Electronic Supplementary Information

Persistent guaiazulene arylmethylium ions as electrophilic traps for metal enolates

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1. General information

If otherwise not noted, chemicals were purchased from commercial sources (Merck, ThermoFischer, TCI) and used without further purification. Reactions were carried out under Ar atmosphere using oven dried glassware and using standard Schlenk techniques. Solvents were purified by standard methods.

NMR spectra were recorded with Varian NMR System 600 instruments (600 MHz for ^{1}H, 150 MHz for ^{13}C) and Bruker Ascend (400 MHz for ^{1}H, 100 MHz for ^{13}C). Chemical shifts (δ) are given in ppm relative to tetramethylsilane.

Compounds were purified by flash chromatography using Isolera Biotage FSKO-1107-0010 or Büchi Pure C-810 Flash systems. Thin-layer chromatography was performed on Merck TLC-plates silica gel 60, F-254.

High-resolution mass spectroscopy was measured by using Orbitrap Thermo Scientific Velos pro with heated electrospray ionization (capillary temperature 350 °C, source heater temperature 300 °C, mass range 80–600 m/z, full scan, positive polarity, resolution 120000).

FT-IR spectra were recorded with Agilent Technologies Cary 630 spectrometer by ATR technique and reported in wave numbers (cm^{-1}).

Enantiomeric purities were determined by Chiralcel and Chiralpak (Daicel Chemical Industries Ltd.) columns on HPLC Agilent Technologies 1200 Infinity series using Chemstation software for LC systems.

Melting points were measured using a Melting Point M-656 apparatus (Büchi).

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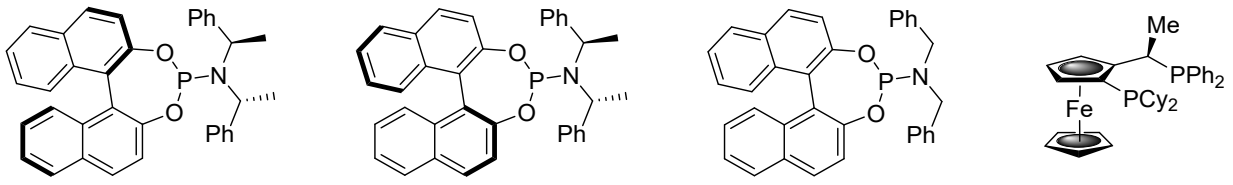
The ligands used in this work were prepared following a literature procedure, except **L4** which was bought from commercial source.[1]



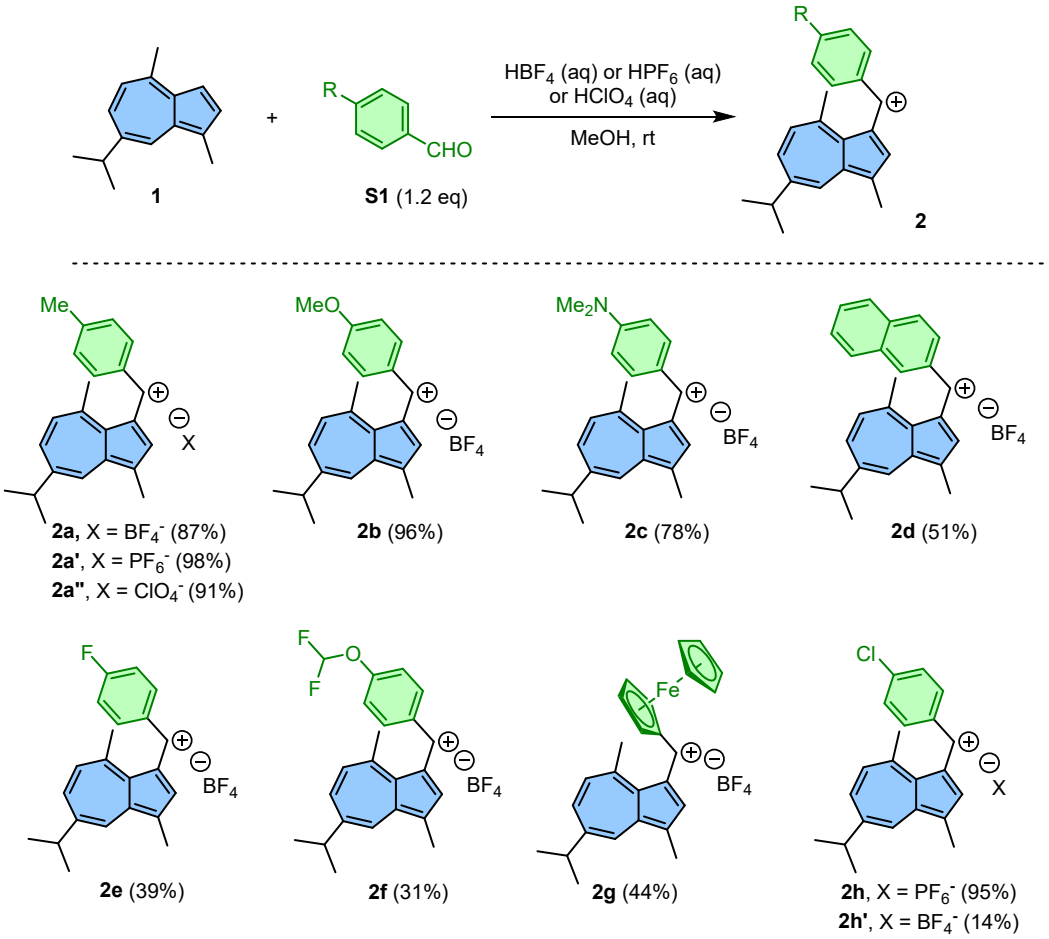
L1 **L2** **L3** (racemic) **L4** (*R*,*S*)-Rev-Josiphos

Figure S1. Structures of the used ligands.

2. General procedure for the preparation of guaiazulene-stabilized carbocations

General procedure 1: reaction of guaiazulene with aldehydes

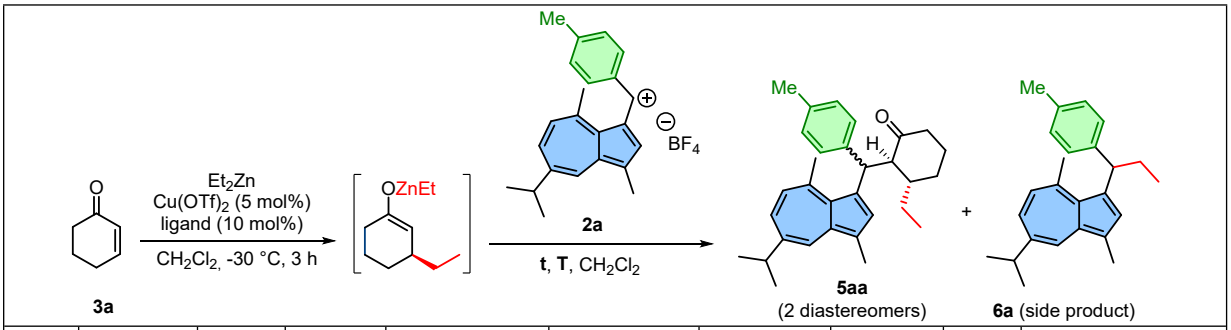
The guaiazulene-stabilized carbocations were prepared based on a literature procedure.[2] Guaiazulene (1 g, 5 mmol, 1 eq) was dissolved in MeOH (20 mL). To this solution, a mixture of the aldehyde (1.2 eq, 6.05 mmol), 50 wt% aqueous HBF_4 (1.7 mL, 14 mmol, 2.7 eq) or 55 wt% aqueous HPF_6 (2.2 mL, 14 mmol, 2.7 eq) or 70 wt% aqueous $HClO_4$ (1.2 mL, 14 mmol, 2.7 eq), and MeOH (40 mL) was slowly added at room temperature and stirred for 1–3 h. The reaction progress was followed by TLC (Hex:EtOAc 4/1). After that, Et_2O was added (100 mL) and the reaction mixture containing the precipitated solid was cooled in the freezer (few hours to overnight). Then, the solid was filtered, washed with Et_2O, and dried under reduced pressure. The crude product can be purified by the following recrystallization process: the crude product is dissolved in minimum amount of CH_3CN and then dropwise added to Et_2O. The mixture containing the precipitated solid is cooled, filtered, and dried under reduced pressure to give the final product. The prepared carbocations were stored in the fridge under Ar atmosphere. During our work, we did not observe any issues with the stability of these compounds.



Scheme S1. Preparation of guaiazulene-stabilized carbocations.

3. Enolate trapping reactions – study of reaction conditions and other Michael acceptors

Table S1. Study of the reaction conditions.



Entry	Ligand	Et_2Zn (eq)	Cation (eq)	T (enolate trap.)	t (enolate trap.)	Isolated yield (%)	ee (%)[a,b]	dr[c]	comment
1.	**L1**	3.0	3.0	-30 °C to rt	o/n	53	-88/-86	~1:1	cation added to enolate
2.	**L2**	1.3	3.0	-30 °C to rt	o/n	46	96/97	~1:1	enolate added to cation
3.	**L2**	1.3	2.0	rt	1 h	83	97/97	~1:1	enolate added to cation
4.	**L2**	1.3	2.0	-30 °C to rt	1 h	58	96/97	~1:1	enolate added to cation
5.	**L3**	1.3	2.0	-30 °C to rt	o/n	33	-	~1:1	racemic

[a] Enantiomeric excesses were determined by chiral HPLC using CHIRALPAK® IA column (Hex:IPA 90/10, 1.0 mL/min, 254 µm). [b] The stereochemistry of the product is based on the work of Alexakis *et al.*[3] and assuming *trans* orientation for the cyclohexanone. [c] Diastereomeric ratios were determined by ^1H NMR.

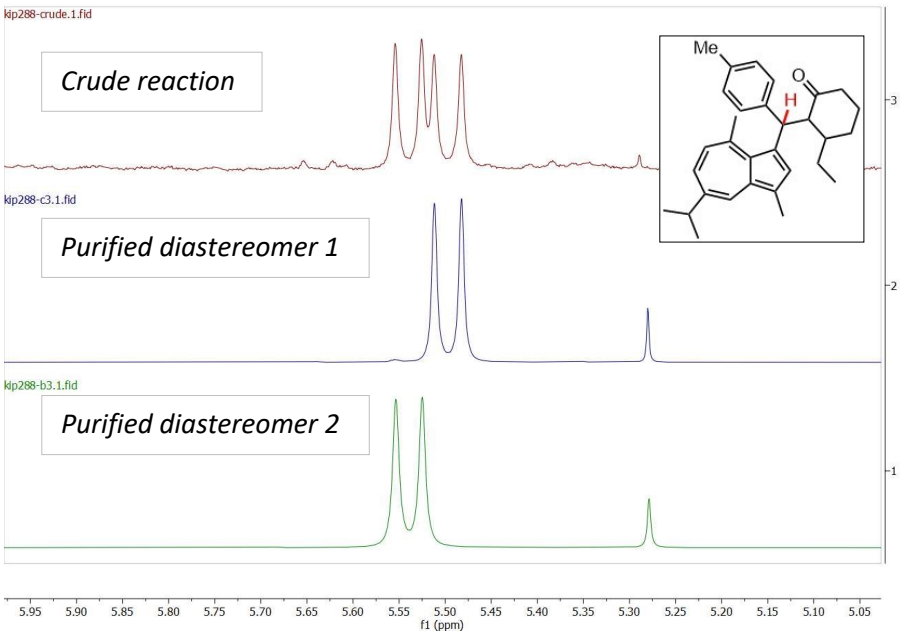
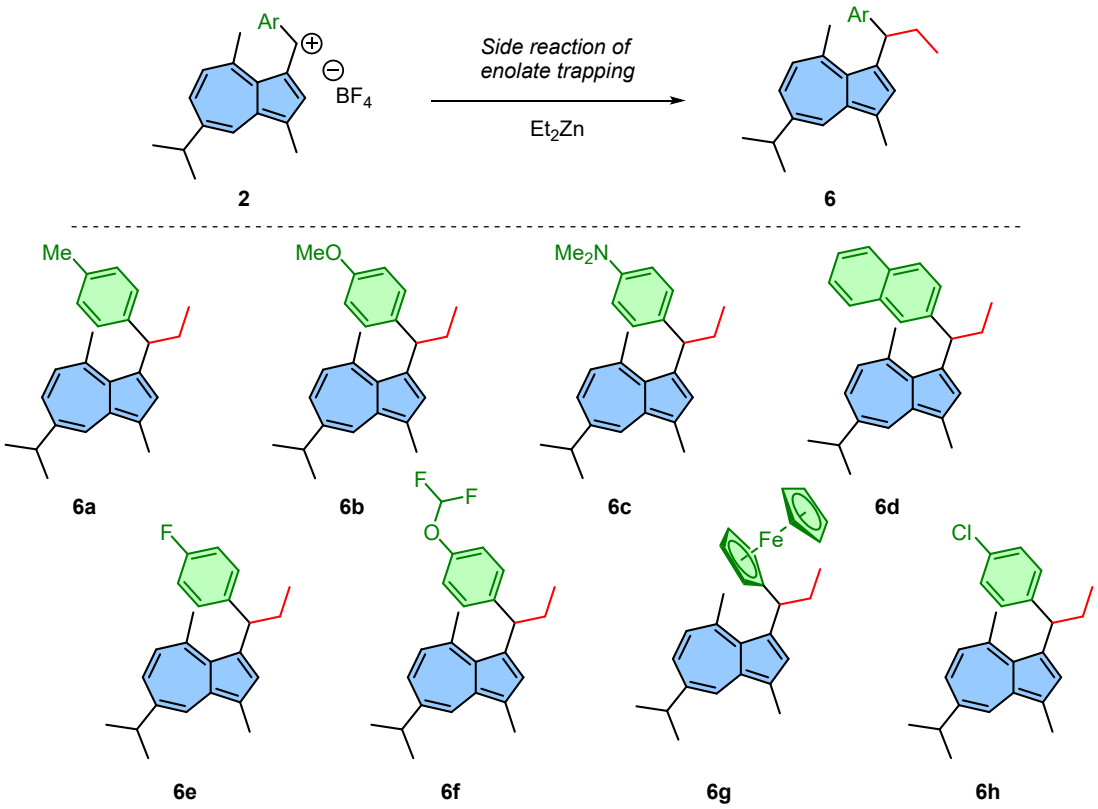
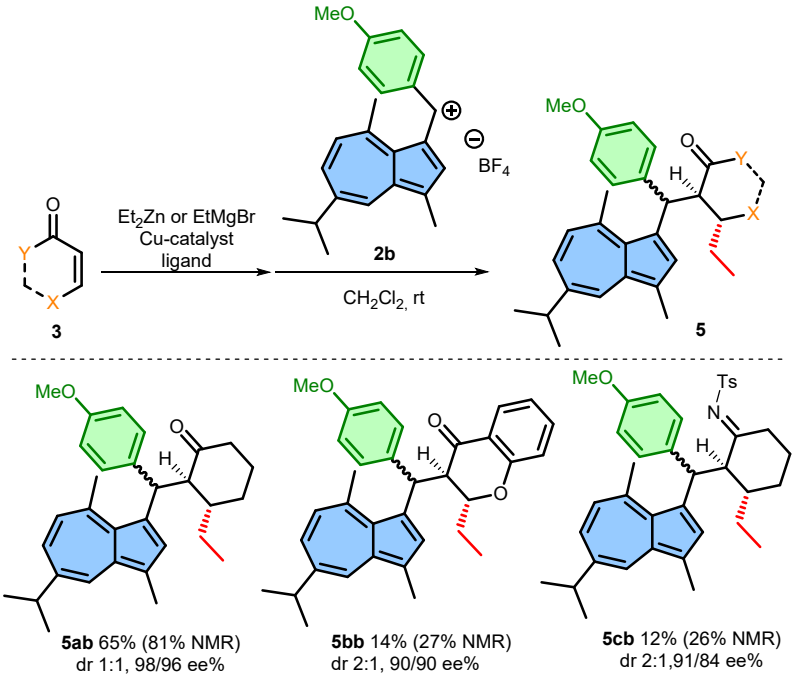


Figure S2. Determination of the dr ratio from the crude reaction mixture (^1H NMR, $CDCl_3$). The observed ^1H signals belong to the hydrogen atom shown in red color (upper right corner).



Scheme S2. Isolated and characterized side products from the cation scope: reaction of the cation with Et_2Zn.



Scheme S3. Other asymmetric conjugate addition (ACA) formed enolates in the enolate trapping reaction.

4. Reaction procedures for the enolate trapping reactions

General procedure 2: tandem conjugate addition and enolate trapping

Copper(I) thiophene-2-carboxylate (5 mg, 0.025 mmol, 5 mol%) and ligand **L2** (27 mg, 0.05 mmol, 10 mol%) were added to a dry Schlenk-tube under Ar atmosphere. Next, dry DCM (1.5 mL) was added, and the mixture was stirred at room temperature for 15 min and then cooled to -30 °C. At this temperature, first 2-cyclohexen-1-one (48 µL, 0.5 mmol, 1.0 eq) and then Et_2Zn (0.9M in hexane, 725 µL, 0.65 mmol, 1.3 eq) were slowly added. The conjugate addition reaction mixture was stirred for 3 h at -30 °C. Next, in another dry Schlenk-tube the guaiazulene-stabilized carbocation (1.0 mmol, 2.0 eq) was dissolved in dry DCM (2–5 mL) at room temperature under Ar atmosphere. Finally, the first reaction mixture (containing the metal enolate) was transferred to the second Schlenk-tube (containing the solution of the carbocation) using a syringe and was stirred for 1 h at room temperature. The reaction was quenched by the addition of saturated aqueous NH_4Cl (~ 10 mL). The phases were separated, and the aqueous phase was further extracted with DCM (3 × 50 mL). The combined organic phase was dried over anhydr. $MgSO_4$, and the solvent was evaporated under reduced pressure. The crude product was purified by flash chromatography (silica gel, mixtures of hexane and ethyl acetate) to gain the final products as a blue oil.

General procedure 3: reaction with silyl enol ether

In a dry Schlenk-tube, carbocation **2a** (100 mg, 0.26 mmol, 1.0 eq) was measured under Ar atmosphere. Next, dry DCM (2 mL) was added and stirred at room temperature for 5 min. Then, silyl enol ether (0.52 mmol, 2.0 eq) was added slowly and the reaction mixture was stirred at the same temperature for 1 h. The reaction was quenched by the addition of sat. aqueous NaCl (~10 mL). The phases were separated, and the aqueous phase was further extracted with EtOAc (3 × 50 mL). The combined organic phase was dried over anhydr. $MgSO_4$, and the solvent was evaporated under reduced pressure. The crude product was purified by flash chromatography (silica gel, mixtures of hexane and ethyl acetate) to gain the final products as a blue oil.

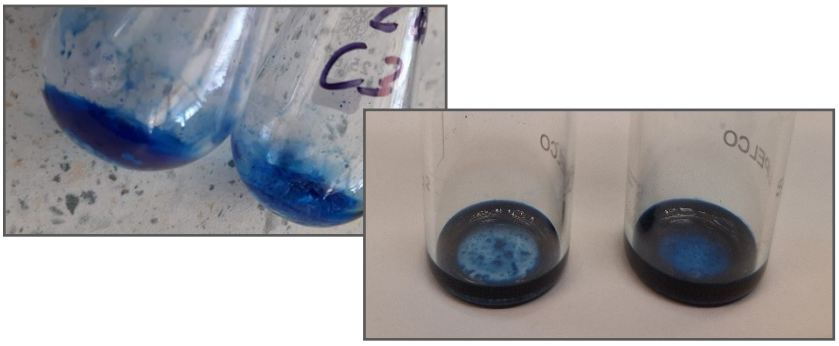
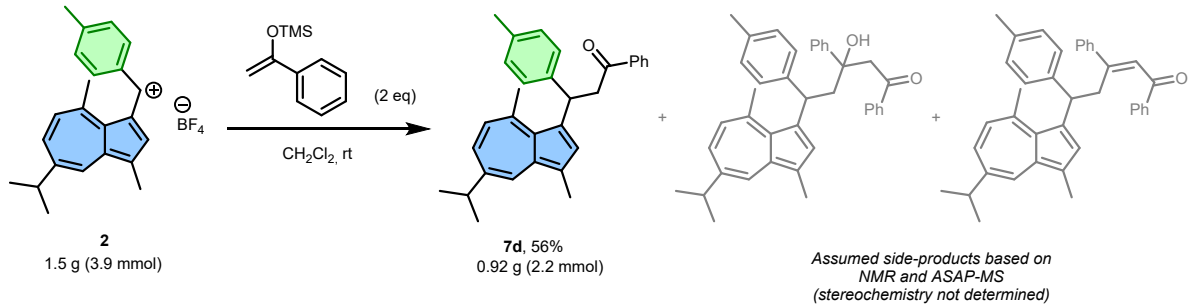


Figure S3. Picture of the diastereomers of **5aa** and **5ac**, respectively, after column chromatography showing the typical blue color of the products.

5. Scale-up reaction



2
1.5 g (3.9 mmol)

7d, 56%
0.92 g (2.2 mmol)

Assumed side-products based on NMR and ASAP-MS (stereochemistry not determined)

Scheme S4. Scale-up reaction.

In a dry round bottom flask, carbocation **2a** (1.5 g, 3.9 mmol, 1.0 eq) was measured under Ar atmosphere. Next, dry DCM (30 mL) was added and stirred at room temperature for 5 min. Then, 1-phenyl-1-trimethylsiloxyethylene (1.6 mL, 7.8 mmol, 2.0 eq) was added slowly and the reaction mixture was stirred at the same temperature for 90 min. The reaction was quenched by the addition of sat. aqueous NaCl (~20 mL). The phases were separated, and the aqueous phase was further extracted with EtOAc (3 × 50 mL). The combined organic phase was dried over anhydr. $MgSO_4$, and the solvent was evaporated under reduced pressure. The crude product was purified by flash chromatography (silica gel, Hex:EtOAc 50:1 to 10:1) to gain the final **7d** product as a blue solid (0.92 g, 56%).

The progress of the reaction can be observed by the color change: the original deep orange color of the carbocation **2a** changes into dark blue showing the formation of the product **7d** (see Fig. S4 for more details).

Based on NMR and ASAP-MS analyses, we assume the formation of two side-products (**Scheme S4**). These might be formed by an additional reaction of the product **7d** with another molecule of silyl enol ether reactant and consecutive H_2O elimination.

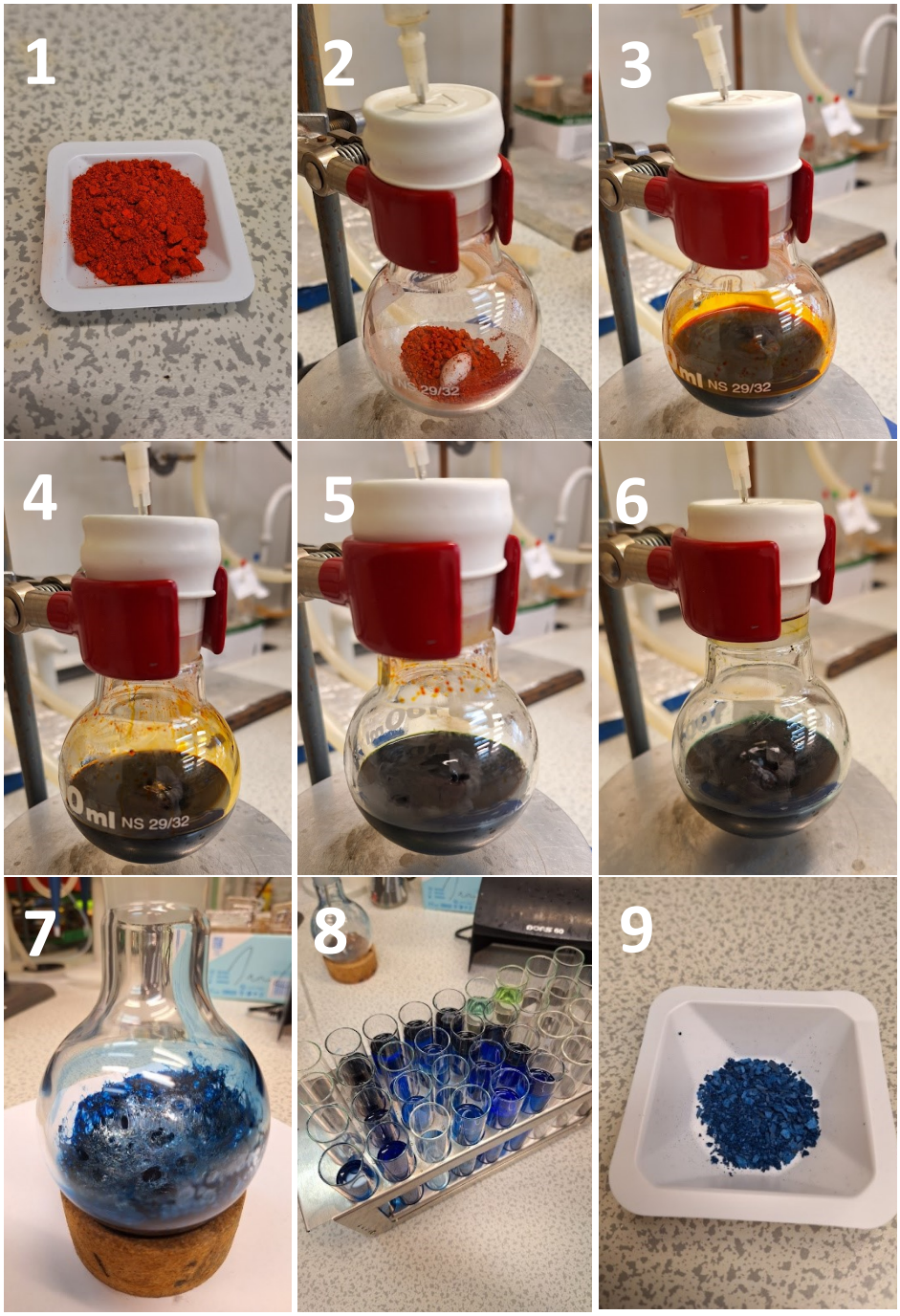
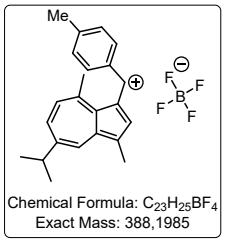


Figure S4. Pictures of the scale-up reaction: 1) Carbocation starting material **2a**; 2) Starting material under Ar atmosphere in a pre-dried flask; 3) After the addition of dry DCM (Note: red/orange color); 4) After the addition of 1-phenyl-1-trimethylsiloxyethylene (start of reaction); 5) Reaction mixture after 10 min (Note: color changed); 6) Reaction mixture after 90 min (Note: blue/green color); 7) Crude reaction mixture after work-up; 8) Column chromatography; 9) Final product (**7d**).

6. Characterization data

6.1. Carbocations

(5-isopropyl-3,8-dimethylazulen-1-yl)(*p*-tolyl)methylium tetrafluoroborate (2a)

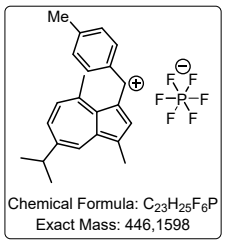


Following the *General procedure 1 (double scale)*: guaiazulene (2.0 g, 10.1 mmol), 48 wt% aqueous HBF_4 (3.4 mL, 2.7 eq), 4-methylbenzaldehyde (1.4 mL, 1.2 eq), MeOH (40 + 80 mL). Isolated: 3.4 g (87%)

Orange solid, **Mp:** 180–187 °C (degr.); **UV-Vis:** λ_{max} (DCM): 488 nm (ε: 32400 M^{-1} cm^{-1}); **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 8.79 (s, 1H), 8.59 (d, *J* = 11.2 Hz, 1H), 8.54 (d, *J* = 2.2 Hz, 1H), 8.42 (dd, *J* = 11.3, 2.3 Hz, 1H), 8.06 – 8.02 (m, 1H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 3.51 (p, *J* = 6.8 Hz, 1H), 3.46 (s, 3H), 2.60 (s, 3H), 2.54 (s, 3H), 1.55 (s, 3H), 1.53 (s, 3H). **^{13}C NMR** (150 MHz, CD_2Cl_2): δ 170.14, 160.04, 156.34, 152.71, 150.64, 149.37, 144.67, 144.22, 143.89, 141.32, 138.44, 138.00, 133.21, 132.51, 130.51, 39.75, 29.49, 23.58, 21.62, 13.62. **^{19}F NMR** (376 MHz, CD_2Cl_2): δ -152.90, -152.95. **IR** (ATR): ν_{max} 2967 (w), 1579 (m), 1556 (m), 1403 (m), 1348 (m), 1323 (m), 1192 (m), 1048 (s), 1035 (s), 819 (m), 520 (m), 507 (m) cm^{-1}. **HRMS** (HESI): m/z $[M+H]^+$ calcd for $C_{23}H_{25}$: 301.1951, found: 301.1946

Spectral data corresponds to the literature (different NMR solvent).[4]

(5-isopropyl-3,8-dimethylazulen-1-yl)(p-tolyl)methylium hexafluorophosphate(V) (2a')

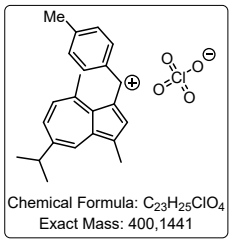


Following the *General procedure 1*: guaiazulene (1.0 g, 5.0 mmol), 55 wt% aqueous HPF_6 (2.2 mL, 2.7 eq), 4-methylbenzaldehyde (0.7 mL, 1.2 eq), MeOH (20 + 40 mL). Isolated: 2.2 g (98%)

Dark red solid, **Mp:** 140–145 °C (degr.); **UV-Vis:** λ_{max} (DCM): 491 nm (ε: 29300 M^{-1} cm^{-1}); **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 8.73 (s, 1H), 8.55 – 8.46 (m, 2H), 8.35 (dd, *J* = 11.3, 2.2 Hz, 1H), 8.01 (s, 1H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 3.47 (p, *J* = 6.9 Hz, 1H), 3.41 (s, 3H), 2.56 (s, 3H), 2.50 (s, 3H), 1.51 (s, 3H), 1.50 (s, 3H). **^{13}C NMR** (150 MHz, CD_2Cl_2): δ 170.60, 160.55, 156.62, 153.18, 151.04, 149.63, 145.18, 144.69, 144.20, 141.83, 138.88, 138.45, 133.63 (2 × C_{Ar}), 132.91, 130.97 (2 × C_{Ar}), 40.19, 29.87, 23.99 (2 × CH_3), 22.03, 14.00. **^{19}F NMR** (376 MHz, CD_2Cl_2): δ -73.31 (d, *J* = 710.8 Hz). **IR** (ATR): ν_{max} 2970 (w), 1572 (w), 1550 (w), 1401 (w), 1347 (w), 1184 (w), 1047 (w), 832 (s), 813 (s), 556 (s), 506 (m) cm^{-1}. **HRMS** (HESI): m/z $[M+H]^+$ calcd for $C_{23}H_{25}$: 301.1951, found: 301.1956

Spectral data corresponds to the literature (different NMR solvent).[4]

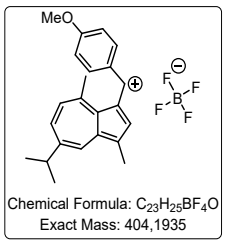
(5-isopropyl-3,8-dimethylazulen-1-yl)(p-tolyl)methylium perchlorate (2a")

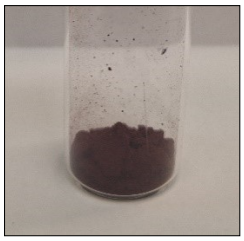


Following the *General procedure 1 (half scale)*: guaiazulene (0.5 g, 2.5 mmol), 70 wt% aqueous $HClO_4$ (0.6 mL, 2.7 eq), 4-methylbenzaldehyde (0.35 mL, 1.2 eq), MeOH (10 + 20 mL). Isolated: 0.9 g (91%)

Dark red solid, **Mp:** 175–180 °C (degr.); **UV-Vis:** λ_{max} (DCM): 487 nm (ε: 29500 M^{-1} cm^{-1}); **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 8.75 (s, 1H), 8.56 (d, *J* = 11.2 Hz, 1H), 8.51 (d, *J* = 2.2 Hz, 1H), 8.39 (dd, *J* = 11.2, 2.2 Hz, 1H), 8.00 (s, 1H), 7.72 (d, *J* = 7.9 Hz, 2H), 7.45 (d, *J* = 7.9 Hz, 2H), 3.52 – 3.45 (m, 1H), 3.43 (s, 3H), 2.56 (s, 3H), 2.50 (s, 3H), 1.51 (s, 3H), 1.50 (s, 3H). **^{13}C NMR** (100 MHz, CD_2Cl_2): δ 170.55, 160.48, 156.77, 153.18, 151.02, 149.82, 145.04, 144.67, 144.31, 141.72, 138.90, 138.46, 133.64 (2 × C_{Ar}), 132.98, 130.92 (2 × C_{Ar}), 40.16, 29.95, 24.01 (2 × CH_3), 22.02, 14.04, 1.16. **IR** (ATR): ν_{max} 2964 (w), 1574 (m), 1551 (m), 1398 (m), 1344 (m), 1321 (m), 1190 (m), 1077 (s), 1045 (s), 847 (m), 815 (m), 620 (s), 504 (m) cm^{-1}. **HRMS** (HESI): m/z $[M+H]^+$ calcd for $C_{23}H_{25}$: 301.1951, found: 301.1957

5-isopropyl-3,8-dimethylazulen-1-yl)(4-methoxyphenyl)methylium tetrafluoroborate (2b)



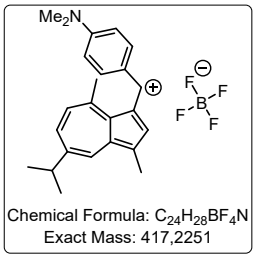


Following the *General procedure 1 (double scale)*: guaiazulene (2.0 g, 10.1 mmol), 48 wt% aqueous HBF_4 (3.4 mL, 2.7 eq), 4-methoxylbenzaldehyde (1.5 mL, 1.2 eq), MeOH (40 + 80 mL). Isolated: 3.9 g (96%)

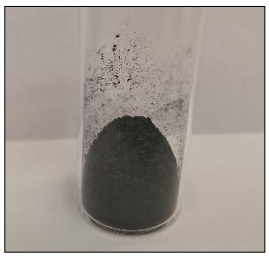
Brown solid, **Mp:** 180–185 °C (degr.); **UV-Vis:** λ_{max} (DCM): 530 nm (ε: 45600 M^{-1} cm^{-1}); **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 8.79 (s, 1H), 8.55 – 8.47 (m, 2H, overlaying signals), 8.36 (dd, *J* = 11.2, 2.2 Hz, 1H), 8.09 (s, 1H), 7.94 – 7.87 (m, 2H), 7.23 – 7.17 (m, 2H), 4.00 (s, 3H), 3.56 – 3.46 (m, 1H), 3.45 (s, 3H), 2.61 (s, 3H), 1.54 (s, 3H), 1.52 (s, 3H). **^{13}C NMR** (100 MHz, CD_2Cl_2): δ 168.42, 164.61, 158.79, 155.81, 152.42, 150.85, 148.24, 143.37, 143.31, 141.31, 137.87, 136.64, 136.28 (2 × C_{Ar}), 128.01 (2 × C_{Ar}), 115.72, 56.01, 53.99, 53.72, 53.45, 53.18, 52.91, 39.59, 29.58, 23.63 (2 × CH_3), 13.56. **^{19}F NMR** (376 MHz, CD_2Cl_2): δ -152.84, -152.89. **IR** (ATR): ν_{max} 2969 (w), 1575 (m), 1550 (m), 1513 (m), 1431 (m), 1399 (m), 1349 (m), 1271 (m), 1177 (m), 1044 (s), 1021 (s), 834 (m), 520 (m) cm^{-1}. **HRMS** (HESI): m/z $[M+H]^+$ calcd for $C_{23}H_{25}O$: 317.1900, found: 317.1896

The carbocation with PF_6^- anion has been described before.[5]

(4-(dimethylamino)phenyl)(5-isopropyl-3,8-dimethylazulen-1-yl)methylium tetrafluoroborate (2c)



Chemical Formula: $C_{24}H_{28}BF_4N$
Exact Mass: 417,2251

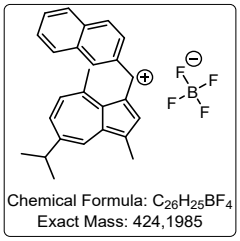


Following the *General procedure 1*: guaiazulene (1.0 g, 5.0 mmol), 50 wt% aqueous HBF_4 (1.7 mL, 2.7 eq), 4-(dimethylamino)benzaldehyde (0.9 g, 1.2 eq), MeOH (20 + 40 mL). Isolated: 1.6 g (78%)

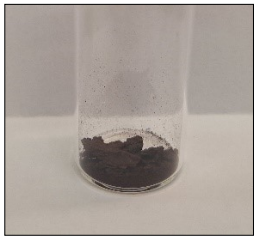
Dark green solid, **Mp:** 163–165 °C (degr.) [lit.[4] mp>160 °C decomp.]; **UV-Vis:** λ_{max} (DCM): 652 nm (ε: 115200 M^{-1} cm^{-1}); **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 8.72 (s, 1H), 8.44 (s, 1H), 8.17 (s, 1H), 8.08 (s, 2H), 7.97 – 7.90 (m, 2H), 7.02 – 6.96 (m, 2H), 3.42 – 3.35 (m, 4H, overlaying signals), 3.34 (s, 6H), 2.64 (s, 3H), 1.50 (s, 3H), 1.48 (s, 3H). **^{13}C NMR** (100 MHz, CD_2Cl_2): δ 160.38, 155.63, 153.06, 152.83, 152.01, 148.99, 142.64, 141.44, 140.98, 138.90 (2 × C_{Ar}), 138.37, 136.99, 131.08, 124.05, 113.95 (2 × C_{Ar}), 40.56 (2 × CH_3), 38.93, 29.66, 23.80 (2 × CH_3), 13.28. **^{19}F NMR** (376 MHz, CD_2Cl_2): δ -153.10, -153.15. **IR** (ATR): ν_{max} 2960 (w), 1610 (m), 1504 (m), 1329 (m), 1164 (m), 1029 (s), 825 (m), 718 (m), 519 (m) cm^{-1}. **HRMS** (HESI): m/z $[M+H]^+$ calcd for $C_{23}H_{26}N$: 316.2060, found: 316.2060

The spectroscopic data corresponds to the literature (different NMR solvent).[4]

(5-isopropyl-3,8-dimethylazulen-1-yl)(naphthalen-2-yl)methylium tetrafluoroborate (2d)



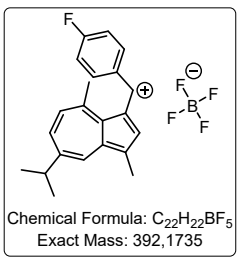
Chemical Formula: $C_{26}H_{25}BF_4$
Exact Mass: 424,1985



Following the *General procedure 1*: guaiazulene (1.0 g, 5.0 mmol), 50 wt% aqueous HBF_4 (1.7 mL, 2.7 eq), 2-naphthaldehyde (0.8 g, 1.2 eq), MeOH (20 + 40 mL). Isolated: 1.1 g (51%)

Dark brown solid, **Mp:** 164–169 °C (degr.); **UV-Vis:** λ_{max} (DCM): 518 nm (ε: 29500 M^{-1} cm^{-1}); **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 8.95 (s, 1H), 8.62 (d, *J* = 11.2 Hz, 1H), 8.55 (d, *J* = 2.2 Hz, 1H), 8.44 (dd, *J* = 11.2, 2.2 Hz, 1H), 8.37 (d, *J* = 1.8 Hz, 1H), 8.15 – 8.05 (m, 3H), 7.99 (d, *J* = 8.1 Hz, 1H), 7.92 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.75 – 7.63 (m, 2H), 3.57 – 3.46 (m, 4H, overlaying signals), 2.61 (s, 3H), 1.56 (s, 4H), 1.54 (s, 3H). **^{13}C NMR** (100 MHz, CD_2Cl_2): δ 170.57, 160.16, 156.66, 152.76, 150.21, 149.67, 144.80, 144.03, 141.24, 139.25, 138.07, 135.67, 134.83, 133.20, 132.84, 129.53, 129.50, 129.46, 127.90, 127.61, 127.55, 39.79, 29.51, 23.59 (2 × CH_3), 13.66. **^{19}F NMR** (376 MHz, CD_2Cl_2): δ -152.60, -152.65. **IR** (ATR): ν_{max} 2971 (w), 1573 (m), 1399 (m), 1344 (m), 1093 (m), 1048 (s), 1034 (s), 928 (m), 831 (m), 762 (m), 658 (m), 517 (m), 450 (m) cm^{-1}. **HRMS** (HESI): m/z $[M+H]^+$ calcd for $C_{26}H_{25}$: 337.1951, found: 337.1944

(4-fluorophenyl)(5-isopropyl-3,8-dimethylazulen-1-yl)methylium tetrafluoroborate (2e)

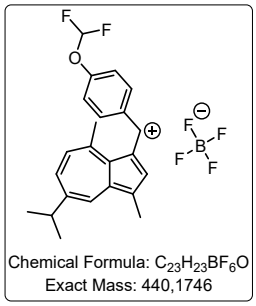


Chemical Formula: $C_{22}H_{22}BF_5$
Exact Mass: 392,1735

Following the *General procedure 1*: guaiazulene (1.0 g, 5.0 mmol), 50 wt% aqueous HBF_4 (1.7 mL, 2.7 eq), 4-fluorobenzaldehyde (0.65 mL, 1.2 eq), MeOH (20 + 40 mL). Isolated: 0.8 g (39%)

Red solid, **Mp:** 165–175 °C (degr.); UV-Vis**:** λ_{max} (DCM): 473 nm (ε: 22200 M^{-1} cm^{-1}); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.78 (s, 1H), 8.63 (d, *J* = 11.2 Hz, 1H), 8.55 (d, *J* = 2.3 Hz, 1H), 8.45 (dd, *J* = 11.3, 2.2 Hz, 1H), 7.95 (s, 1H), 7.90 – 7.82 (m, 2H), 7.36 (t, *J* = 8.6 Hz, 2H), 3.52 (p, *J* = 6.8 Hz, 1H), 3.46 (s, 3H), 2.59 (s, 3H), 1.55 (s, 3H), 1.53 (s, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 171.02, 165.26 (d, *J* = 256.8 Hz), 160.58, 156.90, 152.85, 149.98, 148.72, 144.98, 144.20, 140.69, 139.18, 138.15, 135.24 (d, *J* = 9.1 Hz) (2 × C_{Ar}), 131.60 (d, *J* = 3.3 Hz), 116.99 (d, *J* = 22.2 Hz) (2 × C_{Ar}), 39.83, 29.42, 23.56 (2 × CH_3), 13.64. ^{19}F NMR (376 MHz, CD_2Cl_2): δ -105.34 (ddd, *J* = 13.8, 8.4, 5.4 Hz), -152.61, -152.66. **IR** (ATR): ν_{max} 2971 (w), 1570 (m), 1507 (m), 1454 (m), 1405 (m), 1350 (m), 1195 (m), 1164 (m), 1048 (s), 1035 (s), 910 (m), 840 (m), 663 (m), 514 (m) cm^{-1}. HRMS (HESI): m/z $[M+H]^+$ calcd for $C_{22}H_{22}F$: 305.1700, found: 305.1694

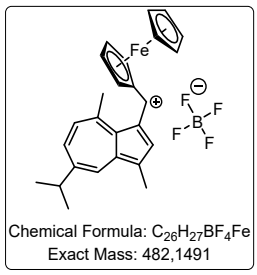
(4-(difluoromethoxy)phenyl)(5-isopropyl-3,8-dimethylazulen-1-yl)methylium tetrafluoroborate (2f)

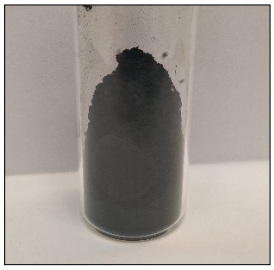


Following the *General procedure 1*: guaiazulene (1.0 g, 5.0 mmol), 50 wt% aqueous HBF_4 (1.7 mL, 2.7 eq), 4-(difluoromethoxy)benzaldehyde (0.8 mL, 1.2 eq), MeOH (20 + 40 mL). Isolated: 0.7 g (31%)

Red-orange solid, **Mp:** 164–175 °C (degr.); UV-Vis**:** λ_{max} (DCM): 479 nm (ε: 24000 M^{-1} cm^{-1}); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.77 (s, 1H), 8.62 (d, *J* = 11.3 Hz, 1H), 8.54 (d, *J* = 2.3 Hz, 1H), 8.44 (dd, *J* = 11.2, 2.2 Hz, 1H), 7.96 (s, 1H), 7.92 – 7.82 (m, 2H), 7.43 – 7.35 (m, 2H), 6.78 (t, *J* = 73.0 Hz, 1H), 3.52 (p, *J* = 6.9 Hz, 1H), 3.47 (s, 3H), 2.59 (s, 3H), 1.55 (s, 3H), 1.54 (s, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 171.01, 160.57, 156.87, 154.31, 152.81, 149.95, 148.64, 144.98, 144.18, 140.72, 139.27, 138.13, 134.81 (2 × C_{Ar}), 132.05, 119.72 (2 × C_{Ar}), 115.51 (t, *J* = 261.3 Hz), 39.84, 29.44, 23.57 (2 × CH_3), 13.66. ^{19}F NMR (376 MHz, CD_2Cl_2): δ -82.64 (d, *J* = 72.9 Hz), -152.68. **IR** (ATR): ν_{max} 2974 (w), 1605 (m), 1585 (m), 1566 (m), 1509 (m), 1406 (m), 1350 (m), 1188 (m), 1051 (s), 838 (m), 662 (m), 521 (m) cm^{-1}. HRMS (HESI): m/z $[M+H]^+$ calcd for $C_{23}H_{23}F_2O$: 353.1712, found: 353.1718

(5-isopropyl-3,8-dimethylazulen-1-yl)(ferrocenyl)methylium tetrafluoroborate (2g)





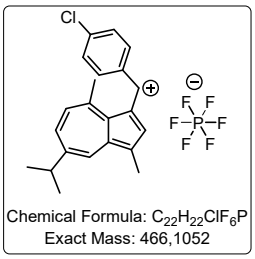
Following the *General procedure 1*: guaiazulene (1.0 g, 5.0 mmol), 50 wt% aqueous HBF_4 (1.7 mL, 2.7 eq), ferrocenecarboxaldehyde (1.3 mL, 1.2 eq), MeOH (20 + 40 mL). Isolated: 1.1 g (44%)

Dark green solid, **Mp:** 188–200 °C (degr.); UV-Vis**:** λ_{max} (DCM): 473 nm (ε: 15300 M^{-1} cm^{-1}) and 2nd long-wavelength maximum due to the ferrocene arm: 723 nm (ε: 8600 M^{-1} cm^{-1}) ; ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.74 (s, 1H), 8.41 (d, *J* = 2.3 Hz, 1H), 8.35 (d, *J* = 11.2 Hz, 1H), 8.13 (dd, *J* = 11.1, 2.2 Hz, 1H), 7.98 (s, 1H), 5.38 (t, *J* = 1.9 Hz, 2H), 5.16

(t, *J* = 2.0 Hz, 2H), 4.43 (s, 5H), 3.39 (s, 3H), 3.34 (p, *J* = 6.9 Hz, 1H), 2.51 (s, 3H), 1.47 (s, 3H), 1.46 (s, 3H). **^{13}C NMR** (100 MHz, CD_2Cl_2): δ 163.08, 155.30, 154.64, 153.95, 148.27, 144.52, 142.80, 140.43, 140.10, 138.22, 133.11, 82.23, 79.64 (2 × C_{Cp}), 74.48 (2 × C_{Cp}), 73.18 (5 × C_{Cp}), 39.47, 29.28, 23.41 (2 × CH_3), 13.46. **^{19}F NMR** (376 MHz, CD_2Cl_2): δ -152.84, -152.89. **IR** (ATR): ν_{max} 3093 (w), 2972 (w), 2878 (w), 1545 (m), 1517 (m), 1394 (m), 1369 (m), 1338 (m), 1305 (m), 1268 (m), 1095 (m), 1032 (s), 894 (m), 835 (s), 662 (m), 630 (m), 499 (m), 471 (m) cm^{-1}. **HRMS** (HESI): m/z $[M+H]^+$ calcd for $C_{26}H_{27}Fe$: 395.1457, found: 395.1464

The spectroscopic data corresponds to the literature (different solvent in NMR).[6]

(4-chlorophenyl)(5-isopropyl-3,8-dimethylazulen-1-yl)methylium hexafluorophosphate (2h)

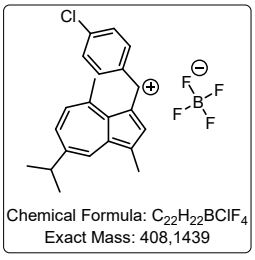


Chemical Formula: $C_{22}H_{22}ClF_6P$
Exact Mass: 466,1052

Following the *General procedure 1 (lower-scale)*: guaiazulene (0.25 g, 1.25 mmol), 55 wt% aqueous HPF_6 (550 µL, 2.7 eq), 4-chlorobenzaldehyde (0.21 g, 1.2 eq), MeOH (5 + 10 mL). Isolated: 0.6 g (95%)

Red solid, **Mp:** 140–145 °C (degr.); **UV-Vis:** λ_{max} (DCM): 474 nm (ε: 21100 M^{-1} cm^{-1}); **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 8.70 (s, 1H), 8.59 (d, *J* = 11.3 Hz, 1H), 8.54 (d, *J* = 2.2 Hz, 1H), 8.43 (dd, *J* = 11.2, 2.3 Hz, 1H), 7.92 (s, 1H), 7.79 – 7.73 (m, 2H), 7.68 – 7.62 (m, 2H), 3.52 (p, *J* = 6.9 Hz, 1H), 3.45 (s, 3H), 2.58 (d, *J* = 1.2 Hz, 3H), 1.55 (s, 3H), 1.54 (s, 3H). **^{13}C NMR** (100 MHz, CD_2Cl_2): δ 171.53, 160.93, 156.81, 152.81, 150.08, 148.21, 145.30, 144.25, 140.61, 139.79, 139.00, 138.22, 133.80 (2 × C_{Ar}), 129.92 (2 × C_{Ar}), 39.92, 29.38, 23.54 (2 × CH_3), 13.67. **^{19}F NMR** (376 MHz, CD_2Cl_2): δ -73.22 (d, *J* = 710.8 Hz). **IR** (ATR): ν_{max} 2977 (w), 1577 (m), 1404 (m), 1345 (m), 1196 (m), 1088 (m), 828 (s), 744 (m), 663 (m), 556 (s), 508 (m) cm^{-1}. **HRMS** (HESI): m/z $[M+H]^+$ calcd for $C_{22}H_{22}Cl$: 321.1405, found: 321.1411

(4-chlorophenyl)(5-isopropyl-3,8-dimethylazulen-1-yl)methylium tetrafluoroborate (2h')



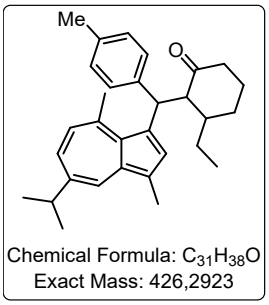
Chemical Formula: $C_{22}H_{22}BClF_4$
Exact Mass: 408,1439

Following the *General procedure 1 (lower-scale)*: guaiazulene (0.25 g, 1.25 mmol), 50 wt% aqueous HBF_4 (424 µL, 2.7 eq), 4-chlorobenzaldehyde (0.21 g, 1.2 eq), MeOH (5 + 10 mL). Isolated: 70 mg (14%)

Red solid, **Mp:** 158–168 °C (degr.); **UV-Vis:** λ_{max} (DCM): 474 nm (ε: 25200 M^{-1} cm^{-1}); **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 8.74 (s, 1H), 8.64 (d, *J* = 11.2 Hz, 1H), 8.54 (d, *J* = 2.2 Hz, 1H), 8.46 (dd, *J* = 11.2, 2.3 Hz, 1H), 7.92 (s, 1H), 7.82 – 7.73 (m, 2H), 7.67 – 7.59 (m, 2H), 3.53 (p, *J* = 6.8 Hz, 1H), 3.46 (s, 3H), 2.58 (s, 3H), 1.55 (s, 3H), 1.53 (s, 3H). **^{13}C NMR** (100 MHz, CD_2Cl_2): δ 171.45, 160.82, 157.07, 152.81, 150.26, 148.27, 145.26, 144.34, 140.51, 139.78, 138.86, 138.18, 133.86 (2 × C_{Ar}), 133.73, 129.86 (2 × C_{Ar}), 39.87, 29.40, 23.55 (2 × CH_3), 13.67. **^{19}F NMR** (376 MHz, CD_2Cl_2): δ -152.56, -152.61. **IR** (ATR): ν_{max} 2976 (w), 1607 (m), 1578 (m), 1454 (m), 1405 (m), 1350 (m), 1048 (s), 847 (m), 827 (m), 662 (m), 508 (m) cm^{-1}. **HRMS** (HESI): m/z $[M+H]^+$ calcd for $C_{22}H_{22}Cl$: 321.1405, found: 321.1413

6.2. Products of tandem conjugate addition and enolate trapping

3-ethyl-2-((5-isopropyl-3,8-dimethylazulen-1-yl)(p-tolyl)methyl)cyclohexan-1-one (5aa)



Chemical Formula: $C_{31}H_{38}O$
Exact Mass: 426,2923

Following the *General procedure 2* using carbocation **2a** (388 mg, 1.0 mmol, 2.0 eq). Based on ^{1}H NMR analysis of the crude reaction mixture, the diastereomeric ratio was 1:1. The crude product was purified by flash chromatography (silica gel, Hex:EtOAc 40:1 to 10:1). Isolated: 136 mg (64%)

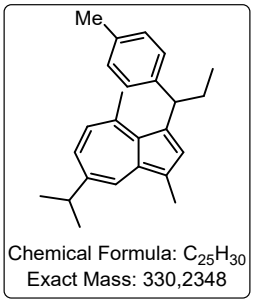
Diastereomer 1:

Blue oil, $\mathbf{R_f}$ (silica, Hex:EtOAc 10/1): 0.37; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.05 (d, *J* = 2.2 Hz, 1H), 7.79 (s, 1H), 7.24 – 7.20 (m, 1H), 7.17 – 7.10 (m, 2H), 6.99 (d, *J* = 7.9 Hz, 2H), 6.81 (d, *J* = 10.7 Hz, 1H), 5.50 (d, *J* = 11.8 Hz, 1H), 3.23 (d, *J* = 11.7 Hz, 1H), 3.15 (s, 3H), 2.99 (p, *J* = 6.9 Hz, 1H), 2.73 (td, *J* = 13.6, 6.8 Hz, 1H), 2.66 (s, 3H), 2.27 – 2.21 (m, 1H), 2.22 (d, *J* = 7.7 Hz, 0H), 2.20 (s, 3H), 2.08 – 1.91 (m, 2H), 1.89 – 1.78 (m, 2H), 1.49 – 1.41 (m, 1H), 1.40 – 1.23 (m, 8H), 0.82 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 214.37, 143.63, 141.17, 139.49, 139.44, 137.85, 135.51, 134.20, 133.44, 132.38, 129.26 (2 × C_{Ar}), 128.50 (2 × C_{Ar}), 126.88, 126.71, 124.91, 63.35, 45.03, 40.99, 39.66, 37.56, 28.44, 24.84, 24.57, 24.54, 23.84, 23.74, 20.95, 13.24, 11.72. **IR** (ATR): ν_{max} 2961 (m), 2929 (m), 2873 (m), 1704 (s), 1511 (m), 1460 (m), 1450 (m), 1377 (m), 1306 (m), 1109 (m), 1085 (m), 1020 (m), 817 (m), 730 (m), 503 (m) cm^{-1}. **HRMS** (HESI): m/z $[M+H]^+$ calcd for $C_{31}H_{39}O$: 427.2995, found: 427.2989; $[M+Na]^+$ calcd for $C_{31}H_{38}ONa$: 449.2815, found: 449.2810; $[M+K]^+$ calcd for $C_{31}H_{38}OK$: 465.2554, found: 465.2551; **HPLC**: Chiralpak IA, hexane/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, t_R(major) = 4.46 min, t_R(minor)= 3.70 min (97% ee).

Diastereomer 2:

Blue oil, $\mathbf{R_f}$ (silica, Hex:EtOAc 10/1): 0.28; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.01 (d, *J* = 2.2 Hz, 1H), 7.98 (s, 1H), 7.23 – 7.14 (m, 3H), 7.04 (d, *J* = 7.8 Hz, 2H), 6.76 (d, *J* = 10.7 Hz, 1H), 5.54 (d, *J* = 11.4 Hz, 1H), 3.18 – 3.05 (m, 4H), 2.95 (h, *J* = 6.9 Hz, 1H), 2.63 (s, 3H), 2.48 – 2.35 (m, 1H), 2.32 – 2.19 (m, 4H), 2.00 – 1.74 (m, 4H), 1.68 – 1.59 (m, 1H), 1.34 – 1.24 (m, 8H), 0.76 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 214.24, 144.36, 140.43, 139.66, 138.22, 136.78, 135.59, 134.50, 133.54, 132.81, 129.41, 127.91, 127.62, 126.91, 125.34, 63.66, 45.59, 40.59, 40.09, 37.57, 28.54, 25.29, 24.58, 24.54, 24.03, 22.86, 20.96, 13.33, 11.71. **IR** (ATR): ν_{max} 2961 (m), 2929 (m), 2872 (m), 1706 (s), 1544 (m), 1513 (m), 1460 (m), 1375 (m), 1307 (m), 1109 (m), 1086 (m), 1021 (m), 814 (m), 741 (m), 658 (m), 558 (m), 505 (m) cm^{-1}. **HRMS** (HESI): m/z $[M+H]^+$ calcd for $C_{31}H_{39}O$: 427.2995, found: 427.2991; $[M+Na]^+$ calcd for $C_{31}H_{38}ONa$: 449.2815, found: 449.2812; $[M+K]^+$ calcd for $C_{31}H_{38}OK$: 465.2554, found: 465.2551; **HPLC**: Chiralpak IA, hexane/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, t_R(major) = 6.26 min, t_R(minor)= 3.94 min (97% ee).

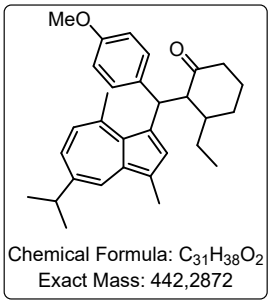
7-isopropyl-1,4-dimethyl-3-(1-(p-tolyl)propyl)azulene (6a)



Following the *General procedure 2* using carbocation **2a** (388 mg, 1.0 mmol, 2.0 eq). This side-product product was isolated by flash chromatography (silica gel, Hex:EtOAc 40:1 to 10:1).

Blue oil, $\mathbf{R_f}$ (silica, Hex:EtOAc 40/1): 0.40; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.05 (d, *J* = 2.2 Hz, 1H), 7.66 (s, 1H), 7.19 (dd, *J* = 10.7, 2.2 Hz, 1H), 7.03 (s, 4H), 6.75 (d, *J* = 10.7 Hz, 1H), 4.81 (t, *J* = 7.6 Hz, 1H), 2.99 (p, *J* = 6.9 Hz, 1H), 2.92 (s, 3H), 2.64 (s, 3H), 2.27 (s, 3H), 2.14 (pd, *J* = 7.3, 1.7 Hz, 2H), 1.33 (s, 3H), 1.31 (s, 3H), 0.94 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 145.02, 144.54, 138.88, 137.81, 137.78, 134.76, 134.33, 133.18, 132.61, 130.66, 128.92 (2 × C_{Ar}), 128.25 (2 × C_{Ar}), 126.45, 124.54, 46.80, 37.61, 31.94, 27.94, 24.60 (2 × CH_3), 20.96, 13.50, 13.24. **IR** (ATR): ν_{max} 2960 (s), 2928 (m), 2871 (m), 1688 (w), 1544 (m), 1511 (s), 1460 (s), 1451 (s), 1373 (m), 1021 (m), 910 (m), 810 (s), 800 (s), 732 (s), 542 (m), 509 (m) cm^{-1}. **HRMS** (HESI): m/z $[M+H]^+$ calcd for $C_{25}H_{31}$: 331.2420, found: 331.2418

3-ethyl-2-((5-isopropyl-3,8-dimethylazulen-1-yl)(4-methoxyphenyl)methyl)cyclohexan-1-one (5ab)



Following the *General procedure 2* using carbocation **2b** (404 mg, 1.0 mmol, 2.0 eq). Based on ^{1}H NMR analysis of the crude reaction mixture, the diastereomeric ratio was 1:1. The crude product was purified by flash chromatography (silica gel, Hex:EtOAc 40:1 to 10:1). Isolated: 144 mg (65%)

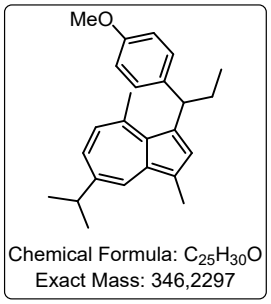
Diastereomer 1:

Blue oil, $\mathbf{R_f}$ (silica, Hex:EtOAc 10/1): 0.28; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.01 (d, *J* = 2.2 Hz, 1H), 7.97 (s, 1H), 7.25 – 7.21 (m, 2H), 7.18 (dd, *J* = 10.7, 2.2 Hz, 1H), 6.82 – 6.72 (m, 3H, overlaying signals), 5.52 (d, *J* = 11.4 Hz, 1H), 3.73 (s, 3H), 3.14 – 3.06 (m, 4H, overlaying signals), 2.97 (p, *J* = 6.8 Hz, 1H), 2.63 (s, 3H), 2.45 – 2.35 (m, 1H), 2.31 – 2.20 (m, 1H), 2.01 – 1.79 (m, 4H), 1.70 – 1.60 (m, 1H), 1.31 – 1.25 (m, 8H, overlaying signals), 0.76 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 214.40, 157.72, 143.65, 139.50, 139.36, 137.77, 136.39, 134.26, 133.48, 132.35, 129.57 (2 × C_{Ar}), 126.87, 126.81, 124.90, 113.95 (2 × C_{Ar}), 63.49, 55.20, 44.65, 41.01, 39.65, 37.56, 28.38, 24.85, 24.56, 24.53, 23.88, 23.77, 13.23, 11.74. **IR** (ATR): ν_{max} 2959 (m), 2931 (m), 2869 (m), 1703 (s), 1608 (m), 1510 (s), 1460 (m), 1303 (m), 1251 (s), 1177 (s), 1033 (m), 909 (m), 830 (m), 729 (s), 646 (m), 531 (m) cm^{-1}. **HRMS** (HESI): m/z $[M+H]^+$ calcd for $C_{31}H_{39}O_2$: 443.2945, found: 443.2940; $[M+Na]^+$ calcd for $C_{31}H_{38}O_2Na$: 465.2764, found: 465.2759; $[M+K]^+$ calcd for $C_{31}H_{38}O_2K$: 481.2503, found: 481.2499; **HPLC**: Chiralpak IA, hexane/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, t_R(major) = 4.19 min, t_R(minor)= 5.27 min (98% ee).

Diastereomer 2:

R_f (silica, Hex:EtOAc 10/1): 0.14; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 2.2 Hz, 1H), 7.78 (s, 1H), 7.25 – 7.20 (m, 1H), 7.19 – 7.11 (m, 2H), 6.82 (d, *J* = 10.7 Hz, 1H), 6.76 – 6.69 (m, 2H), 5.49 (d, *J* = 11.7 Hz, 1H), 3.68 (s, 3H), 3.22 (d, *J* = 11.7 Hz, 1H), 3.15 (s, 3H), 3.00 (p, *J* = 6.9 Hz, 1H), 2.73 (dt, *J* = 13.5, 6.7 Hz, 1H), 2.66 (s, 3H), 2.24 (dd, *J* = 13.3, 3.9 Hz, 1H), 2.08 – 1.92 (m, 2H), 1.89 – 1.78 (m, 2H), 1.50 – 1.41 (m, 1H), 1.40 – 1.22 (m, 8H, overlaying signals), 0.82 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 214.26, 157.70, 144.36, 139.69, 138.17, 136.67, 135.65, 134.55, 133.59, 132.73, 129.00 (2 × C_{Ar}), 127.79, 126.91, 125.37, 114.09 (2 × C_{Ar}), 63.72, 55.08, 45.16, 40.60, 40.09, 37.57, 28.50, 25.29, 24.58, 24.53, 24.03, 22.87, 13.32, 11.71. **IR** (ATR): ν_{max} 2960 (m), 2932 (m), 2874 (m), 1703 (s), 1610 (m), 1511 (s), 1460 (m), 1304 (m), 1250 (s), 1178 (s), 1033 (s), 909 (m), 828 (m), 729 (s), 646 (m), 560 (m), 536 (m) cm^{-1}. **HRMS** (HESI): m/z $[M+H]^+$ calcd for $C_{31}H_{39}O_2$: 443.2945, found: 443.2941; $[M+Na]^+$ calcd for $C_{31}H_{38}O_2Na$: 465.2764, found: 465.2760; $[M+K]^+$ calcd for $C_{31}H_{38}O_2K$: 481.2503, found: 481.2500; **HPLC**: Chiralpak IA, hexane/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, t_R(major) = 12.39 min, t_R(minor)= 5.03 min (96% ee).

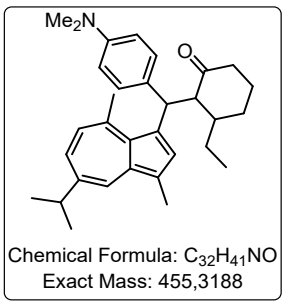
7-isopropyl-3-(1-(4-methoxyphenyl)propyl)-1,4-dimethylazulene (6b)



Following the *General procedure 2* using carbocation 2b (404 mg, 1.0 mmol, 2.0 eq). This side-product product was isolated by flash chromatography (silica gel, Hex:EtOAc 40:1 to 10:1).

R_f (silica, Hex:EtOAc 40/1): 0.31; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.05 (d, *J* = 2.2 Hz, 1H), 7.65 (s, 1H), 7.20 (dd, *J* = 10.7, 2.2 Hz, 1H), 7.08 – 7.02 (m, 2H), 6.81 – 6.73 (m, 3H, overlaying signals), 4.79 (t, *J* = 7.5 Hz, 1H), 3.74 (s, 3H), 3.00 (p, *J* = 6.9 Hz, 1H), 2.92 (s, 3H), 2.64 (s, 3H), 2.19 – 2.06 (m, 2H), 1.33 (s, 3H), 1.32 (s, 3H), 0.93 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 157.31, 145.02, 139.76, 138.88, 137.71 (2 × C_{Ar}), 134.35, 133.19, 132.54, 130.77, 129.22 (2 × C_{Ar}), 126.43, 124.53, 113.57 (2 × C_{Ar}), 55.19, 46.34, 37.58, 31.98, 27.86, 24.58 (2 × CH_3), 13.45, 13.21. **IR** (ATR): ν_{max} 2965 (w), 2935 (w), 2878 (w), 1687 (w), 1611 (m), 1513 (s), 1460 (m), 1378 (m), 1303 (m), 1250 (s), 1179 (s), 1033 (s), 829 (s) cm^{-1}. **HRMS** (HESI): m/z $[M+H]^+$ calcd for $C_{25}H_{31}O$: 347.2369, found: 347.2363

2-((4-(dimethylamino)phenyl)(5-isopropyl-3,8-dimethylazulen-1-yl)methyl)-3-ethylcyclohexan-1-one (5ac)



Following the *General procedure 2* using carbocation **2c** (417 mg, 1.0 mmol, 2.0 eq). Based on ^{1}H NMR analysis of the crude reaction mixture, the diastereomeric ratio was 3:2. The crude product was purified by flash chromatography (silica gel, Hex:EtOAc 40:1 to 10:1). Isolated: 109 mg (49%)

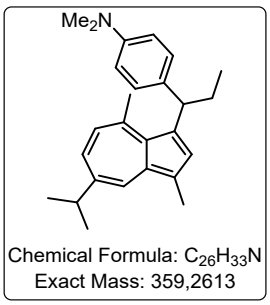
Diastereomer 1:

R_f (silica, Hex:EtOAc 10/1): 0.26; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 2.2 Hz, 1H), 7.96 (s, 1H), 7.20 – 7.13 (m, 3H, overlaying signals), 6.74 (d, *J* = 10.7 Hz, 1H), 6.66 – 6.60 (m, 2H), 5.48 (d, *J* = 11.5 Hz, 1H), 3.15 – 3.06 (m, 4H, overlaying signals), 2.96 (p, *J* = 6.9 Hz, 1H), 2.86 (s, 6H), 2.62 (s, 3H), 2.41 (td, *J* = 12.8, 6.3 Hz, 1H), 2.27 (tt, *J* = 13.7, 4.4 Hz, 1H), 2.00 – 1.75 (m, 4H), 1.63 (d, *J* = 14.5 Hz, 1H), 1.30 – 1.26 (m, 8H, overlaying signals), 0.77 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 214.72, 148.83, 143.67, 139.41, 139.25, 137.78, 134.06, 133.30, 132.22, 129.21 (2 × C_{Ar}), 127.37, 126.69, 124.81, 112.85 (2 × C_{Ar}), 63.59, 44.56, 40.97, 40.64 (2 × CH_3), 39.63, 37.54, 28.39, 24.85, 24.56, 24.53, 23.75, 23.71, 13.22, 11.76. **IR** (ATR): ν_{max} 2959 (m), 2929 (m), 2871 (w), 1704 (s), 1611 (m), 1519 (s), 1455 (m), 1343 (m), 817 (m) cm^{-1}. **HRMS** (HESI): m/z $[M+H]^+$ calcd for $C_{32}H_{42}NO$: 456.3261, found: 456.3258; $[M+Na]^+$ calcd for $C_{32}H_{41}NONa$: 478.3080, found: 478.3076; $[M+K]^+$ calcd for $C_{32}H_{41}NOK$: 494.2820, found: 494.2817; **HPLC:** Chiralpak IA, hexane/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, t_R(major) = 5.05 min, t_R(minor)= 4.04 min (97% ee).

Diastereomer 2:

R_f (silica, Hex:EtOAc 10/1): 0.10; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 2.2 Hz, 1H), 7.78 (s, 1H), 7.21 (dd, *J* = 10.6, 2.2 Hz, 1H), 7.15 – 7.05 (m, 2H), 6.80 (d, *J* = 10.7 Hz, 1H), 6.63 – 6.49 (m, 2H), 5.45 (d, *J* = 11.7 Hz, 1H), 3.23 (d, *J* = 11.7 Hz, 1H), 3.16 (s, 3H), 2.99 (p, *J* = 6.9 Hz, 1H), 2.82 (s, 6H), 2.74 (td, *J* = 13.5, 6.7 Hz, 1H), 2.65 (s, 3H), 2.28 – 2.18 (m, 1H), 2.09 – 1.90 (m, 2H), 1.89 – 1.74 (m, 2H), 1.47 – 1.40 (m, 1H), 1.40 – 1.26 (m, 8H, overlaying signals), 0.82 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 214.46, 148.81, 144.42, 139.41, 138.15, 136.79, 134.36, 133.39, 132.60, 131.39, 128.60 (2 × C_{Ar}), 128.40, 126.71, 125.24, 112.94 (2 × C_{Ar}), 63.69, 45.03, 40.67, 40.55 (2 × CH_3), 40.03, 37.55, 28.52, 25.28, 24.58, 24.53, 24.05, 22.95, 13.32, 11.71. **IR** (ATR): ν_{max} 2962 (w), 2932 (w), 2865 (w), 1712 (m), 1613 (m), 1522 (s), 1459 (m), 1359 (m), 1228 (m), 1168 (m), 1108 (m), 809 (s), 754 (m), 647 (m), 556 (m) cm^{-1}. **HRMS** (HESI): m/z $[M+H]^+$ calcd for $C_{32}H_{42}NO$: 456.3261, found: 456.3257; $[M+Na]^+$ calcd for $C_{32}H_{41}NONa$: 478.3080, found: 478.3074; $[M+K]^+$ calcd for $C_{32}H_{41}NOK$: 494.2820, found: 494.2816; **HPLC:** Chiralpak IA, hexane/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, t_R(major) = 8.73 min, t_R(minor)= 4.68 min (97% ee).

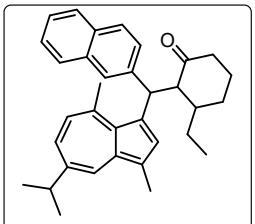
4-(1-(5-isopropyl-3,8-dimethylazulen-1-yl)propyl)-*N*,*N*-dimethylaniline (6c)



Following the *General procedure 2* using carbocation **2c** (417 mg, 1.0 mmol, 2.0 eq). This side-product product was isolated by flash chromatography (silica gel, Hex:EtOAc 40:1 to 10:1).

R_f (silica, Hex:EtOAc 40/1): 0.17; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 2.2 Hz, 1H), 7.66 (s, 1H), 7.18 (dd, *J* = 10.7, 2.2 Hz, 1H), 7.04 – 6.98 (m, 2H), 6.74 (d, *J* = 10.7 Hz, 1H), 6.67 – 6.60 (m, 2H), 4.75 (t, *J* = 7.6 Hz, 1H), 2.99 (p, *J* = 6.9 Hz, 1H), 2.93 (s, 3H), 2.87 (s, 6H), 2.63 (s, 3H), 2.12 (p, *J* = 7.4 Hz, 2H), 1.33 (s, 3H), 1.31 (s, 3H), 0.93 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 148.56, 145.10, 138.68, 137.86, 137.74, 135.88, 134.21, 133.05, 132.51, 131.38, 128.92 (2 × C_{Ar}), 126.30, 124.47, 112.78 (2 × C_{Ar}), 46.17, 40.83 (2 × CH_3), 37.60, 31.94, 27.90, 24.61 (2 × CH_3), 13.52, 13.24. **IR** (ATR): ν_{max} 2959 (m), 2930 (m), 2870 (m), 2799 (w), 1613 (m), 1518 (s), 1461 (m), 1444 (m), 1344 (m), 1163 (m), 1055 (m), 947 (m), 809 (s), 732 (m), 656 (m), 548 (m) cm^{-1}. **HRMS** (HESI): m/z $[M+H]^+$ calcd for $C_{26}H_{34}N$: 360.2686, found: 360.2682

3-ethyl-2-((5-isopropyl-3,8-dimethylazulen-1-yl)(naphthalen-2-yl)methyl)cyclohexan-1-one (5ad)



Chemical Formula: $C_{34}H_{38}O$
Exact Mass: 462,2923

Following the *General procedure 2* using carbocation **2d** (424 mg, 1.0 mmol, 2.0 eq). Based on ^{1}H NMR analysis of the crude reaction mixture, the diastereomeric ratio was 1.2:1. The crude product was purified by flash chromatography (silica gel, Hex:EtOAc 40:1 to 10:1). Isolated: 110 mg (48%)

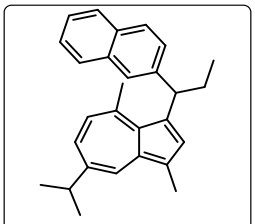
Diastereomer 1:

Blue oil, $\mathbf{R_f}$ (silica, Hex:EtOAc 10/1): 0.36; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.08 (s, 1H), 8.03 (d, *J* = 2.2 Hz, 1H), 7.80 – 7.69 (m, 4H), 7.49 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.46 – 7.36 (m, 2H), 7.18 (dd, *J* = 10.7, 2.2 Hz, 1H), 6.78 (d, *J* = 10.7 Hz, 1H), 5.76 (d, *J* = 11.4 Hz, 1H), 3.26 (d, *J* = 11.3 Hz, 1H), 3.18 (s, 3H), 2.96 (hept, *J* = 7.4, 6.9 Hz, 1H), 2.66 (s, 3H), 2.52 – 2.32 (m, 2H), 2.05 – 1.94 (m, 2H), 1.93 – 1.82 (m, 2H), 1.70 – 1.63 (m, 1H), 1.30 – 1.25 (m, 8H, overlaying signals), 0.71 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 214.13, 143.66, 141.64, 139.67, 139.55, 137.90, 134.33, 133.54, 133.43, 132.68, 132.04, 128.42, 127.76, 127.55, 127.20, 127.03, 126.72, 126.18, 125.93, 125.51, 124.97, 63.06, 45.55, 41.05, 39.74, 37.56, 28.52, 24.83, 24.55, 24.52, 23.98, 23.76, 13.27, 11.64. **IR** (ATR): ν_{max} 3051 (w), 2959 (m), 2932 (m), 2869 (m), 1703 (s), 1460 (m), 1365 (m), 908 (m), 816 (m), 747 (m), 728 (s), 477 (s) cm^{-1}. **HRMS** (HESI): m/z $[M+H]^+$ calcd for $C_{34}H_{39}O$: 463.2995, found: 463.2992; $[M+Na]^+$ calcd for $C_{34}H_{38}ONa$: 485.2815, found: 485.2812; $[M+K]^+$ calcd for $C_{34}H_{38}OK$: 501.2554, found: 501.2553; **HPLC**: Chiralpak IA, hexane/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, t_R(major) = 5.27 min, t_R(minor)= 4.03 min (97% ee).

Diastereomer 2:

Blue oil, $\mathbf{R_f}$ (silica, Hex:EtOAc 10/1): 0.25; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 2.2 Hz, 1H), 7.89 (s, 1H), 7.73 – 7.63 (m, 4H, overlaying signals), 7.46 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.35 (pd, *J* = 6.9, 1.5 Hz, 2H), 7.25 – 7.21 (m, 1H), 6.83 (d, *J* = 10.7 Hz, 1H), 5.71 (d, *J* = 11.7 Hz, 1H), 3.37 (d, *J* = 11.6 Hz, 1H), 3.22 (s, 3H), 3.00 (h, *J* = 6.9 Hz, 1H), 2.81 (td, *J* = 13.5, 6.8 Hz, 1H), 2.69 (s, 3H), 2.29 – 2.18 (m, 1H), 2.12 – 1.82 (m, 4H), 1.49 (d, *J* = 14.1 Hz, 1H), 1.42 – 1.35 (m, 1H), 1.34 – 1.26 (m, 7H, overlaying signals), 0.85 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 213.93, 144.36, 140.95, 139.86, 138.30, 136.87, 134.61, 133.65, 133.51, 133.06, 132.09, 128.54, 127.78, 127.57, 127.17, 127.07, 126.42, 126.36, 125.80, 125.44 (2 × C_{Ar}), 63.37, 46.06, 40.65, 40.14, 37.57, 28.66, 25.31, 24.57, 24.53, 24.13, 22.94, 13.37, 11.75. **IR** (ATR): ν_{max} 3054 (w), 2962 (m), 2931 (m), 2875 (m), 1702 (s), 1460 (m), 1366 (m), 909 (m), 816 (m), 729 (s), 477 (s) cm^{-1}. **HRMS** (HESI): m/z $[M+H]^+$ calcd for $C_{34}H_{39}O$: 463.2995, found: 463.2991; $[M+Na]^+$ calcd for $C_{34}H_{38}ONa$: 485.2815, found: 485.2813; $[M+K]^+$ calcd for $C_{34}H_{38}OK$: 501.2554, found: 501.2553; **HPLC**: Chiralpak IA, hexane/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, t_R(major) = 9.33 min, t_R(minor)= 4.90 min (97% ee).

7-isopropyl-1,4-dimethyl-3-(1-(naphthalen-2-yl)propyl)azulene (6d)

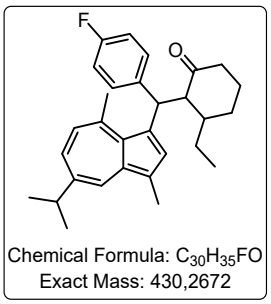


Chemical Formula: $C_{28}H_{30}$
Exact Mass: 366,2348

Following the *General procedure 2* using carbocation **2d** (424 mg, 1.0 mmol, 2.0 eq). This side-product product was isolated by flash chromatography (silica gel, Hex:EtOAc 40:1 to 10:1).

R_f (silica, Hex:EtOAc 40/1): 0.34; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.08 (d, *J* = 2.2 Hz, 1H), 7.80 – 7.67 (m, 4H), 7.55 (s, 1H), 7.43 – 7.33 (m, 3H), 7.21 (dd, *J* = 10.8, 2.2 Hz, 1H), 6.77 (d, *J* = 10.7 Hz, 1H), 5.01 (t, *J* = 7.5 Hz, 1H), 3.01 (p, *J* = 6.9 Hz, 1H), 2.96 (s, 3H), 2.65 (s, 3H), 2.30 – 2.20 (m, 2H), 1.34 (s, 3H), 1.32 (s, 3H), 0.99 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 145.03, 145.00, 139.03, 137.98, 137.81, 134.40, 133.58, 133.26, 131.81, 130.21, 127.76, 127.71, 127.55, 127.49, 126.56, 126.28, 125.67, 125.08, 124.61, 47.32, 37.59, 31.75, 29.71, 27.97, 24.58 (2 × CH_3), 13.49, 13.22. **IR** (ATR): ν_{max} 3058 (w), 2959 (m), 2925 (m), 2857 (m), 1460 (m), 1372 (m), 856 (m), 815 (s), 744 (s), 477 (s) cm^{-1}; **HRMS** (HESI): m/z $[M+H]^+$ calcd for $C_{28}H_{31}$: 367.2420, found: 367.2418; $[M+Na]^+$ calcd for $C_{28}H_{30}Na$: 389.2240, found: 389.2240

3-ethyl-2-((4-fluorophenyl)(5-isopropyl-3,8-dimethylazulen-1-yl)methyl)cyclohexan-1-one (5ae)



Chemical Formula: $C_{30}H_{35}FO$
Exact Mass: 430,2672

Following the *General procedure 2* using carbocation **2e** (392 mg, 1.0 mmol, 2.0 eq). Based on ^{1}H NMR analysis of the crude reaction mixture, the diastereomeric ratio was 1:1. The crude product was purified by flash chromatography (silica gel, Hex:EtOAc 40:1 to 10:1). Isolated: 163 mg (76%)

Diastereomer 1:

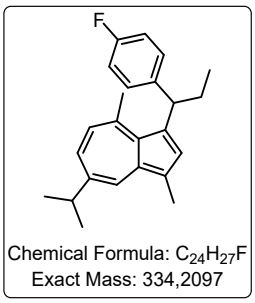
R_f (silica, Hex:EtOAc 10/1): 0.33; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 2.2 Hz, 1H), 7.96 (s, 1H), 7.31 – 7.26 (m, 2H), 7.21 (dd, *J* = 10.7, 2.2 Hz, 1H), 6.98 – 6.89 (m, 2H), 6.79 (d, *J* = 10.7 Hz, 1H), 5.57 (d, *J* = 11.3 Hz, 1H), 3.14 – 3.05 (m, 4H, overlaying signals), 2.97 (dq, *J* = 13.2, 6.6 Hz, 1H), 2.64 (s, 3H), 2.39 (td, *J* = 13.2, 12.5, 6.8 Hz, 1H), 2.24 (tt, *J* = 13.7, 4.4 Hz, 1H), 2.01 – 1.88 (m, 2H), 1.88 – 1.77 (m, 2H), 1.69 – 1.61 (m, 1H), 1.33 – 1.26 (m, 8H, overlaying signals), 0.76 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 213.93, 161.10 (d, *J* = 244.6 Hz), 143.57, 140.03 (d, *J* = 3.4 Hz), 139.78, 139.26, 137.79, 134.43, 133.66, 132.49, 130.04 (d, *J* = 8.0 Hz, 2 × C_{Ar}), 127.06, 126.10, 125.01, 115.35 (d, *J* = 21.2 Hz, 2 × C_{Ar}), 63.32, 44.65, 41.02, 39.66, 37.56, 28.35, 24.84, 24.55, 24.52, 24.04, 23.74, 13.21, 11.69. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -116.98 (ddd, *J* = 13.8, 8.8, 5.4 Hz). **IR** (ATR): ν_{max} 2963 (m), 2930 (m), 2871 (m), 1704 (s), 1508 (s), 1461 (m), 1224 (s), 1159 (m), 837 (m), 517 (m) cm^{-1}. **HRMS** (HESI): m/z $[M+H]^+$ calcd for $C_{30}H_{36}FO$: 431.2745, found: 431.2740; $[M+Na]^+$ calcd for $C_{30}H_{35}FONa$: 453.2564, found: 453.2561; $[M+K]^+$ calcd for $C_{30}H_{35}FOK$: 469.2304, found: 469.2306; **HPLC:** Chiralpak IA, hexane/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, t_R(major) = 4.91 min, t_R(minor)= 3.81 min (97% ee).

Diastereomer 2:

R_f (silica, Hex:EtOAc 10/1): 0.25; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.08 (d, *J* = 2.2 Hz, 1H), 7.76 (s, 1H), 7.27 – 7.24 (m, 1H), 7.23 – 7.17 (m, 2H), 6.93 – 6.80 (m, 3H, overlaying signals), 5.52 (d, *J* = 11.8 Hz, 1H), 3.20 (d, *J* = 11.7 Hz, 1H), 3.13 (s, 3H), 3.01 (p, *J* = 6.9 Hz, 1H), 2.74 – 2.62 (m, 4H, overlaying signals), 2.31 – 2.21 (m, 1H), 2.06 – 1.92 (m, 2H), 1.90 – 1.77 (m, 2H), 1.51 – 1.42 (m, 1H), 1.41 – 1.26 (m, 8H, overlaying signals), 0.83 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 213.99, 161.08 (d, *J* = 245.1 Hz), 144.25, 139.98, 139.30 (d, *J* = 3.2 Hz), 138.20, 136.51, 134.71, 133.78, 132.84, 129.52 (d, *J* = 7.9 Hz, 2 × C_{Ar}), 127.10, 127.06, 125.50, 115.50 (d, *J* = 21.2 Hz, 2 × C_{Ar}), 63.66, 45.21, 40.51, 40.12, 37.58, 28.48, 25.28, 24.57, 24.52, 24.01, 22.77, 13.30, 11.69. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -116.78 (tt, *J* = 8.5, 5.2 Hz). **IR** (ATR): ν_{max} 2962 (m), 2934 (m), 2875 (m), 1704 (s), 1604 (m), 1509 (s), 1461 (m), 1224 (s), 1159 (m), 909 (m), 833 (s), 730 (s), 556 (m) cm^{-1}. **HRMS** (HESI): m/z $[M+H]^+$ calcd for $C_{30}H_{36}FO$:

431.2745, found: 431.2740; $[M+Na]^+$ calcd for $C_{30}H_{35}FONa$: 453.2564, found: 453.2564; $[M+K]^+$ calcd for $C_{30}H_{35}FOK$: 469.2304, found: 469.2302; **HPLC:** Chiralpak IA, hexane/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, t_R(major) = 7.73 min, t_R(minor)= 4.10 min (97% ee).

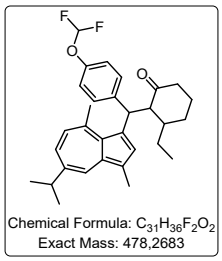
3-(1-(4-fluorophenyl)propyl)-7-isopropyl-1,4-dimethylazulene (6e)



Following the *General procedure 2* using carbocation **2e** (392 mg, 1.0 mmol, 2.0 eq). This side-product product was isolated by flash chromatography (silica gel, Hex:EtOAc 40:1 to 10:1).

R_f (silica, Hex:EtOAc 40/1): 0.17; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 2.2 Hz, 1H), 7.64 (s, 1H), 7.22 (dd, *J* = 10.7, 2.2 Hz, 1H), 7.09 (dd, *J* = 8.5, 5.6 Hz, 2H), 6.90 (t, *J* = 8.7 Hz, 2H), 6.77 (d, *J* = 10.7 Hz, 1H), 4.82 (t, *J* = 7.6 Hz, 1H), 3.00 (p, *J* = 7.0 Hz, 1H), 2.90 (s, 3H), 2.64 (s, 3H), 2.13 (dq, *J* = 15.9, 6.9 Hz, 2H), 1.33 (s, 3H), 1.32 (s, 3H), 0.94 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 160.86 (d, *J* = 243.3 Hz), 144.94, 143.22 (d, *J* = 3.0 Hz), 139.13, 137.75, 137.56, 134.51, 133.35, 132.65, 130.05, 129.65 (d, *J* = 7.7 Hz, 2 × C_{Ar}), 126.61, 124.63, 114.88 (d, *J* = 21.0 Hz, 2 × C_{Ar}), 46.49, 37.60, 32.01, 27.85, 24.58 (2 × CH_3), 13.40, 13.20. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -118.38 (tt, *J* = 8.9, 5.5 Hz). **IR** (ATR): ν_{max} 2962 (m), 2933 (m), 2873 (w), 1507 (s), 1461 (m), 1221 (s), 1157 (s), 909 (m), 831 (s), 731 (s), 544 (m) cm^{-1}. **HRMS** (HESI): m/z $[M+H]^+$ calcd for $C_{24}H_{28}F$: 335.2170, found: 335.2164

2-((4-(difluoromethoxy)phenyl)(5-isopropyl-3,8-dimethylazulen-1-yl)methyl)-3-ethylcyclohexan-1-one (5af)



Following the *General procedure 2* using carbocation **2f** (440 mg, 1.0 mmol, 2.0 eq). Based on ^{1}H NMR analysis of the crude reaction mixture, the diastereomeric ratio was 1:1. The crude product was purified by flash chromatography (silica gel, Hex:EtOAc 40:1 to 100:1). Isolated: 110 mg (46%)

Diastereomer 1:

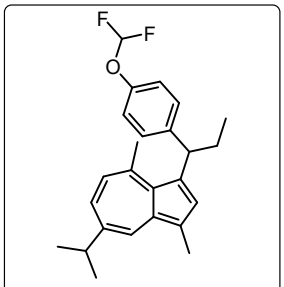
Blue oil, **R_f** (silica, Hex:EtOAc 10/1): 0.35; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.04 (d, *J* = 2.1 Hz, 1H), 7.96 (s, 1H), 7.34 – 7.27 (m, 2H), 7.21 (dd, *J* = 10.8, 2.2 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 2H), 6.79 (d, *J* = 10.8 Hz, 1H), 6.41 (t, *J* = 74.2 Hz, 1H), 5.58 (d, *J* = 11.3 Hz, 1H), 3.16 – 3.07 (m, 4H, overlaying signals), 2.97 (dt, *J* = 13.8, 6.9 Hz, 1H), 2.64 (s, 3H), 2.39 (td, *J* = 13.2, 12.6, 6.8 Hz, 1H), 2.24 (tt, *J* = 13.8, 4.5 Hz, 1H), 2.00 – 1.89 (m, 2H), 1.89 – 1.75 (m, 2H), 1.65 (dd, *J* = 14.5, 3.4 Hz, 1H), 1.41 – 1.15 (m, 8H), 0.76 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 213.75, 149.36 (t, *J* = 2.7 Hz), 143.56, 141.58, 139.86, 139.24, 137.86, 134.47, 133.70, 132.52, 129.95 (2 × C_{Ar}), 127.12, 125.92, 125.07, 119.59 (2 × C_{Ar}), 115.98 (t, *J* = 259.3 Hz), 63.22, 44.71, 41.04, 39.69, 37.57, 28.38, 24.85, 24.55, 24.52, 24.04, 23.71, 13.21, 11.68. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -80.55 (dd, *J* = 74.1, 2.6 Hz). **IR** (ATR): ν_{max} 2963 (m), 2935

(m), 2873 (w), 1704 (m), 1508 (m), 1381 (m), 1219 (m), 1123 (s), 1040 (s), 910 (m), 731 (m) cm^{-1}. **HRMS** (HESI): m/z $[M+H]^+$ calcd for $C_{31}H_{37}F_2O_2$: 479.2756, found: 479.2760; $[M+Na]^+$ calcd for $C_{31}H_{36}F_2O_2Na$: 501.2576, found: 501.2579; $[M+K]^+$ calcd for $C_{31}H_{36}F_2O_2K$: 517.2315, found: 517.2321; **HPLC:** Chiralpak IA, hexane/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, t_R(major) = 5.69 min, t_R(minor)= 4.17 min (95% ee).

Diastereomer 2:

Blue oil, $\mathbf{R_f}$ (silica, Hex:EtOAc 10/1): 0.25; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.08 (d, *J* = 2.2 Hz, 1H), 7.76 (s, 1H), 7.29 – 7.21 (m, 3H, overlaying signals), 6.98 – 6.89 (m, 2H), 6.85 (d, *J* = 10.7 Hz, 1H), 6.37 (t, *J* = 74.3 Hz, 1H), 5.54 (d, *J* = 11.8 Hz, 1H), 3.21 (d, *J* = 11.7 Hz, 1H), 3.13 (s, 3H), 3.00 (p, *J* = 6.8 Hz, 1H), 2.74 – 2.62 (m, 4H, overlaying signals), 2.31 – 2.21 (m, 1H), 1.99 (tdd, *J* = 13.3, 5.7, 2.5 Hz, 2H), 1.85 (tq, *J* = 13.7, 4.2 Hz, 2H), 1.50 – 1.43 (m, 1H), 1.41 – 1.29 (m, 8H, overlaying signals), 0.83 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 213.89, 149.52 (t, *J* = 2.9 Hz), 144.23, 140.82, 140.07, 138.27, 136.50, 134.75, 133.82, 132.88, 129.48 (2 × C_{Ar}), 127.17, 126.87, 125.55, 119.53 (2 × C_{Ar}), 116.08 (t, *J* = 258.6 Hz), 63.56, 45.28, 40.55, 40.12, 37.59, 28.50, 26.94, 25.29, 24.56, 24.52, 24.04, 22.79, 13.30, 11.68. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -80.36 (dd, *J* = 74.2, 3.2 Hz). **IR** (ATR): ν_{max} 2963 (m), 2934 (m), 2874 (w), 1703 (m), 1509 (m), 1461 (m), 1381 (m), 1218 (m), 1122 (s), 1041 (s), 908 (m), 730 (s) cm^{-1}. **HRMS** (HESI): m/z $[M+H]^+$ calcd for $C_{31}H_{37}F_2O_2$: 479.2756, found: 479.2754; $[M+Na]^+$ calcd for $C_{31}H_{36}F_2O_2Na$: 501.2573, found: 501.2579; $[M+K]^+$ calcd for $C_{31}H_{36}F_2O_2K$: 517.2315, found: 517.2312; **HPLC:** Chiralpak IA, hexane/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, t_R(major) = 12.79 min, t_R(minor)= 4.40 min (97% ee).

3-(1-(4-fluorophenyl)propyl)-7-isopropyl-1,4-dimethylazulene (6f)

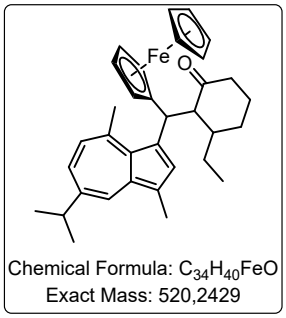


Chemical Formula: $C_{25}H_{28}F_2O$
Exact Mass: 382,2108

Following the *General procedure 2* using carbocation **2f** (440 mg, 1.0 mmol, 2.0 eq). This side-product product was isolated by flash chromatography (silica gel, Hex:EtOAc 100:1 to 10:1).

$\mathbf{R_f}$ (silica, Hex:EtOAc 10/1): 0.73; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 2.2 Hz, 1H), 7.64 (s, 1H), 7.26 – 7.18 (m, 1H), 7.12 (d, *J* = 8.6 Hz, 2H), 6.97 (d, *J* = 8.3 Hz, 2H), 6.78 (d, *J* = 10.7 Hz, 1H), 6.42 (t, *J* = 74.4 Hz, 1H), 4.84 (t, *J* = 7.6 Hz, 1H), 3.00 (p, *J* = 6.9 Hz, 1H), 2.90 (s, 3H), 2.64 (s, 3H), 2.22 – 2.04 (m, 2H), 1.33 (s, 3H), 1.32 (s, 3H), 0.94 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 148.99 (t, *J* = 2.8 Hz), 144.90, 144.85, 139.20, 137.79, 137.52, 134.52, 133.39, 132.66, 129.80, 129.58 (2 × C_{Ar}), 126.65, 124.66, 119.48, 119.25 (2 × C_{Ar}), 116.15 (t, *J* = 258.7 Hz), 46.55, 37.59, 31.90, 27.88, 24.57, 13.40, 13.19. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -80.34 (d, *J* = 74.3 Hz). **IR** (ATR): ν_{max} 2965 (m), 2935 (m), 2875 (w), 1509 (m), 1380 (m), 1219 (m), 1123 (s), 1039 (s), 835 (m) cm^{-1}. **HRMS** (HESI): m/z $[M+H]^+$ calcd for $C_{25}H_{29}F_2O$: 383.2181, found: 383.2180

3-(ferrocenyl(2-ethyl-6-methylenecyclohexyl)methyl)-7-isopropyl-1,4-dimethylazulene (5ag)



Chemical Formula: $C_{34}H_{40}FeO$
Exact Mass: 520,2429

Following the *General procedure 2* using carbocation **2g** (481 mg, 1.0 mmol, 2.0 eq). Based on ^{1}H NMR analysis of the crude reaction mixture, the diastereomeric ratio was 1:1. The crude product was purified by flash chromatography (silica gel, Hex:EtOAc 100:1 to 10:1). Isolated: 31 mg (12%)

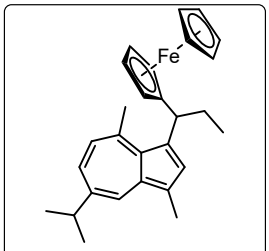
Diastereomer 1:

Blue oil, $\mathbf{R_f}$ (silica, Hex:EtOAc 10/1): 0.43; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 2.2 Hz, 1H), 7.71 (s, 1H), 7.21 (dd, *J* = 10.5, 2.2 Hz, 1H), 6.85 (d, *J* = 10.5 Hz, 1H), 5.16 (d, *J* = 11.1 Hz, 1H), 4.16 (t, *J* = 2.0 Hz, 2H), 4.12 (q, *J* = 2.1 Hz, 1H), 4.07 (q, *J* = 2.0 Hz, 1H), 3.56 (s, 5H), 3.30 (s, 3H), 3.00 (p, *J* = 6.9 Hz, 1H), 2.82 (d, *J* = 11.0 Hz, 1H), 2.65 (s, 3H), 2.26 (td, *J* = 13.3, 6.5 Hz, 1H), 2.11 – 2.00 (m, 1H), 1.88 (s, 2H), 1.84 – 1.76 (m, 1H), 1.76 – 1.69 (m, 1H), 1.59 (s, 1H), 1.34 (s, 3H), 1.32 (s, 3H), 1.24 – 1.19 (m, 2H), 0.79 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 213.70, 142.60, 139.64, 138.48, 138.18, 133.61 (2 × C_{Ar}), 130.64, 129.35, 126.67, 125.21, 95.57, 68.85, 68.47 (5 × C_{Cp}), 67.94, 65.69, 65.56, 64.63, 41.06, 39.63, 38.33, 37.58, 28.77, 24.91, 24.56, 24.53, 23.90, 23.06, 13.25, 11.88. **IR** (ATR): ν_{max} 3091 (w), 2959 (m), 2926 (s), 2861 (m), 1693 (m), 1460 (m), 1107 (m), 810 (s), 481 (s) cm^{-1}. **HRMS** (HESI): m/z $[M]^+$ calcd for $C_{34}H_{40}FeO$: 520.2423, found: 520.2424; $[M+Na]^+$ calcd for $C_{34}H_{40}F_eONa$: 543.2321, found: 543.2320; $[M+K]^+$ calcd for $C_{34}H_{40}F_eOK$: 559.2060, found: 559.2056; **HPLC:** Chiralpak IA, hexane/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, t_R(major) = 4.56 min, t_R(minor)= 3.86 min (97% ee).

Diastereomer 2:

Blue oil, $\mathbf{R_f}$ (silica, Hex:EtOAc 10/1): 0.35; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.10 (d, *J* = 2.1 Hz, 1H), 7.62 (s, 1H), 7.28 (dd, *J* = 10.5, 2.2 Hz, 1H), 6.91 (d, *J* = 10.5 Hz, 1H), 5.11 (d, *J* = 11.4 Hz, 1H), 4.17 – 4.09 (m, 2H), 3.99 (td, *J* = 2.4, 1.1 Hz, 1H), 3.94 (dt, *J* = 2.6, 1.3 Hz, 1H), 3.57 (s, 5H), 3.31 (s, 3H), 3.04 (p, *J* = 6.8 Hz, 1H), 2.89 (d, *J* = 11.2 Hz, 1H), 2.68 (s, 3H), 2.60 (td, *J* = 13.4, 6.6 Hz, 1H), 2.19 (d, *J* = 13.3 Hz, 1H), 1.95 – 1.85 (m, 2H), 1.82 – 1.70 (m, 1H), 1.46 (s, 1H), 1.37 (s, 3H), 1.36 (s, 3H), 1.35 – 1.32 (m, 1H), 1.21 – 1.14 (m, 1H), 1.14 – 1.06 (m, 1H), 0.68 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 214.36, 143.64, 139.63, 138.32, 136.53, 134.01, 133.62, 131.71, 130.03, 126.76, 125.46, 94.35, 68.34 (5 × C_{Cp}), 68.25, 68.01, 66.10, 65.82, 64.86, 41.24, 39.65, 39.06, 37.57, 28.65, 25.06, 24.58, 24.55, 24.35, 23.08, 13.31, 11.54. **IR** (ATR): ν_{max} 3092 (w), 2958 (m), 2925 (s), 2860 (m), 1704 (s), 1544 (m), 1460 (m), 1107 (m), 816 (s), 481 (s) cm^{-1}. **HRMS** (HESI): m/z $[M]^+$ calcd for $C_{34}H_{40}FeO$: 520.2423, found: 520.2422; $[M+Na]^+$ calcd for $C_{34}H_{40}F_eONa$: 543.2321, found: 543.2319; $[M+K]^+$ calcd for $C_{34}H_{40}F_eOK$: 559.2060, found: 559.2054; **HPLC:** Chiralpak IA, hexane/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, t_R(major) = 5.33 min, t_R(minor)= 4.52 min (97% ee).

3-(1-ferrocenylpropyl)-7-isopropyl-1,4-dimethylazulene (6g)

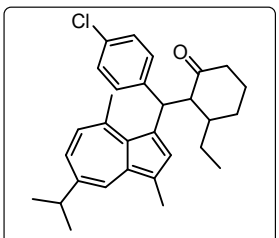


Chemical Formula: $C_{28}H_{32}Fe$
Exact Mass: 424,1853

Following the *General procedure 2* using carbocation **2g** (481 mg, 1.0 mmol, 2.0 eq). This side-product product was isolated by flash chromatography (silica gel, Hex:EtOAc 100:1 to 10:1).

R_f (silica, Hex:EtOAc 10/1): 0.87; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.05 (d, *J* = 2.2 Hz, 1H), 7.52 (s, 1H), 7.25 (dd, *J* = 10.7, 2.0 Hz, 1H), 6.84 (d, *J* = 10.6 Hz, 1H), 4.68 (dd, *J* = 10.2, 4.6 Hz, 1H), 4.12 (dt, *J* = 2.8, 1.4 Hz, 1H), 4.10 – 4.04 (m, 7H), 4.04 – 4.02 (m, 1H), 3.08 (s, 3H), 3.02 (q, *J* = 6.9 Hz, 1H), 2.61 (s, 3H), 2.34 – 2.23 (m, 1H), 2.11 – 1.98 (m, 1H), 1.37 (s, 3H), 1.36 (s, 3H), 0.88 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 142.96, 138.00, 137.50, 136.44, 132.60, 131.99, 131.52, 130.18, 125.12, 123.91, 95.80, 67.42 (5 × C_{cp}), 66.54, 66.34, 66.08, 65.17, 38.65, 36.55, 29.82, 27.43, 23.54 (2 × CH_3), 12.18, 12.10. **IR** (ATR): ν_{max} 3095 (w), 2961 (m), 2930 (m), 2871 (w), 1544 (m), 1460 (m), 1106 (m), 1000 (m), 909 (m), 812 (s), 730 (s), 482 (s) cm^{-1}. **HRMS** (HESI): m/z $[M]^+$ calcd for $C_{28}H_{32}Fe$: 424.1848, found: 424.1850; $[M+Na]^+$ calcd for $C_{28}H_{32}FeNa$: 447.1746, found: 447.1741

3-ethyl-2-((4-chlorophenyl)(5-isopropyl-3,8-dimethylazulen-1-yl)methyl)cyclohexan-1-one (5ah)



Chemical Formula: $C_{30}H_{35}ClO$
Exact Mass: 446,2376

Following the *General procedure 2* using carbocation **2h** (466 mg, 1.0 mmol, 2.0 eq). Based on ^{1}H NMR analysis of the crude reaction mixture, the diastereomeric ratio was 1:1. The crude product was purified by flash chromatography (silica gel, Hex:EtOAc 100:1 to 10:1). Isolated: 18 mg (18%)

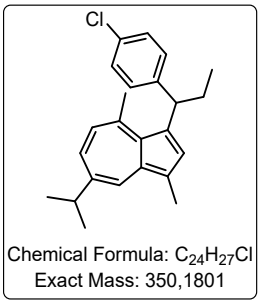
Diastereomer 1:

R_f (silica, Hex:EtOAc 10/1): 0.43; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.08 (d, *J* = 2.2 Hz, 1H), 7.75 (s, 1H), 7.26 (dd, *J* = 10.6, 2.2 Hz, 1H), 7.20 – 7.13 (m, 4H), 6.85 (d, *J* = 10.6 Hz, 1H), 5.51 (d, *J* = 11.8 Hz, 1H), 3.20 (d, *J* = 11.7 Hz, 1H), 3.12 (s, 3H), 3.01 (hept, *J* = 6.9 Hz, 1H), 2.67 (td, *J* = 13.6, 6.7 Hz, 1H), 2.66 (s, 3H), 2.30 – 2.23 (m, 1H), 2.04 – 1.94 (m, 2H), 1.89 – 1.77 (m, 2H), 1.46 (d, *J* = 13.9 Hz, 1H), 1.33 (s, 3H), 1.32 (s, 3H), 1.29 – 1.21 (m, 2H), 0.83 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 213.81, 144.18, 142.03, 140.04, 138.23, 136.47, 134.72, 133.79, 132.87, 131.89, 129.40 (2 × C_{Ar}), 128.81 (2 × C_{Ar}), 127.14, 126.65, 125.50, 63.44, 45.33, 40.49, 40.11, 37.56, 28.46, 25.25, 24.54, 24.50, 23.99, 22.74, 13.28, 11.66. **IR** (ATR): ν_{max} 2961 (m), 2930 (m), 2870 (m), 1705 (s), 1489 (m), 1461 (m), 1090 (s), 1013 (s), 822 (m), 730 (m), 649 (m) cm^{-1}. **HRMS** (HESI): m/z $[M+H]^+$ calcd for $C_{30}H_{36}ClO$: 447.2449, found: 447.2434; $[M+Na]^+$ calcd for $C_{30}H_{35}ClONa$: 469.2269, found: 469.2258; **HPLC:** Chiralpak IA, hexane/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, t_R(major) = 4.95 min, t_R(minor)= 3.82 min (97% ee).

Diastereomer 2:

R_f (silica, Hex:EtOAc 10/1): 0.37; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.04 (d, *J* = 2.2 Hz, 1H), 7.95 (s, 1H), 7.26 – 7.19 (m, 5H), 6.79 (d, *J* = 10.7 Hz, 1H), 5.56 (d, *J* = 11.3 Hz, 1H), 3.10 (d, *J* = 11.2 Hz, 1H), 3.08 (s, 3H), 2.98 (hept, *J* = 6.9 Hz, 1H), 2.63 (s, 3H), 2.39 (td, *J* = 13.3, 12.7, 6.8 Hz, 1H), 2.23 (tt, *J* = 13.9, 4.7 Hz, 1H), 1.98 – 1.91 (m, 2H), 1.88 – 1.77 (m, 2H), 1.68 – 1.63 (m, 1H), 1.30 (s, 3H), 1.29 (s, 3H), 1.29 – 1.27 (m, 2H), 0.77 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 213.70, 143.52, 142.81, 139.84, 139.21, 137.82, 134.45, 133.67, 132.55, 131.74, 129.96 (2 × C_{Ar}), 128.67 (2 × C_{Ar}), 127.11, 125.67, 125.02, 63.08, 44.76, 41.00, 39.66, 37.55, 28.34, 24.81, 24.53, 24.50, 24.02, 23.69, 13.20, 11.65. **IR** (ATR): ν_{max} 2962 (m), 2929 (m), 2872 (m), 1704 (s), 1595 (m), 1491 (m), 1461 (m), 1091 (m), 1014 (m), 908 (m), 824 (m), 730 (s), 648 (m) cm^{-1}. **HRMS** (HESI): m/z $[M+H]^+$ calcd for $C_{30}H_{36}ClO$: 447.2449, found: 447.2433; $[M+Na]^+$ calcd for $C_{30}H_{35}ClONa$: 469.2269, found: 469.2259; **HPLC**: Chiralpak IA, hexane/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, t_R(major) = 6.83 min, t_R(minor)= 4.14 min (97% ee).

3-(1-(4-chlorophenyl)propyl)-7-isopropyl-1,4-dimethylazulene (6h)

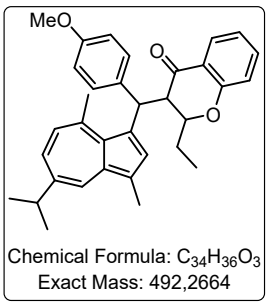


Chemical Formula: $C_{24}H_{27}Cl$
Exact Mass: 350,1801

Following the *General procedure 2* using carbocation **2h** (466 mg, 1.0 mmol, 2.0 eq). This side-product product was isolated by flash chromatography (silica gel, Hex:EtOAc 100:1 to 10:1).

R_f (silica, Hex:EtOAc 10/1): 0.90; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.09 (d, *J* = 2.2 Hz, 1H), 7.65 (s, 1H), 7.24 (dd, *J* = 10.6, 2.2 Hz, 1H), 7.22 – 7.18 (m, 2H), 7.10 – 7.06 (m, 2H), 6.79 (d, *J* = 10.7 Hz, 1H), 4.83 (t, *J* = 7.6 Hz, 1H), 3.02 (p, *J* = 6.9 Hz, 1H), 2.91 (s, 3H), 2.66 (s, 3H), 2.20 – 2.08 (m, 2H), 1.35 (s, 3H), 1.34 (s, 3H), 0.96 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 146.06, 144.89, 139.20, 137.76, 137.53, 134.54, 133.38, 132.68, 131.03, 129.69 (2 × C_{Ar}), 129.59, 128.28 (2 × C_{Ar}), 126.66, 124.63, 46.64, 37.59, 31.81, 27.86, 24.57 (2 × CH_3), 13.38, 13.19. **IR** (ATR): ν_{max} 2962 (m), 2930 (m), 2873 (w), 1687 (w), 1544 (w), 1491 (m), 1461 (m), 1091 (m), 1014 (m), 907 (m), 819 (m), 731 (s), 649 (m), 525 (m) cm^{-1}. **HRMS** (APPI): m/z $[M+H]^+$ calcd for $C_{24}H_{28}Cl$: 351.1874, found: 351.1877

2-ethyl-3-((5-isopropyl-3,8-dimethylazulen-1-yl)(4-methoxyphenyl)methyl)chroman-4-one (5bb)



Chemical Formula: $C_{34}H_{36}O_3$
Exact Mass: 492,2664

Copper(I) bromide dimethyl sulfide complex (4 mg, 0.02 mmol, 5 mol%) and ligand **L4** (14 mg, 0.024 mmol, 6 mol%) were added to a dry Schlenk-tube under Ar atmosphere. Next, dry DCM (2 mL) was added, and the mixture was stirred at room temperature for 15 min and then cooled to -78 °C. At this temperature, EtMgBr (3M in Et_2O, 330 µL, 1.0 mmol, 2.5 eq) was added. After 30 min, a solution of chromone (59 mg, 0.4 mmol, 1.0 eq) in dry DCM (1.5 mL) was added and the reaction mixture was stirred overnight at -78°C. Next, in another dry Schlenk-tube under Ar atmosphere carbocation **2b** (420 mg, 1 mmol, 2.5 eq) was dissolved in dry DCM (2 mL) at room

temperature. Finally, the first reaction mixture (containing the metal enolate) was transferred to the second Schlenk-tube (containing the carbocation) and stirred at room temperature for 1 h. The reaction was quenched by the addition of saturated aqueous NH_4Cl (~ 10 mL). The phases were separated, and the aqueous phase was further extracted with DCM (3 × 50 mL). The combined organic phase was dried over anhydr. $MgSO_4$, and the solvent was evaporated under reduced pressure. Based on ^1H NMR analysis of the crude reaction mixture, the diastereomeric ratio was 2:1. The crude product was purified by flash chromatography (silica gel, mixtures of hexane:DCM 3/1 to 1/1) to gain the final products as blue oils: 28 mg (14%).

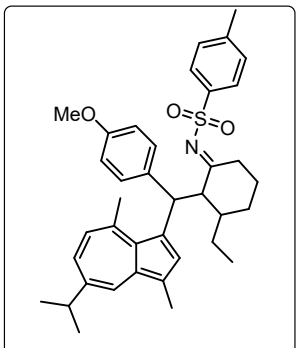
Diastereomer 1:

Blue oil, $\mathbf{R_f}$ (silica, Hex:EtOAc 10/1): 0.32; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.02 – 7.96 (m, 2H), 7.50 – 7.40 (m, 2H), 7.34 – 7.29 (m, 2H), 7.10 (dd, *J* = 10.6, 2.2 Hz, 1H), 7.03 (dd, *J* = 8.4, 1.1 Hz, 1H), 6.89 – 6.80 (m, 3H), 6.57 (d, *J* = 10.7 Hz, 1H), 5.50 (d, *J* = 11.5 Hz, 1H), 4.30 (ddd, *J* = 9.8, 5.2, 1.5 Hz, 1H), 3.75 (s, 3H), 3.31 (dd, *J* = 11.5, 1.6 Hz, 1H), 2.94 (hept, *J* = 6.9 Hz, 1H), 2.67 (s, 3H), 2.46 (s, 3H), 1.83 (tdd, *J* = 14.3, 7.3, 2.0 Hz, 1H), 1.54 – 1.45 (m, 1H), 1.28 (s, 3H), 1.27 (s, 3H), 0.92 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 194.17, 158.07, 157.89, 143.94, 139.45, 138.37, 138.21, 135.77, 135.21, 134.01, 133.43, 131.60, 129.75 (2 × C_{Ar}), 127.12, 126.87, 126.07, 124.81, 120.83, 120.69, 117.62, 114.17 (2 × C_{Ar}), 80.37, 56.63, 55.22, 43.30, 37.52, 27.59, 24.54 (2 × CH_3), 24.29, 13.37, 10.27. **IR** (ATR): ν_{max} 2961 (m), 2934 (m), 2877 (w), 2839 (w), 1688 (m), 1606 (m), 1510 (s), 1461 (s), 1250 (s), 1173 (m), 1030 (m), 729 (m), 523 (m) cm^{-1}. **HRMS** (HESI): m/z $[M+H]^+$ calcd for $C_{34}H_{37}O_3$: 493.2737, found: 493.2739; $[M+Na]^+$ calcd for $C_{34}H_{36}O_3Na$: 515.2557, found: 515.2553; $[M+K]^+$ calcd for $C_{34}H_{36}O_3K$: 531.2296, found: 531.2297; **HPLC**: Chiralpak IA, hexane/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, t_R(major) = 8.40 min, t_R(minor)= 4.29 min).

Diastereomer 2:

Blue oil, $\mathbf{R_f}$ (silica, Hex:EtOAc 10/1): 0.28; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.09 (d, *J* = 2.2 Hz, 1H), 7.77 (s, 1H), 7.72 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.51 (ddd, *J* = 8.6, 7.1, 1.8 Hz, 1H), 7.25 (dd, *J* = 10.7, 2.2 Hz, 1H), 7.01 (td, *J* = 7.3, 1.1 Hz, 1H), 6.98 – 6.93 (m, 3H), 6.81 (d, *J* = 10.7 Hz, 1H), 6.72 – 6.64 (m, 2H), 5.47 (d, *J* = 11.6 Hz, 1H), 4.27 (ddd, *J* = 9.6, 5.7, 1.2 Hz, 1H), 3.69 (s, 3H), 3.34 (dd, *J* = 11.6, 1.3 Hz, 1H), 3.01 (p, *J* = 6.9 Hz, 1H), 2.92 (s, 3H), 2.68 (s, 3H), 1.77 (ddq, *J* = 14.6, 9.5, 7.3 Hz, 1H), 1.49 (dqd, *J* = 14.5, 7.4, 5.6 Hz, 1H), 1.33 (s, 3H), 1.32 (s, 3H), 0.85 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 194.25, 158.18, 157.76, 145.40, 139.82, 138.24, 136.16, 136.00, 134.80, 134.68, 133.76, 132.91, 129.60 (2 × C_{Ar}), 127.37, 127.04, 126.92, 125.31, 120.95, 120.82, 117.83, 113.71 (2 × C_{Ar}), 81.08, 57.70, 55.03, 43.97, 37.58, 27.95, 24.58, 24.54, 24.30, 13.37, 10.11. **IR** (ATR): ν_{max} 2962 (m), 2933 (m), 2875 (w), 2839 (w), 1688 (m), 1606 (m), 1511 (s), 1462 (s), 1251 (s), 1178 (m), 1030 (m), 908 (m), 729 (s), 527 (m) cm^{-1}. **HRMS** (HESI): m/z $[M+H]^+$ calcd for $C_{34}H_{37}O_3$: 493.2737, found: 493.2735; $[M+Na]^+$ calcd for $C_{34}H_{36}O_3Na$: 515.2557, found: 515.2556; $[M+K]^+$ calcd for $C_{34}H_{36}O_3K$: 531.2296, found: 531.2296; **HPLC**: Chiralpak IA, hexane/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, t_R(major) = 12.14 min, t_R(minor)= 4.63 min).

N-(3-ethyl-2-((5-isopropyl-3,8-dimethylazulen-1-yl)(4-methoxyphenyl)methyl)cyclohexylidene)-4-methylbenzenesulfonamide (5cb)



Chemical Formula: $C_{38}H_{45}NO_3S$
Exact Mass: 595,3120

$Cu(OTf)_2$ (9 mg, 0.025 mmol, 5 mol%) and ligand **L2** (27 mg, 0.05 mmol, 10 mol%) were added to a dry Schlenk-tube under Ar atmosphere. Next, dry toluene (1 mL) was added, and the mixture was stirred at room temperature for 15 min. Next, the *N*-sulfonyl imine in dry toluene (3 mL) was added and stirred for 30 min. Next, the reaction mixture was cooled to -30 °C and at this temperature Et_2Zn (0.9M in hexane, 720 µL, 0.65 mmol, 1.3 eq) was added and stirred for 2 h. Next, in another dry Schlenk-tube under Ar atmosphere carbocation **2b** (420 mg, 1 mmol, 2.5 eq) was dissolved in dry DCM (4 mL) at room temperature. Finally, the first reaction mixture (containing the metal enolate) was transferred to the second Schlenk-tube (containing the carbocation) and stirred at room temperature for 1.5 h. The reaction was quenched by the addition of saturated aqueous NH_4Cl (~ 10 mL). The phases were separated, and the aqueous phase was further extracted with DCM (3 × 50 mL). The combined organic phase was dried over anhydr. $MgSO_4$, and the solvent was evaporated under reduced pressure. Based on ^{1}H NMR analysis of the crude reaction mixture, the diastereomeric ratio was 2:1. The crude product was purified by flash chromatography (preparative TLC, hexane:EtOAc 5/1) to gain the final products as blue oils: 37 mg (12%).

Diastereomer 1:

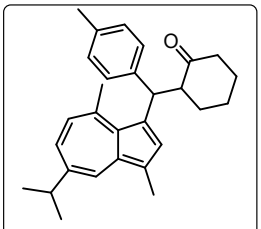
R_f (silica, Hex:EtOAc 5/1): 0.26; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 2.1 Hz, 1H), 7.92 (s, 1H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.24 – 7.17 (m, 3H), 7.12 (d, *J* = 7.9 Hz, 2H), 6.81 – 6.73 (m, 3H), 5.44 (d, *J* = 11.4 Hz, 1H), 3.72 (s, 3H), 3.20 (t, *J* = 12.2 Hz, 2H), 3.06 (s, 3H), 3.03 – 2.96 (m, 1H), 2.55 (s, 3H), 2.38 (s, 3H), 2.26 – 2.11 (m, 2H), 2.00 – 1.80 (m, 4H), 1.62 (d, *J* = 14.8 Hz, 2H), 1.34 (s, 3H), 1.32 (s, 3H), 0.74 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 196.11, 157.81, 143.64, 142.97, 139.79, 139.61, 138.75, 137.87, 136.15, 134.29, 133.45, 132.47, 129.64 (2 × C_{Ar}), 129.23 (2 × C_{Ar}), 127.02, 126.70 (2 × C_{Ar}), 126.24, 124.62, 113.99 (2 × C_{Ar}), 60.70, 55.19, 45.27, 41.91, 37.60, 32.95, 29.71, 28.37, 24.66, 24.63, 24.53, 24.13, 23.44, 21.53, 13.15, 11.82. **IR** (ATR): ν_{max} 2961 (m), 2928 (m), 2871 (m), 1608 (s), 1511 (s), 1460 (m), 1317 (m), 1304 (m), 1252 (s), 1153 (s), 1092 (s), 1033 (m), 811 (s), 726 (s), 676 (s), 544 (m) cm^{-1}. **HRMS** (HESI): m/z $[M+H]^+$ calcd for $C_{38}H_{46}NO_3S$: 596.3193, found: 596.3187; $[M+Na]^+$ calcd for $C_{38}H_{45}NO_3SNa$: 618.3012, found: 618.3005; $[M+K]^+$ calcd for $C_{38}H_{45}NO_3SK$: 634.2752, found: 634.2745; **HRMS** (APPI): m/z $[M+H]^+$ calcd for $C_{38}H_{46}NO_3S$: 596.3193, found: 596.3194; **HPLC:** Chiralpak IC, hexane/*i*-PrOH = 90:10, 1.5 mL/min, 254 nm, t_R(major) = 23.61 min, t_R(minor)= 28.75 min.

Diastereomer 2:

R_f (silica, Hex:EtOAc 5/1): 0.20; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 2.2 Hz, 1H), 7.74 (s, 1H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.24 (dd, *J* = 10.7, 2.0 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.7 Hz, 2H), 6.82 (d, *J* = 10.7 Hz, 1H), 6.74 – 6.67 (m, 2H), 5.47 (d, *J* = 11.7 Hz, 1H), 3.73 (s, 3H), 3.65 (d, *J* = 14.4 Hz, 1H), 3.20 (d, *J* = 11.6 Hz, 1H), 3.12 (s, 3H), 3.00 (p, *J* = 6.8 Hz, 1H), 2.72 – 2.66 (m, 1H), 2.64 (s, 3H), 2.40 (s, 3H), 2.01 – 1.95 (m, 1H), 1.93 – 1.82 (m, 3H), 1.47 – 1.34 (m, 3H), 1.32 (s, 3H), 1.31 (s, 3H), 0.81 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 194.64, 157.83, 144.57, 143.14, 139.90, 138.62, 138.20, 136.71, 135.55, 134.77, 133.76, 132.96, 129.37 (2 × C_{Ar}), 129.19 (2 × C_{Ar}), 127.49, 127.14, 127.03 (2 × C_{Ar}), 125.42, 114.14 (2 × C_{Ar}), 60.57, 55.27, 46.31, 40.66, 37.69, 33.67, 28.59, 25.28, 24.70, 24.65, 23.57, 22.86, 21.69, 13.42, 11.84. **IR** (ATR): ν_{max} 3961 (m), 2930 (m), 2868 (w), 1608 (s), 1511 (s), 1461 (m), 1303 (m), 1253 (s), 1152 (s), 1092 (s), 1034 (m), 908 (m), 826 (m), 813 (m), 727 (s), 667 (s), 588 (s), 539 (s) cm^{-1}. **HRMS** (HESI): m/z $[M+H]^+$ calcd for $C_{38}H_{46}NO_3S$: 596.3193, found: 596.3184; $[M+Na]^+$ calcd for $C_{38}H_{45}NO_3SNa$: 618.3012, found: 618.3003; $[M+K]^+$ calcd for $C_{38}H_{45}NO_3SK$: 634.2752, found: 634.2743; **HRMS** (APPI): m/z $[M+H]^+$ calcd for $C_{38}H_{46}NO_3S$: 596.3193, found: 596.3189; **HPLC:** Chiralpak IC, hexane/*i*-PrOH = 90:10, 1.5 mL/min, 254 nm, t_R(major) = 20.11 min, t_R(minor)= 18.67 min.

6.3. Products of silyl enol ether trapping

2-((5-Isopropyl-3,8-dimethylazulen-1-yl)(*p*-tolyl)methyl)cyclohexan-1-one (7a)



Chemical Formula: $C_{29}H_{34}O$
Exact Mass: 398,2610

Following the *General procedure 3* using 1-(trimethylsiloxy)cyclohexene (101 µL, 0.26 mmol, 2.0 eq). Based on ^{1}H NMR analysis of the crude reaction mixture, the diastereomeric ratio was 1:1. The crude product was purified by flash chromatography (silica gel, Hex:EtOAc 40:1 to 10:1). Isolated: 67 mg (65%)

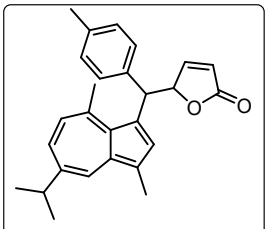
Diastereomer 1:

Blue oil, $\mathbf{R_f}$ (silica, Hex:EtOAc 10/1): 0.45; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.01 (d, *J* = 2.1 Hz, 1H), 7.74 (s, 1H), 7.17 (dd, *J* = 10.7, 2.2 Hz, 1H), 7.05 (d, *J* = 7.9 Hz, 2H), 7.00 (d, *J* = 7.9 Hz, 2H), 6.76 (d, *J* = 10.8 Hz, 1H), 5.46 (d, *J* = 9.2 Hz, 1H), 3.38 (td, *J* = 9.7, 4.4 Hz, 1H), 3.07 (s, 3H), 2.96 (p, *J* = 6.9 Hz, 1H), 2.63 (s, 3H), 2.39 – 2.26 (m, 2H), 2.24 (s, 3H), 2.00 (dt, *J* = 12.2, 6.6 Hz, 1H), 1.93 – 1.83 (m, 2H), 1.82 – 1.72 (m, 1H), 1.72 – 1.64 (m, 1H), 1.49 – 1.39 (m, 1H), 1.29 (d, *J* = 2.1 Hz, 3H), 1.28 (d, *J* = 2.1 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 213.06, 145.47, 141.22, 138.82, 137.37, 136.89, 135.08, 134.62, 133.47, 132.49, 129.53, 129.15 (2 × C_{Ar}), 128.94 (2 × C_{Ar}), 126.88, 124.15, 58.31, 43.44, 42.52, 37.52, 33.77, 29.21, 28.07, 24.71, 24.57, 24.55, 20.91, 13.30. **IR** (ATR): ν_{max} 2957 (m), 2929 (m), 2863 (m), 1706 (m), 1512 (m), 1448 (m), 1125 (m), 909 (m), 820 (m), 728 (s), 647 (m), 504 (m) cm^{-1}. **HRMS** (HESI): m/z $[M+H]^+$ calcd for $C_{29}H_{35}0$: 399.2682, found: 399.2687; $[M+Na]^+$ calcd for $C_{29}H_{34}0Na$: 421.2502, found: 421.2509

Diastereomer 2:

Blue oil, $\mathbf{R_f}$ (silica, Hex:EtOAc 10/1): 0.38; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.01 (d, *J* = 2.2 Hz, 1H), 7.53 (s, 1H), 7.22 (dd, *J* = 10.6, 2.2 Hz, 1H), 7.17 (d, *J* = 7.9 Hz, 2H), 7.00 (d, *J* = 7.9 Hz, 2H), 6.81 (d, *J* = 10.5 Hz, 1H), 5.47 (d, *J* = 10.9 Hz, 1H), 3.44 – 3.37 (m, 1H), 3.12 (s, 3H), 2.98 (hept, *J* = 6.9 Hz, 1H), 2.58 (s, 3H), 2.50 – 2.39 (m, 2H), 2.22 (s, 3H), 2.05 – 1.97 (m, 1H), 1.79 – 1.69 (m, 3H), 1.62 – 1.56 (m, 1H), 1.45 – 1.39 (m, 1H), 1.32 (d, *J* = 1.9 Hz, 3H), 1.31 (d, *J* = 1.9 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 213.14, 144.44, 142.48, 139.53, 138.53, 137.54 (2 × C_{Ar}), 134.83, 134.12, 133.35, 131.79, 128.98 (2 × C_{Ar}), 127.92 (2 × C_{Ar}), 126.72, 125.43, 57.61, 42.95, 42.84, 37.56, 34.20, 29.44, 28.97, 24.88, 24.55, 24.52, 20.93, 13.26. **IR** (ATR): ν_{max} 2958 (m), 2930 (m), 2863 (m), 1709 (m), 1513 (m), 1447 (m), 1124 (m), 909 (m), 815 (m), 728 (s), 647 (m), 546 (m), 521 (m) cm^{-1}. **HRMS** (HESI): m/z $[M+H]^+$ calcd for $C_{29}H_{35}0$: 399.2682, found: 399.2686; $[M+Na]^+$ calcd for $C_{29}H_{34}0Na$: 421.2502, found: 421.2504

5-((5-Isopropyl-3,8-dimethylazulen-1-yl)(*p*-tolyl)methyl)furan-2(5H)-one (7b)

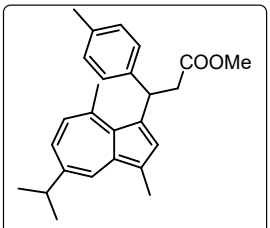


Chemical Formula: $C_{27}H_{28}O_2$
Exact Mass: 384,2089

Following the *General procedure 3* using 2-(trimethylsiloxy)furan (107 µL, 0.26 mmol, 2.0 eq). Based on ^{1}H NMR analysis of the crude reaction mixture, the diastereomeric ratio was 2:3. The crude product was purified by flash chromatography (silica gel, Hex:EtOAc 20:1 to 2:1). Isolated: 60 mg (60%). The diastereomers were not separated (ratio of 2:3).

Blue oil, $\mathbf{R_f}$ (silica, Hex:EtOAc 10/1): 0.12; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.13 (d, *J* = 2.1 Hz, 0.6H), 8.10 (d, *J* = 2.1 Hz, 0.4H), 7.84 (s, 0.4H), 7.79 (s, 0.6H), 7.42 (dd, *J* = 5.8, 1.4 Hz, 0.4H), 7.28 (dd, *J* = 10.7, 2.2 Hz, 0.6H), 7.27 – 7.19 (m, 1H, overlaying), 7.15 (s, 0.4H), 7.14 (s, 0.6H), 7.09 – 7.03 (m, 3H, overlaying), 6.84 (d, *J* = 10.7 Hz, 0.6H), 6.79 (d, *J* = 10.8 Hz, 0.4H), 6.02 (m, 1H, overlaying), 5.75 (dd, *J* = 7.8, 1.7 Hz, 0.4H), 5.70 (dd, *J* = 8.2, 1.7 Hz, 0.6H), 5.17 (d, *J* = 7.9 Hz, 0.4H), 5.05 (d, *J* = 8.2 Hz, 0.6H), 3.01 (dp, *J* = 14.0, 6.9 Hz, 1H, overlaying), 2.85 (s, 1.8H), 2.84 (s, 1.2H), 2.67 (s, 1.2H), 2.66 (s, 1.8H), 2.27 (s, 1.2H), 2.27 (s, 1.8H), 1.34 (d, *J* = 6.8 Hz, 3.6H), 1.32 (dd, *J* = 6.9, 2.2 Hz, 2.4H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 172.98, 172.91, 156.88, 156.02, 145.04, 144.91, 140.15, 139.76, 138.28, 138.24, 137.67, 137.47, 137.12, 136.53, 136.19, 135.13, 134.96, 134.00, 133.77, 133.11, 132.42, 129.44, 129.01, 128.79, 127.56, 127.37, 125.14, 124.78, 124.57, 124.51, 121.90, 86.93, 86.66, 49.54, 49.37, 37.63, 37.58, 28.05, 27.89, 24.58, 24.55, 20.99, 13.24, 13.17. **IR** (ATR): ν_{max} 2956 (m), 2922 (w), 2863 (w), 1753 (s, C=O) , 1511 (m), 1156 (m), 1097 (m), 900 (m), 811 (s), 727 (m) cm^{-1}. **HRMS** (HESI): m/z $[M+H]^+$ calcd for $C_{27}H_{29}O_2$: 385.2162, found: 385.2169; $[M+Na]^+$ calcd for $C_{27}H_{28}O_2Na$: 407.1982, found: 407.1987

Methyl 3-(5-isopropyl-3,8-dimethylazulen-1-yl)-3-(*p*-tolyl)propanoate (7c)

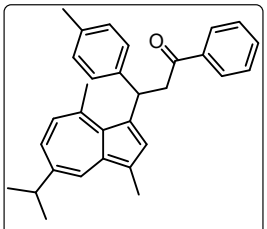


Chemical Formula: $C_{26}H_{30}O_2$
Exact Mass: 374,2246

Following the *General procedure 3* using 1-(*tert*-butyldimethylsilyloxy)-1-methoxyethene (114 µL, 0.26 mmol, 2.0 eq). The crude product was purified by flash chromatography (silica gel, Hex:EtOAc 20:1 to 10:1). Isolated: 73 mg (75%).

Blue oil, $\mathbf{R_f}$ (silica, Hex:EtOAc 10/1): 0.46; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.07 (d, *J* = 2.2 Hz, 1H), 7.61 (s, 1H), 7.23 (dd, *J* = 10.8, 2.2 Hz, 1H), 7.05 – 6.99 (m, 4H), 6.80 (d, *J* = 10.7 Hz, 1H), 5.59 (t, *J* = 7.8 Hz, 1H), 3.56 (s, 3H), 3.19 – 3.07 (m, 2H), 3.04 – 2.98 (m, 1H), 2.97 (s, 3H), 2.62 (s, 3H), 2.26 (s, 3H), 1.33 (d, *J* = 1.3 Hz, 3H), 1.31 (d, *J* = 1.3 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 172.72, 145.35, 142.88, 139.20, 137.65, 137.16, 135.39, 134.75, 133.57, 132.36, 129.14 (2 × C_{Ar}), 128.48, 127.82 (2 × C_{Ar}), 127.03, 124.45, 51.61, 43.58, 41.10, 37.59, 27.65, 24.59 (2 × CH_3), 20.95, 13.19. **IR** (ATR): ν_{max} 2959 (m), 2928 (m), 2871 (w), 1736 (s), 1688 (m), 1513 (m), 1437 (m), 1253 (m), 1157 (s), 1021 (m), 910 (m), 817 (m), 730 (s), 650 (m), 528 (m) cm^{-1}. **HRMS** (HESI): m/z $[M+H]^+$ calcd for $C_{26}H_{31}O_2$: 375.2319, found: 375.2326; $[M+Na]^+$ calcd for $C_{26}H_{30}O_2Na$: 397.2138, found: 397.2144

3-(5-Isopropyl-3,8-dimethylazulen-1-yl)-1-phenyl-3-(*p*-tolyl)propan-1-one (7d)

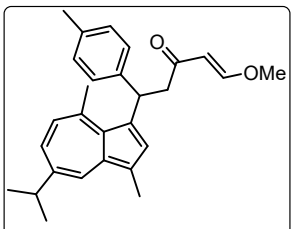


Chemical Formula: $C_{31}H_{32}O$
Exact Mass: 420,2453

Following the *General procedure 3* using 1-phenyl-1-trimethylsiloxyethylene (107 µL, 0.26 mmol, 2.0 eq). The crude product was purified by flash chromatography (silica gel, Hex:EtOAc 40:1 to 10:1). Isolated: 70 mg (64%).

Blue solid, $\mathbf{R_f}$ (silica, Hex:EtOAc 10/1): 0.49; **Mp:** 126–129 °C; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.06 (d, *J* = 2.2 Hz, 1H), 7.95 – 7.91 (m, 2H), 7.61 (s, 1H), 7.55 – 7.51 (m, 1H), 7.45 – 7.39 (m, 2H), 7.23 (dd, *J* = 10.7, 2.2 Hz, 1H), 7.06 (d, *J* = 8.2 Hz, 2H), 7.03 (d, *J* = 8.1 Hz, 2H), 6.81 (d, *J* = 10.8 Hz, 1H), 5.88 (t, *J* = 7.1 Hz, 1H), 3.87 (dd, *J* = 17.0, 7.0 Hz, 1H), 3.78 (dd, *J* = 17.0, 7.1 Hz, 1H), 3.04 – 2.96 (m, 4H, overlaying), 2.60 (s, 3H), 2.27 (s, 3H), 1.33 (d, *J* = 1.8 Hz, 3H), 1.32 (d, *J* = 1.8 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 198.58, 145.57, 143.46, 139.13, 137.66, 137.29, 137.25, 135.22, 134.78, 133.61, 132.91, 132.26, 129.32, 129.14 (2 × C_{Ar}), 128.55 (2 × C_{Ar}), 128.10 (2 × C_{Ar}), 128.03 (2 × C_{Ar}), 126.99, 124.40, 47.88, 39.88, 37.60, 27.75, 24.60 (2 × CH_3), 20.96, 13.20. **IR** (ATR): ν_{max} 2957 (m), 2925 (w), 2866 (w), 1679 (s, C=O), 1657 (m), 1596 (m), 1510 (m), 1448 (m), 1355 (m), 1272 (m), 1023 (m), 1003 (m), 973 (m), 913 (m), 870 (m), 817 (s), 761 (s), 751 (m), 687 (s), 655 (m), 557 (s) cm^{-1}. **HRMS** (HESI): m/z $[M+H]^+$ calcd for $C_{31}H_{33}O$: 421.2526, found: 421.2527; $[M+Na]^+$ calcd for $C_{31}H_{32}ONa$: 443.2345, found: 443.2351

(*E*)-5-(5-Isopropyl-3,8-dimethylazulen-1-yl)-1-methoxy-5-(*p*-tolyl)pent-1-en-3-one (7e)

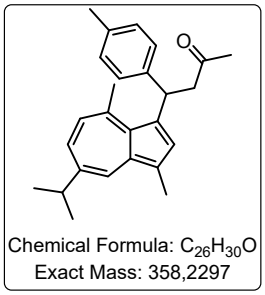


Chemical Formula: $C_{28}H_{32}O_2$
Exact Mass: 400,2402

Following the *General procedure 3* using *trans*-1-methoxy-3-trimethylsiloxy-1,3-butadiene (101 µL, 0.26 mmol, 2.0 eq). The crude product was purified by flash chromatography (silica gel, Hex:EtOAc 20:1 to 2:1). Isolated: 13 mg (12%).

Blue oil, $\mathbf{R_f}$ (silica, Hex:EtOAc 10/1): 0.19; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.05 (d, *J* = 2.3 Hz, 1H), 7.58 (s, 1H), 7.50 (d, *J* = 12.6 Hz, 1H), 7.22 (dd, *J* = 10.7, 2.2 Hz, 1H), 7.02 (s, 4H), 6.79 (d, *J* = 10.8 Hz, 1H), 5.69 (t, *J* = 7.3 Hz, 1H), 5.52 (d, *J* = 12.6 Hz, 1H), 3.61 (s, 3H), 3.30 (dd, *J* = 15.9, 7.2 Hz, 1H), 3.24 (dd, *J* = 15.9, 7.3 Hz, 1H), 3.02 – 2.96 (m, 1H), 2.98 (s, 3H), 2.61 (s, 3H), 2.26 (s, 3H), 1.32 (d, *J* = 1.7 Hz, 3H), 1.31 (d, *J* = 1.7 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 197.91, 162.63, 145.52, 143.48, 139.08, 137.64, 137.38, 135.11, 134.69, 133.52, 132.23, 129.34, 129.04 (2 × C_{Ar}), 127.98 (2 × C_{Ar}), 126.92, 124.34, 105.85, 57.42, 50.50, 40.13, 37.58, 27.75, 24.58 (2 × CH_3), 20.94, 13.20. **IR** (ATR): ν_{max} 2961 (m), 2927 (m), 2869 (w), 1680 (m), 1620 (m), 1591 (s) 1511 (m), 1439 (m), 1309 (m), 1185 (m), 1083 (m), 920 (m), 811 (m), 729 (m) cm^{-1}. **HRMS** (HESI): m/z $[M+H]^+$ calcd for $C_{28}H_{33}O_2$: 401.2475, found: 401.2476; $[M+Na]^+$ calcd for $C_{28}H_{32}O_2Na$: 423.2295, found: 423.2296

4-(5-Isopropyl-3,8-dimethylazulen-1-yl)-4-(p-tolyl)butan-2-one (7f)



Chemical Formula: $C_{26}H_{30}O$
Exact Mass: 358,2297

Following the *General procedure 3* using (isopropenyloxy)trimethylsilane (87 µL, 0.26 mmol, 2.0 eq). The crude product was purified by flash chromatography (silica gel, Hex:EtOAc 20:1 to 10:1). Isolated: 42 mg (45%).

Blue oil, $\mathbf{R_f}$ (silica, Hex:EtOAc 10/1): 0.38; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.06 (d, *J* = 2.2 Hz, 1H), 7.59 (s, 1H), 7.22 (dd, *J* = 10.7, 2.2 Hz, 1H), 7.04 – 6.97 (m, 4H), 6.79 (d, *J* = 10.8 Hz, 1H), 5.62 (t, *J* = 7.4 Hz, 1H), 3.28 (dd, *J* = 16.3, 7.7 Hz, 1H), 3.20 (dd, *J* = 16.3, 7.2 Hz, 1H), 3.03 – 2.97 (m, 1H), 2.97 (s, 3H), 2.62 (s, 3H), 2.26 (s, 3H), 2.04 (s, 3H), 1.32 (d, *J* = 1.5 Hz, 3H), 1.31 (d, *J* = 1.5 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 207.64, 145.45, 143.26, 139.25, 137.66, 137.23, 135.28, 134.81, 133.63, 132.37, 129.15 (2 × C_{Ar}), 128.75, 127.90 (2 × C_{Ar}), 127.04, 124.46, 52.93, 40.20, 37.60, 30.66, 27.72, 24.58 (2 × CH_3), 20.94, 13.19. **IR** (ATR): ν_{max} 2963 (m), 2926 (m), 2872 (w), 1710 (m), 1688 (m), 1513 (m), 1358 (m), 1159 (m), 1020 (m), 910 (m), 818 (m), 729 (s), 647 (m), 544 (m) cm^{-1}. **HRMS** (HESI): m/z $[M+H]^+$ calcd for $C_{26}H_{31}O$: 359.2369, found: 359.2373; $[M+Na]^+$ calcd for $C_{26}H_{30}ONa$: 381.2189, found: 381.2195

7. NMR spectra

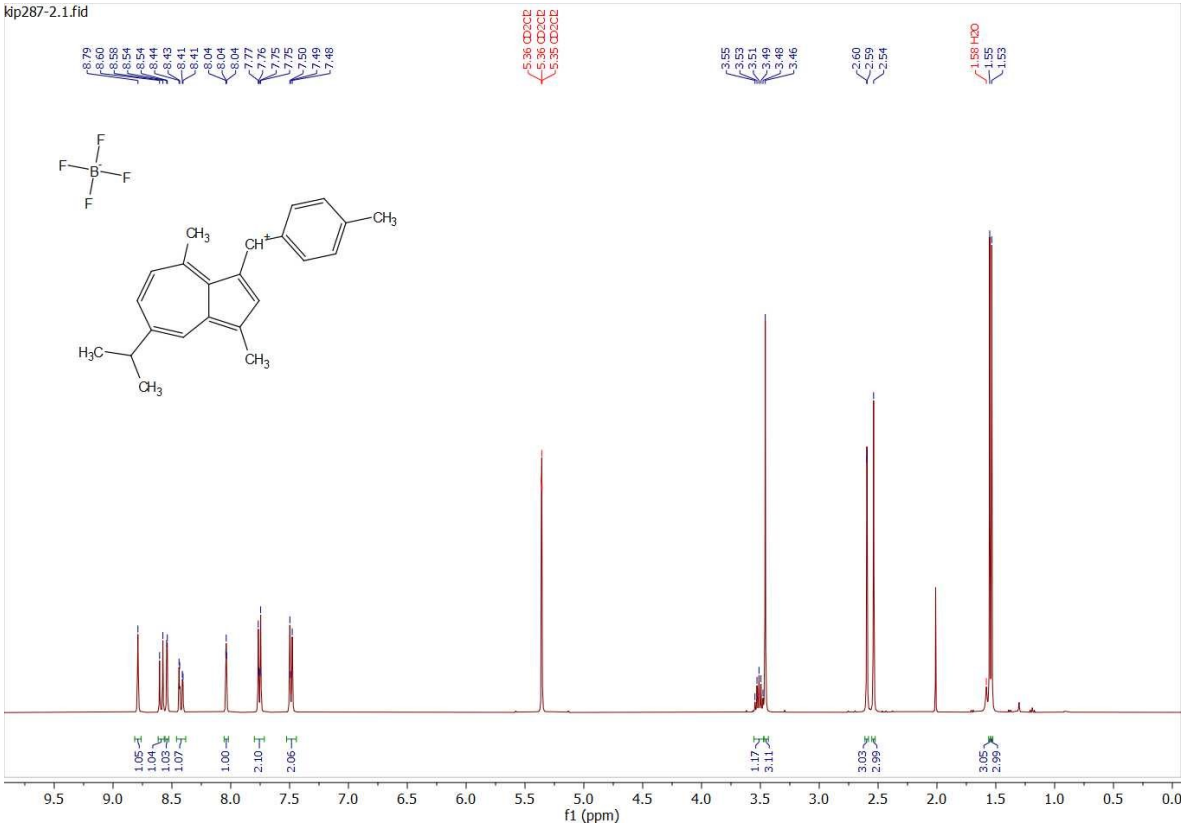


Figure S5. ^{1}H NMR spectrum of compound **2a** (400 MHz, CD_2Cl_2).

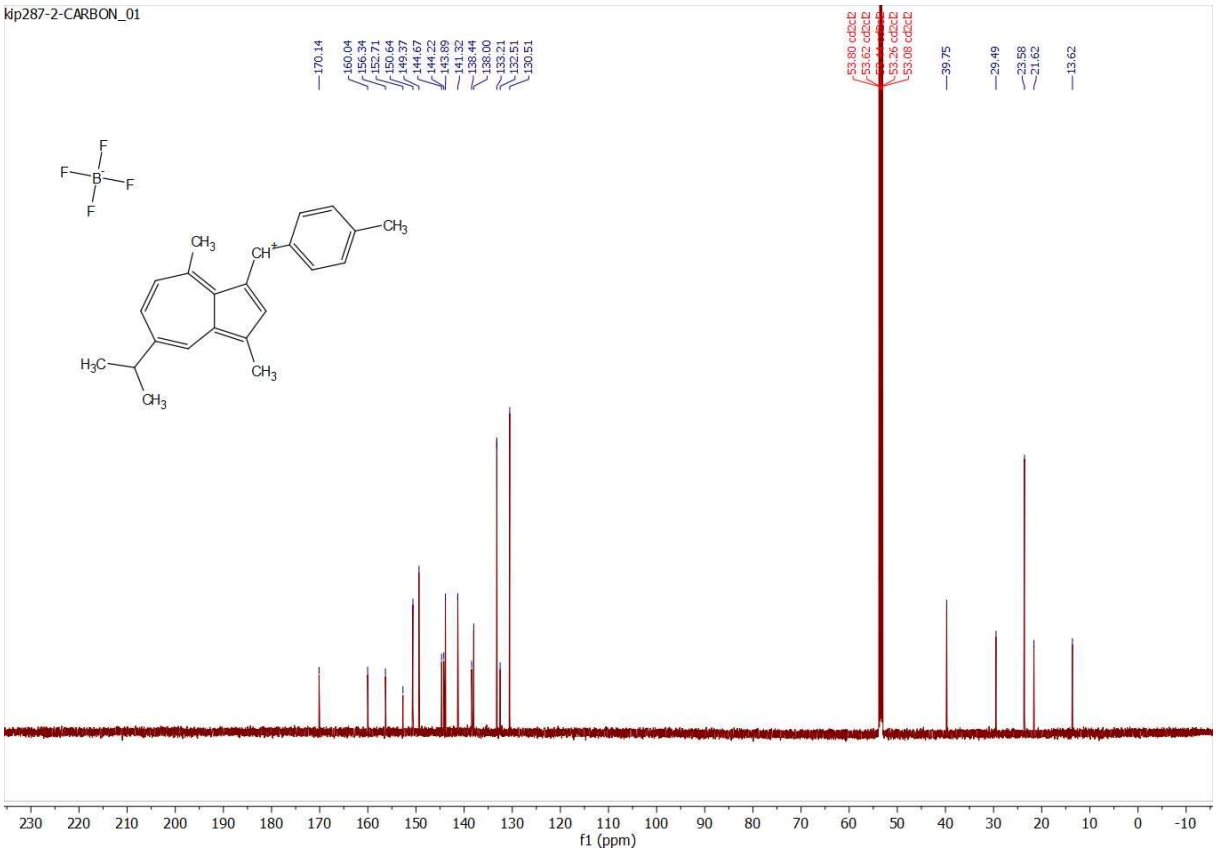


Figure S6. ^{13}C NMR spectrum of compound **2a** (150 MHz, CD_2Cl_2).

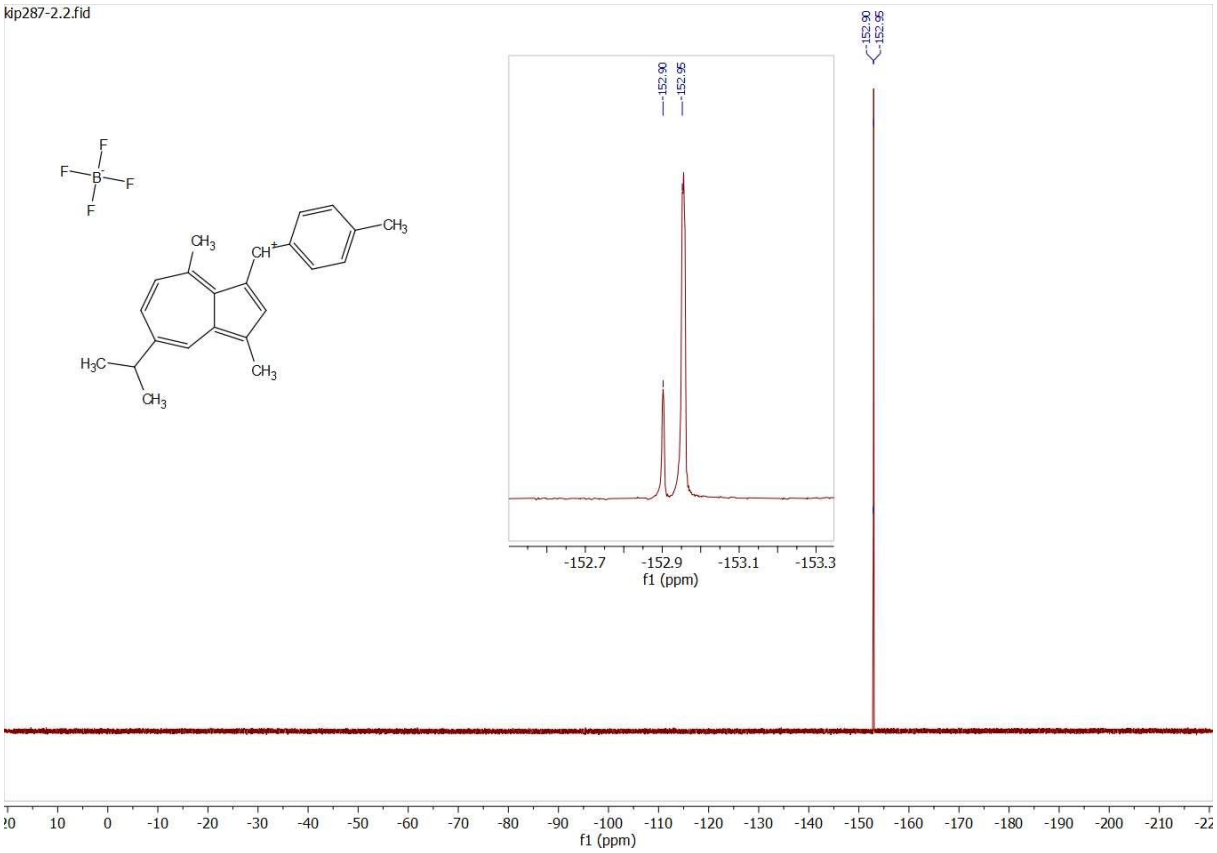


Figure S7. ^{19}F NMR spectrum of compound **2a** (376 MHz, CD_2Cl_2).

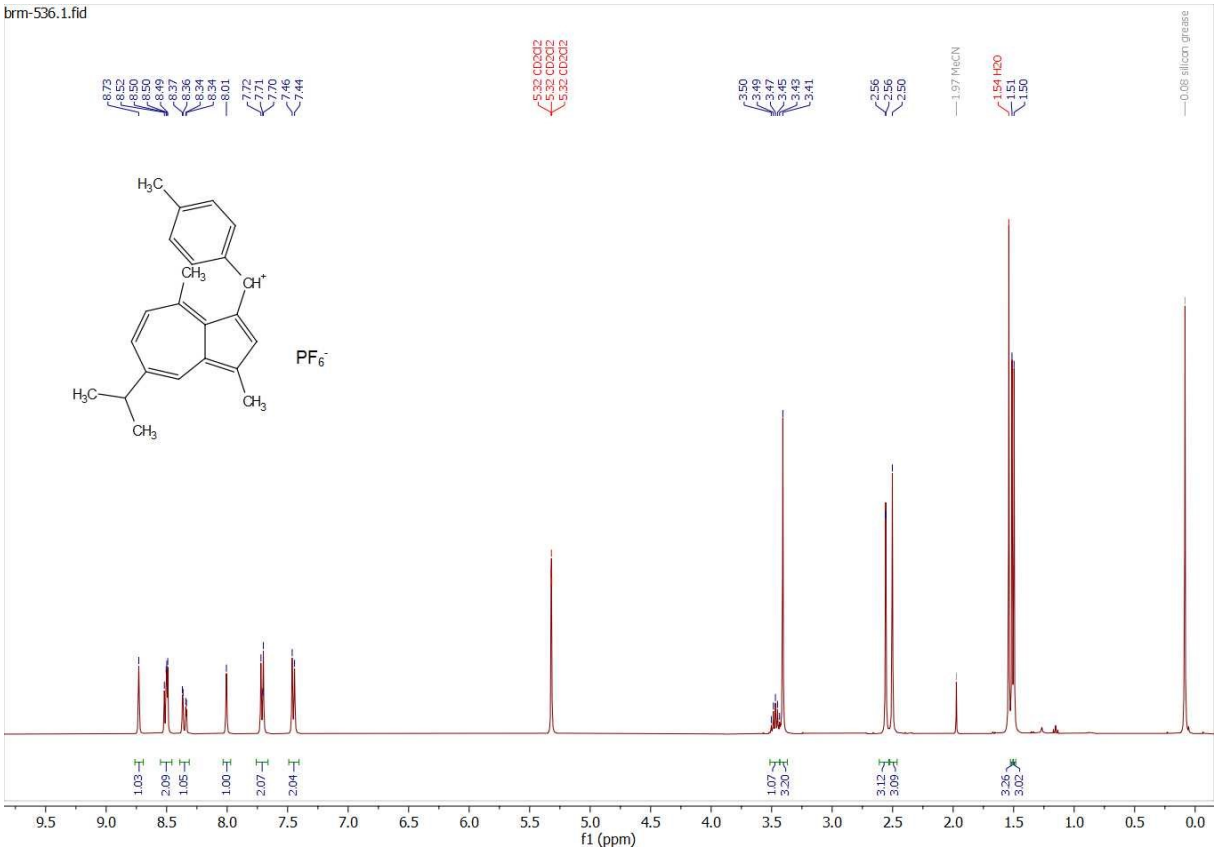


Figure S8. ^{1}H NMR spectrum of compound **2a'** (400 MHz, CD_2Cl_2).

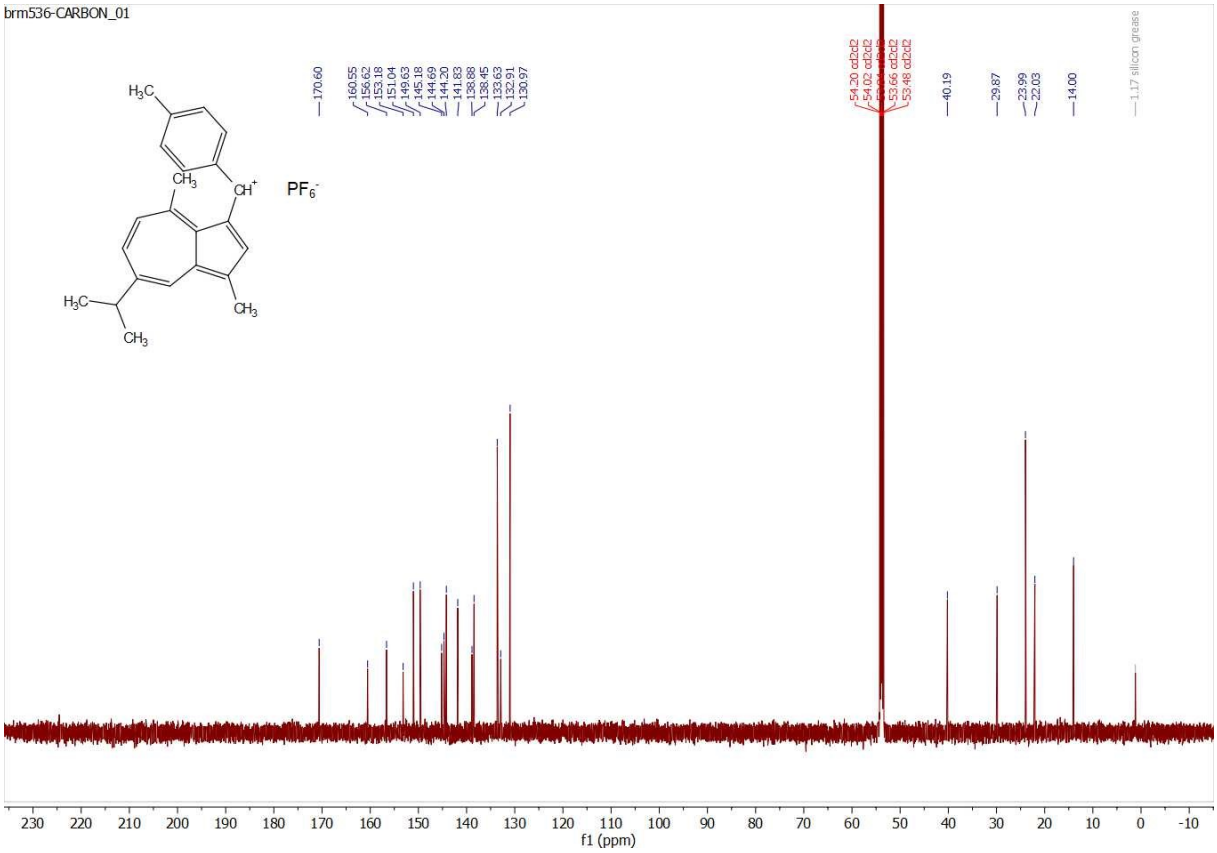


Figure S9. ^{13}C NMR spectrum of compound **2a'** (150 MHz, CD_2Cl_2).

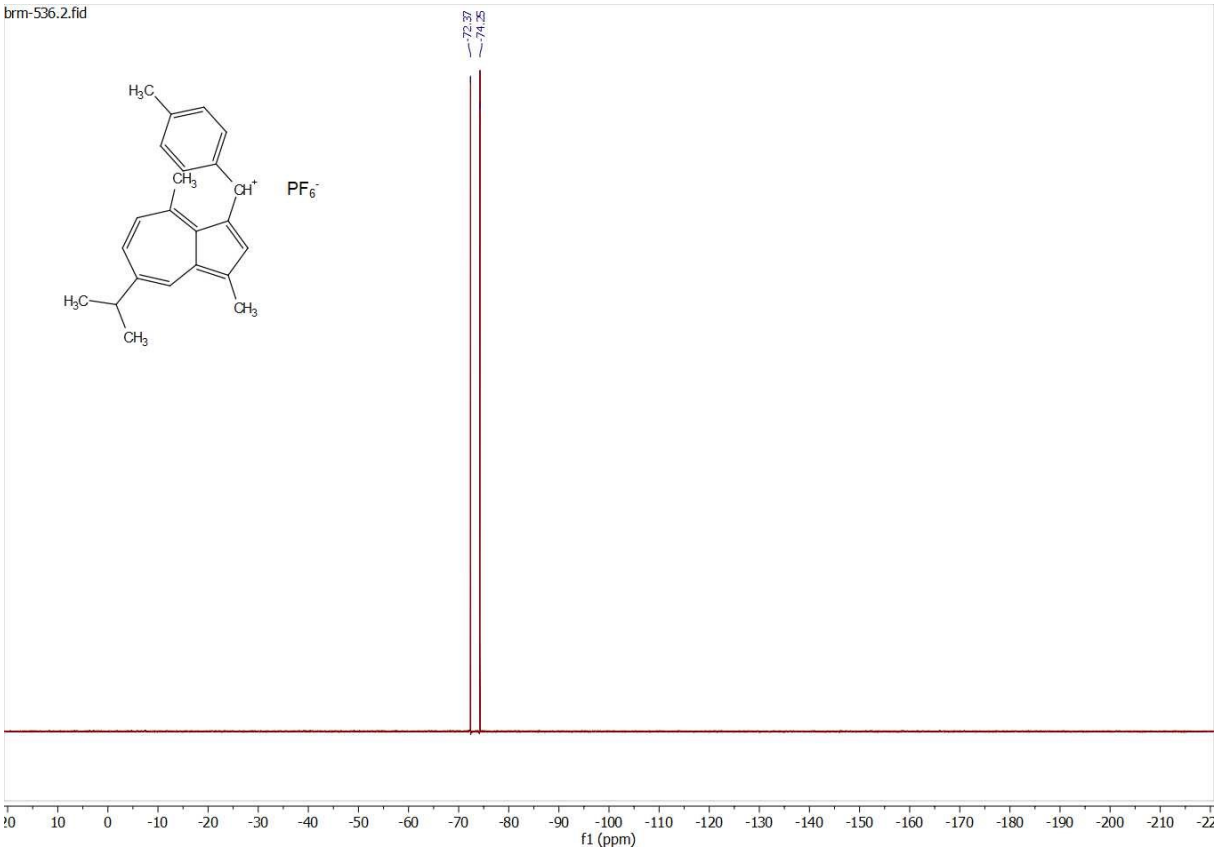


Figure S10. ^{19}F NMR spectrum of compound **2a'** (376 MHz, CD_2Cl_2).

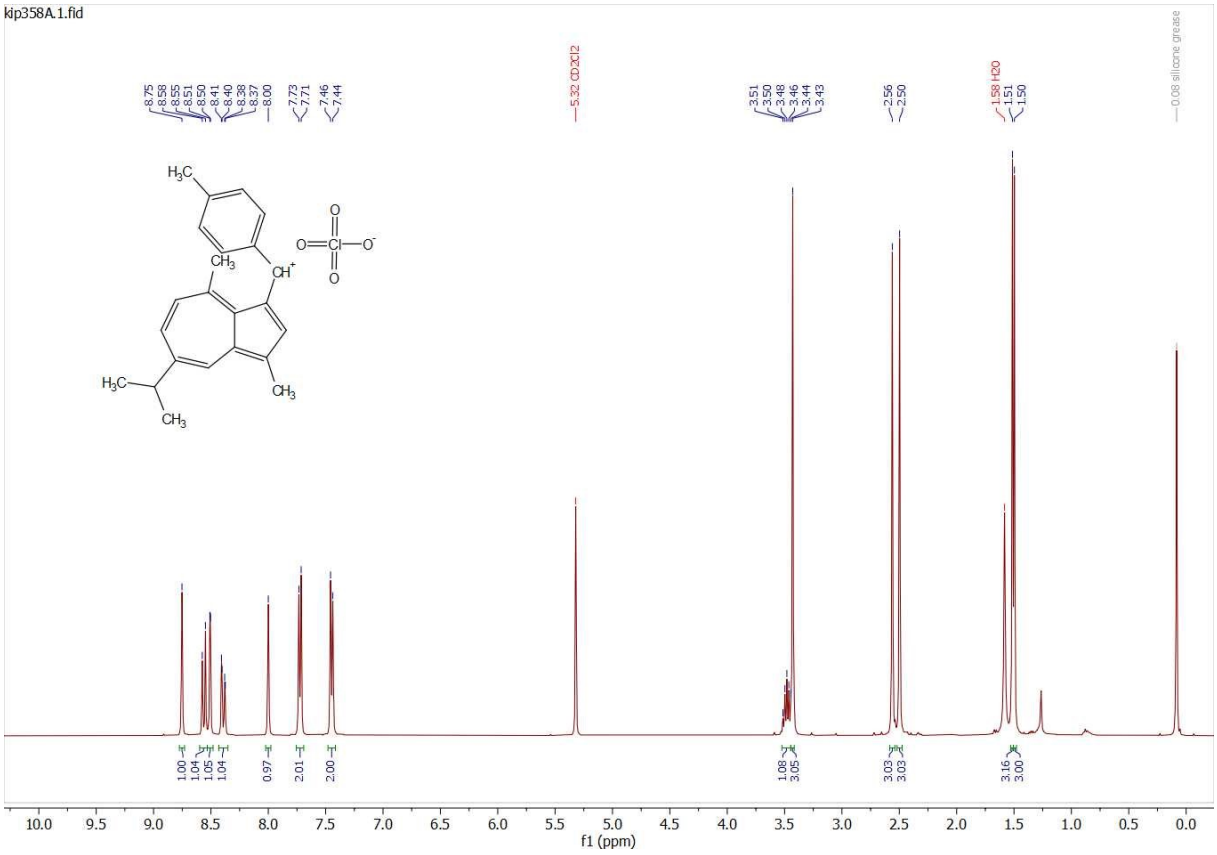


Figure S11. ^{1}H NMR spectrum of compound **2a"** (400 MHz, CD_2Cl_2).

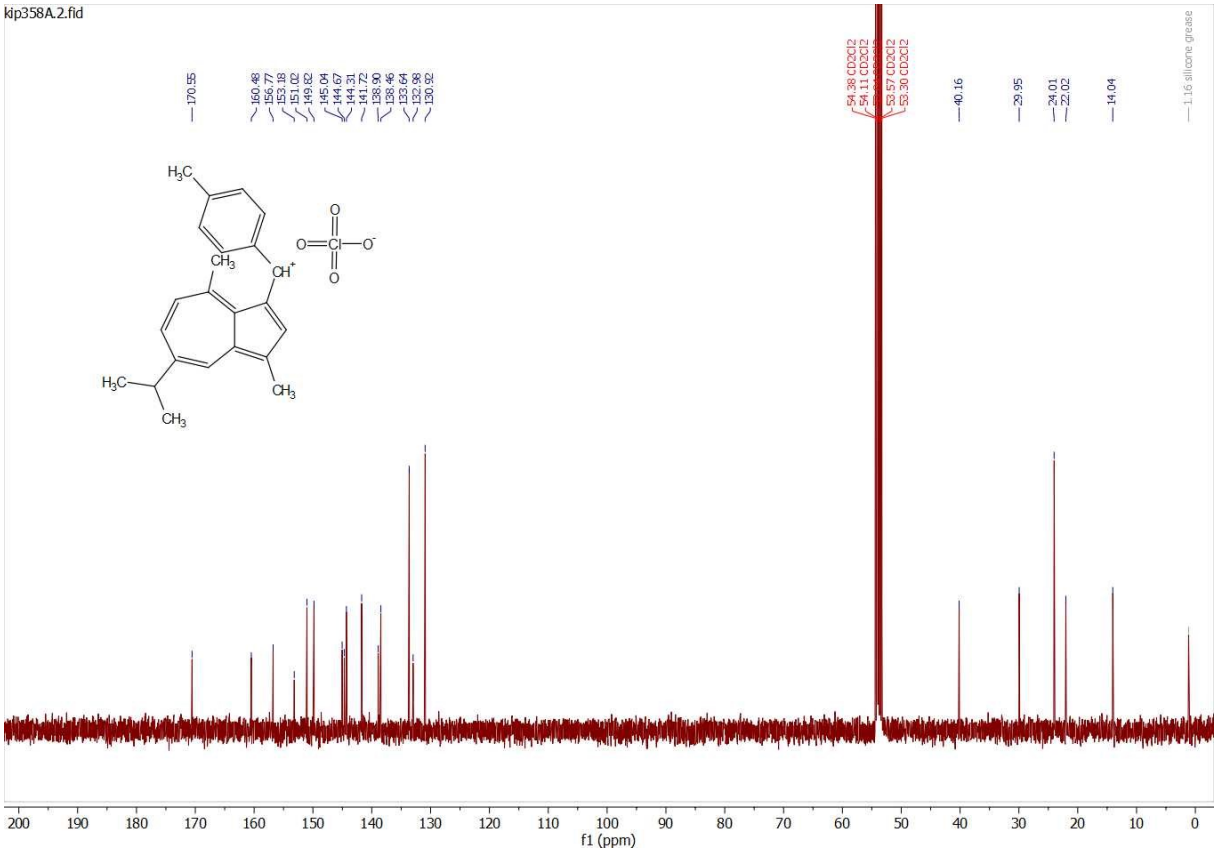


Figure S12. ^{13}C NMR spectrum of compound **2a"** (100 MHz, CD_2Cl_2).

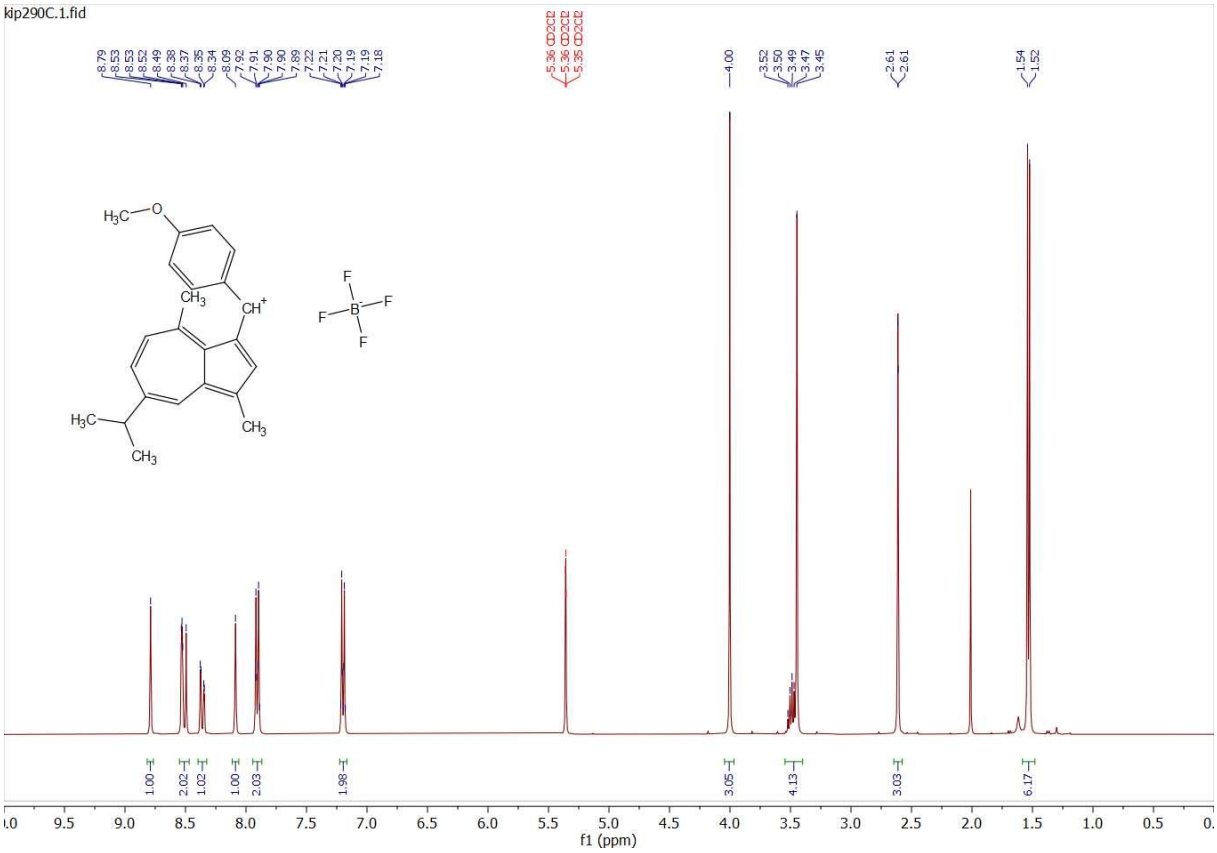


Figure S13. ^{1}H NMR spectrum of compound **2b** (400 MHz, CD_2Cl_2).

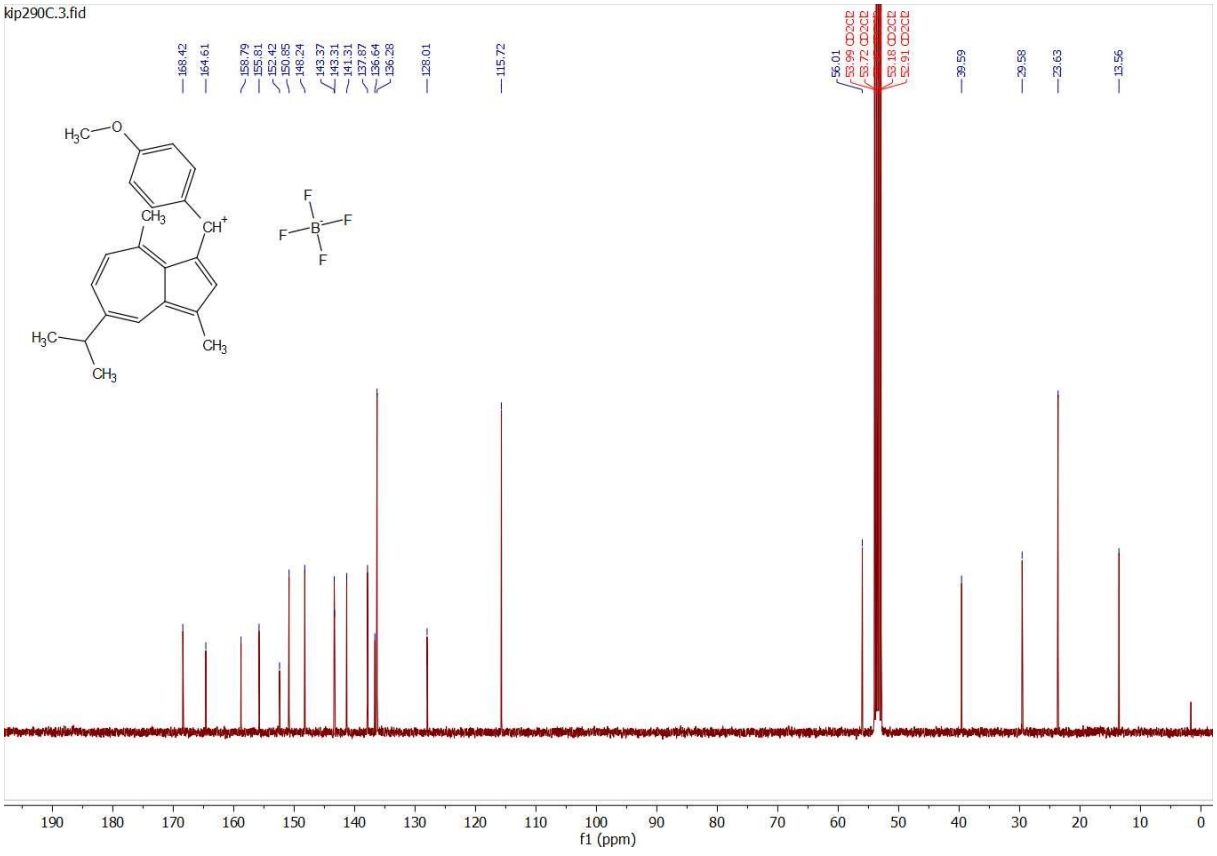


Figure S14. ^{13}C NMR spectrum of compound **2b** (100 MHz, CD_2Cl_2).

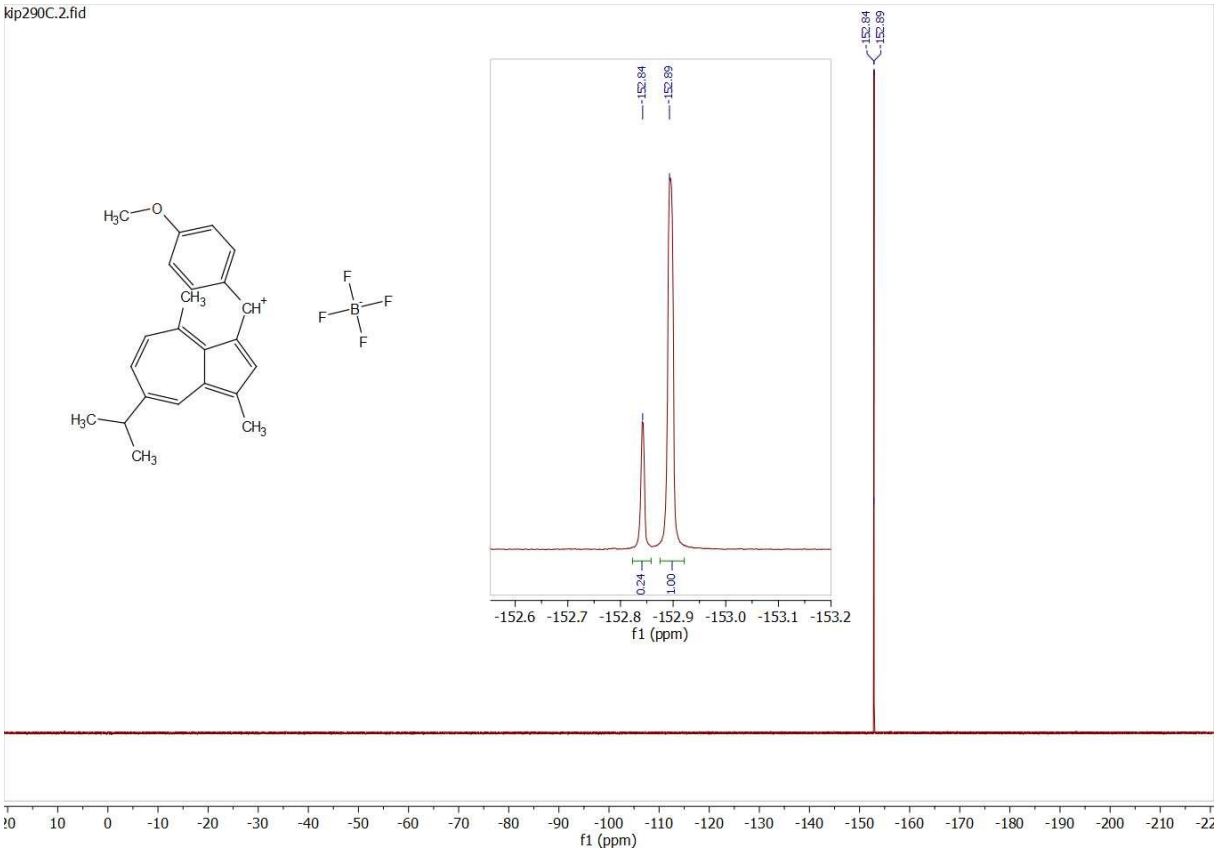


Figure S15. ^{19}F NMR spectrum of compound **2b** (376 MHz, CD_2Cl_2).

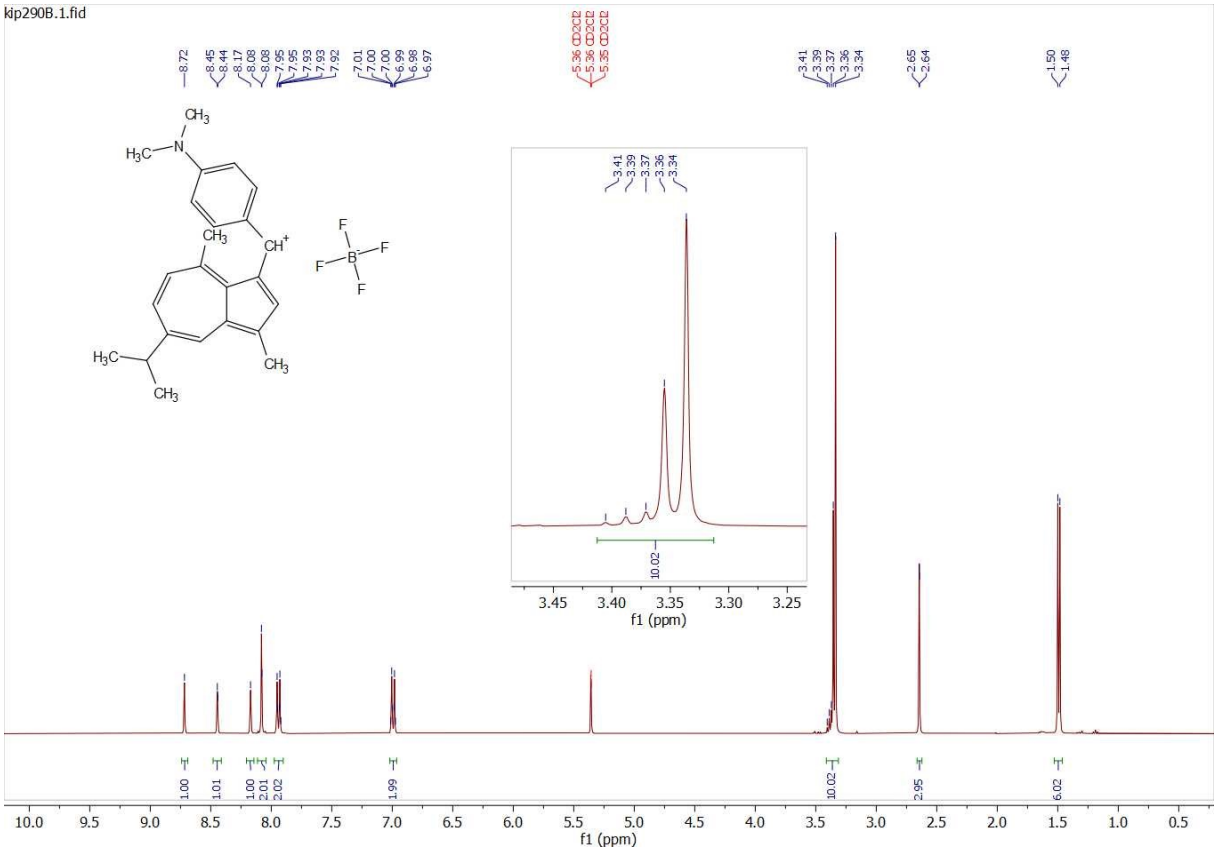


Figure S16. ^{1}H NMR spectrum of compound **2c** (400 MHz, CD_2Cl_2).

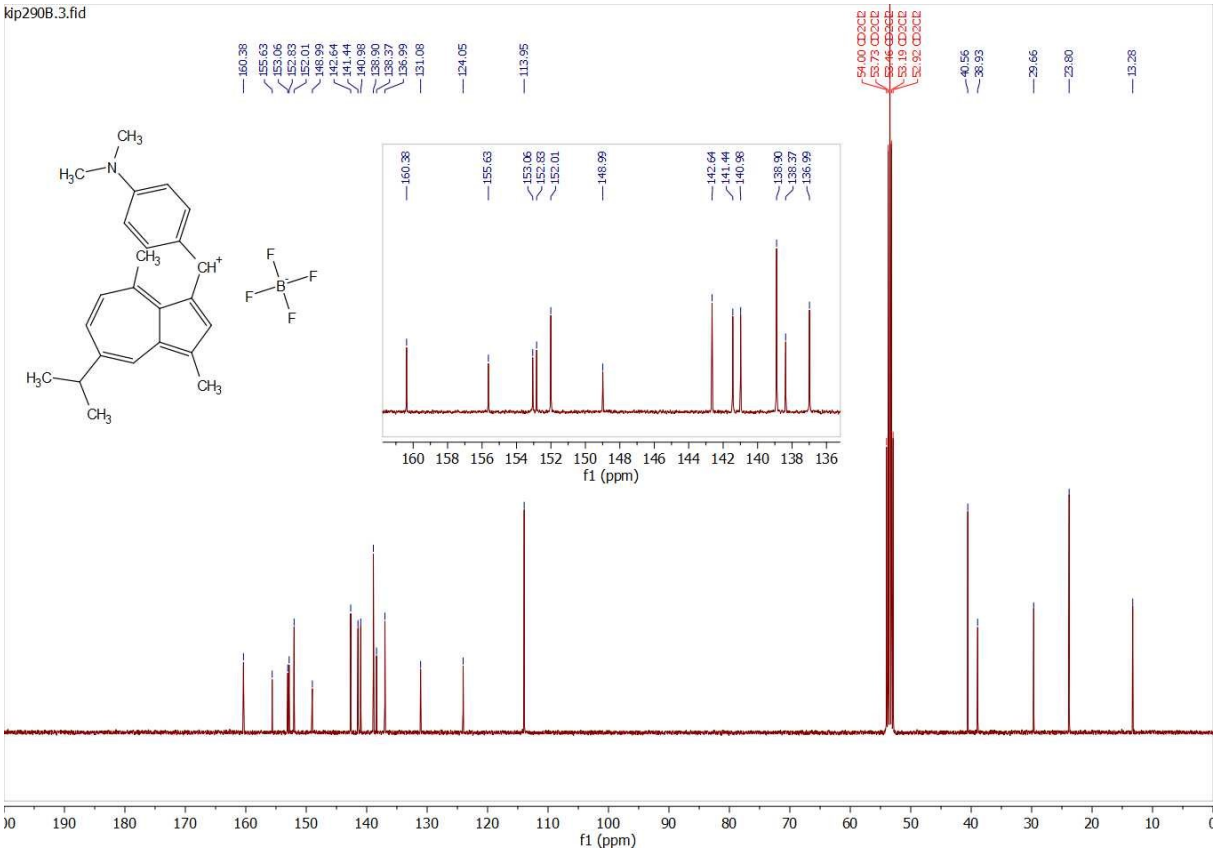


Figure S17. ^{13}C NMR spectrum of compound **2c** (100 MHz, CD_2Cl_2).

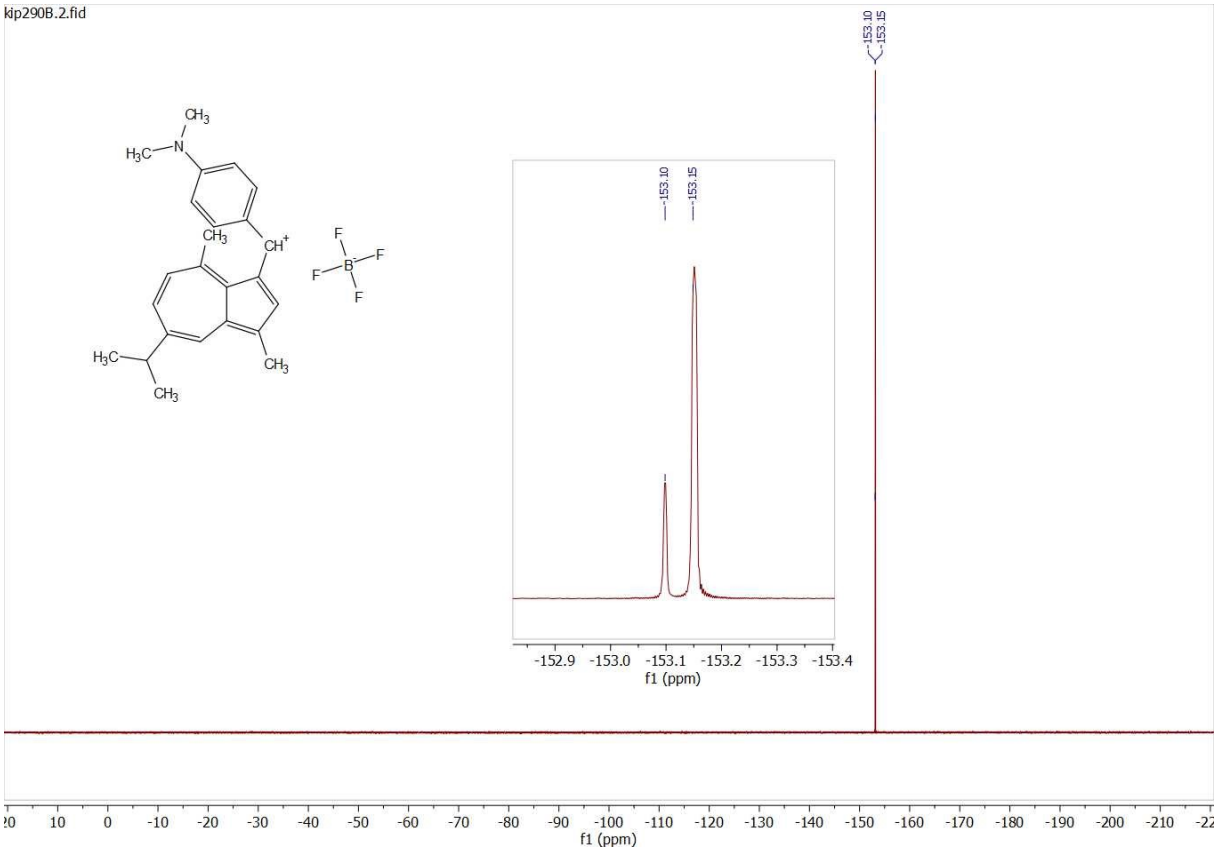


Figure S18. ^{19}F NMR spectrum of compound **2c** (376 MHz, CD_2Cl_2).

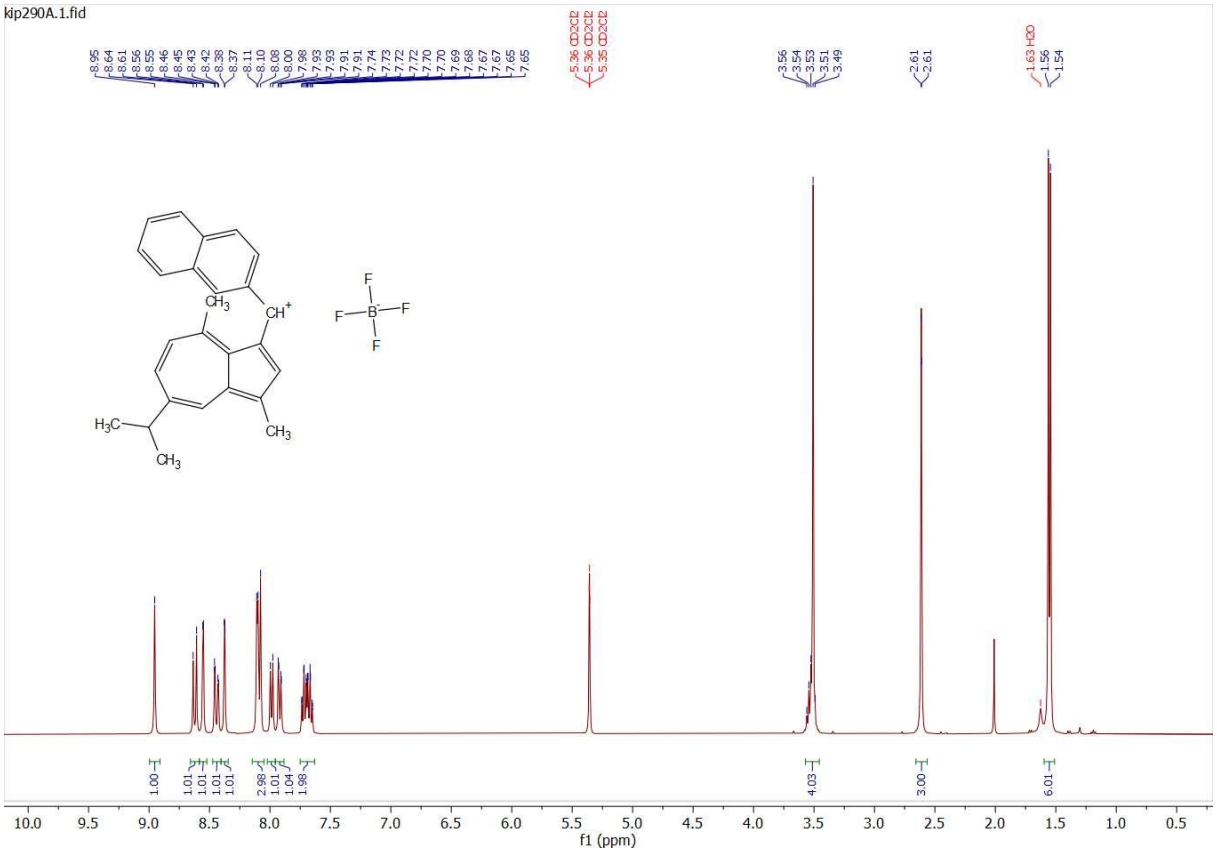


Figure S19. ^{1}H NMR spectrum of compound **2d** (400 MHz, CD_2Cl_2).

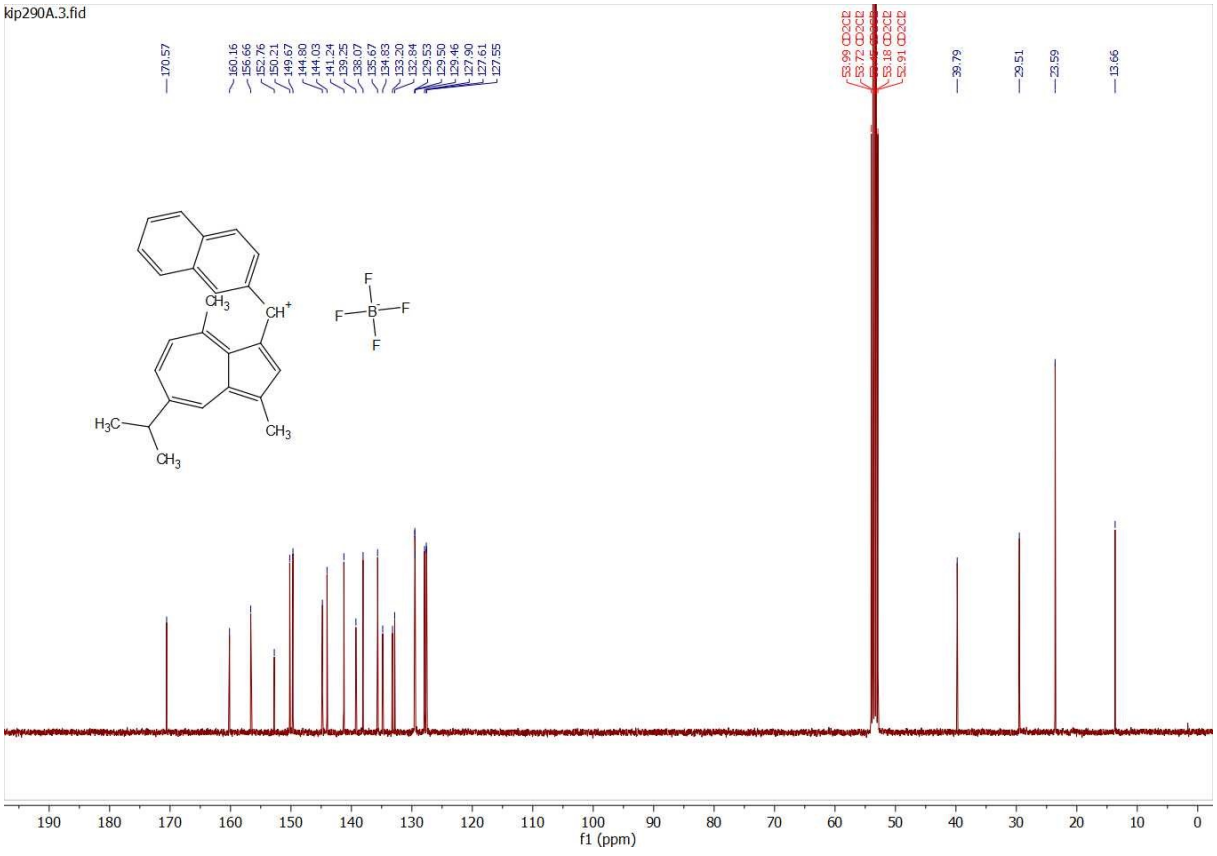


Figure S20. ^{13}C NMR spectrum of compound **2d** (100 MHz, CD_2Cl_2).

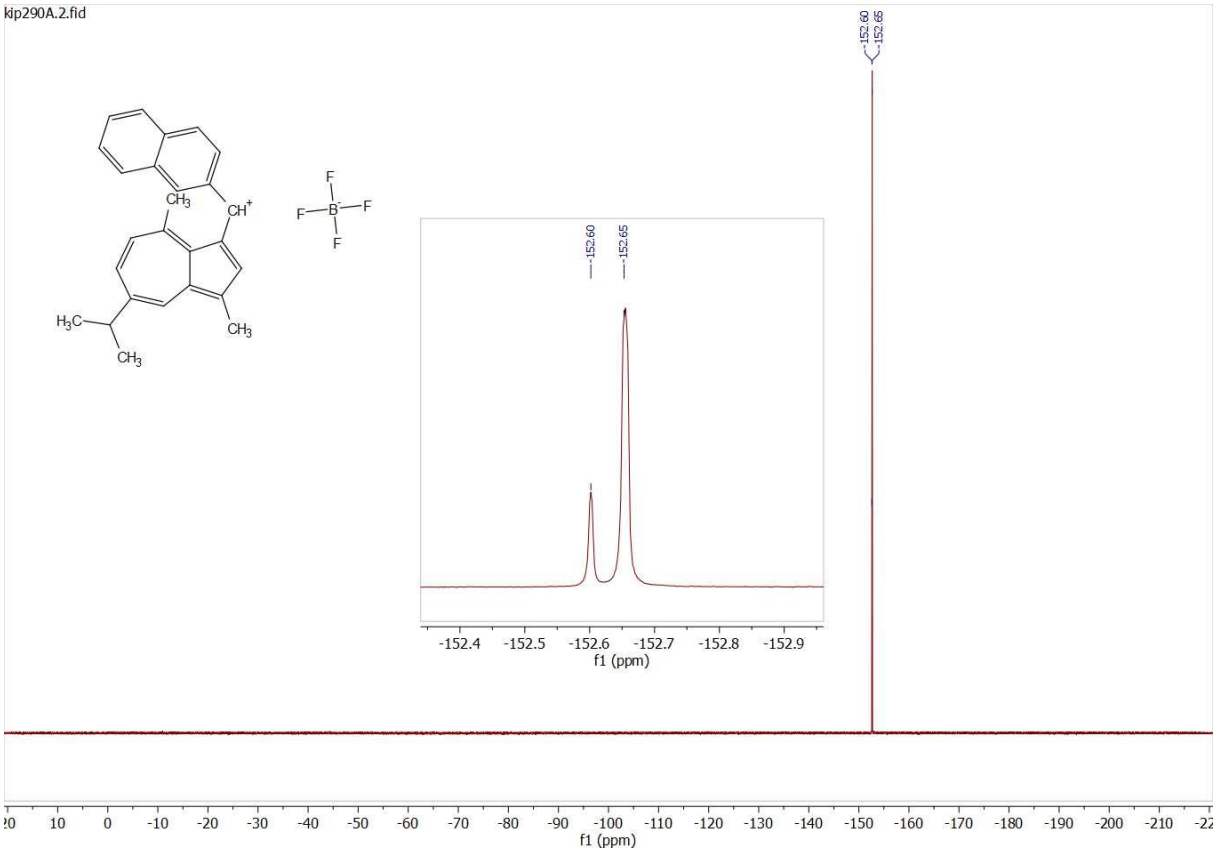


Figure S21. ^{19}F NMR spectrum of compound **2d** (376 MHz, CD_2Cl_2).

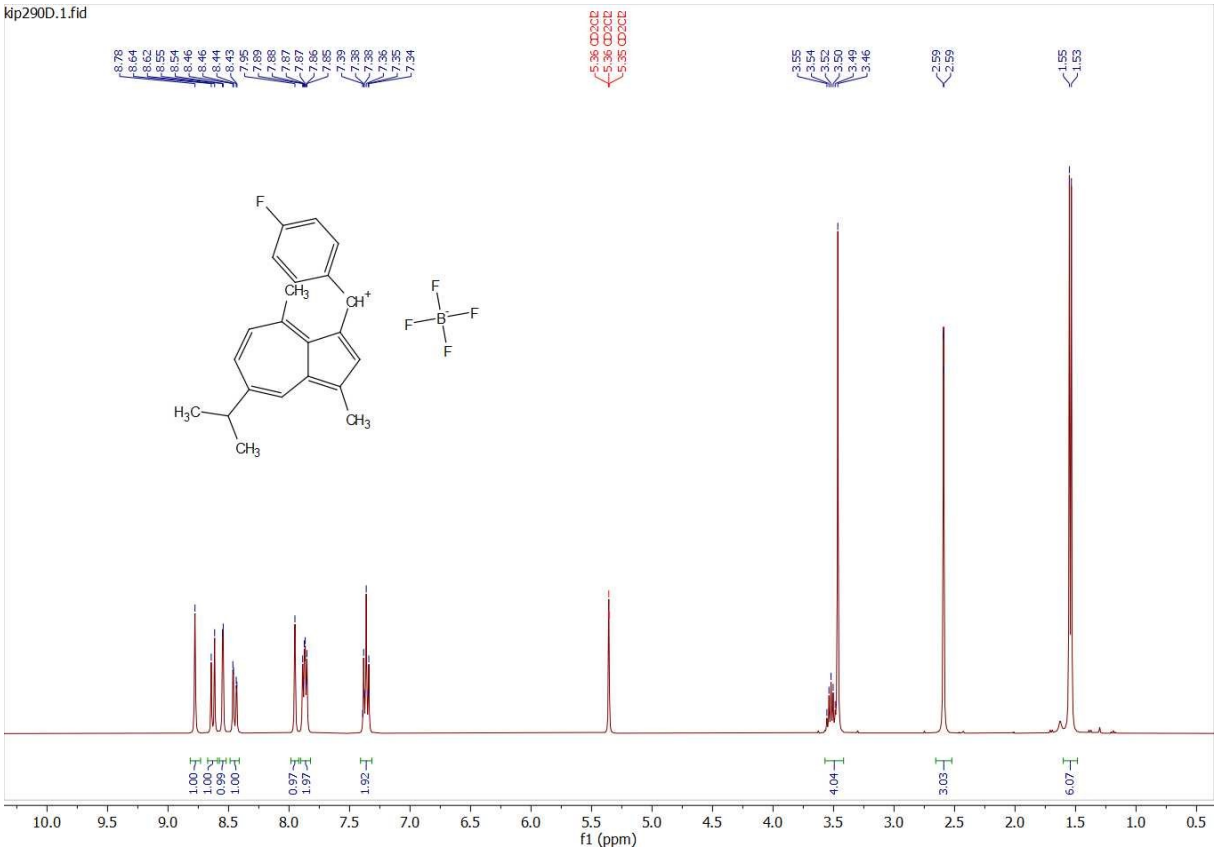


Figure S22. ^{1}H NMR spectrum of compound **2e** (400 MHz, CD_2Cl_2).

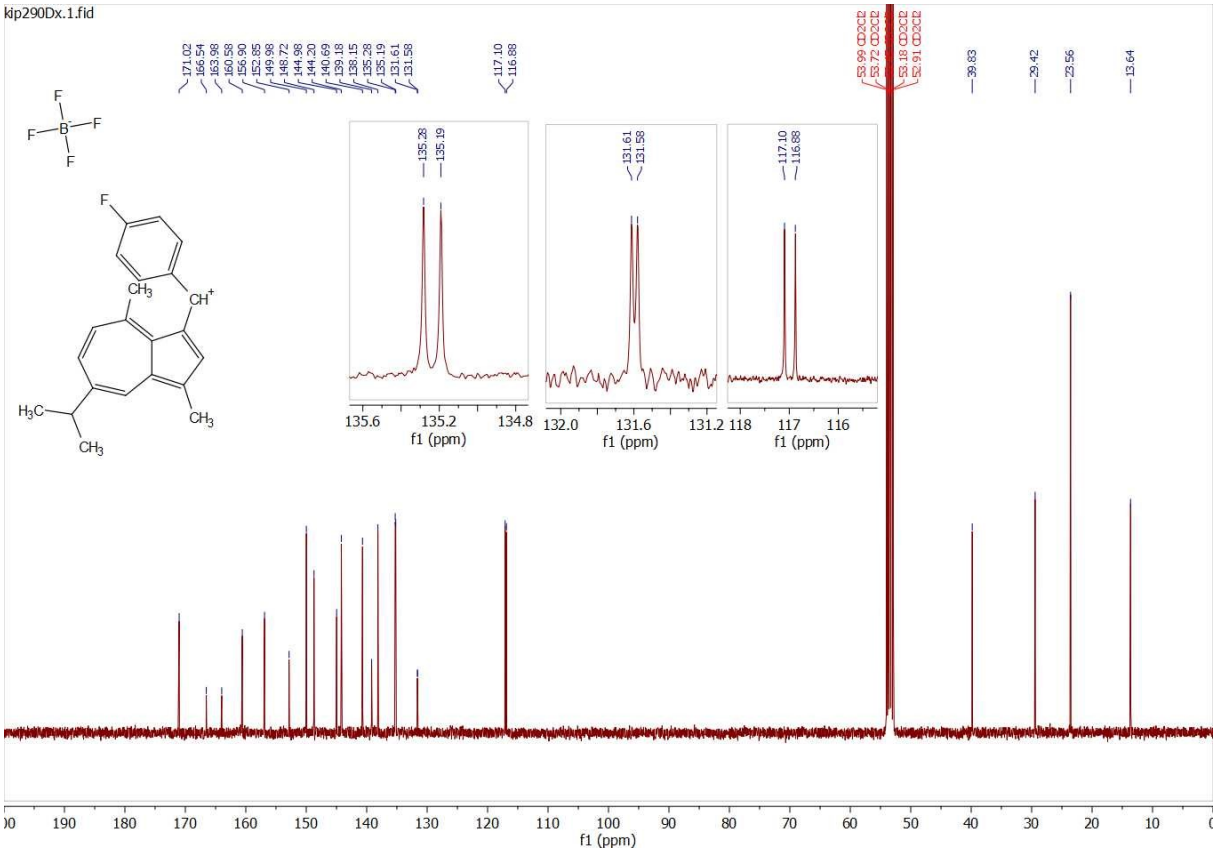


Figure S23. ^{13}C NMR spectrum of compound **2e** (100 MHz, CD_2Cl_2).

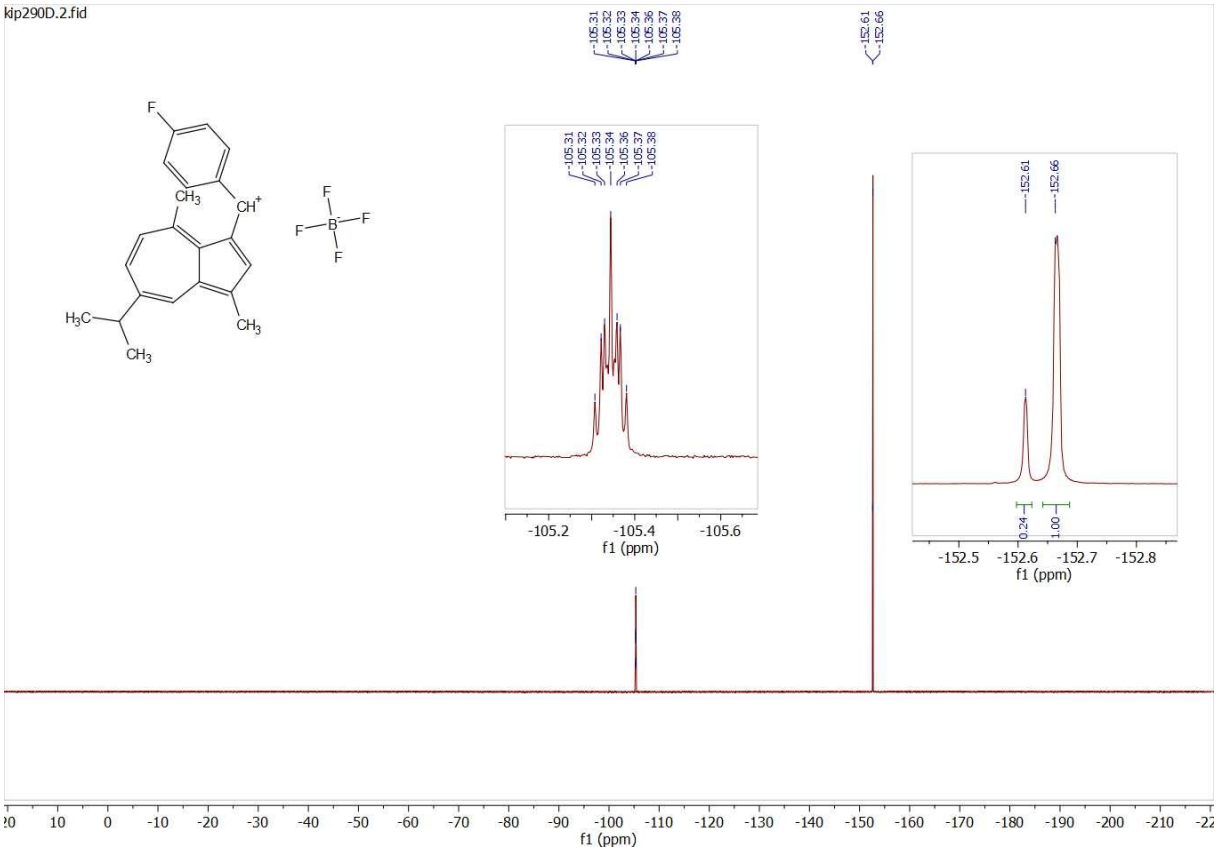


Figure S24. ^{19}F NMR spectrum of compound **2e** (376 MHz, CD_2Cl_2).

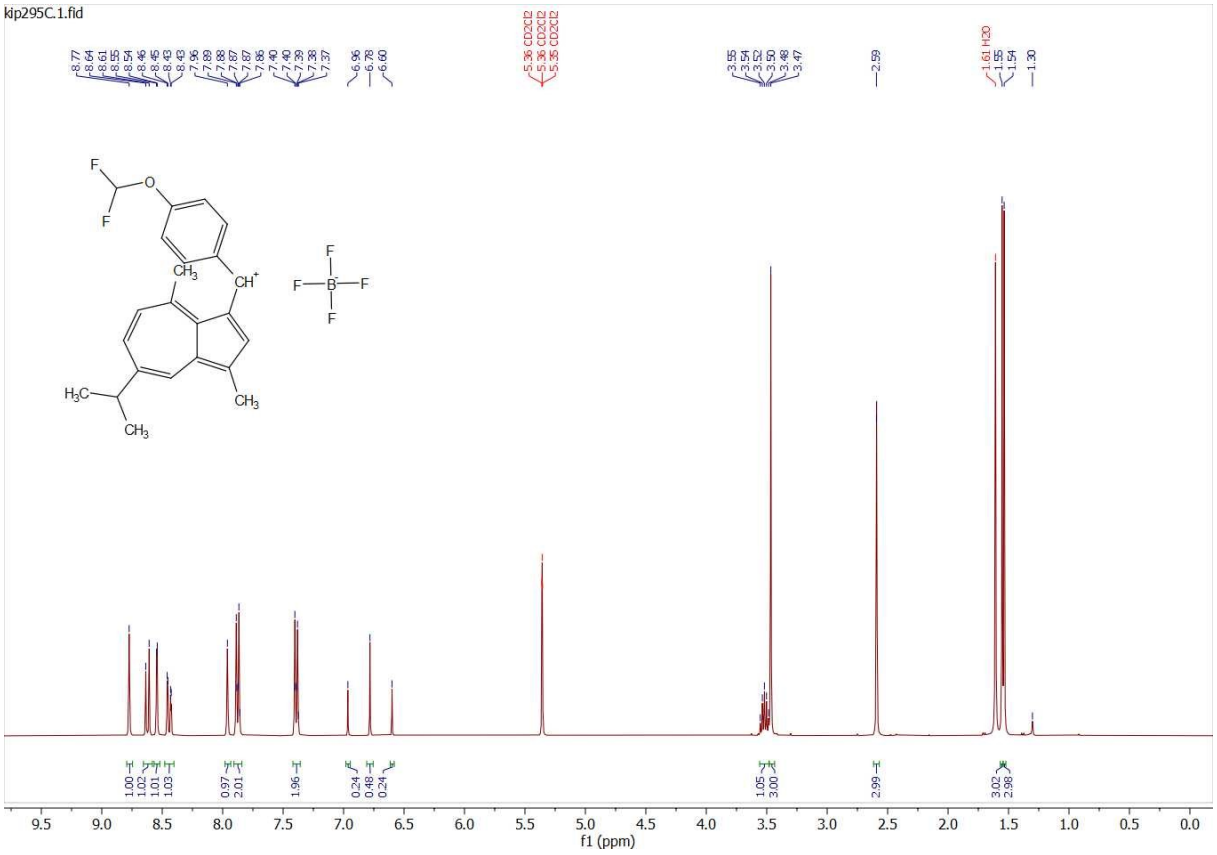


Figure S25. ^{1}H NMR spectrum of compound **2f** (400 MHz, CD_2Cl_2).

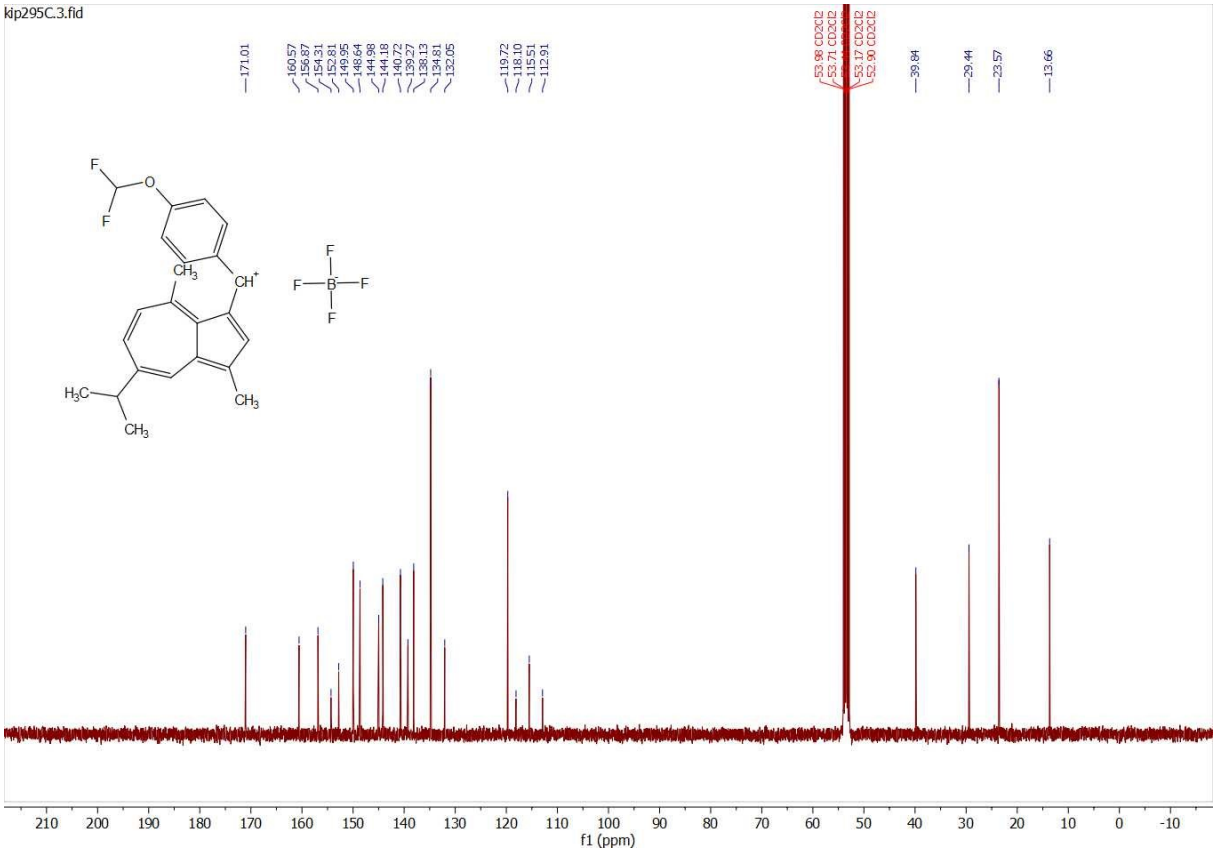


Figure S26. ^{13}C NMR spectrum of compound **2f** (100 MHz, CD_2Cl_2).

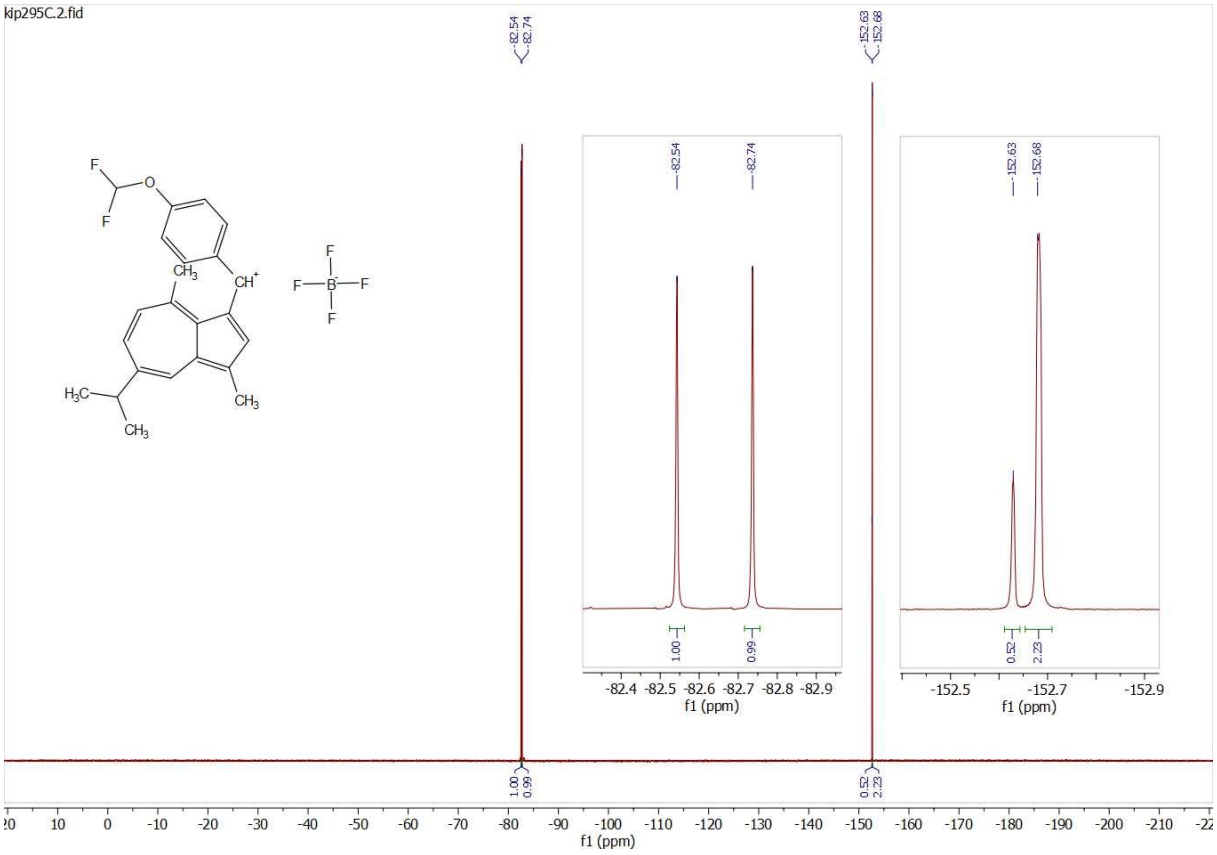


Figure S27. ^{19}F NMR spectrum of compound **2f** (376 MHz, CD_2Cl_2).

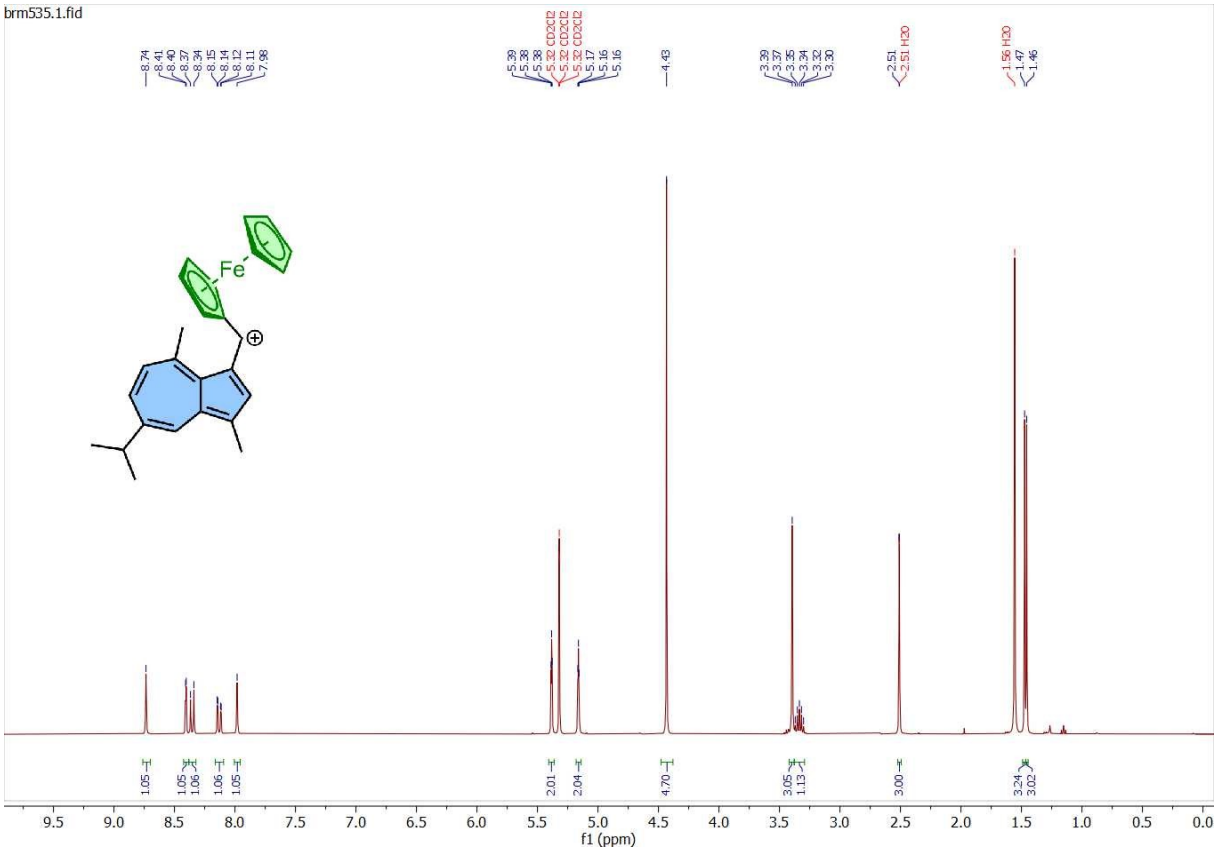


Figure S28. ^{1}H NMR spectrum of compound **2g** (400 MHz, CD_2Cl_2).

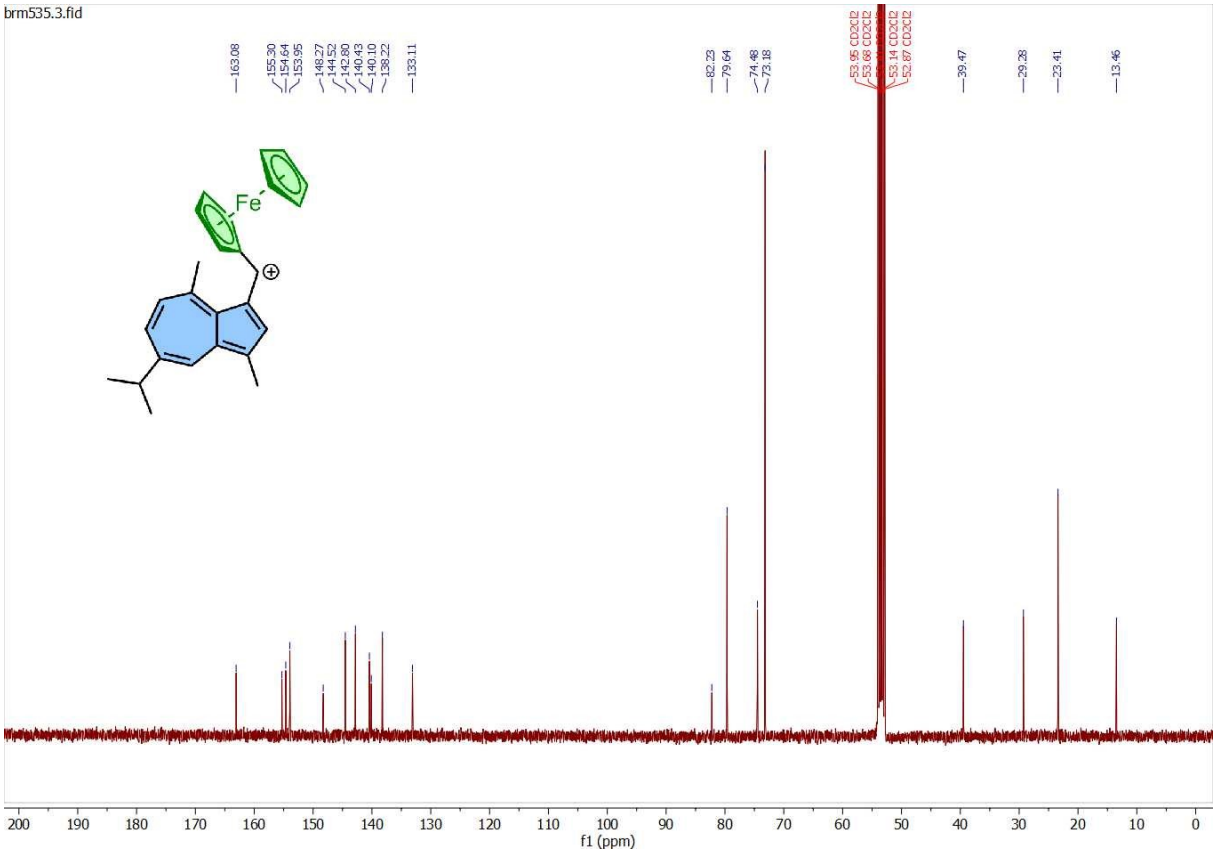


Figure S29. ^{13}C NMR spectrum of compound **2g** (100 MHz, CD_2Cl_2).

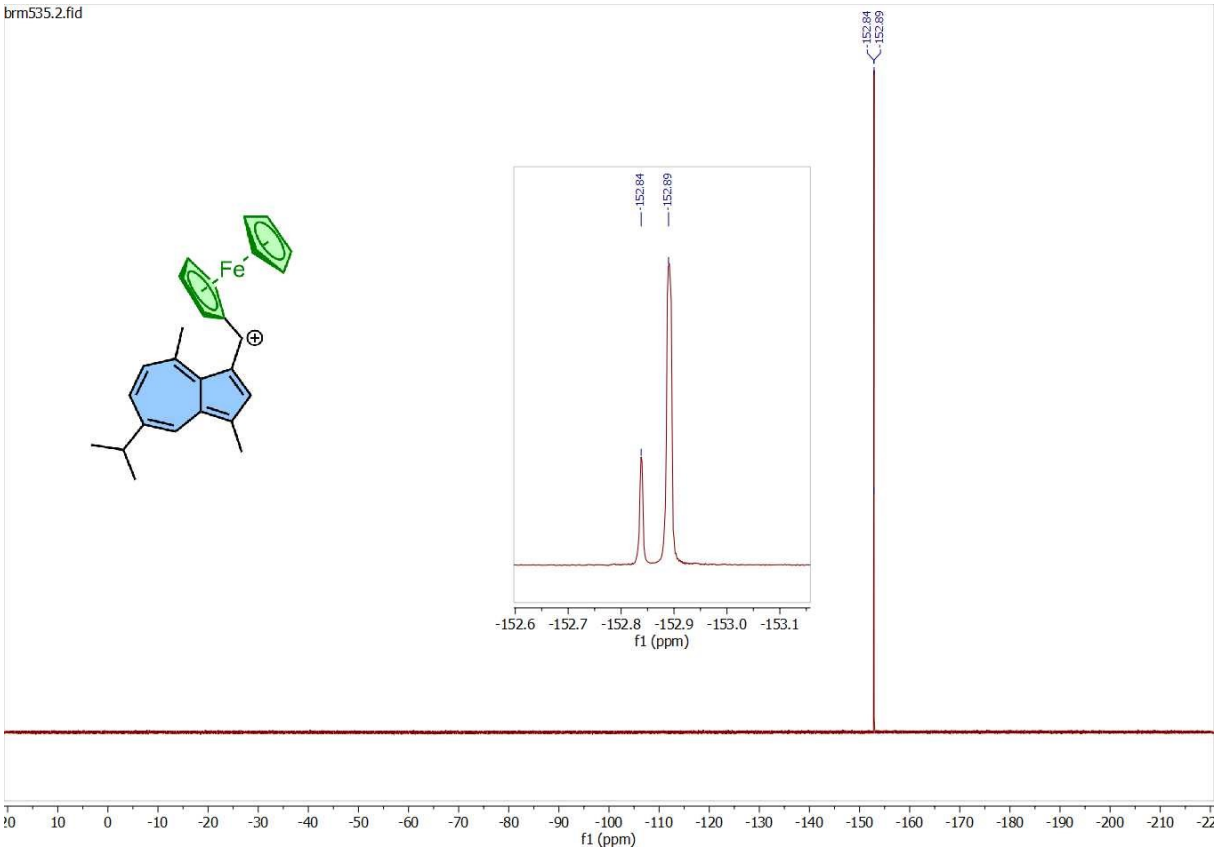


Figure S30. ^{19}F NMR spectrum of compound **2g** (376 MHz, CD_2Cl_2).

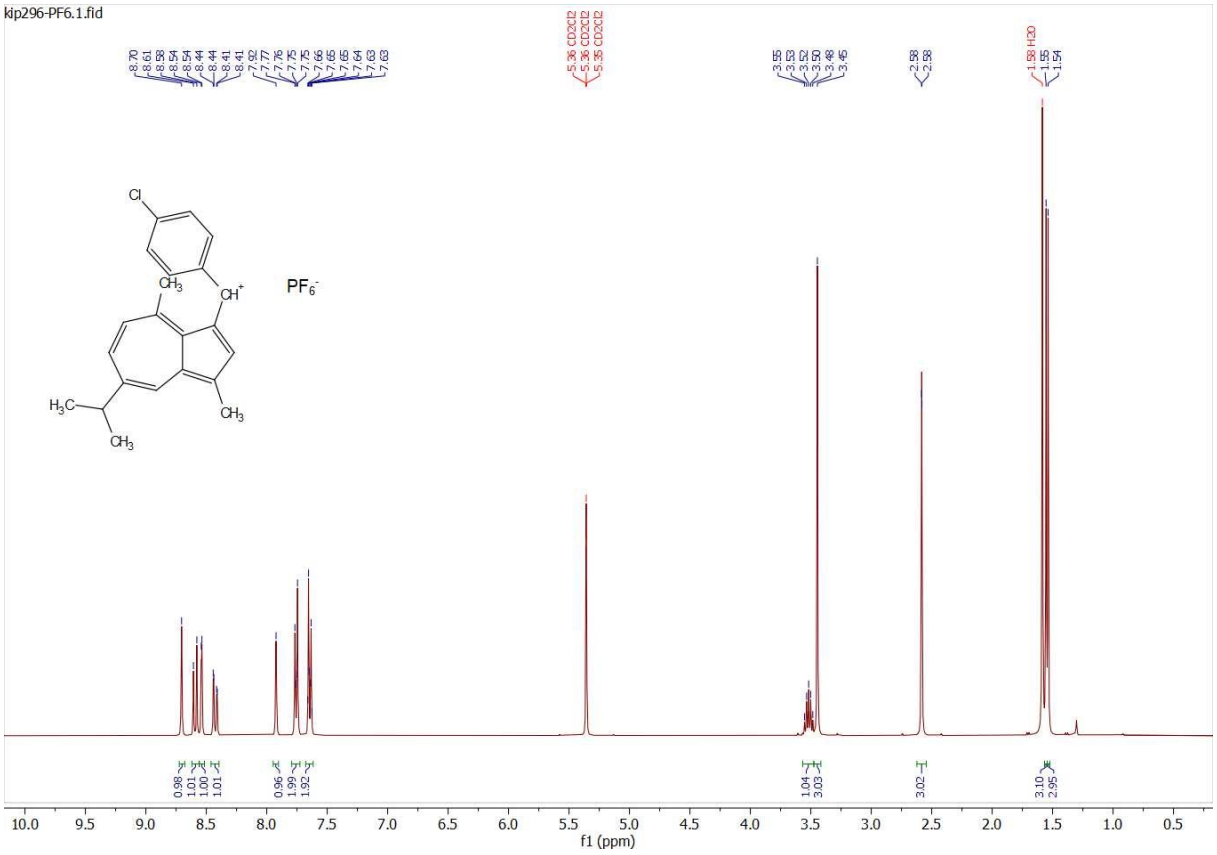


Figure S31. ^{1}H NMR spectrum of compound **2h** (400 MHz, CD_2Cl_2).

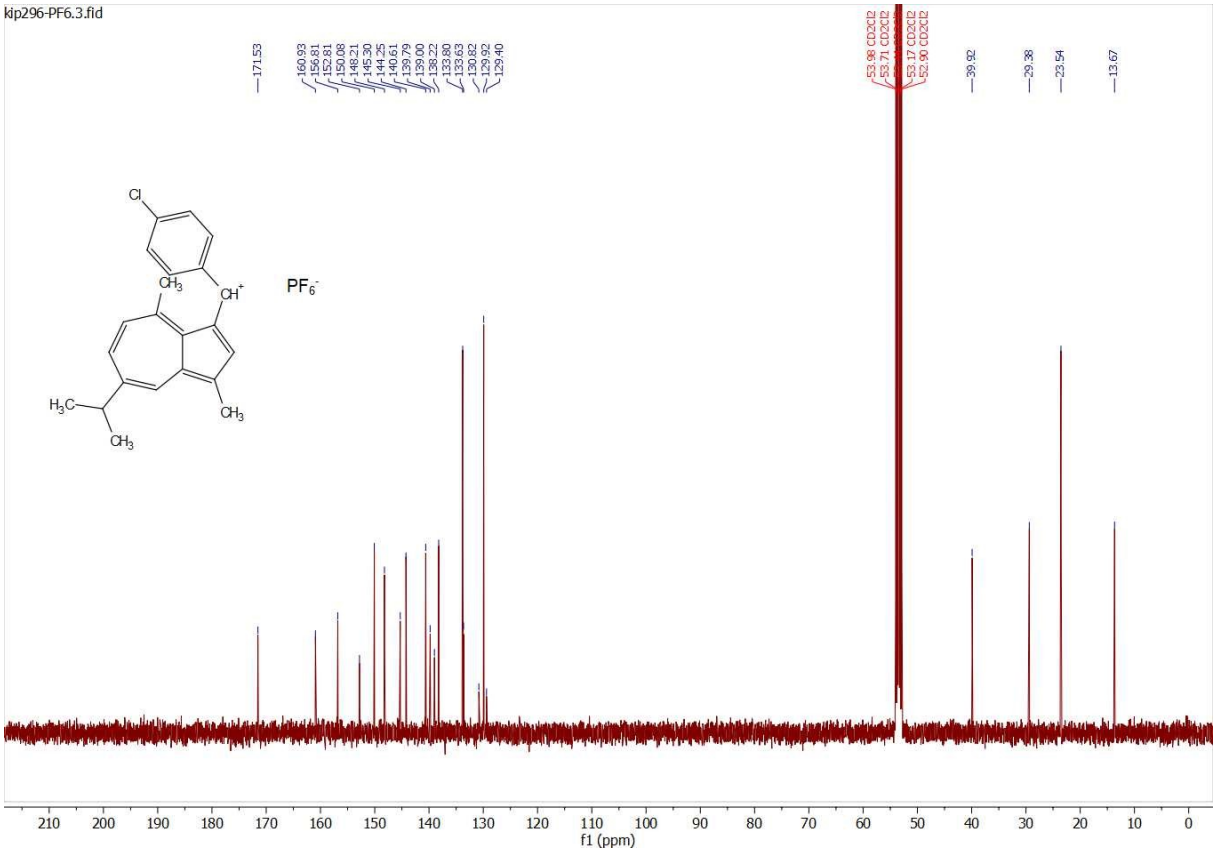


Figure S32. ^{13}C NMR spectrum of compound **2h** (100 MHz, CD_2Cl_2).

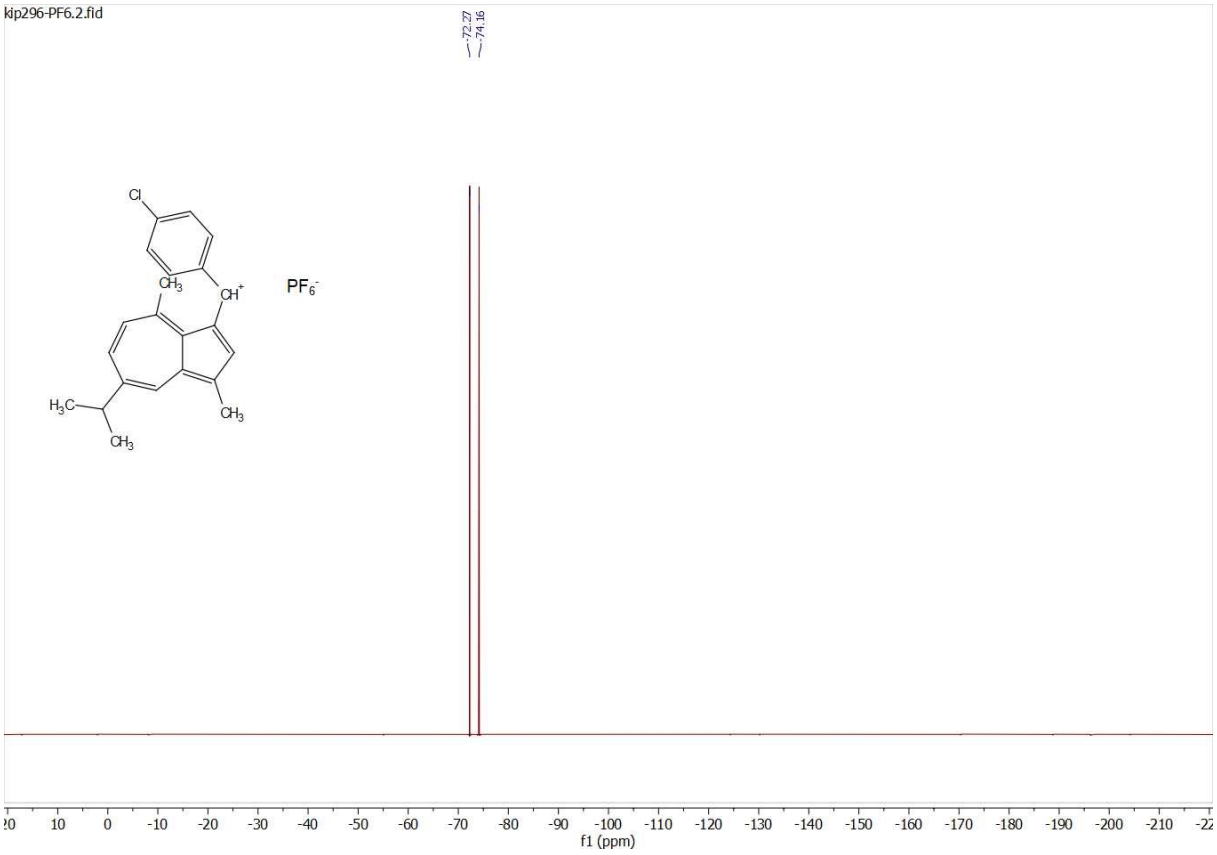


Figure S33. ^{19}F NMR spectrum of compound **2h** (376 MHz, CD_2Cl_2).

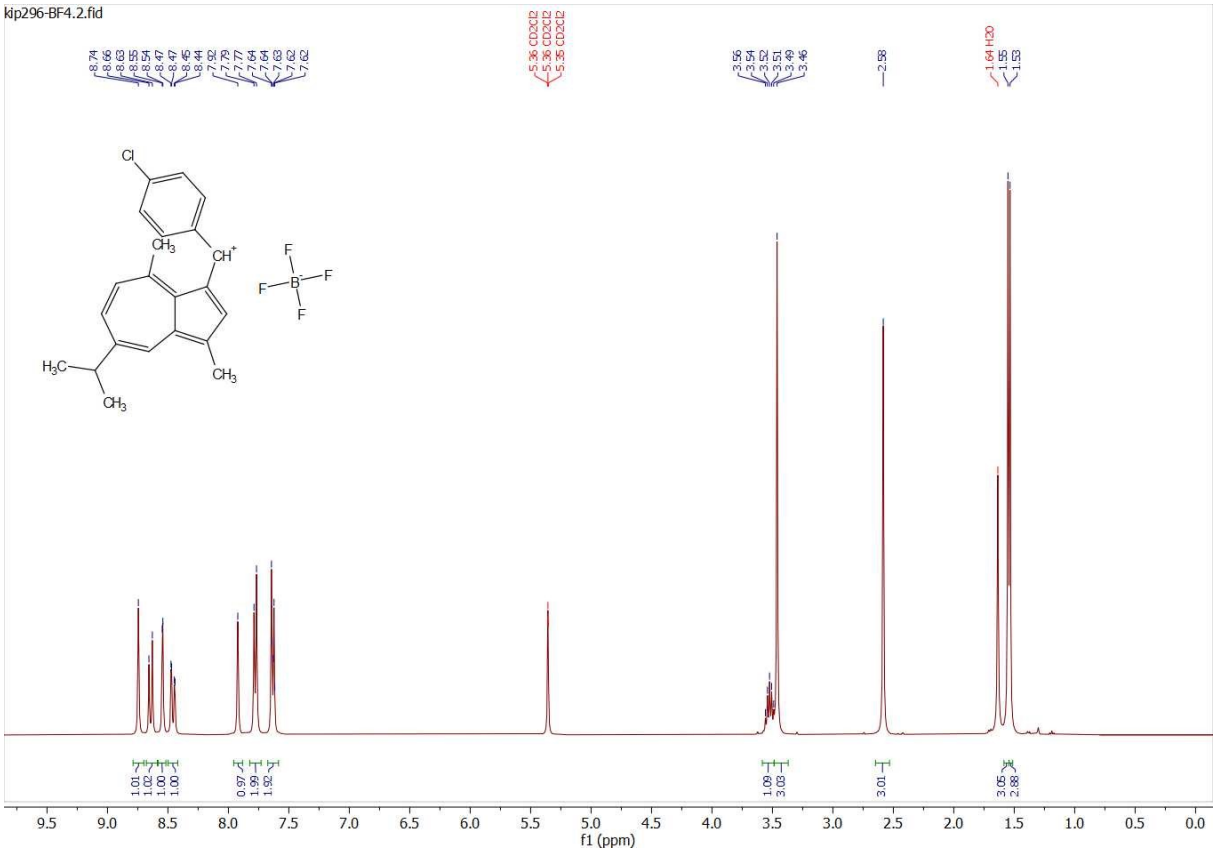


Figure S34. ^{1}H NMR spectrum of compound **2h'** (400 MHz, CD_2Cl_2).

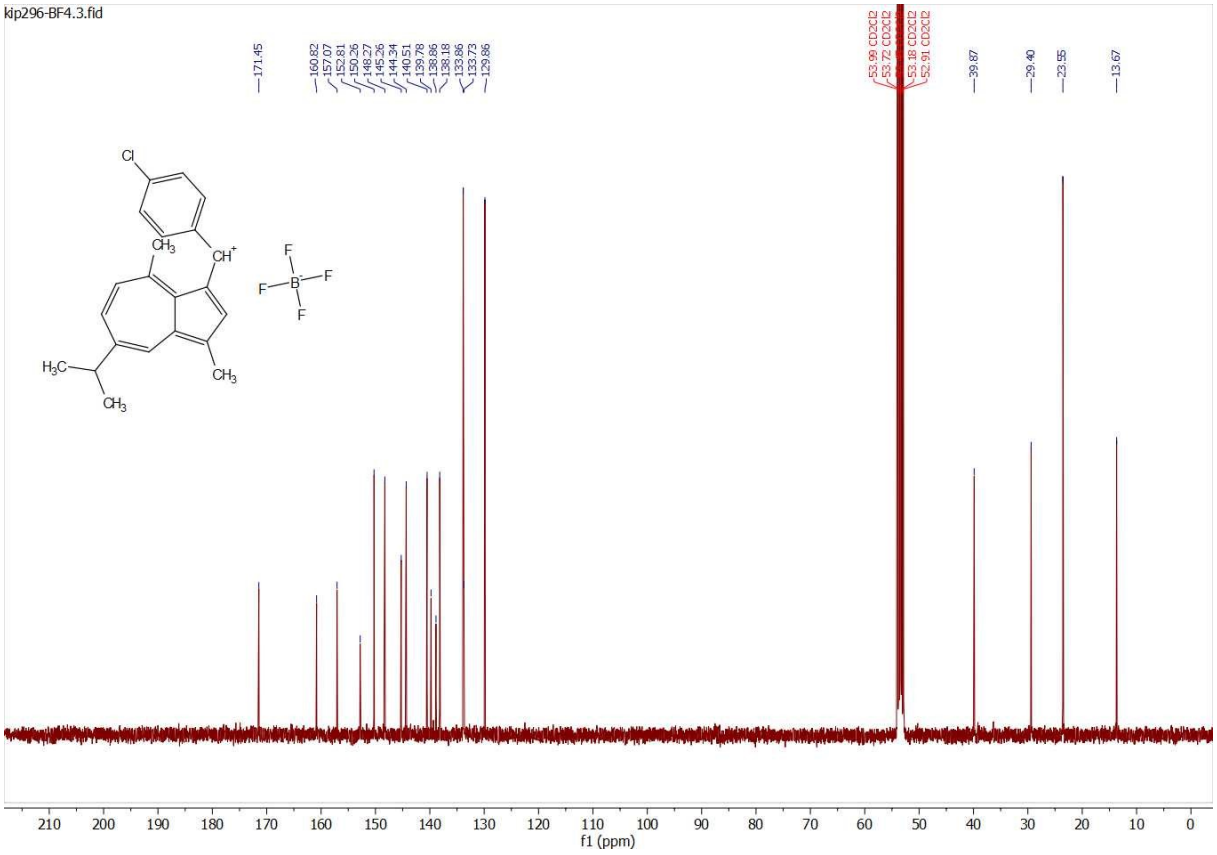


Figure S35. ^{13}C NMR spectrum of compound **2h'** (100 MHz, CD_2Cl_2).

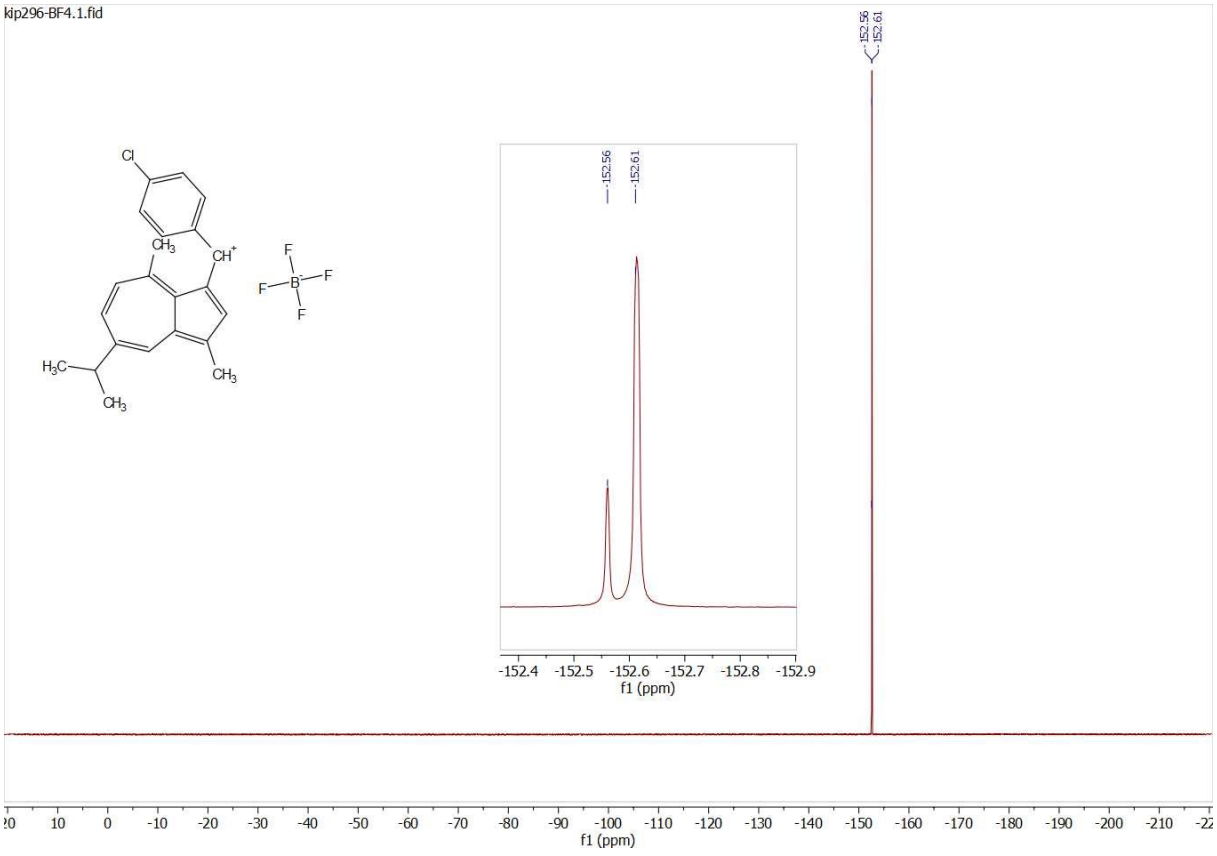


Figure S36. ^{19}F NMR spectrum of compound **2h'** (376 MHz, CD_2Cl_2).

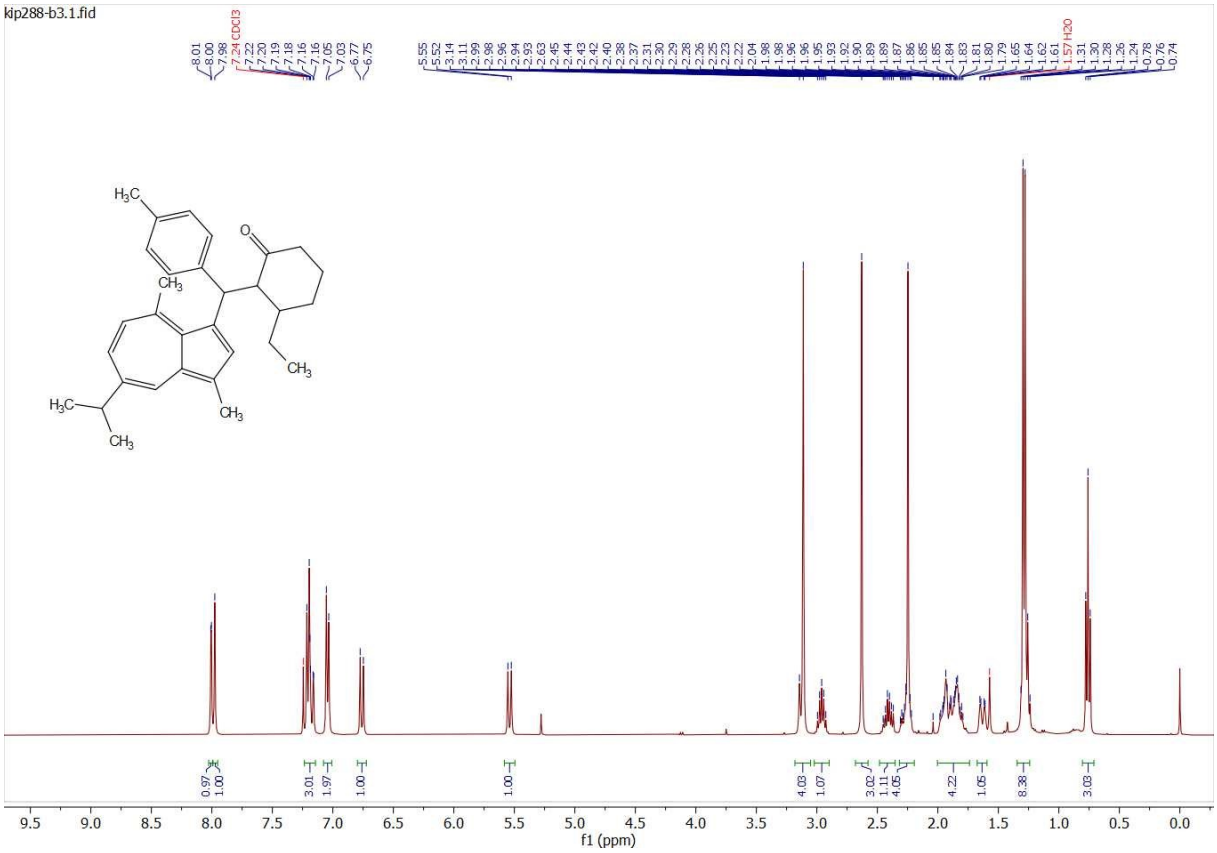


Figure S37. ^{1}H NMR spectrum of compound **5aa/diastereomer 1** (400 MHz, $CDCl_3$).

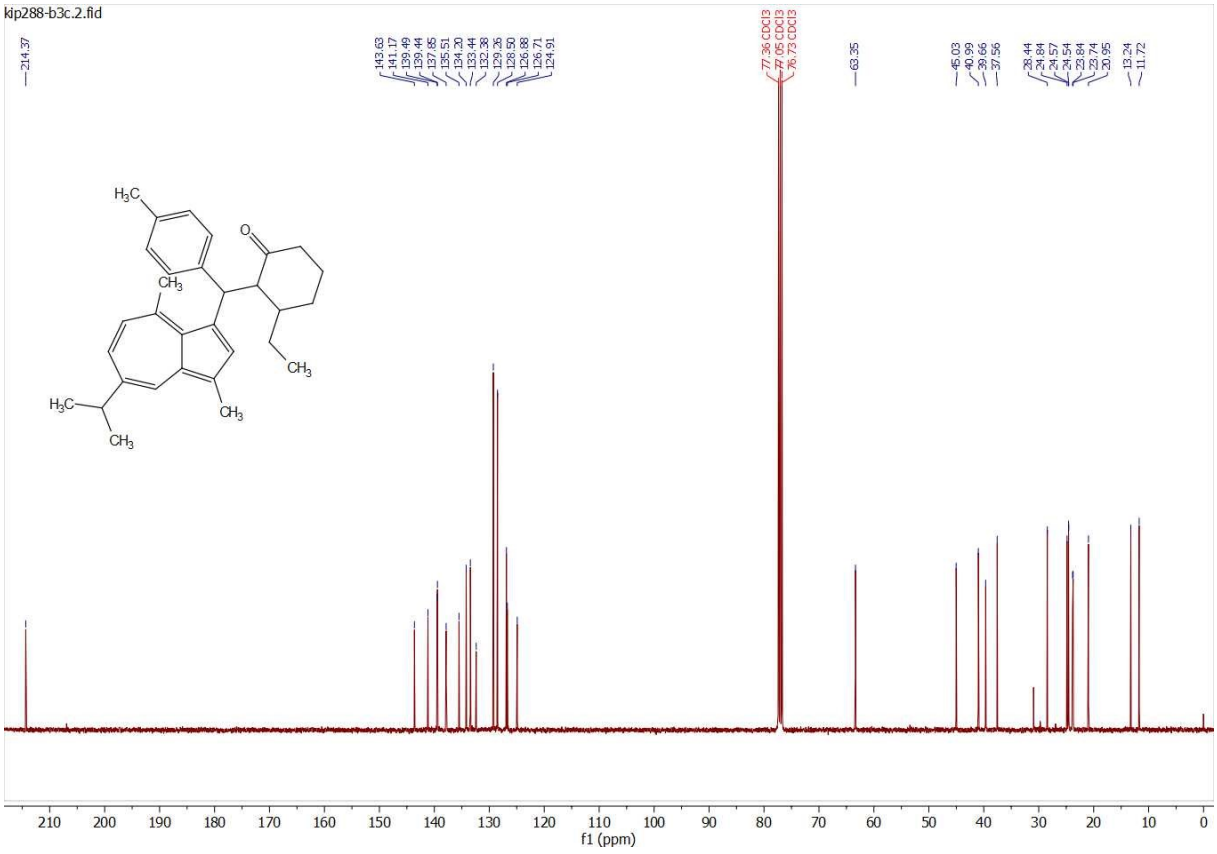


Figure S38. ^{13}C NMR spectrum of compound **5aa/diastereomer 1** (100 MHz, $CDCl_3$).

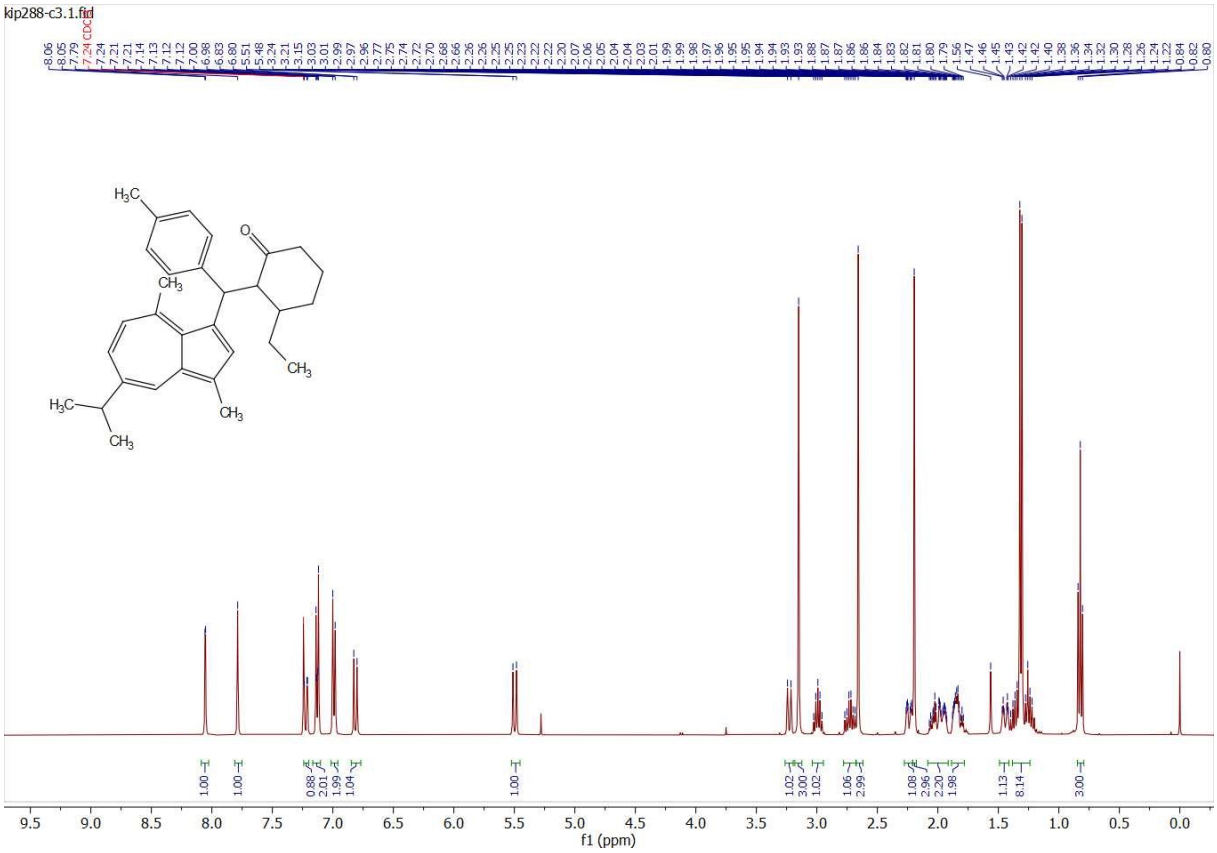


Figure S39. ^{1}H spectrum of compound **5aa/diastereomer 2** (400 MHz, $CDCl_3$).

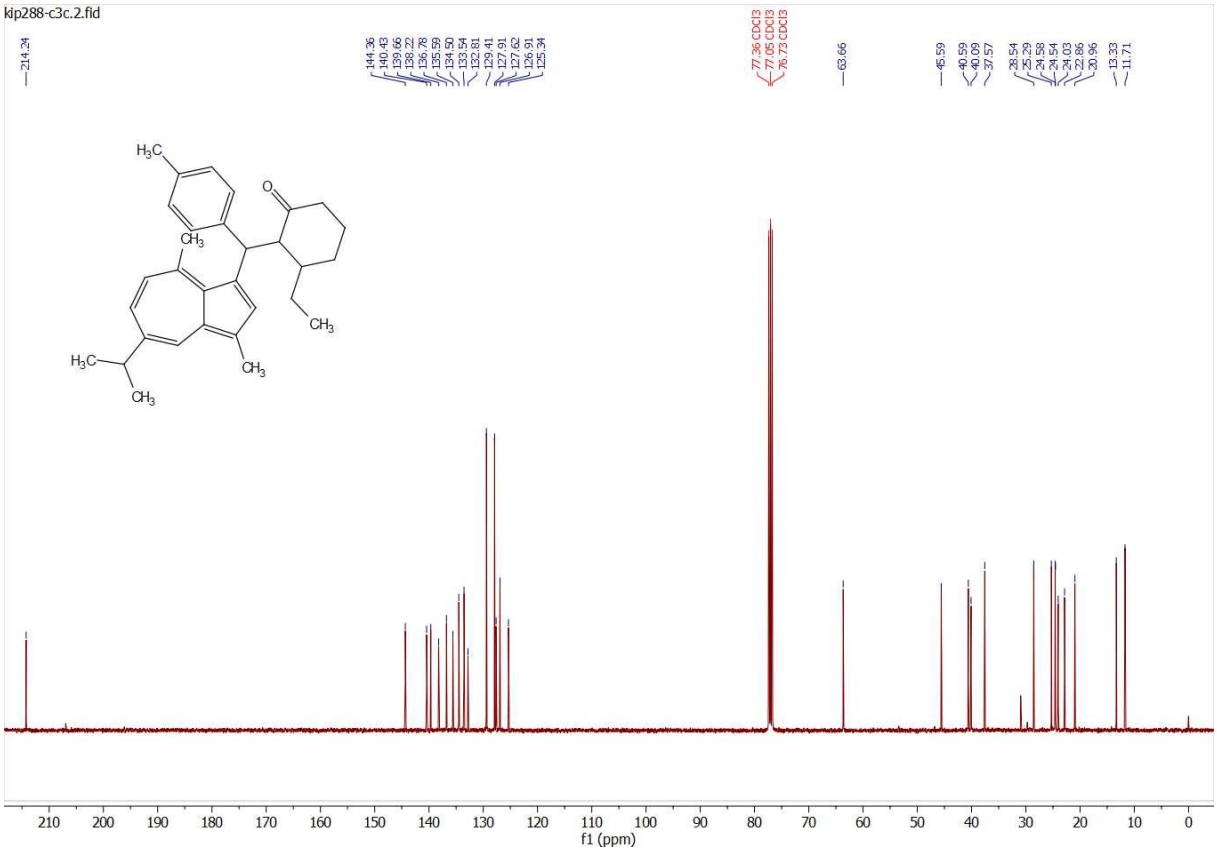


Figure S40. ^{13}C spectrum of compound **5aa/diastereomer 2** (100 MHz, $CDCl_3$).

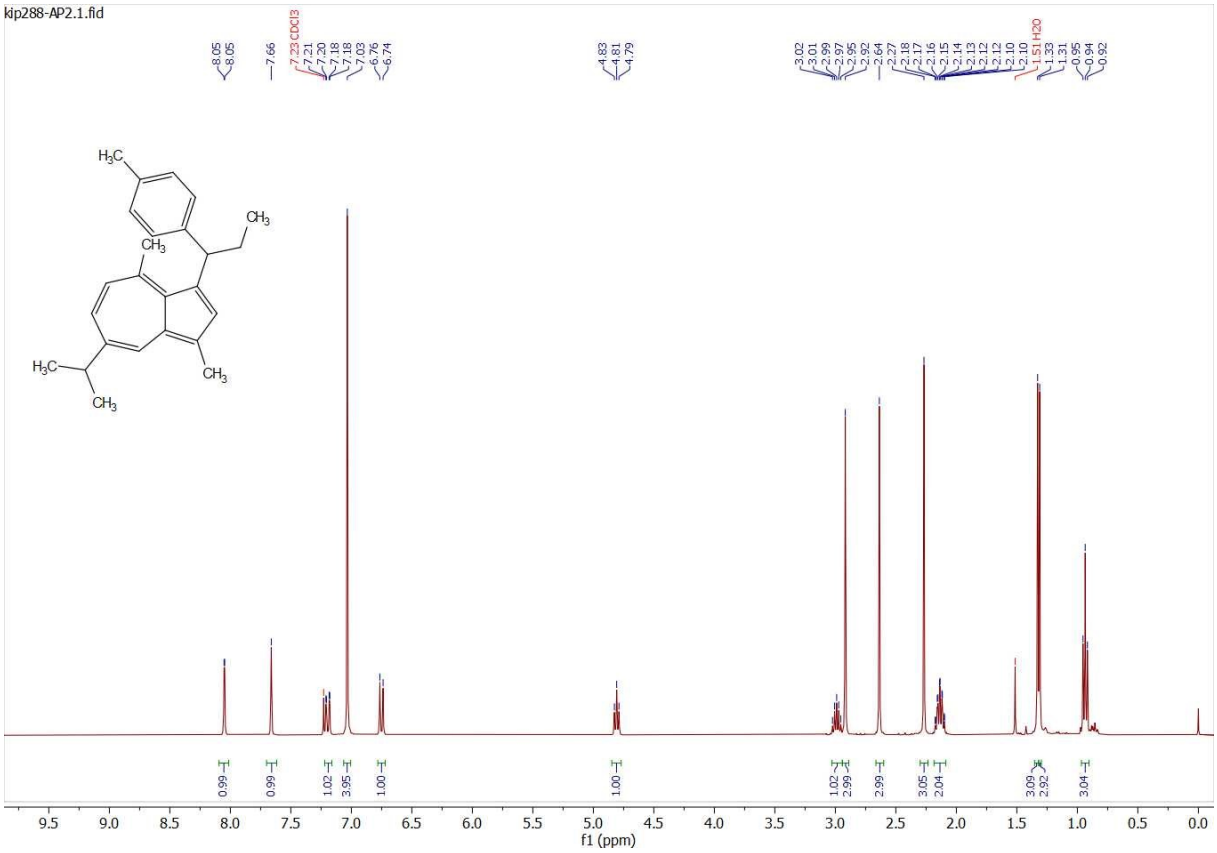


Figure S41. ^{1}H NMR spectrum of compound **6a** (400 MHz, $CDCl_3$).

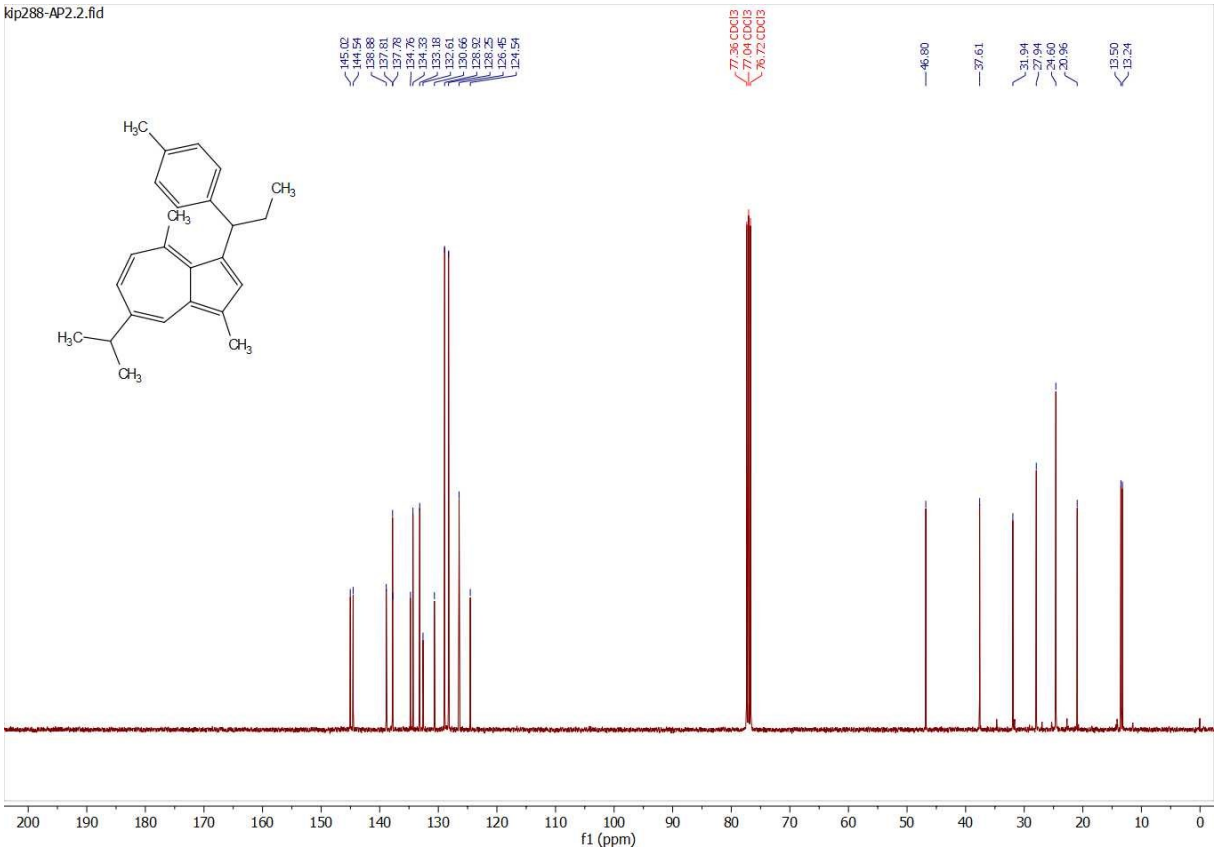


Figure S42. ^{13}C NMR spectrum of compound **6a** (100 MHz, $CDCl_3$).

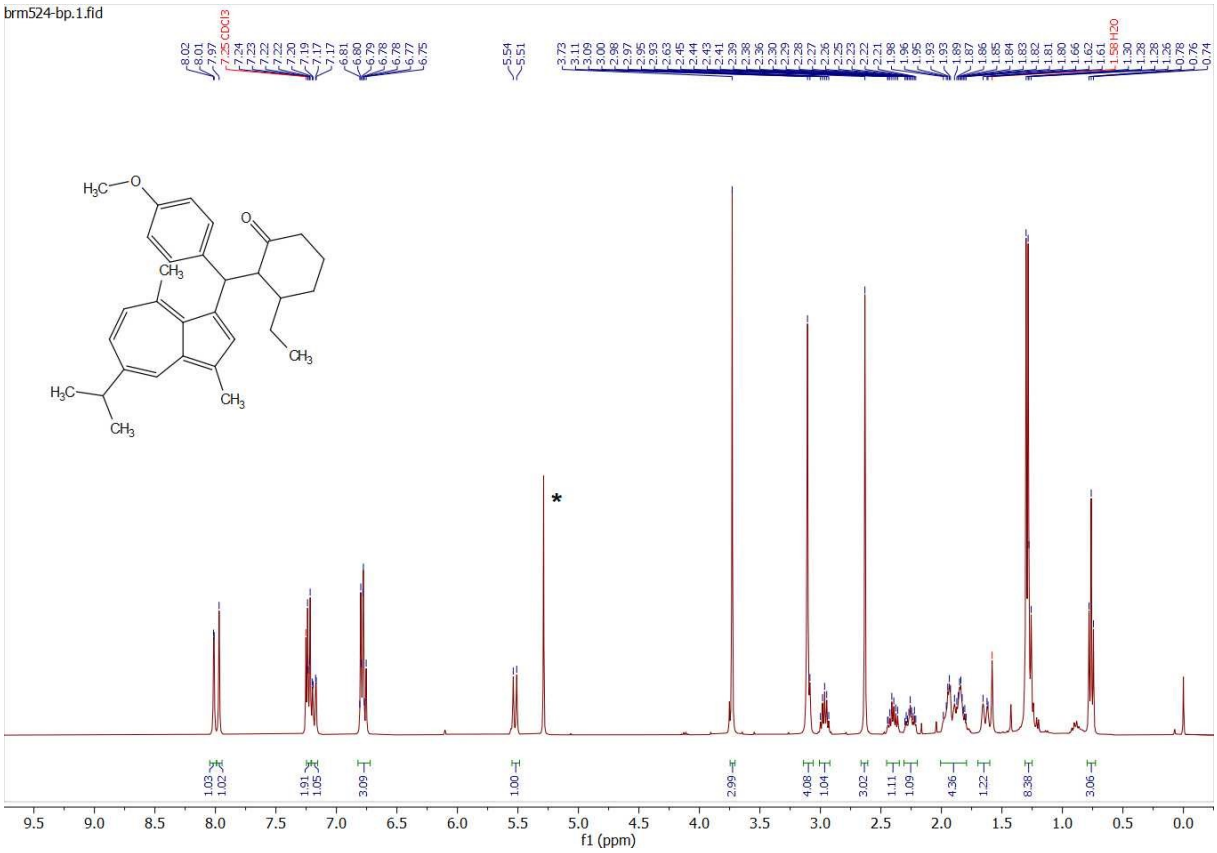


Figure S43. ^{1}H NMR spectrum of compound **5ab/diastereomer 1** (400 MHz, $CDCl_3$).

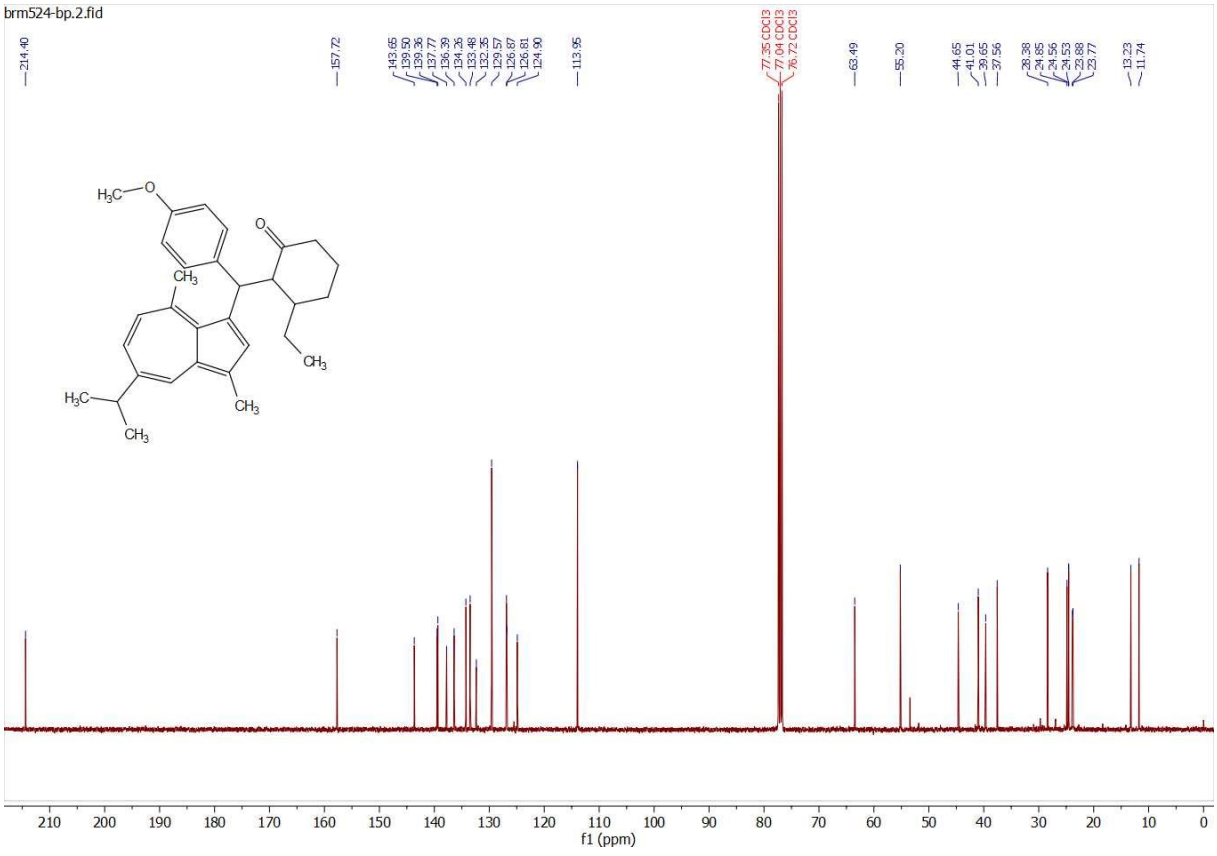


Figure S44. ^{13}C NMR spectrum of compound **5ab/diastereomer 1** (100 MHz, $CDCl_3$).

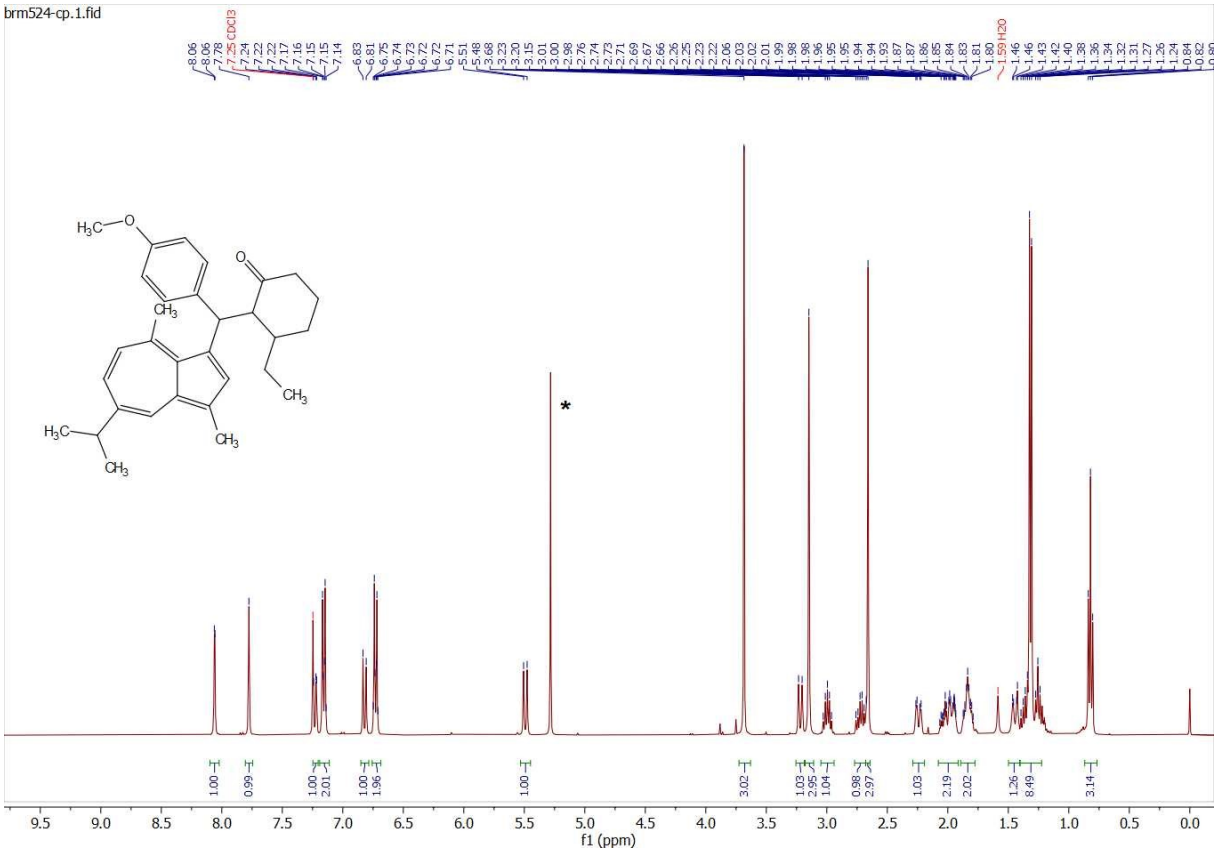


Figure S45. ^{1}H NMR spectrum of compound **5ab/diastereomer 2** (400 MHz, $CDCl_3$).

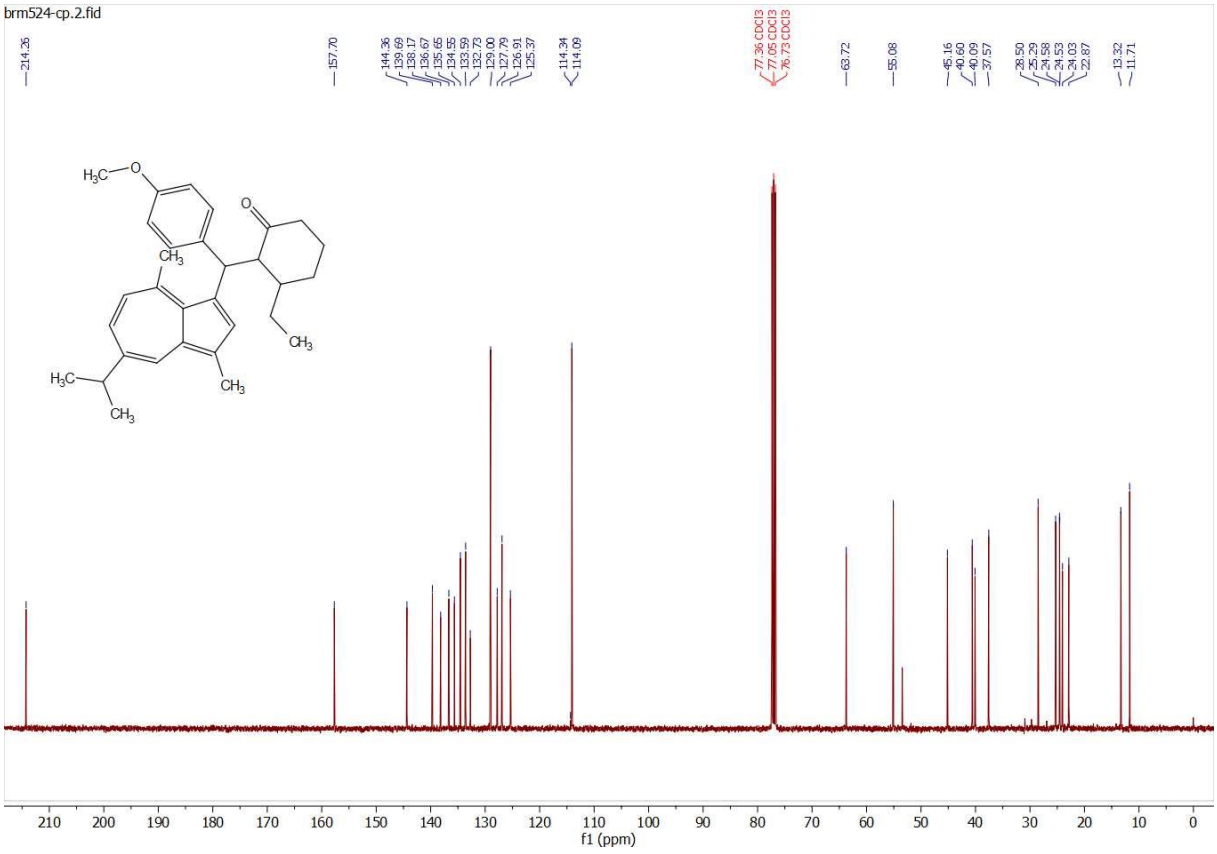


Figure S46. ^{13}C NMR spectrum of compound **5ab/diastereomer 2** (100 MHz, $CDCl_3$).

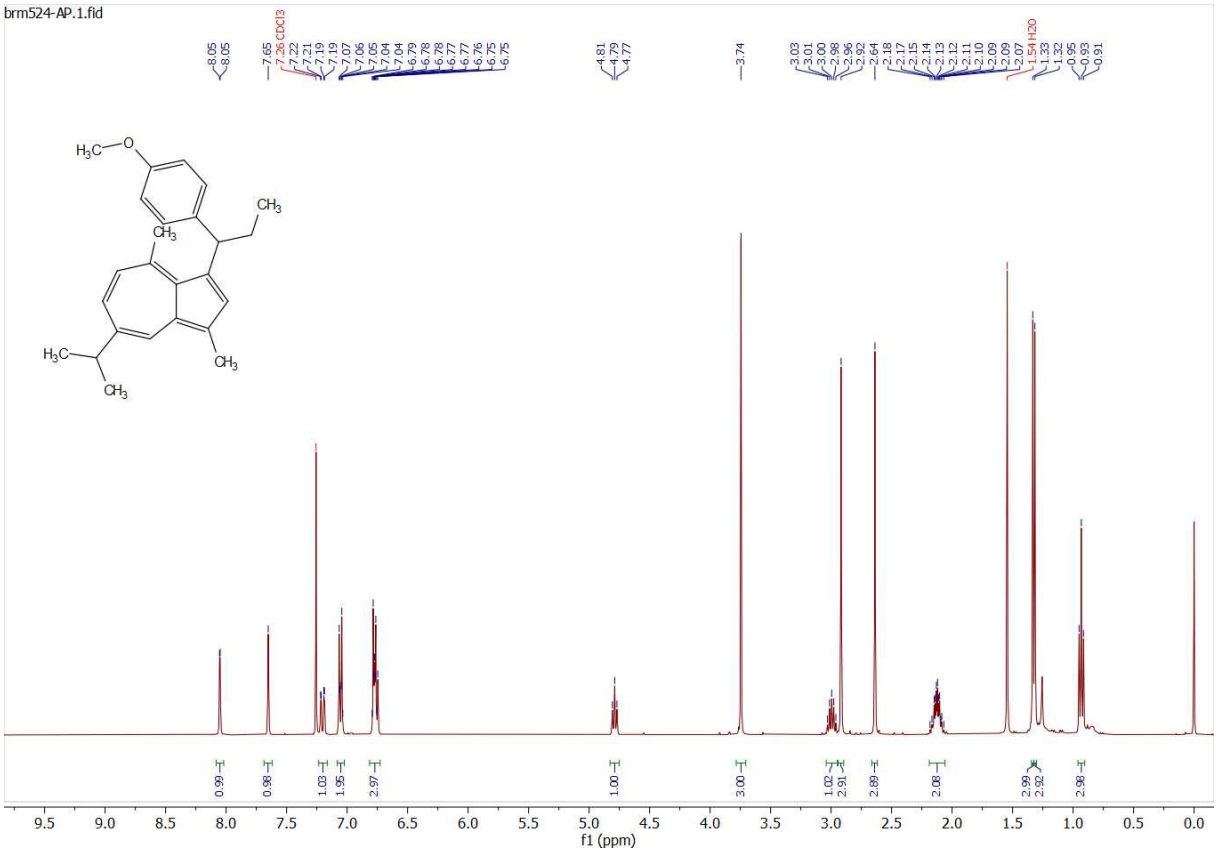


Figure S47. ^{1}H NMR spectrum of compound **6b** (400 MHz, $CDCl_3$).

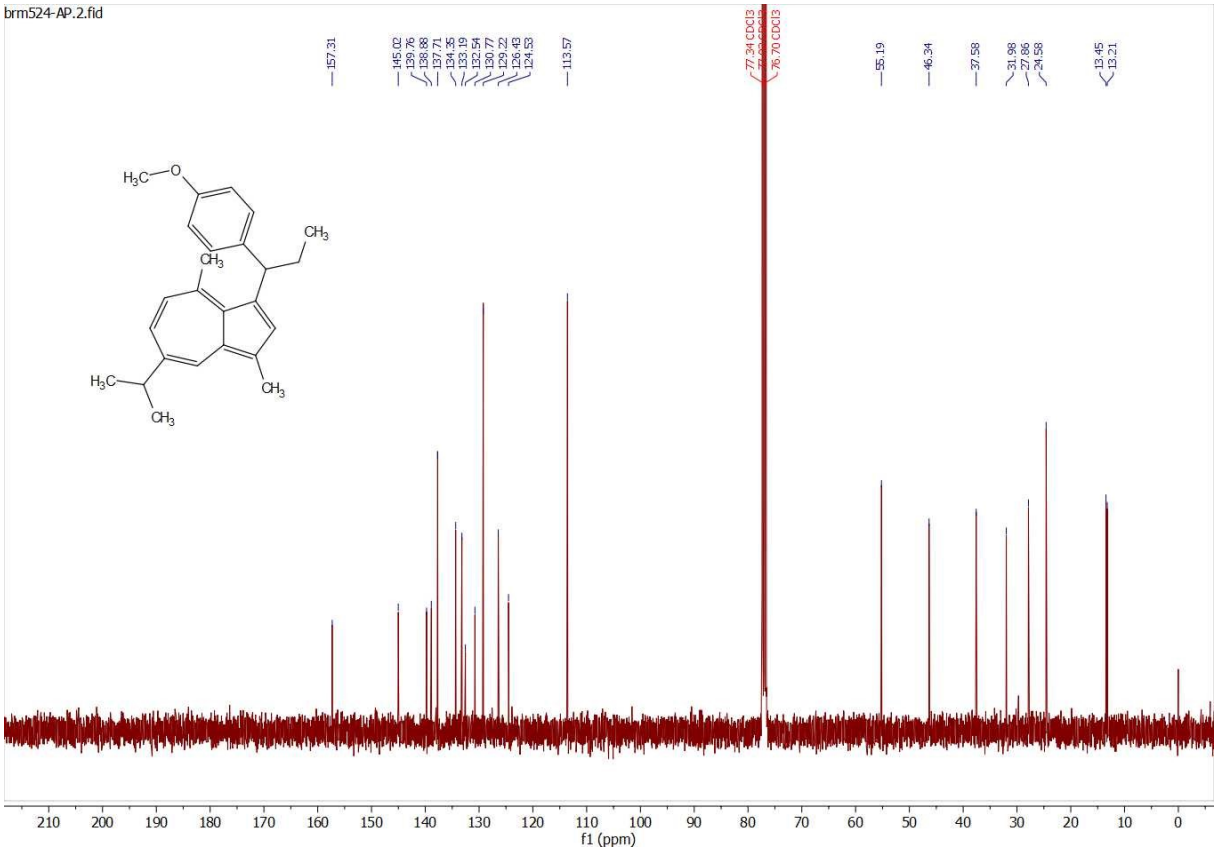


Figure S48. ^{13}C NMR spectrum of compound **6b** (100 MHz, $CDCl_3$).

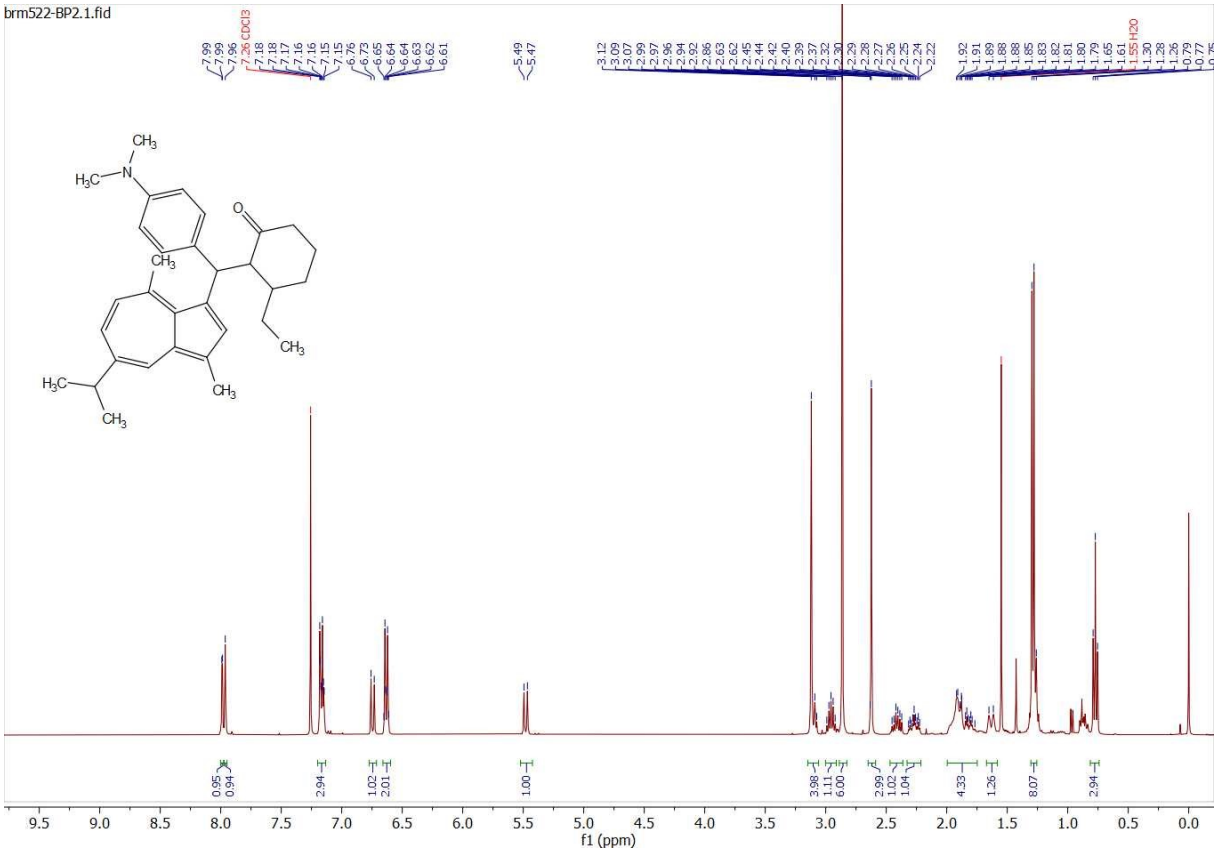


Figure S49. ^{1}H NMR spectrum of compound **5ac/diastereomer 1** (400 MHz, $CDCl_3$).

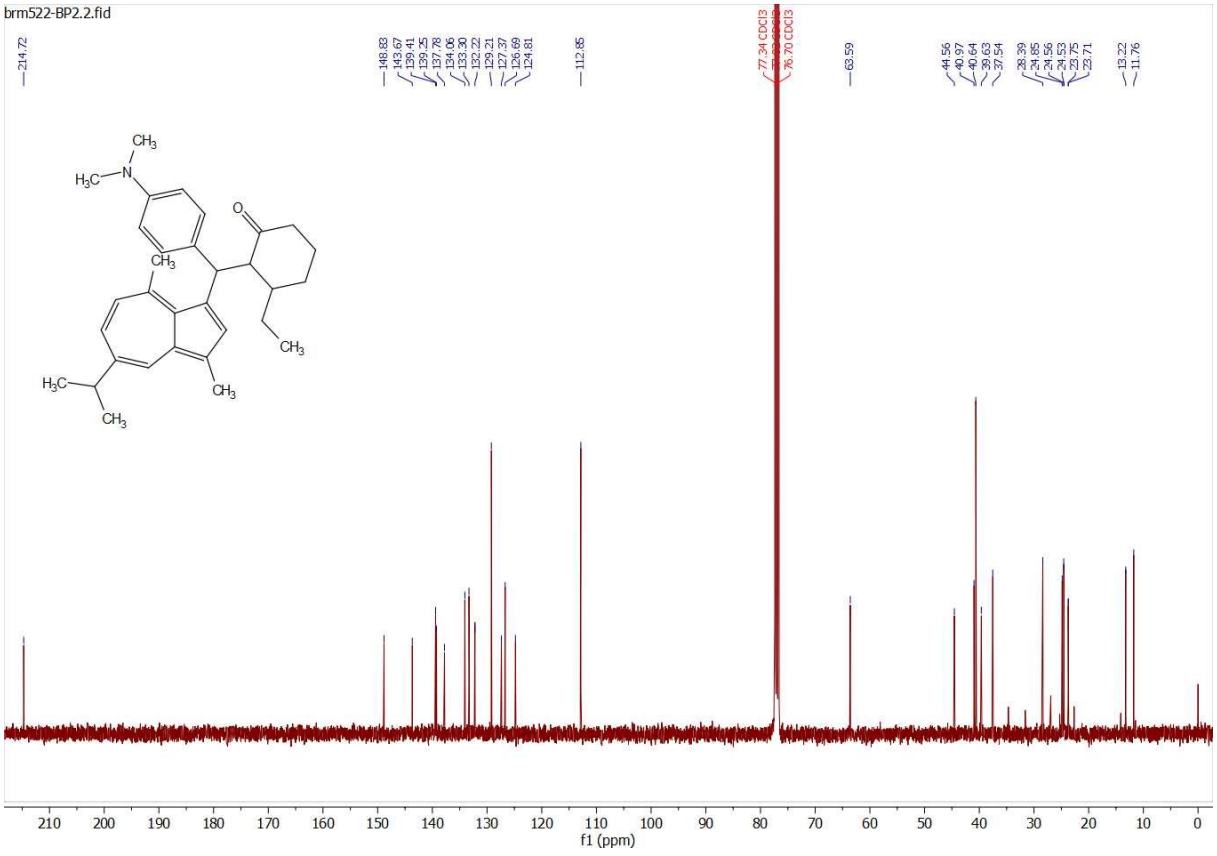


Figure S50. ^{13}C NMR spectrum of compound **5ac/diastereomer 1** (100 MHz, $CDCl_3$).

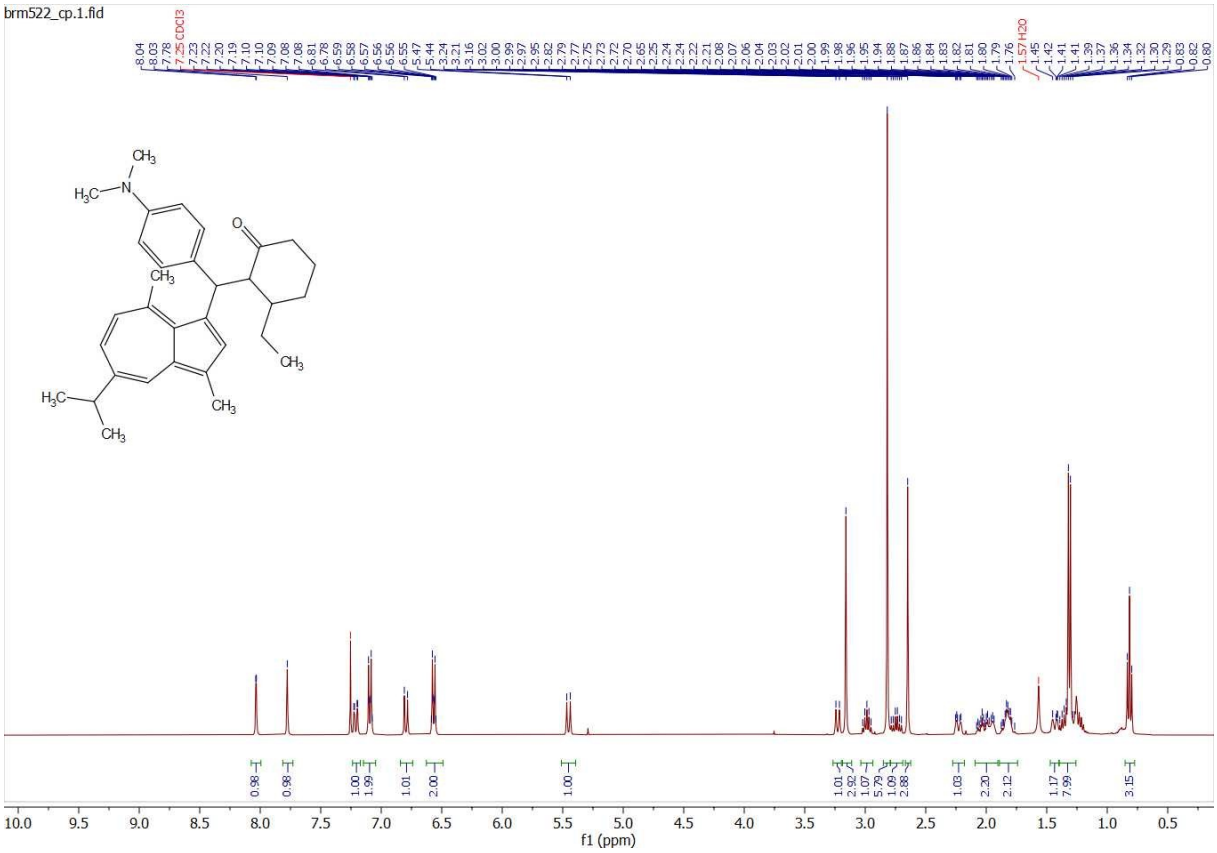


Figure S51. ^{1}H NMR spectrum of compound **5ac/diastereomer 2** (400 MHz, $CDCl_3$).

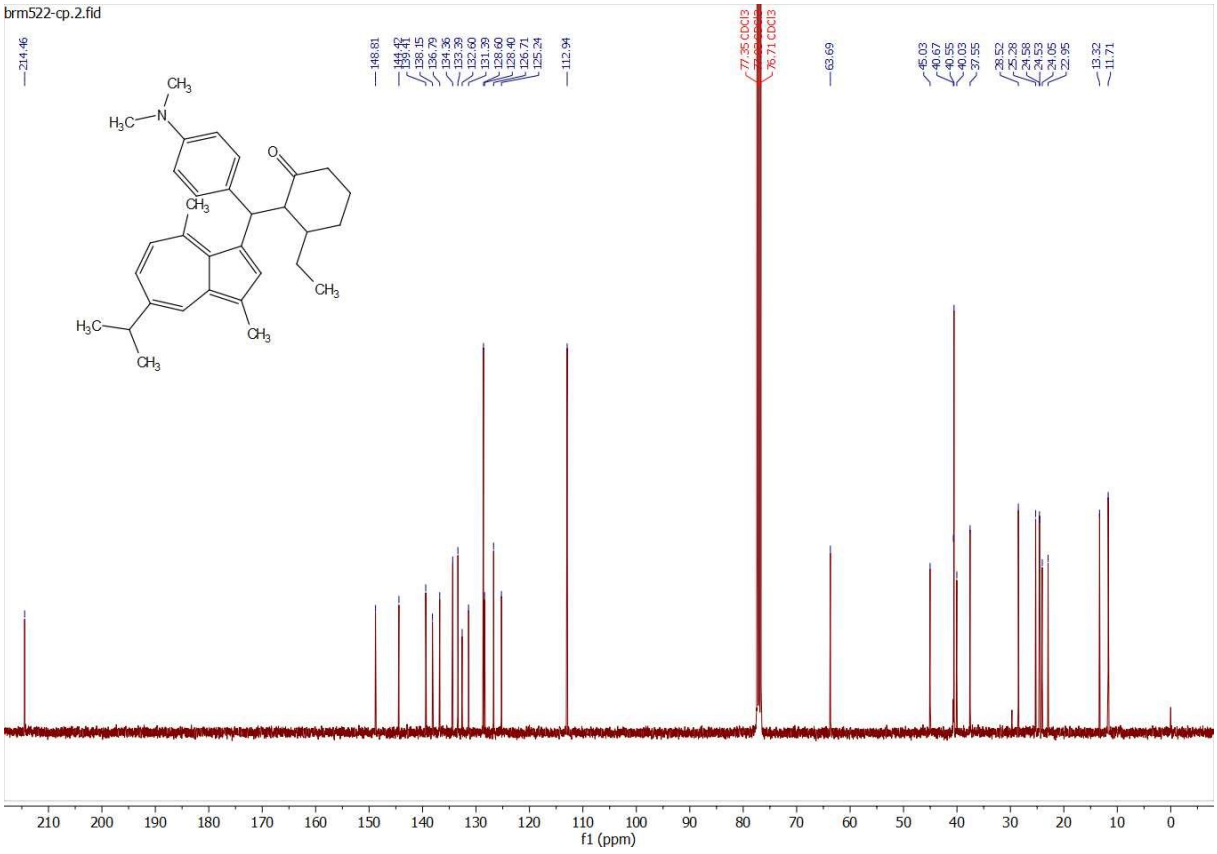


Figure S52. ^{13}C NMR spectrum of compound **5ac/diastereomer 2** (100 MHz, $CDCl_3$).

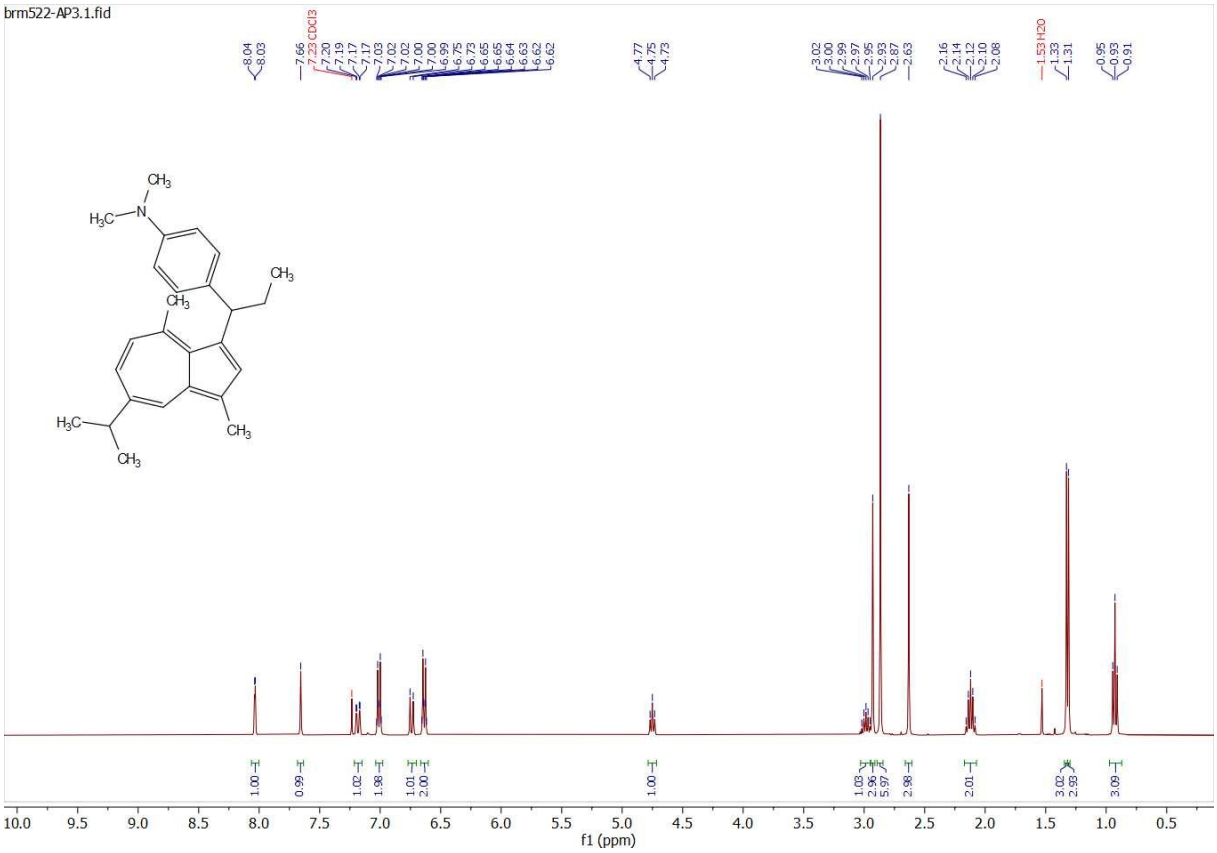


Figure S53. ^{1}H NMR spectrum of compound **6c** (400 MHz, $CDCl_3$).

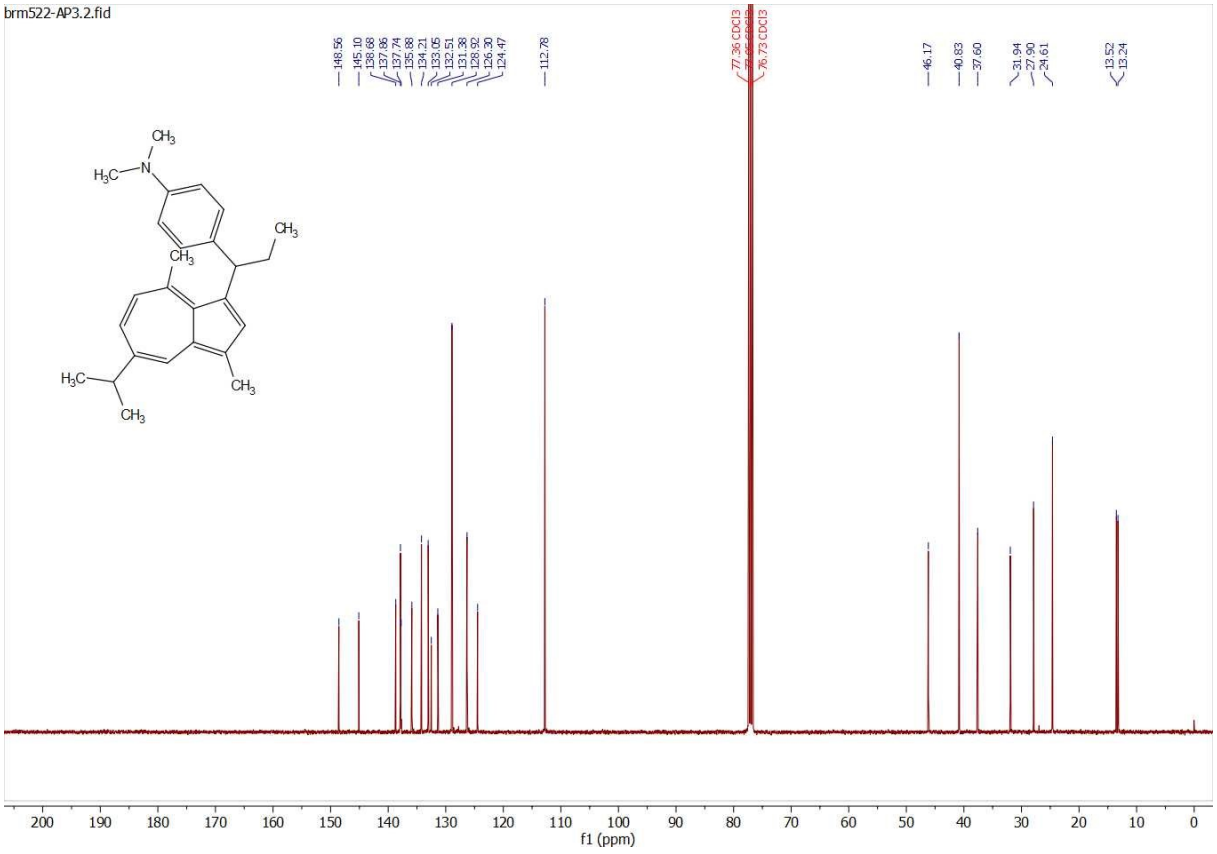


Figure S54. ^{13}C NMR spectrum of compound **6c** (100 MHz, $CDCl_3$).

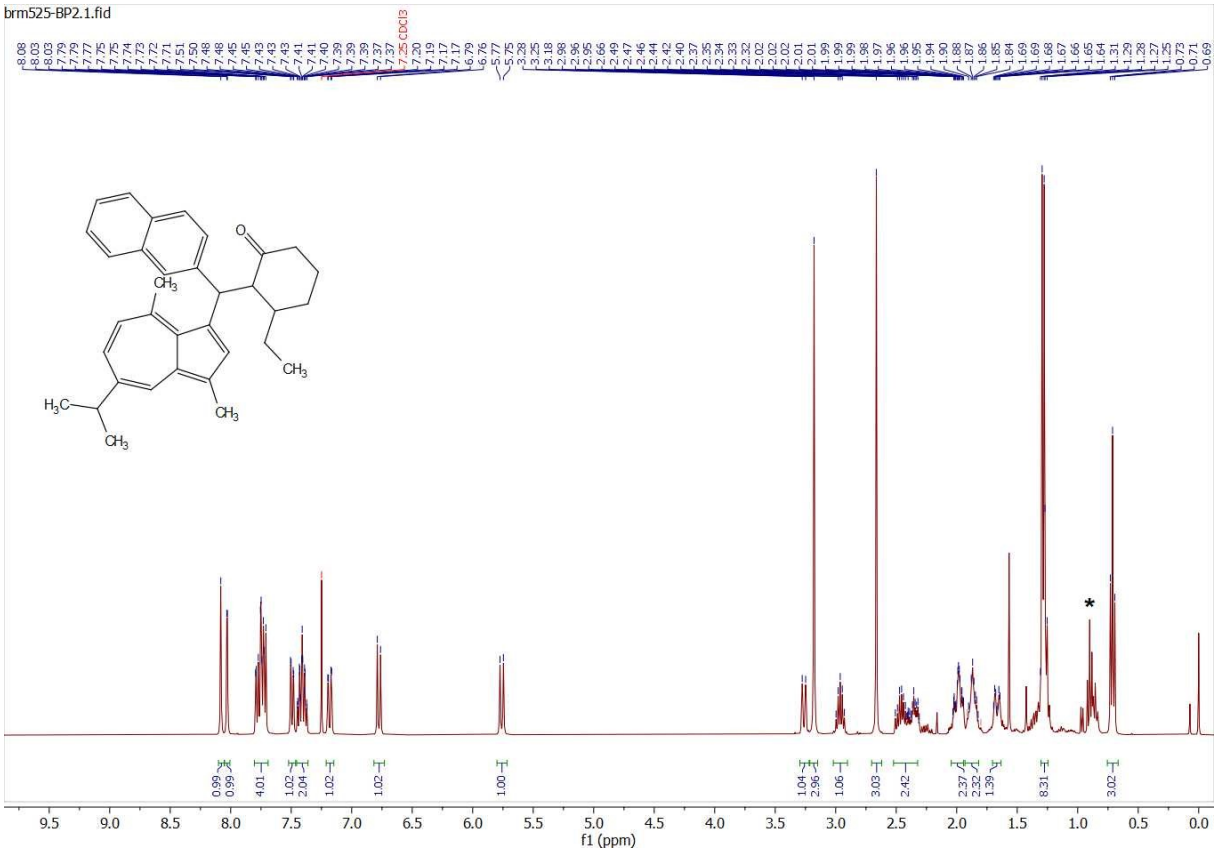


Figure S55. ^{1}H NMR spectrum of compound **5ad/diastereomer 1** (400 MHz, $CDCl_3$).

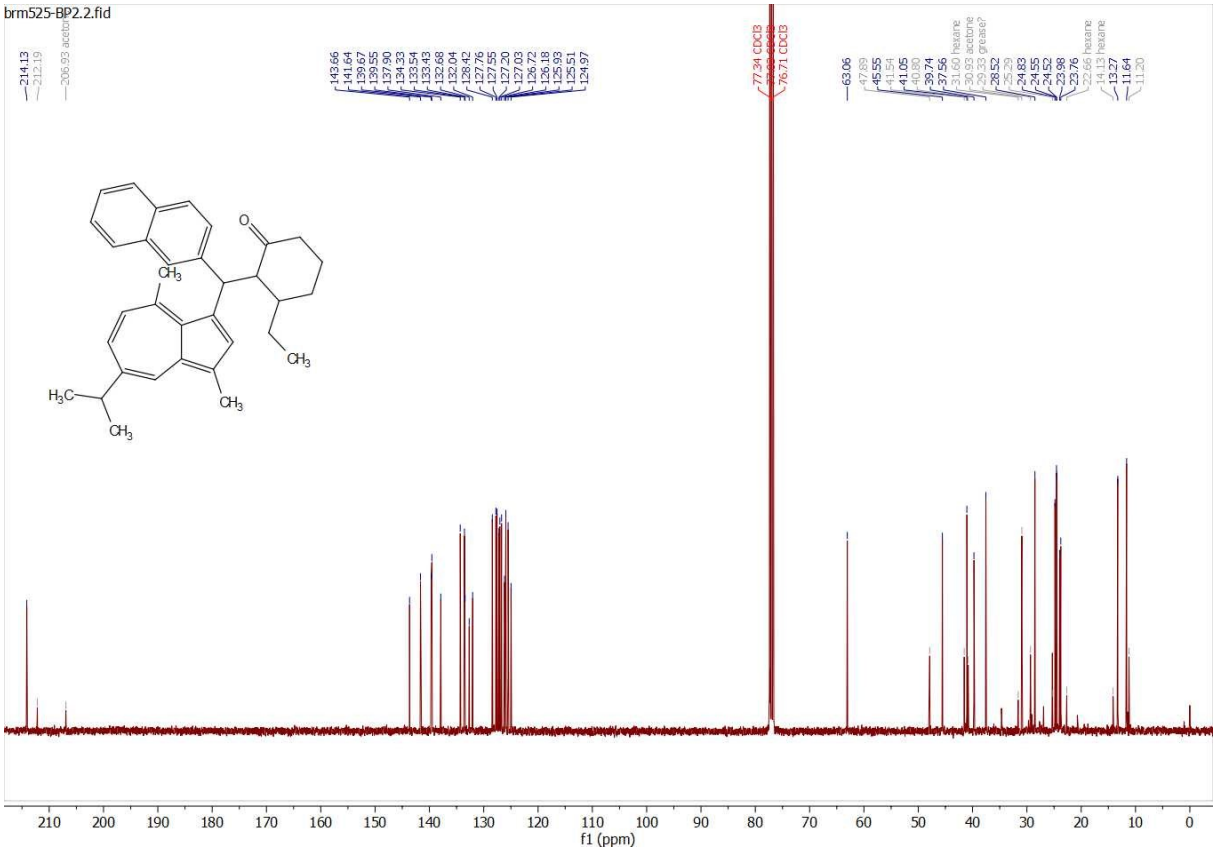


Figure S56. ^{13}C NMR spectrum of compound **5ad/diastereomer 1** (100 MHz, $CDCl_3$).

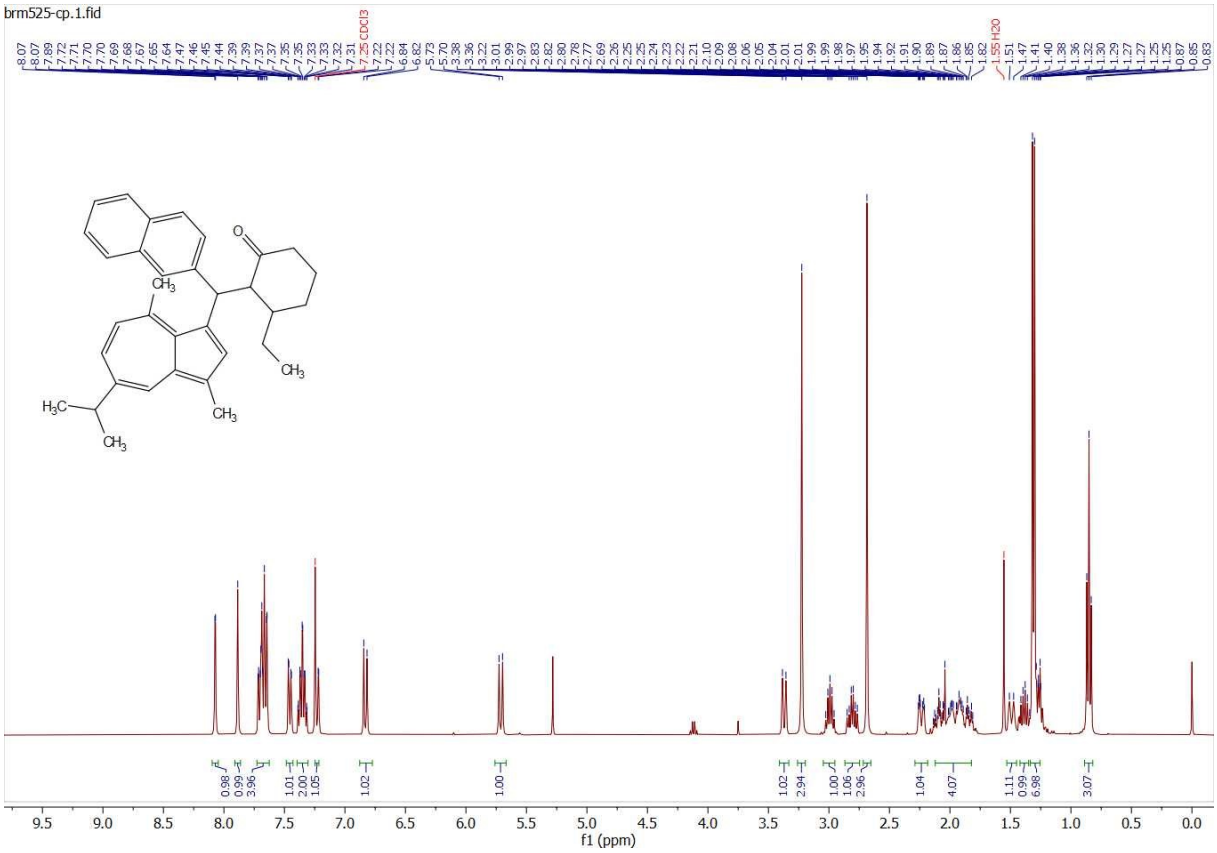


Figure S57. ^{1}H NMR spectrum of compound **5ad/diastereomer 2** (400 MHz, $CDCl_3$).

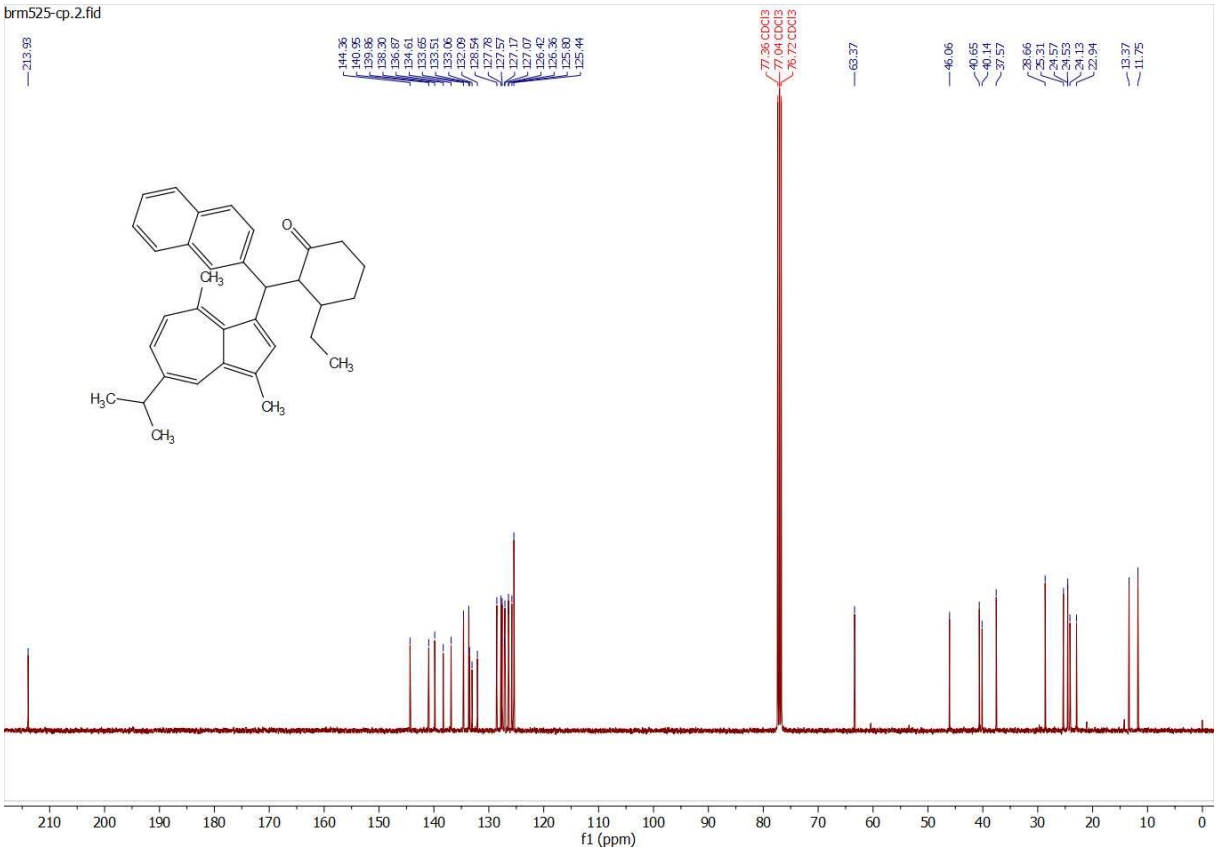


Figure S58. ^{13}C NMR spectrum of compound **5ad/diastereomer 2** (100 MHz, $CDCl_3$).

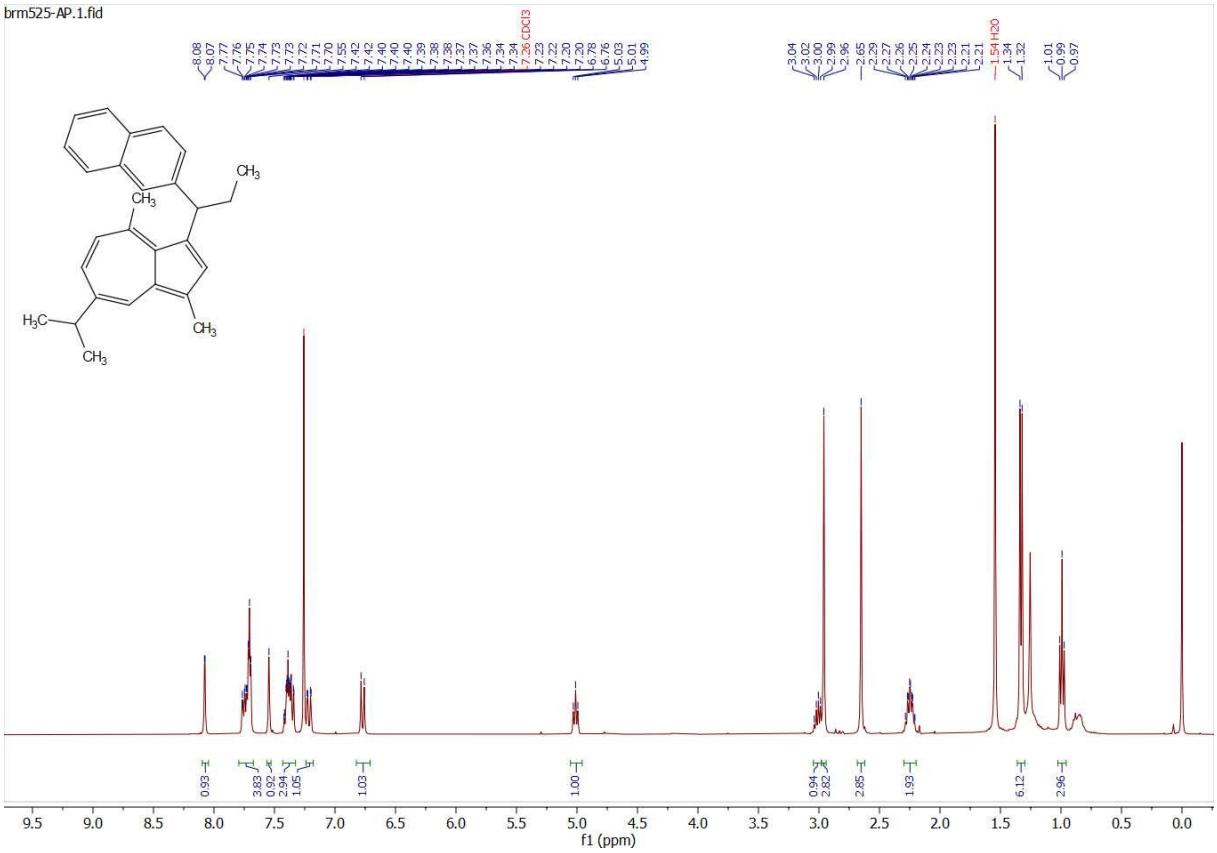


Figure S59. ^{1}H NMR spectrum of compound **6d** (400 MHz, $CDCl_3$).

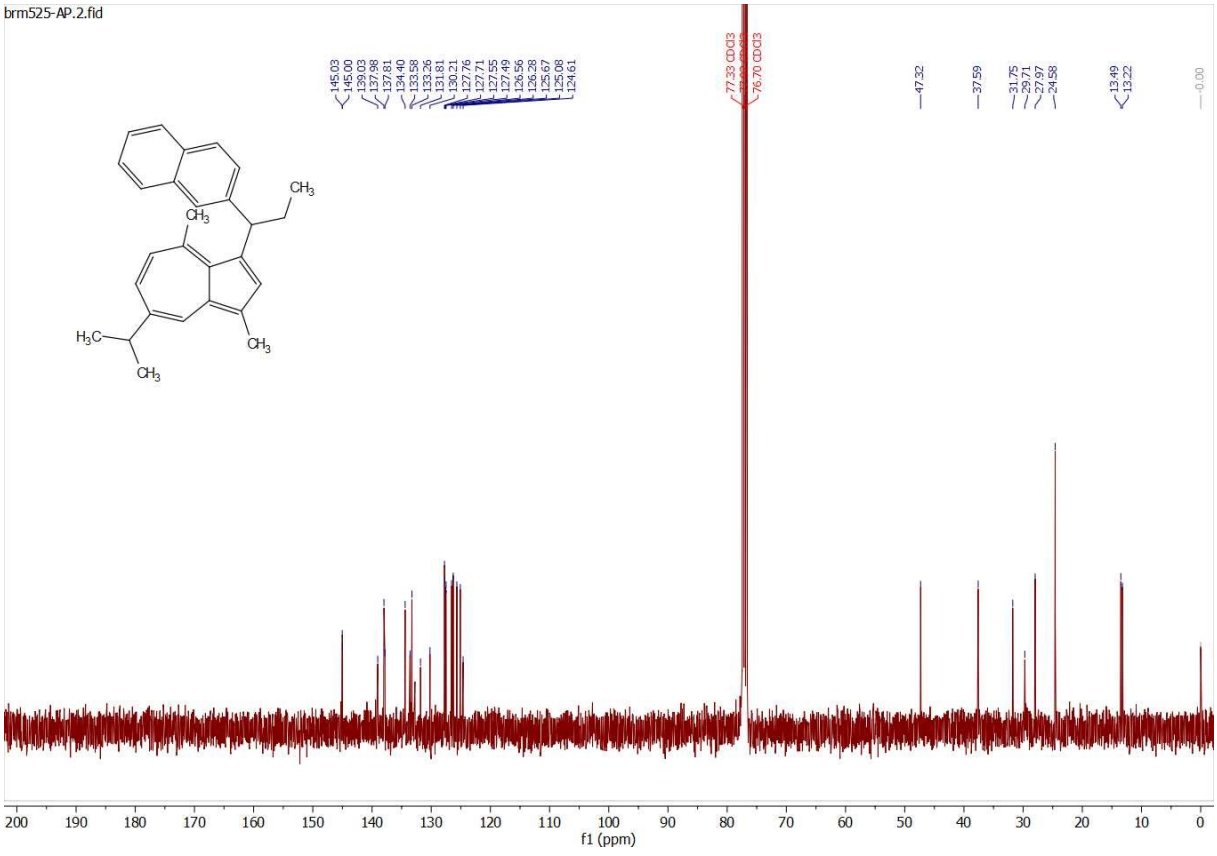


Figure S60. ^{13}C NMR spectrum of compound **6d** (400 MHz, $CDCl_3$).

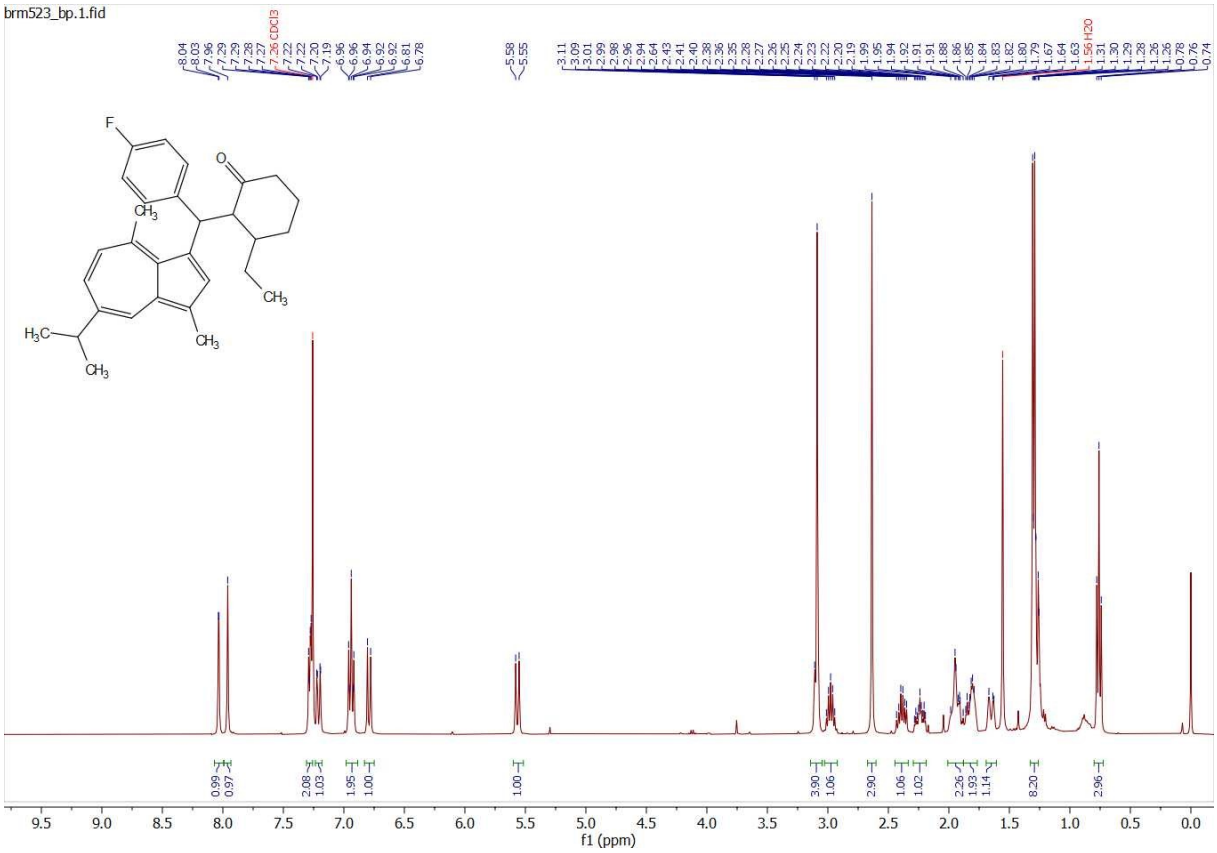


Figure S61. ^{1}H NMR spectrum of compound **5ae/diastereomer 1** (400 MHz, $CDCl_3$).

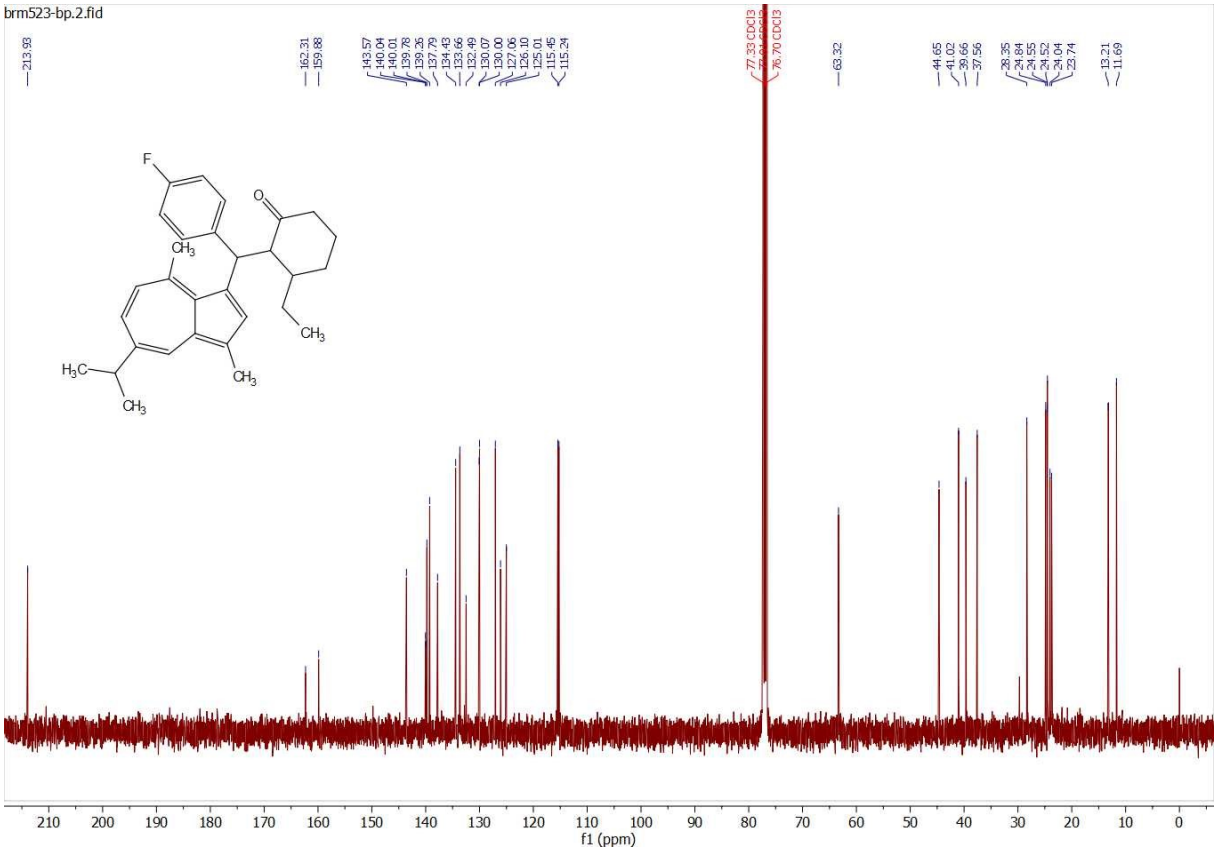


Figure S62. ^{13}C NMR spectrum of compound **5ae/diastereomer 1** (100 MHz, $CDCl_3$).

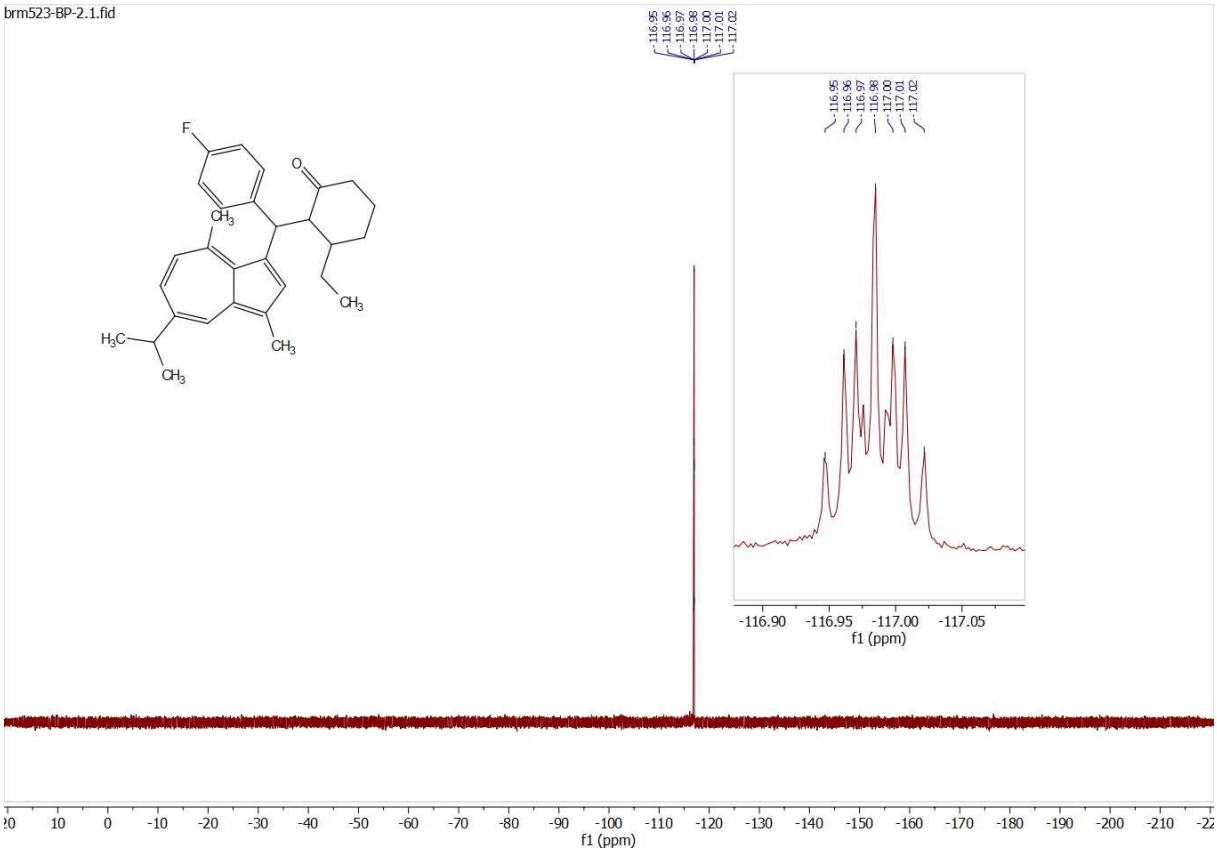


Figure S63. ^{19}F NMR spectrum of compound **5ae/diastereomer 1** (376 MHz, $CDCl_3$).

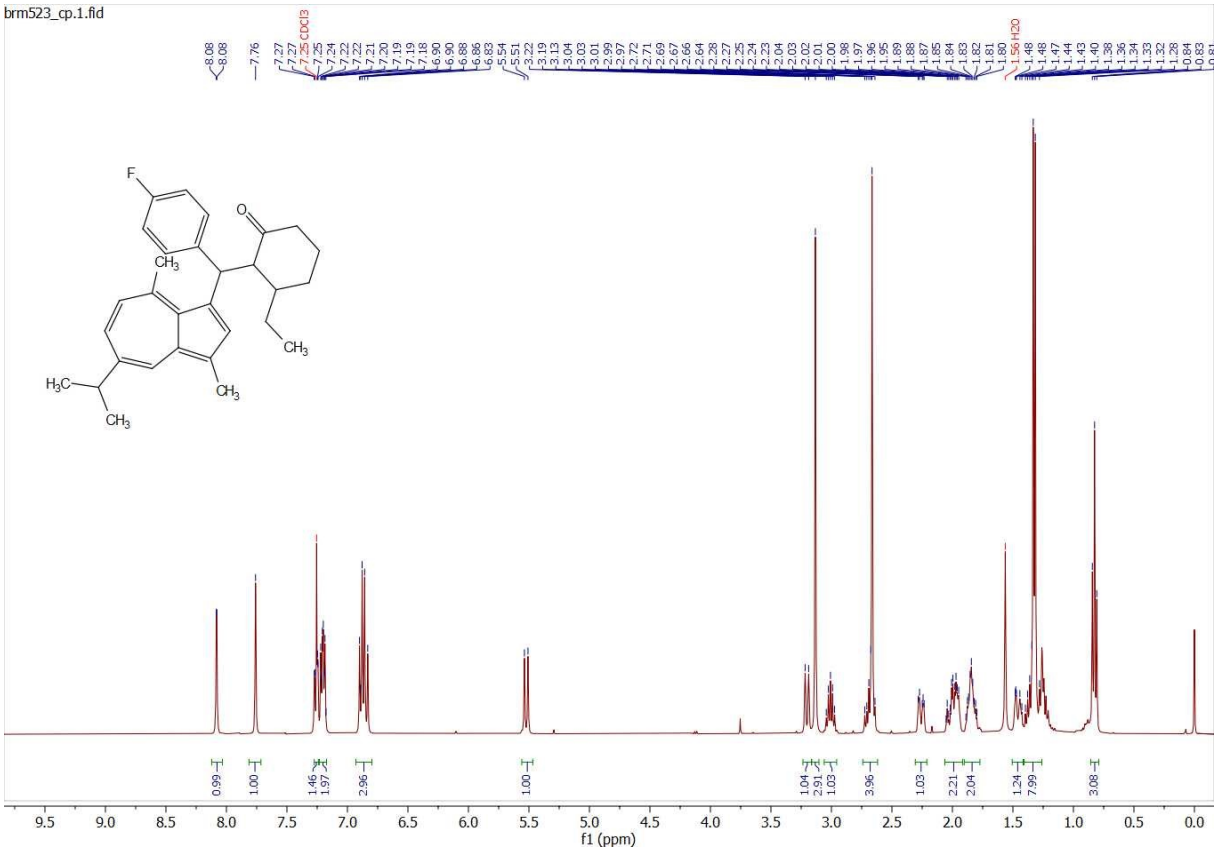


Figure S64. ^{1}H NMR spectrum of compound **5ae/diastereomer 2** (400 MHz, $CDCl_3$).

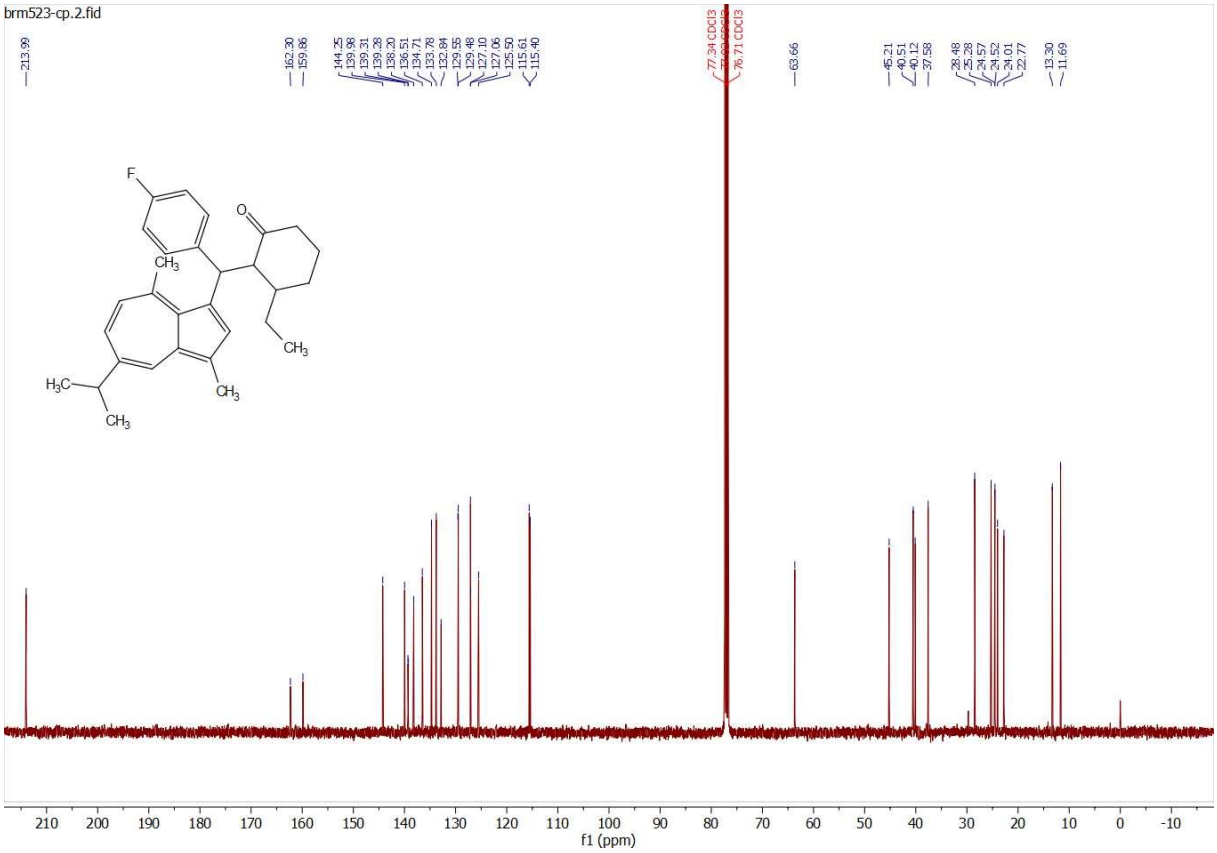


Figure S65. ^{13}C NMR spectrum of compound **5ae/diastereomer 2** (100 MHz, $CDCl_3$).

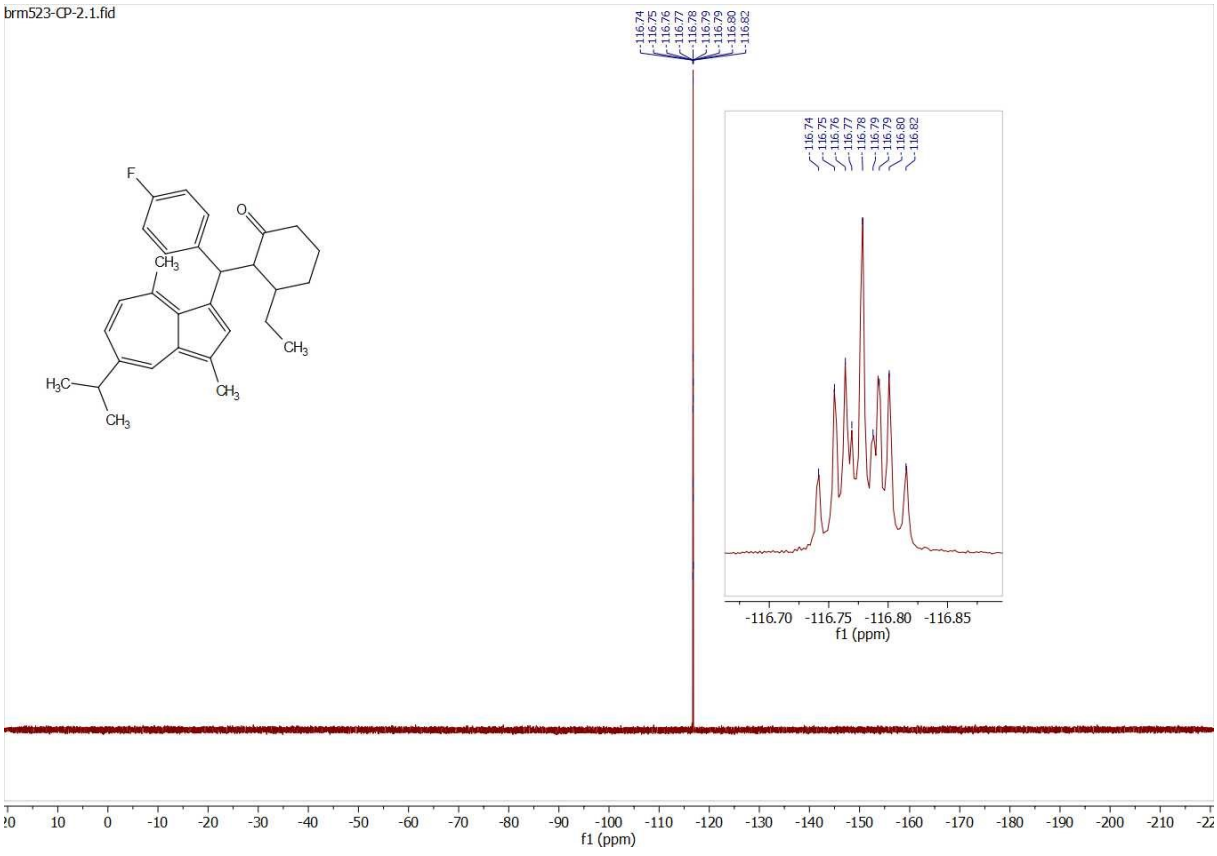


Figure S66. ^{19}F NMR spectrum of compound **5ae/diastereomer 2** (376 MHz, $CDCl_3$).

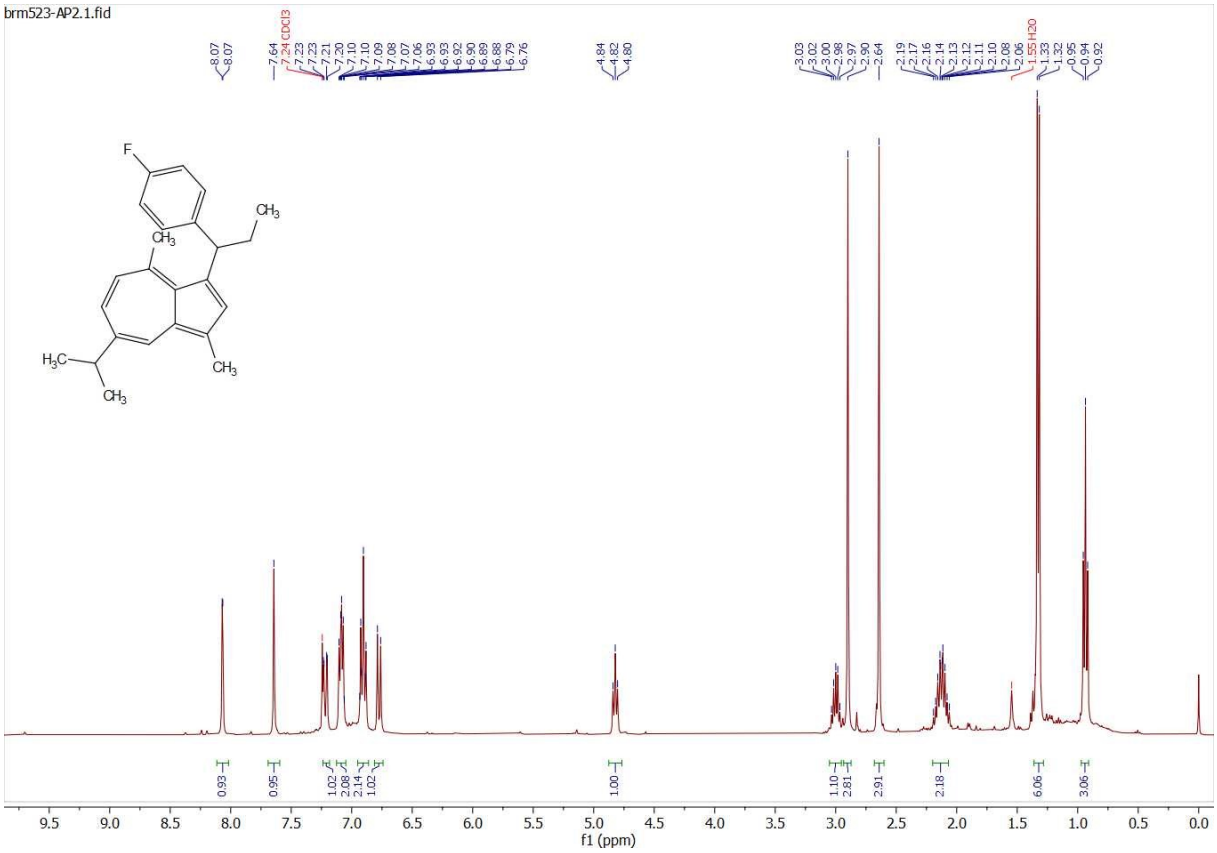


Figure S67. ^{1}H NMR spectrum of compound **6e** (400 MHz, $CDCl_3$).

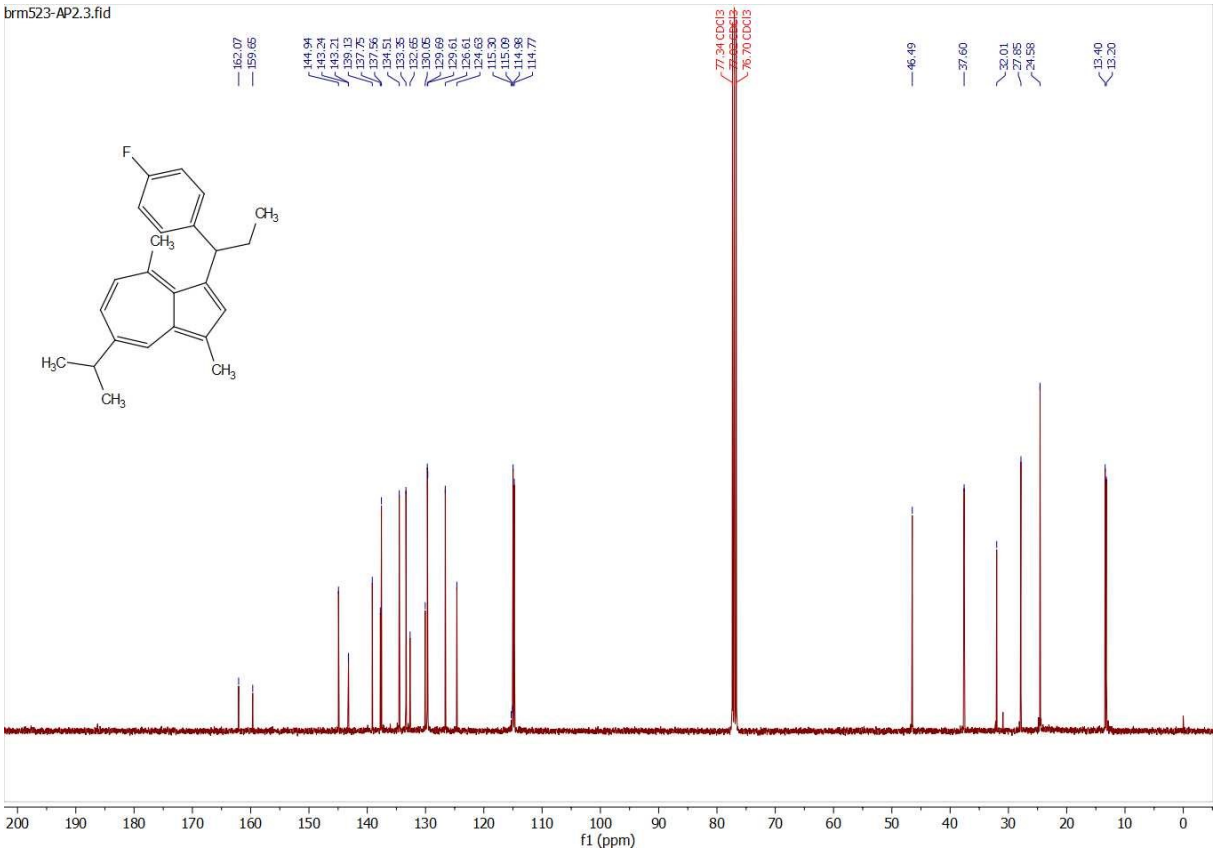


Figure S68. ^{13}C NMR spectrum of compound **6e** (100 MHz, $CDCl_3$).

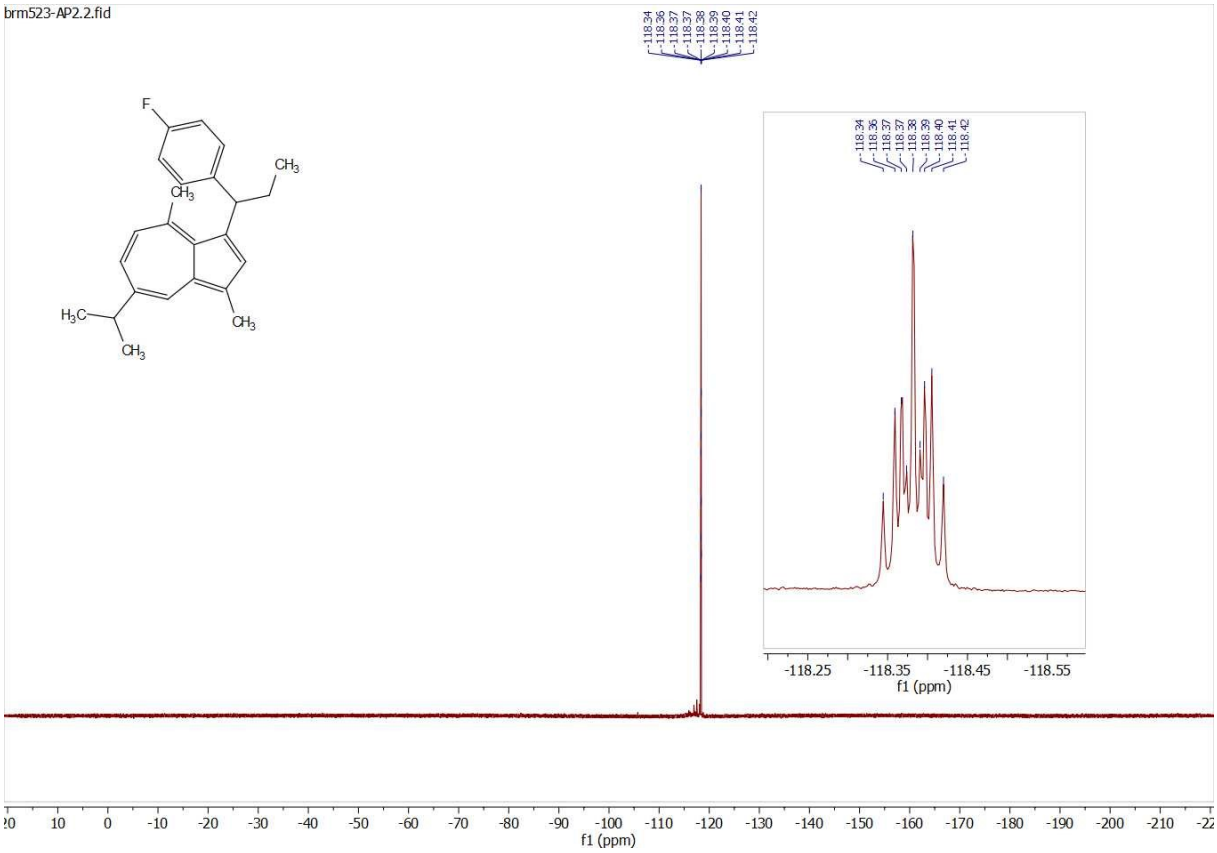


Figure S69. ^{19}F NMR spectrum of compound **6e** (376 MHz, $CDCl_3$).

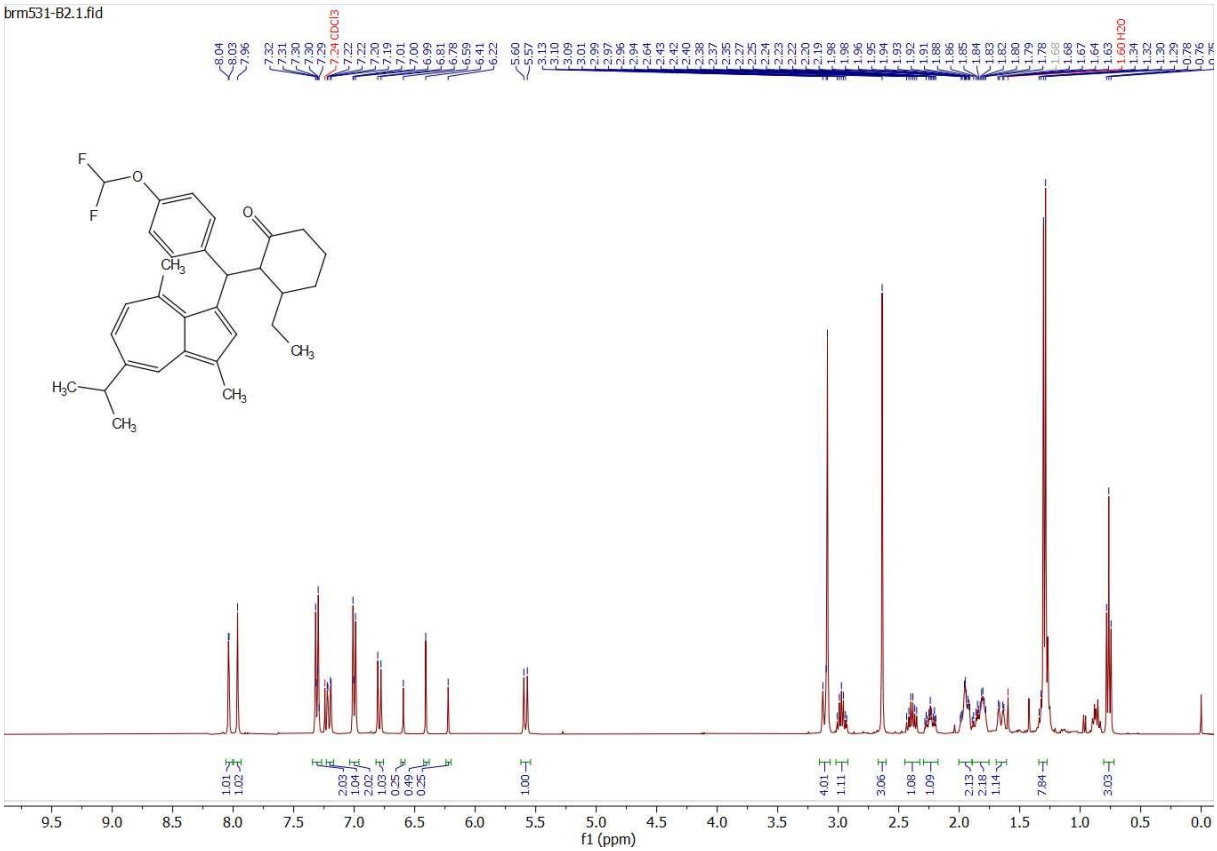


Figure S70. ^{1}H NMR spectrum of compound **5af/diastereomer 1** (400 MHz, $CDCl_3$).

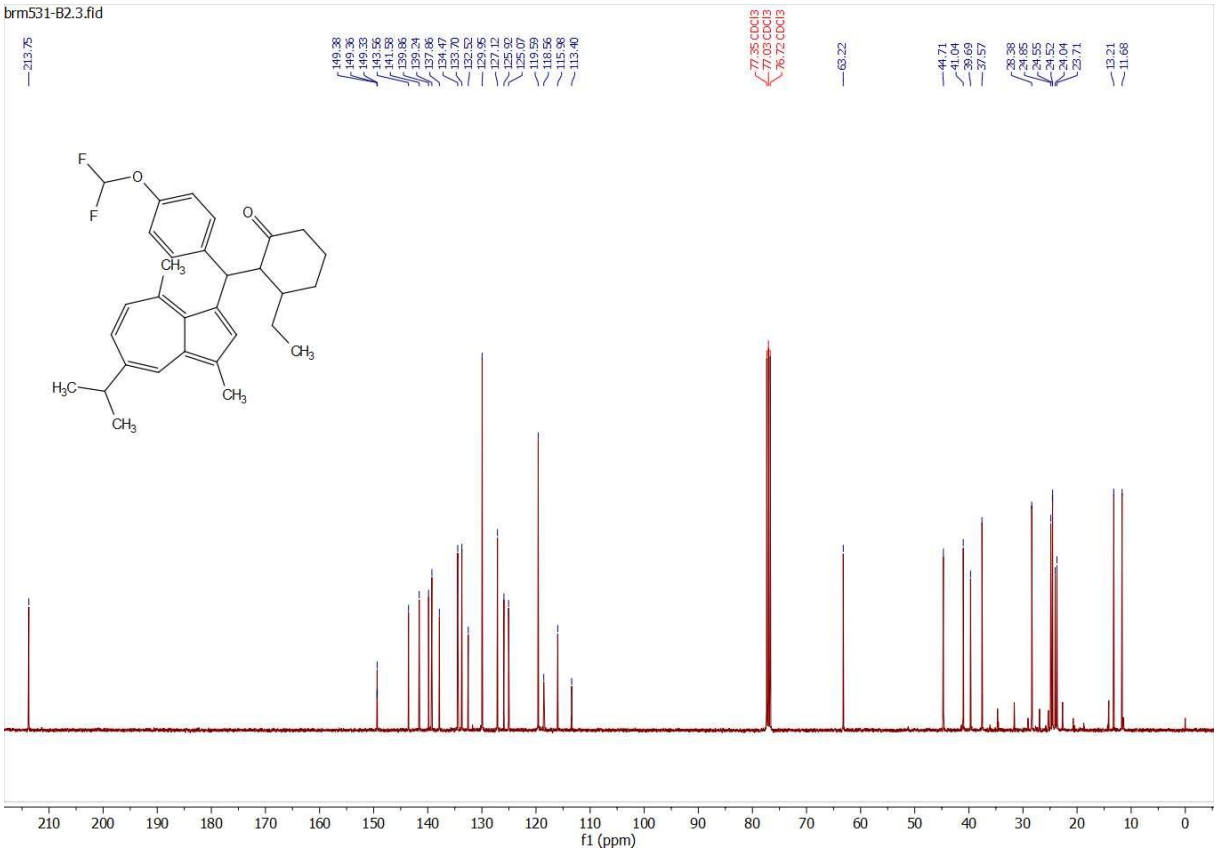


Figure S71. ^{13}C NMR spectrum of compound **5af/diastereomer 1** (100 MHz, $CDCl_3$).

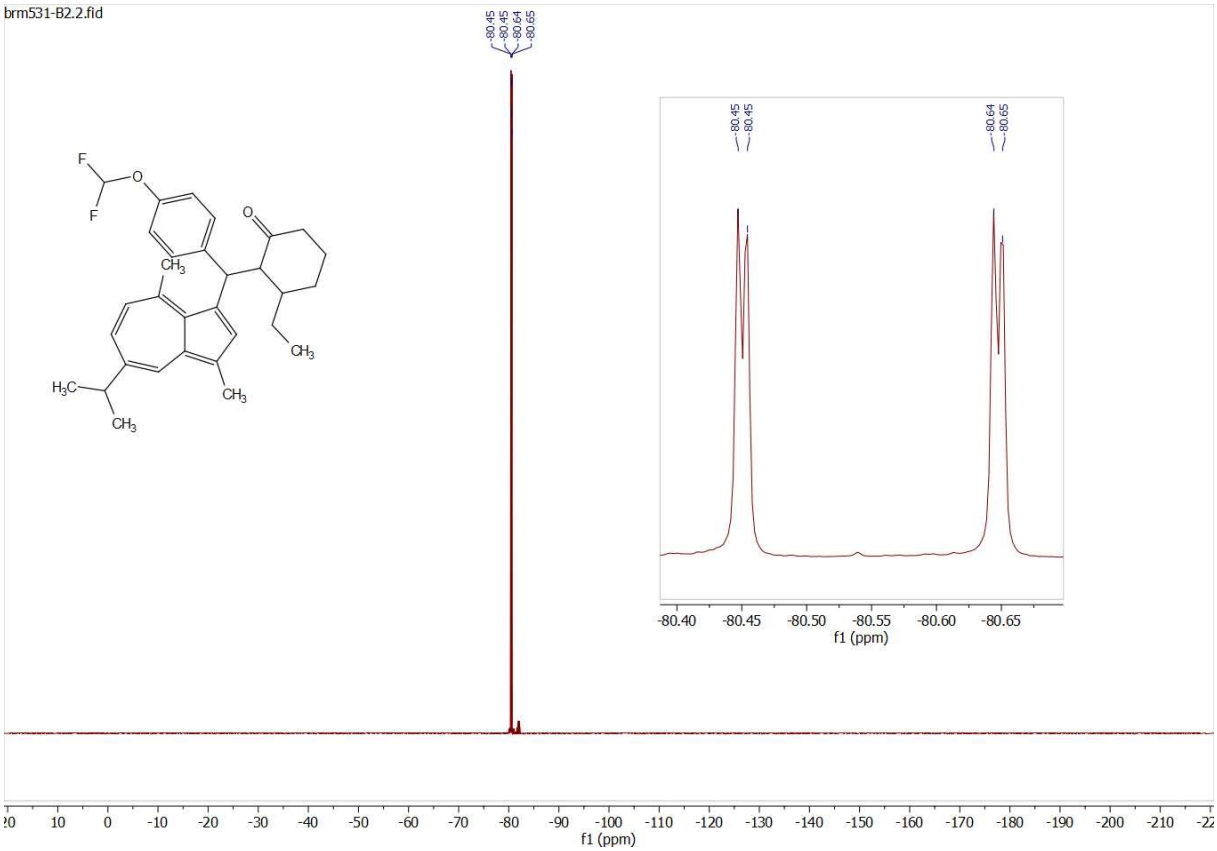


Figure S72. ^{19}F NMR spectrum of compound **5af/diastereomer 1** (376 MHz, $CDCl_3$).

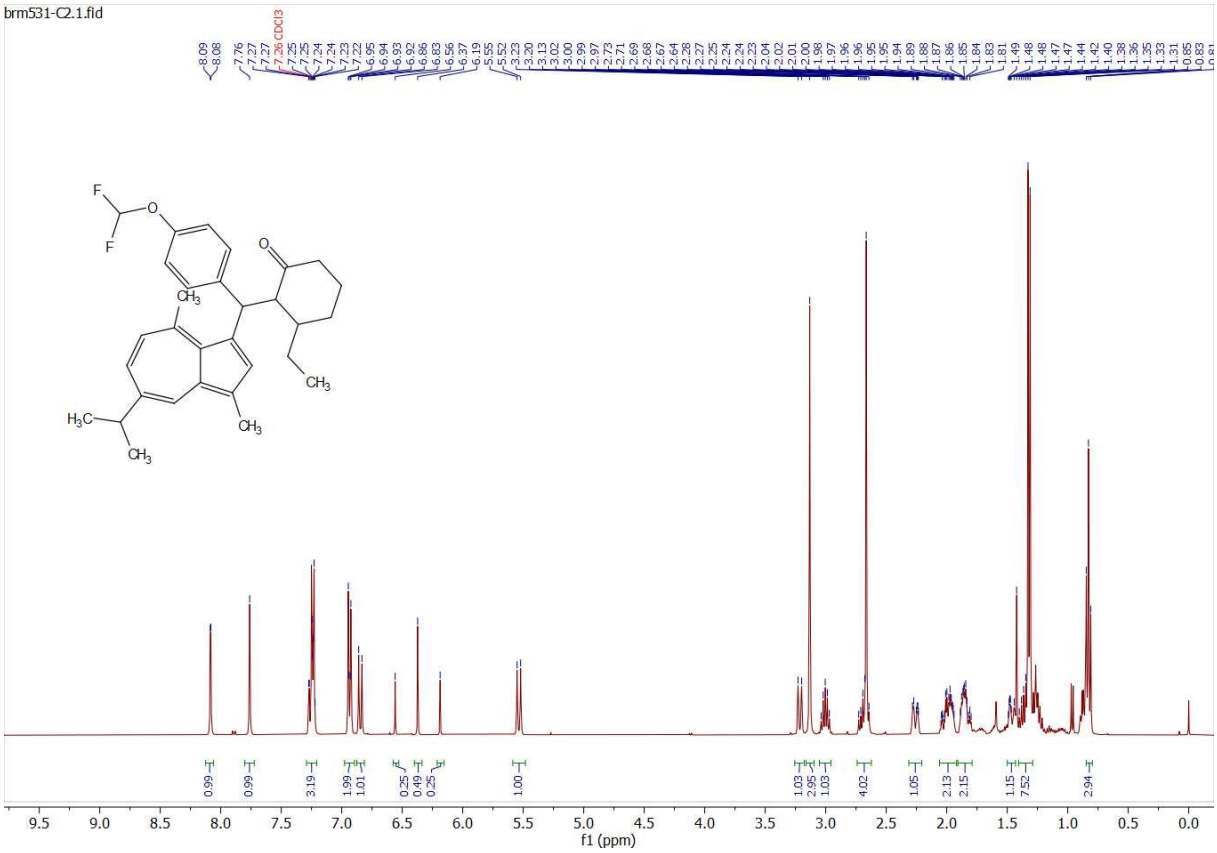


Figure S73. ^{1}H NMR spectrum of compound **5af/diastereomer 2** (400 MHz, $CDCl_3$).

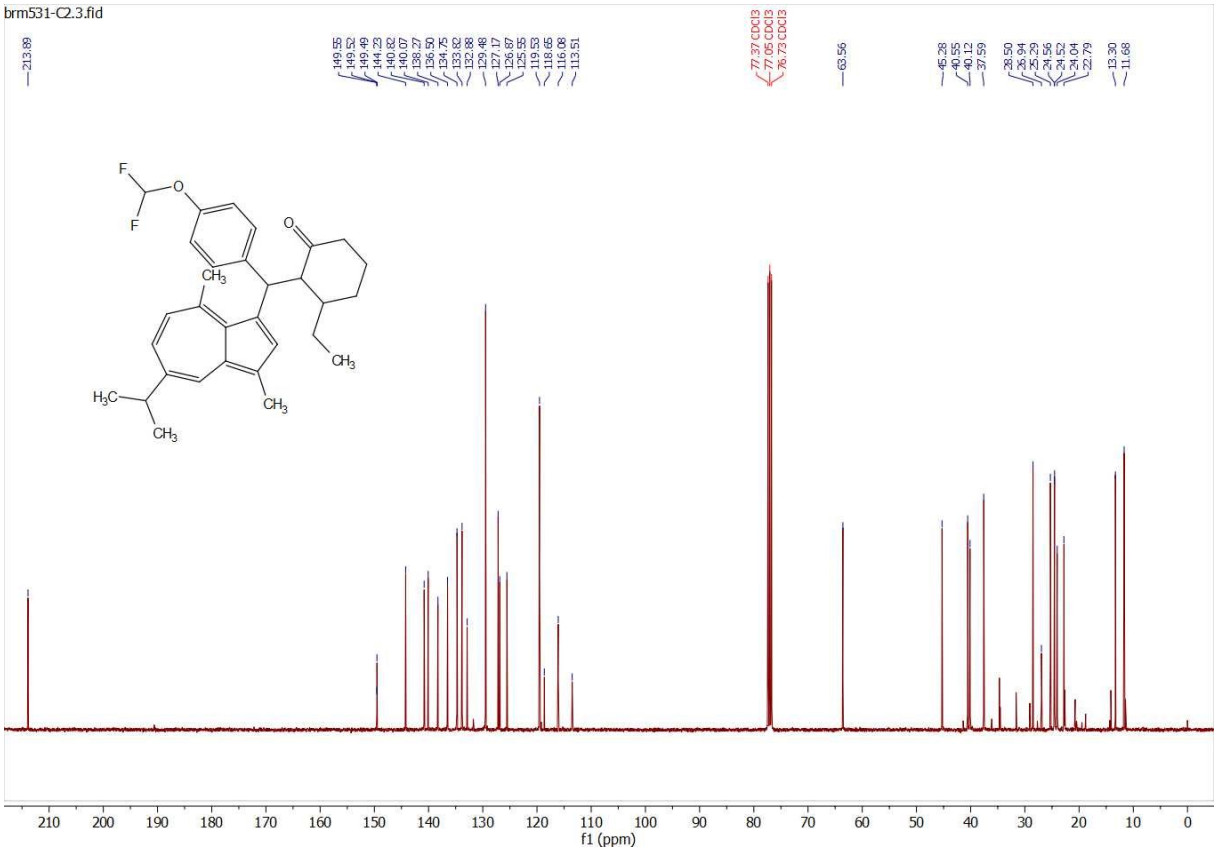


Figure S74. ^{13}C NMR spectrum of compound **5af/diastereomer 2** (100 MHz, $CDCl_3$).

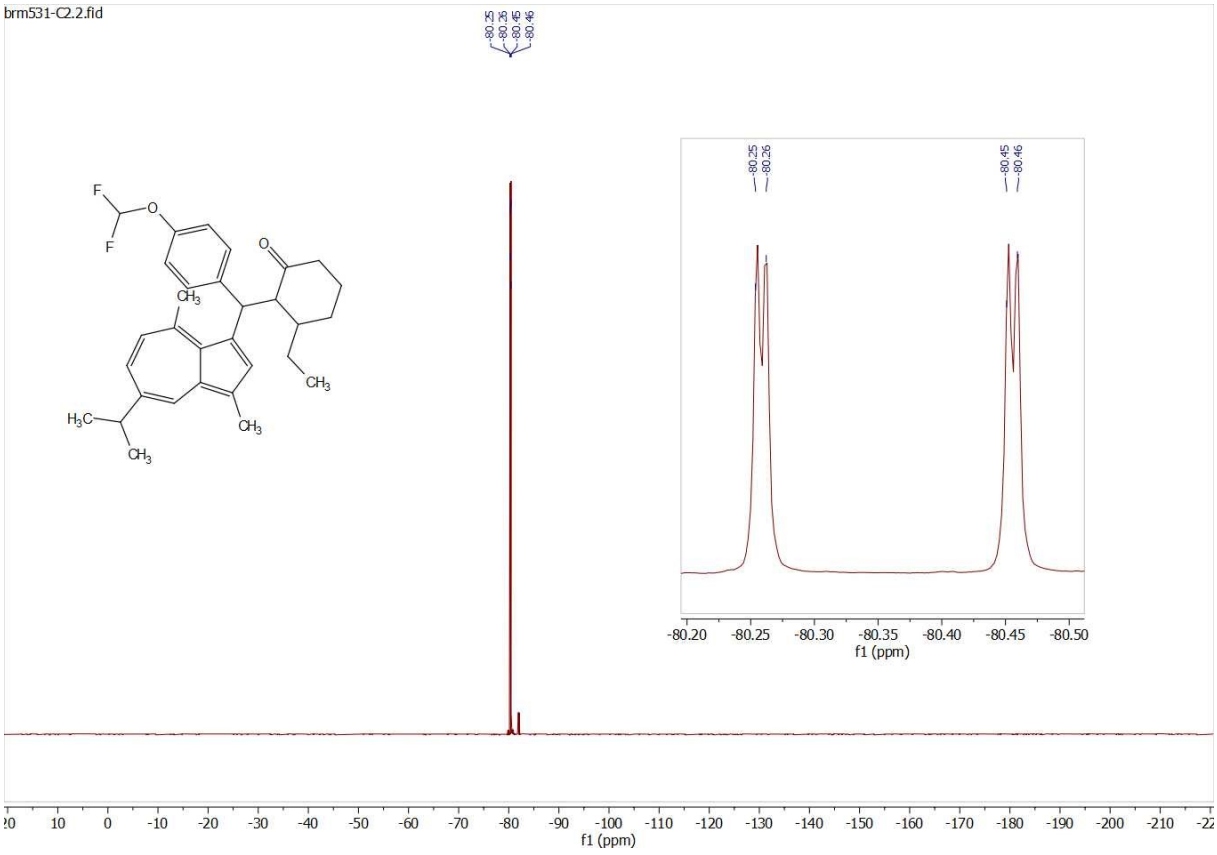


Figure S75. ^{19}F NMR spectrum of compound **5af/diastereomer 2** (376 MHz, $CDCl_3$).

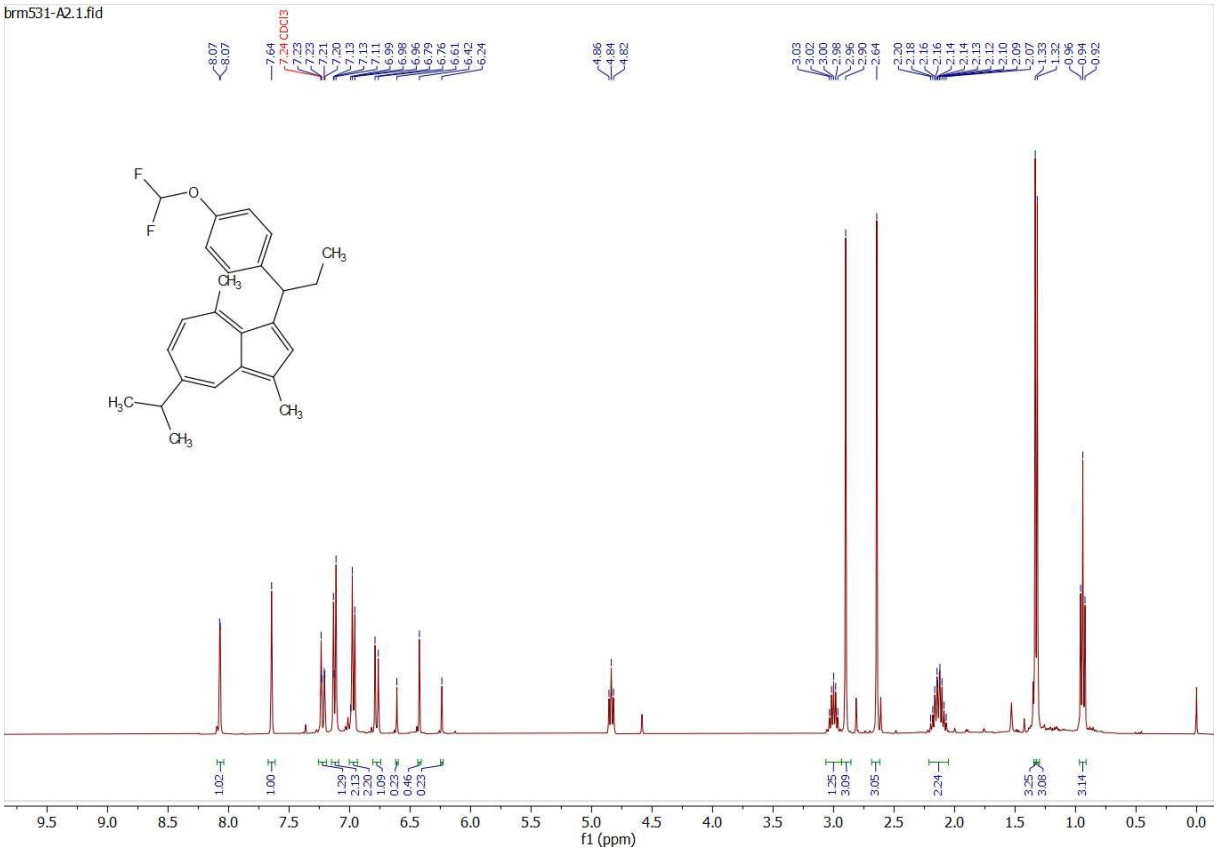


Figure S76. ^{1}H NMR spectrum of compound **6f** (400 MHz, $CDCl_3$).

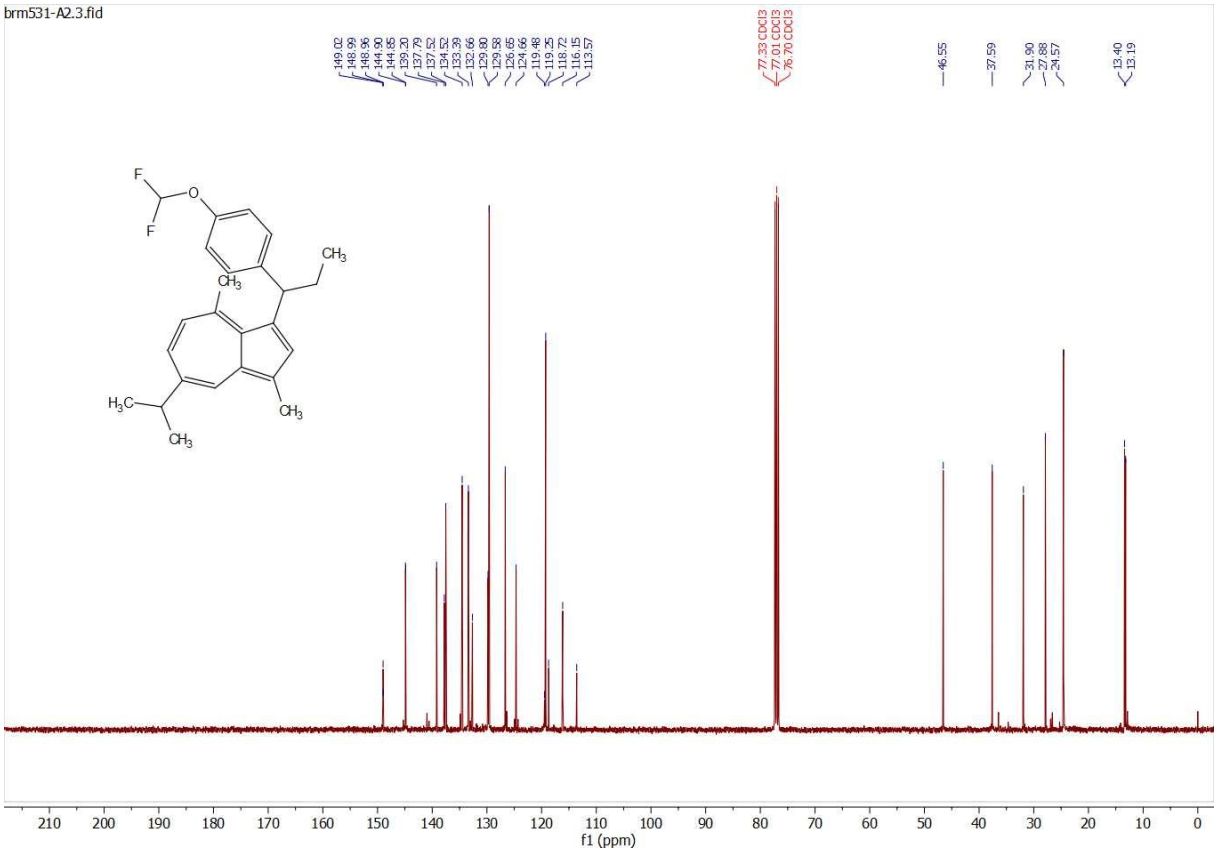


Figure S77. ^{13}C NMR spectrum of compound **6f** (100 MHz, $CDCl_3$).

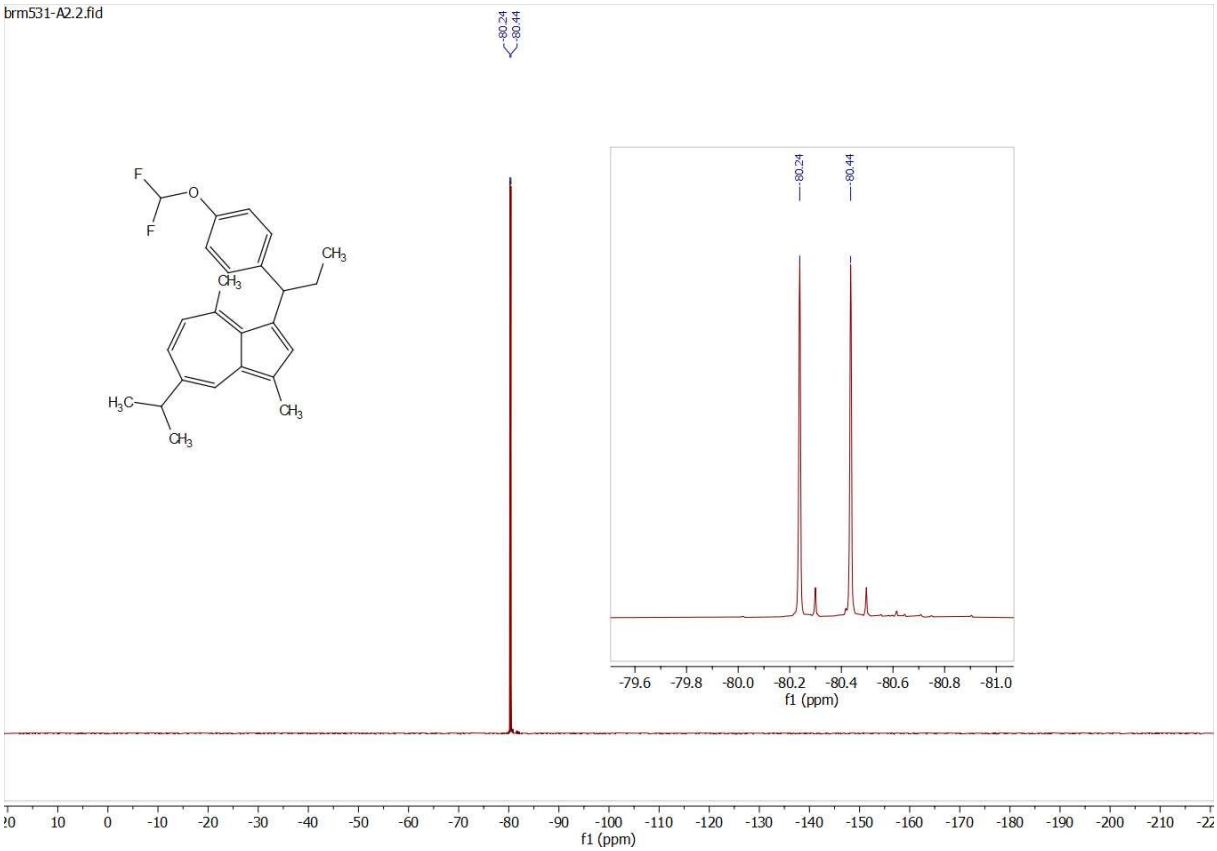


Figure S78. ^{19}F NMR spectrum of compound **6f** (376 MHz, $CDCl_3$).

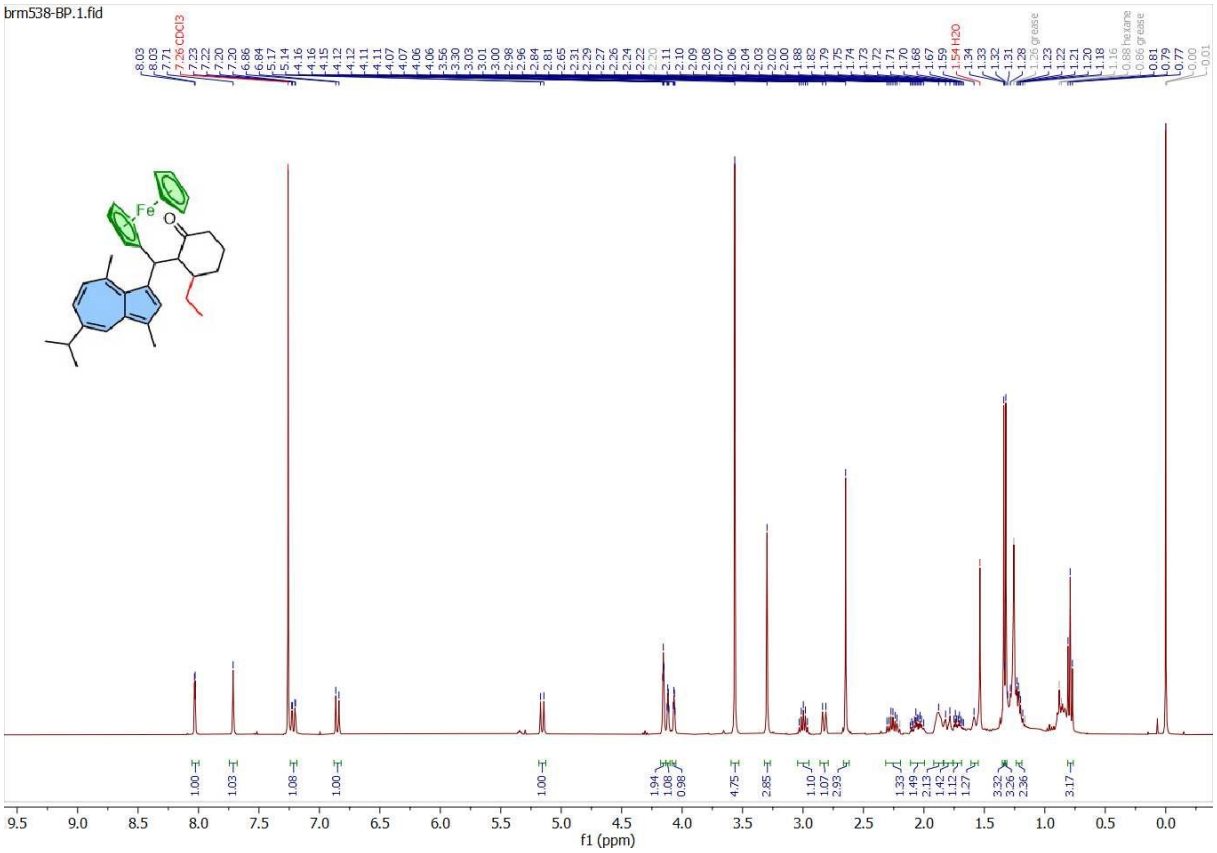


Figure S79. ^{1}H NMR spectrum of compound **5ag/diastereomer 1** (400 MHz, $CDCl_3$).

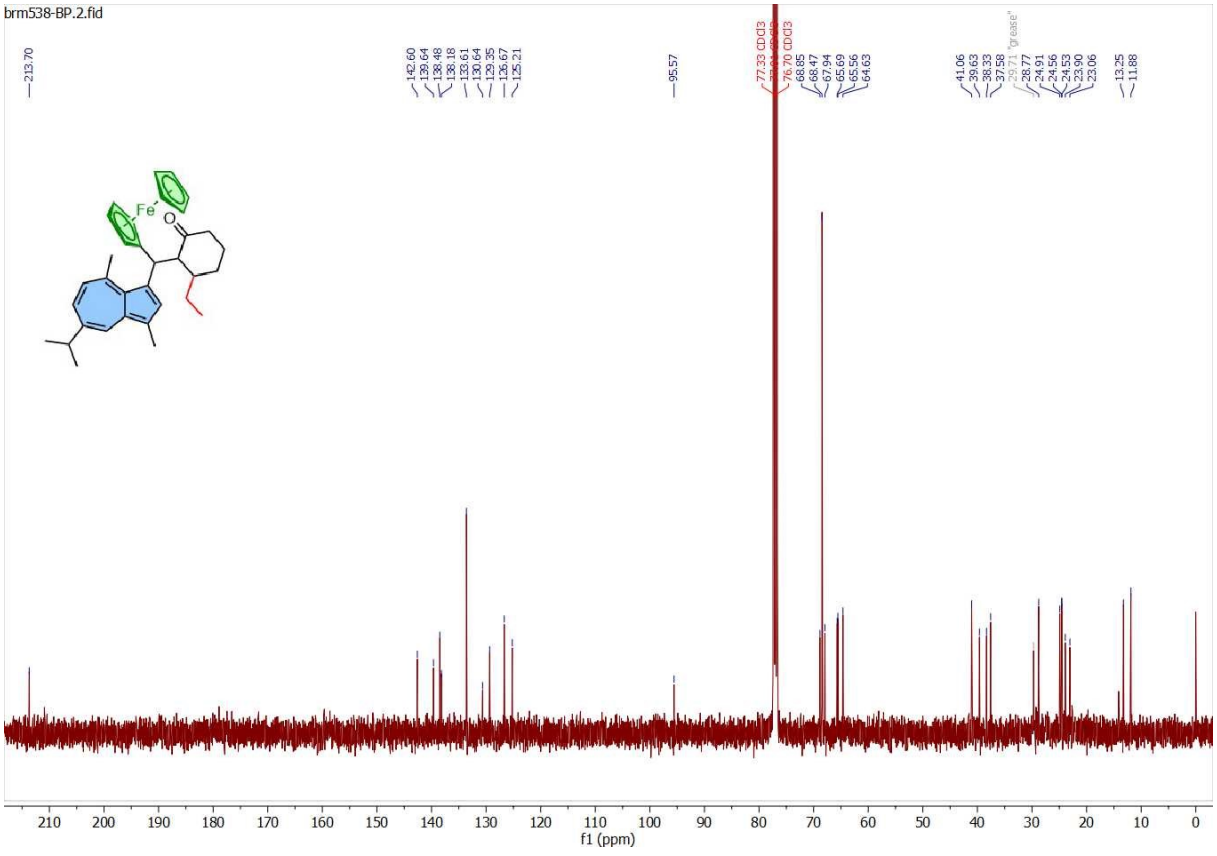


Figure S80. ^{13}C NMR spectrum of compound **5ag/diastereomer 1** (100 MHz, $CDCl_3$).

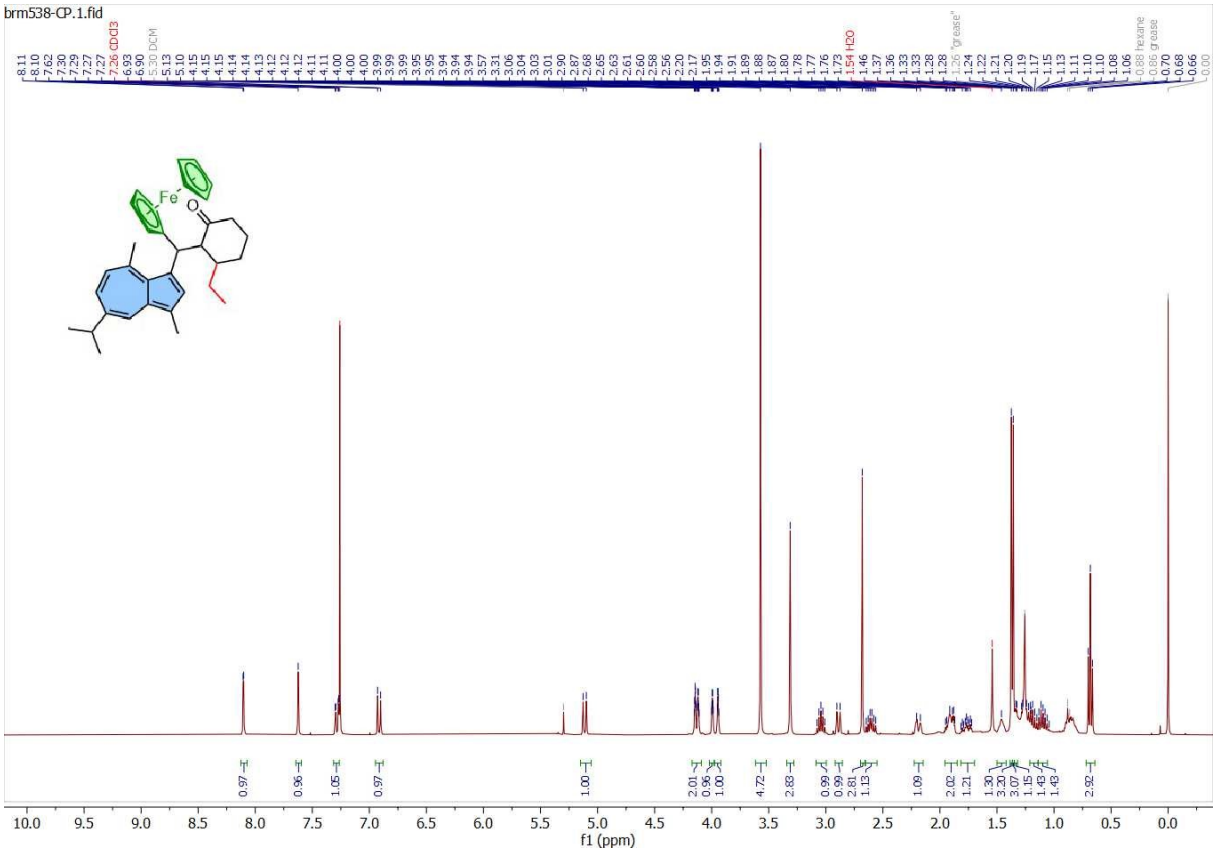


Figure S81. ^{1}H NMR spectrum of compound **5ag/diastereomer 2** (400 MHz, $CDCl_3$).

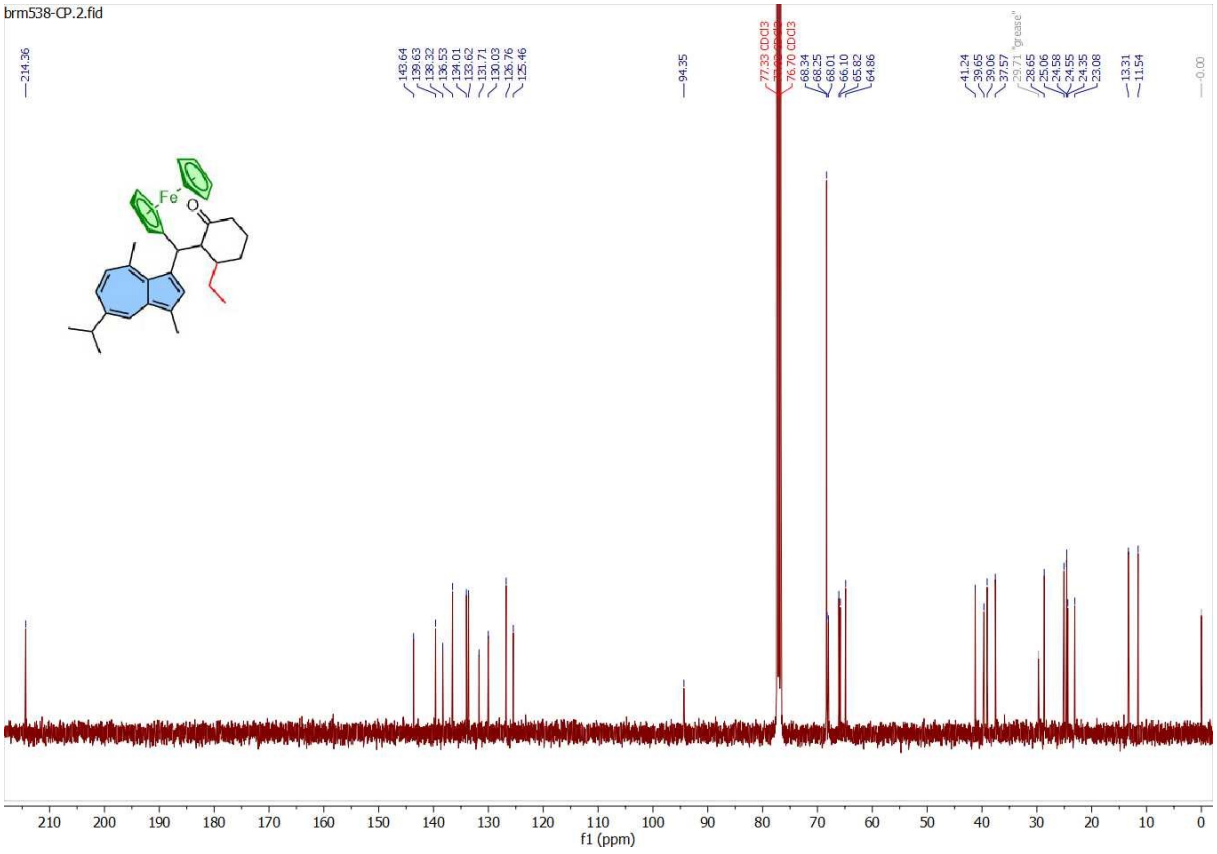


Figure S82. ^{13}C NMR spectrum of compound **5ag/diastereomer 2** (100 MHz, $CDCl_3$).

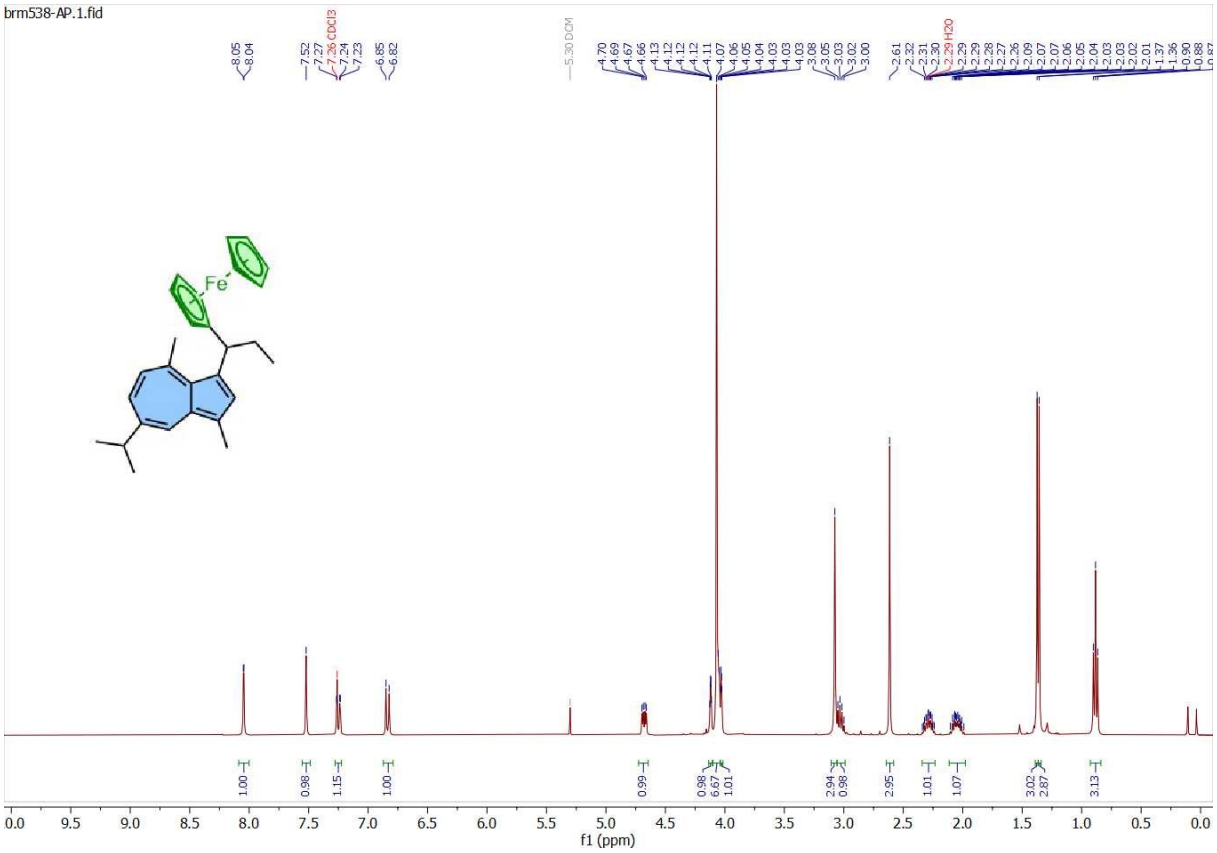


Figure S83. ^{1}H NMR spectrum of compound **6g** (400 MHz, $CDCl_3$).

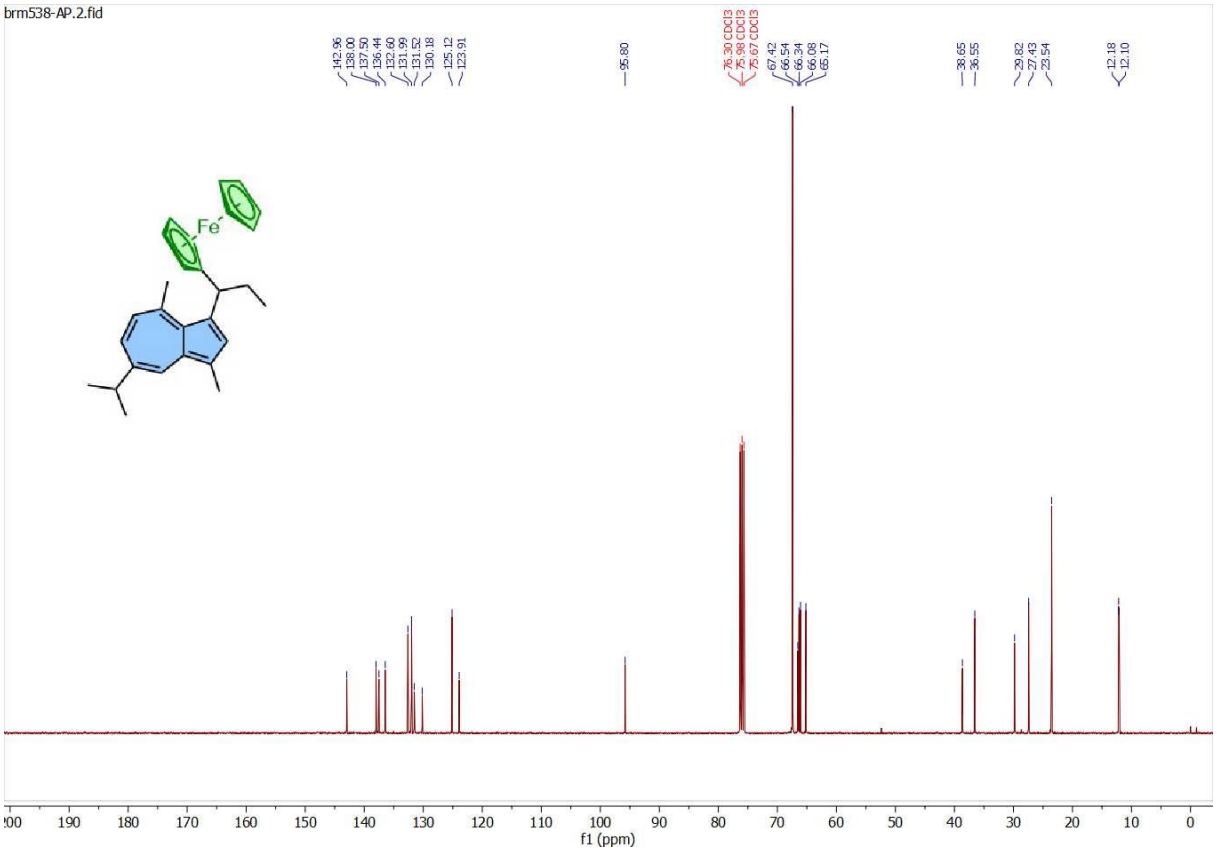


Figure S84. ^{13}C NMR spectrum of compound **6g** (100 MHz, $CDCl_3$).

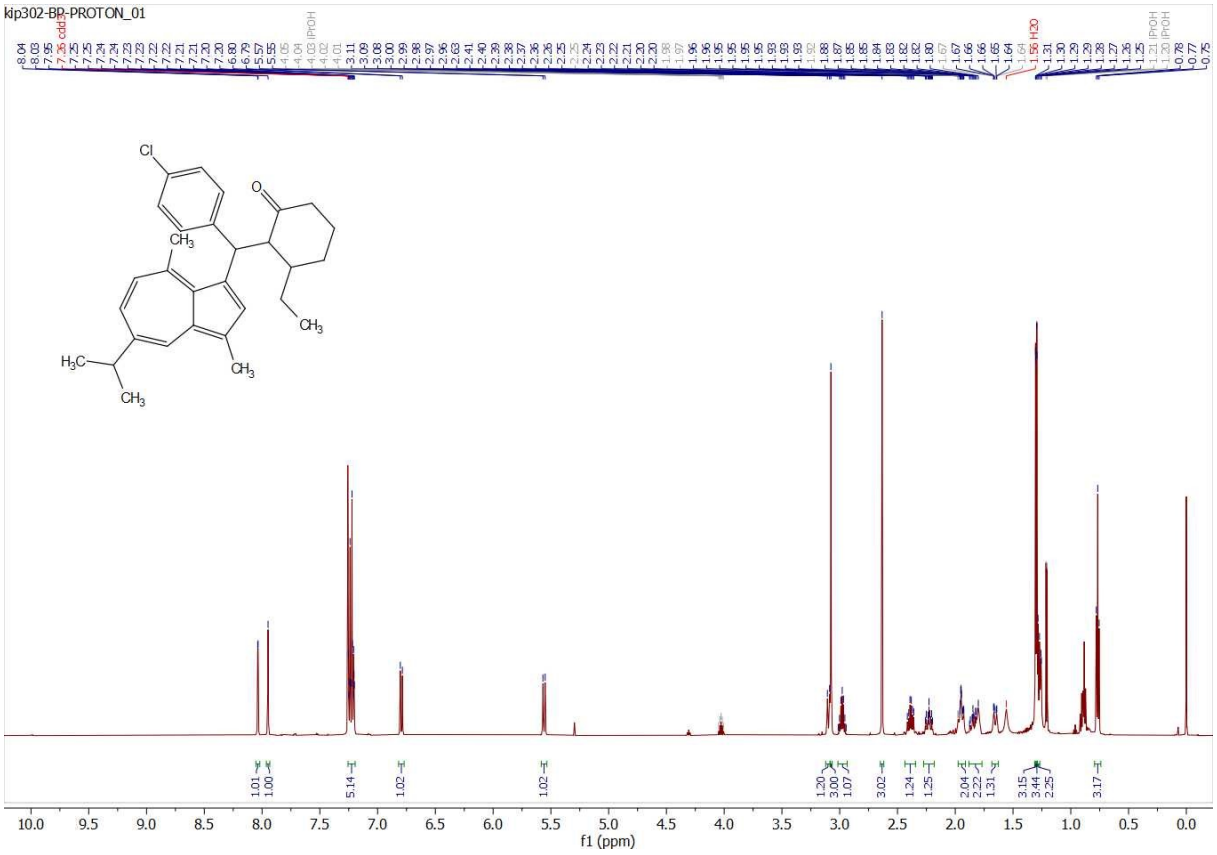


Figure S85. ^{1}H NMR spectrum of compound **5ah/diastereomer 1** (600 MHz, $CDCl_3$).

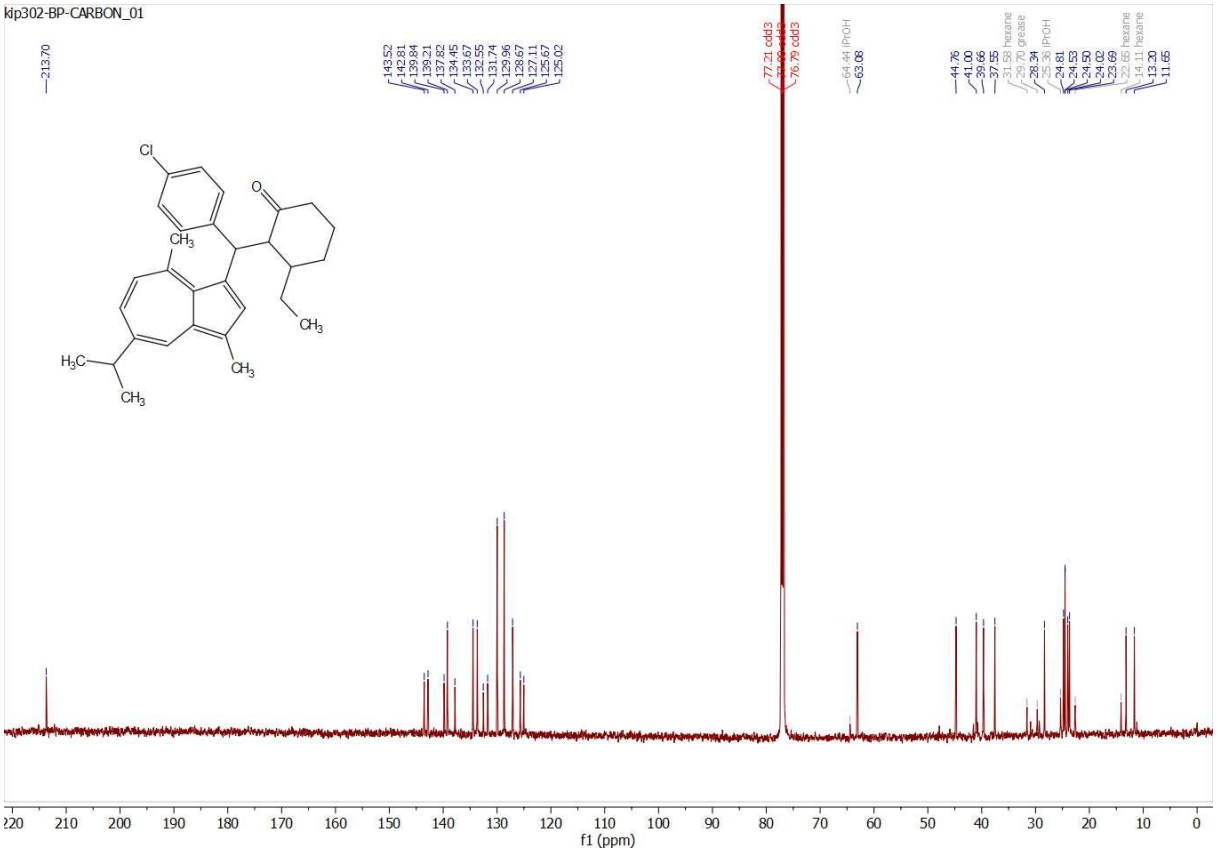


Figure S86. ^{13}C NMR spectrum of compound **5ah/diastereomer 1** (150 MHz, $CDCl_3$).

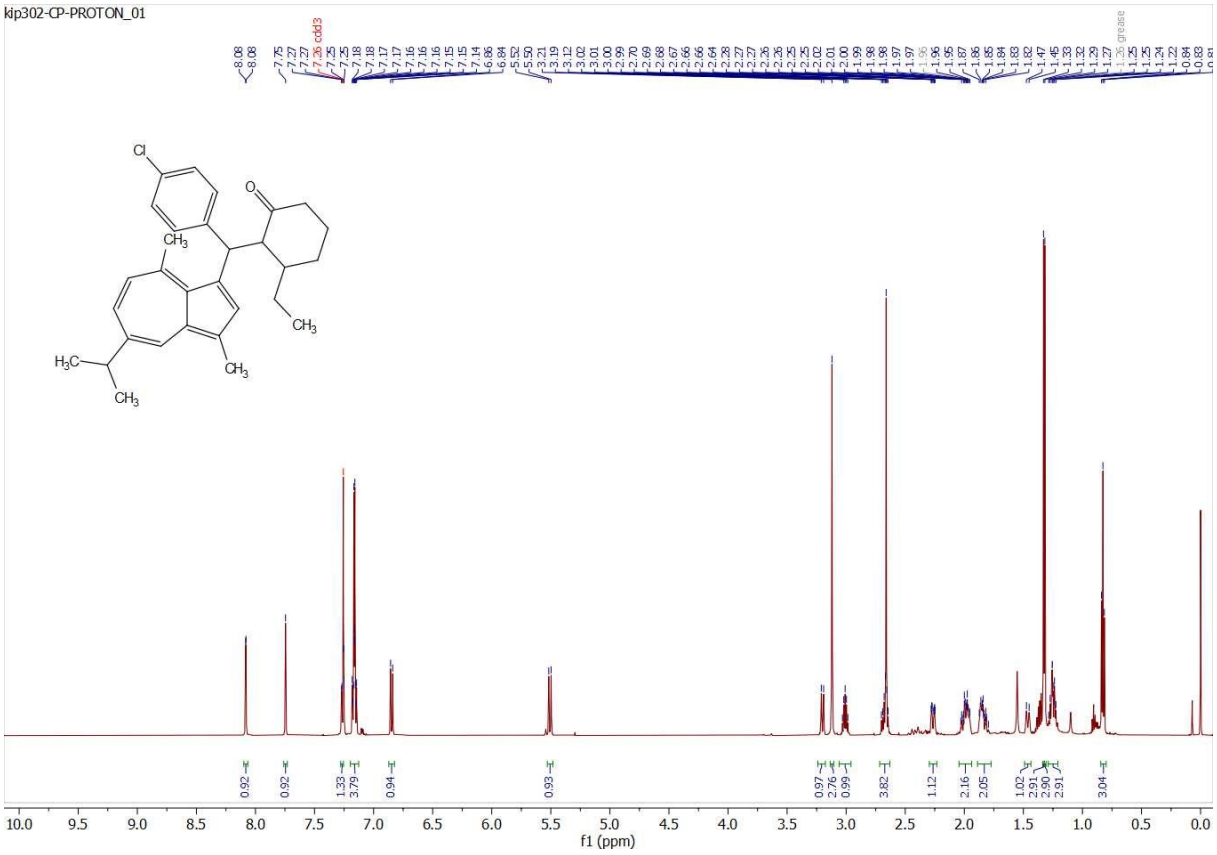


Figure S87. ^{1}H NMR spectrum of compound **5ah/diastereomer 2** (600 MHz, $CDCl_3$).

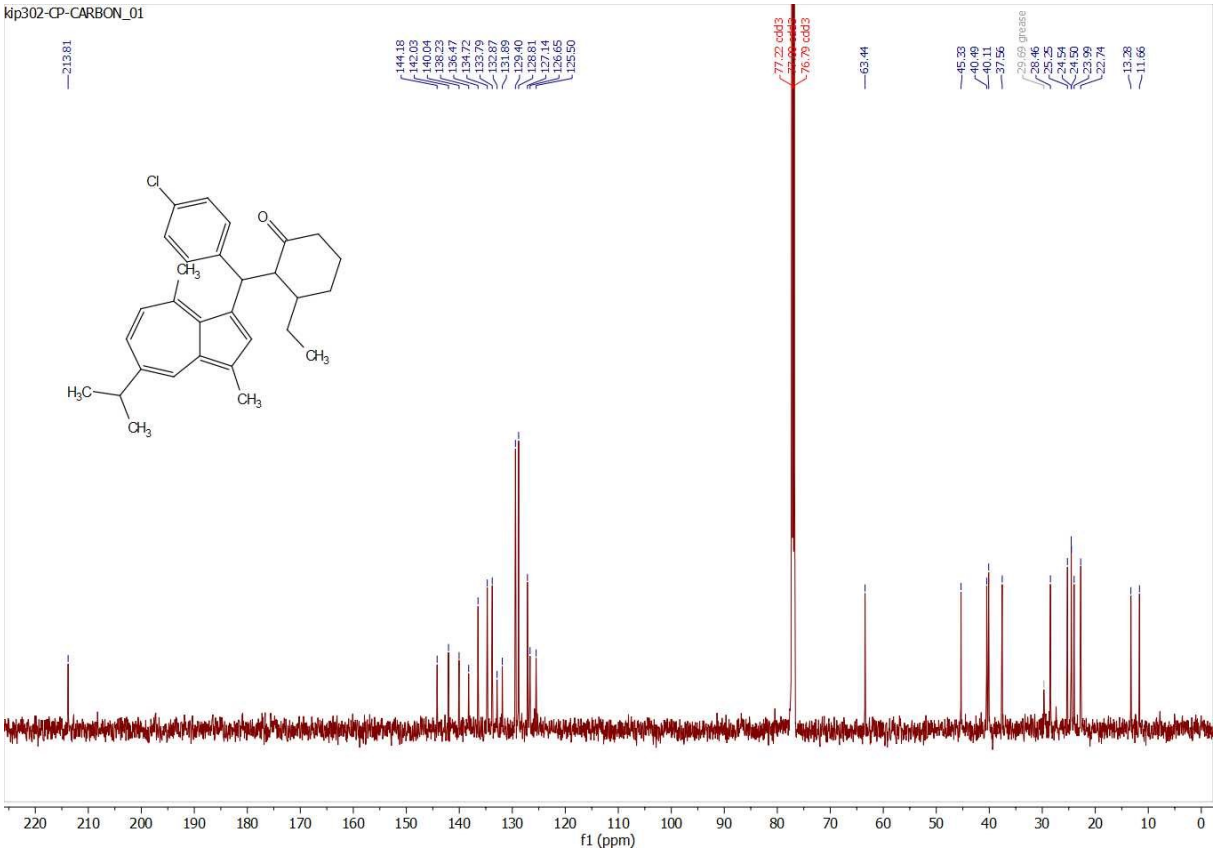


Figure S88. ^{13}C NMR spectrum of compound **5ah/diastereomer 2** (150 MHz, $CDCl_3$).

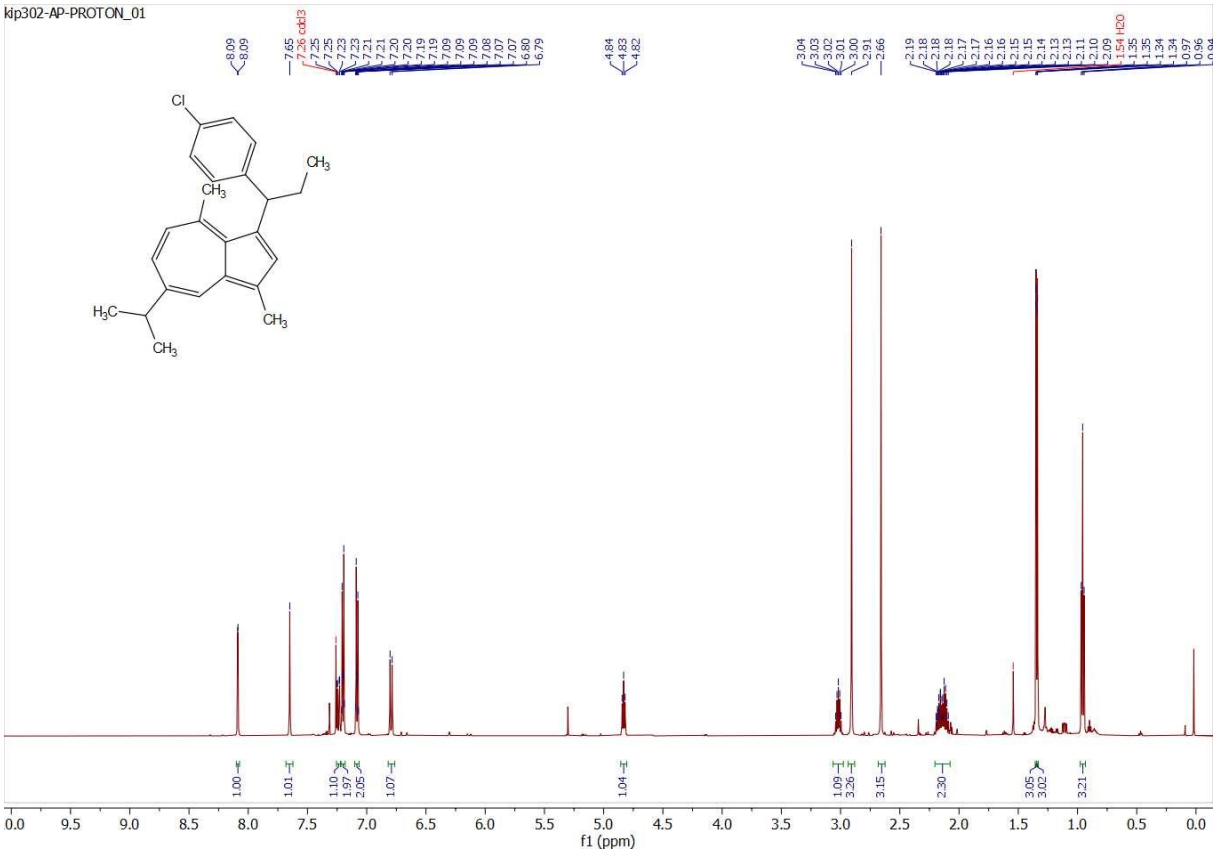


Figure S89. ^{1}H NMR spectrum of compound **6h** (600 MHz, $CDCl_3$).

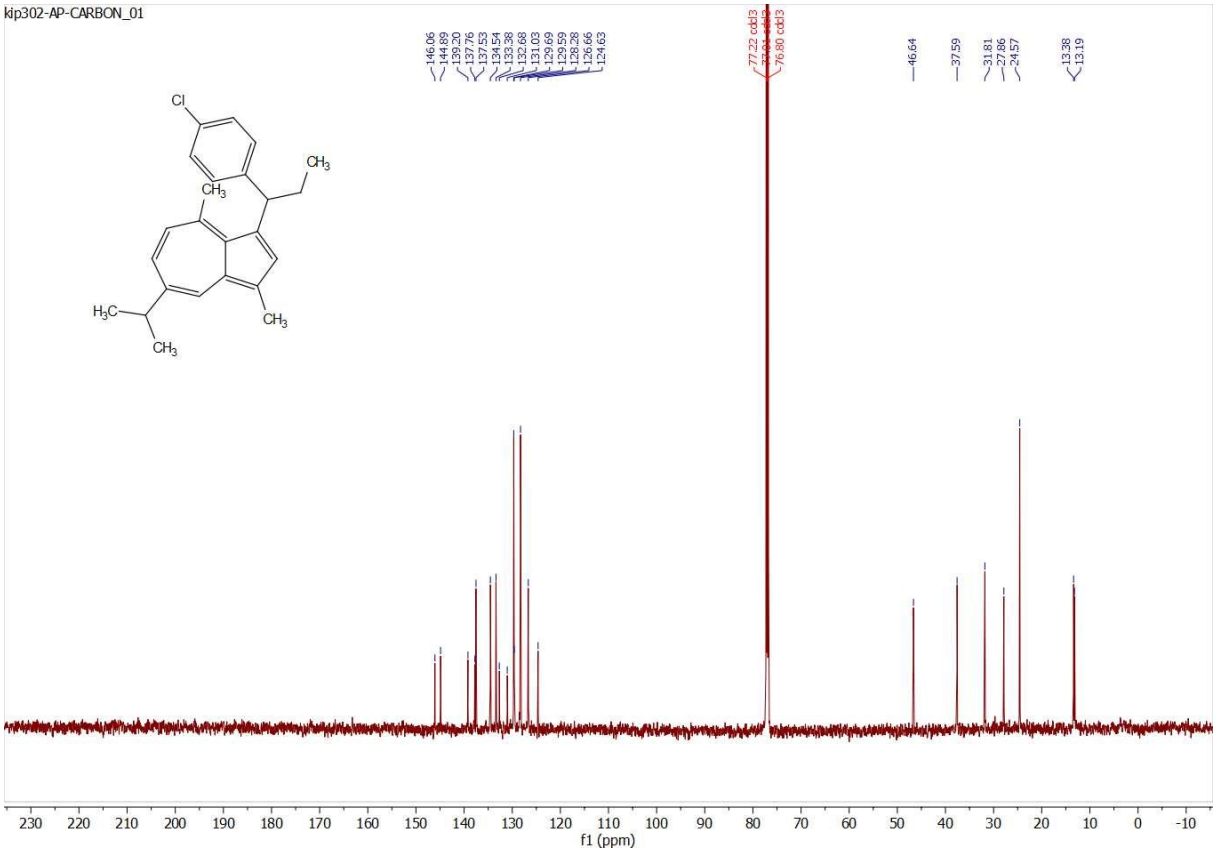


Figure S90. ^{13}C NMR spectrum of compound **6h** (150 MHz, $CDCl_3$).

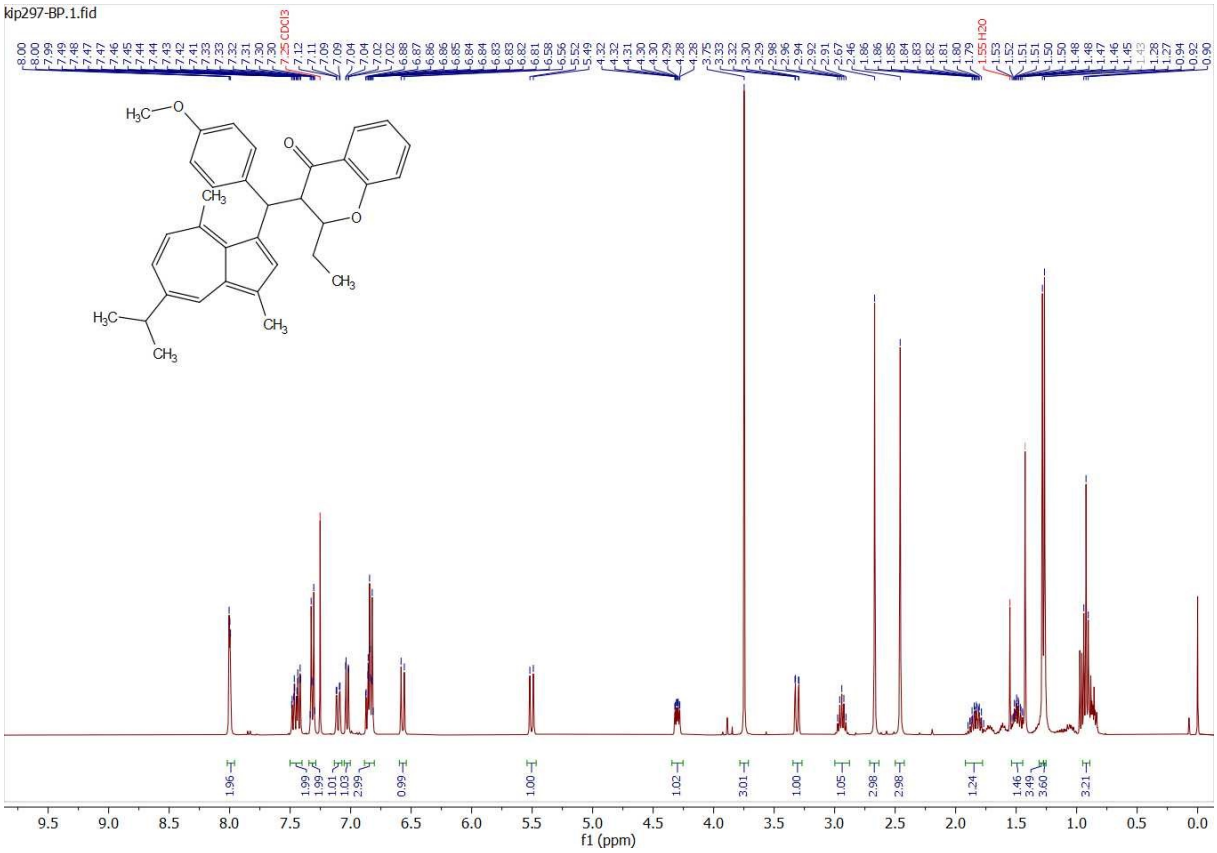


Figure S91. ^{1}H NMR spectrum of compound **5bb/diastereomer 1** (400 MHz, $CDCl_3$).

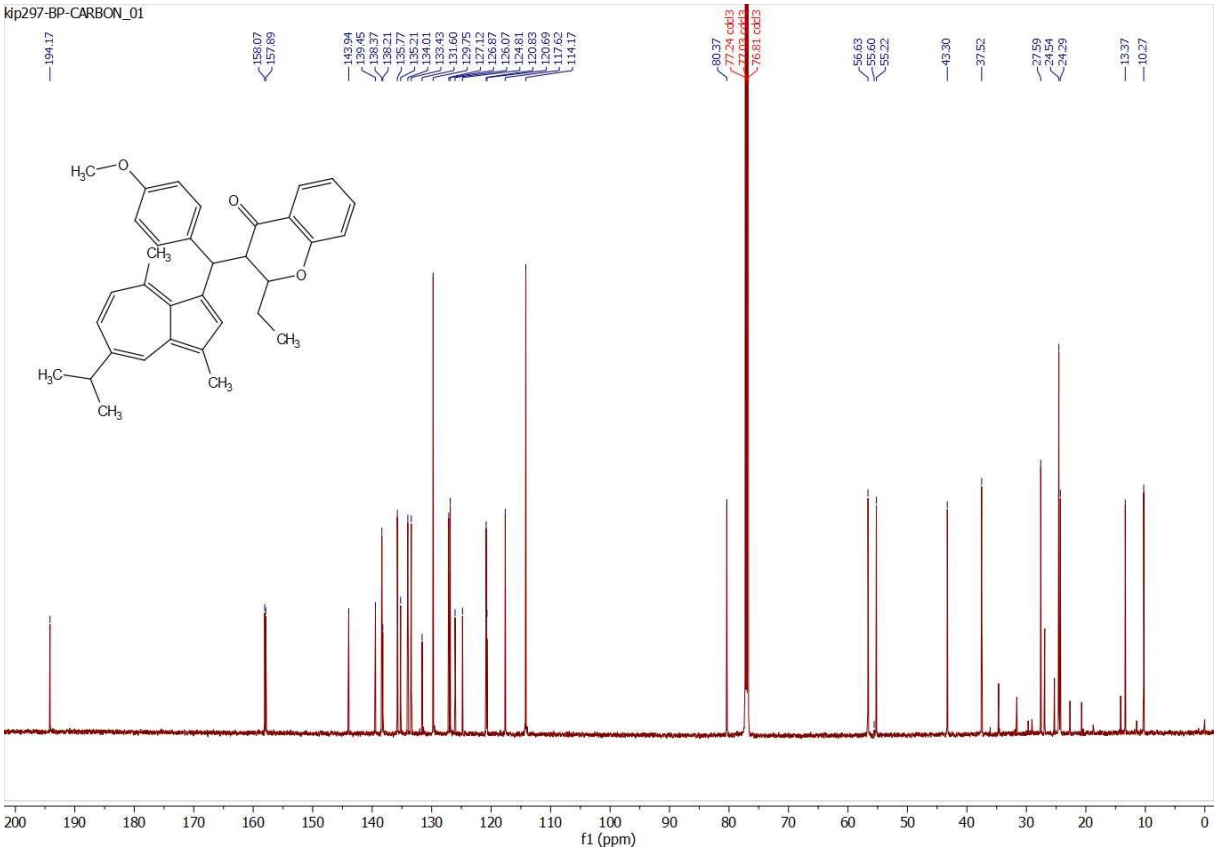


Figure S92. ^{13}C NMR spectrum of compound **5bb/diastereomer 1** (150 MHz, $CDCl_3$).

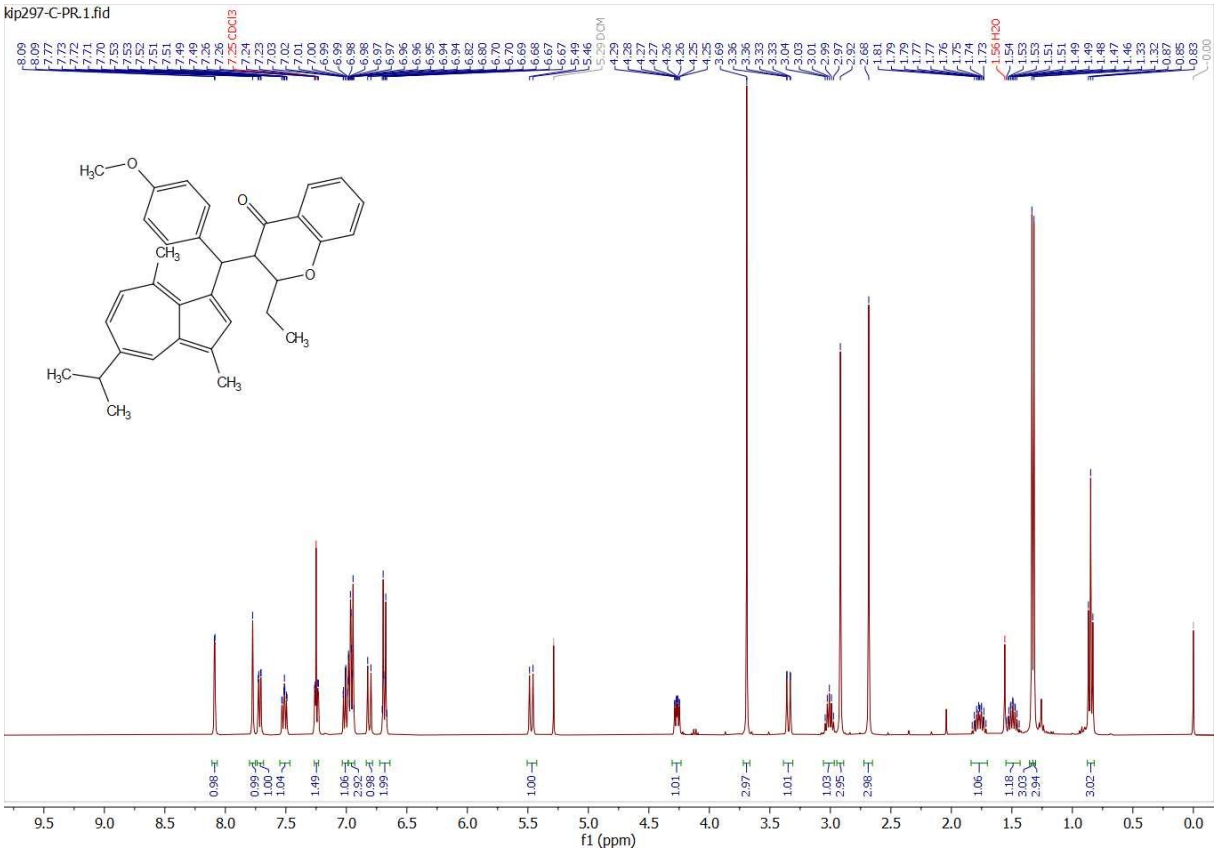


Figure S93. ^{1}H NMR spectrum of compound **5bb/diastereomer 2** (400 MHz, $CDCl_3$).

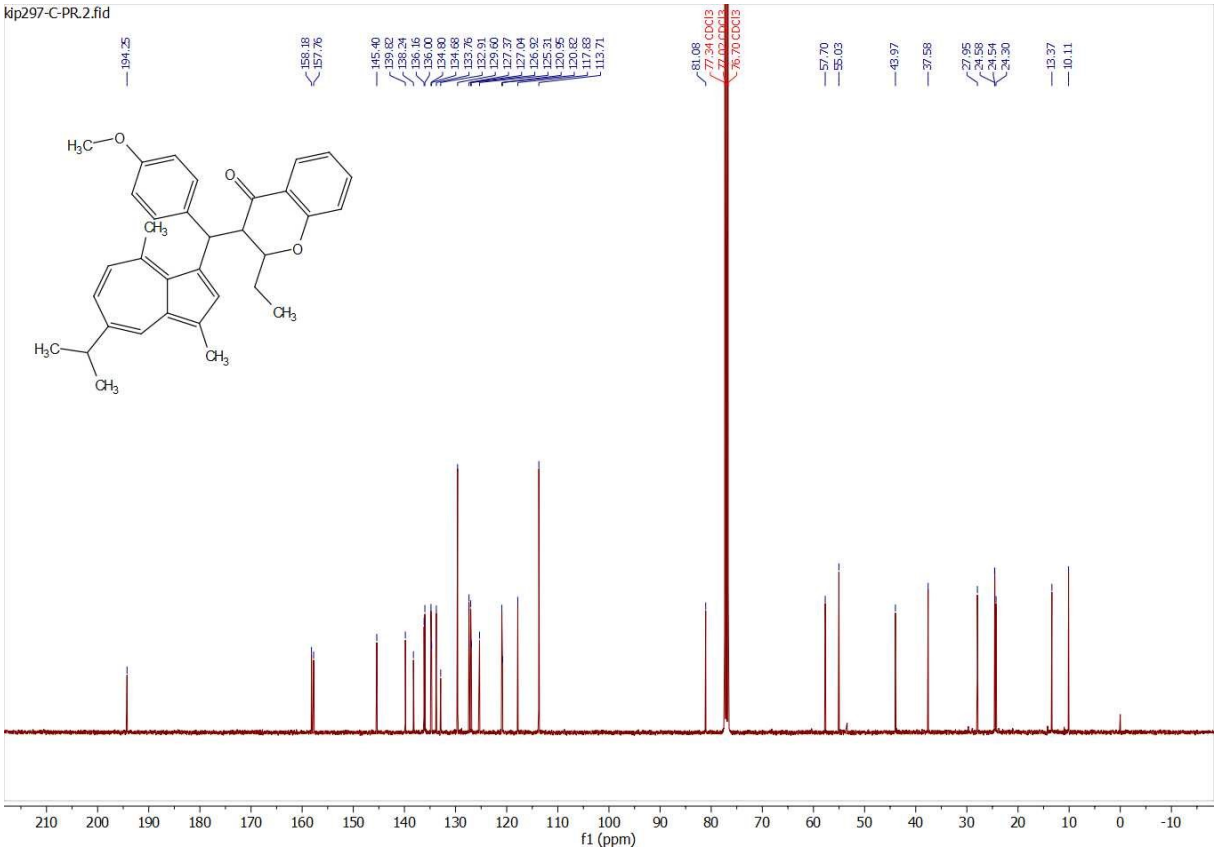


Figure S94. ^{13}C NMR spectrum of compound **5bb/diastereomer 2** (100 MHz, $CDCl_3$).

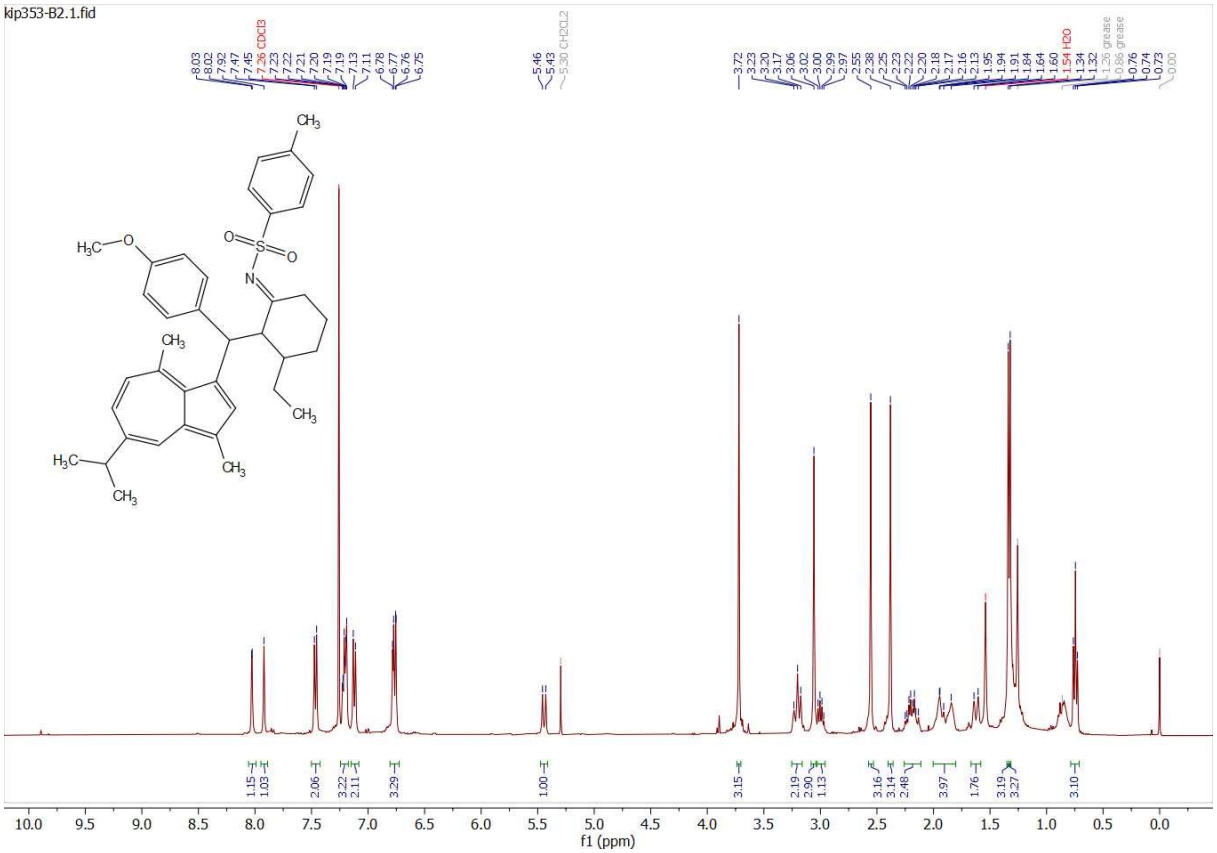


Figure S95. ^{1}H NMR spectrum of compound **5cb/diastereomer 1** (400 MHz, $CDCl_3$).

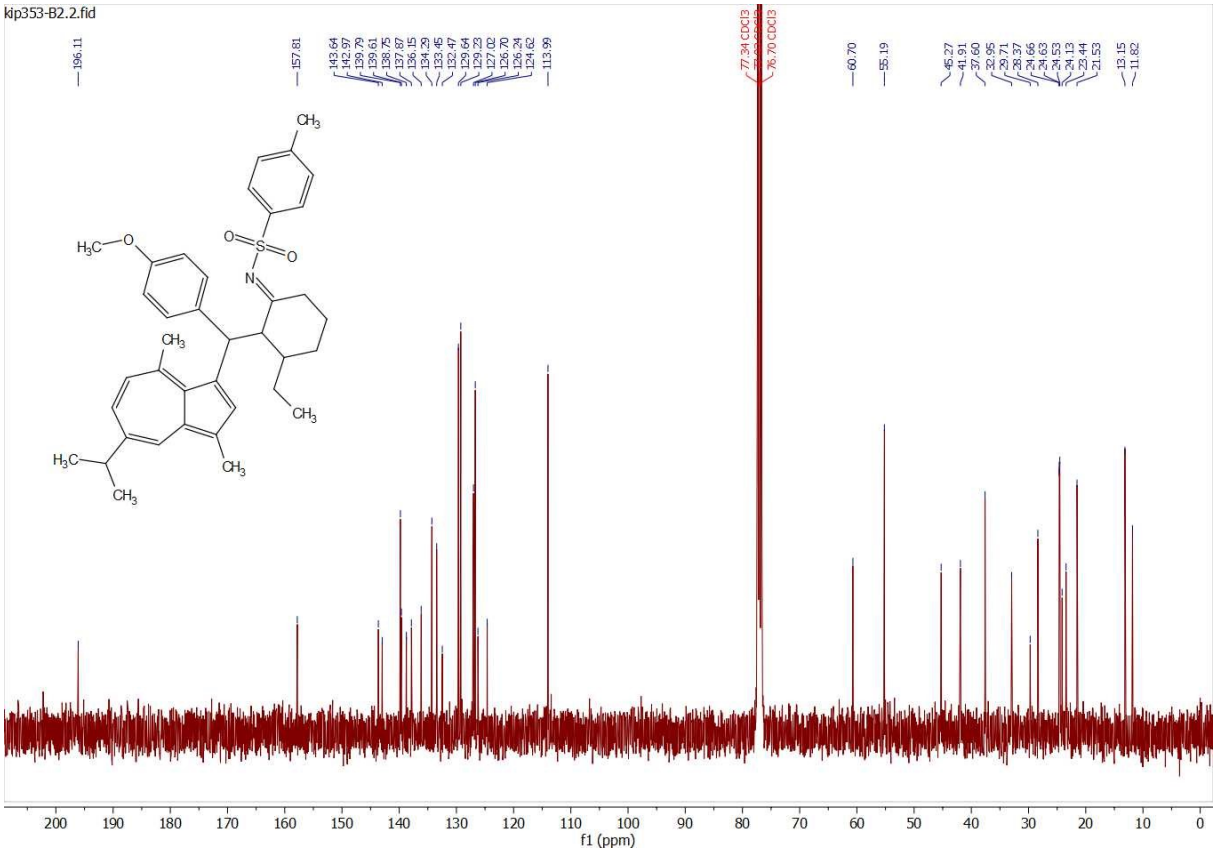


Figure S96. ^{13}C NMR spectrum of compound **5cb/diastereomer 1** (100 MHz, $CDCl_3$).

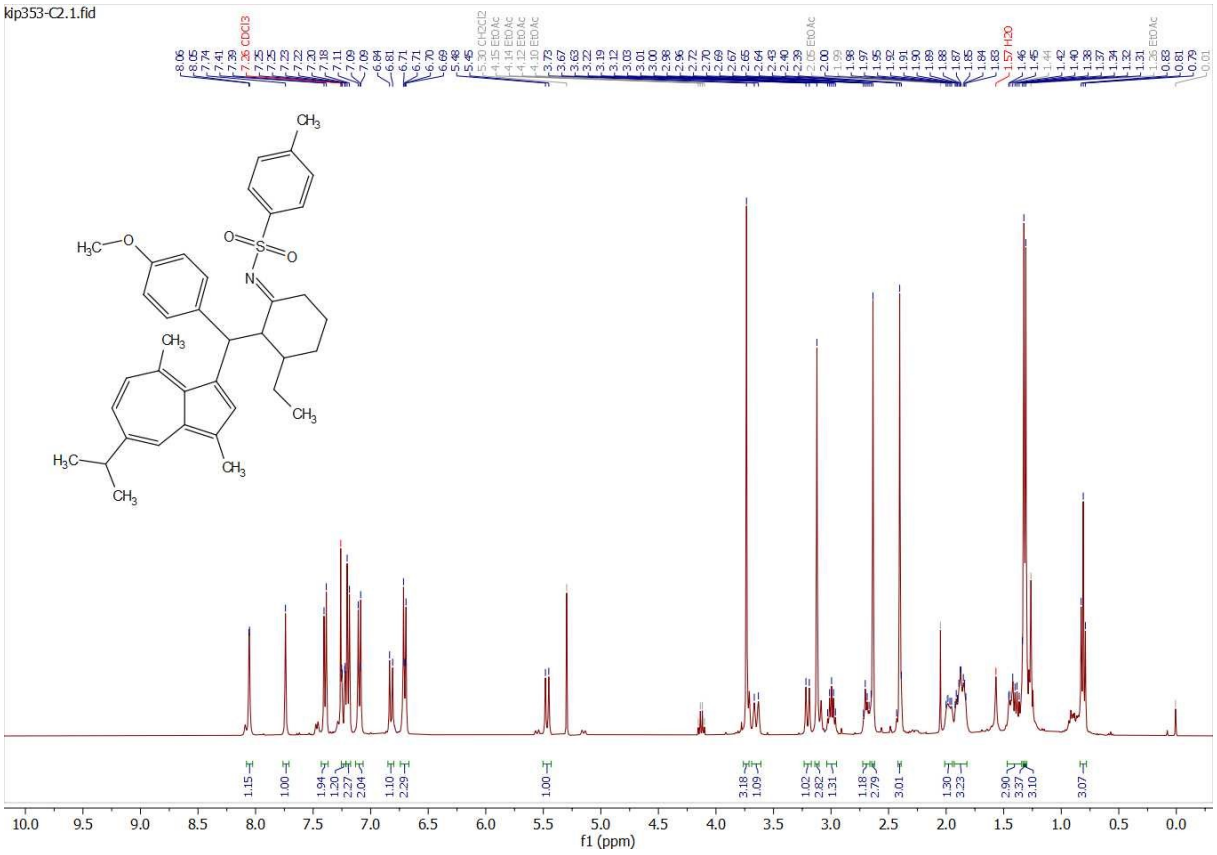


Figure S97. ^{1}H NMR spectrum of compound **5cb/diastereomer 2** (400 MHz, $CDCl_3$).

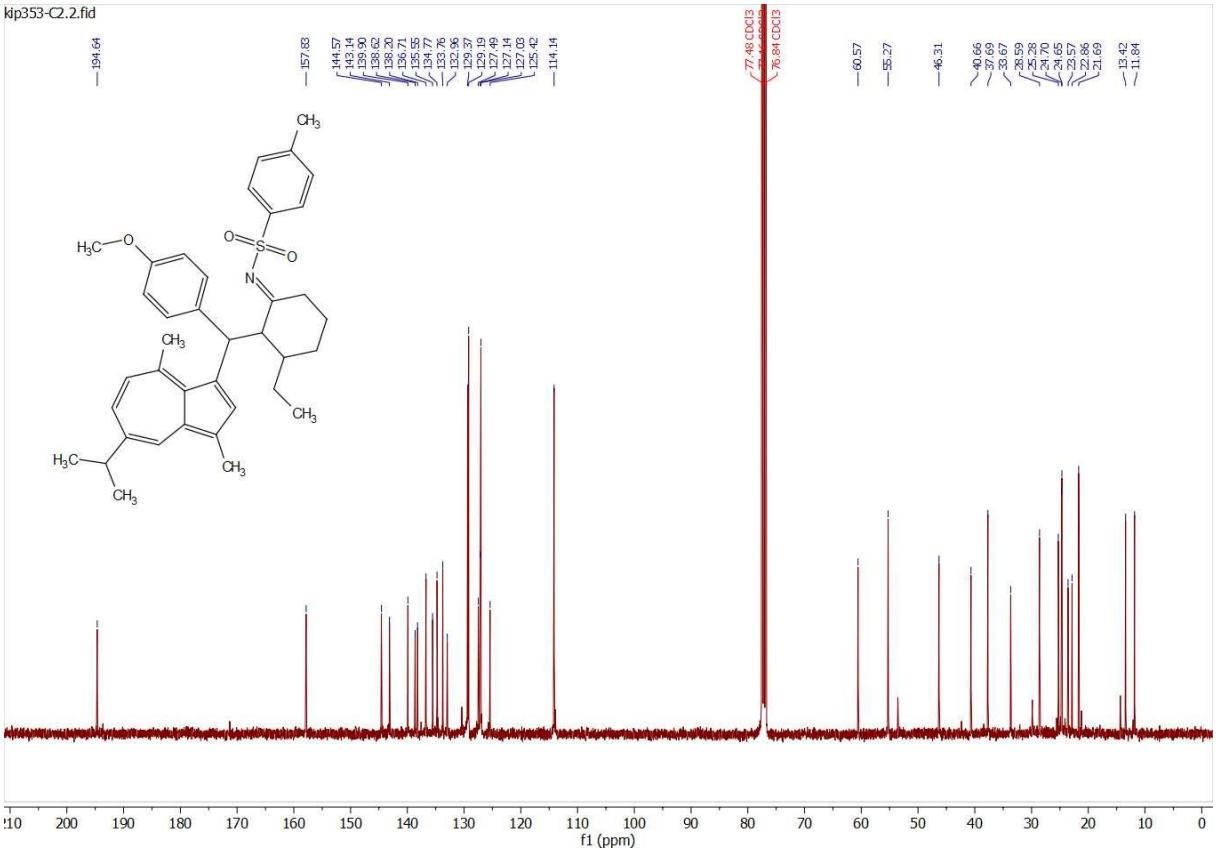


Figure S98. ^{13}C NMR spectrum of compound **5cb/diastereomer 2** (100 MHz, $CDCl_3$).

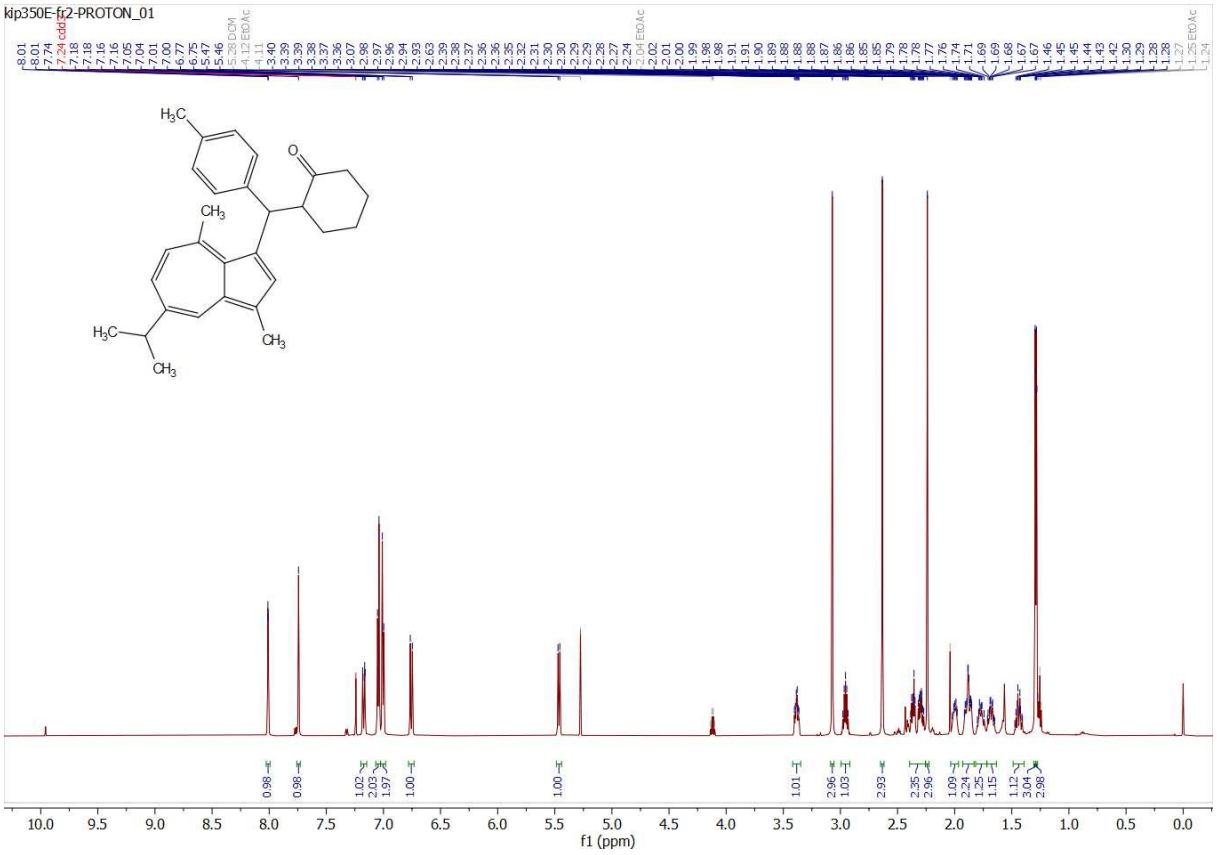


Figure S99. ^{1}H NMR spectrum of compound **7a/diastereomer 1** (600 MHz, $CDCl_3$).

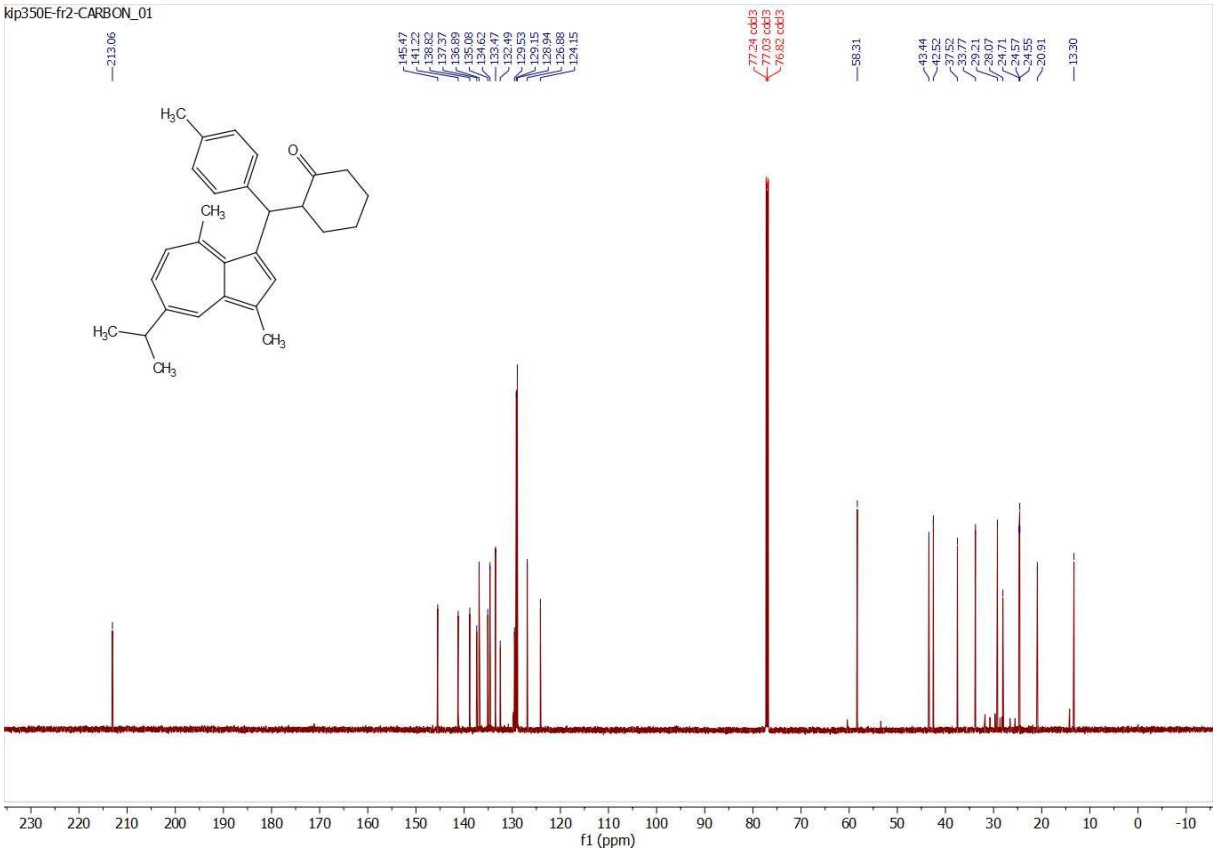


Figure S100. ^{13}C NMR spectrum of compound **7a/diastereomer 1** (150 MHz, $CDCl_3$).

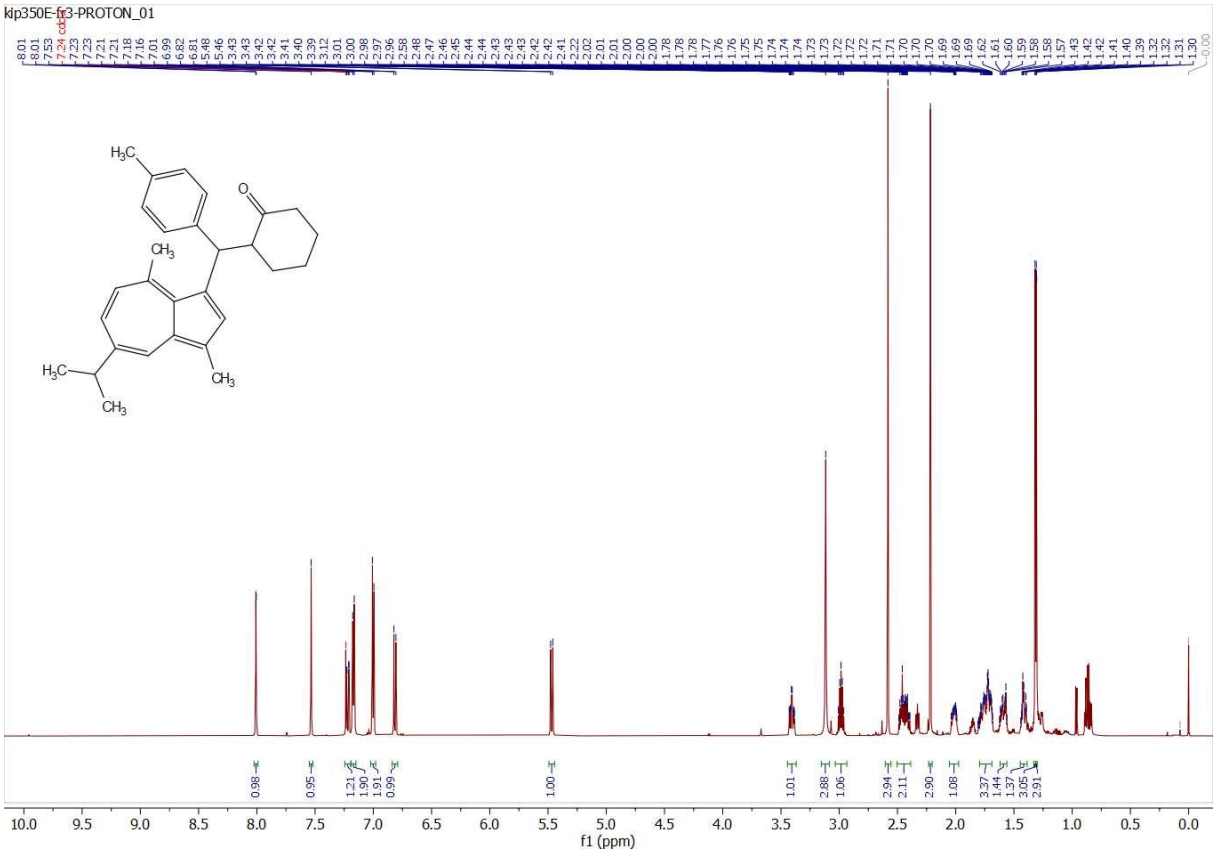


Figure S101. ^{1}H NMR spectrum of compound **7a/diastereomer 2** (600 MHz, $CDCl_3$).

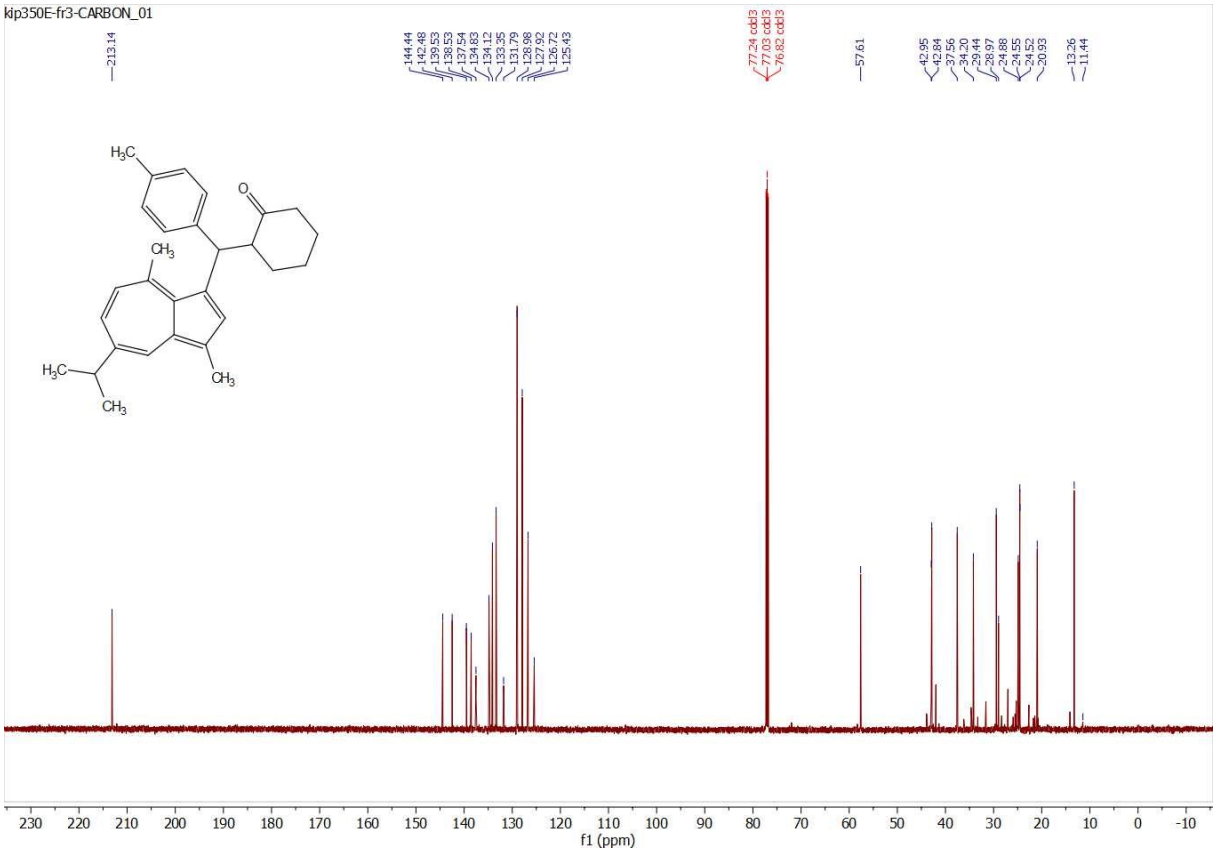


Figure S102. ^{13}C NMR spectrum of compound **7a/diastereomer 2** (150 MHz, $CDCl_3$).

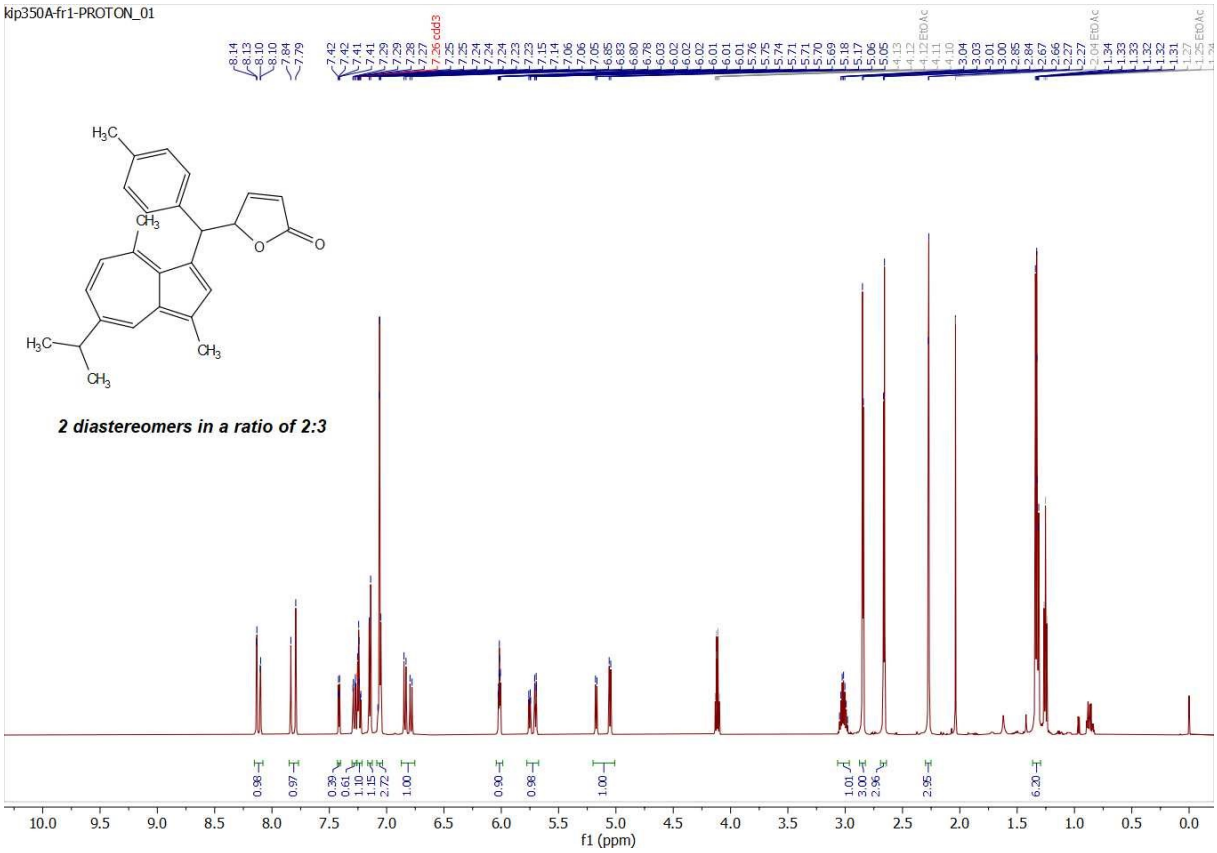


Figure S103. ^{1}H NMR spectrum of compound **7b** (600 MHz, $CDCl_3$).

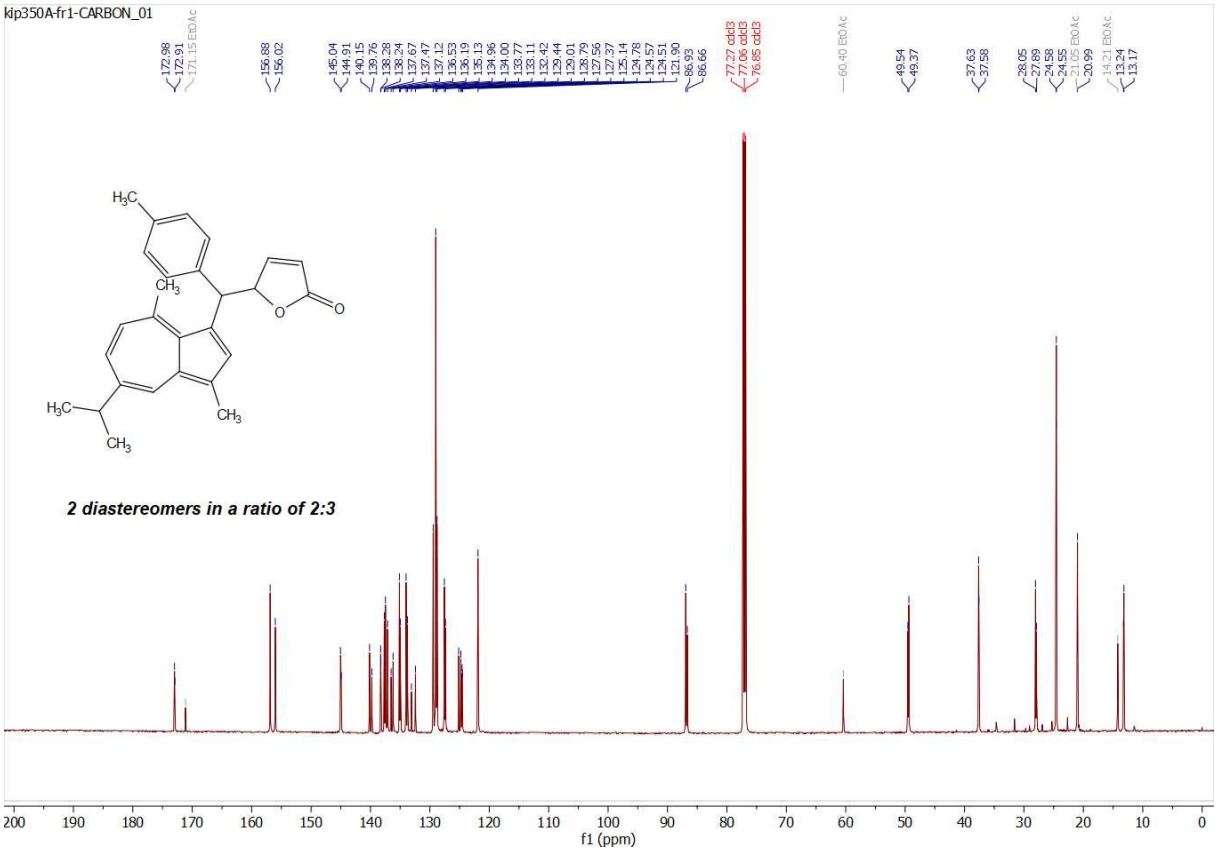


Figure S104. ^{13}C NMR spectrum of compound **7b** (150 MHz, $CDCl_3$).

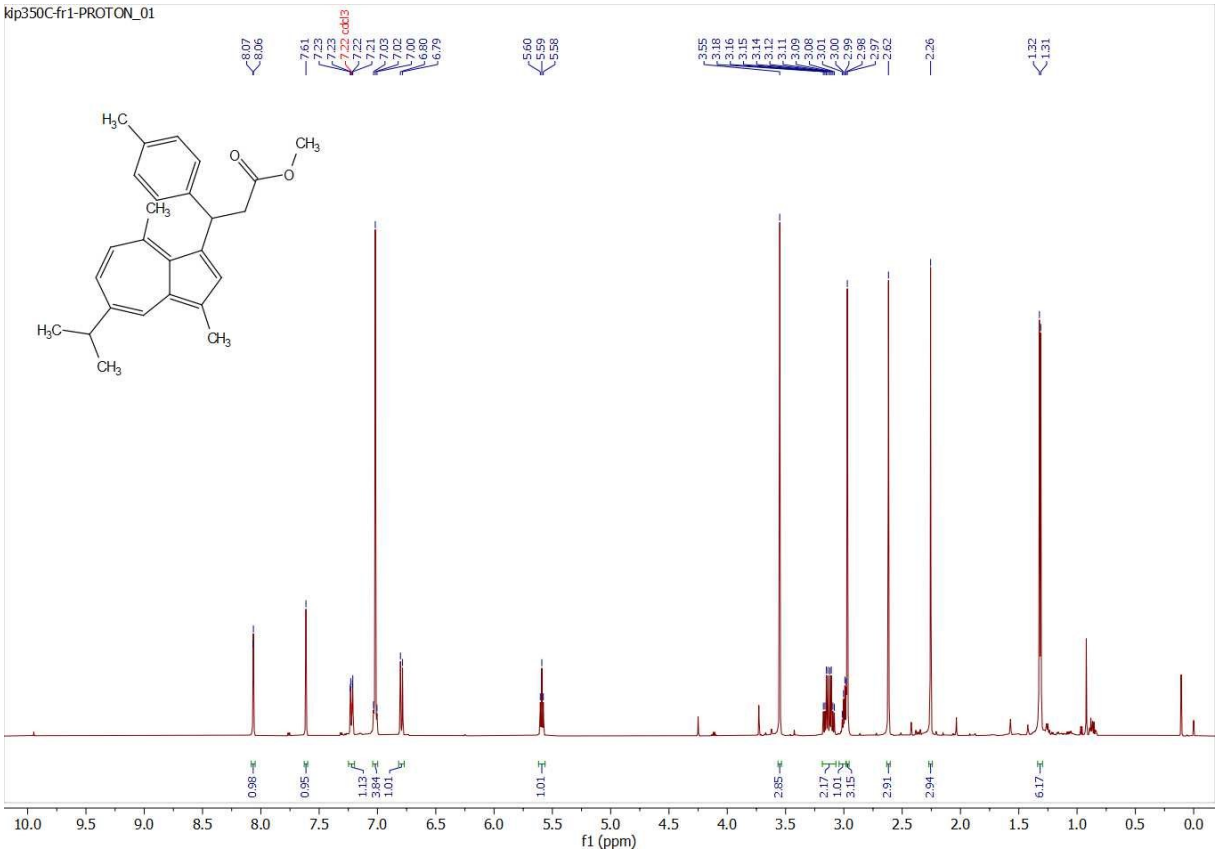


Figure S105. ^{1}H NMR spectrum of compound **7c** (600 MHz, $CDCl_3$).

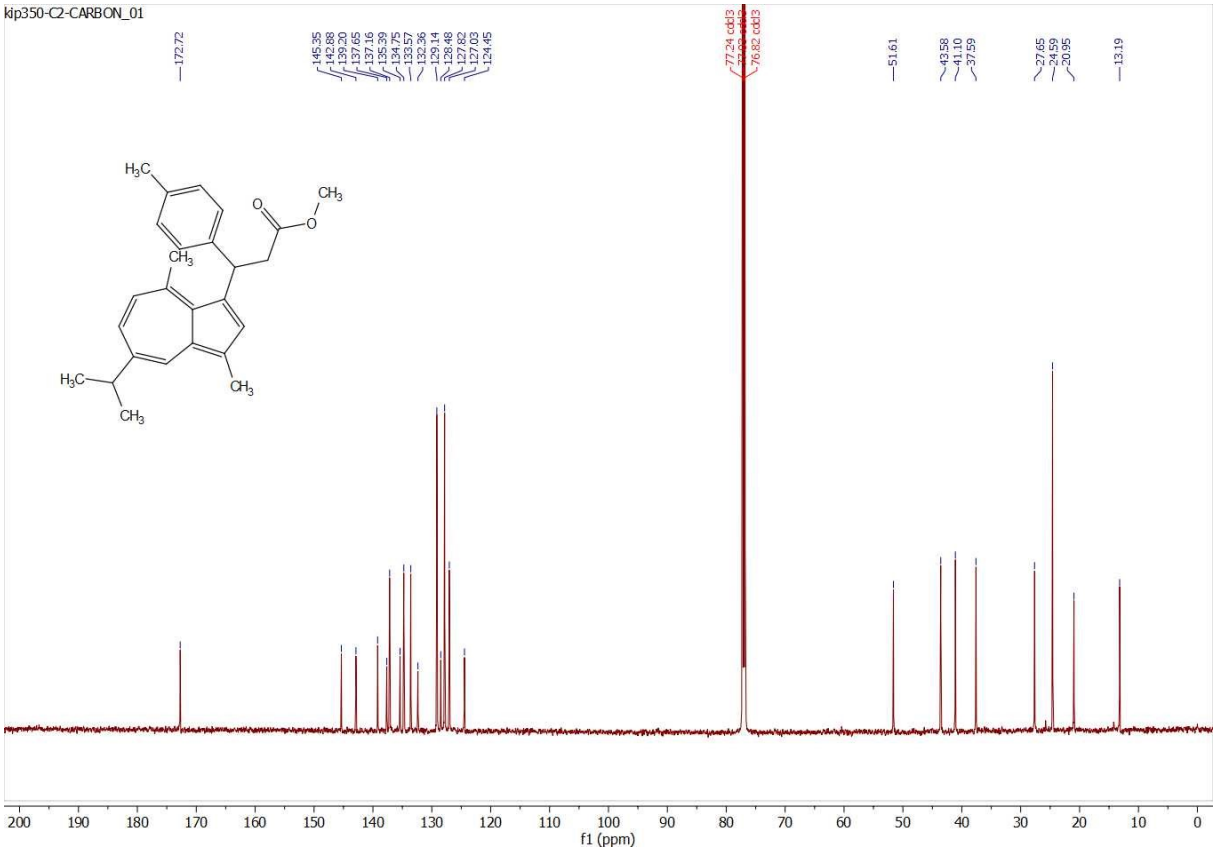


Figure S106. ^{13}C NMR spectrum of compound **7c** (150 MHz, $CDCl_3$).

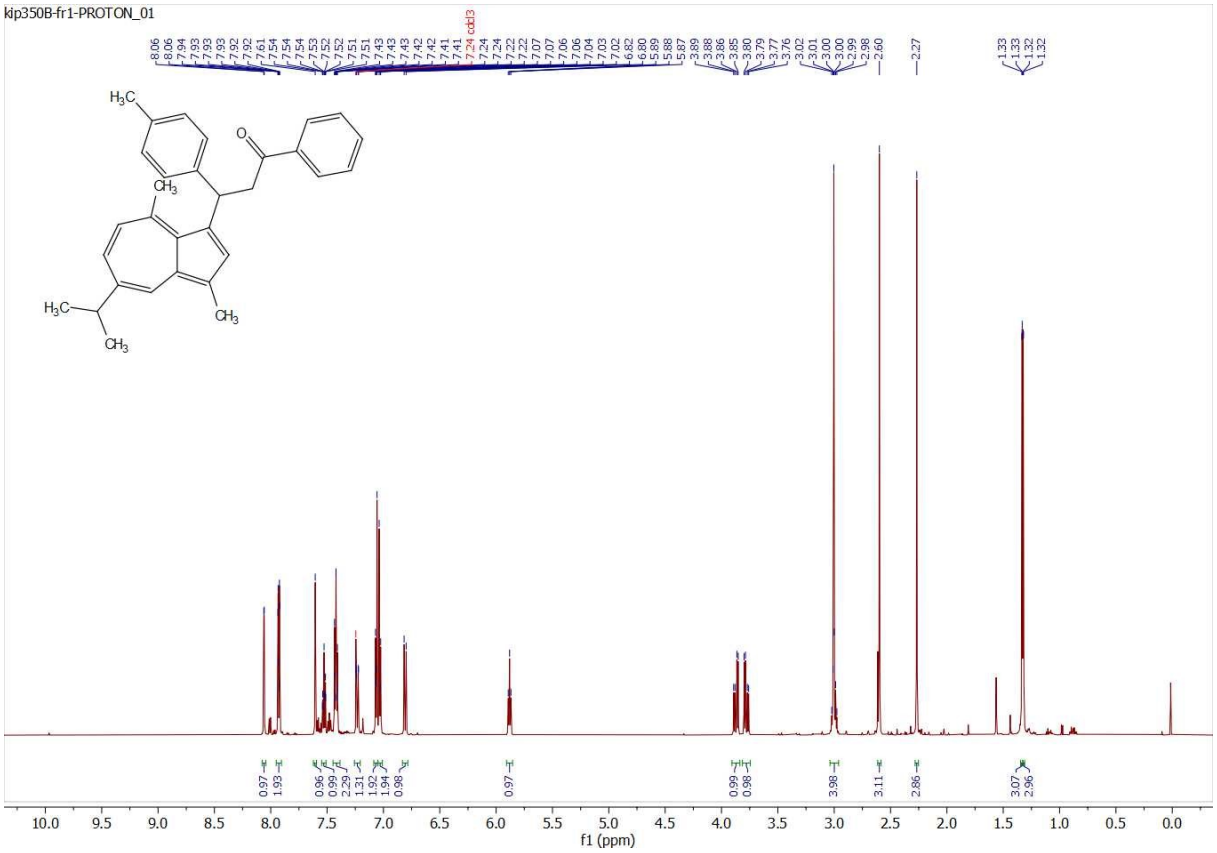


Figure S107. ^{1}H NMR spectrum of compound **7d** (600 MHz, $CDCl_3$).

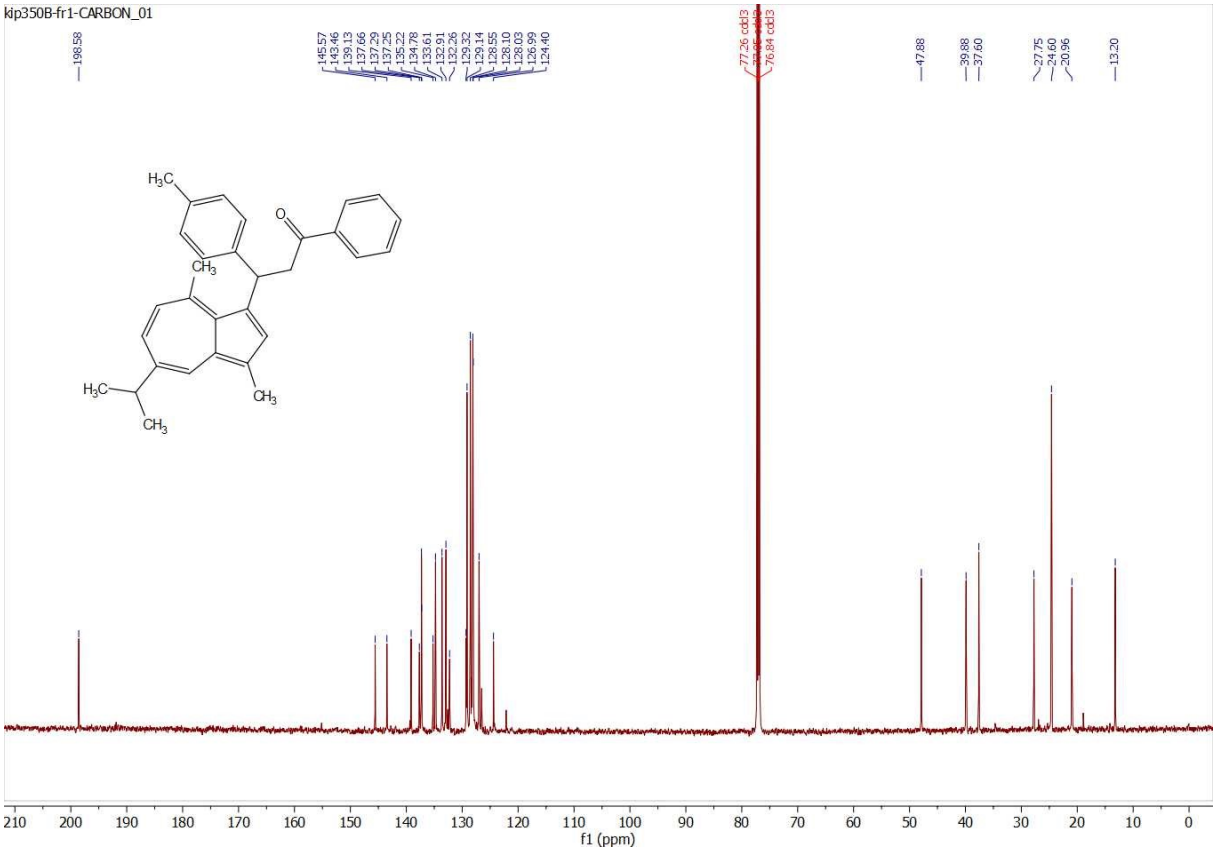


Figure S108. ^{13}C NMR spectrum of compound **7d** (150 MHz, $CDCl_3$).

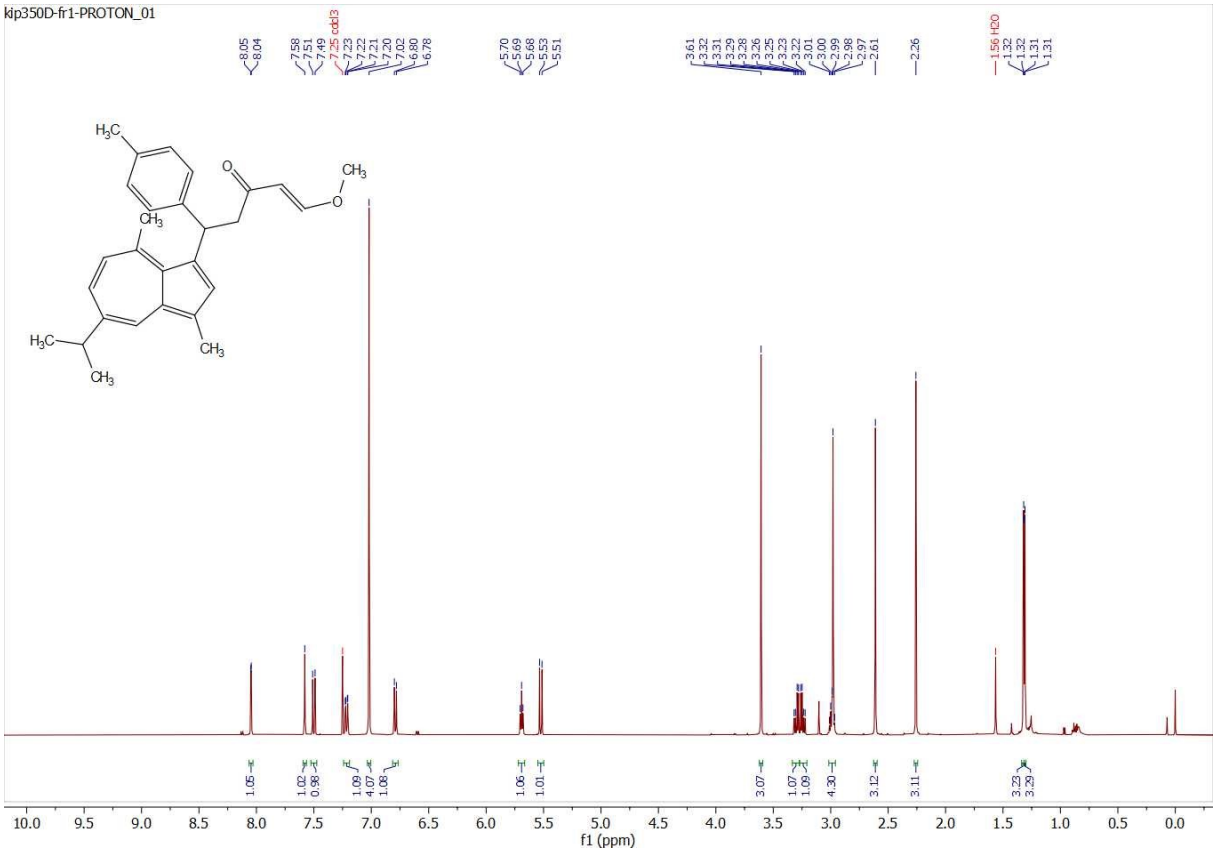


Figure S109. ^{1}H NMR spectrum of compound **7e** (600 MHz, $CDCl_3$).

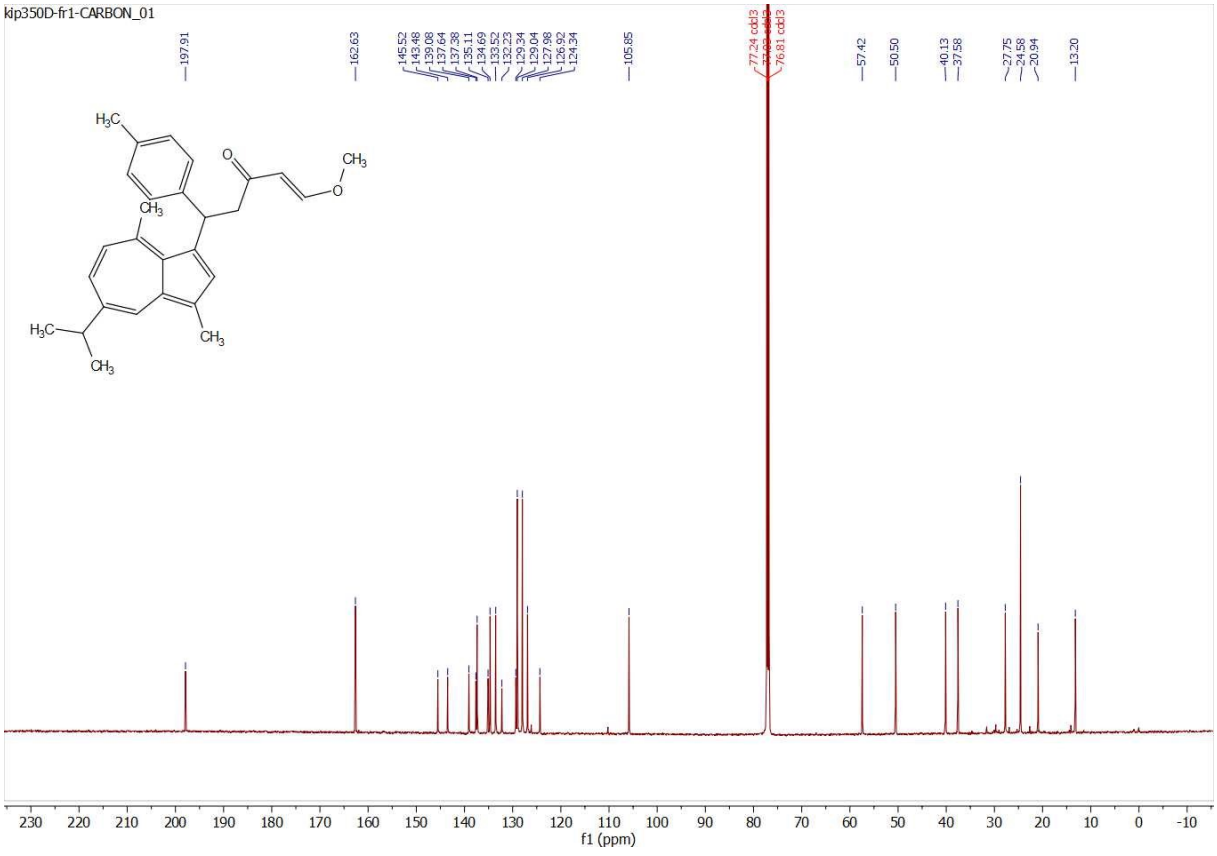


Figure S110. ^{13}C NMR spectrum of compound **7e** (150 MHz, $CDCl_3$).

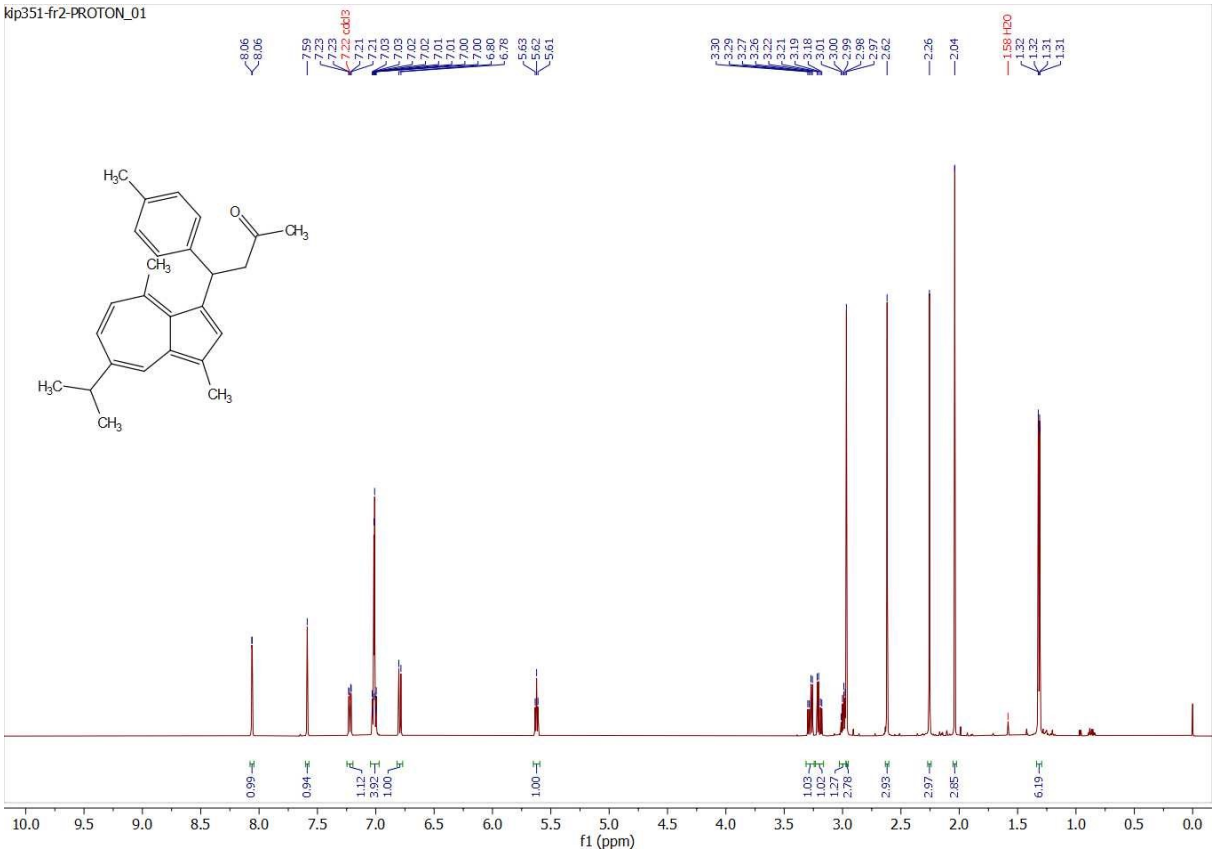


Figure S111. ^{1}H NMR spectrum of compound **7f** (600 MHz, $CDCl_3$).

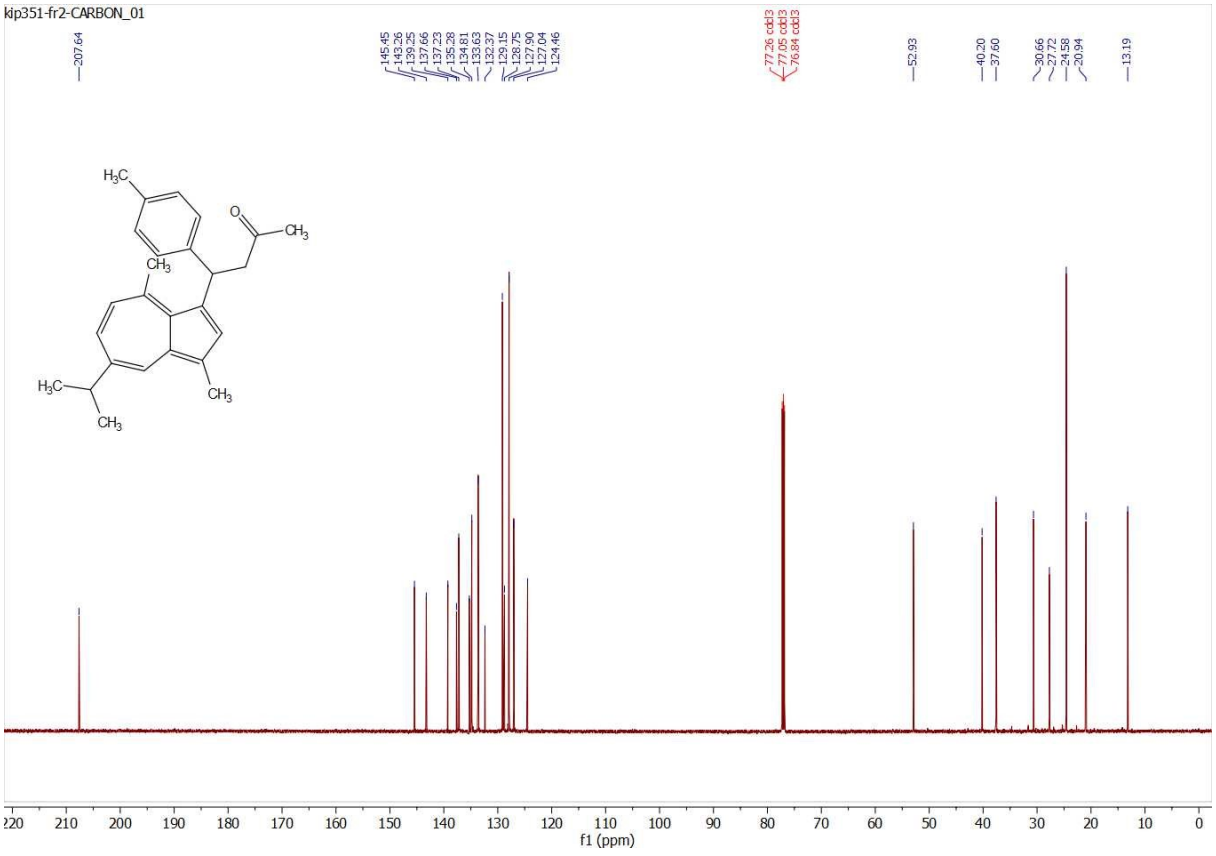


Figure S112. ^{13}C NMR spectrum of compound **7f** (150 MHz, $CDCl_3$).

8. HPLC chromatograms

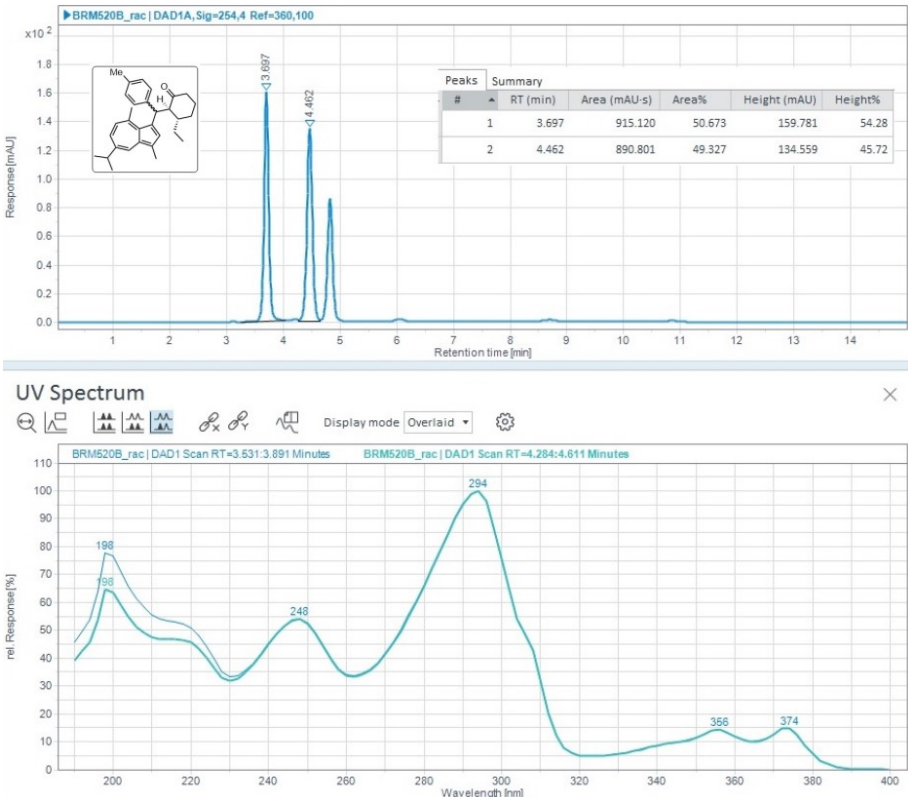


Figure S113. HPLC chromatogram of compound **5aa/diastereomer 1** (racemic, Chiralpak IA, hexane/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, t_R(major) = 3.70 min, t_R(minor)= 4.46 min).

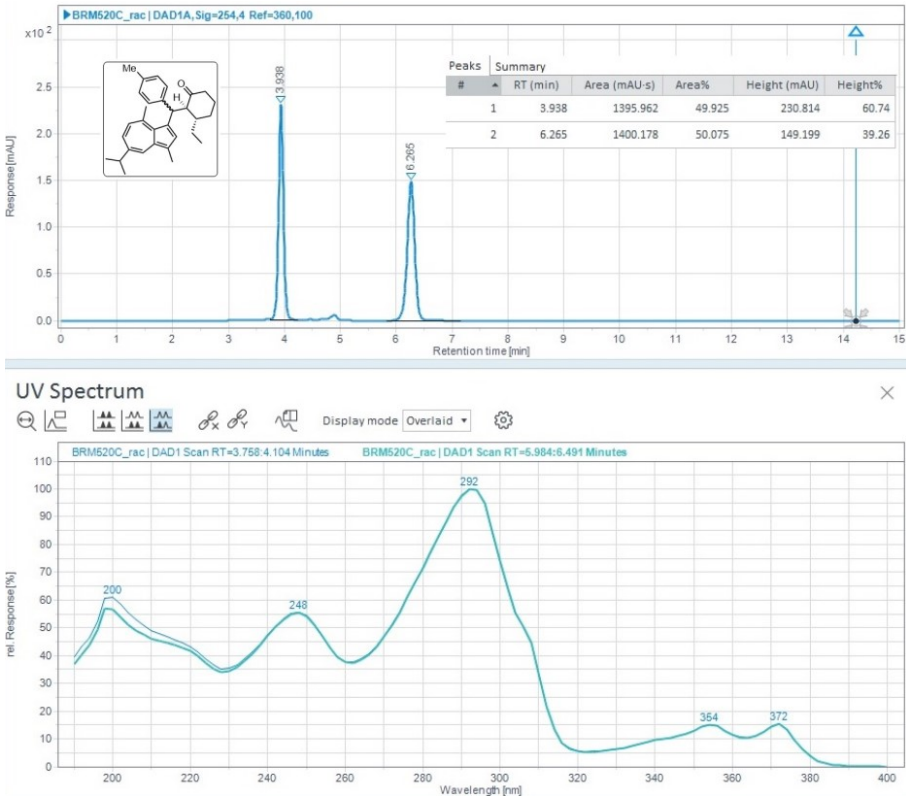


Figure S114. HPLC chromatogram of compound **5aa/diastereomer 2** (racemic, Chiralpak IA, hexane/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, t_R(major) = 3.94 min, t_R(minor)= 6.27 min).

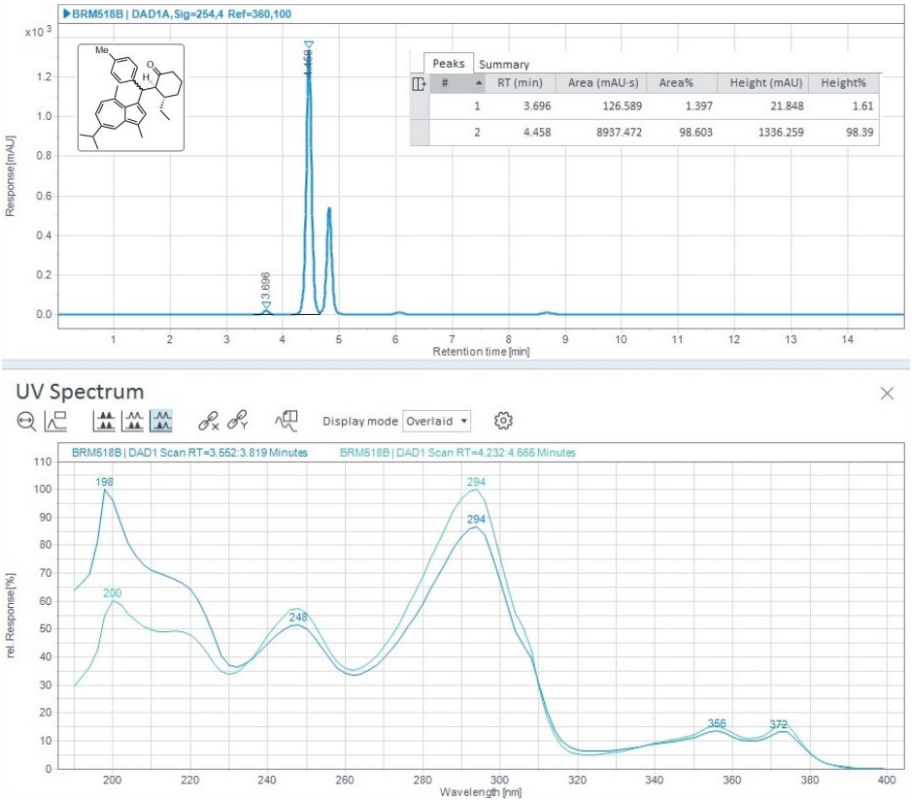


Figure S115. HPLC chromatogram of compound **5aa/diastereomer 1** (97% ee, Chiralpak IA, hexane/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, t_R(major) = 4.46 min, t_R(minor)= 3.70 min).

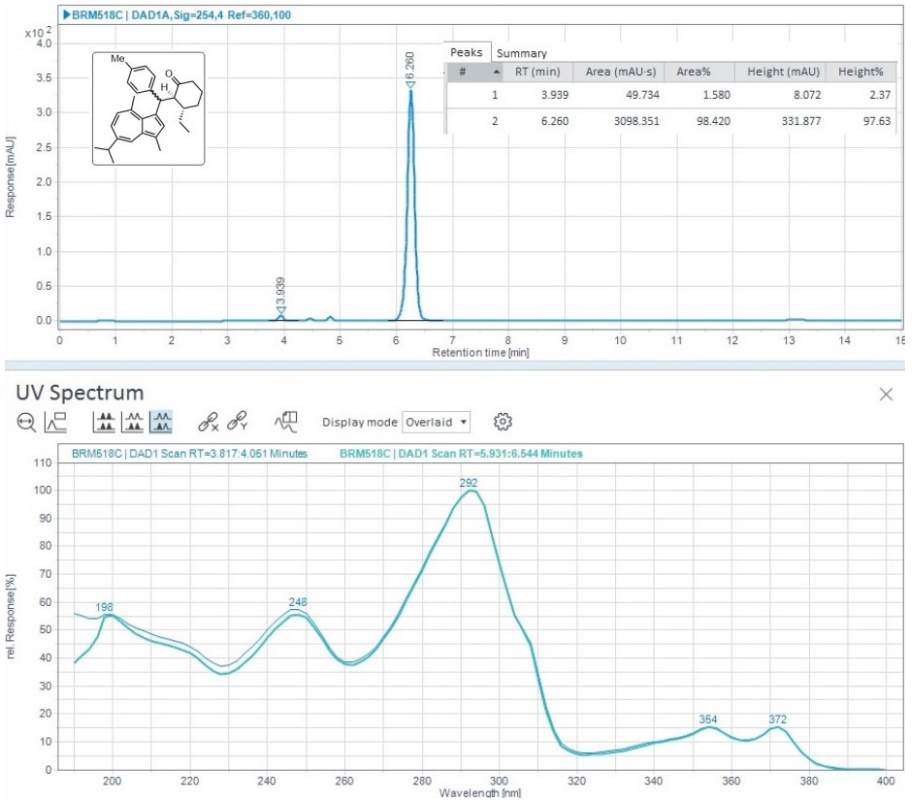


Figure S116. HPLC chromatogram of compound **5aa/diastereomer 2** (97% ee, Chiralpak IA, hexane/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, t_R(major) = 6.26 min, t_R(minor)= 3.94 min).

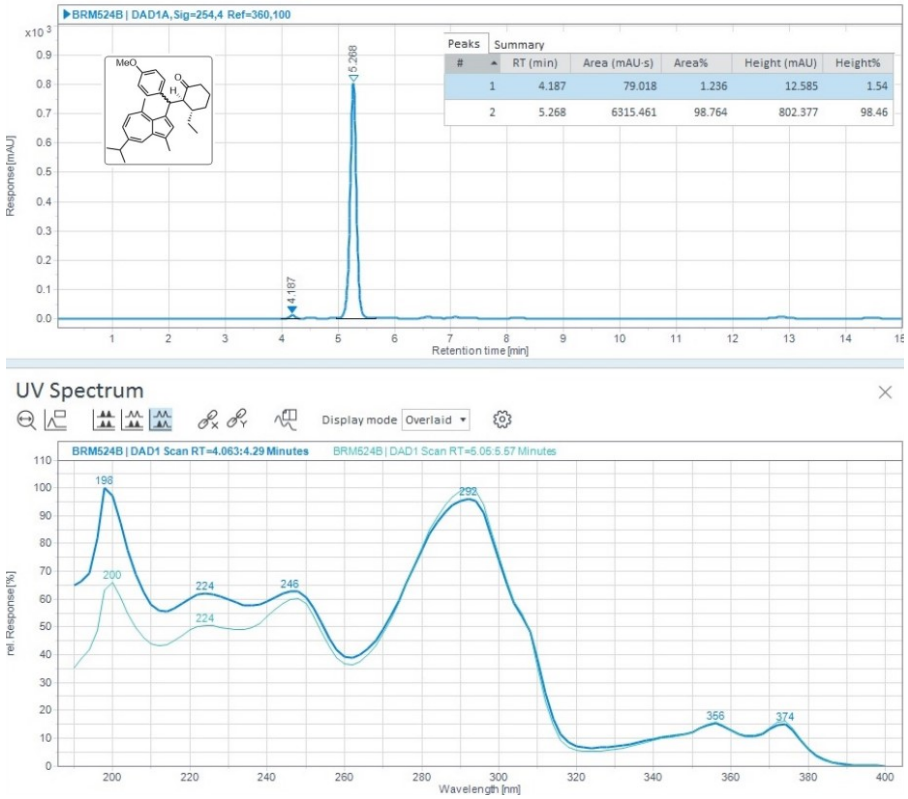


Figure S117. HPLC chromatogram of compound **5ab/diastereomer 1** (98% ee, Chiralpak IA, hexane/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, t_R(major) = 4.19 min, t_R(minor)= 5.27 min).

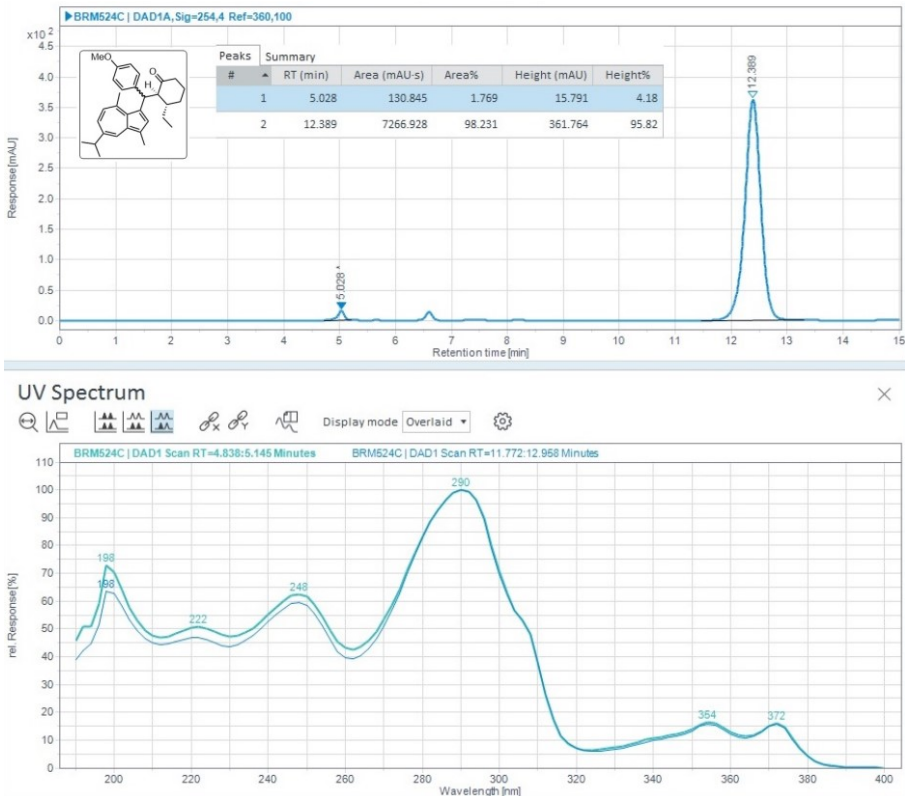


Figure S118. HPLC chromatogram of compound **5ab/diastereomer 2** (96% ee, Chiralpak IA, hexane/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, t_R(major) = 12.39 min, t_R(minor)= 5.03 min).

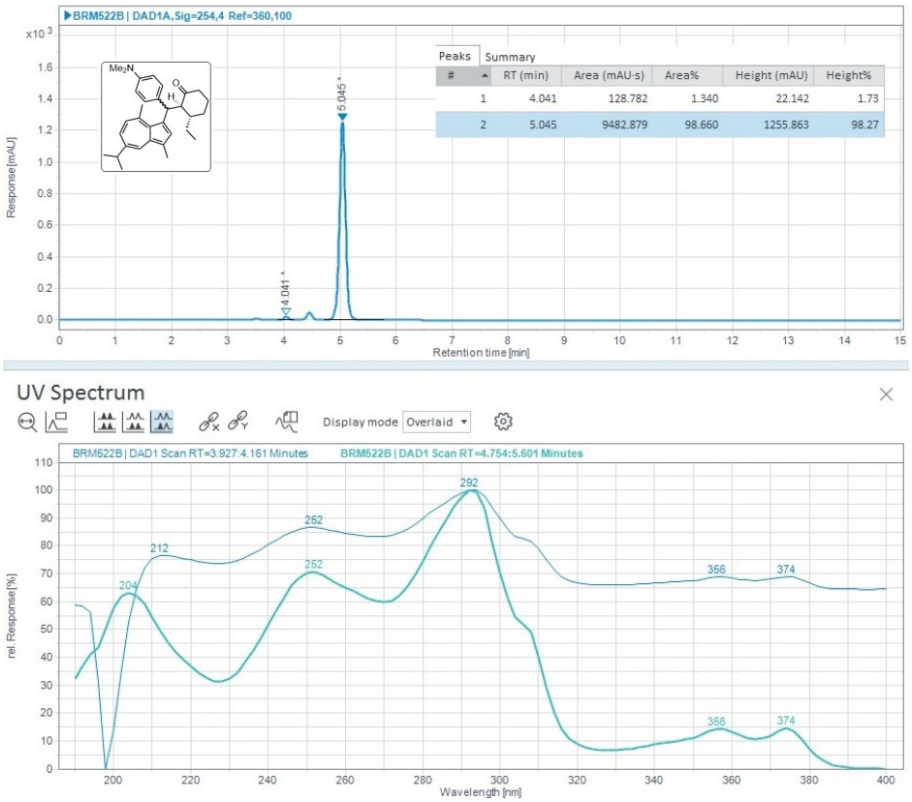


Figure S119. HPLC chromatogram of compound **5ac/diastereomer 1** (97% ee, Chiralpak IA, hexane/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, t_R(major) = 5.05 min, t_R(minor)= 4.04 min).

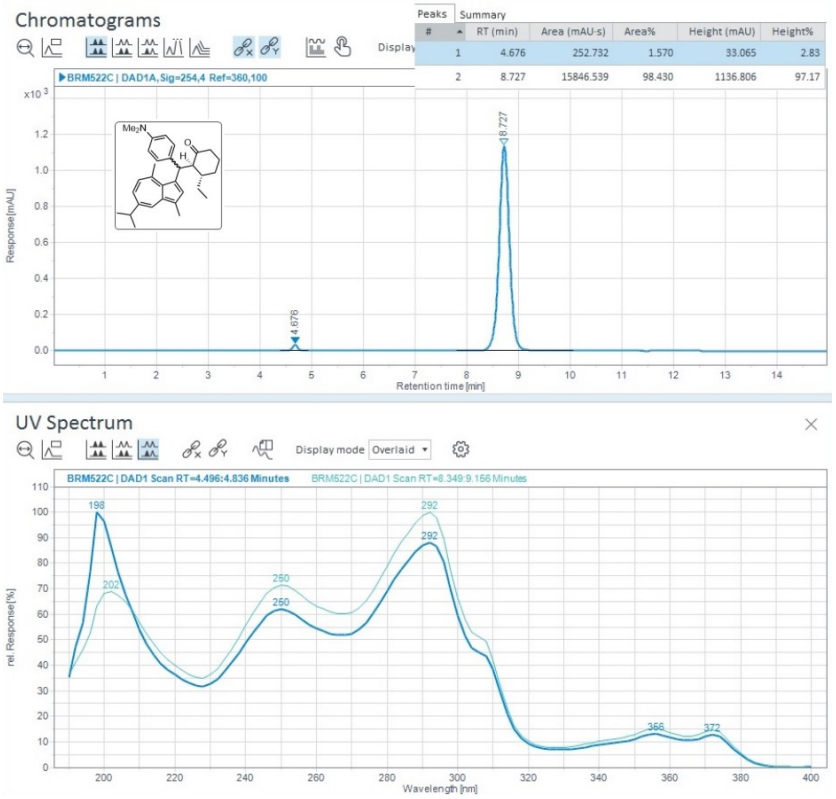


Figure S120. HPLC chromatogram of compound **5ac/diastereomer 2** (97% ee, Chiralpak IA, hexane/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, t_R(major) = 8.73 min, t_R(minor)= 4.68 min).

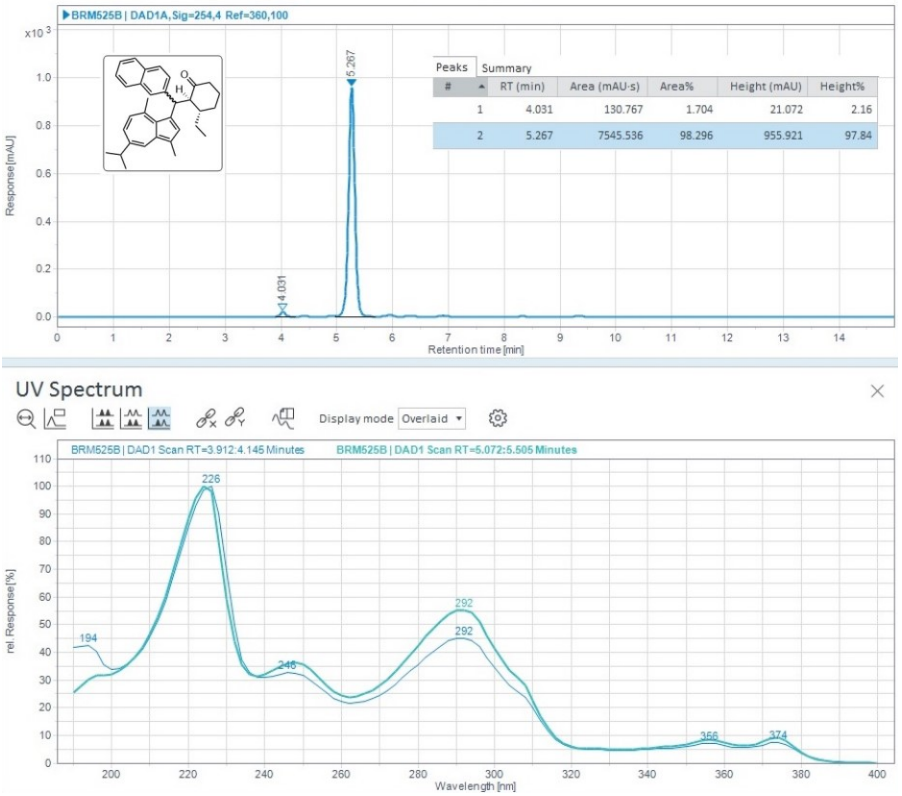


Figure S121. HPLC chromatogram of compound **5ad/diastereomer 1** (97% ee, Chiralpak IA, hexane/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, t_R(major) = 5.27 min, t_R(minor)= 4.03 min).

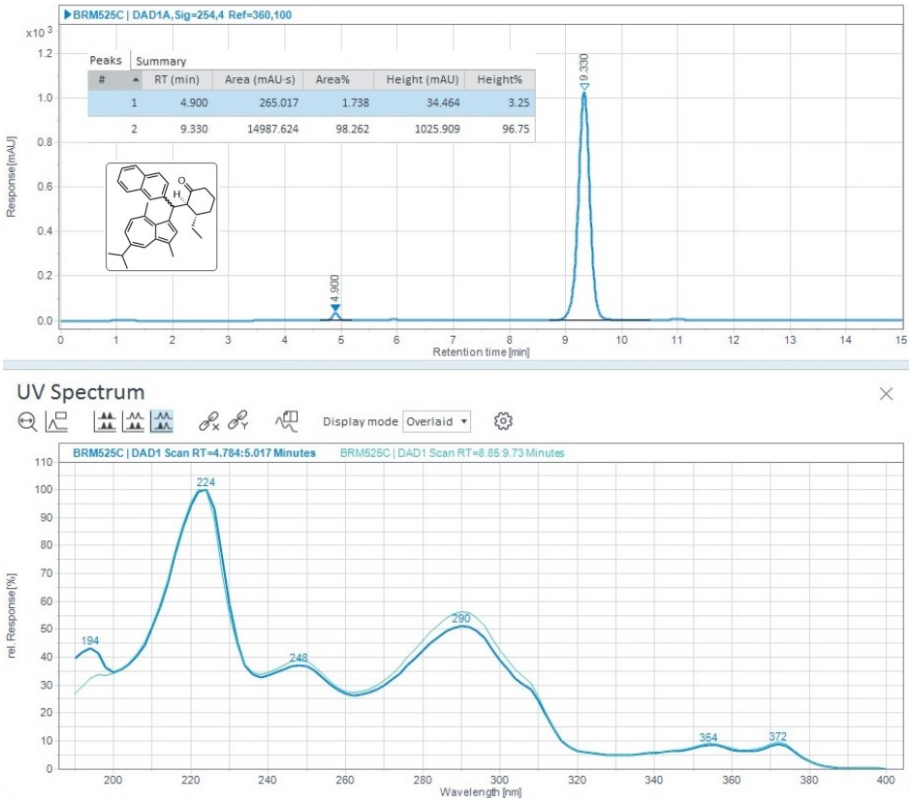


Figure S122. HPLC chromatogram of compound **5ad/diastereomer 2** (97% ee, Chiralpak IA, hexane/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, t_R(major) = 9.33 min, t_R(minor)= 4.90 min).

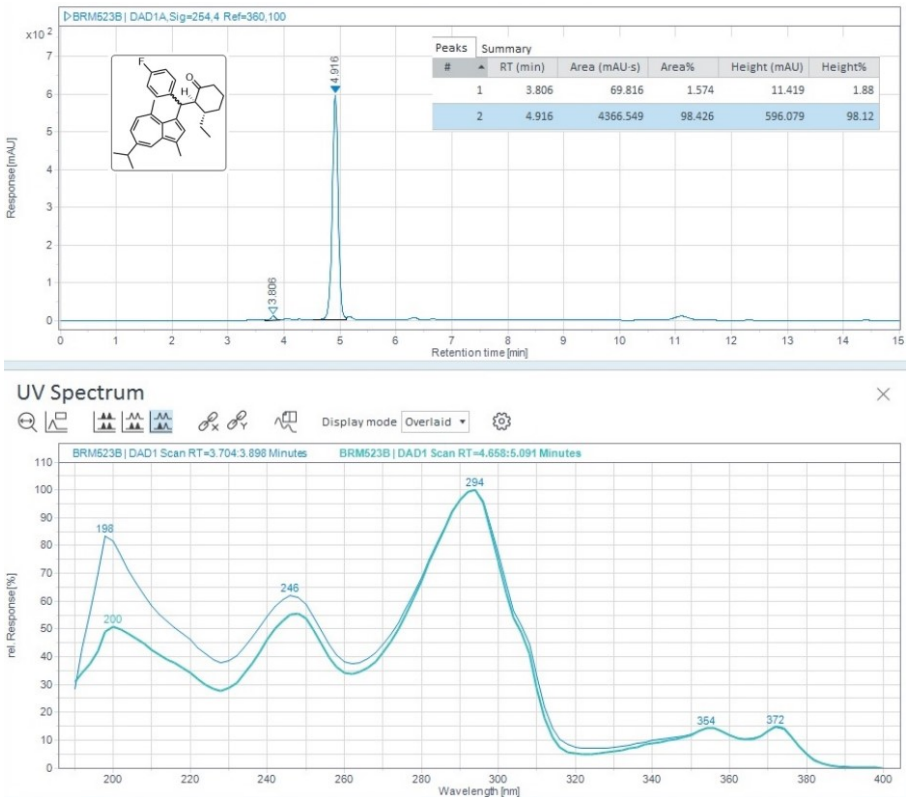


Figure S123. HPLC chromatogram of compound **5ae/diastereomer 1** (97% ee, Chiralpak IA, hexane/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, t_R(major) = 4.91 min, t_R(minor)= 3.81 min).

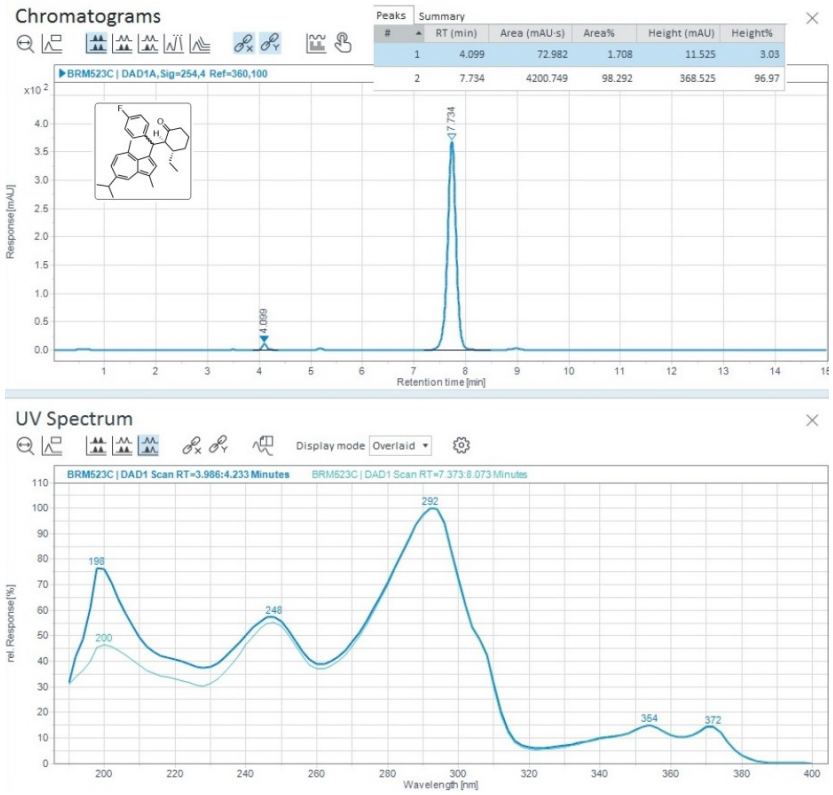


Figure S124. HPLC chromatogram of compound **5ae/diastereomer 2** (97% ee, Chiralpak IA, hexane/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, t_R(major) = 7.73 min, t_R(minor)= 4.10 min).

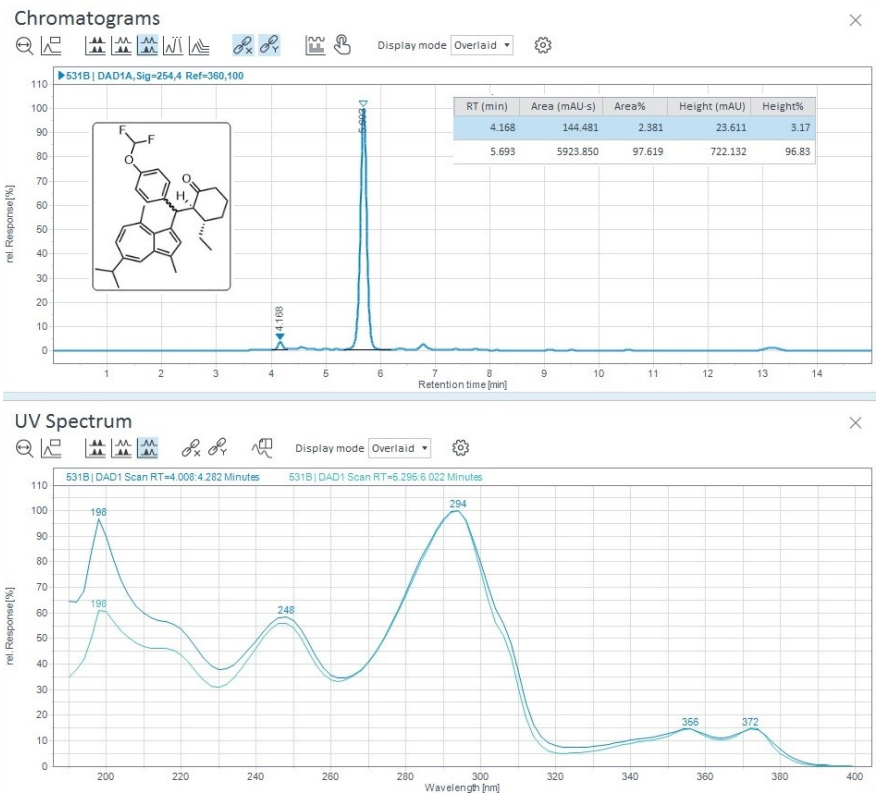


Figure S125. HPLC chromatogram of compound **5af/diastereomer 1** (95% ee, Chiralpak IA, hexane/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, t_R(major) = 5.69 min, t_R(minor)= 4.17 min).

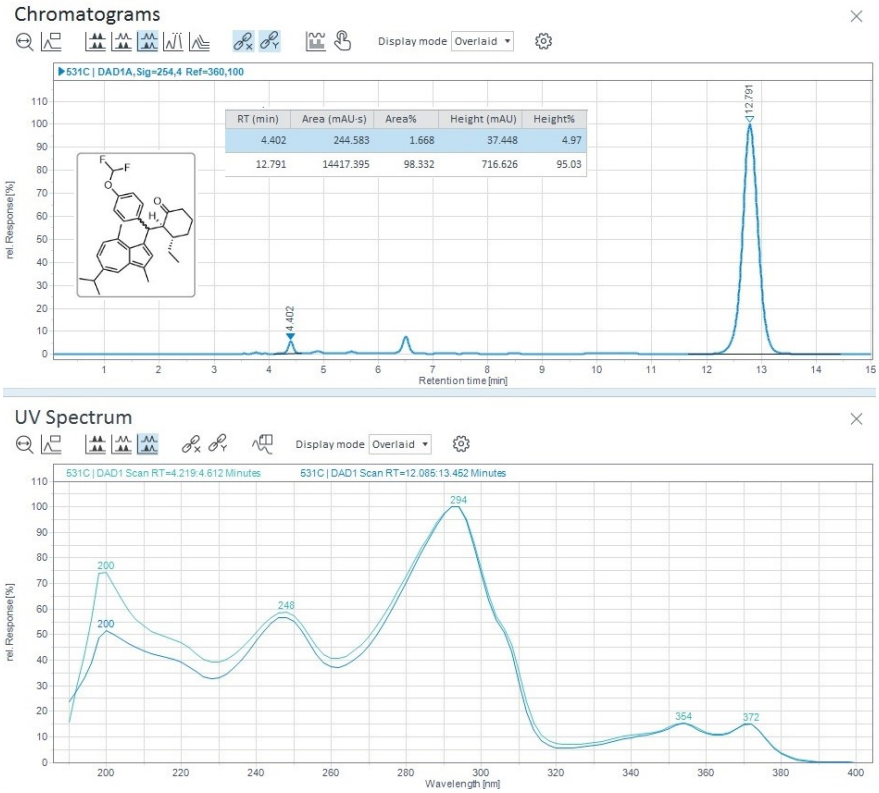


Figure S126. HPLC chromatogram of compound **5af/diastereomer 2** (97% ee, Chiralpak IA, hexane/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, t_R(major) = 12.79 min, t_R(minor)= 4.40 min).

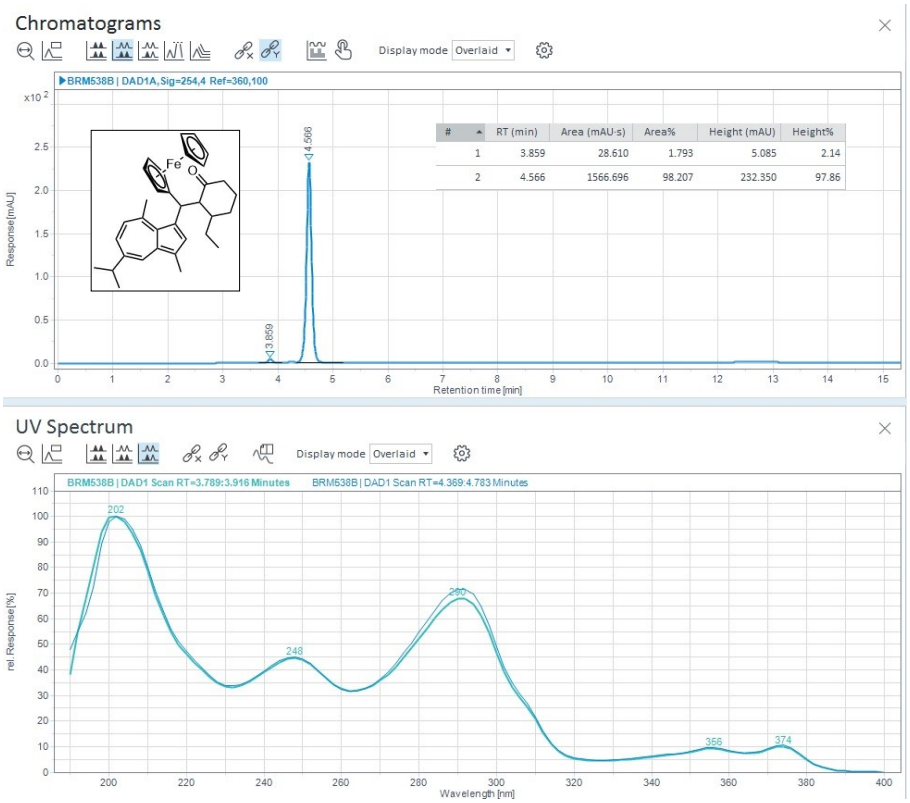


Figure S127. HPLC chromatogram of compound **5ag/diastereomer 1** (96% ee, Chiralpak IA, hexane/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, t_R(major) = 4.57 min, t_R(minor)= 3.86 min).

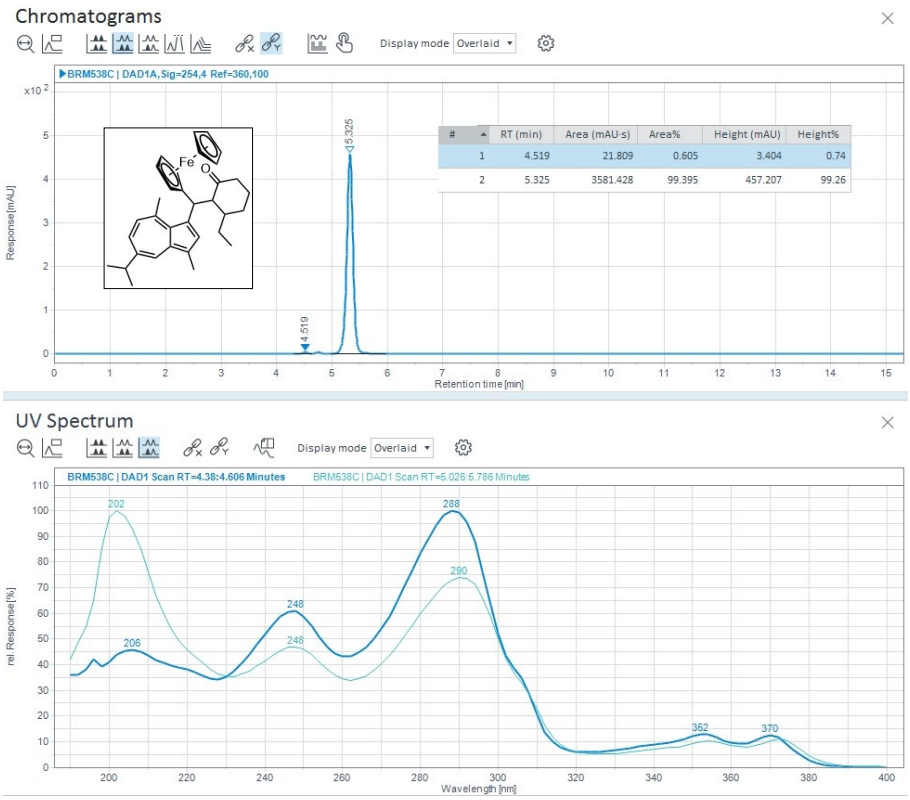


Figure S128. HPLC chromatogram of compound **5ag/diastereomer 2** (99% ee, Chiralpak IA, hexane/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, t_R(major) = 5.33 min, t_R(minor)= 4.52 min).

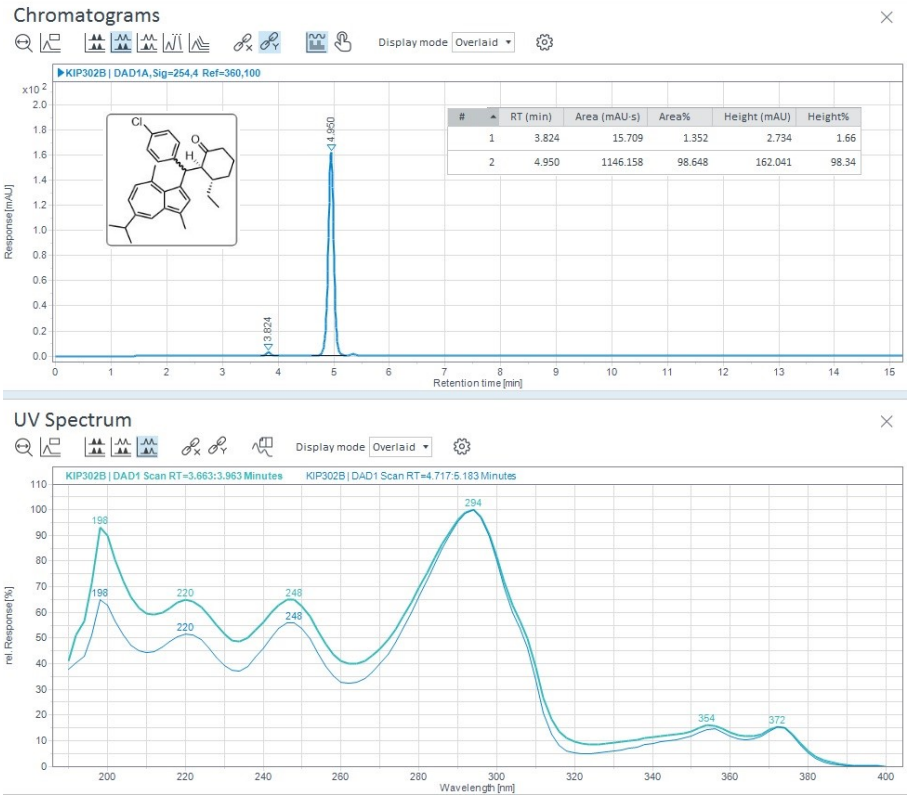


Figure S129. HPLC chromatogram of compound **5ah/diastereomer 1** (97% ee, Chiralpak IA, hexane/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, t_R(major) = 4.95 min, t_R(minor)= 3.82 min).

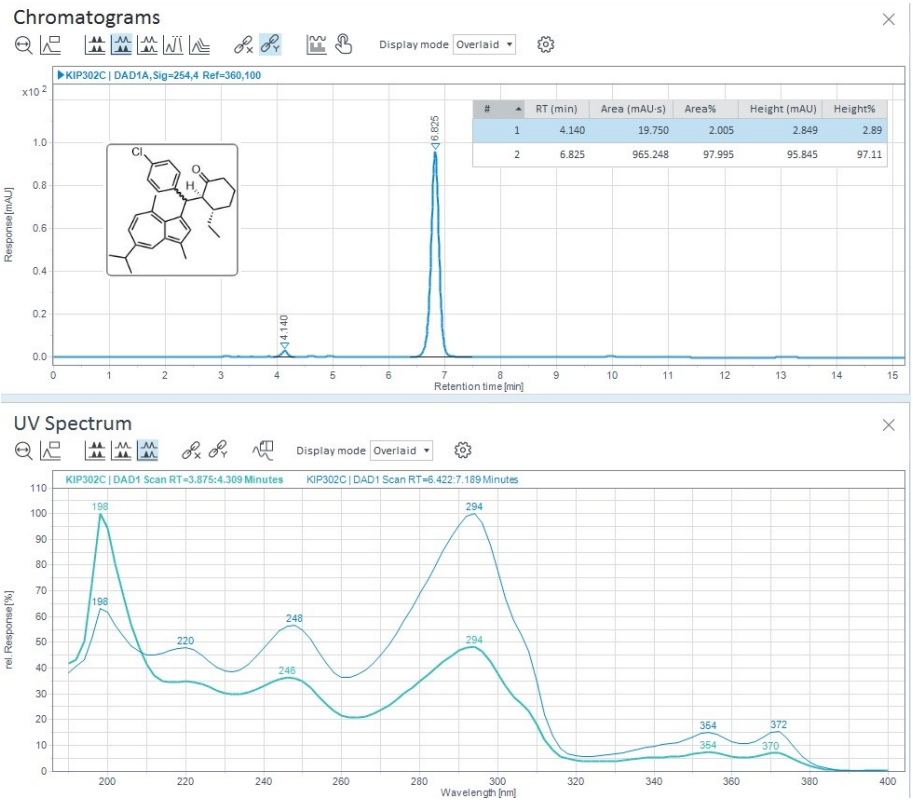


Figure S130. HPLC chromatogram of compound **5ah/diastereomer 2** (96% ee, Chiralpak IA, hexane/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, t_R(major) = 6.83 min, t_R(minor)= 4.14 min).

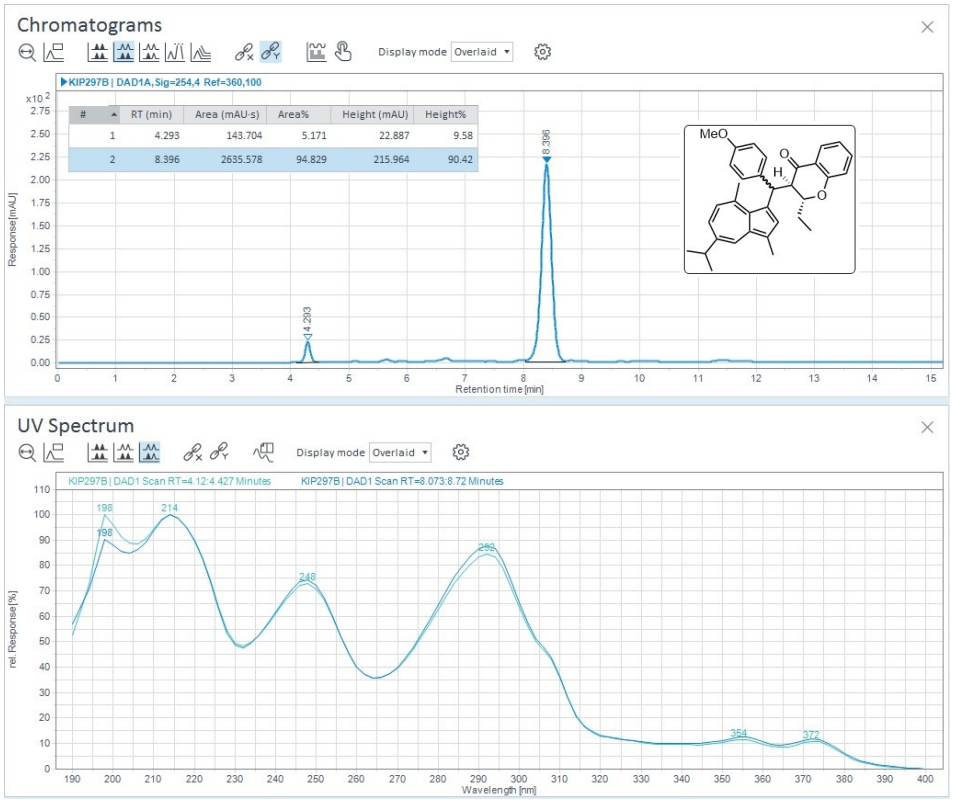


Figure S131. HPLC chromatogram of compound **5bb/diastereomer 1** (90% ee, Chiralpak IA, hexane/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, t_R(major) = 8.40 min, t_R(minor)= 4.29 min).

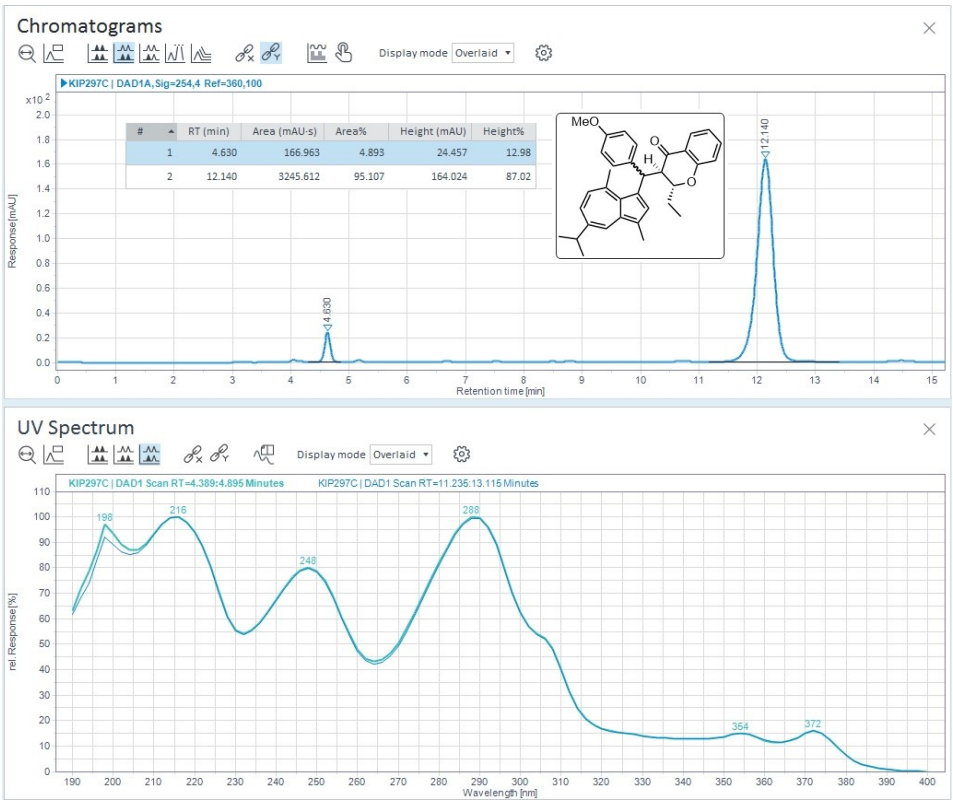


Figure S132. HPLC chromatogram of compound **5bb/diastereomer 2** (90% ee, Chiralpak IA, hexane/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, t_R(major) = 12.14 min, t_R(minor)= 4.63 min).

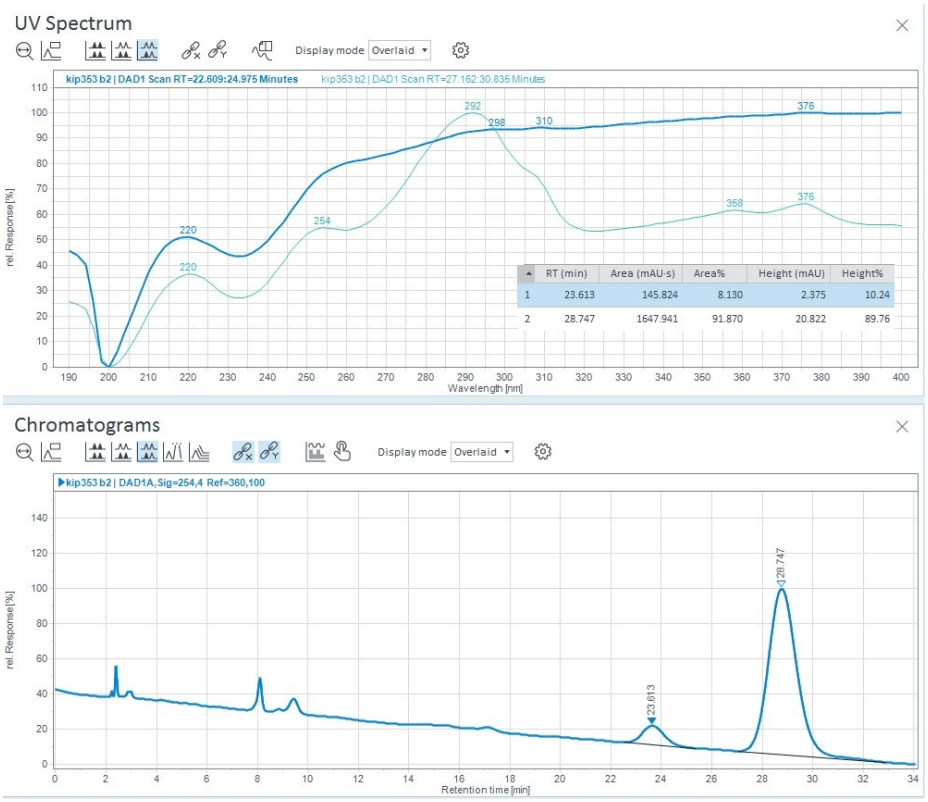


Figure S133. HPLC chromatogram of compound **5cb/diastereomer 1** (84% ee, Chiralpak IC, hexane/*i*-PrOH = 90:10, 1.5 mL/min, 254 nm, t_R(major) = 23.61 min, t_R(minor)= 28.75 min).

Figure S134. HPLC chromatogram of compound **5cb/diastereomer 2** (91% ee, Chiralpak IC, hexane/*i*-PrOH = 90:10, 1.5 mL/min, 254 nm, t_R(major) = 20.11 min, t_R(minor)= 18.67 min).

9. HRMS pictures

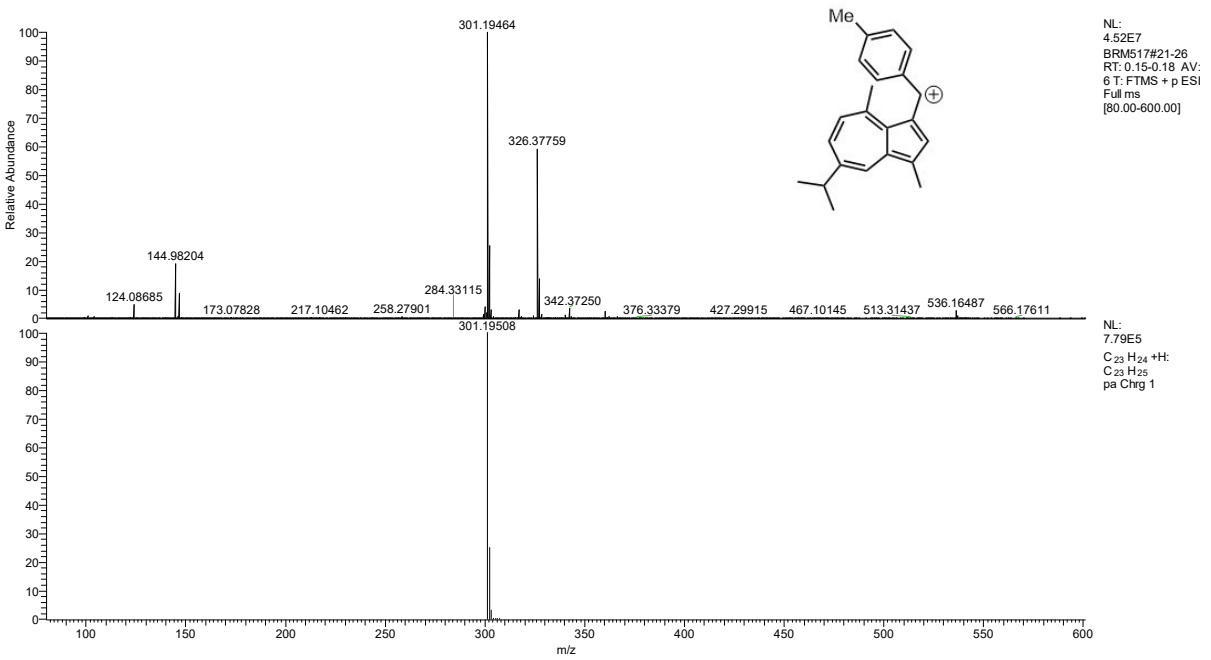


Figure S135. HRMS picture of compound **2a**.

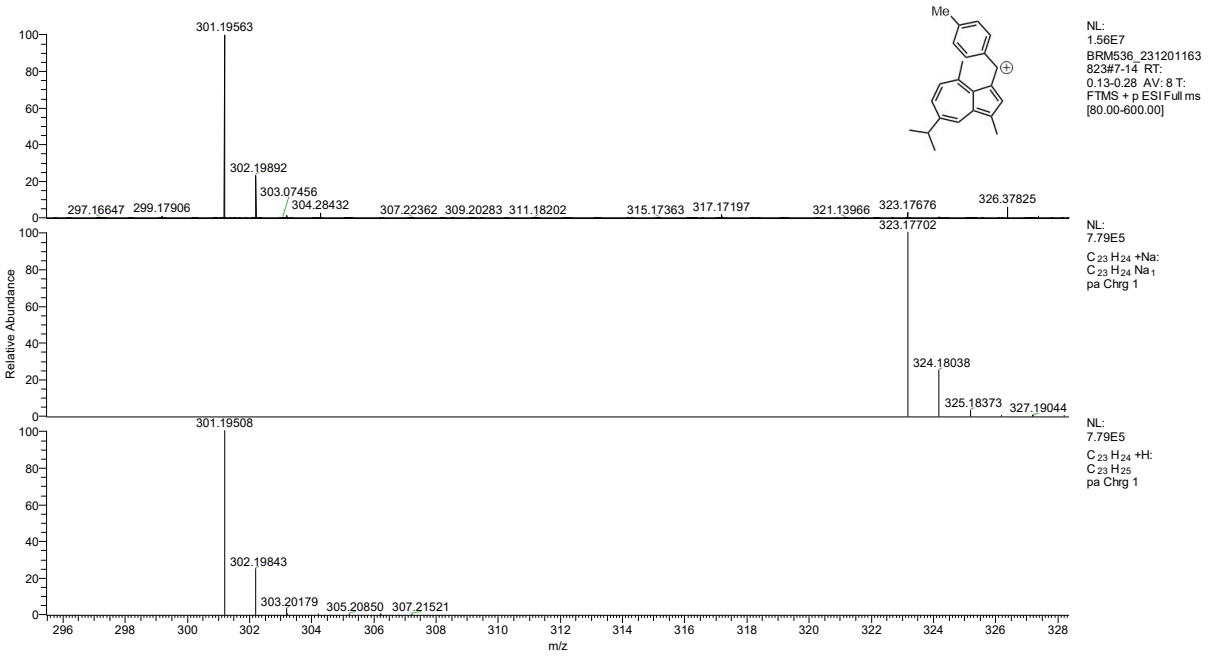


Figure S136. HRMS picture of compound **2a'**.

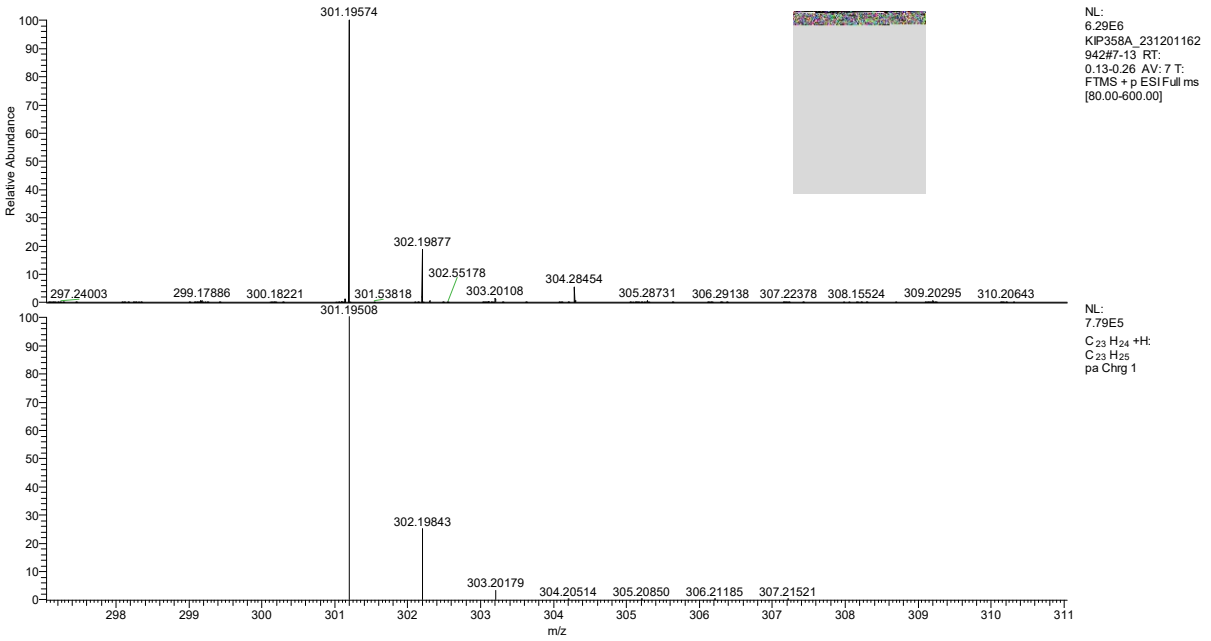


Figure S137. HRMS picture of compound **2a”**.

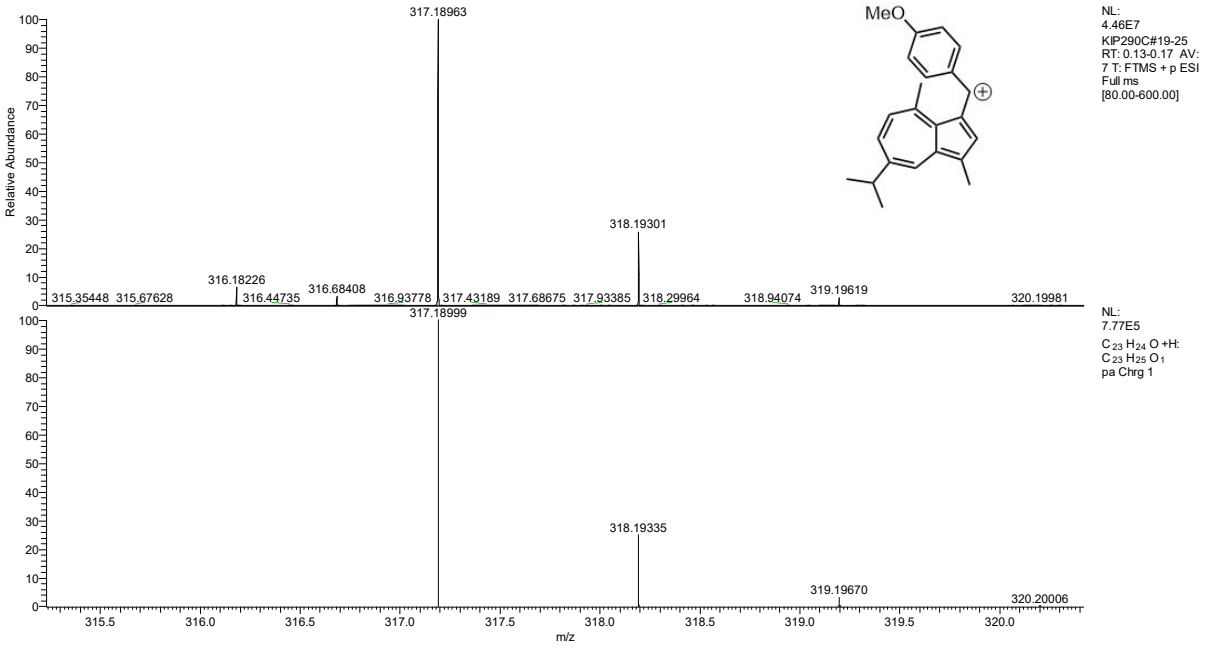


Figure S138. HRMS picture of compound **2b**.

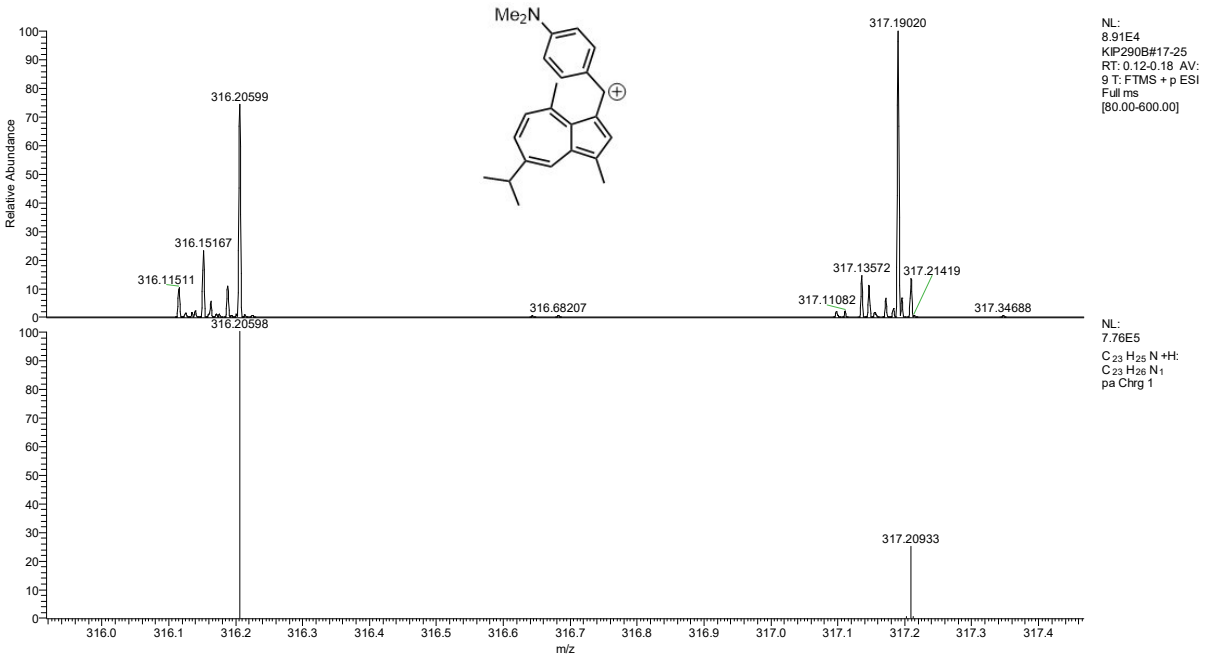


Figure S139. HRMS picture of compound **2c**.

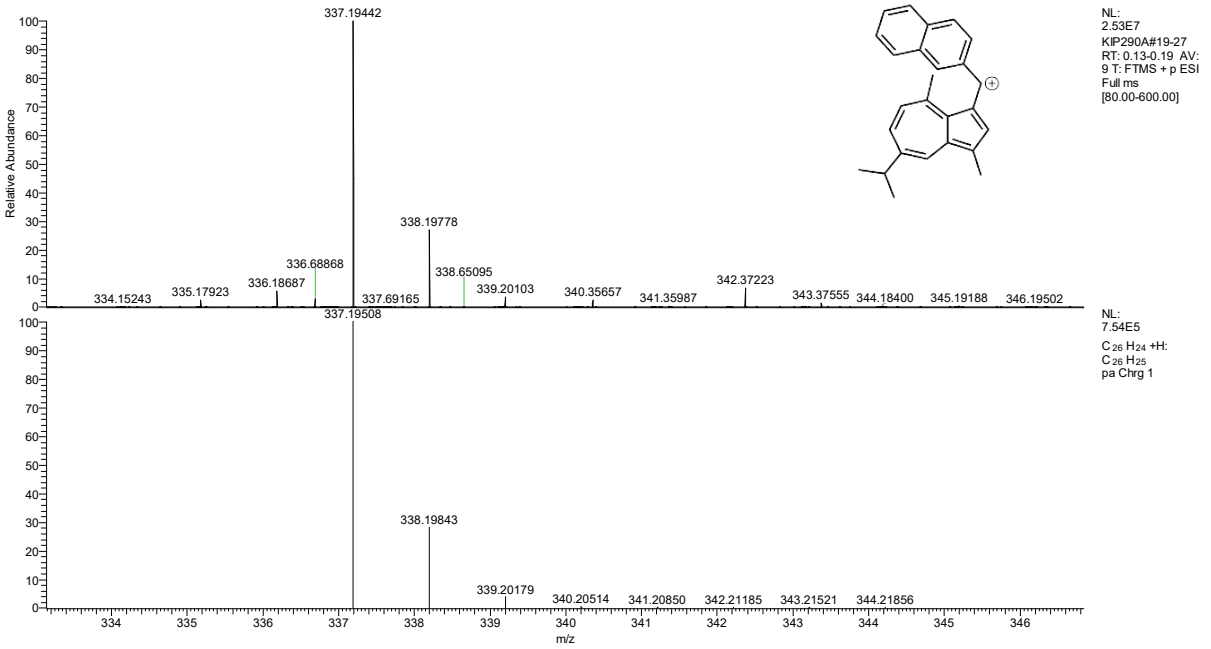


Figure S140. HRMS picture of compound **2d**.

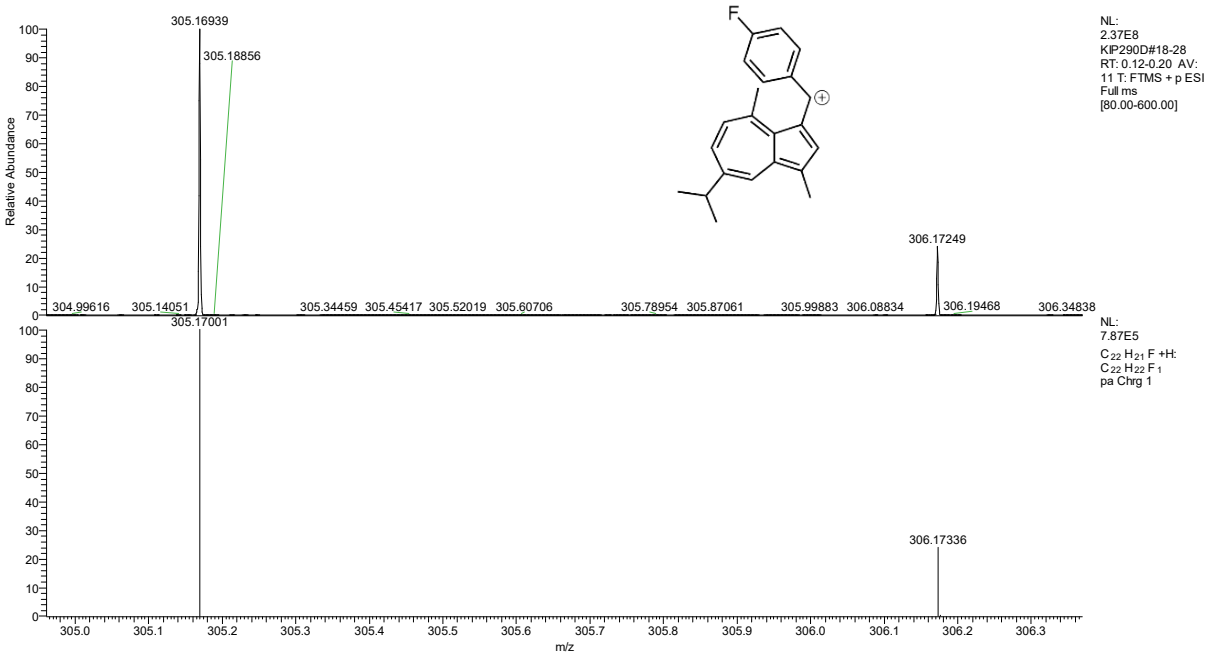


Figure S141. HRMS picture of compound **2e**.

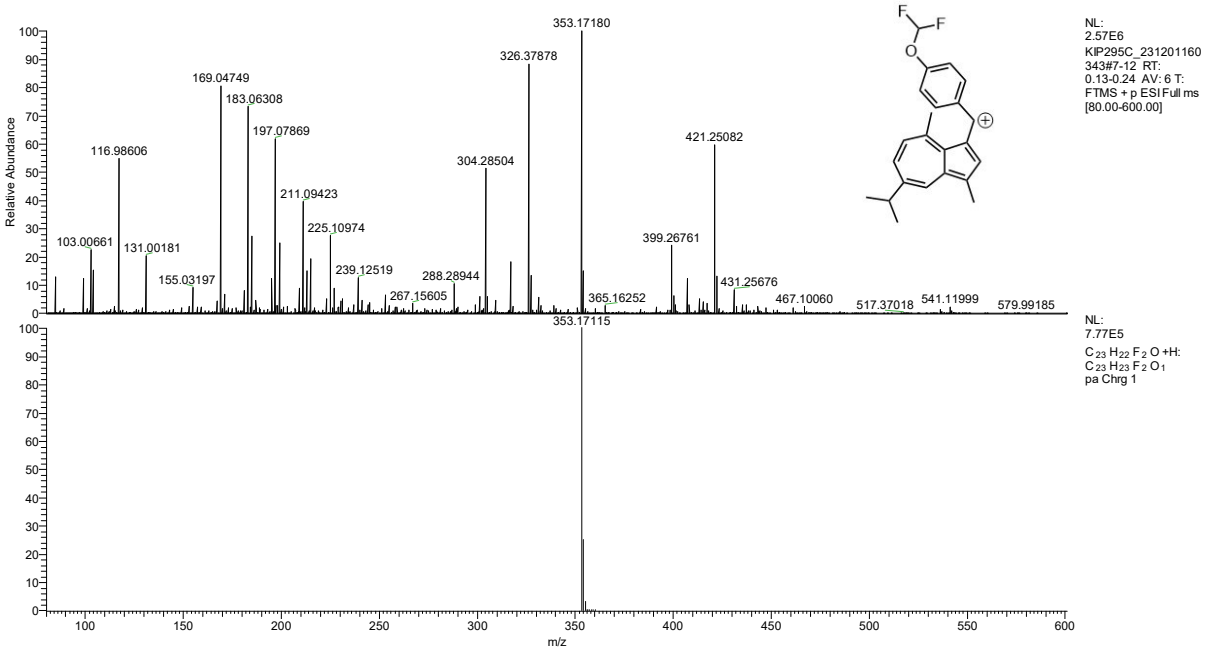


Figure S142. HRMS picture of compound **2f**.

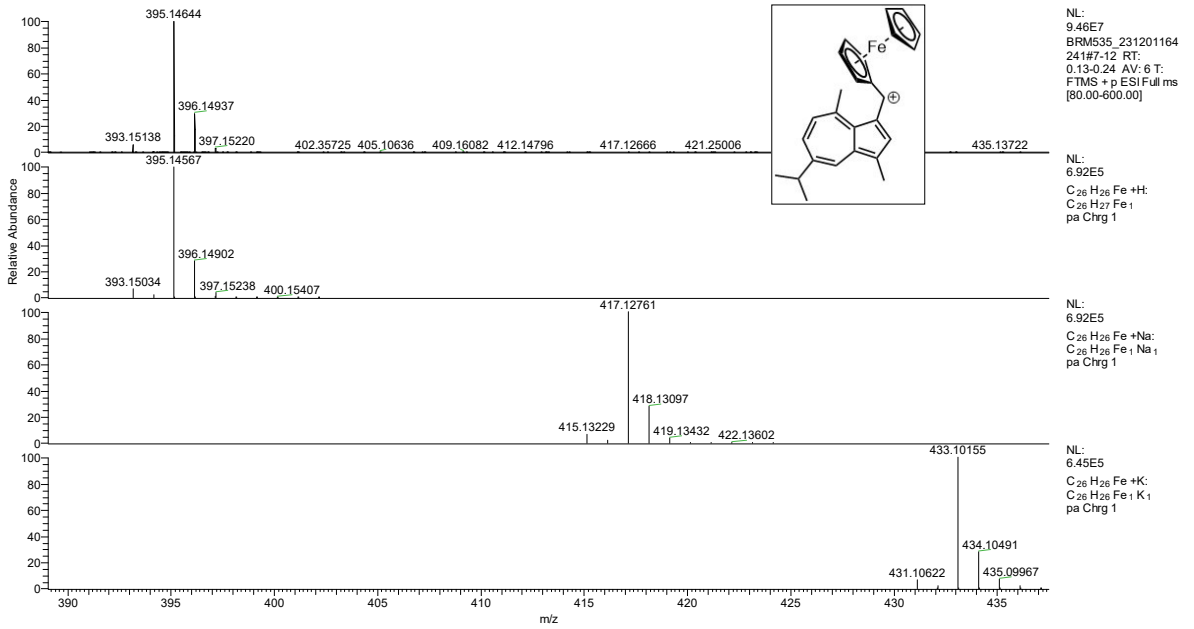


Figure S143. HRMS picture of compound **2g**.

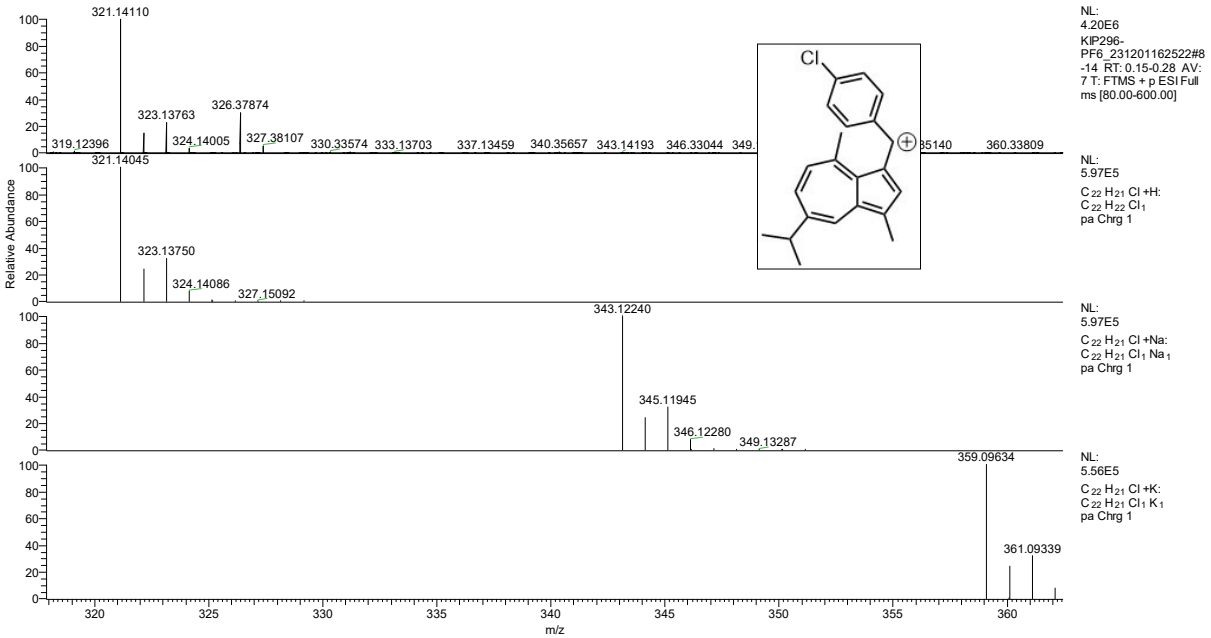


Figure S144. HRMS picture of compound **2h**.

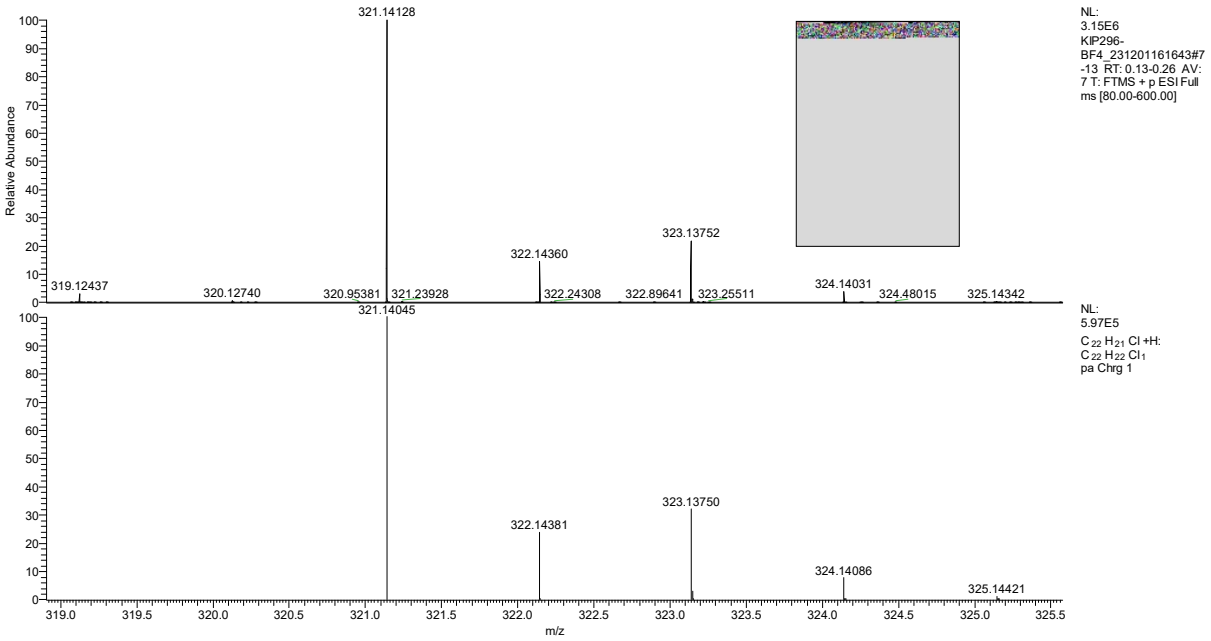


Figure S145. HRMS picture of compound **2h'**.

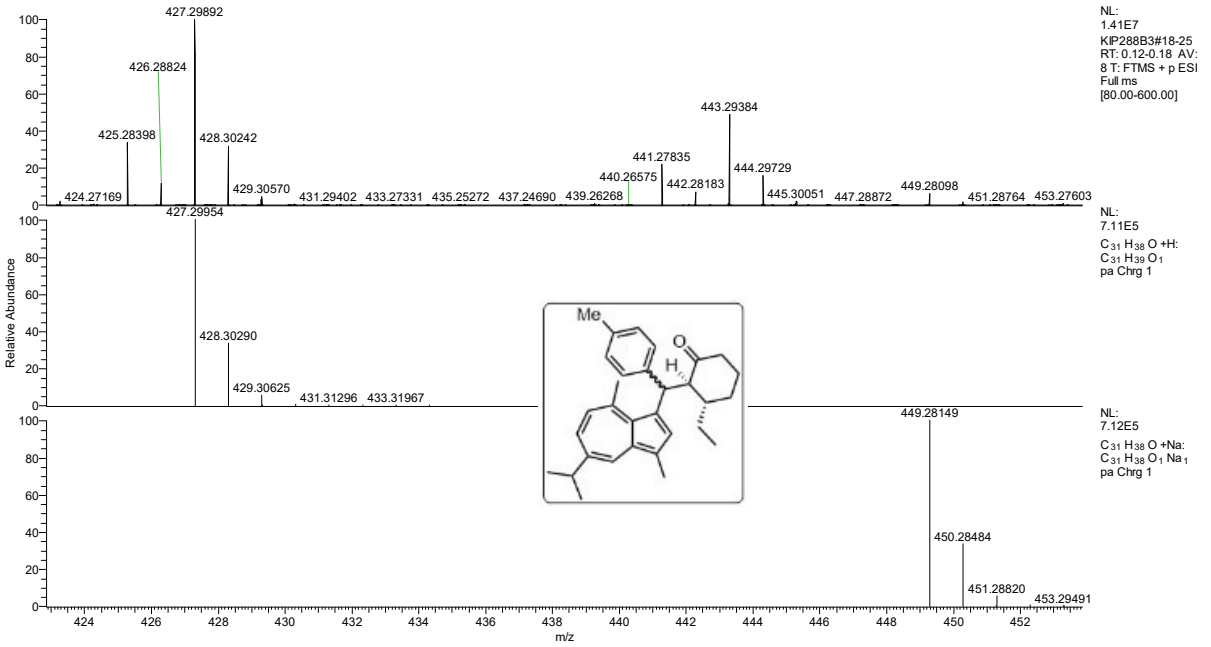


Figure S146. HRMS picture of compound **5aa/diastereomer 1**.

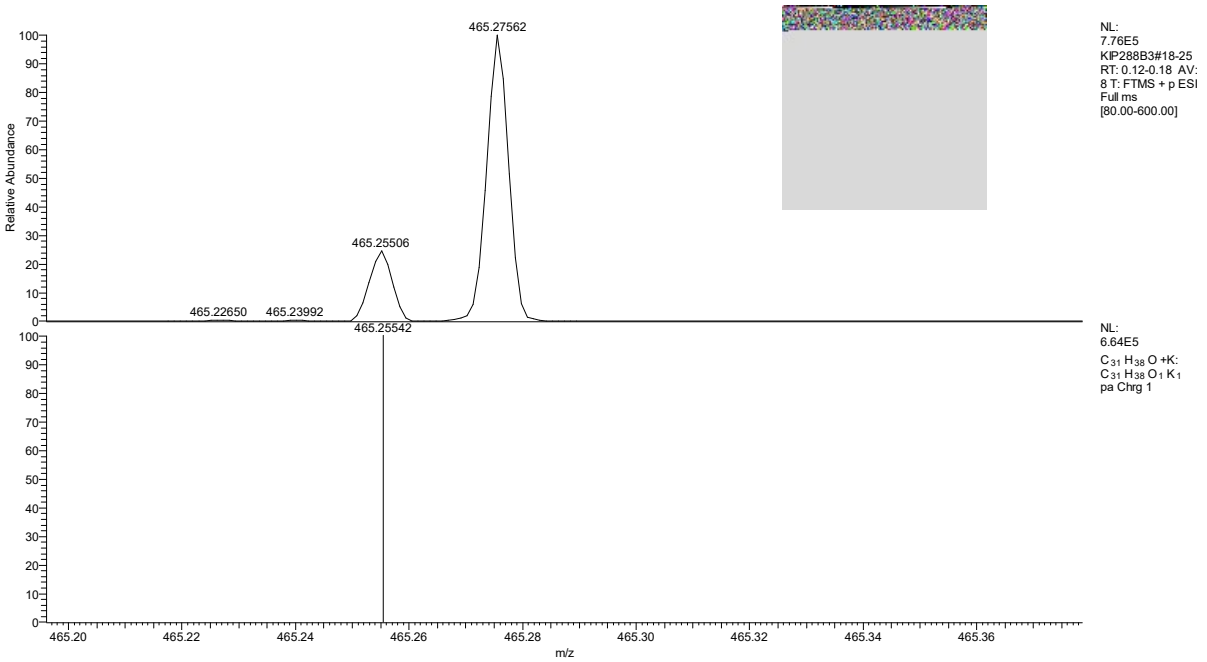


Figure S147. HRMS picture of compound **5aa/diastereomer 1** (enlarged).

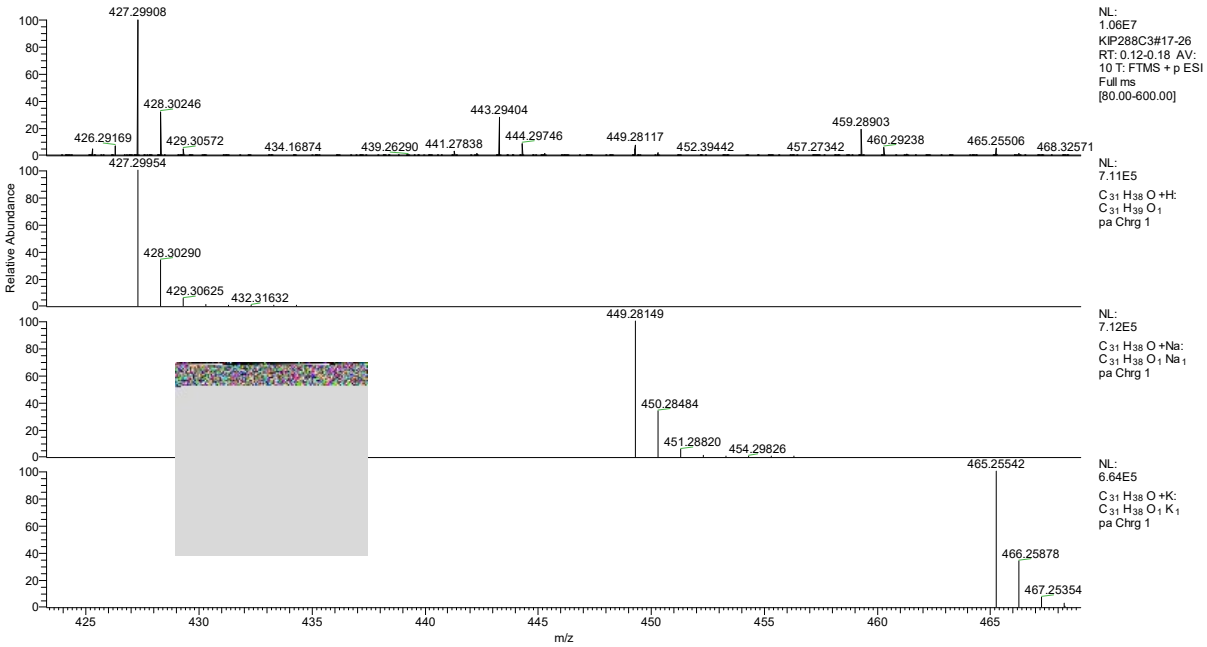


Figure S148. HRMS picture of compound **5aa/diastereomer 2**.

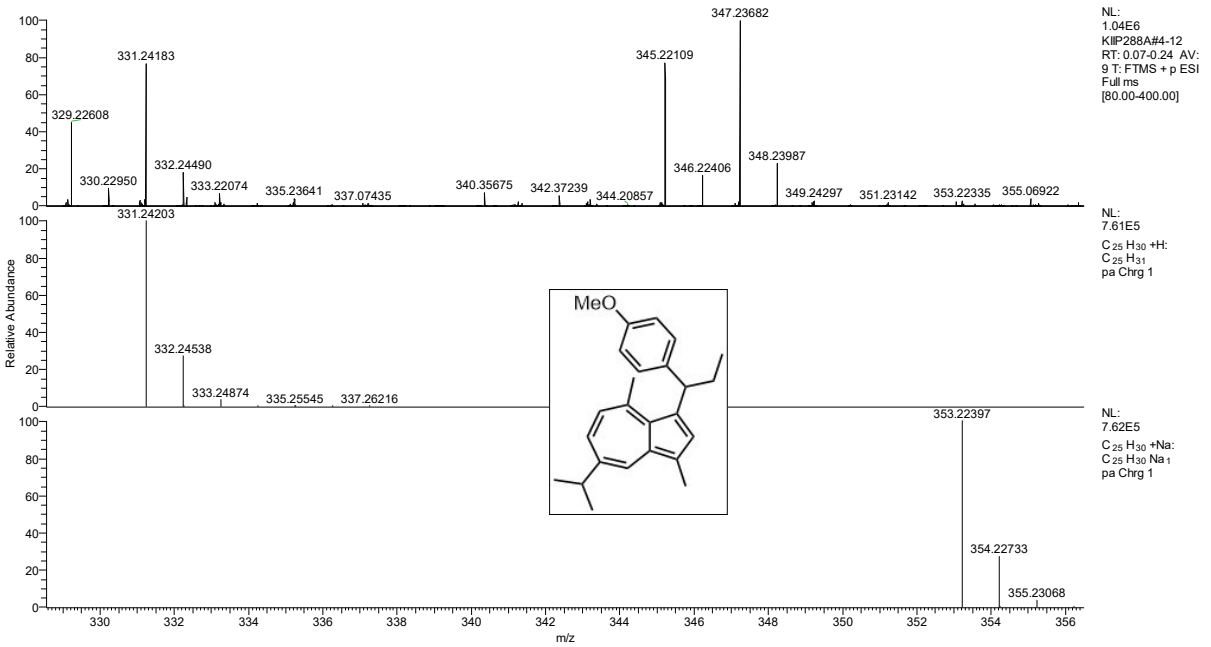


Figure S149. HRMS picture of compound **6a**.

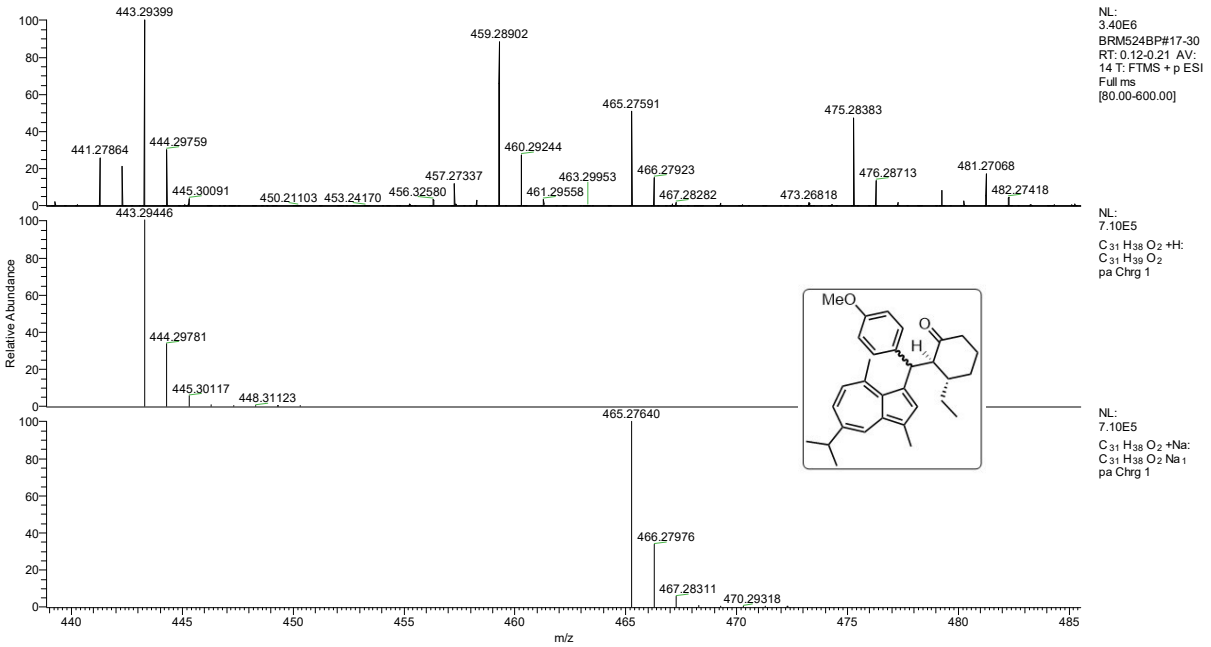


Figure S150. HRMS picture of compound **5ab/diastereomer 1**.

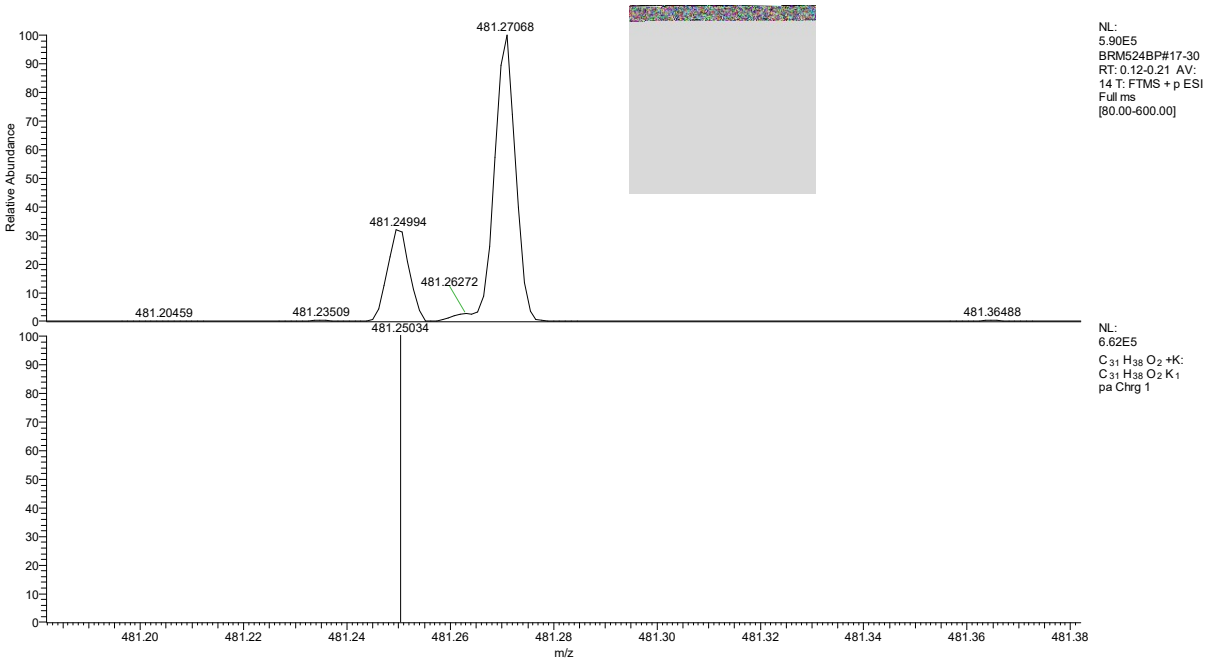


Figure S151. HRMS picture of compound **5ab/diastereomer 1** (enlarged).

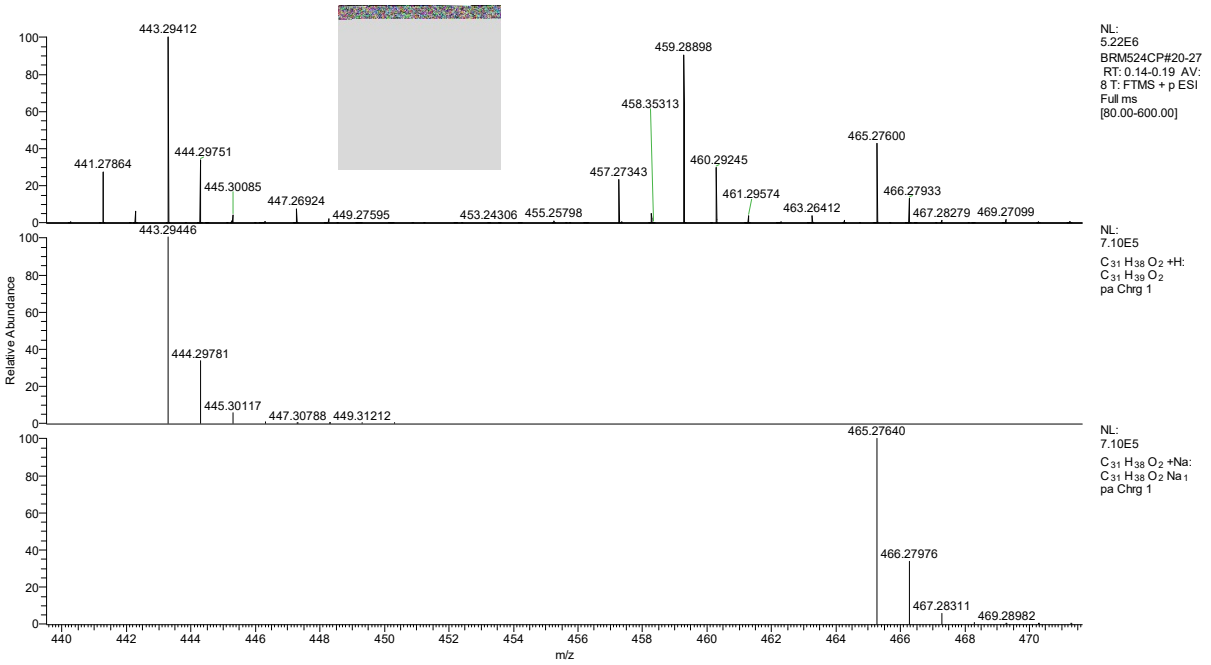


Figure S152. HRMS picture of compound **5ab/diastereomer 2**.

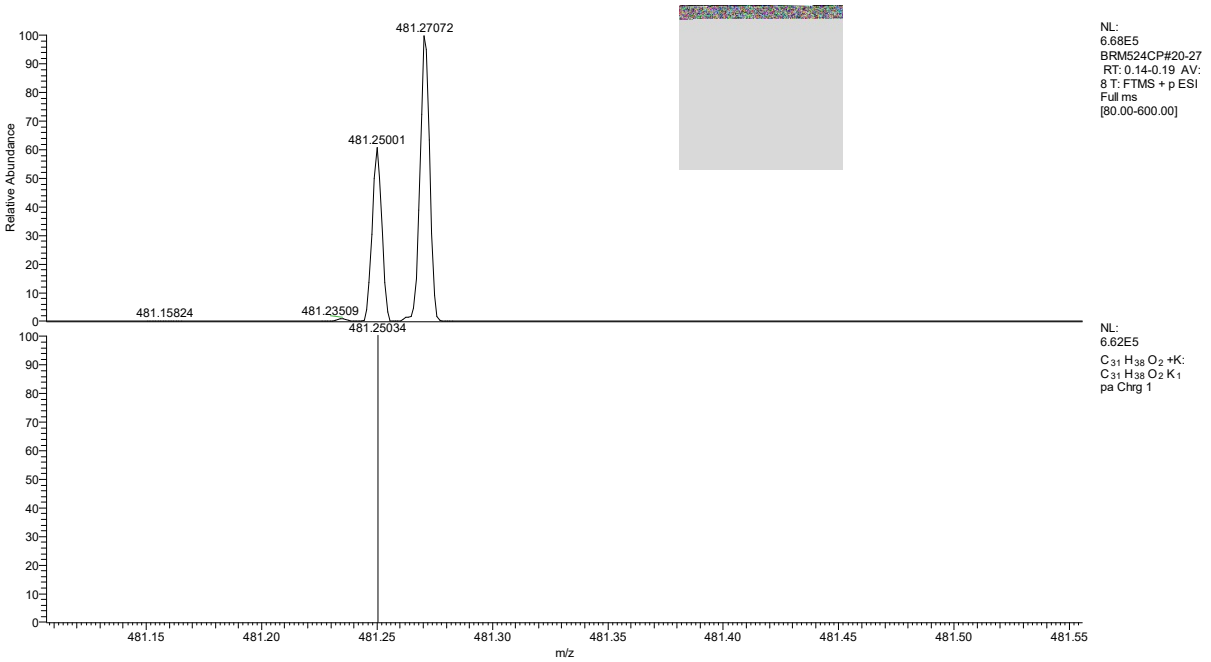


Figure S153. HRMS picture of compound **5ab/diastereomer 2** (enlarged).

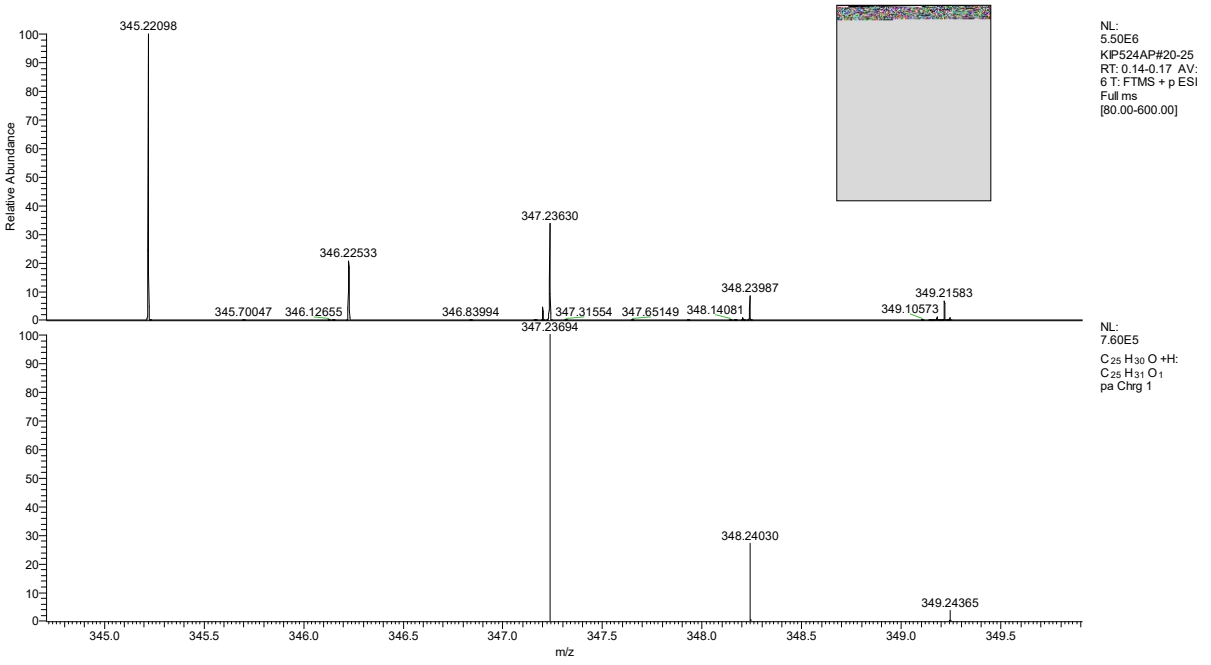


Figure S154. HRMS picture of compound **6b**.

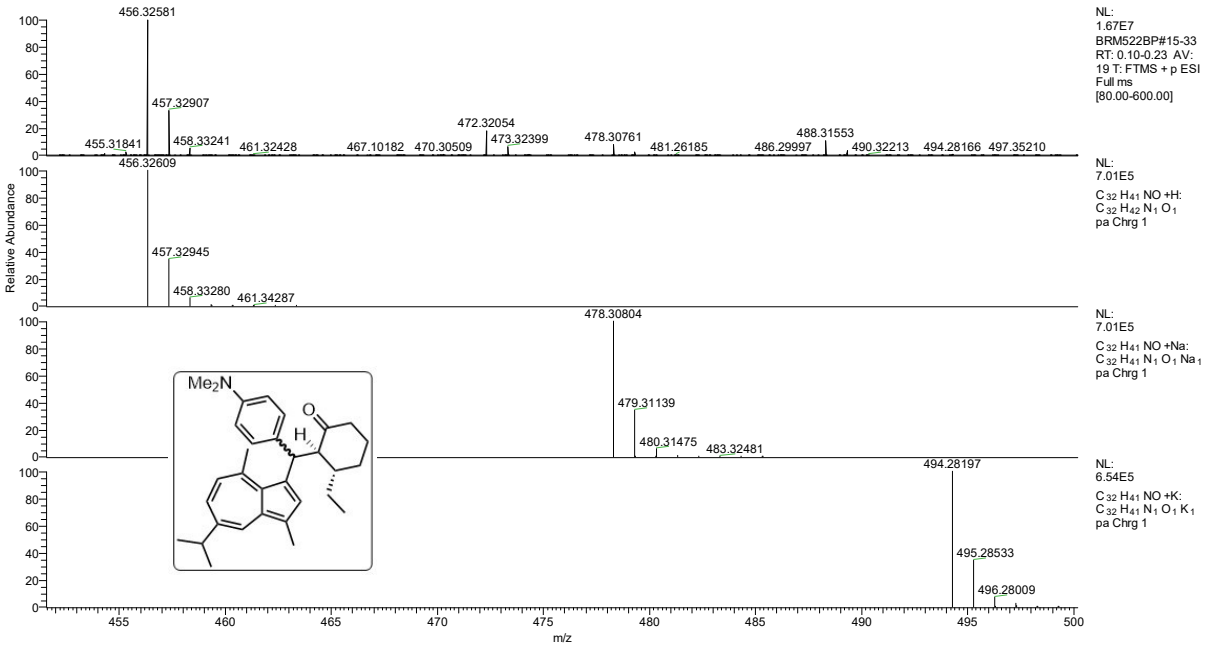


Figure S155. HRMS picture of compound **5ac/diastereomer 1**.

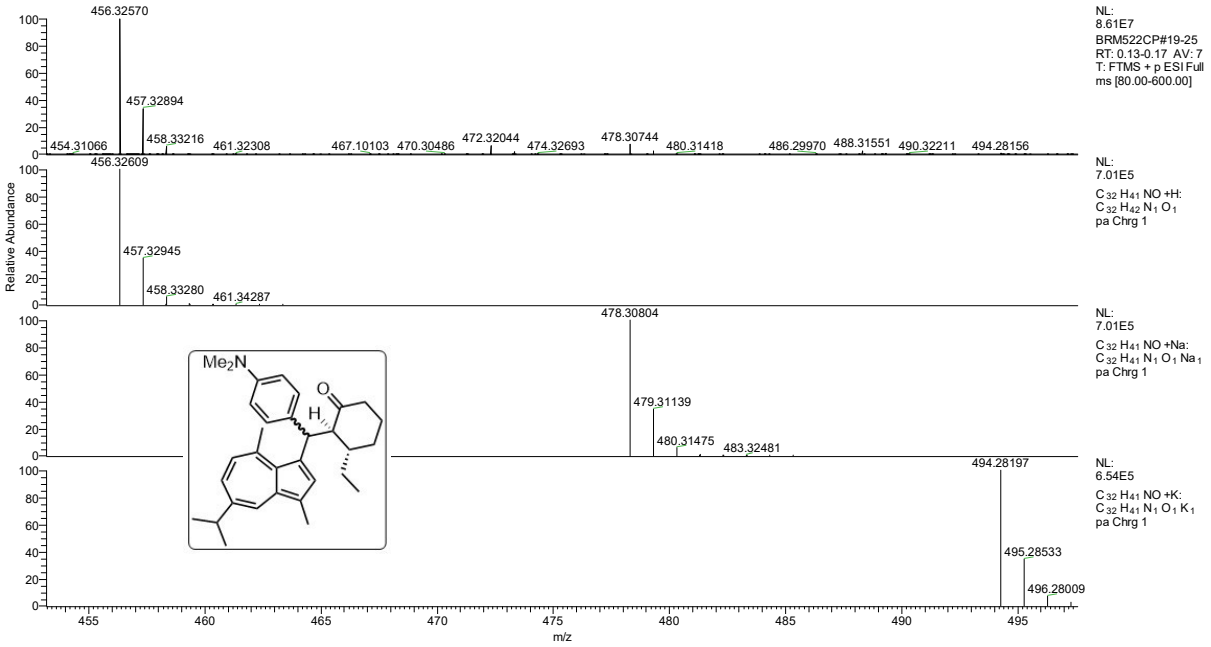


Figure S156. HRMS picture of compound **5ac/diastereomer 2**.

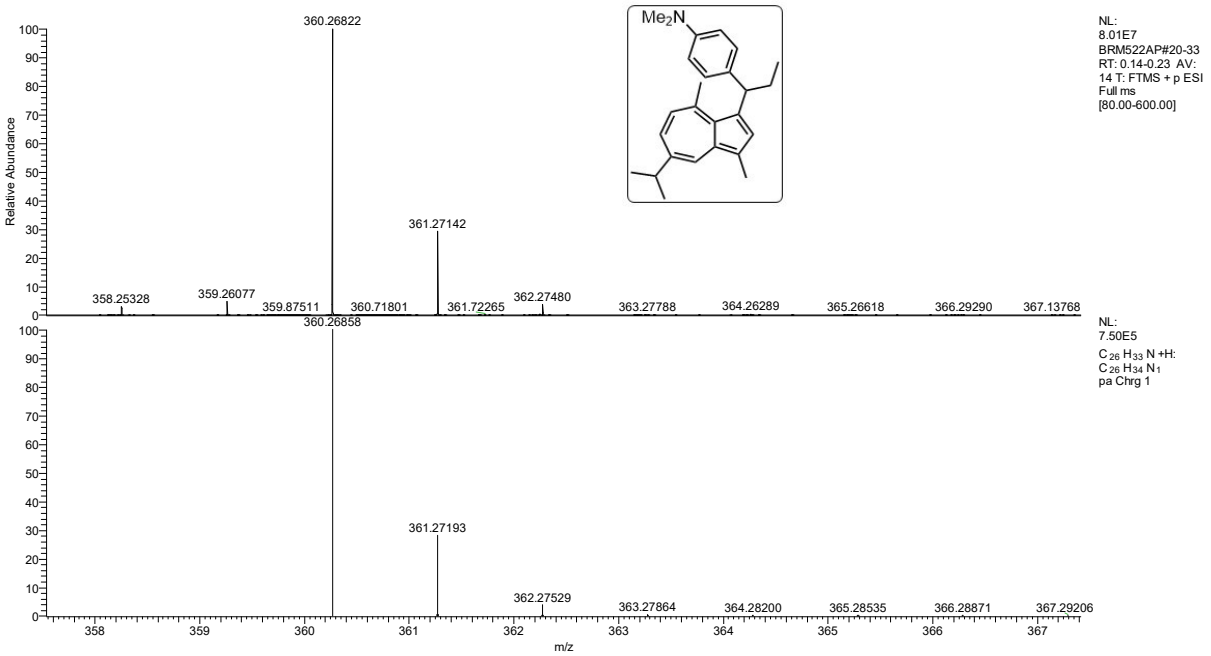


Figure S157. HRMS picture of compound [6c](#).

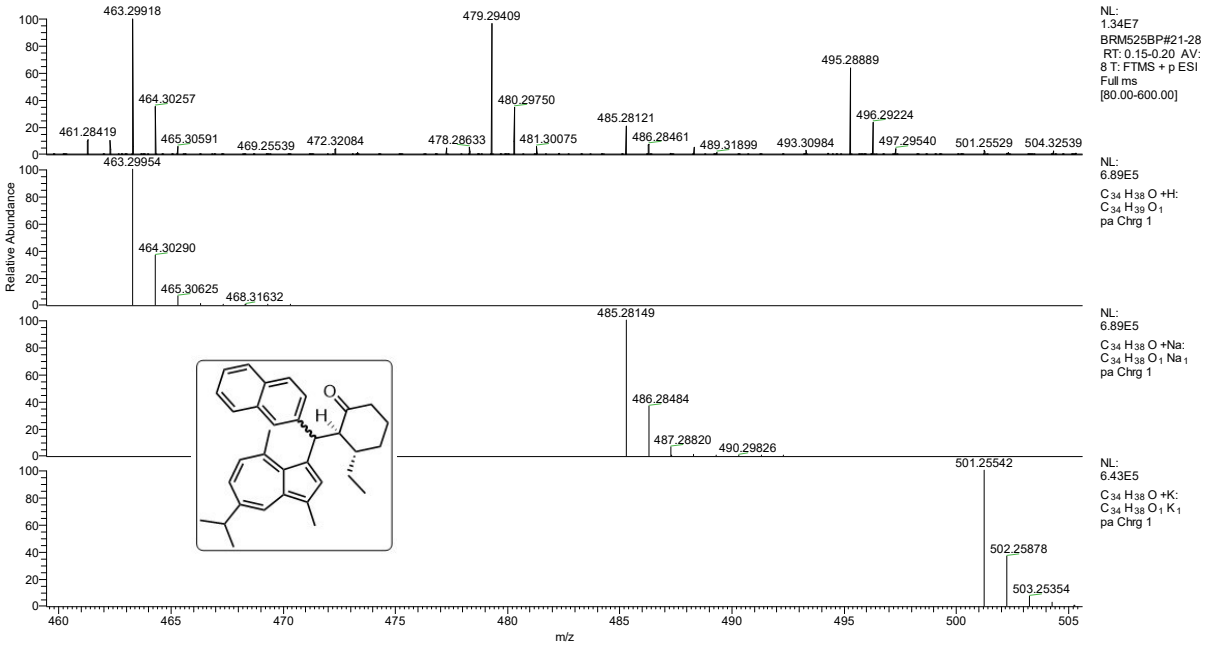


Figure S158. HRMS picture of compound [5ad/diastereomer 1](#).

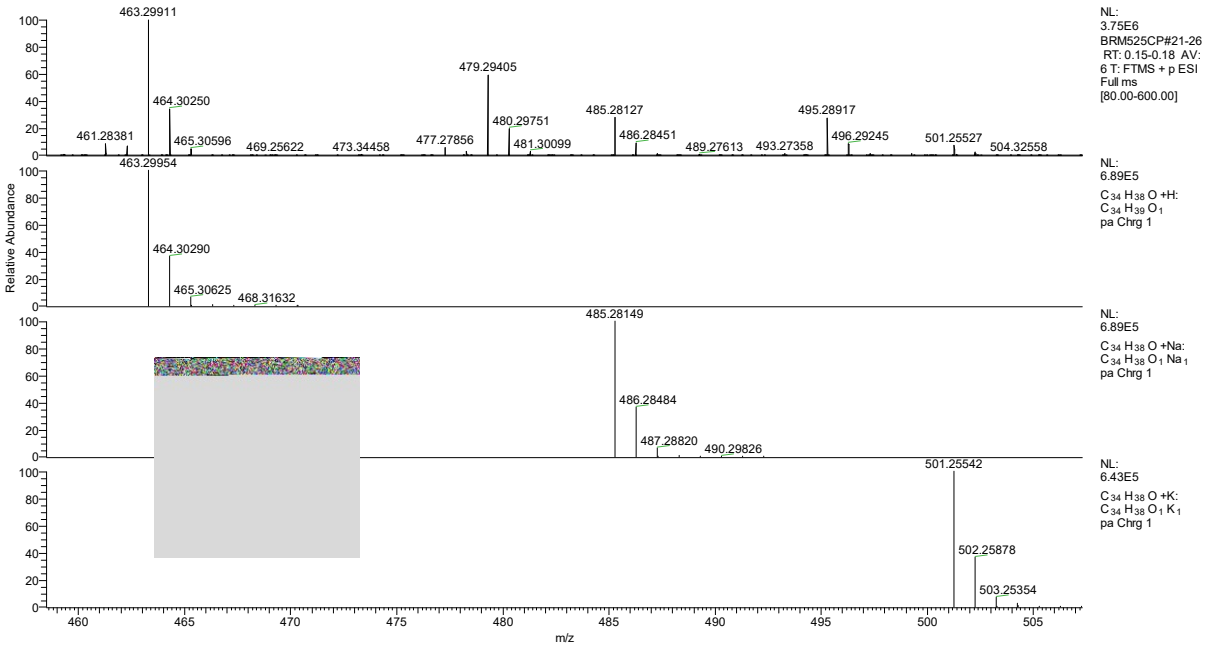


Figure S159. HRMS picture of compound **5ad/diastereomer 2**.

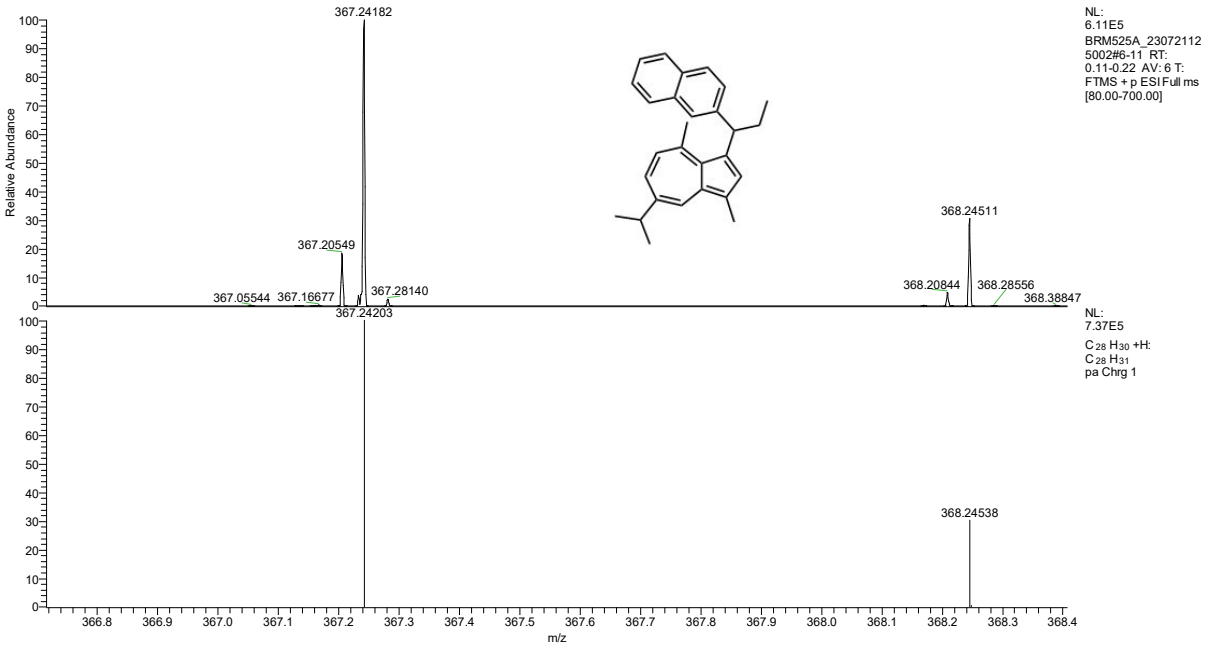


Figure S160. HRMS picture of compound **6d**.

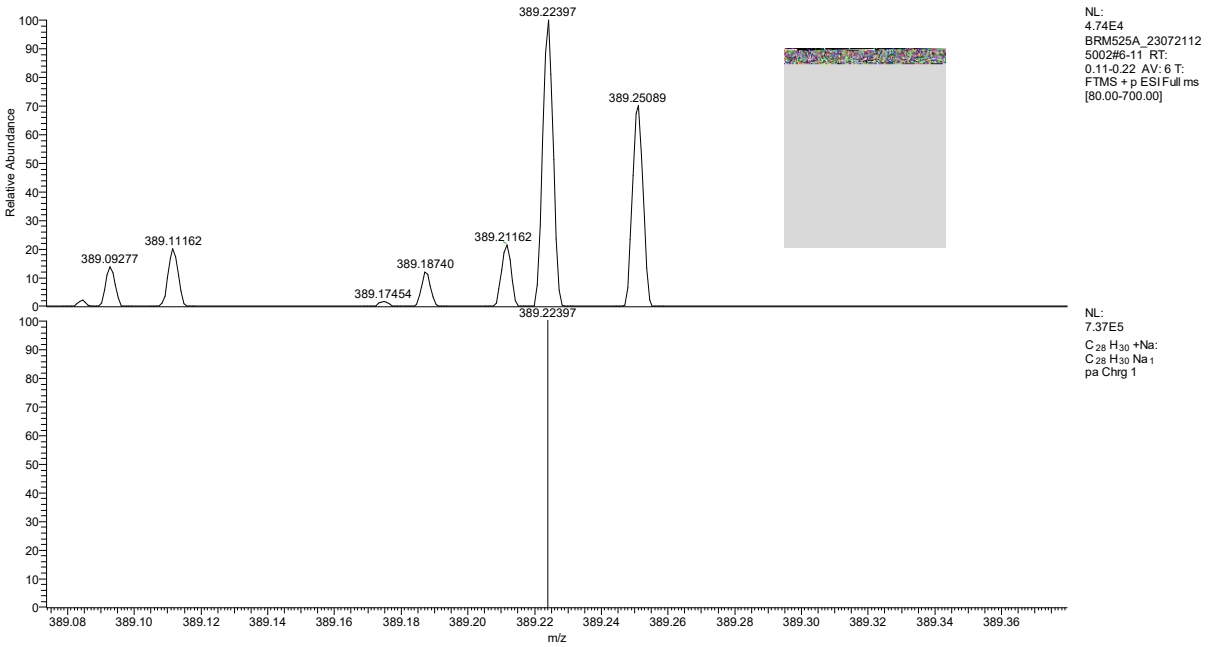


Figure S161. HRMS picture of compound **6d** (Na^+ adduct).

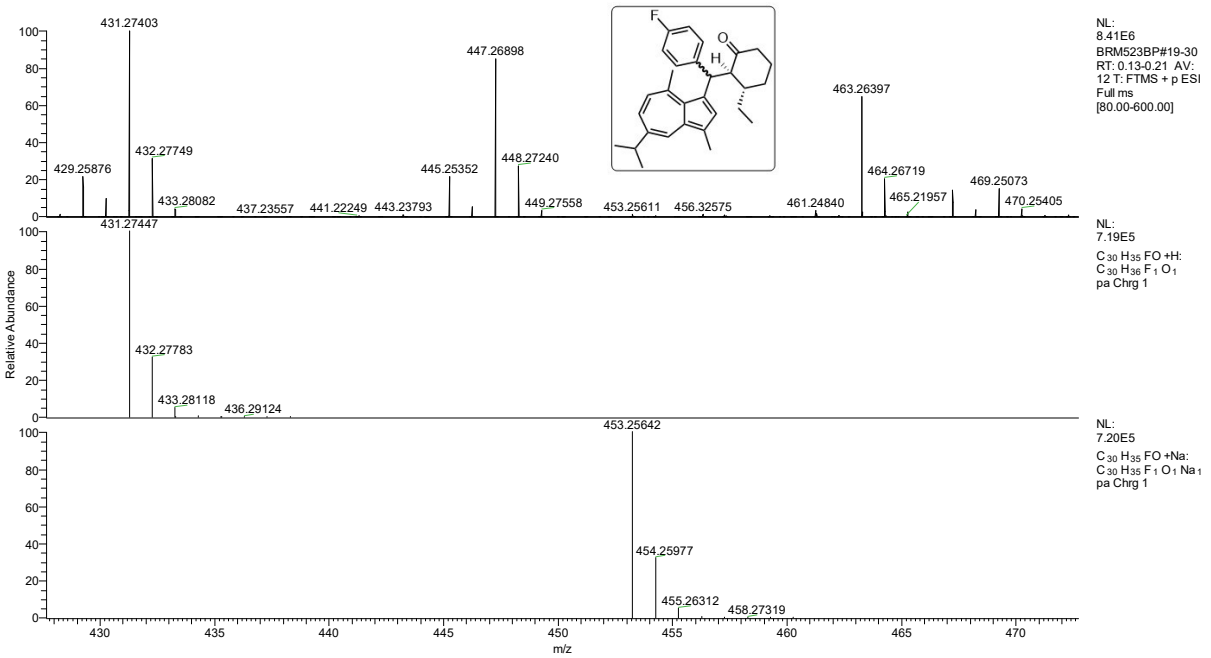


Figure S162. HRMS picture of compound **5ae/diastereomer 1**.

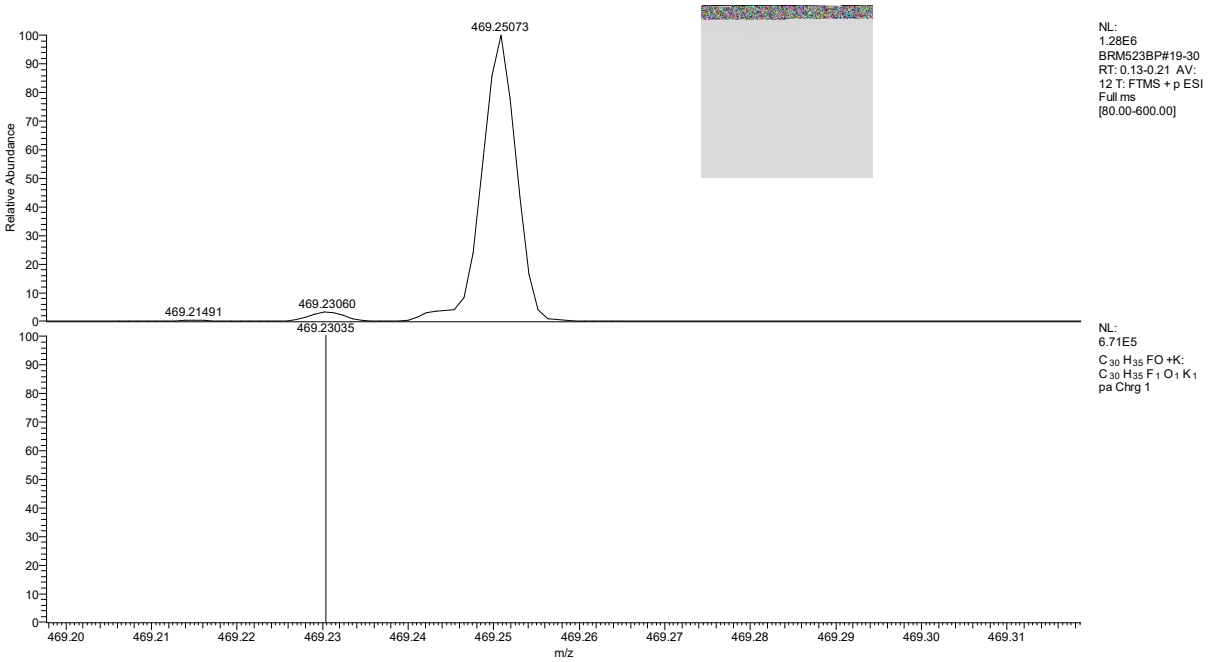


Figure S163. HRMS picture of compound **5ae/diastereomer 1** (enlarged).

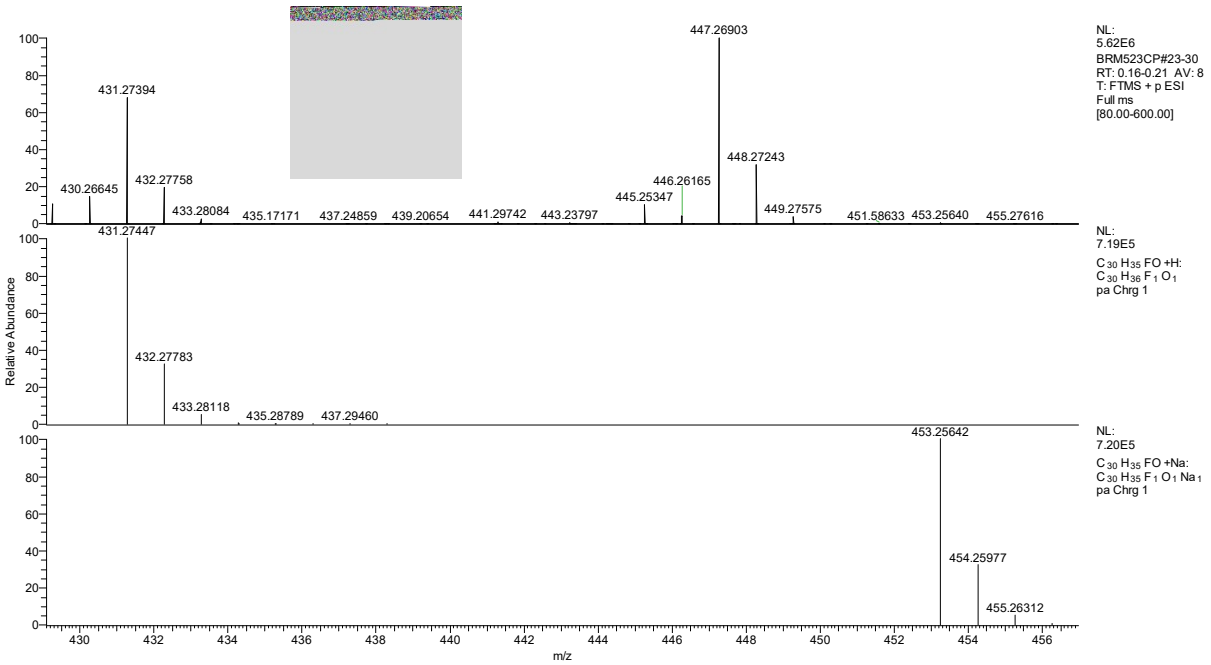


Figure S164. HRMS picture of compound **5ae/diastereomer 2**.

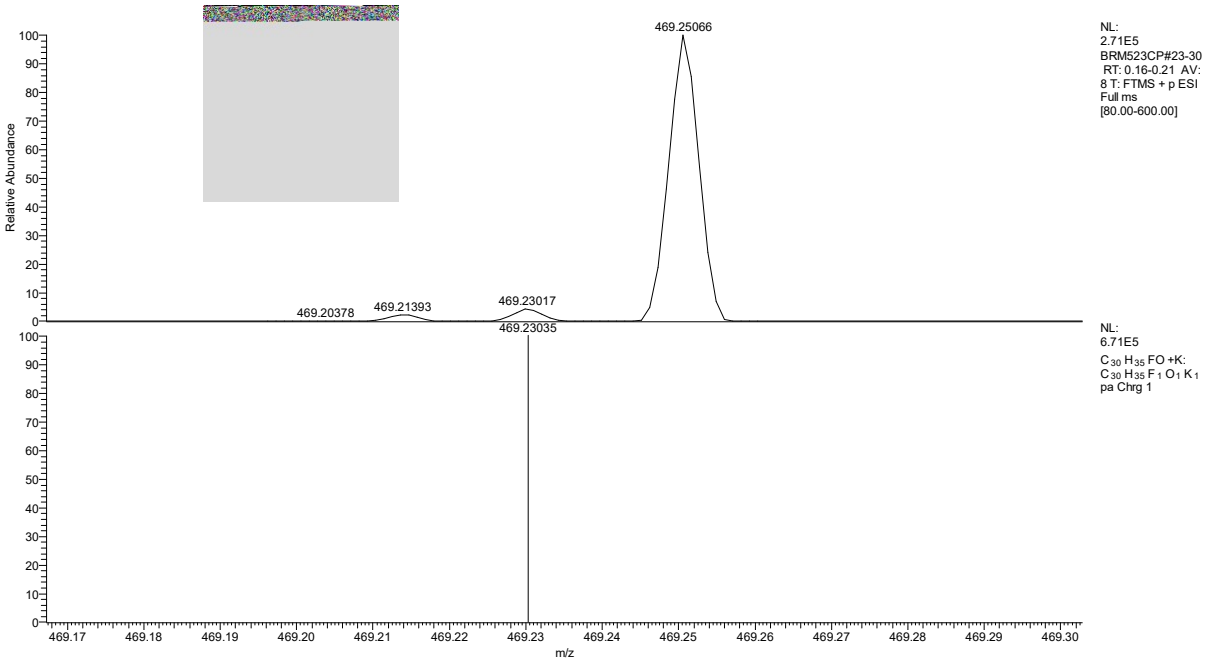


Figure S165. HRMS picture of compound **5ae/diastereomer 2** (enlarged).

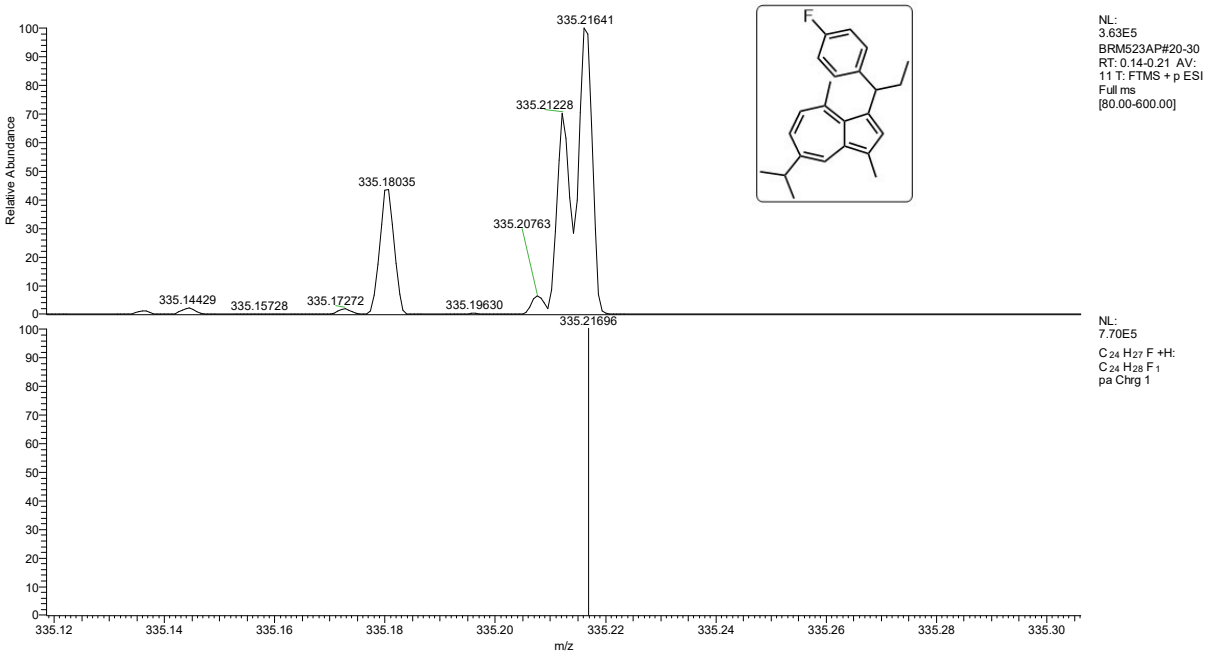


Figure S166. HRMS picture of compound **6e**.

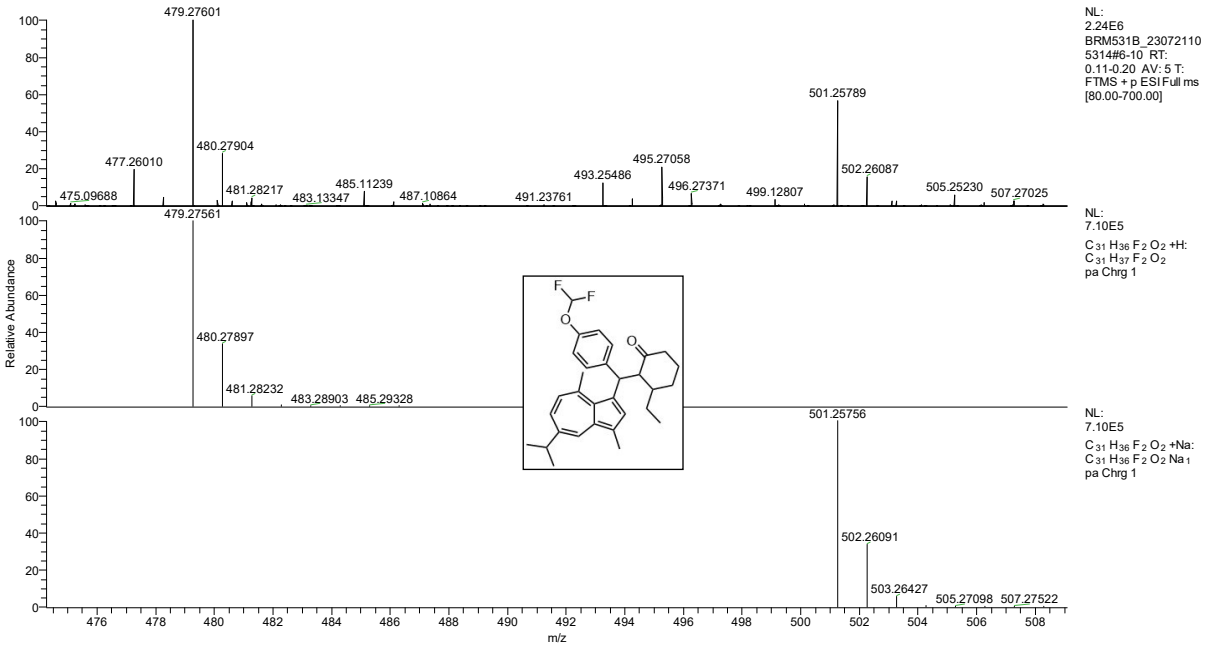


Figure S167. HRMS picture of compound **5af/diastereomer 1**.

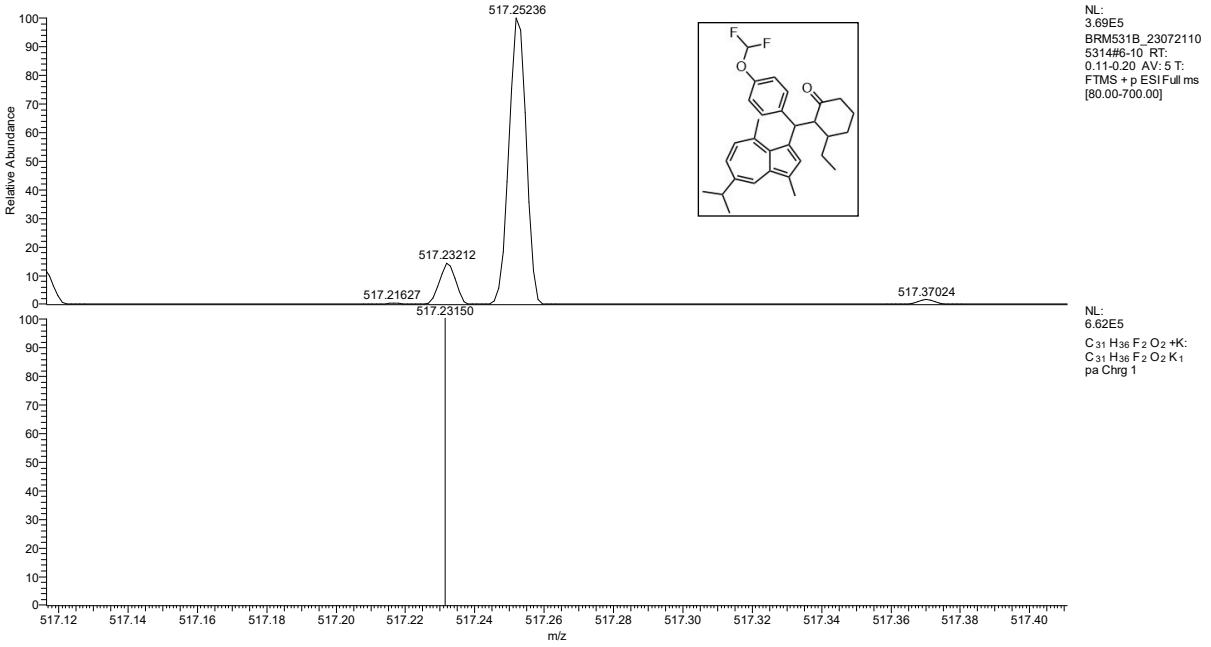


Figure S168. HRMS picture of compound **5af/diastereomer 1** (K^+ adduct).

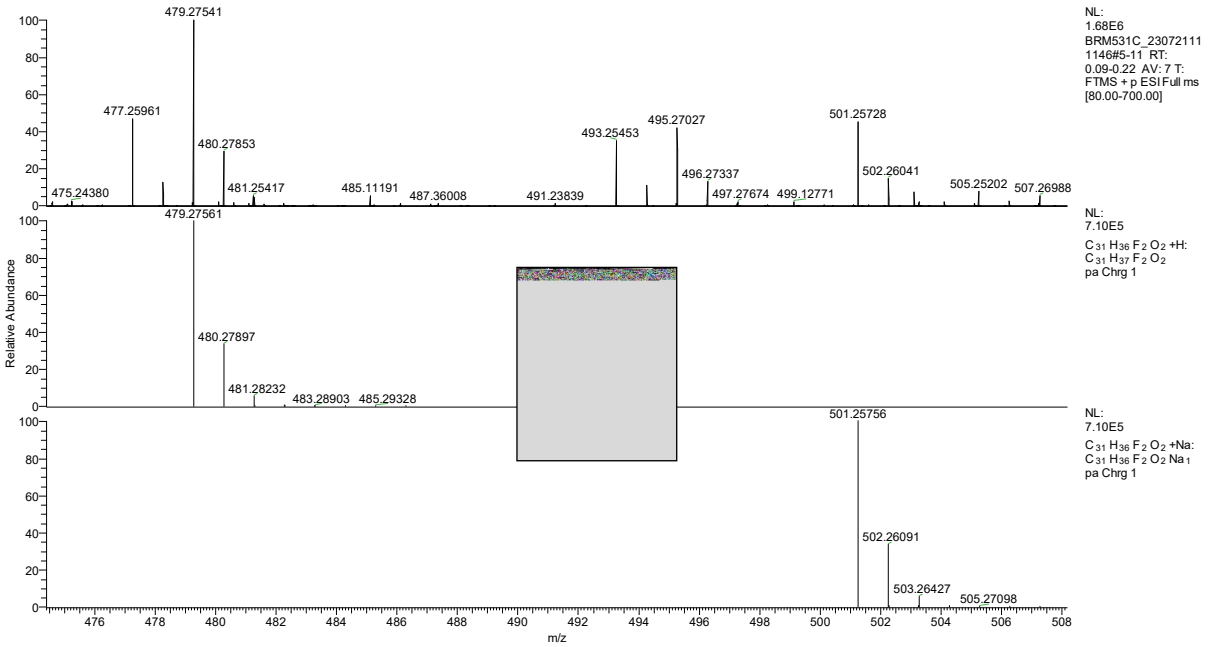


Figure S169. HRMS picture of compound **5af/diastereomer 2**.

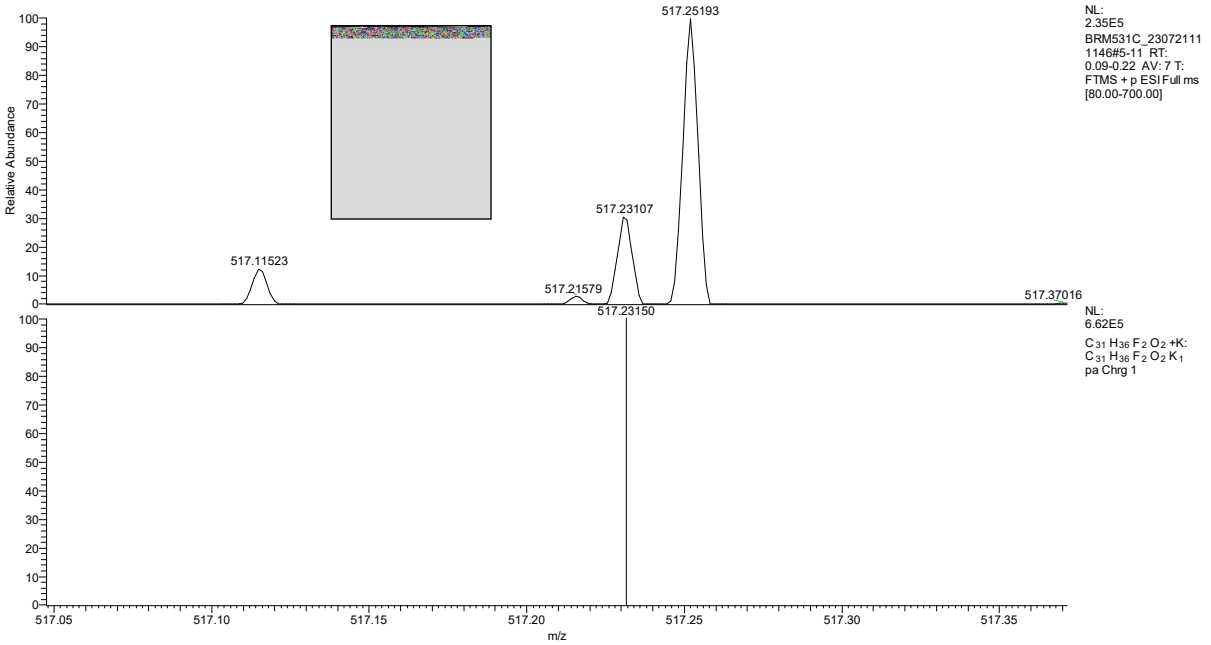


Figure S170. HRMS picture of compound **5af/diastereomer 2** (K^+ adduct).

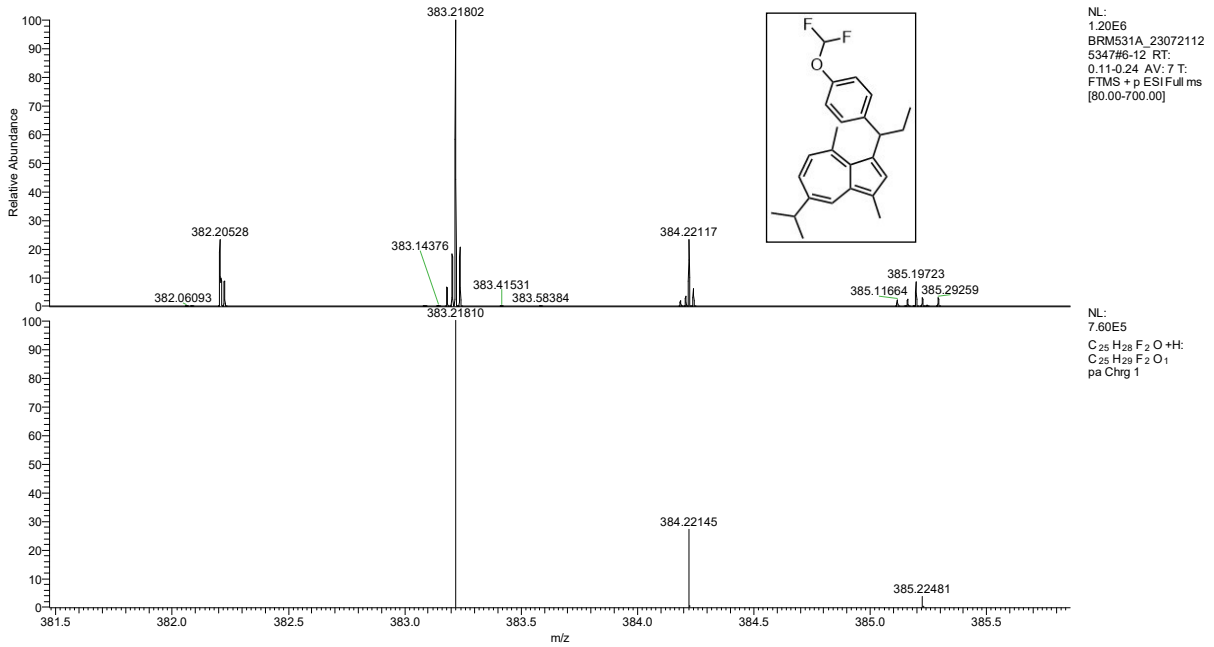


Figure S171. HRMS picture of compound **6f**.

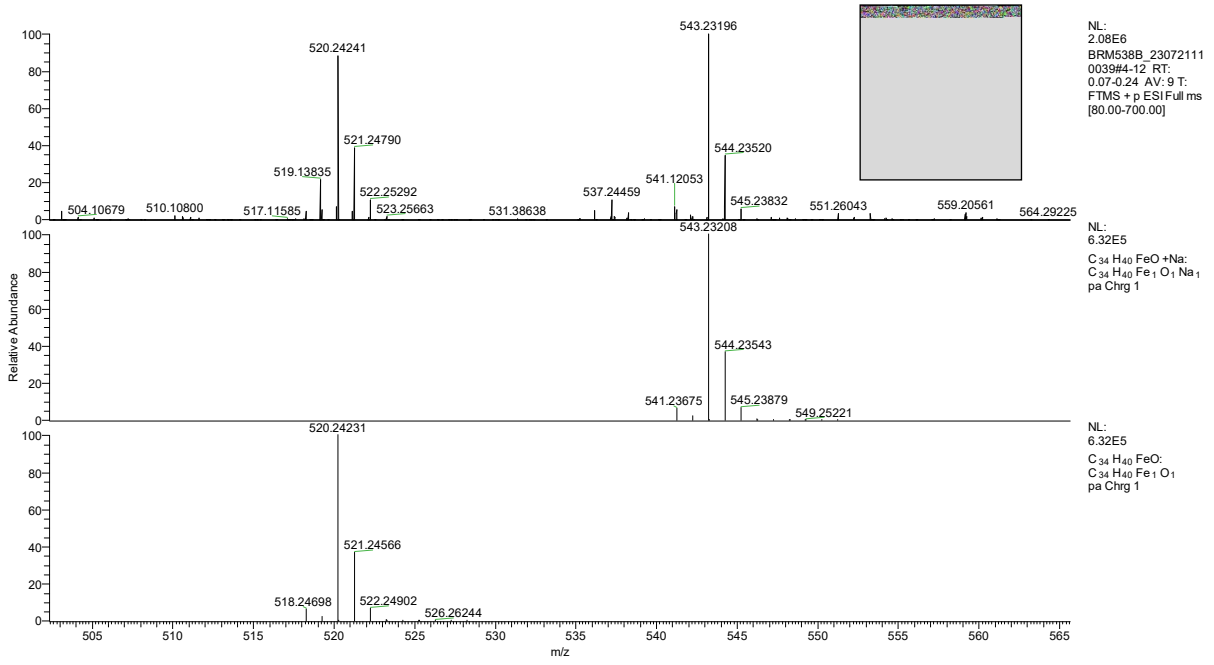


Figure S172. HRMS picture of compound **5ag/diastereomer 1** (M^+ and Na^+ adduct).

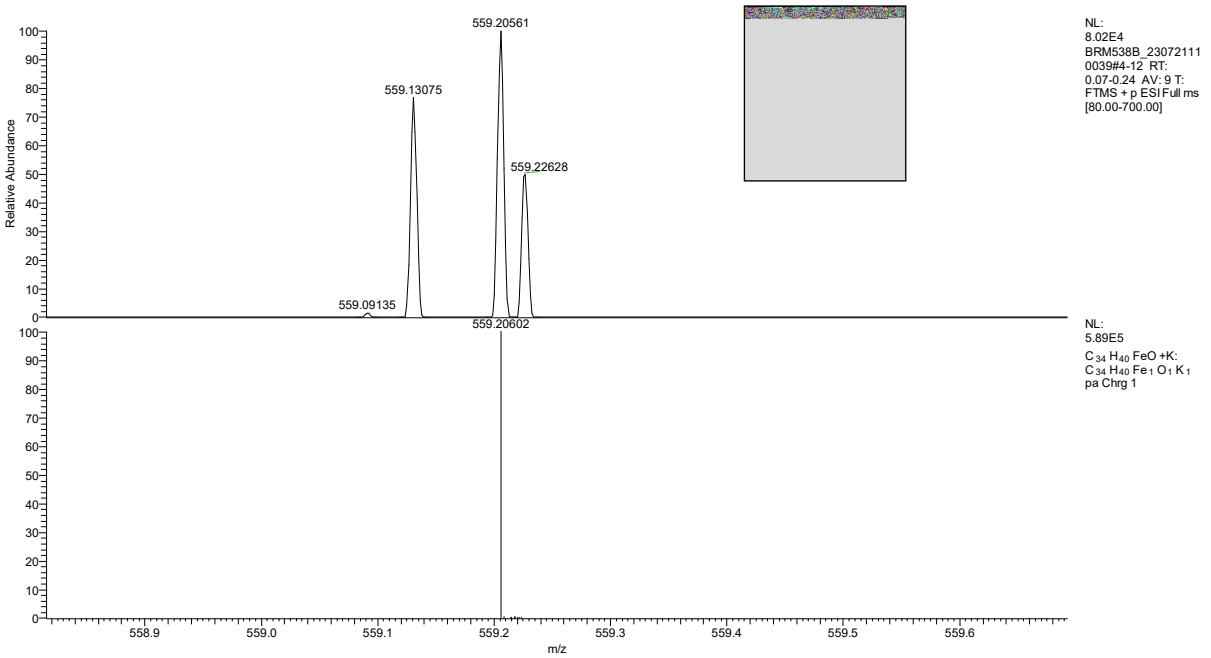


Figure S173. HRMS picture of compound **5ag/diastereomer 1** (K^+ adduct).

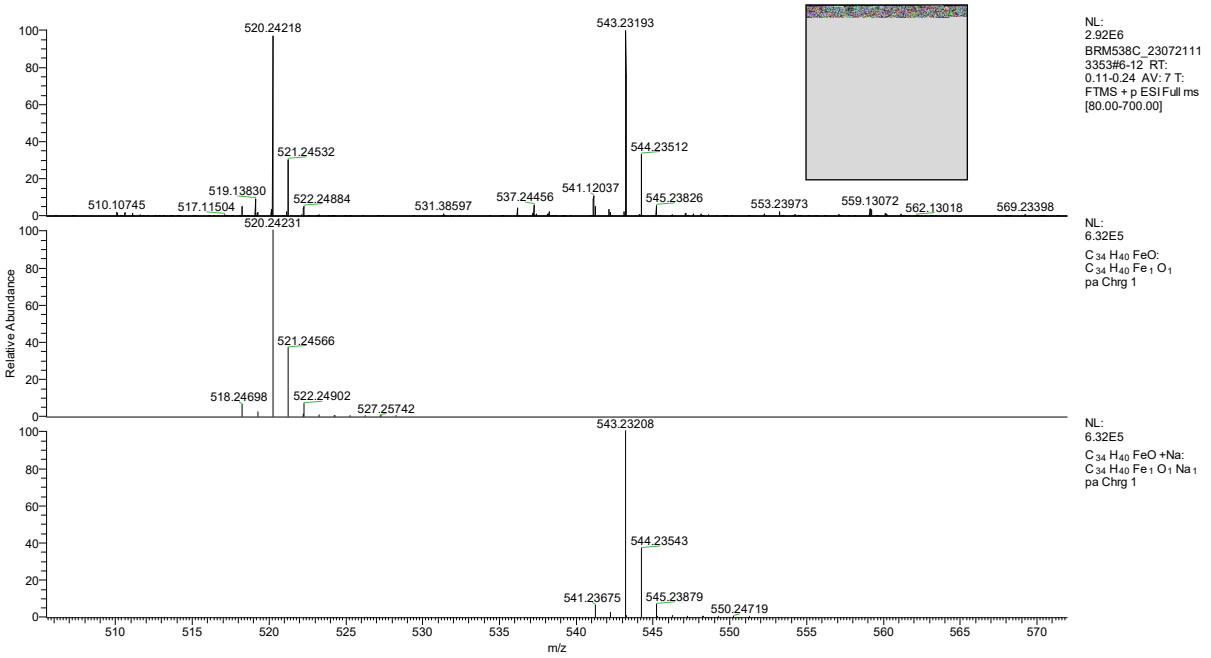


Figure S174. HRMS picture of compound **5ag/diastereomer 2** (M^+ and Na^+ adduct).

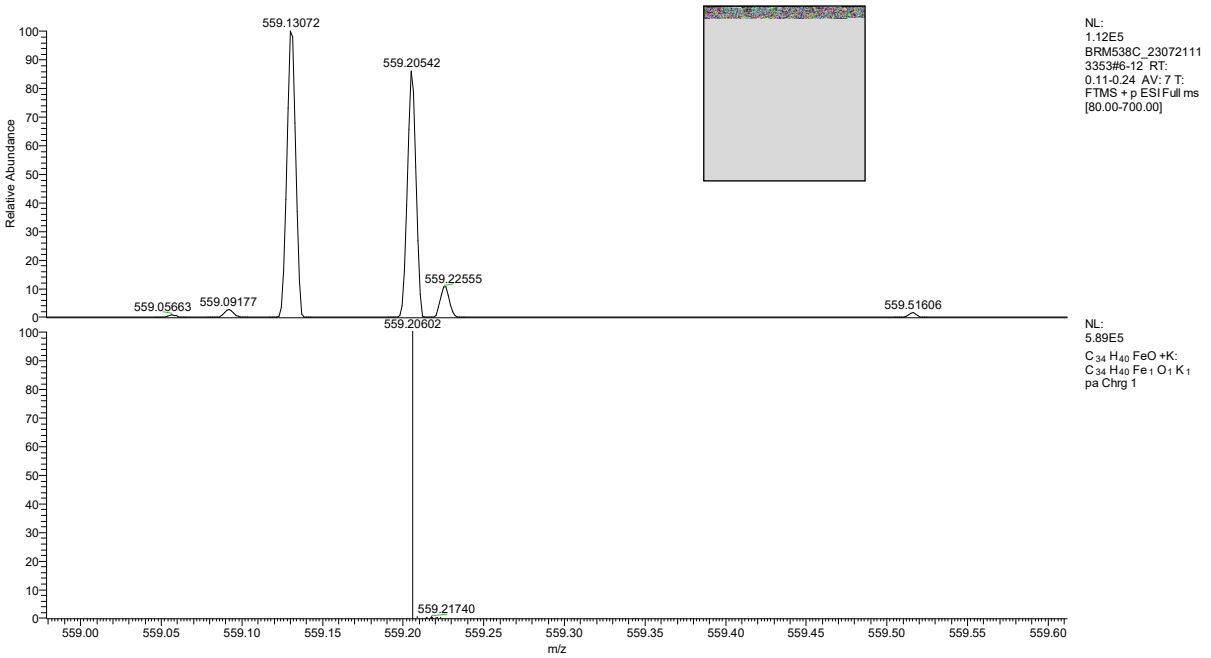


Figure S175. HRMS picture of compound **5ag/diastereomer 2** (K^+ adduct).

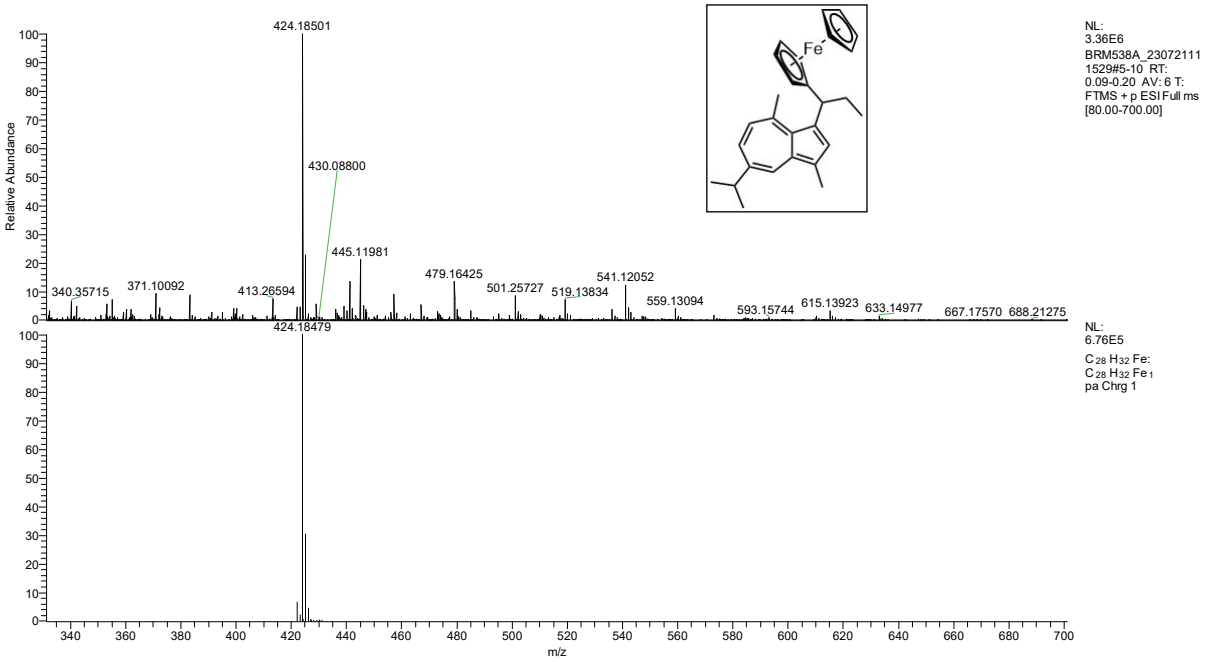


Figure S176. HRMS picture of compound **6g**.

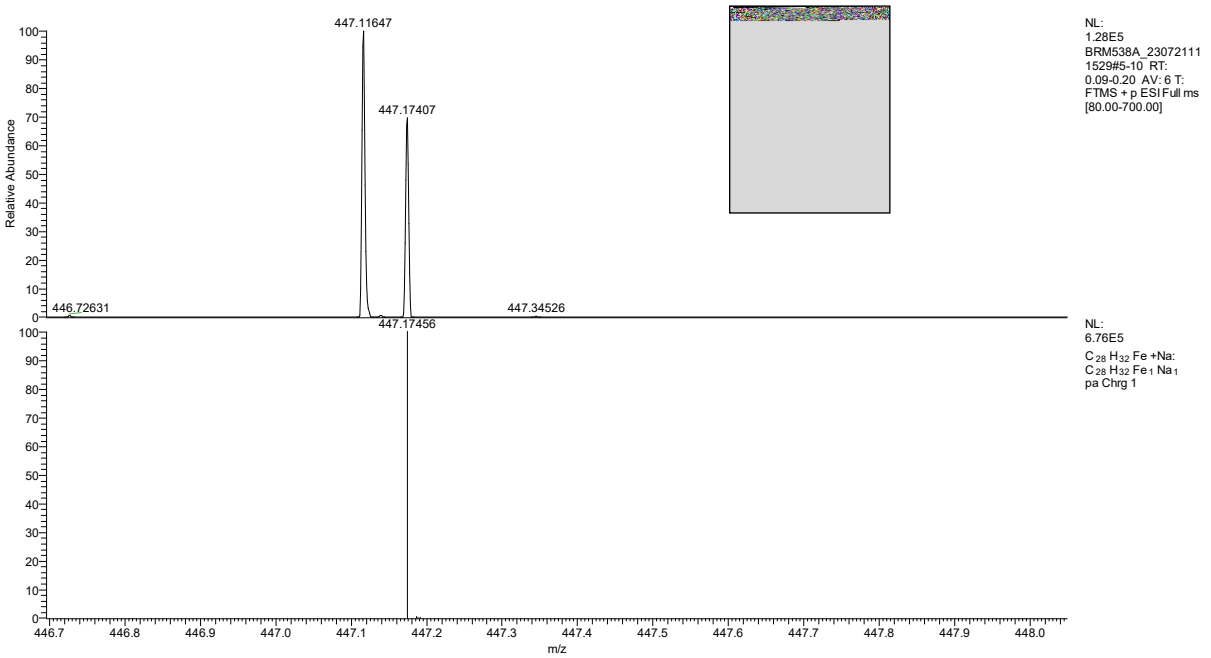


Figure S177. HRMS picture of compound **6g** (Na^+ adduct).

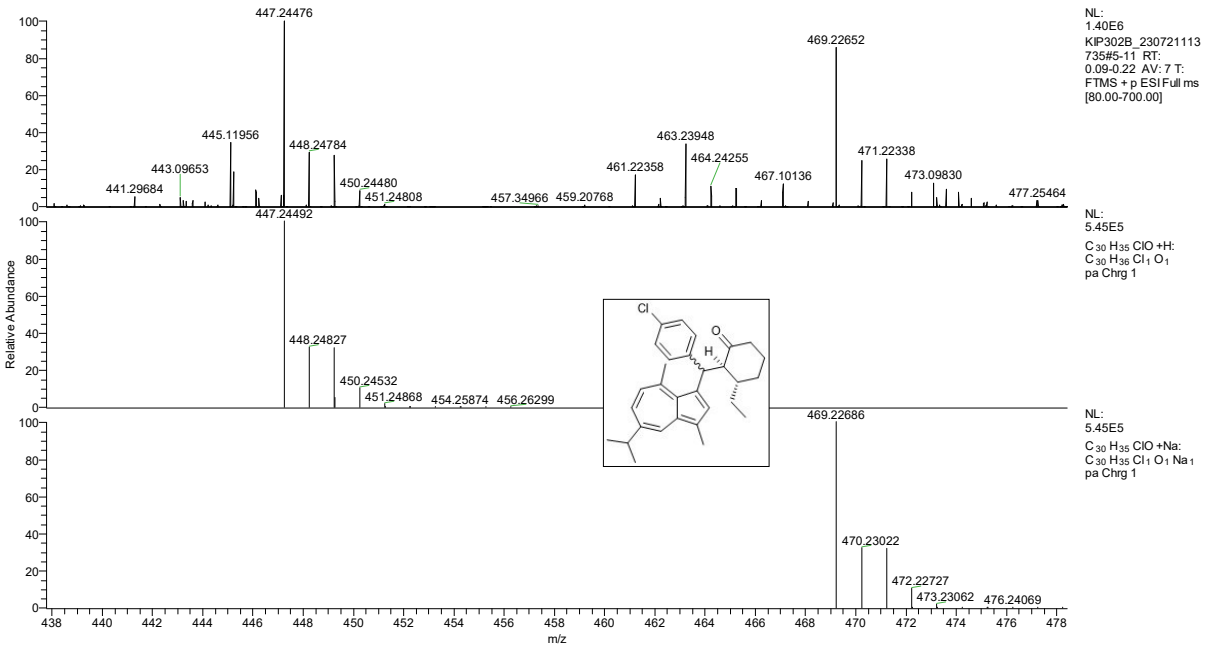


Figure S178. HRMS picture of compound **5ah/diastereomer 1**.

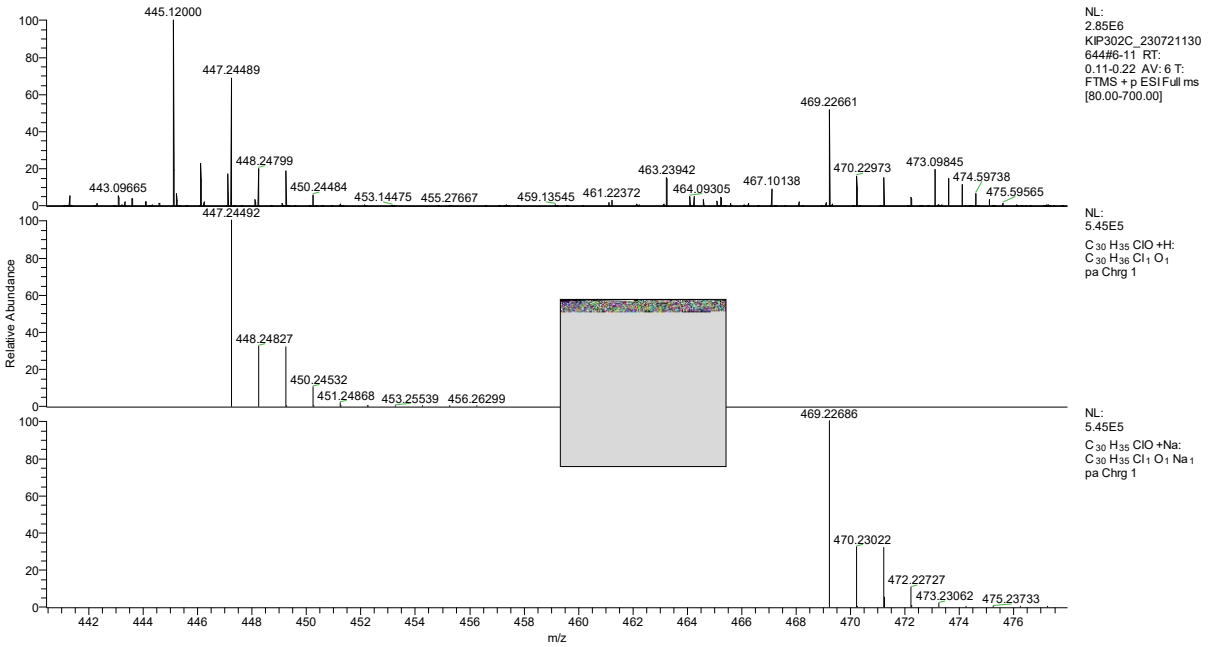


Figure S179. HRMS picture of compound **5ah/diastereomer 2**.

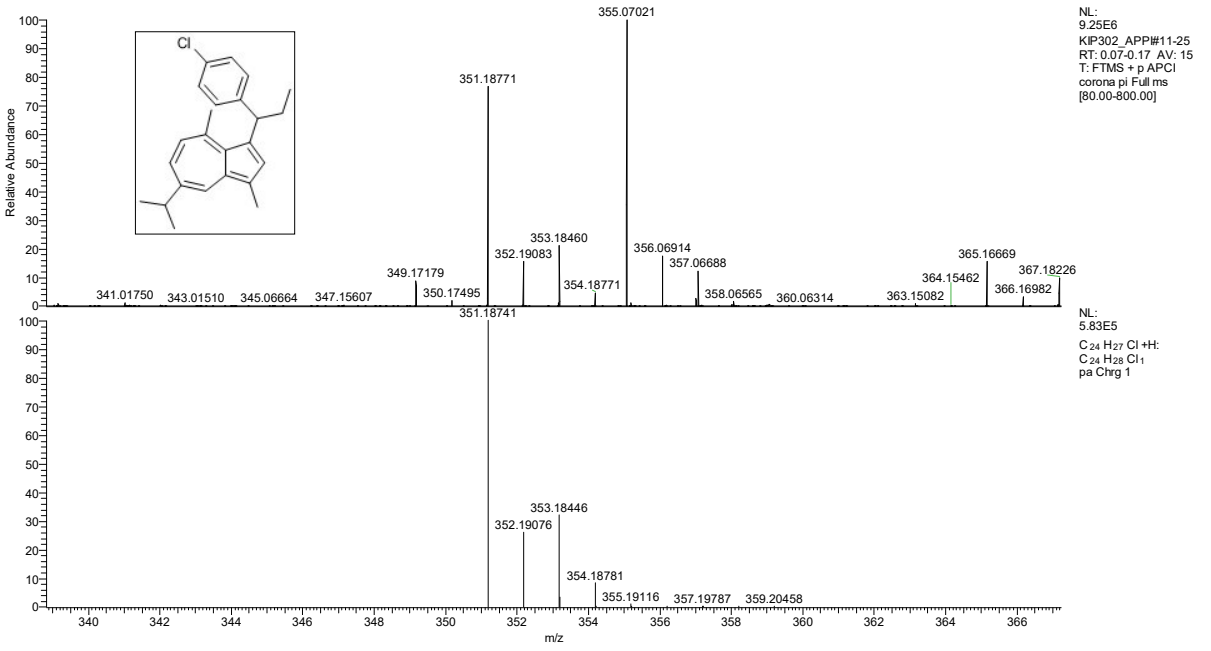


Figure S180. HRMS picture of compound **6h**.

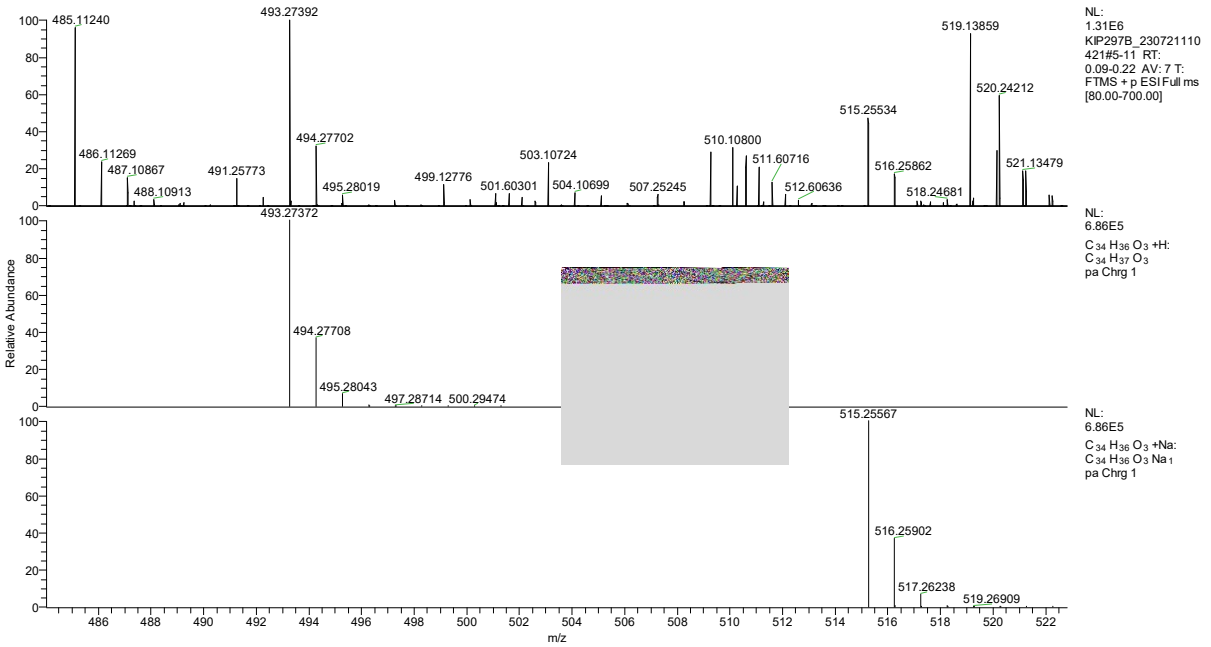


Figure S181. HRMS picture of compound **5bb/diastereomer 1**.

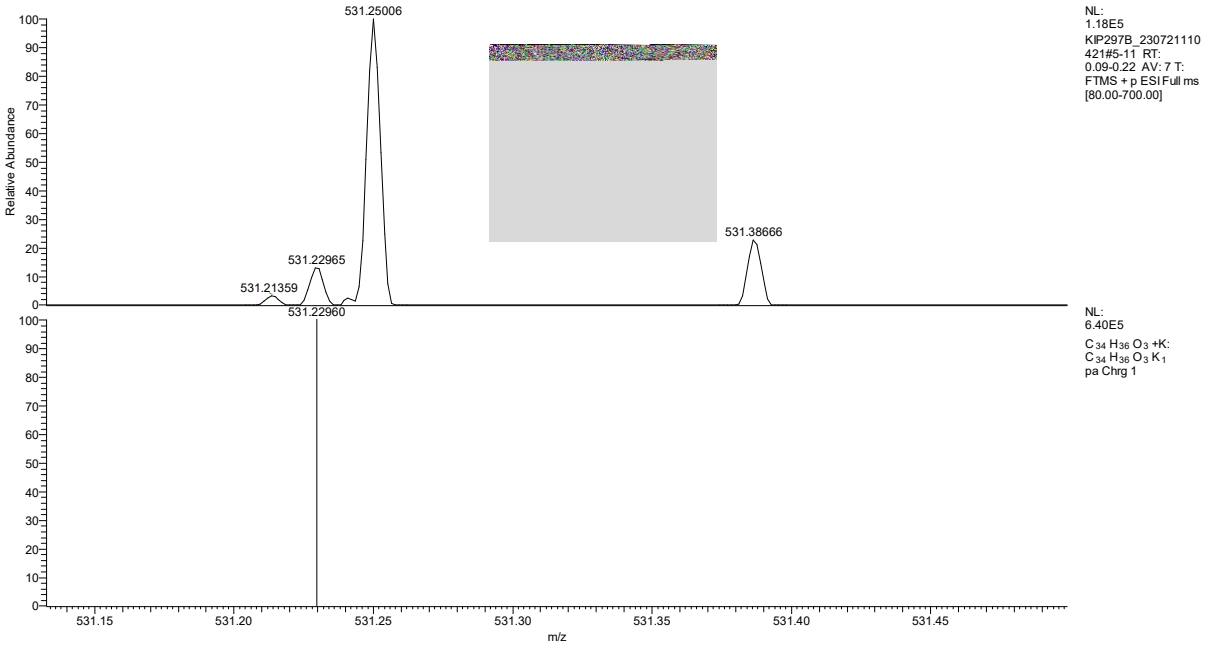


Figure S182. HRMS picture of compound **5bb/diastereomer 1** (K^+ adduct).

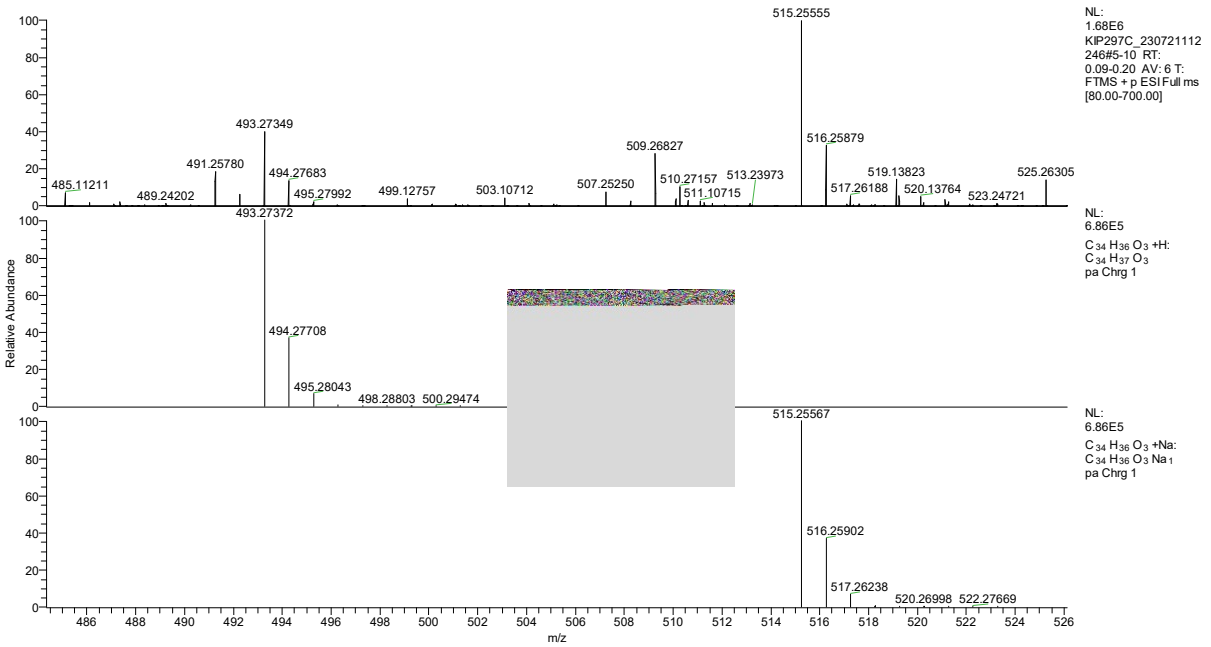


Figure S183. HRMS picture of compound **5bb/diastereomer 2**.

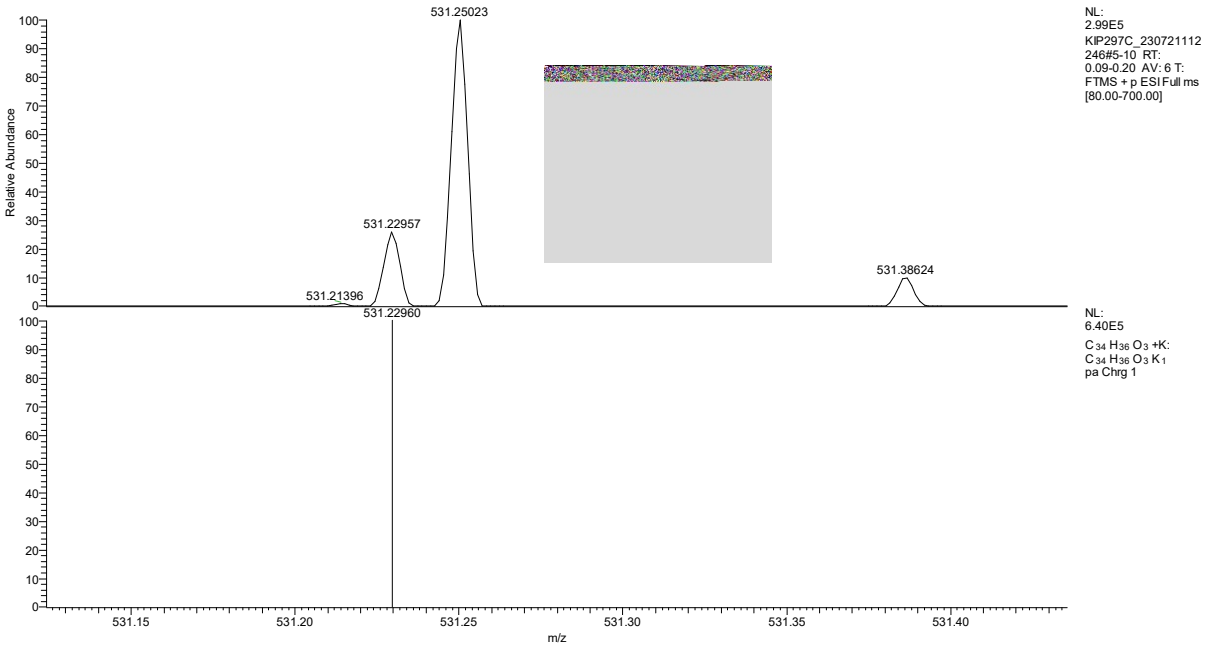


Figure S184. HRMS picture of compound **5bb/diastereomer 2** (K^+ adduct).

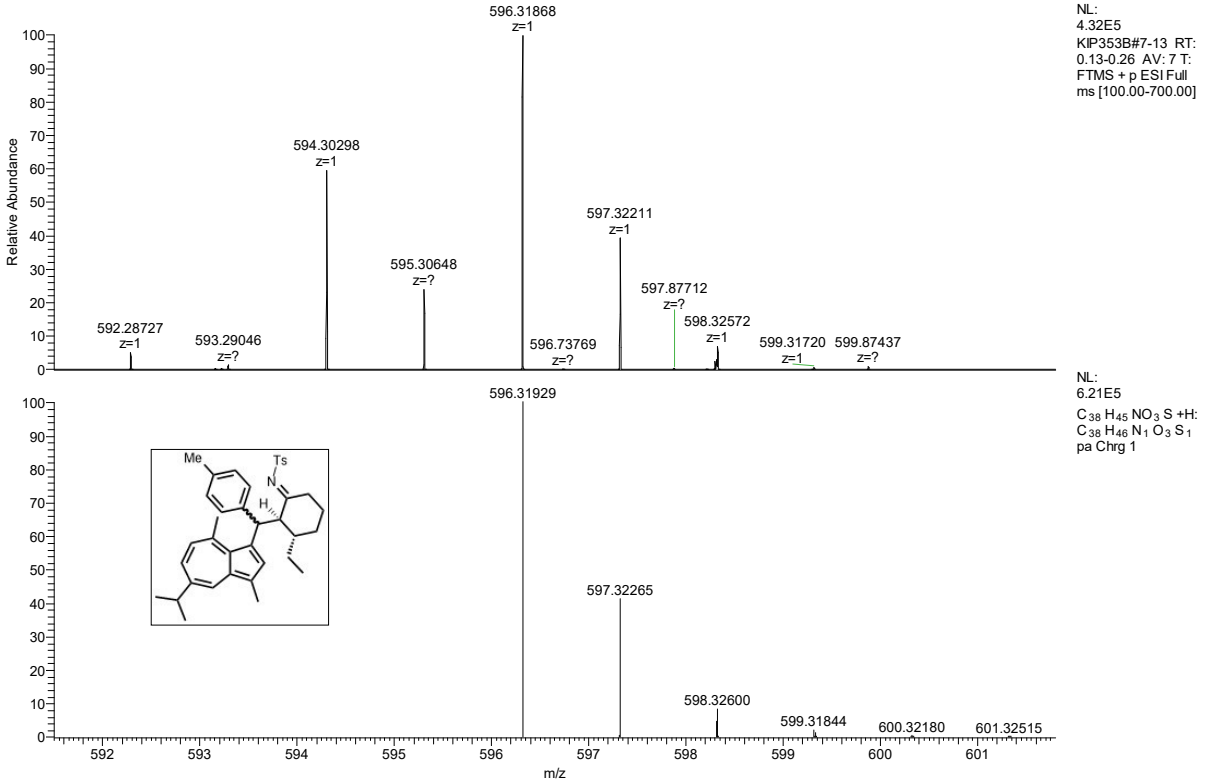


Figure S185. HRMS picture of compound **5cb/diastereomer 1**.

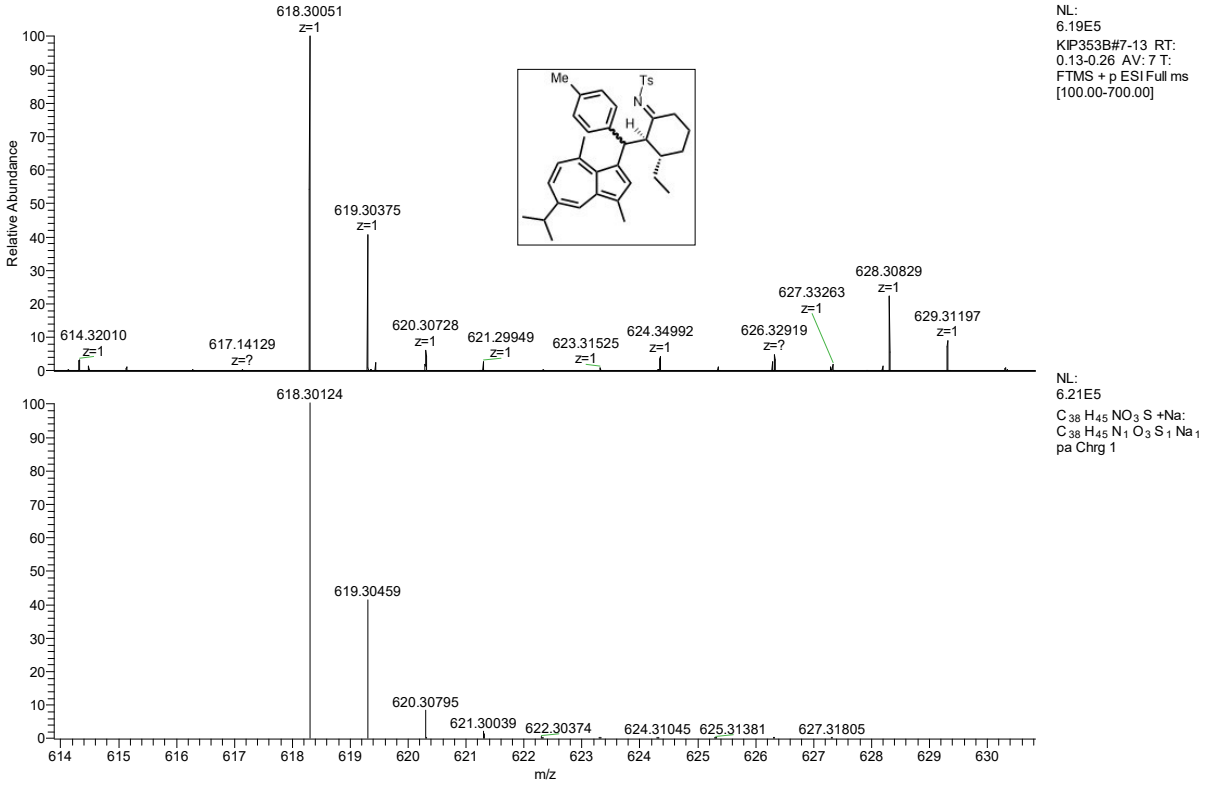


Figure S186. HRMS picture of compound **5cb/diastereomer 1** (Na^+ adduct).

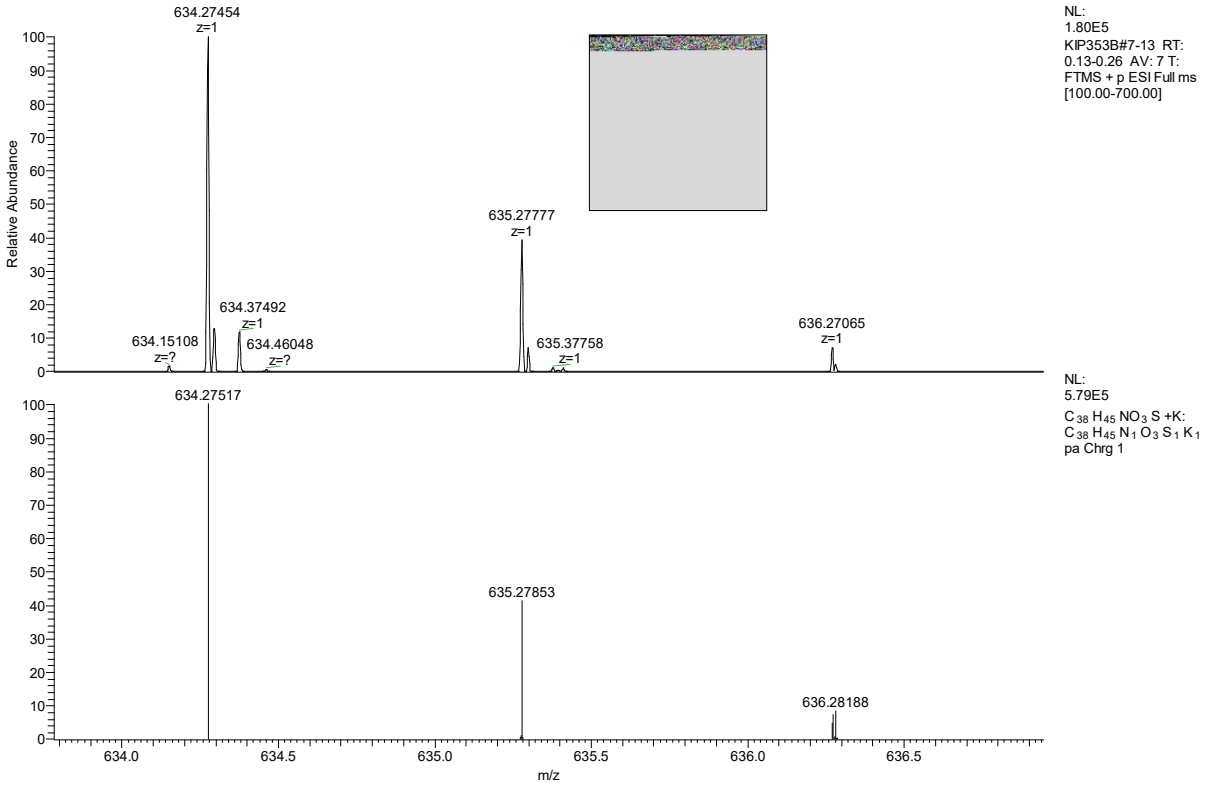


Figure S187. HRMS picture of compound **5cb/diastereomer 1** (K^+ adduct).

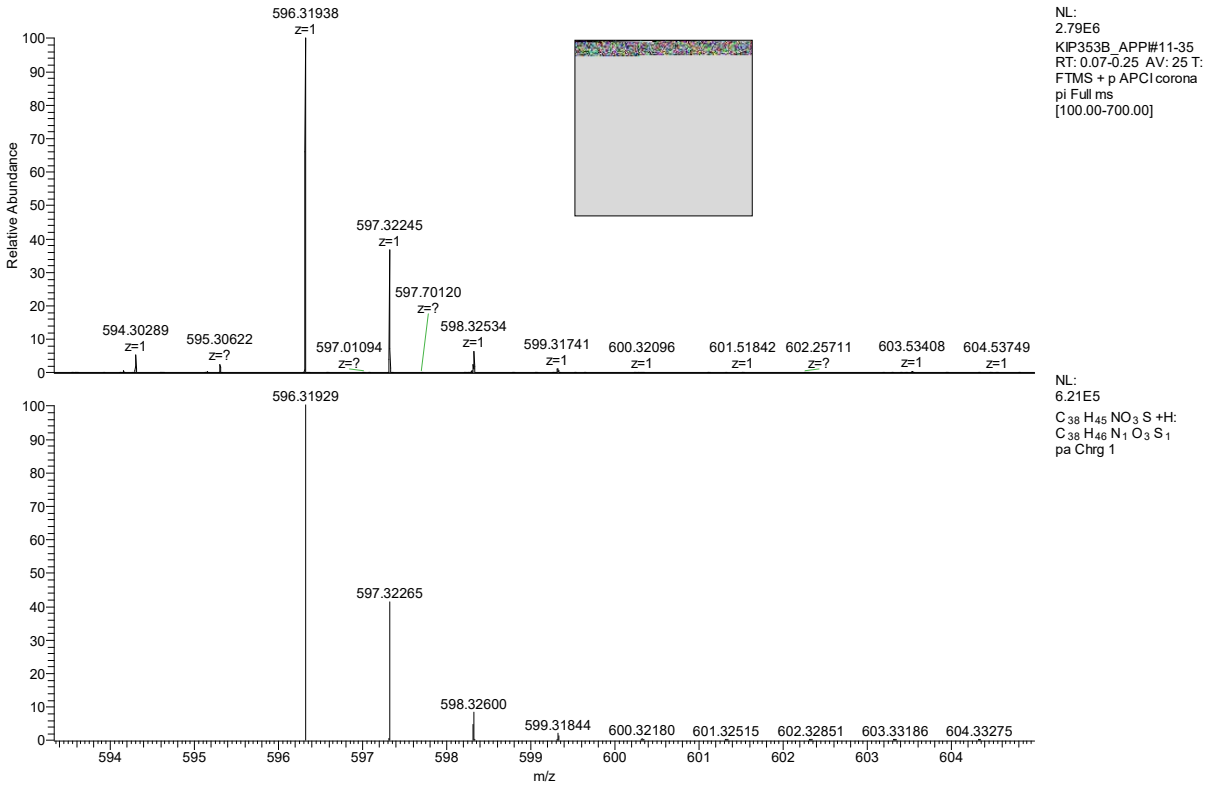


Figure S188. HRMS picture of compound **5cb/diastereomer 1** (APPI).

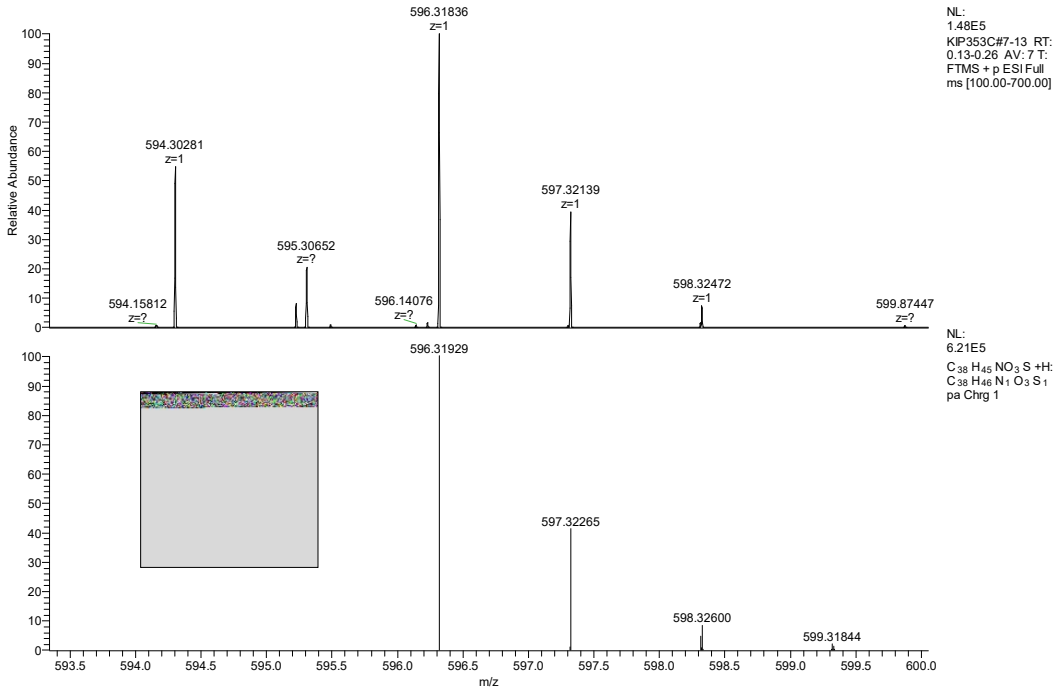


Figure S189. HRMS picture of compound **5cb/diastereomer 2**.

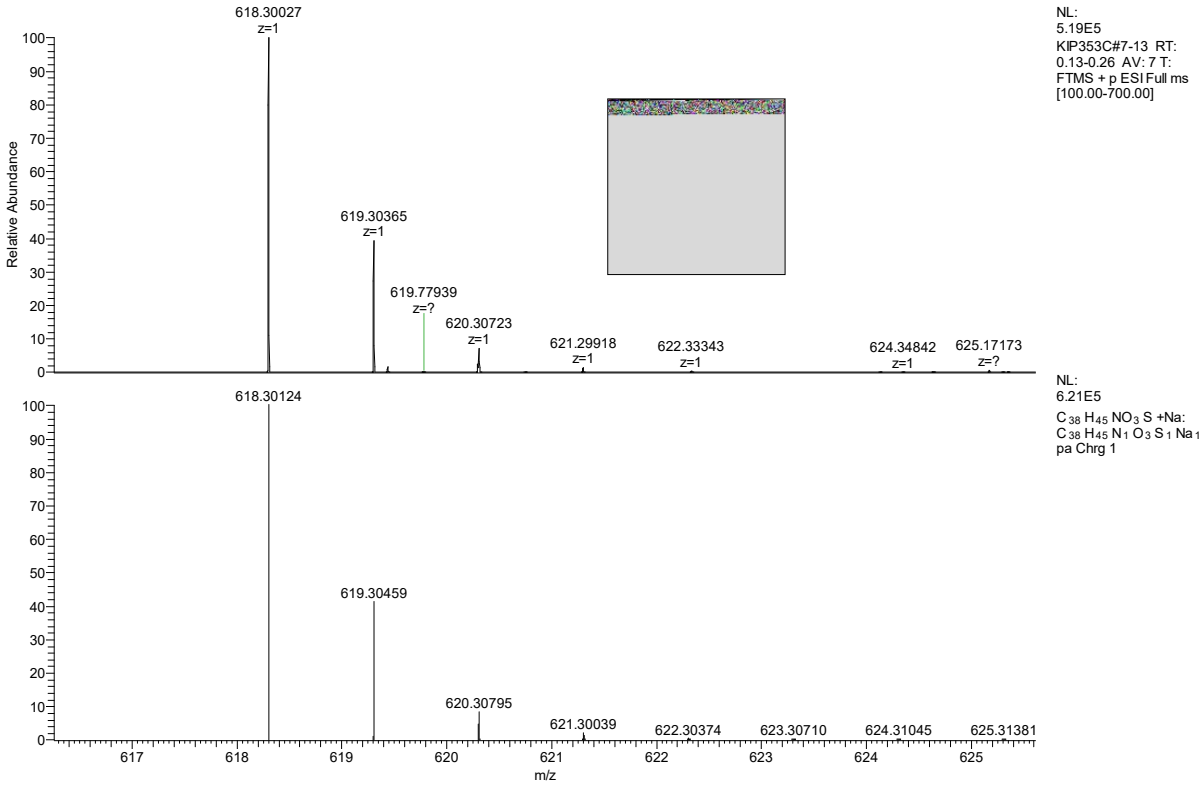


Figure S190. HRMS picture of compound **5cb/diastereomer 2** (Na^+ adduct).

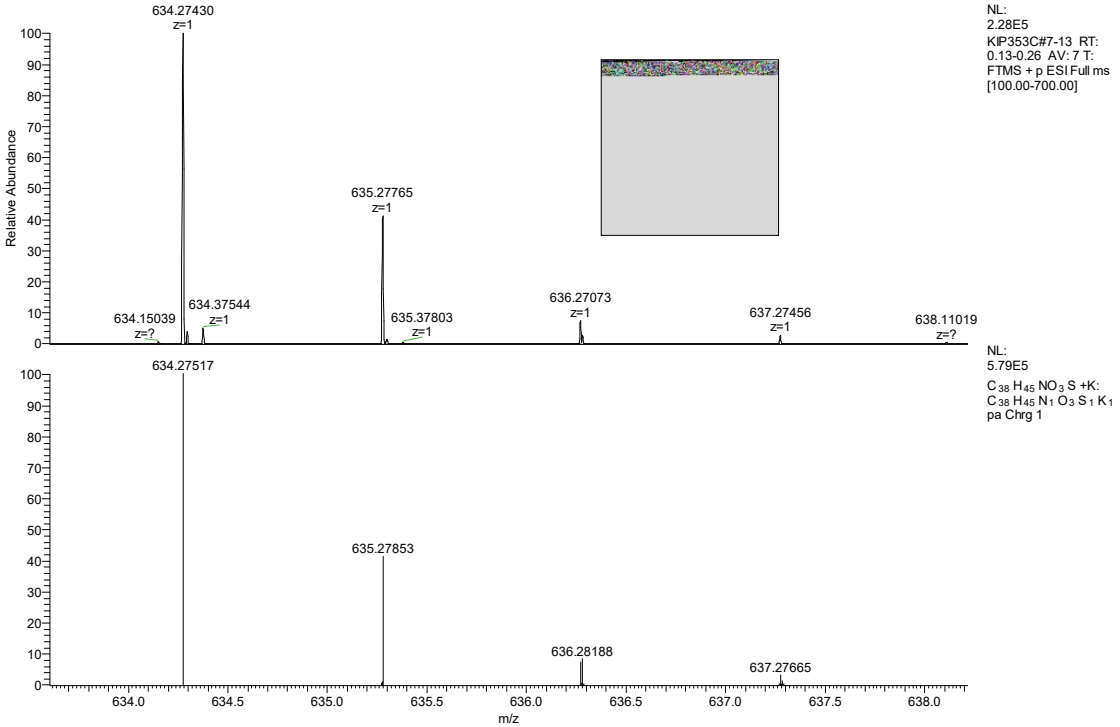


Figure S191. HRMS picture of compound **5cb/diastereomer 2** (K^+ adduct).

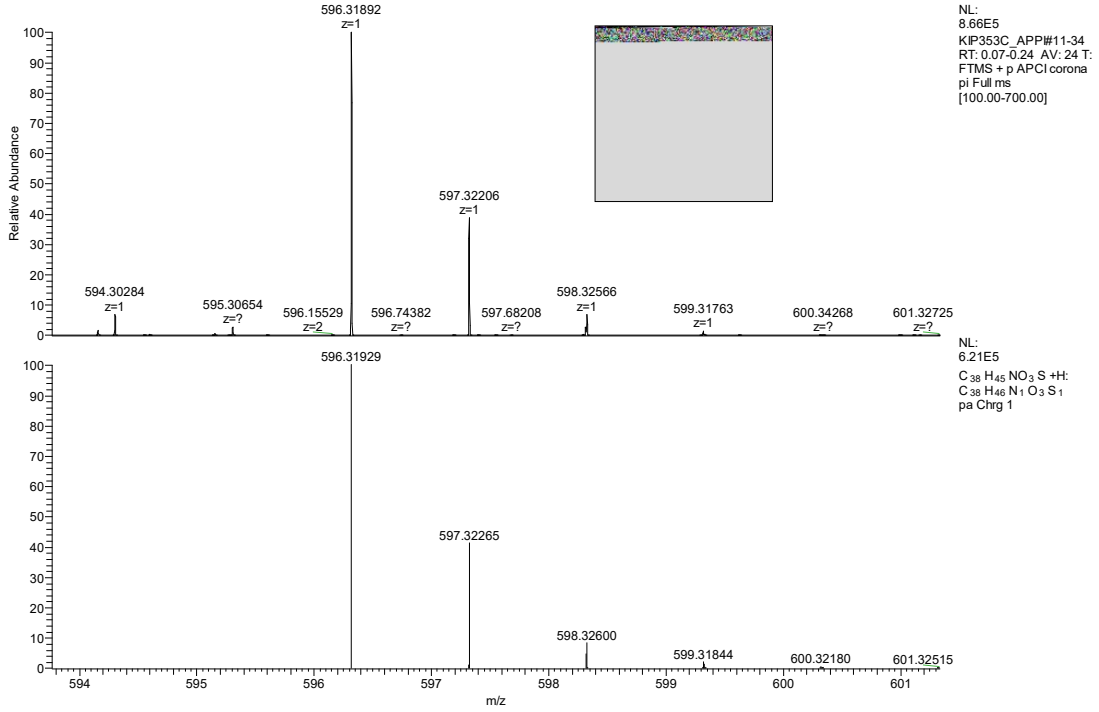


Figure S192. HRMS picture of compound **5cb/diastereomer 2** (APPI).

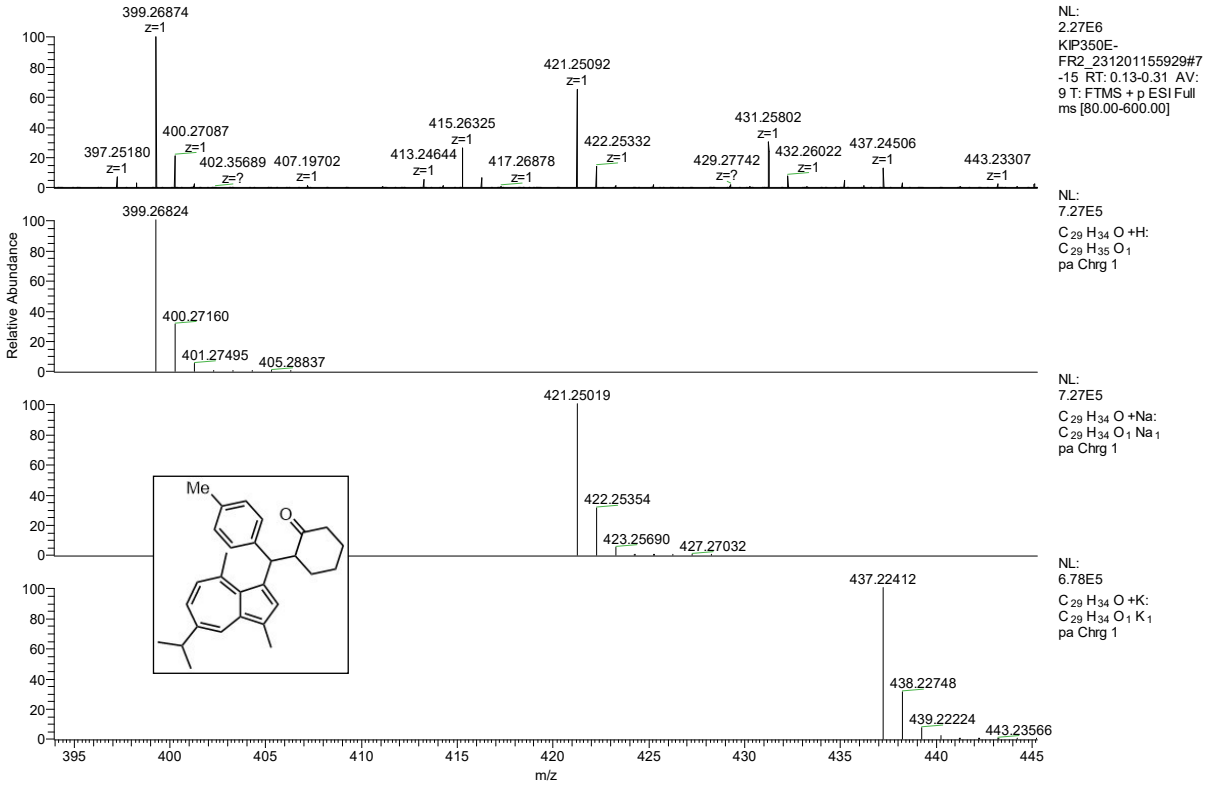


Figure S193. HRMS picture of compound [7a/diastereomer 1].

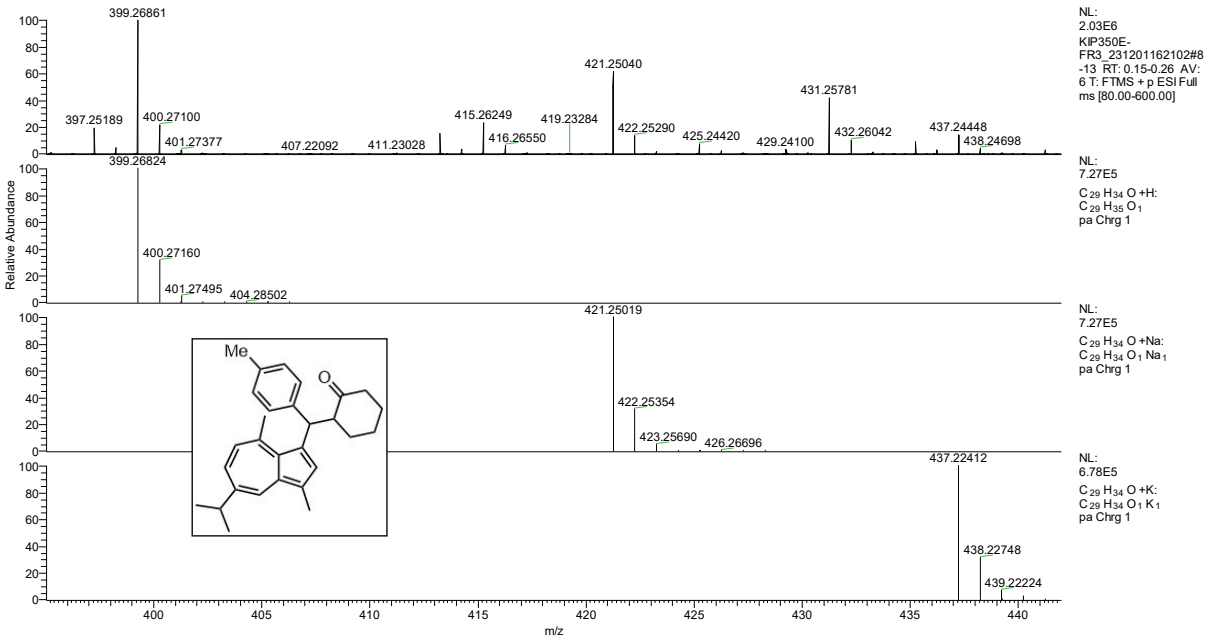


Figure S194. HRMS picture of compound [7a/diastereomer 2].

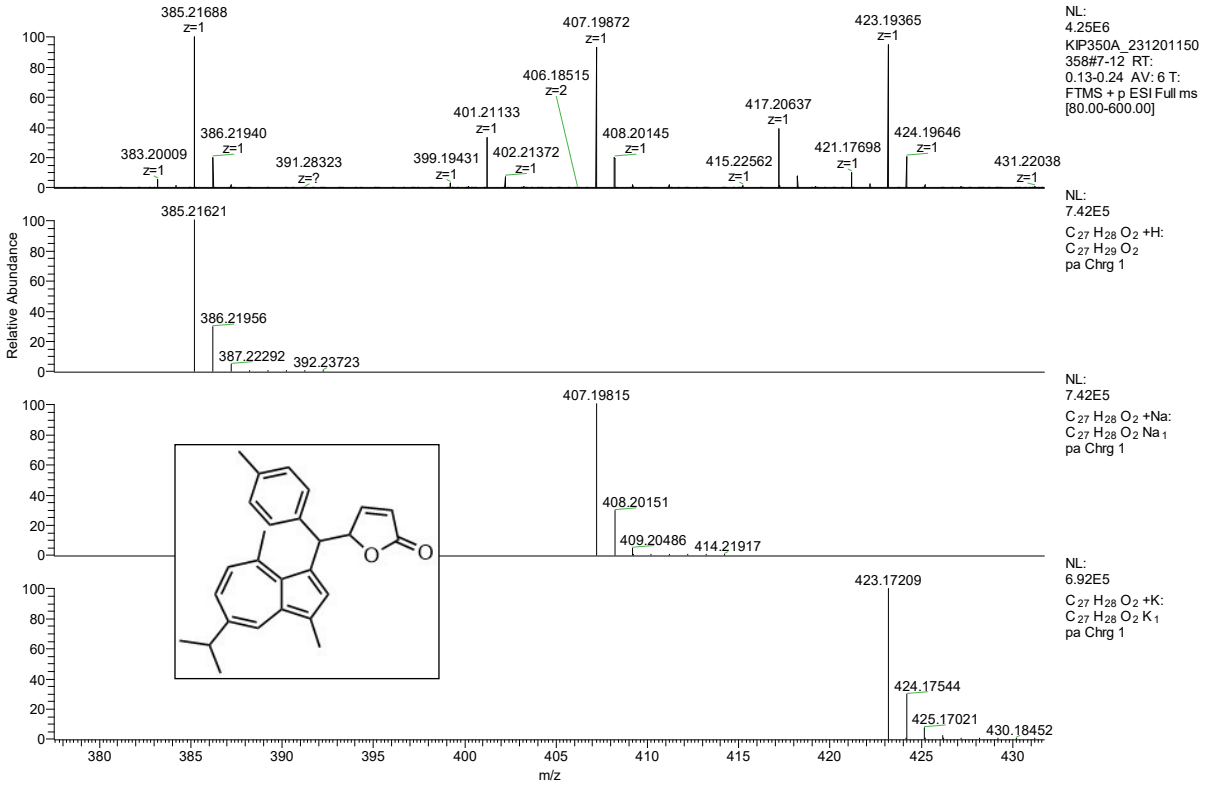


Figure S195. HRMS picture of compound **7b**.

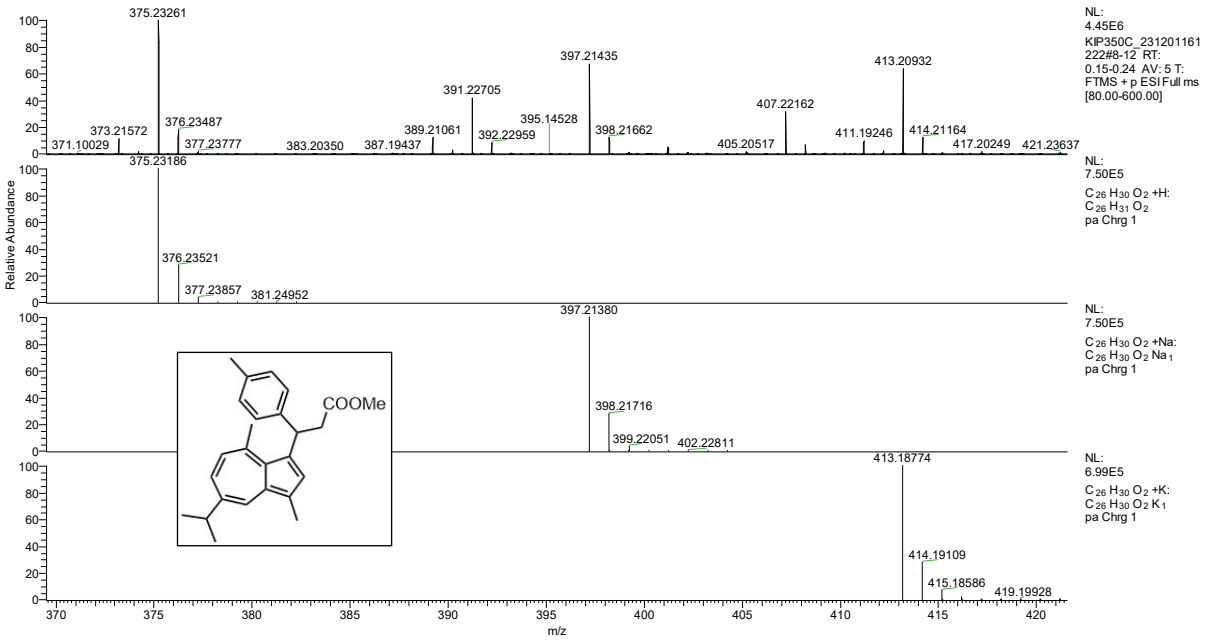


Figure S196. HRMS picture of compound **7c**.

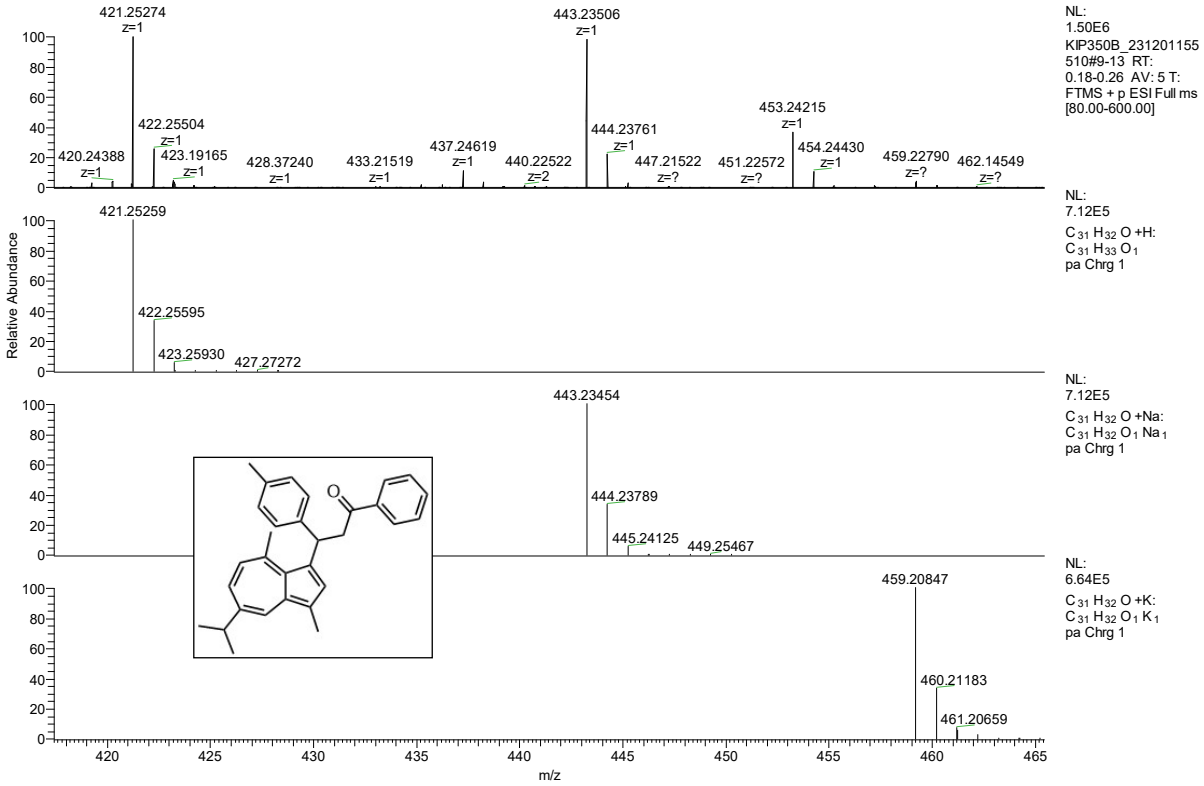


Figure S197. HRMS picture of compound **7d**.

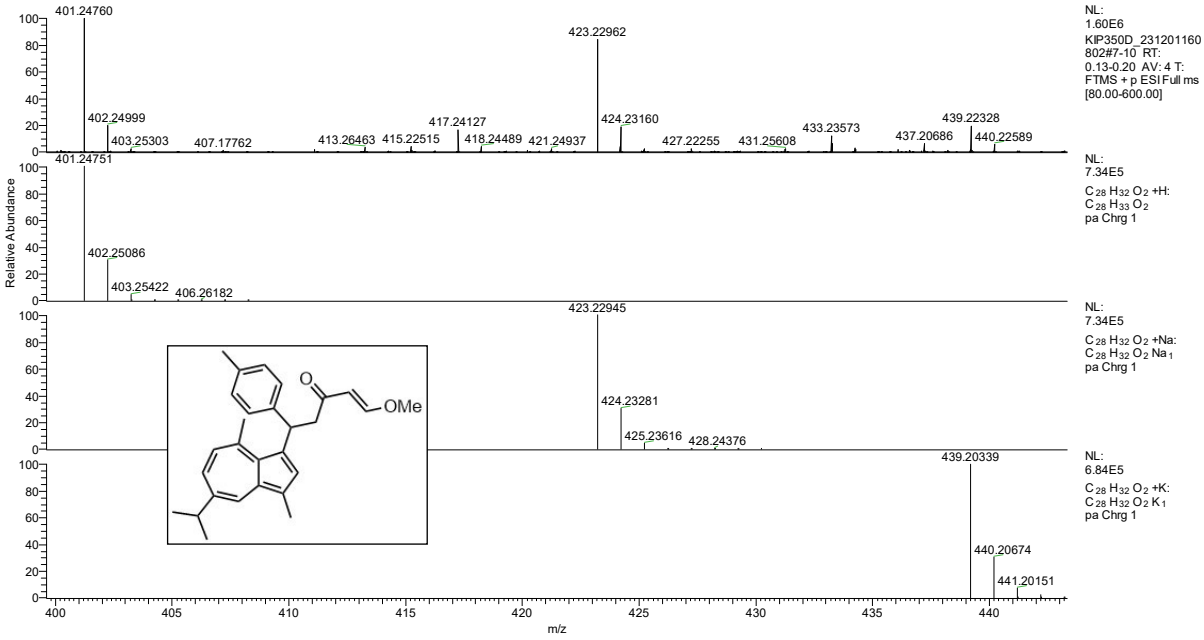


Figure S198. HRMS picture of compound **7e**.

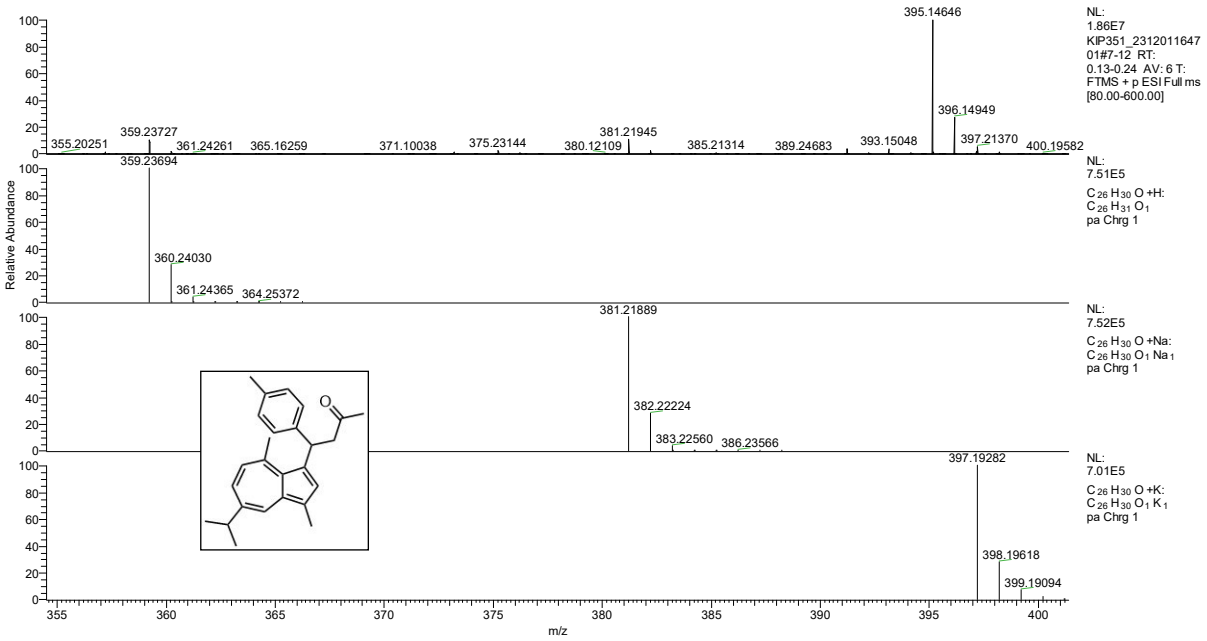


Figure S199. HRMS picture of compound **7f**.

10. Spectroscopic study

Electronic (UV-Vis and fluorescence) spectra were recorded on an Agilent Cary 8454 UV-Visible Spectrophotometer and an Edinburgh Instruments FLS1000 Photoluminiscence Spectrometer in 1 cm fluorescence cuvette (sample fluorescence was measured in a right-angle arrangement). Reaction progress was monitored by both UV-Vis and fluorescence spectroscopy through a decrease in absorbance of carbocation **2a** at 530 nm or an increase in fluorescence of guaiazulene product **7c** at its emission maximum.

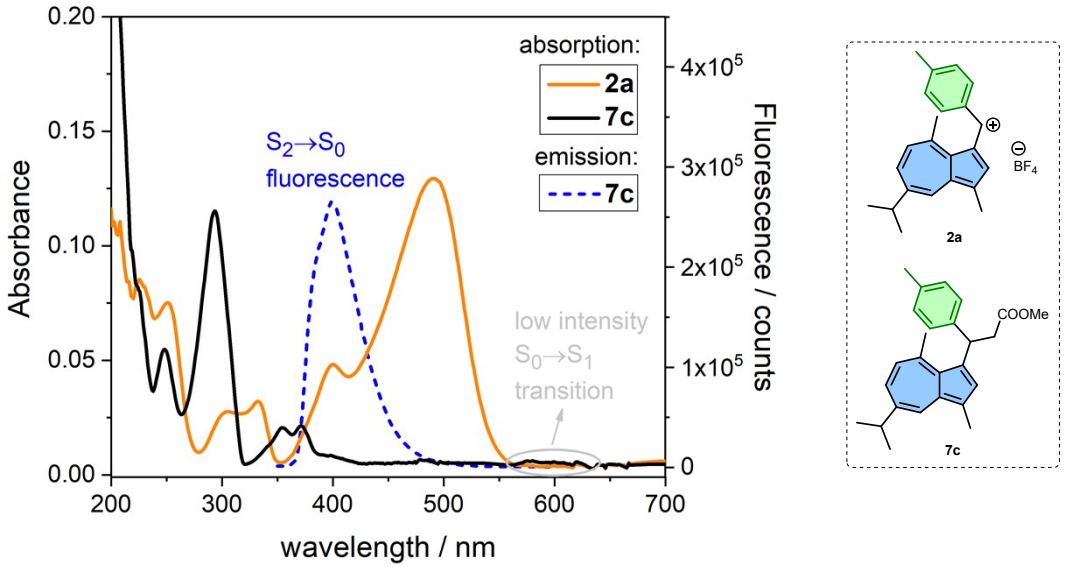


Figure S200. UV-Vis absorption spectra of guaiazulene-based carbocation **2a** and guaiazulene product **7c** (the product **7c** shows typical azulene-like low intensity $S_0 \rightarrow S_1$ transition), and fluorescence spectrum of **7c** (carbocation **2a** is non-emissive).

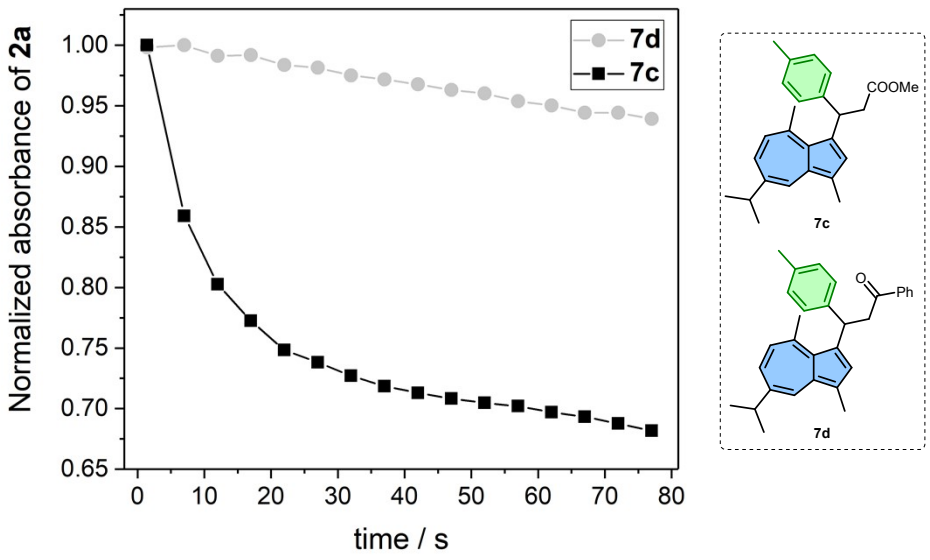


Figure S201. Comparison of initial decrease in absorbance at 530 nm of orange guaiazulene-based carbocation **2a** after addition of the strongest (20 eq Nu, c_{cation}= 0.02 µmol/mL) and the weakest nucleophile (13 eq Nu, c_{cation}= 0.22 µmol/mL) in the series (leading to formation of guaiazulene products **7c** and **7d**, respectively).

Table S2. Basic UV-Vis absorption characteristics of the studied carbocations.

Compound	Absorption maxima λ_A [nm]	Extinction coefficient ε_A [M^{-1} cm^{-1}]
2a	488	32400
2a'	491	29300
2a"	487	29500
2b	530	45600
2c	652	115200
2d	518	29500
2e	473	22200
2f	479	24000
2g	473	15300
	723[a]	8600
2h	474	21100
2h'	474	25200

[a] 2nd long-wavelength maximum due to the ferrocene arm

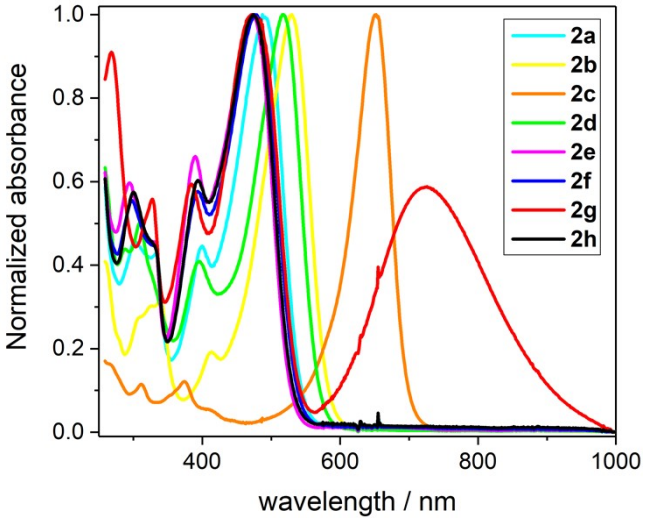


Figure S202. UV-Vis absorption spectra of the studied carbocations (spectra of **2a´**, **2a´´** and **2h´** are almost identical to **2a** and **2h**, respectively) + photo of stock solutions (below).

Electrophilicity parameter

At a nucleophile (Nu) excess, the reaction rate (decrease in concentration of a carbocation C) can be classified as a pseudo-first order reaction with an observed pseudo-first order rate constant k_{obs}:

$$-\frac{d[C]}{dt} = k_{obs}[C] = k_{bi}[Nu][C] \qquad \Rightarrow \qquad k_{bi} = \frac{k_{obs}}{[Nu]}$$

where k_{bi} is the bimolecular rate constant for a reaction between carbocation (C) and a nucleophile (Nu). To determine the electrophilicity parameter (E) of the guaiazulene-based cation **2a**, we used the generally known Mayr-Patz equation:[7]

$$\log k_{bi} = S_N(N + E) \qquad \Rightarrow \qquad E = \frac{(\log k_{bi} - S_N N)}{S_N}$$

where k_{bi} is the bimolecular rate constant mentioned above (determined at the temperature of 20 °C), N is the nucleophilicity parameter, and S_N is the nucleophile-specific sensitivity parameter.

Figure S203 shows the reaction progress at three different excesses of nucleophile 1-phenyl-1-trimethylsiloxyethylene. The experimentally determined electrophilicity parameter of -7.02 is in relatively good agreement with the DFT-calculated value of -5.85 (Table 1 in the main text; k_{bi} = 0.17 L

mol^{-1} s^{-1} - calculated as arithmetic average of k_{bi} values determined at each excess of nucleophile; S_N = 0.96 and N = 6.22).[8]

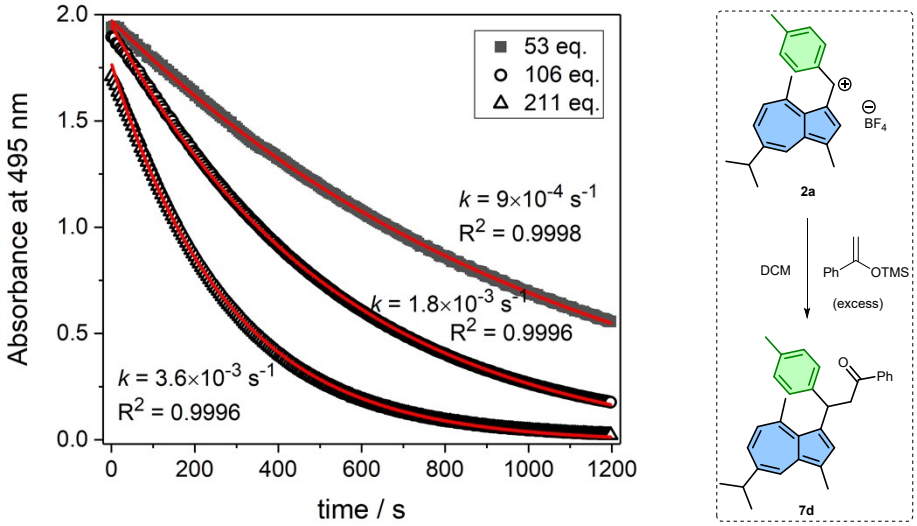
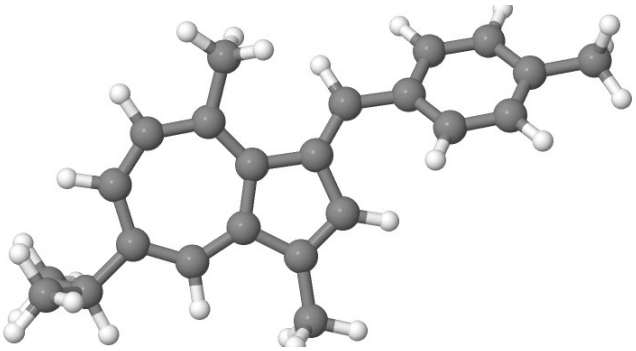


Figure S203. Decreased Vis-light absorption of carbocation reactant **2a** due to guaiazulene product **7d** formation at different excesses of nucleophile 1-phenyl-1-trimethylsiloxyethylene (53, 106, and 211 equivalents, which corresponds to concentration of 5.51×10^{-3} mol L^{-1}, 1.07×10^{-2} mol L^{-1}, and 2.0×10^{-2} mol L^{-1}, respectively). Red lines represent mono-exponential fits of experimental data; *k* is a pseudo-first order rate constant at a nucleophile excess.

11. Computational study

DFT calculations were realized using Turbomole 7.7 program package.[9] Geometric optimizations were performed using PBEh-3c functional,[10] with def2-mSVP basis set.[11] Energies were refined using PBE0 functional[12] with Grimme´s empirical D4 dispersion correction,[13] and def2-TZVP basis set.[14] Influence of solvent was taken into account using COSMO(∞) approach.[15]

Guaiazulene-tol-cation



Geometry optimization: PBEh-3c/mSVP
SCF energy = -889.29975278242 Hartree

Thermochemical properties at 298.15 K
Chemical potential = 0.372536 Hartree
Entropy = 0.000254 Hartree/K
Inner energy = 0.447319 Hartree
ZPE = 0.4255 Hartree
Enthalpy = 0.448263 Hartree

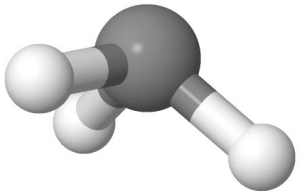
Single point energy at PBE0-D4/TZVP COSMO(∞)
SCF energy = -890.61208876801 Hartree

Coordinates:

	Atom	X	Y	Z
1	C	0.6478	-0.9052	0.2731
2	C	0.7529	0.5319	0.2951
3	C	2.8622	-0.4432	0.1948
4	C	1.9756	-1.4666	0.2186
5	C	2.1825	0.8273	0.2123
6	C	-0.4695	-1.7335	0.2718
7	C	-0.2943	1.4306	0.4803
8	C	-1.6580	1.0799	0.4914
9	C	-1.8186	-1.4265	0.2895
10	C	-2.3170	-0.1223	0.3807
11	H	3.9286	-0.5595	0.0762
12	C	2.2912	-2.9199	0.1512
13	C	2.7934	2.0329	0.0075
14	H	-0.2428	-2.7932	0.2354

15	C	-0.0405	2.8993	0.6845
16	H	-2.3254	1.9259	0.6045
17	C	-2.8168	-2.5616	0.2301
18	H	-3.3972	-0.0343	0.3980
19	H	-0.9155	3.3887	1.1055
20	H	0.7905	3.0817	1.3631
21	H	0.1718	3.4023	-0.2611
22	H	-2.2484	-3.4929	0.1620
23	C	-3.6923	-2.4637	-1.0203
24	C	-3.6601	-2.6283	1.5046
25	H	-4.3454	-3.3336	-1.0837
26	H	-4.3339	-1.5813	-1.0046
27	H	-3.0960	-2.4293	-1.9316
28	H	-3.0405	-2.7128	2.3970
29	H	-4.2989	-1.7513	1.6208
30	H	-4.3141	-3.4992	1.4706
31	H	1.8548	-3.3903	-0.7319
32	H	3.3664	-3.0794	0.1057
33	H	1.9210	-3.4562	1.0271
34	H	2.1791	2.8787	-0.2662
35	C	4.2013	2.3241	0.0531
36	C	4.6881	3.3848	-0.7247
37	C	6.0303	3.6982	-0.7335
38	C	6.9346	2.9997	0.0673
39	C	6.4433	1.9767	0.8810
40	C	5.1067	1.6396	0.8773
41	H	4.0054	3.9486	-1.3488
42	H	6.3857	4.5042	-1.3628
43	C	8.3824	3.3729	0.0943
44	H	7.1219	1.4481	1.5384
45	H	4.7524	0.8796	1.5609
46	H	8.5612	4.1521	0.8383
47	H	8.7162	3.7610	-0.8666
48	H	9.0136	2.5251	0.3554

Methyl-anion



Geometry optimization: PBEh-3c/mSVP
SCF energy = -39.70861194145 Hartree

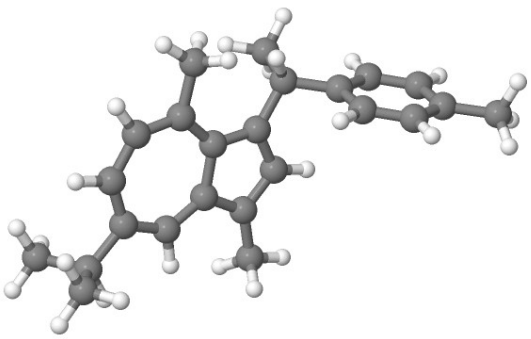
Thermochemical properties at 298.15 K
Chemical potential = 0.010369 Hartree
Entropy = 0.000077 Hartree/K
Inner energy = 0.032414 Hartree
ZPE = 0.029545 Hartree
Enthalpy = 0.033358 Hartree

Single point energy at PBE0-D4/TZVP COSMO(∞)
SCF energy = -39.90919462669 Hartree

Coordinates:

	Atom	X	Y	Z
1	C	0.0225	0.0736	-0.0101
2	H	-0.4527	-0.3968	-0.8966
3	H	-0.7245	-0.0826	0.7966
4	H	0.8372	-0.6341	0.2521

Guaiazulene-tol-Me-product



Geometry optimization: PBEh-3c/mSVP
SCF energy = -929.35289315336 Hartree

Thermochemical properties at 298.15 K
Chemical potential = 0.409731 Hartree
Entropy = 0.000266 Hartree/K
Inner energy = 0.488225 Hartree
ZPE = 0.464697 Hartree
Enthalpy = 0.489169 Hartree

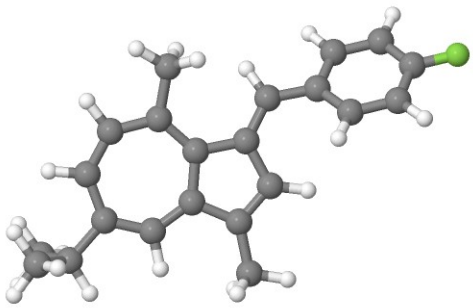
Single point energy at PBE0-D4/TZVP COSMO(∞)
SCF energy = -930.65910166939 Hartree

Coordinates:

	Atom	X	Y	Z
1	C	0.6333	-0.9555	-0.0844
2	C	0.7736	0.5291	0.0396
3	C	2.7686	-0.4056	-0.5066
4	C	1.8971	-1.4747	-0.4239
5	C	2.1223	0.8136	-0.2322
6	C	-0.4663	-1.7707	0.0805
7	C	-0.2779	1.4000	0.3656
8	C	-1.5991	1.0324	0.6214
9	C	-1.7885	-1.4770	0.4087
10	C	-2.2515	-0.1946	0.6432
11	H	3.8221	-0.4906	-0.7405
12	C	2.2450	-2.9094	-0.6437
13	C	2.8777	2.1185	-0.3408
14	H	-0.2614	-2.8263	-0.0762
15	C	-0.0229	2.8816	0.4802
16	H	-2.2537	1.8644	0.8527
17	C	-2.7721	-2.6298	0.5097
18	H	-3.3067	-0.1147	0.8866
19	H	-0.9485	3.4249	0.6586
20	H	0.6458	3.1056	1.3121
21	H	0.4233	3.2939	-0.4235
22	H	-2.2178	-3.5479	0.2917
23	C	-3.8884	-2.5196	-0.5285
24	C	-3.3422	-2.7715	1.9204
25	H	-4.5408	-3.3934	-0.4891
26	H	-4.5121	-1.6406	-0.3577
27	H	-3.4849	-2.4463	-1.5383
28	H	-2.5487	-2.8777	2.6600

29	H	-3.9416	-1.9038	2.2017
30	H	-3.9876	-3.6485	1.9908
31	H	1.6759	-3.3536	-1.4635
32	H	3.3003	-3.0126	-0.8935
33	H	2.0645	-3.5206	0.2434
34	C	4.2787	1.9686	0.2231
35	C	5.4320	2.0913	-0.5389
36	C	6.6893	1.9385	0.0337
37	C	6.8377	1.6628	1.3853
38	C	5.6790	1.5370	2.1497
39	C	4.4286	1.6851	1.5798
40	H	5.3681	2.3064	-1.5974
41	H	7.5694	2.0368	-0.5912
42	C	8.1960	1.5319	2.0102
43	H	5.7584	1.3158	3.2078
44	H	3.5442	1.5629	2.1947
45	H	8.5481	2.4916	2.3941
46	H	8.9366	1.1797	1.2927
47	H	8.1879	0.8337	2.8471
48	C	2.8481	2.6252	-1.7832
49	H	2.4002	2.8773	0.2772
50	H	3.2987	1.9055	-2.4678
51	H	1.8189	2.7685	-2.1119
52	H	3.3710	3.5773	-1.8889

Guaiazulene-F-Ph-cation



Geometry optimization: PBEh-3c/mSVP
SCF energy = -949.11480634047 Hartree

Thermochemical properties at 298.15 K
Chemical potential = 0.338565 Hartree
Entropy = 0.000242 Hartree/K

Inner energy = 0.409847 Hartree
ZPE = 0.389148 Hartree
Enthalpy = 0.410791 Hartree

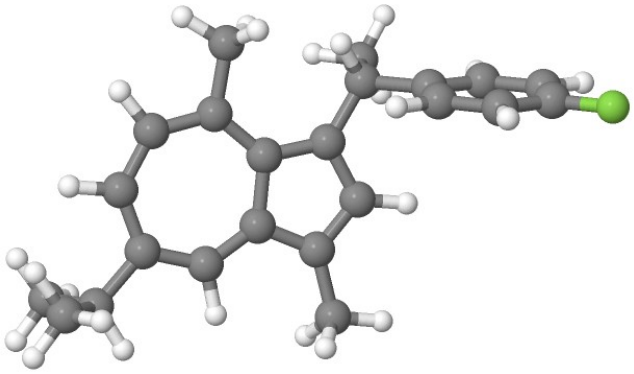
Single point energy at PBE0-D4/TZVP COSMO(∞)
SCF energy = -950.51957606034 Hartree

Coordinates:

	Atom	X	Y	Z
1	C	0.6418	-0.9103	0.2772
2	C	0.7495	0.5252	0.3018
3	C	2.8586	-0.4554	0.2022
4	C	1.9697	-1.4756	0.2237
5	C	2.1814	0.8177	0.2192
6	C	-0.4770	-1.7366	0.2728
7	C	-0.2949	1.4268	0.4872
8	C	-1.6596	1.0791	0.4979
9	C	-1.8255	-1.4265	0.2896
10	C	-2.3211	-0.1211	0.3840
11	H	3.9248	-0.5755	0.0847
12	C	2.2807	-2.9296	0.1562
13	C	2.7934	2.0206	0.0157
14	H	-0.2525	-2.7967	0.2339
15	C	-0.0375	2.8947	0.6923
16	H	-2.3250	1.9264	0.6123
17	C	-2.8261	-2.5586	0.2253
18	H	-3.4011	-0.0309	0.4014
19	H	-0.9129	3.3872	1.1087
20	H	0.7906	3.0745	1.3752
21	H	0.1807	3.3968	-0.2524
22	H	-2.2603	-3.4914	0.1560
23	C	-3.6986	-2.4543	-1.0269
24	C	-3.6723	-2.6257	1.4981
25	H	-4.3539	-3.3223	-1.0940
26	H	-4.3378	-1.5703	-1.0101
27	H	-3.1002	-2.4193	-1.9369
28	H	-3.0551	-2.7138	2.3917
29	H	-4.3094	-1.7476	1.6147
30	H	-4.3283	-3.4949	1.4605
31	H	1.8439	-3.3982	-0.7276
32	H	3.3553	-3.0929	0.1123
33	H	1.9071	-3.4645	1.0315
34	H	2.1823	2.8706	-0.2516

35	C	4.2056	2.3032	0.0552
36	C	4.6984	3.3504	-0.7376
37	C	6.0405	3.6644	-0.7542
38	C	6.8968	2.9488	0.0670
39	C	6.4425	1.9417	0.9048
40	C	5.1014	1.6229	0.8939
41	H	4.0198	3.9101	-1.3690
42	H	6.4242	4.4574	-1.3812
43	F	8.1840	3.2514	0.0706
44	H	7.1323	1.4357	1.5663
45	H	4.7372	0.8764	1.5866

Guaiazulene-F-Ph-Me-product



Geometry optimization: PBEh-3c/mSVP
SCF energy = -989.17319690534 Hartree

Thermochemical properties at 298.15 K
Chemical potential = 0.375523 Hartree
Entropy = 0.000255 Hartree/K
Inner energy = 0.450744 Hartree
ZPE = 0.42834 Hartree
Enthalpy = 0.451689 Hartree

Single point energy at PBE0-D4/TZVP COSMO(∞)
SCF energy = -990.56823012423 Hartree

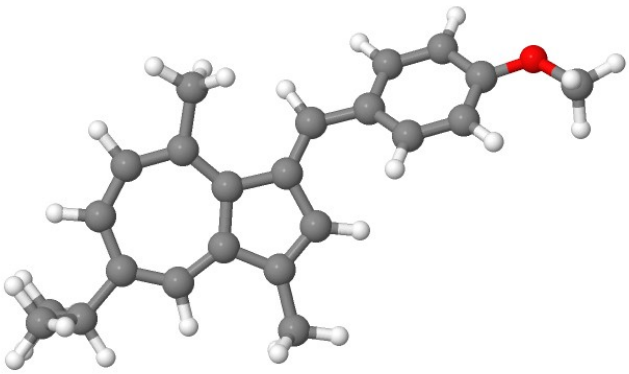
Coordinates:

	Atom	X	Y	Z
1	C	0.6375	-0.9508	-0.0907
2	C	0.7766	0.5337	0.0281
3	C	2.7675	-0.4001	-0.5356

4	C	1.8987	-1.4697	-0.4424
5	C	2.1220	0.8190	-0.2558
6	C	-0.4591	-1.7672	0.0866
7	C	-0.2748	1.4053	0.3551
8	C	-1.5931	1.0369	0.6213
9	C	-1.7793	-1.4741	0.4241
10	C	-2.2429	-0.1916	0.6552
11	H	3.8186	-0.4848	-0.7807
12	C	2.2456	-2.9045	-0.6637
13	C	2.8784	2.1231	-0.3652
14	H	-0.2538	-2.8231	-0.0676
15	C	-0.0216	2.8882	0.4561
16	H	-2.2483	1.8691	0.8502
17	C	-2.7602	-2.6282	0.5364
18	H	-3.2965	-0.1123	0.9057
19	H	-0.9471	3.4316	0.6347
20	H	0.6507	3.1211	1.2828
21	H	0.4189	3.2932	-0.4538
22	H	-2.2045	-3.5468	0.3244
23	C	-3.8782	-2.5272	-0.5009
24	C	-3.3275	-2.7603	1.9492
25	H	-4.5293	-3.4016	-0.4540
26	H	-4.5027	-1.6476	-0.3356
27	H	-3.4764	-2.4609	-1.5119
28	H	-2.5325	-2.8591	2.6883
29	H	-3.9287	-1.8922	2.2250
30	H	-3.9705	-3.6383	2.0270
31	H	1.6695	-3.3502	-1.4776
32	H	3.2987	-3.0074	-0.9228
33	H	2.0737	-3.5143	0.2260
34	C	4.2738	1.9719	0.2128
35	C	5.4342	2.1260	-0.5335
36	C	6.6913	1.9736	0.0410
37	C	6.7774	1.6652	1.3803
38	C	5.6451	1.5053	2.1589
39	C	4.4057	1.6578	1.5655
40	H	5.3794	2.3689	-1.5860
41	H	7.5900	2.0939	-0.5489
42	F	7.9827	1.5155	1.9443
43	H	5.7361	1.2616	3.2089
44	H	3.5137	1.5155	2.1641
45	C	2.8636	2.6228	-1.8100
46	H	2.3965	2.8862	0.2437
47	H	3.3283	1.9036	-2.4859

48	H	1.8371	2.7557	-2.1508
49	H	3.3786	3.5795	-1.9144

Guaiazulene-MeOPh-cation



Geometry optimization: PBEh-3c/mSVP
SCF energy = -964.35210770465 Hartree

Thermochemical properties at 298.15 K
Chemical potential = 0.378772 Hartree
Entropy = 0.000254 Hartree/K
Inner energy = 0.453614 Hartree
ZPE = 0.431212 Hartree
Enthalpy = 0.454558 Hartree

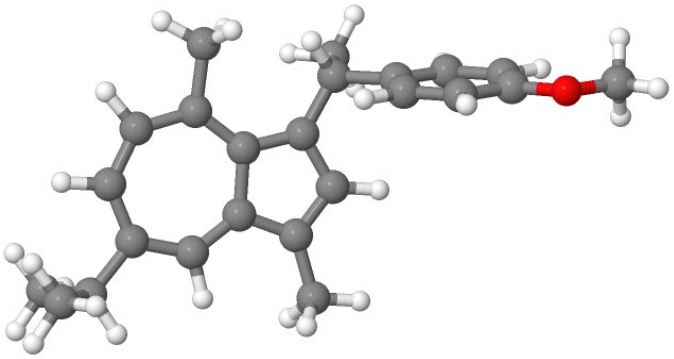
Single point energy at PBE0-D4/TZVP COSMO(∞)
SCF energy = -965.78003448052 Hartree

Coordinates:

	Atom	X	Y	Z
1	C	0.6561	-0.8856	0.3149
2	C	0.7387	0.5563	0.2976
3	C	2.8607	-0.3836	0.2811
4	C	1.9912	-1.4240	0.3108
5	C	2.1607	0.8725	0.2482
6	C	-0.4477	-1.7308	0.3050
7	C	-0.3298	1.4409	0.4277
8	C	-1.6863	1.0674	0.4139
9	C	-1.8018	-1.4463	0.2763
10	C	-2.3225	-0.1495	0.3192
11	H	3.9311	-0.4863	0.1872
12	C	2.3362	-2.8723	0.2891

13	C	2.7587	2.0891	0.0305
14	H	-0.2033	-2.7874	0.3037
15	C	-0.1062	2.9197	0.5931
16	H	-2.3707	1.9040	0.4862
17	C	-2.7794	-2.5998	0.2195
18	H	-3.4041	-0.0788	0.3060
19	H	-1.0014	3.4070	0.9722
20	H	0.7011	3.1370	1.2900
21	H	0.1266	3.3971	-0.3608
22	H	-2.1939	-3.5226	0.1881
23	C	-3.6250	-2.5478	-1.0538
24	C	-3.6534	-2.6512	1.4738
25	H	-4.2622	-3.4299	-1.1123
26	H	-4.2812	-1.6762	-1.0760
27	H	-3.0065	-2.5248	-1.9506
28	H	-3.0549	-2.7045	2.3828
29	H	-4.3079	-1.7817	1.5535
30	H	-4.2932	-3.5328	1.4448
31	H	1.9313	-3.3745	-0.5916
32	H	3.4151	-3.0118	0.2738
33	H	1.9549	-3.3935	1.1694
34	H	2.1362	2.9050	-0.3082
35	C	4.1435	2.4246	0.1343
36	C	4.6248	3.5275	-0.6002
37	C	5.9429	3.8949	-0.5603
38	C	6.8418	3.1953	0.2600
39	C	6.3731	2.1335	1.0456
40	C	5.0498	1.7602	0.9754
41	H	3.9437	4.0834	-1.2330
42	H	6.3062	4.7282	-1.1463
43	H	7.0282	1.6113	1.7284
44	H	4.7013	0.9765	1.6344
45	O	8.0938	3.6213	0.2455
46	C	9.0690	2.9826	1.0482
47	H	8.8364	3.0700	2.1121
48	H	9.1809	1.9282	0.7853
49	H	10.0060	3.4949	0.8514

Guaiazulene-MeOPh-Me-product



Geometry optimization: PBEh-3c/mSVP
SCF energy = -1004.40111676642 Hartree

Thermochemical properties at 298.15 K
Chemical potential = 0.415366 Hartree
Entropy = 0.000268 Hartree/K
Inner energy = 0.494367 Hartree
ZPE = 0.470237 Hartree
Enthalpy = 0.495311 Hartree

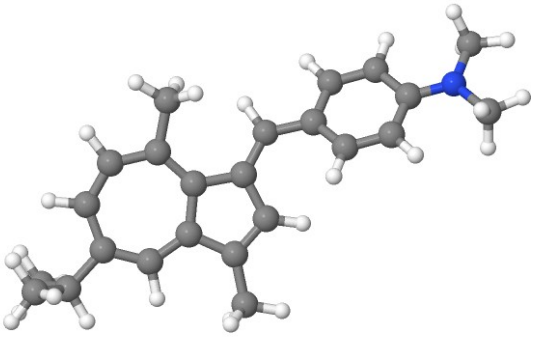
Single point energy at PBE0-D4/TZVP COSMO(∞)
SCF energy = -1005.82471792023 Hartree

Coordinates:

	Atom	X	Y	Z
1	C	0.6542	-0.9078	-0.0950
2	C	0.7446	0.5824	0.0074
3	C	2.7707	-0.2930	-0.5215
4	C	1.9352	-1.3889	-0.4285
5	C	2.0835	0.9078	-0.2628
6	C	-0.4153	-1.7576	0.0885
7	C	-0.3395	1.4231	0.3072
8	C	-1.6464	1.0147	0.5717
9	C	-1.7458	-1.5043	0.4191
10	C	-2.2536	-0.2349	0.6269
11	H	3.8277	-0.3448	-0.7492
12	C	2.3305	-2.8142	-0.6293
13	C	2.8027	2.2331	-0.3709
14	H	-0.1742	-2.8083	-0.0494
15	C	-0.1390	2.9158	0.3784
16	H	-2.3314	1.8280	0.7800

17	C	-2.6861	-2.6897	0.5524
18	H	-3.3101	-0.1873	0.8734
19	H	-1.0863	3.4308	0.5245
20	H	0.5070	3.1907	1.2130
21	H	0.3076	3.3143	-0.5313
22	H	-2.0995	-3.5918	0.3531
23	C	-3.8107	-2.6452	-0.4816
24	C	-3.2437	-2.8182	1.9695
25	H	-4.4312	-3.5404	-0.4172
26	H	-4.4646	-1.7849	-0.3286
27	H	-3.4152	-2.5822	-1.4954
28	H	-2.4429	-2.8777	2.7066
29	H	-3.8726	-1.9663	2.2336
30	H	-3.8563	-3.7161	2.0646
31	H	1.7729	-3.2896	-1.4393
32	H	3.3875	-2.8853	-0.8827
33	H	2.1750	-3.4178	0.2677
34	C	4.1904	2.1342	0.2353
35	C	5.3599	2.3357	-0.4762
36	C	6.6135	2.2378	0.1254
37	C	6.7111	1.9327	1.4748
38	C	5.5403	1.7256	2.2079
39	C	4.3122	1.8240	1.5928
40	H	5.3234	2.5772	-1.5303
41	H	7.4932	2.4051	-0.4810
42	H	5.6127	1.4847	3.2606
43	H	3.4161	1.6440	2.1755
44	C	2.8009	2.7163	-1.8215
45	H	2.2829	2.9866	0.2186
46	H	3.3074	2.0076	-2.4782
47	H	1.7783	2.8087	-2.1871
48	H	3.2840	3.6895	-1.9250
49	C	9.0727	2.0142	1.4645
50	O	7.8695	1.8155	2.1564
51	H	9.8745	1.8763	2.1868
52	H	9.1508	3.0239	1.0479
53	H	9.2095	1.2923	0.6525

Guaiazulene-Me2N-Ph-cation



Geometry optimization: PBEh-3c/mSVP
SCF energy = -983.76073486451 Hartree

Thermochemical properties at 298.15 K
Chemical potential = 0.418637 Hartree
Entropy = 0.000267 Hartree/K
Inner energy = 0.497345 Hartree
ZPE = 0.473217 Hartree
Enthalpy = 0.49829 Hartree

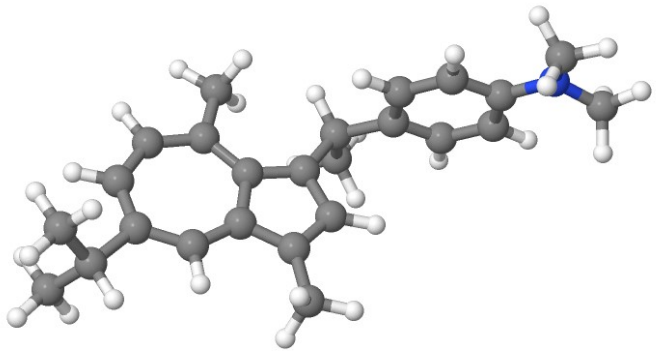
Single point energy at PBE0-D4/TZVP COSMO(∞)
SCF energy = -985.20506378291 Hartree

Coordinates:

	Atom	X	Y	Z
1	C	0.6331	-0.9632	0.3189
2	C	0.7689	0.4758	0.2003
3	C	2.8486	-0.5346	0.2366
4	C	1.9439	-1.5442	0.3436
5	C	2.1932	0.7358	0.1248
6	C	-0.5009	-1.7639	0.3722
7	C	-0.2698	1.4031	0.2768
8	C	-1.6370	1.0791	0.2981
9	C	-1.8449	-1.4327	0.3318
10	C	-2.3170	-0.1194	0.2909
11	H	3.9137	-0.6821	0.1402
12	C	2.2447	-3.0013	0.4184
13	C	2.8351	1.9243	-0.1753
14	H	-0.2951	-2.8267	0.4417
15	C	0.0076	2.8813	0.3395
16	H	-2.2912	1.9424	0.3200
17	C	-2.8635	-2.5527	0.3601
18	H	-3.3956	-0.0099	0.2811
19	H	-0.8634	3.4235	0.7002

20	H	0.8350	3.1156	1.0066
21	H	0.2389	3.2860	-0.6477
22	H	-2.3103	-3.4956	0.3798
23	C	-3.7269	-2.5536	-0.9018
24	C	-3.7195	-2.4957	1.6261
25	H	-4.3952	-3.4145	-0.8956
26	H	-4.3525	-1.6623	-0.9716
27	H	-3.1214	-2.6092	-1.8061
28	H	-3.1087	-2.5126	2.5284
29	H	-4.3410	-1.5994	1.6593
30	H	-4.3905	-3.3538	1.6625
31	H	1.8155	-3.5509	-0.4215
32	H	3.3188	-3.1748	0.4026
33	H	1.8585	-3.4496	1.3358
34	H	2.2374	2.7171	-0.6031
35	C	4.2069	2.2456	-0.0571
36	C	4.7086	3.3487	-0.7822
37	C	6.0245	3.7120	-0.7436
38	C	6.9470	3.0059	0.0699
39	C	6.4350	1.9411	0.8585
40	C	5.1203	1.5784	0.7889
41	H	4.0339	3.9137	-1.4142
42	H	6.3470	4.5521	-1.3401
43	H	7.0762	1.4170	1.5514
44	H	4.7697	0.8000	1.4527
45	N	8.2452	3.3462	0.1147
46	C	9.1686	2.6139	0.9578
47	H	8.9202	2.7133	2.0167
48	H	9.1902	1.5530	0.7026
49	H	10.1716	3.0036	0.8178
50	C	8.7363	4.4660	-0.6630
51	H	8.2557	5.4024	-0.3730
52	H	9.8028	4.5799	-0.4981
53	H	8.5827	4.3119	-1.7329

Guaiazulene-Me2N-Ph-Me-product



Geometry optimization: PBEh-3c/mSVP
SCF energy = -1023.79833045501 Hartree

Thermochemical properties at 298.15 K
Chemical potential = 0.454238 Hartree
Entropy = 0.000283 Hartree/K
Inner energy = 0.537744 Hartree
ZPE = 0.511792 Hartree
Enthalpy = 0.538689 Hartree

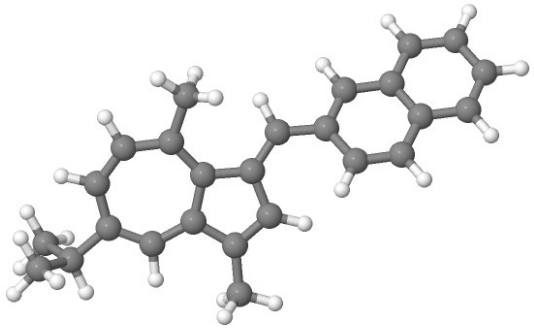
Single point energy at PBE0-D4/TZVP COSMO(∞)
SCF energy = -1025.24143518534 Hartree

Coordinates:

	Atom	X	Y	Z
1	C	0.6054	-0.9354	-0.1195
2	C	0.7199	0.5479	0.0460
3	C	2.7277	-0.3339	-0.5376
4	C	1.8768	-1.4208	-0.4811
5	C	2.0608	0.8655	-0.2252
6	C	-0.4779	-1.7748	0.0270
7	C	-0.3460	1.3896	0.4024
8	C	-1.6590	0.9909	0.6528
9	C	-1.8043	-1.5143	0.3687
10	C	-2.2892	-0.2482	0.6417
11	H	3.7816	-0.3906	-0.7781
12	C	2.2492	-2.8419	-0.7452
13	C	2.7939	2.1859	-0.3015
14	H	-0.2548	-2.8218	-0.1605
15	C	-0.1161	2.8713	0.5599
16	H	-2.3276	1.8039	0.9100
17	C	-2.7663	-2.6875	0.4402

18	H	-3.3445	-0.1945	0.8920
19	H	-1.0489	3.3917	0.7675
20	H	0.5604	3.0819	1.3887
21	H	0.3107	3.3186	-0.3366
22	H	-2.1961	-3.5889	0.1948
23	C	-3.8881	-2.5688	-0.5910
24	C	-3.3291	-2.8794	1.8480
25	H	-4.5249	-3.4549	-0.5740
26	H	-4.5265	-1.7059	-0.3941
27	H	-3.4894	-2.4603	-1.5996
28	H	-2.5312	-2.9927	2.5819
29	H	-3.9422	-2.0306	2.1557
30	H	-3.9590	-3.7692	1.8953
31	H	1.6838	-3.2720	-1.5751
32	H	3.3049	-2.9182	-1.0030
33	H	2.0843	-3.4823	0.1241
34	C	4.2026	2.0488	0.2440
35	C	5.3511	2.2326	-0.5108
36	C	6.6202	2.0937	0.0332
37	C	6.7994	1.7692	1.3830
38	C	5.6361	1.5699	2.1460
39	C	4.3840	1.7098	1.5827
40	H	5.2794	2.4891	-1.5599
41	H	7.4702	2.2451	-0.6168
42	H	5.6993	1.2990	3.1903
43	H	3.5135	1.5329	2.2047
44	C	2.7437	2.7290	-1.7303
45	H	2.3039	2.9197	0.3366
46	H	3.2121	2.0402	-2.4348
47	H	1.7098	2.8532	-2.0524
48	H	3.2410	3.6971	-1.8120
49	C	9.2063	1.6639	1.0796
50	N	8.0547	1.6549	1.9410
51	H	10.1087	1.5802	1.6808
52	H	9.2813	2.6012	0.5235
53	H	9.2110	0.8424	0.3523
54	C	8.1885	1.1084	3.2650
55	H	7.8108	0.0823	3.3516
56	H	9.2387	1.1002	3.5478
57	H	7.6664	1.7193	4.0048

Guaiazulene-Naphth-cation



Geometry optimization: PBEh-3c/mSVP
SCF energy = -1003.37070726947 Hartree

Thermochemical properties at 298.15 K
Chemical potential = 0.393078 Hartree
Entropy = 0.000255 Hartree/K
Inner energy = 0.468278 Hartree
ZPE = 0.445833 Hartree
Enthalpy = 0.469222 Hartree

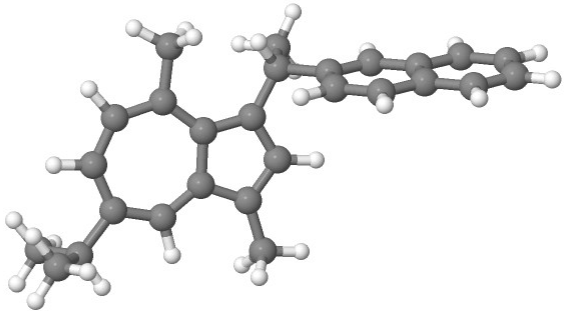
Single point energy at PBE0-D4/TZVP COSMO(∞)
SCF energy = -1004.85298289034 Hartree

Coordinates:

	Atom	X	Y	Z
1	C	0.6845	-0.9119	0.2681
2	C	0.8132	0.5103	0.4651
3	C	2.9057	-0.4759	0.2354
4	C	2.0031	-1.4820	0.1418
5	C	2.2453	0.7933	0.4033
6	C	-0.4466	-1.7146	0.1681
7	C	-0.2166	1.3932	0.7784
8	C	-1.5861	1.0679	0.7492
9	C	-1.7902	-1.3878	0.2229
10	C	-2.2659	-0.0977	0.4815
11	H	3.9694	-0.5960	0.0989
12	C	2.2974	-2.9218	-0.0961
13	C	2.8613	2.0114	0.3098
14	H	-0.2382	-2.7656	0.0005
15	C	0.0637	2.8152	1.1826
16	H	-2.2382	1.9026	0.9775
17	C	-2.8085	-2.4879	0.0187

18	H	-3.3445	0.0059	0.5119
19	H	-0.7883	3.2421	1.7066
20	H	0.9235	2.8930	1.8447
21	H	0.2422	3.4499	0.3122
22	H	-2.2567	-3.4108	-0.1785
23	C	-3.6895	-2.2092	-1.2004
24	C	-3.6454	-2.7116	1.2797
25	H	-4.3546	-3.0540	-1.3768
26	H	-4.3188	-1.3292	-1.0606
27	H	-3.0971	-2.0592	-2.1027
28	H	-3.0218	-2.9279	2.1467
29	H	-4.2653	-1.8463	1.5191
30	H	-4.3168	-3.5571	1.1337
31	H	1.8561	-3.2788	-1.0284
32	H	3.3702	-3.0908	-0.1595
33	H	1.9174	-3.5517	0.7106
34	H	2.2420	2.8796	0.1352
35	C	8.7773	4.4369	-0.3878
36	C	7.8429	5.2649	-1.0404
37	C	8.3695	3.3132	0.2805
38	C	6.5131	4.9542	-1.0142
39	C	7.0066	2.9645	0.3212
40	C	6.0630	3.7985	-0.3348
41	C	6.5402	1.8219	1.0184
42	C	4.7036	3.4539	-0.2815
43	C	5.2209	1.4926	1.0330
44	C	4.2678	2.3004	0.3504
45	H	9.8272	4.6953	-0.4163
46	H	8.1848	6.1484	-1.5616
47	H	9.0931	2.6840	0.7826
48	H	5.7923	5.5884	-1.5148
49	H	7.2530	1.2162	1.5635
50	H	3.9851	4.0992	-0.7750
51	H	4.8894	0.6492	1.6225

Guaiazulene-Naphth-Me-product



Geometry optimization: PBEh-3c/mSVP
SCF energy = -1043.42580461029 Hartree

Thermochemical properties at 298.15 K
Chemical potential = 0.430025 Hartree
Entropy = 0.000269 Hartree/K
Inner energy = 0.509164 Hartree
ZPE = 0.485038 Hartree
Enthalpy = 0.510109 Hartree

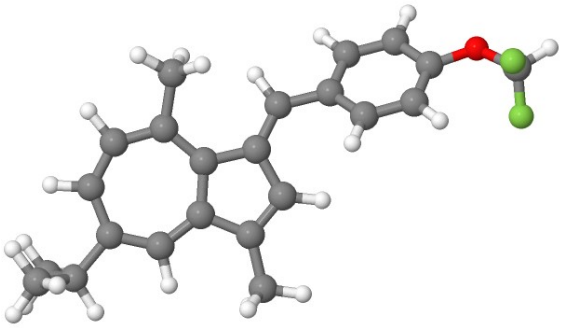
Single point energy at PBE0-D4/TZVP COSMO(∞)
SCF energy = -1044.90247032596 Hartree

Coordinates:

	Atom	X	Y	Z
1	C	0.6930	-0.8603	-0.1821
2	C	0.7605	0.6175	0.0399
3	C	2.7839	-0.1714	-0.6215
4	C	1.9703	-1.2873	-0.5941
5	C	2.0846	0.9898	-0.2428
6	C	-0.3554	-1.7432	-0.0346
7	C	-0.3283	1.4110	0.4355
8	C	-1.6179	0.9565	0.7098
9	C	-1.6773	-1.5441	0.3603
10	C	-2.1998	-0.3057	0.6872
11	H	3.8336	-0.1837	-0.8863
12	C	2.3825	-2.6830	-0.9253
13	C	2.7804	2.3314	-0.2543
14	H	-0.1014	-2.7742	-0.2661
15	C	-0.1539	2.8987	0.6083
16	H	-2.3101	1.7371	1.0024
17	C	-2.5915	-2.7549	0.4305

18	H	-3.2472	-0.2999	0.9732
19	H	-1.1067	3.3824	0.8137
20	H	0.5077	3.1279	1.4446
21	H	0.2612	3.3691	-0.2817
22	H	-1.9990	-3.6255	0.1325
23	C	-3.7590	-2.6467	-0.5501
24	C	-3.0872	-3.0116	1.8531
25	H	-4.3598	-3.5575	-0.5375
26	H	-4.4217	-1.8170	-0.2981
27	H	-3.4074	-2.4897	-1.5698
28	H	-2.2556	-3.1180	2.5497
29	H	-3.7171	-2.1963	2.2132
30	H	-3.6820	-3.9253	1.8968
31	H	1.8079	-3.0996	-1.7556
32	H	3.4321	-2.7129	-1.2149
33	H	2.2646	-3.3620	-0.0778
34	C	2.7575	2.9315	-1.6594
35	H	2.2593	3.0258	0.4035
36	H	3.2694	2.2874	-2.3756
37	H	1.7298	3.0355	-2.0069
38	H	3.2229	3.9181	-1.6868
39	C	9.0953	2.0818	1.4830
40	C	9.0052	2.5189	0.1477
41	C	7.9603	1.7874	2.1874
42	C	7.7837	2.6531	-0.4532
43	C	6.6875	1.9167	1.5915
44	C	6.5952	2.3570	0.2495
45	C	5.4905	1.6214	2.2858
46	C	5.3187	2.4889	-0.3501
47	C	4.2791	1.7555	1.6771
48	C	4.1708	2.1997	0.3347
49	H	10.0662	1.9799	1.9495
50	H	9.9082	2.7493	-0.4022
51	H	8.0268	1.4504	3.2149
52	H	7.7157	2.9904	-1.4804
53	H	5.5485	1.2825	3.3132
54	H	5.2769	2.8296	-1.3773
55	H	3.3731	1.5093	2.2182

Guaiazulene-F2CHO-Ph-cation



Geometry optimization: PBEh-3c/mSVP
SCF energy = -1162.46563291819 Hartree

Thermochemical properties at 298.15 K
Chemical potential = 0.360095 Hartree
Entropy = 0.000269 Hartree/K
Inner energy = 0.439473 Hartree
ZPE = 0.415789 Hartree
Enthalpy = 0.440417 Hartree

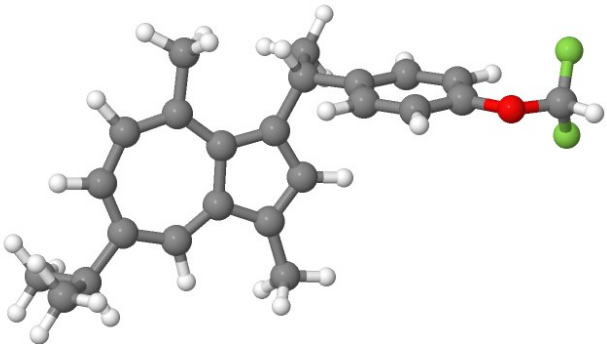
Single point energy at PBE0-D4/TZVP COSMO(∞)
SCF energy = -1164.18215485954 Hartree

Coordinates:

	Atom	X	Y	Z
1	C	0.6456	-0.8866	0.3599
2	C	0.7267	0.5520	0.3500
3	C	2.8537	-0.3877	0.3695
4	C	1.9837	-1.4256	0.3846
5	C	2.1529	0.8702	0.3185
6	C	-0.4574	-1.7328	0.3211
7	C	-0.3411	1.4370	0.4730
8	C	-1.6981	1.0653	0.4212
9	C	-1.8099	-1.4467	0.2576
10	C	-2.3318	-0.1490	0.2954
11	H	3.9259	-0.4906	0.2999
12	C	2.3257	-2.8744	0.3756
13	C	2.7451	2.0813	0.0900
14	H	-0.2134	-2.7894	0.3218
15	C	-0.1201	2.9121	0.6709
16	H	-2.3830	1.9023	0.4867
17	C	-2.7867	-2.5980	0.1665
18	H	-3.4126	-0.0781	0.2527

19	H	-1.0135	3.3858	1.0710
20	H	0.6931	3.1167	1.3642
21	H	0.0998	3.4131	-0.2741
22	H	-2.2022	-3.5216	0.1466
23	C	-3.5952	-2.5362	-1.1305
24	C	-3.6963	-2.6541	1.3952
25	H	-4.2317	-3.4168	-1.2120
26	H	-4.2491	-1.6634	-1.1663
27	H	-2.9513	-2.5096	-2.0092
28	H	-3.1247	-2.7124	2.3210
29	H	-4.3528	-1.7848	1.4599
30	H	-4.3351	-3.5352	1.3430
31	H	1.9413	-3.3777	-0.5136
32	H	3.4041	-3.0167	0.3880
33	H	1.9205	-3.3913	1.2477
34	H	2.1202	2.8998	-0.2379
35	C	4.1410	2.4108	0.1692
36	C	4.6248	3.4701	-0.6145
37	C	5.9524	3.8217	-0.5925
38	C	6.8385	3.1518	0.2517
39	C	6.3733	2.1326	1.0850
40	C	5.0429	1.7744	1.0323
41	H	3.9499	4.0065	-1.2698
42	H	6.3215	4.6235	-1.2175
43	H	7.0134	1.6254	1.7896
44	H	4.6905	1.0221	1.7248
45	O	8.1120	3.6015	0.1852
46	C	9.1409	3.0670	0.9085
47	F	8.9159	3.1856	2.2272
48	F	9.2851	1.7580	0.6450
49	H	10.0468	3.6057	0.6352

Guaiazulene-F2CHO-Ph-Me-product



Geometry optimization: PBEh-3c/mSVP
SCF energy = -1202.52099447504 Hartree

Thermochemical properties at 298.15 K
Chemical potential = 0.398821 Hartree
Entropy = 0.000273 Hartree/K
Inner energy = 0.479415 Hartree
ZPE = 0.454868 Hartree
Enthalpy = 0.480359 Hartree

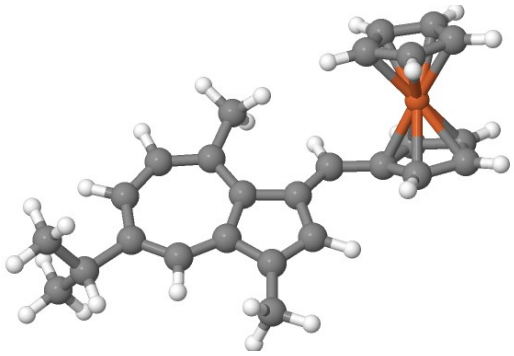
Single point energy at PBE0-D4/TZVP COSMO(∞)
SCF energy = -1204.23029812006 Hartree

Coordinates:

	Atom	X	Y	Z
1	C	0.6580	-0.8756	-0.1962
2	C	0.7382	0.6137	-0.0810
3	C	2.7503	-0.2366	-0.6981
4	C	1.9274	-1.3403	-0.5938
5	C	2.0635	0.9538	-0.3921
6	C	-0.3897	-1.7386	0.0409
7	C	-0.3465	1.4432	0.2478
8	C	-1.6313	1.0188	0.5825
9	C	-1.6999	-1.5028	0.4557
10	C	-2.2134	-0.2399	0.6877
11	H	3.7994	-0.2774	-0.9624
12	C	2.3255	-2.7586	-0.8336
13	C	2.7822	2.2815	-0.4639
14	H	-0.1449	-2.7856	-0.1164
15	C	-0.1716	2.9408	0.2688
16	H	-2.3191	1.8245	0.8107
17	C	-2.6114	-2.7015	0.6543
18	H	-3.2539	-0.2066	0.9963
19	H	-1.1306	3.4439	0.3746
20	H	0.4498	3.2583	1.1077
21	H	0.2883	3.3134	-0.6447
22	H	-2.0244	-3.5957	0.4229
23	C	-3.8002	-2.6809	-0.3059
24	C	-3.0745	-2.8289	2.1050
25	H	-4.3986	-3.5871	-0.2002
26	H	-4.4589	-1.8323	-0.1132
27	H	-3.4712	-2.6140	-1.3429
28	H	-2.2272	-2.8670	2.7897
29	H	-3.7020	-1.9871	2.4030

30	H	-3.6620	-3.7375	2.2453
31	H	1.7381	-3.2257	-1.6272
32	H	3.3714	-2.8166	-1.1323
33	H	2.2127	-3.3776	0.0592
34	C	4.1485	2.1625	0.1857
35	C	5.3436	2.3480	-0.4899
36	C	6.5785	2.2178	0.1398
37	C	6.6180	1.8975	1.4856
38	C	5.4322	1.7113	2.1871
39	C	4.2211	1.8398	1.5406
40	H	5.3421	2.6000	-1.5418
41	H	7.4708	2.3732	-0.4468
42	H	5.4705	1.4596	3.2388
43	H	3.3062	1.6707	2.0961
44	C	2.8278	2.7892	-1.9047
45	H	2.2478	3.0257	0.1238
46	H	3.3447	2.0872	-2.5604
47	H	1.8166	2.8990	-2.2964
48	H	3.3230	3.7590	-1.9779
49	C	9.0008	1.8457	1.7507
50	O	7.7538	1.7325	2.2470
51	H	9.7025	1.6670	2.5654
52	F	9.2306	3.0701	1.2283
53	F	9.2338	0.9573	0.7603

Guaiazulene-Fc-cation



Geometry optimization: PBEh-3c/mSVP
SCF energy = -2267.48535586035 Hartree

Thermochemical properties at 298.15 K
Chemical potential = 0.412013 Hartree
Entropy = 0.000275 Hartree/K
Inner energy = 0.49304 Hartree
ZPE = 0.46877 Hartree
Enthalpy = 0.493984 Hartree

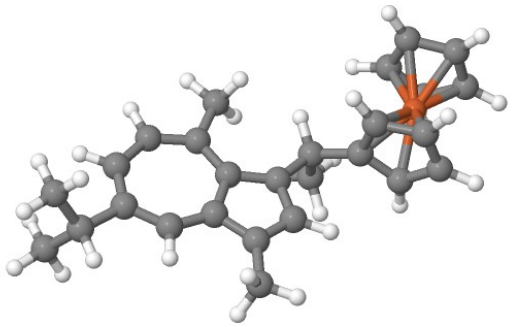
Single point energy at PBE0-D4/TZVP COSMO(∞)
SCF energy = -2269.57793650069 Hartree

Coordinates:

	Atom	X	Y	Z
1	C	0.7525	-0.7090	0.3399
2	C	0.8660	0.6014	-0.2589
3	C	2.9644	-0.2556	0.2390
4	C	2.0733	-1.1957	0.6399
5	C	2.2941	0.8718	-0.3488
6	C	-0.3663	-1.4892	0.6087
7	C	-0.1914	1.4518	-0.5753
8	C	-1.5514	1.0990	-0.5171
9	C	-1.7108	-1.2485	0.3844
10	C	-2.2067	-0.0517	-0.1399
11	H	4.0361	-0.3764	0.2731
12	C	2.3875	-2.5200	1.2438
13	C	2.9365	1.8994	-0.9905
14	H	-0.1435	-2.4533	1.0534
15	C	0.0526	2.8662	-1.0279
16	H	-2.2219	1.8869	-0.8390
17	C	-2.7065	-2.3295	0.7455
18	H	-3.2840	0.0020	-0.2466

19	H	-0.8560	3.4591	-0.9565
20	H	0.8119	3.3631	-0.4265
21	H	0.3673	2.9014	-2.0727
22	H	-2.1382	-3.1813	1.1291
23	C	-3.4779	-2.8080	-0.4854
24	C	-3.6502	-1.8675	1.8573
25	H	-4.1263	-3.6412	-0.2160
26	H	-4.1160	-2.0259	-0.8995
27	H	-2.8092	-3.1489	-1.2751
28	H	-3.1043	-1.5403	2.7419
29	H	-4.2912	-1.0454	1.5354
30	H	-4.3037	-2.6872	2.1540
31	H	2.0276	-3.3451	0.6264
32	H	3.4621	-2.6466	1.3577
33	H	1.9415	-2.6311	2.2339
34	H	2.3606	2.5510	-1.6306
35	Fe	4.9362	3.9348	-0.0829
36	C	3.6529	5.5389	-0.0110
37	C	3.4570	4.7066	1.1221
38	C	4.6757	4.6417	1.8355
39	C	5.6275	5.4331	1.1461
40	C	4.9931	5.9918	0.0109
41	C	4.9248	3.0981	-1.9395
42	C	6.2600	3.3079	-1.5654
43	C	6.5046	2.5955	-0.3620
44	C	5.3265	1.9274	0.0130
45	C	4.3266	2.2064	-0.9794
46	H	2.9096	5.7991	-0.7503
47	H	2.5396	4.2053	1.3969
48	H	4.8519	4.0837	2.7431
49	H	6.6557	5.5875	1.4376
50	H	5.4564	6.6383	-0.7196
51	H	4.4377	3.4927	-2.8197
52	H	6.9758	3.9214	-2.0915
53	H	7.4329	2.5915	0.1892
54	H	5.2033	1.3372	0.9081

Guaiazulene-Fc-Me-product



Geometry optimization: PBEh-3c/mSVP
SCF energy = -2307.53534702153 Hartree

Thermochemical properties at 298.15 K
Chemical potential = 0.450216 Hartree
Entropy = 0.000283 Hartree/K
Inner energy = 0.533708 Hartree
ZPE = 0.507764 Hartree
Enthalpy = 0.534652 Hartree

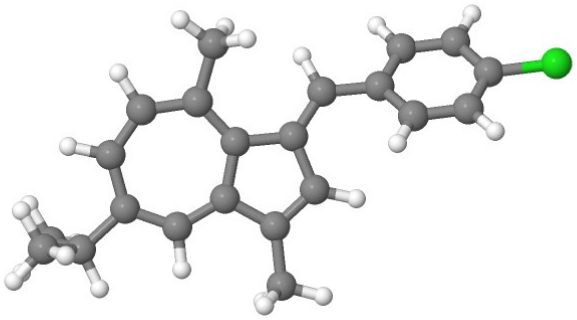
Single point energy at PBE0-D4/TZVP COSMO(∞)
SCF energy = -2309.62239257234 Hartree

Coordinates:

	Atom	X	Y	Z
1	C	0.6777	-1.0290	-0.0008
2	C	0.8688	0.4473	-0.1533
3	C	2.8374	-0.6350	-0.4732
4	C	1.9275	-1.6414	-0.2047
5	C	2.2300	0.6326	-0.4520
6	C	-0.4556	-1.7638	0.2786
7	C	-0.1493	1.3988	0.0065
8	C	-1.4899	1.1285	0.2861
9	C	-1.7735	-1.3719	0.5030
10	C	-2.1917	-0.0524	0.4938
11	H	3.8903	-0.7971	-0.6648
12	C	2.2293	-3.1019	-0.1410
13	C	3.0170	1.8735	-0.8051
14	H	-0.2870	-2.8362	0.3244
15	C	0.1678	2.8691	-0.1000
16	H	-2.1143	2.0111	0.3589
17	C	-2.8050	-2.4543	0.7711

18	H	-3.2488	0.1054	0.6857
19	H	-0.7324	3.4715	0.0010
20	H	0.8539	3.1821	0.6877
21	H	0.6218	3.1266	-1.0556
22	H	-2.2801	-3.4144	0.7472
23	C	-3.8779	-2.4986	-0.3165
24	C	-3.4311	-2.3169	2.1584
25	H	-4.5676	-3.3269	-0.1468
26	H	-4.4693	-1.5814	-0.3356
27	H	-3.4357	-2.6256	-1.3047
28	H	-2.6695	-2.3101	2.9383
29	H	-4.0068	-1.3943	2.2516
30	H	-4.1118	-3.1456	2.3595
31	H	1.6658	-3.6751	-0.8808
32	H	3.2862	-3.2825	-0.3330
33	H	2.0039	-3.5295	0.8387
34	C	2.9279	2.1524	-2.3074
35	H	2.6082	2.7357	-0.2812
36	H	3.3173	1.3128	-2.8843
37	H	1.8922	2.2916	-2.6168
38	H	3.4903	3.0471	-2.5806
39	Fe	5.8122	3.2514	-0.1171
40	C	5.9388	4.7806	-1.4874
41	C	4.8753	5.0221	-0.5820
42	C	5.4194	5.0873	0.7247
43	C	6.8183	4.8856	0.6271
44	C	7.1393	4.6965	-0.7402
45	C	5.5940	1.4854	-1.1366
46	C	6.7210	1.4161	-0.2794
47	C	6.2717	1.6190	1.0479
48	C	4.8708	1.8185	1.0064
49	C	4.4437	1.7414	-0.3448
50	H	5.8493	4.6742	-2.5585
51	H	3.8325	5.1331	-0.8422
52	H	4.8646	5.2545	1.6361
53	H	7.5167	4.8738	1.4508
54	H	8.1252	4.5145	-1.1415
55	H	5.6161	1.3778	-2.2114
56	H	7.7423	1.2455	-0.5868
57	H	6.8898	1.6320	1.9335
58	H	4.2267	1.9943	1.8563

Guaiazulene-Cl-Ph-cation



Geometry optimization: PBEh-3c/mSVP
SCF energy = -1309.16560170125 Hartree

Thermochemical properties at 298.15 K
Chemical potential = 0.336071 Hartree
Entropy = 0.000247 Hartree/K
Inner energy = 0.408622 Hartree
ZPE = 0.387528 Hartree
Enthalpy = 0.409566 Hartree

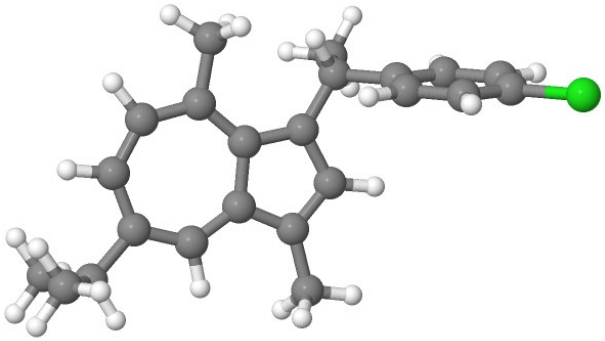
Single point energy at PBE0-D4/TZVP COSMO(∞)
SCF energy = -1310.79515978826 Hartree

Coordinates:

	Atom	X	Y	Z
1	C	0.6423	-0.9090	0.2845
2	C	0.7500	0.5262	0.3101
3	C	2.8596	-0.4546	0.2113
4	C	1.9706	-1.4745	0.2333
5	C	2.1827	0.8189	0.2288
6	C	-0.4762	-1.7356	0.2776
7	C	-0.2948	1.4273	0.4943
8	C	-1.6599	1.0799	0.4956
9	C	-1.8248	-1.4257	0.2876
10	C	-2.3210	-0.1200	0.3771
11	H	3.9258	-0.5749	0.0935
12	C	2.2812	-2.9286	0.1682
13	C	2.7938	2.0216	0.0244
14	H	-0.2514	-2.7957	0.2404
15	C	-0.0388	2.8946	0.7052
16	H	-2.3257	1.9274	0.6069
17	C	-2.8250	-2.5580	0.2204

18	H	-3.4011	-0.0296	0.3869
19	H	-0.9134	3.3832	1.1280
20	H	0.7918	3.0727	1.3852
21	H	0.1740	3.4018	-0.2381
22	H	-2.2587	-3.4908	0.1546
23	C	-3.6925	-2.4558	-1.0354
24	C	-3.6763	-2.6234	1.4898
25	H	-4.3467	-3.3244	-1.1040
26	H	-4.3327	-1.5724	-1.0223
27	H	-3.0906	-2.4214	-1.9431
28	H	-3.0628	-2.7105	2.3861
29	H	-4.3139	-1.7452	1.6027
30	H	-4.3321	-3.4927	1.4506
31	H	1.8449	-3.3984	-0.7153
32	H	3.3558	-3.0923	0.1255
33	H	1.9066	-3.4619	1.0440
34	H	2.1819	2.8726	-0.2377
35	C	4.2071	2.3040	0.0577
36	C	4.6964	3.3514	-0.7350
37	C	6.0393	3.6624	-0.7586
38	C	6.9160	2.9499	0.0515
39	C	6.4494	1.9414	0.8887
40	C	5.1082	1.6226	0.8880
41	H	4.0159	3.9146	-1.3614
42	H	6.4080	4.4577	-1.3909
43	Cl	8.5816	3.3373	0.0432
44	H	7.1339	1.4246	1.5466
45	H	4.7505	0.8758	1.5840

Guaiazulene-Cl-Ph-Me-product



Geometry optimization: PBEh-3c/mSVP
SCF energy = -1349.22534723244 Hartree

Thermochemical properties at 298.15 K
Chemical potential = 0.373025 Hartree
Entropy = 0.00026 Hartree/K
Inner energy = 0.449581 Hartree
ZPE = 0.426768 Hartree
Enthalpy = 0.450525 Hartree

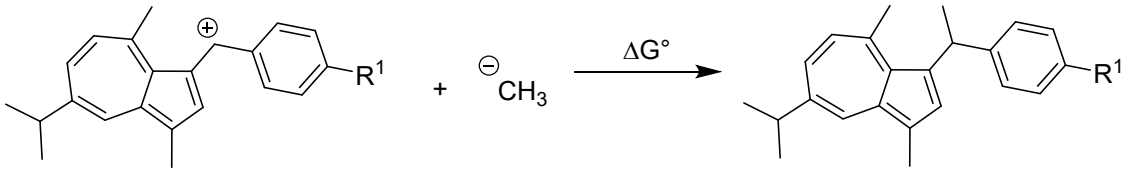
Single point energy at PBE0-D4/TZVP COSMO(∞)
SCF energy = -1350.84496240613 Hartree

Coordinates:

	Atom	X	Y	Z
1	C	0.6365	-0.9521	-0.1015
2	C	0.7781	0.5318	0.0212
3	C	2.7667	-0.4038	-0.5493
4	C	1.8960	-1.4721	-0.4581
5	C	2.1236	0.8154	-0.2643
6	C	-0.4604	-1.7675	0.0788
7	C	-0.2716	1.4043	0.3511
8	C	-1.5892	1.0370	0.6220
9	C	-1.7785	-1.4738	0.4239
10	C	-2.2398	-0.1911	0.6585
11	H	3.8173	-0.4898	-0.7962
12	C	2.2394	-2.9067	-0.6856
13	C	2.8819	2.1182	-0.3722
14	H	-0.2571	-2.8232	-0.0788
15	C	-0.0171	2.8871	0.4497
16	H	-2.2429	1.8696	0.8534
17	C	-2.7595	-2.6272	0.5418
18	H	-3.2919	-0.1111	0.9148
19	H	-0.9416	3.4311	0.6320
20	H	0.6588	3.1209	1.2730
21	H	0.4191	3.2908	-0.4629
22	H	-2.2063	-3.5460	0.3238
23	C	-3.8860	-2.5239	-0.4859

24	C	-3.3152	-2.7609	1.9591
25	H	-4.5375	-3.3977	-0.4344
26	H	-4.5085	-1.6441	-0.3145
27	H	-3.4928	-2.4570	-1.5003
28	H	-2.5143	-2.8620	2.6915
29	H	-3.9130	-1.8924	2.2413
30	H	-3.9587	-3.6382	2.0408
31	H	1.6596	-3.3480	-1.4994
32	H	3.2913	-3.0109	-0.9485
33	H	2.0690	-3.5195	0.2022
34	C	4.2733	1.9675	0.2147
35	C	5.4386	2.1407	-0.5194
36	C	6.6909	1.9952	0.0655
37	C	6.7817	1.6742	1.4061
38	C	5.6339	1.4953	2.1654
39	C	4.3978	1.6402	1.5648
40	H	5.3920	2.3939	-1.5699
41	H	7.5871	2.1326	-0.5238
42	Cl	8.3350	1.4921	2.1454
43	H	5.7086	1.2426	3.2141
44	H	3.5033	1.4821	2.1557
45	C	2.8743	2.6170	-1.8173
46	H	2.3986	2.8825	0.2343
47	H	3.3445	1.8987	-2.4902
48	H	1.8491	2.7470	-2.1630
49	H	3.3868	3.5752	-1.9199

Methyl anion affinity of guaiazulene arylmethylium cations



MAA = -ΔG°; calculated at PBE0-D4/def2-TZVP (COSMO∞) level.

Mayr´s electrophilicity was calculated according to the following equation based on the recommendation of van Vranken and coworkers.[16]

E = MAA*0.11 – 37.9

Cation (Ar)	ε_{LUMO} (Hartree)	ΔG° (Hartree)	MAA (kJ.mol^{-1})	Estimated Mayr´s E
4-CH_3-C_6H_4	-0.1216	-0.110992	291.4	-5.85
4-MeO-C_6H_4	-0.1189	-0.109264	286.9	-6.34
4-Me_2N-C_6H_4	-0.1127	-0.101945	267.7	-8.46
2-Naphthyl	-0.1238	-0.113714	298.6	-5.05
4-F-C_6H_4	-0.1225	-0.112870	296.3	-5.31
4-CHF_2O-C_6H_4	-0.1220	-0.110591	290.4	-5.96
Ferrocenyl	-0.1153	-0.107427	282.1	-6.87
4-Cl-C_6H_4	-0.1243	-0.114182	299.8	-4.92

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