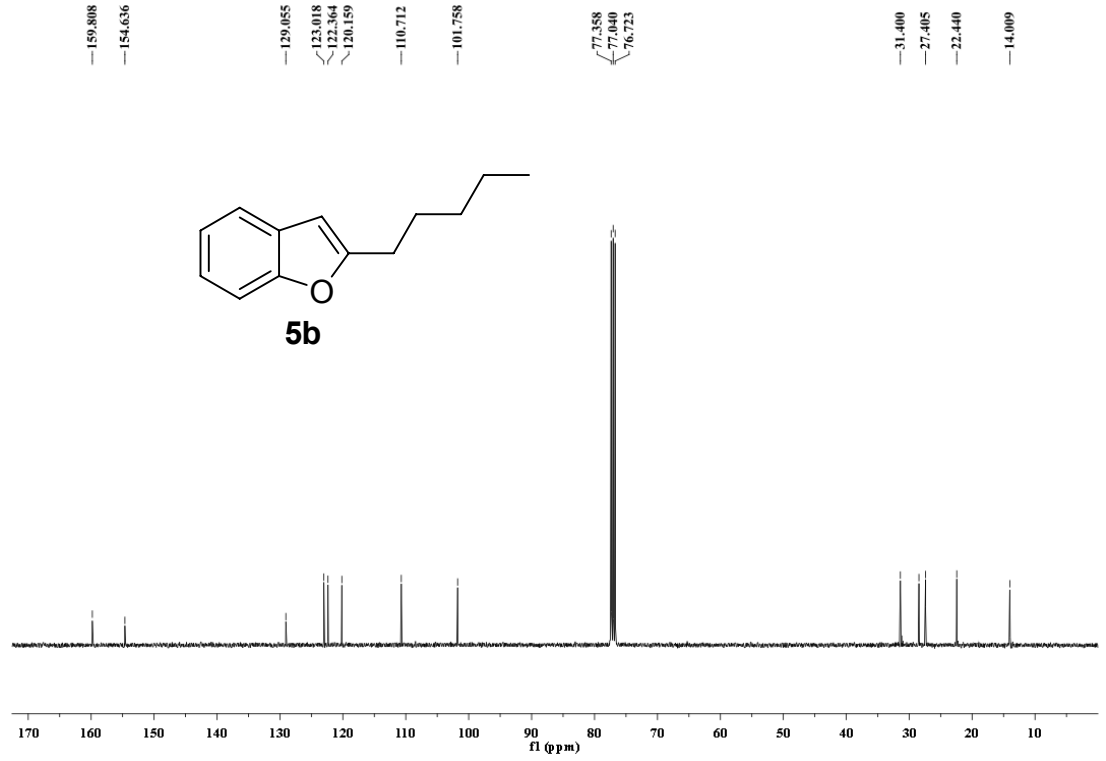
4j

150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.890
7.871
7.526
7.441
7.344
7.275
7.238
7.038
5a
7.604
7.585
7.460
7.380
7.362
7.313
7.295
7.259
7.220
f1 (ppm)
2.00
0.93
1.09
2.05
1.19
1.02
1.20
0.96


155.437
154.405
129.999
128.734
128.303
128.064
124.449
123.773
122.445
120.417
110.691
100.812
76.849
76.532
76.214
5a
f1 (ppm)


7.485
7.473
7.417
7.404
7.260
7.187
7.173
7.161
6.375
2.776
2.763
2.750
1.777
1.765
1.753
1.741
1.729
1.380
1.374
0.927
0.915
0.904
O
5b
f1 (ppm)
0.87
0.86
1.72
0.85
1.76
1.81
3.93
3.00


159.808
154.636
129.055
123.018
122.364
120.159
110.712
101.758
77.358
77.040
76.723
31.400
27.405
22.440
14.009
O
5b
f1 (ppm)