Supporting Information

Palladium-Catalyzed Direct β-Arylation of Ketones with Diaryliodonium Salts: A Stoichiometric Heavy Metal-Free and User-Friendly Approach

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I. Materials and methods

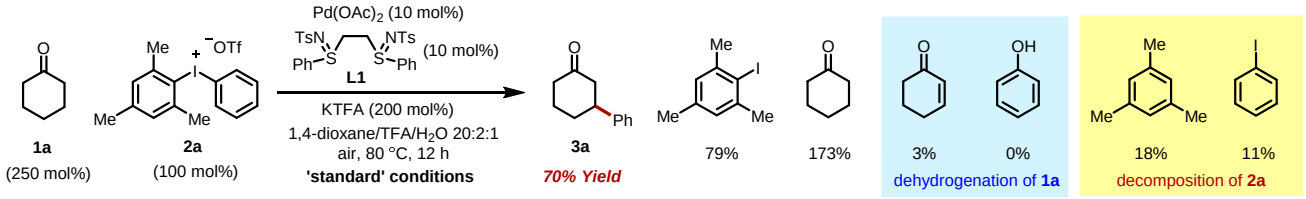
Unless stated otherwise, all reactions were run in vials sealed with PTFE lined caps, purchased from Qorpak. 1,4-Dioxane was distilled from Na and freeze-pump-thawed three times prior to use. Trifluoroacetic acid (TFA, 99%) and palladium acetate (98%) were purchased from Aldrich and used as received. Potassium trifluoroacetate (KTFA) was purchased from Oakwood Chemical and used as received. All commercially available substrates were used without further purification. Thin layer chromatography (TLC) analysis was run on silica gel plates purchased from EMD Chemical (silica gel 60, F254). Gas chromatography (GC) data was obtained from Agilent 7820A GC system, equipped with Agilent 19091J-413 column and a FID detector. GC yield of 3-phenyl cyclohexanone (**3a**) was determined using standard curves with dodecane as internal standard. Mass spectra were recorded on an Autospec or Agilent 6150. Accurate masses from high-resolution mass spectra were reported for the molecular ion $[M+Na]^+$, $[M]^+$ or $[M+H]^+$. ^1H NMR and ^{13}C NMR spectra were recorded on a Varian Gemini (400 MHz for ^1H, 100 MHz for ^{13}C). Chemical shifts are reported as parts per million (ppm) using residual solvent signals as internal standard ($CHCl_3$, δ = 7.26 ppm for ^1H NMR, δ = 77.00 ppm for ^{13}C NMR, DMSO, δ = 40.45 ppm for ^{13}C NMR). Data for ^1H NMR were presented as following: chemical shifts (δ, ppm), multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, tt = triplet of triplets, td = triplet of doublets, m = multiplet), coupling constant (Hz), and integration. The chemical shifts of peaks found were reported for ^{13}NMR spectra. Infrared spectra were obtained from a Nicolet iS5 FTIR spectrometer. Dynamic light scattering experiments were performed on a Zetasizer Nano ZS instrument.

General procedure for reaction condition screening

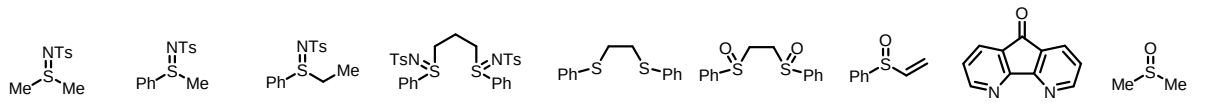
The reaction was run at a 0.2 mmol scale based on the limiting reagent. A 4 mL vial was charged with palladium salt, ligand, additives, cyclohexanones, mesitylphenyliodonium salt, 1 mL 1,4-dioxane and cosolvent. The vial was sealed with a PTFE lined cap and heated in a pie-block at 80 °C for 12 hours under stirring. Then the mixture was allowed to cool to room temperature. The reaction mixture was diluted with 1 mL ethyl acetate and appropriate amount of dodecane (~10 mg) was added as the internal standard. The mixture was stirred for an additional 5 min to fully mix. ~0.2 mL of the resulting mixture was filtered through a small plug of silica gel, eluted with diethyl ether. The filtrate was directly used for GC analysis.

GC instrument conditions: inlet temperature: 250 °C, detector temperature: 300 °C, hydrogen flow: 40 mL/min, air flow: 400 mL/min, column + makeup flow: 30 mL/min. Method: 50 °C hold for 0 min, followed by a temperature increase of 10°C/min to 280 °C, hold 0 min (total run time: 23 min). Yields of product and byproducts are calculated using standard curves with dodecane as the internal standard. Full details of the control reactions are listed below (Table S1).

Table S1. Full Details of the Control Reactions

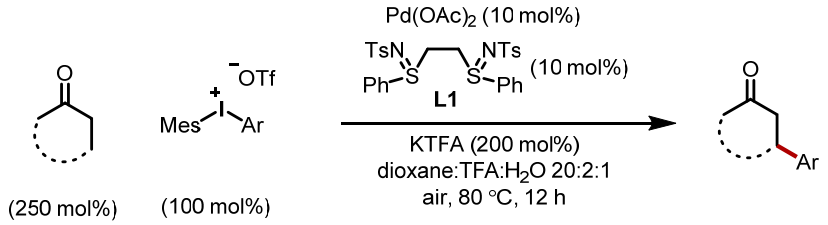


entry	variations from the 'standard' conditions	yield of **3a** (%)	**1a** (%)	iodomesitylene (%)	enone (%)	mesitylene (%)	iodobenzene (%)
1	[MesIPh]BF_4 instead of **2a**	50	158	79	2	18	10
2	[MesIPh]TFA instead of **2a**	56	168	78	3	17	12
3	[Ph_2I]OTf instead of **2a**	36	199	--	0	--	50
4	PhI instead of **2a**	5	240	--	0	--	65
5	w/o $Pd(OAc)_2$	0	244	9	0	1	3
6	w/o **L1**	8	235	33	1	7	6
7	**L2-L10** instead of **L1**	listed below	--	--	--	--	--
8	w/o KTFA and TFA	13	128	73	0	10	9
9	w/o TFA	36	179	86	1	12	10
10	w/o KTFA	34	179	62	0	8	6
11	100 mol% HOTf instead of TFA	2	142	29	0	2	3
12	KOAc instead of KTFA	66	176	76	3	17	9
13	NaOAc instead of KTFA	59	167	72	3	16	8
14	HOAc instead of TFA	40	181	77	5	19	10
15	HFIP instead of TFA	43	195	82	2	16	10
16	w/o H_2O	47	176	71	7	15	11
17	N_2 instead of air	73	170	80	2	18	11
18	**1a**:**2a** = 1:1	48	47	68	0	15	10
19	**L2**	29	212	52	2	15	10
20	**L3**	22	212	58	1	13	12
21	**L4**	41	194	64	4	18	13
22	**L5**	47	187	66	3	17	9
23	**L6**	41	178	74	9	19	20
24	**L7**	60	164	81	4	20	15
25	**L8**	44	199	71	1	15	13
26	**L9**	42	173	71	7	18	20
27	**L10**	36	169	62	1	22	12



L2 (20 mol%) **L3** (20 mol%) **L4** (20 mol%) **L5** (10 mol%) **L6** (10 mol%) **L7** (10 mol%) **L8** (10 mol%) **L9** (10 mol%) **L10** (20 mol%)

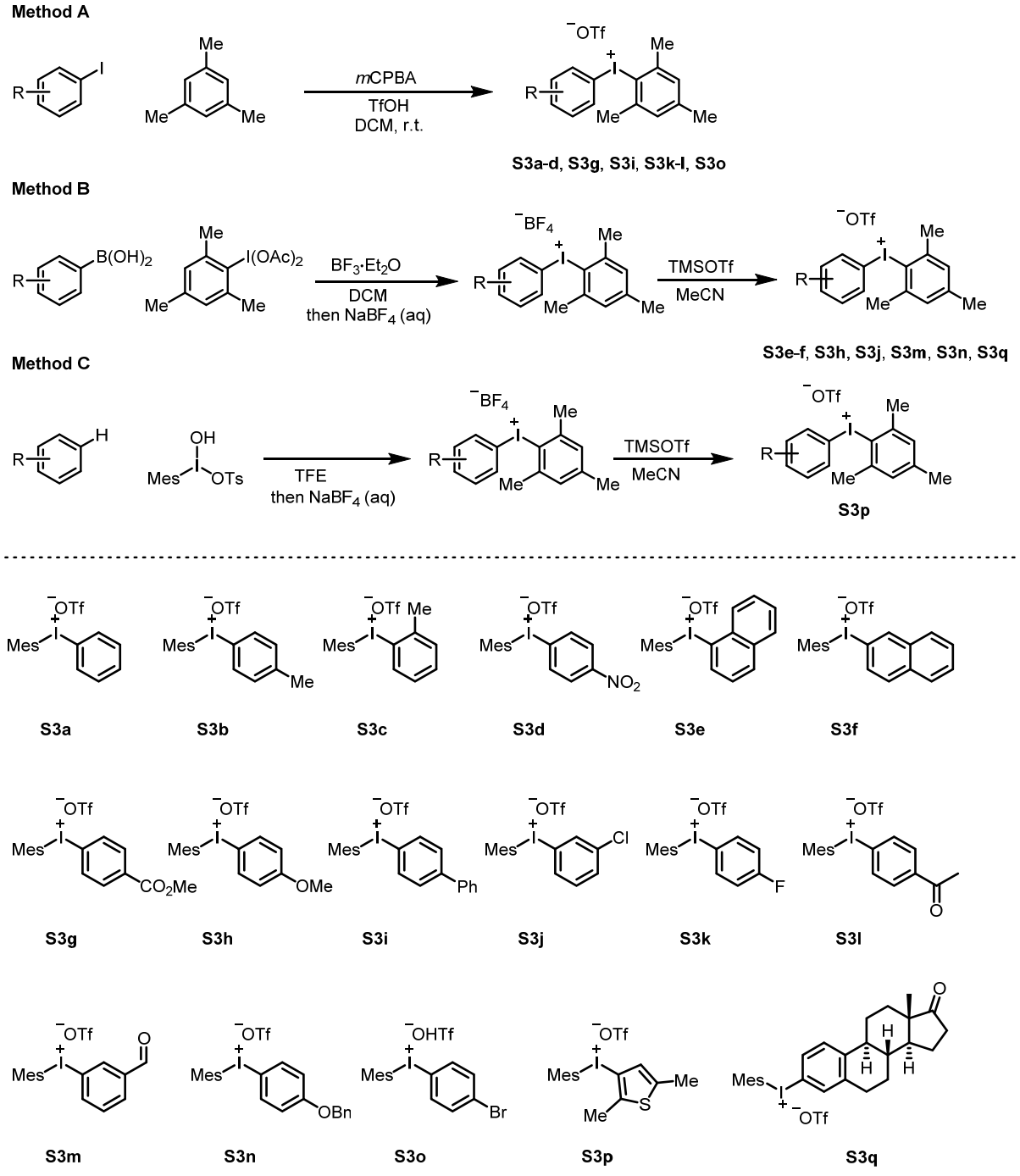
General Procedure for the β-Arylation of Ketones with Mesitylaryliodonium Salts



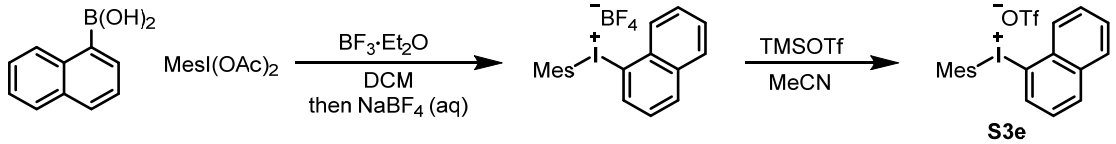
Unless stated otherwise, an 8 mL vial was charged with $Pd(OAc)_2$ (9.0 mg, 0.1 equiv.), KTFA (122 mg, 2.0 equiv.), Mesitylaryliodonium salt (0.4 mmol), **L1** (24 mg, 0.1 equiv.), TFA (200 µL), ketone (1.0 mmol, 2.5 equiv.), H_2O (100 µL) and 1,4-dioxane (2 mL). The vial was sealed with a PTFE lined cap and heated in a pie-block at 80 °C for 12 hours under stirring. Then, the vial was allowed to cool to room temperature and the mixture was filtered through a small plug of silica gel, eluted with diethyl ether. The solvent was then removed *in vacuo* and flash column chromatography (hexane/ethyl acetate or DCM/methanol) of the residue gave the arylation product.

II. Synthesis of mesitylaryliodonium salts

Iodonium salts **S3a-S3d**,[1] **S3f**,[2] **S3g**,[4] **S3h**,[3] **S3i**,[2] **S3k**,[1] **S3l**[1] and **S3o**[1] are known compounds and were synthesized according to the methods in literatures.[10] Procedures of synthesis and full characterization data were provided for previously unknown iodonium salts **S3e**, **S3j**, **S3m**, **S3n**, **S3p** and **S3q**.

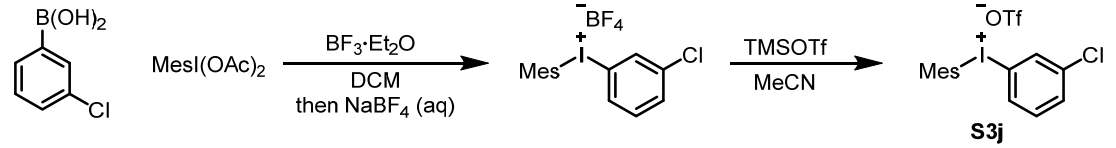


Scheme S1. Methods for the Synthesis of Mesitylaryliodonium Salts



S3e

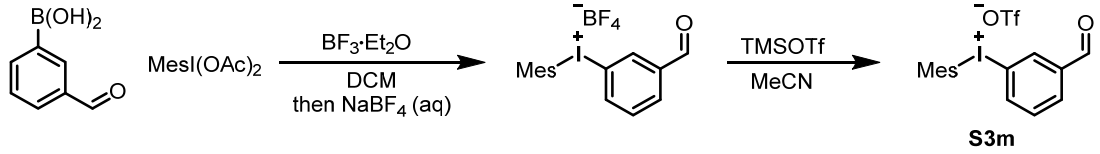
Mesityl(1-naphthyl)iodonium trifluoromethanesulfonate (S3e): A 250 mL round bottom flask was charged with naphthalene-1-boronic acid (860 mg, 5.0 mmol) and 50 mL DCM. The suspension was cooled to 0 °C using an ice bath. Boron trifluoride diethyl etherate (1.2 mL, 2.0 equiv.) was added to the mixture dropwise at 0 °C and the solution was stirred at the same temperature for 10 min. A solution of iodomesitylene diacetate (1.91 g, 1.05 equiv.) in 15 mL DCM was added to the flask dropwise at 0 °C. After the addition, the mixture was warmed to room temperature and stirred for 2 hr. The reaction was quenched by 100 mL saturated $NaBF_4$ solution and the bi-phase mixture was stirred vigorously for 30 min. The organic layer was separated and the aqueous extracted with DCM. The combined organic phase was washed with water and brine, dried and concentrated in vacuo. The residue was triturated with diethyl ether to give a white solid. The solid was filtered, washed with diethyl ether and dried to give mesityl(1-naphthyl)iodonium tetrafluoroborate (1.78 g, 77 % Yield). The tetrafluoroborate salt was dissolved in 20 mL acetonitrile and cooled to 0 °C. Trimethylsilyl trifluoromethanesulfonate (1.1 mL, 1.5 equiv.) was added to the solution dropwise at 0 °C. The mixture was warmed to room temperature and stirred overnight. The solvent was removed in vacuo and the residue triturated with diethyl ether. The suspension was stored at -20 °C for 2 hr and the solid was filtered and washed with diethyl ether to give mesityl(1-naphthyl)iodonium trifluoromethanesulfonate as a white solid (1.85 g, 92 % Yield). Mp. 175-177 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 (d, J = 8.0 Hz, 1H), 7.98-7.92 (m, 2H), 7.81-7.74 (m, 2H), 7.71-7.67 (m, 1H), 7.42 (t, J = 8.0 Hz, 1H), 7.10 (s, 2H), 2.65 (s, 6H), 2.35 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.62, 142.49, 135.11, 133.65, 133.31, 131.70, 130.74, 130.04, 129.46, 128.38, 127.54, 127.29, 120.88, 120.35 (q, $J_{C\text{-}F}$ = 319 Hz), 113.41, 27.23, 21.06. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -78.32. **IR** (KBr, cm^{-1}) 1499, 1450, 1249, 1161, 1030, 912, 741. **HRMS** calcd $C_{19}H_{18}I^+$ [M-CF_3SO_3]$^+$: 373.04480. Found: 373.04470.



S3j

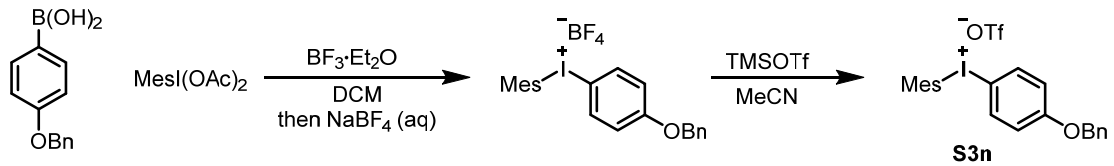
Mesityl(3-chlorophenyl)iodonium trifluoromethanesulfonate (S3j): A 250 mL round bottom flask was charged with 3-chlorophenylboronic acid (780 mg, 5.0 mmol) and 50 mL DCM. The suspension was cooled to 0 °C using an ice bath. Boron trifluoride diethyl etherate (1.2 mL, 2.0 equiv.) was added to the mixture dropwise at 0 °C and the solution was stirred at the same temperature for 10 min. A solution of iodomesitylene diacetate (1.91 g, 1.05 equiv.) in 15 mL DCM was added to the flask dropwise at 0 °C. After the addition, the mixture was warmed to room temperature and stirred for 2 hr. The reaction was quenched by 100 mL saturated $NaBF_4$ solution and the bi-phase mixture was stirred vigorously for 30 min. The organic layer was separated and the aqueous extracted with DCM. The combined organic phase was washed with water and brine, dried and concentrated in vacuo. The residue was triturated with diethyl ether to give a white solid. The solid was filtered, washed with diethyl ether and dried to give mesityl(3-chlorophenyl)iodonium tetrafluoroborate (1.18 g, 53 % Yield). The tetrafluoroborate salt was dissolved in 20 mL acetonitrile and cooled to 0 °C. Trimethylsilyl trifluoromethanesulfonate (0.8 mL, 1.5 equiv.) was added to the solution dropwise at 0 °C. The mixture was warmed to room temperature and stirred

overnight. The solvent was removed in vacuo and the residue triturated with diethyl ether. The suspension was stored at -20 °C for 2 hr and the solid was filtered and washed with diethyl ether to give mesityl(3-chlorophenyl)iodonium trifluoromethanesulfonate as a white solid (1.28 g, 95 % Yield). Mp. 187-189 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (ddd, J_1 = 8.1 Hz, J_2 = 1.8 Hz, J_3 = 0.9 Hz, 1H), 7.60 (t, J = 1.8 Hz, 1H), 7.46 (ddd, J_1 = 8.1 Hz, J_2 = 1.8 Hz, J_3 = 0.9 Hz, 1H), 7.31 (t, J = 8.1 Hz, 1H), 7.09 (s, 2H), 2.61 (s, 6H), 2.34 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.54, 142.47, 137.25, 132.61, 132.29, 132.02, 131.24, 130.36, 120.73, 120.09 (q, $J_{C\text{-}F}$ = 318 Hz), 111.60, 27.10, 21.14. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -78.45. **IR** (KBr, cm^{-1}) 1558, 1250, 1165, 1030, 913, 744. **HRMS** calcd $C_{15}H_{15}ClI^+$ $[M\text{-}CF_3SO_3]^+$: 356.99015. Found: 356.99000.



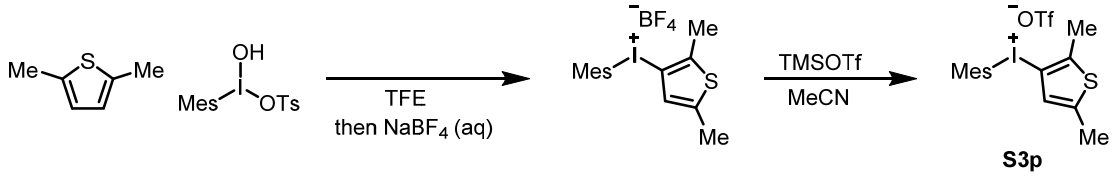
S3m

Mesityl(3-formylphenyl)iodonium trifluoromethanesulfonate (S3m): A 250 mL round bottom flask was charged with 3-formylphenylboronic acid (1.50 g, 10 mmol) and 100 mL DCM. The suspension was cooled to 0 °C using an ice bath. Boron trifluoride diethyl etherate (2.4 mL, 2.0 equiv.) was added to the mixture dropwise at 0 °C and the solution was stirred at the same temperature for 10 min. A solution of iodomesitylene diacetate (3.82 g, 1.05 equiv.) in 30 mL DCM was added to the flask dropwise at 0 °C. After the addition, the mixture was warmed to room temperature and stirred for 2 hr. The reaction was quenched by 150 mL saturated $NaBF_4$ solution and the bi-phase mixture was stirred vigorously for 30 min. The organic layer was separated and the aqueous extracted with DCM. The combined organic phase was washed with water and brine, dried and concentrated in vacuo. The residue was triturated with diethyl ether to give a white solid. The solid was filtered, washed with diethyl ether and dried to give mesityl(3-formylphenyl)iodonium tetrafluoroborate (2.50 g, 57 % Yield). The tetrafluoroborate salt was dissolved in 30 mL acetonitrile and cooled to 0 °C. Trimethylsilyl trifluoromethanesulfonate (1.6 mL, 1.5 equiv.) was added to the solution dropwise at 0 °C. The mixture was warmed to room temperature and stirred overnight. The solvent was removed in vacuo and the residue triturated with diethyl ether. The suspension was stored at -20 °C for 2 hr and the solid was filtered and washed with diethyl ether to give mesityl(3-formylphenyl)iodonium trifluoromethanesulfonate as a white solid (2.42 g, 85 % Yield). Mp. 147-149 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.93 (s, 1H), 8.20 (t, J = 1.6 Hz, 1H), 8.02-7.98 (m, 2H), 7.58 (t, J = 8.0 Hz, 1H), 7.11 (s, 2H), 2.64 (s, 6H), 2.36 (s, 3H). **^{13}C NMR** (100 MHz, DMSO) δ 192.60, 144.32, 142.66, 140.41, 139.40, 135.35, 133.58, 130.84, 123.52, 121.64 (q, $J_{C\text{-}F}$ = 320 Hz), 116.09, 27.31, 21.49. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -78.45. **IR** (KBr, cm^{-1}) 1708, 1701, 1588, 1451, 1271, 1241, 1187, 1029, 742. **HRMS** calcd $C_{16}H_{16}IO^+$ $[M\text{-}CF_3SO_3]^+$: 351.02400. Found: 351.02430.



S3n

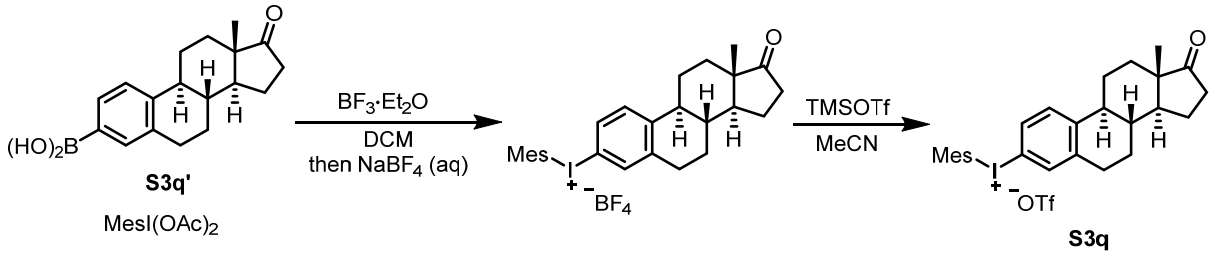
Mesityl(4-benzyloxyphenyl)iodonium trifluoromethanesulfonate (S3n): A 250 mL round bottom flask was charged with 4-benzyloxyphenylboronic acid (1.14 g, 5 mmol) and 50 mL DCM. The suspension was cooled to 0 °C using an ice bath. Boron trifluoride diethyl etherate (1.2 mL, 2.0 equiv.) was added to the mixture dropwise at 0 °C and the solution was stirred at the same temperature for 10 min. A solution of iodomesitylene diacetate (1.91 g, 1.05 equiv.) in 15 mL DCM was added to the flask dropwise at 0 °C. After the addition, the mixture was warmed to room temperature and stirred for 2 hr. The reaction was quenched by 100 mL saturated $NaBF_4$ solution and the bi-phase mixture was stirred vigorously for 30 min. The organic layer was separated and the aqueous extracted with DCM. The combined organic phase was washed with water and brine, dried and concentrated in vacuo. The residue was triturated with diethyl ether to give a white solid. The solid was filtered, washed with diethyl ether and dried to give mesityl(4-benzyloxyphenyl)iodonium tetrafluoroborate (2.12 g, 82 % Yield). The tetrafluoroborate salt was dissolved in 20 mL acetonitrile and cooled to 0 °C. Trimethylsilyl trifluoromethanesulfonate (1.1 mL, 1.5 equiv.) was added to the solution dropwise at 0 °C. The mixture was warmed to room temperature and stirred overnight. The solvent was removed in vacuo and the residue triturated with diethyl ether. The suspension was stored at -20 °C for 2 hr and the solid was filtered and washed with diethyl ether to give mesityl(4-benzyloxyphenyl)iodonium trifluoromethanesulfonate as a white solid (2.25 g, 95 % Yield). Mp. 166-169 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66-7.62 (m, 2H), 7.41-7.32 (m, 5H), 7.08 (s, 2H), 7.00-6.96 (m, 2H), 5.05 (s, 2H), 2.64 (s, 6H), 2.34 (s, 3H). **^{13}C NMR** (100 MHz, DMSO) δ 161.72, 143.81, 142.26, 137.53, 137.07, 130.62, 129.45, 129.06, 128.81, 124.05, 121.63 (q, J_{C-F} = 320 Hz), 119.21, 104.65, 70.61, 27.19, 21.44. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -78.34. **IR** (KBr, cm^{-1}) 1572, 1485, 1246, 1180, 913, 748. **HRMS** calcd $C_{22}H_{22}IO^+$ $[M\text{-}CF_3SO_3]^+$: 429.07100. Found: 429.07090.



S3p

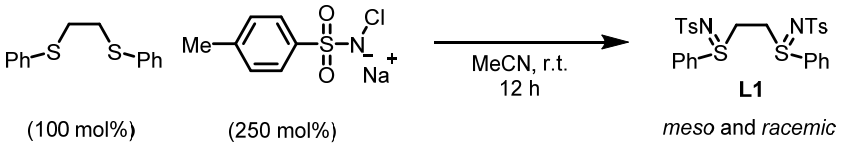
Mesityl(2,5-dimethylthiophen-3-yl)iodonium trifluoromethanesulfonate (S3p): To a stirring solution of 2,5-dimethylthiophene (1.12 g, 10 mmol) in 40 mL trifluoroethanol (TFE) was added (hydroxy(tosyloxy)iodo)mesitylene (4.34 g, 1.0 equiv.). The mixture was stirred at room temperature and monitored by TLC. After 2,5-dimethylthiophene was consumed, the reaction was quenched by 150 mL saturated $NaBF_4$ solution and the mixture was stirred vigorously for 30 min. The mixture was extracted with DCM. The combined organic phase was washed with water and brine, dried and concentrated in vacuo. The residue was triturated with diethyl ether to give a white solid. The solid was filtered, washed with diethyl ether and dried to give mesityl(2,5-dimethylthiophen-3-yl)iodonium tetrafluoroborate (1.20 g, 27 % Yield). The tetrafluoroborate salt was dissolved in 20 mL acetonitrile and cooled to 0 °C. Trimethylsilyl trifluoromethanesulfonate (0.8 mL, 1.5 equiv.) was added to the solution dropwise at 0 °C. The mixture was warmed to room temperature and stirred overnight. The solvent was removed in vacuo and the residue triturated with diethyl ether. The suspension was stored at -20 °C for 2 hr and the solid was filtered and washed with diethyl ether to give mesityl(2,5-dimethylthiophen-3-yl)iodonium trifluoromethanesulfonate as a off-white solid (700 mg, 51 % Yield). Mp. 219-221 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.07 (s, 2H), 6.64-6.63 (m, 1H), 2.65 (s, 6H), 2.59 (s, 3H), 2.41 (s, 3H), 2.34 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.47, 144.02, 142.29, 141.65, 130.41, 127.75, 121.70, 120.29 (q,

$J_{C\text{-}F}$ = 319 Hz), 94.68, 27.08, 21.02, 16.99, 15.42. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -78.36. **IR** (KBr, cm^{-1}) 1275, 1237, 1164, 1032, 913, 744. **HRMS** calcd $C_{15}H_{18}IS^+$ $[M\text{-}CF_3SO_3]^+$: 357.01680. Found: 357.01720.



S3q: A 250 mL round bottom flask was charged with boronic acid **S3q'** (1.67 g, 5.6 mmol)[5] and 50 mL DCM. The suspension was cooled to 0 °C using an ice bath. Boron trifluoride diethyl etherate (1.2 mL, 2.0 equiv.) was added to the mixture dropwise at 0 °C and the solution was stirred at the same temperature for 10 min. A solution of iodomesitylene diacetate (2.14 g, 1.05 equiv.) in 15 mL DCM was added to the flask dropwise at 0 °C. After the addition, the mixture was warmed to room temperature and stirred for 2 hr. The reaction was quenched by 100 mL saturated $NaBF_4$ solution and the bi-phase mixture was stirred vigorously for 30 min. The organic layer was separated and the aqueous extracted with DCM. The combined organic phase was washed with water and brine, dried and concentrated in vacuo. The residue was triturated with diethyl ether to give a white solid. The solid was filtered, washed with diethyl ether and dried to give tetrafluoroborate salt (1.53 g, 47 % Yield). The tetrafluoroborate salt was dissolved in 20 mL acetonitrile and cooled to 0 °C. Trimethylsilyl trifluoromethanesulfonate (0.75 mL, 1.5 equiv.) was added to the solution dropwise at 0 °C. The mixture was warmed to room temperature and stirred overnight. The solvent was removed in vacuo and the residue triturated with diethyl ether. The suspension was stored at -20 °C for 2 hr and the solid was filtered and washed with diethyl ether to give **S3q** as a white solid (1.43 g, 84 % Yield). Mp. 185-188 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.33-7.28 (m, 2H), 7.10 (s, 2H), 2.92-2.88 (m, 2H), 2.63 (s, 6H), 2.50 (dd, J_1 = 19 Hz, J_2 = 8.7 Hz, 1H), 2.35 (s, 3H), 2.33-2.26 (m, 2H), 2.19-1.94 (m, 4H), 1.67-1.37 (m, 6H), 0.88 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 220.16, 144.56, 144.33, 142.44, 141.96, 133.59, 130.32, 129.82, 129.45, 120.30 (q, $J_{C\text{-}F}$ = 320 Hz), 119.99, 108.45, 50.28, 47.73, 44.18, 37.33, 35.72, 31.34, 29.24, 27.17, 25.83, 25.34, 21.48, 21.10, 13.71. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -78.32. **IR** (KBr, cm^{-1}) 2931, 1736, 1250, 1162, 1028, 913, 743. **HRMS** calcd $C_{27}H_{32}IO^+$ $[M\text{-}CF_3SO_3]^+$: 499.14920. Found: 499.14900.

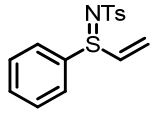
III. Synthesis and pyrolysis of ligand L1



To a stirred solution of 1,2-bis(phenylthio)ethane (5.0 g, 20.3 mmol) in 80 mL of acetonitrile was added Chloramine T trihydrate (14.3 g, 2.5 equiv.). The mixture was stirred overnight at room temperature and a large amount of white precipitate was observed. After the completion of the reaction, 120 mL of dichloromethane was added to the mixture. The white precipitate was filtered off and the solvent was removed in vacuo to give a white solid. The residue was dissolved in about 400 mL of acetone. Brief heat can be used to facilitate the dissolution, but the ligand may decompose under elevated temperature (the ligand pyrolysis proceeds in above 95% conversion within 30 min at 80 ^{o}C). After the majority of the solid was dissolved, the mixture was filtered to remove the insoluble impurities when hot (The filtration step is important since the insoluble impurities were observed to hamper the β-arylation reactions). The filtrate was allowed to cool to room temperature and stand for 1 day to crystalize. The small white crystals were filtered and washed with cold acetone to give a mixture of meso and racemic ligands (5.87 g, 49% Yield). Among the two diastereomers, the meso ligand has worse solubility than the racemic ligand. Thus both ligands can be isolated as pure diastereomers by collecting the early or late portion of the crystalized solids.

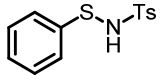
L1-meso: Mp. 165-168 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64-7.53 (m, 14H), 7.09 (d, *J* = 8.0 Hz, 4H), 3.37-3.22 (m, 4H), 2.30 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.09, 140.47, 132.97, 132.61, 130.29, 129.28, 126.12, 126.03, 46.17, 21.40. **IR** (KBr, cm^{-1}) 1305, 1293, 1145, 953, 913, 748. **HRMS** calcd $C_{28}H_{28}N_2NaO_4S_4^+$ $[M+Na]^+$: 607.08240. Found: 607.08230.

L1-racemic: Mp. 141-143 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86-7.84 (m, 4H), 7.79 (d, *J* = 8.0 Hz, 4H), 7.57-7.50 (m, 6H), 7.20 (d, *J* = 8.0 Hz, 4H), 3.92-3.83 (m, 2H), 3.32-3.22 (m, 2H), 2.34 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.19, 140.30, 132.55, 132.23, 130.11, 129.39, 126.28, 126.12, 49.78, 21.39. **IR** (KBr, cm^{-1}) 3061, 2924, 1597, 1446, 1283, 1143, 1088, 968, 913, 747. **HRMS** calcd $C_{28}H_{28}N_2NaO_4S_4^+$ $[M+Na]^+$: 607.08240. Found: 607.08230.



L11

***N*-Tosyl phenyl vinyl sulfilimine (L11)**: White solid. Mp. 109-112 °C. R_f = 0.5 (DCM/MeOH = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.65-7.63 (m, 2H), 7.56-7.47 (m, 3H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.43-6.37 (m, 1H), 6.32-6.28 (m, 1H), 6.05-6.02 (m, 1H), 2.35 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.73, 141.31, 134.64, 133.14, 132.56, 130.01, 129.17, 126.97, 126.22, 125.99, 21.40. **IR** (KBr, cm^{-1}) 3055, 2924, 1723, 1446, 1282, 1142, 1089, 966, 750. **HRMS** calcd $C_{15}H_{16}NO_2S_2$ $[M+H]^+$: 306.0622. Found: 306.0625.

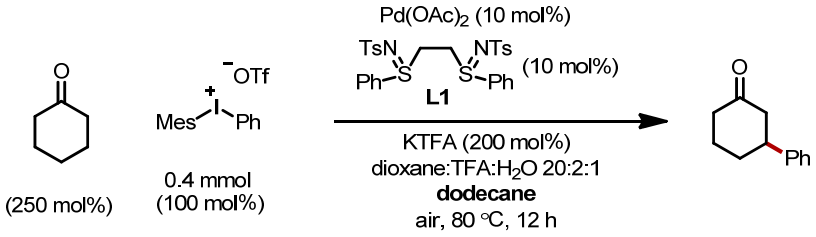


L12

***N*-Phenylsulfanyl tosylamine (L12)**: White solid. Mp. 101-104 °C. R_f = 0.6 (hexane/ethyl acetate = 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80-7.77 (m, 2H), 7.35-7.32 (m, 2H), 7.29-7.23 (m, 4H), 7.23-7.19 (m, 1H). 6.07-6.03 (m, 1H), 2.41 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.26, 137.23, 136.02, 129.62, 128.93, 127.72, 127.49, 126.11, 21.58. **IR** (KBr, cm^{-1}) 1597, 1366, 1293, 1161, 1090, 913, 874, 743. **HRMS** calcd $C_{13}H_{13}NO_2S_2$ $[M]^+$: 279.0388. Found: 279.0387.

IV. Details of mechanistic studies

General procedure for kinetic measurement



An 8 mL vial or 10 mL round-bottom flask was charged with $Pd(OAc)_2$ (9.0 mg, 0.1 equiv.), KTFA (122 mg, 2.0 equiv.), Mesitylphenyliodonium salt (189 mg, 0.4 mmol), **L1** (24 mg, 0.1 equiv.), TFA (200 µL), cyclohexanone (98 mg, 2.5 equiv.), H_2O (100 µL) and 1,4-dioxane (2 mL). Dodecane (~25 mg) was added to the reaction vial as the internal standard. The vial was sealed with a PTFE lined cap and heated in a pie-block at 80 °C (the round-bottom flask sealed with a rubber septum and heated in an oil-bath). Aliquots (~50 µL) were taken from the reaction mixture and directly passed through a small plug of silica gel (~400 mg), eluted with diethyl ether, to give ~10 mL solution. 1-2 mL of the solution was subsequently submitted to the gas chromatography.

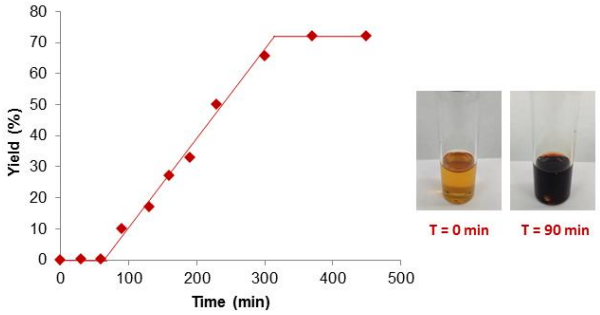


Figure S1. Kinetic Profile

General procedure for the hot filtration test

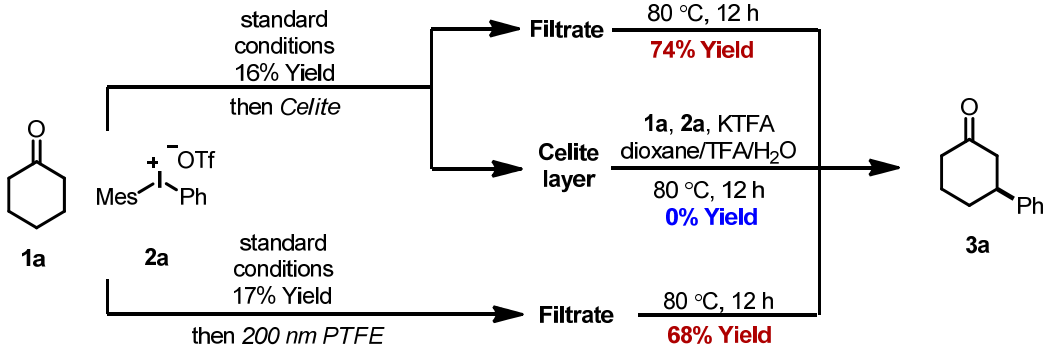


Figure S2. Hot Filtration Test

As the precipitation of palladium black was noted during and after the reaction, hot filtration tests were employed to distinguish between a soluble nanoparticle and a heterogeneous catalyst. Four parallel reactions were set up for the hot filtration test. To the 4 mL vial was charged with $Pd(OAc)_2$ (4.5 mg, 0.1 equiv.), KTFA (61 mg, 2.0 equiv.), Mesitylphenyliodonium salt (95 mg, 0.2 mmol), **L1** (12 mg, 0.1 equiv.), TFA (100 μL), cyclohexanone (49 mg, 2.5 equiv.), H_2O (50 μL) and 1,4-dioxane (1 mL). Dodecane (~10 mg) was added to the reaction vial as the internal standard. The vial was sealed with a PTFE lined cap, heated in a pie-block at 80 °C, and monitored by gas chromatography when necessary.

Vial 1: This reaction was set up as the control reaction. The mixture was monitored at 90 min and 12 h using gas chromatography and the yields calculated.

Vial 2: This reaction was set up as the control reaction to investigate the effect of Celite on the reaction. The reaction was set up as described above. The mixture was monitored, and 100 mg Celite was added to the reaction at 90 min. The resulting mixture was kept stirring at 80 °C and monitored by gas chromatography at 12 h.

Vial 3: This reaction was set up as described above. The mixture was monitored at 90 min and 100 mg Celite was added to the reaction. After stirring for 1 min, the mixture was passed through a small plug of Celite (~100 mg) to a new vial (**Vial 3a**) when hot and the Celite plug was rinsed with ~200 μL of dioxane. The heat was restored to the new vial and reaction monitored at 110 min and 12 h. The remaining Celite layer was added to a new vial (**Vial 3b**) containing KTFA (61 mg, 2.0 equiv.), Mesitylphenyliodonium salt (95 mg, 0.2 mmol), TFA (100 μL), cyclohexanone (49 mg, 2.5 equiv.), H_2O (50 μL) and 1,4-dioxane (1 mL). The new vial was heated at 80 °C and monitored by gas chromatography at 110 min and 12 h.

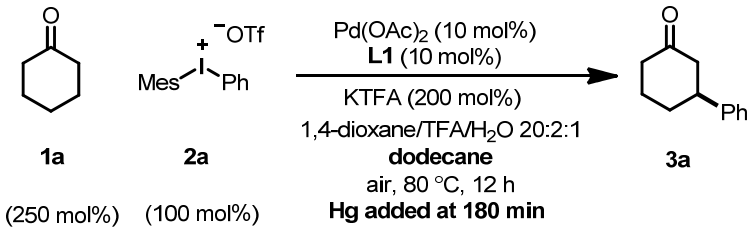
Vial 4: This reaction was set up as described above. The mixture was monitored at 90 min and quickly passed through a PTFE 200 nm filter to a new vial when hot and the filter was rinsed with ~200 μL of dioxane. The heat was restored to the new vial and reaction monitored at 110 min and 12 h.

The yields obtained for different vials at different time point were summarized below. *These results suggested that the active palladium catalyst generated during the induction period sustained the solubility, and those heterogeneous species were not responsible for the transformation.*

Table S2. Results of Hot Filtration Test

Yield (%)	Before filtration	After filtration	
	90 min	100 min	12 h
Vial 1	18	--	76
Vial 2	19	--	74
Vial 3a	16	22	74
Vial 3b		0	0
Vial 4	17	22	68

General procedure for the mercury poisoning test



A supplementary mercury poisoning test was also executed to support the presence of palladium nanoparticles. Molecular mercury is known to inhibit noble metal-nanoparticle-catalyzed reactions through amalgamation. An 8 mL vial was charged with $Pd(OAc)_2$ (9.0 mg, 0.1 equiv.), KTFA (122 mg, 2.0 equiv.), Mesitylphenyliodonium salt (189 mg, 0.4 mmol), **L1** (24 mg, 0.1 equiv.), TFA (200 µL), cyclohexanone (98 mg, 2.5 equiv.), H_2O (100 µL) and 1,4-dioxane (2 mL). Dodecane (~25 mg) was added to the reaction vial as the internal standard. The vial was sealed with a PTFE lined cap and heated in a pie-block at 80 °C. Aliquots (~50 µL) were taken from the reaction mixture and directly passed through a small plug of silica gel (~400 mg), eluted with diethyl ether, to give ~10 mL solution. 1-2 mL of the solution was subsequently submitted to the gas chromatography. When the product formation initiated and the yield reached ~40%, 200 µL of mercury was added to the mixture via syringe. The resulting mixture was heated at 80 °C and monitored by gas chromatography. *The kinetic data showed the product formation was inhibited with the addition of mercury.*

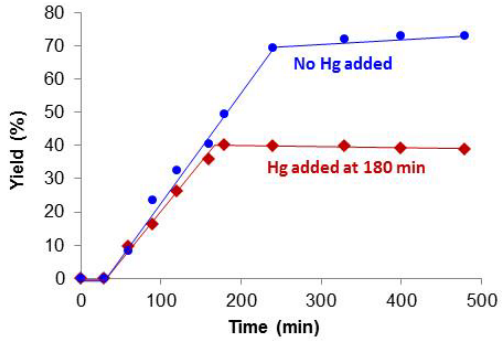
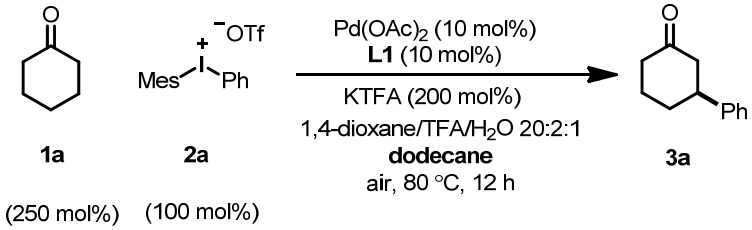


Figure S3. Mercury Poisoning Test

General procedure for dynamic light scattering (DLS) experiment



An 4 mL vial was charged with $Pd(OAc)_2$ (4.5 mg, 0.1 equiv.), KTFA (61 mg, 2.0 equiv.), Mesitylphenyliodonium salt (95 mg, 0.2 mmol), **L1** (12 mg, 0.1 equiv.), TFA (100 µL), cyclohexanone (49 mg, 2.5 equiv.), H_2O (50 µL) and 1,4-dioxane (1 mL). Dodecane (~10 mg) was added to the reaction vial as the internal standard. The vial was sealed with a PTFE lined cap and heated in a pie-block at 80 °C. After the reaction has proceeded for 90 min, the

mixture was allowed to cool to room temperature, and gas chromatography was used to confirm that the product formation had initiated. Subsequently, the reaction solution was directly used for the dynamic light scattering analysis using a Zetasizer Nano ZS instrument. The data was collected at 25 ^{o}C and the medium parameters were set according to the properties of 1,4-dioxane (dispersant refractive index: 1.420, viscosity: 1.1944 mPa•s).

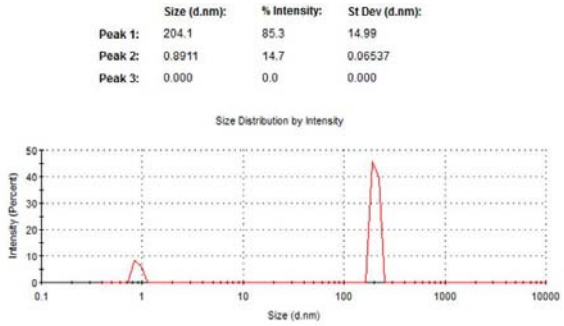
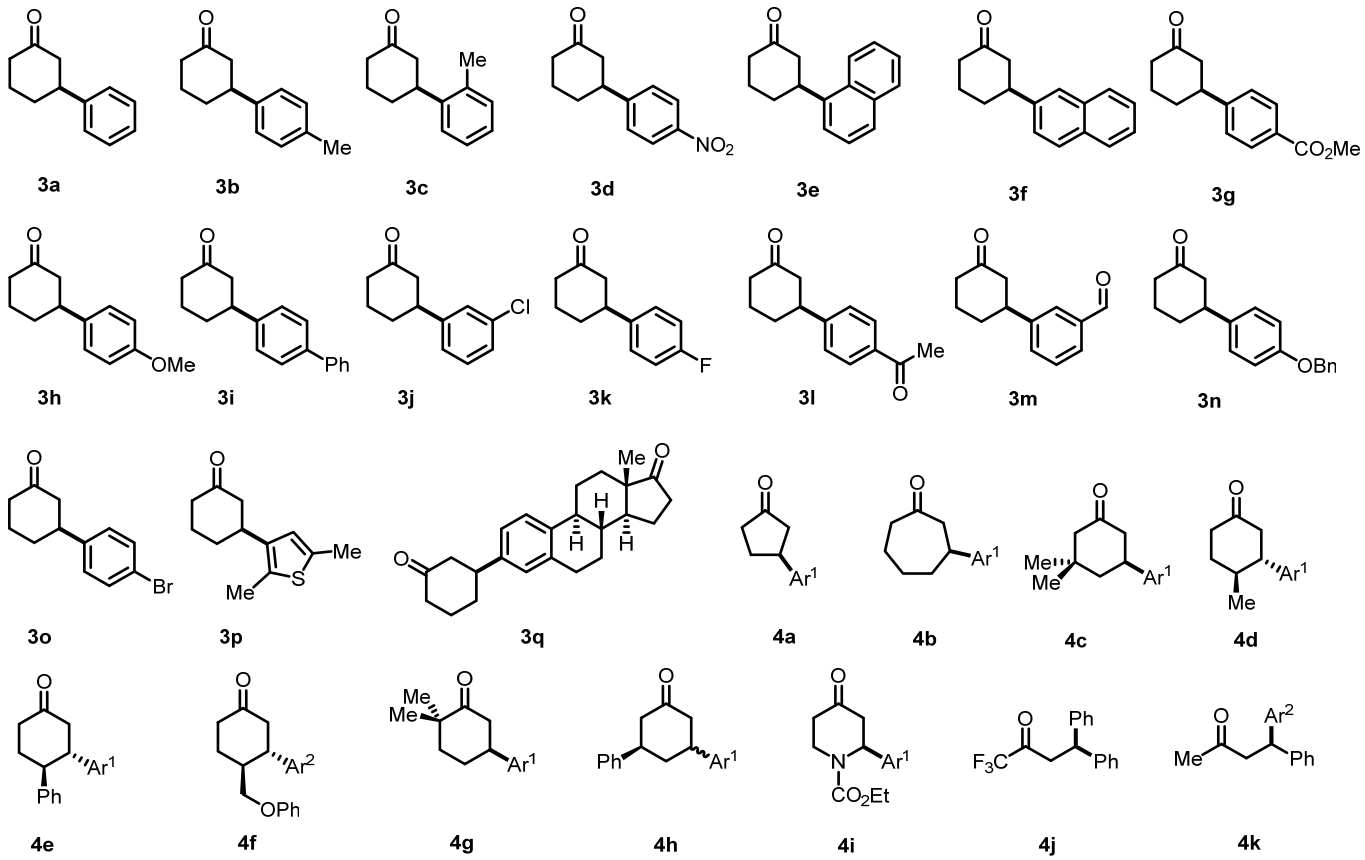


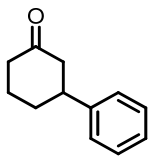
Figure S4. Dynamic Light Scattering Data

V. Characterization of products

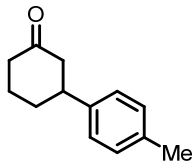
Products **3a-3l**, **4i-k** are known from previous literatures. ^{1}H-NMR and data and spectra, as well as MS data are provided for them. Full characterization data are provided for all the other products.



Scheme S2. β-Arylation Products (Ar^1=*p*-PhC_6H_4, Ar^2=*p*-AcC_6H_4)

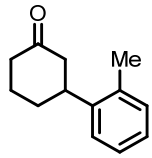


3-Phenylcyclohexan-1-one (3a):[5] 66 % Yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36-7.21 (m, 2H), 7.26-7.22 (m, 3H), 3.06-2.98 (m, 1H), 2.60 (ddt, J_1 = 14.0 Hz, J_2 = 4.6 Hz, J_3 = 1.9 Hz, 1H), 2.53 (dd, J_1 = 12.3 Hz, J_2 = 1.1 Hz, 1H), 2.51-2.44 (m, 1H), 2.43-2.35 (m, 1H), 2.19-2.07 (m, 2H), 1.91-1.73 (m, 2H). **EI-MS** (*m/z*, relative intensity): 174 (M^+, 90), 131 (80), 117 (100), 104 (78), 91 (50), 78 (40).



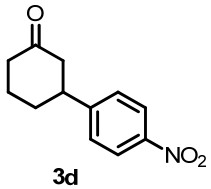
3b

3-(*p*-Tolyl)cyclohexan-1-one (3b): [5] 69 % Yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.16-7.09 (m, 4H), 3.02-2.94 (m, 1H), 2.57 (ddt, J_1 = 10.6 Hz, J_2 = 4.6 Hz, J_3 = 1.9 Hz, 1H), 2.55-2.28 (m, 3H), 2.33 (s, 3H), 2.17-2.25 (m, 2H), 1.89-1.72 (m, 2H). **EI-MS** (*m/z*, relative intensity): 188 (M^+, 65), 145 (40), 131 (100), 118 (46), 105 (20), 91 (30).



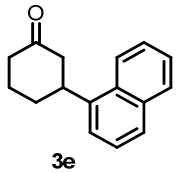
3c

3-(*o*-Tolyl)cyclohexan-1-one (3c): [5] 62 % Yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25-7.12 (m, 4H), 3.26-3.19 (m, 1H), 2.53-2.37 (m, 4H), 2.33 (s, 3H), 2.22-2.15 (m, 1H), 2.05-2.00 (m, 1H), 1.90-1.76 (m, 2H). **EI-MS** (*m/z*, relative intensity): 188 (M^+, 70), 145 (100), 131 (90), 117 (75), 105 (30), 91 (50).



3d

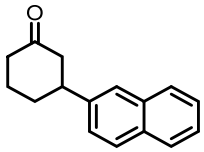
3-(4-Nitrophenyl)cyclohexan-1-one (3d): [5] 49 % Yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (d, J = 8.8 Hz, 2H), 7.39 (d, J = 8.8 Hz, 2H), 3.12 (tt, J_1 = 11.7 Hz, J_2 = 3.9 Hz, 1H), 2.64-2.37 (m, 4H), 2.21-2.10 (m, 2H), 1.94-1.70 (m, 2H). **EI-MS** (*m/z*, relative intensity): 219 (M^+, 90), 176 (100), 163 (30), 115 (25), 91 (20), 77 (23).



3e

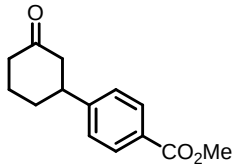
3-(Naphthalen-1-yl)cyclohexan-1-one (3e): [5] 64 % Yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.4 Hz, 1H), 7.90-7.87 (m, 1H), 7.77 (d, J = 8.4 Hz, 1H), 7.56-7.46 (m, 3H), 7.40 (d, J = 7.2 Hz, 1H), 3.87 (ddd, J_1 = 11.7 Hz, J_2 = 7.2 Hz, J_3 = 3.6 Hz 1H), 2.81-2.77 (m, 1H), 2.71-2.65 (m, 1H), 2.61-2.55 (m, 1H), 2.52-2.44 (m, 1H),

2.29-2.18 (m, 2H), 2.06-1.85 (m, 2H). **EI-MS** (*m/z*, relative intensity): 224 (M^+, 85), 181 (25), 167 (100), 153 (70), 141 (30), 128 (20).



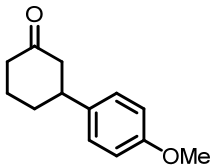
3f

3-(Naphthalen-2-yl)cyclohexan-1-one (3f): [6] 70 % Yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83-7.81 (m, 3H), 7.65 (d, J = 1.3 Hz, 1H), 7.50-7.43 (m, 2H), 7.37 (dd, J_1 = 8.6 Hz, J_2 = 1.8 Hz, 1H), 3.19 (tdd, J_1 = 11.4 Hz, J_2 = 5.2 Hz, J_3 = 3.3 Hz 1H), 2.72-2.61 (m, 2H), 2.51 (dqd, J_1 = 14.3 Hz, J_2 = 3.2 Hz, J_3 = 1.6 Hz, 1H), 2.47-2.33 (m, 1H), 2.22-2.16 (m, 2H), 2.06-1.92 (m, 1H), 1.89-1.77 (m, 1H). **EI-MS** (*m/z*, relative intensity): 224 (M^+, 90), 181 (33), 167 (100), 154 (60), 141 (45), 128 (30), 115 (21).



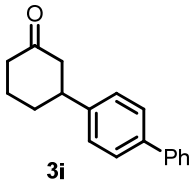
3g

Methyl 4-(3-oxocyclohexyl)benzoate (3g): [5] 60 % Yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.0 Hz, 2H). 7.28 (d, J = 8.0 Hz, 2H), 3.90 (s, 3H), 3.10-3.03 (m, 1H), 2.59 (ddt, J_1 = 14.1 Hz, J_2 = 4.9 Hz, J_3 = 1.9 Hz, 1H), 2.57-2.53 (m, 1H), 2.52-2.45 (m, 1H), 2.44-2.35 (m, 1H), 2.19-2.07 (m, 2H), 1.91-1.73 (m, 2H). **EI-MS** (*m/z*, relative intensity): 232 (M^+, 95), 201 (52), 189 (75), 145 (71), 131 (100), 91 (33), 77 (40).



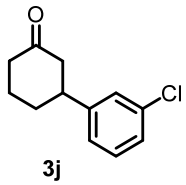
3h

3-(4-Methoxyphenyl)cyclohexan-1-one (3h): [5] 60 % Yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.16-7.12 (m, 2H), 6.89-6.85 (m, 2H), 3.80 (s, 3H), 2.95 (tt, J_1 = 11.7 Hz, J_2 = 4.0 Hz, 1H), 2.59 (ddt, J_1 = 14.0 Hz, J_2 = 4.2 Hz, J_3 = 1.9 Hz, 1H), 2.53-2.33 (m, 3H), 2.18-2.05 (m, 2H), 1.87-1.71 (m, 2H). **EI-MS** (*m/z*, relative intensity): 204 (M^+, 55), 161 (30), 147 (100), 134 (35), 91 (30), 77 (20).



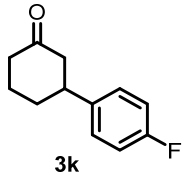
3i

3-([1,1'-Biphenyl]-4-yl)cyclohexan-1-one (3i): [5] 74 % Yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61-7.56 (m, 4H), 7.47-7.43 (m, 2H), 7.34 (ddt, J_1 = 6.6 Hz, J_2 = 5.2 Hz, J_3 = 1.3 Hz, 1H), 7.32-7.30 (m, 2H), 3.12-3.04 (m, 1H), 2.69-2.64 (m, 1H), 2.62-2.55 (m, 1H), 2.54-2.35 (m, 2H), 2.22-2.12 (m, 2H), 1.95-1.76 (m, 2H). **EI-MS** (*m/z*, relative intensity): 250 (M^+, 98), 207 (25), 193 (100), 178 (72), 165 (48), 152 (35), 115 (20).



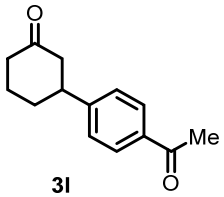
3j

3-(3-Chlorophenyl)cyclohexan-1-one (3j): [5] 62 % Yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28-7.20 (m, 3H), 7.07 (dt, J_1 = 7.4 Hz, J_2 = 1.3 Hz, 1H), 2.99 (tt, J_1 = 11.9 Hz, J_2 = 3.9 Hz, 1H), 2.62-2.56 (m, 1H), 2.53-2.27 (m, 3H), 2.19-2.13 (m, 1H), 2.10-2.06 (m, 1H), 1.88-1.71 (m, 2H). **EI-MS** (*m/z*, relative intensity): 208 (M^+, 85), 165 (100), 151 (46), 138 (60), 115 (50), 103 (52), 77 (33).



3k

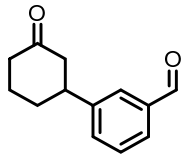
3-(4-Fluorophenyl)cyclohexan-1-one (3k): [5] 66 % Yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19-7.16 (m, 2H), 7.03-6.99 (m, 2H), 3.00 (tt, J_1 = 11.8 Hz, J_2 = 3.9 Hz, 1H), 2.57 (ddt, J_1 = 13.9 Hz, J_2 = 4.2 Hz, J_3 = 2.0 Hz, 1H), 2.52-2.33 (m, 3H), 2.17-2.04 (m, 2H), 1.87-1.71 (m, 2H). **EI-MS** (*m/z*, relative intensity): 192 (M^+, 60), 149 (40), 135 (100), 122 (70), 109 (35), 96 (30), 70 (20).



3l

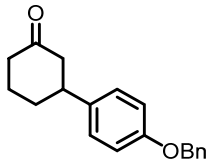
3-(4-Acetylphenyl)cyclohexan-1-one (3l): [5] 53 % Yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94-7.91 (m, 2H), 7.33-7.30 (m, 2H), 3.12-3.04 (m, 1H), 2.64-2.50 (m, 2H), 2.47 (dqd, J_1 = 11.0 Hz, J_2 = 3.3 Hz, J_3 = 1.7 Hz, 1H), 2.42-

2.32 (m, 1H), 2.59 (s, 3H), 2.20-2.13 (m, 1H), 2.12-2.07 (m, 1H), 1.93-1.74 (m, 2H). **EI-MS** (*m/z*, relative intensity): 216 (M^+, 40), 201 (100), 173 (20), 145 (20), 131 (40), 115 (20), 77 (20).



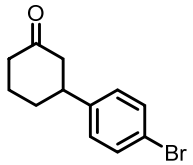
3m

3-(3-Oxocyclohexyl)benzaldehyde (3m): 50 % Yield. Colorless oil. R_f = 0.5 (Hex/EA = 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.01 (s, 1H), 7.76-7.73 (m, 2H), 7.50-7.49 (m, 2H), 3.13-3.05 (m, 1H), 2.64-2.45 (m, 3H), 2.43-2.35 (m, 1H), 2.22-2.14 (m, 1H), 2.13-2.08 (m, 1H), 1.94-1.74 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 210.22, 192.20, 145.34, 136.76, 132.94, 129.39, 128.70, 127.08, 48.59, 44.37, 41.04, 32.56, 25.39. **IR** (KBr, cm^{-1}) 2939, 2868, 1700, 1602, 1448, 1255, 1144, 913, 743. **HRMS** calcd $C_{13}H_{14}O_2$ $[M]^+$: 202.0994. Found: 202.0995.



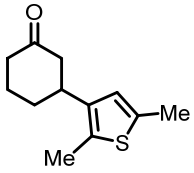
3n

3-(4-(Benzyloxy)phenyl)cyclohexan-1-one (3n): 46 % Yield. White solid. Mp. 96-98 °C. R_f = 0.4 (Hex/EA = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45-7.31 (m, 5H), 7.16-7.13 (m, 2H), 6.97-6.93 (m, 2H), 5.05 (s, 2H), 2.97 (tt, J_1 = 11.8 Hz, J_2 = 3.9 Hz, 1H), 2.61-2.56 (ddt, J_1 = 13.9 Hz, J_2 = 4.2 Hz, J_3 = 1.9 Hz, 1H), 2.53-2.44 (m, 2H), 2.41-2.33 (m, 1H), 2.17-2.11 (m, 1H), 2.09-2.05 (m, 1H), 1.87-1.71 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 211.39, 157.47, 136.98, 136.79, 128.56, 127.94, 127.49, 127.44, 114.91, 70.03, 49.19, 43.96, 41.15, 32.95, 25.47. **IR** (KBr, cm^{-1}) 3033, 2932, 2868, 1710, 1512, 1244, 913, 743. **HRMS** calcd $C_{19}H_{20}O_2$ $[M]^+$: 280.1463. Found: 280.1459.



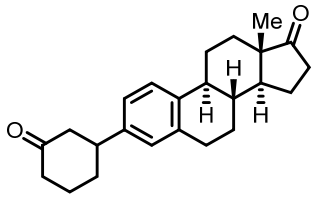
3o

3-(4-Bromophenyl)cyclohexan-1-one (3o):[9] 60 % Yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46-7.43 (m, 2H), 7.11-7.07 (m, 2H), 2.98 (tt, J_1 = 11.7 Hz, J_2 = 3.9 Hz, 1H), 2.61-2.56 (m, 1H), 2.52-2.45 (m, 2H), 2.42-2.34 (m, 1H), 2.18-2.12 (m, 1H), 2.08-2.04 (m, 1H), 1.90-1.70 (m, 2H). **EI-MS** (*m/z*, relative intensity): 252 (M^+, 75), 254 (75), 209 (50), 211 (50), 195 (60), 197 (50), 182 (60), 184 (60), 116 (100), 103 (50), 77 (60).



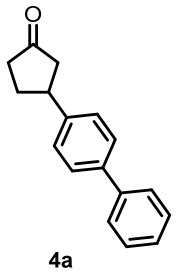
3p

3-(2,5-Dimethylthiophen-3-yl)cyclohexan-1-one (3p): 50 % Yield. Yellow oil. R_f = 0.4 (Hex/EA = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.54 (s, 1H), 3.04-2.96 (m, 1H), 2.46-2.31 (m, 4H), 2.40-2.39 (m, 3H), 2.28 (s, 3H), 2.16-2.10 (m, 1H), 1.98-1.93 (m, 1H), 1.79-1.68 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 211.01, 139.62, 135.88, 130.12, 123.61, 48.61, 41.25, 38.23, 32.19, 25.60, 15.22, 12.60. **IR** (KBr, cm^{-1}) 2937, 2863, 1713, 1447, 1221, 1145, 913, 742. **HRMS** calcd $C_{12}H_{16}OS$ $[M]^+$: 208.0922. Found: 208.0923.



3q

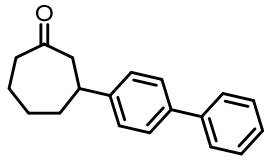
(8R,9S,13S,14S)-13-methyl-3-(3-oxocyclohexyl)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (3q): 51 % Yield as a mixture of two diastereomers. White solid. Mp. 115-117 °C. R_f = 0.3 (Hex/EA = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 (d, J = 8.0 Hz, 1H), 7.03-7.01 (m, 1H), 6.96 (s, 1H), 2.98-2.90 (m, 3H), 2.61-2.26 (m, 7H), 2.20-1.94 (m, 6H), 1.89-1.72 (m, 2H), 1.68-1.40 (m, 6H), 0.91 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 221.02, 211.35, 141.85, 138.14, 136.73, 127.23, 127.20, 125.66, 123.96, 123.92, 50.44, 48.97, 48.95, 47.98, 44.32, 44.28, 41.17, 38.11, 35.83, 32.80, 31.54, 29.45, 26.49, 25.65, 25.59, 21.55, 13.82. **IR** (KBr, cm^{-1}) 2931, 2863, 1738, 1712, 1454, 1256, 1222, 1007, 913, 734. **HRMS** calcd $C_{24}H_{31}O_2$ $[M+H]^+$: 351.2324. Found: 351.2321.



4a

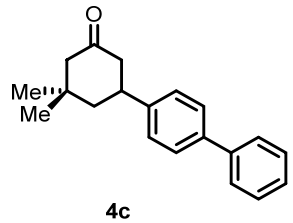
(3-([1,1'-Biphenyl]-4-yl)cyclopentan-1-one (4a): 53 % Yield. White solid. Mp. 120-122 °C. R_f = 0.5 (Hex/EA = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59-7.57 (m, 4H), 7.47-7.43 (m, 2H), 7.37-7.33 (m, 3H), 3.46 (ddd, J_1 = 18.0 Hz, J_2 = 11.1 Hz, J_3 = 7.1 Hz, 1H), 2.72 (dd, J_1 = 18.3 Hz, J_2 = 7.3 Hz, 1H,) 2.54-2.43 (m, 2H), 2.43-2.29 (m, 2H), 2.10-1.98 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 218.37, 142.07, 140.69, 139.72, 128.76, 127.37, 127.24,

127.14, 126.99, 45.81, 41.91, 38.88, 31.22. **IR** (KBr, cm^{-1}) 3031, 2975, 2895, 1737, 1488, 1403, 1135, 912, 843, 774. **HRMS** calcd $C_{17}H_{16}O$ $[M]^+$: 236.1201. Found: 236.1204.



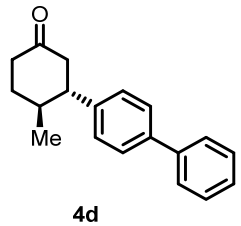
4b

3-([1,1'-Biphenyl]-4-yl)cycloheptan-1-one (4b): 66 % Yield. White solid. Mp. 130-132 °C. R_f = 0.4 (Hex/EA = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59-7.52 (m, 4H), 7.45-7.41 (m, 2H), 7.35-7.31 (m, 1H), 7.27-7.25 (m, 2H). 2.98-2.92 (m, 2H), 2.73-2.60 (m, 3H), 2.15-1.98 (m, 3H), 1.83-1.69 (m, 2H), 1.57-1.48 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 213.43, 145.95, 140.80, 139.30, 128.72, 127.35, 127.14, 126.98, 126.83, 51.21, 43.96, 42.40, 39.19, 29.23, 24.17. **IR** (KBr, cm^{-1}) 2932, 2869, 1692, 1395, 1142, 913, 744. **HRMS** calcd $C_{19}H_{20}O$ $[M]^+$: 264.1514. Found: 264.1513.



4c

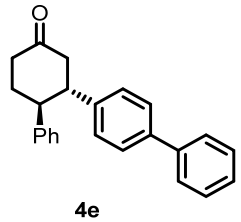
5-([1,1'-Biphenyl]-4-yl)-3,3-dimethylcyclohexan-1-one (4c): 50% Yield. Colorless oil. R_f = 0.5 (Hex/EA = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60-7.56 (m, 4H), 7.46-7.42 (m, 2H), 7.37-7.31 (m, 3H), 3.21 (tt, J_1 = 12.4 Hz, J_2 = 4.5 Hz, 1H) 2.62-2.57 (m, 1H), 2.52-2.45 (m, 1H), 2.37-2.33 (m, 1H), 2.21 (dt, J_1 = 13.5 Hz, J_2 = 2.1 Hz, 1H), 1.92-1.80 (m, 2H), 1.15 (s, 3H), 1.04 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 211.01, 143.22, 140.72, 139.70, 128.74, 127.40, 127.21, 127.07, 127.00, 54.31, 48.15, 46.37, 40.04, 35.46, 32.17, 25.72. **IR** (KBr, cm^{-1}) 3028, 2957, 2869, 1710, 1487, 1142, 913, 762, 743. **HRMS** calcd $C_{20}H_{22}O$ $[M]^+$: 278.1671. Found: 278.1663.



4d

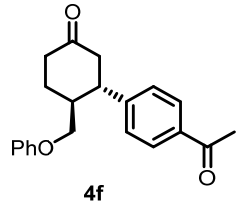
3-([1,1'-Biphenyl]-4-yl)-4-methylcyclohexan-1-one (4d): 70% Yield. The relative stereochemistry was determined by X-ray crystallography. White solid. Mp. 107-109 °C. R_f = 0.5 (Hex/EA = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61-7.55 (m, 4H), 7.46-7.42 (m, 2H), 7.37-7.33 (m, 1H), 7.26-7.24 (m, 2H), 2.62-2.46 (m, 5H), 2.21-2.05 (m, 2H), 1.62-1.52 (m, 1H), 0.83 (d, J = 6.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 210.92, 142.65, 140.72,

139.60, 128.73, 127.61, 127.38, 127.18, 126.96, 51.73, 49.09, 41.38, 36.74, 34.59, 19.32. **IR** (KBr, cm^{-1}) 3028, 2955, 2870, 1714, 1467, 1143, 913, 765, 743. **HRMS** calcd $C_{19}H_{20}O$ $[M]^+$: 264.1514. Found: 264.1510.



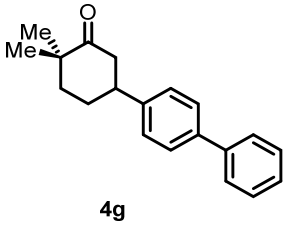
4e

3-([1,1'-Biphenyl]-4-yl)-4-phenylcyclohexan-1-one (4e): 56% Yield. The relative stereochemistry was determined by X-ray crystallography. White solid. Mp. 132-134 °C. R_f = 0.3 (Hex/EA = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49-7.46 (m, 2H), 7.38-7.34 (m, 4H), 7.29-7.25 (m, 1H), 7.15-7.11 (m, 2H), 7.08-7.03 (m, 5H), 3.31-3.19 (m, 2H), 2.79-2.56 (m, 4H), 2.34-2.27 (m, 1H), 2.14-2.04 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 210.12, 142.77, 141.66, 140.57, 139.16, 128.64, 128.30, 127.63, 127.45, 127.09, 126.99, 126.84, 126.38, 50.23, 49.39, 49.18, 41.57, 34.49. **IR** (KBr, cm^{-1}) 3028, 2928, 2870, 1716, 1487, 1142, 913, 742. **HRMS** calcd $C_{24}H_{22}O$ $[M]^+$: 326.1671. Found: 326.1668.



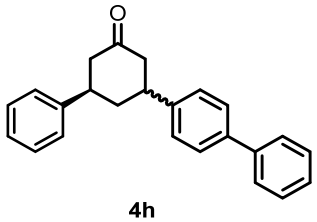
4f

3-(4-Acetylphenyl)-4-(phenoxymethyl)cyclohexan-1-one (4f): 70% Yield. The relative stereochemistry was determined by coupling constants. Yellow oil. R_f = 0.3 (Hex/EA = 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90-7.88 (m, 2H), 7.32-7.30 (m, 2H), 7.22-7.18 (m, 2H), 6.91-6.87 (m, 1H), 6.72-6.68 (m, 2H), 3.72 (dd, J_1 = 9.3 Hz, J_2 = 2.8 Hz, 1H), 3.54 (dd, J_1 = 9.3 Hz, J_2 = 6.1 Hz, 1H), 3.14 (ddd, J_1 = 12.6 Hz, J_2 = 11.5 Hz, J_3 = 4.5 Hz, 1H), 2.68-2.53 (m, 4H), 2.56 (s, 3H), 2.48-2.33 (m, 2H), 1.97-1.86 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 209.51, 197.61, 158.54, 147.76, 136.11, 129.40, 129.08, 127.41, 120.89, 114.26, 68.77, 48.19, 46.31, 41.73, 40.66, 29.19, 26.59. **IR** (KBr, cm^{-1}) 2923, 1716, 1682, 1606, 1496, 1269, 1245, 756. **HRMS** calcd $C_{21}H_{22}O_3Na$ $[M+Na]^+$: 345.14610. Found: 345.14620.



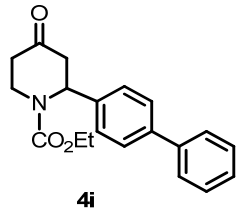
4g

5-([1,1'-Biphenyl]-4-yl)-2,2-dimethylcyclohexan-1-one (4g): 40% Yield. White solid. Mp. 118-121 °C. R_f = 0.7 (Hex/EA = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60-7.55 (m, 4H), 7.46-7.42 (m, 2H), 7.36-7.30 (m, 3H), 3.08-3.00 (m, 1H), 2.81 (dd, J_1 = 14.0 Hz, J_2 = 12.9 Hz, 1H), 2.54 (ddd, J_1 = 14.0 Hz, J_2 = 4.3 Hz, J_3 = 2.0 Hz, 1H), 2.14-2.03 (m, 1H), 2.00-1.94 (m, 1H), 1.88 (dt, J_1 = 13.8 Hz, J_2 = 3.6 Hz, 1H), 1.76-1.69 (m, 1H), 1.28 (s, 3H), 1.14 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 215.00, 143.45, 140.77, 139.61, 128.74, 127.35, 127.19, 127.01, 126.96, 45.18, 44.97, 44.55, 39.85, 29.23, 25.16, 25.15. **IR** (KBr, cm^{-1}) 3028, 2965, 2929, 1707, 1487, 1143, 913, 764, 742. **HRMS** calcd $C_{20}H_{22}O$ $[M]^+$: 278.1671. Found: 278.1673.



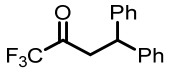
4h

3-([1,1'-Biphenyl]-4-yl)-5-phenylcyclohexan-1-one (4h): 32% Yield as a single diastereomer. Attempts to determine the relative stereochemistry (*cis* or *trans*) were unsuccessful. Colorless oil. R_f = 0.5 (Hex/EA = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59-7.53 (m, 4H), 7.46-7.42 (m, 2H), 7.36-7.31 (m, 3H), 7.27-7.20 (m, 5H), 3.42-3.34 (m, 2H), 2.83-2.71 (m, 4H), 2.38 (t, J = 5.9 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 211.20, 143.77, 142.84, 140.66, 139.47, 128.75, 128.62, 127.42, 127.28, 127.22, 127.00, 126.98, 126.57, 46.62, 46.55, 39.40, 38.86, 38.56. **IR** (KBr, cm^{-1}) 3028, 2923, 1710, 1487, 1275, 913, 764, 748. **HRMS** calcd $C_{24}H_{22}O$ $[M]^+$: 326.1671. Found: 326.1672.



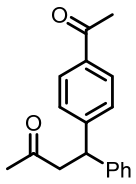
4i

Ethyl 2-([1,1'-biphenyl]-4-yl)-4-oxopiperidine-1-carboxylate (4i):[6] 61% Yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56-7.53 (m, 4H), 7.44-7.40 (m, 2H), 7.35-7.31 (m, 3H), 5.86 (br, 1H), 4.30-4.21 (m, 3H), 3.22-3.15 (m, 1H), 3.04-2.99 (m, 1H), 2.88 (dd, J_1 = 15.5 Hz, J_2 = 7.0 Hz, 1H), 2.59-2.51 (m, 1H), 2.41-2.35 (m, 1H), 1.30 (t, J = 7.1 Hz, 3H). **HRMS** calcd $C_{20}H_{22}NO_3$ $[M+H]^+$: 324.15940. Found: 324.15950.



4j

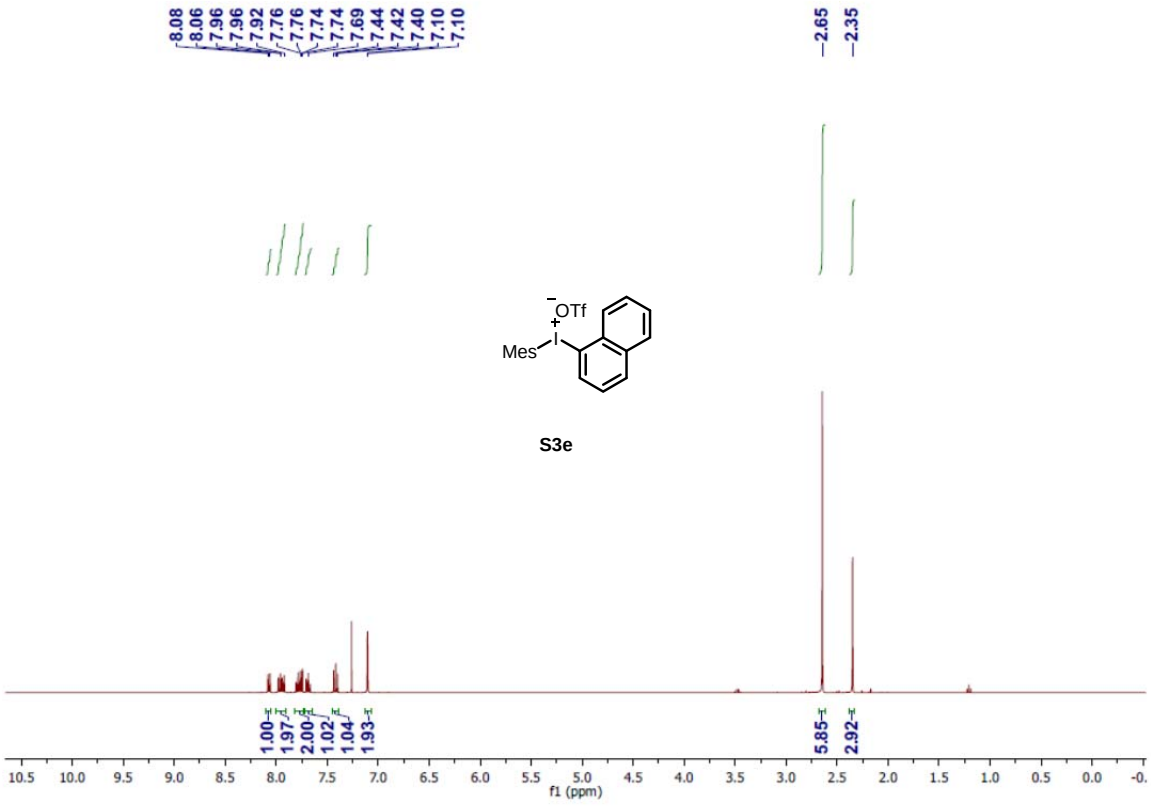
1,1,1-Trifluoro-4,4-diphenylbutan-2-one (4j):[7] 50% Yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31-7.26 (m, 4H), 7.23-7.18 (m, 6H), 4.65 (t, J = 7.5 Hz, 1H), 3.48 (dd, J_1 = 7.5 Hz, J_2 = 0.5 Hz, 2H). **EI-MS** (*m/z*, relative intensity): 278 (M^+, 50), 209 (30), 167 (100), 152 (40), 103 (20), 77 (20).



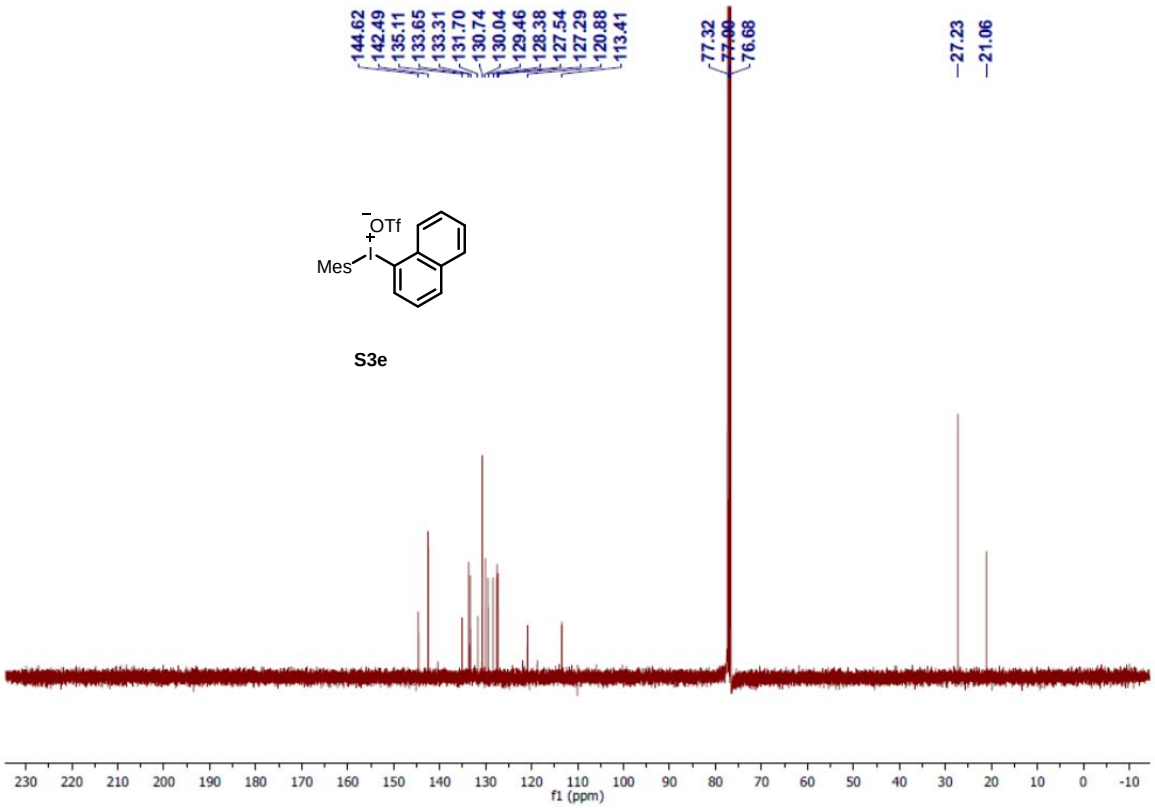
4k

4-(4-Acetylphenyl)-4-phenylbutan-2-one (4k):[8] 38% Yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87-7.84 (m, 2H), 7.32-7.25 (m, 4H), 7.20-7.16 (m, 3H), 4.64 (t, J = 7.5 Hz, 1H), 3.20 (d, J = 7.5 Hz, 2H), 2.54 (s, 3H), 2.09 (s, 3H). **EI-MS** (*m/z*, relative intensity): 266 (M^+, 100), 251 (30), 223 (80), 209 (90), 165 (80).

VI. ^{1}H- and ^{13}C-NMR spectra


8.08
8.06
7.96
7.96
7.92
7.76
7.76
7.74
7.74
7.69
7.44
7.42
7.40
7.10
7.10
2.65
2.35
OTf
Mes
1.00
1.97
2.00
1.02
1.04
1.93
5.85
2.92
f1 (ppm)

S3e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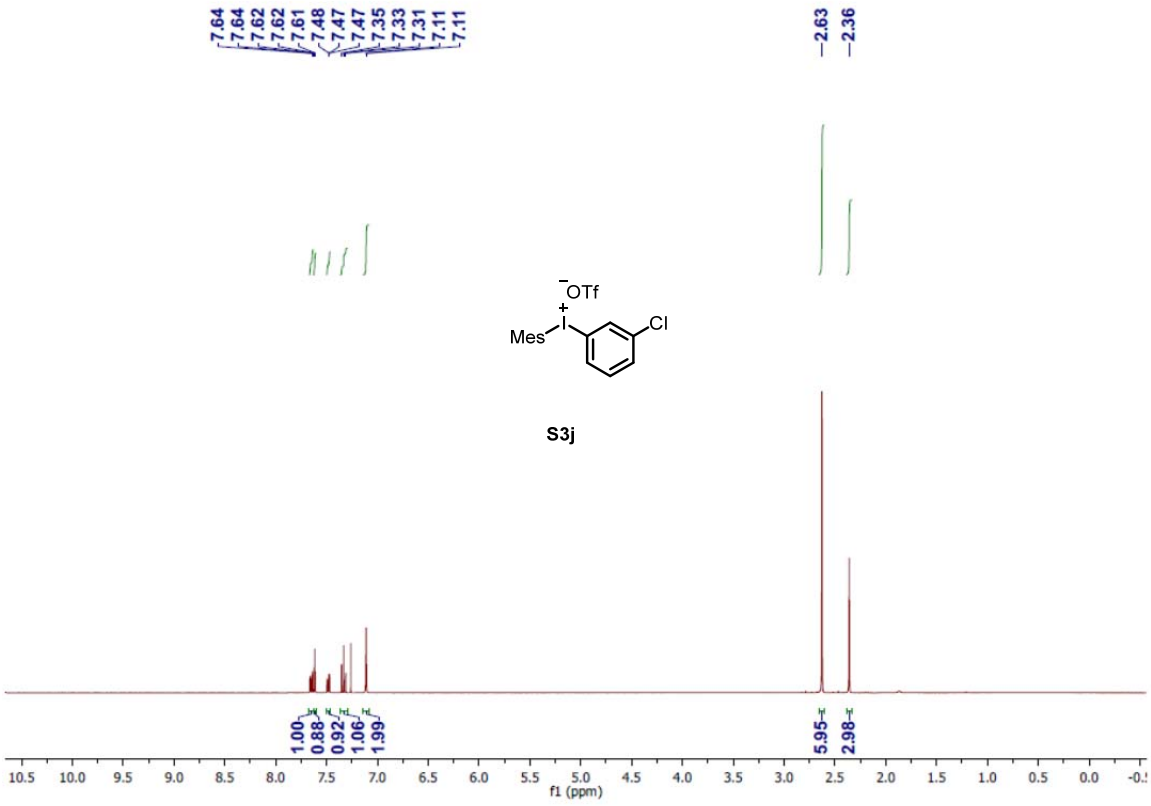
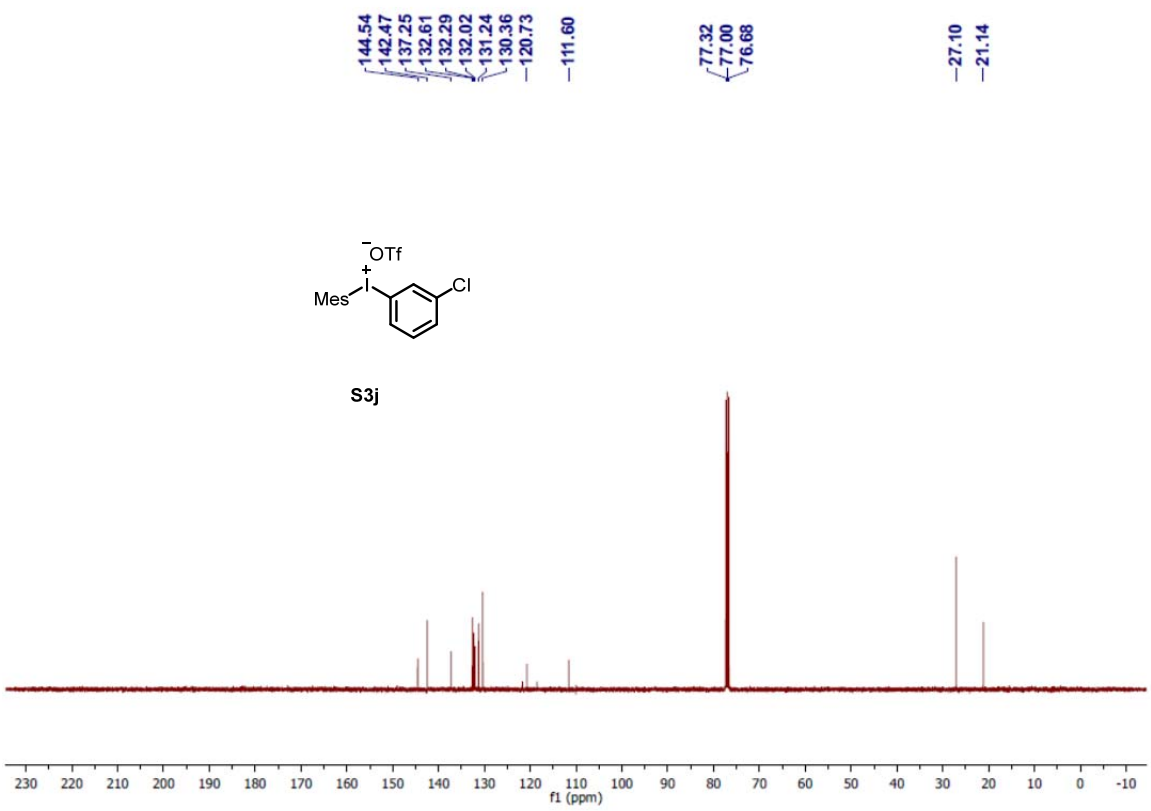
142.49
135.11
133.65
133.31
131.70
130.74
130.04
129.46
128.38
127.54
127.29
120.88
113.41
77.32
77.00
76.68
27.23
21.06
OTf
Mes
f1 (ppm)

S3e


7.64
7.64
7.62
7.62
7.61
7.48
7.47
7.47
7.35
7.33
7.31
7.11
7.11
2.63
2.36
OTf
Mes
I
Cl
1.00
0.88
0.92
1.06
1.99
5.95
2.98
f1 (ppm)

S3j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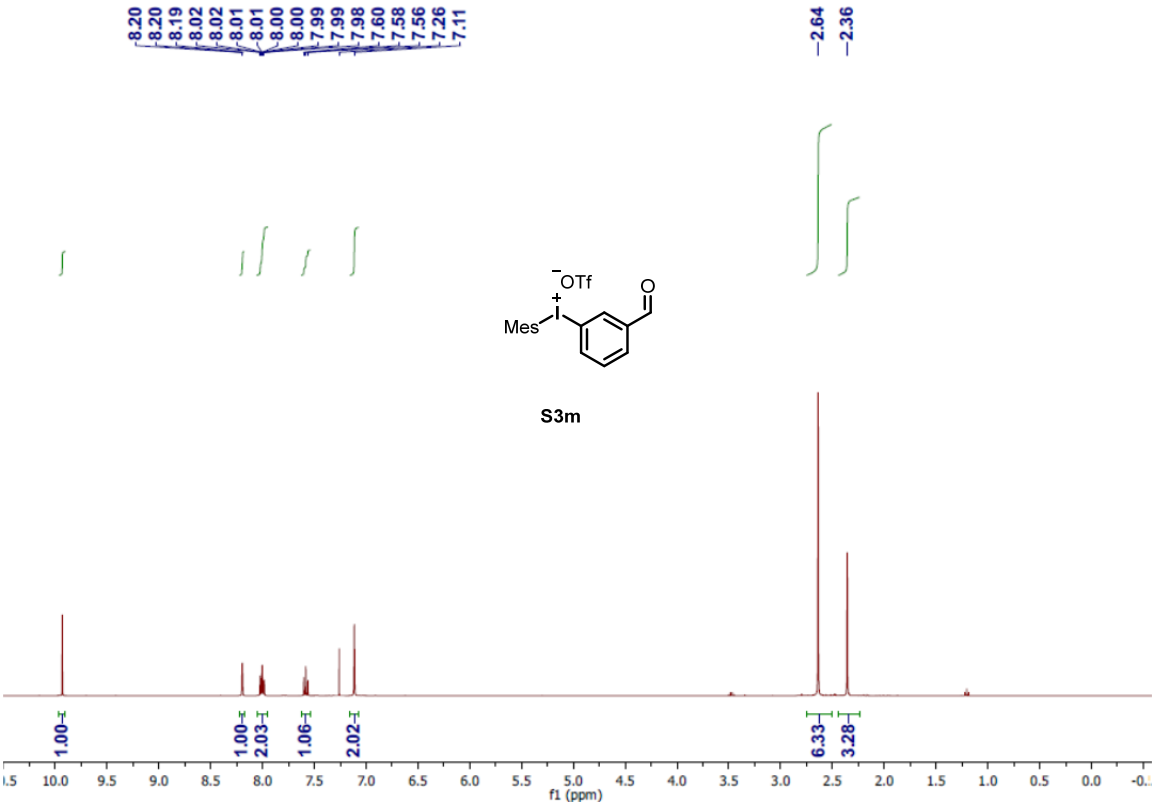
137.25
132.61
132.29
132.02
131.24
130.36
120.73
111.60
77.32
77.00
76.68
27.10
21.14
OTf
Mes
I
Cl
f1 (ppm)

S3j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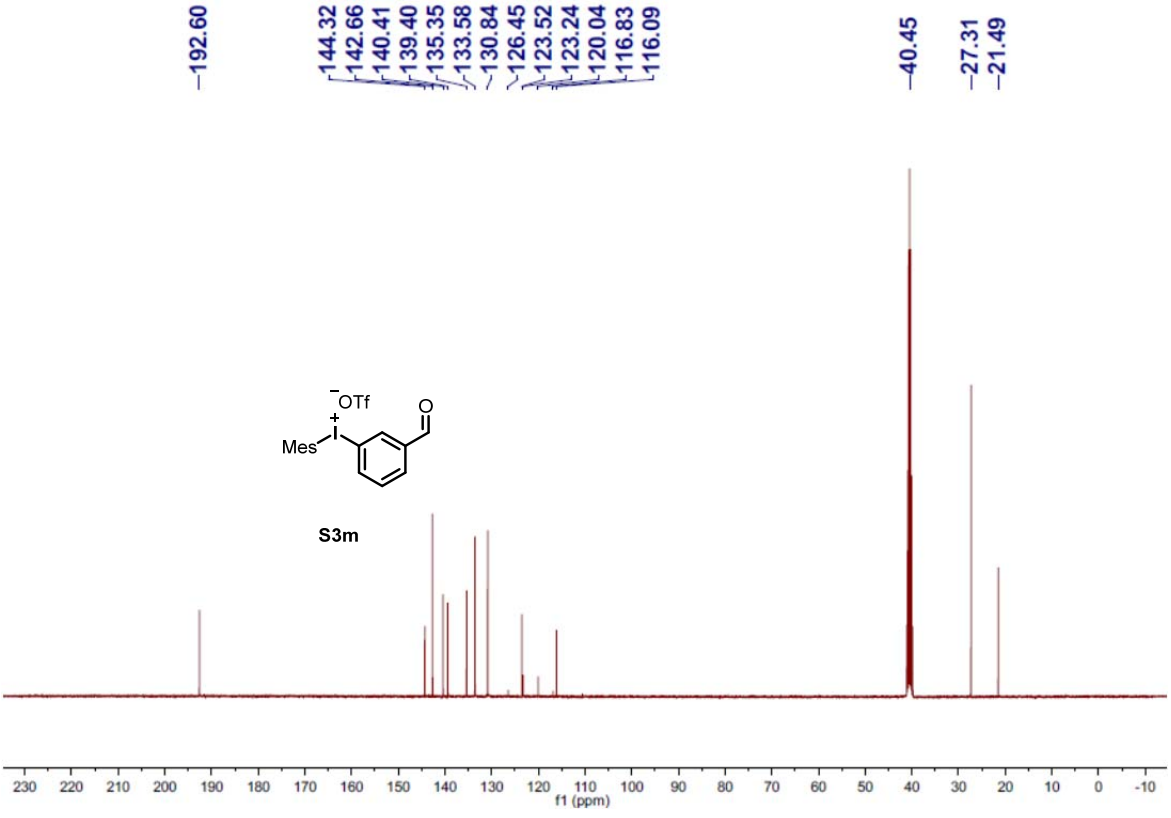
8.20
8.19
8.02
8.02
8.01
8.01
8.00
8.00
7.99
7.99
7.98
7.60
7.58
7.56
7.26
7.11
2.64
2.36
OTf
O
Mes
I
+
1.00
1.00
2.03
1.06
2.02
6.33
3.28
f1 (ppm)

S3m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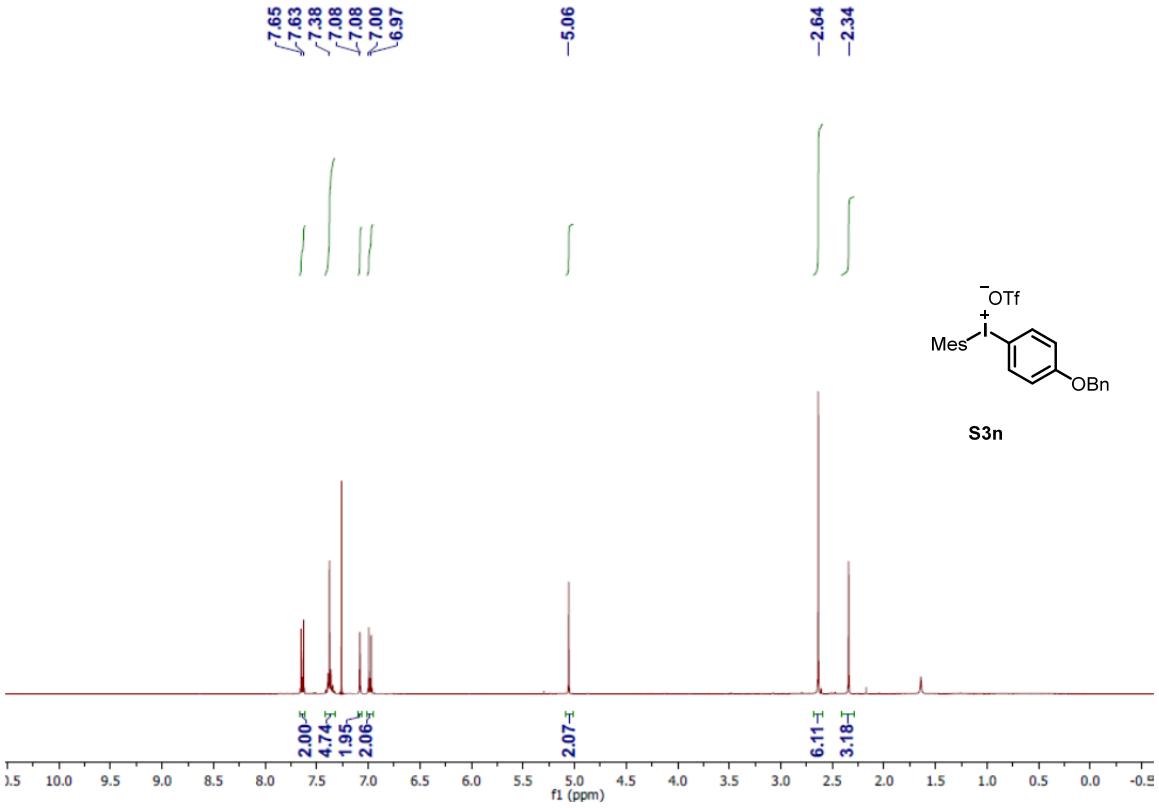
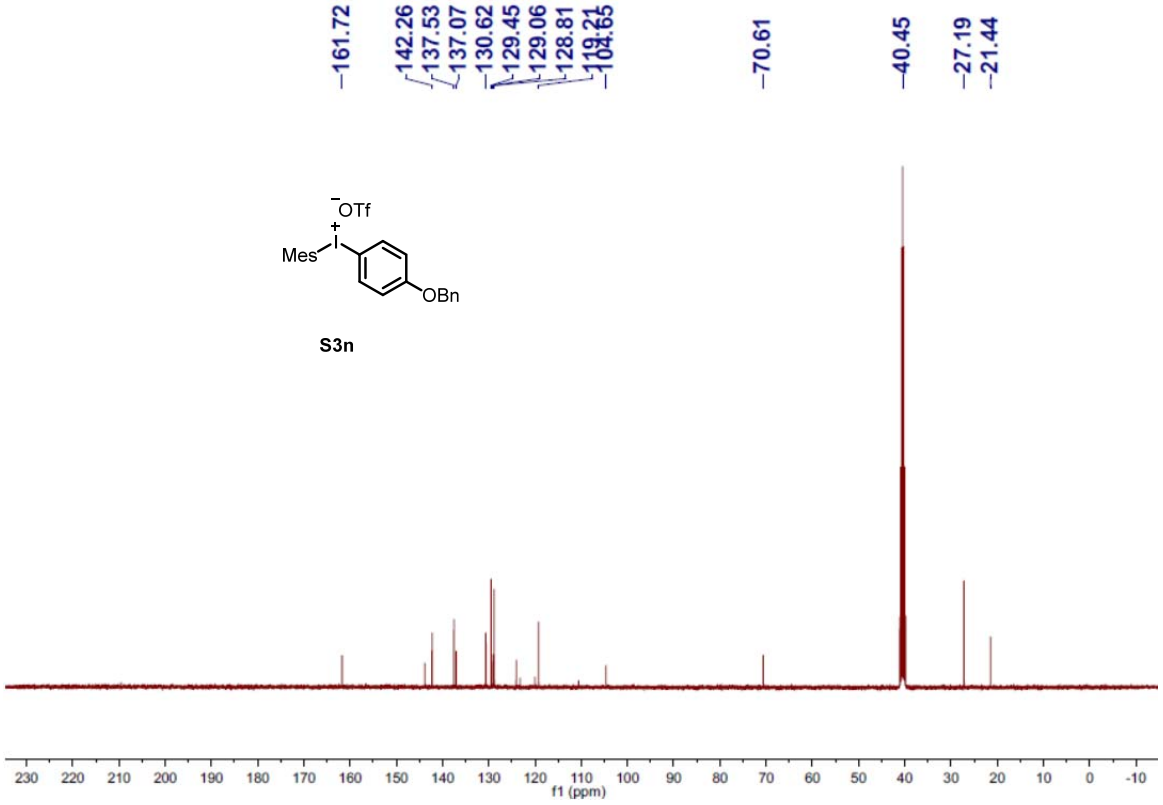
144.32
142.66
140.41
139.40
135.35
133.58
130.84
126.45
123.52
123.24
120.04
116.83
116.09
40.45
27.31
21.49
OTf
O
Mes
I
+
f1 (ppm)

S3m


7.65
7.63
7.38
7.08
7.08
7.00
6.97
5.06
2.64
2.34
OTf
Mes
OBn
2.00
4.74
1.95
2.06
2.07
6.11
3.18
f1 (ppm)

S3n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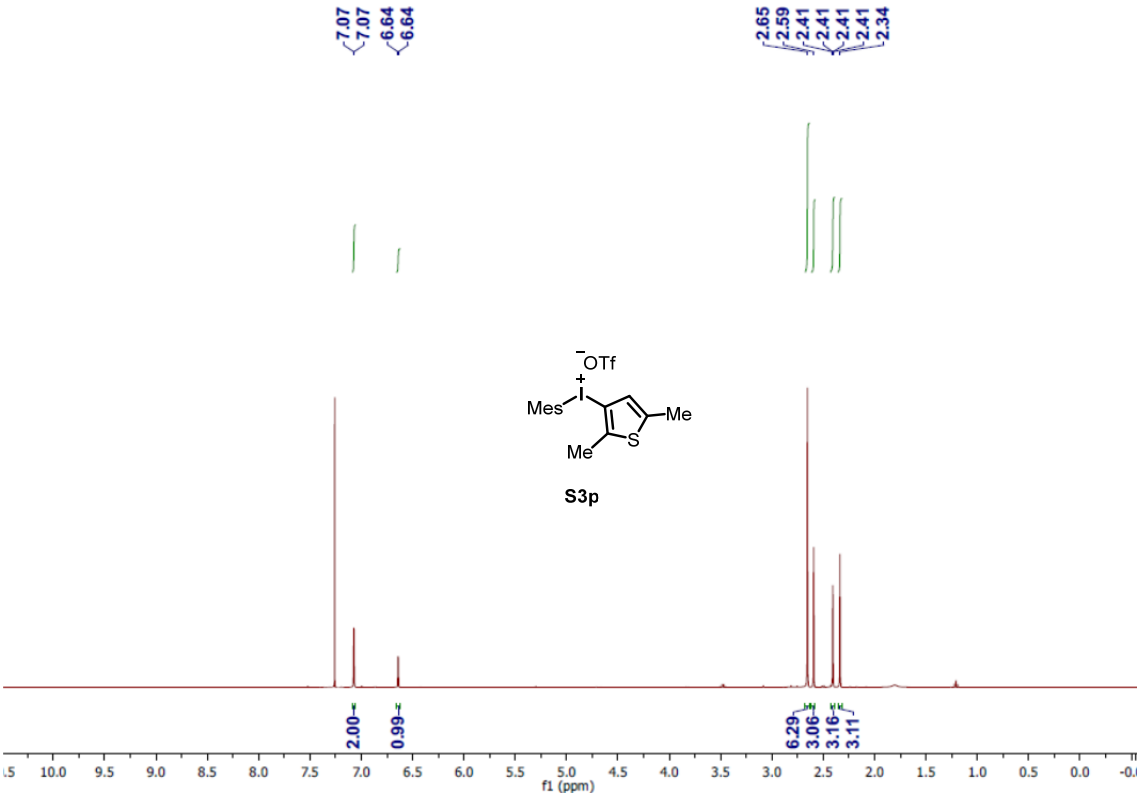
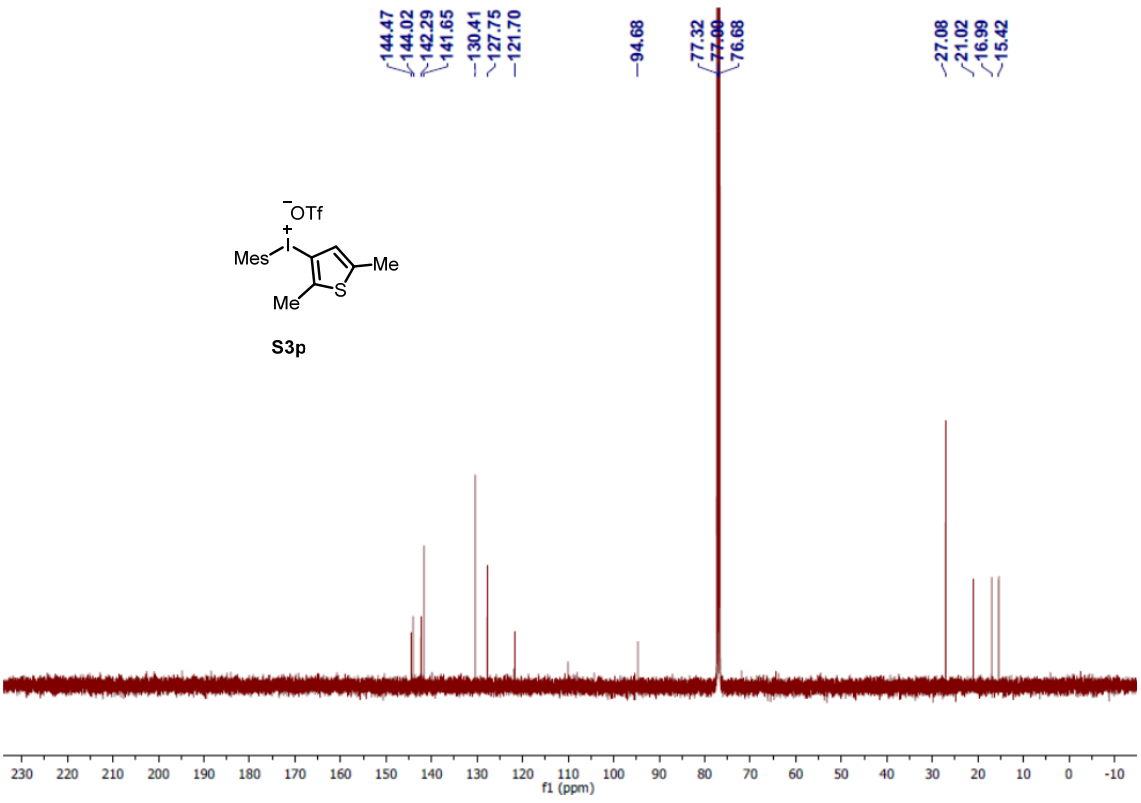
142.26
137.53
137.07
130.62
129.45
129.06
128.81
119.21
104.65
70.61
40.45
27.19
21.44
OTf
Mes
OBn
f1 (ppm)

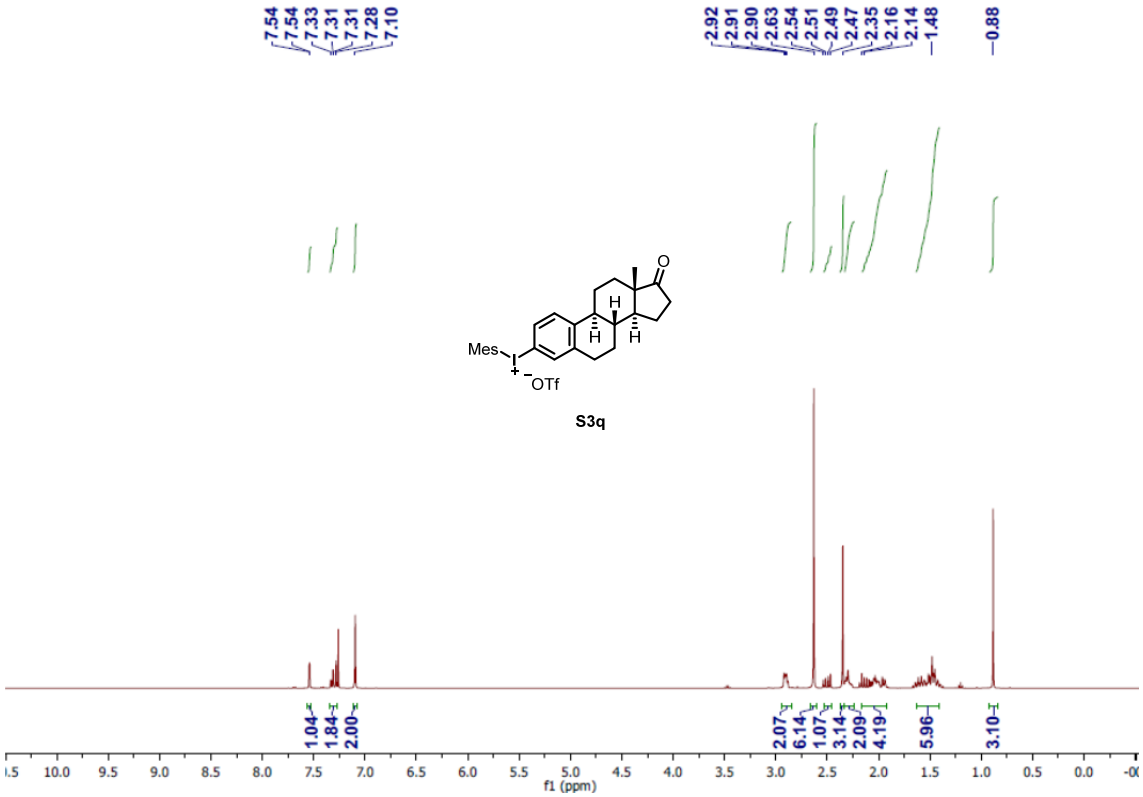
S3n

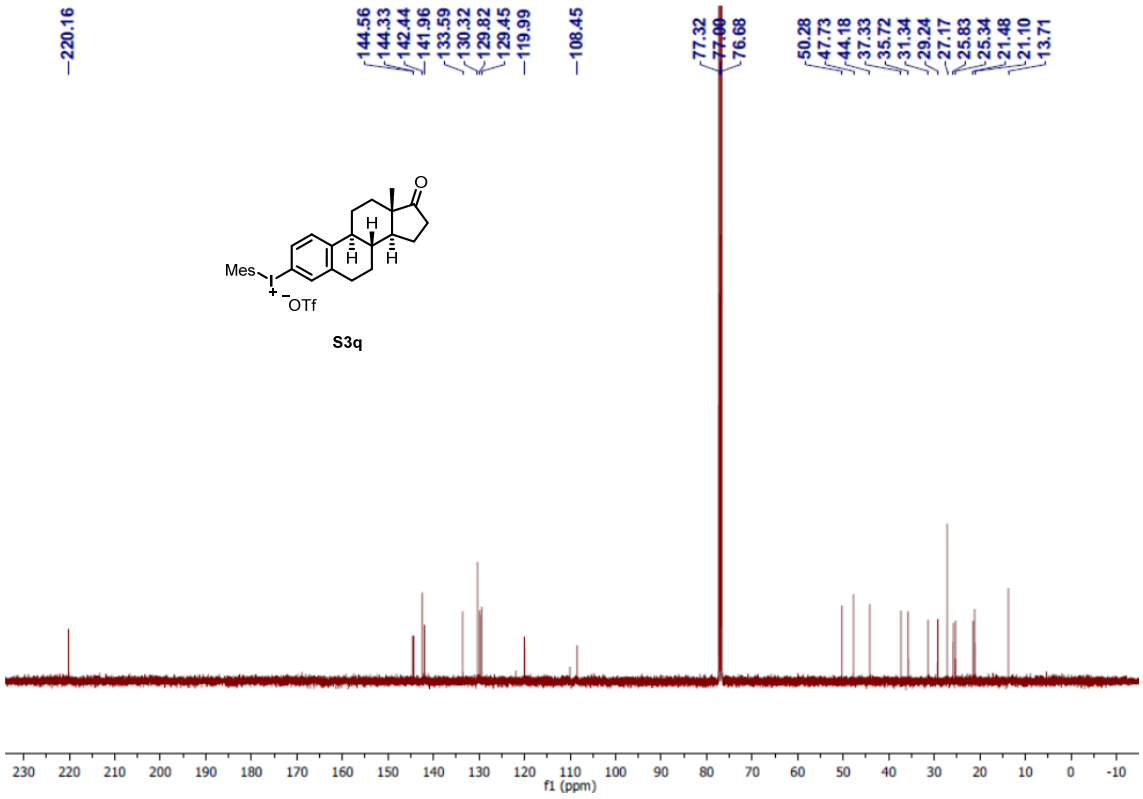

7.07
7.07
6.64
6.64
2.65
2.59
2.41
2.41
2.41
2.41
2.34
OTf
Mes
Me
Me
S
2.00
0.99
6.29
3.06
3.16
3.11
f1 (ppm)

S3p


144.47
144.02
142.29
141.65
130.41
127.75
121.70
94.68
77.32
77.00
76.68
27.08
21.02
16.99
15.42
OTf
Mes
Me
Me
S
f1 (ppm)

S3p


7.54
7.54
7.33
7.31
7.31
7.28
7.10
2.92
2.91
2.90
2.63
2.54
2.51
2.49
2.47
2.35
2.16
2.14
1.48
0.88
Mes
OTf
S3q
1.04
1.84
2.00
2.07
6.14
1.07
3.14
2.09
4.19
5.96
3.10
f1 (ppm)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144.56
144.33
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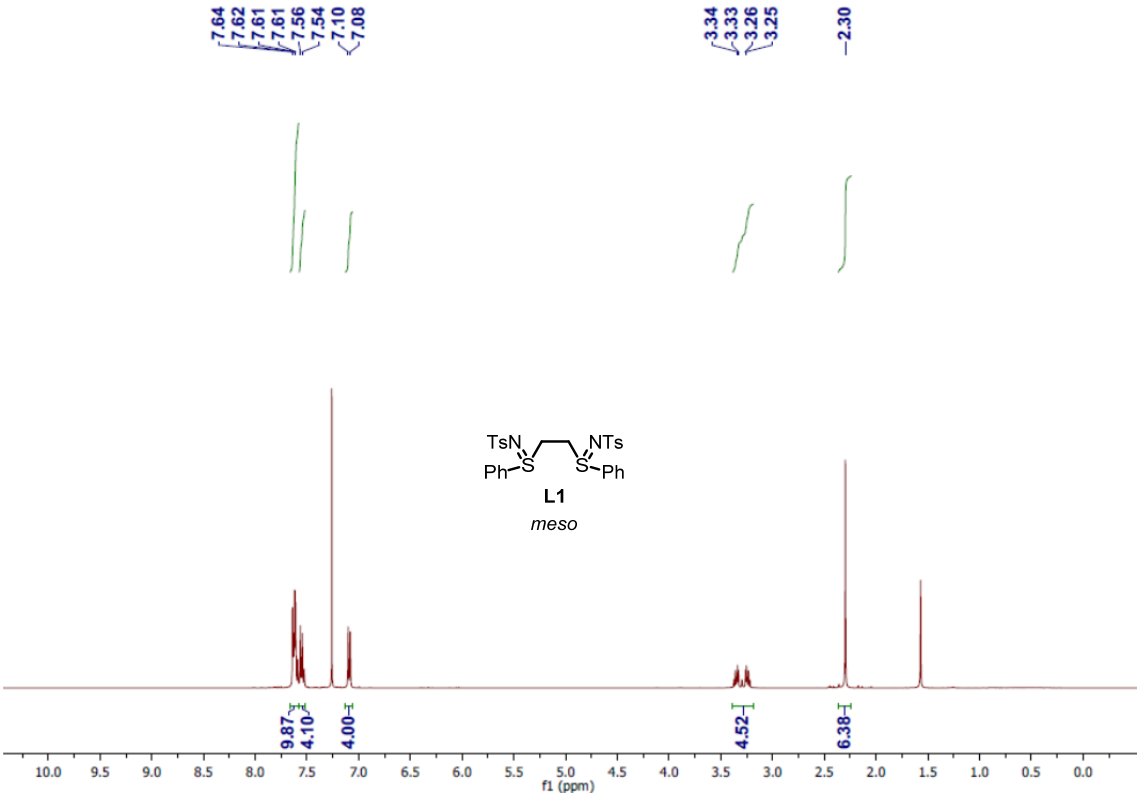
141.96
133.59
130.32
129.82
129.45
119.99
108.45
77.32
77.00
76.68
50.28
47.73
44.18
37.33
35.72
31.34
29.24
27.17
25.83
25.34
21.48
21.10
13.71
Mes
OTf
S3q
f1 (ppm)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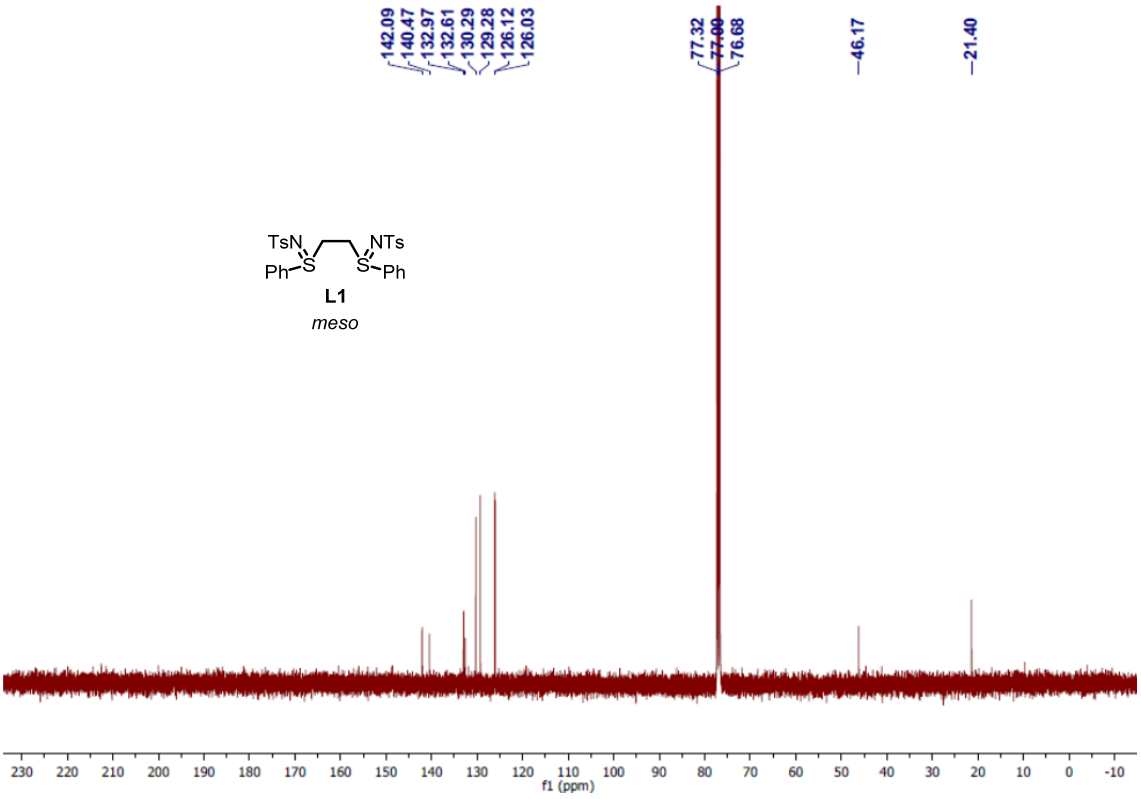
7.62
7.61
7.61
7.56
7.54
7.10
7.08
3.34
3.33
3.26
3.25
2.30
TsN
NTs
Ph
Ph
L1
meso
9.87
4.10
4.00
4.52
6.38
f1 (ppm)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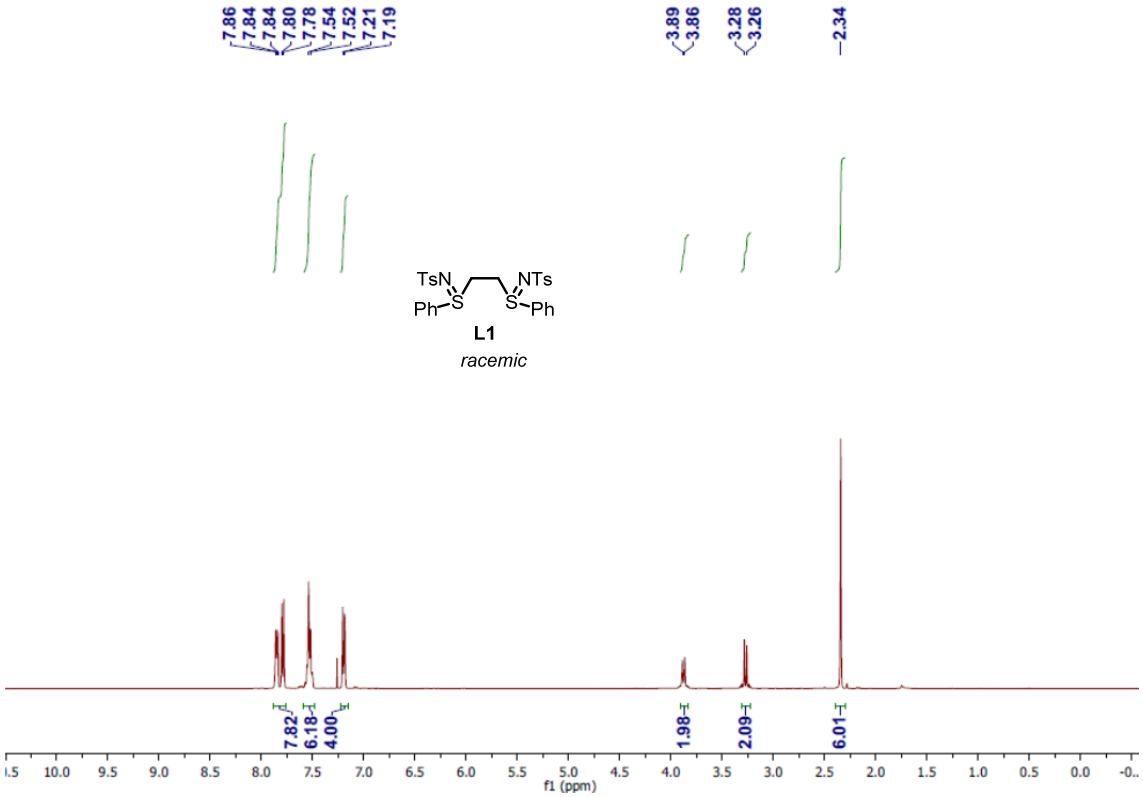
140.47
132.97
132.61
130.29
129.28
126.12
126.03
77.32
77.00
76.68
46.17
21.40
TsN
NTs
Ph
Ph
L1
meso
f1 (ppm)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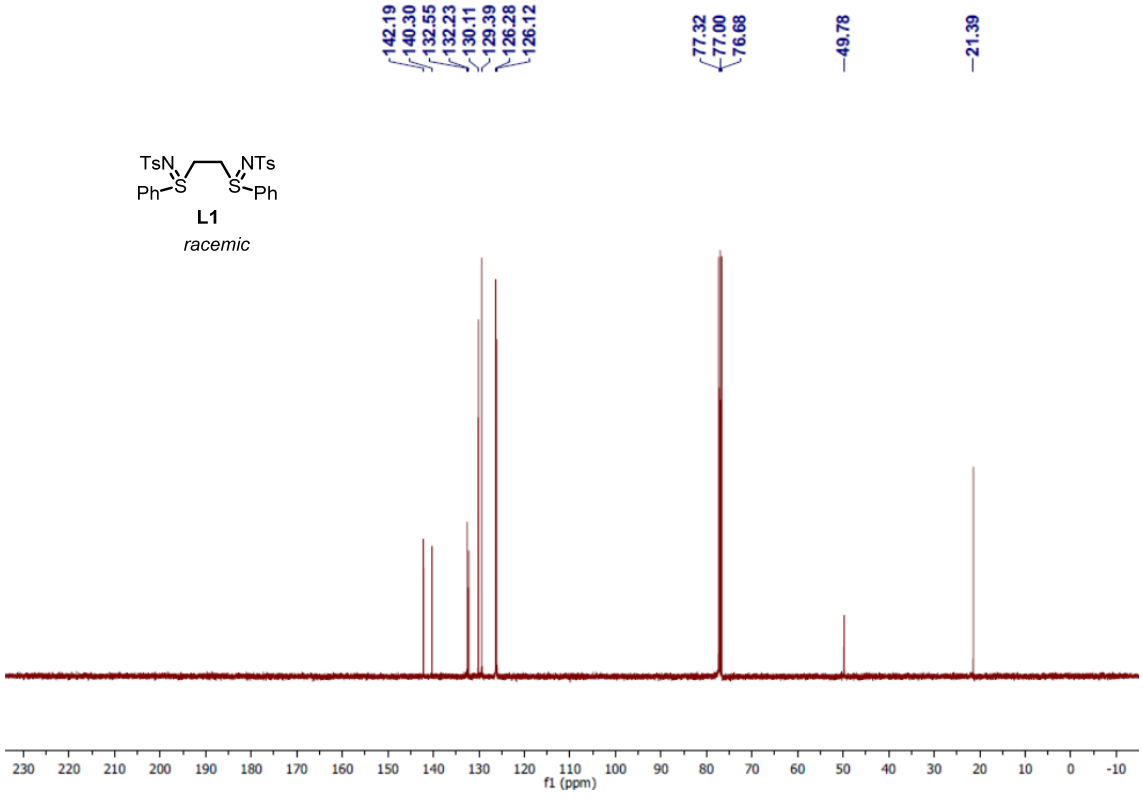
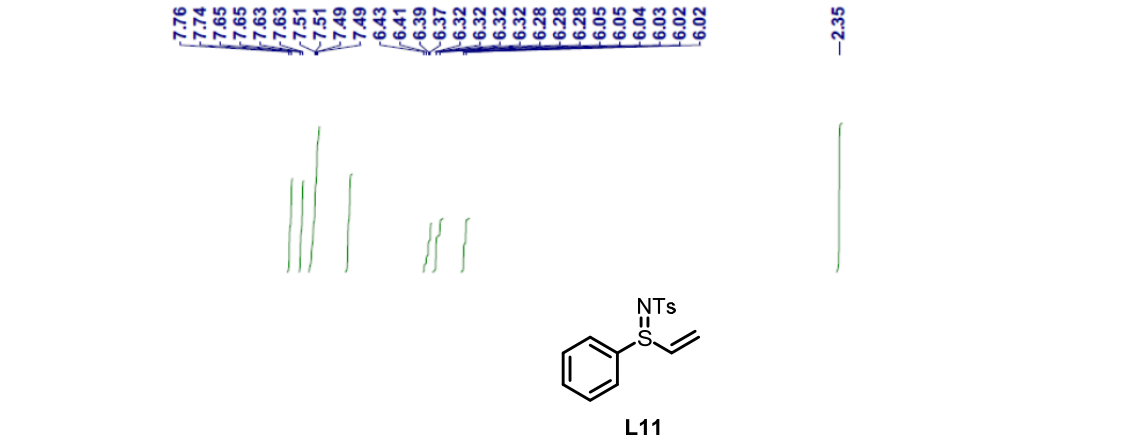
7.84
7.80
7.78
7.54
7.52
7.21
7.19
3.89
3.86
3.28
3.26
2.34
TsN
NTs
Ph
S
S
Ph
L1
racemic
7.82
6.18
4.00
1.98
2.09
6.01
f1 (ppm)


142.19
140.30
132.55
132.23
130.11
129.39
126.28
126.12
77.32
77.00
76.68
49.78
21.39
TsN
NTs
Ph
S
S
Ph
L1
racemic
f1 (ppm)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7.63
7.51
7.51
7.49
7.49
6.43
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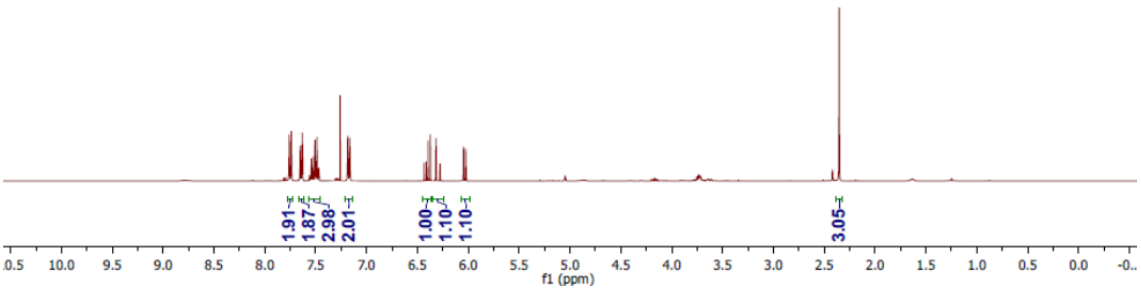
6.39
6.37
6.32
6.32
6.32
6.32
6.28
6.28
6.28
6.05
6.05
6.04
6.03
6.02
6.02
2.35
NTs
S

L11


1.91
1.87
2.98
2.01
1.00
1.10
1.10
3.05
f1 (ppm)


141.73
141.31
134.64
133.14
132.56
130.01
129.17
126.97
126.22
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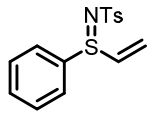
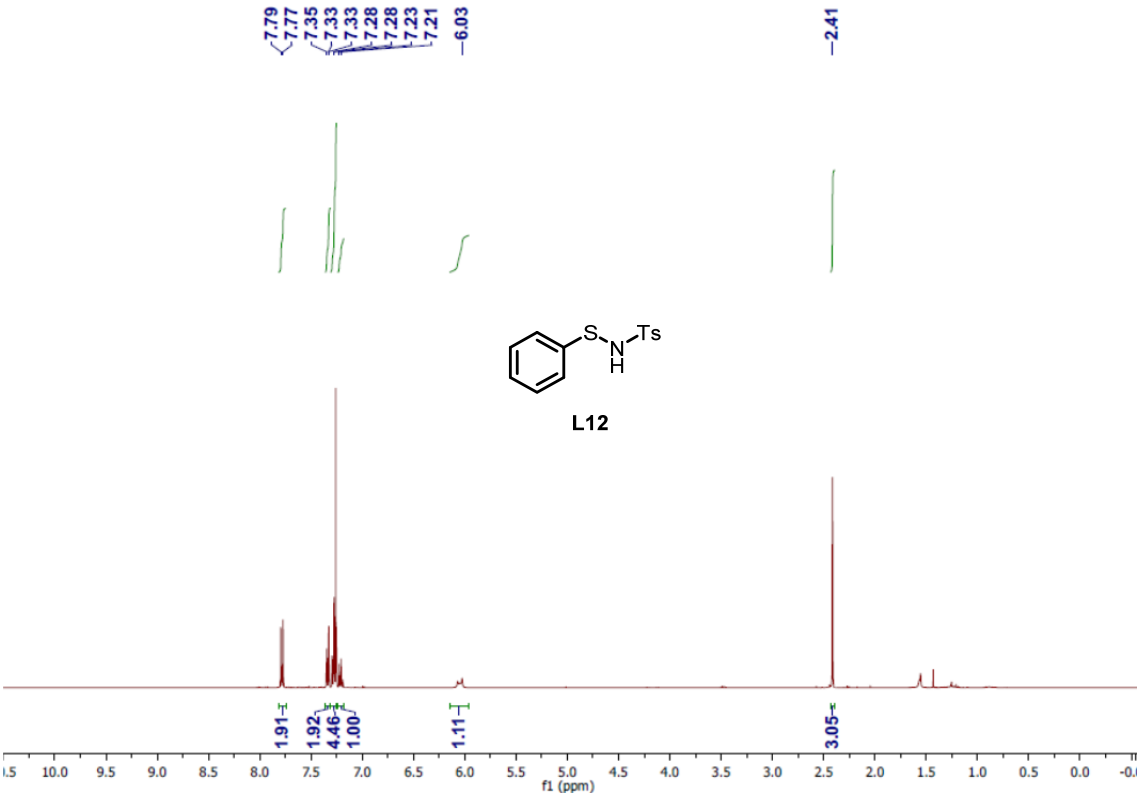
77.00
76.68
21.40


NTs
S

L11

f1 (ppm)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7.28
7.23
7.21
6.03
2.41
S
N
H
Ts
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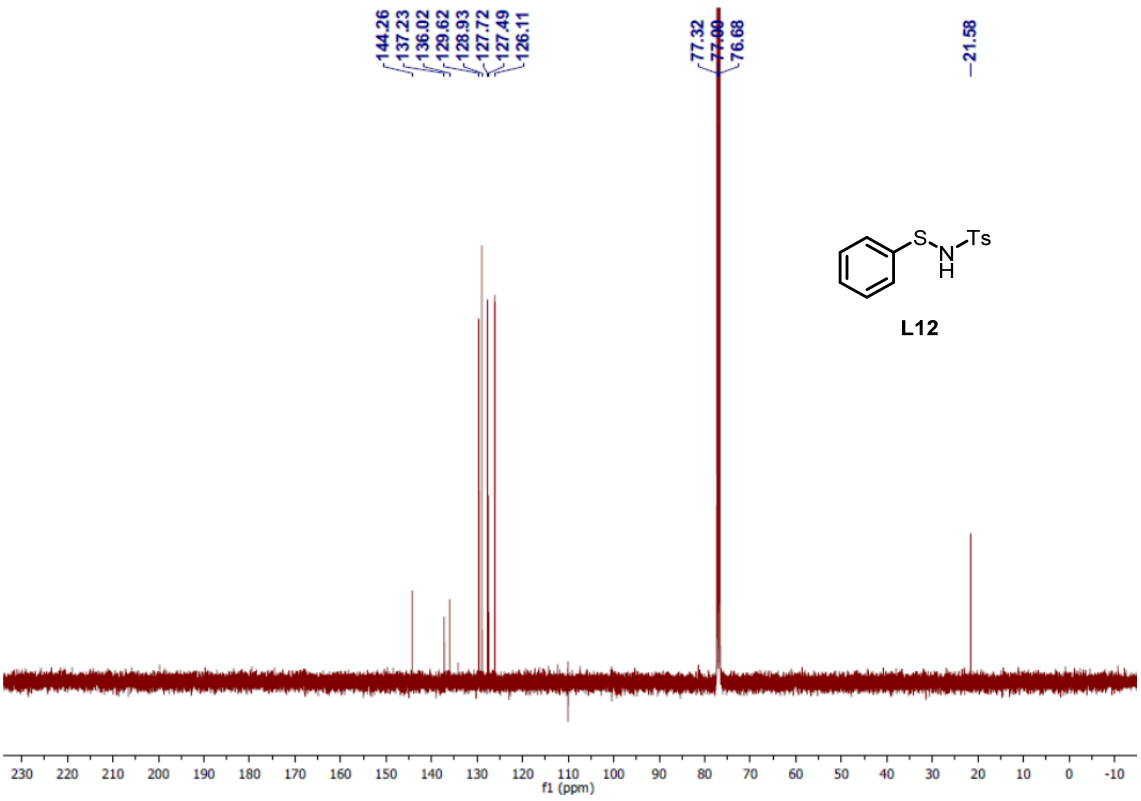
1.00
1.11
3.05
f1 (ppm)

L12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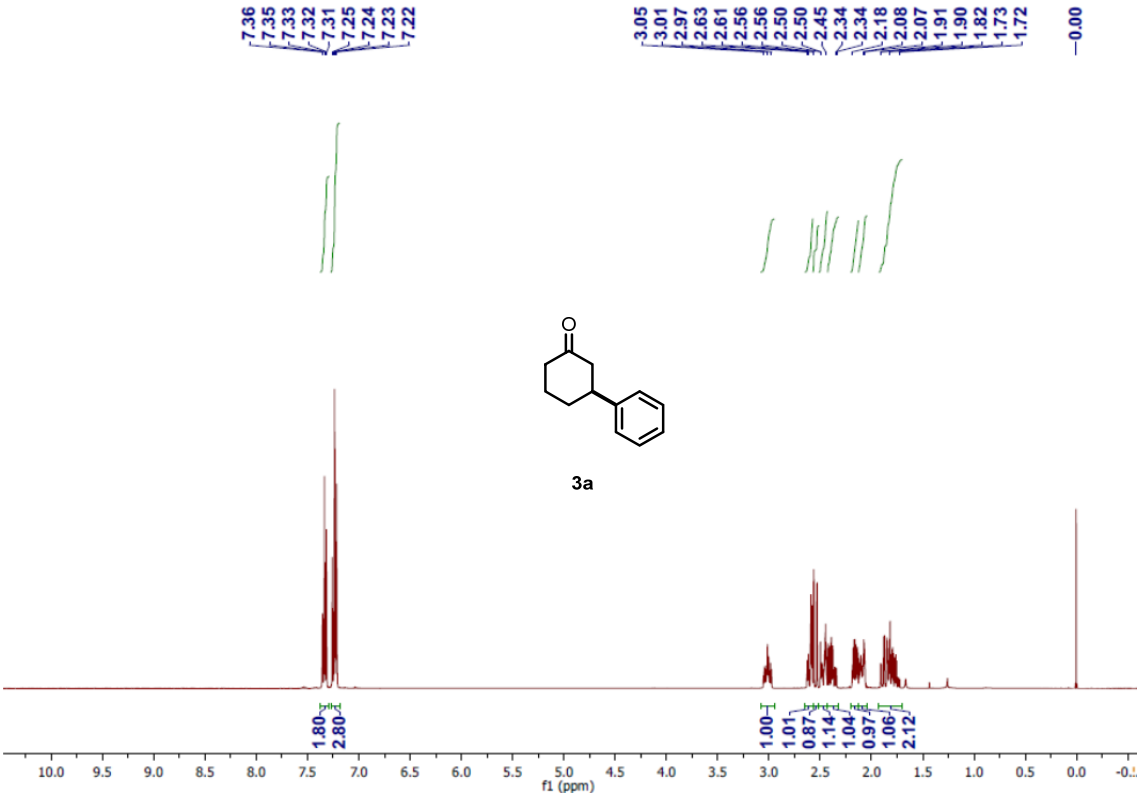
136.02
129.62
128.93
127.72
127.49
126.11
77.32
77.00
76.68
21.58
S
N
H
Ts
f1 (ppm)

L12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7.32
7.31
7.25
7.24
7.23
7.22
3.05
3.01
2.97
2.63
2.61
2.56
2.56
2.50
2.50
2.45
2.34
2.34
2.18
2.08
2.07
1.91
1.90
1.82
1.73
1.72
0.00
1.80
2.80
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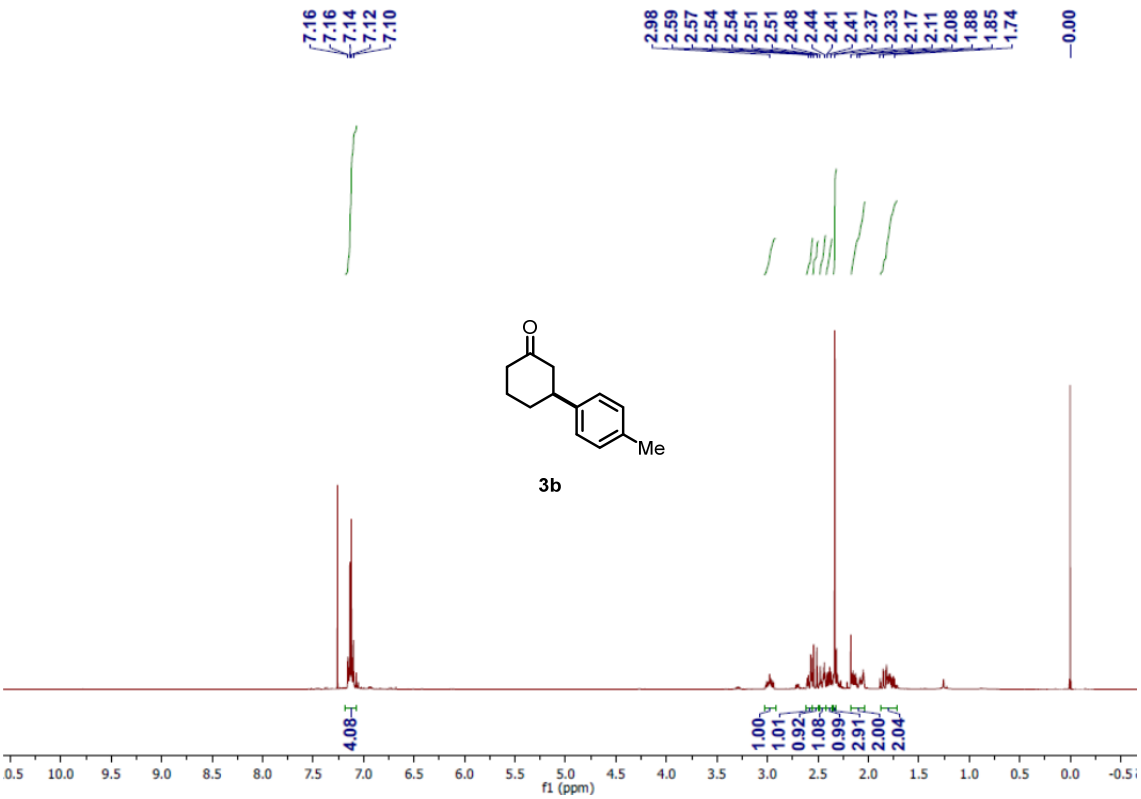
1.01
0.87
1.14
1.04
0.97
1.06
2.12
f1 (ppm)

3a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7.12
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2.57
2.54
2.54
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2.44
2.41
2.41
2.37
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2.17
2.11
2.08
1.88
1.85
1.74
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1.01
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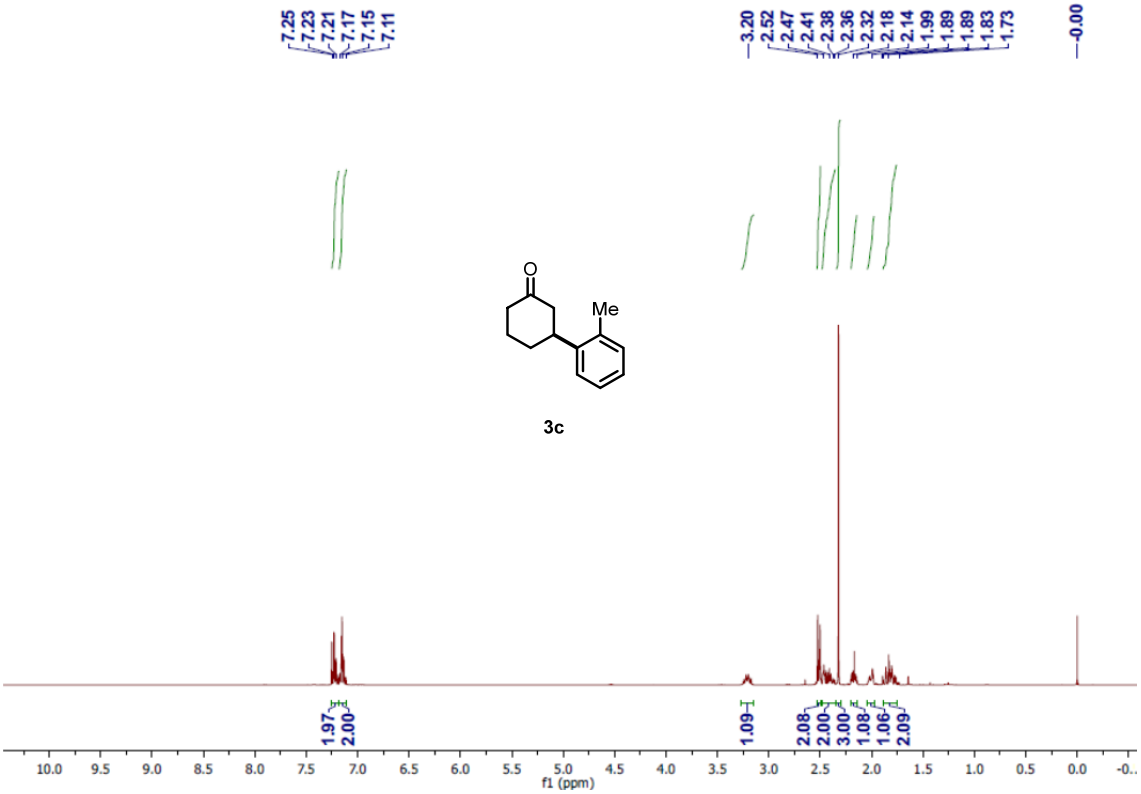
1.08
0.99
2.91
2.00
2.04
f1 (ppm)

3b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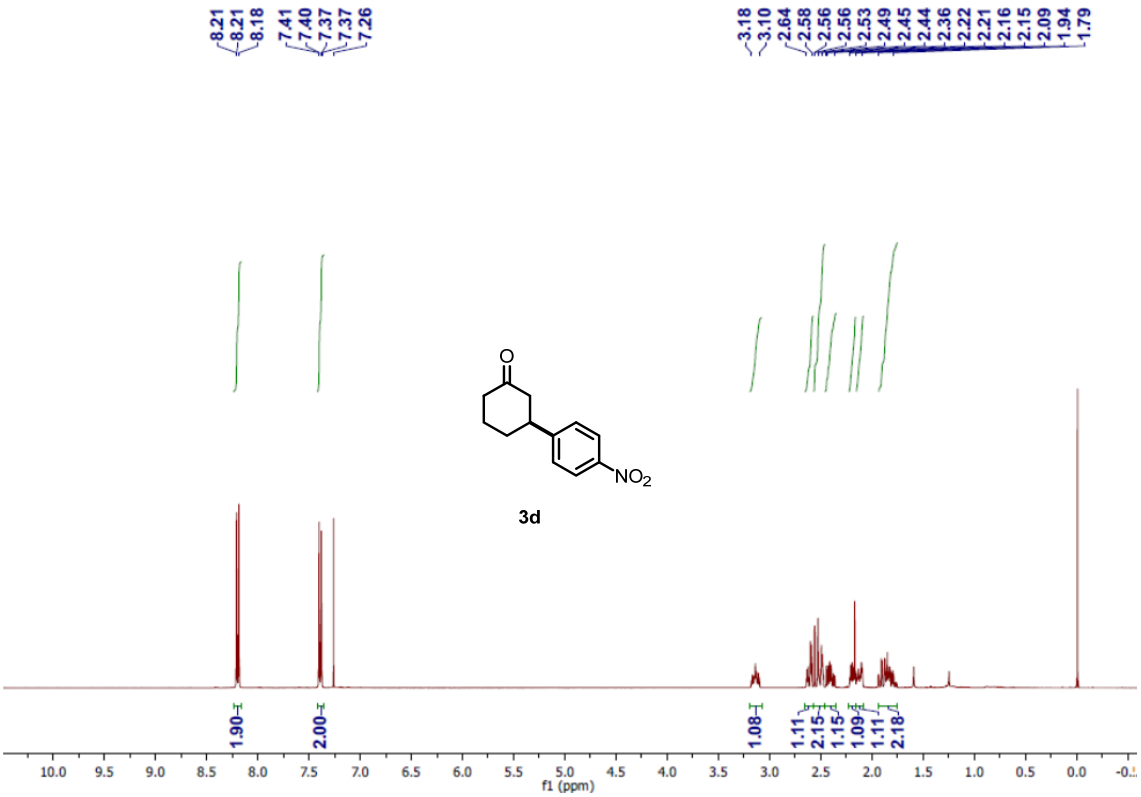
7.23
7.21
7.17
7.15
7.11
3.20
2.52
2.47
2.41
2.38
2.36
2.32
2.18
2.14
1.99
1.89
1.89
1.83
1.73
0.00
O
Me
1.97
2.00
1.09
2.08
2.00
3.00
1.08
1.06
2.09
f1 (ppm)

3c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7.41
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7.37
7.37
7.26
3.18
3.10
2.64
2.58
2.56
2.56
2.53
2.49
2.45
2.44
2.36
2.22
2.21
2.16
2.15
2.09
1.94
1.79
O
NO2
1.90
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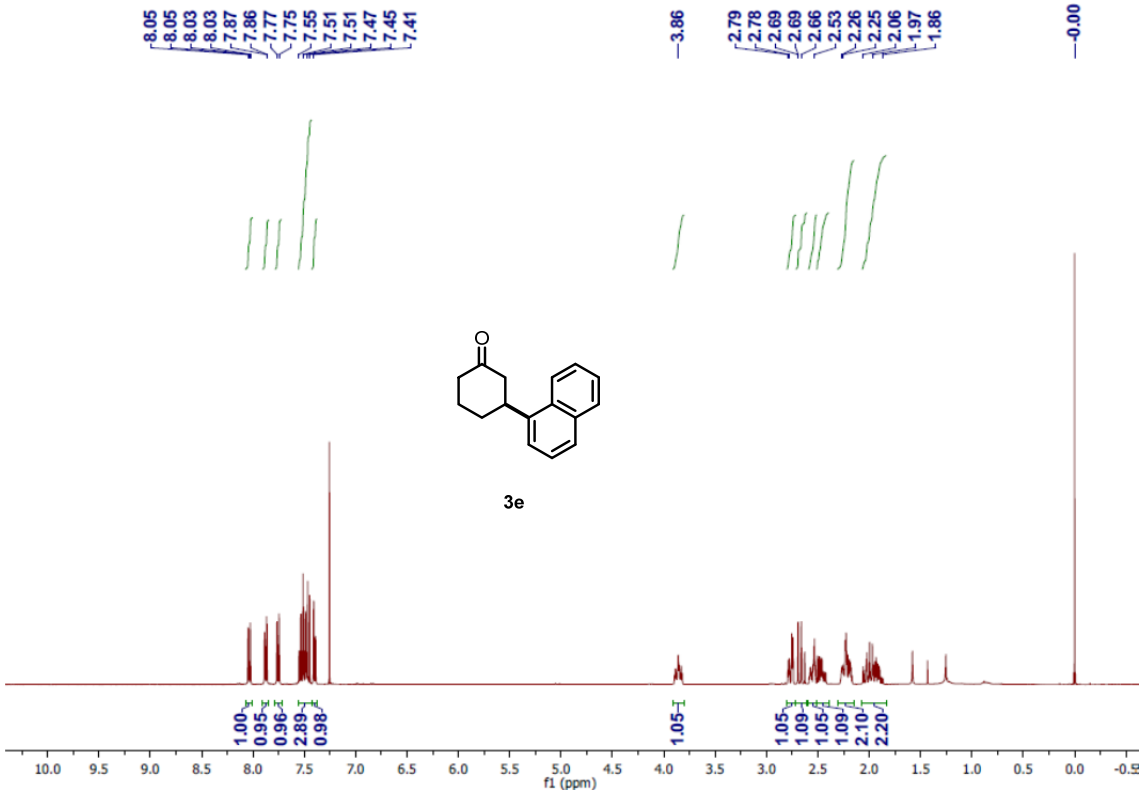
1.08
1.11
2.15
1.15
1.09
1.11
2.18
f1 (ppm)

3d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8.05
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8.03
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7.77
7.75
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7.51
7.51
7.47
7.45
7.41
3.86
2.79
2.78
2.69
2.69
2.66
2.53
2.26
2.25
2.06
1.97
1.86
0.00
1.00
0.95
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2.89
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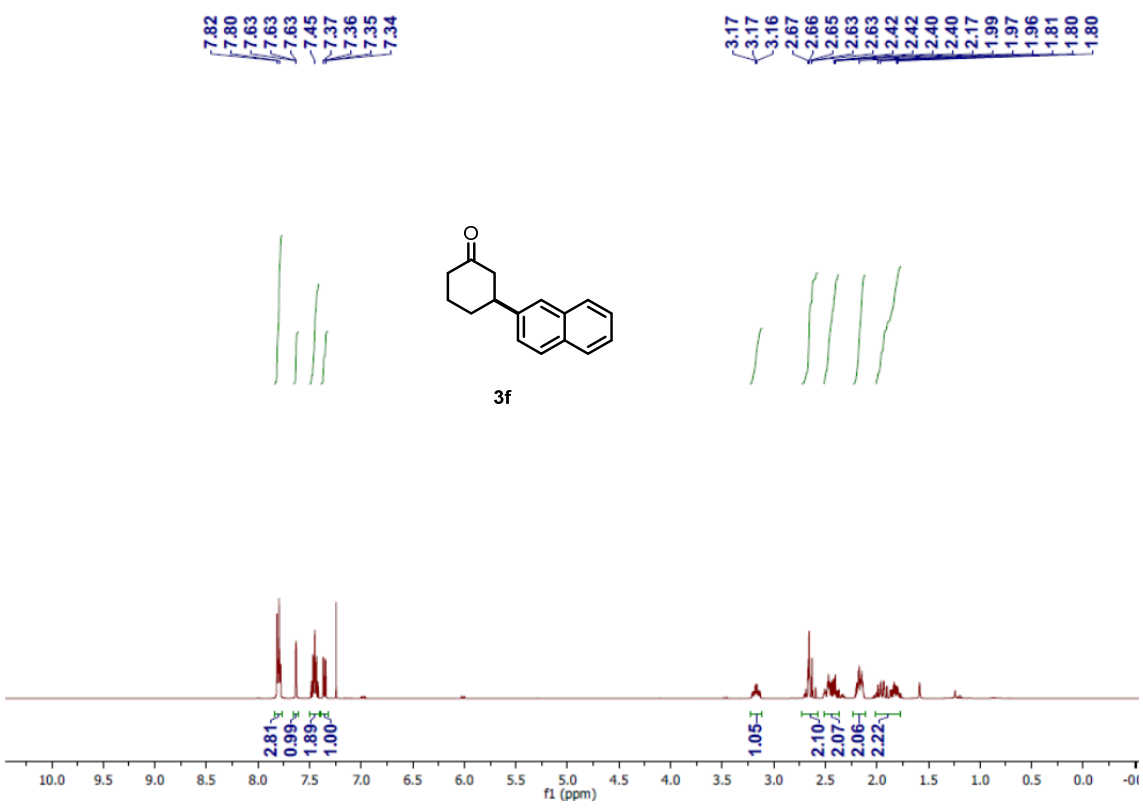
1.05
1.05
1.09
1.05
1.09
2.10
2.20
f1 (ppm)

3e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7.36
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7.34
3.17
3.17
3.16
2.67
2.66
2.65
2.63
2.63
2.42
2.42
2.40
2.40
2.17
1.99
1.97
1.96
1.81
1.80
1.80
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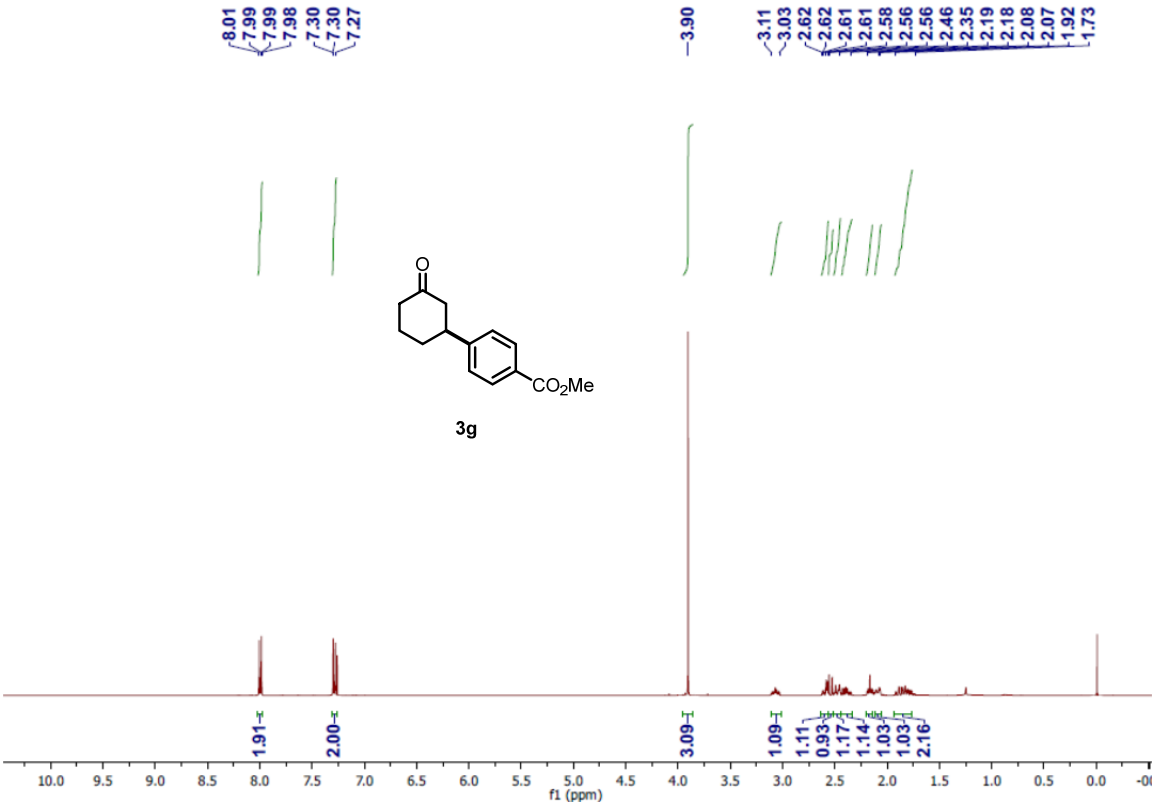
1.89
1.00
1.05
2.10
2.07
2.06
2.22
f1 (ppm)

3f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3.90
3.11
3.03
2.62
2.62
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2.61
2.61
2.58
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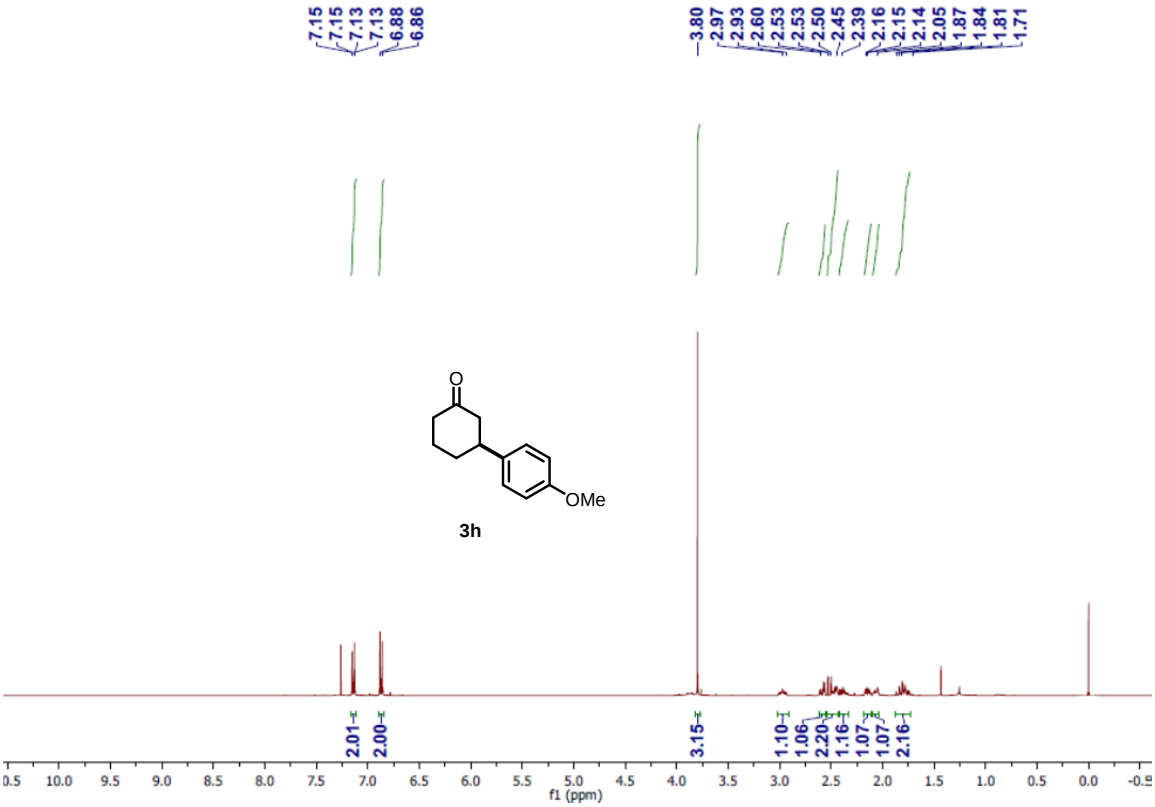
2.19
2.18
2.08
2.07
1.92
1.73
O
CO2Me
1.91
2.00
3.09
1.09
1.11
0.93
1.17
1.14
1.03
1.03
2.16
f1 (ppm)

3g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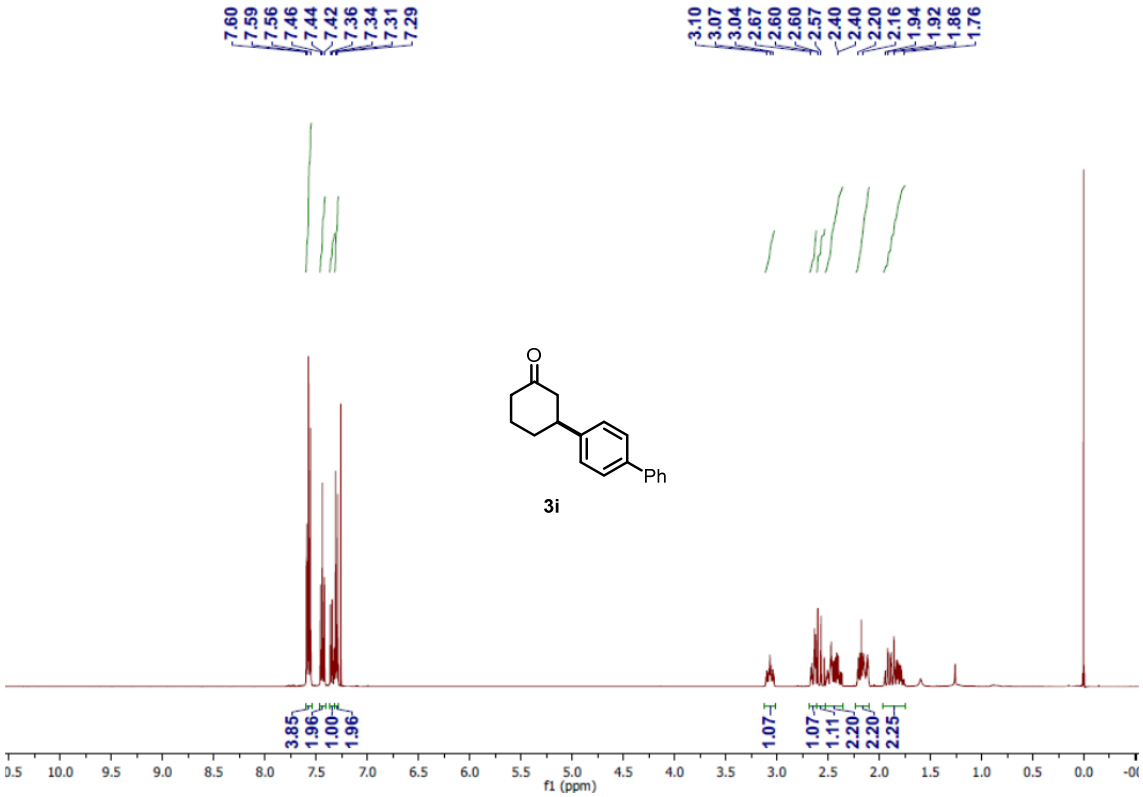
6.86
3.80
2.97
2.93
2.60
2.53
2.53
2.50
2.45
2.39
2.16
2.15
2.14
2.05
1.87
1.84
1.81
1.71
O
OMe
2.01
2.00
3.15
1.10
1.06
2.20
1.16
1.07
1.07
2.16
f1 (ppm)

3h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7.34
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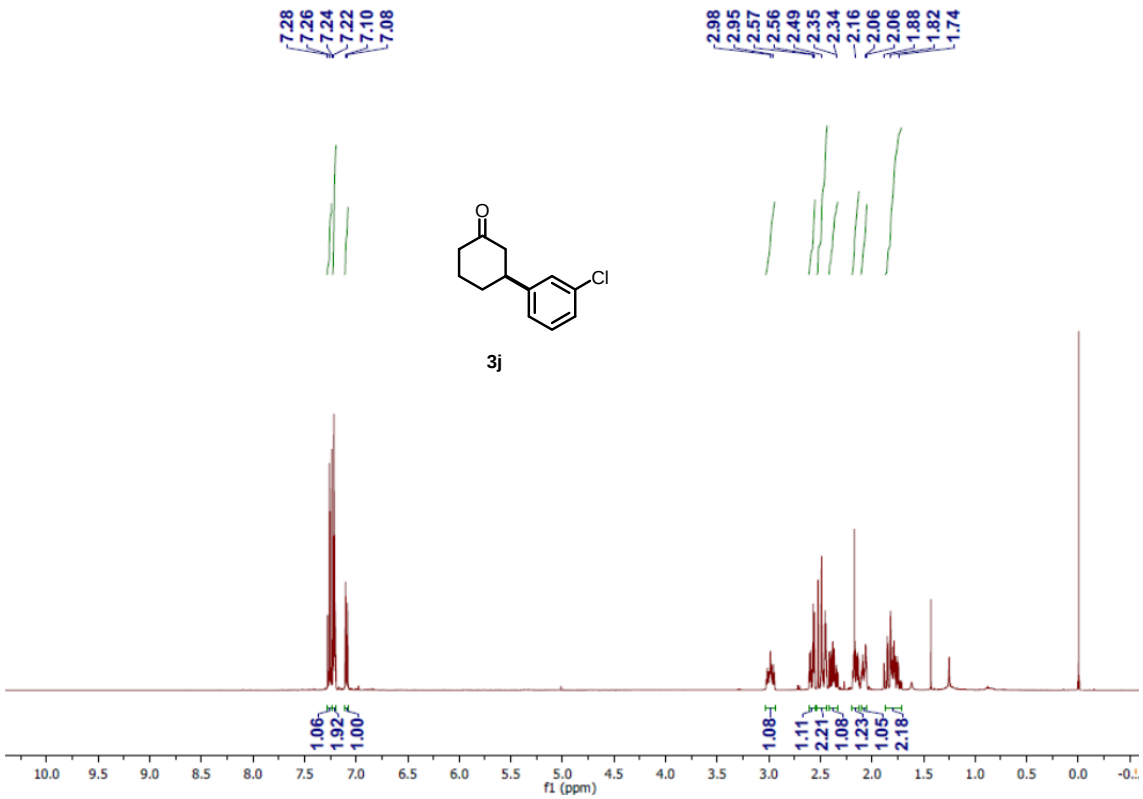
7.29
3.10
3.07
3.04
2.67
2.60
2.60
2.57
2.40
2.40
2.20
2.16
1.94
1.92
1.86
1.76
O
Ph
3.85
1.96
1.00
1.96
1.07
1.07
1.11
2.20
2.20
2.25
f1 (ppm)

3i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7.08
2.98
2.95
2.57
2.56
2.49
2.35
2.34
2.16
2.06
2.06
1.88
1.82
1.74
O
Cl
1.06
1.92
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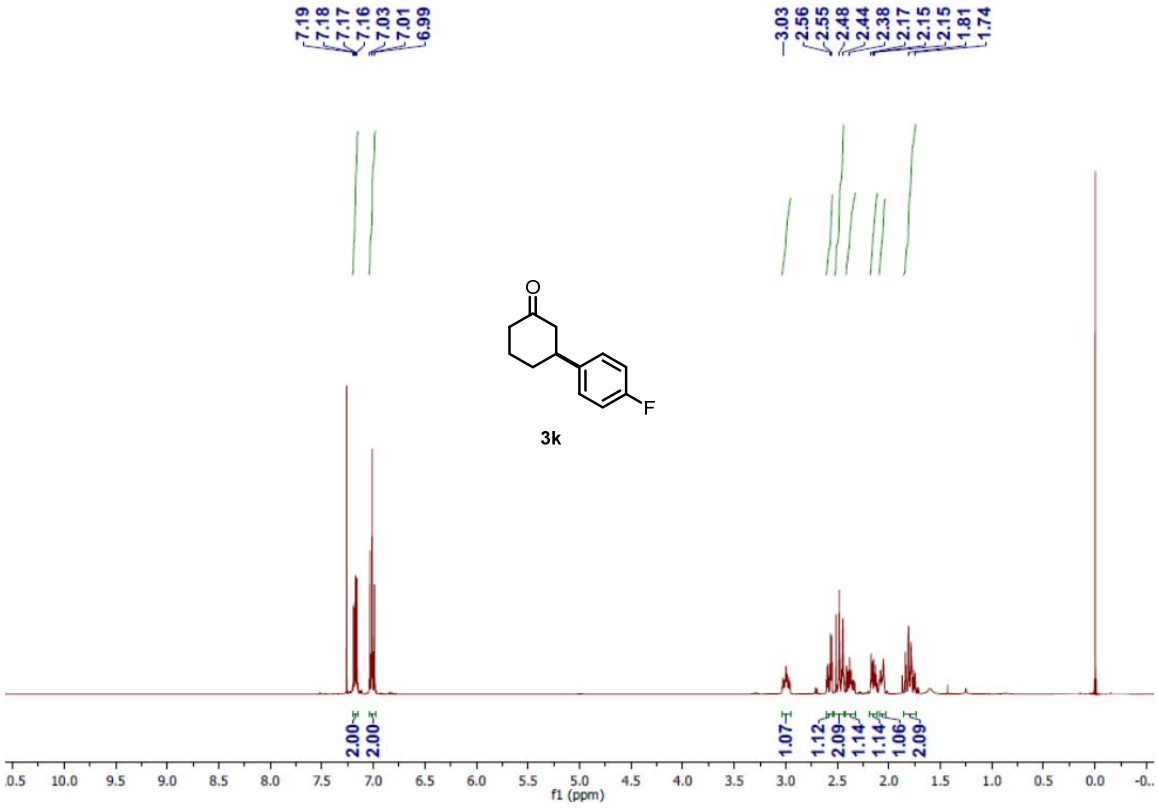
1.08
1.11
2.21
1.08
1.23
1.05
2.18
f1 (ppm)

3j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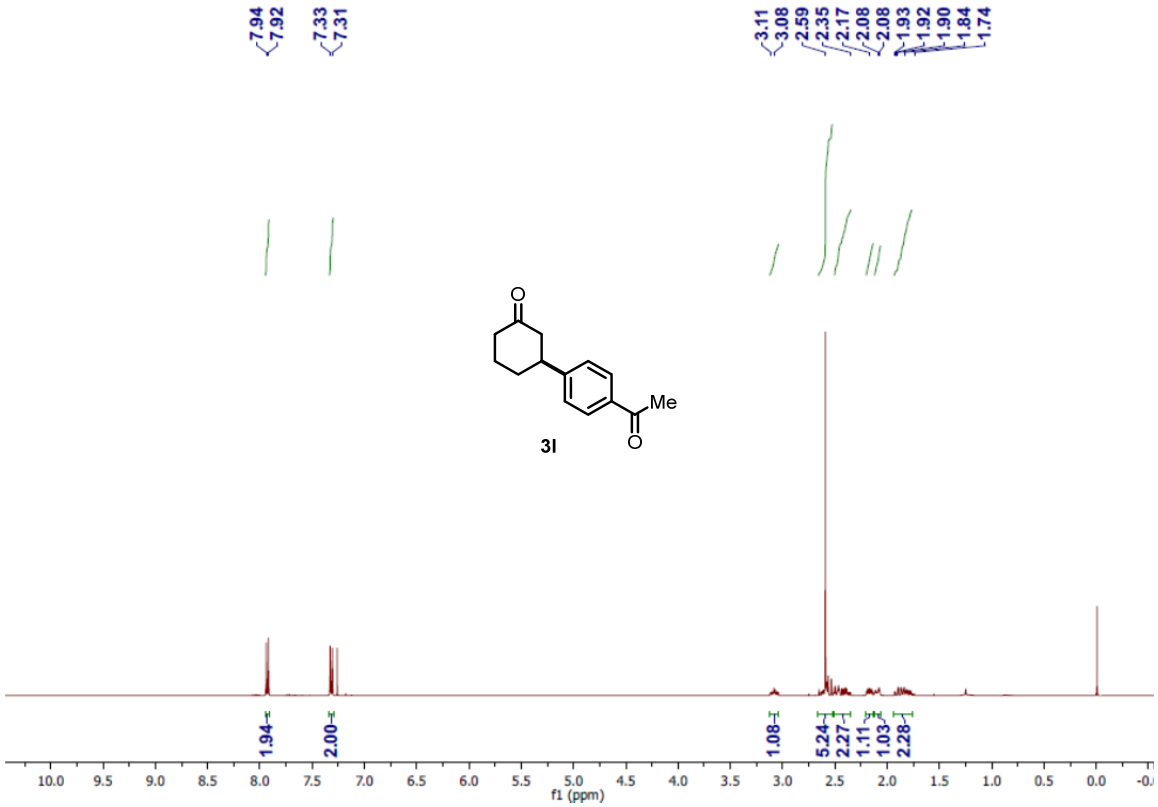
7.18
7.17
7.16
7.03
7.01
6.99
3.03
2.56
2.55
2.48
2.44
2.38
2.17
2.15
2.15
1.81
1.74
O
F
3k
2.00
2.00
1.07
1.12
2.09
1.14
1.14
1.06
2.09
f1 (ppm)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7.92
7.33
7.31
3.11
3.08
2.59
2.35
2.17
2.08
2.08
1.93
1.92
1.90
1.84
1.74
O
Me
O
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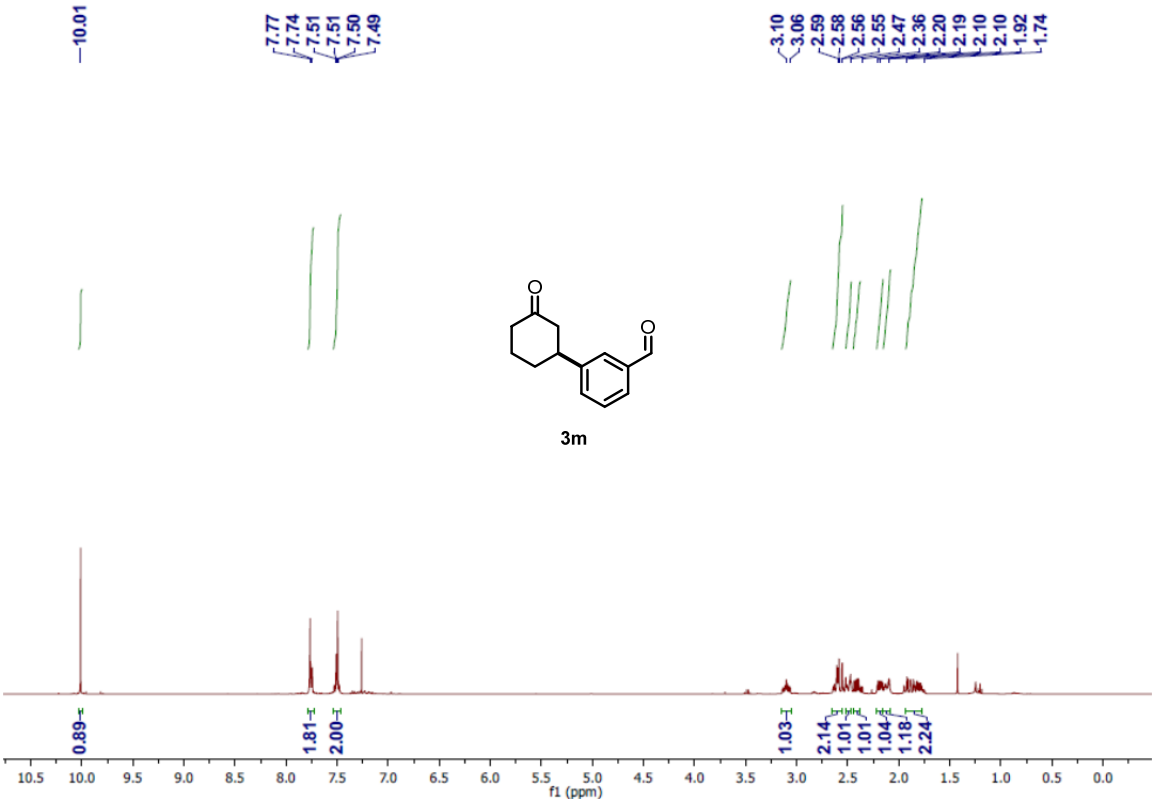
1.94
2.00
1.08
5.24
2.27
1.11
1.03
2.28
f1 (ppm)


10.01
7.77
7.74
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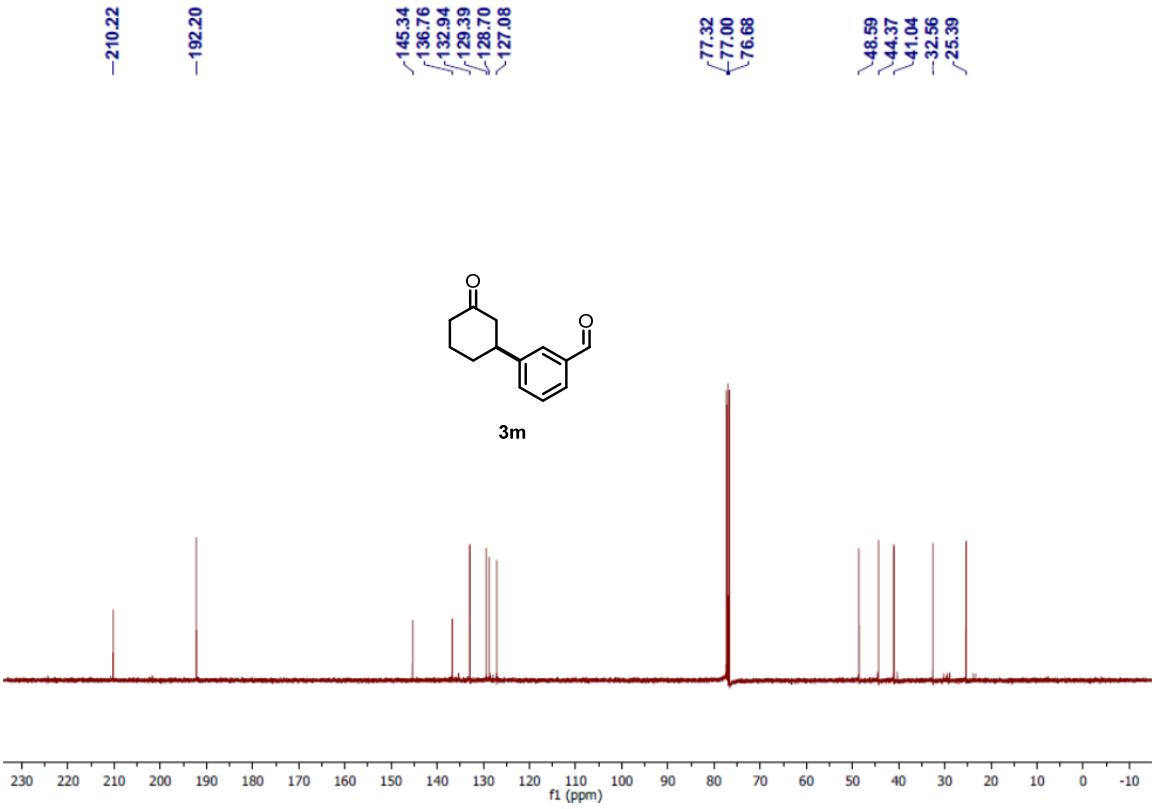
7.49
3.10
3.06
2.59
2.58
2.56
2.55
2.47
2.36
2.20
2.19
2.10
2.10
1.92
1.74
3m
0.89
1.81
2.00
1.03
2.14
1.01
1.01
1.04
1.18
2.24
f1 (ppm)


210.22
192.20
145.34
136.76
132.94
129.39
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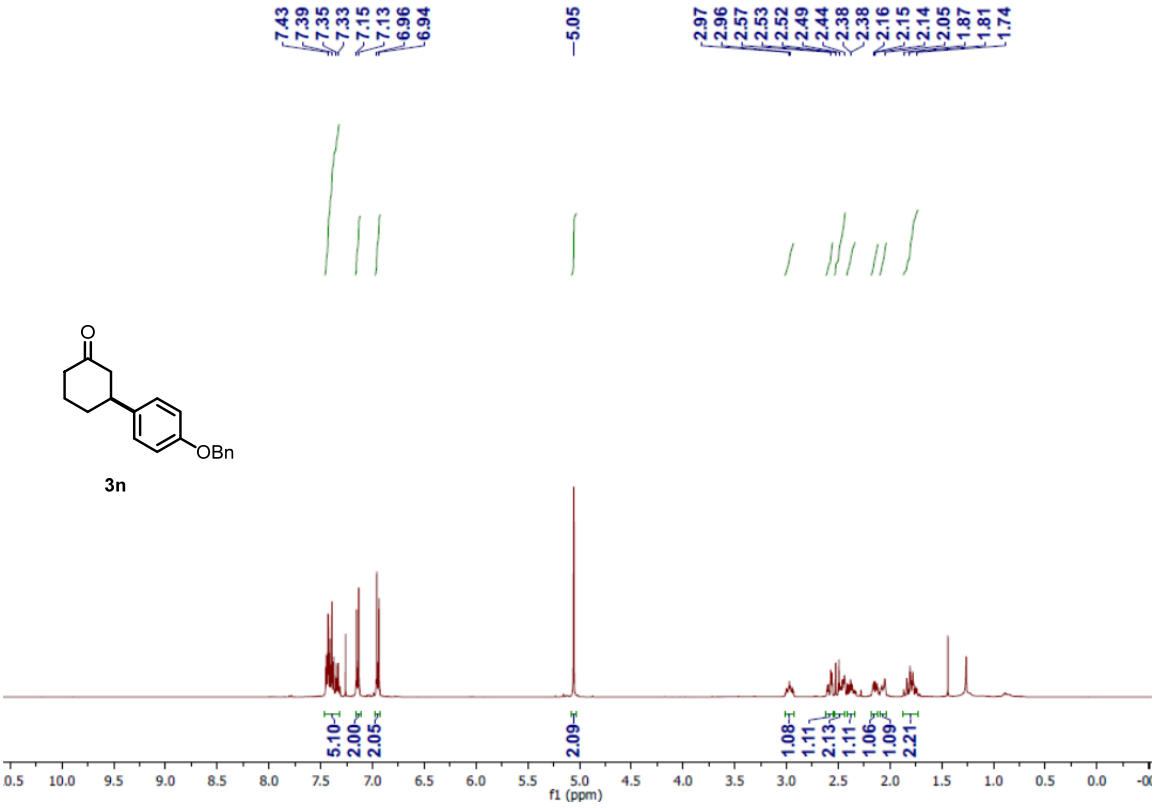
127.08
77.32
77.00
76.68
48.59
44.37
41.04
32.56
25.39
3m
f1 (ppm)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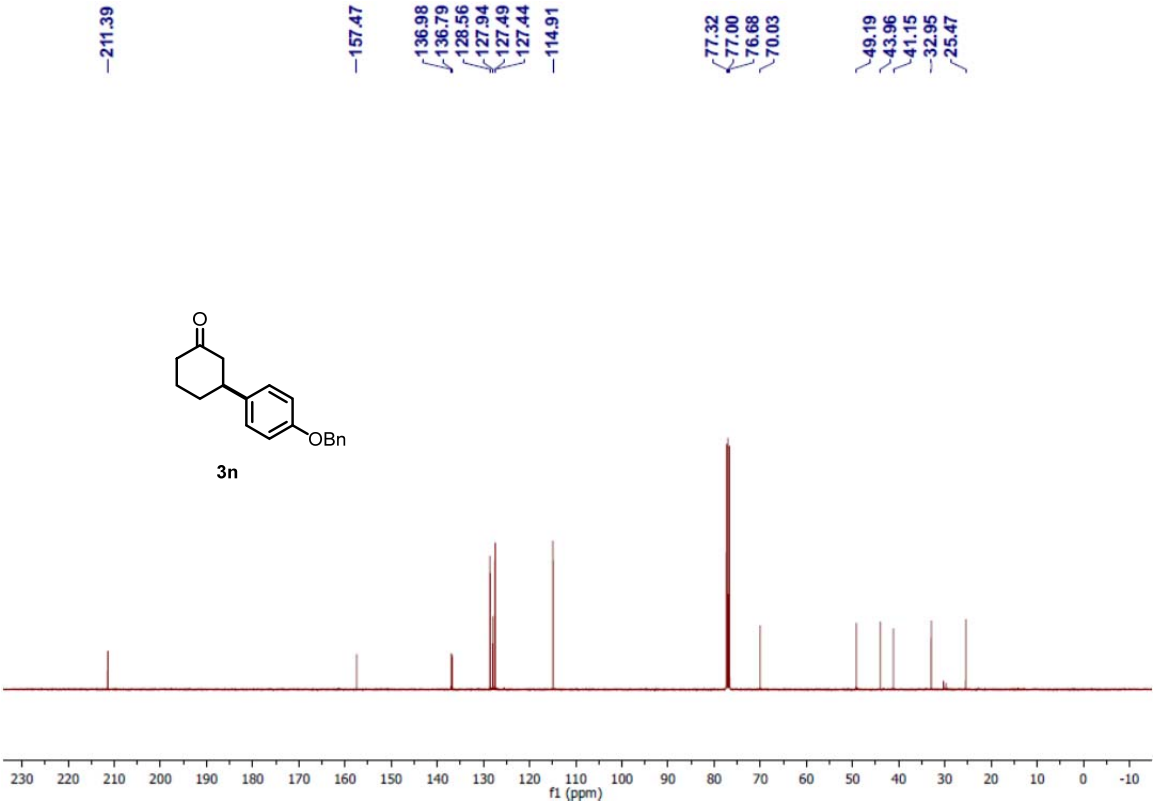
7.39
7.35
7.33
7.15
7.13
6.96
6.94
5.05
2.97
2.96
2.57
2.53
2.52
2.49
2.44
2.38
2.38
2.16
2.15
2.14
2.05
1.87
1.81
1.74
OBn
3n
5.10
2.00
2.05
2.09
1.08
1.11
2.13
1.11
1.06
1.09
2.21
f1 (ppm)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157.47
136.98
136.79
128.56
127.94
127.49
127.44
114.91
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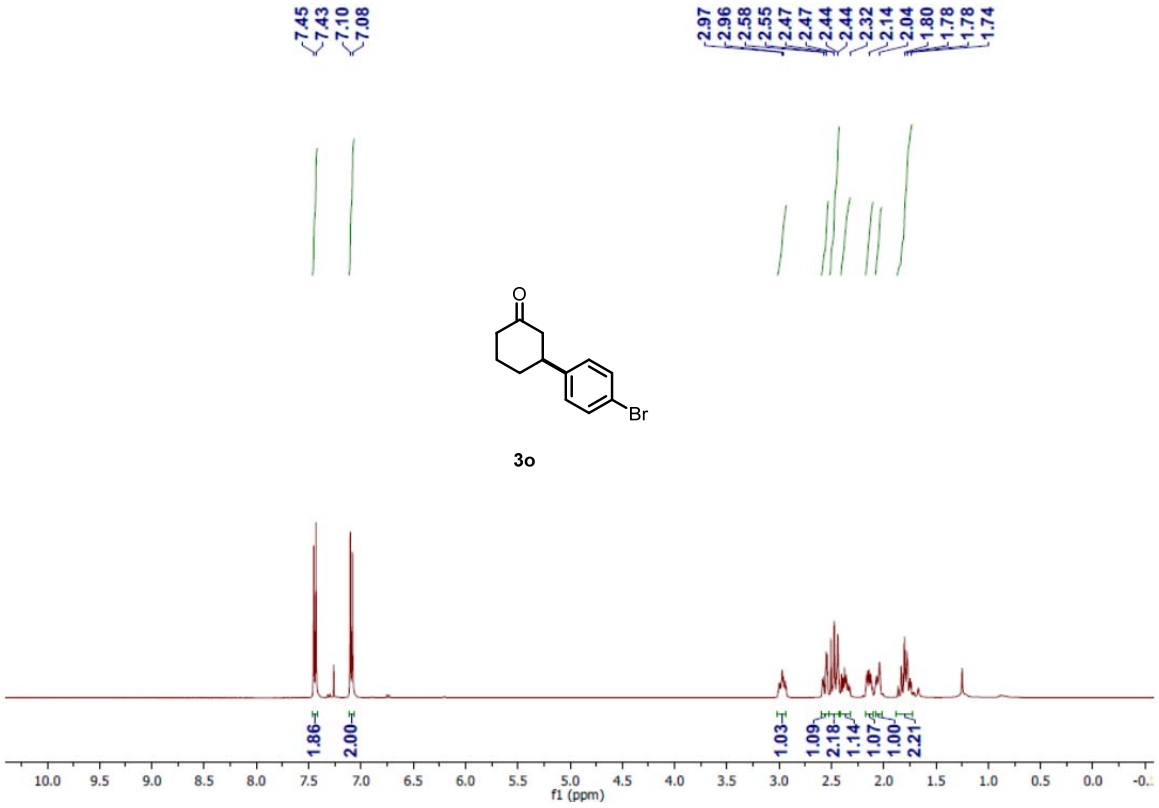
77.00
76.68
70.03
49.19
43.96
41.15
32.95
25.47
OBn
3n
f1 (ppm)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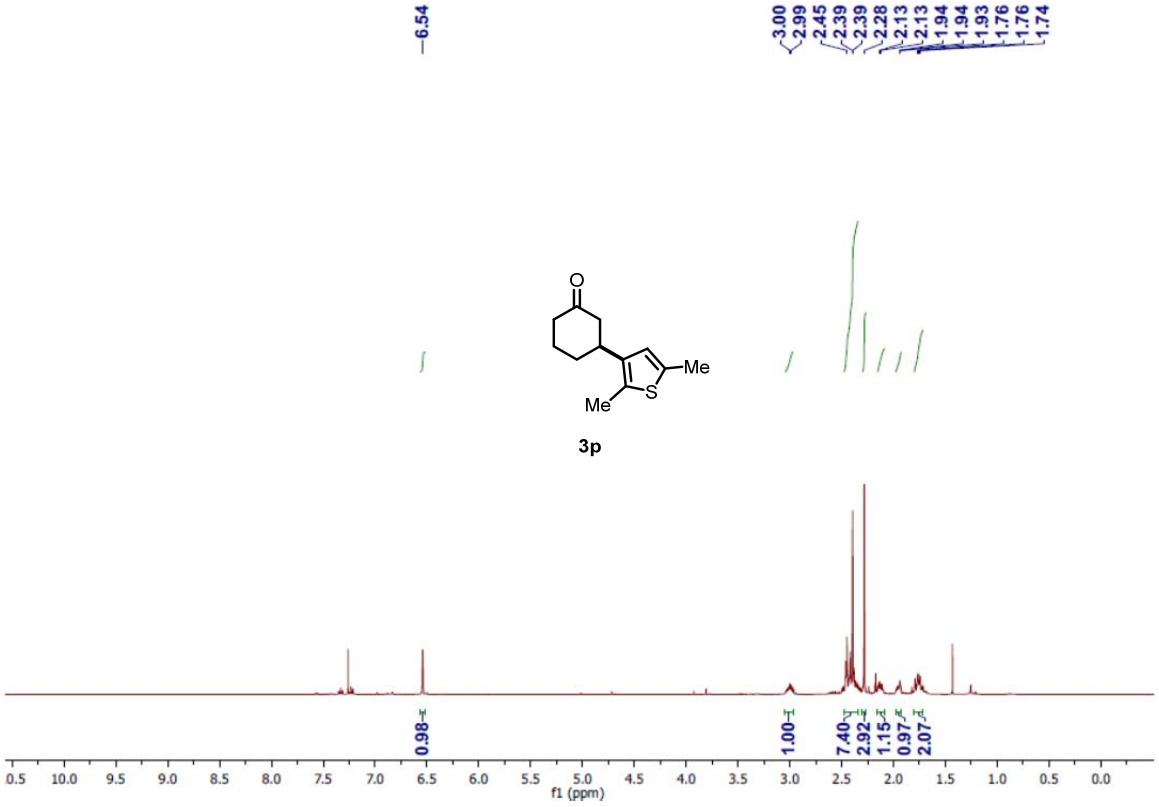
7.43
7.10
7.08
2.97
2.96
2.58
2.55
2.47
2.47
2.44
2.44
2.32
2.14
2.04
1.80
1.78
1.78
1.74
O
Br
1.86
2.00
1.03
1.09
2.18
1.14
1.07
1.00
2.21
f1 (ppm)

3o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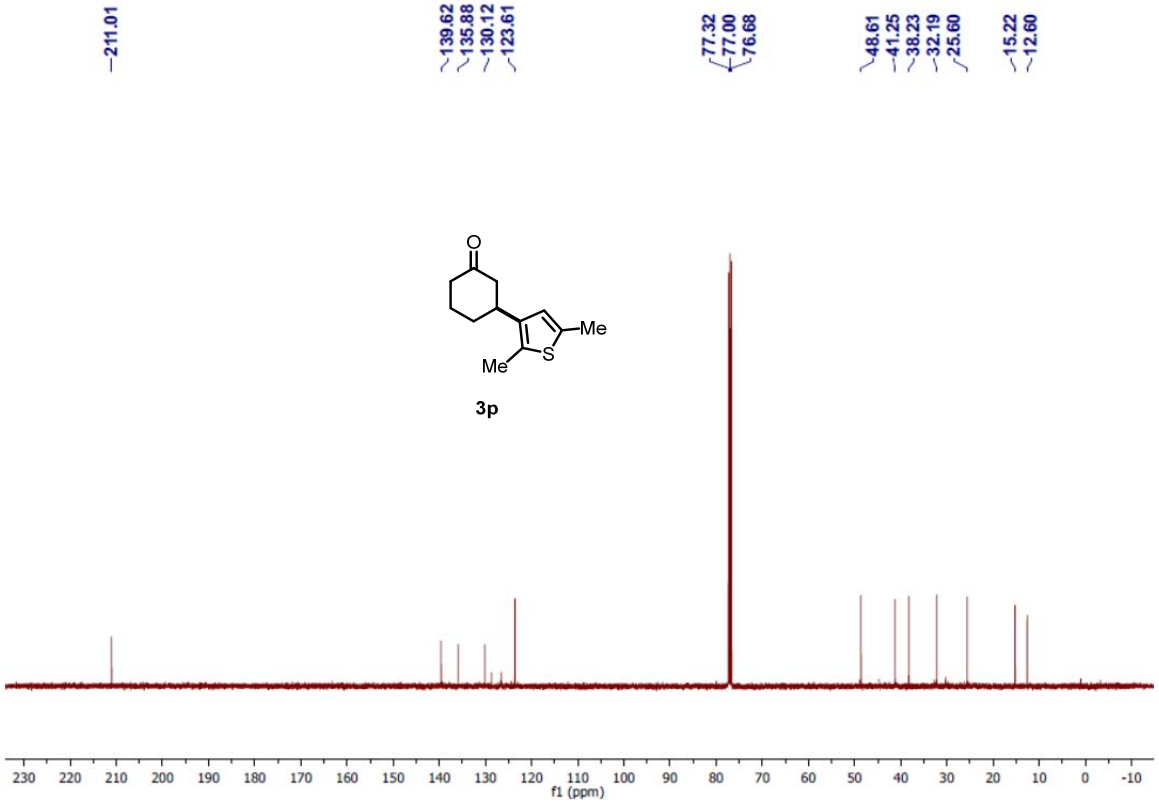
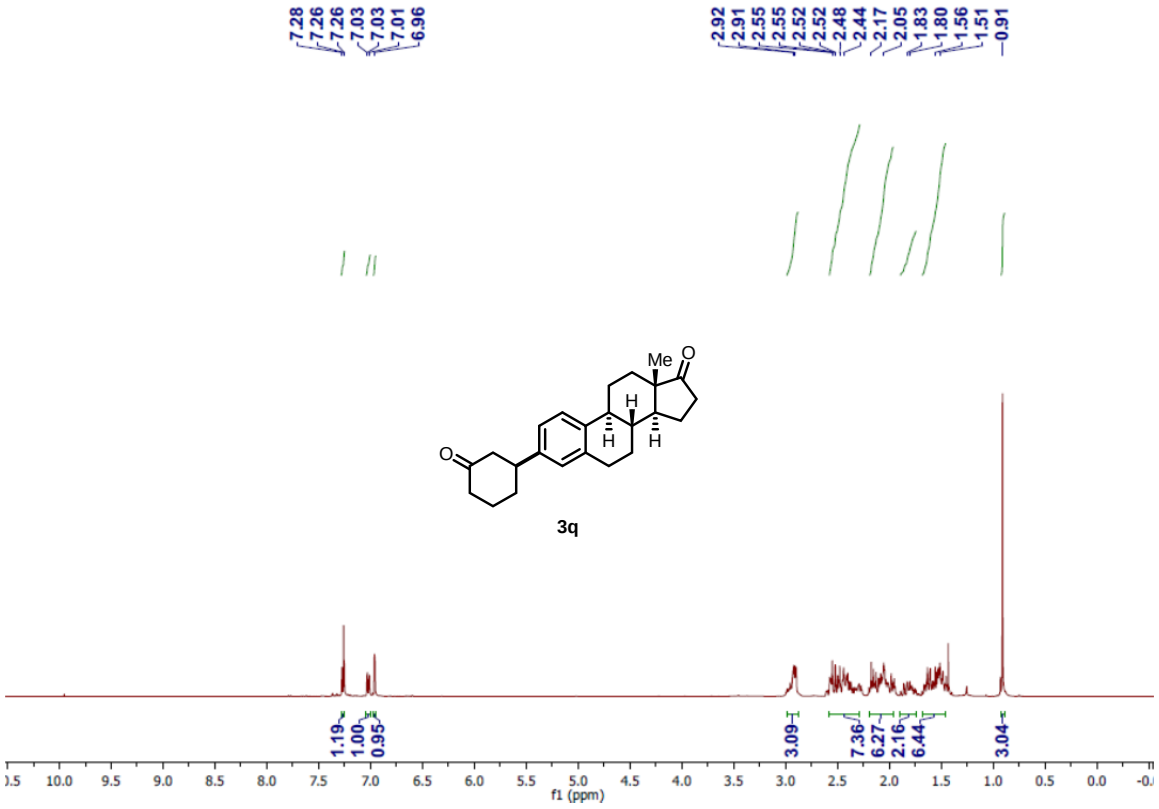
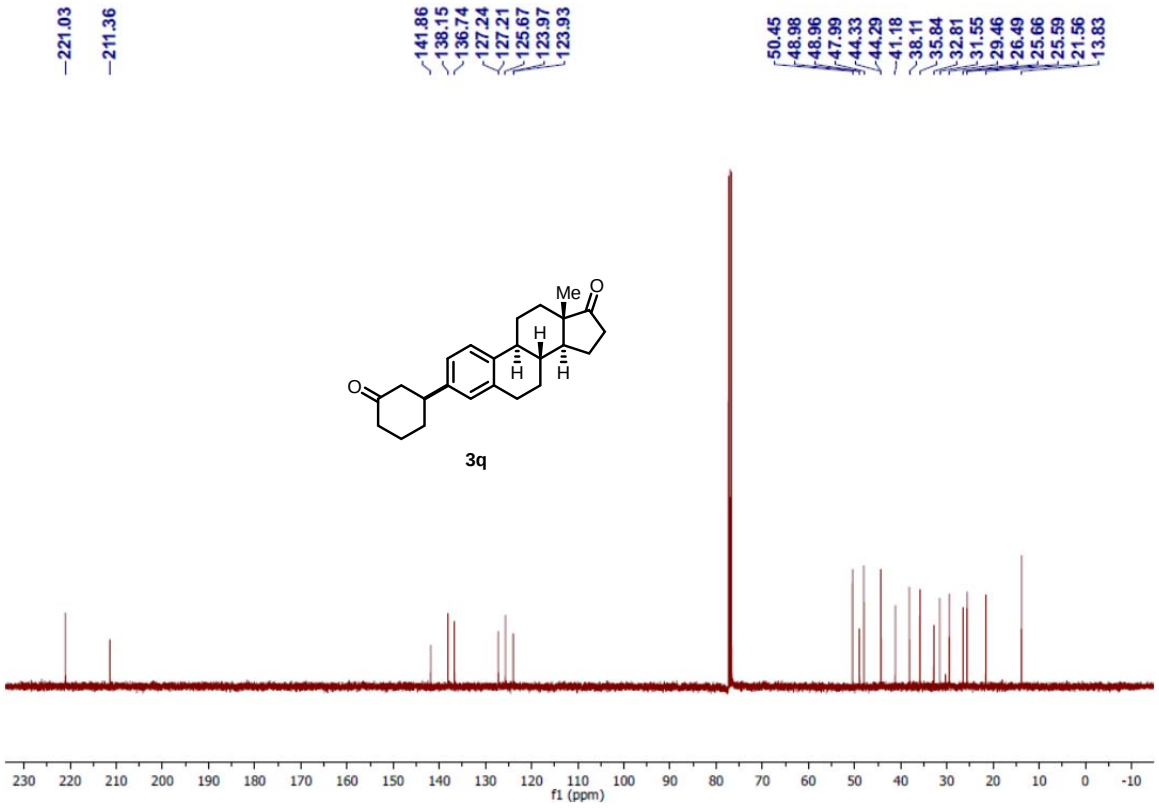
3.00
2.99
2.45
2.39
2.39
2.28
2.13
2.13
1.94
1.94
1.93
1.76
1.76
1.74
O
Me
Me
S
0.98
1.00
7.40
2.92
1.15
0.97
2.07
f1 (ppm)

3p


211.01
139.62
135.88
130.12
123.61
77.32
77.00
76.68
48.61
41.25
38.23
32.19
25.60
15.22
12.60
O
Me
S
Me
3p
f1 (ppm)


7.28
7.26
7.26
7.03
7.03
7.01
6.96
2.92
2.91
2.55
2.55
2.52
2.52
2.48
2.44
2.17
2.05
1.83
1.80
1.56
1.51
0.91
Me
O
H
H
H
O
3q
1.19
1.00
0.95
3.09
7.36
6.27
2.16
6.44
3.04
f1 (ppm)


221.03
211.36
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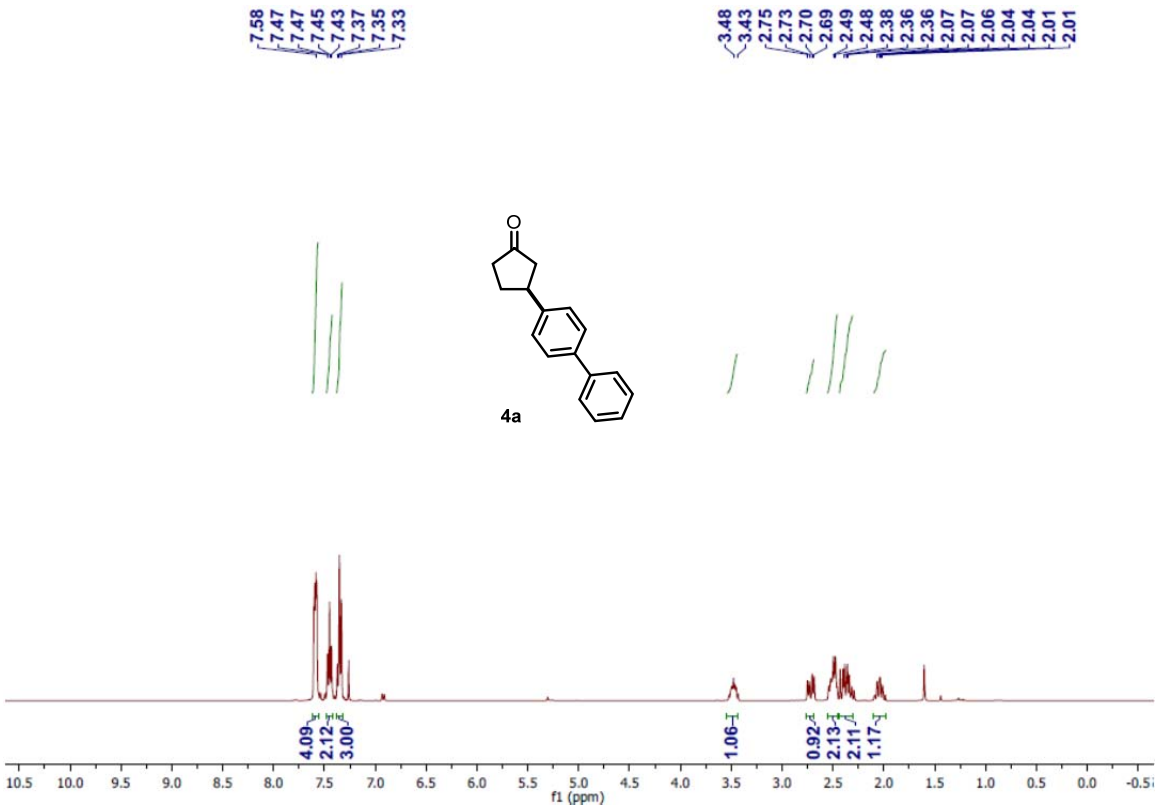
138.15
136.74
127.24
127.21
125.67
123.97
123.93
50.45
48.98
48.96
47.99
44.33
44.29
41.18
38.11
35.84
32.81
31.55
29.46
26.49
25.66
25.59
21.56
13.83
Me
O
H
H
H
O
3q
f1 (ppm)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7.47
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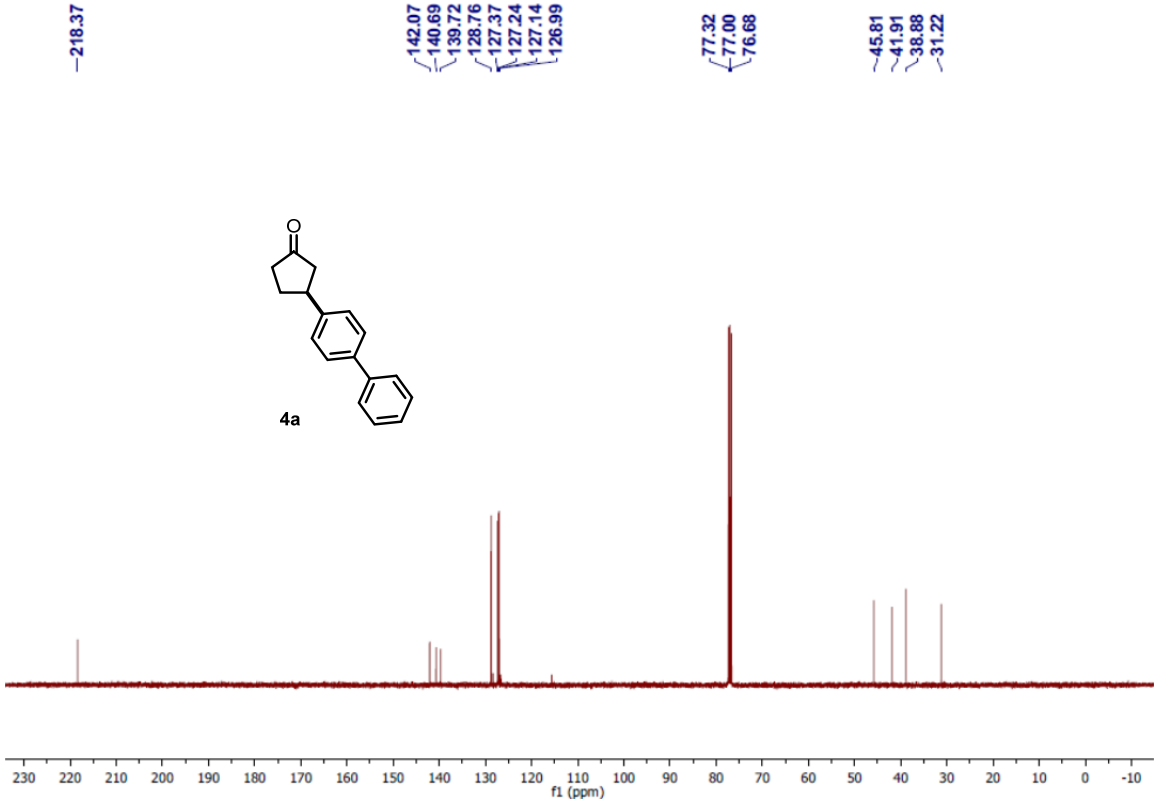
7.37
7.35
7.33
3.48
3.43
2.75
2.73
2.70
2.69
2.49
2.48
2.38
2.36
2.36
2.07
2.07
2.06
2.04
2.04
2.01
2.01
O
4a
4.09
2.12
3.00
1.06
0.92
2.13
2.11
1.17
f1 (ppm)


218.37
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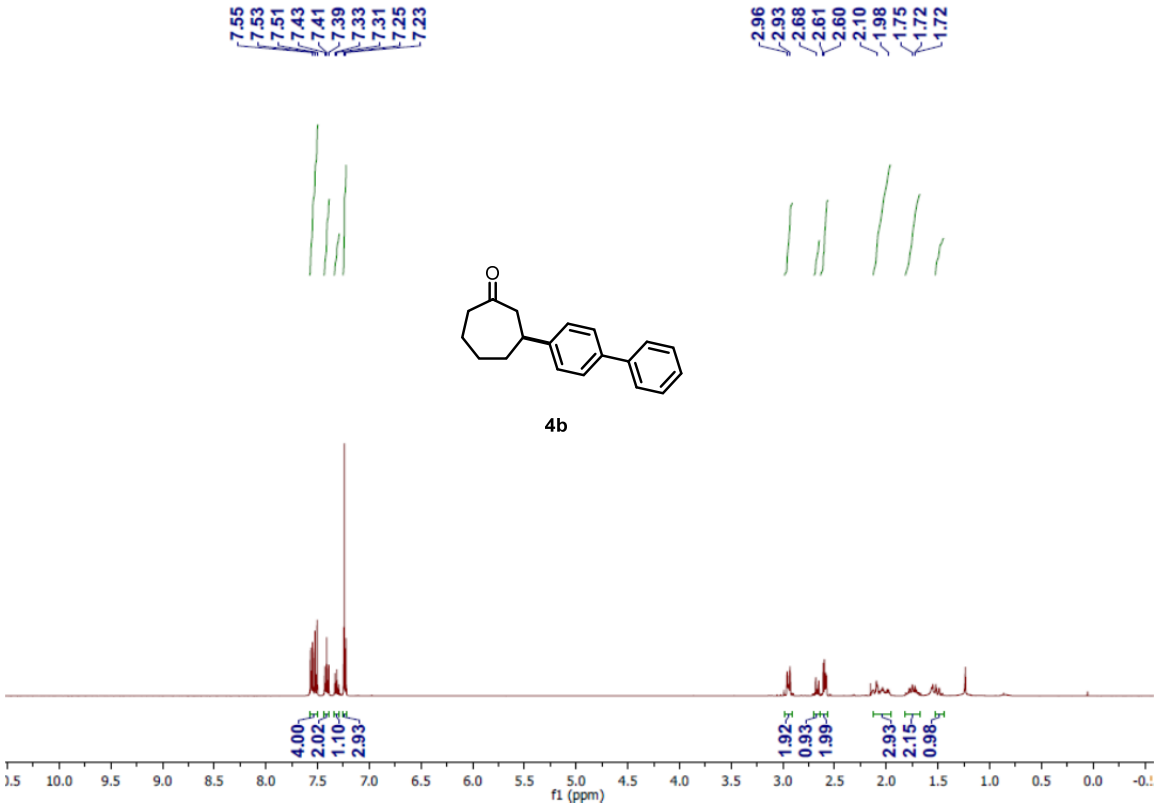
139.72
128.76
127.37
127.24
127.14
126.99
77.32
77.00
76.68
45.81
41.91
38.88
31.22
4a
f1 (ppm)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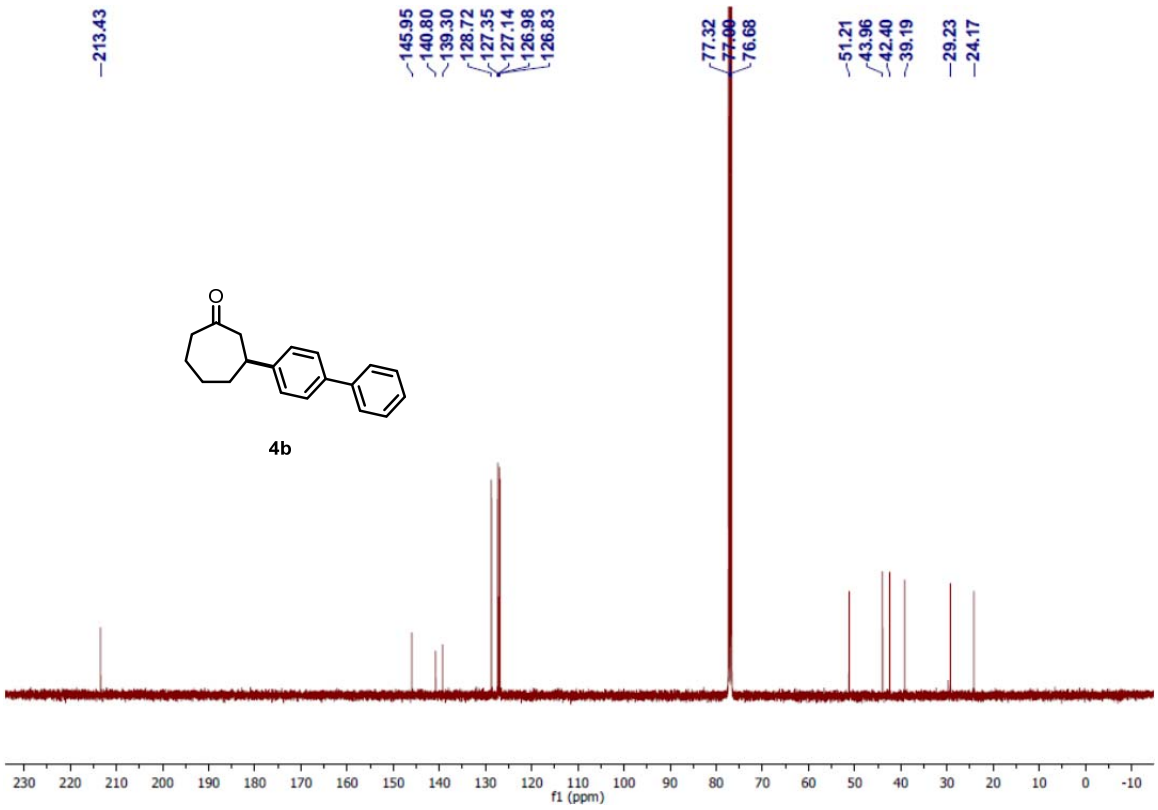
7.41
7.39
7.33
7.31
7.25
7.23
2.96
2.93
2.68
2.61
2.60
2.10
1.98
1.75
1.72
1.72
4b
4.00
2.02
1.10
2.93
1.92
0.93
1.99
2.93
2.15
0.98
f1 (ppm)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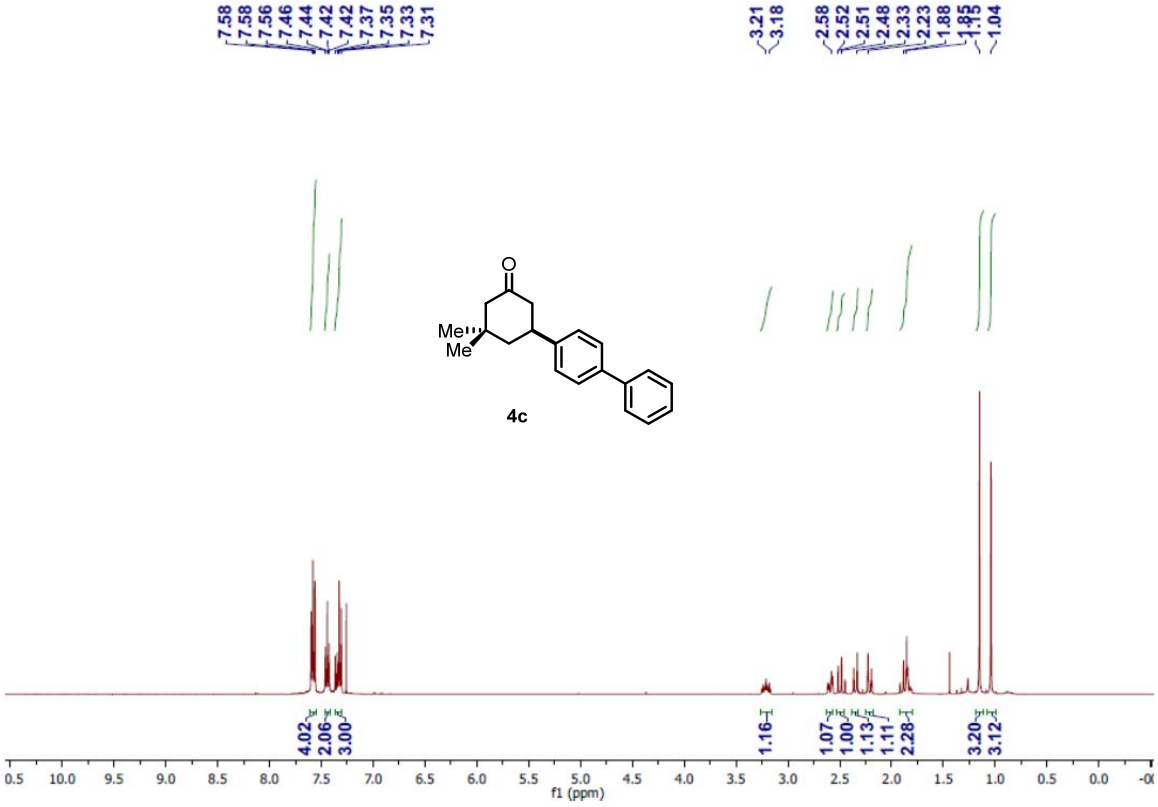
127.14
126.98
126.83
77.32
77.00
76.68
51.21
43.96
42.40
39.19
29.23
24.17
4b
f1 (ppm)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7.58
7.56
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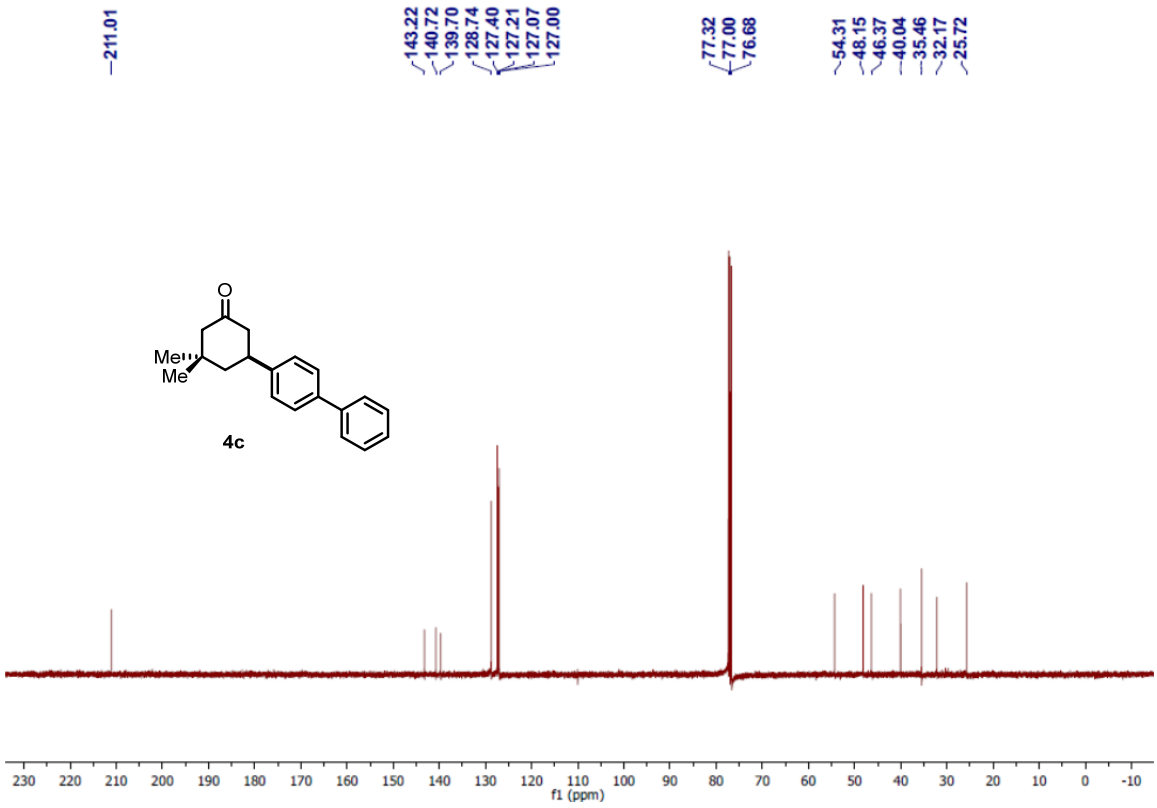
7.44
7.42
7.42
7.37
7.35
7.33
7.31
3.21
3.18
2.58
2.52
2.51
2.48
2.33
2.23
1.88
1.85
1.04
Me
Me
4c
4.02
2.06
3.00
1.16
1.07
1.00
1.13
1.11
2.28
3.20
3.12
f1 (ppm)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127.40
127.21
127.07
127.00
77.32
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76.68
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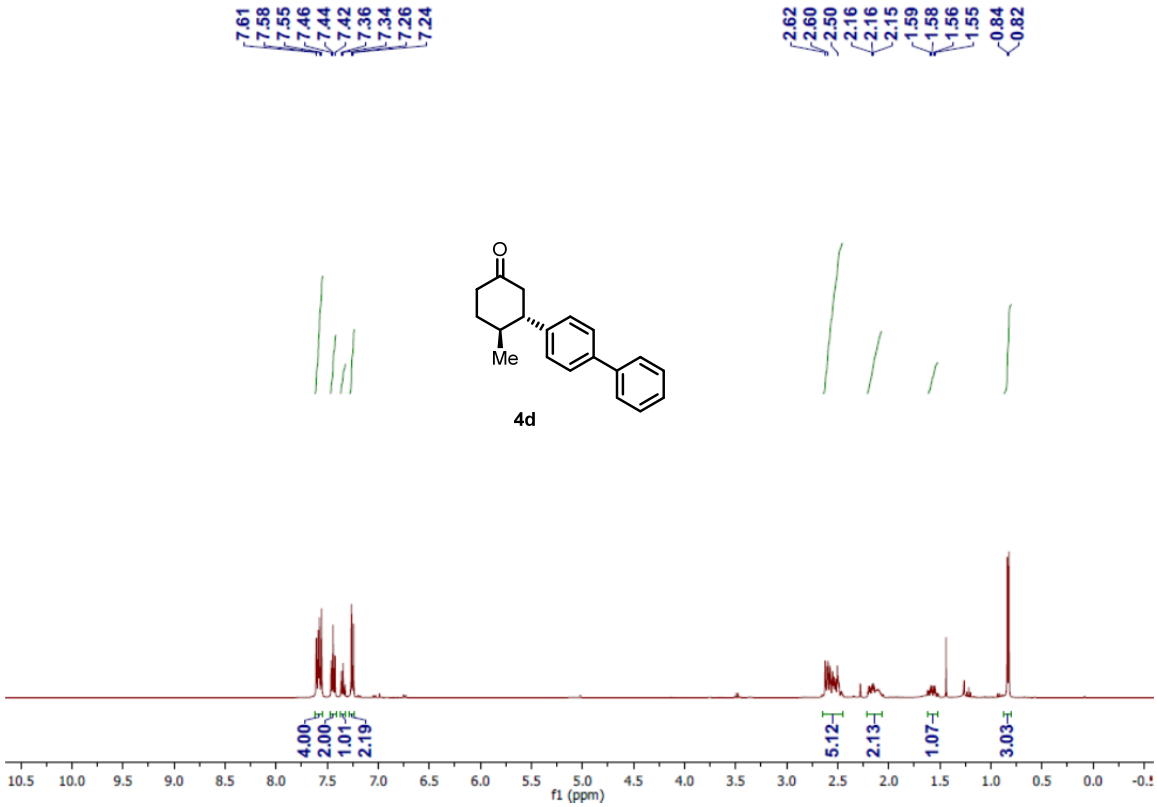
48.15
46.37
40.04
35.46
32.17
25.72
Me
Me
4c
f1 (ppm)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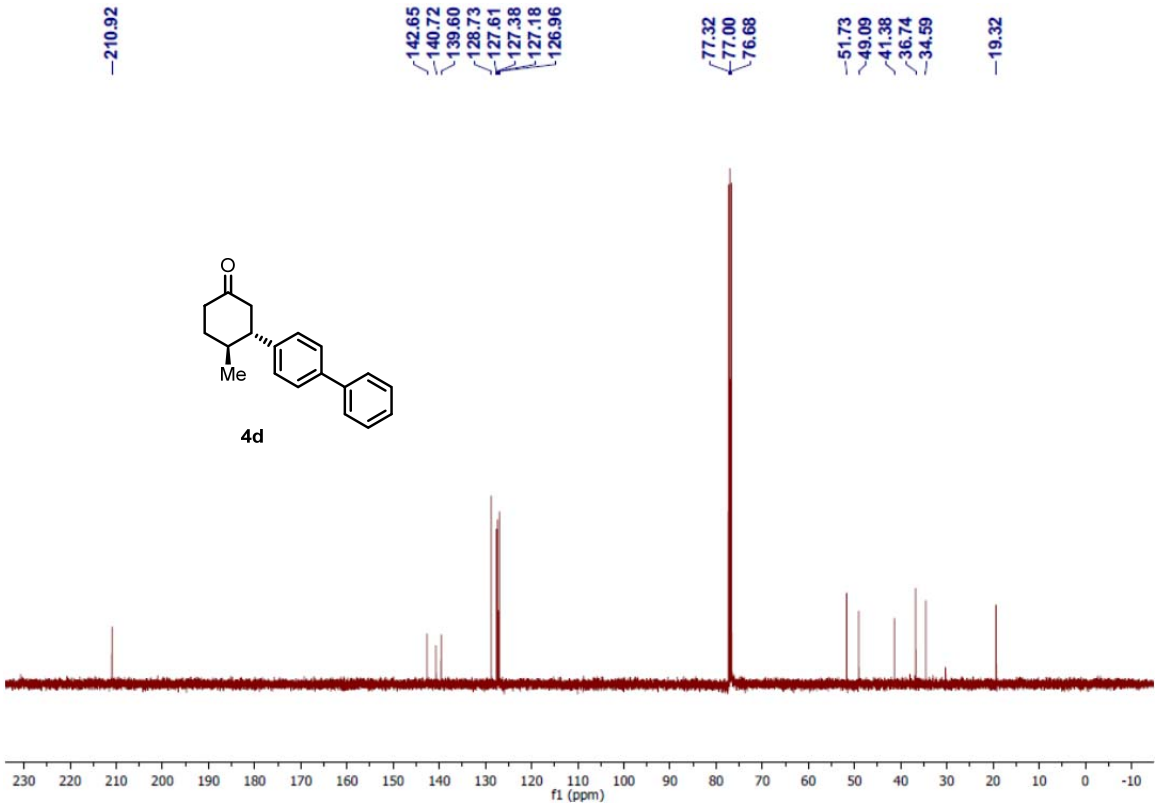
7.44
7.42
7.36
7.34
7.26
7.24
2.62
2.60
2.50
2.16
2.16
2.15
1.59
1.58
1.56
1.55
0.84
0.82
Me
4d
4.00
2.00
1.01
2.19
5.12
2.13
1.07
3.03
f1 (ppm)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127.38
127.18
126.96
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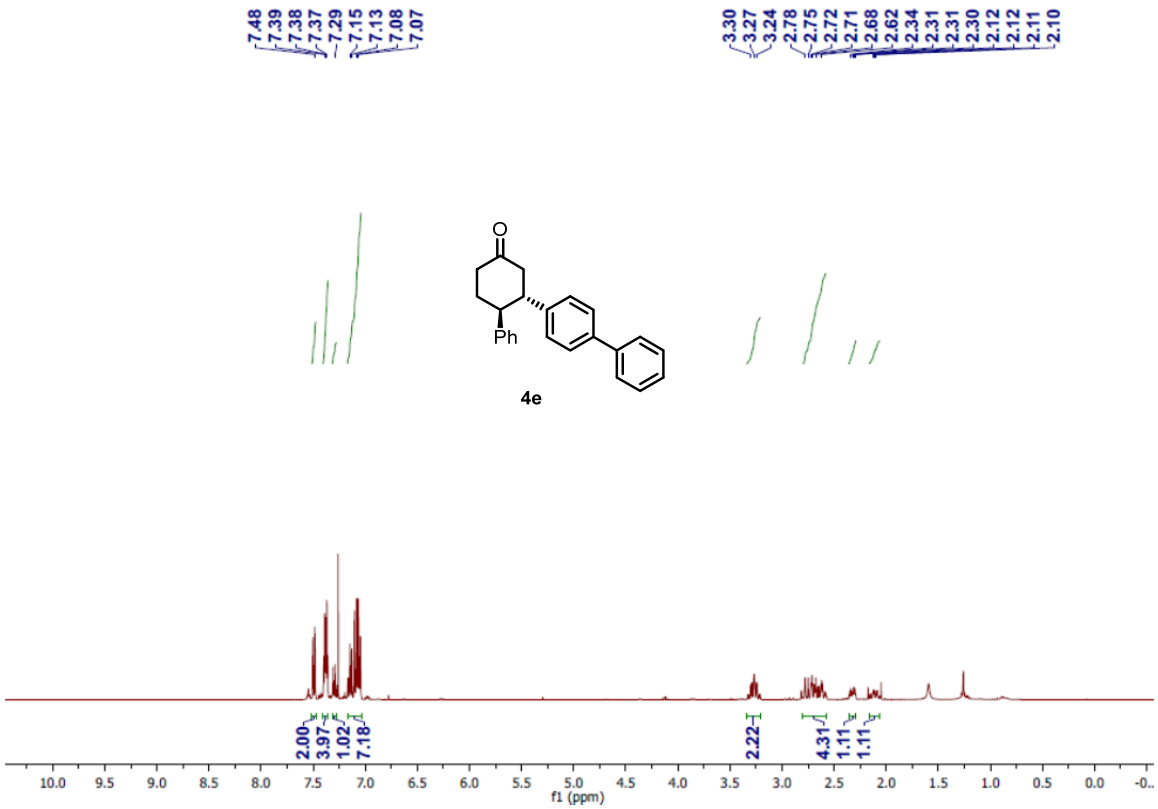
51.73
49.09
41.38
36.74
34.59
19.32
O
Me
4d
f1 (ppm)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7.15
7.13
7.08
7.07
3.30
3.27
3.24
2.78
2.75
2.72
2.71
2.68
2.62
2.34
2.31
2.31
2.30
2.12
2.12
2.11
2.10
O
Ph
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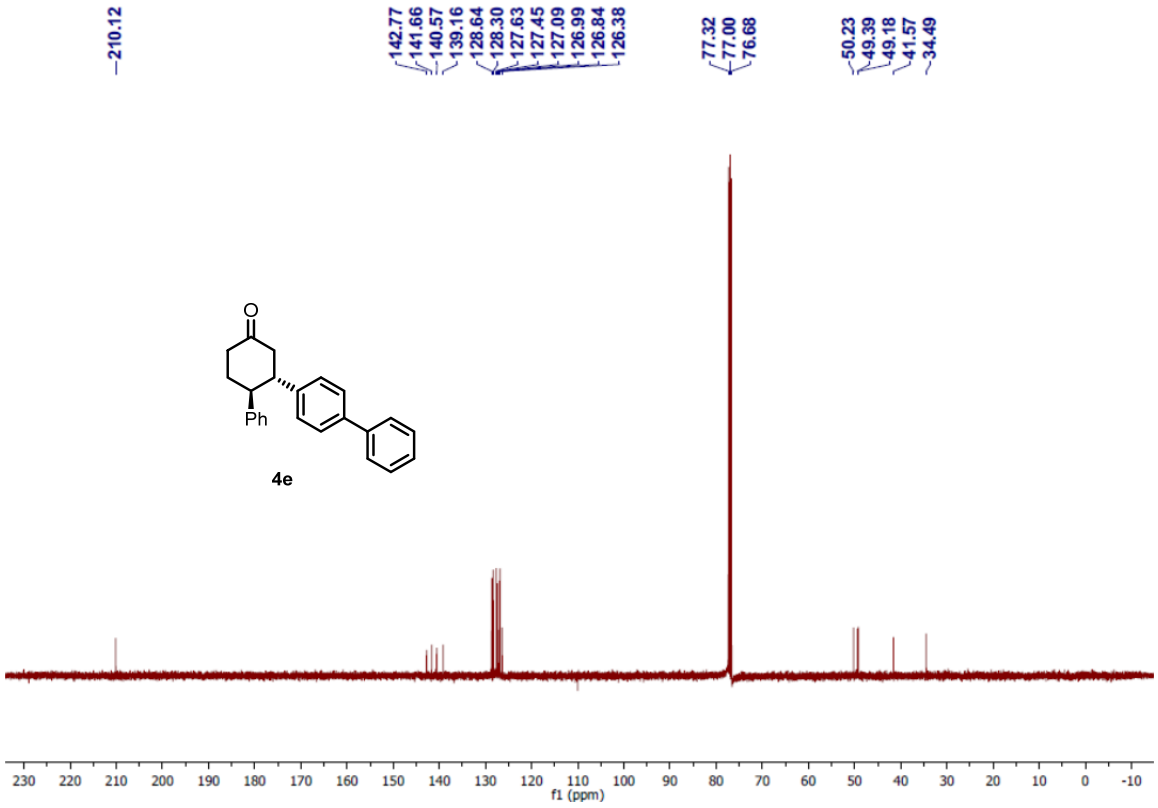
2.00
3.97
1.02
7.18
2.22
4.31
1.11
1.11
f1 (ppm)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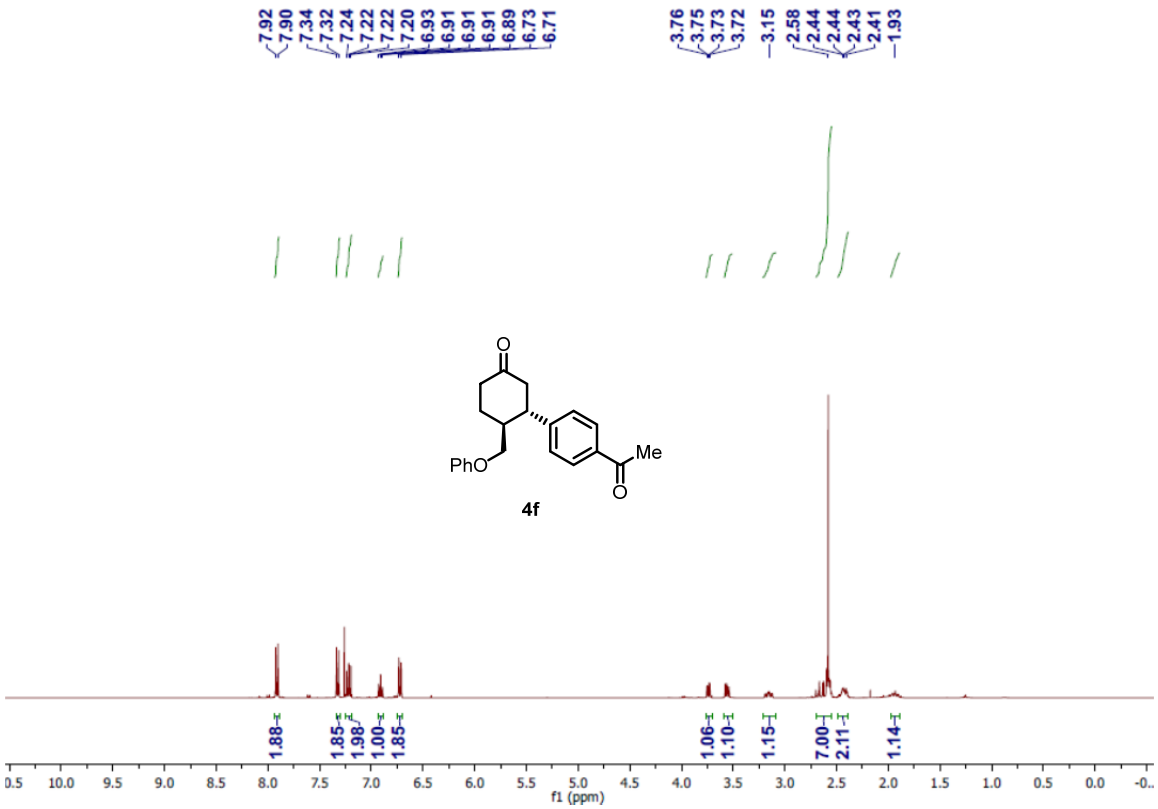
127.09
126.99
126.84
126.38
77.32
77.00
76.68
50.23
49.39
49.18
41.57
34.49
O
Ph
4e
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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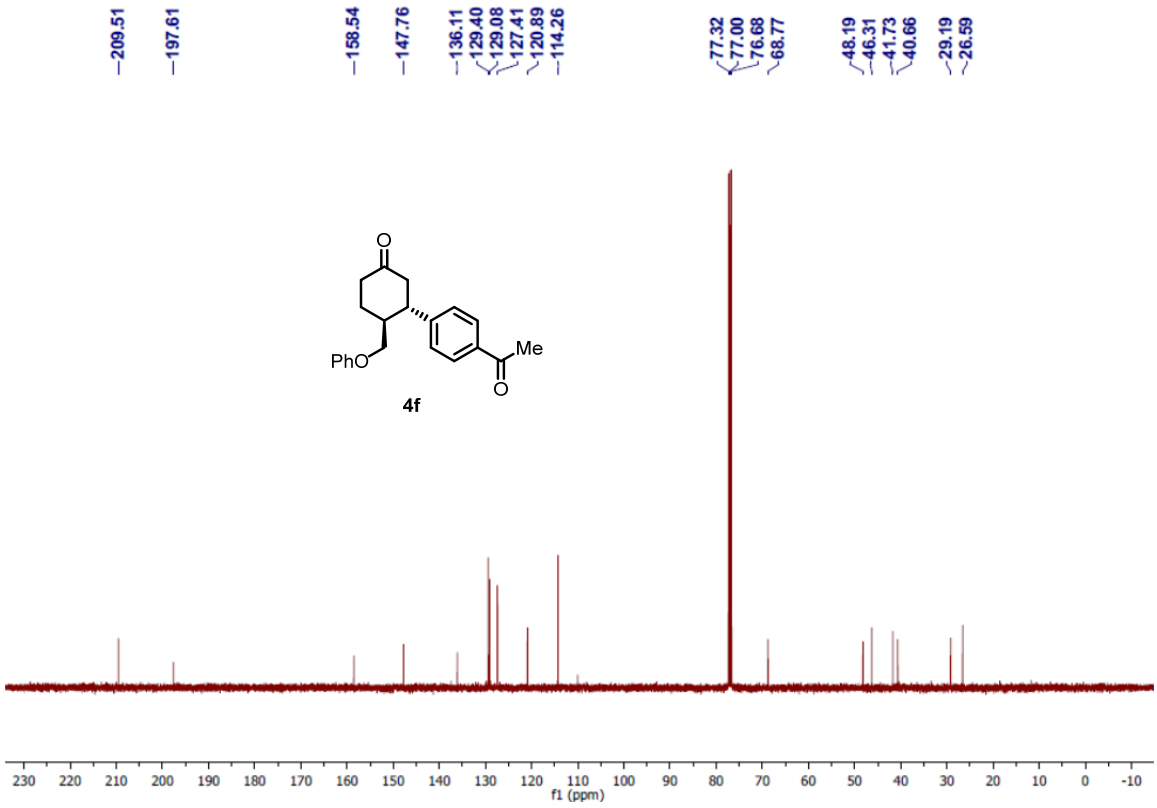
7.22
7.20
6.93
6.91
6.91
6.91
6.89
6.73
6.71
3.76
3.75
3.73
3.72
3.15
2.58
2.44
2.44
2.43
2.41
1.93
O
PhO
Me
O
4f
1.88
1.85
1.98
1.00
1.85
1.06
1.10
1.15
7.00
2.11
1.14
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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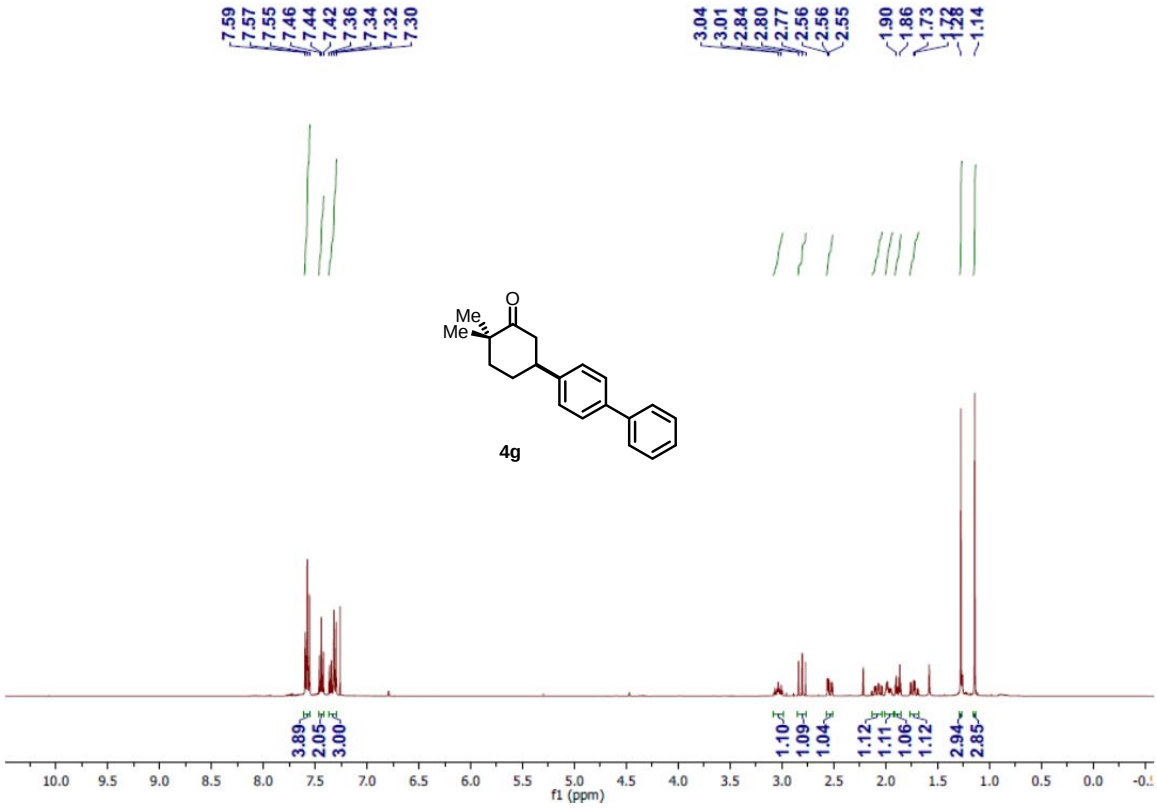
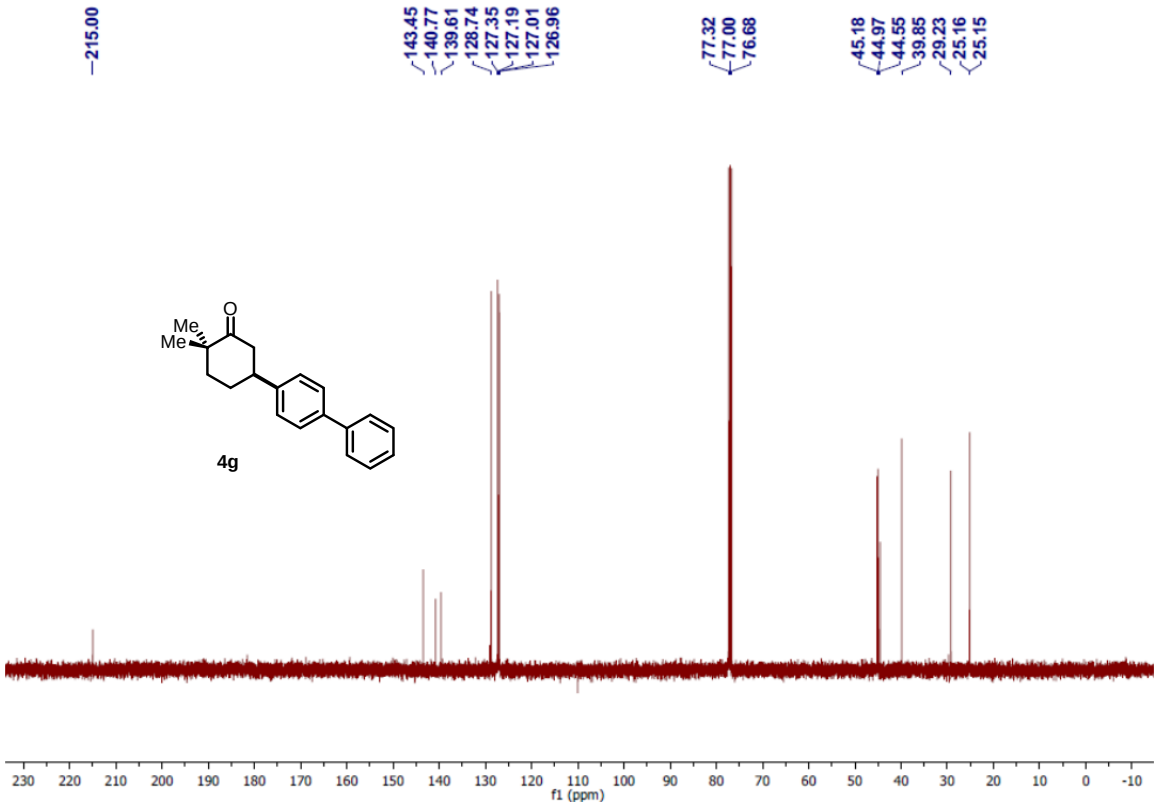
129.08
127.41
120.89
114.26
77.32
77.00
76.68
68.77
48.19
46.31
41.73
40.66
29.19
26.59
PhO
Me
O
O
4f
f1 (ppm)


7.59
7.57
7.55
7.46
7.44
7.42
7.36
7.34
7.32
7.30
3.04
3.01
2.84
2.80
2.77
2.56
2.56
2.55
1.90
1.86
1.73
1.28
1.14
Me
Me
O
4g
3.89
2.05
3.00
1.10
1.09
1.04
1.12
1.11
1.06
1.12
2.94
2.85
f1 (ppm)


215.00
143.45
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127.35
127.19
127.01
126.96
77.32
77.00
76.68
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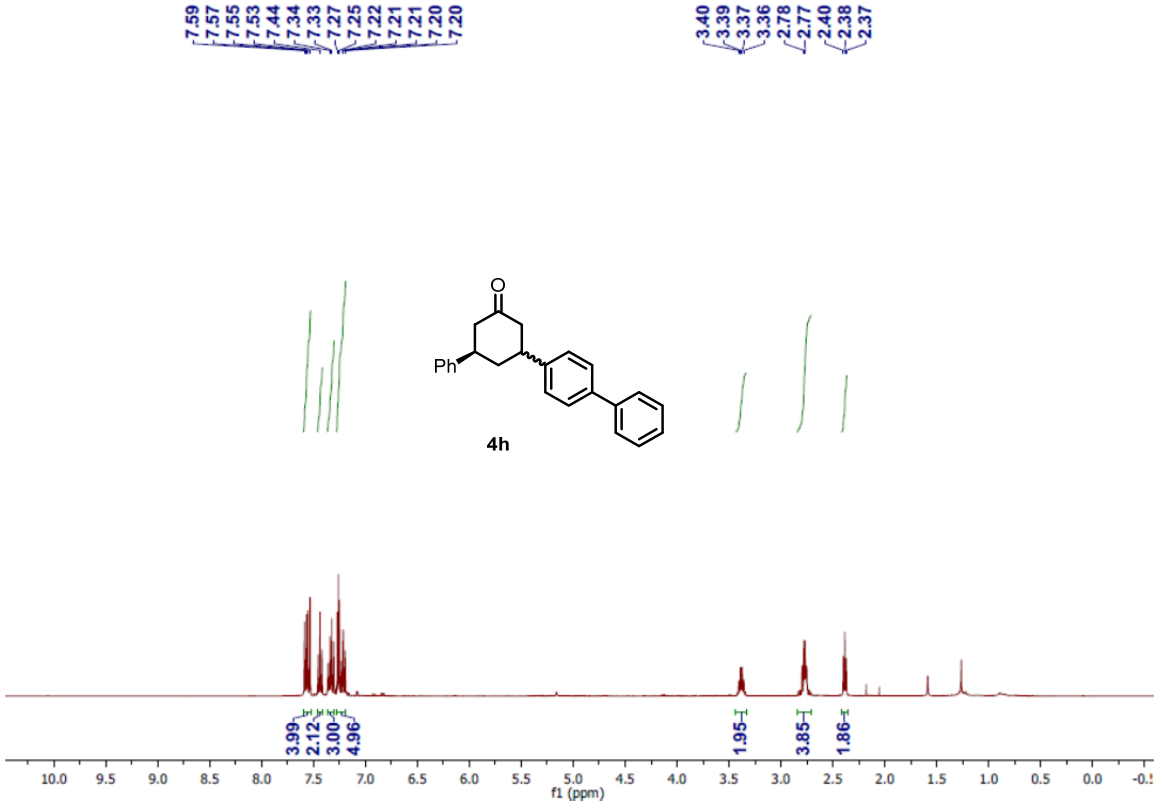
44.97
44.55
39.85
29.23
25.16
25.15
Me
Me
O
4g
f1 (ppm)


7.59
7.57
7.55
7.53
7.44
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7.33
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7.25
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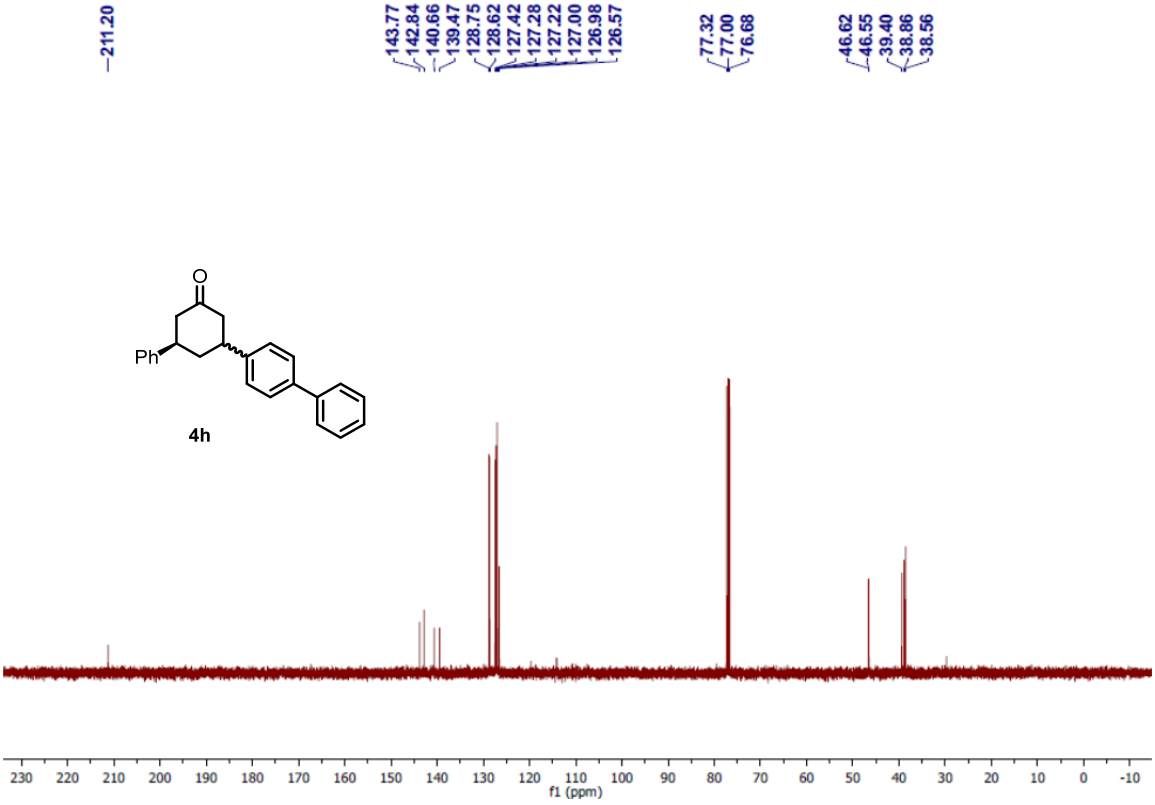
7.21
7.21
7.20
7.20
3.40
3.39
3.37
3.36
2.78
2.77
2.40
2.38
2.37
Ph
O
4h
3.99
2.12
3.00
4.96
1.95
3.85
1.86
f1 (ppm)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127.22
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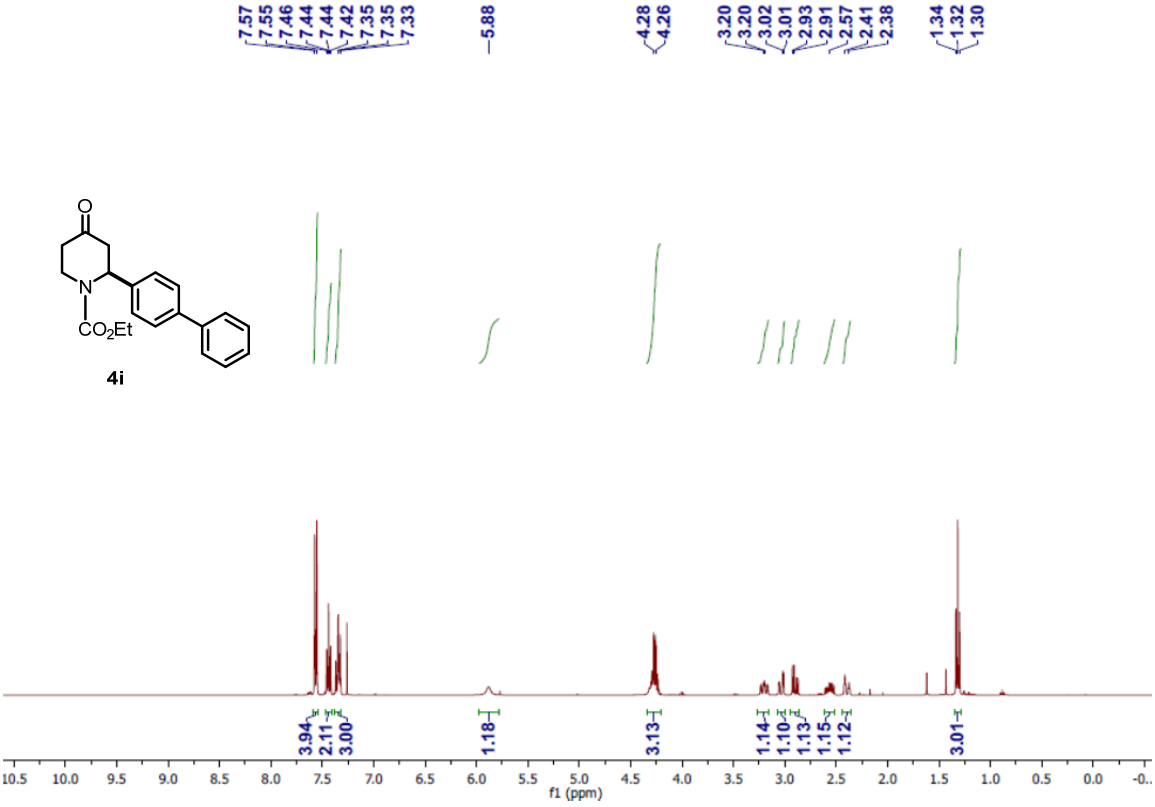
126.57
77.32
77.00
76.68
46.62
46.55
39.40
38.86
38.56
O
Ph
4h
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.46
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7.44
7.42
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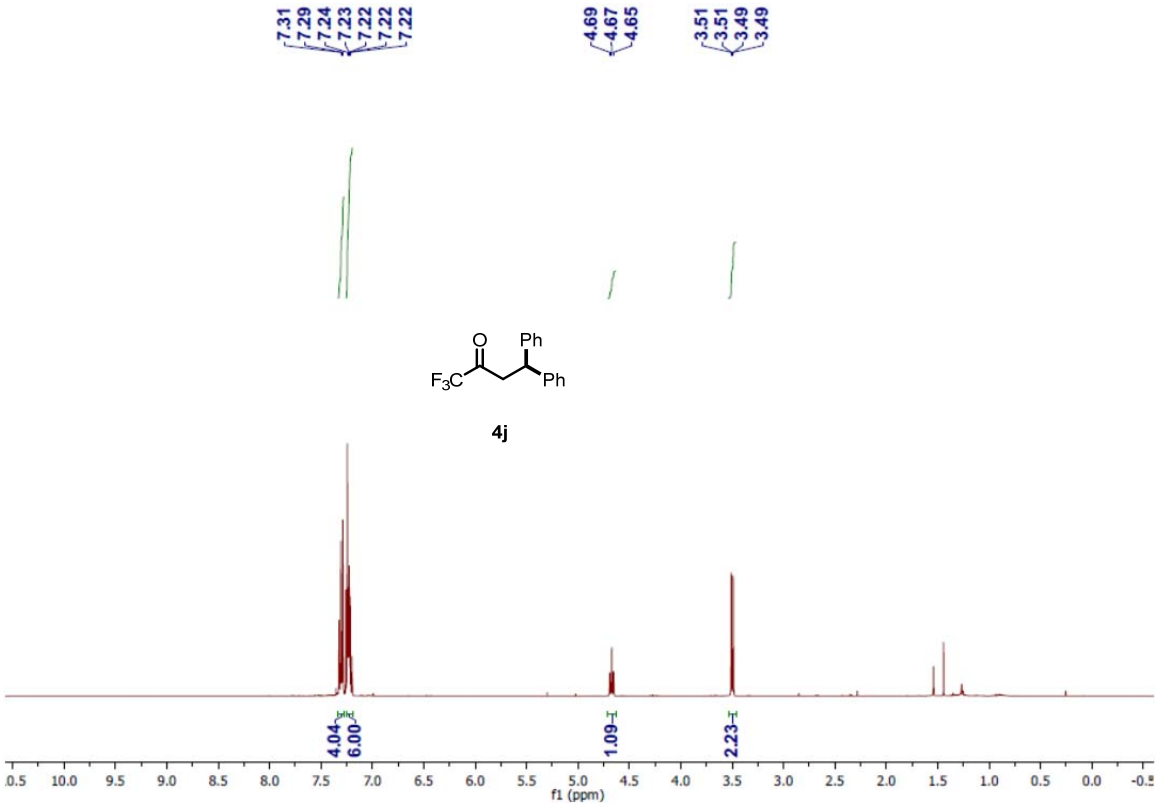
7.35
7.33
5.88
4.28
4.26
3.20
3.20
3.02
3.01
2.93
2.91
2.57
2.41
2.38
1.34
1.32
1.30
O
N
CO2Et
4i
3.94
2.11
3.00
1.18
3.13
1.14
1.10
1.13
1.15
1.12
3.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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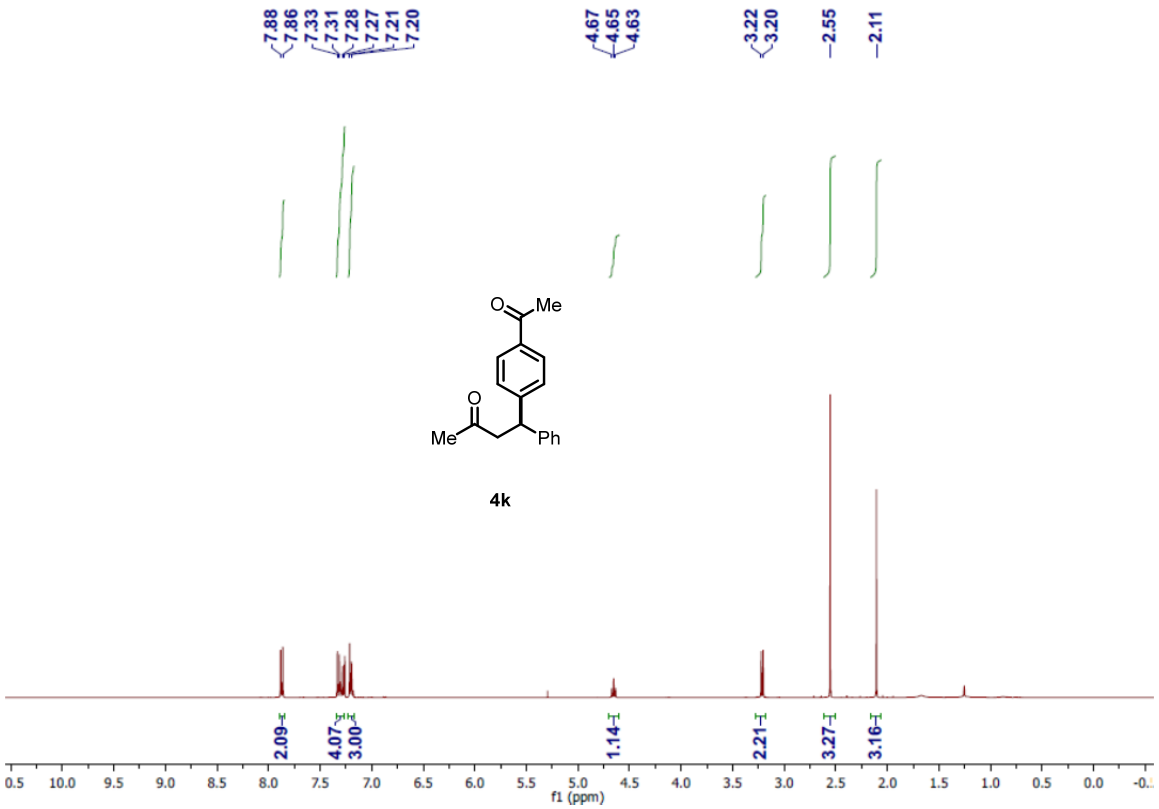
7.29
7.24
7.23
7.22
7.22
7.22
4.69
4.67
4.65
3.51
3.51
3.49
3.49
O
Ph
F3C
Ph
4j
4.04
6.00
1.09
2.23
f1 (ppm)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7.27
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4.67
4.65
4.63
3.22
3.20
2.55
2.11
O
Me
O
Me
Ph
4k
2.09
4.07
3.00
1.14
2.21
3.27
3.16
f1 (ppm)

VII. X-ray data

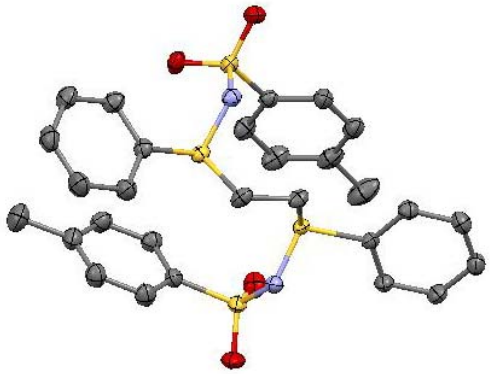

Figure S5. X-ray structure of racemic L1

Empirical formula	C28 H28 N2 O4 S4	
Formula weight	584.76	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	I 2/a	
Unit cell dimensions	a = 15.181(6) Å	α= 90°.
	b = 15.559(5) Å	β= 105.016(18)°.
	c = 23.696(7) Å	γ = 90°.
Volume	5406(3) $Å^3$	
Z	8	
Density (calculated)	1.241 Mg/m^3	
Absorption coefficient	0.390 mm^{-1}	
F(000)	2448.0	
Crystal size	0.73 x 0.27 x 0.20 mm^3	
Theta range for data collection	1.583 to 32.082°.	
Index ranges	-22<=h<=19, -22<=k<=23, -27<=l<=33	
Reflections collected	26405	
Independent reflections	7408 [R(int) = 0.0433]	
Completeness to theta = 32.082°	93.3 %	
Absorption correction	Multi-scan	
Max. and min. transmission	1.000 and 0.705	
Refinement method	Full-matrix least-squares on F^2	

Data / restraints / parameters	8824 / 0 / 345
Goodness-of-fit on F^2	1.065
Final R indices [I>2sigma(I)]	R1 = 0.0431, wR2 = 0.1080
R indices (all data)	R1 = 0.0521, wR2 = 0.1127
Largest diff. peak and hole	0.43 and -0.60 e.Å^{-3}

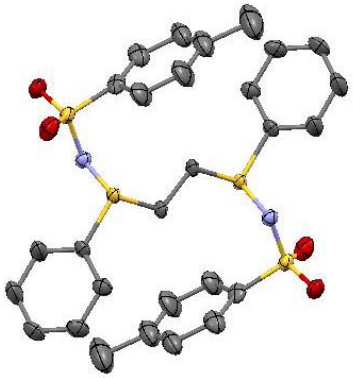

Figure S6. X-ray structure of meso L1

Empirical formula	C28 H28 N2 O4 S4	
Formula weight	584.76	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 6.5498(4) Å	α= 90°.
	b = 20.4037(13) Å	β= 100.469(3)°.
	c = 11.0725(9) Å	γ = 90°.
Volume	1455.10(18) Å^3	
Z	2	
Density (calculated)	1.335 Mg/m^3	
Absorption coefficient	0.362 mm^{-1}	
F(000)	612	
Crystal size	0.340 x 0.230 x 0.180 mm	
Theta range for data collection	3.317 to 27.498°.	
Index ranges	-8<=h<=8, -26<=k<=26, -14<=l<=14	
Reflections collected	20450	
Independent reflections	3345 [R(int) = 0.0550]	

Completeness to theta = 25.242°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00 and 0.848
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3345 / 210 / 265
Goodness-of-fit on F^2	1.023
Final R indices [I>2sigma(I)]	R1 = 0.0359, wR2 = 0.0833
R indices (all data)	R1 = 0.0503, wR2 = 0.0935
Extinction coefficient	n/a
Largest diff. peak and hole	0.417 and -0.330 e.Å^{-3}

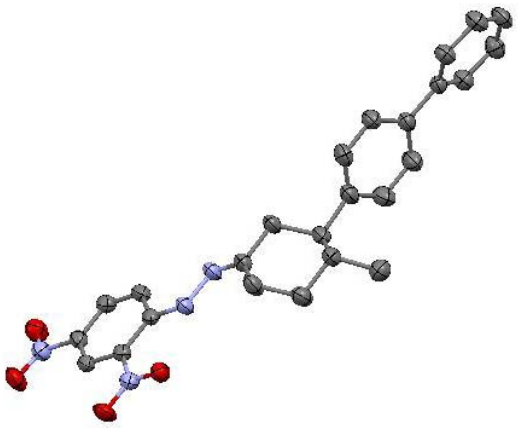

Figure S7. X-ray structure of 4d/DNP adduct

Empirical formula	C25 H24 N4O4	
Formula weight	444.48	
Temperature	100(2) K	
Wavelength	1.5418 Å	
Crystal system	monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 20.3743(10) Å	α= 90°.
	b = 5.7348(4) Å	β= 102.342(6)°.
	c = 19.2424(15) Å	γ = 90°.
Volume	2196.4(3) Å^3	
Z	4	
Density (calculated)	1.344 Mg/m^3	
Absorption coefficient	0.760 mm^{-1}	

F(000)	936
Crystal size	0.190 x 0.130 x 0.024 mm
Theta range for data collection	4.443 to 76.290°.
Index ranges	-25<=h<=25, -7<=k<=7, -23<=l<=23
Reflections collected	22364
Independent reflections	4531 [R(int) = 0.0248]
Completeness to theta = 67.680°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00 and 0.848
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4531 / 57 / 327
Goodness-of-fit on F^2	1.058
Final R indices [I>2sigma(I)]	R1 = 0.0460, wR2 = 0.1146
R indices (all data)	R1 = 0.0500, wR2 = 0.1179
Extinction coefficient	n/a
Largest diff. peak and hole	0.391 and -0.494 e.$Å^{-3}$

VIII. References

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