Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Remote C(sp^3)–H Activation: Palladium-Catalyzed Intermolecular Arylation and Alkynylation with Organolithiums and Terminal Alkynes

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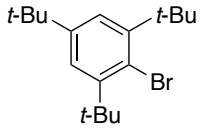
1. General Information

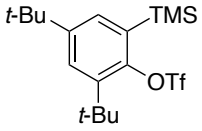
All reactions were carried out under an atmosphere of dry argon with the rigid exclusion of air and moisture using standard Schlenk techniques or in a glovebox unless otherwise specified. Reactions were magnetically stirred and monitored by thin layer chromatography (TLC) on MERCK silica gel 60 F254 coated on aluminum plates. Visualization was accomplished by irradiation with UV light at 254 nm followed by staining with ceric ammonium molybdate (CAM). Organic solvents were concentrated under reduced pressure at appropriate temperature on a rotary evaporator unless otherwise stated. Column chromatography was performed on silica gel (300–400 mesh). Preparative thin-layer chromatography (PTLC) was performed on glass plates (20 × 20 cm) impregnated with silica gel 60 F254 (0.3–0.4 mm thickness). Pentane, diethyl ether, THF and toluene for reactions were dried over sodium wire and distilled under an atmosphere of dry Ar. CH_2Cl_2 was dried over calcium hydride and distilled under an atmosphere of dry Ar. NMR spectra were recorded on a Bruker Ultrashield 400 Plus NMR spectrometer (400 MHz for ^{1}H, 101 MHz for ^{13}C, 377 MHz for ^{19}F) or Bruker Ascend 500 NMR spectrometer (500 MHz for ^{1}H, 126 MHz for ^{13}C, 471 MHz for ^{19}F). Chemical shifts of ^{1}H NMR and ^{13}C NMR spectra were reported as parts per million in δ scale using residual solvent signal as internal standard (note: $CDCl_3$ referenced at δ 7.26 in ^{1}H and δ 77.0 for central line of the triplet in ^{13}C;). Data are represented as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad) and coupling constant (*J*, Hz). High resolution mass spectra (HRMS) were obtained on a Bruker SolariX 9.4T ICR Mass Spectrometer or Thermo Q Exactive Focus Orbitrap Mass Spectrometer. Melting points were measured on a STUART Melting Point Apparatus SMP40 and were uncorrected. GC-MS analyses were performed on an Agilent 7890B system with an Agilent 5977B MSD. Unless otherwise noted, purchased chemicals were used without further purification. All terminal alkynes **8** were commercially available.

2. Preparation of Substrates

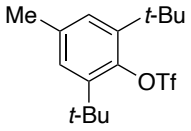
2.1 Synthesis of Aryl bromides and Aryl trifluoromethanesulfonates



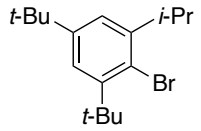
1a



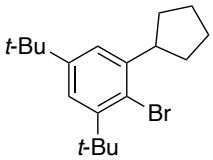
1b



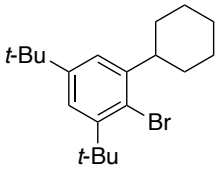
1c



1d



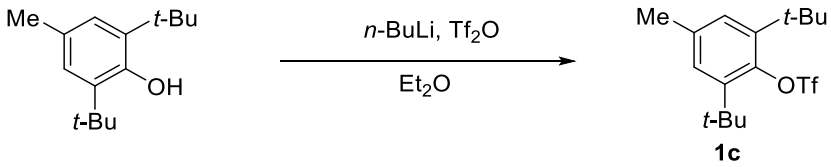
1e



1f

Aryl bromide **1a** was commercially available, and compound **1b, 1d, 1e** and **1f** were known compounds in the literature.[1] Attempt on replacing *t*-Bu group with other groups was also performed, which however only lead to direct cross-coupling reactions with on observation of 1,4-palladium shift product, proving the great significance of steric hindrance for the production of C–H activation in this reaction.

2,6-di-*tert*-butyl-4-methylphenyl trifluoromethanesulfonate (1c)



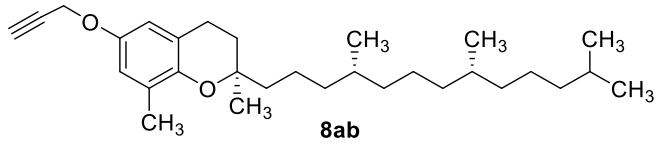
1c

Under an argon atmosphere, to an oven-dried Schlenk flask containing a magnetic stir bar, was added 2,6-di-tert-butyl-4-methylphenol (0.88 g, 4.0 mmol), and diethyl ether (20 mL). The reaction mixture was cooled to −78 ºC, and then a solution of *n*-BuLi (1.6 M in hexanes, 3.75 mL, 6.0 mmol) was added slowly via syringe. The mixture was allowed to warm to room temperature and stirred for 30 min. The mixture was cooled back to −78 ºC, and triflic anhydride (1.35 mL, 8.0 mmol) was added slowly via syringe. The mixture was allowed to warm to room temperature and stirred for 12 h. The reaction was quenched with a saturated aqueous solution of $NaHCO_3$ (30 mL). The organic layer was separated, washed with brine, dried over Na_2SO_4,

filtered and concentrated in vacuo. Chromatographic purification on silica gel (silica gel 20 g; eluent: 100% Hexane) to the product **1c** (422 mg, 30% yield) as a colorless oil. $\mathbf{R}_f$ = 0.8 (Hexane = 100%) **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.18 (s, 2H), 2.35 (s, 3H), 1.46 (s, 18H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 144.8, 137.7, 136.3, 129.7, 127.4, 37.2, 32.6, 21.1 ppm. **^{19}F NMR** (471 MHz, $CDCl_3$) δ = −72.31 ppm. HRMS *m/z* (ESI) calcd. for $C_{16}H_{23}F_3O_3S$ $[M+Na]^+$: 375.1208; found: 375.1212.

2.2 Synthesis of Terminal Alkynes 8

The terminal alkyne **8ab** was synthesized, and the other terminal alkynes are commercially available.



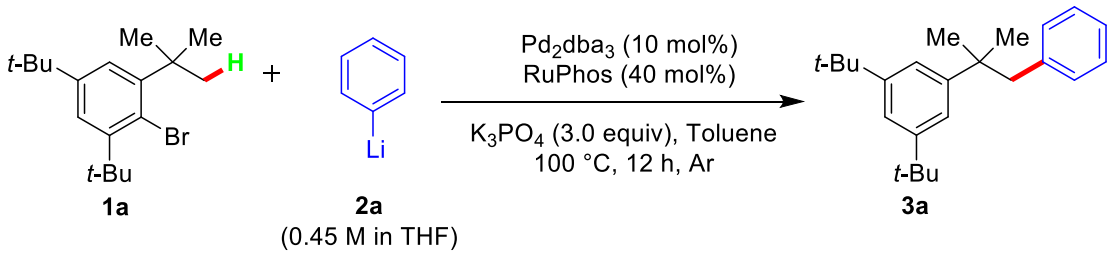
8ab

(R)-2,8-dimethyl-6-(prop-2-yn-1-yloxy)-2-((4R,8R)-4,8,12-trimethyltridecyl)chromane (8ab)

To a mixture of (+) δ-Tocopherol (1.02 g, 2.5 mmol, 1.0 equiv) and anhydrous K_2CO_3 (1.41 g, 10.12 mmol, 4.0 equiv) in acetone (30 mL) was added propargyl bromide (0.30 mL, 3.75 mmol, 1.5 equiv) at 65 °C. After vigorous stirring for 12h, cooled to room temperature. And aqueous NH_4Cl was added to the reaction mixture. The organic layer was separated, and the aqueous layer was extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified through column chromatography (Hexane/Et_2O = 20/1) over silica gel, to afford (R)-2,8-dimethyl-6-(prop-2-yn-1-yloxy)-2-((4R,8R)-4,8,12-trimethyltridecyl)chromane (**8ab**) (0.90 g, 52%) as yellow oil. **R_f =** 0.6 (Hexane/Et_2O = 10/1) **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 6.66 (d, *J* = 2.8 Hz, 1H), 6.56 (dd, *J* = 13.1, 5.6 Hz, 1H), 4.62 (d, *J* = 2.4 Hz, 2H), 2.78 – 2.68 (m, 2H), 2.55 – 2.47 (m, 1H), 2.17 (s, 3H), 1.86 – 1.72 (m, 2H), 1.64 – 1.50 (m, 4H), 1.50 – 1.35 (m, 4H), 1.34 – 1.24 (m, 10H), 1.19 – 1.02 (m, 6H), 0.91 – 0.84 (m, 12H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 150.0, 146.9, 127.3, 121.0, 115.8, 112.5, 79.3, 75.7, 75.0, 56.5, 40.0, 39.4, 37.4, 37.4, 37.3, 32.8, 32.7, 31.2, 28.0, 24.8, 24.4, 24.1, 22.7, 22.7, 22.6, 21.0, 19.7, 19.6, 16.2 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{30}H_{48}O_2$ $[M+H]^+$: 441.3727; found: 441.3725.

3. Optimization of Reaction Conditions

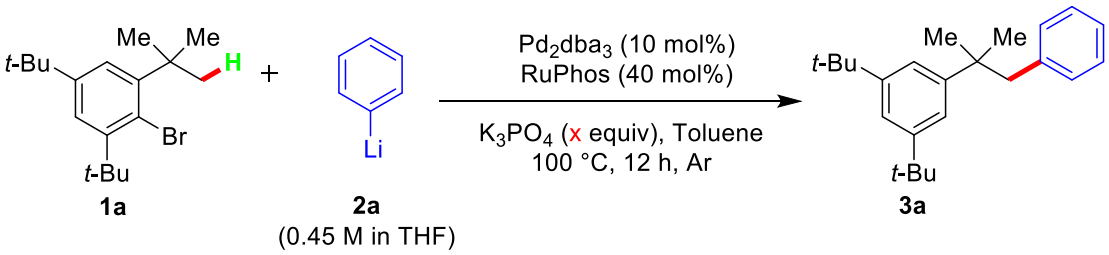
3.1.1 Table S1: Effect of Addition Rate of Organolithium Reagents



[a]Entry	1a	2a	[b]t	[c]Yield (%)
1	1.0 eq.	3.0 eq.	**0.5** + 11.5	53%
2	1.0 eq.	3.0 eq.	**1** + 11 h	65%
3	1.0 eq.	3.0 eq.	**1.5** + 10.5 h	53%
4	1.0 eq.	3.0 eq.	**2** + 10 h	50%
5	1.0 eq.	3.0 eq.	**2.5** + 9.5 h	**77%**
6	1.0 eq.	3.0 eq.	**3** + 9.5 h	63%
7	1.0 eq.	3.0 eq.	**3.5** + 8.5 h	57%
8	1.0 eq.	3.0 eq.	**4** + 8 h	54%
9	1.0 eq.	3.0 eq.	**4.5** + 7.5 h	56%
10	1.0 eq.	3.0 eq.	**5** + 7 h	47%

[a]Reaction conditions unless otherwise noted: **1a** (0.10 mmol), **2a** (0.30 mmol), Pd_2dba_3 (10 mol%), RuPhos (40 mol%), K_3PO_4 (3.0 eq.), toluene (2.0 mL) were used, 100 °C, under Ar for 12 h. [b]For total 12 h reaction time, the first **red** number means the dropwise addition time of **2a**, and the second black number means further continuous reaction time. [c]Yiled was determined by ^1H NMR analysis with CH_2Br_2 as an internal standard.

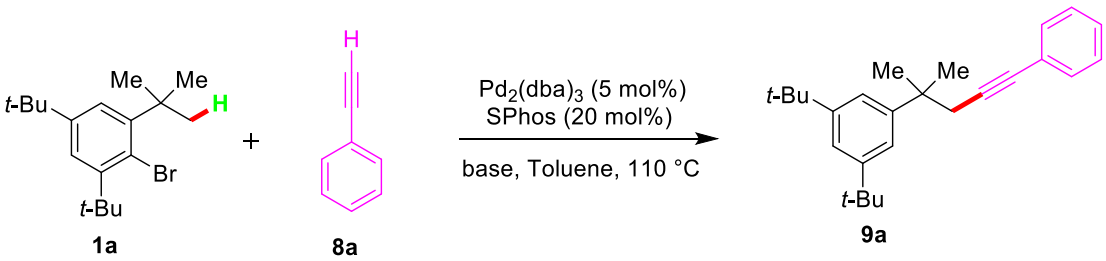
3.1.2 Table S2: Effect of Amounts of Base



[a]Entry	**1a**	**2a**	K_3PO_4	[b]Yield (%)
1	1.0 eq.	3.0 eq.	1.0 eq.	57%
2	1.0 eq.	3.0 eq.	1.5 eq.	59%
3	1.0 eq.	3.0 eq.	2.0 eq.	63%
4	1.0 eq.	3.0 eq.	2.5 eq.	61%
5	1.0 eq.	3.0 eq.	3.0 eq.	77%
6	1.0 eq.	3.0 eq.	3.5 eq.	60%
7	1.0 eq.	3.0 eq.	4.0 eq.	55%

[a]Reaction conditions unless otherwise noted: **1a** (0.10 mmol), **2a** (0.30 mmol), Pd_2dba_3 (10 mol%), RuPhos (40 mol%), K_3PO_4 (x eq.), toluene (2.0 mL) were used, 100 °C, under Ar for 12 h. [b]Yiled was determined by ^1H NMR analysis with CH_2Br_2 as an internal standard.

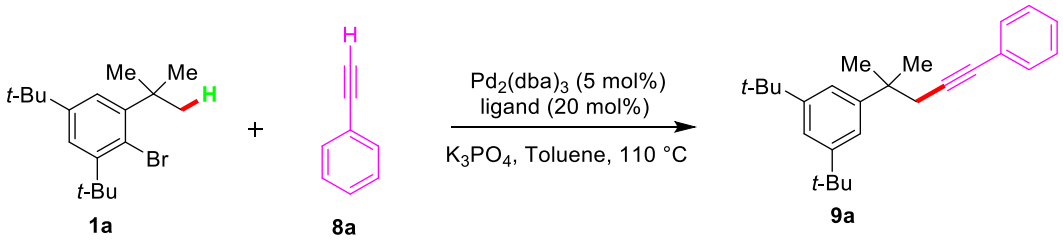
3.2.1 Table S3: Effect of the Base



[a]Entry	**1a**	**8a**	Base	[b]Yield (%)
1	1.0 eq.	1.5 eq.	LiOMe	0
2	1.0 eq.	1.5 eq.	KO^{t}Bu	0
3	1.0 eq.	1.5 eq.	NaO^{t}Bu	0
4	1.0 eq.	1.5 eq.	Et_3N	0
5	1.0 eq.	1.5 eq.	K_2CO_3	18
6	1.0 eq.	1.5 eq.	Cs_2CO_3	32
7	1.0 eq.	1.5 eq.	CsPivO	0
8	1.0 eq.	1.5 eq.	CsF	26
9	1.0 eq.	1.5 eq.	$NaHCO_3$	4
10	1.0 eq.	1.5 eq.	NaOAc	3
11	1.0 eq.	1.5 eq.	KOAc	0
12	1.0 eq.	1.5 eq.	LiOAc	2
13	1.0 eq.	1.5 eq.	KHMDS	0
14	1.0 eq.	1.5 eq.	KF	3
15	1.0 eq.	1.5 eq.	**K_3PO_4**	**37**
16	1.0 eq.	1.5 eq.	K_3PO_4	31[c]

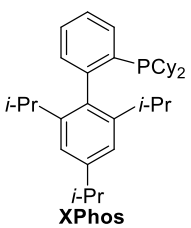
[a]Reaction conditions unless otherwise noted: **1a** (0.10 mmol), **8a** (0.15 mmol), Pd_2dba_3, SPhos, base (0.30 mmol), toluene (2.0 mL) were used, 110 °C, under Ar for 24 h. [b]Yiled was determined by ^1H NMR analysis with CH_2Br_2 as an internal standard. [c]140 °C for 24 h.

3.2.2 Table S4: Effect of the Ligand

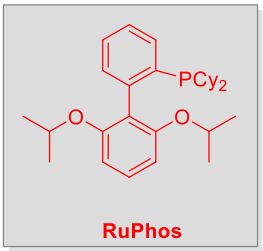


[a]Entry	1a	8a	Ligand	[b]Yield (%)
1	1.0 eq.	1.5 eq.	SPhos	37
2	1.0 eq.	1.5 eq.	CPhos	35
3	1.0 eq.	1.5 eq.	XPhos	49
4	1.0 eq.	1.5 eq.	*t*-ButylMePhos	26
5	1.0 eq.	1.5 eq.	DavePhos	43
6	1.0 eq.	1.5 eq.	*t*-BuxPhos	0
7	1.0 eq.	1.5 eq.	*t*-Bu-xantPhos	0
8	1.0 eq.	1.5 eq.	PhDavePhos	0
9	1.0 eq.	1.5 eq.	RuPhos	**50**
10	1.0 eq.	1.5 eq.	SIMes•HCl	0
11	1.0 eq.	1.5 eq.	IcHex•HCl	0
12	1.0 eq.	1.5 eq.	IPr•HCl	0
13	1.0 eq.	1.5 eq.	IAd•HBF_4	0
14	1.0 eq.	1.5 eq.	CyjohnPhos	37
15	1.0 eq.	1.5 eq.	MePhos	32

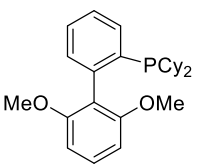
[a]Reaction conditions unless otherwise noted: **1a** (0.10 mmol), **8a** (0.15 mmol), Pd_2dba_3, ligand, K_3PO_4 (0.30 mmol), toluene (2.0 mL) were used, 110 °C, under Ar for 24 h. [b]Yiled was determined by ^1H NMR analysis with CH_2Br_2 as an internal standard.



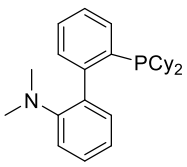
XPhos



RuPhos

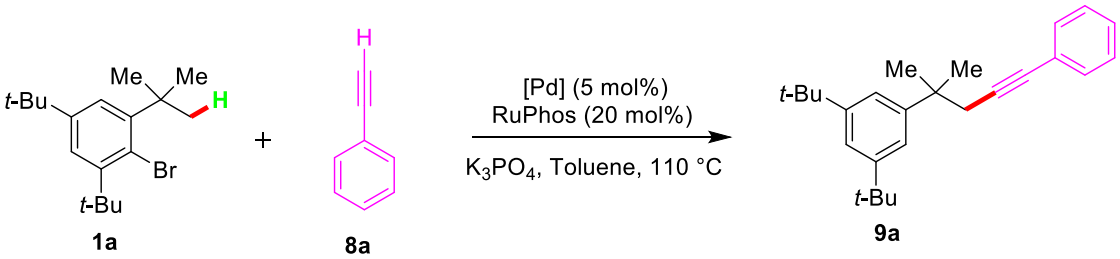


SPhos



DavePhos

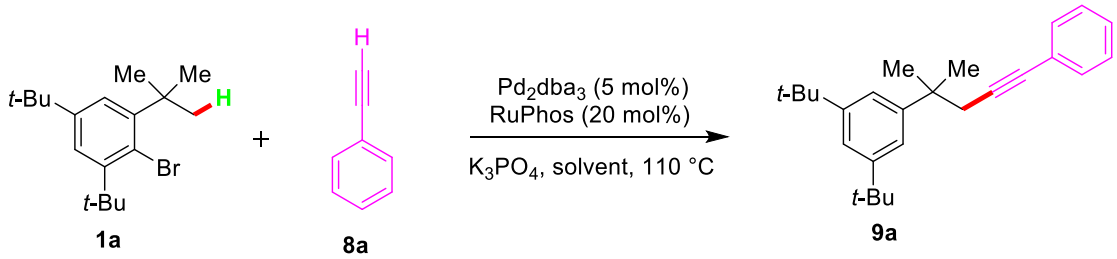
3.2.3 Table S5: Effect of the Palladium Catalyst



[a]Entry	**1a**	**8a**	[Pd]	[b]Yield (%)
1	1.0 eq.	1.5 eq.	$Pd(PPh_3)_4$	22
2	1.0 eq.	1.5 eq.	$Pd(OAc)_2$	0
3	1.0 eq.	1.5 eq.	$Pd(TFA)_2$	22
4	1.0 eq.	1.5 eq.	$Pd(dppf)Cl_2 \cdot DCM$	33
5	1.0 eq.	1.5 eq.	$Pd(dba)_2$	37
6	1.0 eq.	1.5 eq.	$Pd(PPh_3)_2Cl_2$	17
7	1.0 eq.	1.5 eq.	$Pd(PhCN)_2Cl_2$	17
8	1.0 eq.	1.5 eq.	$Pd(Cy_3)_2Cl_2$	39
9	1.0 eq.	1.5 eq.	$Pd(dppf)_2Cl_2$	23
10	1.0 eq.	1.5 eq.	$Pd_2(dba)_3$	50

[a]Reaction conditions unless otherwise noted: **1a** (0.10 mmol), **8a** (0.15 mmol), [Pd], ligand, K_3PO_4 (0.30 mmol), toluene (2.0 mL) were used, 110 °C, under Ar for 24 h. [b]Yiled was determined by ^1H NMR analysis with CH_2Br_2 as an internal standard.

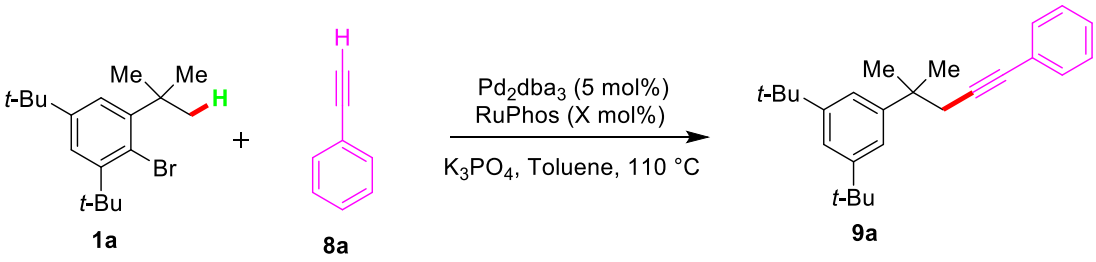
3.2.4 Table S6: Effect of the Solvent



[a]Entry	**1a**	**8a**	Solvent	[b]Yield (%)
1	1.0 eq.	1.5 eq.	Toluene	50
2	1.0 eq.	1.5 eq.	*o*-DCB	0
3	1.0 eq.	1.5 eq.	Benzene	7
4	1.0 eq.	1.5 eq.	DME	10
5	1.0 eq.	1.5 eq.	DMF	0
6	1.0 eq.	1.5 eq.	1,4-dioxane	**60**
7	1.0 eq.	1.5 eq.	MeCN	23
8	1.0 eq.	1.5 eq.	DMSO	0
9	1.0 eq.	1.5 eq.	*m*-Xylene	10

[a]Reaction conditions unless otherwise noted: **1a** (0.10 mmol), **8a** (0.15 mmol), [Pd], ligand, K_3PO_4 (0.30 mmol), solvent (2.0 mL) were used, 110 °C, under Ar for 24 h. [b]Yiled was determined by ^1H NMR analysis with CH_2Br_2 as an internal standard.

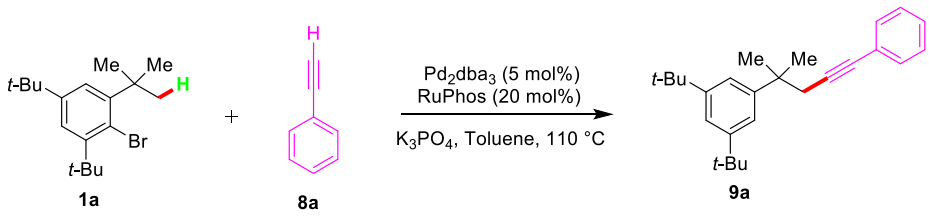
3.2.5. Table S7: Effect of the ratio of Pd_2dba_3/RuPhos



[a]Entry	1a	8a	$Pd_2(dba)_3$	RuPhos	[b]Yield (%)
1	1.0 eq.	1.5 eq.	5 %	5 %	0
2	1.0 eq.	1.5 eq.	5 %	10 %	16
3	1.0 eq.	1.5 eq.	5 %	15 %	25
4	1.0 eq.	1.5 eq.	5 %	20 %	53
5	1.0 eq.	1.5 eq.	5 %	25 %	32
6	1.0 eq.	1.5 eq.	5 %	30 %	19
7	1.0 eq.	1.5 eq.	5 %	40	11

[a]Reaction conditions unless otherwise noted: **1a** (0.10 mmol), **8a** (0.15 mmol), Pd_2dba_3, RuPhos, K_3PO_4 (0.30 mmol), toluene (2.0 mL) were used, 110 °C, under Ar for 24 h. [b]Yiled was determined by ^1H NMR analysis with CH_2Br_2 as an internal standard.

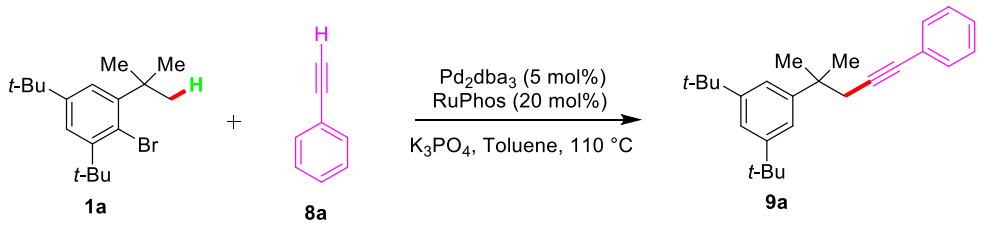
3.2.6 Table S8: Effect of the amount of Toluene



[a]Entry	1a	8a	Toluene (mL)	[b]Yield (%)
1	1.0 eq.	1.5 eq.	1.0	22
2	1.0 eq.	1.5 eq.	1.5	25
3	1.0 eq.	1.5 eq.	2.0	35
4	1.0 eq.	1.5 eq.	2.5	35
5	1.0 eq.	1.5 eq.	3.0	35

[a]Reaction conditions unless otherwise noted: **1a** (0.10 mmol), **8a** (0.15 mmol), Pd_2dba_3, RuPhos, K_3PO_4 (0.30 mmol), toluene, 110 °C, under Ar for 24 h. [b]Yiled was determined by ^1H NMR analysis with CH_2Br_2 as an internal standard.

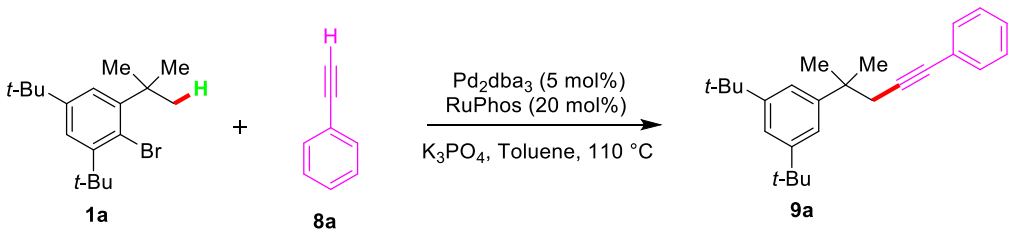
3.2.7 Table S9: Effect of the amount of K_3PO_4



[a]Entry	**1a**	**8a**	K_3PO_4 (equiv.)	[b]Yield (%)
1	1.0 eq.	1.5 eq.	1.0	6
2	1.0 eq.	1.5 eq.	1.5	10
3	1.0 eq.	1.5 eq.	2.0	26
4	1.0 eq.	1.5 eq.	2.5	28
5	1.0 eq.	1.5 eq.	3.0	48
6	1.0 eq.	1.5 eq.	3.5	26
7	1.0 eq.	1.5 eq.	4.0	24
8	1.0 eq.	1.5 eq.	4.5	20

[a]Reaction conditions unless otherwise noted: **1a** (0.10 mmol), **8a** (0.15 mmol), Pd_2dba_3, RuPhos, K_3PO_4, toluene (2.0 mL), 110 °C, under Ar for 24 h. [b]Yiled was determined by ^1H NMR analysis with CH_2Br_2 as an internal standard.

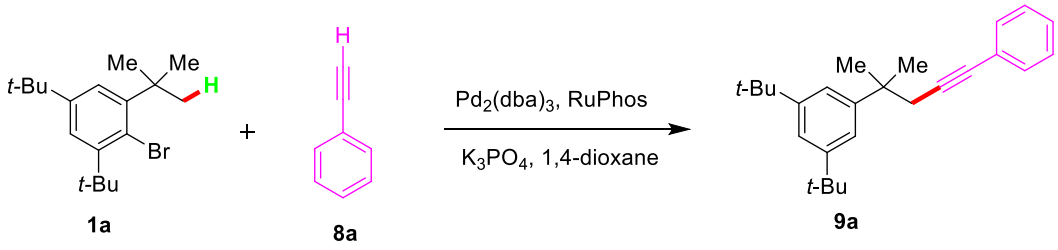
3.2.8 Table S10: Effect of the reaction time



[a]Entry	t (h)	[b]Yield (%)	[a]Entry	t (h)	[b]Yield (%)
1	2	9	9	20	28
2	4	27	10	24	31
3	6	34	11	30	31
4	8	22	12	42	32
5	12	29	13	48	45
6	14	32	14	12	56[c]
7	16	43	15	24	75[c]
8	18	19	16	24	68[d]

[a]Reaction conditions: **1a** (0.10 mmol), **8a** (0.15 mmol), Pd_2dba_3 (5 mol%), RuPhos (20 mol %), K_3PO_4 (0.30 mmol), Toluene 1.0 mL were used, 110 °C, under Ar. [b]Yiled was determined by ^1H NMR analysis with CH_2Br_2 as an internal standard. [c]Compound **8a** was dissolved in 1.0 mL Toluene and added dropwise for 2 h. [d] added dropwise for 1 h.

3.2.9 Table S11: Optimization of the Alkynylation with C(sp^3)–H Activation Reaction Conditions

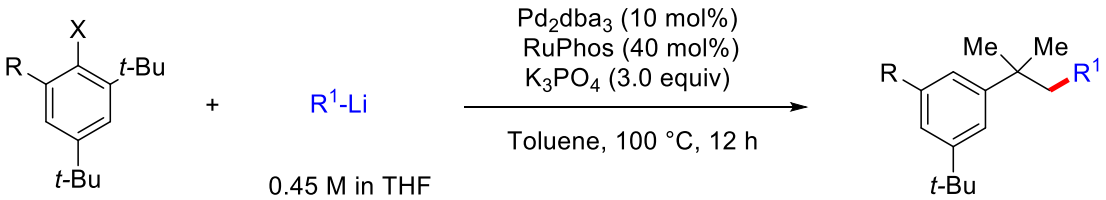


[a]entry	Pd_2dba_3	RuPhos	t (h)	T (°C)	[b]yield (%)[b]
1	5 %	20 %	24	110	54
2	5 %	20 %	24	110	**96 (94)**[c]
3	5 %	20 %	18	110	92 (89)[c]
4	5 %	20 %	12	110	87[c]
5	5 %	20 %	24	110	80[d]
6	2.5 %	10 %	24	110	80[c]
7	1 %	4 %	24	110	68[c]

[a]Reaction conditions unless otherwise noted: **1a** (0.10 mmol), **8a** (0.15 mmol), Pd_2dba_3, RuPhos, K_3PO_4 (0.30 mmol), 1,4-dioxane (1.0 mL) were used, 110 °C, under Ar. [b]Yiled was determined by ^1H NMR analysis with CH_2Br_2 as an internal standard. Yield of isolated **9a** in parentheses. [c]Compound **8a** was dissolved in 1.0 mL 1,4-dioxane and added dropwise over 2 h. [d]Added dropwise for 3 h.

4. Experimental Section

4.1 General Procedure for the Synthesis of 3, 5 and 7



1
X = Br, OTf

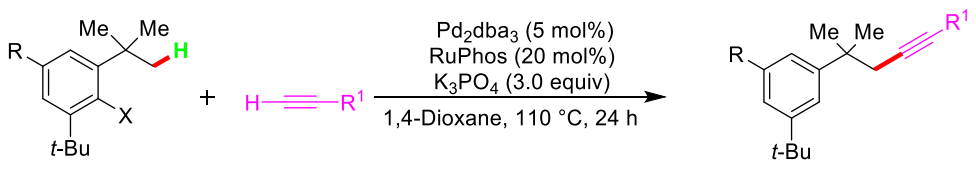
2, 4, 6

3, 5, 7

After three times' evacuation and backfilling with dry argon, an oven-dried test tube equipped with magnetic stir bar was charged with Pd_2dba_3 (0.01mmol), Ruphos (0.04 mmol), K_3PO_4 (0.30 mmol), and aryl bromides/triflates (**1**) (0.10 mmol), were added 2.0 mL toluene via argon-flushed syringes at 100 ℃, and the freshly prepared organolithiums (**2**, **4** or **6**, 0.3 mmol) in THF was added dropwise via a syringe pump over 2.5 h. After 12 h, the test tube was allowed to be cooled down to room temperature, the reaction mixture was quenched by MeOH and passed through a short silica pad using EtOAc as an eluent. After concentrated under reduced pressure, the crude product was purified by column chromatography to afford desired products **3**, **5** or **7**, respectively.

For the preparation of organolithiums (0.45M in THF), procedures are as follows: After three times' evacuation and backfilling with dry argon, an oven-dried Schlenk flask equipped with magnetic stir bar was charged with corresponding aryl bromides (2.0 mmol), were added 2.0 mL THF via argon-flushed syringes, and the resulting solution was cooled to –78 ℃ in an acetone-dry ice bath. Then 2.5 mL *t*-BuLi (2.0 equiv, 1.6M in pentane) was added dropwise via an argon-flushed syringe, and the mixture was stirred at –78 ℃ for 30 min, after which the Schlenk flask was placed at room temperature and kept stirring for 30 min.

4.2 Optimized Procedure for Terminal Alkynes



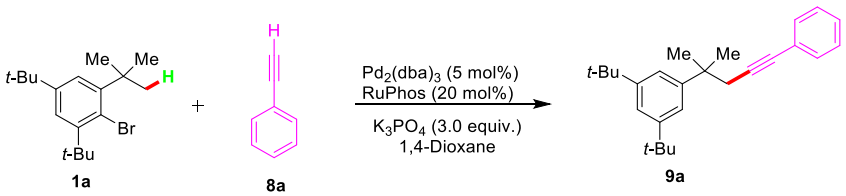
1

8

9

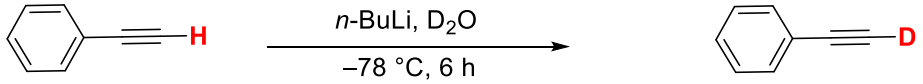
Pd_2dba_3 (5 mol%), Ruphos (20 mol%), K_3PO_4 (0.30 mmol), and **1** (0.10 mmol, 1.0 equiv.) were carried out in test tube in glove box and then 1,4-dioxane (1.0 mL) was added to the test tube at room temperature. Alkynes **8** (0.15 mmol, 1.5 equiv.) dissolve in 1.0 mL 1,4-dioxane and was added dropwise via syringe pump over 2 h at 110 ℃. After addition, the reaction system was stirred at 110 ℃ for another 22 h. It was then filtered through a pad of Celite using EtOAc and CH_2Cl_2. The solvent was removed by reduced pressure and the residue was purified by column chromatograph or preparative thin-layer chromatography to afford the product **9**. Using the compound **1a** as the example: Pd_2dba_3 (0.005 mmol, 4.6 mg), K_3PO_4 (0.30 mmol, 64 mg) and Ruphos (0.02 mmol, 9.4 mg) were carried out in test tube in glove box and then the solution of compound **1a** (0.10 mmol, 33 mg) in 1.0 mL of 1,4-dioxane was added to the test tube at room temperature. Phenylacetylene **8a** (0.15 mmol, 20 *u*l) dissolve in 1.0 mL 1,4-Dioxane and was added dropwise by syringe pump over 2 h at 110 ℃. After addition, the reaction system was stirred at 110 ℃ for another 22 h. It was then filtered through a pad of Celite using CH_2Cl_2. The solvent was removed by reduced pressure and the residue was purified by column chromatograph (silica gel 8 g; eluent: 100% Hexane) to afford the product **9a** (32.6 mg, 94%).

Gram Scale Reaction



Pd_2dba_3 (0.15 mmol, 140 mg), K_3PO_4 (9.15 mmol, 2.07 g) and Ruphos (0.62 mmol, 295 mg) were carried out in round-bottom flask (200 mL) in glove box and then the solution of compound **1a** (3.05 mmol, 1.0 g) in 30.0 mL of 1,4-dioxane was added to the round-bottom flask at room temperature. Phenylacetylene **8a** (4.62 mmol, 0.51 mL) dissolve in 30 mL 1,4-dioxane and was added dropwise by syringe pump over 2 h at 110 ℃. After addition, the reaction system was stirred at 110 ℃ for another 22 h. It was then filtered through a pad of Celite using CH_2Cl_2. The solvent was removed by reduced pressure and the residue was purified by column chromatograph (silica gel 38 g; eluent: 100% Hexane) to afford the product **9a** (695 mg, 65%). $\mathbf{R_f}$ = 0.8 (Hexane = 100%).

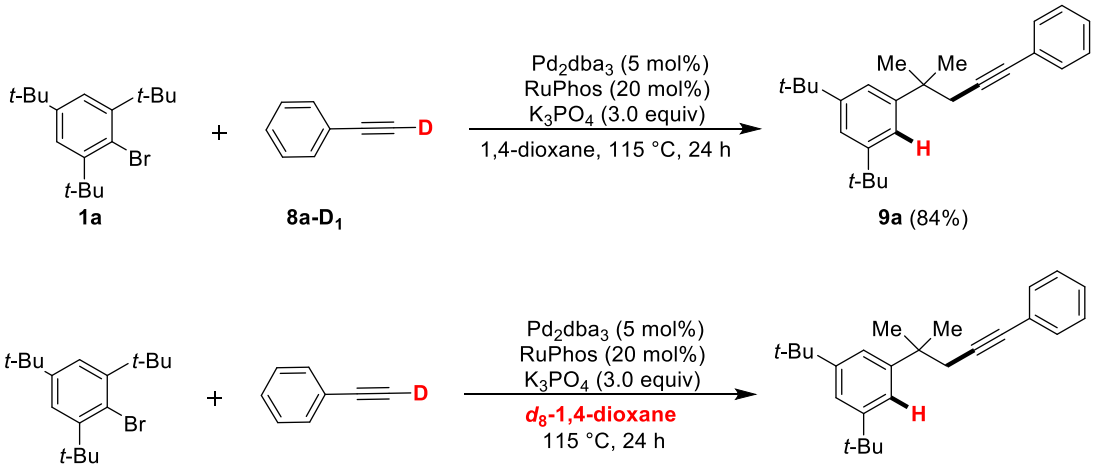
Synthesis of (ethynyl-d)benzene 8a-D_1[4]



8a **8a-D_1**

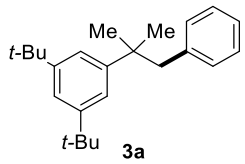
To a solution of phenylacetylene (5.0 mmol, 0.55 mL) in dry THF (25 ml) was added *n*-BuLi (3.43 mL, 5.55 mmol, 1.60 M in hexane solution, 1.1 equiv.) dropwise at −78 ℃ under Ar atmosphere. After being stirred at the same temperature for 30 min, D_2O (2 mL) was added at the room temperature under Ar atmosphere, stirred continuously at the same temperature for 6 h. Then, the organic layer was separated and the aqueous layer was extracted with Et_2O. The combined organic layers were washed with Et_2O (20 mL× 3), dried over anhydrous sodium sulfate and filtered. The solvent was removed under vacuum and the relative integrated intensities of the phenyl protons to the methylidyne protons, which had been 5.0 to 1.0 in the starting phenylacetylene, were now 5.0 to 0, indicating 93% deuteriation at the C–H group and thus a 100% yield of (ethynyl-d)benzene (**8a-D_1**).

H/D-exchanged experiment



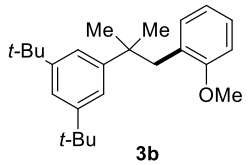
Pd_2dba_3 (0.005 mmol, 4.6 mg), K_3PO_4 (0.30 mmol, 64 mg) and Ruphos (0.02 mmol, 9.4 mg) were carried out in test tube in glove box and then the solution of compound **1a** (0.1 mmol, 33 mg) in 1.0 mL of 1,4-dioxane was added to the test tube at room temperature. Phenylacetylene **8a-D_1** (0.15 mmol) in 1.0 mL 1,4-dioxane and was added dropwise via syringe pump over 2 h at 110 ℃. After addition, the reaction system was stirred at 110 ℃ for another 22 h. It was then filtered through a pad of Celite using CH_2Cl_2. The solvent was removed by reduced pressure

and the residue was purified by column chromatograph (silica gel 8 g; eluent: 100% Hexane) to afford the product **9a** (29.1 mg, 84%). $\mathbf{R_f}$ = 0.8 (Hexane = 100%).



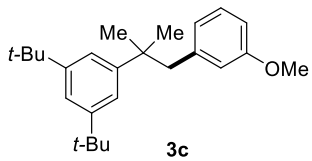
3a

1,3-di-*tert*-butyl-5-(2-methyl-1-phenylpropan-2-yl)benzene (3a): Column chromatography (SiO_2 5 g, eluent: Hexane 100%) afforded **3a** (24.2 mg, 75%) as colorless oil. $\mathbf{R_f}$ = 0.8 (Hexane = 100%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.30 (s, 1H), 7.19-7.11 (m, 5H), 6.80 (m, 2H), 2.87 (s, 2H), 1.38 (s, 6H), 1.34 (s, 18H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 149.8, 147.6, 139.0, 130.4, 127.3, 125.7, 120.4, 119.4, 51.6, 39.1, 34.9, 31.5, 28.1 ppm. Data were in accordance with those reported in the literature.[1]



3b

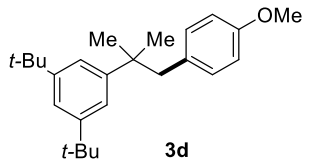
1,3-di-*tert*-butyl-5-(1-(2-methoxyphenyl)-2-methylpropan-2-yl)benzene (3b): Column chromatography (SiO_2 5 g, eluent: Hexane and ethyl acetate (10:1, v/v)) afforded **3b** (32.8 mg, 93%) as colorless oil. $\mathbf{R_f}$ = 0.6 (Hexane/EA = 100/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.24 (s, 1H), 7.16-7.08 (m, 3H), 6.81-6.61 (m, 3H), 3.63 (s, 3H), 2.89 (s, 2H), 1.33 (s, 6H), 1.30 (s, 18H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 158.0, 149.5, 148.4, 132.1, 127.7, 127.0, 120.4, 119.5, 119.3, 110.1, 54.9, 43.7, 39.5, 34.9, 31.6, 28.0 ppm. Data were in accordance with those reported in the literature.[2]



3c

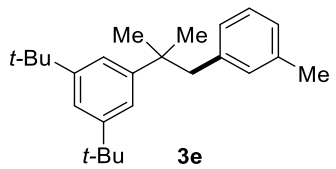
1,3-di-*tert*-butyl-5-(1-(3-methoxyphenyl)-2-methylpropan-2-yl) (3c) Column chromatography (SiO_2 5 g, eluent: Hexane and ethyl acetate (10:1, v/v)) afforded **3c** (24.3 mg, 69%) as colorless oil. $\mathbf{R_f}$ = 0.6 (Hexane/EA = 100/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.27 (s,

J = 2.5 Hz, 1H), 7.10 (d, J = 1.7 Hz, 2H), 7.05 (t, J = 7.9 Hz, 1H), 6.67 (dd, J = 7.9, 2.2 Hz, 1H), 6.46 (d, J = 7.5 Hz, 1H), 6.07 (s, 1H), 3.54 (s, 3H), 2.81 (s, 2H), 1.36 (s, 6H), 1.30 (s, 18H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 158.6, 149.8, 147.5, 140.5, 128.1, 122.9, 120.6, 119.4, 115.1, 111.9, 54.7, 51.7, 39.1, 34.9, 31.5, 28.2 ppm. **HRMS** *m/z* (HESI-II) calcd. for $C_{25}H_{36}O$ $[M+Na]^+$: 375.2659; found: 375.2658.



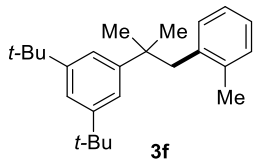
3d

1,3-di-*tert*-butyl-5-(1-(4-methoxyphenyl)-2-methylpropan-2-yl)benzene (3d): Column chromatography (SiO_2 5 g, eluent: Hexane and ethyl acetate (10:1, v/v)) afforded **3d** (22.6 mg, 64%) as colorless oil. **R_f =** 0.6 (Hexane/EA = 100/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.25 (s, 1H), 7.10 (s, 2H), 6.67 (s, 4H), 3.75 (s, 3H), 2.76 (s, 2H), 1.32 (s, 6H), 1.30 (s, 18H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 157.7, 149.7, 147.7, 131.3, 131.2, 120.5, 119.3, 112.8, 55.2, 50.6, 39.1, 34.9, 31.6, 28.0 ppm. Data were in accordance with those reported in the literature.[2]



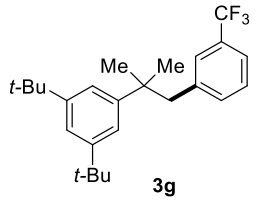
3e

1,3-di-*tert*-butyl-5-(2-methyl-1-(*m*-tolyl)propan-2-yl)benzene (3e): Column chromatography (SiO_2 5 g, eluent: Hexane 100%) afforded **3e** (21.2 mg, 63%) as colorless oil. **R_f =** 0.8 (Hexane 100%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.25 (s, 1H), 7.12 (d, J = 1.7 Hz, 2H), 7.03 (t, J = 7.5 Hz, 1H), 6.93 (d, J = 7.5 Hz, 1H), 6.62 (d, J = 7.5 Hz, 1H), 6.51 (s, 1H), 2.79 (s, 2H), 2.19 (s, 3H), 1.34 (s, 6H), 1.30 (s, 18H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 149.3, 147.4, 138.5, 136.2, 130.9, 127.0, 126.8, 126.0, 120.0, 119.0, 51.0, 38.6, 34.5, 31.1, 27.7, 20.9 ppm. **HRMS** *m/z* (APCI II with DIP) calcd. for $C_{25}H_{36}$ $[M+H]^+$: 337.2890; found: 337.2889.



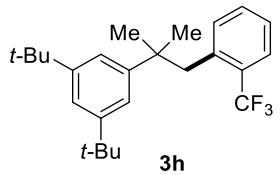
3f

1,3-di-*tert*-butyl-5-(2-methyl-1-(*o*-tolyl)propan-2-yl)benzene (3f): Column chromatography (SiO_2 5 g, eluent: Hexane 100%) afforded **3f** (25.2 mg, 75%) as colorless oil. $\mathbf{R_f}$ = 0.8 (Hexane 100%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.25 (s, 1H), 7.08-6.97 (m, 5H), 6.84 (d, *J* = 7.4 Hz, 1H), 2.83 (s, 2H), 1.74 (s, 3H), 1.43 (s, 6H), 1.27 (s, 18H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 149.7, 147.2, 137.7, 137.3, 131.4, 130.1, 125.8, 124.8, 120.5, 119.5, 47.5, 39.7, 34.9, 31.4, 28.5, 19.4 ppm. **HRMS** *m/z* (APCI II with DIP) calcd. for $C_{25}H_{36}$ $[M+H]^+$: 337.2890; found: 337.2889.



3g

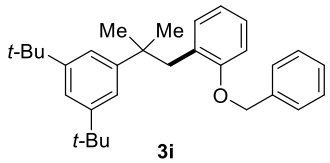
1,3-di-*tert*-butyl-5-(2-methyl-1-(3-(trifluoromethyl)phenyl)propan-2-yl)benzene (3g): Column chromatography (SiO_2 5 g, eluent: Hexane 100%) afforded **3g** (32.4 mg, 83%) as colorless oil. $\mathbf{R_f}$ = 0.7 (Hexane 100%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.35 (d, *J* = 7.7 Hz, 1H), 7.27 (s, 1H), 7.21 (t, *J* = 7.7 Hz, 1H), 7.06 (s, 2H), 6.93 (d, *J* = 7.6 Hz, 1H), 6.82 (s, 1H), 2.89 (s, 2H), 1.37 (s, 6H), 1.28 (s, 18H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 150.1, 146.3, 139.8, 133.5, 129.58 (q, *J* =2.0 Hz), 127.6, 126.7 (q, *J* = 5.0 Hz), 124.2 (q, *J* = 272.2 Hz), 122.52 (q, *J*= 5.0Hz), 120.4, 119.8, 51.4, 39.2, 34.9, 31.5, 28.2 ppm. **^{19}F NMR** (471 MHz, $CDCl_3$) δ = –62.53 (s) ppm. **HRMS** *m/z* (APCI II with DIP) calcd. for $C_{25}H_{33}F_3$ $[M+H]^+$: 391.2607; found: 391.2601.



3h

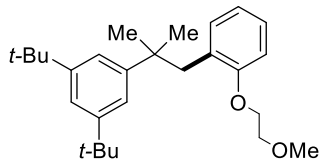
1,3-di-*tert*-butyl-5-(2-methyl-1-(2-(trifluoromethyl)phenyl)propan-2-yl)benzene (3h): Column chromatography (SiO_2 5 g, eluent: Hexane 100%) afforded **3h** (36.7 mg, 94%) as

colorless oil. **R_f =** 0.7 (Hexane 100%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.60 (d, *J* = 7.8 Hz, 1H), 7.32 (s, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.19 (d, *J* = 1.7 Hz, 2H), 7.14 (t, *J* = 7.5 Hz, 1H), 6.44 (d, *J* = 7.8 Hz, 1H), 3.14 (s, 2H), 1.38 (s, 6H), 1.34 (s, 18H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 150.1, 147.9, 138.1, 131.8, 130.5, 129.43 (q, *J* = 29.0 Hz) 125.73 (q, *J* = 4 Hz), 124.69 (q, *J* = 290.0 Hz), 120.7, 119.6, 45.8, 45.7, 39.5, 35.0, 31.5, 28.7 ppm. **^{19}F NMR** (471 MHz, $CDCl_3$) δ = –57.11 (s) ppm. **HRMS** *m/z* (APCI II with DIP) calcd. for $C_{25}H_{33}F_3$ $[M+H]^+$: 391.2607; found: 391.2613.



3i

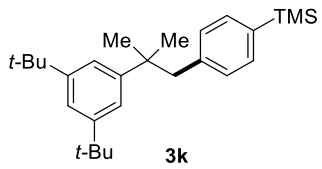
1-(1-(2-(benzyloxy)phenyl)-2-methylpropan-2-yl)-3,5-di-*tert*-butylbenzene (3i): Column chromatography (SiO_2 5 g, eluent: Hexane 100%) afforded **3i** (16.3 mg, 38%) as colorless oil. **R_f =** 0.8 (Hexane/EA =20/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.39 (ddd, *J* = 27.2, 19.4, 7.3 Hz, 6H), 7.18 (d, *J* = 1.4 Hz, 2H), 7.14 (t, *J* = 8.4 Hz, 1H), 6.90 (d, *J* = 8.2 Hz, 1H), 6.77 (t, *J* = 7.4 Hz, 1H), 6.70 (d, *J* = 8.5 Hz, 1H), 5.00 (s, 2H), 2.96 (s, 2H), 1.33 (s, 6H), 1.30 (s, 18H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 157.4, 149.7, 148.9, 137.7, 132.4, 128.5, 128.1, 127.7, 127.1, 127.1, 120.4, 120.0, 119.4, 111.5, 70.0, 43.8, 39.7, 35.0, 31.6, 27.8 ppm. **HRMS** *m/z* (HESI-II) calcd. for $C_{31}H_{40}O$ $[M+Na]^+$: 451.2972; found: 451.2971.



3j

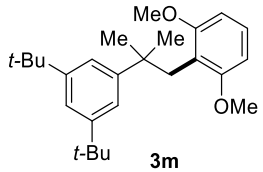
1,3-di-*tert*-butyl-5-(1-(2-(2-methoxyethoxy)phenyl)-2-methylpropan-2-yl)benzene (3j): Column chromatography (SiO_2 5 g, eluent: Hexane 100%) afforded **3j** (25.4 mg, 64%) as colorless oil. **R_f =** 0.8 (Hexane/EA = 50/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.25 (s, 1H), 7.17-7.04 (m, 4H), 6.82-6.74 (m, 1H), 6.67 (d, *J* = 7.4 Hz, 1H), 5.02 (s, 2H), 3.68 (q, *J* = 7.1 Hz, 2H), 2.91 (s, 2H), 1.35 (s, 6H), 1.31 (s, 18H), 1.23 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 156.3, 149.6, 148.4, 132.1, 128.2, 127.1, 120.6, 120.4, 119.4, 113.8, 93.4,

64.0, 43.7, 39.5, 34.9, 31.6, 28.1, 15.1 ppm. **HRMS** *m/z* (HESI-II) calcd. for $C_{27}H_{40}O_2$ $[M+Na]^+$: 419.2920; found: 419.2921.



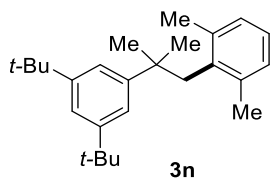
3k

(4-(2-(3,5-di-*tert*-butylphenyl)-2-methylpropyl)phenyl)trimethylsilane (3k): Column chromatography (SiO_2 5 g, eluent: Hexane 100%) afforded **3k** (27.6 mg, 70%) as colorless oil. **R_f =** 0.8 (Hexane 100%). **^{1}H NMR** (400 MHz, CD_2Cl_2) δ = 7.31-7.22 (m, 3H), 7.06 (s, 2H), 6.75 (d, *J* = 7.8 Hz, 2H), 2.80 (s, 2H), 1.33 (s, 6H), 1.27 (s, 18H), 0.21 (s, 9H) ppm. **^{13}C NMR** (101 MHz, CD_2Cl_2) δ = 150.4, 148.1, 140.3, 137.6, 132.9, 130.4, 121.0, 119.9, 51.8, 39.7, 35.4, 31.8, 28.6, –0.9 ppm. **HRMS** *m/z* (APCI II with DIP) calcd. for $C_{27}H_{42}Si$ $[M+H]^+$: 395.3129; found: 395.3132.



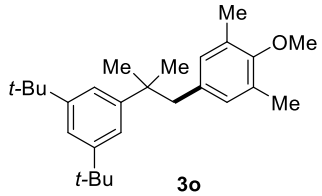
3m

2-(2-(3,5-di-*tert*-butylphenyl)-2-methylpropyl)-1,3-dimethoxybenzene (3m): Column chromatography (SiO_2 5 g, eluent: Hexane 100%) afforded **3m** (37.5 mg, 98%) as colorless oil. **R_f =** 0.8 (Hexane/EA = 20/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.24 (s, 1H), 7.20 (s, 2H), 7.12 (t, *J* = 8.3 Hz, 1H), 6.48 (d, *J* = 8.3 Hz, 2H), 3.60 (s, 6H), 2.97 (s, 2H), 1.33 (s, 6H), 1.32 (s, 18H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 159.0, 149.6, 149.1, 126.8, 120.2, 119.1, 116.4, 103.3, 55.1, 40.1, 36.7, 34.9, 31.6, 28.5 ppm. **HRMS** *m/z* (HESI-II) calcd. for $C_{26}H_{38}O_2$ $[M+Na]^+$: 405.2766; found: 405.2764.



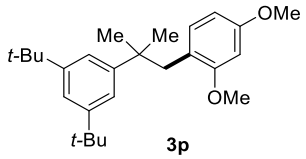
3n

2-(2-(3,5-di-*tert*-butylphenyl)-2-methylpropyl)-1,3-dimethylbenzene (3n): Column chromatography (SiO_2 5 g, eluent: Hexane 100%) afforded **3n** (27.0 mg, 77%) as colorless oil. **R_f =** 0.8 (Hexane 100%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.25 (s, 1H), 6.99-6.94 (m, 3H), 6.89 (d, *J* = 7.4 Hz, 2H), 2.92 (s, 2H), 1.85 (s, 6H), 1.47 (s, 6H), 1.25 (s, 18H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 149.7, 147.5, 138.4, 136.3, 128.1, 125.4, 120.7, 119.6, 43.3, 40.9, 34.8, 31.4, 29.4, 20.7 ppm. **HRMS** *m/z* (APCI II with DIP) calcd. for $C_{26}H_{38}$ $[M+H]^+$: 351.3046; found: 351.3041.



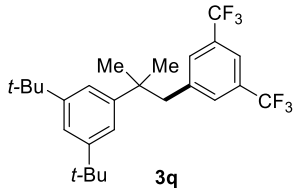
3o

5-(2-(3,5-di-*tert*-butylphenyl)-2-methylpropyl)-2-methoxy-1,3-dimethylbenzene (3o): Column chromatography (SiO_2 5 g, eluent: Hexane 100%) afforded **3o** (26.6 mg, 70%) as colorless oil. **R_f =** 0.7 (Hexane/EA = 50/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.27 (s, 1H), 7.12 (d, *J* = 1.7 Hz, 2H), 6.36 (s, 2H), 3.66 (s, 3H), 2.72 (s, 2H), 2.14 (s, 6H), 1.36 (s, 6H), 1.32 (s, 18H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 155.0, 149.7, 147.7, 134.3, 130.8, 129.1, 120.5, 119.3, 59.6, 50.9, 39.0, 34.9, 31.5, 28.1, 16.0 ppm. **HRMS** *m/z* (HESI-II) calcd. for $C_{27}H_{40}O$ $[M+Na]^+$: 403.2972; found: 403.2971.



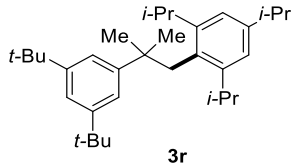
3p

1-(2-(3,5-di-*tert*-butylphenyl)-2-methylpropyl)-2,4-dimethoxybenzene (3p): Column chromatography (SiO_2 5 g, eluent: Hexane 100%) afforded **3p** (33.3 mg, 87%) as colorless oil. **R_f =** 0.7 (Hexane/EA = 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.25 (s, 1H), 7.14 (d, *J* = 1.5 Hz, 2H), 6.55 (d, *J* = 8.3 Hz, 1H), 6.38 (d, *J* = 2.3 Hz, 1H), 6.29 (dd, *J* = 8.3, 2.4 Hz, 1H), 3.77 (s, 3H), 3.63 (s, 3H), 2.82 (s, 2H), 1.32 (s, 24H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 159.0, 158.9, 149.4, 148.6, 132.2, 120.4, 120.2, 119.2, 103.3, 98.0, 55.3, 55.0, 43.1, 39.5, 34.9, 31.6, 27.9 ppm. **HRMS** *m/z* (HESI-II) calcd. for $C_{26}H_{38}O_2$ $[M+Na]^+$: 405.2763; found: 405.2764.



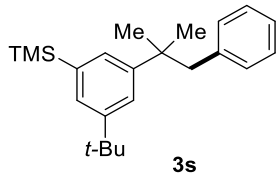
3q

1-(1-(3,5-bis(trifluoromethyl)phenyl)-2-methylpropan-2-yl)-3,5-di-*tert*-butylbenzene (3q): Column chromatography (SiO_2 5 g, eluent: Hexane 100%) afforded **3q** (31.2 mg, 68%) as colorless oil. $\mathbf{R_f}$ = 0.8 (Hexane 100%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.58 (s, 1H), 7.28 (s, 1H), 7.04–7.01 (m, 4H), 2.96 (s, 2H), 1.40 (s, 6H), 1.27 (s, 18H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 150.4, 145.3, 141.3, 130.5, 130.2, 139.9, 122.0 (q, J = 341.5 Hz), 119.65 (q, J = 2.5 Hz), 51.2, 39.3, 34.9, 31.6, 31.4, 28.1 ppm. **^{19}F NMR** (471 MHz, $CDCl_3$) δ = –62.82 (s) ppm. **HRMS** *m/z* (APCI II with DIP) calcd. for $C_{26}H_{32}F_6$ $[M+H]^+$: 459.2481; found: 459.2470.



3r

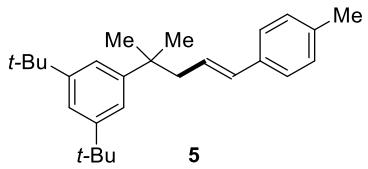
2-(2-(3,5-di-*tert*-butylphenyl)-2-methylpropyl)-1,3,5-triisopropylbenzene (3r): Column chromatography (SiO_2 5 g, eluent: Hexane 100%) afforded **3r** (42.6 mg, 95%) as colorless oil. $\mathbf{R_f}$ = 0.8 (Hexane 100%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.18 (s, 1H), 6.95 (s, 2H), 6.88 (s, 2H), 3.01 (s, 2H), 2.96–2.78 (m, 3H), 1.46 (s, 6H), 1.22 (d, J = 5.2 Hz, 24H), 0.97 (d, J = 6.7 Hz, 12H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 148.7, 147.6, 147.1, 145.6, 130.2, 120.6, 120.6, 120.0, 119.1, 39.8, 39.6, 34.4, 33.7, 31.1, 30.0, 29.4, 23.7 ppm. **HRMS** *m/z* (APCI II with DIP) calcd. for $C_{33}H_{52}$ $[M+H]^+$: 449.4142; found: 449.4060.



3s

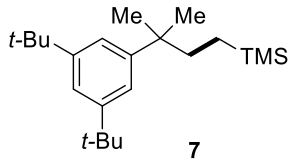
(3-(*tert*-butyl)-5-(2-methyl-1-phenylpropan-2-yl)phenyl)trimethylsilane (3s): Column chromatography (SiO_2 5 g, eluent: Hexane 100%) afforded **3s** (27.1 mg, 80%) as colorless oil. $\mathbf{R_f}$ = 0.8 (Hexane 100%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.38 (s, 1H), 7.33 (d, J = 14.0 Hz, 1H), 7.27 (s, 1H), 7.16-7.11 (m, 3H), 6.79 (dt, J = 7.0, 3.4 Hz, 2H), 2.84 (s, 2H), 1.34 (s, 6H),

1.30 (s, 9H), 0.25 (s, 9H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 149.4, 147.4, 139.0, 130.5, 128.1, 127.4, 127.2, 125.8, 124.1, 51.4, 38.9, 34.8, 31.5, 31.5, 28.1, 0.9 ppm. **HRMS** *m/z* (APCI II with DIP) calcd. for $C_{23}H_{34}Si$ $[M+H]^+$: 339.2430; found: 339.2436.



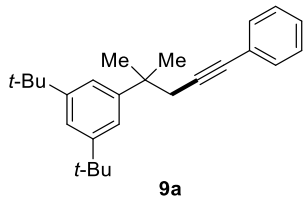
5

(*E*)-1,3-di-*tert*-butyl-5-(2-methyl-5-(*p*-tolyl)pent-4-en-2-yl)benzene (5): Column chromatography (SiO_2 5 g, eluent: Hexane 100%) afforded **5** (24.7 mg, 68%) as colorless oil. **R_f =** 0.8 (Hexane 100%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.27 (s, 1H), 7.24 (d, *J* = 1.6 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.32 (d, *J* = 15.8 Hz, 1H), 5.99 (dt, *J* = 15.4, 7.4 Hz, 1H), 2.48 (d, *J* = 7.4 Hz, 2H), 2.31 (s, 3H), 1.36 (s, 6H), 1.34 (s, 18H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 149.9, 136.5, 131.8, 139.3, 139.1, 126.9, 125.8, 120.0, 119.4, 48.2, 38.5, 35.0, 31.6, 30.3, 28.6, 21.1 ppm. **HRMS** *m/z* (HESI-II) calcd. for $C_{27}H_{38}$ $[M+Na]^+$: 385.2865; found: 385.2866.



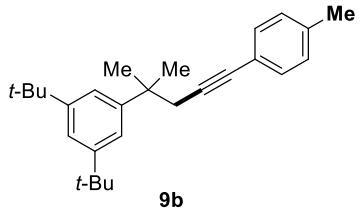
7

(3-(3,5-di-*tert*-butylphenyl)-3-methylbutyl)trimethylsilane (7): Column chromatography (SiO_2 5 g, eluent: Hexane 100%) afforded **7** (26.6 mg, 80%) as colorless oil. **R_f =** 0.8 (Hexane 100%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.24 (s, 1H), 7.17 (d, *J* = 1.7 Hz, 2H), 1.62-1.57 (m, 2H), 1.34 (s, 18H), 1.29 (s, 6H), 0.30-0.22 (m, 2H), –0.06 (s, 9H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 149.7, 148.3, 120.2, 119.1, 38.9, 38.4, 34.9, 31.6, 28.7, 10.9, –1.9 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{22}H_{40}Si$ $[M+H]^+$: 333.2972; found: 333.2972.



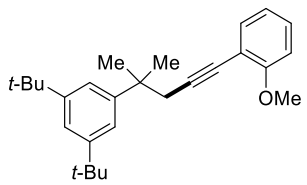
9a

1,3-di-*tert*-butyl-5-(2-methyl-5-phenylpent-4-yn-2-yl)benzene (9a): Column chromatography (SiO_2 5 g, eluent: Hexane 100%) afforded **9a** (32.6 mg, 94%) as yellow oil; **R_f =** 0.8 (Hexane 100%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.34 (d, *J* = 4.9 Hz, 2H), 7.30 (s, 2H), 7.23 (s, 3H), 2.68 (s, 2H), 1.48 (s, 6H), 1.31 (s, 18H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 150.0, 147.5, 131.5, 128.1, 127.5, 124.0, 119.9, 119.9, 88.6, 82.5, 38.4, 35.0, 34.9, 31.6, 28.5 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{26}H_{34}$ $[M+H]^+$: 347.2733; found: 347.2732.



9b

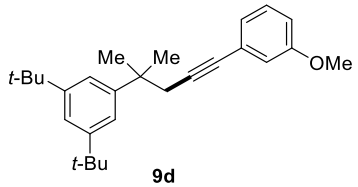
1,3-di-*tert*-butyl-5-(2-methyl-5-(p-tolyl)pent-4-yn-2-yl)benzene (9b): Column chromatography (SiO_2 5 g, eluent: Hexane 100%) afforded **9b** (33.5 mg, 93%) as colourless oil; **R_f =** 0.8 (Hexane 100%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.31 (s, 2H), 7.25 (d, *J* = 7.4 Hz, 3H), 7.07 (d, *J* = 7.6 Hz, 2H), 2.69 (s, 2H), 2.32 (s, 3H), 1.49 (s, 6H), 1.33 (s, 18H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 150.0, 147.6, 137.4, 131.4, 128.9, 121.0, 119.9, 119.9, 87.8, 82.5, 38.4, 35.0, 34.9, 31.6, 28.5, 21.4 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{27}H_{36}$ $[M+H]^+$: 361.2890; found: 361.2884.



9c

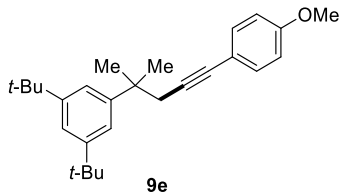
1,3-di-*tert*-butyl-5-(5-(2-methoxyphenyl)-2-methylpent-4-yn-2-yl)benzene (9c): Column chromatography (SiO_2 5 g, eluent: Hexane 100%) afforded **9c** (35.1 mg, 93%) as colourless oil; **R_f =** 0.6 (Hexane/EA = 100/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.31 (d, *J* = 10.3 Hz, 3H), 7.28

(s, 1H), 7.26 – 7.19 (m, 1H), 6.85 (t, *J* = 8.4 Hz, 2H), 3.85 (s, 3H), 2.76 (s, 2H), 1.52 (s, 6H), 1.33 (s, 18H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 159.9, 150.0, 147.7, 133.5, 128.8, 120.3, 119.9, 119.9, 113.2, 110.5, 92.9, 78.6, 55.7, 38.5, 35.2, 35.0, 31.5, 28.4 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{27}H_{36}O$ $[M+H]^+$: 377.2839; found: 377.2835.



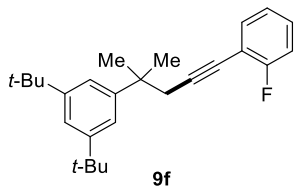
9d

1,3-di-*tert*-butyl-5-(5-(3-methoxyphenyl)-2-methylpent-4-yn-2-yl)benzene (9d): Column chromatography (SiO_2 5 g, eluent: Hexane 100%) afforded **9d** (35.8 mg, 95%) as colourless oil; **R_f =** 0.6 (Hexane/EA = 100/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.29 (d, *J* = 13.2 Hz, 3H), 7.16 (t, *J* = 7.9 Hz, 1H), 6.95 (d, *J* = 7.5 Hz, 1H), 6.88 (s, 1H), 6.81 (d, J = 8.3 Hz, 1H), 3.77 (s, 3H), 2.69 (s, 2H), 1.49 (s, 6H), 1.33 (s, 18H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 159.2, 150.0, 147.5, 129.2, 125.0, 124.1, 119.9, 119.9, 116.3, 114.1, 88.5, 82.4, 55.2, 38.4, 35.0, 34.9, 31.6, 28.5 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{27}H_{36}O$ $[M+H]^+$: 377.2839; found: 377.2834.



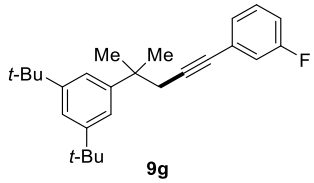
9e

1,3-di-*tert*-butyl-5-(5-(4-methoxyphenyl)-2-methylpent-4-yn-2-yl)benzene (9e): Column chromatography (SiO_2 5 g, eluent: Hexane 100%) afforded **9d** (30.2 mg, 80%) as colourless liquid; **R_f =** 0.6 (Hexane/EA = 100/1) **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.31 – 7.28 (m, 5H), 6.79 (d, *J* = 8.3 Hz, 2H), 3.78 (s, 3H), 2.68 (s, 2H), 1.49 (s, 6H), 1.33 (s, 18H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 158.9, 150.0, 147.6, 132.8, 119.9, 116.2, 113.7, 86.9, 82.2, 55.2, 38.4, 35.0, 34.9, 31.6, 28.5 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{27}H_{36}O$ $[M+H]^+$: 377.2839; found: 377.2835.



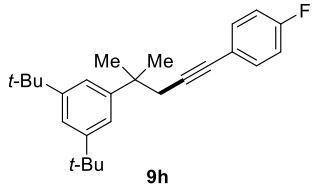
9f

1,3-di-*tert*-butyl-5-(5-(2-fluorophenyl)-2-methylpent-4-yn-2-yl)benzene (9f): Column chromatography (SiO_2 5 g, eluent: hexane 100%) afforded **9f** (31.0 mg, 85%) as colourless liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.38 – 7.35 (m, 3H), 7.32 (s, 1H), 7.26 (dd, *J* = 13.8, 7.8 Hz, 1H), 7.07 (t, *J* = 8.2 Hz, 2H), 2.77 (s, 2H), 1.55 (s, 6H), 1.36 (s, 18H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 163.9, 161.9, 150.1, 147.5, 133.5, 129.1, 129.1, 123.7, 123.7, 120.0, 120.0, 115.4, 115.3, 112.6, 112.5, 94.2, 94.2, 75.8, 38.4, 35.1, 35.0, 31.6, 31.6, 28.4, 22.7, 14.2 ppm. **^{19}F NMR** (471 MHz, $CDCl_3$) δ = -110.76 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{26}H_{33}F$ $[M+H]^+$: 365.2639; found: 365.2642.



9g

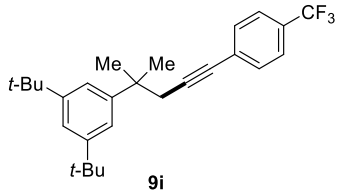
1,3-di-*tert*-butyl-5-(5-(3-fluorophenyl)-2-methylpent-4-yn-2-yl)benzene (9g): Column chromatography (SiO_2 5 g, eluent: Hexane 100%) afforded **9g** (32.9 mg, 90%) as colourless liquid; **R_f =** 0.8 (Hexane 100%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.30 (s, 3H), 7.21 (dd, *J* = 14.5, 7.3 Hz, 1H), 7.11 (d, *J* = 7.6 Hz, 1H), 7.02 (d, *J* = 9.5 Hz, 1H), 6.96 (t, *J* = 8.4 Hz, 1H), 2.69 (s, 2H), 1.49 (s, 6H), 1.33 (s, 18H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 163.3, 161.3, 150.1, 147.3, 129.7, 129.6, 127.4, 127.4, 125.9, 125.9, 120.0, 119.8, 118.4, 118.2, 114.9, 114.7, 89.9, 81.5, 81.4, 38.4, 35.0, 34.9, 31.6, 28.6 ppm. **^{19}F NMR** (471 MHz, $CDCl_3$) δ = −113.52 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{26}H_{33}F$ $[M+H]^+$: 365.2639; found: 365.2638.



9h

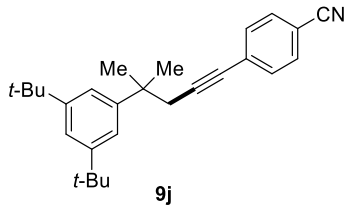
1,3-di-*tert*-butyl-5-(5-(4-fluorophenyl)-2-methylpent-4-yn-2-yl)benzene (9h): Column chromatography (SiO_2 5 g, eluent: Hexane 100%) afforded **9h** (33.9 mg, 93%) as yellow solid: m.p. 54–56 °C; **R_f =** 0.8 (Hexane 100%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.31 (dd, *J* = 11.5,

5.7 Hz, 5H), 6.95 (t, *J* = 8.2 Hz, 1H), 2.68 (s, 2H), 1.49 (s, 6H), 1.33 (s, 18H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 163.0, 161.0, 150.0, 147.4, 133.3, 133.2, 127.9, 127.9, 119.9, 119.8, 115.4, 115.2, 88.3, 81.4, 38.4, 35.0, 34.8, 31.6, 28.5 ppm. **^{19}F NMR** (471 MHz, $CDCl_3$) δ = −112.34 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{26}H_{33}F$ $[M+H]^+$: 365.2639; found: 365.2642.



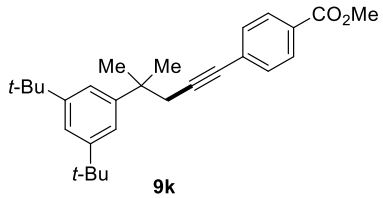
9i

1,3-di-*tert*-butyl-5-(2-methyl-5-(4-(trifluoromethyl)phenyl)pent-4-yn-2-yl)benzene (9i): Column chromatography (SiO_2 5 g, eluent: Hexane 100%) afforded **9i** (39.0 mg, 94%) as yellow solid: m.p. 61–63 °C; **R_f =** 0.8 (Hexane 100%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.51 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.30 (s, 3H), 2.72 (s, 2H), 1.50 (s, 6H), 1.33 (s, 18H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 150.1, 147.2, 131.7, 129.3, 129.1, 127.9, 125.1, 125.0 120.0, 119.8, 91.6, 81.4, 38.4, 35.0, 34.9, 31.6, 28.6 ppm. **^{19}F NMR** (471 MHz, $CDCl_3$) δ = −62.70 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{27}H_{33}F_3$ $[M+H]^+$: 415.2607; found: 415.2606.



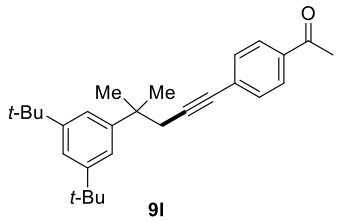
9j

4-(4-(3,5-di-*tert*-butylphenyl)-4-methylpent-1-yn-1-yl)benzonitrile (9j): Column chromatography (SiO_2 5 g, eluent: Hexane/Et_2O = 50/1) afforded **9j** (28.0 mg, 75%) as white solid: m.p. 89–91 °C; **R_f =** 0.7 (Hexane 100%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.55 – 7.53 (m, 2H), 7.40 – 7.38 (m, 2H), 7.29 (s, 3H), 2.73 (s, 2H), 1.49 (s, 6H), 1.33 (s, 18H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 150.2, 147.1, 132.1, 131.9, 129.1, 120.1, 119.8, 118.7, 110.8, 94.1, 81.4, 38.5, 35.0, 31.6, 28.7 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{27}H_{33}N$ $[M+H]^+$: 372.2686; found: 372.2689.



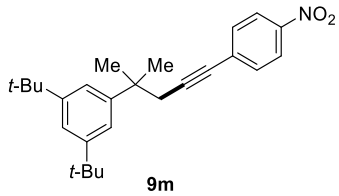
9k

methyl 4-(4-(3,5-di-*tert*-butylphenyl)-4-methylpent-1-yn-1-yl)benzoate (9k): Column chromatography (SiO_2 5 g, eluent: Hexane/Et_2O = 100/1) afforded **9k** (38.0 mg, 94%) as white solid: m.p. 68–70 °C; $\mathbf{R_f}$ = 0.6 (Hexane/EA = 10/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.93 (d, *J* = 7.7 Hz, 2H), 7.39 (d, *J* = 7.7 Hz, 2H), 7.30 (d, *J* = 5.6 Hz, 3H), 3.90 (s, 3H), 2.72 (s, 2H), 1.50 (s, 6H), 1.33 (s, 18H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 166.7, 150.1, 147.2, 131.4, 129.3, 128.9, 128.8, 120.0, 119.8, 92.3, 82.0, 52.1, 38.4, 35.0, 31.6, 28.6 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{28}H_{36}O_2$ $[M+H]^+$: 405.2788; found: 405.2783.



9l

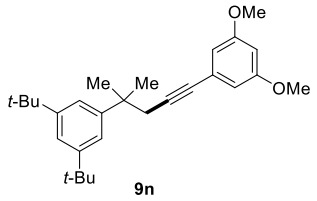
1-(4-(4-(3,5-di-*tert*-butylphenyl)-4-methylpent-1-yn-1-yl)phenyl)ethan-1-one (9l): Column chromatography (SiO_2 5 g, eluent: Hexane/Et_2O = 50/1) afforded **9l** (32.0 mg, 82%) as white solid: m.p. 88–90 °C; $\mathbf{R_f}$ = 0.7 (Hexane/EA = 50/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.86 (d, *J* = 7.7 Hz, 2H), 7.41 (d, *J* = 7.7 Hz, 2H), 7.30 (d, *J* = 5.0 Hz, 3H), 2.73 (s, 2H), 2.58 (s, 3H), 1.50 (s, 6H), 1.33 (s, 18H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 197.4, 150.1, 147.2, 135.6, 131.6, 129.1, 128.1, 120.0, 119.8, 92.7, 82.0, 38.4, 35.0, 35.0, 31.6, 28.6, 26.6 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{28}H_{36}O$ $[M+H]^+$: 389.2839; found: 389.2835.



9m

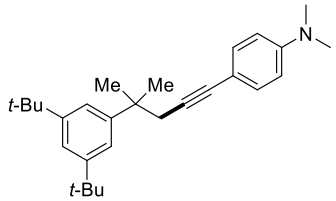
1,3-di-*tert*-butyl-5-(2-methyl-5-(4-nitrophenyl)pent-4-yn-2-yl)benzene (9m): Column chromatography (SiO_2 5 g, eluent: Hexane/Et_2O = 100/1) afforded **9m** (29.0 mg, 74%) as yellow solid: m.p. 123–125 °C; $\mathbf{R_f}$ = 0.5 (Hexane/EA = 100/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ

= 8.13 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.30 (s, 3H), 2.75 (s, 2H), 2.58 (s, 3H), 1.50 (s, 6H), 1.33 (s, 18H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 150.2, 147.0, 146.5, 132.2, 131.1, 123.4, 120.1, 119.8, 95.1, 81.2, 38.5, 35.0, 35.0, 31.6, 28.7 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{26}H_{33}NO_2$ $[M+H]^+$: 392.2584; found: 392.2587.



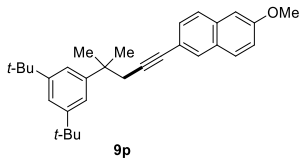
9n

1,3-di-*tert*-butyl-5-(5-(3,5-dimethoxyphenyl)-2-methylpent-4-yn-2-yl)benzene (9n): Column chromatography (SiO_2 5 g, eluent: Hexane/Et_2O = 10/1) afforded **9n** (38.0 mg, 93%) as colourless liquid; **R_f =** 0.6 (Hexane/EA = 50/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.35 (d, *J* = 13.8 Hz, 3H), 6.57 (s, 2H), 6.44 (s, 1H), 3.80 (s, 6H), 2.74 (s, 2H), 1.54 (s, 6H), 1.39 (s, 18H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 160.4, 150.0, 147.4, 125.3, 119.9, 119.9, 109.3, 101.1, 88.3, 82.5, 55.3, 38.4, 35.0, 34.8, 31.6, 28.6 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{28}H_{38}O_2$ $[M+H]^+$: 407.2945; found: 407.2942.



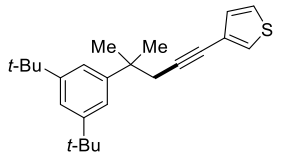
9o

4-(4-(3,5-di-*tert*-butylphenyl)-4-methylpent-1-yn-1-yl)-N,N-dimethylaniline (9o): Column chromatography (SiO_2 5 g, eluent: Hexane/Et_2O = 100/1) afforded **9o** (30.0 mg, 77%) as colourless liquid; **R_f =** 0.6 (Hexane/EA = 50/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.32 (s, 2H), 7.28 (s, 1H), 7.24 (d, *J* = 7.2 Hz, 2H), 2.94 (s, 6H), 2.68 (s, 2H), 1.48 (s, 6H), 1.33 (s, 18H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 149.9, 149.6, 147.8, 132.5, 119.9, 119.8, 111.9, 111.3, 85.8, 83.0, 40.3, 38.4, 35.0, 31.6, 28.5 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{28}H_{39}N$ $[M+H]^+$: 390.3155; found: 390.3147.



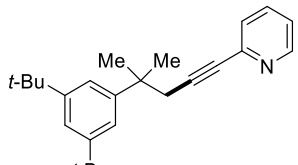
9p

2-(4-(3,5-di-*tert*-butylphenyl)-4-methylpent-1-yn-1-yl)-6-methoxynaphthalene (9p): Column chromatography (SiO_2 5 g, eluent: Hexane/Et_2O = 100/1) afforded **9p** (36.0 mg, 84%) as white solid: m.p. 109−111 °C; $\mathbf{R_f}$ = 0.6 (Hexane/EA = 100/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.79 (s, 1H), 7.63 (t, *J* = 10.1 Hz, 2H), 7.37 (d, *J* = 7.3 Hz, 1H), 7.34 (s, 2H), 7.30 (s, 1H), 7.12 (d, *J* = 8.9 Hz, 1H), 7.08 (s, 1H), 3.90 (s, 3H), 2.74 (s, 2H), 1.53 (s, 6H), 1.34 (s, 18H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 157.9, 150.0, 147.5, 133.7, 130.8, 129.3, 129.1, 128.5, 126.5, 119.9, 119.2, 119.0, 105.7, 88.2, 82.9, 55.3, 38.5, 35.0, 31.6, 28.6 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{31}H_{38}O$ $[M+H]^+$: 427.2995; found: 427.2992.



9q

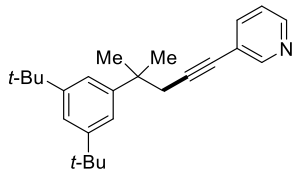
3-(4-(3,5-di-*tert*-butylphenyl)-4-methylpent-1-yn-1-yl)thiophene (9q): Column chromatography (SiO_2 5 g, eluent: Hexane 100%) afforded **9q** (27.0 mg, 77%) as colourless liquid; $\mathbf{R_f}$ = 0.7 (Hexane 100%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.33 (d, *J* = 1.2 Hz, 3H), 7.30 (d, *J* = 7.7 Hz, 1H), 7.24 (dd, *J* = 4.9, 3.0 Hz, 1H), 7.06 (d, *J* = 4.9 Hz, 1H), 2.68 (s, 2H), 1.48 (s, 6H), 1.33 (s, 18H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 150.0, 147.4, 130.0, 127.5, 124.9, 123.0, 119.9, 119.9, 119.0, 88.1, 77.5, 38.3, 35.0, 34.9, 31.6, 28.5 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{24}H_{32}S$ $[M+H]^+$: 353.2298; found: 353.2301.



9r

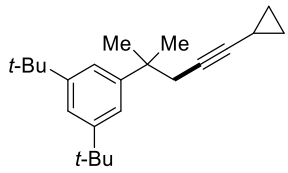
2-(4-(3,5-di-*tert*-butylphenyl)-4-methylpent-1-yn-1-yl)pyridine (9r): Column chromatography (SiO_2 5 g, eluent: Hexane/Et_2O = 15/1) afforded **9r** (28.9 mg, 83%) as colourless liquid; $\mathbf{R_f}$ = 0.8 (Hexane/EA = 100/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.54 (d, *J* =

5.0 Hz, 1H), 7.59 (t, *J* = 8.0 Hz, 1H), 7.31 – 7.29 (m, 4H), 7.17 (t, *J* = 6.0 Hz, 1H), 2.74 (s, 2H), 1.52 (s, 6H), 1.33 (s, 18H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 150.1, 149.8, 147.3, 143.9, 135.9, 126.9, 122.2, 120.0, 119.8, 89.3, 82.3, 38.3, 35.0, 34.8, 31.5, 28.5 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{25}H_{33}N$ $[M+H]^+$: 348.2686; found: 348.2684.



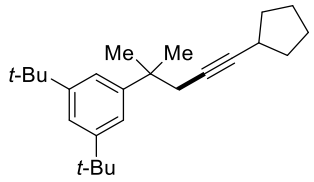
9s

3-(4-(3,5-di-*tert*-butylphenyl)-4-methylpent-1-yn-1-yl)pyridine (9s): Column chromatography (SiO_2 5 g, eluent: Hexane 100%) afforded **9s** (31.0 mg, 89%) as white solid: m.p. 56–58 °C; **R_f =** 0.8 (Hexane/EA = 100/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.57 (s, 1H), 8.47 (d, *J* = 4.5 Hz, 1H), 7.61 (d, *J* = 7.5 Hz, 1H), 7.30 (s, 3H), 7.18 (dd, *J* = 8.0, 5.0 Hz, 1H), 2.72 (s, 2H), 1.50 (s, 6H), 1.33 (s, 18H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 152.3, 150.1, 147.9, 147.1, 138.3, 122.8, 121.1, 120.0, 119.8, 92.4, 79.3, 38.4, 35.0, 34.9, 31.6, 28.6 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{25}H_{33}N$ $[M+H]^+$: 348.2686; found: 348.2685.



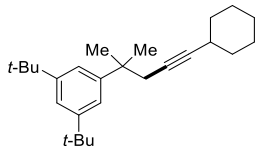
9t

1,3-di-*tert*-butyl-5-(5-cyclopropyl-2-methylpent-4-yn-2-yl)benzene (9t): Column chromatography (SiO_2 5 g, eluent: Hexane 100%) afforded **9t** (27.0 mg, 87%) as colourless liquid; **R_f =** 0.8 (Hexane 100%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.25 (d, *J* = 5.0 Hz, 3H), 2.40 (s, 2H), 1.39 (s, 6H), 1.33 (s, 18H), 1.19 (d, *J* = 7.0 Hz, 1H), 0.67 (t, *J* = 9.3 Hz, 2H), 0.56 (d, *J* = 4.6 Hz, 2H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 149.9, 147.7, 119.9, 119.8, 85.3, 73.7, 38.2, 35.0, 34.3, 31.6, 28.4, 8.0, -0.4 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{23}H_{34}$ $[M+H]^+$: 311.2733; found: 311.2732.



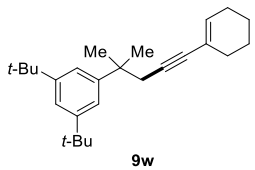
9u

1,3-di-*tert*-butyl-5-(5-cyclopentyl-2-methylpent-4-yn-2-yl)benzene (9u): Column chromatography (SiO_2 5 g, eluent: Hexane 100%) afforded **9u** (24.7 mg, 73%) as colourless liquid; $\mathbf{R_f}$ = 0.8 (Hexane 100%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.26 (s, 3H), 2.56 (d, *J* = 6.3 Hz, 1H), 2.44 (s, 2H), 1.83 (s, 2H), 1.66 (s, 2H), 1.51 (t, *J* = 20.3 Hz, 4H), 1.40 (s, 6H), 1.33 (s, 18H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 149.9, 147.9, 119.9, 119.8, 86.6, 77.9, 38.2, 35.0, 34.3, 34.1, 31.6, 30.4, 28.4, 24.8 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{25}H_{38}$ $[M+H]^+$: 339.3046; found: 339.3047.



9v

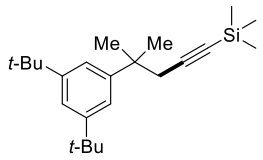
1,3-di-*tert*-butyl-5-(5-cyclohexyl-2-methylpent-4-yn-2-yl)benzene (9v): Column chromatography (SiO_2 5 g, eluent: Hexane 100%) afforded **9v** (29.0 mg, 82%) as colourless liquid; $\mathbf{R_f}$ = 0.8 (Hexane 100%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.25 (s, 3H), 2.46 (s, 2H), 2.34 (d, *J* = 31.7 Hz, 1H), 1.71 (d, *J* = 8.5 Hz, 2H), 1.63 (d, *J* = 6.6 Hz, 2H), 1.45 (t, *J* = 11.3 Hz, 1H), 1.43 – 1.36 (m, 8H), 1.33 (s, 18H), 1.27 (d, *J* = 8.7 Hz, 3H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 149.9, 147.9, 119.9, 119.8, 86.5, 78.3, 38.2, 35.0, 34.3, 33.1, 31.6, 29.1, 28.4, 26.0, 24.7 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{26}H_{40}$ $[M+H]^+$: 353.3203; found: 353.3207.



9w

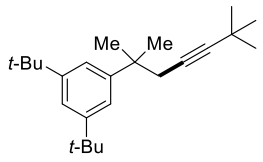
1,3-di-*tert*-butyl-5-(5-(cyclohex-1-en-1-yl)-2-methylpent-4-yn-2-yl)benzene (9w): Column chromatography (SiO_2 5 g, eluent: Hexane 100%) afforded **9w** (29.8 mg, 85%) as colourless liquid; $\mathbf{R_f}$ = 0.8 (Hexane 100%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.26 (s, 3H), 5.98 (t, *J* = 3.5

Hz, 1H), 2.58 (s, 2H), 2.07 – 2.05 (m, 4H), 1.61 – 1.54 (m, 4H), 1.43 (s, 6H), 1.33 (s, 18H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 149.9, 147.7, 133.1, 121.0, 119.9, 119.8, 85.5, 84.3, 38.3, 35.0, 34.8, 31.6, 29.6, 28.4, 25.5, 22.4, 21.6 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{26}H_{38}$ $[M+H]^+$: 351.3046; found: 351.3045.



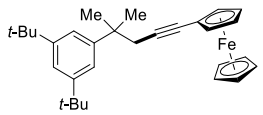
9x

(4-(3,5-di-*tert*-butylphenyl)-4-methylpent-1-yn-1-yl)trimethylsilane (9x): Column chromatography (SiO_2 5 g, eluent: Hexane 100%) afforded **9x** (33.0 mg, 96%) as colourless liquid; **R_f =** 0.8 (Hexane 100%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.26 (s, 3H), 2.52 (s, 2H), 1.43 (s, 6H), 1.33 (s, 18H), 1.12 (s, 9H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 150.0, 147.5, 119.9, 119.8, 105.7, 86.4, 38.0, 35.2, 35.0, 31.6, 28.3, 0.1 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{23}H_{38}Si$ $[M+H]^+$: 343.2816; found: 343.2815.



9y

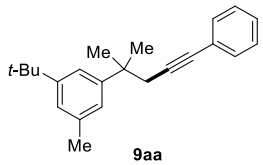
1,3-di-*tert*-butyl-5-(2,6,6-trimethylhept-4-yn-2-yl)benzene (9y): Column chromatography (SiO_2 5 g, eluent: Hexane 100%) afforded **9y** (24.4 mg, 70%) as colourless liquid; **R_f =** 0.8 (Hexane 100%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.30 – 7.28 (m, 3H), 2.47 (s, 2H), 1.44 (s, 6H), 1.36 (s, 18H), 1.20 (s, 9H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 149.9, 148.0, 119.8, 119.7, 90.8, 76.7, 38.2, 35.0, 34.1, 31.6, 31.3, 28.3, 27.4 ppm. **HRMS** *m/z* (ESI) calcd. for $C_{24}H_{38}$ $[M+Na]^+$: 349.2866; found: 349.2863.



9z

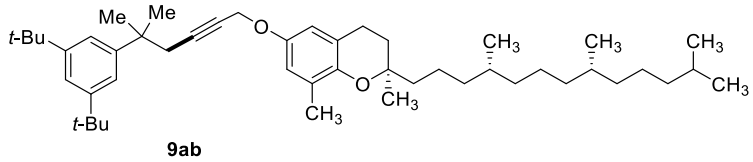
1,3-di-*tert*-butyl-5-(5-ferrocenyl-2-methylpent-4-yn-2-yl)benzene (9z): Column chromatography (SiO_2 5 g, eluent: Hexane 100%) afforded **9z** (36.4 mg, 88%) as dark red oil;

R_f = 0.8 (Hexane 100%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.31 (d, *J* = 6.1 Hz, 3H), 4.31 (dd, *J* = 21.1, 5.0 Hz, 2H), 4.12 (s, 7H), 2.63 (s, 2H), 1.50 (s, 6H), 1.37 (s, 18H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 150.0, 147.6, 119.9, 119.9, 84.5, 80.0, 71.1, 69.6, 68.1, 66.4, 38.3, 35.0, 34.9, 31.6, 28.7 ppm. **HRMS** *m/z* (ESI) calcd. for$C_{30}H_{38}Fe$ $[M]^+$: 454.2318; found: 454.2316.



9aa

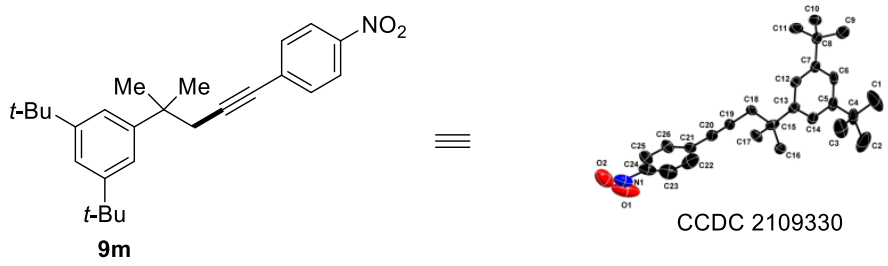
1-(*tert*-butyl)-3-methyl-5-(2-methyl-5-phenylpent-4-yn-2-yl)benzene (9aa): Column chromatography (SiO_2 5 g, eluent: Hexane 100%) afforded **9aa** (13.7 mg, 45%) as colourless liquid; **R_f =** 0.8 (Hexane 100%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.37 – 7.32 (m, 2H), 7.29 (d, *J* = 7.8 Hz, 1H), 7.27 – 7.23 (m, 3H), 7.06 (t, J = 8.8 Hz, 2H), 2.68 (s, 2H), 2.36 (s, 3H), 1.48 (s, 6H), 1.31 (s, 9H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 150.6, 148.1, 136.9, 131.5, 128.1, 127.5, 124.0, 123.8, 123.7, 119.8, 88.5, 82.5, 38.1, 34.8, 34.7, 31.5, 28.4, 21.9 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{23}H_{28}$ $[M+H]^+$: 305.2264; found: 305.2259.



9ab

(R)-6-((5-(3,5-di-*tert*-butylphenyl)-5-methylhex-2-yn-1-yl)oxy)-2,8-dimethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chromane (9ab): Column chromatography (SiO_2 5 g, eluent: Hexane 100%) afforded **9ab** (50.7 mg, 74%) as yellow liquid; **R_f =** 0.4 (Hexane 100%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.30 (d, *J* = 1.5 Hz, 1H), 7.29 – 7.27 (m, 2H), 6.65 (d, *J* = 2.7 Hz, 1H), 6.55 (d, *J* = 2.8 Hz, 1H), 4.61 (s, 2H), 2.81 – 2.64 (m, 2H), 2.54 (s, 2H), 2.16 (s, 3H), 1.87 – 1.70 (m, 2H), 1.60 (s, 3H), 1.58 – 1.52 (m, 2H), 1.43 (s, 6H), 1.35 (s, 18H), 1.33 – 1.02 (m, 19H), 0.91 – 0.85 (m, 12H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 150.3, 150.0, 147.4, 146.6, 127.1, 120.8, 119.9, 119.8, 116.0, 112.6, 85.9, 77.6, 75.6, 57.1, 40.0, 39.4, 38.1, 37.5, 37.4, 37.4, 37.3 35.0, 34.3, 32.8, 32.7, 31.6, 31.3, 28.3, 28.0, 24.8, 24.4, 24.1, 22.7, 22.6, 21.0, 19.7, 19.6, 16.2 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{48}H_{76}O_2$ $[M+H]^+$: 685.5918; found: 685.5914.

5. X-ray Crystallographic Data



9m

Identification code	CCDC 2109330
Empirical formula	$C_{26}H_{33}NO_2$
Formula weight	391.53
Temperature/K	173.15
Crystal system triclinic	
Space group	P-1
a/Å	9.642(14)
b/Å	9.850(15)
c/Å	13.156(18)
α/°	85.36(3)
β/°	76.56(4)
γ/°	74.27(3)
Volume/$Å^3$	1170(3)
Z	2
$\rho_{calc}g/cm^3$	1.112
μ/mm^{-1}	0.069
F(000) 424.0	
Crystal size/mm^3	0.5 × 0.4 × 0.3
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.352 to 50.49
Index ranges	$-11 \le h \le 11$, $-11 \le k \le 11$, $-15 \le l \le 15$
Reflections collected	29741
Independent reflections	4226 [R_{int} = 0.0478, R_{sigma} = 0.0351]
Data/restraints/parameters	4226/0/319
Goodness-of-fit on F_2	1.065
Final R indexes [I>=2σ (I)]	R_1 = 0.1196, wR_2 = 0.3217
Final R indexes [all data]	R_1 = 0.1483, wR_2 = 0.3520
Largest diff. peak/hole / e $Å^{-3}$ 0.84/-0.53	

6. References

1. J. Pan, M. Su, S. L. Buchwald, Palladium(0)-Catalyzed Intermolecular Amination of Unactivated C(sp^3)–H Bonds, *Angew. Chem., Int. Ed*. 2011, **50**, 8647–8651.

2. T. E. Barder, S. D. Walker, J. R. Martinelli, S. L. Buchwald, Catalysts for Suzuki−Miyaura Coupling Processes: Scope and Studies of the Effect of Ligand Structure, *J. Am. Chem. Soc.* 2005, **127**, 4685–4696.

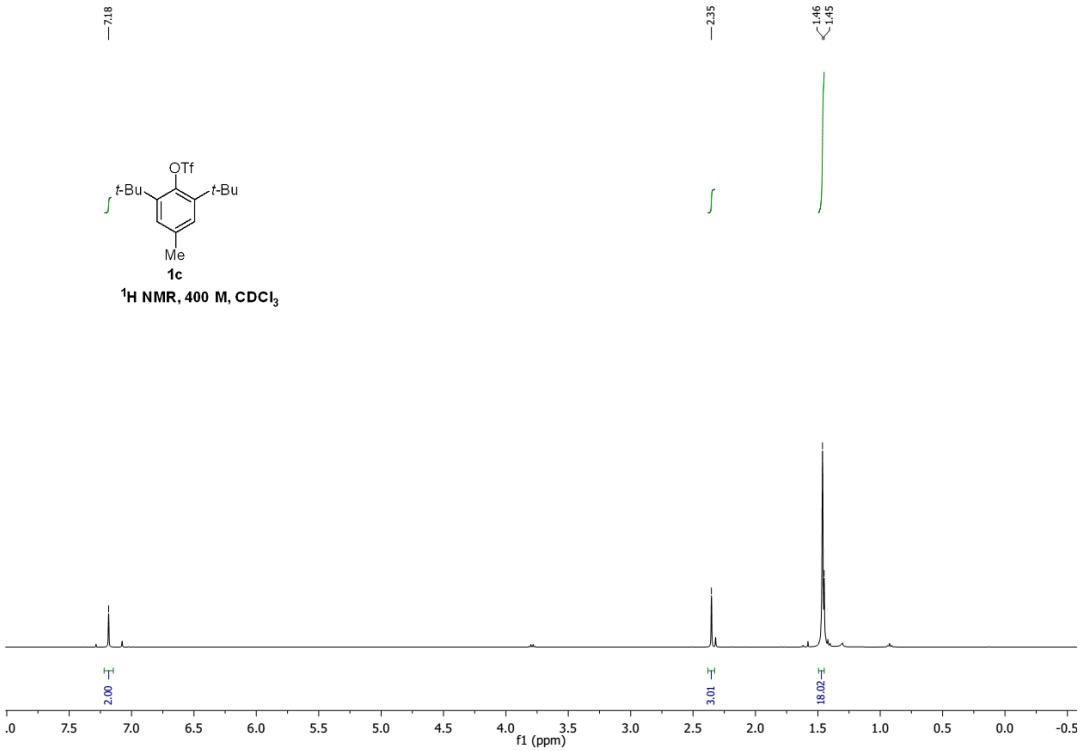
3. T. Hoshi, T. Honma, A. Mori, M. Konishi, T. Sato, H. Hagihira, T. Suzuki, An Active, General, and Long-Lived Palladium Catalyst for Cross-Couplings of Deactivated (Hetero)aryl Chlorides and Bromides with Arylboronic Acids, *J. Org. Chem*. 2013, **78**, 11513–11524.

4. H. Chen, M. Yang, G. Wang, L. Gao, Z. Ni, J. Zou, S. Li, $B(C_6F_5)_3$-Catalyzed Sequential Additions of Terminal Alkynes to *para*-Substituted Phenols: Selective Construction of Congested Phenol-Substituted Quaternary Carbons, *Org. Lett*. 2021, **23**, 5533–5538.

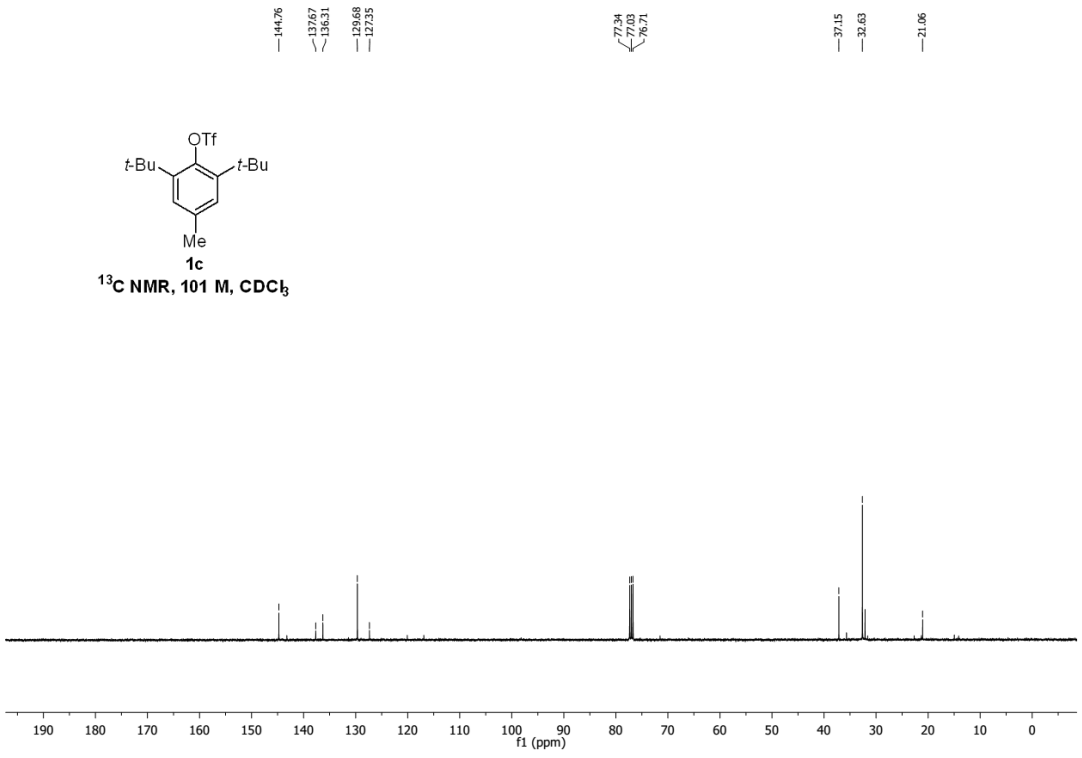
7 . Copies of ^{1}H NMR, ^{13}C NMR, ^{19}F NMR Spectra

2,6-di-*tert*-butyl-4-methylphenyl trifluoromethanesulfonate (1c)

^{1}H NMR (400 MHz, $CDCl_3$)

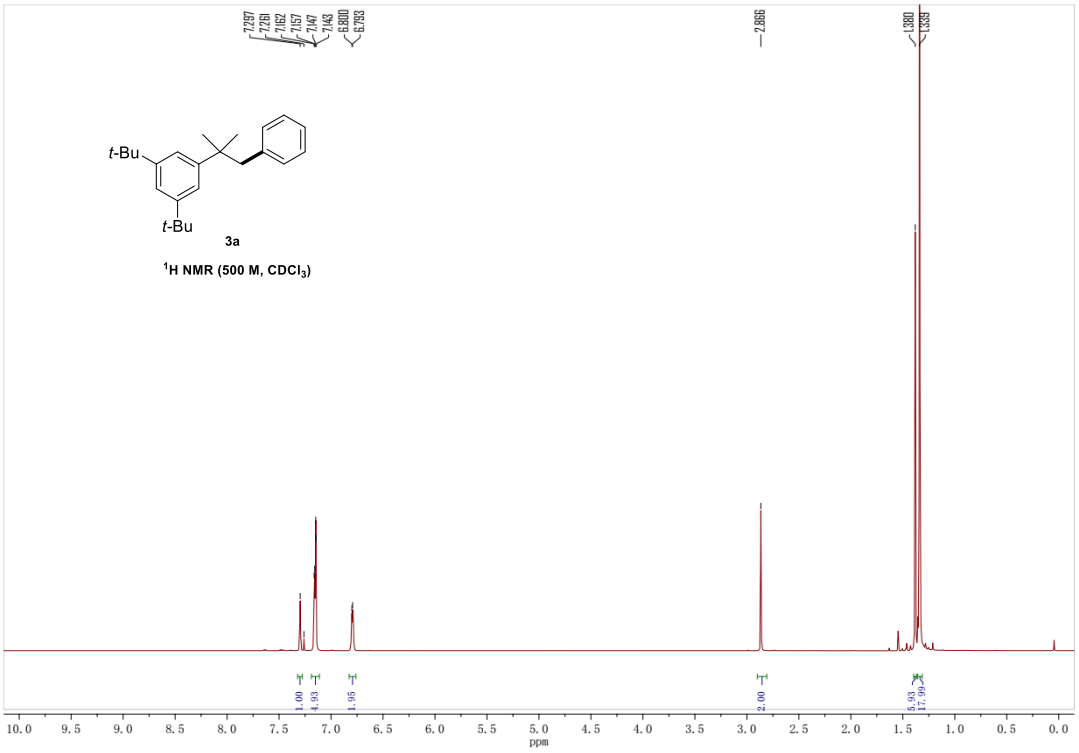


^{13}C NMR (101 MHz, $CDCl_3$)

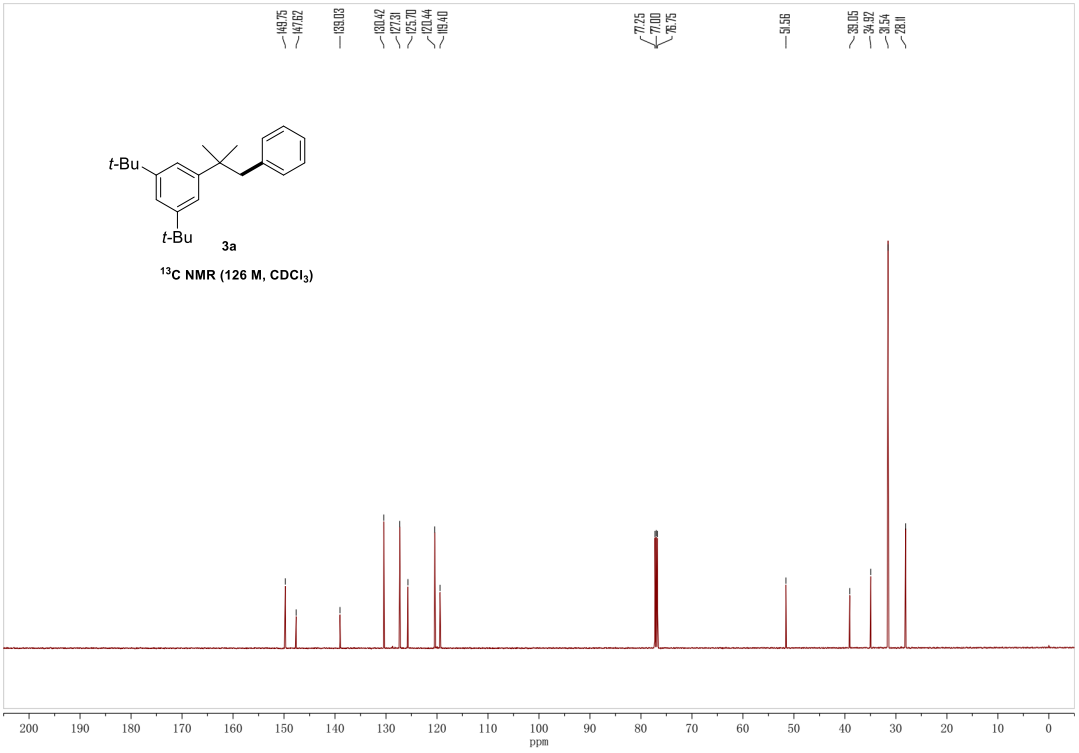


1,3-di-*tert*-butyl-5-(2-methyl-1-phenylpropan-2-yl)benzene (3a)

^{1}H NMR (500 MHz, $CDCl_3$)

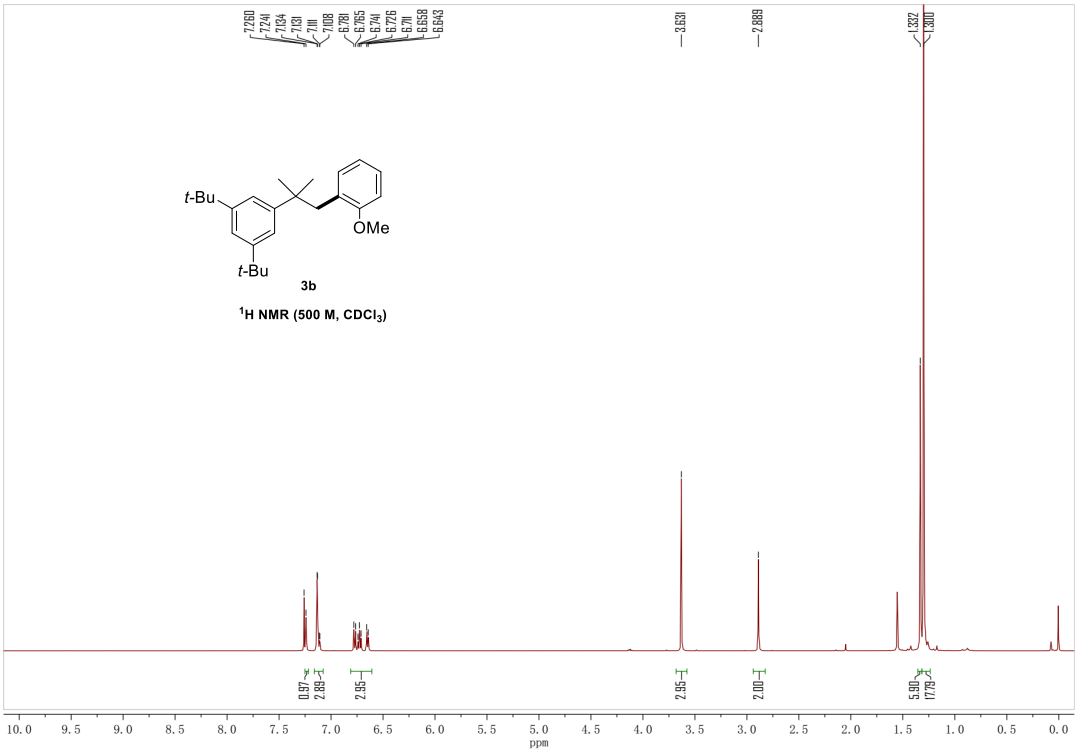


^{13}C NMR (126 MHz, $CDCl_3$)

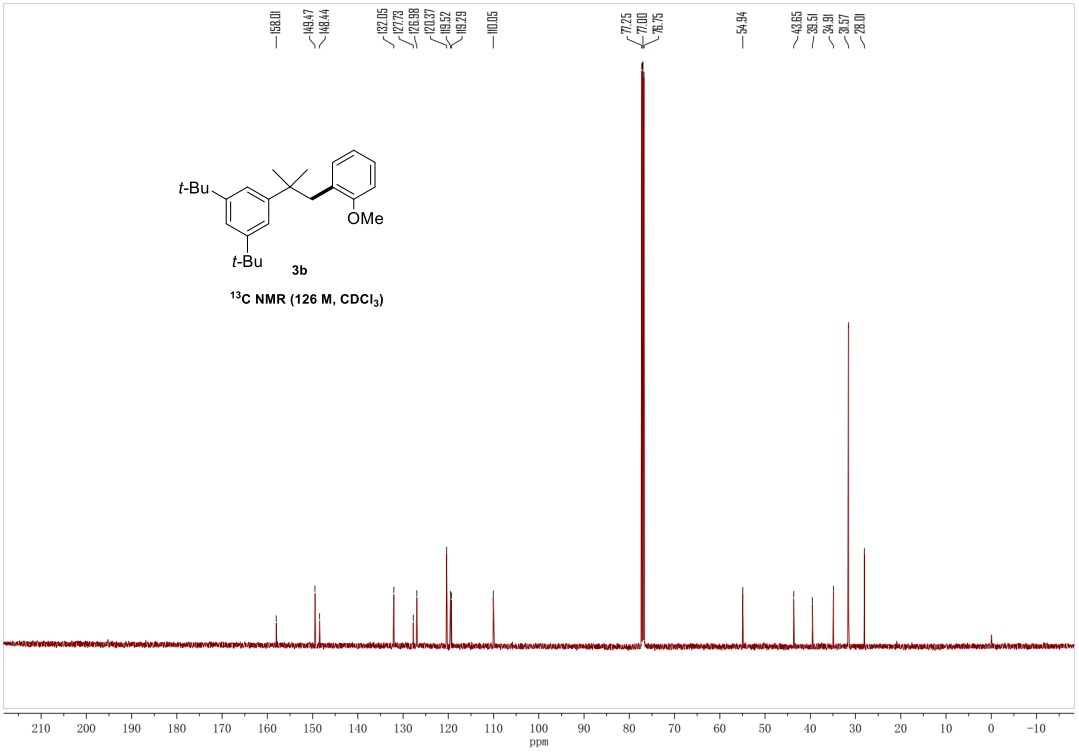


1,3-di-*tert*-butyl-5-(1-(2-methoxyphenyl)-2-methylpropan-2-yl)benzene (3b)

^{1}H NMR (500 MHz, $CDCl_3$)

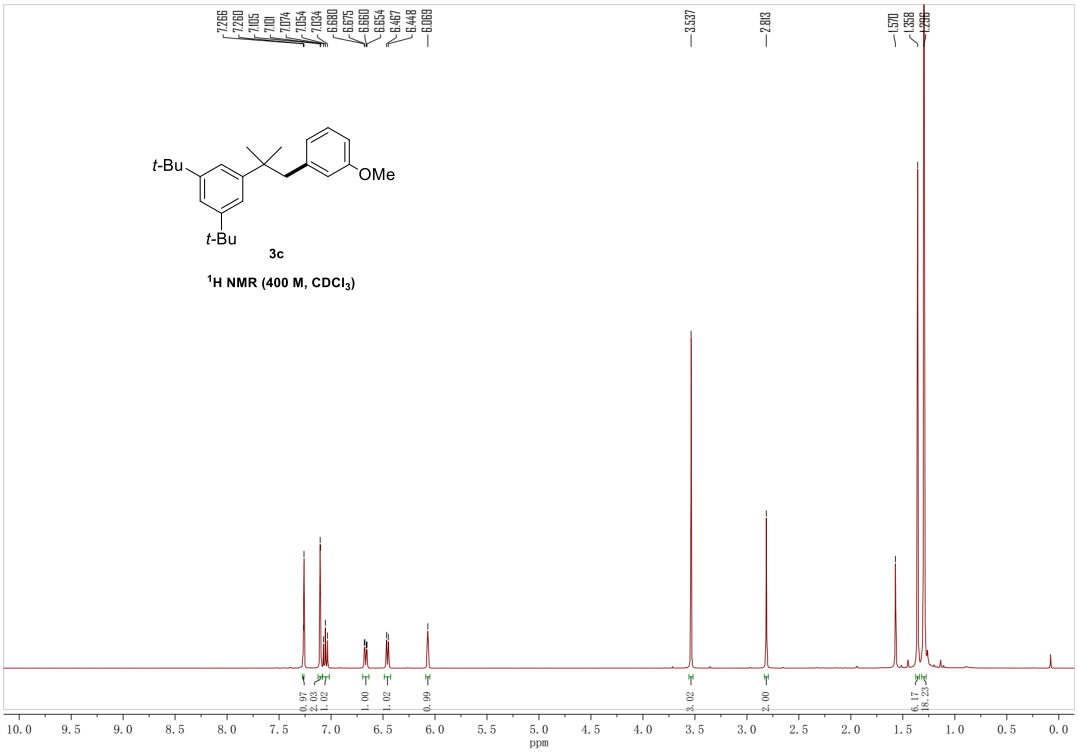


^{13}C NMR (126 MHz, $CDCl_3$)

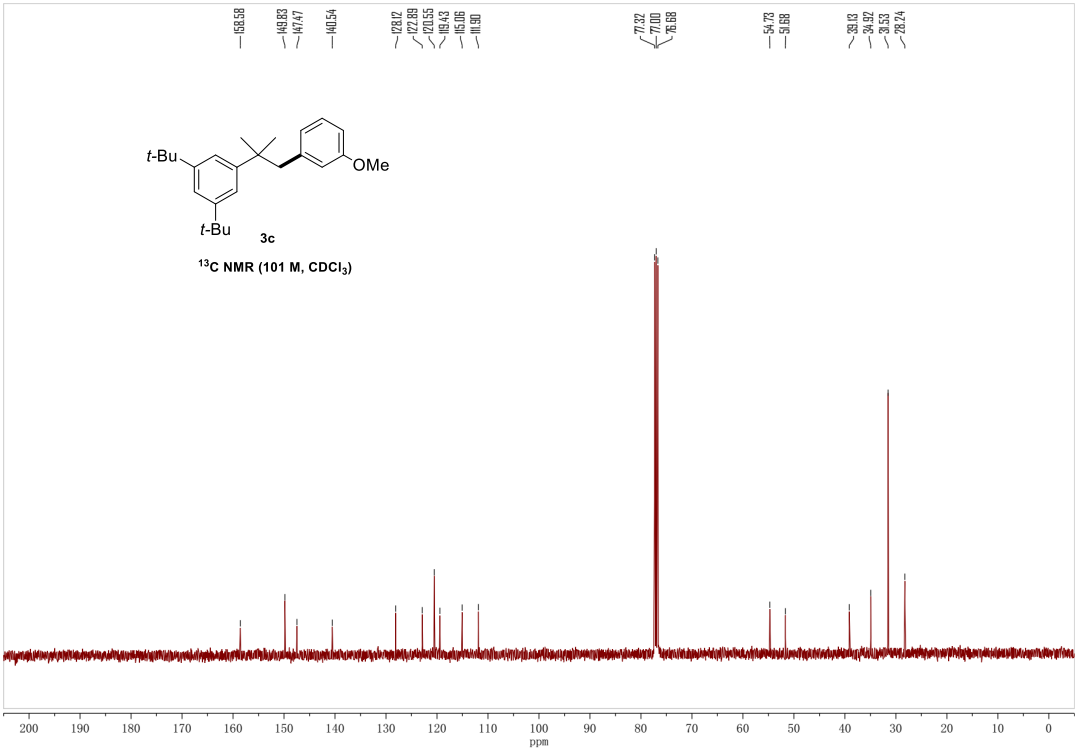


1,3-di-*tert*-butyl-5-(1-(3-methoxyphenyl)-2-methylpropan-2-yl) (3c)

^{1}H NMR (400 MHz, $CDCl_3$)

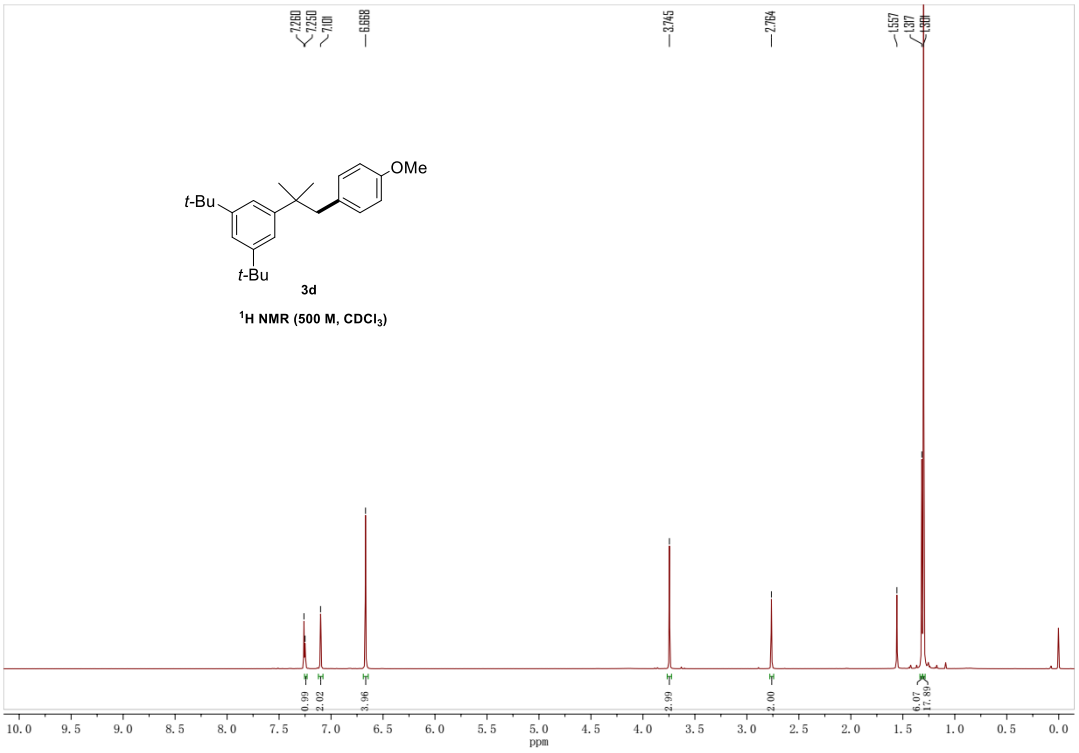


^{13}C NMR (101 MHz, $CDCl_3$)

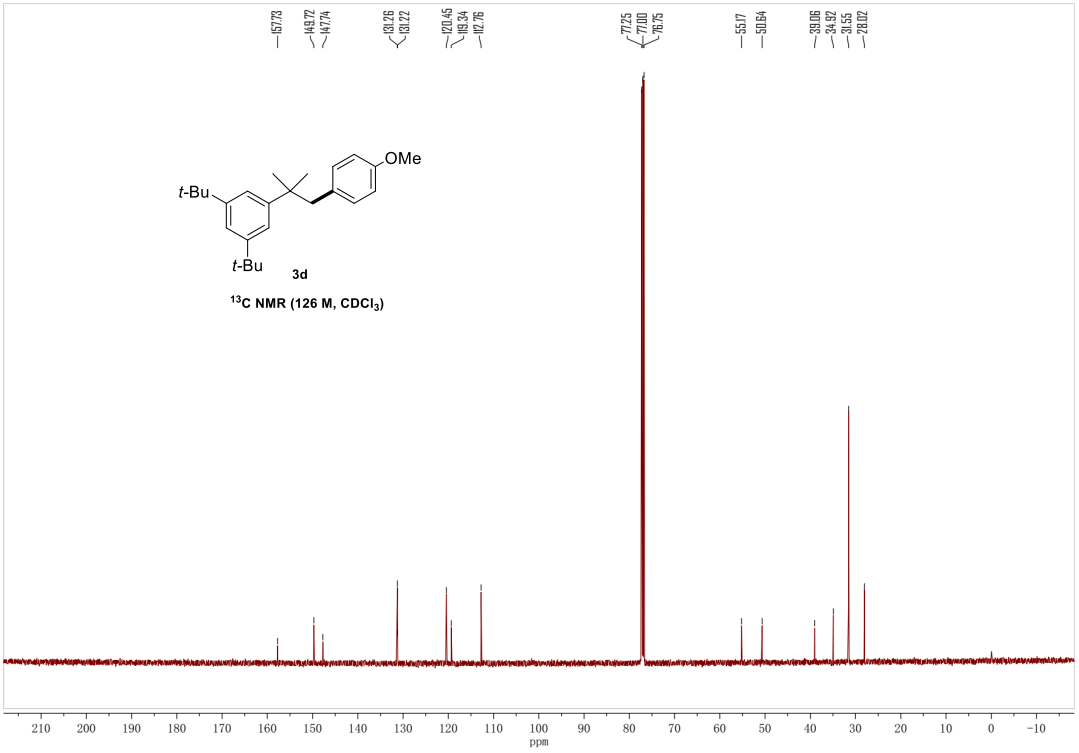


1,3-di-*tert*-butyl-5-(1-(4-methoxyphenyl)-2-methylpropan-2-yl)benzene (3d)

^{1}H NMR (500 MHz, $CDCl_3$)

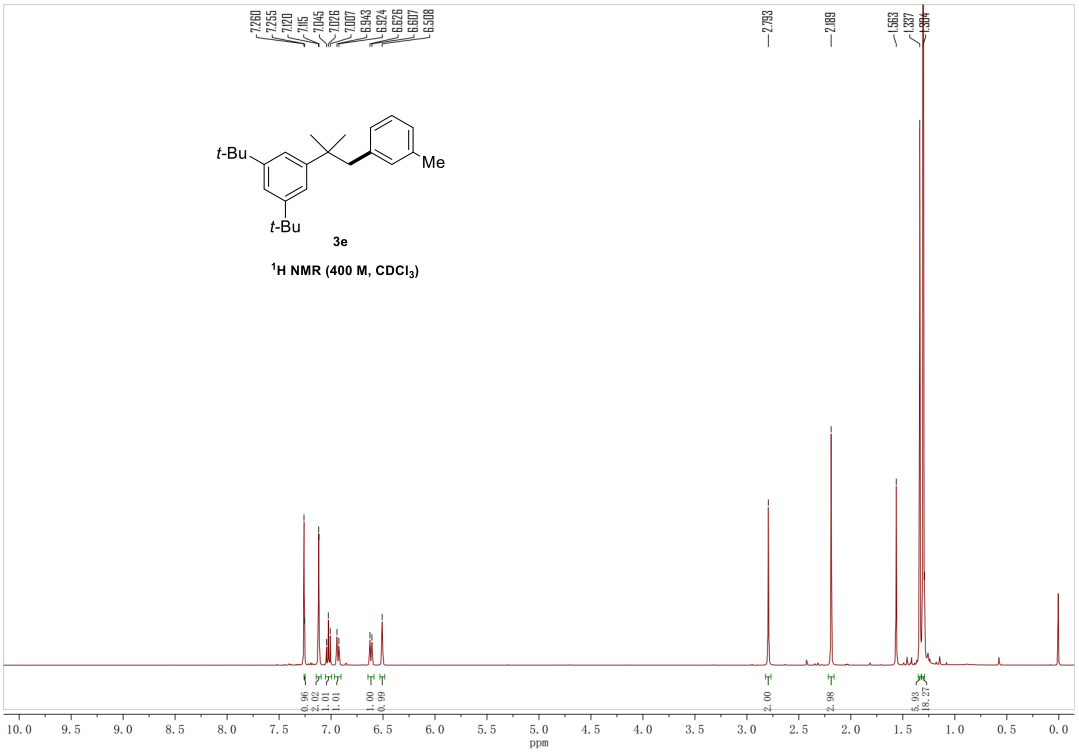


^{13}C NMR (126 MHz, $CDCl_3$)

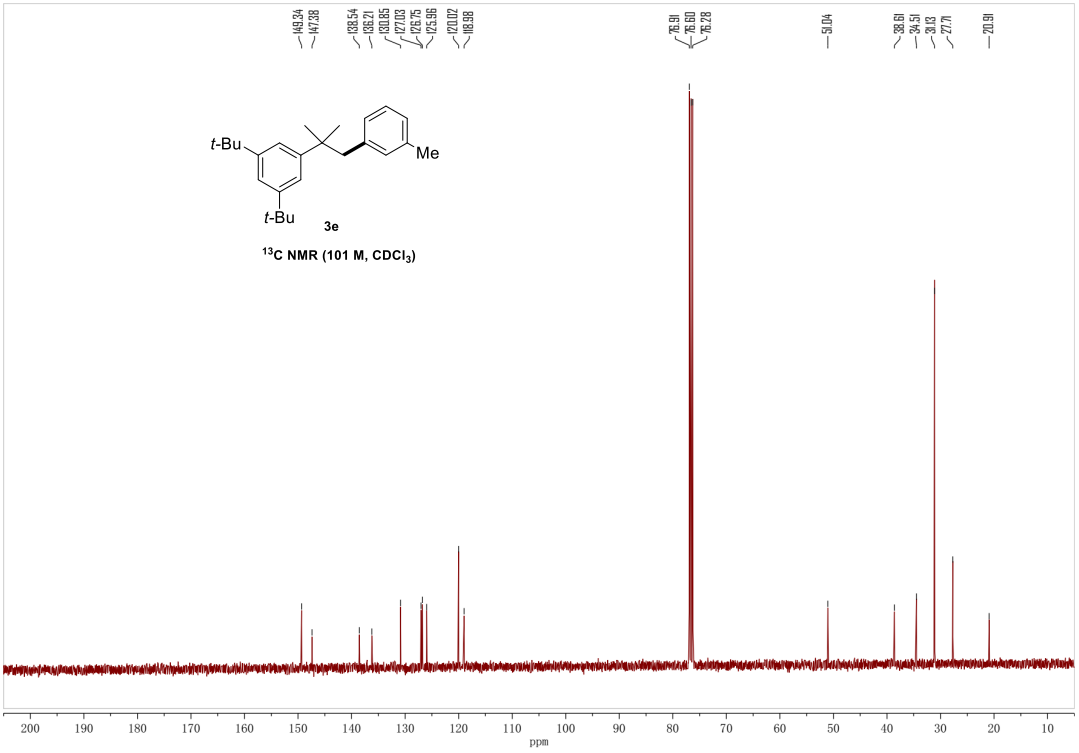


1,3-di-*tert*-butyl-5-(2-methyl-1-(*m*-tolyl)propan-2-yl)benzene (3e)

^{1}H NMR (400 MHz, $CDCl_3$)

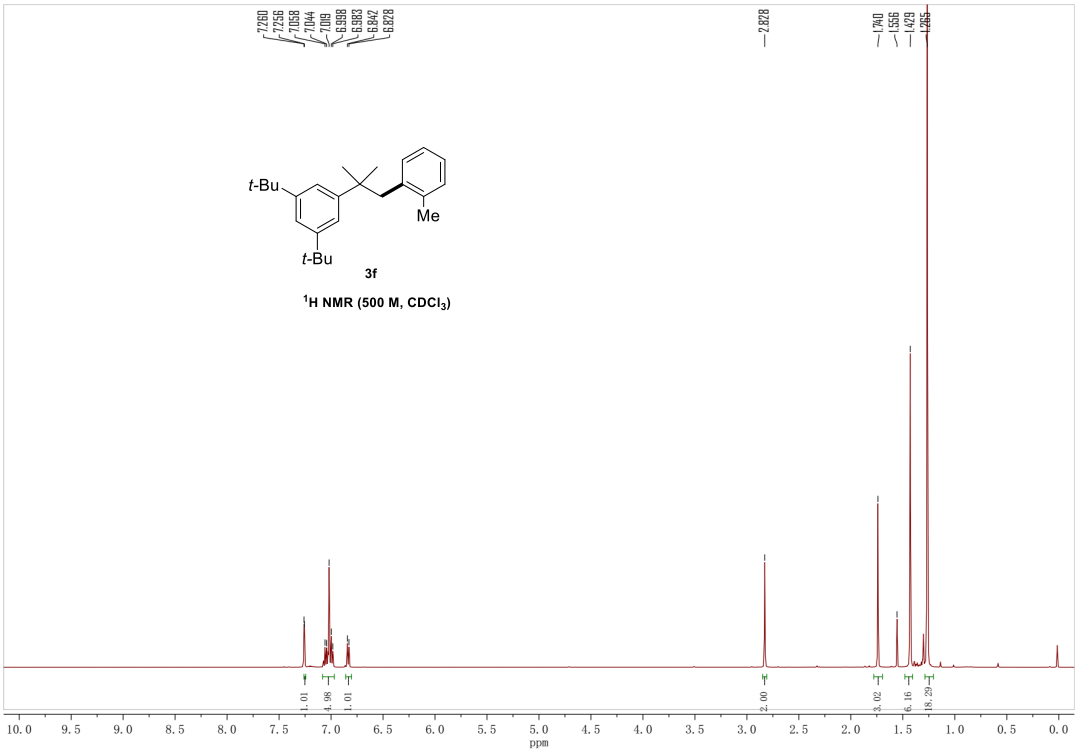


^{13}C NMR (101 MHz, $CDCl_3$)

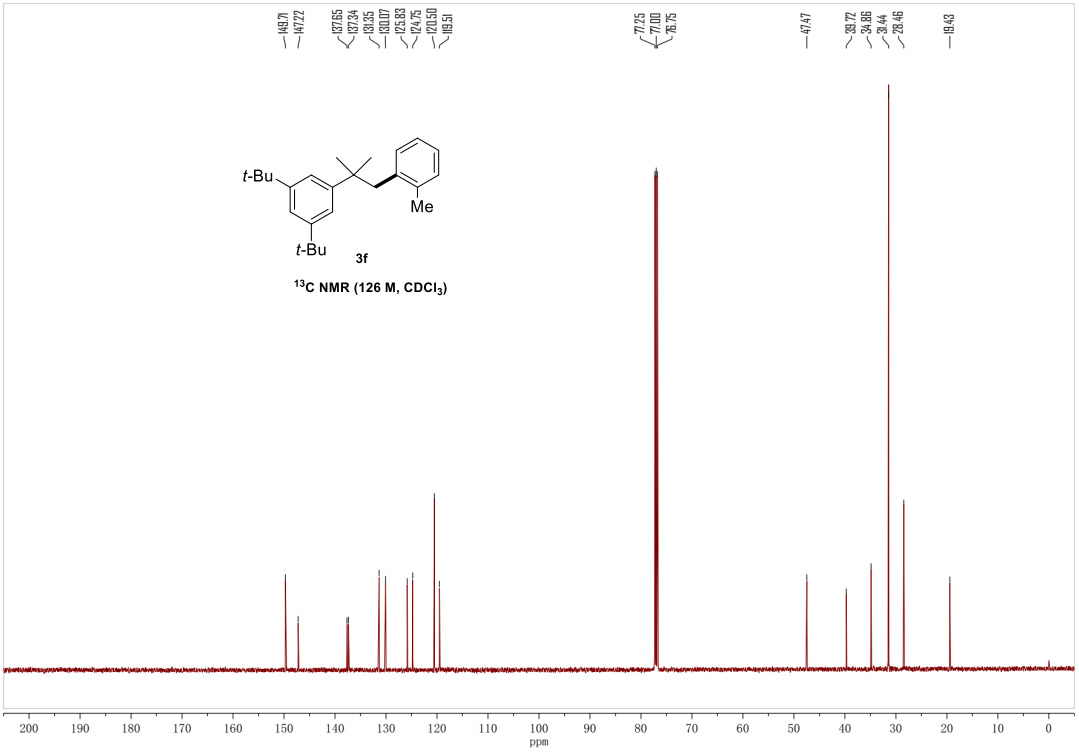


1,3-di-*tert*-butyl-5-(2-methyl-1-(*o*-tolyl)propan-2-yl)benzene (3f)

^{1}H NMR (500 MHz, $CDCl_3$)

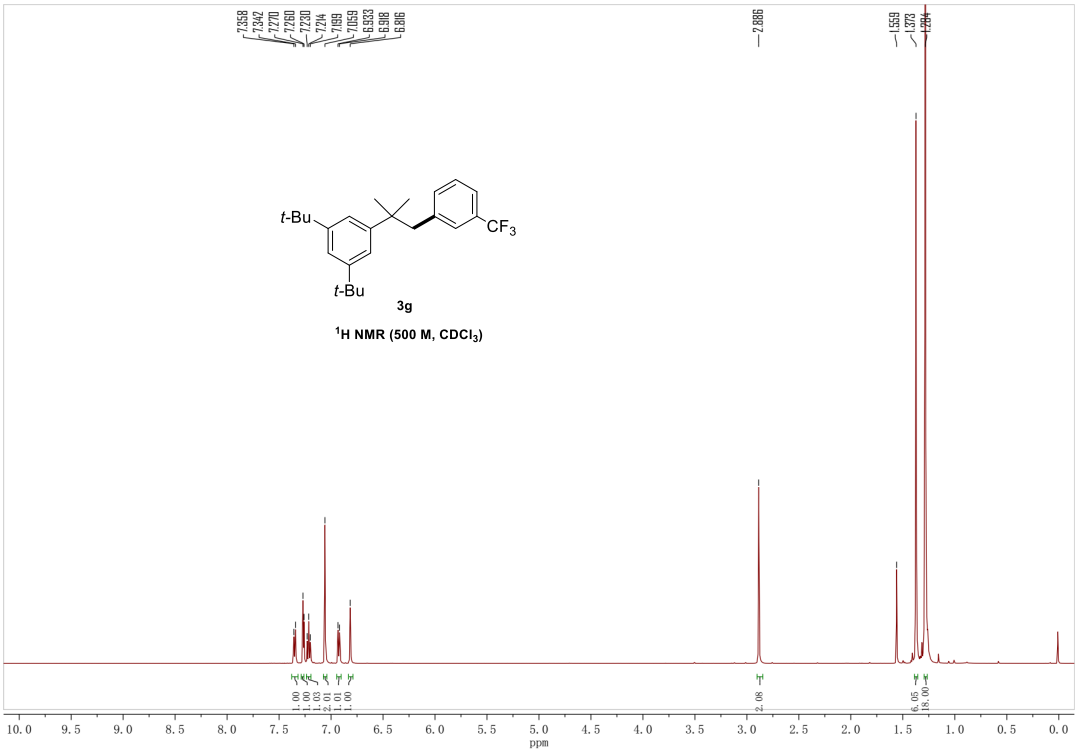


^{13}C NMR (126 MHz, $CDCl_3$)

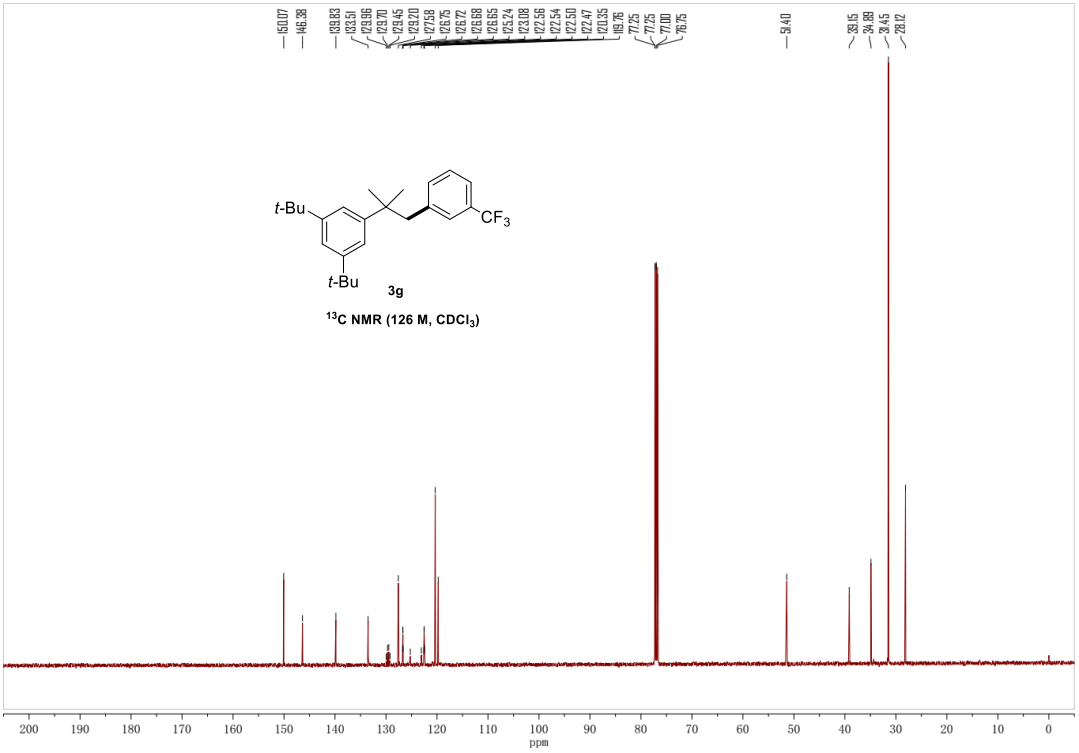


1,3-di-*tert*-butyl-5-(2-methyl-1-(3-(trifluoromethyl)phenyl)propan-2-yl)benzene (3g)

^{1}H NMR (500 MHz, $CDCl_3$)

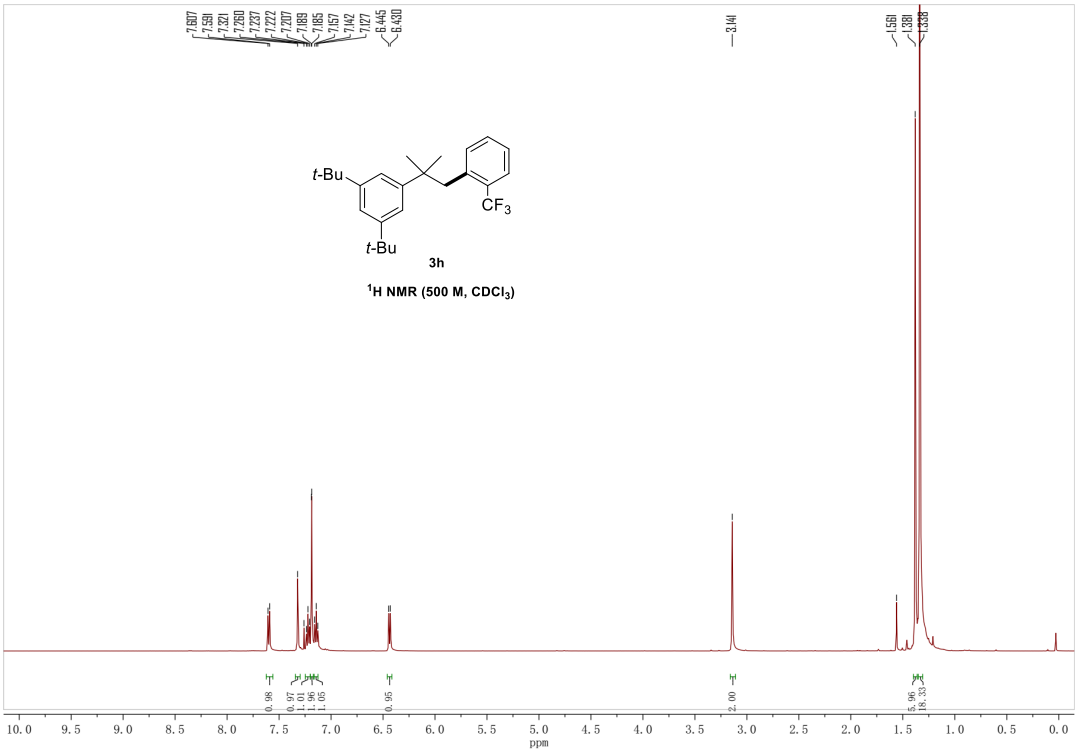


^{13}C NMR (126 MHz, $CDCl_3$)

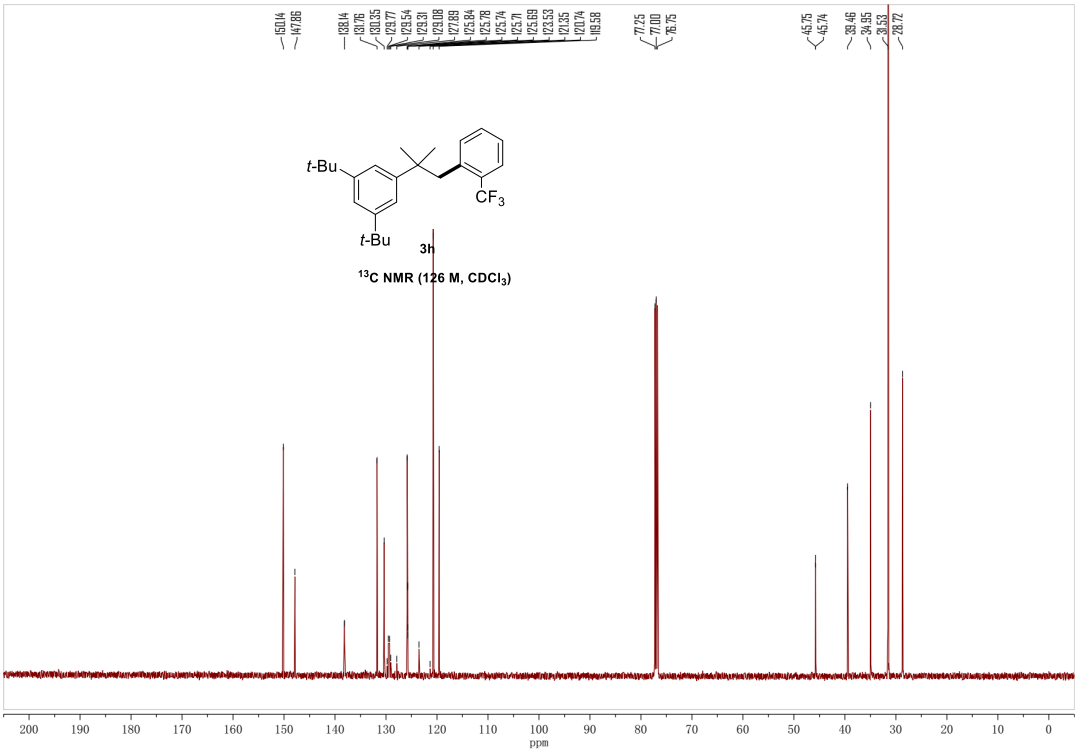


1,3-di-*tert*-butyl-5-(2-methyl-1-(2-(trifluoromethyl)phenyl)propan-2-yl)benzene (3h)

^{1}H NMR (500 MHz, $CDCl_3$)

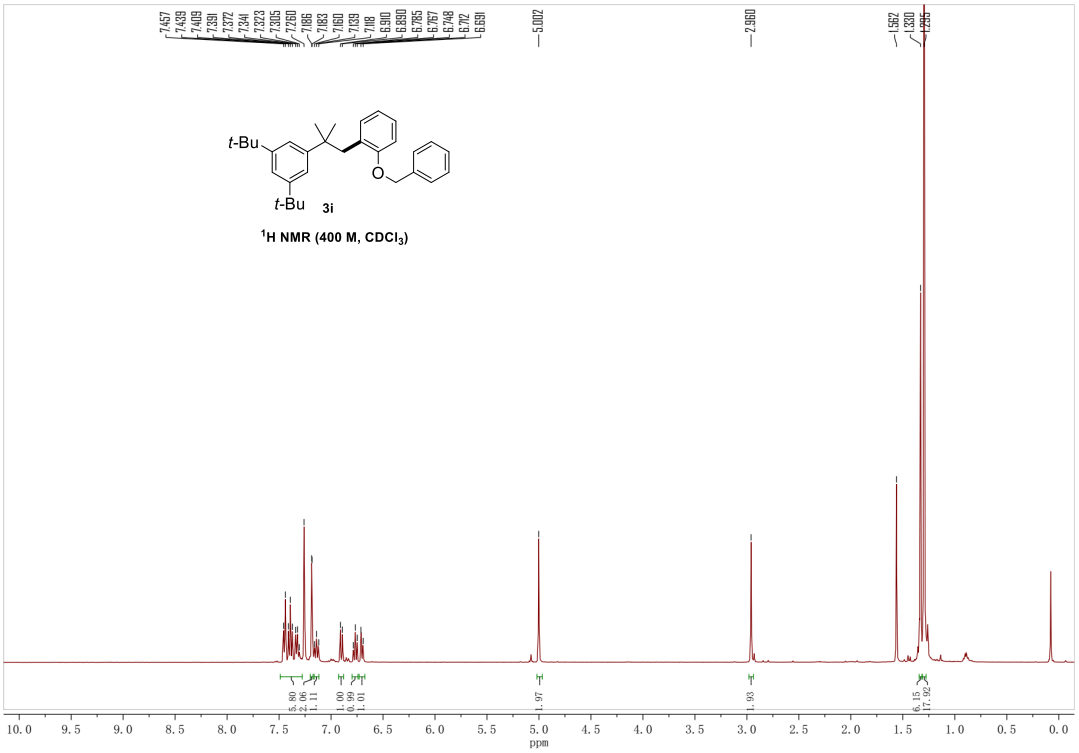


^{13}C NMR (126 MHz, $CDCl_3$)

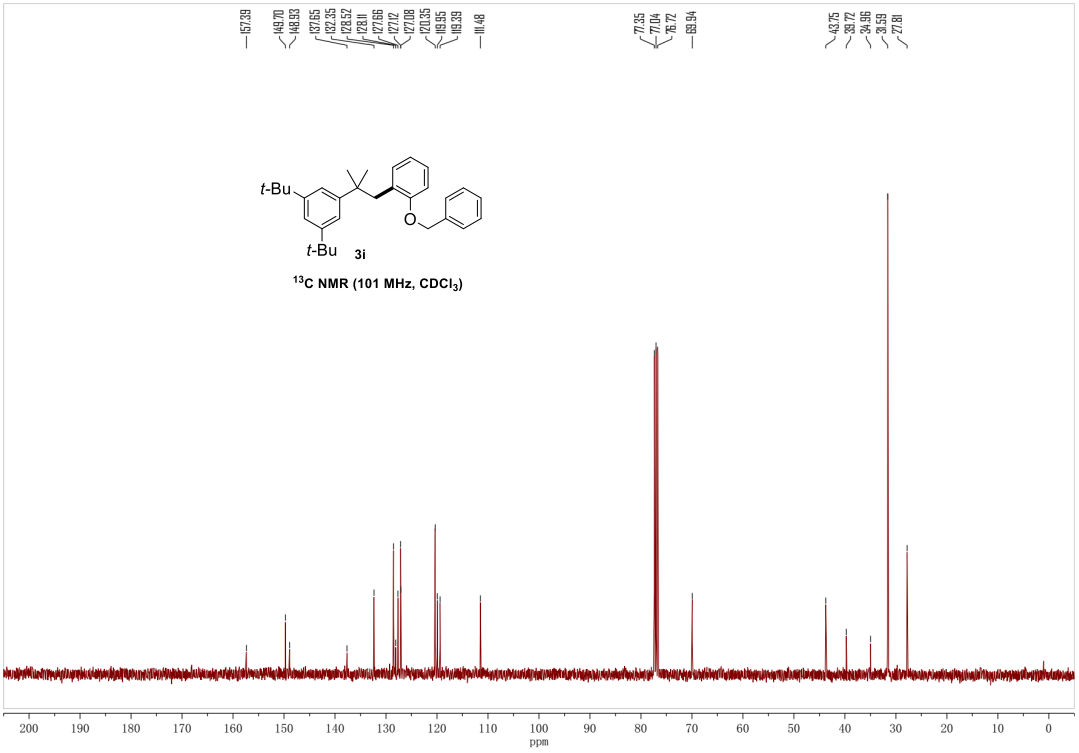


1-(1-(2-(benzyloxy)phenyl)-2-methylpropan-2-yl)-3,5-di-*tert*-butylbenzene (3i)

^{1}H NMR (400 MHz, $CDCl_3$)

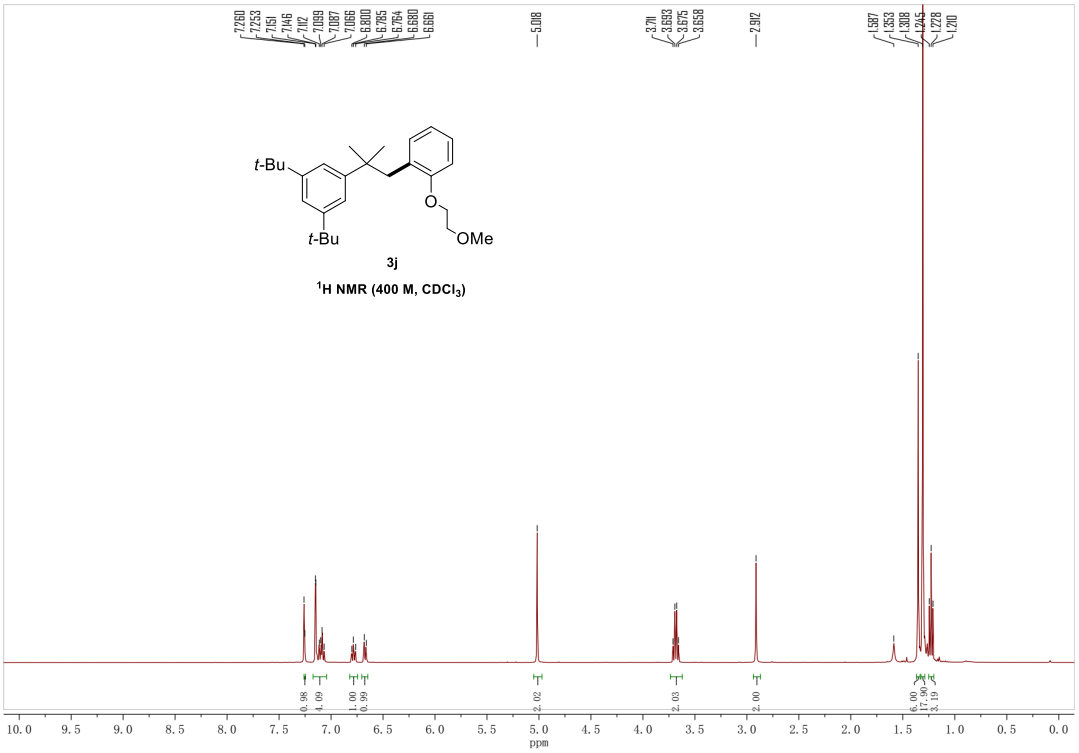


^{13}C NMR (101 MHz, $CDCl_3$)

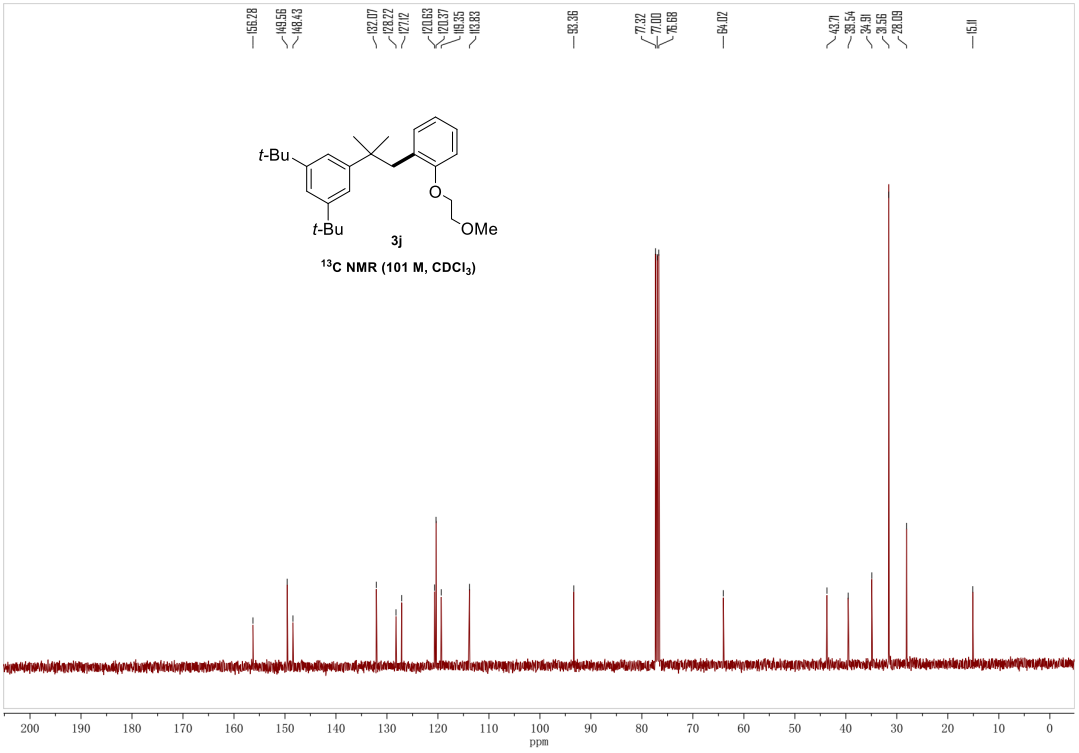


1,3-di-*tert*-butyl-5-(1-(2-(2-methoxyethoxy)phenyl)-2-methylpropan-2-yl)benzene (3j)

^{1}H NMR (400 MHz, $CDCl_3$)

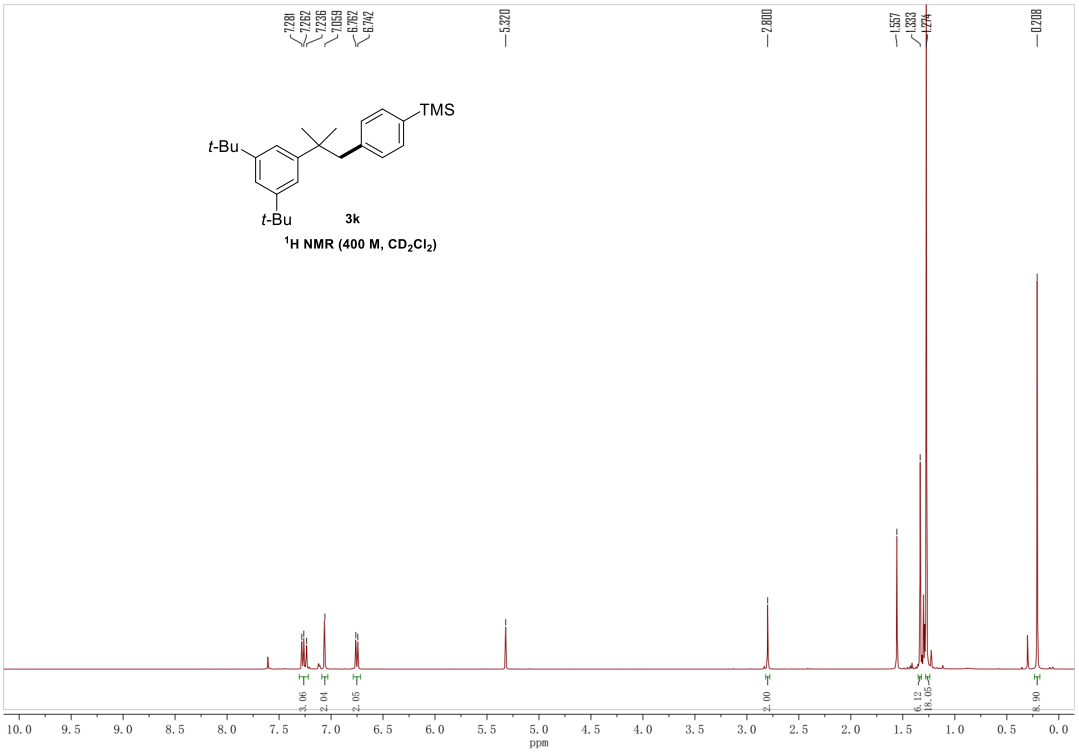


^{13}C NMR (101 MHz, $CDCl_3$)

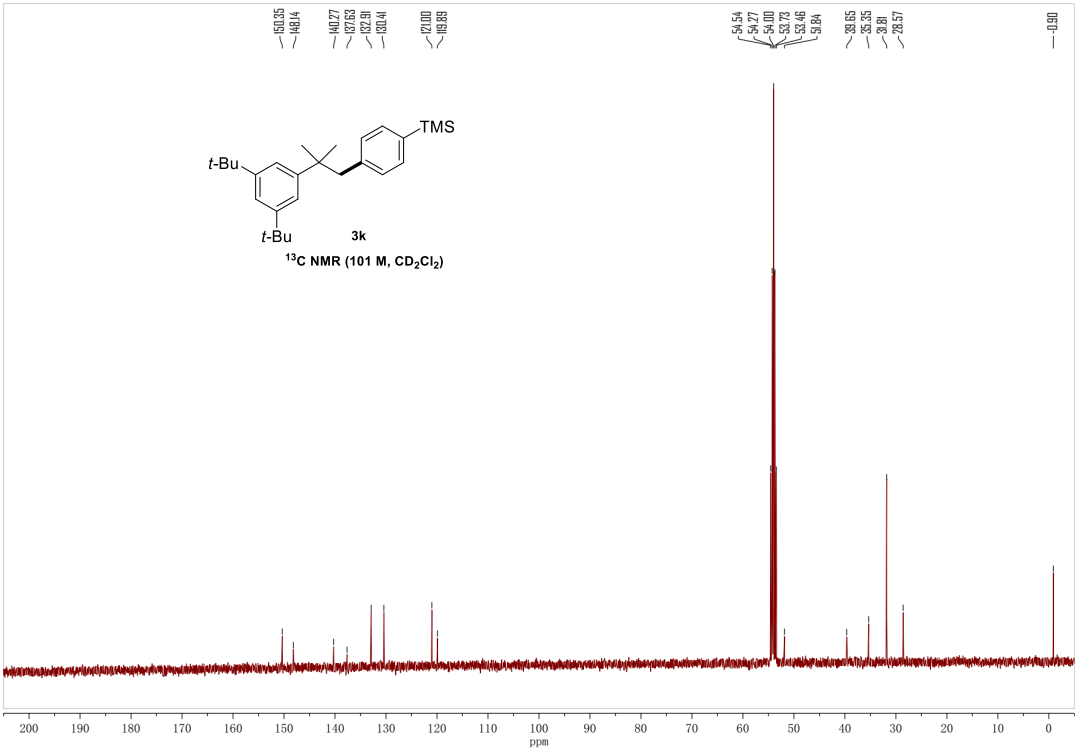


(4-(2-(3,5-di-*tert*-butylphenyl)-2-methylpropyl)phenyl)trimethylsilane (3k)

^{1}H NMR (400 MHz, CD_2Cl_2)

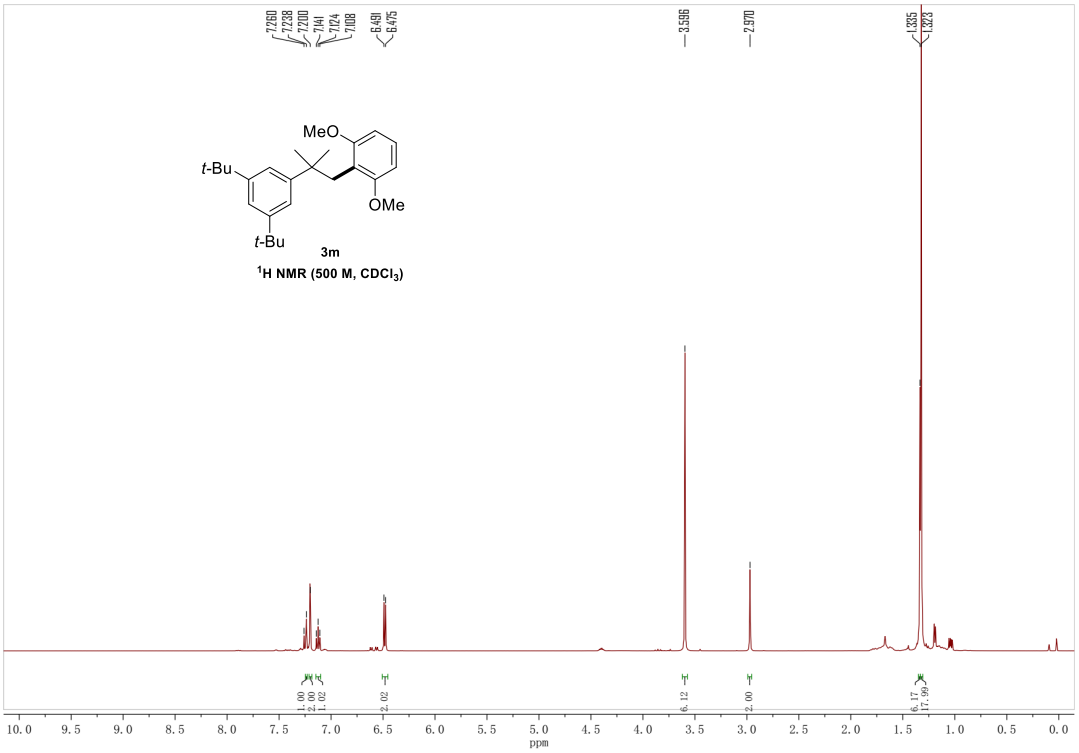


^{13}C NMR (101 MHz, CD_2Cl_2)

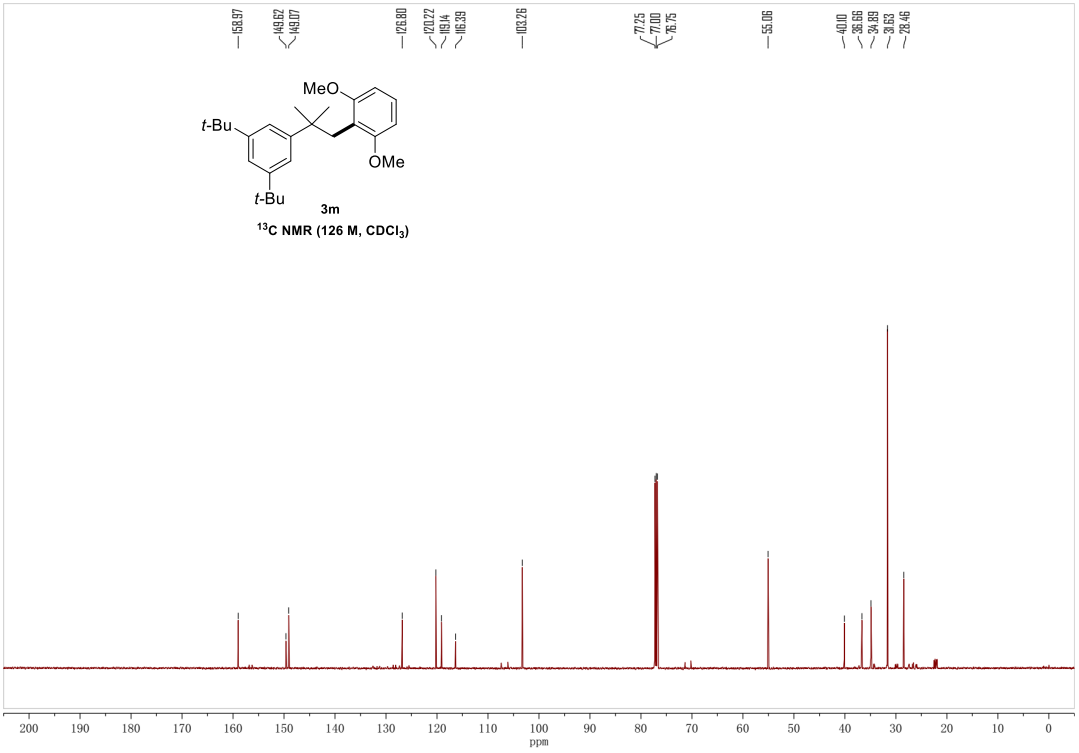


2-(2-(3,5-di-*tert*-butylphenyl)-2-methylpropyl)-1,3-dimethoxybenzene (3m)

^{1}H NMR (500 MHz, $CDCl_3$)

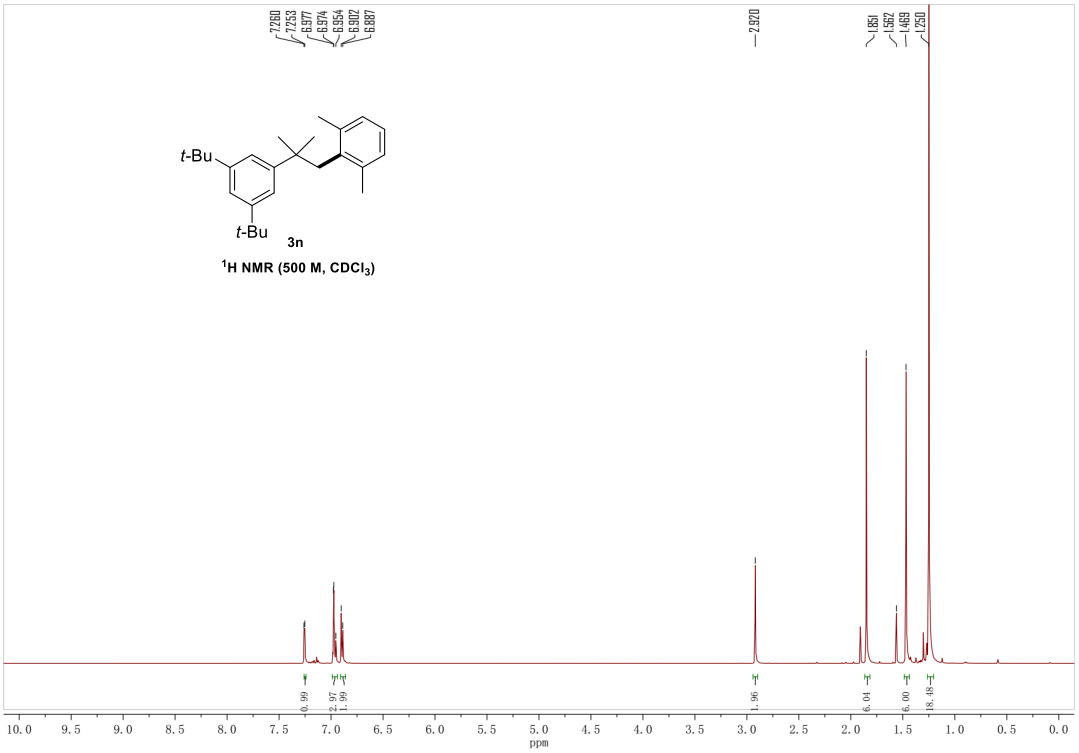


^{13}C NMR (126 MHz, $CDCl_3$)

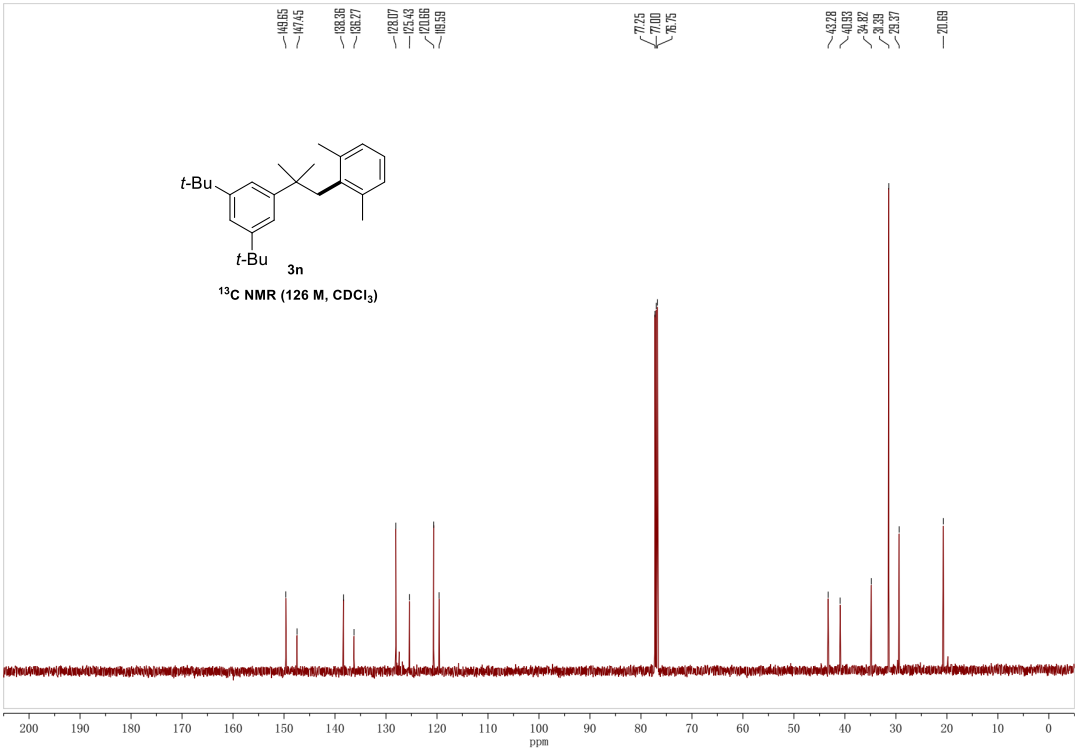


2-(2-(3,5-di-*tert*-butylphenyl)-2-methylpropyl)-1,3-dimethylbenzene (3n)

^{1}H NMR (500 MHz, $CDCl_3$)

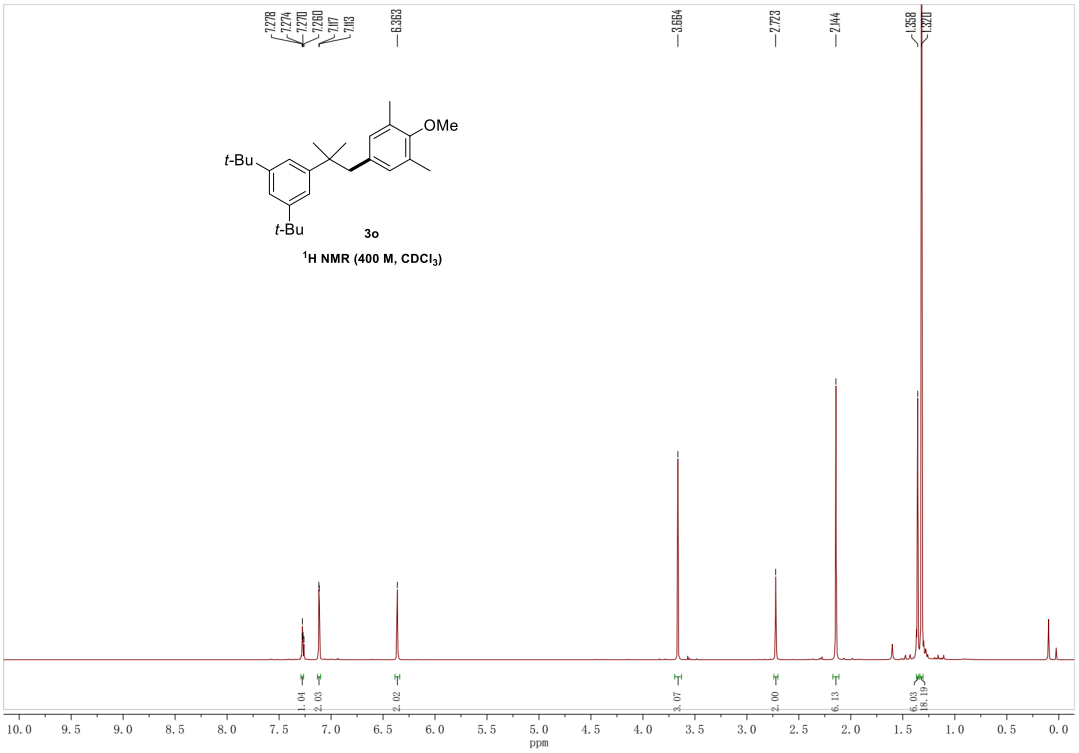


^{13}C NMR (126 MHz, $CDCl_3$)

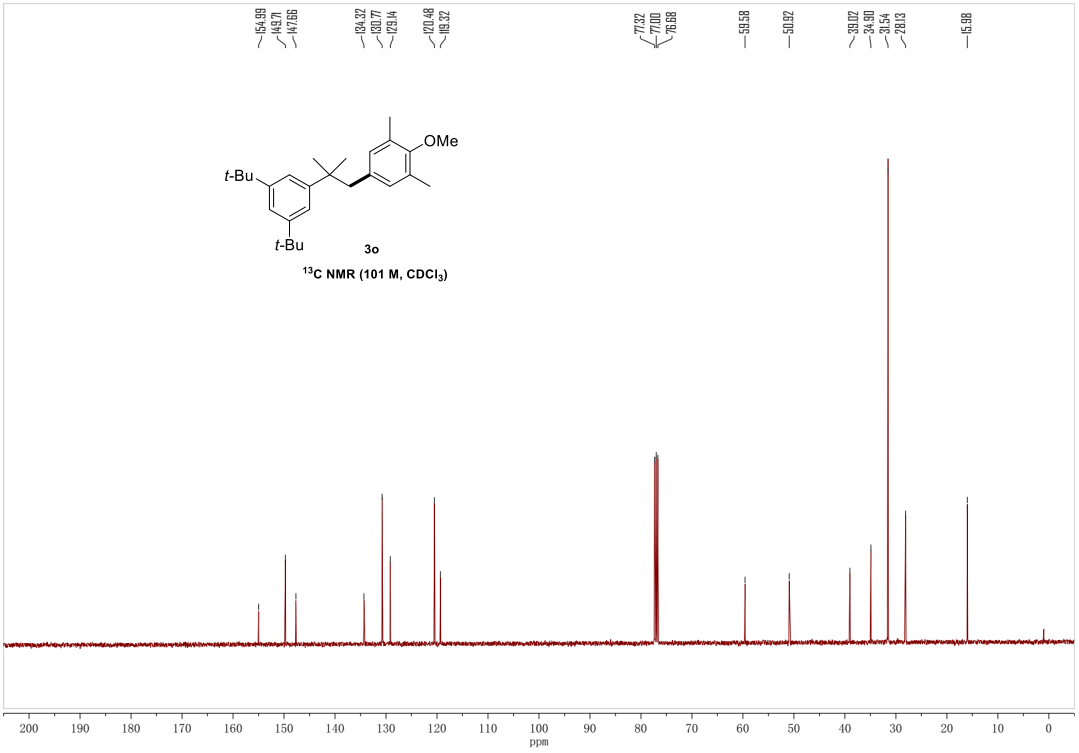


5-(2-(3,5-di-*tert*-butylphenyl)-2-methylpropyl)-2-methoxy-1,3-dimethylbenzene (3o)

^{1}H NMR (400 MHz, $CDCl_3$)

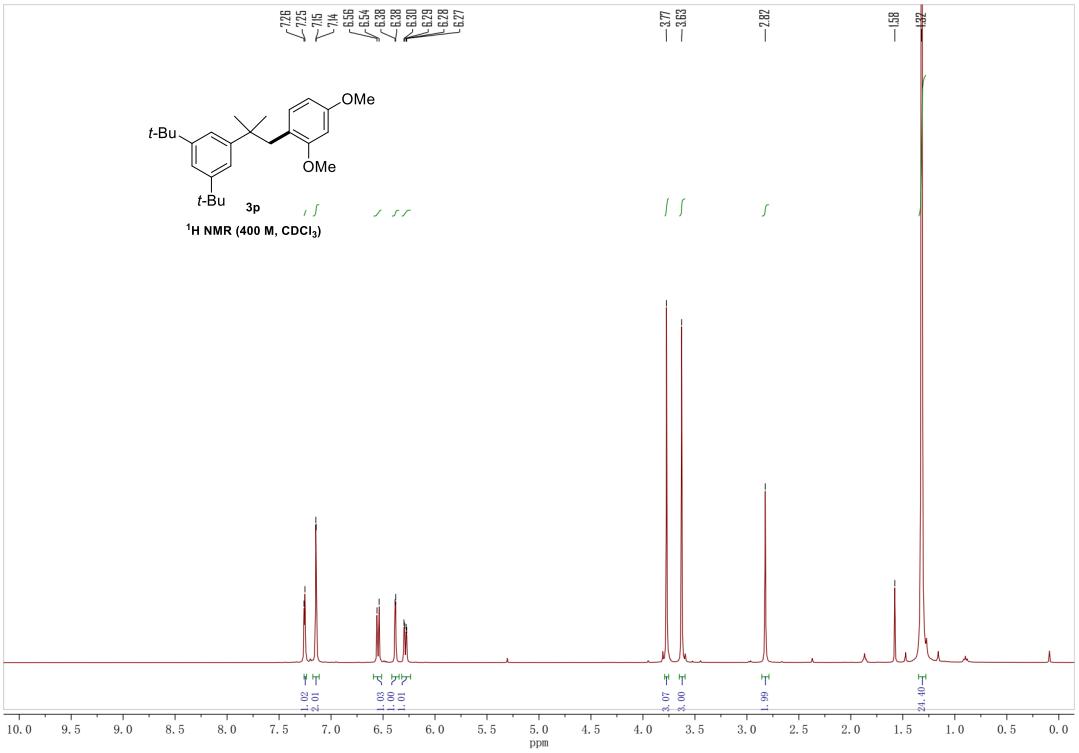


^{13}C NMR (101 MHz, $CDCl_3$)

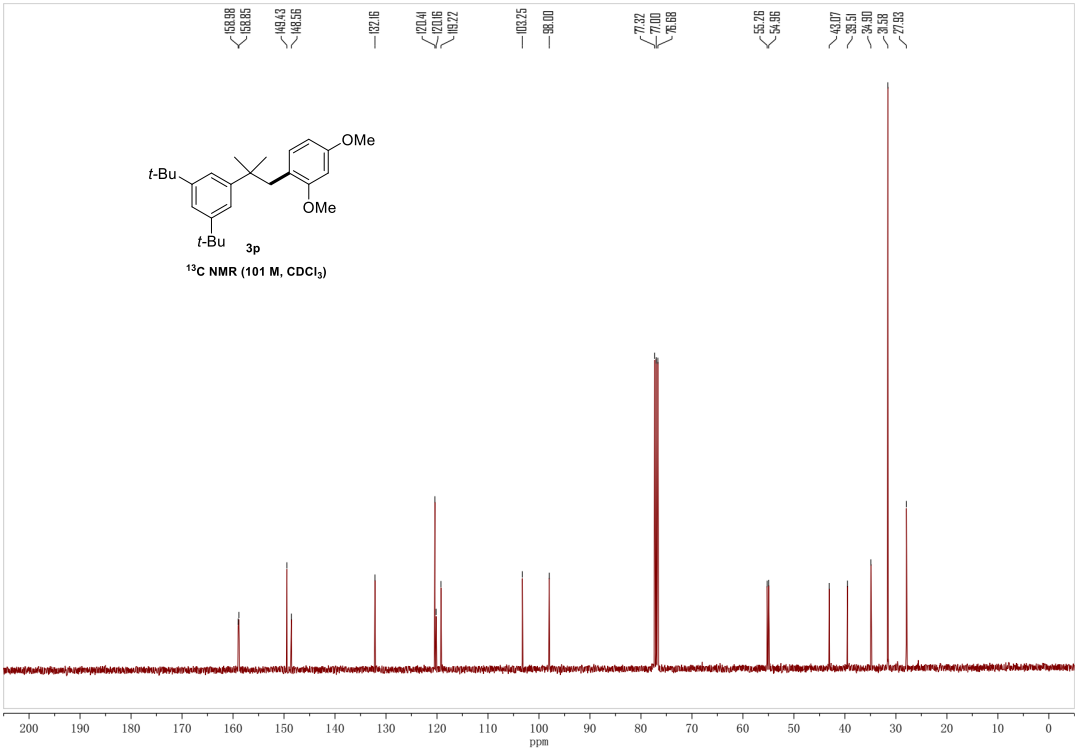


1-(2-(3,5-di-*tert*-butylphenyl)-2-methylpropyl)-2,4-dimethoxybenzene (3p)

^{1}H NMR (400 MHz, $CDCl_3$)

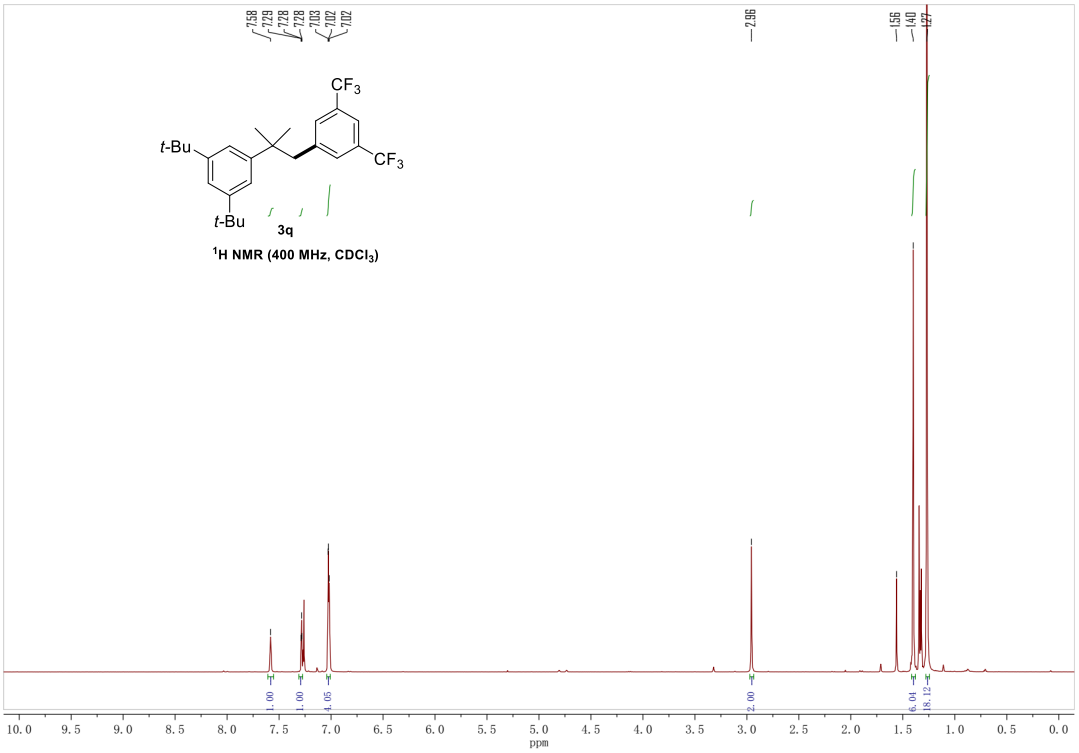


^{13}C NMR (101 MHz, $CDCl_3$)

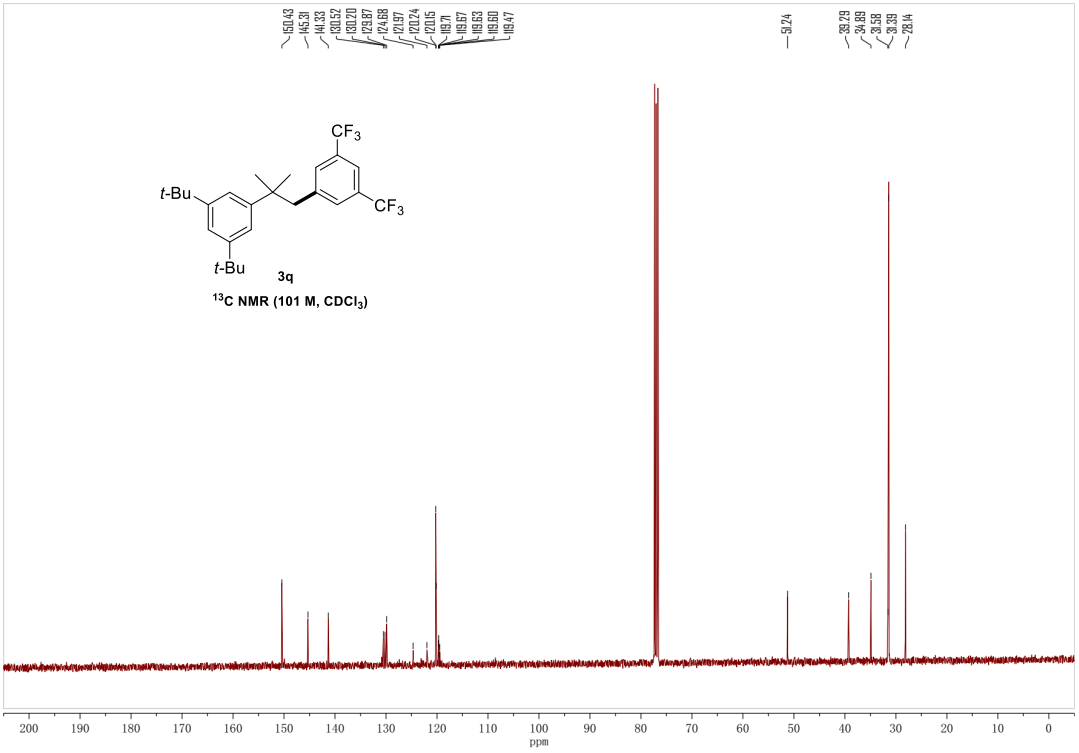


1-(1-(3,5-bis(trifluoromethyl)phenyl)-2-methylpropan-2-yl)-3,5-di-*tert*-butylbenzene (3q)

^{1}H NMR (400 MHz, $CDCl_3$)

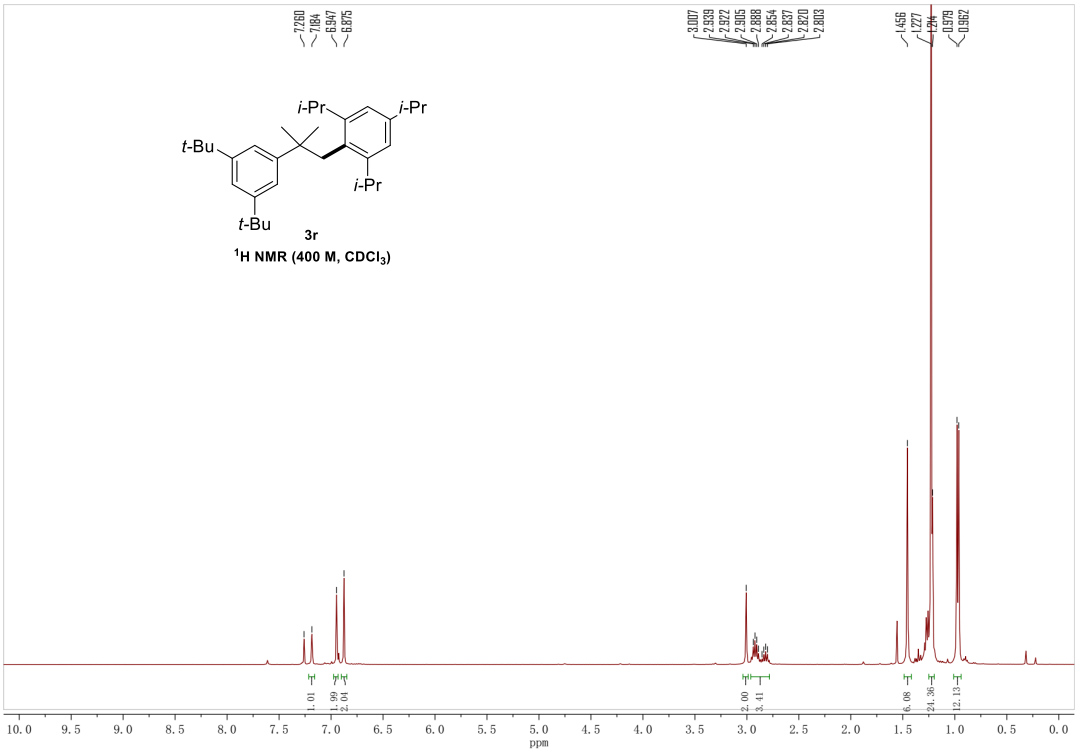


^{13}C NMR (101 MHz, $CDCl_3$)

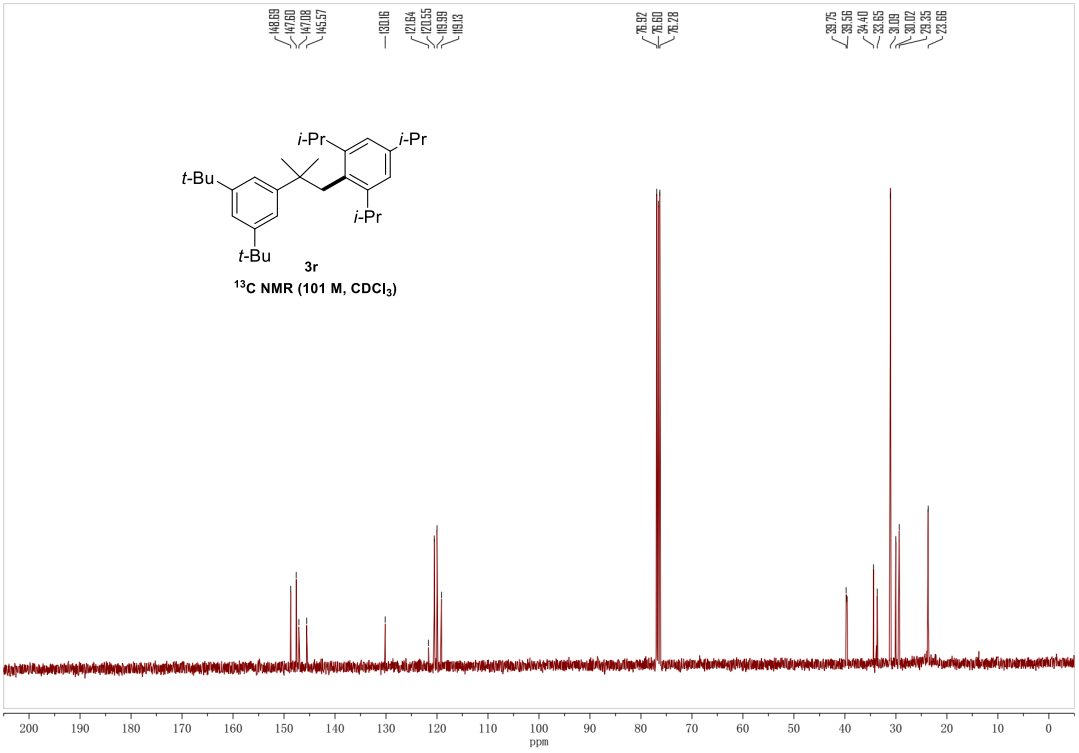


2-(2-(3,5-di-*tert*-butylphenyl)-2-methylpropyl)-1,3,5-triisopropylbenzene (3r)

^{1}H NMR (400 MHz, $CDCl_3$)

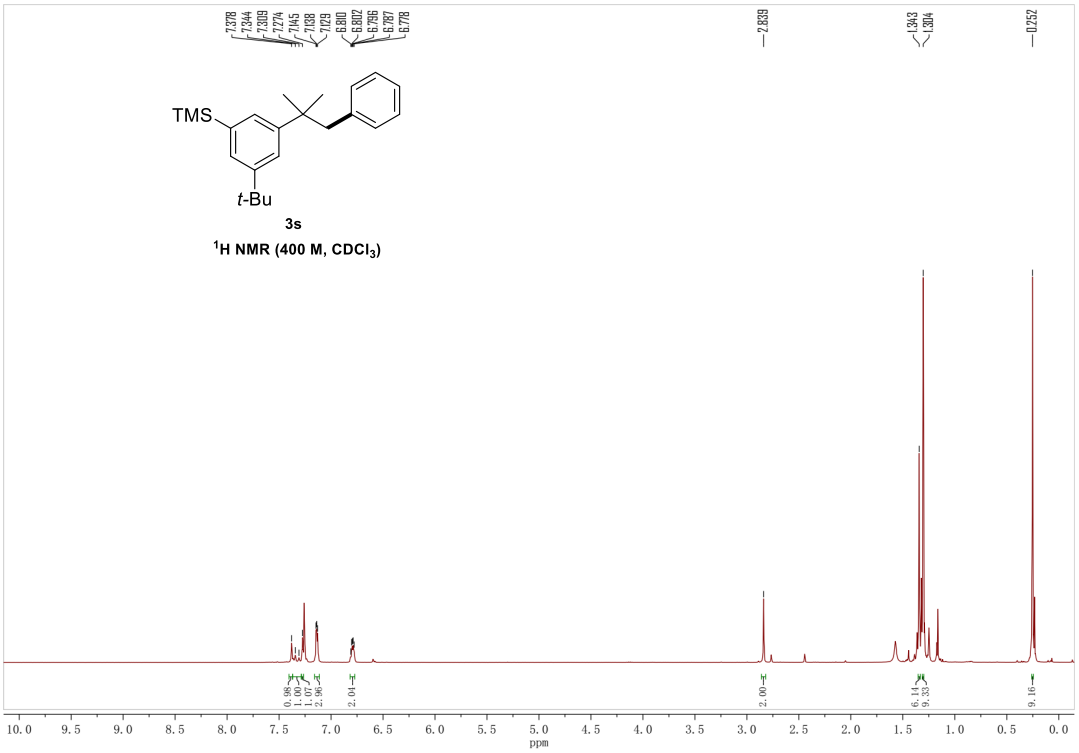


^{13}C NMR (101 MHz, $CDCl_3$)

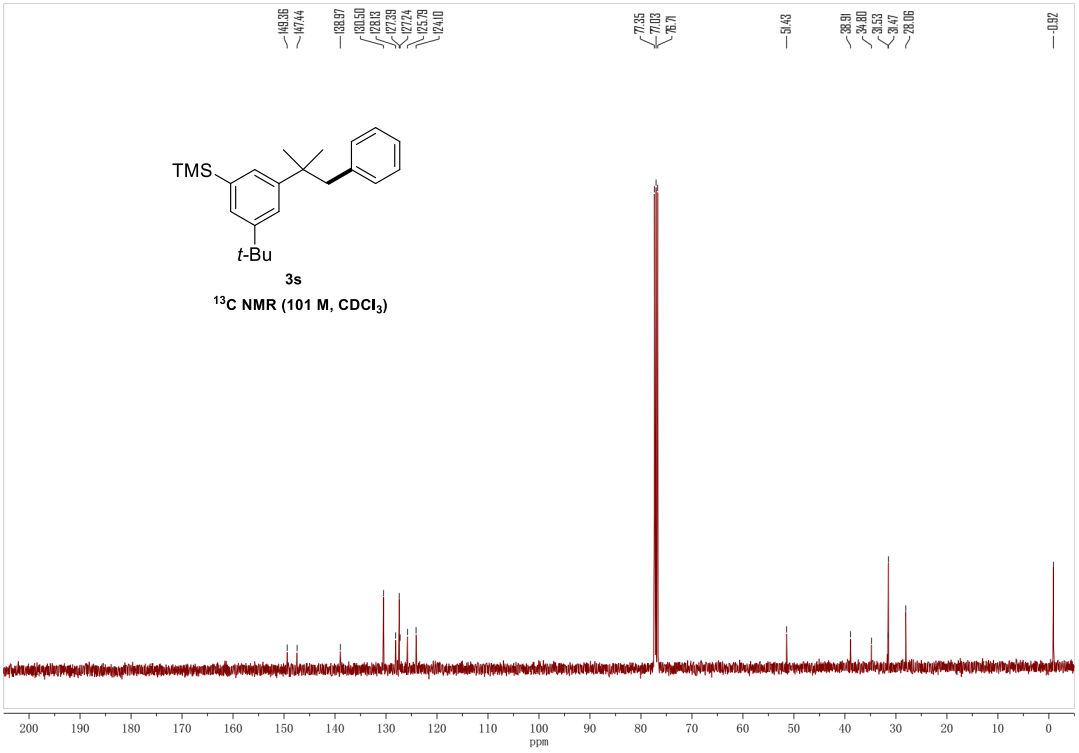


(3-(*tert*-butyl)-5-(2-methyl-1-phenylpropan-2-yl)phenyl)trimethylsilane (3s)

^{1}H NMR (400 MHz, $CDCl_3$)

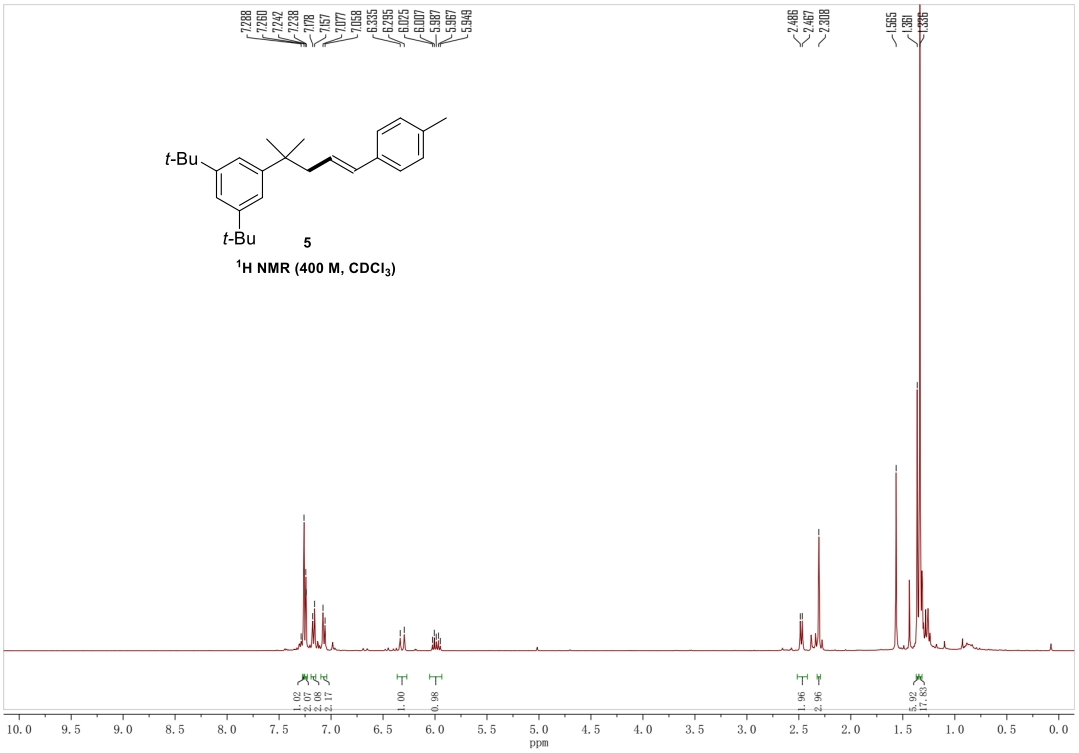


^{13}C NMR (101 MHz, $CDCl_3$)

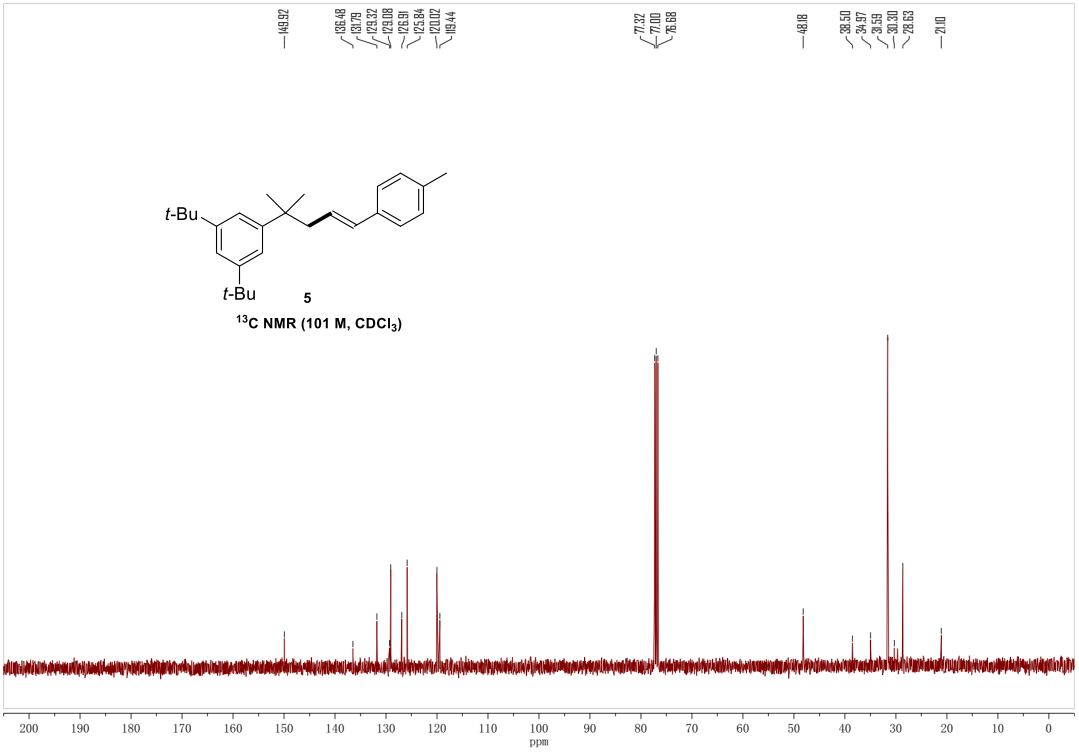


(*E*)-1,3-di-*tert*-butyl-5-(2-methyl-5-(*p*-tolyl)pent-4-en-2-yl)benzene (5)

^{1}H NMR (400 MHz, $CDCl_3$)

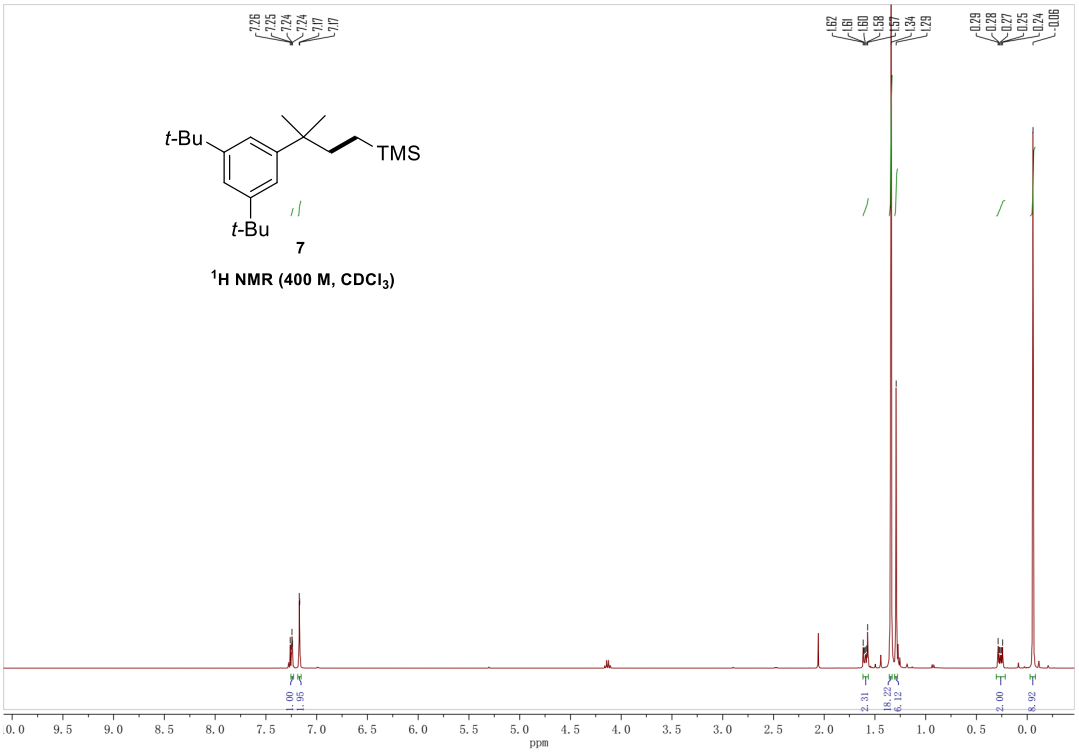


^{13}C NMR (101 MHz, $CDCl_3$)

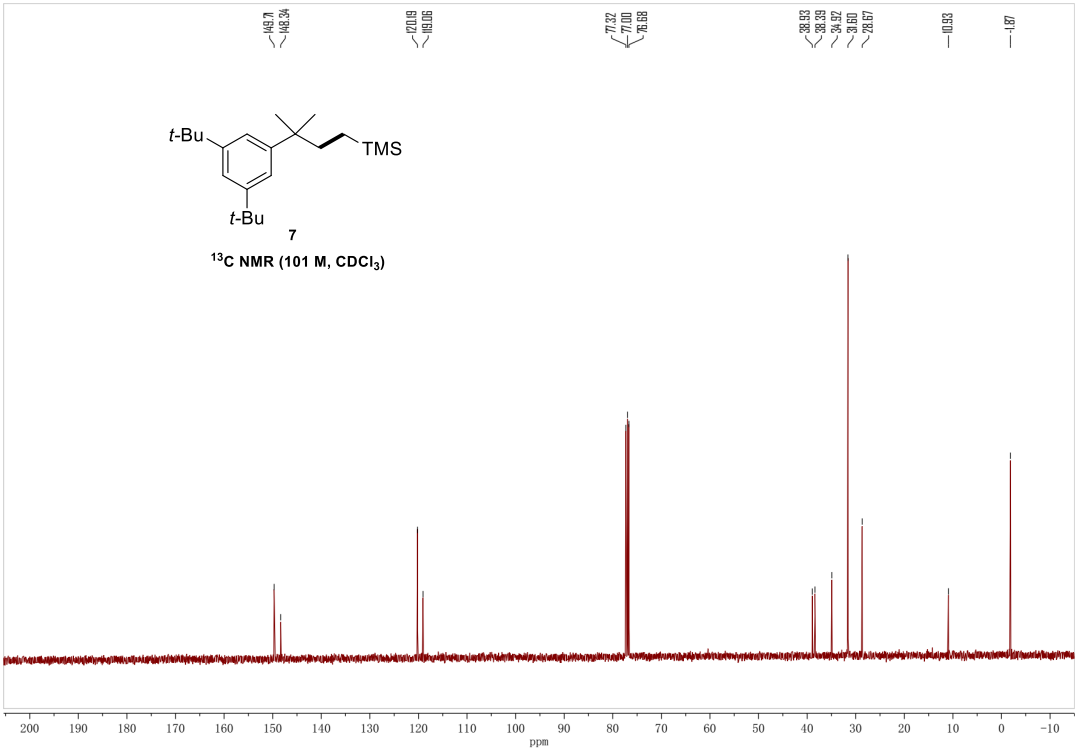


(3-(3,5-di-*tert*-butylphenyl)-3-methylbutyl)trimethylsilane (7)

^{1}H NMR (400 MHz, $CDCl_3$)

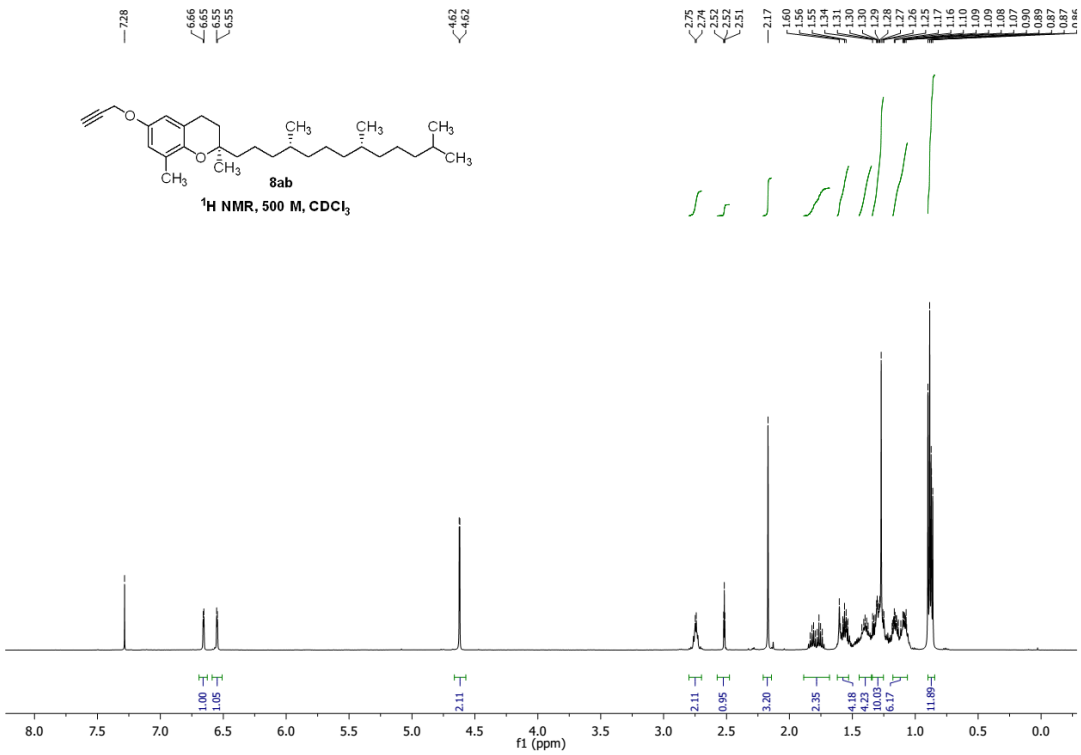


^{13}C NMR (101 MHz, $CDCl_3$)

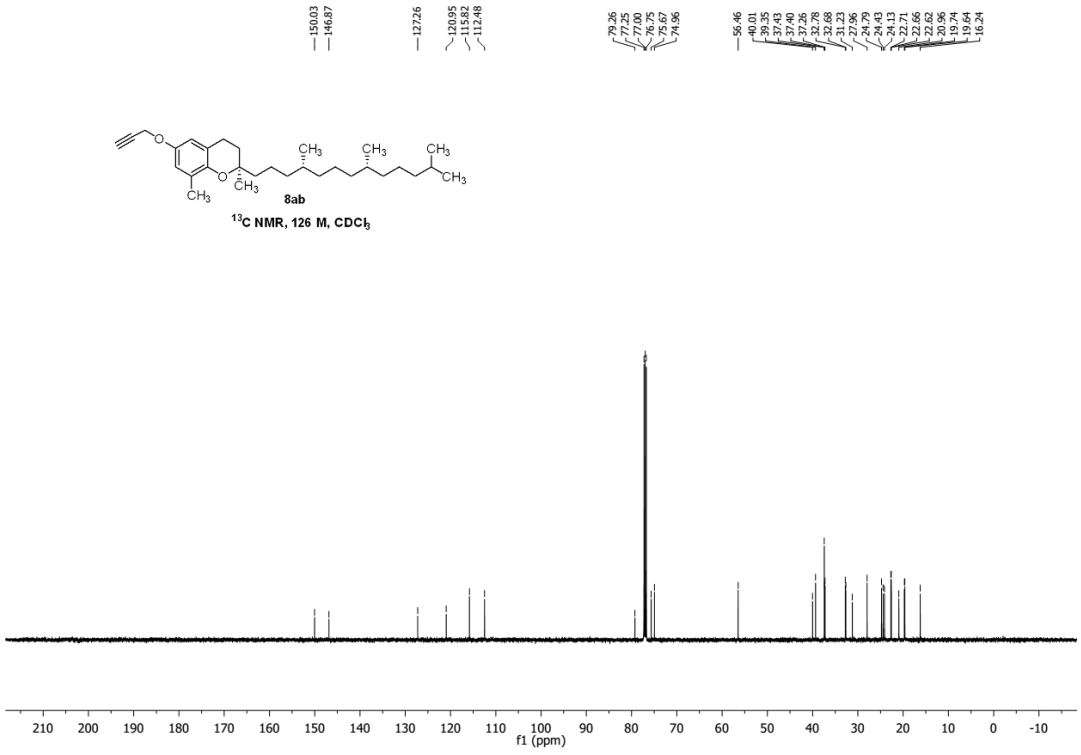


(R)-2,8-dimethyl-6-(prop-2-yn-1-yloxy)-2-((4R,8R)-4,8,12-trimethyltridecyl)chromane (8ab)

^{1}H NMR (500 MHz, $CDCl_3$)

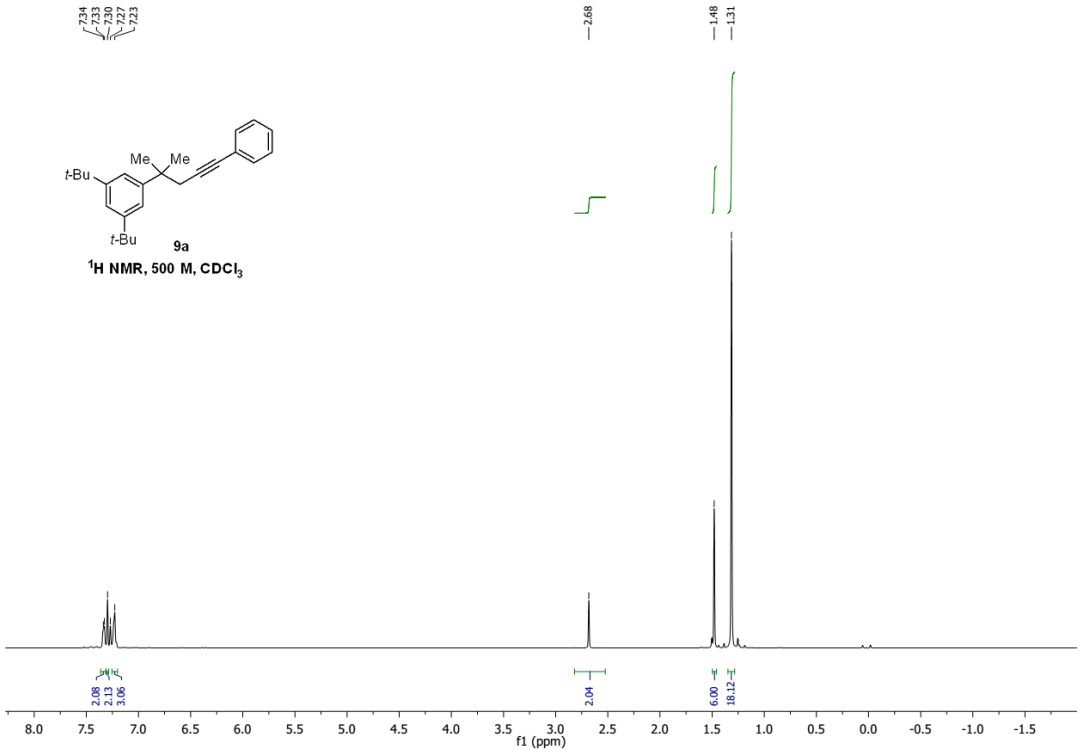


^{13}C NMR (126 MHz, $CDCl_3$)

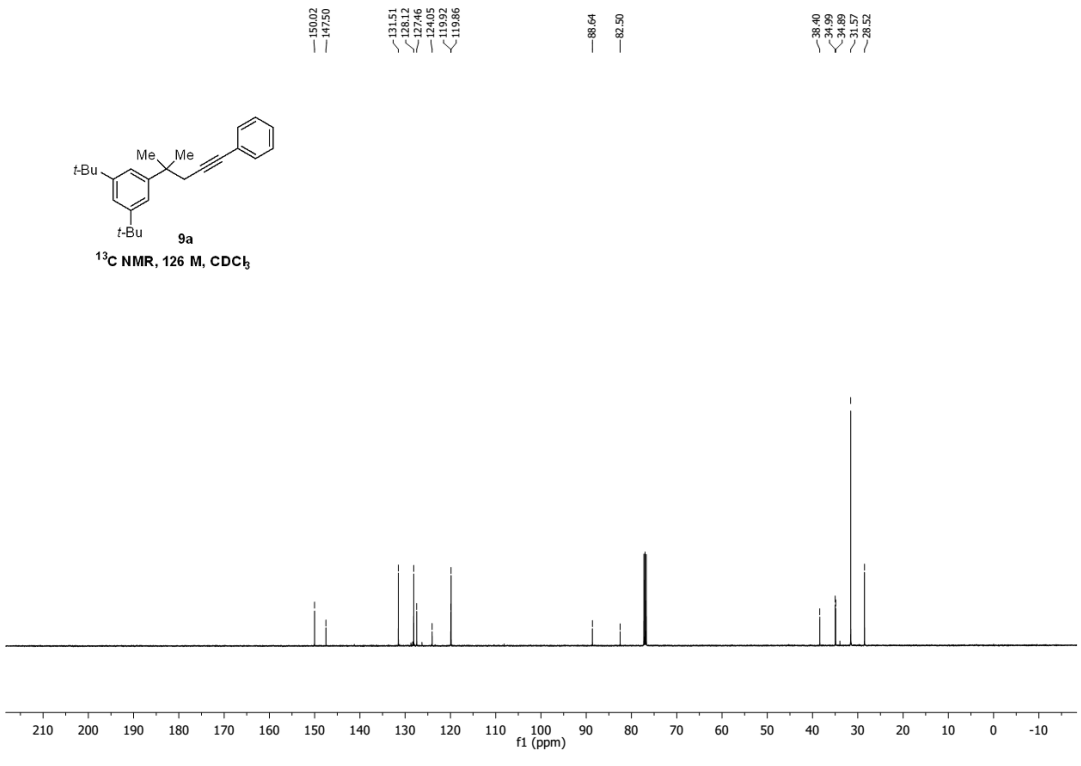


1,3-di-tert-butyl-5-(2-methyl-5-phenylpent-4-yn-2-yl)benzene (9a)

^{1}H NMR (500 MHz, $CDCl_3$)

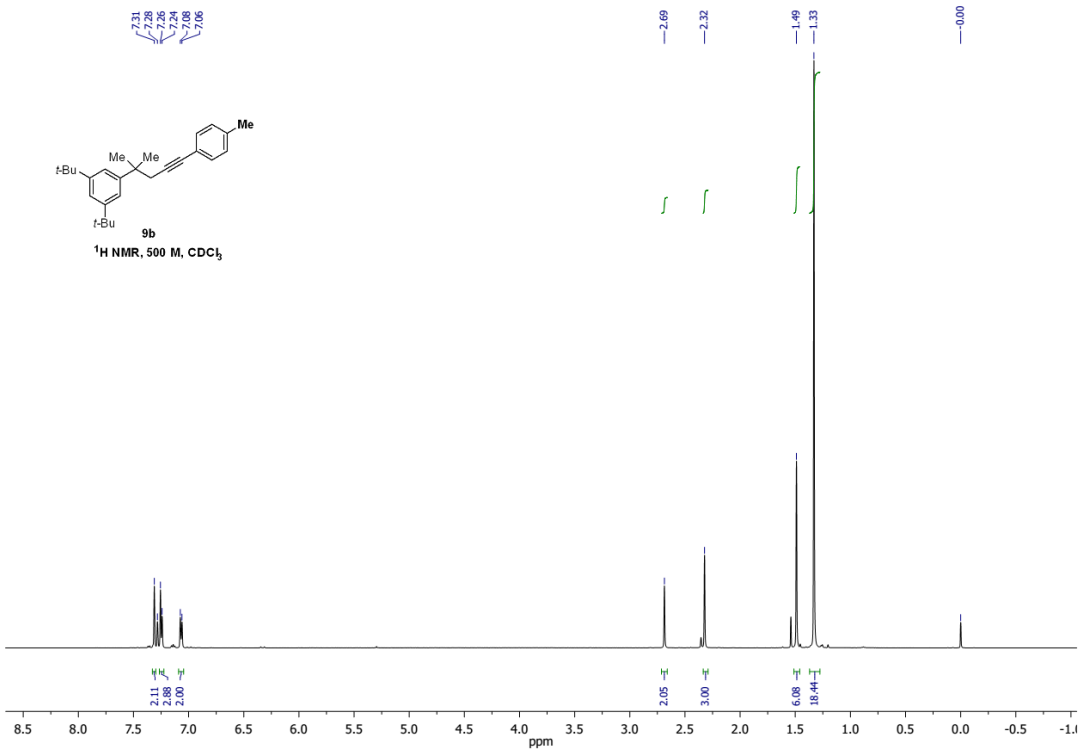


^{13}C NMR (126 MHz, $CDCl_3$)

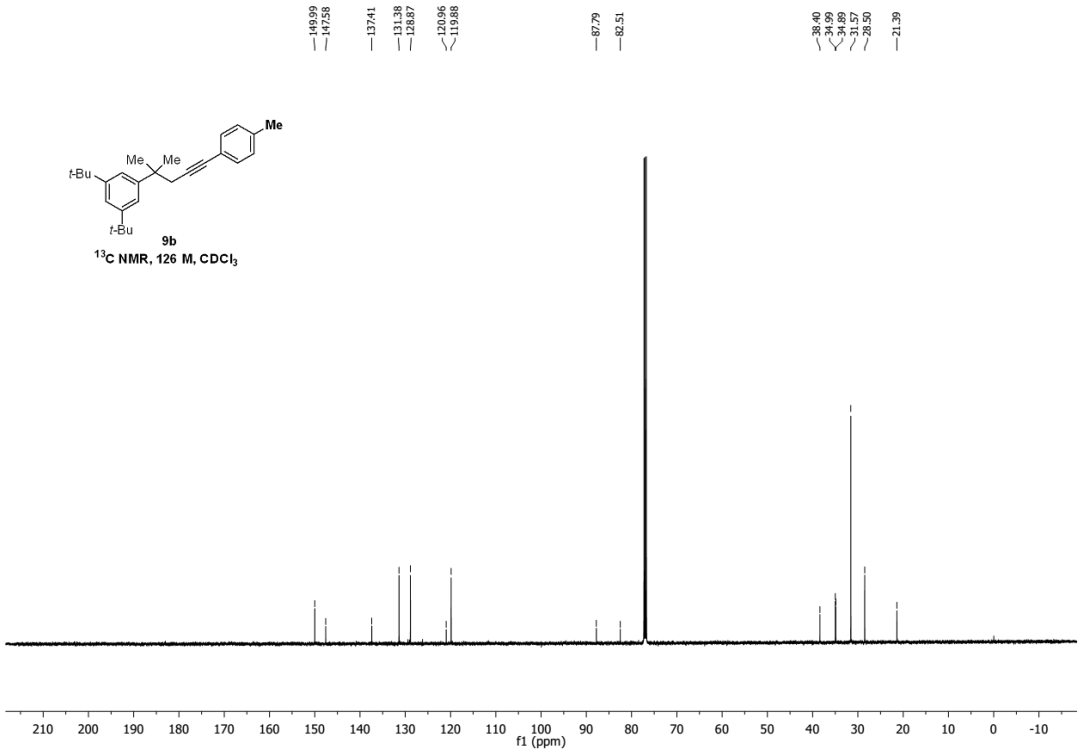


1,3-di-tert-butyl-5-(2-methyl-5-(p-tolyl)pent-4-yn-2-yl)benzene (9b)

^{1}H NMR (500 MHz, $CDCl_3$)

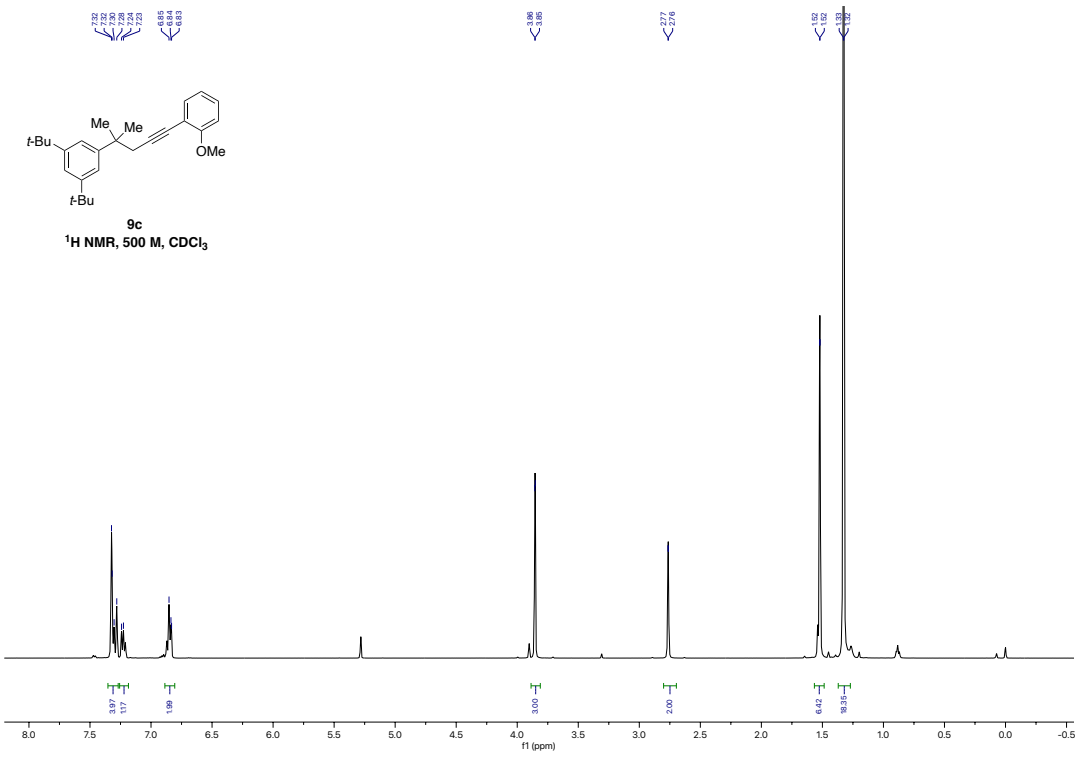


^{13}C NMR (126 MHz, $CDCl_3$)

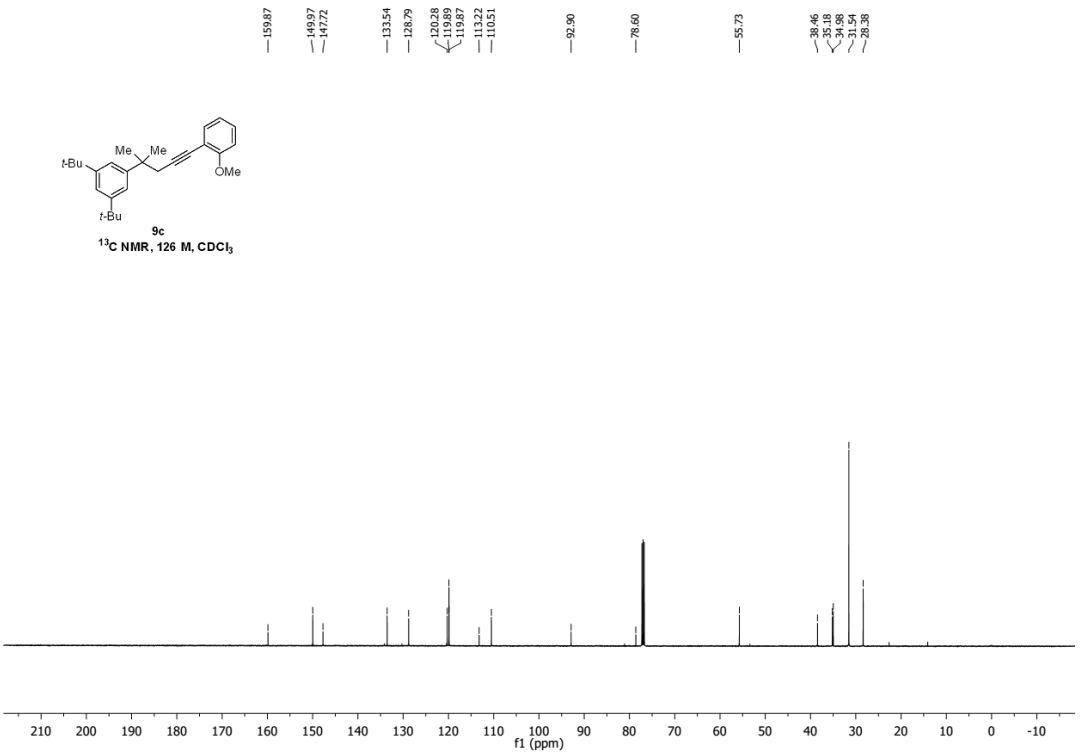


1,3-di-tert-butyl-5-(5-(2-methoxyphenyl)-2-methylpent-4-yn-2-yl)benzene (9c)

^{1}H NMR (500 MHz, $CDCl_3$)

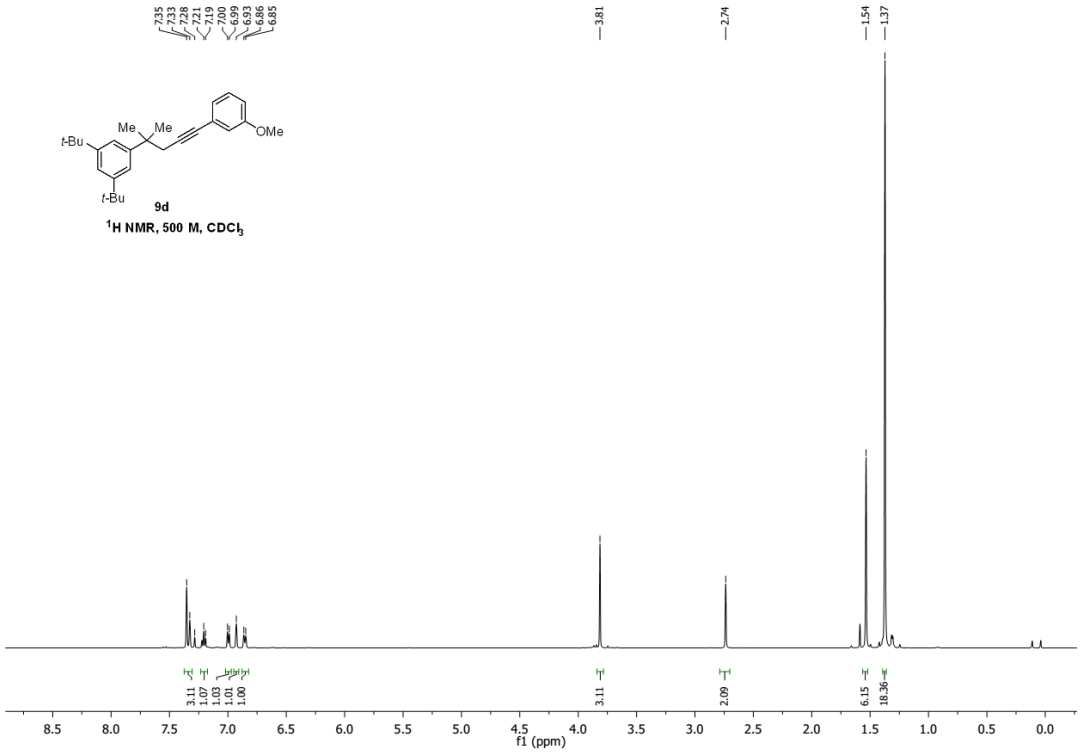


^{13}C NMR (126 MHz, $CDCl_3$)

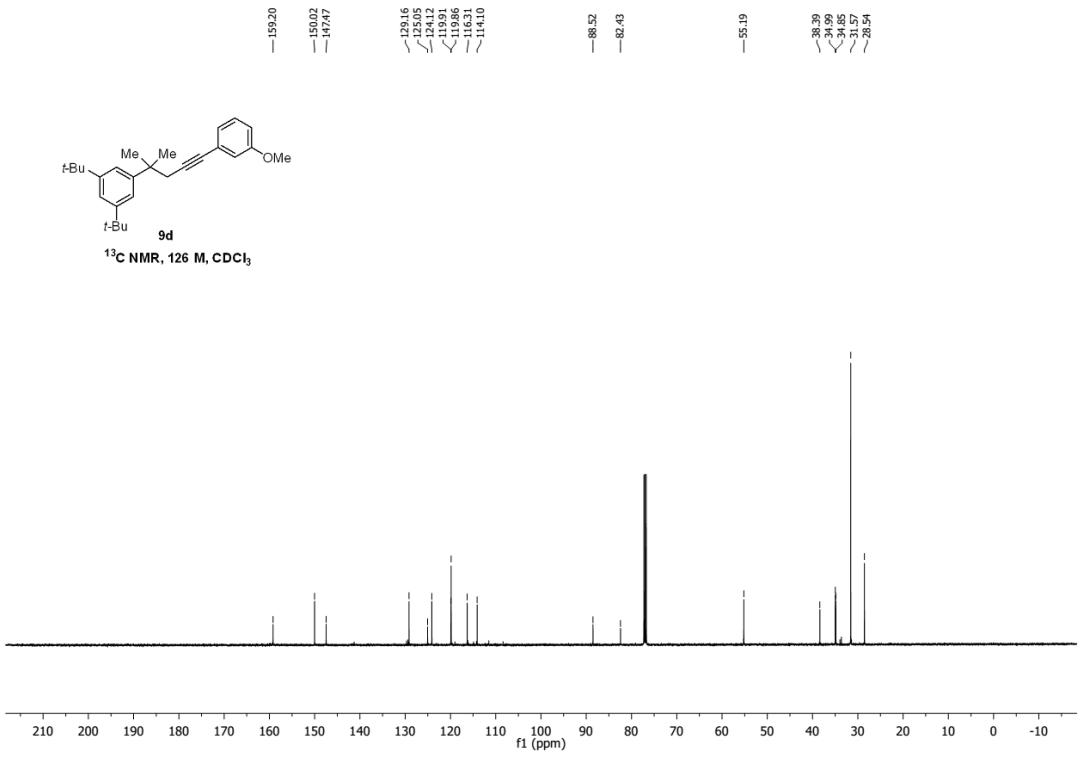


1,3-di-tert-butyl-5-(5-(3-methoxyphenyl)-2-methylpent-4-yn-2-yl)benzene (9d)

^{1}H NMR (500 MHz, $CDCl_3$)

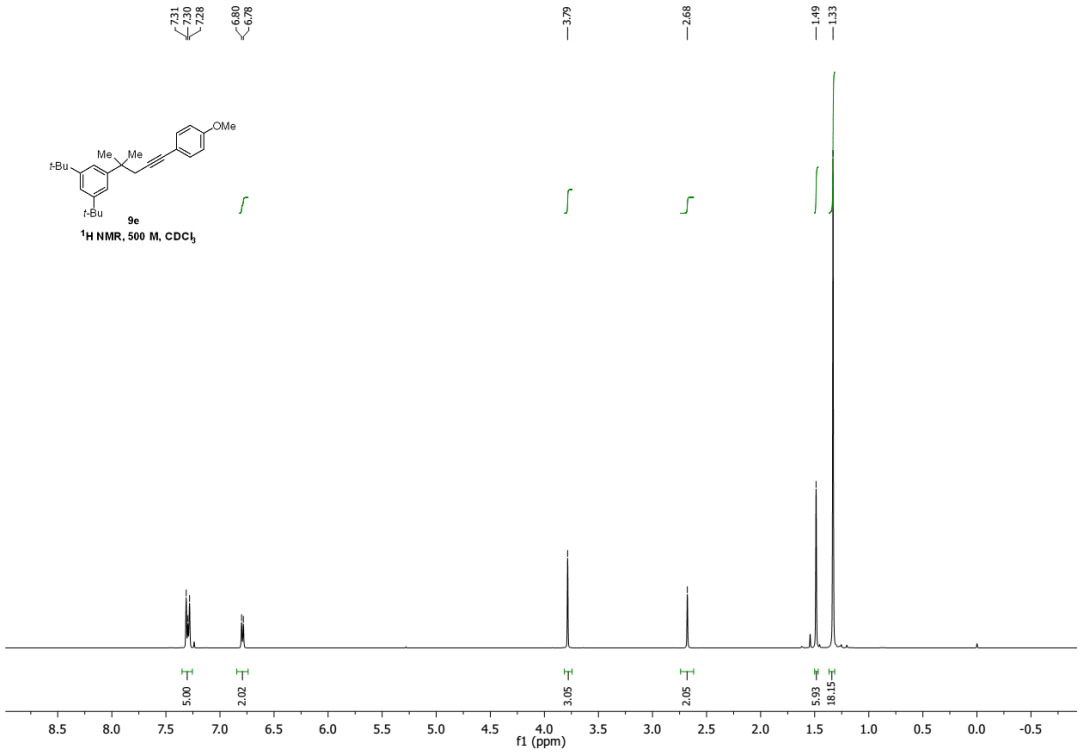


^{13}C NMR (126 MHz, $CDCl_3$)

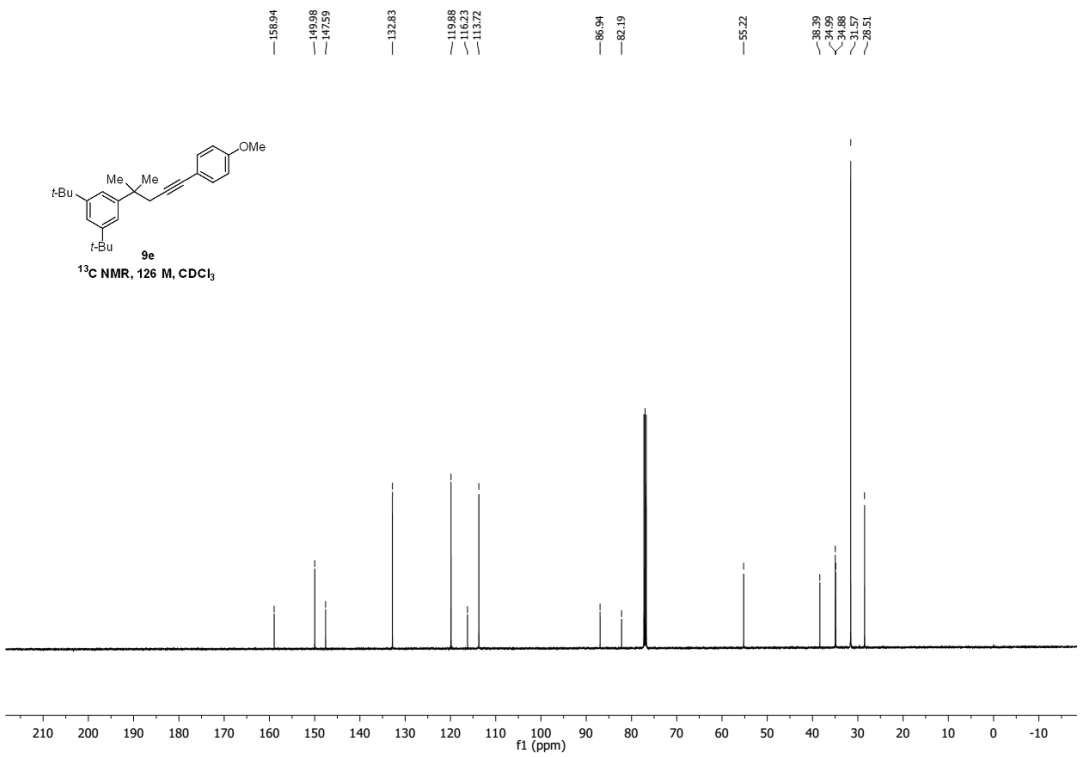


1,3-di-tert-butyl-5-(5-(4-methoxyphenyl)-2-methylpent-4-yn-2-yl)benzene (9e)

^{1}H NMR (500 MHz, $CDCl_3$)

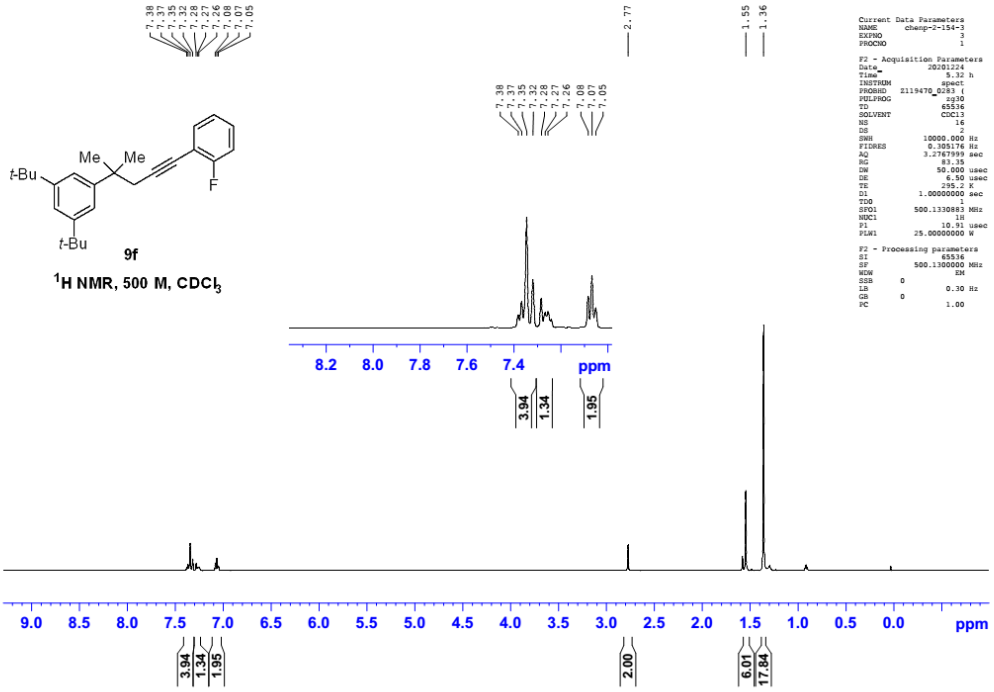


^{13}C NMR (126 MHz, $CDCl_3$)

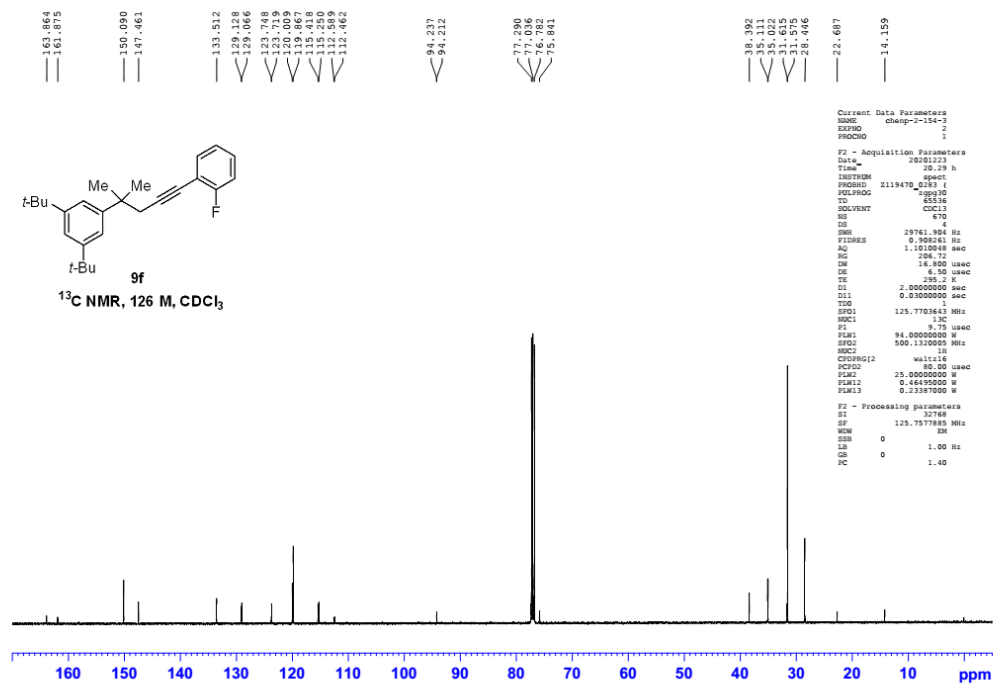


1,3-di-tert-butyl-5-(5-(2-fluorophenyl)-2-methylpent-4-yn-2-yl)benzene (9f)

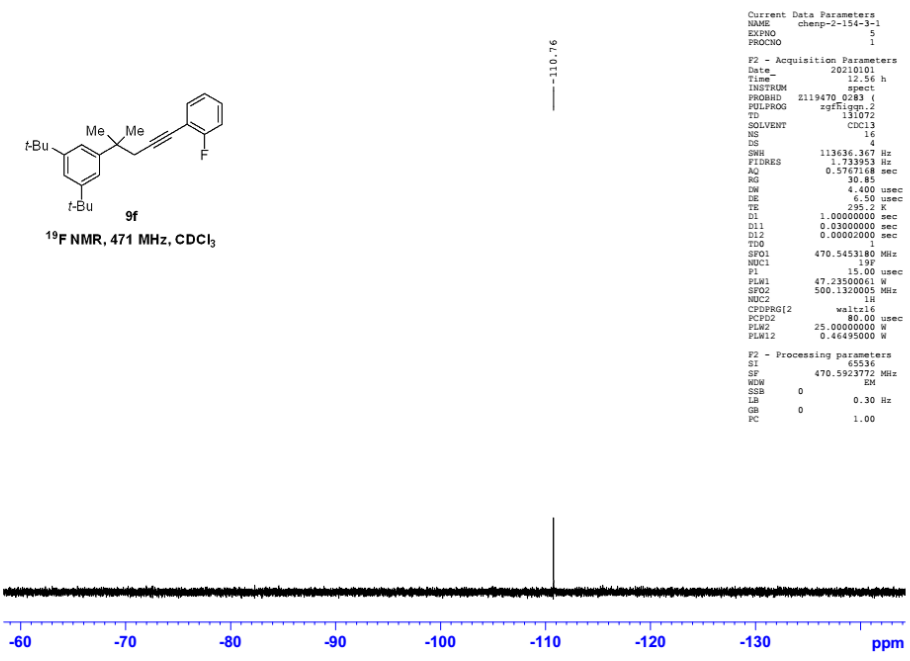
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

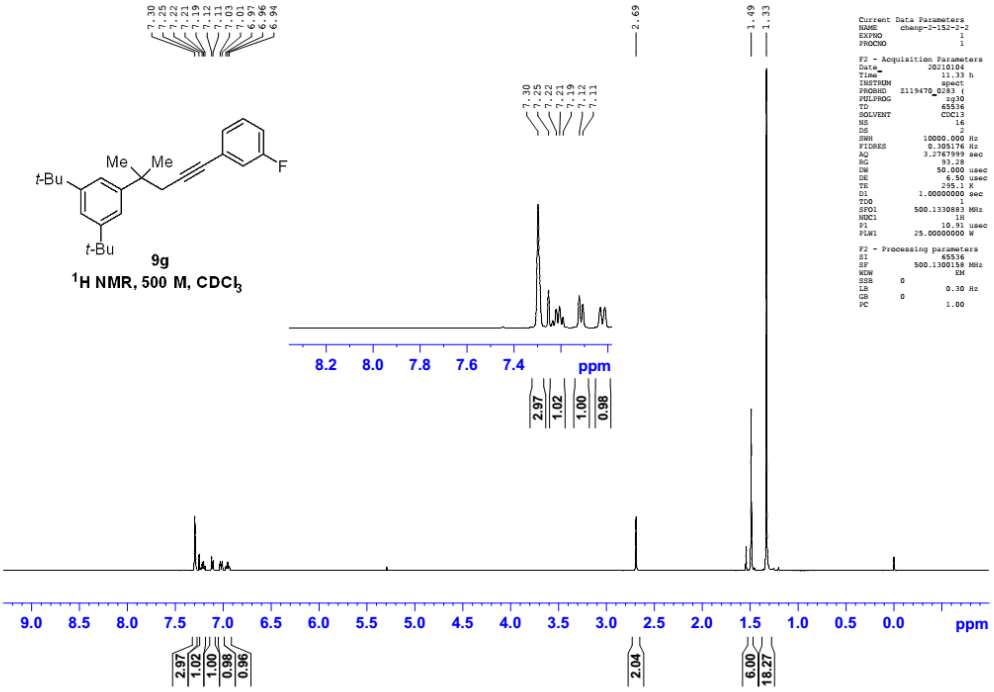


^{19}F NMR (471 MHz, $CDCl_3$)

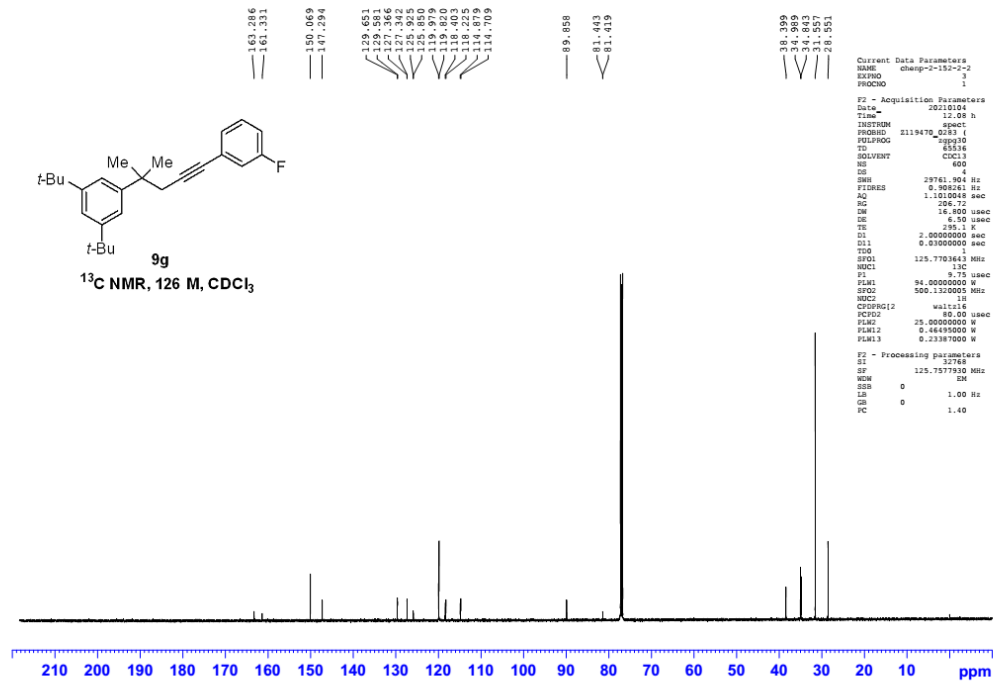


1,3-di-tert-butyl-5-(5-(3-fluorophenyl)-2-methylpent-4-yn-2-yl)benzene (9g)

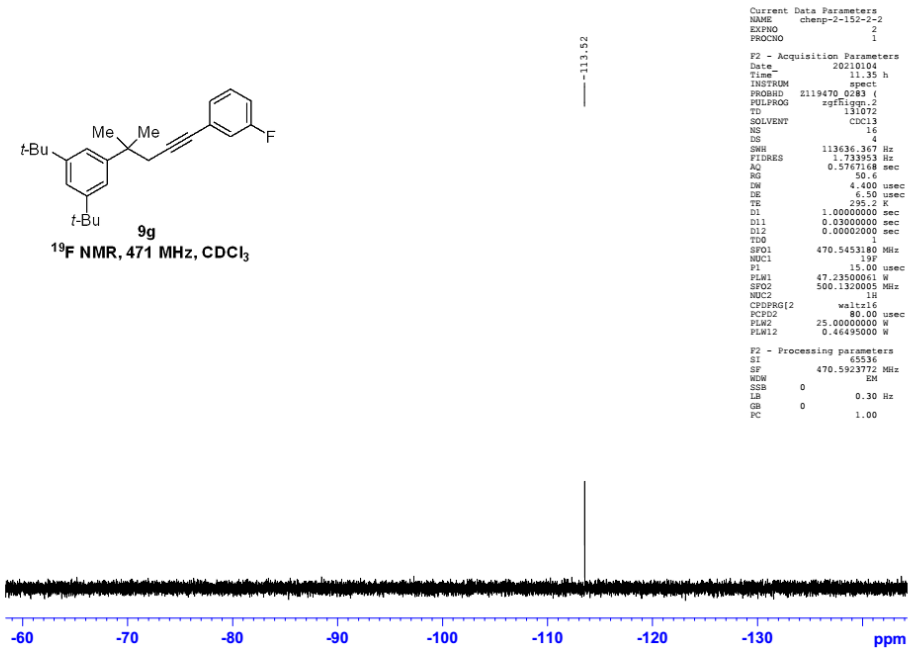
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

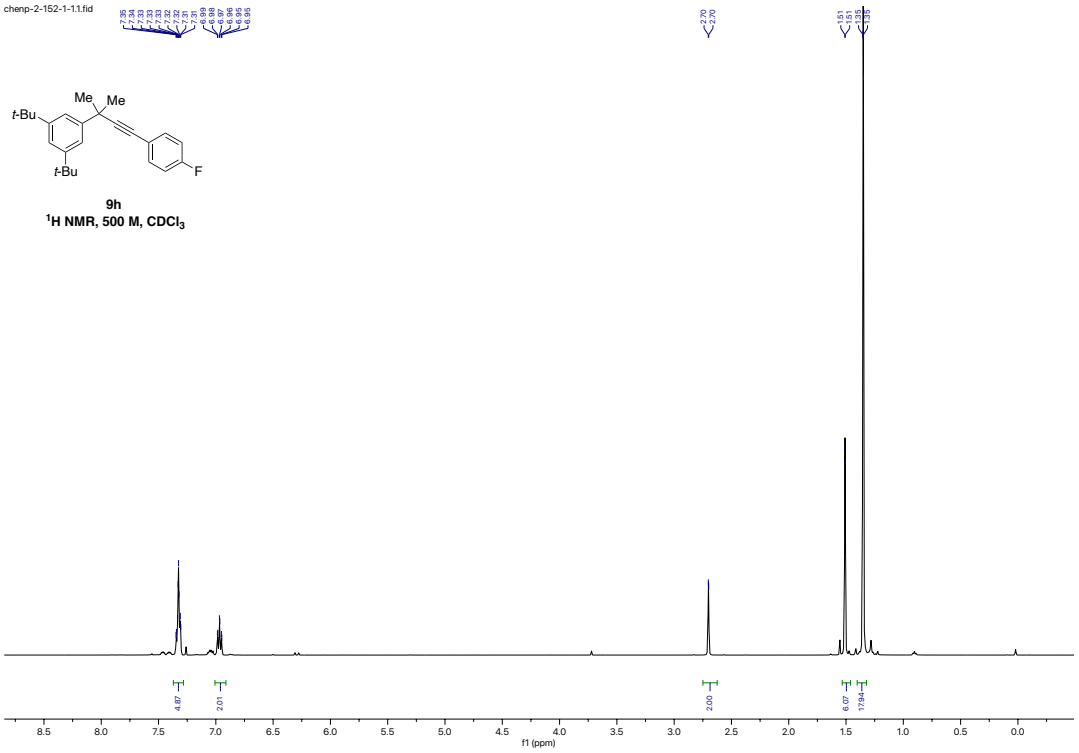


^{19}F NMR (471 MHz, $CDCl_3$)

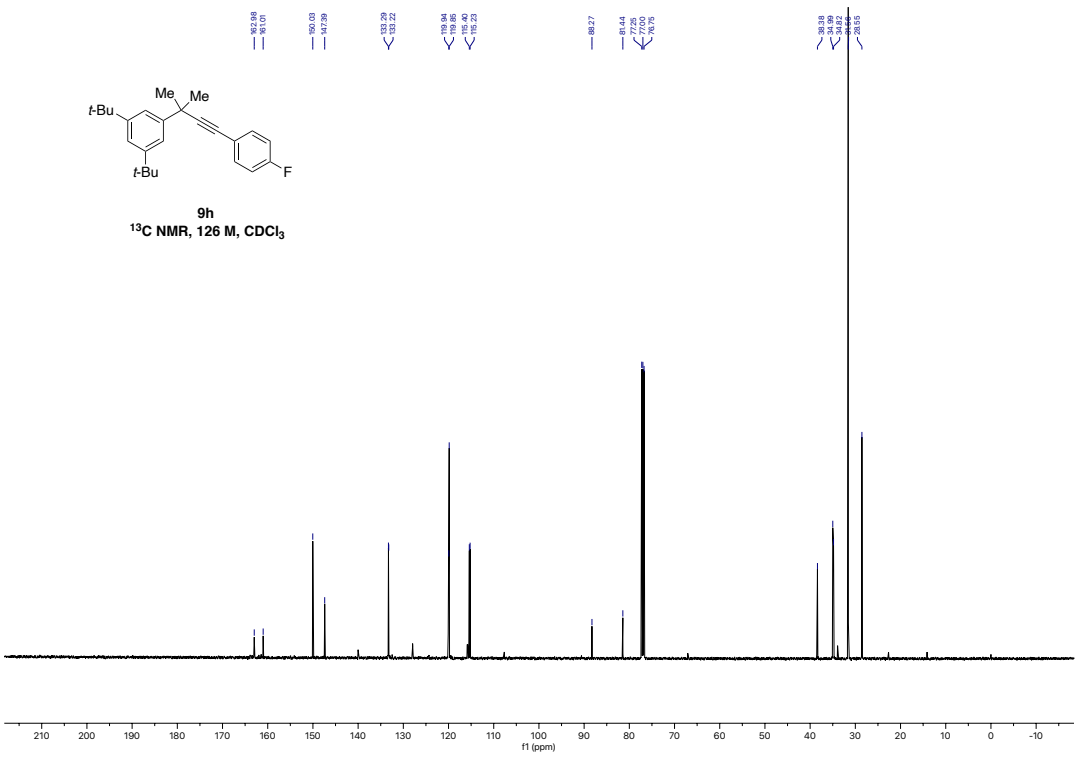


1,3-di-tert-butyl-5-(5-(4-fluorophenyl)-2-methylpent-4-yn-2-yl)benzene (9h)

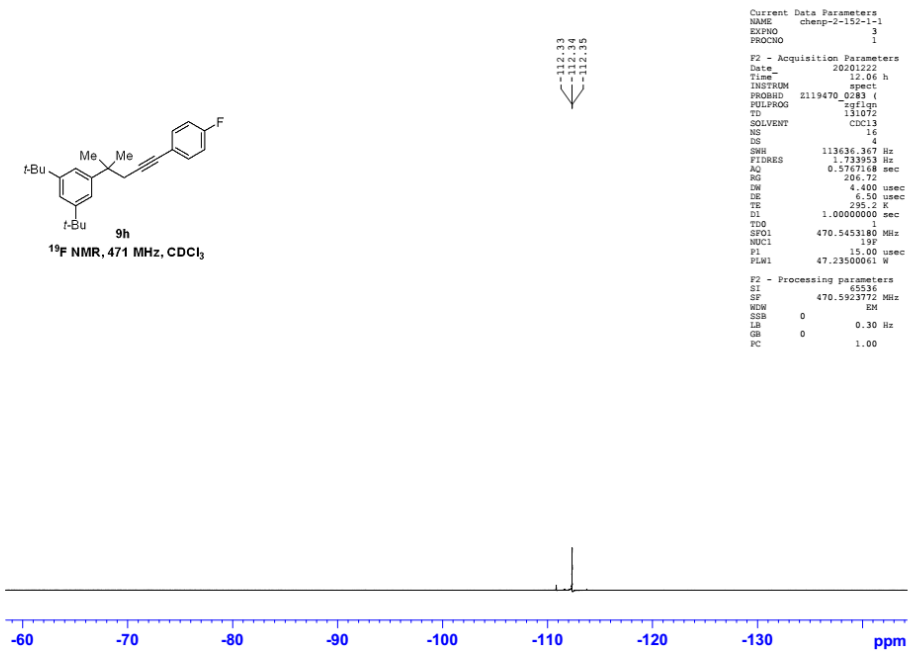
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

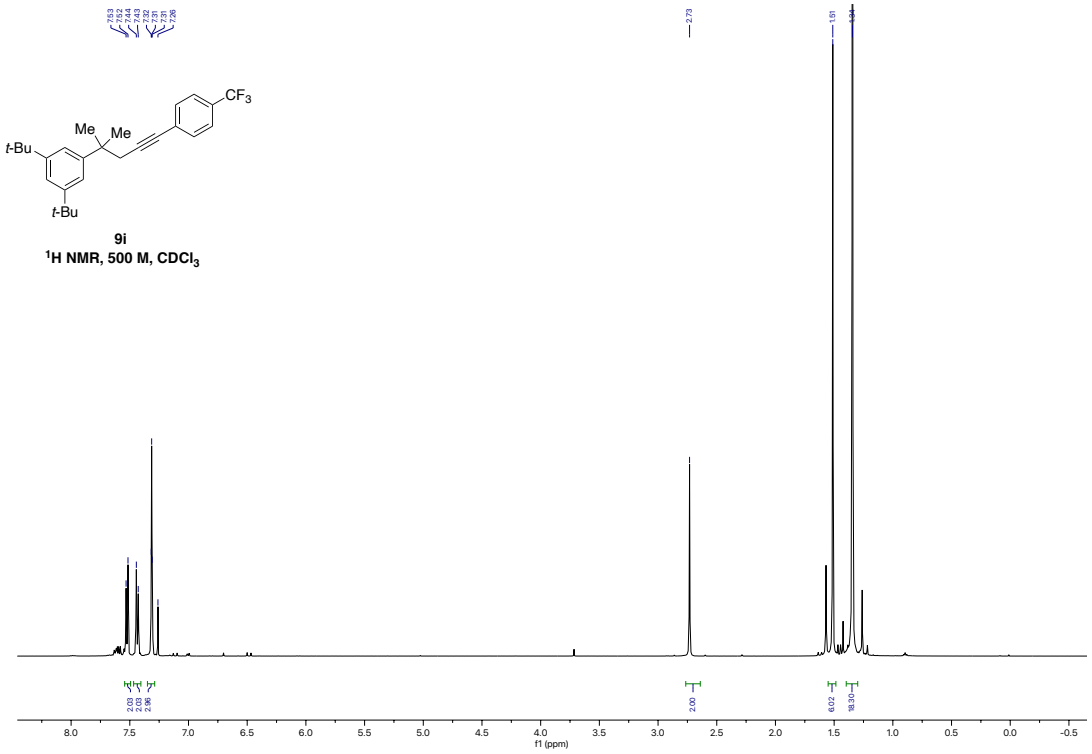


^{19}F NMR (471 MHz, $CDCl_3$)

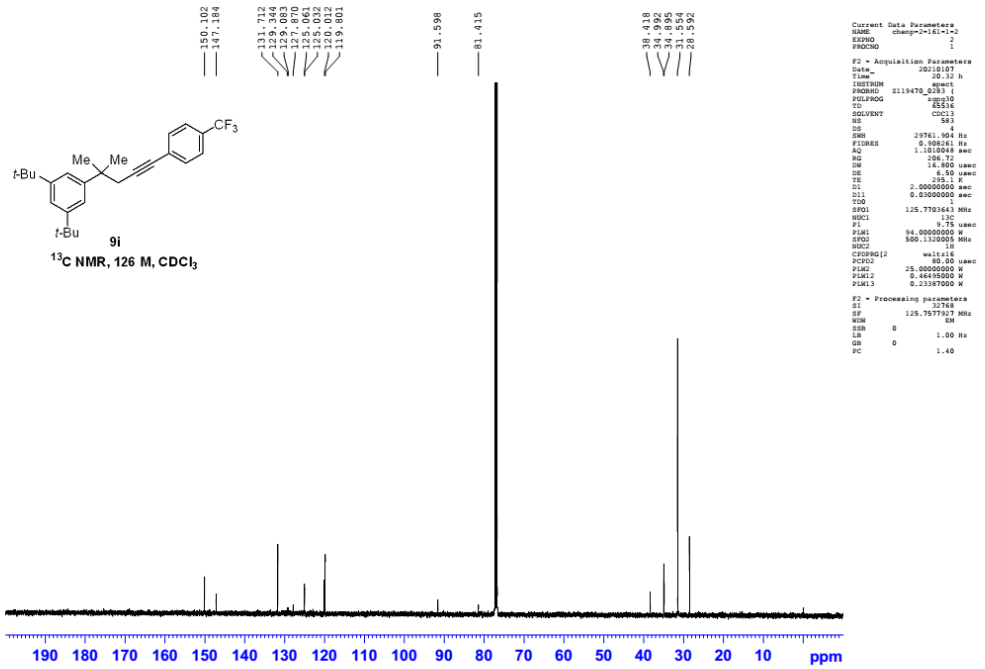


1,3-di-tert-butyl-5-(2-methyl-5-(4-(trifluoromethyl)phenyl)pent-4-yn-2-yl)benzene (9i)

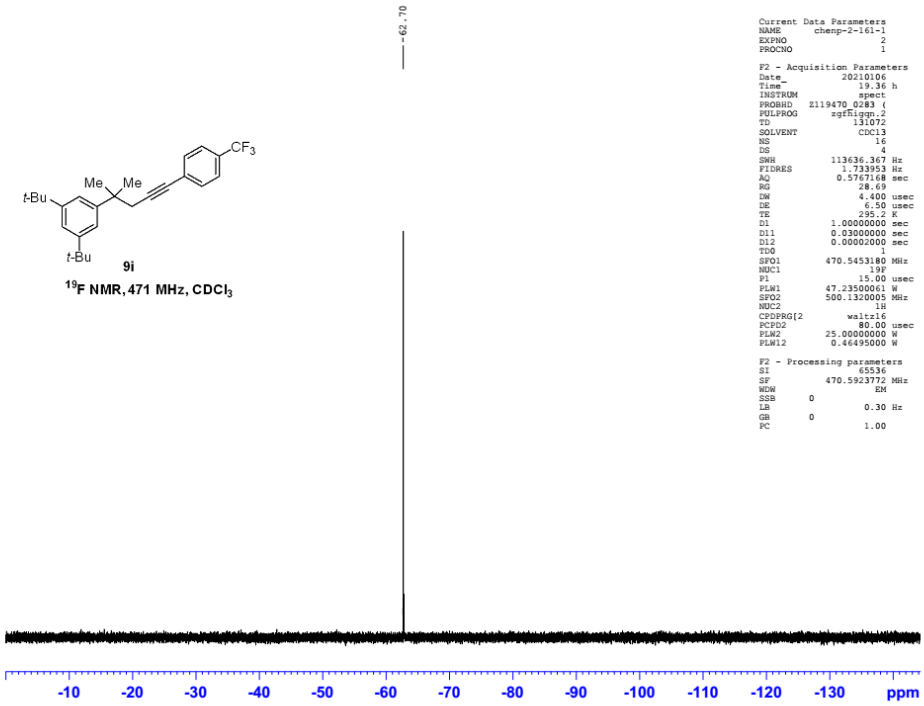
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)



^{19}F NMR (471 MHz, $CDCl_3$)

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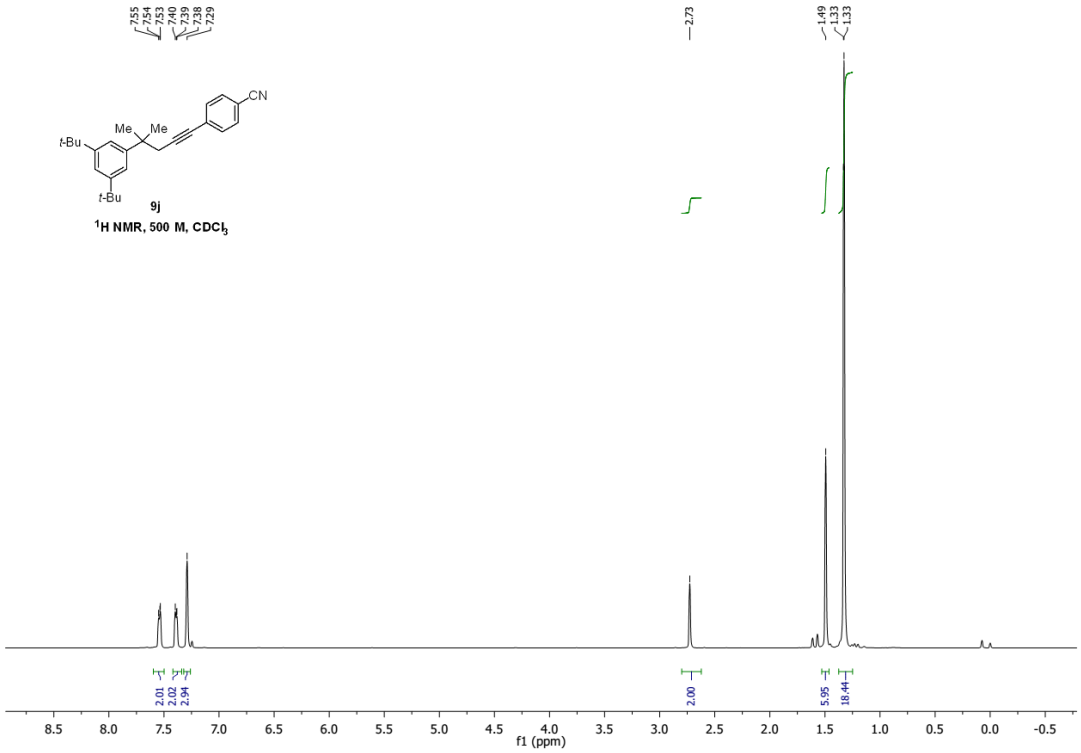
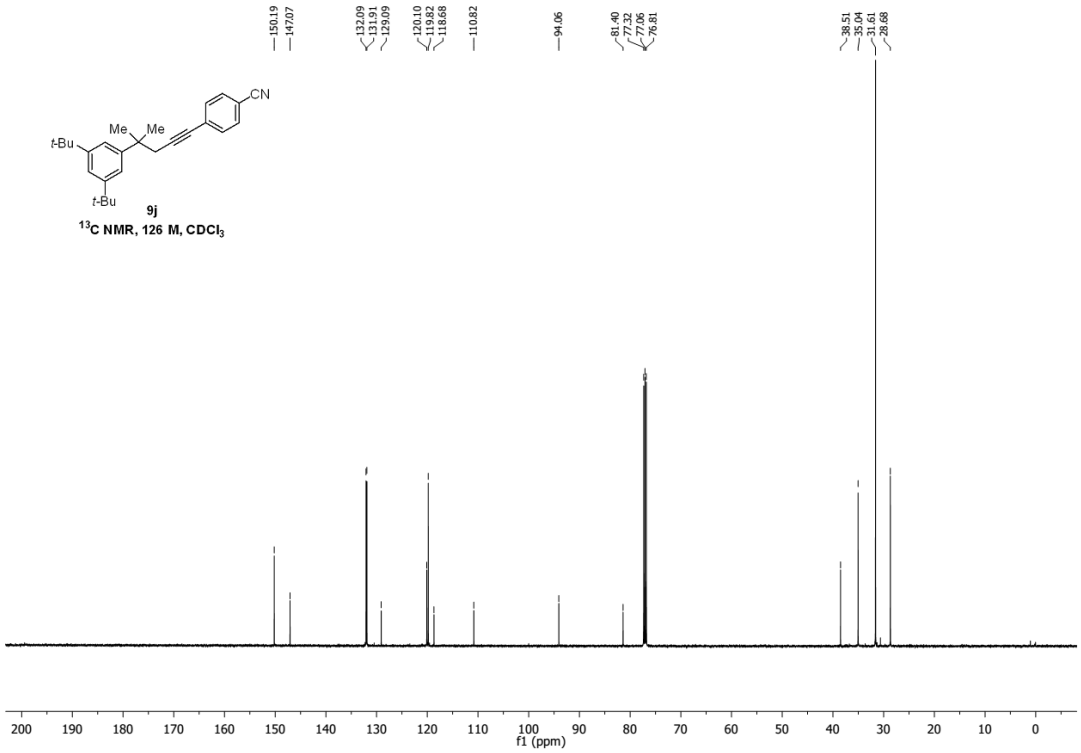
4-(4-(3,5-di-tert-butylphenyl)-4-methylpent-1-yn-1-yl)benzonitrile (9j)

^{1}H NMR (500 MHz, $CDCl_3$)

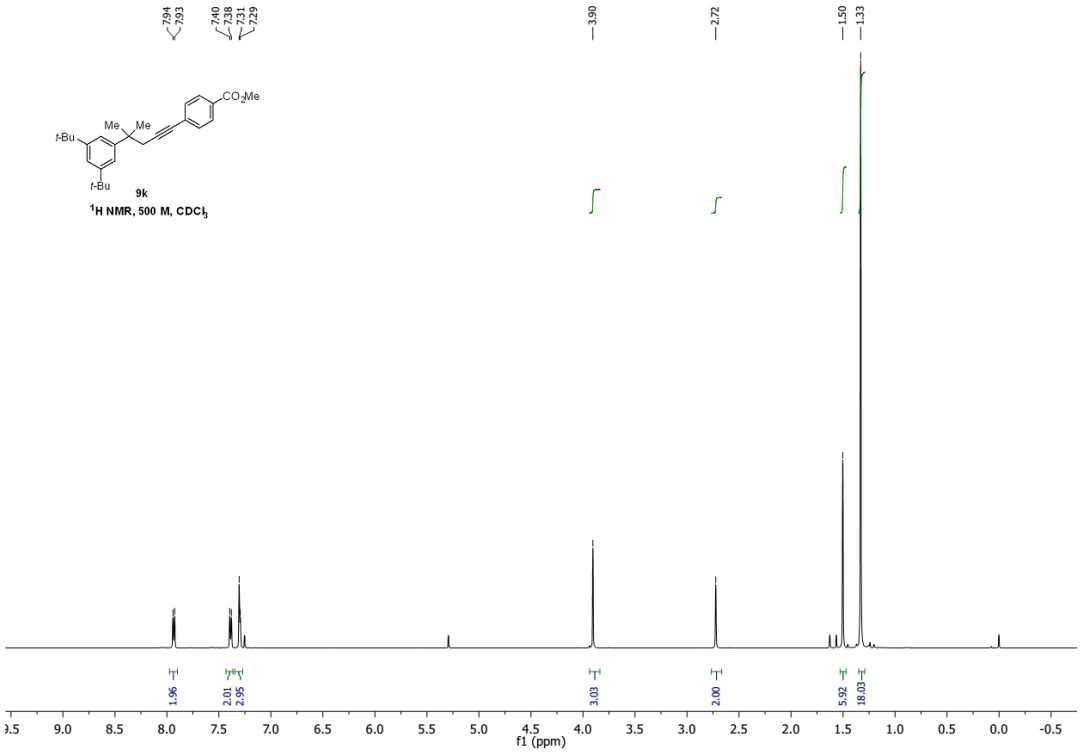


^{13}C NMR (126 MHz, $CDCl_3$)

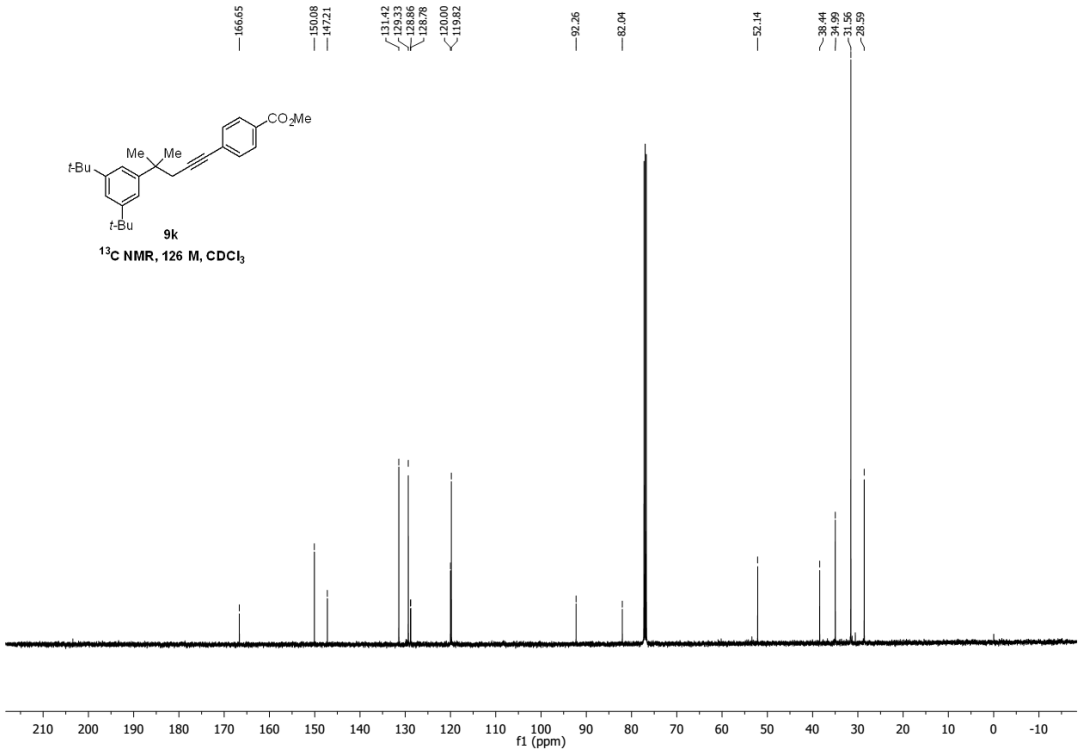


methyl 4-(4-(3,5-di-tert-butylphenyl)-4-methylpent-1-yn-1-yl)benzoate (9k)

^{1}H NMR (500 MHz, $CDCl_3$)

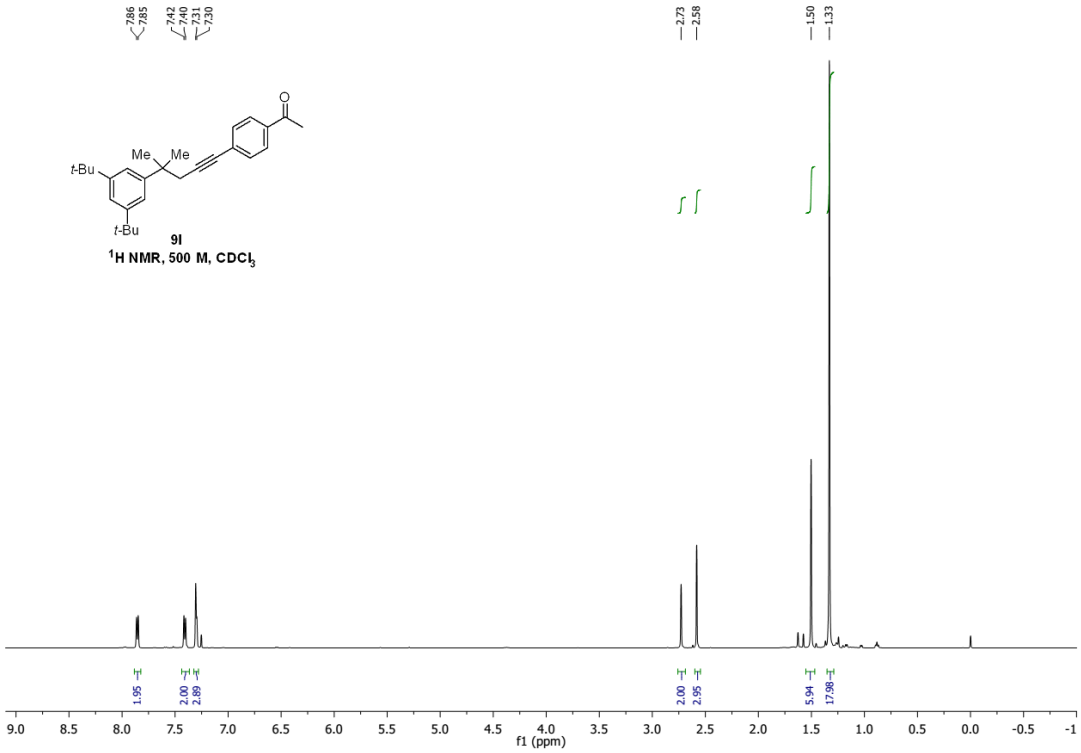


^{13}C NMR (126 MHz, $CDCl_3$)

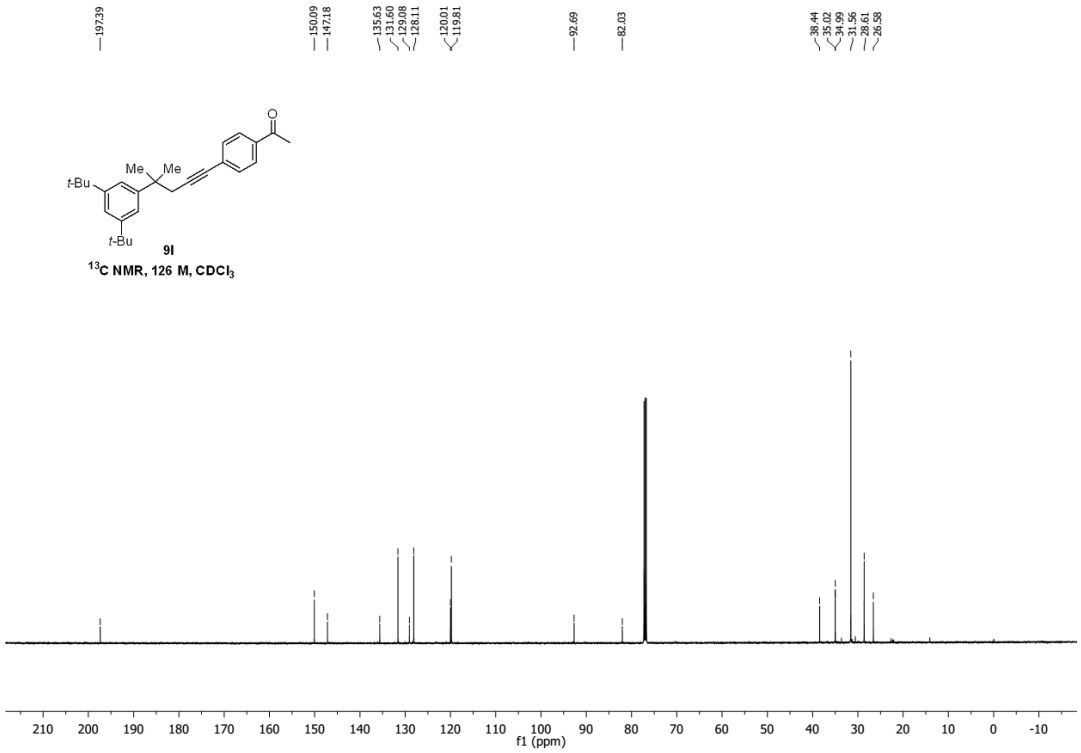


1-(4-(4-(3,5-di-tert-butylphenyl)-4-methylpent-1-yn-1-yl)phenyl)ethan-1-one (9l)

^{1}H NMR (500 MHz, $CDCl_3$)

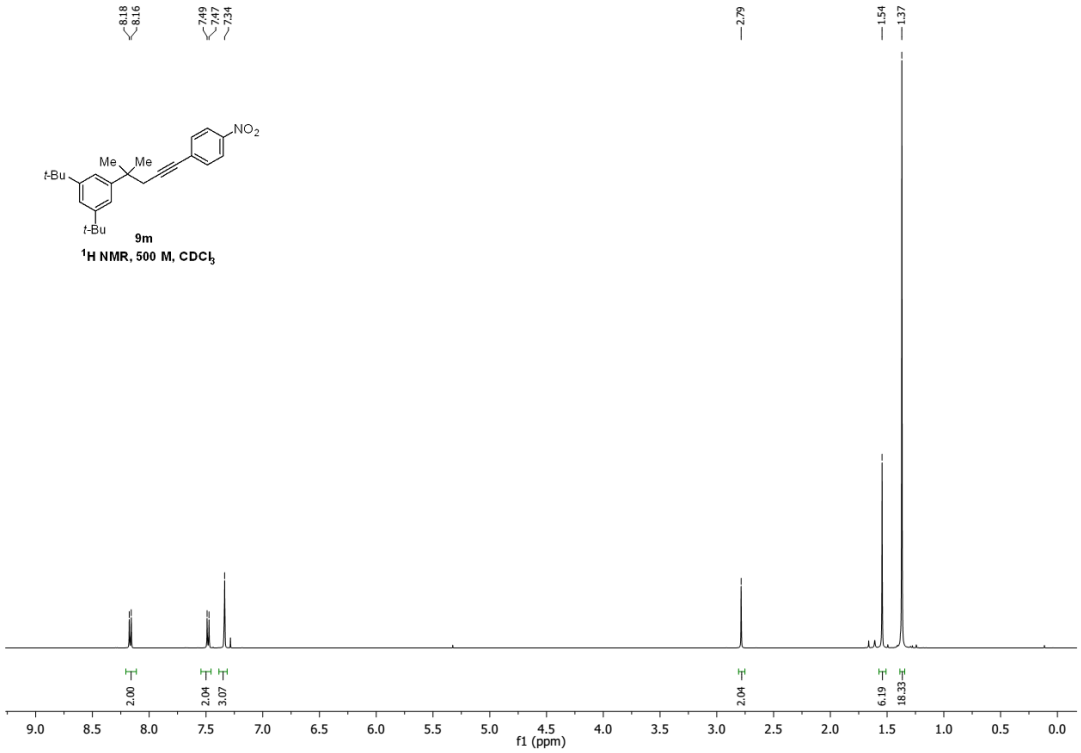


^{13}C NMR (126 MHz, $CDCl_3$)

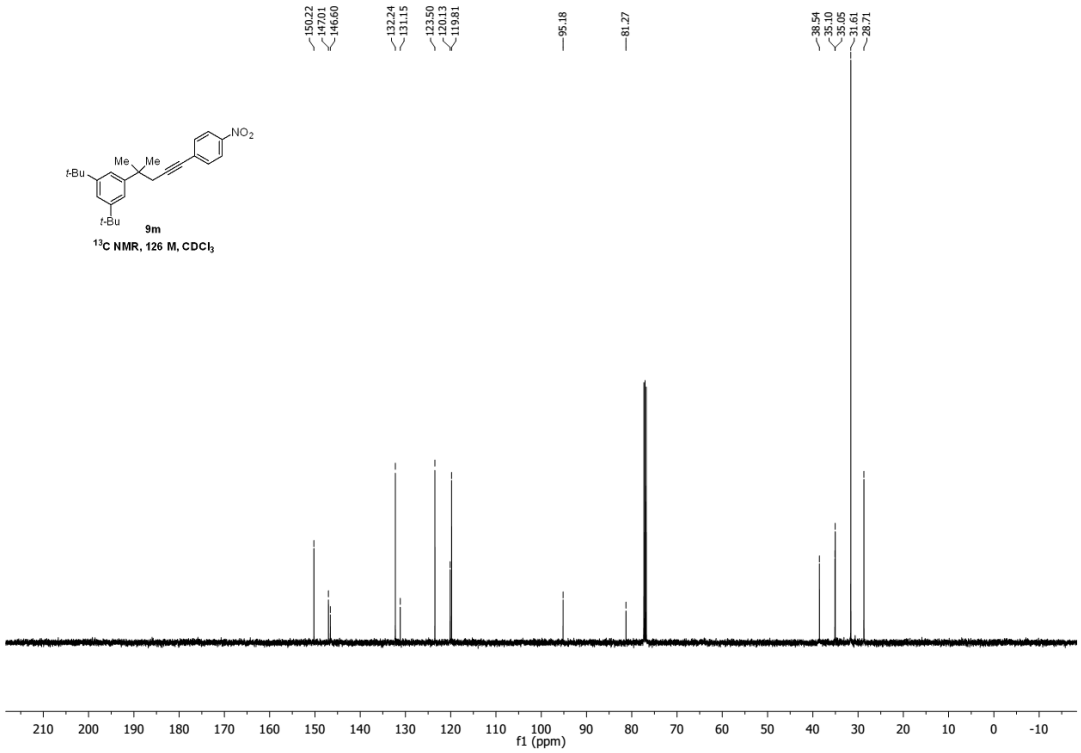


1,3-di-tert-butyl-5-(2-methyl-5-(4-nitrophenyl)pent-4-yn-2-yl)benzene (9m)

^{1}H NMR (500 MHz, $CDCl_3$)

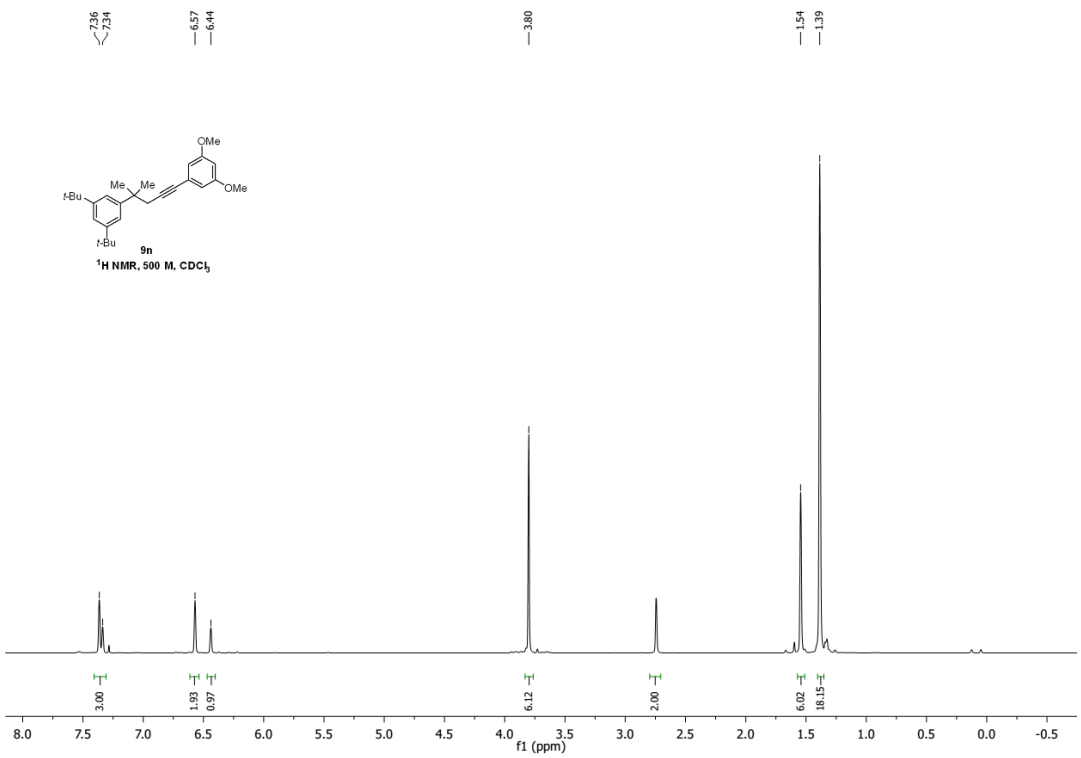


^{13}C NMR (126 MHz, $CDCl_3$)

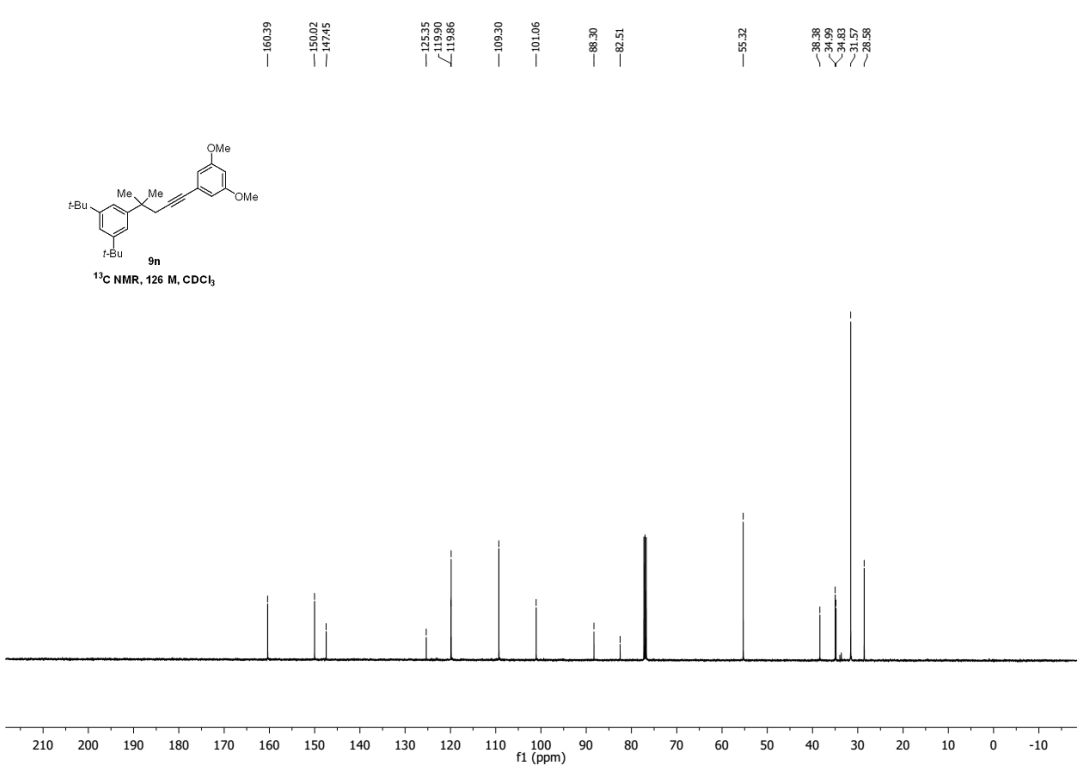


1,3-di-tert-butyl-5-(5-(3,5-dimethoxyphenyl)-2-methylpent-4-yn-2-yl)benzene (9n)

^{1}H NMR (500 MHz, $CDCl_3$)

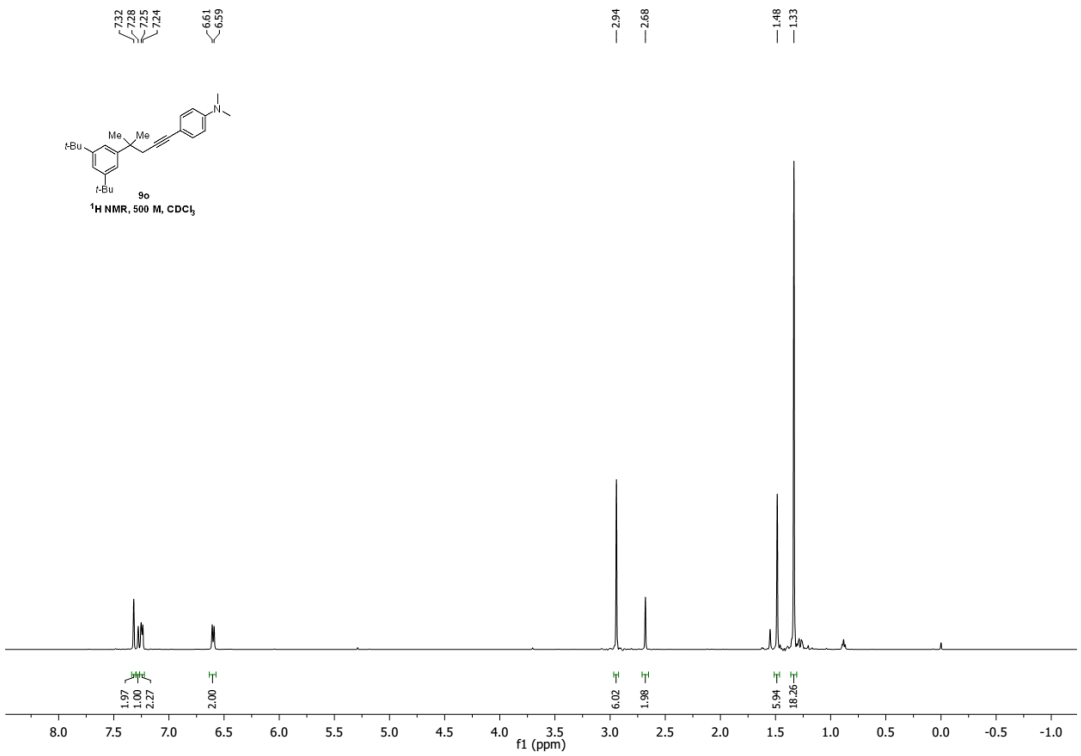


^{13}C NMR (126 MHz, $CDCl_3$)

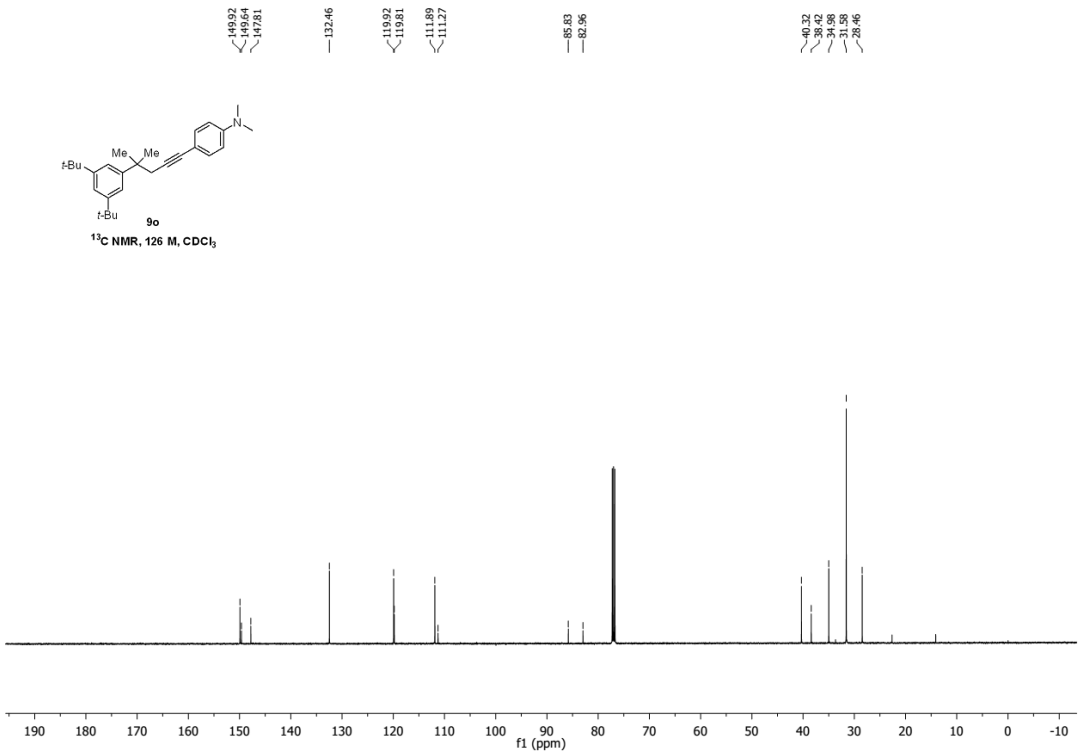


4-(4-(3,5-di-tert-butylphenyl)-4-methylpent-1-yn-1-yl)-N,N-dimethylaniline (9o)

^{1}H NMR (500 MHz, $CDCl_3$)

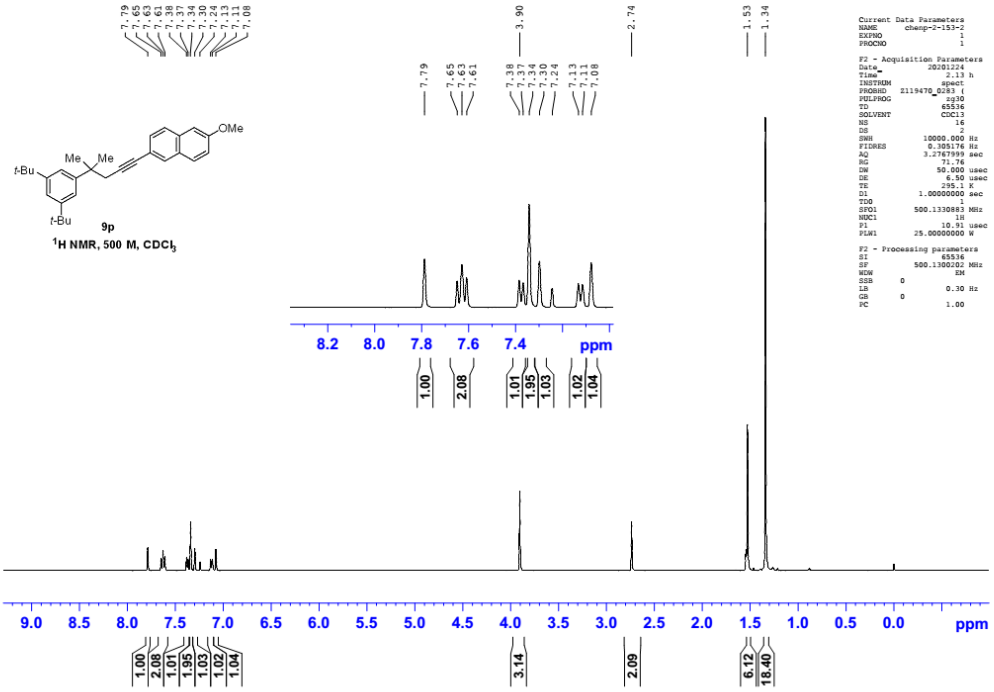


^{13}C NMR (126 MHz, $CDCl_3$)

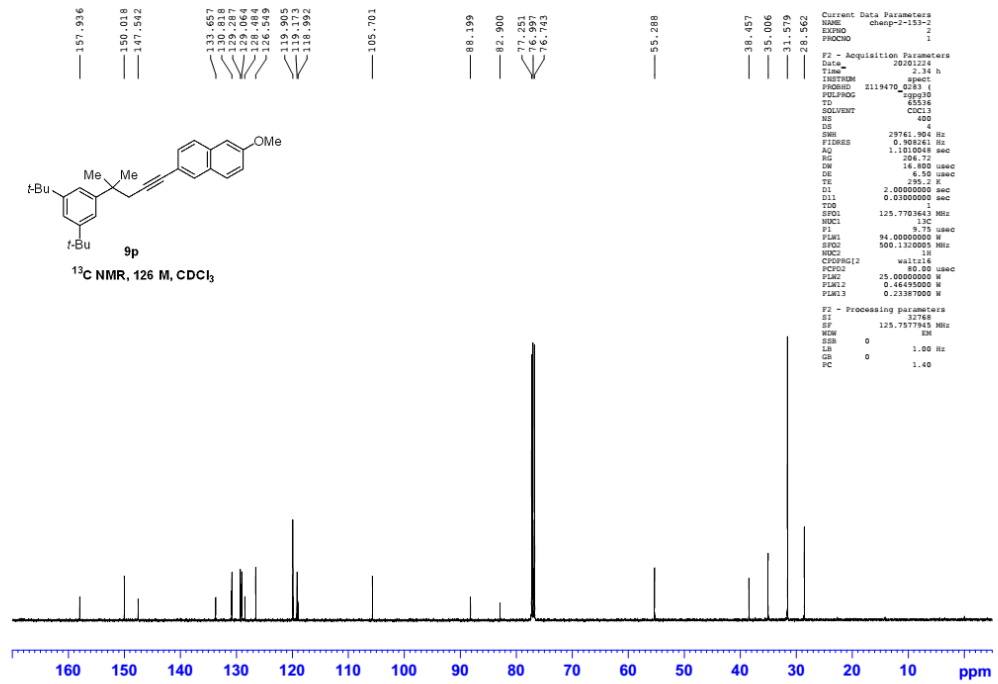


2-(4-(3,5-di-tert-butylphenyl)-4-methylpent-1-yn-1-yl)-6-methoxynaphthalene (9p)

^{1}H NMR (500 MHz, $CDCl_3$)

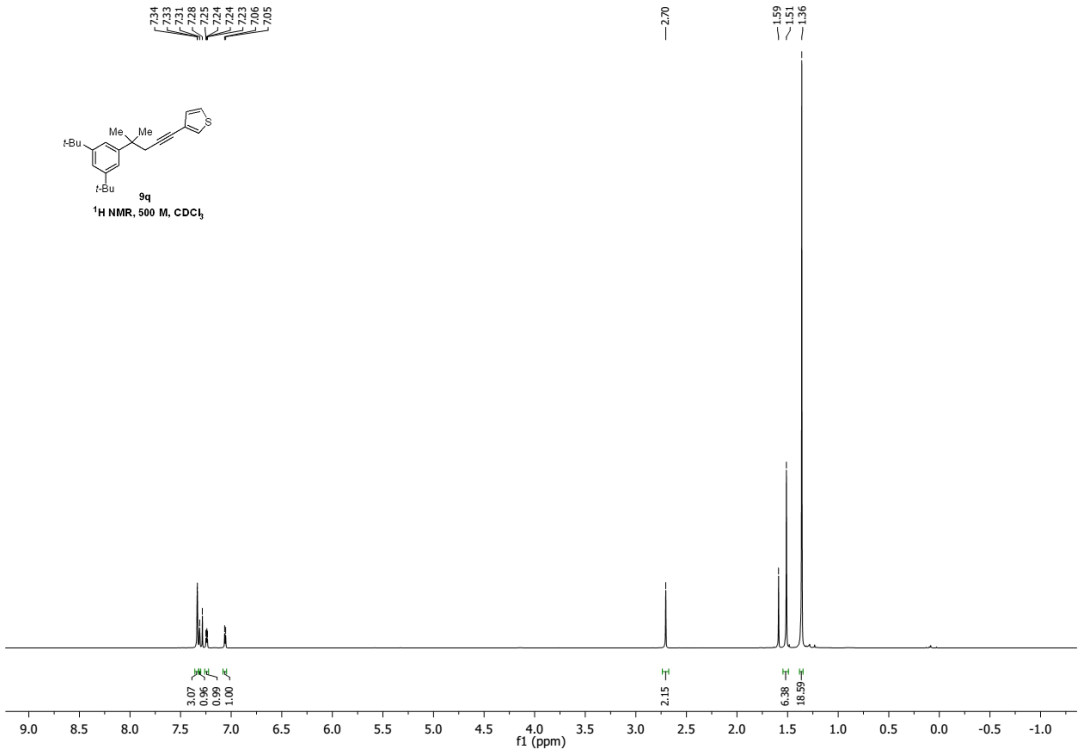


^{13}C NMR (126 MHz, $CDCl_3$)

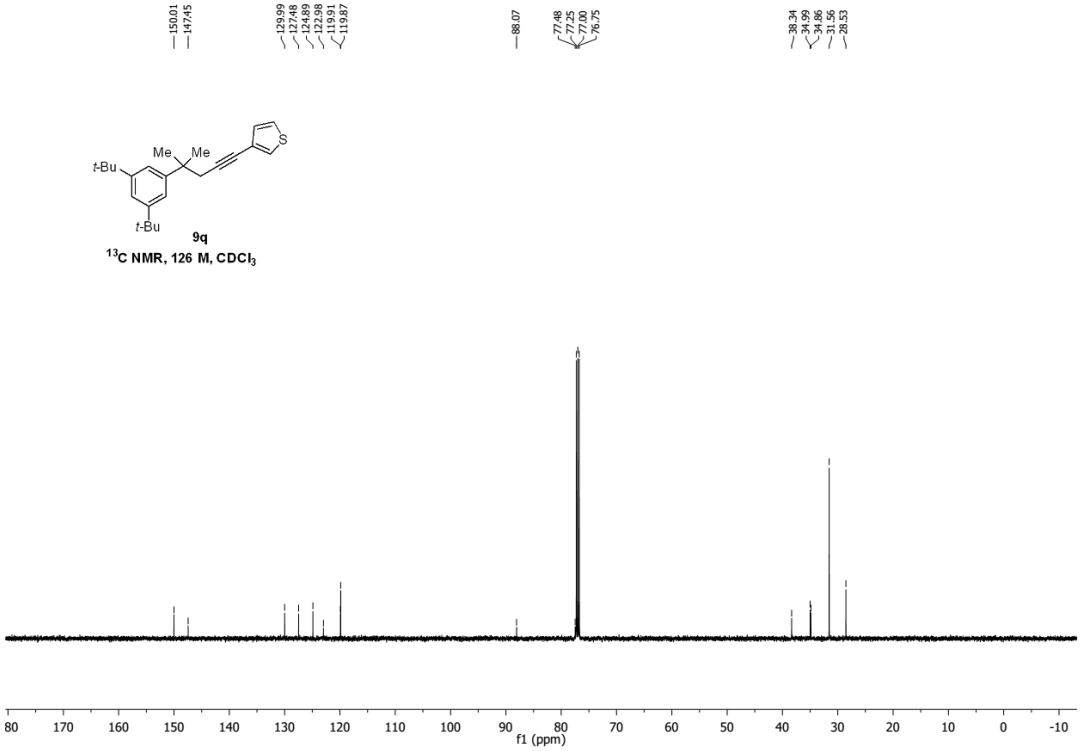


3-(4-(3,5-di-tert-butylphenyl)-4-methylpent-1-yn-1-yl)thiophene (9q)

^{1}H NMR (500 MHz, $CDCl_3$)

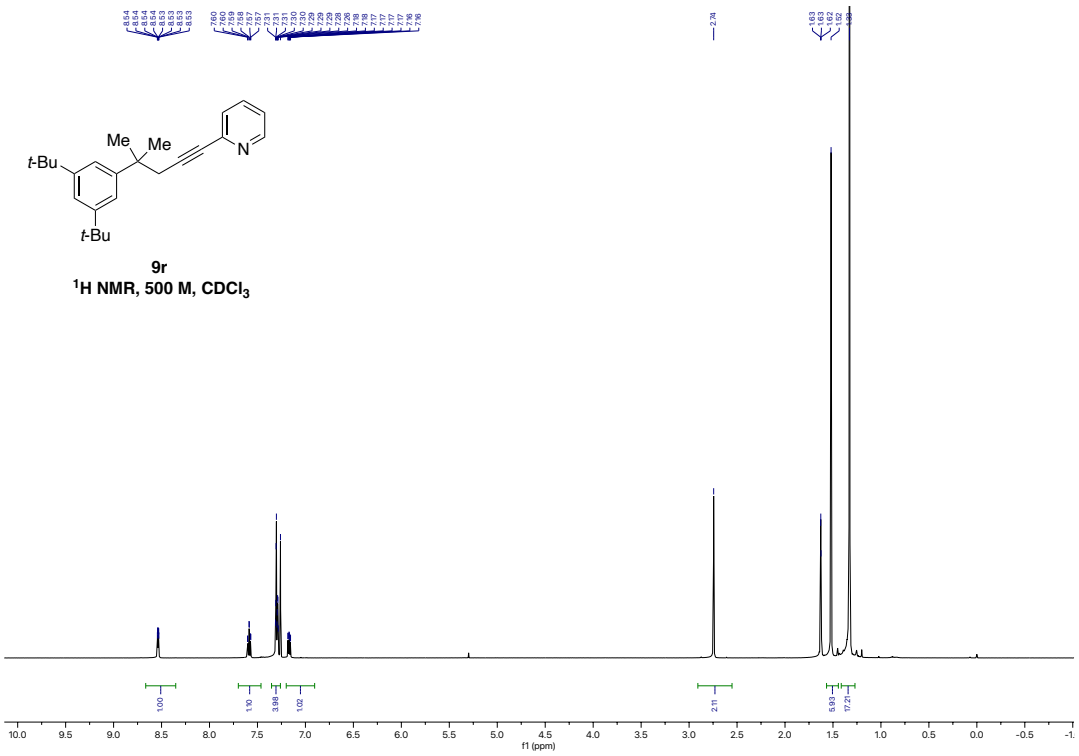


^{13}C NMR (126 MHz, $CDCl_3$)

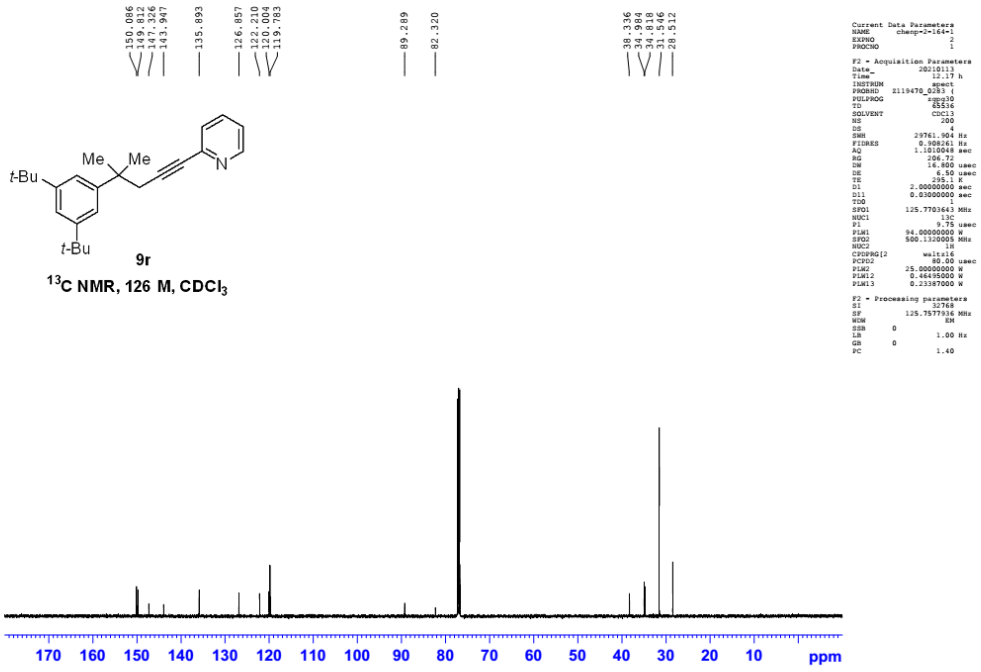


2-(4-(3,5-di-tert-butylphenyl)-4-methylpent-1-yn-1-yl)pyridine (9r)

^{1}H NMR (500 MHz, $CDCl_3$)

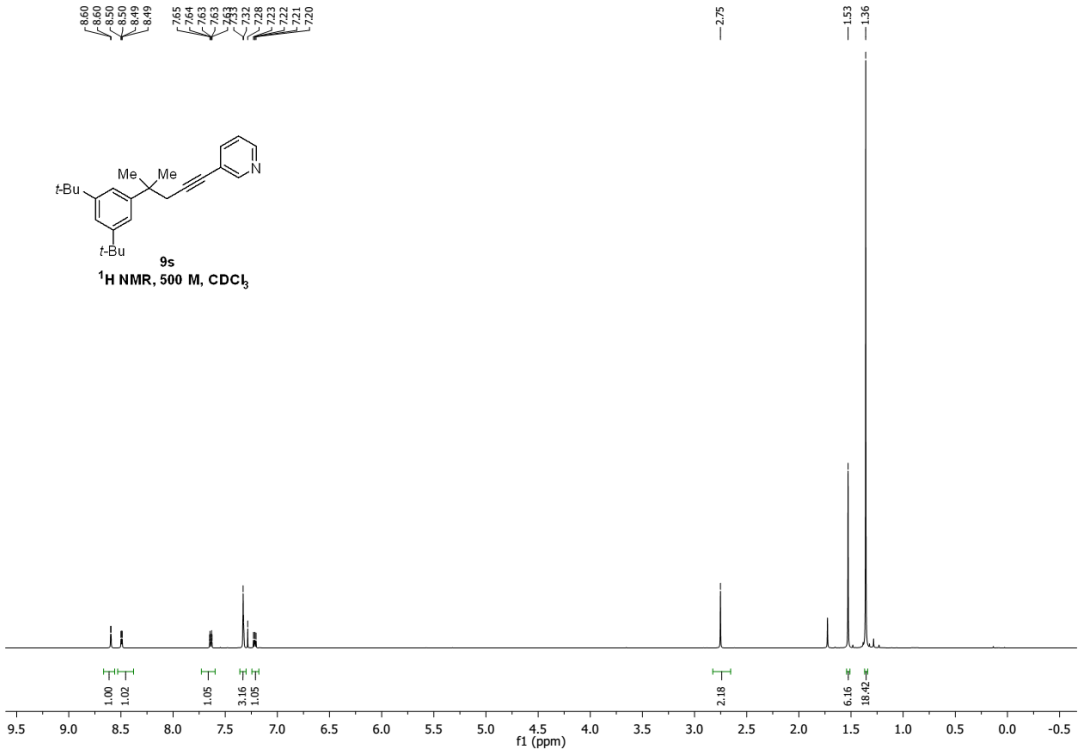


^{13}C NMR (126 MHz, $CDCl_3$)

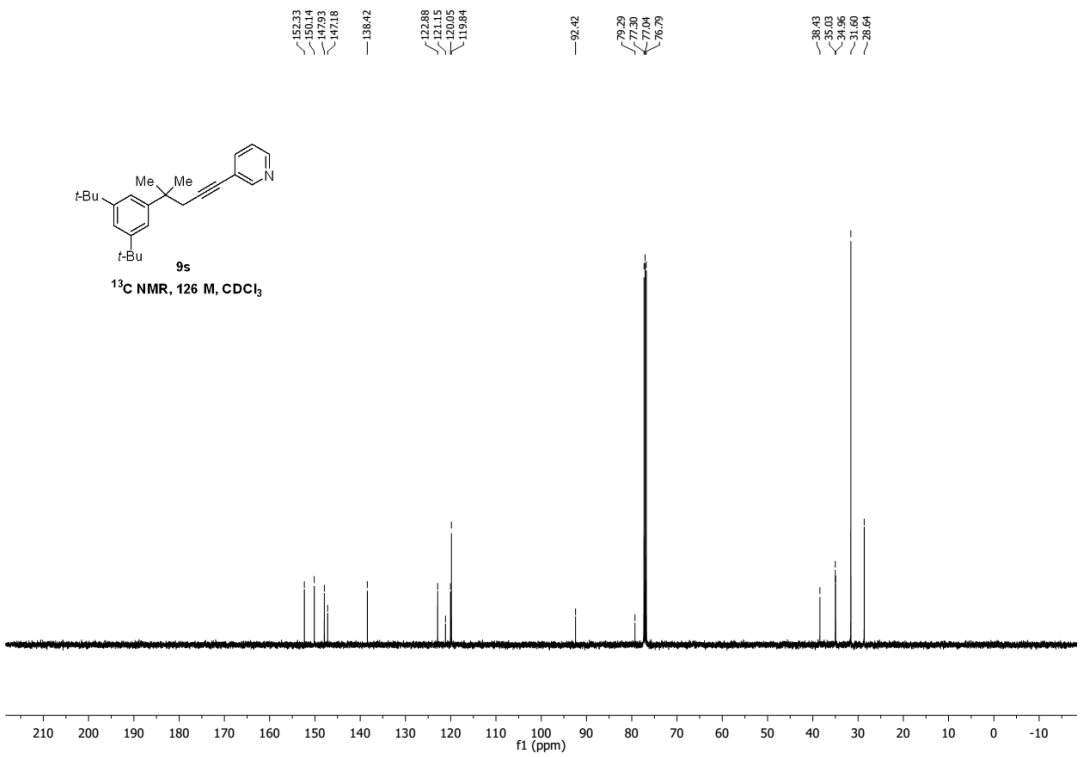


3-(4-(3,5-di-tert-butylphenyl)-4-methylpent-1-yn-1-yl)pyridine (9s)

^{1}H NMR (500 MHz, $CDCl_3$)

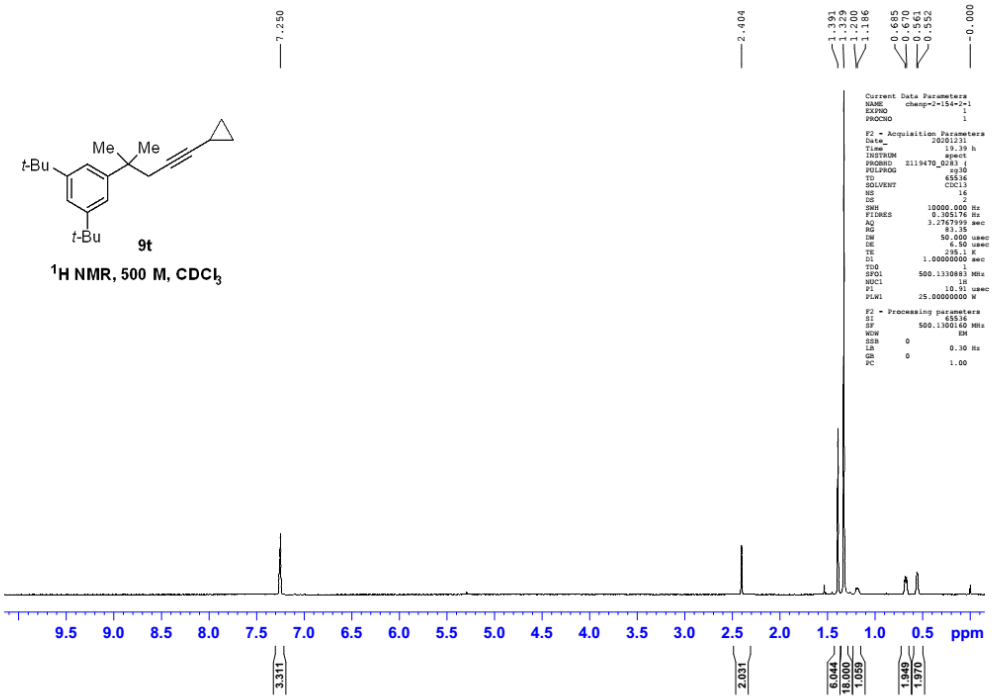


^{13}C NMR (126 MHz, $CDCl_3$)

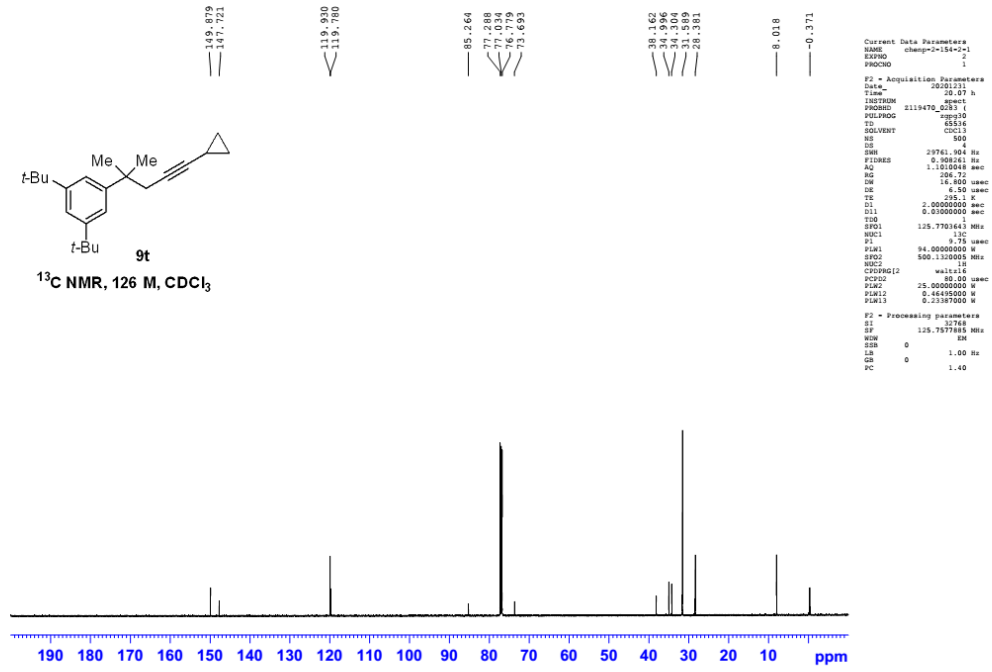


1,3-di-tert-butyl-5-(5-cyclopropyl-2-methylpent-4-yn-2-yl)benzene (9t)

^{1}H NMR (500 MHz, $CDCl_3$)

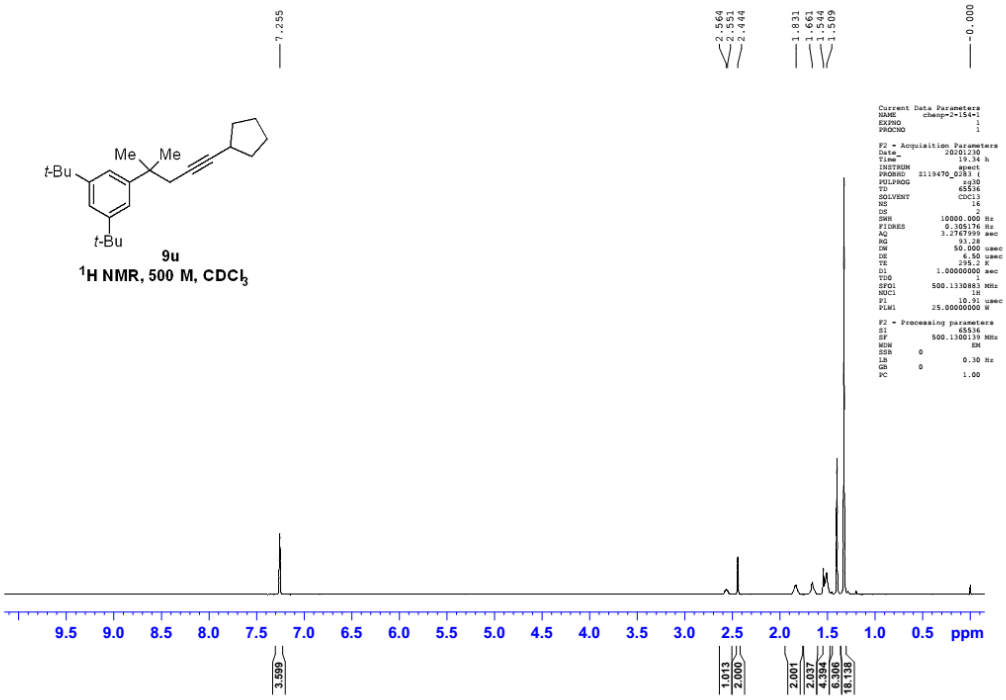


^{13}C NMR (126 MHz, $CDCl_3$)

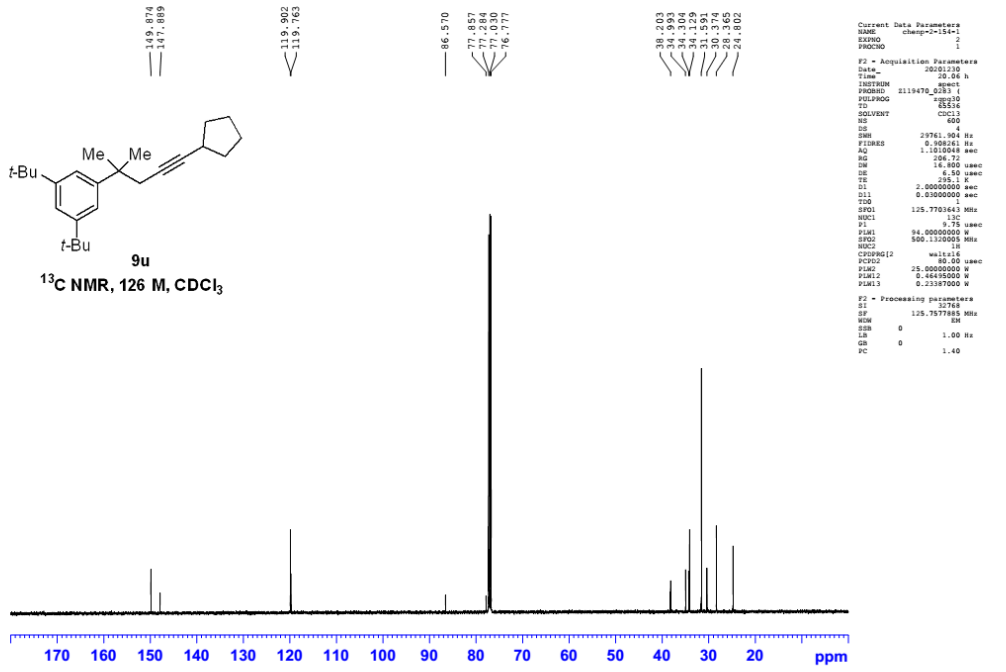


1,3-di-tert-butyl-5-(5-cyclopentyl-2-methylpent-4-yn-2-yl)benzene (9u)

^{1}H NMR (500 MHz, $CDCl_3$)

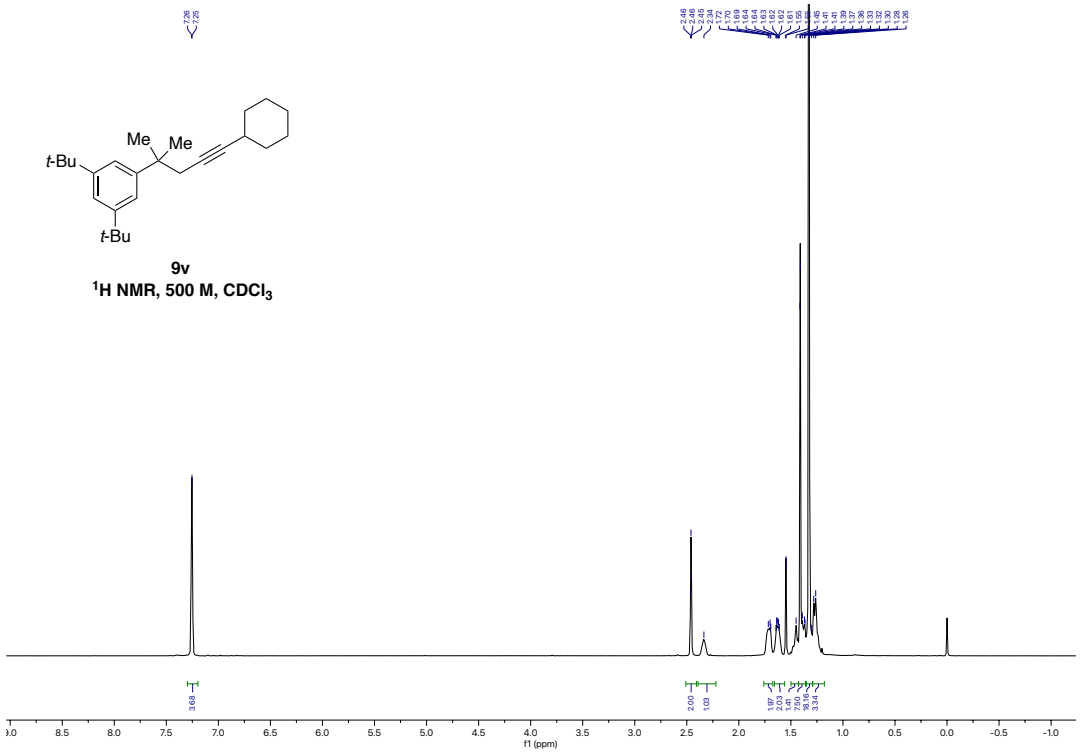


^{13}C NMR (126 MHz, $CDCl_3$)

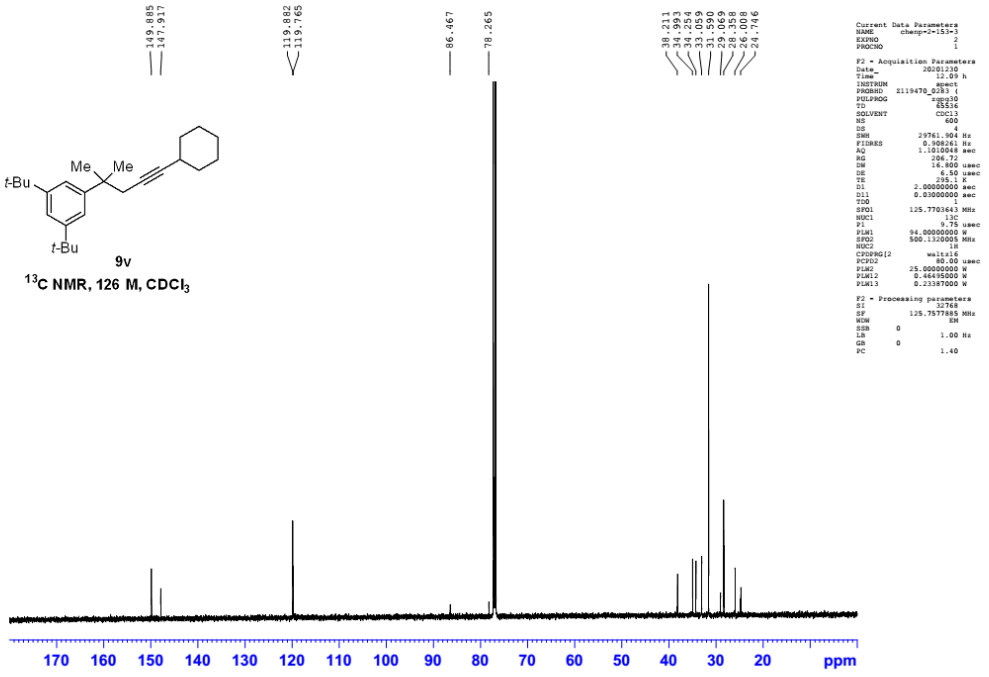


1,3-di-tert-butyl-5-(5-cyclohexyl-2-methylpent-4-yn-2-yl)benzene (9v)

^{1}H NMR (500 MHz, $CDCl_3$)

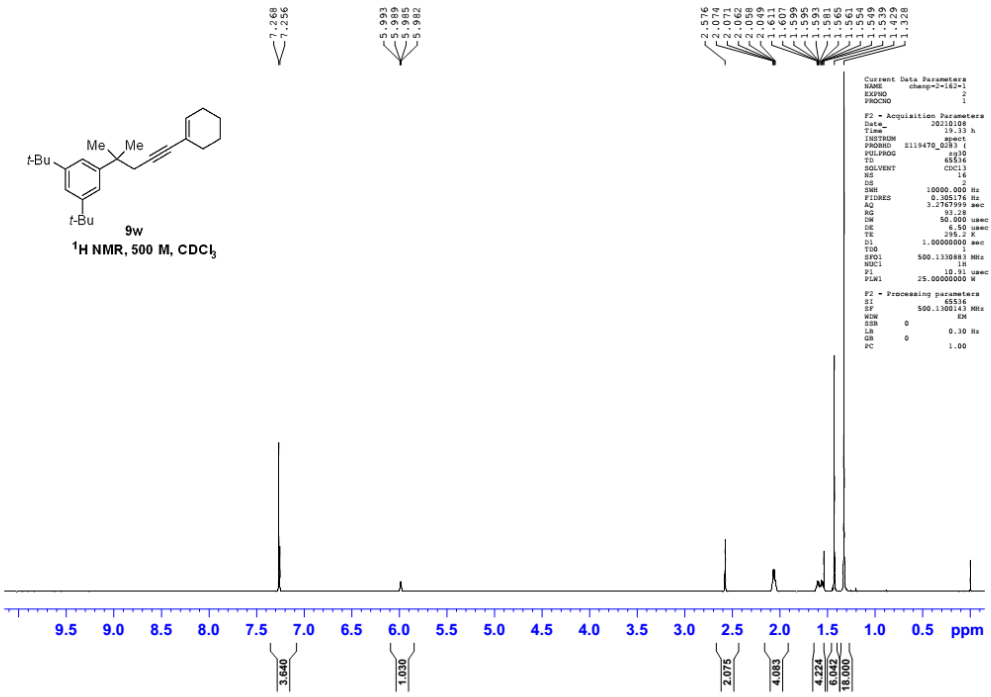


^{13}C NMR (126 MHz, $CDCl_3$)

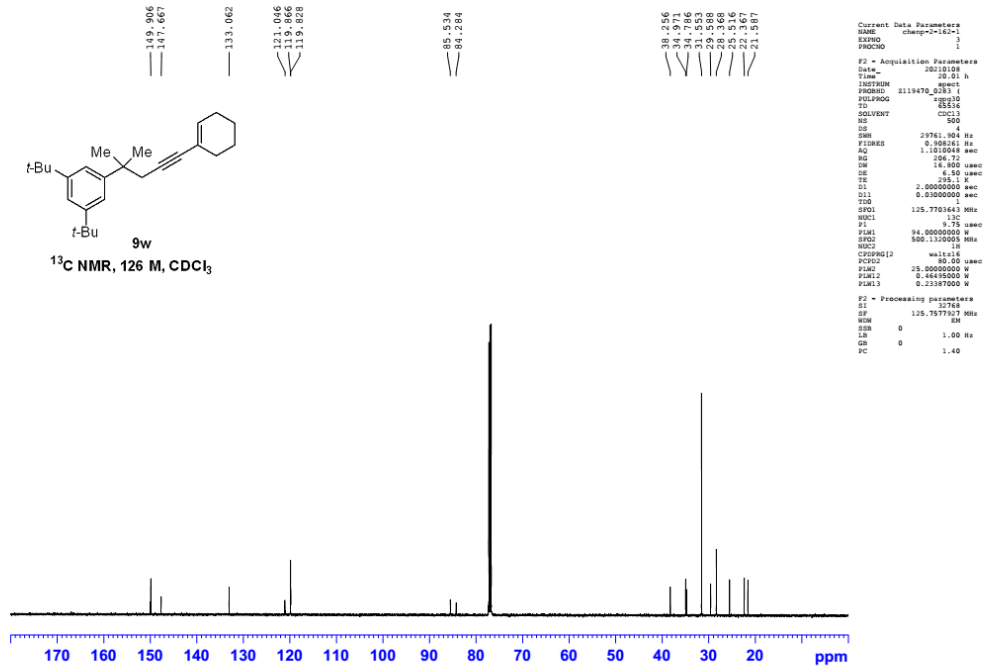


1,3-di-tert-butyl-5-(5-(cyclohex-1-en-1-yl)-2-methylpent-4-yn-2-yl)benzene (9w)

^{1}H NMR (500 MHz, $CDCl_3$)

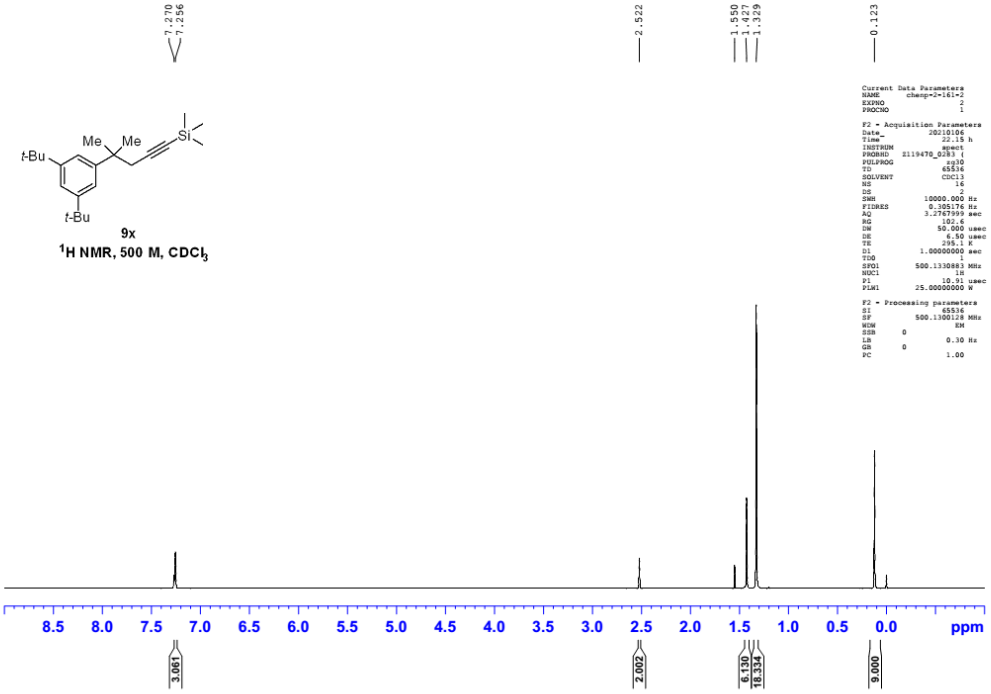


^{13}C NMR (126 MHz, $CDCl_3$)

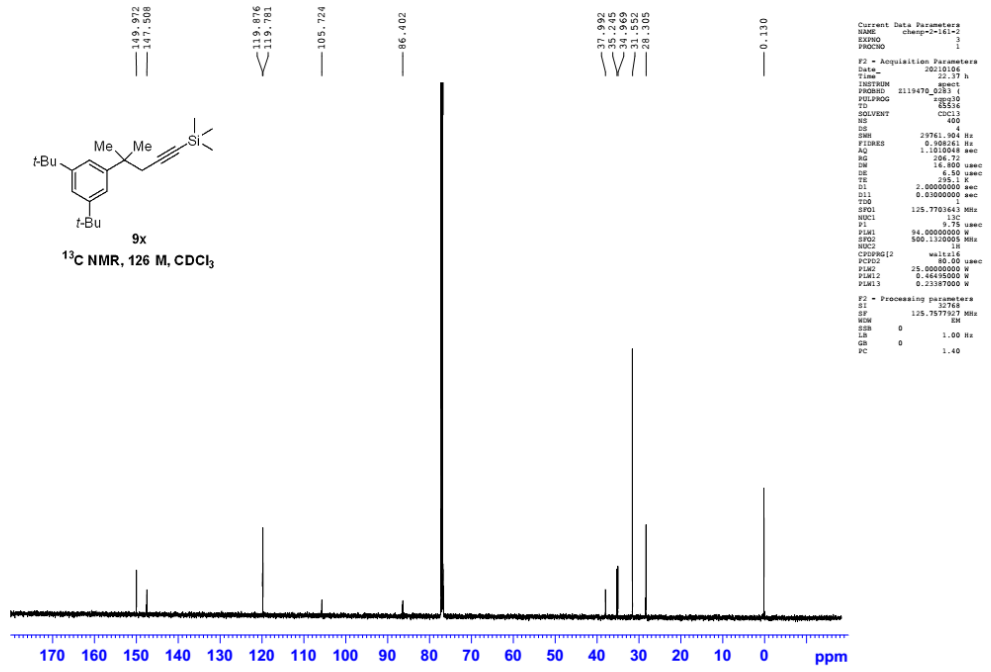


(4-(3,5-di-tert-butylphenyl)-4-methylpent-1-yn-1-yl)trimethylsilane (9x)

^{1}H NMR (500 MHz, $CDCl_3$)

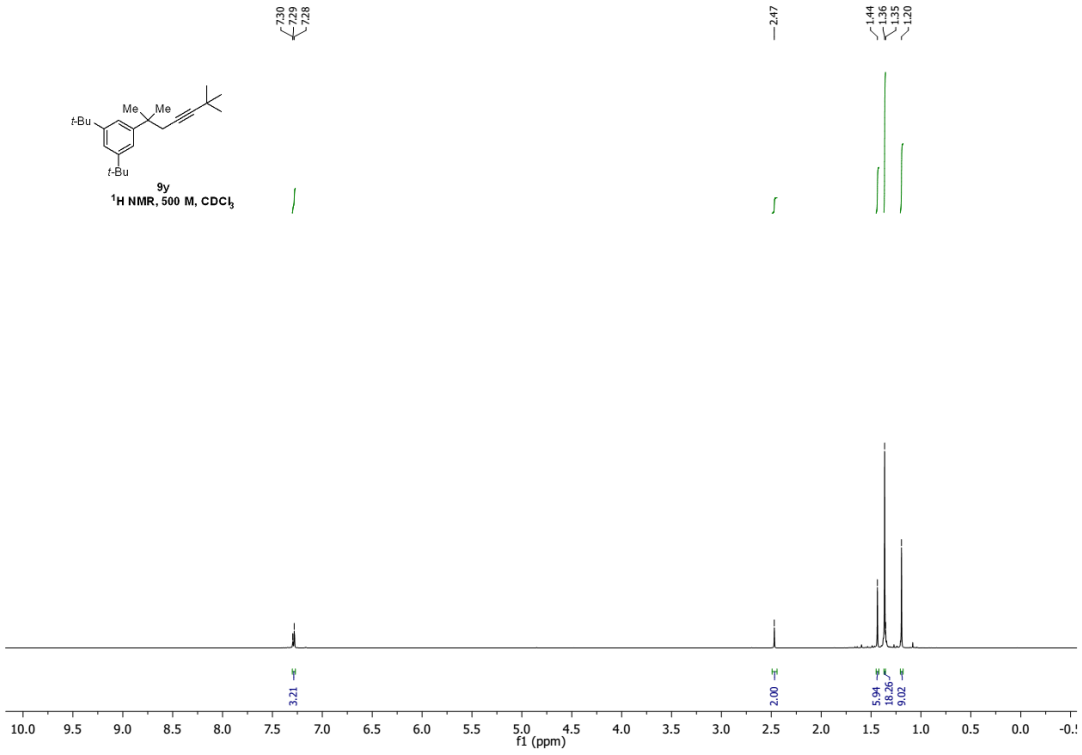


^{13}C NMR (126 MHz, $CDCl_3$)

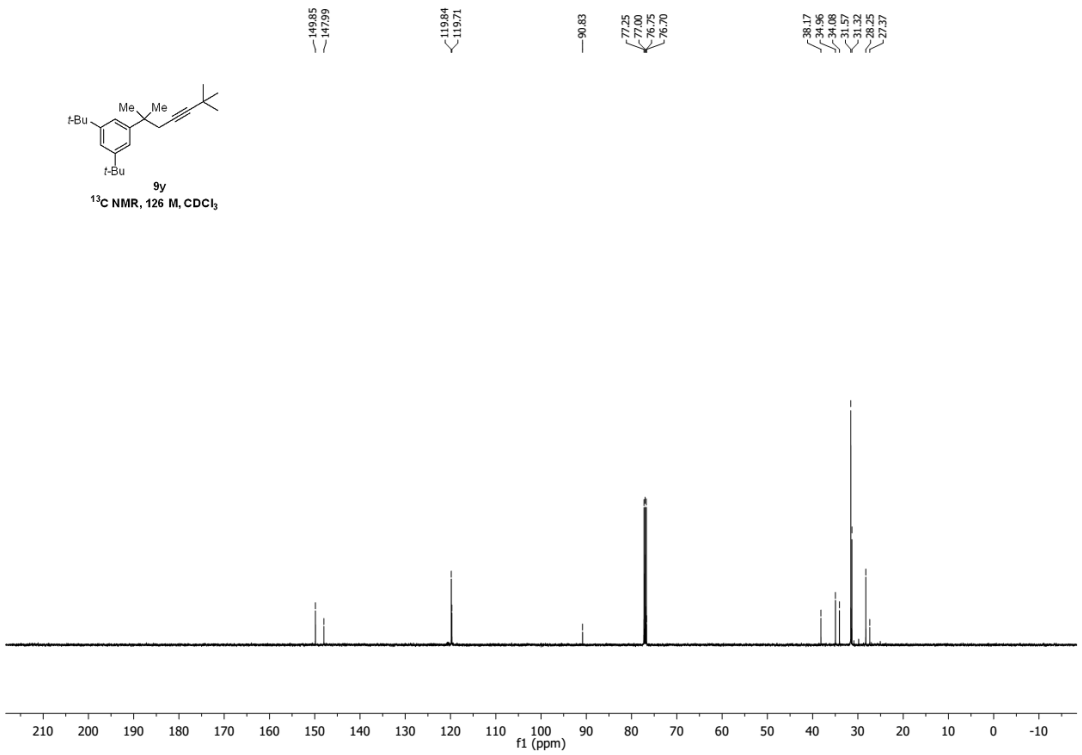


1,3-di-tert-butyl-5-(2,6,6-trimethylhept-4-yn-2-yl)benzene (9y)

^{1}H NMR (500 MHz, $CDCl_3$)

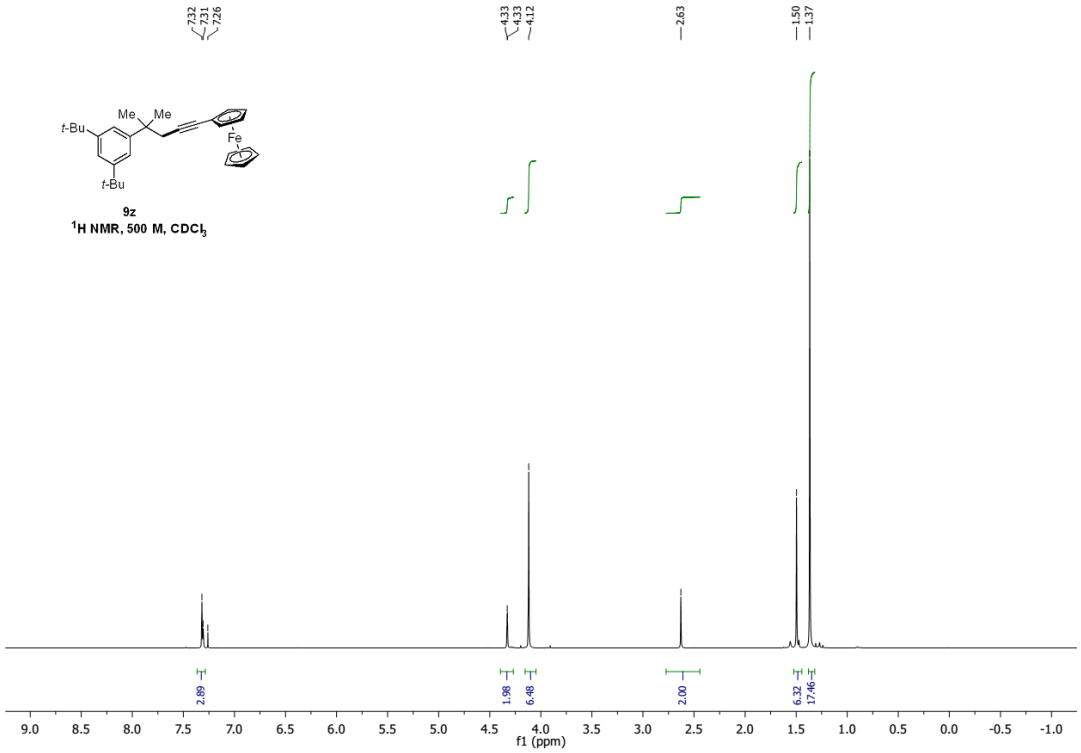


^{13}C NMR (126 MHz, $CDCl_3$)

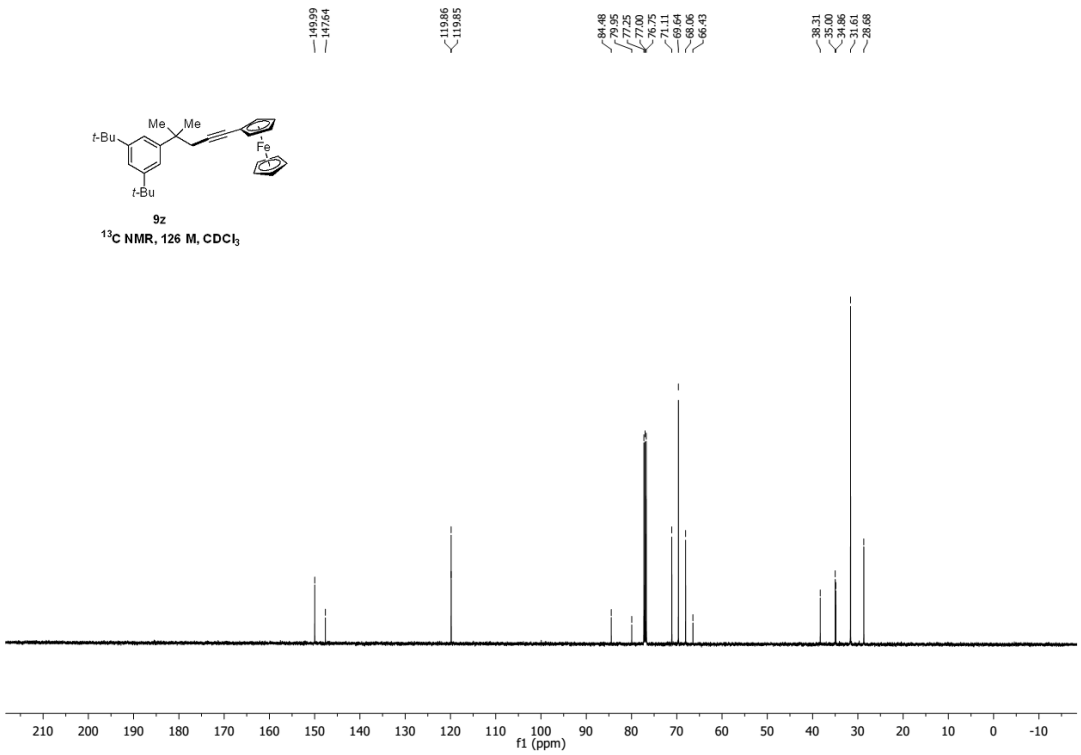


1,3-di-tert-butyl-5-(5-ferrocenyl-2-methylpent-4-yn-2-yl)benzene (9z)

^{1}H NMR (500 MHz, $CDCl_3$)

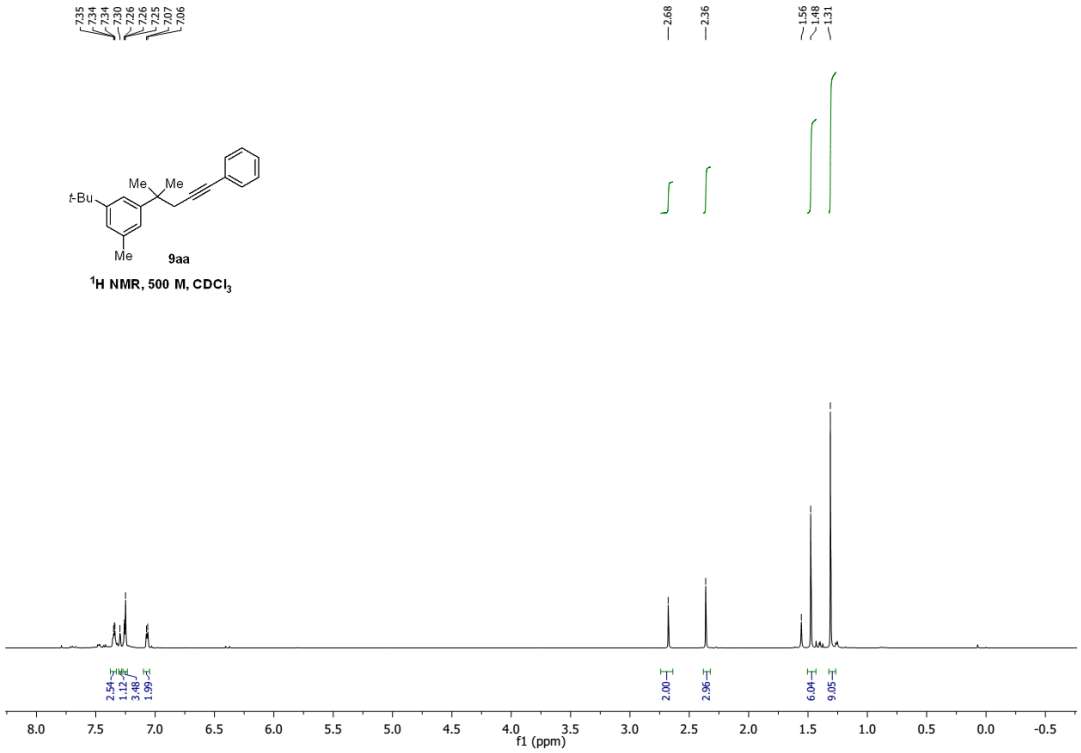


^{13}C NMR (126 MHz, $CDCl_3$)

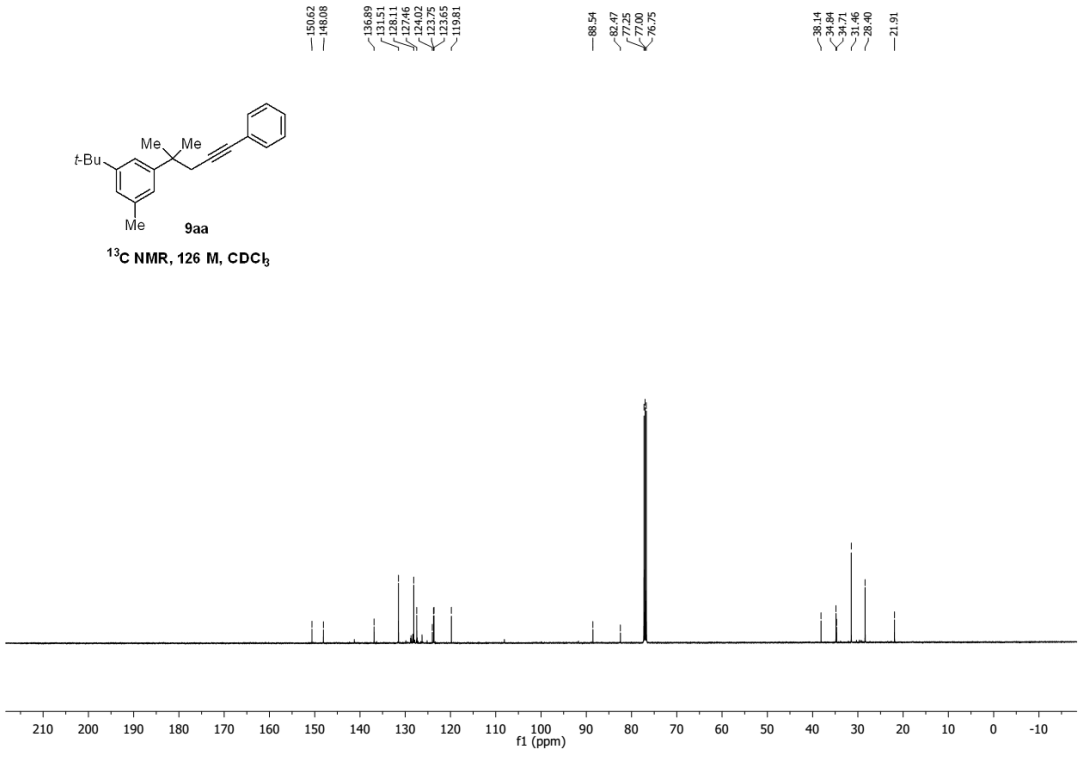


1-(tert-butyl)-3-methyl-5-(2-methyl-5-phenylpent-4-yn-2-yl)benzene (9aa)

^{1}H NMR (500 MHz, $CDCl_3$)

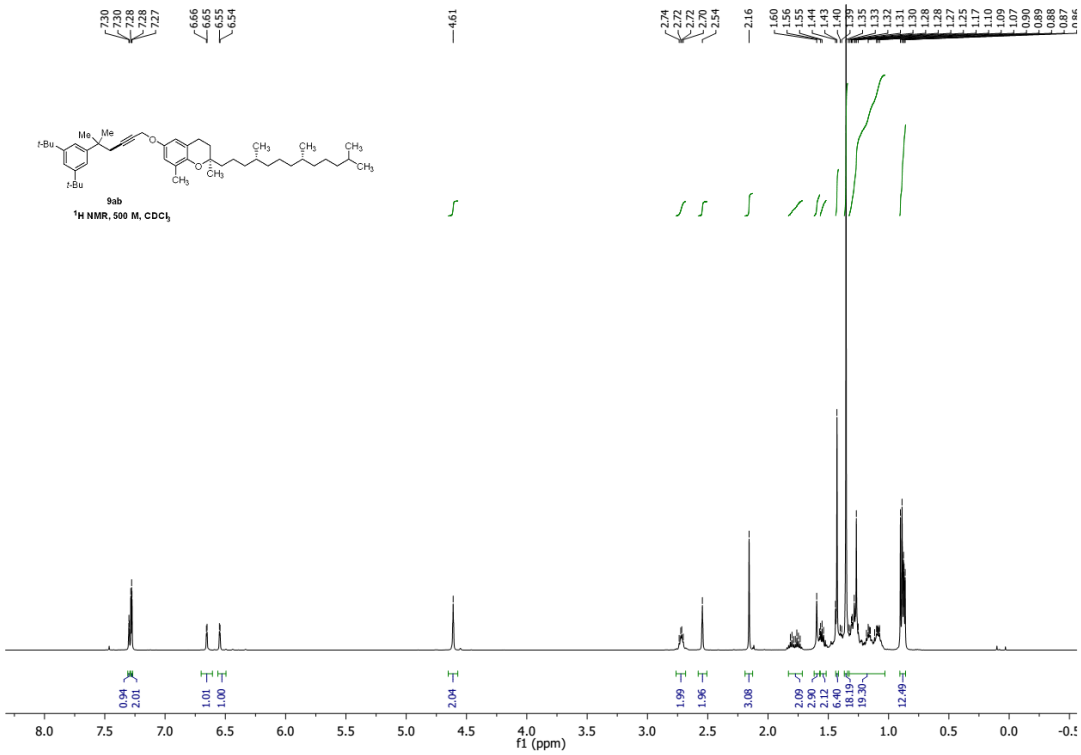


^{13}C NMR (126 MHz, $CDCl_3$)

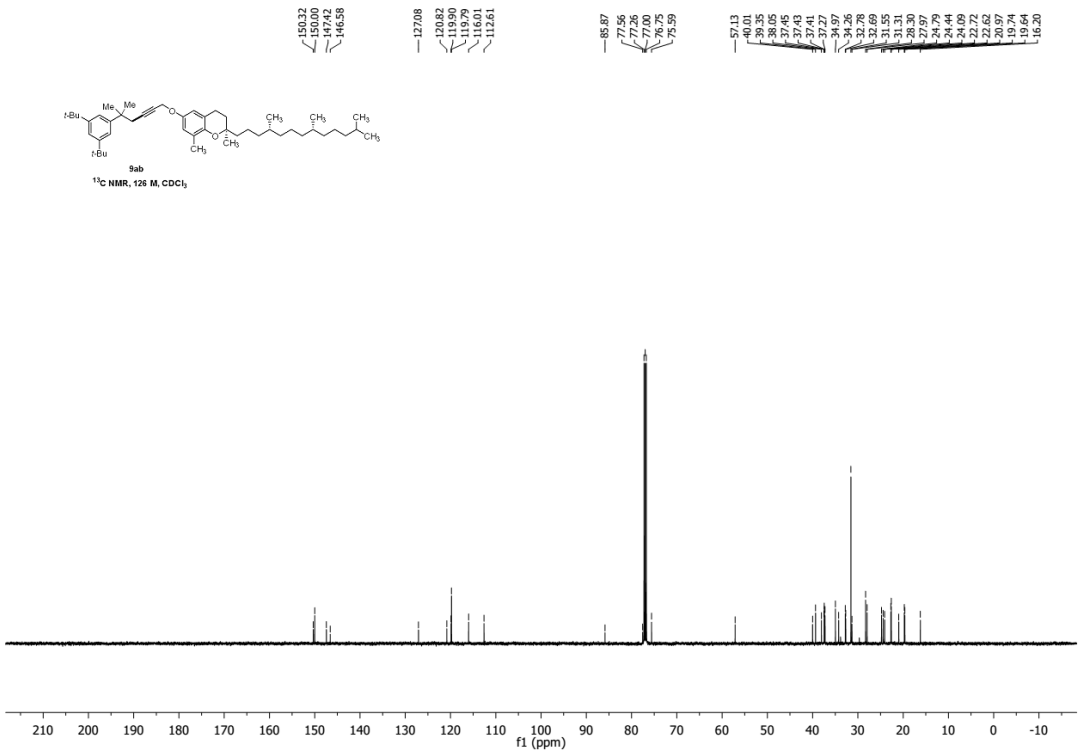


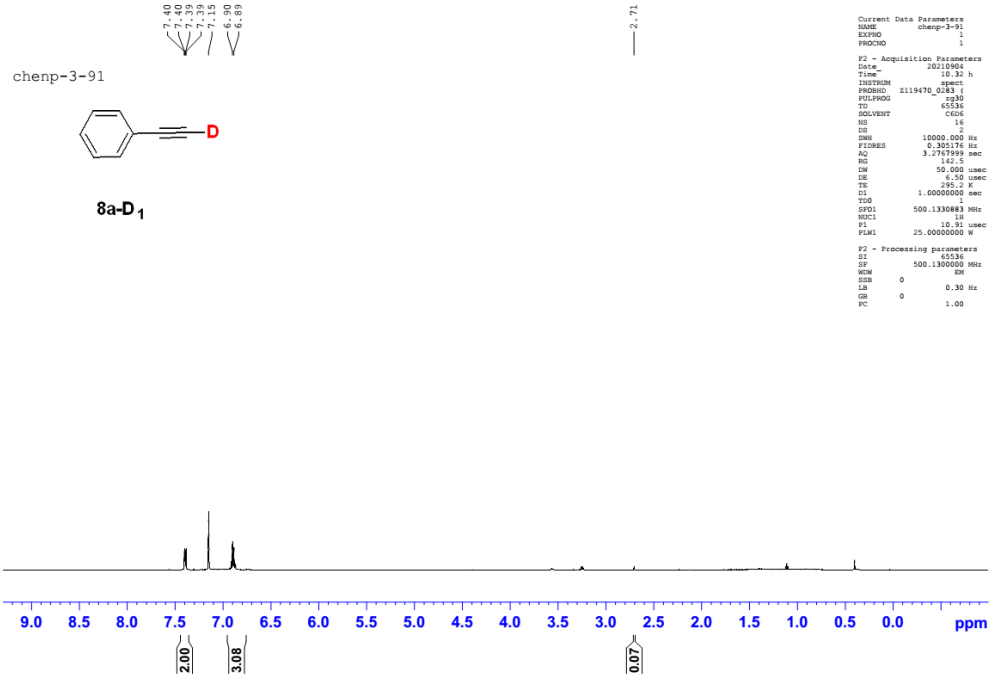
(R)-6-((5-(3,5-di-tert-butylphenyl)-5-methylhex-2-yn-1-yl)oxy)-2,8-dimethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chromane (9ab)

^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

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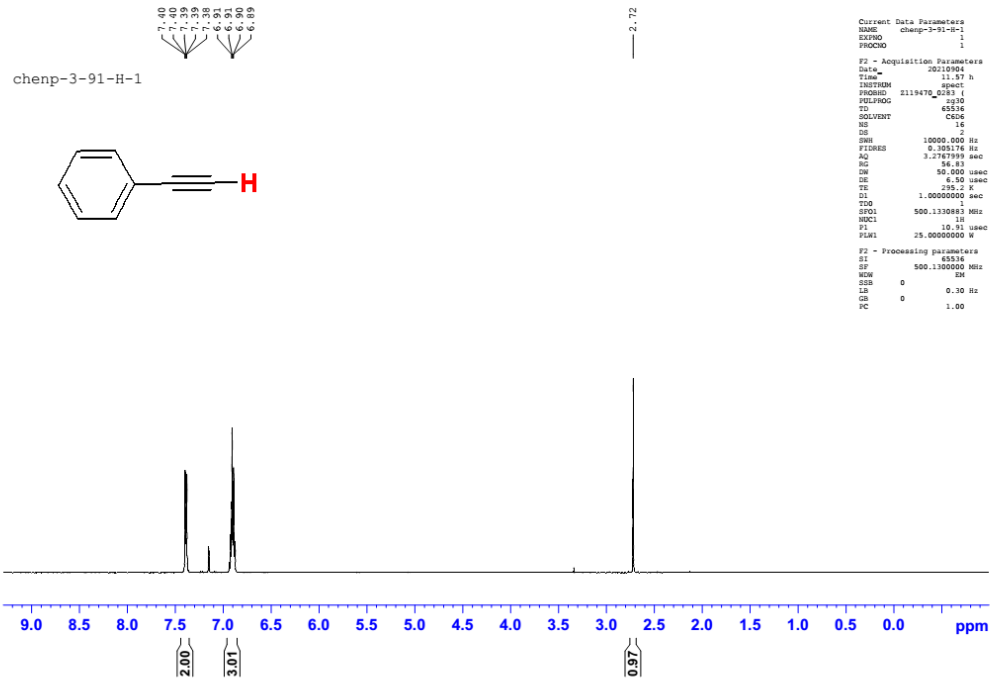
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