An Assay for Aryl Radicals Using BHAS Coupling ESI file (Supporting Information)

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Contents

General Information

All reagents and solvents were obtained from commercial suppliers and were used without further purification unless mentioned otherwise. Where used, diethyl ether and THF were dried using a Pure-Solv 400 solvent purification system (Innovative Technology Inc., USA). Where stated, reactions were prepared in a glovebox supplied by Innovative Technology Inc., USA, which is operated with a nitrogen atmosphere.

Analysis Techniques

Thin Layer Chromatography (TLC) was performed on silica gel pre-coated aluminium plates (60 Å, F254 UV indicator) purchased from Merck. The thin layer chromatograms were analysed by UV (254 nm, UVP mineralight UVG-11 lamp) and staining either with basic $KMnO_4$ [$KMnO_4$ (6 g), K_2CO_3 (40 g), NaOH (5 mL, 10% w/w) in water (600 mL)] or an ethanolic solution of phosphomolybdic acid [phosphomolybdic acid hydrate (10 g) in ethanol (100 mL)].

Flash Column Chromatography purification was performed with 35-70 µm particle size silica gel 60 Å (200-400 mesh) purchased from Prolabo.

Melting points were determined using a Gallenkamp Griffin Melting Point Apparatus.

NMR spectroscopy was performed using Bruker spectrometers, either: an AV3-400 and AV3-400Nano. ^{1}H NMR and ^{13}C NMR spectra were recorded on these spectrometers operating at 400 MHz and 100 MHz, respectively. All spectral data were acquired at 295 K. Chemical shifts (δ) are quoted in parts per million (ppm) relative to the following residual solvent peaks, δ_H 7.26 and δ_C 77.16 for $CDCl_3$ and δ_H 1.72 and δ_C 67.21 for THF-d_8. Coupling constants (*J*) are reported in Hertz (Hz) to the nearest 0.1 Hz. The multiplicity abbreviations used are s (singlet), sept (septet), m (multiplet) and broad (br). In experiments involving C_6D_6 or KO*t*Bu-d_9, workup was performed before ^{2}H NMR spectra were acquired. This involved filtration through a short celite pad, followed by evaporation to remove solvent and HO*t*Bu-d_9.

Infrared (IR) spectra were obtained on a Shimadzu IRAffinity-1 FTIR-ATR spectrometer instrument.

GCMS spectra were obtained on an Agilent 7890A GC system coupled to a 5975C inert XL EI/CI MSD triple axis-mass detector. Electron impact (EI) ionisation was utilised, specifically the method EI320. The column temperature was 320 °C, and the carrier gas was helium with a flow rate of 1 mL/min and was operated in splitless mode. GCMS traces start a few minutes after injection – this is so that the solvents etc are not observed in the chromatography traces and don't over-saturate the mass detector.

GCFID analyses were carried out using an Agilent 7890A gas chromatograph fitted with an Agilent HP5 column (30 m x 0.25 mm x 0.25 µm). Helium was used as the carrier gas (2.0 mL/min flow rate). The injector temperature was 320 °C and was operated in splitless mode. GCFID traces start a few minutes

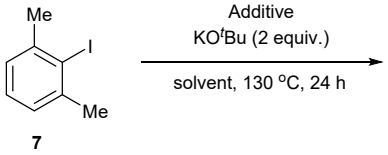
after injection – this is so that the solvents etc are not observed in the chromatography traces and don't over-saturate the mass detector.

Experimental

Assigned peaks in the GCFID spectra have been quantitatively calibrated (for calibrations see pages S34 – S38. During the investigation, the column was changed on the GCFID instrument, and so the retention times for all peaks shifted. A repeat calibration for all calibrated compounds was carried out.

General Procedures

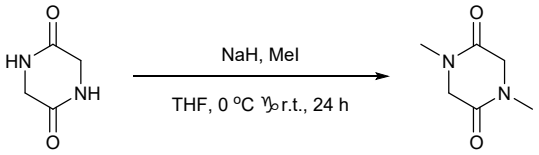
General Procedure A - Reactions of 2-Iodo-m-xylene with KO^{t}Bu



7

To an oven-dried microwave vial, primed with a stirrer bar, in a glovebox was added 2-iodo-*m*-xylene (102 µL, 0.7 mmol, 1 equiv.), an additive, KO^{t}Bu (157 mg, 1.4 mmol, 2 equiv.) and solvent(s) (7 mL) with the vial subsequently sealed and stirred at 130 °C for 24 h. Once complete, the crude mixture was allowed to cool to room temperature and dodecane (23 µL) was added as a GC standard and mixed. A 100 µL aliquot of the crude mixture was then analysed by both GCMS and GCFID.

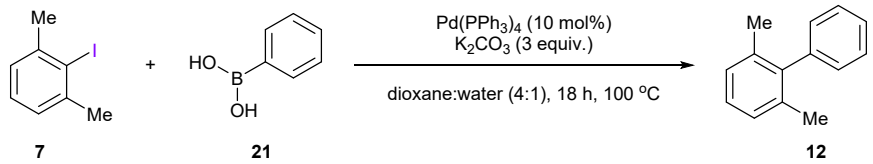
*Preparation of 1,4-Dimethylpiperazine-2,5-dione **16***



20 **16**

To a solution of piperazine-2,5-dione **20** (500 mg, 4.4 mmol, 1 equiv.) in dry THF (10 mL) at 0 °C was added NaH (252 mg, 10.6 mmol, 2.4 equiv.) and the mixture stirred for 30 min. Iodomethane (0.7 mL, 11 mmol, 2.5 equiv.) was then added to the mixture at 0 °C and the reaction left to stir for 24 h, whilst being allowed to warm to room temperature. Once complete, the reaction was quenched with water before being extracted into DCM and concentrated *in vacuo*. The aqueous layer was then concentrated *in vacuo* before being diluted with water and extracted into DCM and again concentrated *in vacuo*, to produce 1,4-dimethylpiperazine-2,5-dione **16** (120 mg, 0.85 mmol, 20%) as a white powder. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.98 (s, 4H), 2.98 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.1, 51.6, 33.2. **ATR-IR** ν_{max} (neat)/cm^{-1} 2967, 2926, 2872, 1618, 1498, 1338, 1251. ***m/z*** (EI) 142 (M^+, 35), 113 (9), 85 (14), 57 (100). **M.p.** 137-140 °C (lit: 136-139 °C).[31] The data for this compound are consistent with those reported in the literature.

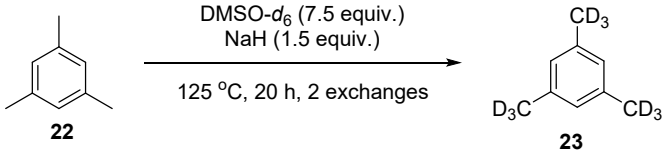
*Preparation of 2,6-Dimethylbiphenyl **12** for calibration experiments*



7 **21** **12**

To an oven-dried microwave vial, primed with a stirrer bar, was added 2-iodo-*m*-xylene **7** (94 µL, 0.65 mmol, 1 equiv.), phenylboronic acid **21** (95 mg, 0.78 mmol, 1.2 equiv.), K_2CO_3 (269 mg, 1.95 mmol, 3 equiv.), $Pd(PPh_3)_4$ (81 mg, 0.07 mmol, 10 mol%) and a dioxane/water (5 mL, 4:1). The vial was subsequently sealed and stirred for 18 h at 100 °C. Once complete, the reaction mixture was diluted with water and extracted with DCM, before being concentrated *in vacuo*. Purification by column chromatography (eluent 100% hexane) afforded 2,6-dimethylbiphenyl **12** as a colourless oil (82 mg, 0.45 mmol, 69%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 – 7.40 (m, 2H), 7.37 – 7.31 (m, 1H), 7.20 – 7.09 (m, 5H) 2.04 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.9, 141.1, 136.1, 129.0, 128.4, 127.3, 127.0, 126.6, 20.8. **ATR-IR** ν_{max} (neat)/cm^{-1} 2920, 2851, 1460, 1377, 1186. ***m/z*** (EI) 182 (M^+, 85), 167 (100), 89 (14), 63 (6), 55 (6). The data for this compound are consistent with those reported in the literature.[32]

*Synthesis of mesitylene-d_9 **23** [33]*



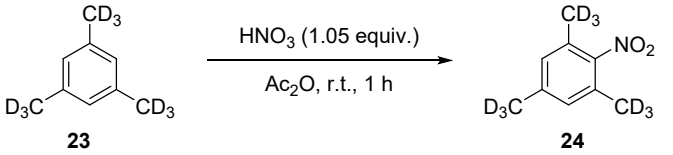
22 **23**

54% yield
96% D incorporation

NaH (540 mg, 22.5 mmol) was added to a 3-necked round-bottomed flask (100 mL) and evacuated. The flask was placed under Ar, then mesitylene **22** (1.80 g, 15 mmol) and DMSO-d_6 (9.47 g, 113 mmol) were added *via* syringe and stirred to give a pale slurry. A condenser was fitted to the flask under Ar flow, and the reaction was slowly heated to 125 °C, gradually changing to a dark brown. After 20 h, the reaction was allowed to cool to room temperature. The volatiles were then removed by vacuum distillation at 100 °C and collected in a trap cooled in liquid nitrogen. This distillate was washed with water (4 x 25 mL) and the upper mesitylene layer was recovered. The exchange was repeated with fresh DMSO-d_6 and NaH. After vacuum distillation and washing with H_2O, the product **23**-d_9 was recovered as a pale-yellow liquid (1.06 g, 8.18 mmol, 54%). Analysis by ^{1}H NMR showed a deuterium incorporation of 96%. ^{2}H NMR showed deuterium incorporation on the methyl groups only. ^{2}H NMR spectrum shows deuterium incorporation in mesitylene-d_9 (a trace of a minor peak at 2.07 ppm likely arises from mesitylene-d_8). **^{1}H NMR** (400 MHz, C_6D_6) δ 6.72 (s, 3H), 2.15 – 2.12 (m, 0.4 H). **^{13}C NMR** (101 MHz, C_6D_6) δ 137.5, 127.4, 21.1 – 19.9 (m). **^{2}H NMR** (61 MHz, C_6H_6) δ 2.09 (br), 2.07 (br). **IR**

ν_{max}/cm^{-1} (neat): 3013, 2924, 2230, 2203, 2127, 2064, 1603, 1443. ***m/z*** (EI): 129.1 [M]$^+$, 111.1, 96.1, 81.1.

Synthesis of nitromesitylene-d_9 ***24*** [34]

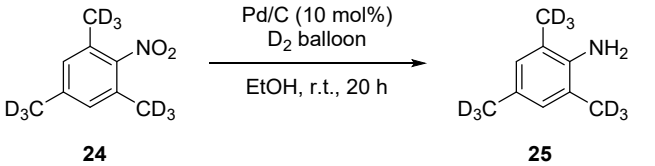


23 → **24**

81% yield
95% D incorporation

A solution of conc. HNO_3 (0.4 mL, 3.7 mmol) and acetic anhydride (2.0 mL) was cooled in an ice bath and added dropwise to a stirred solution of **23**-d_9 (426 mg, 3.3 mmol) and acetic anhydride (1.0 mL) under air, also cooled in an ice bath, quickly turning the solution from colourless to orange. After addition, the solution was allowed to warm to room temperature and stirred for a further 1 h. An aqueous K_2CO_3 solution was added until slightly basic, and then the product was precipitated in ice-water. The precipitate was vacuum filtered, washed with more ice-water and dried *in vacuo* yielding pale yellow crystals of **24** (465 mg, 2.67 mmol, 81%). A signal at 1724 cm^{-1} in the IR spectrum indicates that traces of acetic acid are present in the product. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.91 (s, 2H), 2.28 (quin, 2.2 Hz, 0.15 H), 2.25 (quin, 2.2 Hz, 0.27 H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.7, 129.0, 128.9, 20.0 – 19.3 (m), 16.8 – 15.8 (m). **^{2}H NMR** (61 MHz, $CHCl_3$) δ 2.29 (s, 3D), 2.26 (s, 6D) **IR** ν_{max}/cm^{-1} (neat): 2924, 2870, 2853, 2233, 2112, 2064, 1724, 1599, 1508, 1364. ***m/z*** (EI): 174.1 ([M]$^+$), 156.1, 144.1, 128.1, 96.1, 81.0.

Synthesis of d_9-1,3,5-trimethylaniline ***25***



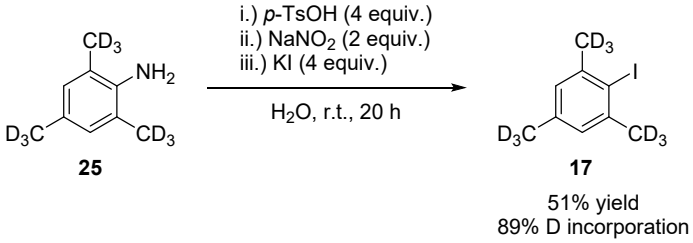
24 → **25**

82% yield
89% D incorporation

Nitroarene **24** (465 mg, 2.67 mmol) and 20% Pd/C (188 mg, 0.267 mmol) were added to a 3-necked round-bottomed flask (250 mL) and evacuated. The flask was placed under Ar flow and degassed ethanol (20 mL) was added. With vigorous stirring, the Ar atmosphere was replaced with D_2 from a balloon. The reaction was left to stir vigorously for 20 h under an atmosphere of D_2. The reaction mixture was then filtered through a short plug of Celite, washed with EtOAc and then concentrated *in vacuo* yielding **25** as a pale-yellow oil (301 mg, 2.19 mmol, 82%). ^{1}H NMR showed a fall in deuterium incorporation to 89%, and also showed that the *ortho*-methyl groups are more labelled than the *para*-methyl group (93% vs 81%). Splitting of peaks in the ^{2}H NMR spectrum is due to presence of minor

isotopologues. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.82 (s, 2H), 3.44 (br, 2H), 2.27 – 2.22 (m, ≈0.5H), 2.19 – 2.17 (m, ≈0.5H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.2, 128.8, 126.8, 121.6, 20.3 – 19.3 (m), 17.3 – 16.5 (m). **^{2}H NMR** (61 MHz, $CHCl_3$) δ 2.23 (br), 2.19 (br), 2.14 (br). ***m/z*** (EI): 144.1 ([M]$^+$), 125.1, 111.1, 95.0, 80.0, 67.0.

Synthesis of 2-iodomesitylene-d_9 ***17***[35]



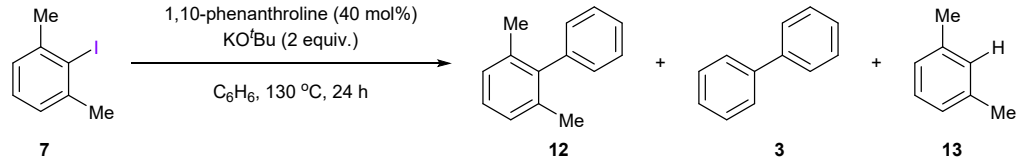
A solution of $NaNO_2$ (302 mg, 4.38 mmol) in H_2O (4 mL) was slowly added dropwise to a stirred suspension of **25** (301 mg, 2.19 mmol) and *p*-TsOH (1.67 g, 8.76 mmol) in H_2O (6 mL) under air at 0 °C, yielding a colourless solution that was left to stir for a further 10 min. A solution of KI (1.45 g, 8.76 mmol) in H_2O (4 mL) was added slowly dropwise, which upon the first addition yielded a dark purple solution that persisted once half the KI solution had been added. Once the addition was complete, the dark purple solution was allowed to slowly warm to room temperature and stirred for a further 20 h. The reaction was then extracted with EtOAc (3 x 5 mL), the combined organic fractions were then washed with sat. $Na_2S_2O_3$ (10 mL) and H_2O (5 mL) twice, then with H_2O (10 mL). The organic fractions were then dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was then purified by column chromatography with hexane eluent to yield **17** as a crystalline white solid (284 mg, 1.11 mmol, 51%). The minor peak in the ^{2}H NMR spectrum is due to incomplete deuterium incorporation. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.88 (s, 2H), 2.43 – 2.37 (m, 0.44 H), 2.24 – 2.19 (m, 0.56 H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.8, 137.4, 128.1, 104.3, 30.1 – 28.5 (m), 20.5 – 20.0 (m). **^{2}H NMR** (61 MHz, $CHCl_3$) δ 2.43 (br), 2.41 (br), 2.24 (br), 2.21 (br). **IR** ν_{max}/cm^{-1} (neat): 3026, 2922, 2228, 2204, 2106, 2062, 1572, 1410, 1271, 1001. ***m/z*** (EI): 255.0 ([M]$^+$), 127.1, 109.0, 96.1, 81.0, 68.0.

2-Iodo-*m*-xylene Reactions

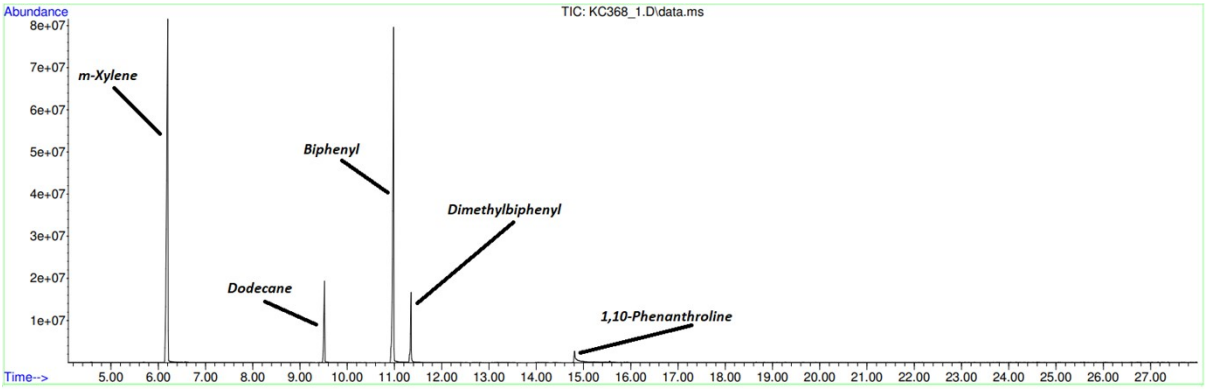
Assigned peaks in the GCFID spectra were quantitatively calibrated (for calibrations see pages S34 – S38). During the investigation, the column was changed on the GCFID and so the retention times for all peaks shifted. A repeat calibration for all calibrated compounds was carried out.

Reaction of 2-Iodo-m-xylene ***7*** *with 1,10-Phenanthroline and KO^{t}Bu (Table 1, Entry 1 and Table 2, Entry 1).*

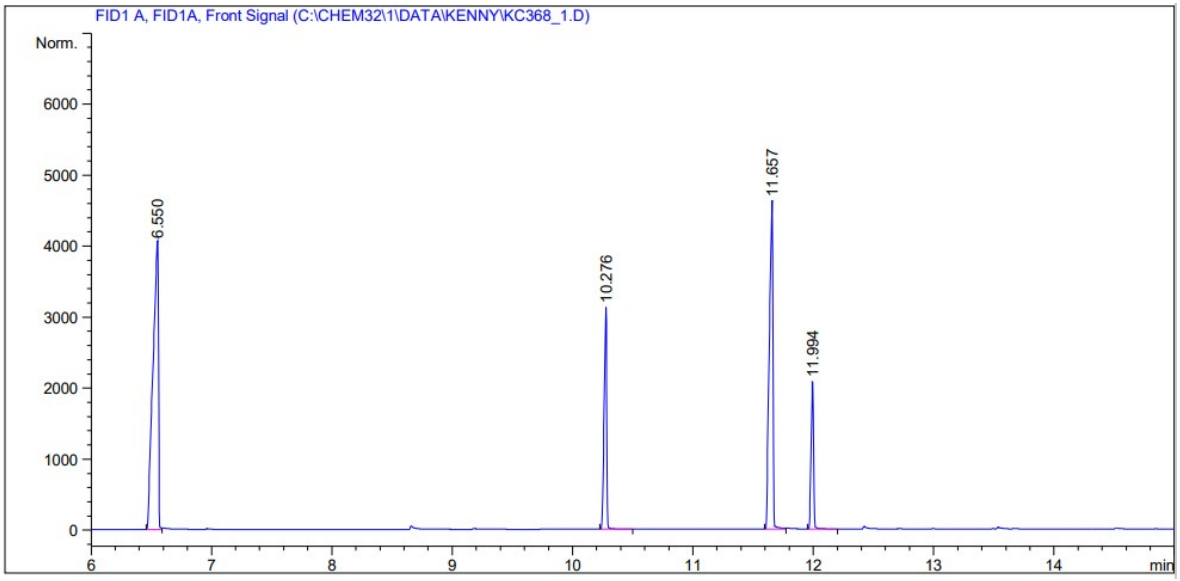
The reaction was conducted according to General Procedure A with 1,10-phenanthroline (50 mg, 0.28 mmol, 40 mol%) and benzene.



GCMS Chromatogram



GCFID data including table quantitating components that had been quantitatively calibrated (for calibrations see pages S34 – S38):



Retention Time	Sample	Peak Area	%Yield
6.550	*m*-Xylene **13**	12741.2	55%
10.276	Dodecane	4566.74072	N/A
11.657	Biphenyl **3**	9882.09375	30%
11.994	2,6-Dimethylbiphenyl **12**	2973.54248	8%

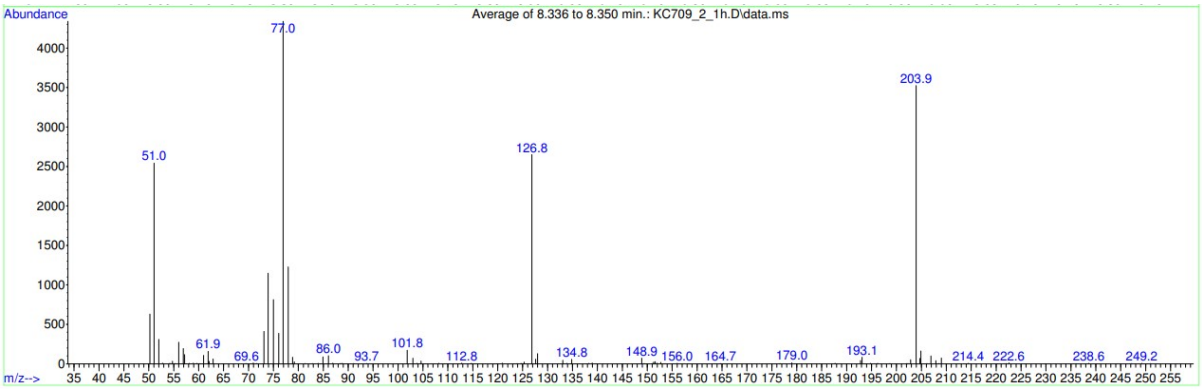
*This reaction was carried out in duplicate with the average below

Sample	%Yield
m-Xylene **13**	58%
2-Iodo-*m*-xylene **7**	0
Biphenyl **3**	32.2%
2,6-Dimethylbiphenyl **12**	8.1%

Investigation by GCMS of the reaction after 5 h, highlighted the mass of iodobenzene , indicating abstraction of iodine atom from substrate **7** by phenyl radicals **14**. The retention time was confirmed by comparison with a commercial sample.

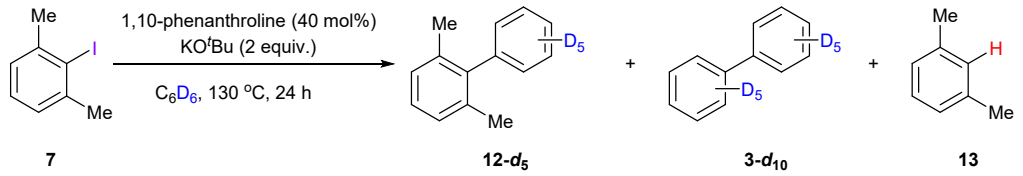
Spectrum of Iodobenzene:

Iodobenzene
Predicted *m/z*: 203.9436 (100.0%), 204.9469 (6.5%)



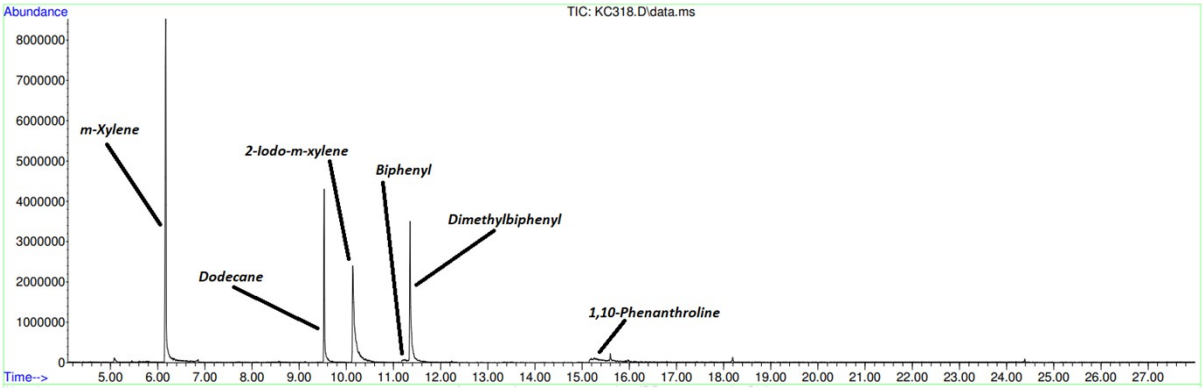
Outcome - The reaction of 2-iodo-*m*-xylene **7** with 1,10-phenanthroline and KO^{t}Bu led to complete conversion of the starting material, **7**, and led to the 3 principal compounds **3**, **12** and **13**. The ratio of **12**:**3** was ~1:3.97.

*Reaction of 2-Iodo-m-xylene **7** with 1,10-Phenanthroline and KO^{t}Bu in C_6D_6 (Table 2, entry 2)*
The reaction was conducted according to General Procedure A with 1,10-phenanthroline (50 mg, 0.28 mmol, 40 mol%) and benzene-d_6.

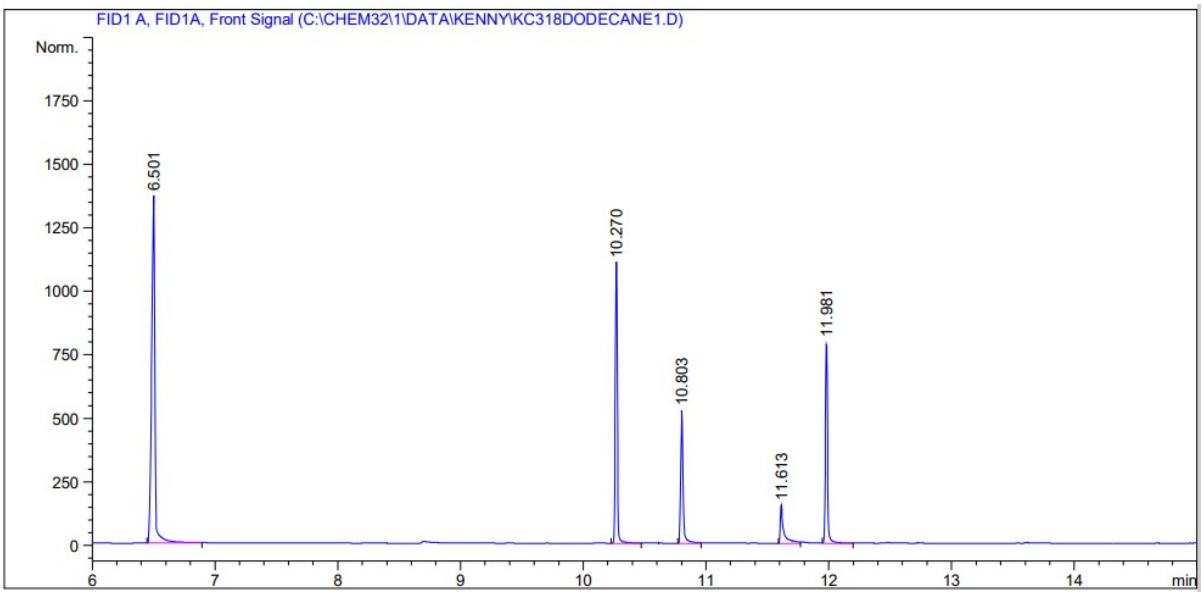


7 **12-d_5** **3-d_{10}** **13**

GCMS Chromatogram



GCFID data including table quantitating components that had been quantitatively calibrated (for calibrations see pages S34 – S38).



Retention Time	Sample	Peak Area	%Yield
6.501	*m*-Xylene	2575.86035	44%
10.270	Dodecane	1263.06714	N/A
10.803	2-Iodo-*m*-xylene	710.42322	11%
11.613	Biphenyl	293.99445	4%
11.981	2,6-Dimethylbiphenyl	962.01141	11%

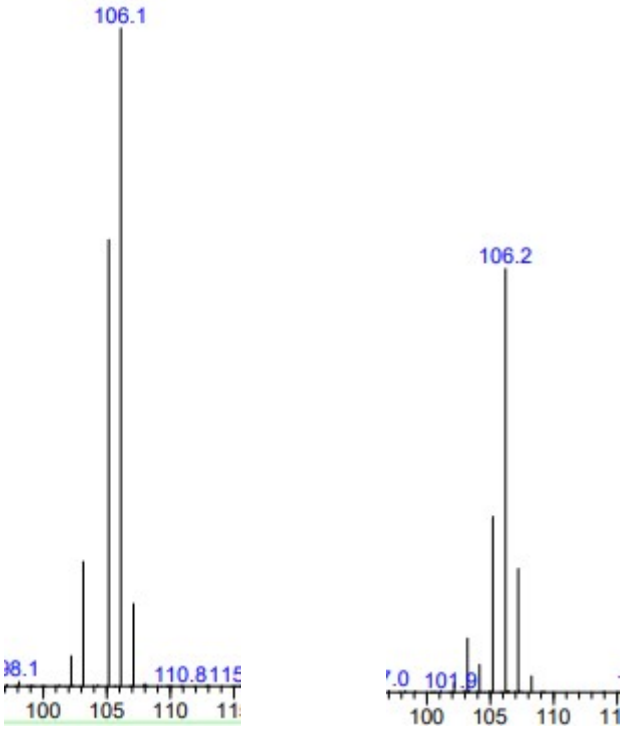
*This reaction was carried out in duplicate with the average below

Sample	%Yield
m-Xylene	45%
2-Iodo-*m*-xylene	12%
Biphenyl	4%
2,6-Dimethylbiphenyl	11%

Level of *m*-xylene D-incorporation

Iodoxylene **7**, Phen, C_6D_6, KO^tBu

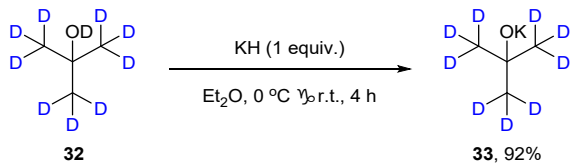
Examination of the mass spectrum of xylene derived from this experiment (shown below), showed the *m/z*= 107 peak to be more intense, relative to *m/z* =106 compared to the unlabelled sample prepared from Phen, C_6H_6, KO^tBu**.** This indicated approx. 12% monodeuteroxylene.



Left: mass spectrum of *m*-xylene, formed by reaction of iodoxylene **7** with KO*t*Bu, and phenanthroline in C_6H_6. Right: mass spectrum of *m*-xylene, formed by reaction of iodoxylene **7** with KO*t*Bu, and phenanthroline in C_6D_6. The level of deuteration (107 mass speak) is 12%.

Outcome - The reaction of 2-iodo-*m*-xylene **7** with 1,10-phenanthroline and KO^{t}Bu in C_6D_6 led to the formation of the 3 principal compounds **3-*d*$_{10}$**, **12-*d*$_5$** and **13**. Some starting material **7** remained after the 24 h. An isotope effect was observed for the formation of deuterated biphenyl **3-*d*$_{10}$** as expected, while the amount of dimethylbiphenyl-d_5 **12-*d*$_5$** remained constant with the amount seen in the parent conditions. The majority of the *m*-xylene **13** formed in this experiment was NOT labelled and the level of mono-deuteration was estimated at 12%.

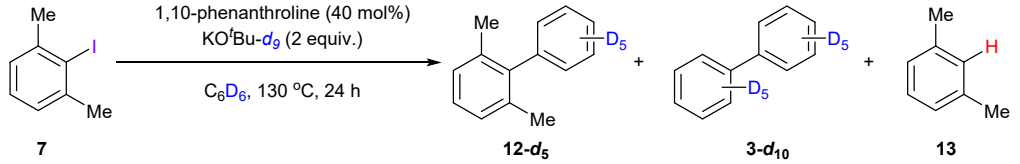
Preparation of Potassium 2-(methyl-d$_3$)propan-2-olate-1,1,1,3,3,3-d$_6$ ***33***



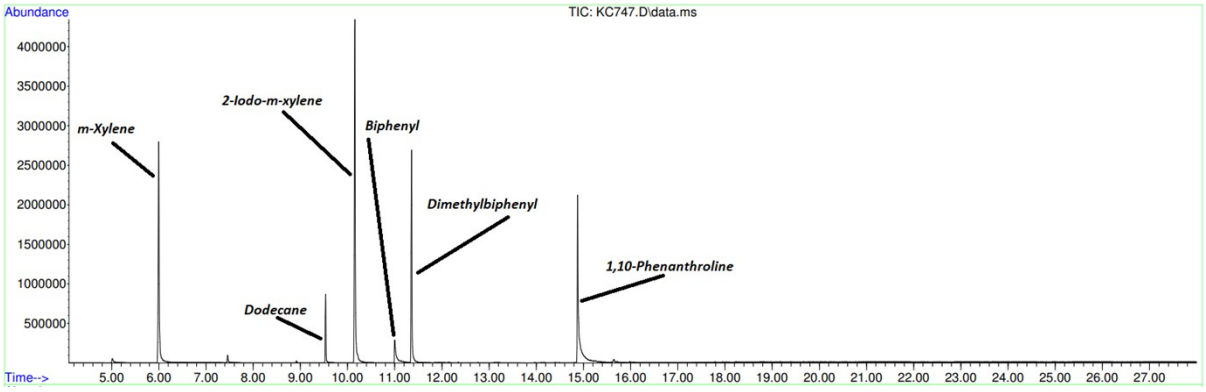
In an oven-dried three necked flask, primed with a stirrer bar, and back filled with nitrogen was added KH (400 mg, 10 mmol, 1 equiv.) and Et_2O (10 mL) and the solution stirred at 0 °C. To this solution was added *tert*-butanol-d_{10} **32** (0.94 mL, 10 mmol, 1 equiv.) and the solution was stirred for 4 h. Once complete, the Et_2O was removed using the house vacuum until dryness. This yielded potassium 2-(methyl-d_3)propan-2-olate-1,1,1,3,3,3-d_6 **33** (KO^{t}Bu-d_9) as a white powder (1.119 mg, 9.2 mmol, 92%).

^{13}C NMR (101 MHz, THF-d_8) δ 66.2, δ 34.6 (sept, J = 18.7 Hz) [Confirmed by comparing with ^{13}C NMR spectrum of *tert-butanol-d_{10}*: **^{13}C NMR** (101 MHz, THF-d_8) δ 57.4, 30.5 (sept, J = 18.9 Hz)].

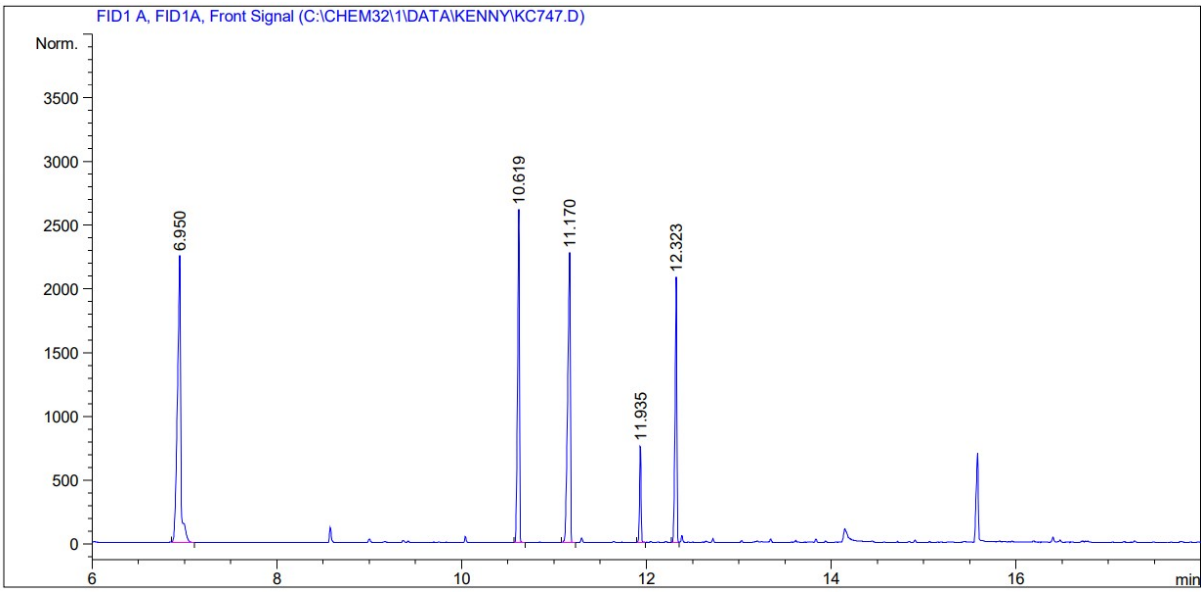
*Reaction of 2-Iodo-m-xylene **7** with 1,10-Phenanthroline and KO^{t}Bu-d_9 in C_6D_6 (Table 2, entry 3)*
The reaction was conducted according to General Procedure A with KO^{t}Bu-d_9 (216 mg, 1.4 mmol, 2 equiv.), 1,10-phenanthroline (50 mg, 0.28 mmol, 40 mol%) and benzene-d_6 (7 mL).



GCMS Chromatogram



GCFID data including table quantitating components that had been quantitatively calibrated (for calibrations see pages S34 – S38):



Retention Time	Sample	Peak Area	%Yield
6.950	*m*-Xylene	4427.48828	28.6%
10.619	Dodecane	3215.67139	N/A
11.170	2-Iodo-*m*-xylene	5234.70898	35.1%
11.935	Biphenyl	664.98743	3.2%
12.323	2,6-Dimethylbiphenyl	2384.65942	10.5%

*This reaction was carried out in duplicate with the average below

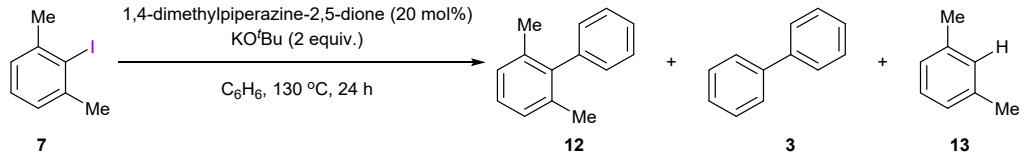
Sample	%Yield
m-Xylene	30.4%
2-Iodo-*m*-xylene	31.0%
Biphenyl	3.5%
2,6-Dimethylbiphenyl	10.7%

For representative mass spectra of **3-d_{10}**, **12-d_5** and **13** see pages S31-S34.

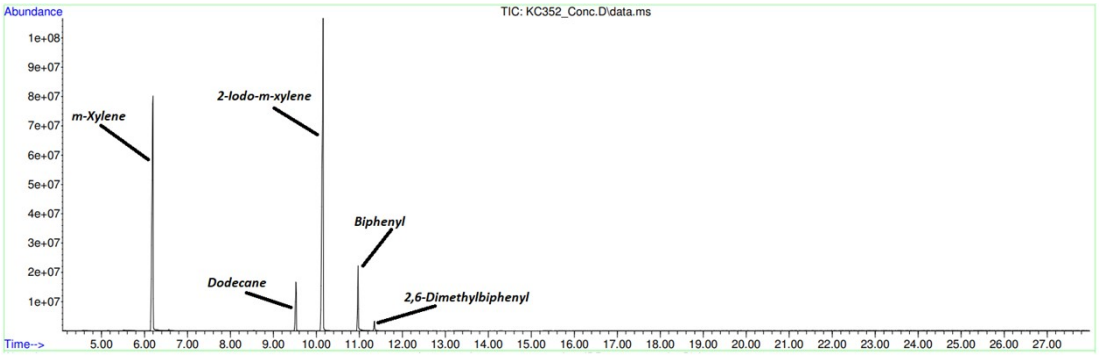
Outcome - The 2-Iodo-*m*-xylene **7** with 1,10-phenanthroline and KO^{t}Bu-d_9 in C_6D_6 led to the formation of the 3 principal compounds **3-d_{10}**, **12-d_5** and **13**. Some starting material was left remaining after the 24 h. The majority of the *m*-xylene **13** formed in this experiment was NOT labelled.

*Reaction of 2-iodo-m-xylene **7** with piperazinedione **16** and KO^{t}Bu (Table 1, Entry 2))*

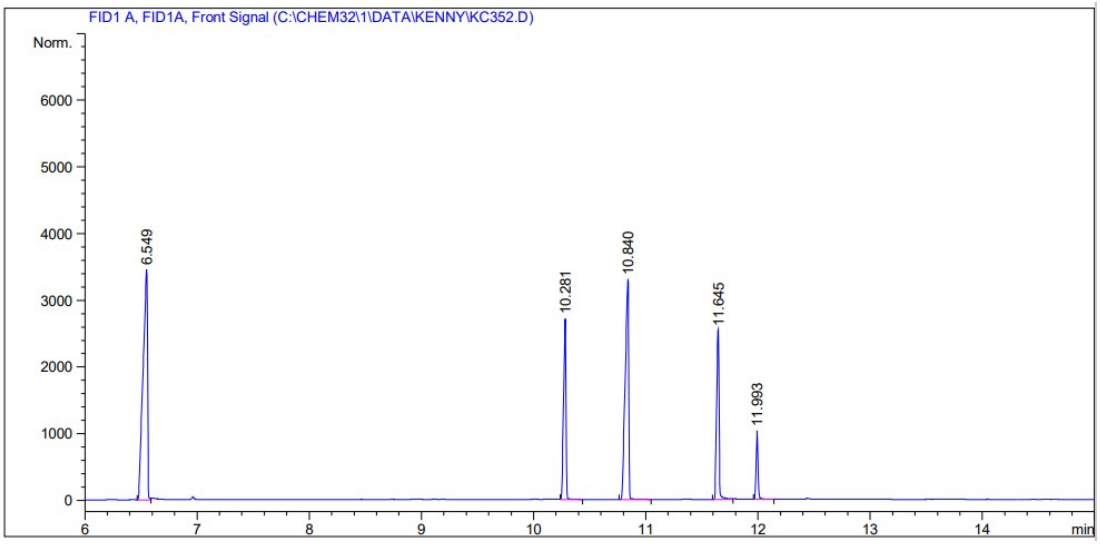
The reaction was conducted according to General Procedure A with 1,4-dimethylpiperazine-2,5-dione **16** (20 mg, 0.14 mmol, 20 mol%), and benzene.



GCMS Chromatogram



GCFID data including table quantitating components that had been calibrated (for calibrations see pages S34 – S38).



Retention Time	Sample	Peak Area	%Yield
6.550	*m*-Xylene	9537.06055	48.2%
10.281	Dodecane	4045.83838	N/A
10.840	2-Iodo-*m*-xylene	7196.21875	38.1%
11.645	Biphenyl	3934.50757	13.9%
11.993	2,6-Dimethylbiphenyl	1204.87329	3.6%

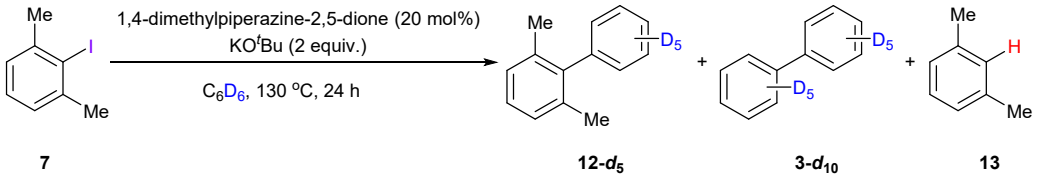
*This reaction was carried out in duplicate with the average below

Sample	%Yield
m-Xylene	47.9%
2-Iodo-*m*-xylene	35.3%
Biphenyl	12.5%
2,6-Dimethylbiphenyl	3.0%

Outcome - The reaction of 2-iodo-*m*-xylene **7** with piperazinedione **16** and KO^{t}Bu led to the formation of the 3 principal compounds **3**, **12** and **13**. Some starting material **7** remained after the 24 h. The ratio of **12**:**3** was ~1:4.17.

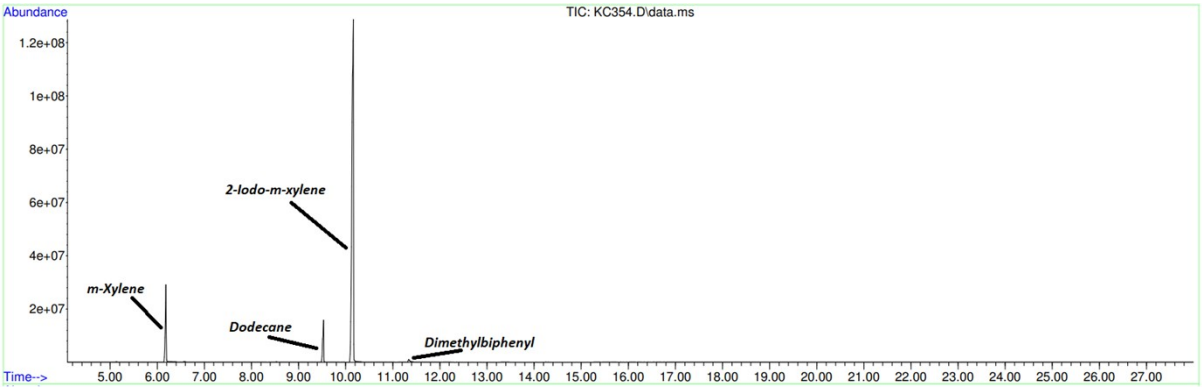
*Reaction of 2-Iodo-m-xylene **7** with Piperazinedione **16** and KO^{t}Bu in C_6D_6*

The reaction was conducted according to General Procedure A with 1,4-dimethylpiperazine-2,5-dione (20 mg, 0.14 mmol, 20 mol%), and benzene-d_6.

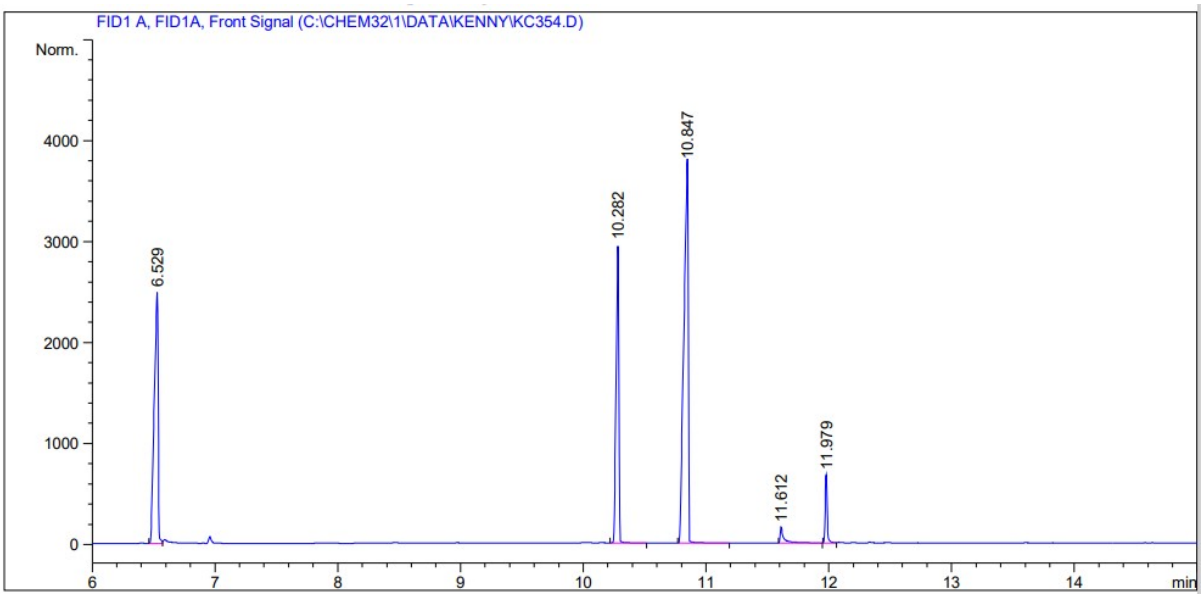


7 **12-d_5** **3-d_{10}** **13**

GCMS Chromatogram



GCFID data including table quantitating components that had been quantitatively calibrated (for calibrations see pages 34– 38).



Retention Time	Sample	Peak Area	%Yield
6.529	*m*-Xylene	5513.38672	24.5%
10.282	Dodecane	4504.60400	N/A
10.847	2-Iodo-*m*-xylene	9336.28711	43.7%
11.612	Biphenyl	330.86661	1%
11.979	2,6-Dimethylbiphenyl	782.20575	2.1%

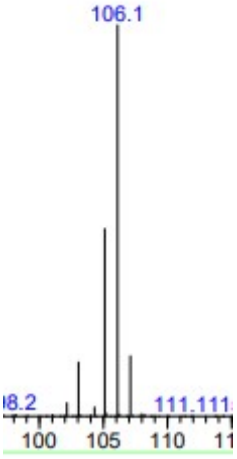
*This reaction was carried out in duplicate with the average below

Sample	%Yield
m-Xylene	25.5%
2-Iodo-*m*-xylene	43.9%
Biphenyl	0.9%
2,6-Dimethylbiphenyl	2.1%

Level of *m*-xylene D-incorporation

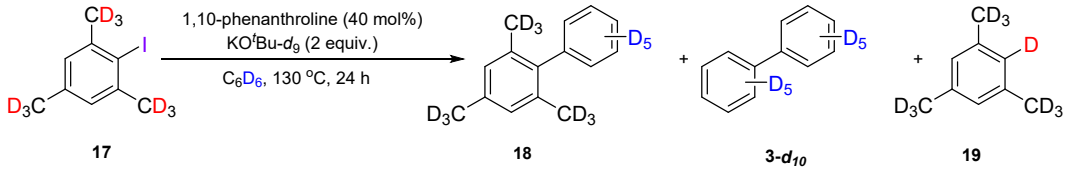
Iodoxylene **7**, *N,N'*-dimethylpiperazinedione, C_6D_6, KO^{t}Bu

Examination of the mass spectrum of xylene (*m/z* 106) derived from this experiment (shown below), showed the *m/z*= 107 peak to be equally intense, but not notably more intense, relative to *m/z* =106 compared to the unlabelled sample prepared from *N,N'*-dimethylpiperazinedione, C_6H_6, KO^{t}Bu**.**



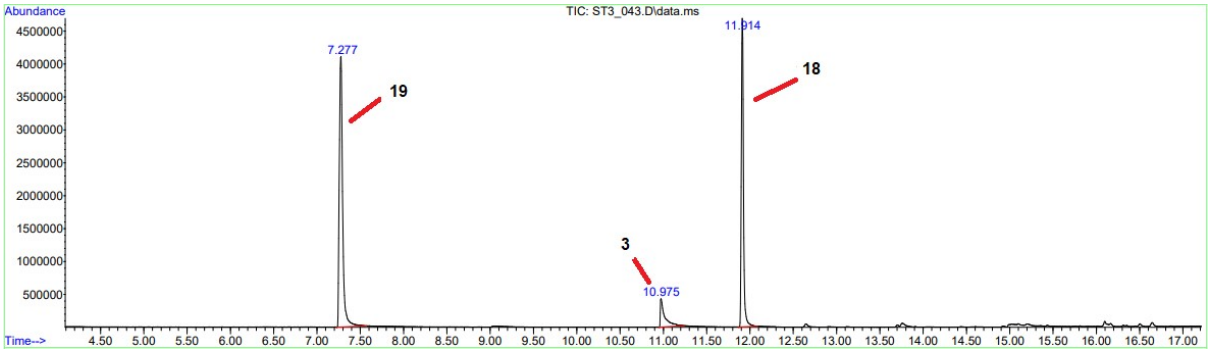
Outcome - The Reaction of 2-Iodo-*m*-xylene **7** with piperazinedione **16** and KO^{t}Bu in C_6D_6 led to the formation of the 3 principal compounds **3-*d*$_{10}$, 12-*d*$_5$** and **13**. Some starting material was left remaining after the 24 h. An isotope effect was observed for the formation of deuterated biphenyl **3-*d*$_{10}$** as expected, while the amount of dimethylbiphenyl-d_5 **12-*d*$_5$** remained constant with the parent conditions. The extent of labelling of *m*-xylene **13** formed in this experiment was low and so could not be accurately determined from the mass spectrum [consistent with formation of low amount (0.9%) of **3-*d*$_{10}$**.].

*Reaction of iodomesitylene-d_9 **17** with 1,10-phenanthroline and KO^{t}Bu-d_9 in C_6D_6*



17 **18** **3-*d*$_{10}$** **19**

The reaction was conducted according to General Procedure A, except that iodomesitylene-d_9 **17** (132 mg, 0.52 mmol) was employed as the substrate, with 1,10-phenanthroline (38 mg, 0.21 mmol, 40 mol%), KO^{t}Bu-d_9 (126 mg, 1.04 mmol) and benzene-d_6 (3.7 mL).



Analysis by GCMS showed complete consumption of the substrate **17**, with production of 2,4,6-trimethylbiphenyl **18**, biphenyl-d_{10} **3** and mesitylene **19**. Due to incomplete deuteration of substrate **17**, it was impossible to use mass spectrometry to determine whether mesitylene **19** was labelled at the aryl position; accordingly, ^{2}H NMR was therefore employed to elucidate this. ^{2}H NMR shows a signal at δ 6.87 ppm in $CHCl_3$ (Figure **S1**), corresponding to the Ar-D position of mesitylene-d_{10} **19**. Peaks at δ 9.26 and 8.32 ppm are also observed, corresponding to deuteration of 1,10-phenanthroline, which was also observed by GC-MS (Figure **S2**). The chemical shifts of these peaks are in agreement with the ^{1}H NMR of commercial 1,10-phenanthroline in $CDCl_3$ (Figure **S3**).

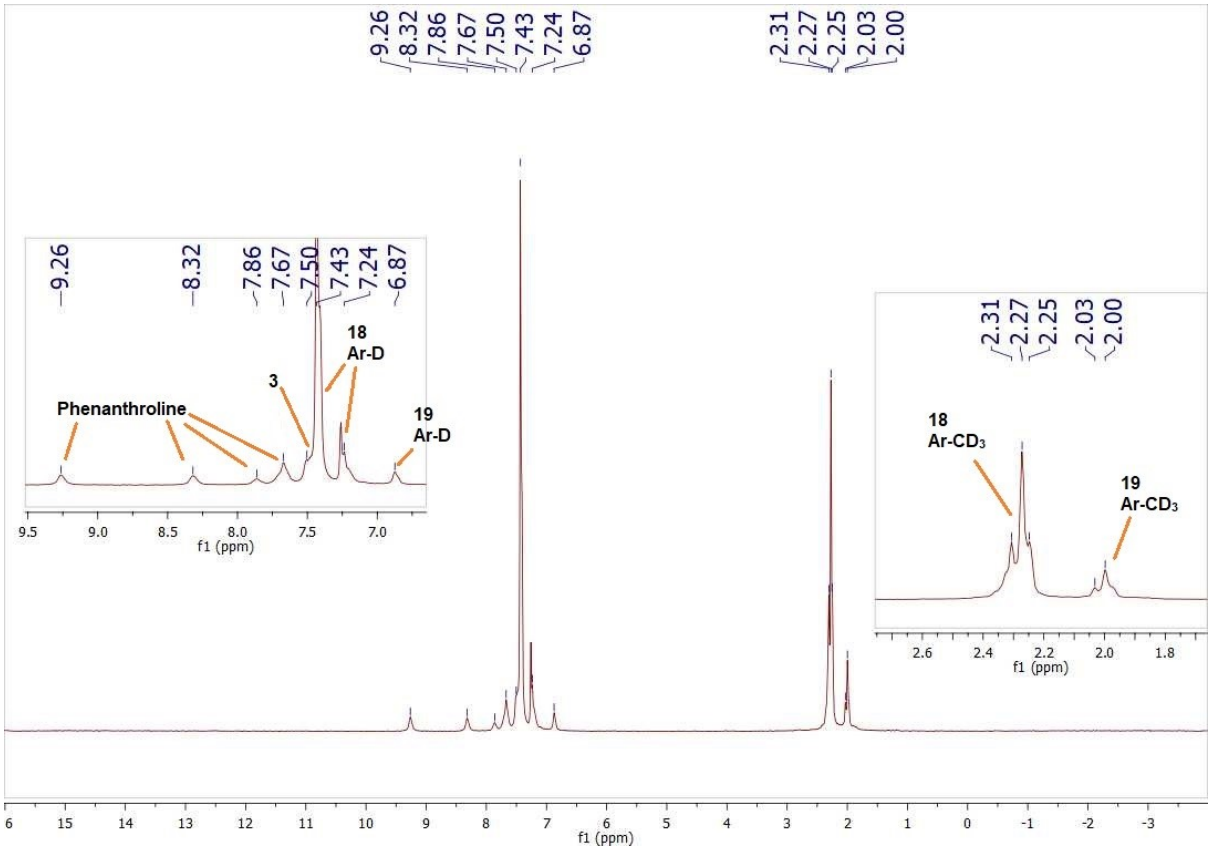


*Figure S1 – ^{2}H spectrum of reaction of iodomesitylene-d_9 **17** with 1,10-phenanthroline and KO^{t}Bu-d_9 in C_6D_6 crude reaction mixture.*

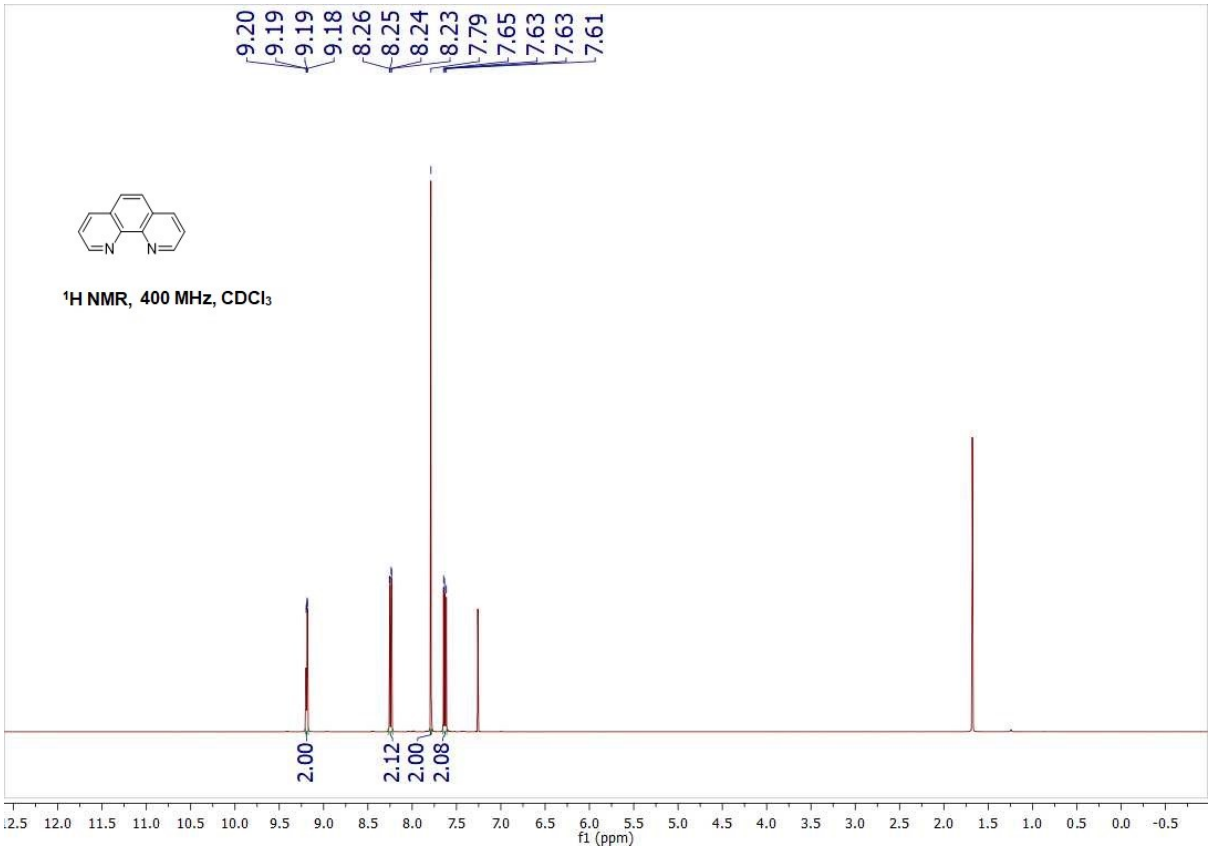


Figure S3 – ^{1}H spectrum of commercial 1,10-phenanthroline in $CDCl_3$.

The ^{1}H NMR spectrum of commercial non-deuterated mesitylene is provided for reference, showing a peak at δ 6.83 ppm (Figure **S4**), and the ^{1}H NMR for our synthesised mesitylene-d_9 shows the same peak at δ 6.72 ppm (in C_6D_6). The literature value for the ^{2}H NMR spectrum of mesitylene-d_3 (1,3,5-$C_6Me_3D_3$) gives a value of δ 7.03 ppm,[36] which is expected to be shifted further downfield than **19** as the longer benzylic C-H bond length (compared to C-D) makes CH_3 a less inductively donating group. Based on this result, it is concluded that under these conditions the mesityl radical favourably abstracts deuterium atoms from the benzylic positions of **19**.

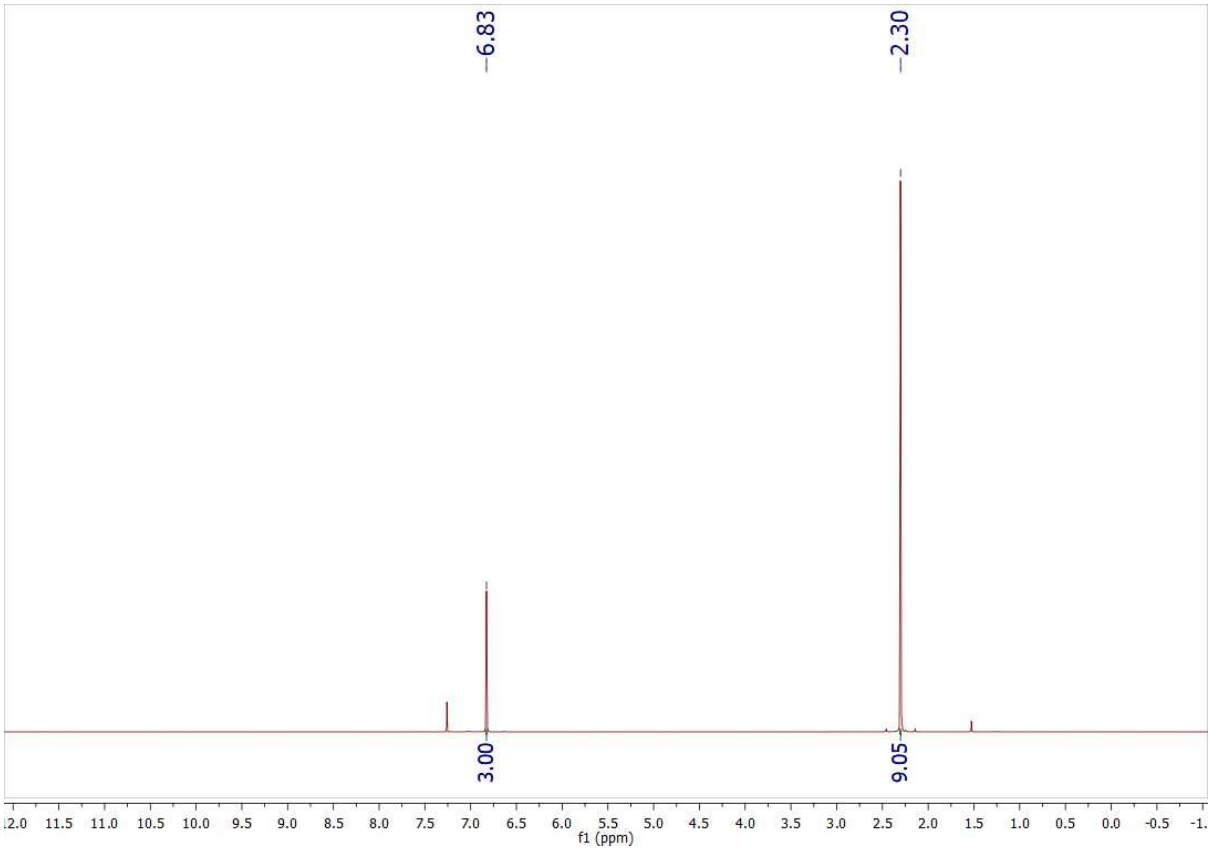
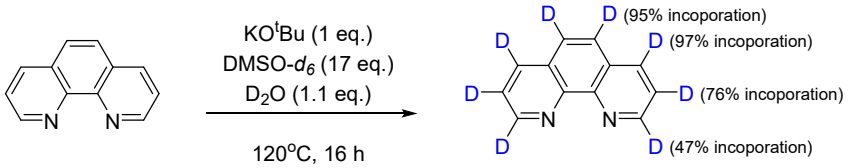


Figure S4- ^{1}H spectrum of commercial mesitylene in $CDCl_3$

Experiments with (i) deuterated phenanthroline that show exchange with iodoxylene and xylene and (ii) and with deuterated mesitylene that show exchange with phenanthroline in the presence of KOtBu acting as base.

Preparation of 1,10-phenanthroline-d_8*

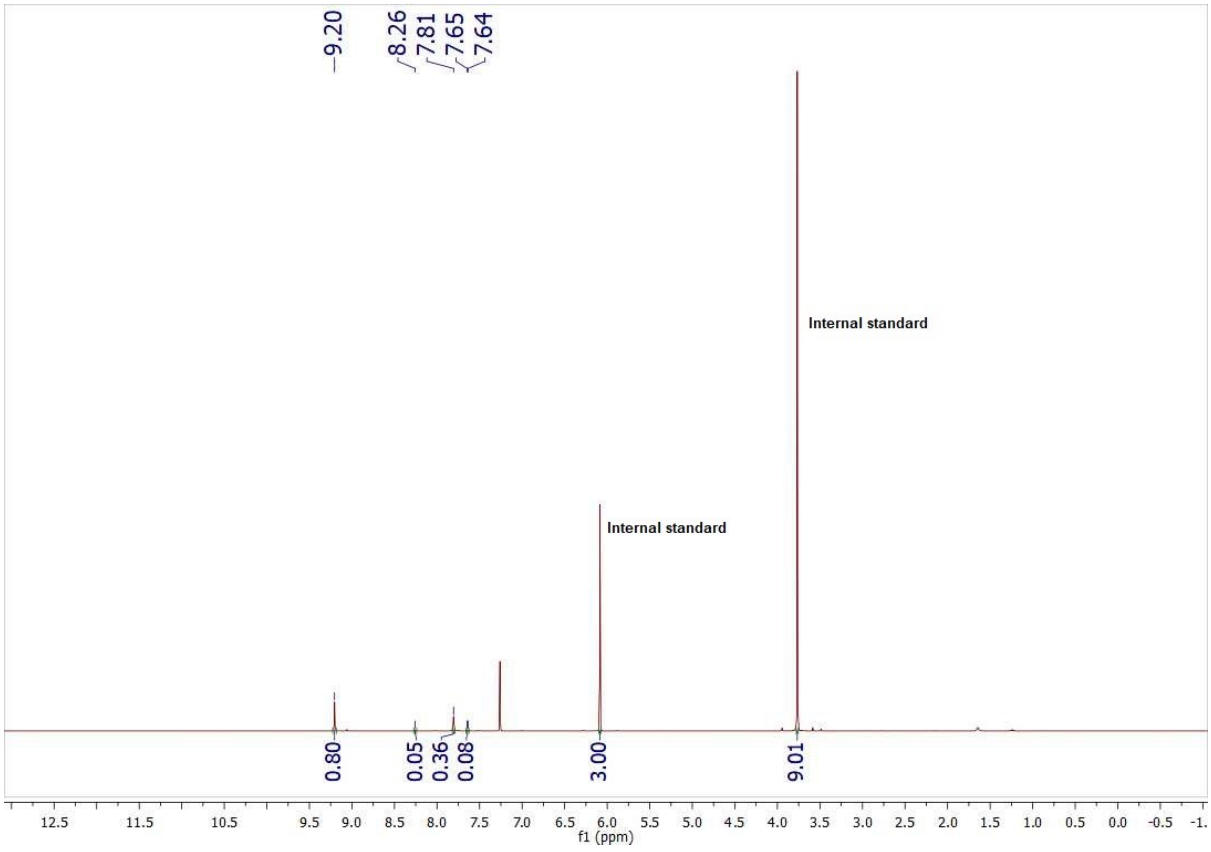


15 **15-d_8**

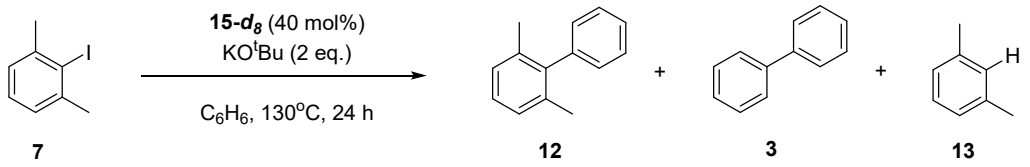
The product was prepared according to a modified literature procedure by Beller *et. al.*[37] An oven-dried 25 mL Schlenk flask was charged with 1,10-phenanthroline (540.9 mg, 3 mmol) and KO^{t}Bu (336.6 mg, 3 mmol, 1 eq.), evacuated for 30 mins and then backfilled with argon. DMSO-d_6 (3.6 mL, 51 mmol, 17 eq.) and D_2O (60 μL, 3.3 mmol, 1.1 eq.) were then added by syringe, immediately giving a red solution and red solids. The mixture was heated at 120°C for 16 h, giving a dark green solution. The solution was cooled, opened to air and diluted with DCM (250 mL), washed with brine (100 mL) and then extracted into DCM (2 x 50 mL). The combined organics were dried over $MgSO_4$ and concentrated *in vacuo*. The product was purified by column chromatography (column 1: DCM to 2% MeOH/DCM, column 2: CHCl3 to 2% MeOH/DCM) yielding **15-d_8** as an off-white solid (171 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.16 (br), 8.22 – 8.19 (m), 7.74 (s), 7.61 – 7.57 (m). **^{2}H NMR** (61 MHz, $CHCl_3$) δ 9.24 (br), 8.31 (br), 7.85 (br), 7.69 (br). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.3, 146.4, 135.9 – 135.3 (m), 128.6 (d, *J* = 6.9 Hz), 126.5 (d, *J* = 12.5 Hz), 123.1 – 122.4 (m). ***m/z*** (EI): 188.1 (M-d_8, 2.8), 187.1 (M-d_7, 22.9), 186.1 (M-d_6, 75.2), 185.1 (M-d_5, 100), 184.1 (M-d_4, 73.4), 183.1 (M-d_3, 36.7), 182.1 (M-d_2, 11.9), 181.1 (M-d_1, 1.8). The data are consistent with those reported.

*Deuterium incorporation was determined by comparison with an internal standard. **15-d_8** (6.0 mg, 0.032 mmol) and 1,3,5-trimethoxybenzene (7.0 mg, 0.045 mmol) were dissolved in $CDCl_3$ and analysed by ^{1}H NMR, giving the following D-incorporations: position 2 = 47%, position 3 = 76%, position 4 = 97%, position 5 = 95%.

Below: 1H NMR spectrum from such an experiment, incorporating 1,3,5-trimethoxy benzene as an internal standard

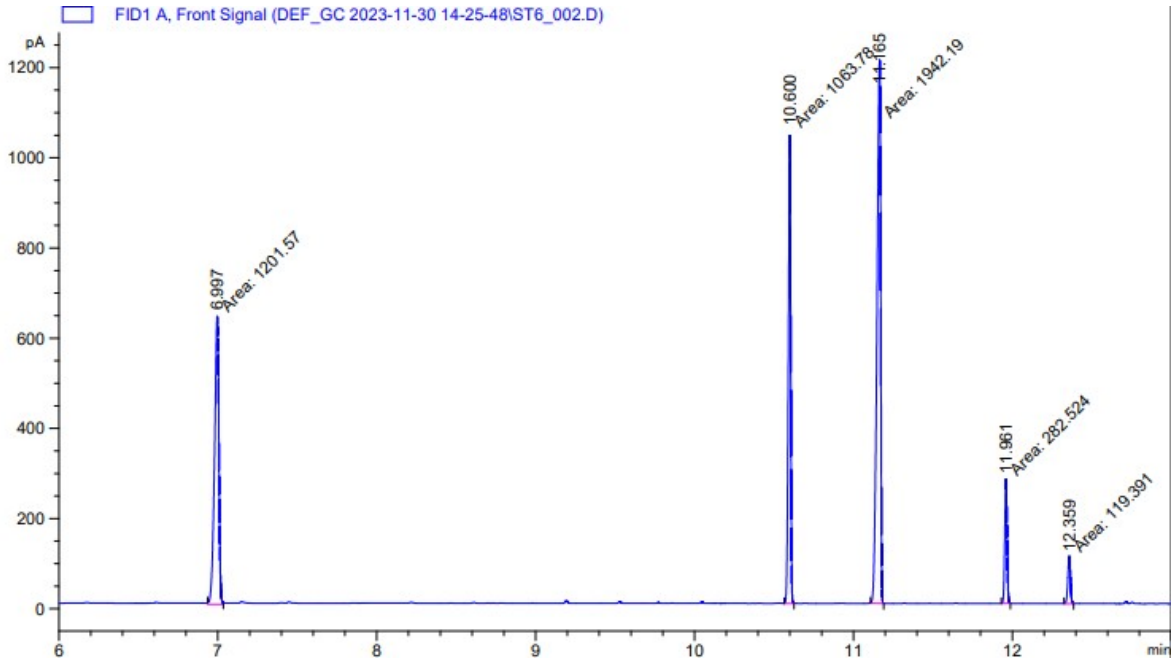


Reaction of iodoxylene 7 with 1,10-phenanthroline-*d*$_8$ and KO^{t}Bu in C_6H_6



7 **12** **3** **13**

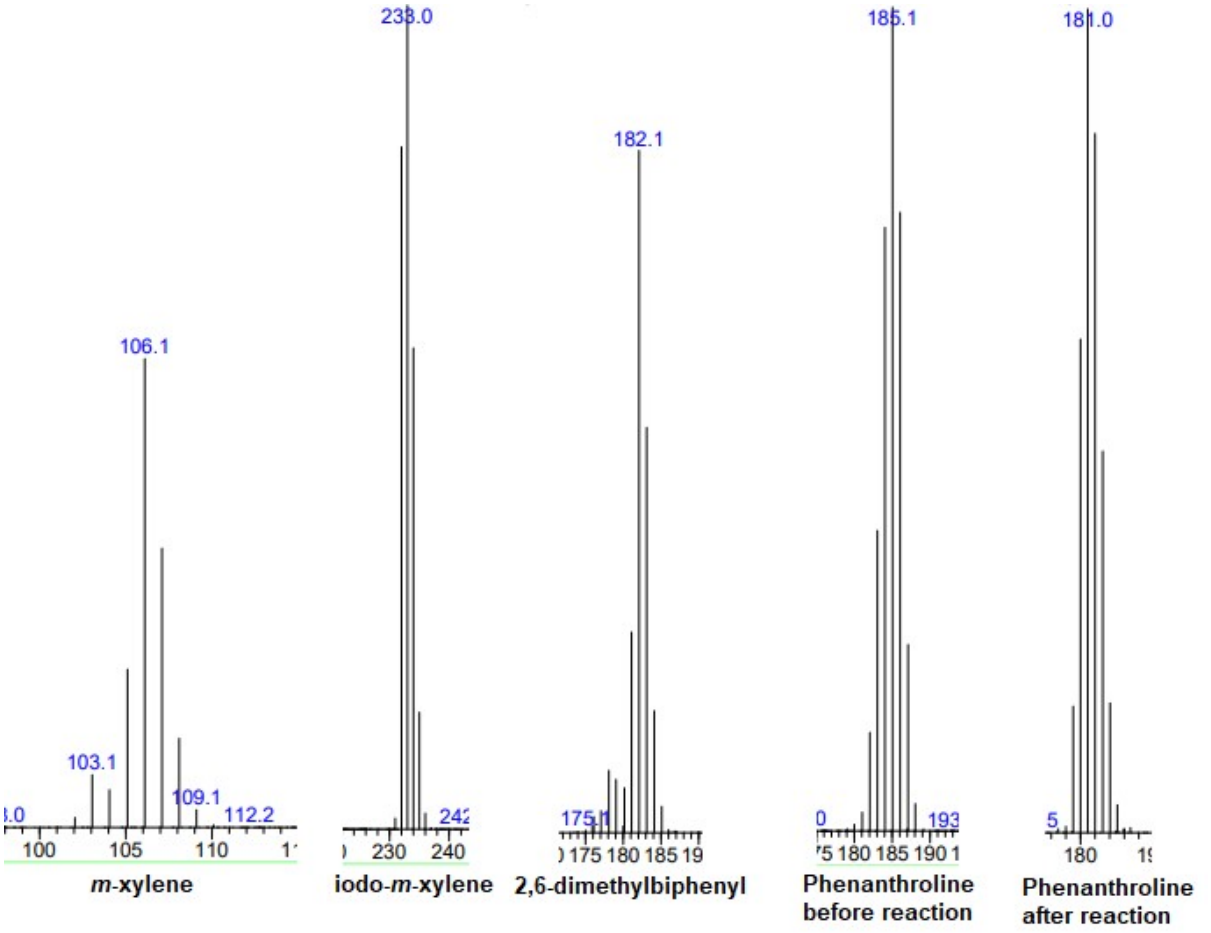
The reaction was conducted according to general procedure A with iodoxylene **7** (50.5 μL, 0.35 mmol), 1,10-phenanthroline-*d*$_8$ **15-*d*$_8$** (25.9 mg, 0.14 mmol, 0.4 eq.), KO^{t}Bu (78.5 mg, 0.7 mmol, 2 eq.) and C_6H_6 (2.5 mL). A dodecane internal standard was added (11.9 mg) and a 100 μL aliquot was used for analysis by GC-FID and GC-MS. The volatiles were then removed from the crude under reduced pressure, which was then diluted with $CHCl_3$ and analysed by ^{2}H NMR.

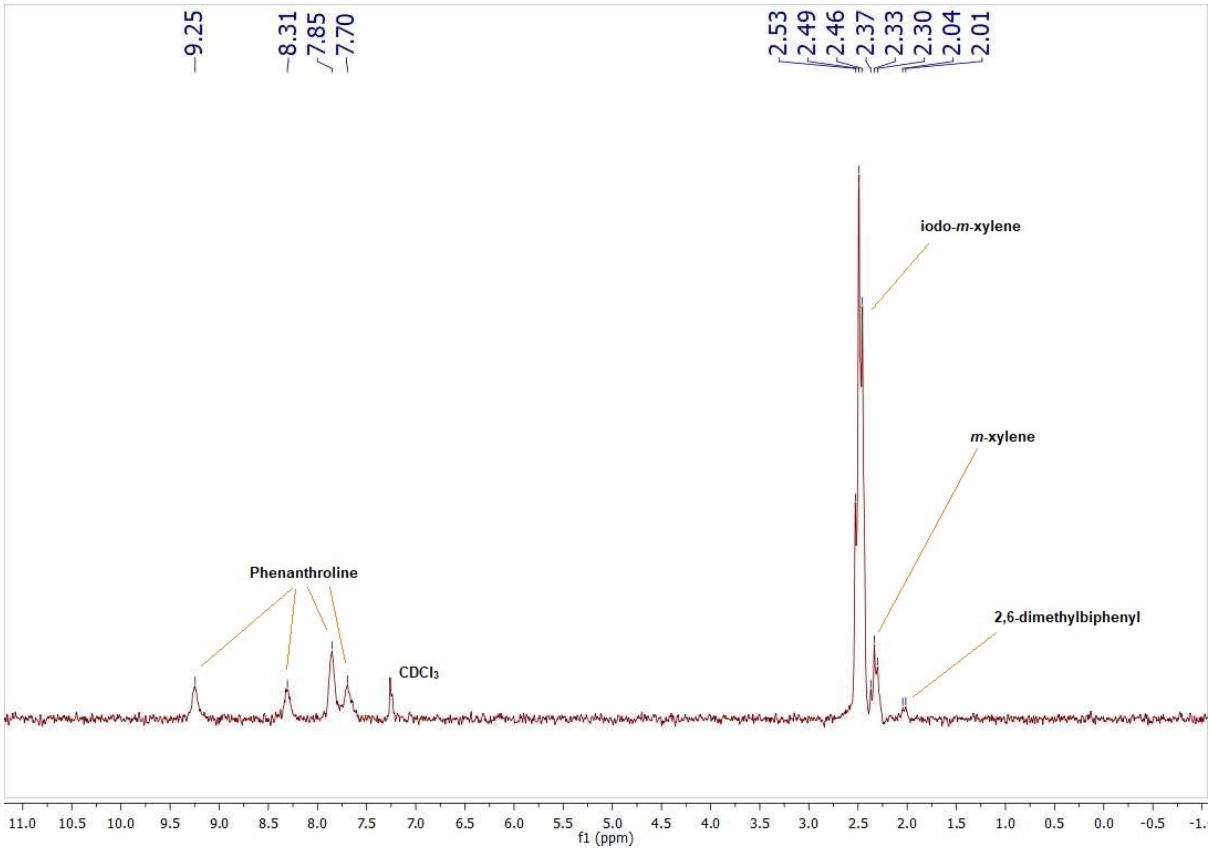


Retention Time	Sample	Peak Area	%Yield
6.997	*m*-Xylene	1201.57	33.6
10.600	Dodecane	1063.78	N/A
11.165	2-Iodo-*m*-xylene	1942.19	56.4
11.961	Biphenyl	282.52	5.9
12.359	2,6-Dimethylbiphenyl	119.39	2.3

GC-MS spectra (below) show deuteration of xylene, iodo-*m*-xylene and 2,6-dimethylbiphenyl by comparison of the intensity of M^+ and $[M+1]^+$ peaks.

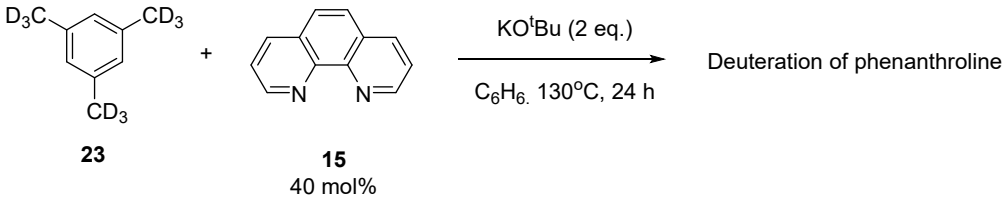
The spectra also show the polydeuterated phenanthroline before the reaction (most intense peak 185) and after the reaction (most intense peak 181) showing significant loss of deuterium label during the reaction. By ^2H NMR, it is observed that D-incorporation on *m*-xylene **13** occurs only at the benzylic positions.


106.1
103.1
109.1
112.2
100
105
110
m-xylene
238.0
230
240
iodo-m-xylene
182.1
175.1
175 180 185
2,6-dimethylbiphenyl
185.1
180 185 190
Phenanthroline
before reaction
181.0
180
Phenanthroline
after reaction


9.25
8.31
7.85
7.70
2.53
2.49
2.46
2.37
2.33
2.30
2.04
2.01
iodo-m-xylene
m-xylene
Phenanthroline
2,6-dimethylbiphenyl
CDCl3
f1 (ppm)

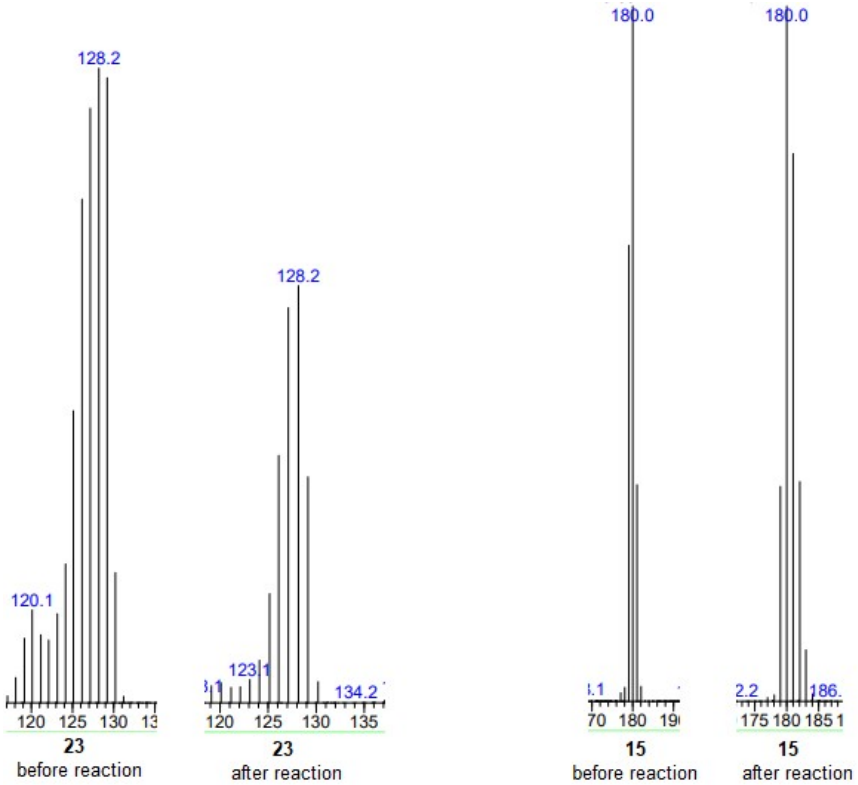
In the above experiment, it is clear that exchange has taken place from perdeuterated phenanthroline into the methyl groups of xylene and iodoxylene.. In an additional experiment, mesitylene-d_9 was used to show that D-exchange to phenanthroline takes place through base-catalysed D^+ transfer.

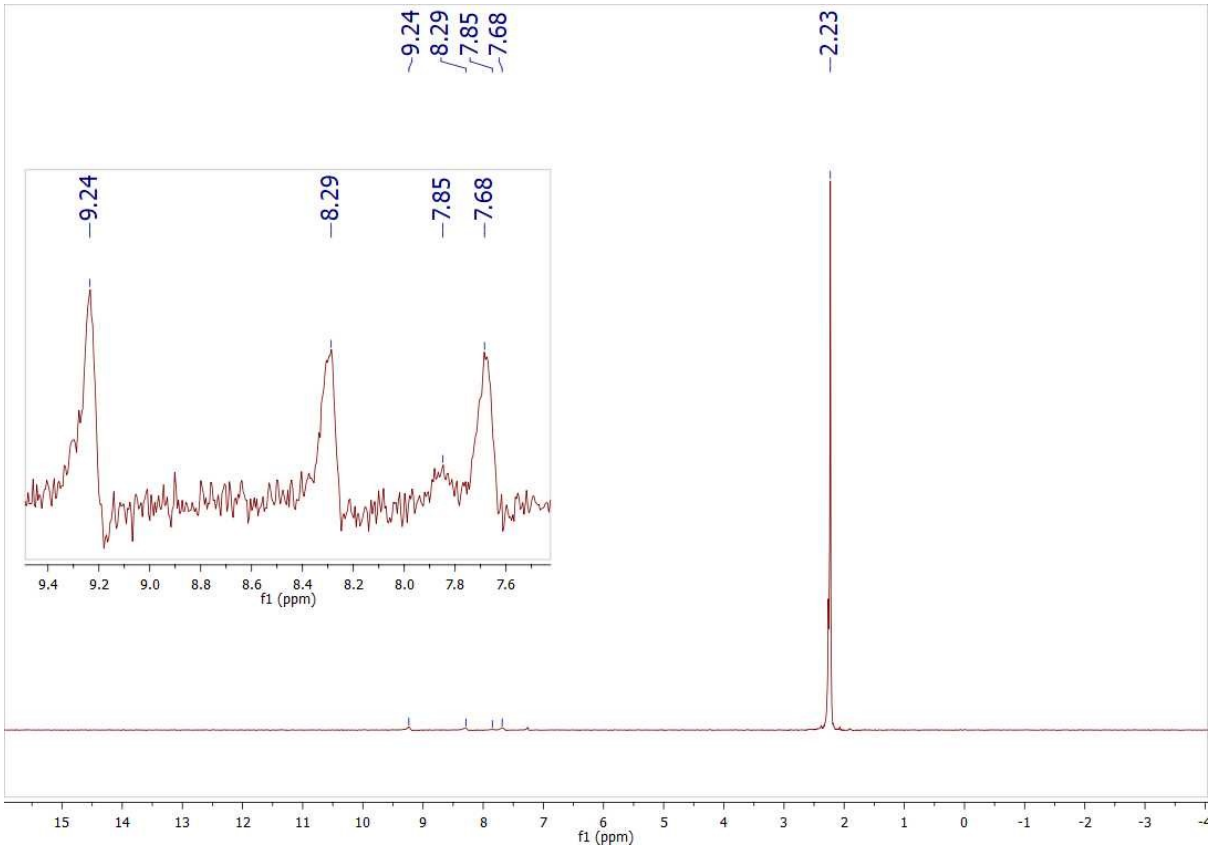
Reaction of 1,10-phenanthroline with *d_9*-mesitylene and KO^{t}Bu in C_6H_6



23 **15** 40 mol%

A 15 mL microwave was charged with **23** (45.2 mg, 0.35 mmol), 1,10-phenanthroline (25.2 mg, 0.14 mmol, 0.4 eq.), KO^{t}Bu (78.5 mg, 0.7 mmol, 2 eq.) and C_6H_6 (2.5 mL) in the glovebox. The flask was capped, removed from the box and stirred at 130^{o}C for 24 h. The reaction was cooled to room temperature and a small aliquot removed for analysis by GC-MS. The volatiles were then removed from the crude, which was diluted with $CHCl_3$ and analysed by ^{2}H NMR. The GC-MS shows an increase in the deuterium incorporation on phenanthroline **15**, (intensity of peak at *m/z* 181 relative to *m/z* 180) and a decrease in the deuterium incorporation on mesitylene **23**, (intensity of peak at *m/z* 129 relative to *m/z* 128). Below the mass spectra, the ^{2}H NMR spectrum of the phenanthroline shows more clearly the incorporation of deuterium at all positions.




9.24
8.29
7.85
7.68
2.23
9.24
8.29
7.85
7.68
9.4 9.2 9.0 8.8 8.6 8.4 8.2 8.0 7.8 7.6
f1 (ppm)
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

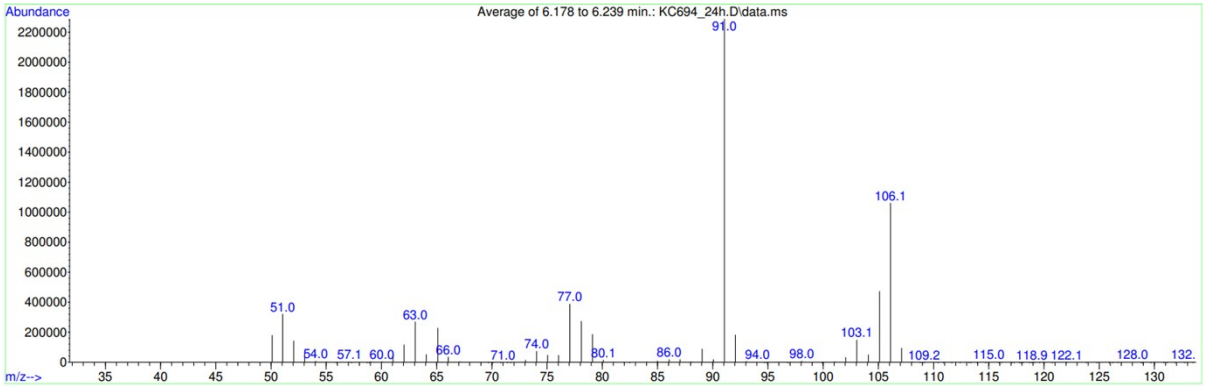
Example GCMS Mass Traces

Mass spectra obtained for the products that were commonly found (together with their approximate retention times on GCMS):

m-Xylene – Retention time = ~6.2 min

13

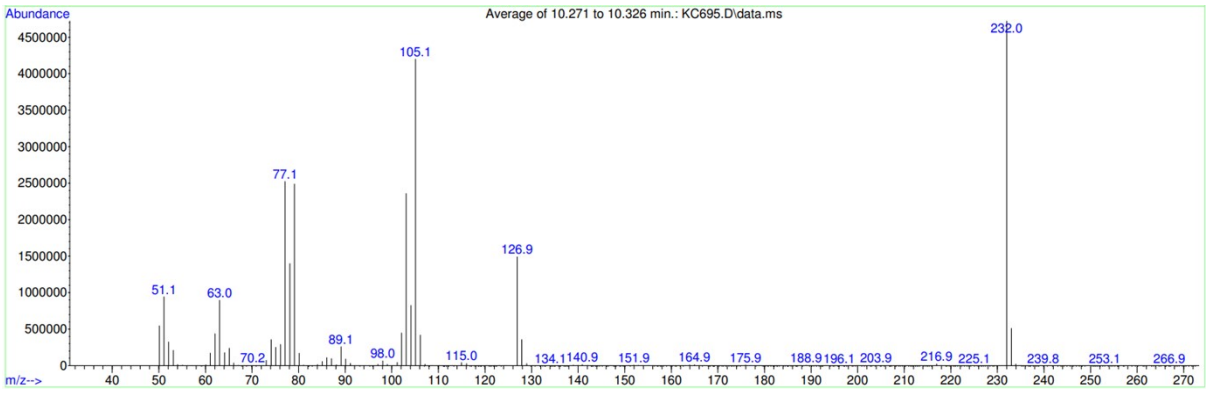
Predicted *m/z*: 106.08 (100.0%), 107.08 (8.8%)



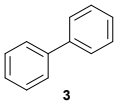
2-Iodo-*m*-xylene – Retention time = ~10.3 min

7

Predicted *m/z*: 231.97 (100.0%), 232.98 (8.8%)

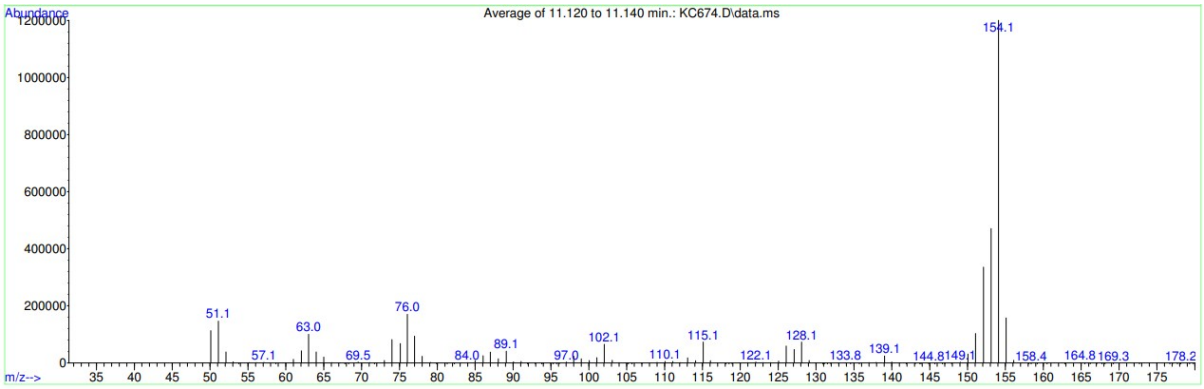


Biphenyl – Retention time = ~11.1 min

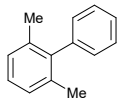


3

Predicted *m/z*: 154.0783 (100.0%), 155.0816 (13.0%)

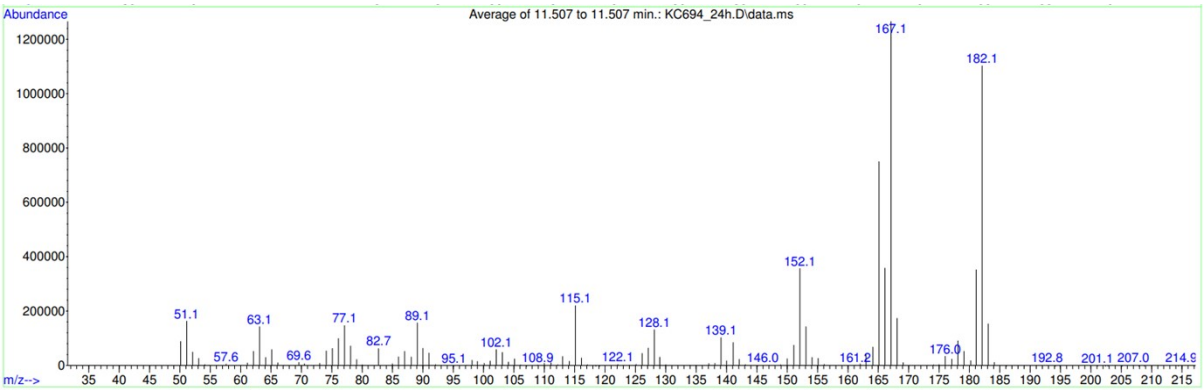


2,6-Dimethylbiphenyl – Retention time = ~11.5 min



12

Predicted *m/z*: 182.11 (100.0%), 183.11 (15.1%), 184.12 (1.1%)



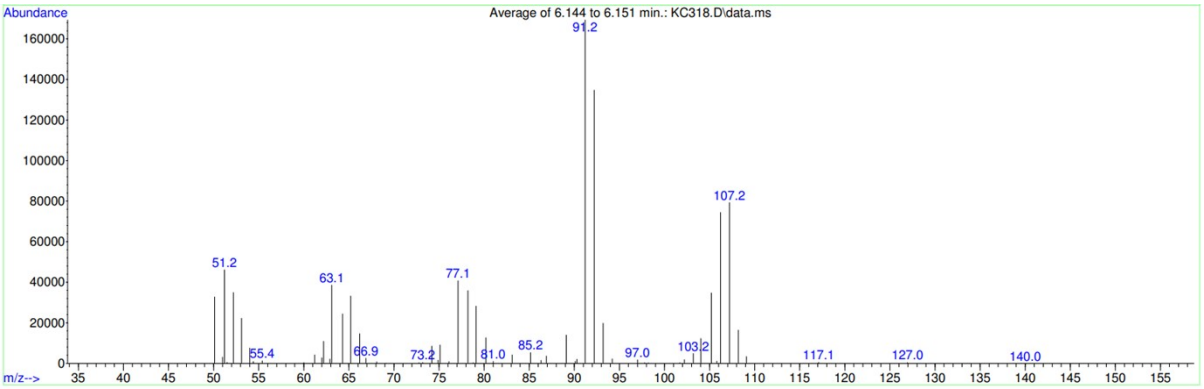
Individual Mass Spectra of Deuterated Compounds

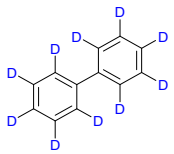
Method of analysis – Picking the peaks on the GCMS software generates an average mass across the peak area. In some cases, the deuterated compounds have slightly differing retention times when compared to their unlabelled counterparts. Analysing across sections of the peak area at different time points can show different isotopologue mass ions.

This is best demonstrated with *m*-xylene **13**: when conducting the reaction of 2-iodo-*m*-xylene **7** with KO^{t}Bu and 1,10-phenanthroline in C_6D_6, the average mass across the whole *m*-xylene peak is the unlabelled compound *m/z* = 106. However, averaging the very start of the peak does indeed highlight that some **13-d_1** has formed as demonstrated with the mass spectrum below showing the *m/z* of 107.

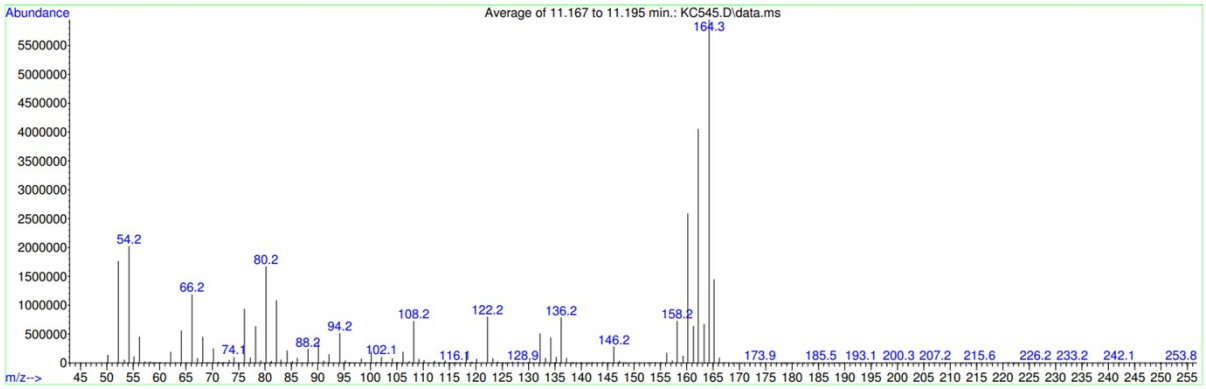
This method of analysis, using averaging across the peak, was used for all isotope studies.

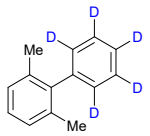
13-d_1
Predicted *m/z*: 107.0845 (100.0%), 108.0879 (8.7%)
Retention Time = ~6.1 min



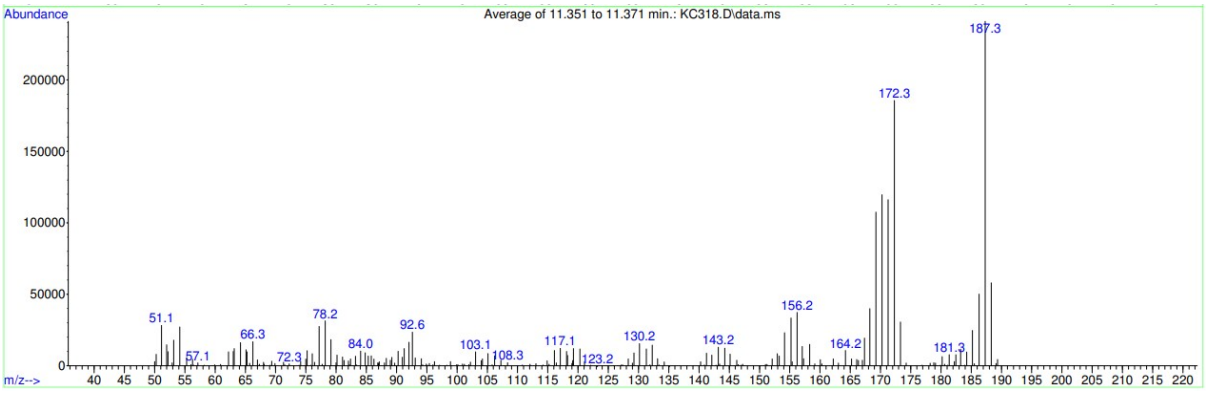


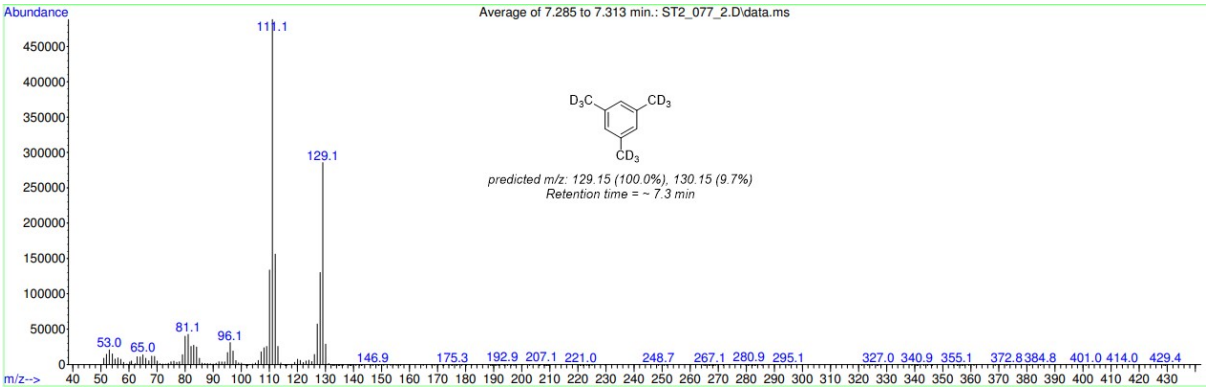
3-d_{10}
Predicted *m/z*: 164.1410 (100.0%), 165.1444 (13.0%)
Retention Time = ~11.2 min

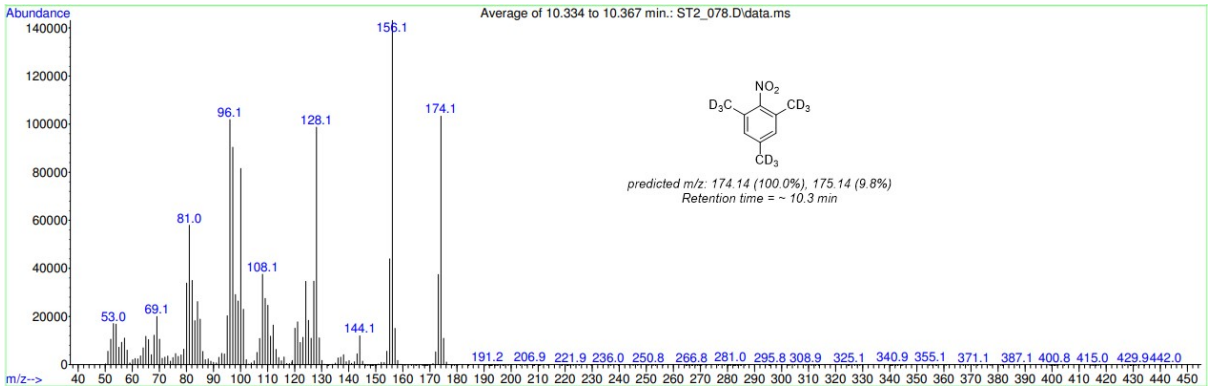


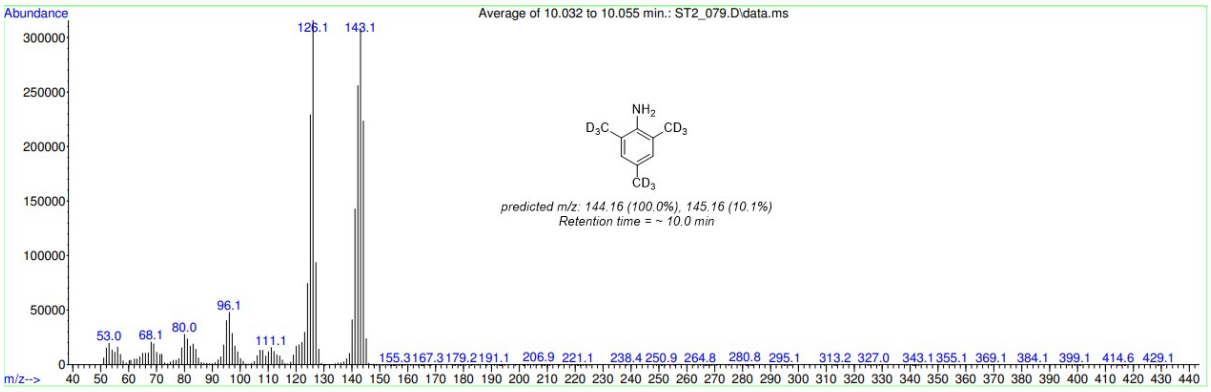


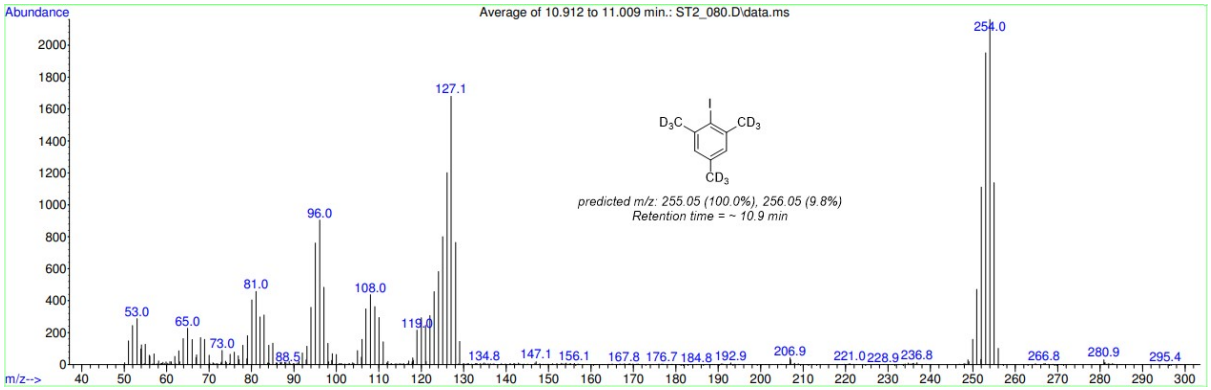
12-d_5
Predicted *m/z*: 187.1409 (100.0%), 188.1443 (15.1%), 189.1476 (1.1%)
Retention Time = ~11.4 min






Abundance
Average of 10.334 to 10.367 min.: ST2_078.D\data.ms
156.1
174.1
96.1
128.1
81.0
108.1
53.0
69.1
144.1
m/z-->
predicted m/z: 174.14 (100.0%), 175.14 (9.8%)
Retention time = ~ 10.3 min


Abundance
Average of 10.032 to 10.055 min.: ST2_079.D\data.ms
126.1
143.1
96.1
53.0
68.1
80.0
111.1
m/z-->
predicted m/z: 144.16 (100.0%), 145.16 (10.1%)
Retention time = ~ 10.0 min


Abundance
Average of 10.912 to 11.009 min.: ST2_080.D\data.ms
254.0
127.1
96.0
81.0
108.0
53.0
65.0
73.0
119.0
m/z-->
predicted m/z: 255.05 (100.0%), 256.05 (9.8%)
Retention time = ~ 10.9 min

Calibration Information

Method

Commercial samples of 2-iodo-*m*-xylene **7**, biphenyl **3** and *m*-xylene **13** were weighed out at several, different mmol and diluted with chloroform. 2,6-Dimethylbiphenyl **12** was prepared and weighed out at several, different mmol and diluted with chloroform. ~17 µL of dodecane was then added to each sample, with the exact weight of dodecane added noted in each case so the exact mmol added was known. 100 µL aliquots of each solution was then taken and made up to 1 mL with chloroform. Each sample was then run on the GCFID using the GC320 method. Once complete, the peak area for both the dodecane and sample was noted in each case.

To plot graphs for each sample:

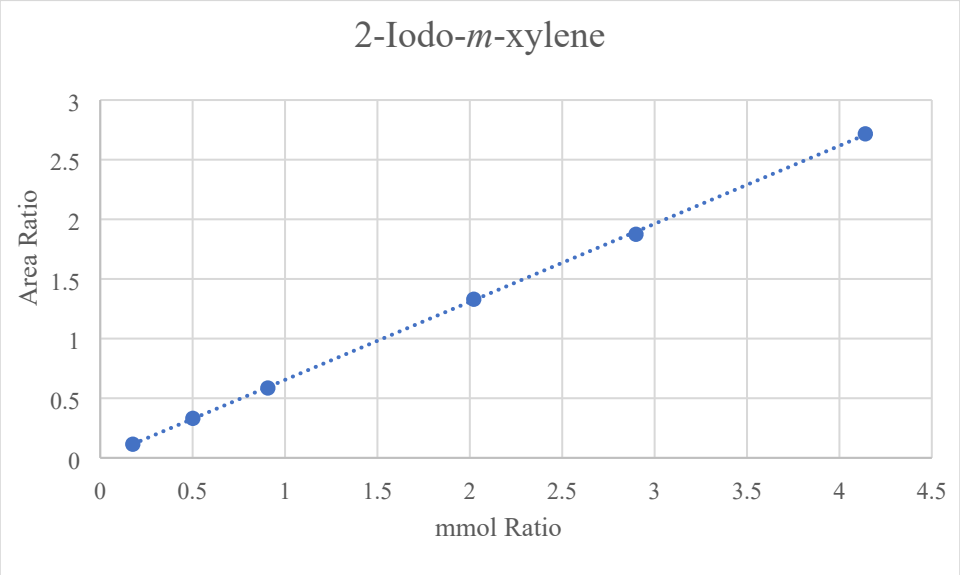
- Mmol ratio was calculated by dividing the mmol of sample by mmol of dodecane.
- The area ratio was then calculated by dividing the sample area by the dodecane area.
- Scatter graphs were then plotted using the mmol ratio against the sample area ratio.

Calibration Graphs

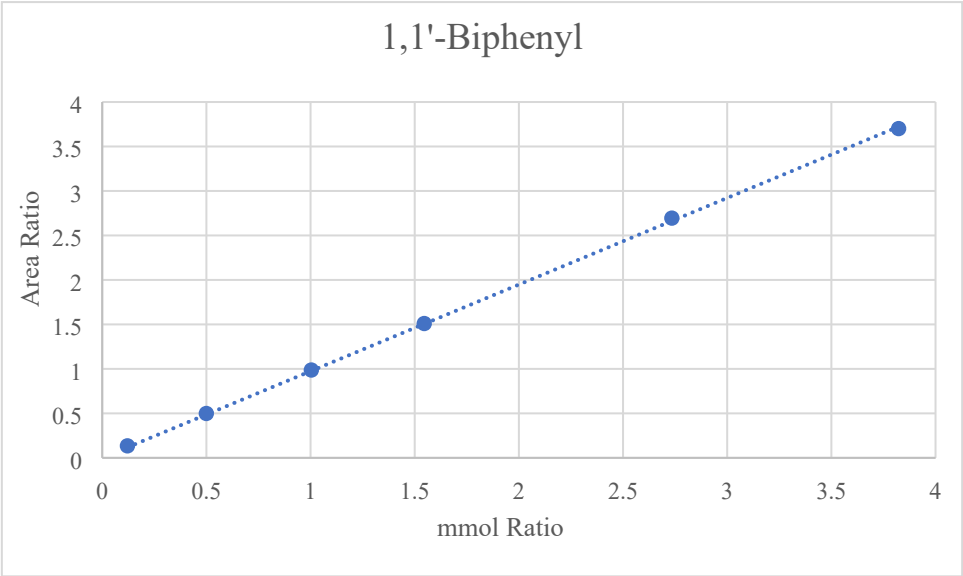
The column was changed on the GCFID and so the retention times for all peaks shifted. A repeat calibration was therefore done.

2-Iodo-m-xylene – First Set of Calibration Graphs

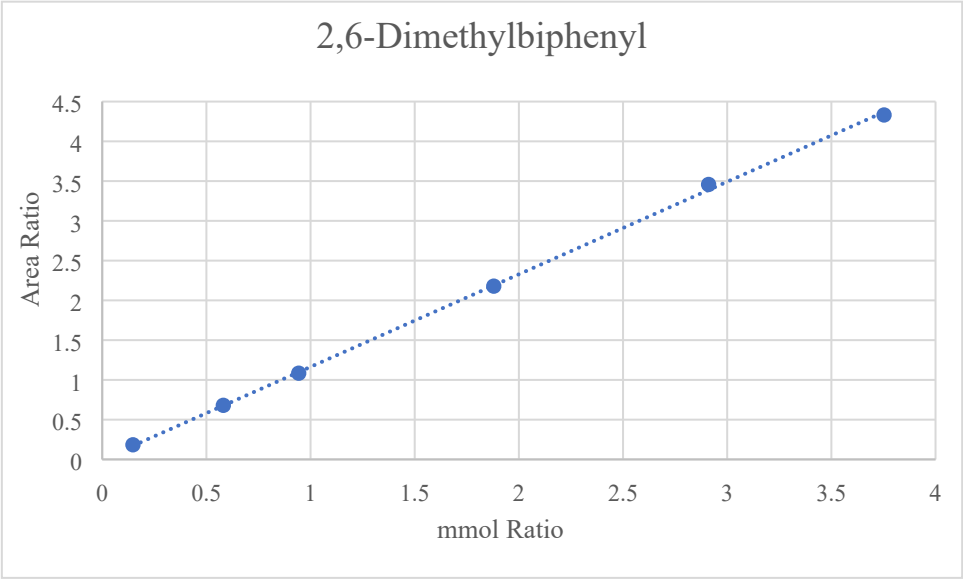
2-iodo-*m*-xylene



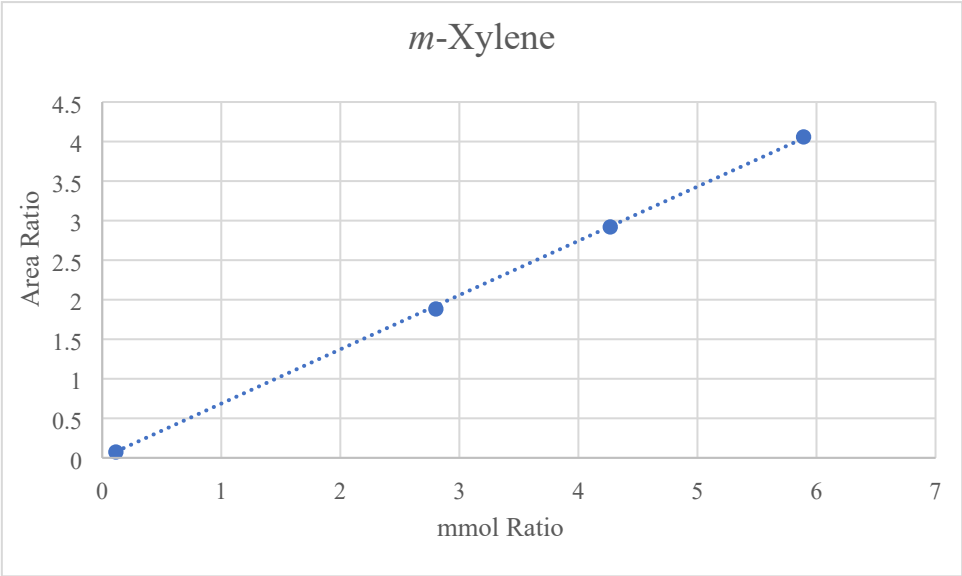
1,1’-Biphenyl



2,6-Dimethylbiphenyl

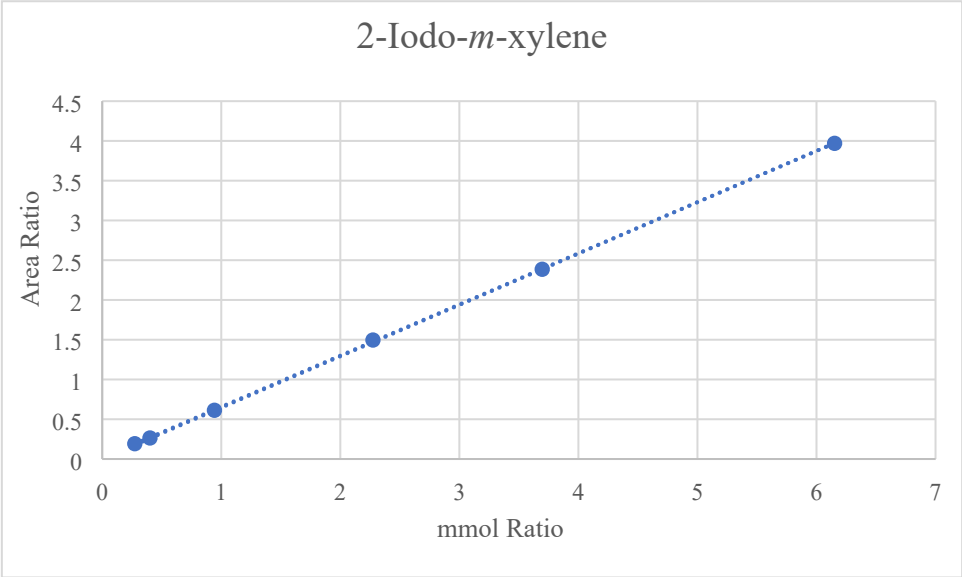


m-Xylene

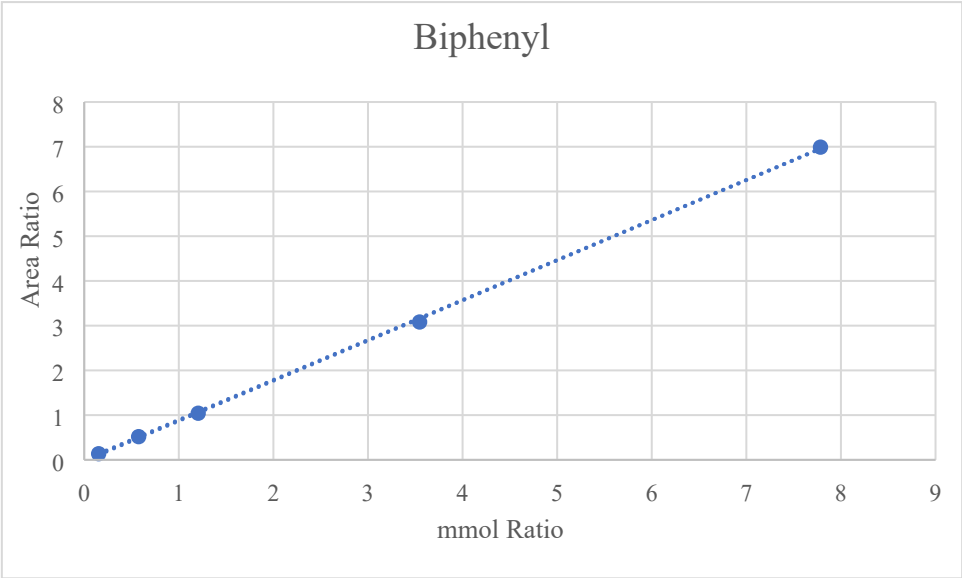


2-Iodo-m-xylene – Second Set of Calibration Graphs

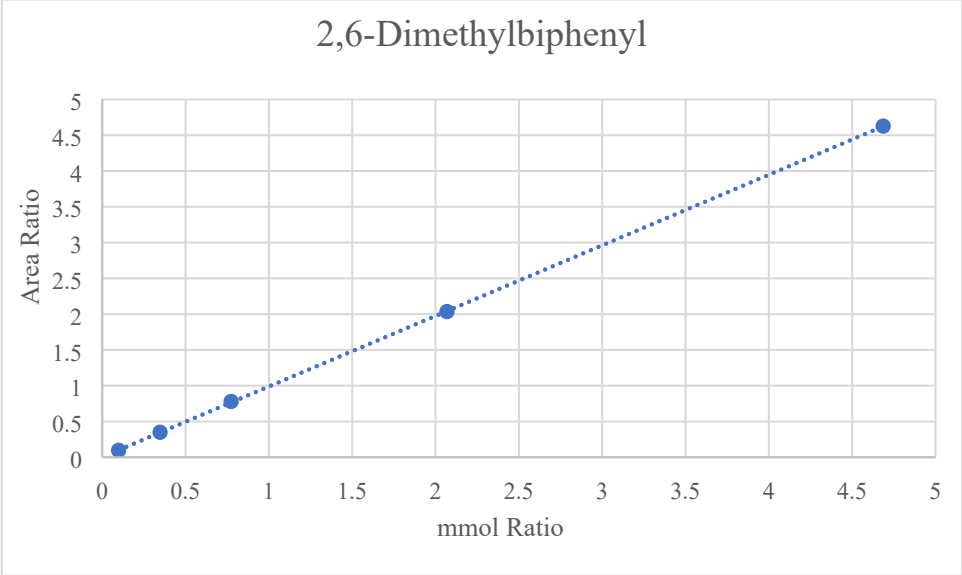
2-iodo-*m*-xylene



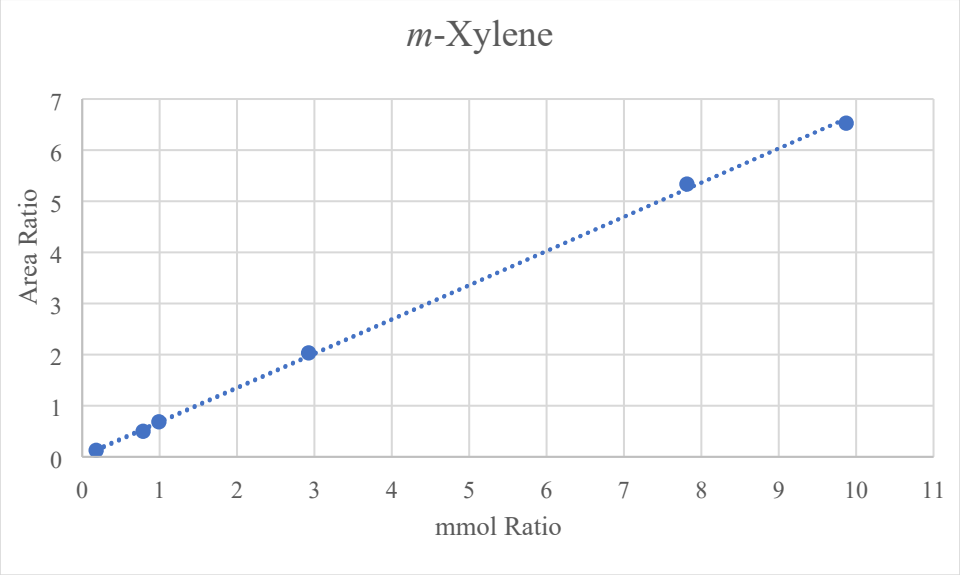
Biphenyl



2,6-Dimethylbiphenyl



m-Xylene

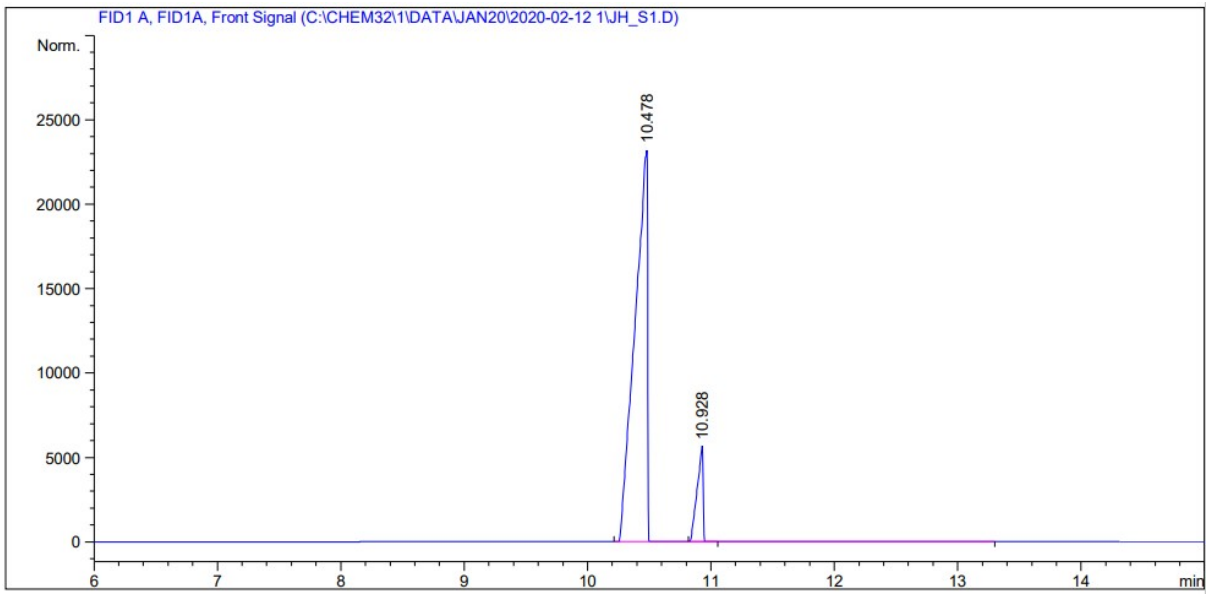

m-Xylene
Area Ratio
mmol Ratio
0
1
2
3
4
5
6
7
8
9
10
11

GC data

2-Iodo-m-xylene – First Set of GCFID Data

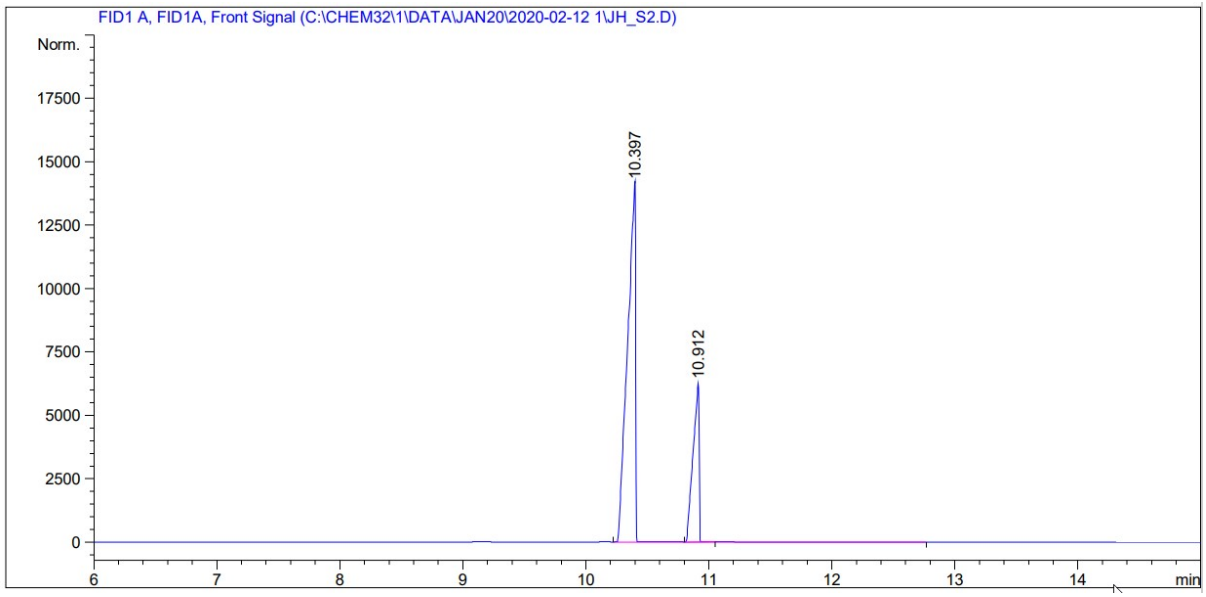
2-Iodo-*m*-xylene

0.02 mmol



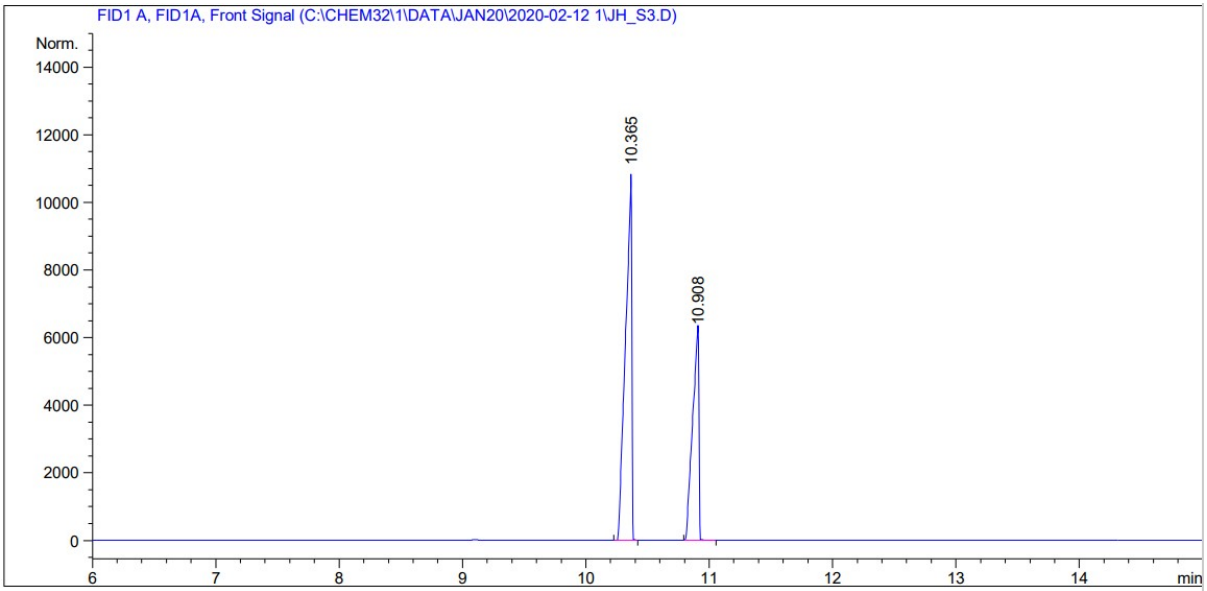
Retention Time	Sample	Peak Area
10.478	Dodecane	164328
10.928	2-Iodo-*m*-xylene	18814.7

0.05 mmol



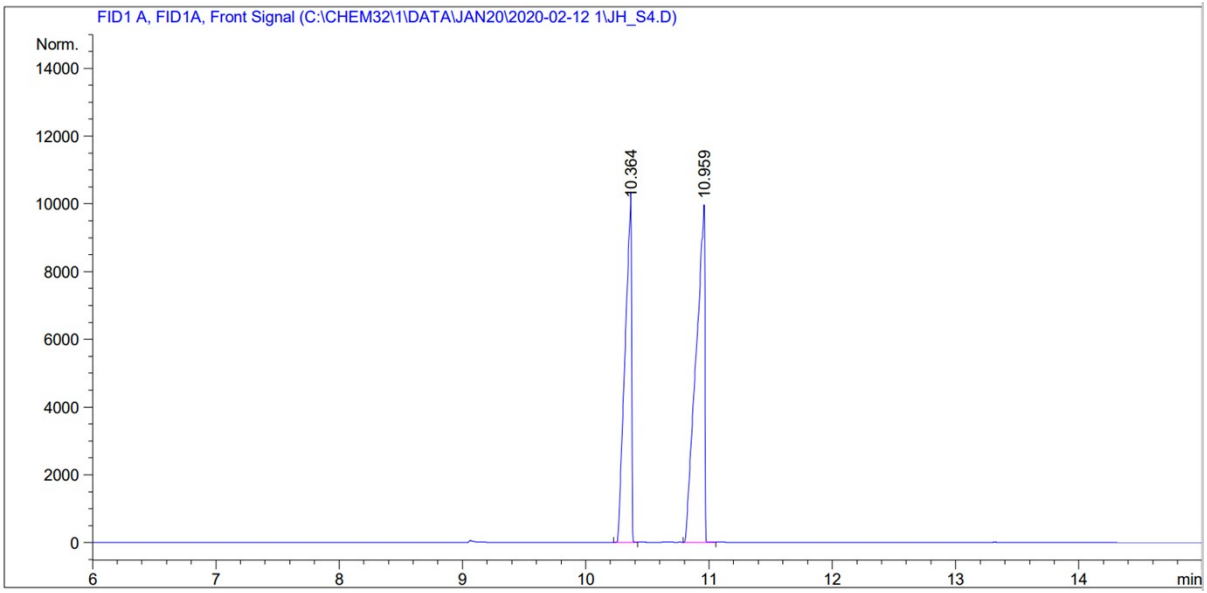
Retention Time	Sample	Peak Area
10.397	Dodecane	64068.3
10.912	2-Iodo-*m*-xylene	21218.7

0.1 mmol



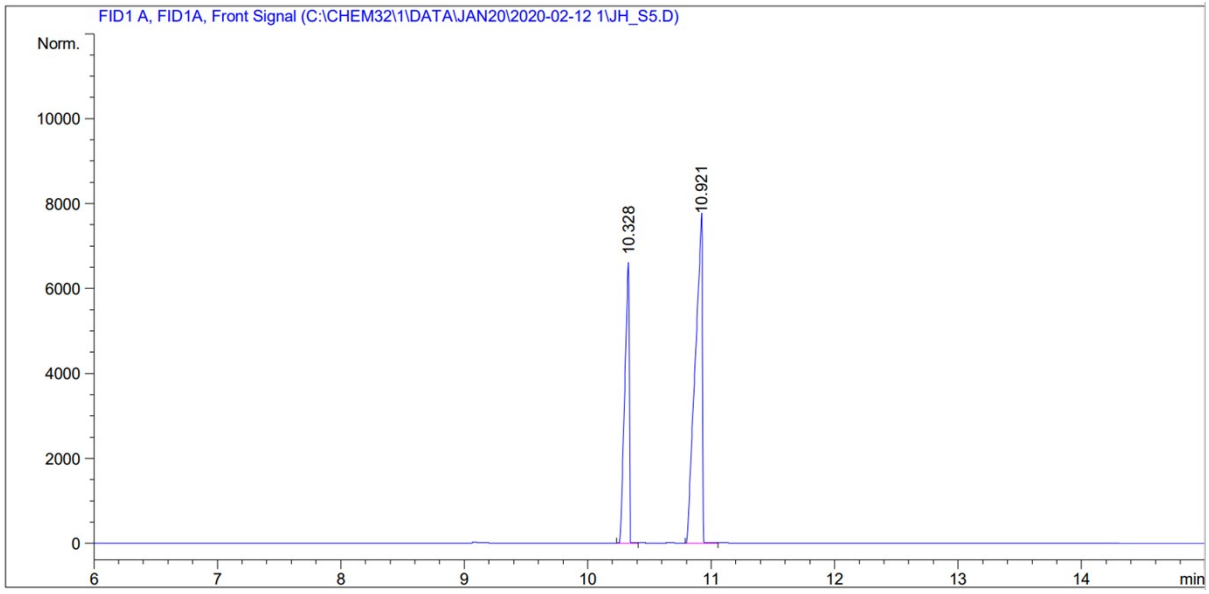
Retention Time	Sample	Peak Area
10.365	Dodecane	37932.2
10.908	2-Iodo-*m*-xylene	22214.8

0.2 mmol



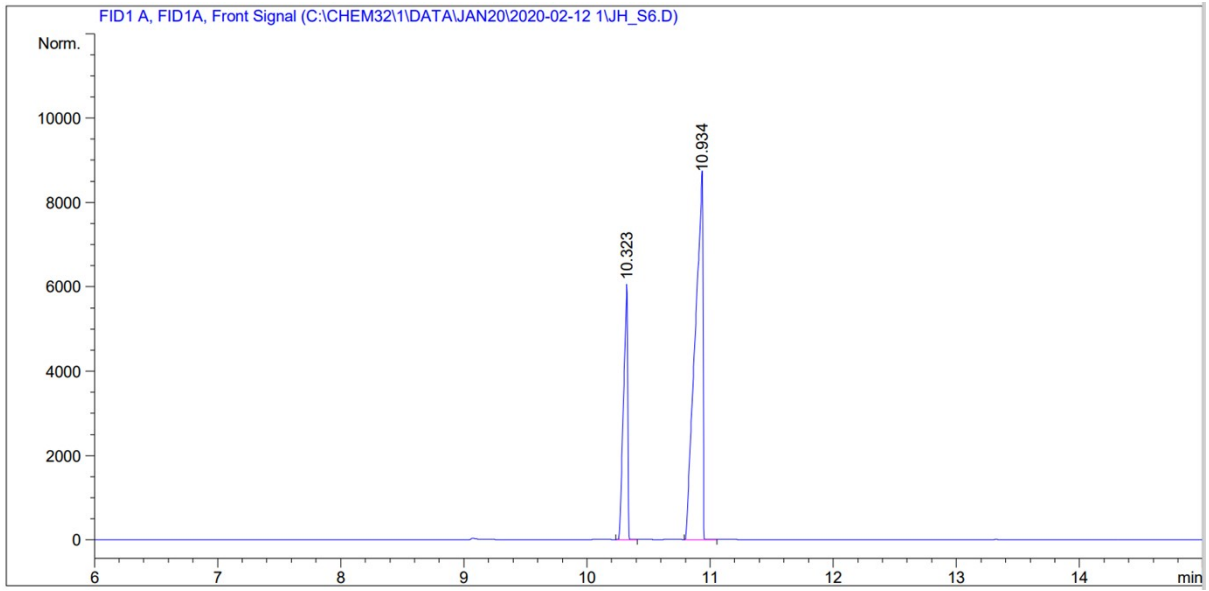
Retention Time	Sample	Peak Area
10.364	Dodecane	37309.1
10.959	2-Iodo-*m*-xylene	49616.7

0.3 mmol



Retention Time	Sample	Peak Area
10.328	Dodecane	16580
10.921	2-Iodo-*m*-xylene	31079.9

0.4 mmol



Retention Time	Sample	Peak Area
10.323	Dodecane	14086.6
10.934	2-Iodo-*m*-xylene	38264.4

For determination of yields:

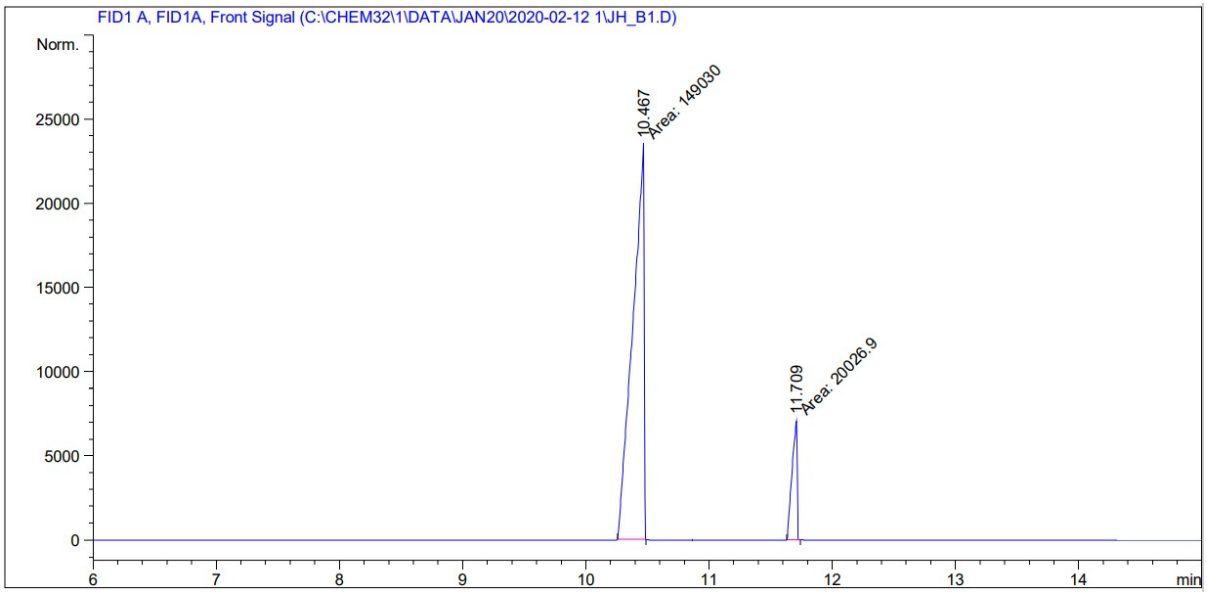
Example used for **Reaction of 2-Iodo-*m*-xylene 7 with Piperazinedione 16 and KO^{t}Bu**

For 2-Iodo-*m*-xylene:

- Area of 2-Iodo-*m*-xylene = **7196.2**
- Area of dodecane = **4045.8**
- Exact mass of dodecane added to vial = 16.7 mg = **0.098** mmol
- Area Ratio: 7196.2/4045.8 = **1.778**
- To determine mmol of sample: (Area ratio*mmol of dodecane)/gradient of the calibration curve = (1.778*0.098)/0.6535= **0.267**
- %yield = (mmol of sample/starting mmol of reaction)*100 = (0.267/0.7)*100 = **38.1%**

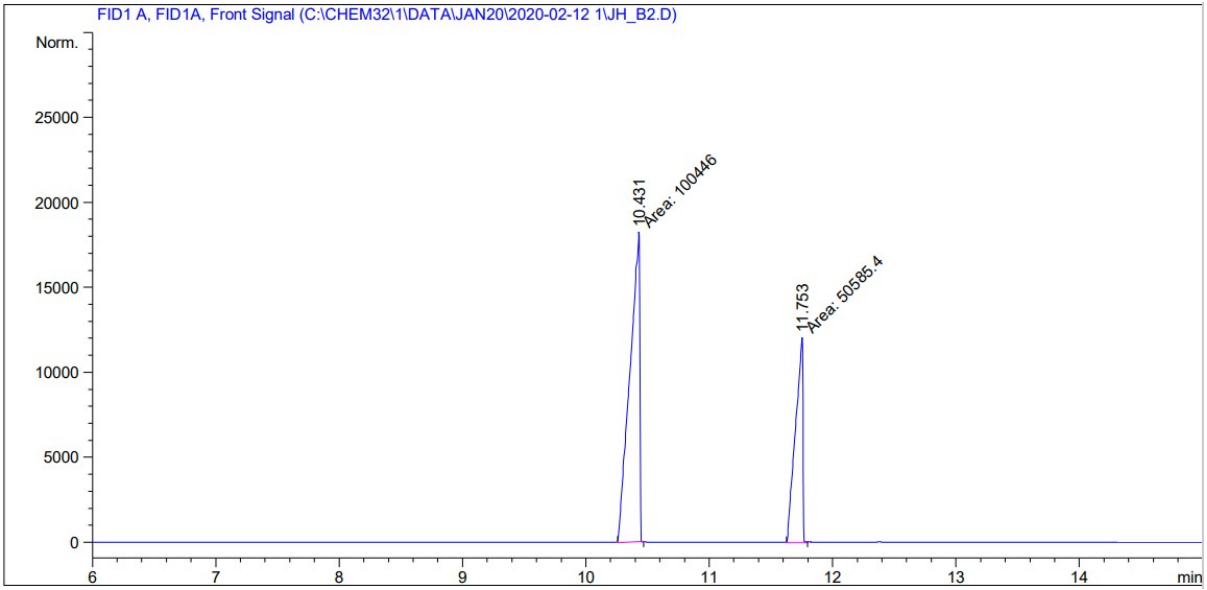
Biphenyl

0.01 mmol



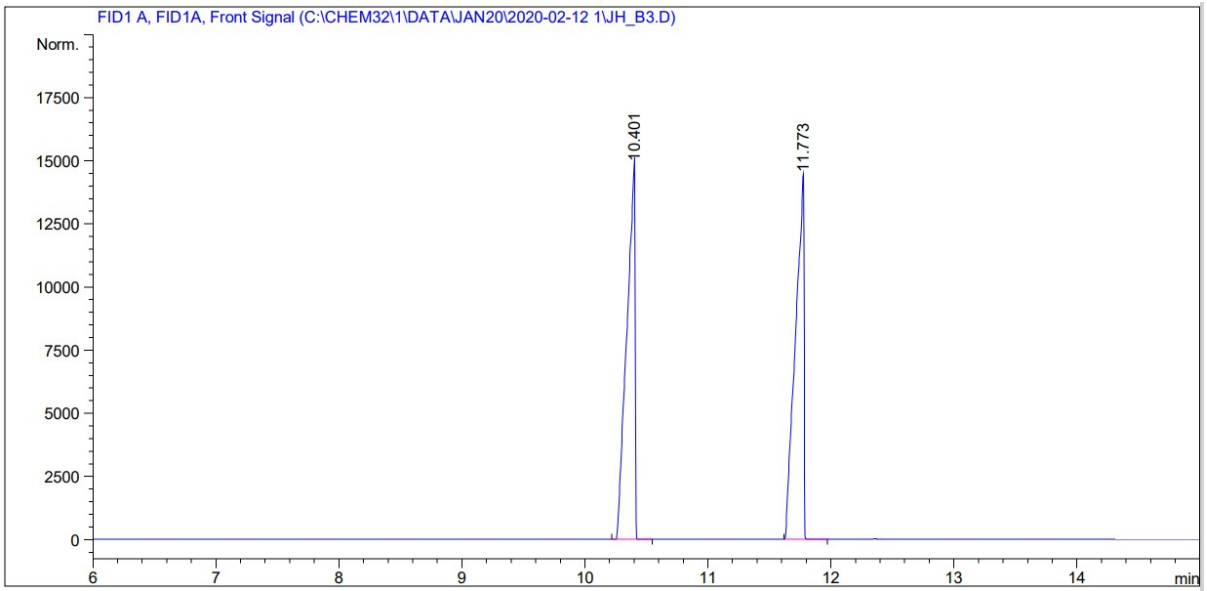
Retention Time	Sample	Peak Area
10.467	Dodecane	149030
11.709	Biphenyl	20026.9

0.05 mmol



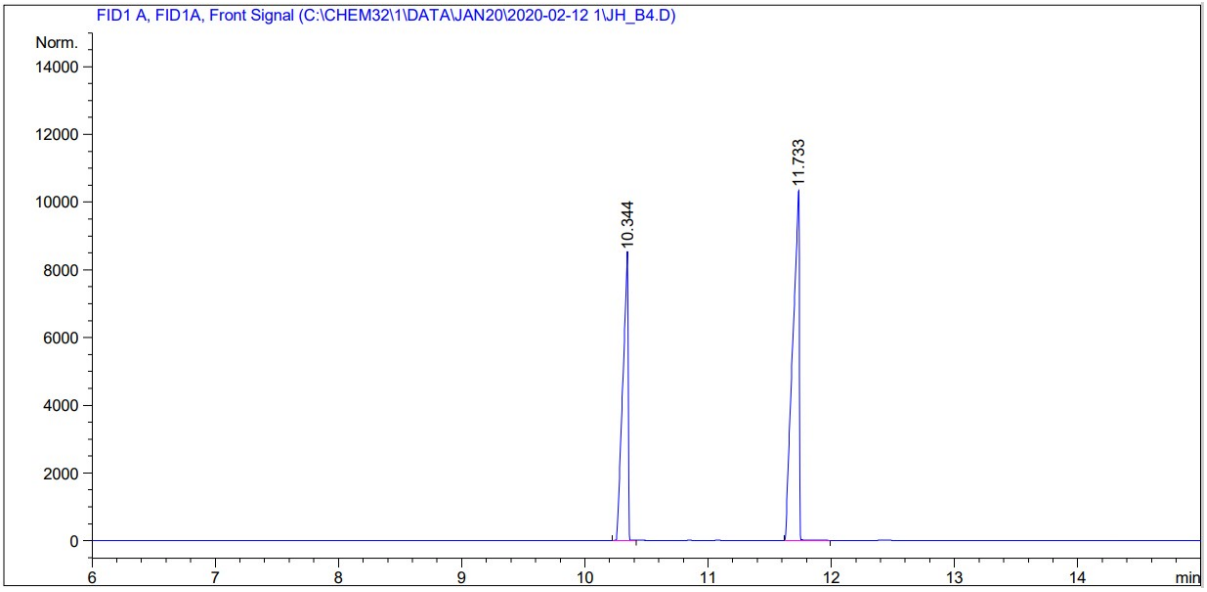
Retention Time	Sample	Peak Area
10.431	Dodecane	100446
11.753	Biphenyl	50585.4

0.1 mmol



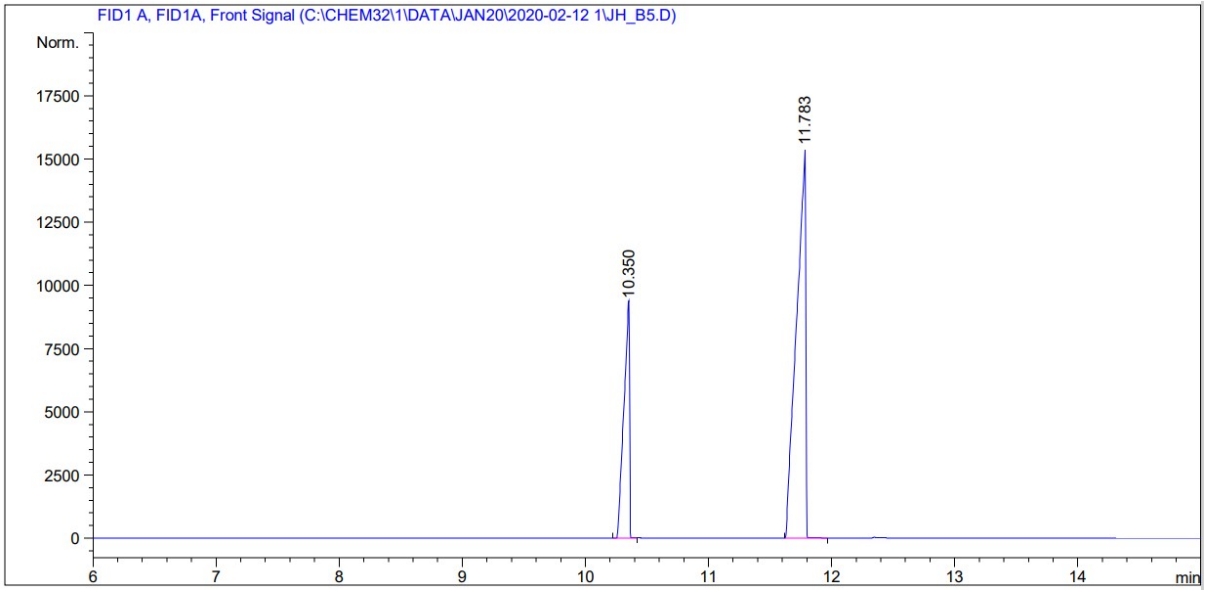
Retention Time	Sample	Peak Area
10.401	Dodecane	70144.2
11.773	Biphenyl	69248.1

0.2 mmol



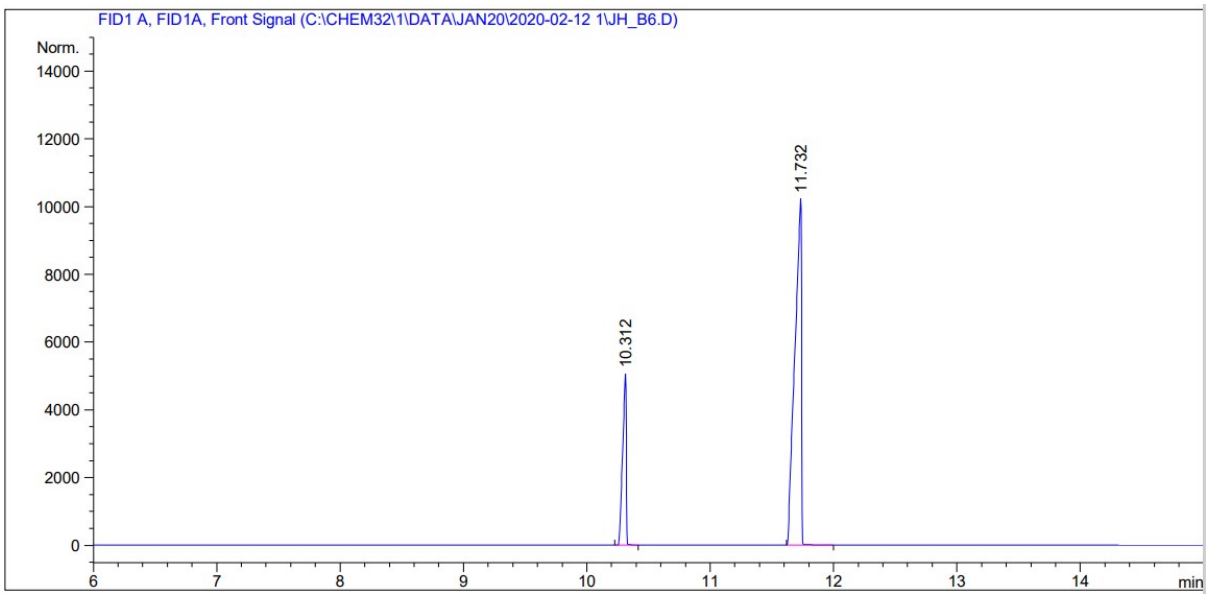
Retention Time	Sample	Peak Area
10.344	Dodecane	25473.5
11.773	Biphenyl	38464.5

0.3 mmol



Retention Time	Sample	Peak Area
10.350	Dodecane	29547.5
11.783	Biphenyl	79621.3

0.4 mmol



Retention Time	Sample	Peak Area
10.312	Dodecane	10280.9
11.732	Biphenyl	38048.0

For determination of yields:

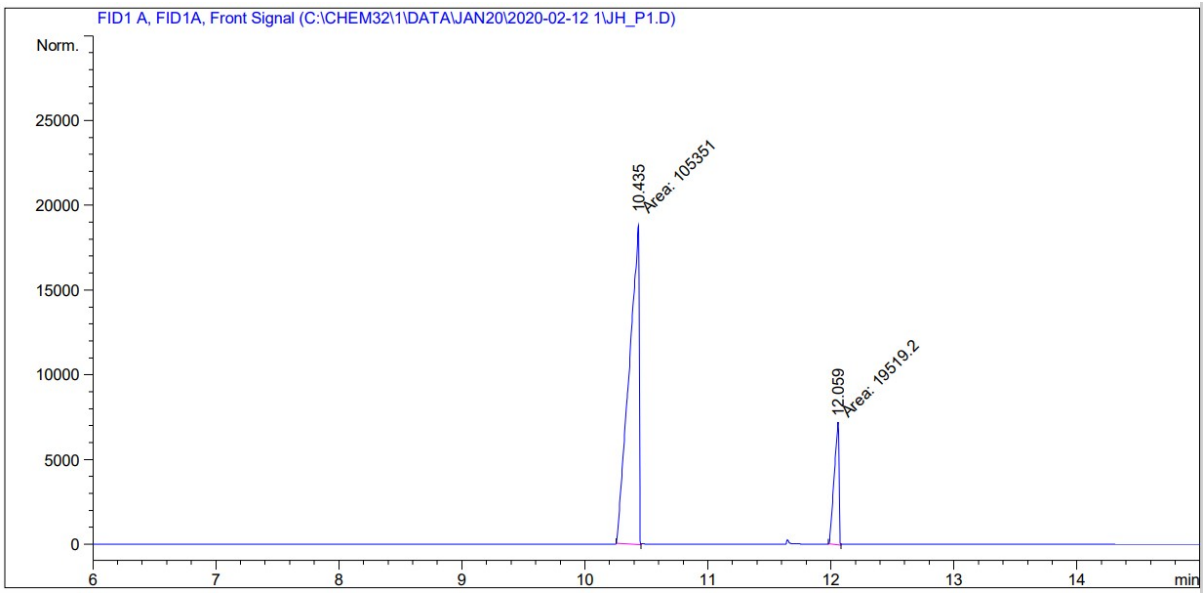
Example used for **Reaction of 2-Iodo-*m*-xylene 7 with Piperazinedione 16 and KO^{t}Bu**

For Biphenyl:

- Area of Biphenyl = **3934.5**
- Area of dodecane = **4045.8**
- Exact mass of dodecane added to vial = 16.7 mg = **0.098** mmol
- Area Ratio: 3934.5/4045.8 = **0.972**
- To determine mmol of sample: (Area ratio*mmol of dodecane)/gradient of the calibration curve = (0.972*0.098)/0.975= **0.098**
- %yield = (mmol of sample/starting mmol of reaction)*100 = (0.098/0.7)*100 = **14.0%**

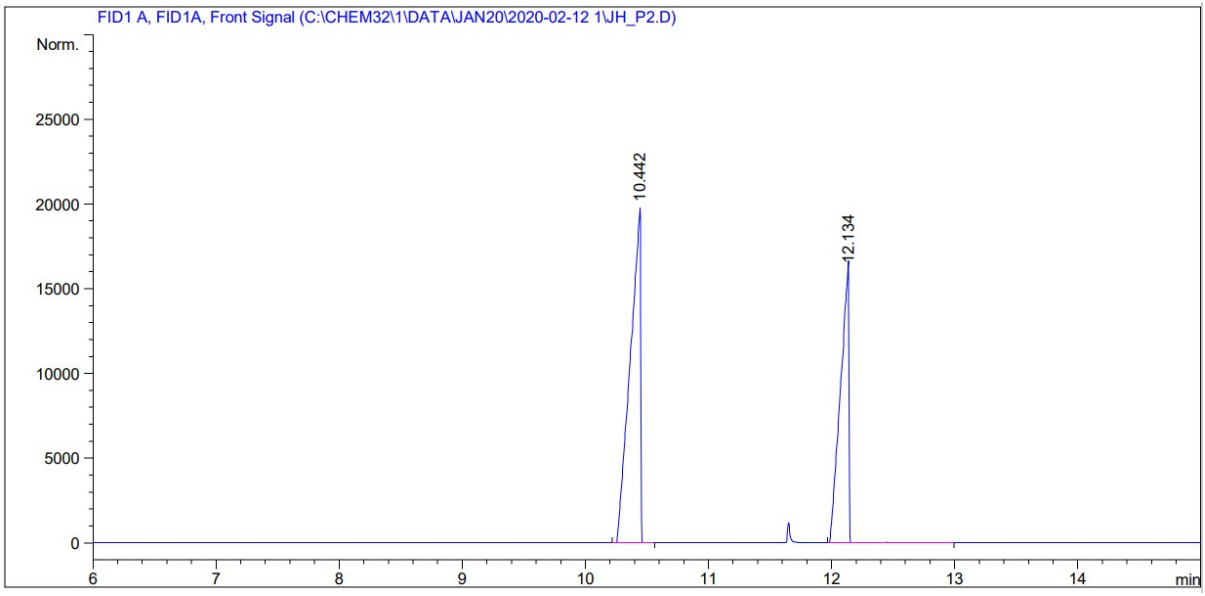
2,6-Dimethylbiphenyl

0.01 mmol



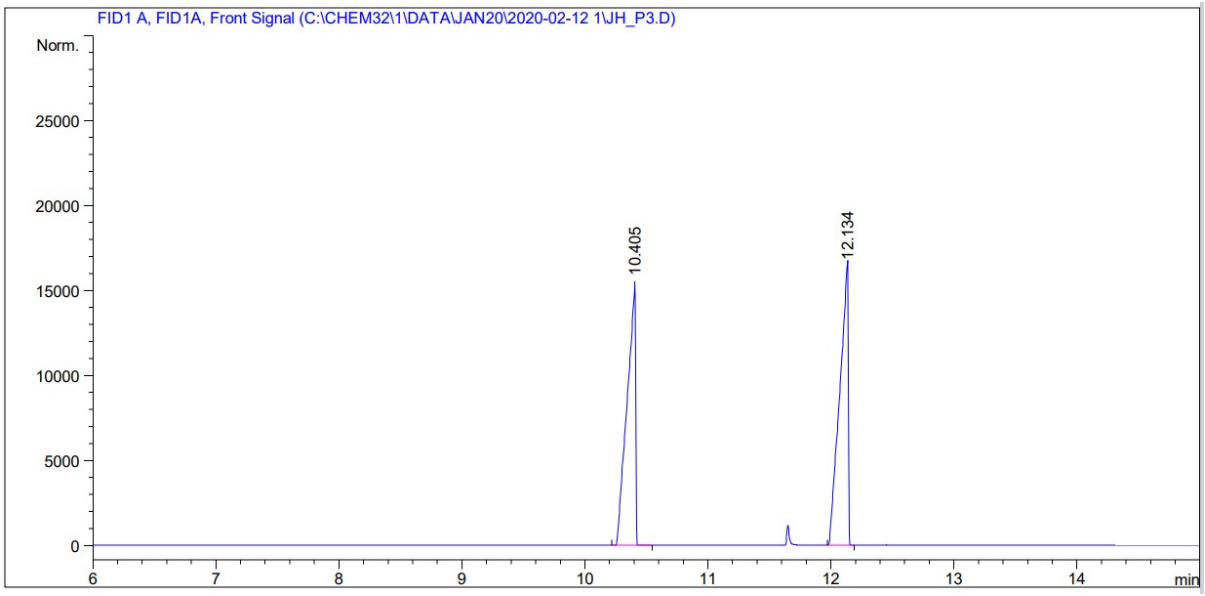
Retention Time	Sample	Peak Area
10.435	Dodecane	105351
12.059	2,6-Dimethylbiphenyl	19519.2

0.06 mmol



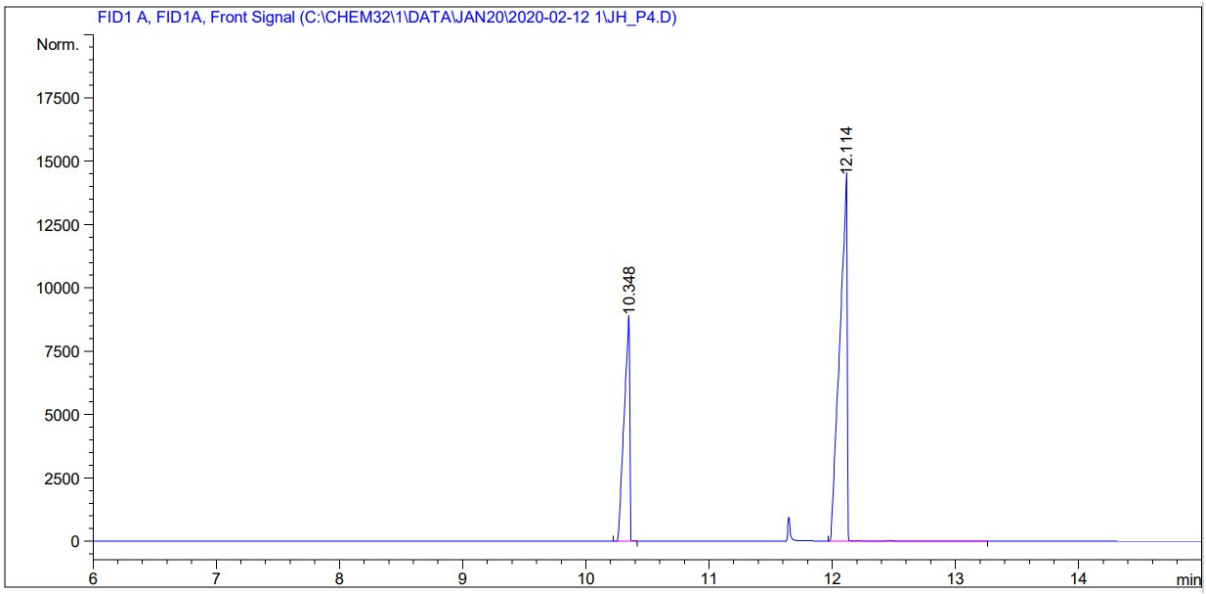
Retention Time	Sample	Peak Area
10.442	Dodecane	115829.0
12.134	2,6-Dimethylbiphenyl	78888.5

0.1 mmol



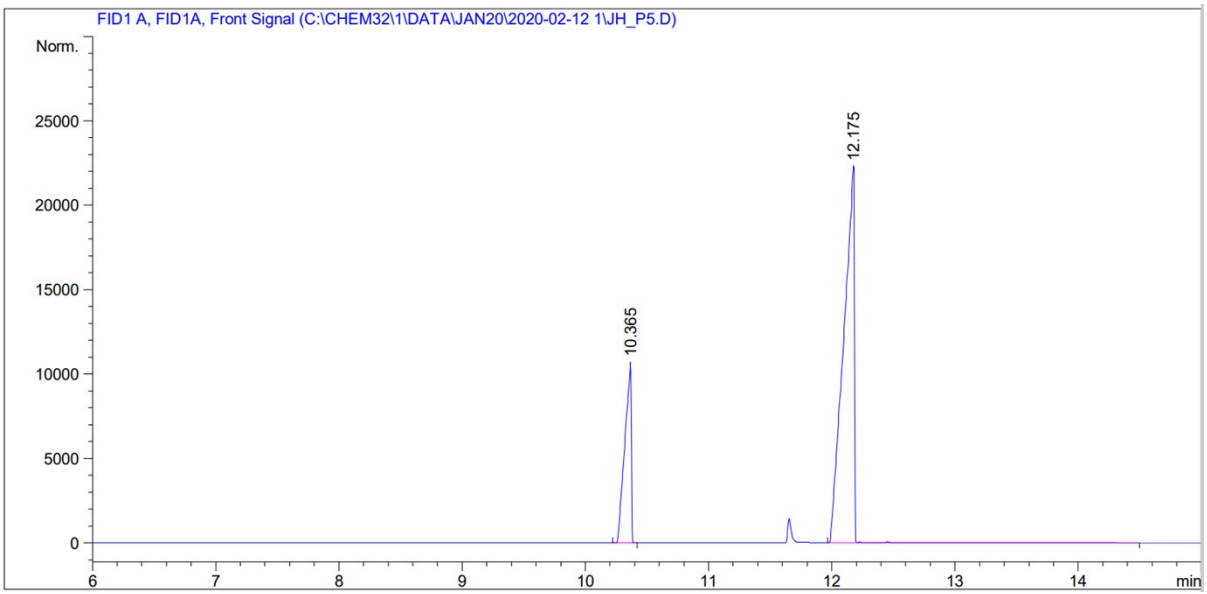
Retention Time	Sample	Peak Area
10.405	Dodecane	74090.1
12.134	2,6-Dimethylbiphenyl	80332.6

0.2 mmol



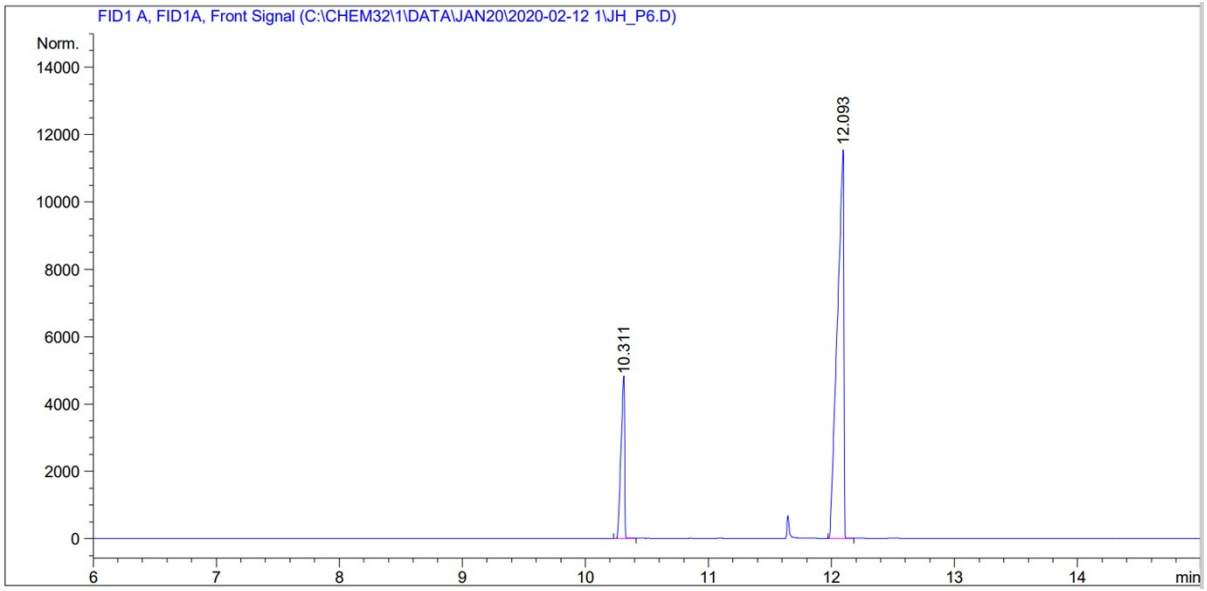
Retention Time	Sample	Peak Area
10.348	Dodecane	27600.9
12.114	2,6-Dimethylbiphenyl	60205.5

0.3 mmol



Retention Time	Sample	Peak Area
10.365	Dodecane	38696.9
12.175	2,6-Dimethylbiphenyl	133795.0

0.4 mmol



Retention Time	Sample	Peak Area
10.311	Dodecane	9779.35352
12.093	2,6-Dimethylbiphenyl	42358.7

For determination of yields:

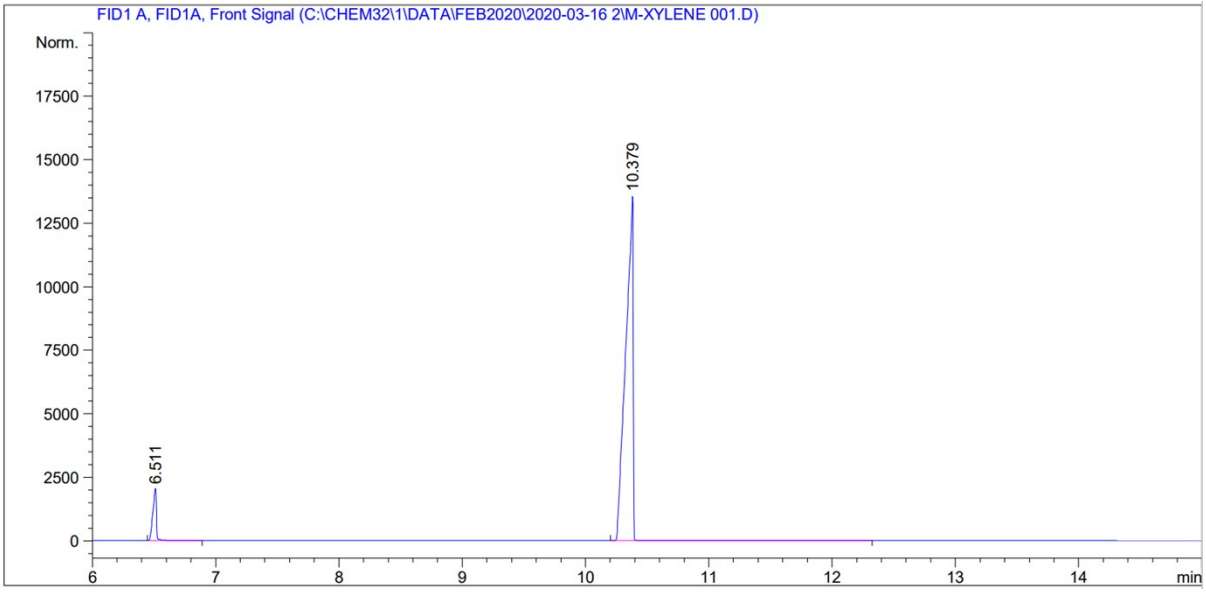
Example used for **Reaction of 2-Iodo-*m*-xylene 7 with Piperazinedione 16 and KO^{t}Bu**

For 2,6-Dimethylbiphenyl:

- Area of 2,6-Dimethylbiphenyl = **820.8**
- Area of dodecane = **4045.8**
- Exact mass of dodecane added to vial = 16.7 mg = **0.098** mmol
- Area Ratio: 820.8/4045.8 = **0.20**
- To determine mmol of sample: (Area ratio*mmol of dodecane)/gradient of the calibration curve = (0.20*0.098)/1.1654= **0.017**
- %yield = (mmol of sample/starting mmol of reaction)*100 = (0.017/0.7)*100 = **2.4%**

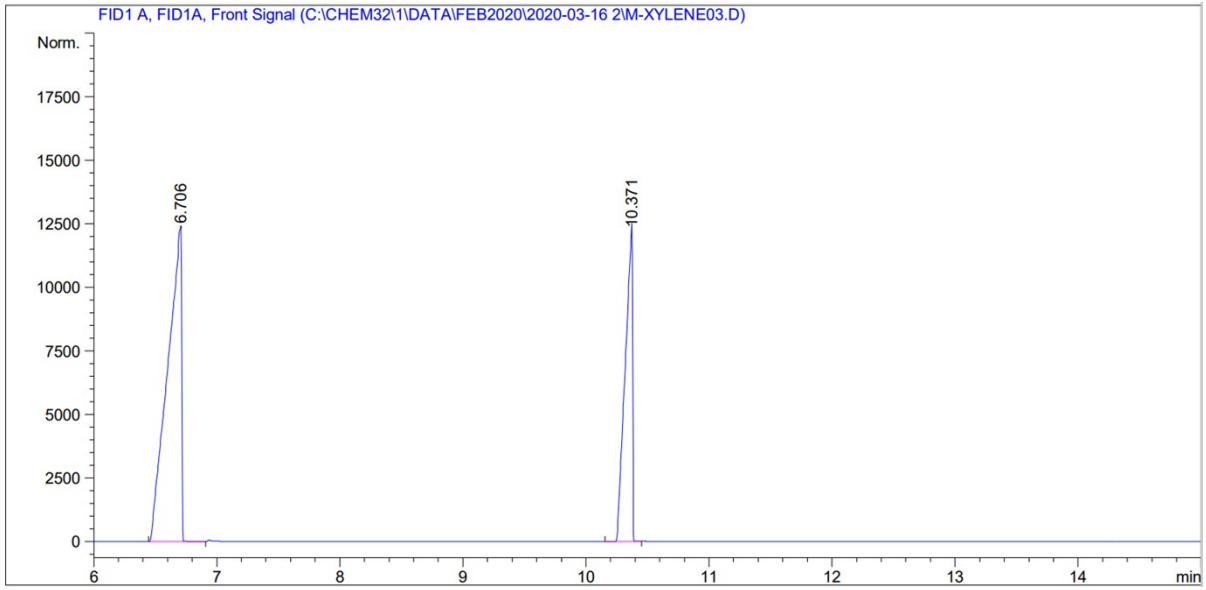
***m*-Xylene**

0.01 mmol



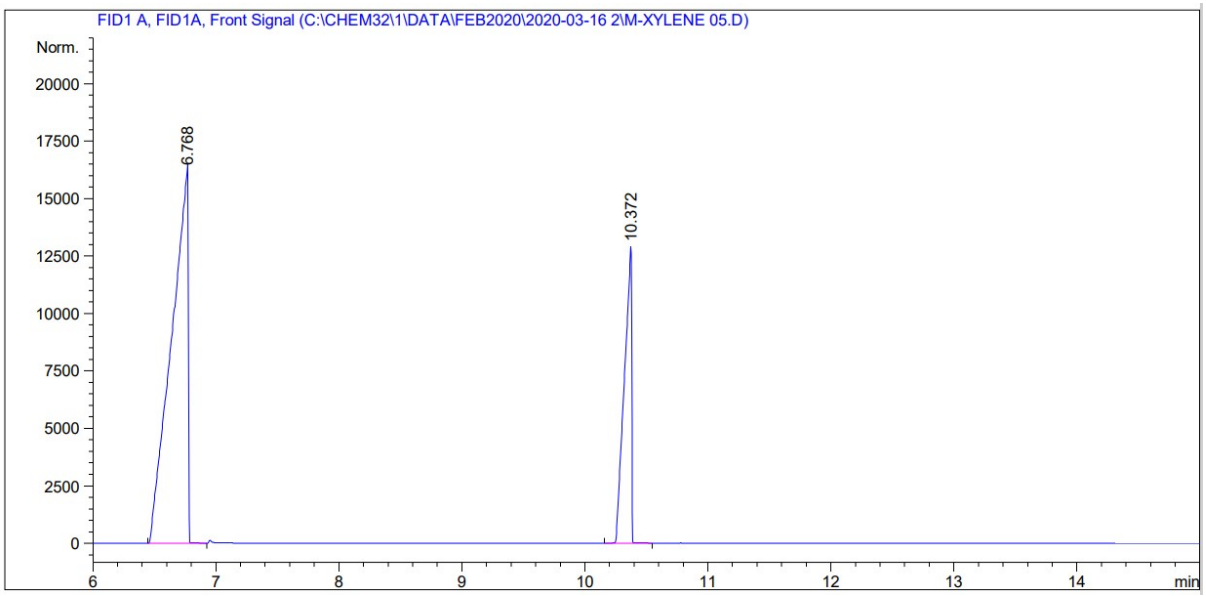
Retention Time	Sample	Peak Area
6.511	*m*-Xylene	4179.44189
10.379	Dodecane	56734.4

0.3 mmol



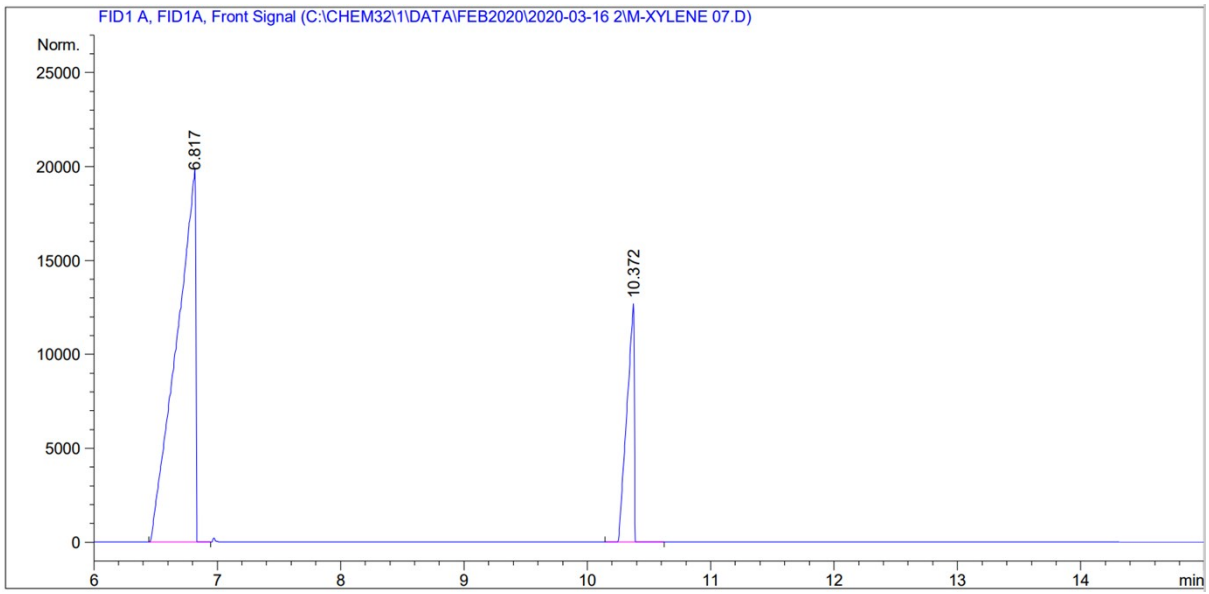
Retention Time	Sample	Peak Area
6.706	*m*-Xylene	97344.0
10.371	Dodecane	51171.6

0.5 mmol



Retention Time	Sample	Peak Area
6.768	*m*-Xylene	153825.0
10.372	Dodecane	52679.4

0.7 mmol



Retention Time	Sample	Peak Area
6.817	*m*-Xylene	211125
10.372	Dodecane	52021.0

For determination of yields:

Example used for **Reaction of 2-Iodo-*m*-xylene 7 with Piperazinedione 16 and KO^{t}Bu**

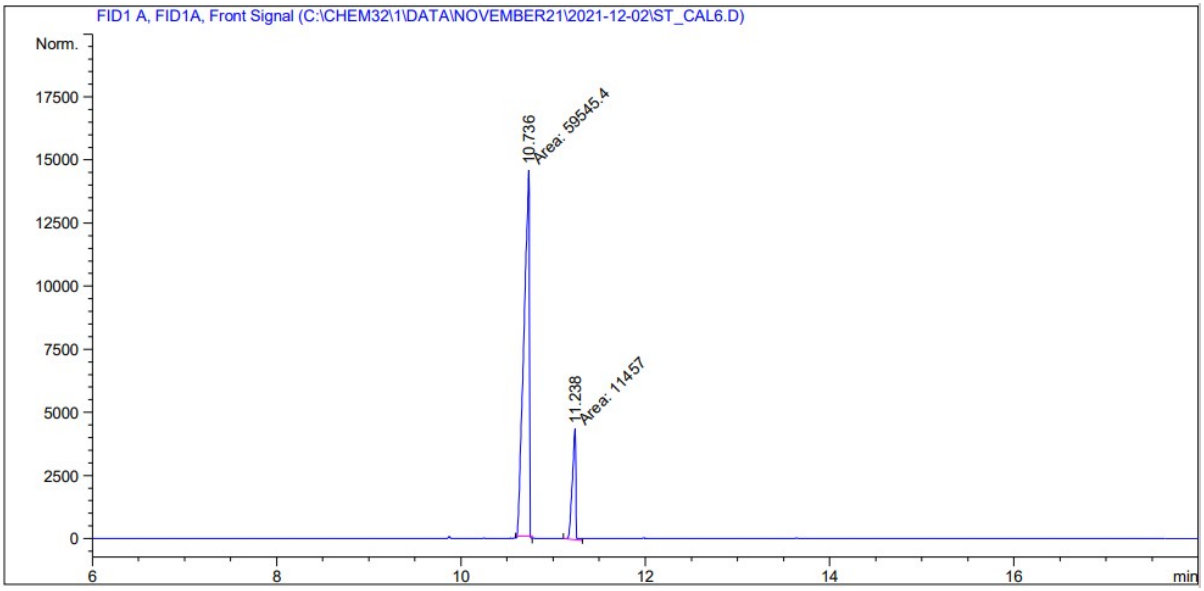
For *m*-Xylene:

- Area of *m*-Xylene = **9449.6**
- Area of dodecane = **4045.8**
- Exact mass of dodecane added to vial = 16.7 mg = **0.098** mmol
- Area Ratio: 9449.6/4045.8 = **2.34**
- To determine mmol of sample: (Area ratio*mmol of dodecane)/gradient of the calibration curve = (2.34*0.098)/0.6853= **0.334**
- %yield = (mmol of sample/starting mmol of reaction)*100 = (0.334/0.7)*100 = **47.7%**

2-Iodo-m-xylene – Second Set of GCFID Data

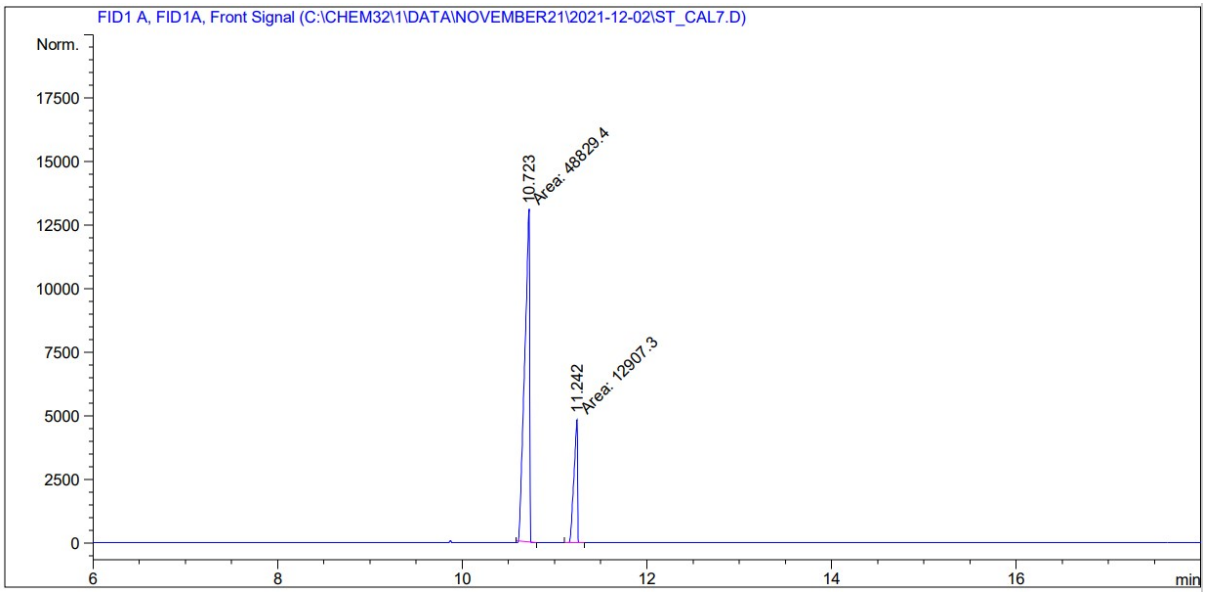
2-Iodo-*m*-xylene

0.02 mmol



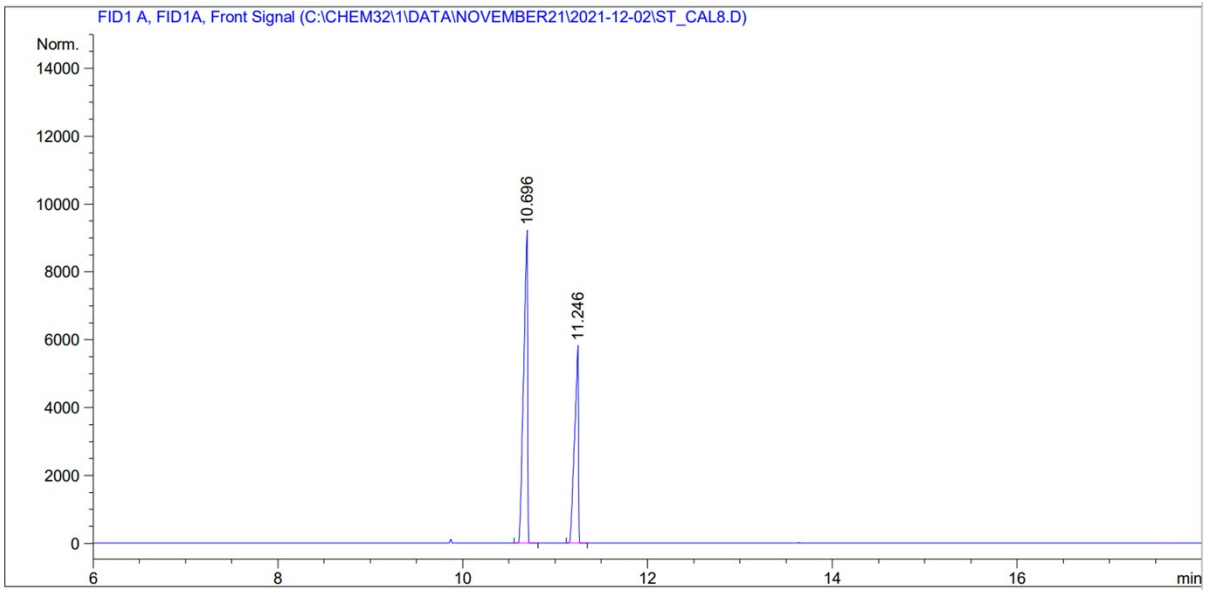
Retention Time	Sample	Peak Area
10.736	Dodecane	59545.4
11.238	2-Iodo-*m*-xylene	11457.0

0.04 mmol



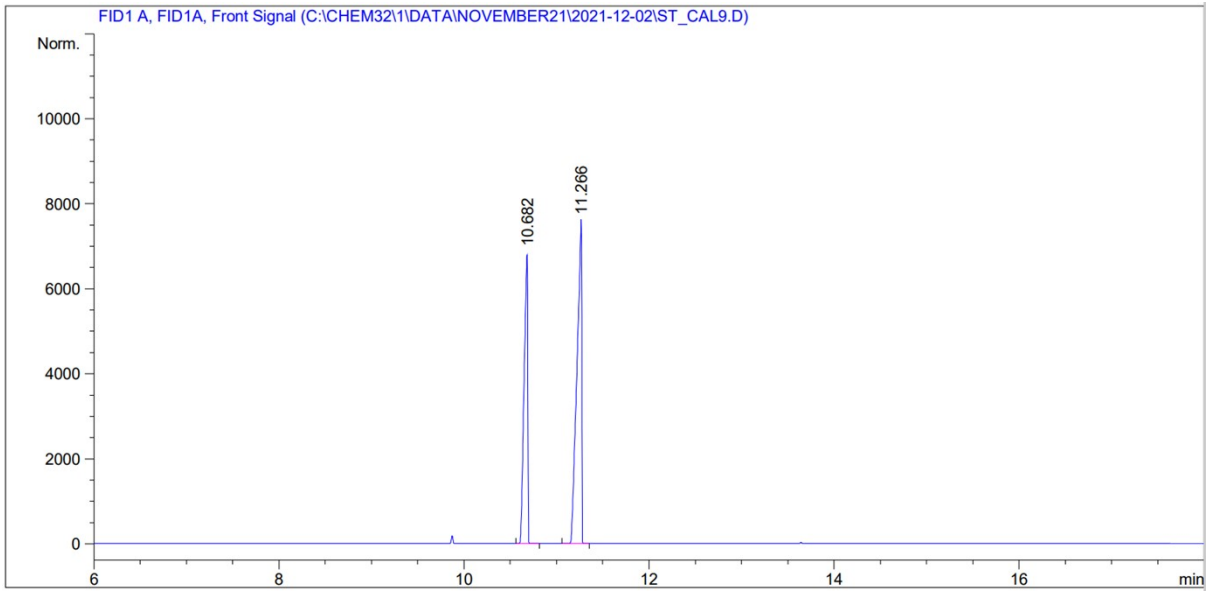
Retention Time	Sample	Peak Area
10.723	Dodecane	48829.4
11.242	2-Iodo-*m*-xylene	12907.3

0.1 mmol



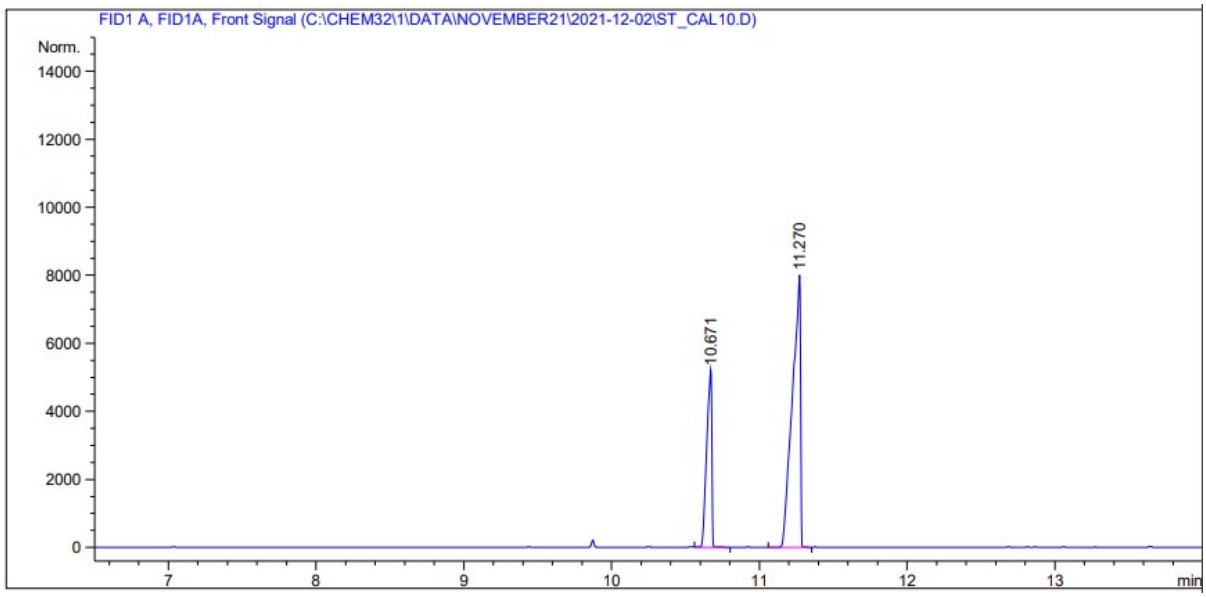
Retention Time	Sample	Peak Area
10.696	Dodecane	27416.6
11.246	2-Iodo-*m*-xylene	16799.3

0.2 mmol



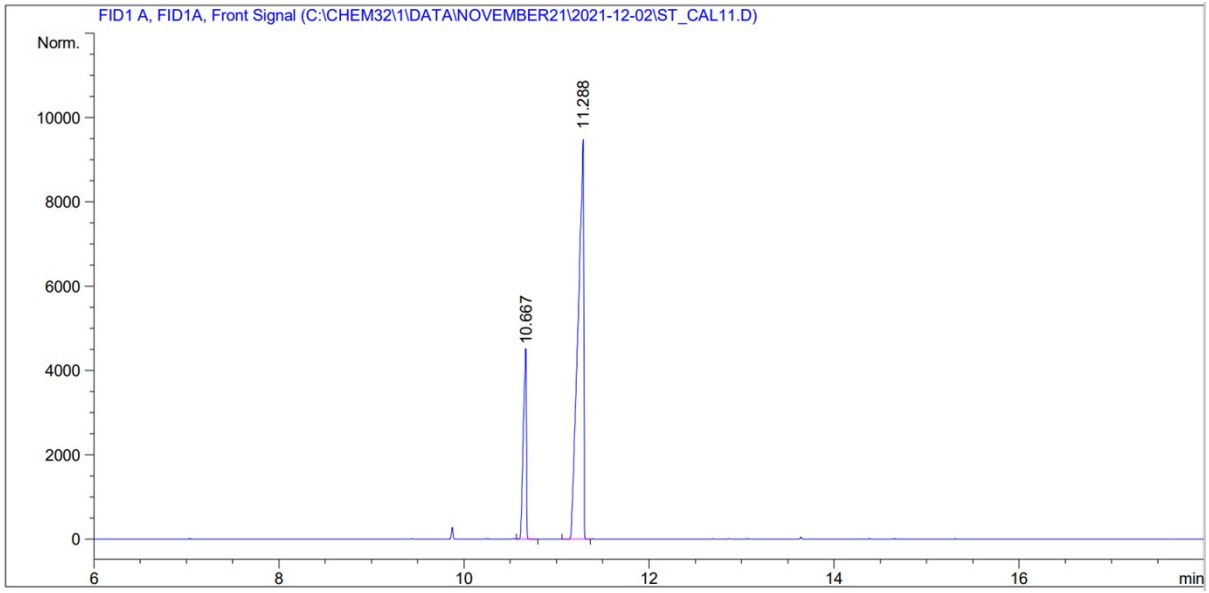
Retention Time	Sample	Peak Area
10.682	Dodecane	18276.5
11.266	2-Iodo-*m*-xylene	27341.3

0.4 mmol



Retention Time	Sample	Peak Area
10.671	Dodecane	12433.8
11.270	2-Iodo-*m*-xylene	29666.8

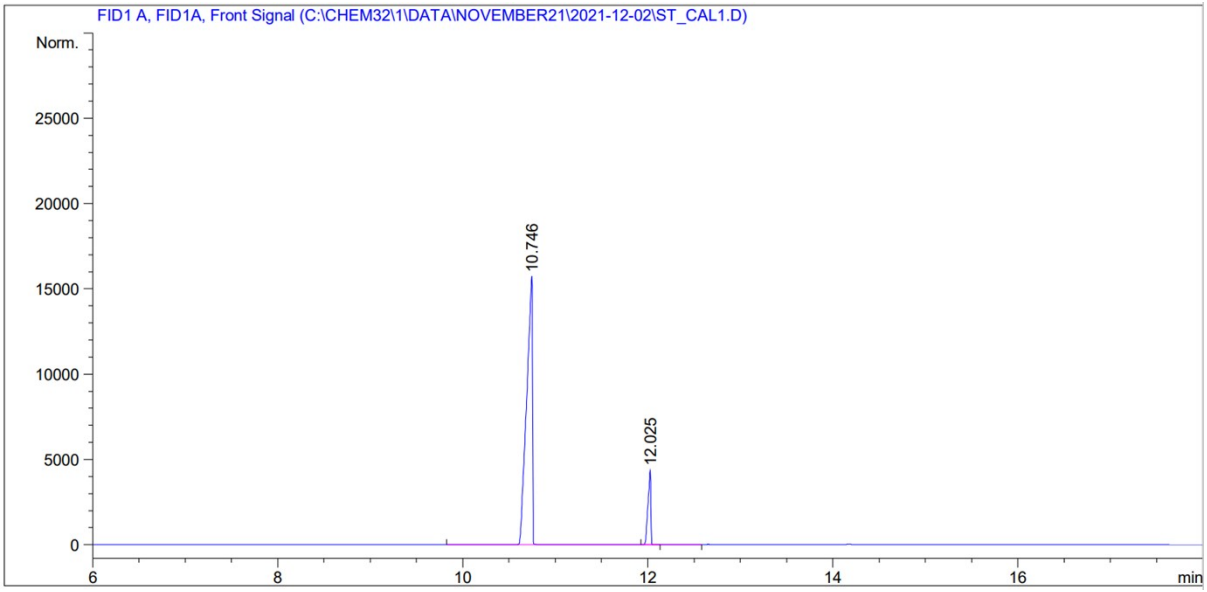
0.6 mmol



Retention Time	Sample	Peak Area
10.667	Dodecane	10198.2
11.288	2-Iodo-*m*-xylene	40482.1

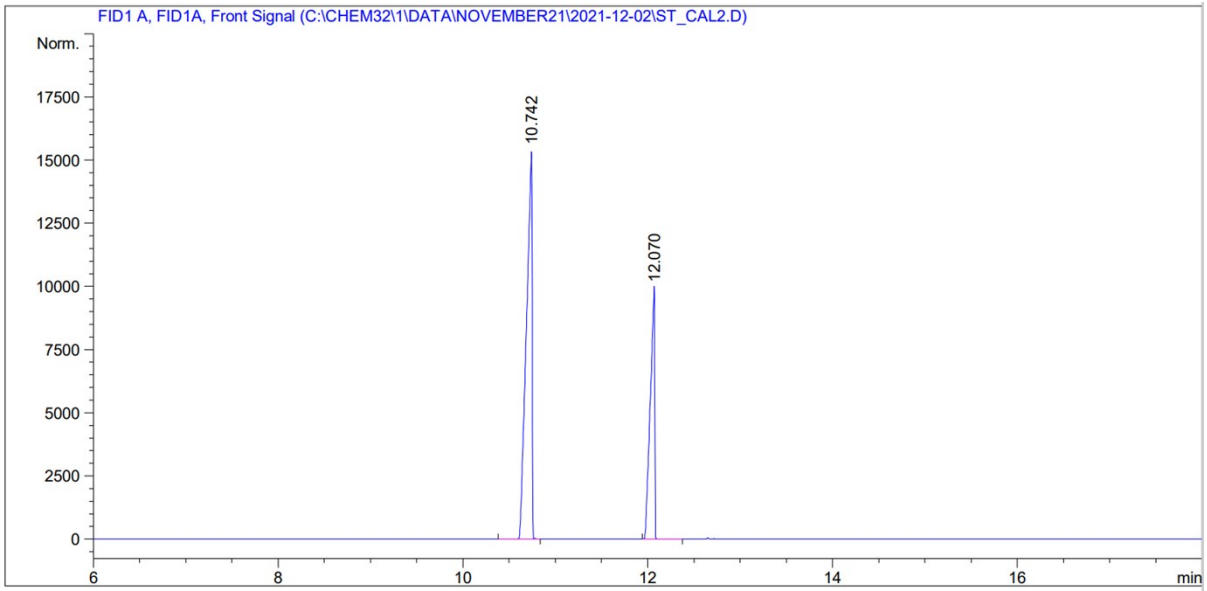
Biphenyl

0.01 mmol



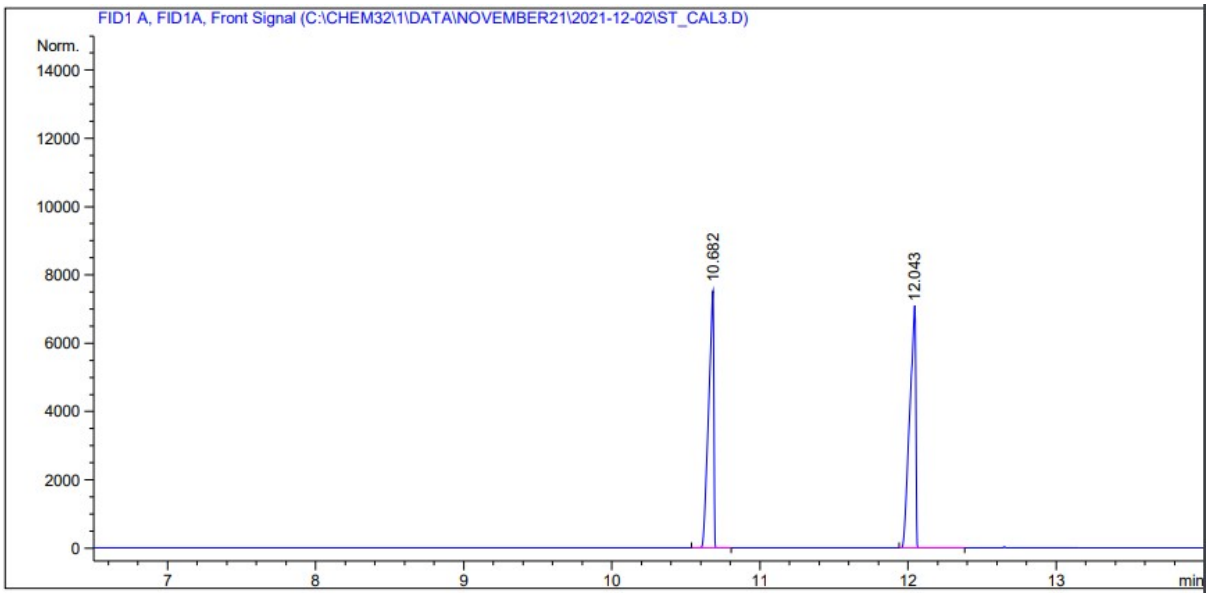
Retention Time	Sample	Peak Area
10.746	Dodecane	68957.4
12.025	Biphenyl	9428.4

0.04 mmol



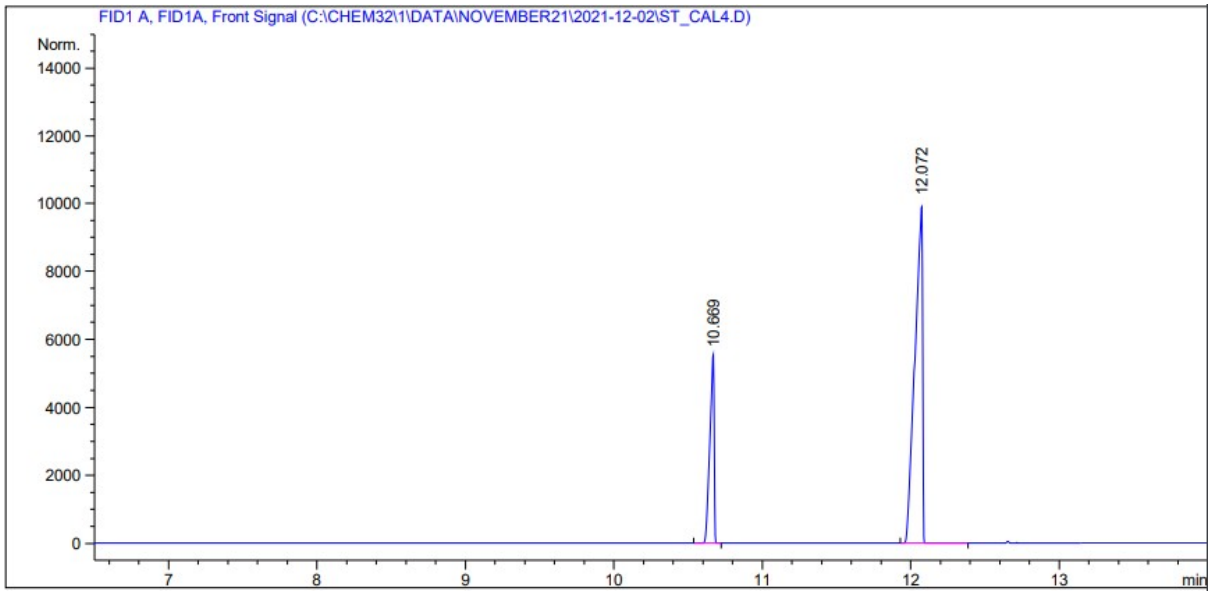
Retention Time	Sample	Peak Area
10.742	Dodecane	65096.8
12.070	Biphenyl	33761.9

0.1 mmol



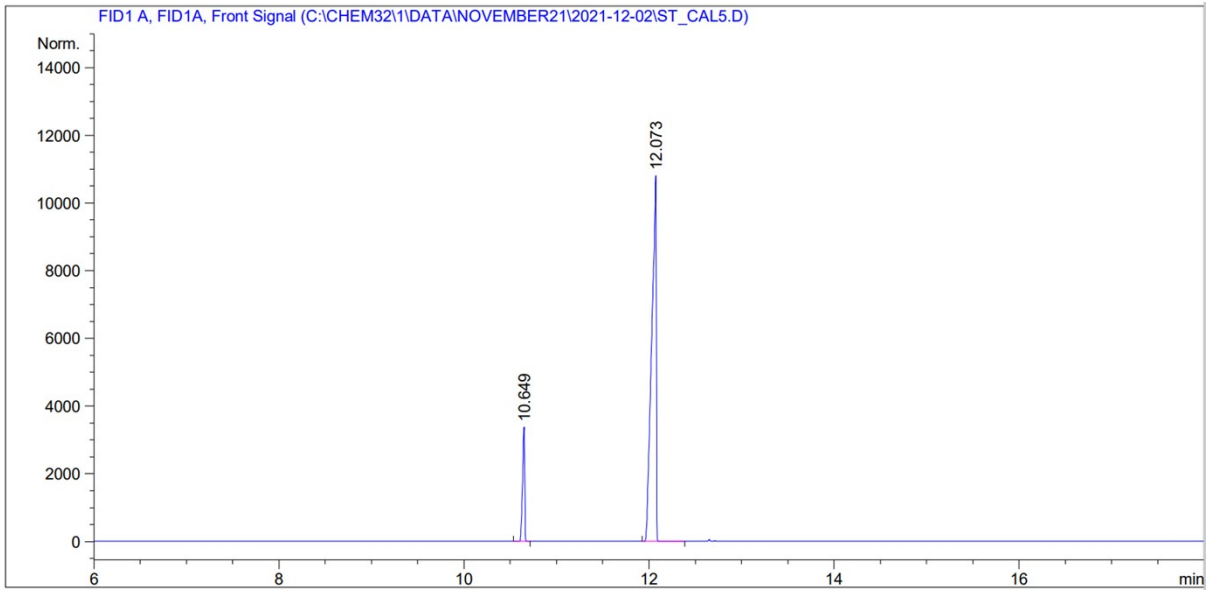
Retention Time	Sample	Peak Area
10.682	Dodecane	18326.8
12.043	Biphenyl	19101.4

0.3 mmol



Retention Time	Sample	Peak Area
10.669	Dodecane	11200.1
12.072	Biphenyl	34515.8

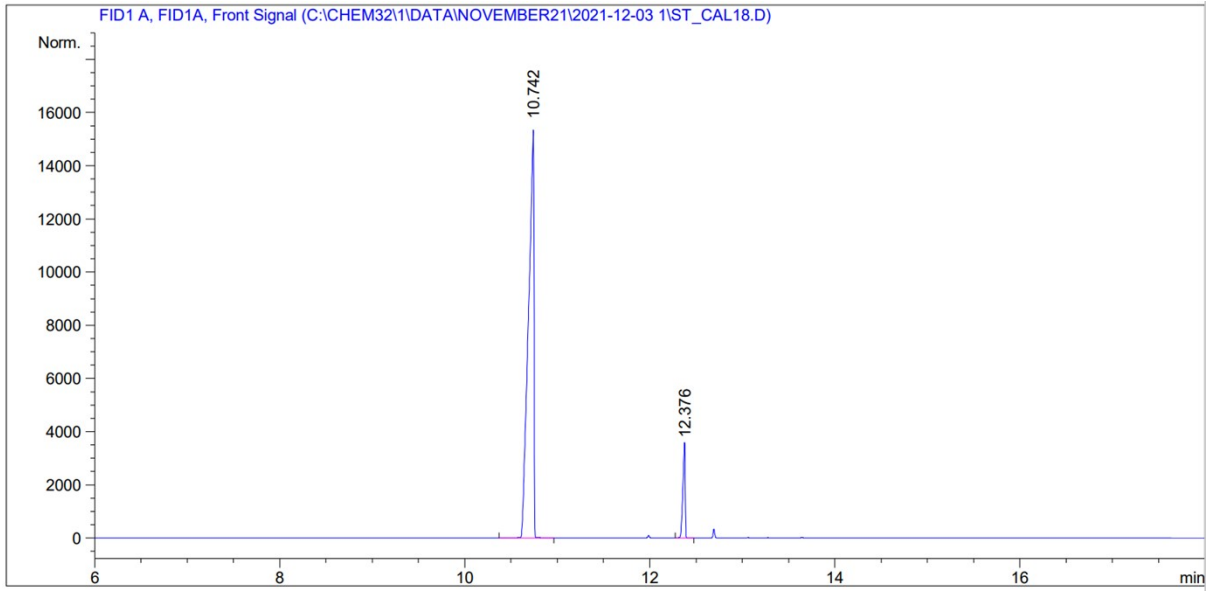
0.7 mmol



Retention Time	Sample	Peak Area
10.649	Dodecane	5400.0
12.073	Biphenyl	37752.0

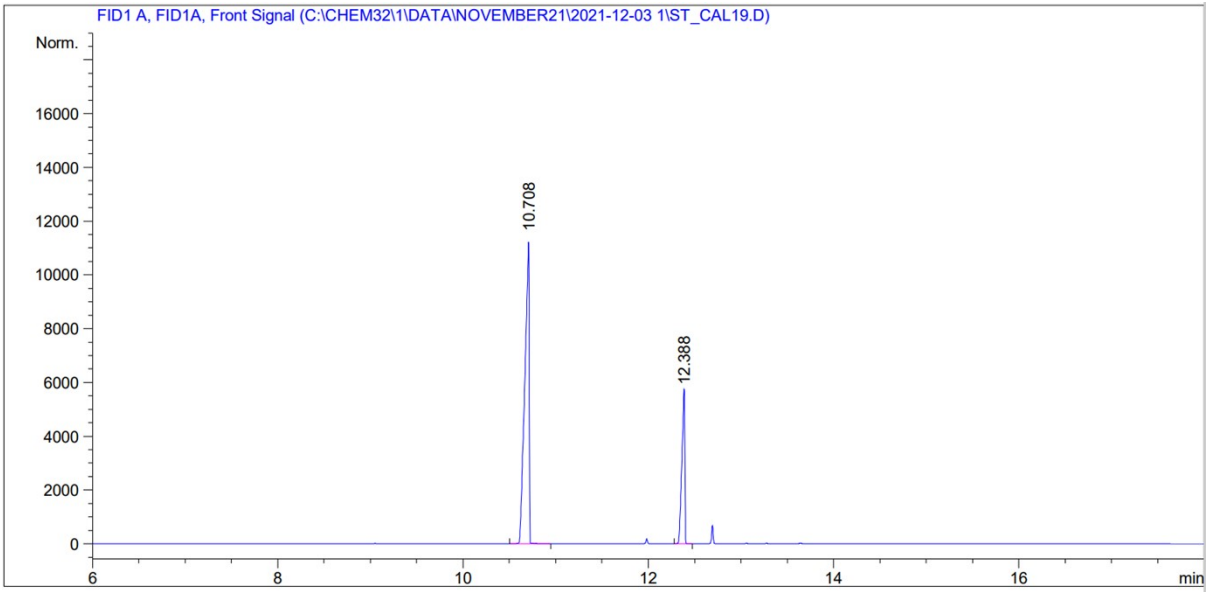
2,6-Dimethylbiphenyl

0.01 mmol



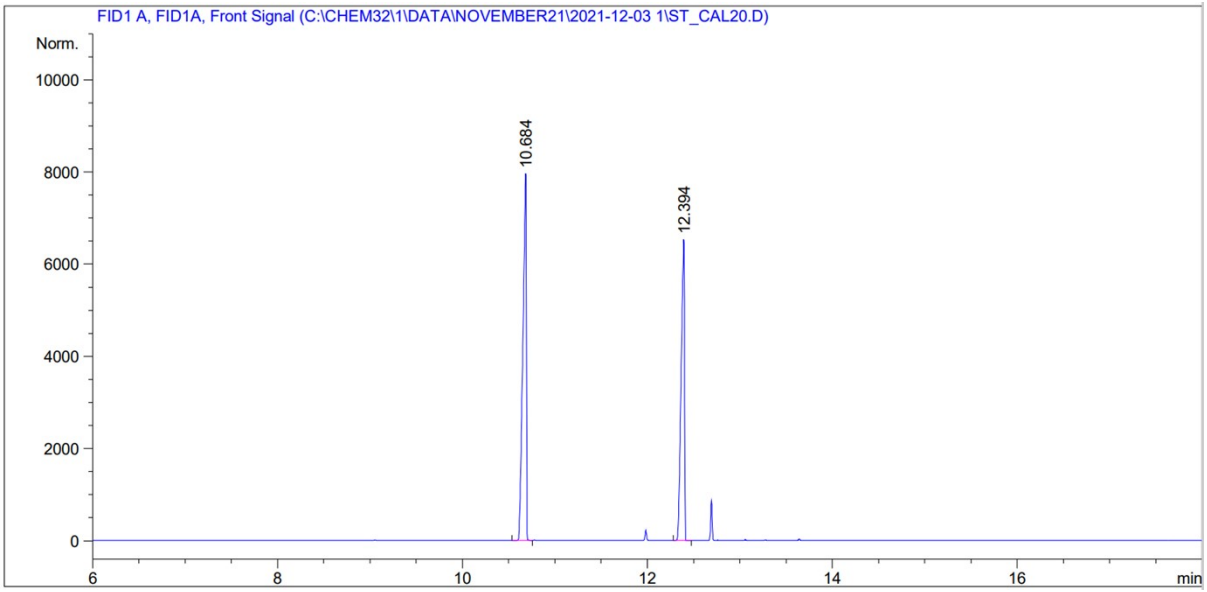
Retention Time	Sample	Peak Area
10.742	Dodecane	62881.5
12.376	2,6-Dimethylbiphenyl	6115.4

0.04 mmol



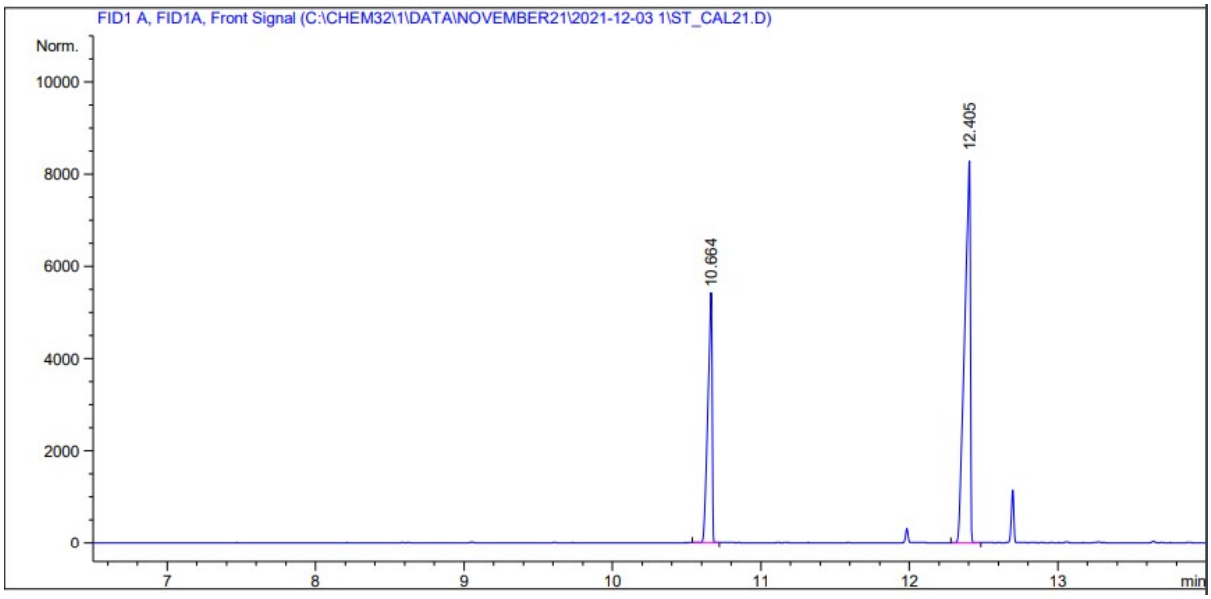
Retention Time	Sample	Peak Area
10.708	Dodecane	36554.7
12.388	2,6-Dimethylbiphenyl	12765.3

0.08 mmol



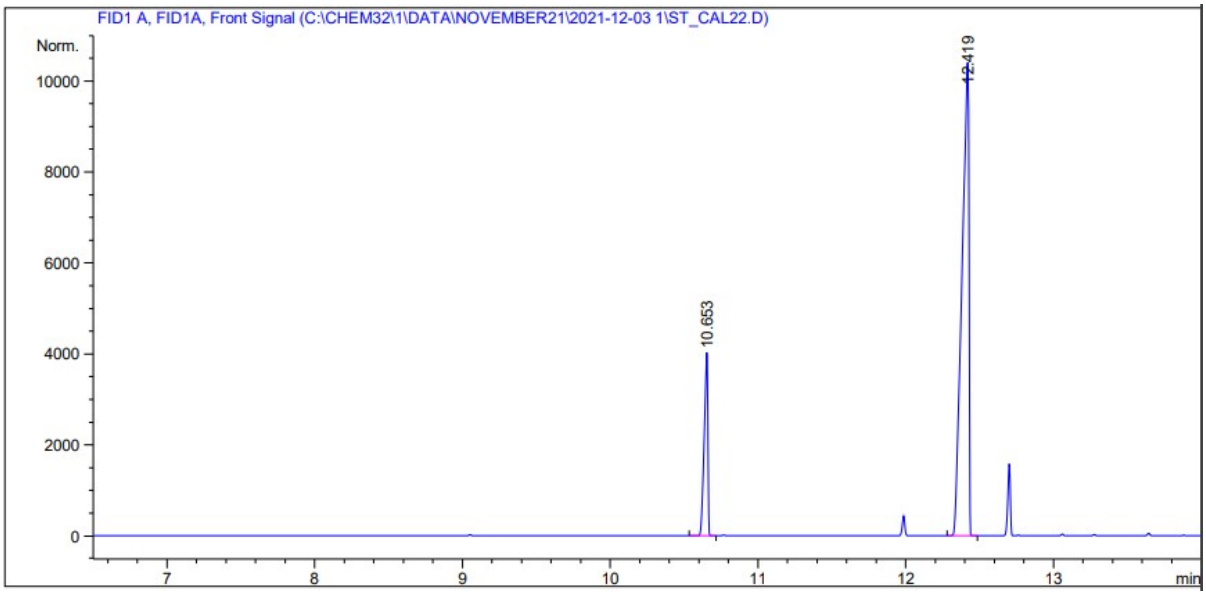
Retention Time	Sample	Peak Area
10.684	Dodecane	20688.2
12.394	2,6-Dimethylbiphenyl	16138

0.2 mmol



Retention Time	Sample	Peak Area
10.664	Dodecane	10923.1
12.405	2,6-Dimethylbiphenyl	22237.2

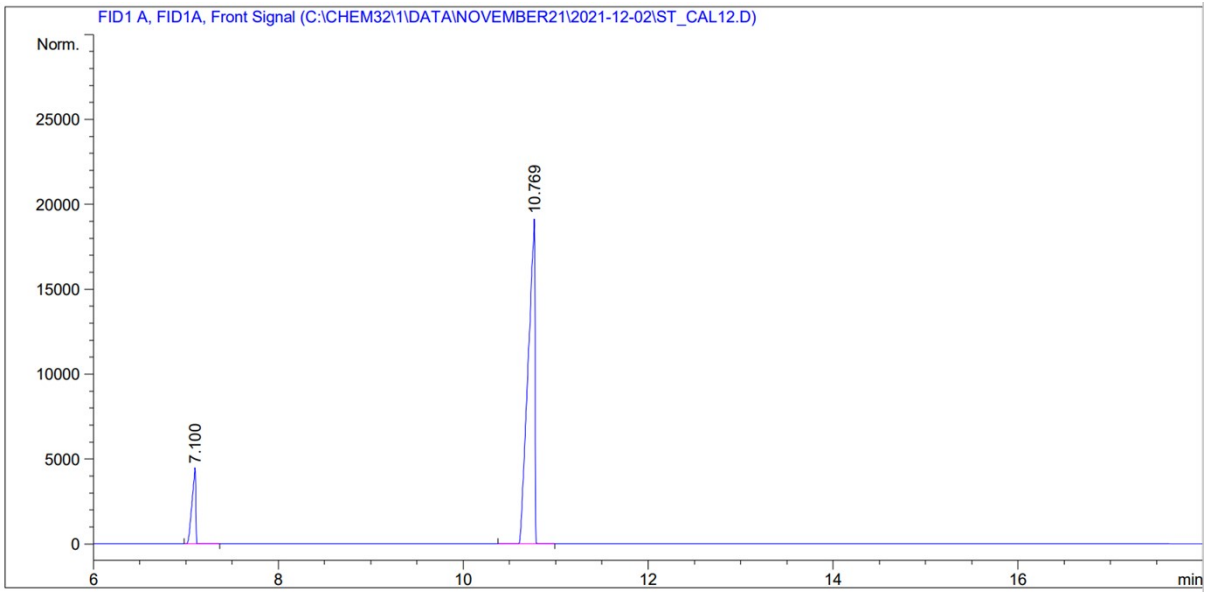
0.5 mmol



Retention Time	Sample	Peak Area
10.653	Dodecane	6931.01709
12.419	2,6-Dimethylbiphenyl	32072.9

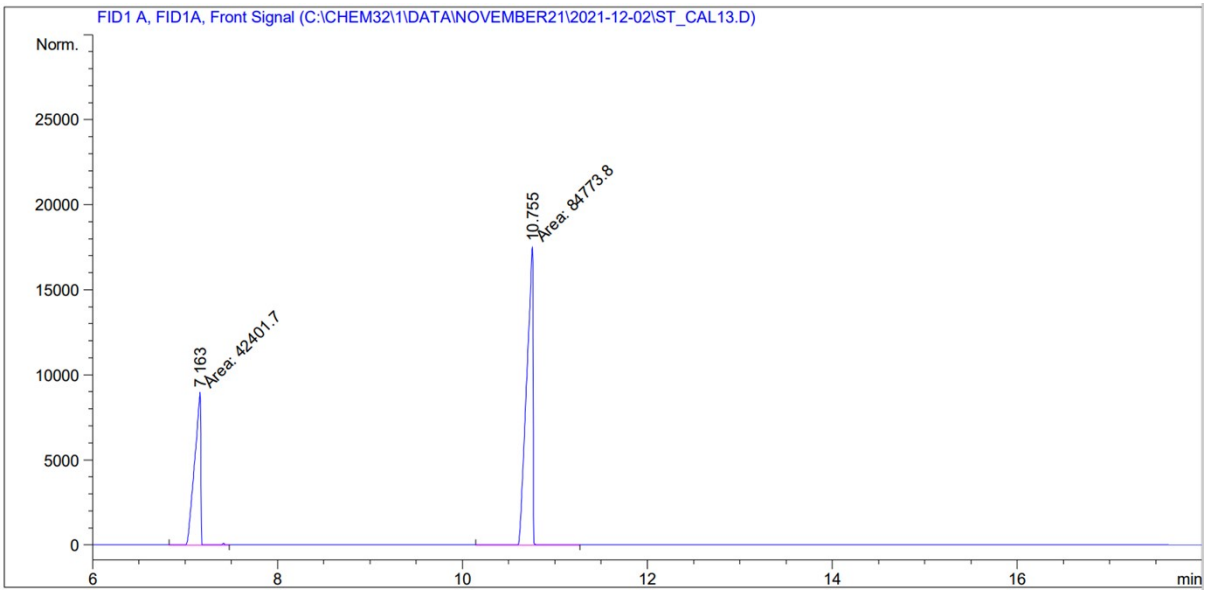
***m*-Xylene**

0.02 mmol



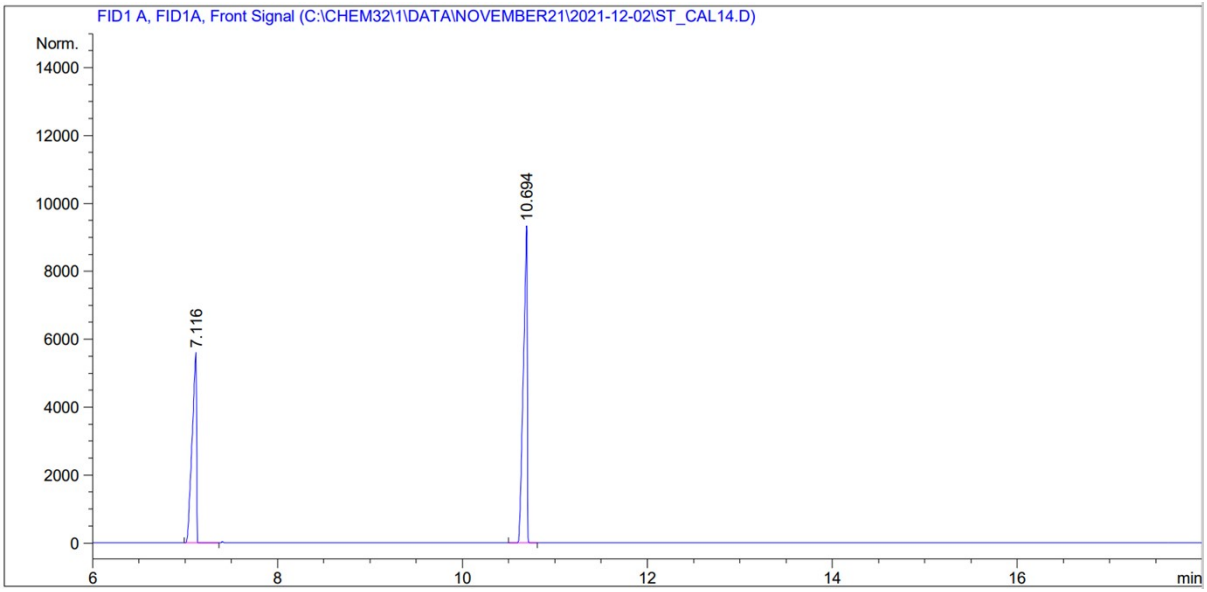
Retention Time	Sample	Peak Area
7.100	*m*-Xylene	12578.9
10.769	Dodecane	98487.2

0.08 mmol



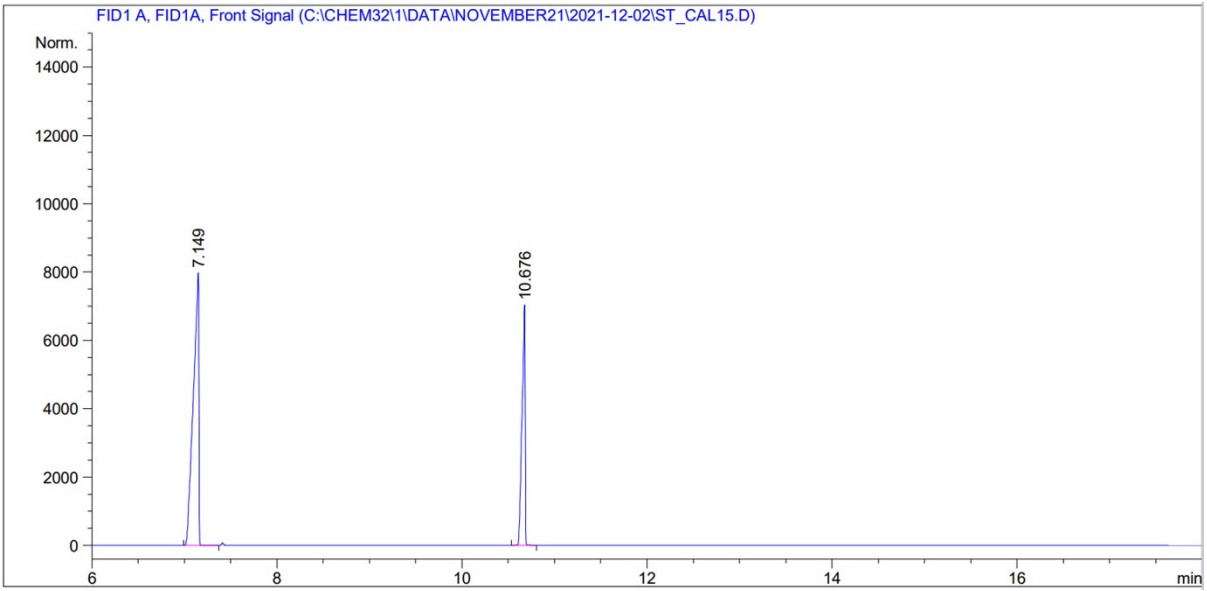
Retention Time	Sample	Peak Area
7.163	*m*-Xylene	42401.7
10.755	Dodecane	84773.8

0.1 mmol



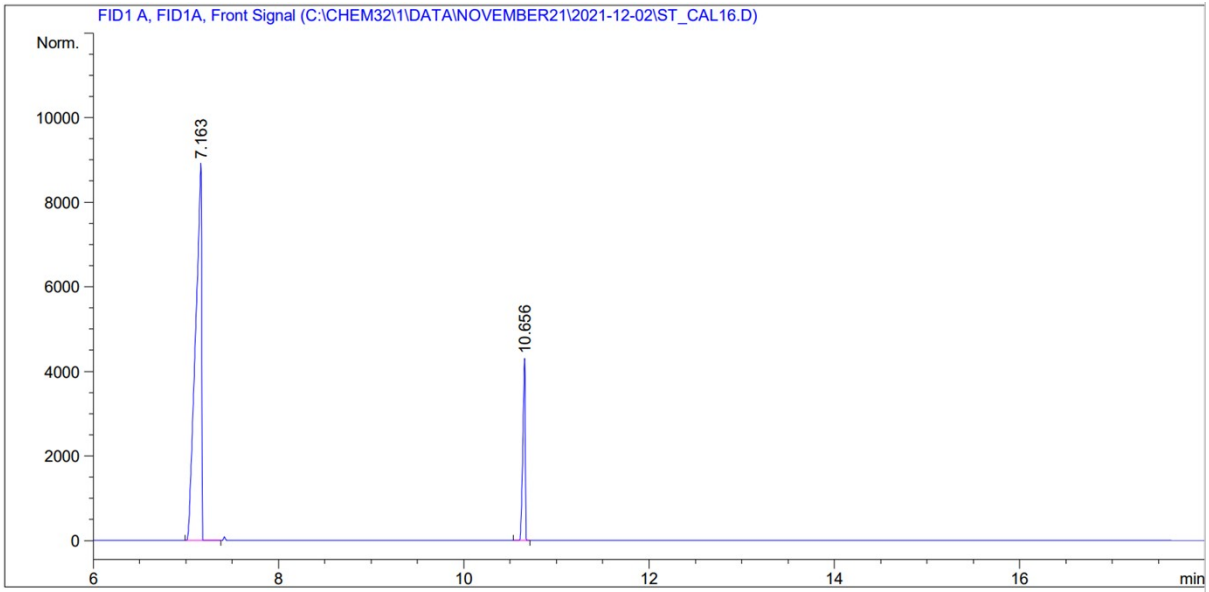
Retention Time	Sample	Peak Area
7.116	*m*-Xylene	18433.6
10.694	Dodecane	26890.0

0.3 mmol



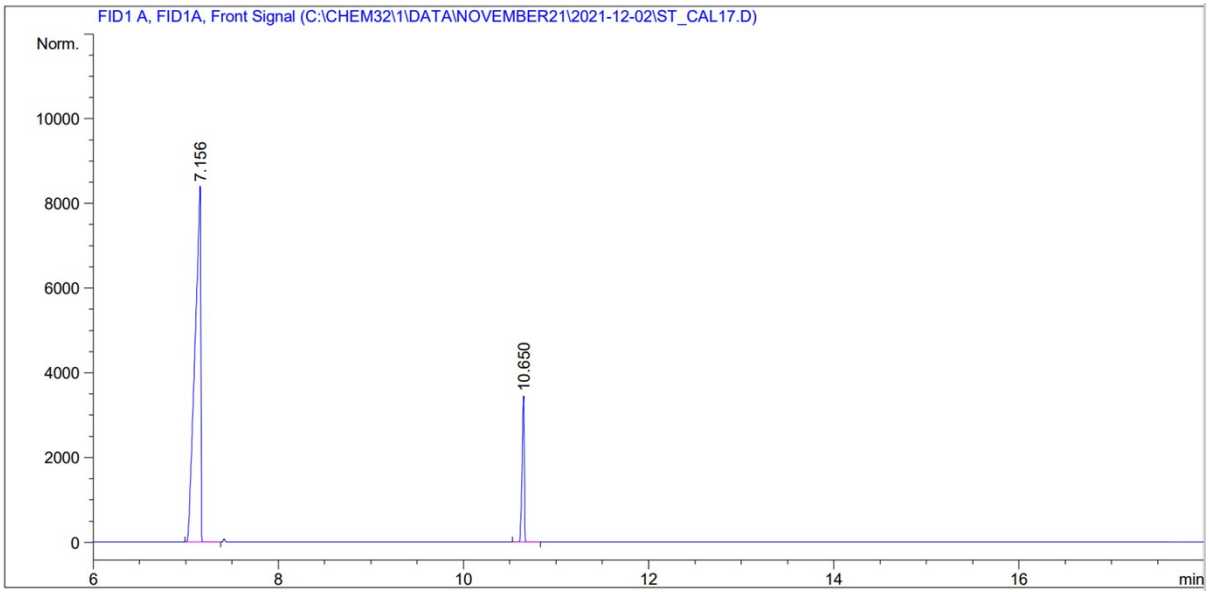
Retention Time	Sample	Peak Area
7.149	*m*-Xylene	32922.7
10.676	Dodecane	16190.1

0.8 mmol



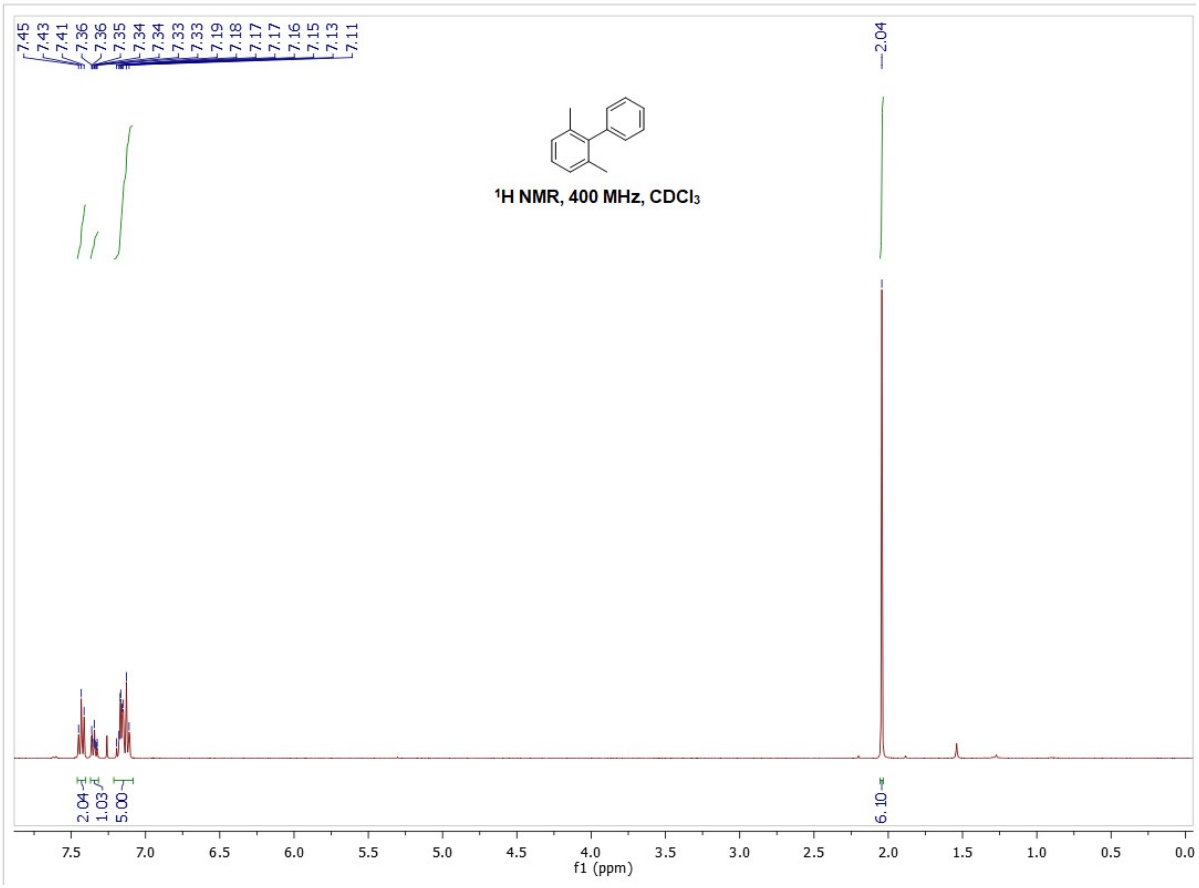
Retention Time	Sample	Peak Area
7.163	*m*-Xylene	40651.0
10.656	Dodecane	7618.8

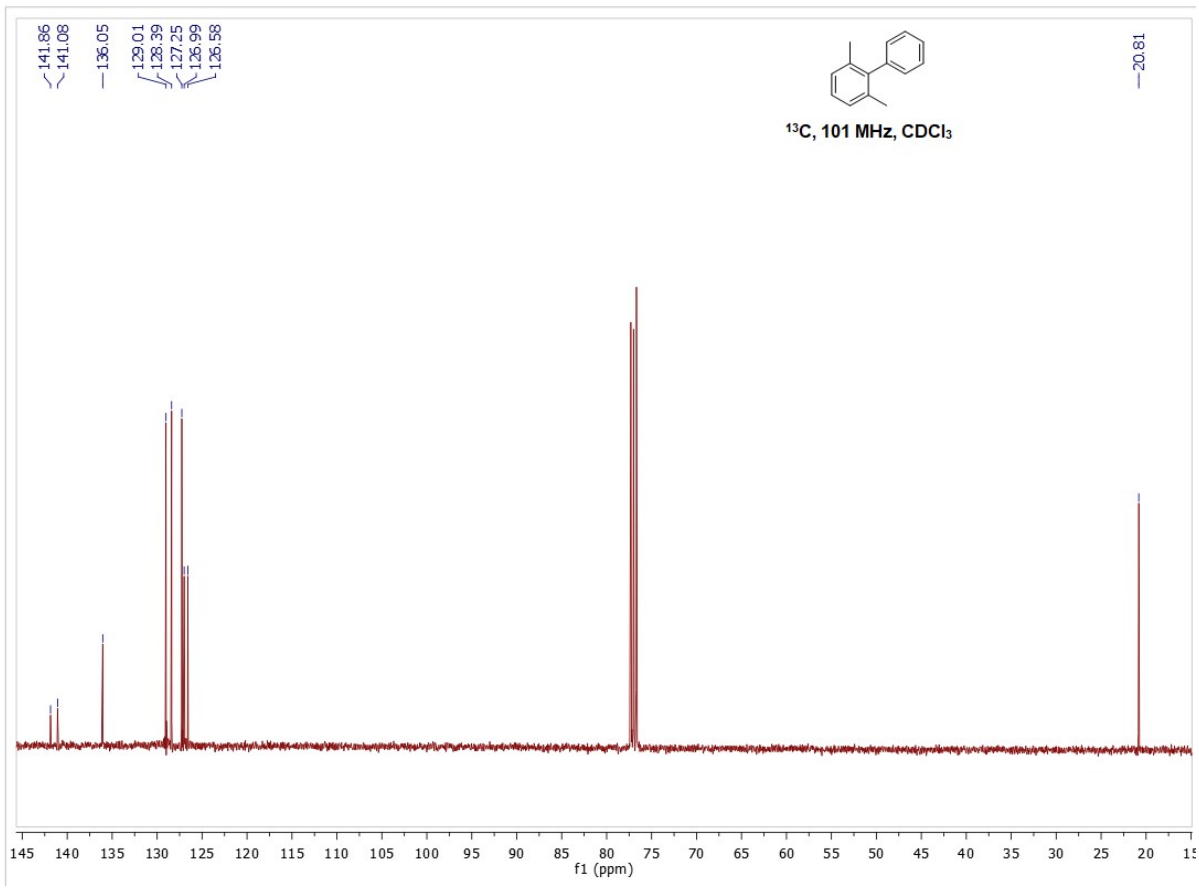
1 mmol

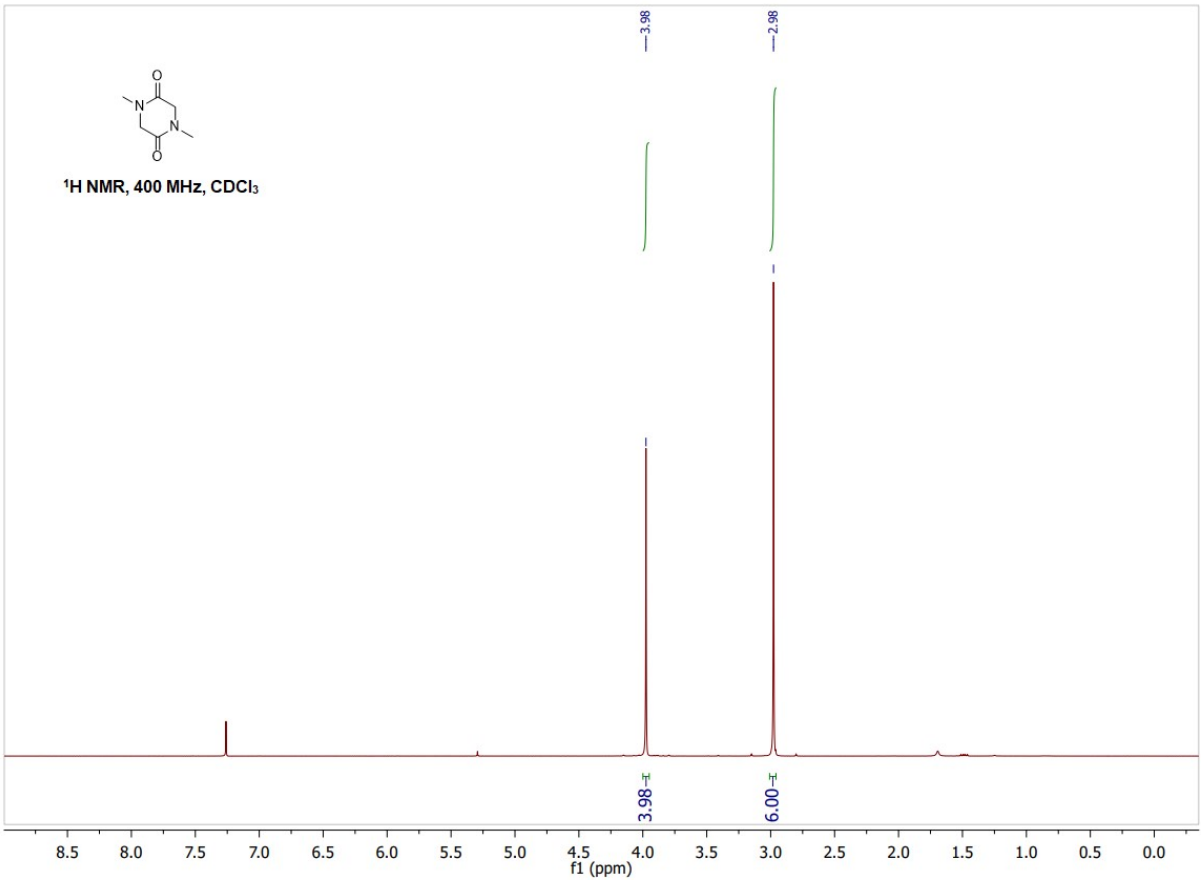


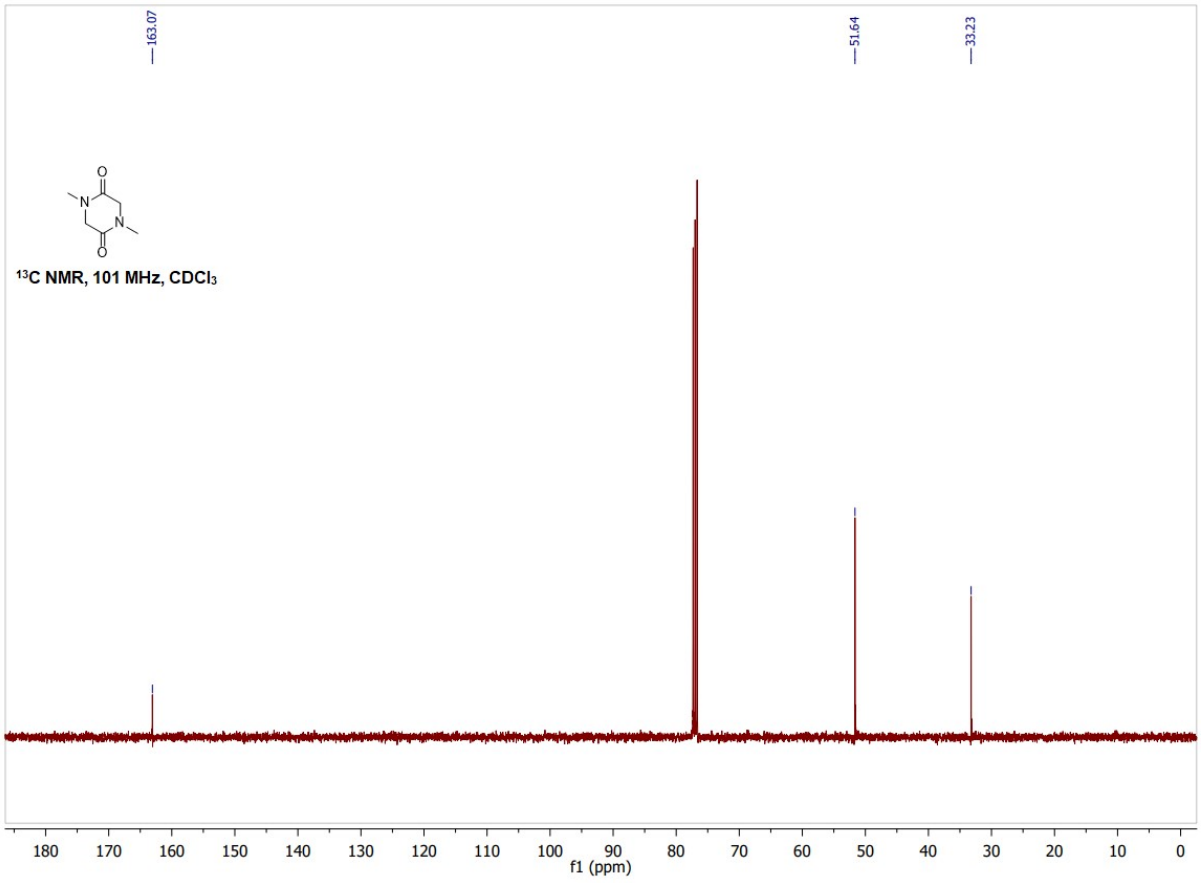
Retention Time	Sample	Peak Area
7.156	*m*-Xylene	36894.7
10.650	Dodecane	5652.2

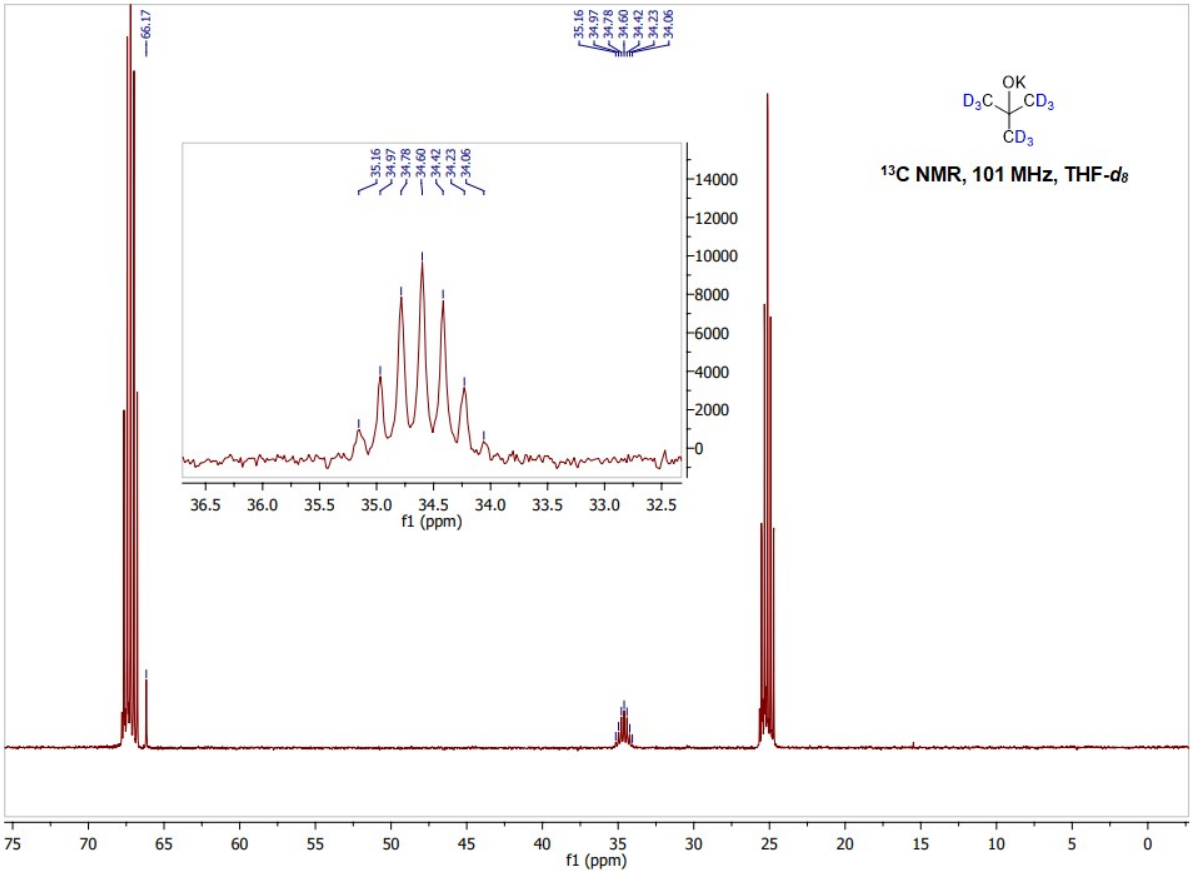
NMR Spectra

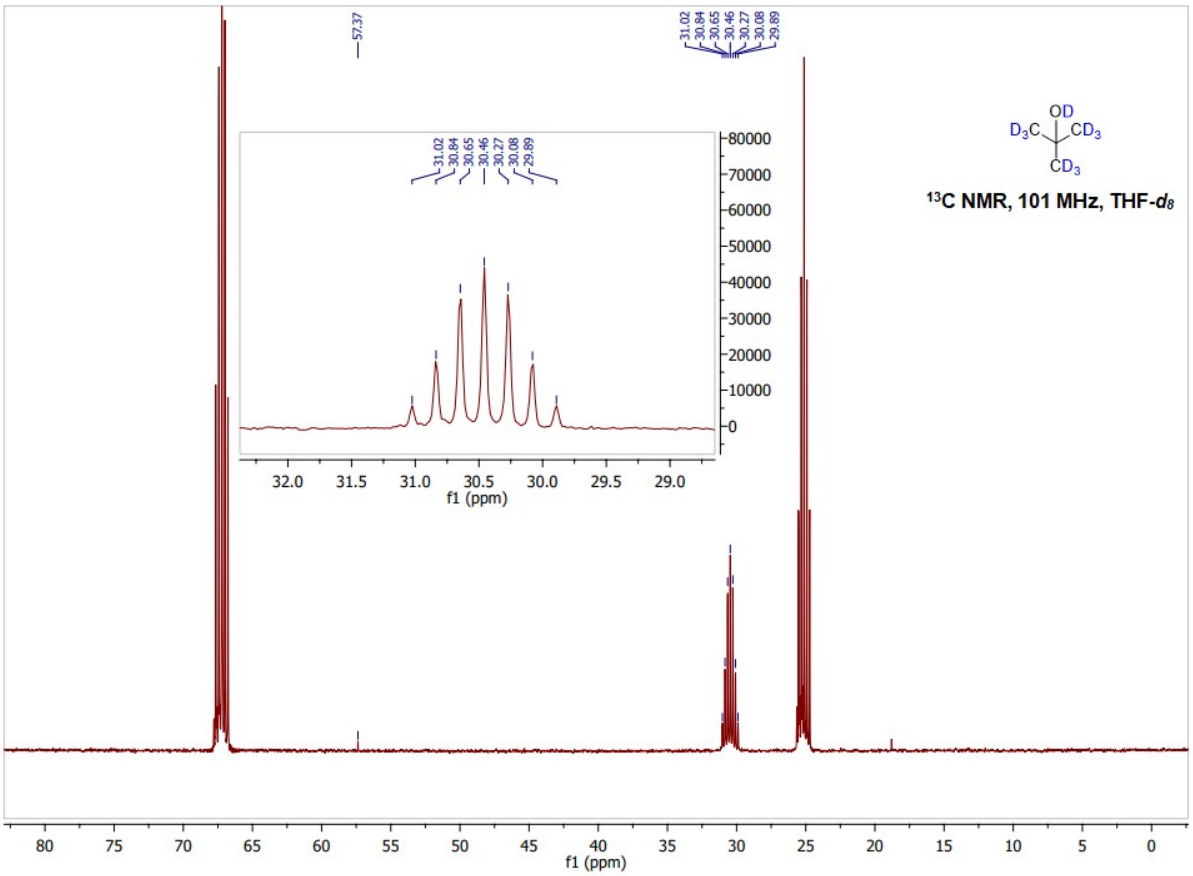

7.45
7.43
7.41
7.36
7.36
7.35
7.34
7.34
7.33
7.33
7.19
7.18
7.17
7.17
7.16
7.15
7.13
7.11
2.04
2.04
1.03
5.00
6.10
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
^{1}H NMR, 400 MHz, CDCl$_3$

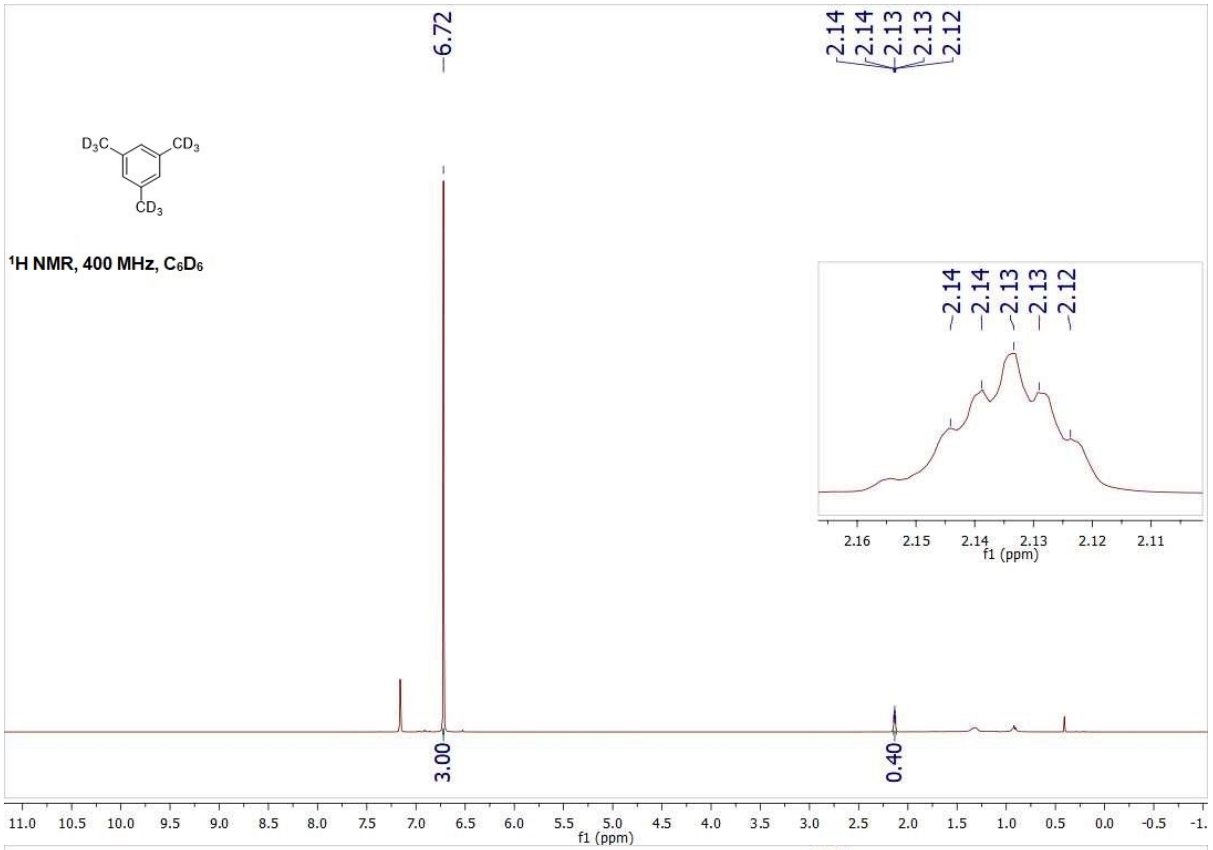

141.86
141.08
136.05
129.01
128.39
127.25
126.99
126.58
20.81
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
f1 (ppm)
^{13}C, 101 MHz, CDCl$_3$

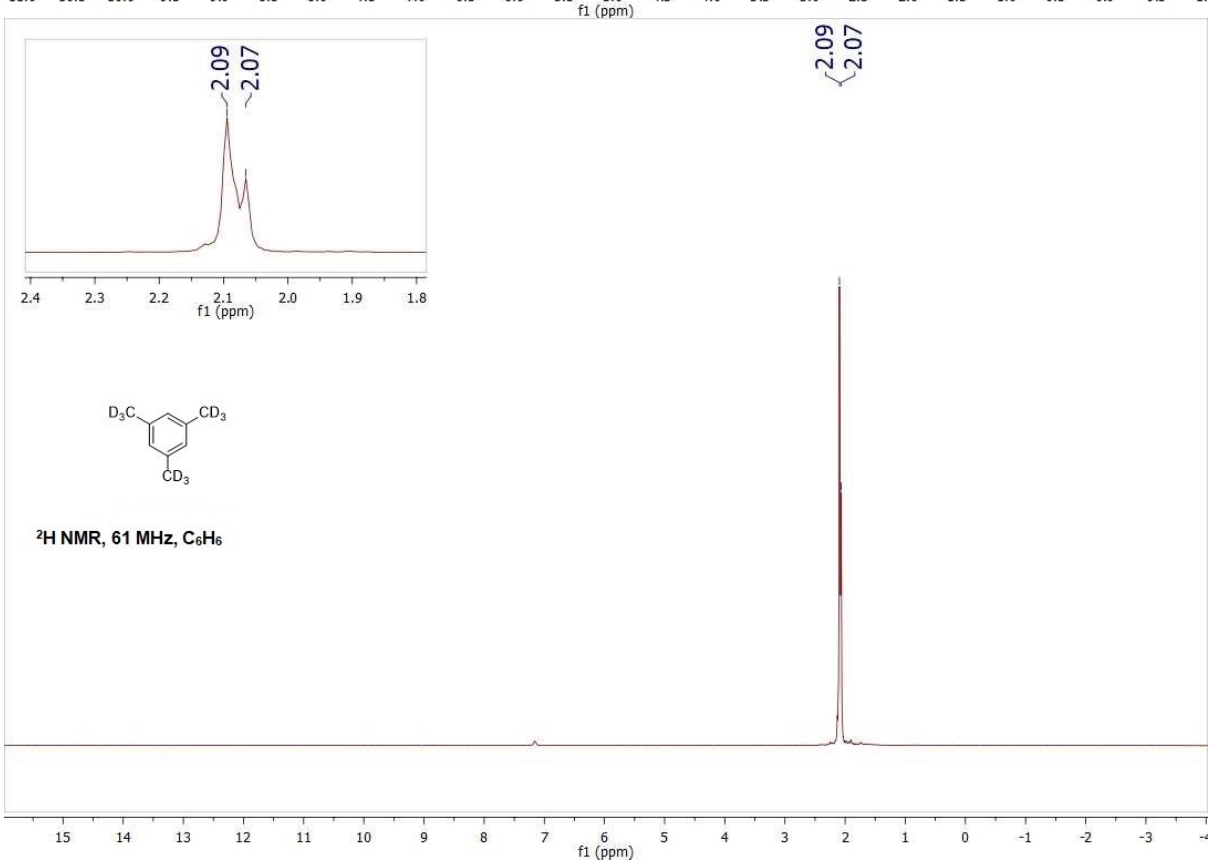

3.98
2.98
^{1}H NMR, 400 MHz, CDCl$_3$
3.98
6.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

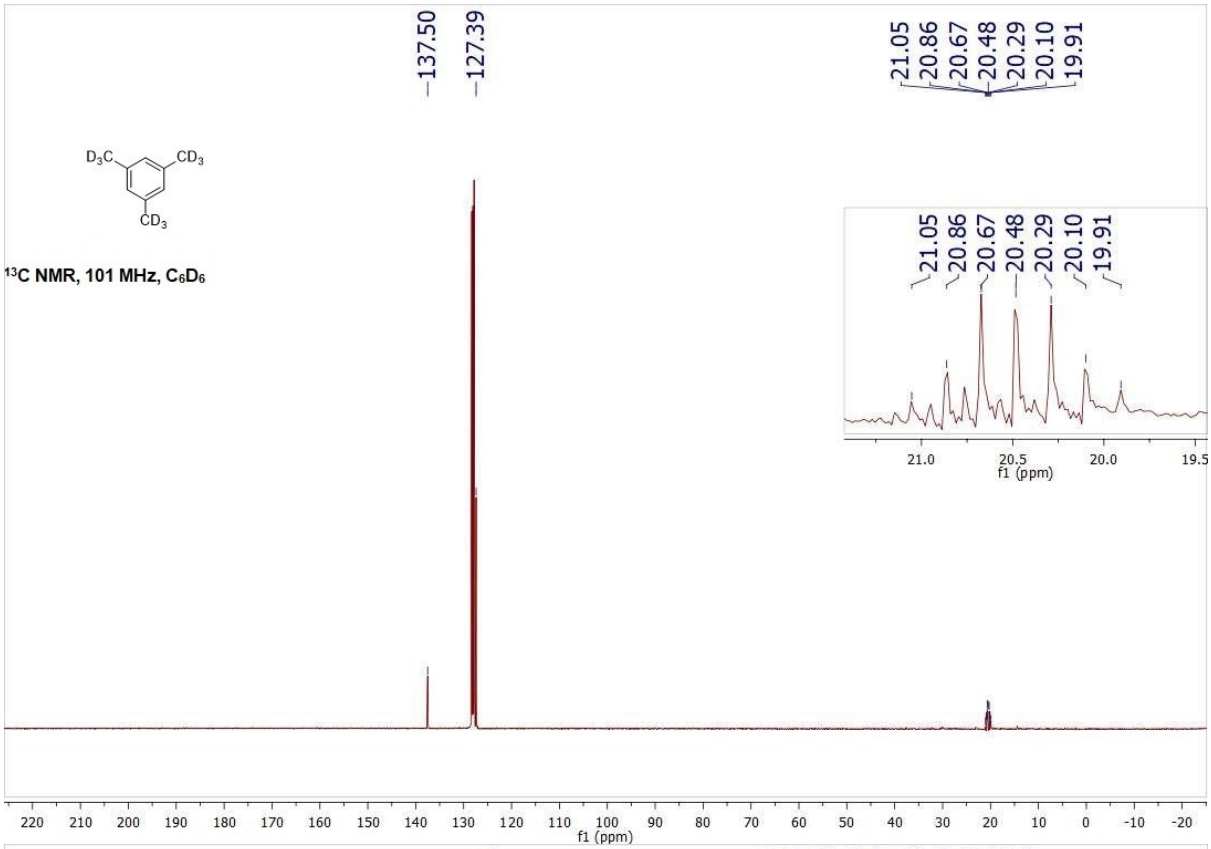

163.07
51.64
33.23
^{13}C NMR, 101 MHz, CDCl$_3$
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

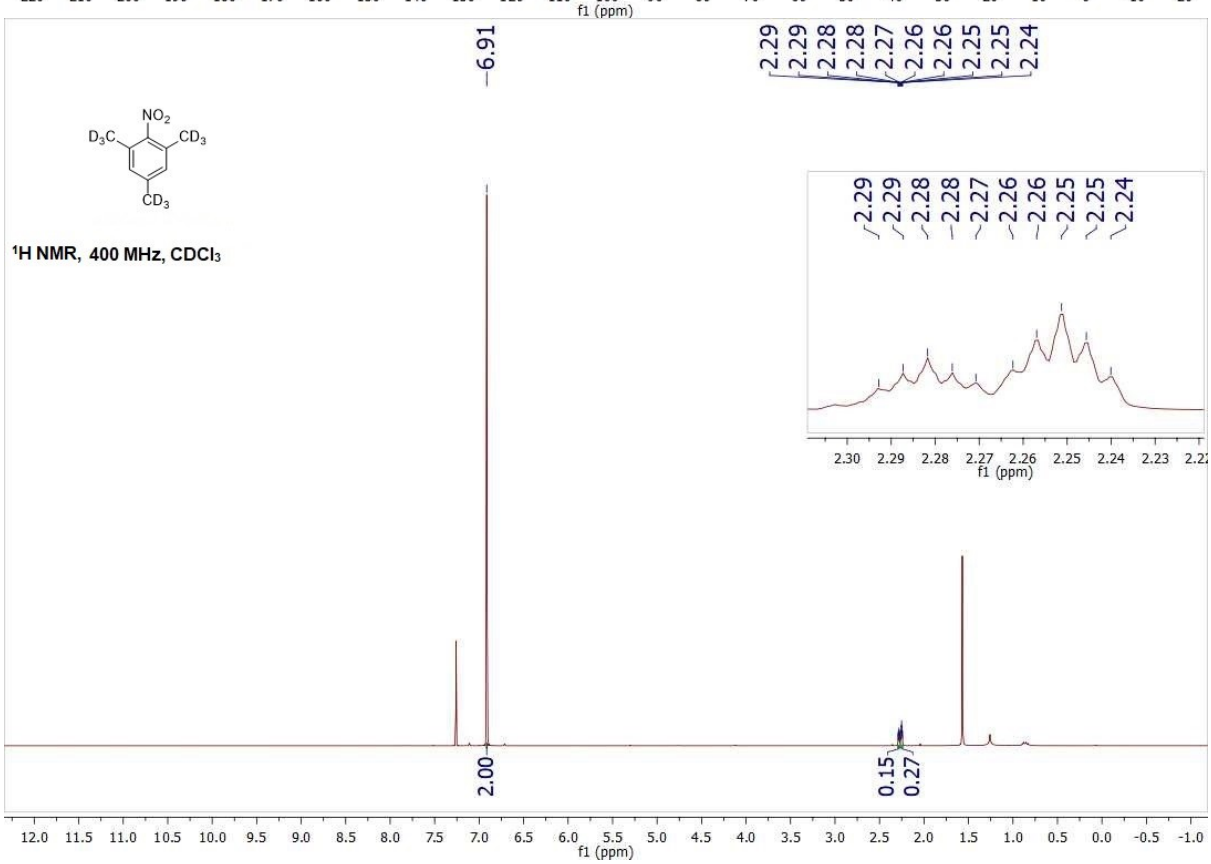

66.17
35.16
34.97
34.78
34.60
34.42
34.23
34.06
OK
D3C
CD3
CD3
13C NMR, 101 MHz, THF-d8
f1 (ppm)

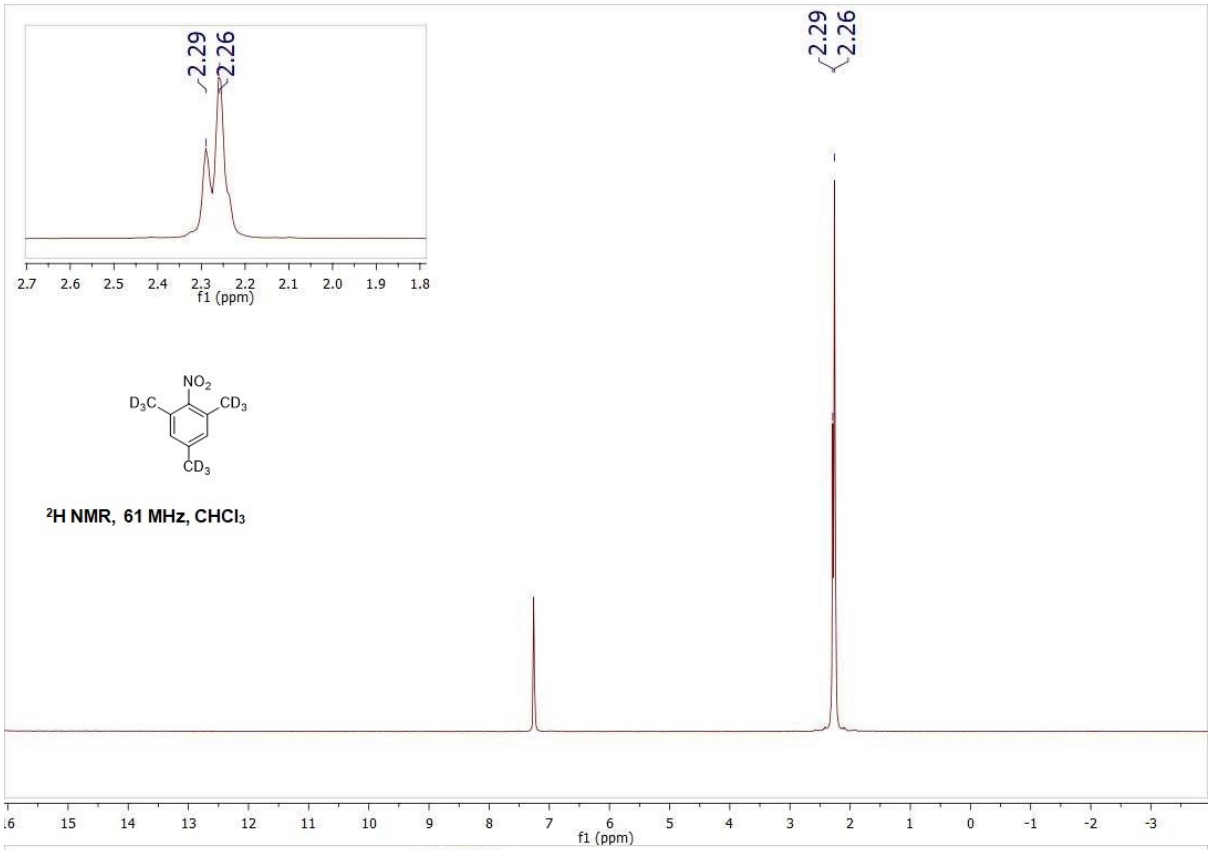

57.37
31.02
30.84
30.65
30.46
30.27
30.08
29.89
OD
D3C
CD3
CD3
13C NMR, 101 MHz, THF-d8
f1 (ppm)

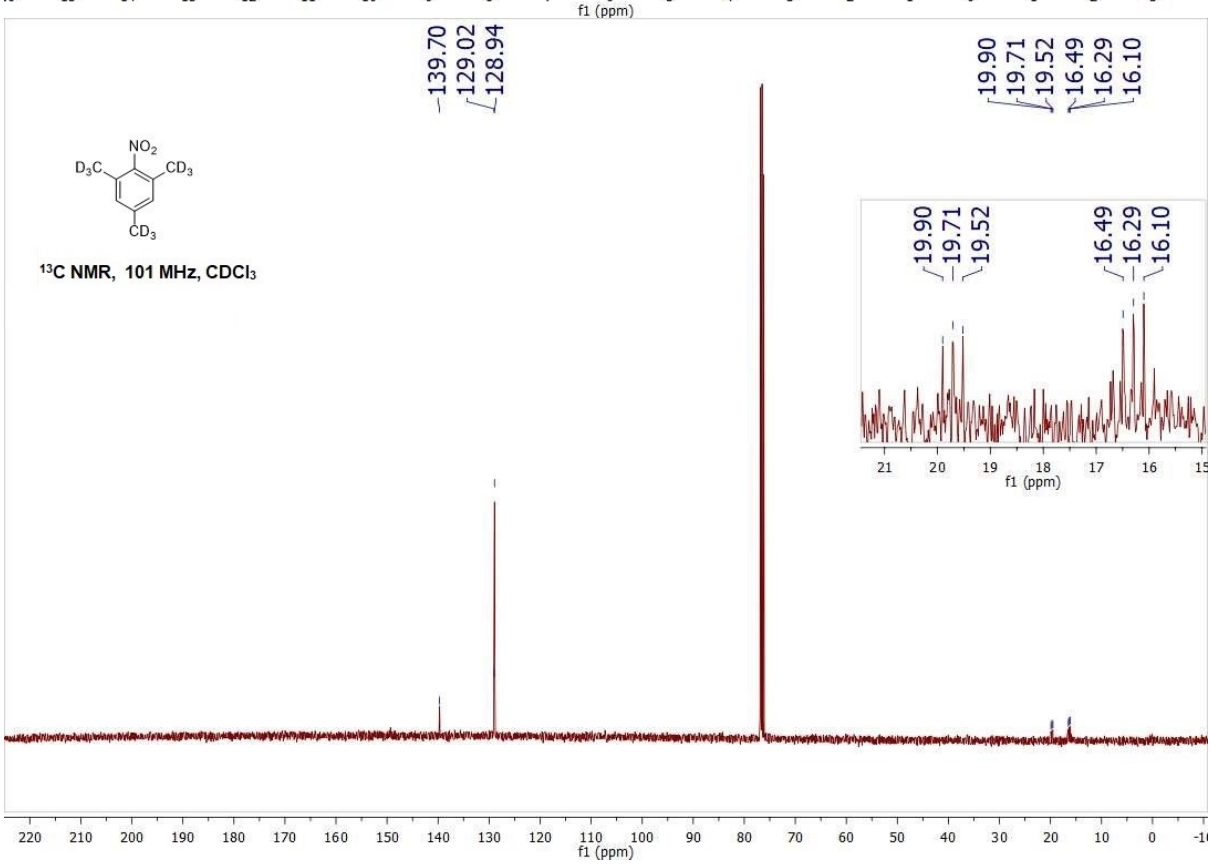

6.72
2.14
2.14
2.13
2.13
2.12
D3C
CD3
CD3
1H NMR, 400 MHz, C6D6
3.00
0.40
f1 (ppm)

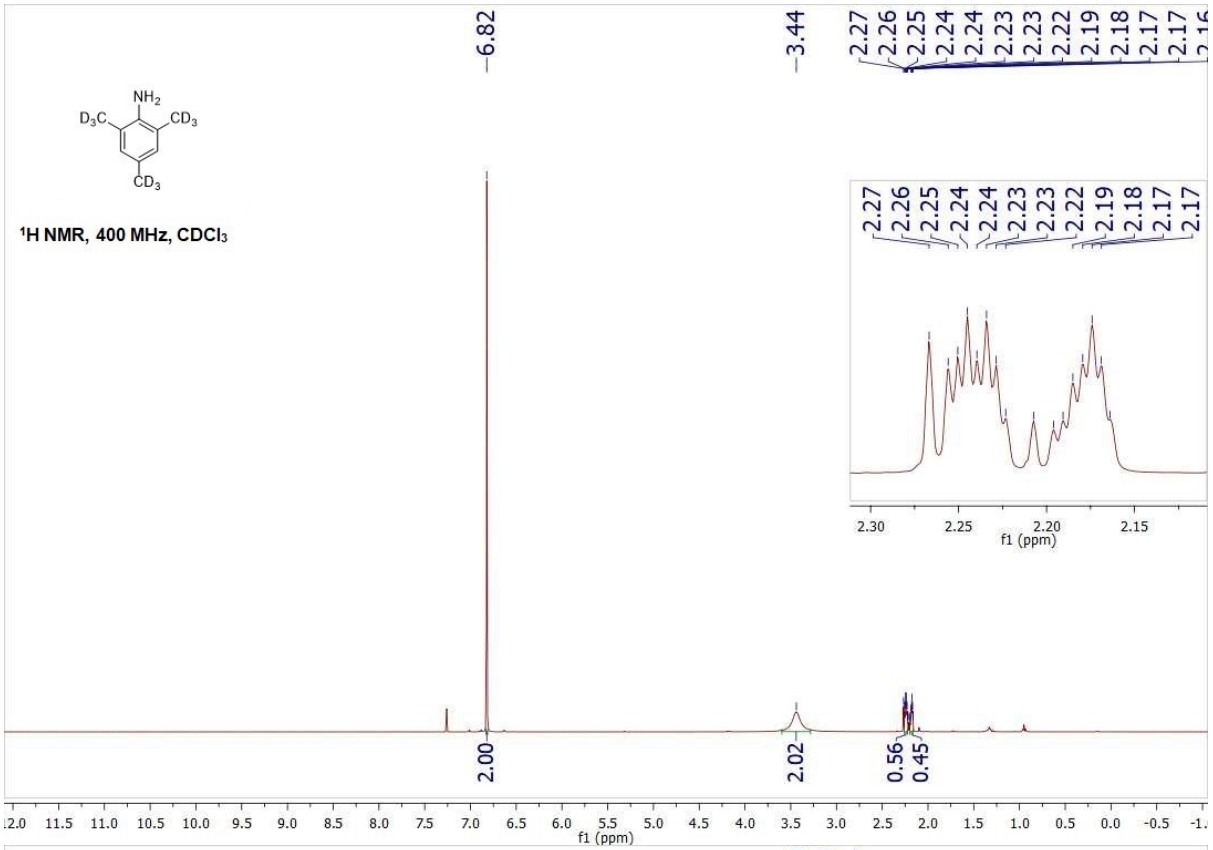

2.09
2.07
D3C
CD3
CD3
2H NMR, 61 MHz, C6H6
f1 (ppm)

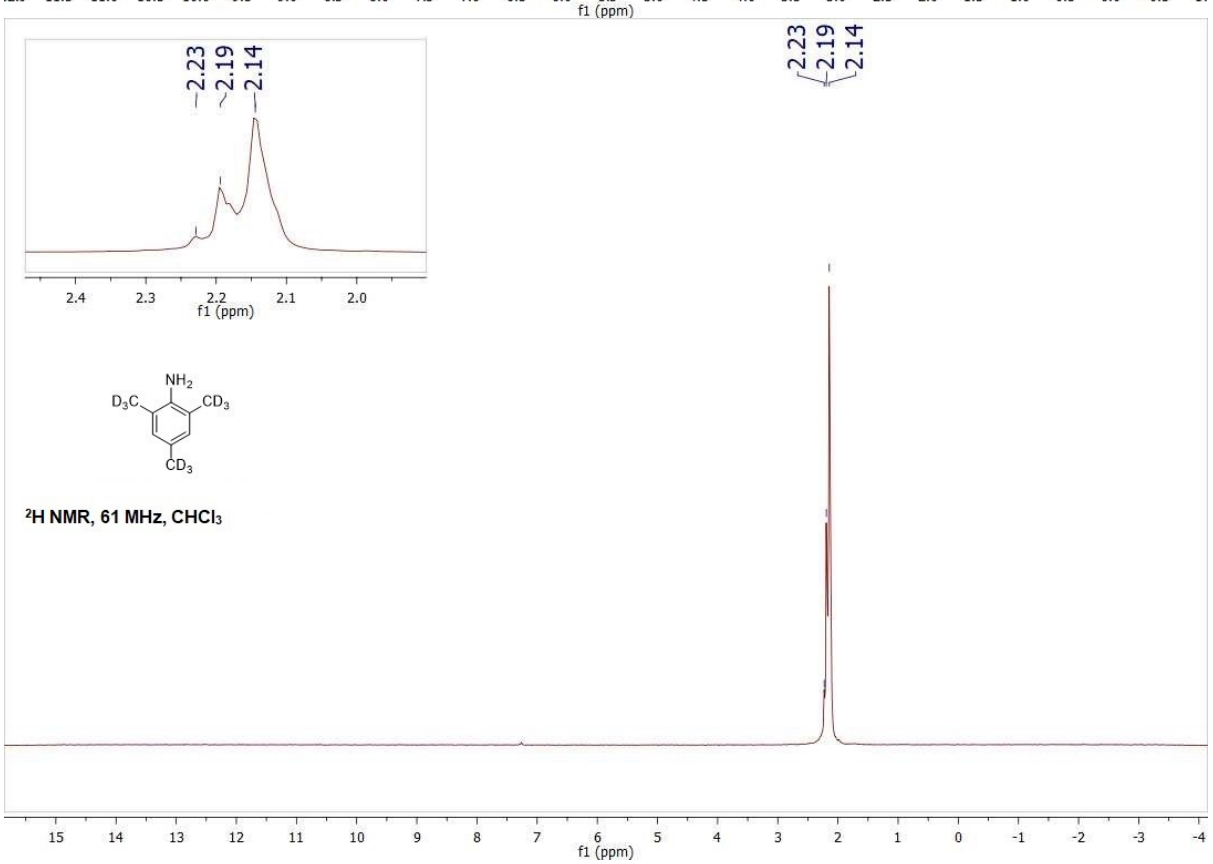

137.50
127.39
21.05
20.86
20.67
20.48
20.29
20.10
19.91
D3C
CD3
CD3
13C NMR, 101 MHz, C6D6
f1 (ppm)

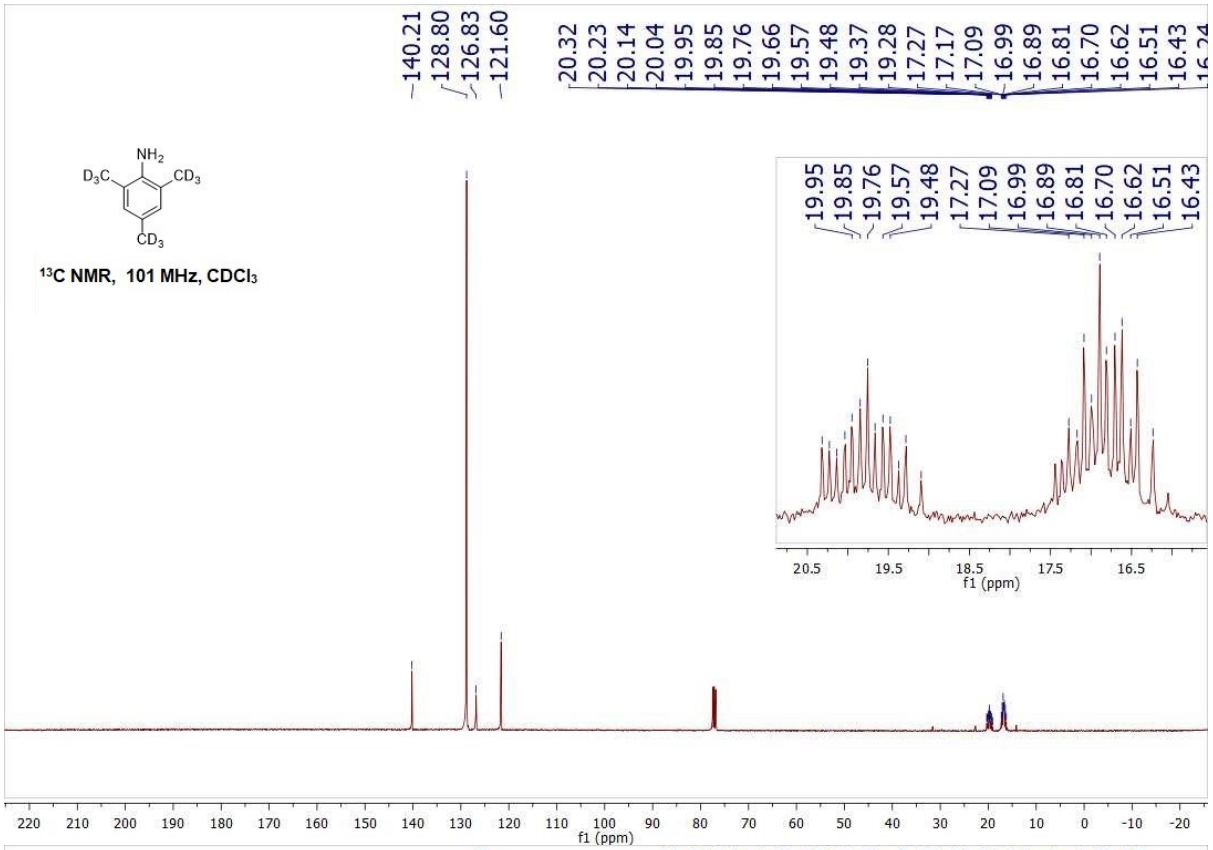

6.91
2.29
2.29
2.28
2.28
2.27
2.26
2.26
2.25
2.25
2.24
NO2
D3C
CD3
CD3
1H NMR, 400 MHz, CDCl3
2.00
0.15
0.27
f1 (ppm)

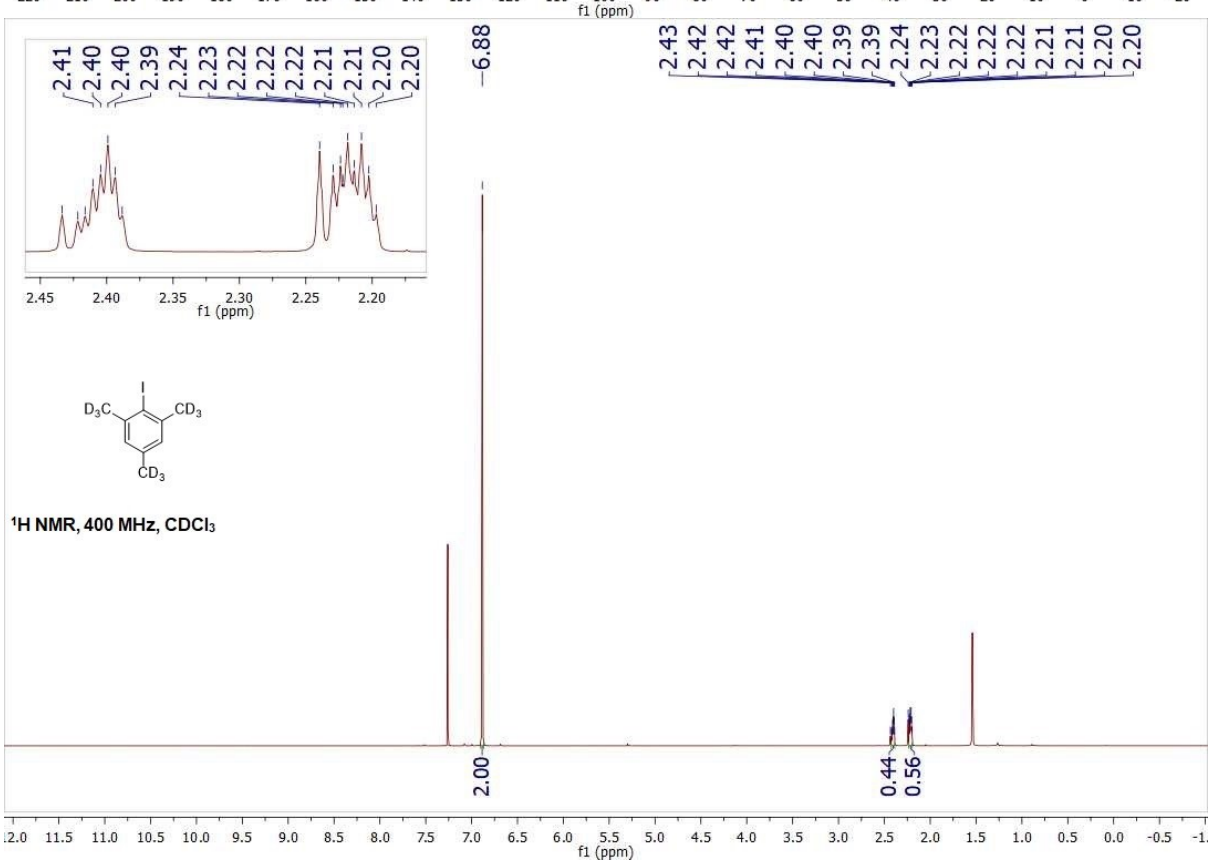

2.29
2.26
2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8
f1 (ppm)
NO2
D3C
CD3
CD3
2H NMR, 61 MHz, CHCl3
2.29
2.26
f1 (ppm)

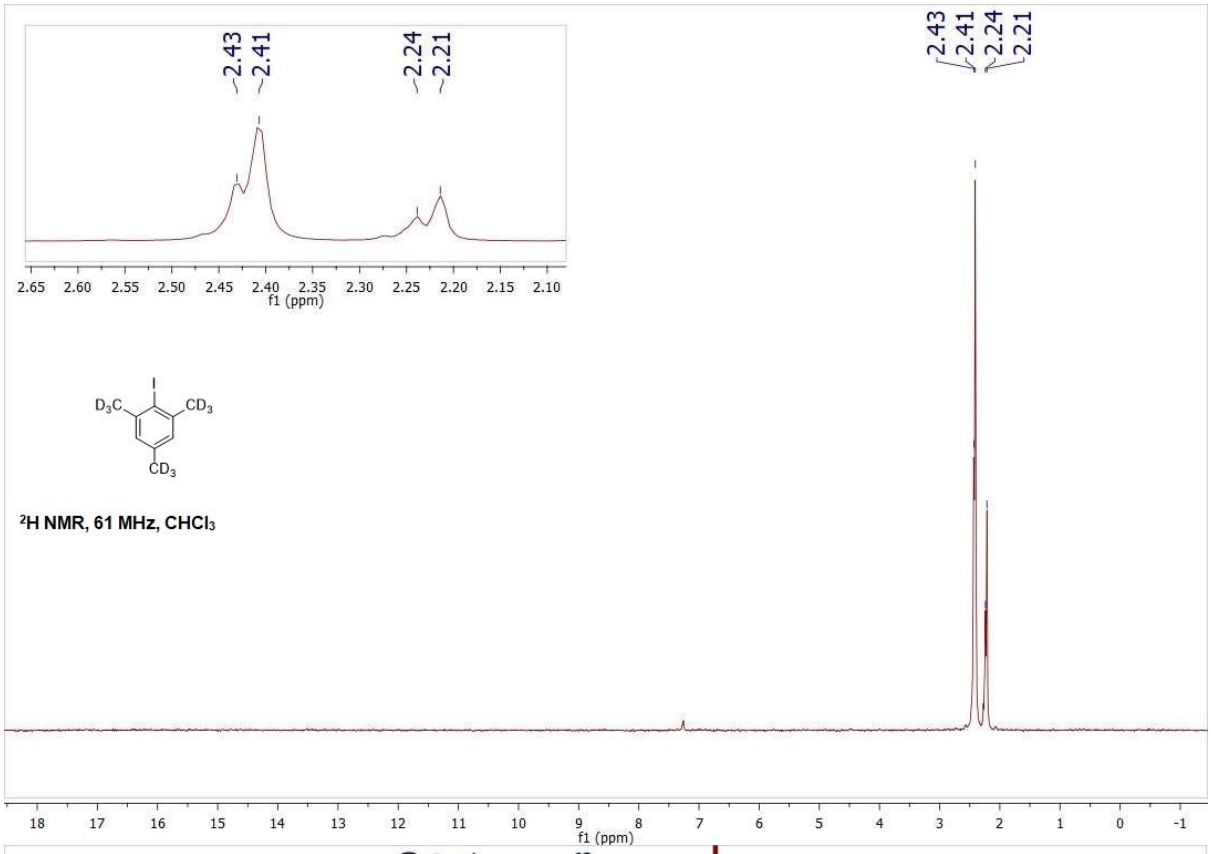

139.70
129.02
128.94
19.90
19.71
19.52
16.49
16.29
16.10
NO2
D3C
CD3
CD3
13C NMR, 101 MHz, CDCl3
19.90
19.71
19.52
16.49
16.29
16.10
21 20 19 18 17 16
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

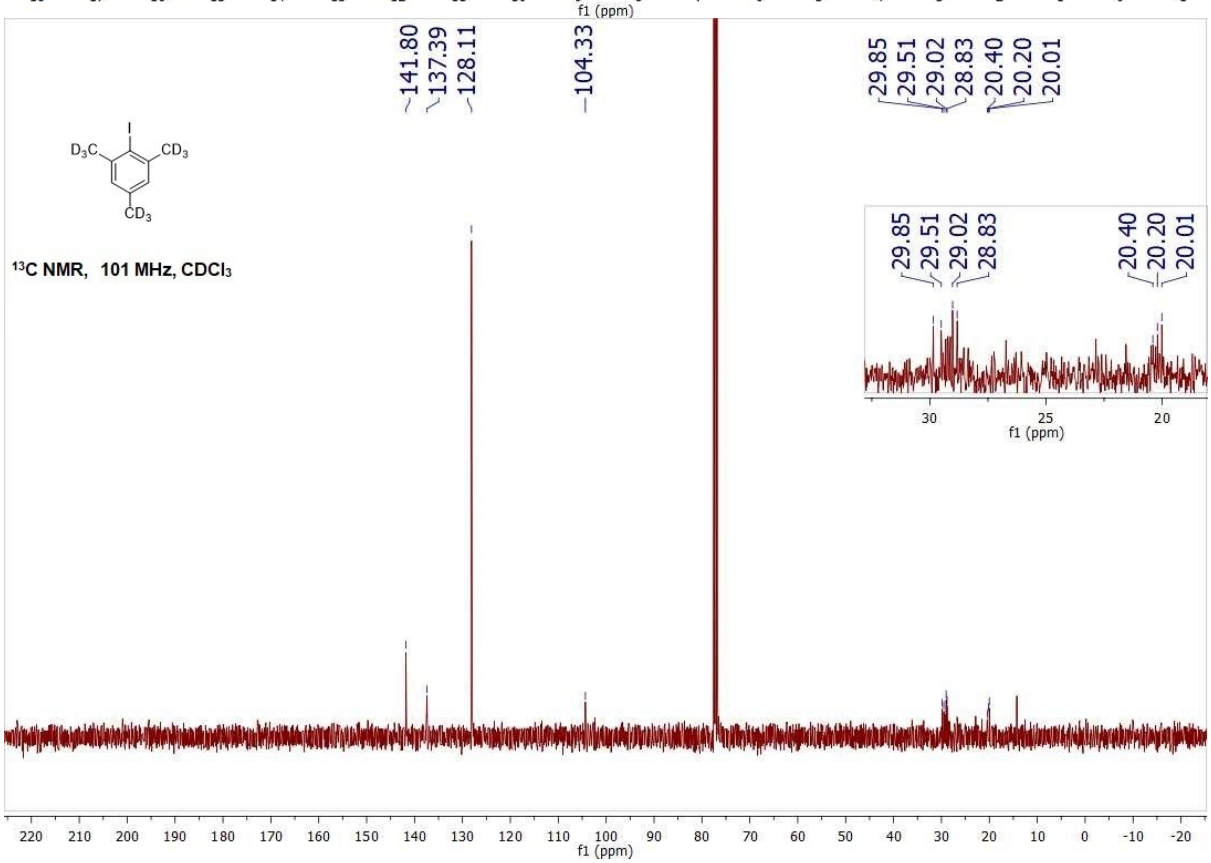

6.82
3.44
2.27
2.26
2.25
2.24
2.24
2.23
2.23
2.22
2.19
2.18
2.17
2.17
NH2
D3C
CD3
CD3
1H NMR, 400 MHz, CDCl3
2.30
2.25
2.20
2.15
f1 (ppm)
2.00
2.02
0.56
0.45
f1 (ppm)

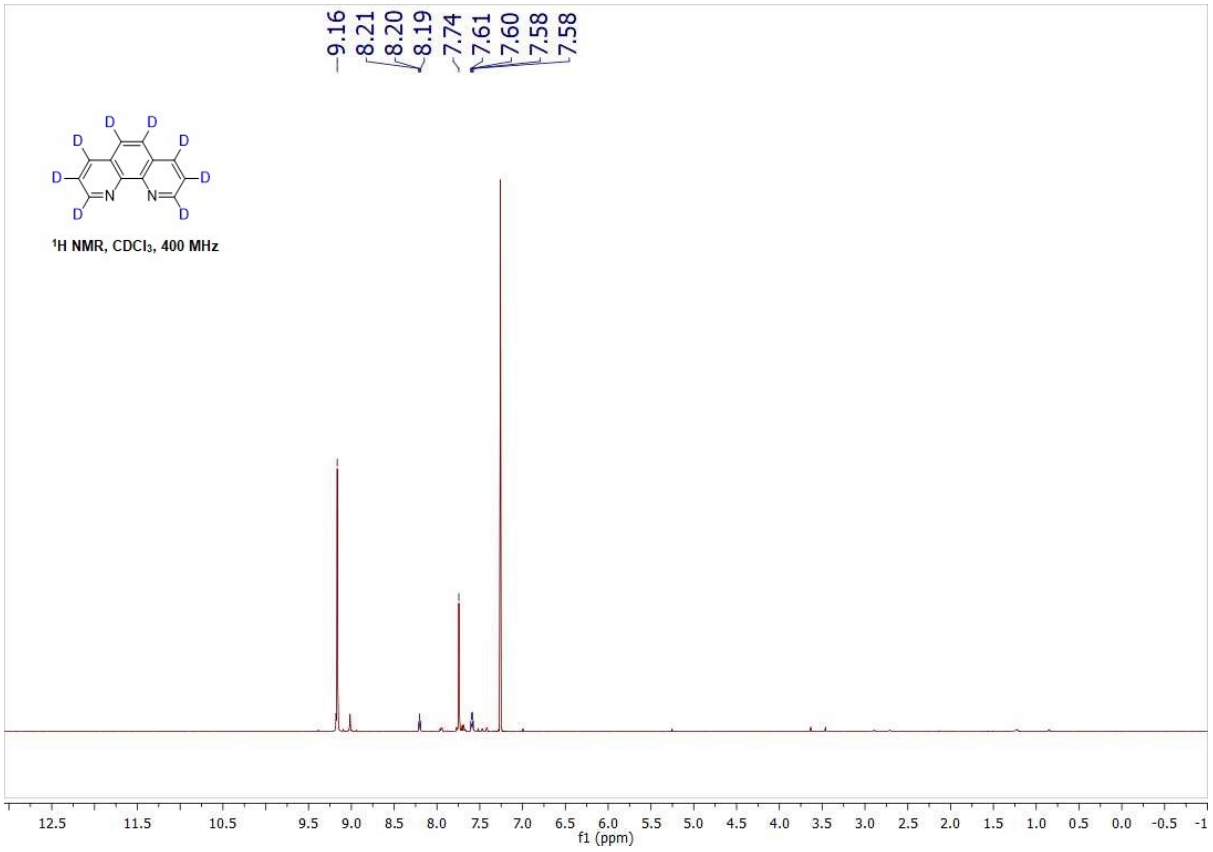

2.23
2.19
2.14
2.4
2.3
2.2
2.1
2.0
f1 (ppm)
NH2
D3C
CD3
CD3
2H NMR, 61 MHz, CHCl3
f1 (ppm)

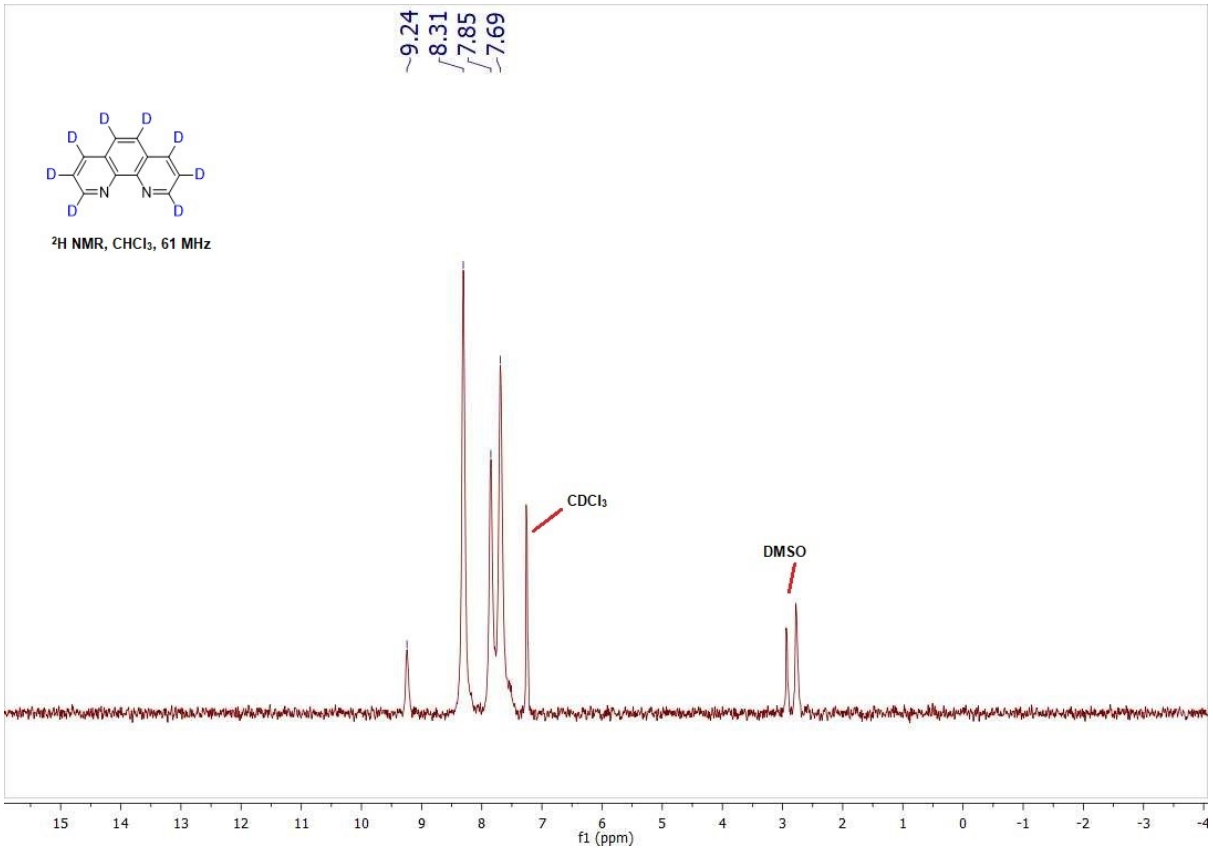

140.21
128.80
126.83
121.60
20.32
20.23
20.14
20.04
19.95
19.85
19.76
19.66
19.57
19.48
19.37
19.28
17.27
17.17
17.09
16.99
16.89
16.81
16.70
16.62
16.51
16.43
NH2
D3C
CD3
CD3
13C NMR, 101 MHz, CDCl3
f1 (ppm)

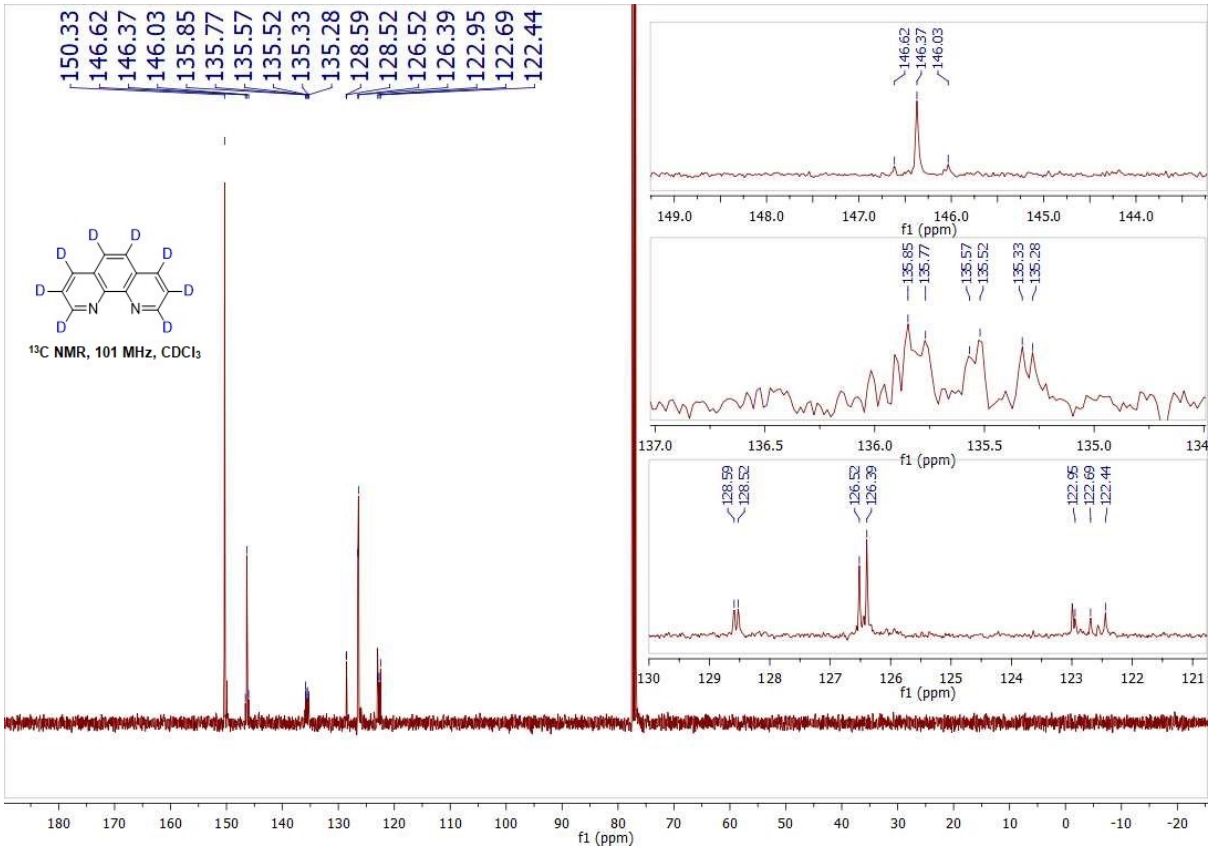

2.41
2.40
2.40
2.39
2.24
2.23
2.22
2.22
2.22
2.21
2.21
2.20
2.20
6.88
2.43
2.42
2.42
2.41
2.40
2.40
2.39
2.39
2.24
2.23
2.22
2.22
2.22
2.21
2.21
2.20
2.20
D3C
CD3
CD3
I
1H NMR, 400 MHz, CDCl3
2.00
0.44
0.56
f1 (ppm)


2.43
2.41
2.24
2.21
2.65 2.60 2.55 2.50 2.45 2.40 2.35 2.30 2.25 2.20 2.15 2.10
f1 (ppm)
D3C
CD3
CD3
I
2H NMR, 61 MHz, CHCl3
18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)


141.80
137.39
128.11
104.33
29.85
29.51
29.02
28.83
20.40
20.20
20.01
D3C
CD3
CD3
I
13C NMR, 101 MHz, CDCl3
30 25 20
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


9.16
8.21
8.20
8.19
7.74
7.61
7.60
7.58
7.58
D
N
^{1}H NMR, CDCl$_3$, 400 MHz
12.5 11.5 10.5 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 -0.5 -1
f1 (ppm)


9.24
8.31
7.85
7.69
D
N
^{2}H NMR, CHCl$_3$, 61 MHz
CDCl$_3$
DMSO
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)


150.33
146.62
146.37
146.03
135.85
135.77
135.57
135.52
135.33
135.28
128.59
128.52
126.52
126.39
122.95
122.69
122.44
D
N
^{13}C NMR, 101 MHz, CDCl$_3$
f1 (ppm)

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