

SUPPORTING INFORMATION:

Aryl Carbonyls and Carbinols as Proelectrophiles for Friedel-Crafts Benzylation and Alkylation

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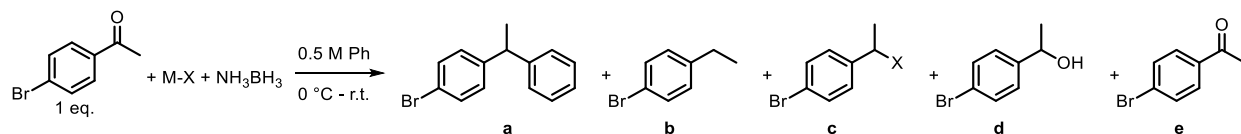
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General information:

All reagents and starting materials were purchased from Sigma-Aldrich (St. Louis, USA), Oakwood (Estill, USA) or Fisher Scientific (Waltham, USA) and used as received. Ammonium chloride, sodium borohydride, sodium bicarbonate, and reagent-grade tetrahydrofuran (75 to 400 ppm BHT) were used as received for preparation of ammonia-borane, which was prepared using a previously reported procedure. Solvents used for all reactions were distilled from sodium/benzophenone (diethyl ether), calcium hydride (dichloromethane), and stored under nitrogen, or used as received (hexanes, ethyl acetate, benzene, *p*-xylenes, mesitylene, chloroform). Thin-layer chromatography (TLC) was performed on F60 silica gel plates purchased from Macherey-Nagel (Allentown, USA) and visualized under UV light or ceric ammonium molybdate solution. Column chromatography was performed using 60 M Kieselgel silica gel. The identities of the products were confirmed by nuclear magnetic resonance (NMR) spectroscopy and measured in δ values in parts per million (ppm). Spectra of products were recorded on a Bruker (Billerica, USA) 400 MHz or a Bruker (Billerica, USA) 300 MHz. The ^1H NMR (400 MHz) spectra were recorded at ambient temperature and calibrated against the residual solvent peak of CDCl_3 ($\delta = 7.26$ ppm) as an internal standard. Coupling constants (J) are given in hertz (Hz), and signal multiplicities are described of NMR data as s = singlet, d = doublet, dd = doublet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, ddt = doublet of doublet of triplets, dqd = doublet of quartet of doublets, dqf = doublet of quartet of triplets, dtd = doublet of triplet of doublets, dddd = doublet of doublet of doublet of doublets, t = triplet, td = triplet of doublets, tt = triplet of triplets, tdd = triplet of doublet of doublets, tdt = triplet of doublet of triplets, q = quartet, p = pentet, h = hexet, m = multiplet, and br = broad. The ^{13}C NMR (101 MHz or 75 MHz) spectra were recorded at ambient temperature and calibrated using CDCl_3 ($\delta = 77.0$ ppm) as an internal standard. ^{19}F NMR (376 MHz or 282 MHz) spectra were recorded at ambient temperature and chemical shifts are reported relative to the external standard CFCl_3 ($\delta = 0$ ppm).

Reaction optimization

One-pot optimization of ketones using 4-bromoacetophenone

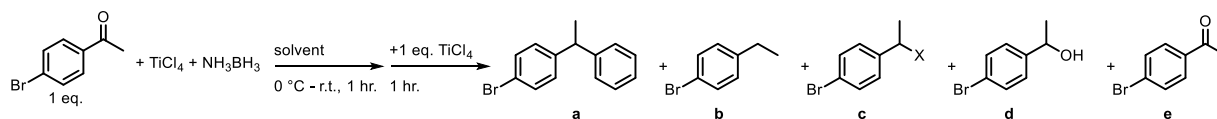


Scheme S1. Reaction scheme and possible products from 4-bromoacetophenone.

Entry	Lewis Acid	LA equiv.	AB equiv.	Time (hr)	product ratios				
					%a	%b	%c	%d	%e
1	TiCl ₄	1	2	1	43	57	--	--	--
2	TiCl ₄	1	1	1	72	28	--	--	--
3	TiCl ₄	0.2	2	1	10	90	--	--	--
4	TiCl ₄	0.5	1	1	--	31	56	13	--
5	TiCl ₄	1	0.5	24	36	--	--	--	64
6	TiCl ₄	1	0.6	24	--	--	40	--	60
7	TiCl ₄	1	0.8	24	72	--	--	--	28
8	TiBr ₄	1	1	24	8	--	45	--	47
9	HfCl ₄	1	1	1	51	17	--	22	--
10	HfCl ₄	1	0.5	24	78	--	--	--	22
11	HfCl ₄	1	0.6	24	80	20	--	--	--
12	HfCl ₄	1	0.8	24	73	27	--	--	--
13	HfCl ₄	1.5	0.5	24	55	--	--	--	45
14	HfCl ₄	1	0.5	24	36	trace	--	--	63
15	HfCl ₄	1	0.5	24	24	61	15	--	24
16	HfCl ₄	1	0.6	24	76	--	--	--	24

Table S1. Outcome of one-pot reduction/alkylation optimization using 4-bromoacetophenone.

Tandem reduction/alkylation optimization of ketones using 4-bromoacetophenone

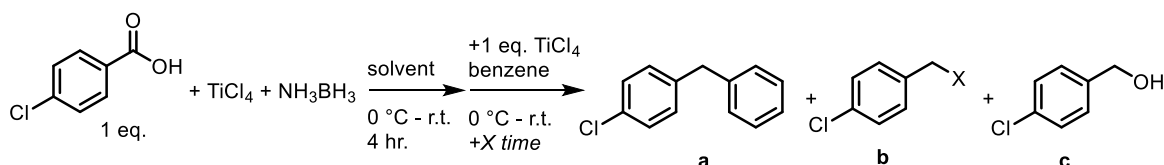


Scheme S2. Reaction scheme and possible products from 4-bromoacetophenone.

Entry	TiCl ₄ equiv.	AB equiv.	Solvent	product ratios					Notes
				%a	%b	%c	%d	%e	
1	10%	0.5	Et ₂ O	--	--	--	--	--	intractable
2	10%	0.5	Ph	82	18	--	--	--	--
3	10%	0.4	Ph	--	31	56	13	--	--
4	10%	0.5	Ph	36	--	--	--	64	--
5	10%	0.5	Ph	--	--	40	--	60	--
6	10%	0.5	Ph	72	--	--	--	28	--

Table S2. Outcome of tandem reduction/alkylation optimization using 4-bromoacetophenone.

Tandem reduction/alkylation optimization of 4-chlorobenzoic acid

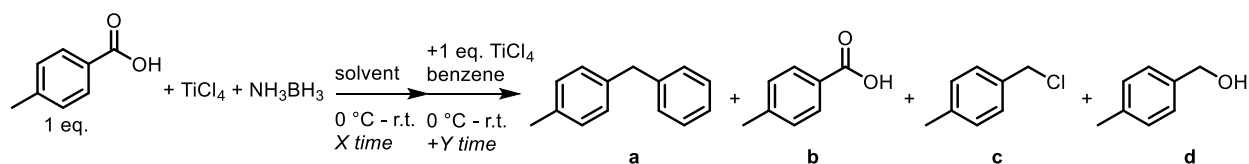


Scheme S3. Reaction scheme and possible products from 4-chlorobenzoic acid.

Entry	Initial TiCl ₄ equiv.	AB equiv.	Solvent	X time	product ratios			Notes
					%a	%b	%c	
1	20%	2	Ph	18	100	--	--	59% yield
2	100%	2	Ph	36	100	--	--	28% yield
3	20%	2	Et ₂ O	16	2	67	31	
4	20%	2	Et ₂ O	16	15	56	29	Initial rxn. time +20 h

Table S3. Outcome of tandem reduction/alkylation optimization using 4-chlorobenzoic acid.

Tandem reduction/alkylation optimization of 4-methylbenzoic acid

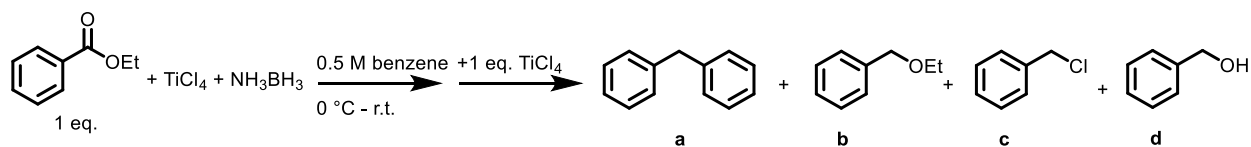


Scheme S4. Reaction scheme and possible products from 4-methylbenzoic acid.

Entry	Solvent	TiCl ₄ eq.	AB eq.	X time (h)	Y time (h)	product ratios				Notes
						%a	%b	%c	%d	
1	Et ₂ O	0.2	2	14	16	4	-	56	--	Messy
2	Ph	0.2	2	20	2	80	20	--	trace	
3	Ph	0.2	2	18	24	69	23	--	8	
4	Ph	0.2	3	24	2	71	23	--	6	
5	Ph	0.4	2	24	2	76	21	--	3	
6	Ph	0.6	2	18	2	90	--	--	10	26% yield 40 °C
7	Ph	0.2	2	20	24	90	--	--	trace	59% yield
8	Ph	0.2	2	24	24	84	--	--	16	+2 eq. TiCl ₄ 42% yield

Table S4. Outcome of tandem reduction/alkylation optimization using 4-methylbenzoic acid.

Tandem reduction/alkylation optimization attempt of ethyl benzoates

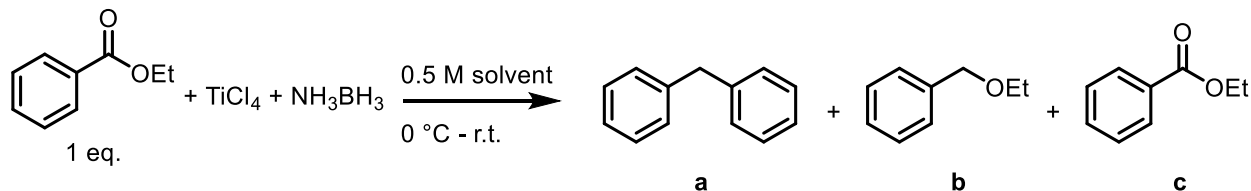


Scheme S5. Reaction scheme and possible products from ethyl benzoate.

Entry	TiCl ₄ eq.	AB eq.	X time (h)	Y time (h)	product ratios				Notes
					%a	%b	%c	%d	
1	0.2	0.5	20	3	61	--	--	--	34% SM
2	0.2	1	24	2	65	--	--	--	35% SM
3	0.2	2	24	2	58	24	--	--	18% SM, 37% yield
4	0.2	0.5	20	3	35	--	--	--	65% SM
5	0.2	0.8	24	2	60	--	--	--	40% SM
6	0.4	0.8	24	2	78	--	--	--	22% SM
7	0.2	1.5	24	2	78	22	--	--	--
8	0.2	1	24	2	25	--	--	--	75% SM
9	0.2	1.5	4	3	94	--	--	--	6% SM

Table S5. Outcome of tandem reduction/alkylation optimization using ethyl benzoate.

One-pot reduction/alkylation optimization attempt of ethyl benzoates



Scheme S6. Reaction scheme and possible products from ethyl benzoate.

Entry	Solvent	TiCl ₄ eq.	AB eq.	Time (h)	product ratios			Notes
					%a	%b	%c	
1	Ph	2	2	16	77	--	23	64% yield
2	Ph	2	1.5	12	100	--	--	Optimal condition

Table S6. Outcome of one-pot reduction/alkylation optimization using ethyl benzoate.

General procedures for Friedel-Crafts reactions

General procedure for the preparation of Friedel-Crafts products from alcohols (solvent nucleophile) (GP1)

To a 15 mL oven dried round bottom flask was added alcohol (1 mmol, 1 equiv.) and a magnetic stirring bar. The reaction container was then sealed with a rubber septum followed by the addition of aryl solvent (3 mL, 0.33 M) to the round bottom flask and its contents were chilled to 0 °C via ice bath. TiCl_4 (0.1 mL, 1 equiv.) was then added dropwise to the reaction mixture. Upon complete addition, the reaction was stirred at 0 °C for 1 minute before being allowed to warm up to room temperature and was stirred until completion as determined by TLC. On completion of the reaction, the mixture was quenched with the addition of DI H_2O (5 mL) and allowed to stir for 1 minute, then transferred to a separatory funnel and extracted with DCM (3 x 5 mL). The combined organic layers were then dried over sodium sulfate, filtered through cotton, and concentrated under rotary evaporation, with the remaining solvent removed on high vacuum. Column chromatography was performed only if further purification was necessary.

General procedure for the preparation of Friedel-Crafts products from alcohols (non-solvent nucleophile) (GP2)

To a 15 mL oven dried round bottom flask was added alcohol (1 mmol, 1 equiv.) and a magnetic stirring bar. This was followed by the addition of dichloromethane (3 mL, 0.33 M) and the arene nucleophile (1 mmol, 1 equiv.) to the round bottom flask. The mixture was stirred and chilled to 0 °C using an ice bath. TiCl_4 (0.55 mL, 0.5 equiv.) was then added dropwise to the reaction mixture. Upon complete addition, the reaction was stirred at 0 °C for 1 minute before being allowed to warm up to room temperature and was stirred until completion as determined by TLC. On completion of the reaction, the mixture was quenched with the addition of DI H_2O (5 mL) and allowed to stir for 1 minute, then transferred to a separatory funnel and extracted with DCM (3 x 5 mL). The combined organic layers were then dried over sodium sulfate, filtered through cotton, and concentrated under rotary evaporation, with the remaining solvent removed on high vacuum. Column chromatography was performed only if further purification was necessary.

General procedure for the preparation of Friedel-Crafts alkylation products from phenyl ethanols (GP3)

To a 15 mL oven dried round bottom flask with side arm and condenser was added alcohol (1 mmol, 1 equiv.) and a magnetic stirring bar, followed by the addition of aryl solvent (5 mL, 0.2 M) to the round bottom flask. The reaction apparatus was sealed and flushed with nitrogen before the dropwise addition of TiCl_4 (0.1 mL, 1 equiv.) to the reaction mixture. Upon complete addition, the reaction was heated to reflux and was stirred for overnight (16 h). The mixture was then allowed to cool to room temperature before quenching with DI H_2O (5 mL) and allowed to stir for 1 minute. Consequently, the reaction mixture was transferred to a separatory funnel and extracted with EtOAc (3 x 5 mL). The combined organic layers were then dried over sodium sulfate, filtered through cotton, and concentrated under rotary evaporation, with the remaining solvent removed on high vacuum.

General procedure for the preparation of Friedel-Crafts alkylation products from aryl aldehydes (GP4)

To a 15 mL oven dried round bottom flask was added aldehyde (1 mmol, 1 equiv.) and a magnetic stirring bar. The reaction container was then sealed with a rubber septum and a needle connected

to an indirect N₂ line leading to an outlet was inserted through the septum. This was followed by the addition of aryl solvent (3 mL, 0.33 M) to the round bottom flask and its contents were chilled to 0 °C via ice bath. TiCl₄ (0.1 mL, 1 equiv.; 0.2 mL (2 equiv. for **2b** and **2c**) was then added dropwise to the reaction mixture. Once the Lewis acid was added, the septum was then removed to allow addition of borane-ammonia (31 mg., 1 equiv.) which was added directly to the reaction mixture followed by resealing of the reaction flask with the rubber septum with attached indirect line outlet. Upon complete addition, the reaction was stirred at 0 °C for 1 minute before being allowed to warm up to room temperature and was stirred until completion as determined by TLC. On completion of the reaction, the mixture was quenched with the addition of DI H₂O (5 mL) and allowed to stir for 1 minute, then transferred to a separatory funnel and extracted with DCM (3 x 5 mL). The combined organic layers were then dried over sodium sulfate, filtered through cotton, and concentrated under rotary evaporation, with the remaining solvent removed on high vacuum. Column chromatography was performed only if further purification was necessary.

General procedure for the preparation of Friedel-Crafts alkylation products from aryl ketones (GP5)

To a 15 mL oven dried round bottom flask was added ketone (1 mmol, 1 equiv.) and a magnetic stirring bar. The reaction container was then sealed with a rubber septum followed by the addition of aryl solvent (3 mL, 0.33 M) to the round bottom flask and its contents were chilled to 0 °C via ice bath. An indirect line leading to an outlet was also attached to the rubber septum. TiCl₄ (0.02 mL, 20 mol%) was then added dropwise to the reaction mixture. Once the Lewis acid was added, the septum was then removed to allow addition of borane-ammonia (16 mg., 0.5 equiv.) which was added directly to the reaction mixture followed by resealing of the reaction flask with the rubber septum with attached indirect line outlet. Upon complete addition, the reaction was stirred at 0 °C for 1 minute before being allowed to warm up to room temperature and stirred until starting material was no longer detectable according to TLC. After full consumption of starting material, the reaction was chilled again to 0 °C followed by the dropwise addition of TiCl₄ (1 mmol, 1 equiv.) and stirred for 1 minute before allowing to warm to room temperature. On completion of the reaction, the mixture was quenched with the addition of DI H₂O (5 mL) and allowed to stir for 1 minute, then transferred to a separatory funnel and extracted with DCM (3 x 5 mL). The combined organic layers were then dried over sodium sulfate, filtered through cotton, and concentrated under rotary evaporation, with the remaining solvent removed on high vacuum.

General procedure for the preparation of Friedel-Crafts alkylation products from aryl carboxylic acids (GP6)

To a 15 mL oven dried round bottom flask was added carboxylic acid (1 mmol, 1 equiv.) and a magnetic stirring bar. The reaction container was then sealed with a rubber septum followed by the addition of aryl solvent (3 mL, 0.33 M) to the round bottom flask and its contents were chilled to 0 °C via ice bath. An indirect line leading to an outlet was also attached to the rubber septum. TiCl₄ (0.02 mL, 20 mol%) was then added dropwise to the reaction mixture. Once the Lewis acid was added, the septum was then removed to allow addition of borane-ammonia (62 mg., 2 equiv.) which was added directly to the reaction mixture followed by resealing of the reaction flask with the rubber septum with attached indirect line outlet. Upon complete addition, the reaction was stirred at 0 °C for 1 minute before being allowed to warm up to room temperature and stirred for 20 h. The reaction was then chilled again to 0 °C followed by the dropwise addition of TiCl₄ (2 mmol, 2 equiv.) and stirred for 1 minute before allowing to warm to room temperature. On completion of the reaction as determined by TLC, the mixture was quenched with the addition of DI H₂O (5 mL) and allowed to stir for 1 minute, then transferred to a separatory funnel followed by 5 mL of saturated NaHCO₃ aqueous solution. The organic layer was extracted with DCM (3 x 5 mL) and the combined organic layers were then dried over sodium sulfate, filtered through

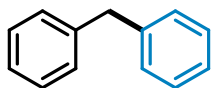
cotton, and concentrated under rotary evaporation, with the remaining solvent removed on high vacuum. Column chromatography was performed only if further purification was necessary.

General procedure for the preparation of Friedel-Crafts alkylation products from aryl esters (GP7)

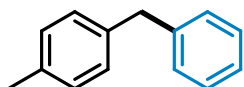
To a 15 mL oven dried round bottom flask was added ester (1 mmol, 1 equiv.) and a magnetic stirring bar. The reaction container was then sealed with a rubber septum followed by the addition of aryl solvent (3 mL, 0.33 M) to the round bottom flask and its contents were chilled to 0 °C via ice bath. An indirect line leading to an outlet was also attached to the rubber septum. TiCl₄ (0.2 mL, 2 equiv.) was then added dropwise to the reaction mixture. Once the Lewis acid was added, the septum was then removed to allow addition of borane-ammonia (47 mg., 1.5 equiv.) which was added directly to the reaction mixture followed by resealing of the reaction flask with the rubber septum with attached indirect line outlet. Upon complete addition, the reaction was stirred at 0 °C for 1 minute before being allowed to warm up to room temperature and stirred for 20 h until completion as determined by TLC. If deemed incomplete by 20 h (**m-F**), the reaction was then chilled again to 0 °C followed by the dropwise addition of TiCl₄ (1 mmol, 1 equiv.) and stirred for 1 minute before allowing to warm to room temperature. On completion of the reaction as determined by TLC, the mixture was quenched with the addition of DI H₂O (5 mL) and allowed to stir for 1 minute, then transferred to a separatory funnel. The organic layer was extracted with DCM (3 x 5 mL) and the combined organic layers were then dried over sodium sulfate, filtered through cotton, and concentrated under rotary evaporation, with the remaining solvent removed on high vacuum. Column chromatography was performed only if further purification was necessary.

Product characterization

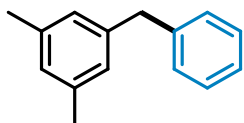
Characterization of Friedel-Crafts products from alcohols



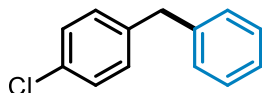
Diphenylmethane (1a); Prepared using method **GP1** and obtained as a colorless oil, mass = 144 mg, 89% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.32 – 7.25 (m, 4H), 7.21 (m, 6H), 4.00 (s, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 141.3, 129.1, 128.6, 126.2, 42.1. The spectral data is in accordance with previous reports.¹



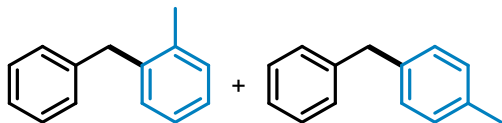
1-benzyl-4-methylbenzene (1b); Prepared using method **GP1** and obtained as a colorless oil, mass = 95 mg, 52% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.33 (m, 2H), 7.28 – 7.21 (m, 3H), 7.15 (s, 4H), 4.01 (s, 2H), 2.38 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 141.5, 138.2, 135.7, 129.3, 129.0, 129.0, 128.6, 126.1, 41.7, 21.1. The spectral data is in accordance with previous reports.¹



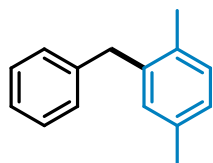
1-benzyl-3,5-dimethylbenzene (1c); Prepared using method **GP1** and obtained as a colorless oil, mass = 81 mg, 42% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.37 – 7.30 (m, 2H), 7.29 – 7.20 (m, 3H), 6.89 (d, J = 8.5 Hz, 3H), 3.97 (s, 2H), 2.34 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 141.5, 141.1, 138.1, 129.0, 128.5, 127.9, 126.9, 126.1, 42.0, 21.4. The spectral data is in accordance with previous reports.²



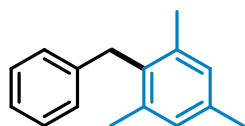
1-benzyl-4-chlorobenzene (1d); Prepared using method **GP1** and obtained as a colorless oil, mass = 188 mg, 93% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.40 – 7.27 (m, 5H), 7.23 (d, J = 6.9 Hz, 2H), 7.17 (d, J = 7.4 Hz, 2H), 4.00 (s, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 140.7, 139.7, 132.0, 130.4, 129.0, 128.7, 126.4, 41.3. The spectral data is in accordance with previous reports.¹



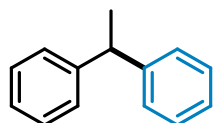
1-benzyl-2-methylbenzene + 1-benzyl-4-methylbenzene (1e); Prepared using method **GP1** and obtained as a colorless oil, mass = 146 mg, 80% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.33 (d, J = 7.6 Hz, 2H), 7.28 – 7.14 (m, 7H), 4.06 (s, 0.8H, *ortho*-isomer), 4.01 (s, 1.2H, *para*-isomer), 2.38 (s, 1.8H, *para*-isomer), 2.31 (s, 1.2H, *ortho*-isomer). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 141.5 (*para*-isomer), 140.5 (*ortho*-isomer), 139.1 (*ortho*-isomer), 138.2 (*para*-isomer), 136.7 (*ortho*-isomer), 135.6 (*para*-isomer), 130.1, 129.3, 129.0, 128.9, 128.5, 126.1, 41.7 (*para*-isomer), 39.6 (*ortho*-isomer), 21.2 (*para*-isomer), 19.8 (*ortho*-isomer). The spectral data is in accordance with previous reports.^{1,3}



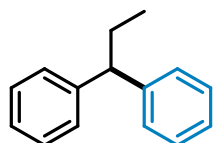
2-benzyl-1,4-dimethylbenzene (1f); Prepared using method **GP1** and obtained as a colorless oil, mass = 122 mg, 64% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.32 (t, $J = 7.3$ Hz, 2H), 7.24 (t, $J = 7.3$ Hz, 1H), 7.18 (d, $J = 7.5$ Hz, 2H), 7.11 (d, $J = 7.7$ Hz, 1H), 7.04 – 6.96 (m, 2H), 4.01 (s, 2H), 2.34 (s, 3H), 2.25 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 140.7, 138.8, 135.5, 133.6, 130.9, 130.3, 128.8, 128.5, 127.2, 126.0, 39.6, 21.1, 19.3. The spectral data is in accordance with previous reports.⁴



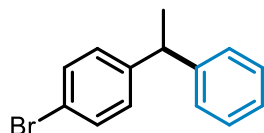
2-benzyl-1,3,5-trimethylbenzene (1g); Prepared using method **GP1** and obtained as a colorless oil, mass = 125 mg, 62% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.30 – 7.23 (m, 2H), 7.21 – 7.15 (m, 1H), 7.08 – 7.03 (m, 2H), 6.93 (s, 2H), 4.06 (s, 2H), 2.33 (s, 3H), 2.24 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 140.3, 137.2, 135.8, 133.9, 129.0, 128.5, 128.0, 125.8, 34.8, 21.0, 20.3. The spectral data is in accordance with previous reports.⁵



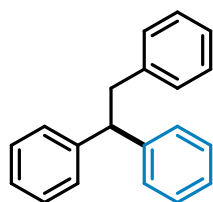
Ethane-1,1-diyl dibenzene (1h); Prepared using method **GP1** and obtained as a colorless oil, mass = 160 mg, 88% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.33 – 7.27 (m, 4H), 7.26 – 7.22 (m, 4H), 7.22 – 7.17 (m, 2H), 4.17 (q, $J = 7.2$ Hz, 1H), 1.66 (d, $J = 7.3$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 146.5, 128.5, 127.8, 126.2, 44.9, 22.0. The spectral data is in accordance with previous reports.⁶



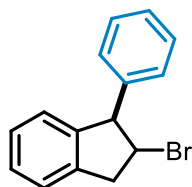
Propane-1,1-diyl dibenzene (1i); Prepared using method **GP1** and obtained as a white solid, mass = 192 mg, 98% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.30 – 7.23 (m, 8H), 7.20 – 7.14 (m, 2H), 3.80 (t, $J = 7.7$ Hz, 1H), 2.08 (p, $J = 7.4$ Hz, 2H), 0.91 (t, $J = 7.3$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 145.1, 128.3, 127.8, 125.9, 53.2, 28.5, 12.7. The spectral data is in accordance with previous reports.⁷



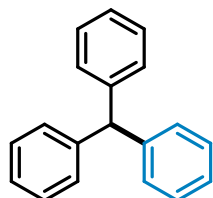
1-bromo-4-(1-phenylethyl)benzene (1j); Prepared using method **GP1** and obtained as a colorless oil, mass = 245 mg, 94% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.40 (d, $J = 7.7$ Hz, 2H), 7.31 – 7.25 (m, 2H), 7.22 – 7.16 (m, 3H), 7.09 (d, $J = 8.5$ Hz, 2H), 4.11 (q, $J = 7.2$ Hz, 1H), 1.62 (d, $J = 7.2$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 145.6, 145.3, 131.3, 129.3, 128.4, 127.4, 126.2, 119.7, 44.1, 21.6. The spectral data is in accordance with previous reports.⁸



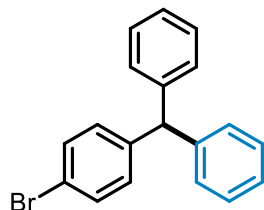
ethane-1,1,2-triyltribenzene (1k); Prepared using method **GP1** and obtained as a pale yellow solid, mass = 178 mg, 69% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.28 (s, 1H), 7.26 – 7.08 (m, 12H), 7.01 (d, $J = 7.4$ Hz, 2H), 4.24 (t, $J = 7.8$ Hz, 1H), 3.38 (d, $J = 7.9$ Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 144.4, 140.2, 129.1, 128.3, 128.0, 126.2, 125.9, 53.1, 42.1. Compound characterization is in accordance with previous reports.⁹



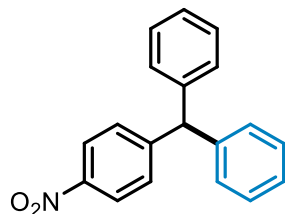
(1R)-2-bromo-1-phenyl-2,3-dihydro-1H-indene (1l); Prepared using method **GP1** and obtained as a white solid (Melting Point = 55-58 °C), mass = 218 mg, 80% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.38 – 7.27 (m, 4H), 7.26 – 7.15 (m, 4H), 6.96 (d, $J = 7.5$ Hz, 1H), 4.57 (d, $J = 7.7$ Hz, 1H), 4.42 (q, $J = 7.6$ Hz, 1H), 3.62 (dd, $J = 16.1, 7.1$ Hz, 1H), 3.39 (dd, $J = 16.1, 8.0$ Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 143.7, 140.9, 140.8, 128.6, 128.4, 127.4, 127.3, 127.3, 124.9, 123.9, 61.5, 55.6, 42.8. **GCMS** m/z: calculated for $\text{C}_{15}\text{H}_{13}\text{Br}$: 272, found 272 (^{79}Br) and 274 (^{81}Br). **HRMS** (APCI+) m/z: calculated for $\text{C}_{15}\text{H}_{13}\text{Br}$: 273.0273, found 273.0268.



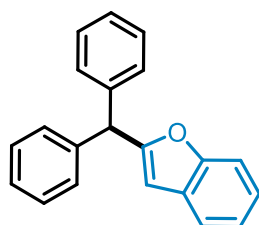
Triphenylmethane (1m); Prepared using method **GP1** and obtained as a white solid, mass = 264 mg, 99% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.33 – 7.26 (m, 6H), 7.25 – 7.19 (m, 3H), 7.16 – 7.11 (m, 6H), 5.57 (s, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 144.1, 129.6, 128.4, 126.4, 57.0. The spectral data is in accordance with previous reports.⁷



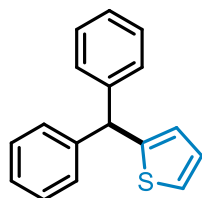
((4-bromophenyl)methylene)dibenzene (1n); Prepared using method **GP1** and obtained as a white solid, mass = 316 mg, 98% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.40 (d, $J = 6.5$ Hz, 2H), 7.31 – 7.27 (m, 4H), 7.26 – 7.21 (m, 2H), 7.09 (d, $J = 8.1$ Hz, 4H), 6.99 (d, $J = 8.4$ Hz, 2H), 5.50 (s, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 143.2, 142.9, 131.3, 131.1, 129.2, 128.3, 126.4, 120.2, 56.2. The spectral data is in accordance with previous reports.¹⁰



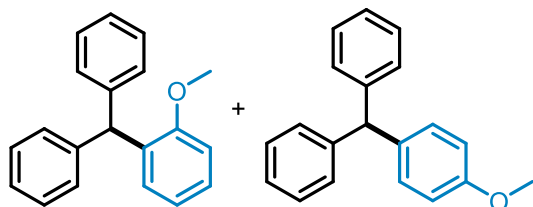
((4-nitrophenyl)methylene)dibenzene (1o); Prepared using method **GP1** and obtained as a pale yellow solid, mass = 283 mg, 98% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.14 (d, $J = 8.7$ Hz, 2H), 7.30 (m, 8H), 7.09 (d, $J = 7.7$ Hz, 4H), 5.64 (s, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 151.5, 146.5, 142.2, 130.2, 129.2, 128.6, 126.9, 123.5, 56.6. Compound characterization is in accordance with previous reports.¹⁰



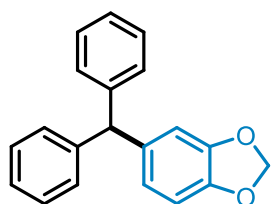
2-benzhydrylbenzofuran (1p); Prepared using method **GP2** and obtained as a white solid, mass = 236 mg, 83% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.48 (d, $J = 7.3$ Hz, 1H), 7.42 (d, $J = 7.7$ Hz, 1H), 7.33 (d, $J = 7.4$ Hz, 4H), 7.25 (d, $J = 7.9$ Hz, 8H), 6.29 (s, 1H), 5.60 (s, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 159.9, 155.1, 141.0, 128.9, 128.5, 126.9, 123.7, 122.6, 120.6, 111.1, 105.6, 51.3. Compound characterization is in accordance with previous reports.¹¹



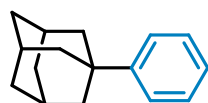
3-benzhydrylthiophene (1q); Prepared using method **GP2** and obtained as a white solid, mass = 235 mg, 94% yield; $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.30 (t, $J = 7.8$ Hz, 4H), 7.26 – 7.18 (m, 7H), 6.94 (t, $J = 4.4$ Hz, 1H), 6.69 (d, $J = 3.9$ Hz, 1H), 5.68 (s, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR ^{13}C NMR (101 MHz, CDCl_3) δ 147.8, 143.7, 128.8, 128.3, 126.6, 126.5, 126.3, 124.5, 52.1. Compound characterization is in accordance with previous reports.¹²



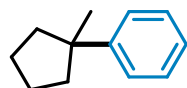
((2-methoxyphenyl)methylene)dibenzene + ((4-methoxyphenyl)methylene)dibenzene (1r); Prepared using method **GP2** and obtained as a whitish oil, mass = 236 mg, 86% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.35 – 7.28 (m, 3H), 7.26 – 7.20 (m, 3H), 7.17 – 7.12 (m, 3H), 7.10 – 7.01 (m, 3H), 6.96 – 6.79 (m, 2H), 5.92 (s, 0.26 H, *ortho*-isomer), 5.54 (s, 0.74 H, *para*-isomer), 3.80 (s, 2.22 H, *para*-isomer), 3.71 (s, 0.78 H, *ortho*-isomer). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 157.9 (*para*-isomer), 144.2 (*para*-isomer), 143.7 (*ortho*-isomer), 136.0, 131.7 (*ortho*-isomer), 130.3 (*para*-isomer), 129.3 (*para*-isomer), 129.2 (*ortho*-isomer), 128.2 (*para*-isomer), 128.1 (*ortho*-isomer), 127.9 (*ortho*-isomer), 126.1 (*para*-isomer), 126.0 (*ortho*-isomer), 125.8 (*ortho*-isomer), 113.6 (*para*-isomer), 110.3 (*ortho*-isomer), 55.9 (*para*-isomer), 55.6 (*ortho*-isomer), 55.1 (*para*-isomer), 49.4 (*ortho*-isomer). Compound characterization is in accordance with previous reports.¹³



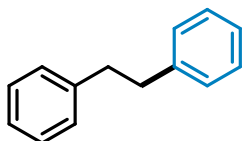
5-benzhydrylbenzo[d][1,3]dioxole (1s); Prepared using method **GP2** and obtained as a colorless oil, mass = 161 mg, 56% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.31 – 7.25 (m, 4H), 7.24 – 7.18 (m, 2H), 7.12 (dd, $J = 7.0, 1.6$ Hz, 4H), 6.73 (d, $J = 7.9$ Hz, 1H), 6.61 (d, $J = 1.8$ Hz, 1H), 6.57 (dd, $J = 8.0, 2.1$ Hz, 1H), 5.92 (s, 2H), 5.47 (s, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 147.6, 145.9, 143.9, 137.9, 129.3, 128.3, 126.3, 122.5, 109.9, 108.0, 100.9, 56.4. Compound characterization is in accordance with previous reports.¹¹



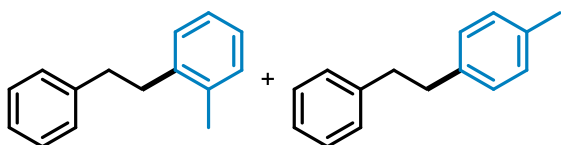
1-phenyladamantane (1t); Prepared using method **GP1** and obtained as a white solid, mass = 207 mg, 94% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.43 – 7.37 (m, 2H), 7.37 – 7.31 (m, 2H), 7.24 – 7.17 (m, 1H), 2.13 (bs, 3H), 1.95 (bs, 6H), 1.85 – 1.77 (m, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 151.2, 128.0, 125.4, 124.8, 43.1, 36.8, 36.1, 28.9. The spectral data is in accordance with previous reports.¹⁴



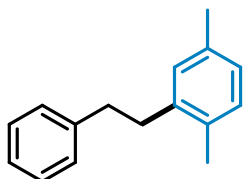
(1-methylcyclopentyl)benzene (1u); Prepared using method **GP1** and obtained as a yellow oil, mass = 106 mg, 63% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.43 – 7.27 (m, 4H), 7.25 – 7.19 (m, 1H), 2.03 – 1.73 (m, 8H), 1.32 (d, $J = 2.2$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 151.6, 128.5, 128.2, 126.2, 125.7, 125.4, 47.3, 39.8, 29.7, 23.9. **GCMS** m/z : calculated for $\text{C}_{12}\text{H}_{16}$: 160, found 160. **HRMS** (APCI+) m/z : calculated for $\text{C}_{12}\text{H}_{16}$: 161.1324, found 161.1320.



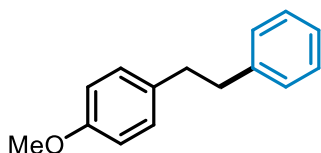
1,2-diphenylethane (1v); Prepared using method **GP3** and obtained as a colorless oil, mass = 123 mg, 68% yield; $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.22 – 7.14 (m, 4H), 7.14 – 7.05 (m, 7H), 2.83 (s, 4H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 141.8, 128.5, 128.4, 126.0, 38.0. The spectral data is in accordance with previous reports.¹⁵



1-methyl-2-phenethylbenzene + 1-methyl-4-phenethylbenzene (1w); Prepared using method **GP3** and obtained as a whitish oil, mass = 157 mg, 80% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.24 – 7.15 (m, 2H), 7.10 (s, 3H), 7.04 (s, 2H), 6.99 (s, 1H), 6.93 (s, 1H), 2.80 (s, 4H), 2.23 (s, 1.65H, *ortho*-isomer), 2.21 (s, 1.35H, *para*-isomer). δ 7.40 – 7.27 (m, 5H), 7.23 (d, $J = 6.9$ Hz, 2H), 7.17 (d, $J = 7.4$ Hz, 2H), 4.00 (s, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 142.1, 142.0, 140.1, 136.0, 135.4, 130.3, 129.3, 129.1, 128.9, 128.5, 128.4, 126.7, 126.2, 126.1, 126.0, 125.9, 125.5, 38.1, 37.6, 36.8, 35.5, 21.1, 19.3. The spectral data is in accordance with previous reports.¹⁵

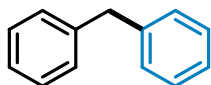


1,4-dimethyl-2-phenethylbenzene (1x); Prepared using method **GP3** and obtained as a brown residue, mass = 167 mg, 73% yield; $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.51 – 7.43 (m, 2H), 7.43 – 7.33 (m, 3H), 7.26 – 7.19 (m, 1H), 7.19 – 7.07 (m, 2H), 3.04 (s, 4H), 2.49 (s, 3H), 2.45 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 142.2, 139.9, 135.4, 132.7, 130.2, 129.7, 128.4, 126.8, 126.0, 37.0, 35.6, 21.0, 18.8. The spectral data is in accordance with previous reports.¹⁶

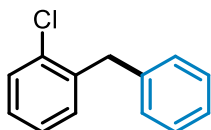


1-methoxy-4-phenethylbenzene (1y); Prepared using method **GP3** and obtained as a white solid, mass = 89 mg, 42% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.31 – 7.26 (m, 2H), 7.22 – 7.17 (m, 3H), 7.10 (d, $J = 8.6$ Hz, 2H), 6.83 (d, $J = 8.6$ Hz, 2H), 3.80 (s, 3H), 2.88 (s, 4H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 157.8, 141.8, 133.8, 129.3, 128.4, 128.2, 125.8, 113.7, 55.2, 38.1, 37.0. The spectral data is in accordance with previous reports.¹⁵

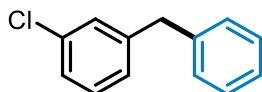
Characterization of Friedel-Crafts products from aryl aldehydes



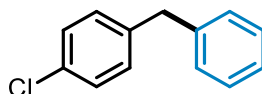
Diphenylmethane (2a); Prepared using method **GP4** and obtained as a colorless oil, mass = 158 mg, 94% yield; The spectral data is identical to **1a**.



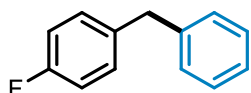
1-benzyl-2-chlorobenzene (2b); Prepared using method **GP4** (20 h and 2 equiv. TiCl_4) and obtained as a colorless oil, mass = 150 mg, 74% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.51 – 7.44 (m, 1H), 7.40 (d, J = 6.4 Hz, 2H), 7.31 (d, J = 6.5 Hz, 3H), 7.28 – 7.22 (m, 3H), 4.22 (s, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 139.6, 138.8, 134.3, 131.1, 129.6, 129.0, 128.6, 127.7, 126.9, 126.3, 39.3. The spectral data is in accordance with previous reports.¹



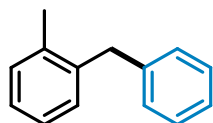
1-benzyl-3-chlorobenzene (2c); Prepared using method **GP4** (20 h and 2 equiv. TiCl_4) and obtained as a colorless oil, mass = 158 mg, 78% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.51 – 7.44 (m, 1H), 7.44 – 7.36 (m, 2H), 7.36 – 7.29 (m, 3H), 7.28 – 7.22 (m, 3H), 4.22 (s, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 143.3, 140.3, 134.4, 129.8, 129.1, 129.0, 128.7, 127.2, 126.5, 126.4, 41.7. The spectral data is in accordance with previous reports.¹



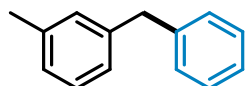
1-benzyl-4-chlorobenzene (2d); Prepared using method **GP4** and obtained as a pale yellow oil, mass = 190 mg, 91% yield; The spectral data is identical to **1d**.



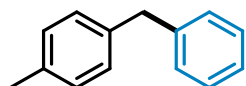
1-benzyl-4-fluorobenzene (2e); Prepared using method **GP4** and obtained as a colorless oil, mass = 162 mg, 84% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.38 (d, J = 7.3 Hz, 2H), 7.34 – 7.18 (m, 5H), 7.06 (t, J = 7.5 Hz, 2H), 4.04 (s, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) ^{13}C NMR (101 MHz, Chloroform- d) δ 161.6 (d, J = 243.8 Hz), 141.1, 136.9, 130.4 (d, J = 7.8 Hz), 129.0, 128.7, 126.3, 115.3 (d, J = 21.0 Hz), 41.2. ^{19}F NMR (282 MHz, CDCl_3) δ -117.3. The spectral data is in accordance with previous reports.¹



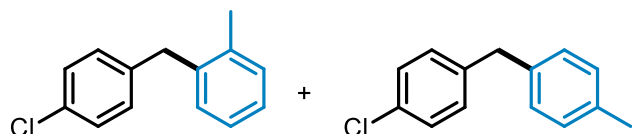
1-benzyl-2-methylbenzene (2f); Prepared using method **GP4** (20 h) and obtained as a colorless oil, mass = 115 mg, 63% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.33 – 7.27 (m, 2H), 7.24 – 7.10 (m, 7H), 4.02 (s, 2H), 2.27 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 140.5, 139.1, 136.8, 130.4, 130.1, 128.9, 128.5, 126.6, 126.13, 126.05, 39.6, 19.8. The spectral data is in accordance with previous reports.³



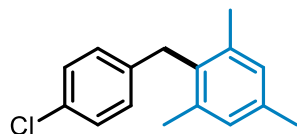
1-benzyl-3-methylbenzene (2g); Prepared using method **GP4** (2 h) and obtained as a colorless oil, mass = 156 mg, 84% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.40 – 7.34 (m, 2H), 7.32 – 7.23 (m, 4H), 7.14 – 7.06 (m, 3H), 4.04 (s, 2H), 2.40 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 141.4, 141.2, 138.1, 129.8, 129.1, 128.6, 128.5, 127.0, 126.1, 42.0, 21.5. The spectral data is in accordance with previous reports.¹⁷



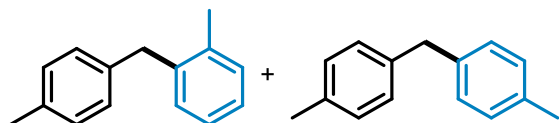
1-benzyl-4-methylbenzene (2h); Prepared using method **GP4** and obtained as a colorless oil, mass = 87 mg, 48% yield; The spectral data is identical to **1b**.



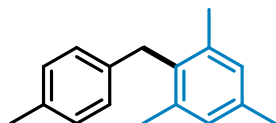
1-(4-chlorobenzyl)-2-methylbenzene + 1-(4-chlorobenzyl)-3-methylbenzene (2i); Prepared using method **GP4** and obtained as a colorless oil, mass = 197 mg, 91% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.32 (m, 2H), 7.27 – 7.23 (m, 1H), 7.15 (m, 5H), 4.02 (s, 0.8H, *ortho*-isomer), 3.98 (s, 1.2H, *para*-isomer), 2.41 (s, 1.8H, *para*-isomer), 2.31 (s, 1.2H, *ortho*-isomer). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) ^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.9, 138.9, 138.3, 137.5, 136.5, 135.8, 131.8, 131.7, 130.4, 130.2, 130.0, 129.9, 129.3, 128.7, 128.5, 128.5, 126.7, 126.1, 40.8 (*para*-isomer), 38.8 (*ortho*-isomer), 21.0 (*para*-isomer), 19.6 (*ortho*-isomer). The spectral data is in accordance with previous reports.¹⁸



2-(4-chlorobenzyl)-1,3,5-trimethylbenzene (2j); Prepared using method **GP4** and obtained as a yellow oil, mass = 168 mg, 66% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.21 (d, $J = 8.5$ Hz, 2H), 6.96 (d, $J = 8.1$ Hz, 2H), 6.92 (s, 2H), 4.00 (s, 2H), 2.32 (s, 3H), 2.21 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 138.7, 137.0, 136.1, 133.4, 131.5, 129.3, 129.1, 128.6, 34.2, 21.0, 20.2. The spectral data is in accordance with previous reports.⁵

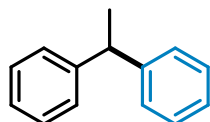


1-methyl-2-(4-methylbenzyl)benzene + 1-methyl-3-(4-methylbenzyl)benzene (2k); Prepared using method **GP4** and obtained as a colorless oil, mass = 153 mg, 78% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.22 (dd, $J = 3.4, 1.8$ Hz, 1H), 7.15 (d, $J = 2.0$ Hz, 6H), 7.08 (dt, $J = 7.9, 2.6$ Hz, 1H), 4.01 (s, 0.6H, *ortho*-isomer), 3.97 (s, 1.4H, *para*-isomer), 2.38 (s, 5H), 2.32 (s, 1H, *ortho*-isomer). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 139.2, 138.4, 137.4, 136.6, 135.5, 135.4, 130.3, 129.9, 129.2, 129.1, 128.8, 128.7, 126.4, 126.0, 41.2 (*para*-isomer), 39.1 (*ortho*-isomer), 21.1, 19.7 (*ortho*-isomer). The spectral data is in accordance with previous reports.¹⁹

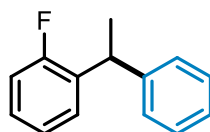


1,3,5-trimethyl-2-(4-methylbenzyl)benzene (2l); Prepared using method **GP4** and obtained as a yellow oil, mass = 136 mg, 60% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.07 (d, $J = 7.8$ Hz, 2H), 6.95 – 6.90 (m, 4H), 4.01 (s, 2H), 2.32 (s, 6H), 2.23 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 137.14, 137.09, 135.7, 135.2, 134.1, 129.2, 129.0, 127.9, 34.4, 21.1, 21.0, 20.3. The spectral data is in accordance with previous reports.⁵

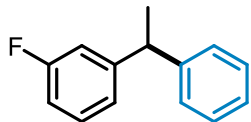
Characterization of Friedel-Crafts products from aryl ketones



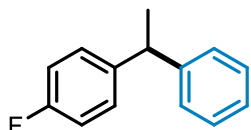
Ethane-1,1-diyl dibenzene (3a); Prepared using method **GP5** and obtained as a colorless oil, mass = 178 mg, 93% yield; The spectral data is identical to **1h**.



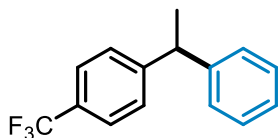
1-fluoro-2-(1-phenylethyl)benzene (3b); Prepared using method **GP5** and obtained as a colorless oil, mass = 159 mg, 75% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.41 – 7.16 (m, 7H), 7.13 – 7.08 (m, 1H), 7.06 – 6.99 (m, 1H), 4.52 (q, $J = 7.4$ Hz, 1H), 1.68 (d, $J = 7.3$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 160.7 (d, $J = 245.8$ Hz), 145.2, 133.4 (d, $J = 14.5$ Hz), 128.6 (d, $J = 4.6$ Hz), 128.5, 127.8 (d, $J = 8.3$ Hz), 127.7, 126.3, 124.2 (d, $J = 3.6$ Hz), 115.5 (d, $J = 22.5$ Hz), 37.7, 20.9. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -119.3. The spectral data is in accordance with previous reports.²⁰



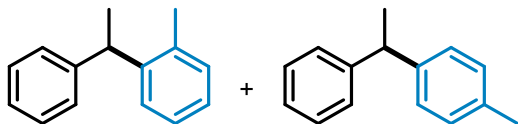
1-fluoro-3-(1-phenylethyl)benzene (3c); Prepared using method **GP5** and obtained as a yellow oil, mass = 142 mg, 71% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.41 – 7.35 (m, 2H), 7.34 – 7.25 (m, 4H), 7.11 – 7.06 (m, 1H), 7.02 (d, J = 10.2 Hz, 1H), 6.96 (t, J = 7.7 Hz, 1H), 4.23 (q, J = 7.3 Hz, 1H), 1.72 (d, J = 7.3 Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 163.1 (d, J = 245.5 Hz), 149.2 (d, J = 6.7 Hz), 145.7, 129.8 (d, J = 8.3 Hz), 128.6, 127.7, 126.4, 123.4 (d, J = 2.8 Hz), 114.6 (d, J = 21.2 Hz), 113.0 (d, J = 21.1 Hz), 44.7, 21.8. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -114.7. The spectral data is in accordance with previous reports.⁶



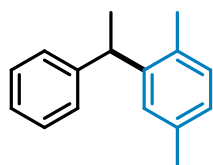
1-fluoro-4-(1-phenylethyl)benzene (3d); Prepared using method **GP5** and obtained as a colorless oil, mass = 151 mg, 76% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.38 – 7.30 (m, 2H), 7.28 – 7.18 (m, 5H), 7.05 – 6.96 (m, 2H), 4.19 (q, J = 7.3 Hz, 1H), 1.67 (d, J = 7.3 Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 161.4 (d, J = 244.0 Hz), 146.3, 142.2, 129.1 (d, J = 7.8 Hz), 128.6, 127.7, 126.3, 115.2 (d, J = 21.1 Hz), 44.2, 22.1. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -118.9. The spectral data is in accordance with previous reports.²¹



1-(1-phenylethyl)-4-(trifluoromethyl)benzene (3e); Prepared using method **GP5** and obtained as a yellow oil, mass = 211 mg, 88% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.38 – 7.30 (m, 2H), 7.28 – 7.18 (m, 5H), 7.05 – 6.96 (m, 2H), 4.19 (q, J = 7.3 Hz, 1H), 1.67 (d, J = 7.3 Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 150.6, 145.4, 128.7, 128.1, 127.7, 126.6, 125.5 (q, J = 3.8 Hz), 125.4, 44.8, 21.7. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -63.8. The spectral data is in accordance with previous reports.²²

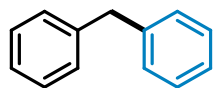


1-methyl-2-(1-phenylethyl)benzene + 1-methyl-4-(1-phenylethyl)benzene (3f); Prepared using method **GP5** and obtained as a colorless oil, mass = 165 mg, 84% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.32 (t, J = 7.4 Hz, 2H), 7.29 – 7.24 (m, 2H), 7.21 (t, J = 6.9 Hz, 1H), 7.15 (t, J = 5.9 Hz, 4H), 4.16 (q, J = 7.2 Hz, 1H), 2.35 (s, 3H), 1.67 (d, J = 7.2 Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 146.6, 143.4, 135.5, 129.1, 128.4, 127.6, 127.5, 126.0, 44.4, 22.0, 21.0. The spectral data is in accordance with previous reports.²²

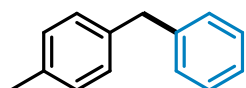


1,4-dimethyl-2-(1-phenylethyl)benzene (3g); Prepared using method **GP5** and obtained as a colorless oil, mass = 214 mg, 99% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.35 – 7.28 (m, 2H), 7.26 – 7.19 (m, 3H), 7.17 – 7.12 (m, 1H), 7.11 – 7.06 (m, 1H), 7.04 – 6.98 (m, 1H), 4.36 (q, J = 7.2 Hz, 1H), 2.39 (s, 3H), 2.26 (s, 3H), 1.68 (d, J = 7.2 Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 146.5, 143.8, 135.4, 133.0, 130.4, 128.4, 127.8, 127.6, 126.9, 125.9, 41.1, 22.2, 21.4, 19.4. The spectral data is in accordance with previous reports.²³

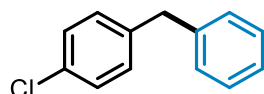
Characterization of Friedel-Crafts products from aryl acids



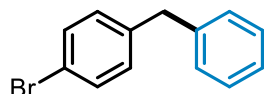
Diphenylmethane (4a); Prepared using method **GP6** and obtained as a pale yellow oil, mass = 94 mg, 56% yield; The spectral data is identical to **1a**.



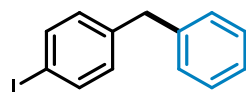
1-benzyl-4-methylbenzene (4b); Prepared using method **GP6** and obtained as a colorless oil, mass = 80 mg, 44% yield; The spectral data is identical to **1b**.



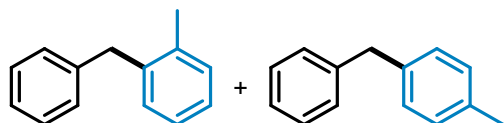
1-benzyl-4-chlorobenzene (4c); Prepared using method **GP6** and obtained as a colorless oil, mass = 152 mg, 75% yield; The spectral data is identical to **1d**.



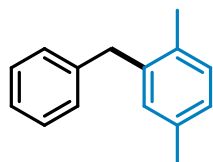
1-benzyl-4-bromobenzene (4d); Prepared using method **GP6** and obtained as a colorless oil, mass = 181 mg, 73% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.46 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 6.1 Hz, 2H), 7.28 (t, J = 5.0 Hz, 1H), 7.23 (d, J = 7.3 Hz, 2H), 7.12 (d, J = 8.4 Hz, 2H), 3.99 (s, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 140.6, 140.2, 131.6, 130.8, 129.0, 128.7, 126.4, 120.1, 41.4. The spectral data is in accordance with previous reports.¹



1-benzyl-4-iodobenzene (4e); Prepared using method **GP6** and obtained as a pale yellow oil, mass = 170 mg, 58% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.67 – 7.60 (m, 2H), 7.37-7.30 (m, 2H), 7.29 – 7.24 (m, 1H), 7.23 – 7.17 (m, 2H), 7.00 – 6.94 (m, 2H), 3.97 (s, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 140.9, 140.5, 137.6, 131.1, 129.0, 128.7, 126.4, 91.4, 41.5. The spectral data is in accordance with previous reports.¹

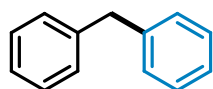


1-benzyl-2-methylbenzene + 1-benzyl-4-methylbenzene (4f); Prepared using method **GP6** and obtained as a colorless oil, mass = 111 mg, 61% yield; The spectral data is identical to **1e**.

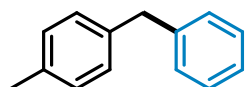


2-benzyl-1,4-dimethylbenzene (4g); Prepared using method **GP6** and obtained as a pale yellow oil, mass = 86 mg, 43% yield; The spectral data is identical to **1f**.

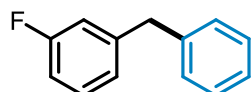
Characterization of Friedel-Crafts products from aryl esters



Diphenylmethane (5a); Prepared using method **GP7** and obtained as a pale yellow oil, mass = 134 mg, 78% yield; The spectral data is identical to **1a**.



1-benzyl-4-methylbenzene (5b); Prepared using method **GP** and obtained as a colorless oil, mass = 88 mg, 47% yield; The spectral data is identical to **1b**.



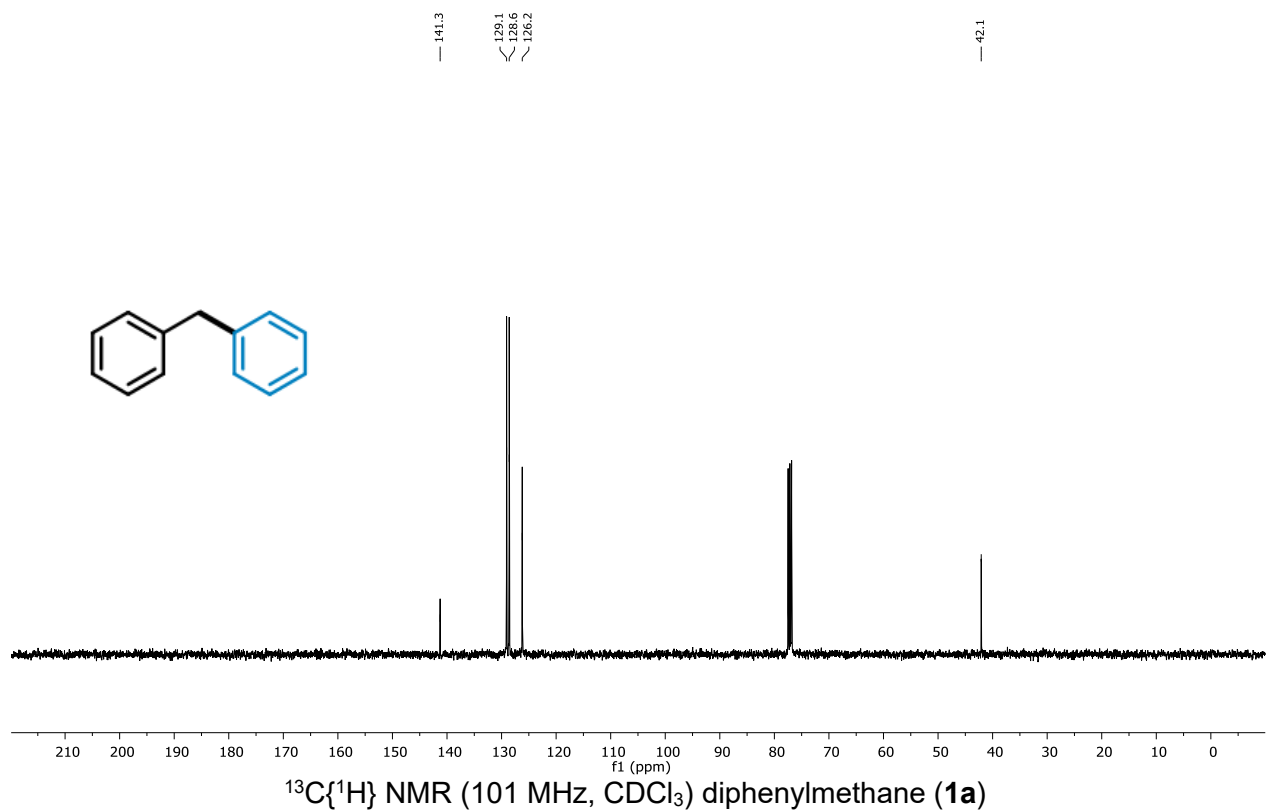
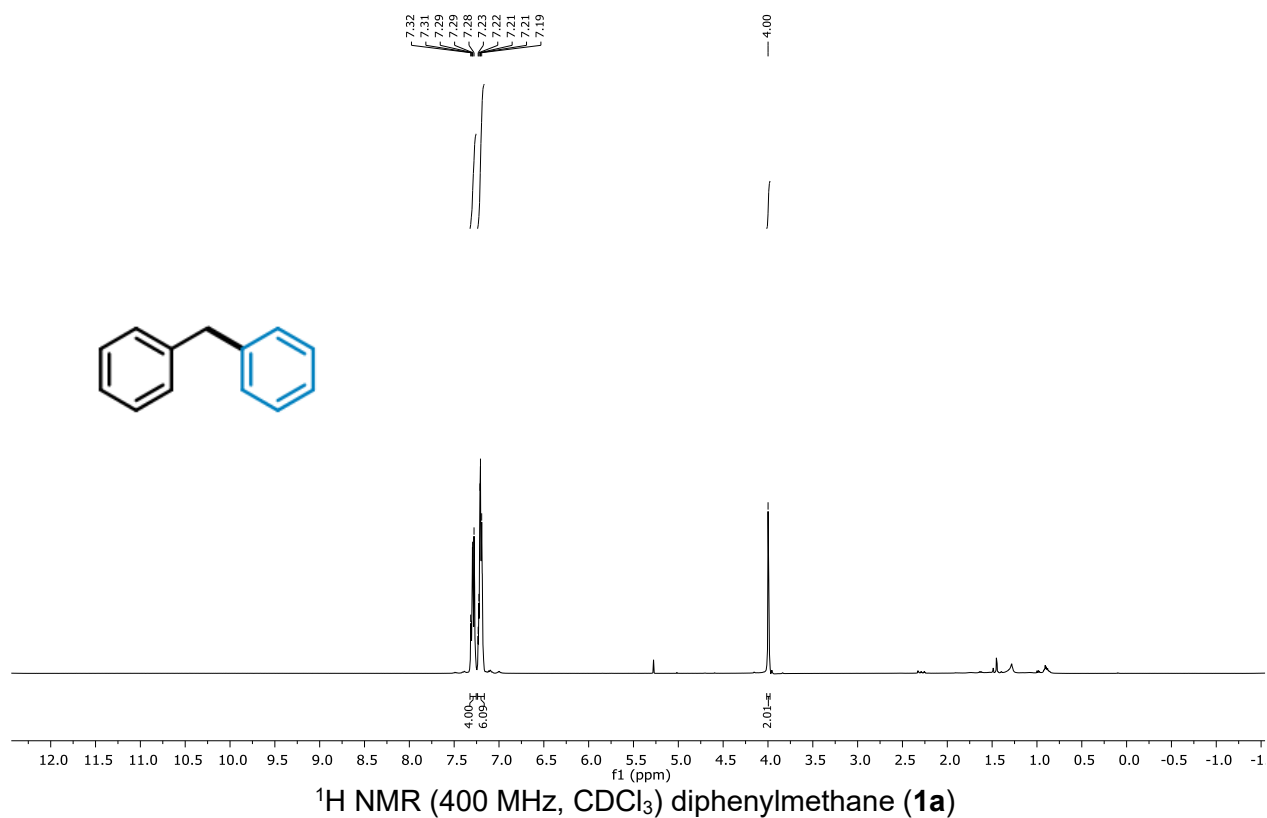
1-benzyl-3-fluorobenzene (5c); Prepared using method **GP7** (20 h, then 1 equiv. TiCl_4 for 2 h) and obtained as a colorless oil, mass = 150 mg, 79% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.35 – 7.29 (m, 2H), 7.29 – 7.23 (m, 2H), 7.23 – 7.18 (m, 2H), 7.02 – 6.97 (m, 1H), 6.94 – 6.87 (m, 2H), 3.99 (s, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 163.1 (d, $J = 245.7$ Hz), 143.8 (d, $J = 7.4$ Hz), 140.4, 130.0 (d, $J = 8.3$ Hz), 129.1, 128.7, 126.5, 124.7 (d, $J = 2.9$ Hz), 115.9 (d, $J = 21.2$ Hz), 113.1 (d, $J = 20.9$ Hz), 41.8. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -115.0. The spectral data is in accordance with previous reports.³

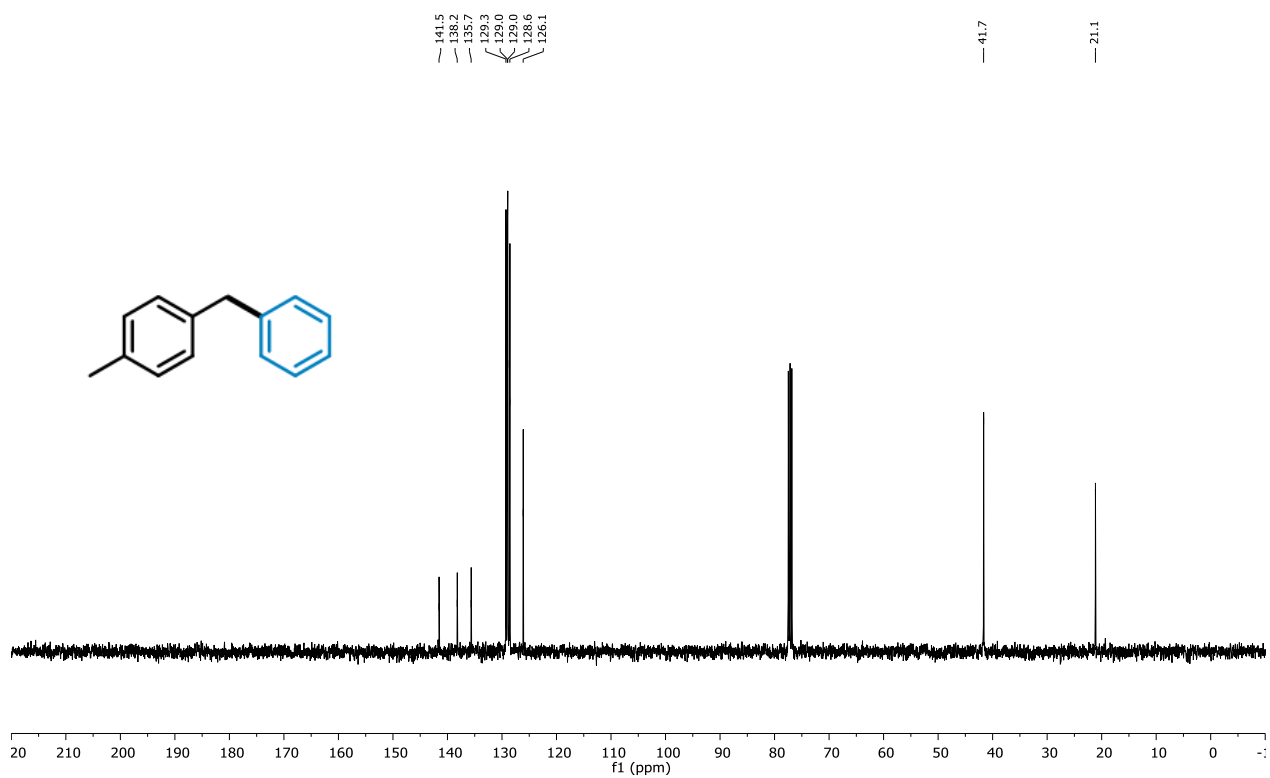
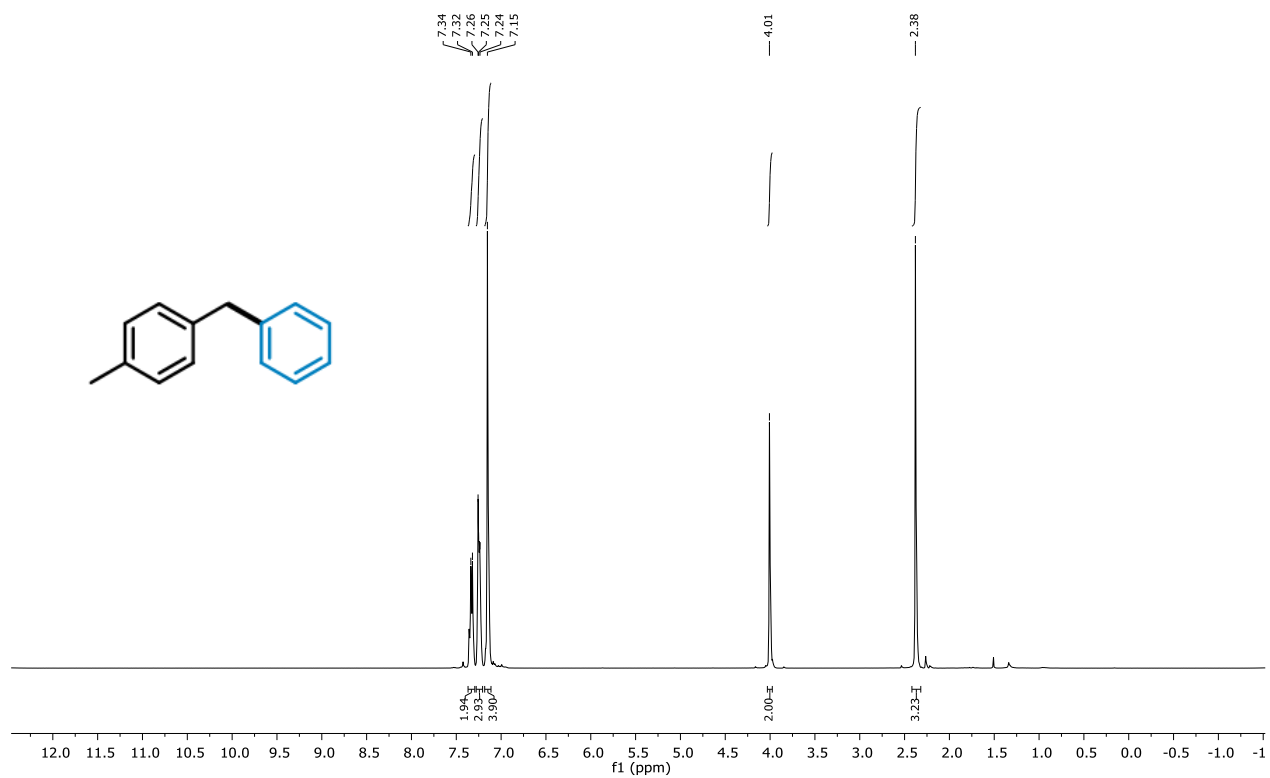
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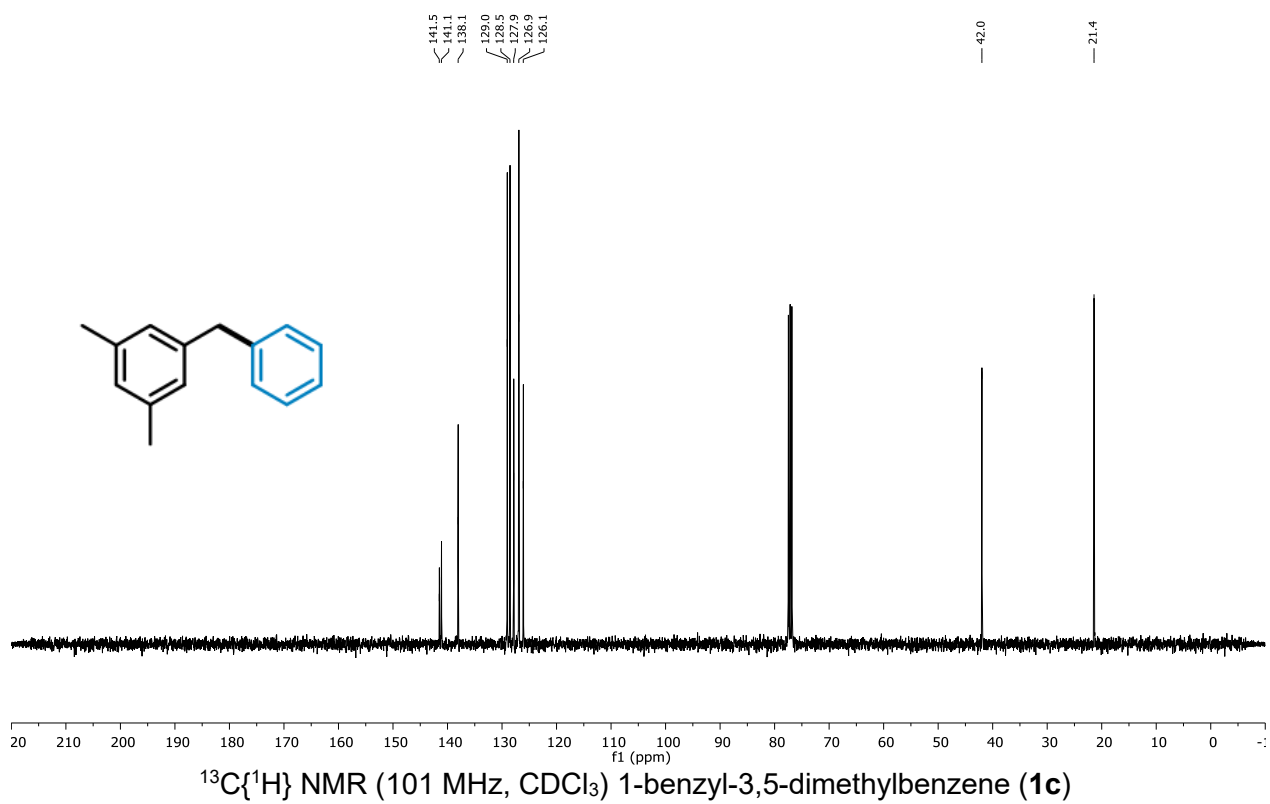
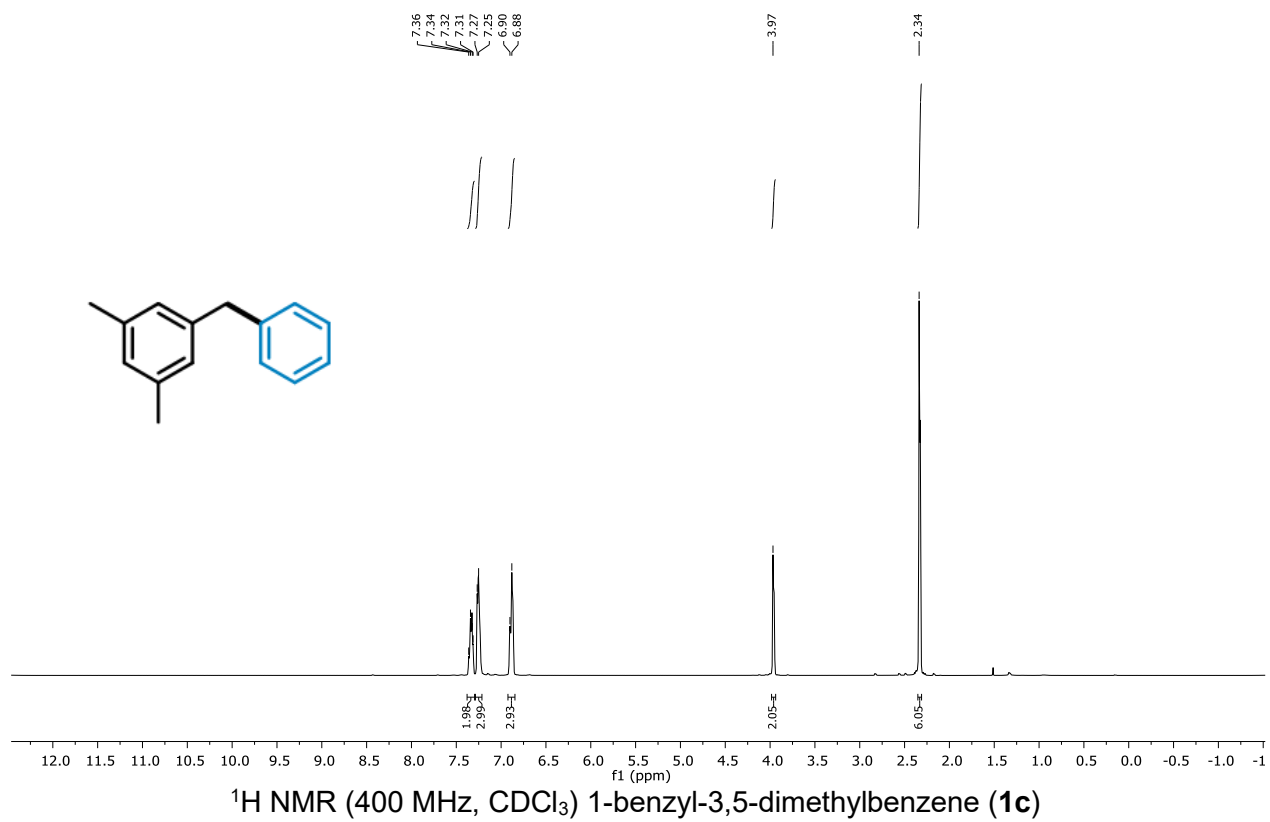
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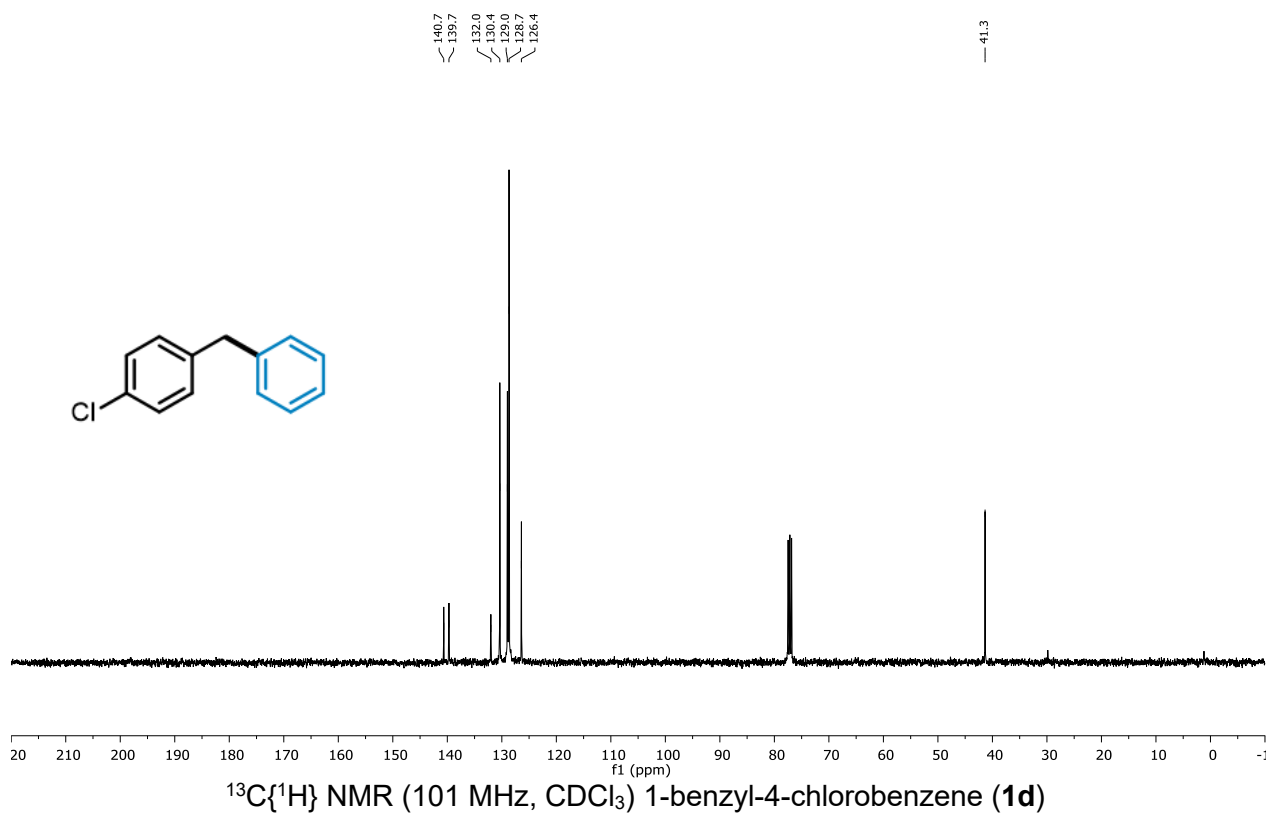
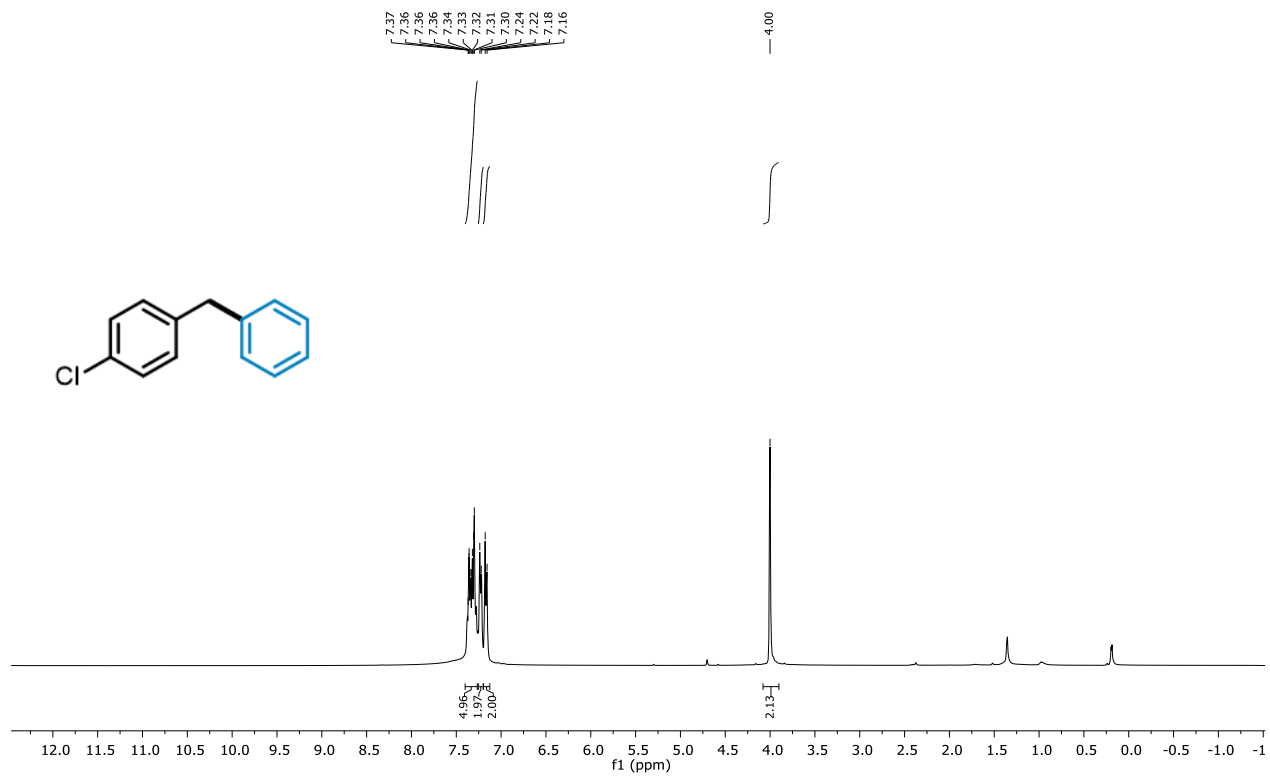
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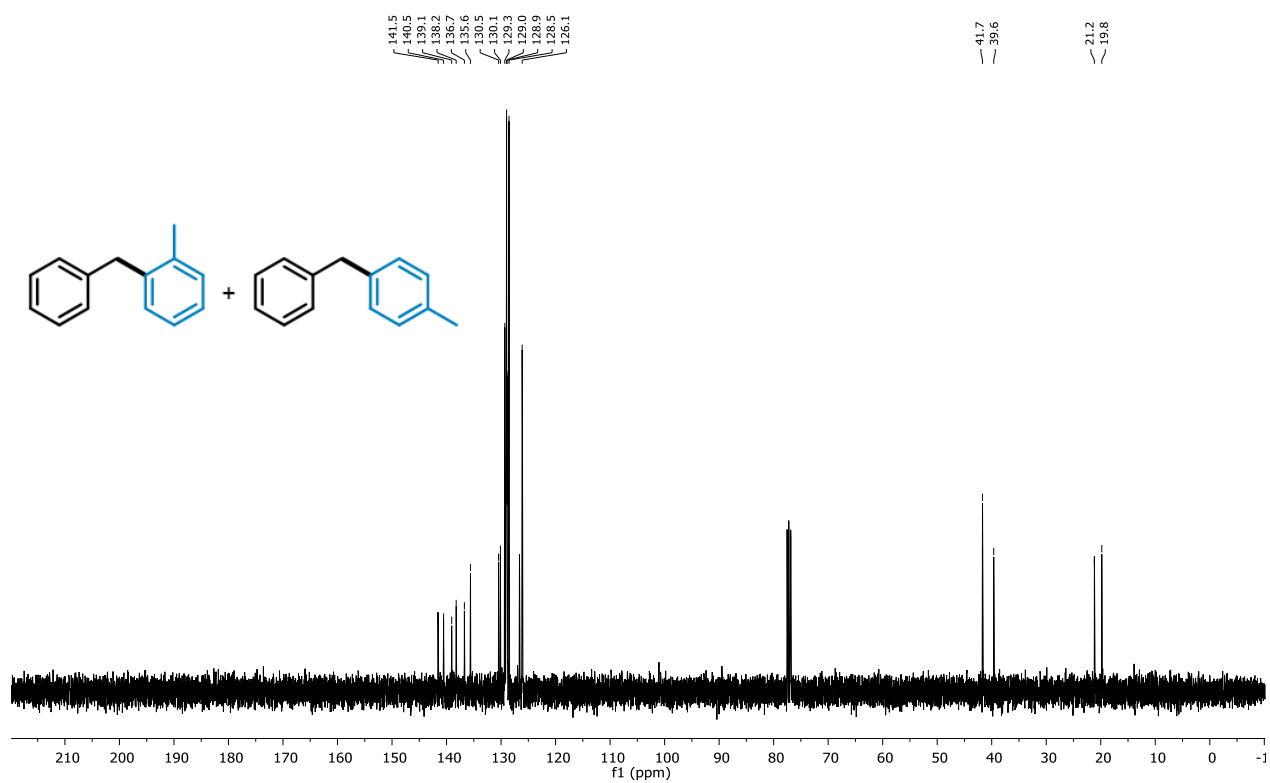
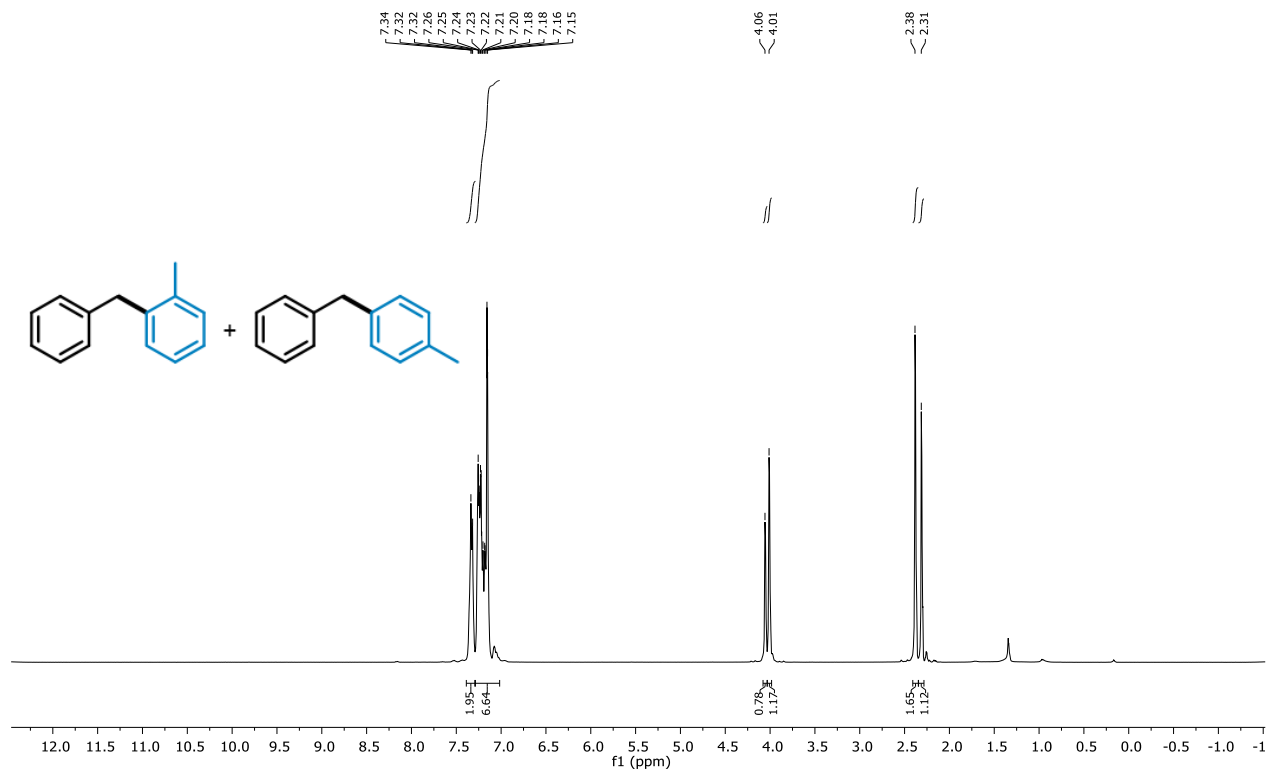
NMR Spectra

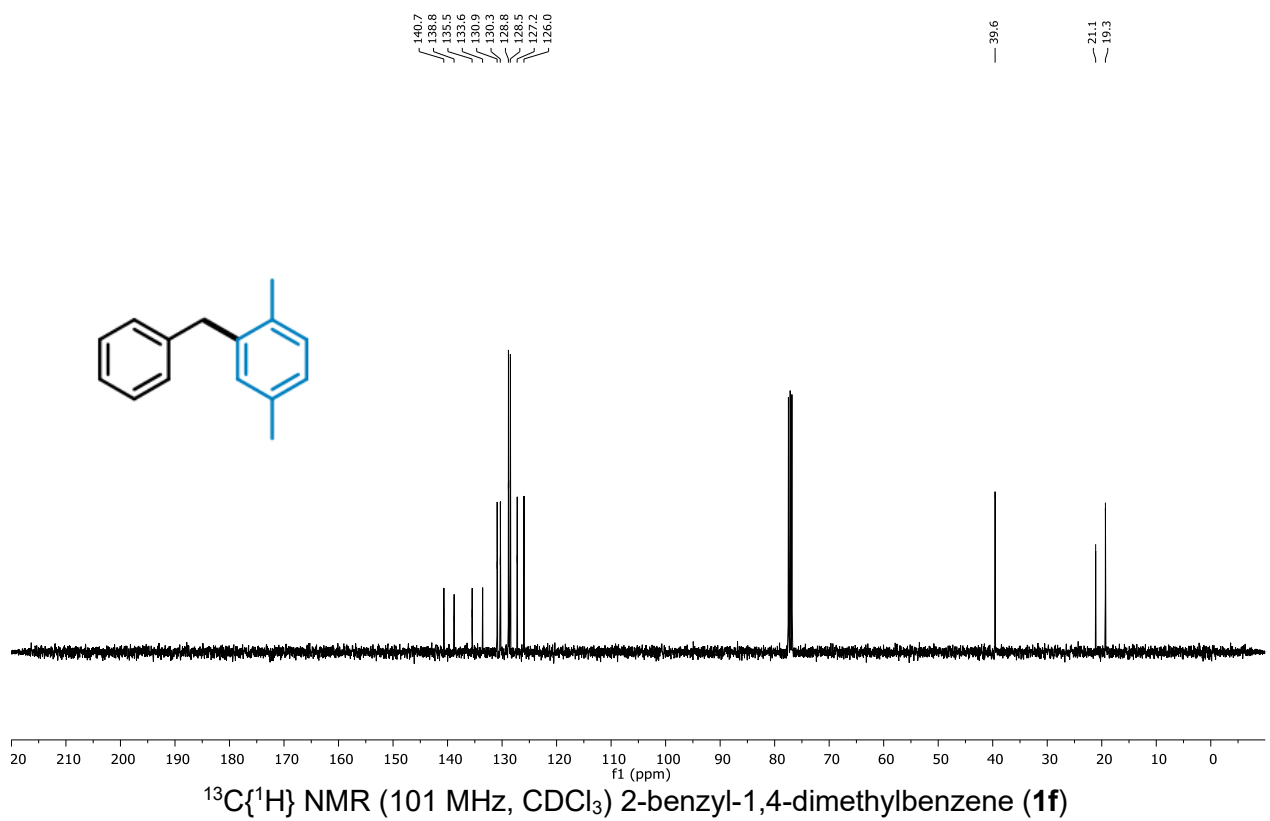
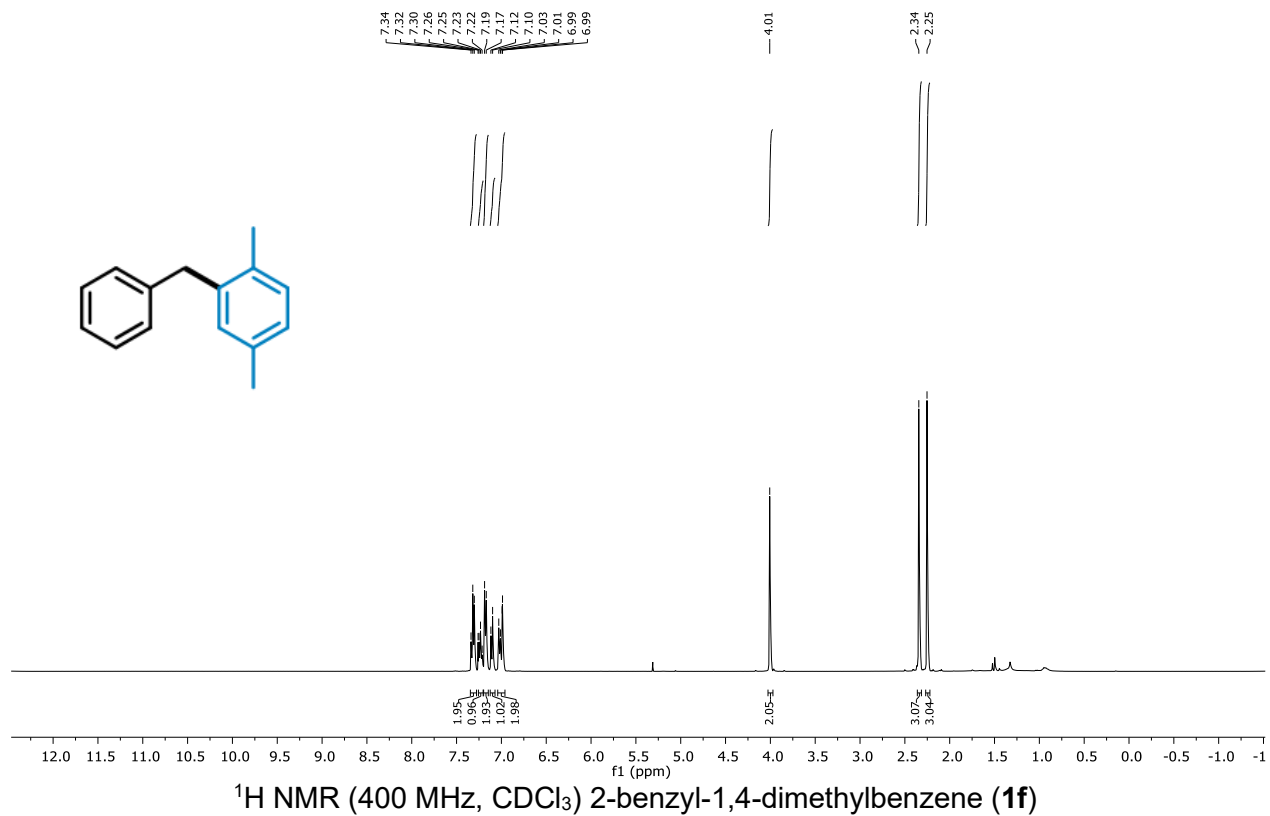


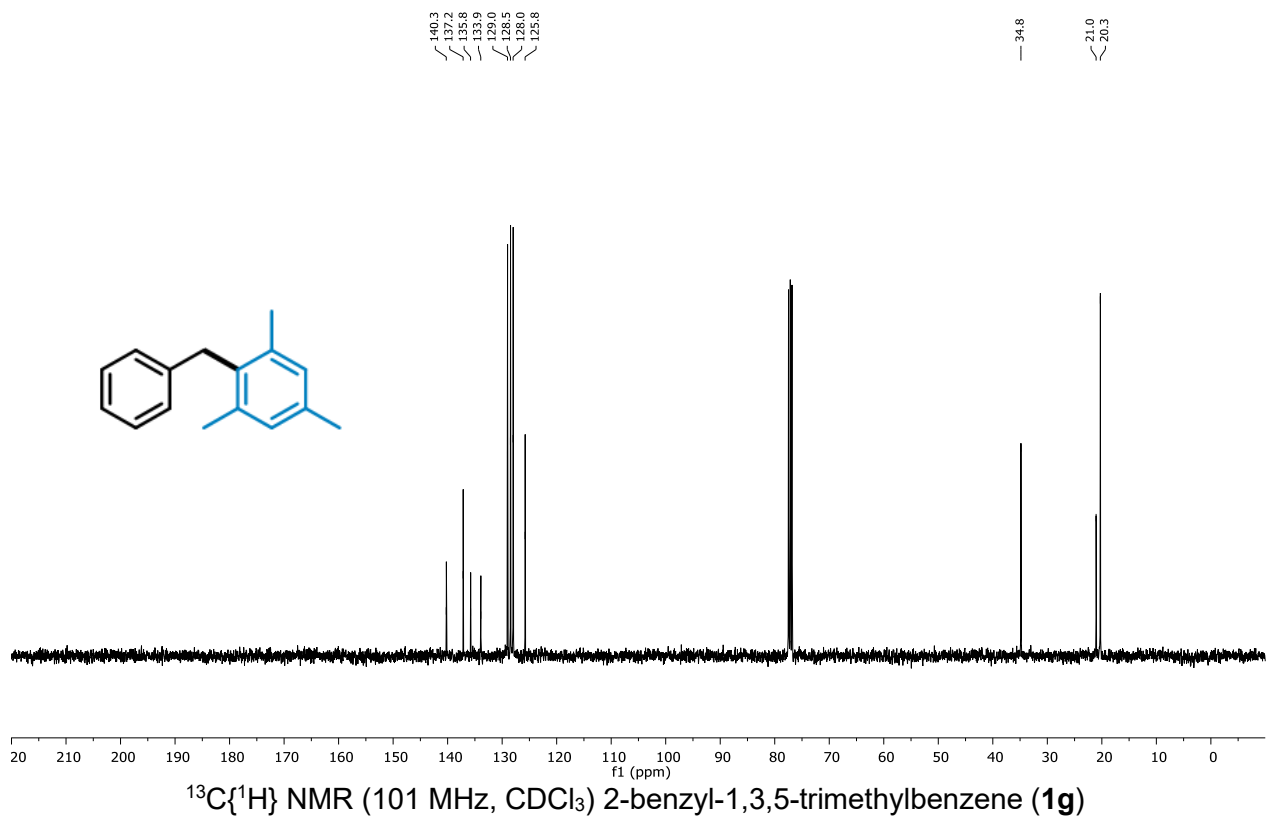
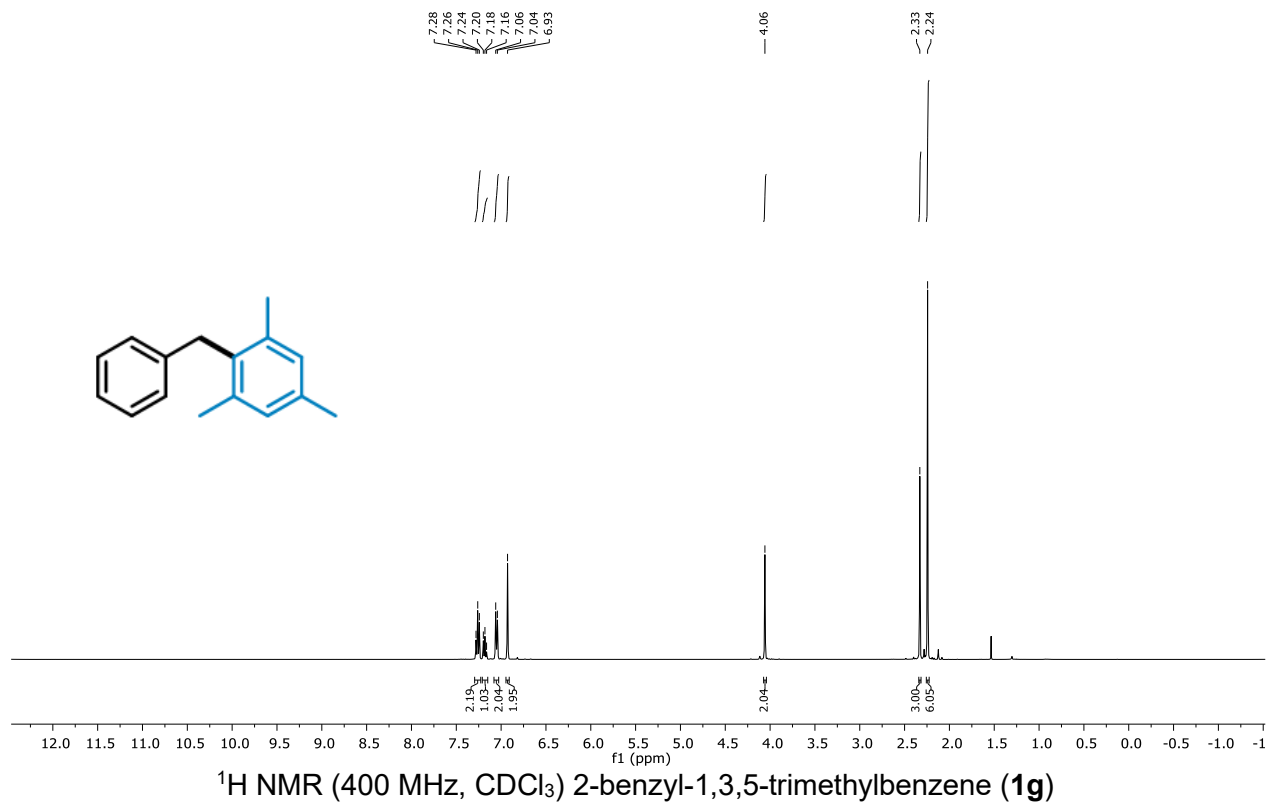


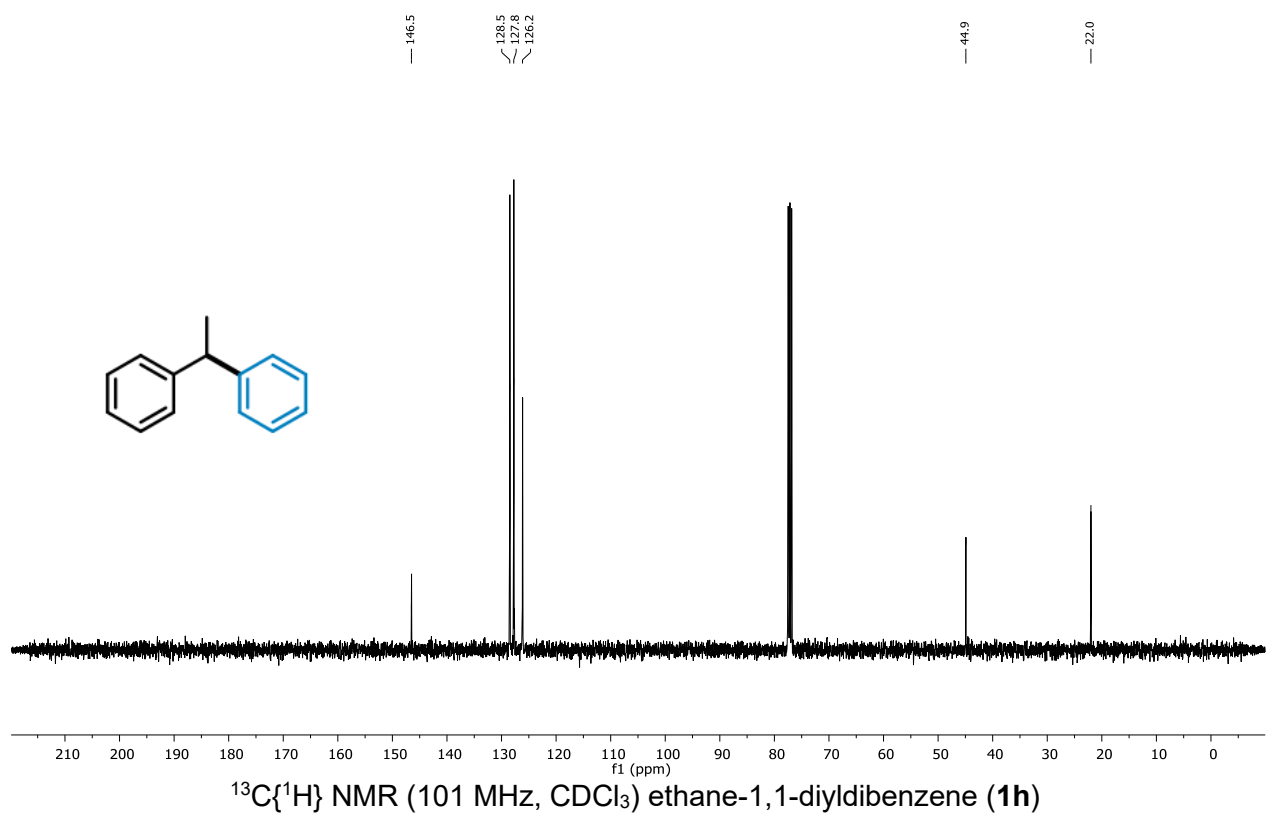
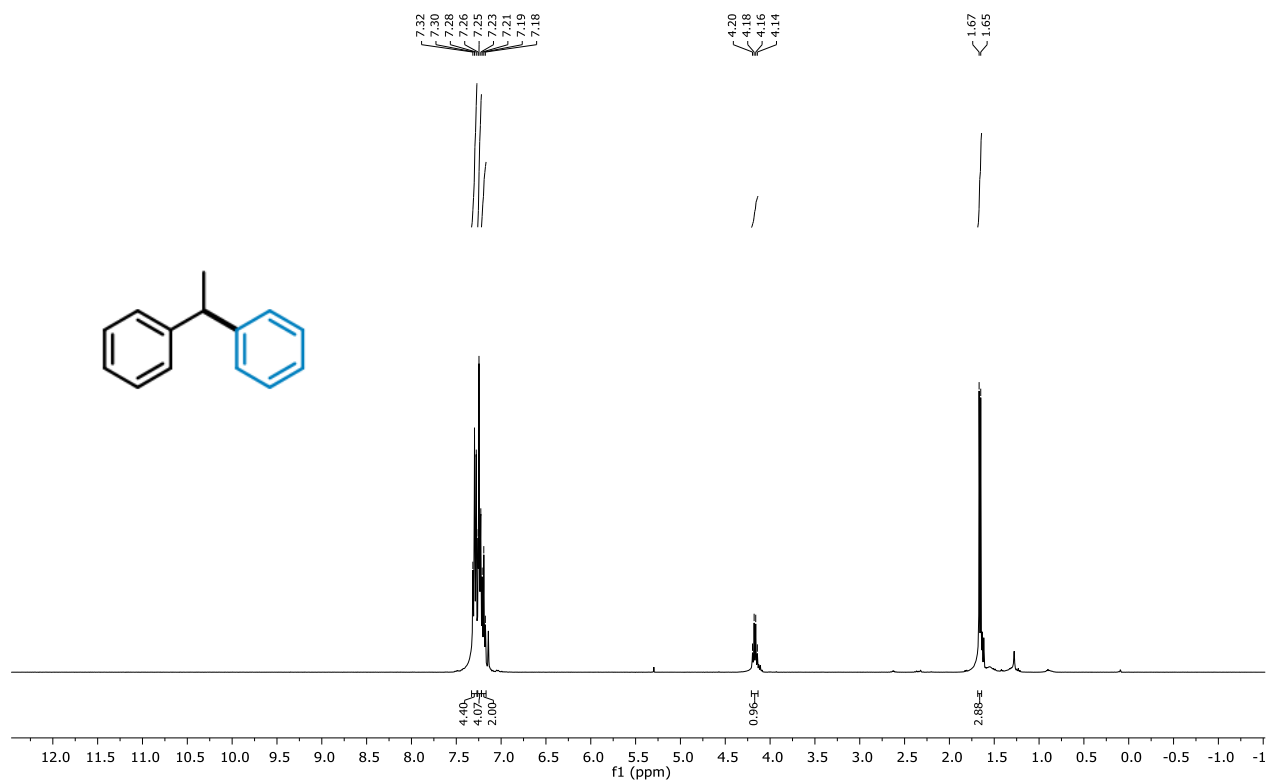


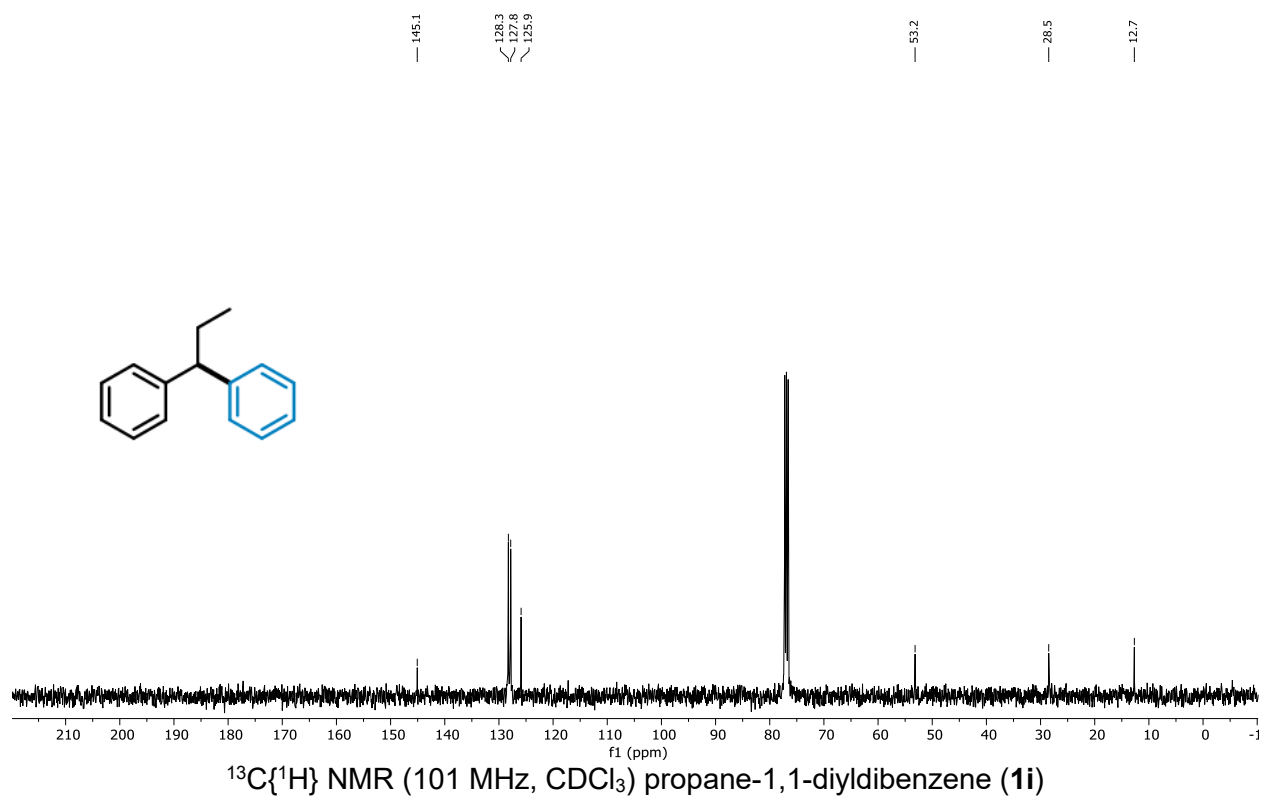
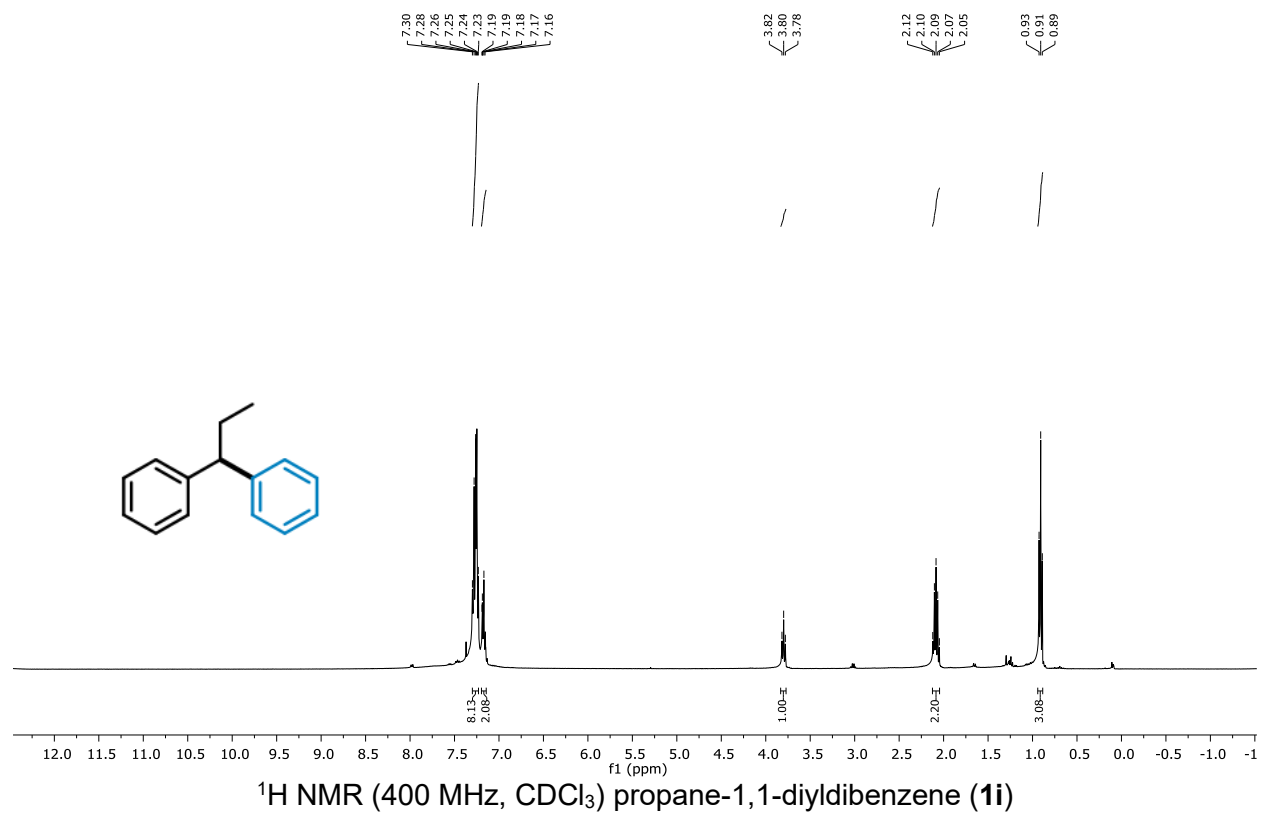


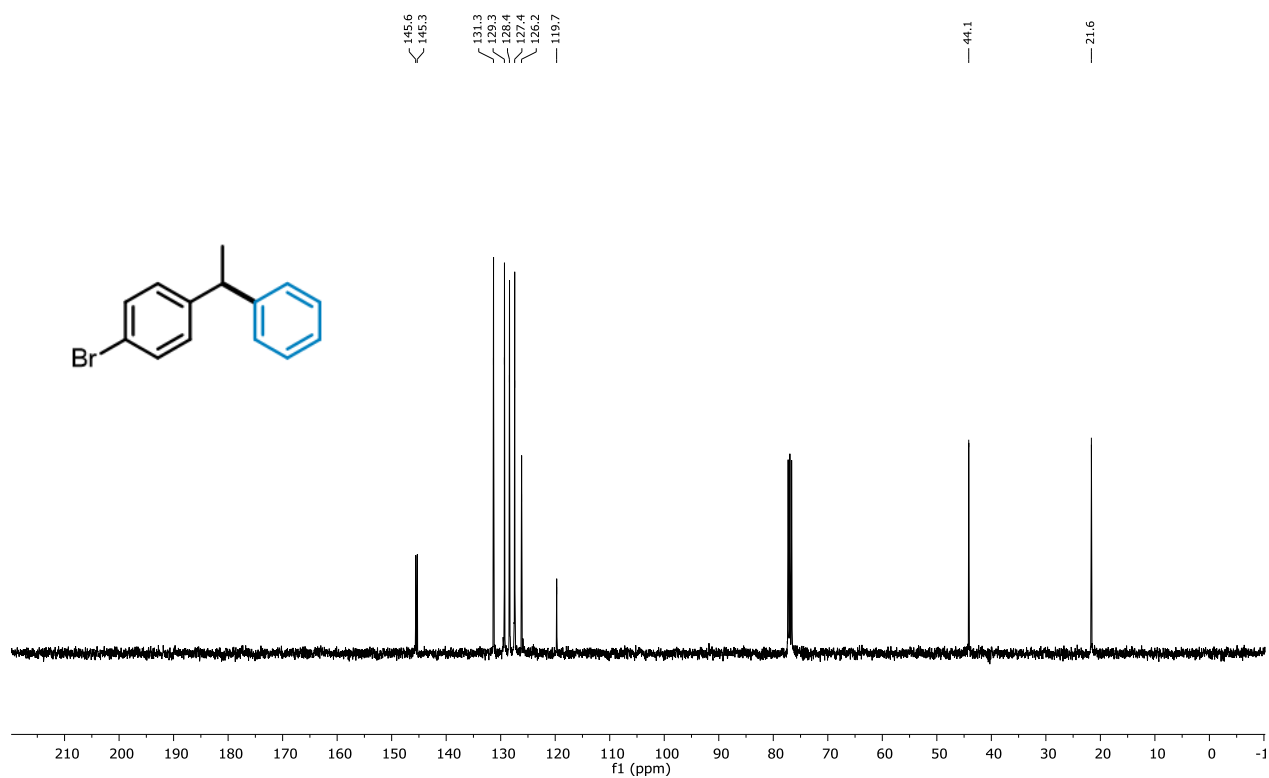
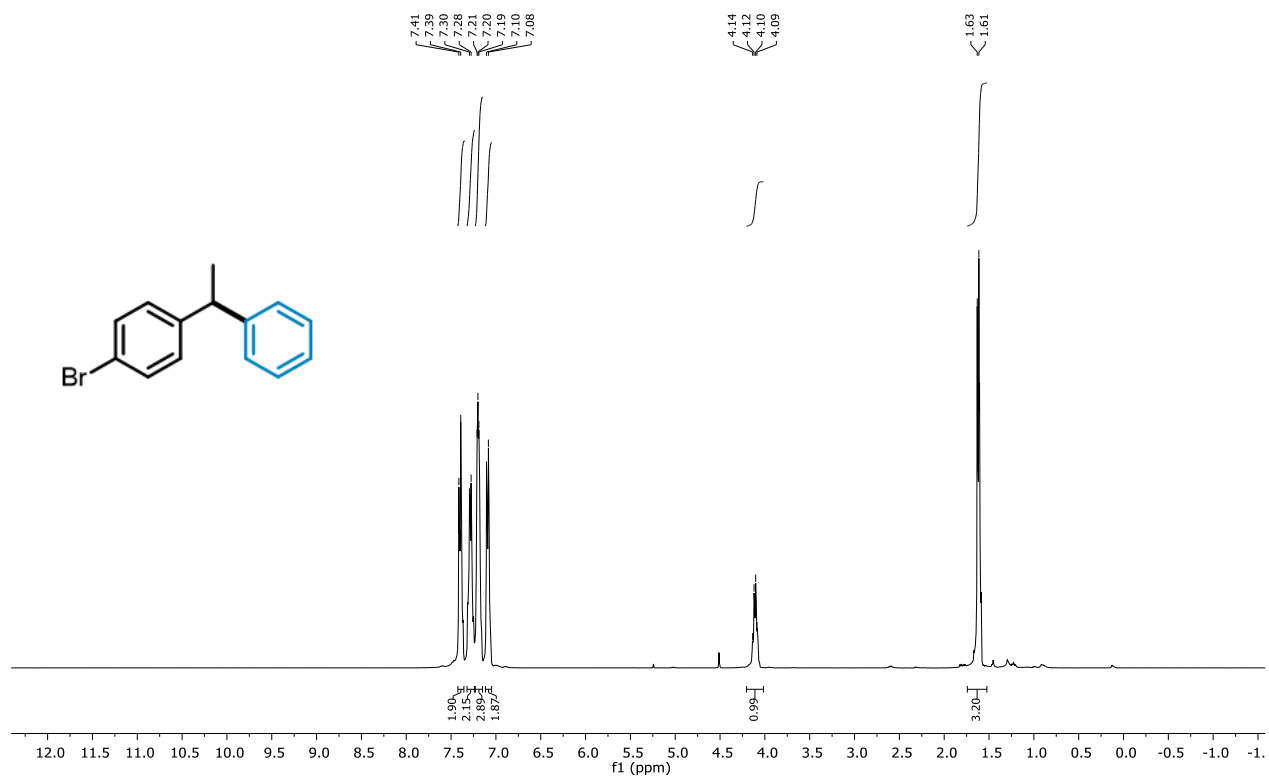


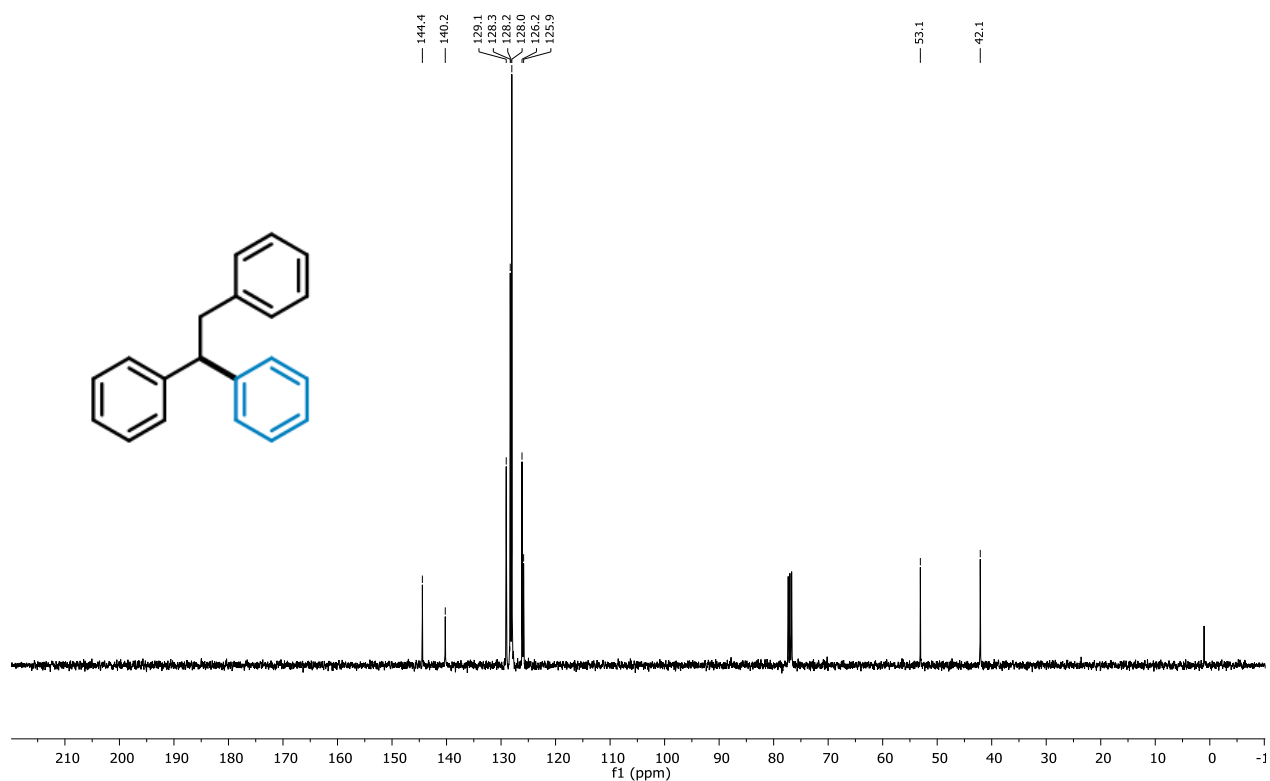
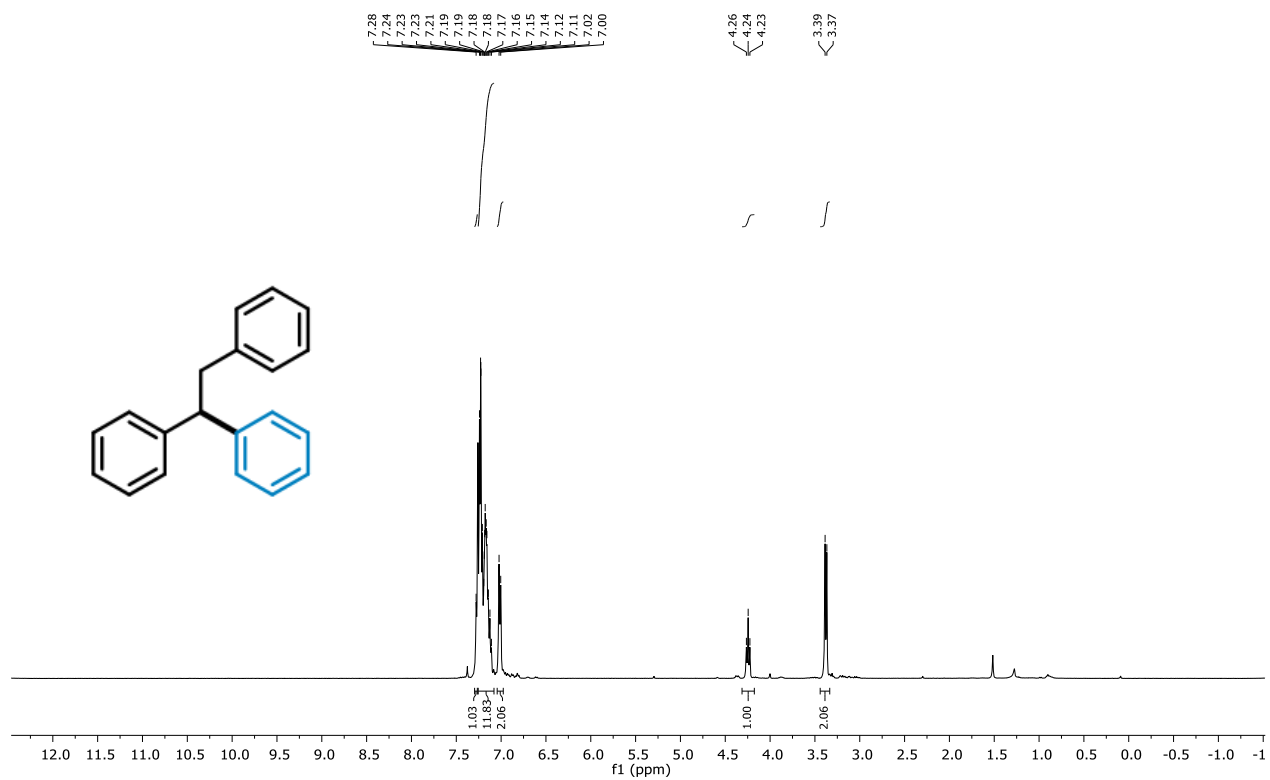


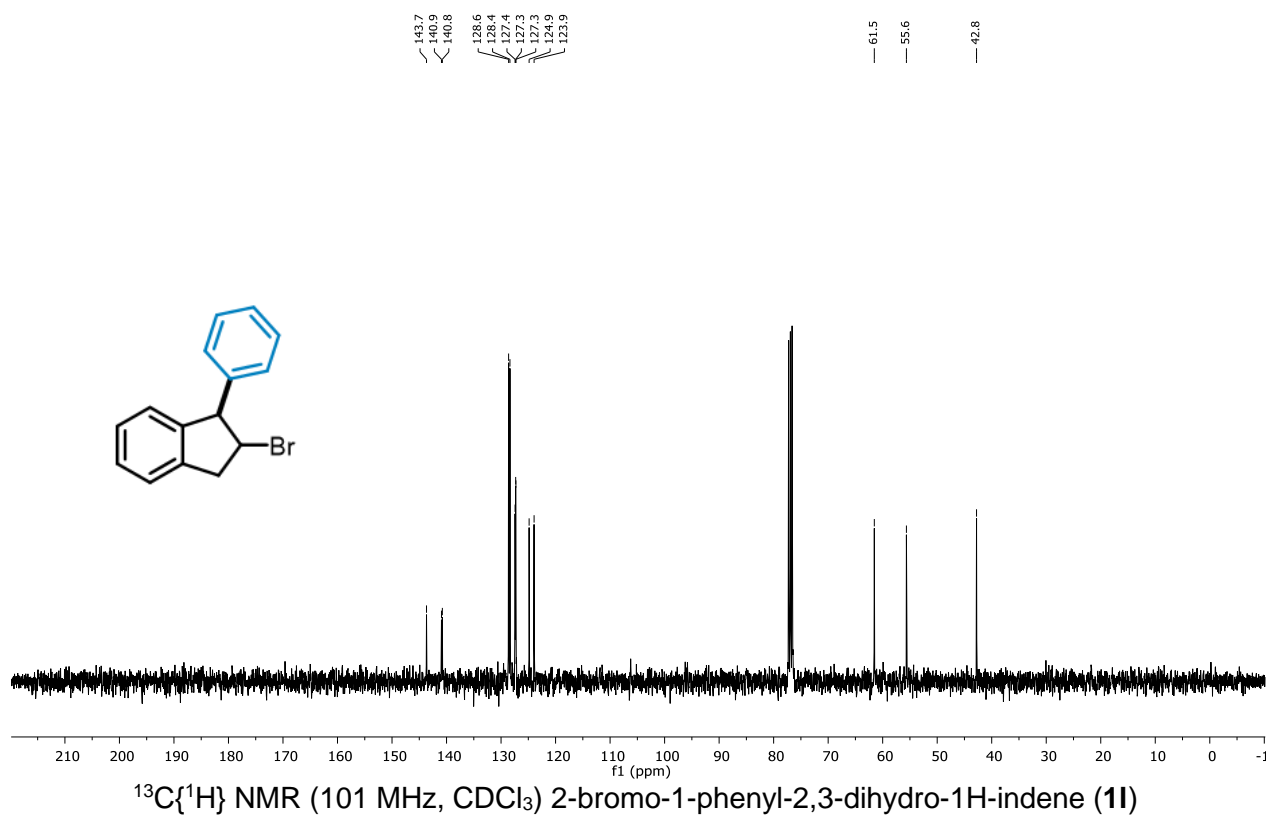
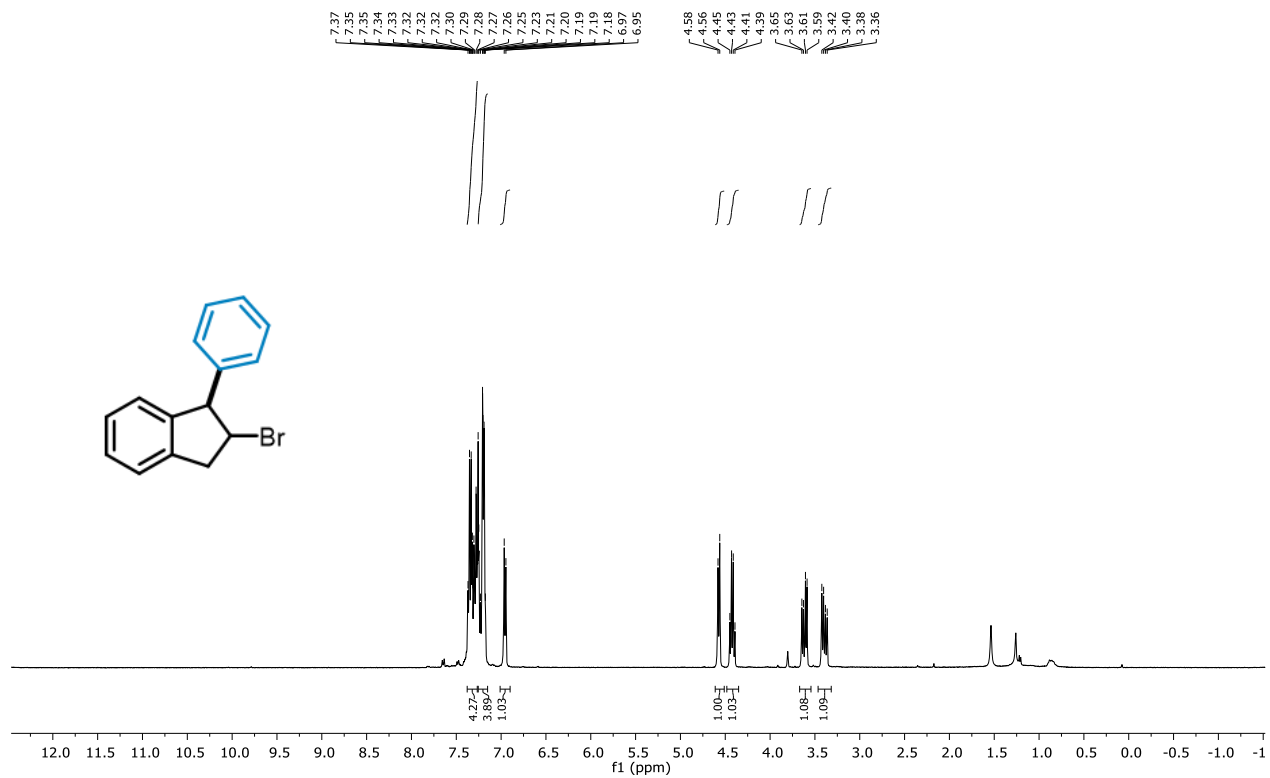


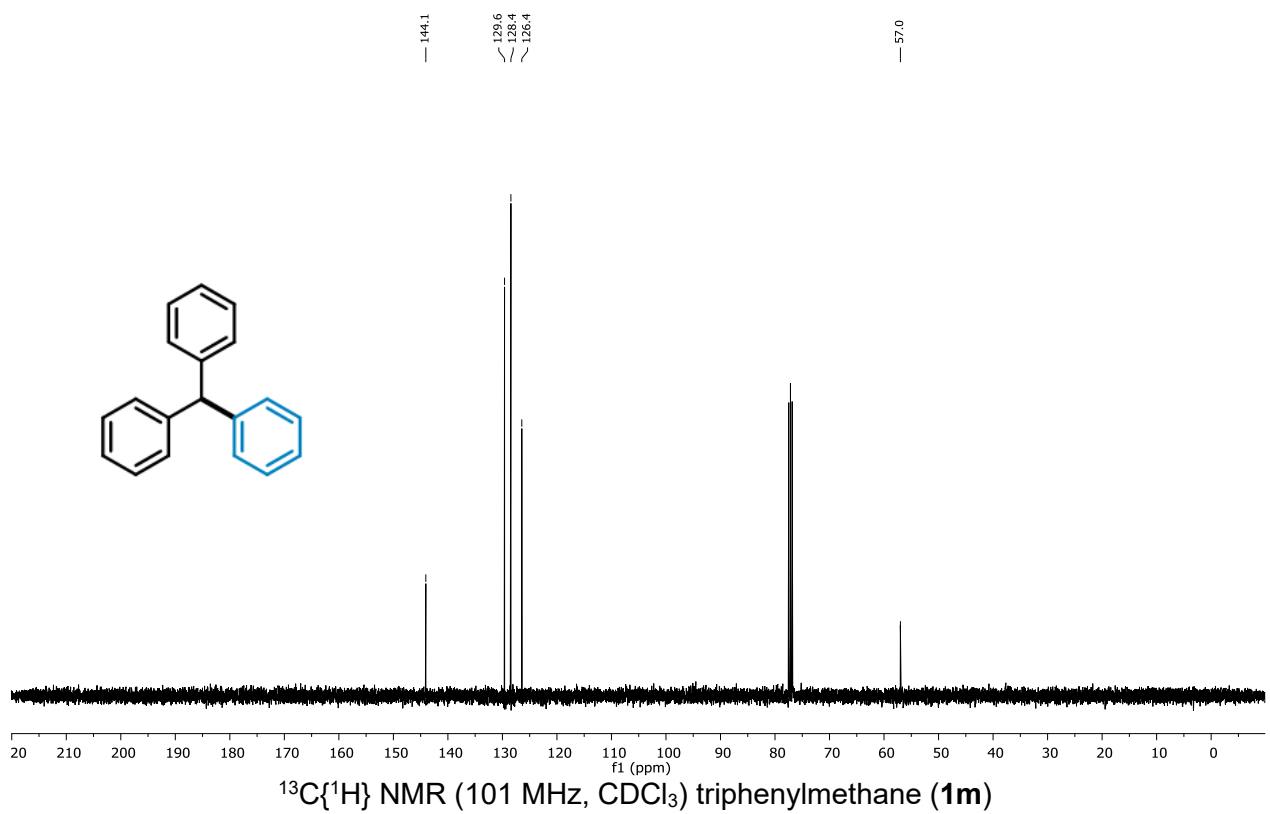
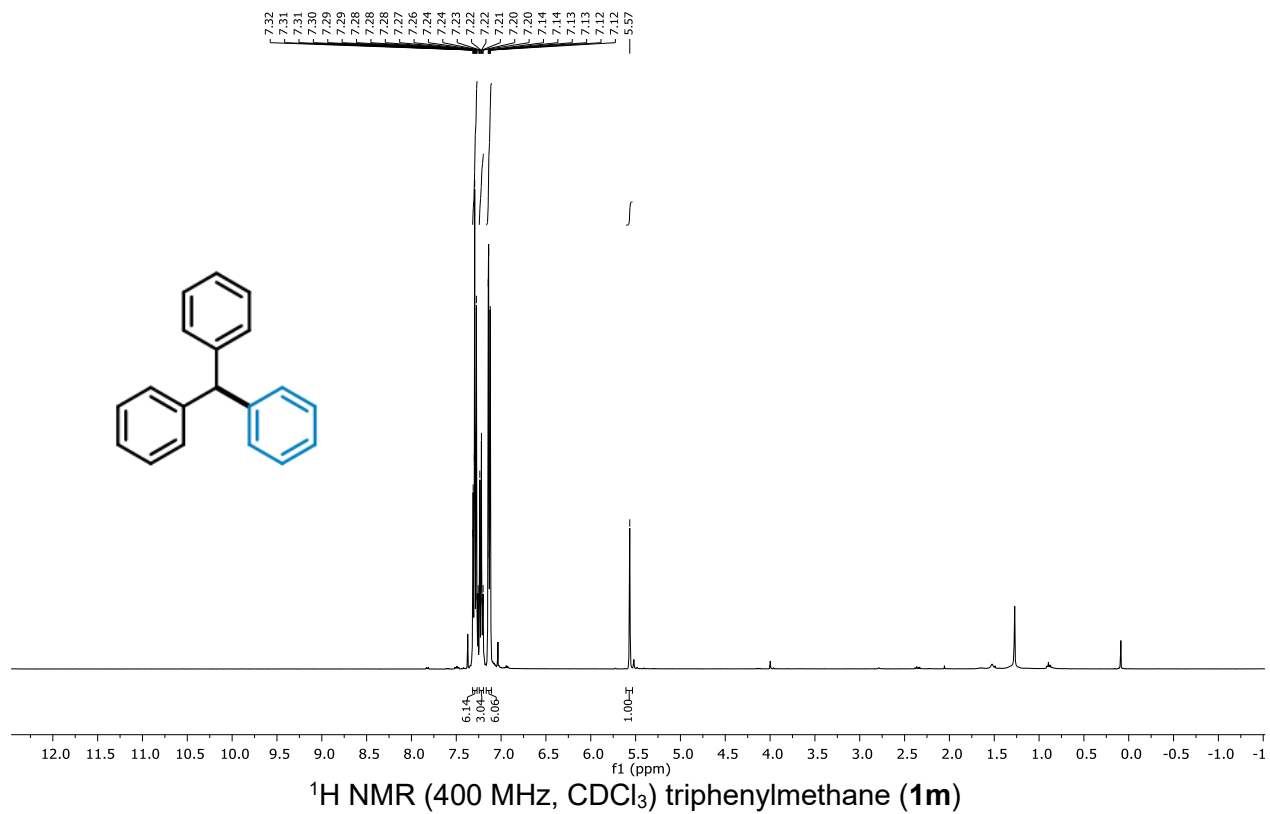


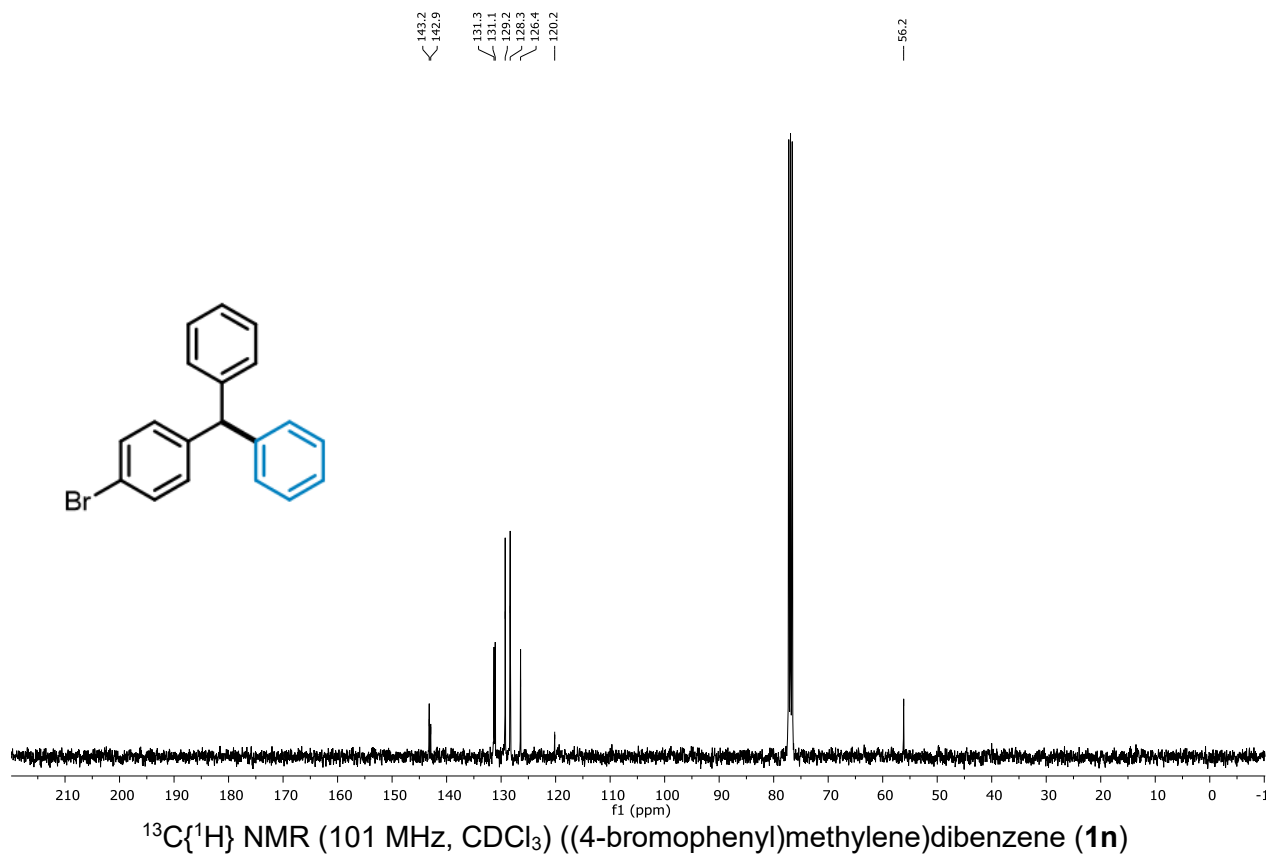
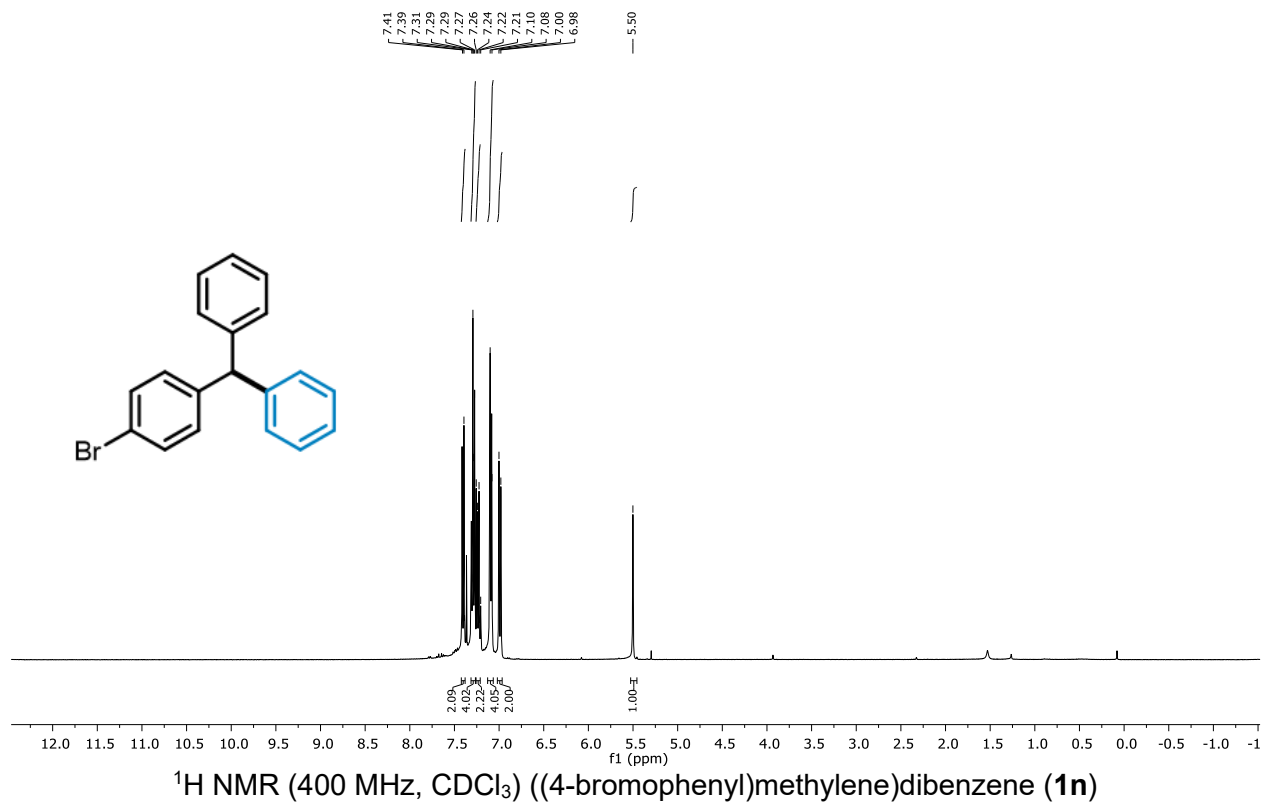


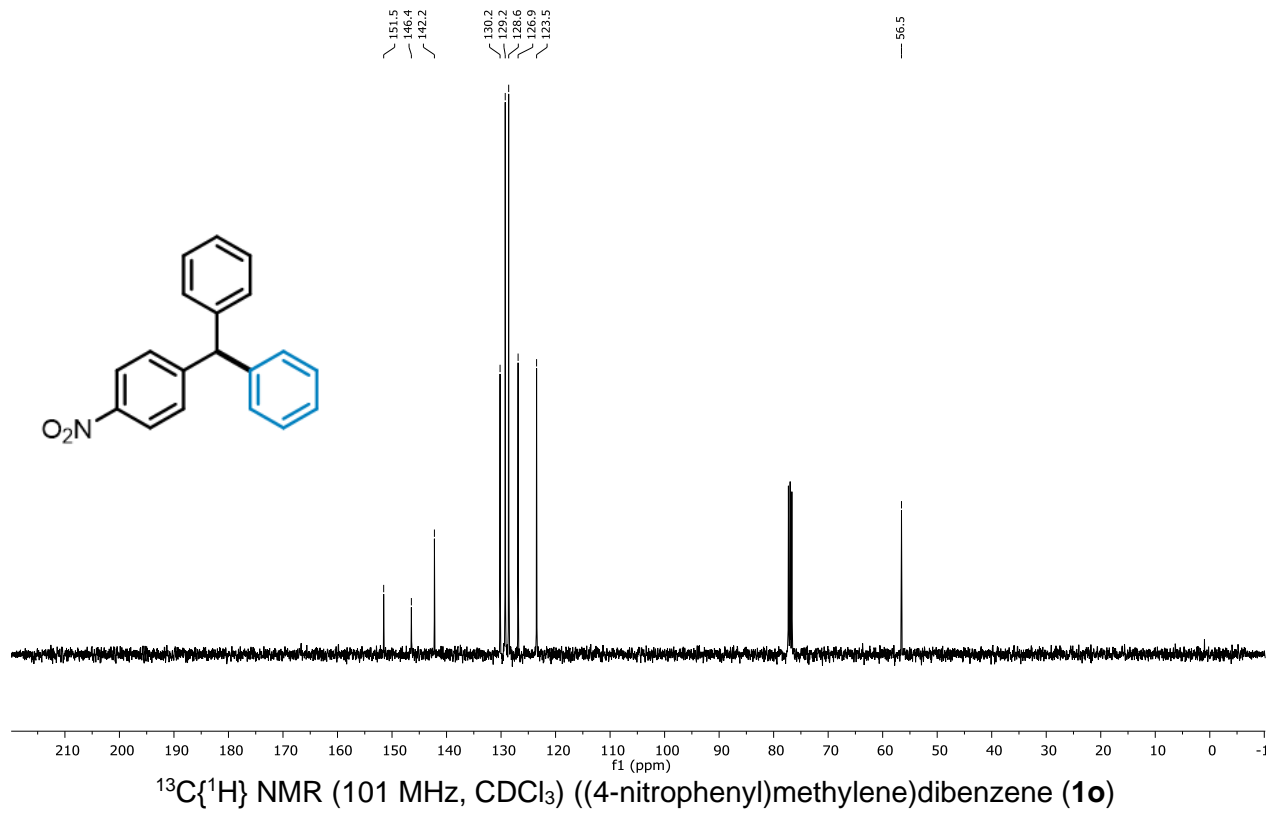
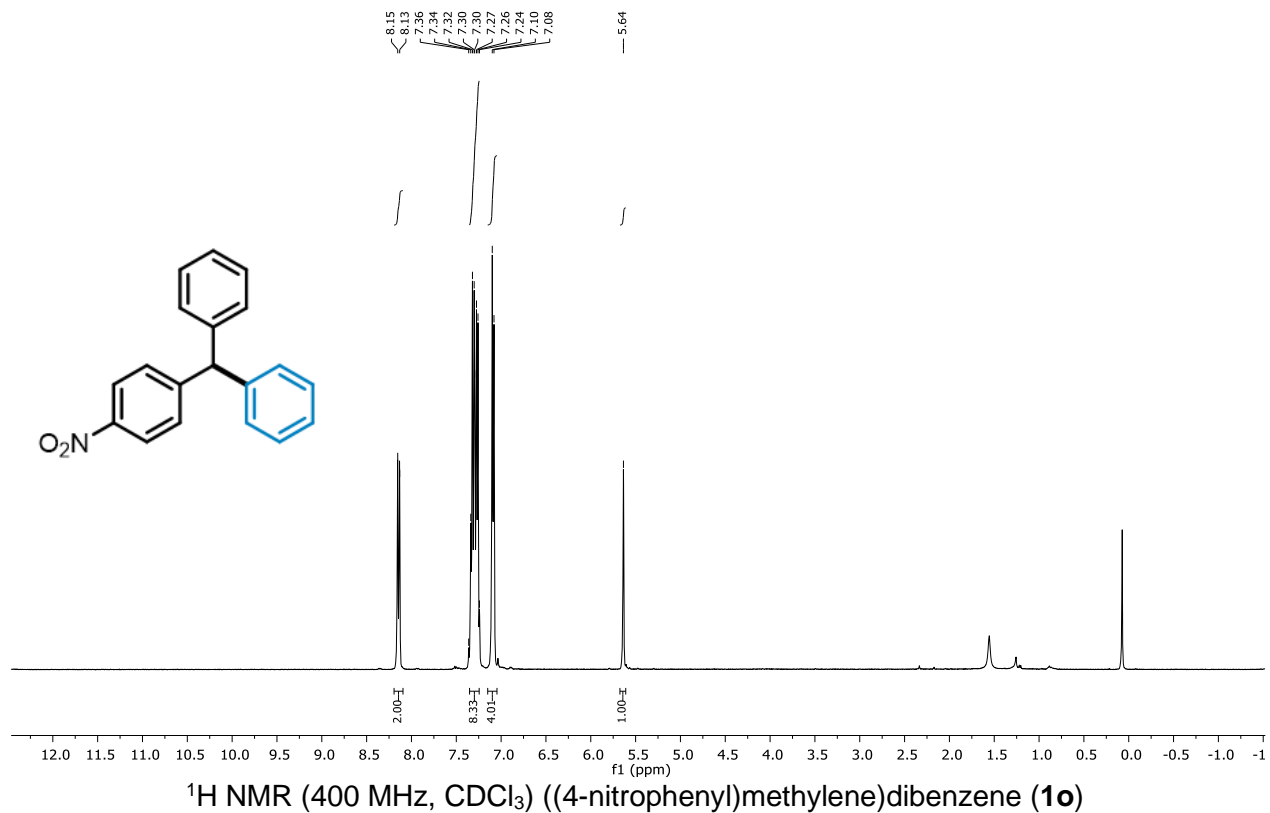


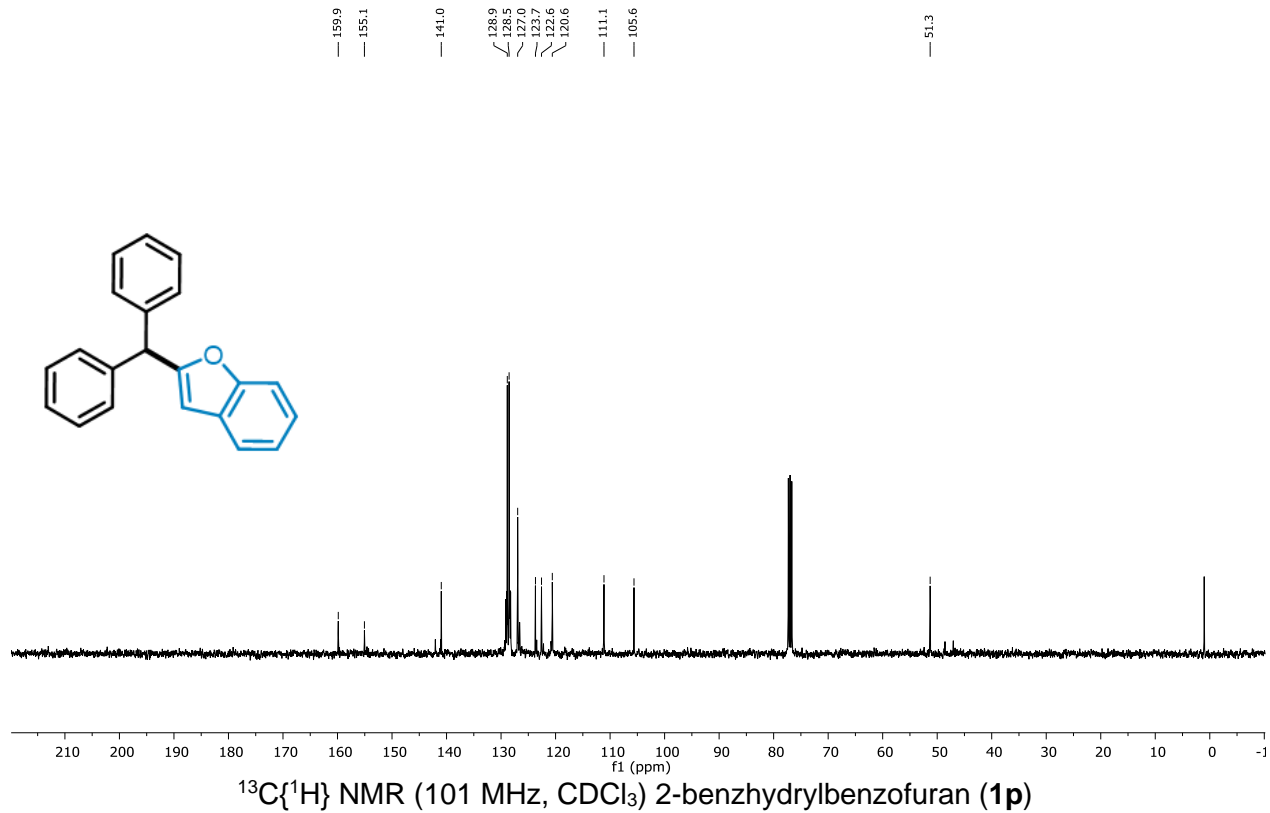
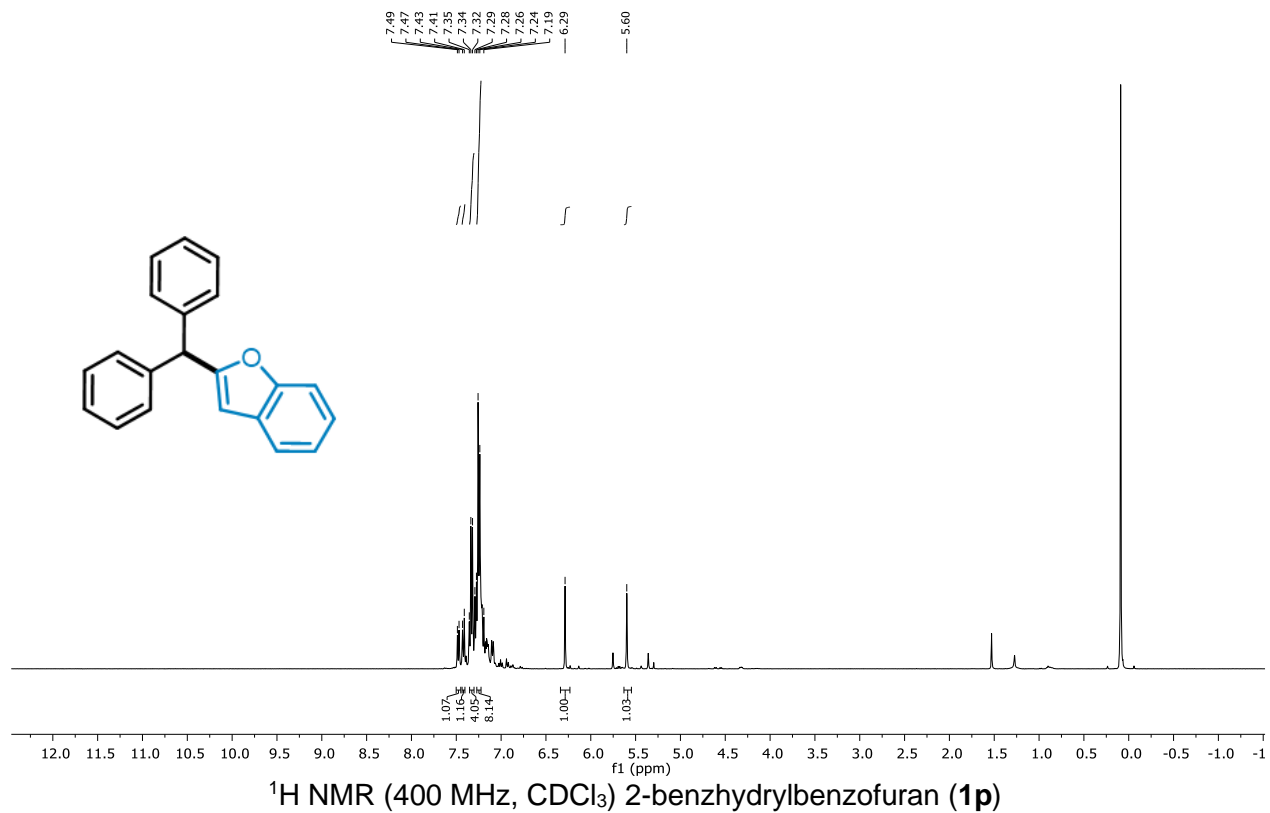


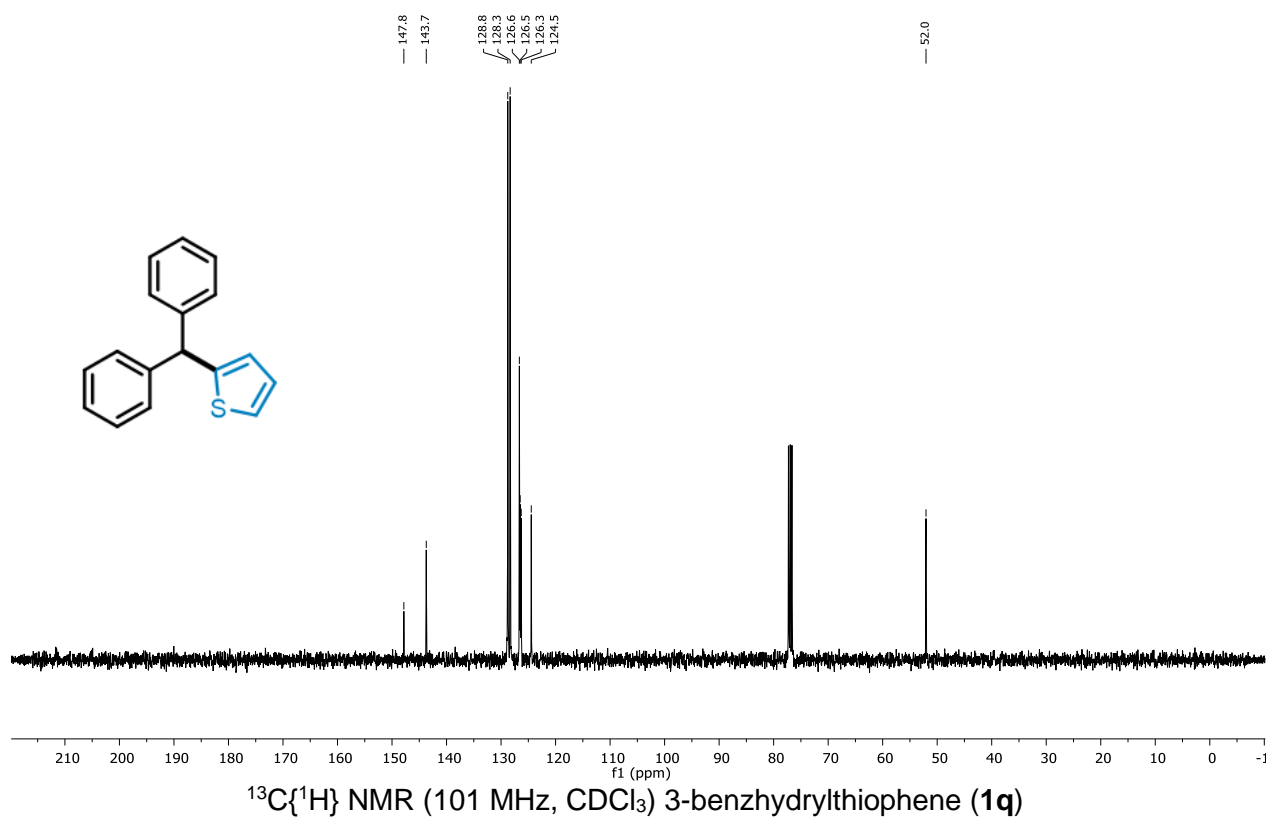
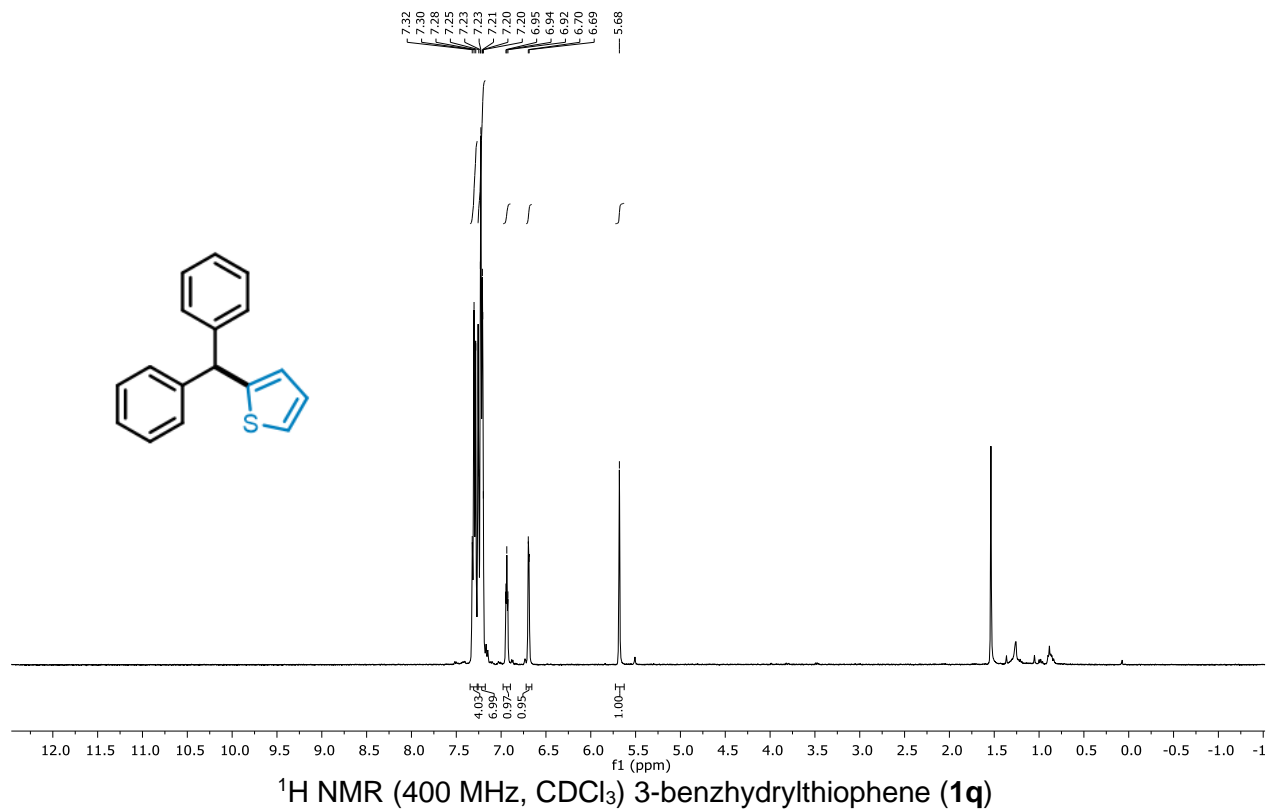


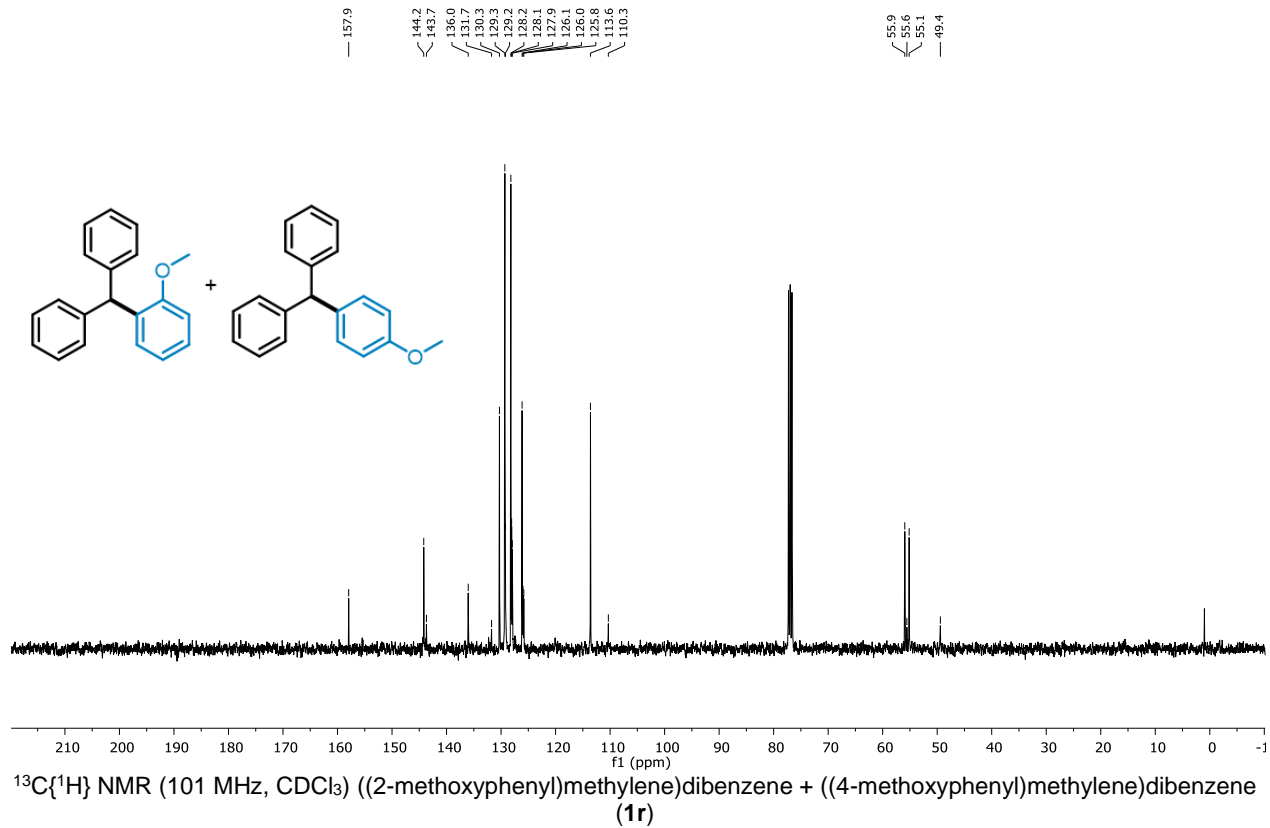
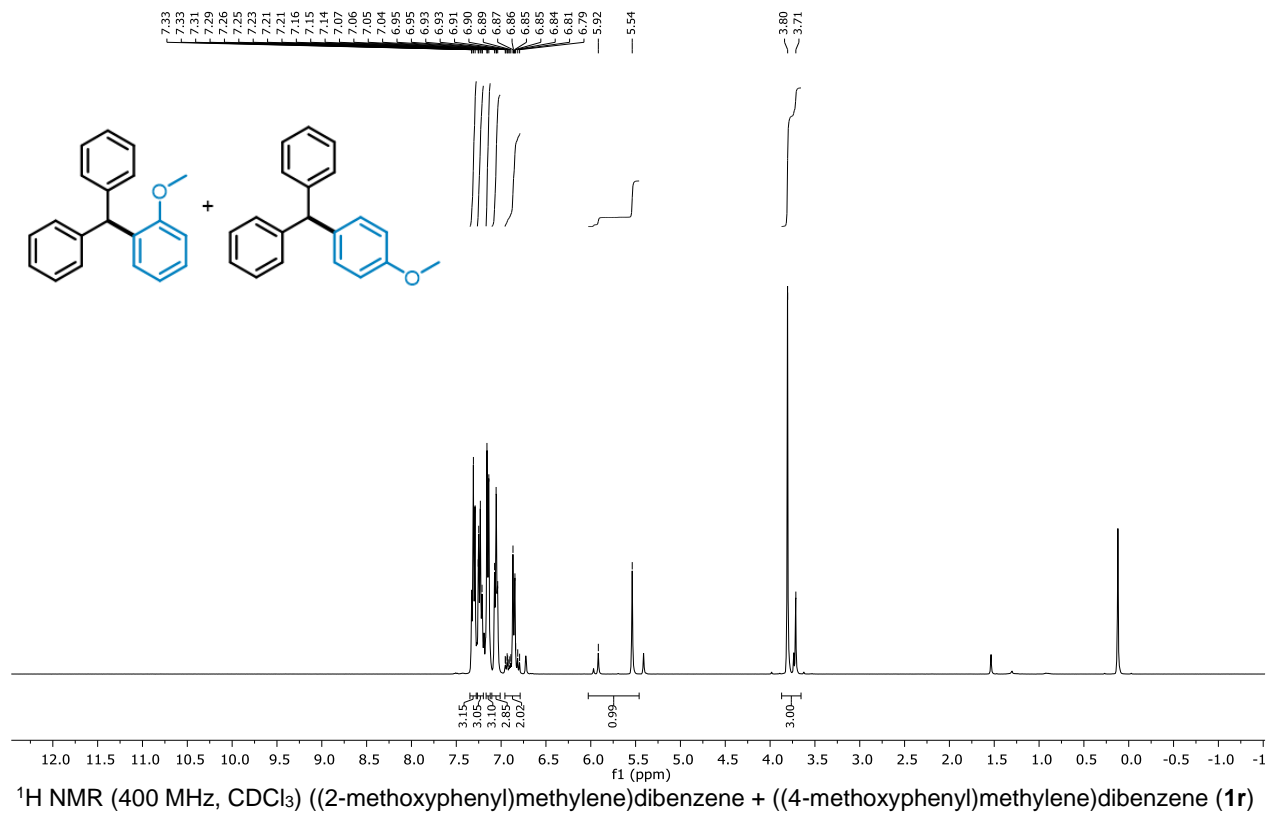


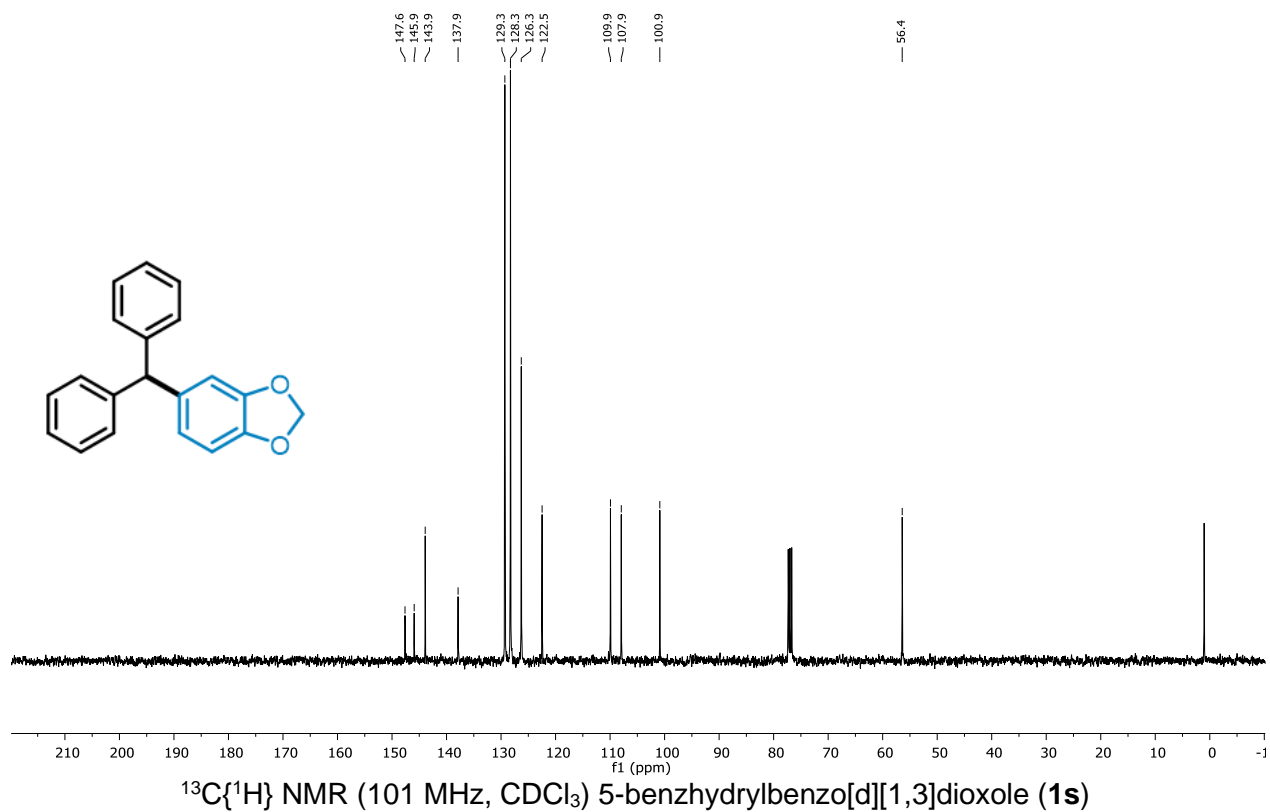
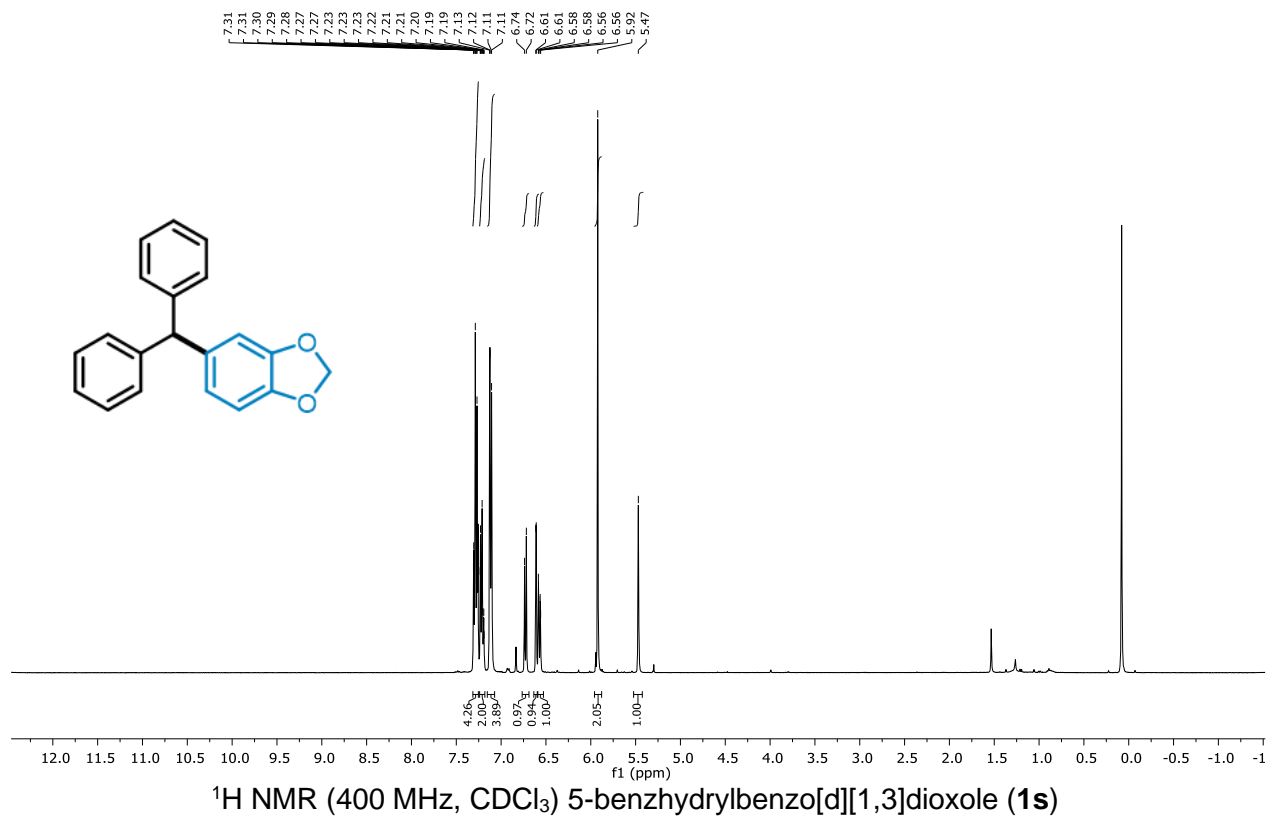


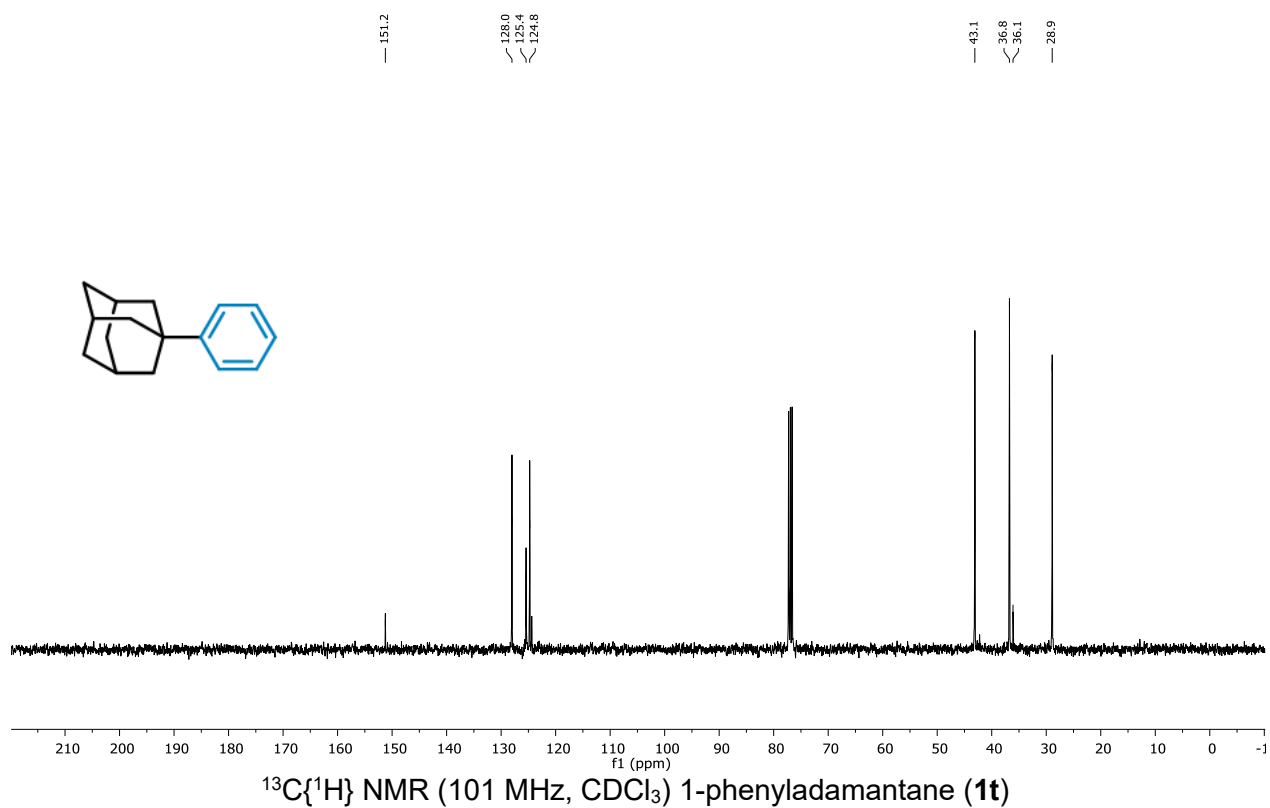
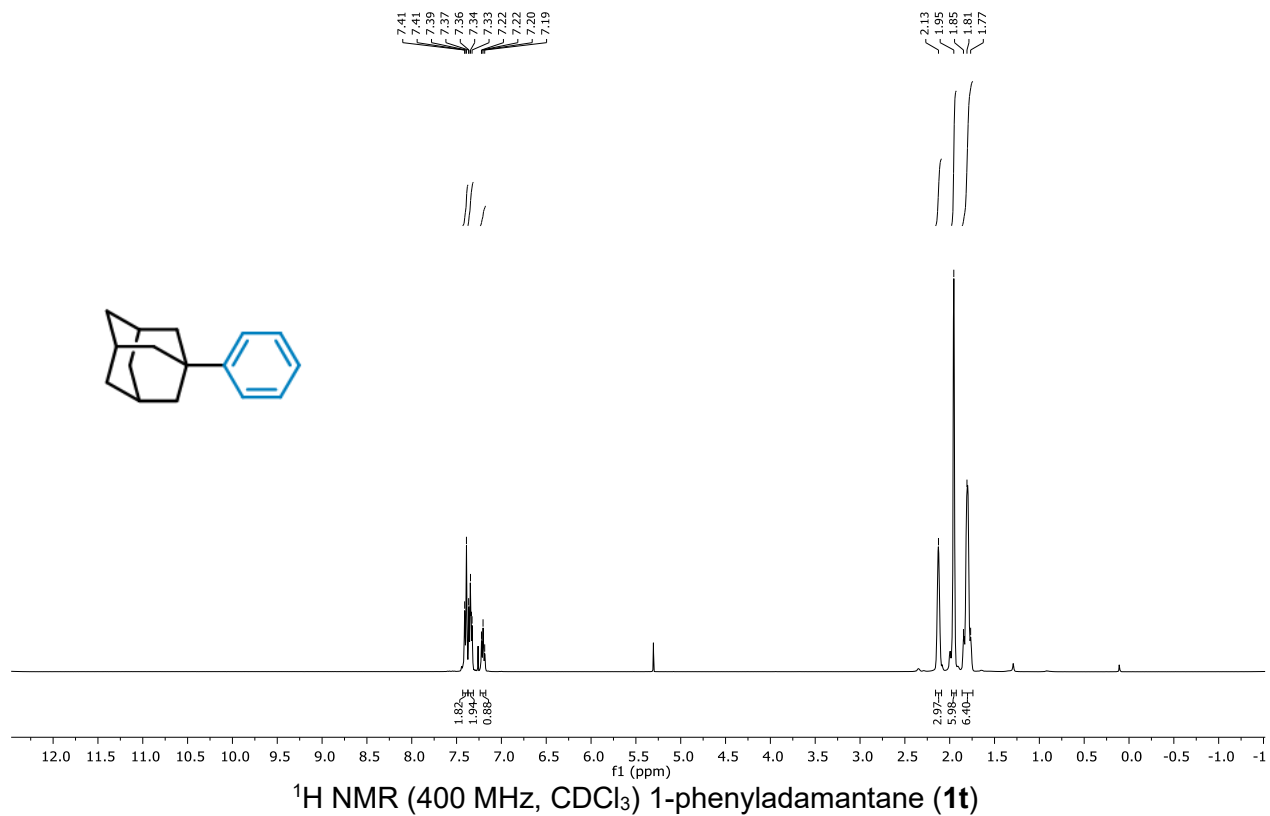


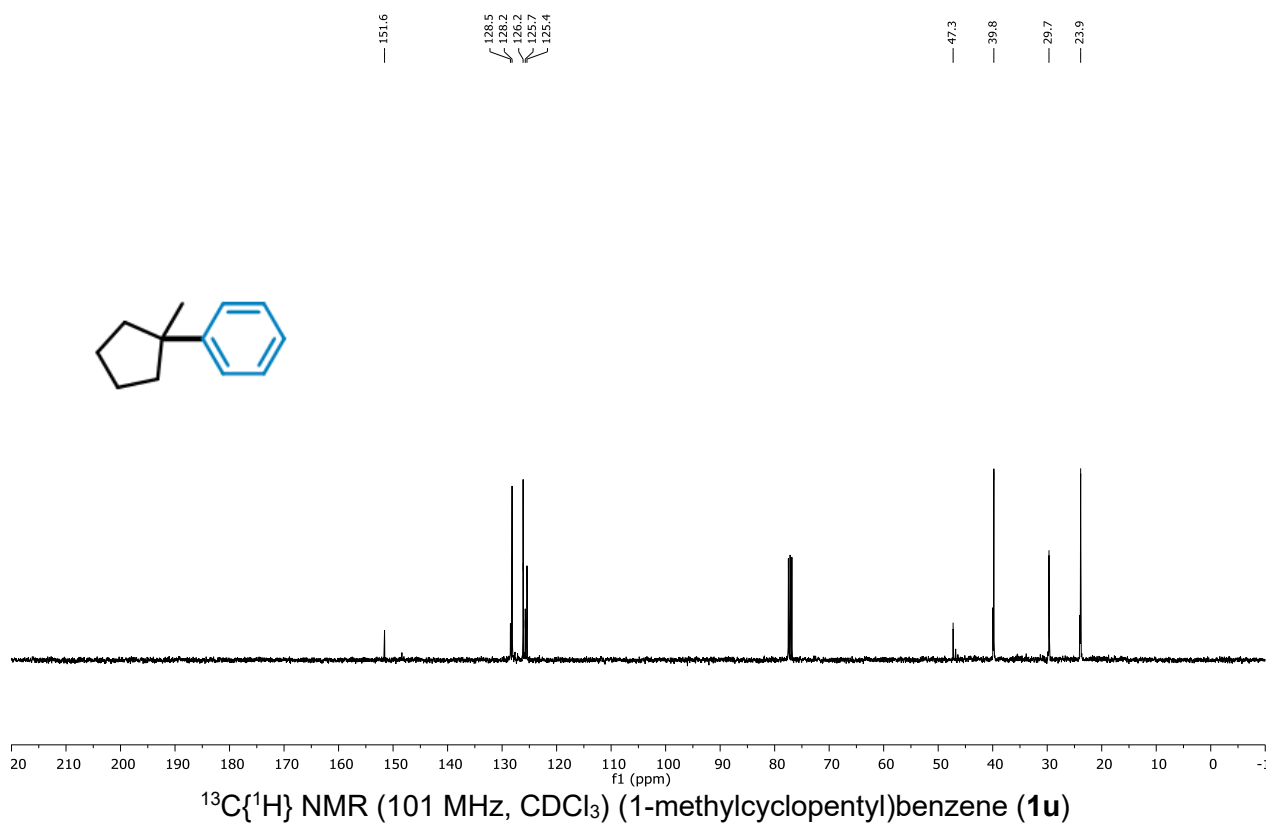
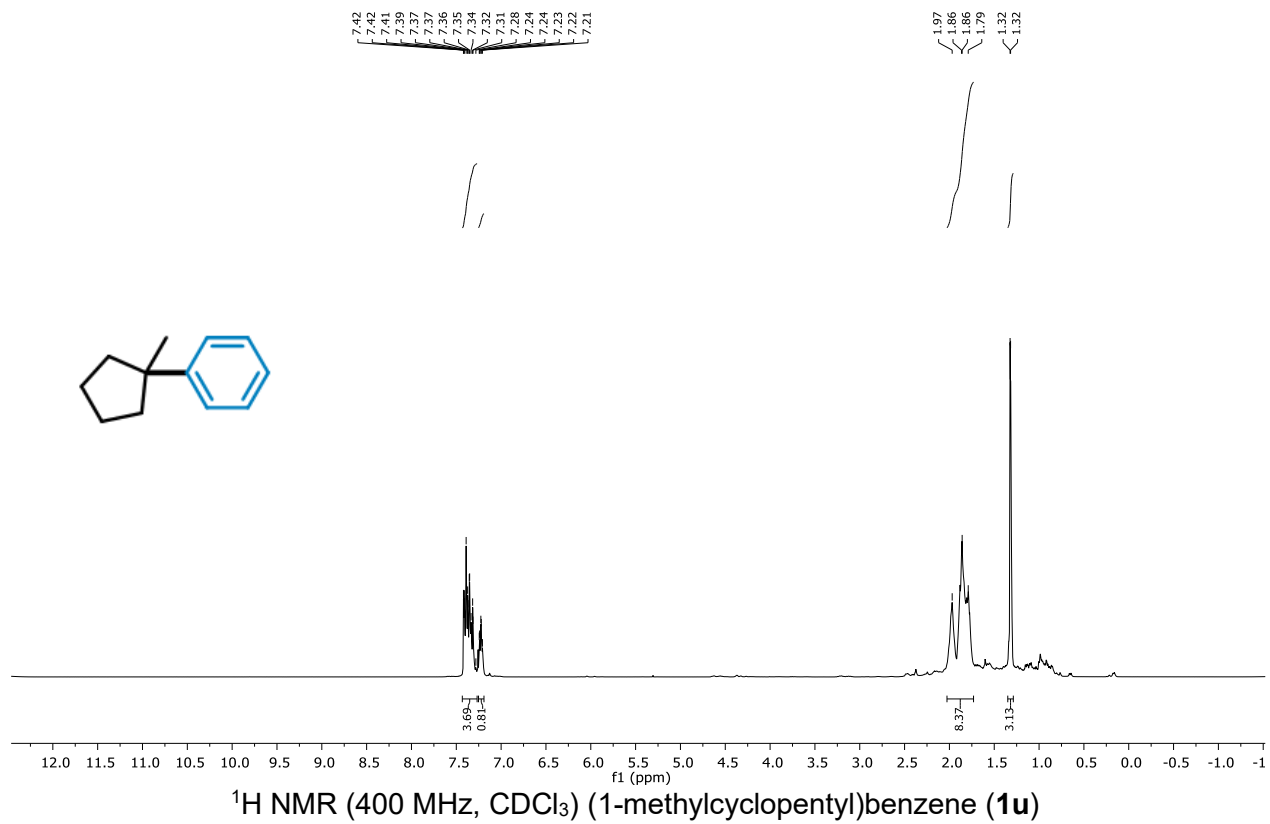


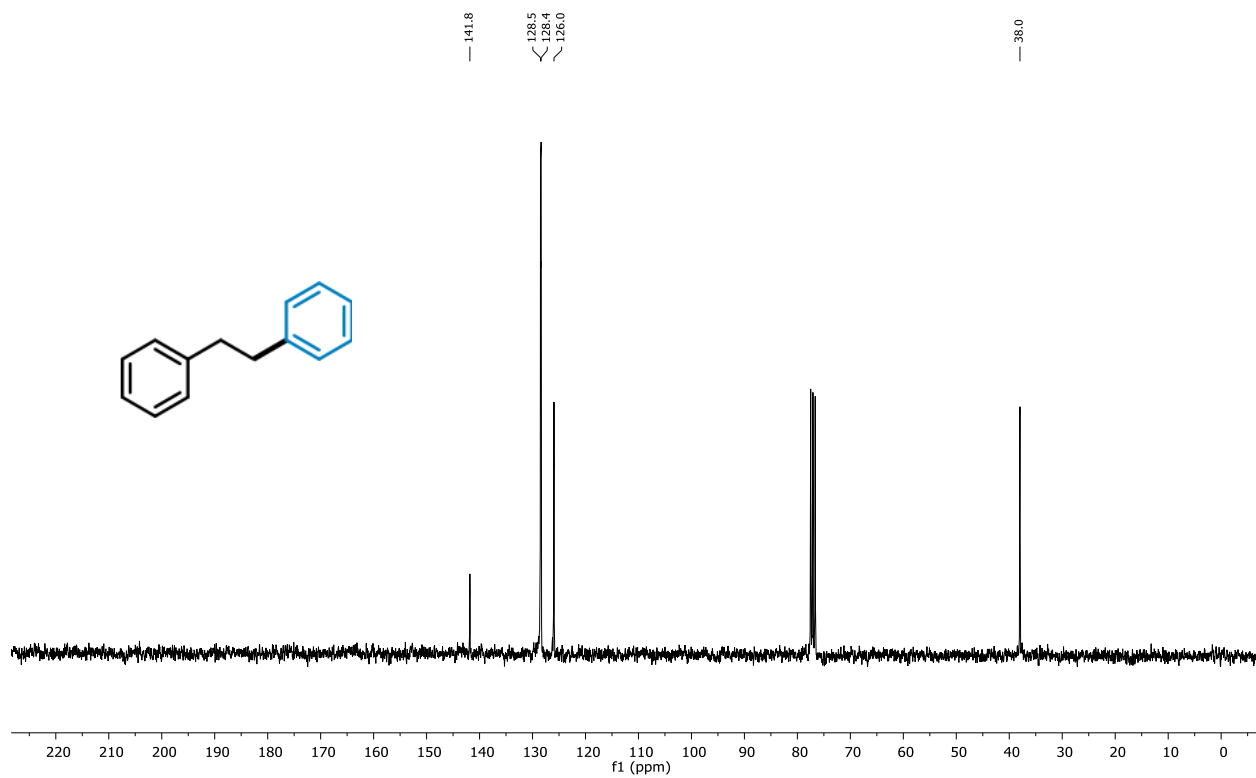
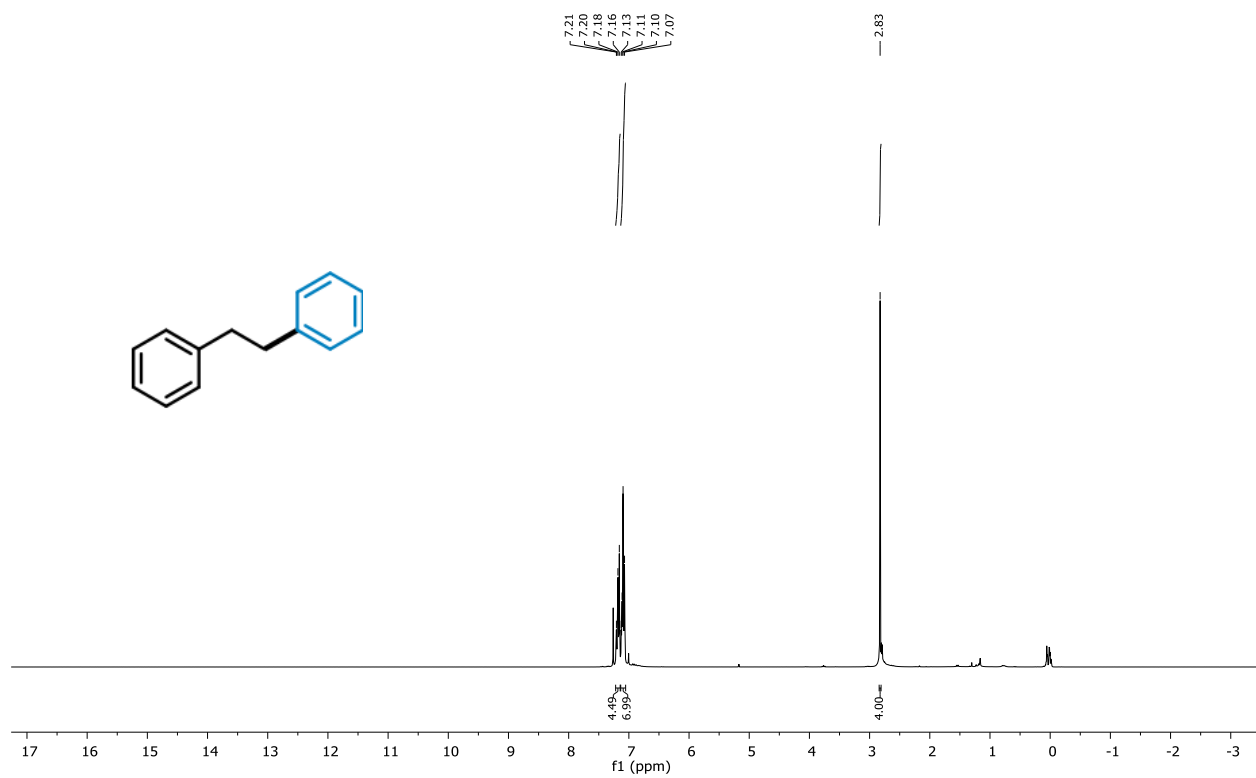


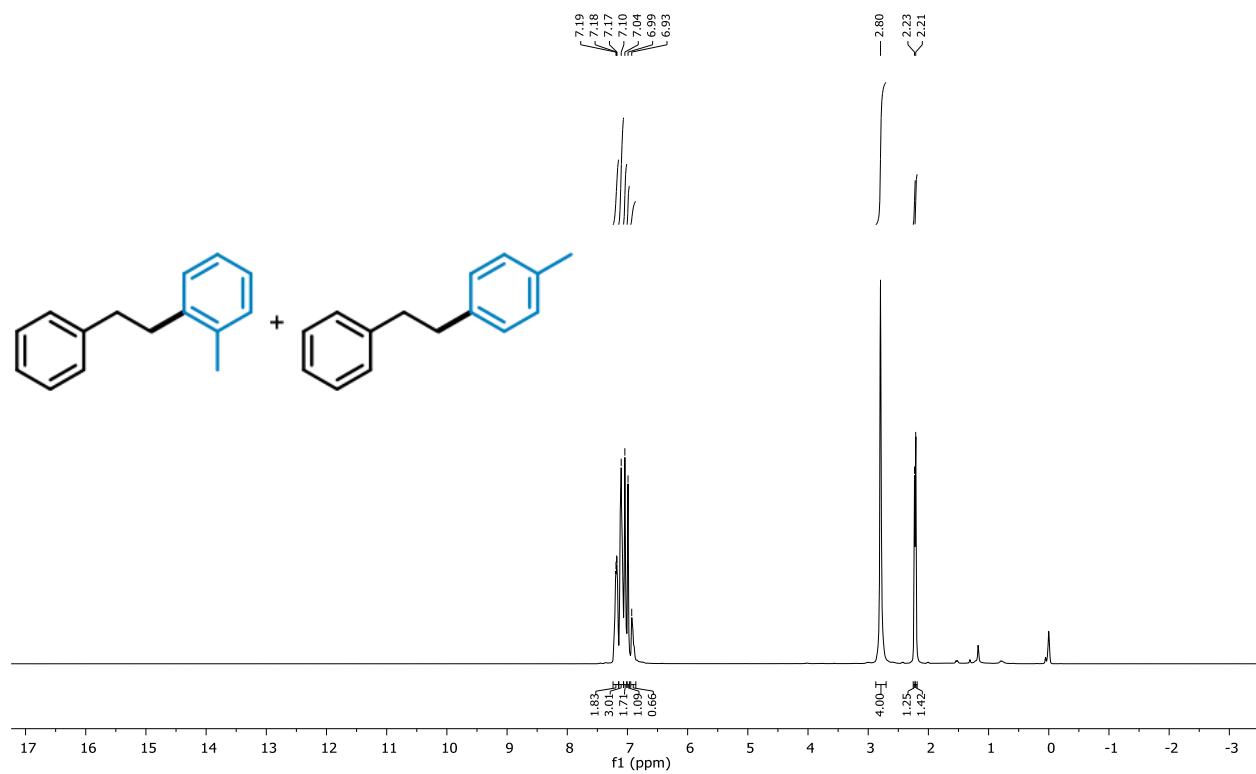




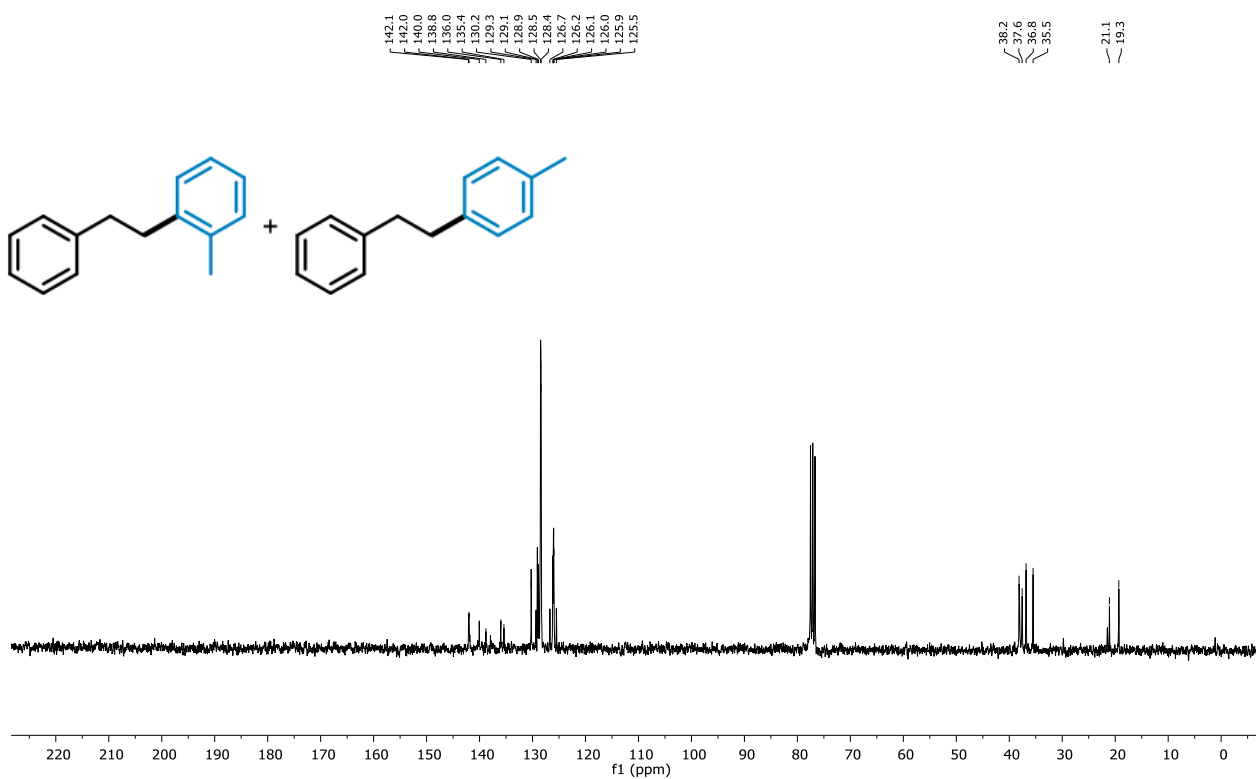




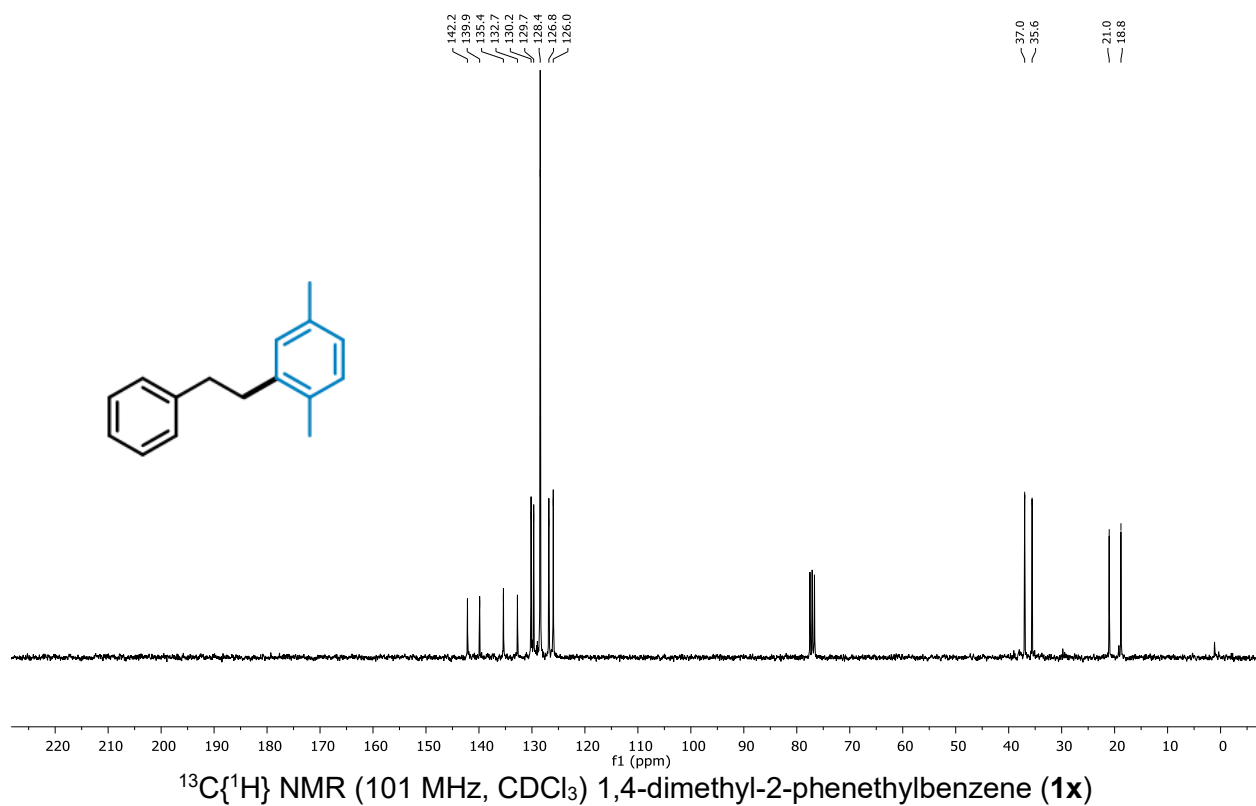
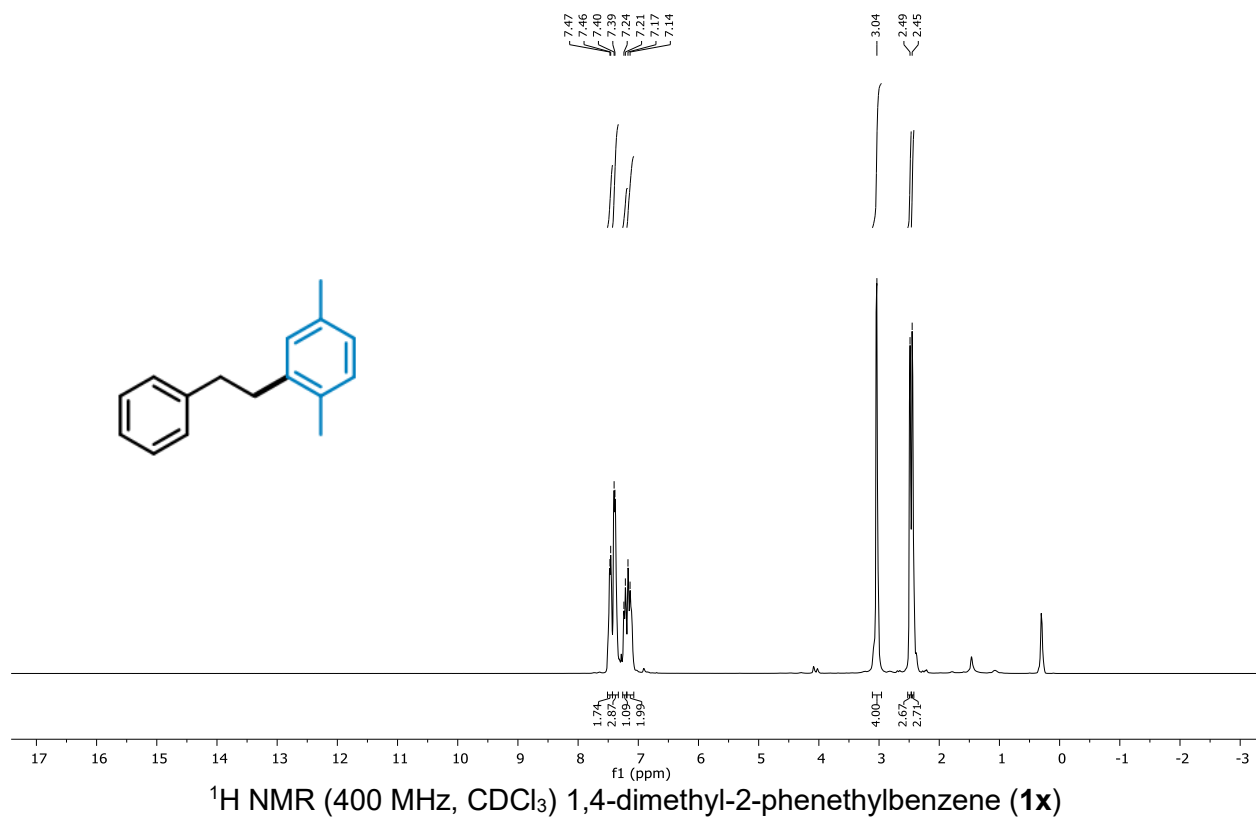


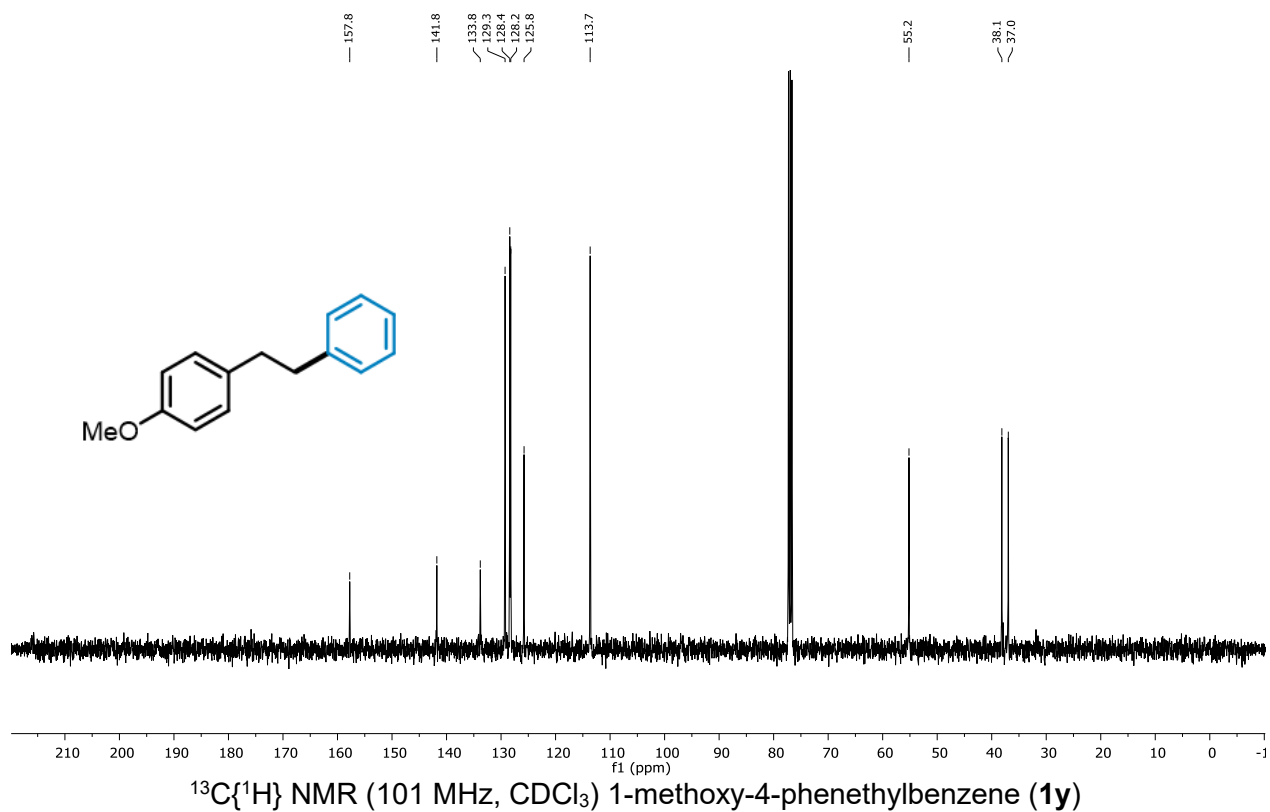
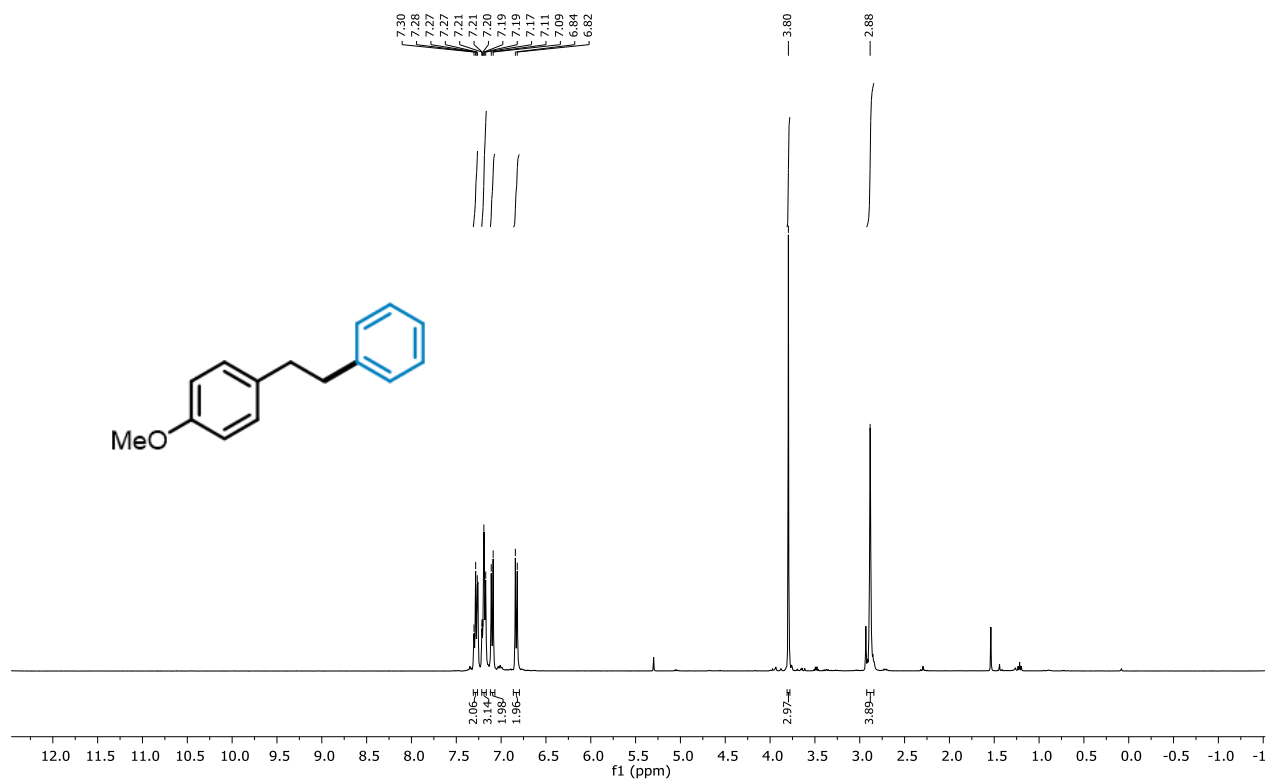


^1H NMR (400 MHz, CDCl_3) 1-methyl-2-phenethylbenzene + 1-methyl-4-phenethylbenzene (**1w**)

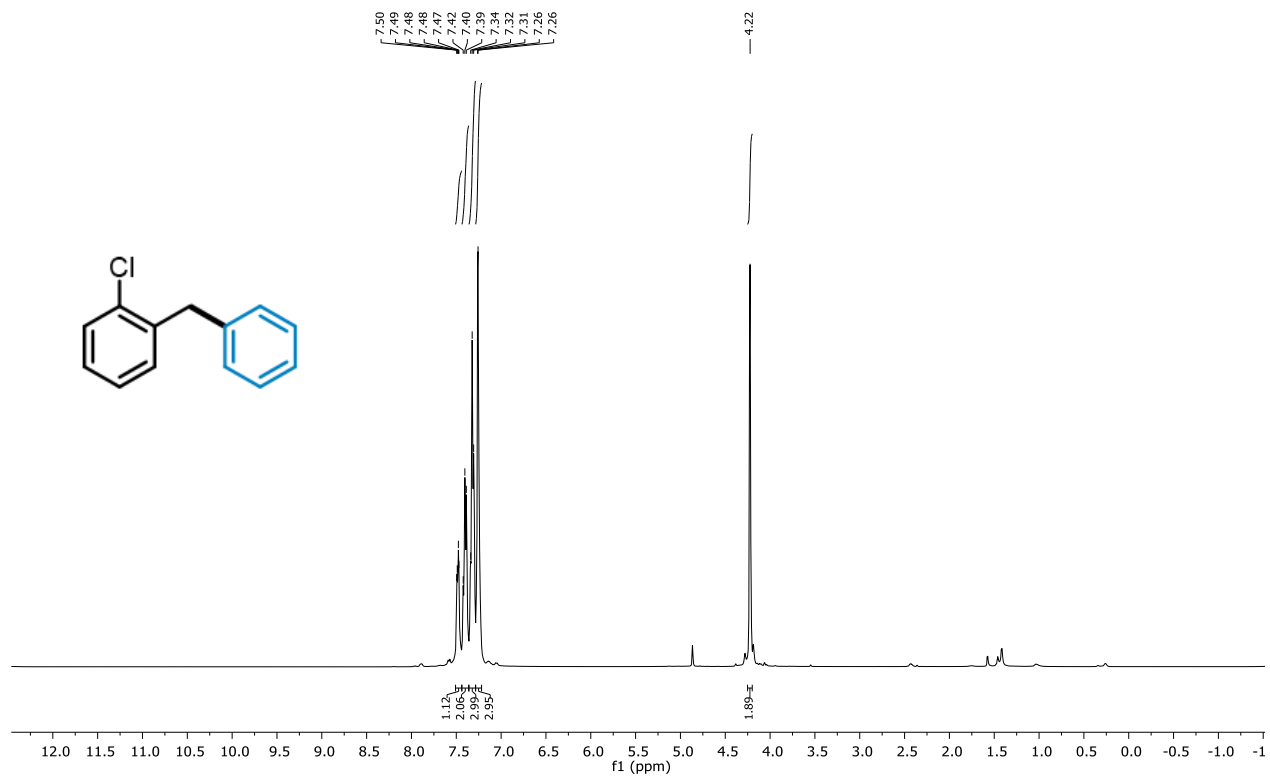


$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) 1-methyl-2-phenethylbenzene + 1-methyl-4-phenethylbenzene (**1w**)

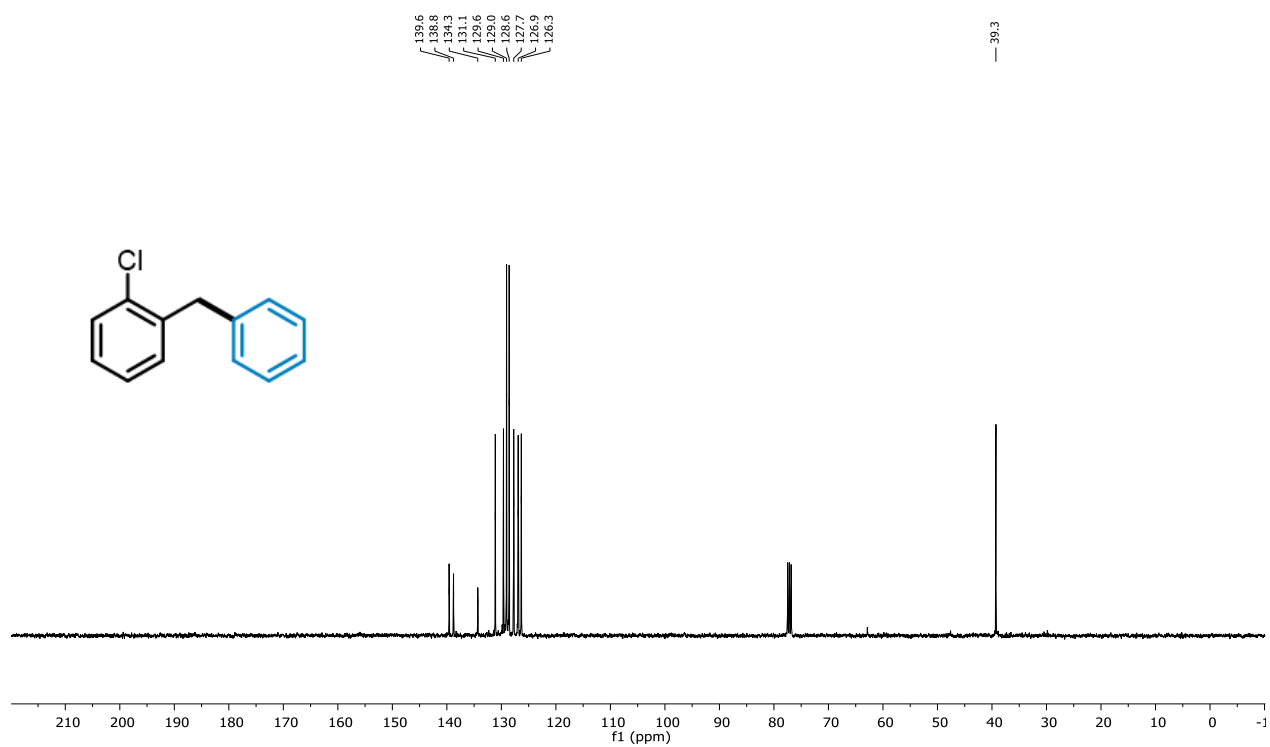




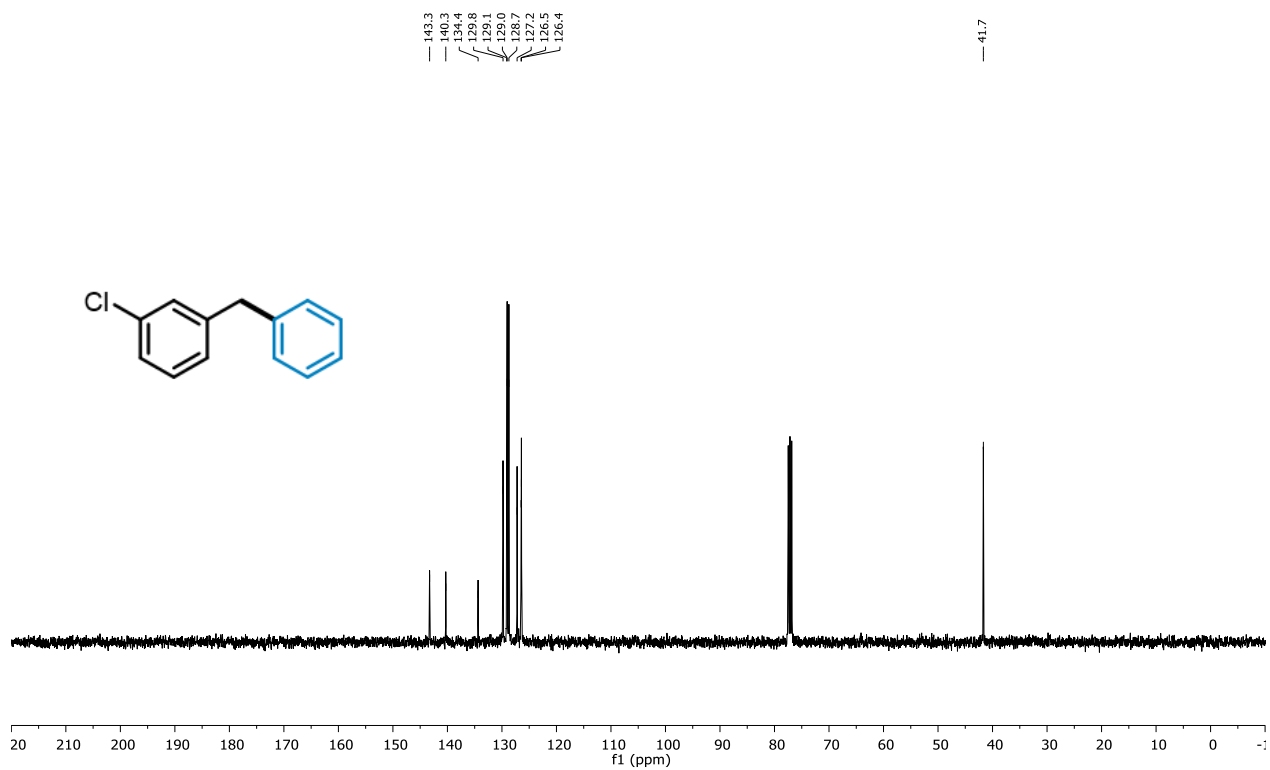
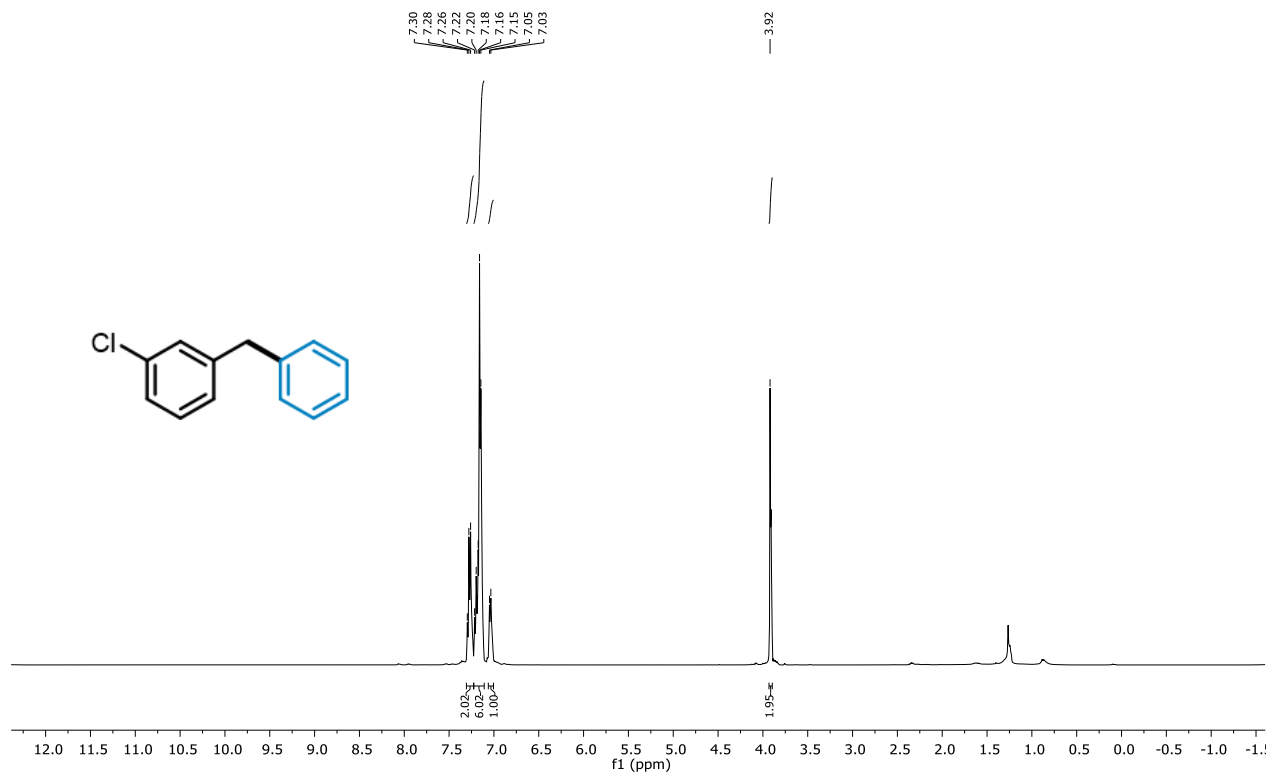
^1H NMR (400 MHz, CDCl_3) diphenylmethane (**2a**) matches with compound **1a**.
 $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) diphenylmethane (**2a**) matches with compound **1a**.



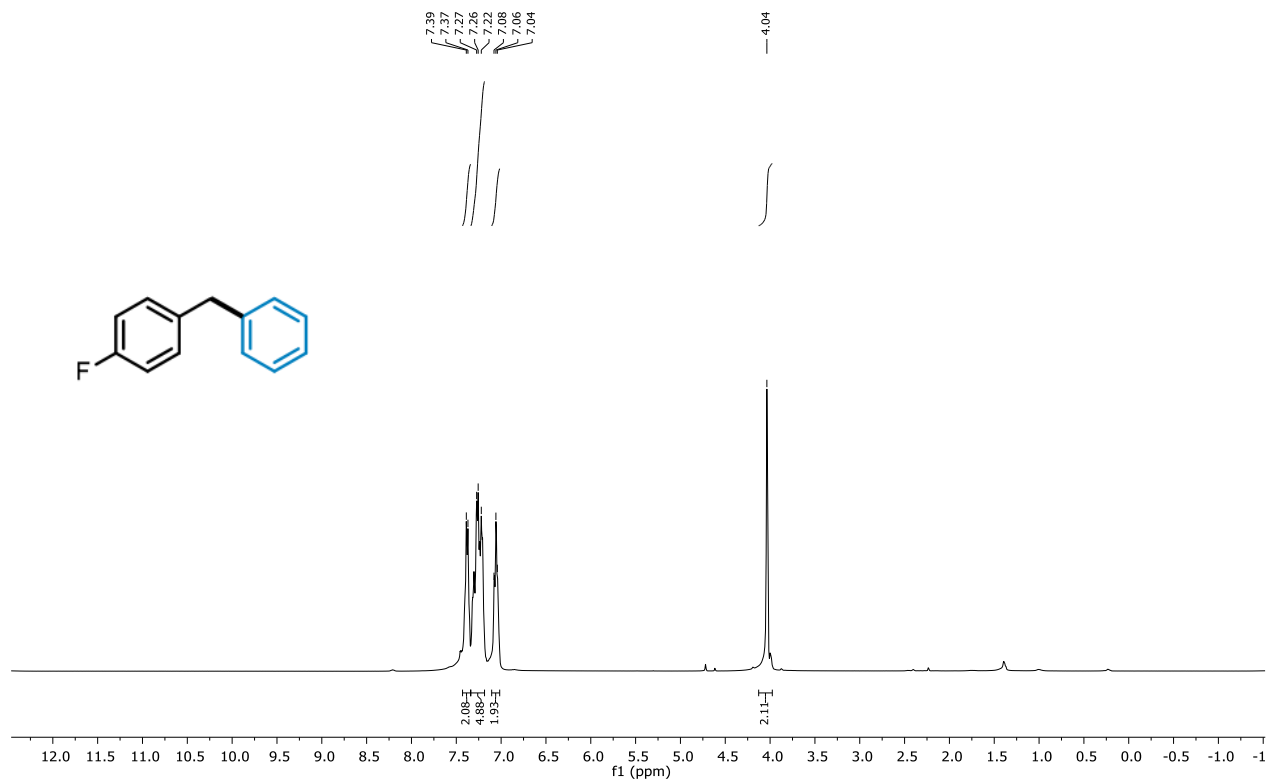
^1H NMR (400 MHz, CDCl_3) 1-benzyl-2-chlorobenzene (**2b**)



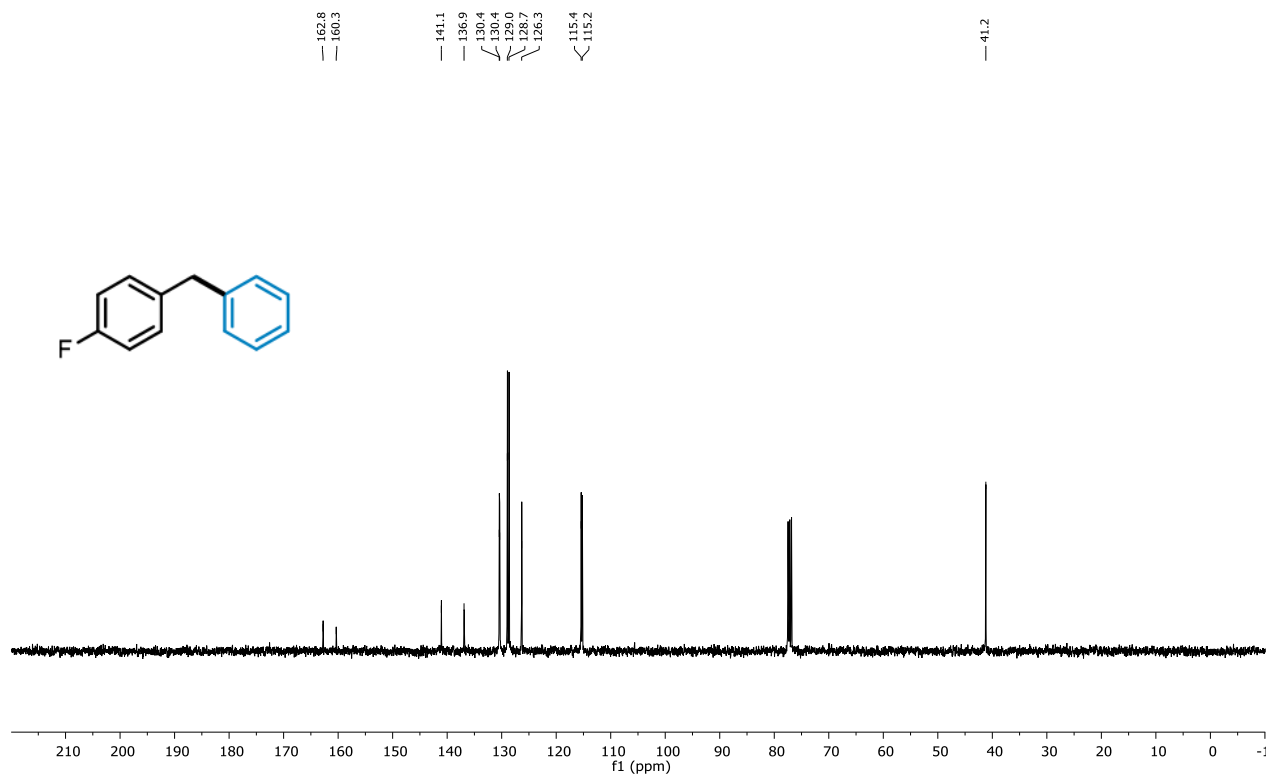
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) 1-benzyl-2-chlorobenzene (**2b**)



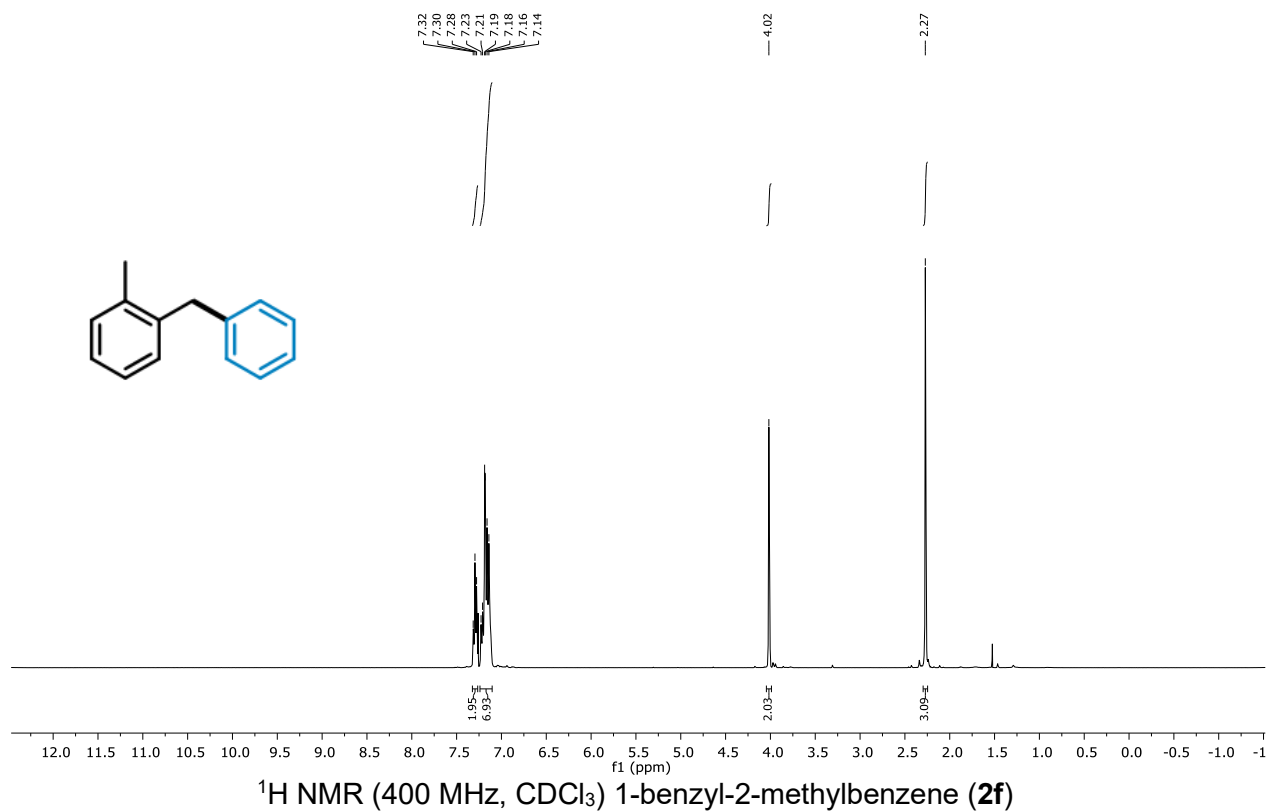
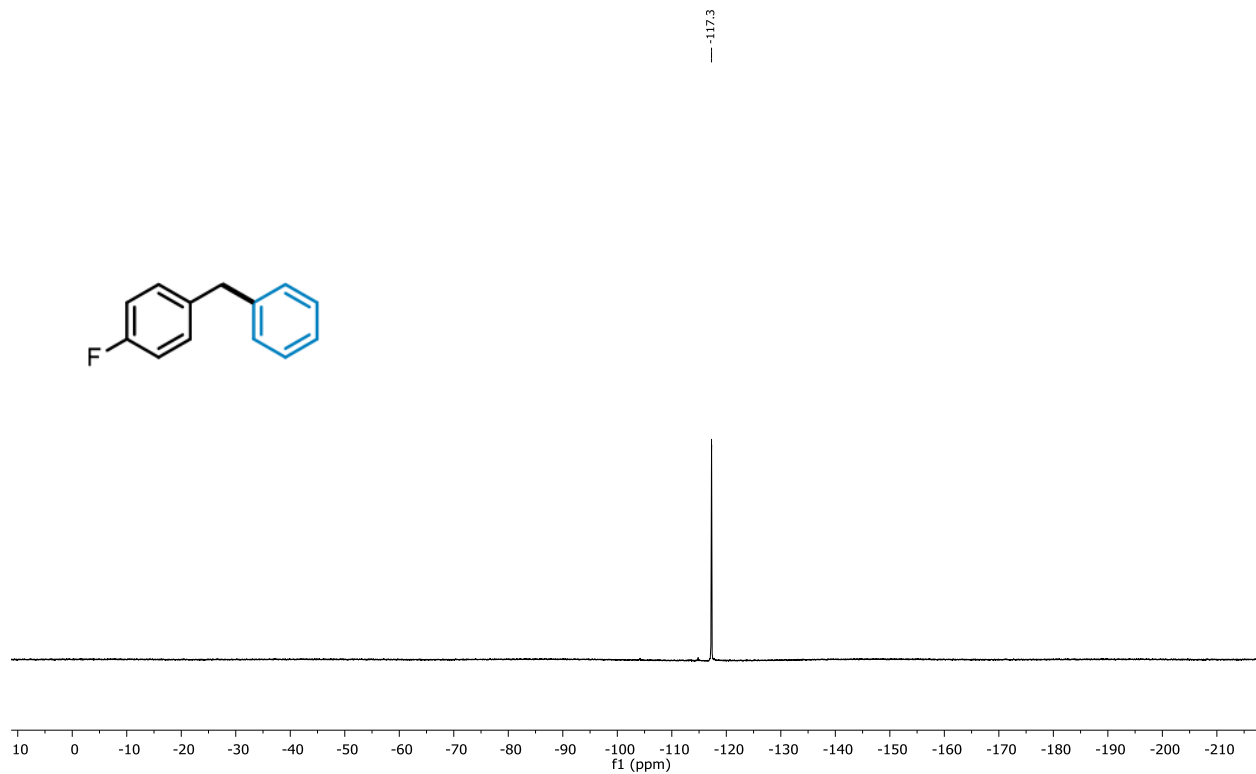
$^1\text{H NMR}$ (400 MHz, CDCl_3) 1-benzyl-4-chlorobenzene (**2d**) matches with compound **1d**.
 $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) 1-benzyl-4-chlorobenzene (**2d**) matches with compound **1d**.

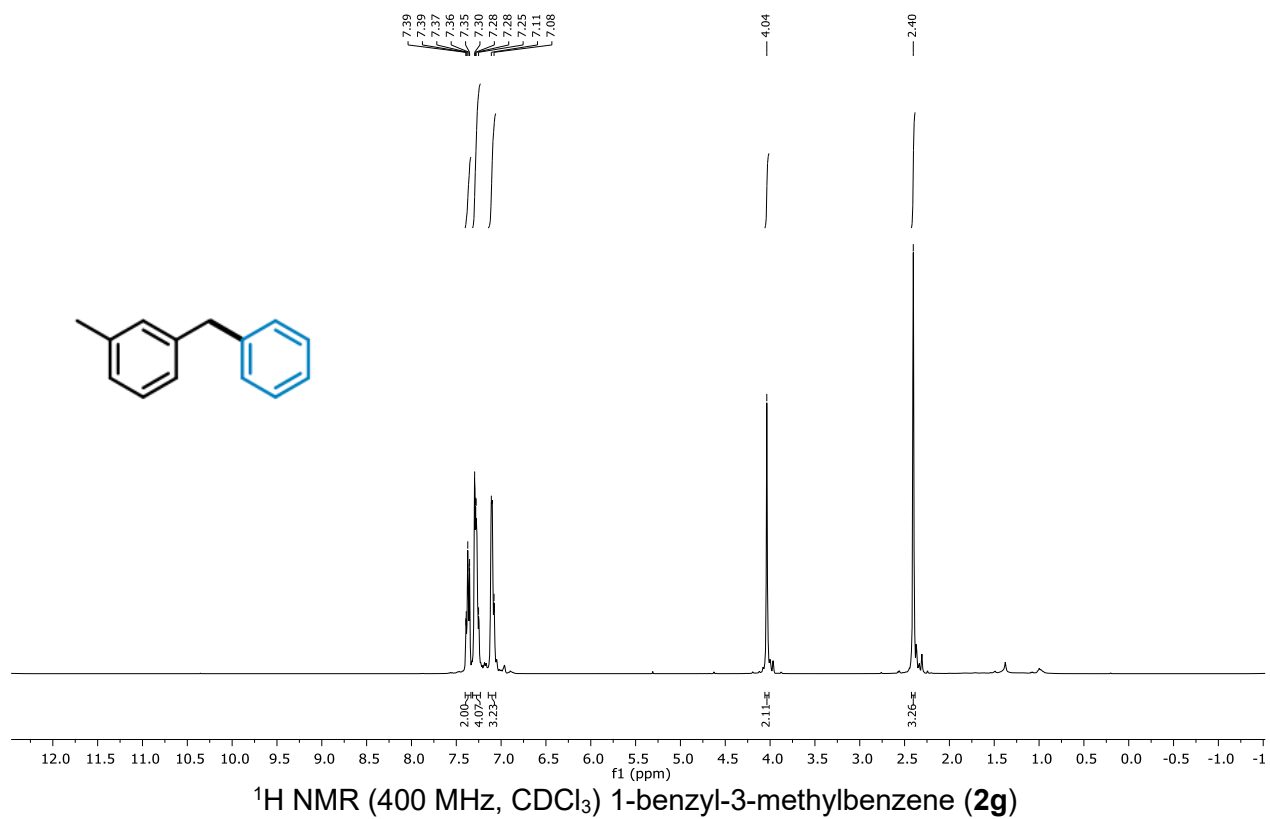
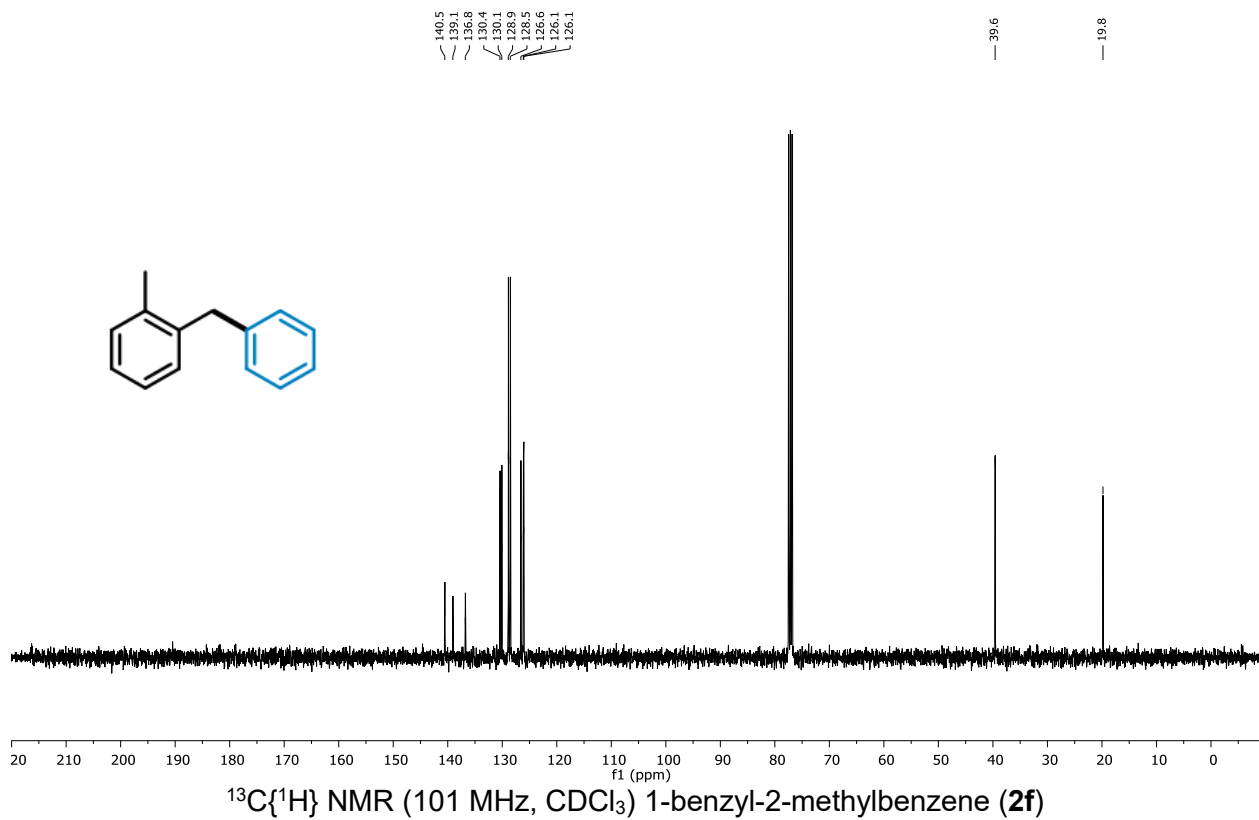


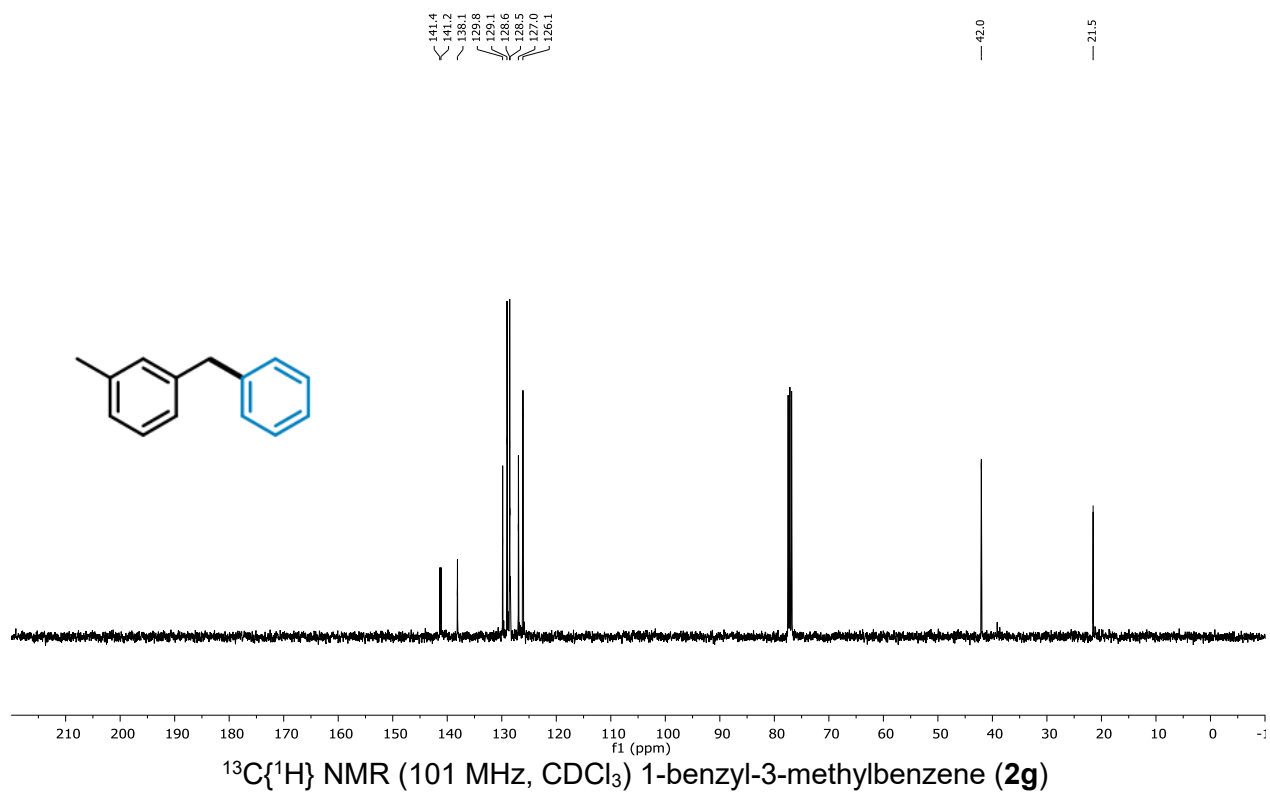
¹H NMR (400 MHz, CDCl₃) 1-benzyl-4-fluorobenzene (**2e**)



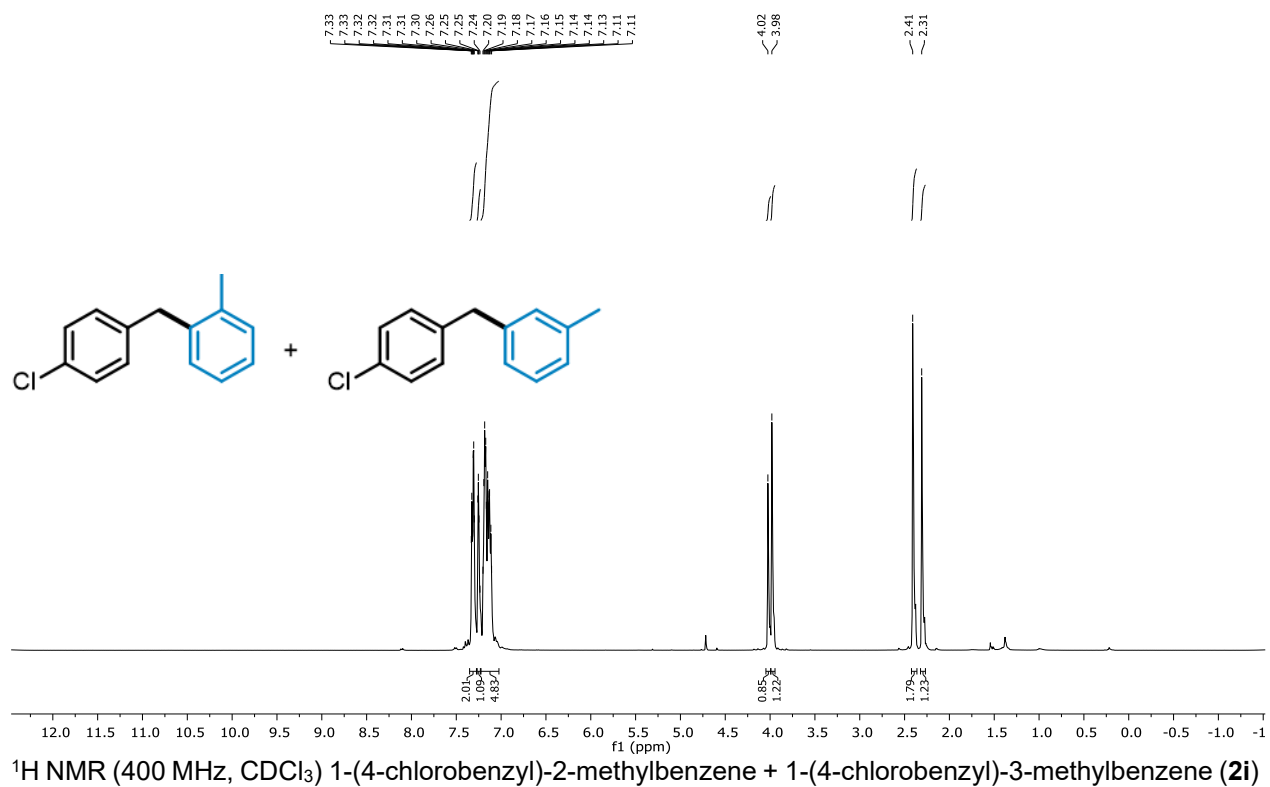
¹³C{¹H} NMR (101 MHz, CDCl₃) 1-benzyl-4-fluorobenzene (**2e**)

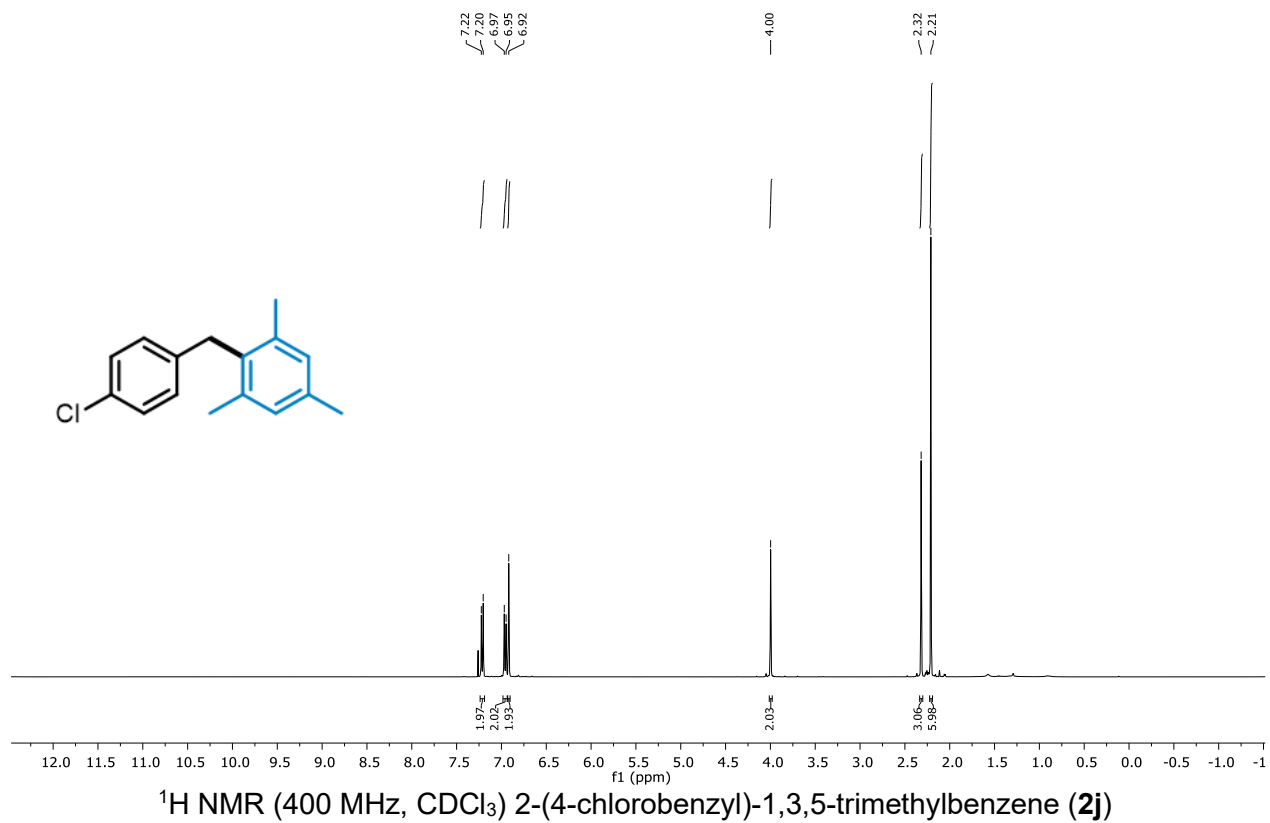
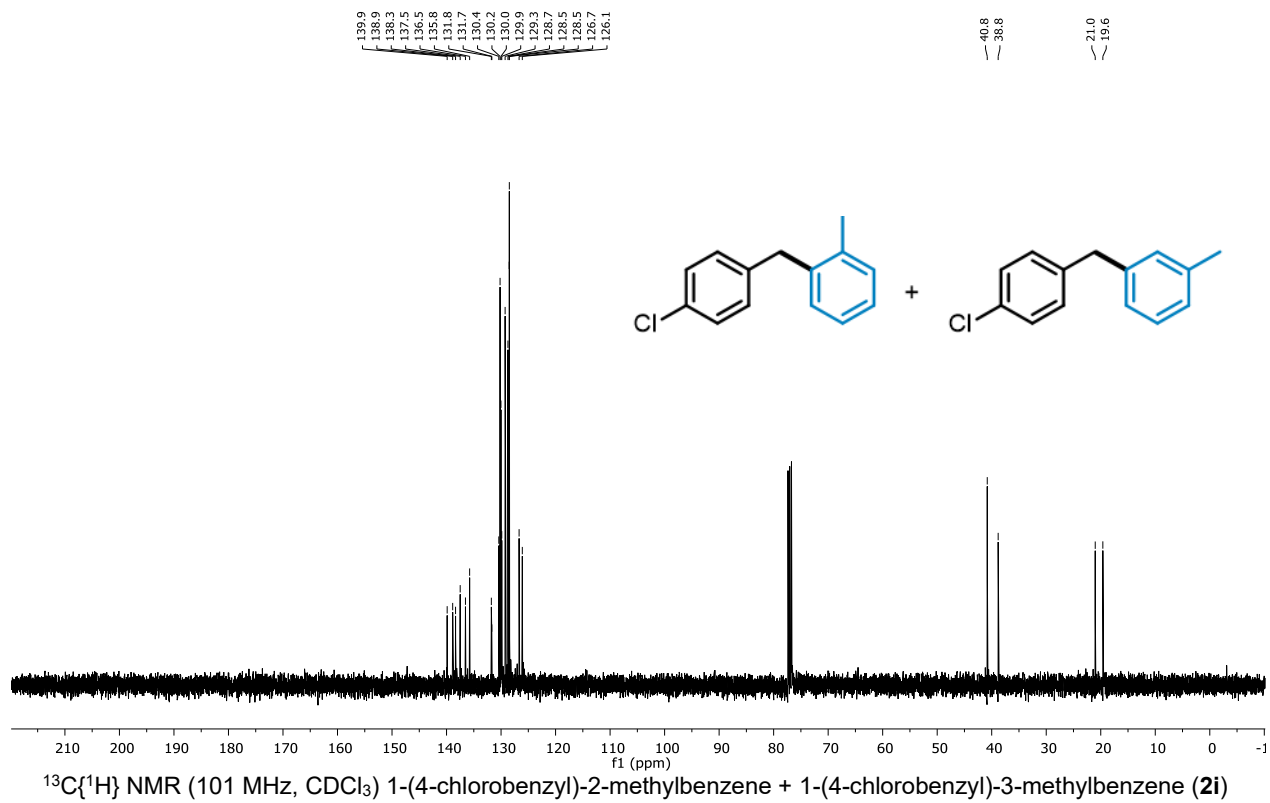


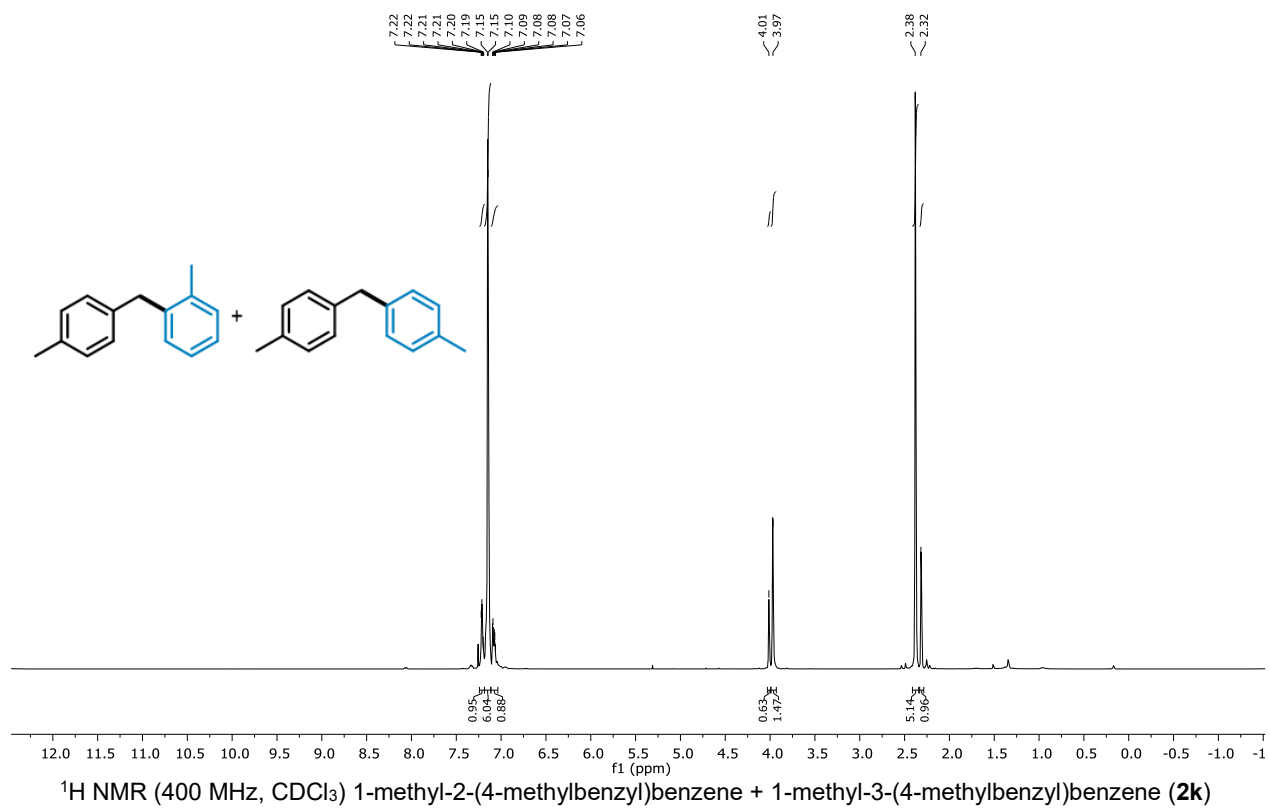
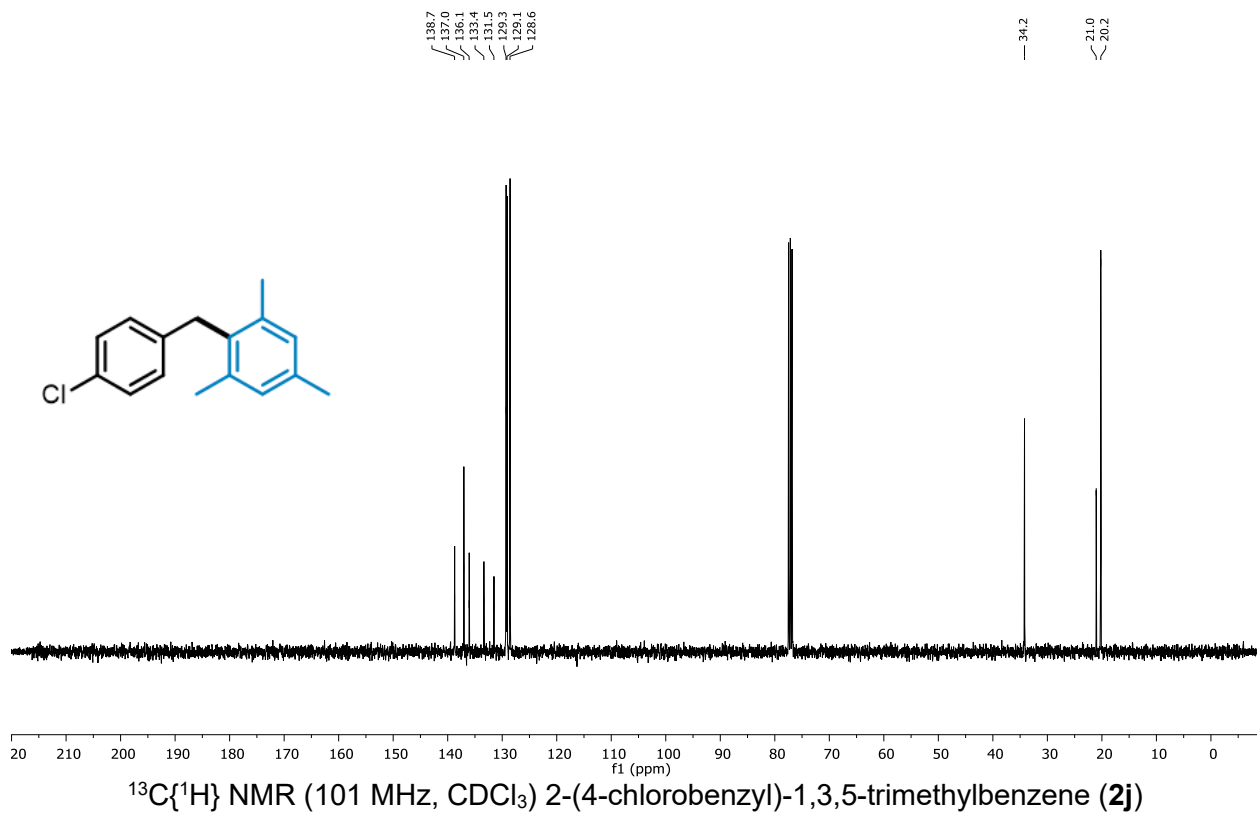


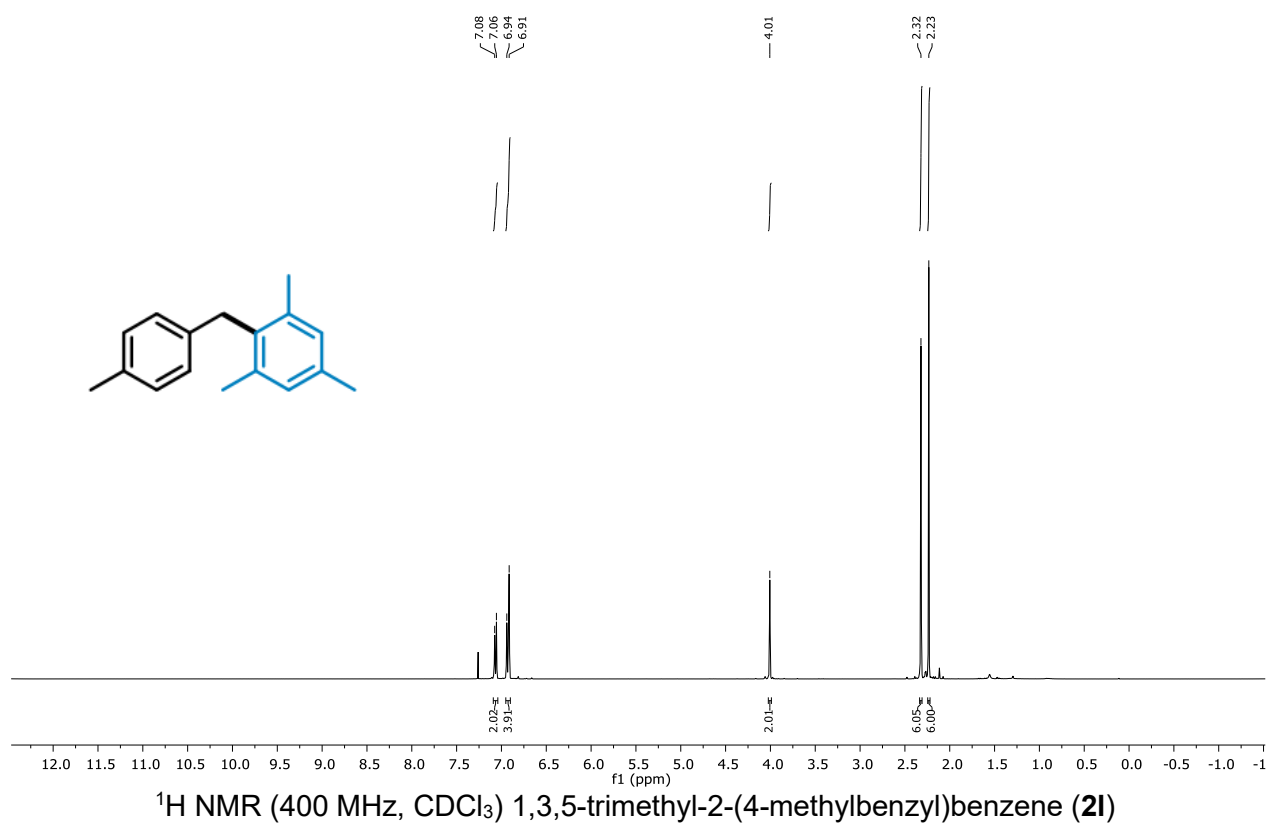
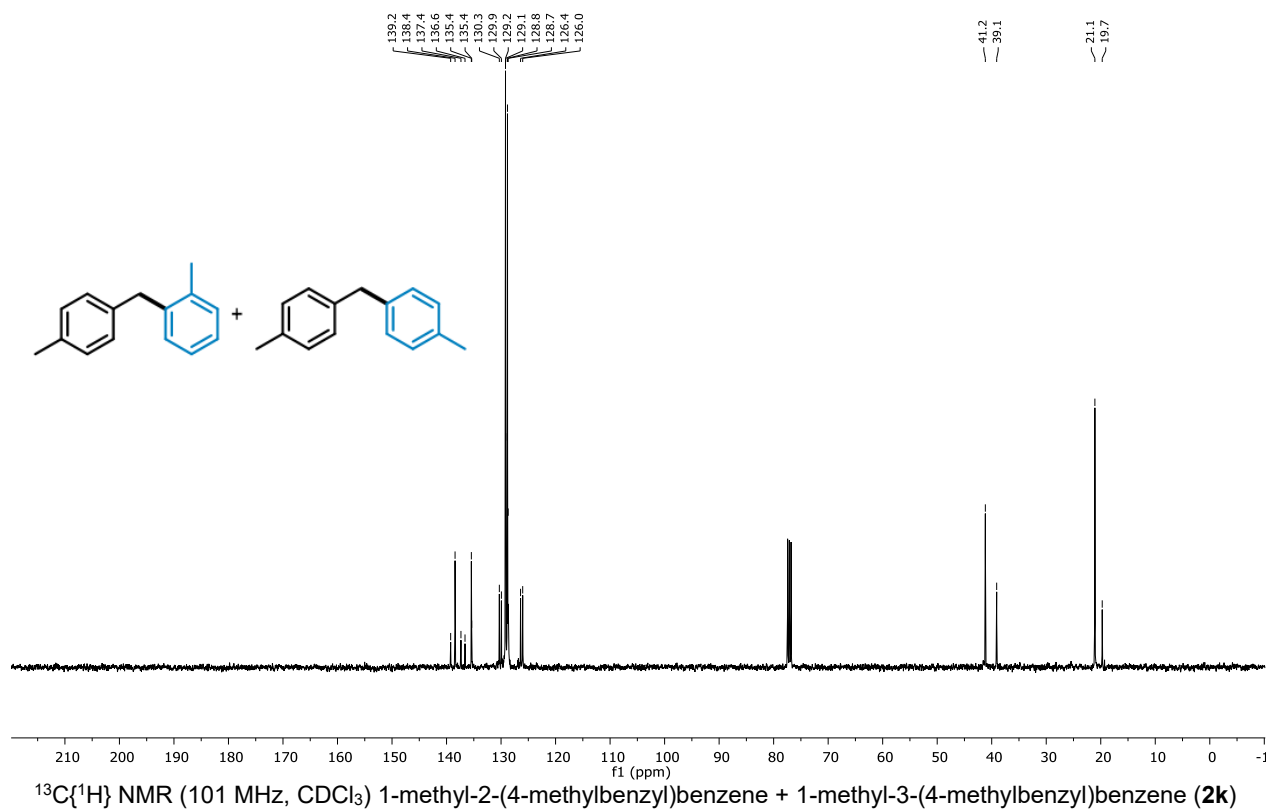


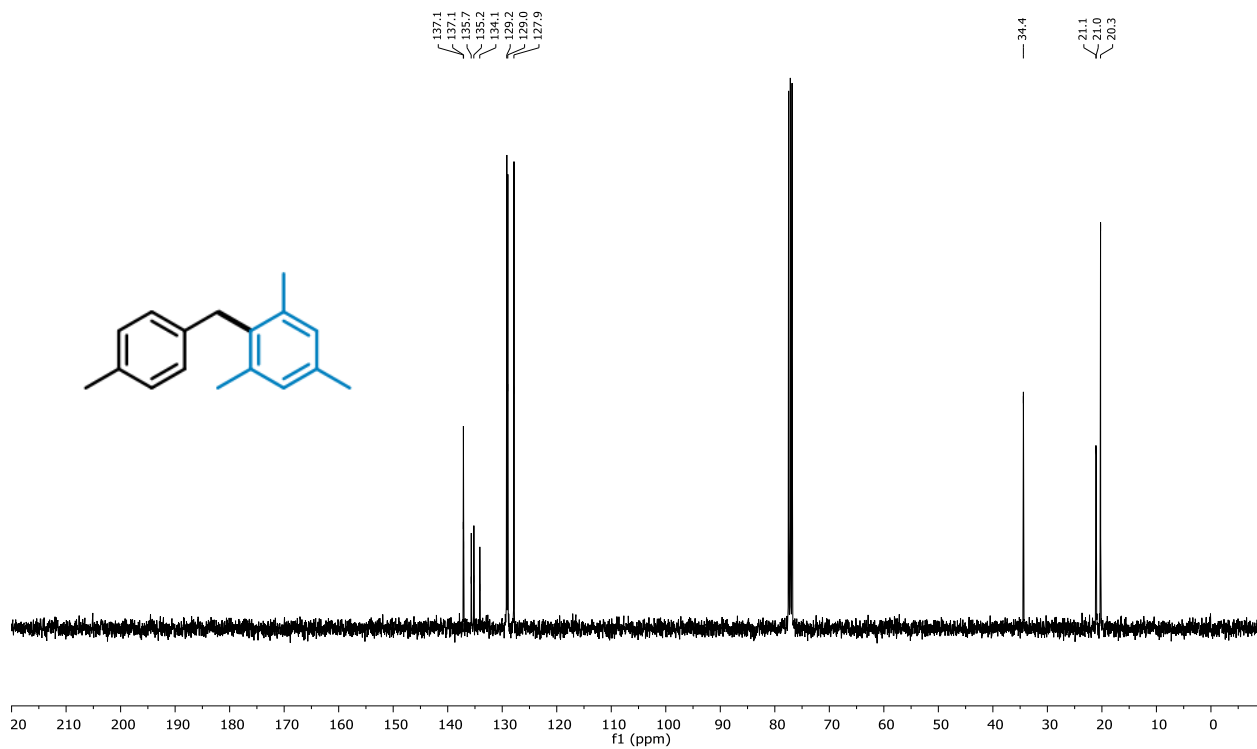
^1H NMR (400 MHz, CDCl_3) 1-benzyl-4-methylbenzene (**2h**) matches with compound **1b**.
 $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) 1-benzyl-4-methylbenzene (**2h**) matches with compound **1b**.





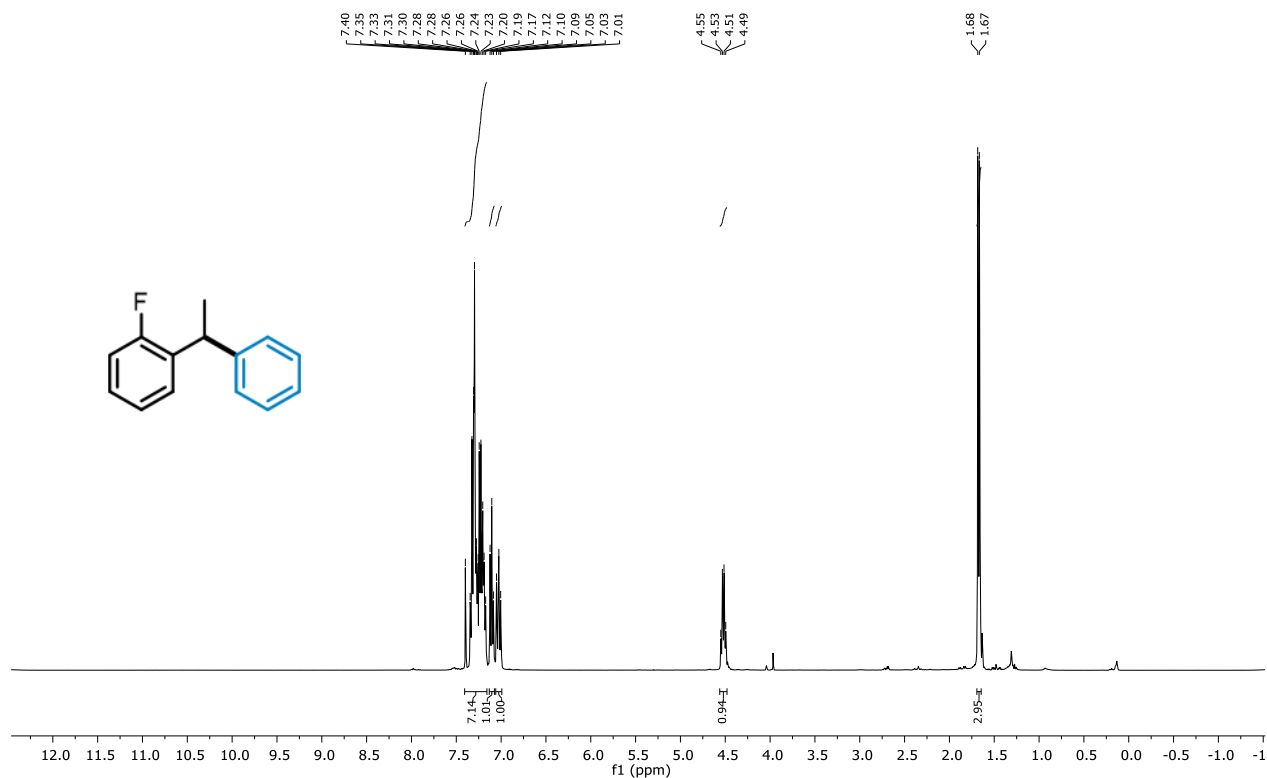




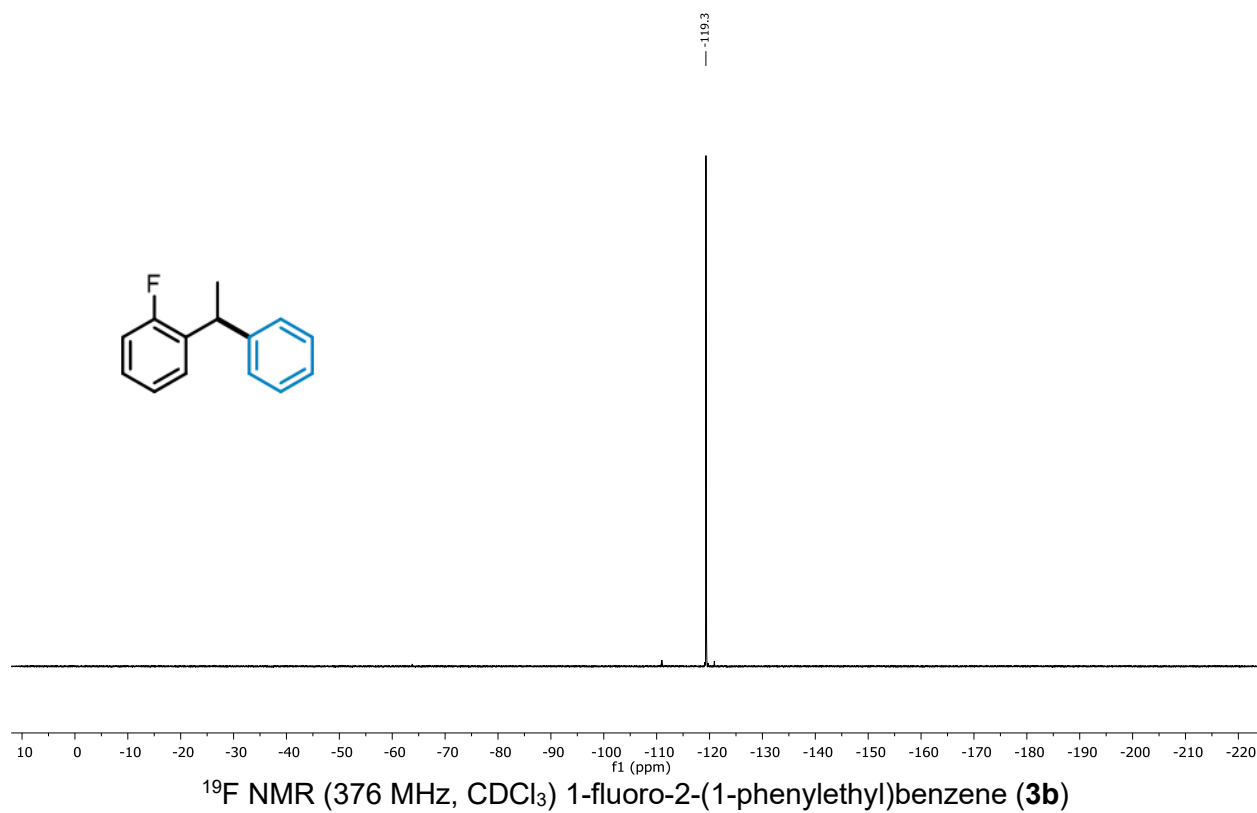
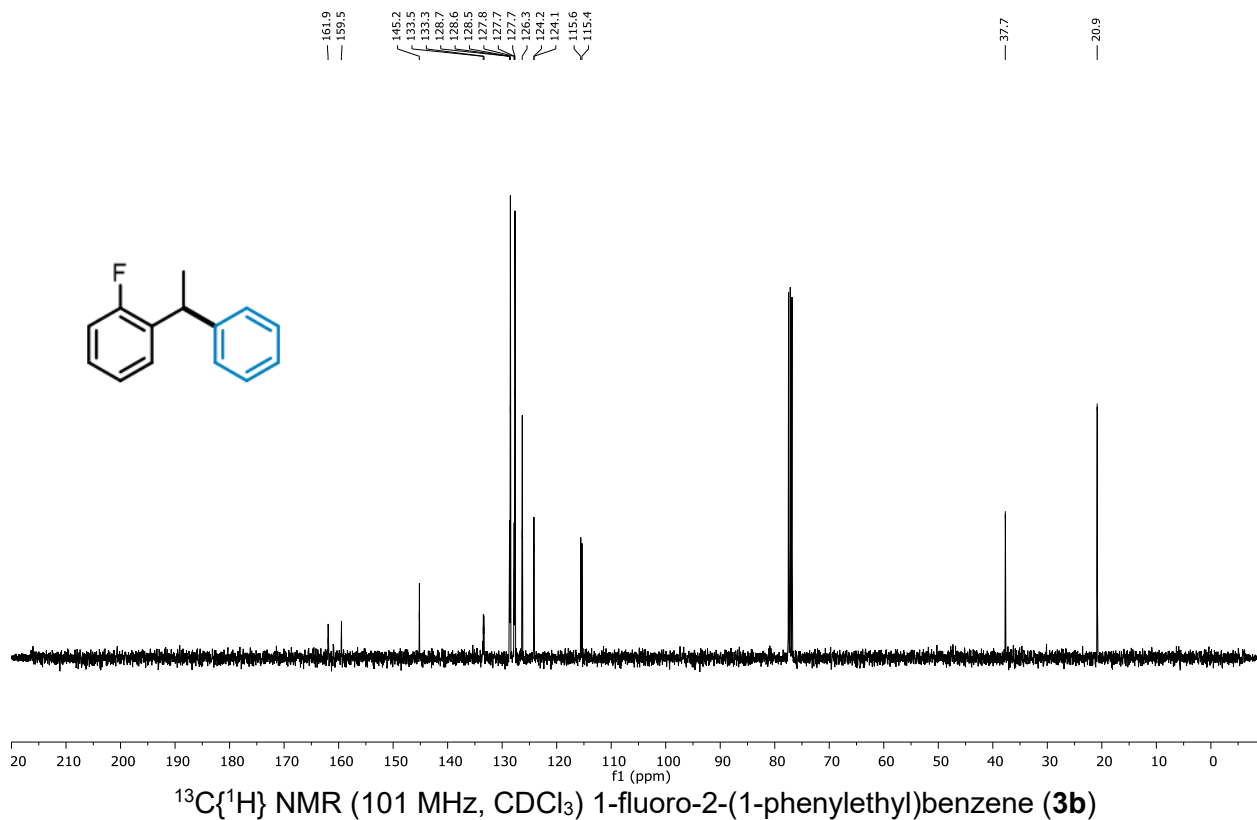


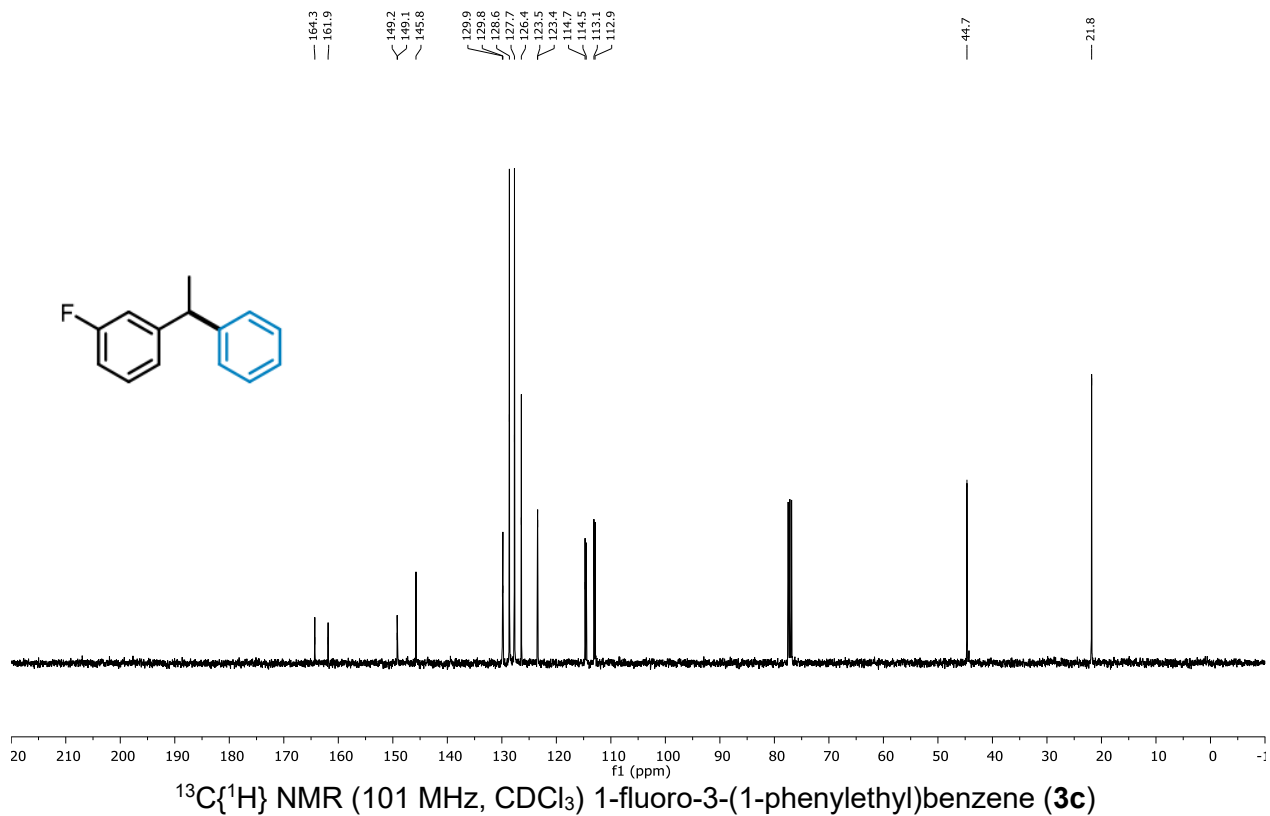
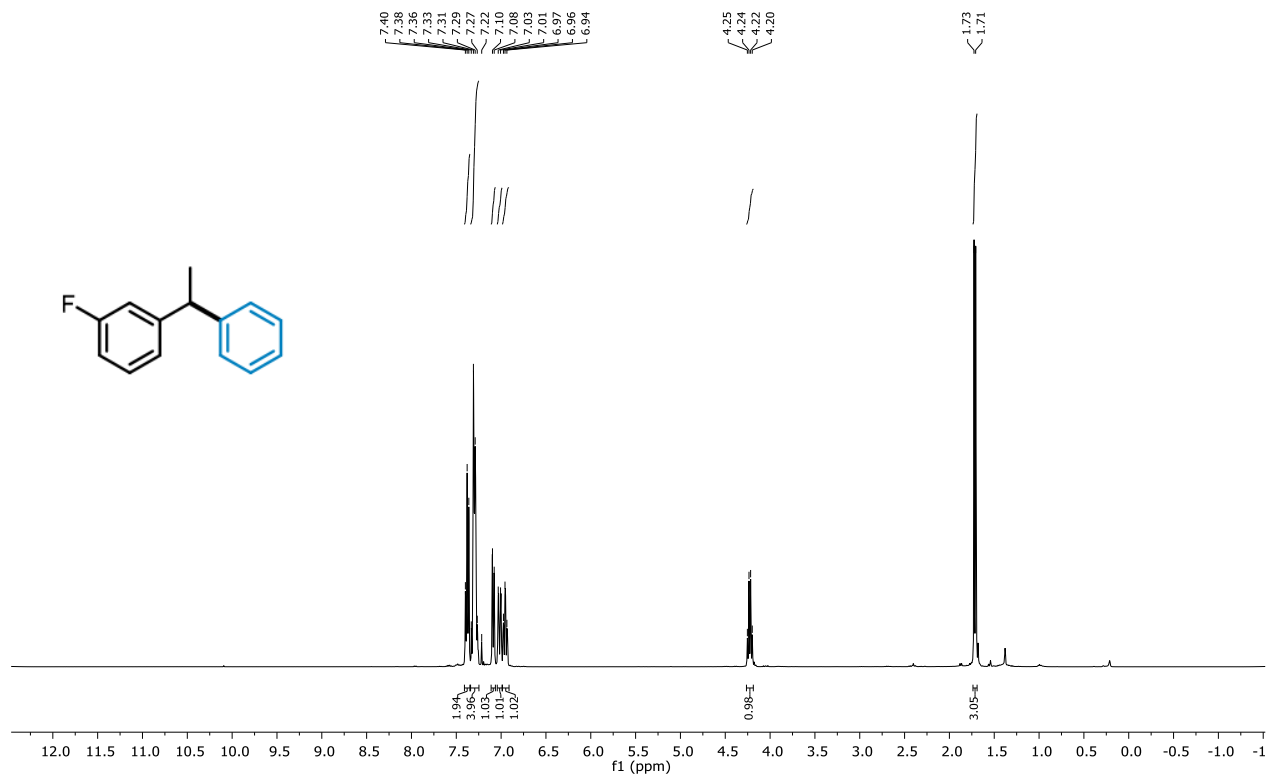
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) 1,3,5-trimethyl-2-(4-methylbenzyl)benzene (**2I**)

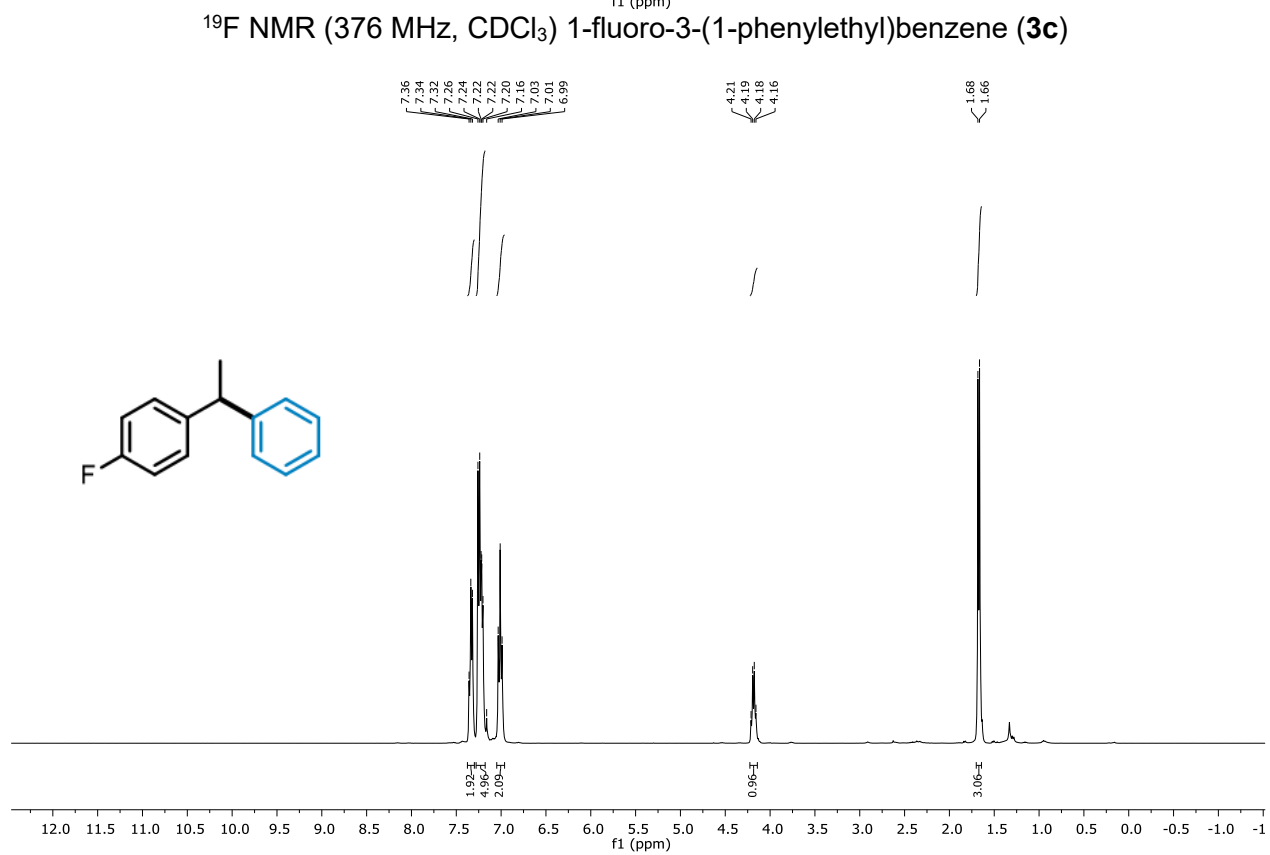
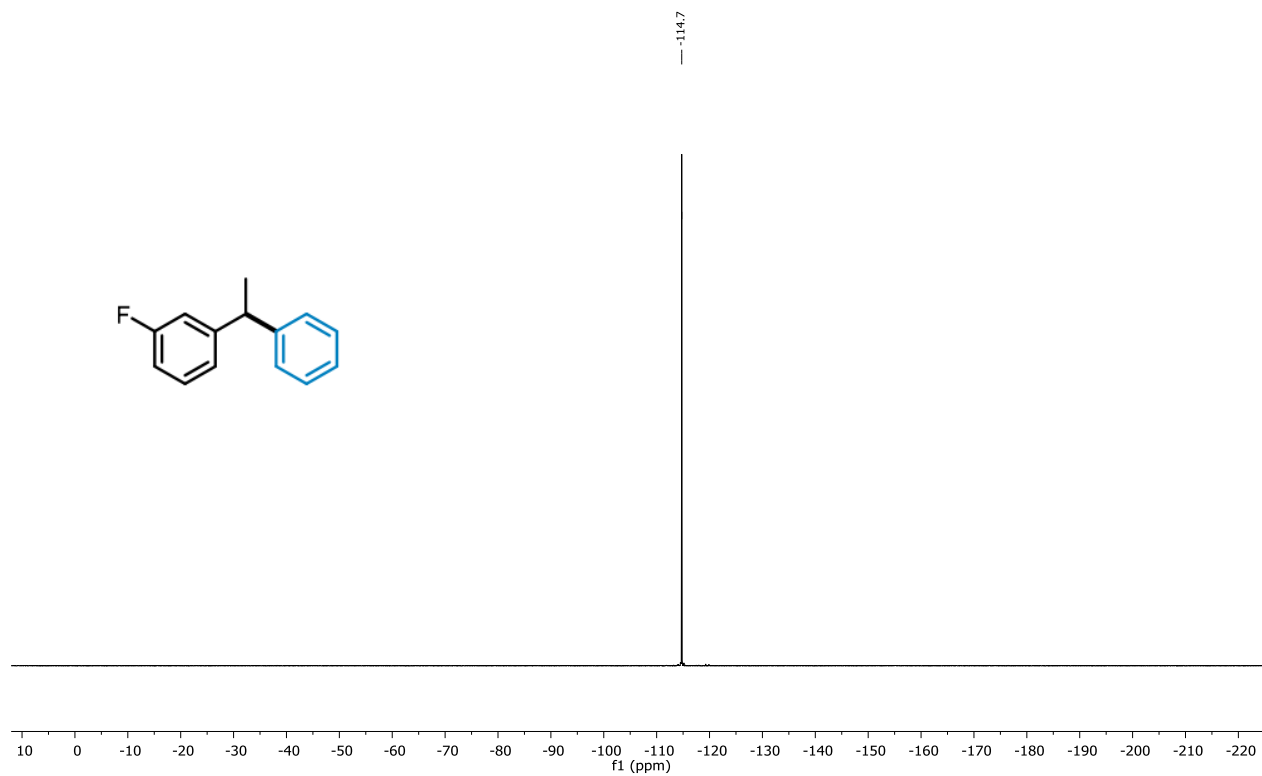
^1H NMR (400 MHz, CDCl_3) ethane-1,1-diyldibenzene (**3a**) matches with compound **1h**.
 $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) ethane-1,1-diyldibenzene (**3a**) matches with compound **1h**.

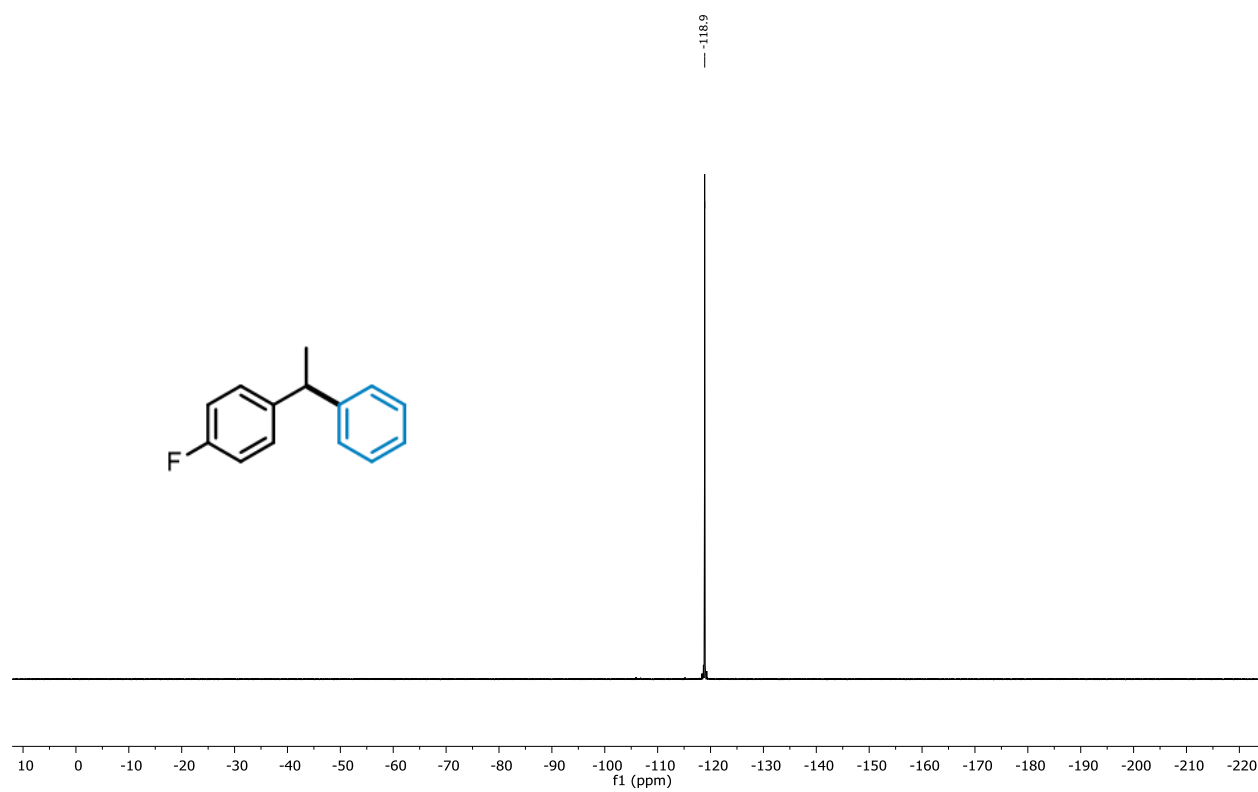
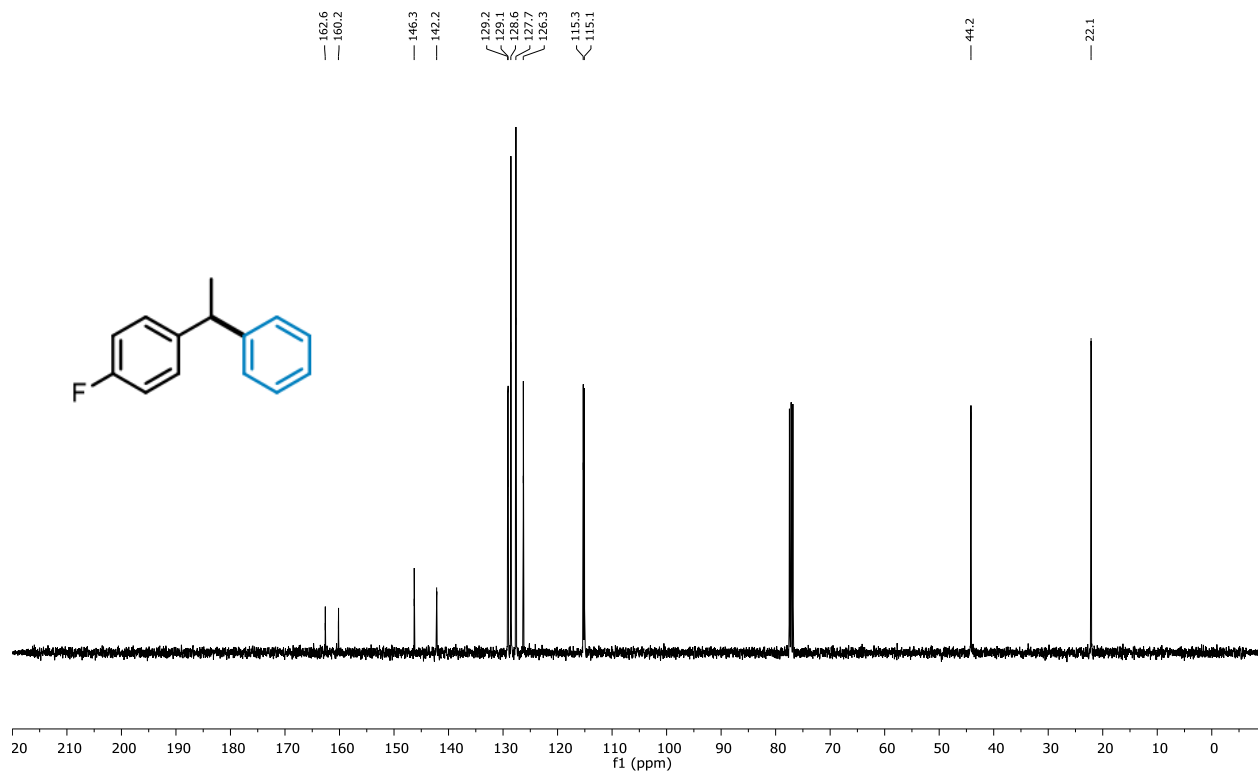


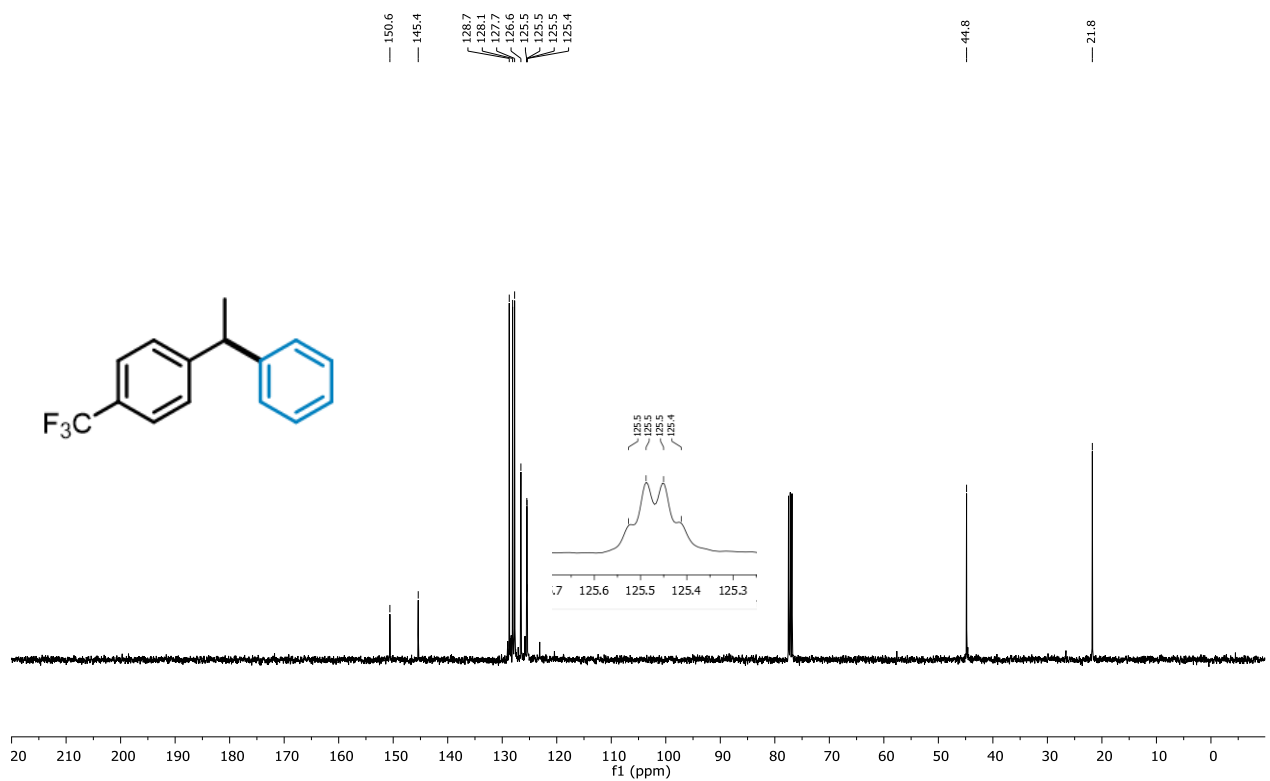
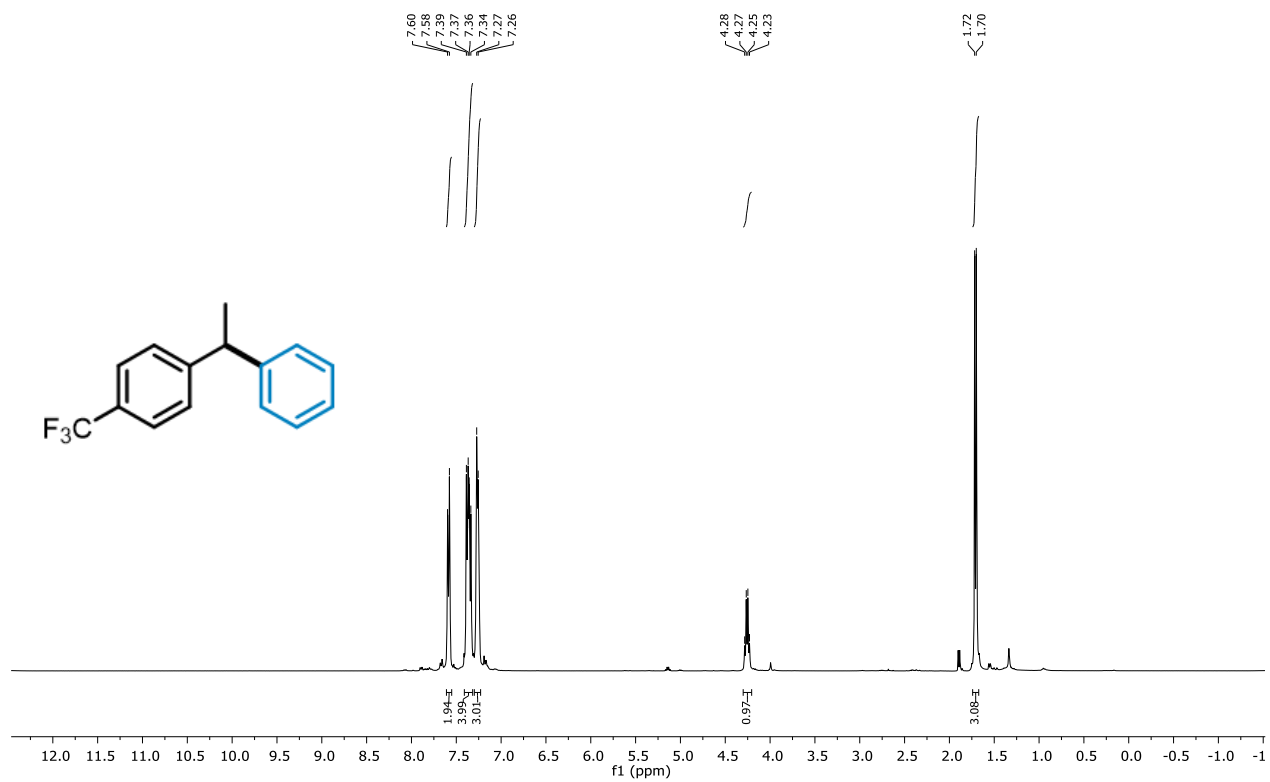
^1H NMR (400 MHz, CDCl_3) 1-fluoro-2-(1-phenylethyl)benzene (**3b**)

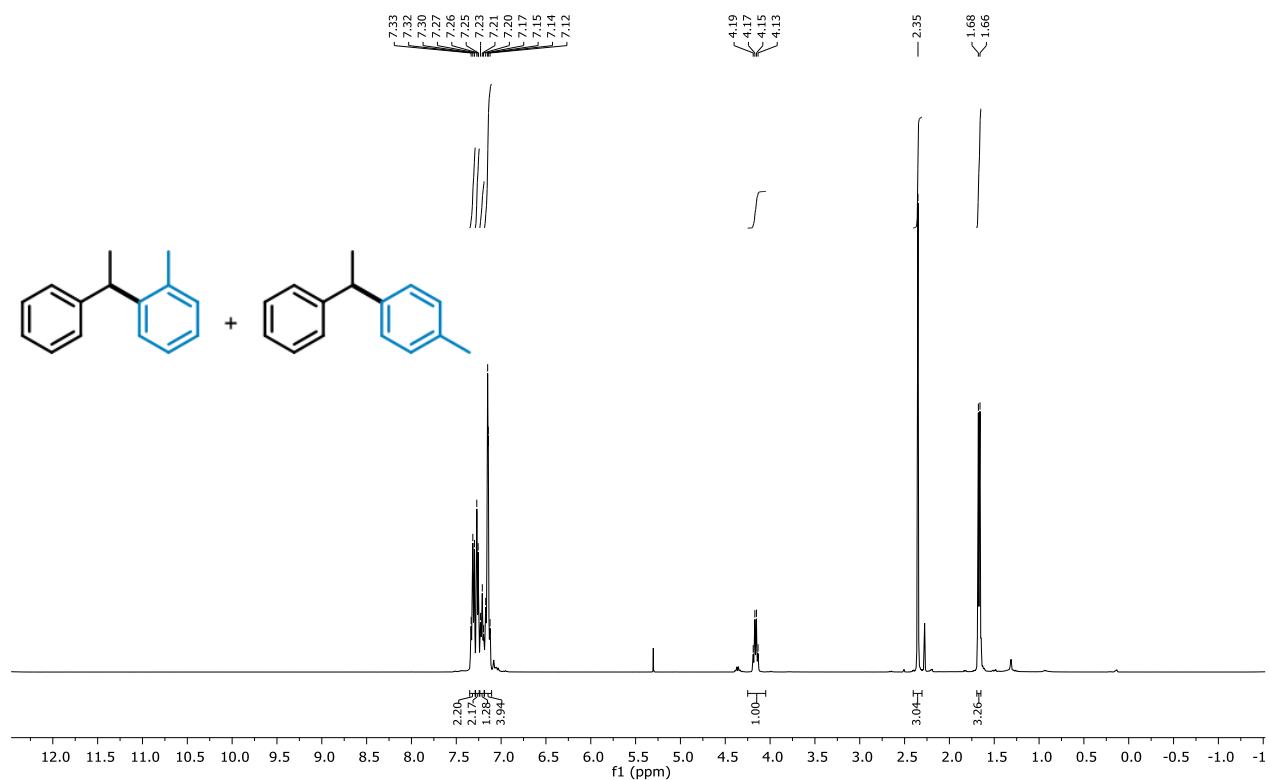
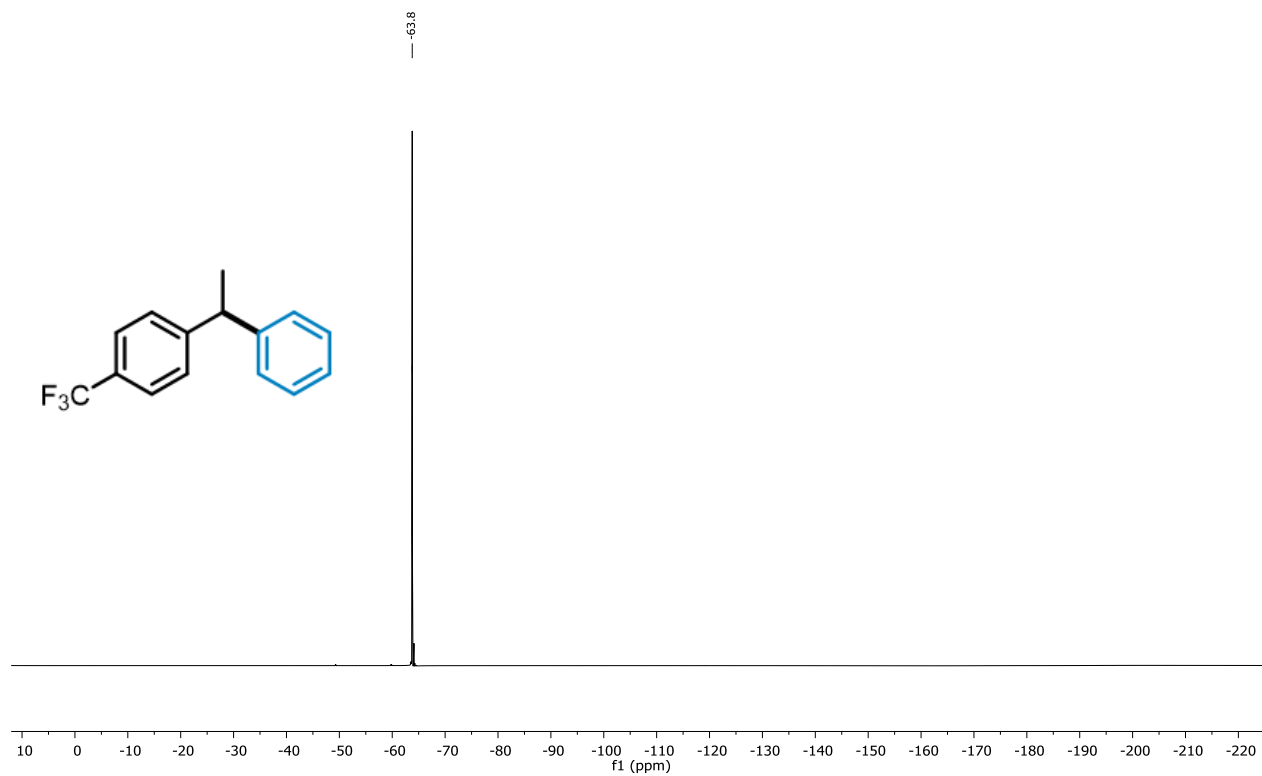


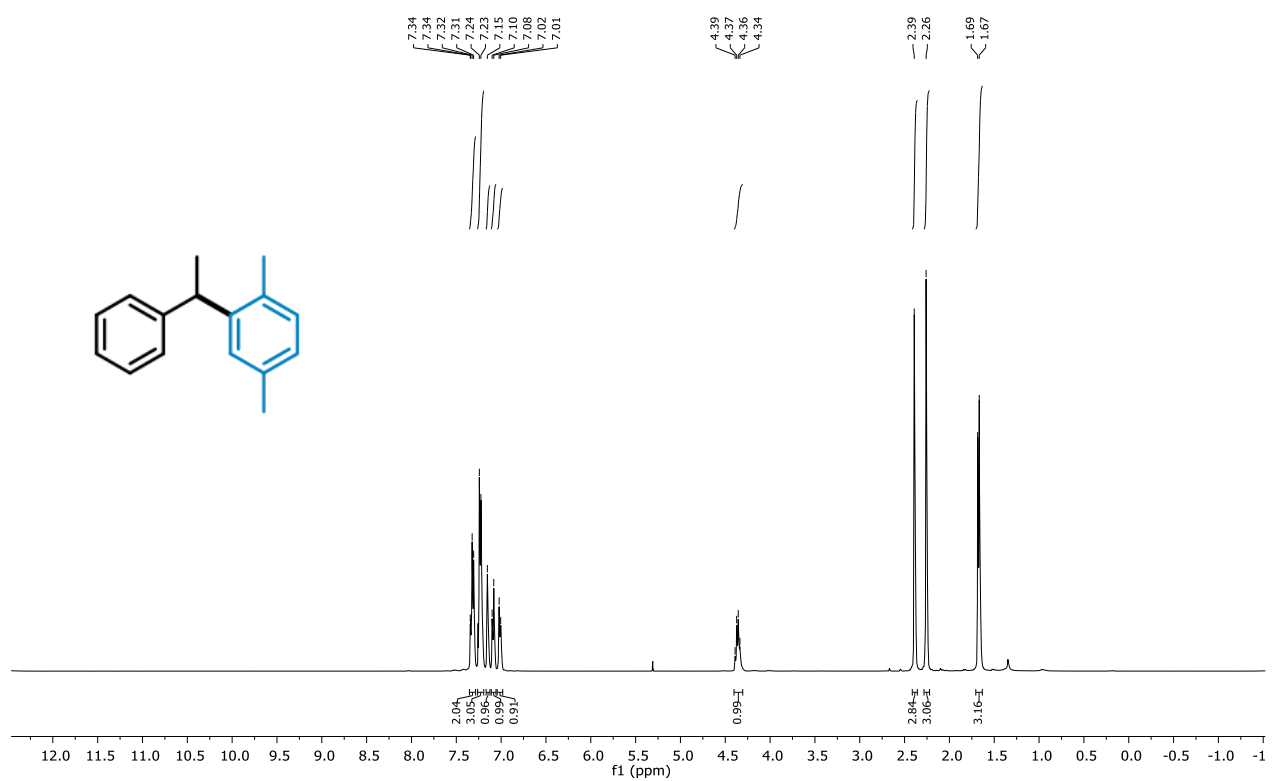
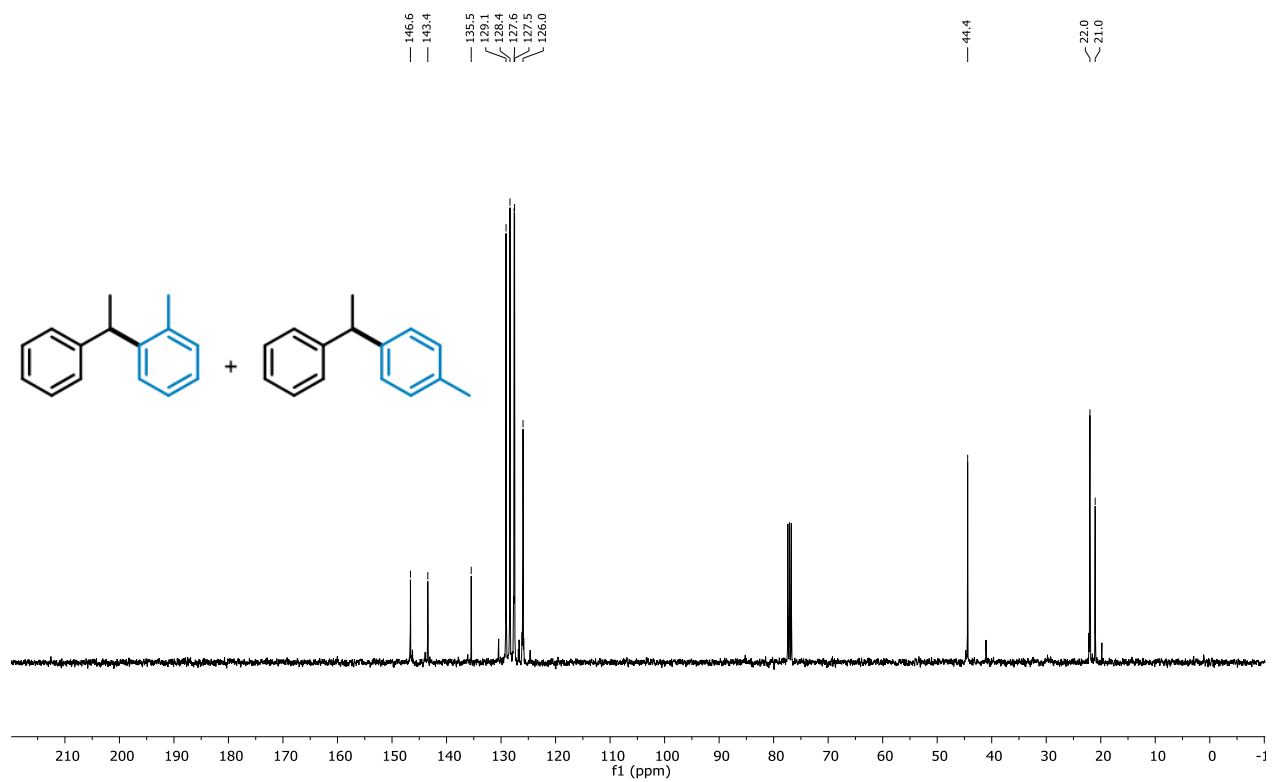


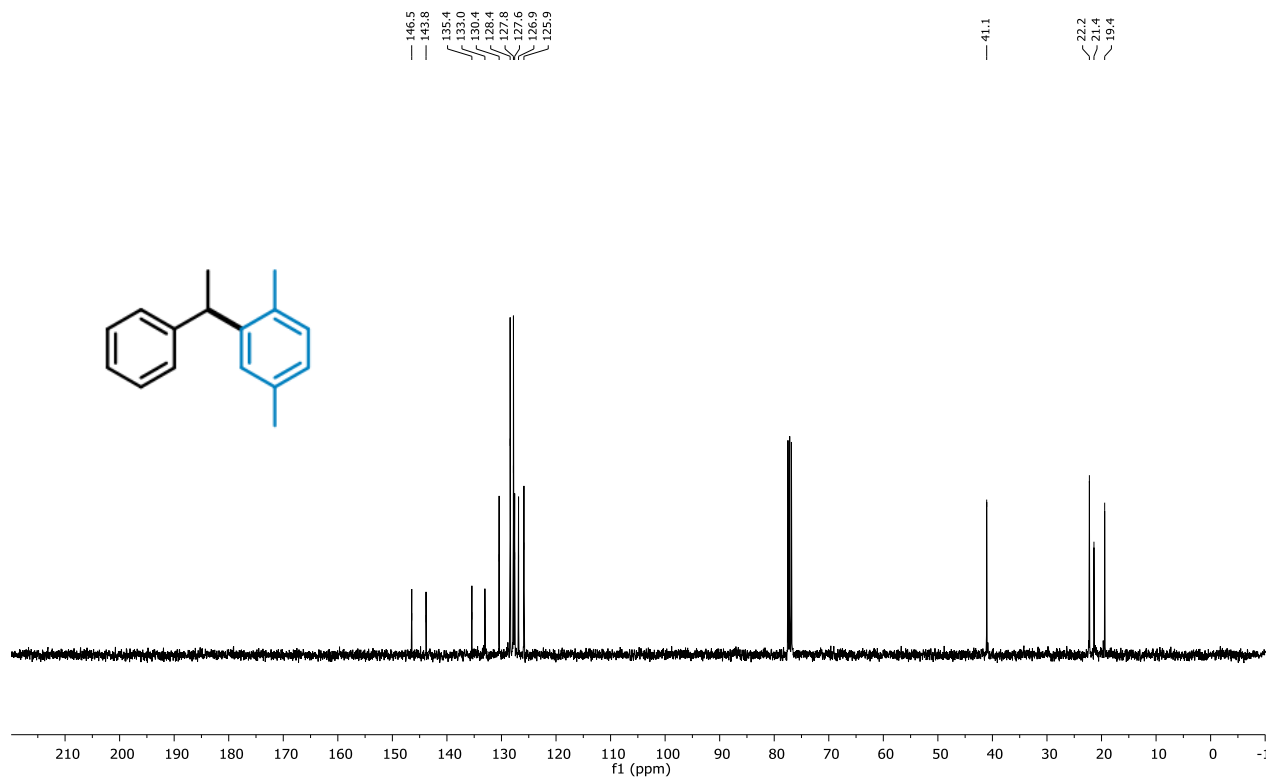












$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) 1,4-dimethyl-2-(1-phenylethyl)benzene (**3g**)

^1H NMR (400 MHz, CDCl_3) diphenylmethane (**4a**) matches with compound **1a**.

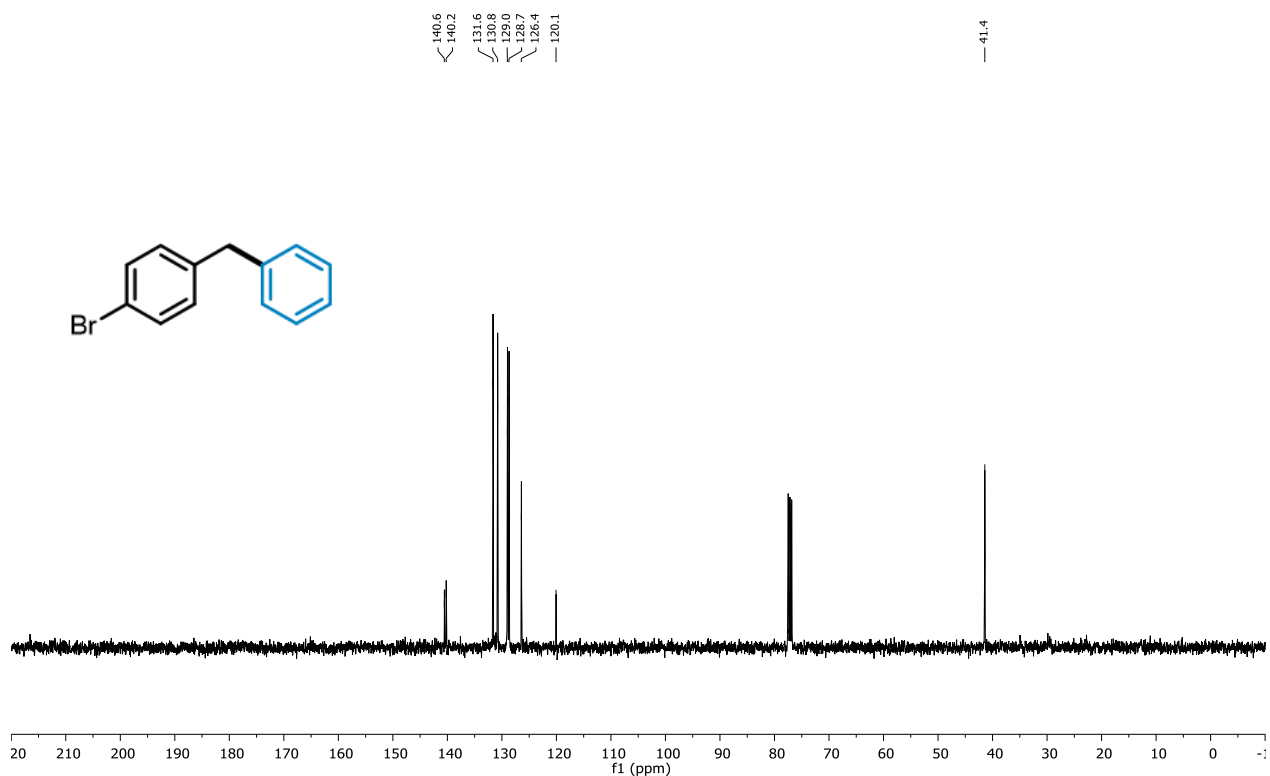
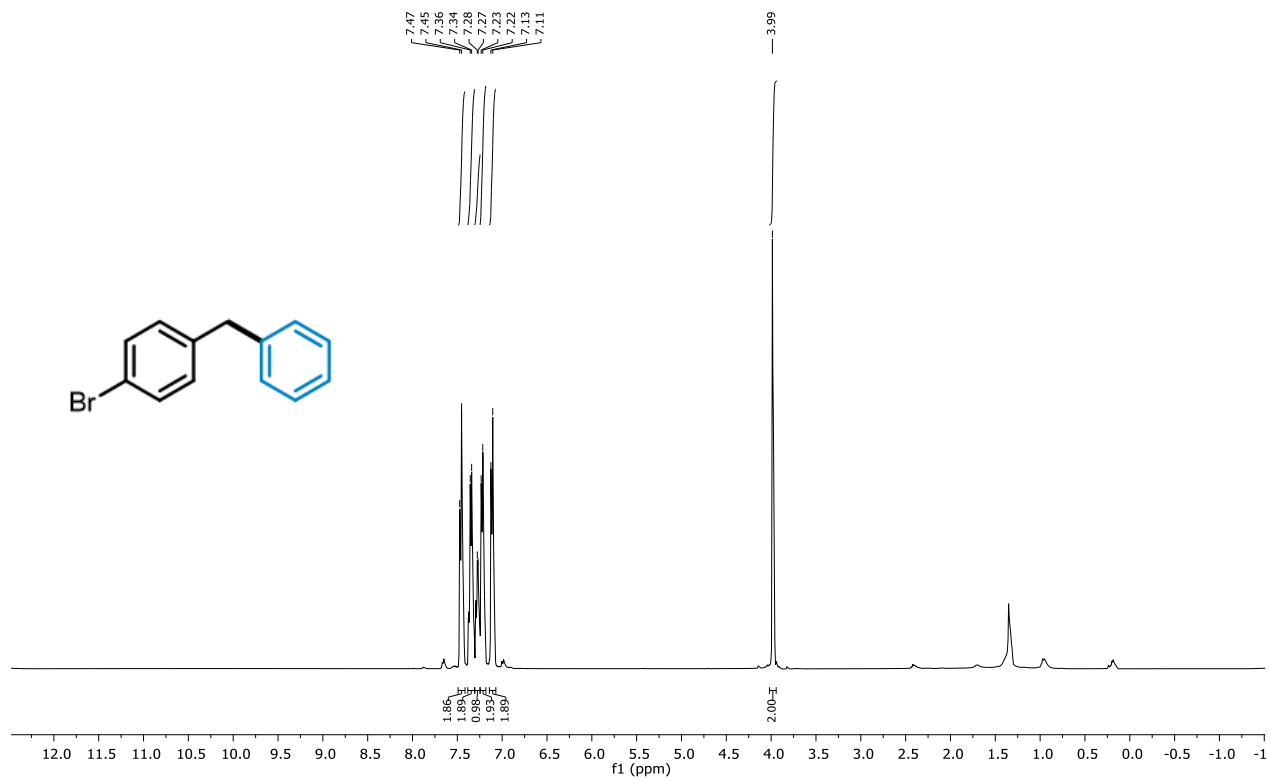
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) diphenylmethane (**4a**) matches with compound **1a**.

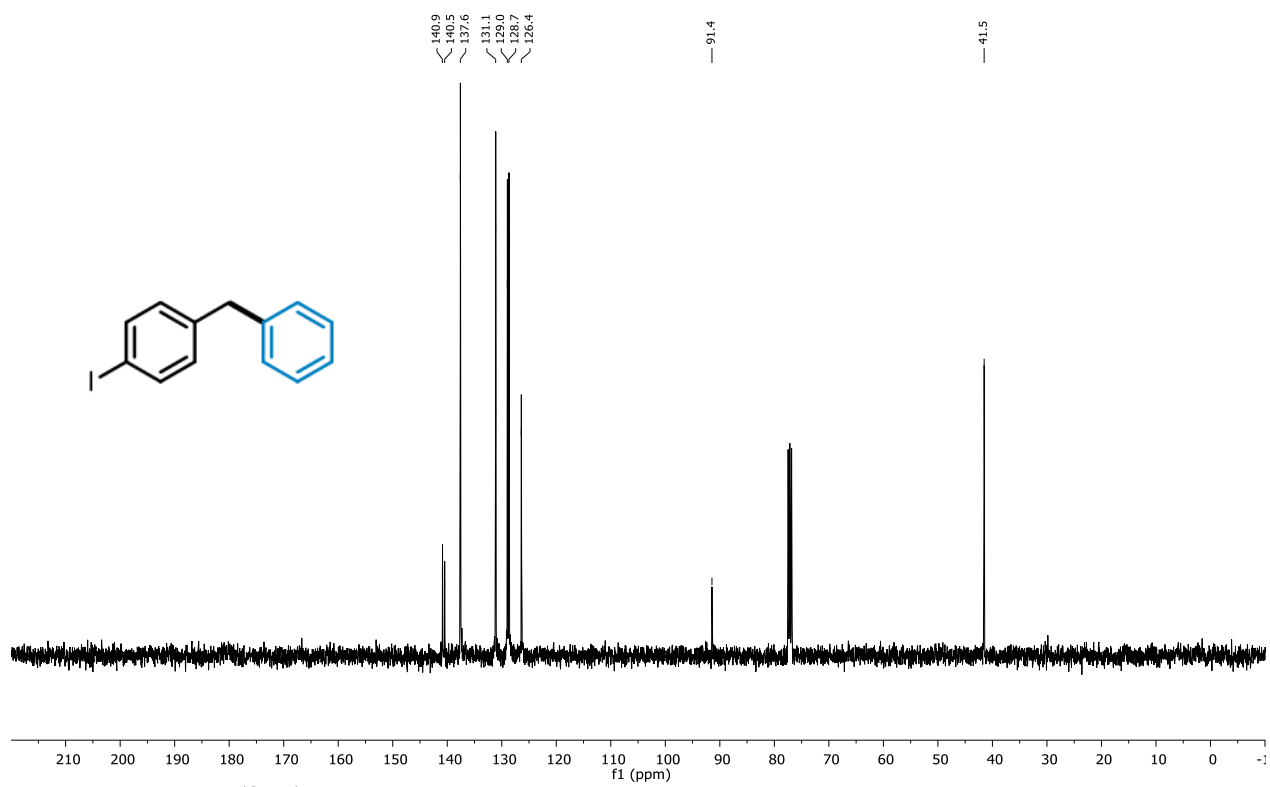
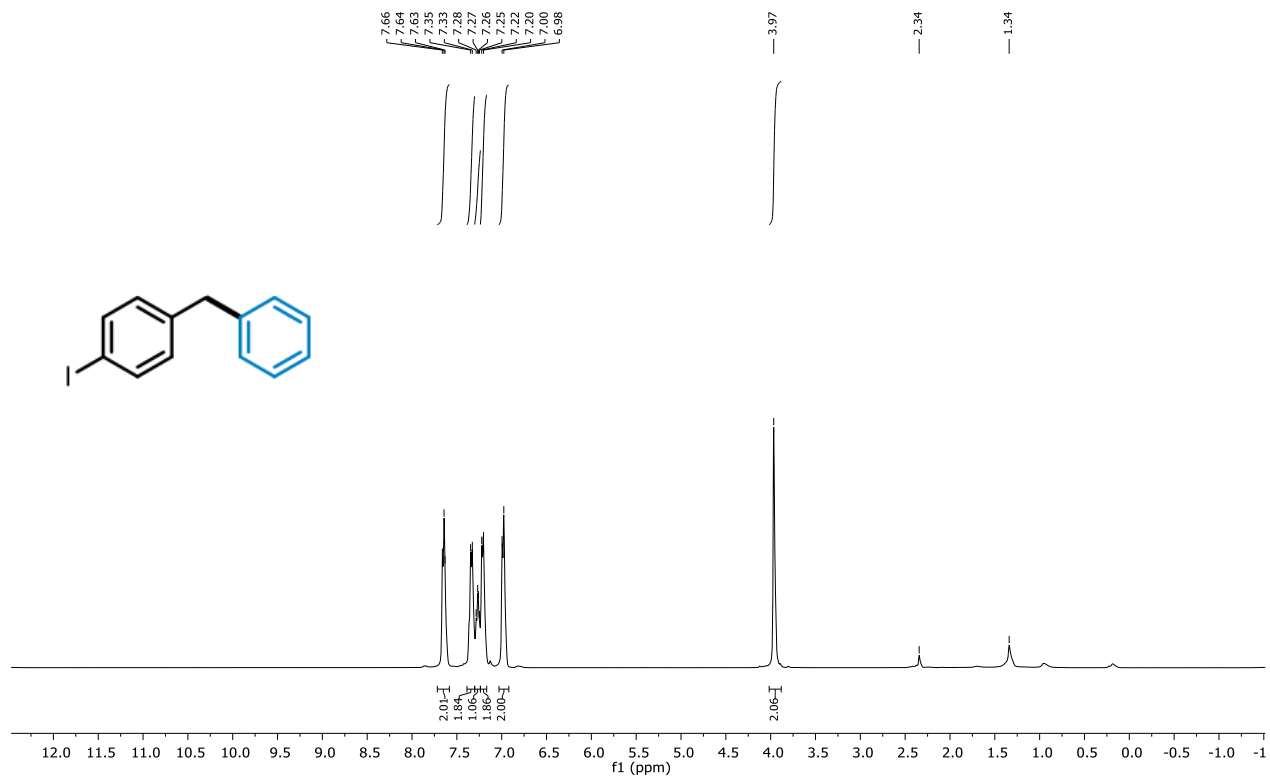
^1H NMR (400 MHz, CDCl_3) 1-benzyl-4-methylbenzene (**4b**) matches with compound **1b**.

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) 1-benzyl-4-methylbenzene (**4b**) matches with compound **1b**.

^1H NMR (400 MHz, CDCl_3) 1-benzyl-4-chlorobenzene (**4c**) matches with compound **1d**.

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) 1-benzyl-4-chlorobenzene (**4c**) matches with compound **1d**.





^1H NMR (400 MHz, CDCl_3) 1-benzyl-2-methylbenzene + 1-benzyl-4-methylbenzene (**4f**) matches with compound **1e**.

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) 1-benzyl-2-methylbenzene + 1-benzyl-4-methylbenzene (**4f**) matches with compound **1e**.

^1H NMR (400 MHz, CDCl_3) 2-benzyl-1,4-dimethylbenzene (**4g**) matches with compound **1g**.

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) 2-benzyl-1,4-dimethylbenzene (**4g**) matches with compound **1g**.

^1H NMR (400 MHz, CDCl_3) diphenylmethane (**5a**) matches with compound **1a**.

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) diphenylmethane (**5a**) matches with compound **1a**.

^1H NMR (400 MHz, CDCl_3) 1-benzyl-4-methylbenzene (**5b**) matches with compound **1b**.

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) 1-benzyl-4-methylbenzene (**5b**) matches with compound **1b**.

