

Palladium-catalysed direct cross-coupling of secondary alkyllithium reagents

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General methods:

All reactions were carried out under a nitrogen atmosphere using oven dried glassware and using standard Schlenk techniques. Et₂O and toluene were dried and distilled over sodium. Pd[P(^tBu)₃]₂ and Qphos was purchased from Strem, Pd₂(dba)₃, JohnPhos, XPhos, and DavePhos were purchased from Aldrich and used without further purification. ⁿBuLi (1.6 M solution in hexane) was purchased from Acros. ^tBuLi (1.7 M in pentane), ^{sec}BuLi (1.4 M in cyclohexane), ⁱPrLi (0.7 M in pentane) and the compounds used as precursor for the preparation of lithium reagents, namely styrene, 2-vinylnaphthalene, indene, or fluorene were purchased from Aldrich. All the bromides were commercially available and were purchased from Aldrich with the exception of 2-bromo-5-phenylthiophene (Maybridge). Organolithium other than the aforementioned were prepared according to described procedures (see below). For volatile compounds **2f**, **2h**, **5d**, **5e** and **5h**, the branched:linear ratio was determined by GC and mass spectra analysis of each compound.

Chromatography: Merck silica gel type 9385 230-400 mesh, TLC: Merck silica gel 60, 0.25 mm. Components were visualized by UV and cerium/molybdenum or potassium permanganate staining. Progress and conversion of the reaction were determined by GC-MS (GC, HP6890; MS HP5973) with an HP1 or HP5 column (Agilent Technologies, Palo Alto, CA). Mass spectra were recorded on an AEI-MS-902 mass spectrometer (EI+) or a LTQ Orbitrap XL (ESI+). ¹H- and ¹³C-NMR were recorded on a Varian AMX400 (400 and 100.59 MHz, respectively) using CDCl₃ as solvent. Chemical shift values are reported in ppm with the solvent resonance as the internal standard (CHCl₃: δ 7.26 for ¹H, δ 77.0 for ¹³C). Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz), and integration. Carbon assignments are based on APT ¹³C-NMR experiments. Melting points were measured using a Büchi Melting Point B-545.

General Procedures for the Cross-Coupling of Secondary Organolithium Reagents

Method A: General procedure for the cross-coupling with ⁱPrLi and ^{sec}BuLi.

In a dry Schlenk flask Pd[P(^tBu)₃]₂ (5 mol%, 0.015 mmol, 7.66 mg) and the substrate (0.3 mmol) were dissolved in 2 mL of dry toluene. The corresponding secondary lithium reagent (1.2 equiv) was diluted with toluene to reach the concentration of 0.36 M; this solution was slowly added over 1 h by the use of a syringe pump. After the addition was completed a saturated aqueous solution of NH₄Cl was added and the mixture was extracted three times with ether. The organic phases were collected, dried over Na₂SO₄ and filtered. The solvent evaporated under reduced pressure afforded the crude product that was then purified by column chromatography.

Method B: General procedure for the cross-coupling with cyclopropyllithium.

In a dry Schlenk flask Pd[P(^tBu)₃]₂ (5 mol%, 0.015 mmol, 7.66 mg) and the substrate (0.3 mmol) were dissolved in 2 mL of dry toluene. The corresponding secondary lithium reagent (1.7 equiv) was diluted with toluene to reach the concentration of 0.36 M; this solution was slowly added over 1 h by the use of a syringe pump. After the addition was completed a saturated aqueous solution of NH₄Cl was added and the mixture was extracted three times with ether. The organic phases were collected, dried over Na₂SO₄ and filtered. The solvent evaporated under reduced pressure afforded the crude product that was then purified by column chromatography.

Method C: General procedure for the cross-coupling with (9H-fluoren-9-yl)lithium.

In a dry Schlenk flask Pd[P(^tBu)₃]₂ (5 mol%, 0.015 mmol, 7.66 mg) and the substrate (0.3 mmol) were dissolved in 2 mL of dry toluene. Fluorenyllithium (1.0 equiv) was slowly added over 1 h by the use of a syringe pump. After the addition was completed a saturated aqueous

solution of NH_4Cl was added and the mixture was extracted three times with ether. The organic phases were collected, dried over Na_2SO_4 and filtered. The solvent evaporated under reduced pressure afforded the crude product that was then purified by column chromatography.

Method D: General procedure for the cross-coupling with (1*H*-inden-1-yl)lithium.

In a dry Schlenk flask $\text{Pd}[\text{P}(\text{tBu})_3]_2$ (5 mol%, 0.015 mmol, 7.66 mg) and the substrate (0.3 mmol) were dissolved in 2 mL of dry toluene at 40 °C. Indenyllithium (1.4 equiv) was slowly added over 2 h by the use of a syringe pump. After the addition was completed a saturated aqueous solution of NH_4Cl was added and the mixture was extracted three times with ether. The organic phases were collected, dried over Na_2SO_4 and filtered. The solvent evaporated under reduced pressure afforded the crude product that was then purified by column chromatography.

Method E: Procedure for the cross-coupling with benzylolithium reagents.

In a dry Schlenk flask $\text{Pd}[\text{P}(\text{tBu})_3]_2$ (5 mol%, 0.015 mmol, 7.66 mg) and the substrate (0.3 mmol) were dissolved in 2 mL of dry toluene. Organolithium reagent (1.3 equiv) was slowly added over 1-1.5 h by the use of a syringe pump. After the addition was completed a saturated aqueous solution of NH_4Cl was added and the mixture was extracted three times with ether. The organic phases were collected, dried over Na_2SO_4 and filtered. The solvent evaporated under reduced pressure afforded the crude product that was then purified by column chromatography.

Method F: General procedure for the cross-coupling of secondary alkylolithium reagents with hindered aryl bromides.

In a dry Schlenk flask $\text{Pd}_2(\text{dba})_3$ (1.25 mol%, 0.00375 mmol, 3.45 mg), Qphos (5 mol%, 0.015 mmol, 10.7 mg) and the substrate (0.3 mmol) were dissolved in 2 mL of dry toluene. The corresponding secondary lithium reagent (1.2 equiv) was diluted with toluene to reach the concentration of 0.36 M; this solution was slowly added over 1 h using a syringe pump. After the addition was completed a saturated aqueous solution of NH_4Cl was added and the mixture was extracted three times with ether. The organic phases were collected, dried over Na_2SO_4 and filtered. The solvent evaporated under reduced pressure afforded the crude product that was then purified by column chromatography.

Preparation of organolithium reagents:

A. Cyclopropyllithium

In a dry Schlenk flask, lithium shot (91 mg) was suspended in dry ether (2 mL) at room temperature. Then bromocyclopropane (7.2 mmol, 0.871 g, 0.577 mL) was dissolved in ether (2 mL) and added slowly over 30 min using a syringe pump. After the addition the mixture was stirring for 15 min.

B. (9*H*-fluoren-9-yl)lithium reagent

In a dry Schlenk flask, fluorene (3.0 mmol, 548 mg) was dissolved in dry ether (10 mL) and the solution was cooled to 0 °C. *n*-BuLi (1 equiv.) was added slowly and the solution was stirred for 10 min. Then the solution was allowed to reach room temperature and stirred for 1h.

C. (1*H*-inden-1-yl)lithium

In a dry Schlenk flask, t BuLi (1.1 eq, 3.3 mmol, 2.21 mL of a solution 1.7 M in pentane) was dissolved in dry ether (5 mL) and the solution was cooled to $-40\text{ }^{\circ}\text{C}$. Indene (3.0 mmol, 0.350 mL) was dissolved in ether (0.7 mL) and added slowly and the solution was stirred for 10 min. Then the solution was allowed to reach room temperature and stirred for 1 h.

D. Organolithium from carbolitiation with i PrLi

In a dry Schlenk flask i PrLi (4.0 mmol, 5.7 mL of 0.7 M solution in pentane) was slowly added to dry ether (5 mL) at $-78\text{ }^{\circ}\text{C}$. The corresponding styrene (4.0 mmol) dissolved in 0.5 mL of ether was added slowly and the solution was stirred for 30 min. Then the solution was allowed to reach room temperature and stirred for 1 h. A sample of the reagent was quenched with MeOH and injected in GC-MS in order to check the purity of the organolithium (polymerisation grade).

E. Organolithium from carbolitiation with n BuLi

In a dry Schlenk flask n BuLi (2.0 mmol, 1.25 mL of 1.6 M solution in pentane) was slowly added to dry ether (3 mL) at $-78\text{ }^{\circ}\text{C}$. The corresponding styrene (2.0 mmol) dissolved in 2 mL of ether was added slowly and the solution was stirred for 30 min. Then the solution was allowed to reach room temperature and stirred for 1 h. A sample of the reagent was quenched with MeOH and injected in GC-MS in order to check the purity of the organolithium (polymerisation grade).

F. Organolithium from carbolitiation with t BuLi

In a dry Schlenk flask t BuLi (2.0 mmol, 1.20 mL of 1.7 M solution in pentane) was slowly added to dry ether (3 mL) at $-78\text{ }^{\circ}\text{C}$. The corresponding styrene (2.0 mmol) dissolved in 2 mL of ether was added slowly and the solution was stirred for 30 min. Then the solution was allowed to reach room temperature and stirred for 1 h. A sample of the reagent was quenched with MeOH and injected in GC-MS in order to check the purity of the organolithium (polymerisation grade).

F. Organolithium from carbolitiation with sec BuLi

In a dry Schlenk flask sec BuLi (2.0 mmol, 1.45 mL of 1.4 M solution in cyclopentane) was slowly added to dry ether (3 mL) at $-78\text{ }^{\circ}\text{C}$. The corresponding styrene (2.0 mmol) dissolved in 2 mL of ether was added slowly and the solution was stirred for 30 min. Then the solution was allowed to reach room temperature and stirred for 1 h. A sample of the reagent was quenched with MeOH and injected in GC-MS in order to check the purity of the organolithium (polymerisation grade).

Control Experiments

Reaction without palladium complex:

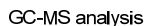
In a dry Schlenk flask p -bromoanisole (0.3 mmol) were dissolved in 2 mL of dry toluene. sec -BuLi (1.2 equiv, 1.2 mmol, 0.26 mL of 1.4 M solution in cyclohexane) was diluted with toluene to reach the concentration of 0.36 M; this solution was slowly added over 1 h by the use of a syringe pump. After the addition was completed a saturated aqueous solution of NH_4Cl was added and the mixture was extracted three times with ether. The organic phases were collected, dried over Na_2SO_4 and filtered. The organic phases were subjected to a GC-MS analysis, where less than 5% of the corresponding product was observed.



Reaction between (4-methoxyphenyl)lithium and 2-bromopropane:

To study whether (or not) the products of Br-Li exchange would also couple under the reaction conditions we performed the following experiment.

(4-methoxyphenyl)lithium was prepared from *p*-bromoanisole and ^tBuLi in THF at -78 °C.¹ In a dry Schlenk flask Pd[P(^tBu)₃]₂ (5 mol%, 0.015 mmol, 7.66 mg) and the 2-bromopropane (0.3 mmol) were dissolved in 2 mL of dry toluene. The (4-methoxyphenyl)lithium solution (1.2 equiv) was slowly added over 1 h by the use of a syringe pump. After the addition was completed a saturated aqueous solution of NH₄Cl was added and the mixture was extracted three times with ether. The combined organic phases were subjected to a GC-MS analysis, where less than 10% of the corresponding product was observed.



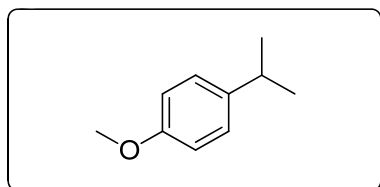
Reaction between ^{sec}BuLi and *p*-bromoanisole catalyzed DPEphos-Pd₂(dba)₃ complex.

In a dry Schlenk flask Pd₂(dba)₃ (2.5 mol%, 0.0075 mmol, 6.9 mg), DPEphos (5 mol%, 0.015 mmol, 8.2 mg) and the *p*-bromoanisole (0.3 mmol) were dissolved in 2 mL of dry toluene. ^{sec}-BuLi (1.2 equiv, 1.2 mmol, 0.26 mL of 1.4 M solution in cyclohexane) was diluted with toluene to reach the concentration of 0.36 M; this solution was slowly added over 1 h by the use of a syringe pump. After the addition was completed a saturated aqueous solution of NH₄Cl was added and the mixture was extracted three times with ether. The organic phases were combined and subjected to a GC-MS analysis, where no cross-coupling product was observed.

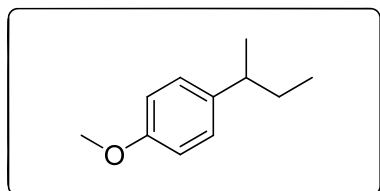


¹ M. Giannerini, M. Fañanás-Mastral, B. L. Feringa, *Nature Chem.* **2013**, 5, 667.

Spectral data of compounds 2a-2z:



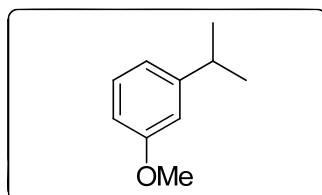
1-Isopropyl-4-methoxybenzene (2a): Synthesized according to **Method A**. Colorless oil obtained after column chromatography (SiO₂, *n*-pentane/EtOAc 100:1), [85% yield]. ¹H NMR (400 MHz, CDCl₃) δ 7.17 (dd, *J* = 9.1, 2.0 Hz, 2H), 6.86 (dd, *J* = 8.6, 2.0 Hz, 2H), 3.82 (s, 3H), 2.89 (septet, *J* = 6.9 Hz, 1H), 1.25 (d, *J* = 6.9 Hz, 6H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 157.6, 141.0, 127.2, 113.7, 55.2, 33.3, 24.2 ppm. The physical data were identical in all respects to those previously reported.²



1-(sec-Butyl)-4-methoxybenzene (2b): Synthesized according to **Method A**. [73% yield] Colorless oil obtained after column chromatography (SiO₂, *n*-pentane/Et₂O 20:1).

Gram scale reaction: In a dry Schlenk flask Pd[P(^{*t*}Bu)₃]₂ (2 mol%, 0.015 mmol, 7.66 mg) and the *p*-bromoanisole (5.5 mmol, 1.03g, 0.690 mL) were dissolved in 18 mL of dry toluene. The corresponding secondary lithium reagent (1.2 equiv, 6.6 mmol, 4.7 mL of 1.4 M solution in cyclopentane) was diluted with toluene to reach the concentration of 0.36 M; this solution was slowly added over 2h by the use of a syringe pump. After the addition was completed a saturated aqueous solution of NH₄Cl was added and the mixture was extracted three times with ether. The organic phases were collected, dried over Na₂SO₄ and filtered. The solvent evaporated under reduced pressure afforded the crude product that was then purified by column chromatography (SiO₂, *n*-pentane/Et₂O 20:1) [4.235 mmol, 695 mg, 77% yield].

¹H NMR (300 MHz, CDCl₃) δ 7.11 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 3.80 (s, 3H), 2.56 (sextet, *J* = 7.0 Hz, 1H), 1.65 – 1.49 (m, 2H), 1.22 (d, *J* = 6.9 Hz, 3H), 0.83 (t, *J* = 7.4 Hz, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 157.6, 139.8, 127.8, 113.6, 55.2, 40.8, 31.3, 22.0, 12.2 ppm. The physical data were identical in all respects to those previously reported.³

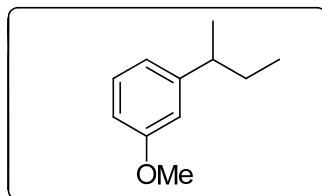


1-Isopropyl-3-methoxybenzene (2c): Synthesized according to **Method A**. [94% yield] Colorless oil obtained after column chromatography (SiO₂, *n*-pentane/Et₂O 20:1). ¹H NMR (400

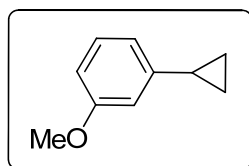
² S. D. Dreher, P. G. Dormer, D. L. Sandrock, G. A. Molander, *J. Am. Chem. Soc.* **2008**, 130, 9257.

³ S. McIntyre, E. Hoermann, F. Menges, S. P. Smidt, A. Pfaltz, *Adv. Synth. Catal.* **2005**, 347, 282.

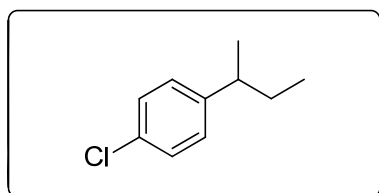
MHz, CDCl₃) δ 7.24 (t, J = 7.9 Hz, 1H), 6.86 (d, J = 8.1 Hz, 1H), 6.81 (br s, 1H), 6.75 (dd, J = 8.2, 2.5 Hz, 1H), 3.83 (s, 3H), 2.91 (septet, J = 6.8 Hz, 1H), 1.28 (d, J = 6.9 Hz, 6H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 159.6, 150.6, 129.2, 118.9, 112.5, 110.7, 55.1, 34.2, 24.0 ppm. The physical data were identical in all respects to those previously reported.⁴



1-(sec-Butyl)-3-methoxybenzene (2d): Synthesized according to **Method A**. [76% yield] Colorless oil obtained after column chromatography (SiO₂, *n*-pentane/Et₂O 20:1). ¹H NMR (400 MHz, CDCl₃) δ 7.23 (t, J = 8.3 Hz, 1H), 6.80 (d, J = 7.6 Hz, 1H), 6.77-6.72 (m, 2H), 3.82 (s, 3H), 2.58 (sextet, J = 7.4 Hz, 1H), 1.65 – 1.57 (m, 2H), 1.25 (d, J = 6.9 Hz, 3H), 0.85 (t, J = 7.4 Hz, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 159.6, 149.5, 129.1, 119.6, 113.0, 110.7, 55.1, 41.8, 31.1, 21.8, 12.3 ppm. The physical data were identical in all respects to those previously reported.⁵



1-Cyclopropyl-3-methoxybenzene (2d): Synthesized according to **Method B**. [55% yield] Colorless oil obtained after column chromatography (SiO₂, *n*-pentane/EtOAc 100:1). ¹H NMR (400 MHz, CDCl₃) δ 7.18 (t, J = 7.9 Hz, 1H), 6.73-6.66 (m, 2H), 6.64 (s, 1H), 3.80 (s, 3H), 1.94-1.81 (m, 1H), 0.96 (m, 2H), 0.76-0.66 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 159.7, 145.8, 129.2, 118.1, 111.5, 110.6, 55.1, 15.5, 9.2 ppm. HRMS (APCI+, m/z): calcd for C₁₀H₁₃O [M+H]⁺: 149.09609; found: 149.09594.

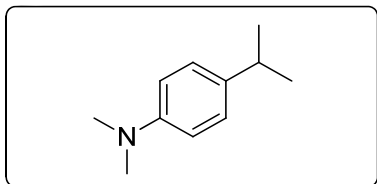


1-(sec-Butyl)-4-chlorobenzene (2g): Synthesized according to **Method A**. [78% yield] Colorless oil obtained after column chromatography (SiO₂, *n*-pentane). ¹H NMR (300 MHz, CDCl₃) δ 7.26 (d, J = 8.5 Hz, 2H), 7.11 (d, J = 8.5 Hz, 2H), 2.58 (sextet, J = 7.0 Hz, 1H), 1.66 – 1.49 (m, 2H), 1.22 (d, J = 6.9 Hz, 3H), 0.81 (t, J = 7.4 Hz, 3H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 146.3, 131.5, 128.6, 128.5, 41.4, 31.3, 22.0, 12.3 ppm. The physical data were identical in all respects to those previously reported.⁶

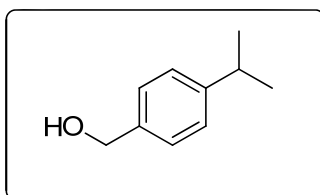
⁴ M. Pompeo, R. D. J. Froese, N. Hadei, M. G. Organ, *Angew. Chem. Int. Ed.* **2012**, 51, 11354.

⁵ A. Joshi-Pangu, M. Ganesh, M. R. Biscoe, *Org. Lett.* **2011**, 13, 1218.

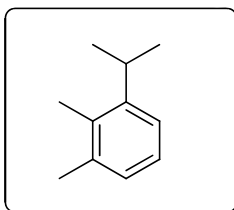
⁶ B. Guan, Y. Wang, B. Li, D. Yu, Z. Shi, *J. Am. Chem. Soc.* **2008**, 130, 14468.



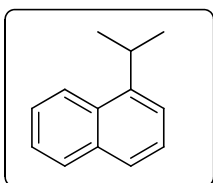
1-Isopropyl-4-methoxybenzene (2i): Synthesized according to **Method A**. Colorless oil obtained after column chromatography (SiO_2 , *n*-pentane/EtOAc 35:1), [75% yield]. ^1H NMR (400 MHz, CDCl_3) δ 7.15 (dd, $J = 8.8, 2.1$ Hz, 2H), 6.76 (dd, $J = 9.0, 2.4$ Hz, 2H), 2.94 (s, 6H), 2.86 (septet, $J = 6.9$ Hz, 1H), 1.26 (d, $J = 7.0$ Hz, 6H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 149.0, 137.2, 126.9, 113.0, 41.0, 33.1, 24.2 ppm. The physical data were identical in all respects to those previously reported.⁷



(4-Isopropylphenyl)methanol (2j): Synthesized according to **Method A** (2.4 equiv of $i\text{PrLi}$ used in this case). [61% yield] Colorless oil obtained after column chromatography (SiO_2 , *n*-pentane/EtOAc 20:1 to 10:1). ^1H NMR (400 MHz, CDCl_3) δ 7.30 (d, $J = 8.1$ Hz, 2H), 7.23 (t, $J = 8.1$ Hz, 1H), 4.65 (s, 2H), 2.92 (septet, $J = 6.8$ Hz, 1H), 1.26 (d, $J = 6.9$ Hz, 6H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 148.5, 138.2, 127.2, 126.6, 65.3, 33.9, 24.0 ppm. The physical data were identical in all respects to those previously reported.⁸



1-Isopropyl-2,3-dimethylbenzene (2k): Synthesized according to **Method A**. [83% yield] Colorless oil obtained after column chromatography (SiO_2 , *n*-pentane). ^1H NMR (400 MHz, CDCl_3) δ 7.17 (d, $J = 7.7$ Hz, 1H), 7.14 (t, $J = 7.5$ Hz, 1H), 7.05 (d, $J = 7.0$ Hz, 1H), 3.26 (septet, $J = 6.8$ Hz, 1H), 2.43 (3H, s), 2.29 (3H, s), 1.28 (d, $J = 6.9$ Hz, 6H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 146.6, 136.6, 133.6, 127.4, 125.6, 122.5, 29.4, 23.4, 21.1, 14.6 ppm. The physical data were identical in all respects to those previously reported.⁹

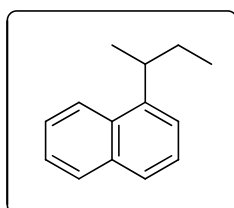


⁷ S. Kanemura, A. Kondoh, H. Yorimitsu, K. Oshima, *Synthesis* **2008**, 2659.

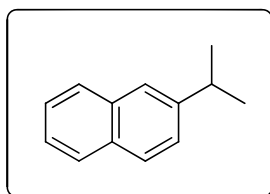
⁸ H. Suzuki, T. Nakamura, *J. Org. Chem.* **2008**, 58, 241.

⁹ H. Cho, R. G. Harvey, P. W. Rabideu, *J. Am. Chem. Soc.* **1975**, 97, 1140.

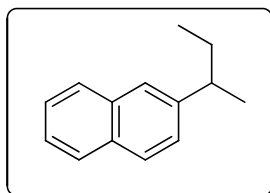
1-Isopropylnaphthalene (2l): Synthesized according to **Method A**. [87% yield, 98:2 branched:linear, 4% of dehalogenation] Colorless oil obtained after column chromatography (SiO_2 , *n*-pentane). ^1H NMR (400 MHz, CDCl_3) δ 8.20 (d, $J = 8.4$ Hz, 1H), 7.92 (dd, $J = 8.3$, 0.9 Hz, 1H), 7.76 (dd, $J = 7.5$, 1.2 Hz, 1H), 7.61-7.46 (4H, m), 3.82 (septet, $J = 6.9$ Hz, 1H), 1.48 (d, $J = 6.9$ Hz, 6H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 144.7, 134.0, 131.4, 129.0, 126.3, 125.7, 125.3, 123.3, 121.7, 28.6, 23.6 ppm. The physical data were identical in all respects to those previously reported.¹⁰



1-(sec-Butyl)naphthalene (2m): Synthesized according to **Method A**. [90% yield, 95:5 branched:linear, 5% of dehalogenation] Colorless oil obtained after column chromatography (SiO_2 , *n*-pentane). ^1H NMR (400 MHz, CDCl_3) δ 8.19 (d, $J = 8.3$ Hz, 1H), 7.91 (d, $J = 8.4$ Hz, 1H), 7.75 (d, $J = 8.0$ Hz, 1H), 7.60-7.47 (m, 3H), 7.44 (d, $J = 7.0$ Hz, 1H), 3.58 (sextet, $J = 6.9$ Hz, 1H), 2.02-1.85 (m, 1H), 1.84-1.70 (m, 1H), 1.43 (d, $J = 6.9$ Hz, 3H), 0.99 (t, $J = 7.4$ Hz, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 143.7, 134.0, 131.8, 129.0, 126.2, 125.6, 125.6, 125.2, 123.3, 122.5, 35.3, 30.6, 21.3, 12.3 ppm. The physical data were identical in all respects to those previously reported.¹¹



2-Isopropylnaphthalene (2n): Synthesized according to **Method A**. [96% yield] Colorless oil obtained after column chromatography (SiO_2 , *n*-pentane). ^1H NMR (400 MHz, CDCl_3) δ 7.87-7.83 (m, 3H), 7.71 (s, 1H), 7.53-7.45 (m, 3H), 3.14 (septet, $J = 6.9$ Hz, 1H), 1.42 (d, $J = 6.9$ Hz, 6H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 146.4, 133.7, 132.1, 127.9, 127.62, 127.61, 125.9, 125.8, 125.1, 124.1, 34.3, 24.0 ppm. The physical data were identical in all respects to those previously reported.¹²



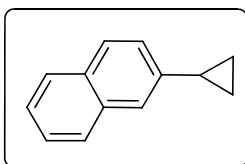
2-(sec-Butyl)naphthalene (2o): Synthesized according to **Method A**. [93% yield, 5% dehalogenation] Colorless oil obtained after column chromatography (SiO_2 , *n*-pentane). ^1H NMR

¹⁰ N. Iwasawa, M. Shido, K. Maeyana, H. Kusana, *J. Am. Chem. Soc.* **2000**, 122, 10226.

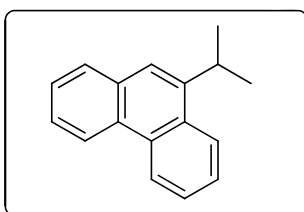
¹¹ W. M. Czaplik, M. Mayer, A. Jacobi von Wangelin, *Synlett* **2009**, 18, 2931.

¹² A. Baroudi, J. Mauldin, I. V. Alabugin, *J. Am. Chem. Soc.* **2010**, 132, 967.

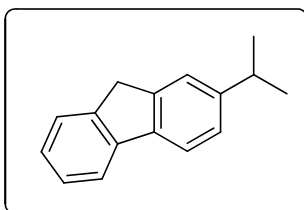
(400 MHz, CDCl_3) δ 7.81-7.77 (m, 3H), 7.61 (1H, s), 7.48-7.38 (m, 2H), 7.35 (d, $J = 8.4\text{ Hz}$, 1H), 2.77 (sextet, $J = 6.9\text{ Hz}$, 1H), 1.78-1.62 (m, 2H), 1.33 (d, $J = 6.9\text{ Hz}$, 3H), 0.86 (t, $J = 7.4\text{ Hz}$, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 145.1, 133.6, 132.1, 127.8, 127.6, 127.5, 125.9, 125.7, 125.2, 125.0, 41.8, 31.0, 21.9, 12.3 ppm. The physical data were identical in all respects to those previously reported.¹³



2-Cyclopropylnaphthalene (2p): Synthesized according to **Method B**. [80% yield] Colorless oil obtained after column chromatography (SiO_2 , *n*-pentane). ^1H NMR (400 MHz, CDCl_3) δ 7.84-7.69 (m, 3H), 7.55 (s, 1H), 7.48-7.37 (m, 2H), 7.21 (d, $J = 8.5\text{ Hz}$, 1H), 2.17-1.98 (m, 1H), 1.08-1.01 (m, 2H), 0.87-0.78 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 141.4, 133.5, 131.9, 127.8, 127.6, 127.2, 125.9, 124.8, 124.6, 123.7, 15.6, 9.2. HRMS (APCI+, *m/z*): calcd for $\text{C}_{13}\text{H}_{13}$ [$\text{M}+\text{H}$] $^+$: 169.10118; found: 169.10098.



9-Isopropylphenanthrene (2q): Synthesized according to **Method A**. [97% yield, 99:1 branched:linear] Colorless oil obtained after column chromatography (SiO_2 , *n*-pentane). ^1H NMR (400 MHz, CDCl_3) δ 8.85-8.78 (m, 1H), 8.74-8.70 (m, 1H), 8.30-8.22 (m, 1H), 7.96-7.90 (m, 1H), 7.74-7.69 (m, 3H), 7.68-7.61 (m, 2H), 3.80 (septet, $J = 6.9\text{ Hz}$, 1H), 1.54 (d, $J = 6.8\text{ Hz}$, 6H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 142.6, 132.0, 131.0, 130.8, 129.4, 128.4, 126.6, 126.5, 126.0, 125.97, 124.0, 123.4, 122.4, 122.3, 28.7, 23.4 ppm. The physical data were identical in all respects to those previously reported.¹⁴

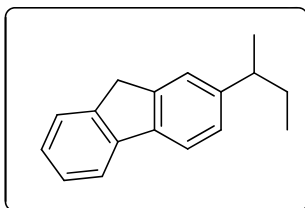


2-Isopropyl-9H-fluorene (2r): Synthesized according to **Method A**. [96% yield] Colorless solid obtained after column chromatography (SiO_2 , *n*-pentane). ^1H NMR (400 MHz, CDCl_3) δ 7.81 (d, $J = 7.5\text{ Hz}$, 1H), 7.76 (d, $J = 7.8\text{ Hz}$, 1H), 7.58 (d, $J = 7.5\text{ Hz}$, 1H), 7.48 (s, 1H), 7.42 (t, $J = 7.5\text{ Hz}$, 1H), 7.36-7.29 (m, 2H), 3.92 (s, 2H), 3.05 (septet, $J = 6.9\text{ Hz}$, 1H), 1.38 (d, $J = 6.9\text{ Hz}$, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 147.8, 143.5, 143.2, 141.9, 139.6, 126.7,

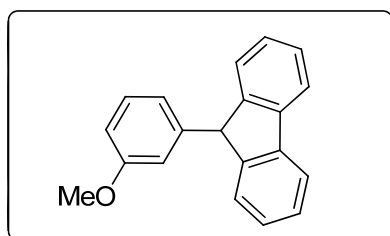
¹³ B. L. H. Taylor, E. C. Swift, J. D. Waetzig, E. R. Jarvo, *J. Am. Chem. Soc.* **2011**, 133, 389.

¹⁴ E. Yoshikawa, K. V. Radhakrishnan, Y. Yamamoto, *J. Am. Chem. Soc.* **2000**, 122, 7280.

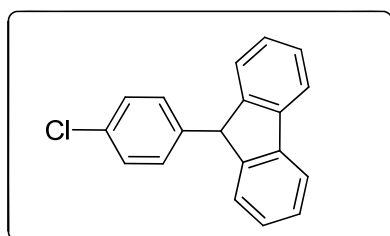
126.3, 125.2, 125.0, 123.1, 119.7, 119.6, 36.9, 34.4, 24.3. The physical data were identical in all respects to those previously reported.¹⁵



2-(sec-Butyl)-9H-fluorene (2s): Synthesized according to **Method A**. [95% yield] Colorless oil obtained after column chromatography (SiO₂, *n*-pentane). ¹H NMR (400 MHz, CDCl₃) δ 7.79 (d, *J* = 7.5 Hz, 1H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.56 (d, *J* = 7.4 Hz, 1H), 7.42-7.36 (m, 2H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.24 (d, *J* = 7.8 Hz, 1H), 3.91 (s, 2H), 2.84-2.63 (m, 1H), 1.78-1.61 (m, 2H), 1.34 (d, *J* = 6.9 Hz, 3H), 0.91 (t, *J* = 7.4 Hz, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 146.6, 143.3, 143.2, 141.9, 139.6, 126.7, 126.2, 125.8, 125.0, 123.7, 119.6, 119.6, 41.9, 36.9, 31.4, 22.2, 12.4 ppm. HRMS (APCI+, *m/z*): calcd for C₁₇H₂₀ [M+H]⁺: 223.1481; found: 223.1488.



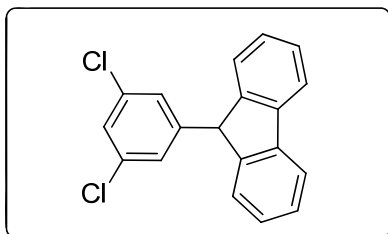
9-(3-Methoxyphenyl)-9H-fluorene (2t): Synthesized according to **Method C**. [94% yield] Yellow solid obtained after column chromatography (SiO₂, *n*-pentane/Et₂O 20:1), m.p = 95-96 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.82 (d, *J* = 7.5 Hz, 2H), 7.43-7.36 (m, 4H), 7.30-7.26 (m, 2H), 7.22 (t, *J* = 7.9 Hz, 1H), 6.80 (dd, *J* = 8.2, 1.6 Hz, 1H), 6.80 (dd, *J* = 8.2, 1.6 Hz, 1H), 6.73 (d, *J* = 7.5 Hz, 1H), 6.67 (br s, 1H), 5.05 (s, 1H), 3.74 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 159.8, 147.7, 143.2, 141.0, 129.7, 127.3, 127.3, 120.8, 119.9, 114.2, 111.9, 55.1, 54.4 ppm. HRMS (APCI+, *m/z*): calcd for C₂₀H₁₇O₁ [M+H]⁺: 273.1274; found: 273.1280.



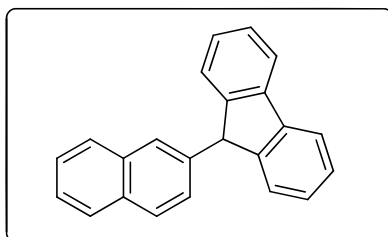
9-(4-Chlorophenyl)-9H-fluorene (2u): Synthesized according to **Method C**. [89% yield] White solid obtained after column chromatography (SiO₂, *n*-pentane). ¹H NMR (400 MHz, CDCl₃) δ 7.82 (d, *J* = 7.6 Hz, 2H), 7.46-7.34 (m, 2H), 7.31-7.27 (m, 4H), 7.25 (d, *J* = 8.3 Hz, 2H), 7.03 (d, *J* = 8.4 Hz, 2H), 5.03 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 147.4, 141.0,

¹⁵ W. T. Ford, T. B. Thompson, K. A. J. Snoble, J. M. Timko, *J. Am. Chem. Soc.* **1975**, 97, 95.

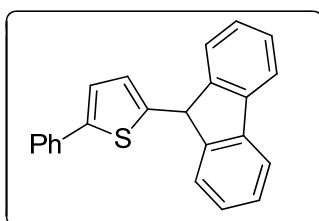
140.2, 132.6, 129.7, 128.9, 127.5, 127.4, 125.2, 120.0, 53.7 ppm. The physical data were identical in all respects to those previously reported.¹⁶



9-(3,5-Dichlorophenyl)-9H-fluorene (2v): Synthesized according to **Method C**. [87% yield]. White solid obtained after column chromatography (SiO₂, *n*-pentane), m.p = 90-92 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, *J* = 7.6 Hz, 2H), 7.46-7.39 (m, 2H), 7.33-7.28 (m, 4H), 7.24 (t, *J* = 1.9 Hz, 1H), 6.98 (d, *J* = 1.8 Hz, 2H), 4.98 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 146.4, 145.2, 141.0, 135.1, 127.8, 127.6, 127.2, 126.8, 125.2, 120.1, 53.6 ppm. MS-EI: *m/z* (%) 310 (M⁺, 100), 275 (65), 239 (50), 165 (40), 119 (38).

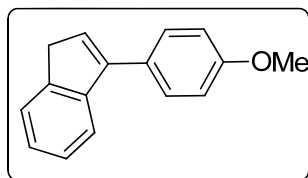


9-(Naphthalen-2-yl)-9H-fluorene (2w): Synthesized according to **Method C**. [93% yield] Colorless oil obtained after column chromatography (SiO₂, *n*-pentane). ¹H NMR (400 MHz, CDCl₃) δ 7.91-7.78 (m, 5H), 7.70 (d, *J* = 8.5 Hz, 1H), 7.51-7.42 (m, 4H), 7.36 (d, *J* = 7.5 Hz, 2H), 7.30-7.27 (m, 3H), 6.93 (d, *J* = 8.5 Hz, 1H), 5.24 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 147.9, 141.1, 139.1, 133.6, 132.6, 128.5, 127.7, 127.6, 127.5, 127.4, 127.3, 126.2, 126.1, 125.6, 125.5, 120.0, 54.6 ppm. MS-EI: *m/z* (%) 292 (M⁺, 100), 165 (10), 145 (15).

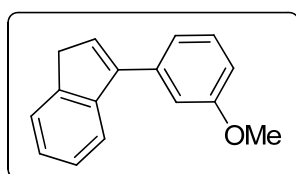


2-(9H-Fluoren-9-yl)-5-phenylthiophene (2x): Synthesized according to **Method C**. [79% yield] Yellow solid obtained after column chromatography (SiO₂, *n*-pentane), m.p = 165-167 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, *J* = 7.6 Hz, 2H), 7.54 (d, *J* = 8.2 Hz, 2H), 7.51 (d, *J* = 7.2 Hz, 2H), 7.43 (d, *J* = 7.4 Hz, 2H), 7.35-7.29 (m, 4H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.18 (d, *J* = 3.6 Hz, 1H), 6.98 (d, *J* = 3.6 Hz, 1H), 5.35 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 146.2, 143.7, 143.1, 140.5, 134.4, 128.8, 127.8, 127.4, 127.2, 126.3, 125.5, 125.3, 122.6, 120.0, 49.3 ppm. HRMS (APCI, *m/z*): calcd for C₂₃H₁₅S [M-H]⁺: 323.08890; found: 323.08875.

¹⁶ G. Li, E. Wang, H. Chen, H. Li, Y. Liu, P. G. Wang, *Tetrahedron*, **2008**, 64, 9033.

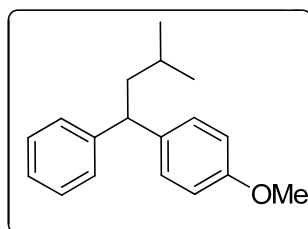


3-(4-Methoxyphenyl)-1H-indene (2y): Synthesized according to **Method D**. [95% yield] Yellow oil obtained after column chromatography (SiO_2 , *n*-pentane/ Et_2O 20:1). ^1H NMR (400 MHz, CDCl_3) δ 7.61 (d, J = 7.6 Hz, 1H), 7.58-7.54 (m, 3H), 7.35 (t, J = 7.5 Hz, 1H), 7.27 (t, J = 7.6 Hz, 1H), 7.01 (d, J = 8.5 Hz, 2H), 6.53 (s, 1H), 3.88 (s, 3H), 3.51 (s, 2H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 159.2, 144.8, 144.6, 144.1, 129.9, 128.8, 128.7, 126.1, 124.7, 124.1, 120.3, 114.0, 55.3, 38.1 ppm. The physical data were identical in all respects to those previously reported.¹⁷



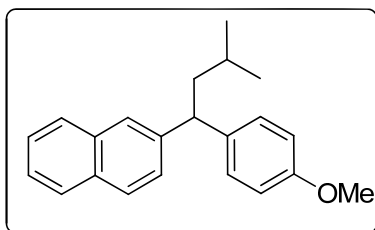
3-(3-Methoxyphenyl)-1H-indene (2z): Synthesized according to **Method D**. [86% yield] Yellow oil obtained after column chromatography (SiO_2 , *n*-pentane/ Et_2O 20:1). ^1H NMR (400 MHz, CDCl_3) δ 7.66 (d, J = 7.6 Hz, 1H), 7.58 (d, J = 7.3 Hz, 1H), 7.44-7.34 (m, 2H), 7.30 (t, J = 7.4 Hz, 1H), 7.25 (d, J = 7.7 Hz, 1H), 7.20 (s, 1H), 6.97 (dd, J = 8.2, 1.8 Hz, 1H), 6.63 (s, 1H), 3.90 (s, 3H), 3.55 (s, 2H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 159.8, 145.1, 144.8, 143.9, 137.5, 131.1, 129.6, 126.2, 124.9, 124.1, 120.4, 120.2, 113.3, 113.2, 55.3, 38.2 ppm. The physical data were identical in all respects to those previously reported.¹⁷

Spectral data of compounds 3a-3f:

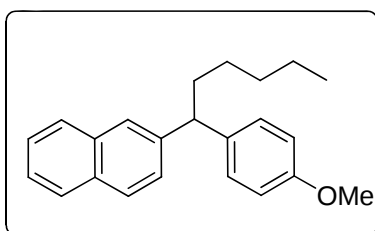


1-Methoxy-4-(3-methyl-1-phenylbutyl)benzene (3a): Synthesized according to **Method E**. [54% yield] Colorless oil obtained after column chromatography (SiO_2 , *n*-pentane to *n*-pentane/ Et_2O 20:1). ^1H NMR (400 MHz, CDCl_3) δ 7.33-7.33 (m, 4H), 7.19-7.14 (m, 3H), 6.83 (d, J = 8.7 Hz, 2H), 3.99 (t, J = 8.0 Hz, 1H), 3.78 (s, 3H), 1.90 (t, J = 7.5 Hz, 2H), 1.51-1.39 (m, 1H), 0.93 (d, J = 6.6 Hz, 6H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 157.8, 145.7, 137.4, 128.7, 128.3, 127.8, 125.9, 113.8, 55.2, 48.0, 45.2, 25.5, 22.7, 22.6 ppm. MS-EI: m/z (%) 254 (M^+ , 10), 197 (100), 165 (15), 153 (12).

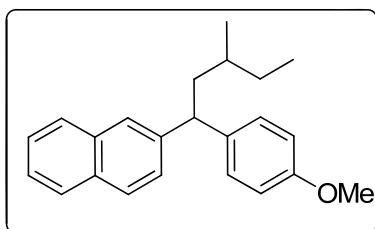
¹⁷ D. R. Arnold, X. Du, K. M. Henseleit, *Can. J. Chem.*, **1991**, 69, 839.



2-(1-(4-Methoxyphenyl)-3-methylbutyl)naphthalene (3b): Synthesized according to **Method E**. [59% yield] Colorless oil obtained after column chromatography (SiO₂, *n*-pentane to *n*-pentane/Et₂O 20:1). ¹H NMR (400 MHz, CDCl₃) δ 7.78 (t, *J* = 7.5 Hz, 2H), 7.74 (t, *J* = 7.5 Hz, 1H), 7.69 (s, 1H), 7.48-7.39 (m, 2H), 7.34 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.21 (d, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 4.14 (t, *J* = 8.0 Hz, 1H), 3.77 (s, 3H), 2.06-1.92 (m, 2H), 1.52-1.44 (m, 1H), 0.96 (d, *J* = 6.6 Hz, 3H), 0.95 (d, *J* = 6.6 Hz, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 157.8, 143.1, 137.3, 133.5, 132.1, 128.9, 127.5, 126.8, 125.9, 125.7, 125.2, 113.8, 55.2, 48.0, 44.9, 25.5, 22.7, 22.67 ppm. MS-EI: *m/z* (%) 304 (M⁺, 15), 247 (100), 215 (20).

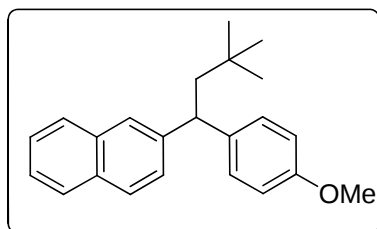


2-(1-(4-Methoxyphenyl)hexyl)naphthalene (3c): Synthesized according to **Method E**. [48% yield] Colorless oil obtained after column chromatography (SiO₂, *n*-pentane to *n*-pentane/Et₂O 20:1). ¹H NMR (400 MHz, CDCl₃) δ 7.79 (t, *J* = 7.9 Hz, 2H), 7.74 (d, *J* = 8.5 Hz, 1H), 7.69 (s, 1H), 7.47-7.40 (m, 2H), 7.33 (d, *J* = 8.5 Hz, 1H), 7.20 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.5 Hz, 2H), 4.02 (t, *J* = 7.7 Hz, 1H), 3.77 (s, 3H), 2.19-2.05 (m, 2H), 1.40-1.24 (m, 6H), 0.87 (t, *J* = 6.8 Hz, 3H), ppm. ¹³C NMR (100 MHz, CDCl₃) δ 157.8, 143.2, 137.4, 133.5, 132.1, 128.9, 128.0, 127.7, 127.5, 126.8, 125.8, 125.7, 125.2, 113.8, 55.2, 50.0, 35.6, 31.9, 27.8, 22.6, 14.1 ppm. MS-EI: *m/z* (%) 318 (M⁺, 10), 247 (100), 215 (15).

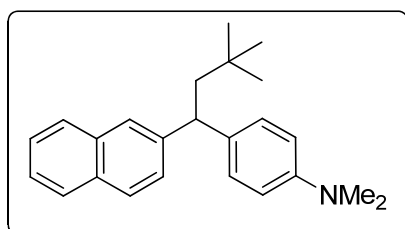


2-(1-(4-Methoxyphenyl)-3-methylpentyl)naphthalene (3d): Synthesized according to **Method E**. [56% yield, dr 1:1] Colorless oil obtained as a 1:1 mixture of diastereoisomers after column chromatography (SiO₂, *n*-pentane to *n*-pentane/Et₂O 20:1). ¹H NMR (400 MHz, CDCl₃) δ 7.75-7.62 (m, 8H, both diaster.), 7.39-7.35 (m, 4H, both diaster.), 7.30-7.27 (m, 2H, both diaster.), 7.17-7.14 (m, 4H, both diaster.), 6.79-6.75 (m, 4H, both diaster.), 4.12-4.08 (m, 2H, both diaster.), 3.71 (s, 3H), 3.70* (s, 3H), 2.16-2.05 (m, 2H, both diaster.), 1.84-1.73 (m, 2H, both diaster.), 1.25-1.11 (m, 4H, both diaster.), 0.88-0.86 (m, 6H, both diaster.), 0.82-0.77 (m, 6H, both diaster.) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 157.8, 157.7*, 143.5, 142.7*, 137.7, 136.8*, 133.5, 132.02, 131.95*, 128.9, 128.7*, 128.0, 127.9*, 127.61, 127.59*, 127.48, 127.45*,

126.8, 126.7*, 125.9, 125.8*, 125.4, 125.18, 125.16*, 113.72, 113.68*, 55.14, 55.13*, 47.71, 47.68*, 42.7, 42.6*, 31.7, 29.54, 29.50*, 19.1, 19.0*, 11.0 ppm. (* indicates the other diastereoisomer) MS-EI: m/z (%) 318 (M^+ , 10), 247 (100), 215 (16).

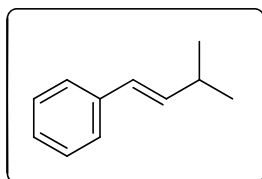


2-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)naphthalene (3e): Synthesized according to **Method E**. [52% yield] Colorless oil obtained after column chromatography (SiO_2 , n -pentane to n -pentane/ Et_2O 20:1). ^1H NMR (400 MHz, CDCl_3) δ 7.81-7.71 (m, 4H), 7.47-7.38 (m, 3H), 7.27 (d, J = 8.8 Hz, 2H), 6.83 (d, J = 8.6 Hz, 2H), 4.21 (t, J = 6.7 Hz, 1H), 3.76 (s, 3H), 2.25-2.13 (m, 2H), 0.88 (s, 9H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 157.7, 144.6, 138.7, 133.6, 132.0, 128.8, 128.0, 127.6, 127.5, 126.7, 125.8, 125.5, 125.2, 113.8, 55.2, 49.3, 47.5, 31.6, 30.3 ppm. MS-EI: m/z (%) 318 (M^+ , 15), 247 (100), 215 (20).



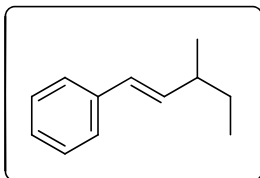
4-(3,3-dimethyl-1-(naphthalen-2-yl)butyl)-N,N-dimethylaniline (3f): Synthesized according to **Method E**. [57% yield] Colorless oil obtained after column chromatography (SiO_2 , n -pentane to n -pentane/ Et_2O 20:1). ^1H NMR (400 MHz, CDCl_3) δ 7.81-7.74 (m, 4H), 7.45-7.22 (m, 3H), 7.23 (d, J = 8.4 Hz, 2H), 6.69 (d, J = 8.5 Hz, 2H), 4.18 (t, J = 6.6 Hz, 1H), 2.90 (s, 6H), 2.28-2.12 (m, 2H), 0.90 (s, 9H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 148.9, 145.0, 134.8, 133.5, 131.9, 128.4, 127.9, 127.7, 127.5, 126.9, 125.7, 125.5, 125.0, 112.9, 49.3, 47.4, 40.8, 31.6, 30.3 ppm. HRMS (APCI+, m/z): calcd for $\text{C}_{24}\text{H}_{30}\text{N}$ [$M+\text{H}$] $^+$: 332.23728; found: 332.23728.

Spectral data of compounds 5a-5k:

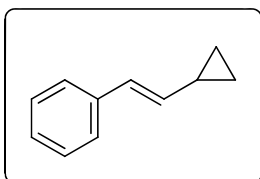


(E)-(3-Methylbut-1-en-1-yl)benzene (5a): (The reaction was carried out on a commercially available 84/16 *trans/cis* mixture). Synthesized according to **Method A**. [91% yield, 88/12 *E/Z*] Colorless oil after column chromatography (SiO_2 , n -pentane). ^1H NMR (400 MHz, CDCl_3) δ 7.38 (d, J = 7.2 Hz, 2H), 7.31 (t, J = 7.6 Hz, 2H), 7.21 (t, J = 7.2 Hz, 1H), 6.37 (d, J = 16.1 Hz, 1H), 6.22 (dd, J = 15.9, 6.8 Hz, 1H), 2.54 – 2.45 (m, 1H), 1.12 (d, J = 6.7 Hz,

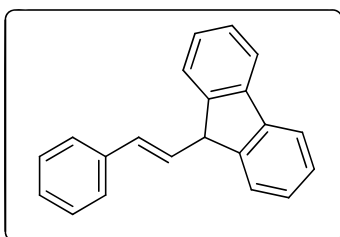
6H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 138.00, 137.95, 128.5, 126.8, 126.7, 126.0, 31.5, 22.5 ppm. The physical data were identical in all respects to those previously reported.¹⁸



(E)-(3-Methylpent-1-en-1-yl)benzene (5b): (The reaction was carried out on a commercially available 84/16 *trans/cis* mixture). Synthesized according to **Method A**. [79% yield, 89/11 *E/Z*] Colorless oil after column chromatography (SiO_2 , *n*-pentane). ^1H NMR (400 MHz, CDCl_3) δ 7.39 (d, J = 7.4 Hz, 2H), 7.32 (t, J = 7.6 Hz, 2H), 7.22 (t, J = 7.2 Hz, 1H), 6.38 (d, J = 16.0 Hz, 1H), 6.13 (dd, J = 15.9, 7.9 Hz, 1H), 2.24 (septet, J = 6.9 Hz, 1H), 1.52-1.39 (m, 1H), 1.11 (d, J = 6.7 Hz, 3H), 0.94 (t, J = 7.4 Hz, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 138.0, 136.8, 128.5, 128.1, 126.7, 126.0, 38.9, 29.8, 20.3, 11.9 ppm. The physical data were identical in all respects to those previously reported.¹⁹



(E)-(2-Cyclopropylvinyl)benzene3-Methylpent-1-en-1-yl)benzene (5c): (The reaction was carried out on a commercially available 84/16 *trans/cis* mixture). Synthesized according to **Method A**. [88% yield] Colorless oil after column chromatography (SiO_2 , *n*-pentane). ^1H NMR (400 MHz, CDCl_3) δ 7.35-7.25 (m, 4H), 7.18 (t, J = 6.8 Hz, 1H), 6.49 (d, J = 15.8 Hz, 1H), 5.75 (dd, J = 15.8, 8.9 Hz, 1H), 1.64-1.54 (m, 1H), 0.89-0.79 (m, 2H), 0.60-0.47 (m, 2H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 137.8, 134.9, 128.5, 127.4, 126.5, 125.6, 14.5, 7.2 ppm. The physical data were identical in all respects to those previously reported.²⁰



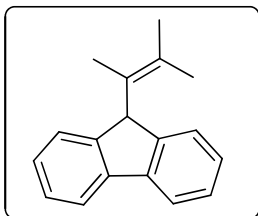
(E)-9-Styryl-9H-fluorene (5c): (The reaction was carried out on a commercially available 84/16 *trans/cis* mixture). Synthesized according to **Method C**. [96% yield, 86/14 *E/Z*]. White solid after column chromatography (SiO_2 , *n*-pentane). ^1H NMR (400 MHz, CDCl_3) δ 7.83 (d, J = 7.4 Hz, 2H), 7.54 (d, J = 7.4 Hz, 2H), 7.46-7.41 (m, 4H), 7.37-7.32 (m, 4H), 7.26 (t, J = 7.3 Hz, 2H), 6.92 (d, J = 15.5 Hz, 1H), 6.08 (dd, J = 15.6, 9.1 Hz, 1H), 4.68 (d, J = 9.1 Hz, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 146.1, 141.0, 137.2, 132.5, 129.0, 128.6, 127.6, 127.4,

¹⁸ G. A. Russell, P. Ngoviwatchai, H. I. Tashtoush, *Organometallics* **1988**, 7, 696.

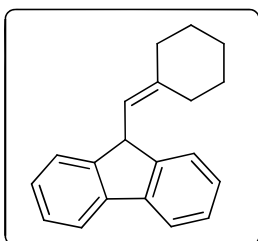
¹⁹ J. Zhou, G. C. Fu, *J. Am. Chem. Soc.* **2004**, 126, 1340.

²⁰ G. Zuo, J. Louie *Angew. Chem. Int. Ed.* **2004**, 43, 2277.

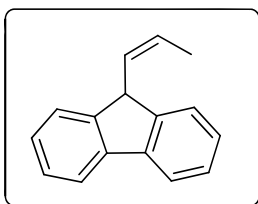
127.2, 126.3, 125.4, 120.0, 52.4 ppm. The physical data were identical in all respects to those previously reported.²¹



9-(3-Methylbut-2-en-2-yl)-9H-fluorene (5f): Synthesized according to **Method C**. [89% yield] Colorless oil after column chromatography (SiO₂, *n*-pentane). ¹H NMR (400 MHz, CDCl₃) δ 7.78 (d, *J* = 7.4 Hz, 2H), 7.42-7.35 (m, 4H), 7.30 (t, *J* = 7.3 Hz, 2H), 5.09 (s, 1H), 2.14 (s, 3H), 1.85 (s, 3H), 0.97 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 147.1, 141.6, 128.1, 126.9, 126.9, 126.4, 124.6, 119.7, 51.7, 21.0, 20.9, 13.4 ppm. HRMS (APCI+, *m/z*): calcd for C₁₈H₁₉ [M+H]⁺: 235.1481; found: 235.1487.

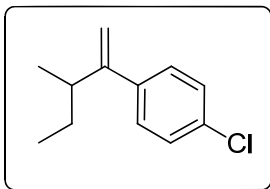


9-(Cyclohexylidenemethyl)-9H-fluorene (5i): Synthesized according to **Method C**. [93% yield] White solid after column chromatography (SiO₂, *n*-pentane), m.p = 97-99 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, *J* = 7.4 Hz, 2H), 7.41 (d, *J* = 7.3 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 2H), 4.90 (d, *J* = 9.6 Hz, 1H), 4.80 (d, *J* = 9.6 Hz, 1H), 2.61-2.54 (m, 1H), 2.18 (t, *J* = 5.7 Hz, 2H), 1.80 (m, 2H), 1.72-1.59 (m, 4H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 147.7, 142.8, 141.0, 127.0, 127.0, 125.0, 120.1, 119.7, 46.9, 37.3, 29.5, 28.8, 28.8, 27.0 ppm. MS-EI: *m/z* (%) 260 (M⁺, 35), 178 (100), 165 (30).

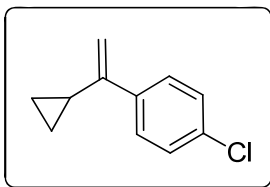


(Z)-9-(Prop-1-en-1-yl)-9H-fluorene (5j): Synthesized according to **Method C**. [91% yield] Colorless oil after column chromatography (SiO₂, *n*-pentane). ¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, *J* = 7.5 Hz, 2H), 7.43 (d, *J* = 7.4 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 2H), 5.87 (dq, *J* = 10.7, 6.8 Hz, 1H), 5.27-5.19 (m, 1H), 4.91 (d, *J* = 9.7 Hz, 1H), 2.05 (dd, *J* = 6.8, 1.8 Hz, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 147.1, 141.1, 129.5, 127.2, 127.1, 126.6, 124.9, 119.8, 46.5, 13.5 ppm. HRMS (APCI+, *m/z*): calcd for C₁₆H₁₅ [M+H]⁺: 207.11683; found: 207.11648.

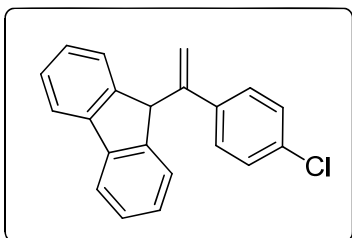
²¹ Z.-Q. Liu, Y. Zhang, L. Zhao, Z. Li, J. Wang, H. Li, L.-M. Wu, *Org. Lett.* **2011**, *13*, 2208.



1-Chloro-4-(3-methylpent-1-en-2-yl)benzene (5k): Synthesized according to **Method A**. [94% yield] Colorless oil after column chromatography (SiO₂, *n*-pentane). ¹H NMR (400 MHz, CDCl₃) δ 7.28 (s, 4H), 5.18 (d, *J* = 0.7 Hz, 1H), 5.04 (s, 1H), 2.63-2.52 (m, 1H), 1.61-1.47 (m, 1H), 1.39-1.30 (m, 1H), 1.11 (d, *J* = 6.8 Hz, 3H), 0.88 (t, *J* = 7.4 Hz, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 153.4, 141.5, 132.8, 128.2, 128.0, 111.6, 39.4, 28.5, 19.3, 11.5 ppm. HRMS (APCI+, *m/z*): calcd for C₁₂H₁₆Cl [M+H]⁺: 195.09350; found: 195.09324.

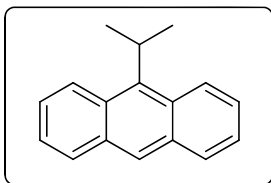


1-Chloro-4-(1-cyclopropylvinyl)benzene (5l): Synthesized according to **Method A**. [73% yield] Colorless oil after column chromatography (SiO₂, *n*-pentane). ¹H NMR (400 MHz, CDCl₃) δ 7.53 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 5.27 (s, 1H), 4.96 (s, 1H), 1.66-1.57 (m, 1H), 0.89-0.81 (m, 2H), 0.61-0.56 (m, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 148.2, 140.0, 133.2, 128.2, 127.4, 109.6, 15.5, 6.6 ppm. MS-EI: *m/z* (%) 178 (M⁺, 45), 143 (100), 128 (90), 115 (40).

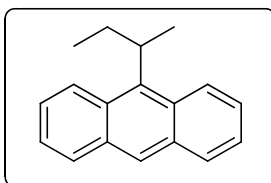


9-(1-(4-Chlorophenyl)vinyl)-9H-fluorene (5m): Synthesized according to **Method C**. [85% yield] white solid after column chromatography (SiO₂, *n*-pentane), m.p = 120-121 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.78 (d, *J* = 7.0 Hz, 2H), 7.40-7.36 (m, 4H), 7.26-7.25 (m, 2H), 7.06 (d, *J* = 8.5 Hz, 2H), 6.92 (d, *J* = 8.5 Hz, 2H), 5.50 (s, 1H), 5.42 (s, 1H), 4.98 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 146.7, 145.7, 141.0, 138.6, 133.2, 128.2, 128.0, 127.4, 127.2, 124.8, 120.1, 117.3, 55.0 ppm. HRMS (APCI+, *m/z*): calcd for C₂₁H₁₆Cl [M+H]⁺: 303.09350; found: 303.09326.

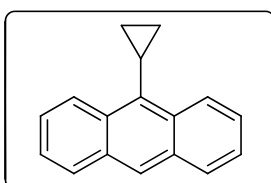
Spectral data of compounds 7a-7h:



9-Isopropylantracene (7a): Synthesized according to **Method F**. [97% yield, 97:3 branched:linear] Colorless solid after column chromatography (SiO₂, *n*-pentane). ¹H NMR (400 MHz, CDCl₃) δ 8.63-8.44 (m, 2H), 8.36 (s, 1H), 8.04 (dd, *J* = 7.9, 1.9 Hz, 2H), 7.59-7.44 (m, 4H), 4.62 (septet, *J* = 7.3 Hz, 1H), 1.80 (d, *J* = 7.3 Hz, 6H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 140.5, 129.6, 129.4, 128.2, 126.4, 126.2, 125.4, 124.5, 28.3, 22.9 ppm. The physical data were identical in all respects to those previously reported.²²



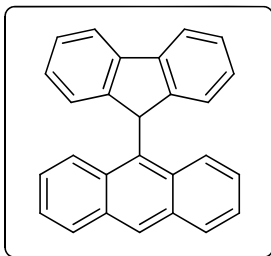
9-(sec-Butyl)anthracene (7b): Synthesized according to **Method F**. [88% yield, 91:9 branched:linear, 3% dehalogenation] Colorless solid after column chromatography (SiO₂, *n*-pentane). ¹H NMR (400 MHz, CDCl₃) δ 8.54 (brs, 1H), 8.46 (s, 1H), 8.40 (s, 1H), 8.05-8.03 (m, 2H), 7.52-7.45 (m, 4H), 4.33 (sextet, *J* = 7.4 Hz, 1H), 2.44-2.16 (m, 1H), 1.77 (d, *J* = 7.3 Hz, 6H), 0.93 (t, *J* = 7.4 Hz, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 139.6, 131.7, 129.2, 128.2, 126.4, 126.2, 125.4, 124.5, 35.9, 30.4, 21.1, 13.6 ppm. HRMS (APCI+, *m/z*): calcd for C₁₈H₁₉ [M+H]⁺: 235.14813; found: 235.14768.



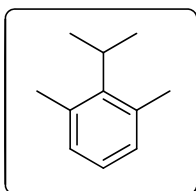
9-Cyclopropylantracene (7c): Synthesized according to **Method F**. [87% yield] Colorless solid after column chromatography (SiO₂, *n*-pentane). ¹H NMR (400 MHz, CDCl₃) δ 8.79 (d, *J* = 8.7 Hz, 2H), 8.38 (s, 1H), 8.02 (d, *J* = 8.2 Hz, 2H), 7.54 (dd, *J* = 8.1, 7.0 Hz, 2H), 7.51-7.46 (m, 2H), 2.57-2.46 (m, 1H), 1.51-1.44 (m, 2H), 0.89-0.82 (m, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 134.7, 131.7, 131.5, 128.9, 126.4, 126.0, 125.0, 124.8, 10.5, 9.3 ppm. The physical data were identical in all respects to those previously reported.²³

²² H. Cho, R. G. Harvey, P. W. Rabideau, *J. Am. Chem. Soc.* **1975**, 97, 1140.

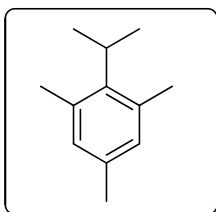
²³ N. L. Bauld, J. D. McDermed, C. E. Hudson, Y. S. Rim, J. Zoeller Jr., R. D. Gordon, J. S. Hyde, *J. Am. Chem. Soc.* **1969**, 91, 6666.



9-(9H-Fluoren-9-yl)anthracene (7d): Synthesized according to **Method F**. [59% yield] Yellow solid after column chromatography (SiO₂, *n*-pentane). ¹H NMR (400 MHz, CDCl₃) δ 8.71 (d, *J* = 8.9 Hz, 1H), 8.49 (s, 1H), 8.15 (d, *J* = 8.3 Hz, 1H), 8.02 (d, *J* = 7.5 Hz, 2H), 7.93 (d, *J* = 8.5 Hz, 1H), 7.68-7.62 (m, 1H), 7.61-7.56 (m, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.27-7.21 (m, 1H), 7.19 (t, *J* = 7.4 Hz, 2H), 7.09 (d, *J* = 7.5 Hz, 2H), 6.90-6.82 (m, 1H), 6.71 (d, *J* = 9.0 Hz, 1H), 6.54 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 149.0, 140.2, 132.3, 132.0, 131.8, 131.6, 129.7, 129.5, 128.8, 127.8, 127.1, 126.5, 125.7, 124.8, 124.5, 123.9, 120.5, 48.9 ppm. The physical data were identical in all respects to those previously reported.²⁴



2-Isopropyl-1,3-dimethylbenzene (7e): Synthesized according to **Method F**. [82% yield, 97:3 branched:linear, 8% dehalogenation] Colorless oil after column chromatography (SiO₂, *n*-pentane). ¹H NMR (400 MHz, CDCl₃) δ 7.01 (s, 3H), 3.48 (septet, *J* = 7.3 Hz, 1H), 2.42 (s, 6H), 1.37 (d, *J* = 7.3 Hz, 6H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 144.1, 136.0, 128.2, 125.4, 29.5, 21.5, 20.8 ppm. The physical data were identical in all respects to those previously reported.²⁵

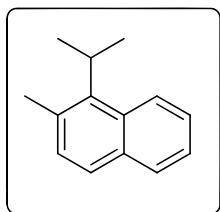


2-Isopropyl-1,3,5-trimethylbenzene (7f): Synthesized according to **Method F**. [85% yield, 96:4 branched:linear, 25% dehalogenation] Colorless oil after column chromatography (SiO₂, *n*-pentane). ¹H NMR (400 MHz, CDCl₃) δ 6.85 (s, 2H), 3.45 (septet, *J* = 7.2 Hz, 1H), 2.40 (s, 6H), 2.28 (s, 3H), 1.36 (d, *J* = 7.3 Hz, 6H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 141.0, 136.0, 134.8, 129.0, 29.2, 23.7, 21.4, 20.6 ppm. The physical data were identical in all respects to those previously reported.²⁶

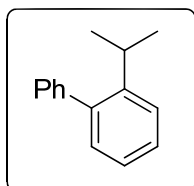
²⁴ J. Wang, W. Wan, H. Jiang, Y. Gao, X. Jiang, H. Lin, W. Zhao, J. Hao, *Org. Lett.* **2010**, 12, 3874.

²⁵ W. W. Schloman Jr., H. Morrison *J. Am. Chem. Soc.* **1977**, 99, 3342.

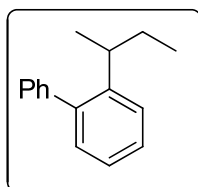
²⁶ J. W. Timberlake, D. Pan, J. Murray, B. S. Jursic, T. Chen, *J. Chem. Org.* **1995**, 60, 5295.



1-Isopropyl-2-methylnaphthalene (7g): (The reaction was carried out on commercially available mixture of isomers 95/5). Synthesized according to **Method F**. [90% yield, 98:2 branched:linear, 8% other isomer] Colorless oil after column chromatography (SiO₂, *n*-pentane). ¹H NMR (400 MHz, CDCl₃, 55 °C) δ 8.31 (d, *J* = 8.6 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.45-7.40 (m, 2H), 7.31 (d, *J* = 8.3 Hz, 1H), 4.05-3.88 (m, 1H), 2.60 (s, 3H), 1.62 (d, *J* = 7.3 Hz, 6H) ppm. ¹³C NMR (100 MHz, CDCl₃, 55 °C) δ 140.8, 133.6, 132.4, 131.9, 129.9, 128.8, 126.2, 124.9, 124.1, 21.8, 21.5 ppm. The physical data were identical in all respects to those previously reported.²⁷



2-Isopropyl-1,1'-biphenyl (7h): Synthesized according to **Method F**. [96% yield, 99:1 branched:linear, 3% homocoupling] Colorless oil after column chromatography (SiO₂, *n*-pentane). ¹H NMR (400 MHz, CDCl₃) δ 7.49-7.44 (m, 3H), 7.41 (d, *J* = 7.2 Hz, 2H), 7.38-7.35 (m, 2H), 7.28-7.22 (m, 2H), 3.13 (septet, *J* = 6.9 Hz, 1H), 1.23 (d, *J* = 6.9 Hz, 6H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 146.4, 142.1, 141.1, 130.0, 129.4, 128.0, 127.7, 126.7, 125.6, 125.3, 29.4, 24.3 ppm. The physical data were identical in all respects to those previously reported.²⁸

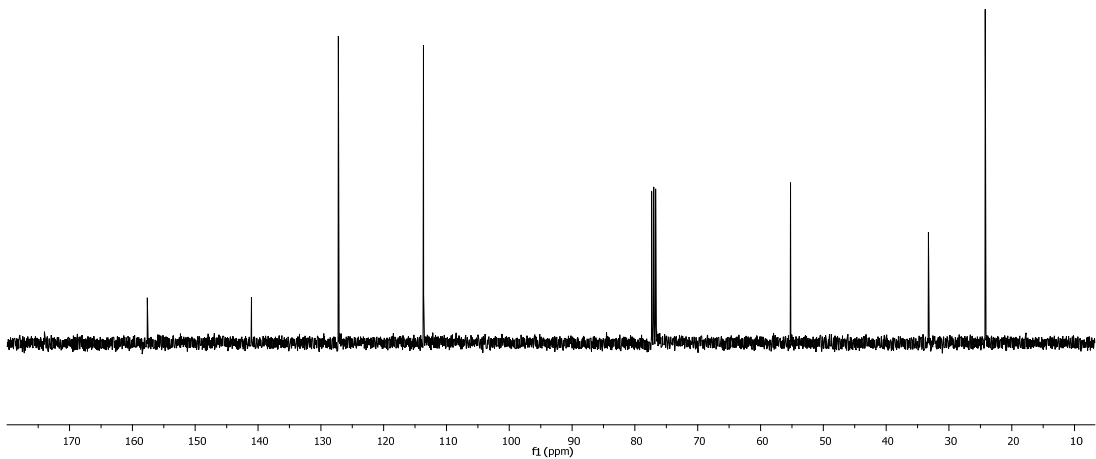
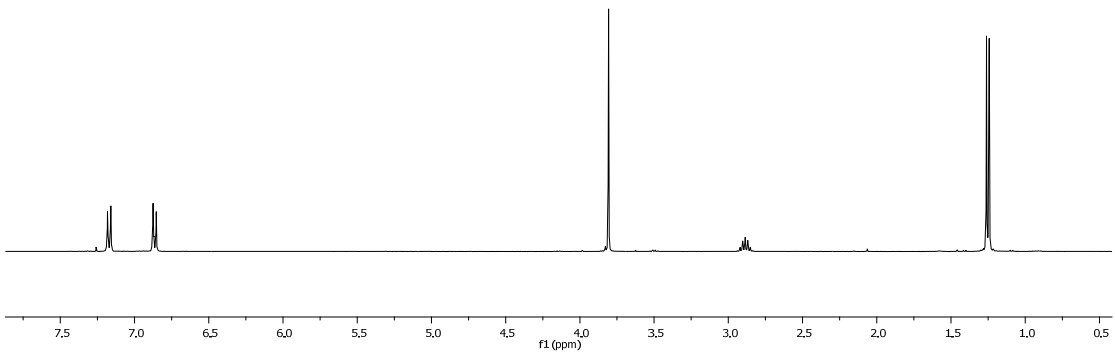
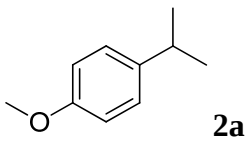


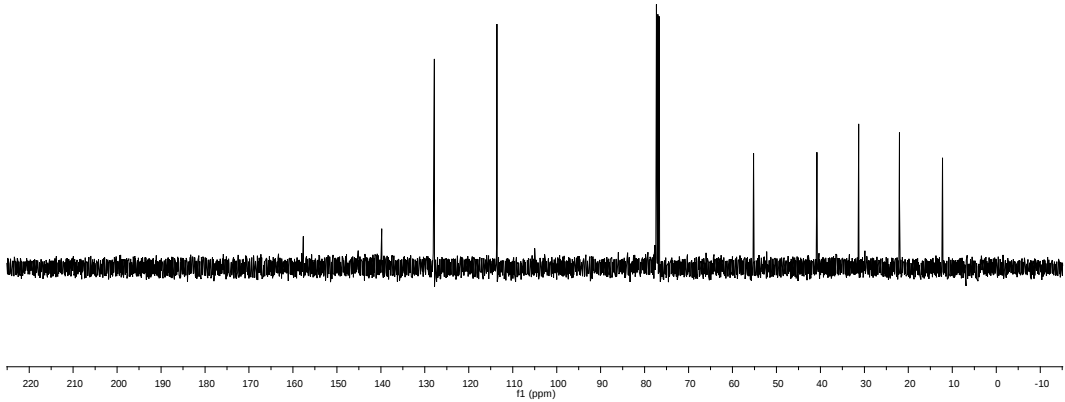
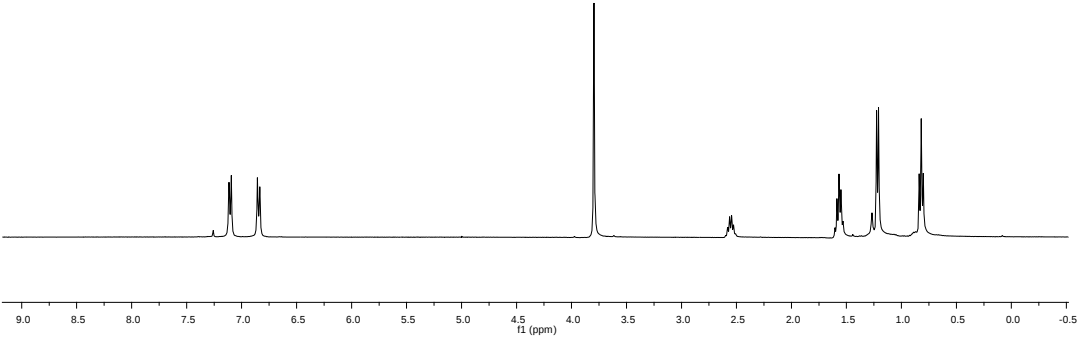
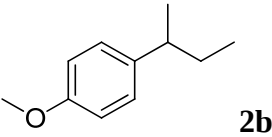
2-(sec-Butyl)-1,1'-biphenyl (7i): Synthesized according to **Method F**. [93% yield, 96:4 branched:linear, 5% homocoupling] Colorless oil after column chromatography (SiO₂, *n*-pentane). ¹H NMR (400 MHz, CDCl₃) δ 7.47-7.43 (m, 2H), 7.42-7.36 (m, 3H), 7.33 (d, *J* = 8.3 Hz, 2H), 7.29-7.21 (m, 2H), 2.91-2.74 (m, 1H), 1.74-1.47 (m, 2H), 1.21 (d, *J* = 6.9 Hz, 3H), 0.75 (t, *J* = 7.4 Hz, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 145.2, 142.3, 141.9, 129.8, 129.5, 127.9, 127.7, 126.6, 125.8, 125.2, 36.4, 31.2, 22.5, 12.3 ppm. HRMS (APCI+, *m/z*): calcd for C₁₆H₁₇ [M-H]⁺: 209.13248; found: 209.13209.

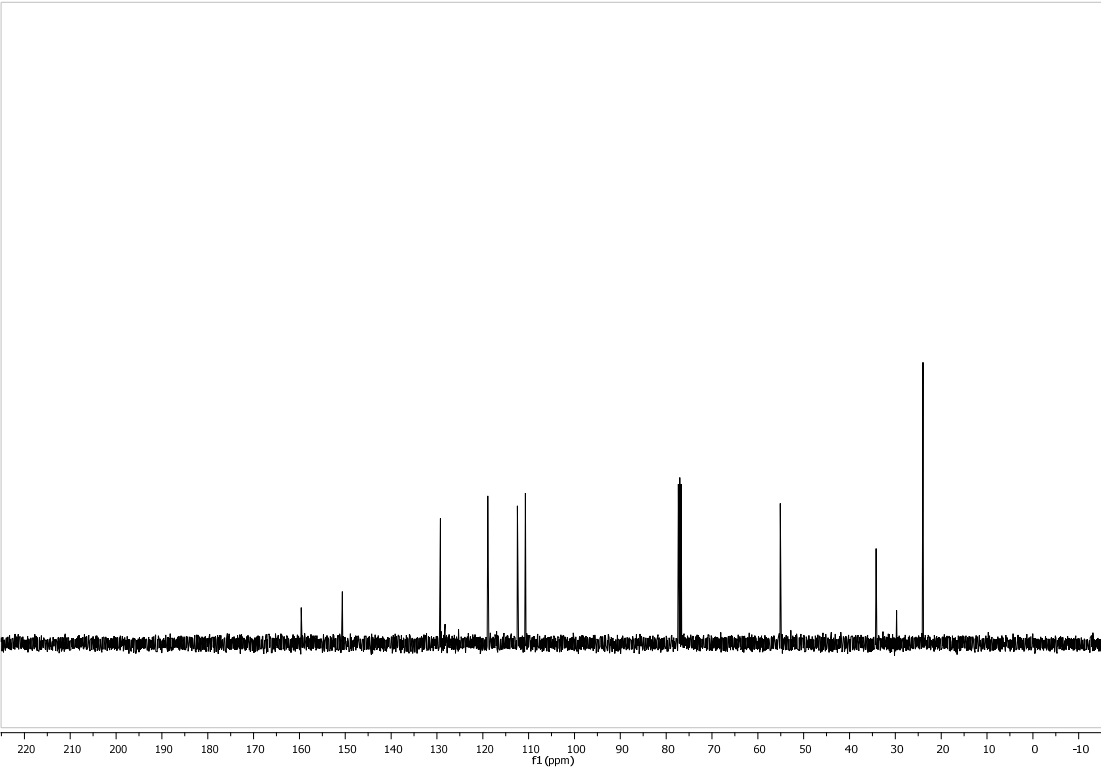
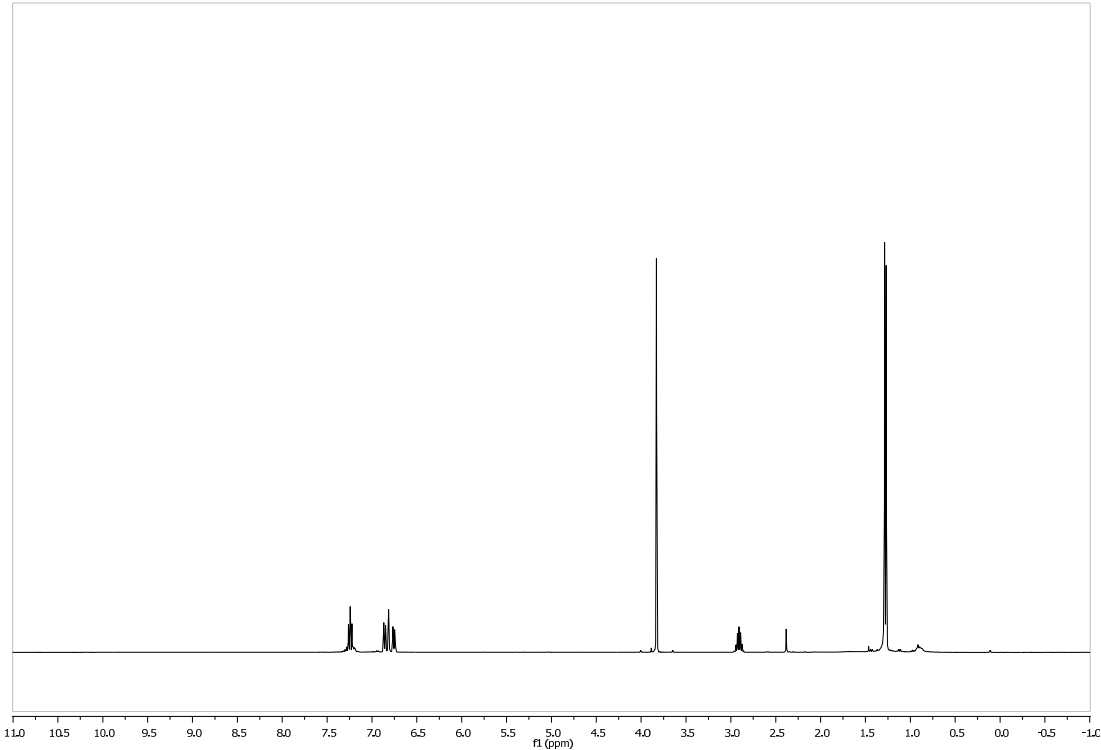
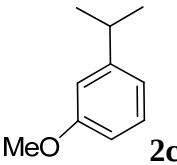
²⁷ D. P. Kelly, D. R. Leslie, B. D. Smith, *J. Am. Chem. Soc.* **1984**, 106, 687.

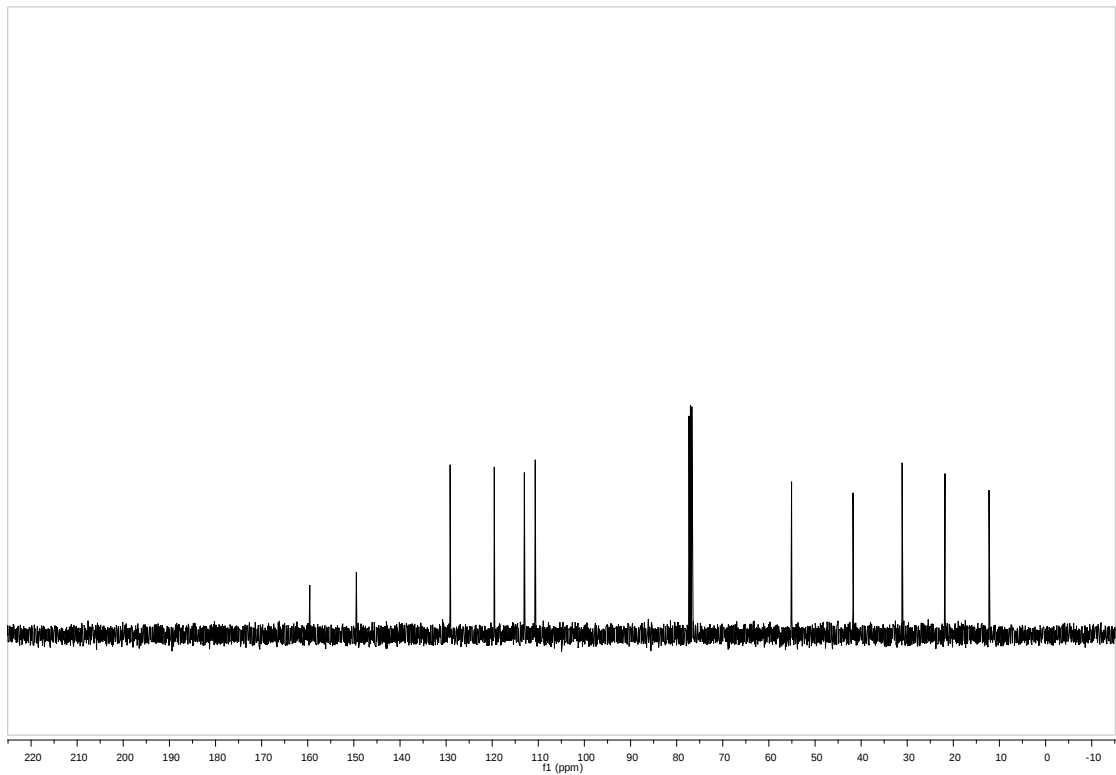
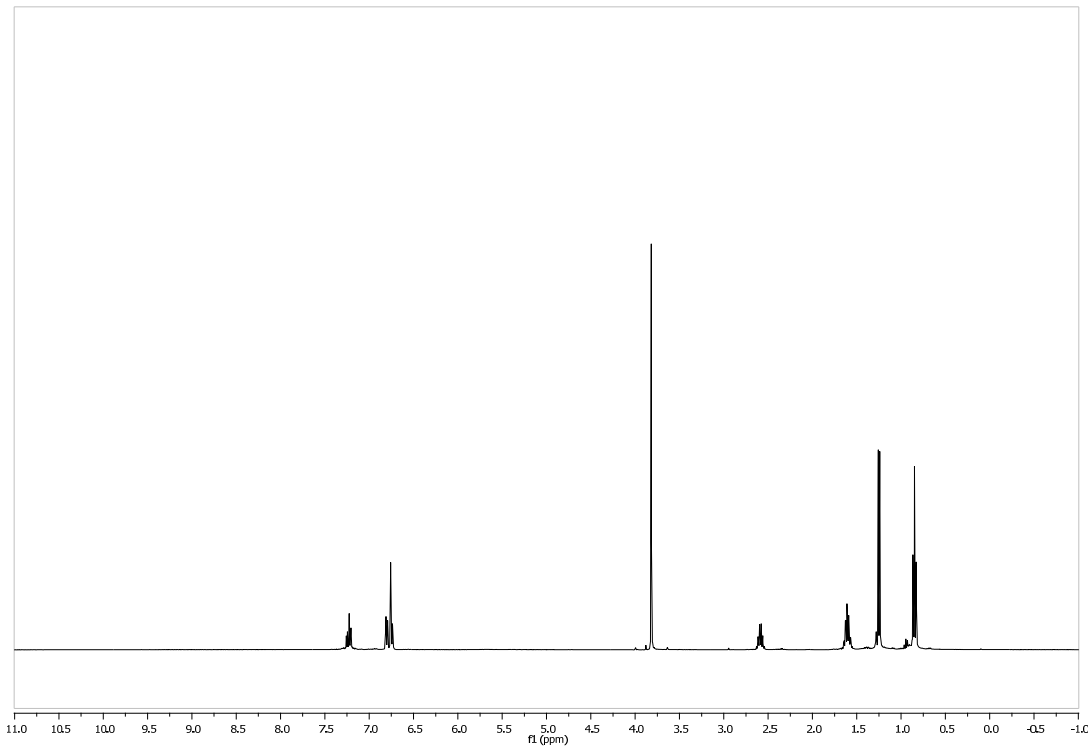
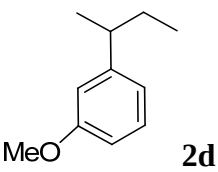
²⁸ Q. Liu, Y. Lan, J. Liu, G. Li, Y.-D. Wu, A. Lei, *J. Am. Chem. Soc.* **2009**, 131, 10201.

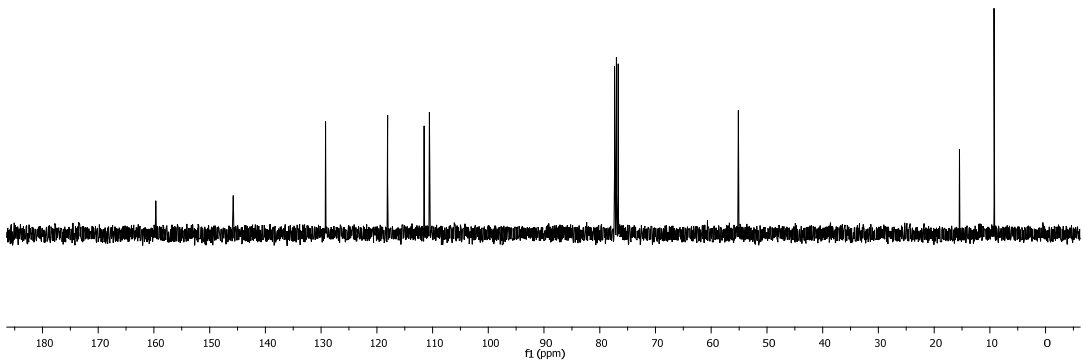
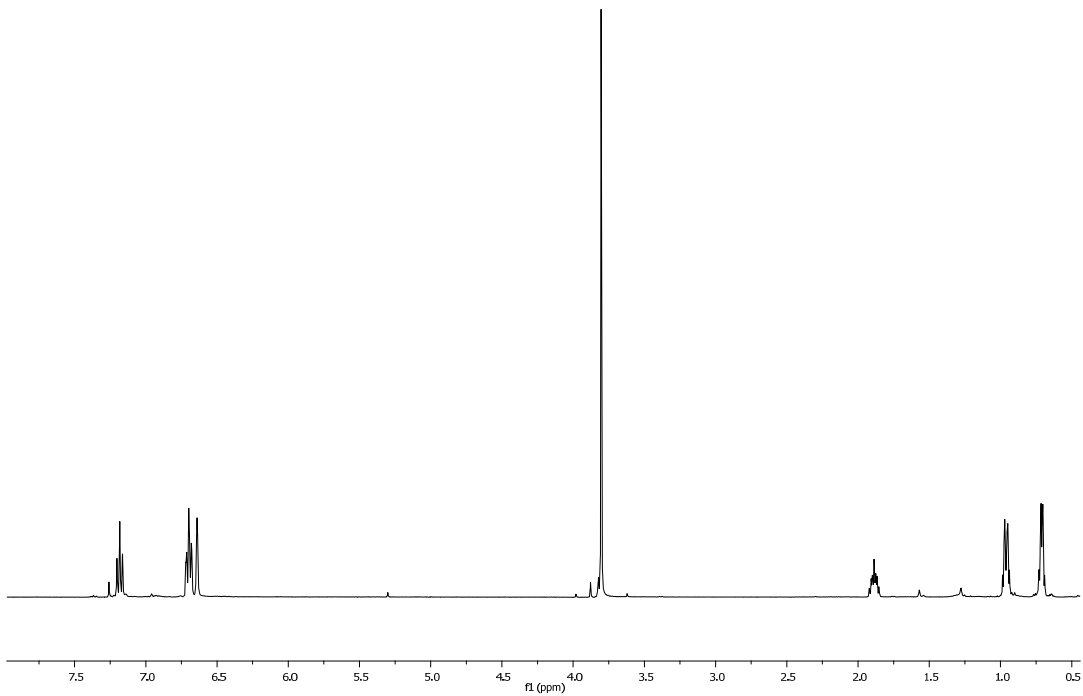
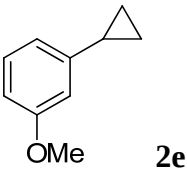
¹H and ¹³C NMR of isolated compounds

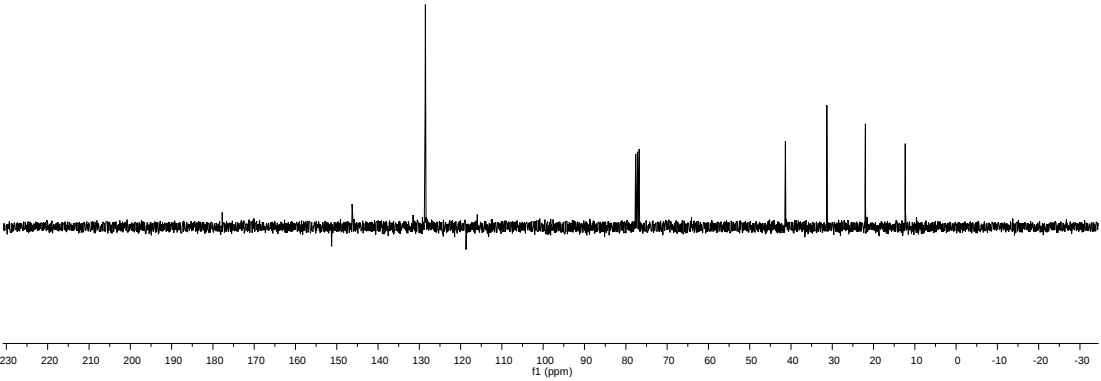
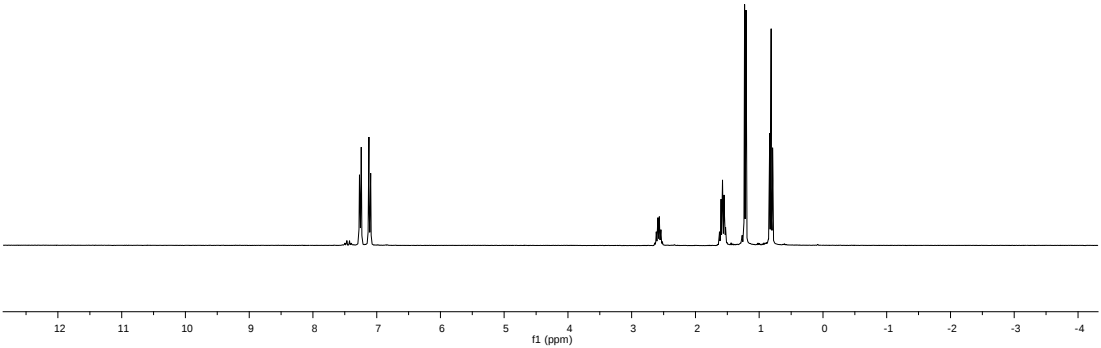
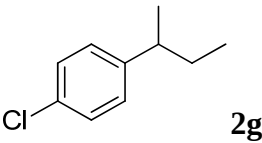


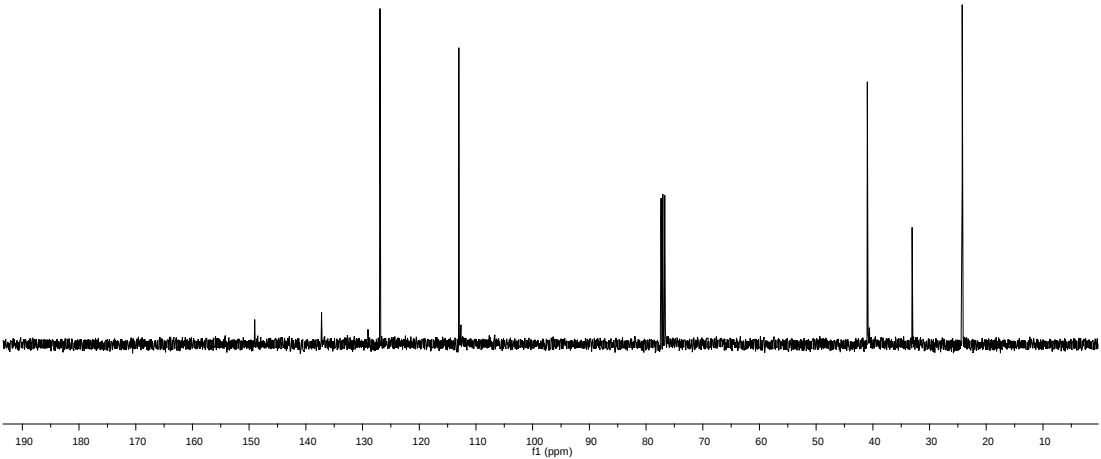
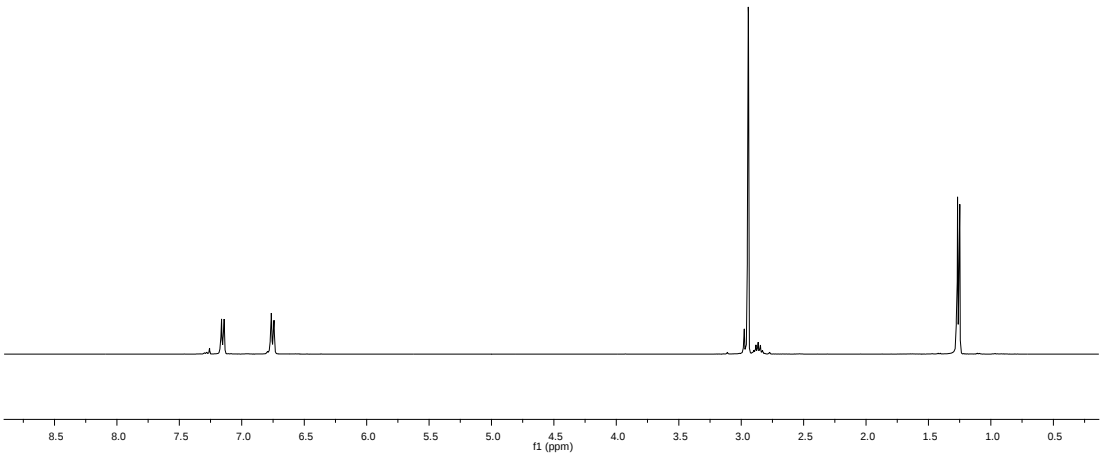
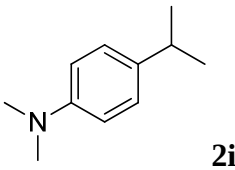


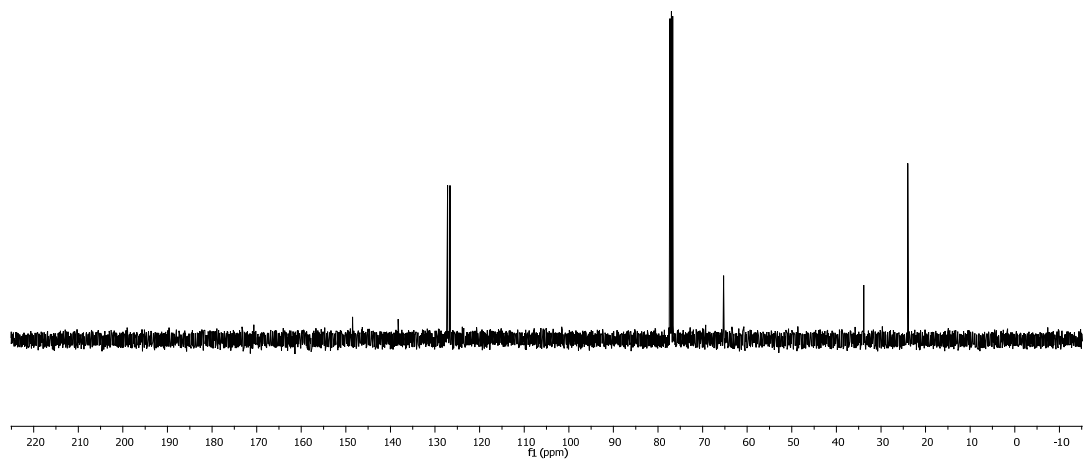
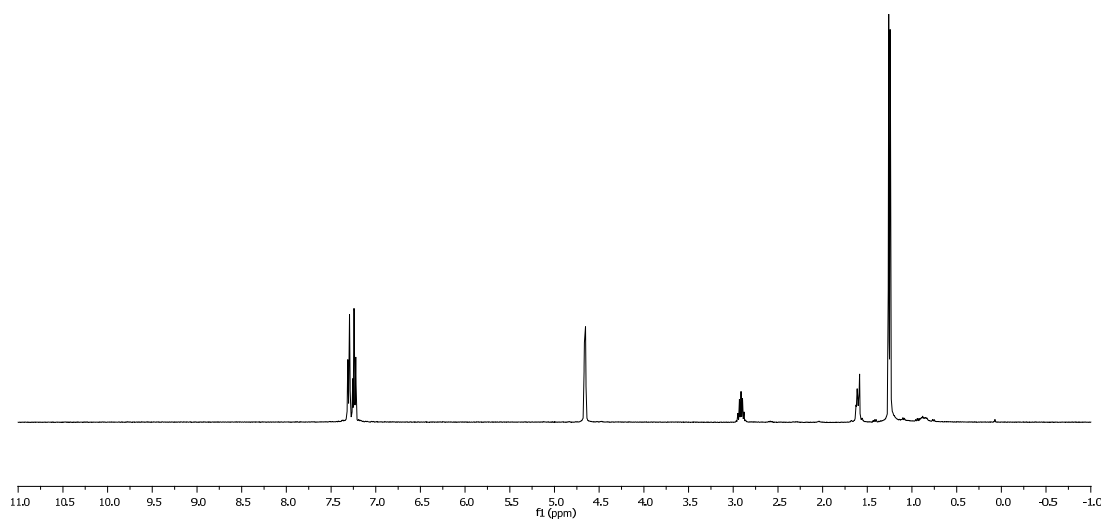
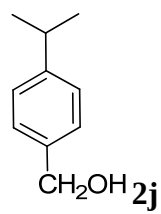


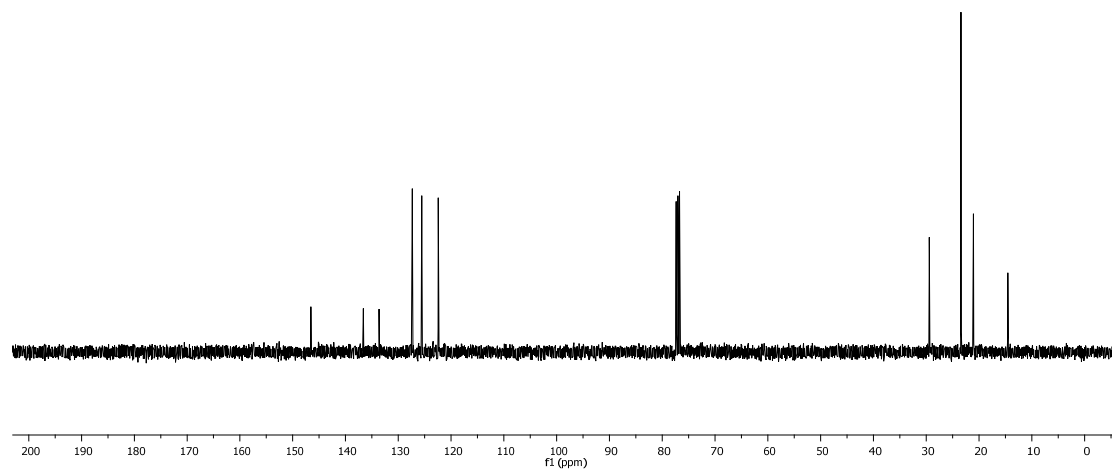
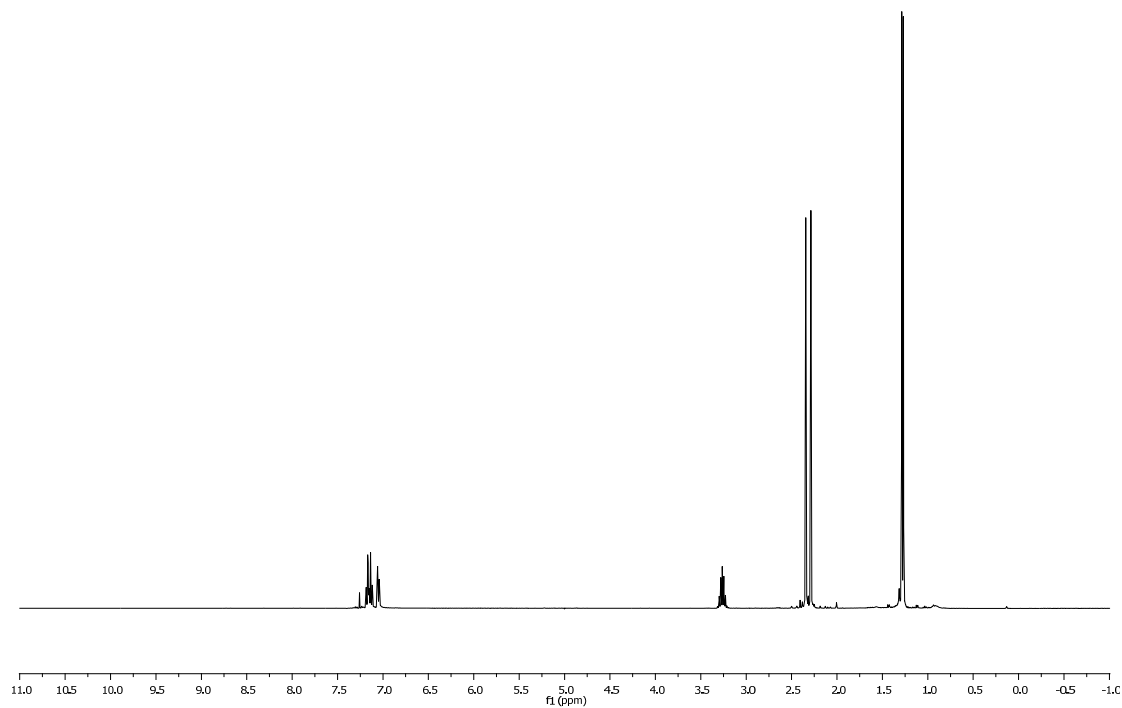
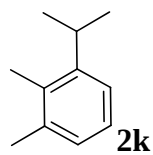


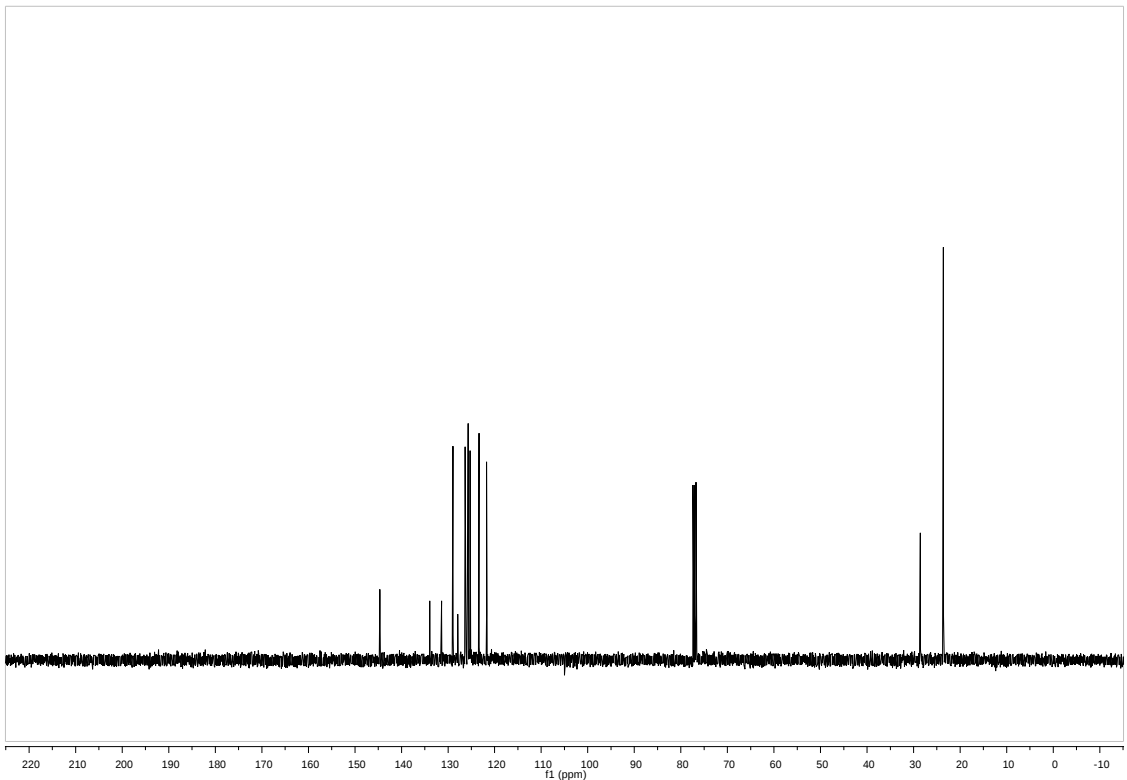
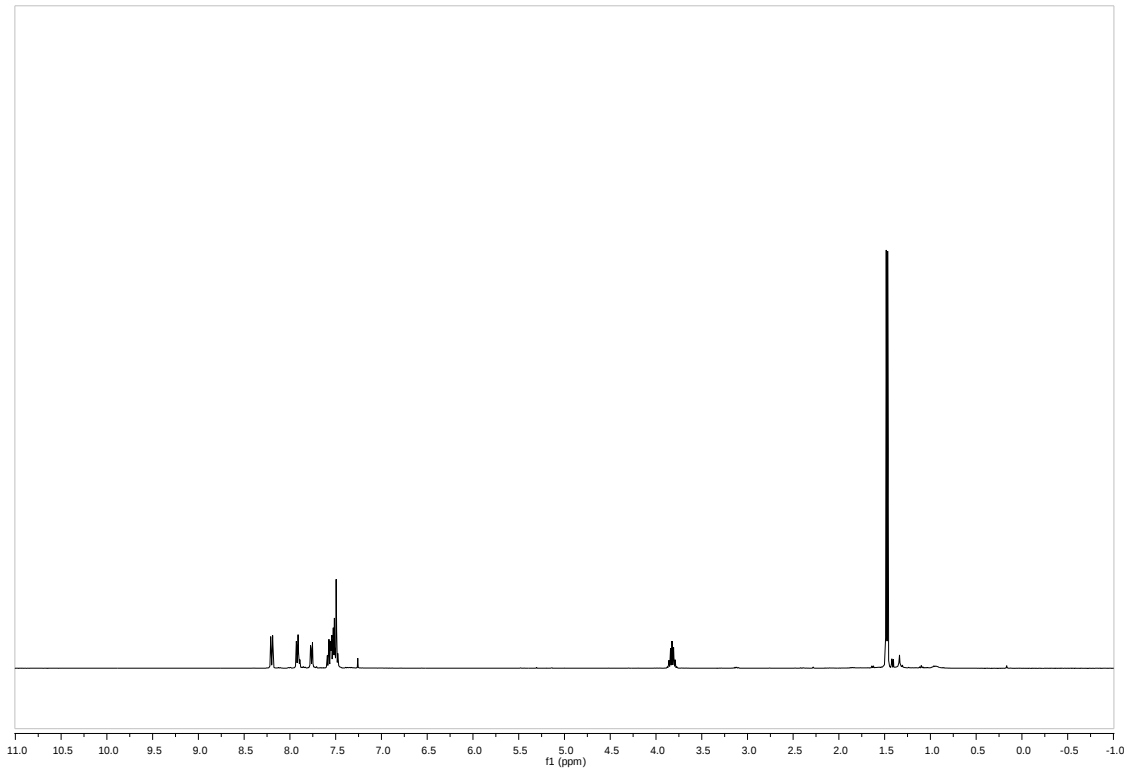
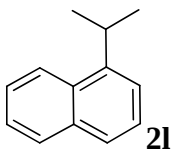


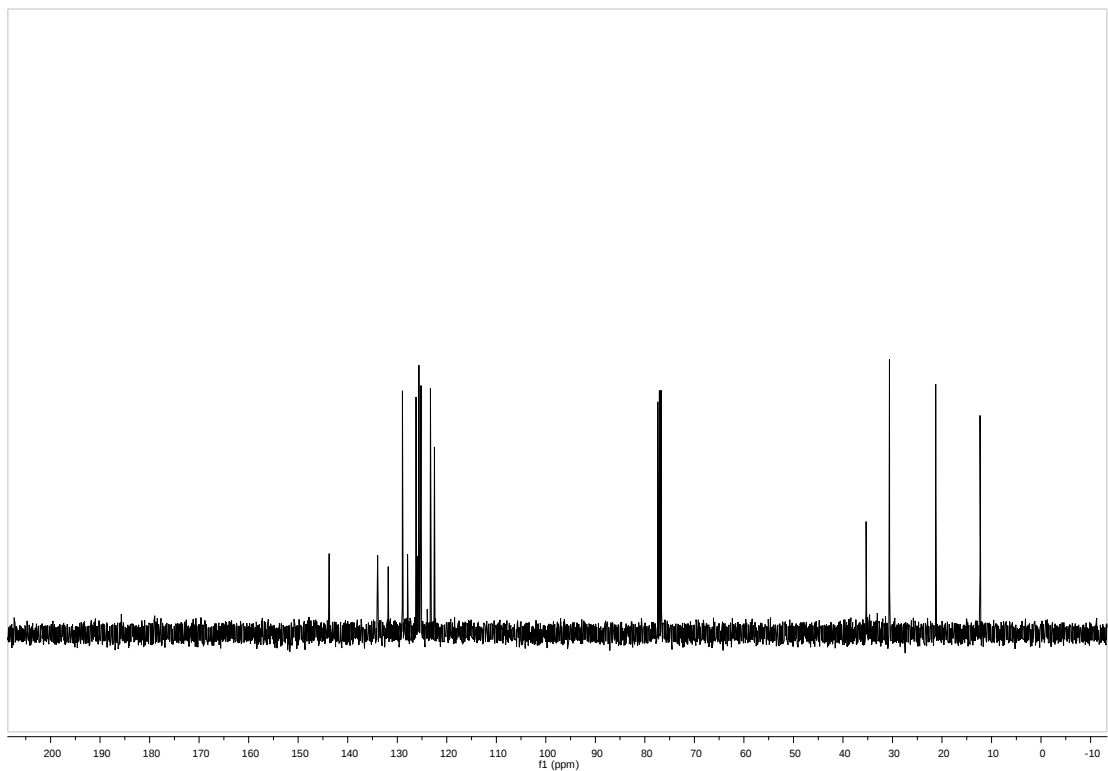
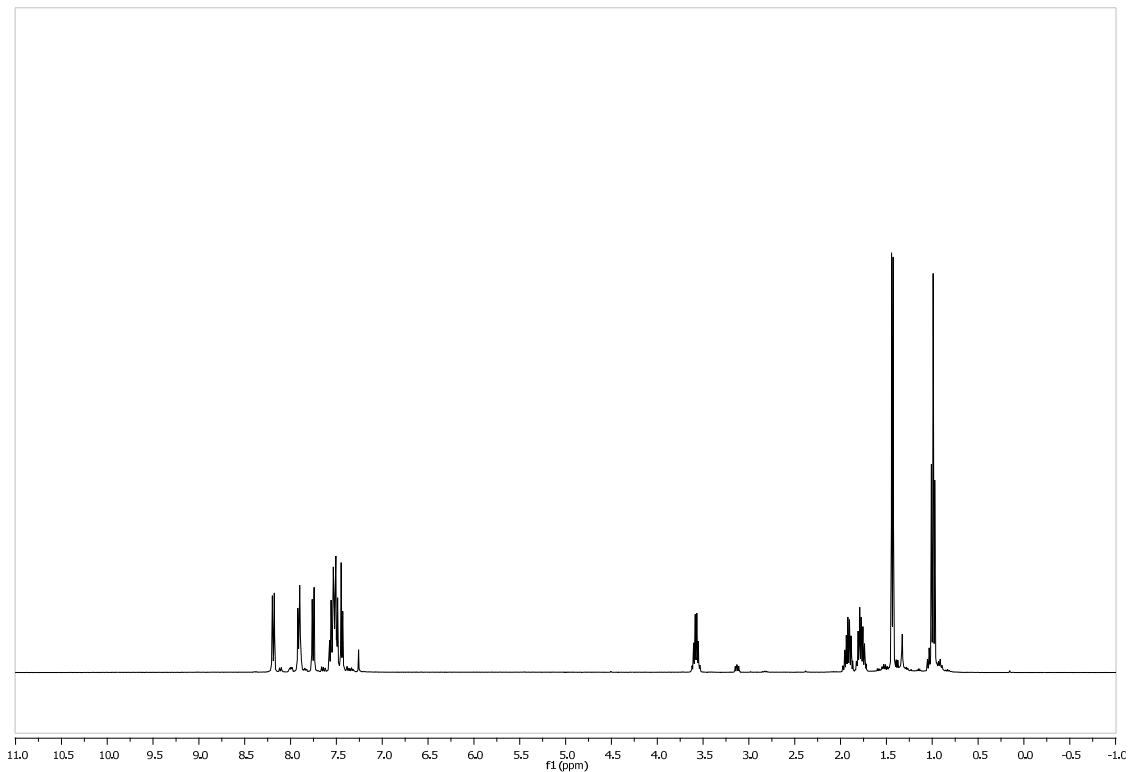
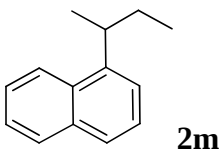


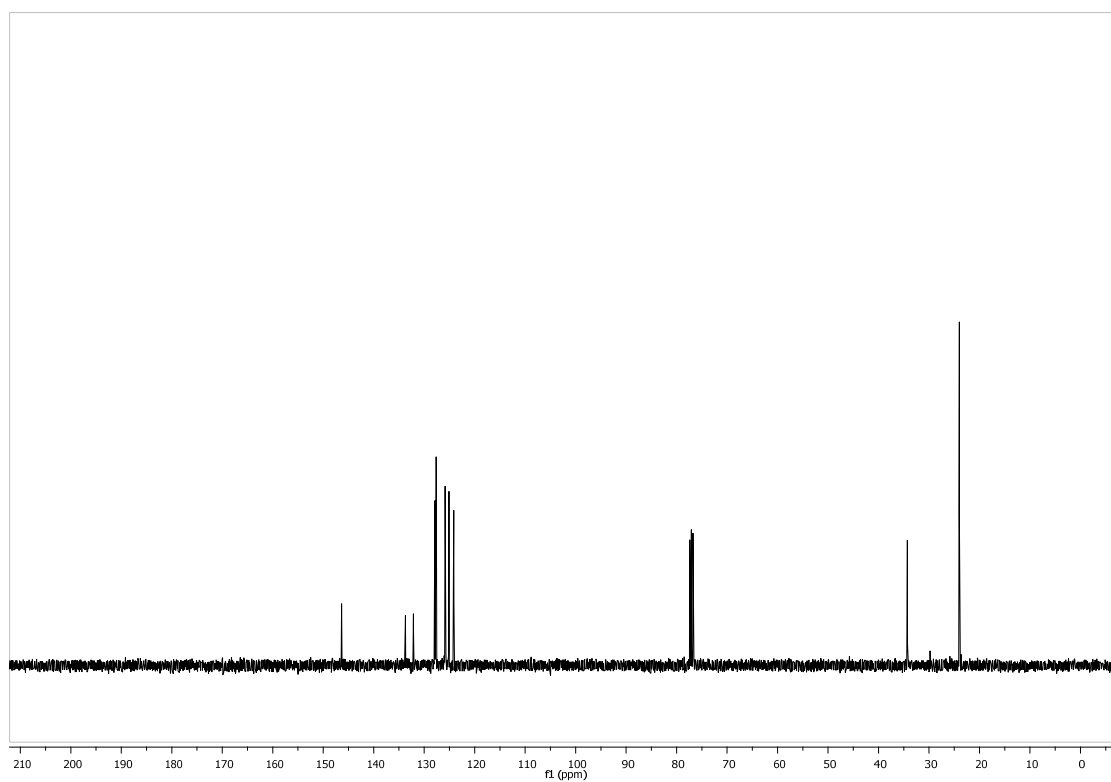
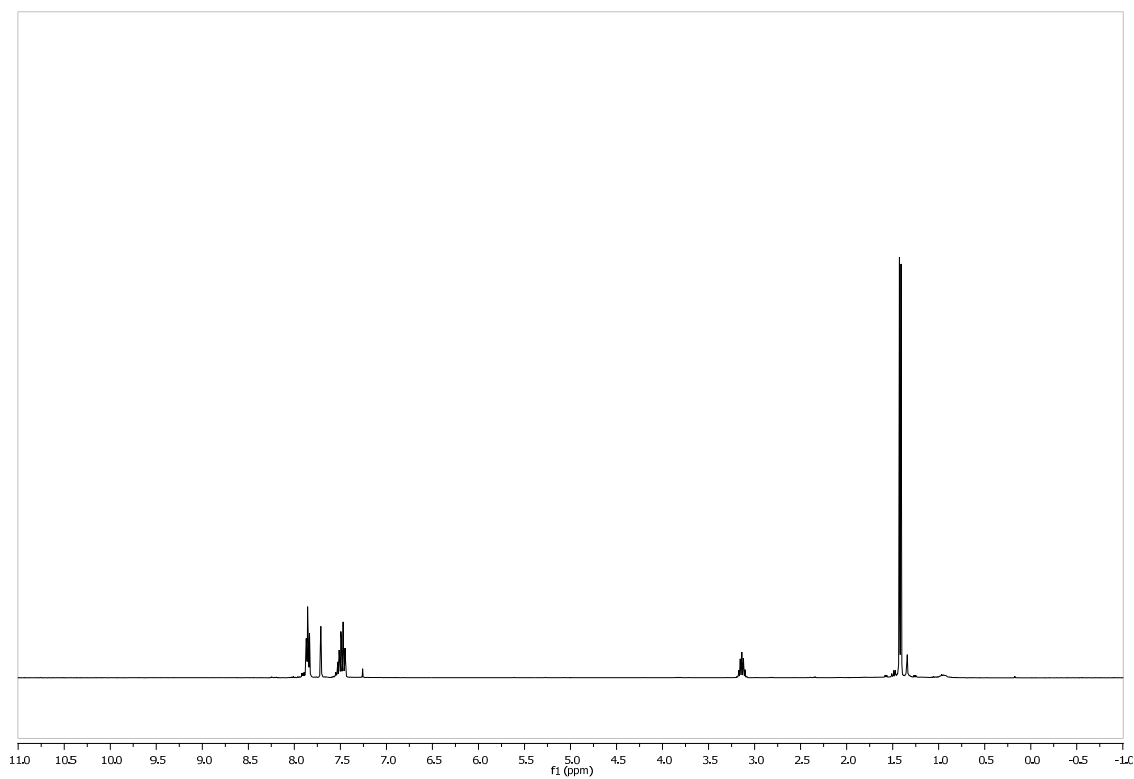
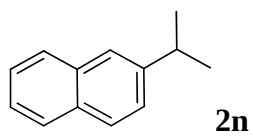


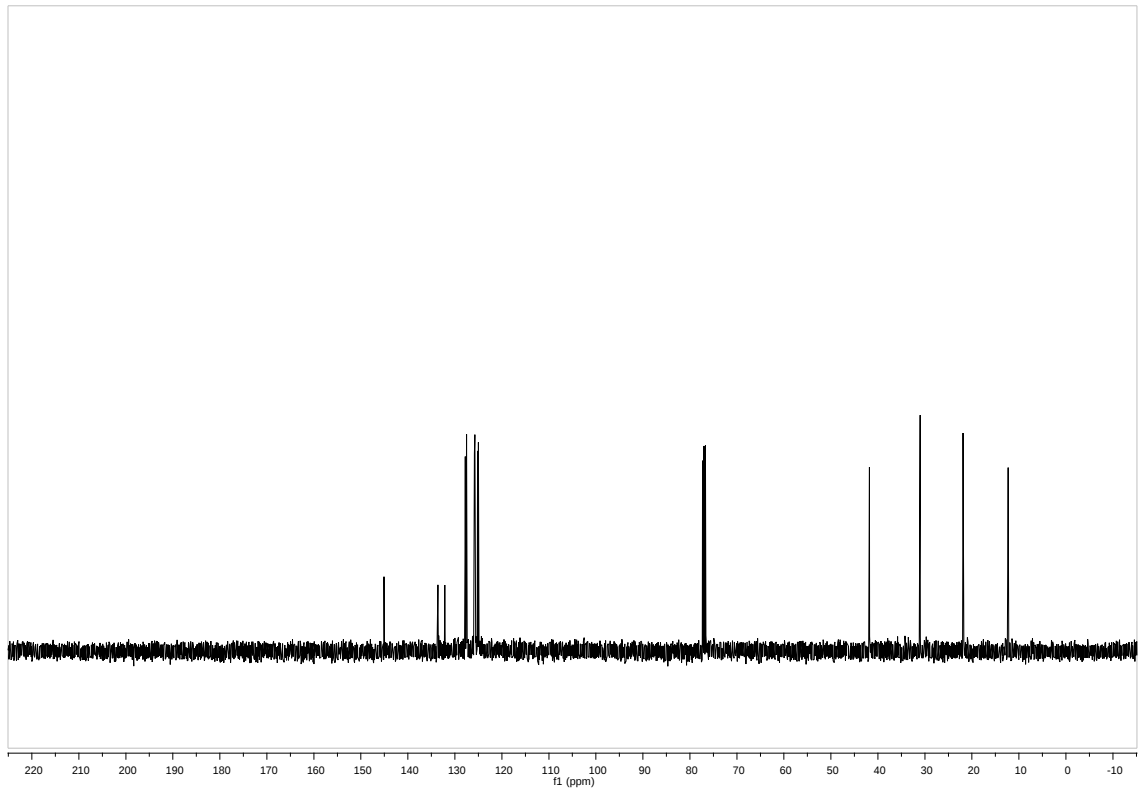
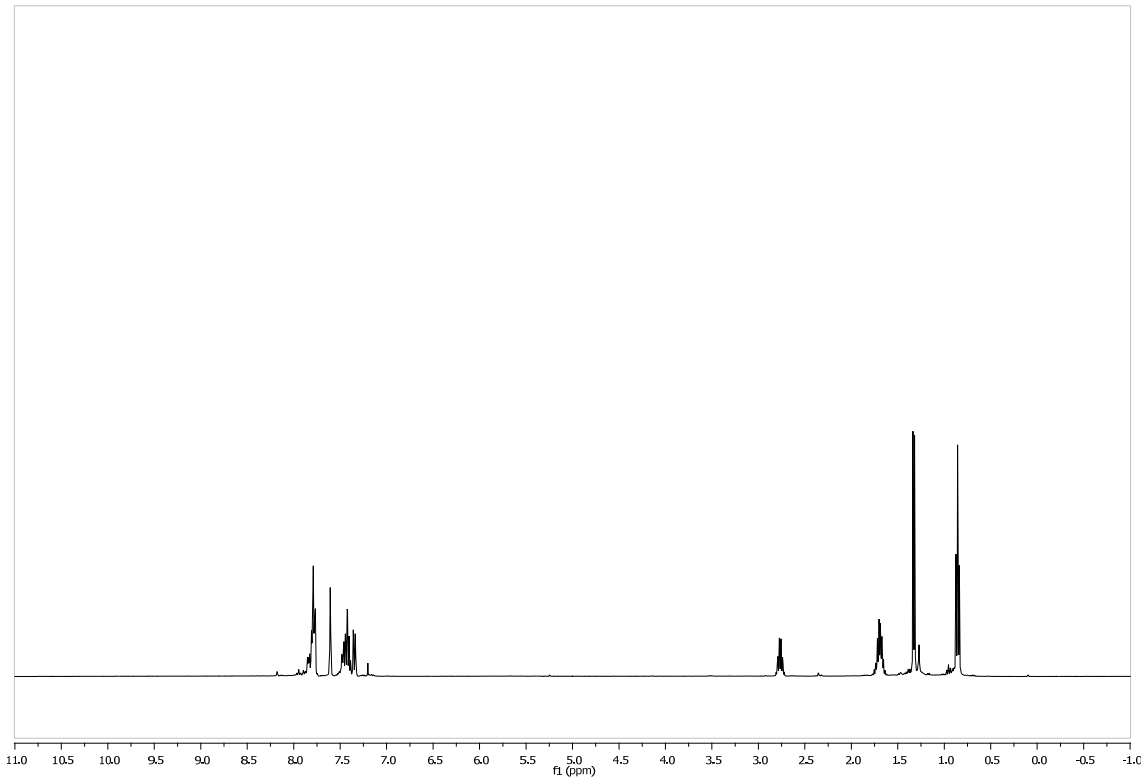
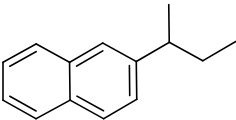


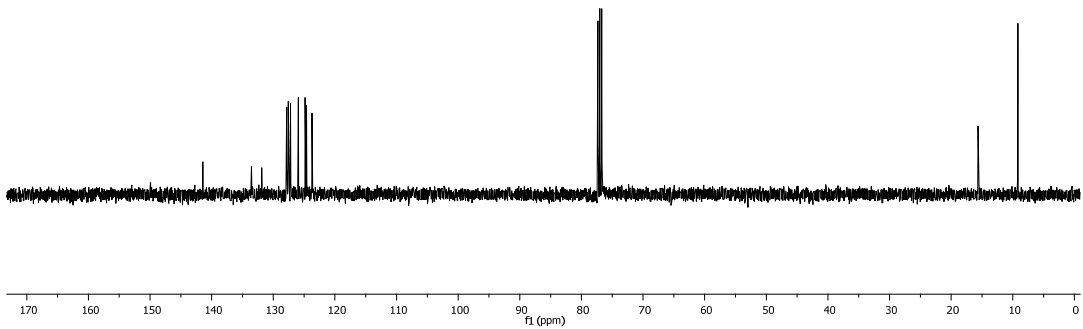
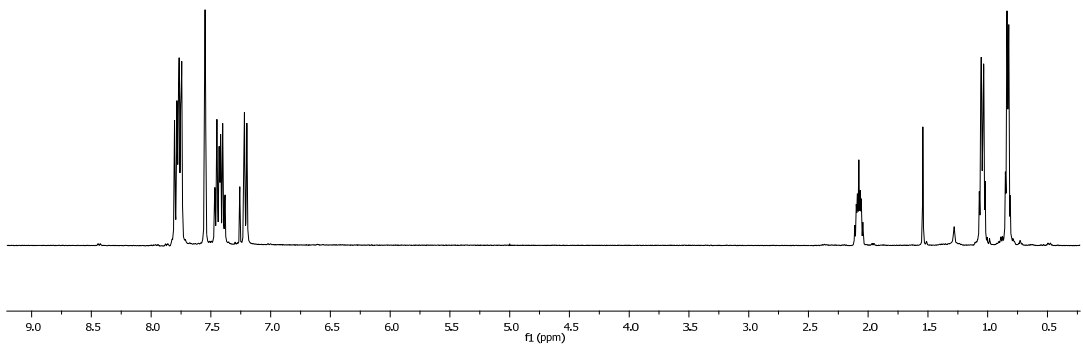
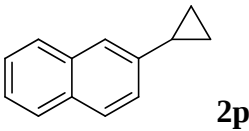


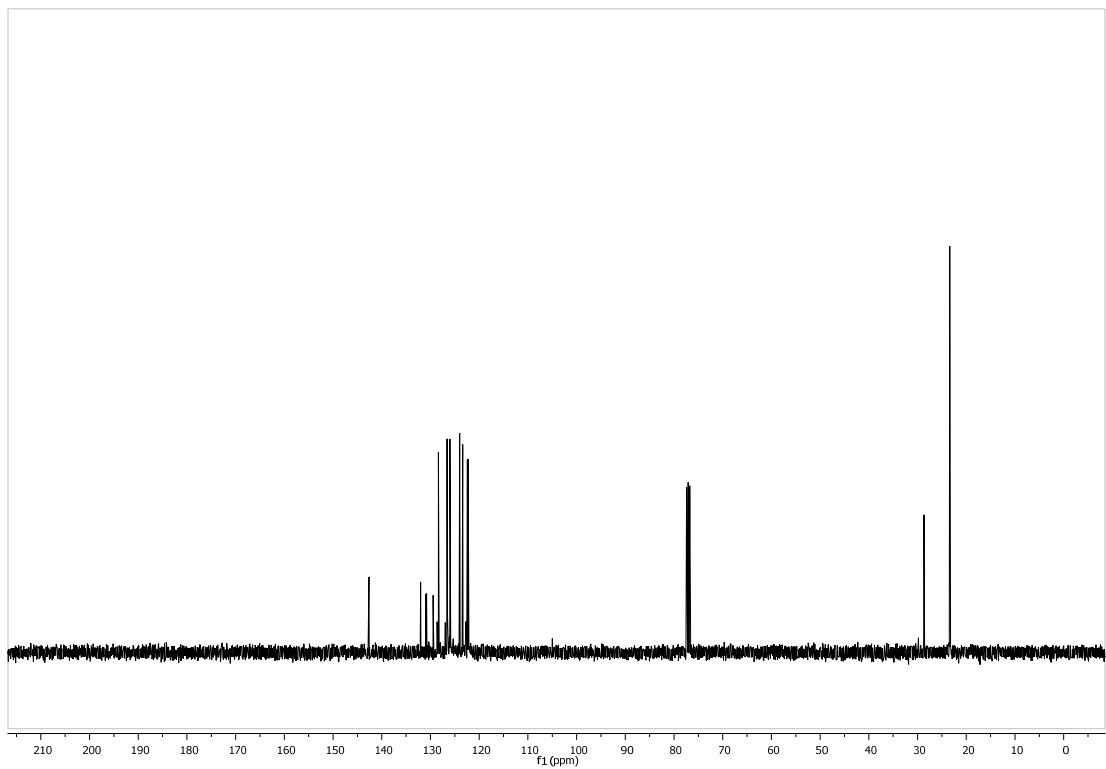
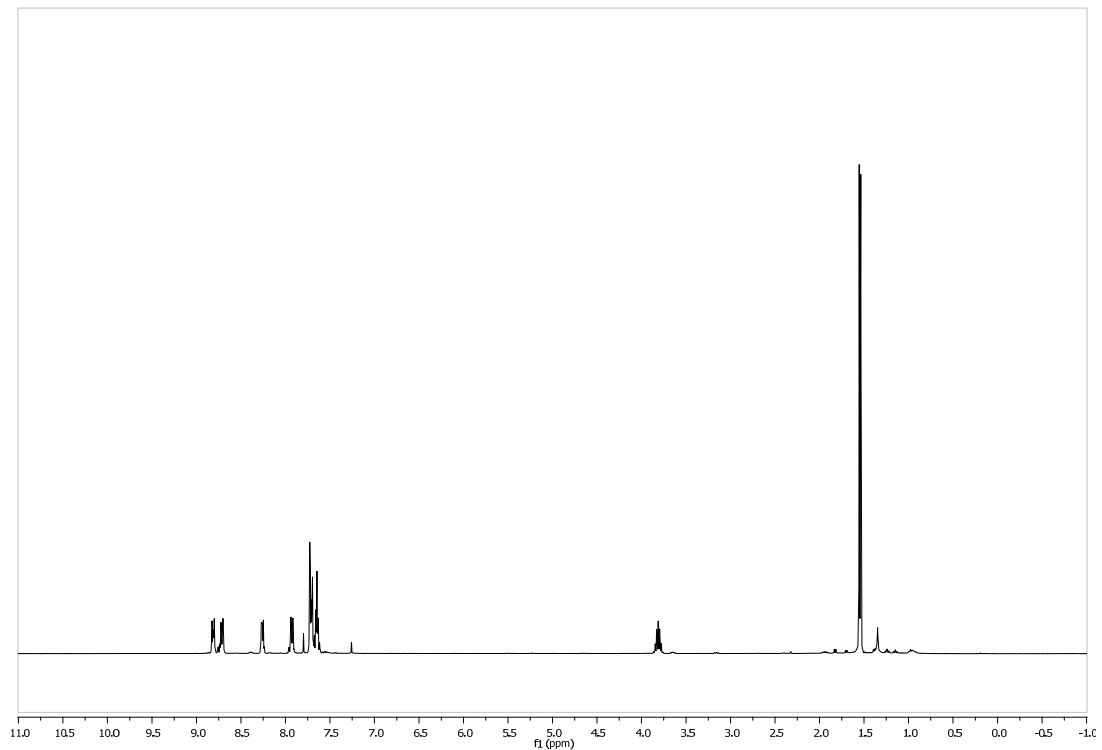
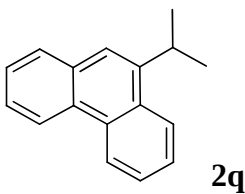


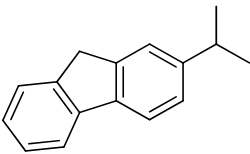




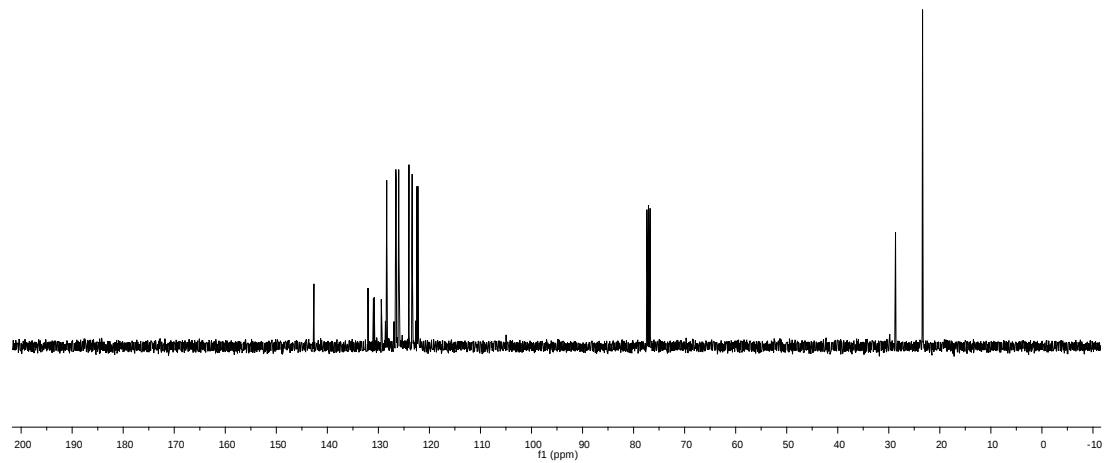
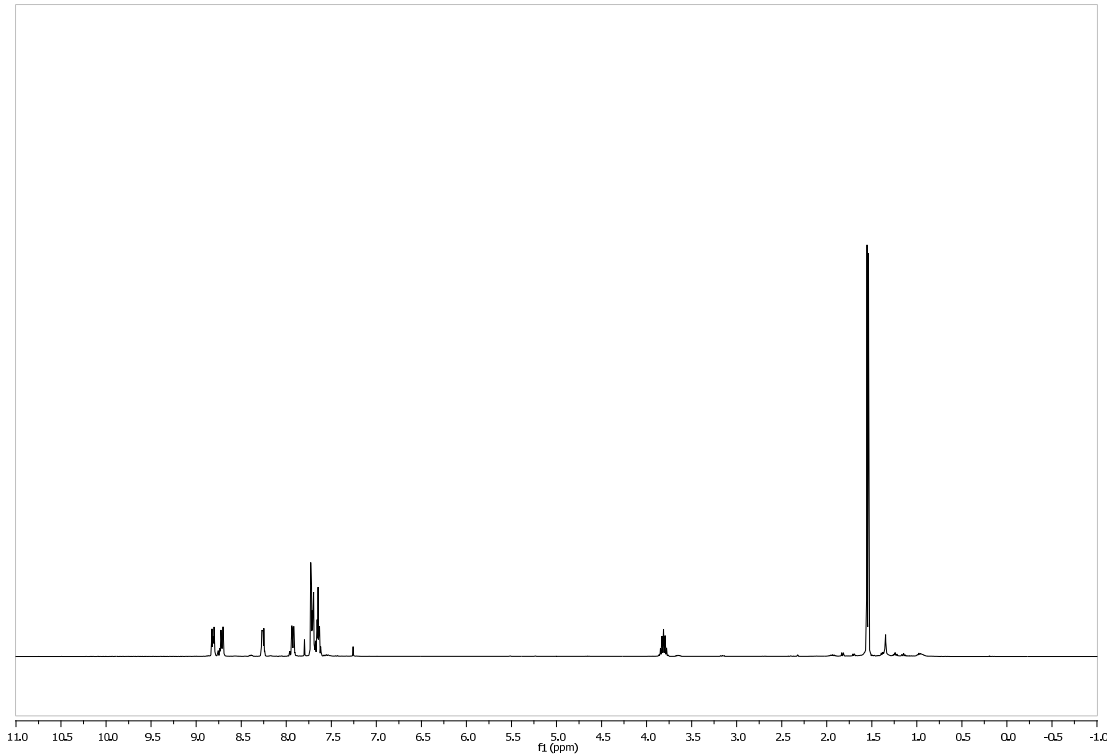


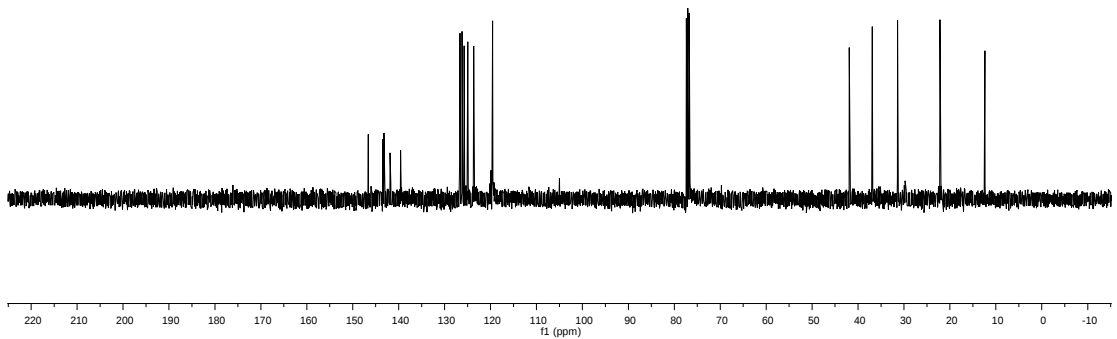
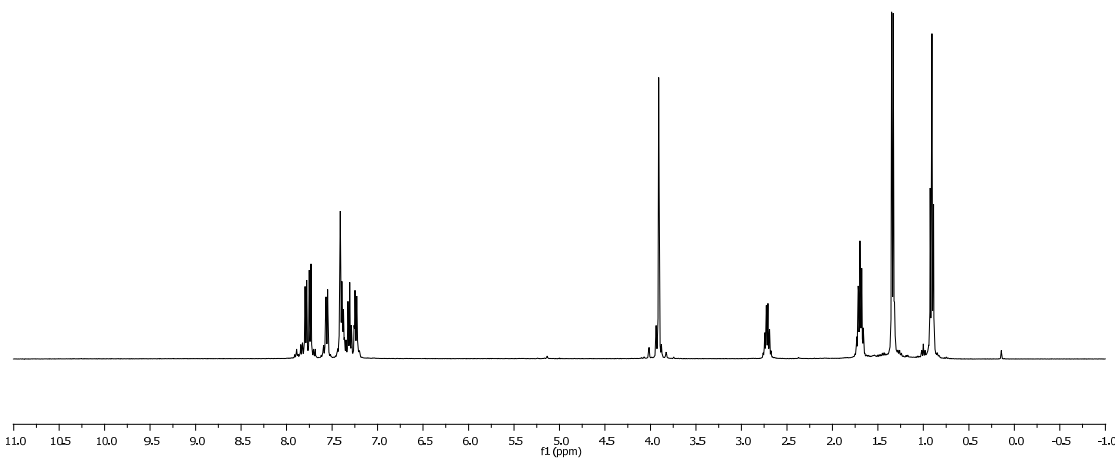
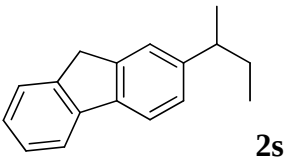


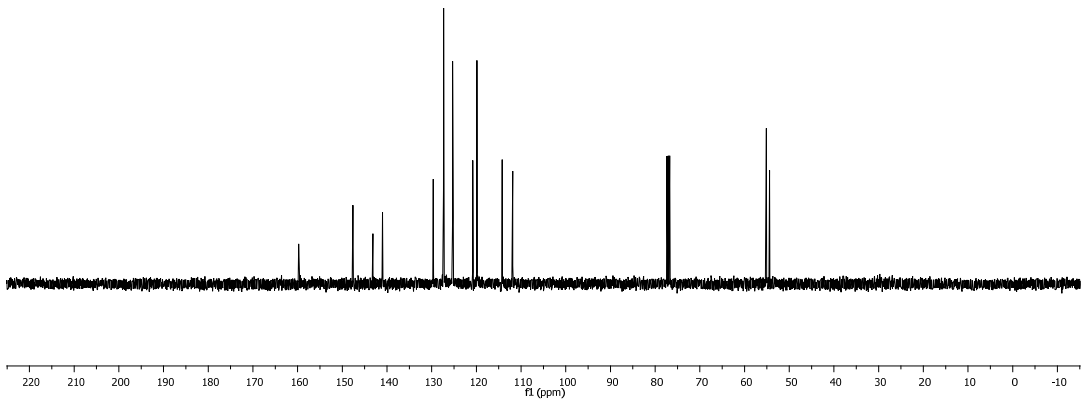
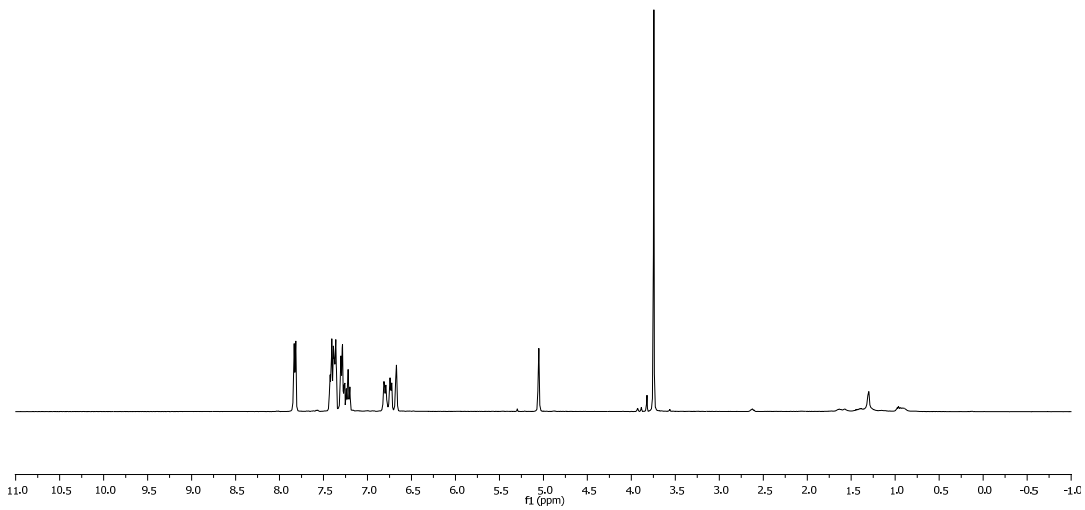
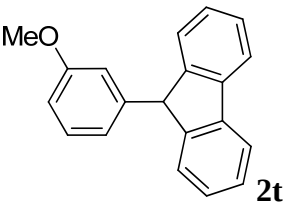


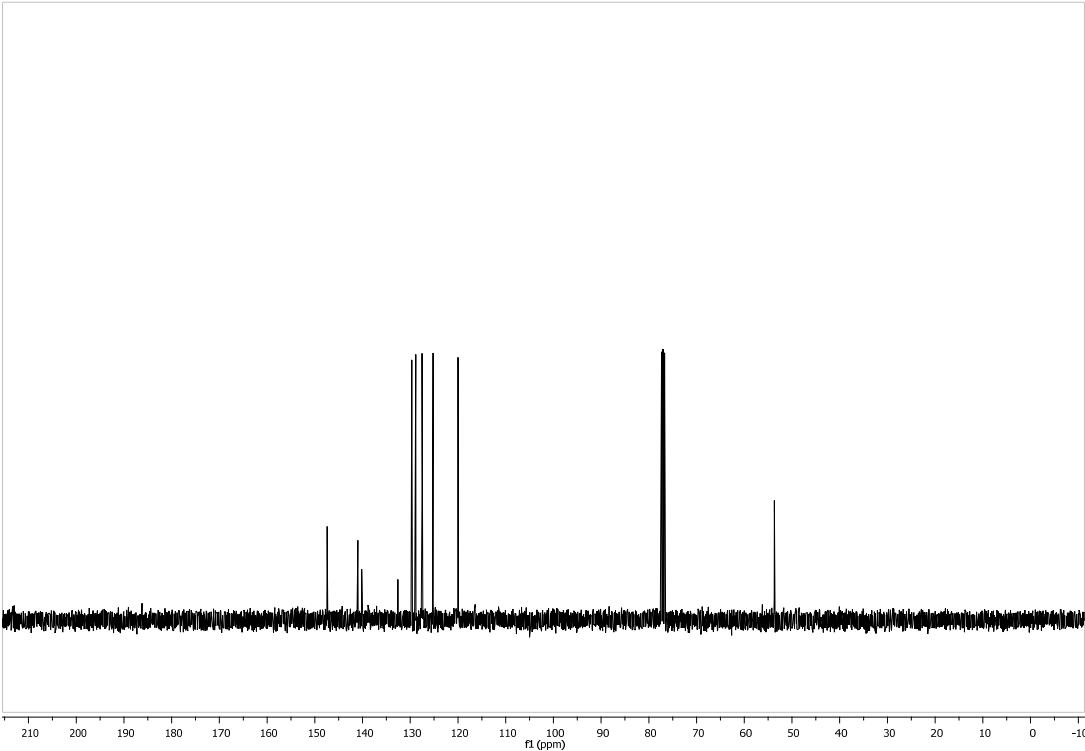
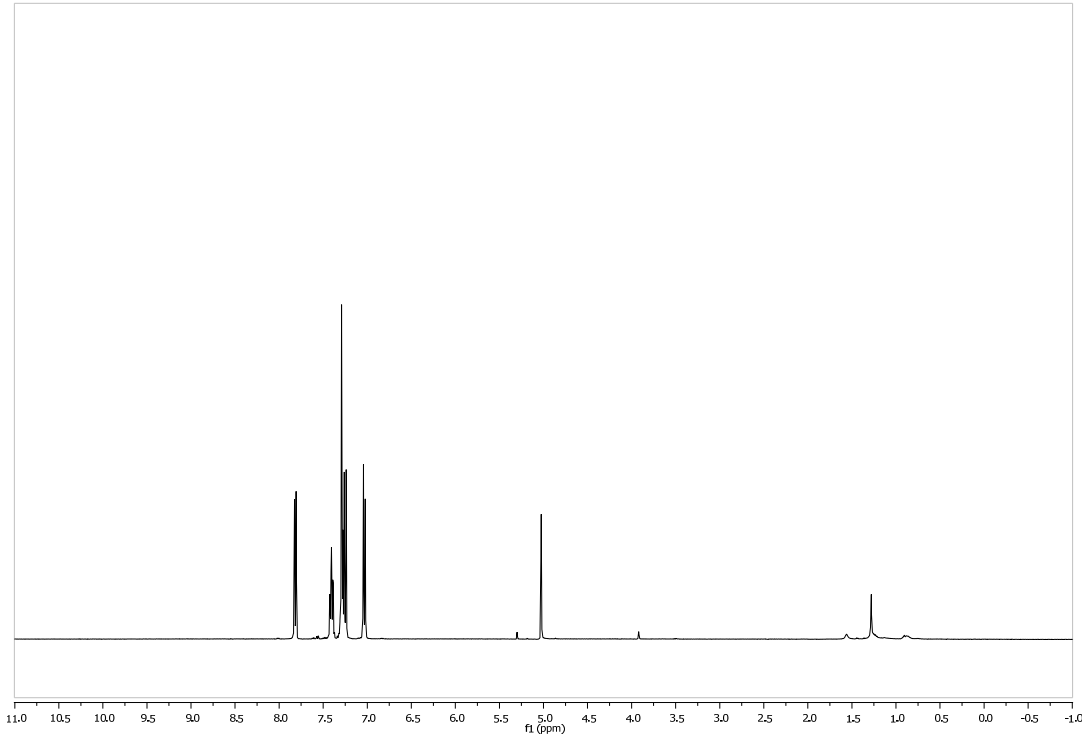
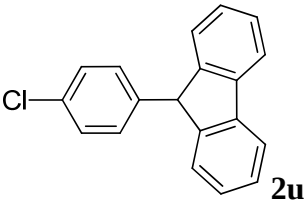


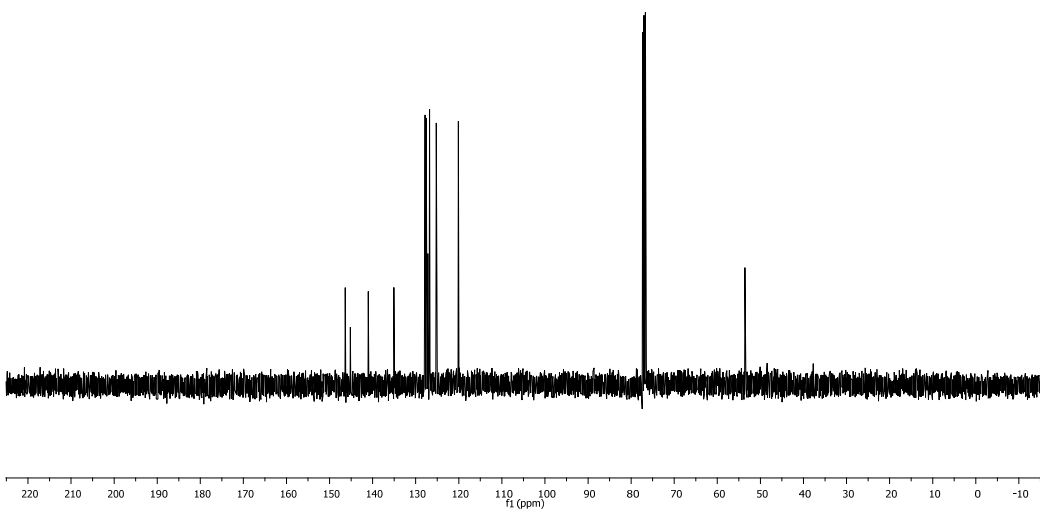
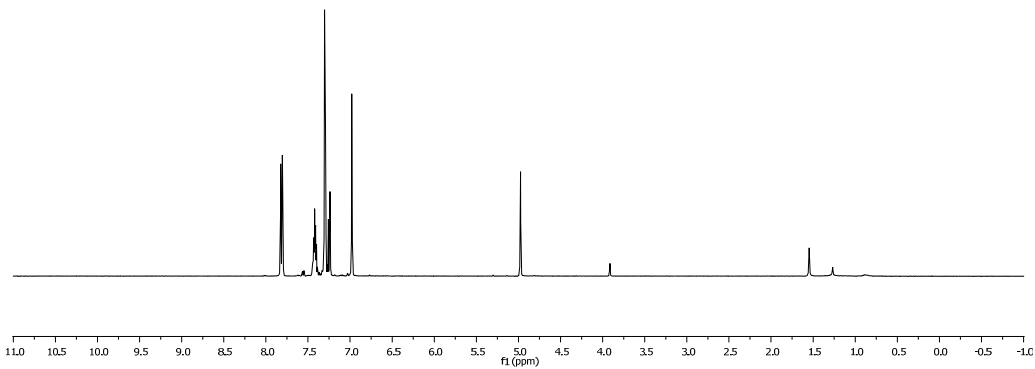
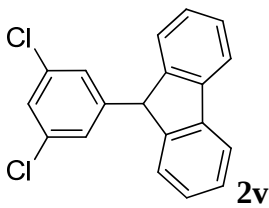
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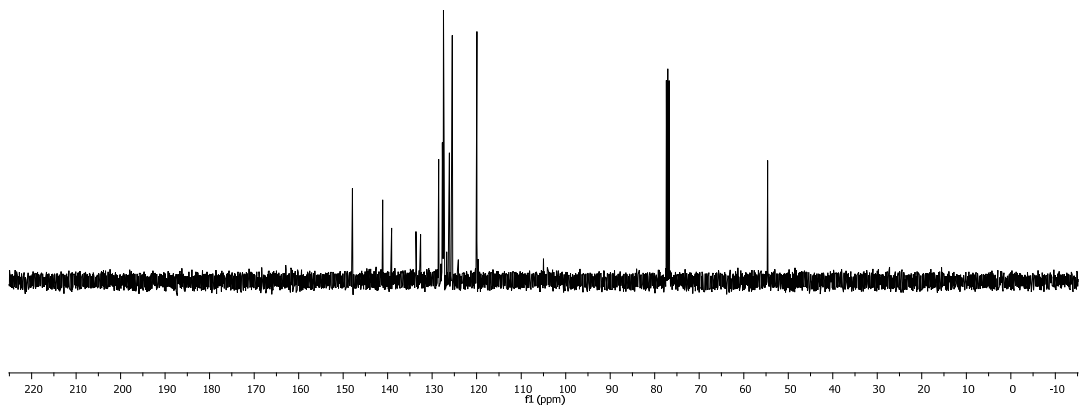
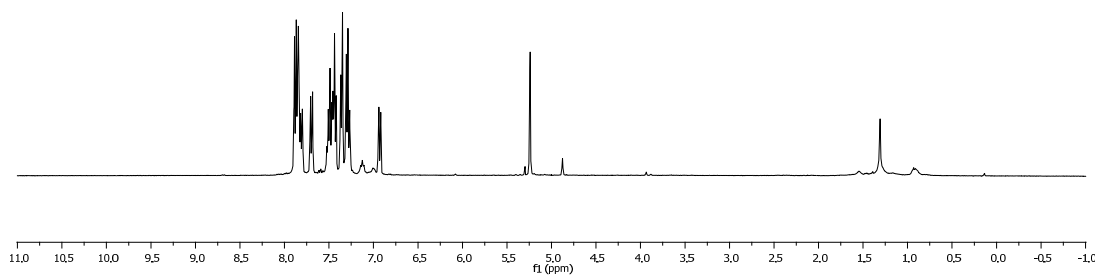
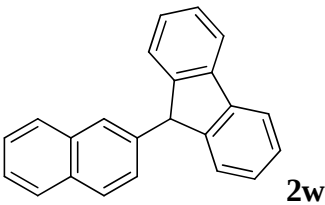


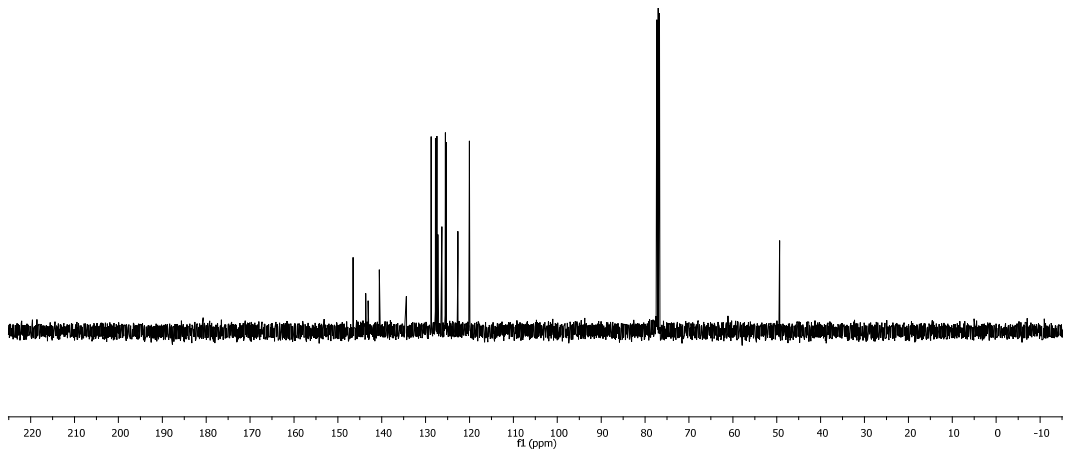
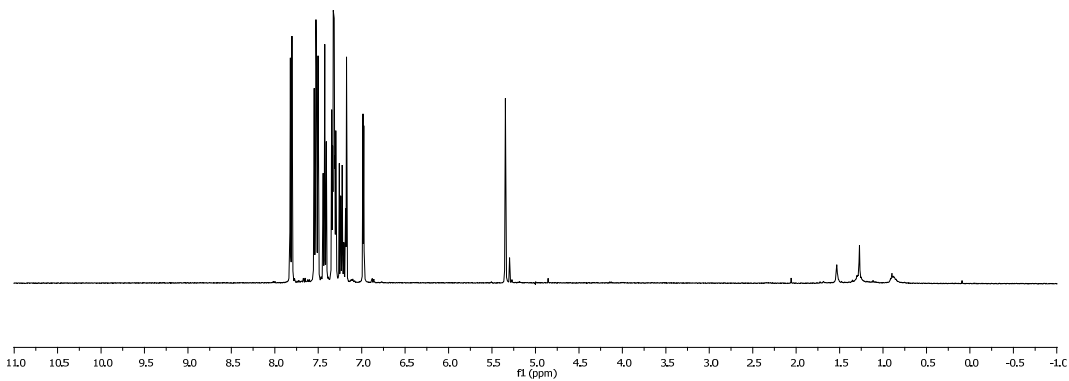
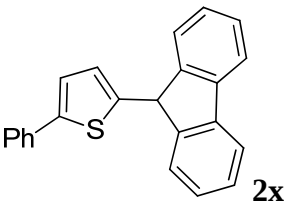


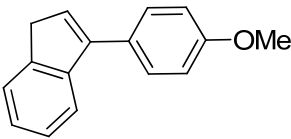












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