Supporting Information for

Domino Synthesis of benzo-fused β,γ-Unsaturated Ketones from Alkenylboronic acids and *N*-Tosylhydrazone-tethered Benzonitriles

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CONTENTS

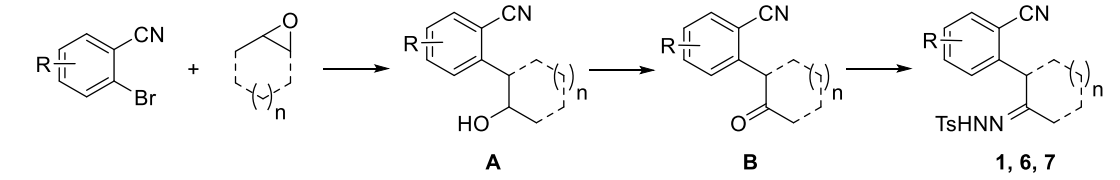
1.- Experimental procedures: General considerations:

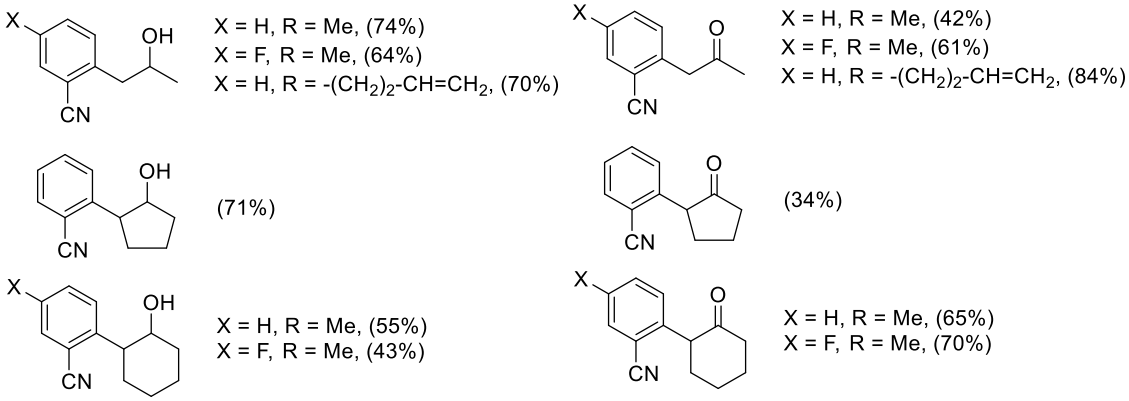
Microwave-assisted reactions were conducted using a focused microwave unit (Biotage InitiatorTM 2.0). The temperature was monitored with an infrared temperature sensor. In all experiments the microwave temperature was held constant. Reactions were performed in (0.5-2 mL) glass vials, which were sealed with a cap with septum. The specific reaction time corresponds to the total irradiation time. 1,4-Dioxane was dried using the corresponding procedure described in D. Perrin, Purification of Laboratory Chemicals, Pergamon Press Ltd. 1980, 2nd Ed. K_2CO_3 was purchased from Fluka and Alfa Aesar Chemical co., stored in a flask purged with nitrogen and weighted in the air. The corresponding boronic acids, epoxides, 2-bromobenzonitriles are commercially available from Aldrich Chemical Co. *N*-Tosylhydrazones were prepared from the corresponding carbonyl compounds and through previously described methodologies.[1] NMR spectra were recorded in CD_2Cl_2 and $CDCl_3$ at 600 MHz and 300 MHz for ^1H, 75 MHz, 100 MHz and 150 MHz for ^{13}C and 282 MHz for ^{19}F, with tetramethylsilane as internal standard for ^1H and the residual solvent signals as standard for ^{13}C. The data is being reported as s = singlet, bs = broad singlet, d = doublet, dd = double doublet, t = triplet, dt = double triplet, q = quatriplet p = quintuplet and m = multiplet or unresolved, chemical shifts in ppm and coupling constant(s) in Hz. HRMS were measured in ESI mode, and the mass analyser of the HRMS was TOF (Bruker model Impact II). Melting points are uncorrected and were measured in a Gallenkamp apparatus.

[1] V. K. Aggarwal, E. Alonso, I. Bae, G. Hynd, K. M. Lydon, M. J. Palmer, M. Patel, M. Porcelloni, J. Richardson, R. A. Stenson, J. R. Studley, J.-L. Vasse and C. L. Winn, *J. Am. Chem. Soc.*, **2003**, *125*, 10926.

2. Experimental procedures for the synthesis and characterization data for the *N*-tosylhydrazones

2.1- General procedure and characterization data for *N*-tosylhydrazones 1, 4, 6 and 7





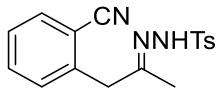
To a solution of the corresponding 2-bromobenzonitrile (5 mmol) in Et_2O (25 mL) was added dropwise BuLi (1.1 equiv.) at -78 °C under nitrogen atmosphere. The resulting mixture was stirred for 30 min at -78 °C and then the epoxide (1.5 equiv.) and boron trifluoride etherate (1.5 equiv.) were added sequentially and dropwise. The reaction was stirred at -78 °C for 1 h and then it was quenched with H_2O. The mixture was extracted with Et_2O (3x20 mL), organic layers were collected, dried with Na_2SO_4 and solvents were evaporated under reduce pressure. The resulting crude was purified by flash chromatography employing as eluent a mixture hexane : ether (1:1) giving the corresponding alcohols **A**.

To a solution of the alcohol **A** in CH_2Cl_2 (0.26 M) was added PCC (1.5 equiv.) at 0 °C. The resulting mixture was stirred for 15 min at 0 °C and after that, at rt for 16 h. The CH_2Cl_2 was evaporated under reduce pressure. The residue was treated with Et_2O and filtered through a short silica gel pad, which was rinsed with additional Et_2O. Solvents were evaporated and the essentially pure corresponding ketone **B** was used without further purification.

The final *N*-tosylhydrazones were prepared following the standard procedure described for Aggarwal:[1] The corresponding ketone **B** (1 mmol) was added to a

stirred solution of *p*-toluensulfonylhydrazide (1,12 mmol) in MeOH (0.65 mL). The reaction was stirred at r.t. until total consumption of the starting carbonyl as monitored by TLC. Then, the solvent was eliminated, giving the *N*-tosylhydrazone **1** as a white solid, which was used in the next step without further purification.

N'-(1-(2-Cyanophenyl)propan-2-ylidene)-4-methylbenzenesulfonohydrazide 1a



Isolated yield after recrystallization in MeOH (starting from the carbonyl compound[2]) = 66 %

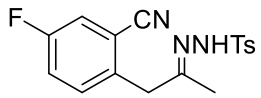
m.p.= 153.2 – 153.4 ºC

^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.65 (d, *J* = 7.8 Hz, 2H), 7.57 – 7.50 (m, 1H), 7.46 – 7.37 (m, 1H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 7.8 Hz, 1H), 3.77 (s, 2H), 2.48 (s, 3H), 1.84 (s, 3H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 155.1 (C), 144.1 (C), 140.2 (C), 135.1 (C), 132.6 (CH), 132.6 (CH), 130.2 (CH), 129.4 (2xCH), 127.9 (2xCH), 127.3 (CH), 117.6 (C), 113.2 (C), 42.8 (CH_2), 21.3 (CH_3), 15.69 (CH_3).

ESI HRMS: calcd. For $[C_{17}H_{18}N_3O_2S]^+$: 328.1114, found: 328.1122.

N'-(1-(2-Cyano-4-fluorophenyl)propan-2-ylidene)-4-methylbenzene sulfonohydrazide 1b



Isolated yield after recrystallization in MeOH = 56%

m.p.= 148.3 – 148.5 ºC

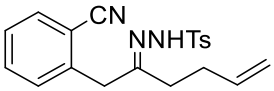
^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.63 (d, *J* = 8.3 Hz, 2H), 7.37 – 7.28 (m, 4H), 7.25 (dd, *J* = 8.3, 2.7 Hz, 1H), 7.18 (dd, *J* = 8.7, 5.3 Hz, 1H), 3.73 (s, 2H), 2.48 (s, 3H), 1.85 (s, 3H).

[2] Mangas-Sanchez, J.; Busto, E.; Gotor-Fernandez, Vicente; Gotor, V. *Catal. Sci. Technol.*, **2012**, *2*, 1590

^{13}C NMR (75 MHz, CD_2Cl_2) δ 160.8 (C, d, $^2J_{C-F}$= 248.2 Hz), 155.0 (C), 144.2 (C), 136.5 (C, d, $^5J_{C-F}$= 3.7 Hz), 135.0 (C), 132.3 (CH, d, $^4J_{C-F}$= 8.3 Hz), 129.4 (CH), 127.9 (CH), 120.2 (CH, d, $^3J_{C-F}$= 21.3 Hz), 119.0 (CH, d, $^3J_{C-F}$= 24.6 Hz), 116.4 (C, d, $^5J_{C-F}$= 2.8 Hz), 114.4 (C, d, $^4J_{C-F}$= 9.4 Hz), 42.1 (CH_2), 21.3 (CH_3), 15.8 (CH_3). ^{19}F NMR (282 MHz, CD_2Cl_2) δ -114.13.

ESI HRMS: calcd. For $[C_{17}H_{17}FN_3O_2S]^+$: 346.1020, found: 346.1017.

***N'*-(1-(2-Cyanophenyl)hex-5-en-2-ylidene)-4-methylbenzenesulfonohydrazide 1c**



Isolated yield after purification by flash chromatography in 2:1 Hex/EtOAc: 49%. Rf = 0.34

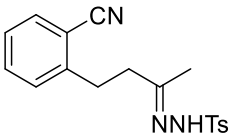
m.p.= 101.7 – 101.9 ºC

^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.59 – 7.48 (m, 1H), 7.45 – 7.32 (m, 3H), 7.06 (d, *J* = 7.7 Hz, 1H), 5.86 – 5.50 (m, 1H), 5.13 – 4.83 (m, 2H), 3.78 (s, 2H), 2.48 (s, 3H), 2.24 (bs, 4H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 157.8 (C), 144.1 (C), 140.4 (C), 136.1 (CH), 134.9 (C), 132.5 (CH), 132.5 (CH), 130.5 (CH), 129.4 (2xCH), 127.9 (2xCH), 127.2 (CH), 117.6 (C), 116.6 (CH_2), 113.2 (C), 41.0 (CH_2), 29.0 (CH_2), 28.9 (CH_2), 21.3 (CH_3).

ESI HRMS: calcd. For $[C_{20}H_{22}N_3O_2S]^+$: 368.1427, found: 368.1423.

***N'*-(4-(2-cyanophenyl)butan-2-ylidene)-4-methylbenzenesulfonohydrazide 4**



Isolated yield after recrystallization in MeOH (starting from the corresponding carbonyl compound[3]) = 66 %

m.p.= 111.8 – 112.2 ºC

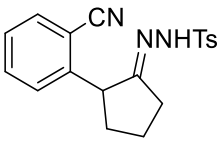
[3] Bell, M. G. et. al. From U.S., 5786356, 20 Jul 1998.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.2 Hz, 2H), 7.64 (s, 1H), 7.56 (d, *J* = 7.7 Hz, 1H), 7.51 – 7.39 (m, 1H), 7.38 – 7.17 (m, 2H), 3.03 (t, *J* = 7.8 Hz, 2H), 2.58 (t, *J* = 7.8 Hz, 2H), 2.46 (s, 3H), 1.84 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 156.0 (C), 145.0 (C), 144.0 (C), 135.2 (C), 132.8 (CH), 132.7 (CH), 129.7 (CH), 129.5 (CH), 129.5 (CH), 128.0 (CH), 126.6 (CH), 117.9 (C), 112.1 (C), 39.0 (CH_2), 30.4 (CH_2), 21.6 (CH_3), 16.1 (CH_3).

ESI HRMS: calcd. For $[C_{18}H_{20}N_3O_2S]^+$: 342.1271, found: 342.1268.

***N'*-(2-(2-Cyanophenyl)cyclopentylidene)-4-methylbenzenesulfonohydrazide 6**



Isolated yield after recrystallization in MeOH, 51%

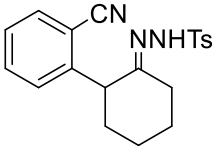
m.p.= 129.7 – 129.9 ºC

^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.60 (d, *J* = 8.4 Hz, 2H), 7.54 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.49 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.43 (bs, 1H), 7.38 (td, *J* = 7.6, 1.3 Hz, 1H), 7.25 (d, *J* = 7.5 Hz, 2H), 7.14 (dd, *J* = 7.9, 1.2 Hz, 1H), 4.01 (t, *J* = 8.4 Hz, 1H), 3.45 (s, 1H), 2.48 (s, 3H), 2.40 – 2.30 (m, 2H), 2.15 – 2.04 (m, 1H), 1.93 – 1.80 (m, 2H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 167.2 (C), 145.5 (C), 143.9 (C), 135.2 (C), 133.1 (CH), 132.6 (CH), 129.4 (2xCH), 129.3 (CH), 127.9 (2xCH), 126.8 (CH), 117.7 (C), 112.3 (C), 50.0 (CH), 34.0 (CH_2), 28.8 (CH_2), 23.2 (CH_2), 21.3 (CH_3).

ESI HRMS: calcd. For $[C_{19}H_{20}N_3O_2S]^+$: 354.1271, found: 354.1268.

(2-(2-cyanophenyl)cyclohexylidene)-4-methylbenzenesulfonohydrazide 7a



Isolated yield after recrystallization in MeOH, 70%

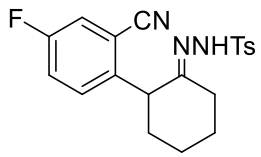
m.p.= 153.2 – 153.5 ºC

^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.71 – 7.60 (m, 2H), 7.45 (td, *J* = 7.6, 1.2 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.33 – 7.25 (m, 3H), 7.22 – 7.15 (m, 2H), 3.80 (dd, *J* = 12.4, 4.7 Hz, 1H), 2.84 – 2.74 (m, 1H), 2.45 (s, 3H), 2.15 – 1.88 (m, 5H), 1.75 – 1.64 (m, 1H), 1.55 (d, *J* = 3.5 Hz, 1H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 161.3 (C), 144.8 (C), 143.9 (C), 134.7(C), 132.3(CH), 132.3 (CH), 129.2 (CH), 129.1 (CH), 127.9 (CH), 126.8 (CH), 117.7 (C), 113.2 (C), 49.1 (CH), 32.9 (CH_2), 27.0 (CH_2), 25.4 (CH_2), 25.1 (CH_2), 21.3 (CH_3).

ESI HRMS: calcd. For $[C_{20}H_{22}N_3O_2S]^+$: 368.1427, found: 368.1436.

(*Z*)-*N'*-(2-(2-Cyano-4-fluorophenyl)cyclohexylidene)-4-methylbenzene-sulfonohydrazide 7b



Isolated yield after recrystallization in MeOH, 45%

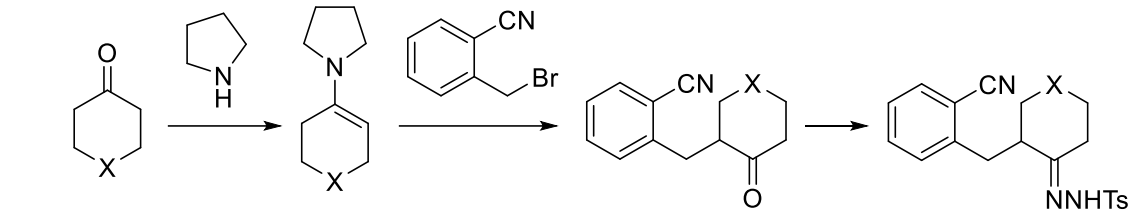
m.p.= 189.0 – 190.3 ºC

^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.40 – 7.33 (m, 4H), 7.33 – 7.27 (m, 1H), 7.22 (d, *J* = 8.3 Hz, 3H), 3.78 (dd, *J* = 12.3, 4.5 Hz, 1H), 2.83 – 2.74 (m, 1H), 2.47 (s, 3H), 2.19 – 1.83 (m, 5H), 1.77 – 1.60 (m, 2H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 161.2 (C), 160.49 (C, d, $^{2}J_{C\text{-}F}$= 247.6 Hz), 144.1 (C), 140.9 (C, d, $^{5}J_{C\text{-}F}$= 3.6 Hz)., 134.7 (C), 131.1 (CH, d, $^{4}J_{C\text{-}F}$= 7.8 Hz), 129.5 (C), 129.1 (2xCH), 127.9 (2xCH), 126.5 (C), 119.7 (CH, d, $^{3}J_{C\text{-}F}$= 21.0 Hz), 118.7 (CH, d, $^{3}J_{C\text{-}F}$= 24.6 Hz), 48.5 (CH), 33.1 (CH_2), 27.0 (CH_2), 25.3 (CH_2), 25.1 (CH_2), 21.3 (CH_3).

ESI HRMS: calcd. For $[C_{20}H_{21}FN_3O_2S]^+$: 386.1333, found: 386.1333.

2.2- Experimental procedure and characterization data for *N*-tosylhydrazones 10

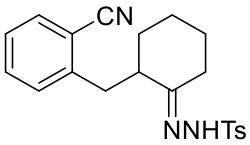


X = CH_2, NBn **D** **E** **10a**, X = CH_2 **10b**, X = NBn

A 100 mL round-bottom flask containing 4 Å molecular sieves and the corresponding cyclic ketone (30 mmol) in toluene (15 mL) was fitted with a Dean−Stark trap with a reflux condenser and heating mantle. Pyrrolidine (4.7 mL, 56 mmol) was added to the above solution. The solution was heated to reflux overnight. The solvent was evaporated to yield crude enamine A[4] as a yellow oil which was transferred to a new 250 mL flask with a magnetic stirrer. To a solution of the enamine A in dioxane (0.5 M solution) was added the 2-(bromomethyl)benzonitrile (30 mmol). The reaction mixture was heated to reflux and stirred for 8 h. Water was added, and the mixture was heated for 2 h. The organic phase was taken up in diethyl ether, washed with brine, dried (MgSO4), and then concentrated to give a brown oil. The resulting crude was purified by flash chromatography employing a convenient eluent to give the corresponding alkylated ketones E[5] 3.82g of **Ea**, 60% yield, yellow oil, hexane: EtOAc 6:1, R*f*: 0.45; 1.21g of **Eb**, 13% yield, brown oil, hexane: EtOAc 3:1, R*f*: 0.40). The corresponding carbonyl compound (1 mmol) was added to a stirred solution of *p*-toluensulfonylhydrazide (1,12 mmol) in MeOH (0.65 mL). The reaction was stirred at r.t. until total consumption of the starting carbonyl. Then, the solvent was eliminated, giving the *N*-tosylhydrazone as a white solid which was used in the next step without further purification.

[4] Chen, L.; Li, L.; Sampson, N. S.;*J. Org. Chem.,* **2018**, *83*, 2892.
[5] Hays, S. J. et al *J. Med. Chem.,* **1993**, *36*, 654.

_N'_-(2-(2-cyanobenzyl)cyclohexylidene)-4-methylbenzenesulfonohydrazide 10a



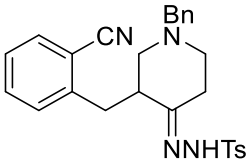
m.p.= 151.2 – 151.5 ºC

^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.81 – 7.67 (m, 2H), 7.57 – 7.53 (m, 1H), 7.48 – 7.39 (m, 1H), 7.34 – 7.24 (m, 4H), 3.29 (dd, *J* = 14.1, 5.8 Hz, 1H), 2.73 (dd, *J* = 14.1, 8.1 Hz,1H), 2.66 – 2.35 (m, 2H), 2.44 (s, 3H), 1.96 – 1.86 (m, 1H), 1.80 – 1.23 (m, 7H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 163.1 (C), 145.3 (C), 144.7 (C), 135.8 (C), 133.2 (CH), 133.0 (CH), 131.1 (CH), 130.0 (2xCH), 128.5 (2xCH), 127.0 (CH), 118.7 (C), 133.3 (C), 45.9 (CH), 36.2 (CH_2), 33.4 (CH_2), 27.2 (CH_2), 26.7 (CH_2), 24.8 (CH_2), 21.9 (CH_3).

ESI HRMS: calcd. For $[C_{21}H_{24}N_3O_2S]^+$: 382.1584, found: 382.1587.

(1-benzyl-3-(2-cyanobenzyl)piperidin-4-ylidene)-4-methylbenzenesulfonohydrazide 10b



m.p.= 160.2 – 160.5 ºC

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 – 7.74 (m, 3H), 7.39 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.34 – 7.30 (m, 2H), 7.29 – 7.27 (m, 2H), 7.25 – 7.24 (m, 2H), 7.22 – 7.10 (m, 3H), 3.60 – 3.55 (m, 1H), 3.44 – 3.13 (m, 3H), 2.84 – 2.73 (m, 2H), 2.64 – 2.47 (m, 3H), 2.42 – 2.32 (m, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 159.8 (C), 144.1 (C), 144.0 (C), 137.8 (C), 135.2 (C), 132.8 (CH), 132.7 (CH), 130.4 (CH), 129.7 (2xCH), 129.1 (2xCH), 128.4 (2xCH), 128.2 (2xCH), 127.4 (CH), 126.6 (CH), 118.3 (C), 112.7 (C), 62.2 (CH_2), 58.1 (CH_2), 52.1 (CH_2), 44.6 (CH), 35.1 (CH_2), 25.9 (CH_2), 21.8 (CH_3).

ESI HRMS: calcd. For $[C_{27}H_{29}N_4O_2S]^+$: 473.2006, found: 473.2006.

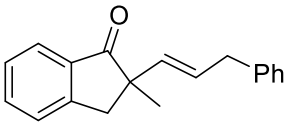
3 – Experimental procedures and characterization data for the final products.

3.1. Experimental procedure and characterization data for ketones 3, 5, 8 and 9.

A microwave vial provided with a triangular stir bar was charged with the tosylhydrazone (0.15 mmol), the alkenyl boronic acid (0.3 mmol) and K_2CO_3 (41.5 mg, 0.3 mmol) in 1.2 mL of dry 1,4-dioxane. The vial was sealed with a septum, placed into the microwave cavity and irradiated to maintain the reaction at the desired temperature (120 ºC) during the reaction time (4h) in a Biotage Initiator microwave apparatus. Once the reaction finished, it was allowed to reach room temperature and the crude was dissolved in DCM and filtered through celite. The solvent was removed under reduced pressure. Finally, the products were purified by flash chromatography on silica gel.

(*E*)-2-Methyl-2-(3-phenylprop-1-en-1-yl)-2,3-dihydro-1*H*-inden-1-one 3a

Following the general method, *N*-tosylhydrazone **1a** (49 mg, 0.15 mmol) and *trans*-3-phenyl-1-propen-1-ylboronic acid (48 mg, 0.3 mmol) were obtained 22 mg of **3a** (56% isolated yield) as a colourless oil. Rf 0.16 (20:1 hexane EtOAc).



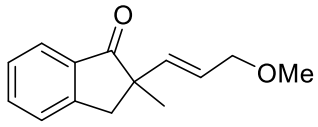
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.8 Hz, 1H), 7.62 (td, *J* = 7.4, 1.2 Hz, 1H), 7.46 (dt, *J* = 7.7, 0.9 Hz, 1H), 7.40 (td, *J* = 7.4, 0.9 Hz, 1H), 7.33 – 7.26 (m, 2H), 7.23 – 7.20 (m, 1H), 7.19 – 7.15 (m, 2H), 5.83 – 5.63 (m, 2H), 3.38 (d, *J* = 5.8 Hz, 2H), 3.33 (d, *J* = 17.4 Hz, 1H), 3.04 (d, *J* = 17.1 Hz, 1H), 1.39 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 208.4 (C), 152.1 (C), 140.2 (C), 135.3 (C), 134.9 (CH), 134.1 (CH), 128.6 (CH), 128.5 (2xCH), 128.3 (2xCH), 127.5 (CH), 126.5 (CH), 126.0 (CH), 124.6 (CH), 51.5 (C), 41.5 (CH2), 38.9 (CH2), 24.0 (CH3).

ESI HRMS: calcd. For $[C_{19}H_{19}O]^+$: 263.1430, found: 263.1421.

(*E*)-2-(3-Methoxyprop-1-en-1-yl)-2-methyl-2,3-dihydro-1*H*-inden-1-one 3b

Following the general method, *N*-tosylhydrazone **1a** (49 mg, 0.15 mmol) and *trans*-3-methoxy-1-propenylboronic acid (35 mg, 0.3 mmol) were obtained 20 mg of **3b** (62% isolated yield) as a colourless oil. Rf 0.17 (8:1 hexane:EtOAc).



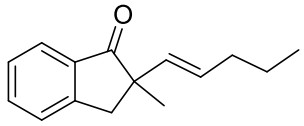
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.8 Hz, 1H), 7.62 (td, *J* = 7.5, 1.3 Hz, 1H), 7.46 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.43 – 7.37 (m, 1H), 5.86 (dt, *J* = 15.8, 1.1 Hz, 1H), 5.72 (dt, *J* = 15.8, 5.7 Hz, 1H), 3.91 (ddd, *J* = 5.9, 3.3, 1.1 Hz, 2H), 3.35 (d, *J* = 17.4 Hz, 1H), 3.31 (s, 3H), 3.05 (d, *J* = 17.1 Hz, 1H), 1.40 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 207.9 (C), 152.0 (C), 135.9 (CH), 135.1 (C), 135.0 (CH), 127.5 (CH), 126.5 (CH), 125.9 (CH), 124.6 (CH), 72.8 (CH_2), 57.9 (CH_3), 51.4 (C), 41.2 (CH_2), 23.7 (CH_3).

ESI HRMS: calcd. For $[C_{14}H_{17}O_2]^+$: 217.1223, found: 217.1206.

(*E*)-2-Methyl-2-(pent-1-en-1-yl)-2,3-dihydro-1*H*-inden-1-one 3c

Following the general method, *N*-tosylhydrazone **1a** (49 mg, 0.15 mmol) and *trans*-1-penten-1-ylboronic acid (34 mg, 0.3 mmol) were obtained 25 mg of **3c** (78% isolated yield) as a colourless oil. Rf 0.31 (20:1 hexane:EtOAc).



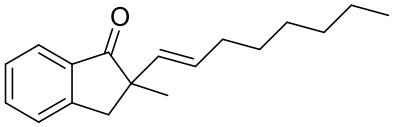
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.0 Hz, 1H), 7.61 (td, *J* = 7.5, 1.3 Hz, 1H), 7.46 (dt, *J* = 7.7, 1.0 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 5.65 – 5.51 (m, 2H), 3.30 (d, *J* = 17.1 Hz, 1H), 3.02 (d, *J* = 17.1 Hz, 1H), 2.04 – 1.96 (m, 2H), 1.42 – 1.29 (m, 5H), 0.87 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 208.6 (C), 152.1 (C), 135.4 (C), 134.8 (CH), 132.6 (CH), 129.9 (CH), 127.4 (CH), 126.4 (CH), 124.6 (CH), 51.4 (C), 41.6 (CH_2), 34.6 (CH_2), 23.9 (CH_3), 22.3 (CH_2), 13.6 (CH_3).

ESI HRMS: calcd. For $[C_{15}H_{19}O]^+$: 215.1430, found: 215.1434

(*E*)-2-Methyl-2-(oct-1-en-1-yl)-2,3-dihydro-1*H*-inden-1-one 3d

Following the general method, *N*-tosylhydrazone **1a** (49 mg, 0.15 mmol) and *trans*-1-octenylboronic acid (47 mg, 0.3 mmol) were obtained 23 mg of **3d** (68% isolated yield) as a yellow oil. Rf 0.34 (20:1 hexane:EtOAc).

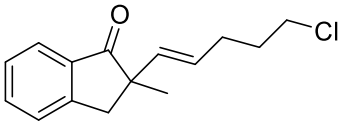


^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.6 Hz, 1H), 7.61 (td, *J* = 7.5, 1.2 Hz, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 7.4 Hz, 1H), 5.66 – 5.50 (m, 2H), 3.30 (d, *J* = 17.1 Hz, 1H), 3.02 (d, *J* = 17.1 Hz, 1H), 2.09 – 1.91 (m, 2H), 1.36 (s, 3H), 1.33 – 1.23 (m, 8H), 0.92 – 0.83 (m, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 208.7 (C), 152.1 (C), 135.4 (C), 134.7 (CH), 132.4 (CH), 130.1 (CH), 127.4 (CH), 126.4 (CH), 124.6 (CH), 51.4 (C), 41.6 (CH_2), 32.6 (CH_2), 31.6 (CH_2), 29.2 (CH_2), 28.7 (CH_2), 23.9 (CH_3), 22.5 (CH_2), 14.0 (CH_3). ESI HRMS: calcd. For $[C_{18}H_{25}O]^+$: 257.1900, found: 257.1876.

(*E*)-2-(5-Chloropent-1-en-1-yl)-2-methyl-2,3-dihydro-1*H*-inden-1-one 3e

Following the general method, *N*-tosylhydrazone **1a** (49 mg, 0.15 mmol) and *trans*-5-chloro-1-penteneboronic acid (44 mg, 0.3 mmol) were obtained 31 mg of **3e** (84% isolated yield) as a colourless oil. Rf 0.21 (20:1 hexane:EtOAc).



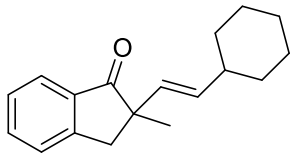
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.4 Hz, 1H), 7.62 (td, *J* = 7.5, 1.2 Hz, 1H), 7.46 (d, *J* = 7.8 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 5.68 – 5.50 (m, 2H), 3.51 (t, *J* = 6.6 Hz, 2H), 3.29 (d, *J* = 17.1 Hz, 1H), 3.04 (d, *J* = 17.1 Hz, 1H), 2.19 (td, *J* = 7.3, 5.8 Hz, 2H), 1.85 (dt, *J* = 8.0, 6.7 Hz, 2H), 1.36 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 208.3 (C), 152.0 (C), 135.3 (C), 134.9 (CH), 134.1 (CH), 128.0 (CH), 127.5 (CH), 126.5 (CH), 124.6 (CH), 51.4 (C), 44.2 (CH_2), 41.6 (CH_2), 31.9 (CH_2), 29.6 (CH_2), 23.8 (CH_3).

ESI HRMS: calcd. For $[C_{15}H_{18}ClO]^+$: 249.1041, found: 249.1029.

(*E*)-2-(2-Cyclohexylvinyl)-2-methyl-2,3-dihydro-1*H*-inden-1-one 3f

Following the general method, *N*-tosylhydrazone **1a** (49 mg, 0.15 mmol) and *trans*-(2-cyclohexylvinyl)boronic acid (46 mg, 0.3 mmol) were obtained 27 mg of **3f** (71% isolated yield) as a colourless oil. Rf 0.32 (20:1, hexane:EtOAc).



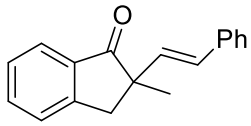
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.7 Hz, 1H), 7.61 (td, *J* = 7.4, 1.2 Hz, 1H), 7.45 (dt, *J* = 7.7, 0.8 Hz, 1H), 7.41 – 7.35 (m, 1H), 5.53 (d, *J* = 2.6 Hz, 2H), 3.30 (d, *J* = 17.2 Hz, 1H), 3.01 (d, *J* = 17.1 Hz, 1H), 1.99 – 1.86 (m, 1H), 1.78 – 1.58 (m, 5H), 1.35 (s, 3H), 1.30 – 1.12 (m, 3H), 1.12 – 0.94 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 208.8 (C), 152.2 (C), 135.7 (CH), 135.4 (C), 134.7 (CH), 130.1 (CH), 127.4 (CH), 126.4 (CH), 124.6 (CH), 51.3 (C), 41.5 (CH_2), 40.6 (CH), 32.9 (CH_2), 32.9 (CH_2), 26.1 (CH_2), 26.0 (2xCH_2), 24.0 (CH_3).

ESI HRMS: calcd. For $[C_{18}H_{23}O]^+$: 255.1743, found: 255.1725.

(*E*)-2-Methyl-2-styryl-2,3-dihydro-1*H*-inden-1-one 3g

Following the general method, *N*-tosylhydrazone **1a** (49 mg, 0.15 mmol) and *trans*-2-phenylvinylboronic acid (44 mg, 0.3 mmol) were obtained 15 mg of **3g** (43% isolated yield) as a colourless oil. Rf 0.18 (30:1 hexane:EtOAc).



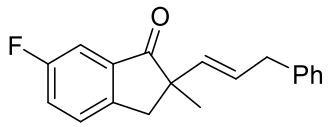
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.6 Hz, 1H), 7.65 (td, *J* = 7.4, 1.2 Hz, 1H), 7.51 (dt, *J* = 7.7, 0.9 Hz, 1H), 7.42 (td, *J* = 7.3, 0.9 Hz, 1H), 7.39 – 7.33 (m, 2H), 7.33 – 7.28 (m, 2H), 7.25 – 7.18 (m, 1H), 6.55 (d, *J* = 16.2 Hz, 1H), 6.35 (d, *J* = 16.2 Hz, 1H), 3.46 (d, *J* = 17.2 Hz, 1H), 3.15 (d, *J* = 17.1 Hz, 1H), 1.50 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 207.9 (C), 152.0 (C), 136.9 (C), 135.3 (C), 135.0 (CH), 132.5 (CH), 129.1 (CH), 128.5 (2xCH), 127.6 (CH), 127.4 (CH), 126.5 (CH), 126.2 (2xCH), 124.8 (CH), 51.8 (C), 41.5 (CH_2), 24.0 (CH_3).

ESI HRMS: calcd. For $[C_{18}H_{17}O]^+$: 249.1274, found: 249.1270.

(*E*)-6-Fluoro-2-methyl-2-(3-phenylprop-1-en-1-yl)-2,3-dihydro-1*H*-inden-1-one 3h

Following the general method, *N*-tosylhydrazone **1b** (52 mg, 0.15 mmol) and *trans*-3-phenyl-1-propen-1-ylboronic acid (48 mg, 0.3 mmol) were obtained 24 mg of **3h** (57% isolated yield) as a colourless oil. Rf 0.47 (8:1 hexane:EtOAc).



^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 – 7.38 (m, 2H), 7.36 – 7.31 (m, 1H), 7.31 – 7.26 (m, 2H), 7.24 – 7.19 (m, 1H), 7.19 – 7.14 (m, 1H), 5.82 – 5.62 (m, 2H), 3.38 (d, *J* = 6.2 Hz, 2H), 3.28 (d, *J* = 15.8 Hz, 1H), 3.00 (d, *J* = 16.9 Hz, 1H), 1.39 (s, 3H).

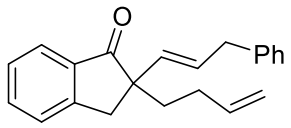
^{13}C NMR (75 MHz, $CDCl_3$) δ 207.4 (C, d, $^{5}J_{C\text{-}F}$= 2.7 Hz), 162.4 (C, d, $^{2}J_{C\text{-}F}$= 247.8 Hz), 147.4 (C, d, $^{5}J_{C\text{-}F}$= 2.2 Hz), 140.1 (C), 137.0 (C, d, $^{4}J_{C\text{-}F}$= 6.8 Hz), 133.6 (CH), 128.9 (CH), 128.5 (2xCH), 128.4 (2xCH), 127.87 (CH, d, $^{4}J_{C\text{-}F}$= 7.9 Hz), 126.0 (CH), 122.6 (CH, d, $^{3}J_{C\text{-}F}$= 23.8 Hz), 110.4 (CH, d, $^{3}J_{C\text{-}F}$= 21.8 Hz), 52.5 (C), 40.9 (CH_2), 38.9 (CH_2), 23.9 (CH_3).

^{19}F NMR (282 MHz, $CDCl_3$) δ -114.32.

ESI HRMS: calcd. For $[C_{19}H_{18}FO]^{+}$: 281.1336, found: 281.1326.

(*E*)-2-(But-3-en-1-yl)-2-(3-phenylprop-1-en-1-yl)-2,3-dihydro-1*H*-inden-1-one 3i

Following the general method, *N*-tosylhydrazone **1c** (55 mg, 0.15 mmol) and *trans*-3-phenyl-1-propen-1-ylboronic acid (48 mg, 0.3 mmol) were obtained 28 mg of **3i** (62% isolated yield) as a colourless oil. Rf 0.36 (20:1 hexane:EtOAc).



^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.6 Hz, 1H), 7.61 (td, *J* = 7.4, 1.2 Hz, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.31 – 7.25 (m, 2H), 7.21 (d, *J* = 7.2 Hz, 1H), 7.18 – 7.12 (m, 2H), 5.84 – 5.70 (m, 3H), 5.05 – 4.89 (m, 2H),

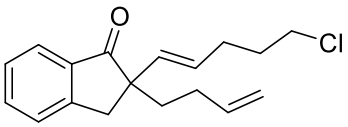
3.38 (d, *J* = 3.2 Hz, 2H), 3.30 (d, *J* = 17.3 Hz, 1H), 3.14 (d, *J* = 17.3 Hz, 1H), 2.18 – 2.05 (m, 1H), 2.05 – 1.93 (m, 1H), 1.91 – 1.76 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 207.8 (C), 152.47 (C), 140.2 (C), 138.1 (CH), 135.7 (C), 134.9 (CH), 133.1 (CH), 129.3 (CH), 128.4 (2xCH), 128.4 (2xCH), 127.5 (CH), 126.3 (CH), 126.0 (CH), 124.5 (CH), 114.7 (CH_2), 55.3 (C), 39.1 (CH_2), 37.9 (CH_2), 37.0 (CH_2), 29.1 (CH_2).

ESI HRMS: calcd. For $[C_{22}H_{23}O]^+$: 303.1743, found: 303.1728.

(*E*)-2-(But-3-en-1-yl)-2-(5-chloropent-1-en-1-yl)-2,3-dihydro-1*H*-inden-1-one 3j

Following the general method, *N*-tosylhydrazone **1c** (55 mg, 0.15 mmol) and *trans*-5-chloro-1-penteneboronic acid (44 mg, 0.3 mmol) were obtained 28 mg of **3j** (65% isolated yield) as a colourless oil. Rf 0.17 (20:1 hexane:EtOAc).

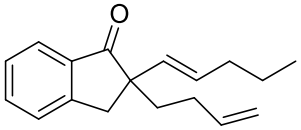


^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.7 Hz, 1H), 7.61 (td, *J* = 7.4, 1.2 Hz, 1H), 7.47 (d, *J* = 7.7 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 5.87 – 5.71 (m, 1H), 5.65 (d, *J* = 15.7 Hz, 1H), 5.53 (dt, *J* = 15.7, 6.4 Hz, 1H), 5.03 – 4.90 (m, 2H), 3.49 (t, *J* = 6.6 Hz, 2H), 3.26 (d, *J* = 17.3 Hz, 1H), 3.14 (d, *J* = 17.3 Hz, 1H), 2.25 – 2.13 (m, 2H), 2.13 – 2.03 (m, 1H), 2.02 – 1.90 (m, 1H), 1.89 – 1.71 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 207.8 (C), 152.3 (C), 138.0 (CH), 135.7 (C), 134.9 (CH), 133.1 (CH), 128.6 (CH), 127.5 (CH), 126.3 (CH), 124.4 (CH), 114.7 (CH_2), 55.2 (C), 44.2 (CH_2), 38.1 (CH_2), 36.9 (CH_2), 31.9 (CH_2), 29.7 (CH_2), 29.0 (CH_2). ESI HRMS: calcd. For $[C_{18}H_{22}ClO]^+$: 289.1354, found: 289.1339.

(*E*)-2-(but-3-en-1-yl)-2-(pent-1-en-1-yl)-2,3-dihydro-1*H*-inden-1-one 3k

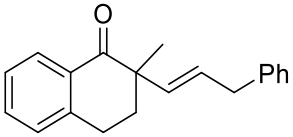
Following the general method and employing *N*-tosylhydrazone **1c** (55 mg, 0.15 mmol) and *trans*-1-penten-1-ylboronic acid (34 mg, 0.3 mmol), 28 mg of **3h** (73% isolated yield) were obtained as a yellow oil. Rf 0.30 (20:1 hexane:EtOAc).



^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.7 Hz, 1H), 7.58 (td, *J* = 7.5, 1.2 Hz, 1H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 5.84 – 5.71 (m, 1H), 5.59 – 5.49 (m, 2H), 5.01 – 4.89 (m, 2H), 3.26 (d, *J* = 17.3 Hz, 1H), 3.10 (d, *J* = 17.3 Hz, 1H), 2.12 – 1.68 (m, 6H), 1.40 – 1.25 (m, 2H), 0.84 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 208.3 (C), 152,7 (C), 138.4 (CH), 136.0 (C), 134.9 (CH), 131.7 (CH), 130.8 (CH), 127.6 (CH), 126.5 (CH), 124.6 (CH), 114.8 (CH_2), 55.4 (C), 38.2 (CH_2), 37.1 (CH_2), 34.9 (CH_2), 29.3 (CH_2), 22.6 (CH_2), 13.7 (CH_3). ESI HRMS: calcd. For $[C_{18}H_{23}O]^+$: 255.1743, found: 255.1734.

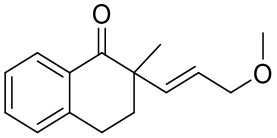
(*E*)-2-Methyl-2-(3-phenylprop-1-en-1-yl)-3,4-dihydronaphthalen-1(2*H*)-one 5a



From *N*-tosylhydrazone **4** (51.2 mg, 0.15 mmol) and *trans*-1-penten-1-ylboronic acid (34.1 mg, 0.30 mmol), **5a** was obtained in 78% isolated yield (31.9 mg) as a colourless oil. **5a** was purified by flash chromatography on silica gel using a mixture of hexanes/ethyl acetate 8:1 as eluent. R*f* (hexanes/ethyl acetate 8:1) = 0.53.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.48 (td, *J* = 7.5, 1.5 Hz, 1H), 7.36-7.15 (m, 5H), 7.12-7.05 (m, 2H), 5.73 (dt, *J* = 15.8, 1.3 Hz, 1H), 5.56 (dt, *J* = 15.8, 6.6 Hz, 1H), 3.35 (dd, *J* = 6.5, 1.2 Hz, 2H), 3.09 (ddd, *J* = 15.7, 9.9, 5.4 Hz, 1H), 2.91 (dt, *J* = 17.1, 4.9 Hz, 1H), 2.20-2.01 (m, 2H), 1.35 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.5 (C), 143.5 (C), 140.1 (CH), 133.9 (CH), 133.0 (C), 131.9 (CH), 129.2 (CH), 128.6 (CH), 128.4 (CH), 128.3 (CH), 127.9 (CH), 126.6 (CH), 125.9 (CH), 47.8 (C), 39.0 (CH_2), 35.6 (CH_2), 26.0 (CH_2), 24.0 (CH_3). HRMS(ESI): calcd. For $[C_{20}H_{21}O]^+$: 277.1586, found: 277.1584.

(*E*)-2-(3-Methoxyprop-1-en-1-yl)-2-methyl-3,4-dihydronaphthalen-1(2*H*)-one 5b

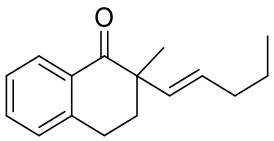


From *N*-tosylhydrazone **4** (51.2 mg, 0.15 mmol) and (51.2 mg, 0.15 mmol) and (*E*)-(3-methoxyprop-1-en-1-yl)boronic acid (34.7 mg, 0.30 mmol), **5b** was obtained in 88% isolated yield (30.0 mg) as a colourless oil. **5b** was purified by flash chromatography on silica gel using a mixture of hexanes/ethyl acetate 5:1 as eluent. R*f* (hexanes/ethyl acetate 5:1) = 0.33.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.1 Hz, 1H), 7.47 (td, *J* = 7.4, 1.6 Hz, 1H), 7.31 (dd, *J* = 13.0, 5.5 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 5.92 (d, *J* = 15.9 Hz, 1H), 5.53 (dt, *J* = 16.0, 5.8 Hz, 1H), 3.89 (dd, *J* = 5.8, 1.5 Hz, 2H), 3.29 (s, 3H), 3.08 (ddd, *J* = 15.4, 9.6, 5.2 Hz, 1H), 2.92 (dt, *J* = 17.2, 5.1 Hz, 1H), 2.20-2.05 (m, 2H), 1.35 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 200.1 (C), 143.4 (C), 135.5 (C), 133.1 (CH), 131.8 (CH), 128.6 (CH), 127.9 (CH), 126.6 (CH), 126.5 (CH), 72.9 (CH_2), 57.8 (CH_3), 47.6 (C), 35.4 (CH_2), 25.9 (CH_2), 23.7 (CH_3). HRMS(ESI): calcd. For $[C_{15}H_{18}NaO_2]^+$: 253.1199, found: 253.1200.

(*E*)-2-Methyl-2-(pent-1-en-1-yl)-3,4-dihydronaphthalen-1(2*H*)-one 5c



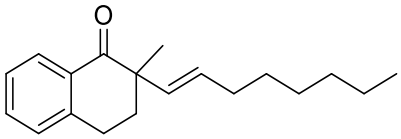
From *N*-tosylhydrazone **4** (51.2 mg, 0.15 mmol) and *trans*-1-penten-1-ylboronic acid (34.1 mg, 0.30 mmol), **5c** was obtained in 70% isolated yield (24.0 mg) as a colourless oil. **5c** was purified by flash chromatography on silica gel using a mixture of hexanes/ethyl acetate 8:1 as eluent. R_f (hexanes/ethyl acetate 8:1) = 0.53.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.7 Hz, 1H), 7.46 (td, *J* = 7.5, 1.4 Hz, 2H), 7.37-7.25 (m, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 5.59 (d, *J* = 15.8 Hz, 1H), 5.36 (dt, *J* = 15.9, 6.7 Hz, 1H), 3.09 (ddd, *J* = 16.2, 9.8, 5.9 Hz, 1H), 2.87 (dt, *J* = 17.0, 4.6 Hz, 1H), 2.20-1.90 (m, 3H), 1.41-1.22 (m, 6H), 0.82 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 200.7 (C), 143.6 (C), 132.9 (C), 132.1 (CH), 132.0 (CH), 130.8 (CH), 128.5 (CH), 127.8 (CH), 126.5 (CH), 47.8 (C), 35.9 (CH_2), 34.8 (CH_2), 26.0(CH_2), 24.2 (CH_3), 22.3 (CH_2), 13.4 (CH_3).

HRMS(ESI): calcd. For $[C_{16}H_{20}NaO]^+$: 251.1392, found: 251.1405.

(*E*)-2-(Hex-1-en-1-yl)-2-methyl-3,4-dihydronaphthalen-1(2*H*)-one 5d



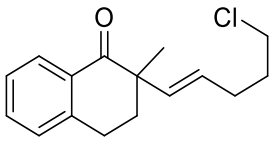
From (*N*-tosylhydrazone **4** (51.2 mg, 0.15 mmol) and *trans*-1-hexen-1-ylboronic acid (38.3 mg, 0.30 mmol), **57d** was obtained in 50% isolated yield (18.2 mg) as a colourless oil. **57d** was purified by flash chromatography on silica gel using a mixture of hexanes/ethyl acetate 8:1 as eluent. R_f (hexanes/ethyl acetate 8:1) = 0.55.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.7 Hz, 1H), 7.46 (td, *J* = 7.5, 1.4 Hz, 2H), 7.37-7.25 (m, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 5.58 (d, *J* = 15.9 Hz, 1H), 5.36 (dt, *J* = 15.8, 6.7 Hz, 1H), 3.09 (ddd, *J* = 16.1, 9.7, 6.0 Hz, 1H), 2.87 (dt, *J* = 17.0, 4.6 Hz, 1H), 2.12-1.90 (m, 4H), 1.32 (s, 3H), 1.30-1.10 (m, 5H), 1.00-0.87 (m, 2H), 0.85 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 200.8 (C), 143.6 (C), 132.9 (CH), 132.0 (C), 131.9 (CH), 131.0 (CH), 128.5 (CH), 127.8 (CH), 126.5 (CH), 47.7 (C), 35.9 (CH_2), 32.4 (CH_2), 31.3 (CH_2), 26.0 (CH_2), 24.2 (CH_3), 22.5 (CH_2), 13.8 (CH_3).

HRMS(ESI): calcd. For $[C_{17}H_{23}O]^+$: 243.1743, found: 243.1742.

(*E*)-2-(5-chloropent-1-en-1-yl)-2-methyl-3,4-dihydronaphthalen-1(2*H*)-one 5e



From *N*-tosylhydrazone **4** (51.2 mg, 0.15 mmol) and (*E*)-(5-chloropent-1-en-1-yl)boronic acid (44.5 mg, 0.30 mmol), **57e** was obtained in 60% isolated yield (24.0 mg) following as a colourless oil. **5e** was purified by flash chromatography on silica gel using a mixture of hexanes/ethyl acetate 6:1 as eluent. R_f (6:1 hexane:EtOAc) = 0.60.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.9 Hz, 1H), 7.47 (td, *J* = 7.5, 1.5 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 1H),), 5.58 (d, *J* = 15.9 Hz, 1H), 5.31 (dt, *J* = 15.8, 6.8 Hz, 1H), 3.50-3.35 (m, 2H), 3.07 (ddd, *J* = 16.0, 9.7, 5.8

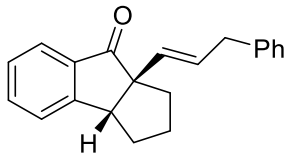
Hz, 1H), 2.89 (dt, *J* = 17.0, 4.7 Hz, 1H), 2,20-1.99 (m, 4H), 1.78 (p, *J* = 6.9 Hz, 2H), 1.32 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 200.5 (C), 143.4 (C), 133.8 (CH), 133.0 (CH), 131.9 (C), 128.7 (CH), 128.6 (CH), 127.8 (CH), 126.5 (CH), 47.8 (C), 44.2 (CH_2), 35.8 (CH_2), 31.7 (CH_2), 29.7 (CH_2), 26.0 (CH_2), 24.1 (CH_3).

HRMS(ESI): calcd. For $[C_{16}H_{19}ClNaO]^+$: 285.1016, found: 285.1015.

(3a*R,8a*S**)-8a-((*E*)-3-Phenylprop-1-en-1-yl)-2,3,3a,8a-tetrahydrocyclopenta [*a*]inden-8(1*H*)-one 8a**

Following the general method, from *N*-tosylhydrazone **6** (53 mg, 0.15 mmol) and *trans*-3-phenyl-1-propen-1-ylboronic acid (48 mg, 0.3 mmol) were obtained 28 mg of **8a** (65% isolated yield) as a colourless oil. R*f* 0.22 (20:1 hexane:EtOAc).



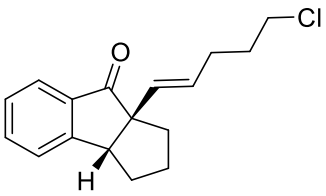
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.9 Hz, 1H), 7.64 (td, *J* = 7.5, 1.3 Hz, 1H), 7.47 (dd, *J* = 7.7, 0.9 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.32 – 7.29 (m, 1H), 7.27 (q, *J* = 1.4 Hz, 1H), 7.23 – 7.17 (m, 3H), 5.85 – 5.69 (m, 2H), 3.66 (d, *J* = 9.1 Hz, 1H), 3.38 (d, *J* = 5.0 Hz, 2H), 2.25 (ddt, *J* = 12.5, 6.0, 1.8 Hz, 1H), 2.21 – 2.05 (m, 1H), 1.88 – 1.81 (m, 1H), 1.81 – 1.71 (m, 1H), 1.71 – 1.62 (m, 1H), 1.21 (ddt, *J* = 18.2, 12.1, 5.9 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 209.3 (C), 157.4 (C), 140.3 (C), 136.5 (C), 135.4 (CH), 132.8 (CH), 128.5 (CH), 128.5 (2xCH), 128.3 (2xCH), 127.5 (CH), 126.0 (CH), 125.9 (CH), 123.6 (CH), 63.5 (C), 50.7 (CH), 39.0 (CH_2), 38.3 (CH_2), 33.3 (CH_2), 25.0 (CH_2).

ESI HRMS: calcd. For $[C_{21}H_{21}O]^+$: 289.1587, found: 289.1577.

(3a*R,8a*S**)-8a-((*E*)-5-Chloropent-1-en-1-yl)-2,3,3a,8a-tetrahydrocyclopenta [*a*]inden-8(1*H*)-one 8b**

Following the general method, from *N*-tosylhydrazone **6** (53 mg, 0.15 mmol) and *trans*-5-chloro-1-penteneboronic acid (44 mg, 0.3 mmol) were obtained 23 mg of **8b** (56% isolated yield) as a colourless oil. R*f* 0.24 (20:1 hexane:EtOAc).



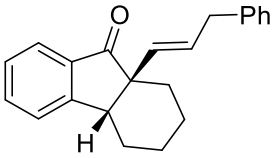
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.7 Hz, 1H), 7.65 (td, *J* = 7.5, 1.3 Hz, 1H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.39 (t, *J* = 7.4 Hz, 1H), 5.75 (dt, *J* = 15.6, 1.3 Hz, 1H), 5.56 (dt, *J* = 15.6, 6.6 Hz, 1H), 3.63 (d, *J* = 8.9 Hz, 1H), 3.52 (t, *J* = 6.6 Hz, 2H), 2.29 – 2.06 (m, 4H), 1.90 – 1.80 (m, 3H), 1.81 – 1.72 (m, 1H), 1.72 – 1.59 (m, 2H), 1.29 – 1.11 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 209.3 (C), 157.3 (C), 136.5 (C), 135.4 (CH), 132.8 (CH), 127.9 (CH), 127.5 (CH), 125.9 (CH), 123.6 (CH), 63.5 (C), 50.8 (CH), 44.3 (CH_2), 38.2 (CH_2), 33.3 (CH_2), 31.9 (CH_2), 29.7 (CH_2), 25.0 (CH_2).

ESI HRMS: calcd. For $[C_{17}H_{20}ClO]^+$: 275.1197, found: 275.1178.

(4a*R,9a*S**)-9a-((*E*)-3-Phenylprop-1-en-1-yl)-1,2,3,4,4a,9a-hexahydro-9*H*-fluoren-9-one 9a**

Following the general method, from *N*-tosylhydrazone **7** (55 mg, 0.15 mmol) and *trans*-3-phenyl-1-propen-1-ylboronic acid (48 mg, 0.3 mmol) were obtained 24 mg of **9a** (56% isolated yield) as a colourless oil. R*f* 0.35 (20:1 hexane:EtOAc).



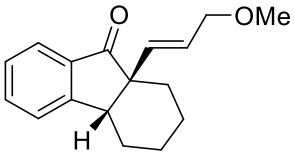
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.6 Hz, 1H), 7.62 (td, *J* = 7.3, 1.2 Hz, 1H), 7.49 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.33 – 7.26 (m, 2H), 7.25 – 7.14 (m, 3H), 5.86 – 5.69 (m, 2H), 3.49 – 3.36 (m, 3H), 2.11 – 1.97 (m, 1H), 1.96 – 1.86 (m, 1H), 1.79 – 1.69 (m, 2H), 1.59 – 1.47 (m, 2H), 1.46 – 1.35 (m, 1H), 1.32 – 1.22 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 207.7 (C), 155.7 (C), 140.4 (C), 135.0 (C), 134.4 (CH), 133.3 (CH), 129.7 (CH), 128.4 (2xCH), 128.3 (2xCH), 127.3 (CH), 126.0 (CH), 124.6 (CH), 124.3 (CH), 55.7 (C), 43.7 (CH), 39.2 (CH_2), 31.2 (CH_2), 26.8 (CH_2), 21.2 (CH_2), 21.2 (CH_2).

ESI HRMS: calcd. For $[C_{22}H_{23}O]^+$: 303.1743, found: 303.1736

(4a*R,9a*S**)-9a-((*E*)-3-Methoxyprop-1-en-1-yl)-1,2,3,4,4a,9a-hexahydro-9*H*-fluoren-9-one 9b**

Following the general method, from *N*-tosylhydrazone **7** (55 mg, 0.15 mmol) and *trans*-3-methoxy-1-propenylboronic acid (35 mg, 0.3 mmol) were obtained 21 mg of **9b** (55% isolated yield) as a colourless oil. R*f* 0.28 (8:1 hexane:EtOAc).



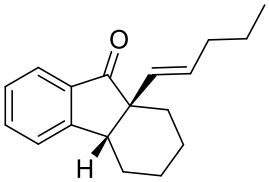
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.6 Hz, 1H), 7.62 (td, *J* = 7.5, 1.2 Hz, 1H), 7.49 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.39 (t, *J* = 7.4 Hz, 1H), 5.90 (dt, *J* = 15.8, 1.2 Hz, 1H), 5.75 (dt, *J* = 15.8, 5.7 Hz, 1H), 3.95 (ddd, *J* = 5.9, 2.1, 1.1 Hz, 2H), 3.44 (t, *J* = 5.5 Hz, 1H), 3.32 (s, 3H), 2.15 – 1.99 (m, 1H), 1.99 – 1.85 (m, 1H), 1.79 – 1.68 (m, 2H), 1.59 – 1.46 (m, 2H), 1.47 – 1.34 (m, 1H), 1.34 – 1.17 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 207.2 (C), 155.6 (C), 135.3 (CH), 134.8 (C), 134.5 (CH), 127.4 (CH), 127.1 (CH), 124.7 (CH), 124.3 (CH), 73.1 (CH_2), 57.7 (CH_3), 55.5 (C), 43.5 (CH), 30.9 (CH_2), 26.7 (CH_2), 21.1 (CH_2), 21.0 (CH_2).

ESI HRMS: calcd. For $[C_{17}H_{20}NaO_2]^+$: 279.1356, found: 279.1337

(4a*R,9a*S**)-9a-((*E*)-Pent-1-en-1-yl)-1,2,3,4,4a,9a-hexahydro-9*H*-fluoren-9-one 9c**

Following the general method, from *N*-tosylhydrazone **7** (55 mg, 0.15 mmol) and *trans*-1-penten-1-ylboronic acid (34 mg, 0.3 mmol) were obtained 20 mg of **9c** (52% isolated yield) as a yellow oil. Rf 0.42 (20:1 hexane:EtOAc).



^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.6 Hz, 1H), 7.61 (td, *J* = 7.4, 1.2 Hz, 1H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.38 (t, *J* = 7.4 Hz, 1H), 5.63 – 5.56 (m, 2H), 3.39 (t, *J* = 5.7 Hz, 1H), 2.10 – 1.97 (m, 3H), 1.94 – 1.81 (m, 1H), 1.74 – 1.65 (m, 2H),

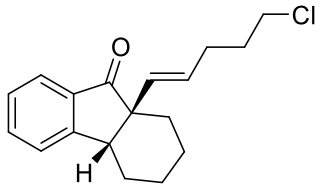
1.58 – 1.45 (m, 2H), 1.44 – 1.34 (m, 3H), 1.31 – 1.23 (m, 1H), 0.88 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 208.0 (C), 155.8 (C), 135.1 (C), 134.3 (CH), 131.8 (CH), 131.1 (CH), 127.3 (CH), 124.6 (CH), 124.3 (CH), 55.6 (C), 43.9 (CH), 34.9 (CH_2), 31.1 (CH_2), 27.1 (CH_2), 22.5 (CH_2), 21.3 (CH_2), 21.2 (CH_2), 13.5 (CH_3).

ESI HRMS: calcd. For $[C_{18}H_{23}O]^+$: 255.1743, found: 255.1738

(4a*R,9a*S**)-9a-((*E*)-5-Chloropent-1-en-1-yl)-1,2,3,4,4a,9a-hexahydro-9*H*-fluoren-9-one 9d**

Following the general method, from *N*-tosylhydrazone **7** (55 mg, 0.15 mmol) and *trans*-5-chloro-1-penteneboronic acid (44 mg, 0.3 mmol) were obtained 23 mg of **9d** (57% isolated yield) as a colourless oil. Rf 0.18 (20:1 hexane:EtOAc).



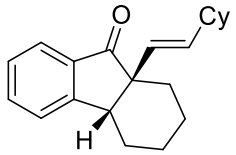
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.5 Hz, 1H), 7.62 (td, *J* = 7.4, 1.2 Hz, 1H), 7.49 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.39 (t, *J* = 6.9 Hz, 1H), 5.78 – 5.46 (m, 2H), 3.52 (t, *J* = 6.6 Hz, 2H), 3.37 (t, *J* = 5.7 Hz, 1H), 2.29 – 2.16 (m, 2H), 2.10 – 1.96 (m, 1H), 1.94 – 1.79 (m, 3H), 1.75 – 1.67 (m, 2H), 1.57 – 1.44 (m, 2H), 1.45 – 1.21 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 207.6 (C), 155.7 (C), 135.0 (C), 134.4 (CH), 133.3 (CH), 129.2 (CH), 127.4 (CH), 124.6 (CH), 124.3 (CH), 55.6 (C), 44.2 (CH_2), 43.9 (CH), 32.0 (CH_2), 31.0 (CH_2), 29.9 (CH_2), 27.0 (CH_2), 21.2 (CH_2), 21.2 (CH_2).

ESI HRMS: calcd. For $[C_{18}H_{22}ClO]^+$: 289.1354, found: 289.1334

(4a*R,9a*S**)-9a-((*E*)-2-Cyclohexylvinyl)-1,2,3,4,4a,9a-hexahydro-9*H*-fluoren-9-one 9e**

Following the general method, from *N*-tosylhydrazone **7** (55 mg, 0.15 mmol) and *trans*-(2-cyclohexylvinyl)boronic acid (46 mg, 0.3 mmol) were obtained 21 mg of **9e** (47% isolated yield) as a yellow oil. Rf 0.31 (20:1 hexane:EtOAc).



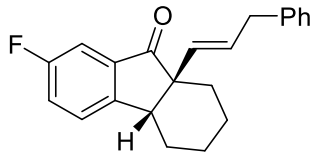
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.6 Hz, 1jH), 7.61 (td, *J* = 7.5, 1.3 Hz, 1H), 7.48 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.38 (t, *J* = 7.3 Hz, 1H), 5.59 – 5.52 (m, 2H), 3.39 (t, *J* = 5.7 Hz, 1H), 2.07 – 1.95 (m, 1H), 1.96 – 1.83 (m, 1H), 1.76 – 1.64 (m, 7H), 1.57 – 1.44 (m, 2H), 1.42 – 1.31 (m, 2H), 1.32 – 1.16 (m, 4H), 1.14 – 1.02 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 208.1 (C), 155.9 (C), 137.1 (CH), 135.1 (C), 134.3 (CH), 129.2 (CH), 127.2 (CH), 124.6 (CH), 124.3 (CH), 55.4 (C), 43.6 (CH), 40.9 (CH), 33.1 (CH2), 33.0 (CH2), 31.2 (CH2), 27.0 (CH2), 26.1 (CH2), 26.0 (2xCH2), 21.3 (CH2), 21.1 (CH2).

ESI HRMS: calcd. For $[C_{21}H_{27}O]^{+}$: 295.2056, found: 295.2023

(4a*R,9a*S**)-7-Fluoro-9a-((*E*)-3-phenylprop-1-en-1-yl)-1,2,3,4,4a,9a-hexahydro-9*H*-fluoren-9-one 9f**

Following the general method, from *N*-tosylhydrazone **7** (57 mg, 0.15 mmol) and *trans*-3-phenyl-1-propen-1-ylboronic acid (48 mg, 0.3 mmol) were obtained 27 mg of **9f** (56% isolated yield) as a yellow oil. Rf 0.5 (8:1 hexane:EtOAc).



^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 – 7.40 (m, 2H), 7.36 – 7.31 (m, 1H), 7.31 – 7.27 (m, 2H), 7.24 – 7.19 (m, 1H), 7.19 – 7.14 (m, 2H), 5.89 – 5.64 (m, 2H), 3.47 – 3.33 (m, 3H), 2.10 – 1.96 (m, 1H), 1.91 – 1.78 (m, 1H), 1.78 – 1.70 (m, 2H), 1.57 – 1.47 (m, 2H), 1.43 – 1.22 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 206.6 (C, d, $^{5}J_{C\text{-}F}$= 2.6 Hz), 162.2 (C, d, $^{2}J_{C\text{-}F}$= 247.4 Hz), 151.1 (C, d, $^{5}J_{C\text{-}F}$= 2.6 Hz), 140.2 (C), 136.8 (C, d, $^{4}J_{C\text{-}F}$= 7.1 Hz), 133.0 (CH), 130.0 (CH), 128.4 (2xCH), 128.4 (2xCH), 126.0 (CH), k125.7 (CH, d, $^{4}J_{C\text{-}F}$= 8.0 Hz), 121.8 (CH, d, $^{3}J_{C\text{-}F}$= 23.5 Hz), 110.6 (CH, d, $^{3}J_{C\text{-}F}$= 21.8 Hz), 56.3 (C), 43.2 (CH), 39.2 (CH_2), 31.1 (CH_2), 27.0 (CH_2), 21.1 (CH_2), 21.1 (CH_2).

^{19}F NMR (282 MHz, $CDCl_3$) δ -114.45.

ESI HRMS: calcd. For $[C_{22}H_{22}FO]^+$: 321.1649, found: 321.1627.

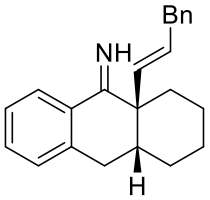
3.2- Experimental procedure and characterization data for ketimines 11 and hexahydroanthracenones 12

3.2.1- General procedure and characterization data for ketimines 11.

The procedure is identical to that described for indanones **3** above but employing *N*-tosylhydrazone **10a**

(4a*S,9a*S**)-9a-((*E*)-3-Phenylprop-1-en-1-yl)-1,3,4,4a,9a,10-hexahydroanthracen-9(2*H*)-imine 11a**

Following the general method and employing *N*-tosylhydrazone **10a** (57.3 mg, 0.15 mmol) and *trans*-3-phenyl-1-propen-1-ylboronic acid (48.6 mg, 0.3 mmol), 46 mg of **11a** (97% isolated yield) were obtained as a colourless oil. R*f* 0.24 (20:1 hexane:EtOAc).



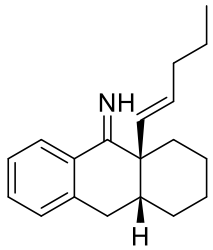
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.29 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.36 (td, *J* = 7.4, 1.4 Hz, 1H), 7.29 – 7.11 (m, 6H), 7.00 – 6.97 (m, 1H), 5.51 (d, *J* = 15.8 Hz, 1H), 5.43 (dt, *J* = 15.8, 5.5 Hz, 1H), 3.28 – 3.20 (d, *J* = 5.8 Hz, 2H; dd, *J* = 18.2, 5.3 Hz, 1H), 2.59 (dd, *J* = 16.8, 2.7 Hz, 1H), 2.25 – 2.16 (m, 1H), 2.05 – 1.97 (m, 1H), 1.68 – 1.60 (m, 1H), 1.53 – 1.21 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 175.8 (C), 140.3 (C), 138.5 (C), 136.6 (CH), 132.0 (C), 131.1 (CH), 129.5 (CH), 129.4 (CH), 128.5 (2xCH), 128.4 (2xCH), 126.4 (CH), 126.2 (CH), 126.1 (CH), 50.2 (C), 41.8 (CH), 38.9 (CH_2), 34.9 (CH_2), 33.3 (CH_2), 28.5 (CH_2), 25.8 (CH_2), 22.2 (CH_2).

ESI HRMS: calcd. For $[C_{23}H_{26}N]^+$: 316.2060, found: 316.2105.

(4a*S,9a*S**)-9a-((*E*)-Pent-1-en-1-yl)-1,3,4,4a,9a,10-hexahydroanthracen-9(2*H*)-imine 11b**

Following the general method and employing *N*-tosylhydrazone **10a** (57.3 mg, 0.15 mmol) and *trans*-1-penten-1-ylboronic acid (34.2 mg, 0.3 mmol), 37 mg of **11b** (74% isolated yield) were obtained as a colourless oil. R*f* 0.20 (20:1 hexane:EtOAc).



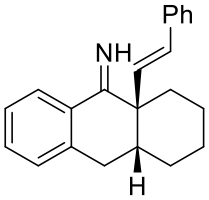
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.30 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.33 (td, *J* = 7.4, 1.5 Hz, 1H), 7.28 – 7.23 (m, 1H), 7.10 (d, *J* = 7.4 Hz, 1H), 5.39 (d, *J* = 15.8 Hz, 1H), 5.23 (dt, *J* = 15.8, 6.5 Hz 1H), 3.21 (dd, *J* = 16.7, 5.2 Hz, 1H), 2.56 (dd, *J* = 16.7, 2.8 Hz, 1H), 2.20 – 2.15 (m, 1H), 1.98 – 1.86 (m, 2H), 1.69 – 1.55 (m, 2H), 1.52 – 1.19 (m, 8H), 0.74 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 175.8 (C), 138.5 (C), 135.1 (CH), 132.4 (C), 130.9 (CH), 130.8 (CH), 129.4 (CH), 126.3 (CH), 126.0 (CH), 50.1 (C), 41.8 (CH), 35.1 (CH_2), 34.8 (CH_2), 33.3 (CH_2), 28.5 (CH_2), 25.8 (CH_2), 22.5 (CH_2), 22.2 (CH_2), 13.6 (CH).

ESI HRMS: calcd. For $[C_{19}H_{26}N]^+$: 268.2060, found: 268.2061.

(4a*S,9a*S**)-9a-((*E*)-Styryl)-1,3,4,4a,9a,10-hexahydroanthracen-9(2*H*)-imine 11c**

Following the general method and employing *N*-tosylhydrazone **10a** (57.3 mg, 0.15 mmol) and *trans*-2-phenylvinylboronic acid (44.4 mg, 0.3 mmol), 35 mg of **11c** (77% isolated yield) were obtained as a colourless oil. R*f* 0.20 (20:1 hexane:EtOAc).



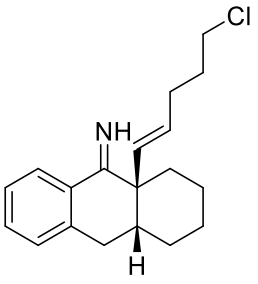
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.36 (d, *J* = 7.7 Hz, 1H), 7.37 – 7.28 (m, 3H), 7.25 – 7.14 (m, 4H), 7.10 (d, *J* = 7.3 Hz, 1H), 6.24 (d, *J* = 16.3 Hz, 1H), 6.17 (d, *J* = 16.3 Hz, 1H), 3.26 (dd, *J* = 16.8, 5.2 Hz, 1H), 2.60 (dd, *J* = 16.8, 2.6 Hz, 1H), 2.32 – 2.28 (m, 1H), 2.16 – 2.09 (m, 1H), 1.74 – 1.64 (m, 2H), 1.60 – 1.50 (m, 2H), 1.47 – 1.26 (m, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 175.3 (C), 138.5 (C), 137.1 (C), 135.0 (CH), 132.0 (C), 131.2 (CH), 130.0 (CH), 129.6 (CH), 128.6 (2xCH), 127.5 (CH), 126.5 (CH), 126.4 (2xCH), 126.1 (CH), 50.5 (C), 42.1 (CH), 35.1 (CH_2), 33.5 (CH_2), 28.5 (CH_2), 25.9 (CH_2), 22.2 (CH_2).

ESI HRMS: calcd. For $[C_{22}H_{24}N]^+$: 302.1903, found: 302.1895.

(4a*S,9a*S**)-9a-((*E*)-5-Chloropent-1-en-1-yl)-1,3,4,4a,9a,10-hexahydroanthracen-9(2*H*)-imine 11d**

Following the general method and employing *N*-tosylhydrazone **10a** (57.3 mg, 0.15 mmol) and *trans*-5-chloro-1-penteneboronic acid (44.5 mg, 0.3 mmol), 40 mg of **11d** (89% isolated yield) were obtained as a colourless oil. R*f* 0.17 (20:1 hexane:EtOAc).



^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28 (d, *J* = 7.8 Hz, 1H), 7.32 (td, *J* = 7.3, 1.5 Hz, 1H), 7.28 – 7.23 (m, 1H), 7.10 (d, *J* = 7.5, 1H), 5.50 (d, *J* = 15.7 Hz, 1H), 5.17 (dt, *J* = 15.7, 6.8 Hz, 2H), 3.40 – 3.25 (m, 2H), 3.21 (dd, *J* = 16.8, 5.3 Hz, 1H), 2.56 (dd, *J* = 16.8, 2.5 Hz, 1H), 2.21 – 2.16 (m, 1H), 2.09 (ddd, *J* = 14.1, 6.9, 1.1 Hz, 2H), 2.00 – 1.93 (m, 1H), 1.74 – 1.58 (m, 4H), 1.51 – 1.22 (m, 5H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 175.5 (C), 138.4(C), 136.7 (CH), 132.2 (C), 131.0 (CH), 129.4 (CH), 128.8 (CH), 126.3 (CH), 125.9 (CH), 50.2 (C), 44.2 (CH_2), 41.8 (CH), 35.1 (CH_2), 33.4 (CH_2), 31.8 (CH_2), 29.6 (CH_2), 28.4 (CH_2), 25.9 (CH_2), 22.2 (CH_2).

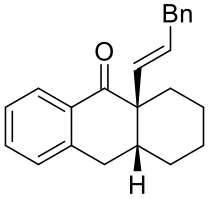
ESI HRMS: calcd. For $[C_{19}H_{25}ClN]^+$: 302.1670, found: 302.1666.

3.2.2 General procedure and characterization data for hexahydroanthracenones 12

A microwave vial provided with a triangular stir bar was charged with the tosylhydrazone **10** (0.15 mmol), the alkenyl boronic acid (0.3 mmol) and K_2CO_3 (41.5 mg, 0.3 mmol) in 1.2 mL of dry 1,4-dioxane. The vial was sealed with a septum, placed into the microwave cavity and irradiated to maintain the reaction at the desired temperature (120 ºC) during the reaction time (4h) in a Biotage Initiator microwave apparatus. Once the reaction finished, it was allowed to reach room temperature and the crude was dissolved in DCM to filter through celite. Solvent was removed under reduced pressure. The crude was dissolved again in DCM and some silica gel was added. It was stirred for an hour and the solvent was removed under reduced pressure (DCM was added and then removed under reduced pressure 2 or 3 times). Finally, the products were purified by flash chromatography on silica gel.

(4a*S*,9a*S***)-9a-((*E*)-3-Phenylprop-1-en-1-yl)-1,3,4,4a,9a,10-hexahydroanthracen-9(2*H*)-one 12a**

Following the general method and employing *N*-tosylhydrazone **10a** (57.3 mg, 0.15 mmol) and *trans*-3-phenyl-1-propen-1-ylboronic acid (48.6 mg, 0.3 mmol), 35 mg of **12a** (74% isolated yield) were obtained as a colourless oil. R*f* 0.46 (20:1 hexane:EtOAc).



^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.45z (td, *J* = 7.4, 1.5 Hz, 1H), 7.30 (d, *J* = 7.6, 1H), 7.23 – 7.11 (m, 4H), 7.0 (d, *J* = 6.5 Hz, 2H), 5.58

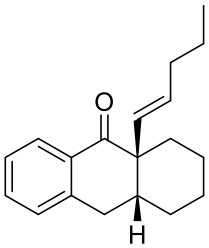
(d, *J* = 15.8 Hz, 1H), 5.45 (dt, *J* = 15.8, 6.5 Hz, 1H), 3.44 (dd, *J* = 16.9, 5.2 Hz, 1H), 3.27 (d, *J* = 6.3 Hz, 2H), 2.60 (dd, *J* = 17.0, 1.8 Hz, 1H), 2.50 – 2.45 (m, 1H), 2.17 – 2.09 (m, 1H), 1.66 – 1.55 (m, 3H), 1.32 – 1.19 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 199.6 (C), 141.6 (C), 140.2 (C), 134.9 (CH), 133.4 (CH), 132.0 (C), 129.7 (CH), 129.4 (CH), 128.5 (2xCH), 128.4 (2xCH), 127.5 (CH), 126.5 (CH), 126.1 (CH), 53.3 (C), 42.5 (CH), 39.0 (CH_2), 34.7 (CH_2), 33.1 (CH_2), 29.0 (CH_2), 25.9 (CH_2), 23.1 (CH_2).

ESI HRMS: calcd. For $[C_{23}H_{25}O]^+$: 317.1900, found: 317.1890.

(4a*S,9a*S**)-9a-((*E*)-Pent-1-en-1-yl)-1,3,4,4a,9a,10-hexahydroanthracen-9(2*H*)-one 12b**

Following the general method and employing *N*-tosylhydrazone **10a** (57.3 mg, 0.15 mmol) and *trans*-1-penten-1-ylboronic acid (34.2 mg, 0.3 mmol), 33 mg of **12b** (82% isolated yield) were obtained as a colourless oil. R*f* 0.41 (20:1 hexane:EtOAc).



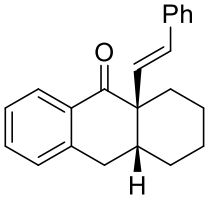
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.44 (td, *J* = 7.4, 1.4 Hz, 1H), 7.29 (d, *J* = 7.5 Hz, 1H), 7.15 (d, *J* = 7.5 Hz, 1H), 5.49 (d, *J* = 16.0 Hz, 1H), 5.24 (dt, *J* = 16.0, 6.7 Hz, 1H), 3.44 (dd, *J* = 16.9, 5.2 Hz, 1H), 2.57 (dd, *J* = 16.9, 2.1 Hz, 1H), 2.46 – 2.42 (m, 1H), 2.14 – 2.07 (m, 1H), 1.92 – 1.85 (m, 2H), 1.66 – 1.54 (m, 3H), 1.30 – 1.17 (m, 6H), 0.75 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 199.8 (C), 141.7 (C), 133.3 (CH), 133.2 (CH), 132.1 (C), 131.2 (CH), 129.4 (CH), 127.4 (CH), 126.4 (CH), 53.3 (C), 42.6 (CH), 35.0 (CH_2), 34.9 (CH_2), 33.1 (CH_2), 29.0 (CH_2), 26.0 (CH_2), 23.2 (CH_2), 22.4 (CH_2), 13.6 (CH).

ESI HRMS: calcd. For $[C_{19}H_{25}O]^+$: 269.1900, found: 269.1909.

(4a*S,9a*S**)-9a-((*E*)-Styryl)-1,3,4,4a,9a,10-hexahydroanthracen-9(2*H*)-one 12c**

Following the general method and employing *N*-tosylhydrazone **10a** (57.3 mg, 0.15 mmol) and *trans*-2-phenylvinylboronic acid (44.4 mg, 0.3 mmol), 30 mg of **12c** (66% isolated yield) were obtained as a colourless oil. R*f* 0.60 (20:1 hexane:EtOAc).



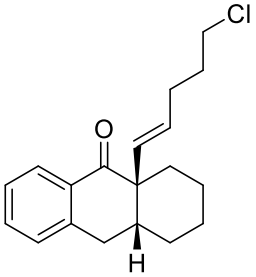
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.47 (td, *J* = 7.5, 1.5 Hz, 1H), 7.35– 7.28 (m, 5H), 7.25 – 7.17 (m, 2H), 6.32 (d, *J* = 15.8 Hz, 1H), 6.24 (d, *J* = 16.5 Hz, 1H), 3.50 (dd, *J* = 16.9, 5.1 Hz, 1H), 2.66 (d, *J* = 17.1, 2.1 Hz, 1H), 2.59 – 2.55 (m, 1H), 2.34 – 2.26 (m, 1H), 1.74 – 1.62 (m, 3H), 1.39 – 1.28 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 199.2 (C), 141.6 (C), 137.1 (C), 133.6 (CH), 133.1 (CH), 131.9 (C), 130.3 (CH), 129.5 (CH), 128.6 (2xCH), 127.6 (2xCH), 126.6 (CH), 126.3 (2xCH), 53.5 (C), 42.7 (CH), 34.8 (CH_2), 33.3 (CH_2), 29.0 (CH_2), 25.9 (CH_2), 23.1 (CH_2).

ESI HRMS: calcd. For $[C_{22}H_{22}NaO]^+$: 325.1563, found: 325.1566.

(4a*S*,9a*S*)-9a-((*E*)-5-Chloropent-1-en-1-yl)-1,3,4,4a,9a,10-hexahydroanthracen-9(2*H*)-one 12d

Following the general method and employing *N*-tosylhydrazone **10a** (57.3 mg, 0.15 mmol) and *trans*-5-chloro-1-penteneboronic acid (44.5 mg, 0.3 mmol), 33 mg of **12d** (72% isolated yield) were obtained as a colourless oil. R*f* 0.68 (20:1 hexane:EtOAc).



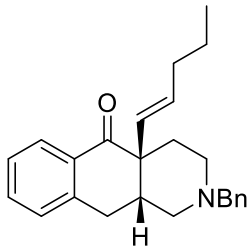
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.43 (td, *J* = 7.4, 1.4 Hz, 1H), 7.29 (d, *J* = 7.6, 1H), 7.16 (d, *J* = 7.6, 1H), 5.58 (d, *J* = 15.9 Hz, 1H), 5.19 (dt, *J* = 15.9, 6.9 Hz, 1H), 3.45 – 3.28 (m, 3H), 2.58 (dd, *J* = 16.9, 1.8 Hz, 1H), 2.45 – 2.40 (m, 1H), 2.12 – 2.05 (m, 3H), 1.75 – 1.53 (m, 5H), 1.33 – 1.14 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 199.5 (C), 141.6 (C), 134.9 (CH), 133.4 (CH), 131.9 (C), 129.5 (CH), 129.1 (CH), 127.4 (CH), 126.5 (CH), 53.3 (C), 44.2 (CH_2), 42.6 (CH), 34.8 (CH_2), 33.1 (CH_2), 31.8 (CH_2), 29.8 (CH_2), 28.9 (CH_2), 25.9 (CH_2), 23.1 (CH_2).

ESI HRMS: calcd. For $[C_{19}H_{24}ClO]^+$: 303.1510, found: 303.1498.

(4a*R,10a*S**)-2-Benzyl-4a-((*E*)-pent-1-en-1-yl)-2,3,4,4a,10,10a-hexahydro-benzo[*g*]isoquinolin-5(1*H*)-one 12e**

Following the general method and employing *N*-tosylhydrazone **10b** (71.0 mg, 0.15 mmol) and *trans*-1-penten-1-ylboronic acid (34.2 mg, 0.3 mmol), 29 mg of **12e** (55% isolated yield) were obtained as a colourless oil. R*f* 0.25 (5:1 hexane:EtOAc).



^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.45 (td, *J* = 7.4, 1.4 Hz, 1H), 7.33 – 7.27 (m, 6H), 7.14 (d, *J* = 7.7 Hz, 1H), 5.48 (d, *J* = 16.0 Hz, 1H), 5.32 (dt, *J* = 16.0, 6.6 Hz, 1H), 3.47 – 3.33 (m, 3H), 2.84 – 2.75 (m, 2H), 2.60 – 2.46 (m, 3H), 2.07 – 1.86 (m, 4H), 1.63 (td, *J* = 13.0, 4.1 Hz, 1H), 1.30 – 1.22 (m, 2H), 0.75 (t, *J* = 7.3 Hz, 3H).

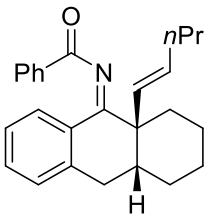
^{13}C NMR (75 MHz, $CDCl_3$) δ 199.1 (C), 141.3 (C), 133.6 (CH), 132.4 (CH), 131.9 (C), 131.8 (CH), 129.4 (CH), 129.2 (CH), 128.4 (CH), 127.6 (CH), 127.3 (CH), 126.7 (CH), 63.3 (CH_2), 55.6 (CH_2), 51.4 (CH_2), 41.0 (CH), 35.0 (CH_2), 33.8 (CH_2), 30.4 (CH_2), 22.3 (CH_2), 13.5 (CH).

ESI HRMS: calcd. For $[C_{25}H_{30}NO]^+$: 360.2322, found: 360.2333.

3.3 Experimental procedures for the synthesis of *N*-benzoylimine 13 and benzamide 14

3.3.1- Experimental procedure and characterization data for *N*-((4a*S**,9a*S**)-9a-((*E*)-pent-1-en-1-yl)-1,3,4,4a,9a,10-hexahydroanthracen-9(2*H*)-ylidene)benzamide 13

To a solution of imine **12b** (0.315 mmol, 85 mg) in toluene (2 mL) were successively added trimethylamine (0.633 mmol, 0.095 mL) and benzoyl chloride (0.333 mmol, 0.038 mL). The solution was stirred and heated to 90 ºC for 4 hours. Once the reaction finished, it was allowed to reach room temperature. Saturated ammonium chloride solution (4 mL) was added and the crude was extracted with DCM (6 mL) three times. The solvent of the combined organic layers was removed under reduced pressure. Finally, the product was purified by flash chromatography on silica gel. 85 mg of **13** (73% isolated yield) were obtained as a colourless oil. R*f* 0.35 (20:1 hexane:EtOAc).



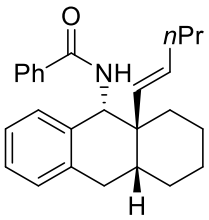
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 – 7.92 (m, 2H), 7.78 (d, *J* = 7.9, 1H), 7.54 – 7.48 (m, 1H), 7.45 – 7.37 (m, 2H), 7.34 (td, *J* = 7.4, 1.2 Hz, 1H), 7.19 – 7.12 (m, 2H), 5.53 – 5.42 (m, 2H), 3.25 (dd, *J* = 16.8, 4.7 Hz 1H), 2.74 (d, *J* = 16.6 Hz, 1H), 2.31 – 2.21 (m, 1H), 2.12 – 2.04 (m, 1H), 1.78 (m, 2H), 1.68 – 1.39 (m, 7H), 1.29 – 1.17 (m, 2H), 0.75 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 176.4 (C), 165.1 (C), 140.7 (C), 134.1 (CH), 134.0 (C), 132.4 (CH), 132.1 (CH), 131.8 (CH), 129.9 (CH), 129.6 (C), 129.0 (2xCH), 128.5 (2xCH), 128.4 (CH), 126.5 (CH), 50.5 (C), 41.7 (CH), 34.9 (CH_2), 34.7 (CH_2), 33.2 (CH_2), 28.7 (CH_2), 24.9 (CH_2), 22.5 (CH_2), 22.3 (CH_2), 13.6 (CH).

ESI HRMS: calcd. For $[C_{26}H_{30}NO]^+$: 372.2300, found: 372.2311.

3.3.2- Experimental procedure and characterization data for *N*-((4a*S**,9*S**,9a*S**)-9a-((*E*)-pent-1-en-1-yl)-1,2,3,4,4a,9,9a,10-octahydroanthracen-9-yl)benzamide 14

To a stirred solution of **13** (0.229 mmol, 85 mg) in anhydrous THF (4.5 mL) was added ground $LiAlH_4$ (1.15 mmol, 435 mg). The solution was stirred at room temperature for 15 mins. After this time, the reaction was carefully quenched with IPA and water, filtered through a pad of celite and extracted twice with EtOAc. The combined organic layers were dried and evaporated under reduced pressure. Finally, the product was purified by flash chromatography on silica gel. 65 mg of **14** (76% isolated yield) were obtained as a colourless oil. R*f* 0.35 (10:1 hexane:EtOAc).



^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 – 7.78 (m, 2H), 7.55 – 7.43 (m, 3H), 7.22 – 7.09 (m, 4H), 6.22 (d, *J* = 10.3, 1H), 5.47 (td, *J* = 16.0, 6.7 Hz, 1H), 5.34 – 5.25 (m, 2H), 3.12 (dd, *J* = 18.2, 11.0 Hz 1H), 2.83 (dd, *J* = 18.2, 7.5 Hz, 1H), 2.27 – 2.17 (m, 1H), 2.02 – 1.95 (m, 2H), 1.92 – 1.81 (m, 1H), 1.70 – 1.39 (m, 7H), 1.34 – 1.20 (m, 3H), 0.80 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 167.6 (C), 135.8 (C), 135.5 (C), 135.3 (CH), 131.5 (CH), 131.3 (CH), 128.8 (4xCH), 127.0 (2xCH), 126.9 (CH), 126.7 (CH), 126.1 (CH), 56.2 (CH), 42.7 (C), 37.2 (CH), 35.4 (CH_2), 29.7 (CH_2), 27.0 (CH_2), 22.8 (CH_2), 22.4 (CH_2), 20.7 (CH_2), 19.6 (CH_2), 13.9 (CH).

ESI HRMS: calcd. For $[C_{26}H_{32}NO]^+$: 374.2401, found: 374.2411.

3.4. Scale up experiments (1 mmol or more)

3.4.1 Experimental procedure for ketone 9a

A 10-20 mL microwave vial provided with an stir bar was charged with the *N*-tosylhydrazone **1a** (0.581 g, 1.58 mmol), the alkenyl boronic acid (0.512 g, 3.16 mmol) and K_2CO_3 (0.436 g, 3.16 mmol) in 12 mL of dry 1,4-dioxane. The vial was

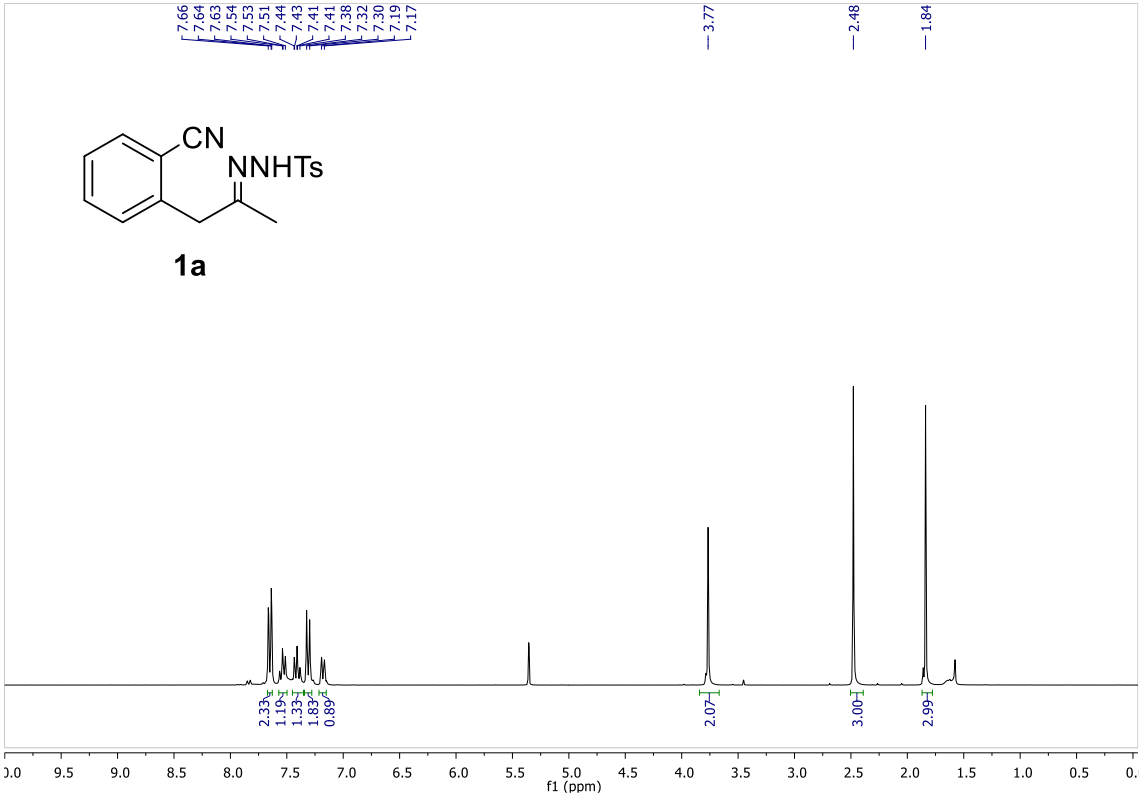
sealed with a septum, placed into the microwave cavity and irradiated to maintain the reaction at the desired temperature (120 ºC) during the reaction time (8h) in a Biotage Initiator microwave apparatus. Once the reaction finished, it was allowed to reach room temperature and the crude was dissolved in EtOAc and filtered through celite. Solvent was removed under reduced pressure. Finally, the product was purified by flash chromatography on silica gel obtaining 0.24 g of **9a** (51% isolated yield R*f* 0.35 (20:1 hexane:EtOAc).

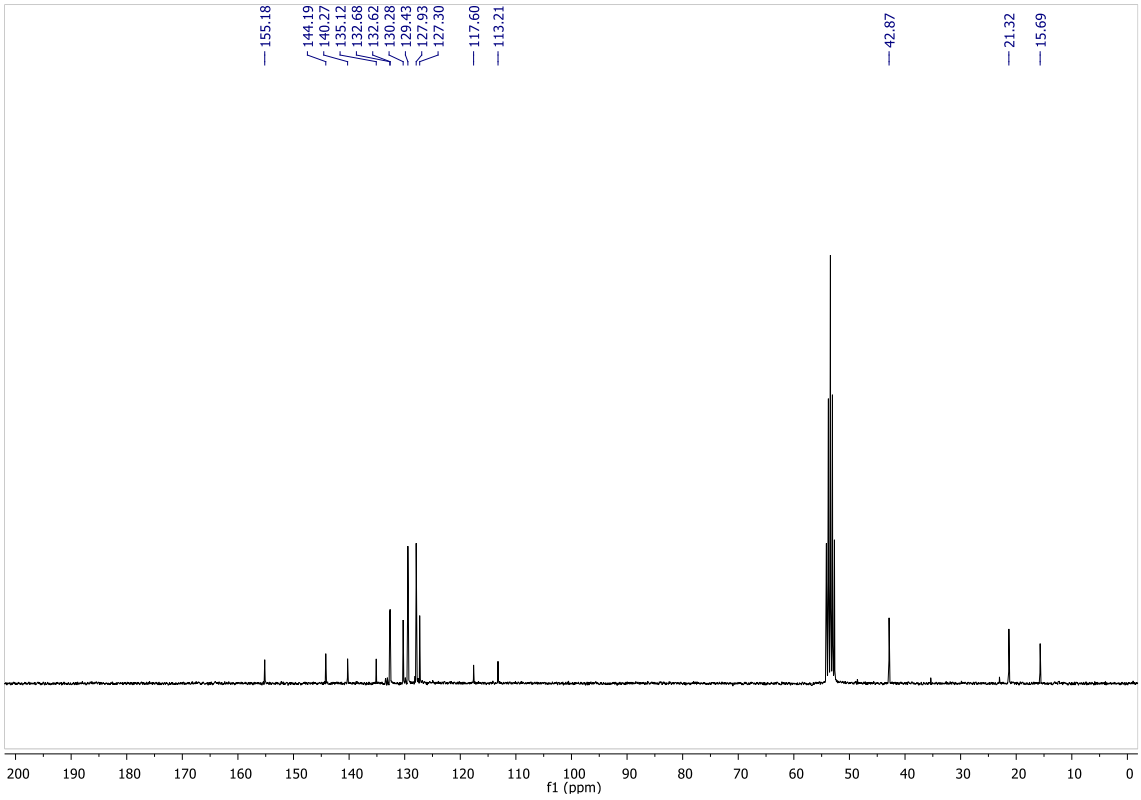
3.4.2 Experimental procedure for imine 11b.

A 10-20 mL microwave vial provided with an stir bar was charged with the *N*-tosylhydrazone **10a** (0.381 g, 1.0 mmol), the alkenyl boronic acid (0.228g, 2.0 mmol) and K_2CO_3 (0.277 g, 2 mmol) in 10 mL of dry 1,4-dioxane. The vial was sealed with a septum, placed into the microwave cavity and irradiated to maintain the reaction at the desired temperature (120 ºC) during the reaction time (8h) in a Biotage Initiator microwave apparatus. Once the reaction finished, it was allowed to reach room temperature and the crude was dissolved in EtOAc and filtered through celite. Solvent was removed under reduced pressure. Finally, the product was purified by flash chromatography on silica gel obtaining 0.175 g of **11b** (65% isolated yield) R*f* 0.20 (20:1 hexane:EtOAc).

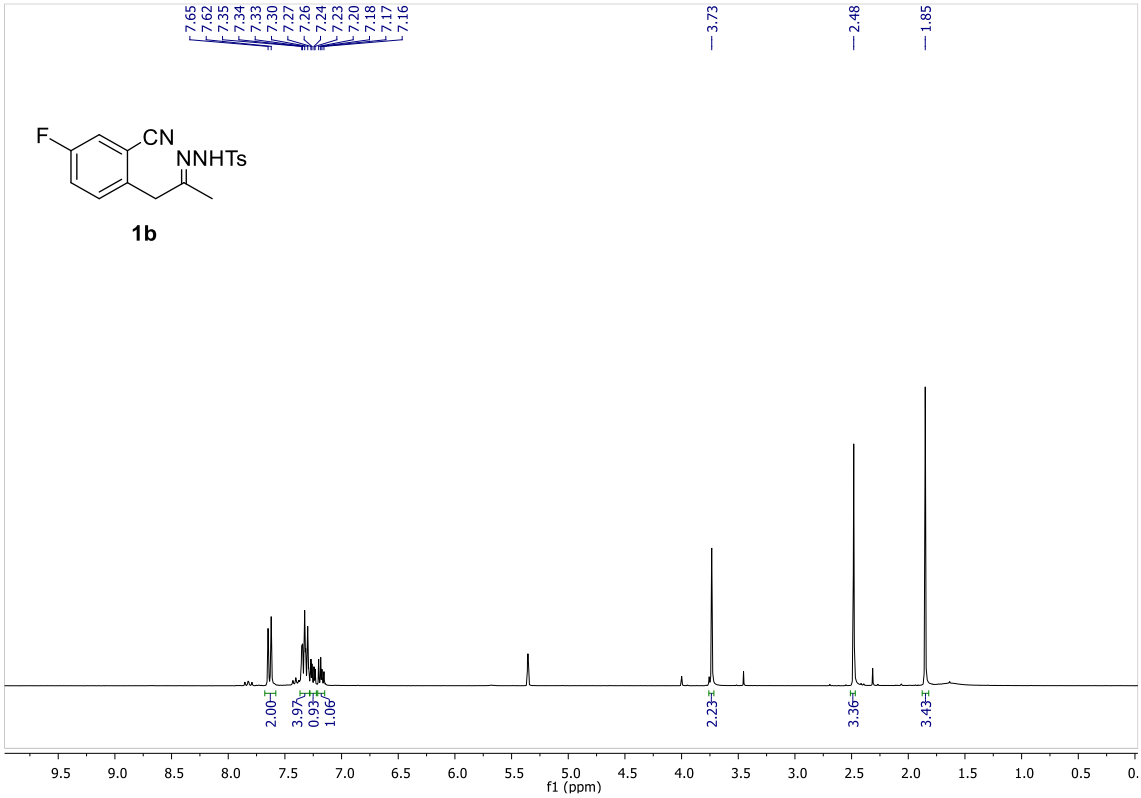
4. Copies of the ^{1}H, ^{13}C, ^{19}F NMR spectra

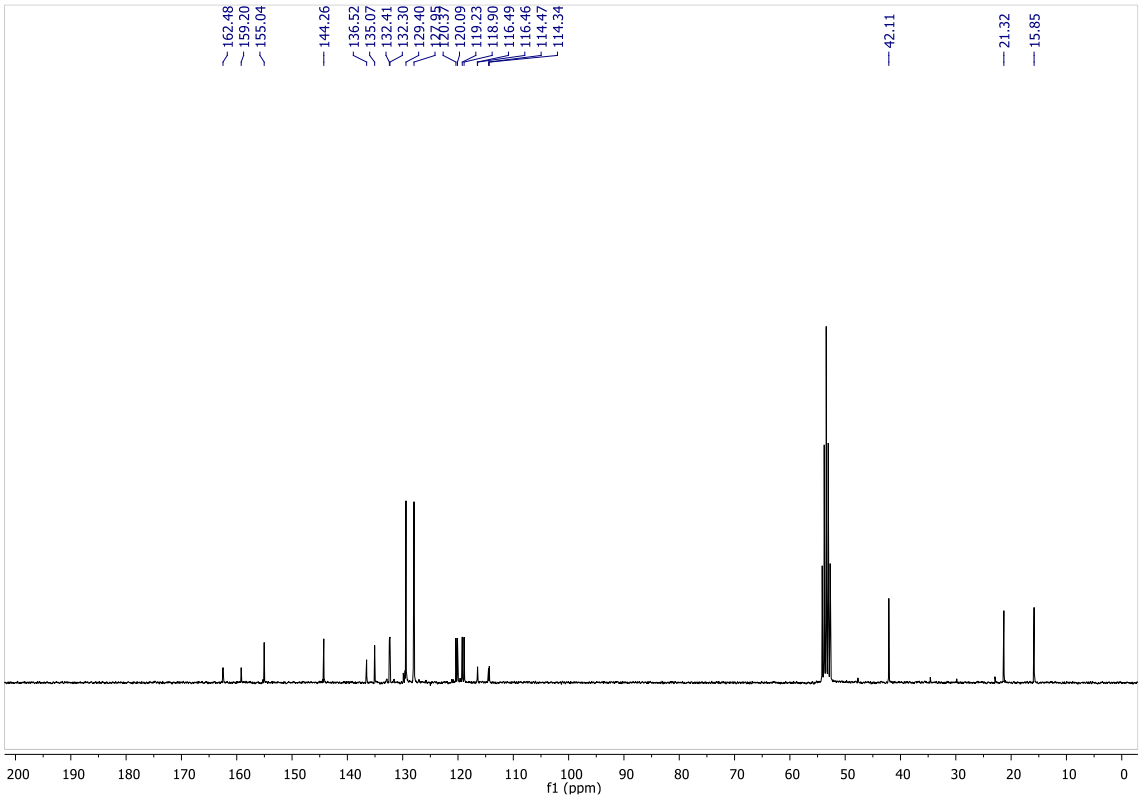
N'-(1-(2-Cyanophenyl)propan-2-ylidene)-4-methylbenzenesulfonohydrazide 1a

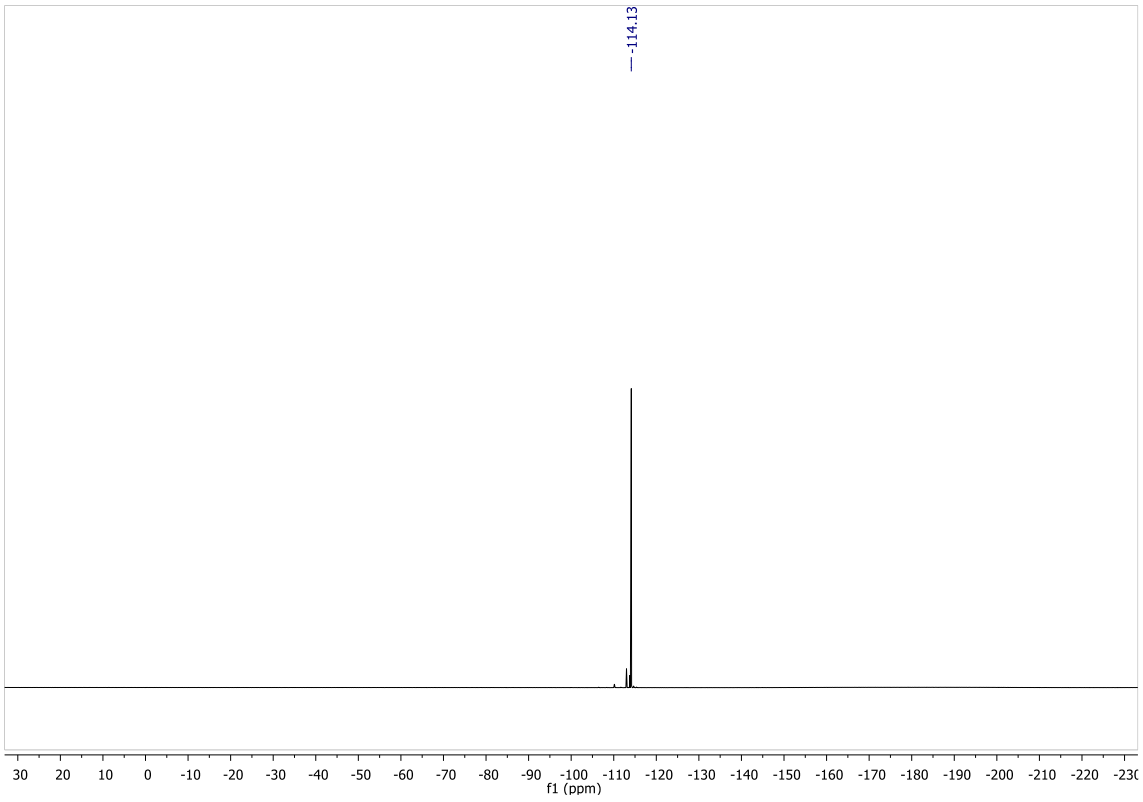




***N*'-(1-(2-Cyano-4-fluorophenyl)propan-2-ylidene)-4-methylbenzenesulfono-hydrazide 1b**






-114.13
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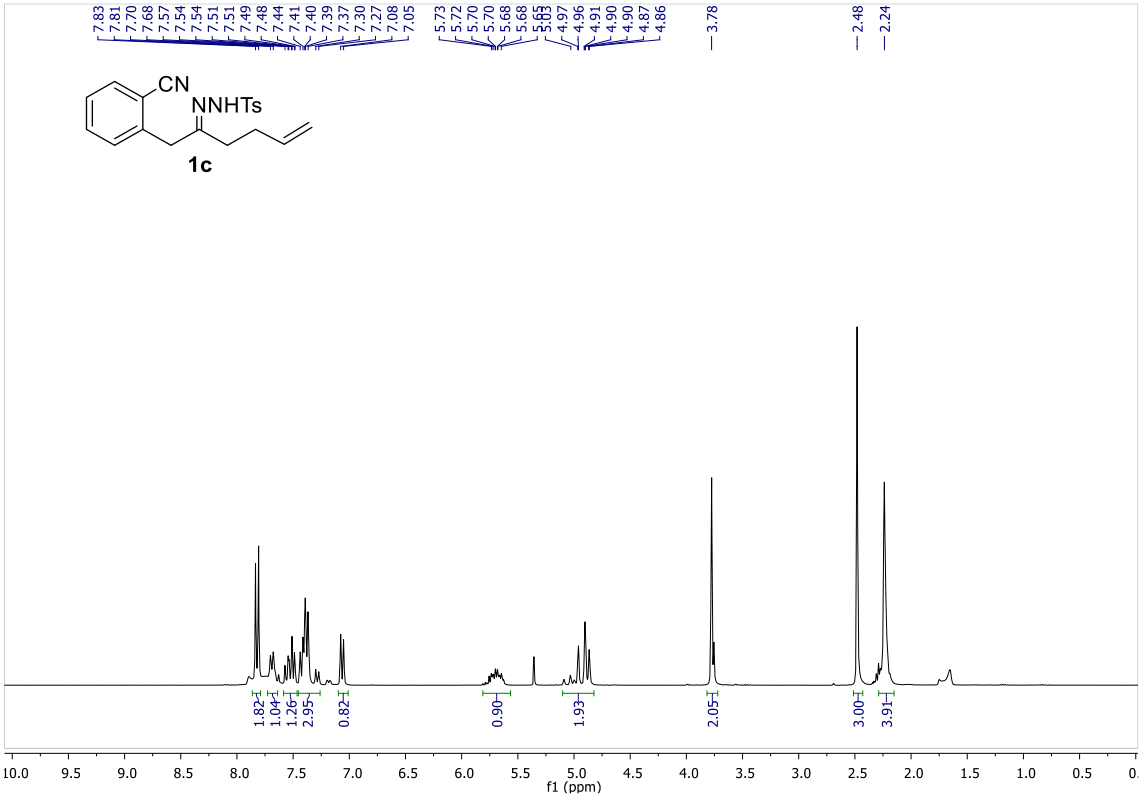
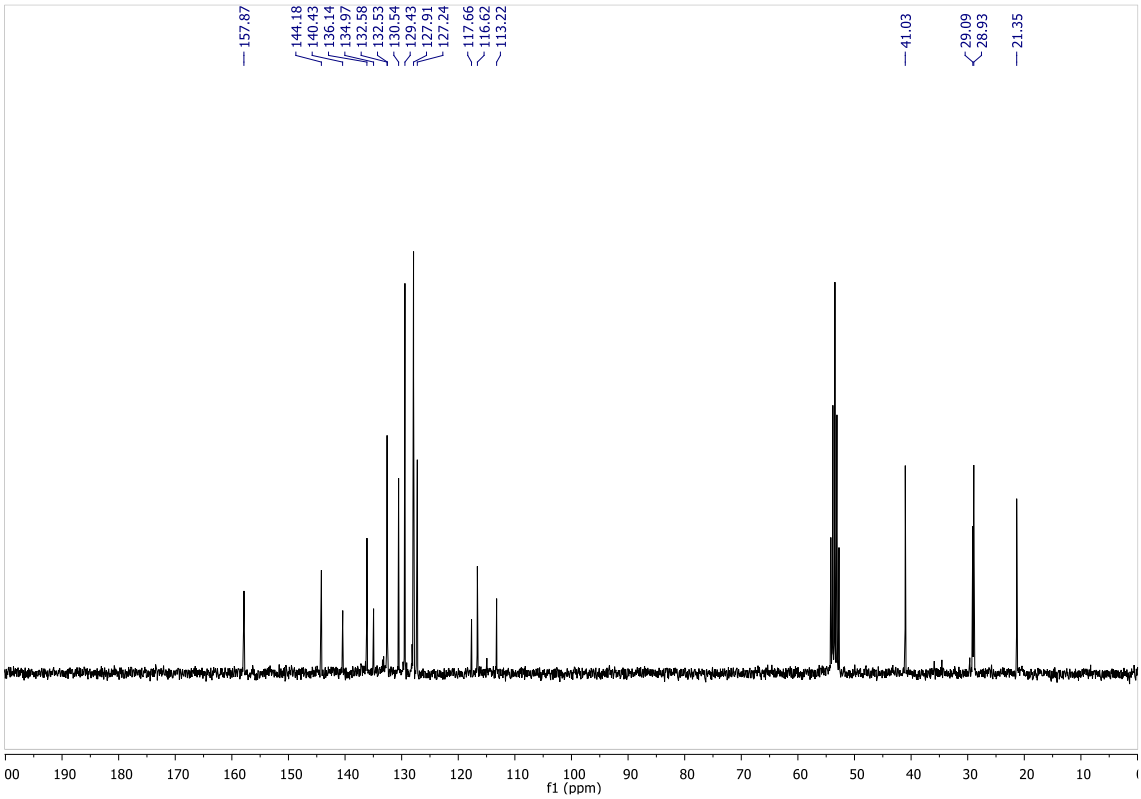
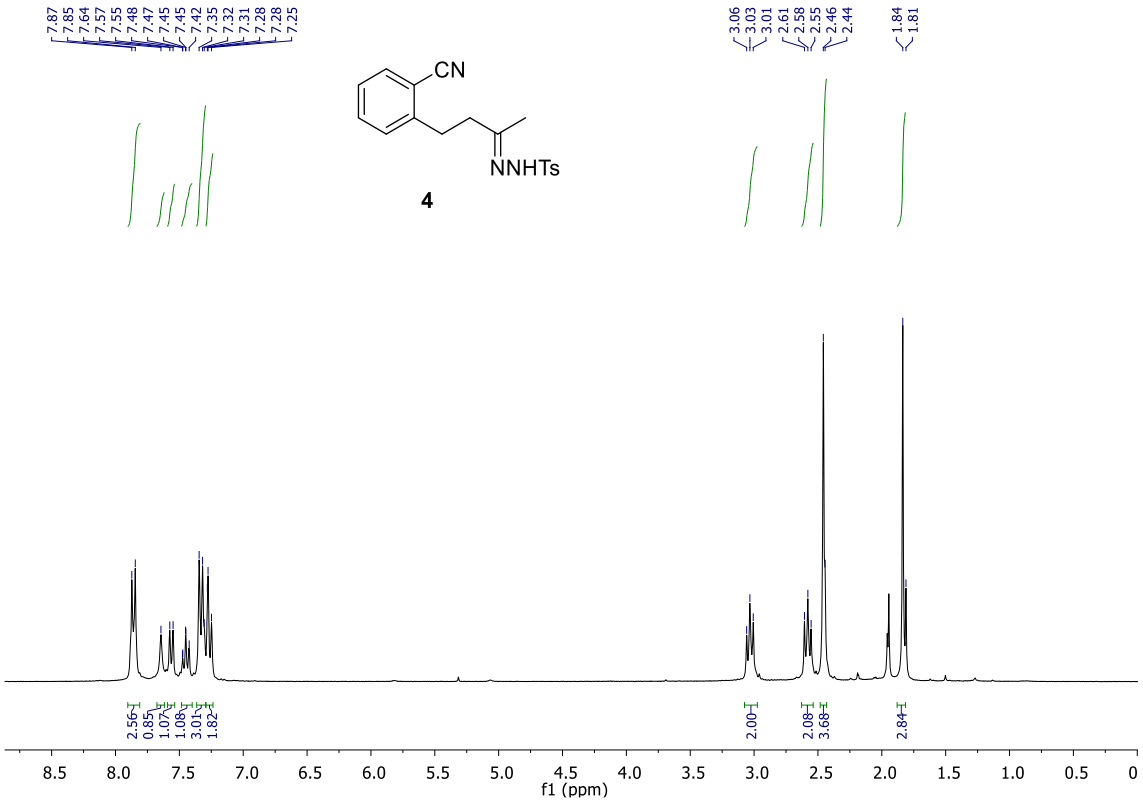
f1 (ppm)

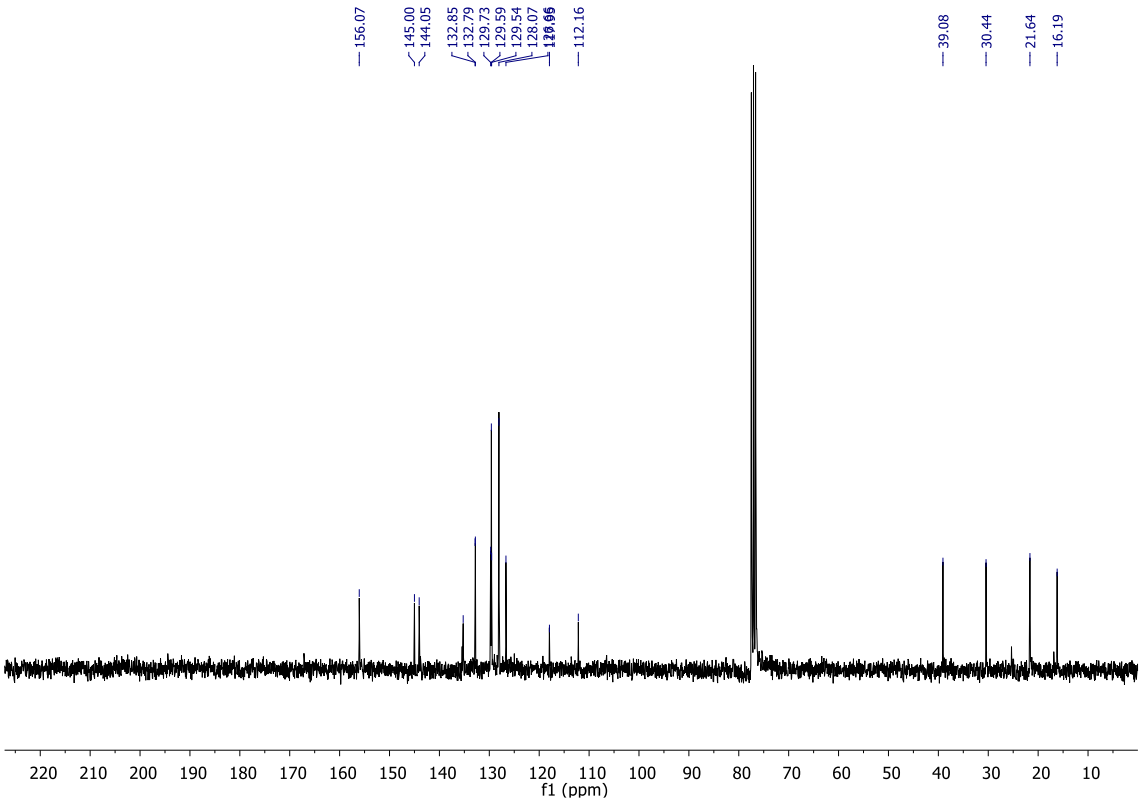
N'-(1-(2-Cyanophenyl)hex-5-en-2-ylidene)-4-methylbenzenesulfonohydrazide 1c



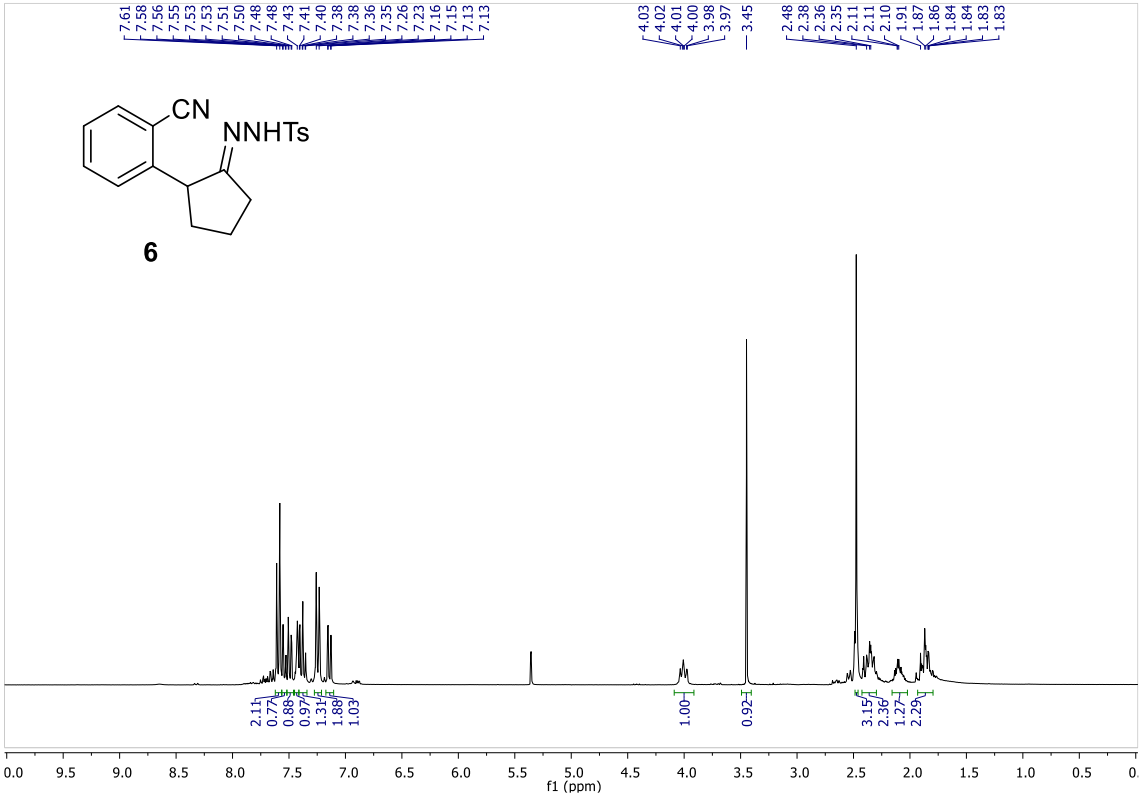


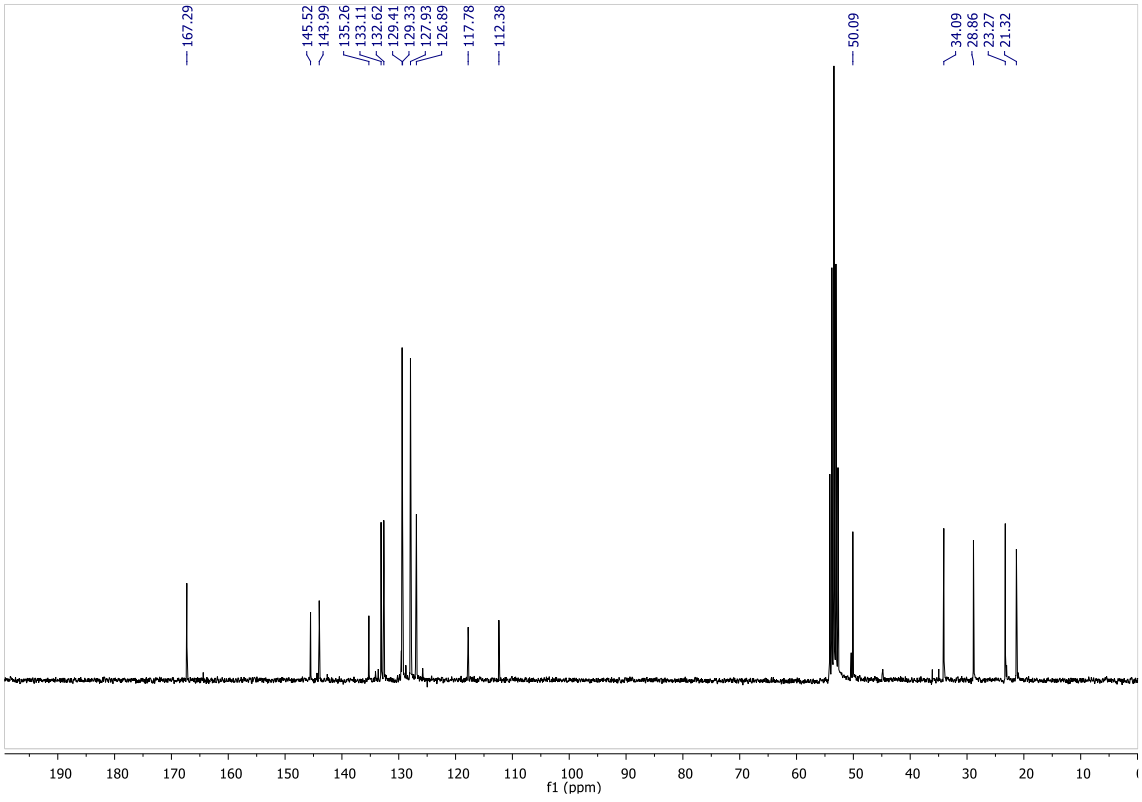
N'-(4-(2-cyanophenyl)butan-2-ylidene)-4-methylbenzenesulfonohydrazide 4



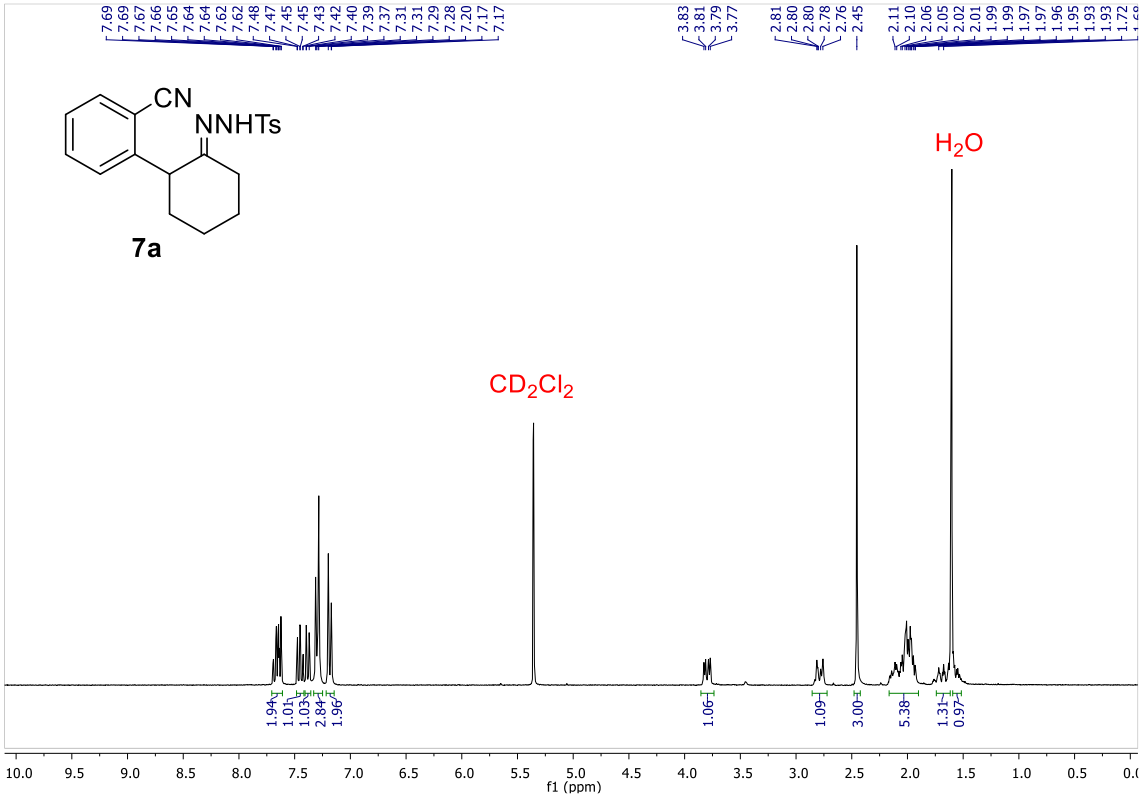


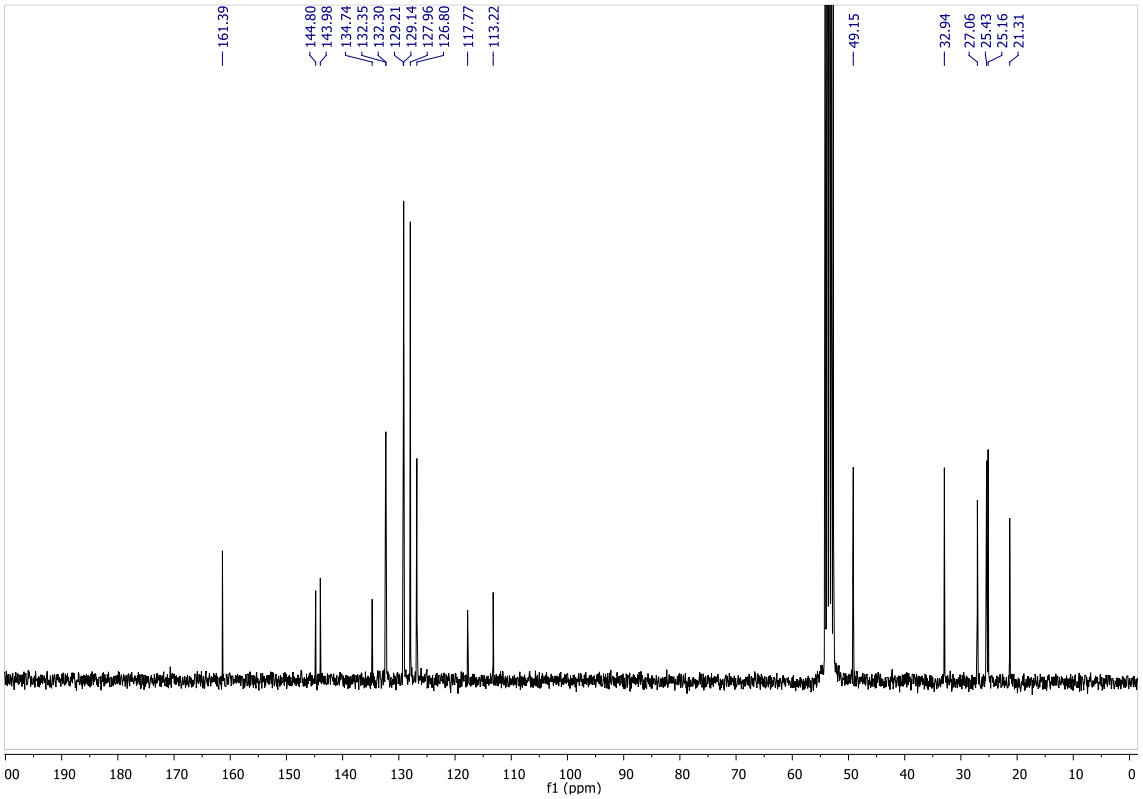
N'-(2-(2-Cyanophenyl)cyclopentylidene)-4-methylbenzenesulfonohydrazide 6



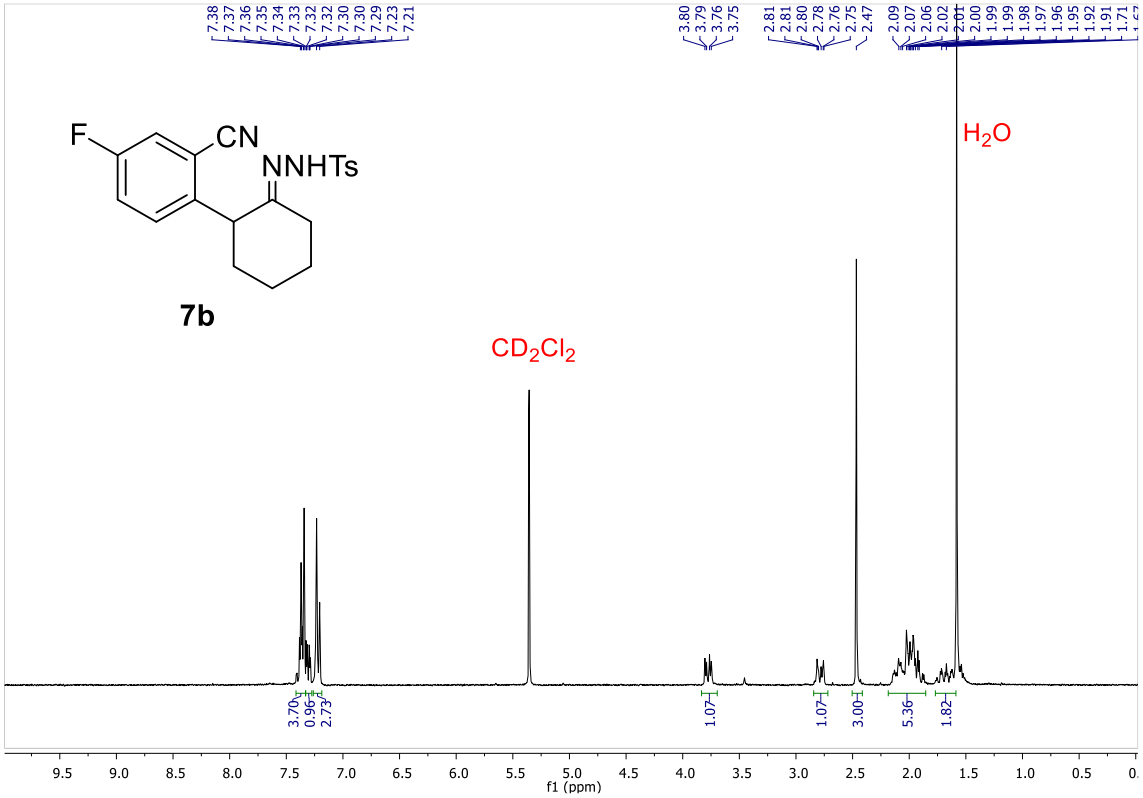


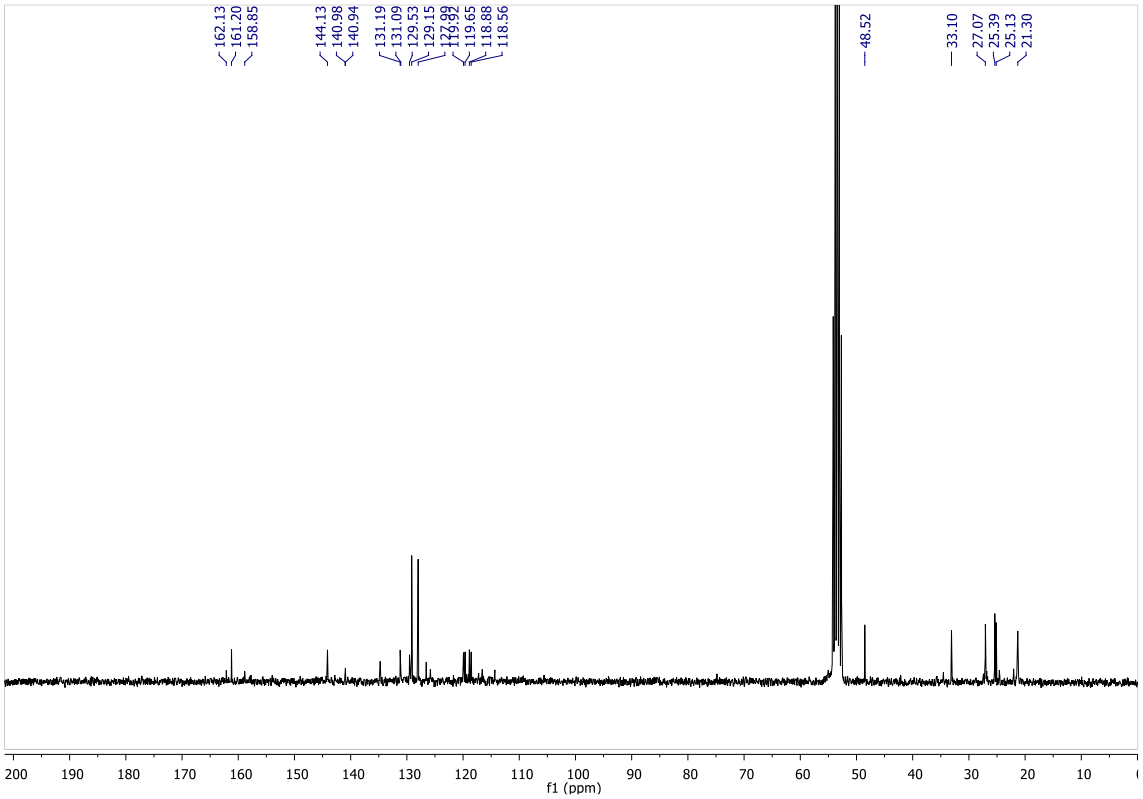
N'-(2-(2-Cyanophenyl)cyclohexylidene)-4-methylbenzenesulfonohydrazide 7a



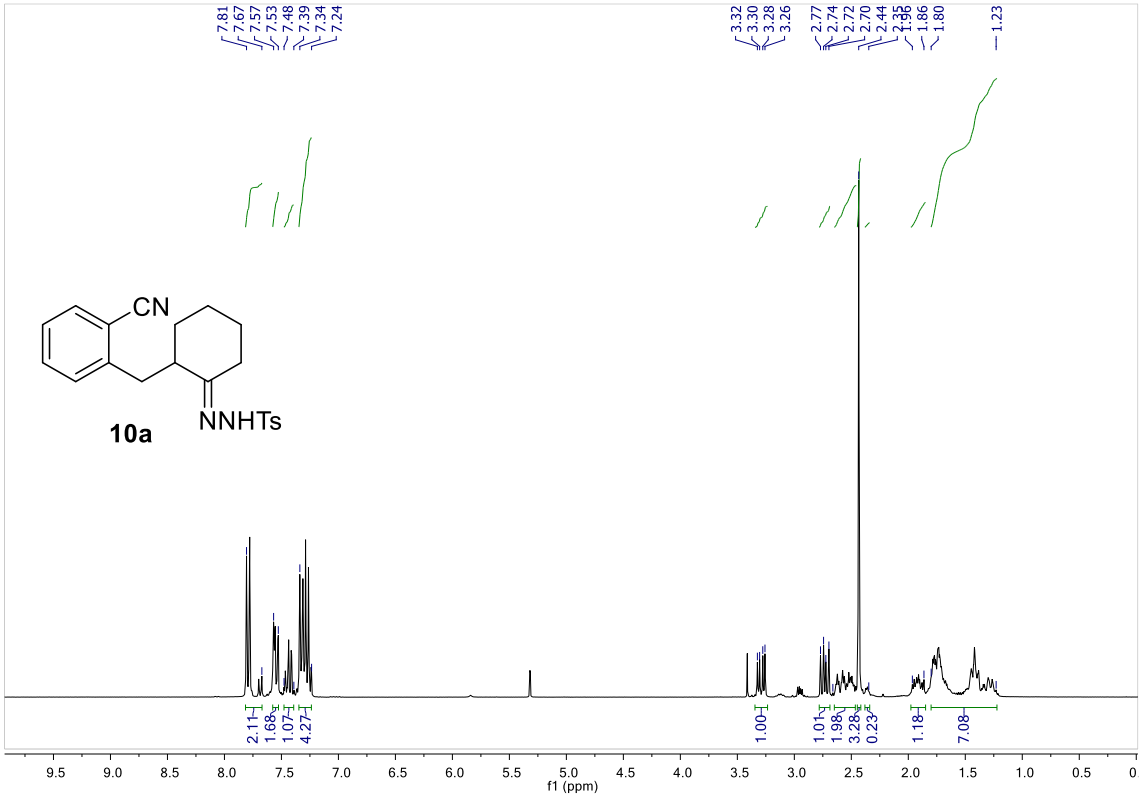


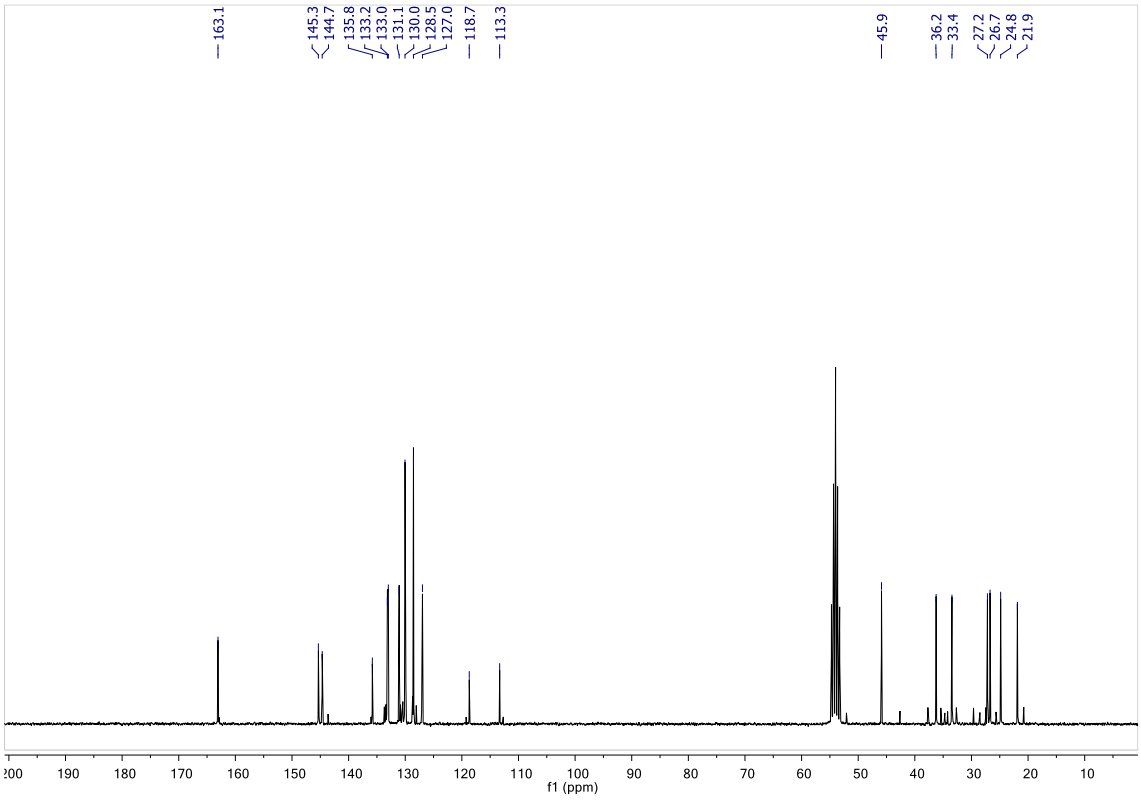
***N'*-(2-(2-Cyano-4-fluorophenyl)cyclohexylidene)-4-methylbenzenesulfono-hydrazide 7b**



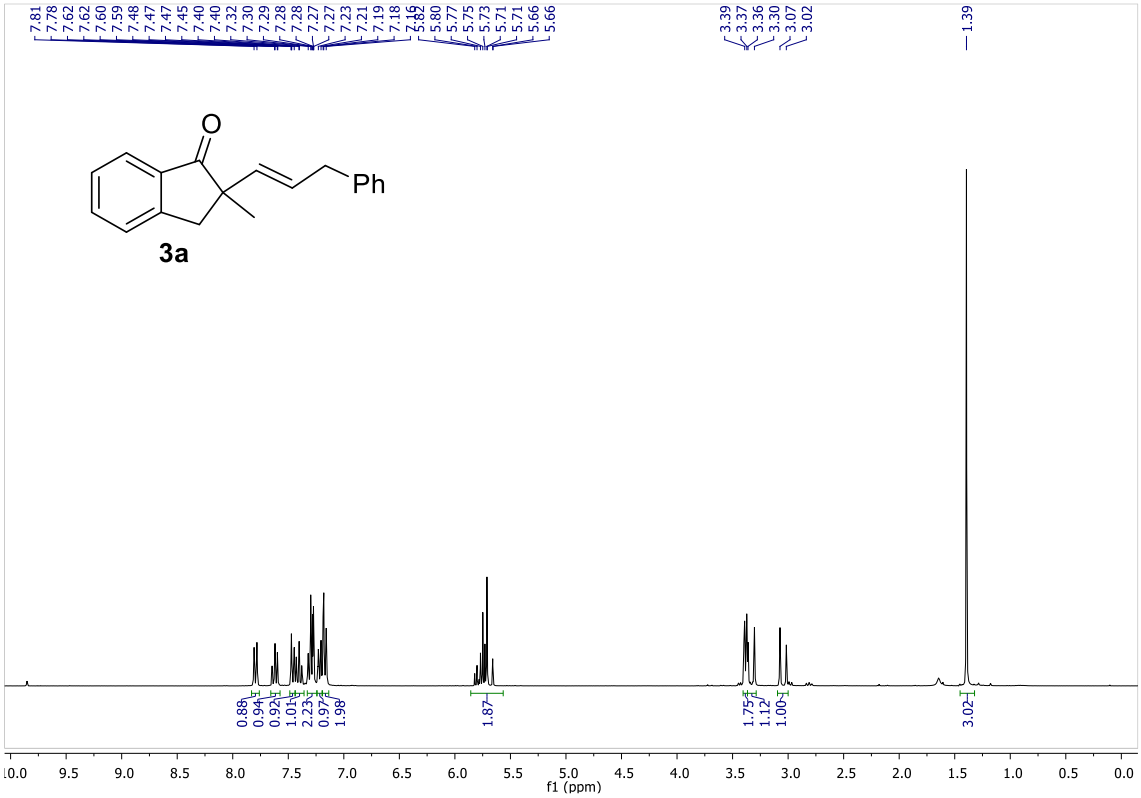


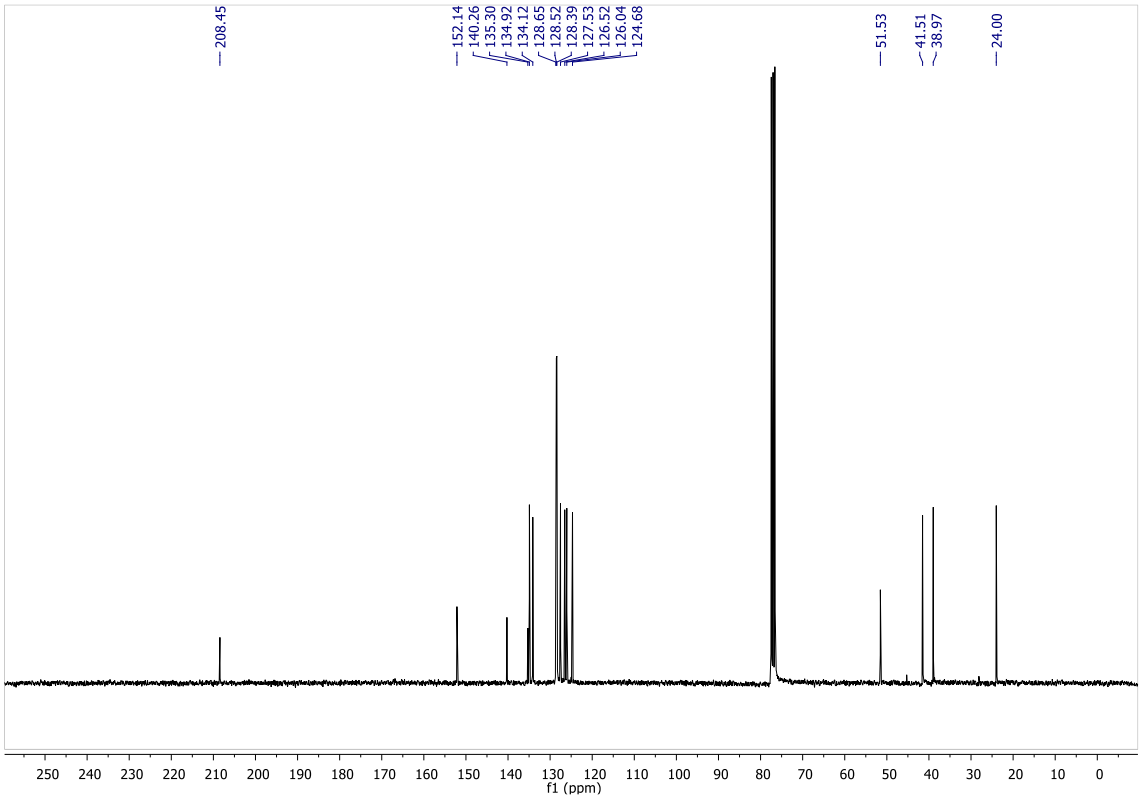
N'-(2-(2-cyanobenzyl)cyclohexylidene)-4-methylbenzenesulfonohydrazide 10a



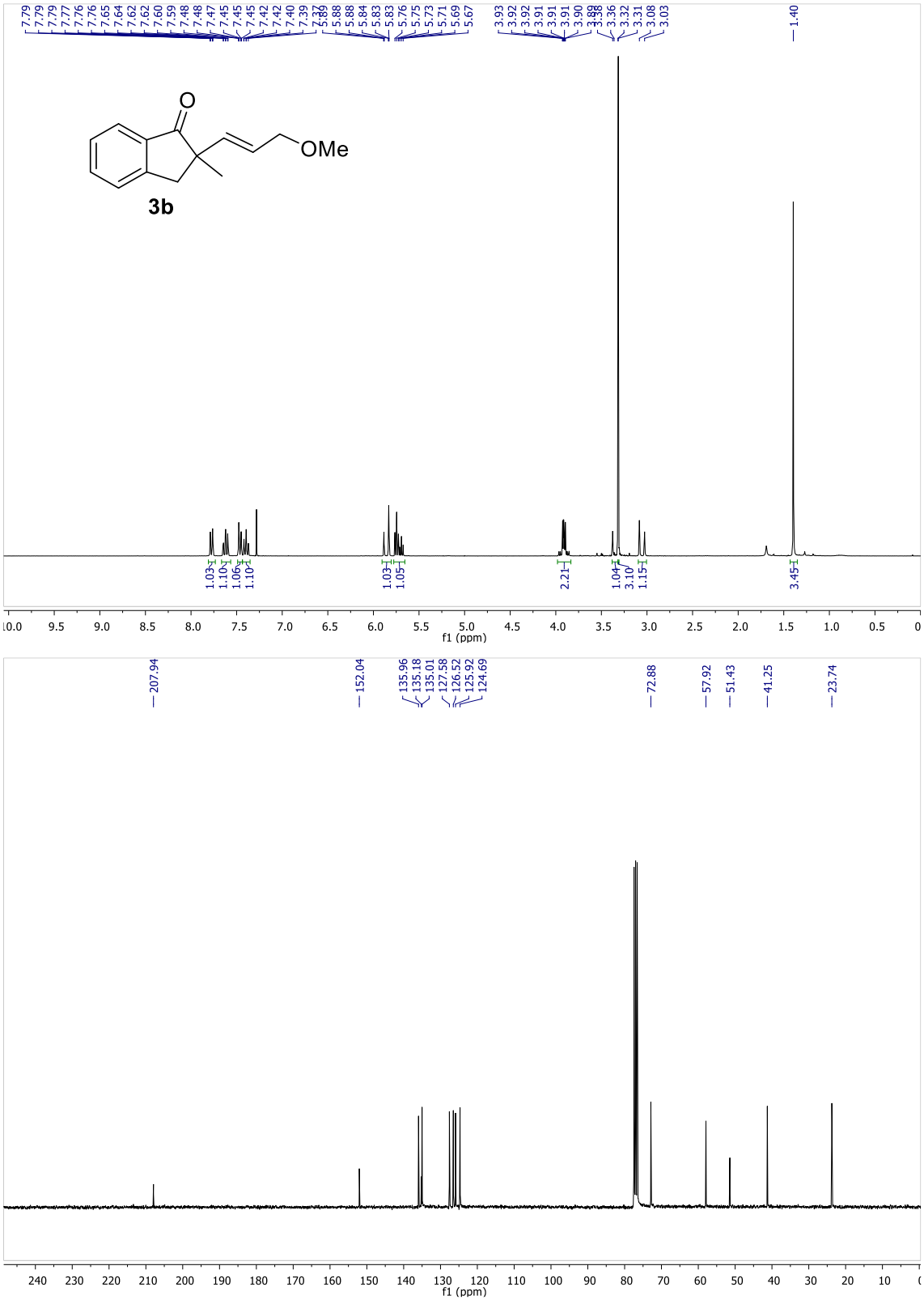


(*E*)-2-Methyl-2-(3-phenylprop-1-en-1-yl)-2,3-dihydro-1*H*-inden-1-one 3a

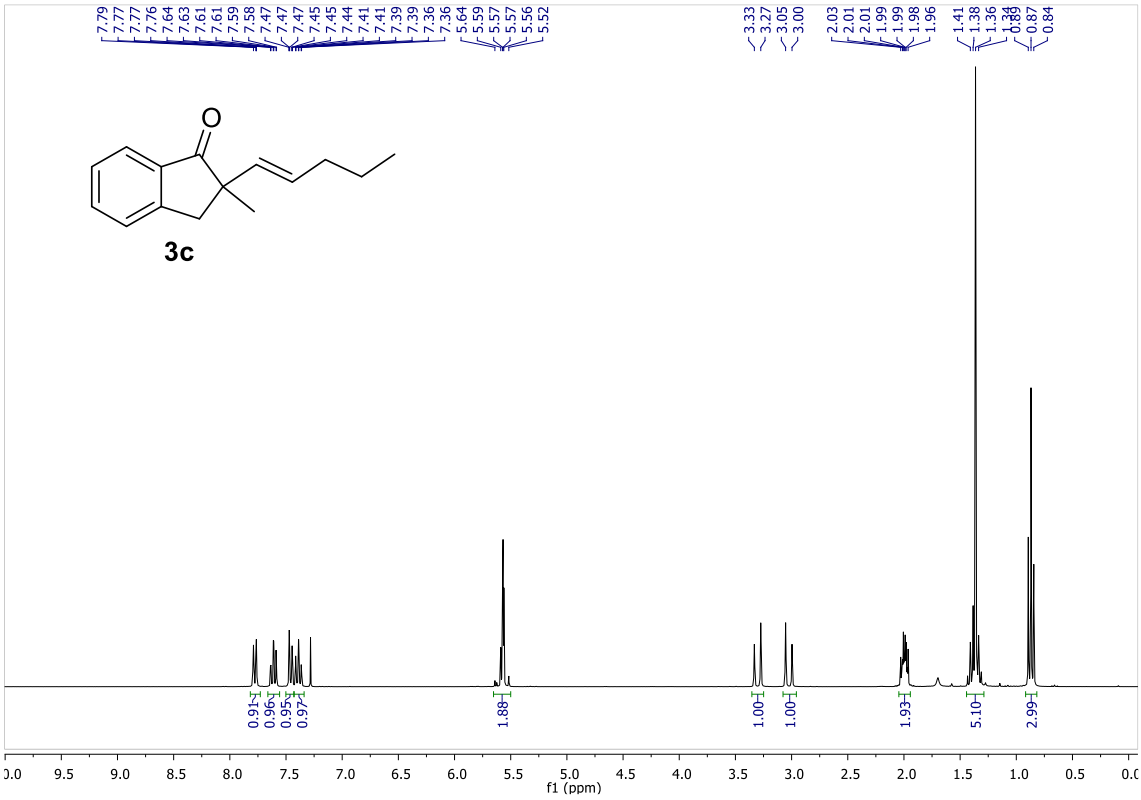


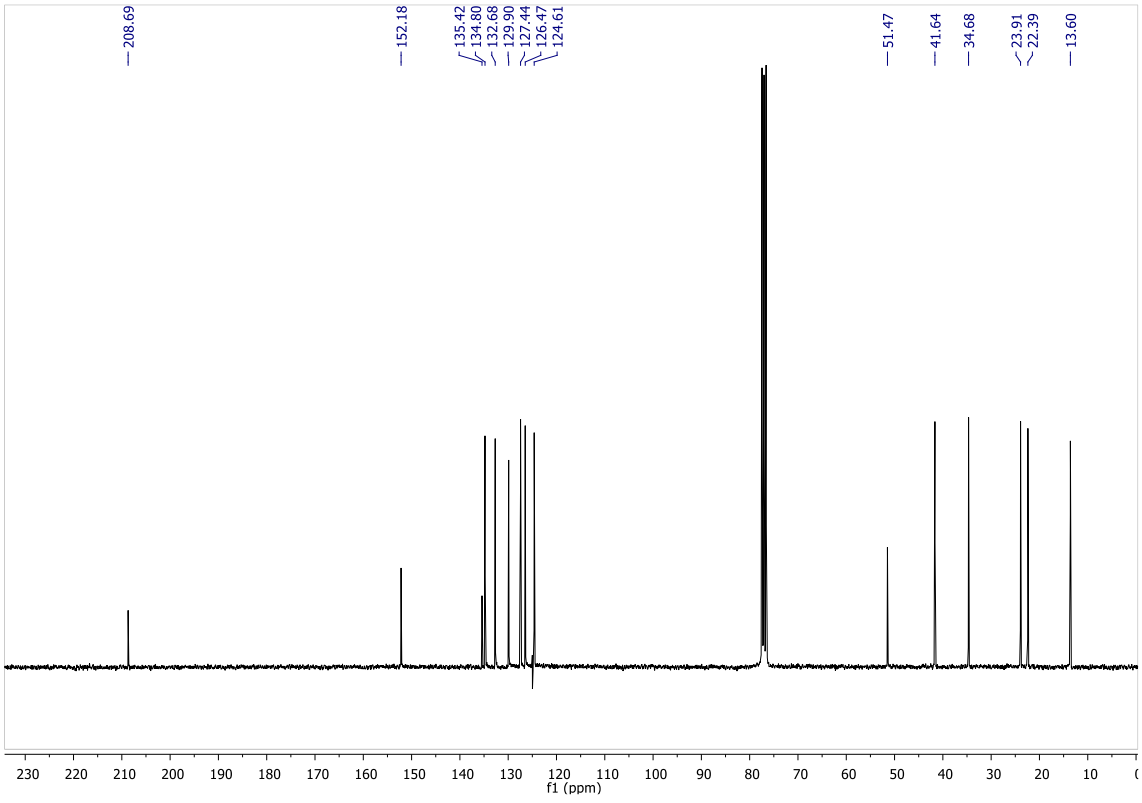


(*E*)-2-(3-Methoxyprop-1-en-1-yl)-2-methyl-2,3-dihydro-1*H*-inden-1-one 3b

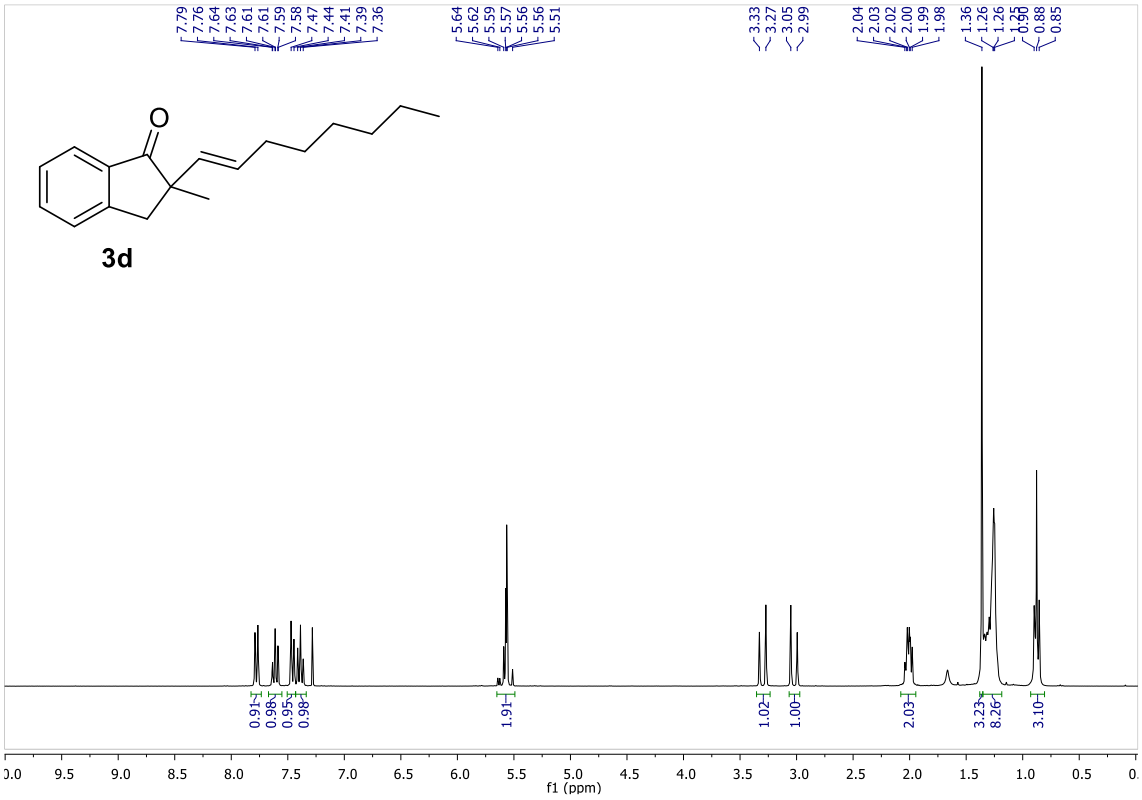


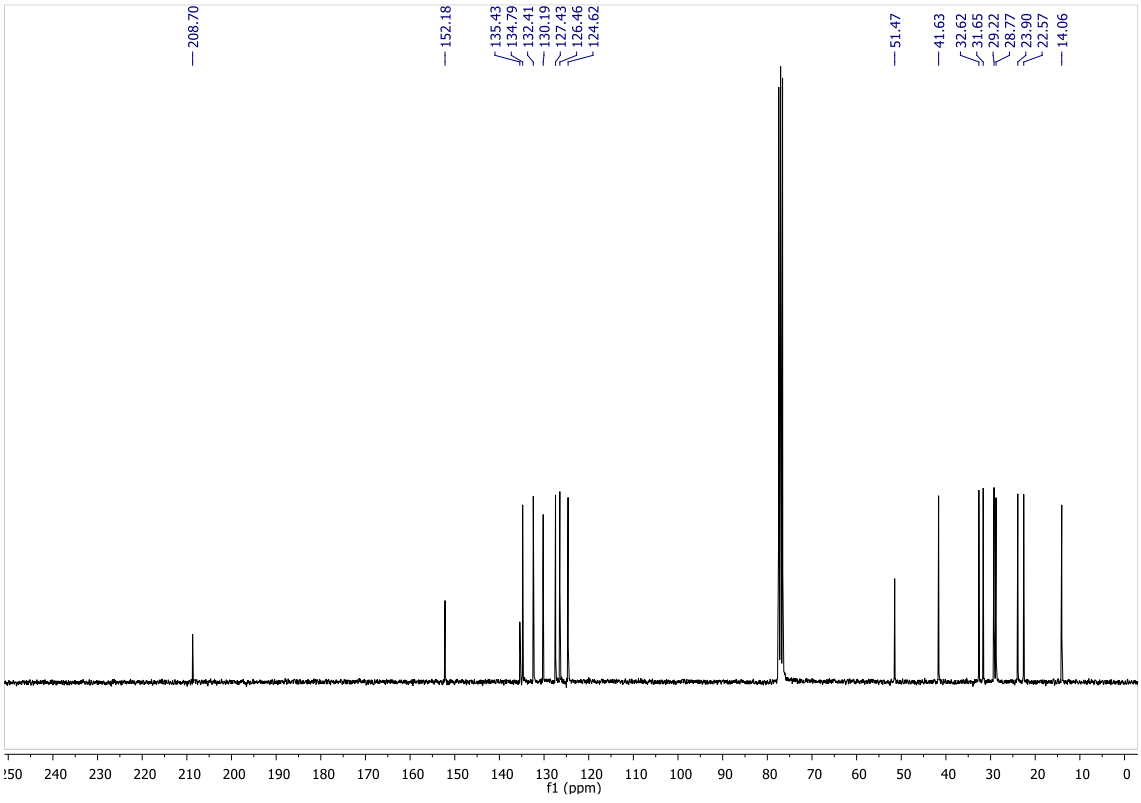
(*E*)-2-Methyl-2-(pent-1-en-1-yl)-2,3-dihydro-1*H*-inden-1-one 3c



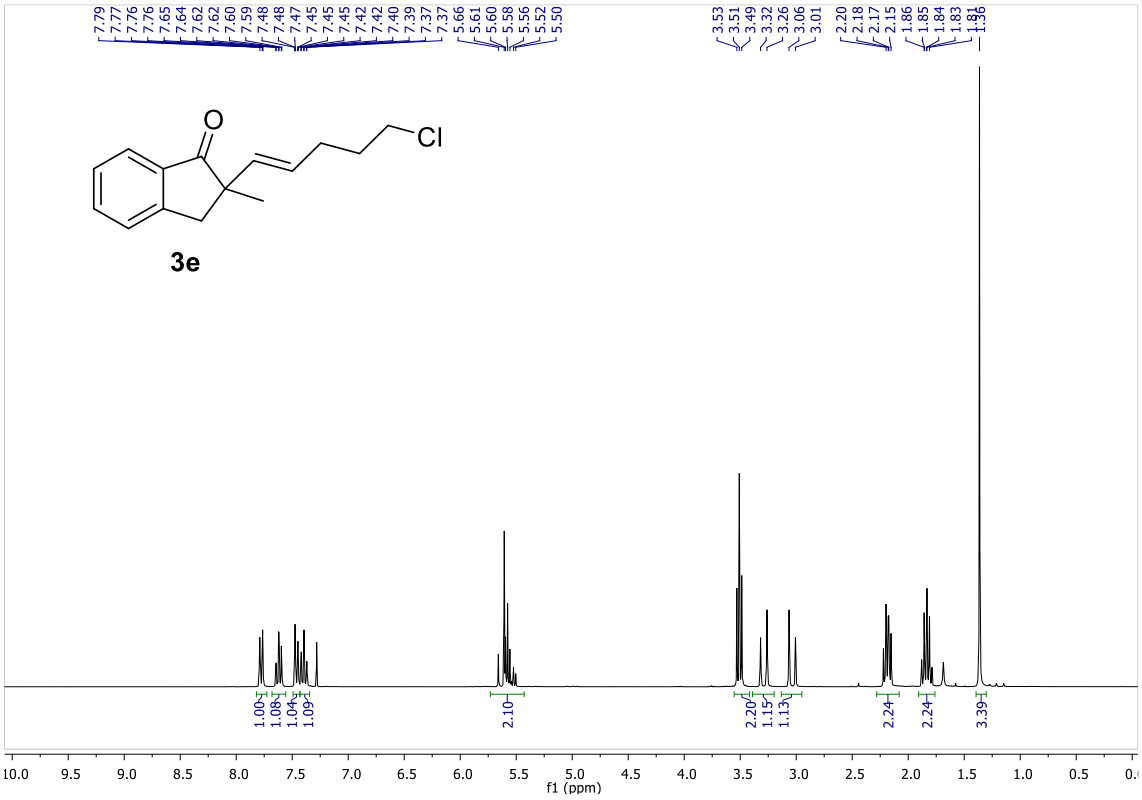


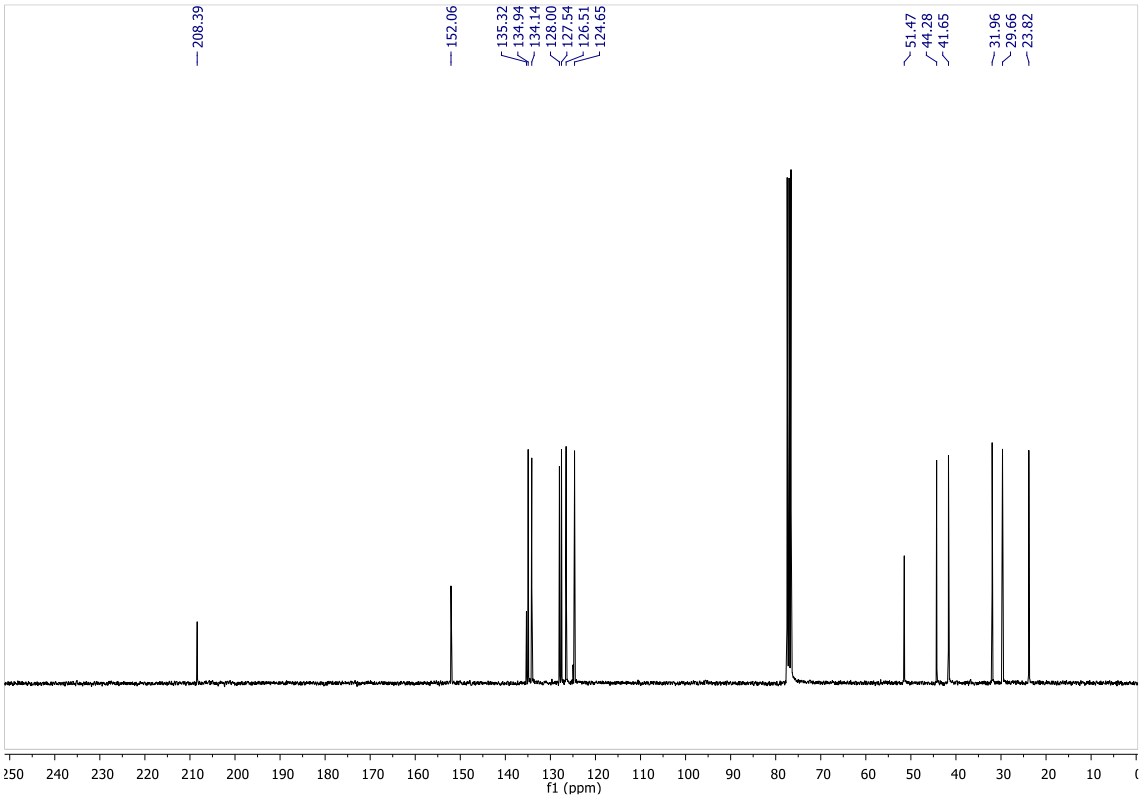
(*E*)-2-Methyl-2-(oct-1-en-1-yl)-2,3-dihydro-1*H*-inden-1-one 3d



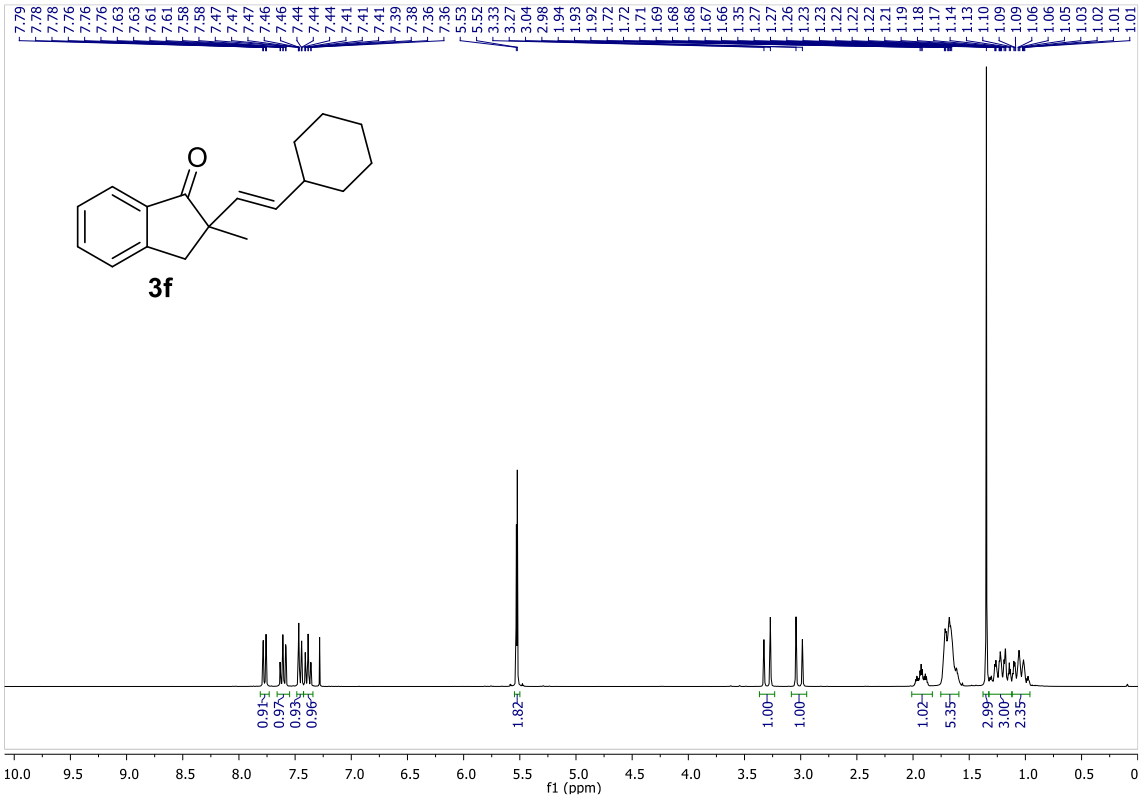


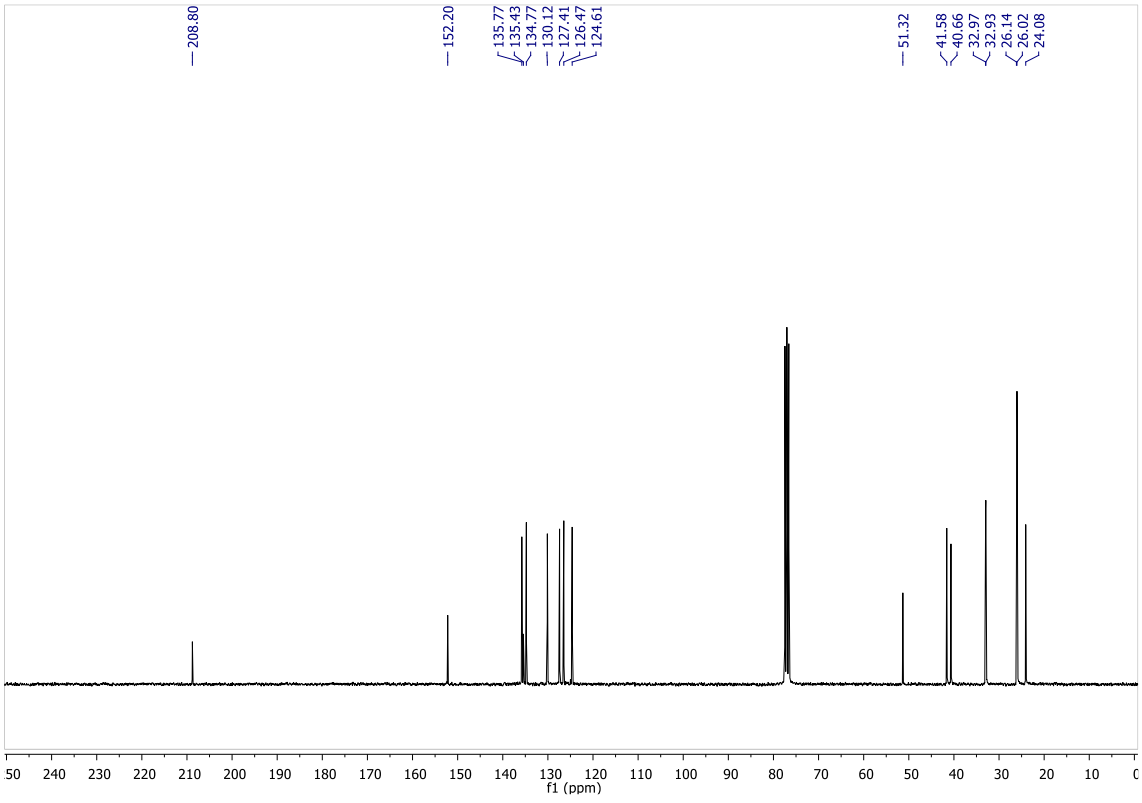
(*E*)-2-(5-Chloropent-1-en-1-yl)-2-methyl-2,3-dihydro-1*H*-inden-1-one 3e



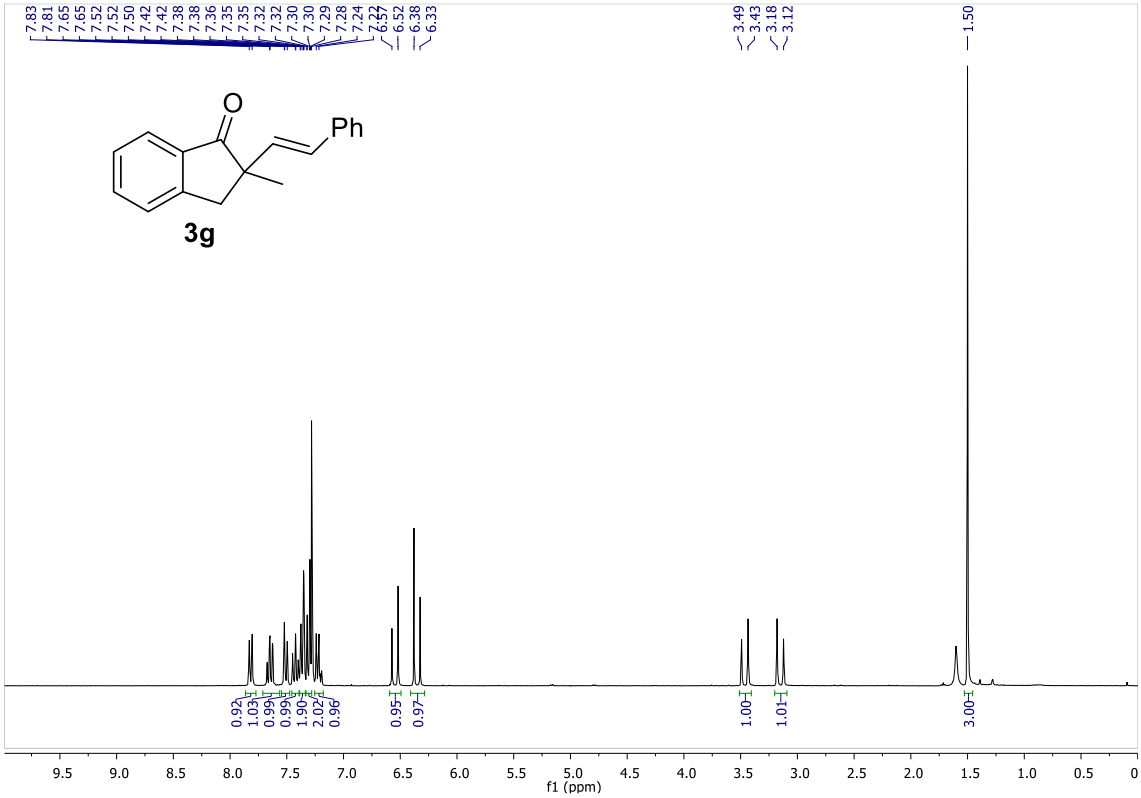


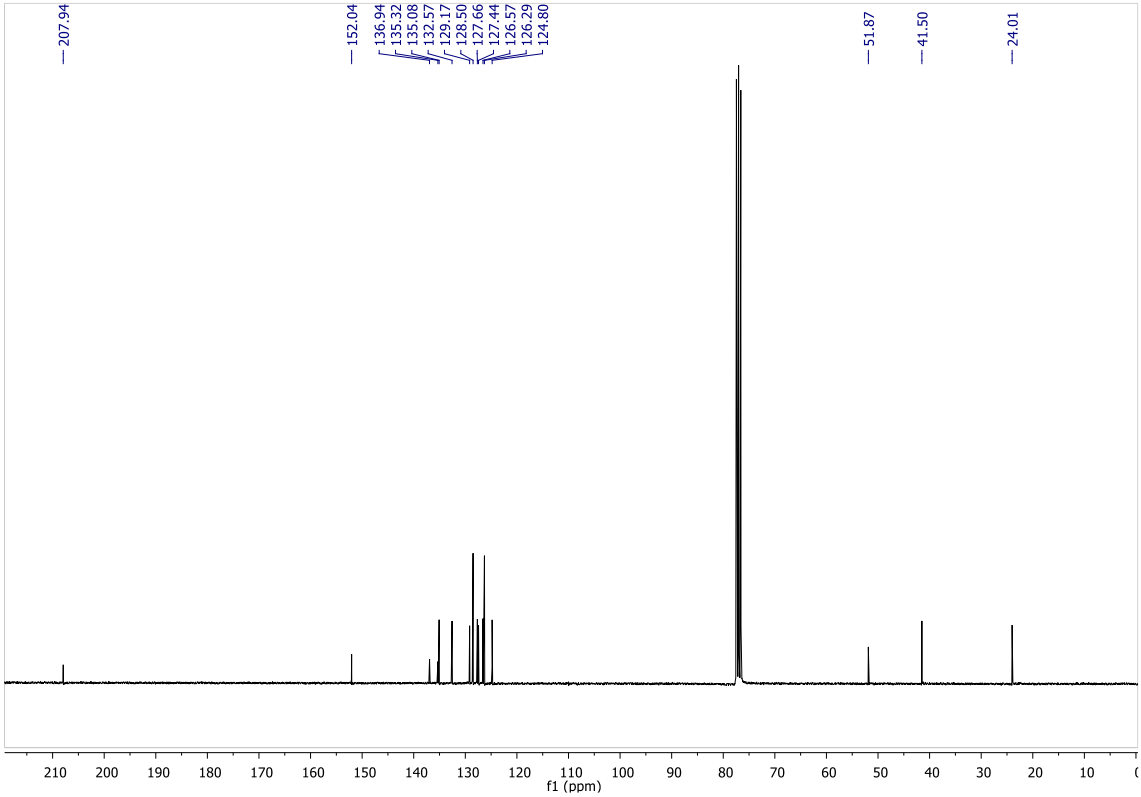
(*E*)-2-(2-Cyclohexylvinyl)-2-methyl-2,3-dihydro-1*H*-inden-1-one 3f



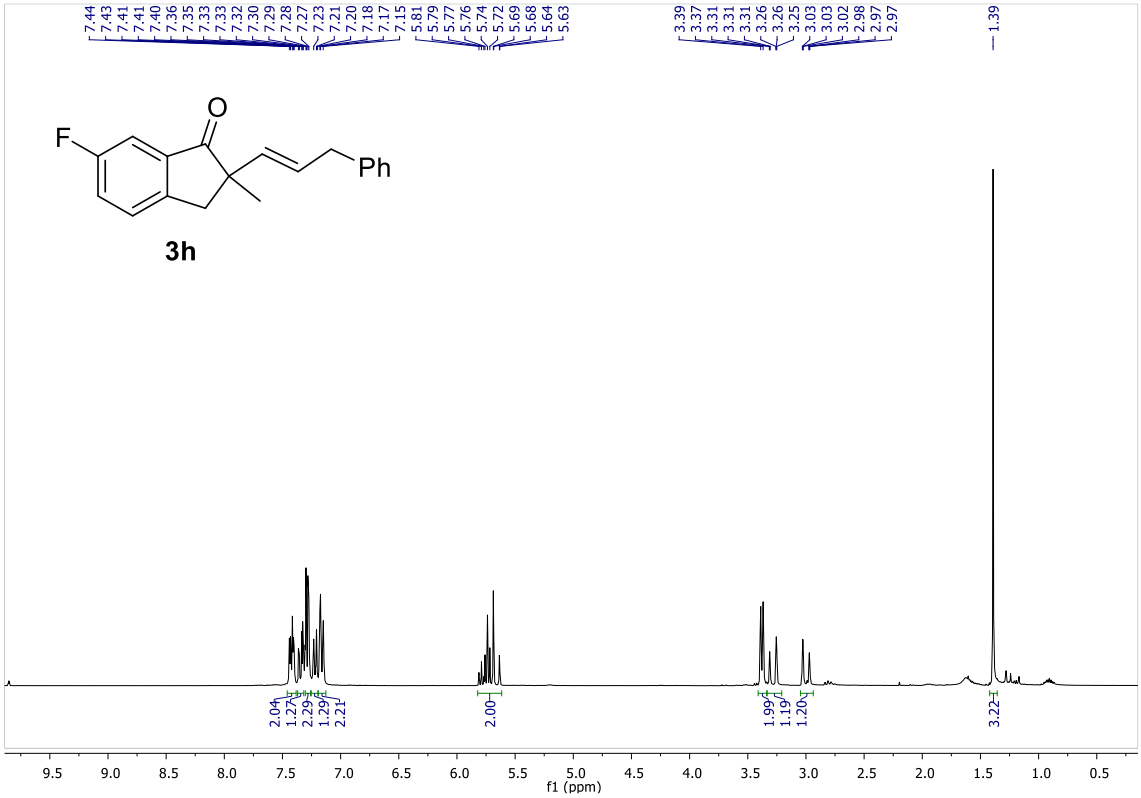


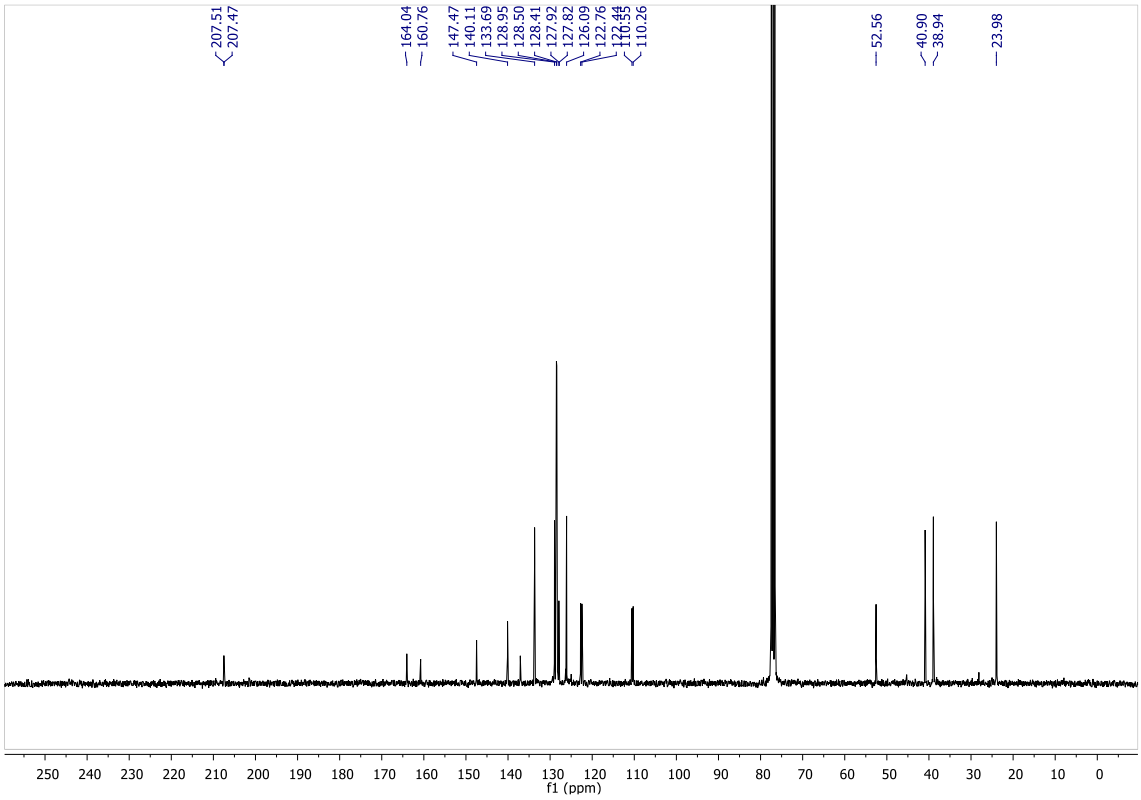
(*E*)-2-Methyl-2-styryl-2,3-dihydro-1*H*-inden-1-one 3g

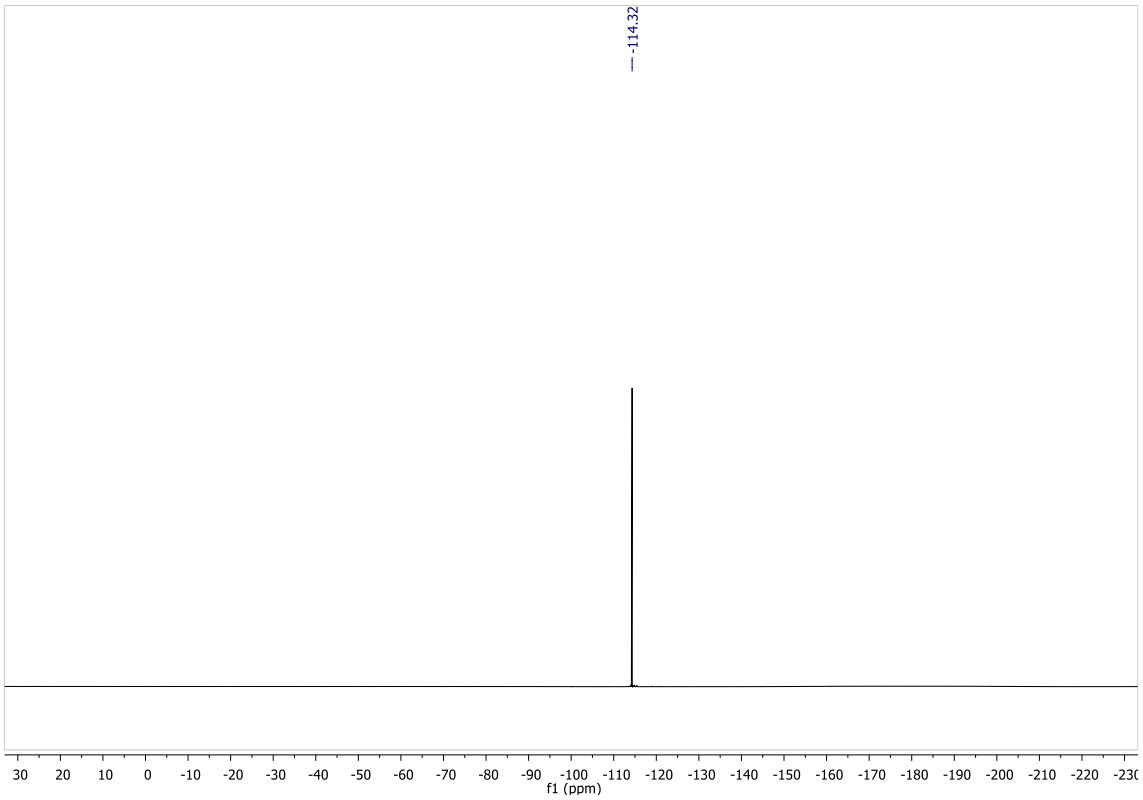




(*E*)-6-Fluoro-2-methyl-2-(3-phenylprop-1-en-1-yl)-2,3-dihydro-1*H*-inden-1-one 3h



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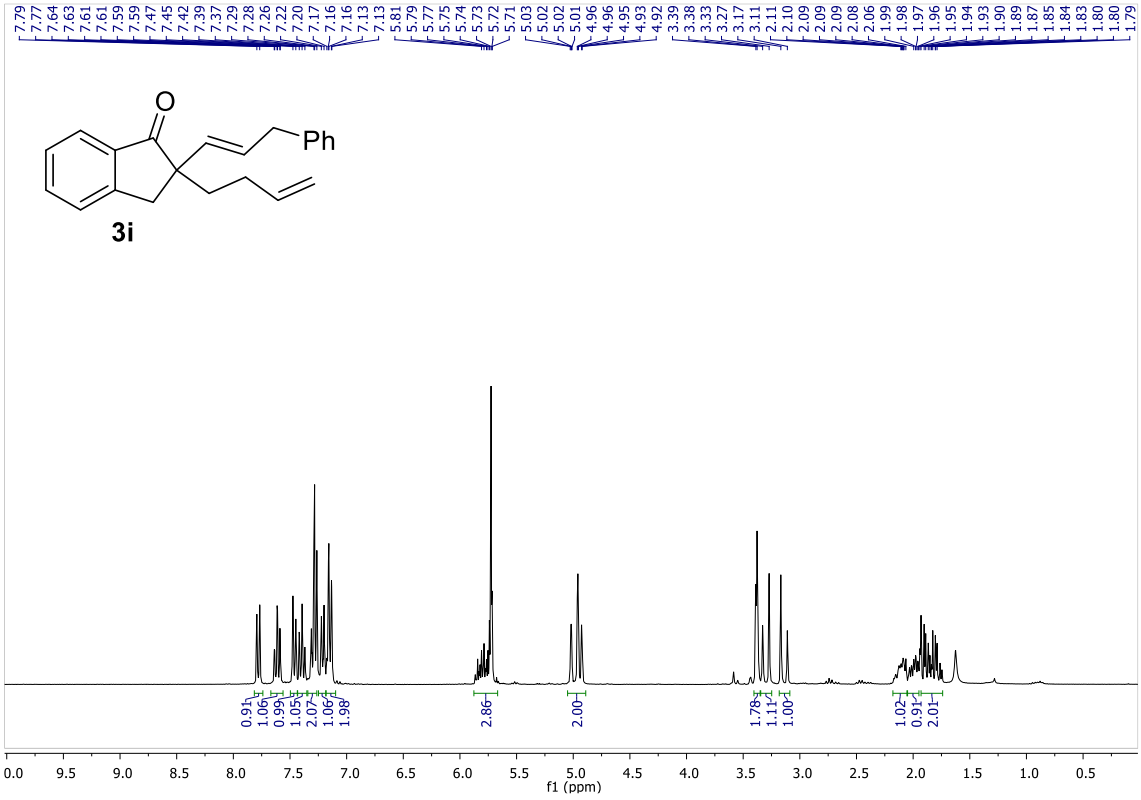
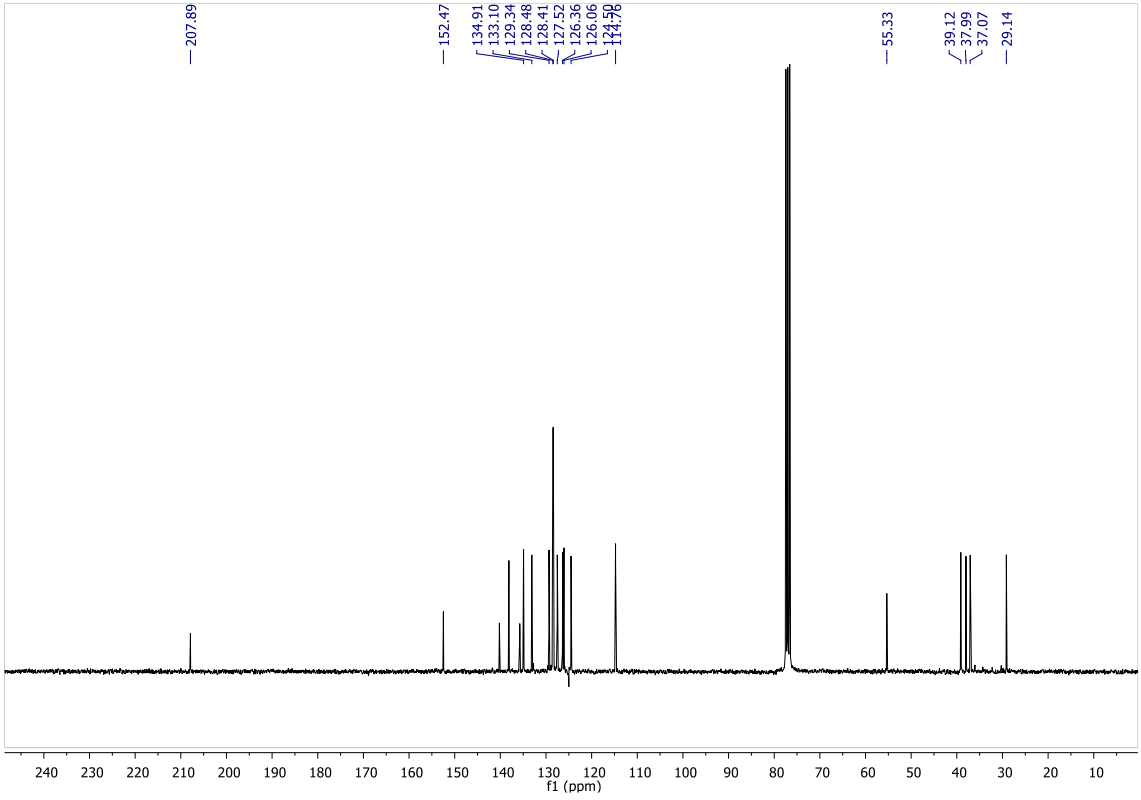
f1 (ppm)

(*E*)-2-(But-3-en-1-yl)-2-(3-phenylprop-1-en-1-yl)-2,3-dihydro-1*H*-inden-1-one

3i





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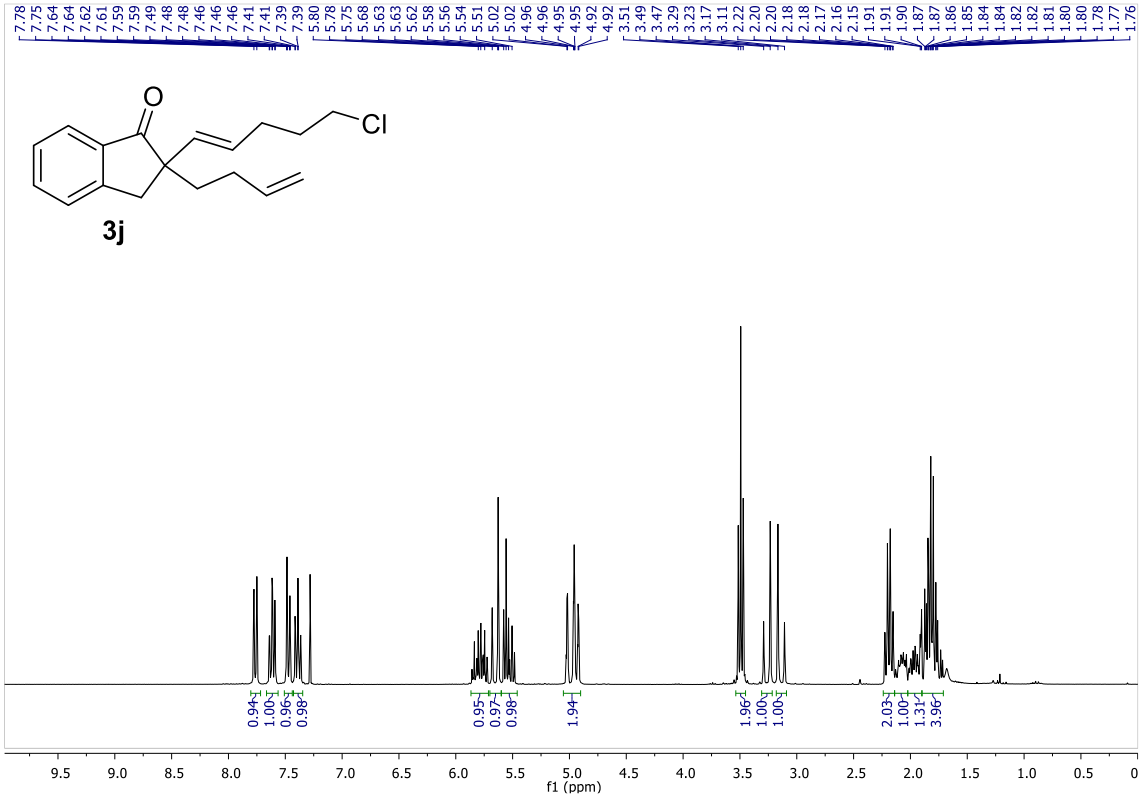
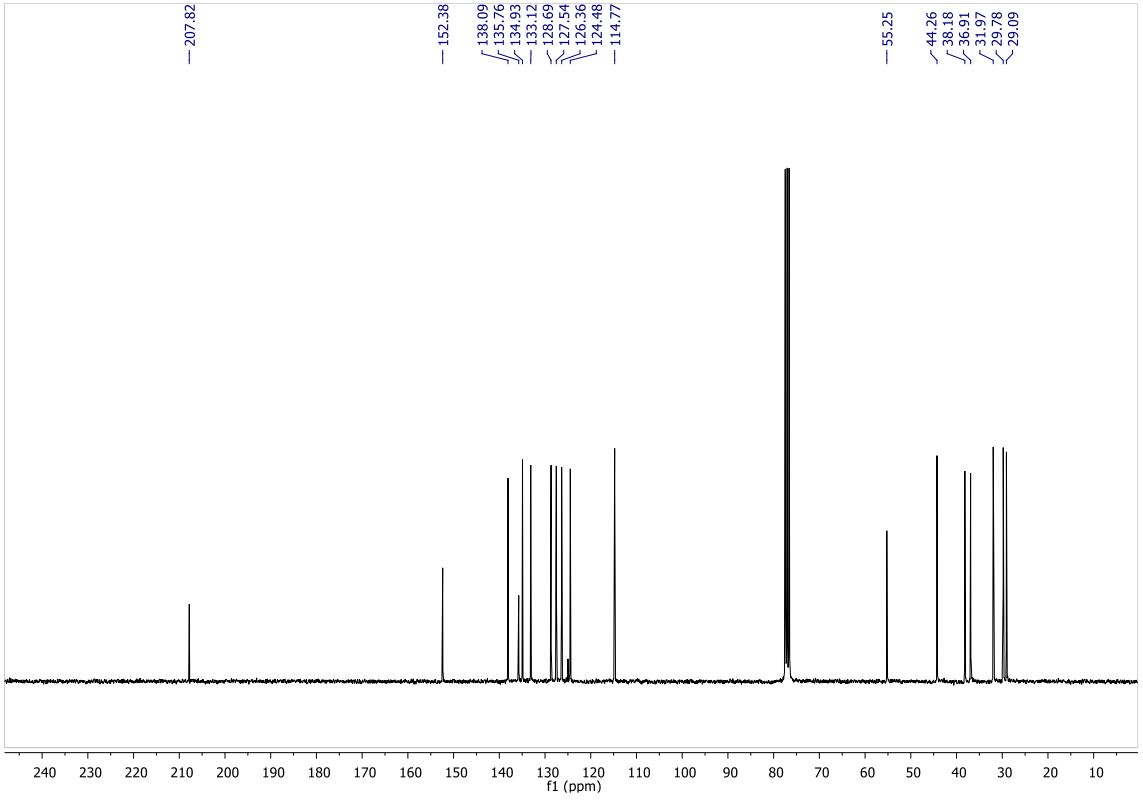
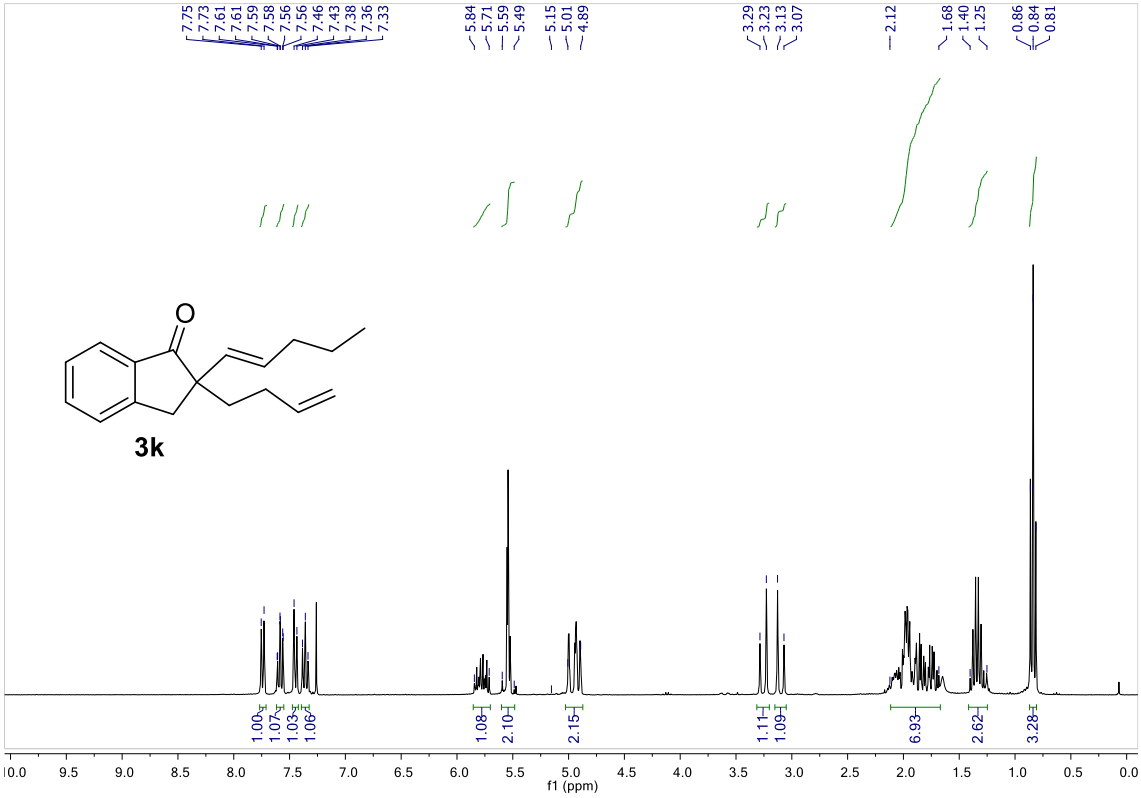
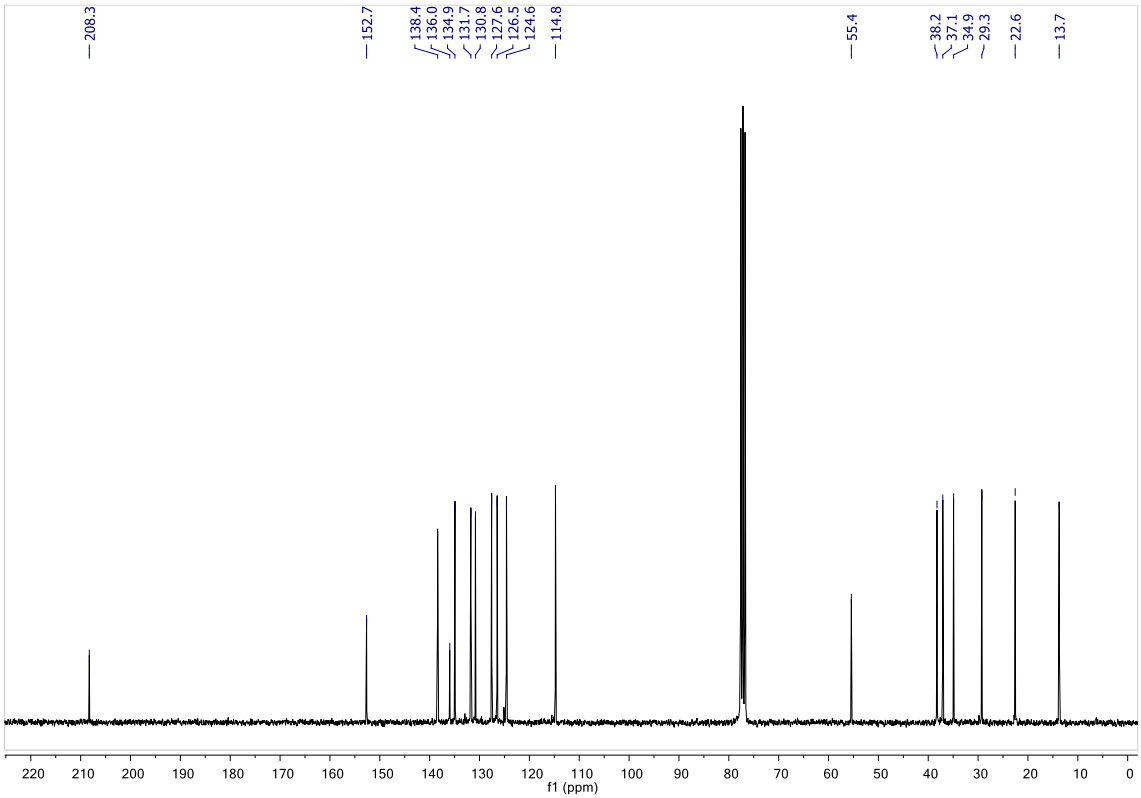
3j





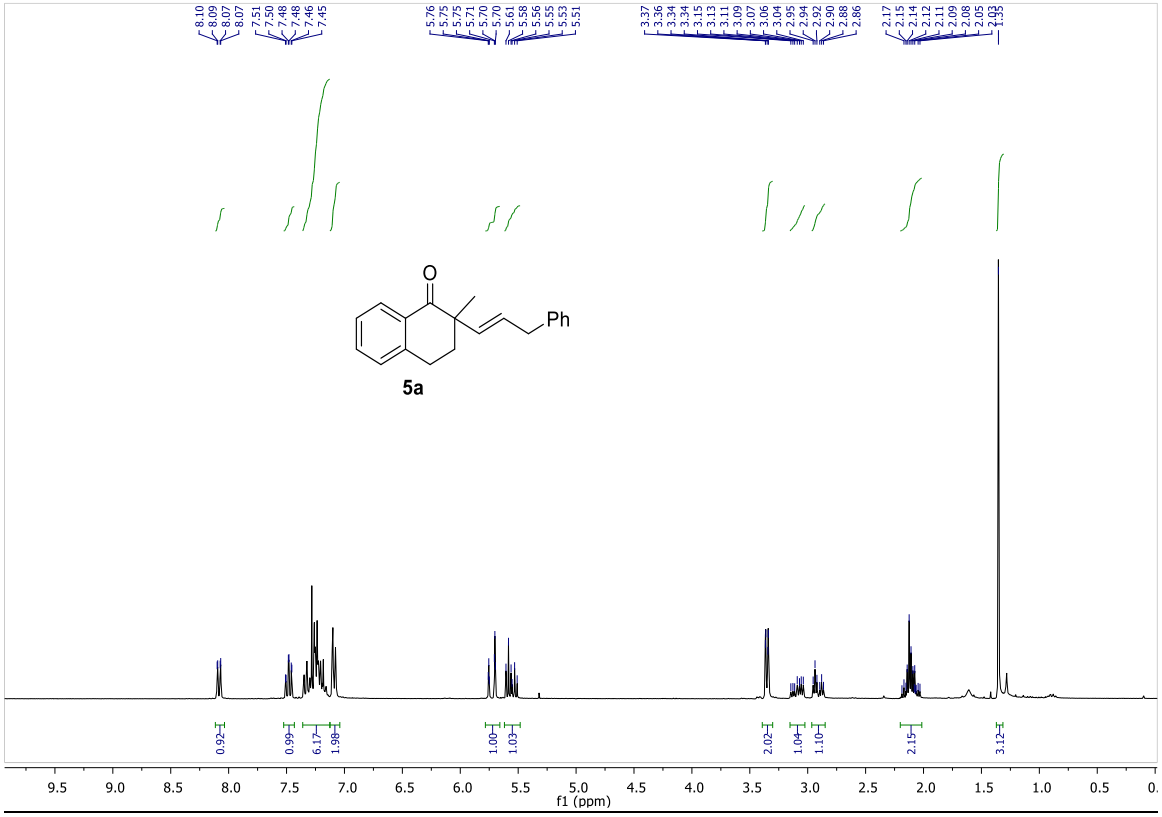
(*R*,*E*)-2-(but-3-en-1-yl)-2-(pent-1-en-1-yl)-2,3-dihydro-1*H*-inden-1-one 3k

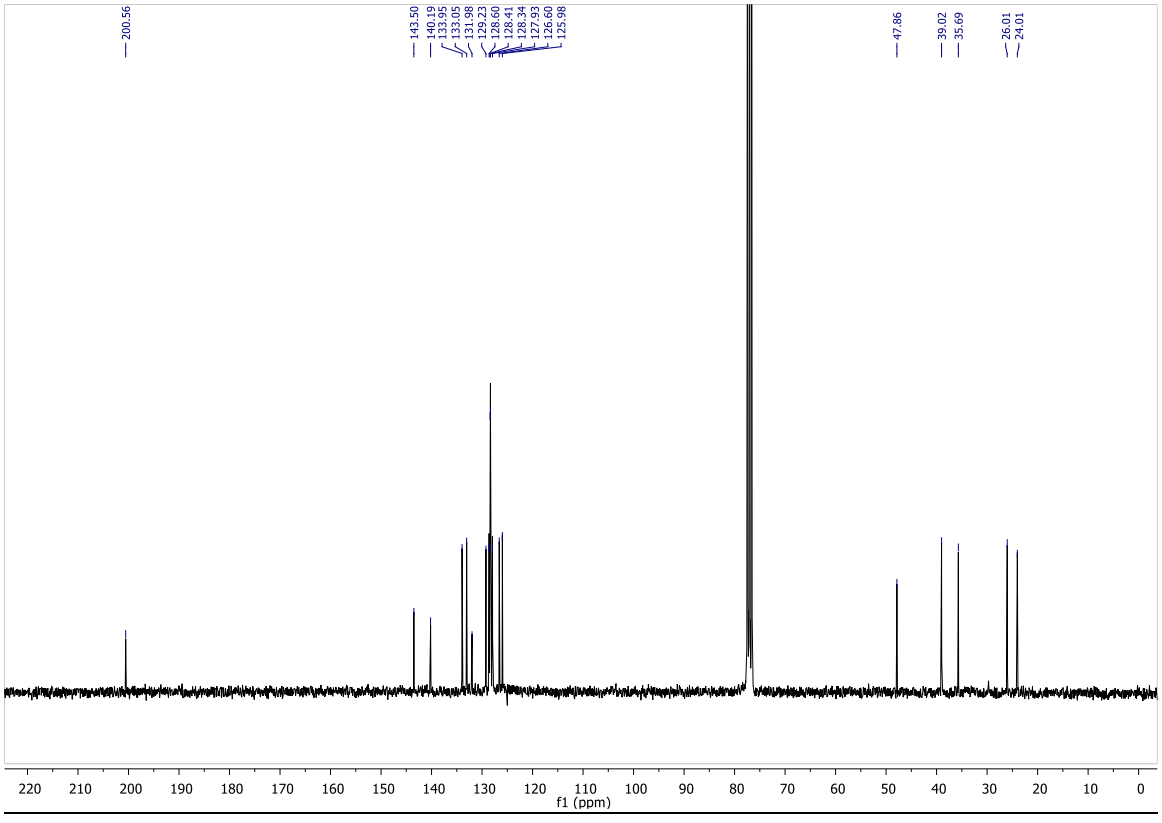




(*E*)-2-methyl-2-(3-phenylprop-1-en-1-yl)-3,4-dihydronaphthalen-1(2*H*)-one

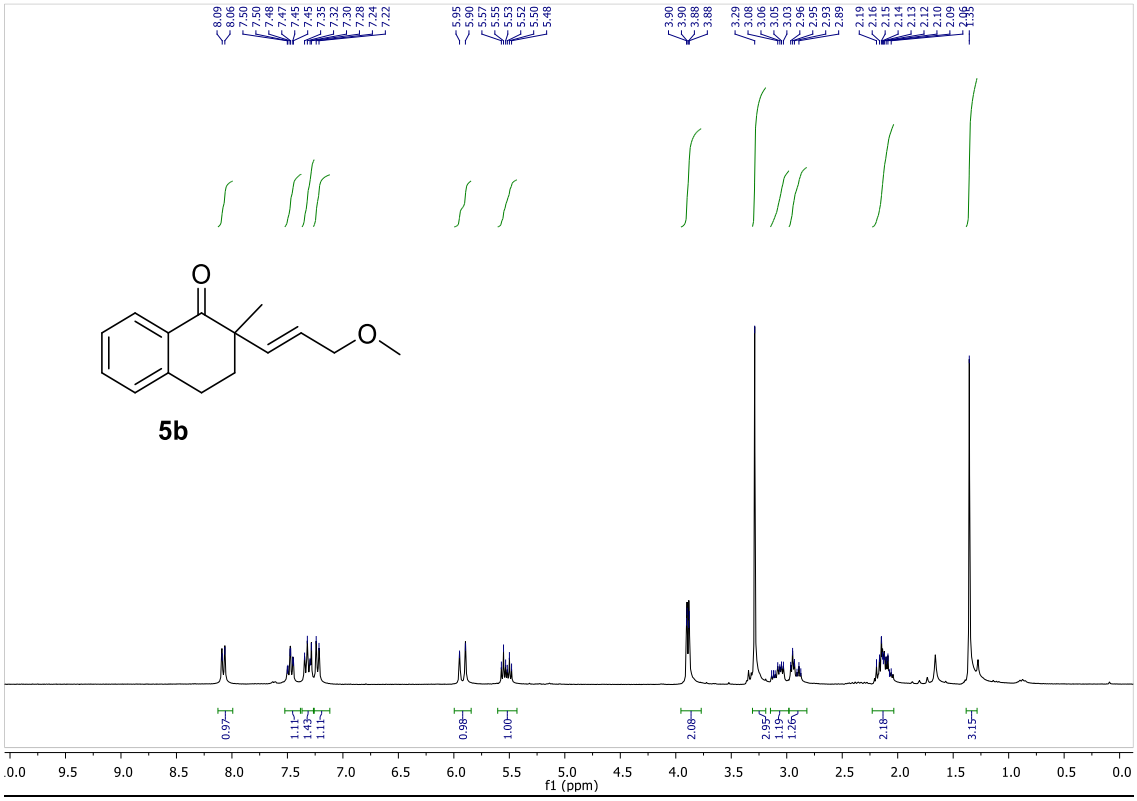
5a

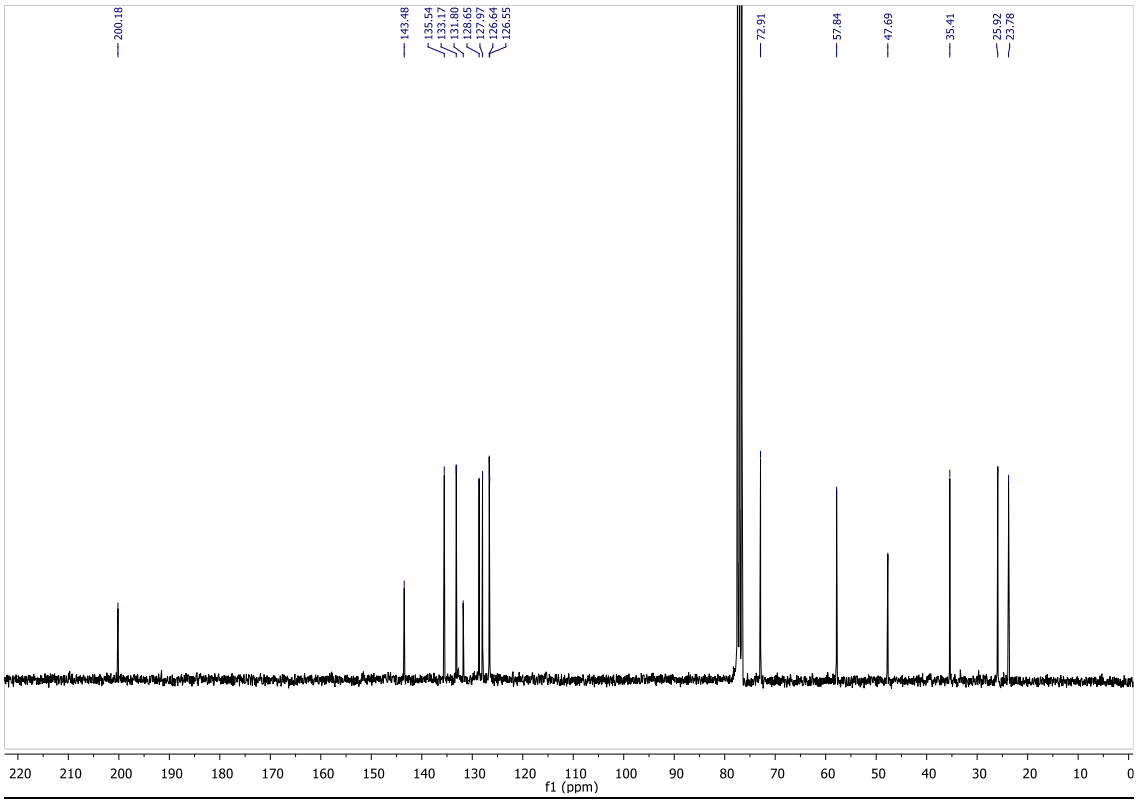




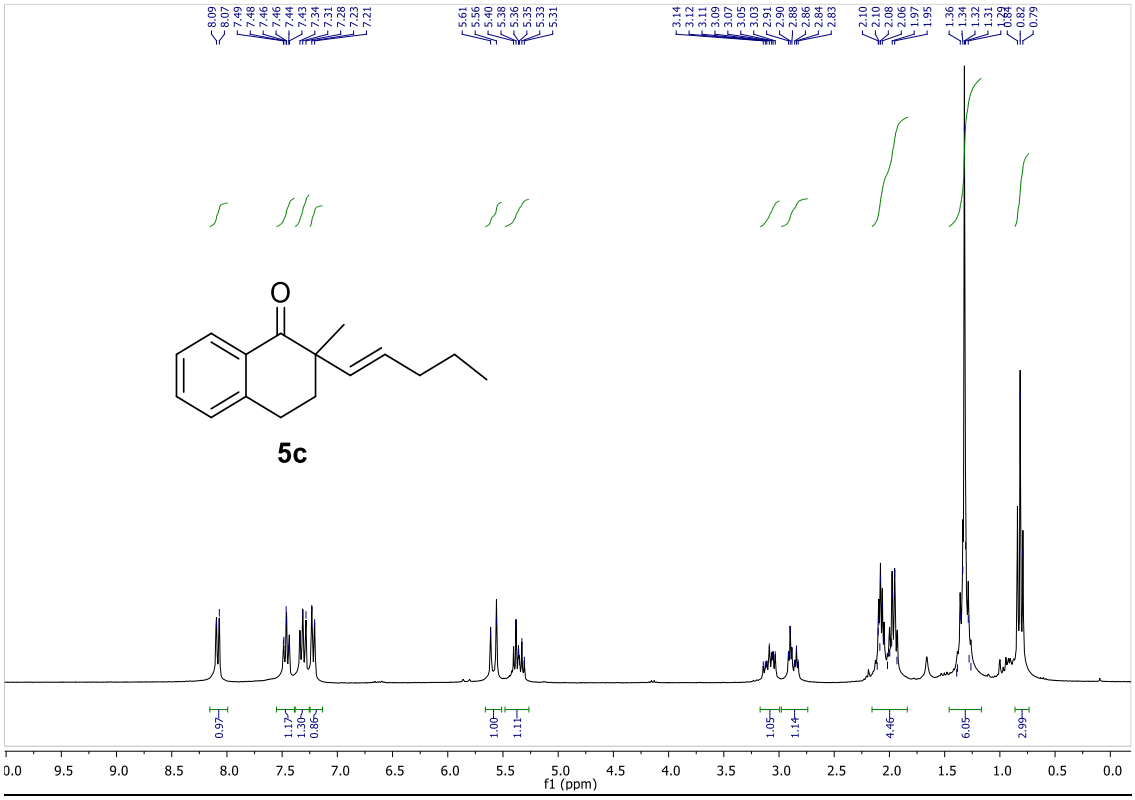
(*E*)-2-(3-Methoxyprop-1-en-1-yl)-2-methyl-3,4-dihydronaphthalen-1(2*H*)-one

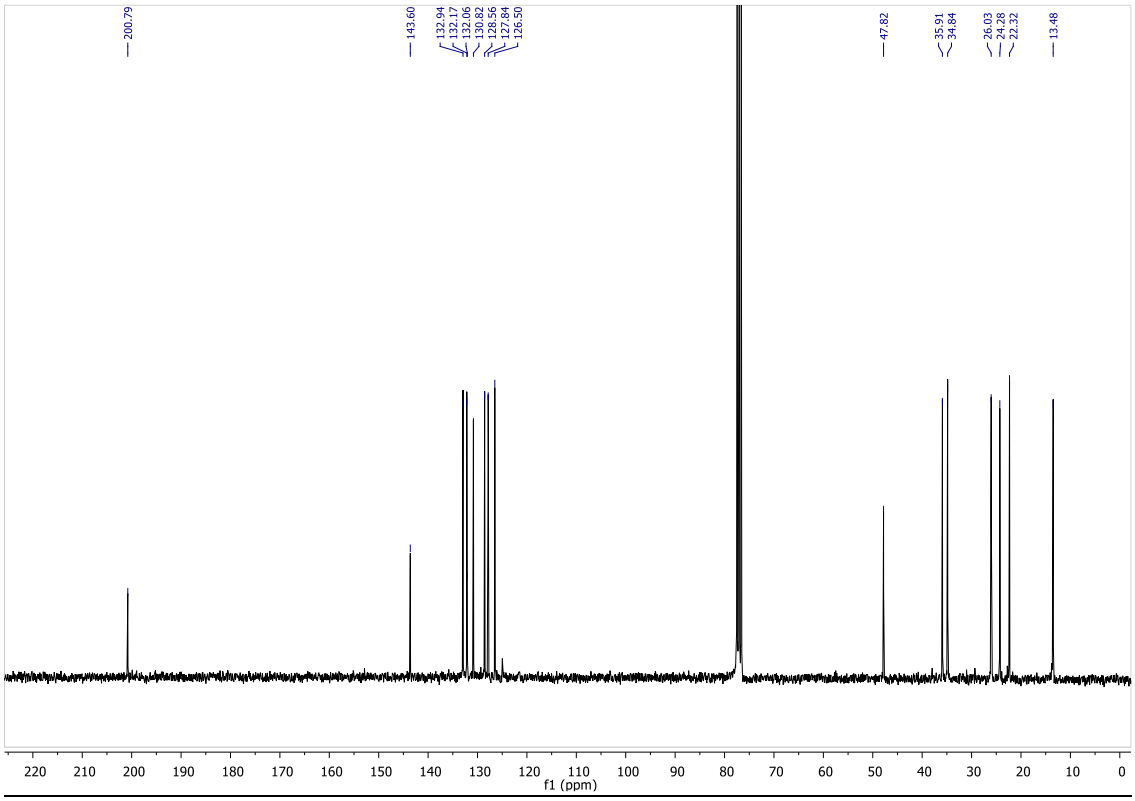
5b



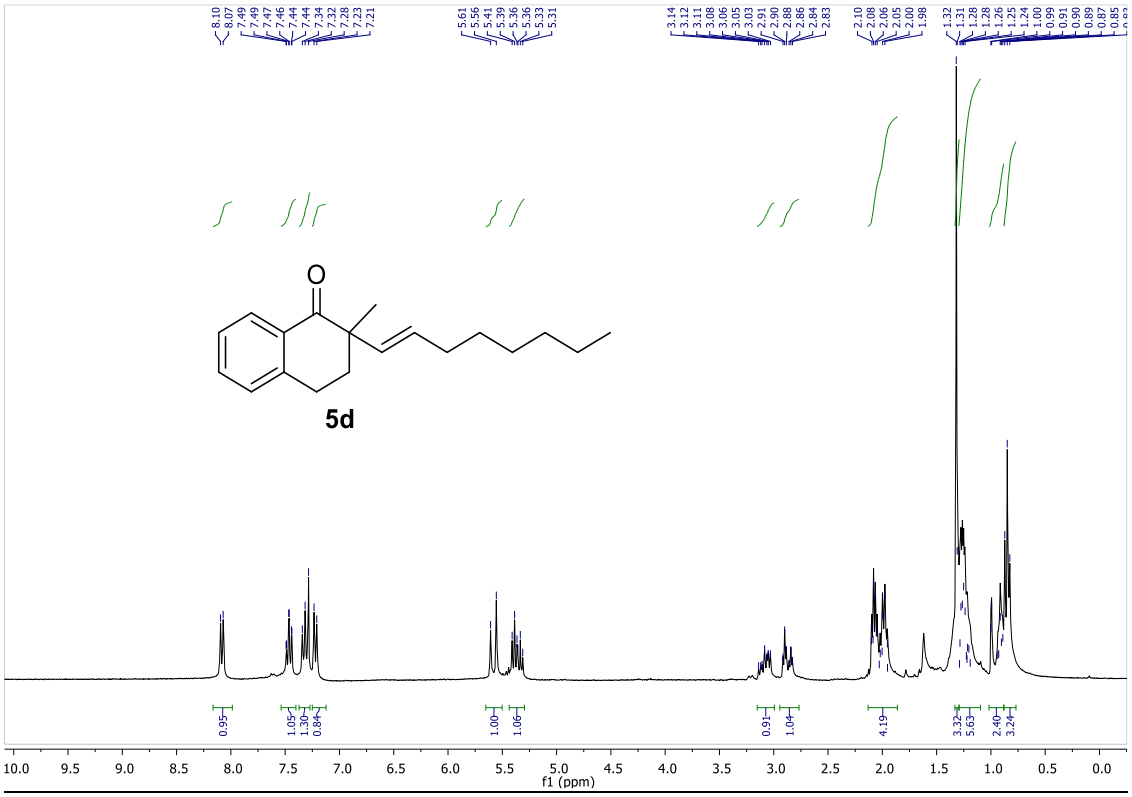


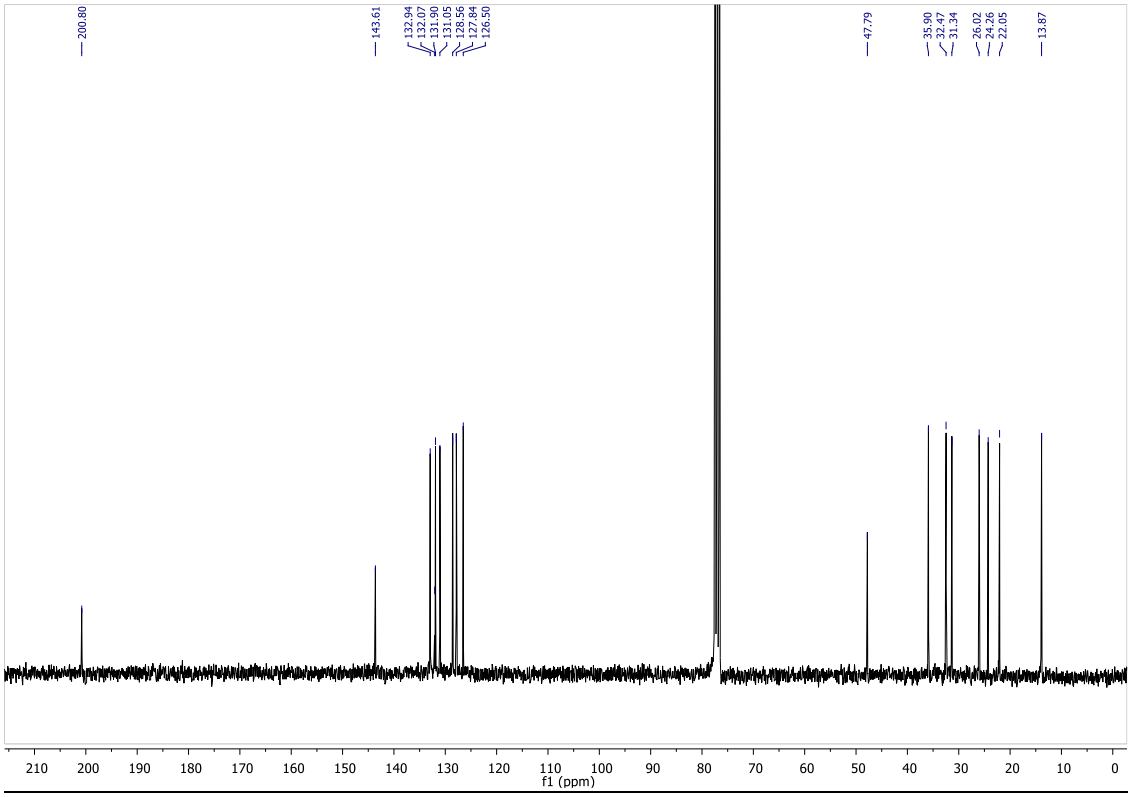
(*E*)-2-Methyl-2-(pent-1-en-1-yl)-3,4-dihydronaphthalen-1(2*H*)-one 5c





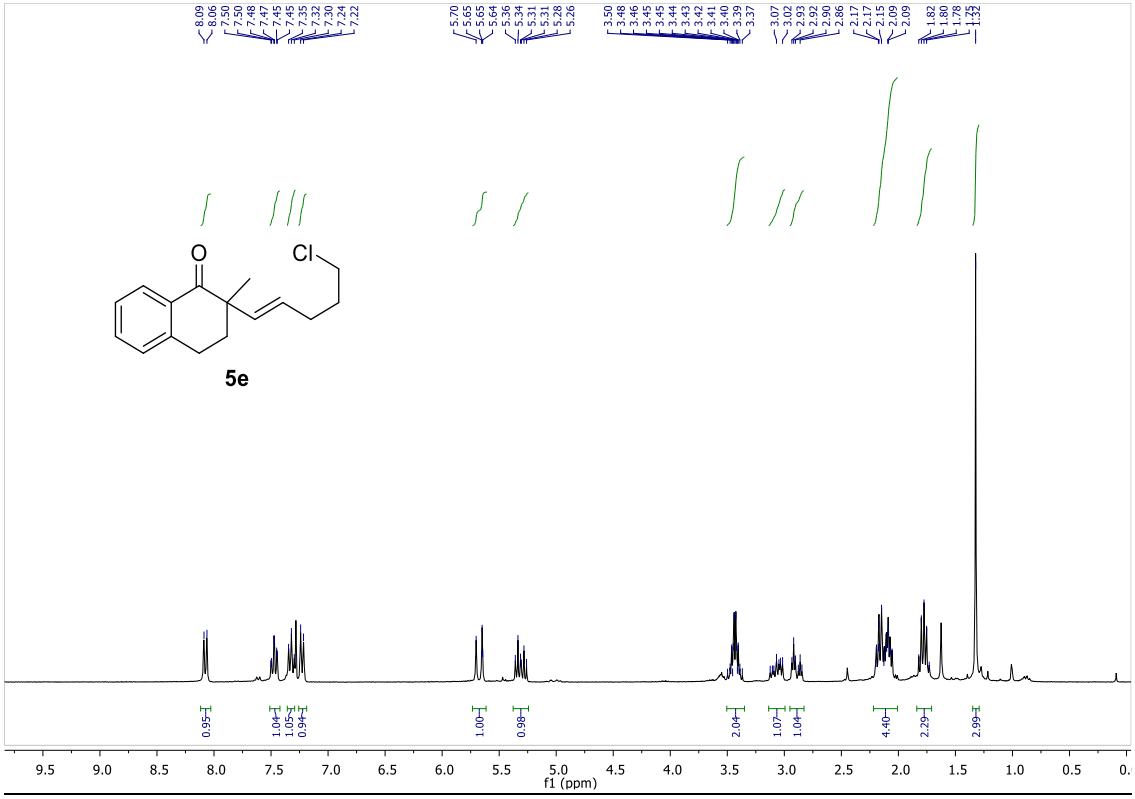
(*E*)-2-(Hex-1-en-1-yl)-2-methyl-3,4-dihydronaphthalen-1(2*H*)-one 5d

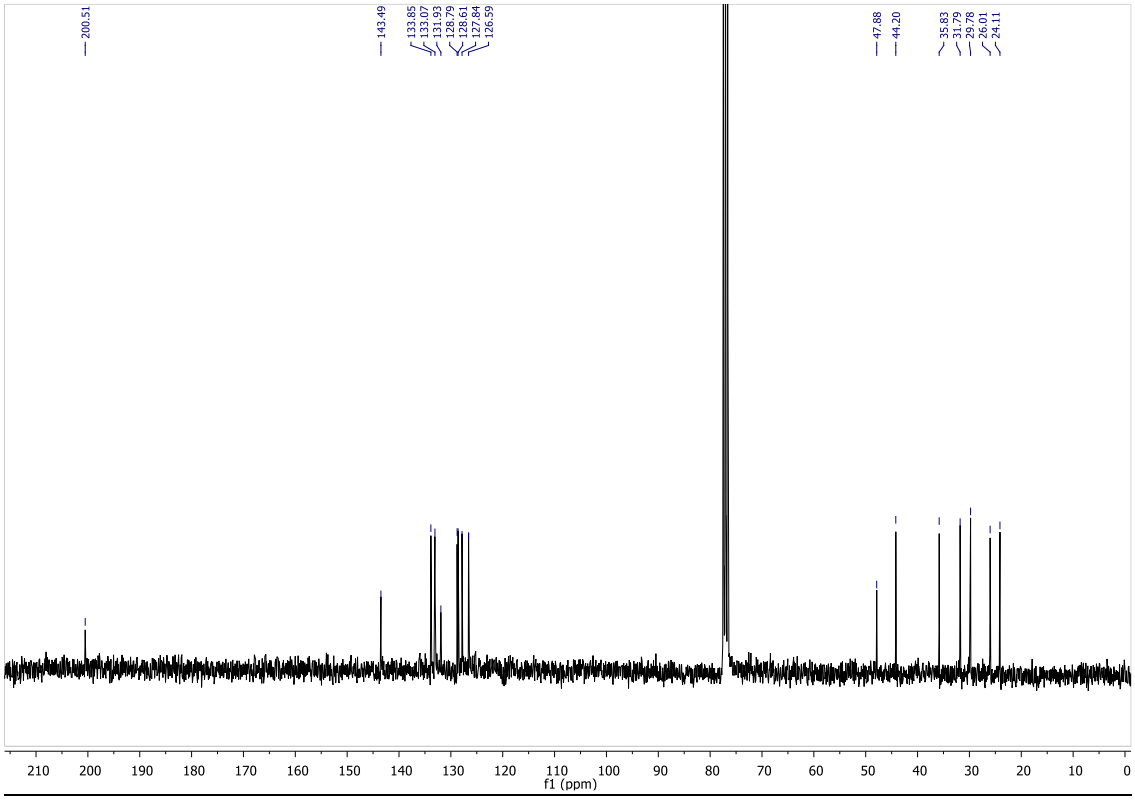




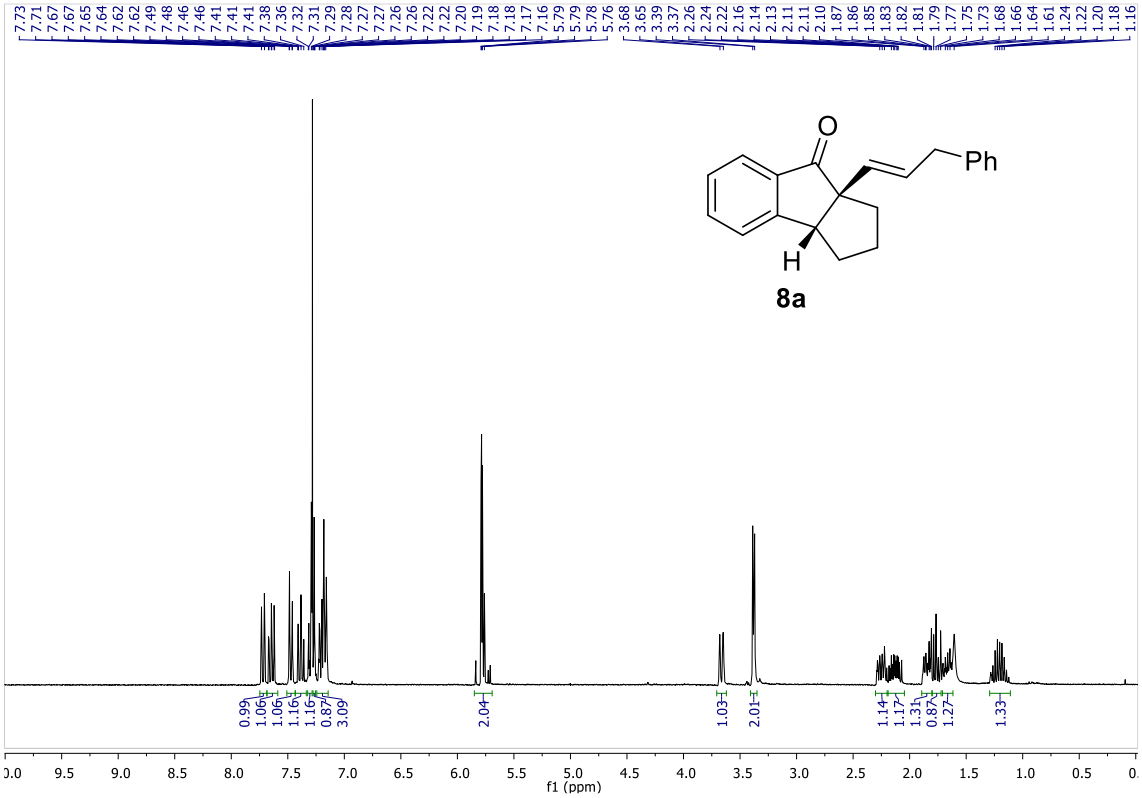
(*E*)-2-(5-chloropent-1-en-1-yl)-2-methyl-3,4-dihydronaphthalen-1(2*H*)-one

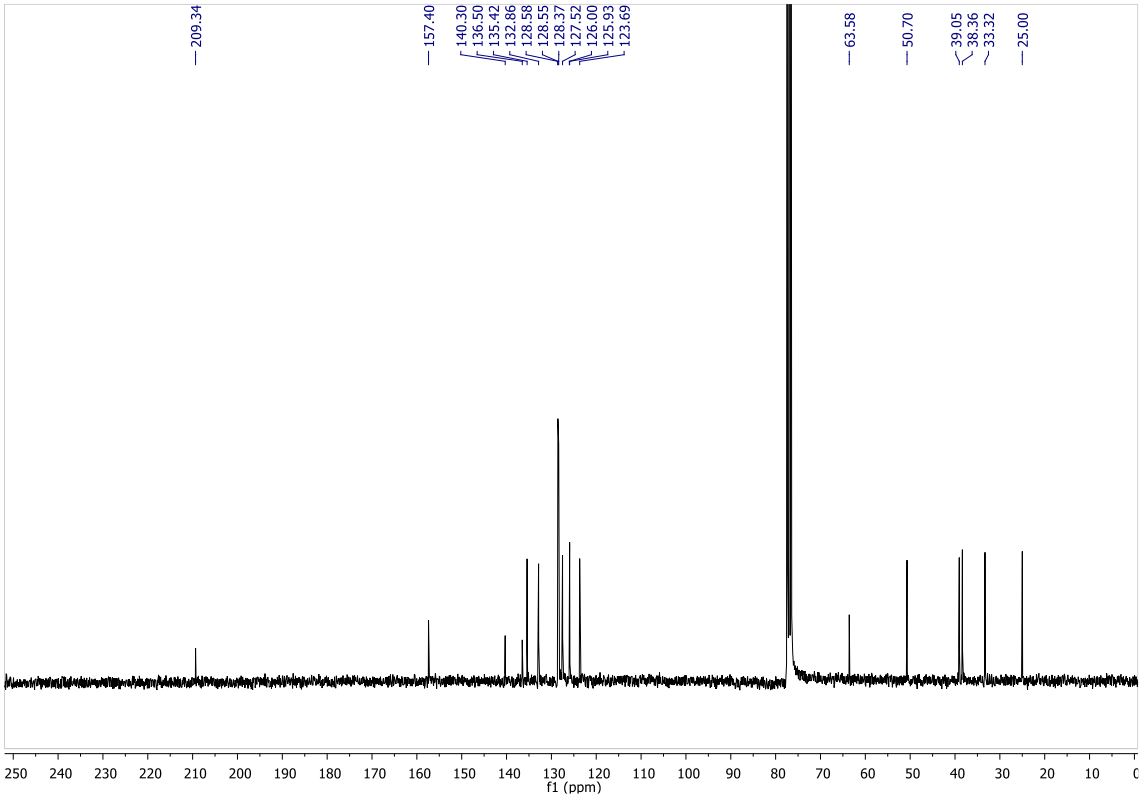
5e



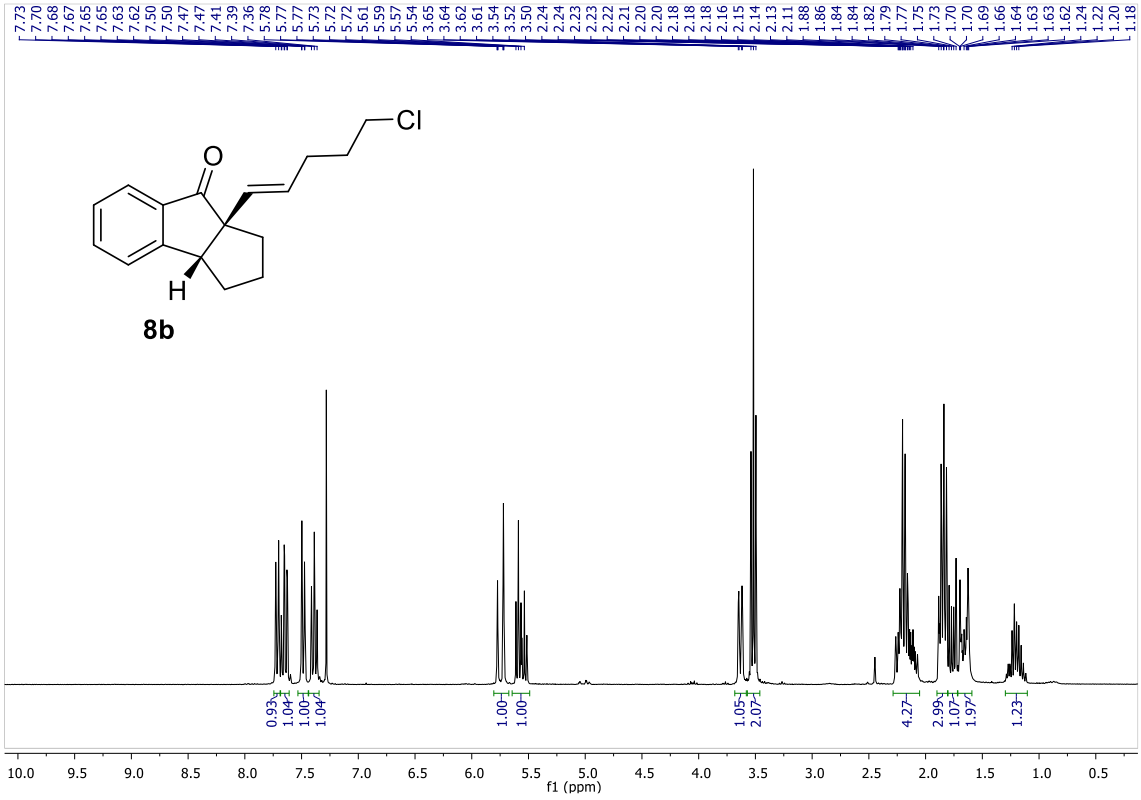


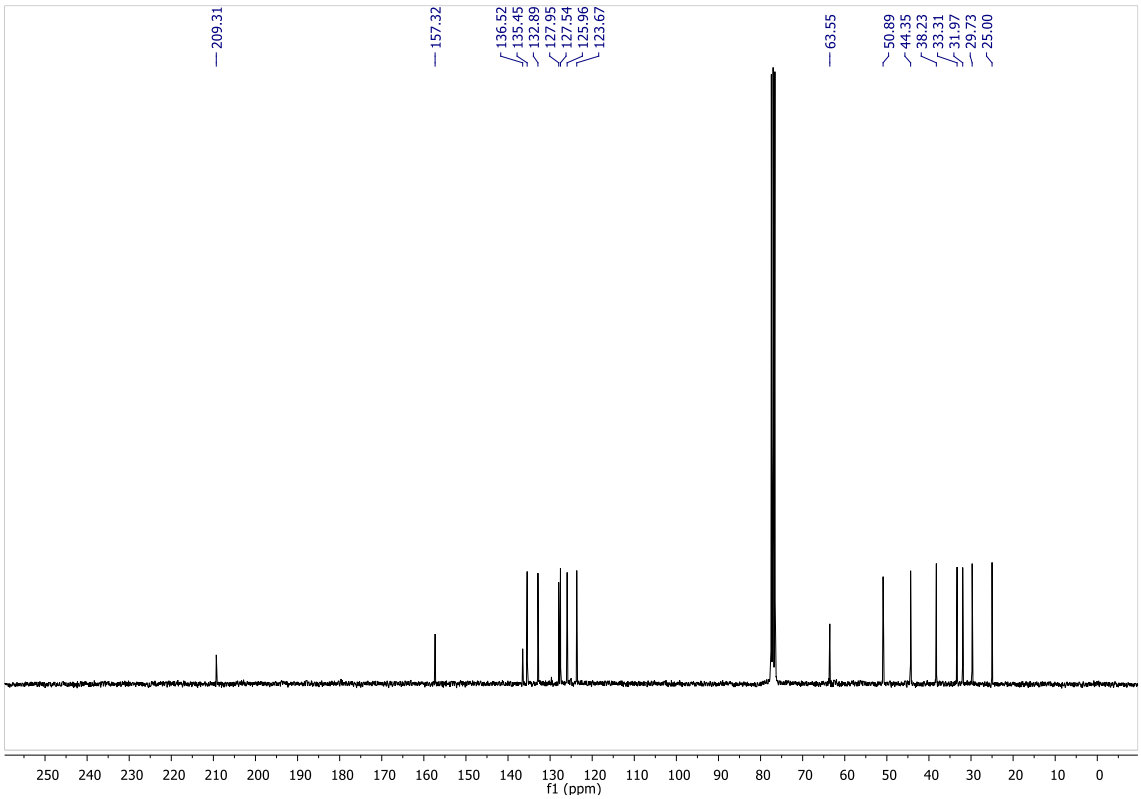
(3a*R,8a*S**)-8a-((*E*)-3-Phenylprop-1-en-1-yl)-2,3,3a,8a-tetrahydro-cyclopenta[a]inden-8(1*H*)-one 8a**



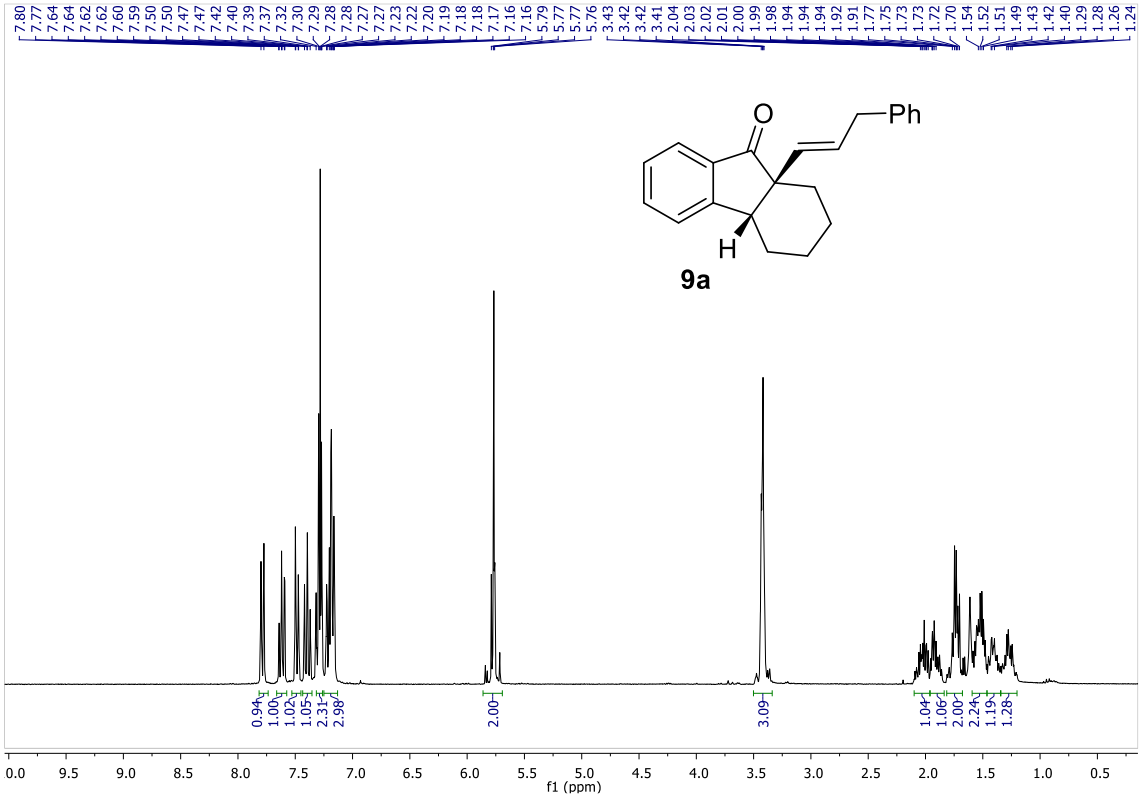


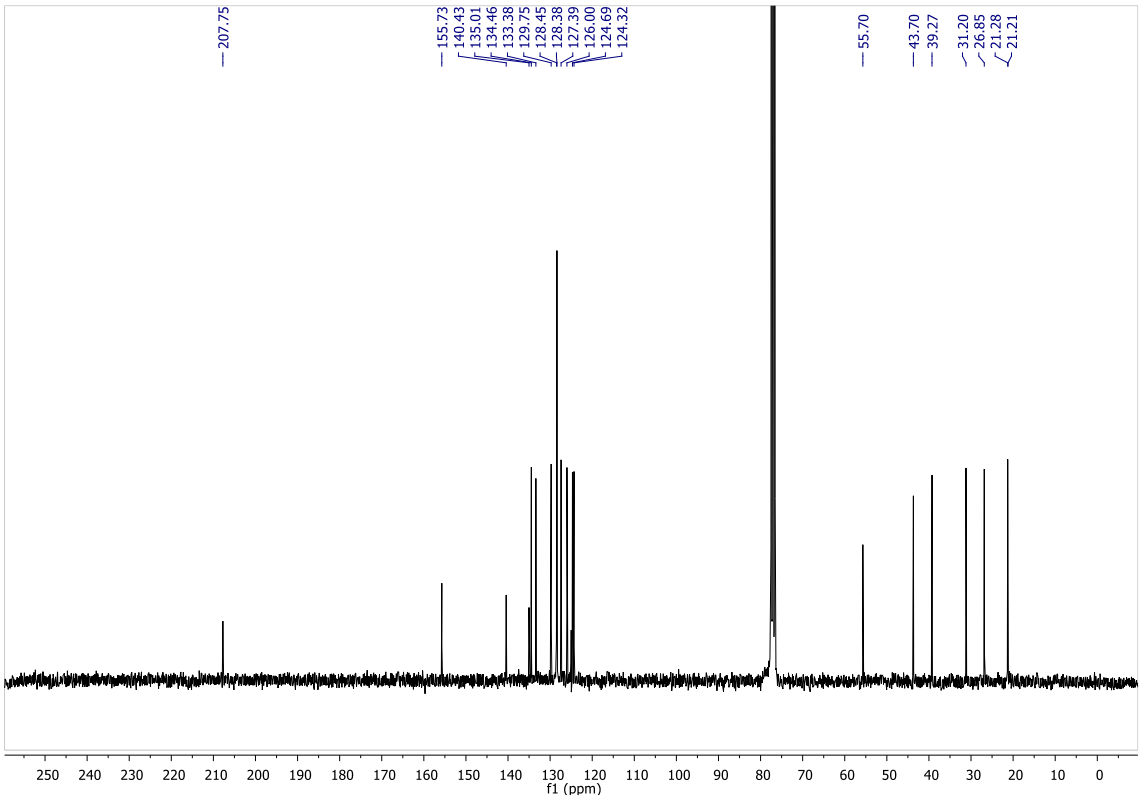
(3a*R,8a*S**)-8a-((*E*)-5-Chloropent-1-en-1-yl)-2,3,3a,8a-tetrahydrocyclopenta[a]inden-8(1*H*)-one 8b**



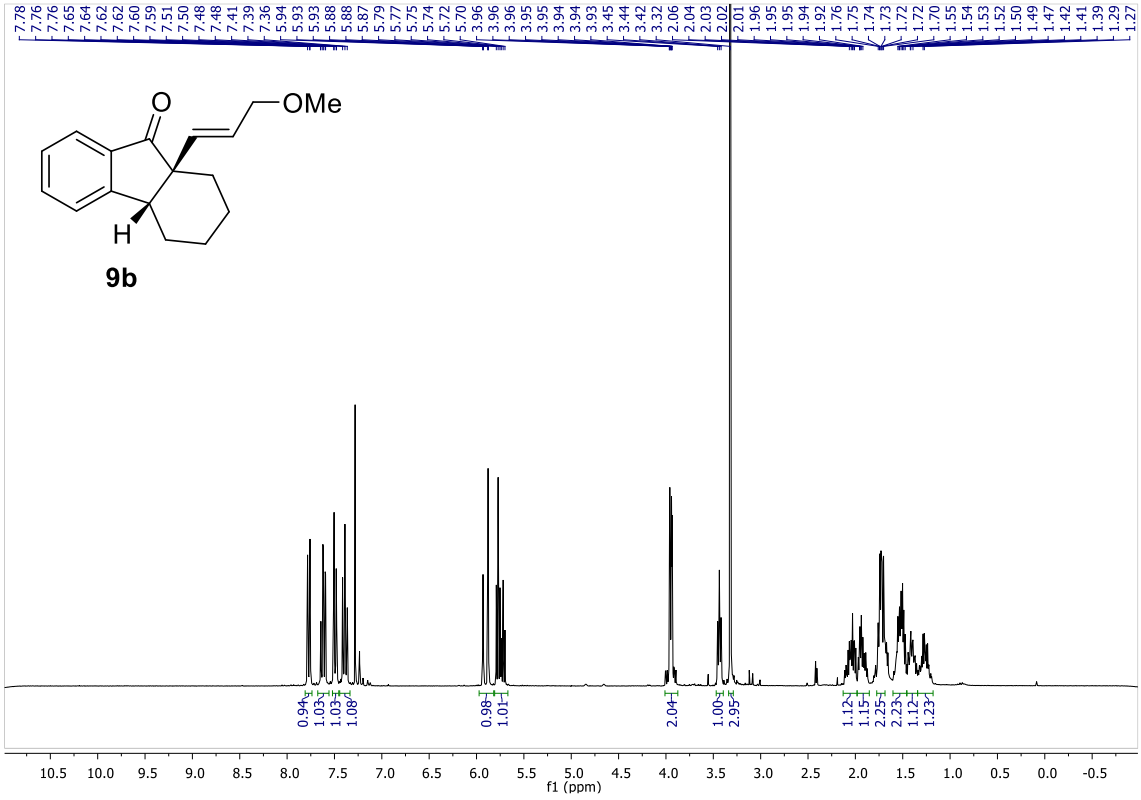


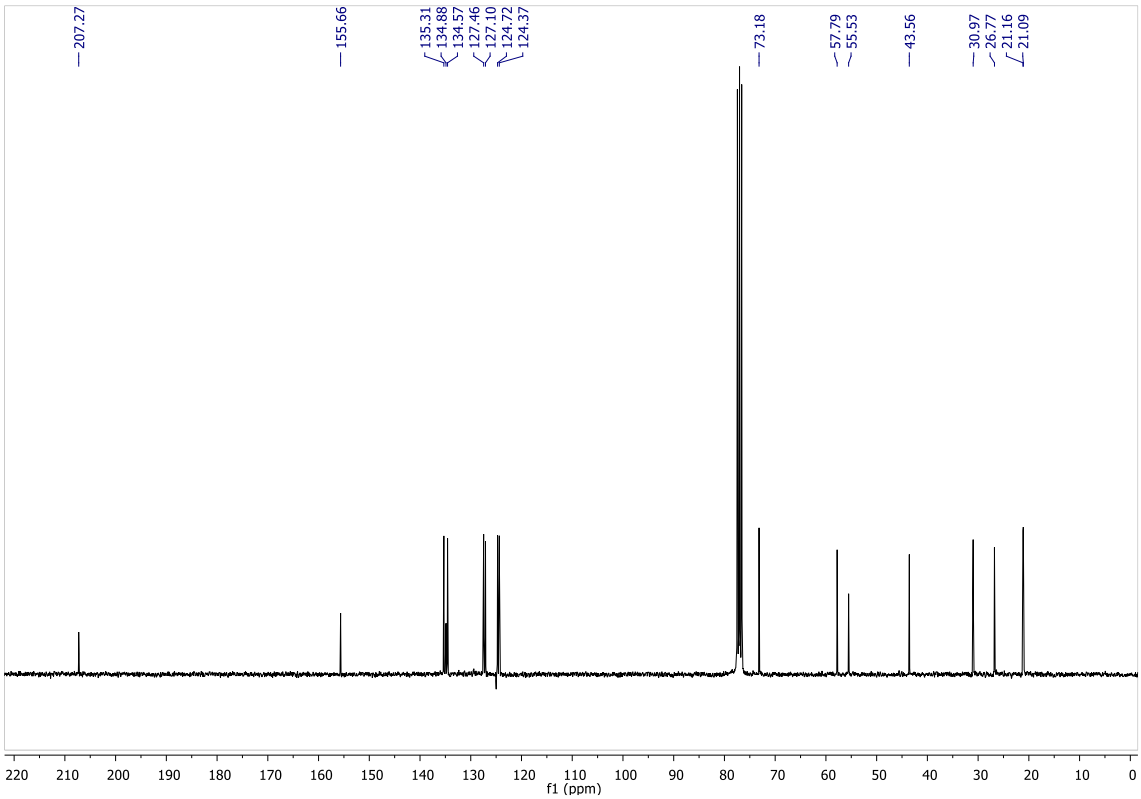
(4a*R,9a*S**)-9a-((*E*)-3-Phenylprop-1-en-1-yl)-1,2,3,4,4a,9a-hexahydro-9*H*-fluoren-9-one 9a**



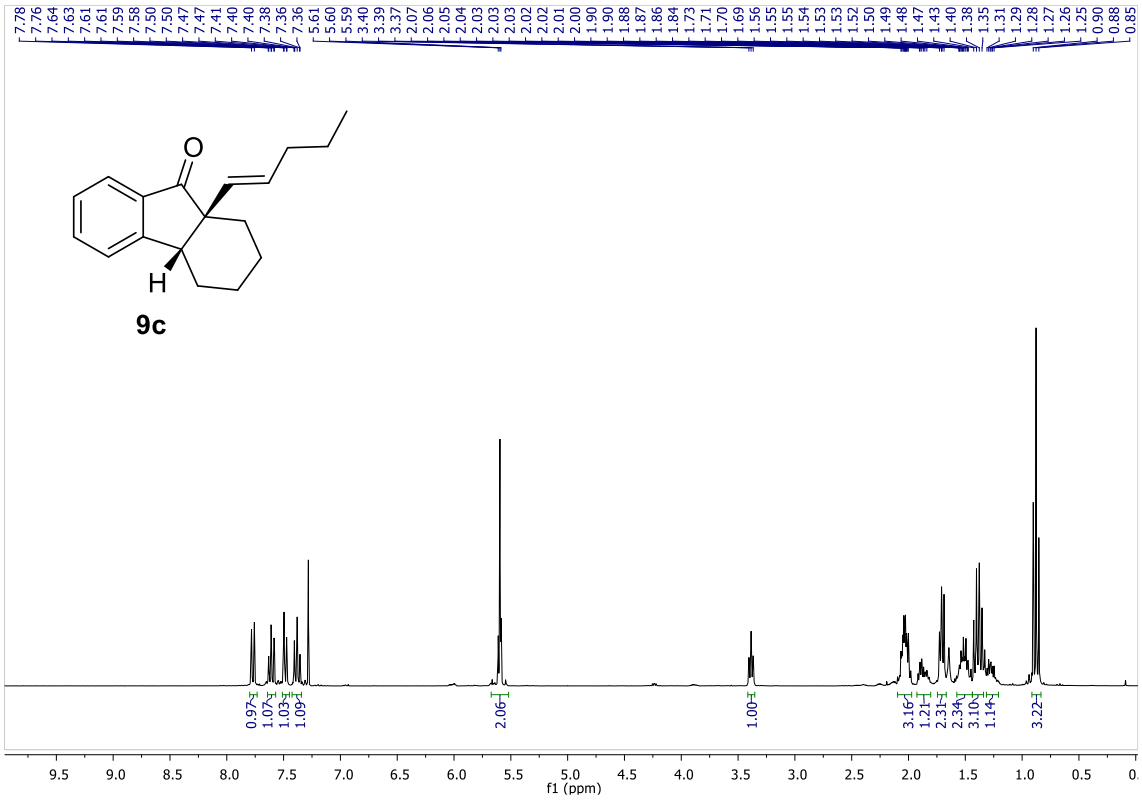


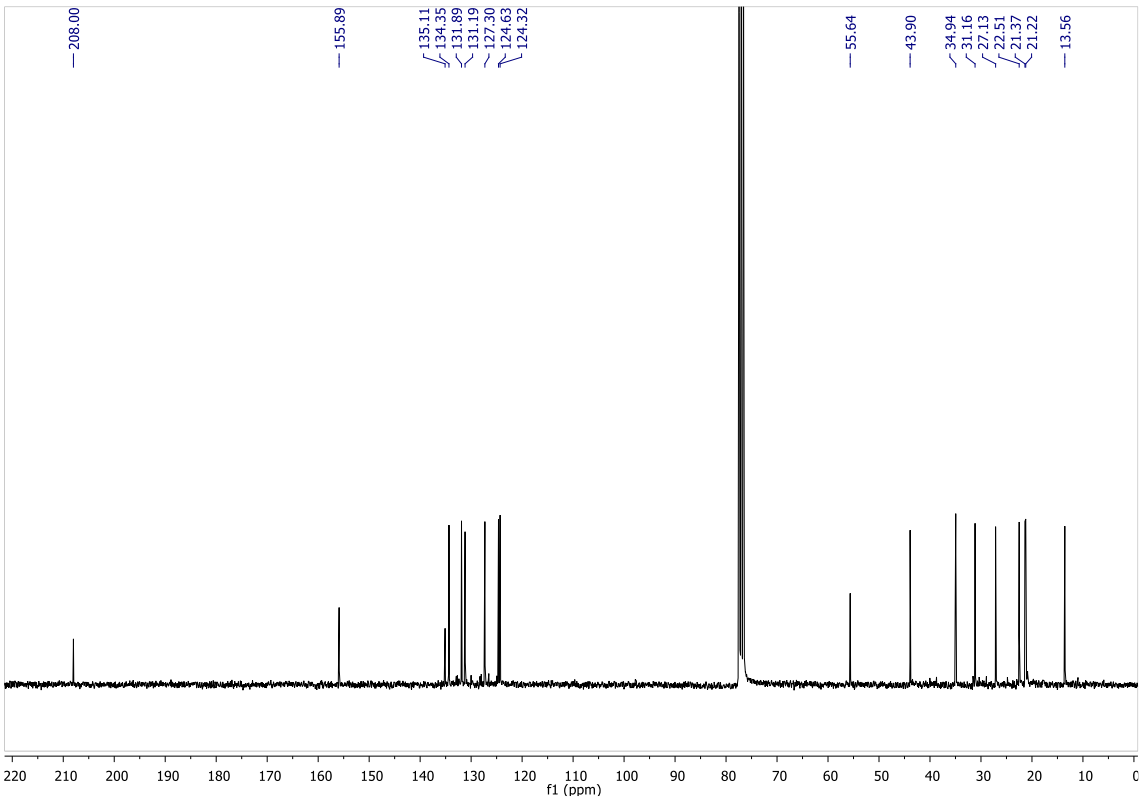
(4a*R,9a*S**)-9a-((*E*)-3-Methoxyprop-1-en-1-yl)-1,2,3,4,4a,9a-hexahydro-9*H*-fluoren-9-one 9b**



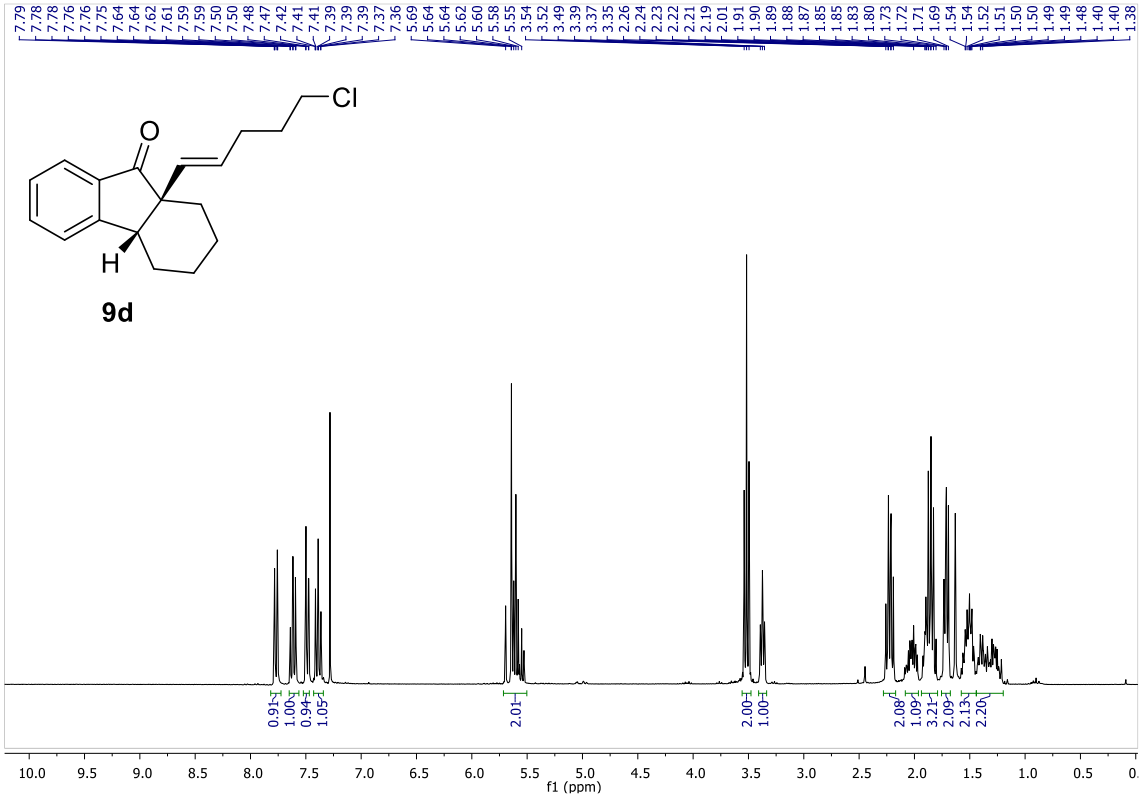


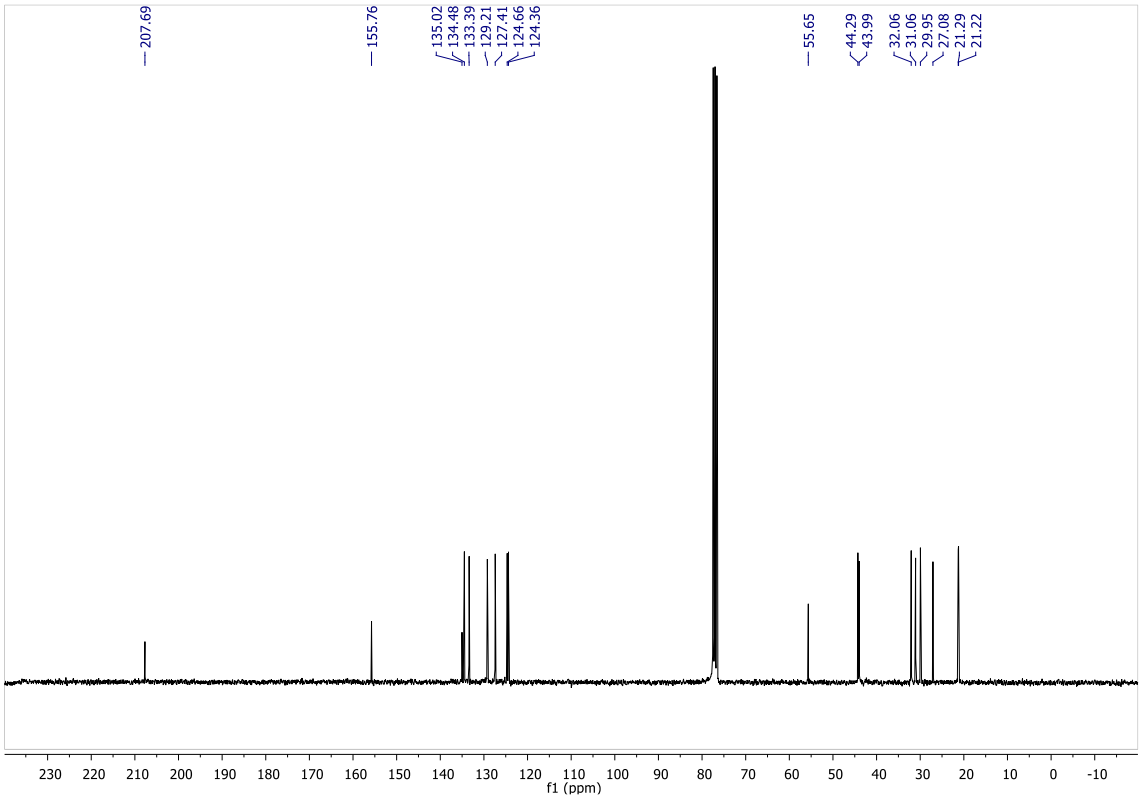
(4a*R,9a*S**)-9a-((*E*)-Pent-1-en-1-yl)-1,2,3,4,4a,9a-hexahydro-9*H*-fluoren-9-one 9c**



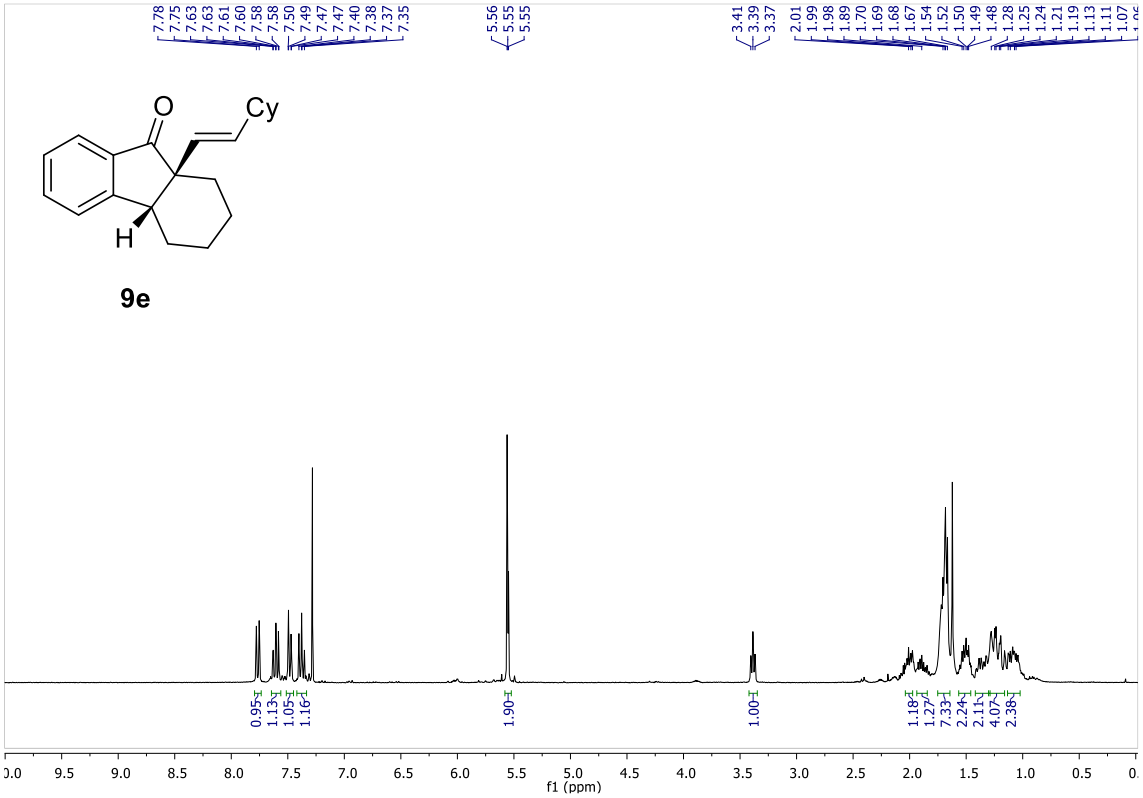


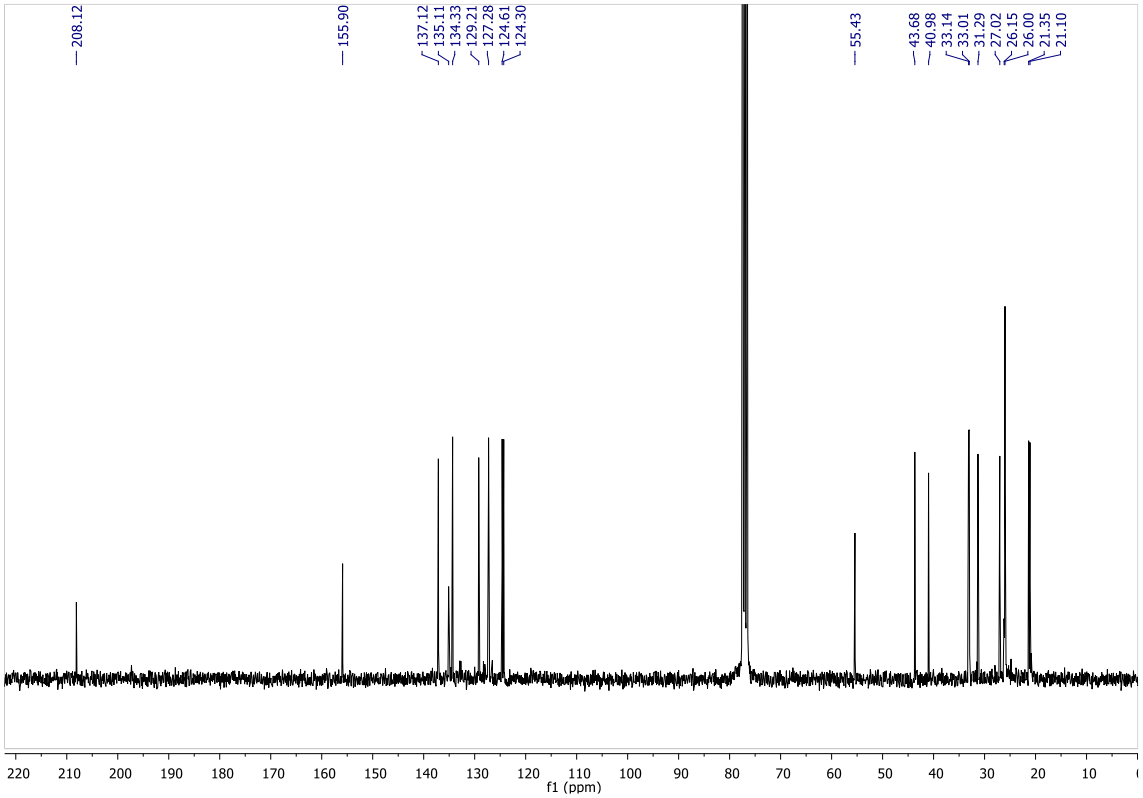
(4a*R,9a*S**)-9a-((*E*)-5-Chloropent-1-en-1-yl)-1,2,3,4,4a,9a-hexahydro-9*H*-fluoren-9-one 9d**



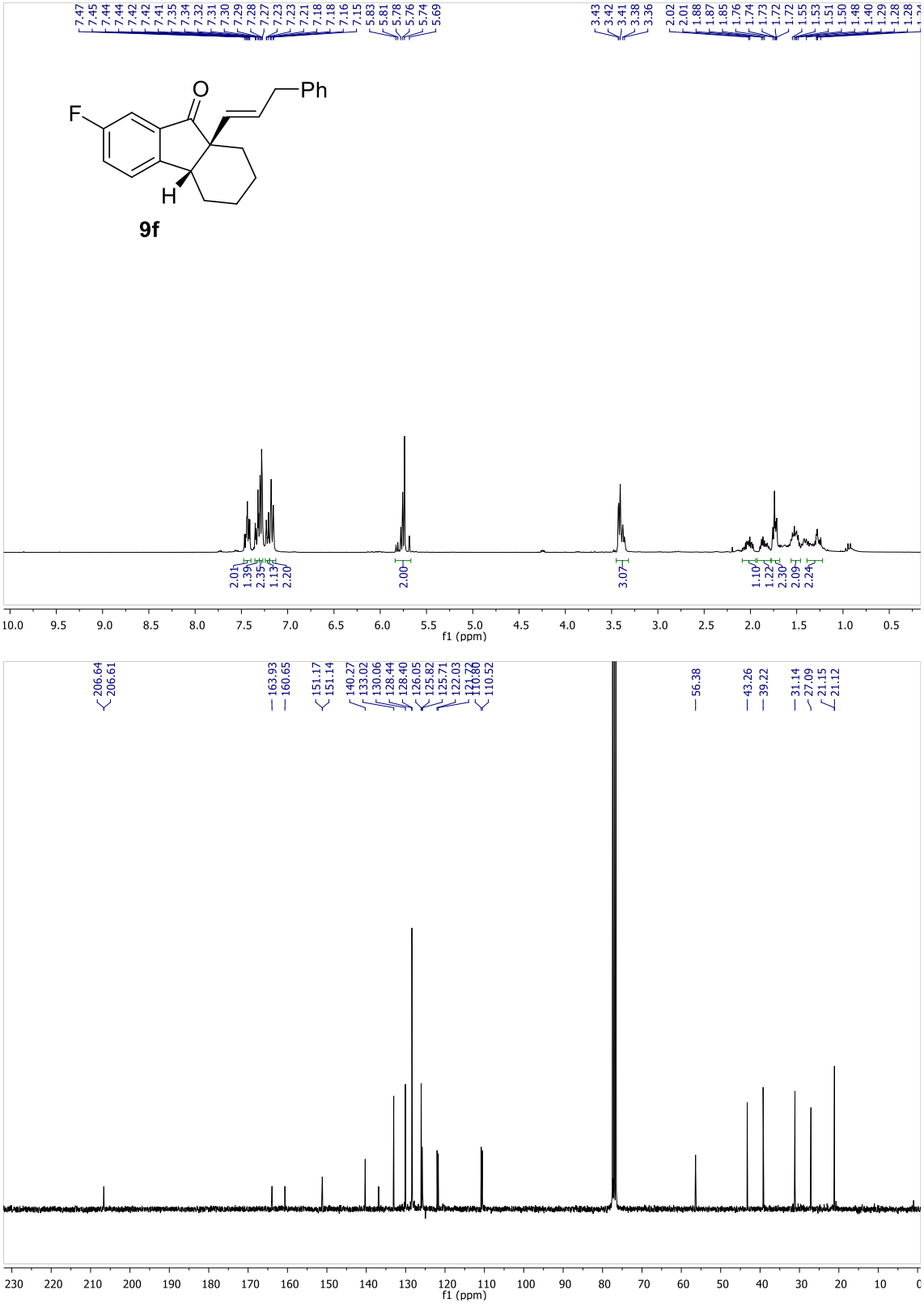


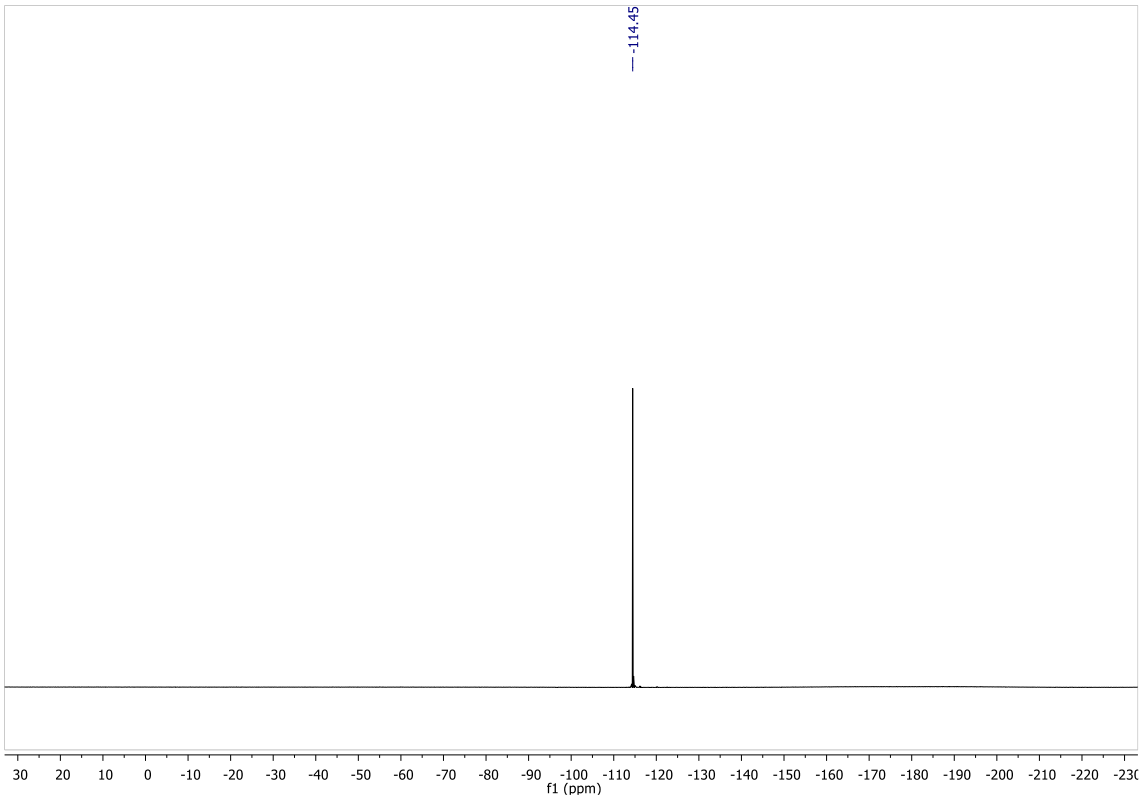
(4a*R,9a*S**)-9a-((*E*)-2-Cyclohexylvinyl)-1,2,3,4,4a,9a-hexahydro-9*H*-fluoren-9-one 9e**



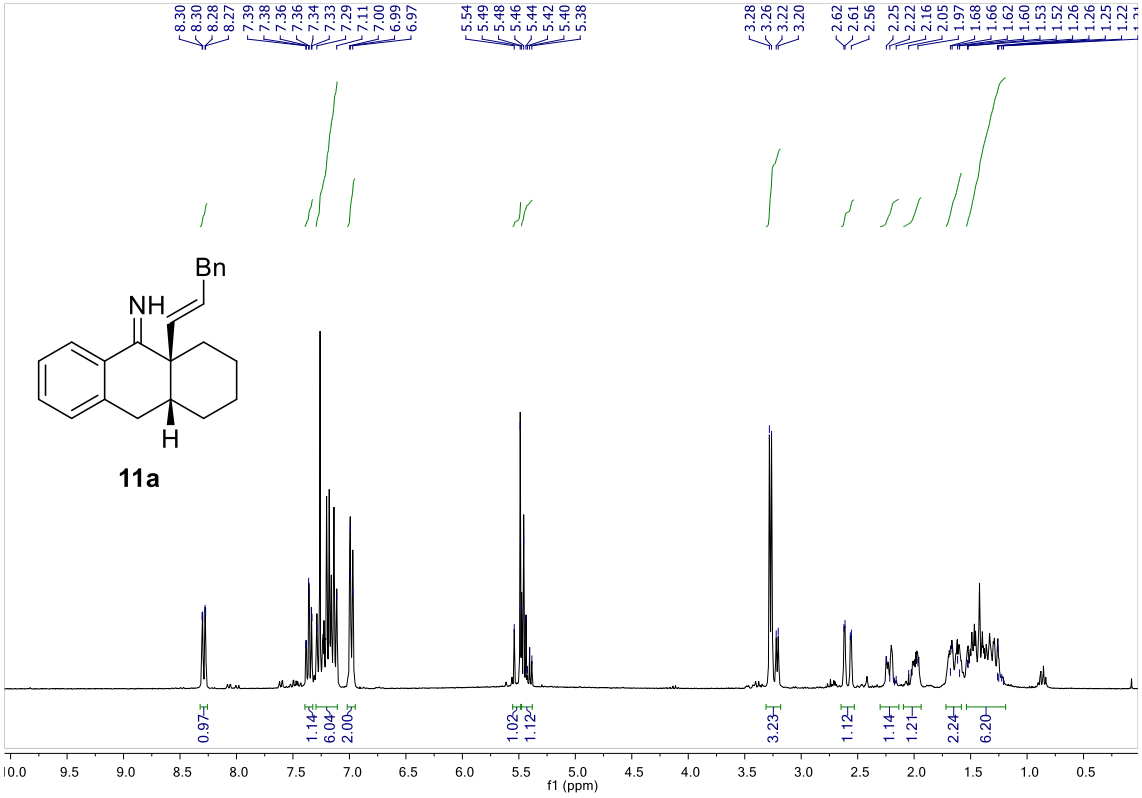


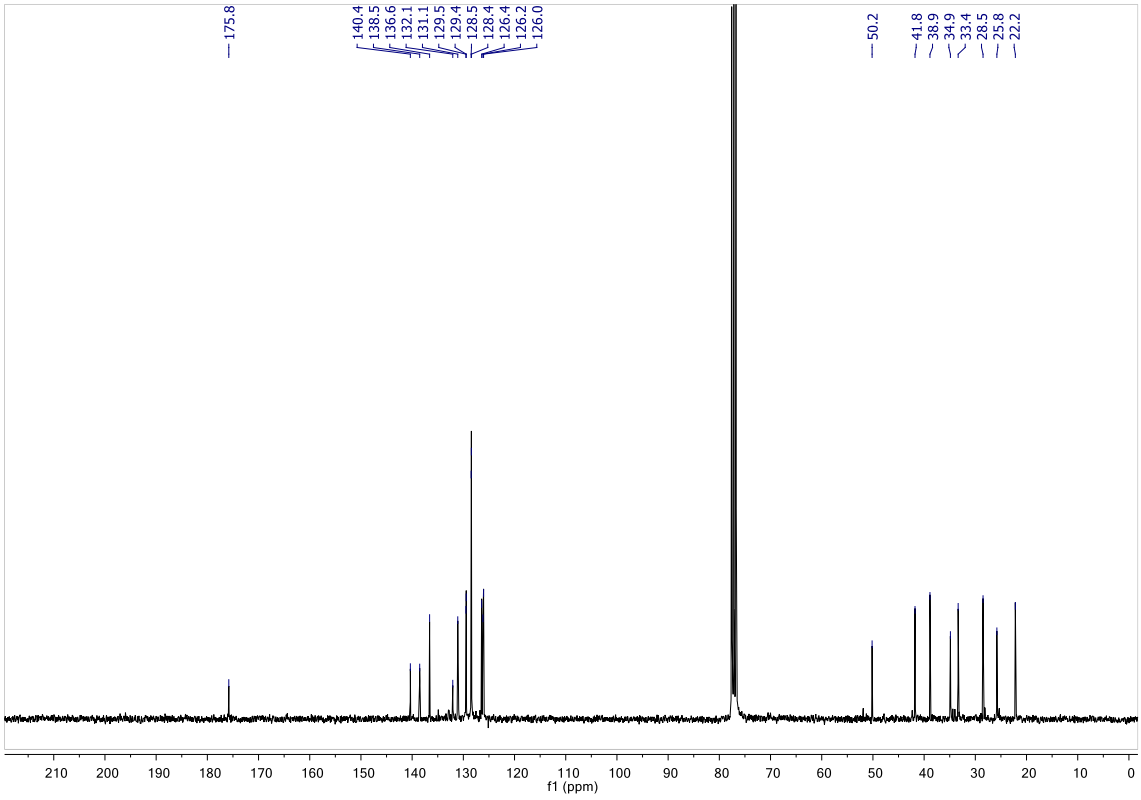
(4a*R,9a*S**)-7-Fluoro-9a-((*E*)-3-phenylprop-1-en-1-yl)-1,2,3,4,4a,9a-hexahydro-9*H*-fluoren-9-one 9f**



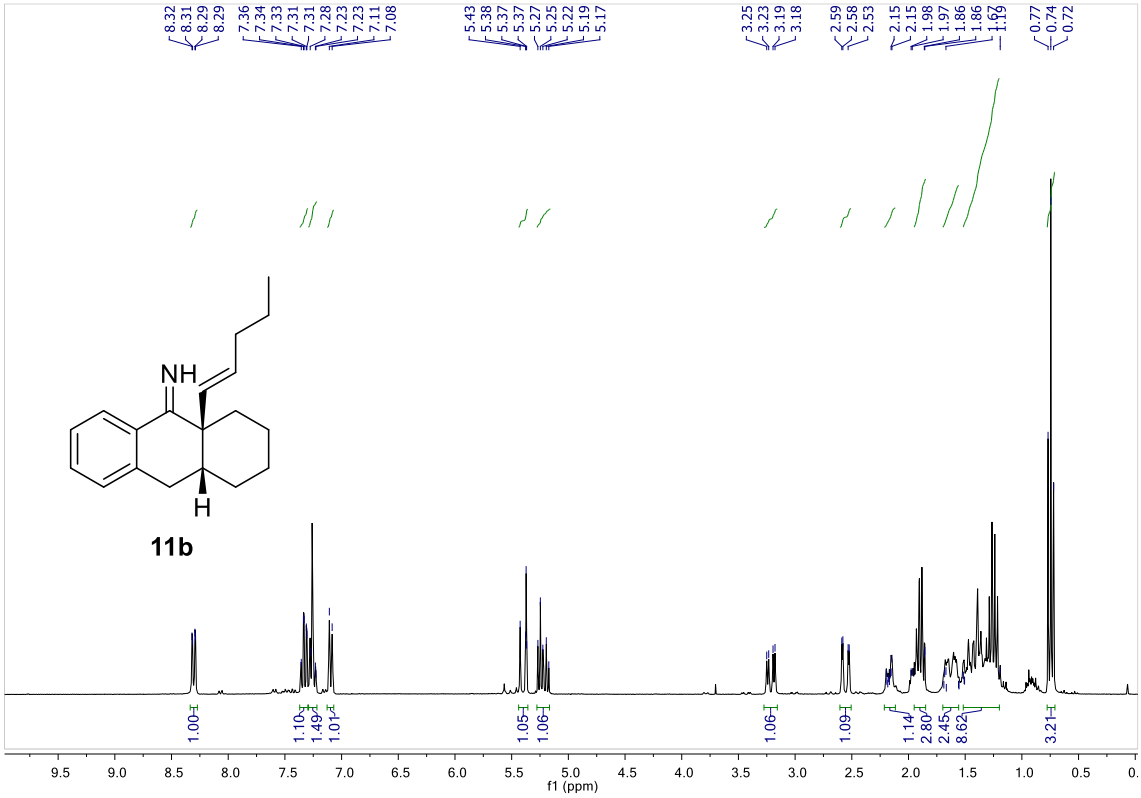

-114.45
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)

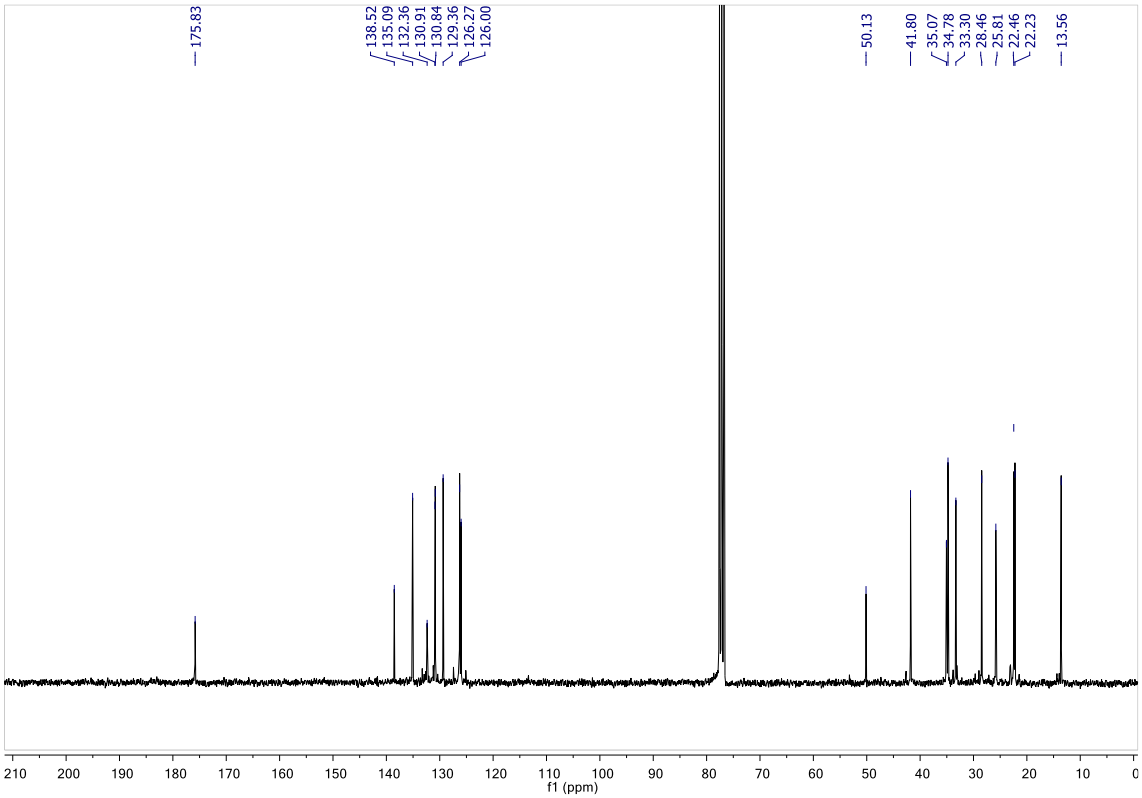
(4a*S,9a*S**)-9a-((*E*)-3-Phenylprop-1-en-1-yl)-1,3,4,4a,9a,10-hexahydroanthracen-9(2*H*)-imine 11a**



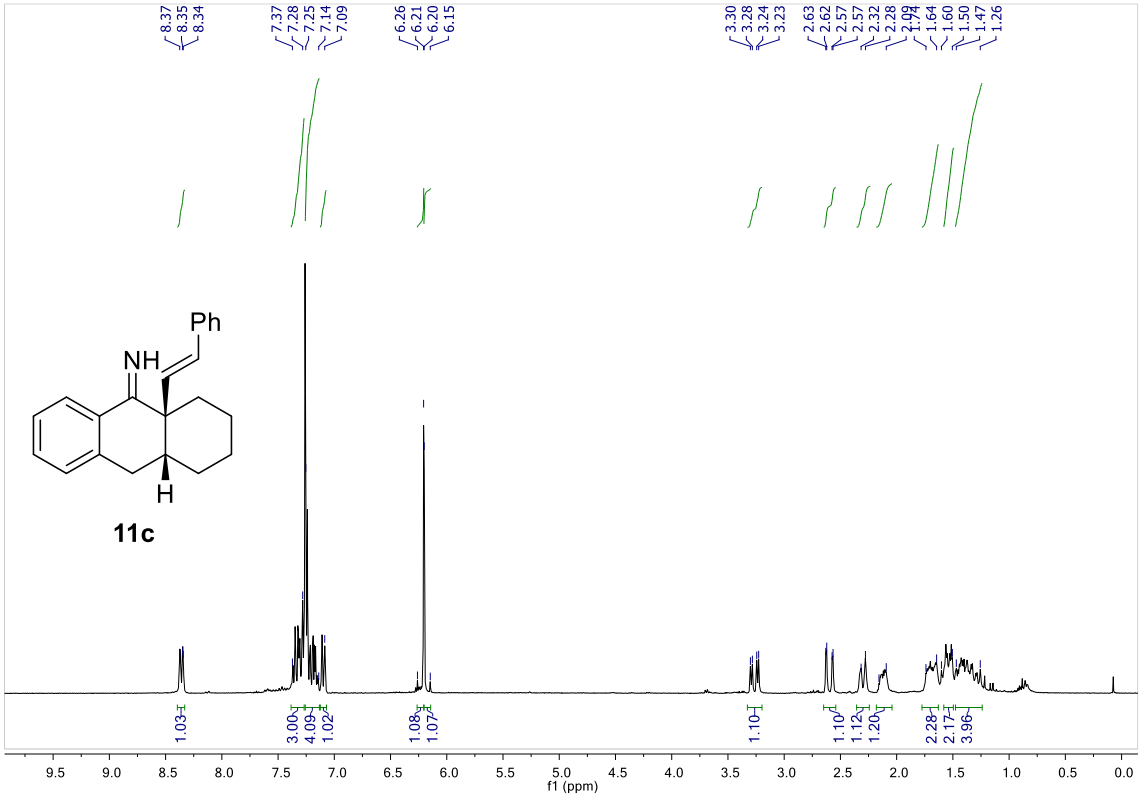


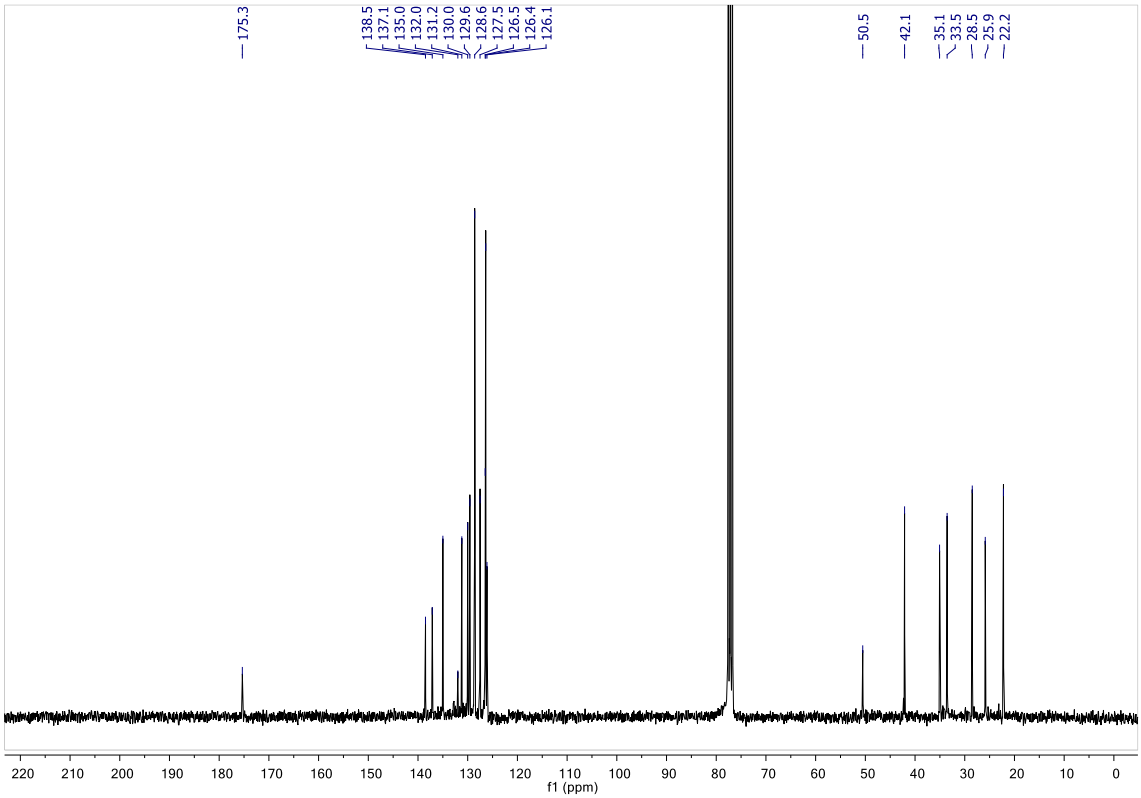
(4a*S,9a*S**)-9a-((*E*)-Pent-1-en-1-yl)-1,3,4,4a,9a,10-hexahydroanthracen-9(2*H*)-imine 11b**



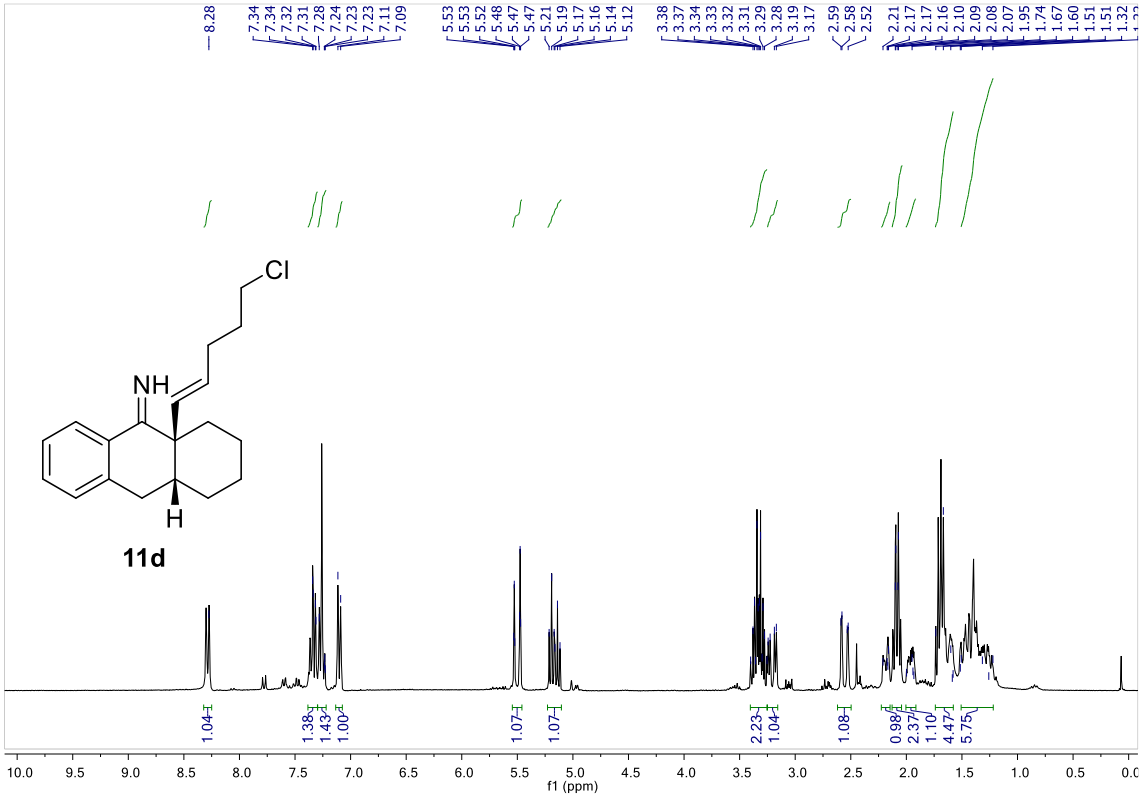


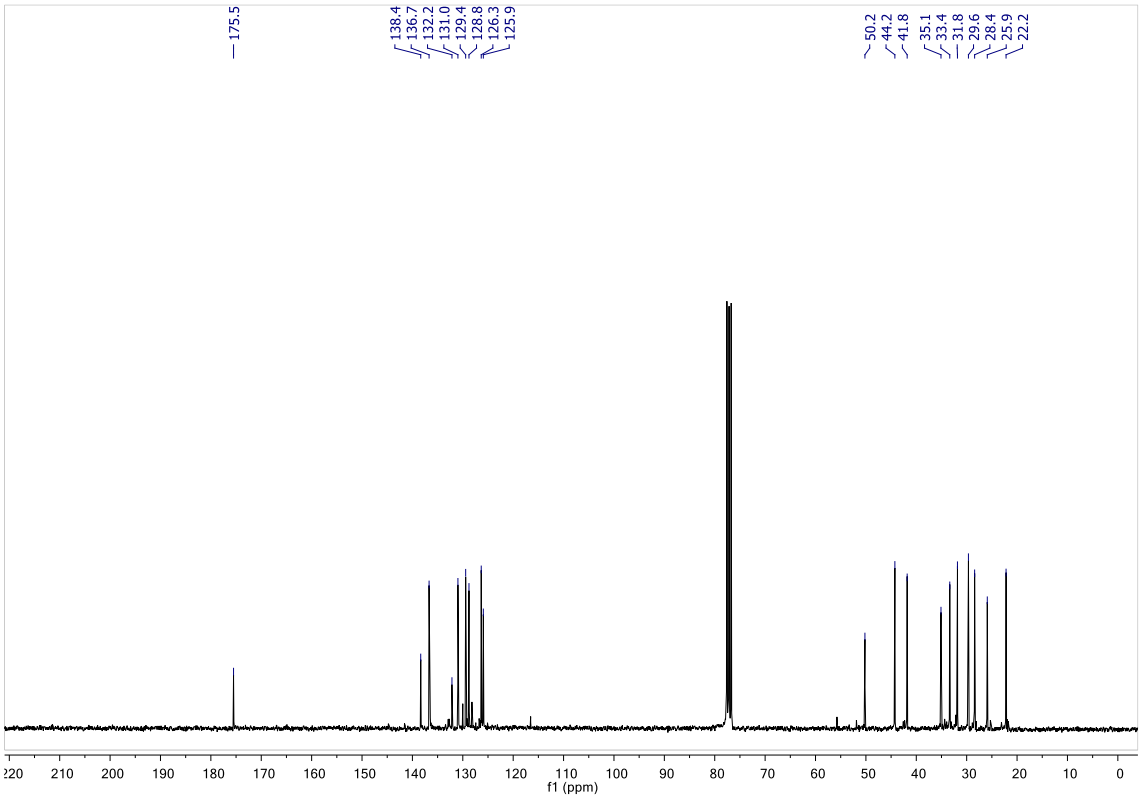
(4a*S,9a*S**)-9a-((*E*)-Styryl)-1,3,4,4a,9a,10-hexahydroanthracen-9(2*H*)-imine 11c**



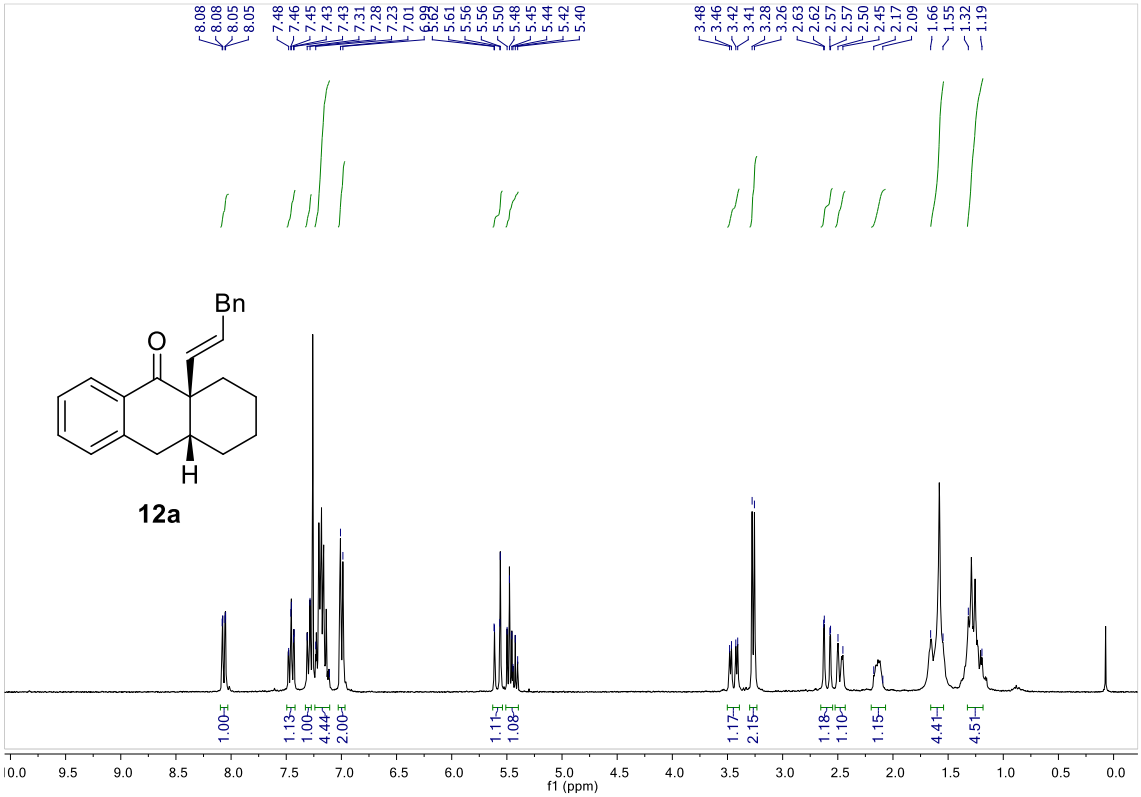


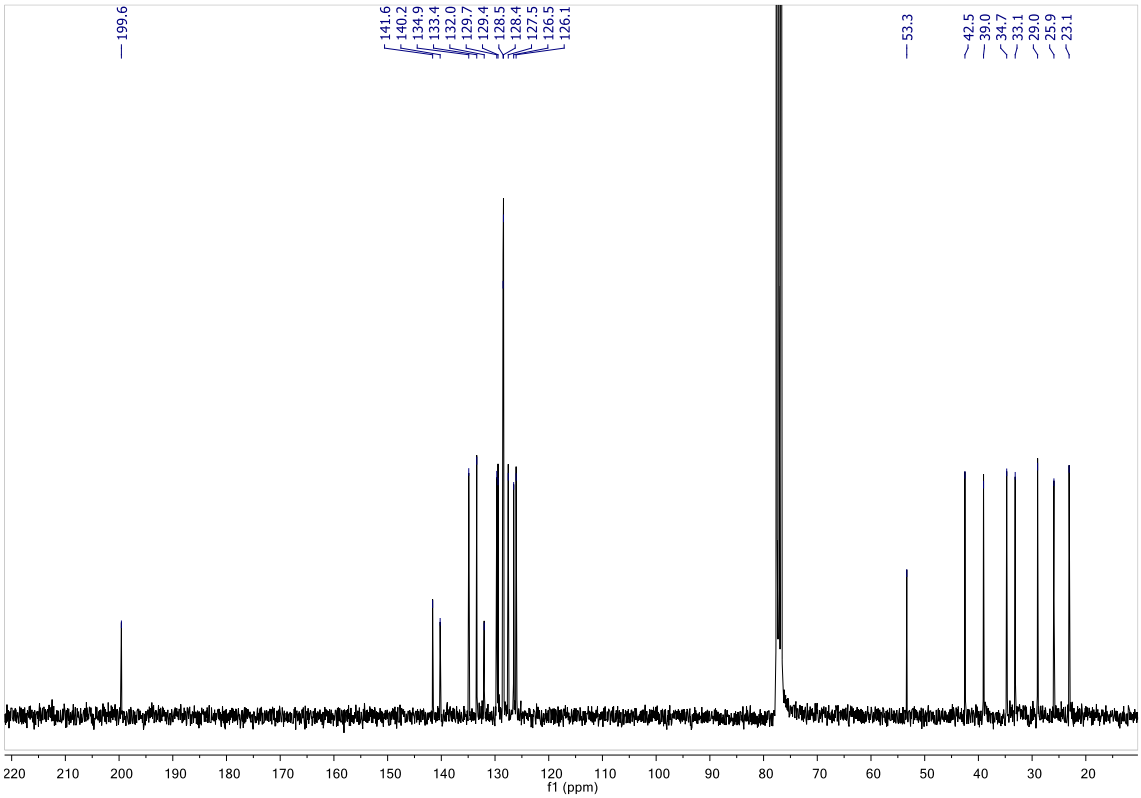
(4a*S,9a*S**)-9a-((*E*)-5-Chloropent-1-en-1-yl)-1,3,4,4a,9a,10-hexahydroanthracen-9(2*H*)-imine 11d**



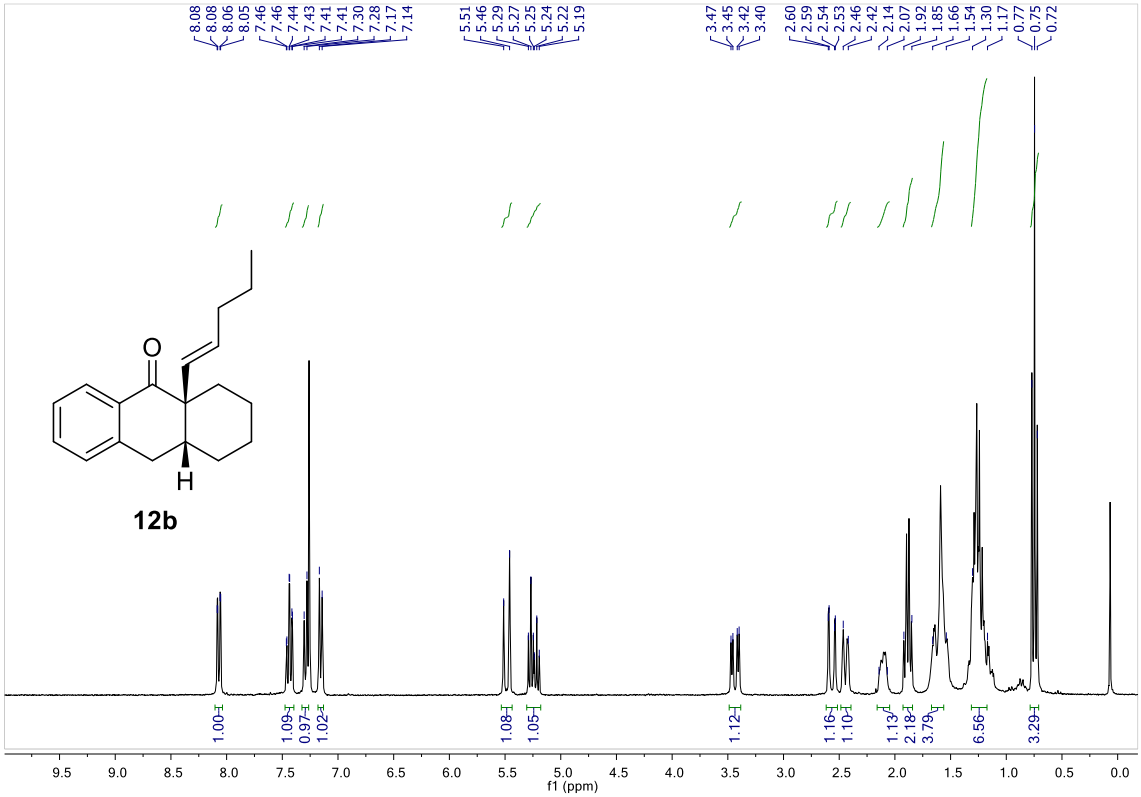


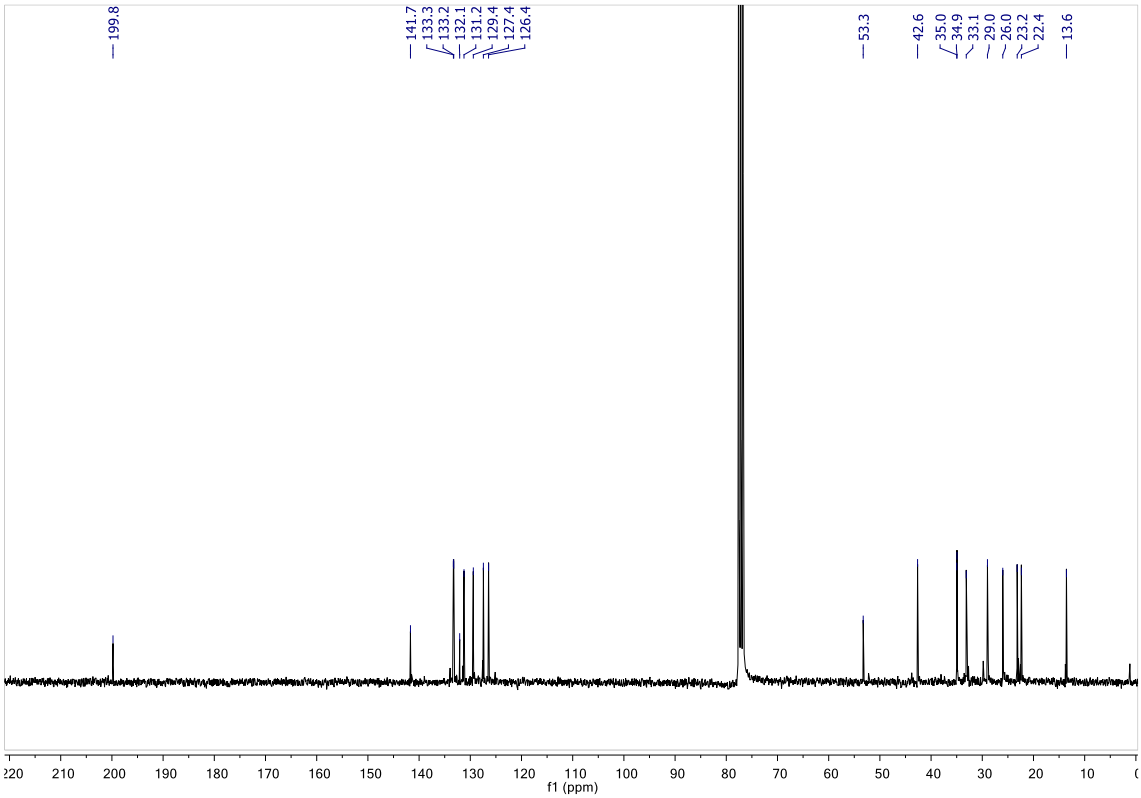
4a*S*,9a*S**)-9a-((*E*)-3-Phenylprop-1-en-1-yl)-1,3,4,4a,9a,10-hexahydroanthracen-9(2*H*)-one 12a**





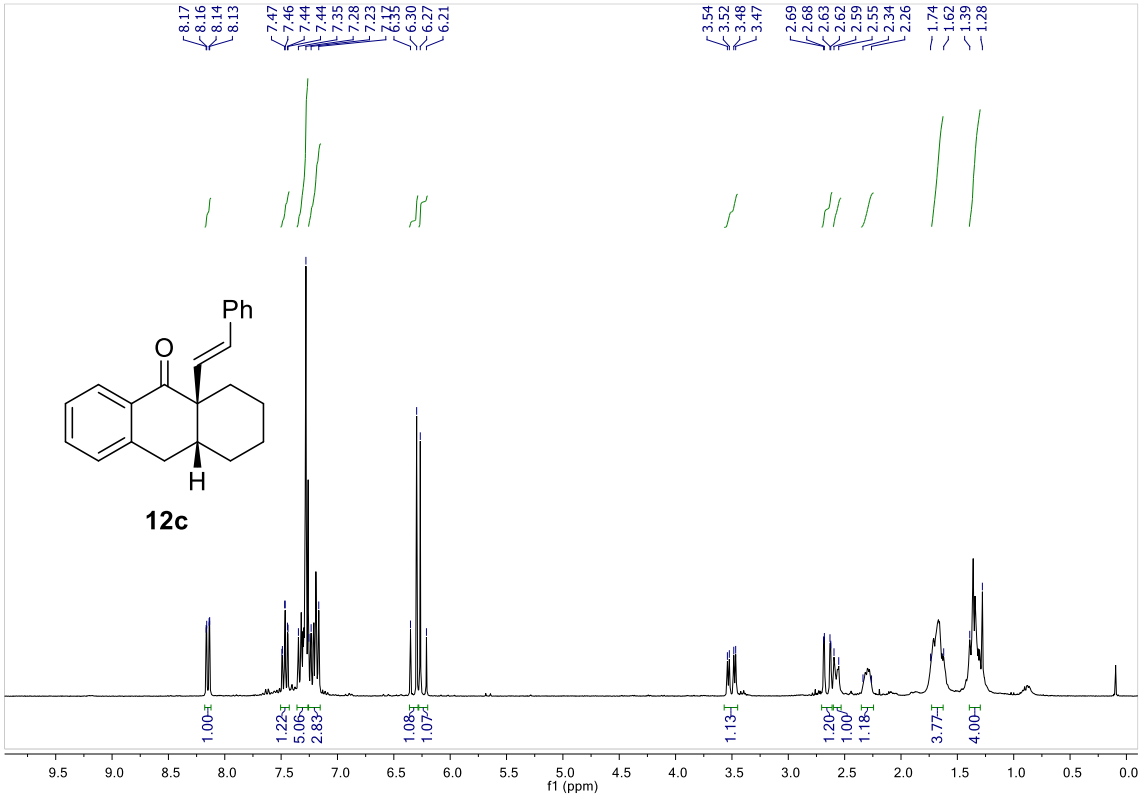
(4a*S,9a*S**)-9a-((*E*)-Pent-1-en-1-yl)-1,3,4,4a,9a,10-hexahydroanthracen-9(2*H*)-one 12b**

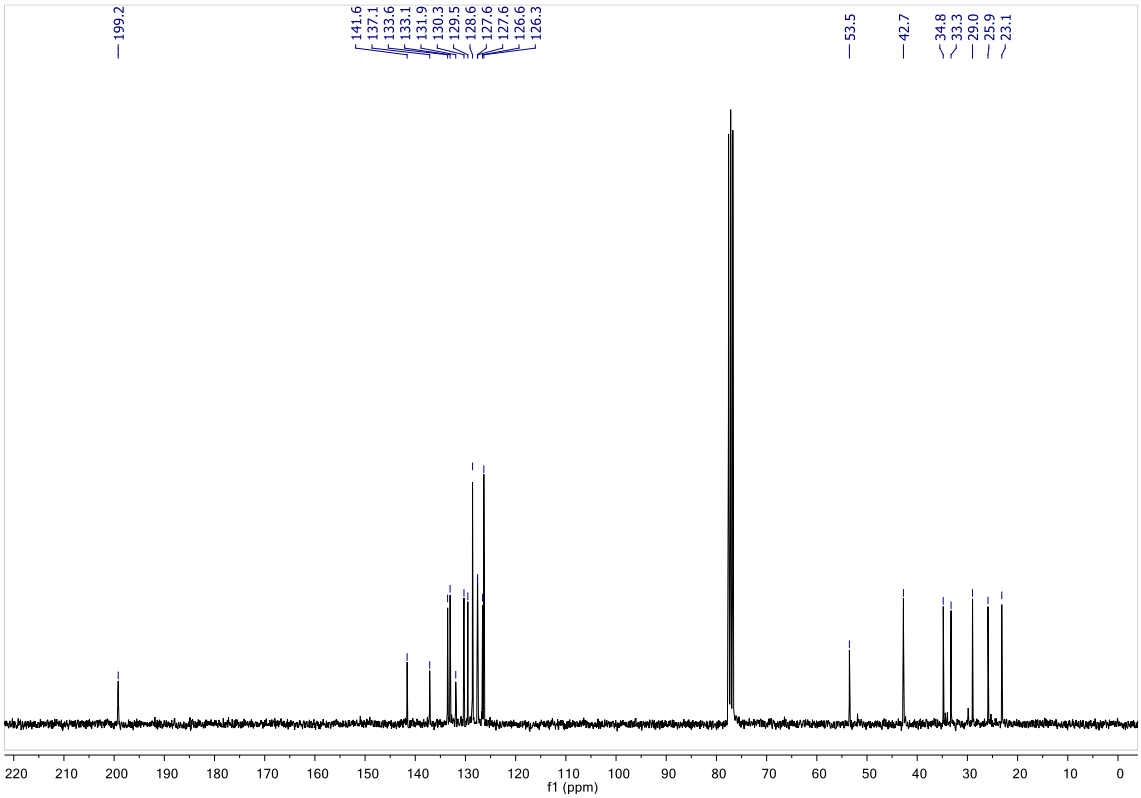




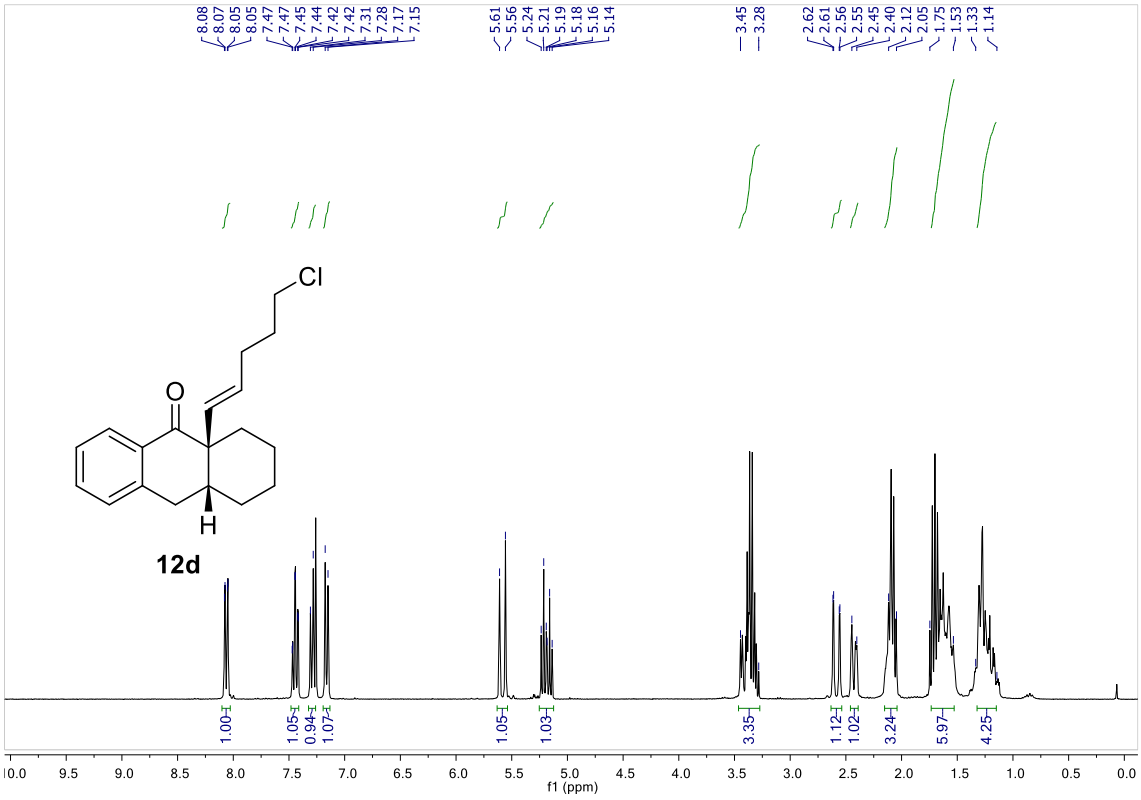
(4a*S,9a*S**)-9a-((*E*)-Styryl)-1,3,4,4a,9a,10-hexahydroanthracen-9(2*H*)-one**

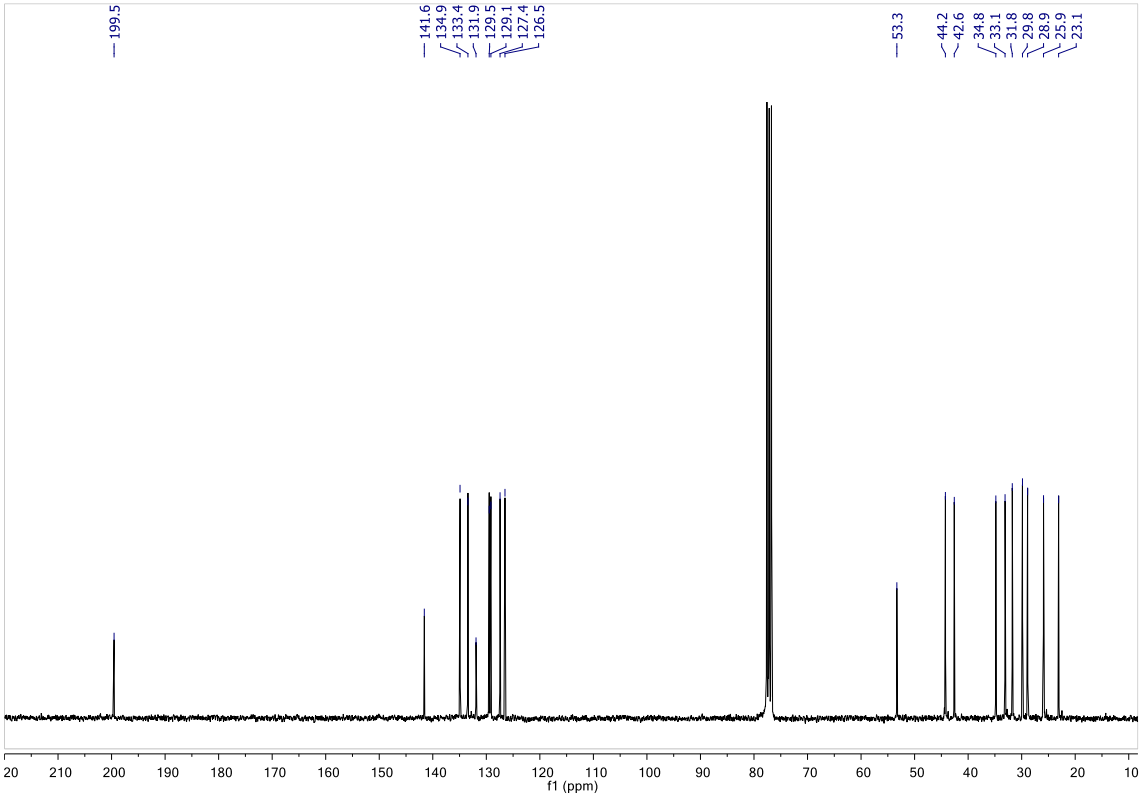
12c



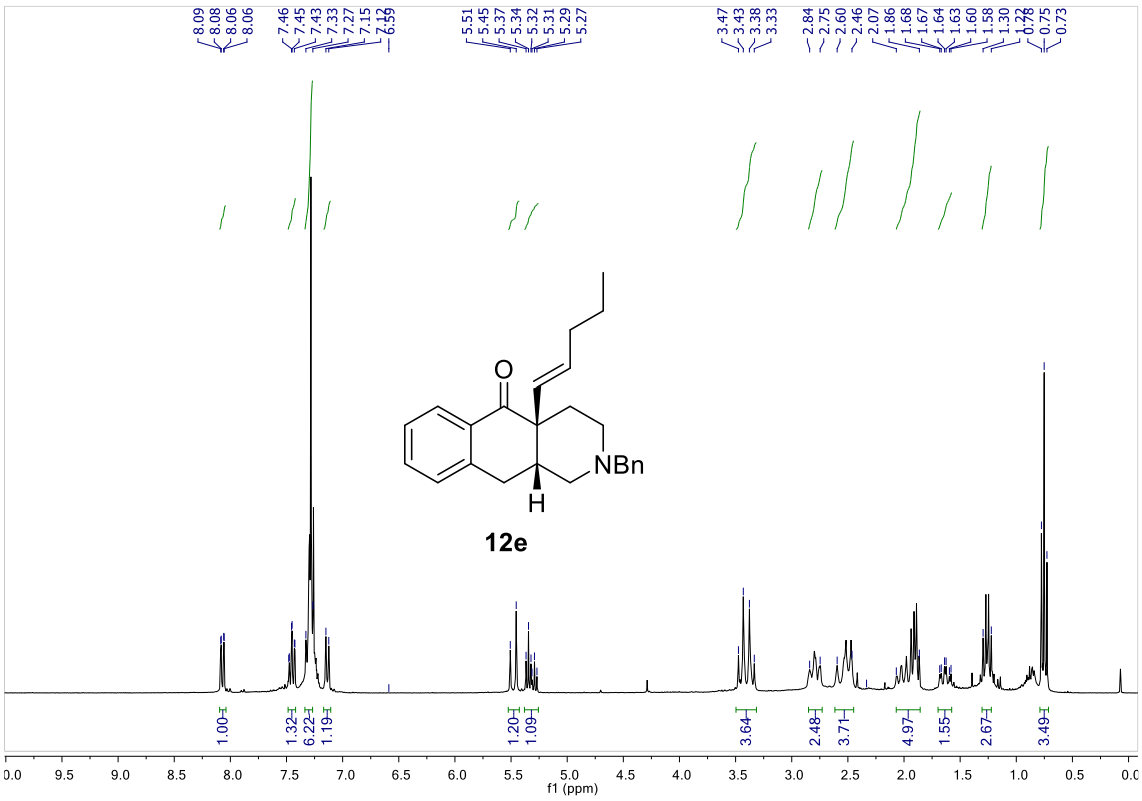


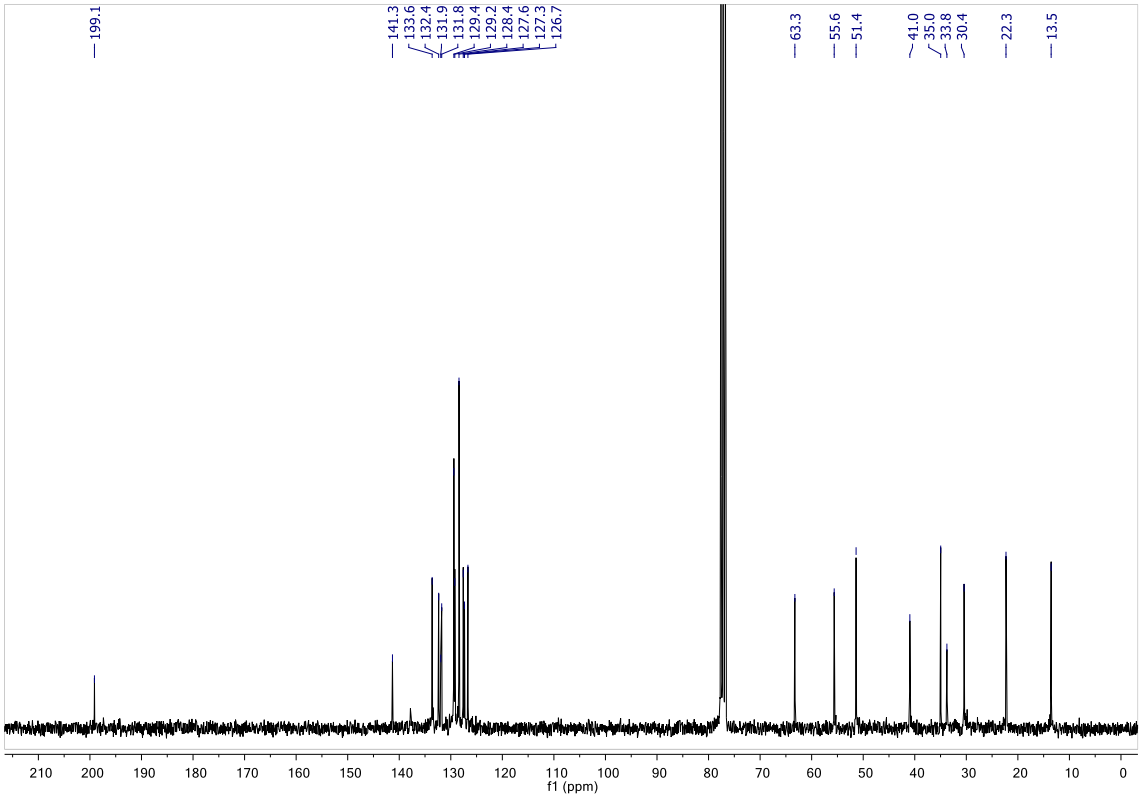
(4a*S*,9a*S*)-9a-((*E*)-5-Chloropent-1-en-1-yl)-1,3,4,4a,9a,10-hexahydroanthracen-9(2*H*)-one 12d



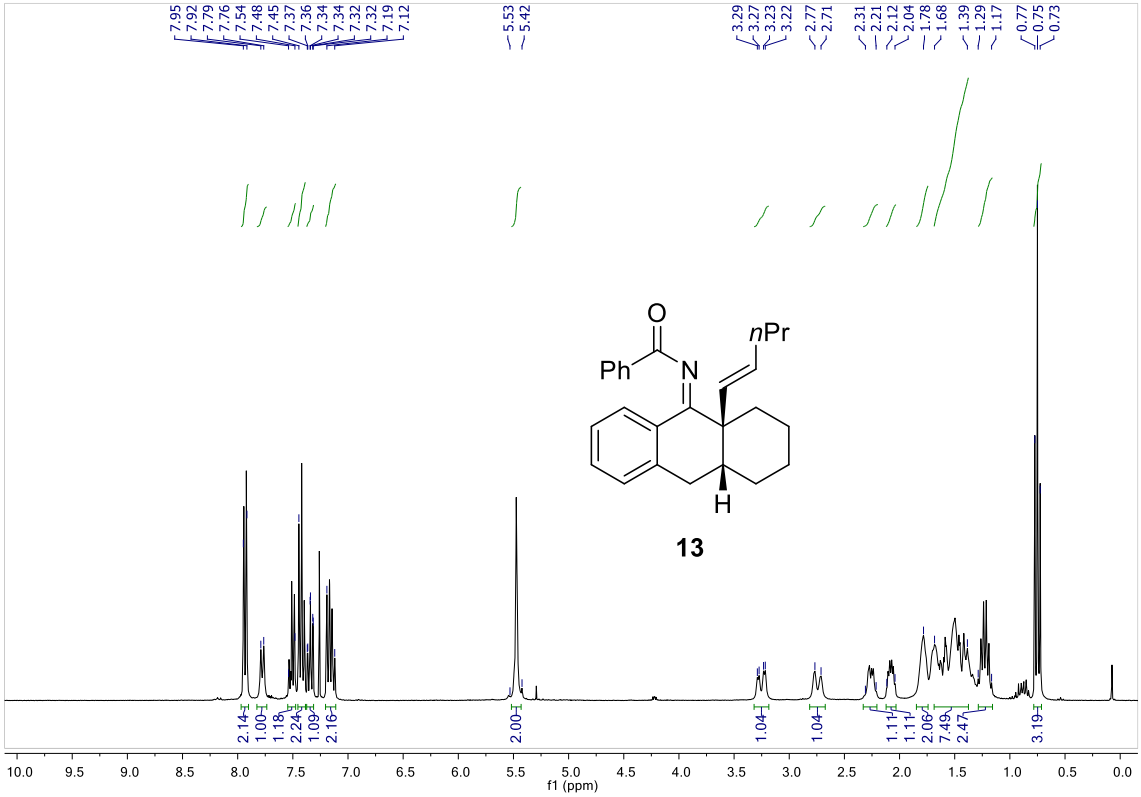


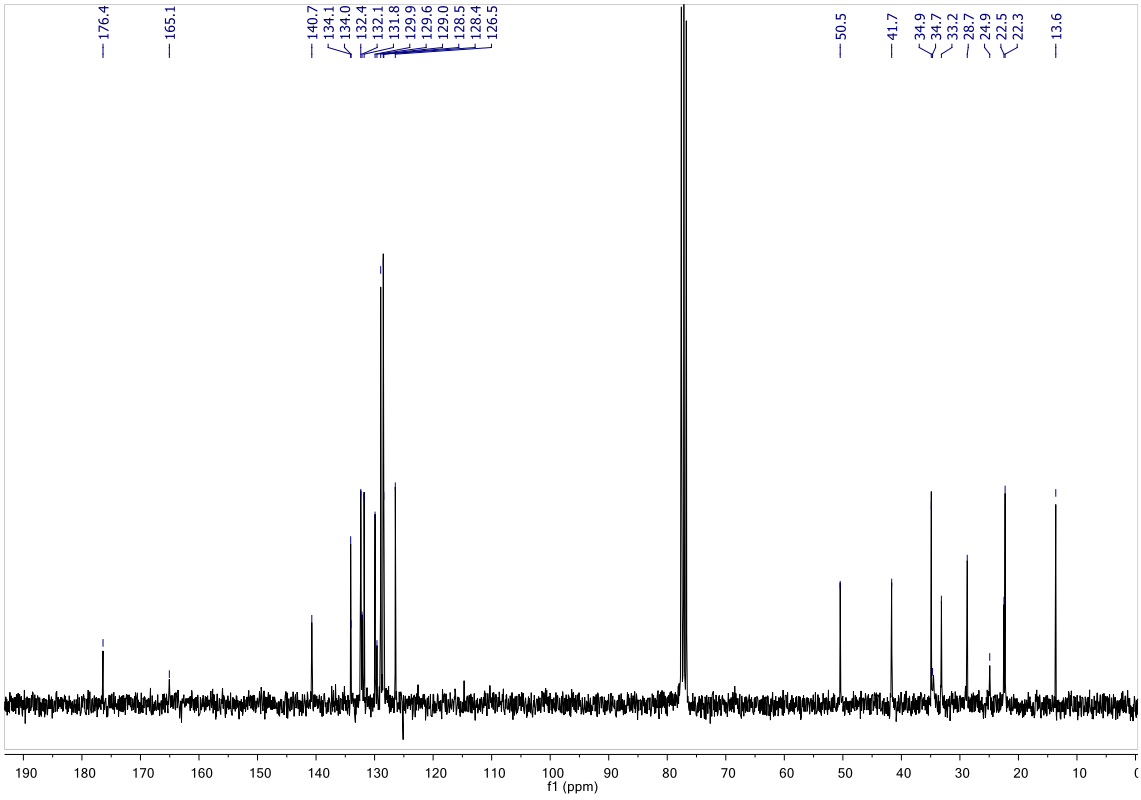
(4a*R,10a*S**)-2-Benzyl-4a-((*E*)-pent-1-en-1-yl)-2,3,4,4a,10,10a-hexahydro-benzo[*g*]isoquinolin-5(1*H*)-one 12e**



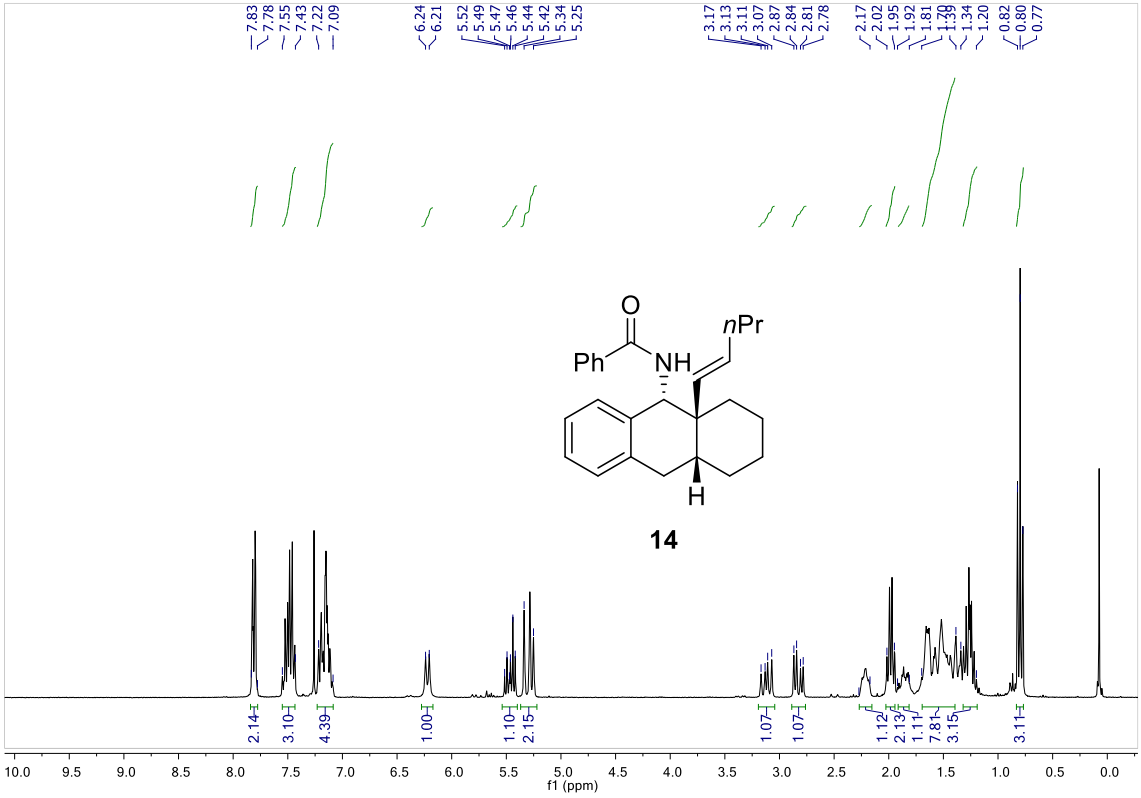


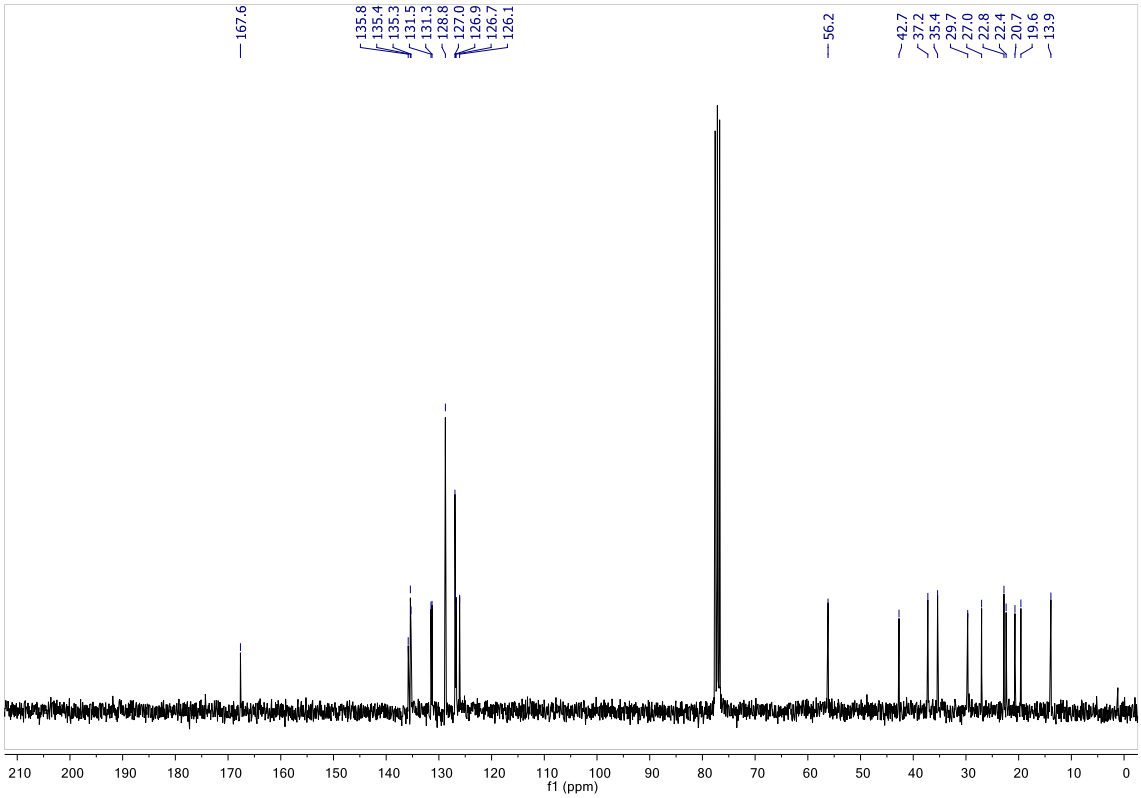
_N_-((4a_S_*,9a_S_*)-9a-((_E_)-pent-1-en-1-yl)-1,3,4,4a,9a,10-hexahydroanthracen-9(2_H_)-ylidene)benzamide 13





_N_-((4a_S_*,9_S_*,9a_S_*)-9a-((_E_)-pent-1-en-1-yl)-1,2,3,4,4a,9,9a,10-octahydro-anthracen-9-yl)benzamide 14





5.- Stereochemical assignment of compound 8a

In order to determine the stereochemistry of compounds **8**, some high field NMR experiments (600 MHz) were carried out. Taking **8a** as model system, the signal corresponding to H1 could be assigned through a HSQC experiment (Figure S1), featuring a chemical shift of 3.67 ppm in the ^{1}H-RMN.

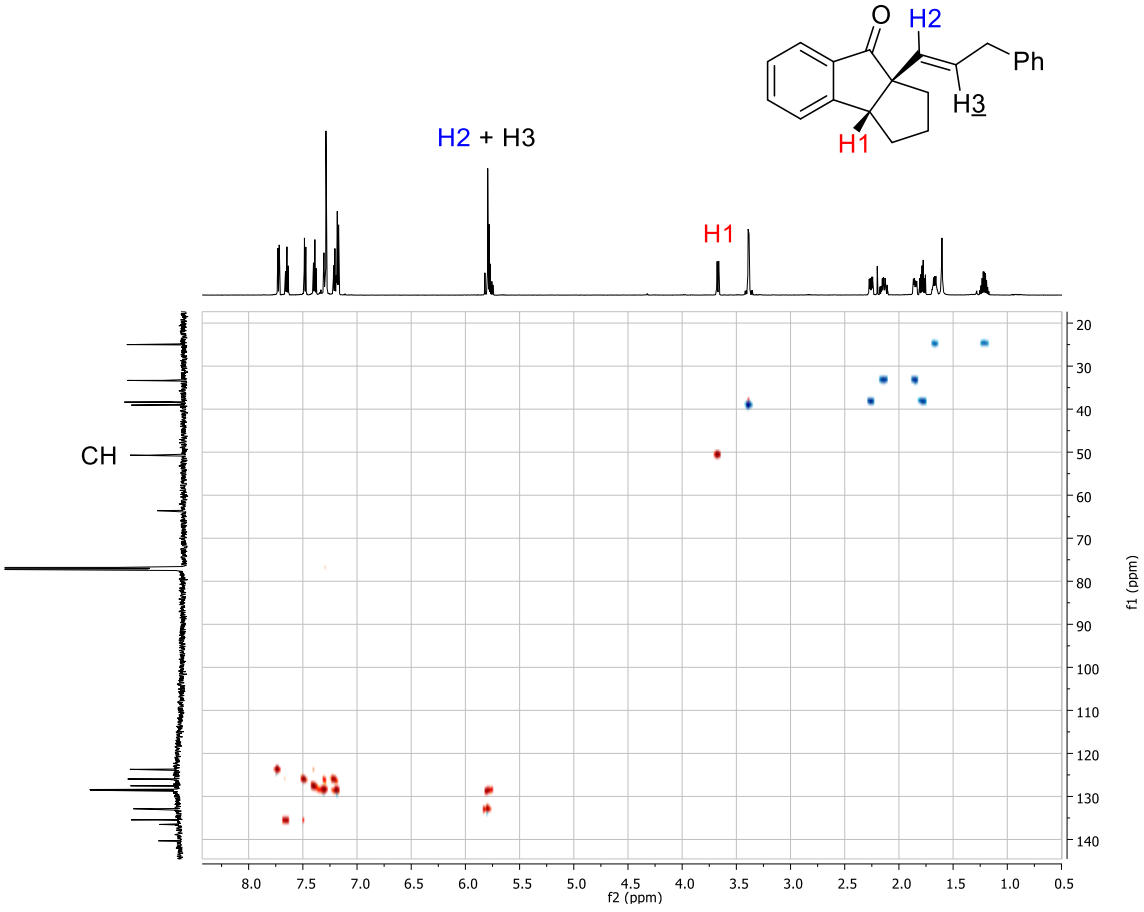


Figure S1. HSQC experiment carried out in compound **8a**.

The *cis*-fusion of the rings was established through selective nOe experiments. Thus, when the signal characteristic of H2 and H3 (δ= 5.79 ppm) was saturated (Figure S2), a strong nOe effect was detected on H1. This observation establishes the *cis* arrangement between H1 and the alkenyl substituent, and therefore the *cis* fusion between the saturated rings.

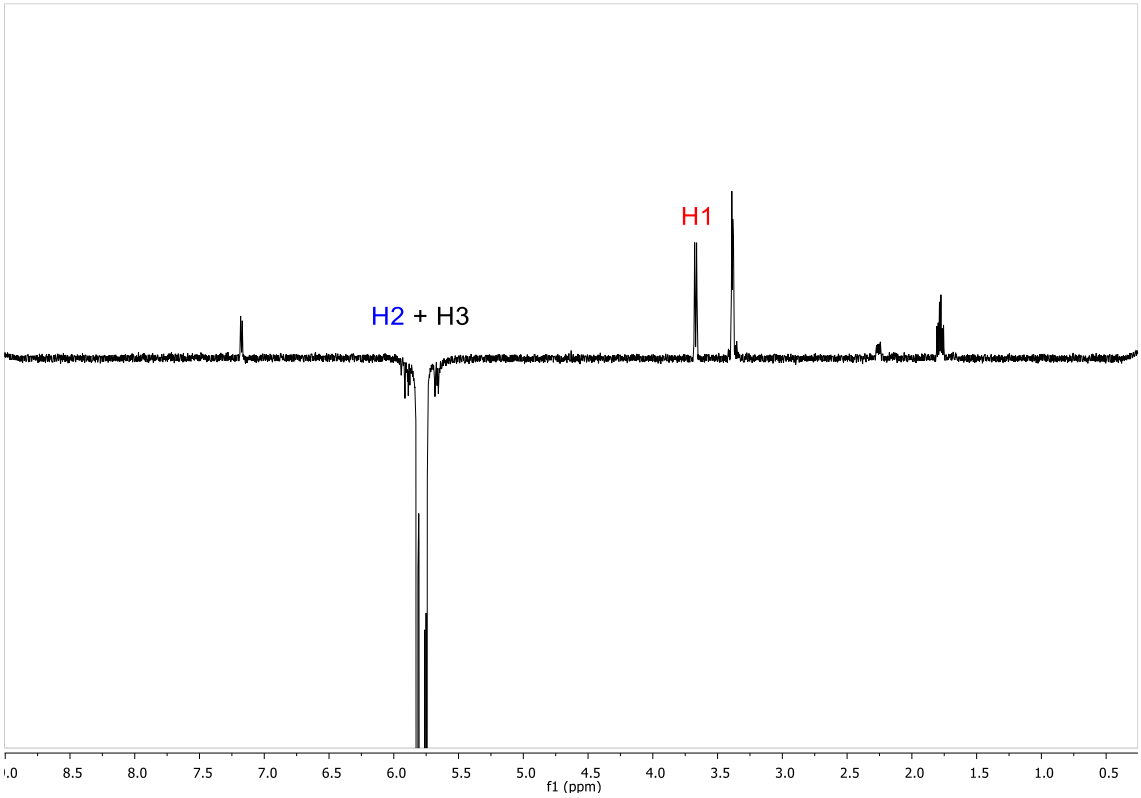


Figure S2. Selective nOe over the signal of H2 and H3.

6.- Stereochemical assignment of compound 9a

The relative stereochemistry of the compound **9a** could be determined through some high field NMR experiments (600 MHz). In this case, the signal corresponding to H1 could be assigned (Figure S3) through a HSQC experiment, featuring a chemical shift of 3.37 ppm in the 1H-RMN spectrum.

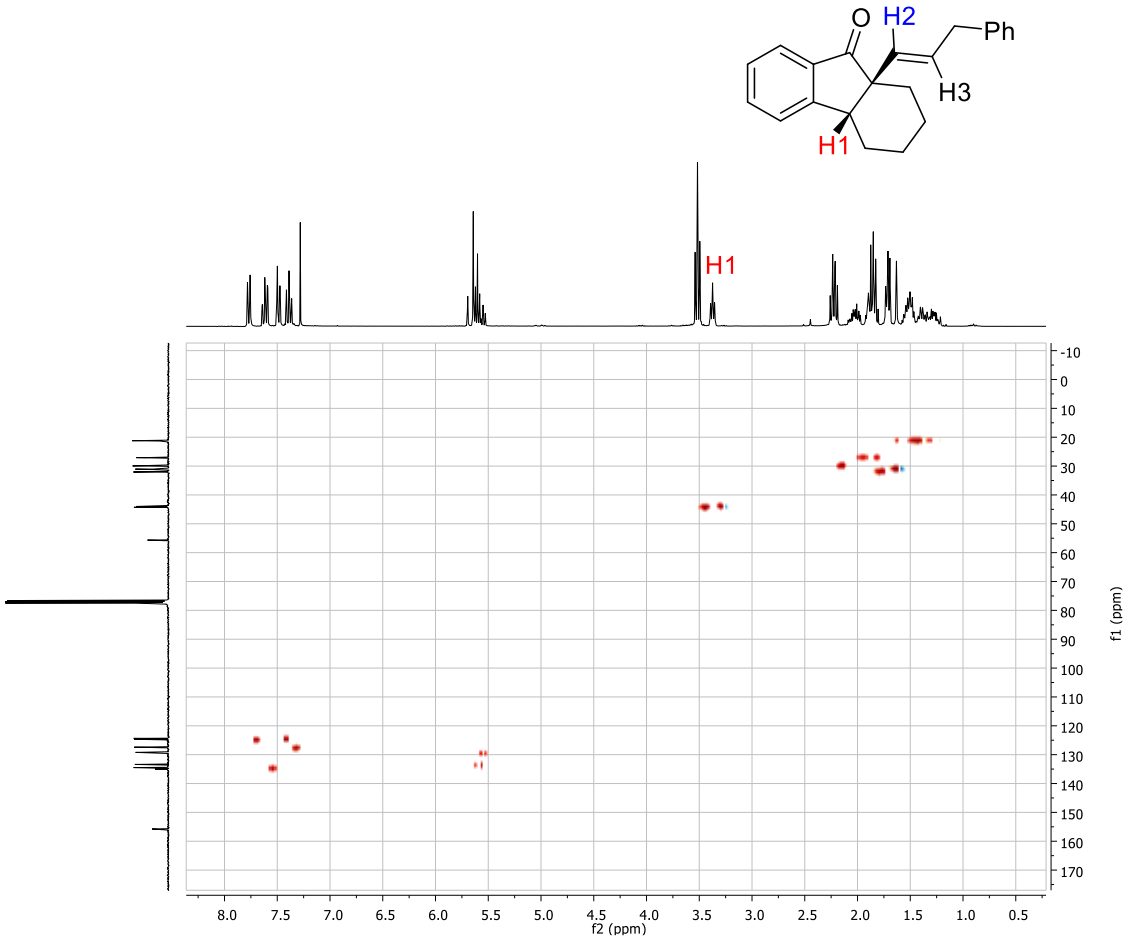


Figure S3. HSQC experiment carried out in compound **9a**.

When a NOESY was carried out a clear nOe was observed between H1 and H2 (Figure S4). These observations establishes the *cis* arrangement between H1 and the alkenyl substituent, and therefore the *cis* fusion between the five and six membered rings.

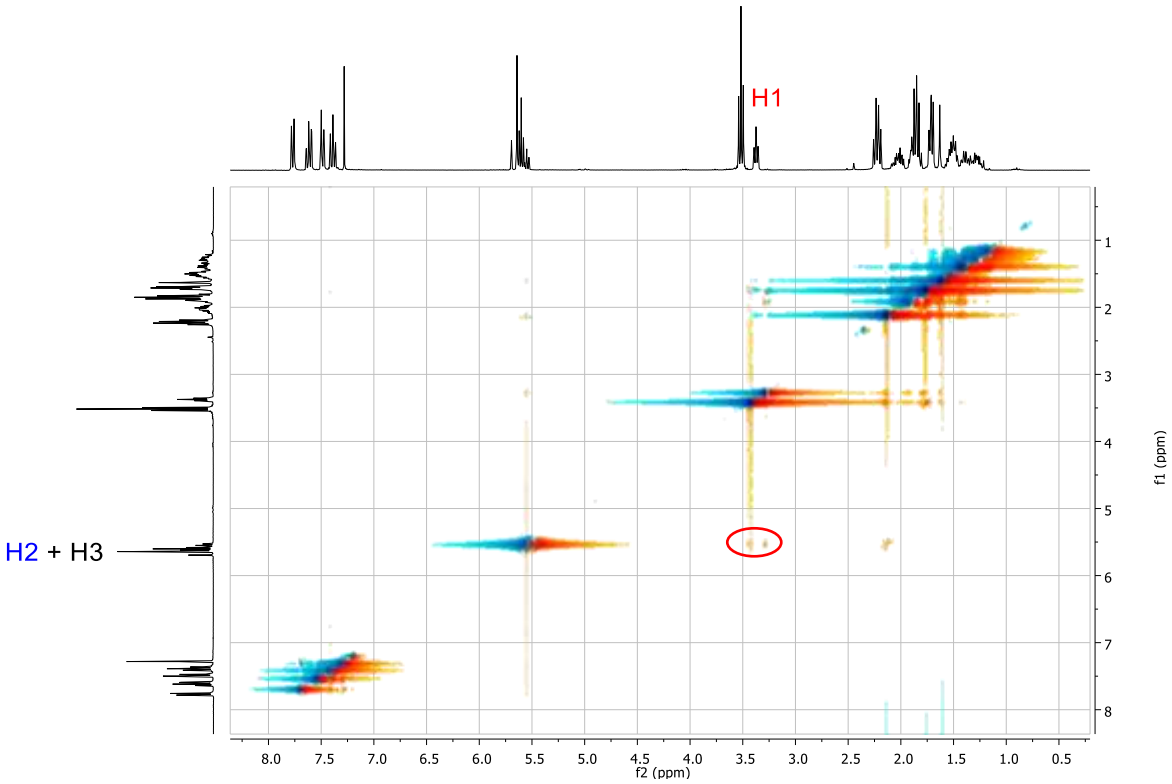


Figure S4. NOESY experiment carried out in compound **9a**.

7. Stereochemical assignment of compound 11b

The relative stereochemistry of the compound **11b** could be determined through some high field NMR experiments (600MHz). In this case, the signal corresponding to H1 could be assigned (Figure S5) through a HSQC experiment, featuring a chemical shift of 1.97 ppm in the ^{1}H-RMN spectrum.

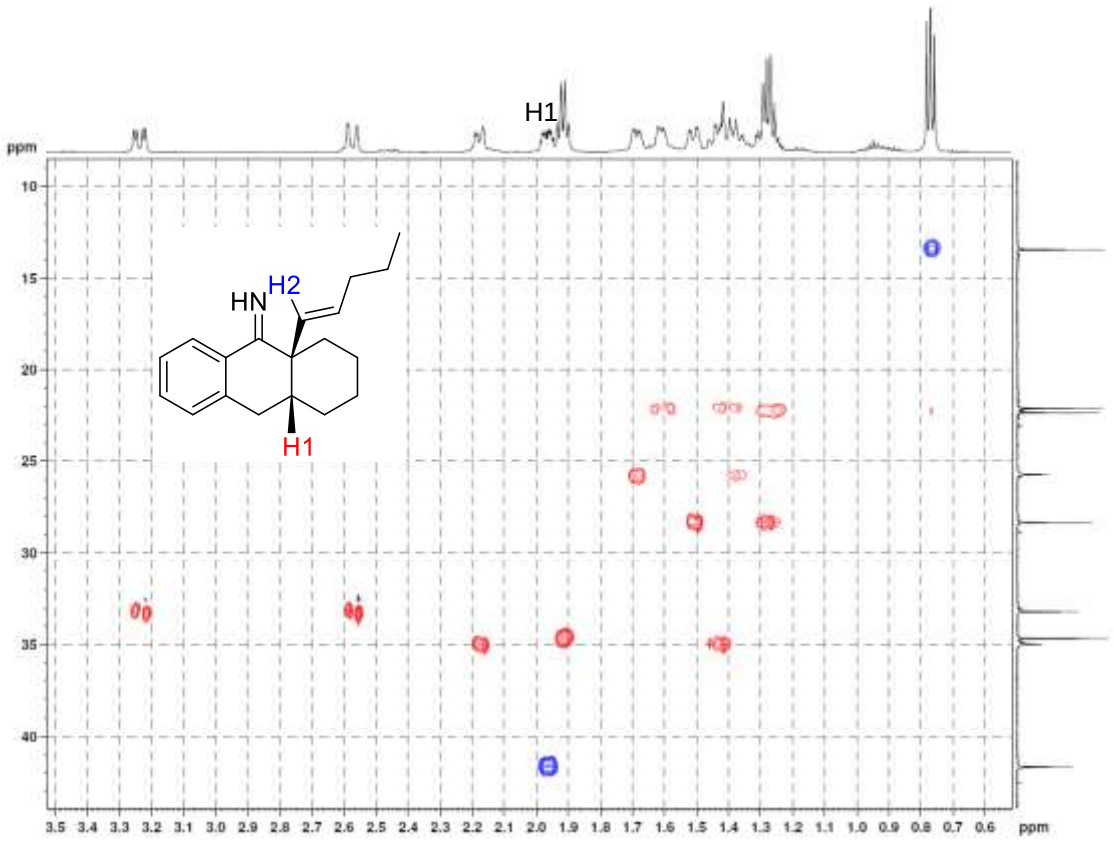


Figure S5. Expansion of the critical area of the HSQC experiment

The *cis*-fusion of the rings was established through selective nOe experiments. Thus, when the signal characteristic of H1 (δ= 1.97 pm) was saturated (Figure S6), a strong nOe effect was detected on H2 (5.41 ppm). This observation establishes the *cis* arrangement between H1 and the alkenyl substituent and therefore the *cis* fusion between the rings (figure S6).

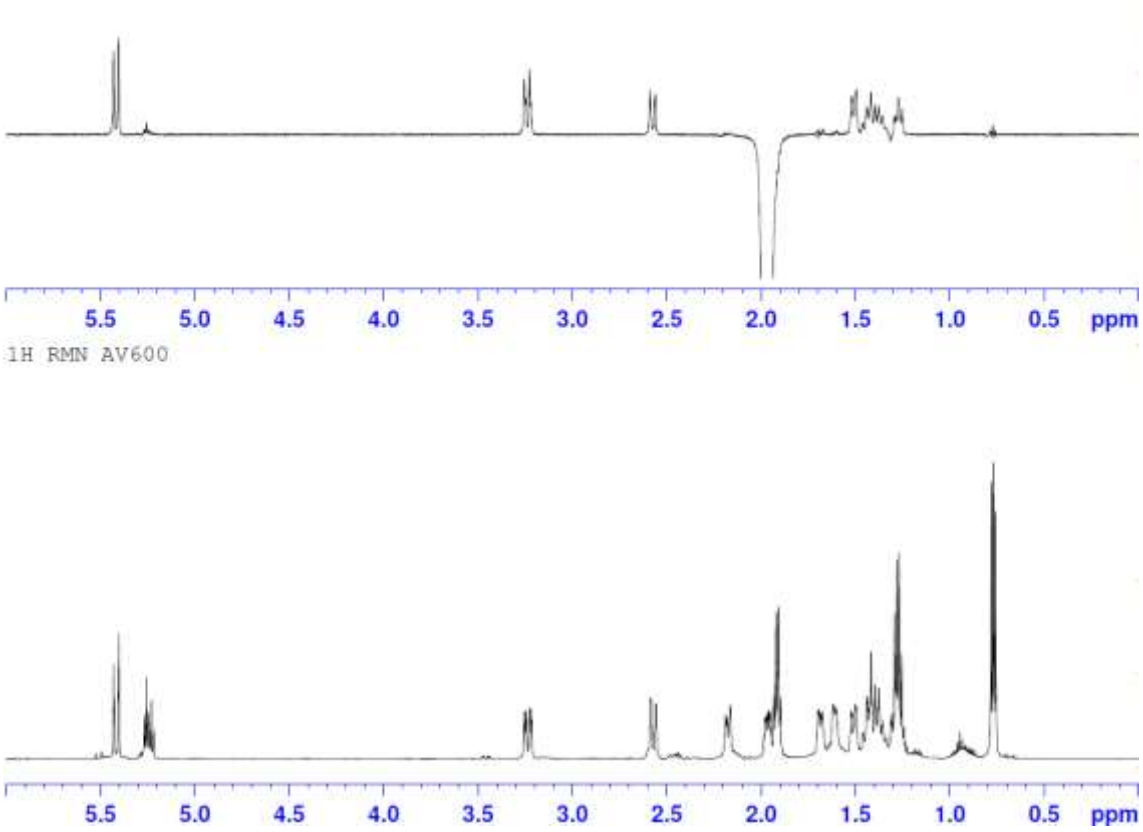
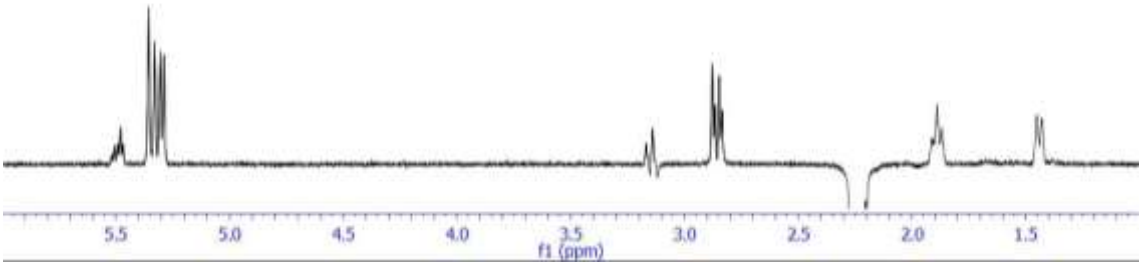
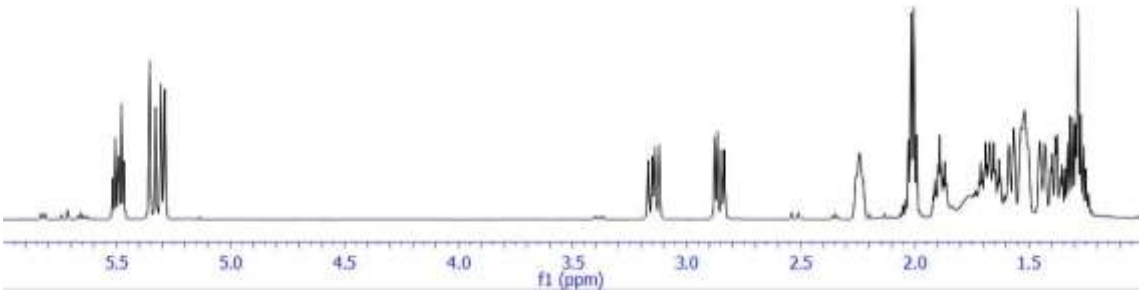


Figure S6: Selective nOe experiment that establishes the stereochemistry of imine **11b**.

8. Stereochemical assignment of amide 14

The relative stereochemistry of the compound **14** could be determined through some high field NMR experiments (600 MHz). In this case, the assignment of the signals on the 1H NMR spectrum could be accomplished through several 2D experiments. Then, relative stereochemistry was established through selective nOe experiments. Thus, when the signal characteristic of H1 (δ= 2.20 pm) was saturated (Figure S8), strong nOe effects were detected on H2 (5.34 ppm) and H3 (5.29 ppm). These observations establish the *cis* arrangement between the alkenyl substituent, H1 and H3 and therefore the proposed stereochemistry.





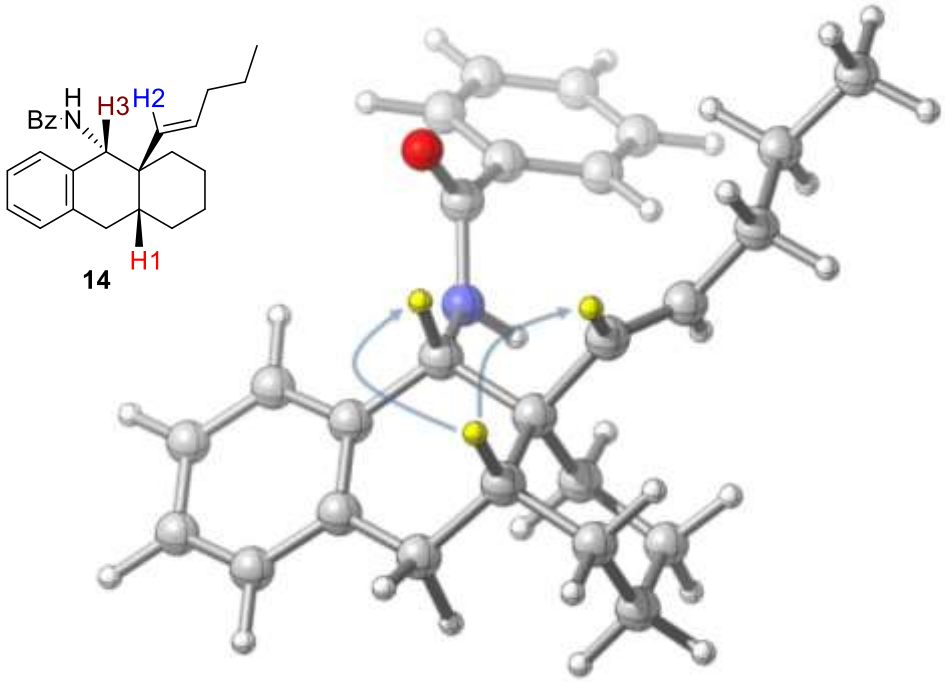


Figure S8: Critical nOes that establish the relative stereochemistry of the three contiguous stereocenters in amide **14**

9. Computational Modeling

General methods

All calculations were performed with the Gaussian09 package of programs.[6] Full geometry optimizations were carried out employing the M06-2X hybrid functional with the 6-311++G(d,p) basis set, denoted as M06-2X/6-311++G**.[7] Harmonic force constants were computed at the optimized geometries employing the same level of theory to characterize the stationary points as minima or saddle points. Zero-point vibrational corrections were determined from the harmonic vibrational frequencies to convert the total energies E_{el} to Gibbs free energies G. Solvation free energies were calculated at the same level considering 1,4-dioxane as the solvent and employing the IEF-PCM model with the United Atom Topological Model (UAHF) to define the cavity. Computational data, three-dimensional models and cartesian coordinates for all the stationary points found are included below. The three-dimensional models have been rendered with CYLview.[8]

9.1 Discussion on the diastereoselectivity of the formation of hexahydroindenones 9 and hexahydroanthracenones 11.

To explain the diastereoselectivity of the formation of hexahydroindenones **9** and hexahydroanthracenones **12** we carried out molecular modeling studies

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[6] Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V.Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

[7] The M06 family of global hybrid functionals have been reported to very give reliable kinetic values for a large number of organic reactions: (a) Zhao Y.; Truhlar, D. *Theor. Chem. Account* **2008**, *120*, 215-241. (b) Xu, X.; Alecu I. M.; Truhlar, D. G. *J. Chem. Theory Comput.* **2011**, *7*, 1667–1676.

[8] CYLview, 1.0b; Legault, C. Y., Université de Sherbrooke, 2009 (http://www.cylview.org)

employing the density functional theory with the M06-2X functional and the 6-311++G** basis set. We chose as model systems the reactions of *trans*-butenylboronic acid **B**, with diazo compounds **A1** and **A2**, which would lead to *N*-boroimines **E** and **H**, that upon hydrolysis would provide cycloadducts **12** and **9** respectively (figure S9).

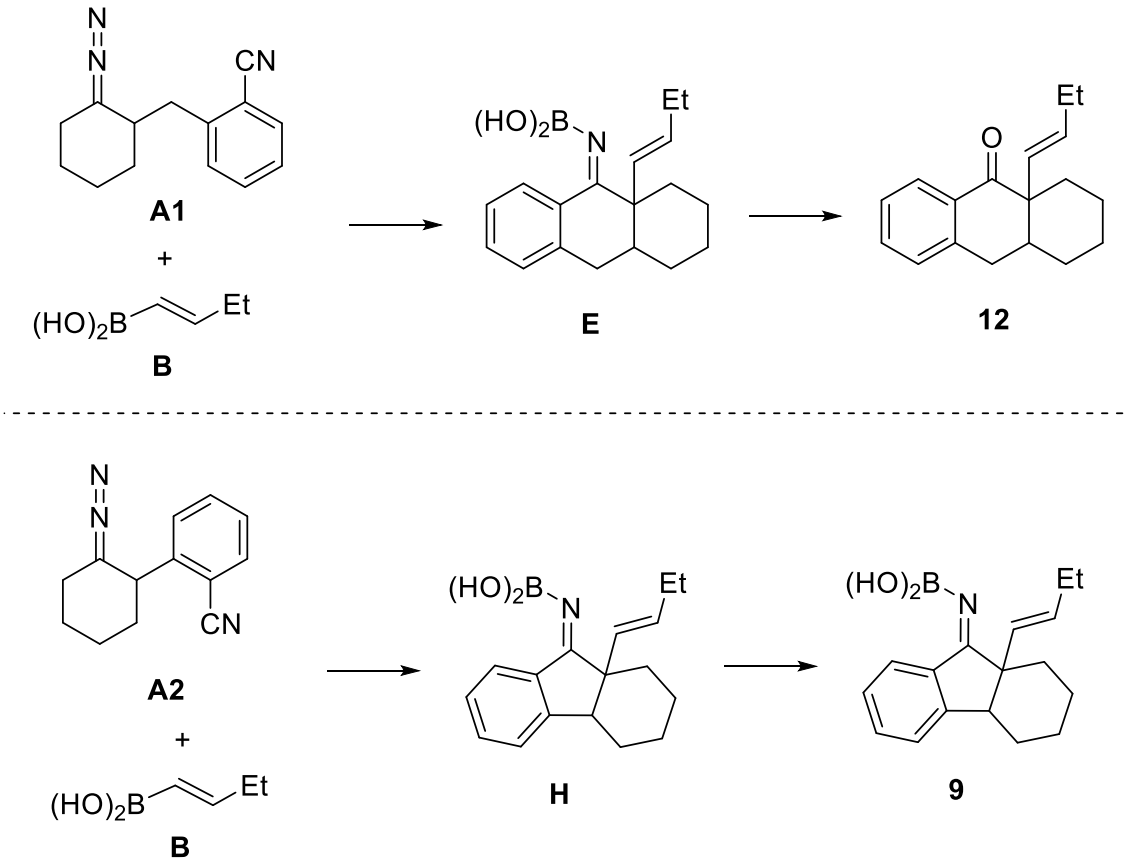
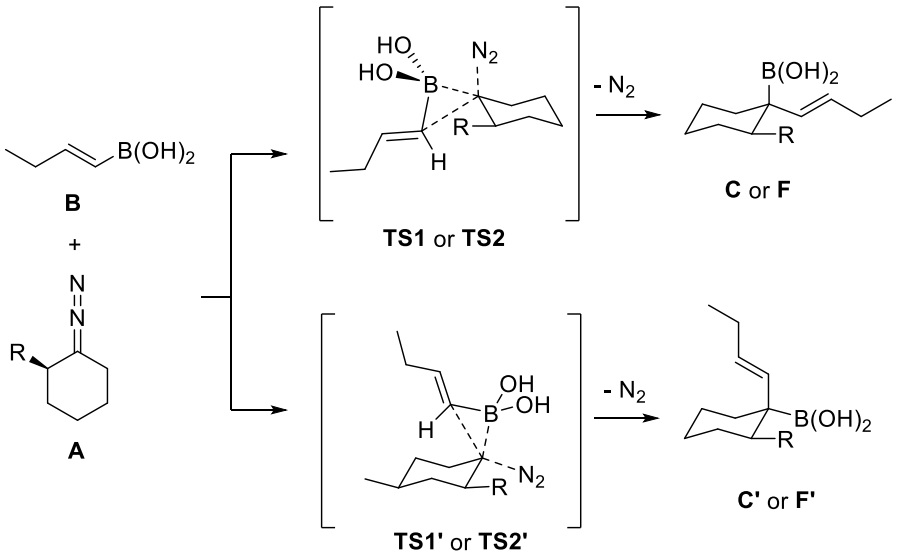


Figure S9: Model systems studied.

First step: carboborylation of the diazo compounds

First of all, the carboborylation of the diazo compounds by reaction with the boronic acid were studied. We had previously studied computationally the carboborylation reaction of 4-substituted-1-diazocyclohexanes during the development of the reductive alkenylation reactions (ref. 15c in the manuscript). We had found that the carboborylation takes place through a concerted but very asynchronous transition state. Moreover, the preference for the formation of one diastereoisomer was also found. Thus, we used these calculations as starting point for the reactions of 2-substituted-1-diazocyclohexanes **A1** and **A2**. Like in

our previous studies, two different approaches were identified for the reactions with the 2-substituted-1-diazocyclohexanes that lead to diastereoisomeric stereoisomeric allyl diazo compounds (**C** and **C'** from **A1,** and **F** and **F'** from **A2** respectively). We found that formation of the isomer that features the boron atom in an axial position and the alkenyl group in the equatorial position, is favoured by more than 3 kcal/mol in the two systems studied (3.5 kcal/mol for **A1** and 3.2 kcal/mol from **A2** respectively). Gibbs free activation energies of 24.5 and 27.7 kcal/mol were determined for the **A1** to **C,** and the **A2** to **F** transformations respectively (Figure S10). Thus, considering that the formation of the diastereoisomers **C** and **F**, that feature the alkenyl and the preexisting substituent in *trans* equatorial positions are clearly favoured, the rest of the study was conducted starting from these allylboronic acids. For both systems the overall process is highly exergonic



R		
A1	ΔGact = G(**TS1**)-G(**A1**) = 24.5 kcal/mol	ΔGreac(**C**) = -57.7 kcal/mol
	ΔΔGact = G(**TS1'**)-G(**TS1**) = 3.5 kcal/mol	ΔGreac(**C'**) = -59.6 kcal/mol
A2	ΔGact = G(**TS2**)-G(**A2**) = 27.7 kcal/mol	ΔGreac(**F**) = -57.2 kcal/mol
	ΔΔGact = G(**TS2'**)-G(**TS2**) = 3.2 kcal/mol	ΔGreac(**F'**) = -56.7 kcal/mol

Figure S10: Computational calculations on the stereoselectivity of the carboborylation of the 2-substituted-1-diazocyclohexanes **A1** and **A2**

1,3-borotropic rearrangement/bora-aza-ene cyclization for the 6-6 fused system

Our previous calculations on the alkylnitrile series (ref. 7b in the manuscript) showed that the formation of the cyclic adducts through α-carboborylation of the nitrile is a highly disfavoured process, and therefore that pathway was discarded. Thus, we considered the 1,3-borotropic rearrangement/carboborylation sequence (Figure S11). Two different stereoisomers **D1** and **D2** can be produced upon the 1,3-borotropic rearrangement on allylboronic acid **C**, which differ in the orientation of the newly formed exocyclic double bond. We found that the formation of **D1**, that features the trisubstituted *E*-double bond, and therefore less steric hindrance through transition state **TS(C-D1)**, is favoured towards the formation of **D2** through **TS(C-D2)** by 1.4 kcal·mol^{-1}. A quite high Gibbs free energy of activation (ΔGact = 36.4 kcal·mol^{-1}) was obtained for this step (Figure S11). The activation energies for the borotropic rearrangement are high and indeed turned out to be the rate determining step in the reaction pathway. This must be the reason why this chemistry works only under microwave irradiation. It is known that the borotropic rearrangement on allylboron derivatives is influenced by the electronic nature of the substituents on the boron, and π-donor substituents rise the activation energy.[9] Nevertheless, the borotropic rearrangement on allylboronic acids has been frequently invoked to explain the formation of mixtures in reactions where the allylboronic acid is generated in situ.[10] Moreover, the 1,3-borotropic rearrangement has been experimentally observed on allylboronates under thermal conditions.[11]

Considering the relatively small energy difference between **TS(C-D1)** and **TS(C-D2)**, both reaction pathways might operate to some extent, and therefore both were calculated after this point.

[9] Hoffmann, R. W.; Zeiss, H. J. *J. Org. Chem.* **1981**, *46*, 1309.
[10] Tran, D. N.; Battilocchio, C.; Lou, S.-B.; Hawkins, J. M.; Ley, S. V. *Chem. Sci.* **2015**, *6*, 1120.
[11] Brown, H. C.; Rangaishenvi, M. V.; Jayaraman, S. *Organometallics*, **1992**, *11*, 1948

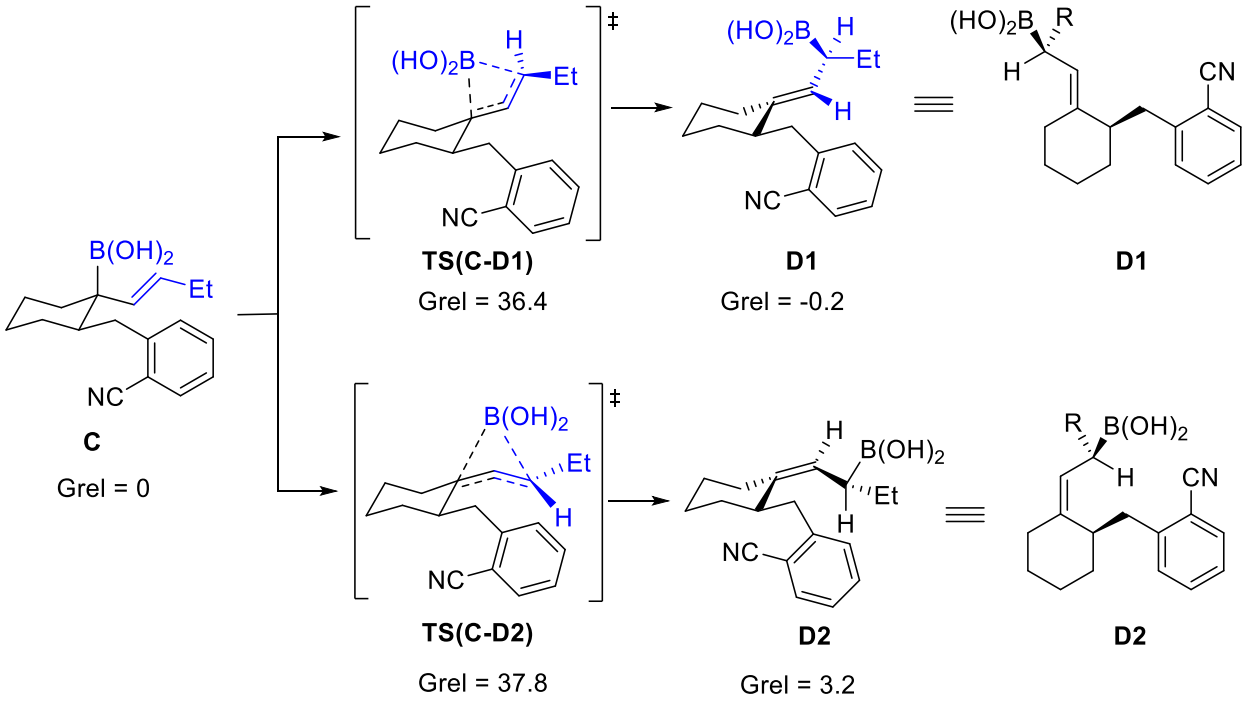
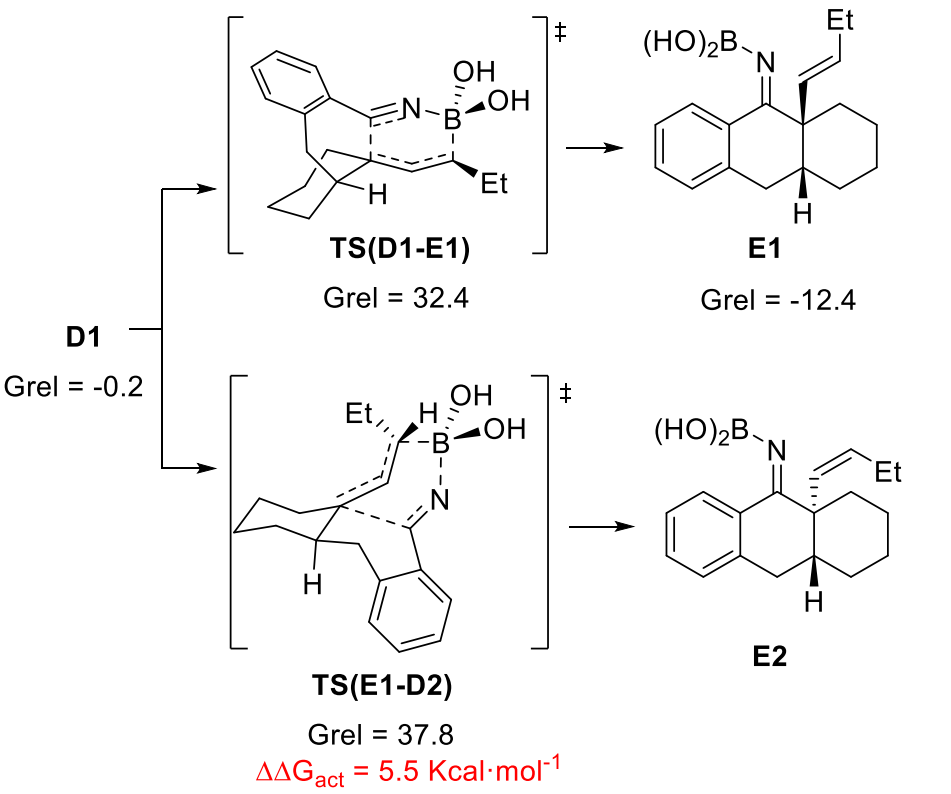


Figure S11: The 1,3-borotropic rearrangement on allylboronic acid **C** to give *Z/E* isomeric allylboronic acids **D1** and **D2** .

Intermediate **D1** can undergo cyclization through two different concerted bora-aza-ene transition states giving rise to *cis*-fused system **E1** or *trans*-fused system **E2**. The formation of the *cis*-fused system **E1** requires a previous conformational chair inversion to place the *o*-cyanobenzyl substituent in an axial arrangement. Then, the cyclization occurs through the transition state **TS(D1-E1).** An energy barrier 32.5 kcal·mol^{-1} from the most stable conformation of **D1** was obtained for this step (Figure S12). For the formation of **E2**, a conformational change by rotation through a sigma bond is needed, to place the boron atom in the appropriate arrangement for the bora-aza-ene reaction. Then, the cyclization might occur through the saddle point **TS(D1-E2)**. Noteworthy, **D2** should feature a *cis* double bond. The Gibbs free energy barrier obtained for this step was 38 kcal·mol^{-1}. Thus, according to our calculations, formation of **E1** is clearly favoured. Indeed, **TS(D1-E1)** is 5.4 kcal·mol^{-1} more stable than **TS(D1-E2)** in spite of the fact that the *o*-cyanobenzyl substituent must be placed in an axial arrangement in the transition state. Inspection of the molecular models clearly show that **TS(D1-E1)** is less distorted from the ideal geometry of the bora-aza-ene reaction than **TS(D1-E2)**. Moreover, the formation of the *cis* double bond provides additional destabilization to **TS(D1-E2)** when compared with **TS(D1-E1)** (Figure S13).



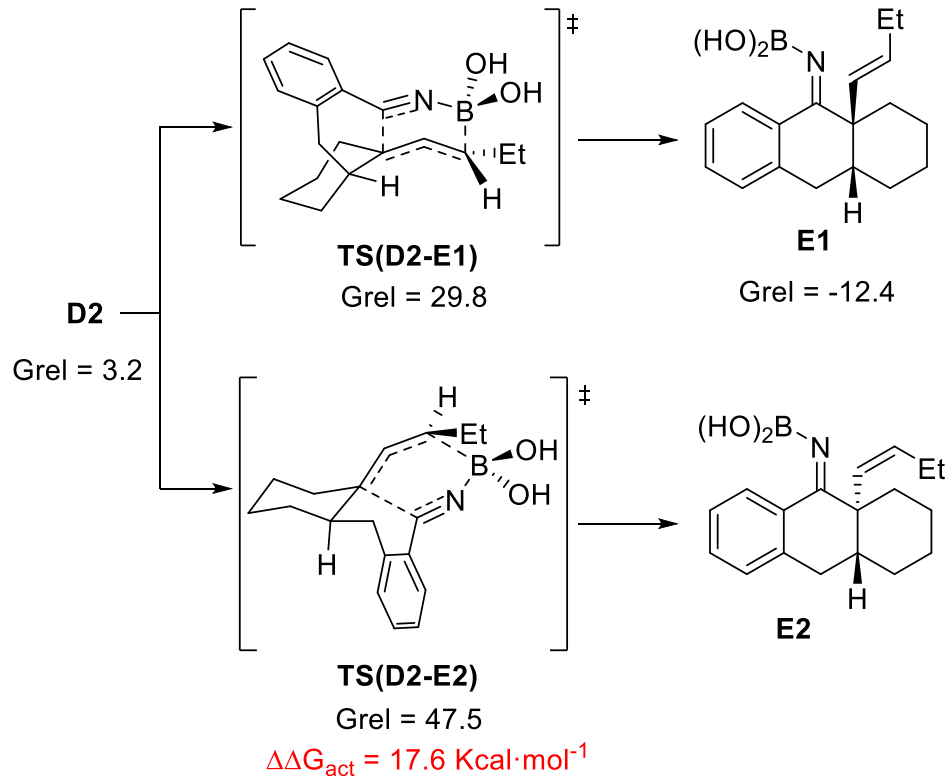


Figure S12: The bora-aza-ene cyclizations for the formation of hexahydroathracenone boroimines derivatives **E1** and **E2** by the alternative pathways from **D1** or **D2**. Energies are given in kcal/mol.

A similar study starting from **D2** led to the identification of another two saddle points, **TS(D2-E1)** that leads again to the *cis*-fused adduct **E1**, and **TS(D2-E2)** that would lead to the non observed isomer **E2** respectively (Figure S12). Again, the saddle point that leads to **E1**, **TS(D2-E1)** is much more stable than **TS(D2-E2)** ($\Delta\Delta G$ = 17.7 kcal ·mol^{-1}) pointing also to the formation of the observed adduct **E1**. Interestingly, **TS(D2-E1)** is also more stable than **TS(D1-E1)** by 2.5 kcal·mol^{-1}. In this case, the destabilization due to the *Z*-double bond in **D2** is compensated by the nearly perfect arrangement of the cyclic moiety of the bora-aza-ene reaction (Figure S13). Thus, both pathways lead to the same final product **E1**, giving support to the proposed mechanism (Figure S14). The overall reaction from the allylboronic acid **C** is exergonic ($\Delta G_{(\mathbf{E1\text{-}C})}$ = -12.5 kcal·mol^{-1}).

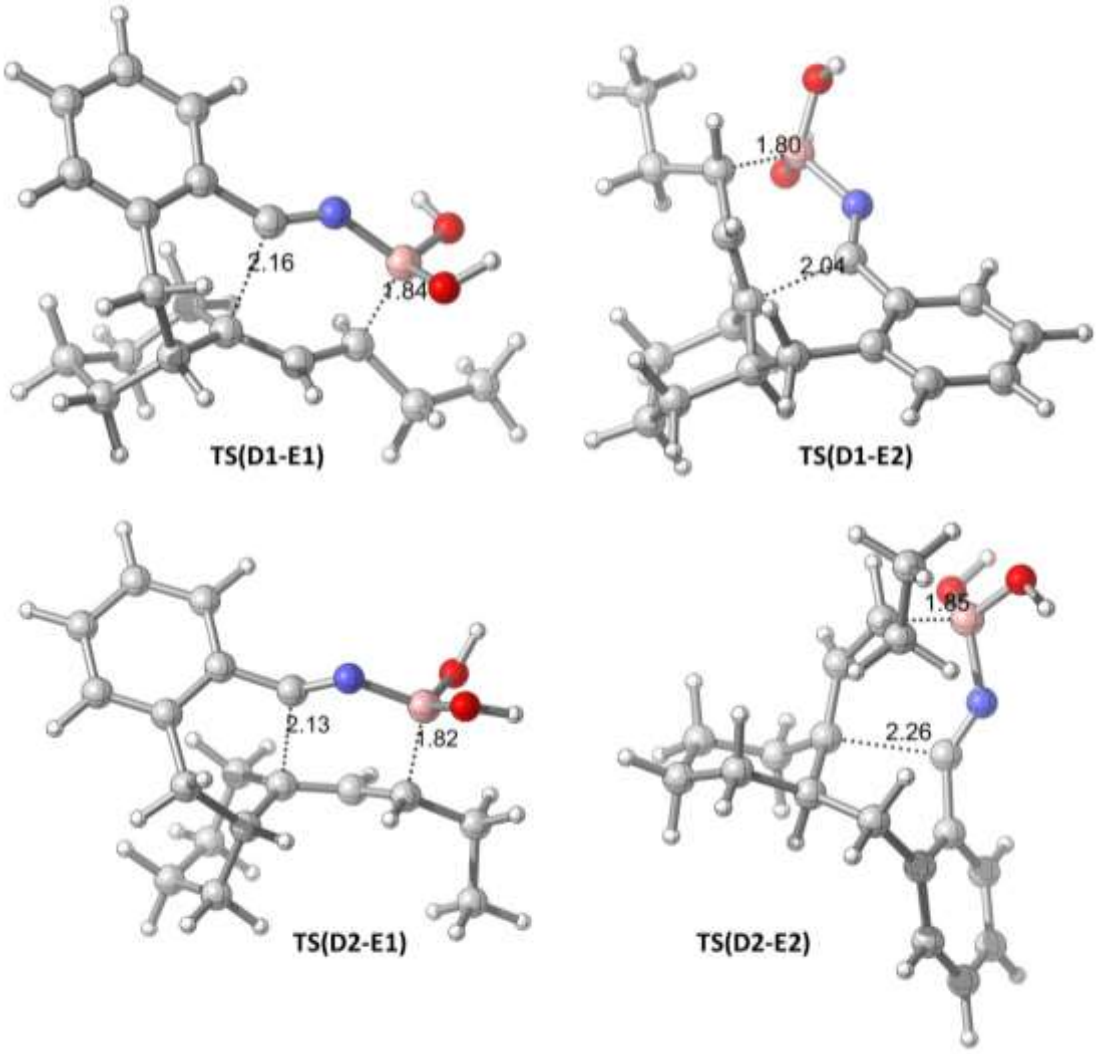


Figure S13: The four possible transition states for the intramolecular bora-aza-ene reaction for the formation of the hexahydroanthracene **E** obtained at the M06-2x/6-311++G** level

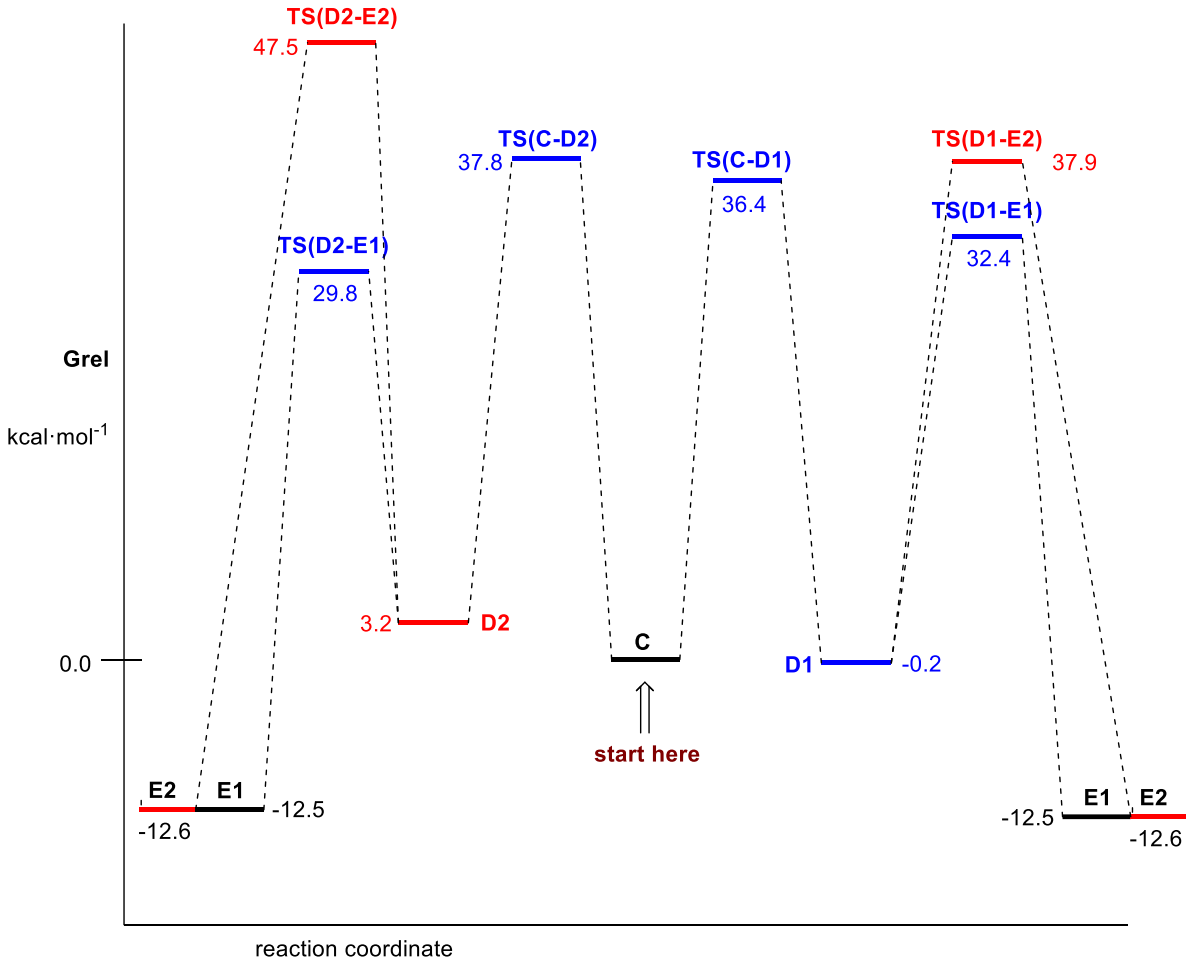


Figure S14: Energy profile for the **C** to **E1** transformation

1,3-borotropic rearrangement/bora-aza-ene cyclization for the 5-6 fused system

A similar study was then conducted for the formation of the indanone **H** obtaining results that parallel those described above. Starting from allylboronic acid **F**, the borotropic rearrangement can occur to give isomeric allylboronic acids **G1** and **G2**, through the transitions states **TS(F-G1)** and **TS(F-G2)** respectively, which are indeed very close in energy. Gibbs energy barriers of 36.2 and 35.2 kcal/mol respectively were found for this step (Figure S15).

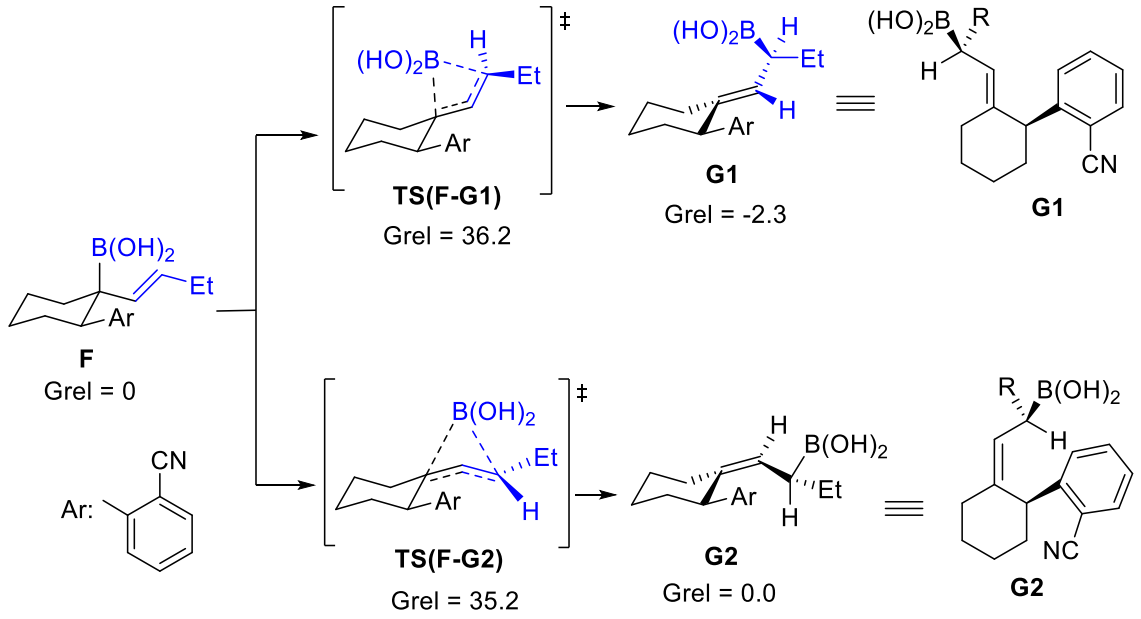


Figure S15: The 1,3-borotropic rearrangement on allylboronic acid **F** to give Z/E isomeric allylboronic acids **G1** and **G2** .

Thus, we considered the isomeric allyl boronic acids **G1** and **G2** and modelled the different saddle points for the cyclization (Figure S16). Starting from **G1**, the saddle points **TS(G1-H1)** and **TS(G1-H2)** were found. This time, and due to the shorter and more rigid tether between the allyl moiety and the cyano group, the saddle point **TS(G1-H2)** features a very distorted structure, which is far from the ideal geometry of the concerted reaction. However, the transition state **TS(G1-H1)**, that requires a previous chair inversion to place the aryl group in an axial arrangement, shows a very favourable geometry for the intramolecular carboborylation through the bora-aza-ene transition state (Figure S17). Indeed, the energy difference between both saddle points was found to be of 20 kcal/mol, justifying clearly the obtention of the *cis*-fused system. Moreover, the Gibbs free energy barrier for the bora-aza-ene reaction obtained in this case (ΔGact = 23.9 kcal·mol^{-1}) is substantially lower than those obtained for the 6-6- fused system, due to the nice arrangement of the TS for the intramolecular reaction. A very similar situation was found starting from isomer **G2** (Figure S16). Again, the saddle point **TS(G2-H2)** was very unfavoured, while **TS(G2-H1)** showed again a favourable geometry (Figure S17).

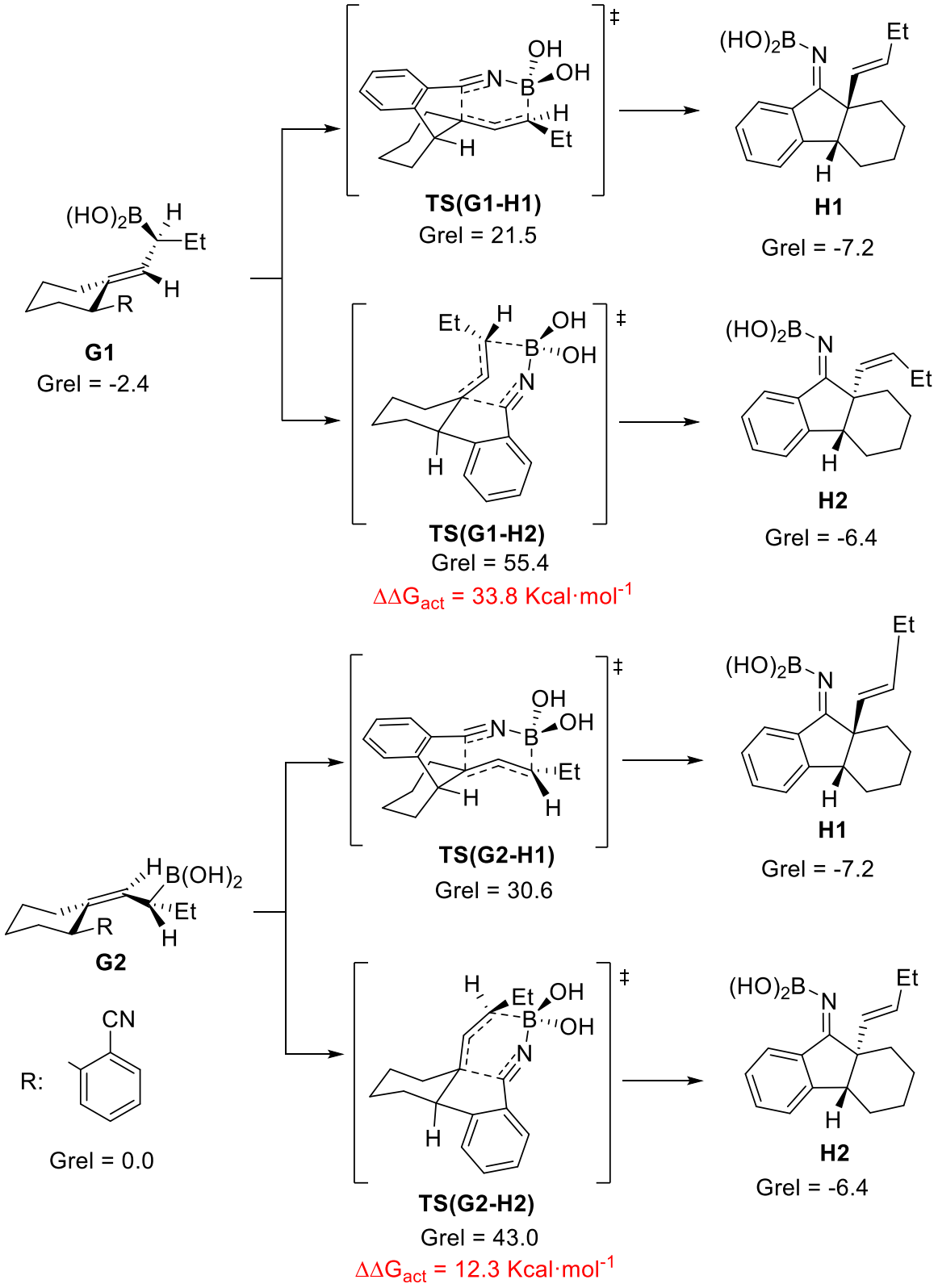


Figure S16: The bora-aza-ene cyclizations for the formation of hexahydroindanone boroimines **H1** and **H2** by the alternative pathways from **G1** or **G2**.

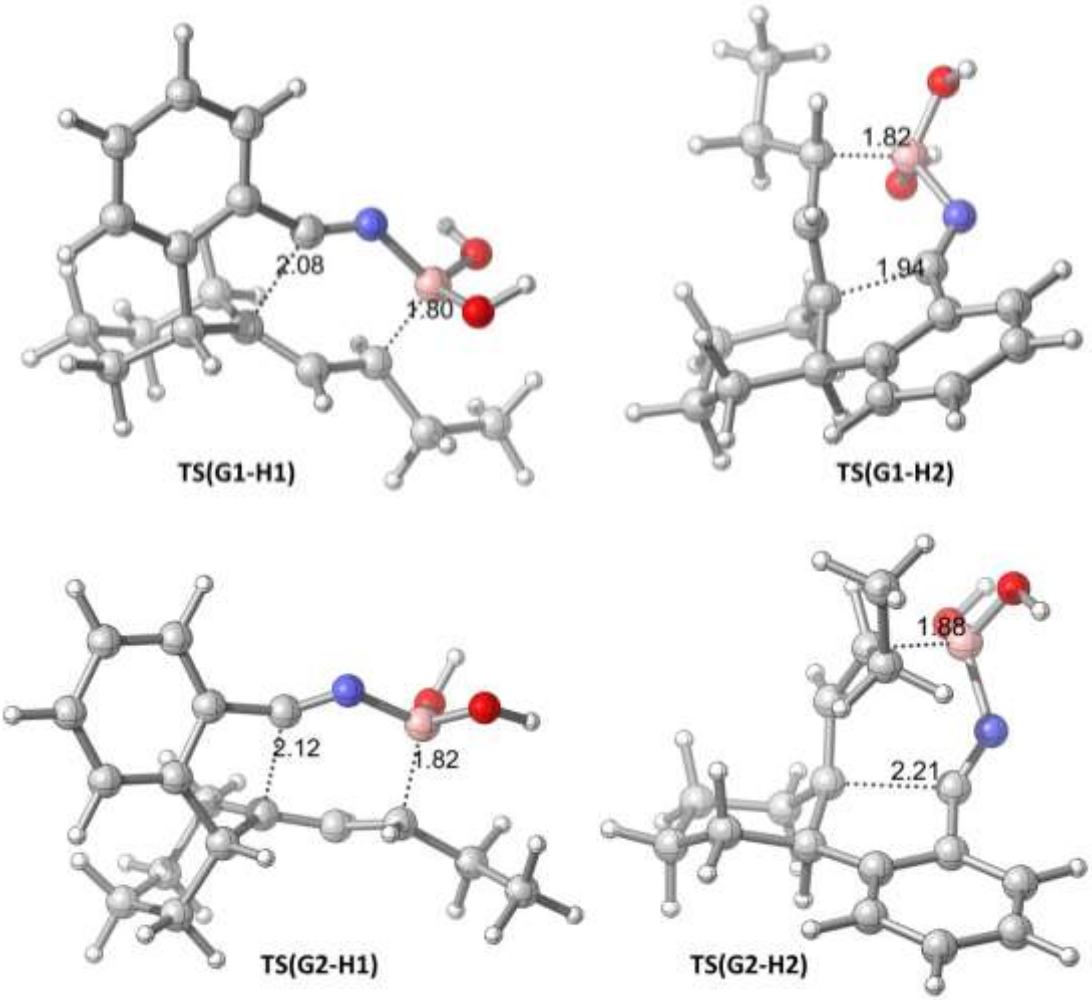


Figure S17: The four possible transition states for the intramolecular bora-aza-ene reaction for the formation of the hexahydroindene **H** obtained at the M06-2x/6-311++G** level

Therefore, like in the 6-6-adduct described above, the diastereoselective formation of the adduct **H1** can be properly explained considering that both reaction pathways, which feature similar energy profiles, can operate, but anyway both lead to the formation of the same final product (Figure S18).

As summary, the stereoselectivity observed in the formation of hexahydroindanones and hexahydroanthracenones can be successfully justified considering the diazo compound carboborylation/1,3-borotropic rearrangement/intramolecular bora-aza-ene domino sequence.

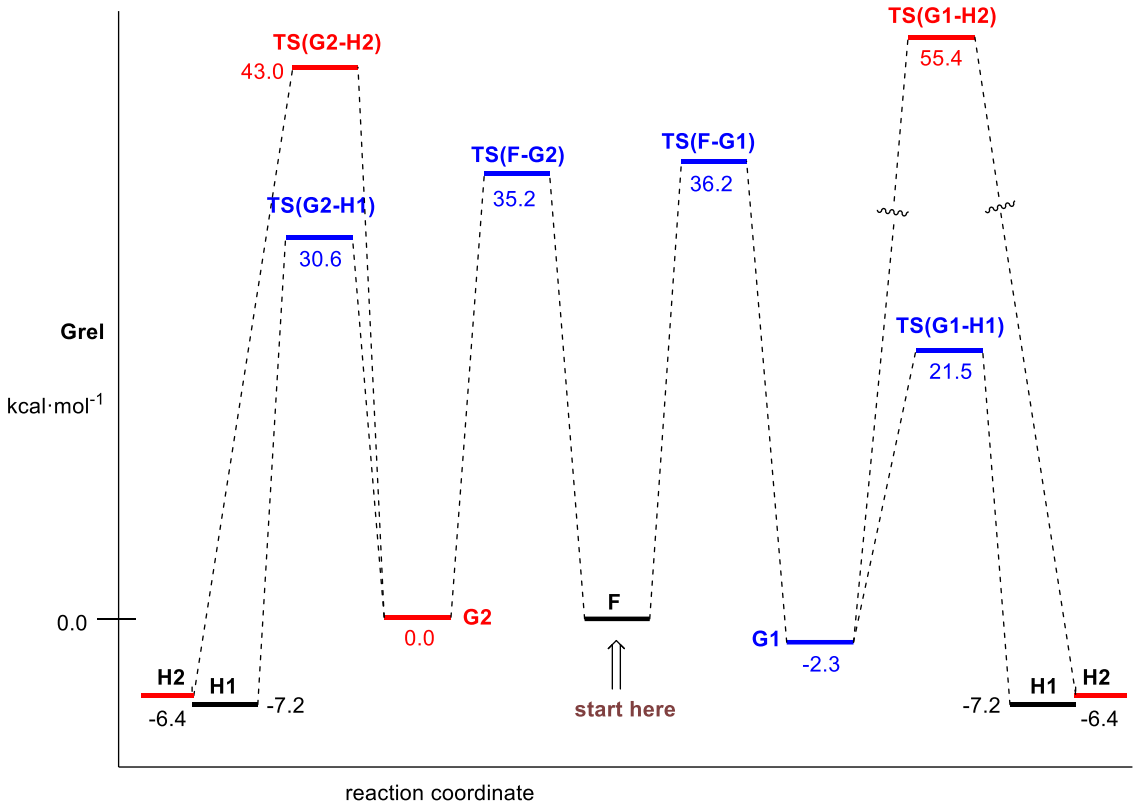
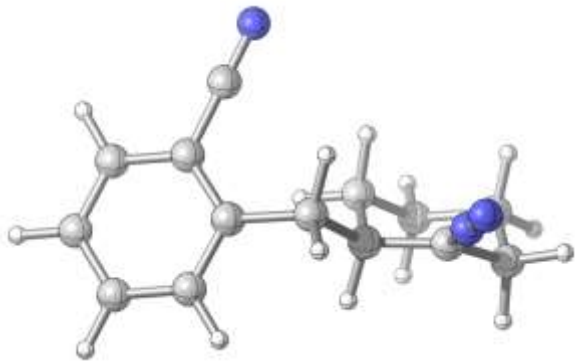


Figure S18: Energy profile for the **F** to **H1** transformation

Cartesian Coordinates and Energy Data

Diazocyclohexane A1



```
E(M062X)=                                          -706.602261178
Zero-point correction=                           0.265738 (Hartree/Particle)
Thermal correction to Energy=                    0.280721
Thermal correction to Enthalpy=                  0.281666
Thermal correction to Gibbs Free Energy=         0.222163
Sum of electronic and zero-point Energies=          -706.336524
Sum of electronic and thermal Energies=             -706.321540
Sum of electronic and thermal Enthalpies=           -706.320596
Sum of electronic and thermal Free Energies=        -706.380098
E(M062X) PCM(1,4-dioxane)=                          -706.6132815

0 1
 C                 -1.95863200    1.94280200    1.19980000
 C                 -3.34257100    1.53852200    0.68836100
 C                 -3.52306900    0.01815100    0.76368400
 C                 -0.95114300   -0.26829700    0.45934100
 C                 -0.84150100    1.26421300    0.40324800
 H                 -4.46231900   -0.29194100    0.30173800
 H                 -3.45330900    1.86213800   -0.35185200
 H                 -4.12398800    2.03340300    1.27132700
 H                 -1.86922800    1.66617100    2.25808600
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 H                 -0.89088300    1.58124700   -0.64517100
 H                  0.13325800    1.57568900    0.79151100
 H                 -3.56342400   -0.28303800    1.81964100
 C                 -2.36252000   -0.66974100    0.09234700
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 C                  2.28452600    0.31509600   -0.64150300
 C                  2.06552700   -1.31601200    1.09477300
 C                  3.58119800    0.61064600   -0.20866800
 C                  3.35160000   -1.02563000    1.53233700
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 H                  4.15485000    1.36468600   -0.73331000
 H                  3.76375300   -1.55773100    2.38158400
 H                  5.11829800    0.16540100    1.21635700
 C                  1.75459300    1.03901500   -1.76569100
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Diazocyclohexane A2

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Thermal correction to Enthalpy=                  0.251961
Thermal correction to Gibbs Free Energy=         0.196110
Sum of electronic and zero-point Energies=           -667.059169
Sum of electronic and thermal Energies=              -667.045485
Sum of electronic and thermal Enthalpies=            -667.044541
Sum of electronic and thermal Free Energies=         -667.100392
E(M062X) PCM(1,4-dioxane)=                           -667.3073241

0 1
 C                 -2.61564200    1.48799600   -1.02759100
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 C                 -3.03322600   -0.40704800    0.57301300
 C                 -0.59778400    0.41507200    0.09630400
 C                 -1.14890000    1.08823000   -1.18009600
 H                 -3.57747600   -1.33857100    0.74120400
 H                 -3.41664300   -0.44421800   -1.54940400
 H                 -4.53680400    0.56452100   -0.63245400
 H                 -2.71195200    2.21988100   -0.21648800
 H                 -0.57909100    1.18366700    0.88136600
 H                 -1.04353000    0.38604300   -2.01484800
 H                 -0.53059100    1.96177700   -1.40552100
 H                 -3.26098600    0.25969600    1.41698200
 C                 -1.54966500   -0.68163200    0.53035200
 N                 -1.09172600   -1.74289800    1.10449900
 N                 -0.68258500   -2.69661300    1.56884000
 H                 -2.95783500    1.97993800   -1.94130400
 C                  0.81584800   -0.05679500   -0.15273000
 C                  1.91785400    0.71744600    0.24101800
 C                  1.06956900   -1.23924300   -0.84874800
 C                  3.22688200    0.31580600   -0.04260600
 C                  2.36801500   -1.64288200   -1.13168800
 H                  0.23250400   -1.85061700   -1.16907300
 C                  3.45118100   -0.86765800   -0.72673000
 H                  4.05283900    0.93875000    0.27769200
 H                  2.53587800   -2.56914500   -1.66805600
 H                  4.46376200   -1.18378500   -0.94399700
 C                  1.71736300    1.96437500    0.92961100
 N                  1.56427000    2.96918400    1.46920200
```

Alkenylboronic acid

```
E(M062X)=                                           -333.202528058
Zero-point correction=                           0.134588 (Hartree/Particle)
Thermal correction to Energy=                    0.143096
Thermal correction to Enthalpy=                  0.144040
Thermal correction to Gibbs Free Energy=         0.100988
Sum of electronic and zero-point Energies=           -333.067940
Sum of electronic and thermal Energies=              -333.059432
Sum of electronic and thermal Enthalpies=            -333.058488
Sum of electronic and thermal Free Energies=         -333.101540
E(M062X) PCM(1,4-dioxane)=                           -333.214092

0 1
 B                 -1.68272100   -0.00993800    0.02730800
 O                 -2.80661200   -0.76120600    0.26679300
 H                 -2.63190000   -1.70100100    0.33614200
 O                 -1.84191700    1.34138300   -0.07891200
 H                 -2.75893100    1.60459300    0.03678200
 C                 -0.26252900   -0.62650700   -0.12509700
 H                 -0.11560200   -1.70549400   -0.05819200
 C                  0.81405800    0.13485300   -0.34322600
```

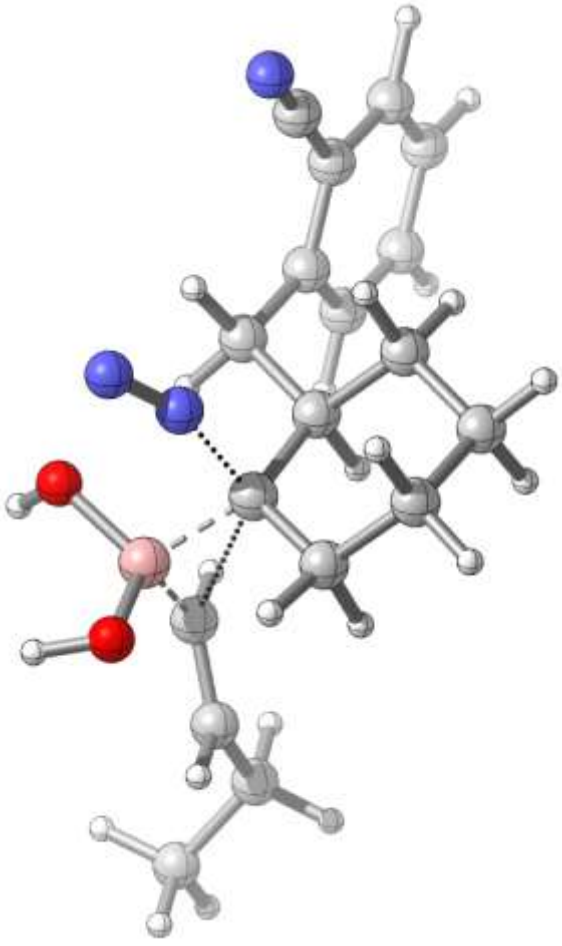
H	0.67468500	1.21490900	-0.40673600
C	2.22277800	-0.35402900	-0.48886400
H	2.24087100	-1.44635700	-0.44668600
H	2.59837000	-0.06127600	-1.47581000
C	3.13983200	0.23595300	0.58856400
H	3.13309200	1.32769900	0.54940300
H	2.80720500	-0.06562400	1.58372200
H	4.16920700	-0.10079600	0.45352800

N_2

```
E(M062X)=                                          -109.522095878
Zero-point correction=                           0.005731 (Hartree/Particle)
Thermal correction to Energy=                    0.008092
Thermal correction to Enthalpy=                  0.009036
Thermal correction to Gibbs Free Energy=        -0.012692
Sum of electronic and zero-point Energies=           -109.516364
Sum of electronic and thermal Energies=              -109.514004
Sum of electronic and thermal Enthalpies=            -109.513060
Sum of electronic and thermal Free Energies=         -109.534788
E(M062X) PCM(1,4-dioxane)=                           -109.5224671

0 1
N                  0.00000000    0.00000000    0.54504900
N                  0.00000000    0.00000000   -0.54504900
```

TS1



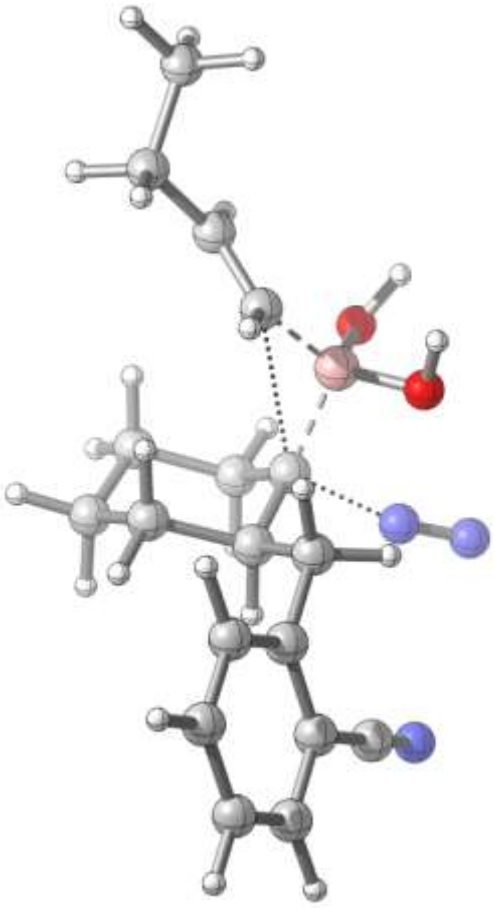
E(M062X)= -1039.79252756
Zero-point correction= 0.398172 (Hartree/Particle)
Thermal correction to Energy= 0.423009
Thermal correction to Enthalpy= 0.423953
Thermal correction to Gibbs Free Energy= 0.342479
Sum of electronic and zero-point Energies= -1039.394356
Sum of electronic and thermal Energies= -1039.369518
Sum of electronic and thermal Enthalpies= -1039.368574
Sum of electronic and thermal Free Energies= -1039.450048
E(M062X) PCM(1,4-dioxane)= -1039.81243981

Imaginary frequency: -312.8194

0 1

N	0.41556900	-2.50298000	-0.80539100
N	0.33106200	-3.19947200	-1.64087200
B	2.09941700	-0.52941600	-0.97984400
O	3.21266900	-1.47281700	-0.92815700
H	3.63685900	-1.51083400	-1.78618800
O	1.45591100	-0.49599600	-2.29513900
H	1.78505200	0.23402000	-2.82071700
C	2.45873300	0.94595300	-0.40099400
C	3.61605100	1.24350100	0.19464000
H	4.34875000	0.44197400	0.30973900
C	1.00221200	-1.11382800	0.15513500
C	1.64041500	-1.80861300	1.33499700
C	-0.28195200	-0.37435300	0.48172400
C	0.68417000	-2.54997300	2.26618100
H	2.12312400	-0.97599800	1.86553100
H	2.45411400	-2.43720700	0.97232800
C	-1.22037700	-1.16000500	1.40788200
H	0.11533700	0.48170800	1.05159700
C	-0.50464600	-1.67654600	2.65344800
H	1.22789000	-2.88474100	3.15265200
H	0.31990400	-3.45457100	1.76339000
H	-2.06018000	-0.52311800	1.69627000
H	-1.64810400	-2.00243100	0.84808400
H	-0.15439700	-0.82596500	3.25018600
H	1.73463500	1.76280200	-0.50894600
C	4.03674600	2.59619300	0.69667700
H	4.23588200	2.53801500	1.77339900
H	3.21891800	3.31014100	0.56035700
C	5.29818300	3.10044700	-0.01199400
H	5.62110500	4.06500200	0.38562200
H	6.12030000	2.39133900	0.11262200
H	5.11602300	3.21322000	-1.08293700
C	-1.00136200	0.18842000	-0.75979900
H	-0.29576900	0.77527300	-1.34575500
H	-1.31800300	-0.63613200	-1.40443200
C	-2.18464900	1.04654300	-0.39518800
C	-3.50028700	0.55992100	-0.42314200
C	-1.99467900	2.36829900	0.00646000
C	-4.58521400	1.36817900	-0.06922200
C	-3.06665700	3.17661800	0.36471900
C	-4.36654400	2.67824200	0.32583400
H	-5.58700700	0.95837500	-0.10756800
H	-2.88909600	4.20133600	0.66923100
H	-5.20404300	3.30769700	0.59944200
H	-0.98473300	2.76556000	0.02971000
C	-3.74500600	-0.80607100	-0.80126100
N	-3.92798500	-1.90585700	-1.08703300
H	-1.20362200	-2.23728800	3.27846700

TS1′



E(M062X)=	-1039.79122032
Zero-point correction=	0.399603 (Hartree/Particle)
Thermal correction to Energy=	0.424110
Thermal correction to Enthalpy=	0.425054
Thermal correction to Gibbs Free Energy=	0.345302
Sum of electronic and zero-point Energies=	-1039.391617
Sum of electronic and thermal Energies=	-1039.367110
Sum of electronic and thermal Enthalpies=	-1039.366166
Sum of electronic and thermal Free Energies=	-1039.445919
E(M062X) PCM(1,4-dioxane)=	-1039.80965

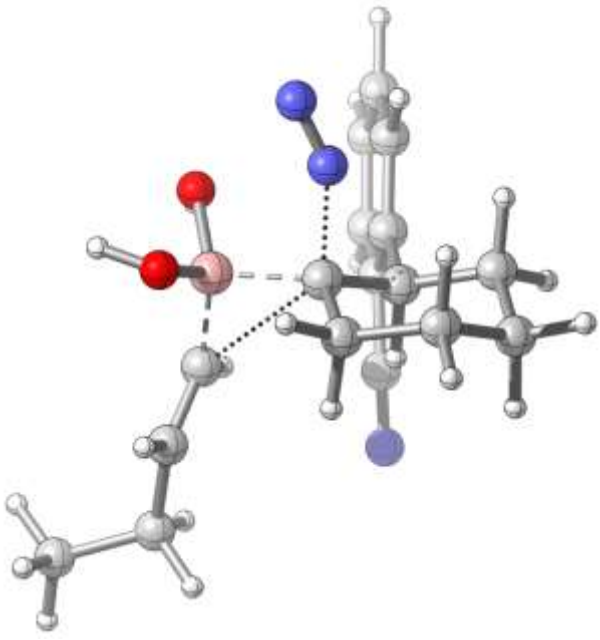
Imaginary frequency: -274.2114

0 1

N	-0.04161500	2.58911600	0.38891500
N	0.15761800	3.49405300	0.96157700
B	-1.90117200	0.85493900	0.79814300
O	-2.87926900	1.90812400	0.52719700
H	-3.44284200	2.03602900	1.29165900
O	-1.22007400	1.01884400	2.09219000
H	-1.61427100	0.45793000	2.76078800
C	-2.50076400	-0.64595300	0.64497900
C	-3.72872100	-0.92360100	0.20048400
C	-4.36537600	-2.28397900	0.14078900
H	-4.34721900	-0.09288500	-0.14694500
C	-0.73501800	1.11989600	-0.38947400
C	0.48723300	0.23989500	-0.55947300
C	-1.19812400	1.70558400	-1.70543500
C	0.07341500	-0.92899100	-1.48405500
H	1.24856100	0.81343500	-1.10445200
C	-1.63993100	0.53180900	-2.60034700

H	-0.37634700	2.22799500	-2.20845100
H	-2.02392000	2.39299200	-1.52829300
C	-0.47903300	-0.43529800	-2.82037100
H	0.95511000	-1.55709800	-1.63998200
H	-0.68012000	-1.53816100	-0.97695300
H	-1.99531900	0.93896500	-3.54959800
H	-2.47770900	0.01415200	-2.12802000
H	0.31716000	0.07163000	-3.37841700
H	-1.90656400	-1.50010400	0.99050400
H	-3.65263000	-3.03659700	0.49141700
H	-4.60186900	-2.52804000	-0.90226700
C	1.09398300	-0.26820400	0.76125000
H	0.42134200	-1.00251500	1.20827300
H	1.15937100	0.55480100	1.47717600
C	2.45567700	-0.87471400	0.54785700
C	3.57150800	-0.05751600	0.29984800
C	2.65975700	-2.25263400	0.56617300
C	4.84092700	-0.59674700	0.07978800
C	3.92000800	-2.79844300	0.34538700
H	1.81392900	-2.90378200	0.75896900
C	5.01339800	-1.97276800	0.10236400
H	5.67698700	0.06700300	-0.10331100
H	4.05021200	-3.87403000	0.36634100
H	5.99503000	-2.39810600	-0.06505700
C	3.39256100	1.36893700	0.27112000
N	3.20904500	2.50490300	0.23846000
H	-0.80087800	-1.28736200	-3.42424500
C	-5.65338700	-2.35440200	0.96729200
H	-6.12306300	-3.33742100	0.88965500
H	-6.37419000	-1.60835400	0.62319800
H	-5.44417300	-2.15465500	2.02049400

TS2



E(M062X)=	-1000.48249089
Zero-point correction=	0.369674 (Hartree/Particle)
Thermal correction to Energy=	0.393123
Thermal correction to Enthalpy=	0.394067
Thermal correction to Gibbs Free Energy=	0.317013
Sum of electronic and zero-point Energies=	-1000.112817
Sum of electronic and thermal Energies=	-1000.089368

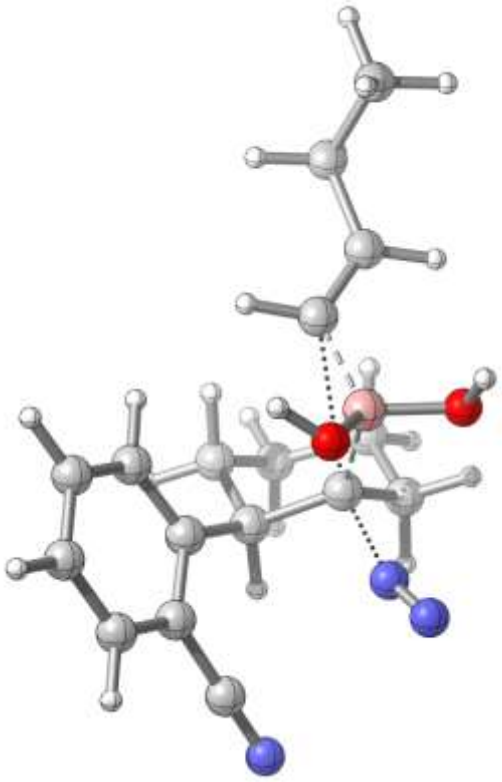
Sum of electronic and thermal Enthalpies= -1000.088424
Sum of electronic and thermal Free Energies= -1000.165478
E(M062X) PCM(1,4-dioxane)= -1000.50221033

Imaginary frequency: -337.08

0 1

N	1.09143200	2.17375900	-1.11671100
N	1.40901100	2.59870300	-2.07181000
B	-0.88686400	0.53971800	-1.34407700
O	-1.57907200	1.66032600	-1.95720000
H	-1.87417200	1.40119000	-2.83197300
O	0.02406300	-0.08670700	-2.29305200
H	0.06865100	-1.03691900	-2.17921800
C	-1.82479800	-0.50762700	-0.53784700
C	-3.08359200	-0.25343700	-0.17283000
H	-3.50644100	0.71997800	-0.43336800
C	-0.02736600	1.27160300	-0.07417300
C	-0.72185400	2.41725700	0.62977500
C	0.84683600	0.45407400	0.86159000
C	0.16345600	3.24644000	1.56111500
H	-1.50991500	1.91089600	1.20212600
H	-1.23345200	3.02581000	-0.11694900
C	1.76546400	1.30922600	1.75373300
H	0.06867100	0.03818500	1.51820400
C	0.96805100	2.36611500	2.51588000
H	-0.45711300	3.94981300	2.12089400
H	0.85102700	3.85243600	0.95803800
H	2.29296500	0.64941100	2.44720700
H	2.53133600	1.78708100	1.12965200
H	0.28565800	1.86223600	3.20982700
H	-1.43157800	-1.49331600	-0.26819000
C	-4.00239700	-1.20708300	0.53717100
H	-4.34268200	-0.75187100	1.47494600
H	-3.45002500	-2.11163500	0.80650000
C	-5.22642200	-1.56327500	-0.31314800
H	-5.90327900	-2.22885600	0.22695300
H	-5.78429900	-0.66435700	-0.58793400
H	-4.91935100	-2.05972100	-1.23622100
C	1.58923300	-0.71445900	0.24789600
C	1.28009700	-2.03506900	0.60987700
C	2.64466200	-0.52516200	-0.64394600
C	1.96570300	-3.12348300	0.05831800
C	3.33079900	-1.59931100	-1.19252900
H	2.93521900	0.47780000	-0.92940600
C	2.98578700	-2.90466800	-0.85178900
H	1.69195300	-4.12731800	0.35860700
H	4.13505600	-1.41770300	-1.89525000
H	3.51548600	-3.74372200	-1.28518400
C	0.26375200	-2.30449100	1.59225900
N	-0.53410700	-2.52453400	2.39198500
H	1.64184800	2.97763600	3.12078800

TS2′



E(M062X)= -1000.48075221
Zero-point correction= 0.370611 (Hartree/Particle)
Thermal correction to Energy= 0.393969
Thermal correction to Enthalpy= 0.394913
Thermal correction to Gibbs Free Energy= 0.318601
Sum of electronic and zero-point Energies= -1000.110142
Sum of electronic and thermal Energies= -1000.086783
Sum of electronic and thermal Enthalpies= -1000.085839
Sum of electronic and thermal Free Energies= -1000.162151
E(M062X) PCM(1,4-dioxane)= -1000.4986731

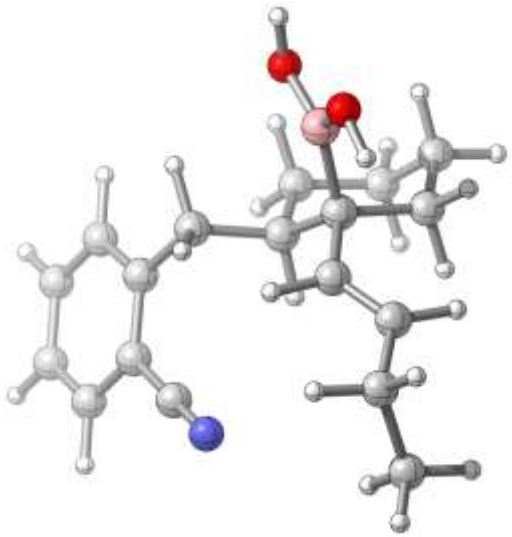
Imaginary frequency: -277.7165

0 1

N	-1.07623000	-1.49347900	1.51090800
N	-1.50854300	-1.64782200	2.49928600
B	0.98459300	-0.03210200	1.15802000
O	1.58606800	-0.95209400	2.11647600
H	1.87078200	-0.45471200	2.88557600
O	0.05566300	0.87743400	1.83010300
H	0.11734300	1.77448400	1.50195800
C	2.06991900	0.74458600	0.23392000
C	3.36969200	0.44090900	0.21199500
C	4.44437800	1.18464200	-0.53017300
H	3.70335400	-0.41637700	0.80087800
C	0.07949800	-1.09869600	0.18200200
C	-0.82824200	-0.64625400	-0.95724700
C	0.65096400	-2.47525300	-0.08539000
C	0.07727100	-0.54494100	-2.21238300
H	-1.54034000	-1.45398500	-1.16530800
C	1.52916500	-2.39637800	-1.34900700
H	-0.15234000	-3.19671200	-0.27409600
H	1.23682800	-2.79205900	0.77680800
C	0.71640100	-1.89290700	-2.53917100
H	-0.54265200	-0.18804400	-3.03872000
H	0.86887600	0.18943700	-2.04716100
H	1.93471500	-3.39146400	-1.54449000
H	2.37077300	-1.72601000	-1.16308500

H	-0.06526500	-2.61969600	-2.78913000
H	1.77515000	1.62033800	-0.35520300
H	3.99698500	2.00922500	-1.09364100
H	4.91193200	0.51374500	-1.26144200
C	-1.62098000	0.61767600	-0.69231400
C	-1.10626200	1.88659500	-0.95242500
C	-2.92896000	0.54407900	-0.18782500
C	-1.83906400	3.03384600	-0.67629400
H	-0.11302500	1.98330400	-1.37062900
C	-3.67070000	1.69457700	0.09710500
C	-3.11982800	2.94281500	-0.13857800
H	-1.40719400	4.00630900	-0.88235900
H	-4.67305000	1.59317000	0.49434900
H	-3.68825400	3.83721400	0.08339000
C	-3.54427800	-0.73736300	0.03000000
N	-4.02293300	-1.77108800	0.19606400
H	1.35499200	-1.79233400	-3.42011700
C	5.52721500	1.71814700	0.41317100
H	6.31733500	2.23315100	-0.13755600
H	5.98591200	0.90126900	0.97598400
H	5.09712700	2.41779100	1.13313900

Allylboronic acid C



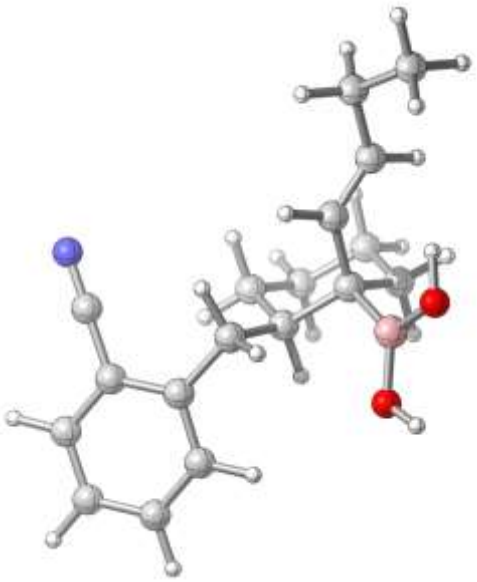
E(M062x)= -930.389111144
Zero-point correction= 0.395476 (Hartree/Particle)
Thermal correction to Energy= 0.416995
Thermal correction to Enthalpy= 0.417939
Thermal correction to Gibbs Free Energy= 0.344817
Sum of electronic and zero-point Energies= -929.993635
Sum of electronic and thermal Energies= -929.972116
Sum of electronic and thermal Enthalpies= -929.971172
Sum of electronic and thermal Free Energies= -930.044294
E(M062x) PCM(1,4-dioxane)= -930.40589748

0 1

C	-0.42710800	-2.06807000	0.94899000
C	1.91866700	-2.44143900	1.73556700
C	2.31854400	-1.07630800	1.18047300
C	1.48273600	-0.63486800	-0.04848100
C	-0.03519900	-0.73532000	0.29229500
H	2.55520500	-2.68921400	2.58937200
H	-0.34828000	-2.86424000	0.20117100
H	-1.47596800	-2.01287000	1.25728100
H	2.17940300	-0.32551300	1.96929900
H	3.38394500	-1.06822700	0.92572800

H	-0.23077800	0.06698800	1.01931900
H	2.07422400	-3.22020900	0.98025500
C	1.80555900	0.80218400	-0.40539300
H	1.16885700	1.26299800	-1.15838600
C	2.77201600	1.57447300	0.09376100
H	3.44031100	1.19431300	0.86432000
C	2.96329600	3.01665000	-0.28234900
H	3.98761100	3.17414300	-0.63829400
H	2.28869700	3.27115500	-1.10393100
B	1.94290200	-1.55313200	-1.27211300
O	1.28200900	-2.70750500	-1.59015100
H	1.69904000	-3.15552100	-2.33356300
O	3.04739100	-1.23975400	-2.01142400
H	3.41458500	-0.38505900	-1.75860900
C	2.69165600	3.93958900	0.90989500
H	3.33620600	3.68520700	1.75566100
H	2.87503000	4.98366400	0.64804100
H	1.65199900	3.84090300	1.22692300
C	0.44923500	-2.42279000	2.14680700
H	0.14757000	-3.39097300	2.55534000
H	0.30781800	-1.68045000	2.94193200
C	-0.93729300	-0.49402300	-0.94190300
H	-0.95697100	-1.40661100	-1.54286600
H	-0.52673400	0.29777600	-1.57275900
C	-2.34210700	-0.11570700	-0.55402100
C	-3.37917000	-1.04677900	-0.55240900
C	-2.64657300	1.19347500	-0.14546900
C	-4.66449600	-0.69656500	-0.15372500
H	-3.16793800	-2.06255700	-0.86882900
C	-3.93546300	1.55373900	0.25536900
C	-4.94591500	0.60402200	0.25346500
H	-5.45117300	-1.44192200	-0.16267100
H	-4.13168500	2.57470000	0.55926500
H	-5.94680600	0.87827000	0.56236200
C	-1.61316600	2.19437400	-0.15450200
N	-0.78217100	2.99102300	-0.17334500

Allylboronic acid C′



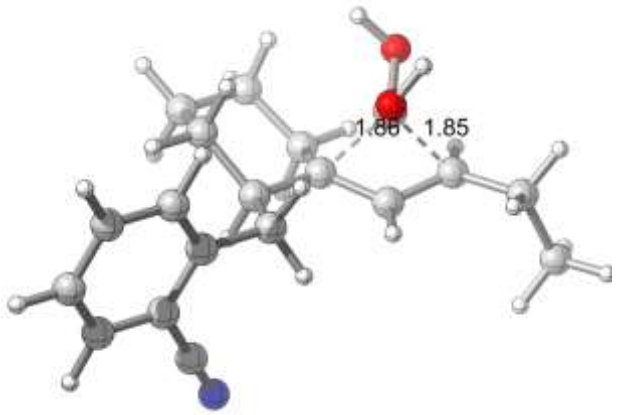
E(M062X)=	-930.390243177
Zero-point correction=	0.394967 (Hartree/Particle)
Thermal correction to Energy=	0.416668
Thermal correction to Enthalpy=	0.417612

Thermal correction to Gibbs Free Energy= 0.343254
Sum of electronic and zero-point Energies= -929.995276
Sum of electronic and thermal Energies= -929.973575
Sum of electronic and thermal Enthalpies= -929.972631
Sum of electronic and thermal Free Energies= -930.046989
E(M062x) PCM(1,4-dioxane)= -930.4073452

0 1

B	-1.48911700	-1.97052700	-0.66027300
O	-0.50189800	-2.91788800	-0.66016100
H	-0.72731800	-3.66394900	-1.22481200
O	-2.58927300	-2.18880800	-1.43483600
H	-3.20104600	-1.44401700	-1.39933100
C	-2.10494700	0.45347000	-0.32130200
C	-3.37008800	0.81212500	-0.09340100
C	-4.08664500	1.91126000	-0.82547100
H	-3.95437700	0.29294700	0.66624000
C	-1.34775800	-0.70100900	0.29376600
C	0.14713200	-0.35841400	0.52178500
C	-1.94542200	-1.15399600	1.65436200
C	0.31879800	0.71258500	1.60285500
H	0.61481500	-1.28337800	0.88264200
C	-1.77365800	-0.10038100	2.75250700
H	-1.42577700	-2.07003300	1.96054400
H	-2.99987700	-1.42416300	1.54096000
C	-0.29998600	0.26737800	2.92824100
H	1.38214300	0.93140100	1.74356500
H	-0.15313000	1.64366200	1.26302500
H	-2.18454400	-0.48135000	3.69183200
H	-2.34146000	0.79819300	2.49327200
H	0.24801700	-0.60703000	3.30085100
H	-1.56885700	1.01545600	-1.08665500
H	-3.38500700	2.42758300	-1.48618400
H	-4.44840800	2.65138900	-0.10373900
C	2.37044400	-0.07344700	-0.63016800
C	2.96999300	-1.33381800	-0.60099200
C	3.20021200	1.04617700	-0.48038700
C	4.34058100	-1.47538900	-0.43359500
H	2.33544800	-2.20848400	-0.70859100
C	4.58284300	0.91056100	-0.31071600
C	5.15209800	-0.35165100	-0.28808800
H	4.78083500	-2.46551100	-0.41673500
H	5.19250300	1.79876400	-0.19891100
H	6.22165000	-0.46084500	-0.15806400
C	2.63097600	2.36719900	-0.48761300
N	2.17558000	3.42416900	-0.48816900
H	-0.19190800	1.05418700	3.67924700
C	-5.27474100	1.37932900	-1.63355000
H	-5.81245500	2.19059700	-2.12813500
H	-5.98167400	0.85216500	-0.98767400
H	-4.93572900	0.68000000	-2.40224700
C	0.87539800	0.03582000	-0.77890600
H	0.60498300	1.05416300	-1.06852300
H	0.56569000	-0.63153100	-1.59002700

TS(C-D1)



E(M062X) =	-930.32701442
Zero-point correction=	0.393375 (Hartree/Particle)
Thermal correction to Energy=	0.414513
Thermal correction to Enthalpy=	0.415458
Thermal correction to Gibbs Free Energy=	0.343293
Sum of electronic and zero-point Energies=	-929.933639
Sum of electronic and thermal Energies=	-929.912501
Sum of electronic and thermal Enthalpies=	-929.911557
Sum of electronic and thermal Free Energies=	-929.983721
E(M062x) PCM(1,4-dioxane)=	-930.40589748

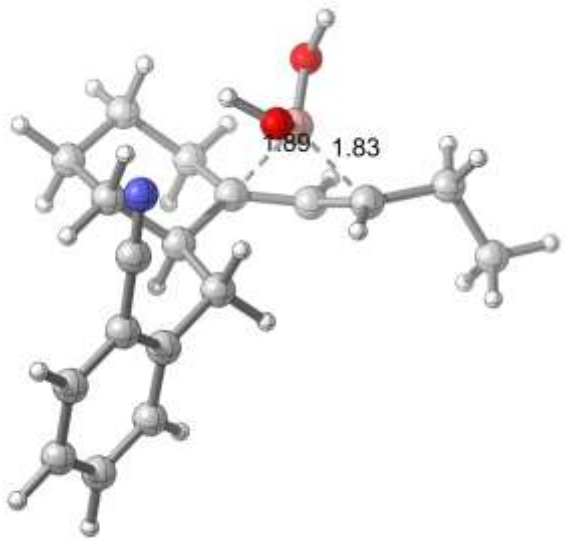
Imaginary frequency: -428.0589 cm^{-1}

0 1

C	0.69460300	1.89920400	0.01304400
C	-1.28940000	2.93132800	1.18831300
C	-1.80845500	1.52566400	1.50172300
C	-1.27526600	0.47351800	0.53817900
C	0.24905900	0.49173400	0.43803800
H	-1.59303100	3.61846500	1.98262500
H	0.27980100	2.11391900	-0.98179900
H	1.78337700	1.93720700	-0.07610000
H	-1.47002000	1.24126200	2.50778800
H	-2.89784900	1.52572900	1.51463100
H	0.63949300	0.32713300	1.45404500
H	-1.75448100	3.29901800	0.26869600
C	-2.00103100	-0.71280000	0.29249000
H	-1.44436100	-1.52431300	-0.17080800
C	-3.37512500	-0.75580700	0.01391400
H	-4.05150200	-0.07709100	0.52267800
C	-3.98140100	-1.97351500	-0.63018200
H	-4.83701800	-1.66489500	-1.23887200
H	-3.25114100	-2.41332200	-1.31783700
B	-2.37972000	0.45147300	-0.96432800
O	-3.22860800	1.58549800	-0.99350000
H	-2.74666500	2.34941300	-1.31923600
O	-1.74324500	0.03689300	-2.16263100
H	-2.32062800	0.18530400	-2.91556400
C	-4.43287600	-3.02092700	0.39209500
H	-5.16623700	-2.59770500	1.08256600
H	-4.88753900	-3.88464400	-0.09778700
H	-3.58279200	-3.36974300	0.98362600
C	0.22898200	2.94783400	1.02333600
H	0.56536100	3.94270800	0.71937500
H	0.70178300	2.73499100	1.98989100
C	0.84173000	-0.60811600	-0.46629000
H	0.57713800	-1.58934700	-0.06124300
H	0.40585200	-0.52972800	-1.46451900
C	2.34315000	-0.53647700	-0.55942300

C	3.15976700	-0.97352600	0.49572400
C	2.97464400	-0.01360700	-1.68682100
C	4.55287700	-0.88303400	0.42803200
C	4.35956700	0.07950700	-1.76233800
H	2.36184200	0.32636900	-2.51469800
C	5.15317300	-0.35285900	-0.70360900
H	5.14890200	-1.23292600	1.26199200
H	4.82187800	0.49050600	-2.65211900
H	6.23218800	-0.28208700	-0.76130900
C	2.55602100	-1.54317700	1.67029200
N	2.06556600	-2.00176800	2.60508300

TS(C-D2)



E(M062X)= -930.3248904
Zero-point correction= 0.392930 (Hartree/Particle)
Thermal correction to Energy= 0.414143
Thermal correction to Enthalpy= 0.415088
Thermal correction to Gibbs Free Energy= 0.343357
Sum of electronic and zero-point Energies= -929.931960
Sum of electronic and thermal Energies= -929.910747
Sum of electronic and thermal Enthalpies= -929.909803
Sum of electronic and thermal Free Energies= -929.981533
E(M062x) PCM(1,4-dioxane)= -930.3441559

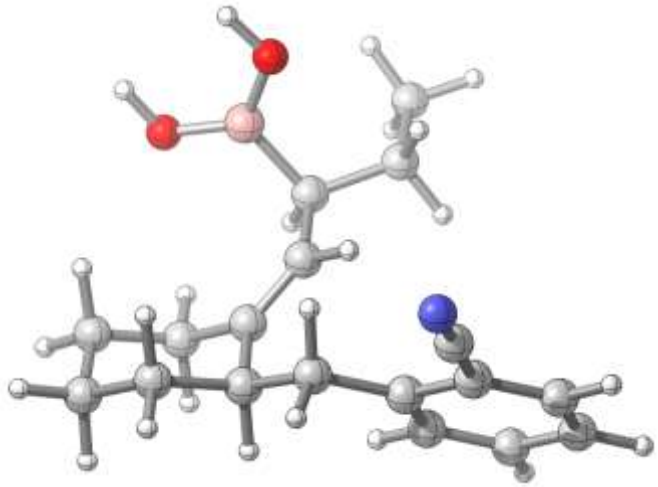
Imaginary frequency: -435.9869 cm^{-1}

0 1

C	-1.36892200	3.14060200	0.81954900
C	0.66165400	1.84248300	0.06119000
C	0.09561300	0.57096000	0.71485800
C	-1.43017800	0.63662600	0.80285300
C	-1.90336500	1.88932800	1.52009100
H	1.75429700	1.81921800	0.10356400
H	-1.78964100	3.17958000	-0.19222300
H	-1.70900500	4.03780000	1.34371500
H	0.42694400	0.60144500	1.76703300
H	-1.54763800	1.88239400	2.56029300
H	0.39818200	1.86581300	-1.00115200
C	-2.32277300	-0.45618600	0.79636000
H	-3.28364900	-0.22421000	1.25783300
C	-2.43712000	-1.45869400	-0.18787000
H	-1.55668800	-1.88374100	-0.65460200
C	-3.70571500	-2.26482900	-0.27967400
H	-3.85331200	-2.57415300	-1.31886100
H	-4.55509100	-1.62422000	-0.02002700

B	-2.34523200	0.26133600	-0.80335600
O	-1.45405600	0.15378100	-1.89385400
H	-1.08596900	1.00152200	-2.15394100
O	-3.52834000	1.02757500	-0.91490600
H	-3.84333800	1.03653600	-1.82159400
C	-3.68870000	-3.50164000	0.62374300
H	-2.84945300	-4.15406500	0.37107000
H	-4.60989000	-4.07983400	0.52433800
H	-3.58025400	-3.20902800	1.67132700
C	0.15605300	3.10947300	0.75181300
H	0.53671400	3.99215100	0.23137000
H	0.55958000	3.14401700	1.77168000
H	-2.99478700	1.91430900	1.53885500
C	0.67718400	-0.72981100	0.12808100
H	0.39654200	-0.81718600	-0.92214100
H	0.24222900	-1.57673200	0.66559000
C	2.17508800	-0.80024700	0.27275700
C	3.03787000	-0.43479400	-0.77206400
C	2.75610500	-1.21508500	1.47071800
C	4.42737200	-0.48881600	-0.62465200
C	4.13575600	-1.26894600	1.62674200
H	2.10814700	-1.50669200	2.29095200
C	4.97625100	-0.90699700	0.57729900
H	5.06001800	-0.20083100	-1.45527300
H	4.55760200	-1.60066000	2.56834100
H	6.05170800	-0.95207600	0.69516300
C	2.49048400	0.03231100	-2.01803200
N	2.05087600	0.42809800	-3.00528800

Allylboronic acid D1



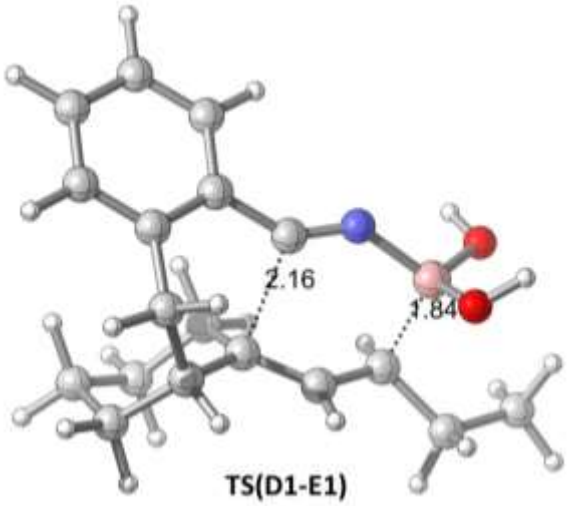
E(M062X)= -930.383322676
Zero-point correction= 0.395077 (Hartree/Particle)
Thermal correction to Energy= 0.416870
Thermal correction to Enthalpy= 0.417814
Thermal correction to Gibbs Free Energy= 0.342422
Sum of electronic and zero-point Energies= -929.988246
Sum of electronic and thermal Energies= -929.966453
Sum of electronic and thermal Enthalpies= -929.965509
Sum of electronic and thermal Free Energies= -930.040901
E(M062x) PCM(1,4-dioxane)= -930.40375952

0 1

C	2.67036800	2.63240800	-0.65696800
C	0.90214800	0.86974600	-0.59101700
C	2.03975900	1.44607700	-1.39961000
H	3.12475000	2.25576500	0.26552800

H	3.47222400	3.06745400	-1.25972000
H	2.80219300	0.69566900	-1.60516700
H	1.65072300	1.80210600	-2.36362000
C	0.45321800	3.08192900	0.45887800
H	-0.31171200	3.84185900	0.64685900
H	0.80595100	2.72867500	1.43568900
C	-0.18118600	1.89040700	-0.28608700
C	0.87841100	-0.38404200	-0.12799500
H	0.03476600	-0.70125800	0.48234700
C	1.92394000	-1.46176200	-0.32899000
H	-0.54348500	2.28415700	-1.24844800
B	2.99428400	-1.21923600	0.80549600
O	4.02925300	-0.35556800	0.54939500
H	4.62209700	-0.18307500	1.28459900
O	2.81167800	-1.84005400	2.01182100
H	3.43915700	-1.61861400	2.70333300
H	2.40779100	-1.32729600	-1.30147700
C	1.28559900	-2.85580600	-0.27238100
H	0.83451300	-2.99884300	0.71466200
H	0.47054100	-2.90758800	-1.00250400
C	2.29364100	-3.97036800	-0.53870200
H	3.08824800	-3.96218000	0.21268800
H	1.81916600	-4.95320400	-0.50755100
H	2.75729300	-3.85190300	-1.52201500
C	1.61850000	3.68832800	-0.32177800
H	2.06666800	4.50639700	0.24883800
H	1.23601400	4.12422300	-1.25310100
C	-1.37806400	1.37320300	0.50704000
H	-1.99577900	2.23327200	0.79188200
H	-1.02906200	0.94836200	1.45554300
C	-2.28591200	0.37337800	-0.17524800
C	-3.34079400	-0.20265400	0.55312100
C	-2.15556400	0.00180100	-1.51189000
C	-4.22772000	-1.11124700	-0.02857400
C	-3.03717500	-0.90051800	-2.09866500
H	-1.34260300	0.40790800	-2.10046100
C	-4.07496600	-1.46079300	-1.36134300
H	-5.02603200	-1.53113500	0.57095700
H	-2.90774300	-1.17056600	-3.14019100
H	-4.75843300	-2.16518800	-1.81884800
C	-3.52000000	0.15513100	1.93424500
N	-3.65733400	0.44926400	3.03839100

TS(D1-E1)



E(M062X)= -930.3393037
Zero-point correction= 0.394476 (Hartree/Particle)
Thermal correction to Energy= 0.414473

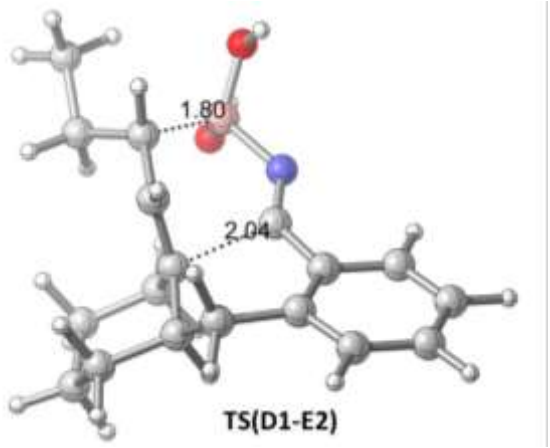
Thermal correction to Enthalpy= 0.415417
Thermal correction to Gibbs Free Energy= 0.347145
Sum of electronic and zero-point Energies= -929.944827
Sum of electronic and thermal Energies= -929.924831
Sum of electronic and thermal Enthalpies= -929.923887
Sum of electronic and thermal Free Energies= -929.992159
E(M062x) PCM(1,4-dioxane)= -930.35660385

Imaginary frequency: -427.4027 cm^{-1}

0 1

C	-0.04212700	1.04355200	0.10392200
C	0.39059400	1.12261000	-1.36150700
H	-0.47115000	0.94213600	-2.00564900
C	1.85799900	0.48903600	1.75985900
H	1.27314000	-0.04274400	2.51790300
H	2.69320000	0.96331200	2.28076600
C	0.93576100	1.58326200	1.15613700
C	1.47302800	-1.34846500	0.10678700
C	0.03629100	-1.10880100	0.18718500
C	-1.38512200	1.04569100	0.45567100
H	-1.61082100	1.30118800	1.49326800
C	-2.47657200	0.50394000	-0.26334500
H	-2.33426400	0.43610700	-1.34462400
C	-3.84662400	1.08312900	0.12167400
H	-3.83813400	2.15227600	-0.11777900
H	-3.95864000	0.99905000	1.20615000
C	-5.04871900	0.44304300	-0.56788600
H	-5.19926400	-0.58474900	-0.24250700
H	-5.95240200	1.01673900	-0.34912900
H	-4.91509000	0.42575800	-1.65332500
H	0.32843200	1.91898700	2.00065700
N	-1.00912300	-1.66538300	0.11805100
B	-2.53145900	-1.27586800	0.20405300
O	-3.31178200	-2.00020100	-0.73284100
H	-2.85546600	-2.16520800	-1.55860100
O	-3.01993300	-1.34191800	1.52394000
H	-3.58989200	-2.10774300	1.62546900
C	2.37954900	-0.53804700	0.79943000
H	1.12891700	0.35145600	-1.60181900
C	1.71217000	2.82231100	0.66805000
H	2.53177000	3.02922900	1.36300700
H	1.03564700	3.68330700	0.71624200
C	1.04264100	2.46571000	-1.70120000
H	1.36688400	2.45383100	-2.74528500
H	0.31355800	3.27700200	-1.59430300
C	2.22296500	2.71385000	-0.76613700
H	2.75214800	3.63033800	-1.03996900
H	2.94018500	1.88837600	-0.85738300
C	1.91461200	-2.34895800	-0.76256000
H	1.18357500	-2.95475600	-1.28436900
C	3.74060600	-0.75551400	0.59838400
C	3.27541800	-2.54899200	-0.94720300
H	3.62158100	-3.32609500	-1.61752000
C	4.18808200	-1.74680300	-0.26861000
H	5.25170000	-1.89693900	-0.41191200
H	4.45594100	-0.14020400	1.13338000

TS(D1-E2)



E(M062X)= -930.332581763
Zero-point correction= 0.394902 (Hartree/Particle)
Thermal correction to Energy= 0.414466
Thermal correction to Enthalpy= 0.415410
Thermal correction to Gibbs Free Energy= 0.349348
Sum of electronic and zero-point Energies= -929.937680
Sum of electronic and thermal Energies= -929.918116
Sum of electronic and thermal Enthalpies= -929.917171
Sum of electronic and thermal Free Energies= -929.983234
E(M062x) PCM(1,4-dioxane)= -930.350105

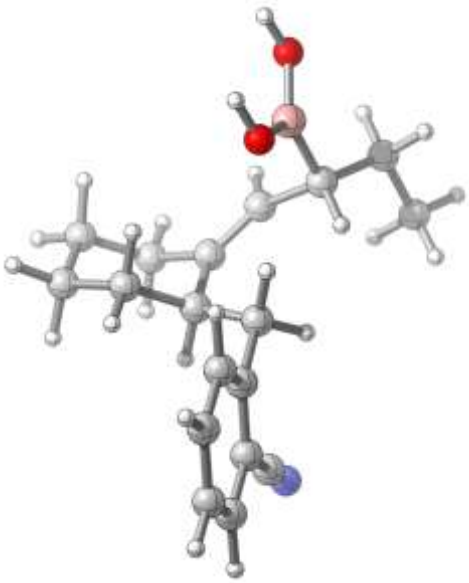
Imaginary frequency: -334.6074

0 1

C	-0.22914600	0.89768900	0.01372200
C	0.95185200	1.82940000	-0.18864100
C	-0.93122900	1.21772600	1.31525900
C	0.55194600	-0.97193500	0.22045900
C	-0.89929000	0.32452700	-1.05586800
H	-0.35526500	0.29578500	-1.99938000
C	-2.08871600	-0.48496800	-0.95973200
N	-0.24825900	-1.84415400	0.39648500
B	-1.83635700	-1.85723200	0.17503200
O	-2.27093100	-3.07270800	-0.42810500
H	-1.71776800	-3.35495000	-1.15734900
O	-2.49970700	-1.62482500	1.40738200
H	-2.91288800	-2.43939100	1.70309800
H	1.47901400	1.88005700	0.77375000
C	-1.51409600	2.63787100	1.16670500
H	-1.99588500	2.94017800	2.10025100
H	-2.29300100	2.60828800	0.39761400
C	0.38487400	3.23350100	-0.44109700
H	1.19986400	3.94453900	-0.61014600
H	-0.23399200	3.21831900	-1.34570500
C	-0.44553200	3.66768700	0.77496100
H	-0.91579500	4.63581500	0.58406700
H	0.23693600	3.81172200	1.62106800
H	-0.19708800	1.20682100	2.12878500
H	-1.69863800	0.48709800	1.56285800
C	1.97392900	1.31000100	-1.19241800
H	1.50902200	1.05418500	-2.14923500
H	2.70981900	2.08943800	-1.40590200
C	2.69206400	0.12179200	-0.59327300
C	2.01831800	-0.87064400	0.13693600
C	4.08103300	0.02952000	-0.69126700
H	4.61514000	0.79190100	-1.24803600
C	2.73155000	-1.90489000	0.75620800
H	2.17707600	-2.65749500	1.30335300

C	4.78784000	-0.99914800	-0.08262000
H	5.86693600	-1.03877900	-0.17415200
C	4.11147200	-1.96769500	0.65283200
H	4.65406100	-2.77037900	1.13711100
H	-2.26136600	-0.96938400	-1.92564500
C	-3.41798000	0.19300300	-0.54469700
H	-3.53484200	1.13184300	-1.09679100
H	-3.42185600	0.43169100	0.51830400
C	-4.60834200	-0.71258500	-0.85333000
H	-5.54429300	-0.23572500	-0.55393900
H	-4.66537200	-0.92651500	-1.92437500
H	-4.51840000	-1.66467500	-0.32920500

Allylboronic acid D2



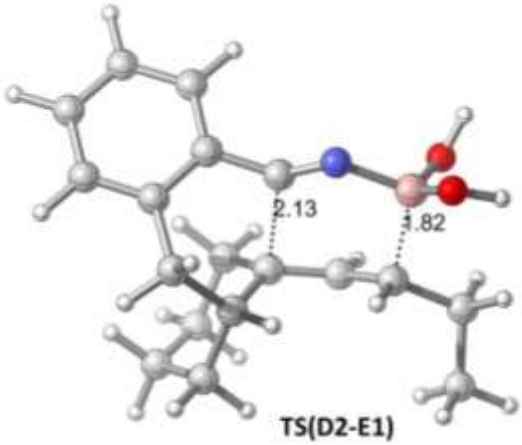
E(M062X)= -930.378500562
Zero-point correction= 0.395163 (Hartree/Particle)
Thermal correction to Energy= 0.416941
Thermal correction to Enthalpy= 0.417885
Thermal correction to Gibbs Free Energy= 0.342627
Sum of electronic and zero-point Energies= -929.983338
Sum of electronic and thermal Energies= -929.961560
Sum of electronic and thermal Enthalpies= -929.960615
Sum of electronic and thermal Free Energies= -930.035874
E(M062x) PCM(1,4-dioxane)= -930.3986417

0 1

C	1.18509900	3.40696100	-0.62431800
C	1.22042200	0.92447000	-0.87936700
C	1.43625900	2.24277700	-1.59425800
H	1.93426100	3.35977900	0.17472400
H	1.31640800	4.36418000	-1.13671400
H	2.44905600	2.29672200	-1.99869900
H	0.73952600	2.32411700	-2.43782700
C	-0.47160200	1.94396800	0.61113300
H	-1.50271200	1.89401800	0.97288400
H	0.18755800	1.78988400	1.47493600
C	-0.21378400	0.80531500	-0.39633000
C	2.27264900	0.12433000	-0.66517100
H	-0.84190600	1.00912200	-1.27599400
C	-0.21428500	3.31573100	-0.01669900
H	-0.35860300	4.10265300	0.72894500

H	-0.95821500	3.48562400	-0.80437500
C	-0.64898700	-0.56230800	0.15531700
H	-0.11679100	-0.77290500	1.08437900
H	-0.38882000	-1.33376900	-0.57562000
C	-2.13020800	-0.62015100	0.42728400
C	-3.06379000	-0.75189100	-0.61304000
C	-2.62630800	-0.52503200	1.72697200
C	-4.43861100	-0.78262700	-0.36140600
C	-3.99175900	-0.55311100	1.98571800
H	-1.91982100	-0.42560100	2.54427000
C	-4.90263700	-0.68087200	0.94099400
H	-5.12755000	-0.88975000	-1.19025000
H	-4.34759700	-0.47705700	3.00653000
H	-5.96675600	-0.70525200	1.13978100
C	-2.60427600	-0.87028100	-1.97085500
N	-2.23527100	-0.96467900	-3.05684300
C	2.46335700	-1.14827100	0.13826000
H	1.54060500	-1.72391500	0.19708500
B	2.84389900	-0.64218300	1.58250700
O	4.16101700	-0.39787400	1.86150100
H	4.35299800	-0.03760600	2.73005500
O	1.83302200	-0.42765100	2.48950700
H	2.10088000	-0.05395900	3.33237800
C	3.55025100	-2.02792100	-0.49947700
H	4.47953000	-1.45277800	-0.56419100
H	3.76355700	-2.87489400	0.16036400
C	3.14707900	-2.53854600	-1.88042400
H	3.92920700	-3.15992100	-2.32162500
H	2.23380400	-3.13741500	-1.82061100
H	2.94806700	-1.70776400	-2.56193000
H	3.21518200	0.47911700	-1.08717700

TS(D2-E1)



E(M062X)= -930.339303667
Zero-point correction= 0.394476 (Hartree/Particle)
Thermal correction to Energy= 0.414473
Thermal correction to Enthalpy= 0.415417
Thermal correction to Gibbs Free Energy= 0.347145
Sum of electronic and zero-point Energies= -929.944827
Sum of electronic and thermal Energies= -929.924831
Sum of electronic and thermal Enthalpies= -929.923887
Sum of electronic and thermal Free Energies= -929.992159
E(M062x) PCM(1,4-dioxane)= -930.35660385

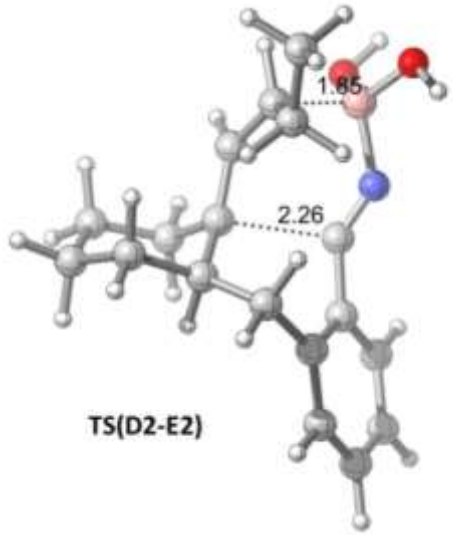
Imaginary frequency: -427.4027

0 1

C	-0.04212700	1.04355200	0.10392200

C	0.39059400	1.12261000	-1.36150700
H	-0.47115000	0.94213600	-2.00564900
C	1.85799900	0.48903600	1.75985900
H	1.27314000	-0.04274400	2.51790300
H	2.69320000	0.96331200	2.28076600
C	0.93576100	1.58326200	1.15613700
C	1.47302800	-1.34846500	0.10678700
C	0.03629100	-1.10880100	0.18718500
C	-1.38512200	1.04569100	0.45567100
H	-1.61082100	1.30118800	1.49326800
C	-2.47657200	0.50394000	-0.26334500
H	-2.33426400	0.43610700	-1.34462400
C	-3.84662400	1.08312900	0.12167400
H	-3.83813400	2.15227600	-0.11777900
H	-3.95864000	0.99905000	1.20615000
C	-5.04871900	0.44304300	-0.56788600
H	-5.19926400	-0.58474900	-0.24250700
H	-5.95240200	1.01673900	-0.34912900
H	-4.91509000	0.42575800	-1.65332500
H	0.32843200	1.91898700	2.00065700
N	-1.00912300	-1.66538300	0.11805100
B	-2.53145900	-1.27586800	0.20405300
O	-3.31178200	-2.00020100	-0.73284100
H	-2.85546600	-2.16520800	-1.55860100
O	-3.01993300	-1.34191800	1.52394000
H	-3.58989200	-2.10774300	1.62546900
C	2.37954900	-0.53804700	0.79943000
H	1.12891700	0.35145600	-1.60181900
C	1.71217000	2.82231100	0.66805000
H	2.53177000	3.02922900	1.36300700
H	1.03564700	3.68330700	0.71624200
C	1.04264100	2.46571000	-1.70120000
H	1.36688400	2.45383100	-2.74528500
H	0.31355800	3.27700200	-1.59430300
C	2.22296500	2.71385000	-0.76613700
H	2.75214800	3.63033800	-1.03996900
H	2.94018500	1.88837600	-0.85738300
C	1.91461200	-2.34895800	-0.76256000
H	1.18357500	-2.95475600	-1.28436900
C	3.74060600	-0.75551400	0.59838400
C	3.27541800	-2.54899200	-0.94720300
H	3.62158100	-3.32609500	-1.61752000
C	4.18808200	-1.74680300	-0.26861000
H	5.25170000	-1.89693900	-0.41191200
H	4.45594100	-0.14020400	1.13338000

TS(D2-E2)



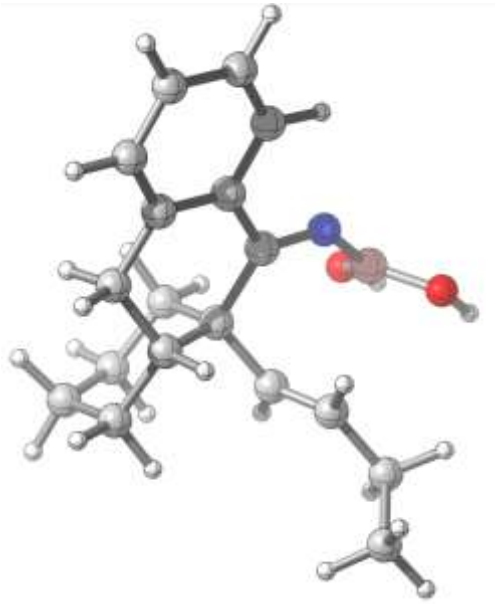
E(M062X)= -930.317607463
Zero-point correction= 0.394947 (Hartree/Particle)
Thermal correction to Energy= 0.414597
Thermal correction to Enthalpy= 0.415541
Thermal correction to Gibbs Free Energy= 0.349269
Sum of electronic and zero-point Energies= -929.922660
Sum of electronic and thermal Energies= -929.903010
Sum of electronic and thermal Enthalpies= -929.902066
Sum of electronic and thermal Free Energies= -929.968338
E(M062x) PCM(1,4-dioxane)= -930.334663996

Imaginary frequency: -392.01

0 1

C	0.11392200	1.02159100	-0.66107800
C	-0.73464300	1.45794300	0.53912400
C	-0.38750100	1.82832100	-1.85525500
C	-0.23617100	-1.20518700	-0.49028200
C	1.48016100	0.76185600	-0.73321200
H	1.88462500	0.91039600	-1.73478600
C	2.38248200	0.04965700	0.08375400
N	0.74129800	-1.87597300	-0.47131800
B	2.28232300	-1.62680600	-0.68996100
O	3.09555600	-2.51672400	0.04794600
H	2.66069800	-2.86556900	0.82716600
O	2.63060900	-1.51797100	-2.04755000
H	3.21838900	-2.23729600	-2.28962900
H	-1.71797500	1.67434400	0.10256100
C	-0.03646300	3.30669900	-1.56209000
H	-0.43548900	3.95744000	-2.34601900
H	1.05534700	3.39177600	-1.60303200
C	-0.22660500	2.84109700	0.97149200
H	-0.74489500	3.18345100	1.87361700
H	0.84488500	2.80906900	1.19075200
C	-0.52495900	3.80771900	-0.19106800
H	-0.09118100	4.79146400	0.00795100
H	-1.61154900	3.94849500	-0.23277200
H	-1.46768900	1.70575200	-1.98502500
H	0.09365800	1.51525100	-2.78427100
C	-1.09468900	0.40866100	1.60866800
H	-0.22614500	-0.12773100	1.98713600
H	-1.57824800	0.90208400	2.45558600
C	-2.07191000	-0.52935000	0.94376200
C	-1.65632200	-1.23589600	-0.19608000
C	-3.40740900	-0.63176200	1.32102700
H	-3.75119000	-0.09598400	2.19933700
C	-4.30122100	-1.40010500	0.58011000
H	-5.33729200	-1.46602000	0.89084300
C	-2.54462800	-2.00098300	-0.95012100
H	-2.18529300	-2.53764300	-1.81975600
C	-3.87516800	-2.07592300	-0.55977000
H	-4.57380000	-2.66986500	-1.13604900
H	3.41437200	0.19094400	-0.24517400
C	2.26721900	-0.06469000	1.59958400
H	1.71926500	0.79175700	2.00483000
H	1.68870700	-0.95445900	1.87867100
C	3.64464600	-0.14037700	2.25886100
H	3.56261100	-0.27174700	3.34001300
H	4.21598400	-0.97539600	1.84819400
H	4.20773100	0.77726200	2.07114600

Cycloadduct E1



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E(M062X)=                                          -930.410455122
Zero-point correction=                             0.396851 (Hartree/Particle)
Thermal correction to Energy=                      0.417453
Thermal correction to Enthalpy=                    0.418397
Thermal correction to Gibbs Free Energy=           0.347471
Sum of electronic and zero-point Energies=             -930.013604
Sum of electronic and thermal Energies=                -929.993002
Sum of electronic and thermal Enthalpies=              -929.992058
Sum of electronic and thermal Free Energies=           -930.062984
E(M062X) PCM(1,4-dioxane)=                                -930.42843737
```

```
0 1
 C                  0.29969200    0.55191900    0.34838100
 C                  0.16227100    1.08009000    1.80134100
 H                  0.61668200    0.34948900    2.47561600
 C                 -1.80405900    1.74798100   -0.47636900
 H                 -2.18457700    2.39612900   -1.27207400
 H                 -2.03850400    2.25594200    0.46483700
 C                 -0.29143300    1.59733600   -0.63522400
 C                 -1.91583000   -0.74697400   -0.10540800
 C                 -0.47238300   -0.78431100    0.29261000
 C                  1.76760500    0.32332100    0.02797900
 H                  2.49696500    0.67323900    0.75557700
 C                  2.21203700   -0.28503600   -1.06747900
 H                  1.49385200   -0.67095900   -1.79265600
 C                  3.65659900   -0.51526100   -1.39340200
 H                  3.81981300   -1.59210800   -1.51299800
 H                  4.27701100   -0.18176900   -0.55570500
 C                  4.07671000    0.20510500   -2.67854300
 H                  3.95395000    1.28516900   -2.57087600
 H                  5.12097900    0.00043200   -2.92313000
 H                  3.46315700   -0.11898400   -3.52268100
 H                 -0.09791700    1.23135500   -1.65071800
 N                  0.03644900   -1.89455700    0.61454200
 B                  1.34394900   -2.28013000    1.04241800
 O                  1.75017800   -1.94782300    2.31881200
 H                  2.55950400   -2.37056700    2.61114100
 O                  2.08129700   -3.09107000    0.20845300
 H                  2.94291400   -3.33821100    0.54652300
 C                 -2.54366500    0.43929200   -0.49732100
 H                 -0.89991700    1.13375200    2.06566300
 C                  0.40812500    2.95350300   -0.46107100
 H                 -0.02239900    3.67449400   -1.16334600
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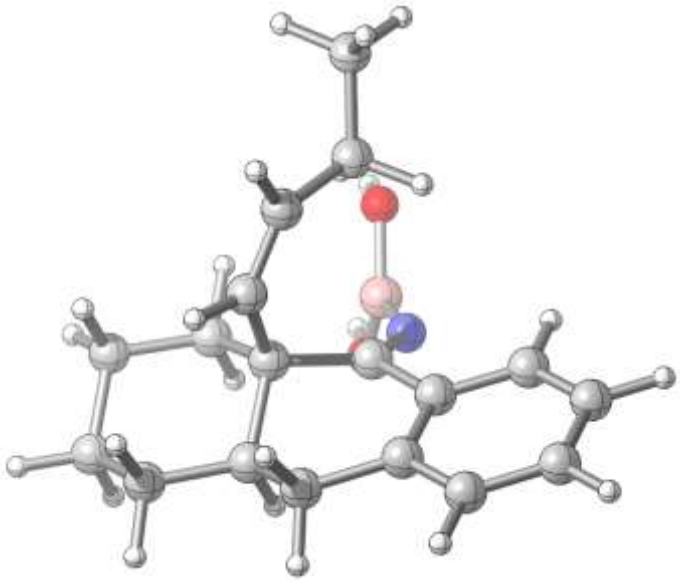
H	1.46447300	2.84302500	-0.72733600
C	0.81036400	2.45784800	1.98593100
H	0.62592200	2.80833700	3.00505700
H	1.89697100	2.36915100	1.88542000
C	0.30302200	3.48614500	0.97241600
H	0.87679300	4.41249000	1.06249900
H	-0.73450300	3.74788100	1.20329300
C	-2.64277500	-1.94493300	-0.10656600
H	-2.12833400	-2.84947200	0.19297300
C	-3.88666800	0.40255500	-0.88437100
C	-3.97284000	-1.96845900	-0.48524900
H	-4.52305100	-2.90181500	-0.48199500
C	-4.59964600	-0.78548300	-0.87875100
H	-5.63944500	-0.79462700	-1.18543500
H	-4.36979700	1.32349200	-1.19508400

Cycloadduct E2



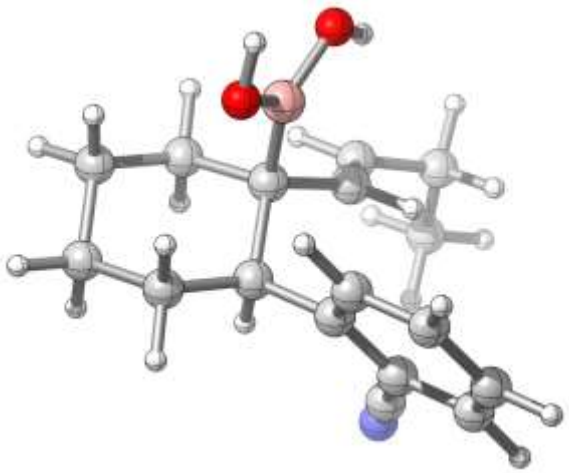
E(M062X)= -930.410546545
Zero-point correction= 0.396800 (Hartree/Particle)
Thermal correction to Energy= 0.417437
Thermal correction to Enthalpy= 0.418381
Thermal correction to Gibbs Free Energy= 0.347540
Sum of electronic and zero-point Energies= -930.013747
Sum of electronic and thermal Energies= -929.993109
Sum of electronic and thermal Enthalpies= -929.992165
Sum of electronic and thermal Free Energies= -930.063007
E(M062X) PCM(1,4-dioxane)= -930.42843737

0 1

C	0.66379000	0.67194000	0.19353000
C	-1.31241500	2.27226200	0.11150600
H	-1.70731200	3.15373100	-0.40371500
H	-1.37443200	2.49339400	1.18432600
C	0.15237900	2.06719900	-0.27492800
C	-1.64801400	-0.16080600	-0.50783600
C	-0.16668000	-0.34382400	-0.60405900
C	0.42067800	0.50967500	1.68693500
H	0.36484900	1.43456700	2.25454800
C	0.28764600	-0.62213900	2.37973400
H	0.22517000	2.06497100	-1.37167400
N	0.29265800	-1.26458400	-1.32759900
B	1.51928300	-1.83696300	-1.74368900
O	2.03051800	-2.88845300	-1.00935900
H	2.80548800	-3.30990500	-1.38343100

O	2.08723200	-1.39110800	-2.91723900
H	2.84809500	-1.88875300	-3.21939600
C	-2.19439700	1.08297900	-0.17877200
C	1.01671800	3.22001300	0.24626100
H	0.64717900	4.15594500	-0.18546900
C	-2.48797300	-1.24723000	-0.76937800
H	-2.03145700	-2.19444200	-1.03282700
C	-3.58362900	1.21394600	-0.12264500
C	-3.86395100	-1.10924700	-0.69322400
H	-4.50877600	-1.95757200	-0.88952700
C	-4.41406700	0.13088800	-0.37057100
H	-5.48998700	0.25204000	-0.31798600
H	-4.01291700	2.18185500	0.11696200
C	2.16293700	0.54067200	-0.12707500
H	2.52407400	-0.42507700	0.24092100
H	2.28818600	0.55015600	-1.21631500
C	2.49831000	3.02739800	-0.07025800
H	3.08315100	3.84808200	0.35353900
H	2.64614500	3.05518500	-1.15647500
C	2.98742100	1.68225700	0.46708300
H	2.90778200	1.66923100	1.55992900
H	4.04305100	1.53630100	0.22382400
H	0.89057900	3.31285700	1.33174700
H	0.11640000	-0.51672800	3.45059700
C	0.33015100	-2.04172100	1.87651500
H	-0.62847900	-2.28206900	1.39907200
H	1.08709700	-2.15695700	1.09908500
C	0.59871200	-3.03471800	3.00657900
H	1.56108600	-2.83154700	3.48319300
H	-0.17538200	-2.97002400	3.77585300
H	0.61770000	-4.05912200	2.63125100

Allylboronic acid F



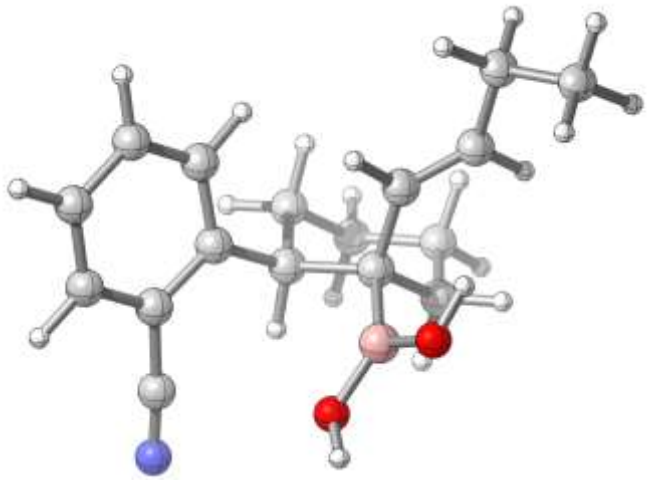
E(M062X)= -891.084449978
Zero-point correction= 0.367593 (Hartree/Particle)
Thermal correction to Energy= 0.387629
Thermal correction to Enthalpy= 0.388573
Thermal correction to Gibbs Free Energy= 0.319607
Sum of electronic and zero-point Energies= -890.716857
Sum of electronic and thermal Energies= -890.696821
Sum of electronic and thermal Enthalpies= -890.695877
Sum of electronic and thermal Free Energies= -890.764843
E(M062X) PCM(1,4-dioxane)= -891.0998726

0 1

C	1.01624500	-1.84886300	-1.53769900
C	-1.18436800	-3.02596300	-1.23397700

C	-1.76222400	-1.77276000	-0.57473400
C	-0.69840800	-0.91523800	0.15799000
C	0.43616100	-0.59023100	-0.87046000
H	-1.98670000	-3.56782100	-1.74205700
H	1.51147400	-2.47895400	-0.79640800
H	1.77300300	-1.53791900	-2.26421800
H	-2.22101100	-1.14578200	-1.35048900
H	-2.56233900	-2.04787500	0.12104200
H	-0.06244900	-0.02129000	-1.66593800
H	-0.77465800	-3.69831400	-0.47315000
C	-1.29064200	0.39074100	0.64440000
H	-0.57380800	1.08924000	1.07906500
C	-2.56762800	0.77311100	0.61769000
H	-3.32587900	0.12064000	0.18826600
C	-3.04980000	2.11873600	1.07973400
H	-3.82823400	1.99115200	1.84020900
H	-2.22370400	2.65758800	1.55278700
B	-0.26207400	-1.74817600	1.45412700
O	0.72668600	-2.69444500	1.42233600
H	0.80743500	-3.13527200	2.27496800
O	-0.93344400	-1.60241000	2.63385800
H	-1.59571100	-0.90356100	2.59001000
C	-3.60905500	2.93913100	-0.08758200
H	-4.44363400	2.41769000	-0.56361400
H	-3.97214500	3.90986800	0.25611400
H	-2.83698100	3.10241200	-0.84208800
C	-0.08258300	-2.65641100	-2.22618100
H	0.34260200	-3.55656200	-2.67750300
H	-0.51474400	-2.06263800	-3.04089700
C	1.52338500	0.29797100	-0.29963800
C	1.54240100	1.68247300	-0.54365400
C	2.55275400	-0.22386800	0.48697600
C	2.54864500	2.50560700	-0.02774000
C	3.55325900	0.59053600	1.00503100
H	2.56428500	-1.28547400	0.69848400
C	3.55716000	1.95812900	0.74844400
H	2.52610300	3.56681500	-0.24350200
H	4.33792400	0.15216300	1.61067400
H	4.33915000	2.59209400	1.14726100
C	0.50392100	2.30408900	-1.32286900
N	-0.32155400	2.82777000	-1.93051400

Allylboronic acid F′



E(M062X)= -891.079507161
Zero-point correction= 0.366688 (Hartree/Particle)

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Thermal correction to Energy=                    0.387107
Thermal correction to Enthalpy=                  0.388051
Thermal correction to Gibbs Free Energy=         0.316840
Sum of electronic and zero-point Energies=           -890.712819
Sum of electronic and thermal Energies=              -890.692400
Sum of electronic and thermal Enthalpies=            -890.691456
Sum of electronic and thermal Free Energies=         -890.762667
E(M062X) PCM(1,4-dioxane)=                             -891.0963967

0 1
 B                -0.33814100   -0.55436900   -1.82670200
 O                 0.78630700   -1.18287300   -2.25765900
 H                 0.92831900   -1.11274000   -3.20627900
 O                -1.13379800    0.08064200   -2.73523400
 H                -1.89816300    0.49246000   -2.31784500
 C                -1.59566700    0.51118300    0.06238700
 C                -2.92251400    0.54698200    0.20214000
 C                -3.71925300    1.80296400    0.41565700
 H                -3.50197700   -0.37398900    0.15474900
 C                -0.72699800   -0.67525100   -0.28089400
 C                 0.55375800   -0.79063900    0.61667900
 C                -1.48136100   -2.02922400   -0.17487300
 C                 0.18096900   -1.14182000    2.06680500
 H                 1.11005700   -1.64213400    0.20984400
 C                -1.82213500   -2.43157700    1.26357600
 H                -0.83790500   -2.80390500   -0.60834800
 H                -2.38633900   -2.00318800   -0.79055900
 C                -0.56421300   -2.47489400    2.12869200
 H                 1.09045400   -1.18217800    2.67309100
 H                -0.45477800   -0.35406500    2.48816900
 H                -2.31471500   -3.40798800    1.25949100
 H                -2.52779900   -1.71807300    1.69874900
 H                 0.09877400   -3.27216400    1.77229600
 H                -1.07713600    1.46835300    0.09827500
 H                -3.04102800    2.65706900    0.49820100
 H                -4.25939600    1.73097400    1.36604800
 C                 1.47827100    0.40878600    0.55777500
 C                 1.16847200    1.60239900    1.21811700
 C                 2.71567300    0.35577800   -0.10862300
 C                 2.00761300    2.70807100    1.16854000
 H                 0.25536900    1.66197000    1.79758700
 C                 3.56432700    1.46780000   -0.16297000
 C                 3.20471200    2.65006200    0.46200900
 H                 1.72975100    3.61544300    1.69196000
 H                 4.50915300    1.38152700   -0.68551300
 H                 3.86201600    3.50961900    0.41938000
 C                 3.21227600   -0.86588400   -0.68753700
 N                 3.68747300   -1.82161400   -1.11651900
 H                -0.82246200   -2.71362500    3.16384900
 C                -4.72857000    2.04047100   -0.71219200
 H                -5.32906400    2.93231500   -0.52298800
 H                -5.40940500    1.19131100   -0.81042300
 H                -4.21757900    2.17275700   -1.66918000
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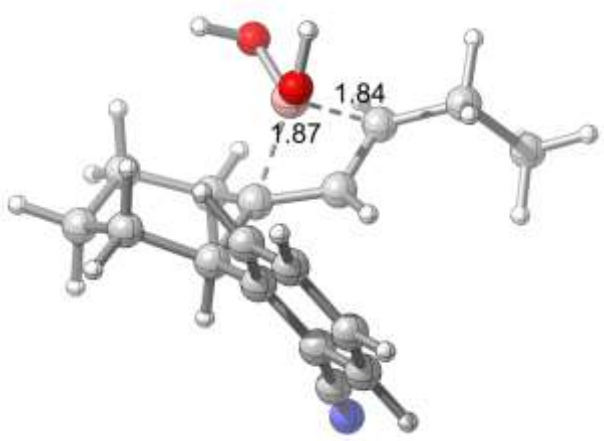
TS(F-G1)



E(M062X)= - 891.0219968
Zero-point correction= 0.364075 (Hartree/Particle)
Thermal correction to Energy= 0.384098
Thermal correction to Enthalpy= 0.385042
Thermal correction to Gibbs Free Energy= 0.315976
Sum of electronic and zero-point Energies= -890.657922
Sum of electronic and thermal Energies= -890.637899
Sum of electronic and thermal Enthalpies= -890.636955
Sum of electronic and thermal Free Energies= -890.706020
E(M062X) PCM(1,4-dioxane)= -891,0400496

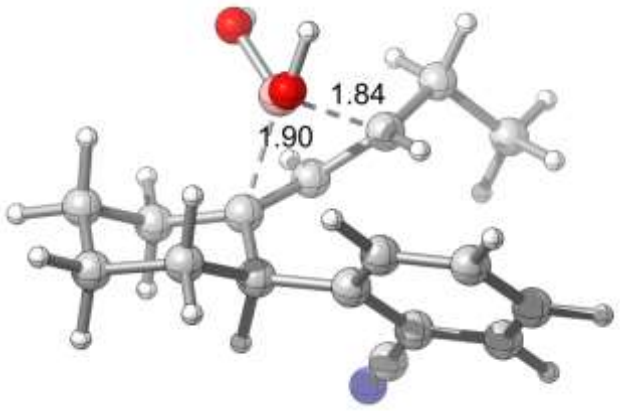
Imaginary frequency: -426.4180

0 1

C	0.02252400	-2.67236500	-0.28668800
C	2.38187800	-2.56013100	0.60606500
C	2.09315800	-1.16162600	1.16375200
C	0.94667000	-0.47279900	0.43948100
C	-0.31121600	-1.34742300	0.41563500
H	3.11602000	-3.06224400	1.24141800
H	0.36774700	-2.46825400	-1.30747300
H	-0.87744300	-3.28980900	-0.35936200
H	1.79825300	-1.25138800	2.21864800
H	2.99674400	-0.55356800	1.12941400
H	-0.51912700	-1.60385500	1.46519400
H	2.84033100	-2.46850400	-0.38305800
C	0.83562400	0.93053700	0.37585400
H	-0.14766200	1.30821300	0.09702700
C	1.88676000	1.79284700	0.02940100
H	2.89296000	1.58246700	0.37696200
C	1.58752800	3.20337900	-0.40417600
H	2.37912000	3.54446200	-1.07825400
H	0.65843200	3.20650900	-0.98441400
B	1.62497600	0.36201200	-1.08955800
O	2.95116900	-0.06379700	-1.35214500
H	2.94128700	-0.90746800	-1.81079100
O	0.69890300	0.43828700	-2.15916400
H	1.12792500	0.77661900	-2.94909100
C	1.46590800	4.17097900	0.77678600
H	2.38617300	4.18275700	1.36543700
H	1.26742800	5.18966600	0.43653100
H	0.65212000	3.86521600	1.43911800
C	1.11474900	-3.40773800	0.49124500
H	1.34370600	-4.36242600	0.01047700
H	0.73718700	-3.63968400	1.49432000
C	-1.56062700	-0.67493700	-0.10955600
C	-2.35455400	0.10312200	0.75141600
C	-1.97854000	-0.79438400	-1.43273100

C	-3.52477900	0.72649100	0.31036200
C	-3.14219300	-0.17854500	-1.87840800
H	-1.37208200	-1.35840900	-2.12863700
C	-3.92107800	0.57981900	-1.00965000
H	-4.10869600	1.31543900	1.00690800
H	-3.44153800	-0.28875400	-2.91398700
H	-4.82911300	1.05561300	-1.35872900
C	-1.94075900	0.29535100	2.11596200
N	-1.59165000	0.46085100	3.20030100

TS(F-G2)



E(M062X)= -891,021366
Zero-point correction= 0.364098 (Hartree/Particle)
Thermal correction to Energy= 0.384154
Thermal correction to Enthalpy= 0.385098
Thermal correction to Gibbs Free Energy= 0.316892
Sum of electronic and zero-point Energies= -890.657268
Sum of electronic and thermal Energies= -890.637212
Sum of electronic and thermal Enthalpies= -890.636268
Sum of electronic and thermal Free Energies= -890.704474
E(M062X) PCM(1,4-dioxane)= -891,0393601

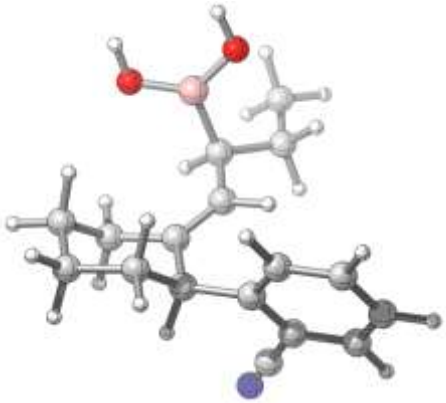
Imaginary frequency: -440.0670

0 1

C	-3.60198100	-0.38376400	-0.50589300
C	-1.84786600	-1.99828300	0.34507200
C	-0.77806800	-1.18568700	-0.39834000
C	-1.19993200	0.28165000	-0.53502900
C	-2.52503900	0.40773200	-1.25700500
H	-1.54833700	-3.05083500	0.36887500
H	-3.73317200	0.06303700	0.48615600
H	-4.55811500	-0.30431900	-1.03002600
H	-0.80293900	-1.54321200	-1.44153800
H	-2.42813500	0.01920400	-2.28038500
H	-1.92901900	-1.64240600	1.37353400
C	-0.33460000	1.38770700	-0.53779400
H	-0.73613900	2.26049900	-1.05727700
C	0.62490800	1.71735100	0.44189300
H	1.20050800	0.93291700	0.92249800
C	1.23605100	3.09333700	0.45253600
H	1.46866500	3.37978200	1.48286500
H	0.50824700	3.82471800	0.08156700
B	-1.05604700	1.29721200	1.06328500
O	-0.92209800	0.31726600	2.07046500
H	-0.80591600	0.75750300	2.91673900
O	-1.98180800	2.32538800	1.33001300
H	-1.85300200	3.12705500	0.82275700
C	2.50625100	3.16112400	-0.40162700

H	3.24804500	2.44514400	-0.03865500
H	2.95352600	4.15718500	-0.37496500
H	2.28129700	2.90850700	-1.44091400
C	-3.20002400	-1.85254800	-0.35835500
H	-3.96674100	-2.39915800	0.19664600
H	-3.14047700	-2.31001800	-1.35404600
H	-2.81755500	1.45856100	-1.33077500
C	0.64549100	-1.41439000	0.05448200
C	1.70743700	-1.10445500	-0.81281400
C	0.96845900	-1.93014200	1.30706800
C	3.04006000	-1.28641100	-0.43569500
C	2.29283500	-2.11936200	1.68687000
H	0.17039200	-2.15830400	2.00106200
C	3.33291900	-1.79494500	0.82042000
H	3.82915200	-1.02864600	-1.13143400
H	2.51447800	-2.51875700	2.66979100
H	4.36342400	-1.94060600	1.11964400
C	1.43289000	-0.54877400	-2.11072500
N	1.21350900	-0.09228200	-3.14467800

Allylboronic acid G1



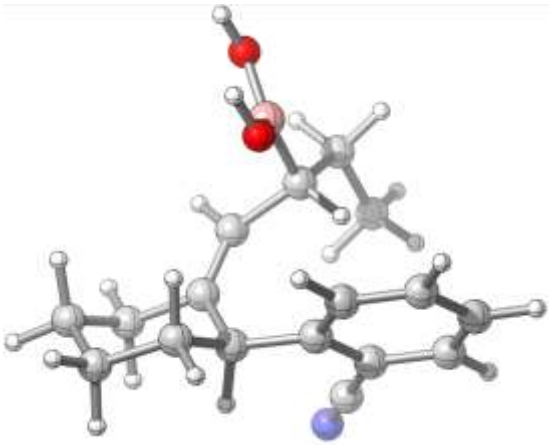
E(M062X)= -891.079318162
Zero-point correction= 0.366423 (Hartree/Particle)
Thermal correction to Energy= 0.386958
Thermal correction to Enthalpy= 0.387902
Thermal correction to Gibbs Free Energy= 0.316223
Sum of electronic and zero-point Energies= -890.712895
Sum of electronic and thermal Energies= -890.692360
Sum of electronic and thermal Enthalpies= -890.691416
Sum of electronic and thermal Free Energies= -890.763095
E(M062X) PCM(1,4-dioxane)= -891,1002534

0 1

C	-1.04450200	3.20003800	0.32045100
C	-0.24873900	0.83637500	0.51544000
C	-1.02938600	1.93505000	1.19244600
H	-1.61632900	2.98523100	-0.58893100
H	-1.56401300	4.00643600	0.84492000
H	-2.05231500	1.62424500	1.40141700
H	-0.54581100	2.16707900	2.15070800
C	1.13913900	2.49664500	-0.72745300
H	2.15863600	2.80871900	-0.97388900
H	0.63572200	2.23505700	-1.66498000
C	1.17876500	1.26269700	0.19229300
C	-0.75071200	-0.35634300	0.18314900
H	-0.11173900	-1.06586200	-0.34028500
C	-2.15785200	-0.85549100	0.43432300
H	1.62014600	1.59839700	1.14217600
B	-3.01672800	-0.32248300	-0.77659200
O	-3.60701100	0.91052600	-0.66298300

H	-4.06734700	1.22886500	-1.44290100
O	-3.09476600	-1.09080200	-1.90845100
H	-3.58100000	-0.71228700	-2.64412600
H	-2.54306000	-0.41217700	1.35770500
C	-2.17937000	-2.38398000	0.56638700
H	-1.81940400	-2.82552400	-0.36852700
H	-1.47779500	-2.68413500	1.35171900
C	-3.57243100	-2.92158500	0.88177400
H	-4.27452400	-2.67675400	0.07969000
H	-3.56482200	-4.00746500	0.99509300
H	-3.95664900	-2.49103300	1.81060800
C	0.37196800	3.63603400	-0.05527300
H	0.33976900	4.50581300	-0.71700300
H	0.90962800	3.94424500	0.84931800
C	2.04436800	0.13594300	-0.31895600
C	2.57227200	-0.80372700	0.58435200
C	2.33105500	-0.04380200	-1.66966100
C	3.35712500	-1.87383300	0.15235200
C	3.11117700	-1.11015200	-2.10814000
H	1.93856100	0.65828700	-2.39452500
C	3.62717400	-2.02758300	-1.20011400
H	3.74846800	-2.57323000	0.88106900
H	3.31640500	-1.22334800	-3.16622300
H	4.23646800	-2.85583500	-1.53972500
C	2.30057200	-0.66994100	1.99100400
N	2.09501800	-0.55974000	3.11784000

Allylboronic acid G2



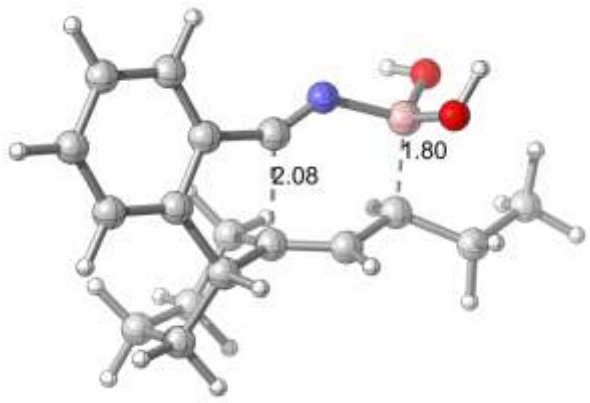
E(M062X)= -891.077175847
Zero-point correction= 0.366173 (Hartree/Particle)
Thermal correction to Energy= 0.386504
Thermal correction to Enthalpy= 0.387448
Thermal correction to Gibbs Free Energy= 0.317189
Sum of electronic and zero-point Energies= -890.711003
Sum of electronic and thermal Energies= -890.690672
Sum of electronic and thermal Enthalpies= -890.689728
Sum of electronic and thermal Free Energies= -890.759987
E(M062X) PCM(1,4-dioxane)= -891.09738313

0 1

C	3.74914100	-0.43860500	0.39419000
C	1.31053300	-0.10575800	0.77678300
C	2.63833200	-0.35541700	1.45410900
H	3.84509400	0.54374400	-0.08251700
H	4.70848900	-0.66358800	0.86836900
H	2.85585500	0.43921200	2.17053700

H	2.59475100	-1.29972400	2.01132700
C	2.04093800	-1.27413900	-1.28389900
H	1.81636300	-2.07446600	-1.99602100
H	2.01488500	-0.32352600	-1.82841100
C	0.97595300	-1.24876100	-0.17362500
C	0.66527100	1.05089600	0.96418100
H	1.12727500	-2.16601000	0.41468500
C	3.42839800	-1.48817400	-0.67225400
H	4.18915400	-1.47278700	-1.45748000
H	3.46321700	-2.48540200	-0.21744700
C	-0.55661000	1.66314400	0.31311900
H	-1.17475800	0.90360200	-0.16515700
B	0.03182200	2.59256200	-0.81668500
O	0.27209600	3.90829900	-0.52558200
H	0.67268700	4.43173300	-1.22332500
O	0.32046500	2.03092300	-2.03784900
H	0.74043100	2.61662000	-2.67228700
C	-1.40504800	2.40951800	1.35400700
H	-0.78020900	3.15363500	1.85868300
H	-2.19360500	2.97097200	0.84324200
C	-2.02323200	1.45563800	2.37362800
H	-2.60603800	1.99224300	3.12537000
H	-2.68825600	0.74242000	1.87656700
H	-1.25185800	0.87681600	2.88888900
H	1.12815600	1.72897300	1.68452100
C	-0.45176600	-1.30271000	-0.65790700
C	-1.46716200	-1.66215500	0.24480600
C	-0.82587200	-0.98938700	-1.96145100
C	-2.80964500	-1.67634800	-0.13555600
C	-2.16281700	-1.00320700	-2.34707900
H	-0.06894000	-0.68631600	-2.67285200
C	-3.15855500	-1.33981800	-1.43632600
H	-3.56537700	-1.94841400	0.59135900
H	-2.42810300	-0.73889600	-3.36417400
H	-4.19924400	-1.34462300	-1.73634200
C	-1.12847300	-1.99276800	1.60320700
N	-0.85941200	-2.26921300	2.68767700

TS(G1-H1)



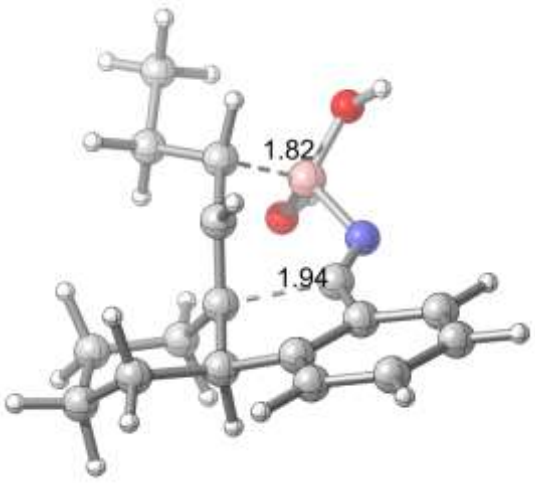
E(M062X)= -891.046814777
Zero-point correction= 0.364852 (Hartree/Particle)
Thermal correction to Energy= 0.383700
Thermal correction to Enthalpy= 0.384644
Thermal correction to Gibbs Free Energy= 0.319294
Sum of electronic and zero-point Energies= -890.681963
Sum of electronic and thermal Energies= -890.663115
Sum of electronic and thermal Enthalpies= -890.662171
Sum of electronic and thermal Free Energies= -890.727521
E(M062X) PCM(1,4-dioxane)= -891.0651835

Imaginary frequency: -381.3377

0 1

C	-0.09462600	0.94090700	-0.13369700
C	-0.29067400	1.41924900	1.29880800
H	0.66043100	1.43310200	1.83008600
C	-1.36364300	0.97650000	-0.96776100
C	-1.51714700	-1.26986900	0.06341000
C	-0.08100000	-1.10801000	0.24367100
C	1.14040000	0.83472000	-0.73456700
H	1.14624400	0.69968000	-1.81844600
C	2.37864500	0.57509500	-0.07232400
H	2.42670500	0.97078000	0.94534400
C	3.62417500	0.96450000	-0.88673800
H	3.58544700	2.04128500	-1.08504000
H	3.57413400	0.45402100	-1.85201400
C	4.95172900	0.64024300	-0.20760800
H	5.09165600	-0.43438000	-0.09999900
H	5.78213600	1.04568800	-0.79034300
H	4.99743900	1.07885600	0.79346500
H	-1.09453000	0.79848500	-2.01575200
N	0.95435900	-1.61259600	0.51959600
B	2.47817700	-1.20568800	0.19131300
O	3.34278300	-1.53126900	1.26769900
H	2.98115900	-1.30296700	2.12460800
O	2.86500300	-1.78838400	-1.03623100
H	3.36629100	-2.59105200	-0.87423600
C	-2.21071800	-0.21164400	-0.52784000
H	-0.94763400	0.73010500	1.84342800
C	-2.07706300	2.33419800	-0.87431700
H	-3.02720400	2.30452900	-1.41413100
H	-1.45118200	3.07206400	-1.38693200
C	-0.94922300	2.80571100	1.31894800
H	-1.09687500	3.12441300	2.35414200
H	-0.28013200	3.53393000	0.84678800
C	-2.28365900	2.77662800	0.57351200
H	-2.75683400	3.76152600	0.59675100
H	-2.96563200	2.08220600	1.07924300
C	-2.15737700	-2.44680100	0.45266400
H	-1.57988800	-3.24701400	0.89978800
C	-3.58331900	-0.34333300	-0.71412800
C	-3.52683800	-2.55961900	0.26180600
H	-4.04389600	-3.46204600	0.56368400
C	-4.23405300	-1.50839100	-0.31877000
H	-5.30391600	-1.59911800	-0.46681500
H	-4.15125800	0.45923900	-1.16950600

TS(G1-H2)



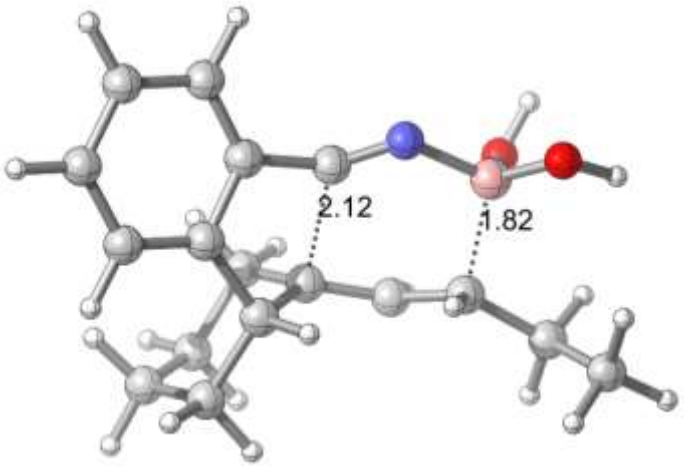
E(M062X)= -891.016588636
Zero-point correction= 0.365759 (Hartree/Particle)
Thermal correction to Energy= 0.384290
Thermal correction to Enthalpy= 0.385234
Thermal correction to Gibbs Free Energy= 0.321532
Sum of electronic and zero-point Energies= -890.650829
Sum of electronic and thermal Energies= -890.632299
Sum of electronic and thermal Enthalpies= -890.631355
Sum of electronic and thermal Free Energies= -890.695057
E(M062X) PCM(1,4-dioxane)= -891.0333522

Imaginary frequency: -371.71 cm^{-1}

0 1

C	0.01728800	0.78260900	0.21544900
C	1.44760500	1.29631800	0.21404000
C	-0.80587800	1.58414200	1.19302200
C	0.40004200	-1.07674600	0.59866900
C	-0.55477800	0.19786600	-0.91484700
H	0.15522400	-0.11403900	-1.68433600
C	-1.88475000	-0.35150900	-0.97022000
N	-0.50433500	-1.84851000	0.79776100
B	-2.04321600	-1.53723100	0.40026000
O	-2.69223200	-2.71500600	-0.06127400
H	-2.10571900	-3.30209300	-0.53960700
O	-2.73291800	-0.93151100	1.47883800
H	-3.34710800	-1.56381300	1.86025100
H	1.67145800	1.53806700	1.26301200
C	-0.84950800	3.00224700	0.57168600
H	-1.38217800	3.68364900	1.24025500
H	-1.43254500	2.94094600	-0.35381800
C	1.47173600	2.63488300	-0.52234900
H	2.48109600	3.05491200	-0.56244700
H	1.12268400	2.50042900	-1.55148000
C	0.54353800	3.58565400	0.26221400
H	0.42895300	4.52856400	-0.27793400
H	1.03970900	3.82747700	1.20950900
H	-0.30363000	1.61318800	2.16481500
H	-1.79931100	1.17565400	1.35287600
C	2.37258100	0.14882800	-0.08750200
C	1.84369700	-1.08052700	0.32172500
C	3.67438700	0.20821900	-0.56348900
H	4.09520400	1.15323900	-0.88816000
C	2.60593700	-2.24450500	0.28820800
H	2.16668500	-3.18361000	0.60353600
C	4.43901500	-0.95655000	-0.61062200
H	5.45492800	-0.91522500	-0.98567400
C	3.91464600	-2.17252600	-0.17577800
H	4.52295200	-3.06805200	-0.21366700
H	-1.97363000	-0.96744800	-1.86980800
C	-3.11830400	0.57681200	-0.92040200
H	-2.99366900	1.38372500	-1.65090400
H	-3.23002400	1.03496300	0.06072300
C	-4.39572200	-0.19374200	-1.24901300
H	-4.56587500	-0.98986000	-0.52376200
H	-5.25994800	0.47410600	-1.24643200
H	-4.32680900	-0.65576900	-2.23782500

TS(G2-H1)



E(M062X)=	-891.033866262
Zero-point correction=	0.365505 (Hartree/Particle)
Thermal correction to Energy=	0.384146
Thermal correction to Enthalpy=	0.385091
Thermal correction to Gibbs Free Energy=	0.320394
Sum of electronic and zero-point Energies=	-890.668361
Sum of electronic and thermal Energies=	-890.649720
Sum of electronic and thermal Enthalpies=	-890.648776
Sum of electronic and thermal Free Energies=	-890.713472
E(M062X) PCM(1,4-dioxane)=	-891.0518985

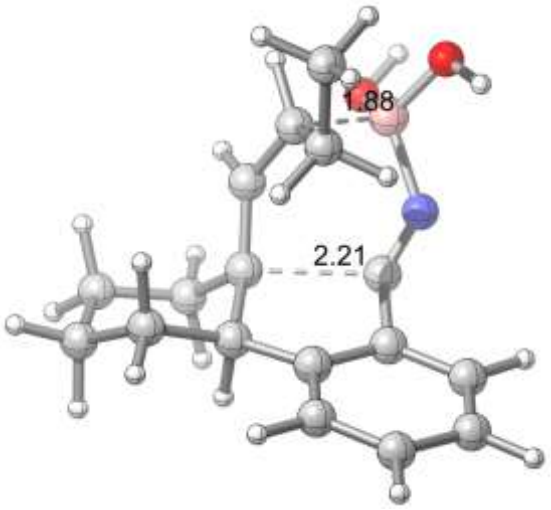
Imaginary frequency: -434.49 cm^{-1}

0 1

C	-0.07966600	0.88739200	0.43757300
C	-0.84636600	1.39580100	1.65037000
H	-0.18618600	1.41648800	2.51980100
C	-0.95482800	0.85496000	-0.81755700
C	-1.44737700	-1.36542600	0.08792000
C	-0.02795700	-1.23337500	0.38359000
C	1.29976100	1.01847400	0.45890400
H	1.72269200	1.42314900	1.38021100
C	2.24698800	0.39869400	-0.39305400
H	1.86481700	0.08676200	-1.36833900
C	3.65071900	1.02330100	-0.48002100
H	4.27863000	0.64115700	0.33151300
H	3.58877400	2.10408400	-0.32616000
C	4.30519200	0.75399700	-1.83486600
H	3.74025300	1.23789000	-2.63600700
H	5.32636400	1.14013900	-1.86512200
H	4.33108400	-0.31561200	-2.05310300
H	-0.33783200	0.59677900	-1.68539900
N	1.02961100	-1.76611100	0.36190900
B	2.49175500	-1.19684600	0.44619800
O	2.88913400	-0.91370600	1.78278400
H	3.28964700	-1.68483800	2.19102000
O	3.35048700	-2.01735900	-0.32802300
H	4.26613600	-1.76178700	-0.20192300
C	-1.95821000	-0.27537400	-0.61885000
H	-1.66520500	0.70661000	1.89096600
C	-1.59863700	2.22782000	-1.06736400
H	-2.25819000	2.17858500	-1.93922800
H	-0.79584400	2.92691000	-1.32312700
C	-1.44357500	2.78411700	1.38530000
H	-2.00191900	3.12621900	2.26112100
H	-0.62838800	3.49843500	1.22020400
C	-2.35248700	2.75330800	0.15610300
H	-2.74673700	3.75103900	-0.05419200

H	-3.21410200	2.10943000	0.36717900
C	-2.20118700	-2.50213900	0.35620300
H	-1.75922400	-3.33412800	0.89062100
C	-3.27122100	-0.33400200	-1.06641700
C	-3.52125400	-2.53614800	-0.07971200
H	-4.13747700	-3.40160800	0.13069500
C	-4.04704000	-1.45956000	-0.78907900
H	-5.07570000	-1.49449200	-1.12874200
H	-3.70174600	0.49327200	-1.61870100

TS(G2-H2)



E(M062X)= -890.994576293
Zero-point correction= 0.365356 (Hartree/Particle)
Thermal correction to Energy= 0.384096
Thermal correction to Enthalpy= 0.385040
Thermal correction to Gibbs Free Energy= 0.320222
Sum of electronic and zero-point Energies= -890.629220
Sum of electronic and thermal Energies= -890.610481
Sum of electronic and thermal Enthalpies= -890.609536
Sum of electronic and thermal Free Energies= -890.674354
E(M062X) PCM(1,4-dioxane)= -891.012175

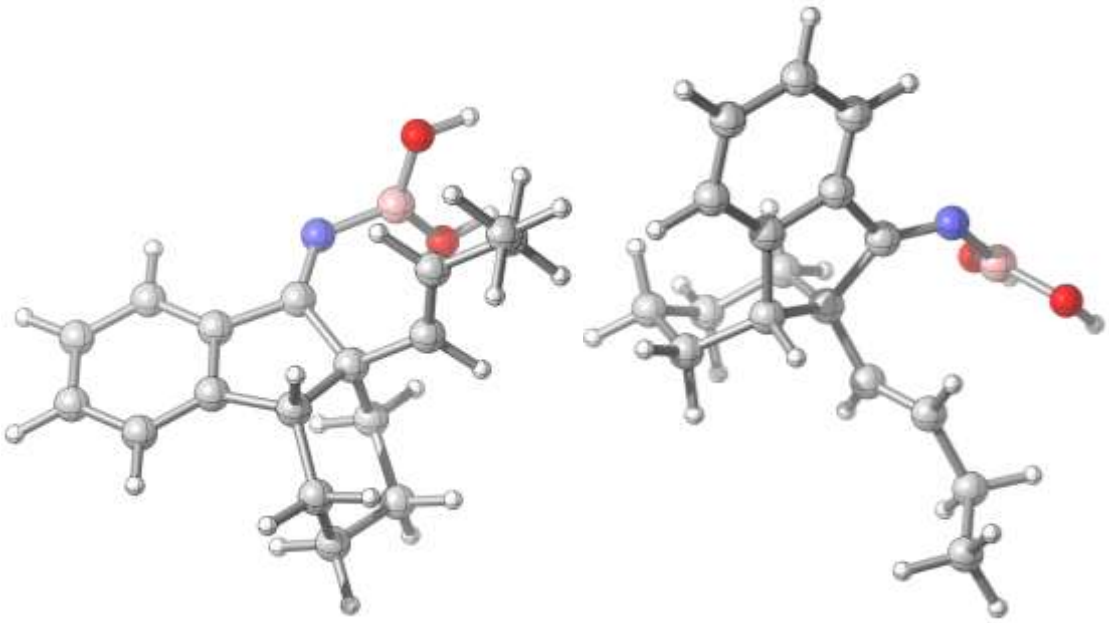
Imaginary frequency: -473.96 cm^{-1}

0 1

C	-0.18384100	1.29870100	-0.54532300
C	-1.54223800	0.81638500	-0.02857200
C	-0.48175400	2.56836800	-1.34695200
C	0.34232100	-0.73641400	-1.22304900
C	1.05723100	1.38517400	0.09477700
H	1.67056100	2.20134400	-0.28693900
C	1.82512100	0.47183500	0.83910400
N	1.49531400	-1.01487000	-1.26914800
B	2.75999600	-0.31197500	-0.59100100
O	3.64595100	-1.26447800	-0.04574900
H	3.21965700	-2.09753100	0.16155300
O	3.37091400	0.68471500	-1.35903500
H	4.25837000	0.41073400	-1.60278800
H	-2.23423300	1.09859400	-0.83605400
C	-0.99328700	3.61182600	-0.32404400
H	-1.28891300	4.53385000	-0.83394600
H	-0.14865000	3.86640100	0.32601900
C	-1.97176700	1.71073600	1.13739600
H	-2.91282100	1.37648100	1.58529700
H	-1.20491100	1.70407700	1.91776900
C	-2.16475300	3.12297400	0.54777500
H	-2.34562300	3.84718100	1.34624900

H	-3.07409600	3.10112500	-0.06481500
H	-1.23557500	2.38534500	-2.11895000
H	0.40988100	2.95060000	-1.84734600
C	-1.75003400	-0.67197000	-0.03573200
C	-0.92776600	-1.37981500	-0.91341400
C	-2.79961900	-1.34514600	0.58377900
H	-3.44708700	-0.81894900	1.27534800
C	-3.02683100	-2.68809900	0.30252400
H	-3.84572000	-3.20517900	0.78932400
C	-1.14932100	-2.72666100	-1.20397000
H	-0.47337500	-3.25056300	-1.86909600
C	-2.21869800	-3.37506800	-0.60348400
H	-2.40931800	-4.41915900	-0.81945900
H	2.71467800	0.93100000	1.27340700
C	1.21006600	-0.61129000	1.71860800
H	0.20266000	-0.31742800	2.03233100
H	1.07722000	-1.54731000	1.16138100
C	2.07205000	-0.88493600	2.95105000
H	1.65714200	-1.69388600	3.55584900
H	3.08557400	-1.16089700	2.65028200
H	2.14120800	0.00665100	3.57906500

Cycloadduct H1



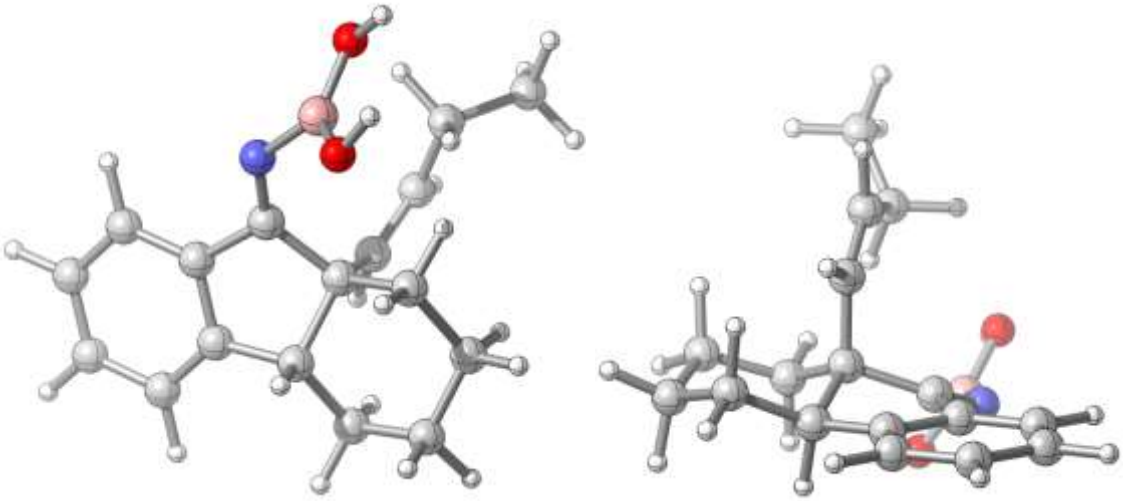
E(M062X)= -891.105947302
Zero-point correction= 0.367547 (Hartree/Particle)
Thermal correction to Energy= 0.387128
Thermal correction to Enthalpy= 0.388072
Thermal correction to Gibbs Free Energy= 0.320080
Sum of electronic and zero-point Energies= -890.738400
Sum of electronic and thermal Energies= -890.718820
Sum of electronic and thermal Enthalpies= -890.717875
Sum of electronic and thermal Free Energies= -890.785867
E(M062X) PCM(1,4-dioxane)= -891.1119016

0 1

C	0.12835000	0.46919500	0.38225900
C	-0.25621600	0.71351000	1.86805700
H	0.54112400	0.30014000	2.49088300
C	-0.88720000	1.17523700	-0.57121800
C	-1.56533500	-1.10394300	-0.32120600
C	-0.16038300	-1.02878000	0.14446600
C	1.55784900	0.87670700	0.13535000

H	1.99882000	1.57248800	0.84841000
C	2.30464400	0.43495800	-0.87408600
H	1.87760400	-0.27848700	-1.58013300
C	3.72677000	0.83242400	-1.13215800
H	4.35172300	-0.06793600	-1.11053400
H	4.07574700	1.49164300	-0.33197400
C	3.89064900	1.51906100	-2.49190800
H	3.30481100	2.43989900	-2.52975900
H	4.93587300	1.76809400	-2.68561100
H	3.54446300	0.86756400	-3.29788600
H	-0.41442400	1.22004600	-1.55999900
N	0.58864000	-2.02095600	0.34596000
B	1.93502600	-2.03690500	0.84613300
O	2.14461600	-1.72977100	2.17285000
H	3.03839200	-1.87404800	2.48870100
O	2.93188400	-2.47508200	0.00629100
H	3.80656900	-2.49988800	0.39638900
C	-2.01568900	0.16765800	-0.67111300
H	-1.16301400	0.14359900	2.09927500
C	-1.26630100	2.59953900	-0.16715900
H	-2.07004800	2.96068700	-0.81594800
H	-0.40251500	3.24844700	-0.35398100
C	-0.52680000	2.18337300	2.18387600
H	-0.78001000	2.28457200	3.24254000
H	0.37437200	2.78563100	2.01558500
C	-1.65843800	2.71198700	1.30437900
H	-1.88780000	3.75214600	1.55006300
H	-2.56669700	2.12710300	1.49284800
C	-2.38409300	-2.22174600	-0.41201800
H	-1.99653200	-3.19669900	-0.13859200
C	-3.32458200	0.34359000	-1.10200300
C	-3.69381500	-2.04444400	-0.84440000
H	-4.36246200	-2.89410500	-0.91604000
C	-4.15824600	-0.77103000	-1.18119200
H	-5.18319600	-0.64899500	-1.51264300
H	-3.69738000	1.32436200	-1.37665600

Cycloadduct H2



E(M062X)=	-891.093404054
Zero-point correction=	0.367882 (Hartree/Particle)
Thermal correction to Energy=	0.387392
Thermal correction to Enthalpy=	0.388336
Thermal correction to Gibbs Free Energy=	0.320502
Sum of electronic and zero-point Energies=	-890.725522
Sum of electronic and thermal Energies=	-890.706012
Sum of electronic and thermal Enthalpies=	-890.705068

Sum of electronic and thermal Free Energies= -890.772902
E(M062X) PCM(1,4-dioxane)= -891.1109771

0 1

C	0.15252400	0.53089500	-0.12487300
C	-1.13774000	1.16319600	-0.71952900
C	-1.67691300	-0.99079100	0.09534900
C	-0.21832600	-0.95641900	-0.21672000
C	0.22182300	0.87202000	1.36585700
H	-0.64076400	1.40386700	1.75833100
C	1.17992700	0.56473100	2.23979700
H	-1.10964500	0.93504600	-1.79578700
N	0.47489800	-1.94640200	-0.55797300
B	1.76286300	-2.15729600	-1.12493800
O	2.76626500	-2.66264000	-0.32843000
H	3.57882400	-2.88446900	-0.78526800
O	1.91451300	-1.93646500	-2.47690600
H	2.75900700	-2.20395100	-2.84259000
C	-2.21964800	0.27771000	-0.14242700
C	-1.15143800	2.68015400	-0.60498800
H	-2.06203700	3.09072600	-1.05127500
C	-2.46190300	-2.04705800	0.52730300
H	-2.01932200	-3.02364300	0.68843900
C	-3.56681200	0.51220800	0.08209900
C	-3.81506000	-1.80839000	0.76079600
H	-4.45234300	-2.60916700	1.11673700
C	-4.35755000	-0.54165100	0.54556000
H	-5.41136600	-0.37448500	0.73732300
H	-4.00281000	1.48895900	-0.09809600
C	1.35567900	1.03067300	-0.92094600
H	2.29271800	0.61910600	-0.53718600
H	1.25712100	0.68966500	-1.95778800
C	0.08687800	3.21617300	-1.34379400
H	0.15259300	4.30130900	-1.23036100
H	-0.03585800	3.01699200	-2.41527000
C	1.39470600	2.56682000	-0.86344200
H	1.58951600	2.87310700	0.17006800
H	2.22739300	2.93671300	-1.46768400
H	-1.13532600	2.99842300	0.44162500
H	1.03490100	0.91612700	3.26047000
C	2.45529800	-0.18972500	2.00365100
H	2.57566500	-0.92458500	2.80605200
H	2.41071800	-0.76505000	1.08100800
C	3.67072900	0.74580500	1.99896900
H	3.59334000	1.48002700	1.19270000
H	3.74189000	1.29697700	2.94008800
H	4.59792100	0.18434300	1.86567300