

Nickel-Catalyzed Stereoselective Diarylation of Alkenylarenes

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General Considerations: Infrared (IR) spectra were recorded on a Bruker Tensor II FT-IR Spectrometer, ν_{\max} in cm^{-1} . Bands are characterized as broad (br), strong (s), medium (m), and weak (w). ^1H NMR spectra were recorded at room temperature on a Varian I400 (400 MHz), Varian VXR400 (400 MHz), Varian I500 (500 MHz), or a Varian I600 (600 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the residual solvent resonance as the internal standard (CHCl_3 : 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz), and integration. ^{13}C NMR spectra were recorded on a Varian I400 (100 MHz), Varian VXR400 (100 MHz), or a Varian I500 (125 MHz) spectrometer with complete proton decoupling. ^{19}F NMR spectra were recorded on a Varian VXR400 (375 MHz) spectrometer or a Varian I500 (470 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl_3 : 77.16 ppm). Most of High-resolution mass spectrometry (HRMS) was performed on either a Waters/Micromass LCT Classic (ESI-TOF) or a Thermo Electron Corporation MAT 95XP-Trap (GC/MS). Samples 15 and 16 were analyzed by low energy electron ionization (EI, 15 V) on an Agilent G7250 QTOF mass spectrometer. This instrument was purchased with funds from NSF award CHE 1726633. Melting points were obtained on a Thomas Hoover capillary melting point apparatus without correction. The diastereomeric and regioisomeric ratios were determined using NMR, GC or GC-MS analysis of unpurified reaction mixtures. GC analyses were performed by means of Agilent 6850 Gas Chromatograph equipped with Agilent 19091Z-413E, 30 m x 320 μm x 0.25 μm column. Helium was used as the GC carrier gas and maintained at a constant flow rate of 25.0 mL/min. The initial temperature was 60 $^\circ\text{C}$ and subsequently ramped at a rate of 20 $^\circ\text{C}/\text{min}$ to a final temperature of 300 $^\circ\text{C}$, and held for 5 min. Total run time was 17 min.

Unless otherwise noted, all reactions have been carried out with distilled and degassed solvents under an atmosphere of dry N_2 in oven- (135 $^\circ\text{C}$) and flame-dried glassware with standard vacuum-line techniques. Tetrahydrofuran and dioxane were purified under a positive pressure of dry argon by passage through two columns of activated alumina. Dioxane was degassed via five consecutive freeze/pump/thaw cycles prior to use. Toluene was purified under a positive pressure of dry argon by passage through columns of activated alumina and Q5 (Grubbs apparatus). All work-up and purification procedures were carried out with reagent grade solvents (purchased from Sigma-Aldrich) in air. Standard column chromatography techniques using ZEOprep 60/40-63 μm silica gel were used for purification.

■ Reagents and Catalysts:

Styrene was purchased from Sigma-Aldrich and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.

1-bromo-3,5-dimethylbenzene was purchased from Oakwood and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use

Nickel(II) dichloride (NiCl₂) was purchased from Strem and used as received.

Nickel(II) dibromide (NiBr₂) was purchased from Sigma-Aldrich and used as received.

Nickel(II) chloride ethylene glycol dimethyl ether complex (NiCl₂DME) was purchased from Strem and used as received.

Bis(1,5-cyclooctadiene)nickel(0) was purchased from Strem and used as received.

Bis(tricyclohexylphosphine)nickel(II) dichloride (NiCl₂(PCy₃)₂) was purchased from Sigma-Aldrich and used as received.

Potassium ethoxide was purchased from Sigma-Aldrich and used as received.

Sodium ethoxide was purchased from Strem and used as received.

Potassium tert-butoxide was purchased from Strem and used as received.

Potassium methoxide was purchased from Alfa Aesar and used as received.

Dodecane was purchased from Aldrich and used as received.

5,5,5',5'-tetramethyl-2,2'-bi(1,3,2-dioxaborinane) was purchased from Oakwood and purified via recrystallization from pentane prior to use.

Bis(pinacolato)diboron was purchased from Oakwood and purified via recrystallization from pentane prior to use.

4-Methoxystyrene was purchased from Alfa Aesar and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.

4-Chlorostyrene was purchased from TCI America and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.

2-Methylstyrene was purchased from Sigma-Aldrich and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.

4-(Trifluoromethyl)styrene was purchased from Combi-Blocks and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.

α-Methylstyrene was purchased from Sigma-Aldrich and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.

trans-β-methylstyrene was purchased from TCI America and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.

3,5-Dimethoxystyrene was prepared in accordance with literature procedures.¹

(E)-1-chloro-4-(prop-1-en-1-yl)benzene was prepared in accordance with literature procedures.²

2-Vinylnaphthalene was purchased from Alfa Aesar and used as received.

trans-Stilbene was purchased from Sigma-Aldrich and used as received.

cis-Stilbene was purchased from Combi-Blocks and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.

tert-Butyl(cinnamyloxy)dimethylsilane was prepared in accordance with literature procedures.³

1-Tosyl-3-vinyl-1H-indole was prepared in accordance with literature procedures.⁴

(E)-1-Methoxy-4-(3-methylbut-1-en-1-yl)benzene was prepared in accordance with literature procedures.⁵

2H-Chromene was prepared in accordance with literature procedures.⁶

7-Methoxy-1,2-dihydronaphthalene was prepared in accordance with literature procedures.⁷

Dibromomethane was purchased from Oakwood and stored over activated 4Å molecular sieves.

(4-(Benzyloxy)phenyl)boronic acid was purchased from Ark Pharm and used as received.

(4-(Trifluoromethyl)phenyl)boronic acid was purchased from Matrix Scientific and used as received.

(4-Methoxyphenyl)boronic acid was purchased from Oakwood and used as received.

(Cyclohex-1-en-1-yl)boronic acid was purchased from Synthonix and used as received.

1-Bromo-2-methylbenzene was purchased from TCI America and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.

1-Bromo-3,5-di-tert-butylbenzene was purchased from Ark Pharm and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.

1-Naphthalenylboronic acid was purchased from Combi-Blocks and used as received.

2,2-Dimethyl-1,3-propanediol was purchased from Alfa Aesar and used as received.

2-Tolylboronic acid was purchased from Matrix Scientific and used as received.

3,5-Dimethoxybenzeneboronic acid was purchased from Ark Pharm and used as received.

3-Bromoanisole was purchased from Combi-Blocks and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.

3-Ethoxycarbonylphenylboronic acid was purchased from Ark Pharm and used as received.

3-Methoxyphenylboronic acid was purchased from Combi-Blocks and used as received.

4-(4-Bromobenzyl)morpholine was prepared in accordance with literature procedures.⁸

4-Bromo-1,2-methylenedioxybenzene was purchased from Combi-Blocks and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.

4-Bromobenzotrifluoride was purchased from Sigma-Aldrich and used as received.

4-Bromofluorobenzene was purchased from Acros and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.

4-Chlorophenylboronic acid was purchased from Combi-Blocks and used as received.

4-hydroxyphenylboronic acid was purchased from Combi-Blocks and used as received.

4-Methylphenylboronic acid was purchased from Combi-Blocks and used as received.

Benzo[d][1,3]dioxol-5-ylboronic acid was purchased from Ark Pharm and used as received.

Boronic esters were prepared in accordance with literature procedures and purified by silica gel column chromatography or recrystallization prior to use.⁹

Bromobenzene was purchased from Sigma-Aldrich and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.

Ethyl 3-bromobenzoate was purchased from Oakwood and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.

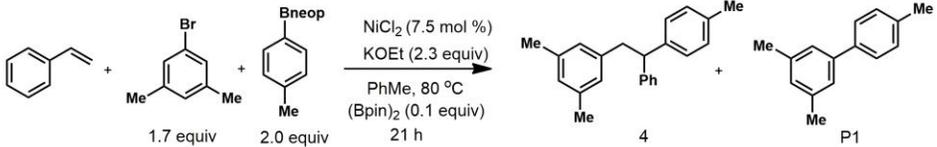
N-(4-Bromophenyl)pyrrolidine was purchased from Ark Pharm and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.

Phenylboronic acid was purchased from Combi-Blocks and used as received.

tert-butyl (4-bromophenyl)(methyl)carbamate was prepared in accordance with literature procedures.¹⁰

■ Optimization Studies

Table S1: Change from Standard Conditions



entry	Change from Standard Reaction	Yield of 4 (%) ^[a]	Yield of P1 (%) ^[a]
1	none	77	26
2	No (Bpin) ₂	trace	trace
3	(Bpin) ₂ (0.5 equiv) was added	48	20
4	B ₂ neop ₂ (0.1 equiv) instead of (Bpin) ₂	70	23
5	Zn or Mn (1 equiv) instead of (Bpin) ₂	trace	trace
6	Ni(cod) ₂ instead of (Bpin) ₂ and NiCl ₂	53	18
7	Ni(cod) ₂ instead of NiCl ₂	54	19
8	NiCl ₂ (DME) instead of NiCl ₂	73	16
9	NiBr ₂ instead of NiCl ₂	76	18
10	PdCl ₂ instead of NiCl ₂	trace	50
11	NiCl ₂ (PCy ₃) ₂ instead of NiCl ₂	trace	18
12	bpy (0.1 equiv) was added	trace	31
13	KOtBu (2.3 equiv) instead of KOEt	38	18
14	KOMe (2.3 equiv) instead of KOEt	71	trace
15	NaOEt (2.3 equiv) instead of KOEt	16	trace
16	KOH (2.3 equiv) instead of KOEt	15	trace
17	DMA instead of PhMe	15	107
18	THF instead of PhMe	71	36
19	1,4-dioxane instead of PhMe	72	24
20	<i>p</i> -tolylboronic acid instead of <i>p</i> -tolylBneop	19	9
21	<i>p</i> -tolylBPin instead of <i>p</i> -tolylBneop	trace	trace
22	arylbromide (1.2 equiv) was used	68	15
23	<i>p</i> -tolylBneop(1.8 equiv) was used	72	24
24	NiCl ₂ (5 mol %) was used	68	23
25	NiCl ₂ (10 mol %) was used	74	25
26	at 60 °C	66	18
27	reaction for 12 h	67	20
28	setup the reaction outside of glovebox	72	21

^[a] Yield was determined by GC analysis using dodecane as internal standard.

Procedure A for Table S1: In an N₂-filled glovebox, to a 16 x 100 mm screw-capped vial containing a magnetic stirbar was added NiCl₂ (2.0 mg, 0.015 mmol, 7.5 mol %), bis(pinacolato)diboron (5.1 mg, 0.020 mmol, 10 mol %), KOEt (38.6 mg, 0.460 mmol, 2.30 equiv) and 2-(4-Methylphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (81.6 mg, 0.400 mmol, 2.00 equiv). The vial was sealed with a rubber septum and removed from the glovebox. In a separate vial, styrene (35 μL, 0.30 mmol, 1.5 equiv) and 3,5-dimethylbromobenzene (69 μL, 0.51 mmol, 2.6 equiv) were dissolved in toluene to a final volume of 1.5 mL. 1.0 mL of the toluene solution (0.20 M in styrene, 0.20 mmol, 1.0 equiv, and 0.34 M in aryl bromide, 0.34 mmol, 1.7 equiv.) was added to the reaction vial containing Ni catalyst via syringe under an N₂ atmosphere. The septum was quickly replaced by a Teflon-lined screw cap and the reaction was stirred at 80 °C for 21 h in a preheated aluminum block. The reaction was quenched upon the addition of 2 M HCl (2 mL), and the mixture was extracted with EtOAc (3 x 3 mL). Dodecane (46 μL, 0.20 mmol, 1.00 equiv.) was added via syringe, and a small aliquot was analyzed via GC.

Discussion: NiCl₂ and B₂Pin₂ were found optimal at promoting the diarylation reaction. Other amounts of (Bpin)₂, B₂neop₂ and metal reductants were found to give lower yield or

none of product (Table S1, entries 1-5). Other catalysts and ligands were also evaluated. Ni(cod)₂ with or without B₂Pin₂ shows similar catalytic reactivity. NiBr₂ and NiCl₂DME can also promote the diarylation reaction; however PdCl₂ cannot promote this transformation. When ligands were added, no product was detected (Table S1, entries 6-12). Various bases and solvents were also screened and provided product in moderate to good yield (Table S1, entries 13-19). Replacing the arylBneop with arylBpin or arylboronic acid resulted in a significant decrease in yield (Table S1, entries 18-19). With respect to ArBpin we suspect that a slower rate of transmetalation relative to ArBneop results in low yield. Lowering the amount of arylbromide and arylBneop or changing the catalyst loading cannot increase the yield (Table S1, entries 22-25). Shorter the reaction time or lower the temperature give lower yield of product (Table S1, entries 26-27). To our delight, the reaction could be setup outside of the glovebox using standard Schlenk techniques to afford product in comparable yield (Table S1, entries 28). It should be noted that the main side product observed in the optimized reaction is biaryl compound P1, which results from direct cross-coupling.

Procedure for Ni-Catalyzed Diarylation of Alkenes outside of glovebox

A 16 x 100 mm screw-capped vial containing a magnetic stirbar was flame-dried. After cooling to room temperature, the vial was removed from vacuum-line. NiCl₂ (2.0 mg, 0.015 mmol, 7.5 mol %), bis(pinacolato)diboron (5.1 mg, 0.020 mmol, 10 mol %), KOEt (38.6 mg, 0.460 mmol, 2.30 equiv) and 2-(4-Methylphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (81.6 mg, 0.400 mmol, 2.00 equiv) were added to the vial. The vial was sealed with a rubber septum, and evacuated under high vacuum and backfilled with nitrogen. The evacuate-refill cycle was repeated three times. In a separate flame-dried vial under nitrogen, styrene (35 μ L, 0.30 mmol, 1.5 equiv) and 3,5-dimethylbromobenzene (69 μ L, 0.51 mmol, 2.6 equiv) were dissolved in toluene to a final volume of 1.5 mL. 1.0 mL of the toluene solution (0.20 M in styrene, 0.20 mmol, 1.0 equiv, and 0.34 M in aryl bromide, 0.34 mmol, 1.7 equiv.) was added to the reaction vial containing Ni catalyst via syringe. The septum was quickly replaced by a Teflon-lined screw cap and the reaction was stirred at 80 $^{\circ}$ C for 21 h in a preheated aluminum block. The reaction was quenched upon the addition of 2 M HCl (2 mL), and the mixture was extracted with EtOAc (3 x 3 mL). Dodecane (46 μ L, 0.20 mmol, 1.00 equiv.) was added via syringe, and a small aliquot was analyzed via GC.

■ General Procedure B: Ni-Catalyzed Diarylation of Alkenes :

In an N₂-filled glovebox, to an oven dried 16 x 100 mm screw-capped vial containing a magnetic stirbar was added NiCl₂ (4.9 mg, 0.038 mmol, 7.5 mol %), bis(pinacolato)diboron, (12.7 mg, 0.0500 mmol, 10.0 mol %), KOEt (96.6 mg, 1.15 mmol, 2.30 equiv.) and arylBneop (1.0 mmol, 2.0 equiv.). The vial was sealed with a rubber septum and removed from the glovebox. In a separate oven dried 10.0 mL vial under N₂, alkene (0.60 mmol, 1.2 equiv.) and arylbromide (1.0 mmol, 2.0 equiv.) were dissolved in toluene to a final volume of 3.0 mL. 2.5 mL of the toluene solution (0.2 M in alkene, 0.50 mmol, 1.0 equiv., and 0.34 M in aryl bromide, 0.85 mmol, 1.7 equiv.) was added to the reaction vial containing Ni catalyst via syringe under an N₂ atmosphere. Note: if the alkene and arylbromide is a solid, it was added to the vial in the glovebox. The septum was quickly replaced by a Teflon-lined screw cap and the reaction was

stirred at 80 °C for 24 h in a preheated aluminum block. The reaction was quenched upon the addition of 2 M HCl (2 mL) or water (3 mL) for the products that are sensitive to acid (**26**, **27** and **33**), and the mixture was extracted with EtOAc (3 x 3 mL), dried over MgSO₄, gravity filtered, and concentrated. Dibromomethane was added as an internal standard and a small aliquot was analyzed via ¹H NMR, Crude material was purified via silica gel column chromatography.

■ Substrate Limitations:

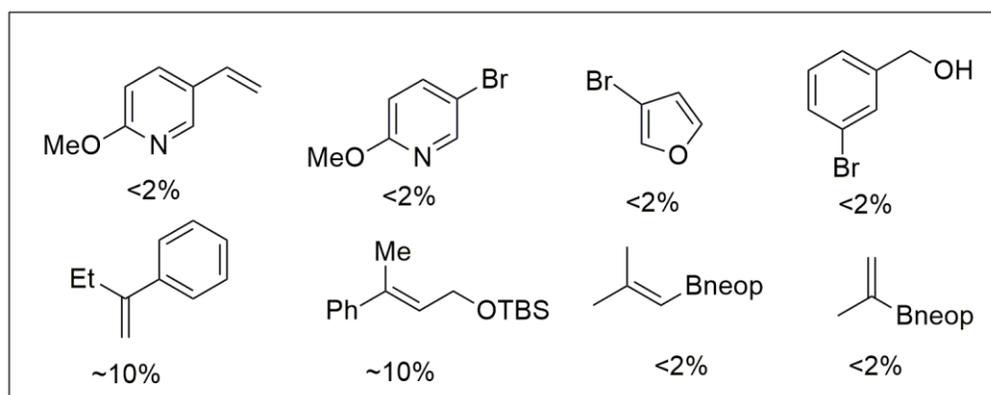
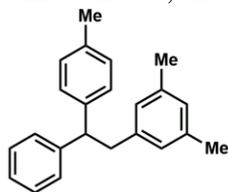


Figure S1: Unreactive substrates for Ni-catalyzed diarylation

■ Characterization Data:

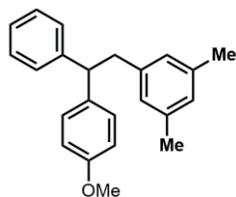
Unless noted, the minor diastereomer is not detected via NMR.



1,3-dimethyl-5-(2-phenyl-2-(p-tolyl)ethyl)benzene (4): The title compound was prepared according to general procedure B. NMR yield of the unpurified reaction mixture was determined using dibromomethane as an NMR standard. Purification by column chromatography (200:1 hexanes/Et₂O) yields **4** as a colorless oil.

Average over 2 runs: 76% NMR yield, 64% isolated yield.

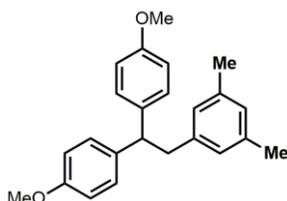
IR (neat): 3020 (m), 2917 (m), 2859 (m), 2976 (m), 1603 (m), 1511 (m), 1450 (m), 840 (s), 840 (s), 696 (s), 537 (s). **¹H NMR (400 MHz, CDCl₃):** δ 7.35 – 7.28 (m, 4H), 7.25 – 7.20 (m, 3H), 7.17 – 7.15 (m, 2H), 6.85 (s, 1H), 6.74 (s, 2H), 4.30 (t, *J* = 7.7 Hz, 1H), 3.37 (d, *J* = 7.7 Hz, 2H), 2.38 (s, 3H), 2.30 (s, 6H). **¹³C NMR (100 MHz, CDCl₃):** δ 145.0, 141.8, 140.4, 137.4, 135.6, 129.1, 128.4, 128.2, 128.0, 127.6, 127.1, 126.1, 52.6, 42.1, 21.4, 21.1. **HRMS (APCI):** Calculated for C₂₃H₂₄Na [M+Na]⁺: 323.1770, Found 323.1773.



1-(2-(4-methoxyphenyl)-2-phenylethyl)-3,5-dimethylbenzene(6): The title compound was prepared according to general procedure B. NMR yield of the unpurified reaction mixture was determined using dibromomethane as an NMR standard. Purification by column chromatography (200:1 hexanes/Et₂O) yields **6** as a colorless oil.

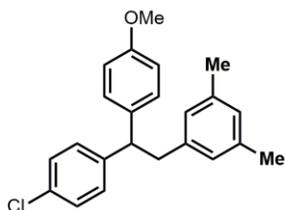
Average for 2 runs: 79% NMR, 72% isolated.

IR (neat): 3024 (m), 2915 (m), 2857 (m), 2976 (m), 1606 (m), 1509 (s), 1451 (m), 1246 (s), 1177 (s), 841 (s), 696 (s), 540 (s). **¹H NMR (400 MHz, CDCl₃):** δ 7.31 – 7.23 (m, 4H), 7.21 – 7.15 (m, 3H), 6.86 – 6.83 (m, 2H), 6.81 (s, 1H), 6.68 (s, 2H), 4.23 (t, *J* = 7.7 Hz, 1H), 3.79 (s, 3H), 3.30 (d, *J* = 7.7 Hz, 2H), 2.25 (s, 6H). **¹³C NMR (100 MHz, CDCl₃):** δ 158.0, 145.2, 140.3, 137.4, 137.0, 129.1, 128.4, 128.1, 127.6, 127.1, 126.1, 113.8, 55.3, 52.2, 42.3, 21.4. **HRMS (APCI):** Calculated for C₂₃H₂₄ONa [M+Na]⁺: 339.1719, Found 339.1720.



4,4'-(2-(3,5-dimethylphenyl)ethane-1,1-diyl)bis(methoxybenzene) (7): The title compound was prepared according to general procedure B. NMR yield of the unpurified reaction mixture was determined using dibromomethane as an NMR standard. Purification by column chromatography (100:1 hexanes/Et₂O) yields **7** as a colorless oil. Average for 2 runs: 77% NMR, 66% isolated.

IR (neat): 3000 (m), 2913 (m), 2834 (m), 1607 (m), 1508 (s), 1462 (m), 1244 (s), 1175 (s), 824 (s), 840 (s), 729 (s), 575 (s). **¹H NMR (400 MHz, CDCl₃):** δ 7.16 (d, *J* = 8.6 Hz, 4H), 6.85 – 6.82 (m, 5H), 6.70 (s, 2H), 4.20 (t, *J* = 7.7 Hz, 1H), 3.80 (s, 6H), 3.27 (d, *J* = 7.7 Hz, 2H), 2.3 (s, 6H). **¹³C NMR (100 MHz, CDCl₃):** δ 157.9, 140.5, 137.5, 137.4, 129.0, 127.6, 127.1, 113.8, 55.3, 51.3, 42.5, 21.4. **HRMS (APCI):** Calculated for C₂₃H₂₆O₂Na [M+Na]⁺: 369.1825, Found 369.1826.

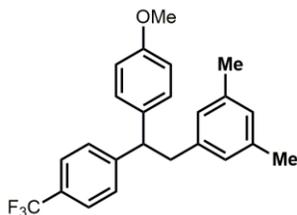


1-(2-(4-chlorophenyl)-2-(4-methoxyphenyl)ethyl)-3,5-dimethylbenzene (8):

The title compound was prepared according to general procedure B. NMR yield of the unpurified reaction mixture was determined using dibromomethane as an NMR standard.

Purification by column chromatography (200:1 hexanes/Et₂O) yields **8** as a colorless oil. Average for 2 runs: 80% NMR, 66% isolated.

IR (neat): 3011 (m), 2915 (m), 2834 (m), 1607 (m), 1510 (s), 1462 (m), 1247 (s), 1177 (s), 820 (s), 731 (s), 562 (s). **¹H NMR (400 MHz, CDCl₃):** δ 7.23 (d, *J* = 8.5 Hz, 2H), 7.14 – 7.11 (m, 4H), 6.84 (d, *J* = 8.7 Hz, 2H), 6.80 (s, 1H), 6.66 (s, 2H), 4.20 (t, *J* = 7.8 Hz, 1H), 3.79 (s, 3H), 3.30 – 3.19 (m, 2H), 2.24 (s, 6H). **¹³C NMR (100 MHz, CDCl₃):** δ 158.2, 143.6, 139.9, 137.6, 136.5, 131.8, 129.5, 129.0, 128.5, 127.7, 127.0, 113.9, 55.4, 51.6, 42.2, 21.4. **HRMS (APCI):** Calculated for C₂₃H₂₃OClNa [M+Na]⁺: 373.1330, Found 373.1330.

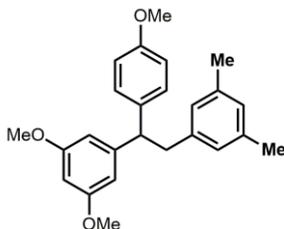


1-(2-(4-methoxyphenyl)-2-(4-(trifluoromethyl)phenyl)ethyl)-3,5-dimethylbenzene

(9): The title compound was prepared according to general procedure B. NMR yield of the unpurified reaction mixture was determined using dibromomethane as an NMR standard. Purification by column chromatography (180:1 hexanes/Et₂O) yields **9** as a colorless oil.

Average over 2 runs: 71% NMR yield, 62% isolated yield.

IR (neat): 3011 (m), 2917 (m), 2836 (m), 1608 (m), 1510 (s), 1463 (m), 1323 (s), 1248 (s), 1161 (s), 1109 (s), 1067 (s), 825 (s), 697 (m). **¹H NMR (400 MHz, CDCl₃):** δ 7.53 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 6.82 (s, 1H), 6.66 (s, 2H), 4.29 (t, *J* = 7.8 Hz, 1H), 3.80 (s, 3H), 3.36 – 3.24 (m, 2H), 2.25 (s, 6H). **¹³C NMR (100 MHz, CDCl₃):** δ 158.3, 149.2 (d, *J* = 1.6 Hz), 139.7, 137.7, 136.0, 129.0, 128.6, 128.4 (q, *J* = 32.1 Hz), 127.8, 127.0, 125.3 (q, *J* = 3.8 Hz), 124.4 (q, *J* = 270.2 Hz), 114.0, 55.3, 52.1, 42.0, 21.3. **¹⁹F NMR (376 MHz, CDCl₃)** δ – 62.3. **HRMS (APCI):** Calculated for C₂₄H₂₇ONF₃ [M+NH₄]⁺: 402.2039, Found 402.2040.



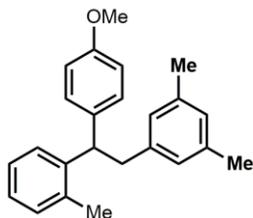
1-(2-(3,5-dimethoxyphenyl)-2-(4-methoxyphenyl)ethyl)-3,5-dimethylbenzene (**10**):

The title compound was prepared according to general procedure B. NMR yield of the unpurified reaction mixture was determined using dibromomethane as an NMR standard. Purification by column chromatography (80:1 hexanes/Et₂O) yields **10** as a colorless oil.

Average over 2 runs: 90% NMR yield, 78% isolated yield.

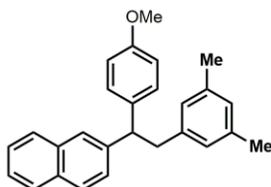
IR (neat): 3000 (m), 2915 (m), 2835 (m), 1594 (s), 1510 (s), 1458 (m), 1246 (s), 1178 (s), 828 (s), 729 (s). **¹H NMR (400 MHz, CDCl₃):** δ 7.19 (d, *J* = 8.6 Hz, 2H), 6.86 – 6.82 (m, 3H), 6.72 (s, 2H), 6.44 (d, *J* = 2.2 Hz, 2H), 6.34 (t, *J* = 2.3 Hz, 1H), 4.19 (t, *J* = 7.7 Hz, 1H), 3.80 (s, 3H), 3.77 (s, 6H), 3.33 – 3.24 (m, 2H), 2.27 (s, 6H). **¹³C NMR (100 MHz,**

CDCl₃): δ 160.7, 158.0, 147.7, 140.3, 137.4, 136.5, 129.0, 127.6, 127.0, 113.8, 106.4, 97.9, 55.3, 55.2, 52.4, 42.1, 21.3. **HRMS (APCI)**: Calculated for C₂₅H₂₉O₃ [M+H]⁺: 377.2111, Found 377.2114.



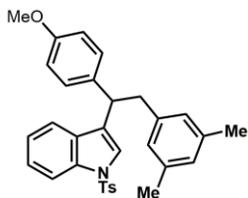
1-(2-(4-methoxyphenyl)-2-(o-tolyl)ethyl)-3,5-dimethylbenzene (11): The title compound was prepared according to general procedure B. NMR yield of the unpurified reaction mixture was determined using dibromomethane as an NMR standard. Purification by column chromatography (200:1 hexanes/Et₂O) yields **11** as a colorless oil. Average for 2 runs: 56% NMR, 47% isolated.

IR (neat): 3013 (m), 2915 (m), 2833 (m), 1607 (s), 1509 (s), 1460 (m), 1246 (s), 1176 (s), 1034 (s), 825 (s), 733 (s). **¹H NMR (400 MHz, CDCl₃)**: δ 7.41 (d, J = 7.7 Hz, 1H), 7.26 – 7.21 (m, 1H), 7.15 – 7.09 (m, 2H), 7.03 (d, J = 8.6 Hz, 2H), 6.80 – 6.77 (m, 3H), 6.63 (s, 2H), 4.38 (t, J = 7.6 Hz, 1H), 3.78 (s, 3H), 3.29 – 3.20 (m, 2H), 2.23 (s, 6H), 2.18 (s, 3H). **¹³C NMR (100 MHz, CDCl₃)**: δ 157.9, 143.2, 140.4, 137.4, 136.3, 130.5, 129.4, 127.6, 127.1, 127.0, 126.09, 126.07, 113.6, 55.3, 47.8, 42.6, 21.4, 20.0. **HRMS (APCI)**: Calculated for C₂₄H₂₅O [M-H]⁺: 329.1900, Found: 329.1901.



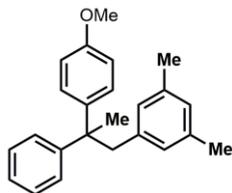
2-(2-(3,5-dimethylphenyl)-1-(4-methoxyphenyl)ethyl)naphthalene (12): The title compound was prepared according to general procedure B. NMR yield of the unpurified reaction mixture was determined using dibromomethane as an NMR standard. Purification by column chromatography (180:1 hexanes/Et₂O) yields **12** as colorless oil. Average for 2 runs: 93% NMR yield, 82% isolated yield.

IR (neat): 3011 (m), 2914 (m), 2834 (m), 1606 (s), 1509 (s), 1440 (m), 1245 (s), 1177 (s), 1034 (m), 830 (s), 729 (s). **¹H NMR (400 MHz, CDCl₃)**: δ 7.84 – 7.82 (m, 2H), 7.79 (d, J = 8.5 Hz, 1H), 7.73 (s, 1H), 7.52 – 7.44 (m, 2H), 7.40 (dd, J = 8.5, 1.8 Hz, 1H), 7.22 (d, J = 8.6 Hz, 2H), 6.86 (d, J = 8.7 Hz, 2H), 6.83 (s, 1H), 6.75 (s, 2H), 4.44 (t, J = 7.7 Hz, 1H), 3.80 (s, 3H), 3.43 (qd, J = 13.7, 7.7 Hz, 2H), 2.26 (s, 6H). **¹³C NMR (100 MHz, CDCl₃)**: δ 158.0, 142.7, 140.3, 137.5, 136.8, 133.6, 132.2, 129.3, 128.0, 127.9, 127.6, 127.10, 127.08, 126.1, 125.9, 125.4, 113.8, 55.3, 52.2, 42.1, 21.4. **HRMS (APCI)**: Calculated for C₂₇H₂₅O [M-H]⁺: 365.1900, Found: 365.1901.



3-(2-(3,5-dimethylphenyl)-1-(4-methoxyphenyl)ethyl)-1-tosyl-1H-indole (13): The title compound was prepared according to general procedure B. NMR yield of the unpurified reaction mixture was determined using dibromomethane as an NMR standard. Purification by column chromatography (20:1 hexanes/Et₂O) yields **13** as a white solid. Average for 2 runs: 50% NMR, 46% isolated.

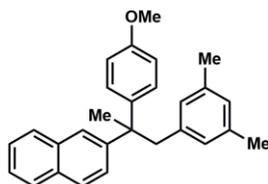
m. p.: 61-63 °C. **IR (neat):** 3005 (m), 2916 (m), 2835 (m), 1606 (m), 1509 (s), 1446 (m), 1248 (s), 1172 (s), 1130 (s), 1096 (m), 1034 (m), 810 (m), 745 (s), 571 (s). **¹H NMR (400 MHz, CDCl₃):** δ 7.95 (d, *J* = 8.3 Hz, 1H), 7.63 (d, *J* = 8.1 Hz, 2H), 7.52 (s, 1H), 7.24 – 7.22 (m, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 8.5 Hz, 2H), 6.83 (s, 1H), 6.77 (d, *J* = 8.5 Hz, 2H), 6.72 (s, 2H), 4.36 (t, *J* = 7.7 Hz, 1H), 3.76 (s, 3H), 3.35 (dd, *J* = 13.8, 7.7 Hz, 1H), 3.18 (dd, *J* = 13.8, 7.7 Hz, 1H), 2.35 (s, 3H), 2.24 (s, 6H). **¹³C NMR (100 MHz, CDCl₃):** δ 158.2, 144.7, 139.9, 137.6, 135.6, 135.24, 135.19, 130.8, 129.8, 129.0, 127.8, 126.9, 126.8, 126.3, 124.6, 123.5, 123.1, 120.4, 113.82, 113.79, 55.3, 43.4, 42.3, 21.7, 21.4. **HRMS (APCI):** Calculated for C₃₂H₃₀O₃NS [M-H]⁺: 508.1941, Found: 508.1942.



1-(2-(4-methoxyphenyl)-2-phenylpropyl)-3,5-dimethylbenzene (14):

The title compound was prepared according to general procedure B. NMR yield of the unpurified reaction mixture was determined using dibromomethane as an NMR standard. Purification by column chromatography (200:1 hexanes/Et₂O) yields **14** as a white solid. Average over 2 runs: 75% NMR, 58% isolated.

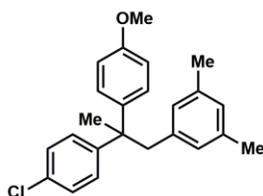
m. p.: 75-77 °C. **IR (neat):** 3023 (m), 3001 (m), 2916 (m), 2833 (m), 1605 (m), 1506 (s), 1444 (m), 1246 (s), 1105 (s), 809 (m), 700 (s), 572 (s). **¹H NMR (400 MHz, CDCl₃):** δ 7.33 – 7.29 (m, 2H), 7.25 – 7.22 (m, 3H), 7.15 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.81 (s, 1H), 6.24 (s, 2H), 3.84 (s, 3H), 3.40 – 3.33 (m, 2H), 2.18 (s, 6H), 1.56 (s, 3H). **¹³C NMR (100 MHz, CDCl₃):** δ 157.7, 149.9, 141.9, 138.1, 136.5, 128.93, 128.89, 127.9, 127.8, 127.5, 125.8, 113.2, 55.4, 47.9, 46.7, 27.3, 21.3. **HRMS (APCI):** Calculated for C₂₄H₃₀ON [M+NH₄]⁺: 348.2322, Found 348.2323.



2-(1-(3,5-dimethylphenyl)-2-(4-methoxyphenyl)propan-2-yl)naphthalene (15):

The title compound was prepared according to general procedure B. NMR yield of the unpurified reaction mixture was determined using dibromomethane as an NMR standard. Purification by column chromatography (200:1 hexanes/Et₂O) yields **15** as a white solid. Average over 2 runs: 95% NMR, 86% isolated.

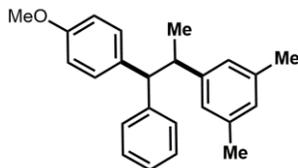
m. p.: 43-45 °C. **IR (neat):** 2999 (m), 2915 (m), 2833 (m), 1604 (s), 1509 (s), 1461 (m), 1245 (s), 1181 (s), 1033 (m), 819 (s), 745 (s). **¹H NMR (400 MHz, CDCl₃):** δ 7.89 – 7.82 (m, 2H), 7.80 – 7.71 (m, 2H), 7.56 – 7.45 (m, 2H), 7.28 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.15 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.80 (s, 1H), 6.26 (s, 2H), 3.84 (s, 3H), 3.65 – 3.36 (m, 2H), 2.13 (s, 6H), 1.66 (s, 3H). **¹³C NMR (100 MHz, CDCl₃):** δ 157.7, 147.3, 141.3, 138.0, 136.6, 133.2, 131.9, 129.1, 128.9, 128.1, 127.8, 127.6, 127.5, 125.9, 125.6, 125.0, 113.2, 55.4, 47.6, 46.9, 27.1, 21.3. **HRMS (EI):** Calculated for C₂₈H₂₈O [M]⁺: 380.2135, Found 380.2132.



1-(2-(4-chlorophenyl)-2-(4-methoxyphenyl)propyl)-3,5-dimethylbenzene (16):

The title compound was prepared according to general procedure B. NMR yield of the unpurified reaction mixture was determined using dibromomethane as an NMR standard. Purification by column chromatography (200:1 hexanes/Et₂O) yields **16** as a white solid. Average over 2 runs: 65% NMR, 56% isolated.

m. p.: 66-68 °C. **IR (neat):** 2999 (m), 2918 (m), 2834 (m), 1605 (m), 1510 (s), 1462 (m), 1246 (s), 1182 (s), 827 (s), 730 (s), 572 (s). **¹H NMR (400 MHz, CDCl₃):** δ 7.22 (d, *J* = 8.8 Hz, 2H), 7.16 – 7.01 (m, 4H), 6.82 (d, *J* = 8.8 Hz, 2H), 6.77 (s, 1H), 6.20 (s, 2H), 3.81 (s, 3H), 3.28 (m, 2H), 2.14 (s, 6H), 1.49 (s, 3H). **¹³C NMR (100 MHz, CDCl₃):** δ 157.8, 148.4, 141.4, 137.7, 136.7, 131.6, 129.4, 128.8, 127.9, 127.7, 113.3, 55.4, 47.8, 46.5, 27.3, 21.3. **HRMS (EI):** Calculated for C₂₄H₂₅ClO [M]⁺: 364.1588, Found 364.1586.

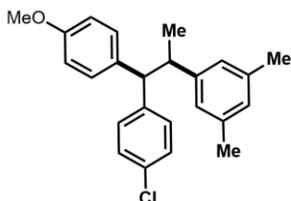


1-(1-(4-methoxyphenyl)-1-phenylpropan-2-yl)-3,5-dimethylbenzene (17):

The title compound was prepared according to general procedure B. NMR yield of the unpurified reaction mixture was determined using dibromomethane as an NMR standard. Purification by column chromatography (200:1 hexanes/Et₂O) yields **17** as a white solid. Average for 2 runs: 95% NMR yield, 81% isolated yield, >20:1 dr. The diastereoselectivity was determined by GC-MS of crude mixture (see attached spectrum), which was compared to the sample prepared from diarylation of *cis*-β-methylstyrene under general procedure B (51% NMR yield and 5:1 dr)

m. p.: 58-60 °C. **IR (neat):** 3003 (m), 2918 (m), 2833 (m), 1605 (m), 1511 (s), 1441 (m), 1244 (s), 1107 (s), 1037 (m), 801 (m), 699 (s), 590 (s). **¹H NMR (400 MHz, CDCl₃):** δ

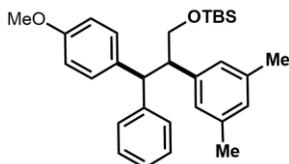
7.38 (d, $J = 7.6$ Hz, 2H), 7.32 (t, $J = 7.5$ Hz, 2H), 7.20 (t, $J = 7.2$ Hz, 1H), 7.07 (d, $J = 8.4$ Hz, 2H), 6.79 (s, 2H), 6.73 (s, 1H), 6.65 (d, $J = 8.4$ Hz, 2H), 4.04 (d, $J = 11.3$ Hz, 1H), 3.68 (s, 3H), 3.49 (dq, $J = 13.5, 6.9$ Hz, 1H), 2.24 (s, 6H), 1.17 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 157.5, 146.1, 145.0, 137.4, 136.5, 129.2, 128.6, 128.3, 127.6, 126.2, 125.6, 113.5, 58.3, 55.2, 44.3, 22.5, 21.5. HRMS (APCI): Calculated for $\text{C}_{24}\text{H}_{30}\text{ON}$ $[\text{M}+\text{NH}_4]^+$: 348.2322, Found 348.2320.



1-(1-(4-chlorophenyl)-1-(4-methoxyphenyl)propan-2-yl)-3,5-dimethylbenzene (18):

The title compound was prepared according to general procedure B. NMR yield of the unpurified reaction mixture was determined using dibromomethane as an NMR standard. Purification by column chromatography (200:1 hexanes/ Et_2O) yields **18** as a white solid. Average for 2 runs: 66% NMR yield, 56% isolated yield, >20:1 dr.

m. p.: 68-70 °C. **IR (neat):** 3012 (m), 2959, 2915 (m), 2836 (m), 1606 (m), 1511 (s), 1461 (m), 1251 (s), 1177 (m), 1031 (m), 808 (s), 731 (m), 595 (s). ^1H NMR (400 MHz, CDCl_3): δ 7.35 – 7.30 (m, 4H), 7.07 (d, $J = 8.7$ Hz, 2H), 6.80 (s, 2H), 6.76 (s, 1H), 6.68 (d, $J = 8.7$ Hz, 2H), 4.06 (d, $J = 11.2$ Hz, 1H), 3.69 (s, 3H), 3.48 (dq, $J = 11.2, 6.8$ Hz, 1H), 2.26 (s, 6H), 1.19 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 157.6, 145.7, 143.5, 137.5, 135.9, 131.8, 129.7, 129.1, 128.7, 127.7, 125.6, 113.6, 57.6, 55.1, 44.2, 22.3, 21.5. HRMS (APCI): Calculated for $\text{C}_{24}\text{H}_{29}\text{ONCl}$ $[\text{M}+\text{NH}_4]^+$: 382.1932, Found 382.1933.

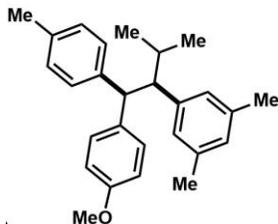


tert-butyl(2-(3,5-dimethylphenyl)-3-(4-methoxyphenyl)-3-phenylpropoxy)dimethylsilane (19): The title compound was prepared according to general procedure B. NMR yield of the unpurified reaction mixture was determined using dibromomethane as an NMR standard. Purification by column chromatography (120:1 hexanes/ Et_2O) yields **19** as a colorless oil.

Average over 2 runs: 65% NMR yield, 54% isolated yield, >20:1 dr.

IR (neat): 3027 (m), 2952 (m), 2855 (m), 1608 (m), 1510 (s), 1442 (m), 1301(s), 1245 (s), 1105 (s), 832 (s), 774 (s), 733 (s), 699 (s). ^1H NMR (400 MHz, CDCl_3): δ 7.43 – 7.41 (m, 2H), 7.32 (t, $J = 7.6$ Hz, 2H), 7.22 – 7.20 (m, 1H), 7.14 (d, $J = 8.7$ Hz, 2H), 6.89 (s, 2H), 6.74 (s, 1H), 6.67 (d, $J = 8.7$ Hz, 2H), 4.52 (d, $J = 11.6$ Hz, 1H), 3.67 (s, 3H), 3.63 (d, $J = 4.0$ Hz, 2H), 3.47 (dt, $J = 11.7, 4.0$ Hz, 1H), 2.25 (s, 6H), 0.87 (s, 9H), -0.21 (s, 3H), -0.23 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 157.4, 144.8, 142.3, 136.7, 135.9, 129.6, 128.5, 128.4, 127.6, 127.2, 126.2, 113.5, 66.0, 55.1, 51.9, 51.6, 26.0, 21.5, 18.4, -

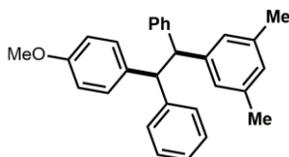
5.73, -5.79. **HRMS (APCI):** Calculated for C₃₀H₄₄O₂NSi [M+NH₄]⁺: 478.3136, Found 478.3135.



1-(1-(4-methoxyphenyl)-3-methyl-1-(p-tolyl)butan-2-yl)-3,5-dimethylbenzene (20):

The title compound was prepared according to general procedure B. NMR yield of the unpurified reaction mixture was determined using dibromomethane as an NMR standard. Purification by column chromatography (150:1 hexanes/Et₂O) yields **20** as a white solid. Average over two runs: 47% NMR yield, 43% isolated yield, >20:1 dr.

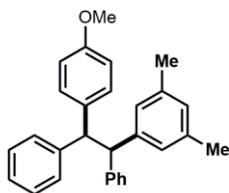
m. p.: 105-107 °C. **IR (neat):** 3005 (m), 2952 (m), 2821 (m), 1606 (m), 1508 (s), 1450 (m), 1258 (s), 1176 (s), 1034 (s), 822 (s), 766 (s), 730 (m), 573 (s). **¹H NMR (400 MHz, CDCl₃):** δ 7.31 (d, *J* = 8.6 Hz, 2H), 7.08 (d, *J* = 7.9 Hz, 2H), 6.87 – 6.64 (m, 4H), 6.76 (s, 2H), 6.71 (s, 1H), 4.37 (d, *J* = 12.3 Hz, 1H), 3.77 (s, 3H), 3.42 (dd, *J* = 12.4, 3.2 Hz, 1H), 2.23 (s, 6H), 2.14 (s, 3H), 1.85 – 1.80 (m, 1H), 0.79 (d, *J* = 6.8 Hz, 3H), 0.75 (d, *J* = 6.9 Hz, 3H). **¹³C NMR (100 MHz, CDCl₃):** δ 157.9, 141.8, 139.4, 137.6, 136.2, 134.6, 128.9, 128.1, 127.4, 114.2, 55.3, 54.5, 52.8, 28.5, 22.7, 21.6, 21.0, 16.1. **HRMS (APCI):** Calculated for C₂₇H₃₆ON [M+NH₄]⁺: 390.2791, Found 390.2793.



1-(3,5-dimethylphenyl)-2-(4-methoxyphenyl)ethane-1,2-diyl)dibenzene (21): The title compound was prepared according to general procedure B. NMR yield of the unpurified reaction mixture was determined using dibromomethane as an NMR standard. Purification by column chromatography (70:1 hexanes/Et₂O) yields **21** as a white solid.

Average over two runs: 96% NMR yield, 85% isolated yield, >20:1 dr.

m. p.: 147-150 °C. **IR (neat):** 3022 (m), 2962 (m), 2916 (m), 1606 (m), 1512 (s), 1255 (s), 1028 (s), 824 (s), 699 (m), 606 (s). **¹H NMR (400 MHz, CDCl₃):** δ 7.16 – 7.07 (m, 10H), 7.02 – 6.98 (m, 2H), 6.80 (s, 2H), 6.08 – 6.66 (m, 3H), 4.72 (d, *J* = 12.2 Hz, 1H), 4.64 (d, *J* = 12.2 Hz, 1H), 3.70 (s, 3H), 2.17 (s, 6H). **¹³C NMR (100 MHz, CDCl₃):** δ 157.6, 144.2, 144.0, 143.4, 137.4, 136.0, 129.5, 128.63, 128.56, 128.2, 127.7, 126.5, 125.78, 125.75, 113.6, 56.5, 55.5, 55.2, 21.5. **HRMS (APCI):** Calculated for C₂₉H₃₂ON [M+NH₄]⁺: 410.2478, Found 410.2480. X-ray crystal structure is available (see attached spectrum).

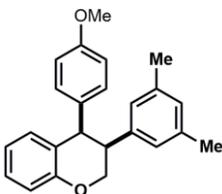


1-(3,5-dimethylphenyl)-2-(4-methoxyphenyl)ethane-1,2-diyl dibenzene (22):

The title compound was prepared according to general procedure B. NMR yield of the unpurified reaction mixture was determined using dibromomethane as an NMR standard. Purification by column chromatography (70:1 hexanes/Et₂O) yields **22** as a white solid.

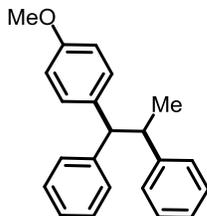
Average over two runs: 70% NMR yield, 59% isolated yield, 8:1 dr. The dr of the isolated product was determined by analysis of the ¹H NMR. The characterization data shown below is of a single major diastereomer obtained after recrystallization from hexanes.

m. p.: 47-49 °C. **IR (neat):** 3029 (m), 2959 (m), 2914 (m), 1606 (m), 1510 (s), 1259 (s), 1040 (s), 827 (s), 696 (m), 609 (s). **¹H NMR (400 MHz, CDCl₃):** δ 7.20 – 7.16 (m, 4H), 7.15 – 7.11 (m, 4H), 7.08 – 7.02 (m, 4H), 6.79 (s, 2H), 6.67 – 6.65 (m, 3H), 4.73 (d, *J* = 12.2 Hz, 1H), 4.66 (d, *J* = 12.2 Hz, 1H), 3.68 (s, 3H), 2.16 (s, 6H). **¹³C NMR (100 MHz, CDCl₃):** δ 157.6, 144.1, 144.0, 143.4, 137.4, 136.1, 129.5, 128.7, 128.5, 128.22, 128.16, 127.6, 126.5, 125.79, 125.76, 113.6, 56.5, 55.5, 55.2, 21.5. **HRMS (APCI):** Calculated for C₂₉H₃₂ON [M+NH₄]⁺: 410.2478, Found 410.2479. X-ray crystal structure is available (see attached spectrum).



cis-3-(3,5-dimethylphenyl)-4-(4-methoxyphenyl)chroman (23): The title compound was prepared according to general procedure B. NMR yield of the unpurified reaction mixture was determined using dibromomethane as an NMR standard. Purification by column chromatography (200:1 hexanes/Et₂O) yields **23** as a colorless oil. Average over two runs: 61% NMR yield, 46% isolated yield, >20:1 dr.

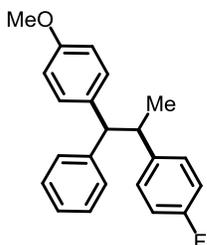
IR (neat): 3004 (m), 2950 (m), 2834 (m), 1606 (m), 1509 (s), 1487 (m), 1247 (s), 1176 (s), 1035 (s), 830 (s), 729 (s), 704 (s). **¹H NMR (400 MHz, CDCl₃):** δ 7.21 (ddd, *J* = 8.6, 7.2, 1.7 Hz, 1H), 7.01 – 6.98 (m, 2H), 6.89 – 6.85 (m, 2H), 6.66 (d, *J* = 8.7 Hz, 2H), 6.55 (d, *J* = 8.7 Hz, 2H), 6.28 (s, 2H), 4.43 (dd, *J* = 12.0, 10.5 Hz, 1H), 4.43 – 4.23 (m, 2H), 3.75 (s, 3H), 3.58 – 3.52 (m, 1H), 2.20 (s, 6H). **¹³C NMR (100 MHz, CDCl₃):** δ 158.3, 154.6, 139.2, 137.5, 133.7, 131.6, 131.0, 128.4, 128.1, 126.3, 125.1, 120.6, 116.7, 112.7, 64.8, 55.3, 47.1, 43.4, 21.4. **HRMS (APCI):** Calculated for C₂₄H₂₅O₂ [M+H]⁺: 345.1849, Found 345.1850.



1-(4-methoxyphenyl)propane-1,2-diyl)dibenzene (26): The title compound was prepared according to general procedure B. NMR yield of the unpurified reaction mixture was determined using dibromomethane as an NMR standard. Purification by column chromatography (80:1 hexanes/Et₂O) yields **26** as a white solid

Average over 2 runs: 92% NMR yield, 79% isolated yield, >20:1 dr.

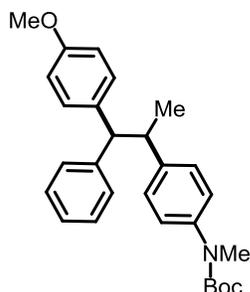
m.p.: 41-44 °C. **IR (neat):** 2959 (w), 2834 (w), 1509 (m), 1244 (m), 1033 (m), 734 (m), 697 (s), 579 (m). **¹H NMR (400 MHz, CDCl₃):** δ 7.39 (dd, *J* = 8.1, 1.4 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.23 – 7.14 (m, 5H), 7.11 – 7.06 (m, 1H), 7.06 – 7.02 (m, 2H), 6.66 – 6.60 (m, 2H), 4.04 (d, *J* = 11.4 Hz, 1H), 3.66 (s, 3H), 3.56 (dq, *J* = 11.4, 6.8 Hz, 1H), 1.21 (d, *J* = 6.8 Hz, 3H). **¹³C NMR (100 MHz, CDCl₃):** δ 157.5, 146.2, 144.7, 136.3, 129.2, 128.7, 128.3, 128.2, 127.8, 126.3, 125.9, 113.5, 58.6, 55.1, 44.6, 22.3. **HRMS (ESI):** Calculated for C₂₂H₂₂ONa [M+Na]⁺: 325.1563, Found: 325.1561.



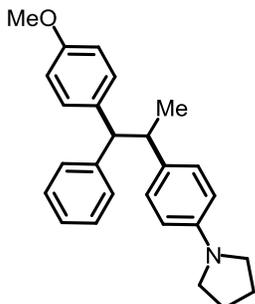
1-fluoro-4-(1-(4-methoxyphenyl)-1-phenylpropan-2-yl)benzene (27): The title compound was prepared according to general procedure B. NMR yield of the unpurified reaction mixture was determined using dibromomethane as an NMR standard. Purification by column chromatography (80:1 hexanes/Et₂O) yields **27** as a white solid

Average over 2 runs: 76% NMR yield, 65% isolated yield, >20:1 dr.

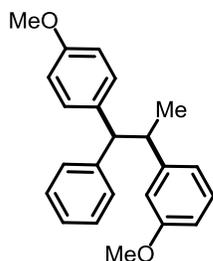
m.p.: 53-55 °C. **IR (neat):** 2960 (s), 2890 (s), 1611 (m), 1507 (s), 1249 (s), 1219 (s), 1157 (m), 1021 (m), 829 (s), 801 (s), 697 (s), 551 (s). **¹H NMR (500 MHz, CDCl₃):** δ 7.38 – 7.35 (m, 2H), 7.33 – 7.28 (m, 2H), 7.22 – 7.16 (m, 1H), 7.11 – 7.05 (m, 2H), 7.02 – 6.96 (m, 2H), 6.88 – 6.81 (m, 2H), 6.65 – 6.59 (m, 2H), 3.95 (d, *J* = 11.2 Hz, 1H), 3.67 (s, 3H), 3.53 (dq, *J* = 11.2, 6.8 Hz, 1H), 1.17 (d, *J* = 6.8 Hz, 3H). **¹³C NMR (125 MHz, CDCl₃):** δ 161.1 (d, *J* = 241.9 Hz), 157.6, 144.4, 141.8 (d, *J* = 3.3 Hz), 136.1, 129.2, 129.0 (d, *J* = 7.7 Hz), 128.7, 128.3, 126.4, 115.0 (d, *J* = 20.8 Hz), 113.6, 58.9, 55.2, 44.0, 22.3. **¹⁹F NMR (470 MHz, CDCl₃):** δ -180.6. **HRMS (APCI):** Calculated for C₂₂H₂₅ONF [M+NH₄]⁺: 338.1915, Found: 338.1915.



tert-butyl(4-(1-(4-methoxyphenyl)-1-phenylpropan-2-yl)phenyl)(methyl)carbamate (28): The title compound was prepared according to general procedure B. NMR yield of the unpurified reaction mixture was determined using dibromomethane as an NMR standard. Purification by column chromatography (5:1 hexanes/EtOAc) yields **28** as a colorless oil. Average over 2 runs: 47% NMR yield, 42% isolated yield, >20:1 dr. **IR (neat):** 3001 (m), 2929 (m), 1691 (s), 1510 (s), 1362(s), 1245 (s), 1149 (s), 1108 (s), 1034 (m), 805 (m), 724 (s), 699 (s), 529 (m). **¹H NMR (400 MHz, CDCl₃):** δ 7.37 (d, *J* = 7.1 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.09 (d, *J* = 8.1 Hz, 2H), 7.05 – 6.98 (m, 4H), 6.64 – 6.59 (m, 2H), 3.99 (d, *J* = 11.3 Hz, 1H), 3.65 (s, 3H), 3.58 – 3.49 (m, 1H), 3.18 (s, 3H), 1.40 (s, 9H), 1.18 (d, *J* = 6.8 Hz, 3H). **¹³C NMR (125 MHz, CDCl₃):** δ 157.5, 155.0, 144.6, 143.3, 141.5, 136.2, 129.2, 128.6, 128.3, 127.8, 126.3, 125.3, 113.5, 80.0, 58.7, 55.1, 44.1, 37.3, 28.4, 22.2. **HRMS (ESI):** Calculated for C₂₈H₃₃O₃NNa [M+Na]⁺: 454.2353, Found: 454.2352.

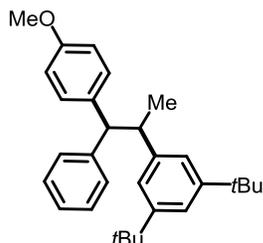


1-(4-(1-(4-methoxyphenyl)-1-phenylpropan-2-yl)phenyl)pyrrolidine (29): The title compound was prepared according to general procedure B. NMR yield of the unpurified reaction mixture was determined using dibromomethane as an NMR standard. Purification by column chromatography (20:1 hexanes/Et₂O) yields **29** as a yellow solid. Average over 2 runs: 78% NMR yield, 65% isolated yield, >20:1 dr. **m.p.:** 96-99 °C. **IR (neat):** 3020 (m), 2921 (m), 2831 (m), 1610 (m), 1509 (s), 1380 (s), 1019 (m), 733 (m). **¹H NMR (500 MHz, CDCl₃):** δ 7.37 – 7.33 (m, 2H), 7.28 (t, *J* = 7.7 Hz, 2H), 7.17 – 7.13 (m, 1H), 7.08 – 7.04 (m, 2H), 7.02 – 6.97 (m, 2H), 6.64 – 6.59 (m, 2H), 6.42 – 6.37 (m, 2H), 3.99 (d, *J* = 11.2 Hz, 1H), 3.64 (s, 3H), 3.45 (dq, *J* = 11.2, 6.8 Hz, 1H), 3.22 – 3.17 (m, 4H), 1.97 – 1.89 (m, 4H), 1.13 (d, *J* = 6.8 Hz, 3H). **¹³C NMR (125 MHz, CDCl₃):** δ 157.4, 146.2, 145.3, 136.8, 132.9, 129.3, 128.5, 128.4, 128.3, 126.1, 113.5, 111.6, 58.7, 55.1, 47.7, 43.5, 25.5, 22.7. **HRMS (ESI):** Calculated for C₂₆H₃₀ON [M+H]⁺: 372.2322, Found: 372.2321.



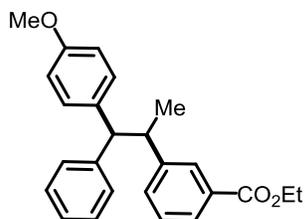
1-methoxy-3-(1-(4-methoxyphenyl)-1-phenylpropan-2-yl)benzene (30): The title compound was prepared according to general procedure B. NMR yield of the unpurified reaction mixture was determined using dibromomethane as an NMR standard. Purification by column chromatography (50:1 hexanes/Et₂O) yields **30** as a colorless oil. Average over 2 runs: 79% NMR yield, 75% isolated yield, >20:1 dr.

IR (neat): 2958 (m), 2833 (m), 1608 (m), 1509 (s), 1244 (s), 1156 (m), 1034 (s), 779 (s), 697 (s), 581 (m). **¹H NMR (400 MHz, CDCl₃):** δ 7.44 – 7.39 (m, 2H), 7.37 – 7.32 (m, 2H), 7.24 – 7.20 (m, 1H), 7.16 – 7.07 (m, 3H), 6.83 – 6.80 (m, 1H), 6.75 (t, *J* = 2.1 Hz, 1H), 6.69 – 6.64 (m, 3H), 4.06 (d, *J* = 11.3 Hz, 1H), 3.75 (s, 3H), 3.68 (s, 3H), 3.58 (dq, *J* = 11.4, 6.8 Hz, 1H), 1.23 (d, *J* = 6.8 Hz, 3H). **¹³C NMR (100 MHz, CDCl₃):** δ 159.4, 157.5, 147.9, 144.7, 136.2, 129.14, 129.12, 128.6, 128.3, 126.3, 120.3, 113.9, 113.5, 110.9, 58.5, 55.2, 55.1, 44.6, 22.3. **HRMS (ESI):** Calculated for C₂₃H₂₄O₂Na [M+Na]⁺: 355.1669, Found: 355.1668.



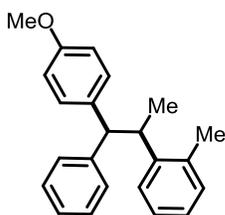
1,3-di-tert-butyl-5-(1-(4-methoxyphenyl)-1-phenylpropan-2-yl)benzene (31): The title compound was prepared according to general procedure B. NMR yield of the unpurified reaction mixture was determined using dibromomethane as an NMR standard. Purification by column chromatography (50:1 hexanes/Et₂O) yields **31** as a colorless oil. Average over 2 runs: 86% NMR yield, 76% isolated yield, >20:1 dr.

IR (neat): 2960 (s), 2867 (m), 1597 (m), 1509 (s), 1245 (s), 1176 (m), 1036 (s), 876 (m), 736 (s), 714 (s), 589 (m). **¹H NMR (500 MHz, CDCl₃):** δ 7.41 – 7.38 (m, 2H), 7.34 – 7.29 (m, 2H), 7.21 – 7.17 (m, 1H), 7.08 (t, *J* = 1.8 Hz, 1H), 6.92 – 6.88 (m, 2H), 6.87 (d, *J* = 1.8 Hz, 2H), 6.58 – 6.54 (m, 2H), 3.90 (d, *J* = 10.9 Hz, 1H), 3.64 (s, 3H), 3.50 (dq, *J* = 10.9, 6.8 Hz, 1H), 1.26 (d, *J* = 6.8 Hz, 3H), 1.22 (s, 18H). **¹³C NMR (125 MHz, CDCl₃):** δ 157.5, 150.0, 144.52, 144.50, 136.6, 129.2, 128.6, 128.5, 126.2, 122.4, 119.4, 113.3, 59.7, 55.2, 45.2, 34.8, 31.6, 21.1. **HRMS (ESI):** Calculated for C₃₀H₃₈O₂Na [M+Na]⁺: 437.2815, Found: 437.2816.



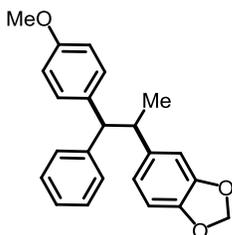
Ethyl 3-(1-(4-methoxyphenyl)-1-phenylpropan-2-yl)benzoate (32): The title compound was prepared according to general procedure B. NMR yield of the unpurified reaction mixture was determined using dibromomethane as an NMR standard. Purification by column chromatography (20:1 hexanes/Et₂O) yields **32** as a colorless oil. Average over 2 runs: 42% NMR yield, 38% isolated yield, >20:1 dr.

IR (neat): 2920 (s), 2851 (s), 1712 (s), 1509 (s), 1245 (s), 1177 (s), 1031 (s), 812 (m), 753 (s), 696 (s), 586 (m). **¹H NMR (400 MHz, CDCl₃):** δ 7.89 (s, 1H), 7.76 (dt, *J* = 7.6, 1.4 Hz, 1H), 7.42 – 7.37 (m, 2H), 7.35 – 7.28 (m, 3H), 7.24 – 7.17 (m, 2H), 7.06 – 7.00 (m, 2H), 6.65 – 6.56 (m, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 4.05 (d, *J* = 11.4 Hz, 1H), 3.68 – 3.58 (m, 4H), 1.40 (t, *J* = 7.1 Hz, 3H), 1.21 (d, *J* = 6.8 Hz, 3H). **¹³C NMR (100 MHz, CDCl₃):** δ 166.9, 157.6, 146.5, 144.3, 135.9, 132.5, 130.4, 129.2, 128.8, 128.7, 128.19, 128.18, 127.2, 126.4, 113.6, 61.0, 58.5, 55.1, 44.5, 22.2, 14.5. **HRMS (ESI):** Calculated for C₂₅H₂₆O₃Na [M+Na]⁺: 397.1774, Found: 397.1777.



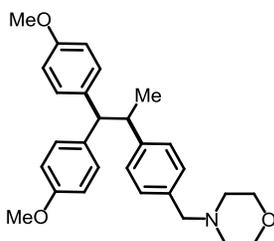
1-(1-(4-methoxyphenyl)-1-phenylpropan-2-yl)-2-methylbenzene (33): The title compound was prepared according to general procedure B. NMR yield of the unpurified reaction mixture was determined using dibromomethane as an NMR standard. Purification by column chromatography (80:1 hexanes/Et₂O) yields **33** as a colorless oil. Average over 2 runs: 88% NMR yield, 81% isolated yield, >20:1 dr.

IR (neat): 3023, (m), 2959 (m), 1609 (m), 1509 (s), 1243 (s), 1176 (s), 1032 (s), 805 (m), 781 (s), 725 (s), 698 (s), 556 (s). **¹H NMR (500 MHz, CDCl₃):** δ 7.40 – 7.37 (m, 2H), 7.34 – 7.30 (m, 2H), 7.27 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.22 – 7.18 (m, 1H), 7.10 (td, *J* = 7.3, 1.8 Hz, 1H), 7.03 – 6.97 (m, 4H), 6.61 – 6.58 (m, 2H), 4.16 (d, *J* = 11.3 Hz, 1H), 3.85 – 3.77 (m, 1H), 3.65 (s, 3H), 2.29 (s, 3H), 1.12 (d, *J* = 6.7 Hz, 3H). **¹³C NMR (125 MHz, CDCl₃):** δ 157.5, 144.8, 144.4, 136.3, 135.3, 130.3, 129.0, 128.6, 128.5, 126.3, 126.2, 126.1, 125.5, 113.4, 57.8, 55.1, 39.0, 21.8, 19.9. **HRMS (ESI):** Calculated for C₂₃H₂₄O₂Na [M+Na]⁺: 339.1719, Found: 339.1716.



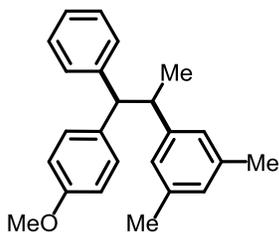
5-(1-(4-methoxyphenyl)-1-phenylpropan-2-yl)benzo[d][1,3]dioxole (34): The title compound was prepared according to general procedure B. NMR yield of the unpurified reaction mixture was determined using dibromomethane as an NMR standard. Purification by column chromatography (20:1 hexanes/Et₂O) yields **34** as a colorless oil. Average over 2 runs: 97% NMR yield, 82% isolated yield, >20:1 dr.

IR (neat): 2958 (m), 2927 (m), 2875 (w), 1609 (m), 1509 (m), 1486 (m), 1243 (s), 1037 (s), 733 (s), 699 (s). **¹H NMR (500 MHz, CDCl₃):** δ 7.37 – 7.34 (m, 2H), 7.32 – 7.28 (m, 2H), 7.20 – 7.17 (m, 1H), 7.07 – 7.03 (m, 2H), 6.69 (d, *J* = 1.4 Hz, 1H), 6.67 – 6.63 (m, 2H), 6.62 – 6.58 (m, 2H), 5.86 (s, 2H), 3.95 (d, *J* = 11.3 Hz, 1H), 3.68 (s, 3H), 3.49 (dq, *J* = 11.3, 6.8 Hz, 1H), 1.15 (d, *J* = 6.8 Hz, 3H). **¹³C NMR (125 MHz, CDCl₃):** δ 157.6, 147.5, 145.5, 144.7, 140.2, 136.3, 129.2, 128.7, 128.2, 126.3, 120.9, 113.6, 108.0, 107.8, 100.8, 58.8, 55.2, 44.3, 22.6. **HRMS (ESI):** Calculated for C₂₃H₂₂O₃Na [M+Na]⁺: 369.1461, Found: 369.1461.



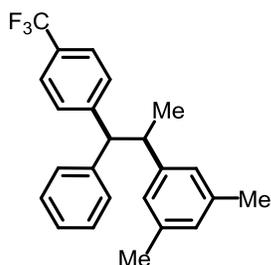
4-(4-(1,1-bis(4-methoxyphenyl)propan-2-yl)benzyl)morpholine (35): The title compound was prepared according to general procedure B. NMR yield of the unpurified reaction mixture was determined using dibromomethane as an NMR standard. Purification by column chromatography (4:1 hexanes/EtOAc) yields **35** as a white solid. Average over 2 runs: 56% NMR yield, 43% isolated yield.

m.p.: 91-94 °C. **IR (neat):** 2956 (m), 2856 (m), 1508 (s), 1245 (s), 1175 (m), 1115 (s), 1034 (s), 847 (m), 733 (s), 566 (m). **¹H NMR (400 MHz, CDCl₃):** δ 7.25 (d, *J* = 8.7 Hz, 2H), 7.10 – 7.02 (m, 4H), 6.97 – 6.92 (m, 2H), 6.86 – 6.81 (m, 2H), 6.58 – 6.53 (m, 2H), 3.93 (d, *J* = 11.2 Hz, 1H), 3.76 (s, 3H), 3.67 (t, *J* = 4.7 Hz, 4H), 3.62 (s, 3H), 3.45 (dq, *J* = 11.5, 6.8 Hz, 1H), 3.37 (s, 2H), 2.35 (t, *J* = 4.6 Hz, 4H), 1.16 (d, *J* = 6.8 Hz, 3H). **¹³C NMR (100 MHz, CDCl₃):** δ 158.0, 157.4, 145.2, 136.8, 136.7, 134.9, 129.2, 129.1, 127.6, 114.0, 113.4, 67.1, 63.3, 57.8, 55.3, 55.1, 53.7, 44.5, 22.1. **HRMS (ESI):** Calculated for C₂₈H₃₄O₃N [M+H]⁺: 432.2533, Found: 432.2531.



1-(1-(4-methoxyphenyl)-1-phenylpropan-2-yl)-3,5-dimethylbenzene (36): The title compound was prepared according to general procedure B. NMR yield of the unpurified reaction mixture was determined using dibromomethane as an NMR standard. Purification by column chromatography (80:1 hexanes/Et₂O) yields **36** as a colorless oil. Average over 2 runs: 94% NMR yield, 86% isolated yield, >20:1 dr.

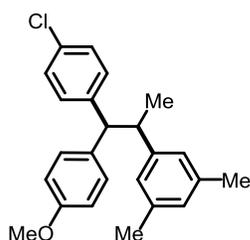
IR (neat): 2958 (m), 2875 (w), 1509 (m), 1243 (s), 1178 (m), 1037 (s), 936 (m), 733 (s), 699 (s), 569 (m). **¹H NMR (500 MHz, CDCl₃):** δ 7.33 – 7.28 (m, 2H), 7.15 – 7.12 (m, 2H), 7.11 – 7.07 (m, 2H), 7.00 – 6.96 (m, 1H), 6.89 – 6.85 (m, 2H), 6.77 (s, 2H), 6.71 (s, 1H), 4.03 (d, *J* = 11.3 Hz, 1H), 3.79 (s, 3H), 3.49 (dq, *J* = 11.2, 6.8 Hz, 1H), 2.22 (s, 6H), 1.19 (d, *J* = 6.9 Hz, 3H). **¹³C NMR (125 MHz, CDCl₃):** δ 158.1, 146.0, 144.5, 137.4, 136.8, 129.3, 128.3, 128.0, 127.5, 125.7, 125.6, 114.0, 58.4, 55.3, 44.3, 22.3, 21.4. **HRMS (ESI):** Calculated for C₂₄H₂₆ONa [M+Na]⁺: 353.1876, Found: 353.1874.



1,3-dimethyl-5-(1-phenyl-1-(4-(trifluoromethyl)phenyl)propan-2-yl)benzene (37):

The title compound was prepared according to general procedure B. NMR yield of the unpurified reaction mixture was determined using dibromomethane as an NMR standard. Purification by column chromatography (80:1 hexanes/Et₂O) yields **37** as a white solid
Average over 2 runs: 63% NMR yield, 56% isolated yield, >20:1 dr.

m.p.: 82-84 °C. **IR (neat):** 3025 (m), 2960 (m), 2923 (m), 2854 (m), 1600 (m), 1322 (s), 1158 (m), 1107 (s), 1065 (s), 734 (m), 697 (s). **¹H NMR (400 MHz, CDCl₃):** δ 7.42 – 7.37 (m, 2H), 7.37 – 7.30 (m, 4H), 7.27 – 7.18 (m, 3H), 6.76 (s, 2H), 6.73 (s, 1H), 4.14 (d, *J* = 11.4 Hz, 1H), 3.53 (dq, *J* = 11.4, 6.8 Hz, 1H), 2.22 (s, 6H), 1.21 (d, *J* = 6.8 Hz, 3H). **¹³C NMR (100 MHz, CDCl₃):** δ 148.3 (d, *J* = 1.5 Hz), 145.3, 143.5, 137.7, 128.9, 128.6, 128.4, 128.0 (q, *J* = 33.0 Hz), 127.9, 126.7, 125.0 (q, *J* = 3.8 Hz), 124.3 (q, *J* = 270.2 Hz), 59.2, 44.2, 22.2, 21.4. **¹⁹F NMR (376 MHz, CDCl₃):** δ – 62.3. **HRMS (APCI):** Calculated for C₂₄H₂₈F₃ [M+NH₄]⁺: 386.2090, Found: 386.2088. X-ray crystal structure is available (see attached spectrum).

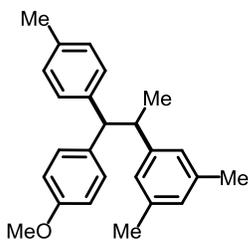


1-(1-(4-chlorophenyl)-1-(4-methoxyphenyl)propan-2-yl)-3,5-dimethylbenzene (38):

The title compound was prepared according to general procedure B. NMR yield of the unpurified reaction mixture was determined using dibromomethane as an NMR standard. Purification by column chromatography (50:1 hexanes/Et₂O) yields **38** as a colorless oil
Average over 2 runs: 71% NMR yield, 61% isolated yield, >20:1 dr.

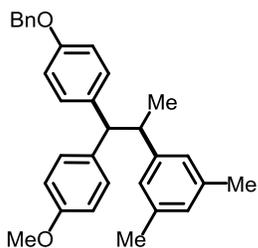
IR (neat): 2956 (m), 2916 (s), 2870 (w), 1606 (m), 1509 (s), 1247 (s), 1176 (m), 1090 (m), 1034 (s), 804 (s), 732 (s), 563 (m). **¹H NMR (400 MHz, CDCl₃):** δ 7.27 – 7.23 (m, 2H), 7.14 – 6.99 (m, 4H), 6.88 – 6.83 (m, 2H), 6.76 – 6.69 (m, 3H), 3.99 (d, *J* = 11.3 Hz, 1H), 3.79 (s, 3H), 3.40 (dq, *J* = 11.2, 6.8 Hz, 1H), 2.21 (s, 6H), 1.15 (d, *J* = 6.8 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 158.2, 145.6, 143.1, 137.6, 136.2, 131.2, 129.6, 129.2, 128.2, 127.7, 125.5, 114.1, 57.7, 55.4, 44.4, 22.4, 21.5. **HRMS (APCI):** Calculated for C₂₄H₂₉ONCl [M+NH₄]⁺: 382.1932, Found: 382.1933.



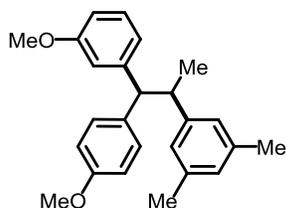
1-(1-(4-methoxyphenyl)-1-(p-tolyl)propan-2-yl)-3,5-dimethylbenzene (39): The title compound was prepared according to general procedure B. NMR yield of the unpurified reaction mixture was determined using dibromomethane as an NMR standard. Purification by column chromatography (60:1 hexanes/Et₂O) yields **39** as a colorless oil. Average over 2 runs: 92% NMR yield, 84% isolated yield, >20:1 dr.

IR (neat): 3011 (m), 2957 (m), 2918 (m), 2868 (m), 1606 (m), 1508 (s), 1246 (s), 1176 (m), 1034 (m), 805 (s), 703 (m). **¹H NMR (400 MHz, CDCl₃):** δ 7.26 (d, *J* = 8.2 Hz, 2H), 7.01 (d, *J* = 7.7 Hz, 2H), 6.88 (d, *J* = 7.8 Hz, 2H), 6.84 (d, *J* = 8.3 Hz, 2H), 6.76 (s, 2H), 6.70 (s, 1H), 4.00 (d, *J* = 11.2 Hz, 1H), 3.77 (s, 3H), 3.45 (dq, *J* = 11.2, 6.8 Hz, 1H), 2.21 (s, 6H), 2.16 (s, 3H), 1.14 (d, *J* = 6.8 Hz, 3H). **¹³C NMR (100 MHz, CDCl₃):** δ 158.0, 146.2, 141.5, 137.3, 137.1, 134.9, 129.2, 128.8, 128.1, 127.5, 125.6, 114.0, 57.8, 55.3, 44.2, 22.5, 21.5, 21.0. **HRMS (ESI):** Calculated for C₂₅H₂₈ONa [M+Na]⁺: 367.2032, Found: 367.2031.



1-(1-(4-(benzyloxy)phenyl)-1-(4-methoxyphenyl)propan-2-yl)-3,5-dimethylbenzene (40): The title compound was prepared according to general procedure B. NMR yield of the unpurified reaction mixture was determined using dibromomethane as an NMR standard. Purification by column chromatography (30:1 hexanes/Et₂O) yields **40** as a colorless oil. Average over 2 runs: 91% NMR yield, 80% isolated yield, >20:1 dr.

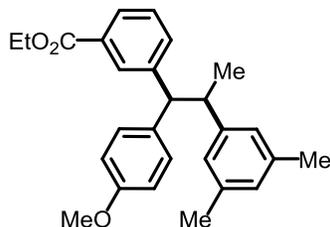
IR (neat): 2958 (m), 2908 (m), 2870 (m), 1605 (m), 1507 (s), 1244 (s), 1175 (m), 1034 (m), 732 (s), 698 (m). **¹H NMR (400 MHz, CDCl₃):** δ 7.47 – 7.35 (m, 4H), 7.35 – 7.24 (m, 3H), 7.09 – 7.00 (m, 2H), 6.91 – 6.83 (m, 2H), 6.77 (s, 2H), 6.75 – 6.70 (m, 3H), 4.92 (s, 2H), 4.00 (d, *J* = 11.2 Hz, 1H), 3.80 (s, 3H), 3.44 (dq, *J* = 11.1, 6.8 Hz, 1H), 2.24 (s, 6H), 1.17 (d, *J* = 6.8 Hz, 3H). **¹³C NMR (100 MHz, CDCl₃):** δ 158.0, 156.7, 146.2, 137.4, 137.1, 129.2, 129.1, 128.6, 127.9, 127.6, 127.5, 125.7, 114.4, 114.0, 70.0, 57.4, 55.3, 44.5, 22.4, 21.5. **HRMS (ESI):** Calculated for C₃₁H₃₂O₂Na [M+Na]⁺: 459.2295, Found: 459.2296.



1-(1-(3-methoxyphenyl)-1-(4-methoxyphenyl)propan-2-yl)-3,5-dimethylbenzene (41):

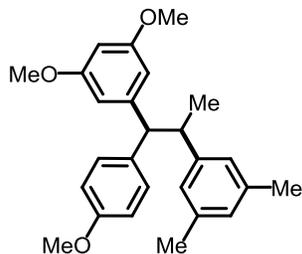
The title compound was prepared according to general procedure B. NMR yield of the unpurified reaction mixture was determined using dibromomethane as an NMR standard. Purification by column chromatography (20:1 hexanes/Et₂O) yields **41** as a colorless oil. Average over 2 runs: 91% NMR yield, 77% isolated yield, >20:1 dr.

IR (neat): 3000 (m), 2956 (m), 2833 (m), 1604 (m), 1509 (s), 1452 (m), 1247 (s), 1177 (m), 1034 (s), 828 (m), 694 (s), 524 (m). **¹H NMR (400 MHz, CDCl₃):** δ 7.37 – 7.32 (m, 2H), 7.05 (t, *J* = 7.9 Hz, 1H), 6.93 – 6.88 (m, 2H), 6.83 (s, 2H), 6.80 (dt, *J* = 7.7, 1.2 Hz, 1H), 6.77 – 6.72 (m, 2H), 6.59 – 6.54 (m, 1H), 4.06 (d, *J* = 11.3 Hz, 1H), 3.81 (s, 3H), 3.69 (s, 3H), 3.51 (dq, *J* = 11.2, 6.8 Hz, 1H), 2.27 (s, 6H), 1.22 (d, *J* = 6.8 Hz, 3H). **¹³C NMR (100 MHz, CDCl₃):** δ 159.2, 158.1, 146.1, 146.0, 137.4, 136.6, 129.3, 128.9, 127.5, 125.6, 120.8, 114.4, 114.0, 110.8, 58.2, 55.3, 55.1, 44.3, 22.4, 21.4. **HRMS (ESI):** Calculated for C₂₅H₂₈O₂Na [M+Na]⁺: 383.1982, Found: 383.1982.



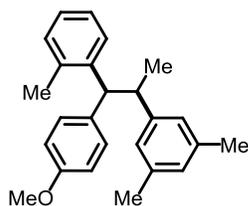
Ethyl 3-(2-(3,5-dimethylphenyl)-1-(4-methoxyphenyl)propyl)benzoate (42): The title compound was prepared according to general procedure B. NMR yield of the unpurified reaction mixture was determined using dibromomethane as an NMR standard. Purification by column chromatography (10:1 hexanes/Et₂O) yields **42** as a colorless oil. Average over 2 runs: 88% NMR yield, 79% isolated yield, >20:1 dr.

IR (neat): 2959 (m), 2912 (m), 2871 (w), 1713 (s), 1605 (m), 1509 (s), 1278 (s), 1247 (s), 1178 (s), 1105 (m), 1031 (m), 842 (m), 746 (s), 795 (m), 597 (m). **¹H NMR (400 MHz, CDCl₃):** δ 7.89 (s, 1H), 7.70 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.38 – 7.30 (m, 3H), 7.16 (t, *J* = 7.7 Hz, 1H), 6.92 – 6.86 (m, 2H), 6.81 (s, 2H), 6.71 (s, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 4.13 (d, *J* = 11.4 Hz, 1H), 3.79 (s, 3H), 3.53 (dq, *J* = 11.4, 6.8 Hz, 1H), 2.23 (s, 6H), 1.38 (t, *J* = 7.1 Hz, 3H), 1.22 (d, *J* = 6.8 Hz, 3H). **¹³C NMR (100 MHz, CDCl₃):** δ 166.8, 158.2, 145.6, 144.8, 137.5, 136.1, 132.7, 130.1, 129.5, 129.2, 128.0, 127.6, 126.9, 125.6, 114.1, 60.8, 58.1, 55.3, 44.3, 22.3, 21.4, 14.4. **HRMS (ESI):** Calculated for C₂₇H₃₀O₃Na [M+Na]⁺: 425.2087, Found: 425.2090.



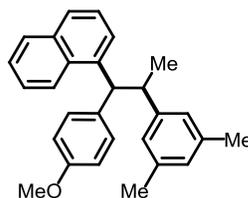
1-(1-(3,5-dimethoxyphenyl)-1-(4-methoxyphenyl)propan-2-yl)-3,5-dimethylbenzene (43): The title compound was prepared according to general procedure B. NMR yield of the unpurified reaction mixture was determined using dibromomethane as an NMR standard. Purification by column chromatography (10:1 hexanes/Et₂O) yields **43** as a white solid. Average over 2 runs: 91% NMR yield, 77% isolated yield, >20:1 dr.

IR (neat): 2999 (m), 2956 (m), 2834 (m), 1593 (s), 1509 (s), 1457 (m), 1247 (s), 1202 (s), 1152 (s), 1059 (m), 826 (s), 731 (m), 689 (m), 539 (m). **¹H NMR (400 MHz, CDCl₃):** δ 7.38 – 7.32 (m, 2H), 6.94 – 6.89 (m, 2H), 6.86 (s, 2H), 6.77 (s, 1H), 6.37 (s, 2H), 6.15 (s, 1H), 4.03 (d, *J* = 11.2 Hz, 1H), 3.81 (s, 3H), 3.68 (s, 6H), 3.48 (dq, *J* = 11.2, 7.0 Hz, 1H), 2.28 (s, 6H), 1.21 (d, *J* = 6.7 Hz, 3H). **¹³C NMR (100 MHz, CDCl₃):** δ 160.2, 158.1, 146.8, 146.0, 137.4, 136.4, 129.2, 127.6, 125.6, 114.0, 106.8, 97.5, 58.3, 55.2, 55.1, 44.3, 22.4, 21.4. **HRMS (ESI):** Calculated for C₂₆H₃₀O₃Na [M+Na]⁺: 413.2090, Found: 413.2089.



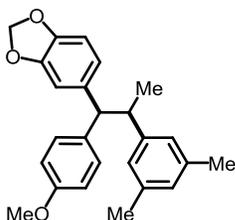
1-(1-(4-methoxyphenyl)-1-(o-tolyl)propan-2-yl)-3,5-dimethylbenzene (44): The title compound was prepared according to general procedure B. NMR yield of the unpurified reaction mixture was determined using dibromomethane as an NMR standard. Purification by column chromatography (60:1 hexanes/Et₂O) yields **44** as a colorless oil. Average over 2 runs: 82% NMR yield, 69% isolated yield, >20:1 dr.

IR (neat): 3014 (m), 2959 (m), 2871 (m), 1606 (m), 1509 (s), 1264 (s), 1177 (m), 1034 (m), 846 (m), 733 (s), 703 (m), 567 (m). **¹H NMR (400 MHz, CDCl₃):** δ 7.42 (d, *J* = 7.8 Hz, 1H), 7.28 – 7.22 (m, 2H), 7.06 – 7.00 (m, 1H), 6.90 – 6.86 (m, 2H), 6.84 – 6.79 (m, 2H), 6.75 (s, 2H), 6.66 (s, 1H), 4.25 (d, *J* = 11.2 Hz, 1H), 3.76 (s, 3H), 3.46 (dq, *J* = 11.2, 6.8 Hz, 1H), 2.19 (s, 3H), 2.18 (s, 6H), 1.12 (d, *J* = 6.8 Hz, 3H). **¹³C NMR (100 MHz, CDCl₃):** δ 157.9, 146.3, 142.4, 137.4, 135.9, 135.8, 130.2, 129.8, 127.5, 127.1, 125.7, 125.5, 125.4, 113.8, 55.3, 52.6, 44.5, 22.9, 21.5, 20.2. **HRMS (ESI):** Calculated for C₂₅H₂₈ONa [M+Na]⁺: 367.2032, Found: 367.2031.



1-(2-(3,5-dimethylphenyl)-1-(4-methoxyphenyl)propyl)naphthalene (45): The title compound was prepared according to general procedure B. NMR yield of the unpurified reaction mixture was determined using dibromomethane as an NMR standard. Purification by column chromatography (20:1 hexanes/Et₂O) yields **45** as a white solid. Average over 2 runs: 81% NMR yield, 68% isolated yield, >20:1 dr.

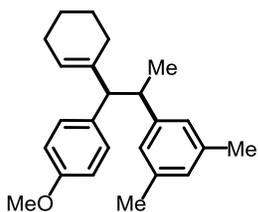
m.p.: 109-111 °C. **IR (neat):** 2960 (m), 2922 (m), 2899 (w), 1599 (m), 1510 (s), 1250 (s), 1165 (m), 1034 (s), 844 (m), 781 (s), 702 (m), 549 (m). **¹H NMR (400 MHz, CDCl₃):** δ 8.27 (d, *J* = 8.5 Hz, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.66 (d, *J* = 7.3 Hz, 1H), 7.57 (d, *J* = 8.2 Hz, 1H), 7.48 – 7.43 (m, 1H), 7.41 – 7.33 (m, 4H), 6.87 – 6.81 (m, 4H), 6.66 – 6.61 (m, 1H), 5.00 (d, *J* = 11.0 Hz, 1H), 3.75 (s, 3H), 3.68 (dq, *J* = 11.0 Hz, 6.8 Hz, 1H), 2.16 (s, 6H), 1.25 (d, *J* = 6.8 Hz, 3H). **¹³C NMR (100 MHz, CDCl₃):** δ 158.0, 146.5, 139.8, 137.5, 136.3, 134.0, 132.1, 129.7, 128.8, 127.5, 126.5, 125.6, 125.3, 125.0, 124.9, 123.6, 113.8, 55.3, 51.2, 44.6, 23.5, 21.4. **HRMS (ESI):** Calculated for C₂₈H₂₈O₂Na [M+Na]⁺: 403.2032, Found:403.2033.



5-(2-(3,5-dimethylphenyl)-1-(4-methoxyphenyl)propyl)benzo[d][1,3]dioxole (46):

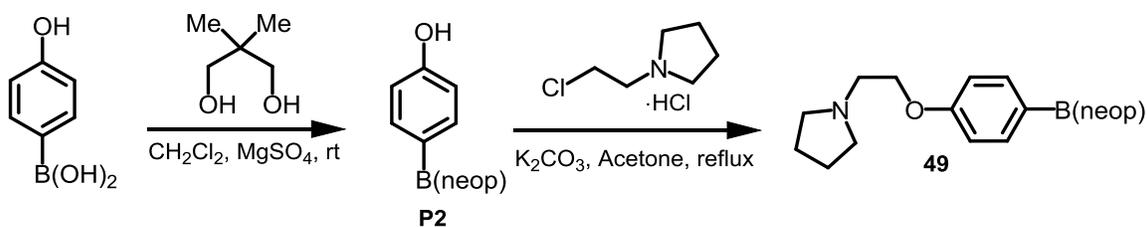
The title compound was prepared according to general procedure B. NMR yield of the unpurified reaction mixture was determined using dibromomethane as an NMR standard. Purification by column chromatography (10:1 hexanes/Et₂O) yields **46** as a white solid. Average over 2 runs: 87% NMR yield, 80% isolated yield, >20:1 dr.

m.p.: 89-91 °C. **IR (neat):** 2959 (m), 2914 (m), 2872 (m), 1607 (m), 1509 (m), 1246 (s), 1036 (s), 842 (m), 733(s). **¹H NMR (400 MHz, CDCl₃):** δ 7.33 – 7.27 (m, 2H), 6.92 – 6.86 (m, 2H), 6.82 (d, *J* = 1.8 Hz, 2H), 6.76 (d, *J* = 1.8 Hz, 1H), 6.70 (d, *J* = 1.7 Hz, 1H), 6.62 (dd, *J* = 8.0, 1.7 Hz, 1H), 6.56 (d, *J* = 8.0 Hz, 1H), 5.79 (s, 2H), 4.00 (d, *J* = 11.4 Hz, 1H), 3.81 (s, 3H), 3.44 (dq, *J* = 11.2, 6.8 Hz, 1H), 2.27 (s, 6H), 1.18 (d, *J* = 6.8 Hz, 3H). **¹³C NMR (100 MHz, CDCl₃):** δ 158.1, 147.3, 146.0, 145.3, 138.7, 137.4, 136.9, 129.1, 127.6, 125.6, 121.2, 114.0, 108.6, 107.9, 100.6, 57.8, 55.3, 44.4, 22.6, 21.5. **HRMS (ESI):** Calculated for C₂₅H₂₆O₃Na [M+Na]⁺: 397.1774, Found: 397.1773.



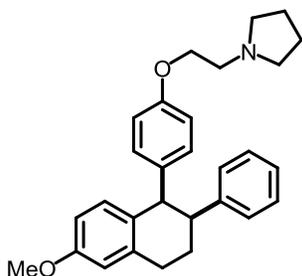
1-(1-(cyclohex-1-en-1-yl)-1-(4-methoxyphenyl)propan-2-yl)-3,5-dimethylbenzene (47): The title compound was prepared according to general procedure B. NMR yield of the unpurified reaction mixture was determined using dibromomethane as an NMR standard. Purification by column chromatography (100:1 hexanes/Et₂O) yields **47** as a colorless oil. Average over 2 runs: 80% NMR yield, 67% isolated yield, >20:1 dr.

IR (neat): 2952 (s), 2855 (m), 2833 (m), 1606 (m), 1509 (s), 1245 (s), 1176 (m), 1036 (m), 844 (s), 732 (m). **¹H NMR (400 MHz, CDCl₃):** δ 7.20 (d, *J* = 8.3 Hz, 2H), 6.86 (d, *J* = 8.3 Hz, 2H), 6.83 – 6.79 (m, 3H), 5.39 – 5.34 (m, 1H), 3.82 (s, 3H), 3.27 – 3.15 (m, 2H), 2.31 (s, 6H), 1.90 – 1.68 (m, 3H), 1.67 – 1.57 (m, 1H), 1.45 – 1.34 (m, 1H), 1.34 – 1.22 (m, 3H), 1.02 (d, *J* = 5.8 Hz, 3H). **¹³C NMR (100 MHz, CDCl₃):** δ 158.0, 146.9, 139.1, 137.2, 135.7, 129.4, 127.3, 125.5, 122.8, 113.6, 60.3, 55.3, 41.9, 26.9, 25.4, 23.0, 22.5, 21.8, 21.5. **HRMS (ESI):** Calculated for C₂₄H₃₀ONa [M+Na]⁺: 357.2189, Found: 357.2187.



1-(2-(4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)phenoxy)ethyl)pyrrolidine (49): In a oven dried 150 mL round bottom flask containing a magnetic stirbar, 4-hydroxyphenylboronic acid (2.57 g, 18.6 mmol), 2,2-Dimethyl-1,3-propanediol (2.04 g, 19.6 mmol, 1.10 equiv.) and MgSO₄ (4.0 g) were suspended in CH₂Cl₂ (80 mL) and stirred overnight at room temperature. The reaction mixture was filtered through a 3 cm x 3 cm pad of silica gel, washed with hexane/CH₂Cl₂ (1:2, 120 mL), and dried under vacuum, affording **P2** as a yellowish-brown solid, which was used directly for next step without further purification. To the stirred solution of compound **P2** (3.00 g, 14.6 mmol) in dry acetone (100 ml), anhydrous K₂CO₃ (6.04 g, 43.7 mmol, 3.00 equiv.) and 1-(2-Chloroethyl)pyrrolidine hydrochloride (3.22 g, 18.9 mmol, 1.30 equiv.) were added. The reaction mixture was refluxed for 24h and then cooled to room temperature. The mixture was filtered through a 3 cm x 3 cm pad of celite and washed with EtOAc (100 mL). The solvent was removed under rotovap and water (60 ml) was added to the residue. The aqueous solution was extracted with EtOAc (3 x 30 ml) and the combined organic layers were dried over Na₂SO₄, gravity filtered, and concentrated. The crude product was purified by flash chromatography on a basic aluminum oxide column (50:1 CH₂Cl₂/MeOH) to give a white solid [*Note:* silica gel column result in significant decomposition of the boronic ester, therefore the column must be completed rapidly]. The product was further purified by recrystallization from diethyl ether to afford a white crystalline solid **49** (3.12 g, 68%).

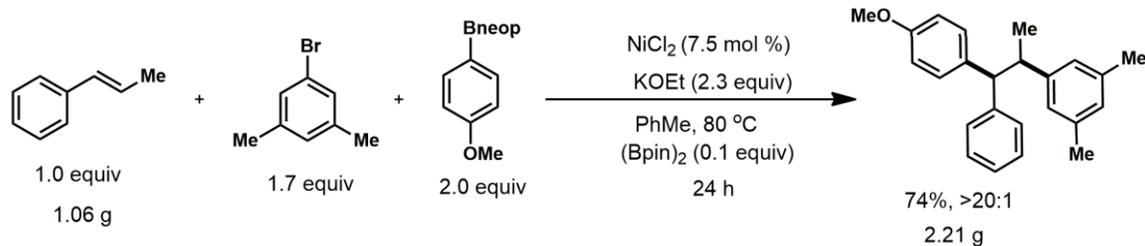
m.p.: 62-64 °C. **IR (neat):** 2960 (m), 2877 (m), 1602 (m), 1317 (s), 1242 (s), 1134 (m). **¹H NMR (400 MHz, CDCl₃):** δ 7.75 – 7.70 (m, 2H), 6.94 – 6.87 (m, 2H), 4.13 (t, *J* = 6.1 Hz, 2H), 3.75 (s, 4H), 2.90 (t, *J* = 6.1 Hz, 2H), 2.65 – 2.58 (m, 4H), 1.84 – 1.76 (m, 4H), 1.01 (s, 6H). **¹³C NMR (100 MHz, CDCl₃):** δ 161.2, 135.6, 114.0, 72.4, 67.0, 55.2, 54.9, 32.1, 23.7, 22.1 (The signal of carbon directly bonded to boron was not detected because of quadrupolar relaxation). **HRMS (ESI):** Calculated for C₁₇H₂₇O₃BN [M+H]⁺: 304.2079, Found: 304.2077.



1-(4-[2-Pyrrolidinoethoxy]phenyl)-2-phenyl-(6-methoxy-1,2,3,4-tetrahydronaphthalene (52) In an N₂-filled glovebox, to a 16 x 100 mm screw-capped vial containing a magnetic stirbar was added NiCl₂ (4.9 mg, 0.025 mmol, 7.5 mol %), bis(pinacolato)diboron (12.7 mg, 0.0500 mmol, 0.100 equiv.), KOEt (96.6 mg, 1.15 mmol, 2.30 equiv.), and **49** (303 mg, 1.00 mmol, 2.00 equiv.). In a separate oven dried 10.0 mL vial under N₂, 7-methoxy-1,2-dihydronaphthalene **50** (91 μL, 0.60 mmol, 1.2 equiv.) and bromobenzene **51** (107 μL, 1.00 mmol, 2.00 equiv.) were dissolved in toluene to a final volume of 3.0 mL. 2.5 mL of the toluene solution (0.2 M in alkene, 0.50 mmol, 1.00 equiv., and 0.34 M in aryl bromide, 0.85 mmol, 1.7 equiv.) was added to the reaction vial containing Ni catalyst via syringe under an N₂ atmosphere. The septum was quickly replaced by a Teflon-lined screw cap and the reaction was stirred at 80 °C for 24 h in a preheated aluminum block. The reaction was quenched upon the addition of water (2.0 mL), and the mixture was extracted with EtOAc (3 x 3.0 mL), dried over MgSO₄, gravity filtered, and concentrated. Dibromomethane was added as an internal standard and a small aliquot ¹H-NMR indicated 41% yield. The residue was purified by silica gel flash chromatography (1:80→1:40 MeOH/CH₂Cl₂) to give **52** (77.1 mg, 36%, >20:1 dr.) as a colorless oil. All characterization data are in agreement with previous literature.¹¹ (*Note:* When the CDCl₃ peak on ¹³C NMR was referenced to 77.00 ppm, the data is consistent with literature values (which was referenced to 77.00 ppm). The ¹³C NMR data and spectrum were provided here, in which the CDCl₃ peak was set to 77.16 ppm in order to keep it uniform).

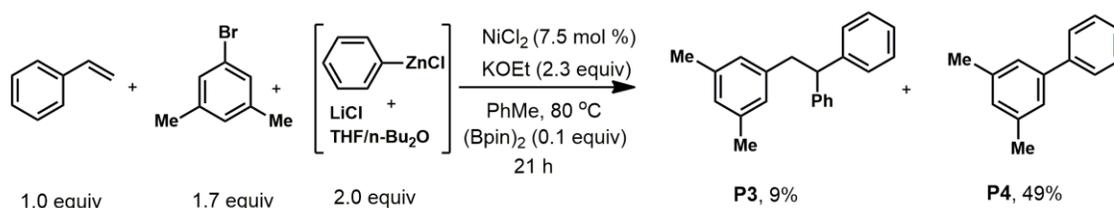
¹H NMR (500 MHz, CDCl₃) δ 7.20 – 7.12 (m, 3H), 6.88 (d, *J* = 8.5 Hz, 1H), 6.83 – 6.75 (m, 3H), 6.69 (dd, *J* = 8.4, 2.7 Hz, 1H), 6.55 (d, *J* = 8.7 Hz, 2H), 6.32 (d, *J* = 8.7 Hz, 2H), 4.25 (d, *J* = 5.0 Hz, 1H), 4.04 – 3.96 (m, 2H), 3.82 (s, 3H), 3.41– 3.32 (m, 1H), 3.14 – 3.00 (m, 2H), 2.85 (t, *J* = 6.2 Hz, 2H), 2.68 – 2.56 (m, 4H), 2.26 – 2.13 (m, 1H), 1.88 – 1.74 (m, 5H). ¹³C NMR (125 MHz, CDCl₃) δ 158.0, 157.1, 144.4, 137.8, 134.8, 132.4, 131.6, 131.4, 128.3, 127.8, 126.1, 113.10, 113.05, 112.7, 67.0, 55.3, 55.2, 54.8, 50.3, 45.6, 30.3, 23.6, 22.1.

■ Gram-Scale Reaction:



In an N₂-filled glovebox, to a flame-dried 100 mL round bottom flask containing a magnetic stirbar was added NiCl₂ (87.8 mg, 0.675 mmol, 7.50 mol %), bis(pinacolato)diboron, (229 mg, 0.900 mmol, 0.100 equiv.), KOEt (1.74 g, 20.7 mmol, 2.30 equiv), and 2-(4-Methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (3.96 g, 18.0 mmol, 2.00 equiv). The flask was sealed with a rubber septum and removed from the glovebox. Toluene (40 mL), *trans*- β -methylstyrene (1.17 mL, 9.00 mmol, 1.00 equiv) and 3,5-dimethylbromobenzene (2.10 mL, 15.3 mmol, 1.70 equiv) were added simultaneously via syringes under an N₂ atmosphere. The reaction was stirred at 80 °C for 24 hours in an oil bath. The reaction was quenched upon the addition of 2 M HCl (50 mL), and the mixture was extracted with EtOAc (3 x 150 mL), dried over MgSO₄, gravity filtered, and concentrated. Purification by silica gel column chromatography (200:1 hexanes/Et₂O) yields **17** as a white solid. (74% isolated yield, 2.21 g).

■ 1,2-Diarylation with arylzinc reagent.

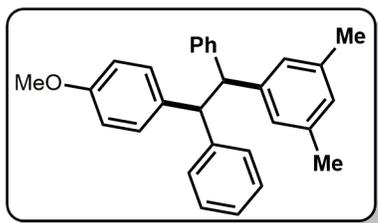


Procedure for the organozinc reagent: In a glovebox, ZnCl₂ (429 mg, 3.15 mmol) was weighed to a pre-dried 2-dram vial containing a magnetic stirbar. The vial was sealed with a rubber septum and removed from the glovebox. THF (4.3 mL) was added in the N₂ atmosphere and stirred for 10 min. PhLi in *n*-Bu₂O (1.75 M/L, 3.00 mmol, 1.70 mL) was then added dropwise at room temperature. After stirring for 2 h, titration of an aliquot (0.50 mL) of the organozinc reagent with iodine¹² showed that the concentration of arylzinc in THF/Bu₂O was 0.50 M/L.

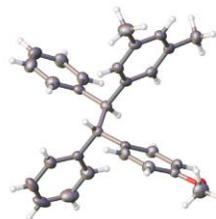
Procedure for the nickel-catalyzed reaction: In an N₂-filled glovebox, to a 16 x 100 mm screw-capped vial containing a magnetic stirbar was added NiCl₂ (2.0 mg, 0.015 mmol, 7.5 mol %), bis(pinacolato)diboron (5.1 mg, 0.020 mmol, 10 mol %), KOEt (38.6 mg, 0.460 mmol, 2.30 equiv). The vial was sealed with a rubber septum and removed from the glovebox. In a separate vial, styrene (35 μ L, 0.30 mmol, 1.5 equiv) and 3,5-dimethylbromobenzene (69 μ L, 0.51 mmol, 2.6 equiv) were dissolved in toluene to a final volume of 1.5 mL. 1.0 mL of the toluene solution (0.20 M in styrene, 0.20 mmol, 1.0 equiv, and 0.34 M in aryl bromide, 0.34 mmol, 1.7 equiv.) was added to the reaction vial containing Ni catalyst via syringe under an N₂ atmosphere. Arylzinc reagent (0.5M/L, 0.8 mL, 2.0 equiv) was then added immediately. The septum was quickly replaced by a Teflon-lined screw cap and the reaction was stirred at 80 °C for 21 h in a preheated aluminum block. The reaction was quenched upon the addition of 2 M HCl (2 mL), and the mixture was extracted with EtOAc (3 x 3 mL). dried over MgSO₄, gravity filtered, and concentrated for the further analysis.

The GC-MS and ¹H NMR analysis of the mixture show only 9% of diarylation product **P3** was formed, the major products were the cross-coupling product **P4** along with 30% of homo-coupling product; additionally, 21% of heck-reaction product was also detected.

■ Crystal of 21, 22 and 37:



21



Datablock: 18045

Bond precision: C-C = 0.0028 Å

Wavelength=0.71073

Cell: a=11.1132 (5)
alpha=90

b=16.9436 (8)
beta=104.743 (2)

c=12.0212 (6)
gamma=90

Temperature: 173 K

	Calculated	Reported
Volume	2189.04 (18)	2189.04 (18)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C ₂₉ H ₂₈ O	C ₂₉ H ₂₈ O
Sum formula	C ₂₉ H ₂₈ O	C ₂₉ H ₂₈ O
Mr	392.51	392.51
Dx, g cm ⁻³	1.191	1.191
Z	4	4
Mu (mm ⁻¹)	0.070	0.070
F000	840.0	840.0
F000'	840.32	
h, k, lmax	14, 22, 15	14, 22, 15
Nref	5060	5047
Tmin, Tmax	0.978, 0.979	0.531, 0.746
Tmin'	0.978	

Correction method= # Reported T Limits: Tmin=0.531 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.997

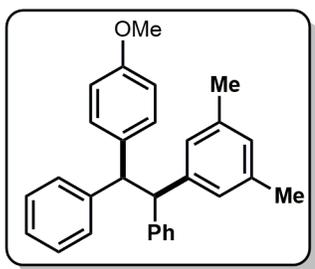
Theta(max)= 27.552

R(reflections)= 0.0596 (4108)

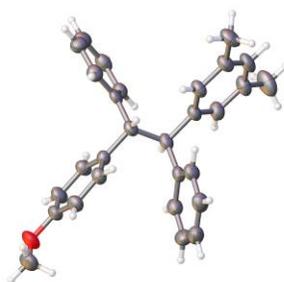
wR2(reflections)= 0.1549 (5047)

S = 1.036

Npar= 274



22



Datablock: 18052

Bond precision: C-C = 0.0035 Å

Wavelength=0.71073

Cell: a=9.2426 (13)

b=11.0042 (15)

c=22.027 (3)

alpha=90

beta=90.723 (9)

gamma=90

Temperature: 173 K

	Calculated	Reported
Volume	2240.1 (5)	2240.1 (5)
Space group	P 21/n	P 21/n
Hall group	-P 2yn	-P 2yn
Moiety formula	C29 H28 O	C29 H28 O
Sum formula	C29 H28 O	C29 H28 O
Mr	392.51	392.51
Dx, g cm ⁻³	1.164	1.164
Z	4	4
Mu (mm ⁻¹)	0.068	0.068
F000	840.0	840.0
F000'	840.32	
h, k, lmax	11, 13, 27	11, 13, 26
Nref	4444	4170
Tmin, Tmax	0.980, 0.983	0.574, 0.745
Tmin'	0.980	

Correction method= # Reported T Limits: Tmin=0.574 Tmax=0.745

AbsCorr = MULTI-SCAN

Data completeness= 0.938

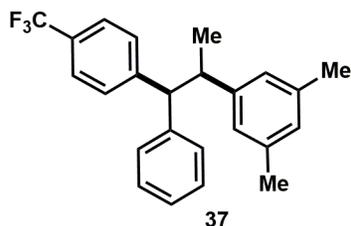
Theta(max)= 26.072

R(reflections)= 0.0576 (2448)

wR2(reflections)= 0.1721 (4170)

S = 1.012

Npar= 274



Datablock: 18034

Bond precision:	C-C = 0.0042 Å	Wavelength=0.71073	
Cell:	a=18.8921 (14)	b=14.4381 (7)	c=14.5290 (11)
	alpha=90	beta=97.589 (2)	gamma=90
Temperature:	173 K		

	Calculated	Reported
Volume	3928.3 (5)	3928.3 (5)
Space group	C 2/c	C 2/c
Hall group	-C 2yc	-C 2yc
Moiety formula	C ₂₄ H ₂₃ F ₃	C ₂₄ H ₂₃ F ₃
Sum formula	C ₂₄ H ₂₃ F ₃	C ₂₄ H ₂₃ F ₃
Mr	368.42	368.42
Dx, g cm ⁻³	1.246	1.246
Z	8	8
Mu (mm ⁻¹)	0.091	0.091
F ₀₀₀	1552.0	1552.0
F ₀₀₀ '	1552.86	
h, k, lmax	22, 17, 17	22, 17, 17
Nref	3488	3481
Tmin, Tmax	0.989, 0.997	0.624, 0.745
Tmin'	0.989	

Correction method= # Reported T Limits: Tmin=0.624 Tmax=0.745
AbsCorr = MULTI-SCAN

Data completeness= 0.998	Theta(max)= 25.052
R(reflections)= 0.0580 (1885)	wR2(reflections)= 0.1502 (3481)
S = 1.019	Npar= 257

¹ Roberts, J. C., Pincock, J. A. *J. Org. Chem.* **2006**, *71*, 1480-1492.

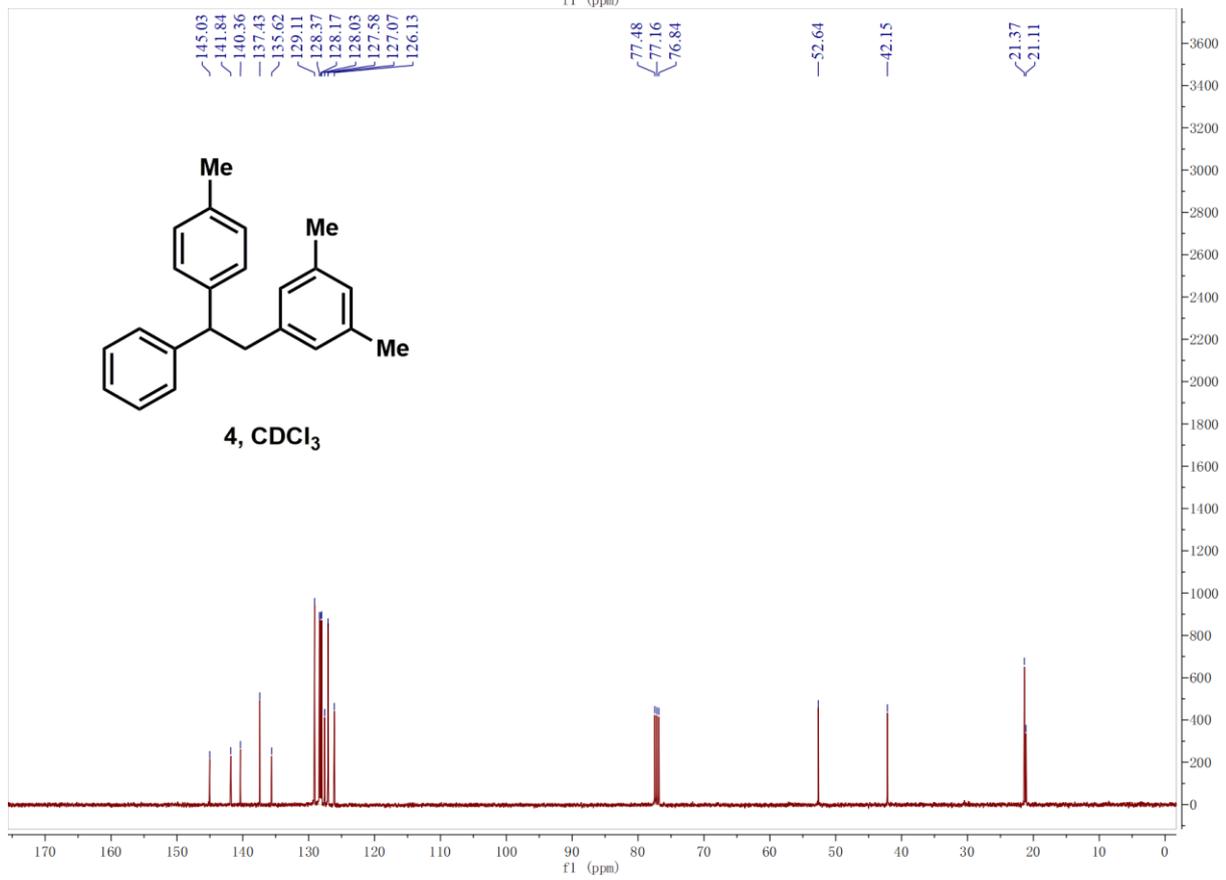
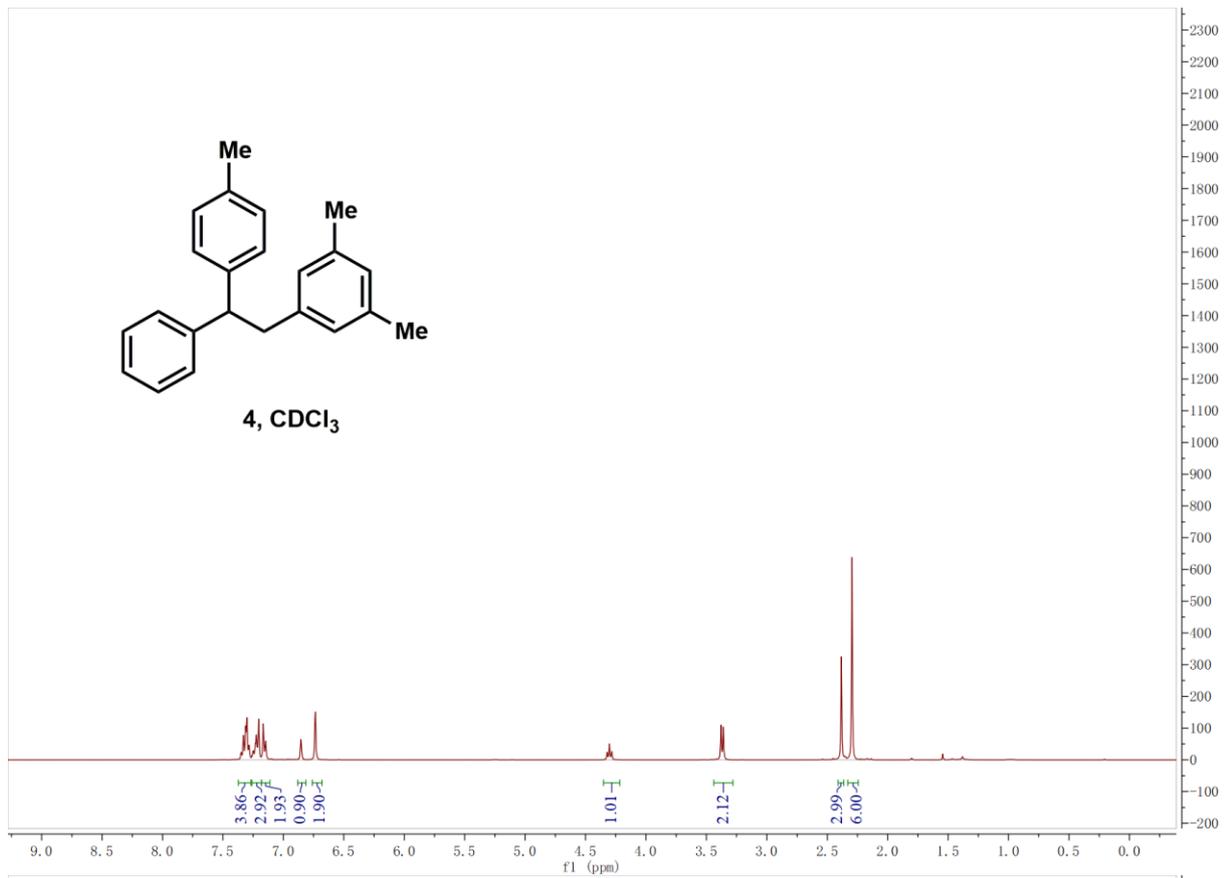
² Zhang, L., Gao, F., Yang, C., Gao, G.-L., Zhao, Y., Gao, Y., Xia, W. *Org. Lett.* **2017**, *19*, 5086-5089.

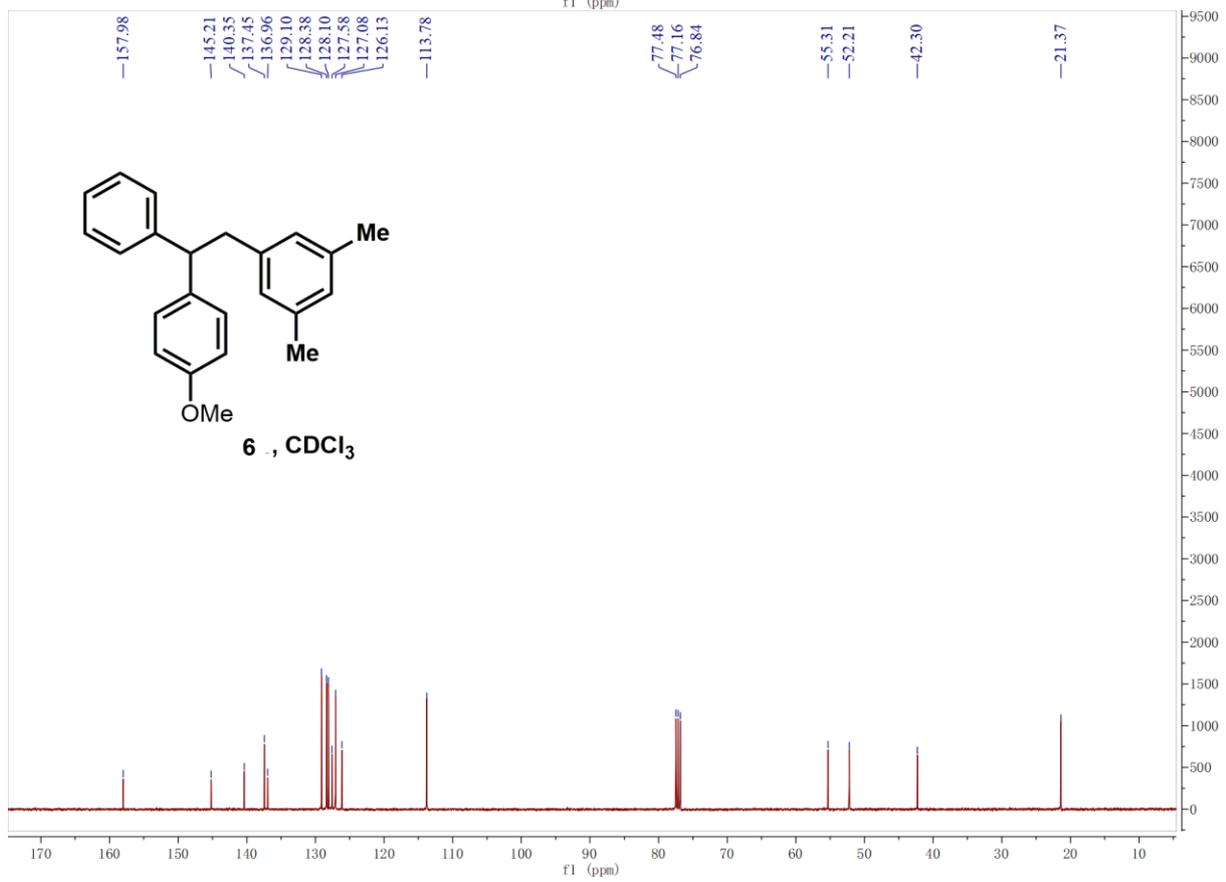
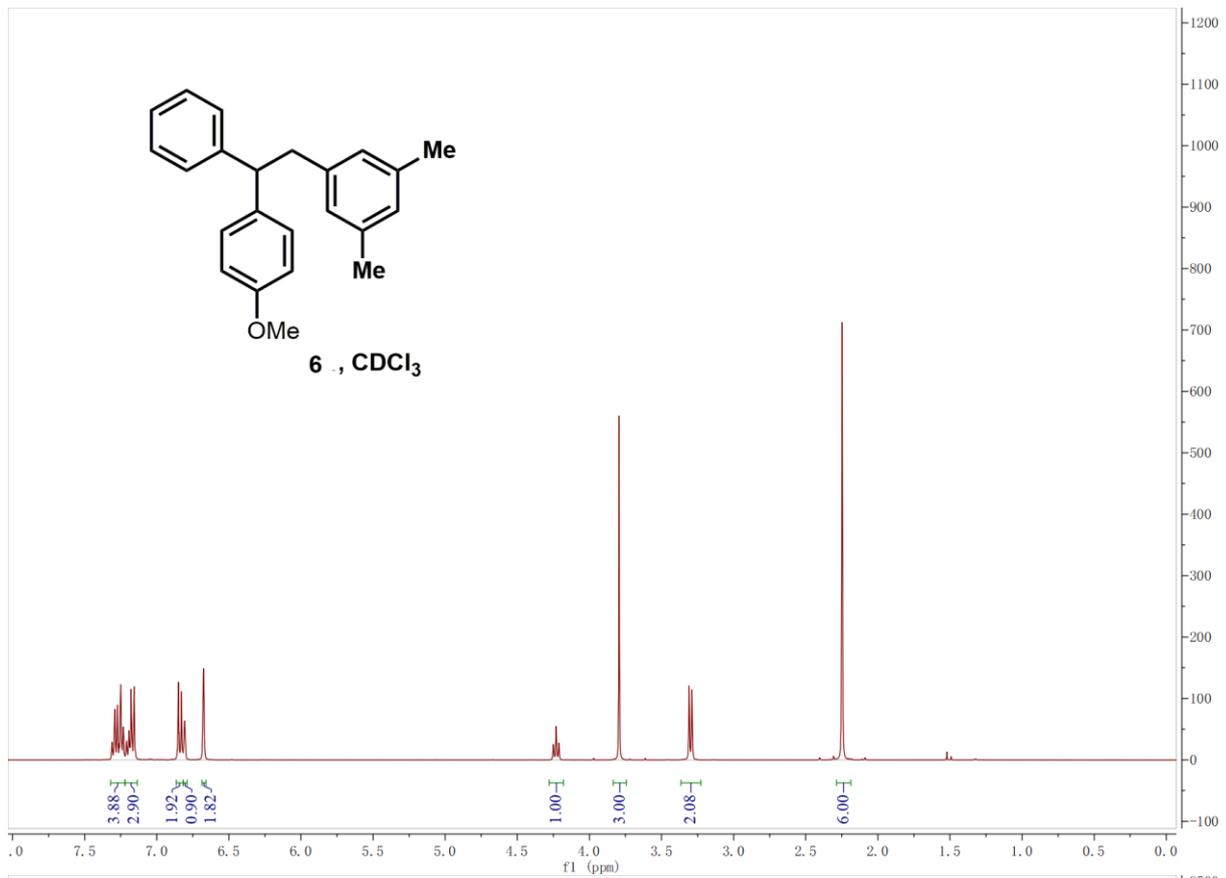
³ Benoit, G., Charette, A. B. *J. Am. Chem. Soc.* **2017**, *139*, 1364-1367.

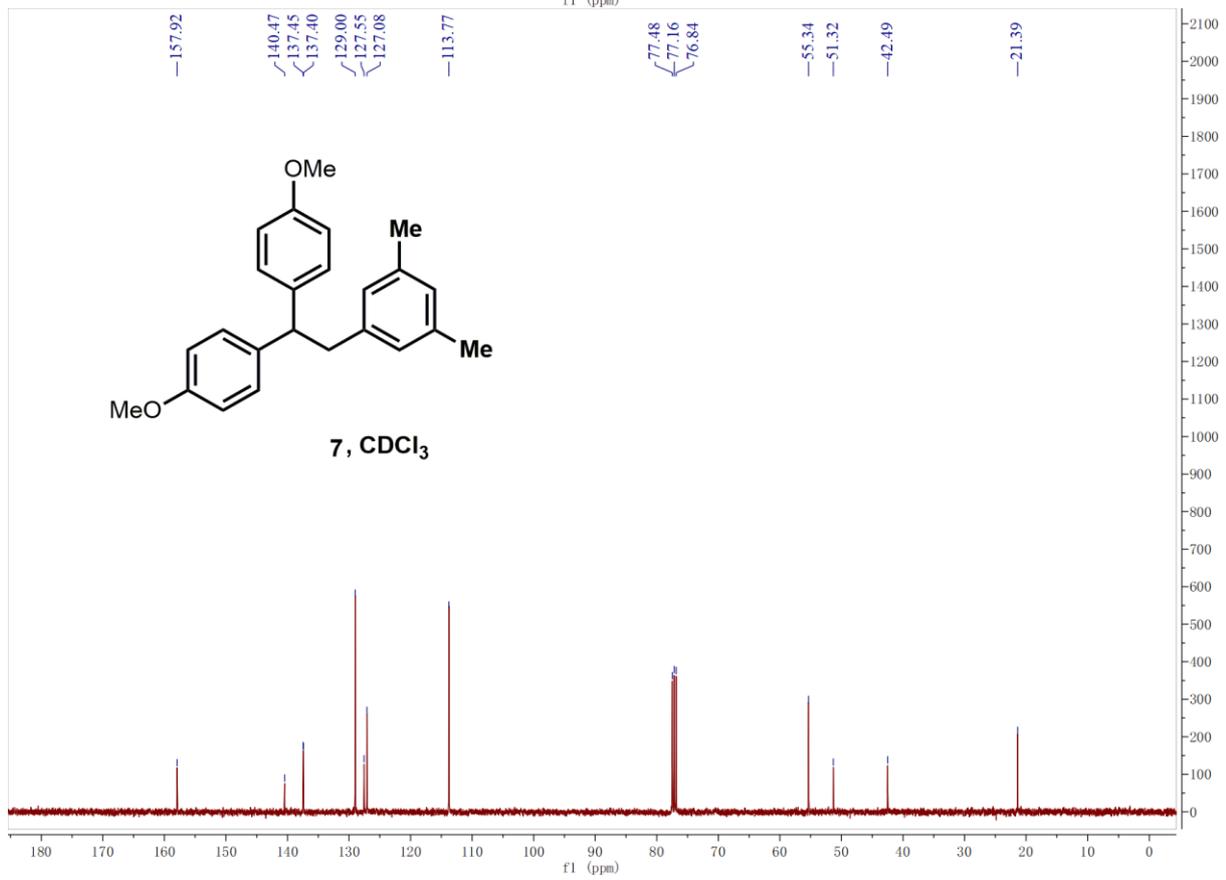
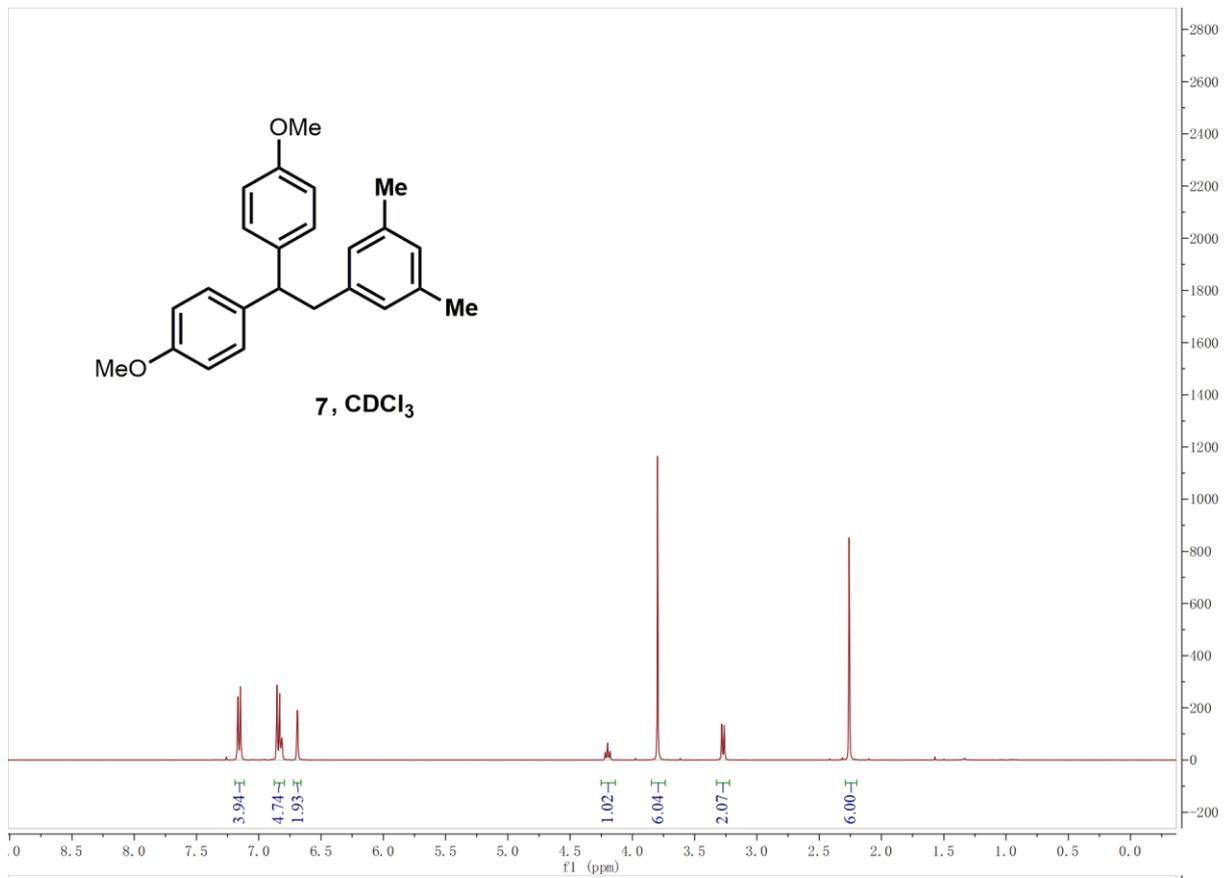
⁴ Waser, J., Gaspar, B., Nambu, H., Carreira, E. M. *J. Am. Chem. Soc.* **2006**, *128*, 11693-11712.

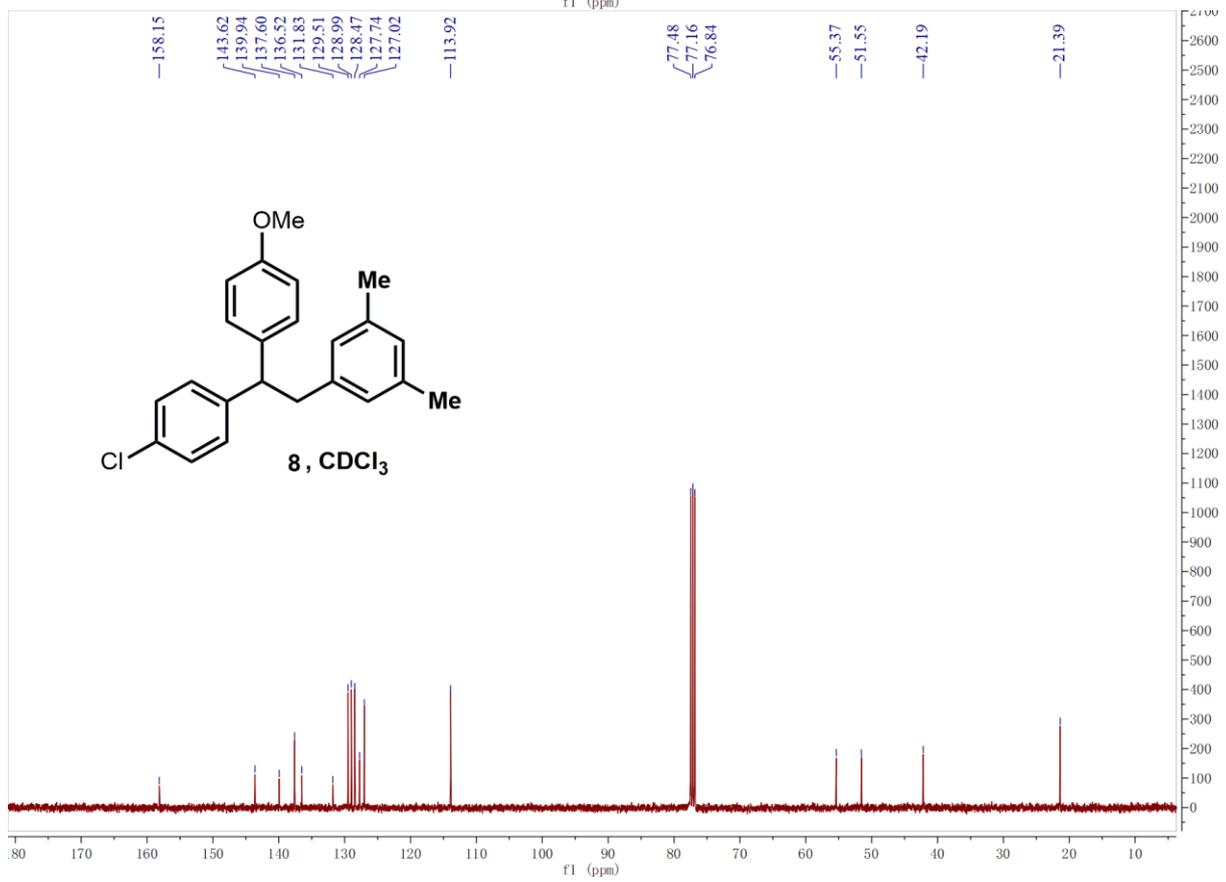
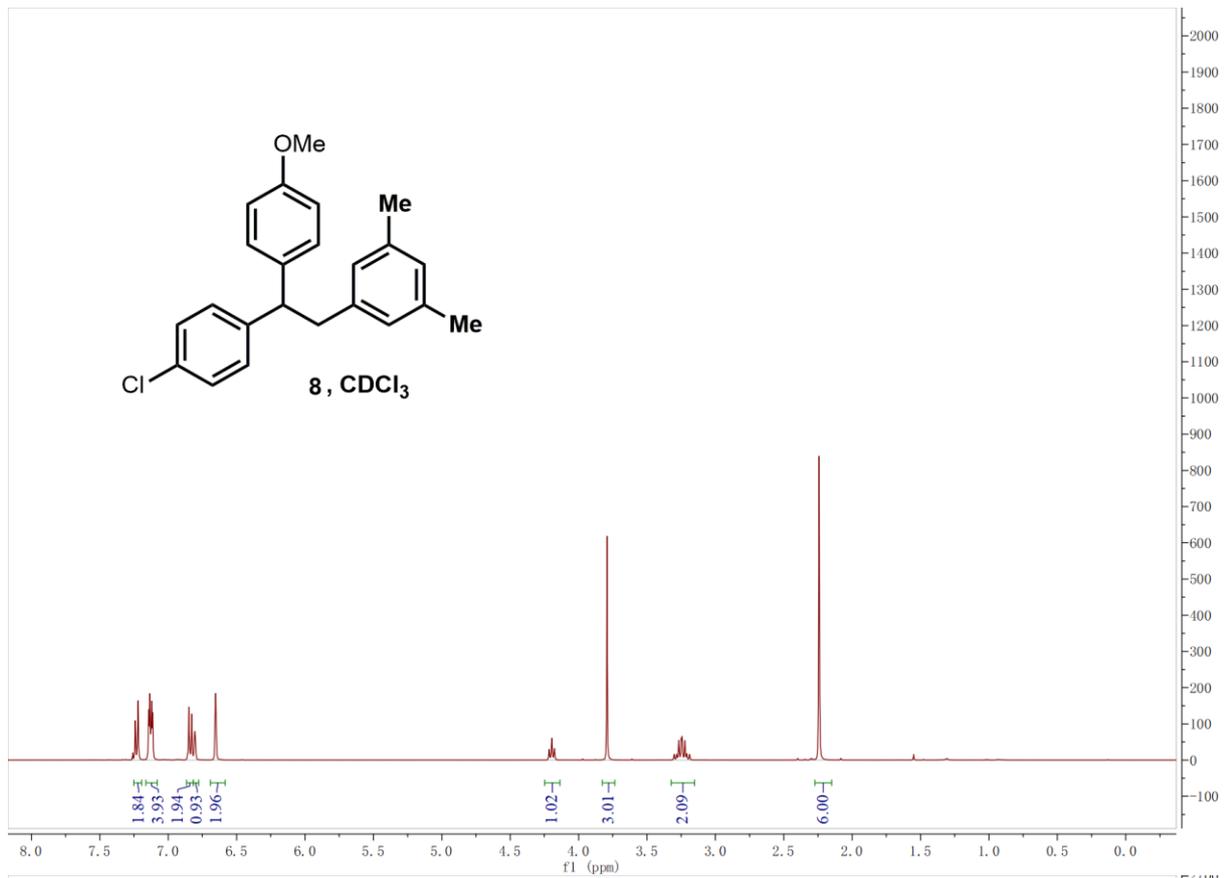
⁵ Daniel, P. E., Weber, A. E., Malcolmson, S. J. *Org. Lett.* **2017**, *19*, 3490-3493.

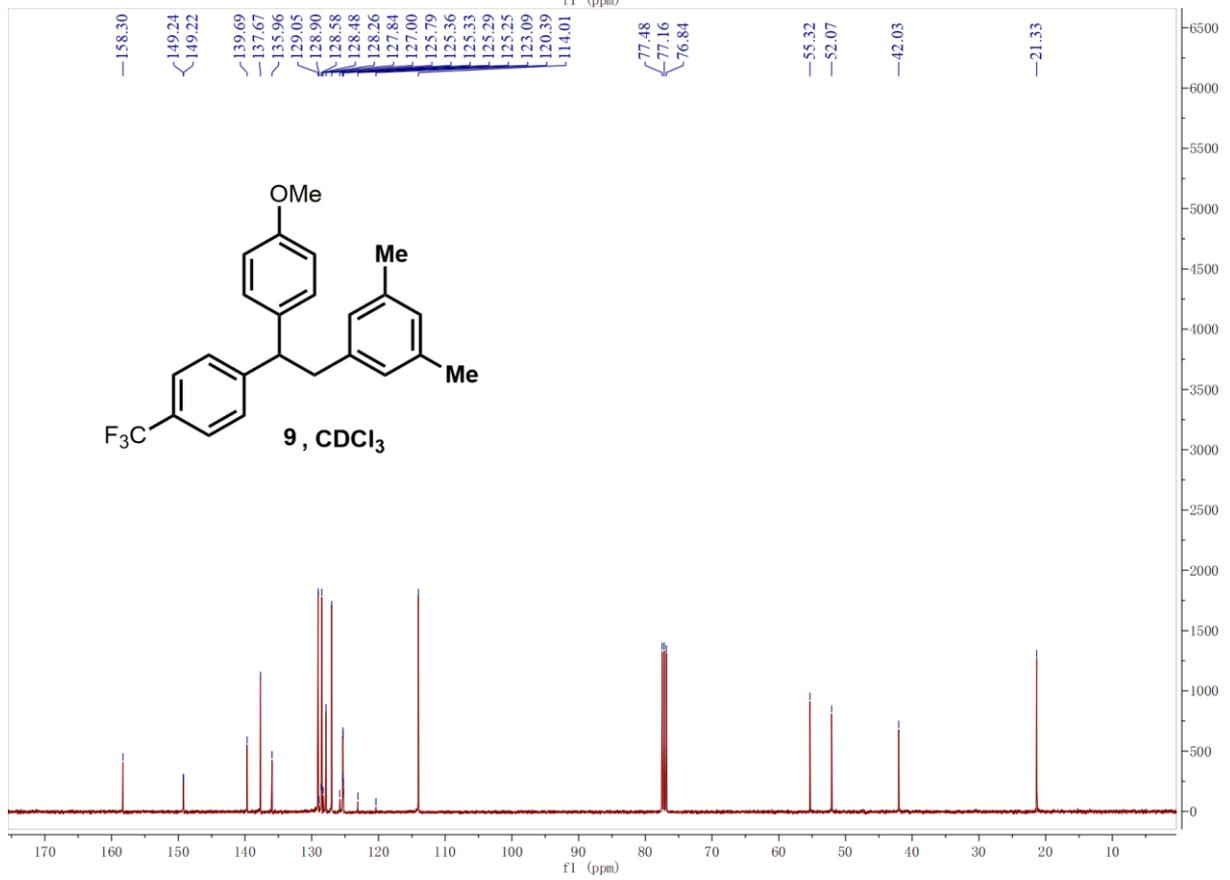
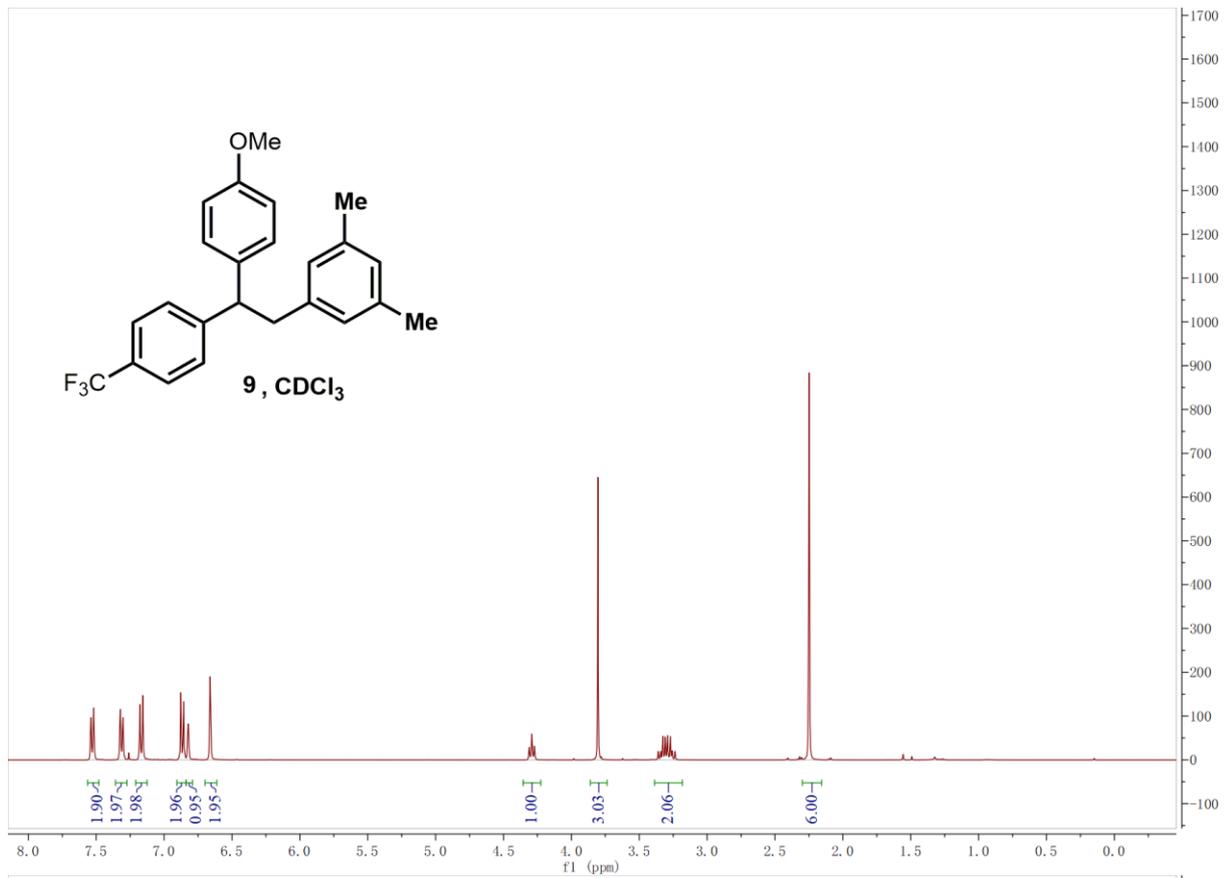
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- ⁶ Lykakis, L. N., Efe, C., Gryparis, C., Stratakis, M. *Eur. J. Org. Chem.* **2011**, 2334-2338.
- ⁷ Phipps, R. J., McMurray, L., Ritter, S., Duong, H. A., Gaunt, M. J. *J. Am. Chem. Soc.*, **2012**, *134*, 10773-10776.
- ⁸ Kalinin, D. V., Wagner, S., Riemann, B., Hermann, S., Schmidt, F., Becker-Pauly, C., Rose-John, S., Schafers, M., Holl, R. *J. Med. Chem.* **2016**, *59*, 9541-9559.
- ⁹ Makida, Y., Marelli, E., Slawin, A. M., Nolan, S. P. *Chemical Communications*, **2014**, *50*, 8010-8013.
- ¹⁰ Chen, M., Ren, Z. H., Wang, Y. Y., Guan, Z. H. *J. Org. Chem.*, **2015**, *80*, 1258-1263.
- ¹¹ a) Yoshida, H., Yoshida, R., Mukae, M., Ohshita, J., Takaki, K. *Chem. Lett.*, **2011**, *40*, 1272-1274; b) Zanotti-Gerosa, A., Smilović, I. G., Časar, Z. *Org. Chem. Front.*, **2017**, *4*, 2311-2322.
- ¹² Krasovskiy, A., Knochel, P. *Synthesis* **2006**, 890-891.

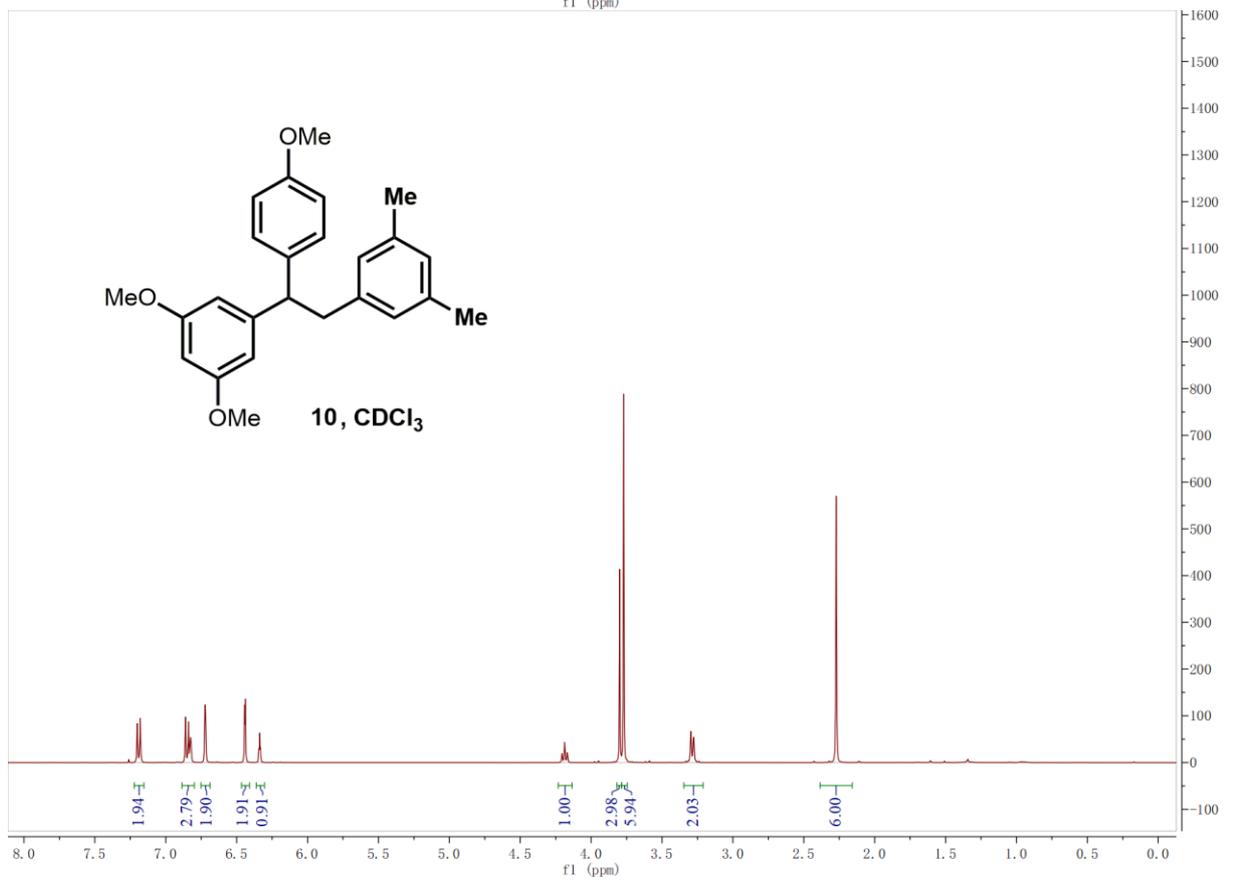
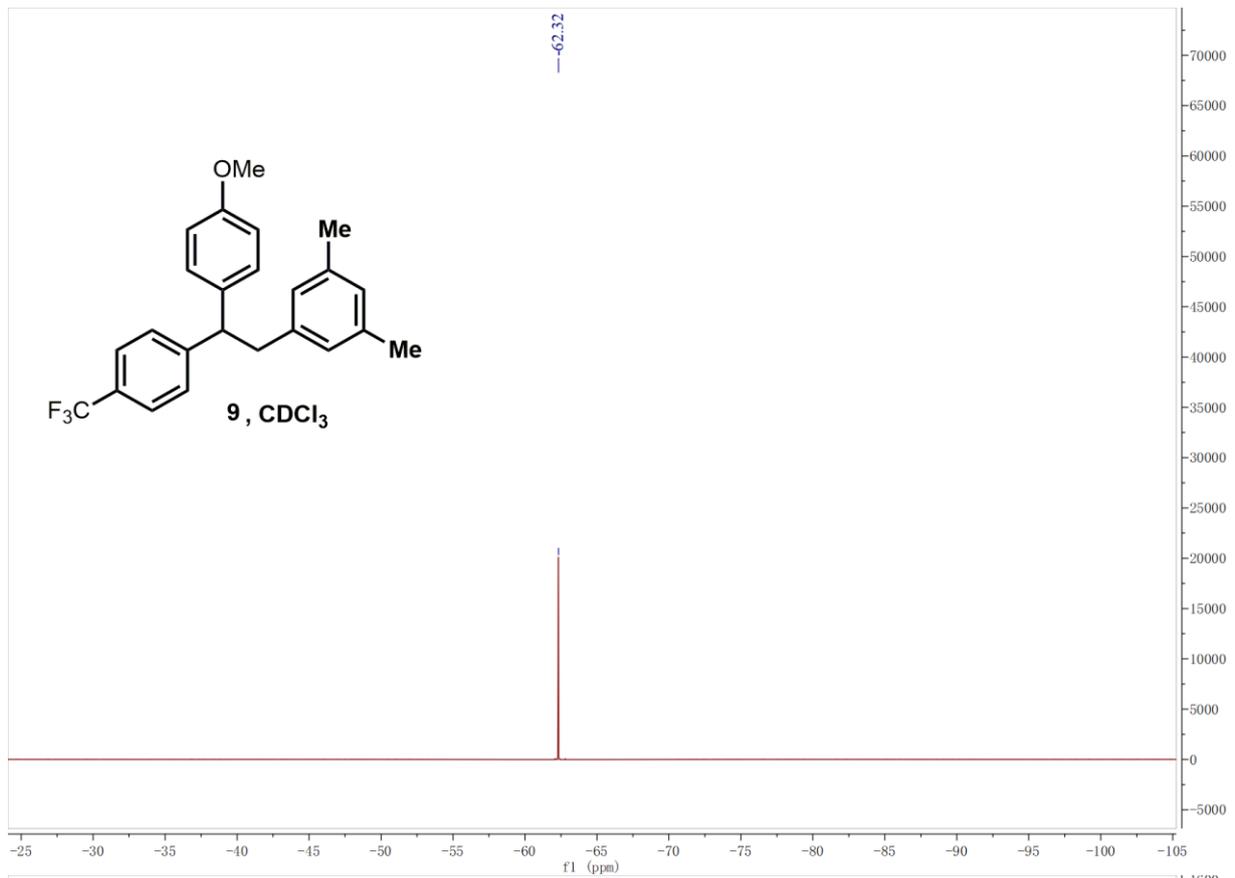


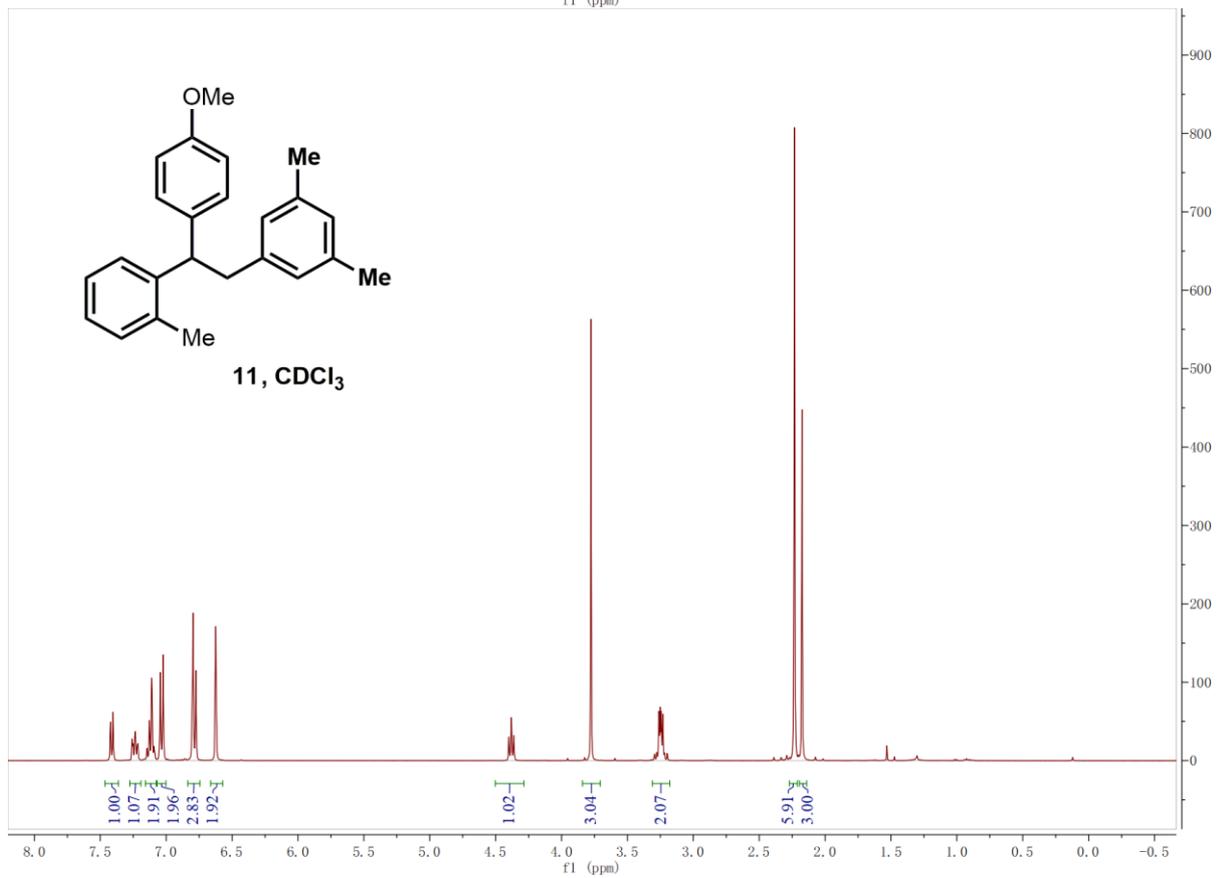
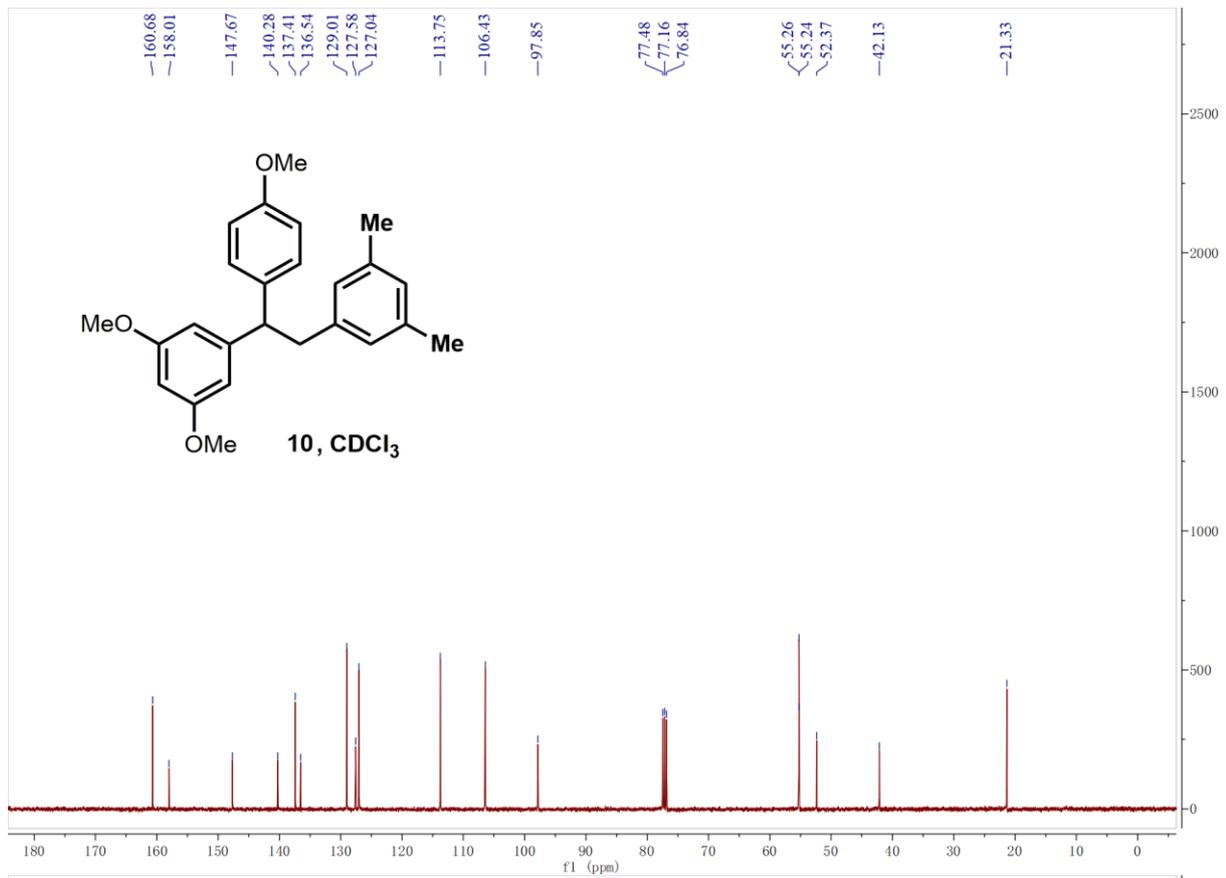


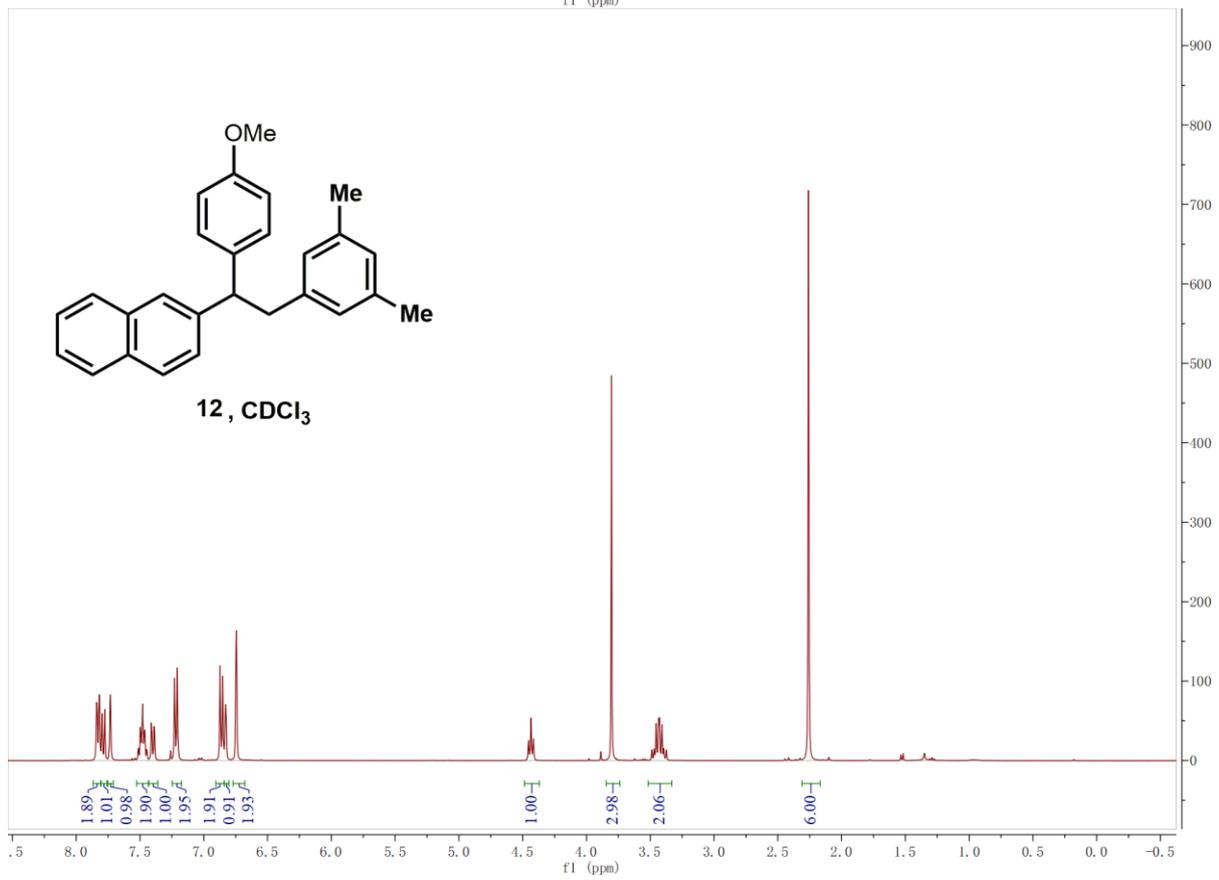
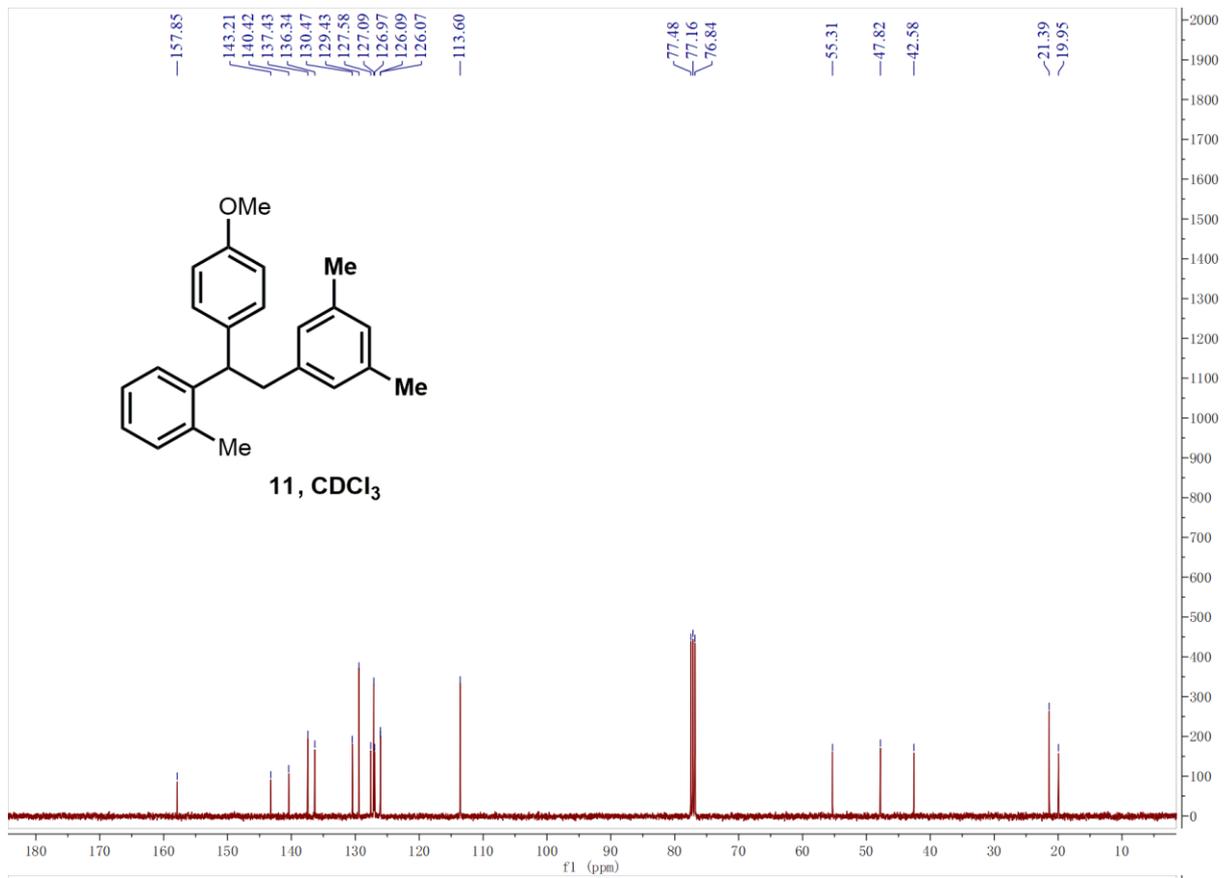


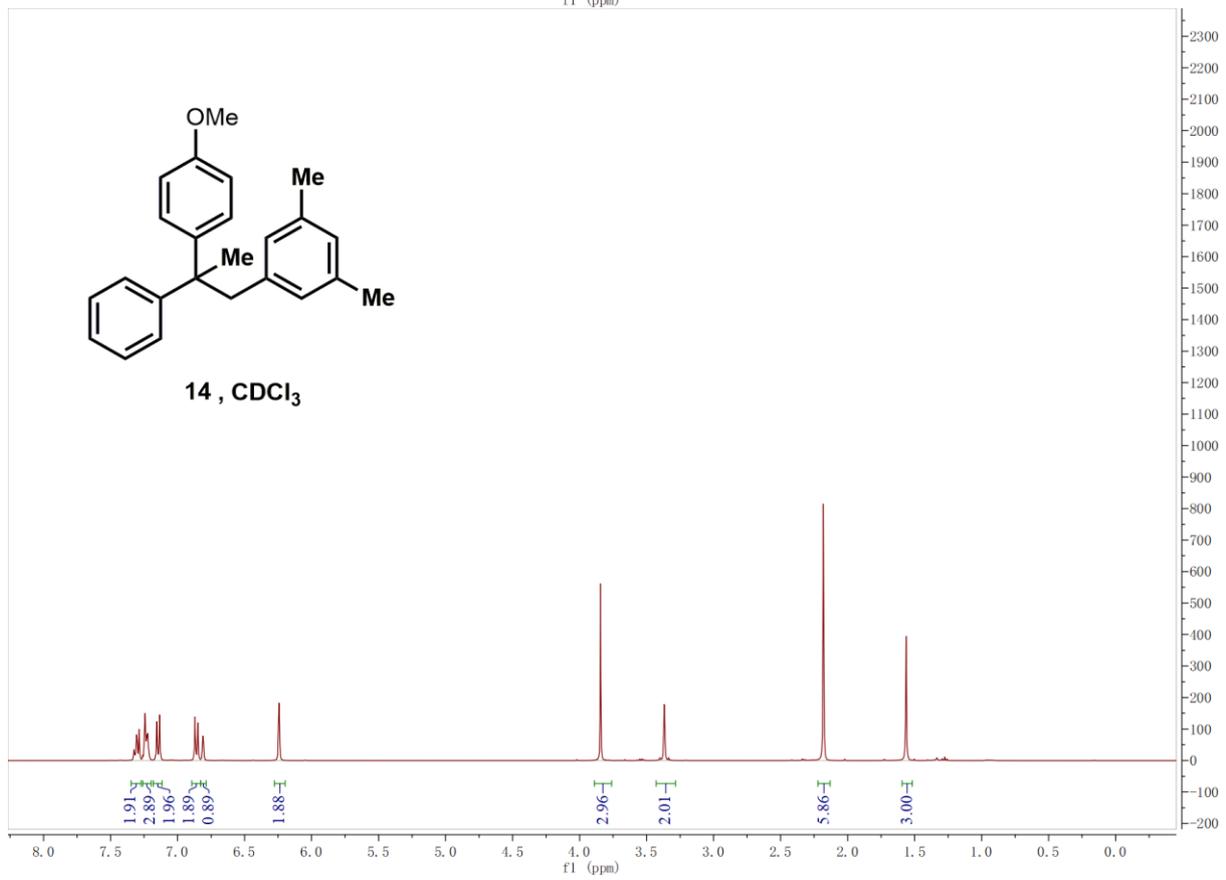
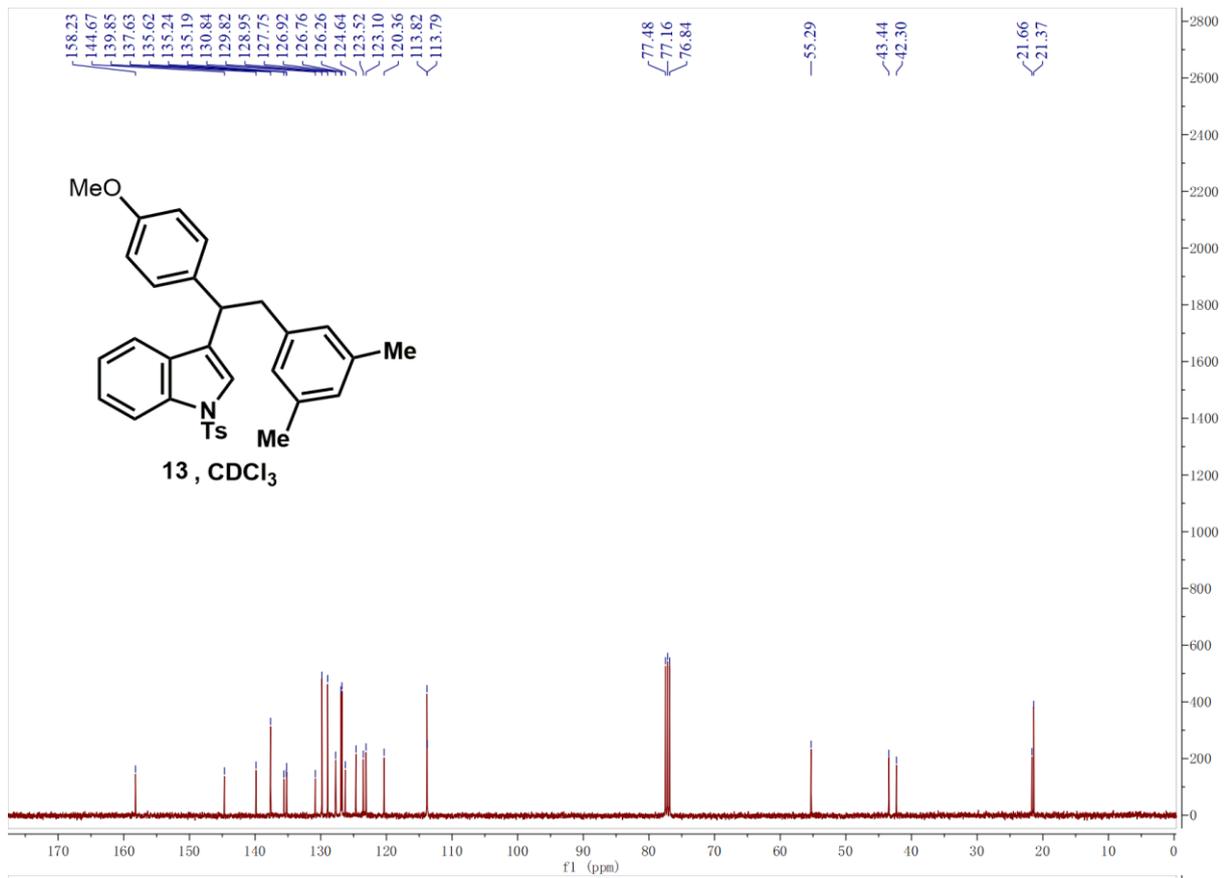


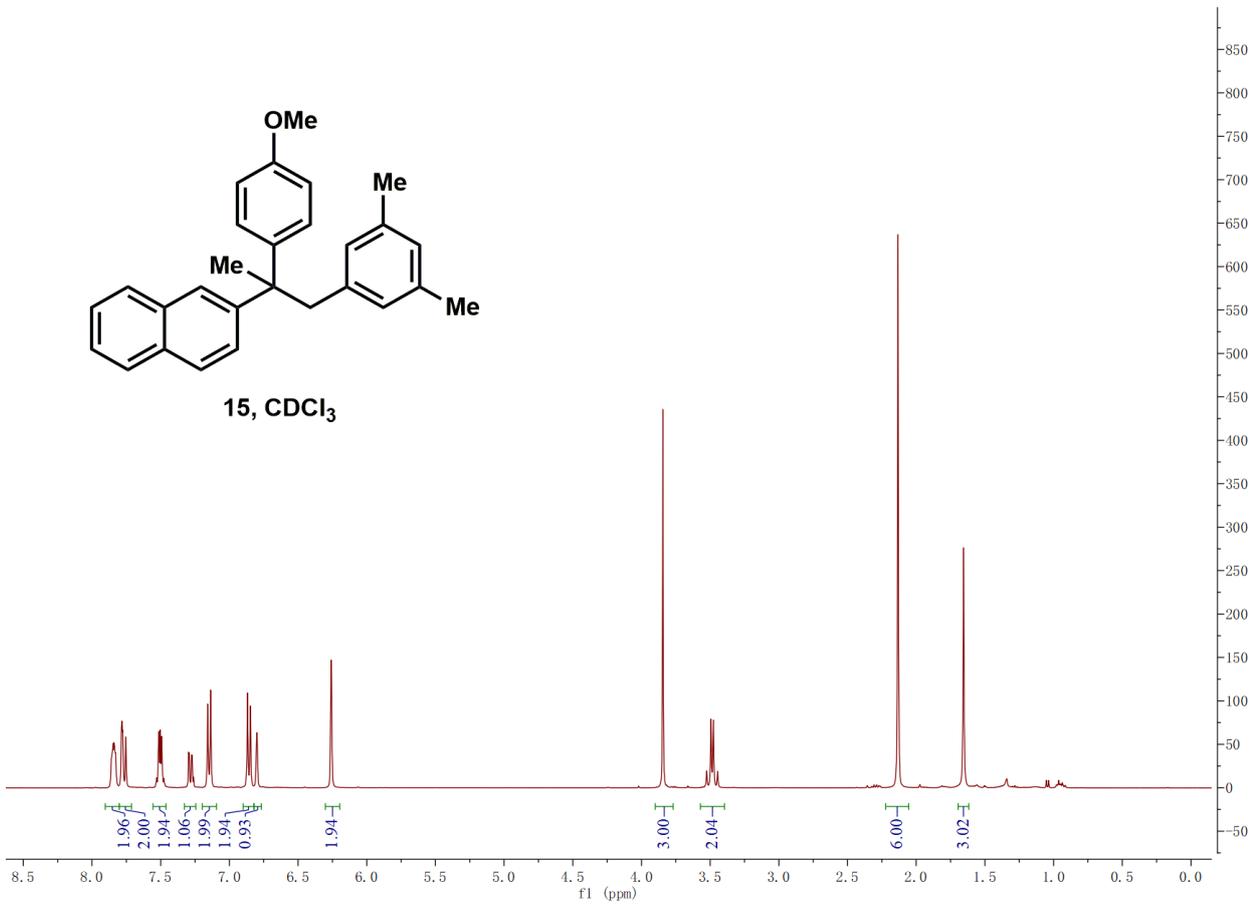
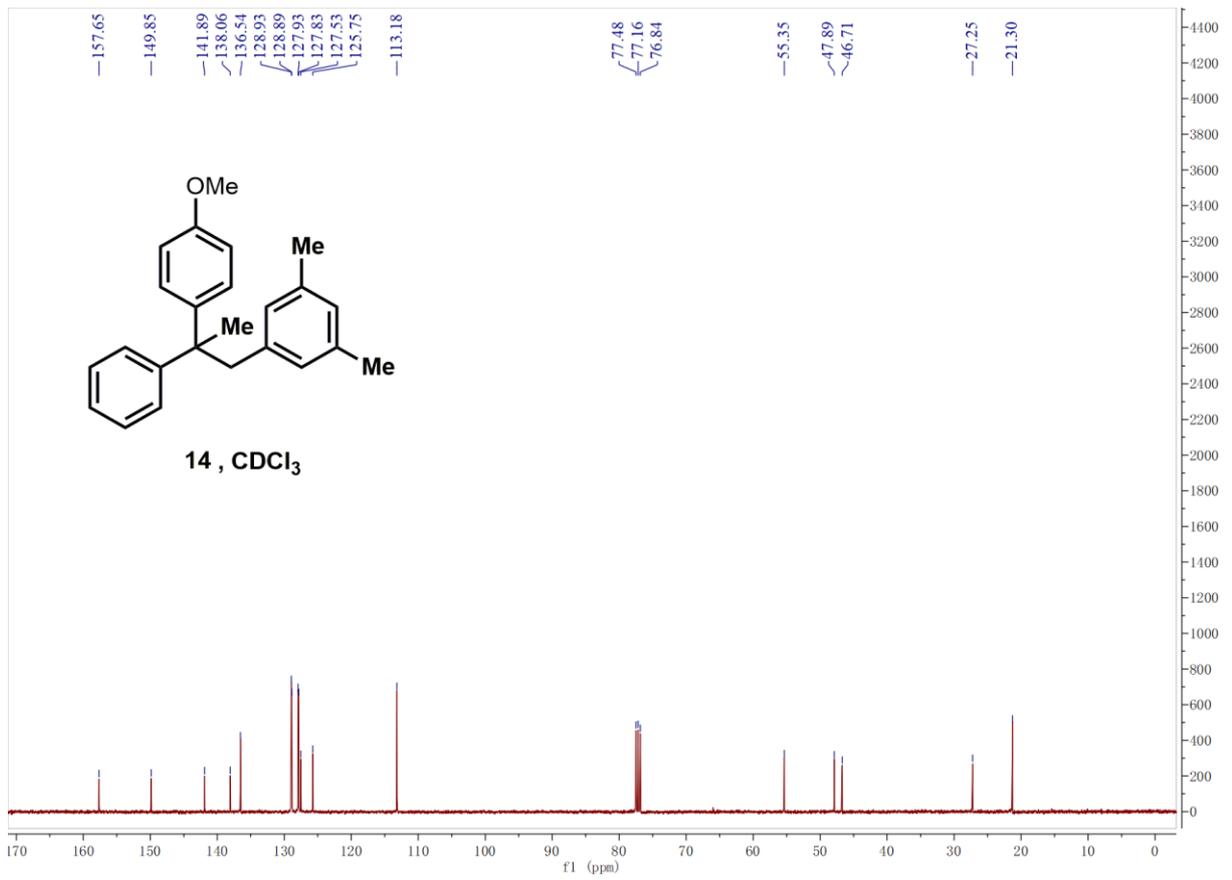


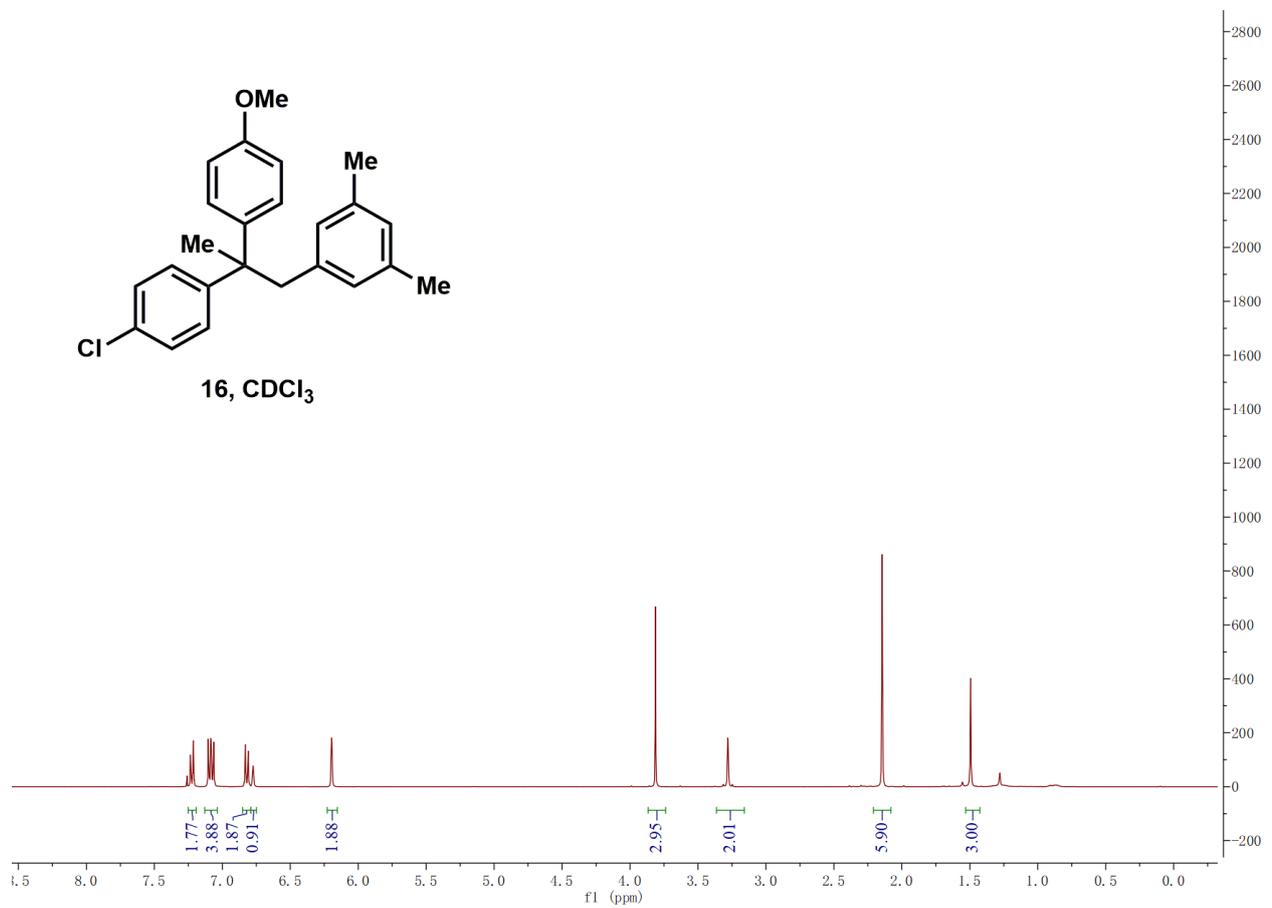
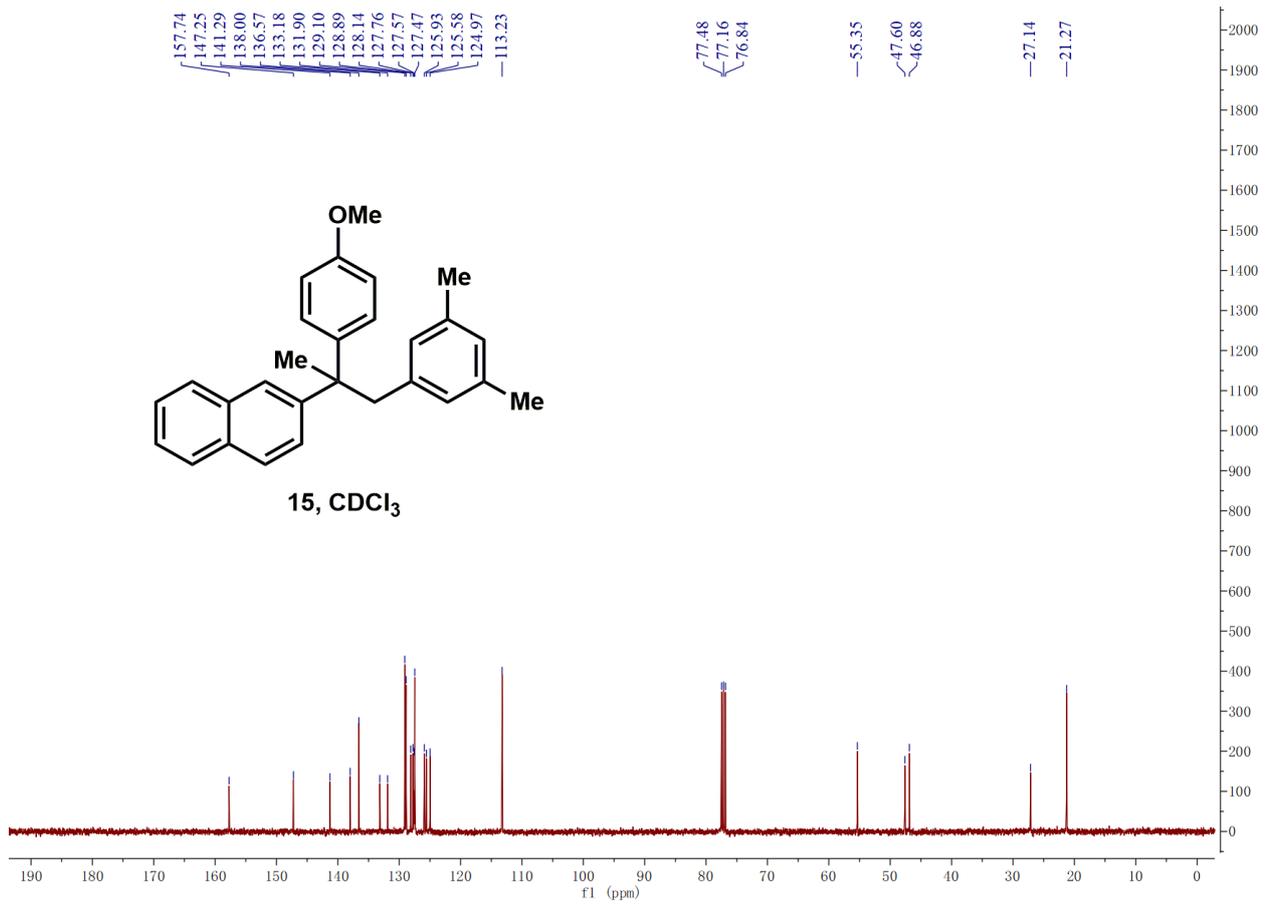


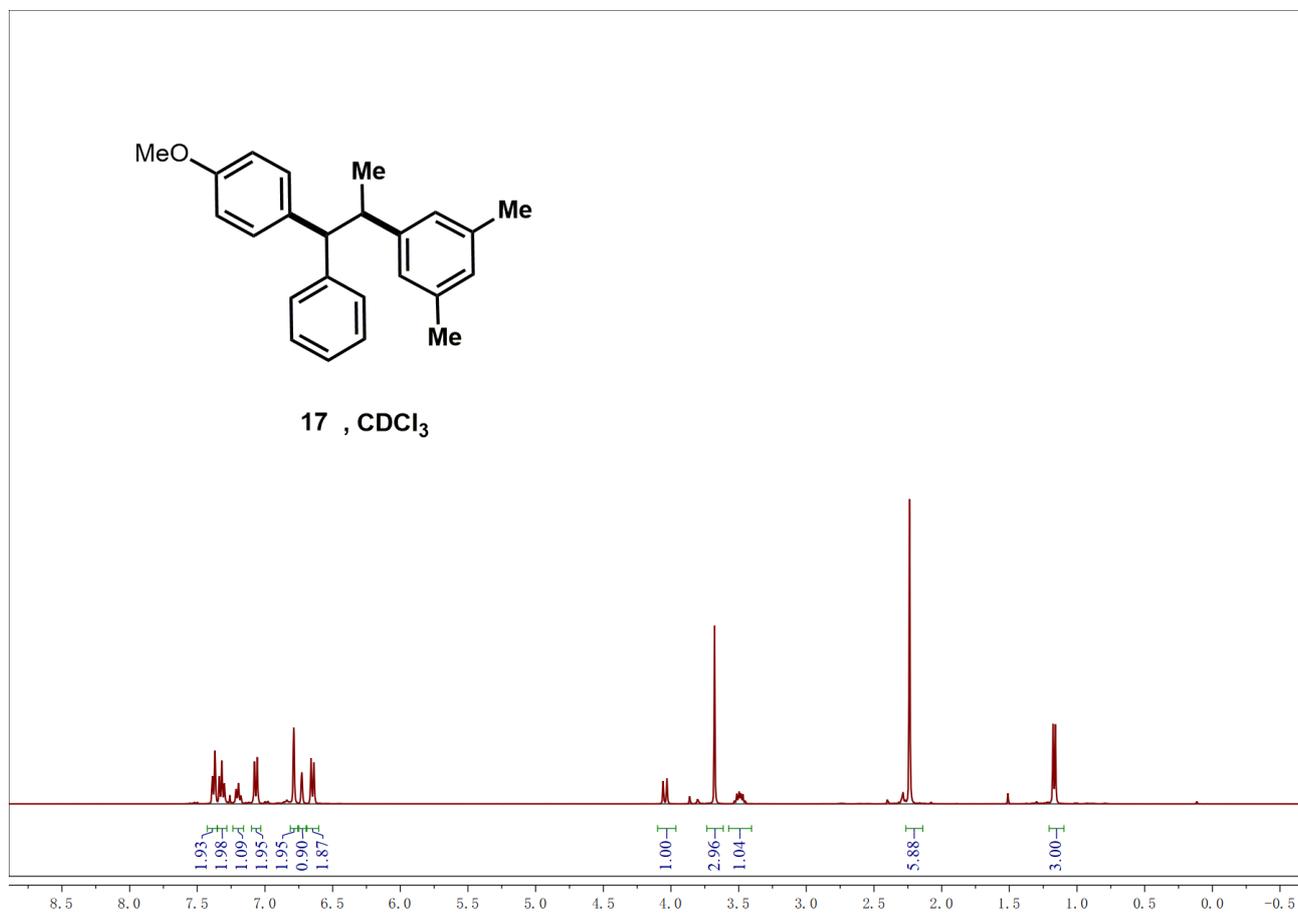
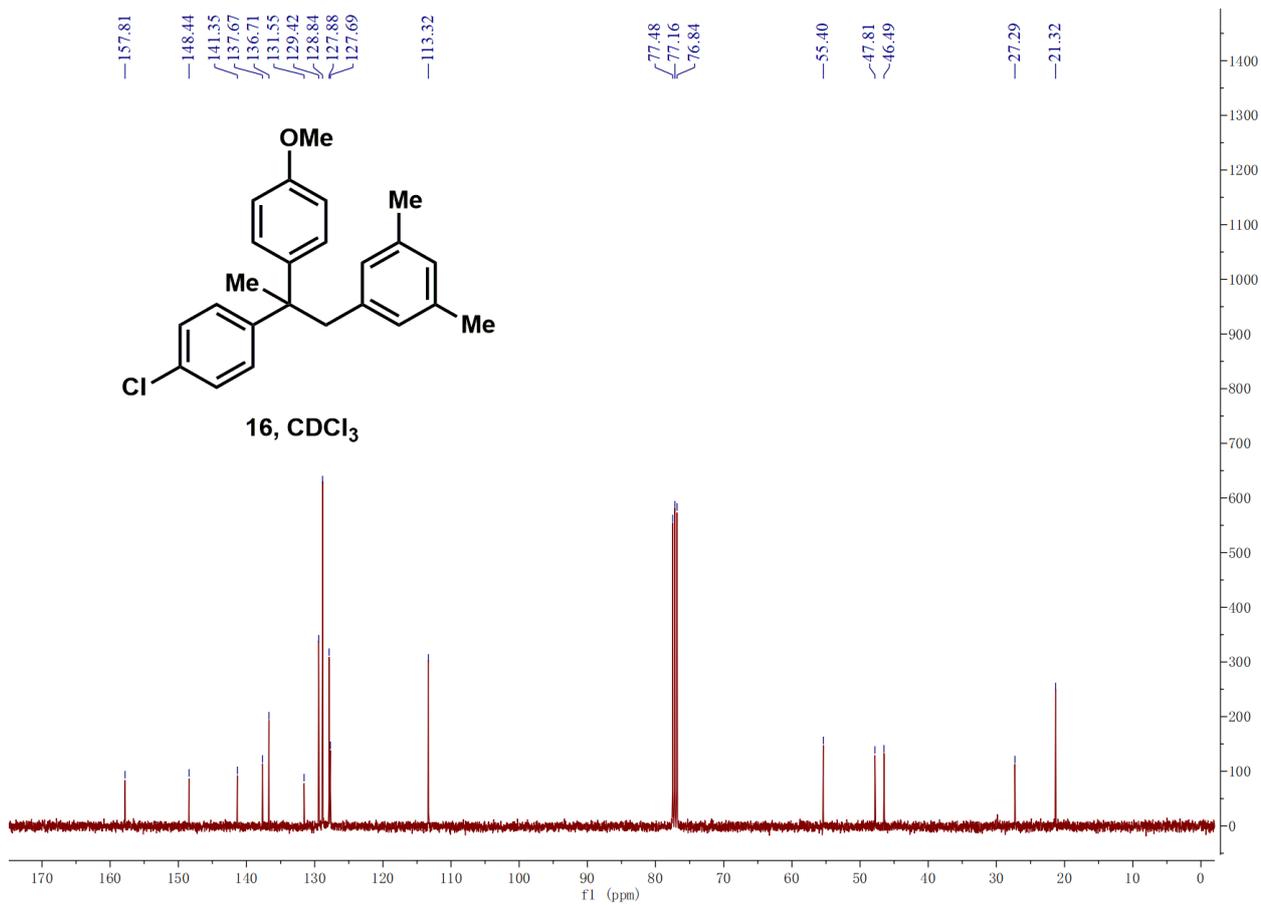


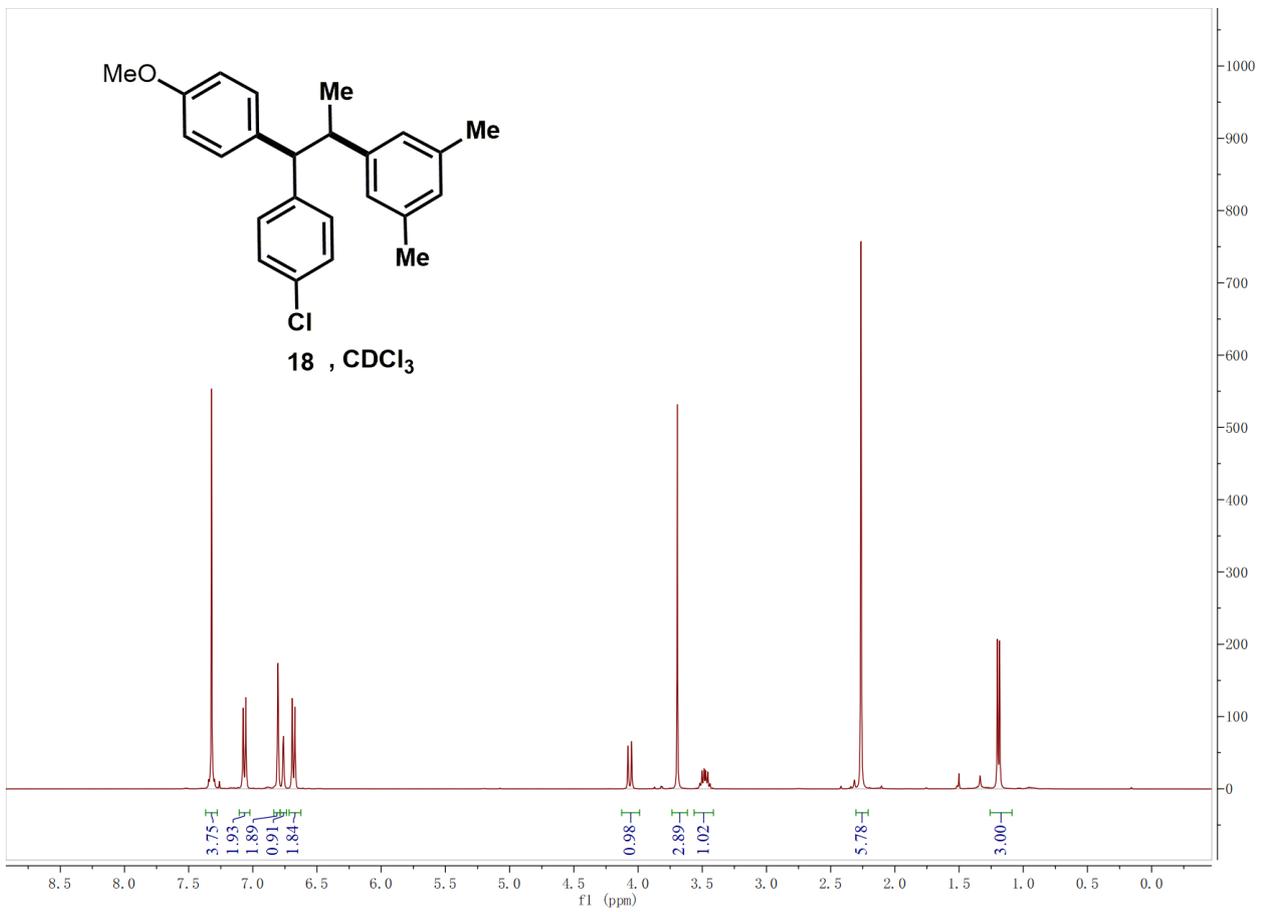
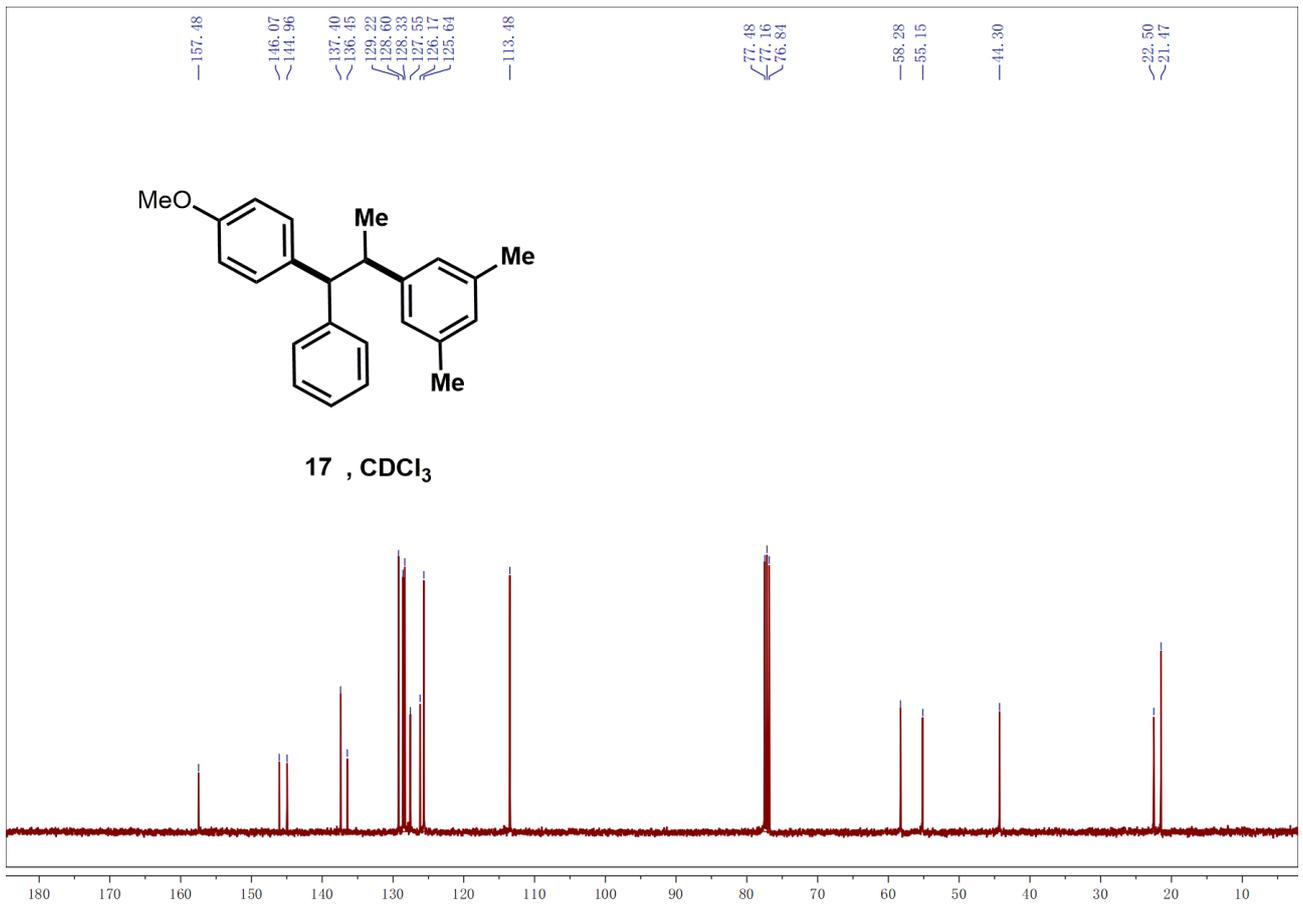


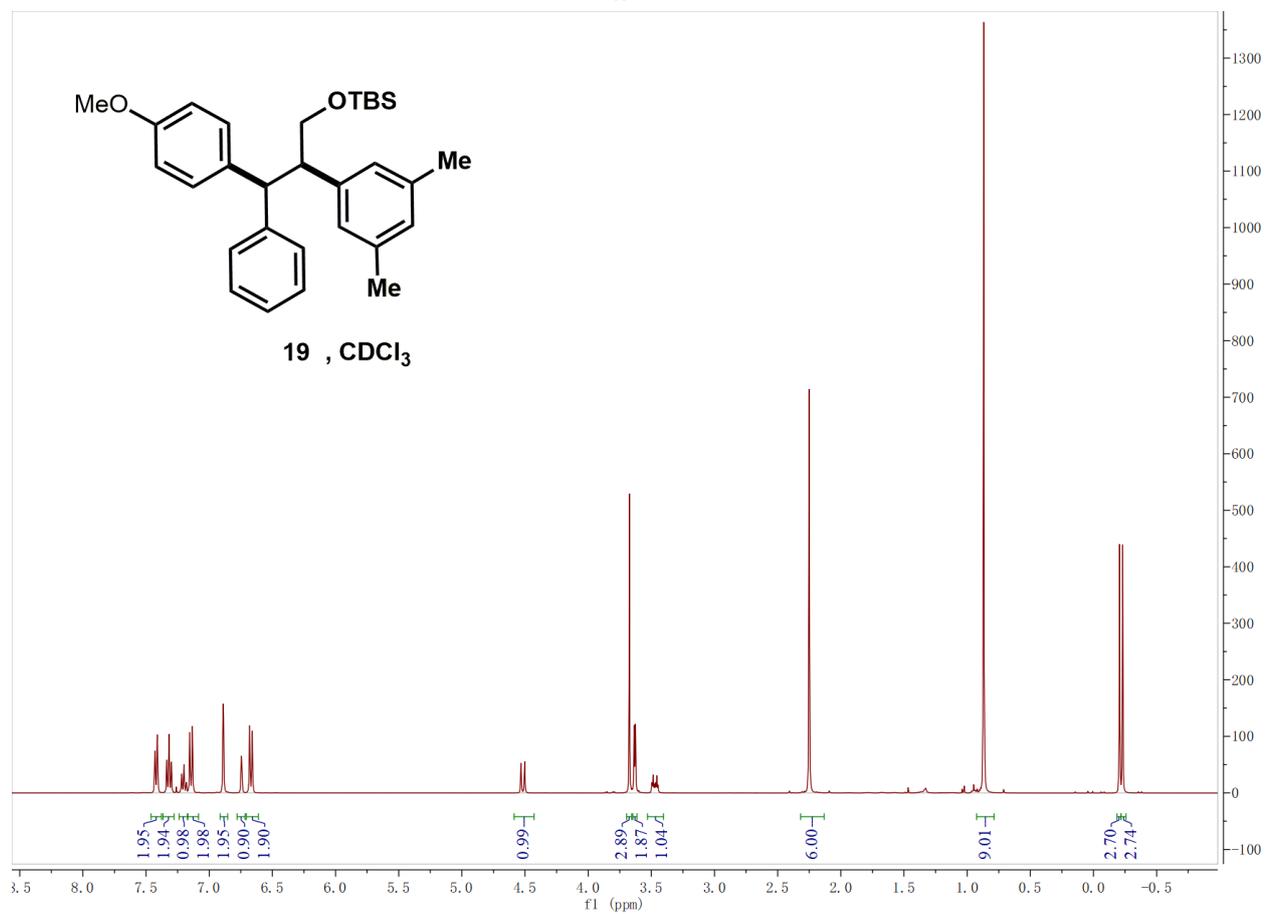
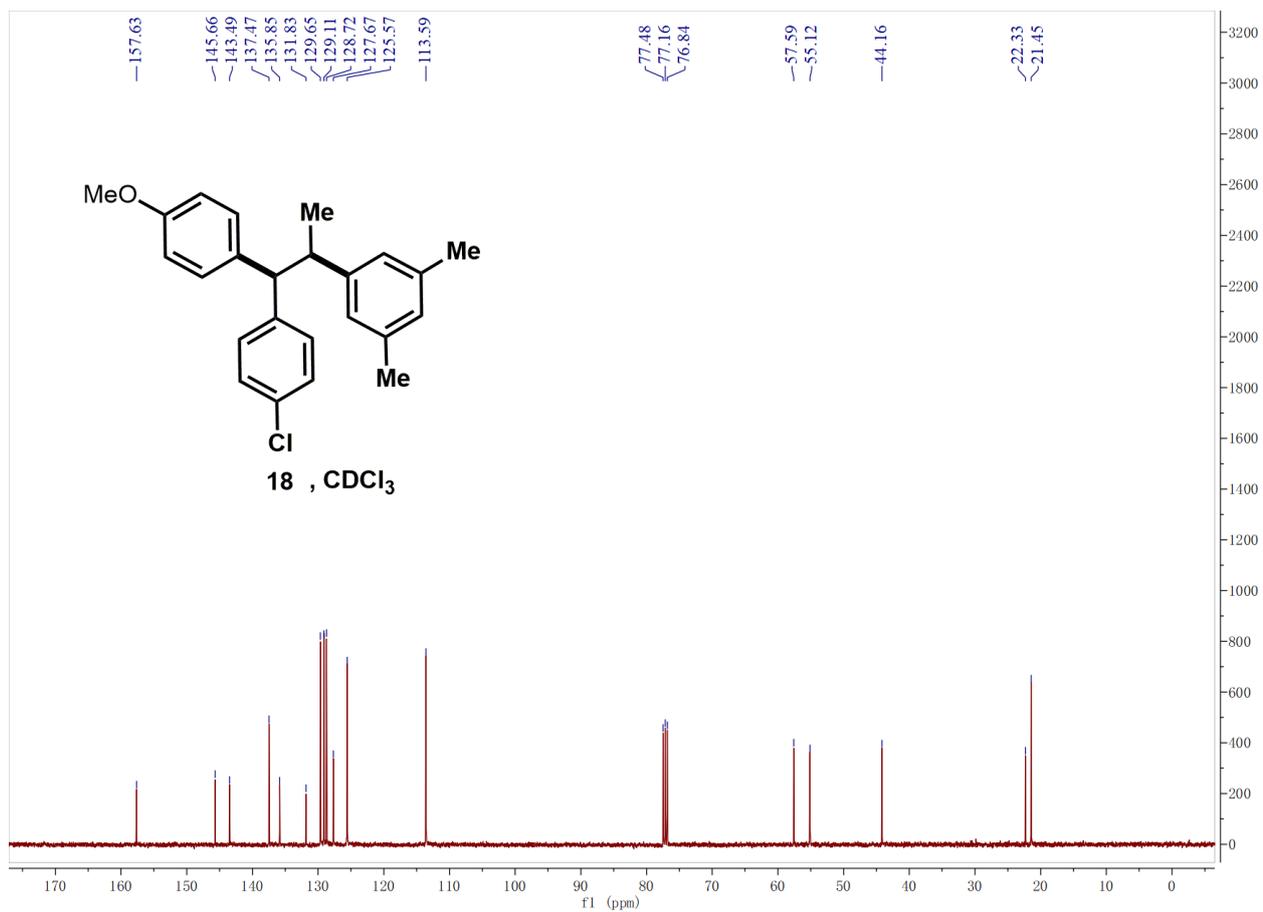


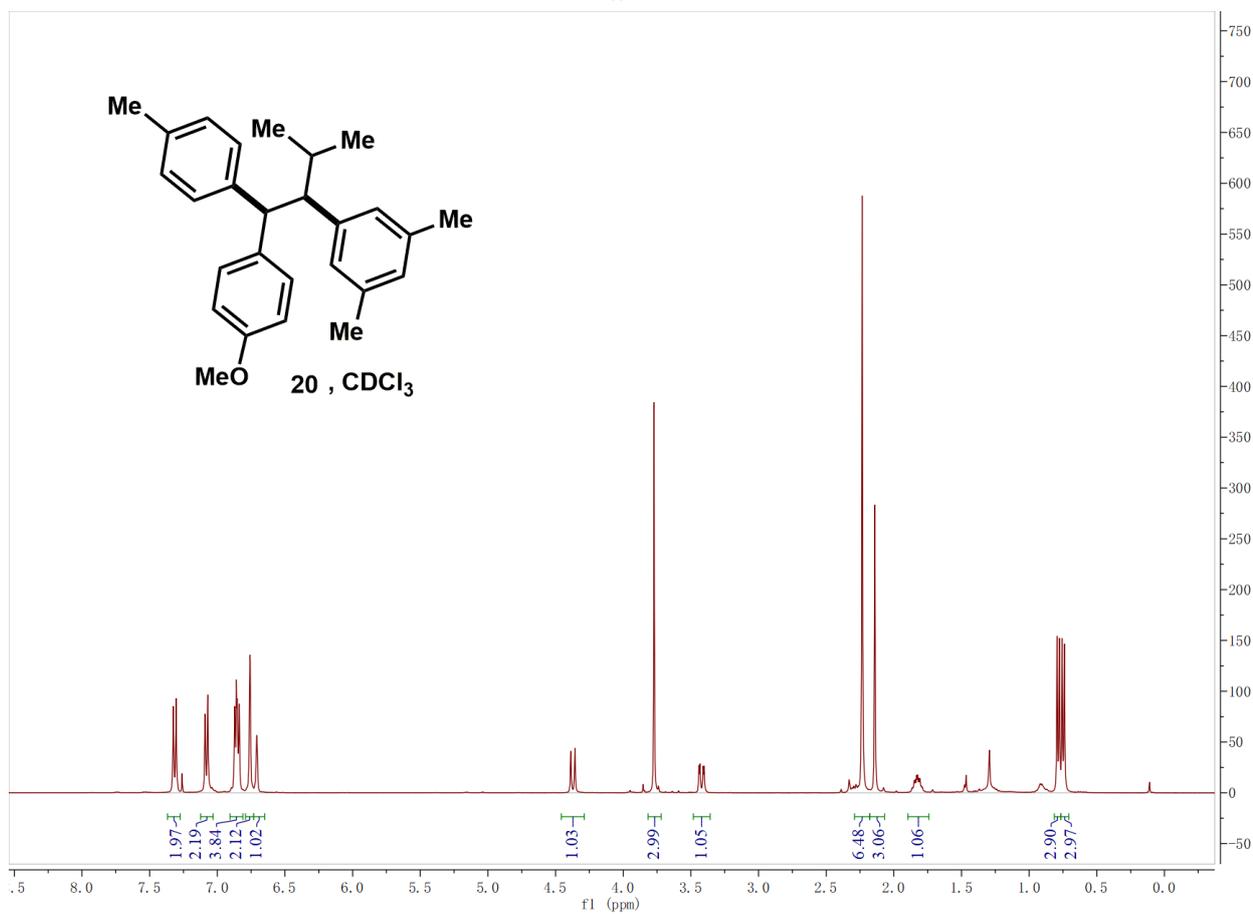
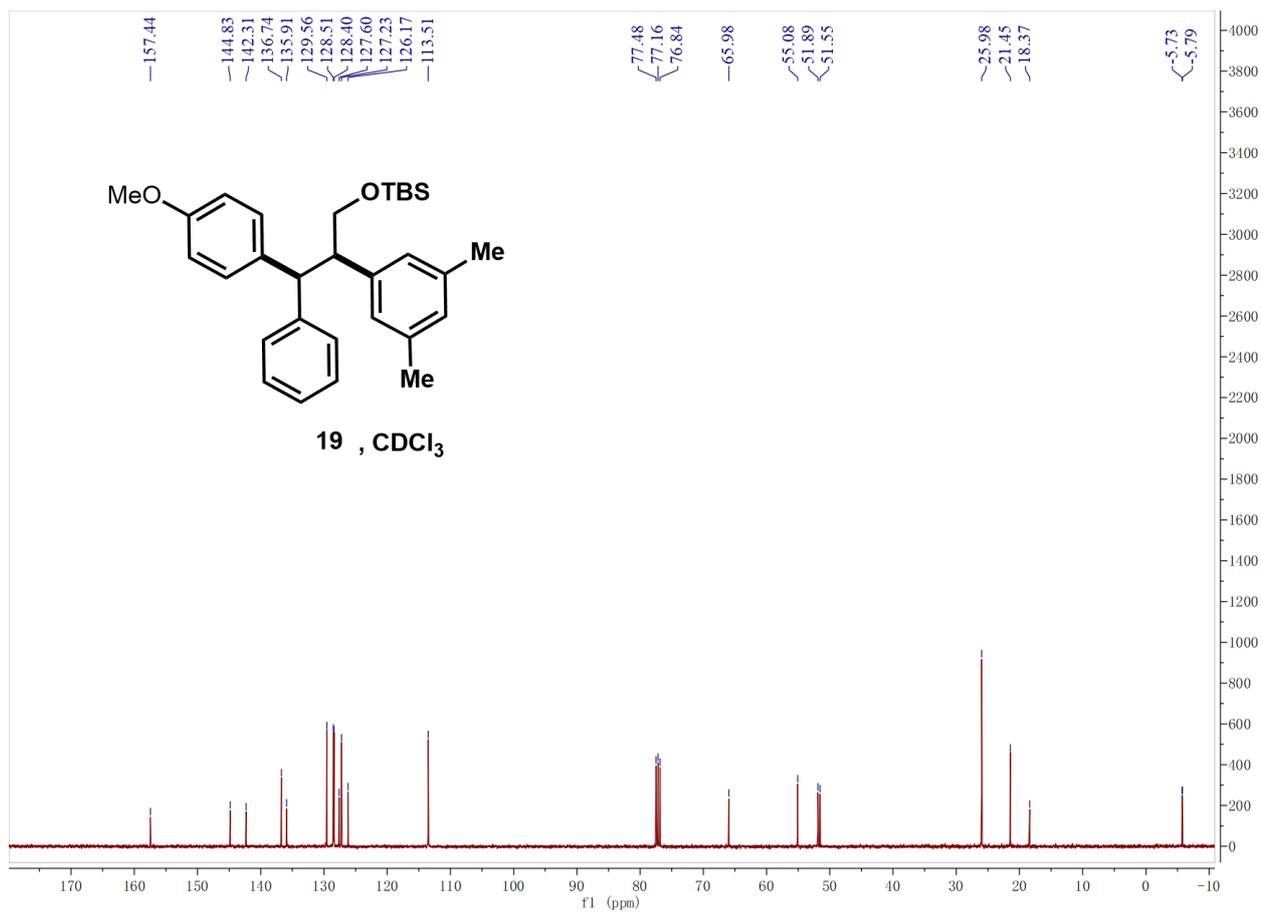


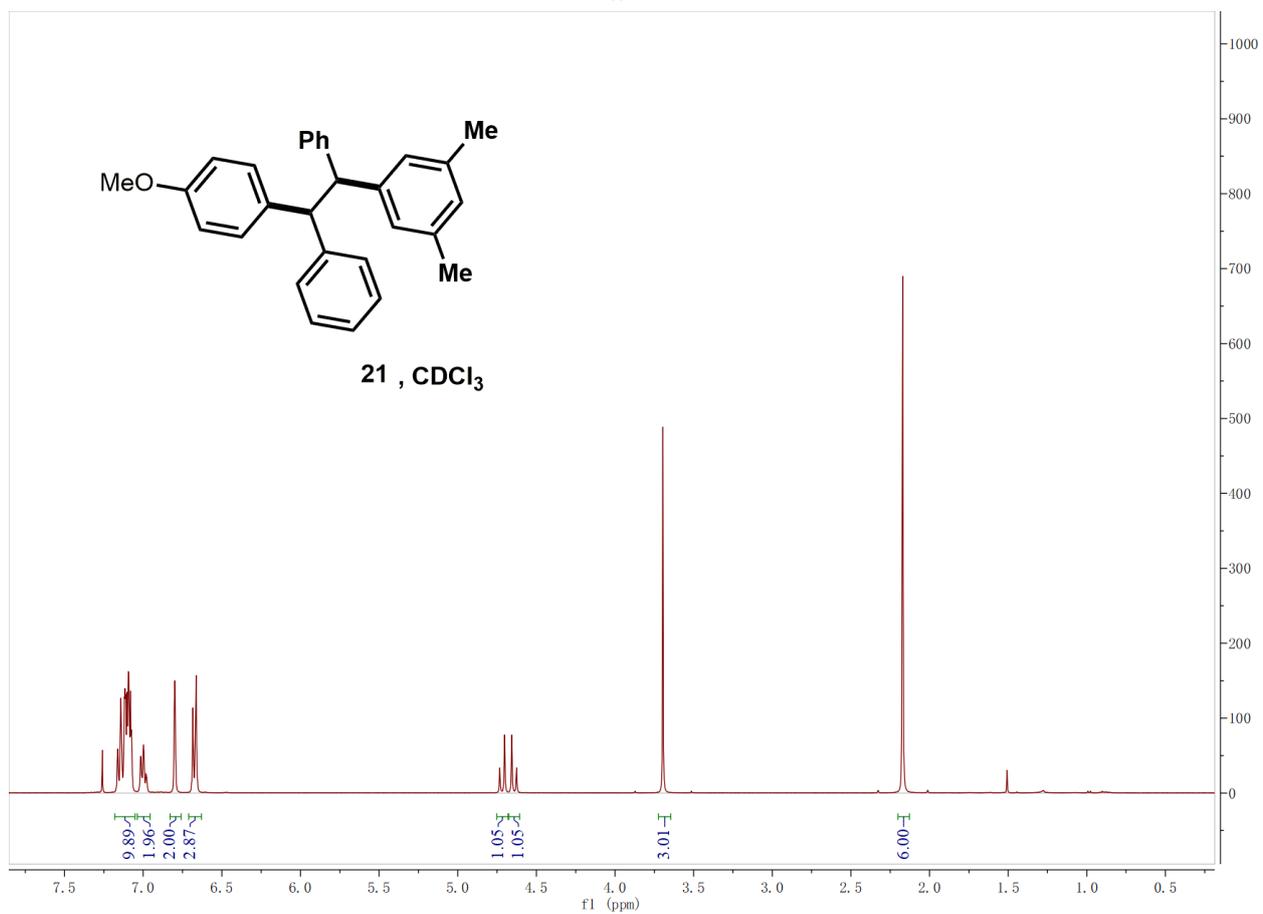
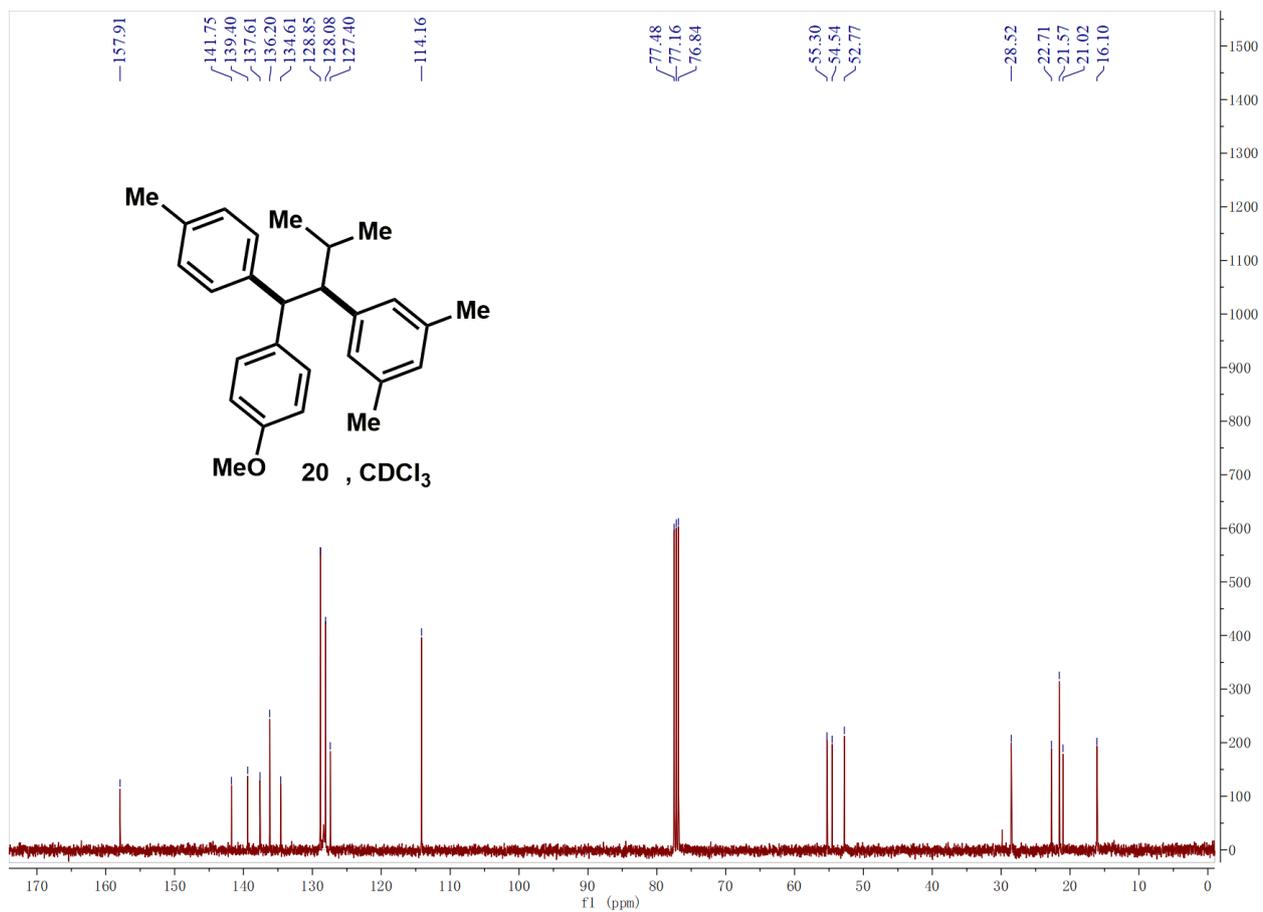


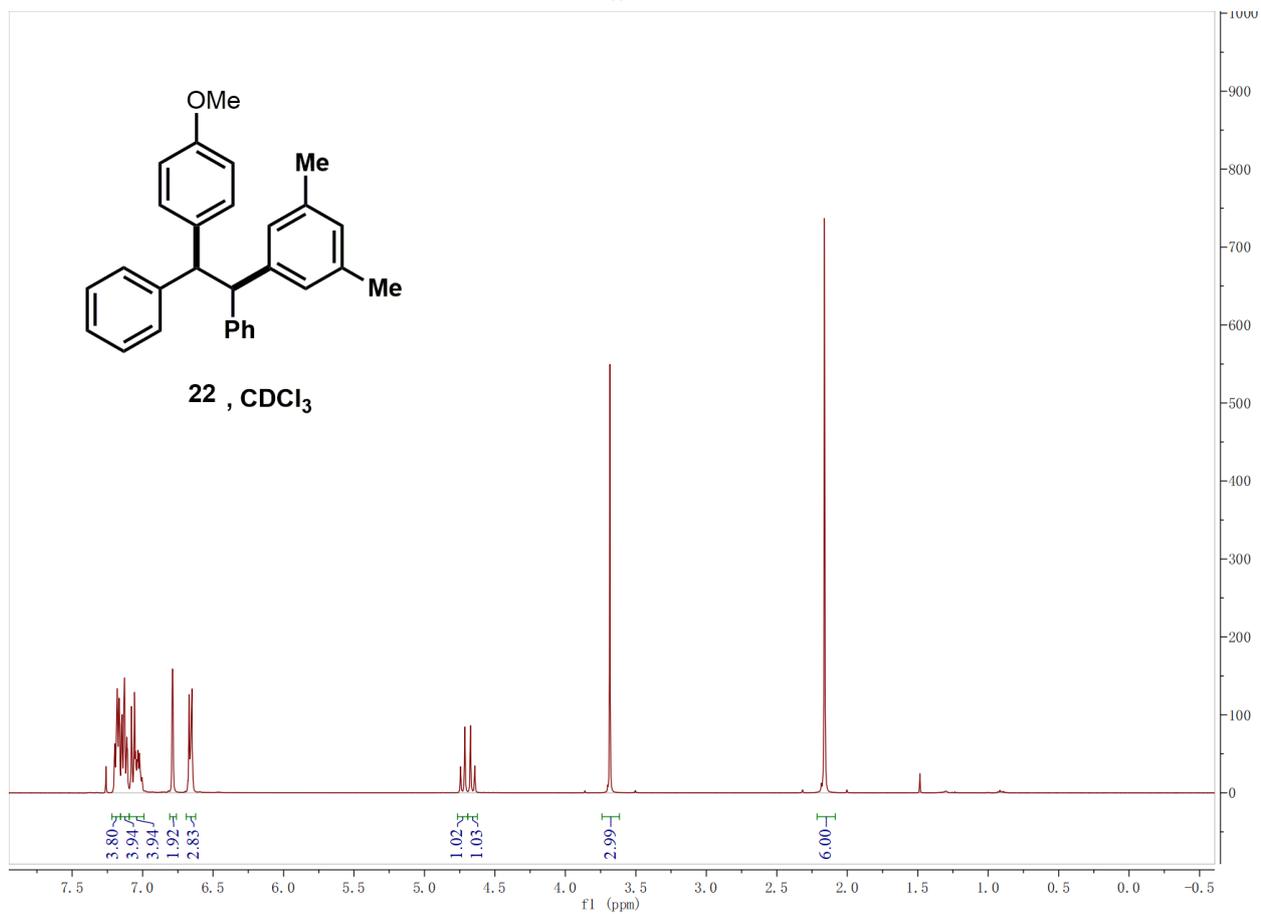
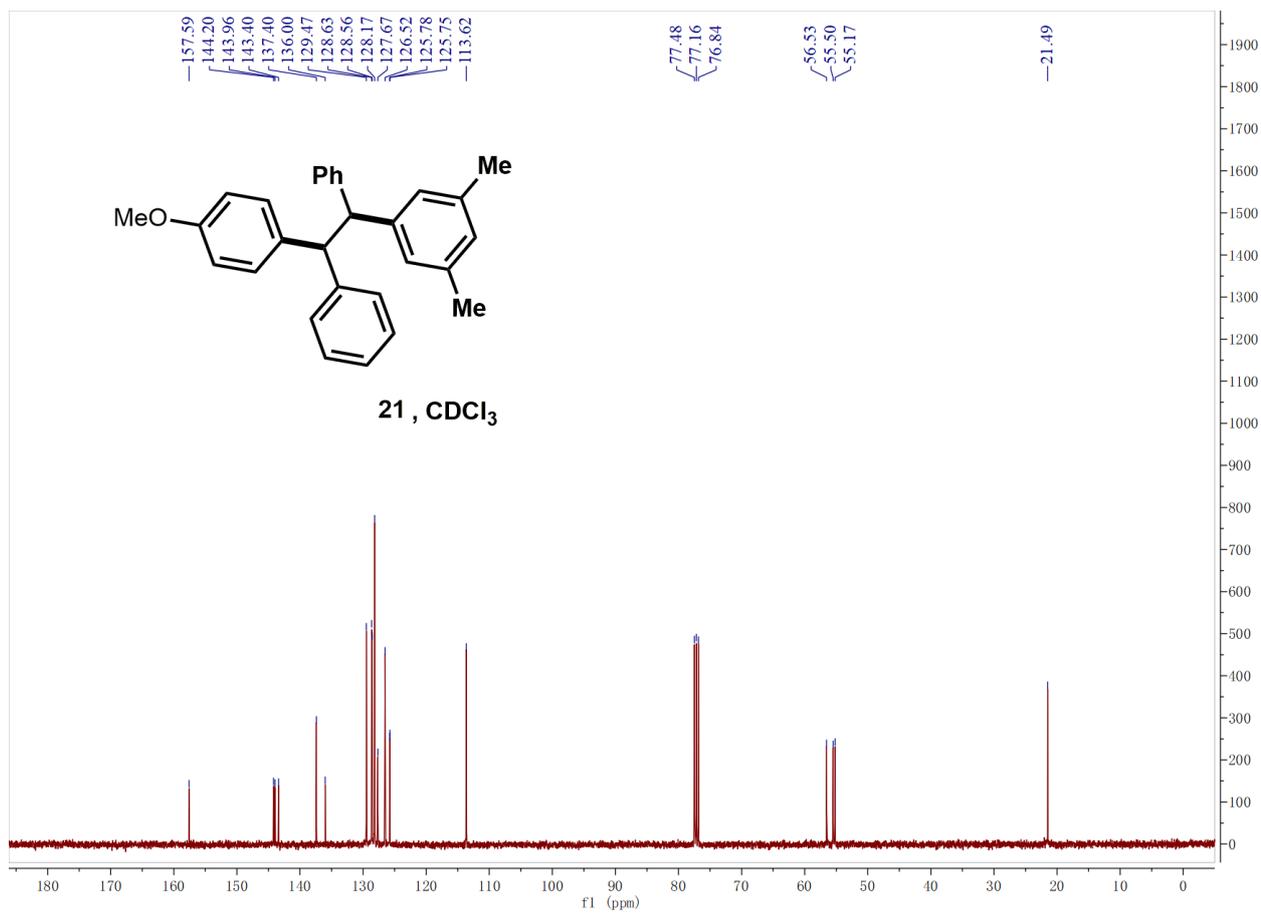


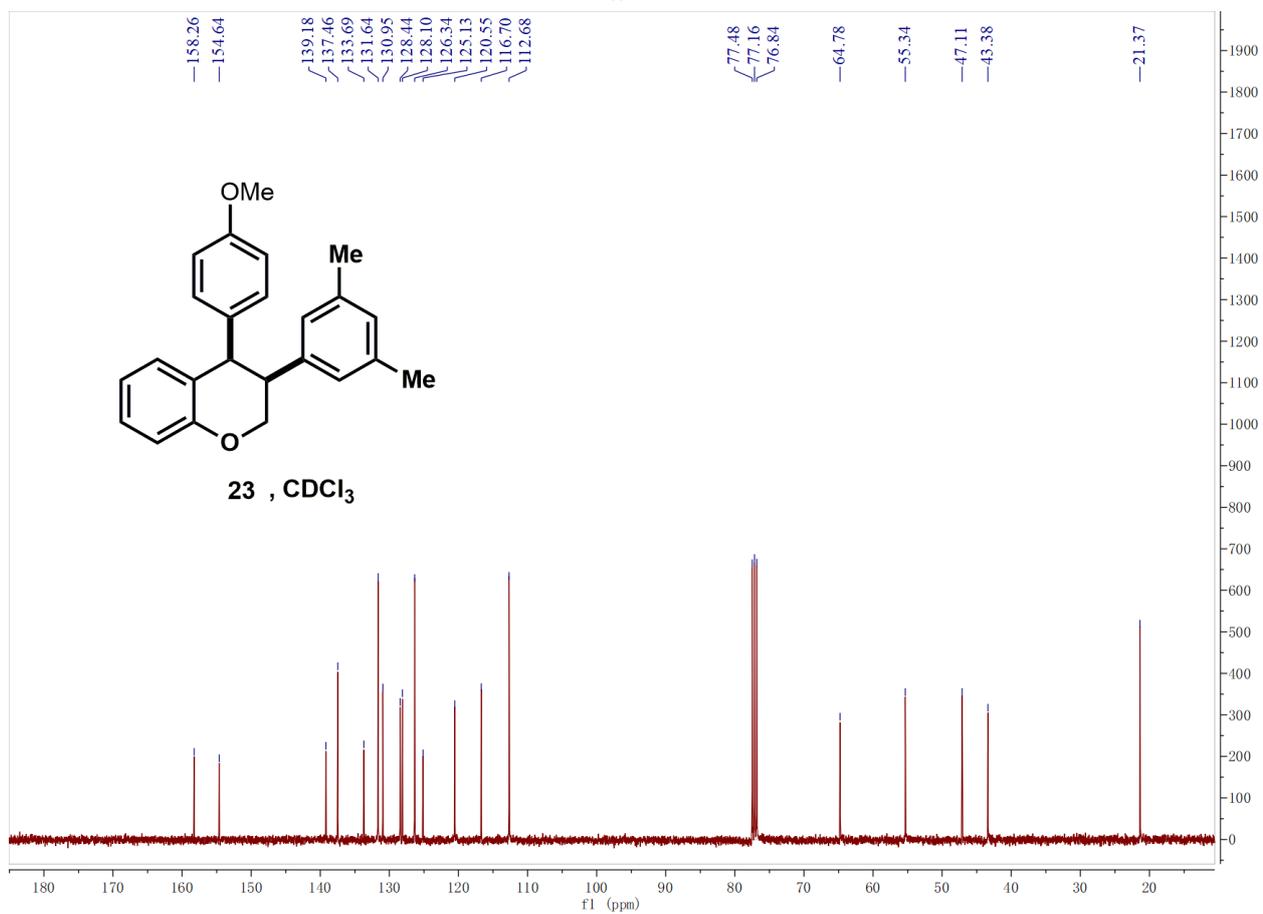
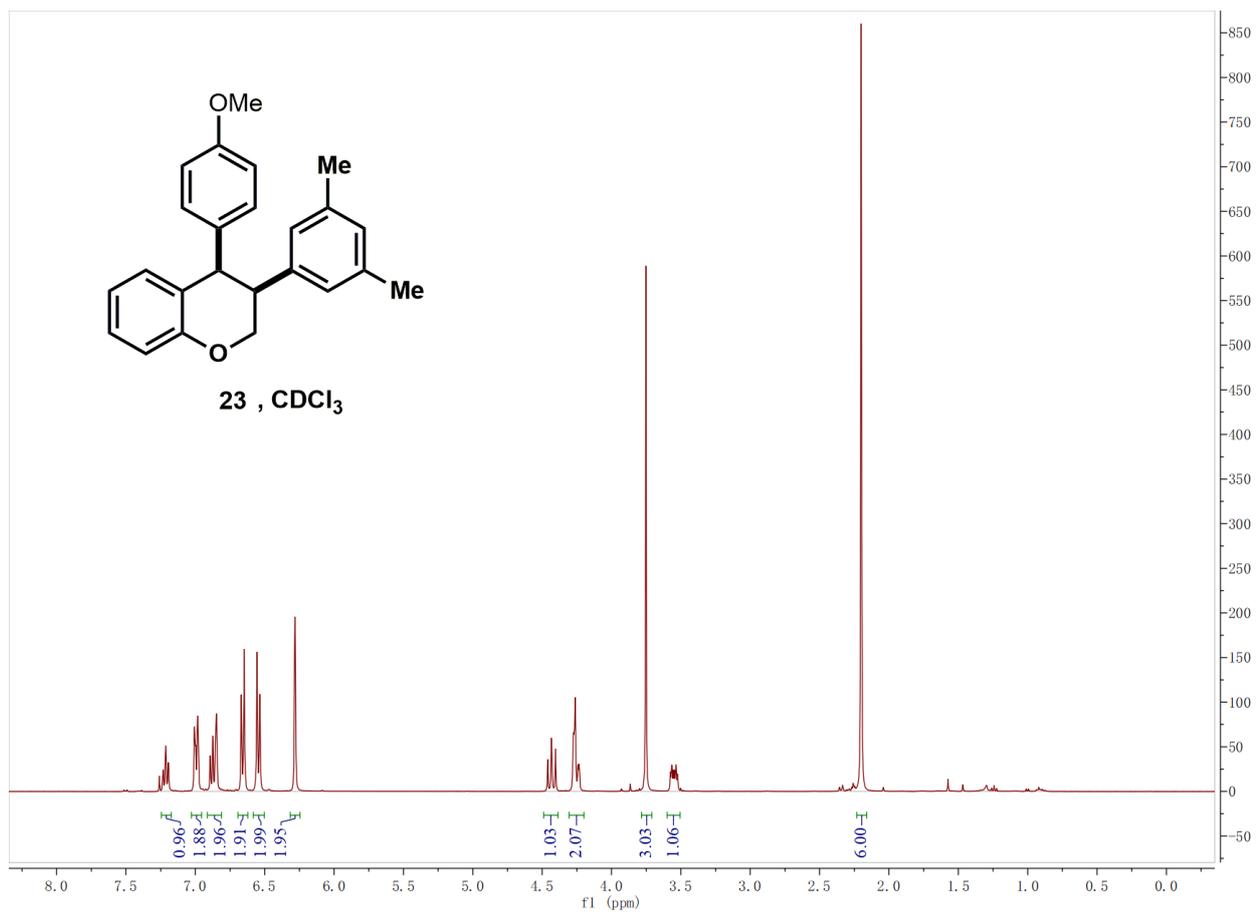


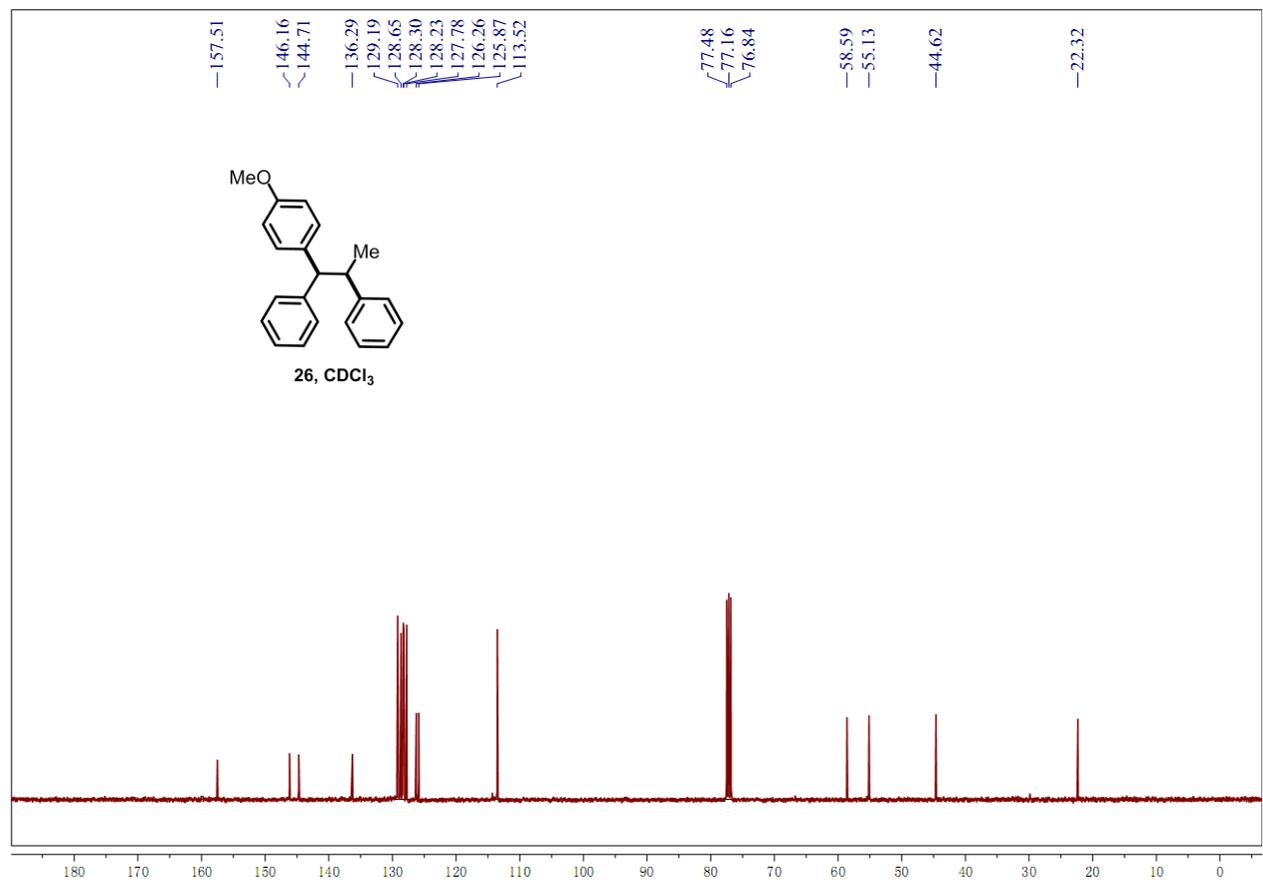
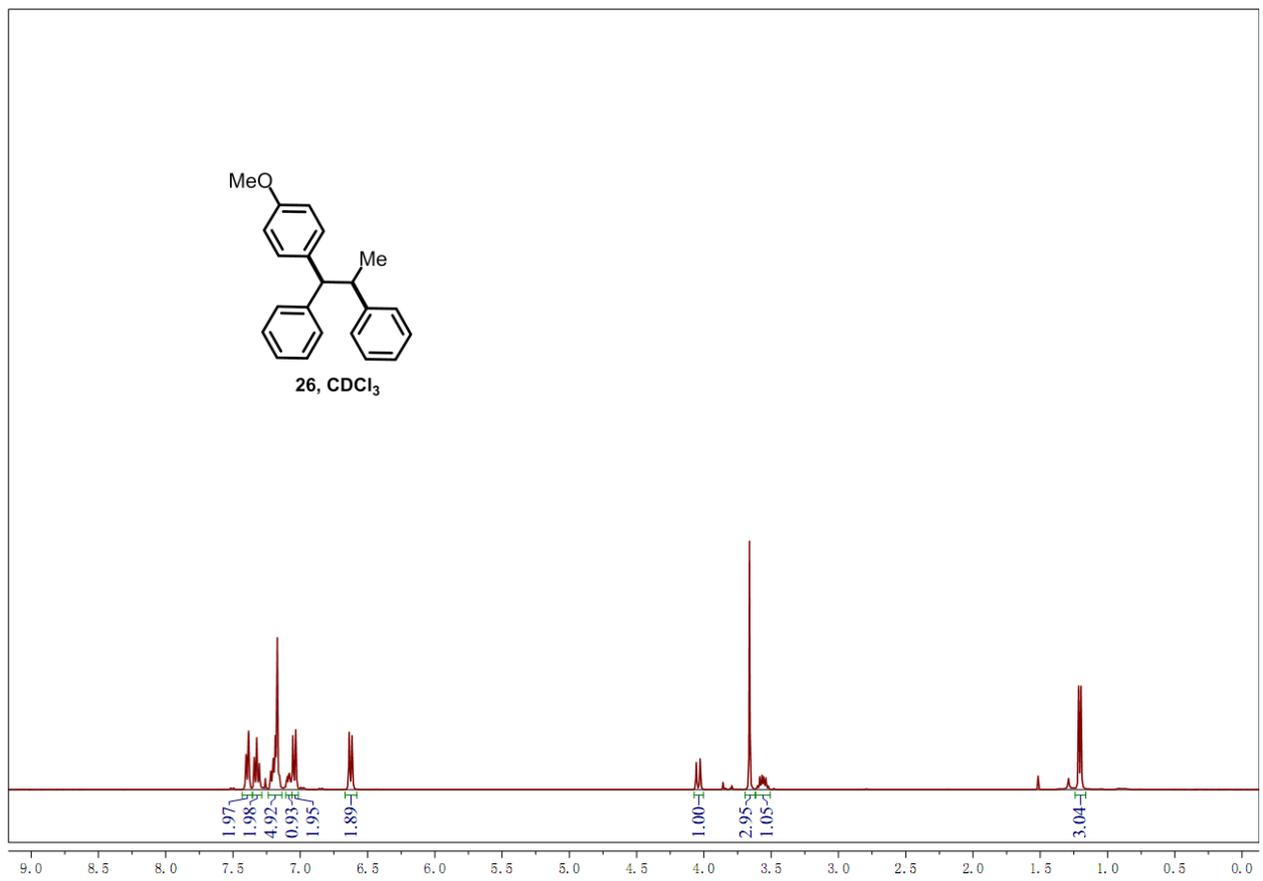


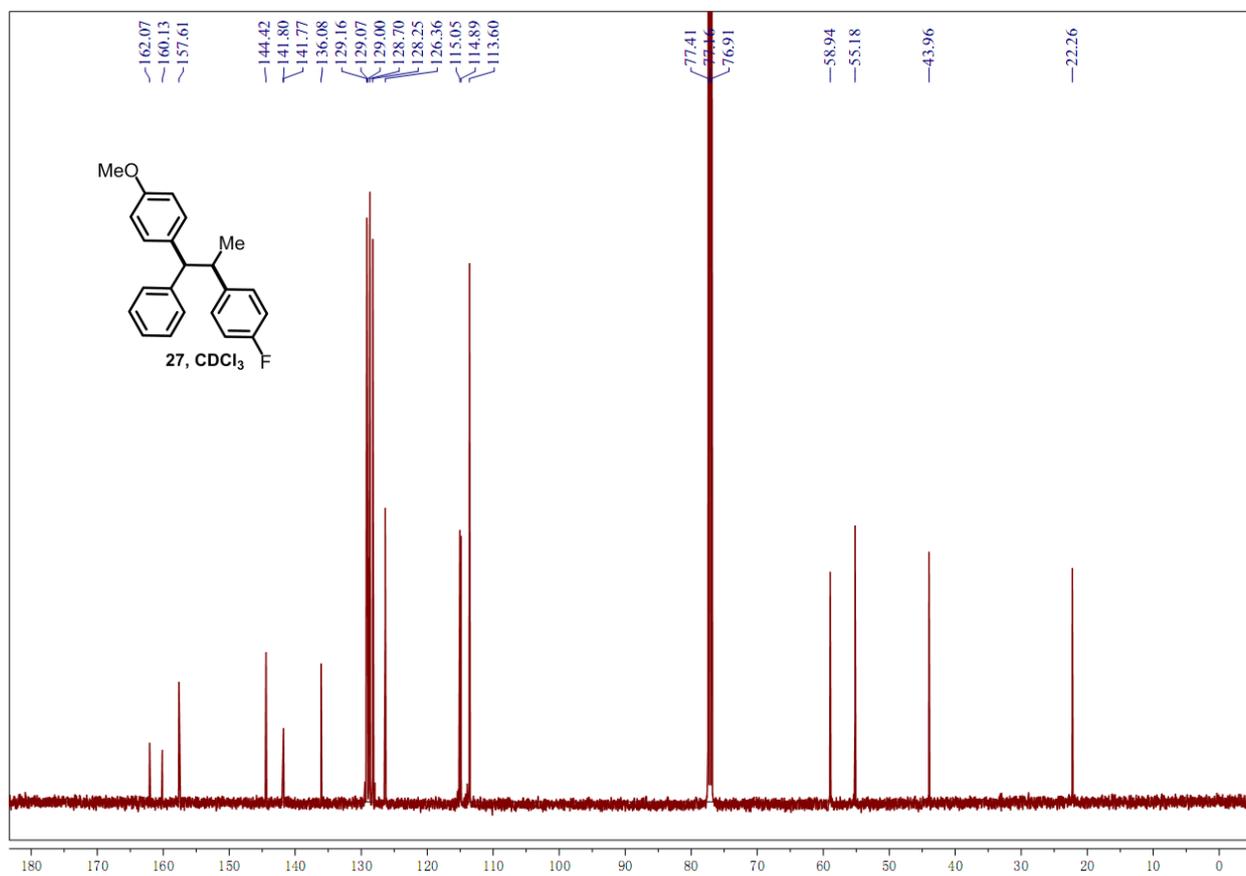
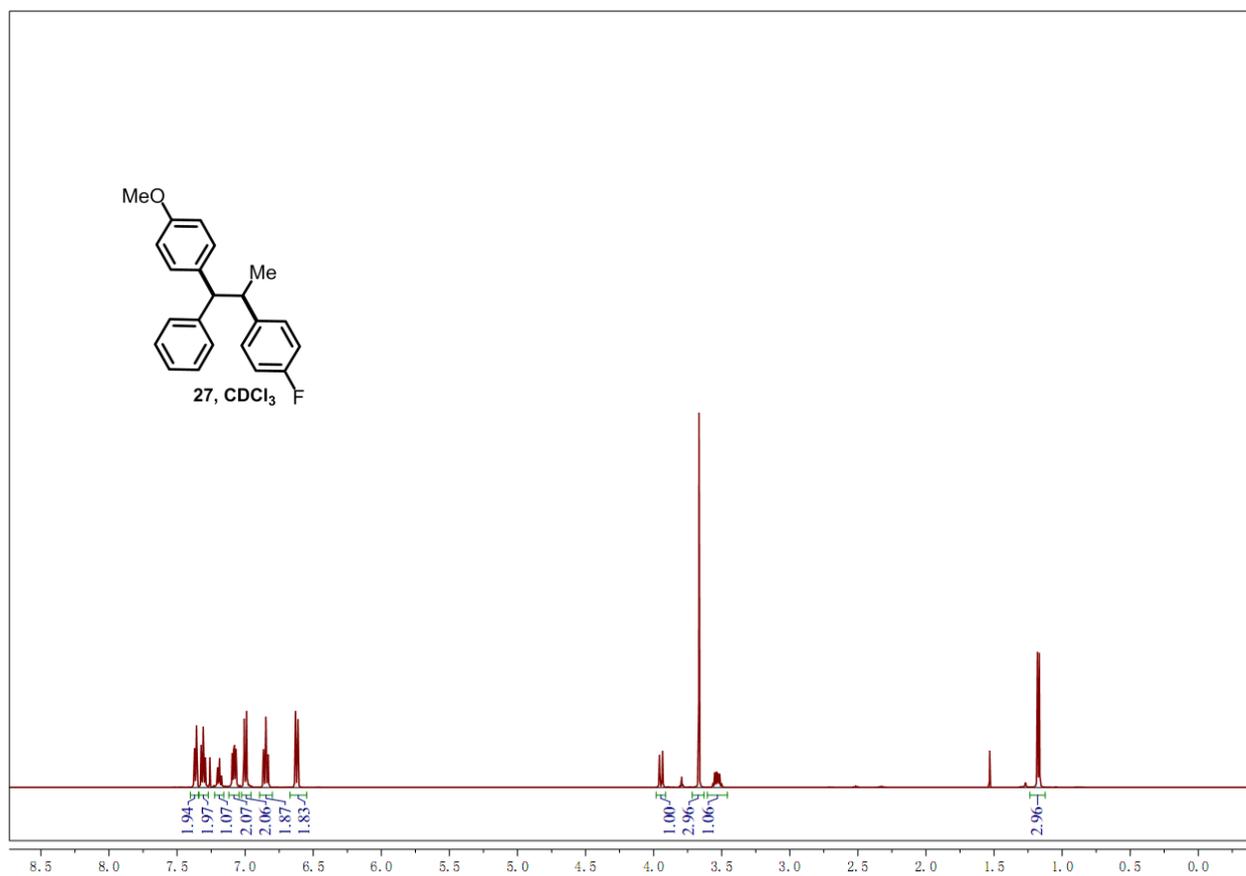


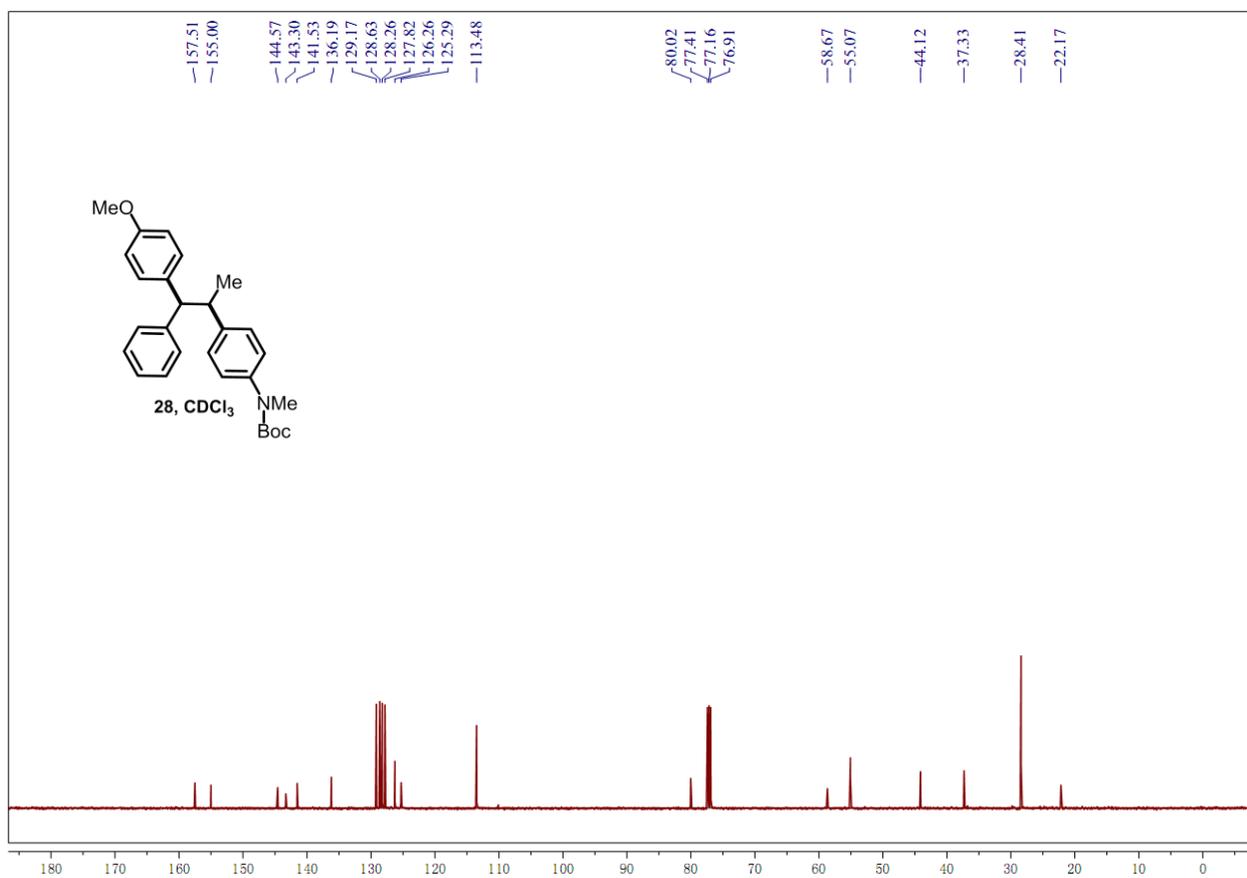
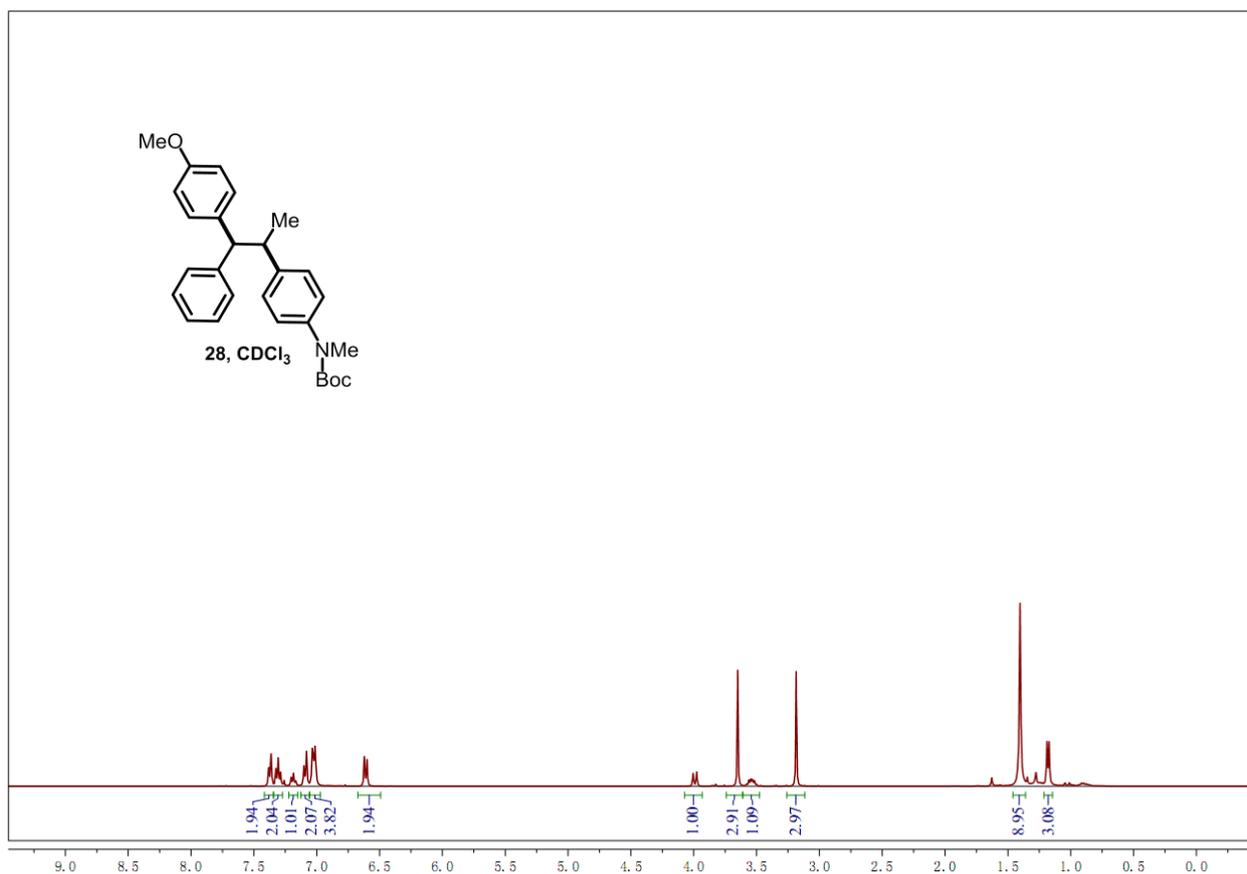


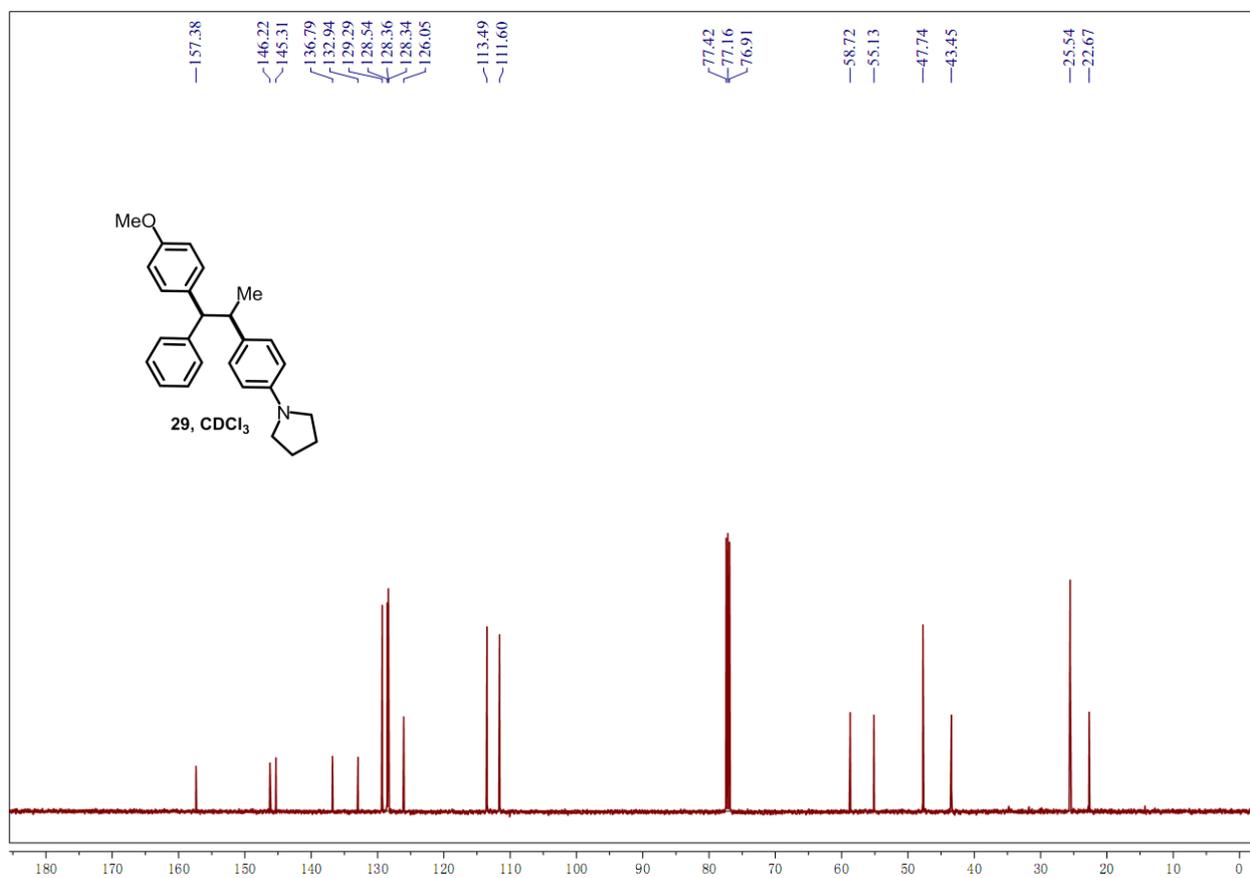
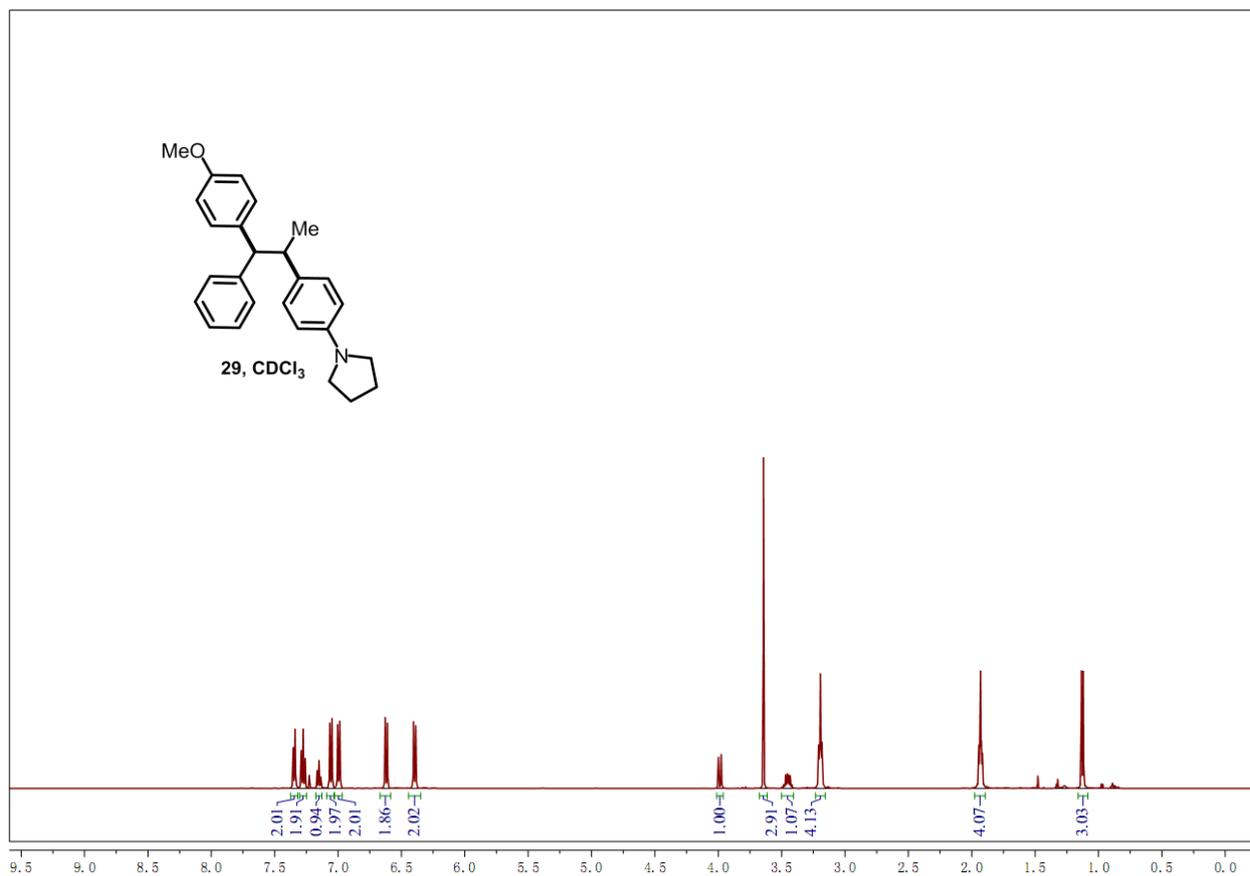


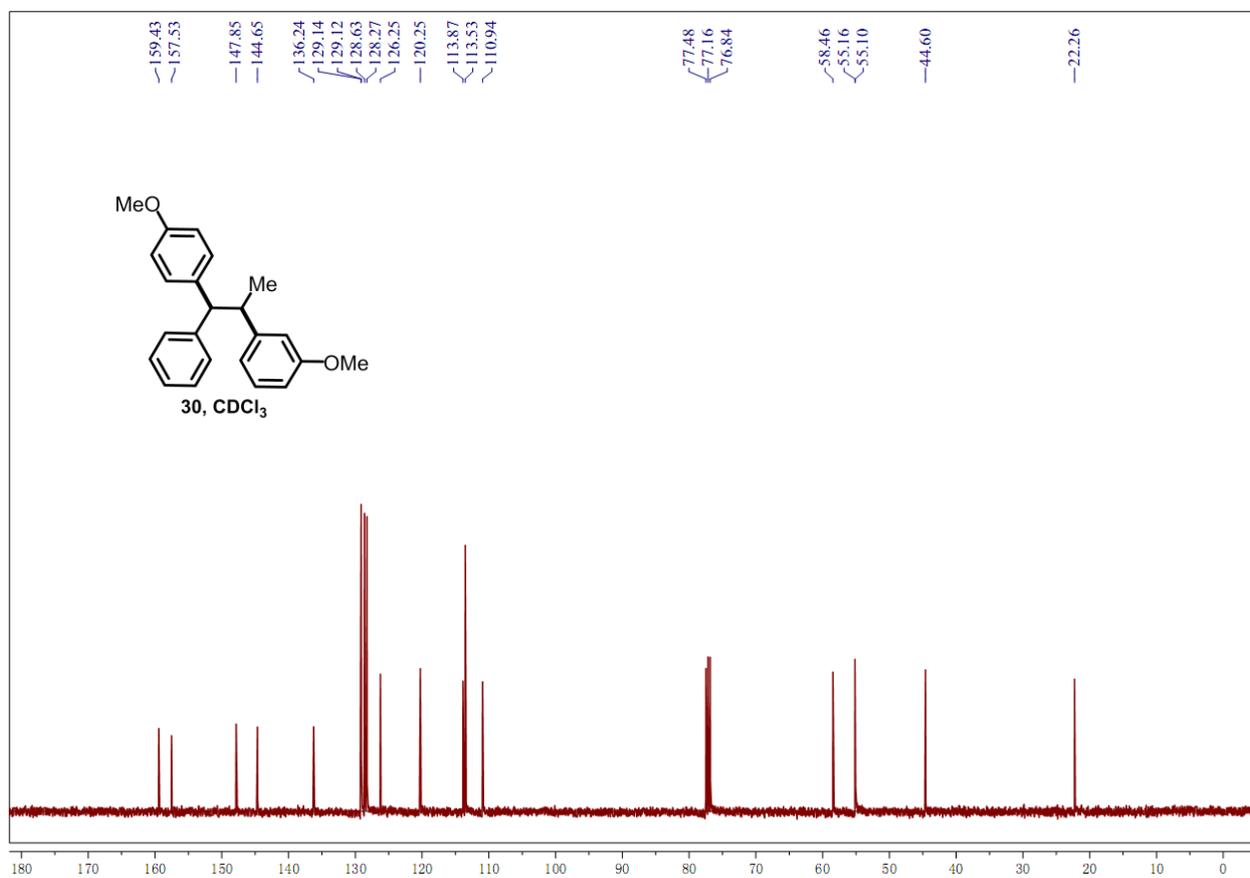
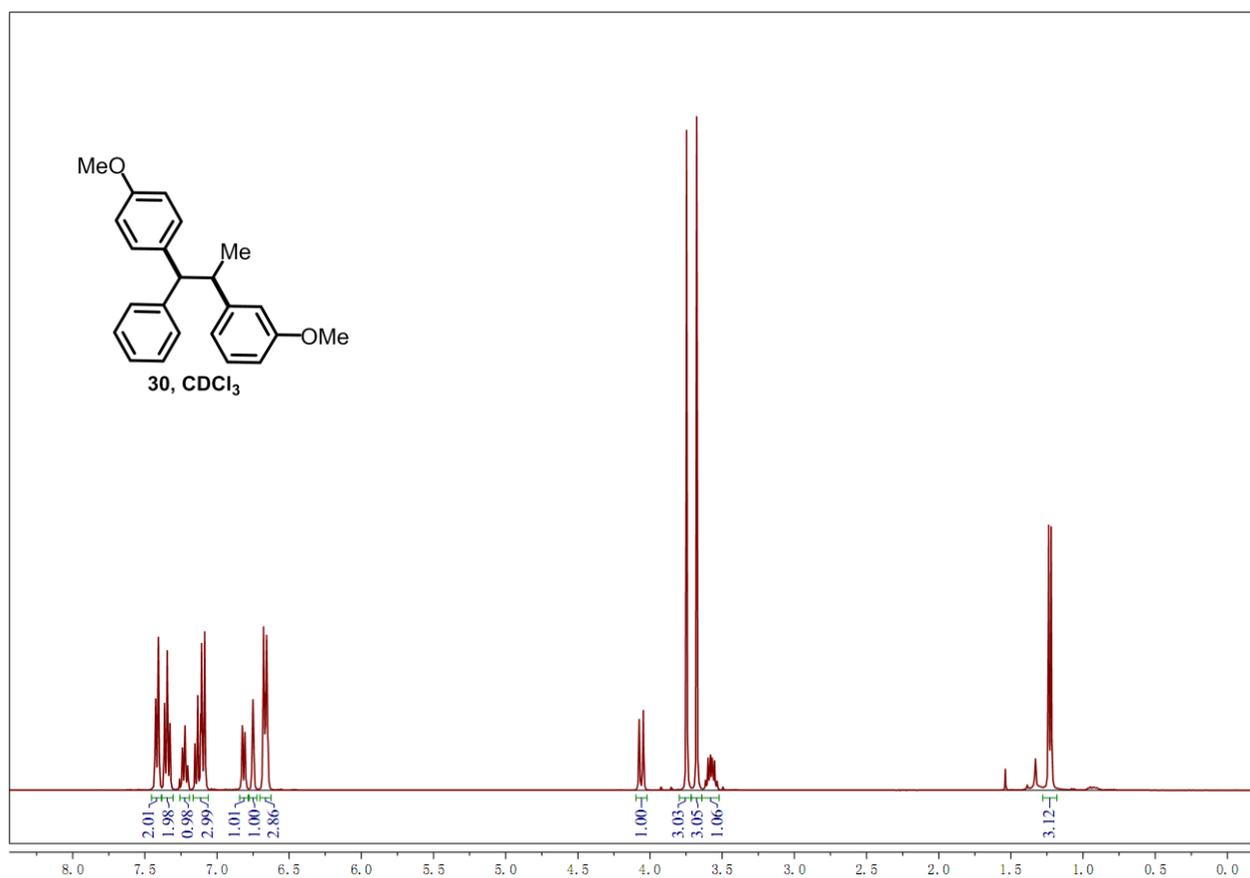


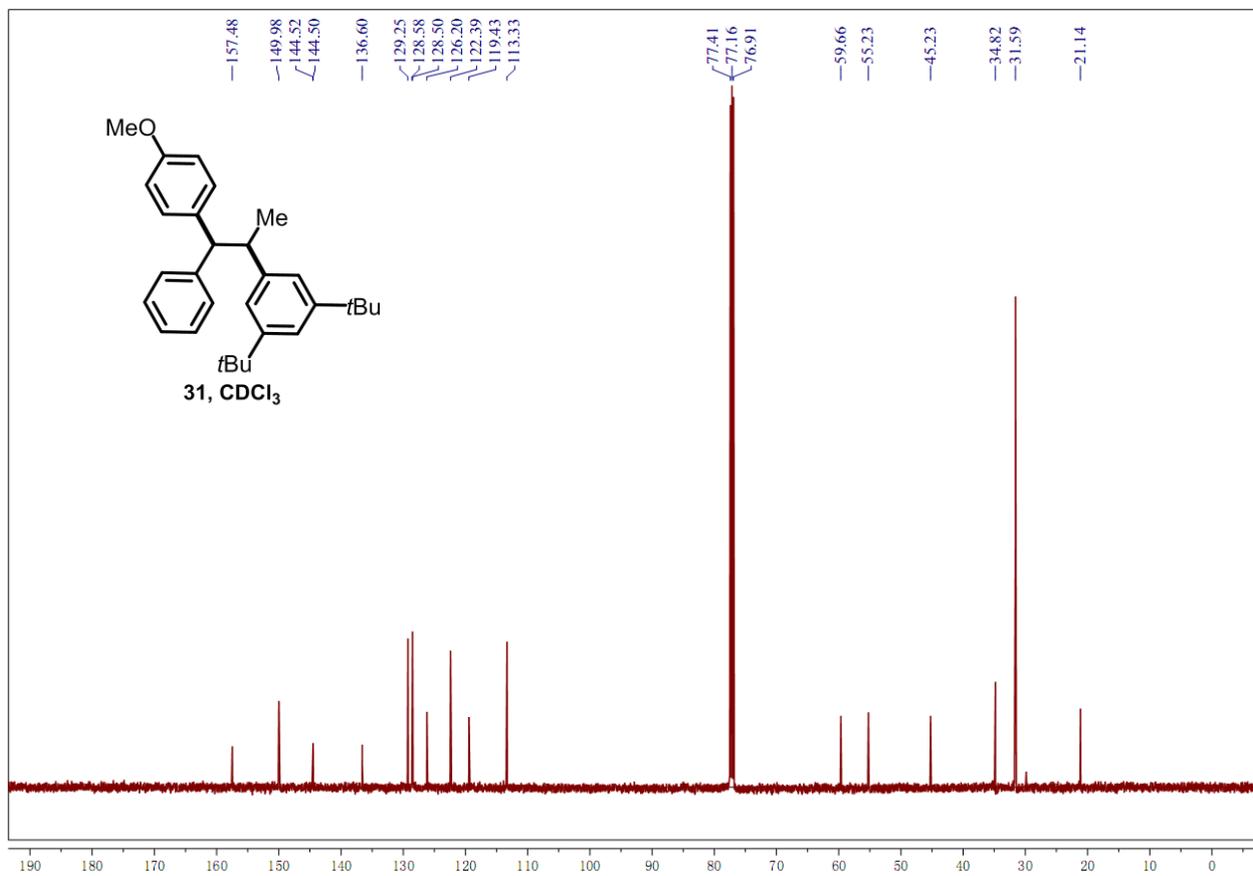
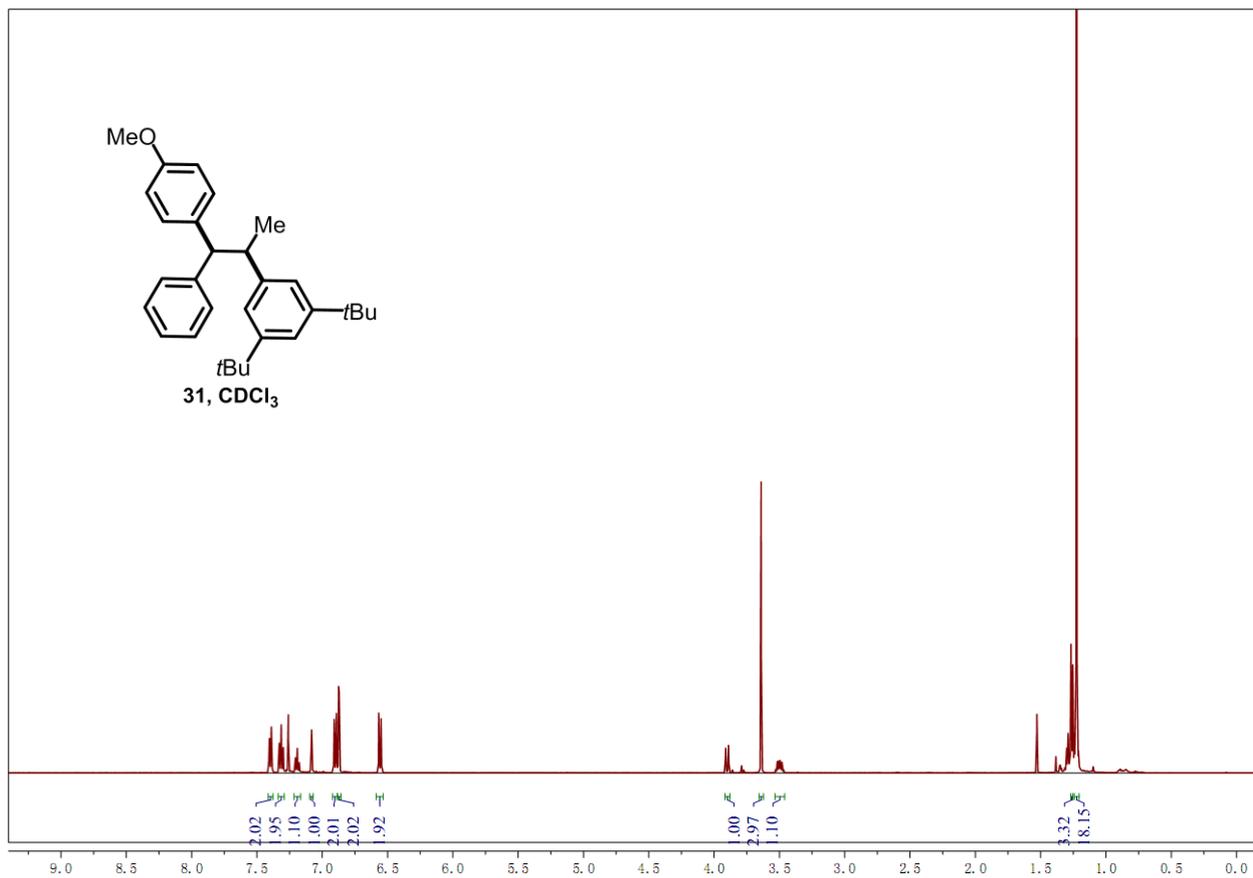


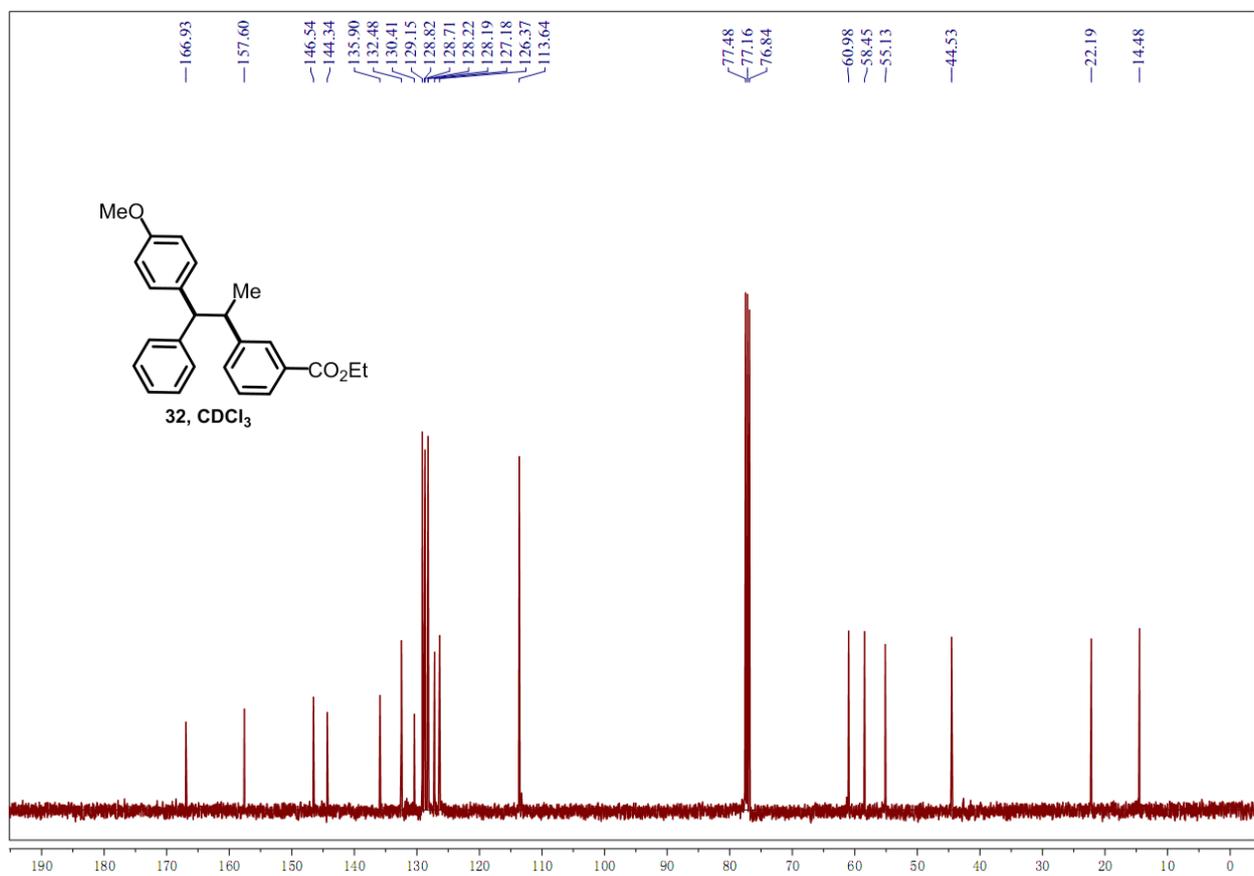
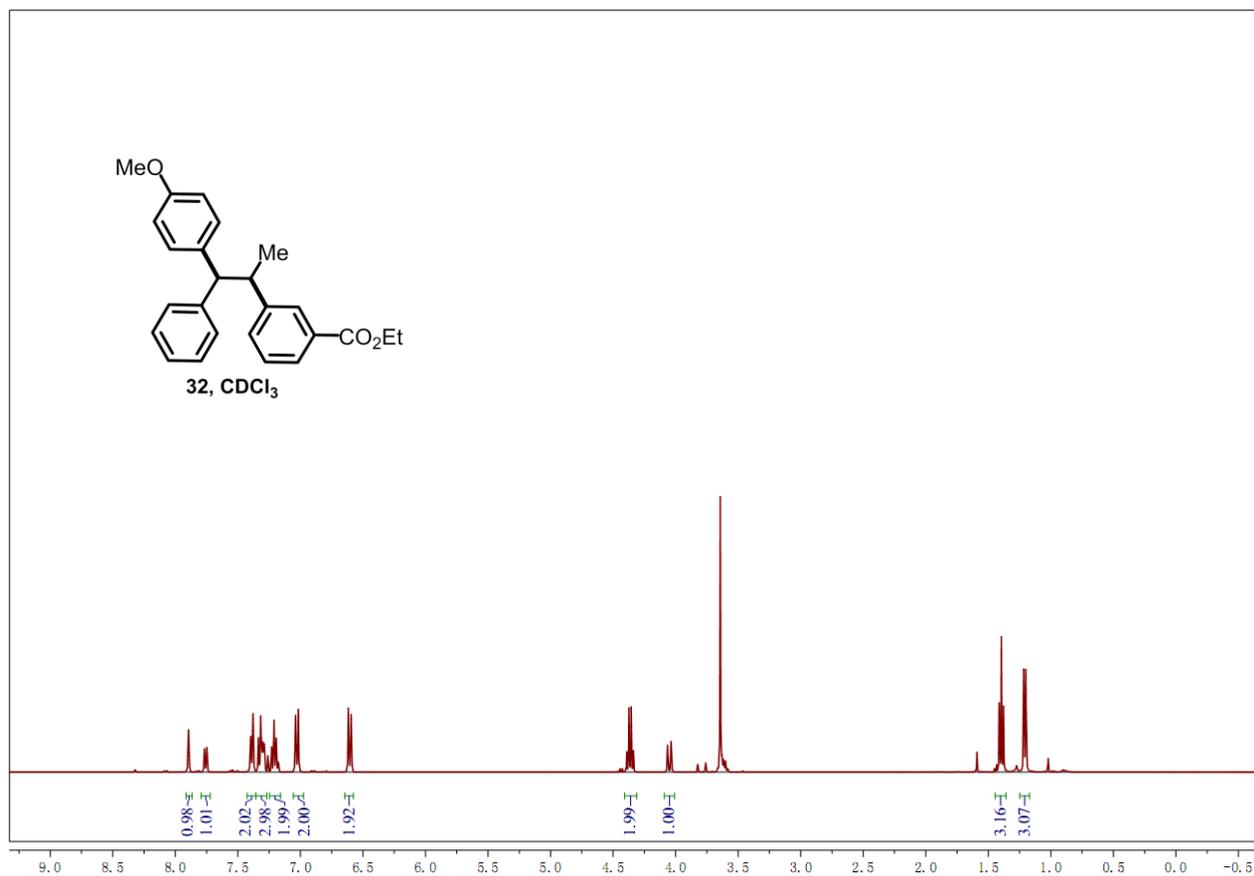


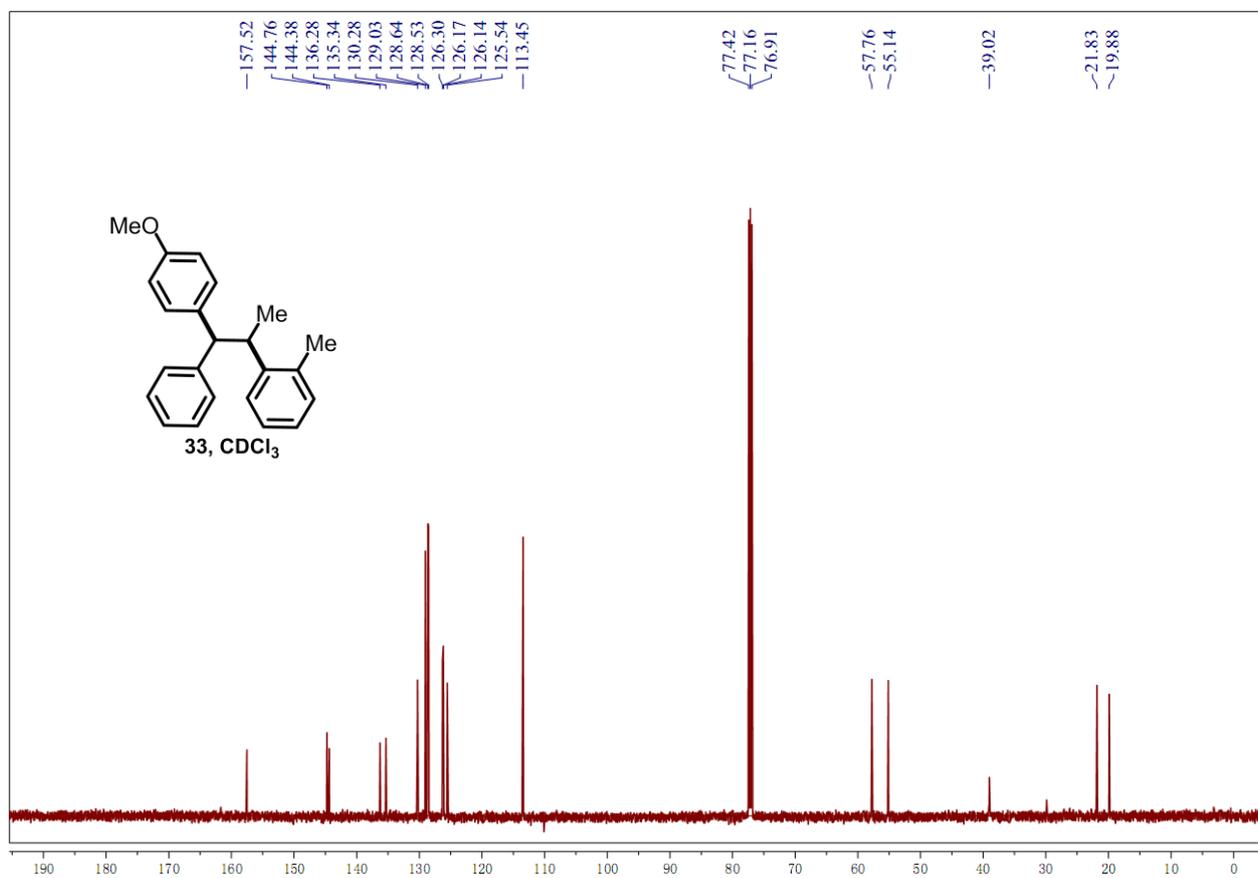
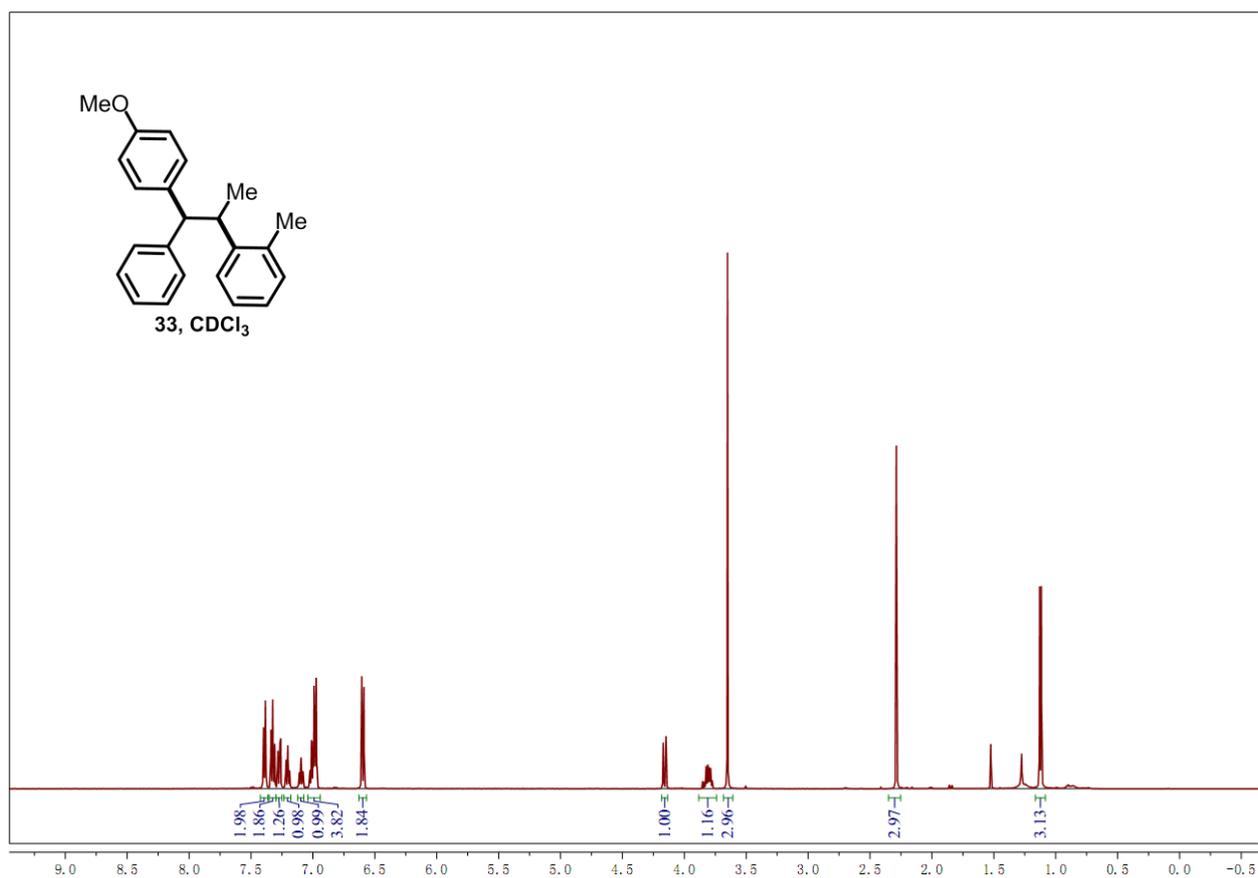


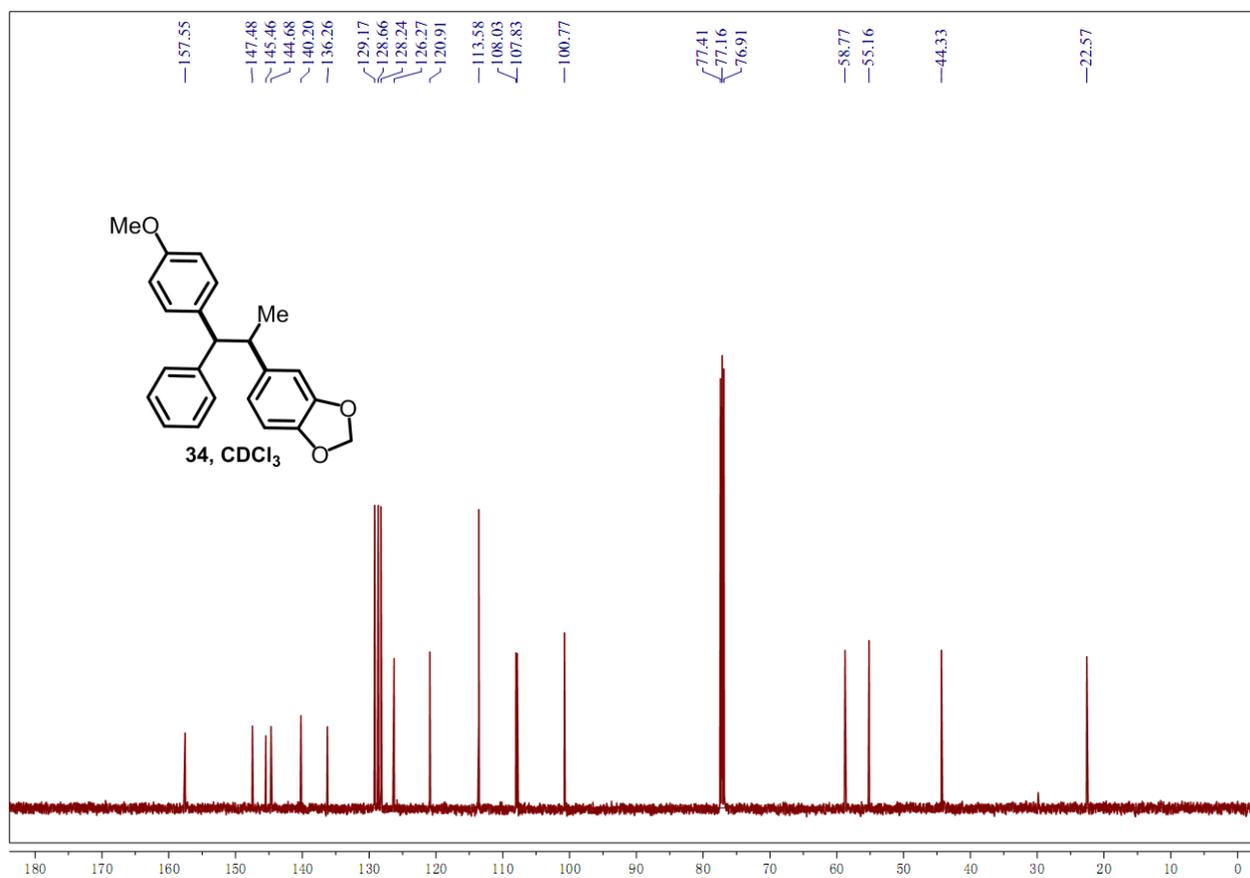
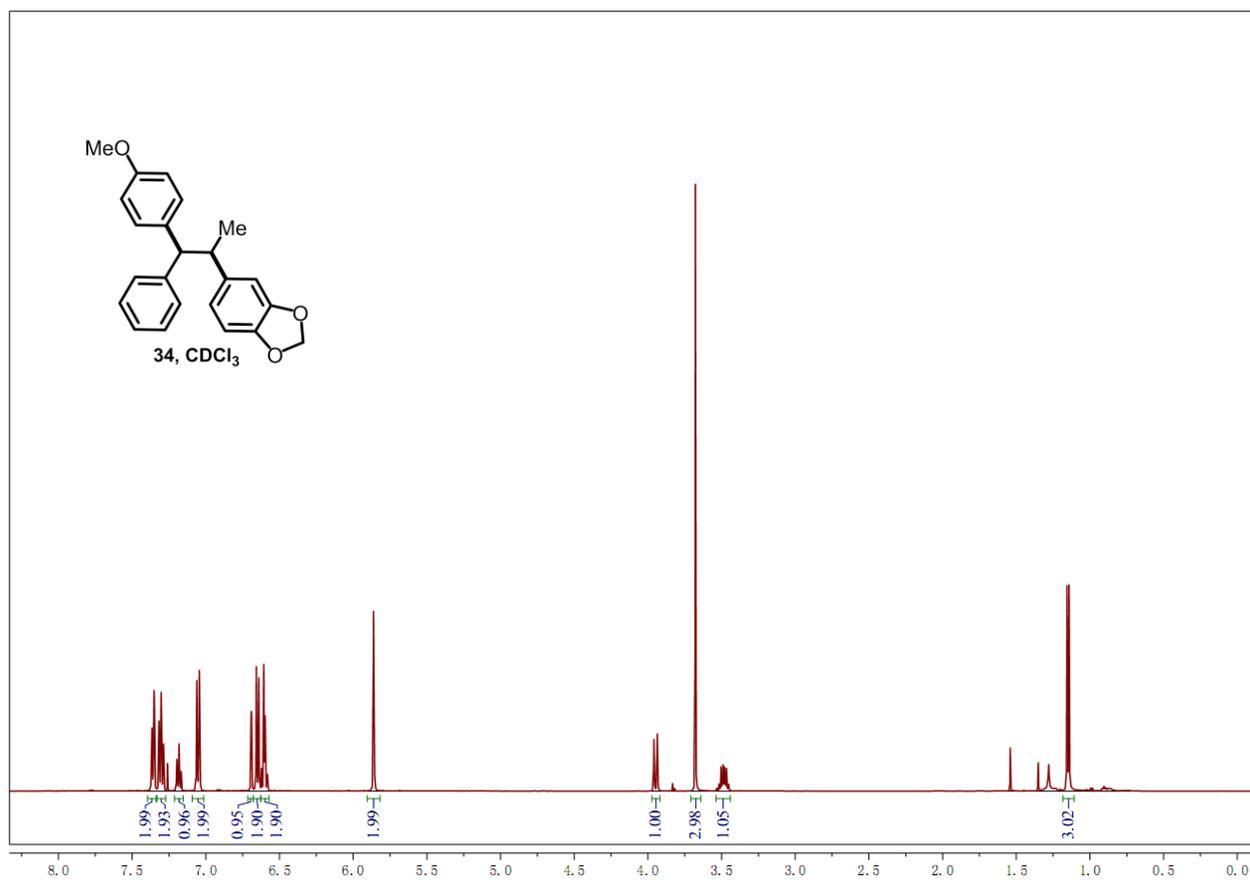


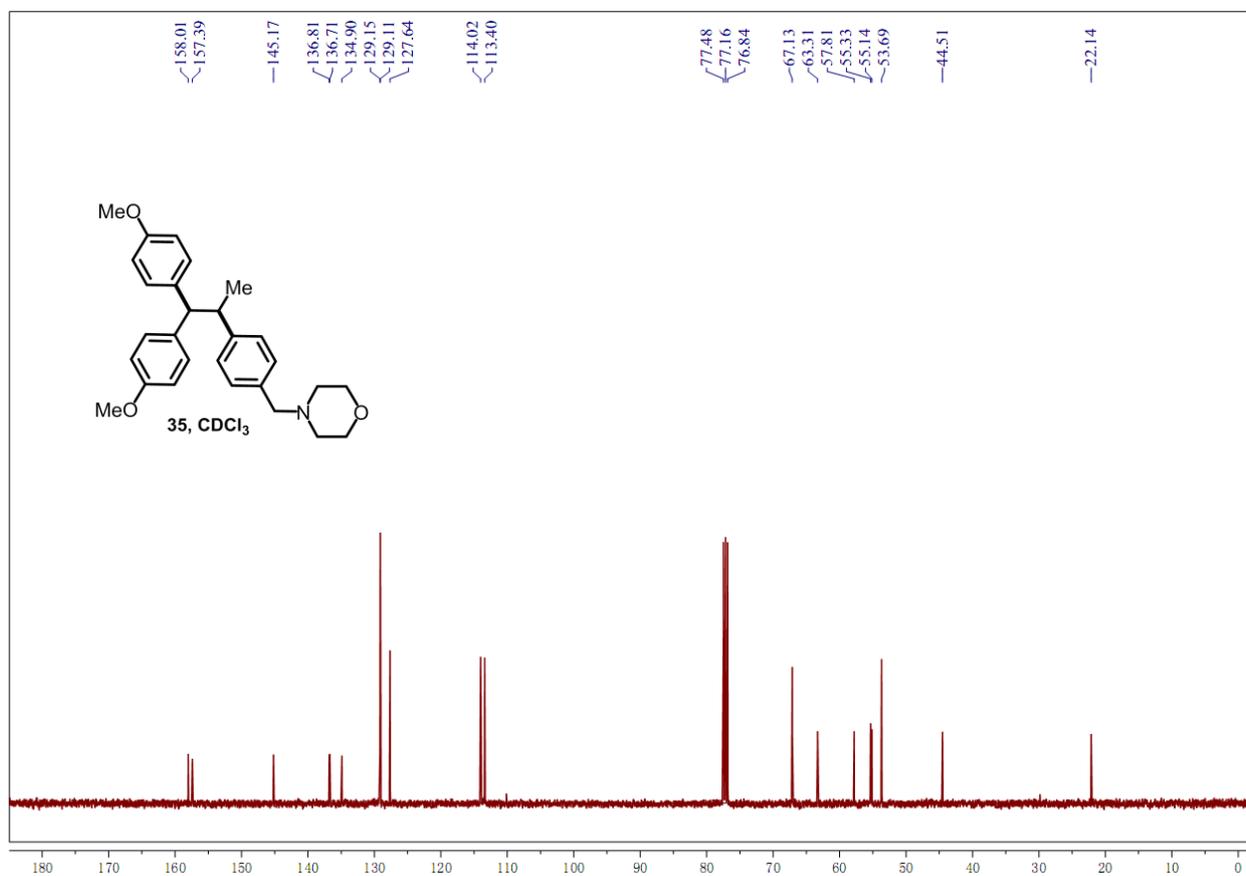
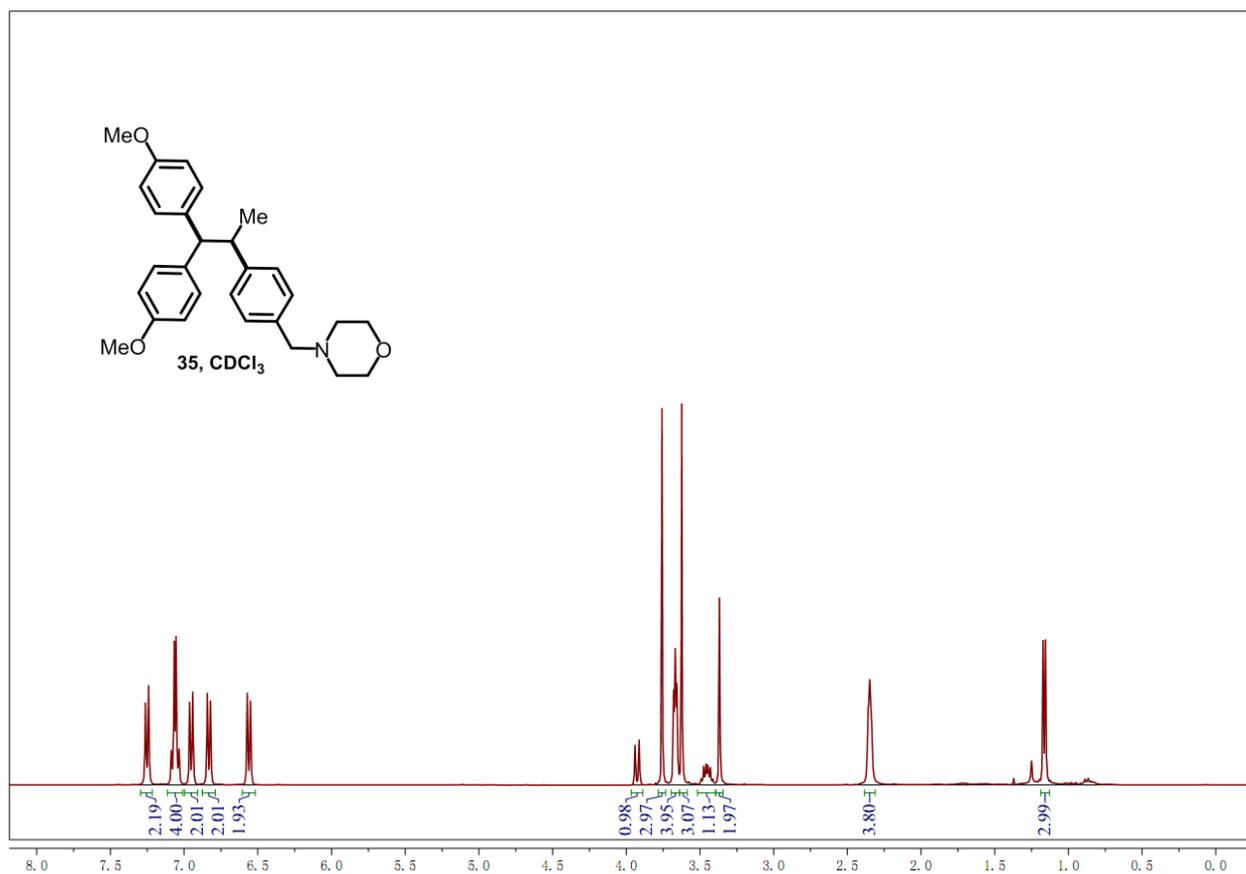


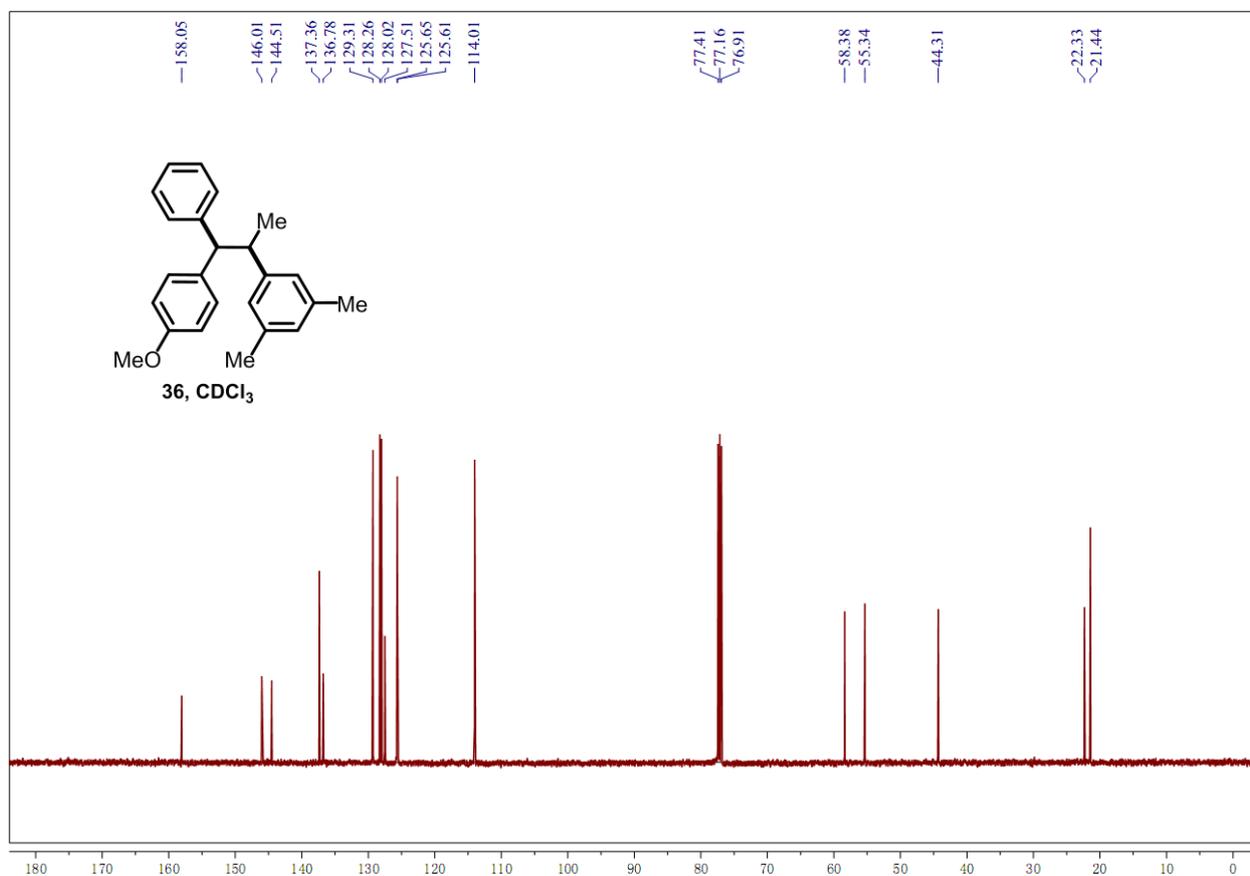
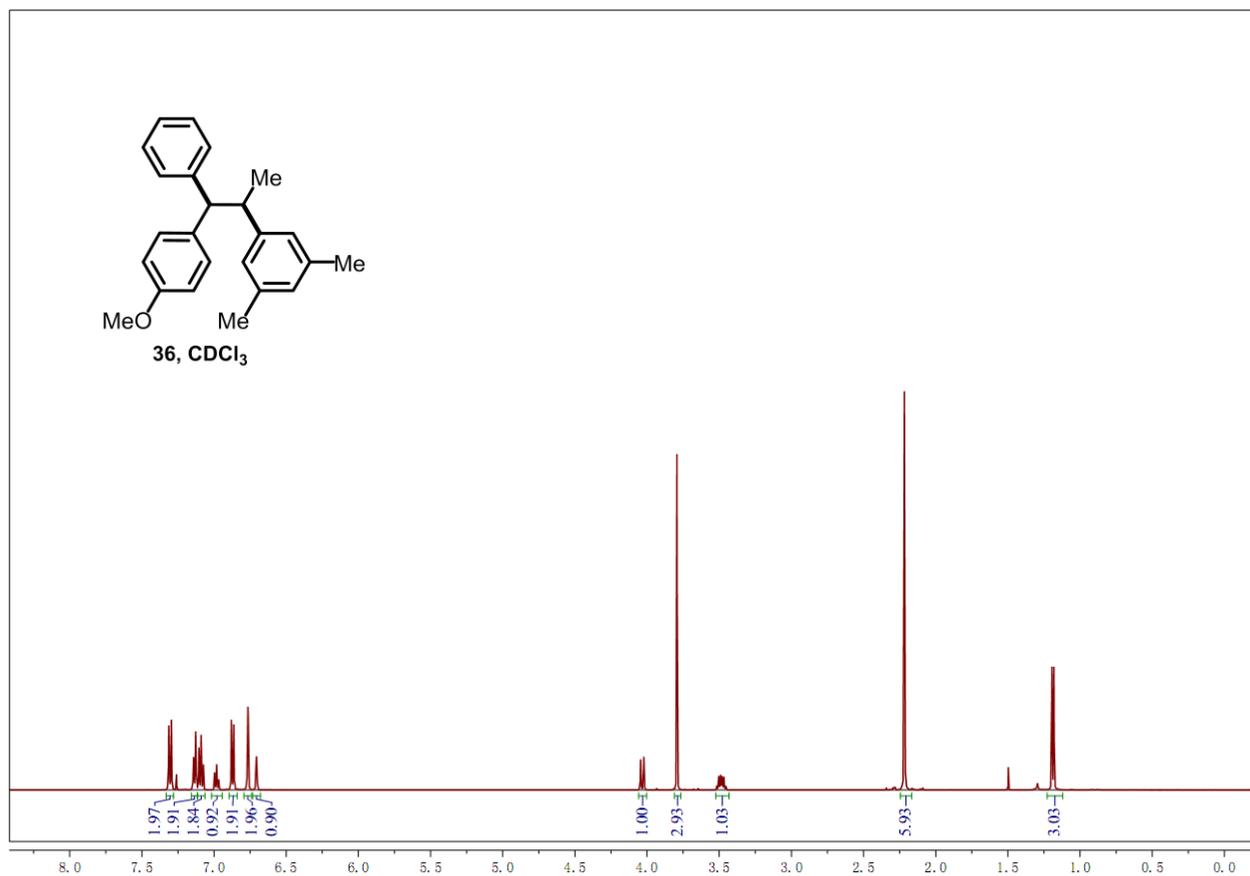


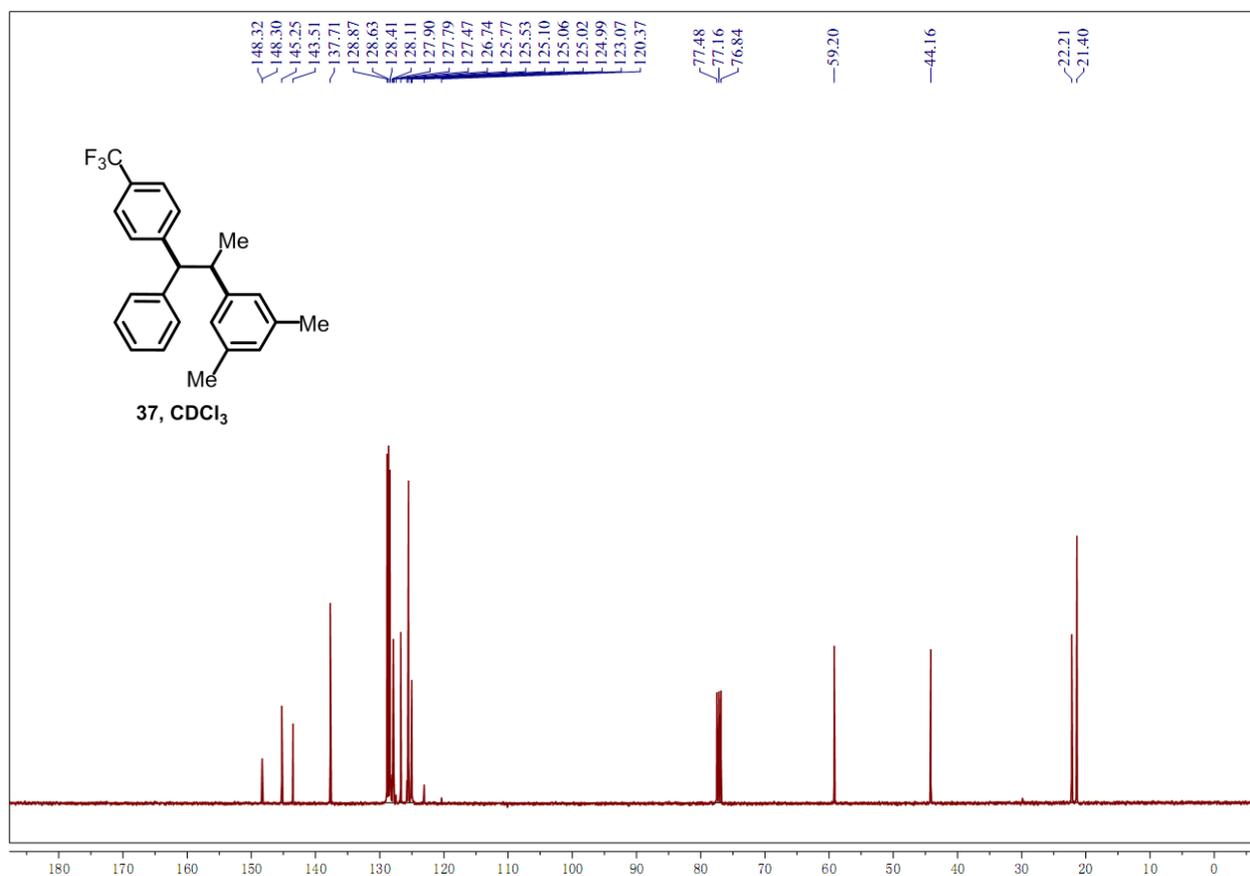
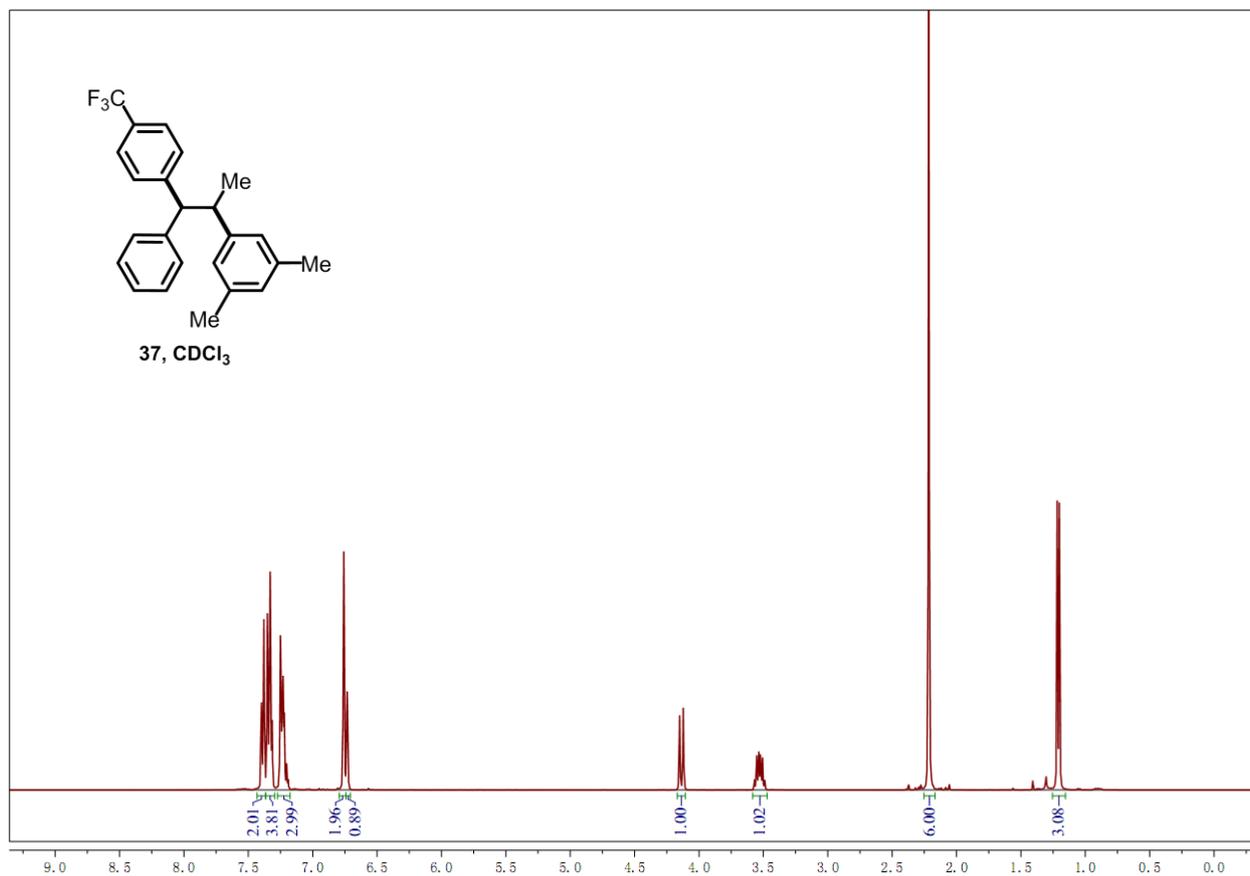


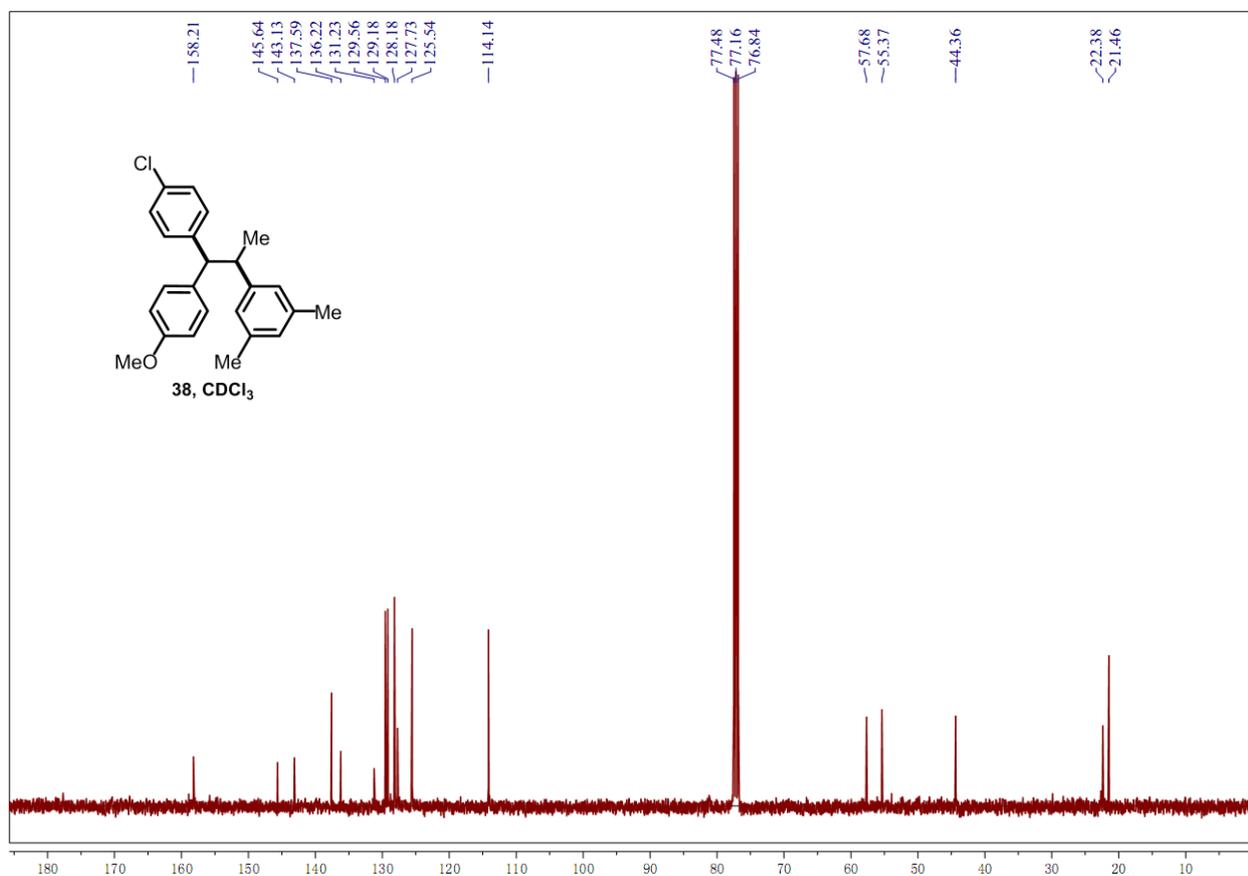
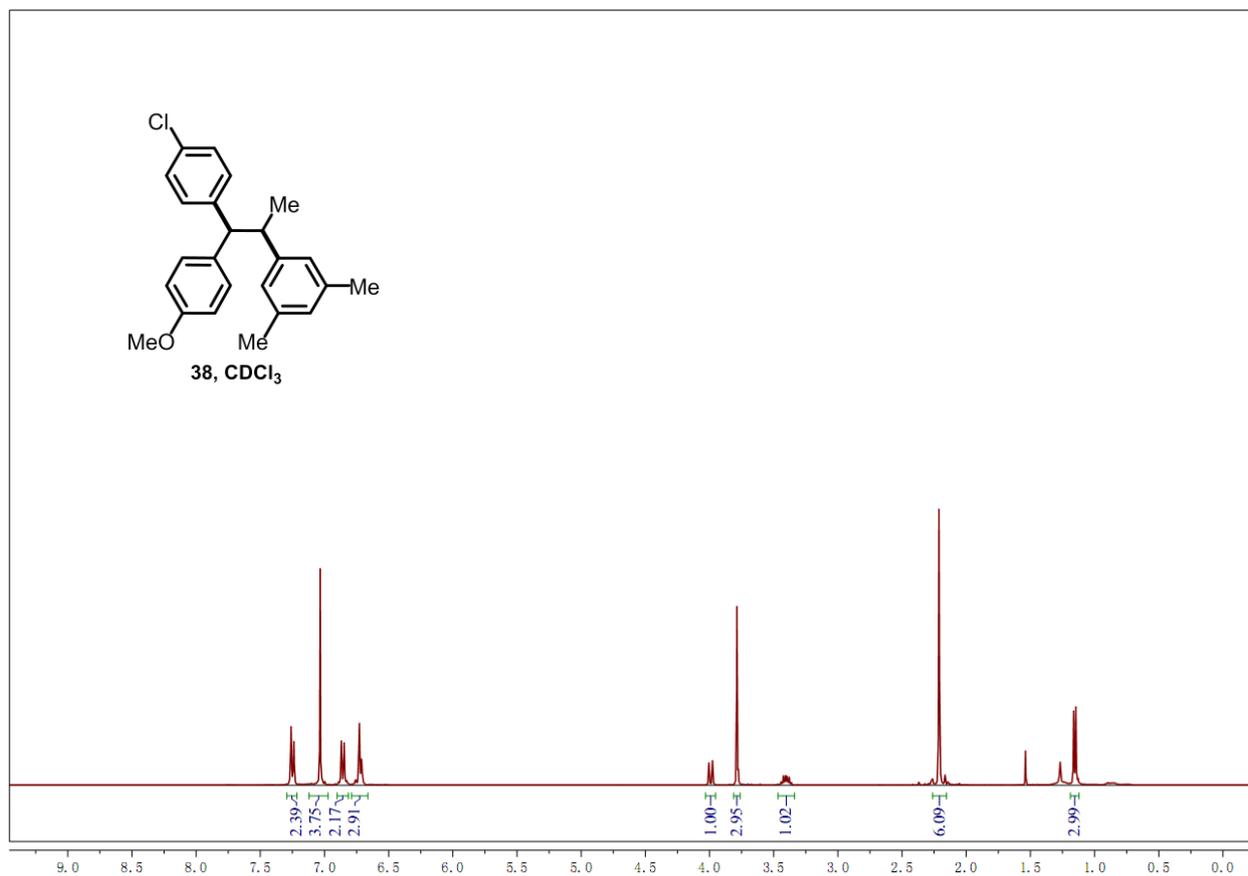


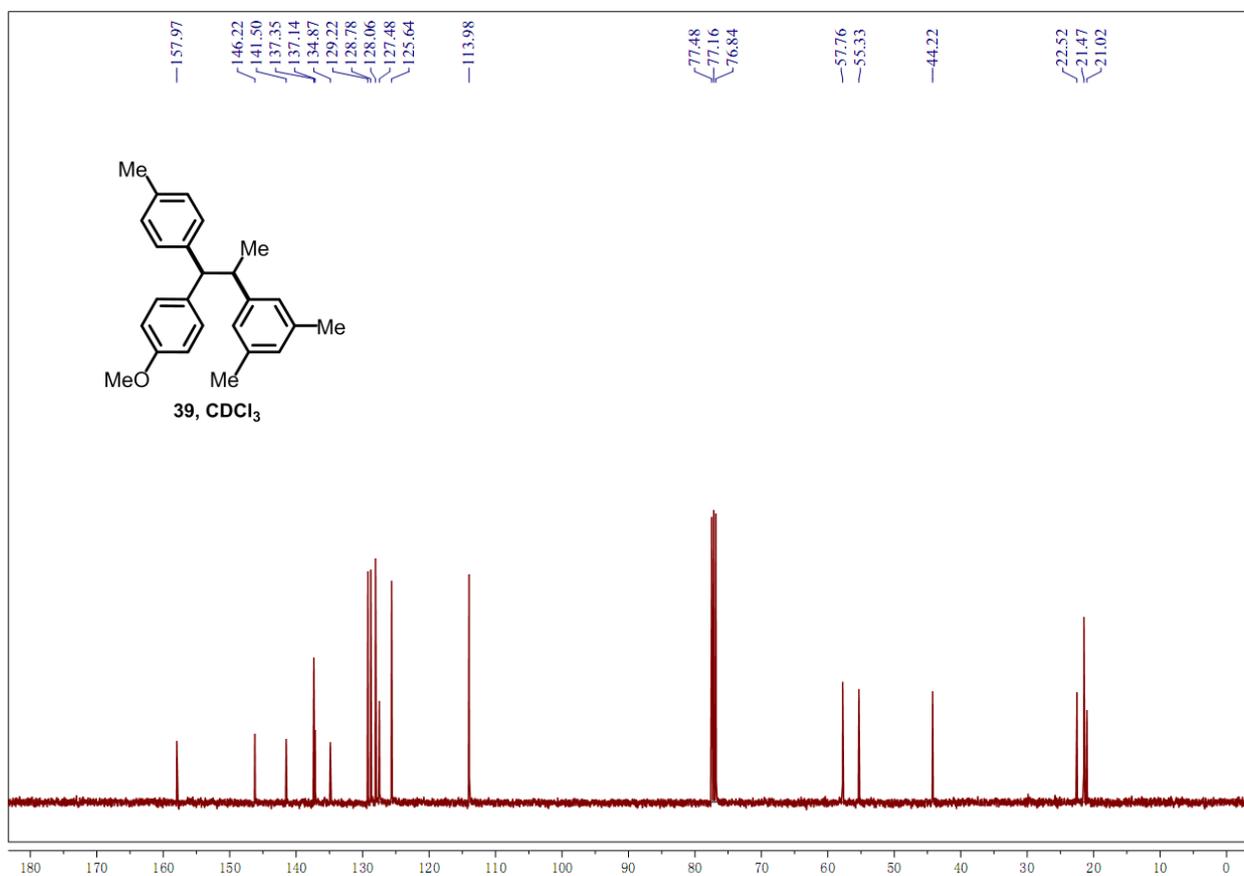
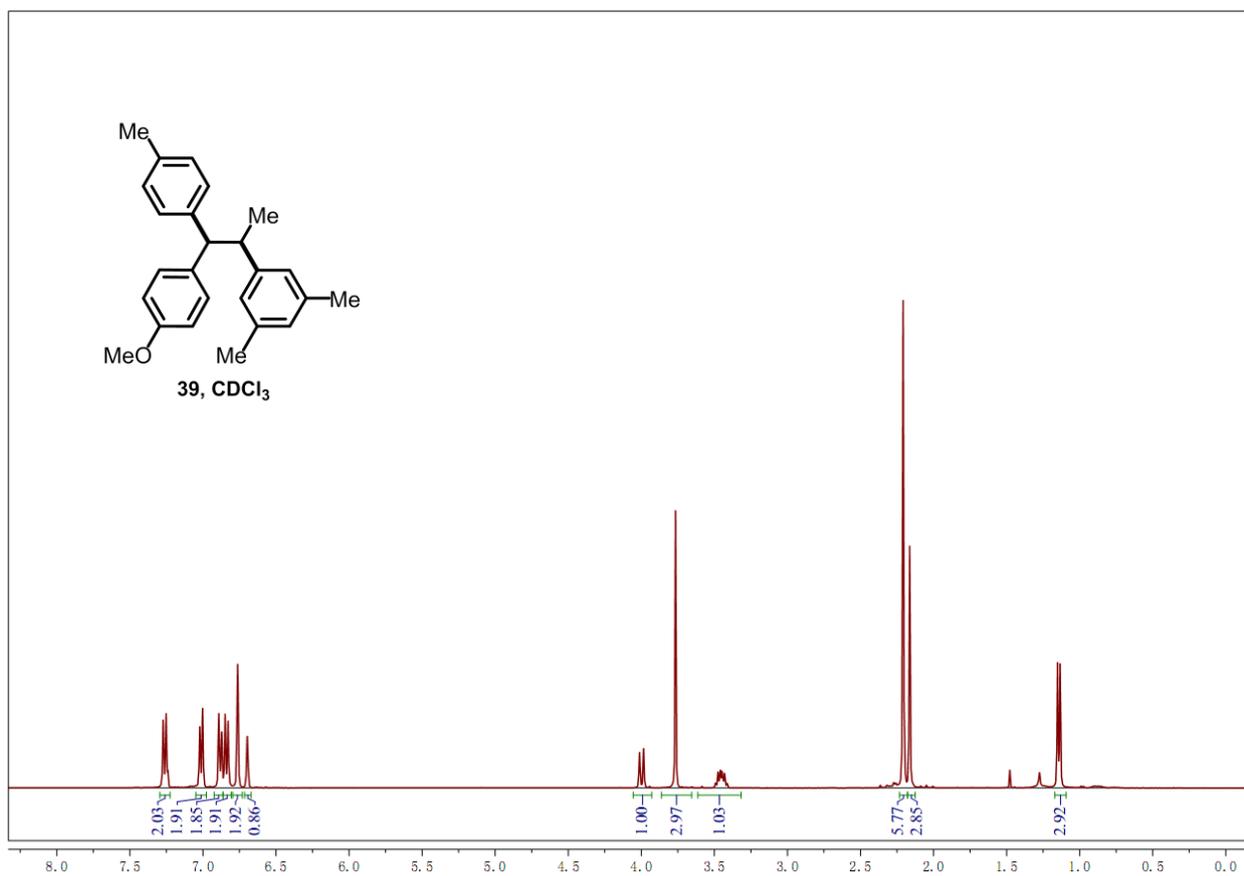


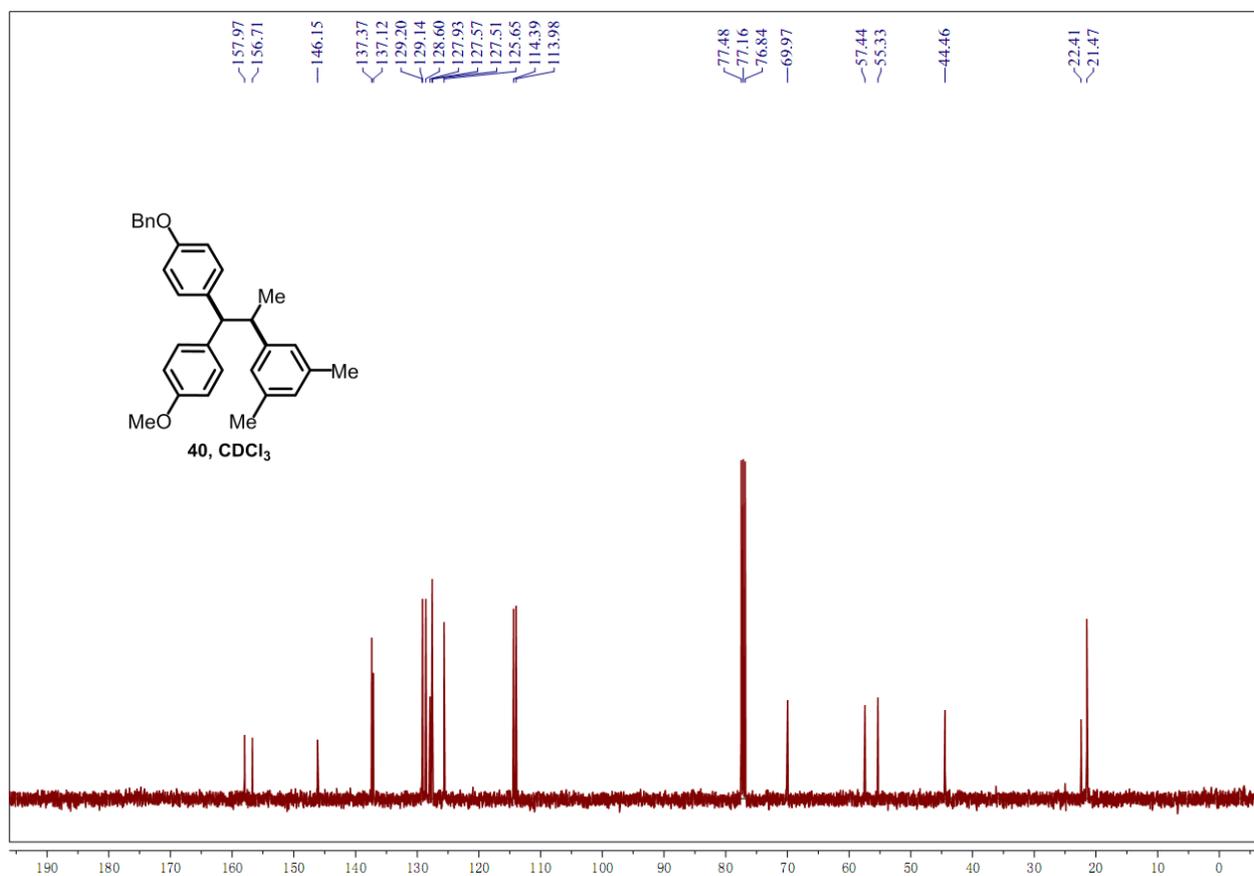
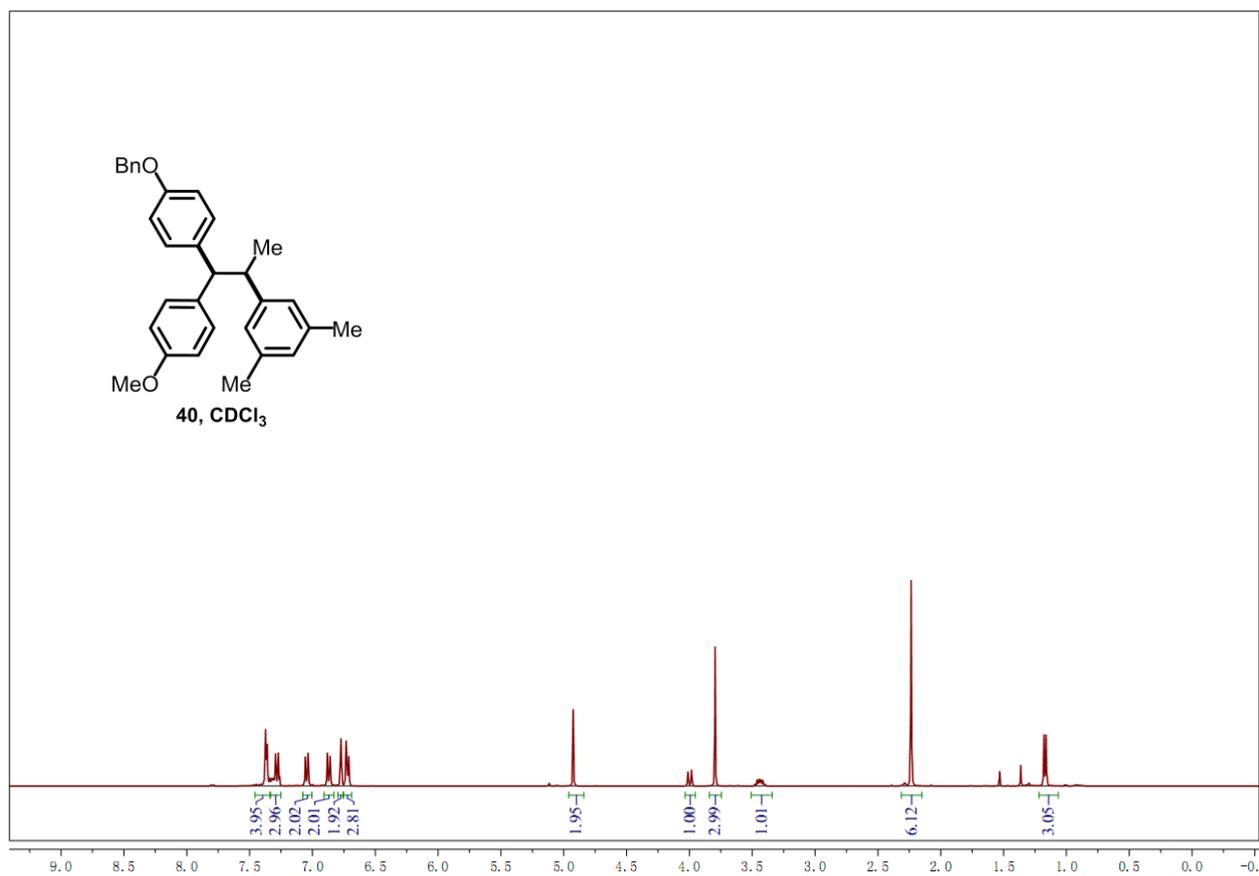


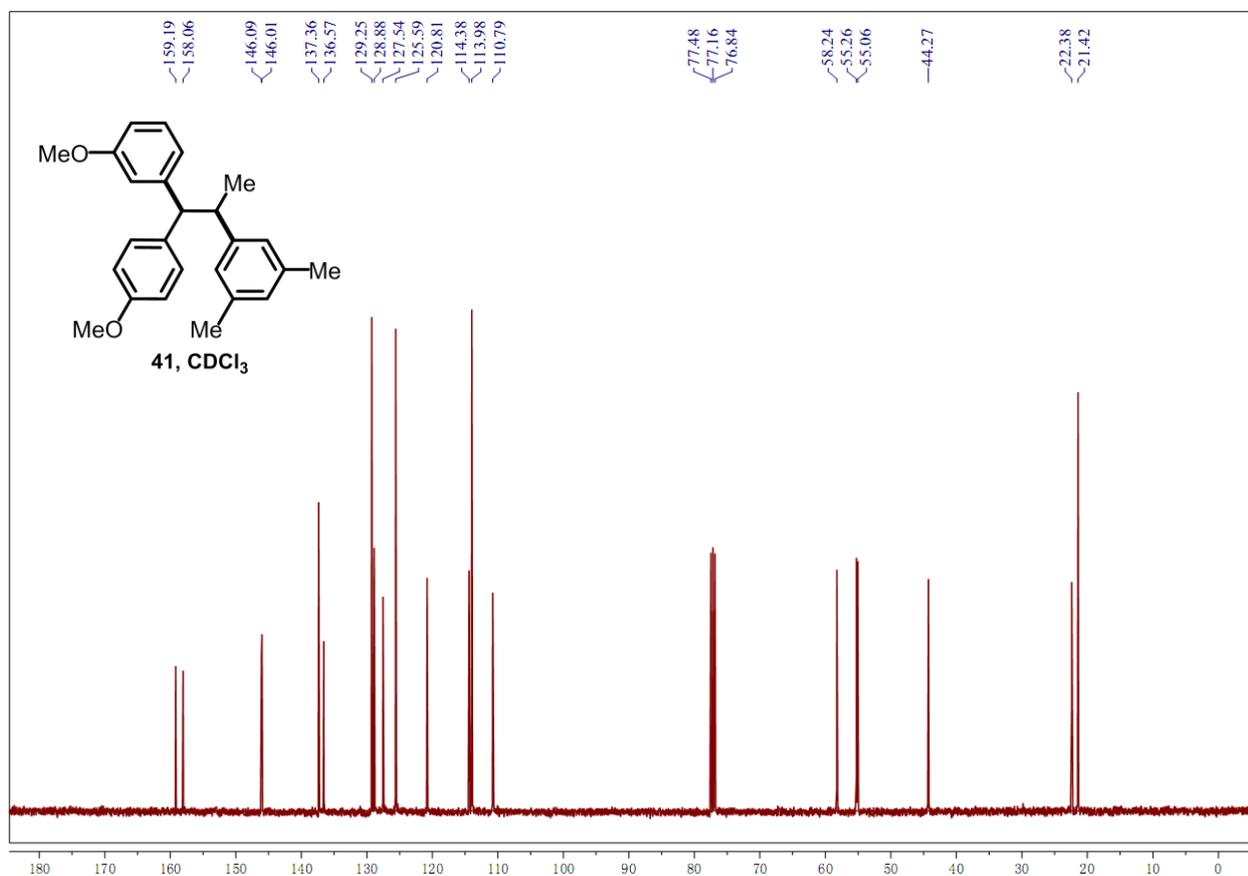
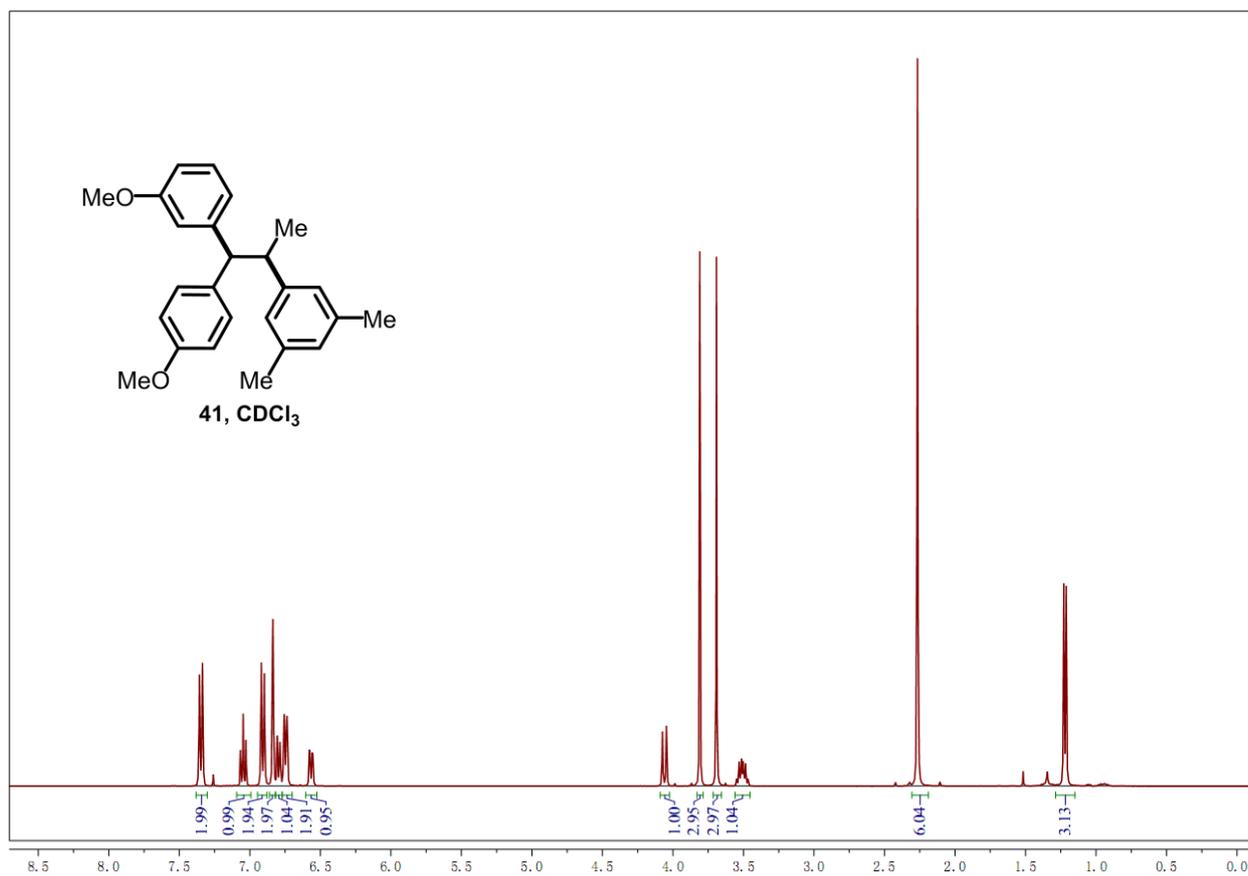


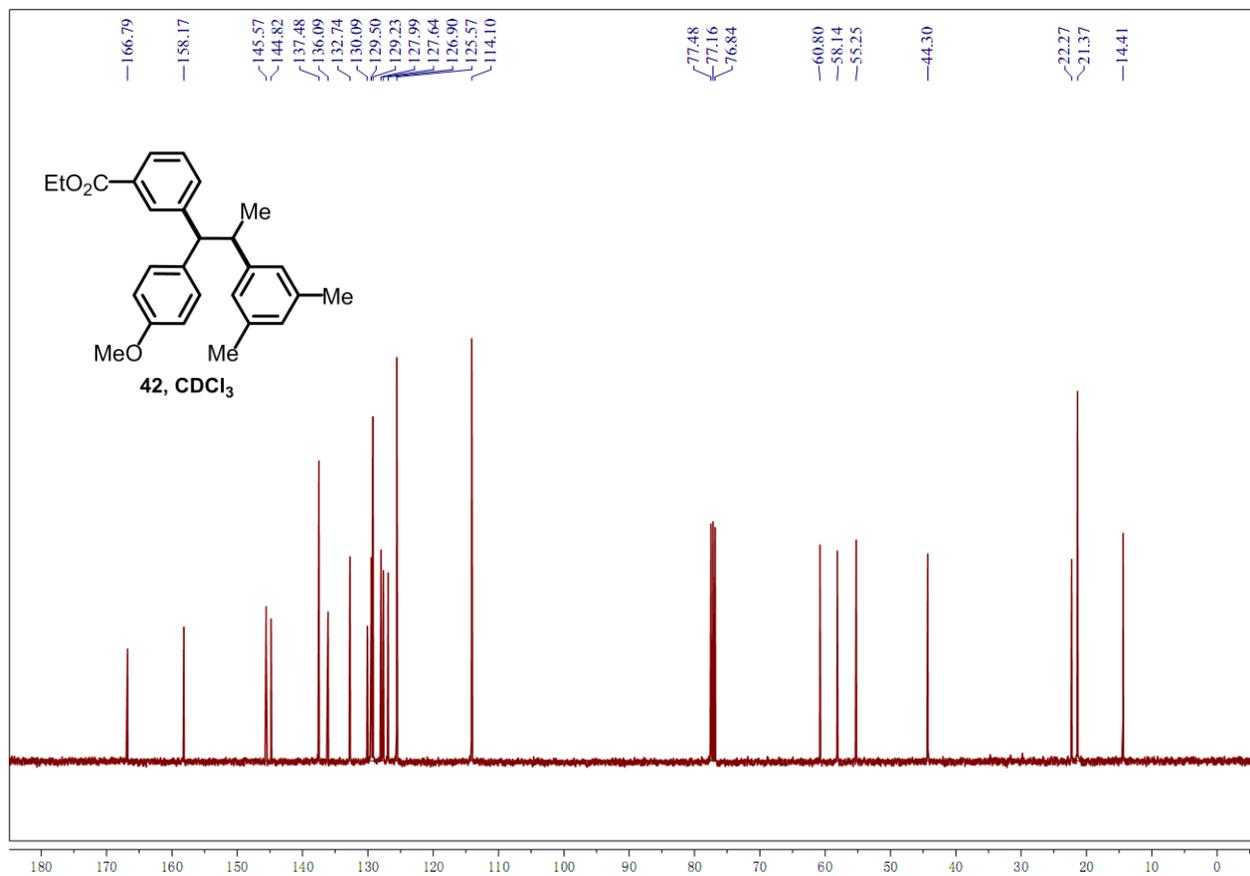
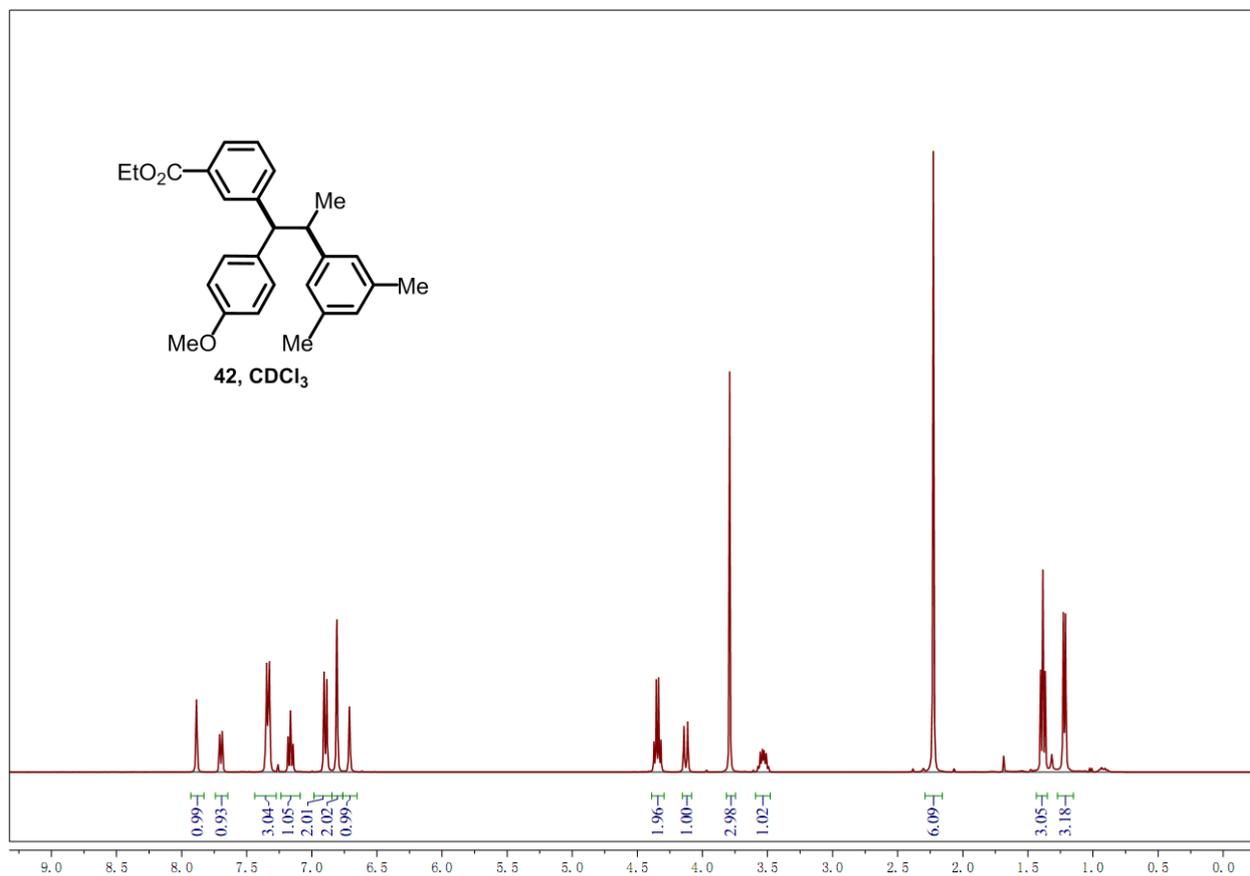


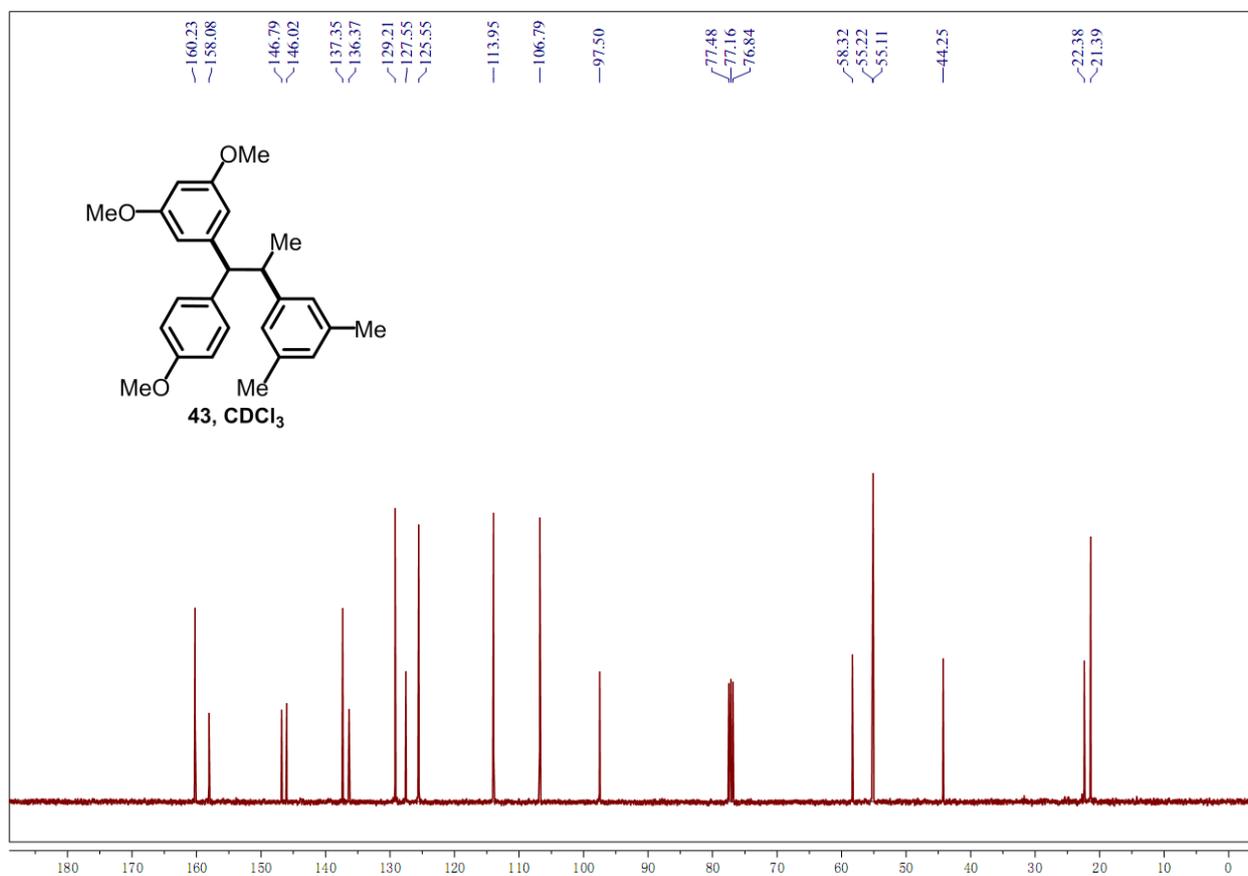
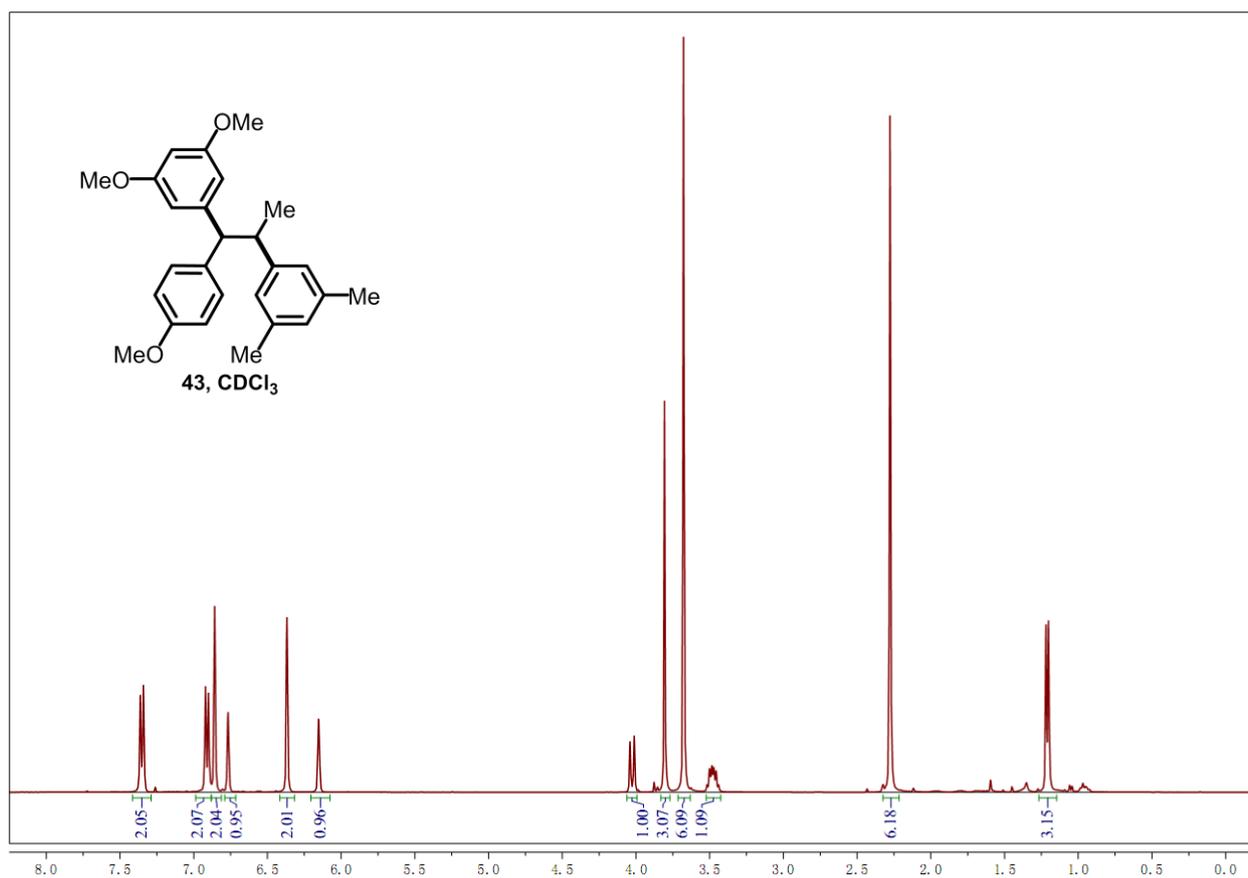


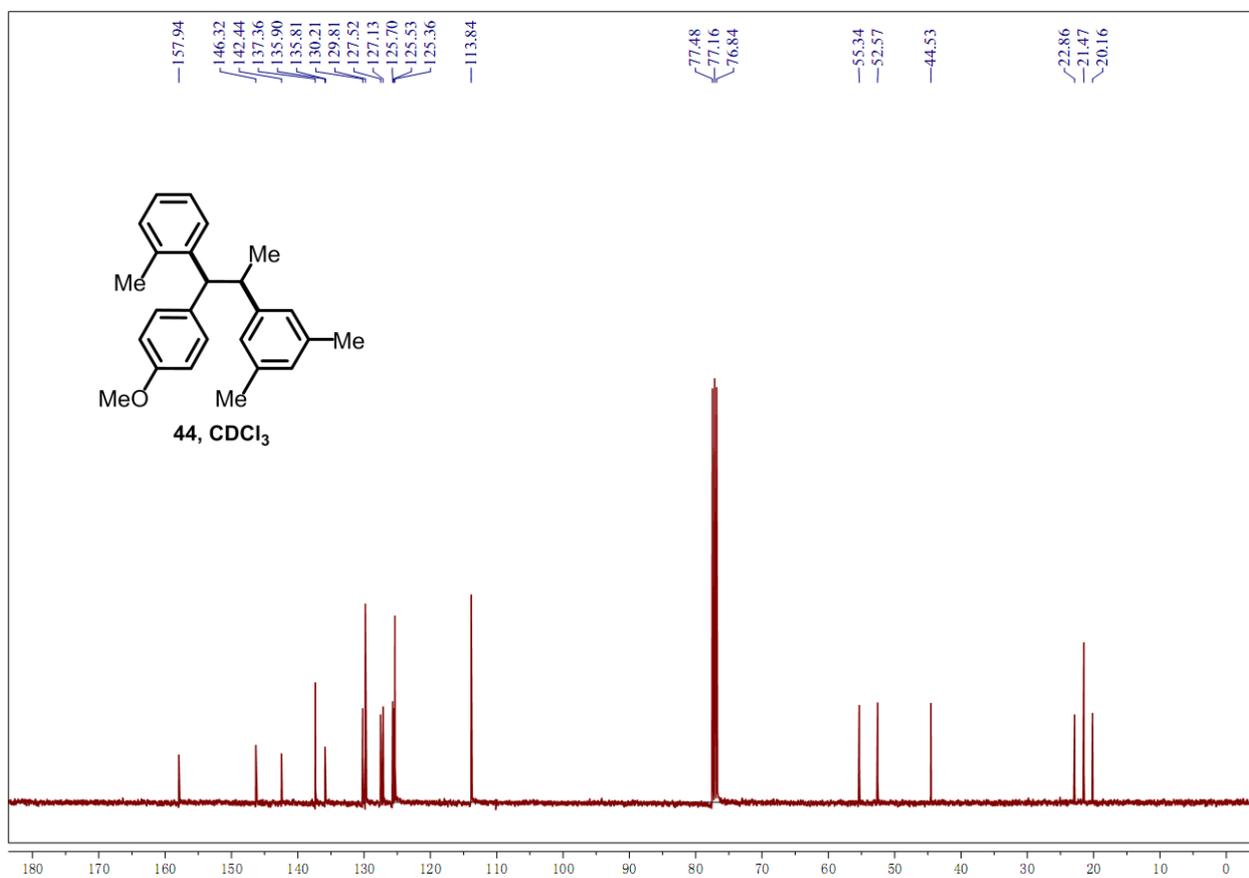
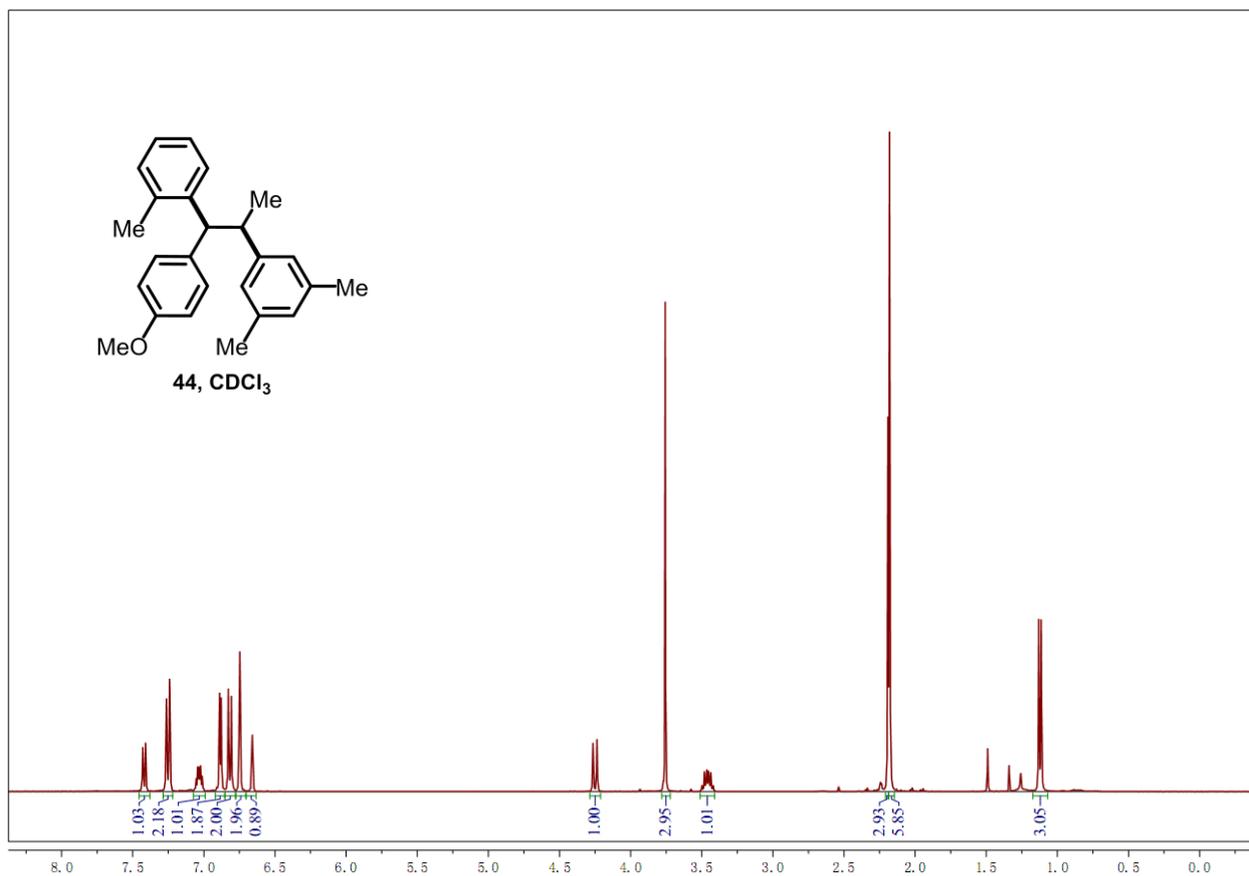


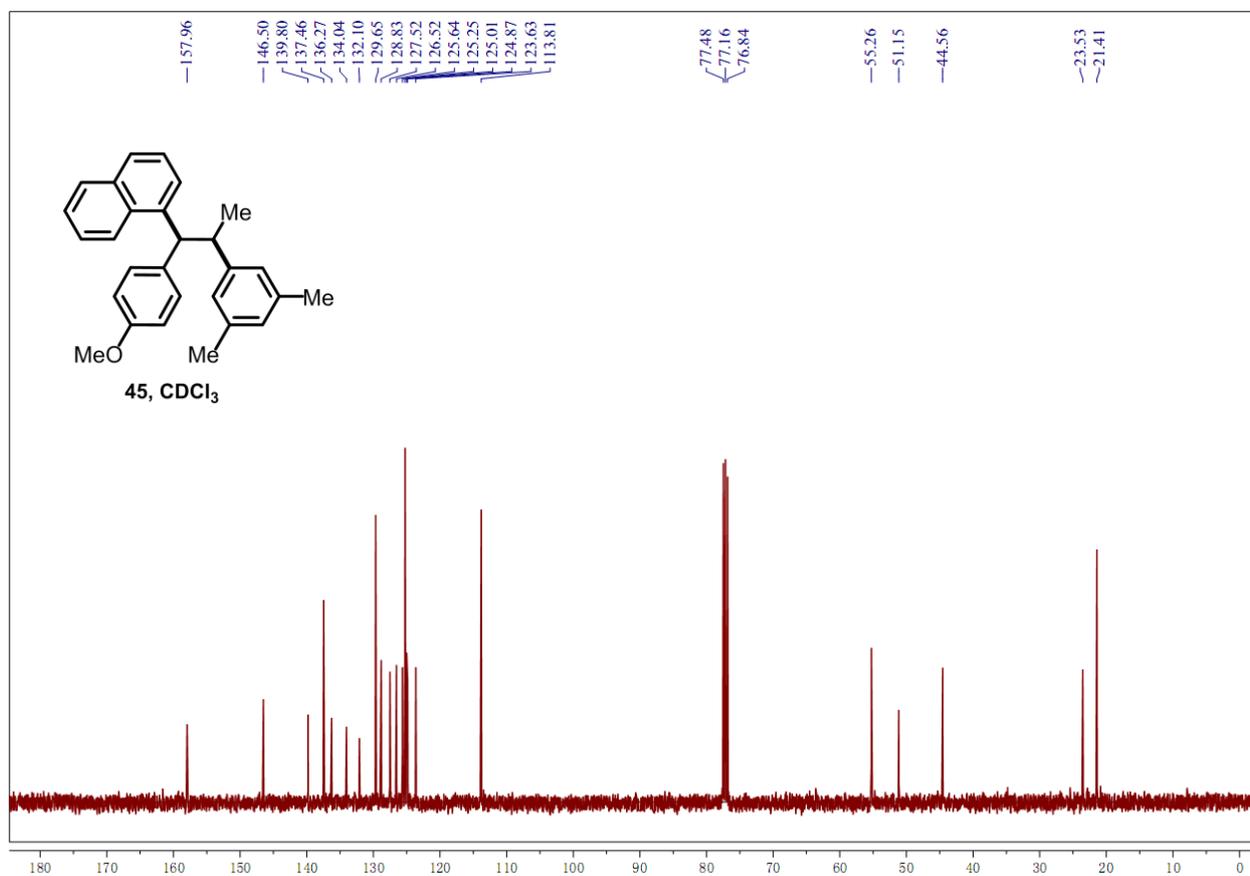
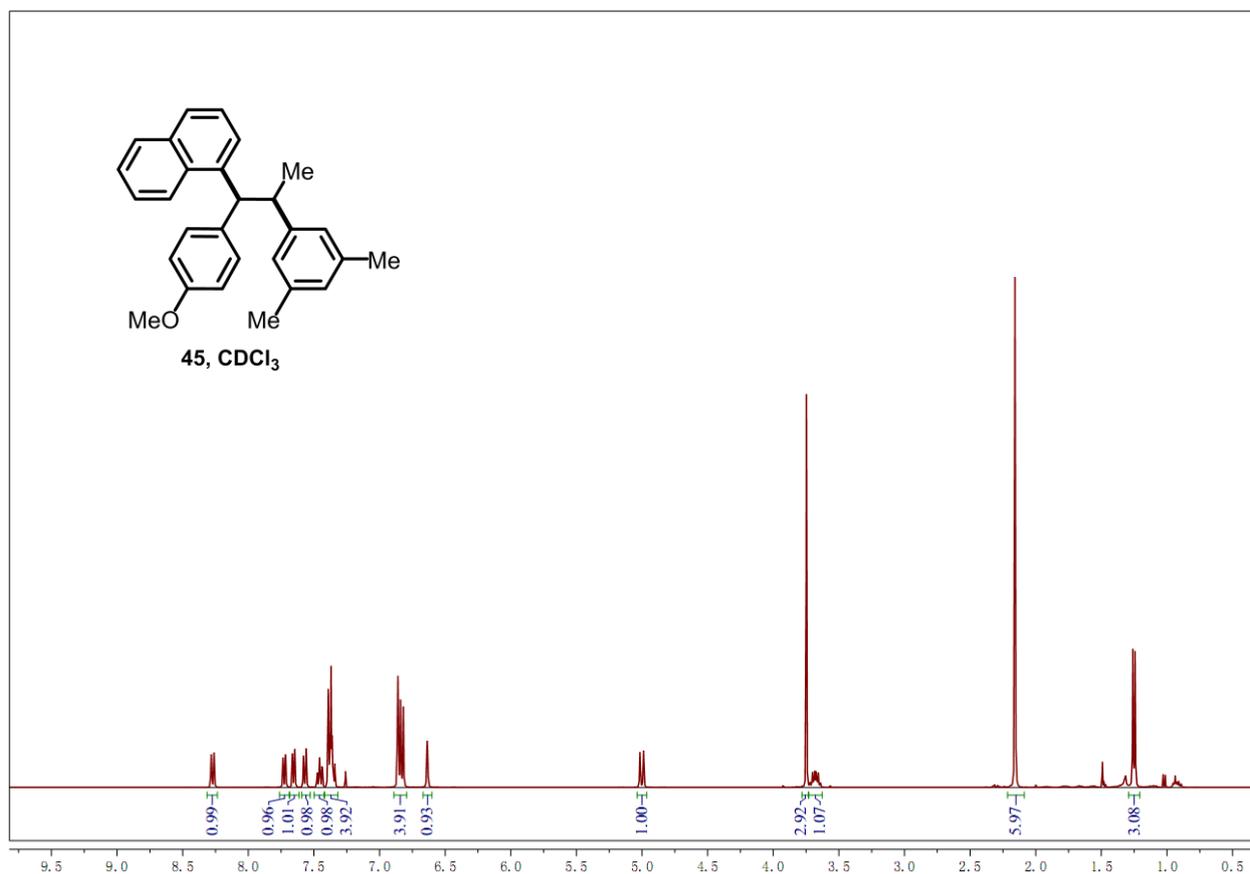


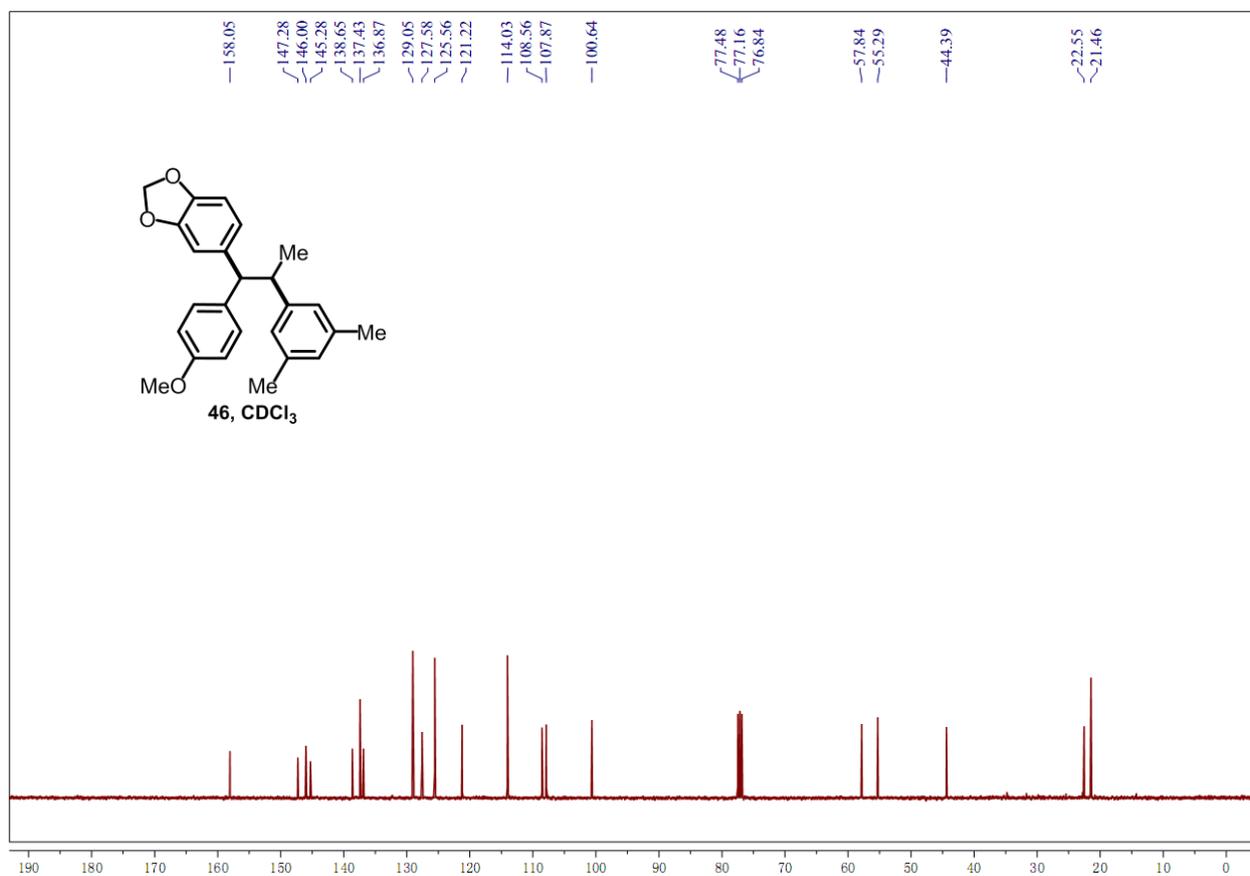
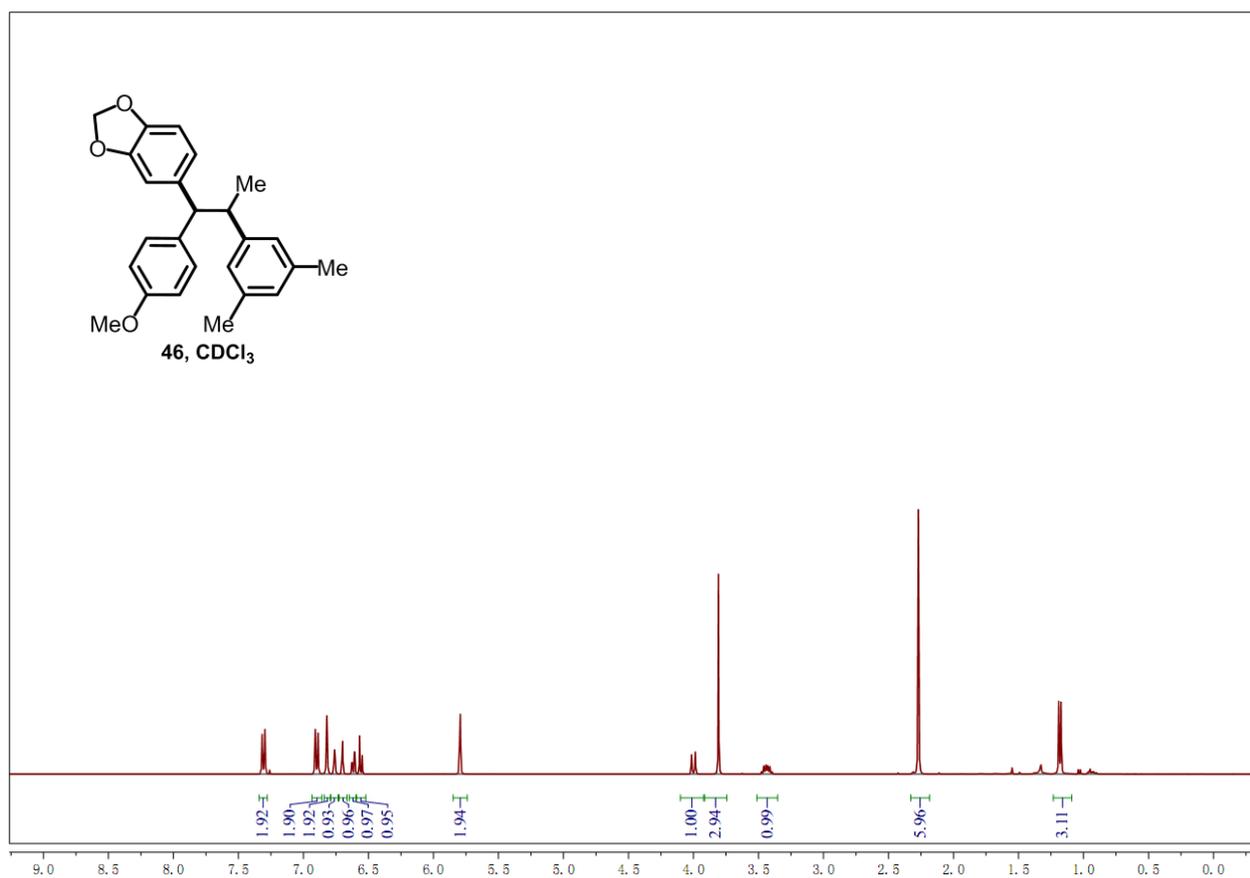


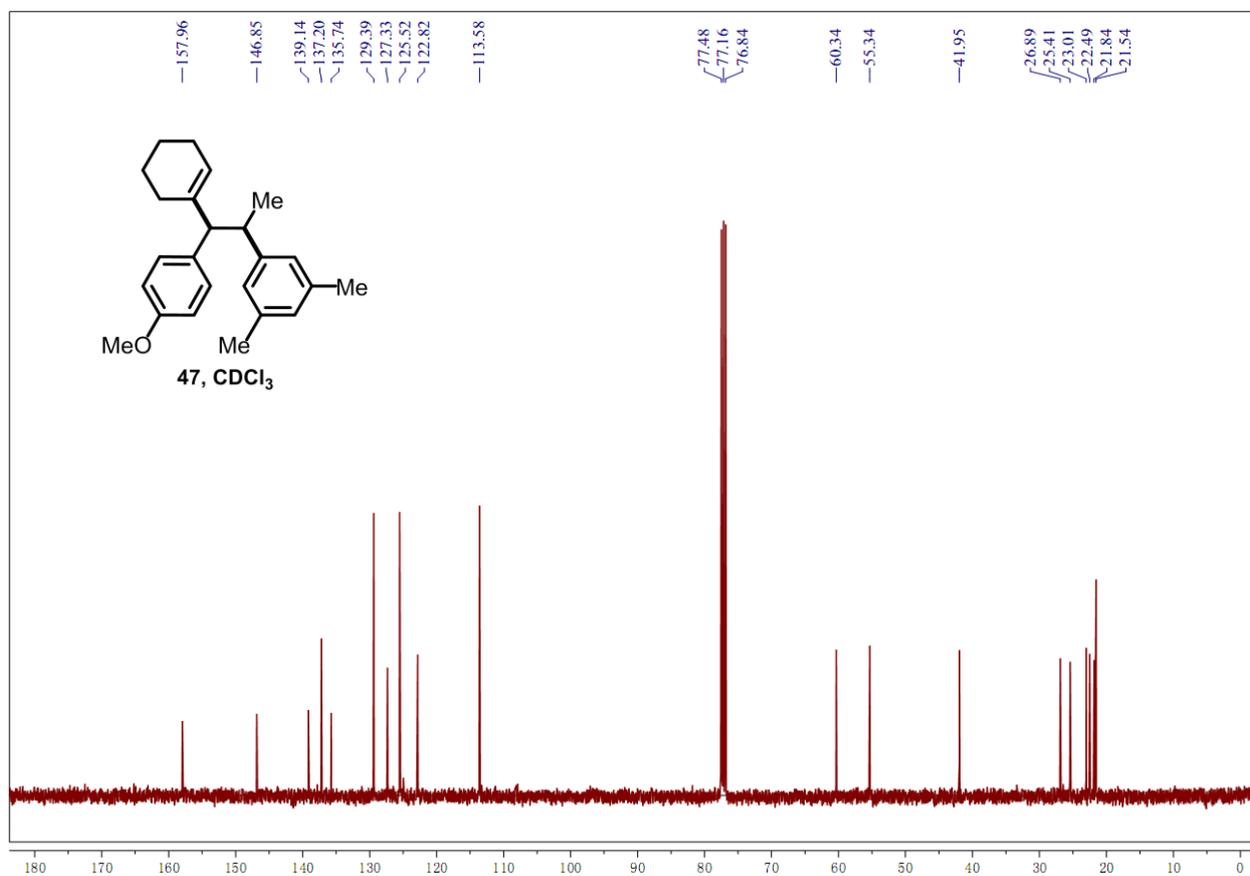
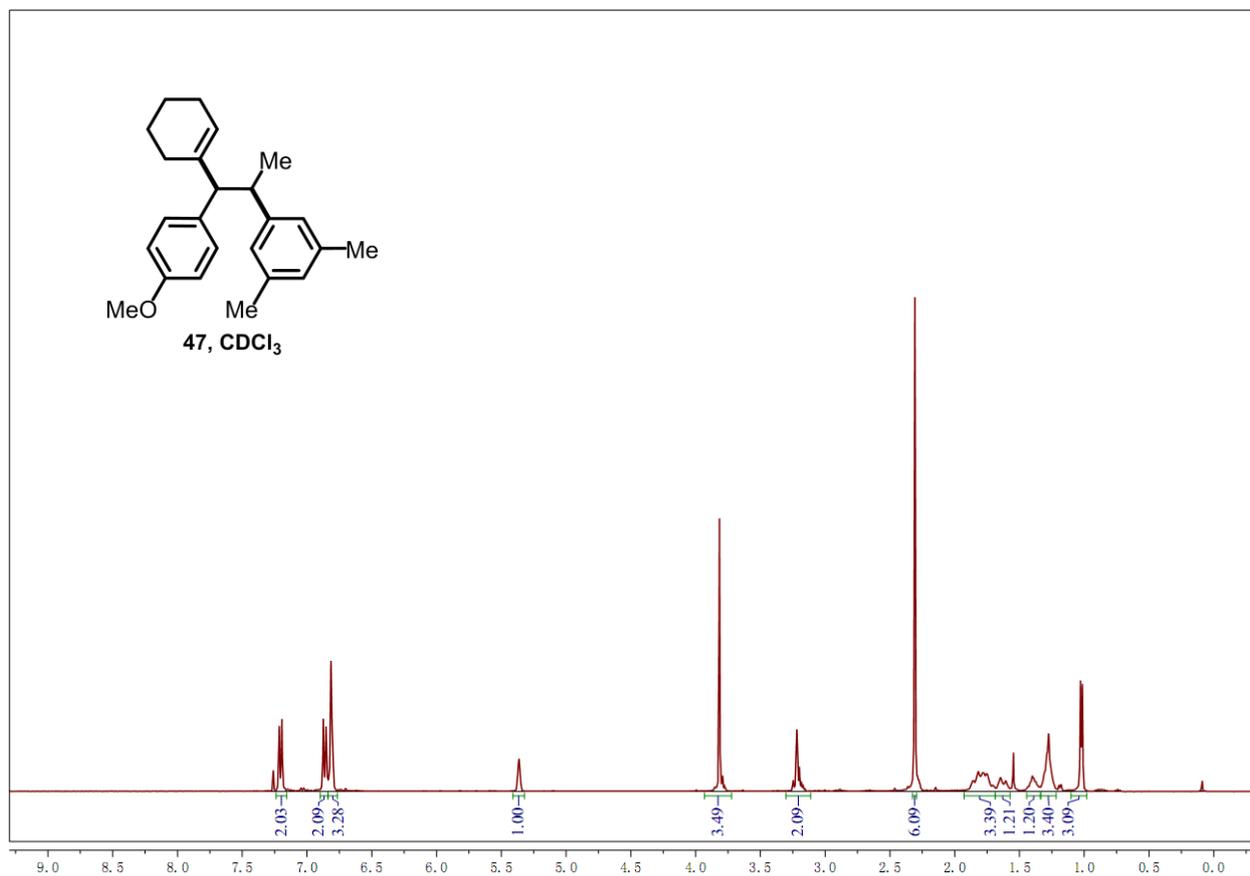


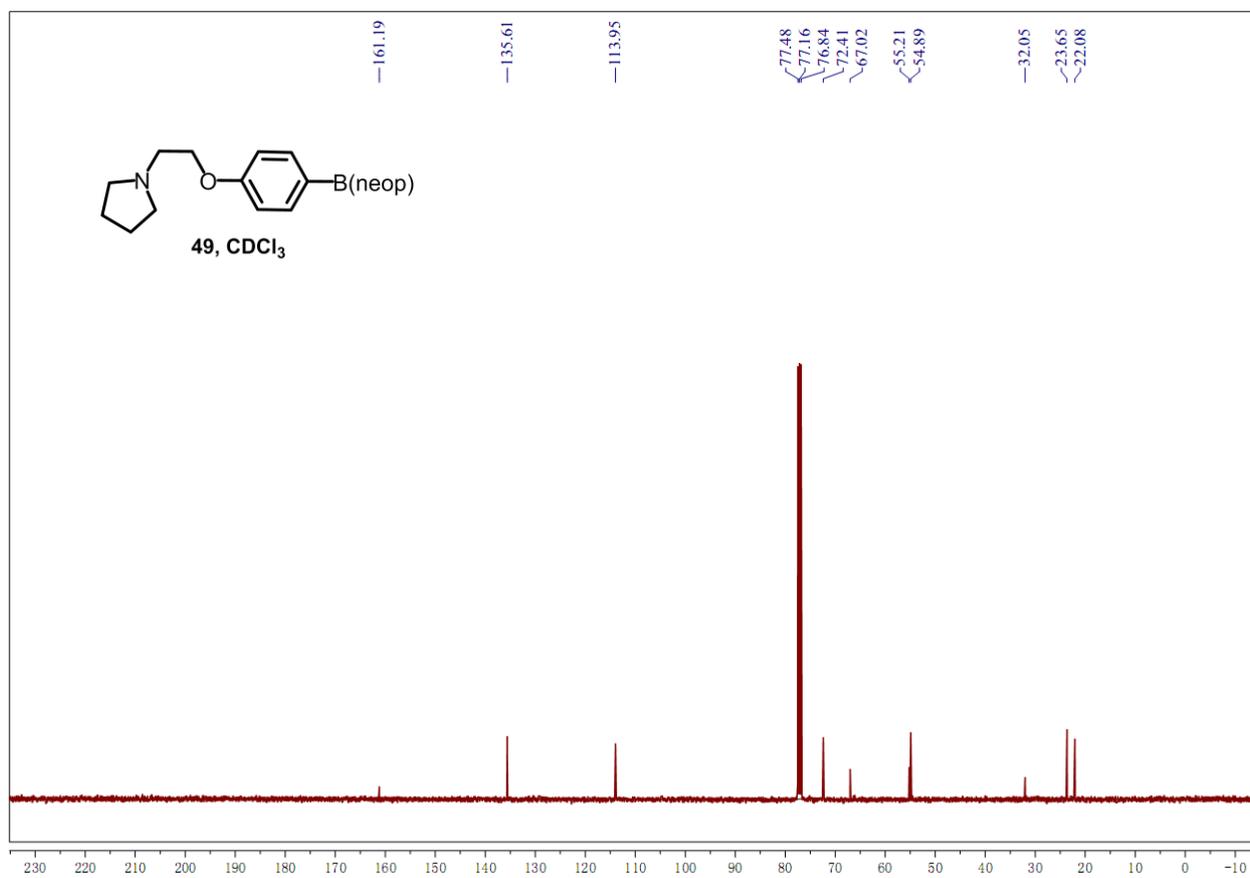
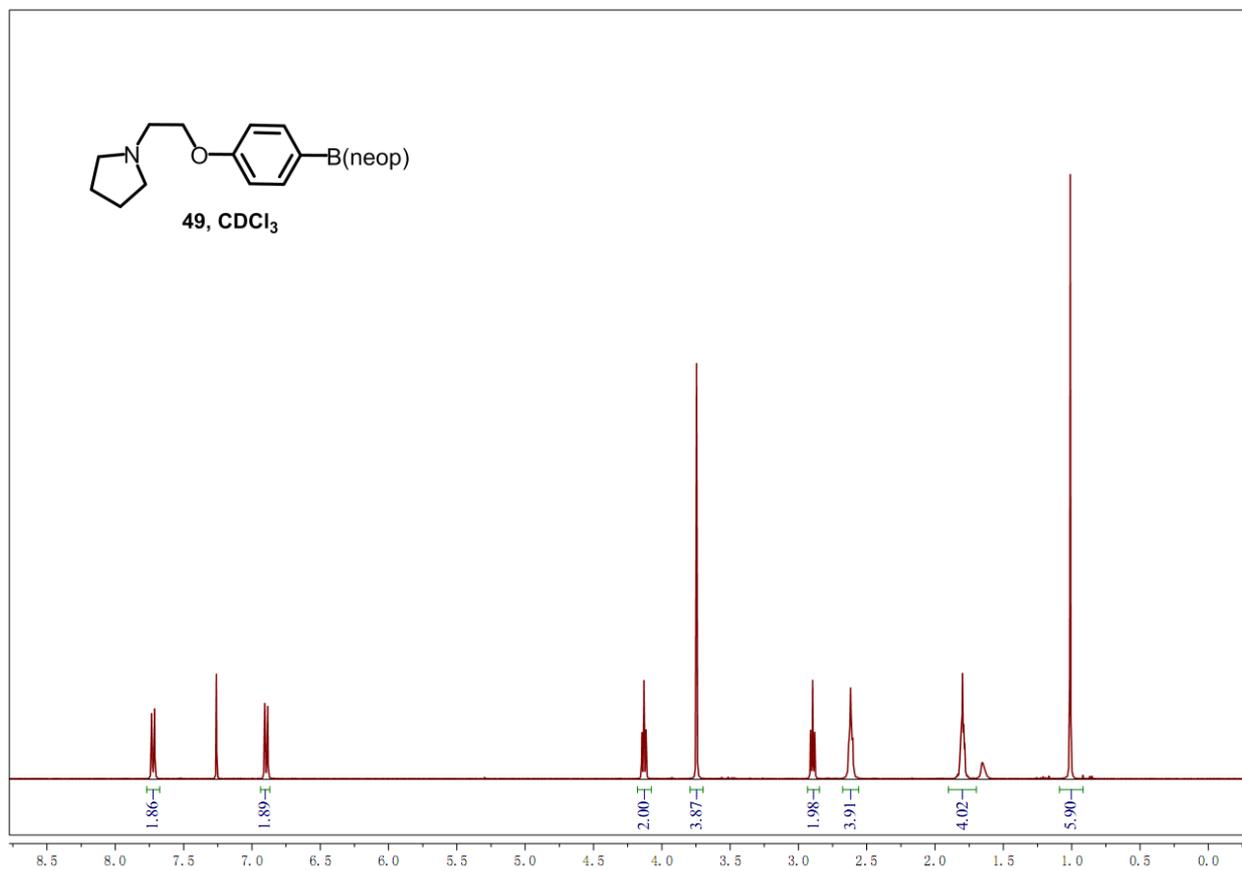


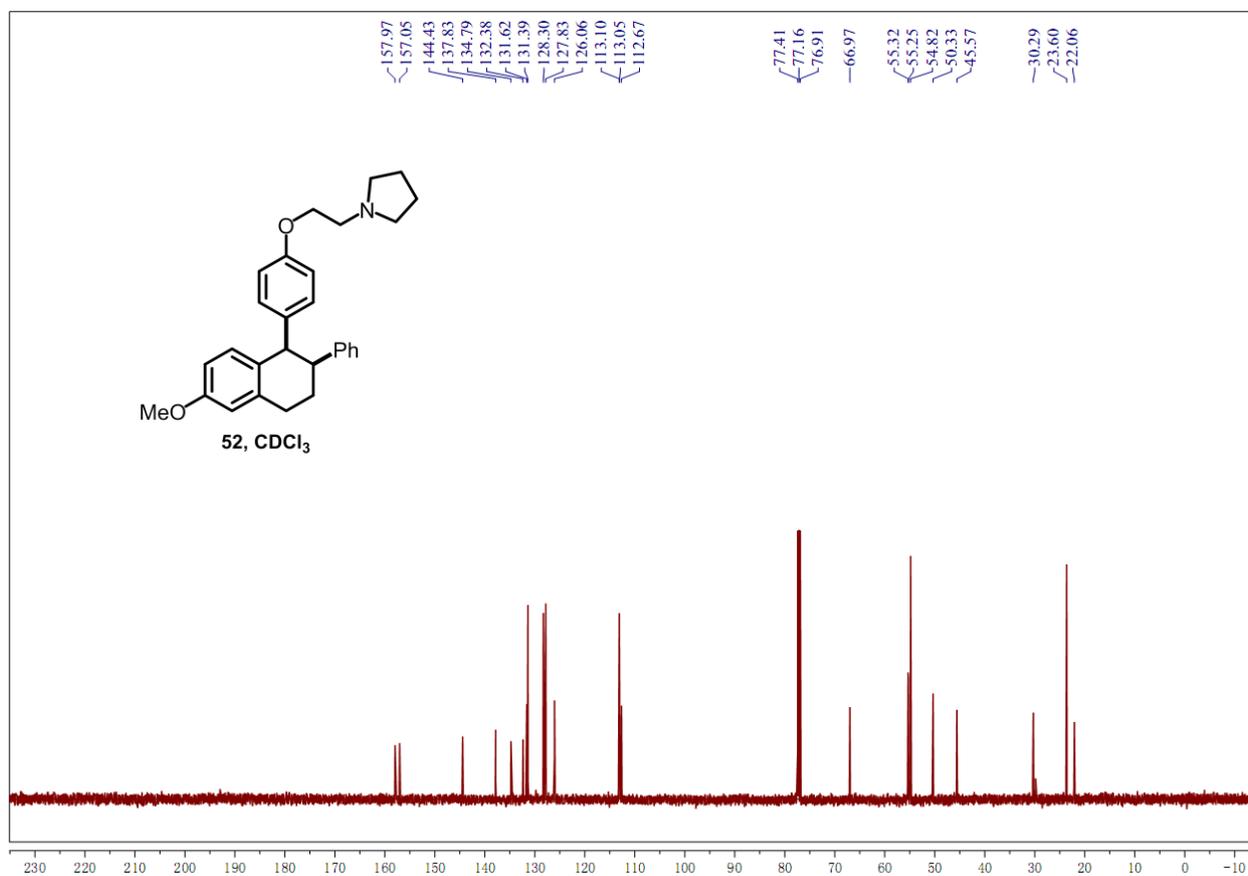
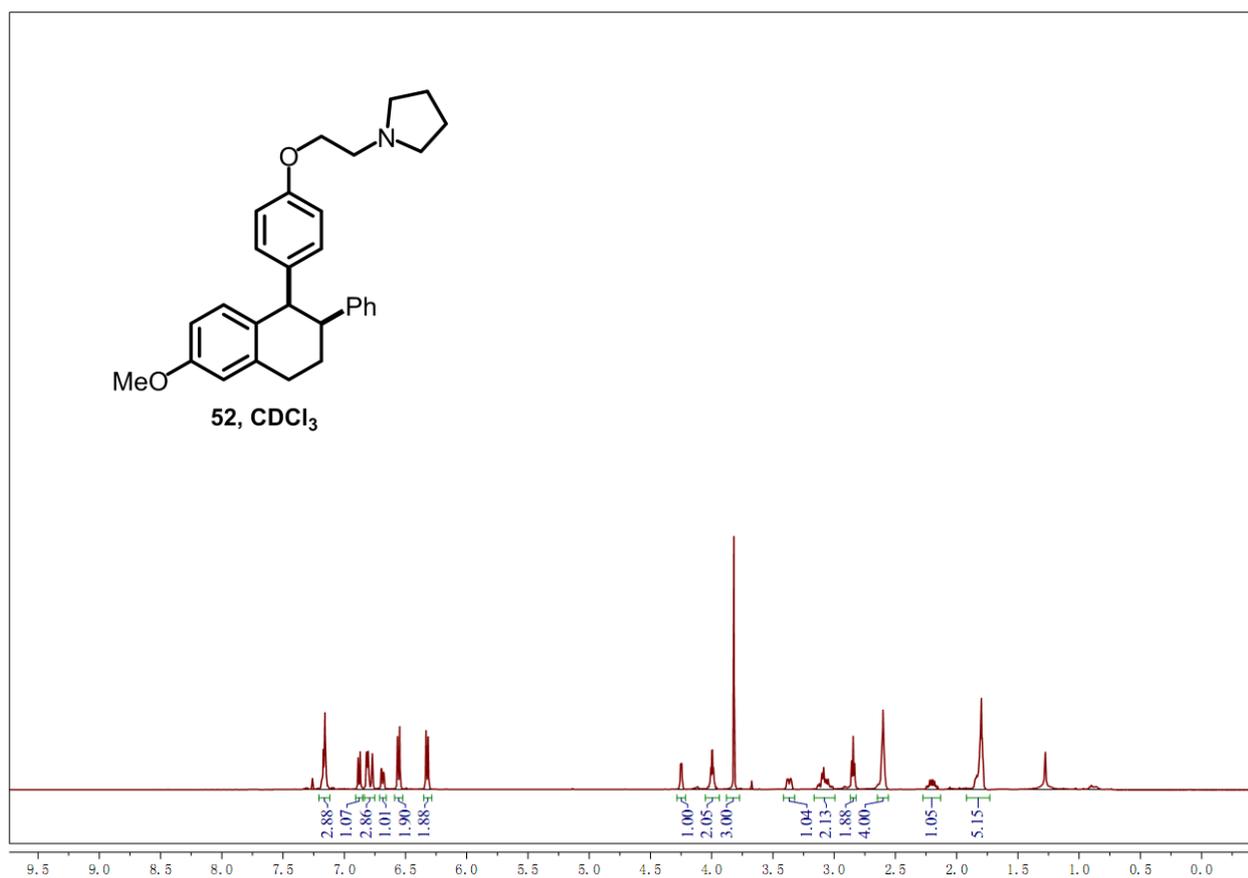












■ Determination of Diastereoselectivity:

