Synthesis of Spiroindanes by Palladium-Catalyzed Oxidative Annulations of Non- or Weakly Activated 1,3-Dienes Involving C–H Functionalization

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Supplementary Information

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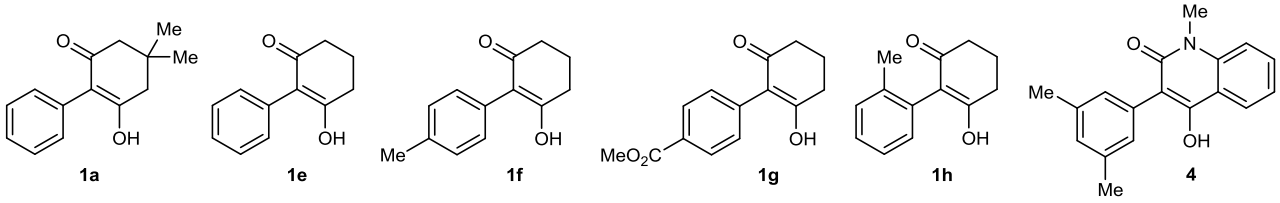
General Information

All non-aqueous reactions were carried out under a nitrogen atmosphere using oven-dried apparatus. All commercially available reagents were used as received. Thin layer chromatography (TLC) was performed on Merck DF-Alufoilien $60F_{254}$ 0.2 mm precoated plates. Product spots were visualized by UV light at 254 nm, and subsequently developed using potassium permanganate or vanillin solution as appropriate. Flash column chromatography was carried out using silica gel (Fisher Scientific 60Å particle size 35-7 micron) employing the method of Still and co-workers.[1] 'Petrol' refers to that fraction of light petroleum ether boiling in the range 40–60 °C. Melting points were recorded on a Gallenkamp melting point apparatus and are uncorrected. Infra-red spectra were recorded on a Nicolet Avatar 360 FT instrument on the neat compound, using the attenuated total reflectance (ATR) technique. ^{1}H NMR spectra were recorded on a Bruker AVA500 (500 MHz) spectrometer or a Bruker AVA400 spectrometer. Chemical shifts (δ) are quoted in parts per million (ppm) downfield of tetramethylsilane, using residual protonated solvent as internal standard ($CDCl_3$ at 7.27 ppm). Abbreviations used in the description of resonances are: s (singlet), d (doublet), t (triplet), q, (quartet), quin (quintet), app (apparent), br (broad), m (multiplet). Coupling constants (*J*) are quoted to the nearest 0.1 Hz. Proton-decoupled ^{13}C NMR spectra were recorded on a Bruker AVA500 (125.8 MHz) spectrometer or a Bruker AVA400 (100.6 MHz) spectrometer. Chemical shifts (δ) are quoted in parts per million (ppm) downfield of tetramethylsilane, using deuterated solvent as internal standard ($CDCl_3$ at 77.0 ppm). Assignments were made using the DEPT sequence with secondary pulses at 90° and 135°. High-resolution mass spectra were recorded using the electrospray ionization (ESI) technique at the School of Chemistry, University of Nottingham.

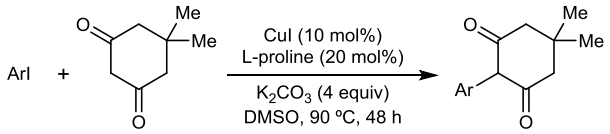
Preparation of 2-Aryl Cyclic 1,3-Dicarbonyl Compounds



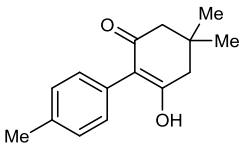
Substrates **1a**,[2] **1e**,[2] **1f**,[2] **1g**,[2] **1h**[3] and **4**[4] were prepared as described previously.

1. Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923–2925.
2. Reddy Chidipudi, S.; Khan, I.; Lam, H. W. *Angew. Chem., Int. Ed.* **2012**, *51*, 12115–12119.
3. Reddy Chidipudi, S.; Wieczysty, M. D.; Khan, I.; Lam, H. W. *Org. Lett.* **2013**, *15*, 570–573.
4. Dooley, J. D.; Reddy Chidipudi, S.; Lam, H. W. *J. Am. Chem. Soc.* **2013**, *135*, 10829–10836.

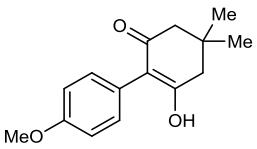
General Procedure A



The appropriate aryl iodide (1.0 equiv) was added to a stirred solution of CuI (10 mol%), L-proline (20 mol%), K_2CO_3 (4.0 equiv), and dimedone (3.0 equiv) in anhydrous DMSO (4 mL/mmol), and the reaction mixture was then stirred at 90 °C for 48 h. The reaction was cooled to 0 °C and acidified with 2 N HCl to pH 3–4 and the aqueous layer was separated and extracted with EtOAc (2 × 100 mL). The combined organic extracts were washed with brine (50 mL), dried ($MgSO_4$), filtered, and concentrated in *vacuo*. Purification of the residue by column chromatography (40% EtOAc/hexane) gave the 2-aryl-1,3-dicarbonyl compound.

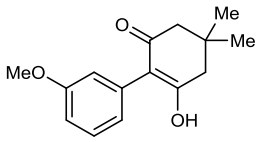


3-Hydroxy-5,5-dimethyl-2-(4-methylphenyl)cyclohex-2-en-1-one (1b). The title compound was prepared according to General Procedure A from 4-iodotoluene (5.45 g, 25.0 mmol) and dimedone (10.51 g, 75.0 mmol), and purified by column chromatography (40% EtOAc/hexane) to give an off-white solid (3.66 g, 64%). R_f = 0.40 (40% EtOAc/hexane); m.p. 202-204 °C (EtOAc/petrol); IR 1718 (C=O), 1575, 1514, 1406, 1336, 1300, 1273, 1254, 1144, 1027 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (2H, d, *J* = 7.9 Hz, Ar**H**), 7.09 (2H, d, *J* = 7.9 Hz, Ar**H**), 6.33 (1H, br s, O**H**) 2.40 (4H, br s, C$\mathbf{H}_2$C$(CH_3)_2$C$\mathbf{H}_2$), 2.37 (3H, s, ArC$\mathbf{H}_3$), 1.16 (6H, s, C$(C\mathbf{H}_3)_2$); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 137.9 (C), 130.4 (2 × CH), 130.0 (2 × CH), 127.6 (C), 116.7 (C), 31.7 (CH_2), 28.3 (2 × CH_3), 21.2 (CH_3), some signals not observed due to keto–enol tautomerism; HRMS (ESI) Exact mass calcd for $C_{15}H_{18}O_2Na$ $[M+Na]^+$: 253.1199, found: 253.1190.



3-Hydroxy-2-(4-methoxyphenyl)-5,5-dimethylcyclohex-2-en-1-one (1c). The title compound was prepared according to General Procedure A from 4-iodoanisole (4.68 g, 20.0 mmol) and dimedone (8.41 g, 60.0 mmol), and purified by column chromatography (40% EtOAc/hexane) to give an off-white solid (2.45 g, 50%). R_f = 0.43 (60% EtOAc/hexane); m.p. 150-152 °C (EtOAc/petrol); IR 2953, 1611 (C=O), 1568, 1512, 1465, 1361, 1331, 1282, 1248, 1174, 1025, 885, 831 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (2H, d, *J* = 8.5 Hz, Ar**H**), 6.97 (2H, d, *J* = 8.5 Hz, Ar**H**), 6.19 (1H, br s, O**H**), 3.82 (3H, s, OC$\mathbf{H}_3$), 2.47 (2H, br s, C$\mathbf{H}_2$), 2.38 (2H, br s, C$\mathbf{H}_2$), 1.16 (6H, s, C$(C\mathbf{H}_3)_2$); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 159.4 (C), 131.8 (2 × CH), 122.5 (C), 116.4 (C), 114.8 (2 × CH), 55.3 (CH_3), 50.8 (C), 31.7 (CH_2), 28.3 (2 × CH_3), some

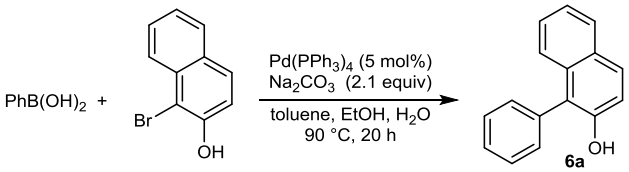
signals not observed due to keto–enol tautomerism; HRMS (ESI) Exact mass calcd for $C_{15}H_{19}O_3$ $[M+H]^+$: 247.1329, found: 247.1314.



3-Hydroxy-2-(3-methoxyphenyl)-5,5-dimethylcyclohex-2-en-1-one (1d). The title compound was prepared according to General Procedure A from 3-iodoanisole (4.68 g, 20.0 mmol) and dimedone (8.41 g, 60.0 mmol), and purified by column chromatography (40% EtOAc/hexane) to give an off-white solid (3.20 g, 65%). R_f = 0.42 (60% EtOAc/hexane); m.p. 122-124 °C (EtOAc/petrol); IR 2959, 1606 (C=O), 1575, 1488, 1339, 1309, 1282, 1252, 1029, 835, 779 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.30 (1H, m, Ar**H**), 6.87 (1H, ddd, *J* = 8.3, 2.6, 0.8 Hz, Ar**H**), 6.79-6.74 (1H, m, Ar**H**), 6.72 (1H, dd, *J* = 2.4, 1.5 Hz, Ar**H**), 6.64 (1H, br s, O**H**), 3.79 (3H, s, OC**H**$_3$), 2.40 (4H, br s, C**H**$_2$C(CH$_3$)$_2$C**H**$_2$), 1.15 (6H, C(C**H**$_3$)$_2$); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 160.1 (C), 132.3 (C), 130.2 (CH), 122.6 (CH), 116.7 (C), 116.0 (CH), 113.9 (CH), 55.2 (CH_3), 31.7 (CH_2), 28.3 (2 × CH_3), some signals not observed due to keto–enol tautomerism; HRMS (ESI) Exact mass calcd for $C_{15}H_{19}O_3$ $[M+H]^+$: 247.1329, found: 247.1323.

Preparation of 1-Aryl-2-Naphthols

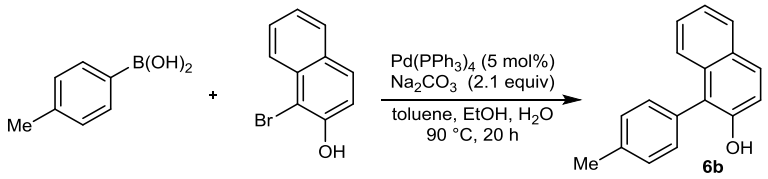
1-Phenylnaphthalen-2-ol (6a)



A 100 mL oven-dried round bottom flask with a stir bar was fitted with a rubber septum, and the flask was purged with nitrogen and charged with $Pd(PPh_3)_4$ (260 mg, 0.22 mmol), Na_2CO_3 (997 mg, 9.41 mmol), 1-bromonaphthalen-2-ol (1.00 g, 4.48 mmol), phenylboronic acid (1.09 g, 8.96 mmol), toluene (45 mL), EtOH (9 mL), and deoxygenated H_2O (10 mL). The mixture was heated at 90 °C for 20 h and cooled to room temperature. The organic layer was separated and the aqueous layer was extracted with EtOAc (3 × 20 mL), and the combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification of the residue by column chromatography (3% (EtOAc/petrol) gave 1-phenyl-2-naphthol (**6a**) as an off-white solid (1.67 g, 85%) that displayed spectroscopic data consistent with those reported previously.[5]

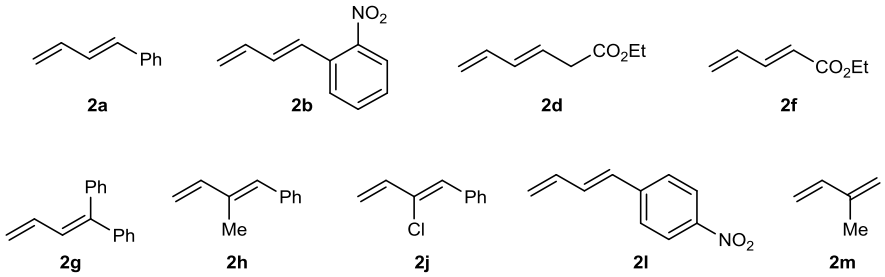
5. Kyhn Rasmussen, L.; Begtrup, M.; Ruhland, T. *J. Org. Chem.* **2004**, *69*, 6890–6893.

1-(4-Methylphenyl)naphthalen-2-ol (6b)



A 100 mL oven-dried round bottom flask with a stir bar was fitted with a rubber septum, and the flask was purged with nitrogen and charged with $Pd(PPh_3)_4$ (77 mg, 0.07 mmol), Na_2CO_3 (298 mg, 2.81 mmol), 1-bromonaphthalen-2-ol (300 mg, 1.34 mmol), *p*-tolylboronic acid (364 mg, 2.68 mmol), toluene (7 mL), EtOH (1.5 mL), and deoxygenated H_2O (1.7 mL). The mixture was heated at 90 °C for 20 h and cooled to room temperature. The organic layer was separated and the aqueous layer was extracted with EtOAc (3 × 15 mL), and the combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification of the residue by column chromatography (2% (EtOAc/petrol) gave 1-*p*-tolyl-2-naphthol (**6b**) as an off-white solid (202 mg, 64%) that displayed spectroscopic data consistent with those reported previously.[5]

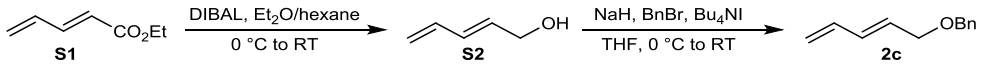
Preparation of 1,3-Dienes



1,3-Dienes **2a**,[6] **2b**,[7] **2d**,[8] **2g**,[9] **2h**,[10] and **2j**[11] were prepared according to previously reported procedures. 1,3-Diene **2l** was prepared by the Wittig reaction of methyltriphenylphosphonium bromide and 4-nitrocinnamaldehyde according to a literature procedure reported for similar compounds,[12] and displayed spectroscopic data consistent with those reported previously.[13] Isoprene (**2m**) is commercially available.

6. Zhu, S.; Lu, X.; Luo, Y.; Zhang, W.; Jiang, H.; Yan, M.; Zeng, W. *Org. Lett.* **2013**, *15*, 1440–1443.
7. Preuß, T.; Saak, W.; Doye, S. *Chem. Eur. J.* **2013**, *19*, 3833–3837.
8. Miller, C. A.; Batey, R. A. *Org. Lett.* **2004**, *6*, 699–702.
9. Wang, T.; Hu, Y.; Zhang, S. *Org. Biomol. Chem.* **2010**, *8*, 2312–2315.
10. Watkins, A. L.; Landis, C. R. *Org. Lett.* **2011**, *13*, 164–167.
11. Krijnen, E. S.; Zuilhof, H.; Lodder, G. *J. Org. Chem.* **1994**, *59*, 8139–8150.
12. Okamoto, T.; Kobayashi, K.; Oka, S.; Tanimoto, S. *J. Org. Chem.* **1988**, *53*, 4897–4901.
13. Borg, T.; Tuzina, P.; Somfai, P. *J. Org. Chem.* **2011**, *76*, 8070–8075.

(*E*)-[(Penta-2,4-dien-1-yloxy)methyl]benzene (2c)

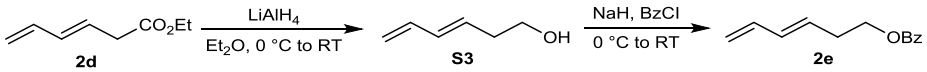


S1 **S2** **2c**

To a solution of the ester **S1**[14] (5.67 g, 45.0 mmol) in Et_2O (100 mL) at 0 °C was added DIBAL (1.0 M in hexane, 90 mL, 90 mmol) over *ca.* 5 min and the mixture was stirred at this temperature for 20 min, and at room temperature for 4 h. The reaction was cooled to 0 °C and quenched carefully with 1 N aqueous HCl solution until the pH of the mixture was 5-6. The aqueous layer was separated and extracted with Et_2O (2 × 50 mL), and the combined organic layers were washed with brine (50 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo* to leave (*E*)-penta-2,4-dien-1-ol (**S2**) (3.29 g, 87% crude yield) as a colorless oil which was taken onto the next step without purification.

To a suspension of NaH (60% in mineral oil, 457 mg, 11.9 mmol) in THF (10 mL) at 0 °C was added a solution of **S2** (500 mg, 5.9 mmol) in THF (5 mL), and the mixture was stirred for 30 min. To this mixture was added Bu_4NI (219 mg, 0.59 mmol) in one portion followed by BnBr (0.85 mL, 7.16 mmol) dropwise and the mixture was stirred at room temperature for 12 h. The reaction was quenched carefully with H_2O (10 mL) and the aqueous layer was separated and washed with Et_2O (2 × 20 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification of the residue by column chromatography (hexane) gave the benzyl ether **2c** as a colorless oil (450 mg, 44%) that displayed spectroscopic data consistent with those reported previously.[15]

(*E*)-Hexa-3,5-dien-1-yl benzoate (2e)



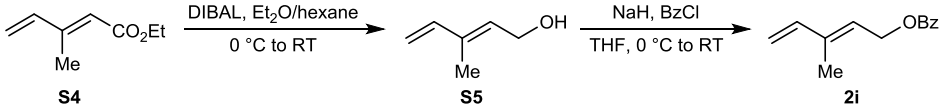
2d **S3** **2e**

To a solution of the ester **2d** (1.50 g, 10.7 mmol) in Et_2O (30 mL) at 0 °C, was added $LiAlH_4$ (2.4 M in Et_2O, 7.0 mL, 16.8 mmol) over *ca.* 2 min, and the mixture was stirred at this temperature for 20 min and at room temperature for 4 h. The reaction was cooled to 0 °C, and quenched carefully with 1 N aqueous HCl solution until the pH of the mixture was 5-6. The aqueous layer was separated and extracted with Et_2O (2 × 50 mL) and the combined organic layers were washed with brine (50 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo* to leave (*E*)-hexa-3,5-dien-1-ol (**S3**) (886 mg, 9.04 mmol, 82% crude yield) as a colorless oil which was taken onto the next step without purification.

14. Prepared according to: Wrigglesworth, J. W.; Cox, B.; Lloyd-Jones, G. C.; Booker-Milburn, K. I. *Org. Lett.* **2011**, *13*, 5326–5329.
15. Constantino, M. G.; de Oliveira, K. T.; Polo, E. C.; da Silva, G. V. J.; Brocksom, T. J. *J. Org. Chem.* **2006**, *71*, 9880–9883.

To a suspension of NaH (60% in mineral oil, 700 mg, 18.1 mmol) in THF (20 mL) at 0 °C was added a solution of **S3** (886 mg, 9.04 mmol) in THF (5 mL) and the mixture was stirred at this temperature for 30 min. Benzoyl chloride (1.6 mL, 13.6 mmol) was added dropwise over *ca*. 1 min and the mixture was stirred at room temperature for 12 h. The reaction was quenched with H_2O (10 mL) and the aqueous layer was separated and extracted with Et_2O (2 × 20 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification of the residue by column chromatography (2% EtOAc/petrol) gave the *benzoyl ester* **2e** as a colorless oil (1.43 g, 78%, *ca*. 93–95% purity). R_f = 0.51 (30% EtOAc/hexane); IR 1718 (C=O), 1602, 1451, 1368, 1314, 1267, 1176, 1109, 1070, 1026, 953, 835, 709, 644 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.09-8.03 (2H, m, Ar**H**), 7.59-7.52 (1H, m, Ar**H**), 7.48-7.41 (2H, m, Ar**H**), 6.35 (1H, dt, *J* = 16.8, 10.2 Hz, =C**H**CH_2), 6.20 (1H, app dd, *J* = 15.2, 10.4 Hz, CH_2=C**H**), 5.82-5.70 (1H, m, C**H**=$CHCH_2$), 5.16 (1H, d, *J* = 16.6 Hz, C$\mathbf{H}_2$=CH), 5.04 (1H, d, *J* = 9.9 Hz, C$\mathbf{H}_2$=CH), 4.38 (2H, t, *J* = 6.8 Hz, C$\mathbf{H}_2$O), 2.57 (2H, q, *J* = 6.8 Hz, C$\mathbf{H}_2CH_2O$); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 166.5 (C), 136.7 (CH), 133.5 (CH), 132.8 (CH), 130.3 (C), 129.6 (CH), 129.5 (2 × CH), 128.3 (2 × CH), 116.1 (CH_2), 64.0 (CH_2), 31.9 (CH_2); HRMS (ESI) Exact mass calcd for $C_{13}H_{14}O_2Na$ $[M+Na]^+$: 225.0886, found: 225.0891.

(*E*)-3-Methylpenta-2,4-dien-1-yl benzoate (2i)



S4 **S5** **2i**

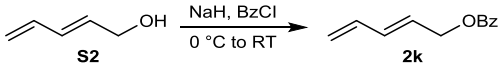
To a solution of the ester **S4**,[16] (2.80 g, 20.0 mmol) in Et_2O (50 mL) at 0 °C was added DIBAL (1.0 M in hexane, 40.0 mL, 40 mmol) over *ca.* 5 min and the mixture was stirred at this temperature for 20 min, and at room temperature for 4 h. The reaction was cooled to 0 °C, and slowly quenched with 1 N aqueous HCl solution until the pH of the mixture was 5-6. The aqueous layer was separated and extracted with Et_2O (2 × 60 mL) and the combined organic layers were washed with brine (50 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo* to leave (*E*)-3-methylpenta-2,4-dien-1-ol (**S5**) (1.92 g, 98% crude yield) as a colorless oil which was taken onto the next step without purification.

To a suspension of NaH (60% in mineral oil, 392 mg, 10.2 mmol) in THF (10 mL) at 0 °C was added a solution of **S5** (500 mg, 5.09 mmol) in THF (5 mL) and the mixture was stirred at this temperature for 30 min. Benzoyl chloride (0.71 mL, 6.12 mmol) was added dropwise over *ca.* 1 min and the mixture was stirred at room temperature for 12 h. The reaction was quenched with H_2O (10 mL) and the aqueous layer was separated and extracted with Et_2O (2 × 20 mL). The combined organic layers were

16. Prepared according to: Yildizhan, S.; Schulz, S. *Synlett*, **2011**, 2831–2833.

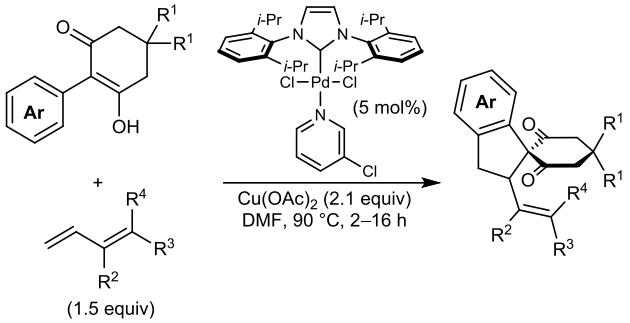
dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification of the residue by column chromatography (2% EtOAc/petrol) gave the *benzoyl ester* **2i** as a colorless oil (585 mg, 57%). R_f = 0.71 (20% EtOAc/hexane); IR 1717 (C=O), 1608, 1451, 1339, 1314, 1268, 1176, 1109, 1069, 1026, 991, 904, 709, 644 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.09-8.04 (2H, m, Ar**H**), 7.53 (1H, t, *J* = 7.4 Hz, Ar**H**), 7.47-7.42 (2H, m, Ar**H)**, 6.43 (1H, dd, *J* = 17.4, 10.7 Hz, CH_2=C**H**), 5.75 (1H, t, *J* = 7.0 Hz, =C**H**CH_2), 5.29 (1H, d, *J* = 17.4 Hz, C**H**$_2$=CH), 5.13 (1H, d, *J* = 10.7 Hz, C**H**$_2$=CH), 4.98 (2H, d, *J* = 7.0 Hz, C**H**$_2$O), 1.90 (3H, m, C**H**$_3$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 166.5 (C), 140.3 (CH), 138.7 (C), 132.9 (CH), 130.2 (C), 129.6 (2 × CH), 128.3 (2 × CH), 125.2 (CH), 113.9 (CH_2), 61.6 (CH_2), 12.1 (CH_3); HRMS (ESI) Exact mass calcd for $C_{13}H_{14}O_2Na$ $[M+Na]^+$: 225.0886, found: 225.0882.

(*E*)-Penta-2,4-dien-1-yl benzoate (2k)

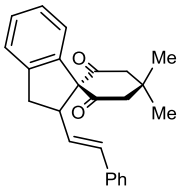


To a suspension of NaH (60% in mineral oil, 457 mg, 11.9 mmol) in THF (10 mL) at 0 °C was added a solution of crude **S2** (500 mg, 5.94 mmol, prepared as described above) in THF (5 mL), and the mixture was stirred at this temperature for 30 min. Benzoyl chloride (0.83 mL, 7.1 mmol) was added dropwise over *ca*. 1 min and the mixture was stirred at room temperature for 12 h. The reaction was quenched with H_2O (10 mL), and the aqueous layer was separated and extracted with Et_2O (2 × 20 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification of the residue by column chromatography (hexane) gave the benzoyl ether **2k** as a colorless oil (780 mg, 70%). This material contained a small quantity (~5%) of an isomeric impurity. R_f = 0.58 (10% EtOAc/hexane); IR 1718 (C=O), 1602, 1451, 1368, 1314, 1267, 1176, 1109, 1070, 1026, 953, 835, 709, 644 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.12-8.05 (2H, m, Ar**H**), 7.58 (1H, t, *J* = 7.4 Hz, Ar**H**), 7.47 (2H, t, *J* = 7.7 Hz, Ar**H**), 6.46-6.33 (2H, m, C**H**=C**H**CH_2), 5.99-5.85 (1H, m, CH_2=C**H**), 5.36-5.25 (1H, m, C**H**$_2$=CH), 5.23-5.14 (1H, m, C**H**$_2$=CH), 4.88 (2H, d, *J* = 6.0 Hz, C**H**$_2$); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 166.2 (C), 135.9 (CH), 134.6 (CH), 132.9 (CH), 130.1 (C), 129.6 (2 × CH), 128.3 (2 × CH), 127.1 (CH), 118.6 (CH_2), 64.9 (CH_2); HRMS (ESI) Exact mass calcd for $C_{12}H_{12}O_2Na$ $[M+Na]^+$: 211.0730, found: 211.0722.

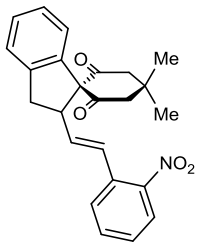
Pd-Catalyzed Oxidative Annulations: General Procedure B



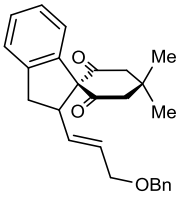
To a mixture of the appropriate 2-aryl-1,3-dicarbonyl compound (0.50 mmol), $Cu(OAc)_2$ (191 mg, 1.05 mmol), and PEPPSI-IPr (17.0 mg, 0.025 mmol) in degassed DMF (1 mL) was added the appropriate diene (0.75 mmol) in degassed DMF (0.5 mL), and the resulting mixture was stirred at 90 ºC for the indicated reaction time (2–16 h). The reaction was filtered through a pad of silica gel eluting with Et_2O (100 mL), washed with H_2O (50 mL), and brine (20 mL). The organic layer was dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification of the residue by column chromatography gave the spiroindane.



4,4-Dimethyl-2'-[(*E*)-2-phenylethenyl]-2',3'-dihydrospiro[cyclohexane-1,1'-indene]-2,6-dione (3a). The title compound was prepared according to General Procedure B from dione **1a** (108 mg, 0.50 mmol) and 1,3-diene **2a** (98 mg, 0.75 mmol) for a reaction time of 2 h, and purified by column chromatography (6% EtOAc/hexane) to give an off-white solid (114 mg, 66%). R_f = 0.55 (30% EtOAc/hexane); m.p. 140-142 °C (EtOAc/petrol); IR 2960, 1721 (C=O), 1688 (C=O), 1495, 1457, 1369, 1328, 1250, 1206, 1099, 982, 753, 747 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.38-7.29 (6H, m, Ar**H**), 7.28-7.22 (2H, m, Ar**H**), 7.07 (1H, d, *J* = 7.4 Hz, Ar**H**), 6.61 (1H, d, *J* = 15.8 Hz, =C**H**Ph), 6.28 (1H, dd, *J* = 15.8, 9.8 Hz, C**H**=CHPh), 3.83-3.75 (1H, m, CH_2C**H**), 3.23-3.14 (2H, m, C**H**$_2$CH), 2.83 (1H, d, *J* = 15.3 Hz, C**H**$_2$C=O), 2.76-2.67 (2H, m, C**H**$_2$C=O), 2.52 (1H, d, *J* = 15.1 Hz, C**H**$_2$C=O), 1.11 (3H, s, C**H**$_3$), 1.05 (3H, s, C**H**$_3$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 207.8 (C), 206.6 (C), 144.0 (C), 140.3 (C), 136.4 (C), 133.2 (CH), 128.7 (CH), 128.6 (2 × CH), 128.3 (CH), 127.8 (CH), 126.7 (CH), 126.4 (2 × CH), 125.0 (CH), 124.8 (CH), 80.1 (C), 53.7 (CH_2), 53.58 (CH), 53.56 (CH_2), 38.3 (CH_2), 30.5 (C), 29.3 (CH_3), 28.4 (CH_3); HRMS (ESI) Exact mass calcd for $C_{24}H_{24}O_2Na$ $[M+Na]^+$: 367.1669, found: 367.1654.

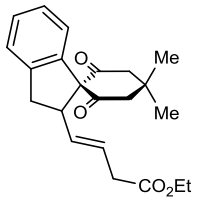


4,4-Dimethyl-2'-[(*E*)-2-(2-nitrophenyl)ethenyl]-2',3'-dihydrospiro[cyclohexane-1,1'-indene]-2,6-dione (3b). The title compound was prepared according to General Procedure B from dione **1a** (108 mg, 0.50 mmol) and 1,3-diene **2b** (131 mg, 0.75 mmol) for a reaction time of 4 h, and purified by column chromatography (8% EtOAc/hexane) to give an off-white solid (128 mg, 66%). R_f = 0.39 (30% EtOAc/hexane); m.p. 148-150 °C (EtOAc/petrol); IR 2957, 1721 (C=O), 1689 (C=O), 1517, 1480, 1346, 1330, 1205, 1097, 1066, 967, 862, 748 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (1H, dd, *J* = 8.2, 1.2 Hz, Ar**H**), 7.52 (1H, td, *J* = 7.8, 1.2 Hz, Ar**H**), 7.46 (1H, dd, *J* = 7.8, 1.3 Hz, Ar**H**), 7.41-7.36 (1H, m, Ar**H**), 7.32-7.22 (3H, m, Ar**H**), 7.10 (1H, d, *J* = 7.4 Hz, Ar**H**), 7.06 (1H, d, *J* = 15.6 Hz, =C**H**Ar), 6.18 (1H, dd, *J* = 15.6, 9.8 Hz, C**H**=CHAr), 3.85 (1H, dt, *J* = 9.8, 7.0 Hz, CH_2C**H**), 3.26 (1H, dd, *J* = 15.5, 7.6 Hz, C**H**$_2$CH), 3.12 (1H, dd, *J* = 15.5, 6.6 Hz, C**H**$_2$CH), 2.98 (1H, d, *J* = 15.3 Hz, C**H**$_2$C=O), 2.77-2.67 (2H, m, C**H**$_2$C=O), 2.57 (1H, d, *J* = 14.9 Hz, C**H**$_2$C=O), 1.10 (6H, s, C(C**H**$_3$)$_2$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 206.7 (C), 206.5 (C), 147.5 (C), 143.5 (C), 139.6 (C), 134.2 (CH), 133.2 (CH), 132.4 (C), 129.0 (CH), 128.42 (CH), 128.36 (CH), 128.2 (CH), 126.8 (CH), 125.1 (CH), 125.0 (CH), 124.5 (CH), 80.4 (C), 53.5 (CH_2), 53.0 (CH_2), 52.2 (CH), 37.9 (CH_2), 30.5 (C), 29.2 (CH_3), 28.2 (CH_3); HRMS (ESI) Exact mass calcd for $C_{24}H_{23}NO_4Na$ $[M+Na]^+$: 412.1519, found 412.1520.

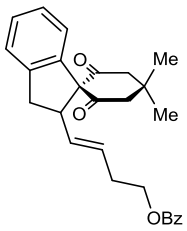


2'-[(*E*)-3-(Benzyloxy)prop-1-en-1-yl]-4,4-dimethyl-2',3'-dihydrospiro[cyclohexane-1,1'-indene]-2,6-dione (3c). The title compound was prepared according to General Procedure B from dione **1a** (109 mg, 0.50 mmol) and 1,3-diene **2c** (131mg, 0.75 mmol) for a reaction time of 12 h, and purified by column chromatography (8% EtOAc/petrol) to give a light yellow viscous liquid (144 mg, 74%). R_f = 0.54 (30% EtOAc/petrol); IR 2965, 2915, 1720 (C=O), 1690 (C=O), 1602, 1550, 1512, 1454, 1370, 1227, 1203, 1062, 828, 793 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40-7.20 (8H, m, Ar**H**), 7.06 (1H, d, *J* = 7.5 Hz, Ar**H**), 5.89-5.77 (2H, m, C**H**=C**H**), 4.51 (2H, s, C**H**$_2$Ph), 4.04-3.95 (2H, m, C**H**$_2$OBn), 3.63 (1H, dd, *J* = 16.2, 7.8 Hz, C**H**CH=CH), 3.13 (1H, dd, *J* = 15.4, 7.6 Hz, C**H**$_2$CHCH=), 3.07 (1H, dd, *J* = 15.4, 7.8 Hz, C**H**$_2$CHCH=), 2.82 (1H, d, *J* = 15.3 Hz, C**H**$_2$C=O), 2.71 (1H, dd, *J* = 10.3, 1.7 Hz, C**H**$_2$C=O), 2.68 (1H, dd, *J* = 10.3, 1.7 Hz, C**H**$_2$C=O), 2.55 (1H, d, *J* = 15.3 Hz, C**H**$_2$C=O), 1.11 (6H, s, 2 × C**H**$_3$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 207.4 (C), 206.3 (C), 143.8 (C), 140.1 (C), 138.1 (C), 132.3 (CH), 130.3 (CH), 128.3 (2 × CH), 128.2 (CH), 127.6 (2 × CH), 127.5 (CH), 126.6 (CH), 124.8 (2 × CH), 79.9 (C),

72.1 (CH_2), 69.9 (CH_2), 53.5 (CH_2), 53.4 (CH_2), 52.7 (CH), 37.8 (CH_2), 30.4 (C), 29.3 (CH_3), 28.2 (CH_3); HRMS (ESI) Exact mass calcd for $C_{26}H_{29}O_3$ $[M+H]^+$: 389.2111, found: 389.2115.

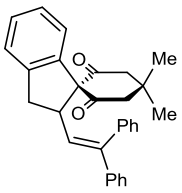


Ethyl (*E*)-4-{4,4-dimethyl-2,6-dioxo-2',3'-dihydrospiro[cyclohexane-1,1'-indene]-2'-yl}but-3-enoate (3d). The title compound was prepared according to General Procedure B from dione **1a** (108 mg, 0.50 mmol) and 1,3-diene **2d** (105 mg, 0.75 mmol) for a reaction time of 12 h, and purified by column chromatography (8% EtOAc/petrol) to give a light yellow viscous liquid (111 mg, 63%). R_f = 0.50 (30% EtOAc/petrol); IR 2956, 1734 (C=O), 1688 (C=O), 1478, 1367, 1315, 1208, 1177, 1142, 983, 893, 759, 644 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.29-7.17 (3H, m, Ar**H**), 7.00 (1H, d, *J* = 7.4 Hz, Ar**H**), 5.84-5.73 (1H, m, =C**H**CH_2), 5.59 (1H, ddt, *J* = 15.3, 9.8, 1.2 Hz, C**H**=$CHCH_2$), 4.14 (2H, q, *J* = 7.1 Hz, OC**H**$_2$), 3.53 (1H, dt, *J* = 9.6, 7.7 Hz, C**H**CH=CH), 3.15-2.96 (4H, m, C**H**$_2$CHCH=CHC**H**$_2$C=O), 2.87 (1H, d, *J* = 15.3 Hz, $(CH_3)_2$CC**H**$_2$C=O), 2.71-2.61 (2H, m, $(CH_3)_2$CC**H**$_2$C=O), 2.57 (1H, d, *J* = 15.3 Hz, $(CH_3)_2$CC**H**$_2$C=O), 1.27 (3H, t, *J* = 7.1 Hz, CH_2C**H**$_3$), 1.12 (3H, s, C**H**$_3$), 1.08 (3H, s, C**H**$_3$); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 208.0 (C), 206.7 (C), 171.3 (C), 143.9 (C), 140.1 (C), 133.2 (CH), 128.2 (CH), 126.7 (CH), 126.1 (CH), 125.0 (CH), 124.7 (CH), 79.9 (C), 60.7 (CH_2), 53.7 (CH_2), 53.6 (CH), 53.4 (CH_2), 37.9 (CH_2), 37.6 (CH_2), 30.5 (C), 29.5 (CH_3), 28.2 (CH_3), 14.2 (CH_3); HRMS (ESI) Exact mass calcd for $C_{22}H_{27}O_4$ $[M+H]^+$: 355.1904, found: 355.1907.

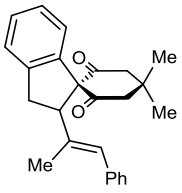


(*E*)-4-{4,4-Dimethyl-2,6-dioxo-2',3'-dihydrospiro[cyclohexane-1,1'-indene]-2'-yl}but-3-en-1-yl benzoate (3e). The title compound was prepared according to General Procedure B from dione **1a** (108 mg, 0.50 mmol) and 1,3-diene **2e** (151 mg, 0.75 mmol) for a reaction time of 12 h, and purified by column chromatography (6% EtOAc/petrol) to give a light yellow viscous liquid (153 mg, 73%). R_f = 0.58 (30% EtOAc/petrol); IR 2951, 2928, 1718 (C=O), 1692 (C=O), 1602, 1451, 1371, 1272, 1227, 1114, 1070, 978, 712 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.07-8.01 (2H, m, Ar**H**), 7.61-7.40 (1H, m, Ar**H**), 7.49-7.42 (2H, m, Ar**H**), 7.29-7.18 (3H, m, Ar**H**), 7.03 (1H, d, *J* = 7.4 Hz, Ar**H**), 5.78-5.60 (2H, m, C**H**=C**H**), 4.34 (2H, t, *J* = 6.6 Hz, C**H**$_2$O), 3.56 (1H, dt, *J* = 9.2, 7.5 Hz, C**H**CH=), 3.09 (1H, dd, *J* = 15.4, 7.6 Hz, C**H**$_2$CHCH=), 2.98 (1H, dd, *J* = 15.4, 7.5 Hz, C**H**$_2$CHCH=), 2.78 (1H, d, *J* = 15.2 Hz, C**H**$_2$C=O), 2.66 (1H, dd, *J* = 15.2, 1.8 Hz, C**H**$_2$C=O), 2.60 (1H, dd, *J* = 15.0, 1.8 Hz, C**H**$_2$C=O), 2.56-2.41 (3H, m, C**H**$_2$C=O and C**H**$_2$$CH_2$O), 1.06 (3H, s, C**H**$_3$), 1.04 (3H, s, C**H**$_3$); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 207.5 (C), 206.3 (C), 166.4 (C), 143.9 (C), 140.0 (C), 132.9 (CH), 132.1 (CH), 130.1 (C),

129.58 (CH), 129.55 (2 × CH), 128.3 (2 × CH), 128.2 (CH), 126.6 (CH), 124.9 (CH), 124.8 (CH), 80.0 (C), 64.0 (CH_2), 53.6 (CH_2), 53.4 (CH_2), 53.1 (CH), 38.1 (CH_2), 31.8 (CH_2), 30.4 (C), 29.4 (CH_3), 28.2 (CH_3); HRMS (ESI) Exact mass calcd for $C_{27}H_{28}O_4Na$ $[M+Na]^+$: 439.1880, found: 439.1890.



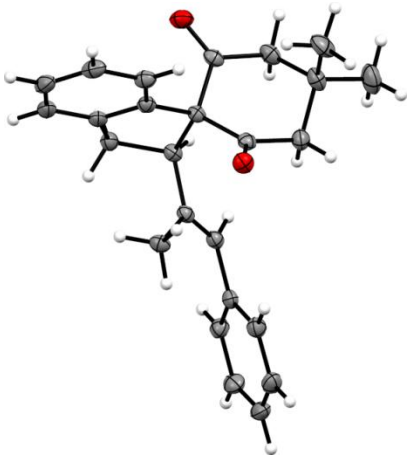
2'-(2,2-Diphenylethenyl)-4,4-dimethyl-2',3'-dihydrospiro[cyclohexane-1,1'-indene]-2,6-dione (3g). The title compound was prepared according to General Procedure B from dione **1a** (108 mg, 0.50 mmol) and 1,3-diene **2g** (154 mg, 0.75 mmol) for a reaction time of 3 h, and purified by column chromatography (5% EtOAc/petrol) to give a yellow solid (154 mg, 73%). R_f = 0.66 (30% EtOAc/petrol); m.p. 152-154 °C (EtOAc/petrol); IR 2957, 1723 (C=O), 1694 (C=O), 1558, 1457, 1372, 1203, 1065, 835, 772, 709 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.38 (3H, m, Ar**H**), 7.35-7.15 (10H, m, Ar**H**), 7.12-7.05 (1H, m, Ar**H**), 6.04 (1H, d, *J* = 11.2 Hz, C**H**=), 3.78 (1H, ddd, *J* = 11.4, 7.5, 4.0 Hz, CH_2C**H**), 3.27 (1H, dd, *J* = 15.5, 7.5 Hz, C**H**$_2$CH), 3.06 (1H, dd, *J* = 15.5, 4.0 Hz, C**H**$_2$CH), 2.68-2.56 (2H, m, C**H**$_2$C=O), 2.48 (1H, d, *J* = 14.8 Hz, C**H**$_2$C=O), 2.41 (1H, dd, *J* = 14.8, 1.3 Hz, C**H**$_2$C=O), 1.06 (3H, s, C**H**$_3$), 1.01 (3H, s, C**H**$_3$); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 206.6 (C), 206.5 (C), 143.8 (C), 143.5 (C), 141.4 (C), 139.0 (C), 138.5 (C), 129.8 (2 × CH), 128.5 (2 × C), 128.3 (CH), 128.2 (2 × CH), 127.79 (CH), 127.75 (CH), 127.4 (2 × CH), 127.3 (CH), 126.7 (CH), 126.4 (CH), 124.7 (CH), 80.8 (C), 53.8 (CH_2), 52.2 (CH_2), 49.0 (CH), 38.4 (CH_2), 30.2 (C), 30.1 (CH_3), 27.0 (CH_3); HRMS (ESI) Exact mass calcd for $C_{30}H_{28}O_2Na$ $[M+Na]^+$: 443.1982, found: 443.1983.

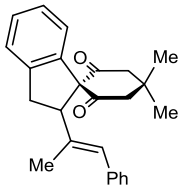


4,4-Dimethyl-2'-[(*E*)-1-phenylprop-1-en-2-yl]-2',3'-dihydrospiro[cyclohexane-1,1'-indene]-2,6-dione (3h). The title compound was prepared according to General Procedure B from dione **1a** (108 mg, 0.50 mmol) and 1,3-diene **2h** (108 mg, 0.75 mmol) for a reaction time of 3 h, and purified by column chromatography (6% EtOAc/hexane) to give a white solid (125 mg, 70%). R_f = 0.54 (30% EtOAc/hexane); m.p. 158-160 °C (EtOAc/petrol); IR 2947, 1717 (C=O), 1689 (C=O), 1481, 1457, 1368, 1242, 1194, 1079, 868, 788, 759, 742 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.20 (8H, m, Ar**H**), 7.01 (1H, d, *J* = 7.2 Hz, Ar**H**), 6.57 (1H, s, =C**H**), 3.68 (1H, dd, *J* = 7.4, 5.3 Hz, CH_2C**H**), 3.22 (1H, dd, *J* = 15.8, 7.5 Hz, C**H**$_2$CH), 3.13 (1H, dd, *J* = 15.8, 5.3 Hz, C**H**$_2$CH), 3.00 (1H, d, *J* = 15.2 Hz, C**H**$_2$C=O), 2.81 (1H, d, *J* = 14.3 Hz, C**H**$_2$C=O), 2.67 (1H, dd, *J* = 15.2, 2.8 Hz, C**H**$_2$C=O), 2.60 (1H, dd, *J* = 14.3, 2.8 Hz, C**H**$_2$C=O), 1.60 (3H, d, *J* = 1.6 Hz, C**H**$_3$), 1.19 (3H, s, C**H**$_3$), 1.04 (3H, s, C**H**$_3$); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 208.0 (C), 206.5 (C), 144.2 (C), 139.5 (C), 137.4 (C), 136.9 (C), 130.6 (CH), 128.9 (2 × CH), 128.24 (2 ×

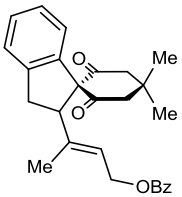
CH), 128.21 (CH), 126.8 (CH), 126.6 (CH), 125.9 (CH), 124.0 (CH), 81.1 (C), 61.2 (CH), 54.4 (CH_2), 52.9 (CH_2), 35.8 (CH_2), 30.7 (C), 30.4 (CH_3), 27.1 (CH_3), 15.0 (CH_3); HRMS (ESI) Exact mass calcd for $C_{25}H_{26}O_2Na$ $[M+Na]^+$: 381.1825, found: 381.1820.

Slow diffusion of petrol into a solution of **3h** in EtOAc gave crystals that were suitable for X-ray crystallography.

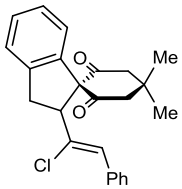




3h
CCDC 992451

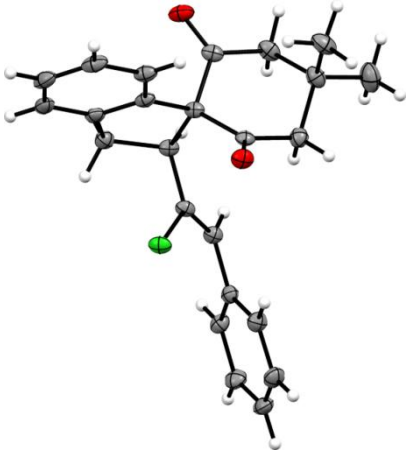


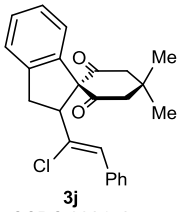
(*E*)-3-{4,4-Dimethyl-2,6-dioxo-2',3'-dihydrospiro[cyclohexane-1,1'-indene]-2'-yl}but-2-en-1-yl benzoate (3i). The title compound was prepared according to General Procedure B from dione **1a** (108 mg, 0.50 mmol) and 1,3-diene **2i** (151 mg, 0.75 mmol) for a reaction time of 12 h, and purified by column chromatography (10% EtOAc/hexane) to give a yellow viscous liquid (125 mg, 60%). R_f = 0.45 (30% EtOAc/hexane); IR 2957, 1718 (C=O), 1689 (C=O), 1517, 1456, 1347, 1265, 1097, 1066, 823 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07-8.02 (2H, m, Ar**H**), 7.61-7.56 (1H, m, Ar**H**), 7.49-7.43 (2H, m, Ar**H**), 7.31-7.21 (3H, m, Ar**H**), 6.96 (1H, d, *J* = 7.5 Hz, Ar**H**), 5.76 (1H, t, *J* = 6.7 Hz, =C**H**), 4.89 (1H, dd, *J* = 12.8, 7.0 Hz, C**H**$_2$O), 4.81 (1H, dd, *J* = 12.8, 6.5 Hz, C**H**$_2$O), 3.55 (1H, dd, *J* = 7.3, 6.0 Hz, ArCH$_2$C**H**), 3.17-3.03 (2H, m, ArC**H**$_2$), 2.87 (1H, d, *J* = 15.3 Hz, C**H**$_2$C=O), 2.72 (1H, d, *J* = 14.4 Hz, C**H**$_2$C=O), 2.60 (1H, dd, *J* = 15.2, 2.7 Hz, C**H**$_2$C=O), 2.54 (1H, dd, *J* = 14.4, 2.7 Hz, C**H**$_2$C=O), 1.55 (3H, s, C**H**$_3$), 1.12 (3H, s, C**H**$_3$), 1.01 (3H, s, C**H**$_3$); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 208.1 (C), 206.6 (C), 166.4 (C), 144.0 (C), 140.7 (C), 139.6 (C), 133.0 (CH), 130.0 (C), 129.5 (2 × CH), 128.4 (2 × CH), 128.2 (CH), 126.7 (CH), 125.7 (CH), 124.8 (CH), 124.1 (CH), 80.7 (C), 61.0 (CH_2), 60.0 (CH), 54.2 (CH_2), 52.9 (CH_2), 35.5 (CH_2), 30.3 (C and CH_3), 27.2 (CH_3), 13.9 (CH_3); HRMS (ESI) Exact mass calcd for $C_{27}H_{28}O_4Na$ $[M+Na]^+$: 439.1880, found: 439.1891.



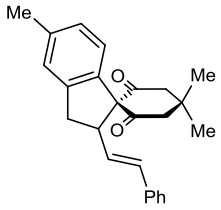
2'-[(*Z*)-1-Chloro-2-phenylethenyl]-4,4-dimethyl-2',3'-dihydrospiro[cyclohexane-1,1'-indene]-2,6-dione (3j). The title compound was prepared according to General Procedure B from dione **1a** (108 mg, 0.50 mmol) and 1,3-diene **2j** (123 mg, 0.75 mmol) for a reaction time of 4 h, and purified by column chromatography (5% EtOAc/hexane) to give an off-white solid (127 mg, 67%). R_f = 0.55 (30% EtOAc/hexane); m.p. 144-146 °C (EtOAc/petrol); IR 2953, 1724 (C=O), 1693 (C=O), 1558, 1482, 1369, 1322, 1211, 1193, 1066, 932, 757 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.64-7.56 (2H, m, Ar**H**), 7.44-7.22 (6H, m, Ar**H**), 6.97 (1H, d, *J* = 7.5 Hz, Ar**H**), 6.79 (1H, s, =C**H**), 4.06 (1H, dd, *J* = 9.8, 7.6 Hz, CH_2C**H**), 3.60 (1H, dd, *J* = 15.3, 10.0 Hz, C**H**$_2$CH), 3.20 (1H, dd, *J* = 15.3, 7.5 Hz, C**H**$_2$CH), 2.93 (1H, d, *J* = 16.3 Hz, C**H**$_2$C=O), 2.79 (1H, d, *J* = 16.3 Hz, C**H**$_2$C=O), 2.71 (2H, s, C**H**$_2$C=O), 1.17 (3H, s, C**H**$_3$), 1.13 (3H, s, C**H**$_3$); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 209.5 (C), 205.8 (C), 143.1 (C), 140.7 (C), 134.1 (C), 131.5 (C), 129.2 (2 × CH), 128.8 (CH), 128.34 (CH), 128.30 (2 × CH), 128.28 (CH), 127.0 (CH), 124.6 (CH), 124.5 (CH), 78.5 (C), 60.9 (CH), 54.0 (CH_2), 53.9 (CH_2), 36.3 (CH_2), 30.3 (C), 30.1 (CH_3), 28.3 (CH_3); HRMS (ESI) Exact mass calcd for $C_{24}H_{23}ClO_2Na$ $[M+Na]^+$: 401.1279, found: 401.1272.

Slow diffusion of petrol into a solution of **3j** in EtOAc gave crystals that were suitable for X-ray crystallography.



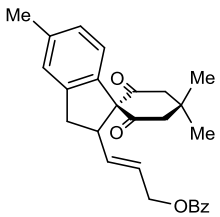


3j
CCDC 992452

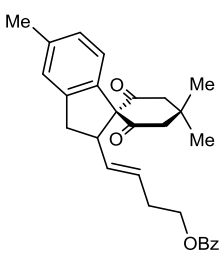


4,4,5'-Trimethyl-2'-[(*E*)-2-phenylethenyl]-2',3'-dihydrospiro[cyclohexane-1,1'-indene]-2,6-dione (3k). The title compound was prepared according to General Procedure B from dione **1b** (115 mg, 0.50 mmol) and 1,3-diene **2a** (98 mg, 0.75 mmol) for a reaction time of 2 h, and purified by column chromatography (7% EtOAc/hexane) to give a light yellow viscous liquid (145 mg, 81%). R_f = 0.59 (30% EtOAc/hexane); IR 2960, 1728 (C=O), 1690 (C=O), 1495, 1371, 1324, 1223, 1074, 973, 909, 751, 733, 692, 632 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.41-7.32 (4H, m, Ar**H**), 7.31-7.25 (1H, m, Ar**H**), 7.15

(1H, s, Ar**H**), 7.09 (1H, d, *J* = 7.8 Hz, Ar**H**), 6.99 (1H, d, *J* = 7.8 Hz, Ar**H**), 6.63 (1H, d, *J* = 15.8 Hz, =C**H**Ph), 6.31 (1H, dd, *J* = 15.8, 9.8 Hz, C**H**=CHPh), 3.81 (1H, dd, *J* = 17.6, 7.9 Hz, CH_2C**H**), 3.17 (2H, d, *J* = 7.9 Hz, C**H**$_2$CH), 2.84 (1H, d, *J* = 15.4 Hz, C**H**$_2$C=O), 2.79-2.69 (2H, m, C**H**$_2$C=O), 2.54 (1H, d, *J* = 15.2 Hz, C**H**$_2$C=O), 2.39 (3H, s, ArC**H**$_3$), 1.13 (3H, s, C(C**H**$_3$)$_2$), 1.07 (3H, s, C(C**H**$_3$)$_2$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 207.8 (C), 206.8 (C), 144.1 (C), 138.2 (C), 137.4 (C), 136.5 (C), 133.1 (CH), 128.8 (CH), 128.6 (2 × CH), 127.7 (CH), 127.6 (CH), 126.3 (2 × CH), 125.7 (CH), 124.4 (CH), 79.8 (C), 53.6 (CH_2), 53.6 (CH), 53.5 (CH_2), 38.1 (CH_2), 30.5 (C), 29.2 (CH_3), 28.4 (CH_3), 21.3 (CH_3); HRMS (ESI) Exact mass calcd for $C_{25}H_{26}O_2Na$ $[M+Na]^+$: 381.1825, found: 381.1819.

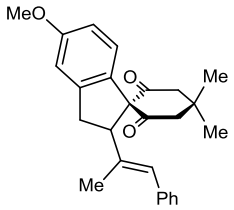


(*E*)-3-{4,4,5'-Trimethyl-2,6-dioxo-2',3'-dihydrospiro[cyclohexane-1,1'-indene]-2'-yl}prop-2-en-1-yl benzoate (3l). The title compound was prepared according to General Procedure B from dione **1b** (115 mg, 0.50 mmol) and 1,3-diene **2k** (141 mg, 0.75 mmol) for a reaction time of 12 h, and purified by column chromatography (7% EtOAc/hexane) to give an off-white solid (154 mg, 74%). R_f = 0.56 (30% EtOAc/hexane); m.p. 108-110 °C (EtOAc/petrol); IR 2962, 1710 (C=O), 1694 (C=O), 1274, 1262, 1227, 1118, 978, 808, 714, 638 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (2H, dt, *J* = 8.4, 1.5 Hz, Ar**H**), 7.60-7.55 (1H, m, Ar**H**), 7.48-7.42 (2H, m, Ar**H**), 7.09 (1H, s, Ar**H**), 7.02 (1H, d, *J* = 7.8 Hz, Ar**H**), 6.92 (1H, d, *J* = 7.8 Hz, Ar**H**), 6.01-5.87 (2H, m, C**H**=C**H**), 4.78 (2H, d, *J* = 5.4 Hz, C**H**$_2$O), 3.69 (1H, q, *J* = 8.6 Hz, ArCH$_2$C**H**), 3.13-3.04 (2H, m, ArC**H**$_2$), 2.78-2.65 (3H, m, 2 × C**H**$_2$C=O), 2.50 (1H, d, *J* = 15.3 Hz, C**H**$_2$C=O), 2.33 (3H, s, ArC**H**$_3$), 1.09 (3H, s, C(C**H**$_3$)$_2$, 1.04 (3H, s, C(C**H**$_3$)$_2$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 207.8 (C), 206.7 (C), 166.2 (C), 144.0 (C), 138.3 (C), 137.7 (C), 134.3 (CH), 133.0 (CH), 130.0 (C), 129.6 (2 × CH), 128.4 (2 × CH), 127.9 (CH), 127.6 (CH), 125.8 (CH), 124.1 (CH), 79.4 (C), 64.7 (CH_2), 53.8 (CH_2), 53.3 (CH_2), 52.4 (CH), 37.7 (CH_2), 30.6 (C), 28.9 (CH_3), 28.7 (CH_3), 21.3 (CH_3); HRMS (ESI) Exact mass calcd for $C_{27}H_{28}O_4Na$ $[M+Na]^+$: 439.1880, found: 439.1882.

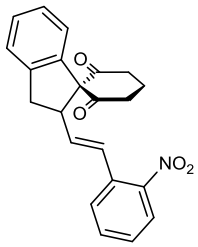


(*E*)-4-{4,4,5'-Trimethyl-2,6-dioxo-2',3'-dihydrospiro[cyclohexane-1,1'-indene]-2'-yl}but-3-en-1-yl benzoate (3m). The title compound was prepared according to General Procedure B from dione **1b** (115 mg, 0.50 mmol) and 1,3-diene **2e** (151 mg, 0.75 mmol) for a reaction time of 12 h, and purified by column chromatography (6% EtOAc/petrol) to give a light yellow viscous liquid (169 mg, 79%). R_f = 0.60 (30% EtOAc/petrol); IR 2989, 2923, 1712 (C=O), 1694 (C=O), 1678 (C=O), 1585, 1560, 1545, 1469,

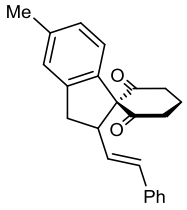
1370, 1276, 1193, 1123, 1069, 968, 703 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.07-8.02 (2H, m, Ar**H**), 7.61-7.55 (1H, m, Ar**H**), 7.49-7.43 (2H, m, Ar**H**), 7.06 (1H, s, Ar**H**), 7.03 (1H, d, *J* = 7.8 Hz, Ar**H**), 6.91 (1H, d, *J* = 7.8 Hz, Ar**H**), 5.79-5.61 (2H, m, C**H**=C**H**), 4.34 (2H, t, *J* = 6.6 Hz, C$\mathbf{H}_2$O), 3.55 (1H, dt, *J* = 9.0, 7.6 Hz, ArCH_2C**H**), 3.05 (1H, dd, *J* = 15.4, 7.6 Hz, ArC$\mathbf{H}_2$), 2.94 (1H, dd, *J* = 15.4, 7.5 Hz, ArC$\mathbf{H}_2$), 2.77 (1H, d, *J* = 15.2 Hz, C$\mathbf{H}_2$C=O), 2.66 (1H, dd, *J* = 15.2, 1.8 Hz, C$\mathbf{H}_2$C=O), 2.60 (1H, dd, *J* = 15.0, 1.8 Hz, C$\mathbf{H}_2$C=O), 2.55-2.43 (3H, m, C$\mathbf{H}_2$C=O and C$\mathbf{H}_2$CH_2O), 2.33 (3H, s, ArC$\mathbf{H}_3$), 1.05 (3H, s, C(C$\mathbf{H}_3$)$_2$), 1.03 (3H, s, C(C$\mathbf{H}_3$)$_2$); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 207.7 (C), 206.5 (C), 164.4 (C), 143.9 (C), 138.0 (C), 137.1 (C), 132.9 (CH), 132.2 (CH), 130.1 (C), 129.5 (2 x CH), 129.4 (CH), 128.3 (2 × CH), 127.5 (CH), 125.5 (CH), 124.5 (CH), 79.7 (C), 64.0 (CH_2), 53.6 (CH_2), 53.4 (CH_2), 53.2 (CH), 38.0 (CH_2), 31.8 (CH_2), 30.4 (C), 29.3 (CH_3), 28.2 (CH_3), 21.3 (CH_3); HRMS (ESI) Exact mass calcd for $C_{28}H_{31}O_4$ $[M+H]^+$: 431.2217, found: 431.2227.



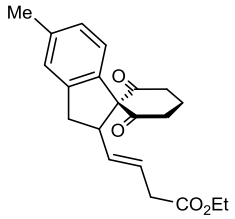
5'-Methoxy-4,4-dimethyl-2'-[(*E*)-1-phenylprop-1-en-2-yl]-2',3'-dihydrospiro[cyclohexane-1,1'-indene]-2,6-dione (3n). The title compound was prepared according to General Procedure B from dione **1c** (123 mg, 0.50 mmol) and 1,3-diene **2h** (108 mg, 0.75 mmol) for a reaction time of 4 h, and purified by column chromatography (7% EtOAc/petrol) to give a light yellow solid (109 mg, 56%). R_f = 0.60 (30% EtOAc/petrol); m.p. 118-120 °C (EtOAc/petrol); IR 2957, 1699 (C=O), 1687 (C=O), 1616, 1493, 1463, 1318, 1257, 1220, 1196, 1082, 1032, 855, 820 748 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.39-7.32 (2H, m, Ar**H**), 7.29-7.20 (3H, m, Ar**H**), 6.92 (1H, d, *J* = 8.4 Hz, Ar**H**), 6.86-6.80 (2H, m, Ar**H**), 6.56 (1H, s, =C**H**Ph), 3.84 (3H, s, OC$\mathbf{H}_3$), 3.68 (1H, dd, *J* = 7.5, 5.0 Hz, CH_2C**H**), 3.19 (1H, dd, *J* = 15.9, 7.6 Hz, C$\mathbf{H}_2$CH), 3.07 (1H, dd, *J* = 15.9, 5.1 Hz, C$\mathbf{H}_2$CH), 3.00 (1H, d, *J* = 15.1 Hz, C$\mathbf{H}_2$C=O), 2.81 (1H, d, *J* = 14.3 Hz, C$\mathbf{H}_2$C=O), 2.65 (1H, dd, *J* = 15.1, 2.8 Hz, C$\mathbf{H}_2$C=O), 2.59 (1H, dd, *J* = 14.2, 2.8 Hz, C$\mathbf{H}_2$C=O), 1.61 (3H, d, *J* = 1.2 Hz, =CC$\mathbf{H}_3$), 1.18 (3H, s, C(C$\mathbf{H}_3$)$_2$), 1.03 (3H, s, C(C$\mathbf{H}_3$)$_2$); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 208.1 (C), 206.7 (C), 159.8 (C), 145.7 (C), 137.5 (C), 136.9 (C), 131.5 (C), 130.5 (CH), 128.9 (2 × CH), 128.2 (2 × CH), 126.8 (CH), 126.5 (CH), 112.8 (CH), 109.2 (CH), 80.5 (C), 61.4 (CH), 55.2 (CH_3), 54.3 (CH_2), 52.8 (CH_2), 35.9 (CH_2), 30.6 (C), 30.5 (CH_3), 27.0 (CH_3), 14.9 (CH_3); HRMS (ESI) Exact mass calcd for $C_{26}H_{28}O_3Na$ $[M+Na]^+$: 411.1931, found: 411.1936.



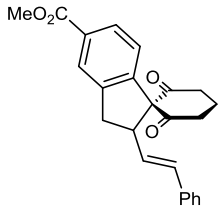
2'-[(*E*)-2-(2-Nitrophenyl)ethenyl]-2',3'-dihydrospiro[cyclohexane-1,1'-indene]-2,6-dione (3o). The title compound was prepared according to General Procedure B from dione **1e** (94 mg, 0.50 mmol) and 1,3-diene **2b** (131 mg, 0.75 mmol) for a reaction time of 2 h, and purified by column chromatography (10% EtOAc/hexane) to give a yellow viscous liquid (110 mg, 61%). R_f = 0.26 (30% EtOAc/hexane); IR 2970, 1722 (C=O), 1694 (C=O), 1606, 1520, 1457, 1344, 1313, 1264, 1204, 1044, 970, 909, 861, 735 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.94 (1H, dd, *J* = 8.2, 1.1 Hz, Ar**H**), 7.56-7.45 (2H, m, Ar**H**), 7.39 (1H, ddd, *J* = 8.6, 7.2, 1.6 Hz, Ar**H**), 7.33-7.21 (3H, m, Ar**H**), 7.07 (1H, d, *J* = 7.3 Hz, Ar**H**), 7.02 (1H, d, *J* = 15.6 Hz, =C**H**Ph), 6.15 (1H, dd, *J* = 15.6, 9.6 Hz, C**H**=CHPh), 3.93-3.84 (1H, m, $ArCH_2C\mathbf{H}$), 3.29 (1H, dd, *J* = 15.5, 7.6 Hz, $ArC\mathbf{H}_2$), 3.14 (1H, dd, *J* = 15.5, 6.3 Hz, $ArC\mathbf{H}_2$), 3.06-2.95 (1H, m, $C\mathbf{H}_2C$=O), 2.90-2.72 (2H, m, $C\mathbf{H}_2C$=O), 2.70-2.59 (1H, m, $C\mathbf{H}_2C$=O), 2.27-2.14 (1H, m, $CH_2C\mathbf{H}_2CH_2$), 2.13-1.98 (1H, m, $CH_2C\mathbf{H}_2CH_2$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 207.4 (C), 206.8 (C), 147.5 (C), 143.5 (C), 140.1 (C), 134.2 (CH), 133.2 (CH), 132.5 (C), 129.1 (CH), 128.4 (CH), 128.3 (CH), 128.2 (CH), 126.9 (CH), 125.2 (CH), 125.0 (CH), 124.5 (CH), 81.7 (C), 52.5 (CH), 39.8 (CH_2), 39.3 (CH_2), 38.1 (CH_2), 17.0 (CH_2); HRMS (ESI) Exact mass calcd for $C_{22}H_{19}NO_4Na$ $[M+Na]^+$: 384.1206, found: 384.1203.



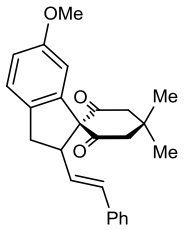
5'-Methyl-2'-[(*E*)-2-phenylethenyl]-2',3'-dihydrospiro[cyclohexane-1,1'-indene]-2,6-dione (3q). The title compound was prepared according to General Procedure B from dione **1f** (101 mg, 0.50 mmol) and 1,3-diene **2a** (98 mg, 0.75 mmol) for a reaction time of 2 h, and purified by column chromatography (9% EtOAc/hexane) to give an off-white solid (120 mg, 73%). R_f = 0.51 (30% EtOAc/hexane); m.p. 142-144 °C (EtOAc/petrol); IR 2929, 1718 (C=O), 1690 (C=O), 1493, 1449, 1413, 1317, 1269, 1223, 1186, 1097, 1075, 815, 753, 746 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.38-7.29 (4H, m, Ar**H**), 7.28-7.23 (1H, m, Ar**H**), 7.12 (1H, s, Ar**H**), 7.05 (1H, d, *J* = 7.8 Hz, Ar**H**), 6.90 (1H, d, *J* = 7.8 Hz, Ar**H**), 6.58 (1H, d, *J* = 15.8 Hz, =C**H**Ph), 6.24 (1H, dd, *J* = 15.8, 9.8 Hz, C**H**=CHPh), 3.82-3.73 (1H, m, C**H**CH=CH), 3.21-3.10 (2H, m, $C\mathbf{H}_2CH$), 2.89-2.70 (3H, m, $C\mathbf{H}_2C$=O), 2.63-2.54 (1H, m, $C\mathbf{H}_2C$=O), 2.36 (3H, s, $C\mathbf{H}_3$), 2.17-2.07 (1H, m, $CH_2C\mathbf{H}_2CH_2$), 2.06-1.97 (1H, m, $CH_2C\mathbf{H}_2CH_2$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 208.7 (C), 207.2 (C), 144.1 (C), 138.2 (C), 138.0 (C), 136.4 (C), 132.9 (CH), 128.6 (2 × CH), 128.6 (CH), 127.8 (CH), 127.7 (CH), 126.4 (2 × CH), 125.6 (CH), 124.5 (CH), 80.9 (C), 54.5 (CH), 40.0 (CH_2), 39.9 (CH_2), 38.3 (CH_2), 21.4 (CH_3), 17.1 (CH_2); HRMS (ESI) Exact mass calcd for $C_{23}H_{22}O_2Na$ $[M+Na]^+$: 353.1512, found: 353.1510.



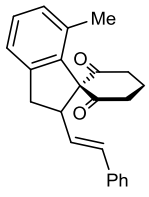
Ethyl (*E*)-4-{5'-methyl-2,6-dioxo-2',3'-dihydrospiro[cyclohexane-1,1'-indene]-2'-yl}but-3-enoate (3r). The title compound was prepared according to General Procedure B from dione **1f** (101 mg, 0.50 mmol) and 1,3-diene **2d** (105 mg, 0.75 mmol) for a reaction time of 12 h, and purified by column chromatography (15% EtOAc/petrol) to give a yellow viscous liquid (100 mg, 59%). R_f = 0.34 (30% EtOAc/petrol); IR 2973, 1732 (C=O), 1718 (C=O), 1693 (C=O), 1496, 1323, 1177, 1022, 990, 823, 640 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.08 (1H, s, Ar**H**), 7.02 (1H, dd, *J* = 7.8, 0.7 Hz, Ar**H**), 6.86 (1H, d, *J* = 7.8 Hz, Ar**H**), 5.81-5.72 (1H, m, =C**H**CH_2), 5.57 (1H, ddt, *J* = 15.3, 9.6, 1.2 Hz, C**H**=$CHCH_2$), 4.14 (2H, q, *J* = 7.1 Hz, C**H**$_2CH_3$), 3.58 (1H, dt, *J* = 9.4, 7.5 Hz, $ArCH_2$C**H**), 3.14-2.94 (4H, m, ArC**H**$_2$ and =CHC**H**$_2$), 2.92-2.58 (4H, m, C**H**$_2CH_2$C**H**$_2$), 2.33 (3H, s, ArC**H**$_3$), 2.22-2.10 (1H, m, CH_2C**H**$_2CH_2$), 2.06-1.93 (1H, m, CH_2C**H**$_2CH_2$), 1.27 (3H, t, *J* = 7.1 Hz, C**H**$_2CH_3$); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 208.6 (C), 207.2 (C), 171.3 (C), 143.9 (C), 138.1 (C), 137.7 (C), 133.2 (CH), 127.6 (CH), 125.6 (CH), 125.5 (CH), 124.6 (CH), 80.8 (C), 60.7 (CH_2), 53.8 (CH), 40.0 (CH_2), 39.7 (CH_2), 38.0 (CH_2), 37.6 (CH_2), 21.3 (CH_3), 17.1 (CH_2), 14.1 (CH_3); HRMS (ESI) Exact mass calcd for $C_{21}H_{25}O_4$ $[M+H]^+$: 341.1747, found: 341.1744.



Methyl 2,6-dioxo-2'-[(*E*)-2-phenylethenyl]-2',3'-dihydrospiro[cyclohexane-1,1'-indene]-5'-carboxylate (3s). The title compound was prepared according to General Procedure B from dione **1g** (123 mg, 0.50 mmol) and 1,3-diene **2a** (98 mg, 0.75 mmol) for a reaction time of 3 h, and purified by column chromatography (12% EtOAc/hexane) to give an off-white solid (101 mg, 54%). R_f = 0.30 (30% EtOAc/hexane); m.p. 138-140 °C (EtOAc/petrol); IR 2989, 1721 (C=O), 1684 (C=O), 1653, 1558, 1506, 1436, 1294, 1198, 986, 765, 751, 656, 640 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (1H, s, Ar**H**), 7.94 (1H, d, *J* = 8.0 Hz, Ar**H**), 7.37-7.23 (5H, m, Ar**H**), 7.07 (1H, d, *J* = 8.0 Hz, Ar**H**), 6.61 (1H, d, *J* = 15.7 Hz, =C**H**Ph), 6.16 (1H, dd, *J* = 15.7, 9.9 Hz, C**H**=CHPh), 3.92 (3H, s, OC**H**$_3$), 3.76 (1H, dt, *J* = 9.7, 7.4 Hz, $ArCH_2$C**H**), 3.25 (1H, dd, *J* = 15.6, 7.5 Hz, ArC**H**$_2$), 3.14 (1H, dd, *J* = 15.6, 7.3 Hz, ArC**H**$_2$), 2.92-2.68 (3H, m, C**H**$_2CH_2$C**H**$_2$), 2.66-2.56 (1H, m, C**H**$_2CH_2$C**H**$_2$), 2.23-2.10 (1H, m, CH_2C**H**$_2CH_2$), 2.08-1.93 (1H, m, CH_2C**H**$_2CH_2$); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 207.7 (C), 206.2 (C), 166.8 (C), 145.6 (C), 144.4 (C), 136.0 (C), 133.4 (CH), 130.2 (C), 128.6 (2 × CH), 128.4 (CH), 128.0 (CH), 127.6 (CH), 126.4 (2 × CH), 125.9 (CH), 125.3 (CH), 81.2 (C), 55.0 (CH), 52.1 (CH_3), 40.1 (CH_2), 39.6 (CH_2), 38.1 (CH_2), 17.1 (CH_2); HRMS (ESI) Exact mass calcd for $C_{24}H_{22}O_4Na$ $[M+Na]^+$: 397.1410, found: 397.1415.

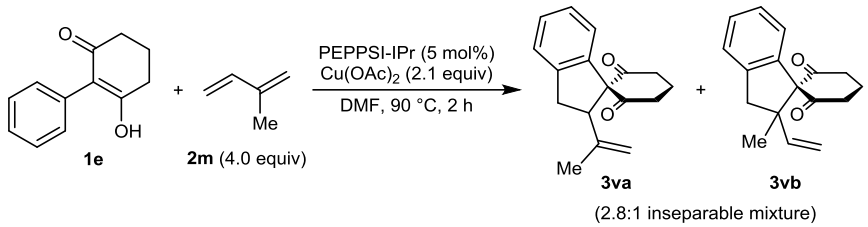


6'-Methoxy-4,4-dimethyl-2'-[(*E*)-2-phenylethenyl]-2',3'-dihydrospiro[cyclohexane-1,1'-indene]-2,6-dione (3t). The title compound was prepared according to General Procedure B from dione **1d** (125 mg, 0.50 mmol) and 1,3-diene **2a** (98 mg, 0.75 mmol) for a reaction time of 3 h, and purified by column chromatography (5% EtOAc/petrol) to give an off-white solid (87 mg, 46%). R_f = 0.63 (30% EtOAc/petrol); m.p. 178-180 °C (EtOAc/petrol); IR 2958, 1688 (C=O), 1600, 1487, 1465, 1330, 1220, 1025, 970, 829, 752, 643, 639 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.22 (5H, m, Ar**H**), 7.20 (1H, d, *J* = 8.3 Hz, Ar**H**), 6.85 (1H, dd, *J* = 8.3, 2.4 Hz, Ar**H**), 6.62-6.55 (2H, m, Ar**H** and =C**H**Ph), 6.25 (1H, dd, *J* = 15.8, 9.8 Hz, C**H**=CHPh), 3.86-3.72 (1H, m, CH_2C**H**), 3.81 (3H, s, OC**H**$_3$), 3.23-3.01 (2H, m, C**H**$_2$CH), 2.82 (1H, d, *J* = 15.4 Hz, C**H**$_2$$CH_2$C**H**$_2$), 2.74-2.65 (2H, m, C**H**$_2$$CH_2$C**H**$_2$), 2.52 (1H, d, *J* = 15.2 Hz, C**H**$_2$$CH_2$C**H**$_2$), 1.09 (3H, s, CC**H**$_3$), 1.05 (3H, s, CC**H**$_3$); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 207.6 (C), 206.5 (C), 158.6 (C), 141.4 (C), 136.4 (C), 136.0 (C), 133.1 (CH), 128.7 (CH), 128.6 (2 × CH), 127.8 (CH), 126.4 (2 × CH), 125.4 (CH), 113.7 (CH), 111.0 (CH), 80.2 (C), 55.4 (CH_3), 54.2 (CH), 53.7 (CH_2), 53.6 (CH_2), 37.4 (CH_2), 30.5 (C), 29.4 (CH_3), 28.3 (CH_3); HRMS (ESI) Exact mass calcd for $C_{25}H_{26}O_3Na$ $[M+Na]^+$: 397.1774, found: 397.1779.



7'-Methyl-2'-[(*E*)-2-phenylethenyl]-2',3'-dihydrospiro[cyclohexane-1,1'-indene]-2,6-dione (3u). The title compound was prepared according to General Procedure B from dione **1h** (101 mg, 0.50 mmol) and 1,3-diene **2a** (98 mg, 0.75 mmol) for a reaction time of 16 h, and purified by column chromatography (7% EtOAc/petrol) to give an off-white solid (99 mg, 60%). R_f = 0.67 (30% EtOAc/petrol); m.p. 156-158 °C (EtOAc/petrol); IR 2988, 1717 (C=O), 1689 (C=O), 1558, 1506, 1394, 1319, 1260, 1231, 1074, 867, 754, 658 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.27 (5H, m, Ar**H**), 7.23 (1H, t, *J* = 7.5 Hz, Ar**H**), 7.14 (1H, d, *J* = 7.4 Hz, Ar**H**), 7.05 (1H, d, *J* = 7.4 Hz, Ar**H**), 6.62 (1H, d, *J* = 15.7 Hz, =C**H**Ph), 6.17 (1H, dd, *J* = 15.7, 10.3 Hz, C**H**=CHPh), 3.58-3.47 (1H, m, ArCH_2C**H**), 3.24 (1H, dd, *J* = 15.6, 7.8 Hz, ArC**H**$_2$), 3.08 (1H, dd, *J* = 15.6, 8.3 Hz, ArC**H**$_2$), 2.93-2.72 (3H, m, C**H**$_2$$CH_2$C**H**$_2$), 2.63 (1H, ddd, *J* = 16.9, 11.5, 5.6 Hz, C**H**$_2$$CH_2$C**H**$_2$), 2.28-2.12 (1H, m, CH_2C**H**$_2$$CH_2$), 2.06-1.92 (1H, m, CH_2C**H**$_2$$CH_2$), 1.97 (3H, s, C**H**$_3$); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 209.5 (C), 207.6 (C), 144.3 (C), 140.4 (C), 136.0 (C), 133.6 (C), 133.4 (CH), 128.7 (2 × CH), 128.62 (CH), 128.57 (CH), 128.47 (CH), 128.1 (CH), 126.4 (2 × CH), 121.7 (CH), 80.9 (C), 56.9 (CH), 40.8 (CH_2), 39.9 (CH_2), 39.0 (CH_2), 20.6 (CH_3), 17.4 (CH_2); HRMS (ESI) Exact mass calcd for $C_{23}H_{22}O_2Na$ $[M+Na]^+$: 353.1512, found: 353.1513.

2'-(Prop-1-en-2-yl)-2',3'-dihydrospiro[cyclohexane-1,1'-indene]-2,6-dione (3va) and 2'-methyl-2'-vinyl-2',3'-dihydrospiro[cyclohexane-1,1'-indene]-2,6-dione (3vb)

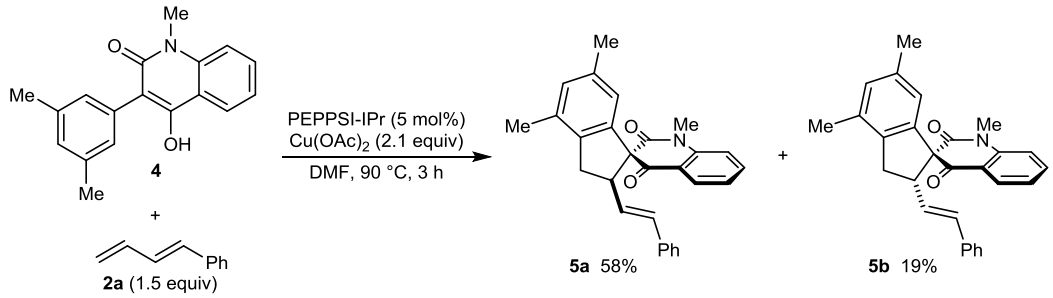


A slight modification of General Procedure B (in that the quantity of the 1,3-diene was increased) was followed using dione **1e** (94 mg, 0.50 mmol) and isoprene (**2m**) (0.2 mL, 2.0 mmol) for a reaction time of 2 h and purified by column chromatography (10% EtOAc/petrol) to give a 2.8:1 inseparable mixture of spiroindanes **3va** and **3vb**, respectively, as a pale yellow gum (70 mg; additional inseparable, unidentified impurities were also present, and therefore the yield was calculated by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. Yield = 50%). R_f = 0.40 (20% EtOAc/petrol); IR 3011, 2962, 2929, 2360, 2340, 1722 (C=O), 1695 (C=O), 1460, 1422, 1378, 1315, 1281, 928, 907, 660 cm^{-1}; HRMS (ESI) Exact mass calcd for $C_{17}H_{19}O_2$ $[M+H]^+$: 255.1380, found 255.1391.

Major product **3va**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.14 (3H, m, Ar**H**), 7.03 (1H, d, *J* = 7.5 Hz, Ar**H**), 4.91 (2H, s, =C**H**$_2$), 3.85 (1H, t, *J* = 7.4 Hz, ArCH$_2$C**H**), 3.24-3.19 (1H, m, ArC**H**$_2$), 3.13 (1H, dd, *J* = 15.4, 7.7 Hz, ArC**H**$_2$), 2.99-2.92 (1H, m, C**H**$_2$CH$_2$C**H**$_2$), 2.85-2.65 (3H, m, C**H**$_2$CH$_2$C**H**$_2$), 2.25-1.97 (2H, m, CH$_2$C**H**$_2$CH$_2$), 1.52 (3H, s, C**H**$_3$); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 208.1 (C), 206.3 (C), 144.1 (C), 144.0 (C), 140.8 (C), 128.2 (CH), 126.5 (CH), 124.7 (CH), 124.5 (CH), 114.4 (CH$_2$), 80.5 (C), 56.1 (CH), 39.5 (2 × CH$_2$), 35.9 (CH$_2$), 21.2 (CH$_3$), 17.3 (CH$_2$).

Minor product **3vb**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.14 (3H, m, Ar**H**), 6.94 (1H, d, *J* = 7.3 Hz, Ar**H**), 6.03 (1H, dd, *J* = 10.6, 17.5 Hz, C**H**=CH$_2$), 5.34-5.26 (2H, m, CH=C**H**$_2$), 3.22 (1H, d, *J* = 15.3 Hz, ArC**H**$_2$), 2.99-2.92 (1H, m, C**H**$_2$CH$_2$C**H**$_2$), 2.85-2.65 (4H, m, 3 of C**H**$_2$CH$_2$C**H**$_2$ and 1 of ArC**H**$_2$), 2.25-1.97 (2H, m, CH$_2$C**H**$_2$CH$_2$), 1.17 (3H, s, C**H**$_3$); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 207.4 (C), 206.6 (C), 143.3 (C), 142.5 (CH), 139.9 (C), 127.9 (CH), 126.6 (CH), 126.4 (CH), 124.3 (CH), 115.7 (CH$_2$), 85.0 (C), 55.3 (C), 45.7 (CH$_2$), 40.6 (CH$_2$), 40.4 (CH$_2$), 22.1 (CH$_3$), 17.4 (CH$_2$).

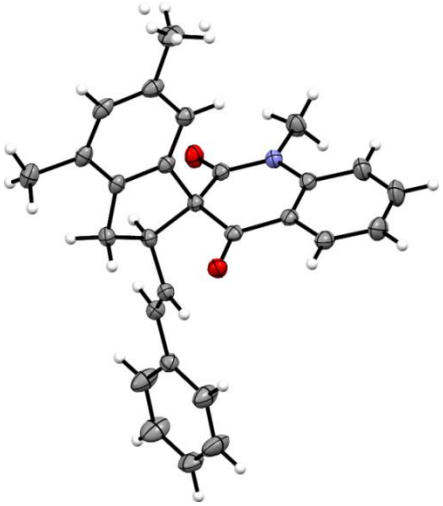
(±)-(1*R*,2*R*)-1',4,6-Trimethyl-2-[(*E*)-2-phenylethenyl]-2,2',3,4'-tetrahydro-1'*H*-spiro[indene-1,3'-quinoline]-2',4'-dione (5a) and (±)-(1*R*,2*S*)-1',4,6-trimethyl-2-[(*E*)-2-phenylethenyl]-2,2',3,4'-tetrahydro-1'*H*-spiro[indene-1,3'-quinoline]-2',4'-dione (5b)

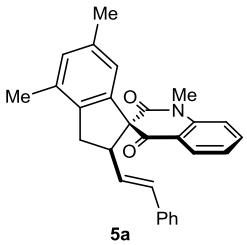


To a mixture of the ketoamide **4** (140 mg, 0.50 mmol), $Cu(OAc)_2$ (191 mg, 1.05 mmol), and PEPPSI-IPr (17.0 mg, 0.025 mmol) in degassed DMF (1 mL) was added the diene **2a** (98 mg, 0.75 mmol) in degassed DMF (0.5 mL), and the resulting mixture was stirred at 90 ºC for 3 h. The reaction was filtered through a pad of silica gel eluting with Et_2O (100 mL), the diethyl ether solvent was washed with H_2O (50 mL), and brine (20 mL). The organic layer was dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification of the residue by column chromatography (5% EtOAc/petrol) gave the *spiroindane* **5b** (38 mg, 19%) as a pale yellow amorphous solid followed by the *spiroindane* **5a** (118 mg, 58%) as an off-white solid.

Data for **5a**: R_f = 0.20 (10% EtOAc/petrol); m.p. 170-172 °C (EtOAc/petrol); IR 1691 (C=O), 1658, 1599, 1468, 1349, 1302, 1173, 983, 753 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (1H, dd, *J* = 7.7, 1.6 Hz, Ar**H**), 7.63 (1H, ddd, *J* = 8.7, 7.4, 1.7 Hz, Ar**H**), 7.26-7.13 (7H, m, Ar**H**), 6.91 (1H, s, Ar**H**), 6.58 (1H, d, *J* = 15.8 Hz, =C**H**Ph), 6.53 (1H, s, Ar**H**), 6.45 (1H, dd, *J* = 15.8, 9.0 Hz, C**H**=CHPh), 4.33-4.26 (1H, m, CH_2C**H**), 3.59 (3H, s, NC**H**$_3$), 3.35 (1H, dd, *J* = 15.2, 10.5 Hz, C**H**$_2$CH), 3.17 (1H, dd, *J* = 15.2, 8.1 Hz, C**H**$_2$CH), 2.30 (3H, s, ArC**H**$_3$), 2.21 (3H, s, ArC**H**$_3$); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 193.4 (C), 172.0 (C), 143.5 (C), 142.1 (C), 140.2 (C), 136.9 (C), 136.7 (C), 136.1 (CH), 134.5 (C), 132.6 (CH), 130.5 (CH), 128.5 (CH), 128.4 (2 × CH), 128.2 (CH), 127.3 (CH), 126.3 (2 × CH), 123.2 (CH), 121.0 (CH), 120.7 (C), 114.8 (CH), 73.5 (C), 54.6 (CH), 36.6 (CH_2), 30.3 (CH_3), 21.2 (CH_3), 19.2 (CH_3); HRMS (ESI) Exact mass calcd for $C_{28}H_{26}NO_2$ $[M+H]^+$: 408.1958, found: 408.1966.

Vapor diffusion of petrol into a solution of **5a** in EtOAc gave crystals that were suitable for X-ray crystallography.

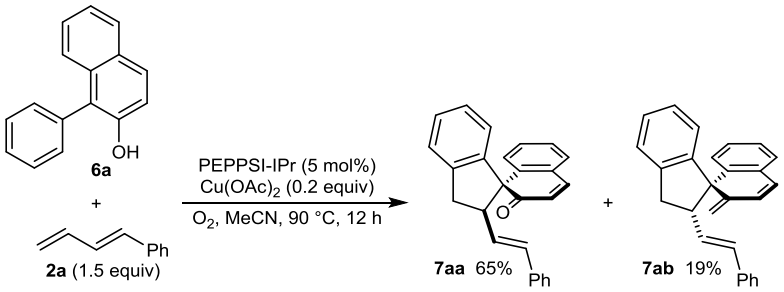




5a
CCDC 992453

Data for **5b**: R_f = 0.21 (10% EtOAc/petrol); IR 3021, 1692 (C=O), 1658, 1599, 1470, 1348, 970, 747 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.12 (1H, dd, *J* = 7.7, 1.6 Hz, Ar**H**), 7.64 (1H, ddd, *J* = 8.8, 7.4, 1.7 Hz, Ar**H**), 7.27-7.16 (6H, m, Ar**H** and C**H**=C**H**Ph), 7.12 (1H, d, *J* = 8.3 Hz, Ar**H**), 6.93 (1H, s, Ar**H**), 6.50 (1H, s, Ar**H**), 6.43 (1H, d, *J* = 2.4 Hz, Ar**H**), 6.42 (1H, s, Ar**H**), 4.15-4.05 (1H, m, CH_2C**H**), 3.43-3.31 (1H, m, C**H**$_2$CH), 3.39 (3H, s, NC**H**$_3$), 3.17 (1H, dd, *J* = 15.1, 8.1 Hz, C**H**$_2$CH), 2.30 (3H, s, ArC**H**$_3$), 2.22 (3H, s, ArC**H**$_3$); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 195.7 (C), 170.3 (C), 143.8 (C), 142.5 (C), 140.4 (C), 136.9 (C), 136.8 (C), 136.3 (CH), 134.1 (C), 132.9 (CH), 130.5 (CH), 128.4 (2 × CH), 128.3 (CH), 128.1 (CH), 127.4 (CH), 126.2 (2 × CH), 123.0 (CH), 121.5 (CH), 121.2 (C), 114.8 (CH), 73.5 (C), 54.3 (CH), 36.8 (CH_2), 29.5 (CH_3), 21.2 (CH_3), 19.3 (CH_3); HRMS (ESI) Exact mass calcd for $C_{28}H_{26}NO_2$ $[M+H]^+$: 408.1958, found: 408.1969.

(±)-(1*S*,2*R*)-2-[(*E*)-2-Phenylethenyl]-2,3-dihydro-2'*H*-spiro[indene-1,1'-naphthalene]-2'-one (7aa) and (±)-(1*S*,2*S*)-2-[(*E*)-2-phenylethenyl]-2,3-dihydro-2'*H*-spiro[indene-1,1'-naphthalene]-2'-one (7ab)

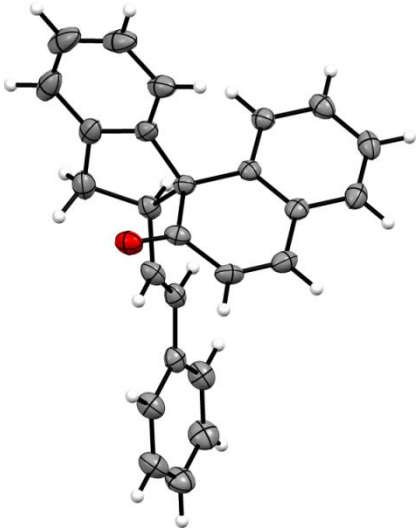


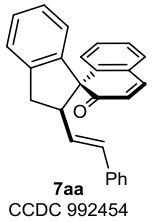
To a mixture of the 1-phenyl-2-naphthol (**6a**) (110 mg, 0.50 mmol), $Cu(OAc)_2$ (18.2 mg, 0.10 mmol), and PEPPSI-IPr (17.0 mg, 0.025 mmol) in MeCN (2.0 mL) at room temperature was added a solution

of 1,3-diene **2a** (97.5 mg, 0.75 mmol) in MeCN (0.5 mL), and the resulting mixture was stirred at 90 ºC for 12 h under an O_2 atmosphere (balloon). The reaction was filtered through a pad of silica gel eluting with Et_2O (100 mL) and concentrated *in vacuo*. Purification of the residue by column chromatography (3% acetone/petrol) gave the *spiroindane* **7aa** (113 mg, 65%) as a pale yellow solid followed by the *spiroindane* **7ab** (33 mg, 19%) as an amorphous pale yellow solid.

Data for **7aa**: R_f = 0.40 (10% acetone/petrol); m.p. 108-110 °C (EtOAc/petrol); IR 1697 (C=O), 1650, 1617, 1560, 1545, 1481, 1430, 1394, 816, 773 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.46-7.17 (13H, m, Ar**H** and C**H**=CHC=O), 6.80 (1H, d, *J* = 7.5 Hz, Ar**H**), 6.24-6.10 (3H, m, CH=C**H**C=O and C**H**=C**H**Ph), 3.60-3.45 (2H, m, C$\mathbf{H}_2$C**H**), 3.15 (1H, dd, *J* = 14.0, 6.3 Hz, C$\mathbf{H}_2$); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 200.3 (C), 146.0 (C), 145.4 (C), 145.3 (CH), 145.1 (C), 136.9 (C), 131.4 (CH), 130.9 (C), 130.0 (CH), 128.9 (CH), 128.8 (CH), 128.4 (2 × CH), 127.8 (CH), 127.4 (CH), 127.3 (CH), 127.2 (CH), 126.9 (CH), 126.3 (2 × CH), 125.2 (CH), 124.9 (CH), 124.4 (CH), 69.4 (C), 64.2 (CH), 36.3 (CH_2); HRMS (ESI) Exact mass calcd for $C_{26}H_{20}ONa$ $[M+Na]^+$: 371.1406, found: 371.1388.

Vapor diffusion of petrol into a solution of **7aa** in EtOAc gave crystals that were suitable for X-ray crystallography.



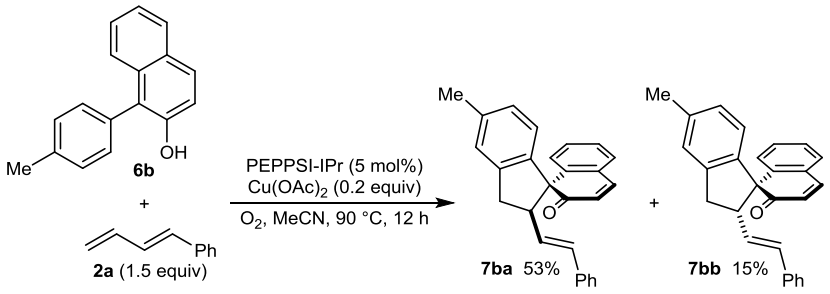


7aa
CCDC 992454

Data for **7ab**: R_f = 0.38 (10% acetone/petrol); IR 2900, 1698 (C=O), 1658, 1565, 1479, 1448, 1395, 1248, 1204, 966, 909, 759, 728 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 (1H, d, *J* = 9.8 Hz, C**H**=CHC=O), 7.42 (1H, d, *J* = 7.4 Hz, Ar**H**), 7.39-7.16 (8H, m, Ar**H**), 7.07-7.01 (2H, m, Ar**H**), 6.98 (1H, d, *J* = 7.5 Hz, Ar**H**), 6.68-6.62 (1H, m, Ar**H**), 6.35 (1H, d, *J* = 15.8 Hz, =C**H**Ph), 6.34 (1H, d, *J* = 9.8 Hz, =C**H**C=O), 5.48 (1H, dd, *J* = 15.8, 9.1 Hz, C**H**=CHPh), 3.70-3.60 (1H, m, CH_2C**H**), 3.28 (1H, dd, *J* = 15.8, 7.8 Hz, C$\mathbf{H}_2$), 3.15 (1H, dd, *J* = 15.8, 10.2 Hz, C$\mathbf{H}_2$); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ

204.1 (C), 145.8 (CH), 144.8 (C), 144.0 (C), 141.7 (C), 136.8 (C), 132.4 (CH), 130.1 (C), 129.5 (CH), 129.4 (CH), 128.4 (2 × CH), 128.3 (C), 128.0 (CH), 127.70 (CH), 127.65 (CH), 127.3 (CH), 127.2 (CH), 126.1 (2 × CH), 125.8 (CH), 125.6 (CH), 124.3 (CH), 70.3 (C), 59.8 (CH), 37.6 (CH_2); HRMS (ESI) Exact mass calcd for $C_{26}H_{20}ONa$ $[M+Na]^+$: 371.1406, found: 371.1399.

(±)-(1*S*,2*R*)-2-[(*E*)-2-(4-Methylphenyl)ethenyl]-2,3-dihydro-2'*H*-spiro[indene-1,1'-naphthalene]-2'-one (7ba) and (±)-(1*S*,2*S*)-2-[(*E*)-2-4-(methylphenyl)ethenyl]-2,3-dihydro-2'*H*-spiro[indene-1,1'-naphthalene]-2'-one (7bb)

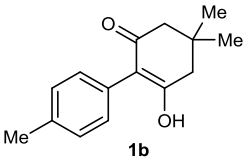


To a mixture of the 1-*p*-tolyl-2-naphthol (**6b**) (117 mg, 0.50 mmol), $Cu(OAc)_2$ (18.2 mg, 0.10 mmol), and PEPPSI-IPr (17.0 mg, 0.025 mmol) in MeCN (2.0 mL) at room temperature was added a solution of 1,3-diene **2a** (97.5 mg, 0.75 mmol) in MeCN (0.5 mL), and the resulting mixture was stirred at 90 ºC for 12 h under an O_2 atmosphere (balloon). The reaction was filtered through a pad of silica gel eluting with Et_2O (100 mL) and concentrated *in vacuo*. Purification of the residue by column chromatography (2% EtOAc/petrol) gave the *spiroindane* **7ba** (96 mg, 53%) as a pale yellow solid followed by the *spiroindane* **7bb** (27 mg, 15%) as an amorphous pale yellow solid.

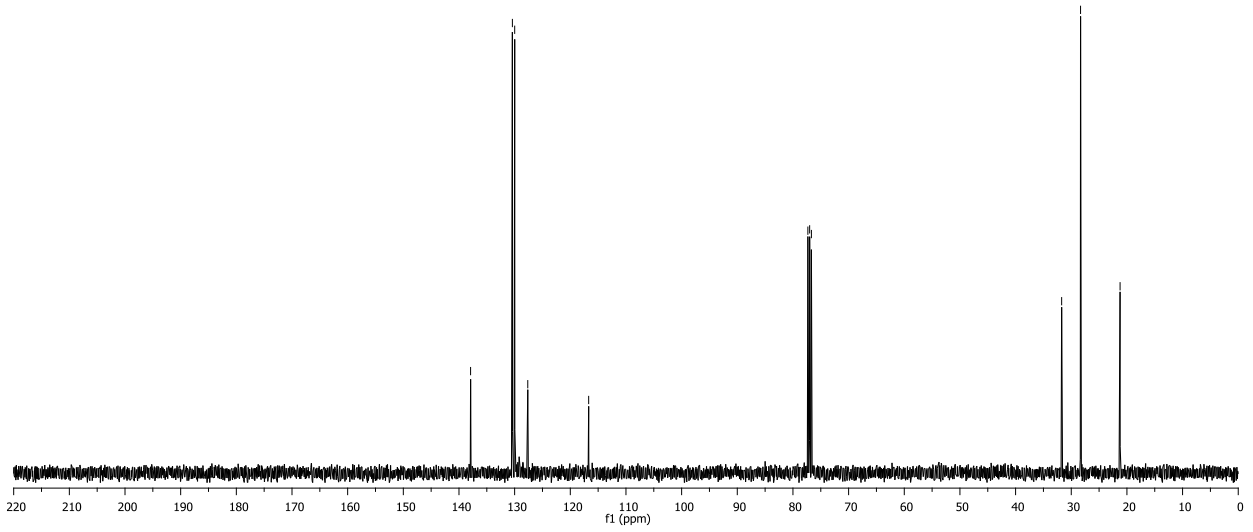
Data for **7ba**: R_f = 0.30 (5% EtOAc/petrol); m.p. 117-119 °C (EtOAc/petrol); IR 2905, 1700 (C=O), 1652, 1617, 1565, 1492, 1448, 1396, 974 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (1H, d, *J* = 9.8 Hz, C**H**=CHC=O), 7.40-7.36 (1H, m, Ar**H**), 7.35-7.31 (2H, m, Ar**H**), 7.30-7.17 (7H, m, Ar**H**), 7.01 (1H, d, *J* = 7.7 Hz, Ar**H**), 6.67 (1H, d, *J* = 7.7 Hz, Ar**H**), 6.21-6.08 (3H, m, =C**H**C=O and C**H**=C**H**Ph), 3.56-3.37 (2H, m, C$\mathbf{H}_2$C**H**), 3.09 (1H, dd, *J* = 14.5, 6.8 Hz, C$\mathbf{H}_2$), 2.41 (3H, s, C$\mathbf{H}_3$); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 200.6 (C), 145.5 (C), 145.3 (CH), 143.0 (C), 137.6 (C), 136.9 (C), 131.3 (CH), 130.9 (C), 130.0 (CH), 128.9 (CH), 128.7 (CH), 128.4 (2 × CH), 127.8 (CH), 127.6 (CH), 127.3 (CH), 127.1 (CH), 126.3 (2 × CH), 125.21 (CH), 125.20 (CH), 124.6 (CH), 69.1 (CH), 64.5 (C), 36.2 (CH_2), 21.4 (CH_3), one quaternary carbon (C) could not be located due to a likely overlap with another signal; HRMS (ESI) Exact mass calcd for $C_{27}H_{23}O$ $[M+H]^+$: 363.1743, found: 363.1741.

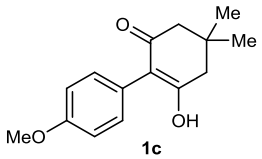
Data for **7bb**: R_f = 0.28 (5% EtOAc/petrol); IR 2924, 1700 (C=O), 1659, 1617, 1563, 1493, 1448, 1395, 1240, 964 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 (1H, d, *J* = 9.8 Hz, C**H**=CHC=O), 7.34 (1H, dd, *J* = 7.3, 1.7 Hz, Ar**H**), 7.31 (1H, dd, *J* = 7.2, 1.4 Hz, Ar**H**), 7.29-7.15 (5H, m, Ar**H**), 7.10 (1H, d, *J* = 7.7 Hz, Ar**H**), 7.04-6.99 (2H, m, Ar**H**), 6.85 (1H, d, *J* = 7.8 Hz, Ar**H**), 6.68-6.63 (1H, m, Ar**H**), 6.35-6.28 (2H, m, CH=C**H**Ph and =C**H**C=O), 5.45 (1H, dd, *J* = 15.7, 9.2 Hz, C**H**=CHPh), 3.67-3.56 (1H, m, CH_2C**H**), 3.22 (1H, dd, *J* = 15.8, 7.8 Hz, C$\mathbf{H}_2$), 3.10 (1H, dd, *J* = 15.8, 10.2 Hz, C$\mathbf{H}_2$), 2.42 (3H, s, C$\mathbf{H}_3$); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 204.4 (C), 145.8 (CH), 144.1 (C), 142.0 (C), 141.8 (C), 137.8 (C), 136.9 (C), 132.3 (CH), 130.1 (C), 129.5 (CH), 129.4 (CH), 128.7 (CH), 128.4 (2 × CH), 128.3 (CH), 127.9 (CH), 127.3 (CH), 127.2 (CH), 126.1 (2 × CH), 125.7 (CH), 125.5 (CH), 125.0 (CH), 70.0 (C), 60.0 (CH), 37.5 (CH_2), 21.4 (CH_3); HRMS (ESI) Exact mass calcd for $C_{27}H_{23}O$ $[M+H]^+$: 363.1743, found: 363.1734.

NMR Spectra of New Compounds



1b

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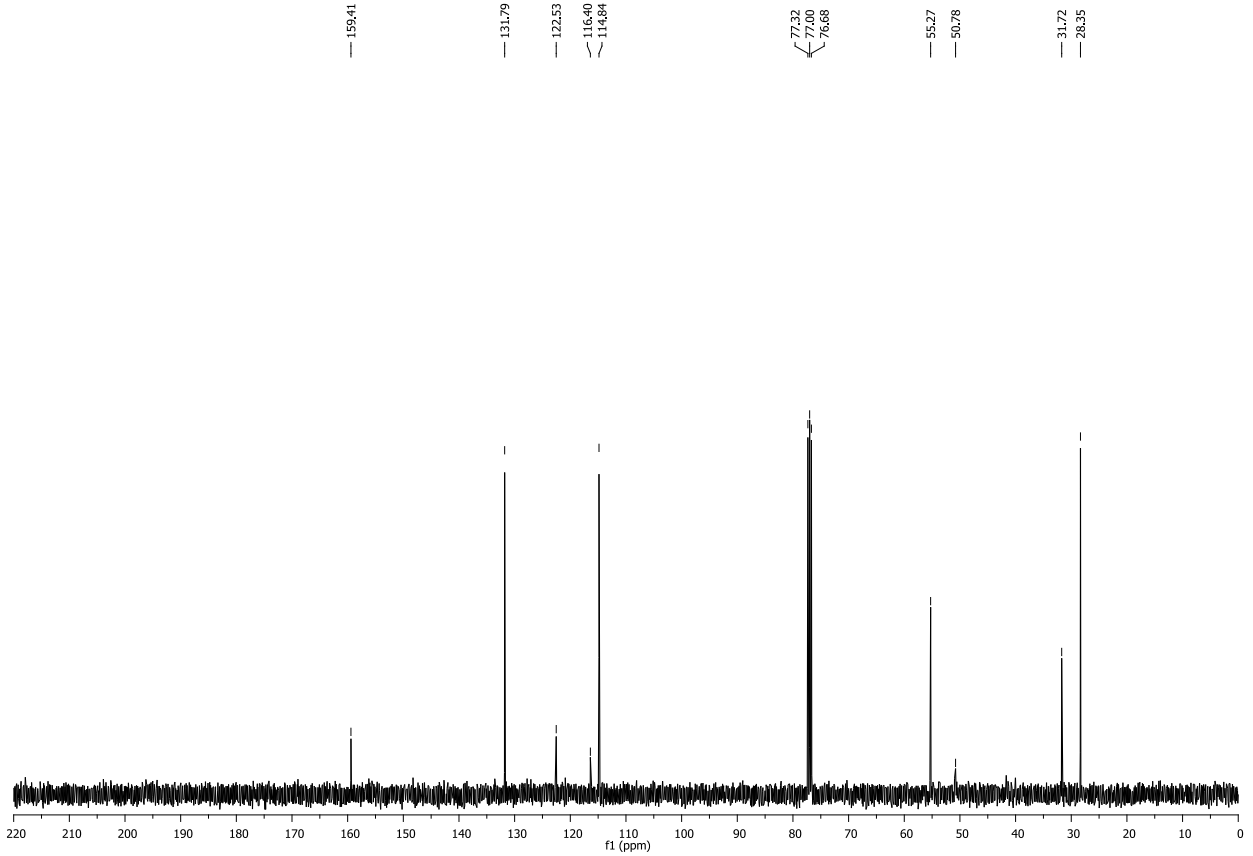
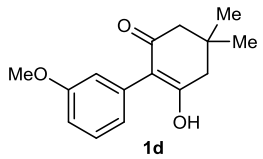
Me
Me
OH
MeO

1c

1.88
1.93
0.89
3.05
4.09
6.00
f1 (ppm)


159.41
131.79
122.53
116.40
114.84
77.32
77.00
76.68
55.27
50.78
31.72
28.35
f1 (ppm)


O
Me
Me
MeO
OH

1d

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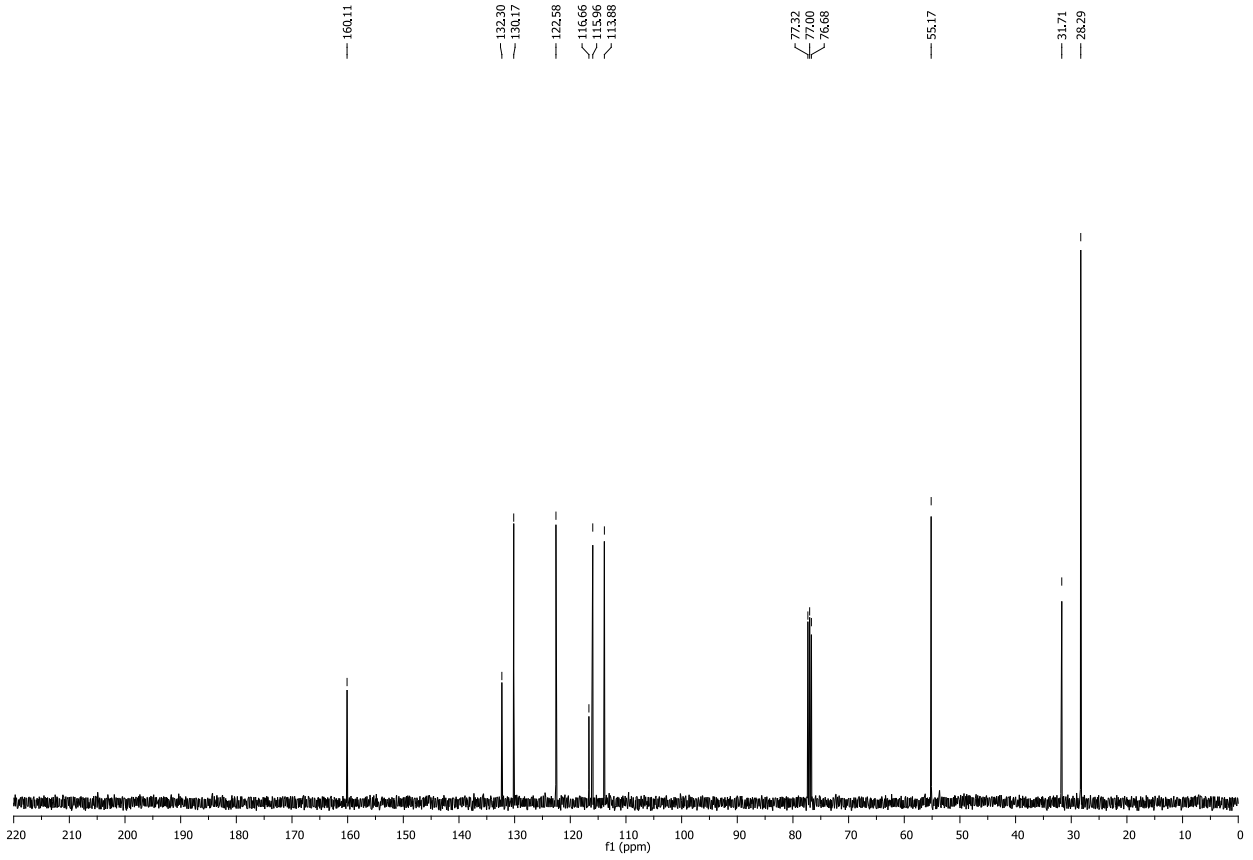
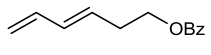
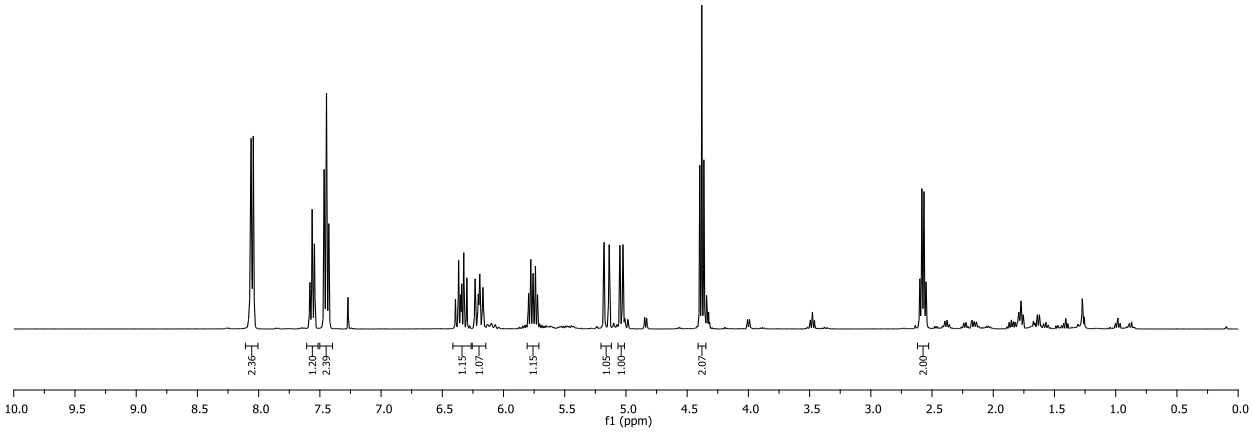
0.93
0.98
0.89
0.90
3.07
4.11
6.00
f1 (ppm)

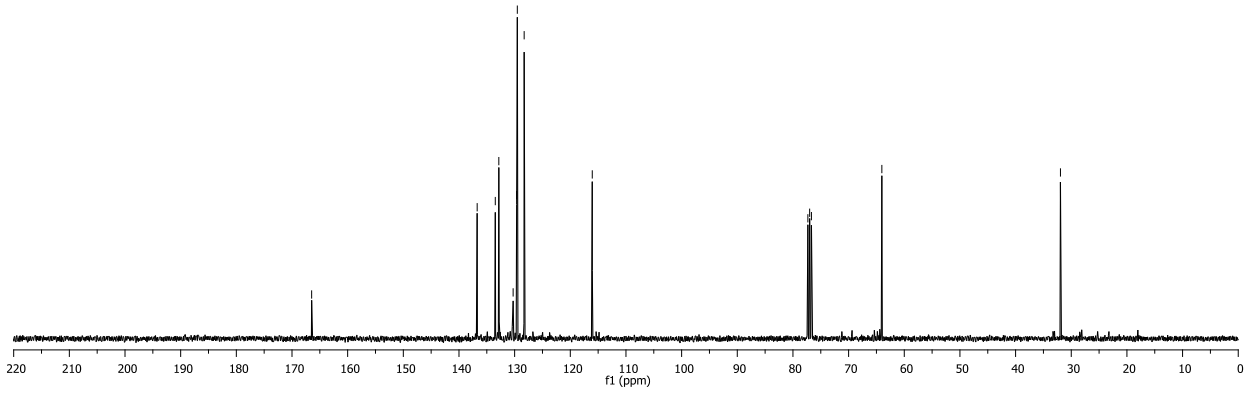

160.11
132.30
130.17
122.58
116.66
115.96
113.88
77.32
77.00
76.68
55.17
31.71
28.29
f1 (ppm)


OBz

2e


2.36
1.20
2.39
1.15
1.07
1.15
1.05
1.00
2.07
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


166.47
136.73
132.84
130.27
129.64
129.52
128.29
116.05
77.32
77.00
76.68
64.03
31.94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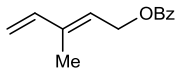
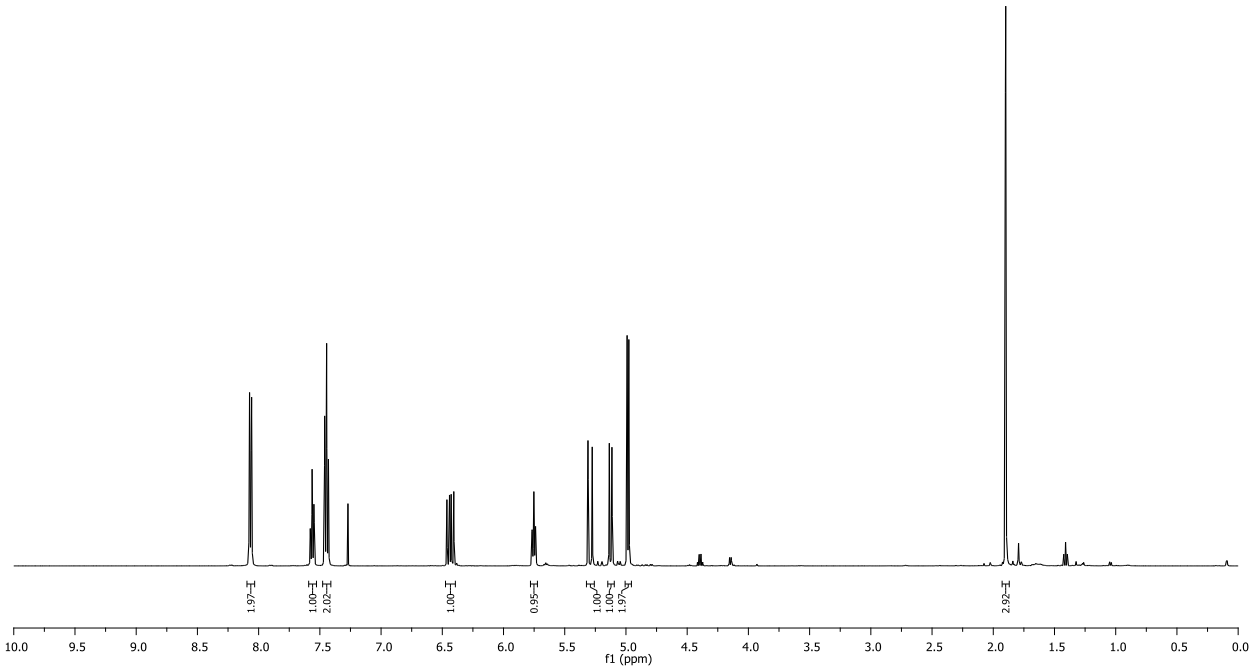
f1 (ppm)


OBz
Me

2i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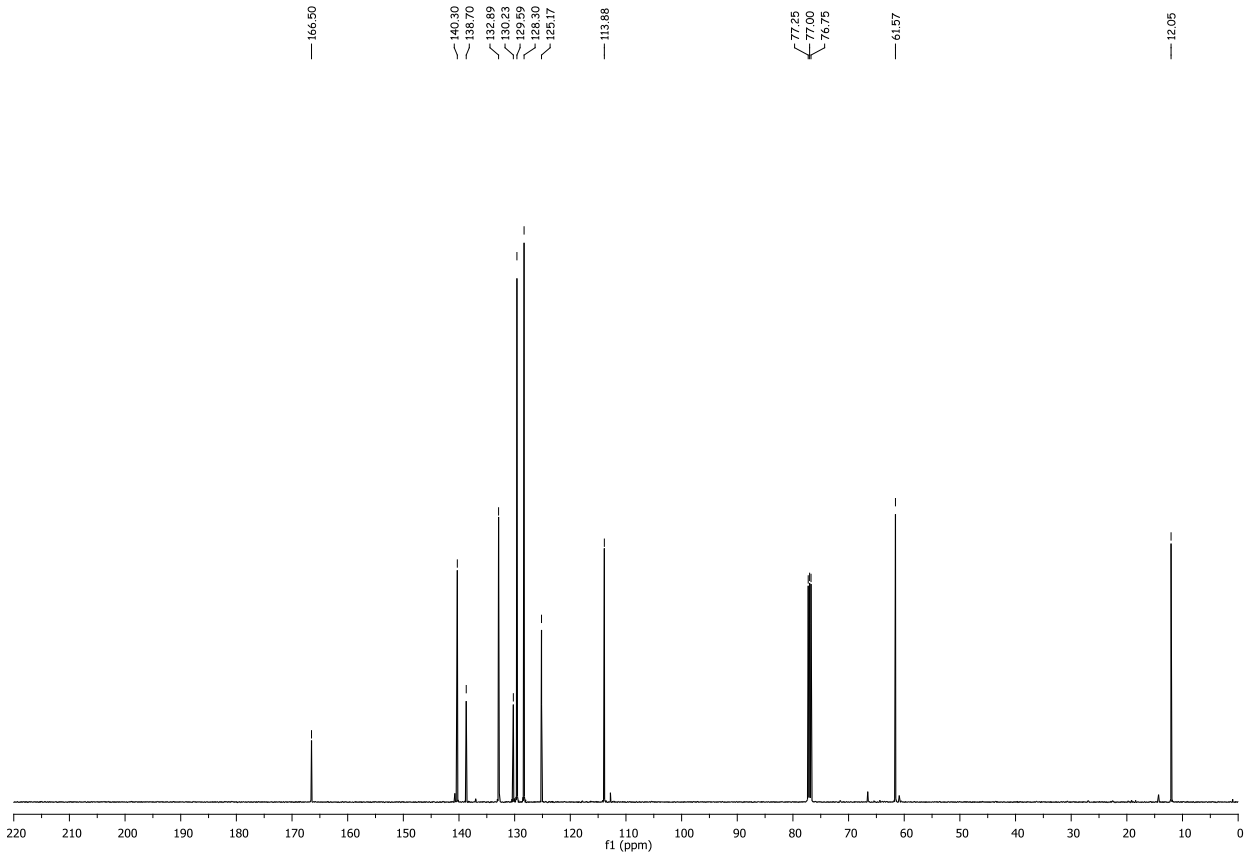
1.00
0.95
1.00
1.00
1.97
2.92
f1 (ppm)


166.50
140.30
138.70
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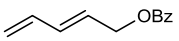
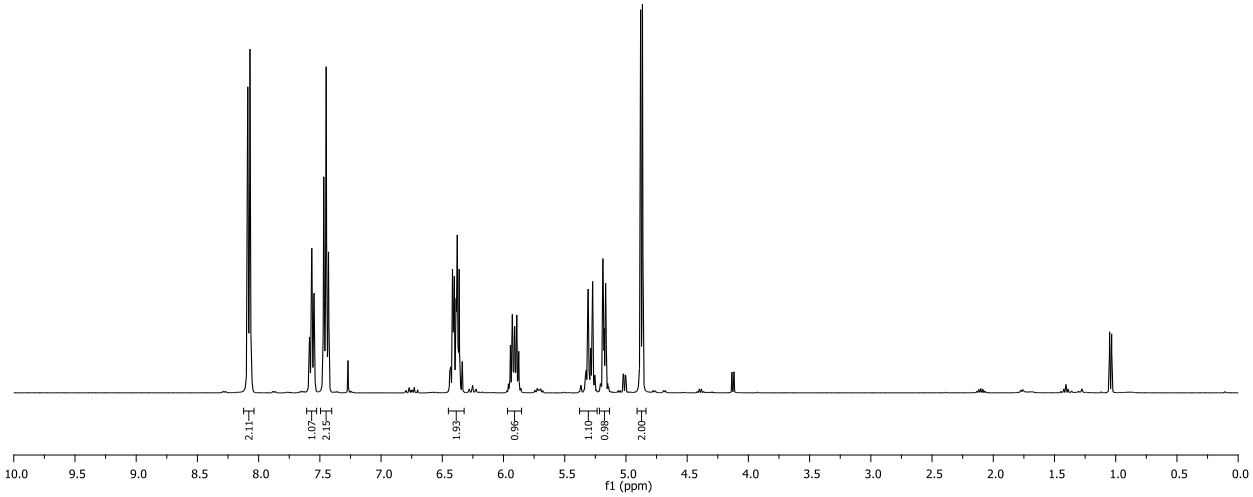
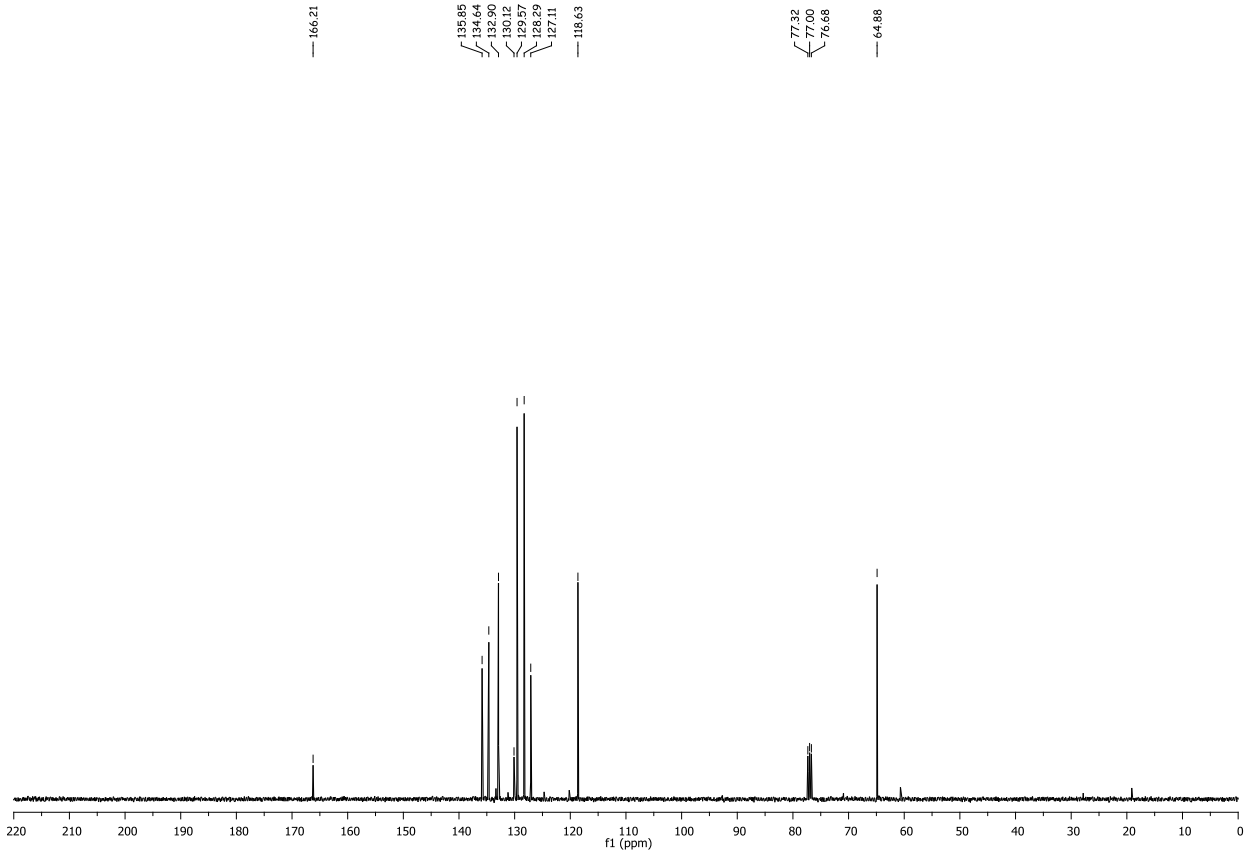
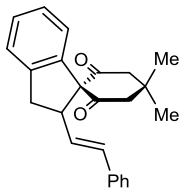
130.23
129.59
128.30
125.17
113.88
77.25
77.00
76.75
61.57
12.05
f1 (ppm)


OBz

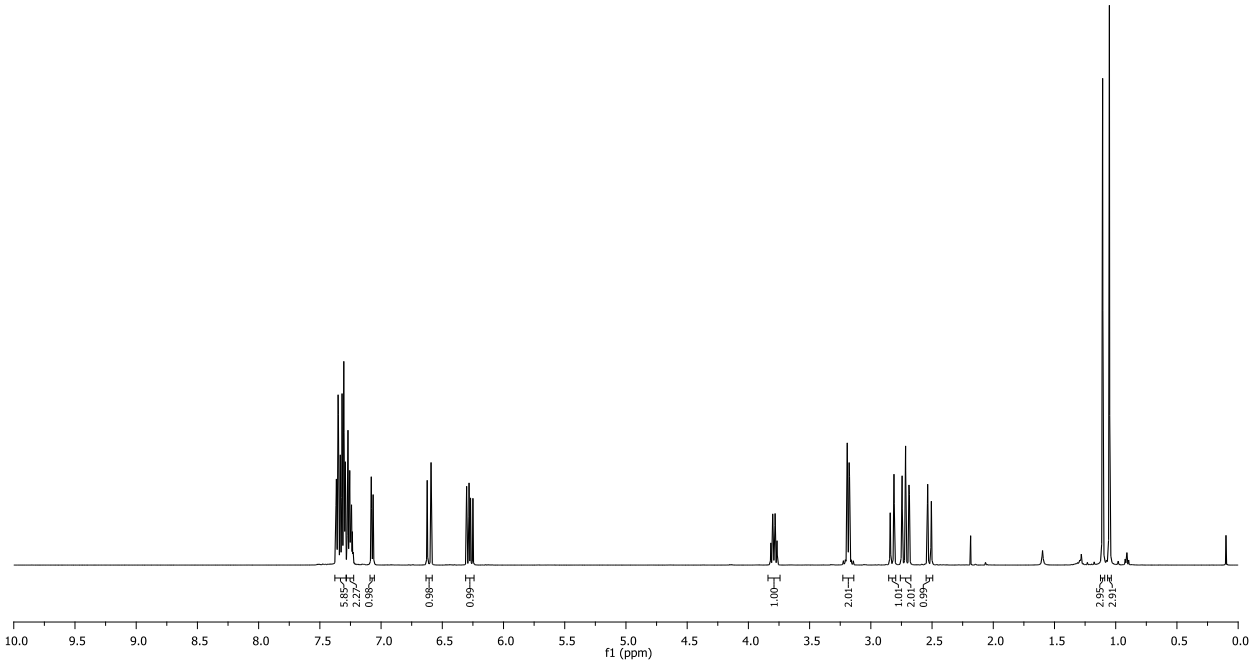
2k

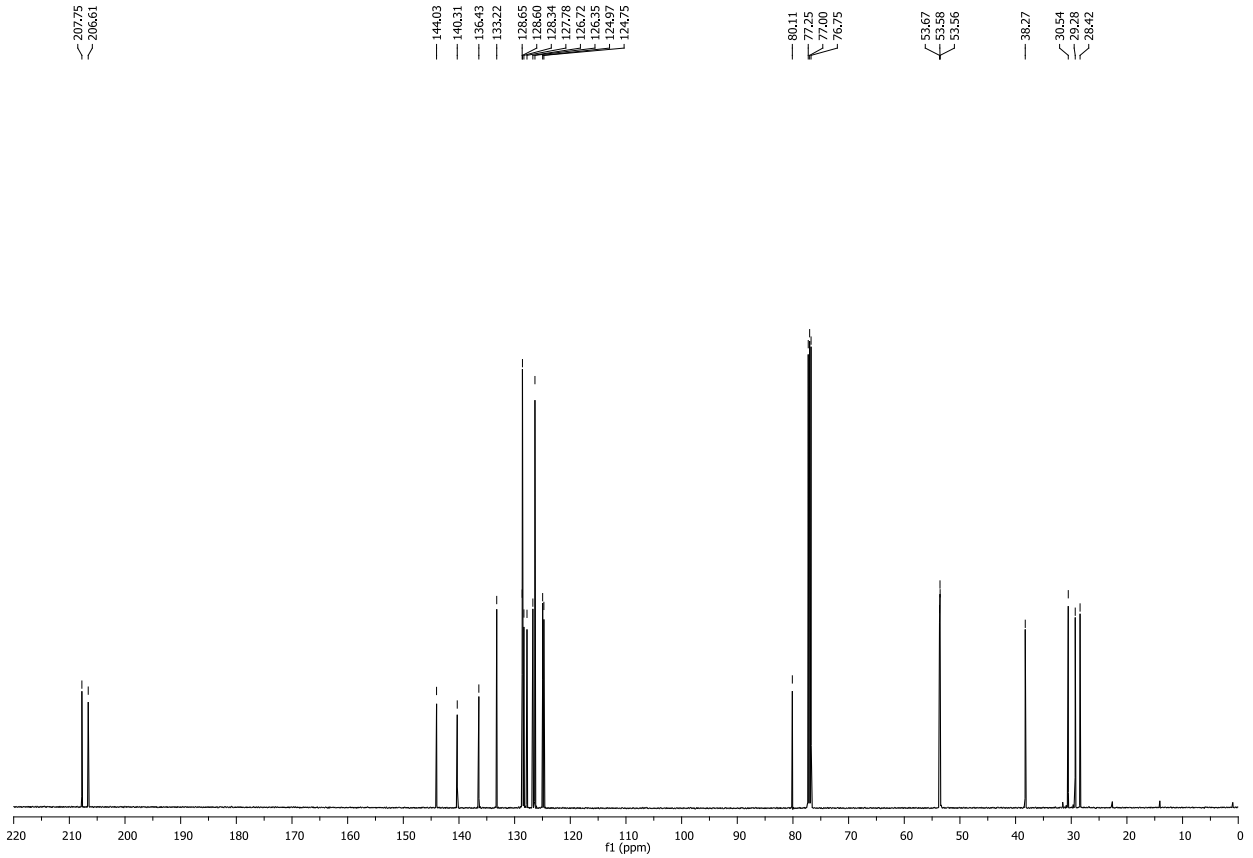

2.11
1.07
2.15
1.93
0.96
1.10
0.98
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


166.21
135.85
134.64
132.90
130.12
129.57
128.29
127.11
118.63
77.32
77.00
76.68
64.88
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)


O
O
Me
Me
Ph

3a


5.85
2.22
0.98
0.98
0.99
1.00
2.01
1.01
2.01
0.99
2.95
2.91
f1 (ppm)


207.75
206.61
144.03
140.31
136.43
133.22
128.65
128.60
128.34
127.78
126.72
126.35
124.97
124.75
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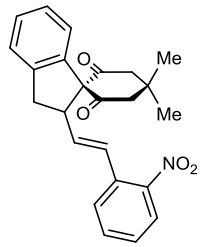
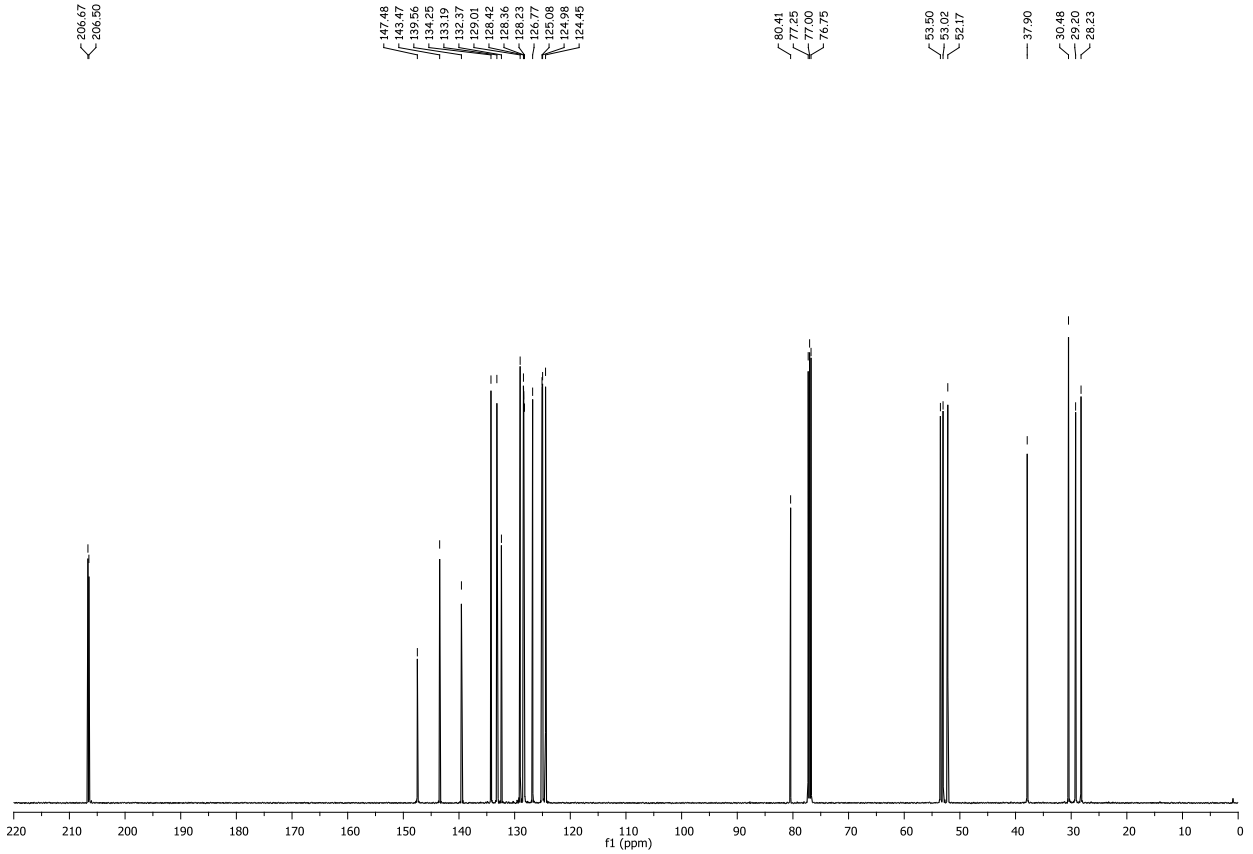
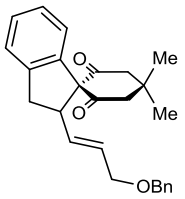
38.27
30.54
29.28
28.42
f1 (ppm)


O
Me
Me
O
NO2

3b

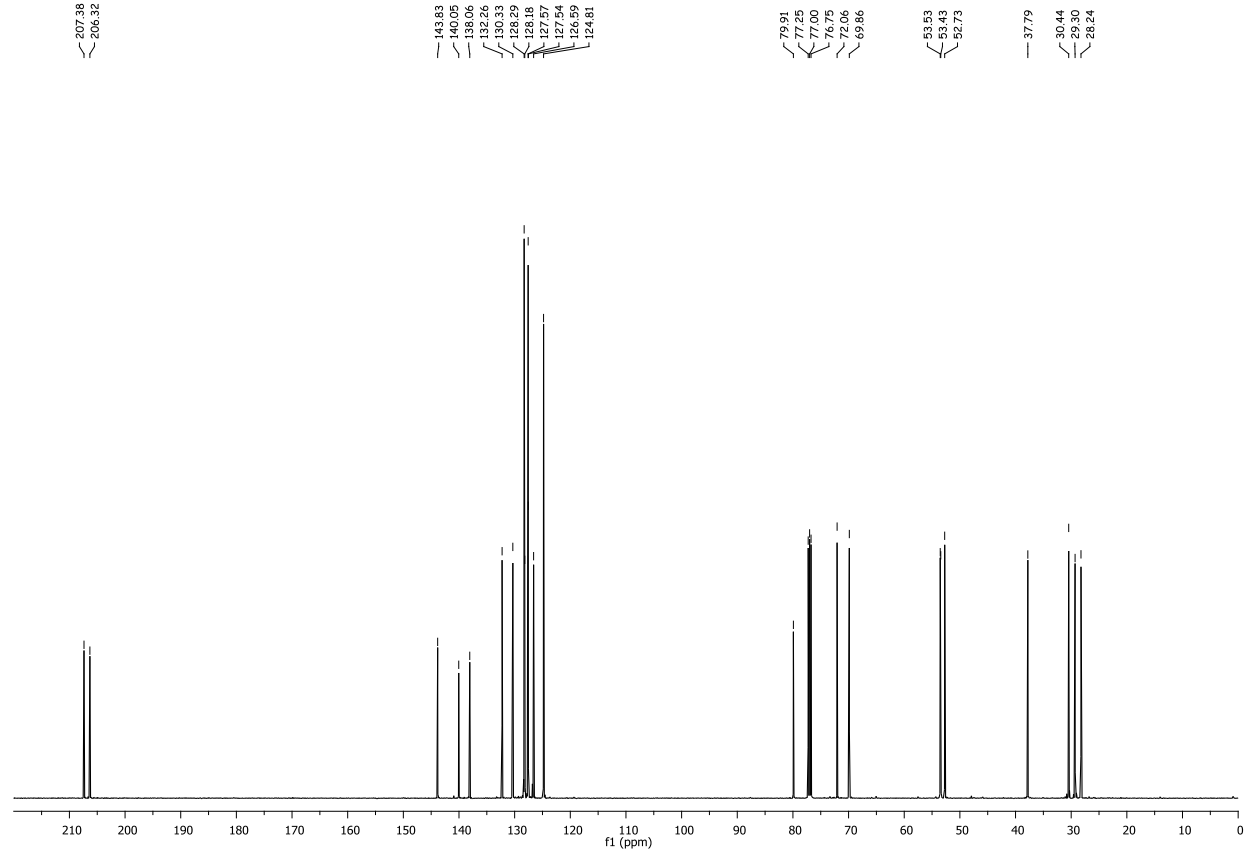
0.96
1.00
1.02
0.99
3.09
1.00
1.02
1.00
1.01
1.01
1.02
1.01
2.03
1.02
6.00
f1 (ppm)


206.67
206.50
147.48
143.47
139.56
134.25
133.19
132.37
129.01
128.42
128.36
128.23
126.77
125.08
124.98
124.45
80.41
77.25
77.00
76.75
53.50
53.02
52.17
37.90
30.48
29.20
28.23
f1 (ppm)


O
Me
O
Me
OBn

3c

8.31
1.04
2.05
2.05
2.04
1.02
1.02
1.04
1.02
1.05
1.02
1.05
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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206.32
143.83
140.05
138.06
132.26
130.33
128.29
128.18
127.57
127.54
126.59
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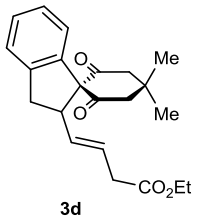
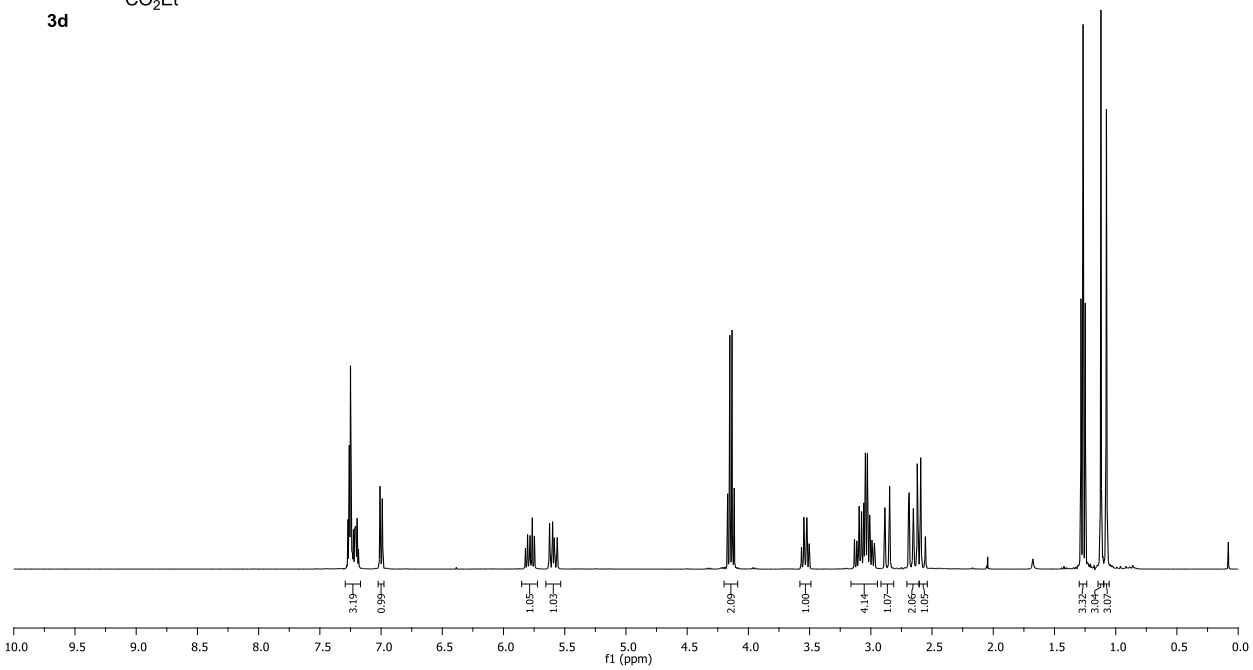
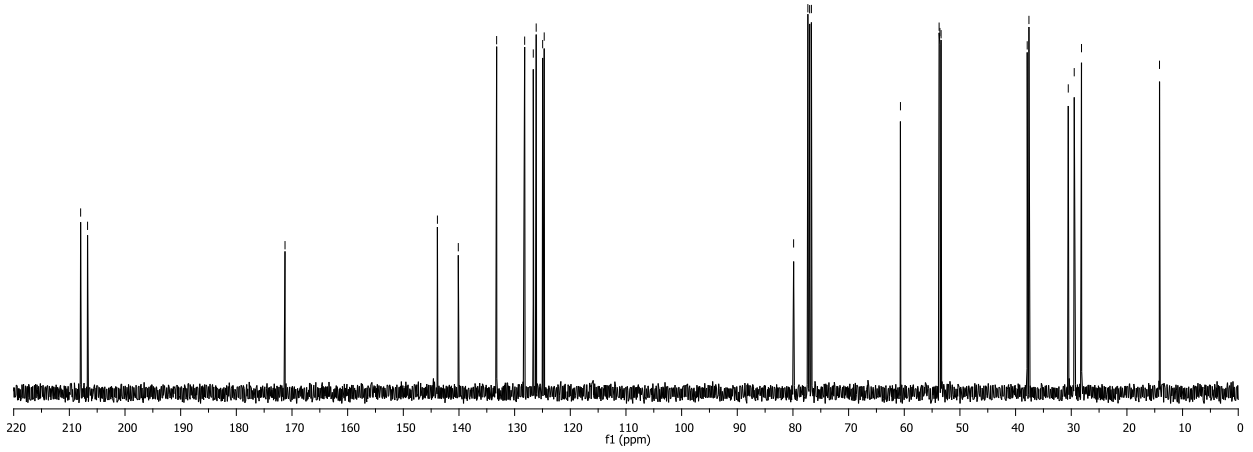
79.91
77.25
77.00
76.75
72.06
69.86
53.53
53.43
52.73
37.79
30.44
29.30
28.24
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

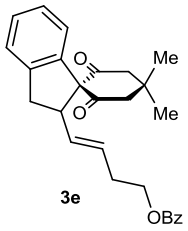

O
O
Me
Me
CO2Et

3d

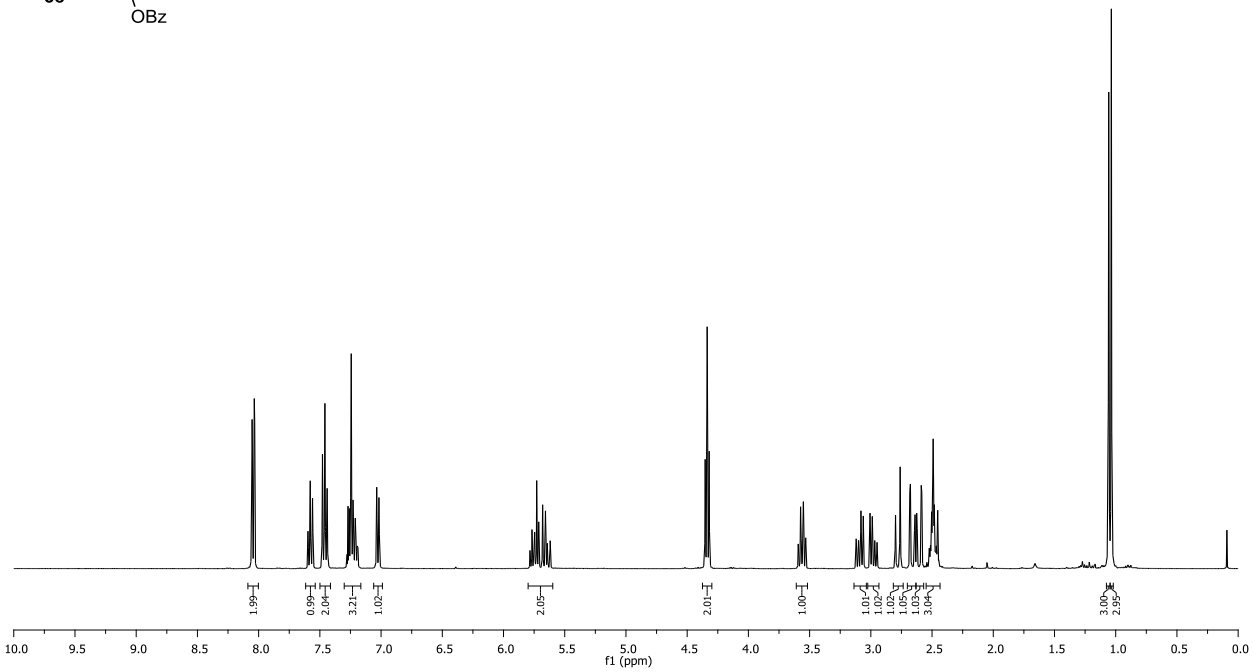

3.19
0.99
1.05
1.03
2.09
1.00
4.14
1.07
2.06
1.05
3.32
3.04
3.07
f1 (ppm)

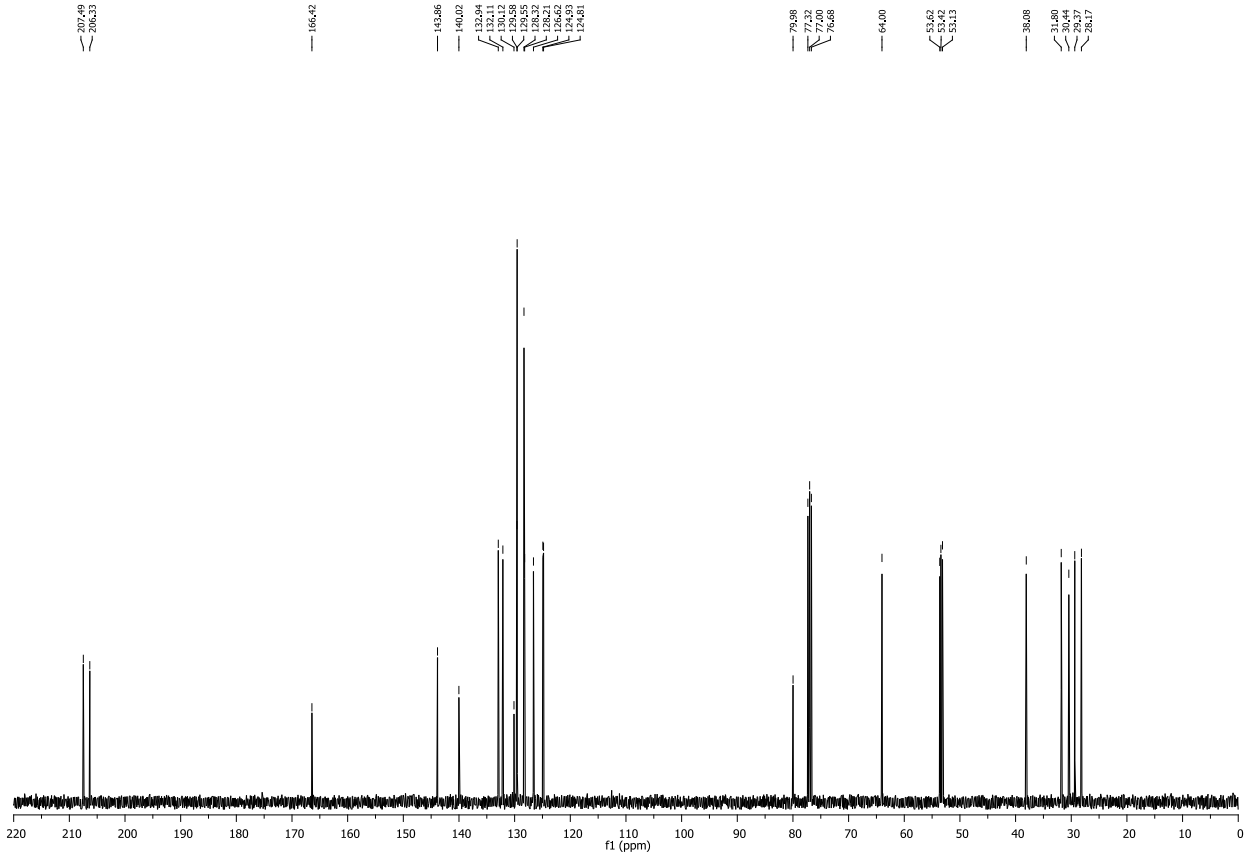

207.97
206.73
171.25
143.87
140.12
133.23
128.20
126.65
126.13
124.97
124.69
79.88
77.32
77.00
76.68
60.69
53.74
53.60
53.39
37.91
37.60
30.54
29.47
28.16
14.15

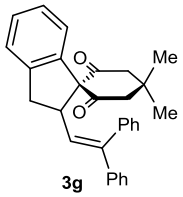

f1 (ppm)


O
Me
Me
O
OBz

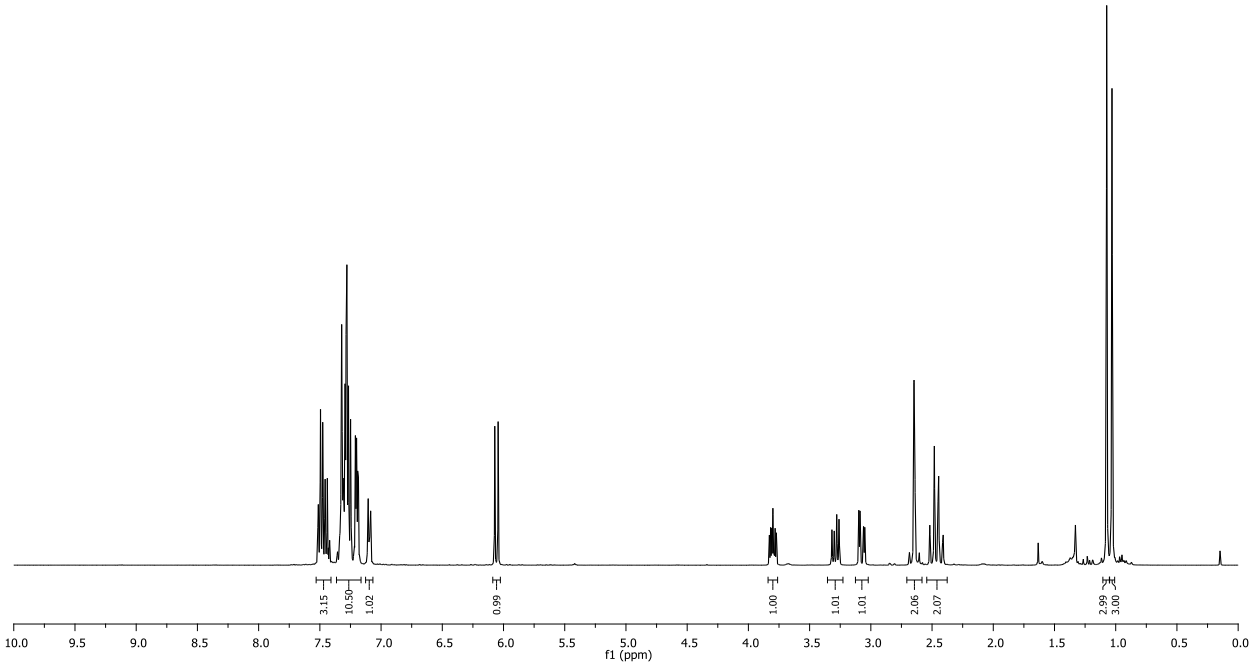
3e


1.99
0.99
2.04
3.21
1.02
2.05
2.01
1.00
1.01
1.02
1.05
1.05
3.04
3.00
2.95
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

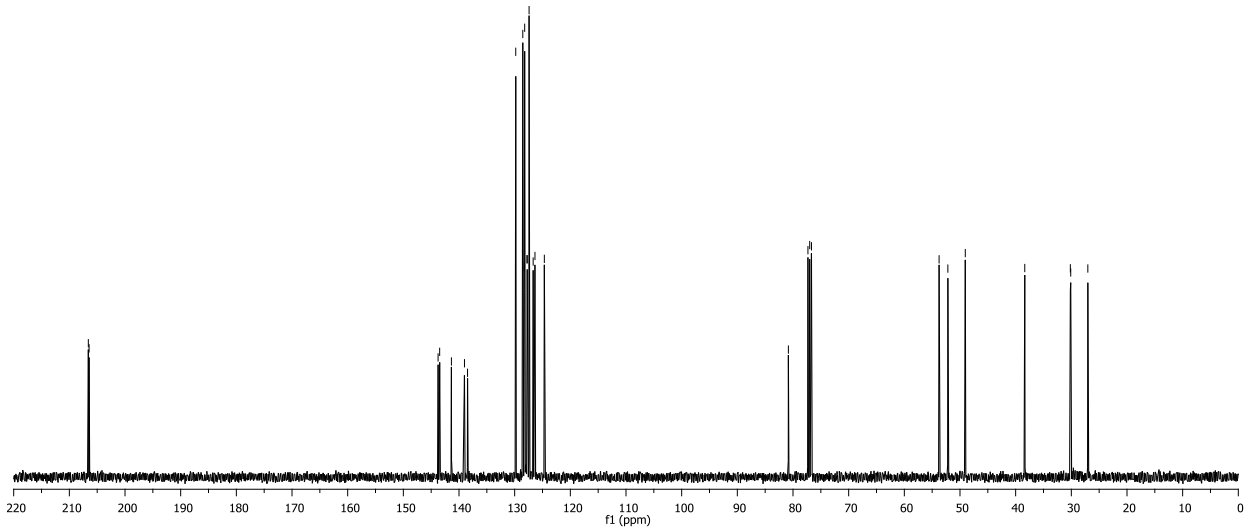

207.49
206.33
166.42
143.86
140.02
132.94
132.11
130.12
129.58
129.55
128.32
128.21
126.62
124.93
124.81
79.98
77.32
77.00
76.68
64.00
53.62
53.42
53.13
38.08
31.80
30.44
29.37
28.17
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

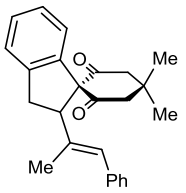

O
O
Me
Me
Ph
Ph

3g

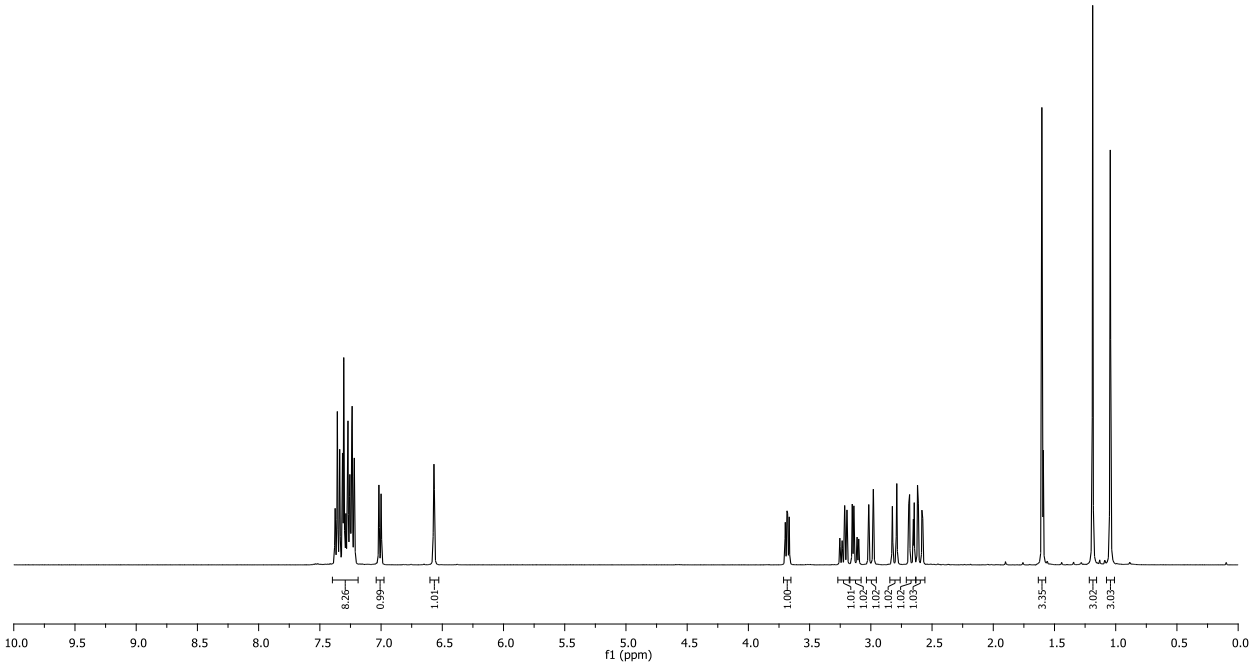

3.15
10.50
1.02
0.99
1.00
1.01
1.01
2.06
2.07
2.99
3.00
f1 (ppm)


206.59
206.45
143.76
143.48
141.36
139.02
138.47
129.81
128.54
128.27
128.20
127.79
127.75
127.41
127.34
126.88
126.36
124.67
80.83
77.32
77.00
76.68
53.75
52.18
49.05
38.36
30.18
30.11
27.03

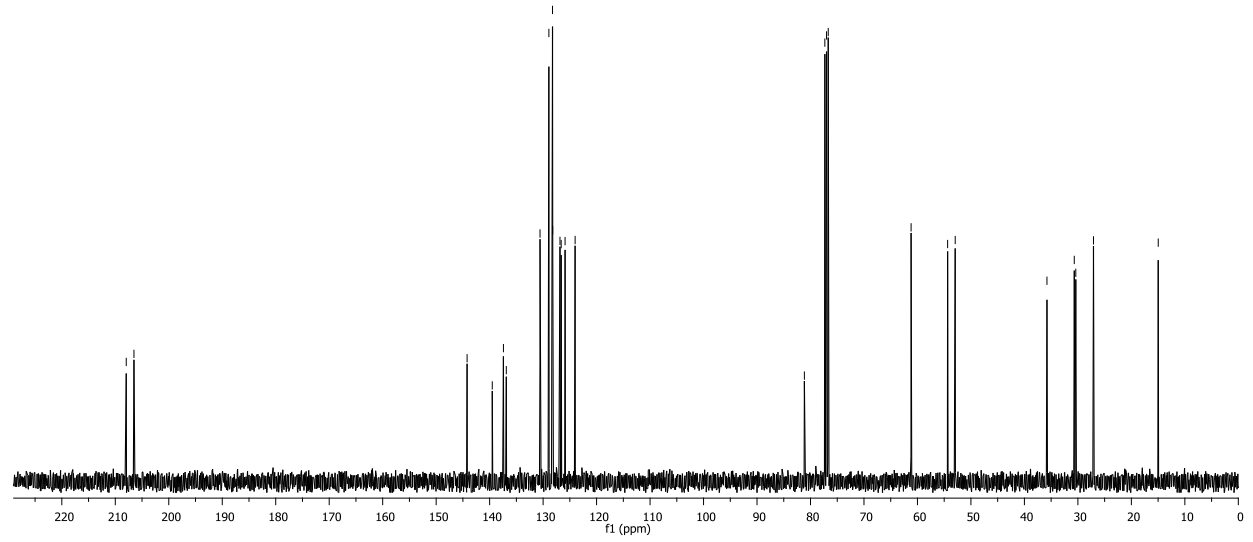

f1 (ppm)

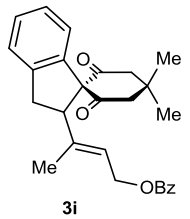

O
O
Me
Me
Me
Ph

3h

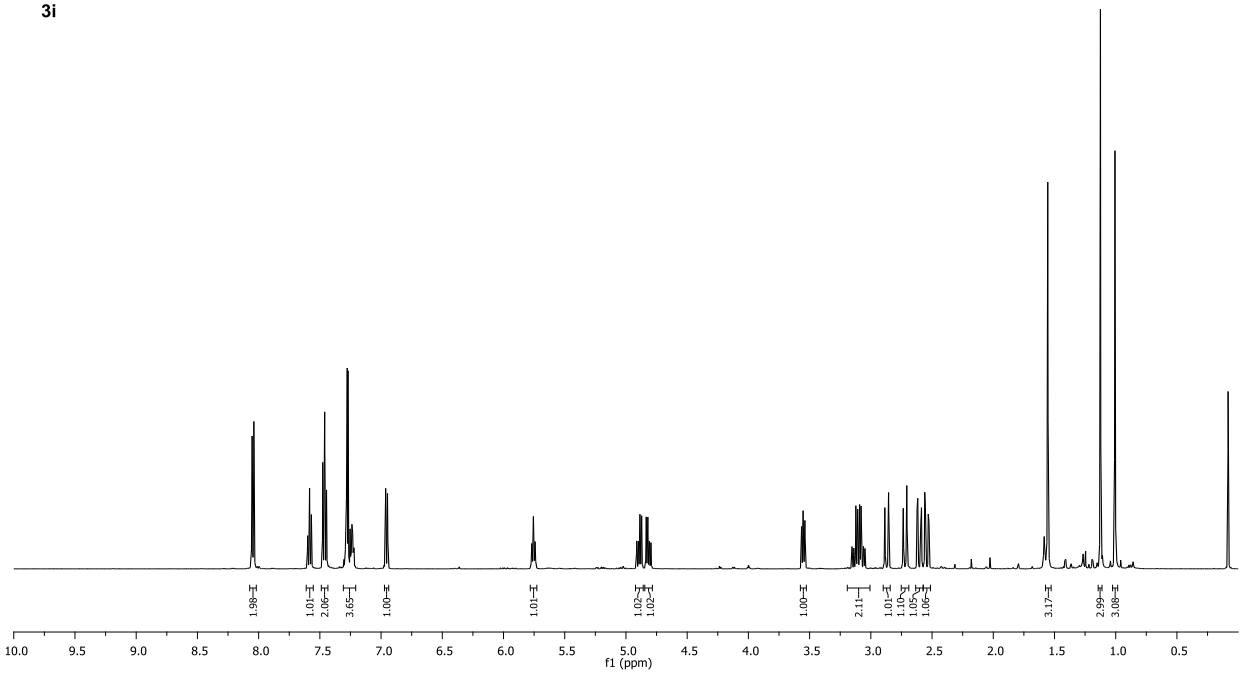

8.26
0.99
1.01
1.00
1.01
1.02
1.02
1.02
1.03
3.35
3.02
3.03
f1 (ppm)

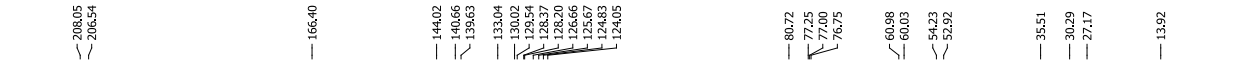

207.95
206.51
144.21
139.51
137.42
136.88
130.58
128.92
128.24
128.21
126.84
126.62
125.89
124.01
81.14
77.32
77.00
76.68
61.19
54.36
52.94
35.78
30.68
30.39
27.08
14.97


f1 (ppm)


O
Me
O
Me
Me
OBz

3i


1.98
1.01
2.06
3.65
1.00
1.01
1.02
1.02
1.00
2.11
1.01
1.05
1.05
1.06
3.17
2.99
3.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


208.05
206.54
166.40
144.02
140.66
139.63
133.04
130.02
129.54
128.37
128.20
126.66
125.67
124.83
124.05
80.72
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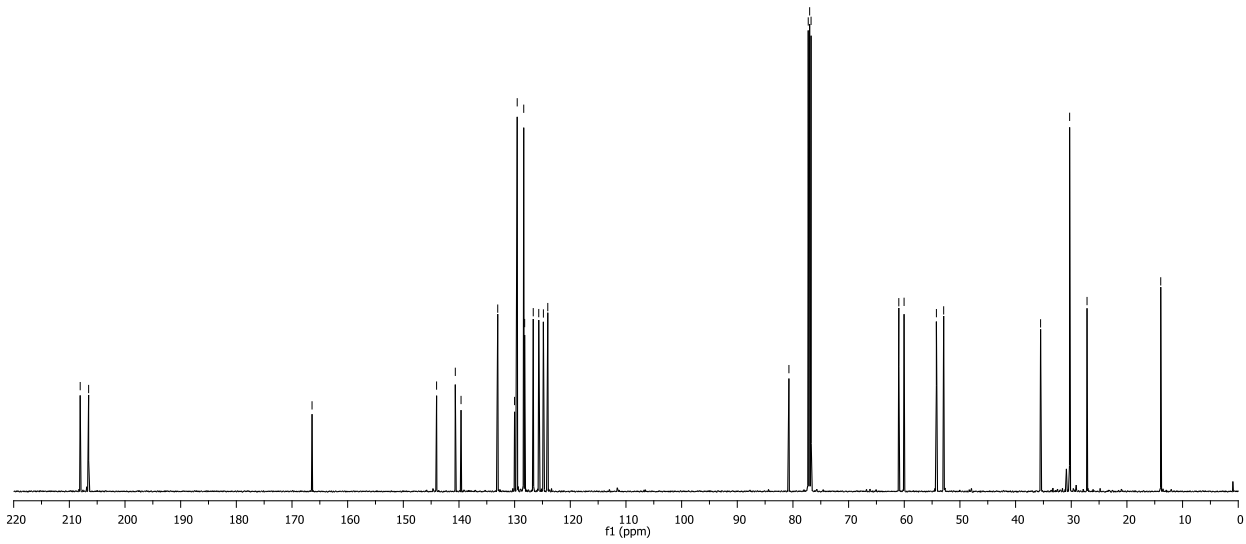
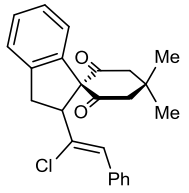
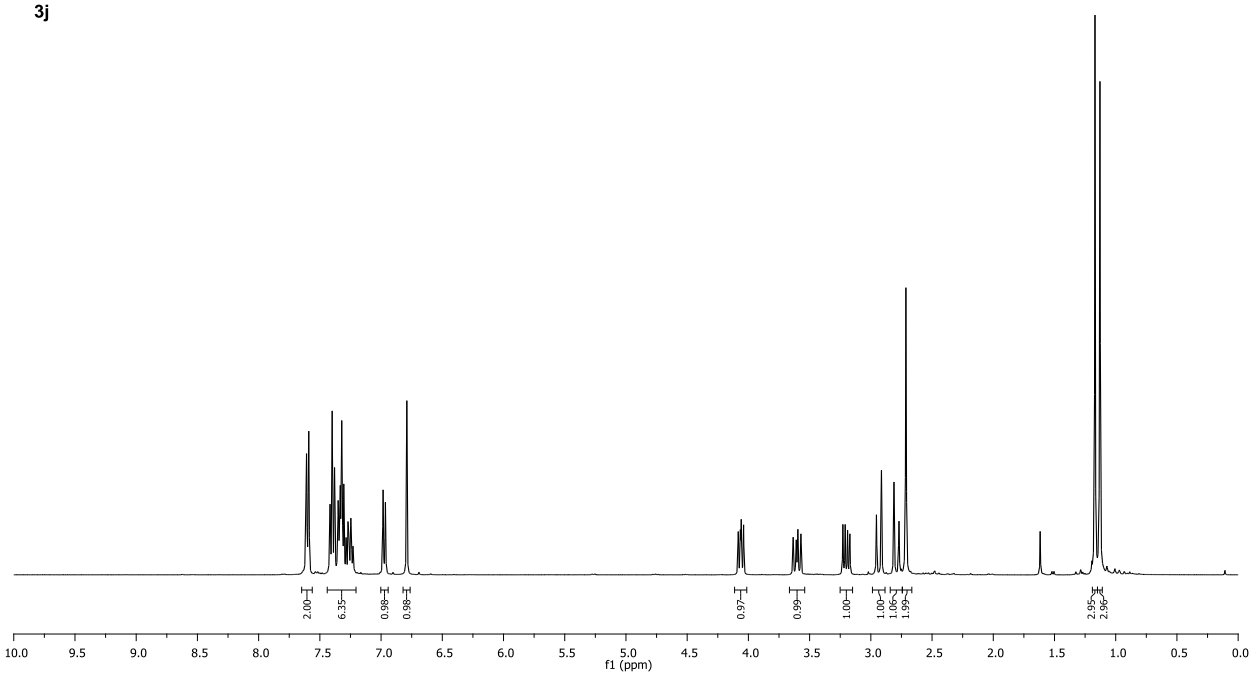
77.00
76.75
60.98
60.03
54.23
52.92
35.51
30.29
27.17
13.92

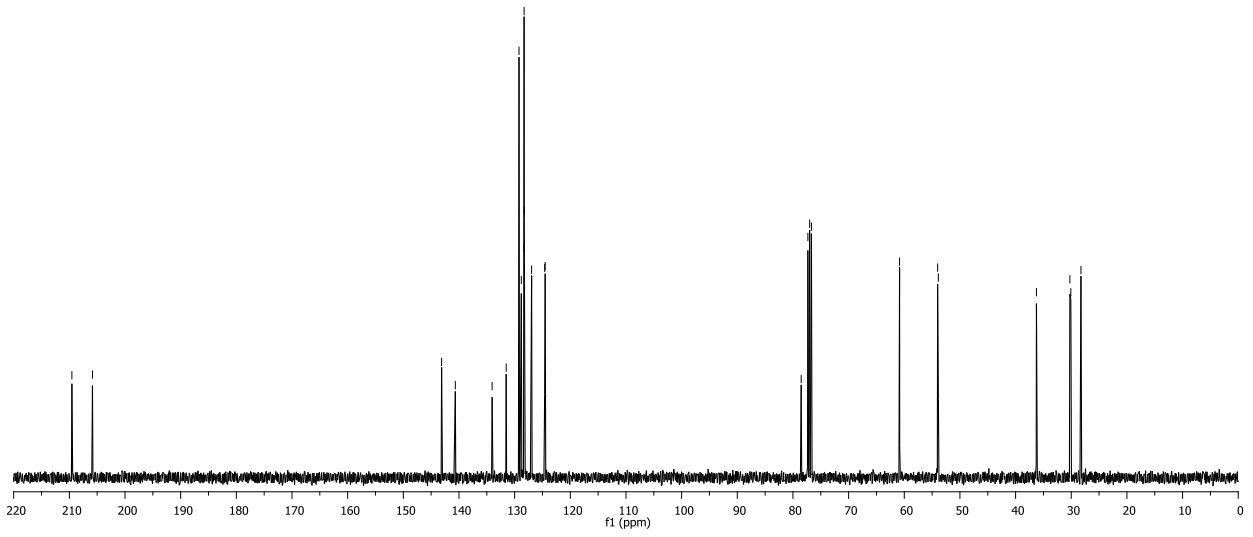

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

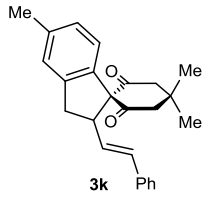

O
O
Me
Me
Cl
Ph

3j

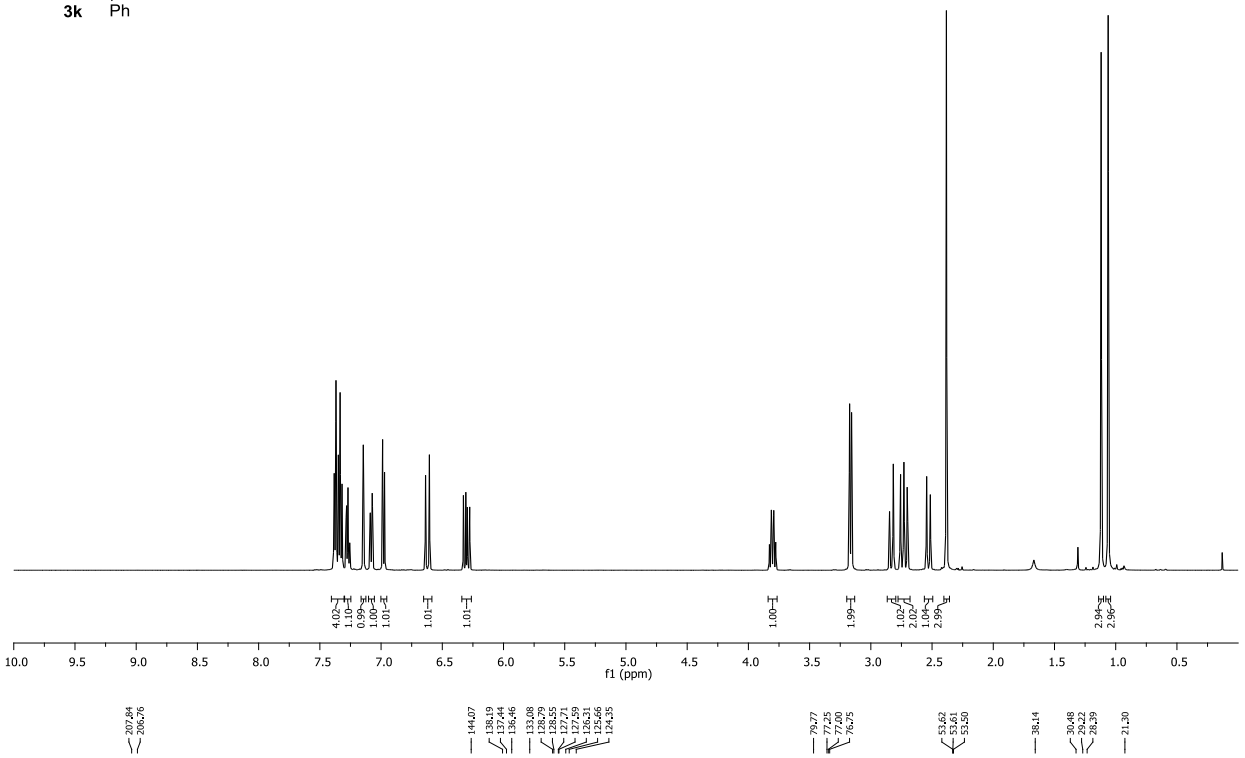

2.00
6.35
0.98
0.98
0.97
0.99
1.00
1.00
1.06
1.99
2.95
2.96
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


209.54
205.84
143.12
140.66
134.05
131.52
129.21
128.80
128.34
128.30
128.28
126.95
124.60
124.51
78.52
77.32
77.00
76.68
60.85
54.00
53.88
36.25
30.25
30.08
28.26

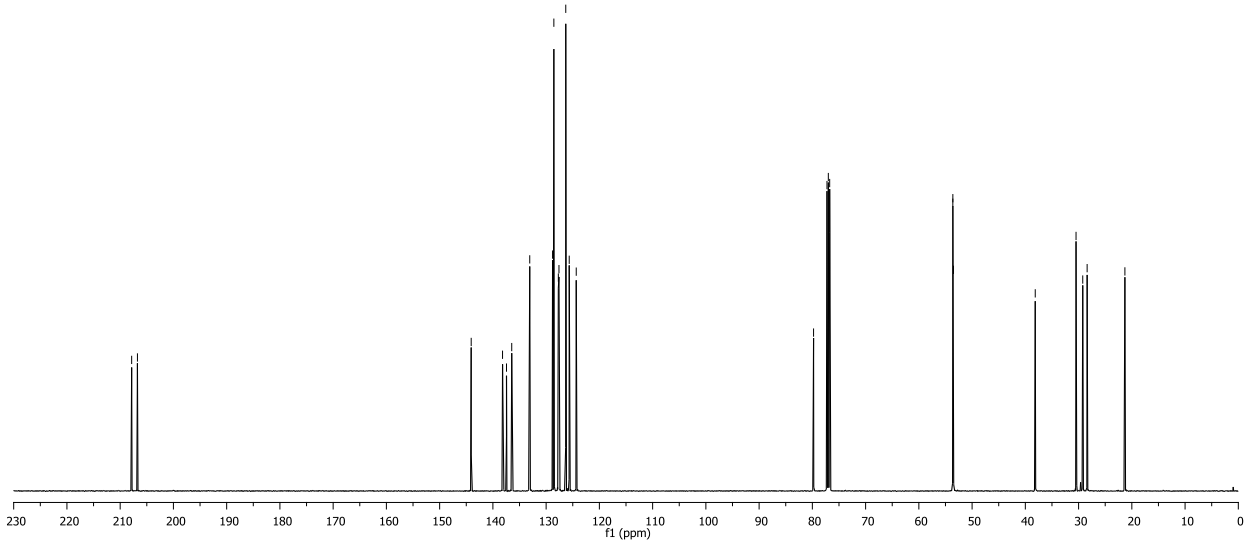

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

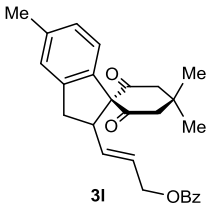

Me
O
Me
O
Me
Ph

3k

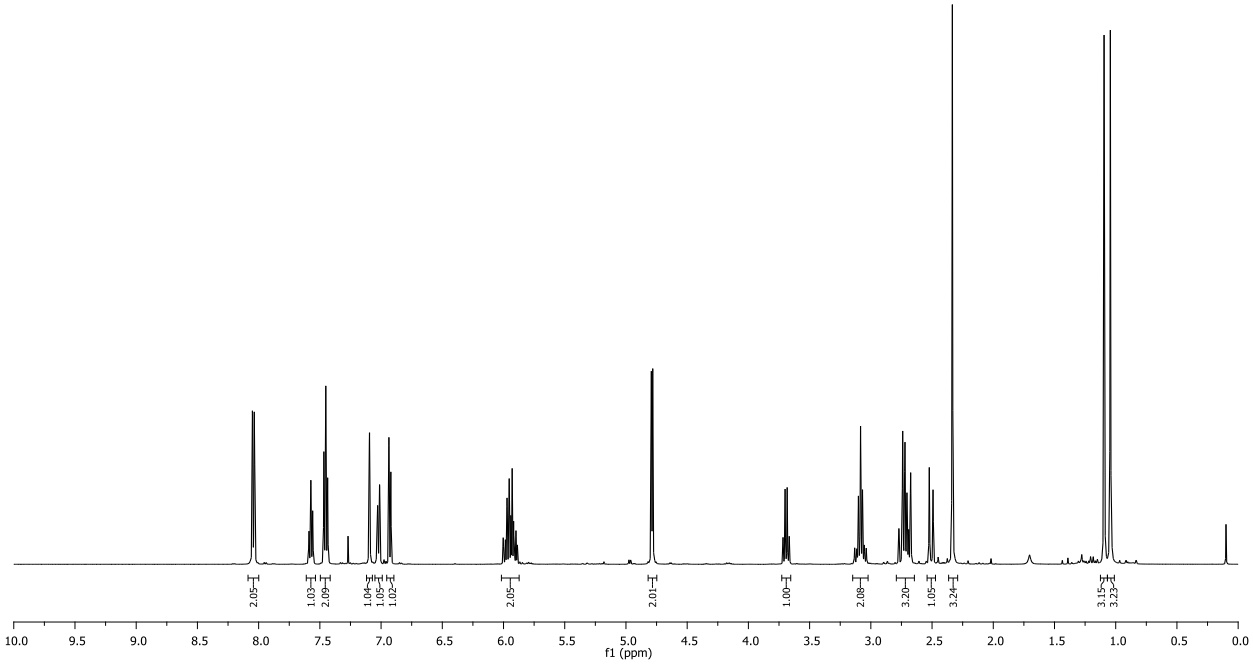

4.02
1.10
0.99
1.00
1.01
1.01
1.01
1.00
1.99
1.02
2.02
1.04
2.99
2.04
2.96
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

207.84
206.76
144.07
138.19
137.44
136.46
133.08
128.79
128.55
127.71
127.59
126.31
125.66
124.35
79.77
77.25
77.00
76.75
53.62
53.61
53.50
38.14
30.48
29.22
28.39
21.30

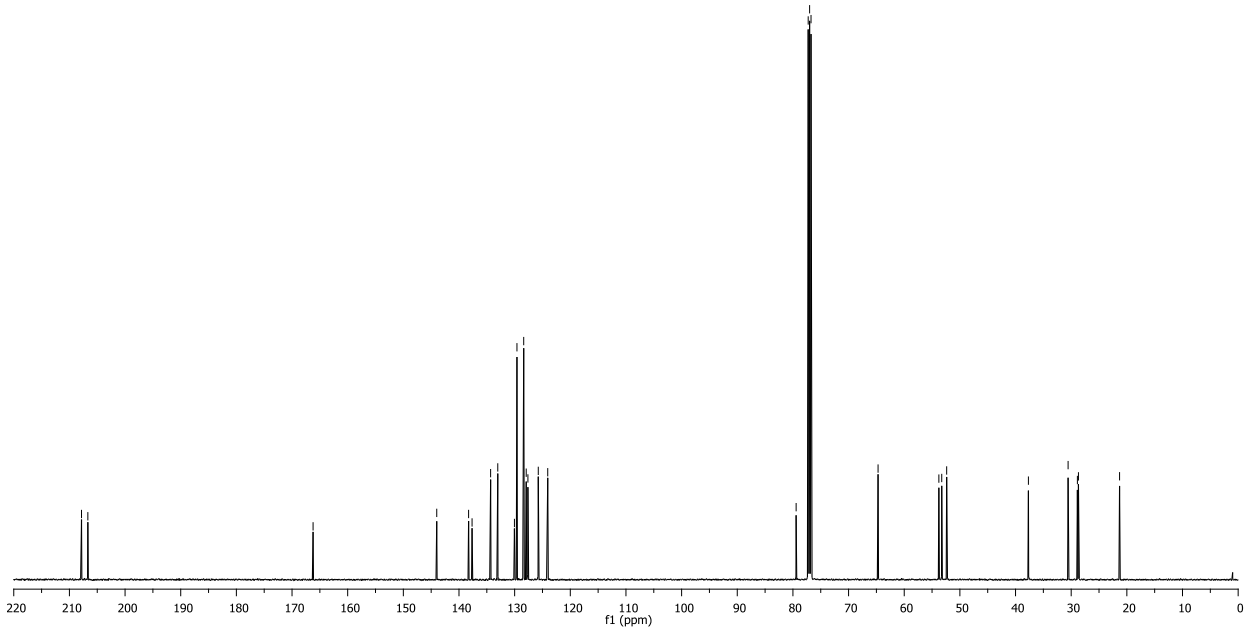

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

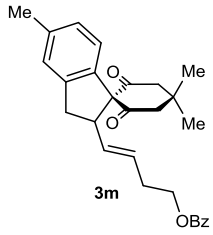

Me
O
Me
Me
O
OBz

3l


2.05
1.03
2.09
1.04
1.05
1.02
2.05
2.01
1.00
2.08
3.20
1.05
3.24
3.15
3.23
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

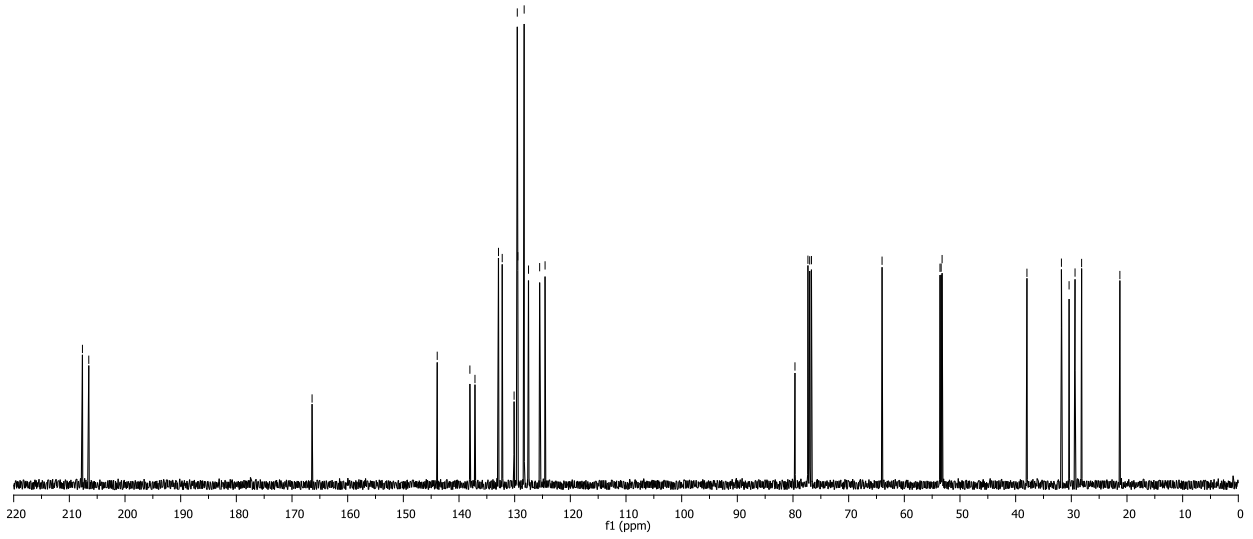

207.83
206.69
166.22
144.00
138.27
137.65
134.32
133.03
130.04
129.58
128.37
127.92
127.62
125.76
124.05
79.42
77.25
77.00
76.75
64.70
53.77
53.26
52.37
37.69
30.55
28.88
28.69
21.31

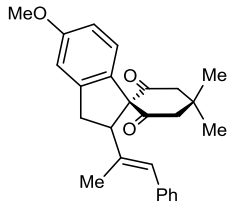

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Me
O
Me
O
Me
3m
OBz

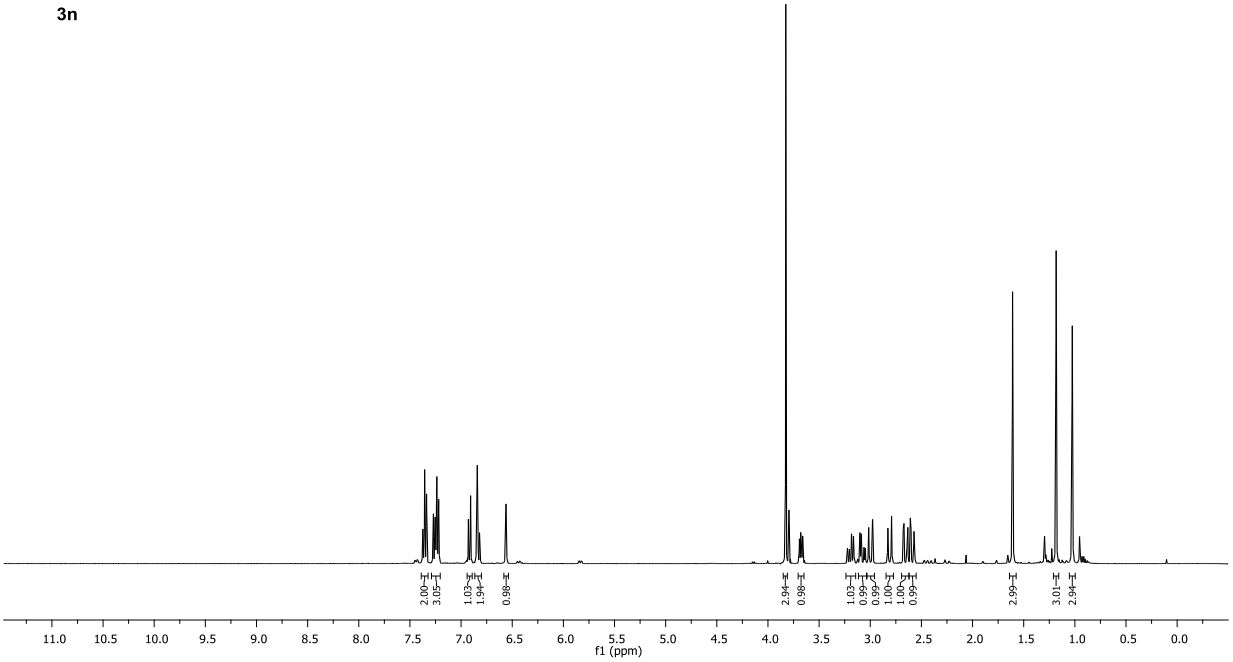
1.99
1.00
2.03
2.02
1.02
2.05
2.02
1.00
1.01
1.03
1.02
1.03
1.04
3.02
3.06
3.01
2.92
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

207.65
206.51
166.39
143.91
138.04
137.13
132.91
132.24
130.10
129.53
129.43
128.30
127.51
125.51
124.54
79.65
77.32
77.00
76.68
64.00
53.59
51.39
53.21
37.97
31.78
30.40
29.33
28.15
21.28

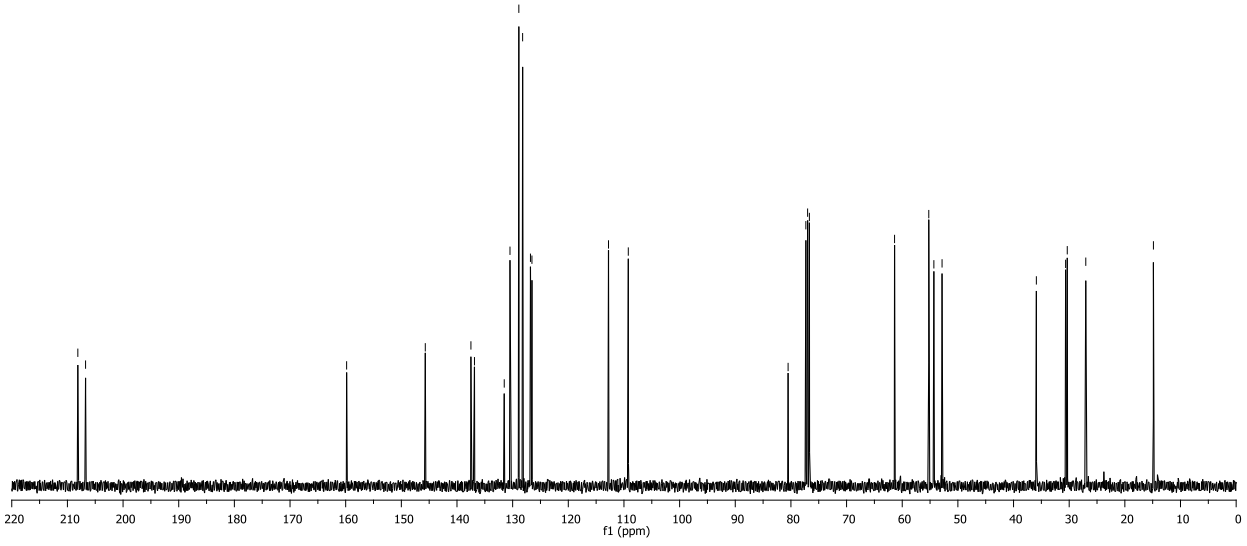

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

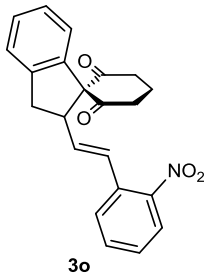

MeO
O
O
Me
Me
Me
Ph

3n

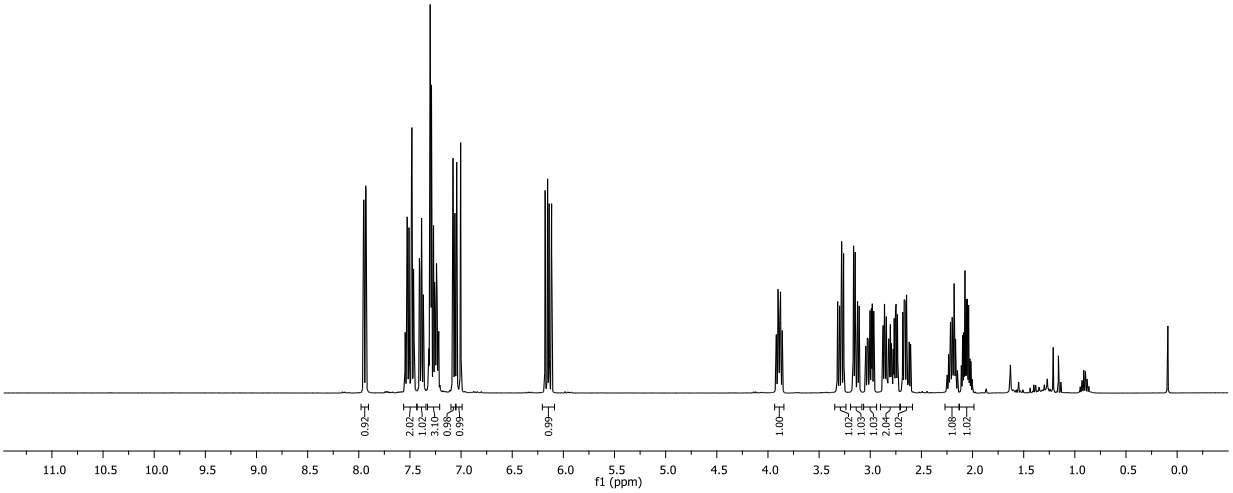

2.00
3.05
1.03
1.94
0.98
2.94
0.98
1.03
0.99
0.99
1.00
1.00
0.99
2.99
3.01
2.94
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


208.13
206.74
159.83
145.70
137.50
136.86
131.51
130.48
128.89
128.21
126.80
126.53
112.78
109.22
80.51
77.32
77.00
76.68
61.38
55.23
54.31
52.84
35.90
30.64
30.35
27.02
14.86

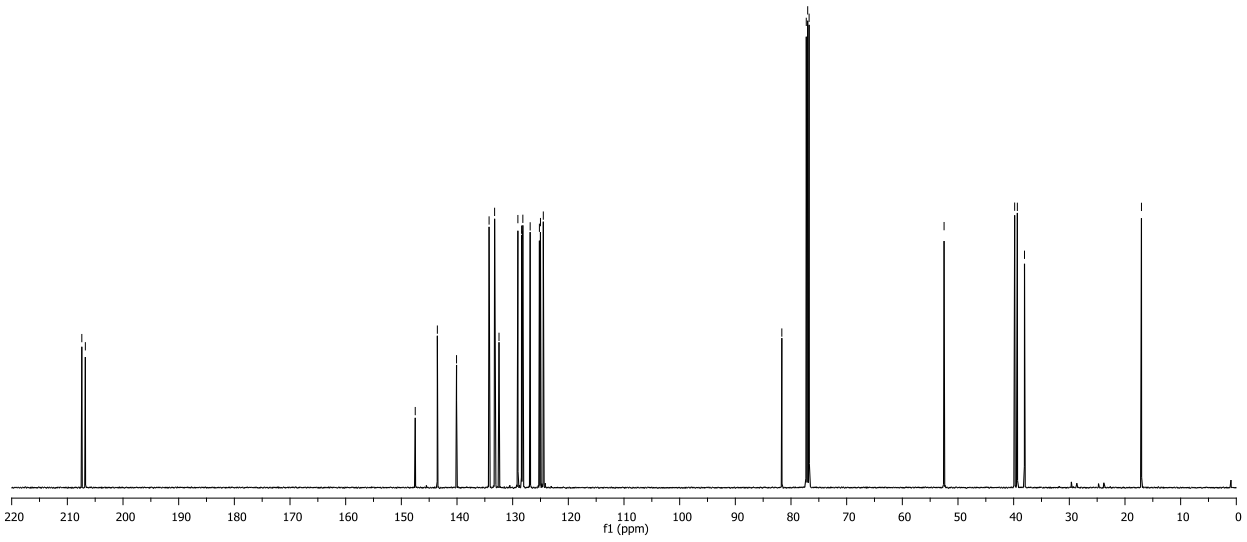

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

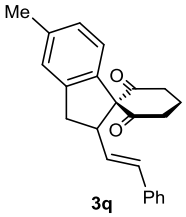

O
O
NO2

3o


0.92
2.02
1.02
3.10
0.98
0.99
0.99
1.00
1.02
1.03
1.03
2.04
1.02
1.08
1.02
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

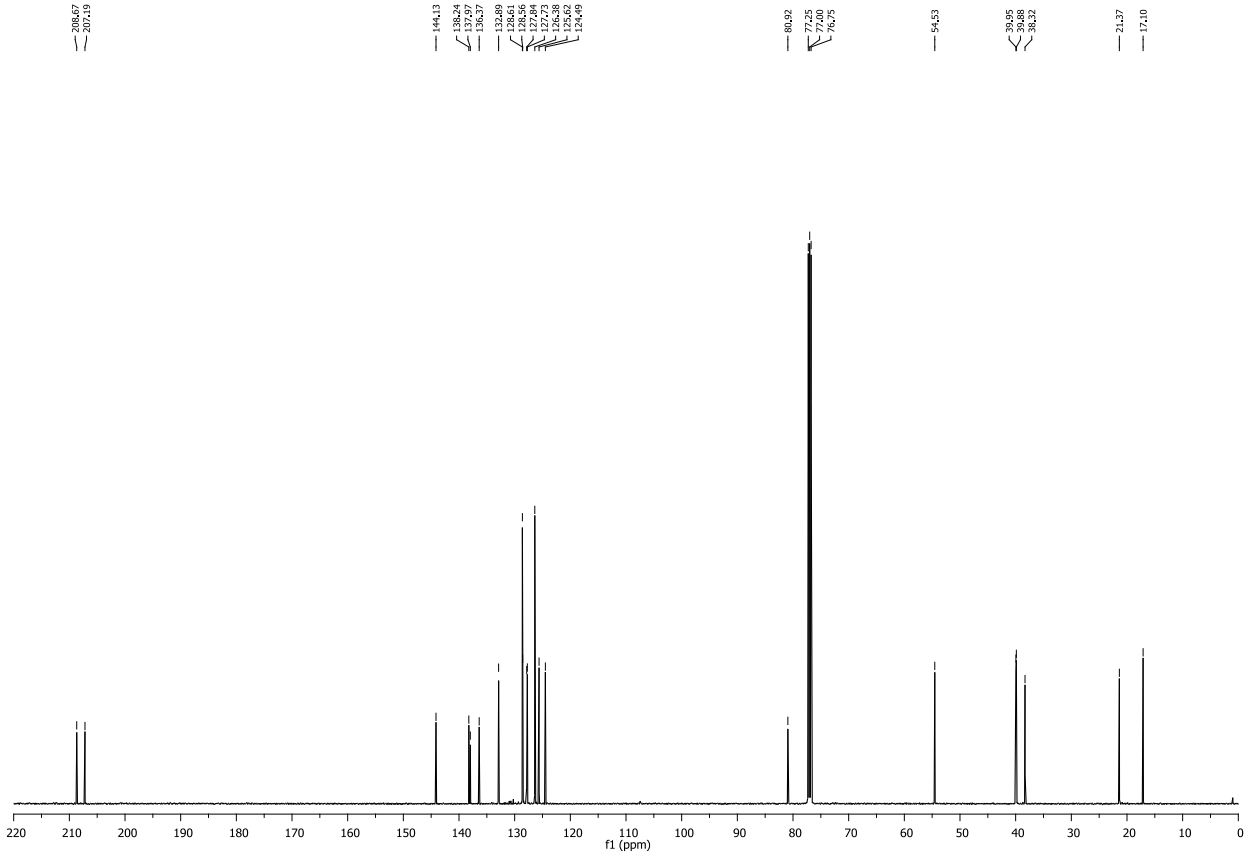

207.40
206.77
147.50
143.53
140.08
134.24
133.24
132.45
129.06
128.40
128.28
126.17
125.85
125.19
125.01
124.50
81.65
77.25
77.00
76.75
52.50
39.82
39.24
38.05
17.04


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)


Me
O
O
Ph

3q

4.12
1.29
0.97
0.99
0.98
1.02
0.99
1.00
2.04
3.10
1.07
3.04
1.02
1.01
f1 (ppm)


208.67
207.19
144.13
138.24
137.97
136.37
132.89
128.61
128.55
127.84
127.73
126.38
125.62
124.49
80.92
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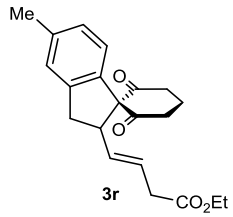
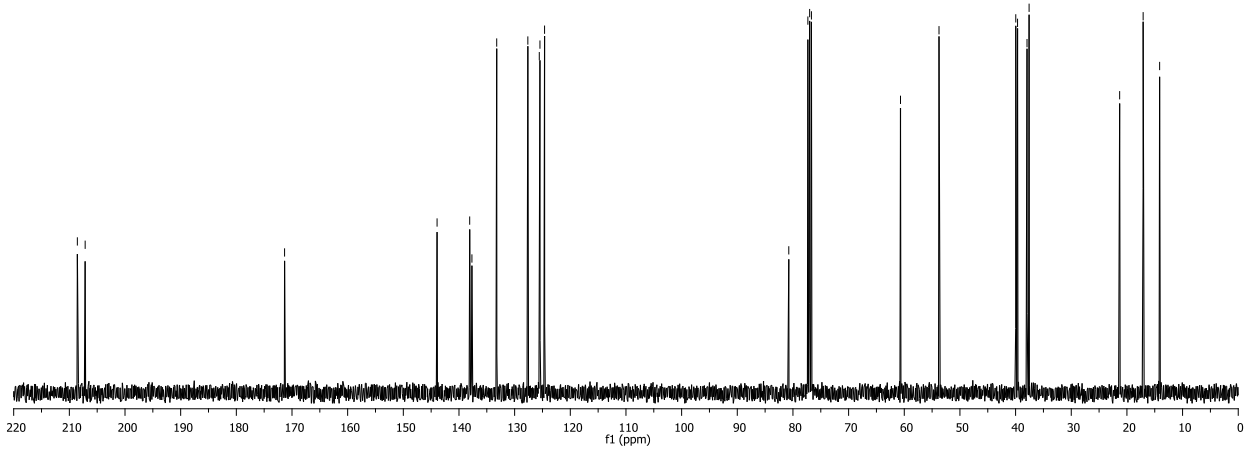
77.00
76.75
54.53
39.95
39.88
38.32
21.37
17.10
f1 (ppm)

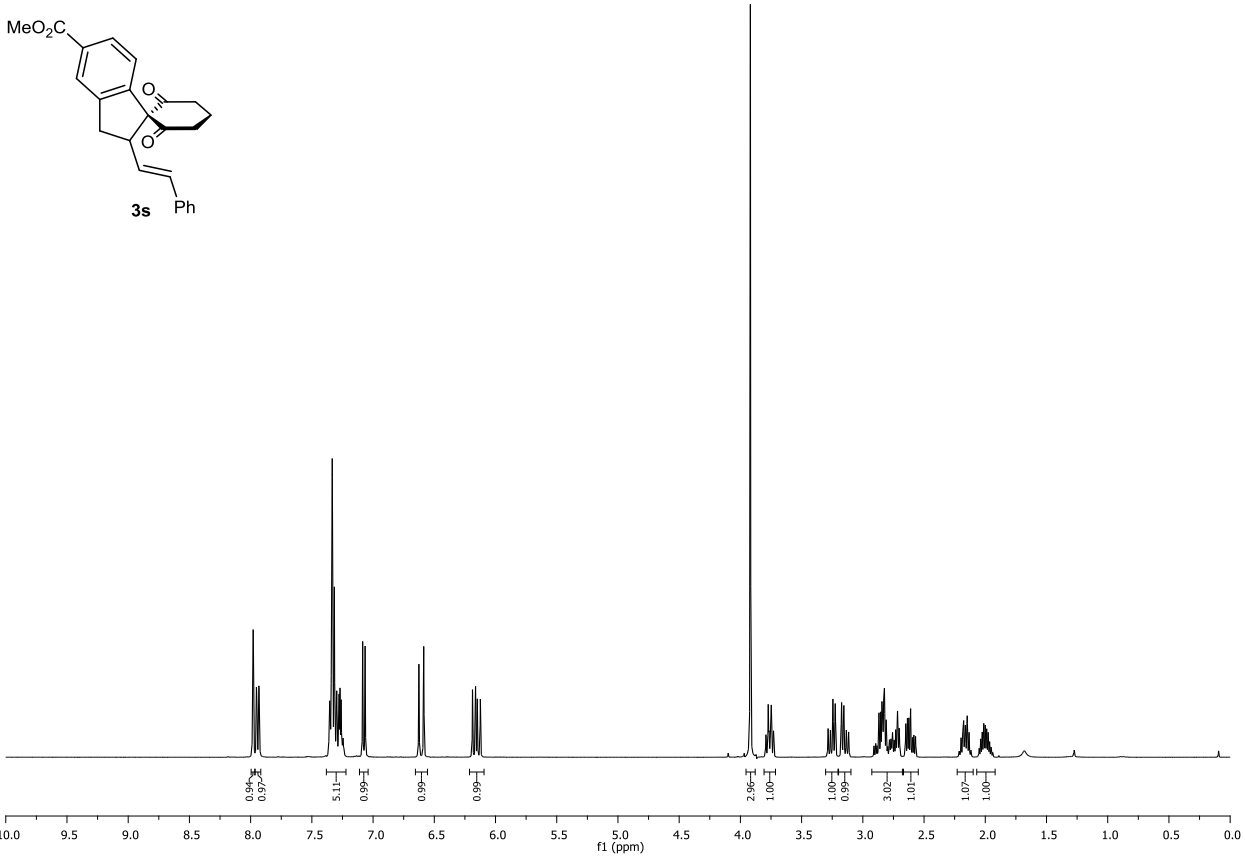

Me
O
O
CO2Et

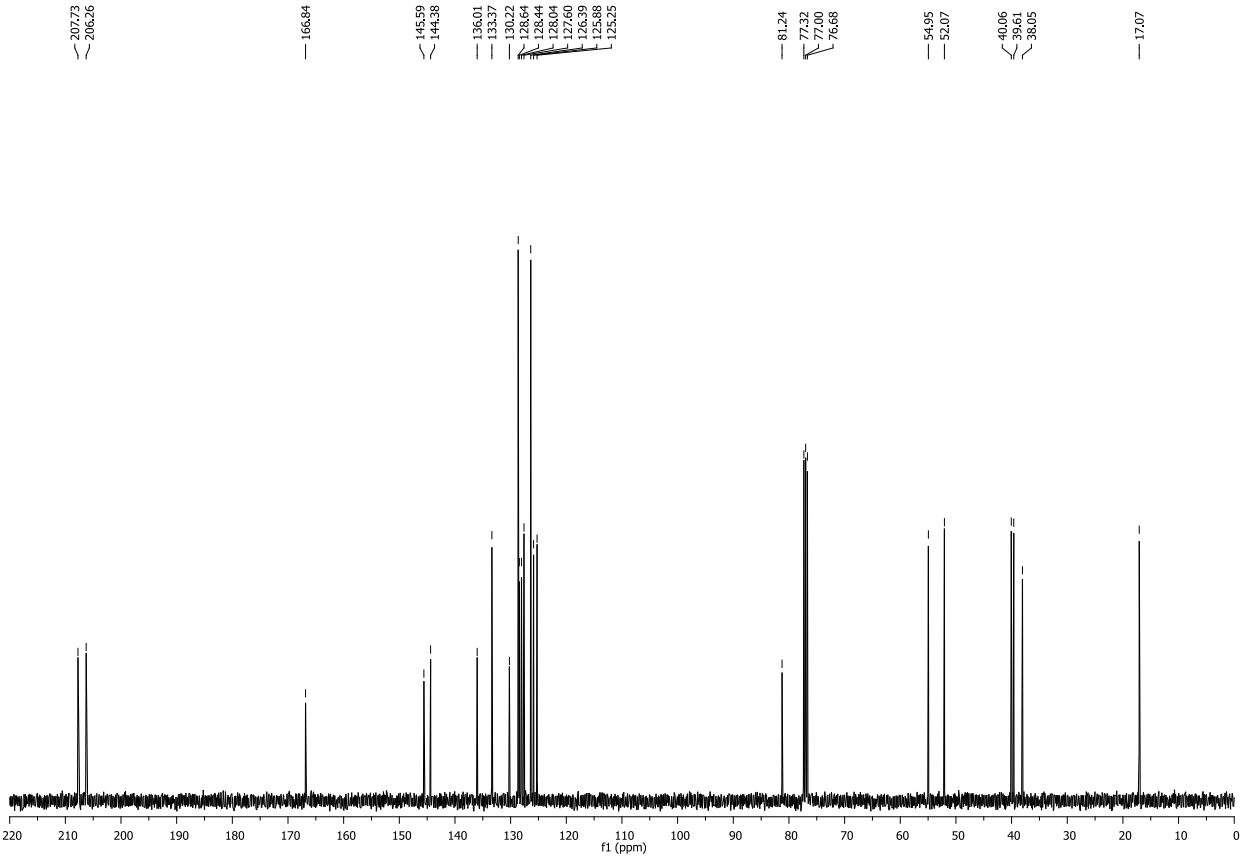
3r

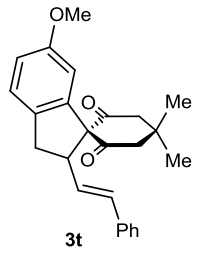
0.98
1.00
1.08
1.01
1.00
2.00
1.00
4.13
4.23
3.06
1.05
1.08
3.20
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


208.56
207.16
171.33
143.93
138.07
137.67
133.22
127.63
125.57
125.45
124.62
80.75
77.32
77.00
76.68
60.68
53.76
39.97
39.65
37.95
37.57
21.30
17.08
14.12


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)

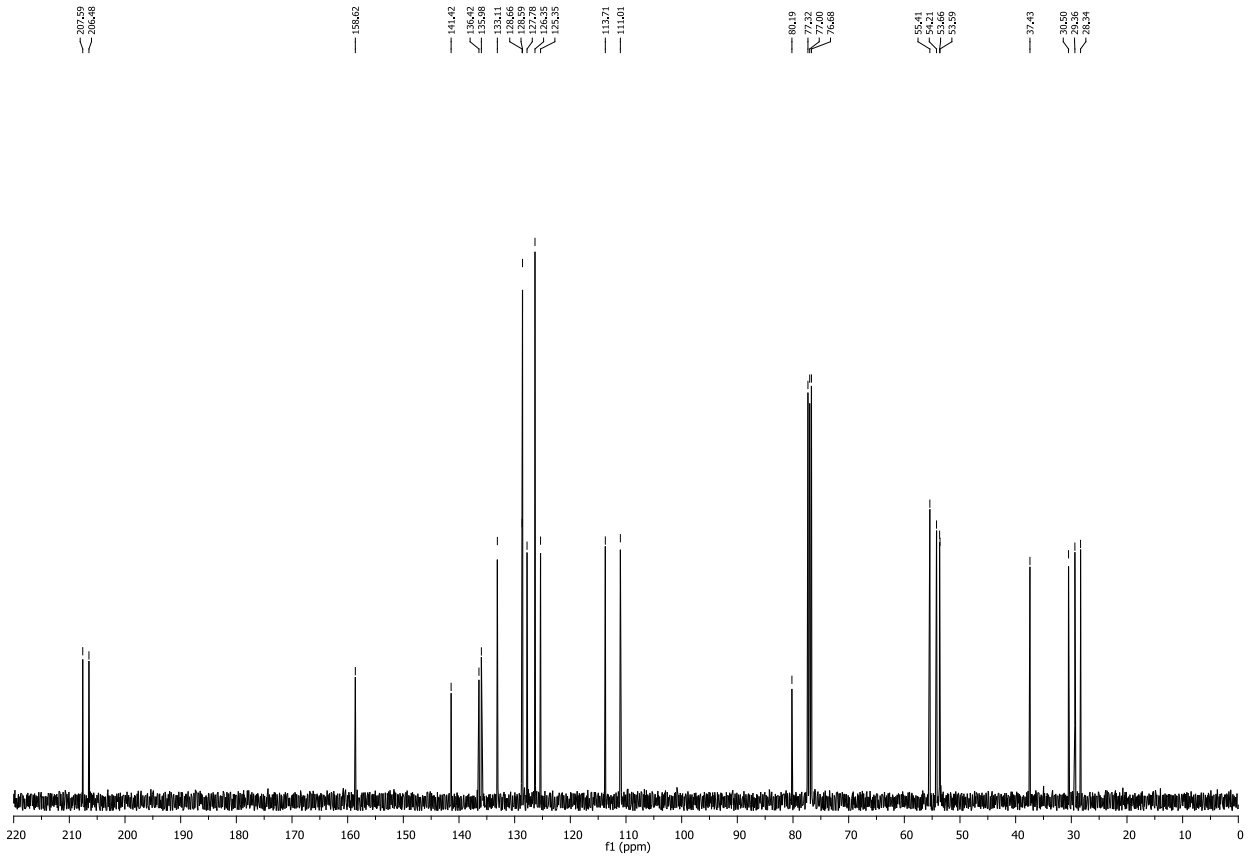

MeO2C
O
O
Ph
3s
0.94
0.97
5.11
0.99
0.99
0.99
2.96
1.00
1.00
0.99
3.02
1.01
1.07
1.00
f1 (ppm)

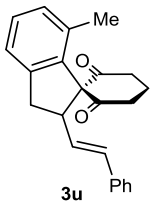

207.73
206.26
166.84
145.59
144.38
136.01
133.37
130.22
128.64
128.44
128.04
127.60
126.39
125.88
125.25
81.24
77.32
77.00
76.68
54.95
52.07
40.06
39.61
38.05
17.07
f1 (ppm)


OMe
O
O
Me
Me
Ph

3t

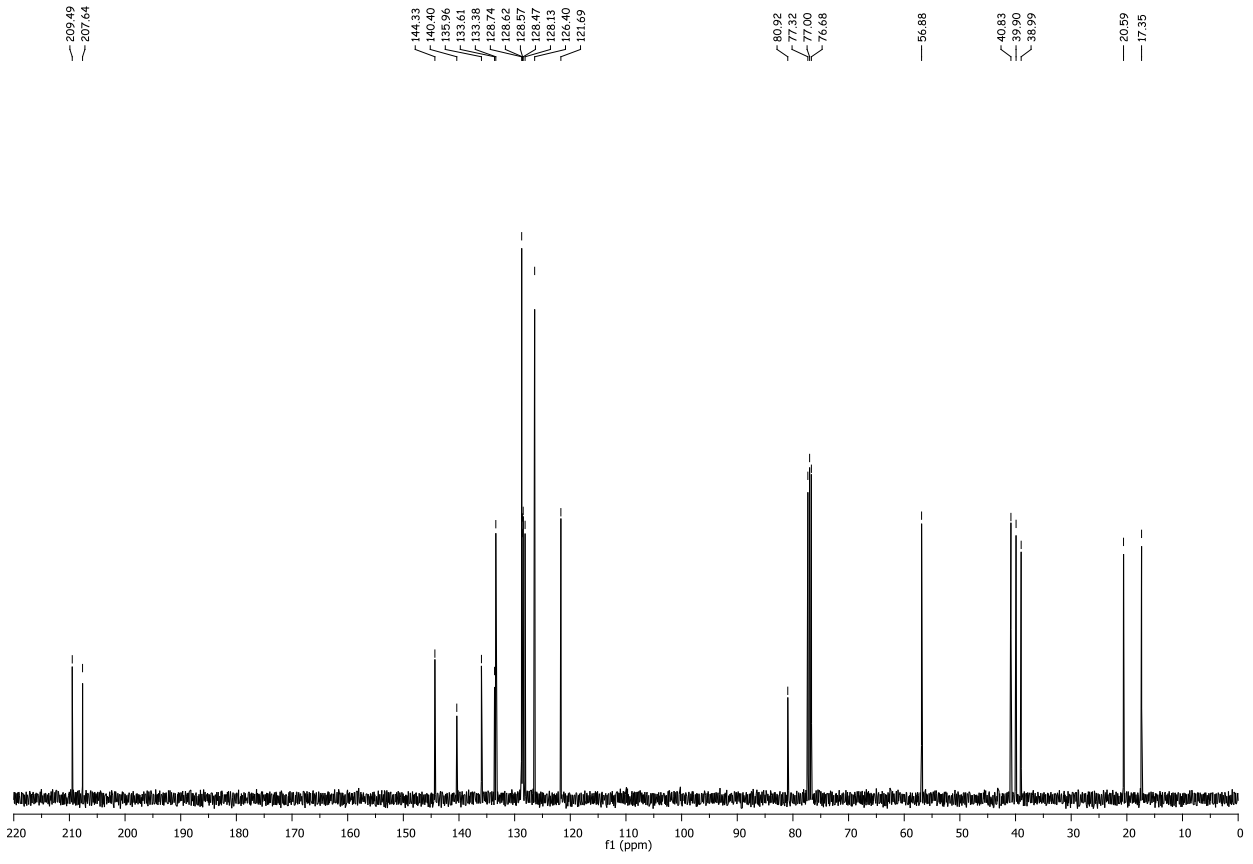
5.27
0.98
0.92
1.93
1.00
4.05
2.00
1.04
2.03
1.05
3.03
2.97
f1 (ppm)

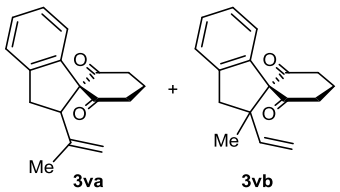

207.59
206.48
158.62
141.42
136.42
135.98
133.11
128.66
128.59
127.78
126.35
125.35
113.71
111.01
80.19
77.32
77.00
76.68
55.41
54.21
53.46
53.59
37.43
30.50
29.36
28.34
f1 (ppm)


Me
O
O
Ph

3u

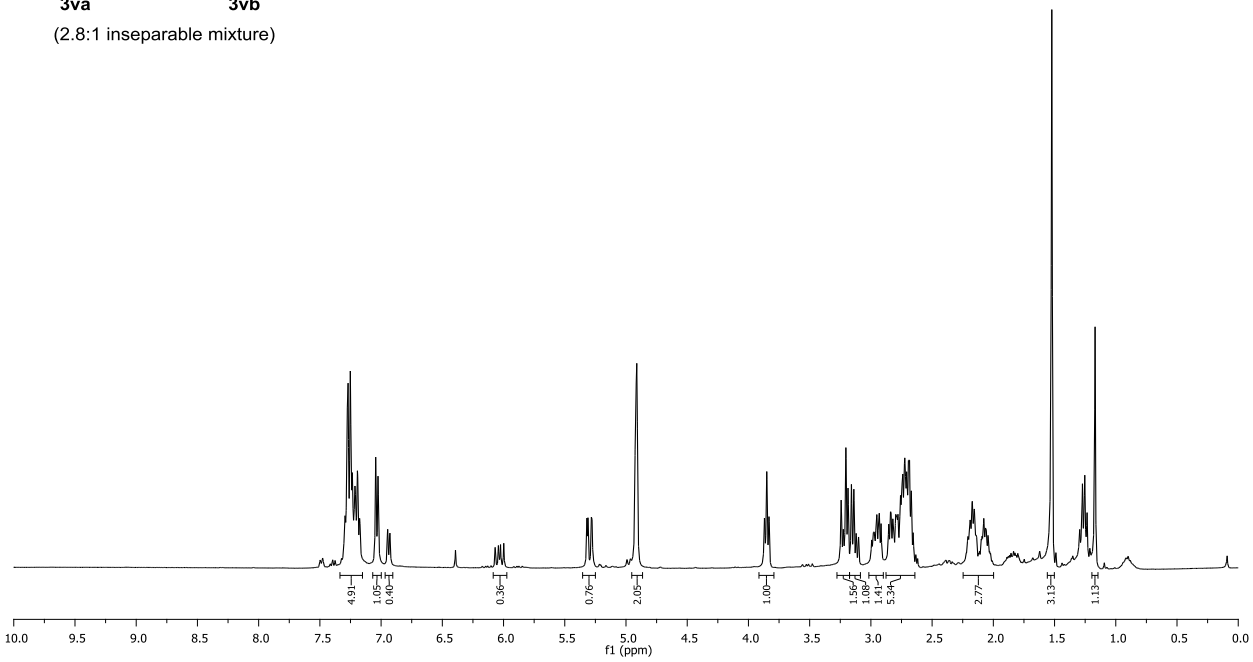
5.26
1.04
1.02
1.00
1.00
1.00
1.03
1.06
1.06
3.16
1.05
1.10
4.11
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


209.49
207.64
144.33
140.40
135.96
133.61
133.38
128.74
128.62
128.57
128.47
128.13
126.40
121.69
80.92
77.32
77.00
76.68
56.88
40.83
39.90
38.99
20.59
17.35
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)

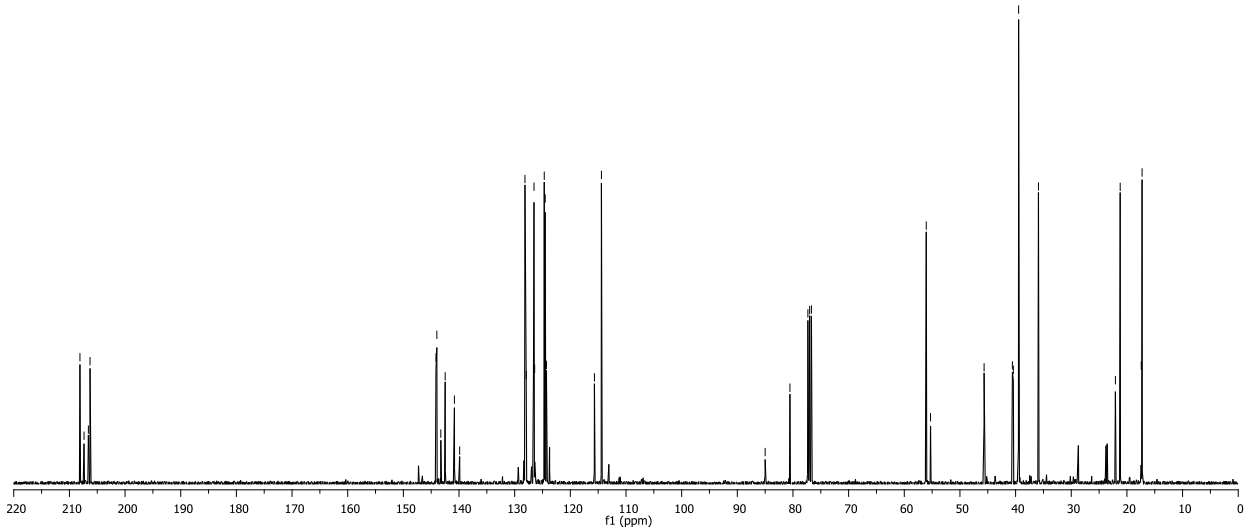


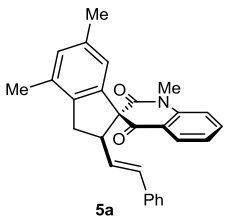
3va **3vb**

(2.8:1 inseparable mixture)

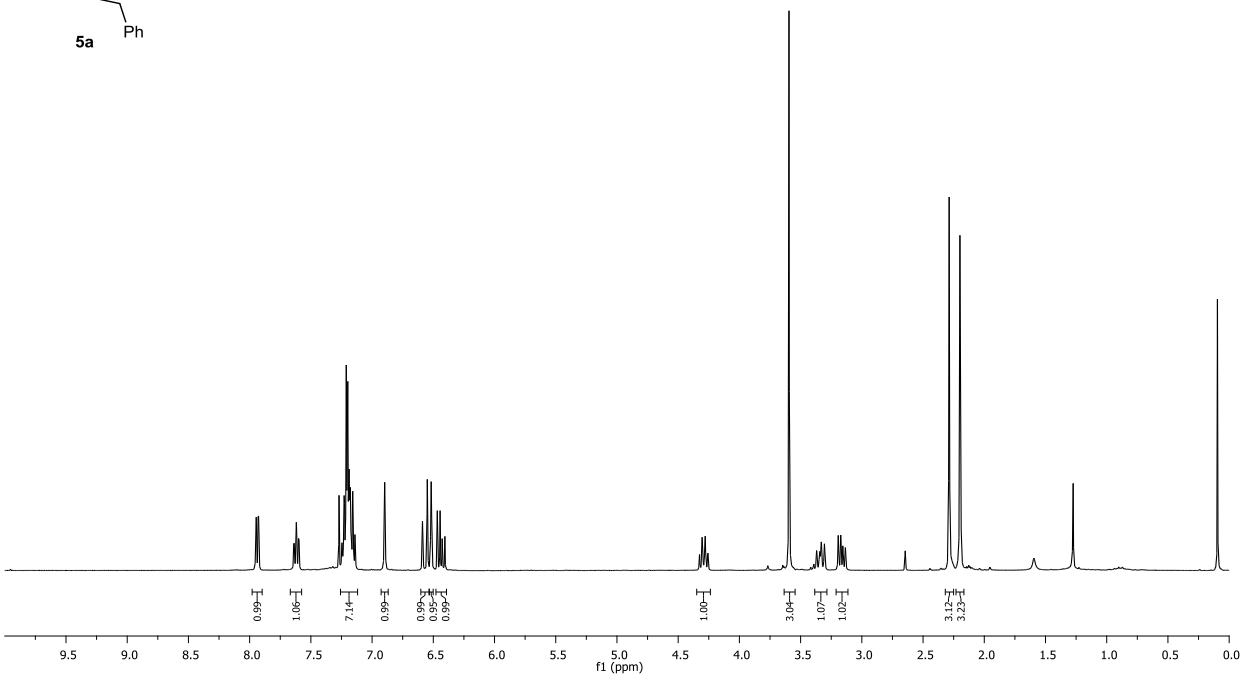


208.11
207.37
206.59
206.30
144.14
143.98
143.27
142.49
140.83
139.89
128.15
126.53
126.41
124.69
124.52
114.41
85.00
80.54
77.32
77.00
76.68
56.05
55.29
45.66
40.58
40.41
39.46
35.89
22.06
21.21
17.43
17.28

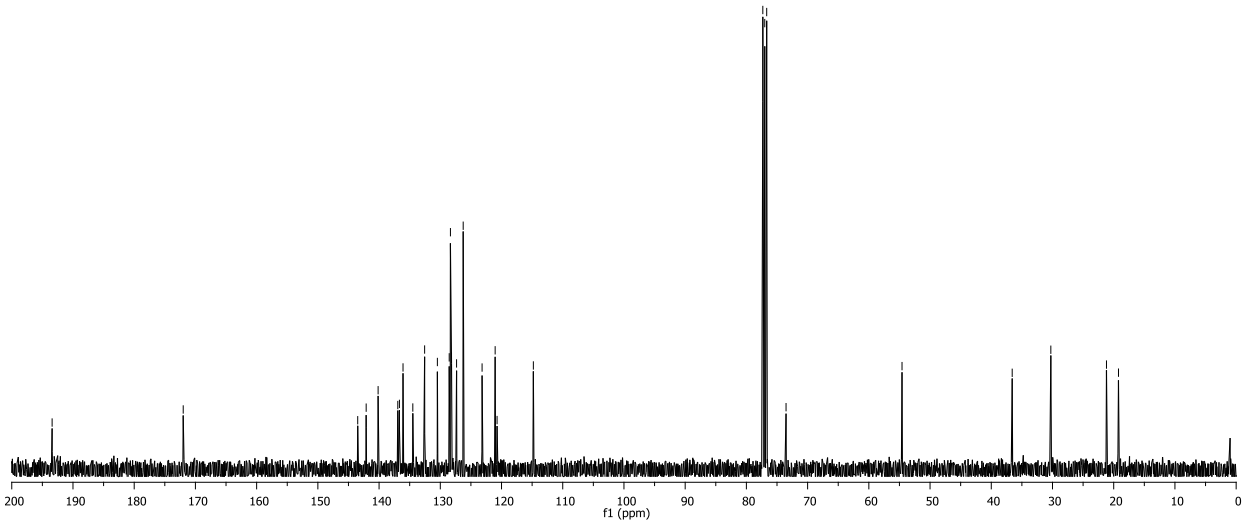


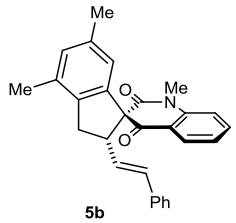

Me
Me
O
Me
N
O
Ph

5a

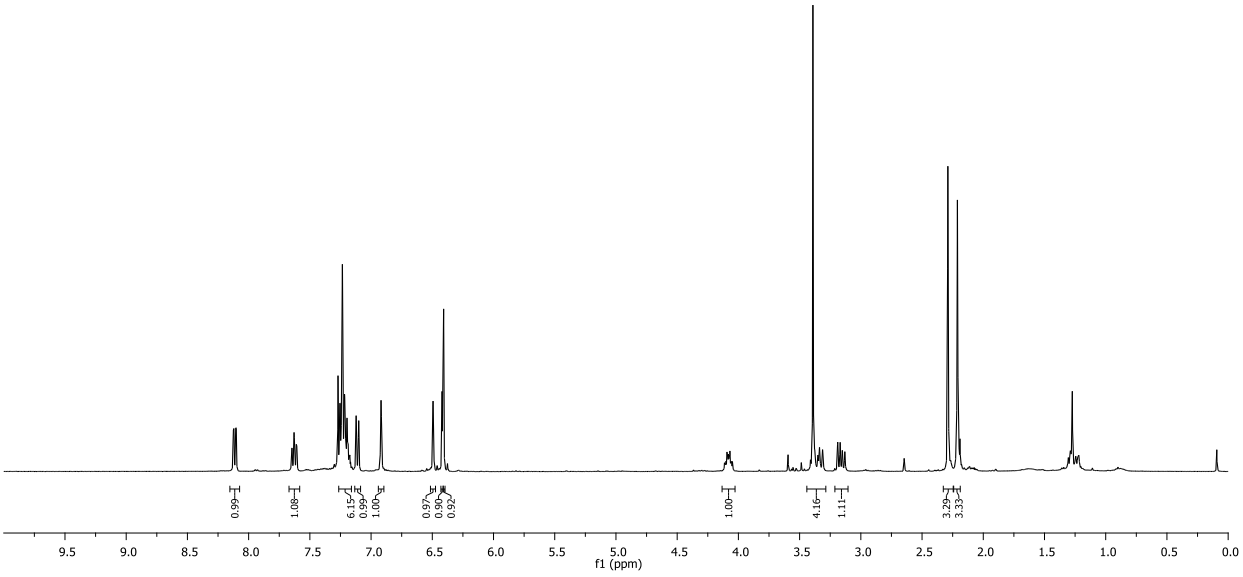

0.99
1.06
7.14
0.99
0.95
0.95
0.99
1.00
3.04
1.07
1.02
3.12
3.23
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


193.41
171.99
143.49
142.11
140.16
136.94
136.67
136.09
134.49
132.56
130.48
128.54
128.35
128.17
127.34
126.26
123.18
121.04
120.73
114.80
77.32
77.00
76.68
73.52
54.58
36.58
30.27
21.18
19.22

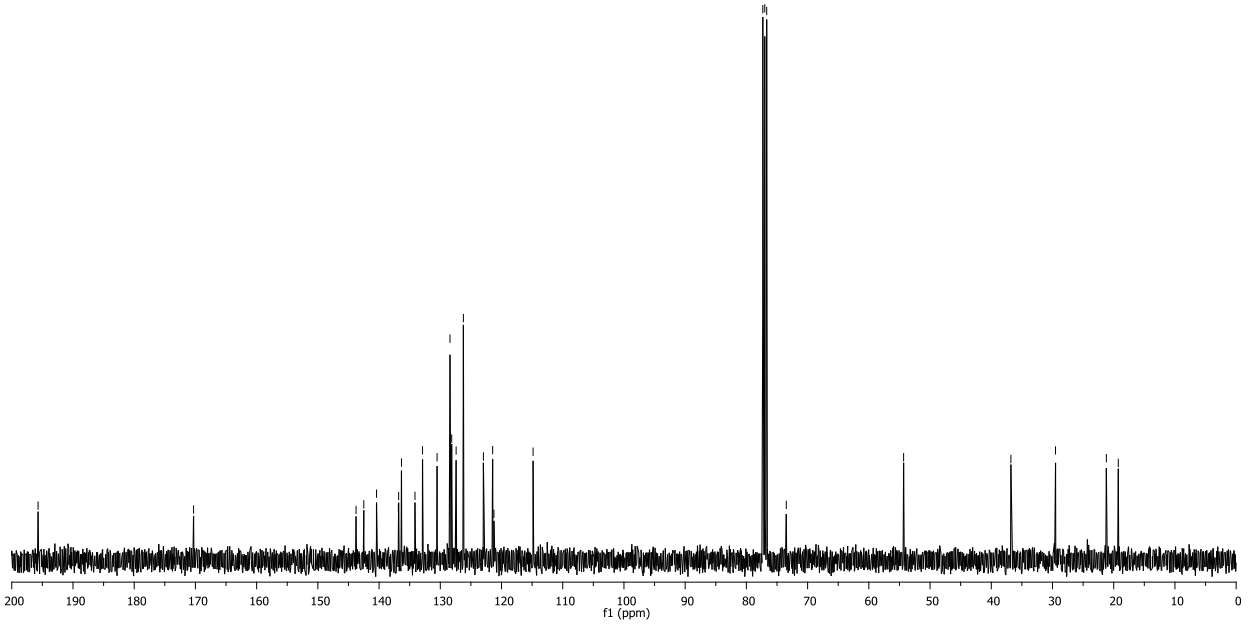

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

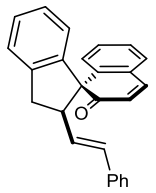

Me
Me
O
Me
N
O
Ph

5b

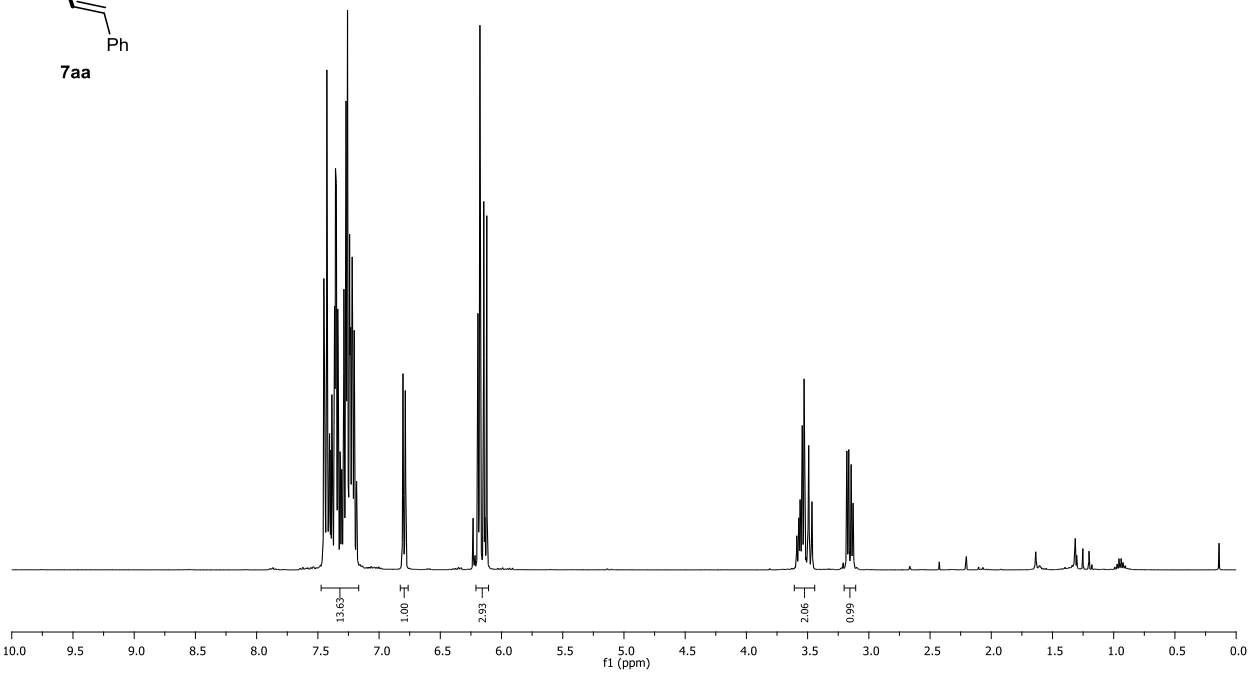

0.99
1.08
6.15
0.99
1.00
0.97
0.90
0.92
1.00
4.16
1.11
3.29
3.33
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


195.70
170.30
143.76
142.50
140.41
136.85
136.80
136.34
134.14
132.90
130.52
128.41
128.34
128.14
127.41
126.23
122.96
121.45
121.24
114.84
77.32
77.00
76.68
73.49
54.32
36.79
29.50
21.20
19.25

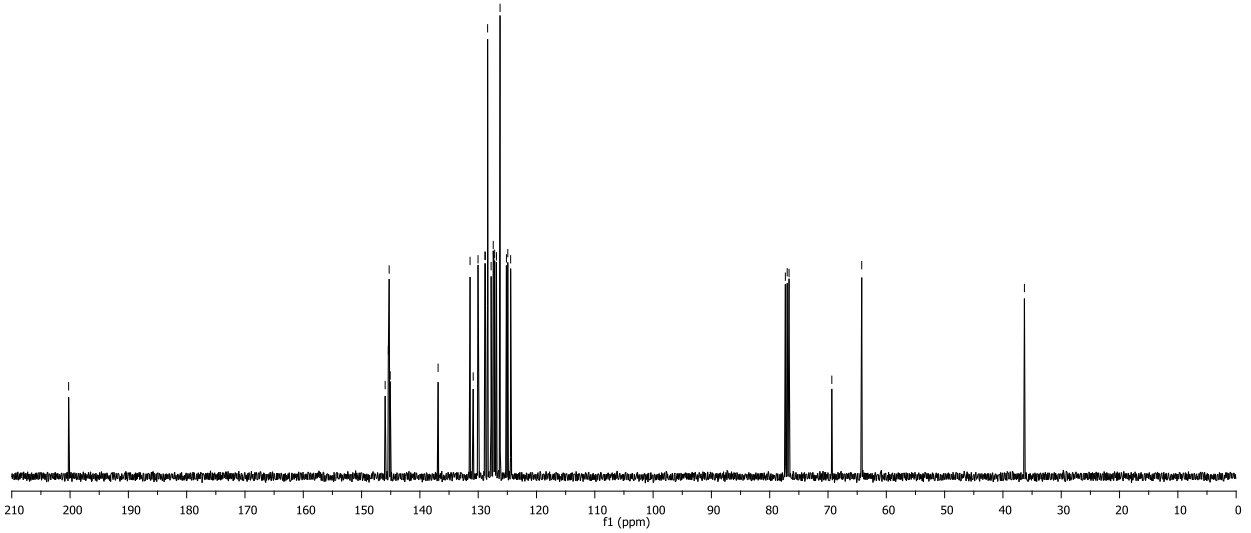

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

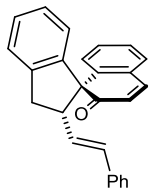

O
Ph

7aa

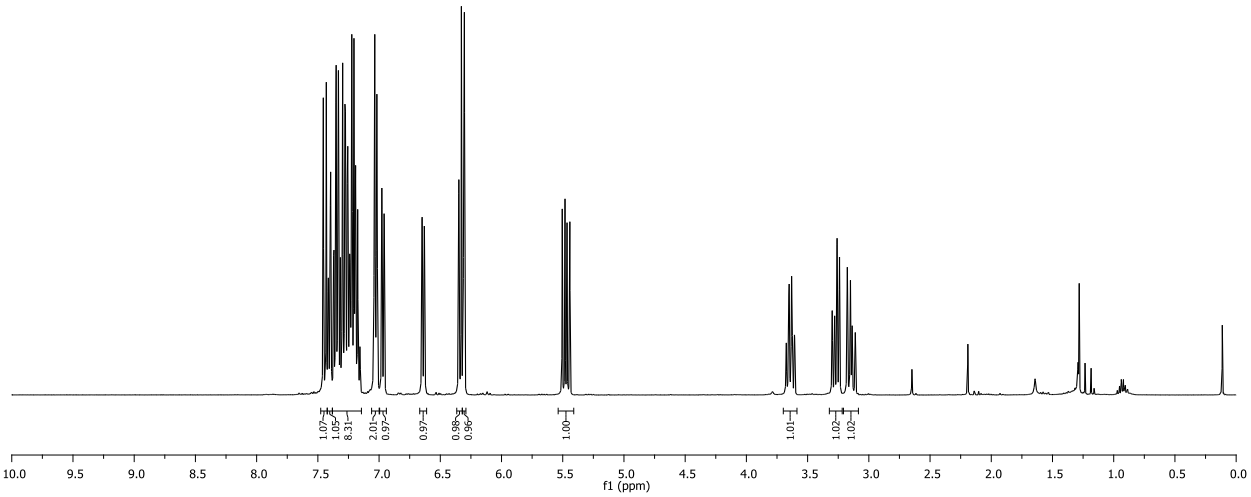

13.63
1.00
2.93
2.06
0.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

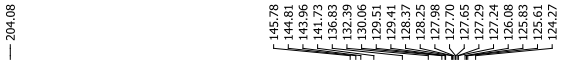

200.25
145.96
145.41
145.27
145.10
136.88
131.39
130.86
130.03
128.86
128.77
128.38
127.78
127.42
127.32
127.18
126.87
126.25
125.16
124.92
124.43
77.32
77.00
76.68
69.35
64.22
36.31

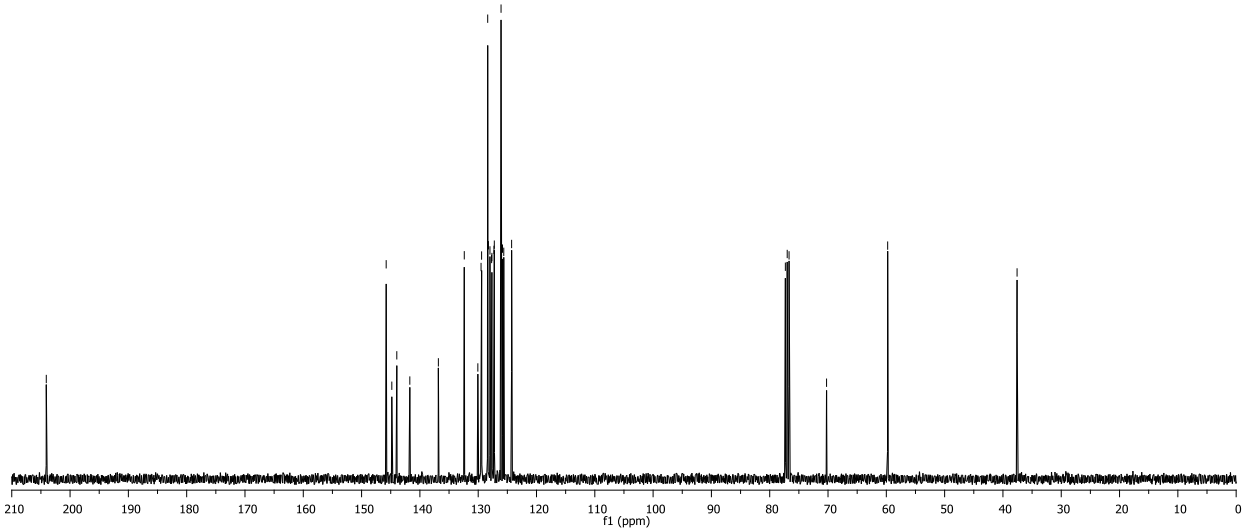

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

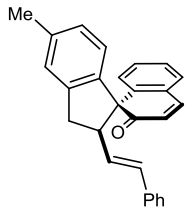

O
Ph

7ab

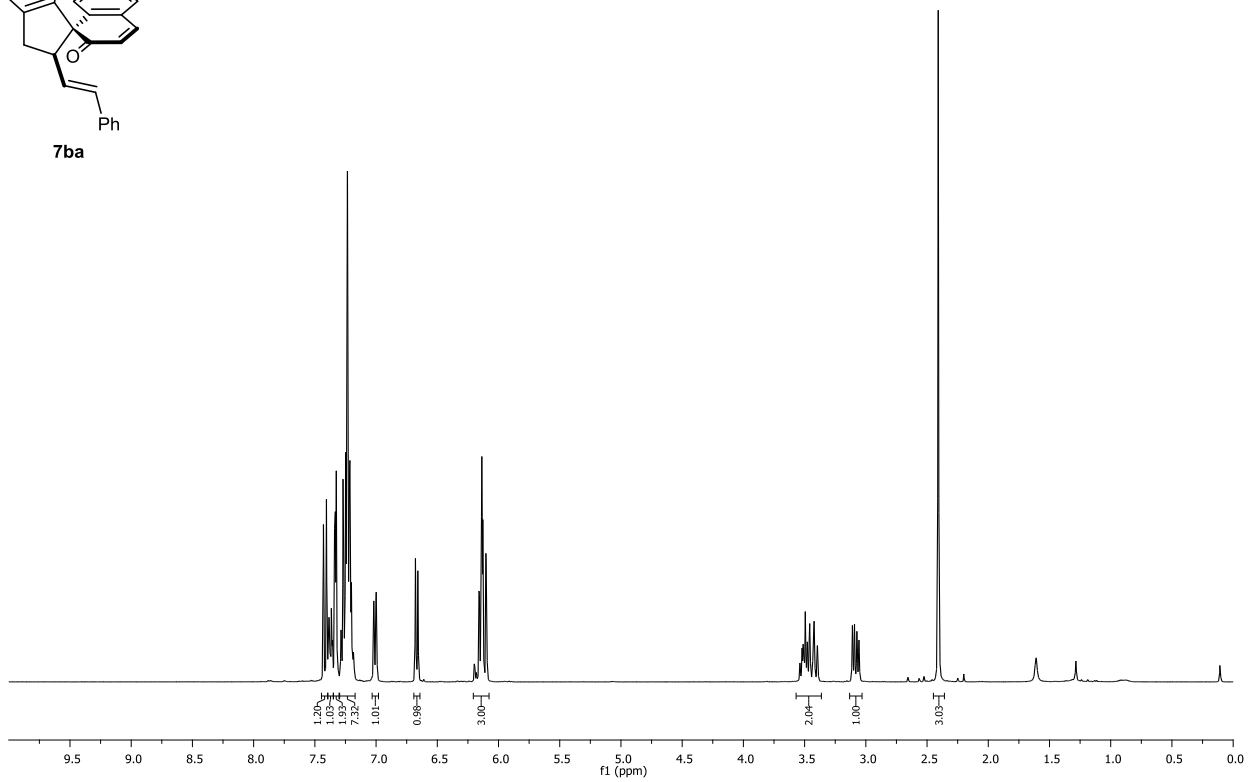

1.07
1.05
8.31
2.01
0.97
0.97
0.98
0.96
1.00
1.01
1.02
1.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

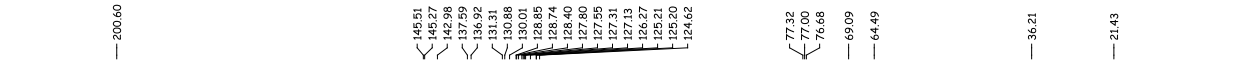

204.08
145.78
144.81
143.96
141.73
136.83
132.39
130.06
129.51
129.41
128.37
128.25
127.98
127.70
127.65
127.29
127.24
126.08
125.83
125.61
124.27
77.32
77.00
76.68
70.25
59.77
37.58

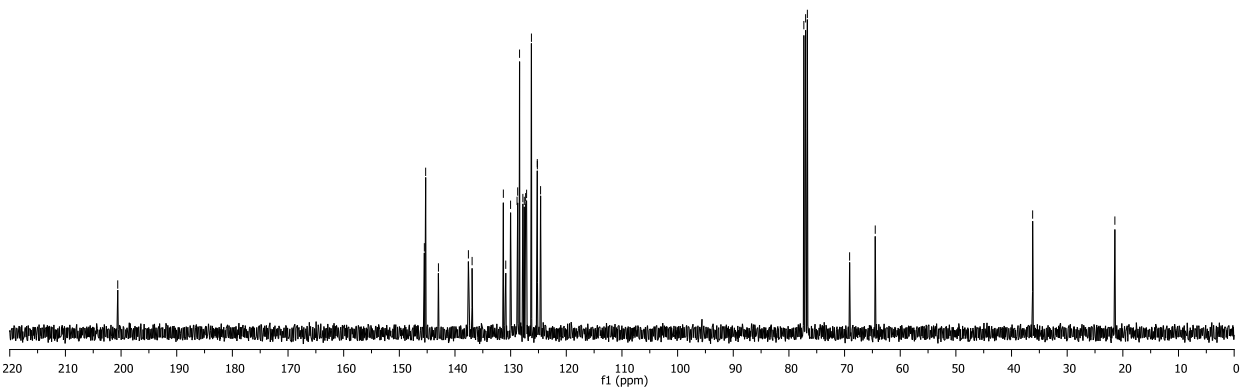

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

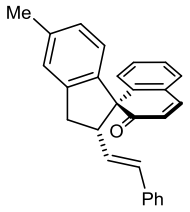

Me
O
Ph

7ba

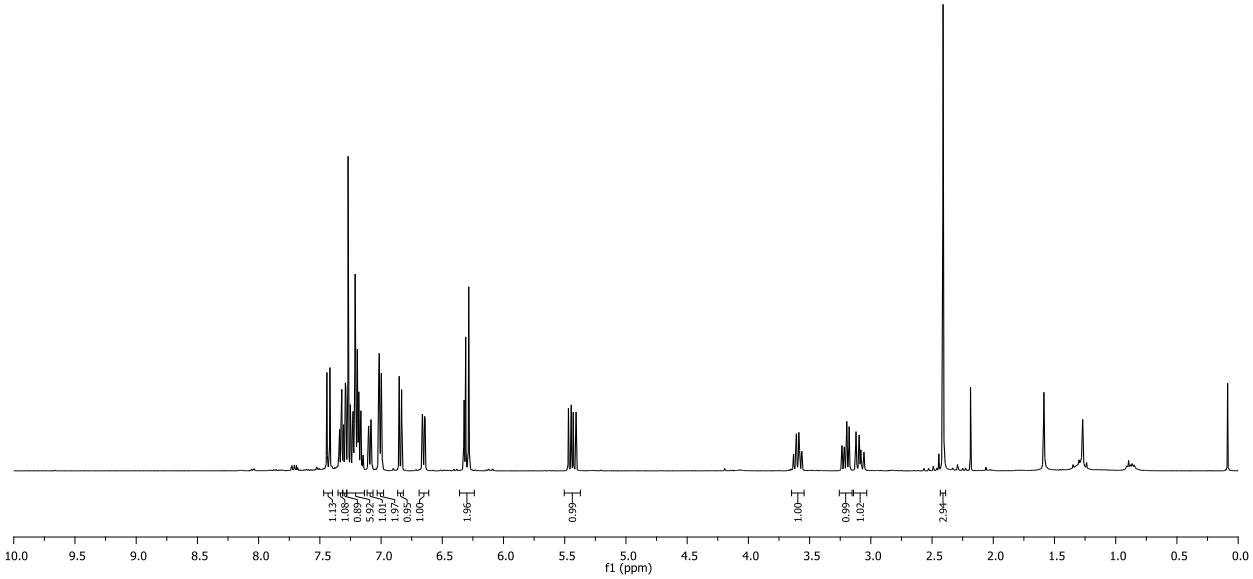

1.20
1.03
1.93
7.32
1.01
0.98
3.00
2.04
1.00
3.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

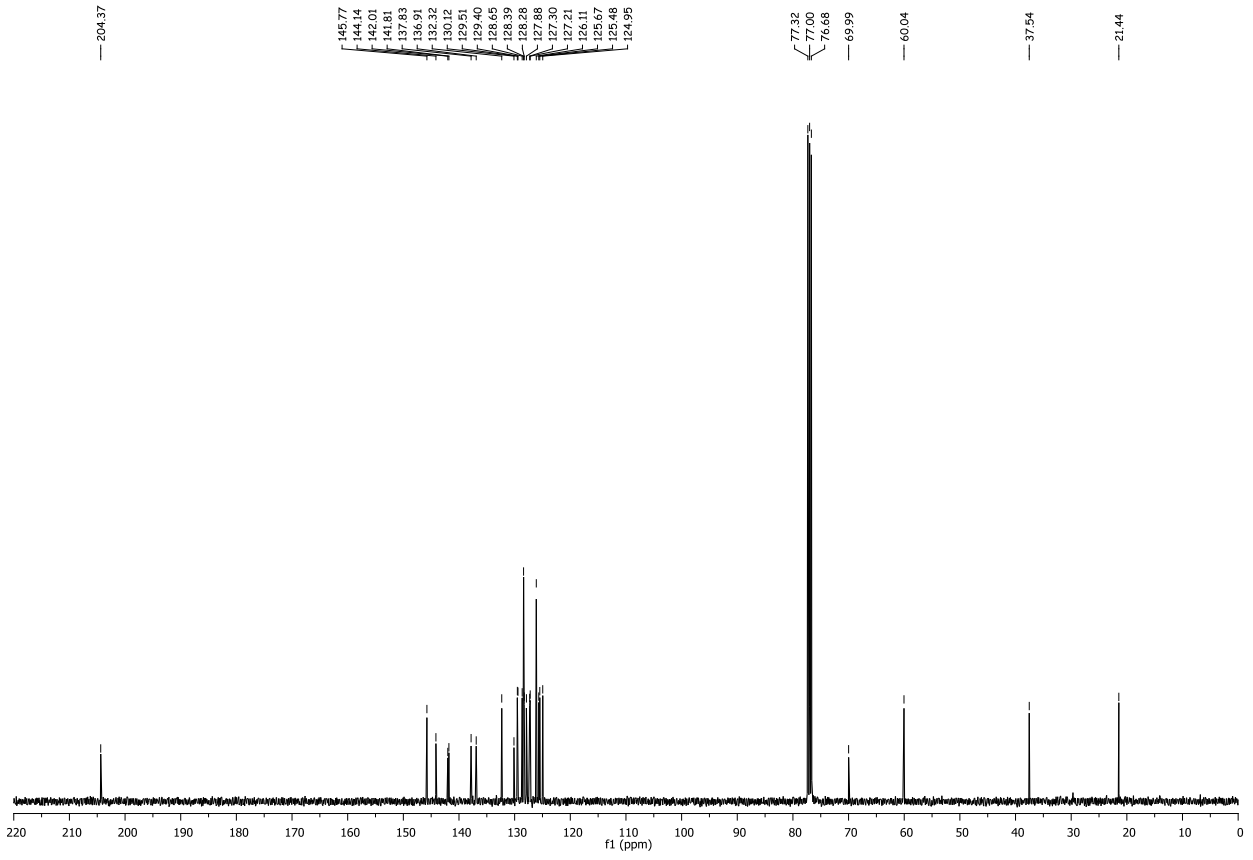

200.60
145.51
145.27
142.98
137.59
136.92
131.31
130.88
130.01
128.85
128.74
128.40
127.80
127.55
127.31
127.13
126.27
125.21
125.20
124.62
77.32
77.00
76.68
69.09
64.49
36.21
21.43


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)


Me
O
Ph

7bb


1.13
1.08
0.89
5.00
1.01
1.97
0.95
1.00
1.96
0.99
1.00
0.99
1.02
2.94
f1 (ppm)


204.37
145.77
144.14
142.01
141.81
137.83
136.91
132.32
130.12
129.51
129.40
128.65
128.39
128.28
127.88
127.30
127.21
126.11
125.67
125.48
124.95
77.32
77.00
76.68
69.99
60.04
37.54
21.44
f1 (ppm)