Supplementary Information

Divergent Functionalization of Terminal Alkynes Enabled Alkynylative [5+1] Benzannulation of 3-Acetoxy-1,4-enynes

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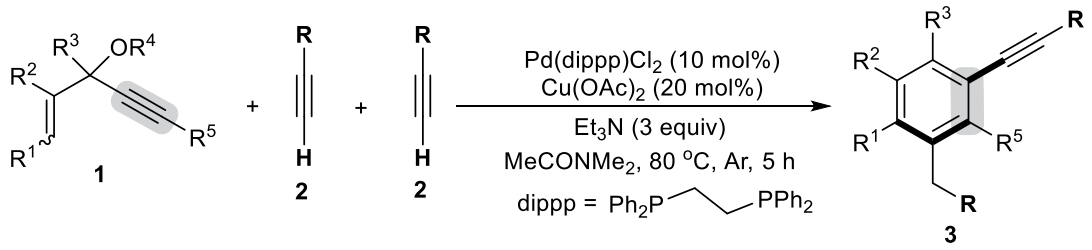
(A) Typical experimental procedure

All the 3-acetoxy-1,4-enynes **1** were synthesized according to the known methods.[1]

(a) Typical Experimental Procedure for the Synthesis of Products 3:



To a Schlenk tube were added 3-acetoxy-1,4-enyne **1** (0.2 mmol), alkyne **2** (2 equiv), Pd(dippp)Cl_2 (10 mol%; 0.02 mmol), Cu(OAc)$_2$ (20 mol%; 0.04 mmol), Et_3N (0.6 mmol) and $MeCONMe_2$ (2 mL). Then the tube was charged with argon and was stirred at 80 °C (oil bar temperature) for 5 h until complete consumption of starting material as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the reaction mixture was cooled to room temperature, quenched by water and extracted with ethyl acetate. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuum, the resulting residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 100/1) to afford the desired product **3**.

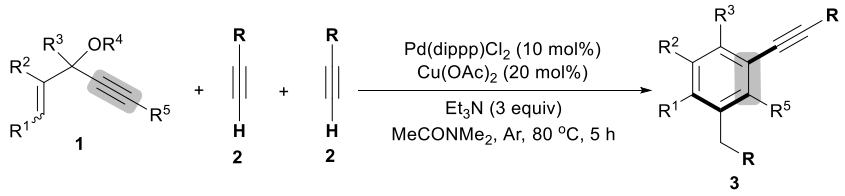
(b) Experimental Procedure for the 1 mmol Scale:

To a Schlenk tube were added 1,5-diphenylpent-1-en-4-yn-3-yl acetate **1a** (1 mmol), phenylacetylene **2a** (2 equiv), Pd(dippp)Cl_2 (10 mol%), Cu(OAc)$_2$ (20 mol%), Et_3N (3 equiv) and $MeCONMe_2$ (5 mL). Then the tube was charged with argon and was stirred at 80 °C (oil bar temperature) for 24 h until complete consumption of starting material as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the reaction mixture was cooled to room temperature, quenched by water and extracted with ethyl acetate. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuum, the resulting residue was

purified by silica gel column chromatography (petroleum ether/ethyl acetate) to afford the desired product **3aa** (302.4 mg, 72% yield).

(c) Screening of Optimal Reaction Conditions

Table S1. Screening of Optimal Reaction Conditions[a]

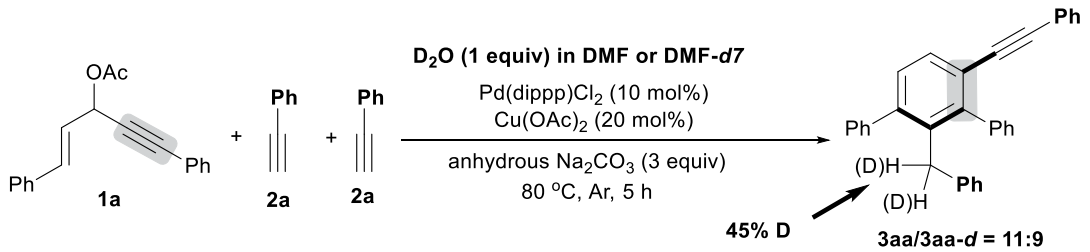


Entry	Variation from the standard conditions	Yield (%)
1	none	78/72[b]
2	without $Pd(dippp)Cl_2$, $Cu(OAc)_2$ or Et_3N	0
3	$Pd(dippp)Cl_2$ (5 mol%)	65
4	$Pd(dippp)Cl_2$ (15 mol%)	73
5	$Pd(PPh_3)_2Cl_2$ instead of $Pd(dippp)Cl_2$	51
6	$PdCl_2/PPh_3$ or $PdCl_2$ instead of $Pd(dippp)Cl_2$	40-45
7	$Pd(PCy_3)_2Cl_2$ instead of $Pd(PPh_3)_2Cl_2$	20
8	$Pd(PPh_3)_4$ instead of $Pd(PPh_3)_2Cl_2$	28
9	$Cu(OAc)_2$ (10 mol%)	55
10	$Cu(OAc)_2$ (30 mol%)	74
11	CuF_2 or $CuCl_2$ instead of $Cu(OAc)_2$	43-46
12	CuOAc instead of $Cu(OAc)_2$	52
13	CuI instead of $Cu(OAc)_2$	62
14	Et_3N (2 equiv)	71
15	Et_3N (4 equiv)	77
16	pyridine, NaOAc or K_2CO_3 instead of Et_3N	33-46
17	$HCONMe_2$ instead of $MeCONMe_2$	76
18	MeCN or DMSO instead of $MeCONMe_2$	49-51
19	at 60 °C	67

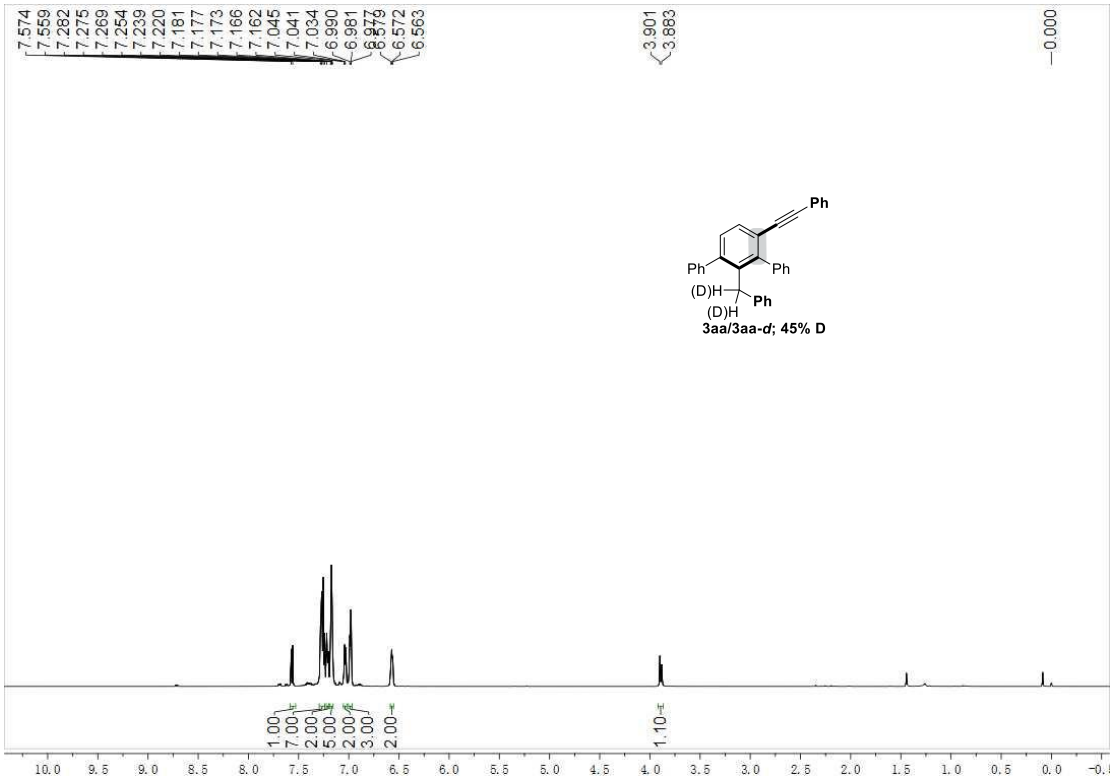
20 at 100 °C 52

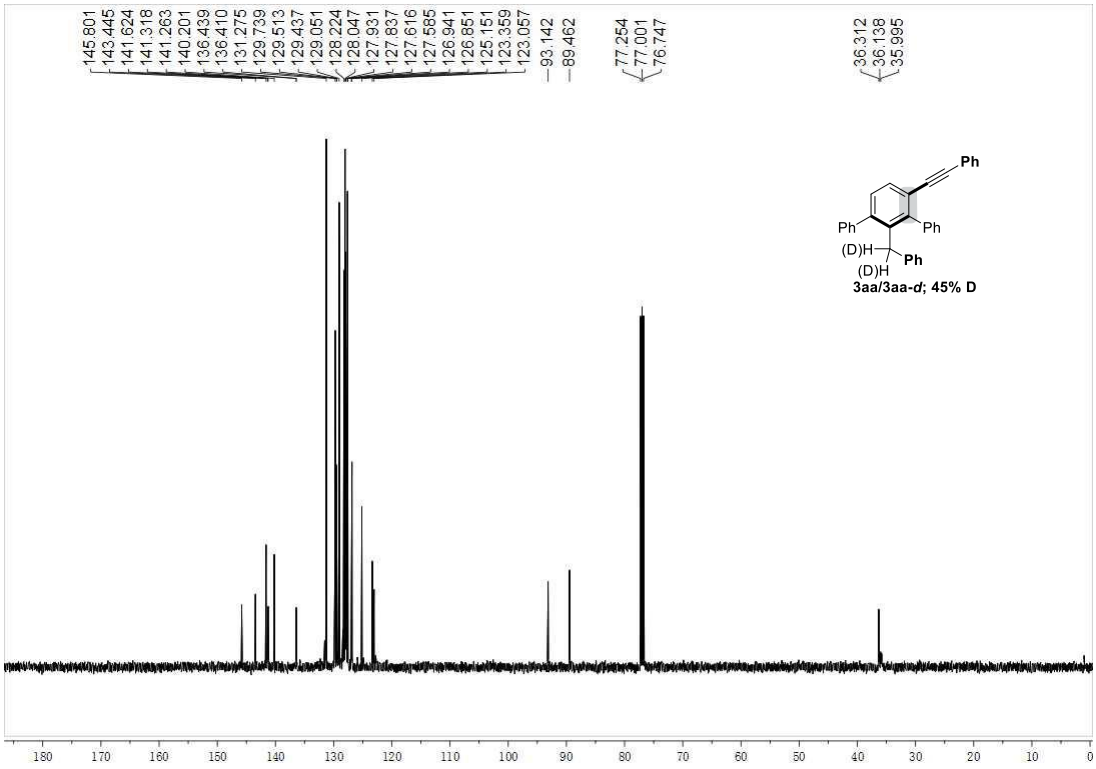
[a] Reaction conditions: **1a** (0.2 mmol), **2a** (2 equiv), Pd(dippp)Cl_2 (10 mol%), Cu(OAc)$_2$ (20 mol%), MeCONMe$_2$ (2 mL), 80 °C, and 5 h under argon atmosphere. [b] **1a** (1 mmol) and MeCONMe$_2$ (5 mL) for 24 h.

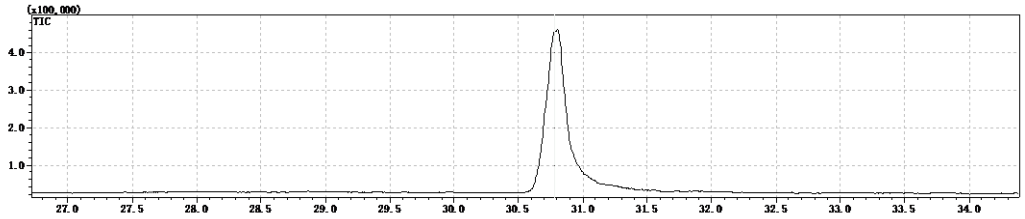
(d) Control Experiments

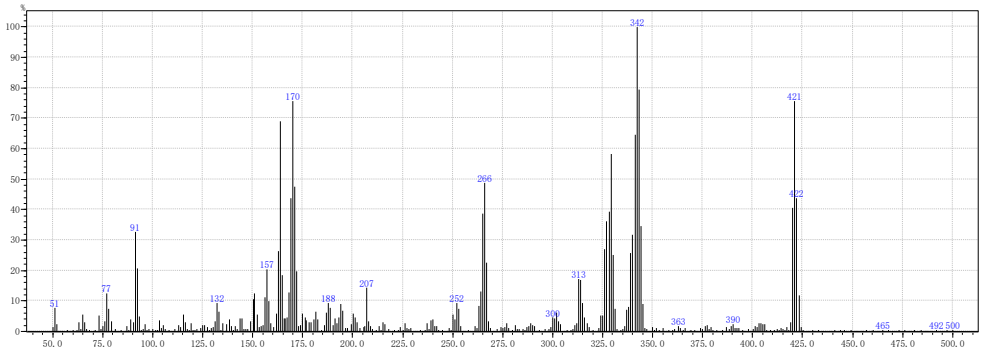


3aa/3aa-*d*: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.57 (d, *J* = 7.5 Hz, 1H), 7.28-7.24 (m, 7H), 7.22-7.20 (m, 2H), 7.18-7.16 (m, 5H), 7.05-7.03 (m, 2H), 6.99-6.98 (m, 3H), 6.58-6.56 (m, 2H), 3.89 (d, *J* = 9.0 Hz, 1.1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 145.8, 143.5, 141.6, 141.3, 141.3, 140.2, 136.4, 136.4, 131.3, 129.7, 129.5, 129.4, 129.1, 128.2, 128.0, 127.9, 127.8, 127.6, 127.6, 126.9, 126.8, 125.2, 123.4, 123.1, 93.1, 89.5, 36.3, 36.1 (d, *J* = 17.9 Hz).









[MS Spectrum]

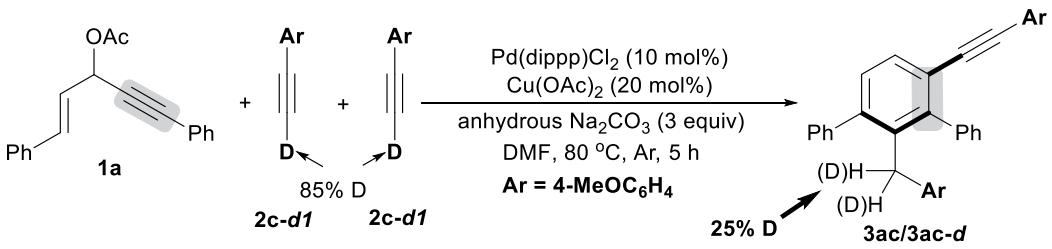
# of Peaks 387

Raw Spectrum 30.785 (scan : 4558) Base Peak m/z 342.10 (Inten : 23,620)

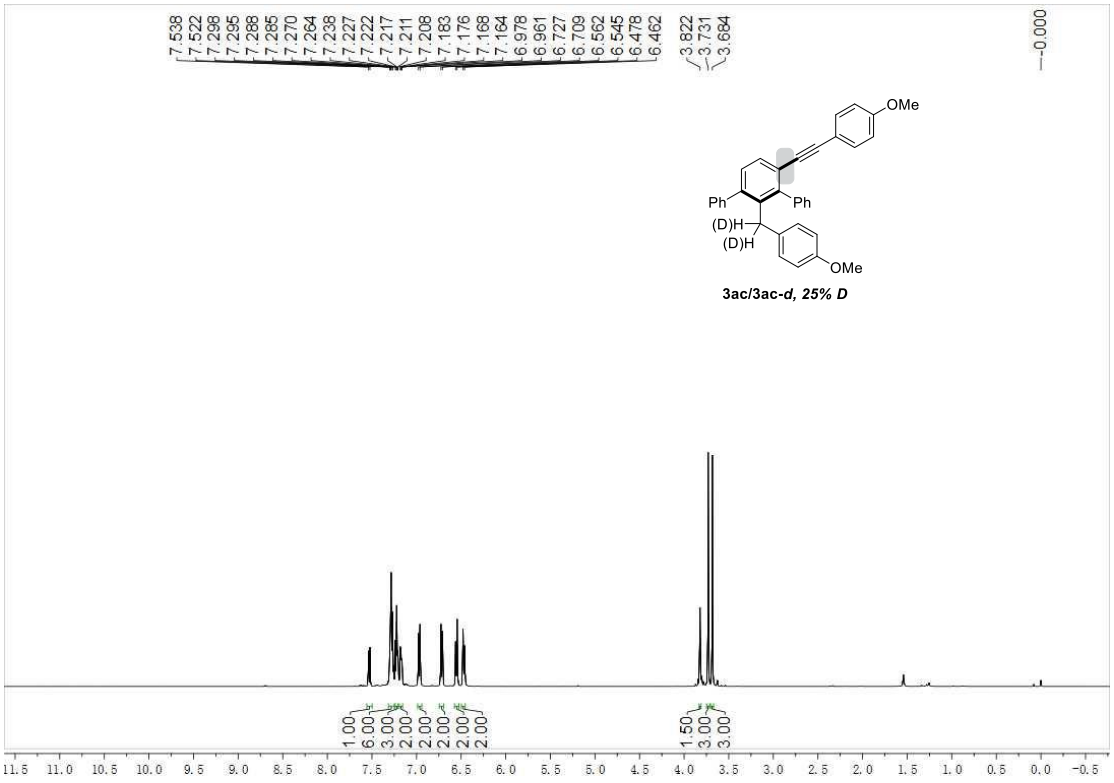
Background No Background Spectrum

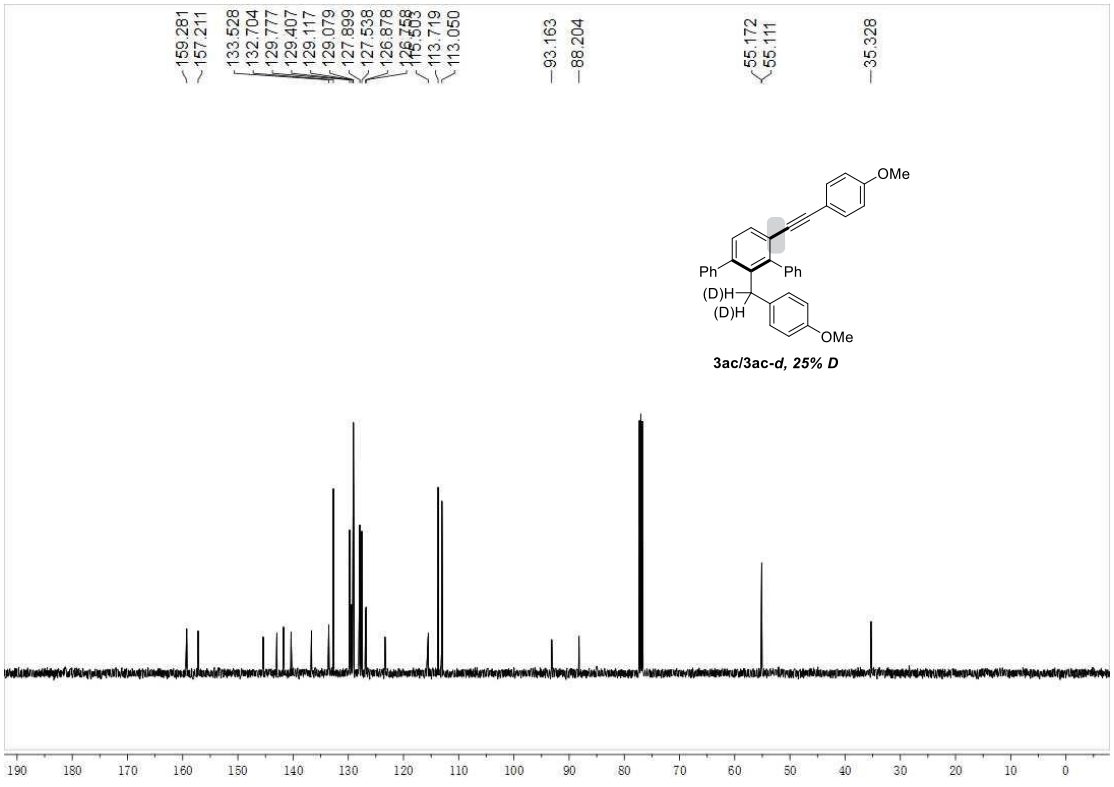
m/z	Absolute Intensity		63.10	746	3.16	77.10	2948	12.48
	Relative Intensity		65.10	1342	5.68	78.05	1786	7.56
50.10	348	1.47	66.10	762	3.23	79.15	833	3.53
51.05	1866	7.90	73.15	1253	5.30	89.05	981	4.15
52.10	583	2.47	76.15	799	3.38	90.15	768	3.25

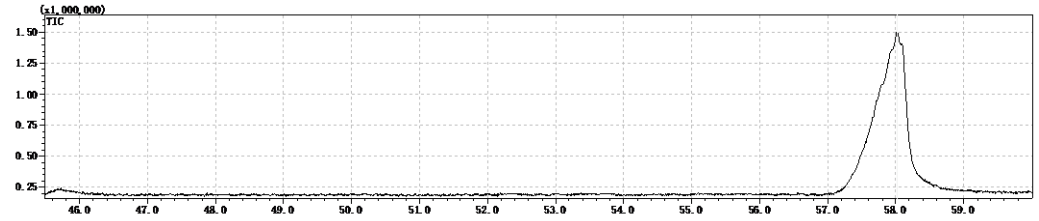
91.10	7738	32.76	178.15	760	3.22	302.10	1498	6.34
92.15	4900	20.75	179.25	746	3.16	303.10	802	3.40
93.15	1225	5.19	180.55	980	4.15	304.10	582	2.46
96.20	580	2.46	181.45	1536	6.50	311.10	490	2.07
103.10	903	3.82	182.45	943	3.99	312.15	688	2.91
105.10	537	2.27	185.90	502	2.13	313.10	4129	17.48
113.10	546	2.31	186.95	1514	6.41	314.10	4031	17.07
115.10	1310	5.55	187.90	2262	9.58	315.10	2274	9.63
116.10	756	3.20	188.85	1895	8.02	316.10	1154	4.89
125.10	551	2.33	190.00	502	2.13	317.10	670	2.84
126.10	492	2.08	191.05	1060	4.49	318.10	393	1.66
131.15	810	3.43	192.25	673	2.85	324.10	1266	5.36
132.05	2257	9.56	193.25	1145	4.85	325.15	1255	5.31
133.05	1529	6.47	194.20	2137	9.05	326.10	6396	27.08
137.10	564	2.39	195.15	1630	6.90	327.10	8561	36.24
138.20	964	4.08	200.35	1442	6.10	328.15	9348	39.58
143.60	1042	4.41	201.45	1112	4.71	329.15	13782	58.35
144.60	1052	4.45	202.35	754	3.19	330.15	5973	25.29
149.15	839	3.55	207.00	3415	14.46	331.10	1769	7.49
150.15	2519	10.66	208.00	801	3.39	336.10	462	1.96
151.05	3018	12.78	209.00	438	1.85	337.10	1742	7.38
152.05	1346	5.70	215.00	751	3.18	338.15	1932	8.18
155.00	502	2.13	216.00	596	2.52	339.10	6105	25.85
156.05	2647	11.21	226.00	634	2.68	340.10	7543	31.93
157.05	4848	20.52	237.00	681	2.88	341.10	15284	64.71
157.95	2401	10.17	239.00	913	3.87	**342.10**	**23620**	**100.00**
158.95	705	2.98	240.10	1001	4.24	343.10	18812	79.64
161.65	1409	5.97	250.00	1374	5.82	344.10	8212	34.77
162.65	6234	26.39	251.15	935	3.96	345.15	2134	9.03
163.55	16327	69.12	252.05	2269	9.61	377.10	538	2.28
164.55	4424	18.73	253.05	1784	7.55	390.10	572	2.42
165.55	1044	4.42	263.10	2022	8.56	403.10	673	2.85
166.10	1073	4.54	264.15	3147	13.32	404.10	644	2.73
167.15	1121	4.75	265.15	9185	38.89	405.10	626	2.65
168.15	3055	12.93	266.10	11532	48.82	406.10	586	2.48
169.15	10370	43.90	267.10	5334	22.58	414.10	295	1.25
170.10	17911	75.83	268.10	798	3.38	417.10	383	1.62
171.05	11227	47.53	277.10	639	2.71	419.15	731	3.09
172.05	4715	19.96	281.10	519	2.20	**420.15**	**9595**	**40.62**
173.10	457	1.93	288.10	482	2.04	**421.15**	**17867**	**75.64**
174.00	511	2.16	289.10	686	2.90	**422.10**	**10346**	**43.80**
175.00	1394	5.90	290.10	532	2.25	423.15	2815	11.92
176.05	1099	4.65	300.05	1088	4.61	424.10	396	1.68
176.95	890	3.77	301.05	1053	4.46			

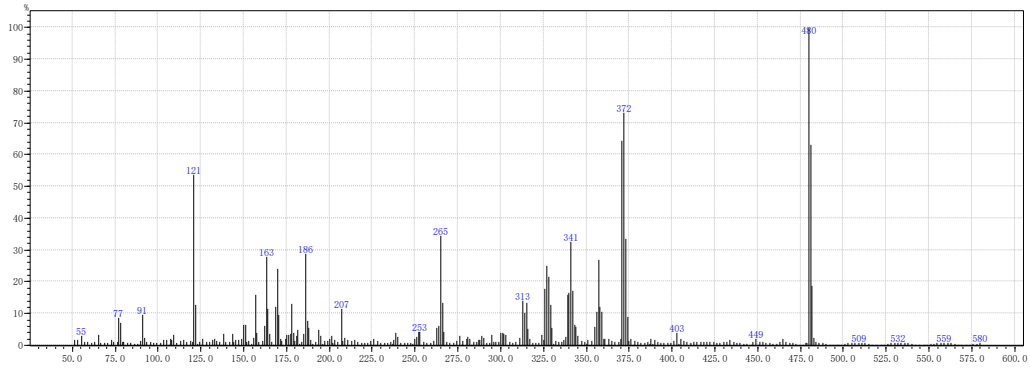


3ac/3ac-*d*: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.53 (d, *J* = 8.0 Hz, 1H), 7.30-7.26 (m, 6H), 7.24-7.21 (m, 3H), 7.18-7.16 (m, 2H), 6.97 (d, *J* = 8.5 Hz, 2H), 6.72 (d, *J* = 9.0 Hz, 2H), 6.55 (d, *J* = 8.5 Hz, 2H), 6.47 (d, *J* = 8.0 Hz, 2H), 3.82 (s, 1.5H), 3.73 (s, 3H), 3.68 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 159.3, 157.2, 145.4, 142.9, 141.7, 140.4, 136.7, 133.5, 132.7, 129.8, 129.4, 129.1, 129.0, 127.9, 127.5, 126.9, 126.8, 123.4, 115.5, 113.7, 113.1, 93.2, 88.2, 55.2, 55.1, 35.3.









[MS Spectrum]

# of Peaks 354

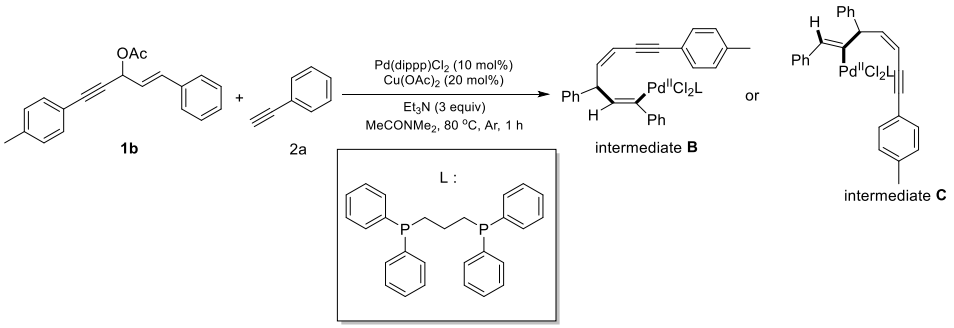
Raw Spectrum 58.030 (scan : 10007) Base Peak m/z 479.95 (Inten : 105,242)

Background No Background Spectrum

m/z	Absolute Intensity		65.00	3500	3.33	121.05	56484	53.67
	Relative Intensity		77.05	9429	8.96	122.10	13546	12.87
51.15	2136	2.03	78.10	7599	7.22	126.15	2204	2.09
53.15	1968	1.87	91.10	10303	9.79	138.00	3833	3.64
55.10	3183	3.02	92.00	2610	2.48	143.55	3874	3.68

147.20	21182	2.01	193.60	53695	5.10	339.00	16879	16.04
149.05	21732	2.06	195.10	32413	3.08	339.95	17524	16.65
150.05	70566	6.70	200.05	23662	2.25	341.00	34319	32.61
151.05	68106	6.47	201.10	31863	3.03	342.00	18082	17.18
155.65	26612	2.53	206.95	12269	11.66	343.05	68136	6.47
156.70	16767	15.93	251.90	46174	4.39	343.95	64286	6.11
157.65	41463	3.94	252.95	47364	4.50	345.10	33673	3.20
162.15	67146	6.38	262.95	58345	5.54	355.00	63996	6.08
163.10	29452	27.99	264.00	66126	6.28	355.95	11153	10.60
164.05	12261	11.65	265.00	36510	34.69	357.00	28442	27.03
165.05	41093	3.90	266.00	14330	13.62	358.00	12913	12.27
166.45	13421	1.28	266.90	45964	4.37	358.95	11374	10.81
168.65	12899	12.26	299.90	44394	4.22	370.95	67757	64.38
169.65	25575	24.30	301.00	43164	4.10	371.95	77291	73.44
170.55	10425	9.91	301.95	40763	3.87	373.00	35524	33.75
175.15	36103	3.43	303.00	35593	3.38	374.00	97119	9.23
176.15	35683	3.39	310.90	27942	2.65	403.00	41933	3.98
177.25	41163	3.91	312.95	15001	14.25	405.00	21642	2.06
178.25	14058	13.36	314.00	10820	10.28	449.05	23272	2.21
179.15	43834	4.16	314.95	14131	13.43	464.85	22972	2.18
179.75	17791	1.69	316.00	56895	5.41	**479.95**	**105242**	**100.00**
180.65	31723	3.01	316.90	22502	2.14	**480.95**	**66592**	**63.28**
181.70	51864	4.93	326.00	18871	17.93	**481.95**	**19734**	**18.75**
185.15	41213	3.92	326.95	26620	25.29	482.95	2509	2.38
186.05	30473	28.96	328.00	22983	21.84	483.90	1466	1.39
187.05	84408	8.02	329.00	13428	12.76			
187.95	60985	5.79	330.00	58125	5.52			
189.20	20301	1.93	337.95	29792	2.83			

(d) Intermediate captured by HRMS



HRMS m/z (ESI) calcd for the intermediate **B or C** $[M+H]^+$ 922.1638, found 922.1629.

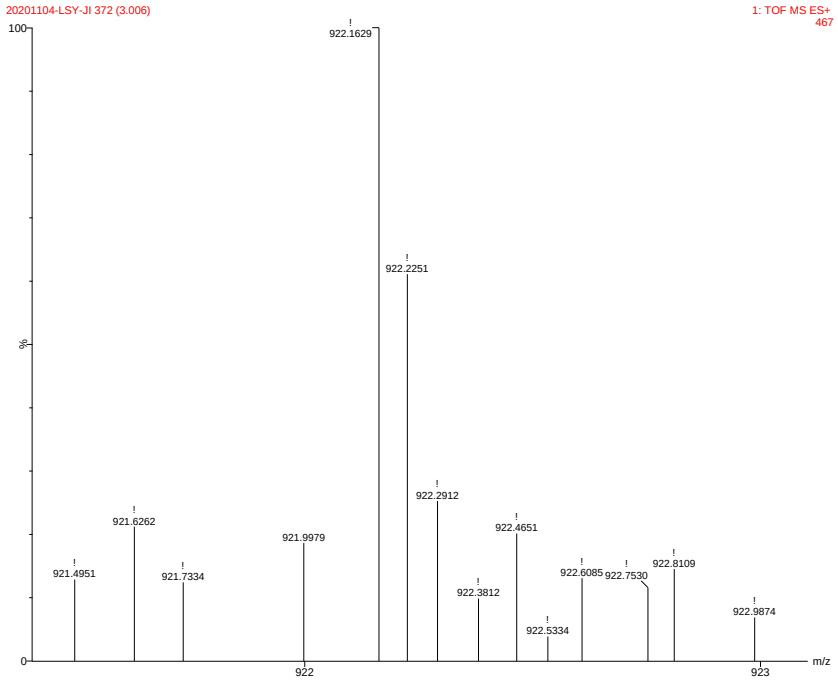
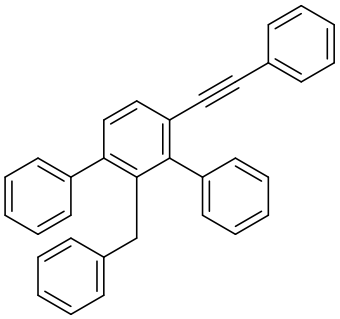


Figure S1. The HRMS Analysis.

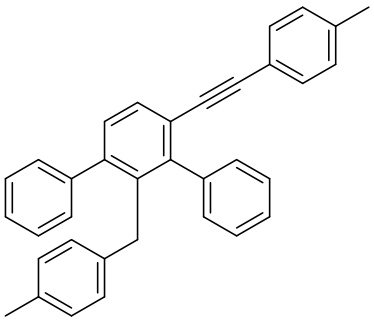
(B) Analytical data

2'-benzyl-4'-(phenylethynyl)-1,1':3',1''-terphenyl (3aa):



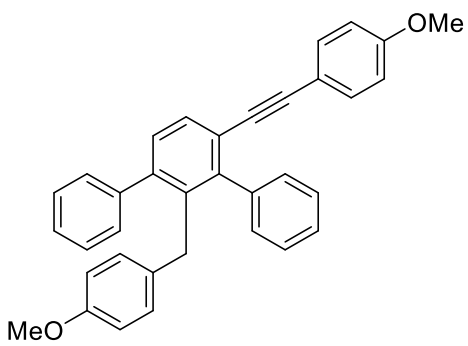
65.5 mg, 78%; mp 92.5-93.6 ^{o}C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.57 (d, *J* = 7.6 Hz, 1H), 7.30-7.17 (m, 14H), 7.05-6.99 (m, 5H), 6.59-6.56 (m, 2H), 3.90 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 145.8, 143.5, 141.6, 141.3, 140.2, 136.5, 131.3, 129.7, 129.5, 129.4, 129.1, 128.2, 128.1, 127.9, 127.8, 127.6, 127.6, 127.0, 126.9, 125.2, 123.4, 123.1, 93.1, 89.5, 36.3; LRMS (EI, 70 eV) m/z (%): 420 (M^+, 100), 342 (95), 265 (77), 170 (29); HRMS m/z (ESI) calcd for $C_{33}H_{25}$ ($[M+H]^+$) 421.1951, found 421.1960.

2'-(4-methylbenzyl)-4'-(p-tolylethynyl)-1,1':3',1''-terphenyl (3ab):



71.7 mg, 80%; mp 103.5-104.4 ^{o}C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55 (d, *J* = 8.0 Hz, 1H), 7.28-7.16 (m, 11H), 6.99 (d, *J* = 7.6 Hz, 2H), 6.93 (d, *J* = 8.0 Hz, 2H), 6.81 (d, *J* = 7.6 Hz, 2H), 6.46 (d, *J* = 7.6 Hz, 2H), 3.85 (s, 2H), 2.26 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 145.7, 143.2, 141.7, 140.3, 138.3, 137.9, 136.5, 134.5, 131.2, 129.8, 129.4, 129.3, 129.1, 128.8, 128.3, 128.0, 127.9, 127.5, 126.9, 126.8, 123.2, 120.3, 93.3, 88.9, 35.8, 21.4, 20.9; LRMS (EI, 70 eV) m/z (%): 448 (M^+, 98), 356 (100), 265 (51), 170 (46); HRMS m/z (ESI) calcd for $C_{35}H_{29}$ ($[M+H]^+$) 449.2264, found 449.2273.

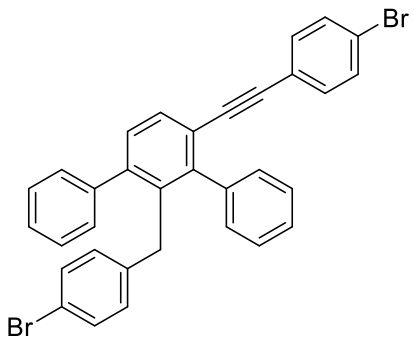
2'-(4-methoxybenzyl)-4'-((4-methoxyphenyl)ethynyl)-1,1':3',1''-terphenyl (3ac):



72.0 mg, 75%; mp 110.6-112.0 ^{o}C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.53 (d, *J* = 8.0 Hz, 1H), 7.30-7.27 (m, 6H), 7.23-7.21 (m, 3H), 7.18-7.16 (m, 2H), 6.97 (d, *J* = 8.5 Hz, 2H), 6.72 (d, *J* = 8.5 Hz, 2H), 6.55 (d, *J* = 8.5 Hz, 2H), 6.47 (d, *J* = 8.5 Hz, 2H), 3.82 (s, 2H), 3.74 (s, 3H), 3.69 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 159.3, 157.2, 145.4, 143.0, 141.8, 140.4, 136.7, 133.6, 132.7, 129.8, 129.4, 129.1, 129.1, 127.9, 127.5, 126.9, 126.8, 123.4, 115.5, 113.7, 113.1, 93.2, 88.2, 55.2, 55.1, 35.3;

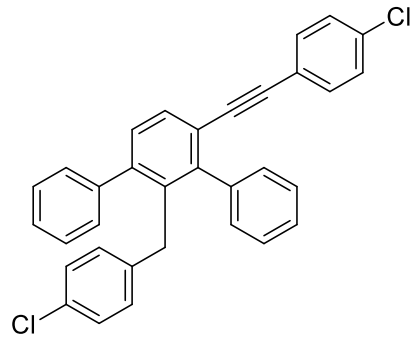
LRMS (EI, 70 eV) m/z (%): 480 (M^+, 100), 372 (67), 207 (62), 121 (94); HRMS m/z (ESI) calcd for $C_{35}H_{29}O_2$ ($[M+H]^+$) 481.2162, found 481.2175.

2'-(4-bromobenzyl)-4'-((4-bromophenyl)ethynyl)-1,1':3',1''-terphenyl (3ad):



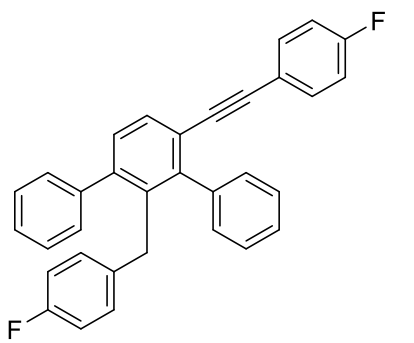
78.3 mg, 68%; mp 168.3-168.9 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.56 (d, *J* = 8.0 Hz, 1H), 7.33-7.01 (m, 15H), 6.87 (d, *J* = 8.0 Hz, 2H), 6.42 (d, *J* = 8.0 Hz, 2H), 3.83 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 145.8, 143.6, 141.3, 140.2, 140.0, 135.9, 132.7, 131.3, 130.7, 129.9, 129.6, 129.6, 128.9, 128.1, 127.7, 127.1, 127.1, 122.8, 122.2, 122.1, 119.0, 92.2, 90.4, 35.7; LRMS (EI, 70 eV) m/z (%): 578 (M^+ + 2, 31), 576 (M^+, 17), 339 (51), 207 (100); HRMS m/z (ESI) calcd for $C_{33}H_{23}{}^{79}Br_2$ ($[M+H]^+$) 577.0161, found 577.0172.

2'-(4-chlorobenzyl)-4'-((4-chlorophenyl)ethynyl)-1,1':3',1''-terphenyl (3ae):



71.2 mg, 73%; mp 146.6-148.2 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.62 (d, *J* = 8.0 Hz, 1H), 7.37-7.33 (m, 7H), 7.30 (d, *J* = 6.4 Hz, 1H), 7.27-7.20 7.62 (m, 5H), 7.01 (t, *J* = 7.6 Hz, 4H), 6.54 (d, *J* = 8.0 Hz, 2H), 3.91 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 145.8, 143.6, 141.4, 140.0, 139.7, 136.0, 133.9, 132.5, 131.0, 129.7, 129.6, 129.6, 129.5, 129.0, 128.4, 128.1, 127.7, 127.1, 127.1, 122.9, 121.8, 92.2, 90.3, 35.7; LRMS (EI, 70 eV) m/z (%): 490 (M^+ + 2, 38), 488 (M^+, 52), 265 (66), 170 (100); HRMS m/z (ESI) calcd for $C_{33}H_{23}{}^{35}Cl_2$ ($[M+H]^+$) 489.1171, found 489.1185.

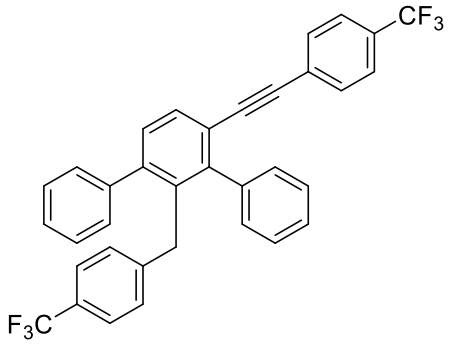
2'-(4-fluorobenzyl)-4'-((4-fluorophenyl)ethynyl)-1,1':3',1''-terphenyl (3af):



68.4 mg, 75%; mp 113.7-119.4 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.55 (d, *J* = 7.5 Hz, 1H), 7.31-7.27 (m, 6H), 7.25 (d, *J* = 8.0 Hz, 1H), 7.22-7.19 (m, 2H), 7.17-7.15 (m, 2H), 7.01-6.98 (m, 2H), 6.88 (t, *J* = 8.5 Hz, 2H), 6.68 (t, *J* = 8.5 Hz, 2H), 6.50-6.47 (m, 2H), 3.86 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 162.2 (d, *J* = 247.8 Hz), 160.8 (d, *J* = 241.8 Hz), 145.7, 143.4, 141.5, 140.2, 136.8 (d, *J* = 3.1 Hz), 136.4, 133.1, 133.0, 129.7, 129.5, 129.5, 129.4, 129.0, 128.0, 127.7, 127.1 (d, *J* = 22.1 Hz), 123.0, 119.4 (d, *J* = 12.3 Hz), 115.4 (d, *J* =

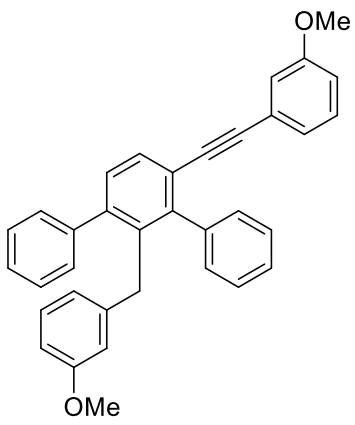
22.1 Hz), 114.3 (d, *J* = 22.1 Hz), 92.2, 89.0, 35.5; LRMS (EI, 70 eV) m/z (%): 456 (M^+, 100), 360 (87), 265 (55), 109 (19); HRMS m/z (ESI) calcd for $C_{33}H_{23}F_2$ ($[M+H]^+$) 457.1762, found 457.1771.

2'-(4-(trifluoromethyl)benzyl)-4'-((4-(trifluoromethyl)phenyl)ethynyl)-1,1':3',1''-terphenyl (3ag):



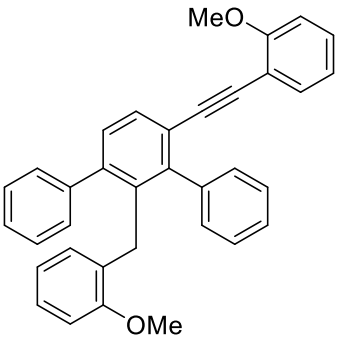
72.3 mg, 65%; mp 142.3-143.3 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.82-7.69 (m, 2H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.54-7.18 (m, 14H), 6.75 (d, *J* = 7.6 Hz, 2H), 4.06 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 146.1, 145.3, 144.1, 141.2, 139.9 139.7 (d, *J* = 147.1 Hz), 136.9 (d, *J* = 127.0 Hz), 135.9, 131.4, 130.0, 129.7, 129.6, 128.9, 128.4, 128.2, 127.9 (q, *J* = 39.0 Hz), 127.8, 127.3, 127.2, 127.0, 125.0 (q, *J* = 3.5 Hz), 124.6 (q, *J* = 3.8 Hz), 123.0 (d, *J* = 88.1 Hz), 122.6, 92.0, 91.6, 36.3; LRMS (EI, 70 eV) m/z (%): 556 (M^+, 100), 397 (62), 265 (19), 170 (34); HRMS m/z (ESI) calcd for $C_{35}H_{23}F_6$ ($[M+H]^+$) 557.1698, found 557.1711.

2'-(3-methoxybenzyl)-4'-((3-methoxyphenyl)ethynyl)-1,1':3',1''-terphenyl (3ah):



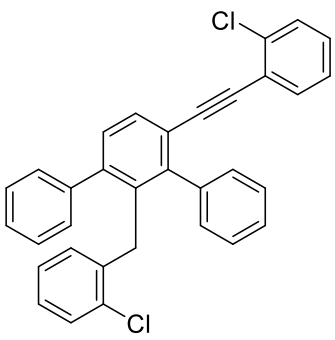
68.2 mg, 71%; mp 116.8-118.2 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.56 (d, *J* = 8.0 Hz, 1H), 7.31-7.19 (m, 11H), 7.09 (t, *J* = 8.5 Hz, 1H), 6.92 (t, *J* = 8.0 Hz, 1H), 6.76 (d, *J* = 8.5 Hz, 1H), 6.67 (d, *J* = 7.5 Hz, 1H), 6.55 (d, *J* = 8.0 Hz, 1H), 6.50 (s, 1H), 6.19 (d, *J* = 7.5 Hz, 1H), 6.11 (s, 1H), 3.88 (s, 2H), 3.70 (s, 3H), 3.60 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 159.0, 145.9, 143.4, 142.9, 141.6, 140.3, 136.3, 129.8, 129.5, 129.4, 129.1, 128.5, 127.9, 127.6, 127.0, 126.8, 124.3, 123.7, 122.9, 120.8, 115.8, 114.8, 113.8, 110.9, 93.1, 89.3, 55.2, 54.9, 36.3; LRMS (EI, 70 eV) m/z (%): 480 (M^+, 100), 359 (63), 265 (35), 169 (8); HRMS m/z (ESI) calcd for $C_{35}H_{29}O_2$ ($[M+H]^+$) 481.2162, found 481.2171.

2'-(2-methoxybenzyl)-4'-((2-methoxyphenyl)ethynyl)-1,1':3',1''-terphenyl (3ai):



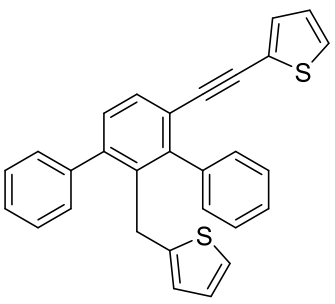
58.6 mg, 61%; mp 123.2-123.9 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.63 (d, *J* = 8.0 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 1H), 7.22-7.20 (m, 8H), 7.17-7.15 (m, 3H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 7.5 Hz, 1H), 6.78-6.70 (m, 3H), 6.67 (d, *J* = 7.5 Hz, 1H), 6.51 (d, *J* = 8.0 Hz, 1H), 3.81 (s, 2H), 3.73 (s, 3H), 3.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 159.5, 156.4, 145.6, 143.4, 141.7, 140.2, 136.6, 133.5, 130.3, 129.6, 129.5, 129.4, 129.3, 128.9, 127.7, 127.3, 126.7, 126.4, 126.2, 123.2, 120.2, 119.9, 112.7, 110.6, 109.5, 93.5, 89.3, 55.6, 55.0, 29.7; LRMS (EI, 70 eV) m/z (%): 480 (M^+, 75), 344 (54), 241 (100), 91 (36); HRMS m/z (ESI) calcd for $C_{35}H_{29}O_2$ ($[M+H]^+$) 481.2162, found 481.2169.

2'-(2-chlorobenzyl)-4'-((2-chlorophenyl)ethynyl)-1,1':3',1''-terphenyl (3aj):



55.6 mg, 57%; mp 131.2-132.5 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.68 (d, *J* = 7.5 Hz, 1H), 7.31(d, *J* = 8.0 Hz, 1H), 7.28-7.25 (m, 7H), 7.20-7.18 (m, 2H), 7.15-7.12 (m, 3H), 7.09-7.01 (m, 4H), 6.99-6.96 (m, 1H), 6.77 (d, *J* = 7.0 Hz, 1H), 3.92 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 146.0, 144.1, 141.2, 139.7, 139.0, 135.6, 135.4, 133.6, 133.3, 130.5, 129.9, 129.6, 129.3, 129.1, 129.0, 128.8, 128.6, 128.0, 127.8, 127.2, 127.1, 126.7, 126.2, 126.2, 123.3, 122.9, 94.3, 89.8, 33.9; LRMS (EI, 70 eV) m/z (%): 490 (M^+ + 2, 29), 488 (M^+, 46), 341 (92), 170 (100); HRMS m/z (ESI) calcd for $C_{33}H_{23}{}^{35}Cl_2$ ($[M+H]^+$) 489.1171, found 489.1179.

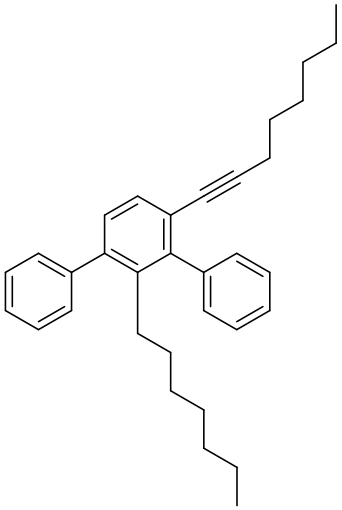
2-((4'-(thiophen-2-ylethynyl)-[1,1':3',1''-terphenyl]-2'-yl)methyl)thiophene (3ak):



54.4 mg, 63%; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.54 (d, *J* = 8.0 Hz, 1H), 7.35-7.31 (m, 6H), 7.29-7.27 (m, 2H), 7.25-7.23 (m, 3H), 7.16 (d, *J* = 6.0 Hz, 1H), 6.93 7.54 (d, *J* = 6.0 Hz, 1H), 6.88-6.85 (m, 2H), 6.67-6.65 (m, 1H), 6.12-6.11 (m, 1H), 4.01 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 145.2, 144.3, 143.1, 141.3, 139.7, 136.2, 131.5, 129.6, 129.6, 129.4, 129.1, 128.0, 127.7, 127.1, 127.1, 127.1, 126.9, 126.0, 124.8, 123.4, 123.0, 122.9, 93.1, 86.4, 31.1; LRMS (EI, 70 eV) m/z

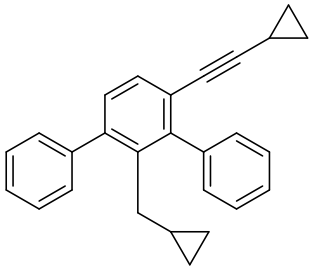
(%): 432 (M^+, 60), 348 (100), 207 (27), 97 (24); HRMS m/z (ESI) calcd for $C_{29}H_{21}S_2$ ($[M+H]^+$) 433.1079, found 433.1087.

2'-heptyl-4'-(oct-1-yn-1-yl)-1,1':3',1''-terphenyl (3al):



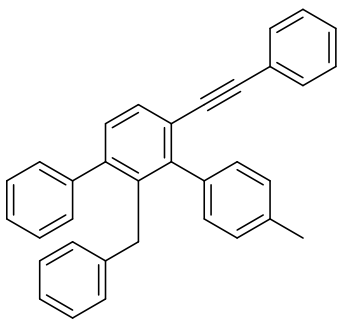
41.0 mg, 47%; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.43-7.265 (m, 11H), 7.09 (d, *J* = 8.0 Hz, 1H), 2.37-2.34 (m, 1H), 2.14-2.10 (m, 2H), 1.26-1.05 (m, 13H), 0.91-0.74 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 144.6, 142.2, 141.8, 140.8, 138.9, 129.7, 129.2, 129.0, 128.7, 127.9, 127.6, 126.7, 126.6, 123.4, 93.8, 80.3, 31.4, 31.3, 30.2, 30.2, 29.3, 28.4, 28.2, 28.2, 22.5, 22.5, 19.3, 14.1, 14.0; LRMS (EI, 70 eV) m/z (%): 436 (M^+, 77), 367 (20), 267 (100), 97 (17); HRMS m/z (ESI) calcd for $C_{33}H_{41}$ ($[M+H]^+$) 437.3203, found 437.3212.

4'-(cyclopropylethynyl)-2'-(cyclopropylmethyl)-1,1':3',1''-terphenyl (3am):



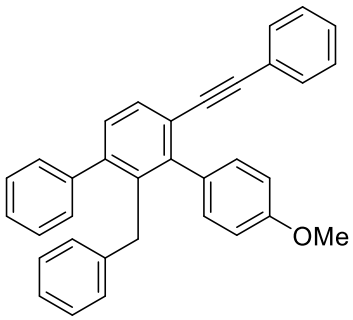
38.3 mg, 55%; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.38-7.29 (m, 9H), 7.25 (d, *J* = 7.5 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 1H), 2.40 (d, *J* = 6.5 Hz, 2H), 1.16-1.10 (m, 1H), 0.62-0.60 (m, 2H), 0.39-0.27 (m, 3H), 0.05-0.02 (m, 2H), -0.58-(-0.59) (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 144.9, 142.5, 141.9, 141.2, 138.2, 130.0, 129.4, 129.3, 128.7, 128.0, 127.6, 126.8 126.7, 123.5, 97.3, 75.3, 34.2, 11.3, 8.53, 4.9, 0.1; LRMS (EI, 70 eV) m/z (%): 348 (M^+, 100), 278 (49), 145 (57), 91 (22); HRMS m/z (ESI) calcd for $C_{27}H_{25}$ ($[M+H]^+$) 349.1951, found 349.1957.

2'-benzyl-4-methyl-6'-(phenylethynyl)-1,1':3',1''-terphenyl (3ba):



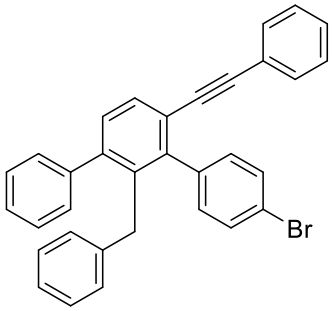
67.7 mg, 78%; mp 98.8-99.7 ^{o}C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.56 (d, *J* = 8.0 Hz, 1H), 7.26-7.17 (m, 9H), 7.10-7.05 (m, 6H), 7.01-6.99 (m, 3H), 6.60-6.57 (m, 2H), 3.90 (s, 2H), 2.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 145.8, 143.4, 141.4, 140.2, 138.7, 136.6, 136.5, 131.3, 129.7, 129.5, 129.5, 129.0, 128.7, 128.2, 128.0, 127.8, 127.6, 127.5, 126.8, 125.1, 123.4, 122.9, 93.0, 89.5, 36.3, 21.1; LRMS (EI, 70 eV) m/z (%): 434 (M^+, 100), 341 (15), 279 (32), 170 (85); HRMS m/z (ESI) calcd for $C_{34}H_{27}$ ($[M+H]^+$) 435.2107, found 435.2118.

2'-benzyl-4-methoxy-6'-(phenylethynyl)-1,1':3',1''-terphenyl (3ca):



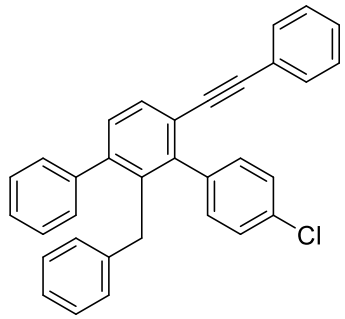
72.9 mg, 81%; mp 102.8-103.9 ºC (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.56 (d, *J* = 8.0 Hz, 1H), 7.27-7.25 (m, 4H), 7.21-7.19 (m, 5H), 7.11-7.09 (m, 4H), 7.01-6.99 (m, 3H), 6.84-6.82 (m, 2H), 6.60-6.58 (m, 2H), 3.91 (s, 2H), 3.79 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 158.5, 145.4, 143.5, 141.7, 141.4, 136.8, 132.6, 131.3, 130.9, 129.6, 129.3, 129.0, 128.2, 128.1, 127.9, 127.8, 127.6, 126.9, 125.1, 123.5, 123.4, 113.1, 92.9, 89.6, 55.3, 36.3; LRMS (EI, 70 eV) m/z (%): 450 (M^+, 100), 372 (62), 295 (27), 169 (16); HRMS m/z (ESI) calcd for $C_{34}H_{27}O$ ($[M+H]^+$) 451.2056, found 451.2065.

2'-benzyl-4-bromo-6'-(phenylethynyl)-1,1':3',1''-terphenyl (3da):



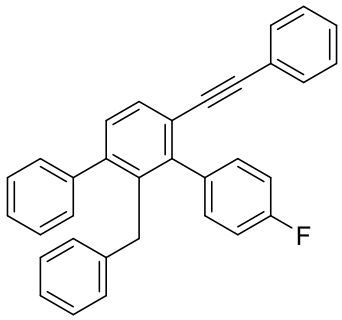
64.7 mg, 65%; mp 151.2-153.0 ºC (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.57 (d, *J* = 7.6 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.29-7.27 (m, 4H), 7.24-7.23 (m, 5H), 7.08-7.06 (m, 2H), 7.03-7.01 (m, 5H), 6.60-6.57 (m, 2H), 3.87 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 144.5, 143.6, 141.4, 141.1, 139.2, 136.4, 131.6, 131.3, 130.8, 129.8, 129.7, 129.1, 128.3, 128.2, 128.1, 128.1, 127.8, 127.2, 125.4, 123.2, 123.1, 121.1, 93.6, 89.1, 36.4; LRMS (EI, 70 eV) m/z (%): 500 (M^+ + 2, 51), 498 (M^+, 52), 328 (90), 91 (100); HRMS m/z (ESI) calcd for $C_{35}H_{24}{}^{79}Br$ ($[M+H]^+$) 499.1056, found 499.1067.

2'-benzyl-4-chloro-6'-(phenylethynyl)-1,1':3',1''-terphenyl (3ea):



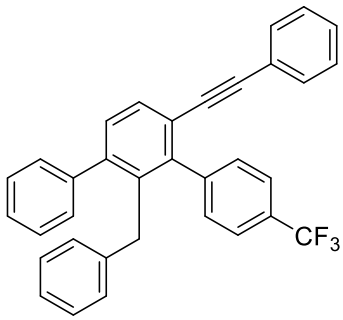
63.6 mg, 70%; mp 136.1-136.9 ºC (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.57 (d, *J* = 8.0 Hz, 1H), 7.30-7.22 (m, 11H), 7.08-7.01 (m, 7H), 6.59-6.57 (m, 2H), 3.87 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 144.4, 143.5, 141.4, 141.1, 138.7, 136.4, 132.8, 131.2, 131.1, 129.7, 129.7, 129.0, 128.2, 128.1, 128.1, 128.0, 127.8, 127.1, 125.3, 123.1, 123.1, 93.5, 89.0, 36.3; LRMS (EI, 70 eV) m/z (%): 456 (M^+ + 2, 33), 454 (M^+, 82), 341 (100), 170 (61); HRMS m/z (ESI) calcd for $C_{33}H_{24}{}^{35}Cl$ ($[M+H]^+$) 455.1561, found 455.1569.

2'-benzyl-4-fluoro-6'-(phenylethynyl)-1,1':3',1''-terphenyl (3fa):



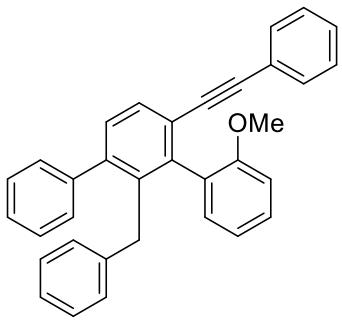
63.9 mg, 73%; mp 115.2-116.1 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.57 (d, *J* = 8.0 Hz, 1H), 7.30-7.20 (m, 9H), 7.11-7.06 (m, 4H), 7.03-6.94 (m, 5H), 6.59-6.57 (m, 2H), 3.88 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 161.9 (d, *J* = 244.0 Hz), 144.7, 143.5, 141.5, 141.2, 136.6, 136.1 (d, *J* = 2.0 Hz), 131.4, 131.3, 131.2, 129.6, 129.0, 128.2, 128.1, 128.0, 127.7, 127.1, 125.3, 123.2 (d, *J* = 12.8 Hz), 114.5 (d, *J* = 21.1 Hz), 93.3, 89.1, 36.3; LRMS (EI, 70 eV) m/z (%): 438 (M^+, 100), 359 (74), 283 (71), 179 (40); HRMS m/z (ESI) calcd for $C_{33}H_{24}F$ ($[M+H]^+$) 439.1857, found 439.1869.

2'-benzyl-6'-(phenylethynyl)-4-(trifluoromethyl)-1,1':3',1''-terphenyl (3ga):



63.4 mg, 65%; mp 139.1-140.7 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.59 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 7.6 Hz, 2H), 7.33-7.30 (m, 4H), 7.27-7.24 (m, 4H), 7.21-7.18 (m, 3H), 7.02-7.01 (m, 3H), 6.98-6.96 (m, 2H), 6.58-6.56 (m, 2H), 3.87 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 144.4, 144.2, 143.6, 141.3, 140.9, 136.2, 131.2, 130.2, 130.0, 129.6, 129.2, 129.0, 128.9, 128.2, 128.1, 128.1, 127.8, 127.2, 125.4, 125.4, 124.5 (q, *J* = 3.1 Hz), 123.2, 122.9, 93.9, 88.8, 36.4; LRMS (EI, 70 eV) m/z (%): 488 (M^+, 100), 409 (41), 333 (40), 170 (32); HRMS m/z (ESI) calcd for $C_{34}H_{24}F_3$ ($[M+H]^+$) 489.1825, found 489.1836.

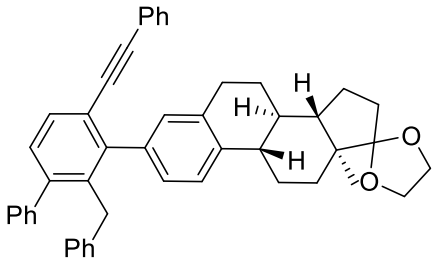
2'-benzyl-2-methoxy-6'-(phenylethynyl)-1,1':3',1''-terphenyl (3ha):



45.9 mg, 51%; mp 108.2-109.4 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.56 (d, *J* = 8.0 Hz, 1H), 7.29-7.22 (m, 6H), 7.19-7.18 (m, 3H), 7.07-7.04 (m, 3H), 6.97-6.95 (m, 3H), 6.90 (t, *J* = 7.5 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 2H), 6.59-6.57 (m, 2H), 3.93 (d, *J* = 16.0 Hz, 1H), 3.81 (d, *J* = 16.0 Hz, 1H), 3.59 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 156.9, 143.3, 142.7, 141.9, 141.2, 137.4, 131.4, 131.3, 129.4, 129.3, 129.1, 129.1, 128.7, 128.7, 128.0, 127.9, 127.7, 127.4, 126.8, 124.9, 123.6, 123.5, 120.0, 110.5, 92.2, 89.5, 55.4, 36.5; LRMS (EI, 70 eV) m/z (%): 450 (M^+, 98),

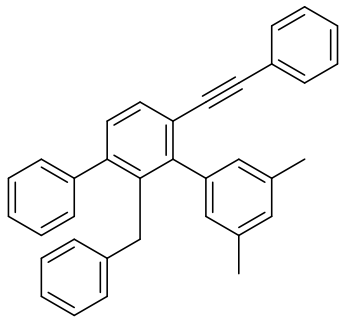
341 (100), 170 (43), 91 (30); HRMS m/z (ESI) calcd for $C_{34}H_{27}O$ ($[M+H]^+$) 451.2056, found 451.2061.

(8R,9S,13S,14S)-3-(2-benzyl-4-(phenylethynyl)-[1,1'-biphenyl]-3-yl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[a]phenanthrene-17,2'-[1,3]dioxolane] (3ia):



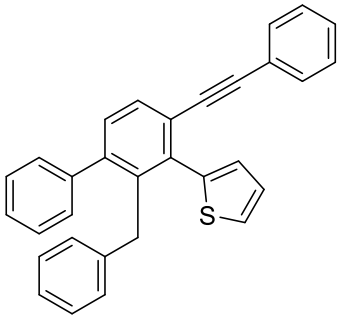
90.8 mg, 71%; Yellow oil; dr = 1.1 : 1; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.55-7.53 (m, 1H), 7.27-7.17 (m, 10H), 7.03-6.99 (m, 6H), 6.85 (d, *J* = 7.5 Hz, 1H), 6.62-6.57 (m, 2H), 3.97-3.90 (m, 6H), 2.78-2.66 (m, 2H), 2.38-2.33 (m, 2H), 2.05-2.02 (m, 1H), 1.88-1.78 (m, 4H), 1.68-1.66 (m, 1H), 1.38-1.34 (m, 4H), 0.95 (s, 1.6H), 0.93 (s, 1.4H), 0.88-0.84 0.95 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 146.3, 146.0, 143.4, 143.4, 141.8, 141.8, 141.6, 141.6, 139.0, 138.8, 137.4, 137.3, 136.7, 136.5, 135.7, 135.7, 131.4, 131.3, 130.6, 130.4, 129.4, 129.2, 129.2, 129.1, 129.1, 129.1, 128.3, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 126.9, 126.9, 125.1, 125.0, 124.5, 124.5, 123.6, 123.6, 123.2, 123.1, 119.5, 119.4, 93.2, 93.0, 90.1, 90.0, 65.3, 64.6, 49.5, 49.5, 46.2, 46.2, 44.3, 44.0, 39.2, 39.0, 36.5, 34.3, 30.8, 30.8, 29.6, 29.3, 27.2, 26.9, 26.2, 26.0, 22.4, 22.4, 14.4, 14.4; HRMS m/z (ESI) calcd for $C_{47}H_{45}O_2$ ($[M+H]^+$) 641.3414, found 641.3421.

2'-benzyl-3,5-dimethyl-6'-(phenylethynyl)-1,1':3',1''-terphenyl (3ja):



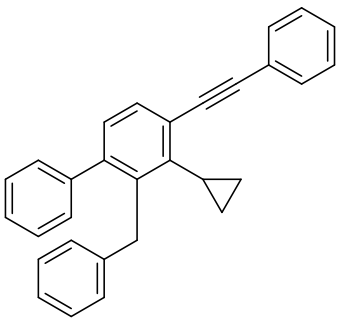
69.0 mg, 77%; mp 115.4-116.6 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55 (d, *J* = 8.0 Hz, 1H), 7.28-7.19 (m, 9H), 7.08-7.07 (m, 2H), 7.01-6.99 (m, 3H), 6.92 (s, 1H), 6.76 (s, 2H), 6.59-6.57 (m, 2H), 3.90 (s, 2H), 2.22 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 146.1, 143.4, 141.8, 141.7, 139.8, 136.8, 136.6, 131.3, 129.5, 129.2, 129.1, 128.3, 128.1, 127.9, 127.8, 127.6, 127.5, 126.9, 125.0, 123.6, 122.9, 92.9, 89.7, 36.4, 21.3; LRMS (EI, 70 eV) m/z (%): 448 (M^+, 45), 357 (100), 279 (16), 170 (10); HRMS m/z (ESI) calcd for $C_{35}H_{29}$ ($[M+H]^+$) 449.2264, found 449.2269.

2-(2-benzyl-4-(phenylethynyl)-[1,1'-biphenyl]-3-yl)thiophene (3ka):



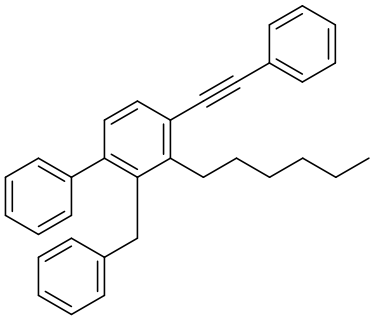
42.6 mg, 50%; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.57 (d, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 5.0 Hz, 1H), 7.28-7.26 (m, 4H), 7.24-7.23 (m, 4H), 7.19-7.16 (m, 4H), 7.07-7.03 (m, 3H), 6.99-6.97 (m, 1H), 6.82 (d, *J* = 3.0 Hz, 1H), 6.67 (d, *J* = 7.0 Hz, 2H), 3.98 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 143.6, 141.6, 141.4, 140.4, 138.6, 138.2, 131.5, 130.5, 129.6, 129.0, 128.2, 128.2, 128.1, 128.0, 127.8, 127.1, 126.4, 125.6, 125.3, 125.0, 123.4, 93.6, 88.9, 36.7; LRMS (EI, 70 eV) m/z (%): 426 (M^+, 100), 347 (58), 271 (25), 174 (36); HRMS m/z (ESI) calcd for $C_{31}H_{23}S$ ($[M+H]^+$) 427.1515, found 427.1522.

2-benzyl-3-cyclopropyl-4-(phenylethynyl)-1,1'-biphenyl (3la):



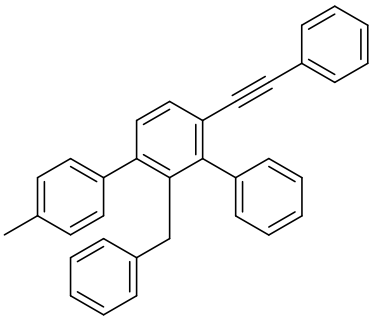
48.4 mg, 63%; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.54-7.52 (m, 2H), 7.49 (d, *J* = 7.5 Hz, 1H), 7.36-7.28 (m, 6H), 7.22-7.20 (m, 2H), 7.17-7.14 (m, 3H), 7.10 (d, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 7.5 Hz, 2H), 4.28 (s, 2H), 1.59-1.55 (m, 1H), 1.04-1.01 (m, 2H), 0.94-0.93 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 143.5, 143.4, 141.8, 141.5, 139.4, 131.3, 130.9, 129.0, 128.4, 128.3, 128.1, 128.0, 128.0, 128.0, 126.9, 125.4, 124.1, 123.9, 94.0, 89.6, 35.6, 13.9, 9.0; LRMS (EI, 70 eV) m/z (%): 384 (M^+, 24), 293 (32), 215 (22), 91 (100); HRMS m/z (ESI) calcd for $C_{30}H_{25}$ ($[M+H]^+$) 385.1951, found 385.1960.

2-benzyl-3-hexyl-4-(phenylethynyl)-1,1'-biphenyl (3ma):



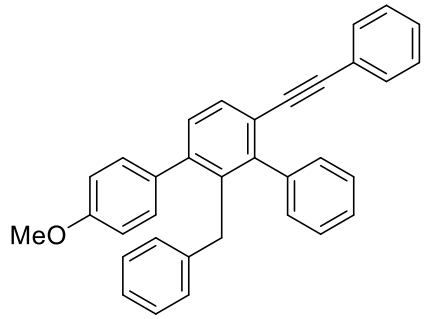
49.6 mg, 58%; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.52-7.50 (m, 3H), 7.36-7.31 (m, 3H), 7.27-7.26 (m, 3H), 7.22-7.16 (m, 4H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 7.0 Hz, 2H), 4.04 (s, 2H), 2.84-2.81 (m, 2H), 1.56-1.52 (m, 2H), 1.37-1.34 (m, 2H), 1.26-1.24 (m, 4H), 0.84-0.81 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 144.9, 143.8, 142.0, 141.4, 135.4, 131.4, 130.4, 128.9, 128.3, 128.2, 128.1, 128.0, 127.9, 126.9, 125.6, 123.7, 122.8, 92.6, 89.0, 35.7, 32.3, 31.6, 30.4, 30.0, 22.6, 14.1; LRMS (EI, 70 eV) m/z (%): 428 (M^+, 79), 371 (12), 279 (15), 91 (100); HRMS m/z (ESI) calcd for $C_{33}H_{33}$ ($[M+H]^+$) 429.2577, found 429.2584.

2'-benzyl-4-methyl-4'-(phenylethynyl)-1,1':3',1''-terphenyl (3oa):



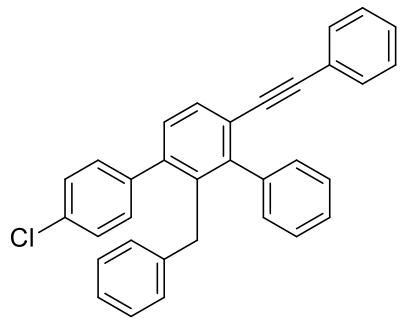
62.5 mg, 72%; mp 146.5-148.0 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.56 (d, *J* = 8.0 Hz, 1H), 7.28-7.24 (m, 4H), 7.20-7.08 (m, 9H), 7.04-6.99 (m, 5H), 6.60-6.57 (m, 2H), 3.90 (s, 2H), 2.33 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 145.8, 143.4, 141.4, 140.2, 138.7, 136.6, 136.5, 131.3, 129.7, 129.5, 129.5, 129.0, 128.7, 128.2, 128.0, 127.8, 127.6, 127.5, 126.8, 125.1, 123.4, 122.9, 93.0, 89.5, 36.3, 21.1; LRMS (EI, 70 eV) m/z (%): 434 (M^+, 89), 341 (63), 170 (100), 91 (38); HRMS m/z (ESI) calcd for $C_{34}H_{27}$ ($[M+H]^+$) 435.2107, found 435.2121.

2'-benzyl-4-methoxy-4'-(phenylethynyl)-1,1':3',1''-terphenyl (3pa):



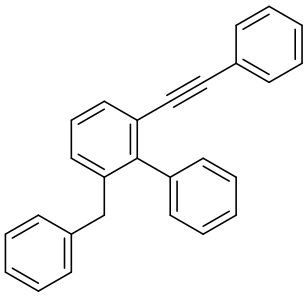
66.6 mg, 74%; mp 155.6-156.9 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.56 (d, *J* = 8.0 Hz, 1H), 7.29-7.27 (m, 3H), 7.25 (d, *J* = 8.0 Hz, 1H), 7.20-7.18 (m, 3H), 7.17-7.14 (m, 4H), 7.04-7.00 (m, 5H), 6.82 (d, *J* = 8.5 Hz, 2H), 6.61-6.59 (m, 2H), 3.90 (s, 2H), 3.79 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 158.7, 145.8, 143.2, 141.5, 140.3, 136.6, 134.1, 131.3, 130.2, 129.7, 129.6, 129.5, 128.2, 128.1, 127.8, 127.7, 127.6, 126.8, 125.2, 123.4, 122.8, 113.4, 93.0, 89.5, 55.2, 36.4; LRMS (EI, 70 eV) m/z (%): 450 (M^+, 100), 372 (54), 295 (27), 169 (12); HRMS m/z (ESI) calcd for $C_{34}H_{27}O$ ($[M+H]^+$) 451.2056, found 451.2064.

2'-benzyl-4-chloro-4'-(phenylethynyl)-1,1':3',1''-terphenyl (3qa):



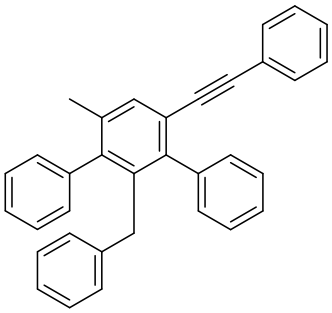
61.7 mg, 68%; mp 160.3-161.2 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.58 (d, *J* = 8.0 Hz, 1H), 7.32-7.29 (m, 3H), 7.28-7.22 (m, 8H), 7.08-7.06 (m, 4H), 7.03-7.02 (m, 3H), 6.59-6.57 (m, 2H), 3.87 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 145.9, 142.2, 141.1, 140.1, 140.0, 136.4, 133.1, 131.3, 130.4, 129.7, 129.6, 129.3, 128.2, 128.1, 128.1, 128.0, 127.8, 127.7, 127.0, 125.3, 123.5, 123.3, 93.4, 89.3, 36.3; LRMS (EI, 70 eV) m/z (%): 456 (M^+ + 2, 15), 454 (M^+, 38), 341 (100), 170 (71); HRMS m/z (ESI) calcd for $C_{33}H_{24}{}^{35}Cl$ ($[M+H]^+$) 455.1561, found 455.1570.

2-benzyl-6-(phenylethynyl)-1,1'-biphenyl (3ra):



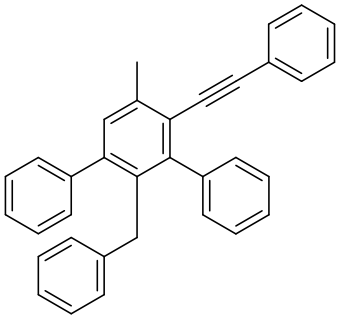
43.3 mg, 63%; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.49 (d, *J* = 7.5 Hz, 1H), 7.41-7.36 (m, 3H), 7.28-7.25 (m, 3H), 7.21-7.18 (m, 6H), 7.15-7.12 (m, 1H), 7.07-7.05 (m, 2H), 6.95 (d, *J* = 7.5 Hz, 2H), 3.84 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 144.5, 140.9, 139.8, 139.2, 131.3, 130.1, 129.8, 129.7, 128.9, 128.2, 128.1, 127.9, 127.8, 127.3, 127.1, 125.8, 123.5, 123.4, 92.8, 89.4, 39.4; LRMS (EI, 70 eV) m/z (%): 344 (M^+, 70), 266 (100), 253 (86), 132 (49); HRMS m/z (ESI) calcd for $C_{27}H_{21}$ ($[M+H]^+$) 345.1638, found 345.1646.

2'-benzyl-4'-methyl-6'-(phenylethynyl)-1,1':3',1''-terphenyl (3sa):



41.7 mg, 48%; mp 100.5-101.8 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.49 (s, 1H), 7.30-7.29 (m, 3H), 7.25-7.19 (m, 9H), 7.06-7.05 (m, 2H), 6.99-6.97 (m, 4H), 6.56-6.54 (m, 2H), 3.71 (s, 2H), 2.04 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 143.2, 141.4, 140.4, 140.2, 136.9, 135.9, 131.3, 131.1, 129.9, 129.7, 129.1, 128.7, 128.2, 128.1, 127.8, 127.6, 127.5, 126.8, 126.7, 125.0, 123.5, 122.6, 92.6, 89.6, 36.9, 20.9; LRMS (EI, 70 eV) m/z (%): 434 (M^+, 70), 341 (74), 207 (100), 170 (95); HRMS m/z (ESI) calcd for $C_{34}H_{27}$ ($[M+H]^+$) 435.2107, found 435.2114.

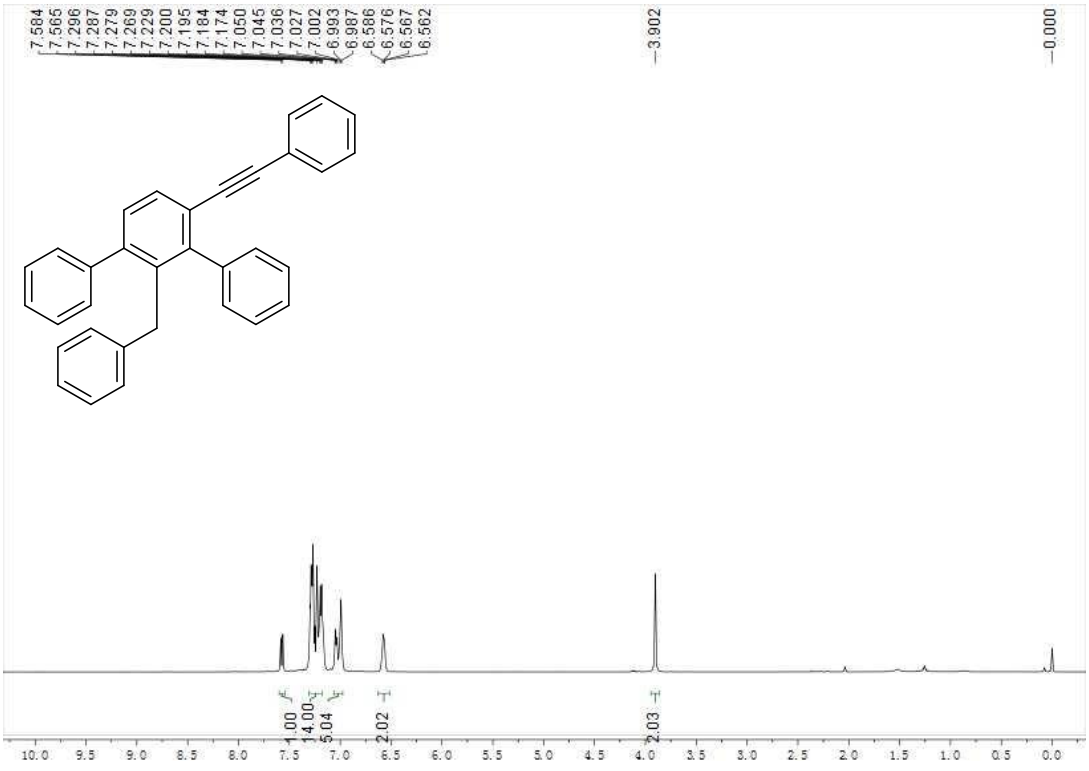
2'-benzyl-5'-methyl-4'-(phenylethynyl)-1,1':3',1''-terphenyl (3ta):

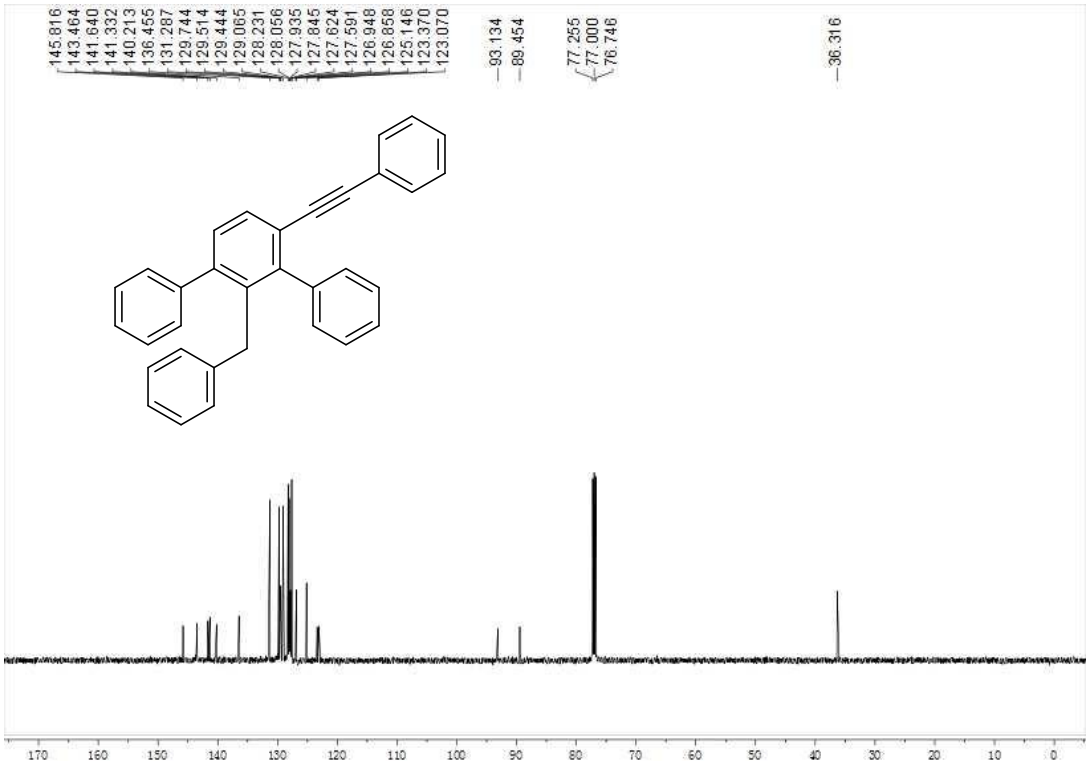


57.3 mg, 66%; mp 103.6-104.9 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.28-7.25 (m, 6H), 7.22-7.20 (m, 2H), 7.19-7.15 (m, 6H), 7.04-7.02 (m, 2H), 6.99-6.98 (m, 3H), 6.59-6.56 (m, 2H), 3.85 (s, 2H), 2.58 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 145.9, 143.0, 141.8, 141.6, 140.8, 137.8, 133.6, 131.2, 130.6, 129.8, 129.1, 128.2, 128.1, 127.9, 127.8, 127.6, 127.6, 126.9, 126.7, 125.1, 123.6, 123.0, 97.6, 88.2, 36.1, 20.9; LRMS (EI, 70 eV) m/z (%): 434 (M^+, 100), 343 (80), 265 (36), 170 (34); HRMS m/z (ESI) calcd for $C_{34}H_{27}$ ($[M+H]^+$) 435.2107, found 435.2115.

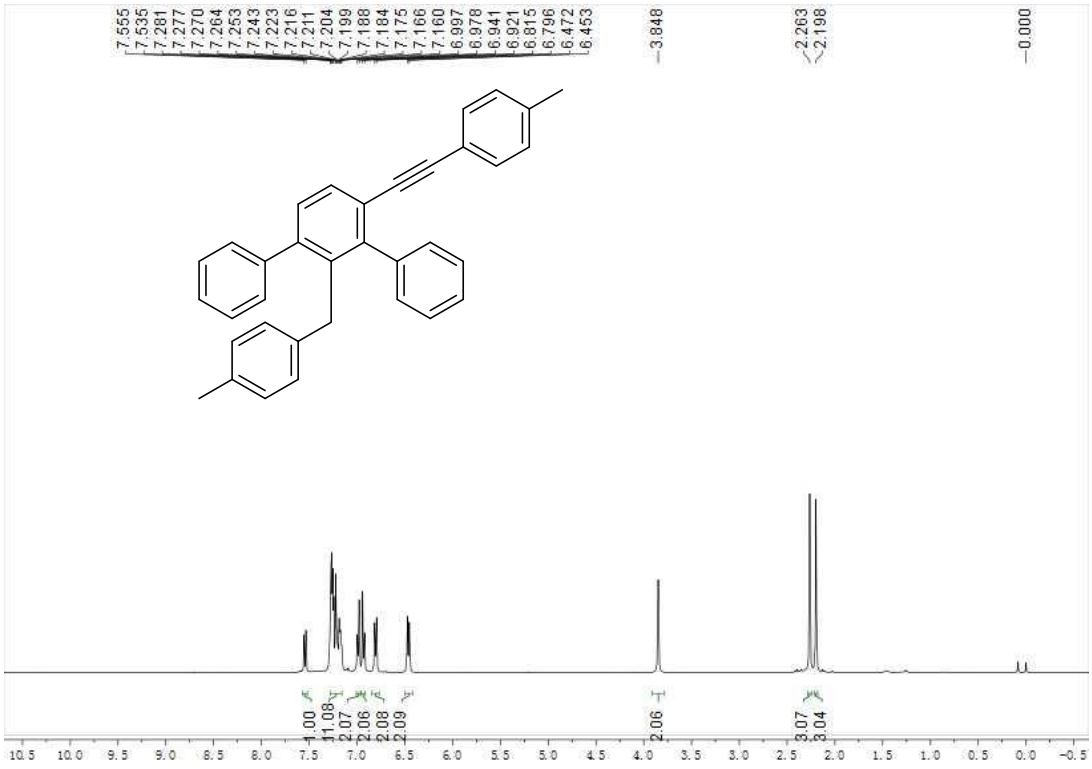
(C) Spectra

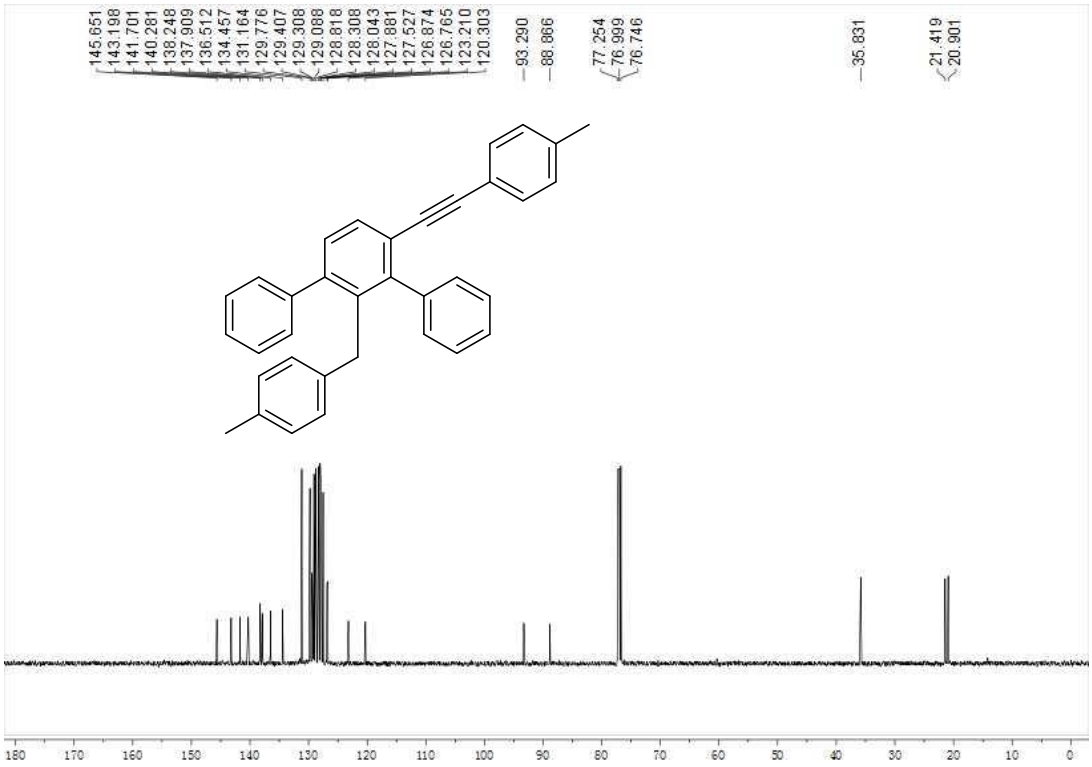
2'-benzyl-4'-(phenylethynyl)-1,1':3',1''-terphenyl (3aa):



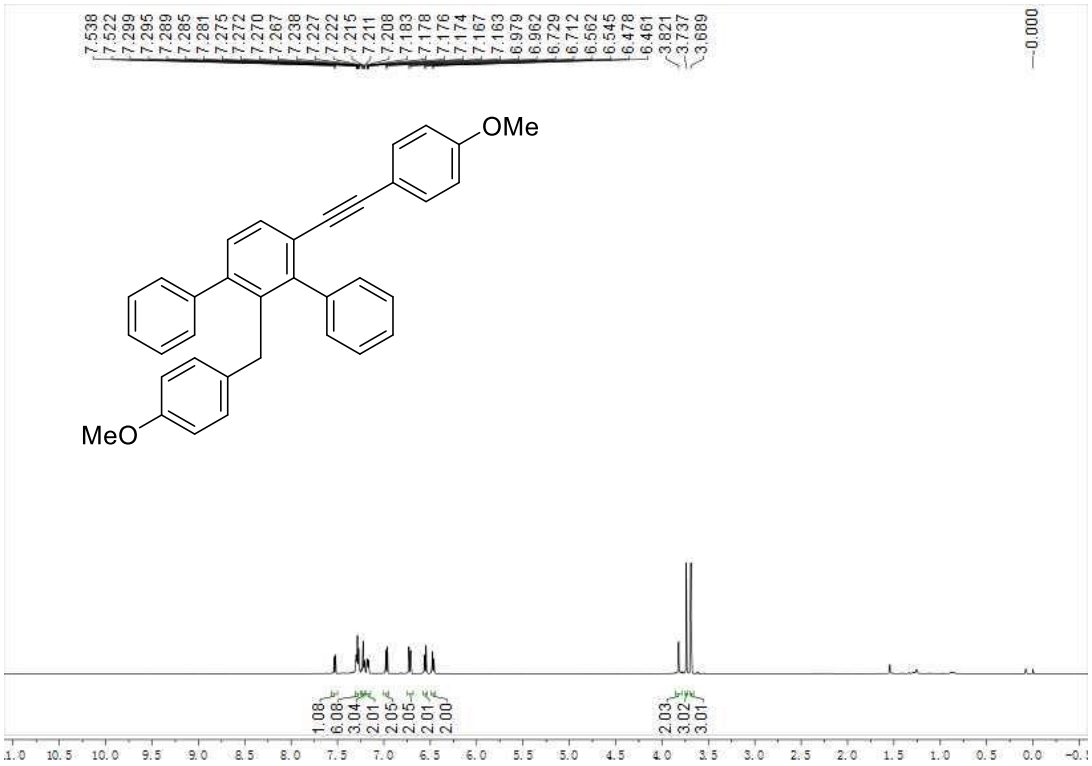


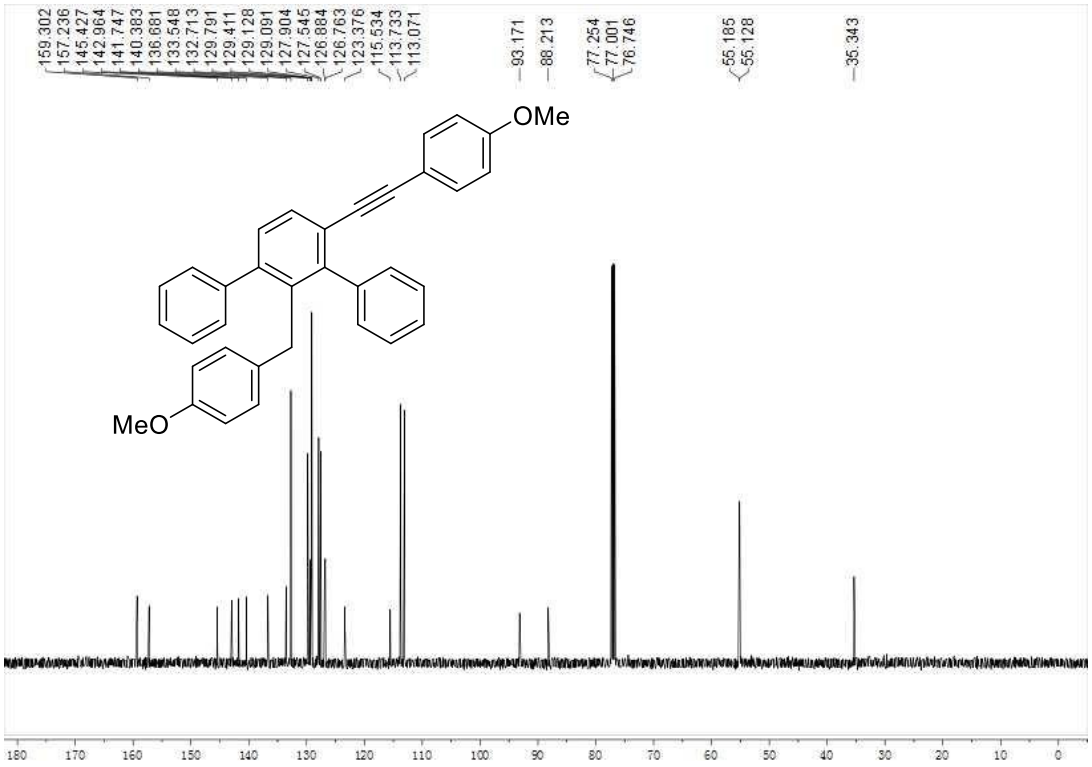
2'-(4-methylbenzyl)-4'-(p-tolylethynyl)-1,1':3',1''-terphenyl (3ab):



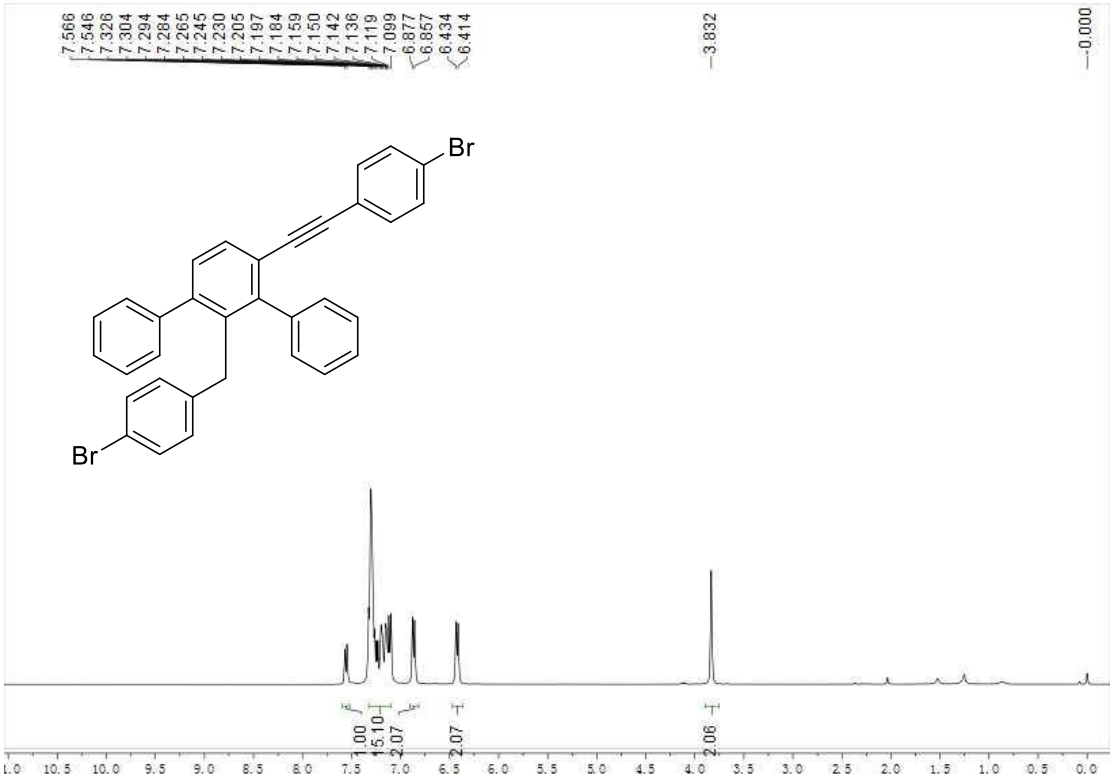


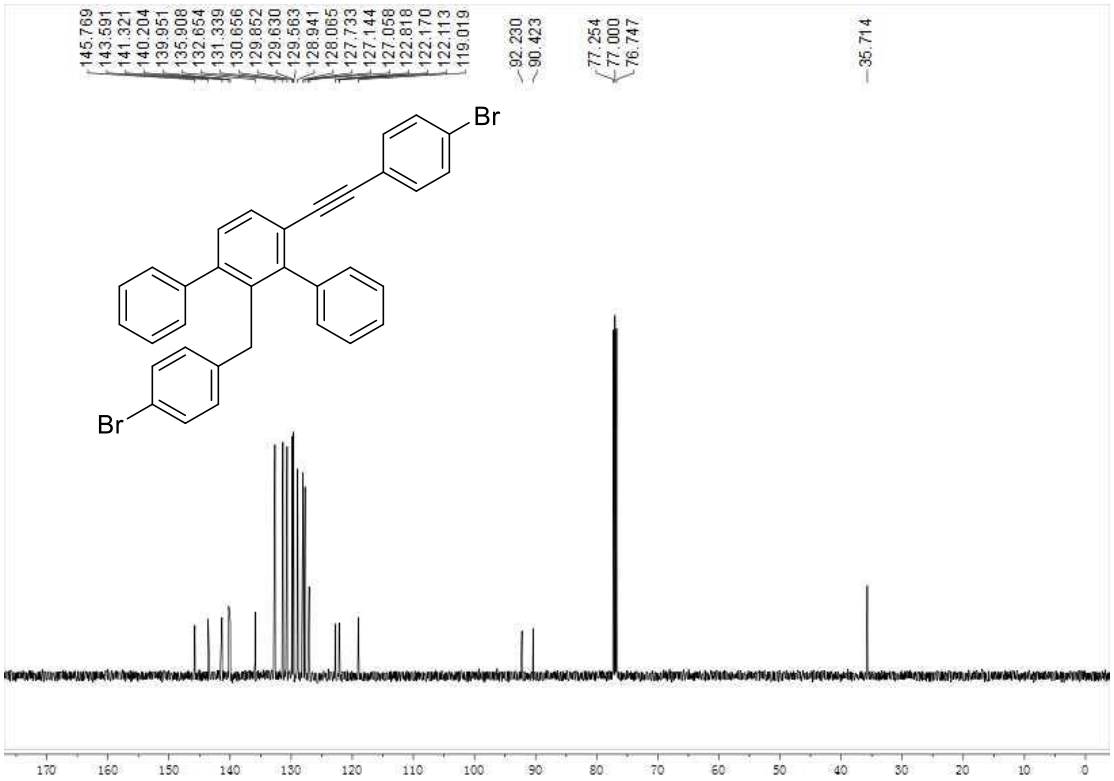
2'-(4-methoxybenzyl)-4'-((4-methoxyphenyl)ethynyl)-1,1':3',1''-terphenyl (3ac):



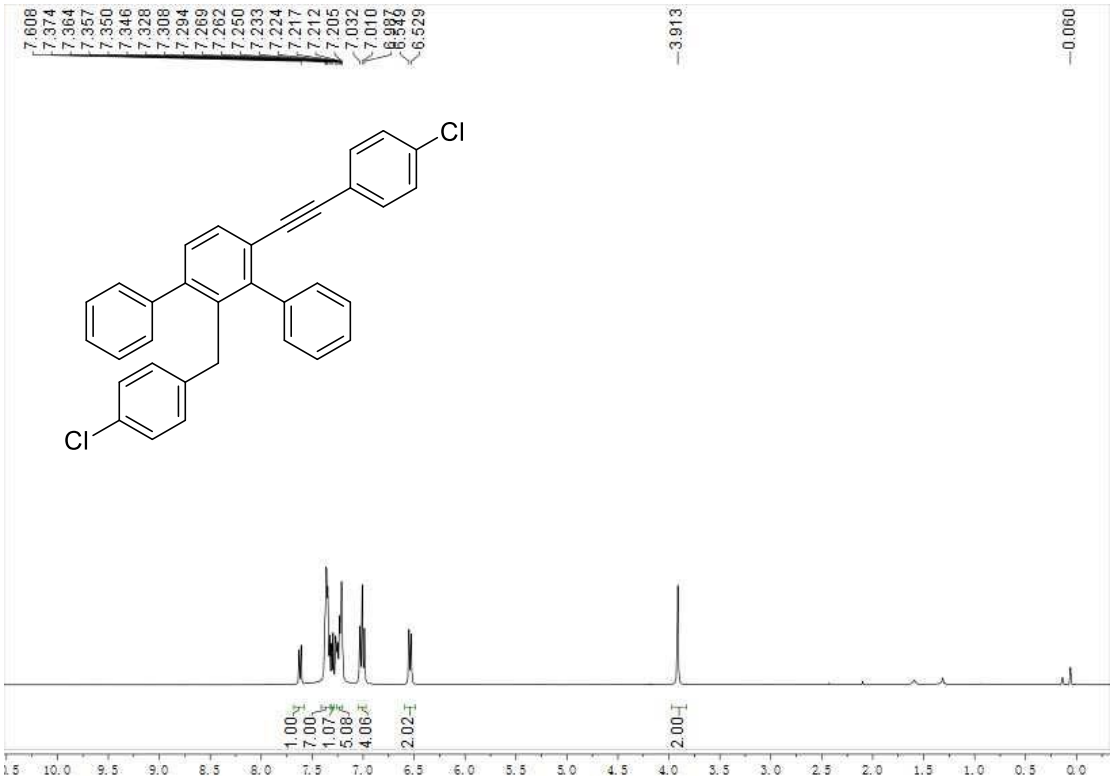


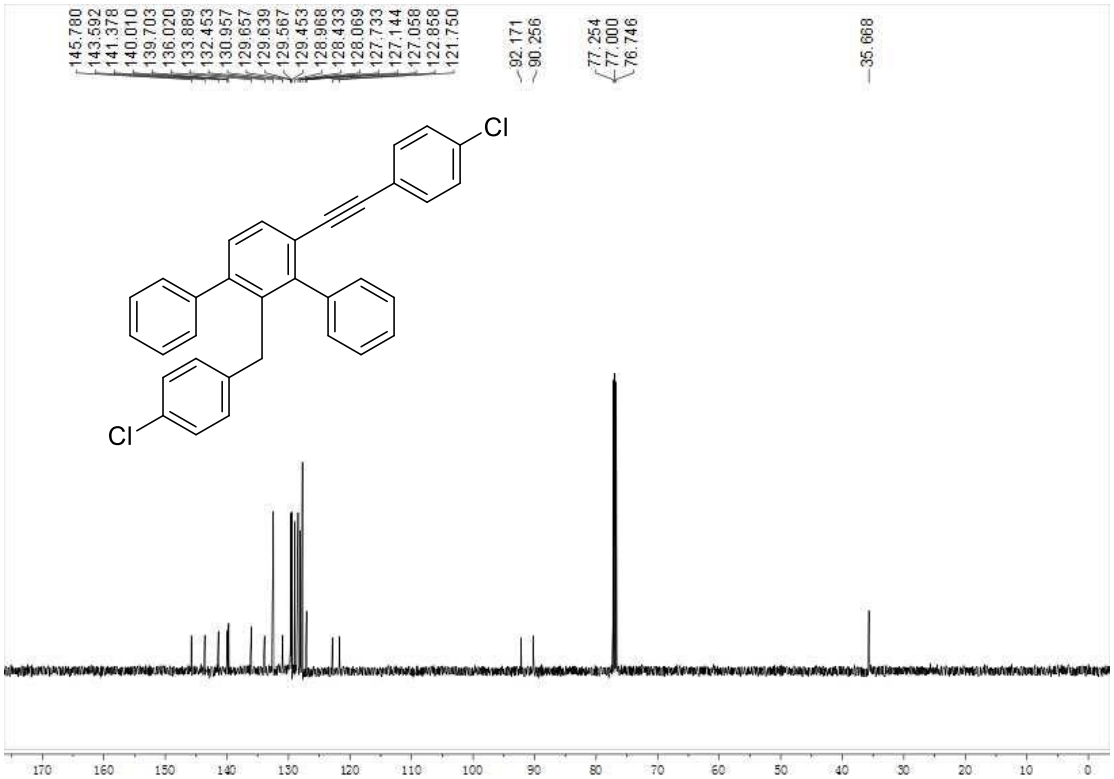
2'-(4-bromobenzyl)-4'-((4-bromophenyl)ethynyl)-1,1':3',1''-terphenyl (3ad):



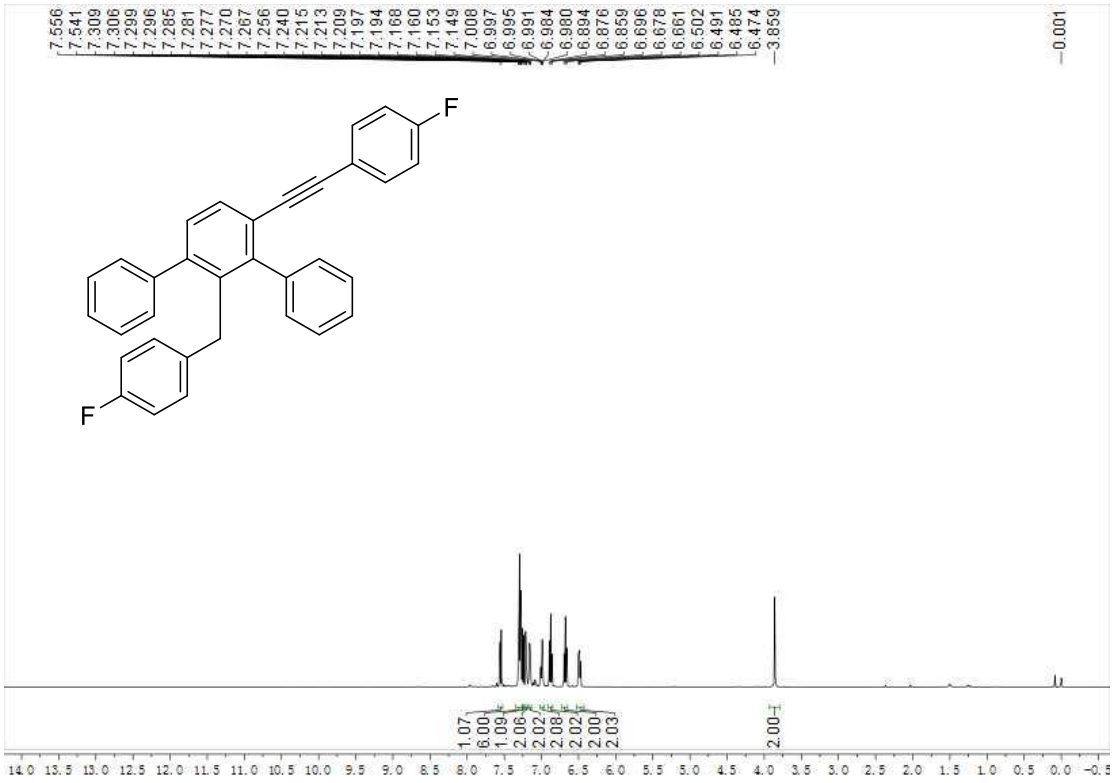


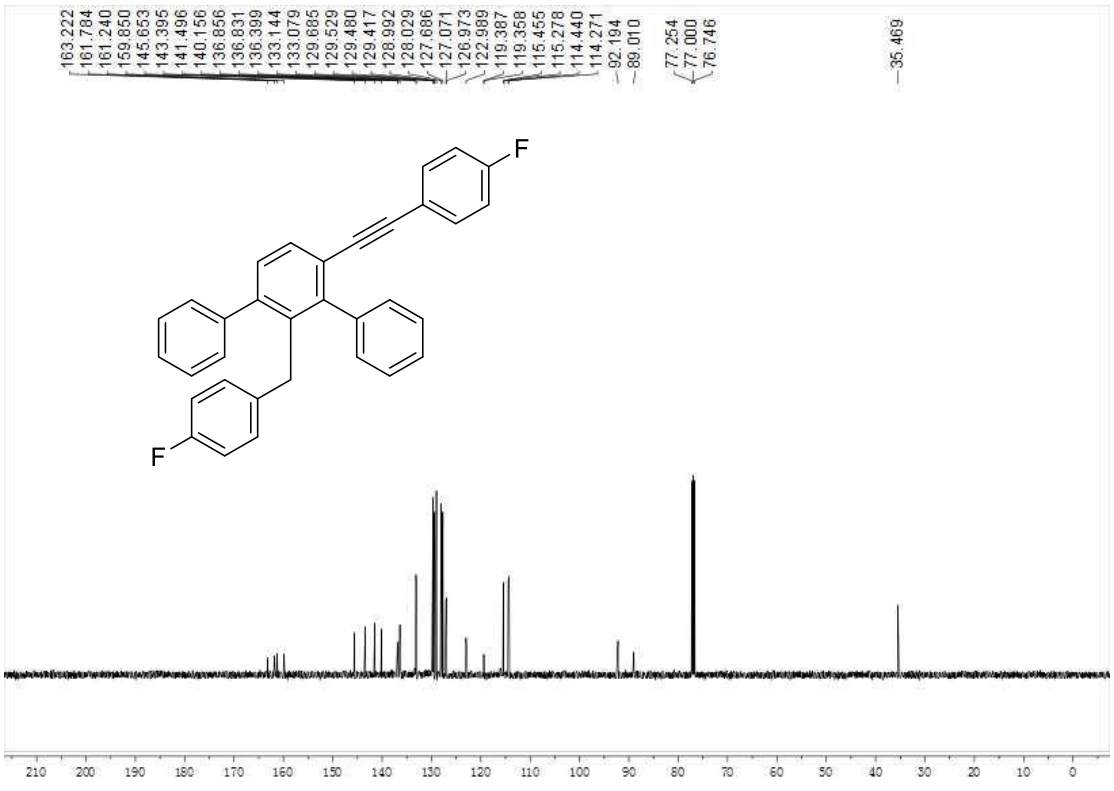
2'-(4-chlorobenzyl)-4'-((4-chlorophenyl)ethynyl)-1,1':3',1''-terphenyl (3ae):



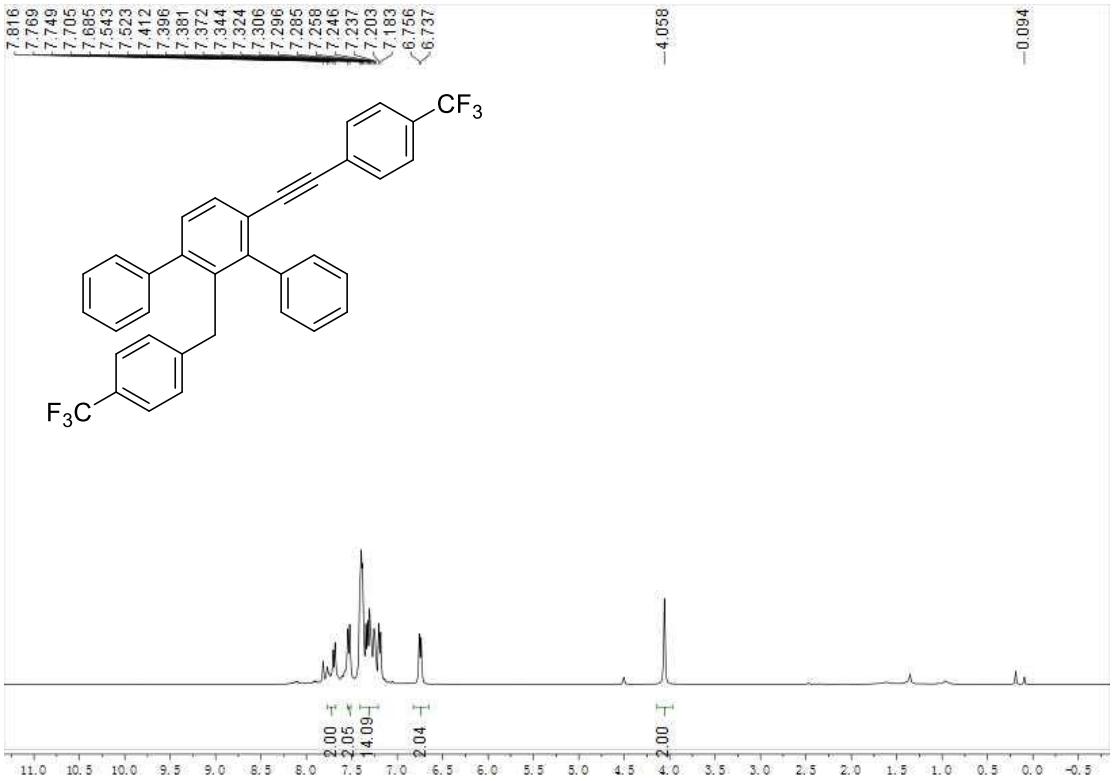


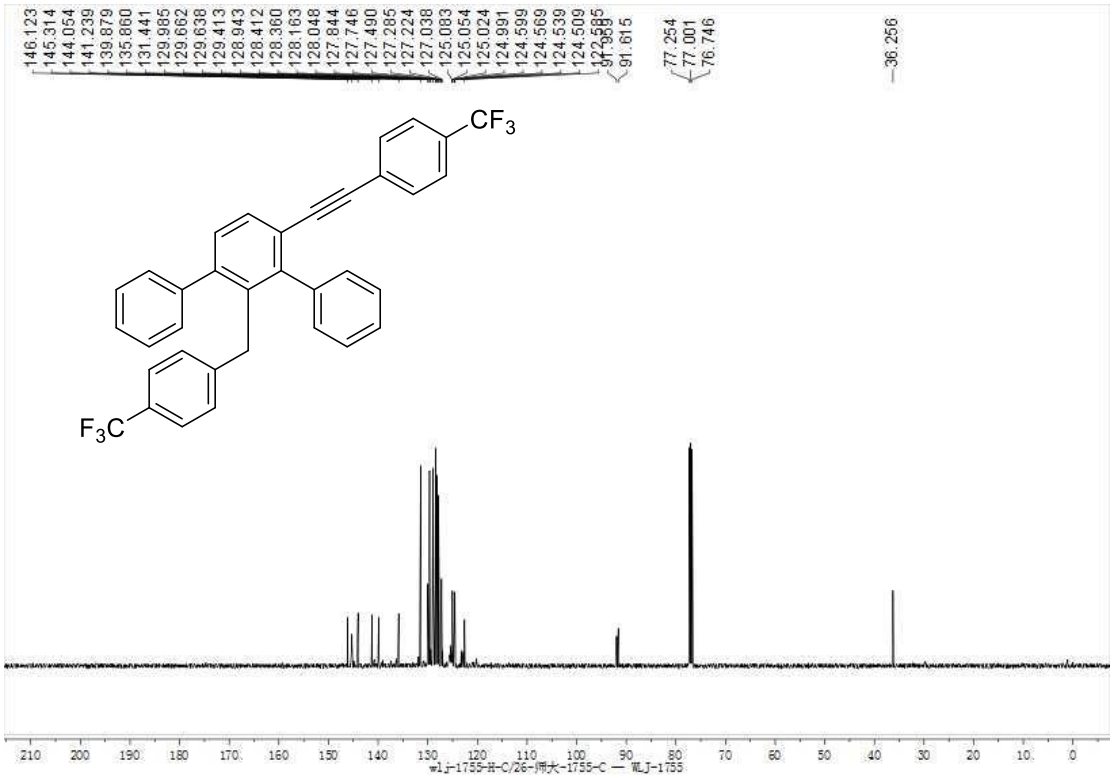
2'-(4-fluorobenzyl)-4'-((4-fluorophenyl)ethynyl)-1,1':3',1''-terphenyl (3af):



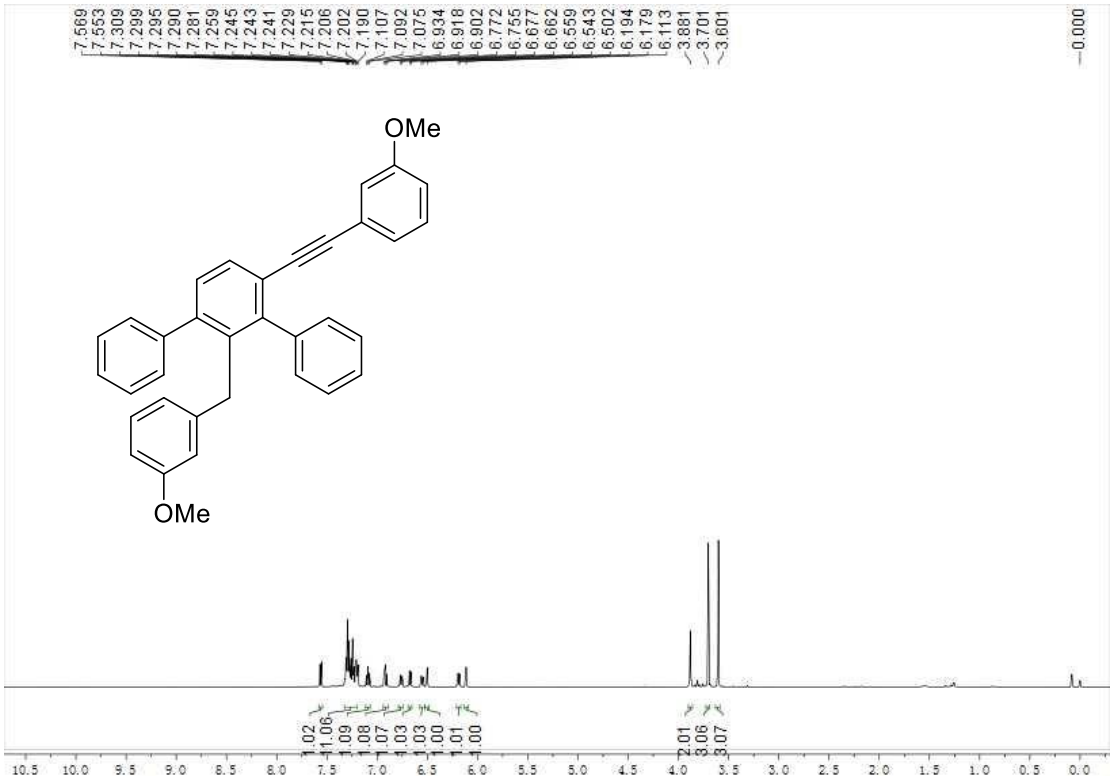


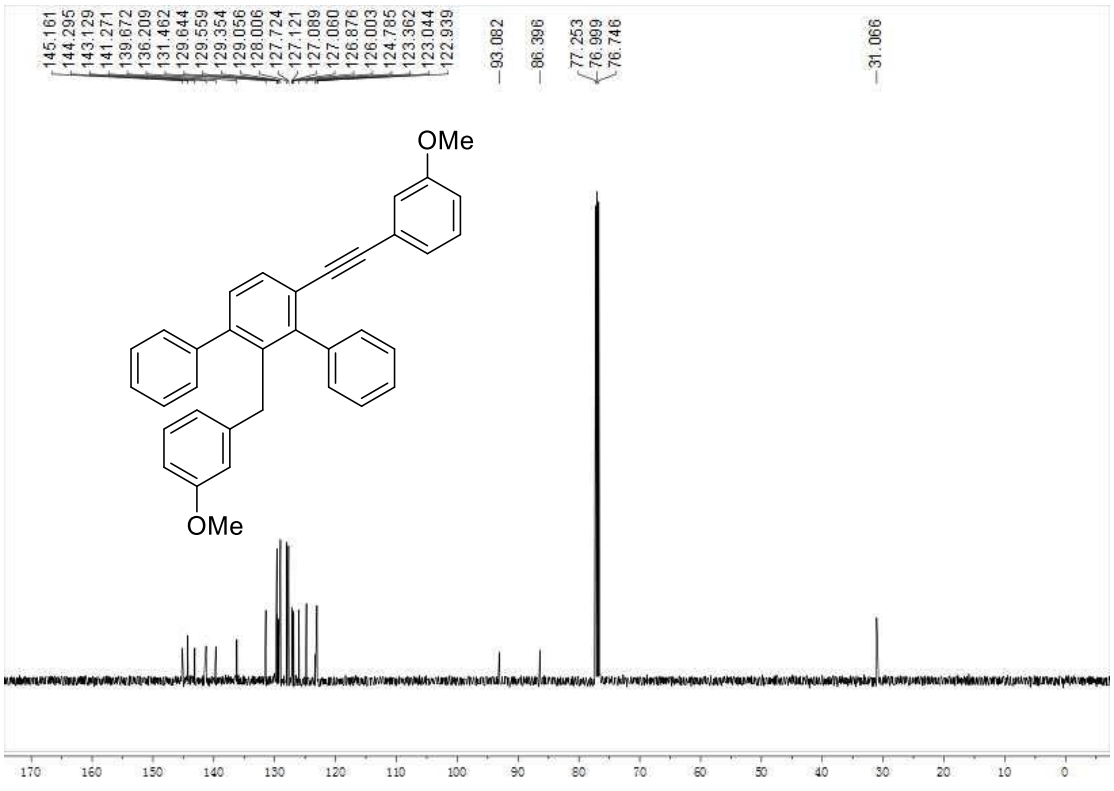
2'-(4-(trifluoromethyl)benzyl)-4'-((4-(trifluoromethyl)phenyl)ethynyl)-1,1':3',1''-terphenyl (3ag):



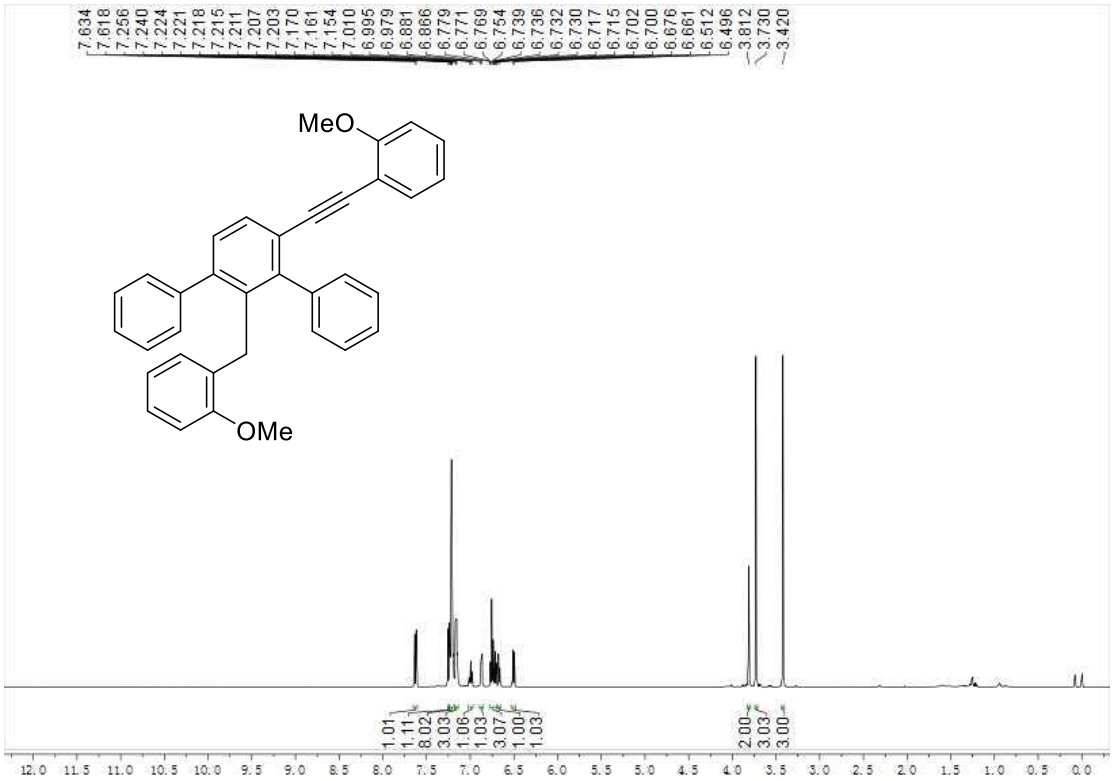


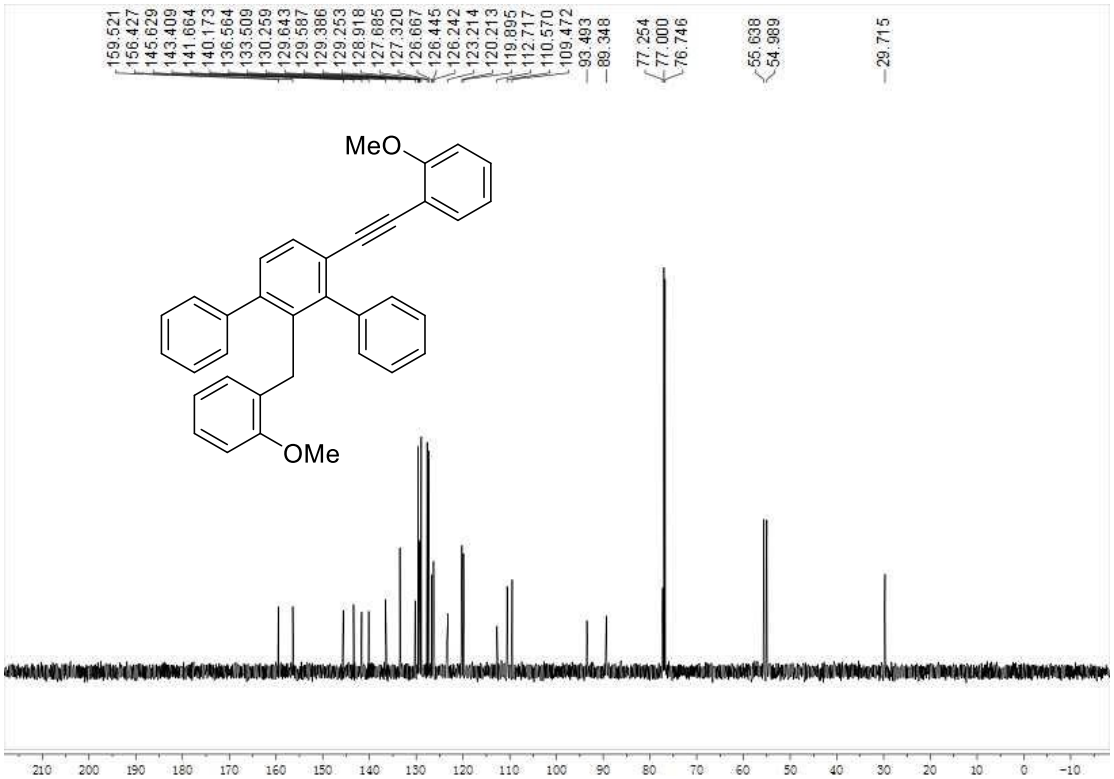
2'-(3-methoxybenzyl)-4'-((3-methoxyphenyl)ethynyl)-1,1':3',1''-terphenyl (3ah):



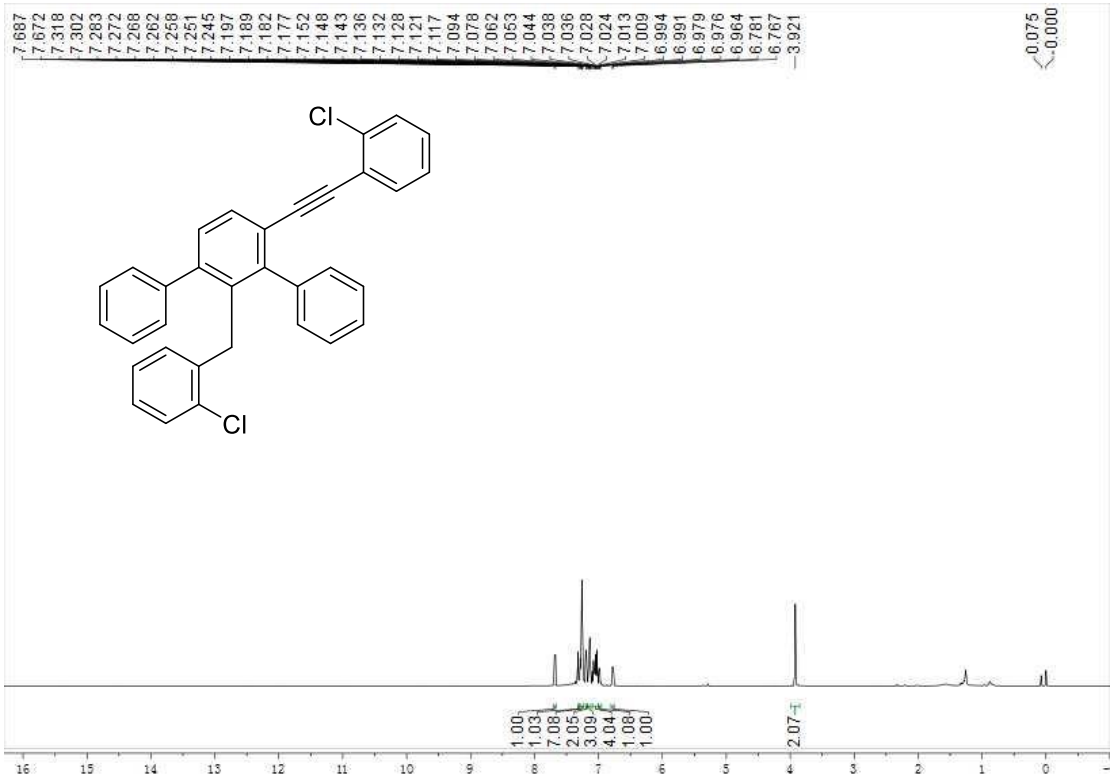


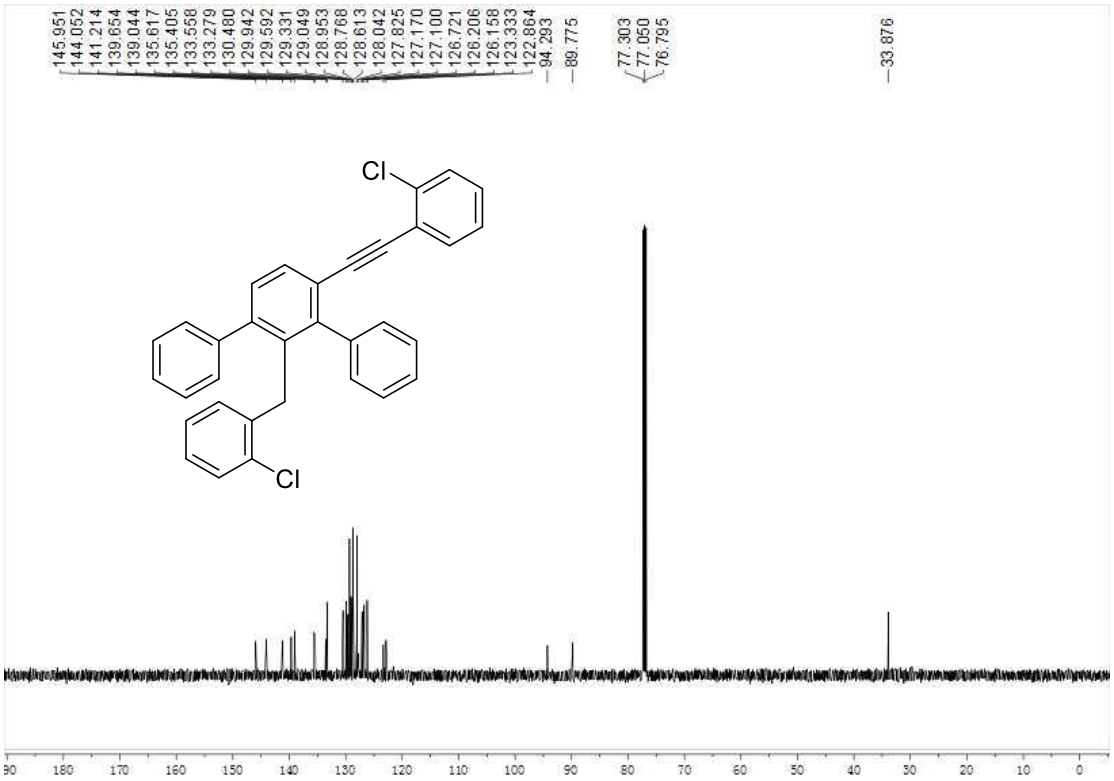
2'-(2-methoxybenzyl)-4'-((2-methoxyphenyl)ethynyl)-1,1':3',1''-terphenyl (3ai):



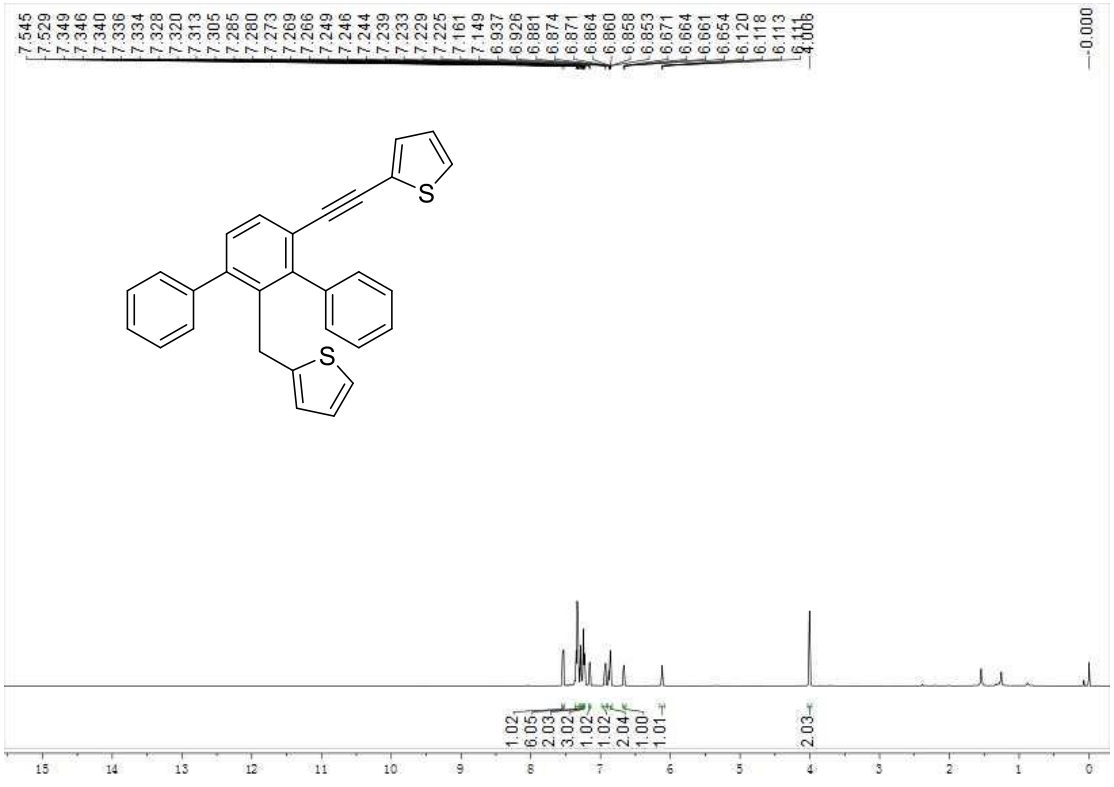


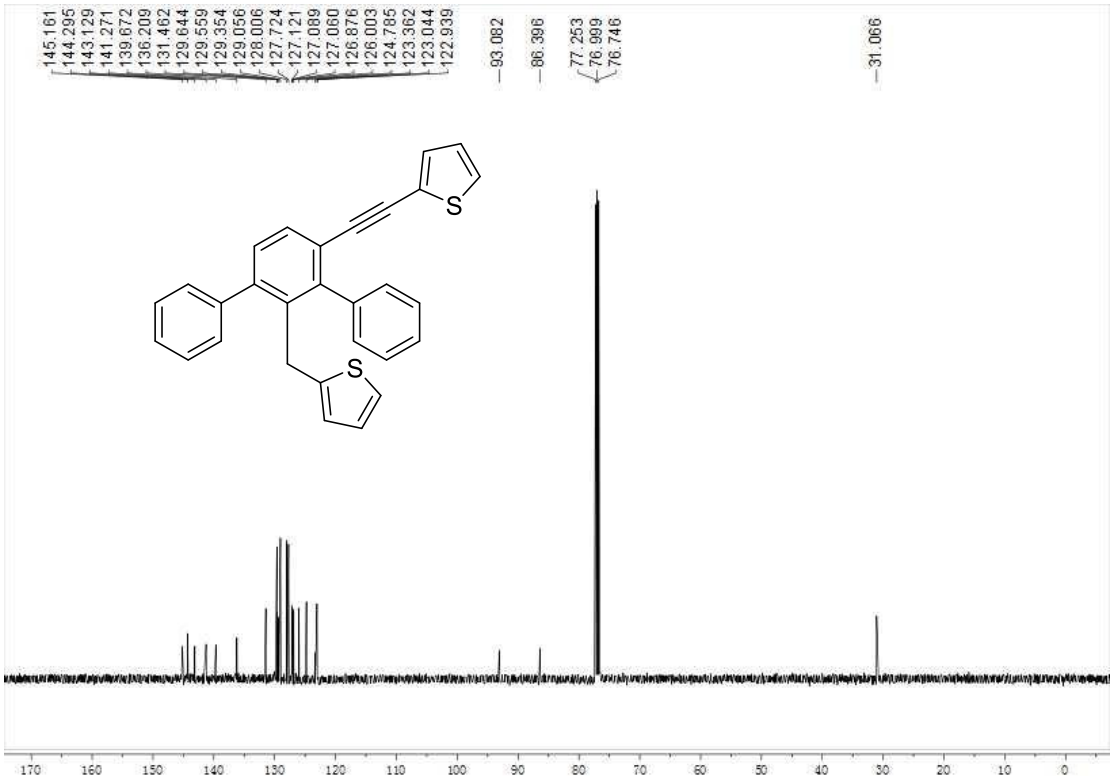
2'-(2-chlorobenzyl)-4'-((2-chlorophenyl)ethynyl)-1,1':3',1''-terphenyl (3aj):



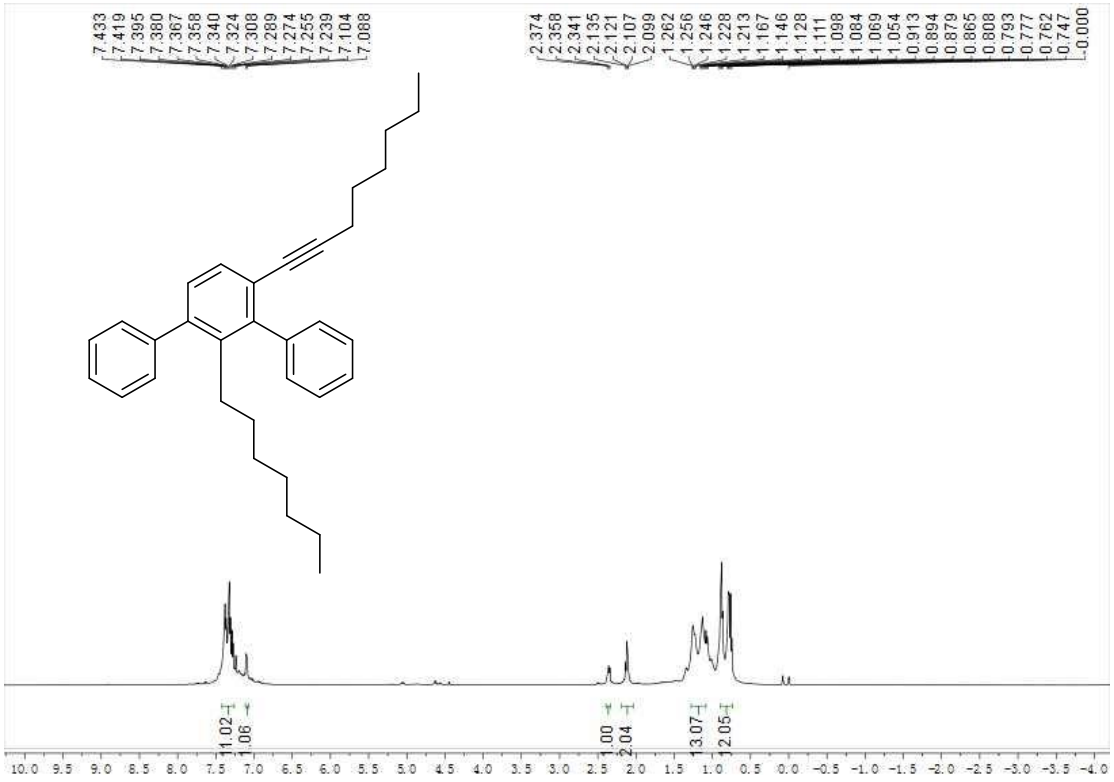


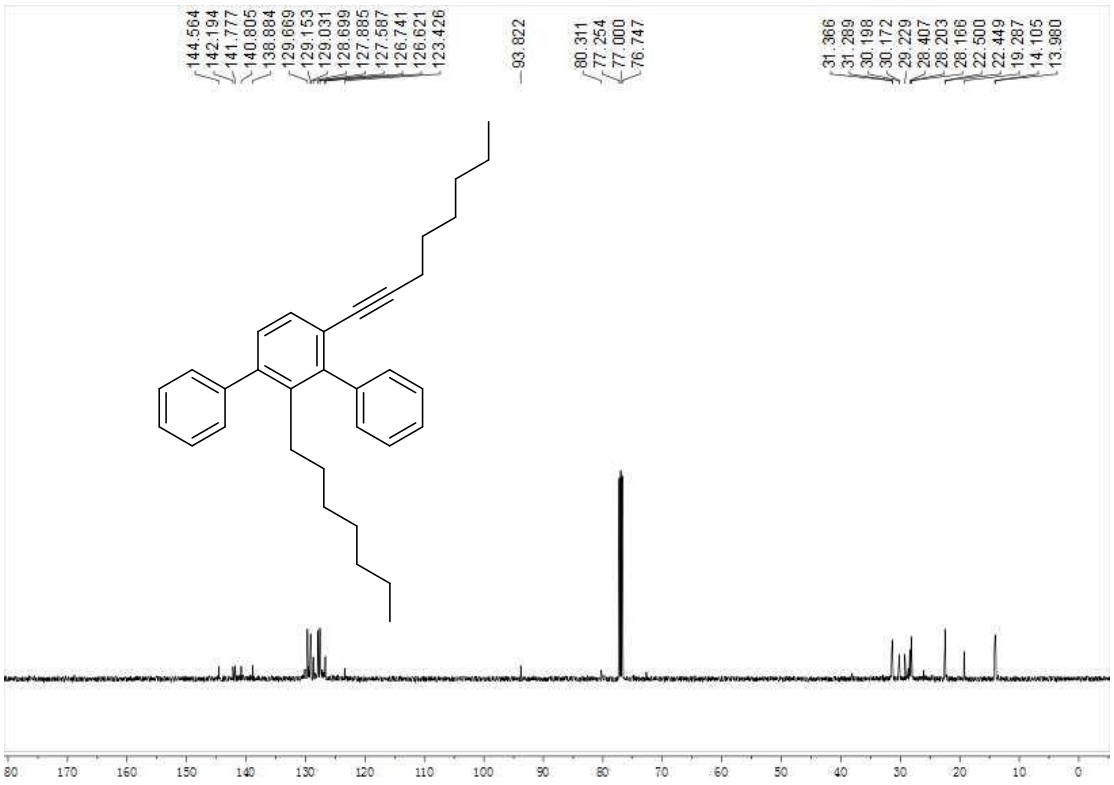
2-((4'-(thiophen-2-ylethynyl)-[1,1':3',1''-terphenyl]-2'-yl)methyl)thiophene (3ak):



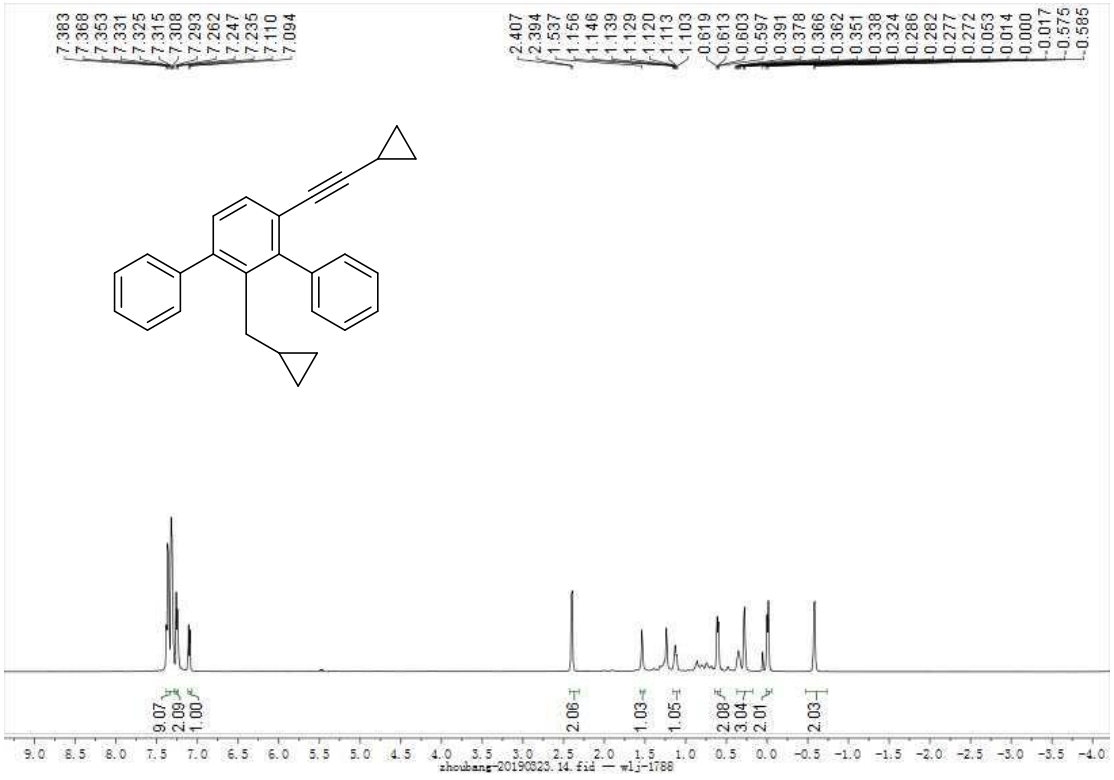


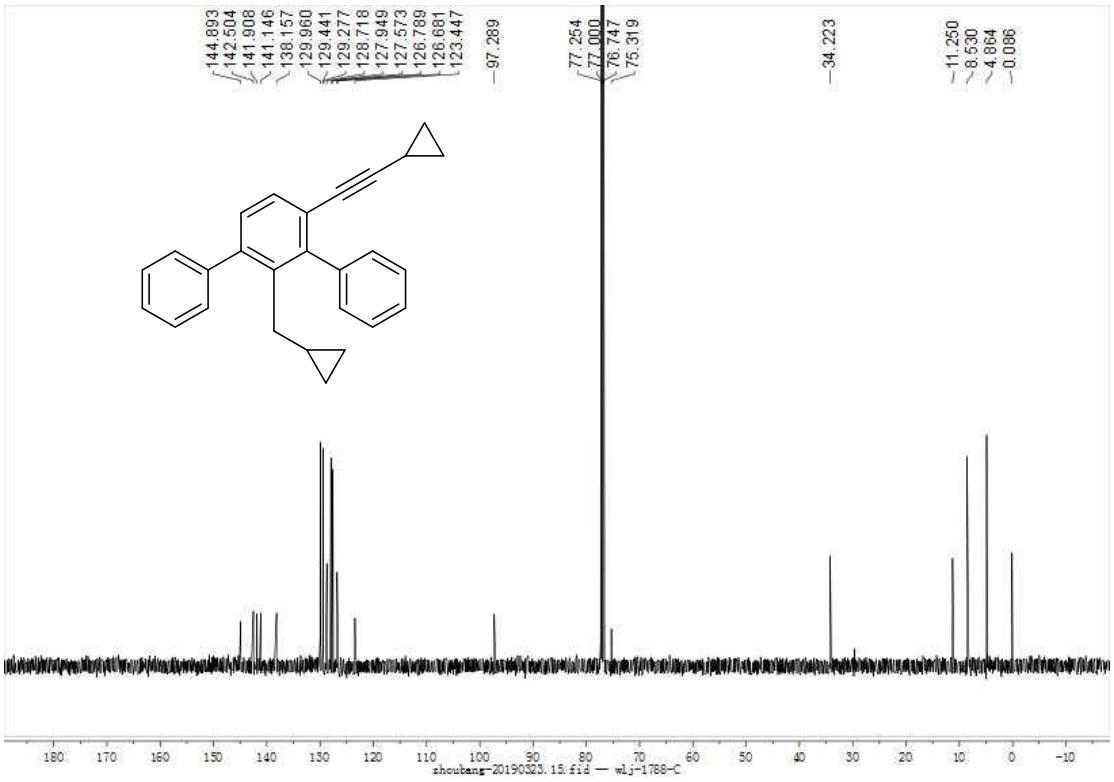
2'-heptyl-4'-(oct-1-yn-1-yl)-1,1':3',1''-terphenyl (3al):



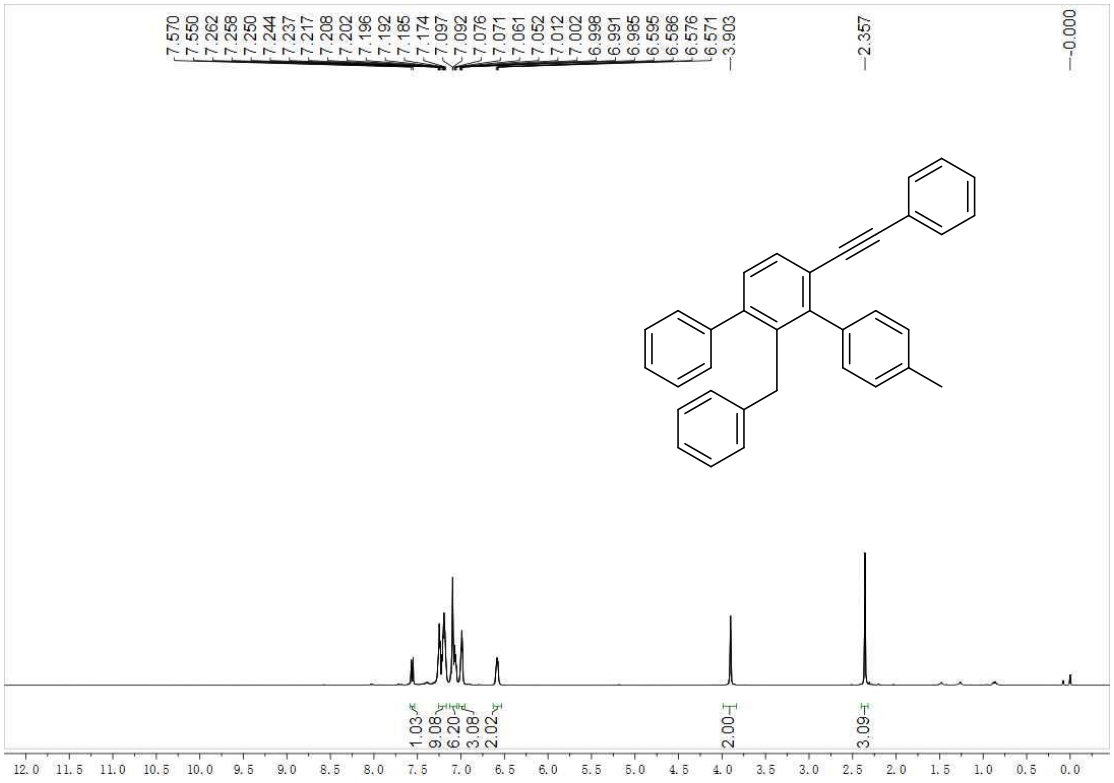


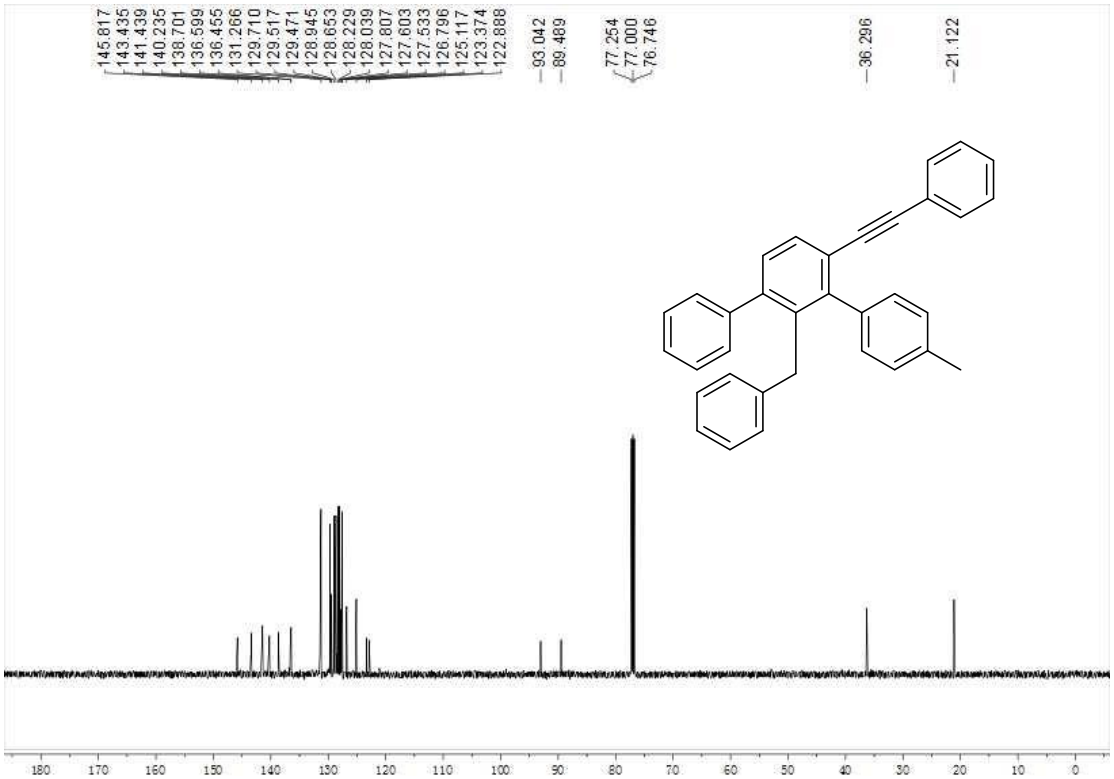
4'-(cyclopropylethynyl)-2'-(cyclopropylmethyl)-1,1':3',1''-terphenyl (3am):



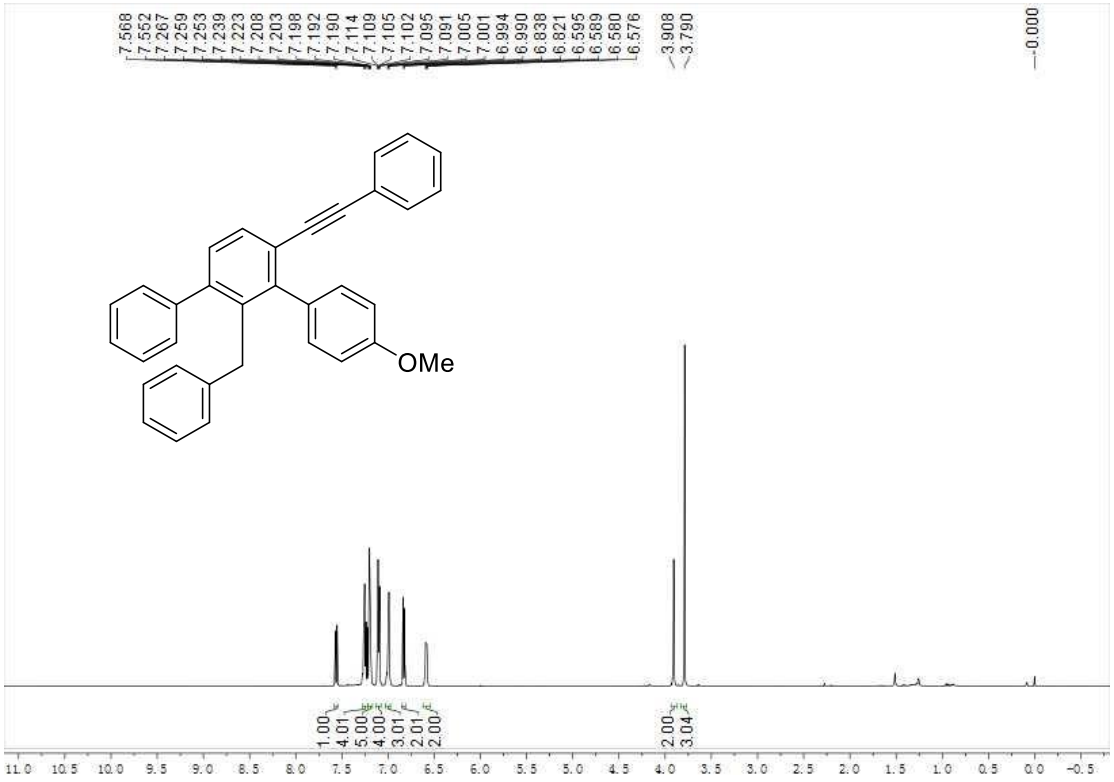


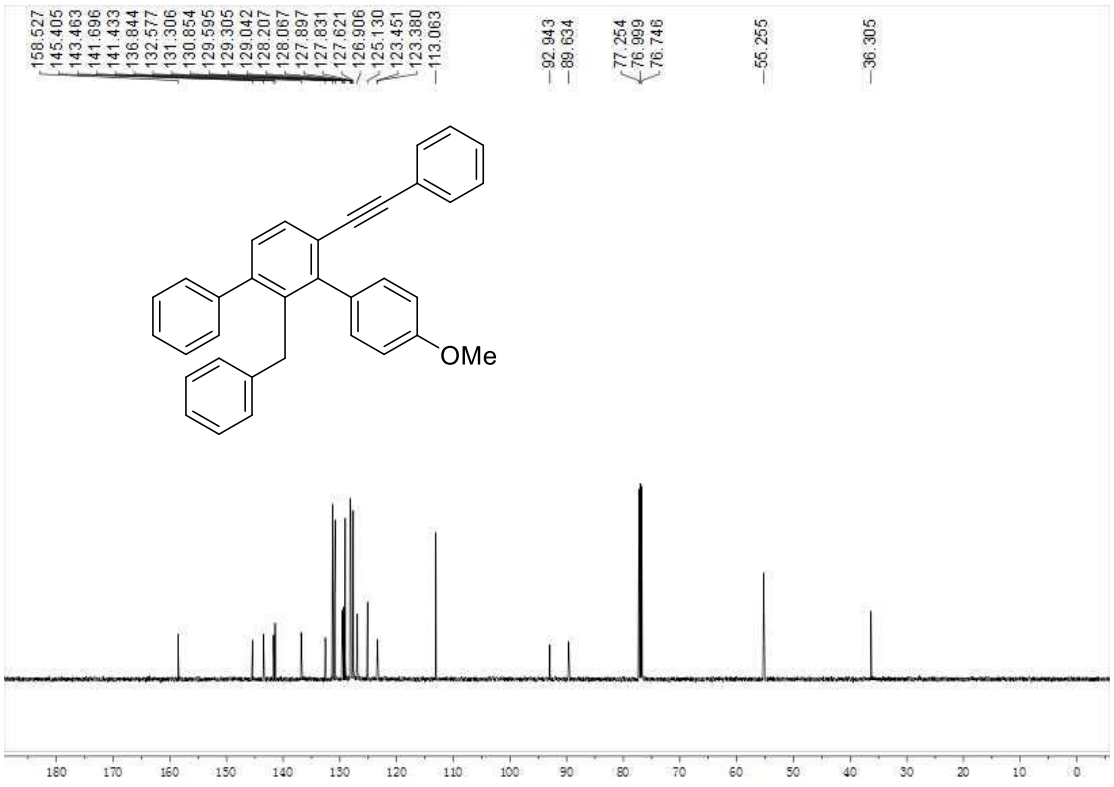
2'-benzyl-4-methyl-6'-(phenylethynyl)-1,1':3',1''-terphenyl (3ba):



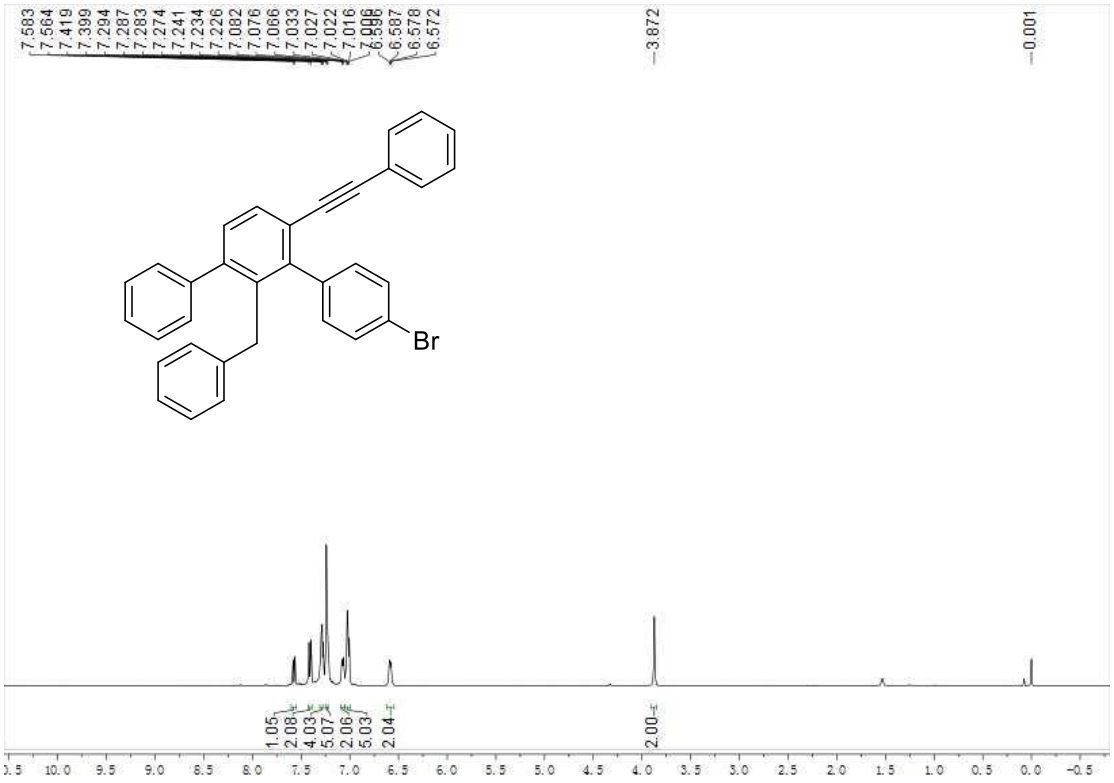


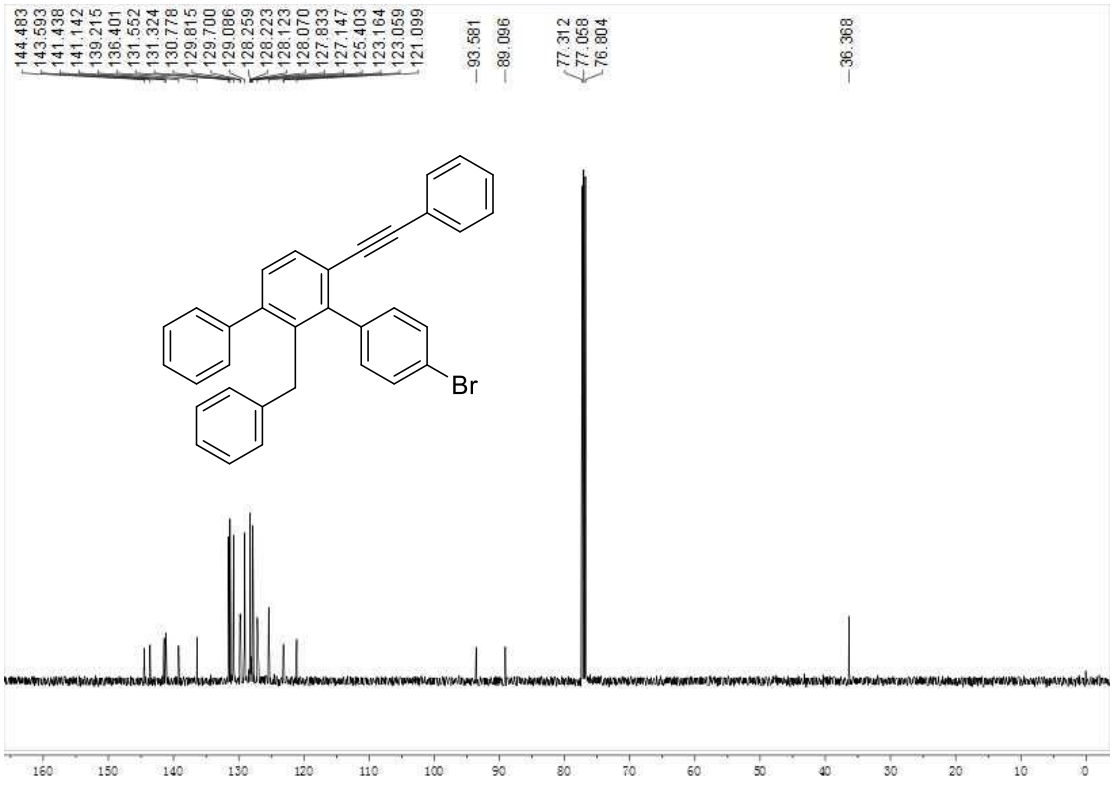
2'-benzyl-4-methoxy-6'-(phenylethynyl)-1,1':3',1''-terphenyl (3ca):



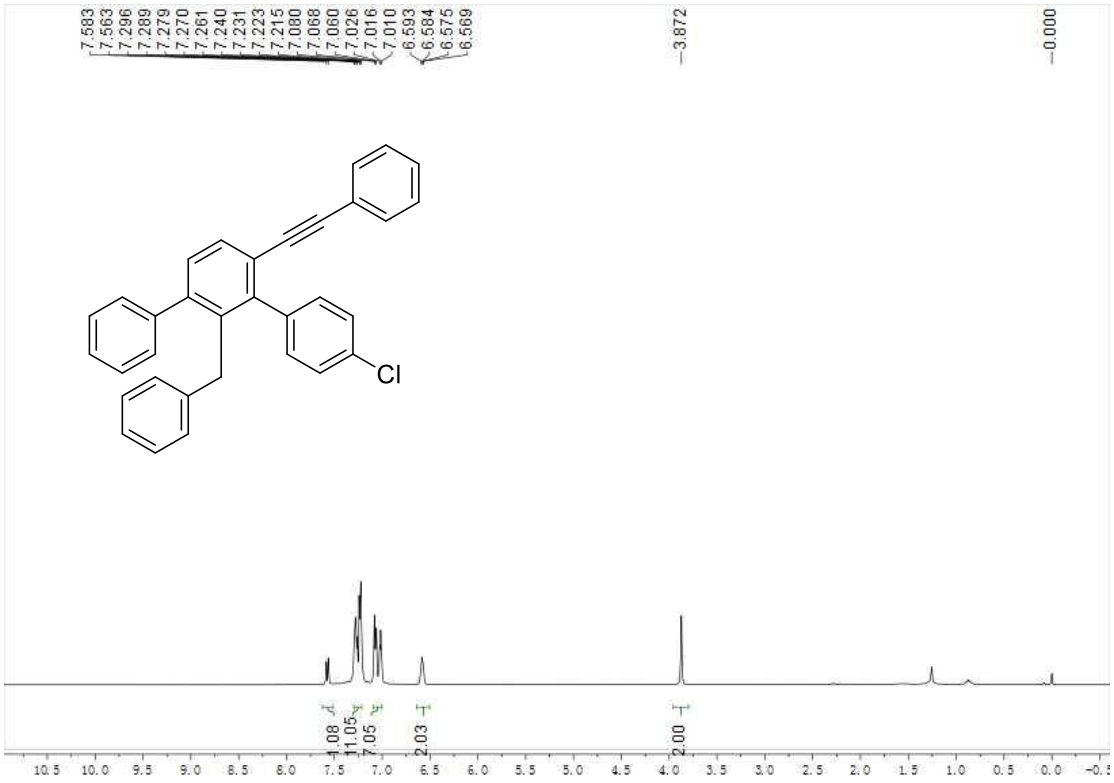


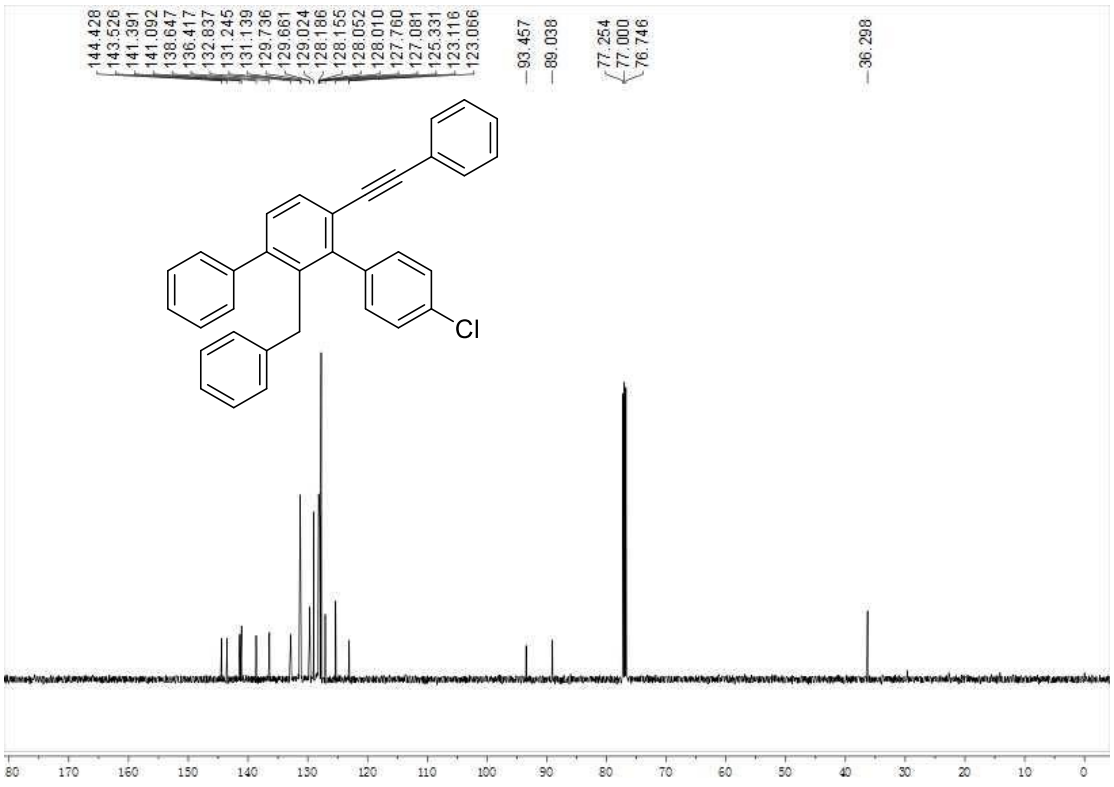
2'-benzyl-4-bromo-6'-(phenylethynyl)-1,1':3',1''-terphenyl (3da):



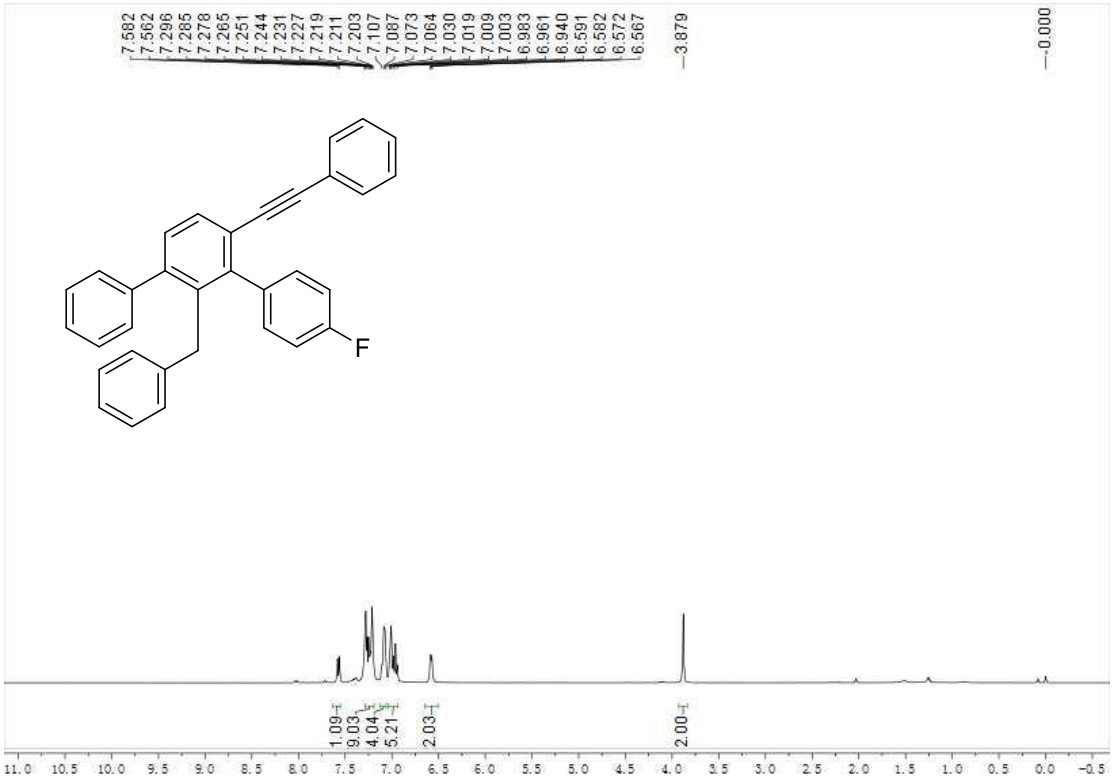


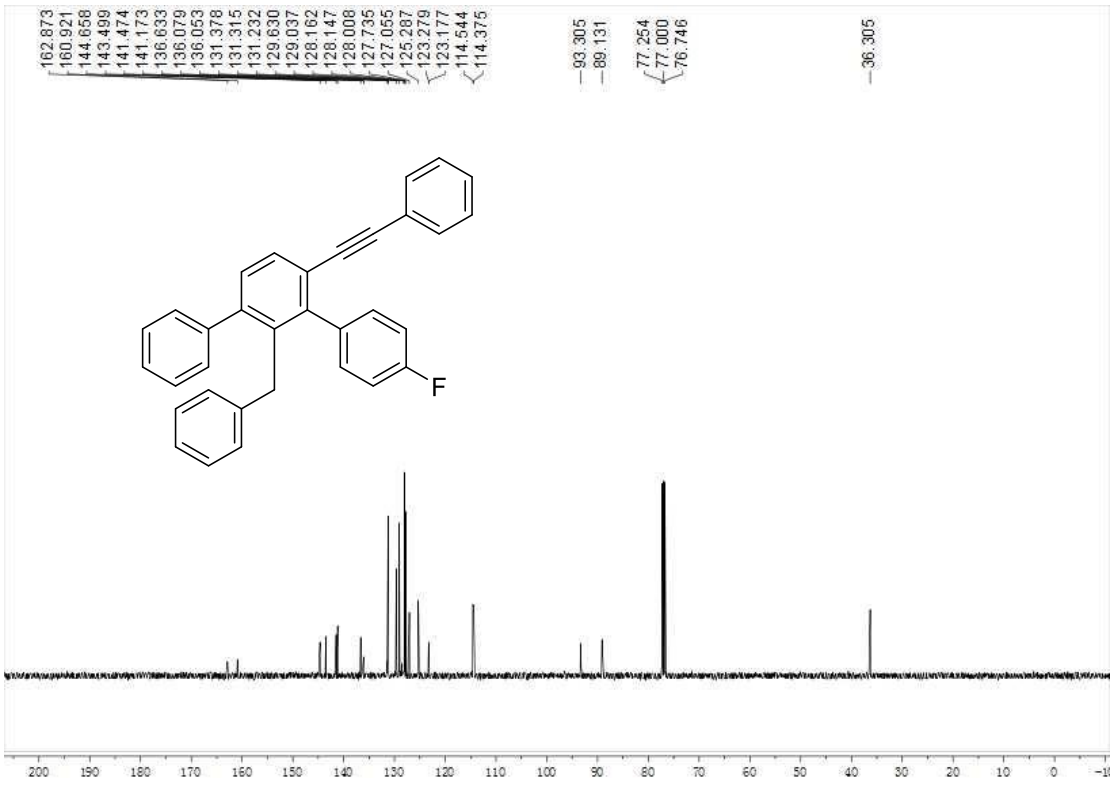
2'-benzyl-4-chloro-6'-(phenylethynyl)-1,1':3',1''-terphenyl (3ea):



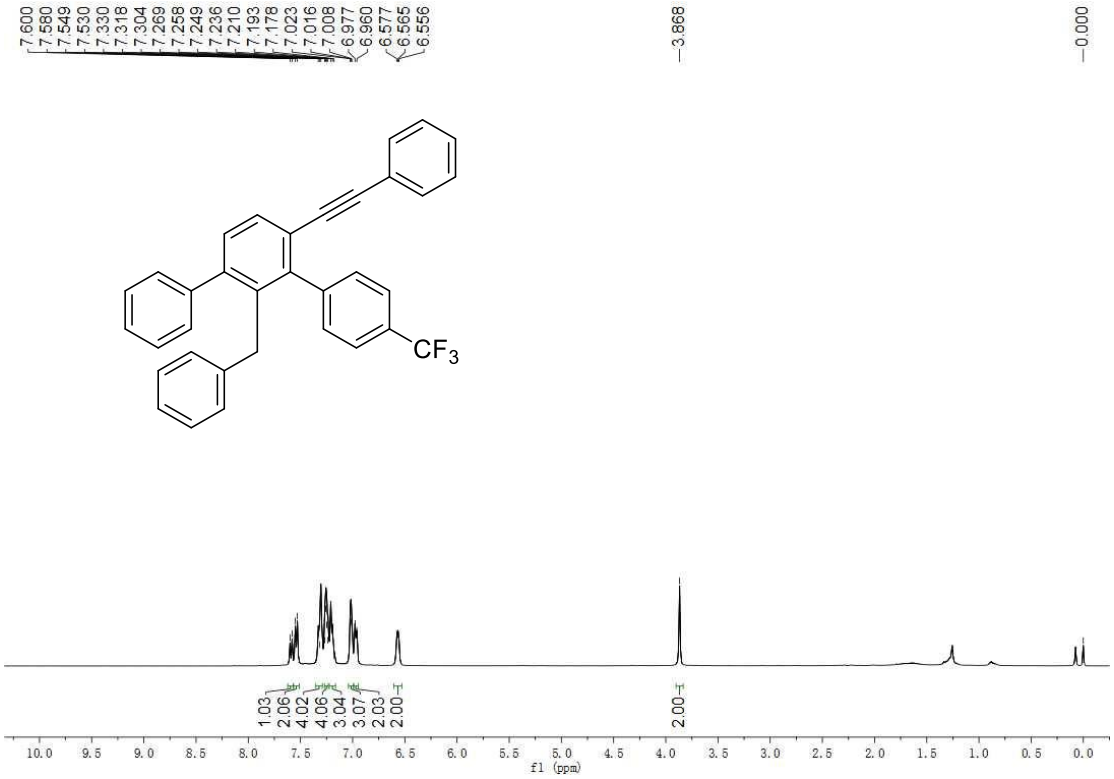


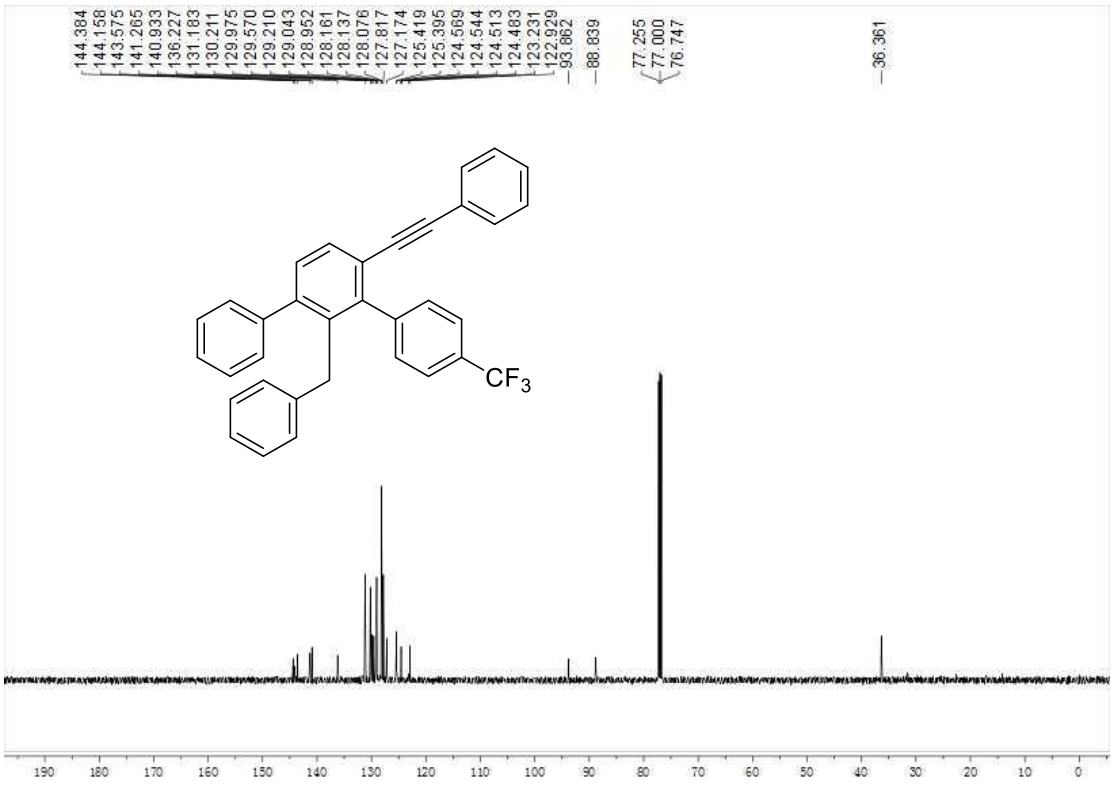
2'-benzyl-4-fluoro-6'-(phenylethynyl)-1,1':3',1''-terphenyl (3fa):



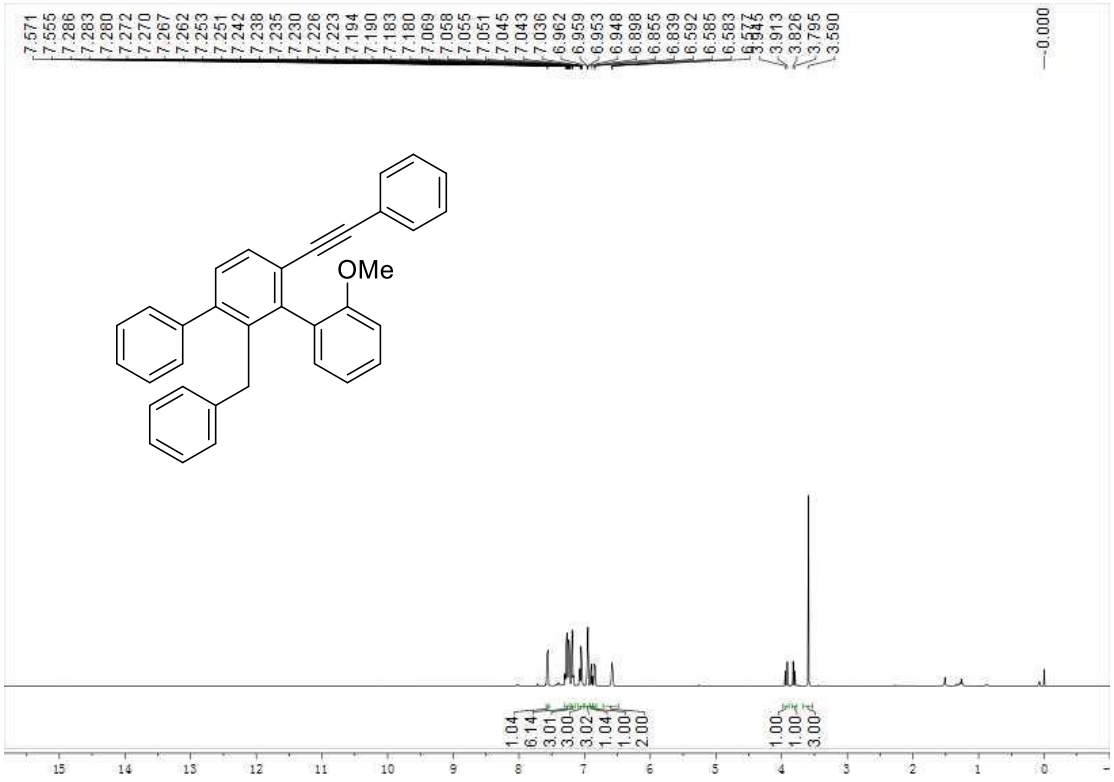


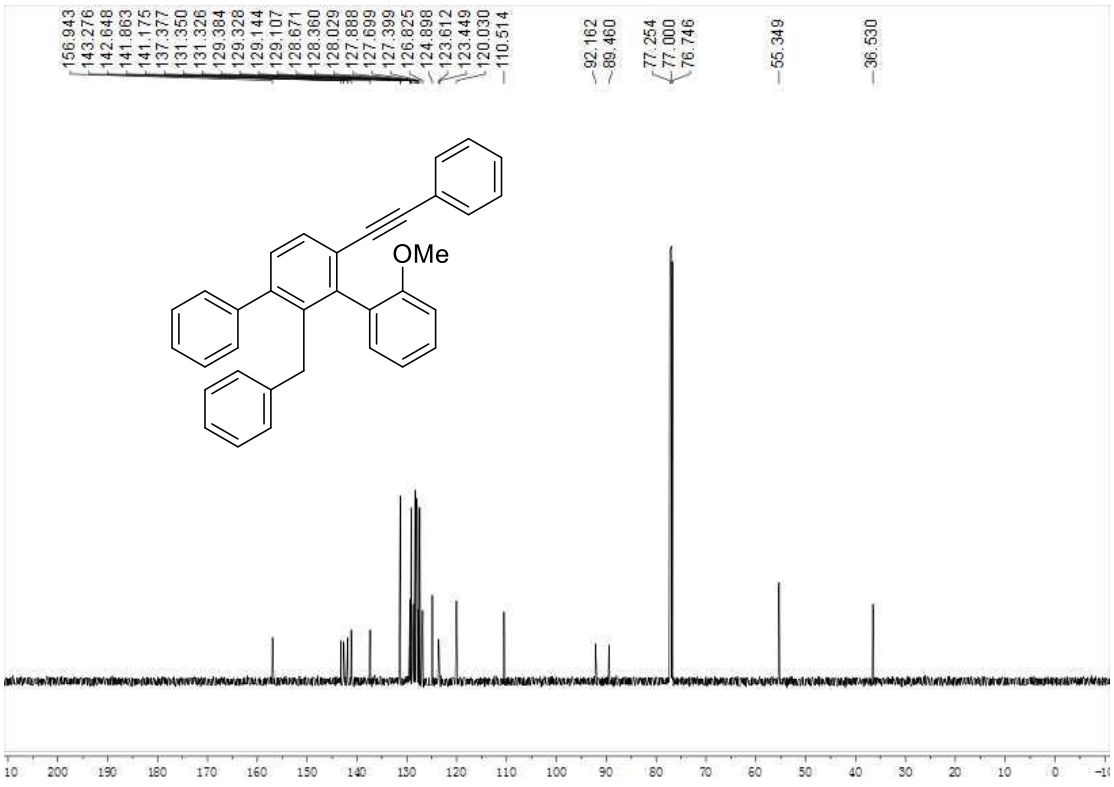
2'-benzyl-6'-(phenylethynyl)-4-(trifluoromethyl)-1,1':3',1''-terphenyl (3ga):



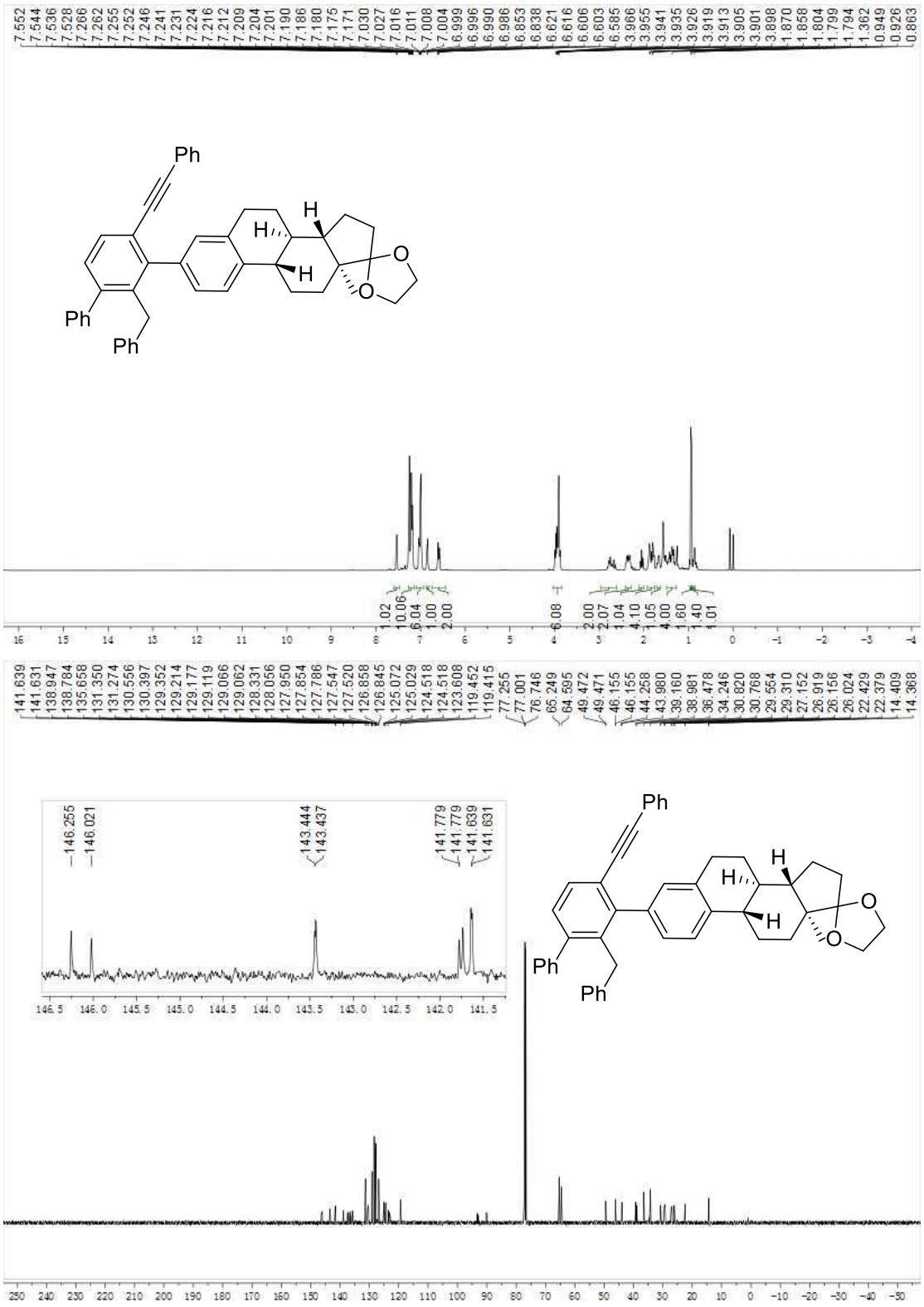


2'-benzyl-2-methoxy-6'-(phenylethynyl)-1,1':3',1''-terphenyl (3ha):

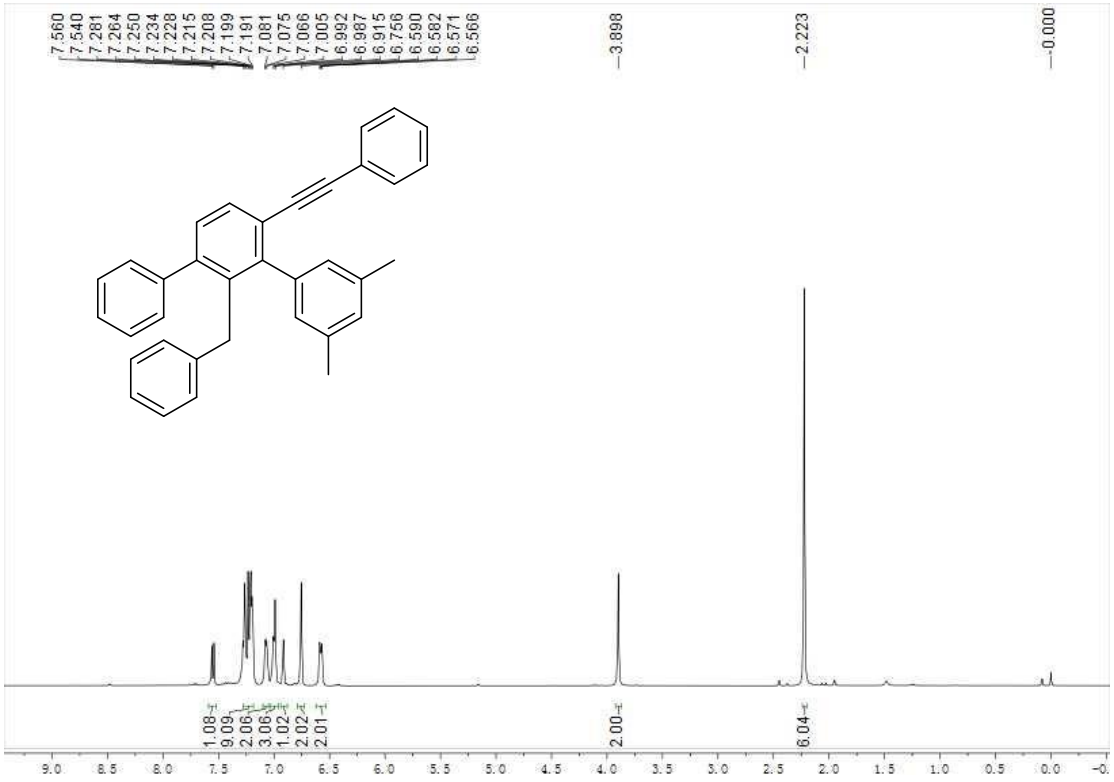


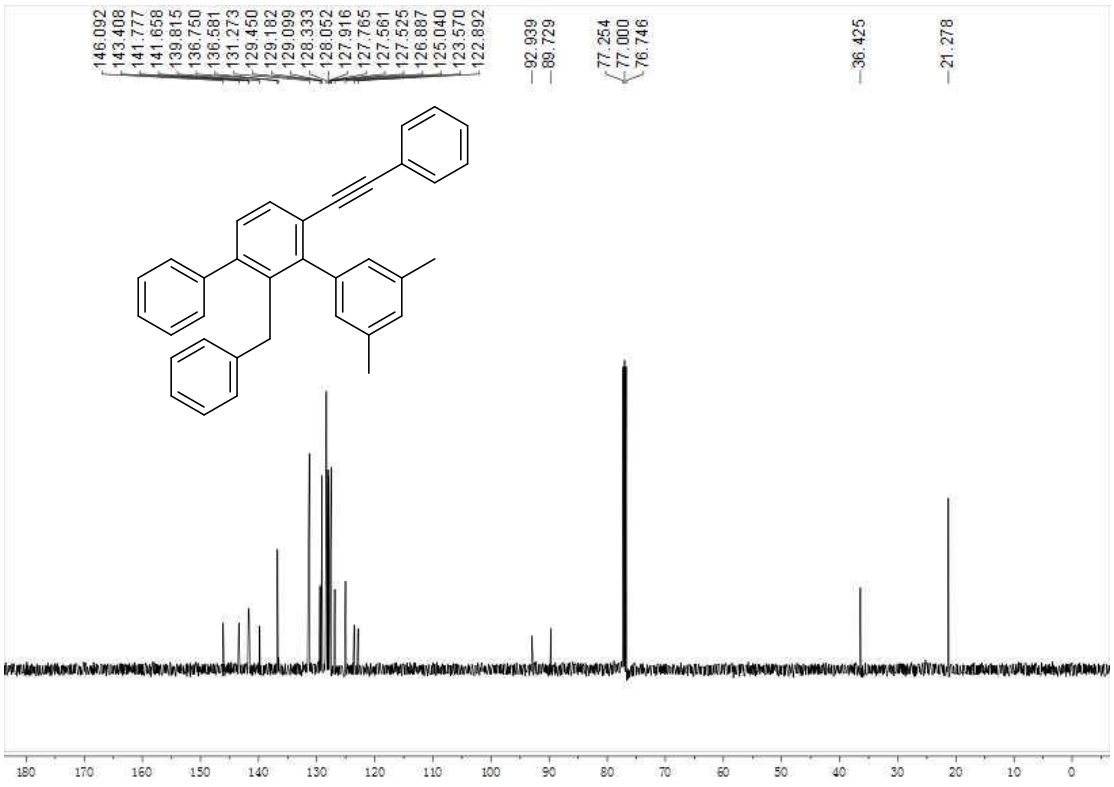


(8R,9S,13S,14S)-3-(2-benzyl-4-(phenylethynyl)-[1,1'-biphenyl]-3-yl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[a]phenanthrene-17,2'-[1,3]dioxolane] (3ia):

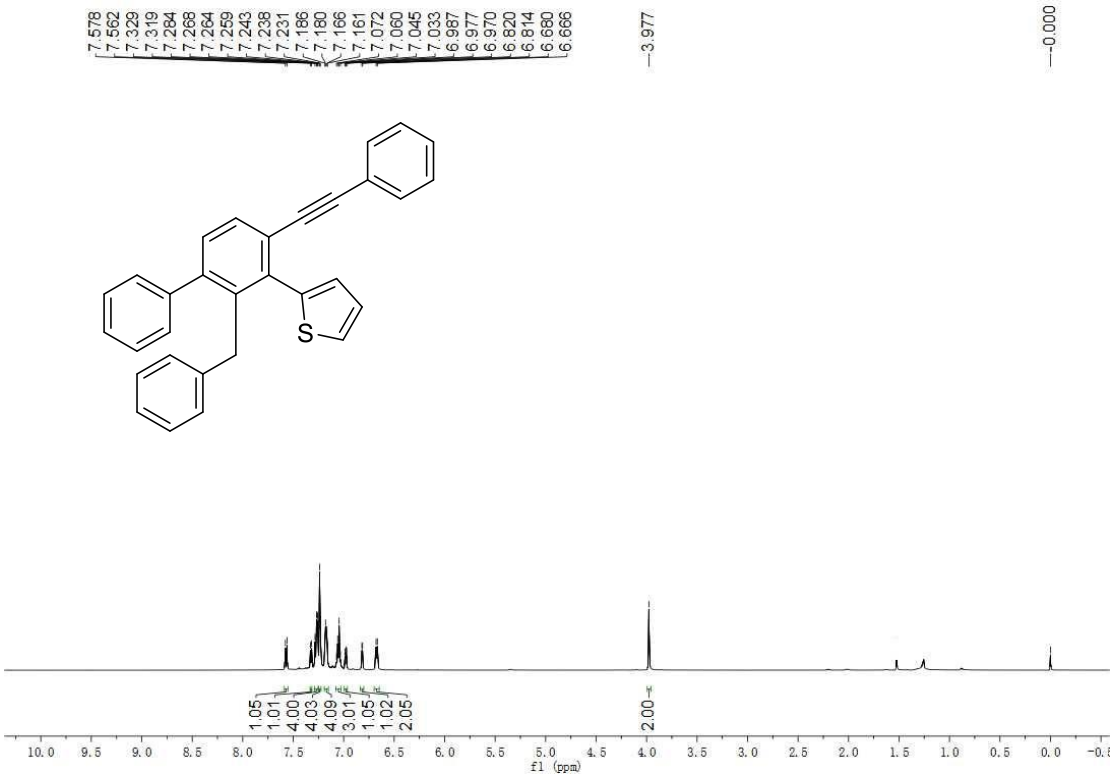


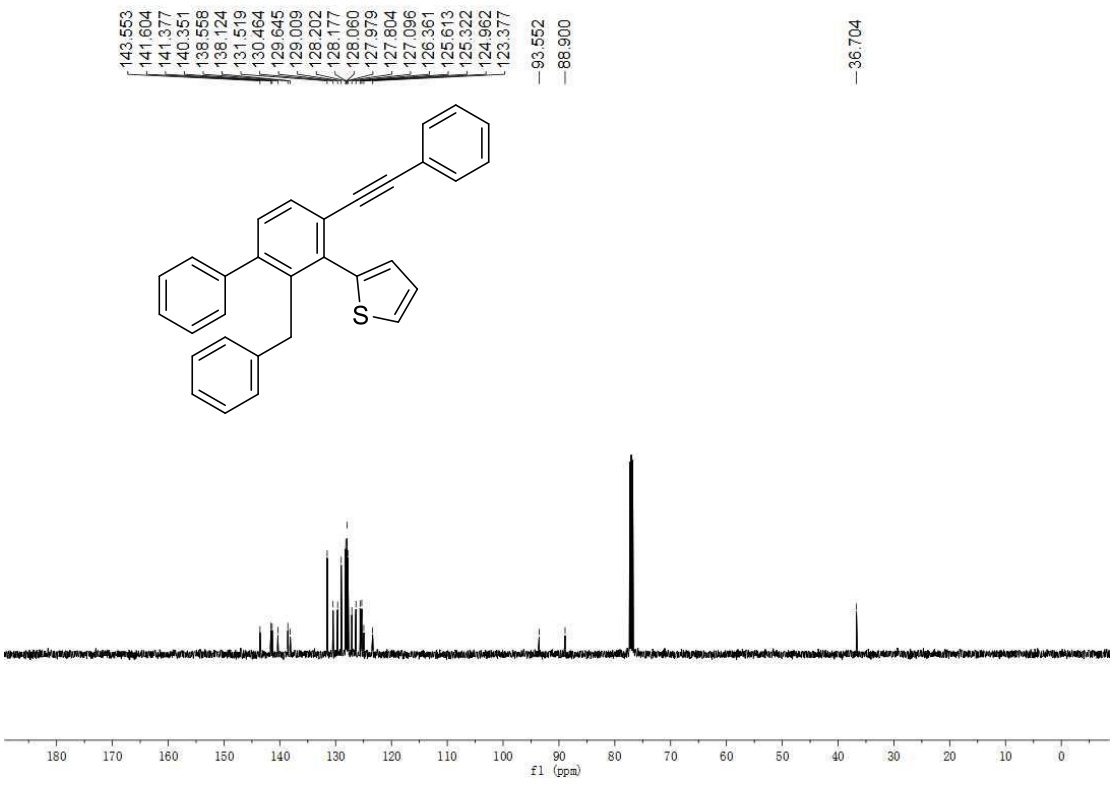
2'-benzyl-3,5-dimethyl-6'-(phenylethynyl)-1,1':3',1''-terphenyl (3ja):



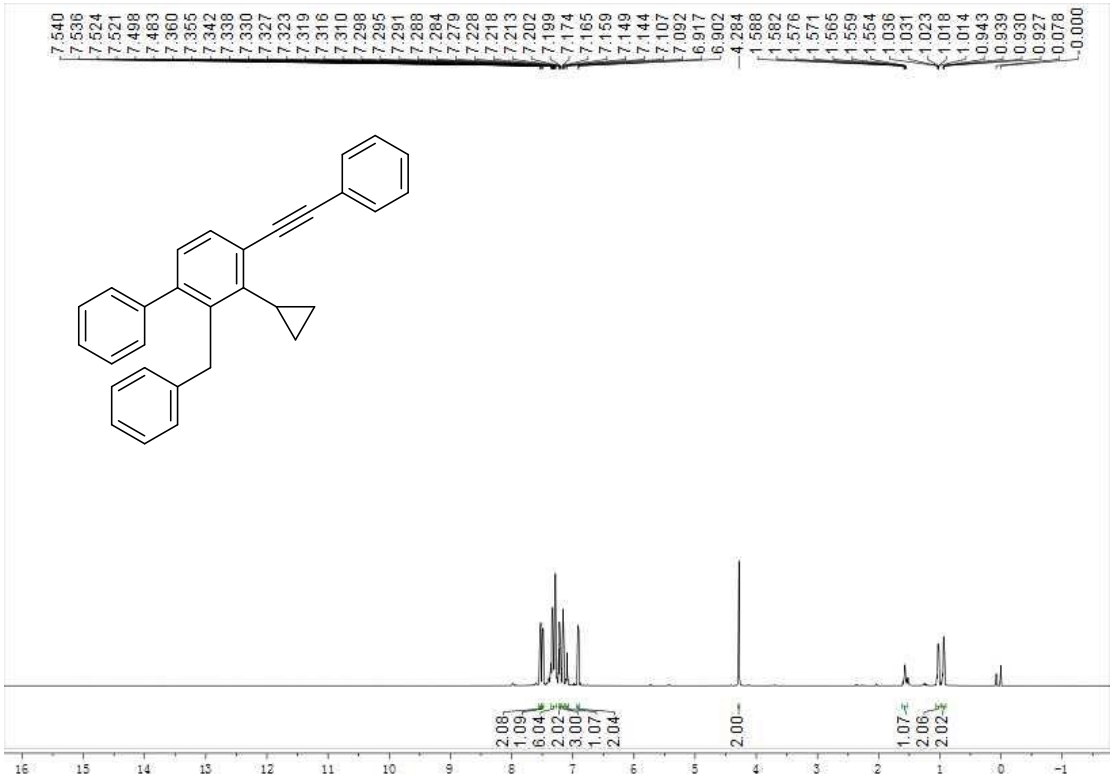


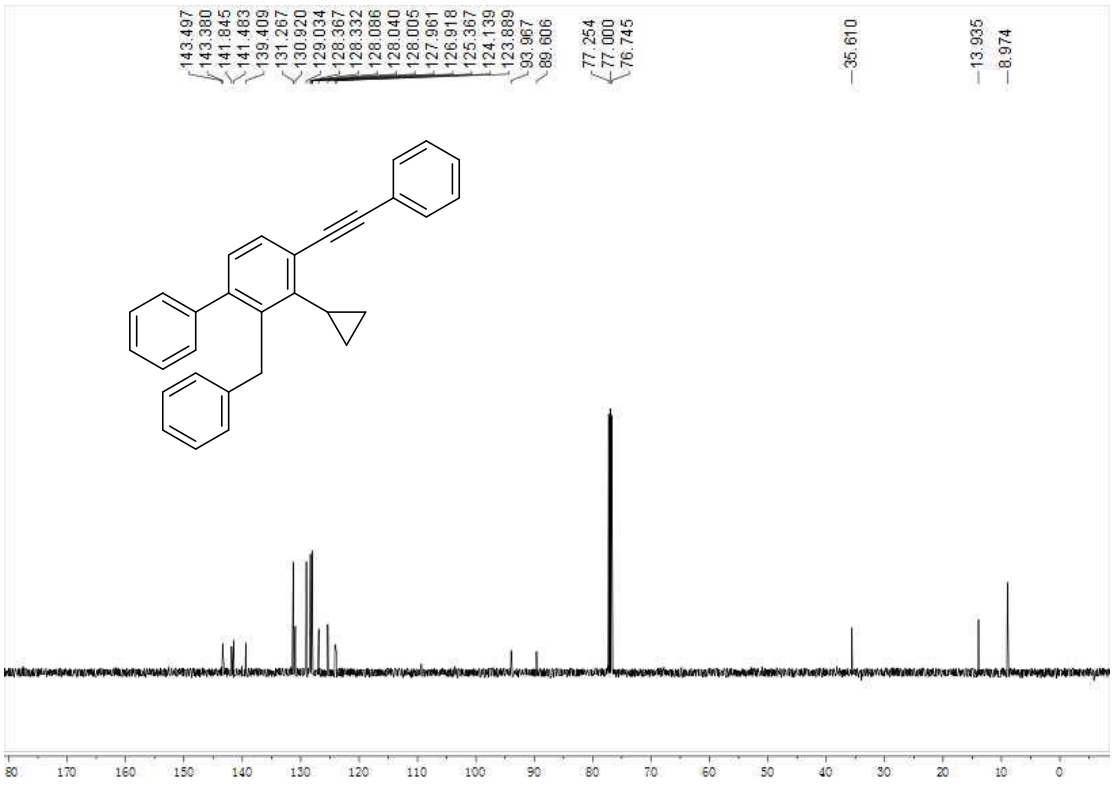
2-(2-benzyl-4-(phenylethynyl)-[1,1'-biphenyl]-3-yl)thiophene (3ka):



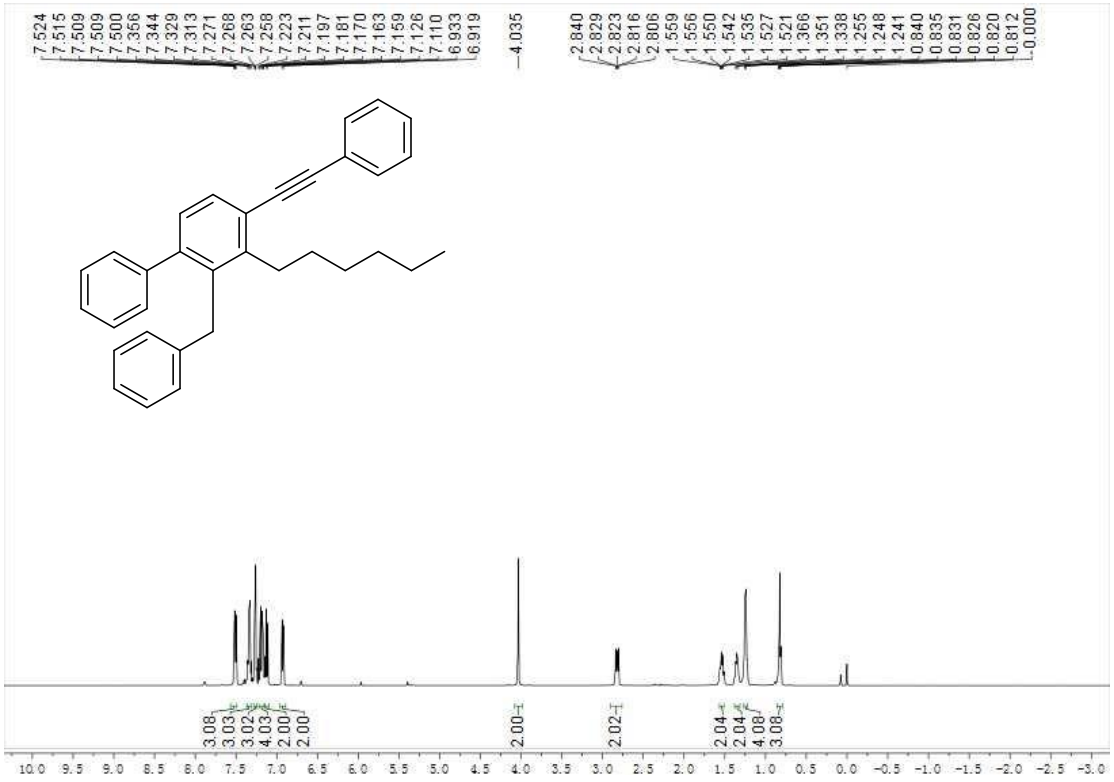


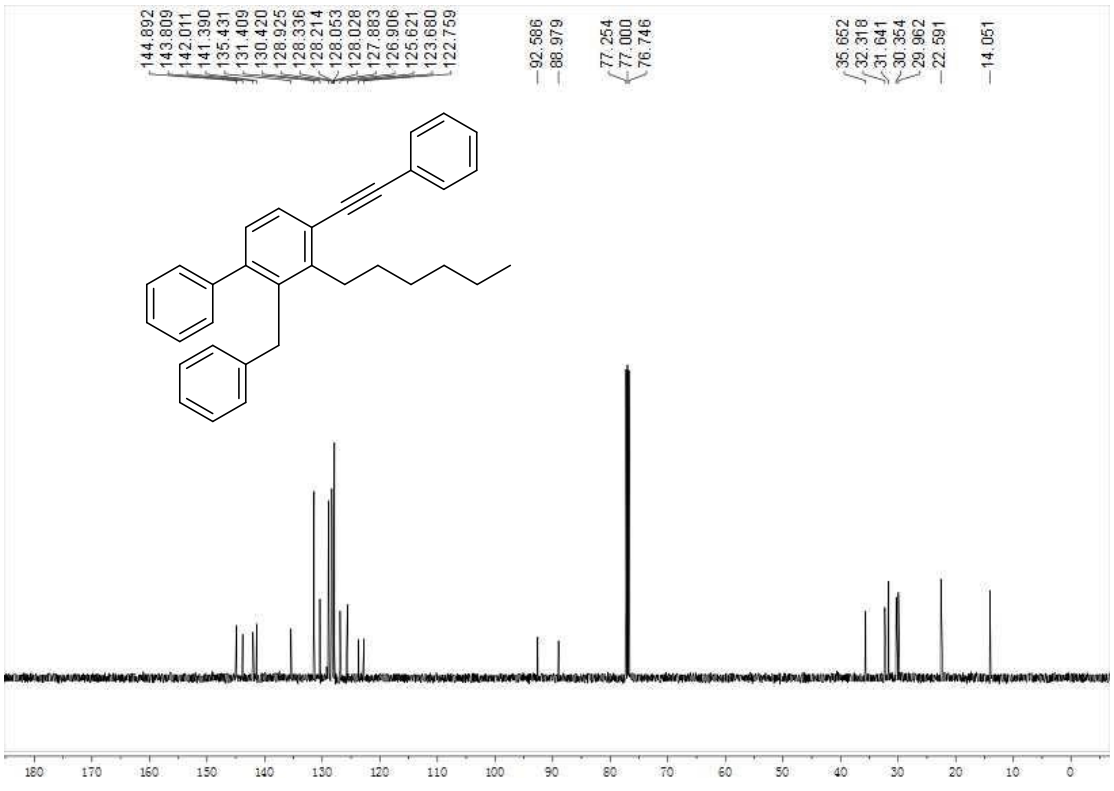
2-benzyl-3-cyclopropyl-4-(phenylethynyl)-1,1'-biphenyl (3la):



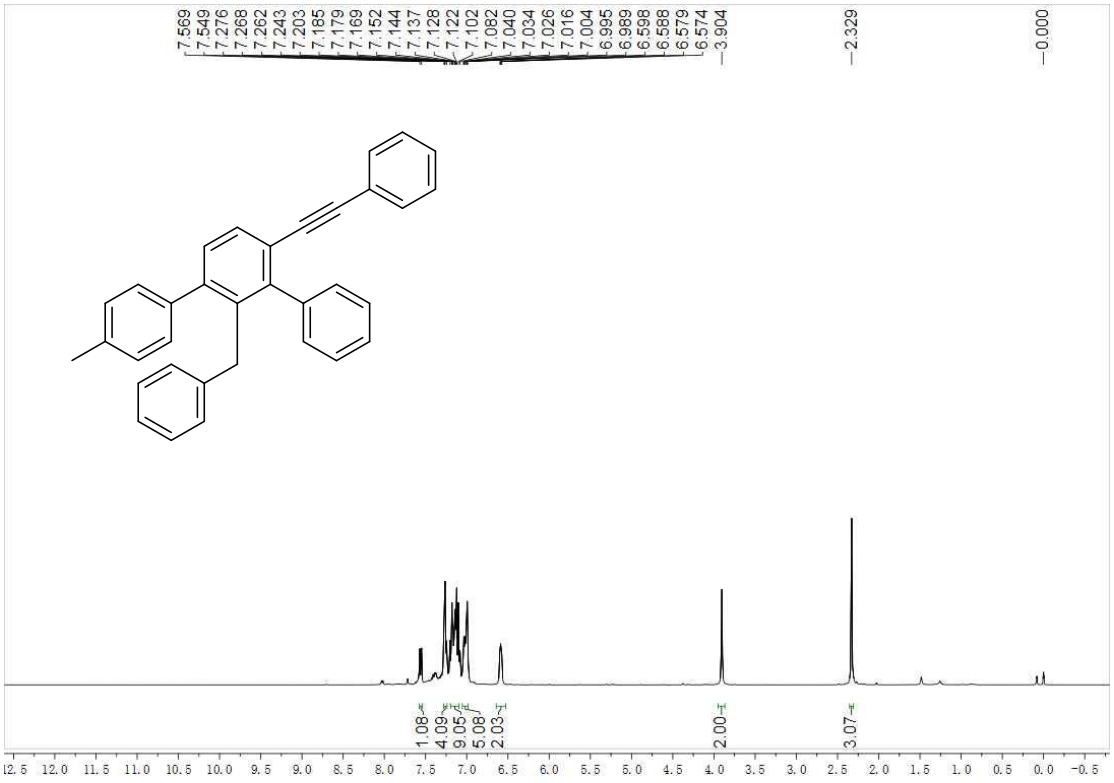


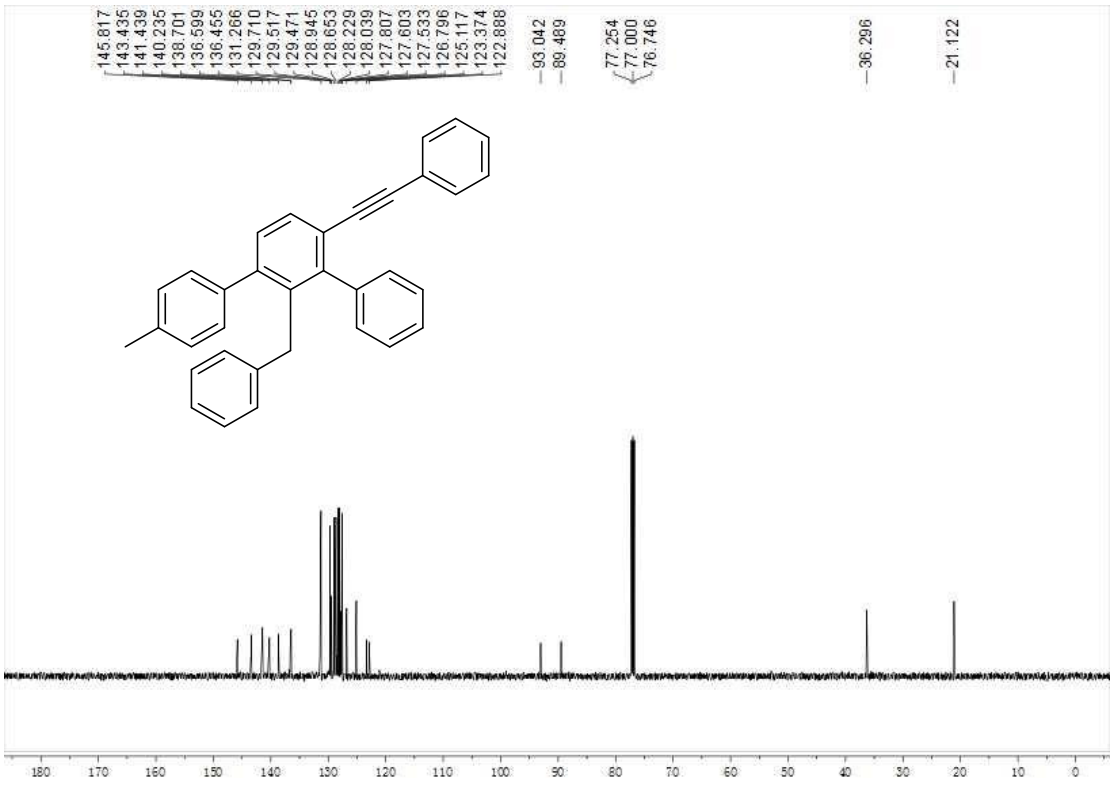
2-benzyl-3-hexyl-4-(phenylethynyl)-1,1'-biphenyl (3ma):



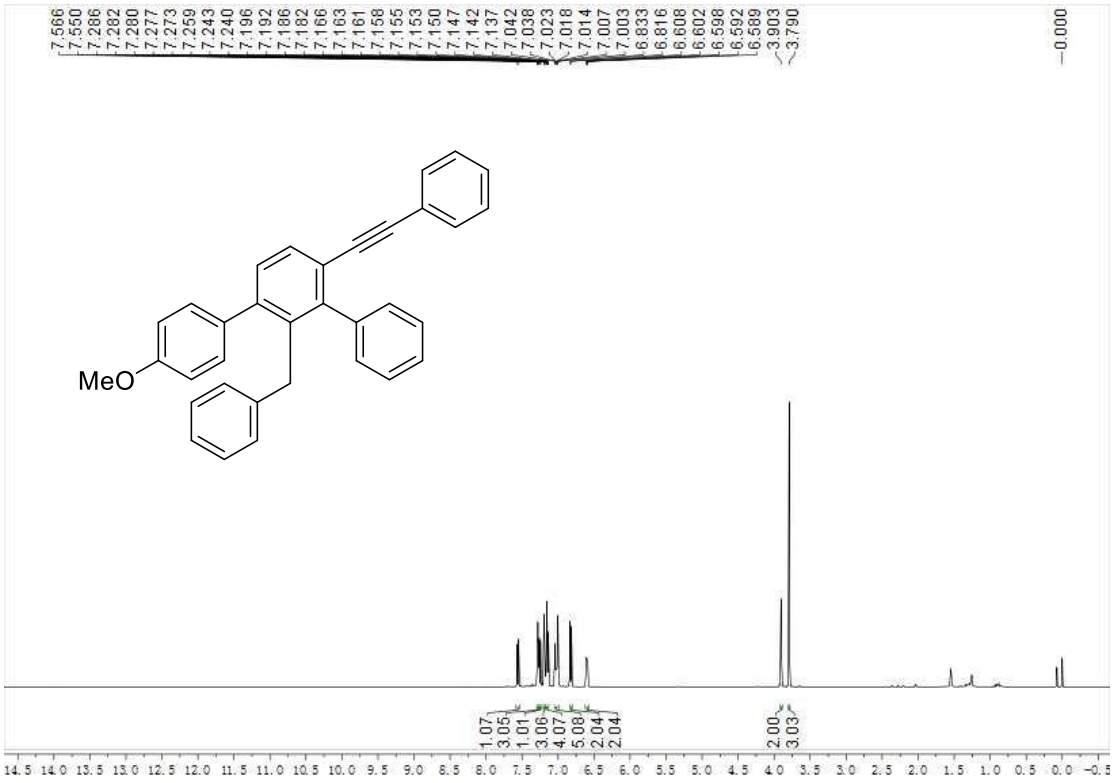


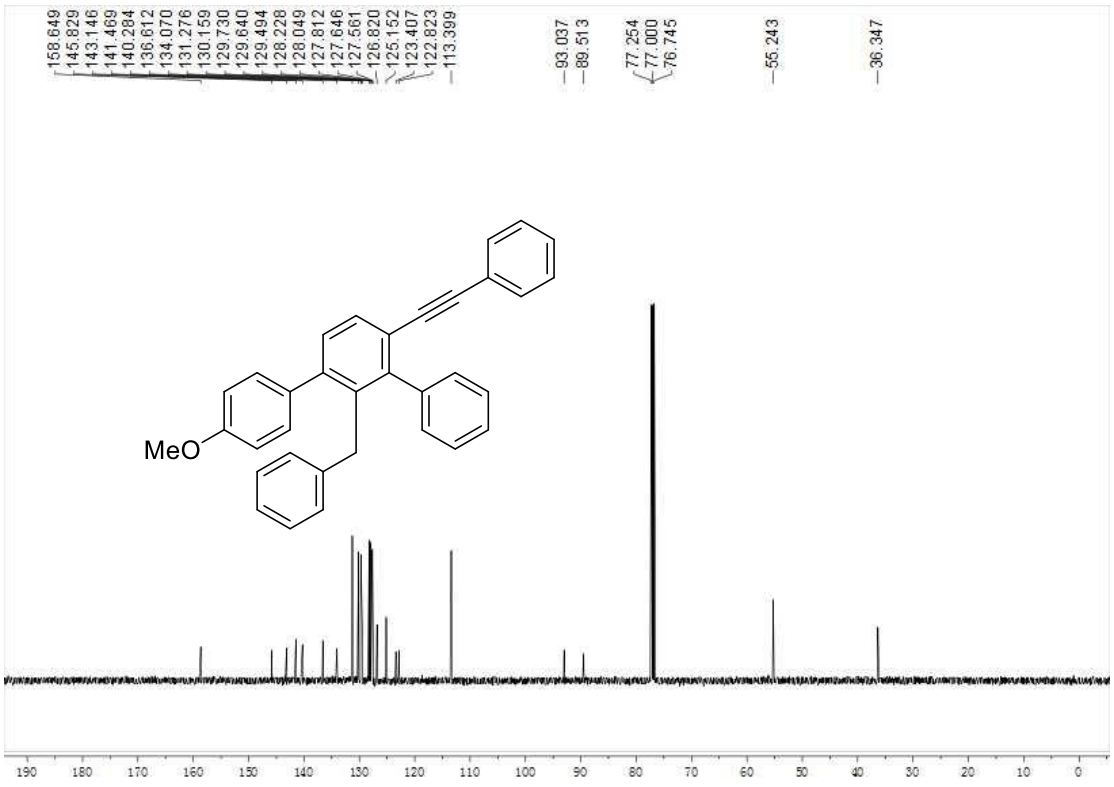
2'-benzyl-4-methyl-4'-(phenylethynyl)-1,1':3',1''-terphenyl (3oa):



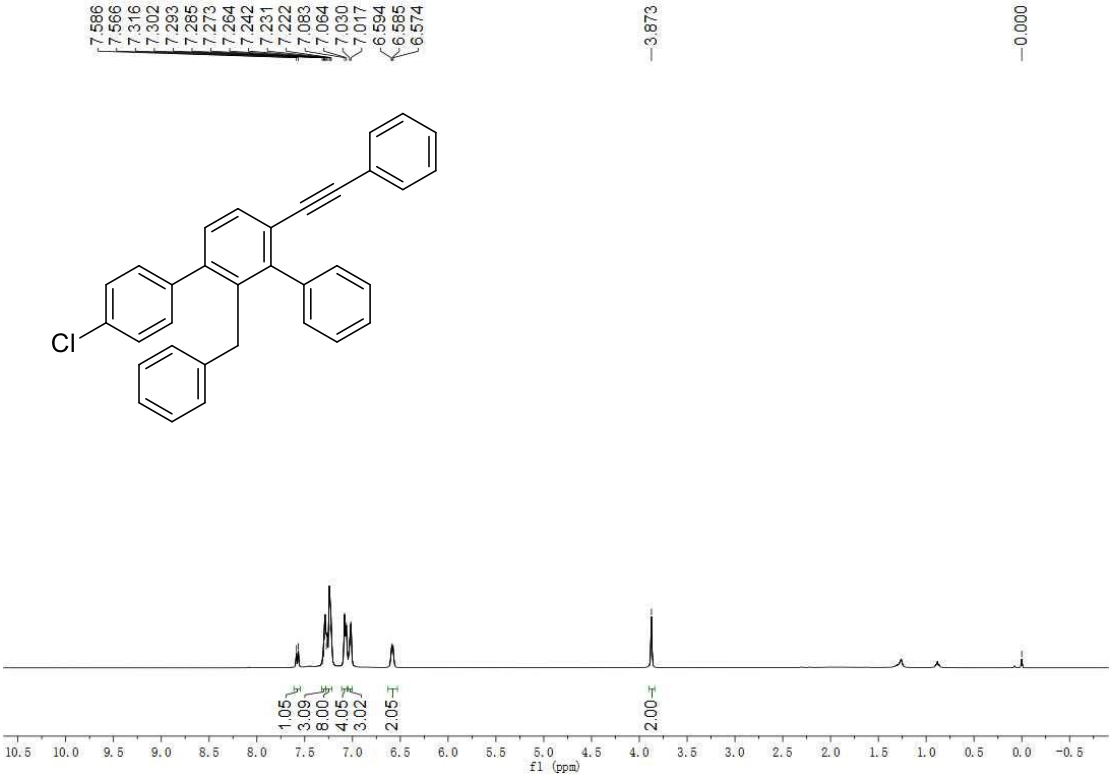


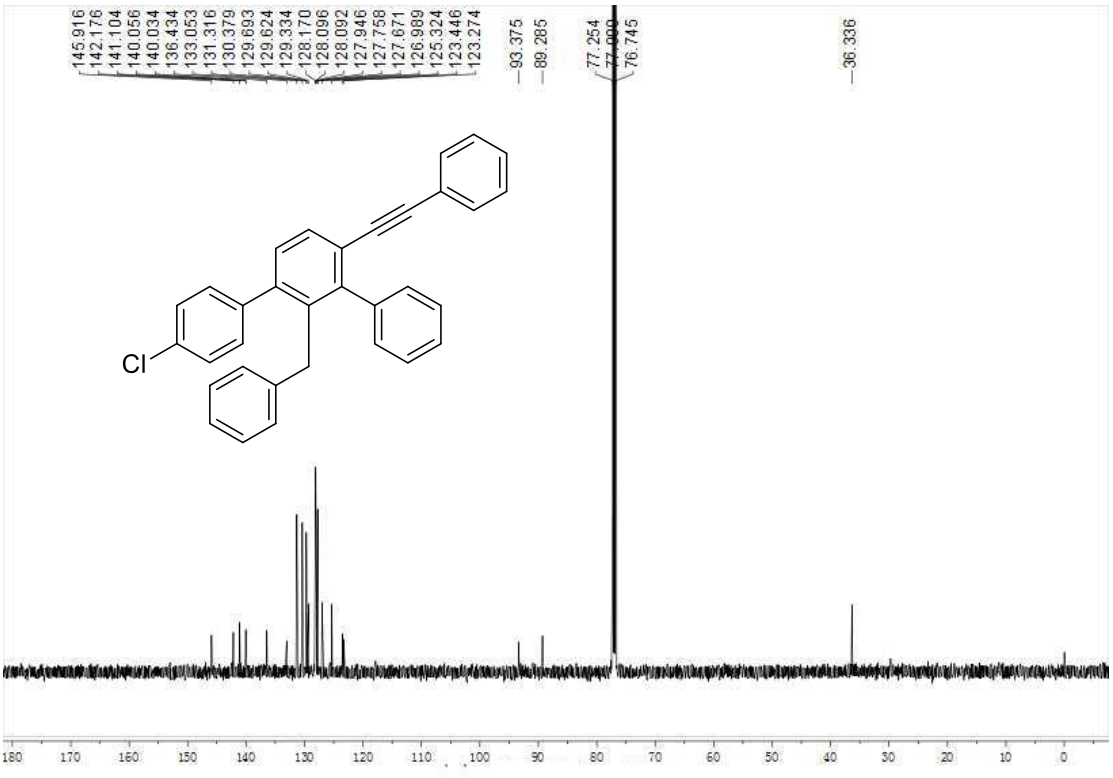
2'-benzyl-4-methoxy-4'-(phenylethynyl)-1,1':3',1''-terphenyl (3pa):



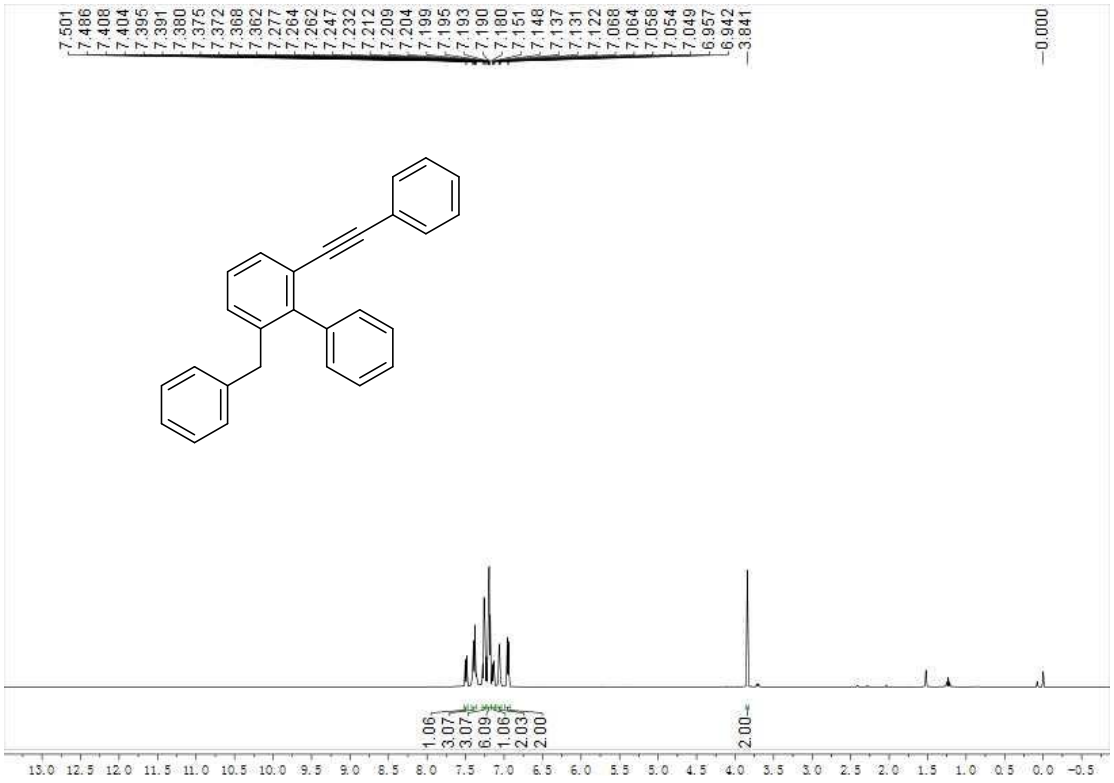


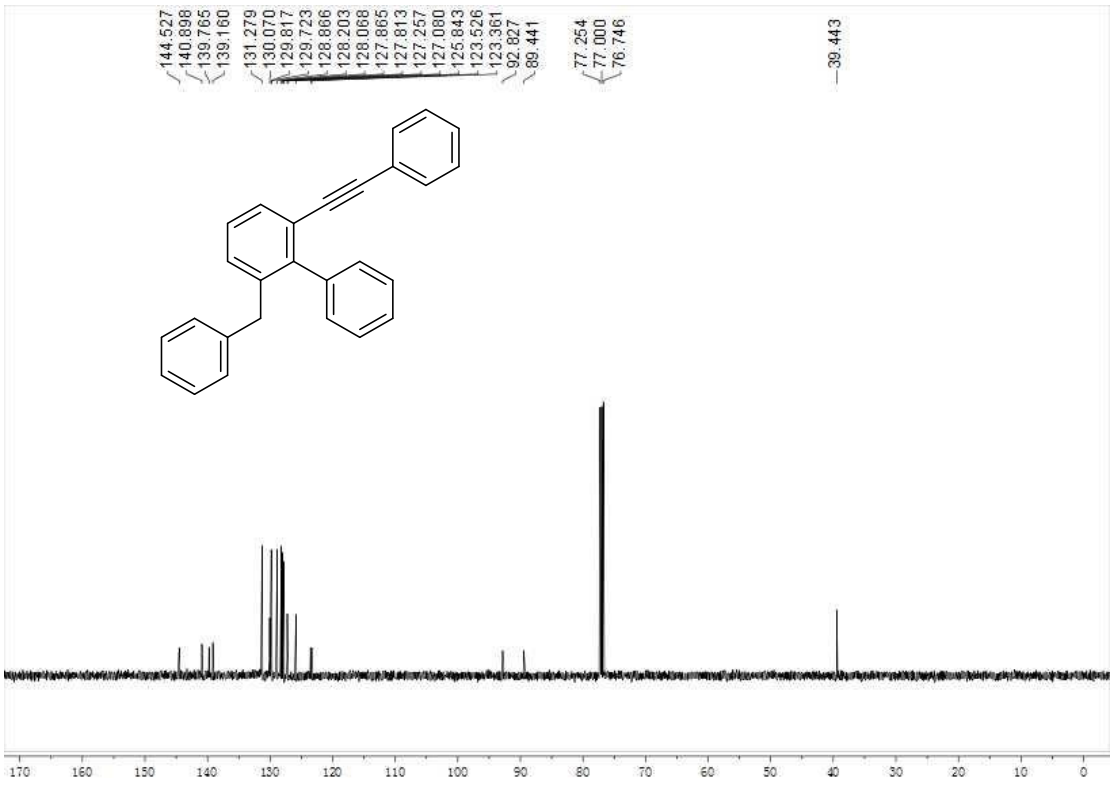
2'-benzyl-4-chloro-4'-(phenylethynyl)-1,1':3',1''-terphenyl (3qa):



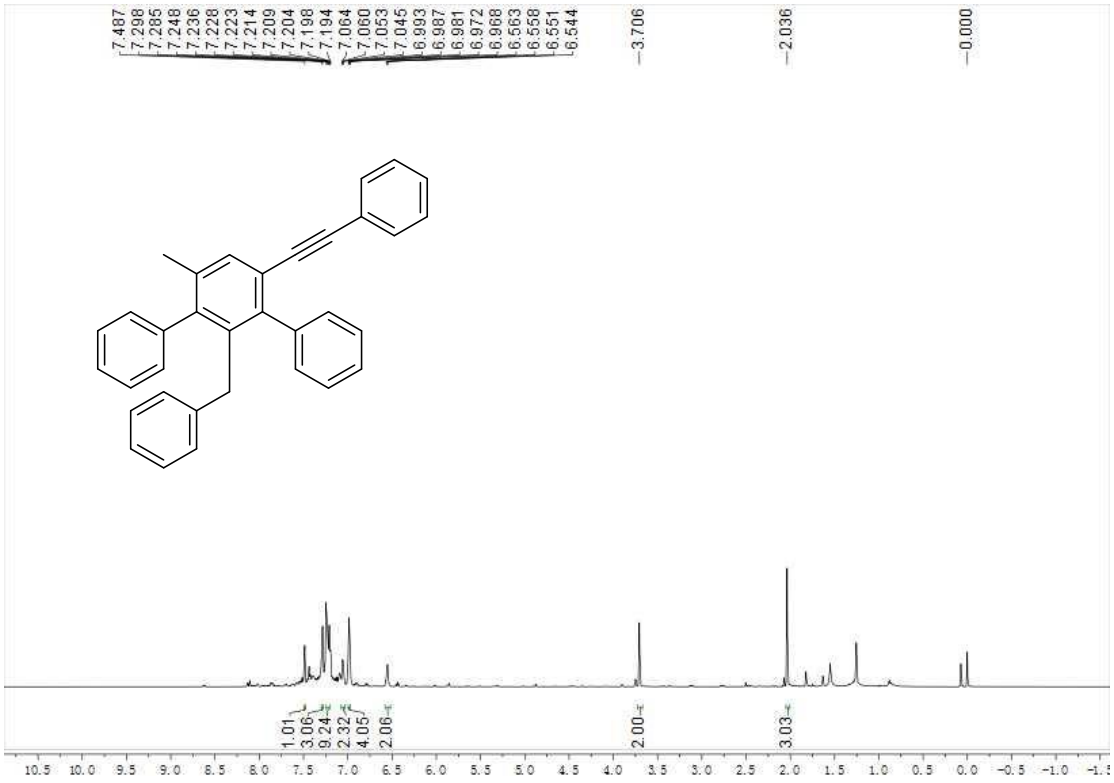


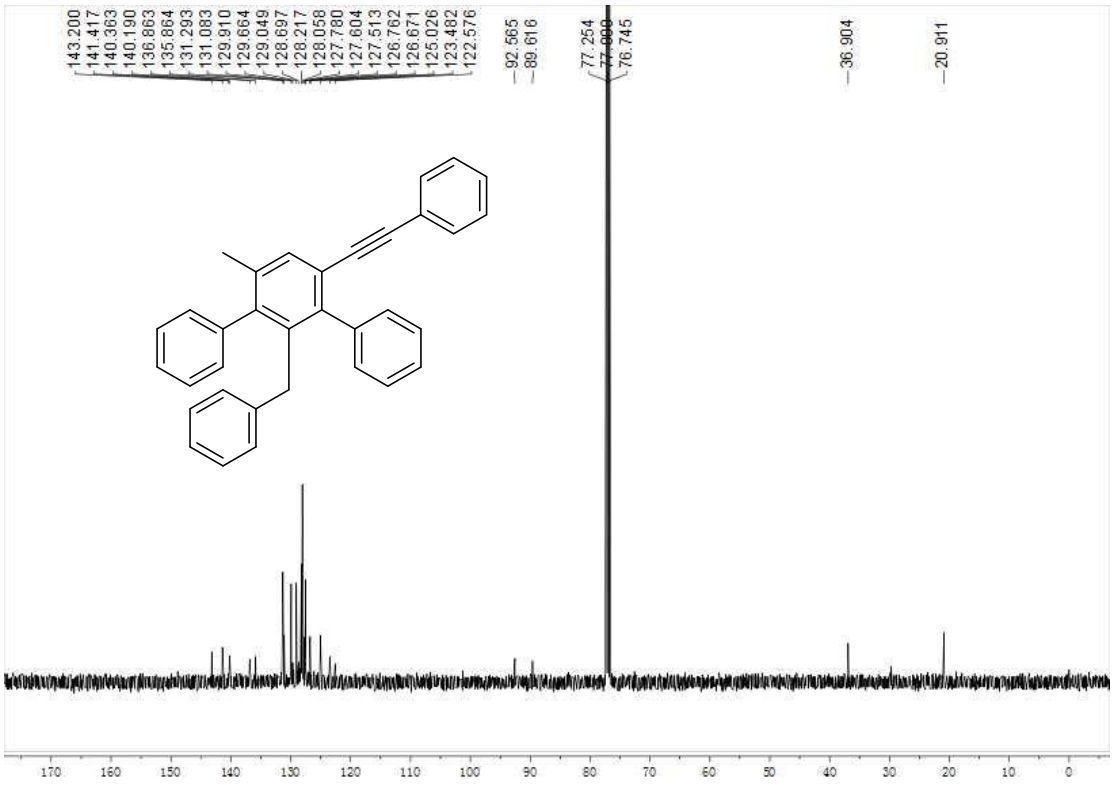
2-benzyl-6-(phenylethynyl)-1,1'-biphenyl (3ra):



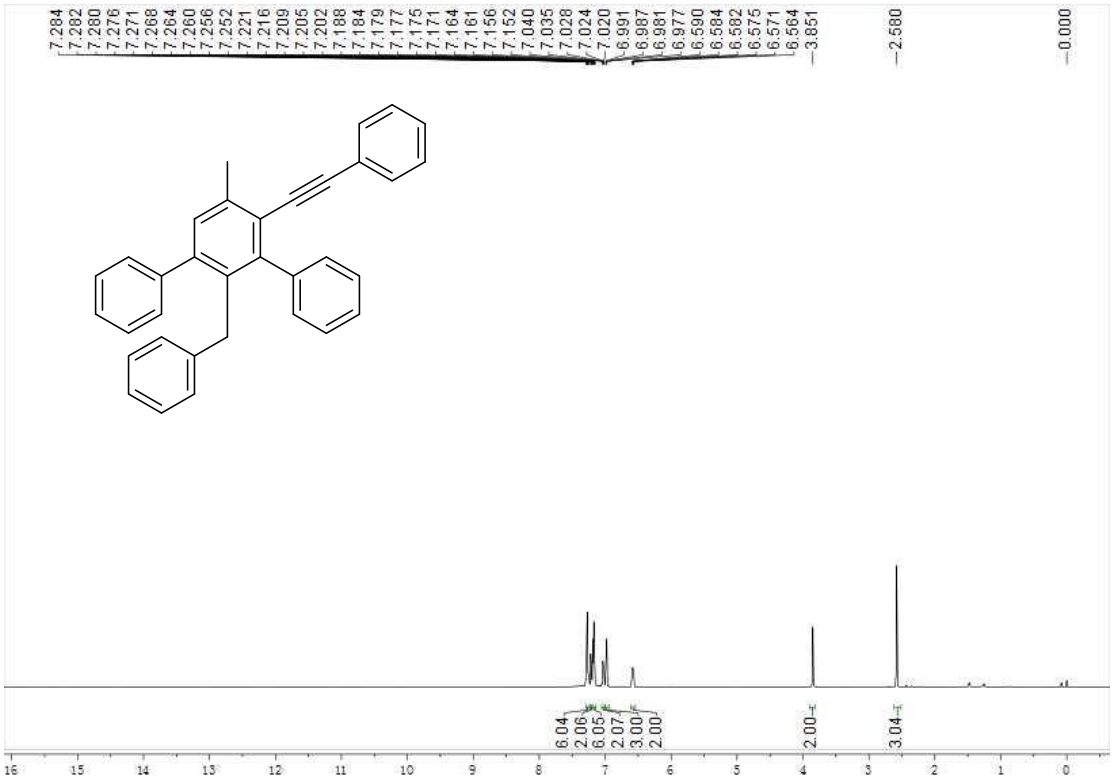


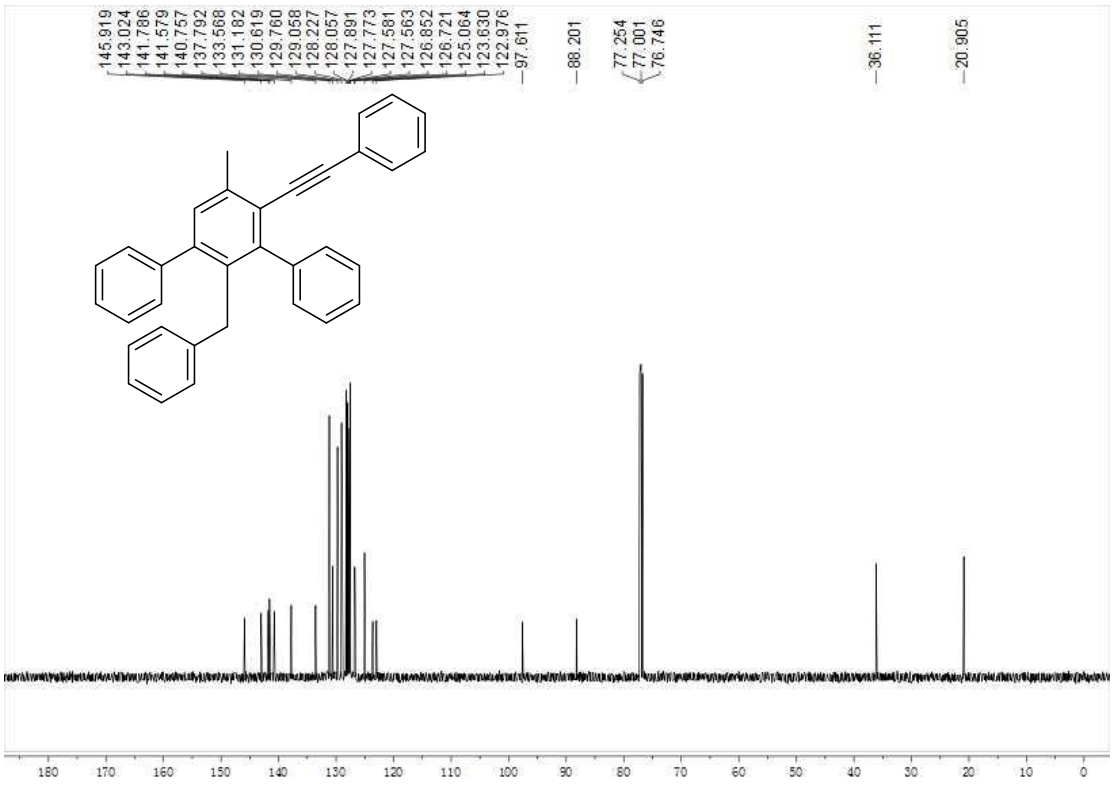
2'-benzyl-4'-methyl-6'-(phenylethynyl)-1,1':3',1''-terphenyl (3sa):





2'-benzyl-5'-methyl-4'-(phenylethynyl)-1,1':3',1''-terphenyl (3ta):





(D) The X-ray single-crystal diffraction analysis of 3aa

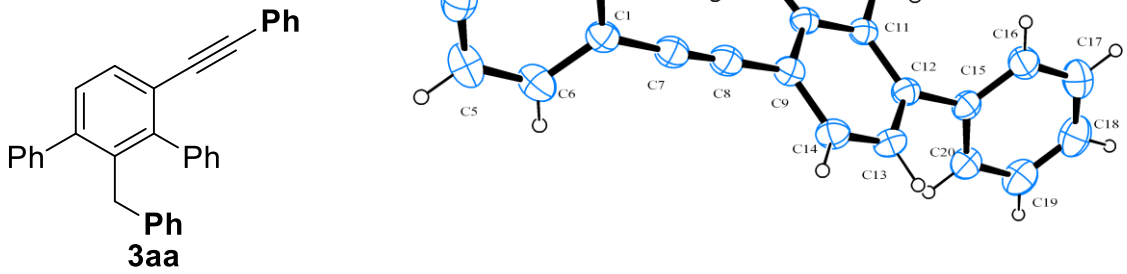


Table S2. Crystal data and structure refinement for A.

Identification code	A	
Empirical formula	C33 H24	
Formula weight	420.52	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 6.9996(8) Å	α= 91.7620(10)°.
	b = 10.3778(12) Å	β= 99.0220(10)°.
	c = 17.063(2) Å	γ = 105.2660(10)°.
Volume	1177.6(2) $Å^3$	
Z	2	
Density (calculated)	1.186 Mg/m^3	
Absorption coefficient	0.067 mm^{-1}	
F(000)	444	
Crystal size	0.160 x 0.140 x 0.110 mm^3	
Theta range for data collection	2.293 to 25.492°.	
Index ranges	-8<=h<=8, -11<=k<=12, -20<=l<=20	
Reflections collected	9179	
Independent reflections	4363 [R(int) = 0.0187]	
Completeness to theta = 25.242°	99.4 %	
Absorption correction	None	

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4363 / 0 / 298
Goodness-of-fit on F^2	0.994
Final R indices [I>2sigma(I)]	R1 = 0.0388, wR2 = 0.0902
R indices (all data)	R1 = 0.0550, wR2 = 0.1003
Extinction coefficient	n/a
Largest diff. peak and hole	0.124 and -0.164 e.$Å^{-3}$

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for A. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	46(2)	2632(1)	129(1)	52(1)
C(2)	-1566(2)	2766(2)	462(1)	64(1)
C(3)	-2943(2)	3354(2)	68(1)	74(1)
C(4)	-2729(3)	3814(2)	-668(1)	73(1)
C(5)	-1151(3)	3666(2)	-1009(1)	78(1)
C(6)	226(2)	3077(2)	-619(1)	70(1)
C(7)	1531(2)	2079(1)	563(1)	56(1)
C(8)	2791(2)	1679(1)	953(1)	55(1)
C(9)	4311(2)	1190(1)	1419(1)	50(1)
C(10)	5514(2)	1937(1)	2104(1)	45(1)
C(11)	6970(2)	1432(1)	2561(1)	46(1)
C(12)	7232(2)	193(1)	2317(1)	49(1)
C(13)	6061(2)	-498(1)	1618(1)	58(1)
C(14)	4617(2)	-24(1)	1179(1)	59(1)
C(15)	8725(2)	-425(1)	2768(1)	52(1)
C(16)	8601(2)	-813(2)	3531(1)	68(1)
C(17)	9938(3)	-1446(2)	3916(1)	82(1)
C(18)	11428(3)	-1691(2)	3547(1)	85(1)
C(19)	11579(2)	-1307(2)	2795(1)	78(1)
C(20)	10239(2)	-681(1)	2406(1)	62(1)
C(21)	8242(2)	2242(1)	3306(1)	52(1)
C(22)	7072(2)	2478(1)	3945(1)	50(1)
C(23)	5392(2)	1525(2)	4083(1)	62(1)
C(24)	4305(3)	1763(2)	4651(1)	73(1)
C(25)	4881(3)	2961(2)	5096(1)	79(1)
C(26)	6556(3)	3916(2)	4976(1)	78(1)
C(27)	7643(2)	3680(2)	4403(1)	65(1)
C(28)	5272(2)	3282(1)	2324(1)	46(1)
C(29)	3594(2)	3418(1)	2618(1)	56(1)
C(30)	3413(2)	4667(2)	2831(1)	65(1)
C(31)	4884(2)	5796(2)	2754(1)	66(1)
C(32)	6552(2)	5687(2)	2454(1)	64(1)
C(33)	6736(2)	4437(1)	2238(1)	55(1)

Table S4. Bond lengths [Å] and angles [°] for A.

C(1)-C(2)	1.3765(19)
C(1)-C(6)	1.384(2)
C(1)-C(7)	1.434(2)
C(2)-C(3)	1.373(2)
C(2)-H(2)	0.9300
C(3)-C(4)	1.373(2)
C(3)-H(3)	0.9300
C(4)-C(5)	1.367(2)
C(4)-H(4)	0.9300
C(5)-C(6)	1.371(2)
C(5)-H(5)	0.9300
C(6)-H(6)	0.9300
C(7)-C(8)	1.1914(19)
C(8)-C(9)	1.4374(19)
C(9)-C(14)	1.3921(18)
C(9)-C(10)	1.4028(17)
C(10)-C(11)	1.4069(18)
C(10)-C(28)	1.4938(17)
C(11)-C(12)	1.4060(17)
C(11)-C(21)	1.5167(17)
C(12)-C(13)	1.3924(18)
C(12)-C(15)	1.4920(18)
C(13)-C(14)	1.3687(19)
C(13)-H(13)	0.9300
C(14)-H(14)	0.9300
C(15)-C(20)	1.3854(19)
C(15)-C(16)	1.383(2)
C(16)-C(17)	1.377(2)
C(16)-H(16)	0.9300
C(17)-C(18)	1.373(3)
C(17)-H(17)	0.9300
C(18)-C(19)	1.367(3)
C(18)-H(18)	0.9300
C(19)-C(20)	1.377(2)
C(19)-H(19)	0.9300
C(20)-H(20)	0.9300

C(21)-C(22)	1.5129(19)
C(21)-H(21A)	0.9700
C(21)-H(21B)	0.9700
C(22)-C(23)	1.3806(19)
C(22)-C(27)	1.3805(18)
C(23)-C(24)	1.377(2)
C(23)-H(23)	0.9300
C(24)-C(25)	1.367(2)
C(24)-H(24)	0.9300
C(25)-C(26)	1.369(2)
C(25)-H(25)	0.9300
C(26)-C(27)	1.383(2)
C(26)-H(26)	0.9300
C(27)-H(27)	0.9300
C(28)-C(33)	1.3856(18)
C(28)-C(29)	1.3849(18)
C(29)-C(30)	1.3781(19)
C(29)-H(29)	0.9300
C(30)-C(31)	1.367(2)
C(30)-H(30)	0.9300
C(31)-C(32)	1.375(2)
C(31)-H(31)	0.9300
C(32)-C(33)	1.3812(19)
C(32)-H(32)	0.9300
C(33)-H(33)	0.9300

C(2)-C(1)-C(6)	118.56(14)
C(2)-C(1)-C(7)	120.29(13)
C(6)-C(1)-C(7)	121.12(13)
C(3)-C(2)-C(1)	120.75(14)
C(3)-C(2)-H(2)	119.6
C(1)-C(2)-H(2)	119.6
C(4)-C(3)-C(2)	120.16(16)
C(4)-C(3)-H(3)	119.9
C(2)-C(3)-H(3)	119.9
C(5)-C(4)-C(3)	119.50(16)
C(5)-C(4)-H(4)	120.2
C(3)-C(4)-H(4)	120.2

C(4)-C(5)-C(6)	120.58(15)
C(4)-C(5)-H(5)	119.7
C(6)-C(5)-H(5)	119.7
C(5)-C(6)-C(1)	120.41(15)
C(5)-C(6)-H(6)	119.8
C(1)-C(6)-H(6)	119.8
C(8)-C(7)-C(1)	176.39(15)
C(7)-C(8)-C(9)	179.60(15)
C(14)-C(9)-C(10)	119.80(12)
C(14)-C(9)-C(8)	119.62(12)
C(10)-C(9)-C(8)	120.57(12)
C(9)-C(10)-C(11)	119.81(12)
C(9)-C(10)-C(28)	119.37(12)
C(11)-C(10)-C(28)	120.79(11)
C(10)-C(11)-C(12)	119.53(11)
C(10)-C(11)-C(21)	119.30(11)
C(12)-C(11)-C(21)	121.17(12)
C(13)-C(12)-C(11)	119.06(12)
C(13)-C(12)-C(15)	117.75(12)
C(11)-C(12)-C(15)	123.19(12)
C(14)-C(13)-C(12)	121.65(13)
C(14)-C(13)-H(13)	119.2
C(12)-C(13)-H(13)	119.2
C(13)-C(14)-C(9)	120.09(12)
C(13)-C(14)-H(14)	120.0
C(9)-C(14)-H(14)	120.0
C(20)-C(15)-C(16)	118.18(14)
C(20)-C(15)-C(12)	119.62(13)
C(16)-C(15)-C(12)	122.13(13)
C(17)-C(16)-C(15)	120.80(16)
C(17)-C(16)-H(16)	119.6
C(15)-C(16)-H(16)	119.6
C(18)-C(17)-C(16)	120.16(17)
C(18)-C(17)-H(17)	119.9
C(16)-C(17)-H(17)	119.9
C(19)-C(18)-C(17)	119.79(16)
C(19)-C(18)-H(18)	120.1
C(17)-C(18)-H(18)	120.1

C(18)-C(19)-C(20)	120.27(17)
C(18)-C(19)-H(19)	119.9
C(20)-C(19)-H(19)	119.9
C(19)-C(20)-C(15)	120.79(16)
C(19)-C(20)-H(20)	119.6
C(15)-C(20)-H(20)	119.6
C(22)-C(21)-C(11)	114.75(11)
C(22)-C(21)-H(21A)	108.6
C(11)-C(21)-H(21A)	108.6
C(22)-C(21)-H(21B)	108.6
C(11)-C(21)-H(21B)	108.6
H(21A)-C(21)-H(21B)	107.6
C(23)-C(22)-C(27)	117.66(14)
C(23)-C(22)-C(21)	121.85(12)
C(27)-C(22)-C(21)	120.48(13)
C(22)-C(23)-C(24)	121.46(14)
C(22)-C(23)-H(23)	119.3
C(24)-C(23)-H(23)	119.3
C(25)-C(24)-C(23)	120.17(16)
C(25)-C(24)-H(24)	119.9
C(23)-C(24)-H(24)	119.9
C(24)-C(25)-C(26)	119.40(16)
C(24)-C(25)-H(25)	120.3
C(26)-C(25)-H(25)	120.3
C(25)-C(26)-C(27)	120.42(15)
C(25)-C(26)-H(26)	119.8
C(27)-C(26)-H(26)	119.8
C(22)-C(27)-C(26)	120.89(16)
C(22)-C(27)-H(27)	119.6
C(26)-C(27)-H(27)	119.6
C(33)-C(28)-C(29)	118.03(12)
C(33)-C(28)-C(10)	120.46(12)
C(29)-C(28)-C(10)	121.51(12)
C(30)-C(29)-C(28)	120.68(14)
C(30)-C(29)-H(29)	119.7
C(28)-C(29)-H(29)	119.7
C(31)-C(30)-C(29)	120.61(14)
C(31)-C(30)-H(30)	119.7

C(29)-C(30)-H(30)	119.7
C(30)-C(31)-C(32)	119.73(14)
C(30)-C(31)-H(31)	120.1
C(32)-C(31)-H(31)	120.1
C(31)-C(32)-C(33)	119.83(14)
C(31)-C(32)-H(32)	120.1
C(33)-C(32)-H(32)	120.1
C(32)-C(33)-C(28)	121.10(14)
C(32)-C(33)-H(33)	119.4
C(28)-C(33)-H(33)	119.4

Symmetry transformations used to generate equivalent atoms:

Table S5. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for A. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	51(1)	50(1)	47(1)	-4(1)	4(1)	6(1)
C(2)	67(1)	72(1)	53(1)	6(1)	13(1)	20(1)
C(3)	68(1)	81(1)	78(1)	-1(1)	13(1)	28(1)
C(4)	72(1)	62(1)	77(1)	6(1)	-8(1)	18(1)
C(5)	80(1)	90(1)	60(1)	22(1)	6(1)	15(1)
C(6)	64(1)	90(1)	55(1)	9(1)	13(1)	18(1)
C(7)	56(1)	59(1)	49(1)	-3(1)	5(1)	10(1)
C(8)	55(1)	57(1)	48(1)	-3(1)	6(1)	10(1)
C(9)	48(1)	51(1)	48(1)	1(1)	9(1)	9(1)
C(10)	44(1)	45(1)	47(1)	1(1)	14(1)	6(1)
C(11)	44(1)	46(1)	47(1)	1(1)	12(1)	7(1)
C(12)	48(1)	47(1)	52(1)	3(1)	14(1)	10(1)
C(13)	63(1)	49(1)	61(1)	-7(1)	10(1)	16(1)
C(14)	62(1)	55(1)	53(1)	-9(1)	2(1)	10(1)
C(15)	50(1)	43(1)	62(1)	1(1)	9(1)	8(1)
C(16)	70(1)	71(1)	65(1)	11(1)	15(1)	22(1)
C(17)	85(1)	83(1)	76(1)	22(1)	4(1)	25(1)
C(18)	66(1)	74(1)	110(2)	16(1)	-6(1)	24(1)
C(19)	56(1)	74(1)	107(2)	6(1)	15(1)	22(1)
C(20)	55(1)	58(1)	75(1)	6(1)	16(1)	14(1)
C(21)	48(1)	49(1)	56(1)	-2(1)	5(1)	8(1)
C(22)	54(1)	51(1)	43(1)	-2(1)	-1(1)	16(1)
C(23)	71(1)	58(1)	52(1)	-2(1)	13(1)	11(1)
C(24)	81(1)	82(1)	57(1)	8(1)	23(1)	19(1)
C(25)	96(1)	98(1)	54(1)	2(1)	20(1)	44(1)
C(26)	100(1)	75(1)	61(1)	-18(1)	3(1)	34(1)
C(27)	70(1)	58(1)	60(1)	-10(1)	0(1)	15(1)
C(28)	48(1)	47(1)	41(1)	1(1)	7(1)	11(1)
C(29)	53(1)	56(1)	59(1)	0(1)	14(1)	12(1)
C(30)	65(1)	71(1)	66(1)	-4(1)	17(1)	27(1)
C(31)	82(1)	54(1)	63(1)	-5(1)	7(1)	26(1)
C(32)	73(1)	47(1)	67(1)	4(1)	10(1)	8(1)
C(33)	56(1)	52(1)	58(1)	3(1)	16(1)	12(1)

Table S6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for A.

	x	y	z	U(eq)
H(2)	-1724	2455	960	76
H(3)	-4024	3441	300	89
H(4)	-3651	4223	-932	87
H(5)	-1011	3967	-1510	94
H(6)	1288	2976	-859	84
H(13)	6266	-1303	1445	70
H(14)	3840	-513	719	70
H(16)	7602	-645	3786	81
H(17)	9832	-1707	4427	98
H(18)	12332	-2117	3808	102
H(19)	12591	-1470	2545	94
H(20)	10352	-426	1893	75
H(21A)	9219	1782	3527	63
H(21B)	8978	3103	3158	63
H(23)	4985	704	3785	74
H(24)	3176	1106	4733	87
H(25)	4142	3127	5477	94
H(26)	6966	4730	5282	94
H(27)	8773	4339	4326	78
H(29)	2580	2659	2673	67
H(30)	2279	4742	3028	78
H(31)	4758	6635	2903	79
H(32)	7554	6452	2397	77
H(33)	7862	4370	2031	66

Table S7. Torsion angles [°] for A.

C(6)-C(1)-C(2)-C(3)	-1.4(2)
C(7)-C(1)-C(2)-C(3)	176.79(14)
C(1)-C(2)-C(3)-C(4)	0.2(2)
C(2)-C(3)-C(4)-C(5)	0.8(2)
C(3)-C(4)-C(5)-C(6)	-0.7(3)
C(4)-C(5)-C(6)-C(1)	-0.5(3)
C(2)-C(1)-C(6)-C(5)	1.5(2)
C(7)-C(1)-C(6)-C(5)	-176.63(14)
C(14)-C(9)-C(10)-C(11)	-2.46(19)
C(8)-C(9)-C(10)-C(11)	178.87(12)
C(14)-C(9)-C(10)-C(28)	175.67(12)
C(8)-C(9)-C(10)-C(28)	-2.99(18)
C(9)-C(10)-C(11)-C(12)	1.27(18)
C(28)-C(10)-C(11)-C(12)	-176.84(11)
C(9)-C(10)-C(11)-C(21)	-179.20(11)
C(28)-C(10)-C(11)-C(21)	2.69(18)
C(10)-C(11)-C(12)-C(13)	1.07(18)
C(21)-C(11)-C(12)-C(13)	-178.45(12)
C(10)-C(11)-C(12)-C(15)	-179.45(12)
C(21)-C(11)-C(12)-C(15)	1.03(19)
C(11)-C(12)-C(13)-C(14)	-2.3(2)
C(15)-C(12)-C(13)-C(14)	178.19(13)
C(12)-C(13)-C(14)-C(9)	1.1(2)
C(10)-C(9)-C(14)-C(13)	1.3(2)
C(8)-C(9)-C(14)-C(13)	179.96(13)
C(13)-C(12)-C(15)-C(20)	60.02(17)
C(11)-C(12)-C(15)-C(20)	-119.46(15)
C(13)-C(12)-C(15)-C(16)	-116.90(16)
C(11)-C(12)-C(15)-C(16)	63.62(18)
C(20)-C(15)-C(16)-C(17)	-0.5(2)
C(12)-C(15)-C(16)-C(17)	176.49(14)
C(15)-C(16)-C(17)-C(18)	0.4(3)
C(16)-C(17)-C(18)-C(19)	-0.1(3)
C(17)-C(18)-C(19)-C(20)	-0.2(3)
C(18)-C(19)-C(20)-C(15)	0.2(2)
C(16)-C(15)-C(20)-C(19)	0.1(2)

C(12)-C(15)-C(20)-C(19)	-176.90(13)
C(10)-C(11)-C(21)-C(22)	62.07(16)
C(12)-C(11)-C(21)-C(22)	-118.41(14)
C(11)-C(21)-C(22)-C(23)	35.46(18)
C(11)-C(21)-C(22)-C(27)	-143.35(13)
C(27)-C(22)-C(23)-C(24)	0.6(2)
C(21)-C(22)-C(23)-C(24)	-178.21(14)
C(22)-C(23)-C(24)-C(25)	-0.2(2)
C(23)-C(24)-C(25)-C(26)	-0.6(3)
C(24)-C(25)-C(26)-C(27)	0.8(3)
C(23)-C(22)-C(27)-C(26)	-0.4(2)
C(21)-C(22)-C(27)-C(26)	178.50(14)
C(25)-C(26)-C(27)-C(22)	-0.4(2)
C(9)-C(10)-C(28)-C(33)	-108.15(14)
C(11)-C(10)-C(28)-C(33)	69.97(16)
C(9)-C(10)-C(28)-C(29)	71.82(17)
C(11)-C(10)-C(28)-C(29)	-110.06(14)
C(33)-C(28)-C(29)-C(30)	-1.1(2)
C(10)-C(28)-C(29)-C(30)	178.94(13)
C(28)-C(29)-C(30)-C(31)	0.1(2)
C(29)-C(30)-C(31)-C(32)	0.6(2)
C(30)-C(31)-C(32)-C(33)	-0.4(2)
C(31)-C(32)-C(33)-C(28)	-0.6(2)
C(29)-C(28)-C(33)-C(32)	1.3(2)
C(10)-C(28)-C(33)-C(32)	-178.70(13)

Symmetry transformations used to generate equivalent atoms:

(E) Reference

(1) X.-Z. Shu, X.-Y. Liu, H.-Q. Xiao, K.-G. Ji, L.-N. Guo, C.-Z. Qi and Y.-M. Liang, *Adv. Synth. Catal.*, 2007, **349**, 2493.