Supporting Information

Base-Mediated Insertion Reaction of Alkynes into Carbon-Carbon σ-Bonds of Ethanones: Synthesis of Hydroxydienone and Chromone Derivatives

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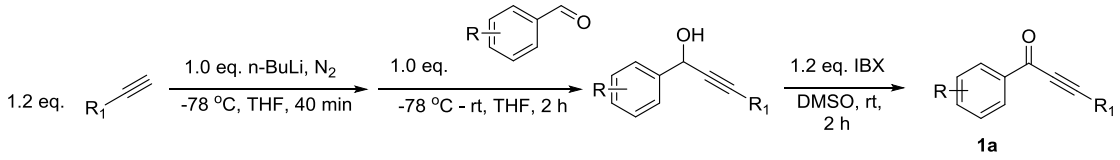
1. General Details.

All reactions under N_2 were performed in flame-dried glassware under an atmosphere of dry nitrogen, and the workup was carried out in air, unless otherwise noted. Dimethylformamide (DMF) were dried and distilled from calcium hydride. Column chromatographic purification of products was carried out using silica gel (200~300 mesh). The reagents were used without further purification.

^{1}H NMR spectra was recorded at 400 MHz, ^{13}C NMR spectra was recorded at 100 MHz, and in $CDCl_3$ (containing 0.03% TMS) solutions. ^{1}H NMR spectra was recorded with tetramethylsilane (δ = 0.00 ppm) as internal reference; ^{13}C NMR spectra was recorded with $CDCl_3$ (δ = 77.00 ppm) as internal reference. High-resolution mass spectra were performed on a mass spectrometer with a TOF (for EI or ESI) or FT-ICR (for MALDI) analyzer. Single crystal X-ray diffraction data was collected in Bruker SMARTAPEX diffractiometers with molybdenum cathodes.

2. **Preparation of Acetyenic ketones**

General procedure for the preparation of Acetyenic Ketones

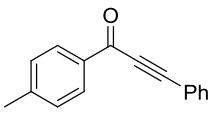


1a

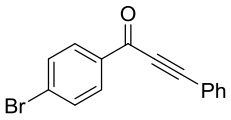
To a solution of alkyne (12 mmol) in anhydrous THF (30 mL), n-BuLi (2.5M, 10 mmol, 4 mL) was added at -78 °C. The resulting mixture was stirred at -78 °C for 1 hour, then the aldehyde (10 mmol) was added and the reaction temperature was raised to room temperature till aldehyde disappeared by TLC analysis. The resulting mixture was quenched with a saturated solution of NH_4Cl and extracted with ethyl acetate (20 mL × 3). The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by

column chromatography with petroleum ether/ethyl acetate = 5/1-10:1 as the eluent afforded the substituted alkynol .

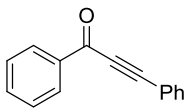
To a solution of substituted alkynol (10 mmol) in DMSO (20 mL) in round-bottom flask, IBX (12 mmol, 3.36 g) was added at room temperature. The reaction was stirred in air until the full conversion of substituted alkynol monitored by thin-layer chromatography. The resulting mixture was quenched with water (20 mL) and filtered. Then the filtrate was extracted with ethyl acetate (20 mL × 3). The organic layers was combined, washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification by column chromatography with petroleum ether/ethyl acetate = 10/1-20:1 as the eluent afforded the acetyenic ketones .



1a (69%)



1b (84%)



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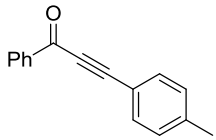

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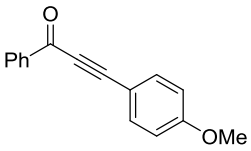

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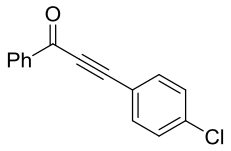

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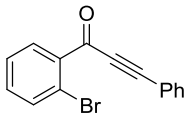

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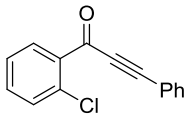
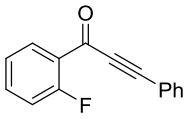
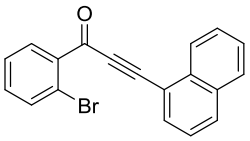


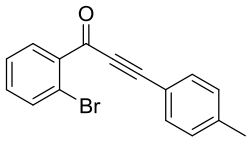
4b (76%)



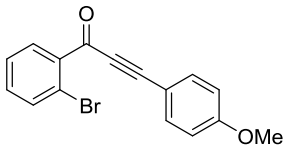
4c(78%)



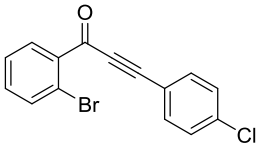
4d (59%)



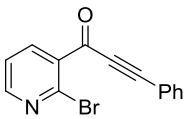
4e (71%)



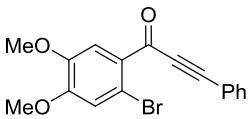
4f (89%)



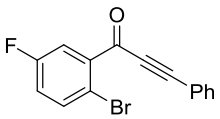
4g (70%)



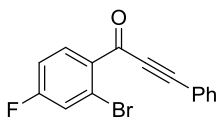
4h (78%)



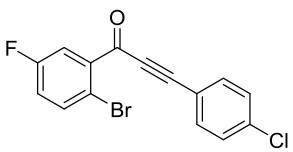
4i (72%)



4j (68%)

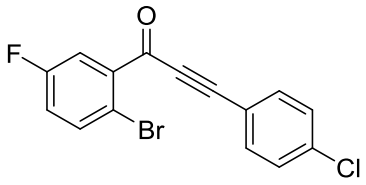


4k (66%)



4l (70%)

Compounds **1a-1f,**[1] and **4a-4k**,[2] are known compounds and the spectroscopic data are in agreement with that previously reported. The analytical data of other products are as follows.

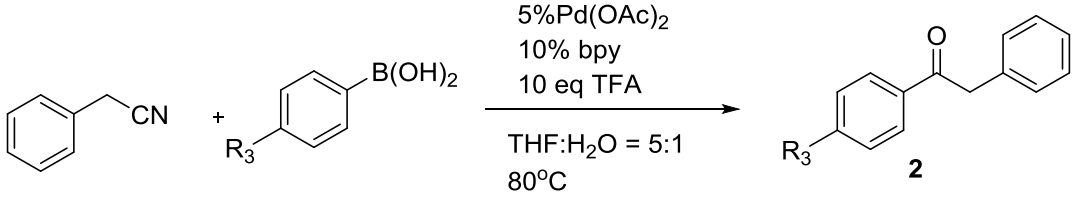


4l

1-(2-bromo-5-fluorophenyl)-3-(4-chlorophenyl)prop-2-yn-1-one (4l): Yellow solid, 70% yield; mp 104-105 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11-7.17 (m, 1H), 7.35-7.46 (m, 2H), 7.55-7.64 (m, 2H), 7.68 (dd, J = 8.8, 4.8 Hz, 1H), 7.74 (dd, J = 8.4, 2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 88.24, 93.67, 115.65 ($J_{C\text{-}F}$ = 3.3 Hz), 118.31, 119.57 ($J_{C\text{-}F}$ = 24.3 Hz), 120.95 ($J_{C\text{-}F}$ = 22.3 Hz), 129.48, 134.63, 136.64 ($J_{C\text{-}F}$ = 7.4 Hz), 138.01, 138.98 ($J_{C\text{-}F}$ = 6.3 Hz), 161.86 ($J_{C\text{-}F}$ = 249.6 Hz), 176.43. HRMS (ESI) calcd for $C_{15}H_8BrClFO$ $[M+H]^+$: 336.9426; found: 336.9423.

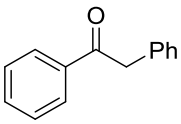
3. **Preparation of Alkyl Aryl Ketones 2**

General procedure for the preparation of Alkyl Aryl Ketones 2

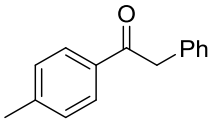


To a Schlenk tube with a magnetic stirring bar were charged the respective nitrile **1** (1.0 mmol), arylboronic acid **2** (2.0 mmol), $Pd(OAc)_2$ (5 mol %, 11.2 mg), bpy (10 mol%, 15.6 mg), TFA (10 equiv, 0.74 ml), THF (5 mL), and H_2O (1 mL) under N_2 atmosphere. The reaction mixture was stirred at 80 ℃ for 36 h. After cooling to r.t., the mixture was poured into EtOAc (5 mL), which was washed with sat. aq $NaHCO_3$ (2 × 10 mL) and then brine (1 × 10 mL). After extracting the aqueous layer with EtOAc (3 × 10 mL), the combined organic layers were dried over anhydrous Na_2SO_4, and evaporated under vacuum. Purification by column chromatography with

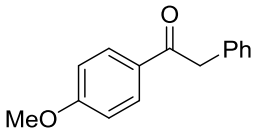
petroleum ether/ethyl acetate = 5/1-10:1 as the eluent afforded the alkyl aryl ketones **2**.[3]



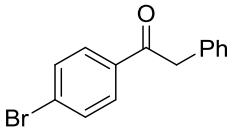
2a



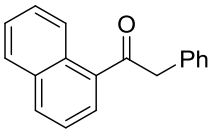
2b (97%)



2c (96%)



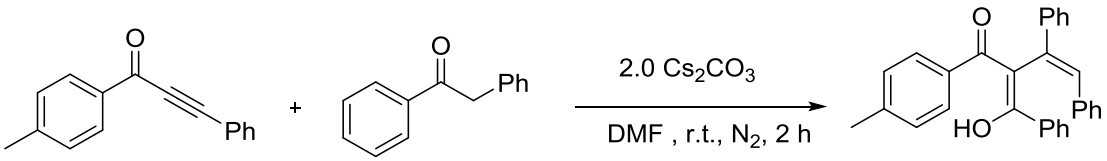
2d (57%)



2e (50%)

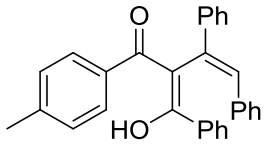
Compounds **2a-2e,**[4] are known compounds and the spectroscopic data are in agreement with that previously reported.

4 Synthesis of hydroxydienones 3



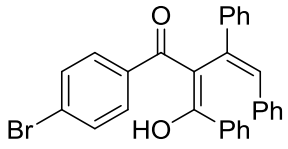
1a **2a** **3a**

In a schlenk tube acetyenic ketone **1a** (0.30 mmol, 66.1 mg), Cs_2CO_3 (0.6 mmol, 195.5 mg), DMF (3.0 mL) and **2a** (0.30 mmol, 58.9 mg) was stirred at room temperature under N_2. After the reaction was completed as monitored by thin-layer chromatography, the reaction mixture was then quenched by water, and the water layers were extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) afforded desired compound **3a**.



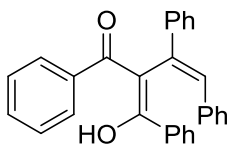
3a

(*2Z,3Z*)-2-(hydroxy(phenyl)methylene)-3,4-diphenyl-1-(p-tolyl)but-3-en-1-one (3a): Yellow solid, obtained in 2.0 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 20:1), 67.4 mg (81% yield); mp 122-123^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.23 (s, 3H), 6.66 (s, 1H), 6.90 (d, J = 7.6 Hz, 2H), 7.04-7.20 (m, 11H), 7.31-7.43 (m, 6H), 18.05 (d, J = 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.16, 110.42, 126.96, 127.14, 127.37, 127.55, 127.64, 127.72, 128.44, 128.49, 128.72, 130.44, 132.20, 134.34, 137.16, 137.35, 137.88, 141.28, 143.00, 190.48, 190.52. HRMS (ESI) calcd for $C_{30}H_{24}NaO_2$ $[M+Na]^+$: 439.1669; found: 439.1691.



3b

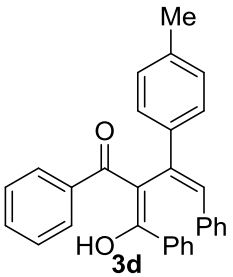
(*2Z,3Z*)-1-(4-bromophenyl)-2-(hydroxy(phenyl)methylene)-3,4-diphenylbut-3-en-1-one (3b): Yellow solid, obtained in 1.0 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 20:1), 78.1 mg (54% yield); mp 136-137 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.66 (s, 1H), 7.06-7.26 (m, 15H), 7.37-7.42 (m, 4H), 17.85 (s,1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 110.65, 125.22, 126.86, 127.33, 127.50, 127.78, 128.64, 128.68, 129.08, 130.86, 130.94, 132.44, 136.01, 136.74, 136.97, 137.67, 142.68, 189.35, 190.80. HRMS (ESI) calcd for $C_{29}H_{21}BrNaO_2$ $[M+Na]^+$: 503.0617; found: 503.0618.



3c

(*2Z,3Z*)-2-(hydroxy(phenyl)methylene)-1,3,4-triphenylbut-3-en-1-one

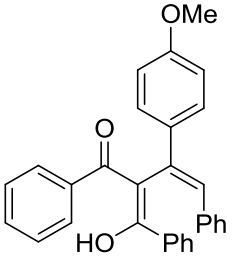
(3c) : Yellow solid, obtained in 3.0 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 20:1), 101.6 mg (84% yield); mp 156-157^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.64 (s, 1H), 7.05-7.24 (m, 14H), 7.34-7.42 (m, 6H), 17.95 (d, J = 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 110.66, 126.97, 127.17, 127.46, 127.56, 127.70, 128.49, 128.54, 128.70, 130.64, 132.28, 137.02, 137.20, 137.85, 142.98, 190.68. HRMS (ESI) calcd for $C_{29}H_{22}NaO_2$ $[M+Na]^+$: 425.1512; found: 425.1505.



3d

(*2Z,3Z*)-2-(hydroxy(phenyl)methylene)-1,4-diphenyl-3-(p-tolyl)but-3-en-1-one

(3d) : Yellow solid, obtained in 3.0 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 20:1), 92.4 mg (74% yield); mp 115-116^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.25 (s, 3H), 6.62 (s, 1H), 6.98 (d, J = 5.6 Hz, 2H), 7.05-7.24 (m, 11H), 7.26-7.32 (m, 2H)，7.35-7.44 (m, 4H), 17.99 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.78, 110.65, 126.81, 127.01, 127.50,,127.68, 128.50, 128.68, 129.25, 130.64, 131.47, 136.86, 137.23, 137.47, 137.95, 140.08, 190.56. HRMS (ESI) calcd for $C_{30}H_{24}NaO_2$ $[M+Na]^+$: 439.1669; found: 439.1670.

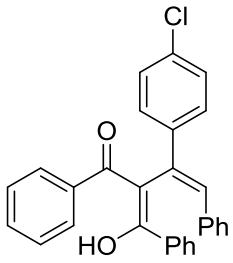


3e

(*2Z,3Z*)-2-(hydroxy(phenyl)methylene)-1,4-diphenyl-3-(p-tolyl)but-3-en-1-one

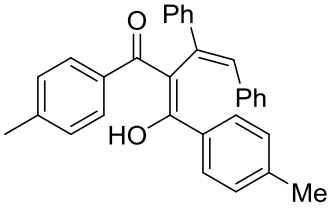
(3e) : Yellow solid, obtained in 3.0 h and purified by chromatography on silica gel

(petroleum ether/ethyl acetate = 10:1), 95.9 mg (74% yield); mp 172-173°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.75 (s, 3H), 6.56 (s, 1H), 6.72 (d, J = 7.2 Hz, 2H), 7.07-7.18 (m, 9H),7.20-7.25 (m, 2H), 7.34 (d, J = 6.4 Hz, 2H), 7.40 (d, J = 4.8 Hz, 4H), 17.97 (d, J = 6.4 Hz,1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.10, 110.66, 113.85, 126.90, 127.47, 127.70, 128.11, 128.51, 128.63, 130.63, 130.68, 135.50, 136.46, 137.23, 138.02, 159.38, 190.55. HRMS (ESI) calcd for $C_{30}H_{24}NaO_3$ $[M+Na]^+$: 455.1618; found: 455.1625.



3f

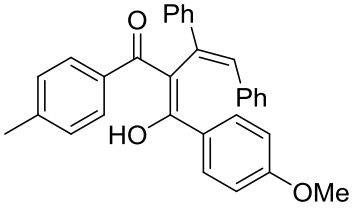
(*2Z,3Z*)-3-(4-chlorophenyl)-2-(hydroxy(phenyl)methylene)-1,4-diphenylbut-3-en-1-one (3f) :Yellow solid, obtained in 1.0 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 20:1), 82.2 mg (63% yield); mp 153-154°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.62 (s, 1H), 7.05-7.18 (m, 11H), 7.23 (d, J = 7.2 Hz, 2H), 7.30-7.37 (m, 6H), 17.95 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 110.21, 127.37, 127.42, 127.81, 128.05, 128.61, 128.69, 128.73, 130.83, 132.68, 133.32, 135.92, 137.03, 137.53, 141.50, 190.67. HRMS (ESI) calcd for $C_{29}H_{21}ClNaO_2$ $[M+Na]^+$: 459.1122; found: 459.1117.



3g

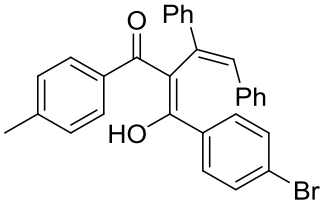
(*2Z,3Z*)-2-(hydroxy(p-tolyl)methylene)-3,4-diphenyl-1-(p-tolyl)but-3-en-1-one (3g) :Yellow solid, obtained in 3.0 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 20:1), 103.9 mg (80% yield); mp 163-164°C. ^{1}H

NMR (400 MHz, $CDCl_3$) δ 2.23 (s, 6H), 6.68 (s, 1H), 6.82-6.90 (m, 4H), 7.06-7.21 (m, 8H), 7.32 (d, J = 6.0 Hz, 4H), 7.43 (d, J = 6.8 Hz, 2H), 18.12 (d, J = 5.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.14, 110.22, 126.96, 127.11, 127.53, 127.62, 128.37, 128.45, 128.74, 132.12, 134.50, 137.29, 137.92, 141.02, 143.03, 190.35. HRMS (ESI) calcd for $C_{31}H_{26}NaO_2$ $[M+Na]^+$: 453.1825; found: 458.1831.



3h

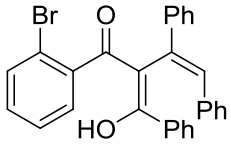
(*2Z,3Z*)-2-(hydroxy(4-methoxyphenyl)methylene)-3,4-diphenyl-1-(p-tolyl)but-3-en-1-one (3h) :Yellow solid, obtained in 3.0 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1), 88.7 mg (66% yield); mp 168-169^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.23 (s, 3H), 3.73 (s, 3H), 6.60 (d, J = 8.8 Hz, 2H), 6.70 (s, 1H), 6.87 (d, J = 8.0 Hz, 2H), 7.08-7.22 (m, 8H), 7.28 (d, J = 7.6 Hz, 2H), 7.40-7.50 (m, 4H), 18.19 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.13, 55.11, 109.92, 113.01, 126.93, 127.12, 127.54, 127.59, 128.34, 128.45, 128.53, 128.71, 129.75, 129.85, 132.12, 134.55, 137.47, 137.92, 140.84, 143.00, 161.87, 189.75, 189.92. HRMS (ESI) calcd for $C_{31}H_{26}NaO_3$ $[M+Na]^+$: 469.1774; found: 469.1782.



3i

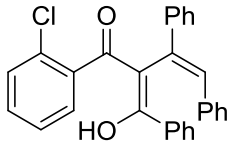
(*2Z,3Z*)-2-((4-bromophenyl)(hydroxy)methylene)-3,4-diphenyl-1-(p-tolyl)but-3-en-1-one (3i) :Yellow solid, obtained in 1.0 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 20:1), 141.4 mg (95% yield); mp 169-170^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.23 (s, 3H), 6.68 (s, 1H), 6.90 (d, J = 7.6 Hz, 2H),

7.08-7.25 (m, 12H), 7.35-7.45 (m, 4H), 17.96 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.17, 110.39, 124.97, 126.85, 127.30, 127,78, 128.52, 128.59, 128.63, 128.71, 129.00, 130.86, 132.35, 134.12, 136.18, 136.89, 137.71, 141.57, 142.69, 189.21, 190.55 . HRMS (ESI) calcd for $C_{30}H_{23}BrNaO_2$ $[M+Na]^+$: 517.0774; found: 517.0788.



3j

(*2Z,3Z*)-1-(2-bromophenyl)-2-(hydroxy(phenyl)methylene)-3,4-diphenylbut-3-en-1-one (3j): Yellow solid, obtained in 1.0 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 20:1), 125.2 mg (87% yield); mp 164-165^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.49 (s, 1H), 6.96-7.01 (m, 1H), 7.03--7.08 (m, 3H), 7.11-7.24 (m, 11H), 7.31 (d, J = 7.2 Hz, 2H), 7.38 (d, J = 7.6 Hz, 2H), 17.54 (s,1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 111.66, 120.33, 126.32, 126.97, 127.27, 127.51, 127.65, 127.73, 128.29, 128.42, 128.68, 128.73, 130.61, 131.09, 132.37, 133.18, 136.18, 136.38, 137.63, 138.10, 142.93, 189.80, 191.18. HRMS (ESI) calcd for $C_{29}H_{21}BrNaO_2$ $[M+Na]^+$: 503.0617; found: 503.0615.

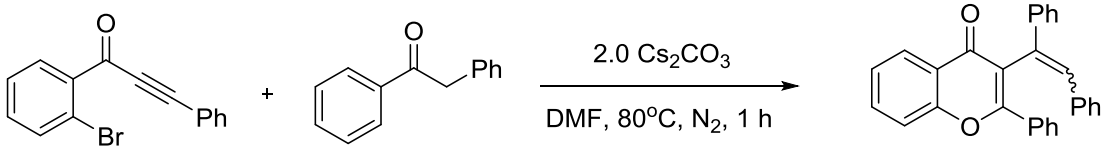


3k

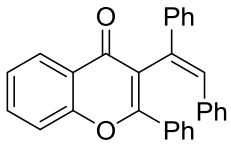
(*2Z,3Z*)-1-(2-chlorophenyl)-2-(hydroxy(phenyl)methylene)-3,4-diphenylbut-3-en-1-one (3k): Yellow solid, obtained in 1.0 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 20:1), 115.7 mg (88% yield); mp 158-159^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.50 (s, 1H), 6.93-7.07 (m, 5H), 7.10-7.24 (m, 10H), 7.30 (d, J = 6.8 Hz, 2H), 7.38 (d, J = 7.6 Hz, 2H), 17.55 (s,1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 111.97, 125.78, 126.90, 127.28, 127.52, 127.67, 127.73, 128.23, 128.40, 128.66, 128.75, 129.86, 130.51, 131.10, 131.56, 132.33, 136.28, 137.65, 143.02,

190.03, 190.37. HRMS (ESI) calcd for $C_{29}H_{21}ClNaO_2$ $[M+Na]^+$: 459.1122; found: 459.1118.

5 Synthesis of Chromones 5

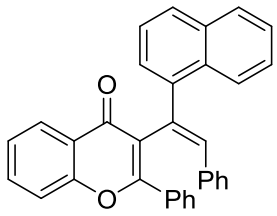


In a Schlenk tube acetyenic ketone **1a** (0.30 mmol, 85.5 mg), Cs_2CO_3 (0.6 mmol, 195.5 mg), DMF (3.0 mL) and **2a** (0.30 mmol, 58.9 mg) was stirred at room temperature under N_2. After the reaction was completed as monitored by thin-layer chromatography, the reaction mixture was then quenched by water, and the water layers were extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) afforded desired compound **5a**.



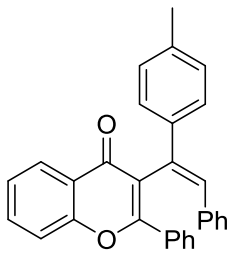
5a

(*Z*)-3-(1,2-diphenylvinyl)-2-phenyl-4H-chromen-4-one (5a): White solid, obtained in 1.0 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 5:1), 75.0 mg (94% yield, *Z/E* = 9:1); mp 187-188°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 (d, *J* = 4.0 Hz, 2H), 6.08-7.10 (m, 4H), 7.12-7.20 (m, 2H), 7.23-7.36 (m, 6H), 7.40-7.54 (m, 4H), 7.67-7.72 (m, 1H), 8.26 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 118.18, 121.25, 123.18, 125.31, 126.29, 126.65, 127.04, 127.85, 128.05 128.09, 128.23, 128.42, 128.80, 130.34, 132.62, 133.17, 133.97, 134.52, 137.55, 141.54, 156.56, 162.94, 178.18. HRMS (ESI) calcd for $C_{29}H_{20}NaO_2$ $[M+Na]^+$: 423.1356; found: 423.1352.



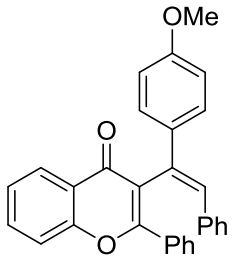
5b

(*Z*)-3-(1-(naphthalen-1-yl)-2-phenylvinyl)-2-phenyl-4H-chromen-4-one (5b): White solid, obtained in 2.0 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 5:1), 120.7 mg (89% yield, *Z/E* = 9:1); mp 170-171^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94 (d, J = 4.4 Hz, 2H), 7.01-7.10 (m, 3H), 7.12-7.17 (m, 3H), 7.24-7.31 (m, 1H), 7.35 (d, J = 7.6 Hz, 2H), 7.40-7.47 (m, 3H), 7.53 (d, J = 8.4 Hz, 1H), 7.70-7.84 (m, 5H), 7.90 (s, 1H), 8.28 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 118.25, 121.24, 123.24,124.56, 125.19, 125.37, 126.06. 126.28, 126.75, 127.10, 127.76, 128.09, 128.27, 128.49, 128.56, 130.41, 133.19, 133.32, 133.83, 134.04, 134.59, 137.60, 138.90, 156.65, 163.08, 178.30 HRMS (ESI) calcd for $C_{33}H_{22}NaO_2$ $[M+Na]^+$: 473.1512; found: 473.1497.



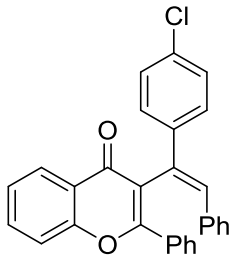
5c

(*Z*)-2-phenyl-3-(2-phenyl-1-(p-tolyl)vinyl)-4H-chromen-4-one (5c): White solid, obtained in 2.0 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 5:1), 122.2 mg (98% yield, *Z/E* = 9:1); mp 182-183^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 3H), 6.87 (d, J = 5.2 Hz, 2H), 6.98 (s, 1H), 7.00-7.06 (m, 3H), 7.10-7.19 (m, 4H), 7.24-7.32 (m, 3H), 7.40-7.51 (m, 4H), 7.67-7.72 (m, 1H), 8.26 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.90, 118.17, 121.22, 123.19, 125.27, 126.14, 126.67, 126.84, 128.02, 128.09, 128.17, 128.41, 129.61, 130.28, 131.70, 133.20, 133.94, 134.51, 137.65, 137.76, 138.64, 156.56, 162.86, 178.34. HRMS (ESI) calcd for $C_{30}H_{22}NaO_2$ $[M+Na]^+$: 437.1512; found: 437.1495.



5d

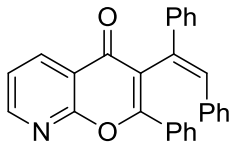
(*Z*)-3-(1-(4-methoxyphenyl)-2-phenylvinyl)-2-phenyl-4H-chromen-4-one (5d): White solid, obtained in 1.0 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 5:1), 110.7 mg (86% yield, *Z/E* = 12:1); mp 177-178^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.78 (s, 3H), 6.83-6.95 (m, 4H), 6.94 (d, *J* = 2.4 Hz, 1H), 7.00-7.05 (m, 3H), 7.15-7.20 (m, 2H), 7.27-7.33 (m, 3H), 7.39-7.50 (m, 4H), 7.66-7.71 (m, 1H), 8.27 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.07, 114.14, 118.13, 121.23, 123.11, 125.24, 126.58, 126.73, 127.40, 127.98, 128.02, 128.13, 128.31, 130.28, 130.78, 133.13, 133.92, 133.97, 137.67, 156.49, 159.59, 162.76, 178.24. HRMS (ESI) calcd for $C_{30}H_{22}NaO_3$ $[M+Na]^+$: 453.1461; found: 453.1466.



5e

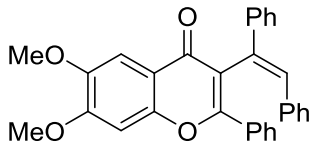
(*Z*)-3-(1-(4-chlorophenyl)-2-phenylvinyl)-2-phenyl-4H-chromen-4-one (5e): White solid, obtained in 1.0 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 5:1), 108.9 mg (83% yield, *Z/E* = 9:1); mp 186-187^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.85-7.10 (m, 6H), 7.13-7.36 (m, 7H), 7.38-7.57 (m, 4H), 7.64-7.75 (m, 1H), 8.26 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 118.18, 120.78, 123.05, 125.41, 126.54, 127.24, 127.51, 127.96, 128.09, 128.26, 128.37, 128.92, 130.47, 132.95, 133.01, 133.38, 133.55, 134.09, 137.19, 140.06, 156.50, 163.14, 178.04. HRMS (ESI) calcd for $C_{29}H_{19}ClNaO_2$ $[M+Na]^+$: 457.0966;

found: 457.0976.



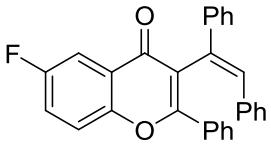
5f

(*Z*)-3-(1,2-diphenylvinyl)-2-phenyl-4H-pyrano[2,3-b]pyridin-4-one (5f): Yellow solid, obtained in 1.0 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 5:1), 100.1 mg (83% yield, *Z/E* = 14:1); mp 196-197^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 (d, J = 6.0 Hz, 2H), 7.01-7.10 (m, 4H), 7.17-7.22 (m, 2H), 7.25-7.36 (m, 4H), 7.42-7.52 (m, 5H), 8.62 (dd, J_1 = 7.6, 1.6 Hz, 1H), 8.72-8.75 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 117.83, 121.69, 122.36, 126.25, 127.27, 128.02, 128.12, 128.27, 128.34, 128.36, 128.88, 130.79, 132.43, 132.99, 133.91, 137.34, 137.42, 141.12, 153.78, 160.96, 163.56, 178.58. HRMS (ESI) calcd for $C_{28}H_{19}NNaO_2$ $[M+Na]^+$: 424.1308; found: 424.1317.



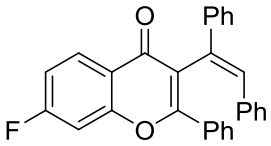
5g

(*Z*)-3-(1,2-diphenylvinyl)-6,7-dimethoxy-2-phenyl-4H-chromen-4-one (5g): White solid, obtained in 2.0 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 2:1), 106.6 mg (77% yield, *Z/E* = 8:1); mp 215-216^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.97 (s, 3H), 3.98 (s, 3H), 6.88-6.98 (m, 3H), 7.02 (s,1H), 7.05-7.11 (m, 3H), 7.14-7.19 (m, 2H), 7.24-7.36 (m, 6H), 7.52 (d, J = 7.6 Hz, 2H), 7.60 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.12, 56.30, 99.66, 105.05, 116.52, 120.62, 126.25, 126.95, 127.74, 127.96, 127.98, 128.18, 128.40, 128.72, 130.10, 132.41, 133.25, 134.63, 137.60, 141.61, 147.88, 152.58, 154.82, 162.20, 177.29. HRMS (ESI) calcd for $C_{31}H_{24}NaO_4$ $[M+Na]^+$: 483.1576; found: 483.1569.



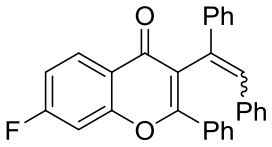
5h

(*Z*)-3-(1,2-diphenylvinyl)-6-fluoro-2-phenyl-4H-chromen-4-one (5h): White solid, obtained in 4.0 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 5:1), 109.6 mg (87% yield, *Z/E* = 9:1); mp 181-182^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89 (d, J = 6.0 Hz, 2H), 6.98-7.10 (m, 4H), 7.13-7.20 (m, 2H), 7.22-7.35 (m, 6H), 7.38-7.44 (m, 1H), 7.45-7.55 (m,3H), 7.88 (dd, J = 8.0, 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 111.25 ($J_{C\text{-}F}$ = 23.6 Hz), 120.33 ($J_{C\text{-}F}$ = 8.0 Hz), 120.58, 122.19 ($J_{C\text{-}F}$ = 25.6 Hz), 124.23 ($J_{C\text{-}F}$ = 7.3 Hz), 126.22, 127.10, 127.92, 128.05, 128.08, 128.23, 128.34, 128.82, 130.50, 132.76, 132.87, 134.22, 137.43, 141.30, 152.72, 159.86 ($J_{C\text{-}F}$ = 246.6 Hz), 163.25, 177.45. HRMS (ESI) calcd for $C_{29}H_{19}FNaO_2$ $[M+Na]^+$: 441.1261; found: 441.1264.



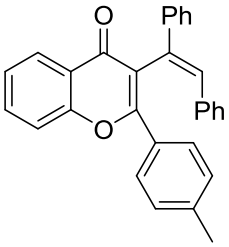
5i

(*Z*)-3-(1,2-diphenylvinyl)-7-fluoro-2-phenyl-4H-chromen-4-one (5i): White solid, obtained in 2.0 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 5:1), 118.1 mg (94% yield, *Z/E* = 6:1); mp 152-153^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (d, J = 5.2 Hz, 2H), 6.98--7.08 (m, 4H), 7.13-7.20 (m, 4H), 7.22-7.35 (m, 6H), 7.51 (d, J = 6.8 Hz, 2H), 8.24-8.29 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 104.71 ($J_{C\text{-}F}$ = 25.2 Hz), 114.11 ($J_{C\text{-}F}$ = 22.8 Hz), 120.00, 121.33, 126.24, 127.12, 127.93, 128.03, 128.10, 128.26, 128.37, 128.84, 129.25 ($J_{C\text{-}F}$ = 10.6 Hz), 130.50, 132.74, 132.79, 134.21, 137.46, 141.35, 157.50 ($J_{C\text{-}F}$ = 13.4 Hz), 163.15, 166.11 ($J_{C\text{-}F}$ = 254.8 Hz), 177.27. HRMS (ESI) calcd for $C_{29}H_{19}FNaO_2$ $[M+Na]^+$: 441.1261; found: 441.1271.



5i

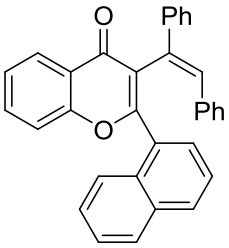
^{1}H NMR (400 MHz, $CDCl_3$) major isomers: δ 6.90 (d, J = 5.6 Hz, 2H), 7.02--7.07 (m, 4H), 7.12-7.17 (m, 4H), 7.22-7.32 (m, 6H), 7.51 (d, J = 7.6 Hz, 2H), 8.21-8.29 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) major isomers: δ 104.69 ($J_{C\text{-}F}$ = 25.2 Hz), 114.08 ($J_{C\text{-}F}$ = 22.8 Hz), 119.97, 121.30, 126.22, 127.10, 127.91, 128.01, 128.08, 128.23, 128.34, 128.81, 129.22 ($J_{C\text{-}F}$ = 10.7 Hz), 130.48, 132.71, 132.76, 134.19, 137.44, 141.32, 157.48 ($J_{C\text{-}F}$ = 13.5 Hz), 163.13, 166.08 ($J_{C\text{-}F}$ = 254.9 Hz), 177.25; ^{1}H NMR (400 MHz, $CDCl_3$) minor isomer: δ 6.61 (s, 1H), 7.81 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) major isomers: δ 104.59 ($J_{C\text{-}F}$ = 25.2 Hz), 113.97 ($J_{C\text{-}F}$ = 22.9 Hz), 127.23, 127.45, 128.15, 128.46, 129.06, 129.33, 129.37, 130.67, 133.23, 133.56, 134.56, 137.09, 139.32, 163.13, 176.94; other peaks are overlapped with the signals of the major isomer; HRMS (ESI) calcd for $C_{29}H_{19}FNaO_2$ $[M+Na]^+$: 441.1261; found: 441.1271.



5j

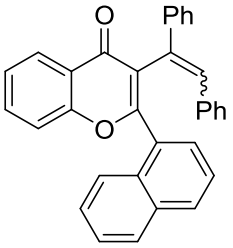
(*Z*)-3-(1,2-diphenylvinyl)-2-(p-tolyl)-4H-chromen-4-one (5j): White solid, obtained in 2.0 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 5:1), 114.8 mg (92% yield, *Z/E* = 14:1); mp 187-188 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.30 (s, 3H), 6.93-7.01 (m, 4H), 7.02-7.10 (m, 4H), 7.22-7.34 (m, 5H), 7.38-7.43 (m, 1H), 7.44-7.53 (m, 3H), 7.66-7.70 (m, 1H), 8.25 (m, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.12, 118.13, 120.90, 123.13, 125.20, 126.30, 126.61, 127.04, 127.78, 128.05, 128.21, 128.41, 128.75, 128.77, 130.28, 132.46, 133.88,

134.53, 137.58, 140.77, 141.55, 156.50, 163.00, 178.09. HRMS (ESI) calcd for $C_{30}H_{22}NaO_2$ $[M+Na]^+$: 437.1512; found: 437.1519.



5k

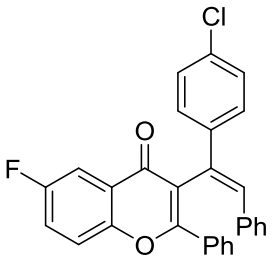
(*Z*)-3-(1,2-diphenylvinyl)-2-(naphthalen-1-yl)-4H-chromen-4-one (5k): White solid, obtained in 2.0 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 5:1), 115.8 mg (86% yield, *Z/E* = 7:1); mp: 182-183 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 6.84 (d, J = 7.2 Hz, 2H), 6.94-7.07 (m, 4H), 7.25-7.36 (m, 3H), 7.43-7.79 (m, 12H), 8.29 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 118.23, 121.50, 123.24, 124.76, 125.36, 126.36, 126.49, 126.72, 127.06, 127.61, 127.76, 127.93, 128.22, 128.36, 128.74, 128.85, 128.98, 130.63, 132.65, 132.89, 133.94, 134.03, 134.66, 137.62, 141.53, 156.67, 162.93, 178.33. HRMS (ESI) calcd for $C_{33}H_{22}NaO_2$ $[M+Na]^+$: 473.1512; found: 473.1516.



5k

^1H NMR (400 MHz, $CDCl_3$) major isomer: δ 6.84 (d, J = 7.2 Hz, 2H), 6.93-7.12 (m, 4H), 7.20-7.31 (m, 3H), 7.40-7.82 (m, 12H), 8.29 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) major isomer δ 118.16, 121.45, 123.16, 124.89, 125.30, 126.30, 126.44, 126.61, 127.01, 127.55, 127.69, 127.86, 128.15, 128.29, 128.69, 128.78, 128.90, 130.55, 132.57, 132.81, 133.87, 133.97, 134.60, 137.55, 141.46, 156.59, 162.86, 178.26; ^1H NMR (400 MHz, $CDCl_3$) minor isomer: δ 6.66 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) minor isomer: δ 118.08, 125.21, 125.65, 126.82, 127.13, 127.25,

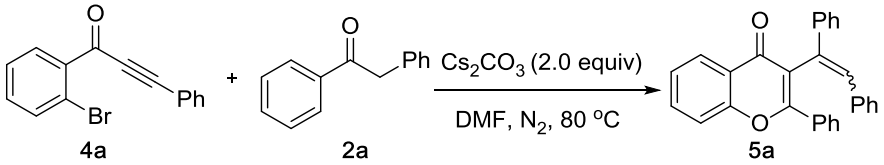
127.43, 127.98, 128.04, 129.06, 129.34, 129.46, 129.65, 129.82, 130.85, 134.50; other peaks are overlapped with the signals of the major isomer; HRMS (ESI) calcd for $C_{33}H_{22}NaO_2$ $[M+Na]^+$: 473.1512; found: 473.1516.



5l

(*Z*)-3-(1-(4-chlorophenyl)-2-phenylvinyl)-6-fluoro-2-phenyl-4H-chromen-4-one (5l): White solid, obtained in 4.0 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1), 104.8 mg (77% yield, *Z/E* = 9:1); mp 182-183^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89 (d, J = 6.8 Hz, 2H), 7.00 (s, 1H), 7.02--7.11 (m, 3H), 7.17-7.35 (m, 7H), 7.41-7.54 (m, 4H), 7.88 (dd, J = 8.0, 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 111.32 ($J_{C\text{-}F}$ = 23.7 Hz), 120.26, 120.39 ($J_{C\text{-}F}$ = 7.9 Hz), 122.36 ($J_{C\text{-}F}$ = 25.7 Hz), 124.25 ($J_{C\text{-}F}$ = 7.4 Hz), 127.38, 127.54, 128.03, 128.20, 128.35, 128.39, 129.03, 130.69, 132.79, 133.18, 133.26, 133.74, 137.19, 139.94, 152.77, 159.98 ($J_{C\text{-}F}$ = 246.9 Hz), 163.49, 177.38. HRMS (ESI) calcd for $C_{29}H_{18}ClFNaO_2$ $[M+Na]^+$: 475.0872; found: 475.0874.

Table S1 Screening of reation conditions for the formation of **5a** [a]



Entry	Solvent	Base	Temp. (°C)	Time (h)	Yileld [b](%)(*Z*/*E*)
1	DMF	Cs_2CO_3	100	1	94(10:1)
2	DMF	Cs_2CO_3	100	1	80(10:1) [c]
3	DMAc	Cs_2CO_3	100	1	95(7:1)
4	DMSO	Cs_2CO_3	100	1	86(5:1)
5	CH_3NO_2	Cs_2CO_3	100	24	trace
6	Tol	Cs_2CO_3	100	24	trace
7	DMF	Cs_2CO_3	100	1	84(8:1) [d]
8	DMF	Cs_2CO_3	100	2	77(14:1) [e]
9	DMF	Cs_2CO_3	120	1	91(7:1)
10	**DMF**	**Cs_2CO_3**	80	**1**	**94(9:1)**
11	DMF	Cs_2CO_3	50	20	80(9:1)

[a] Unless otherwise noted, reations were conducted on a 0.2 mmol scale with the ratio of **4a**:**2a** = 1:1 in 2.0 mL of solvent at 100 °C under N_2. [b] Isolated yields of two isomers. [c] Under air. [d] Using 3.0 equiv of Cs_2CO_3. [e] Using 1.0 equiv of Cs_2CO_3.

6 References

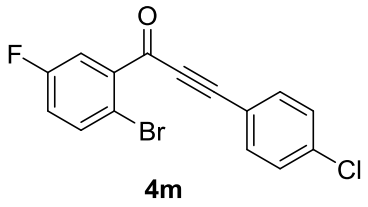
[1] H. Tan; H. Li; W. Ji; L. Wang. *Angew. Chem. Int. Ed.* **2015**, *54*, 8374.

[2] X. Cheng; Y. Zhou; F. Zhang; K. Zhu; Y. Liu; Y. Li. *Chem. Eur. J.* **2016**, *22*, 12655.

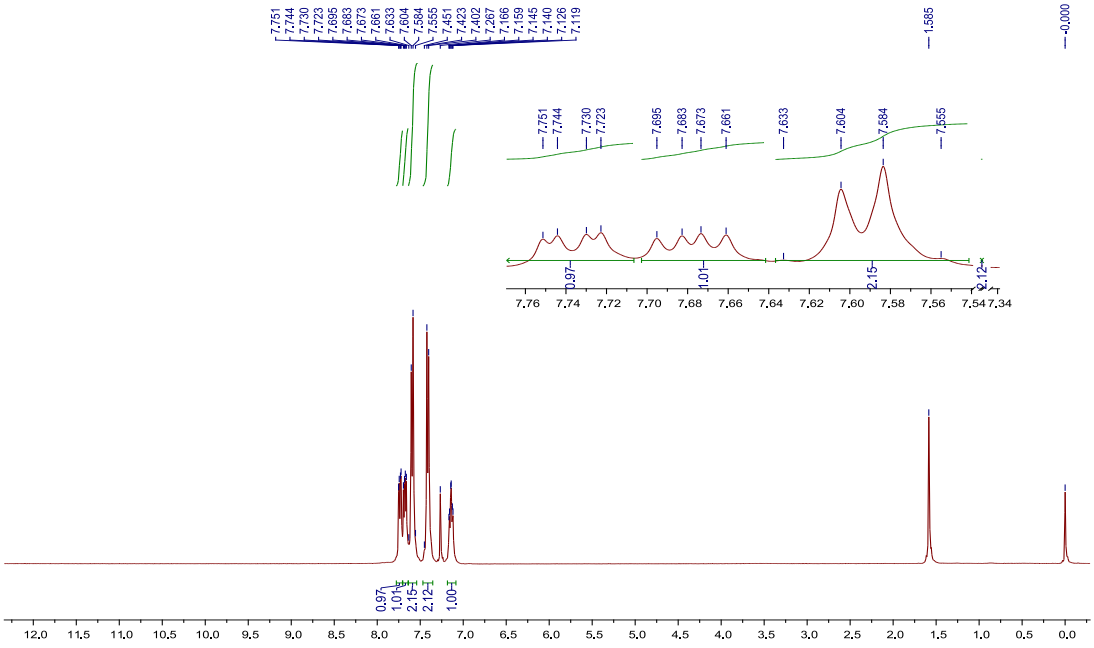
[3] X. Wang, X. Wang; M. Liu; J. Ding; J. Chen; H. Wu. *Synthesis.* **2013**, *45*, 2241.

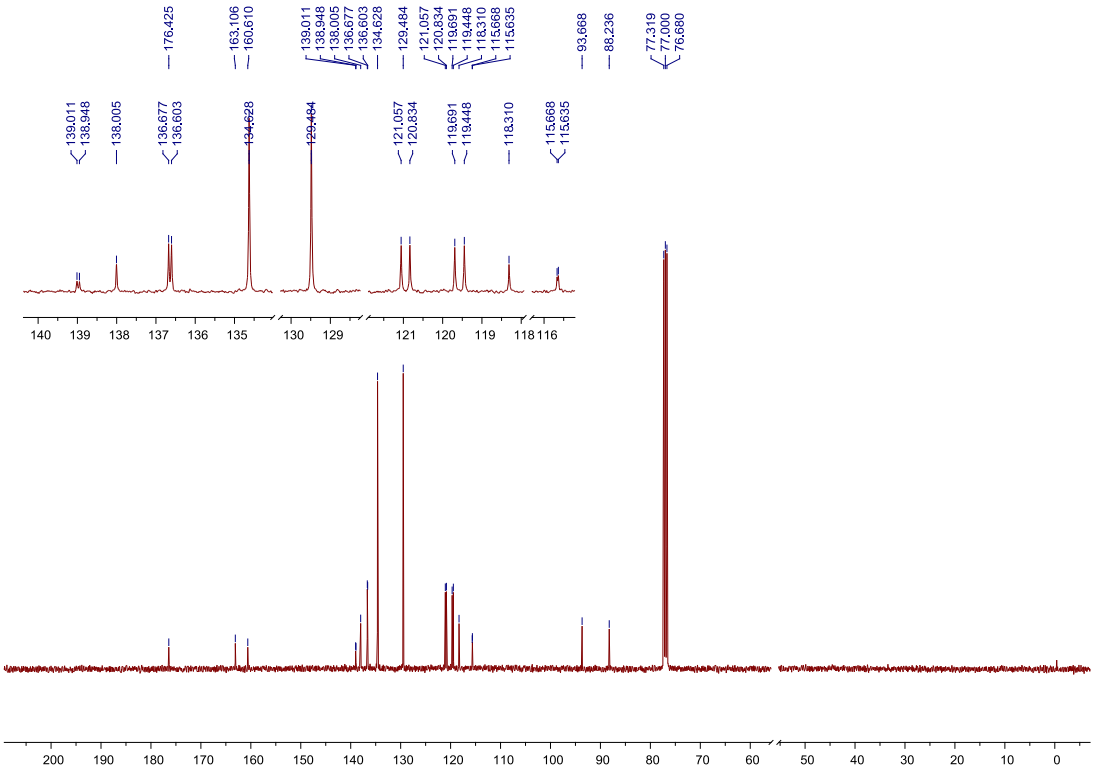
[4] Y. Wong; K. Parthasarathy ; C. Cheng. *Org. Lett.* **2012**, *12*, 1736.

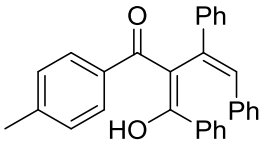
7 Copies of Spectra of New Products



4m



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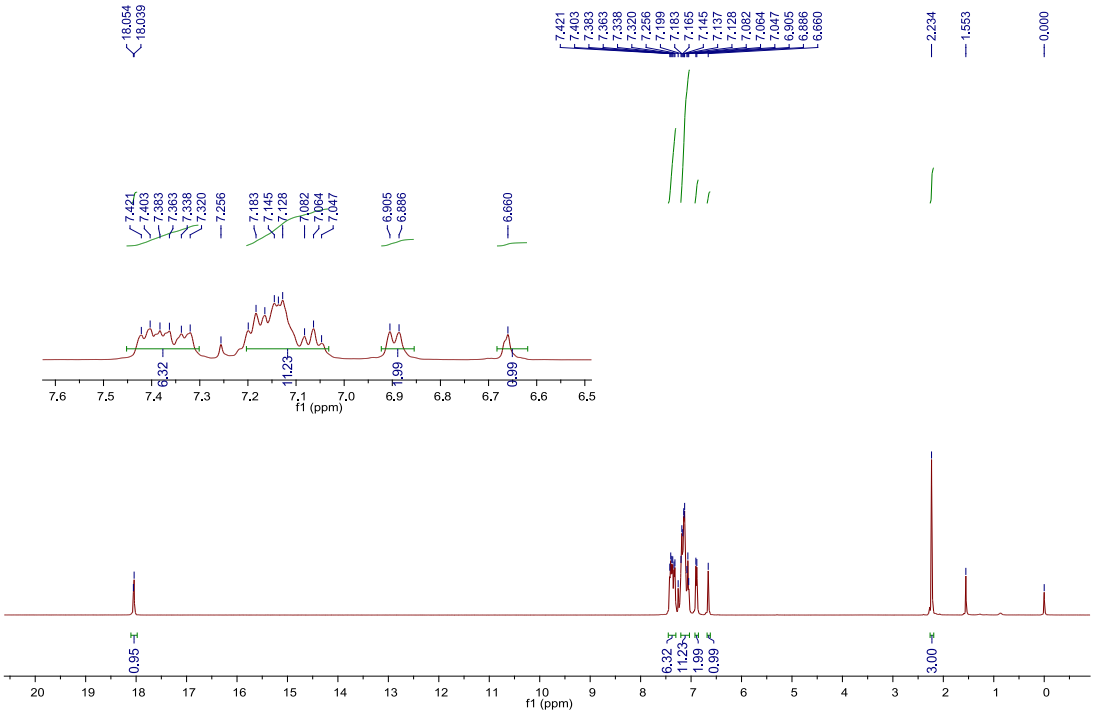
Ph
HO
Ph
Ph

3a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7.145
7.137
7.128
7.082
7.064
7.047
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2.234
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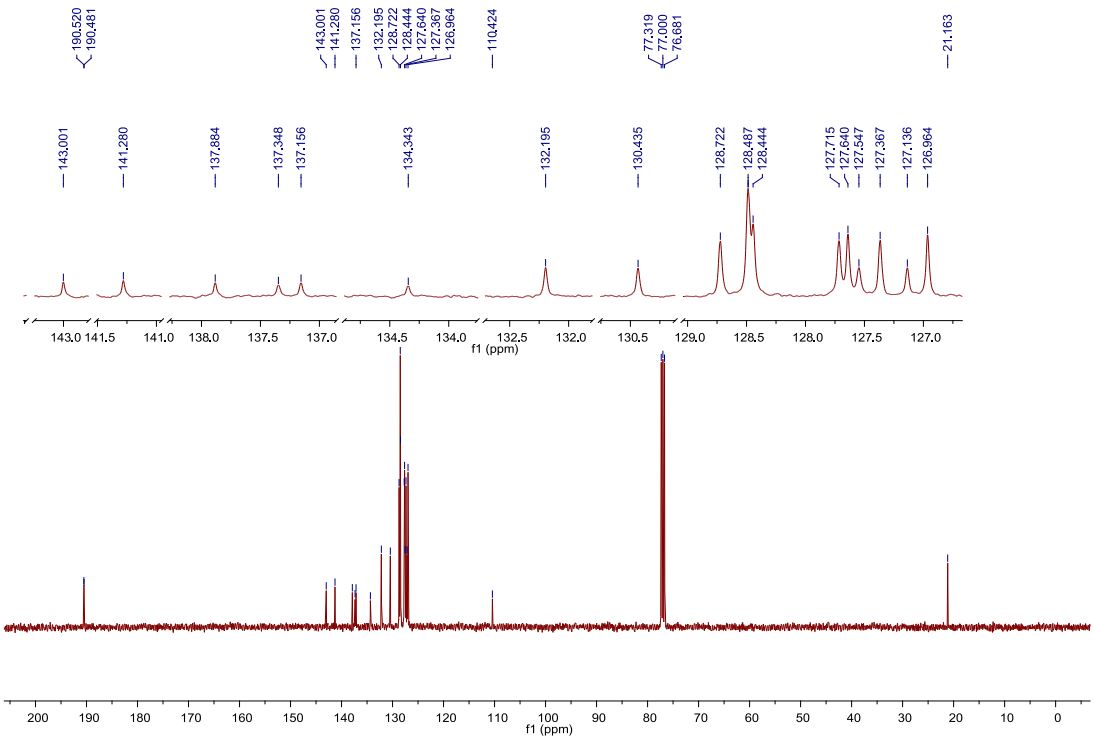
0.000
6.32
11.23
1.99
0.99
3.00
f1 (ppm)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127.367
126.964
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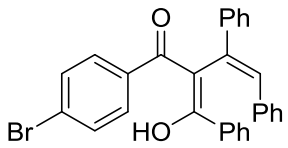
21.163
f1 (ppm)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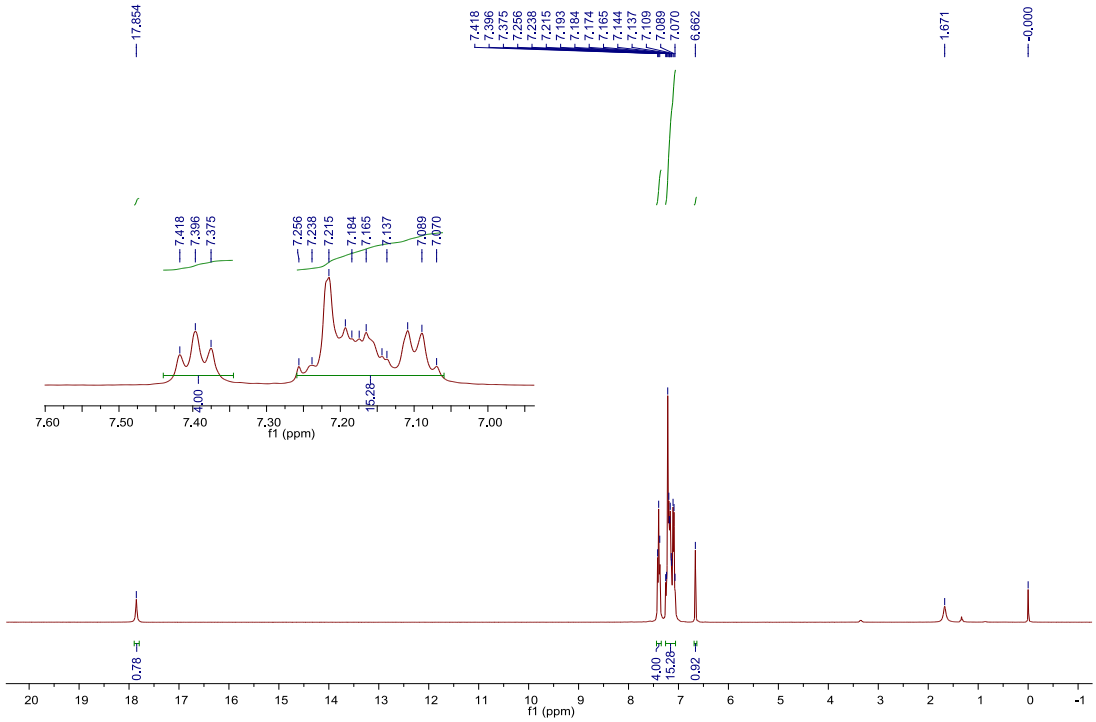
Ph
Br
HO
Ph

3b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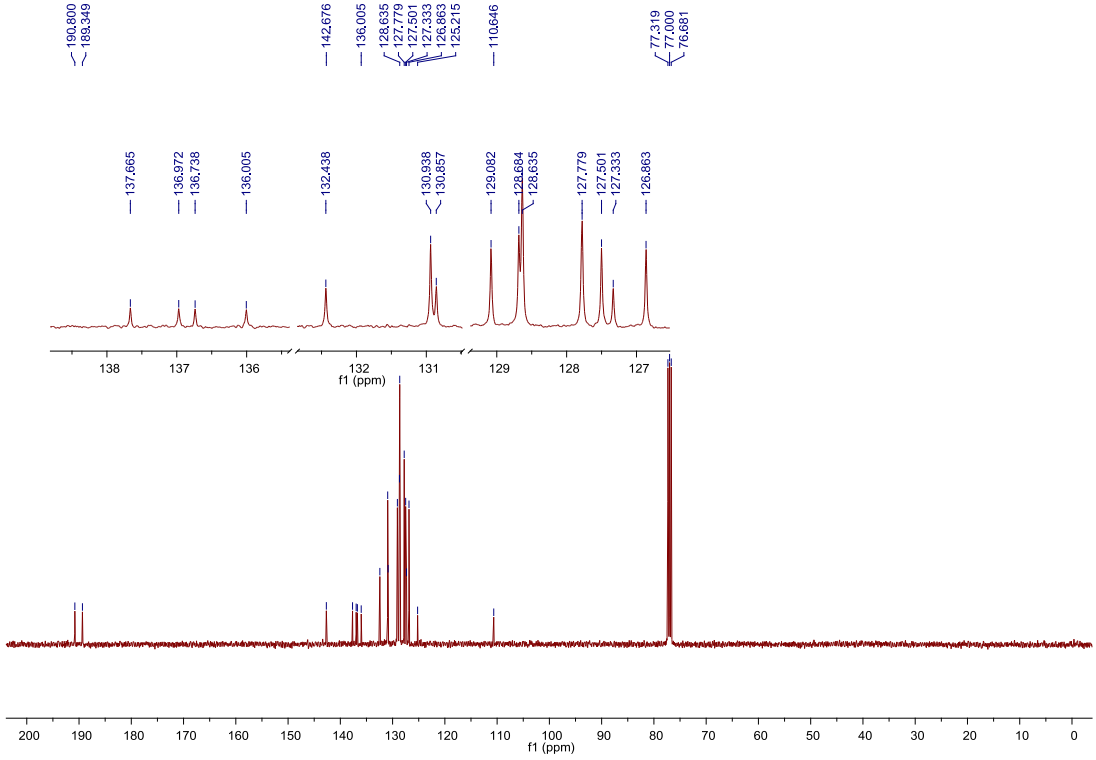
15.28
0.92
f1 (ppm)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125.215
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77.000
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136.972
136.738
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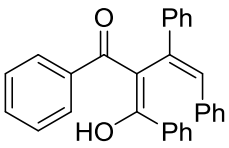
f1 (ppm)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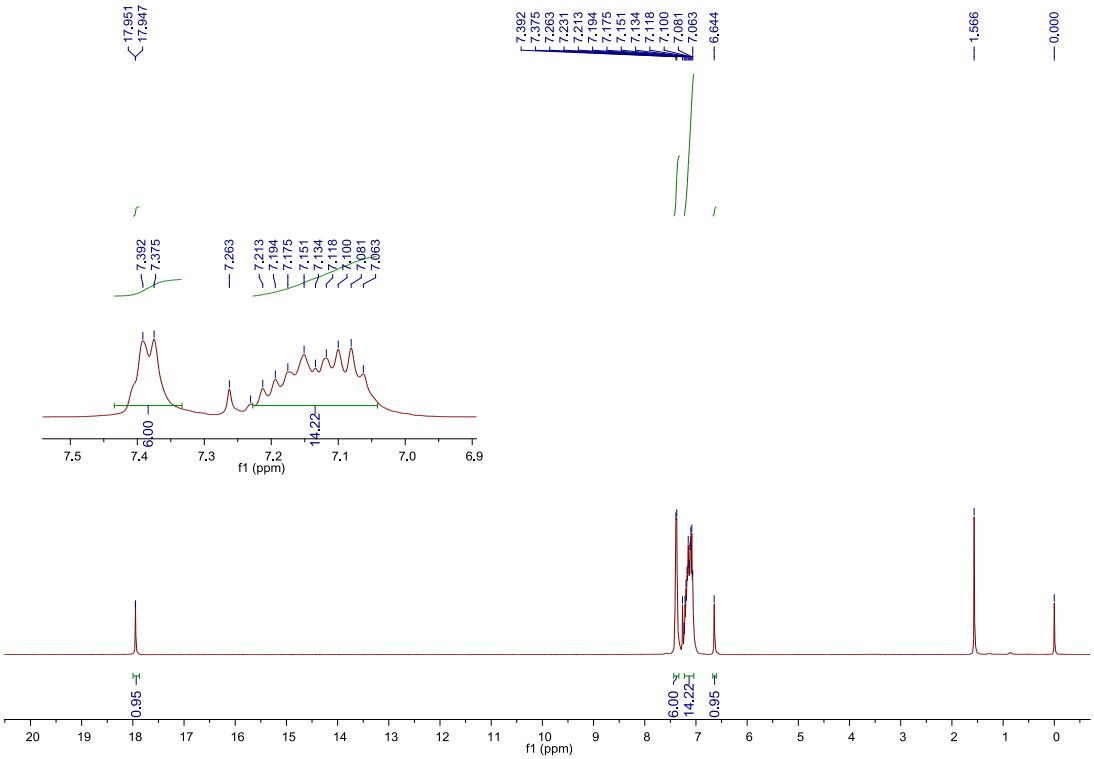
Ph
HO
Ph

3c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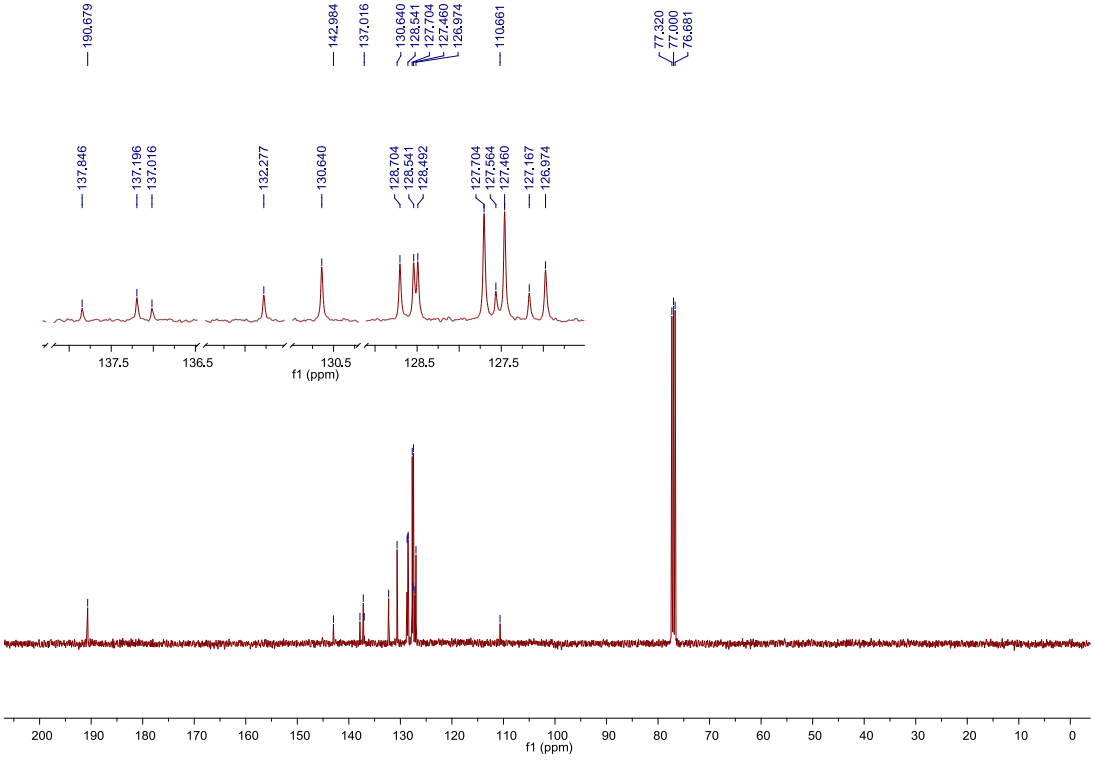
f1 (ppm)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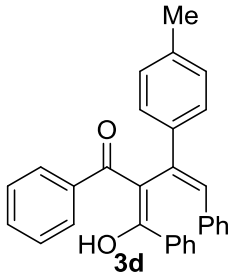
f1 (ppm)
f1 (ppm)


Me
O
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Ph
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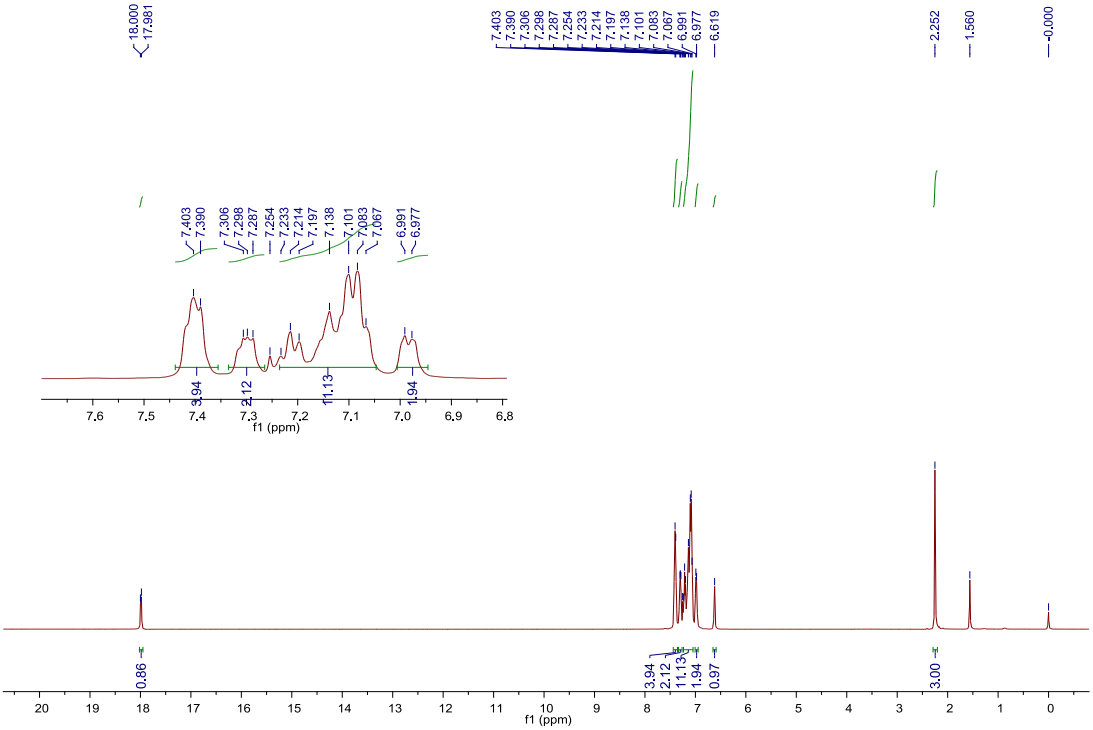
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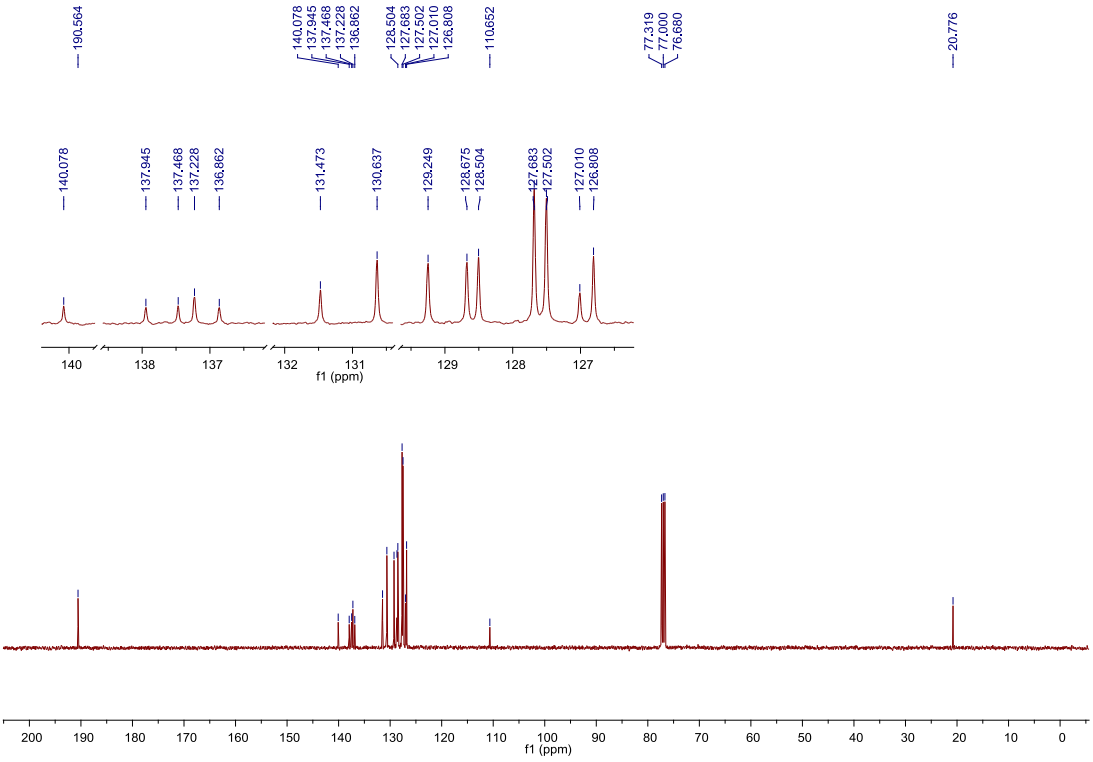
f1 (ppm)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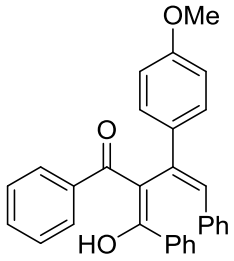
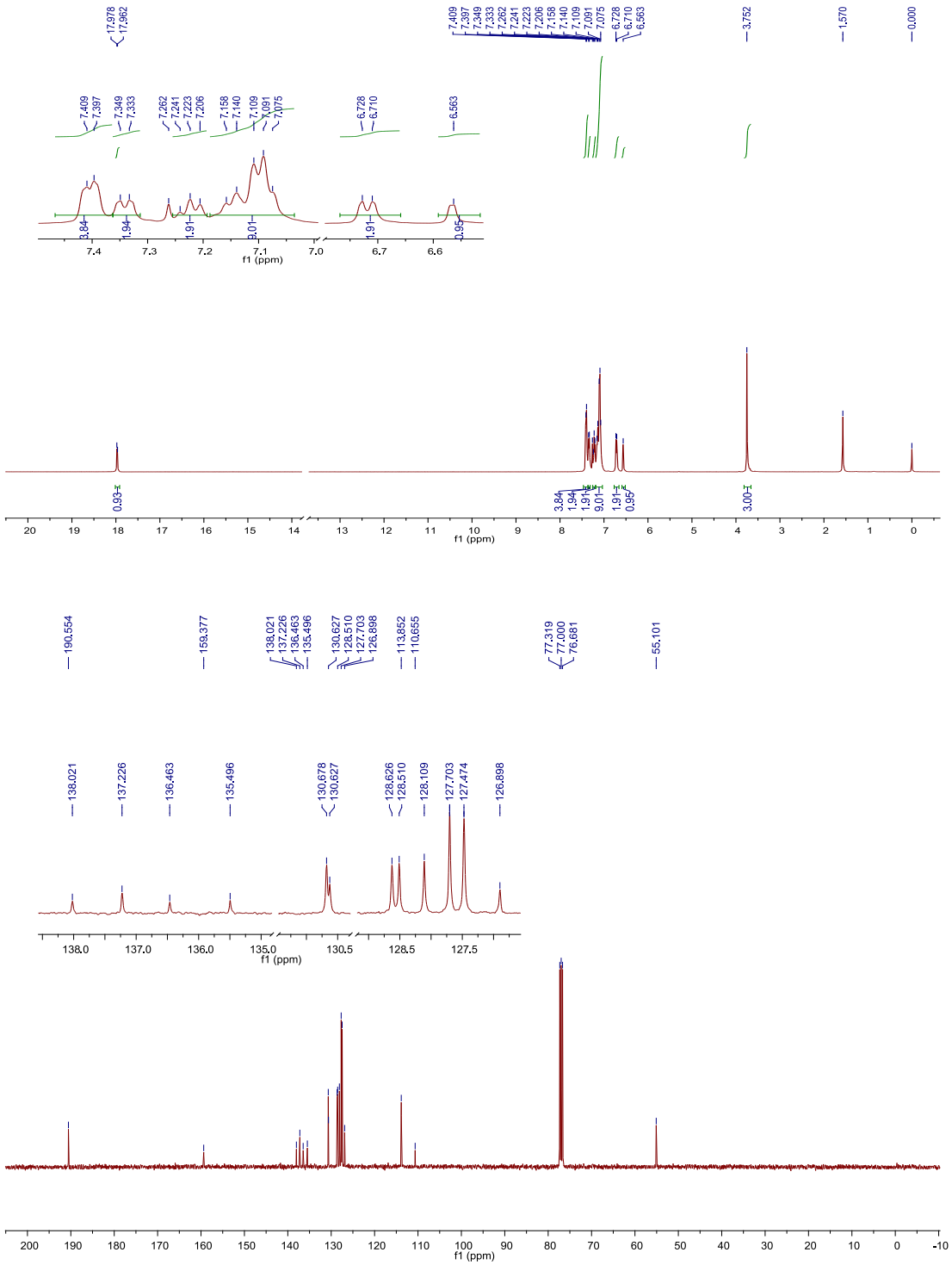
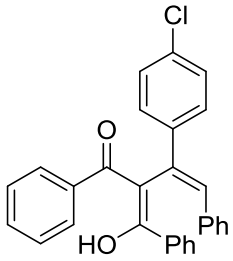


3e

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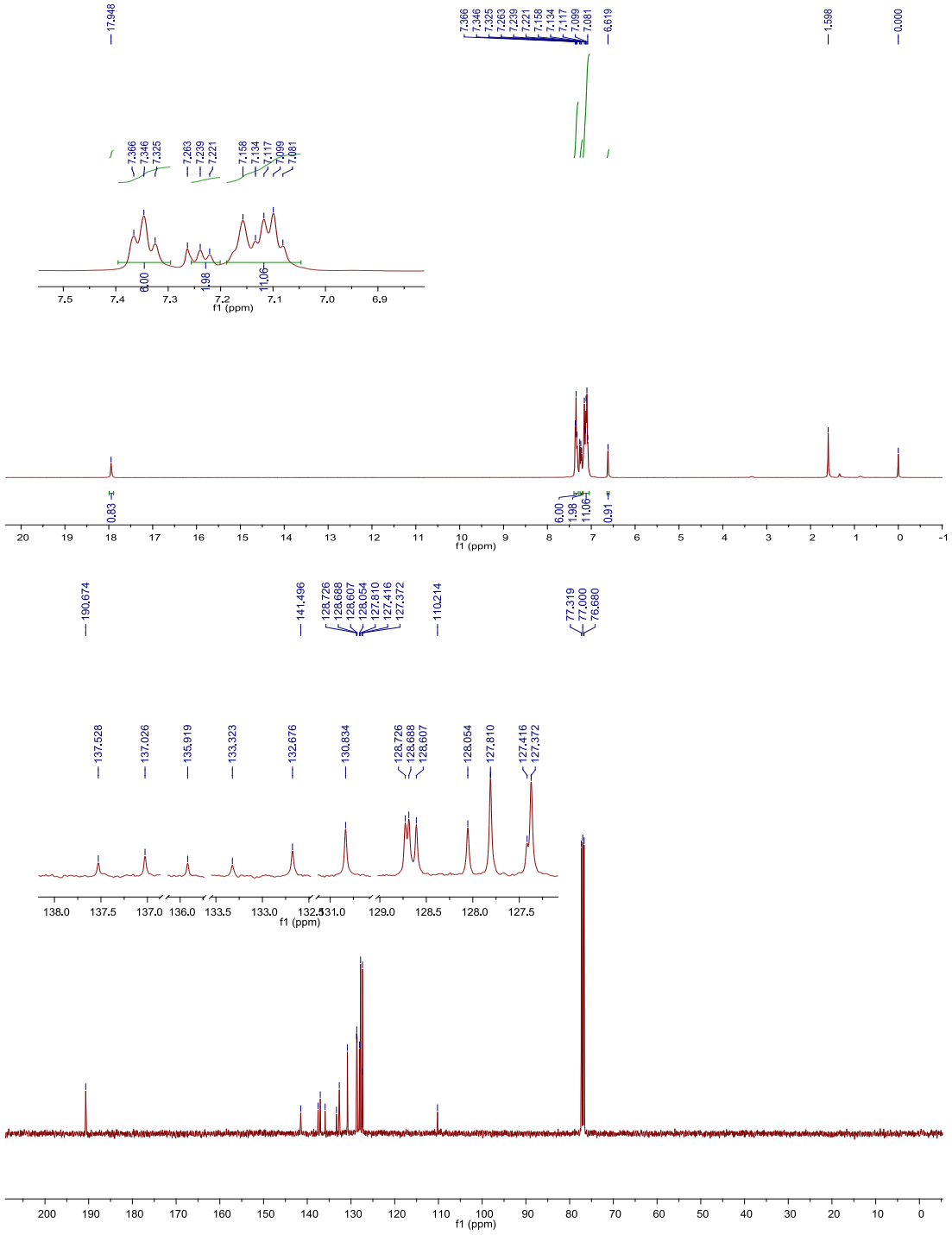
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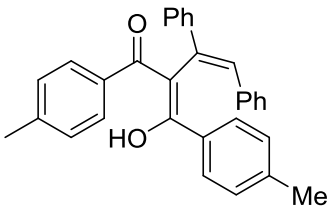
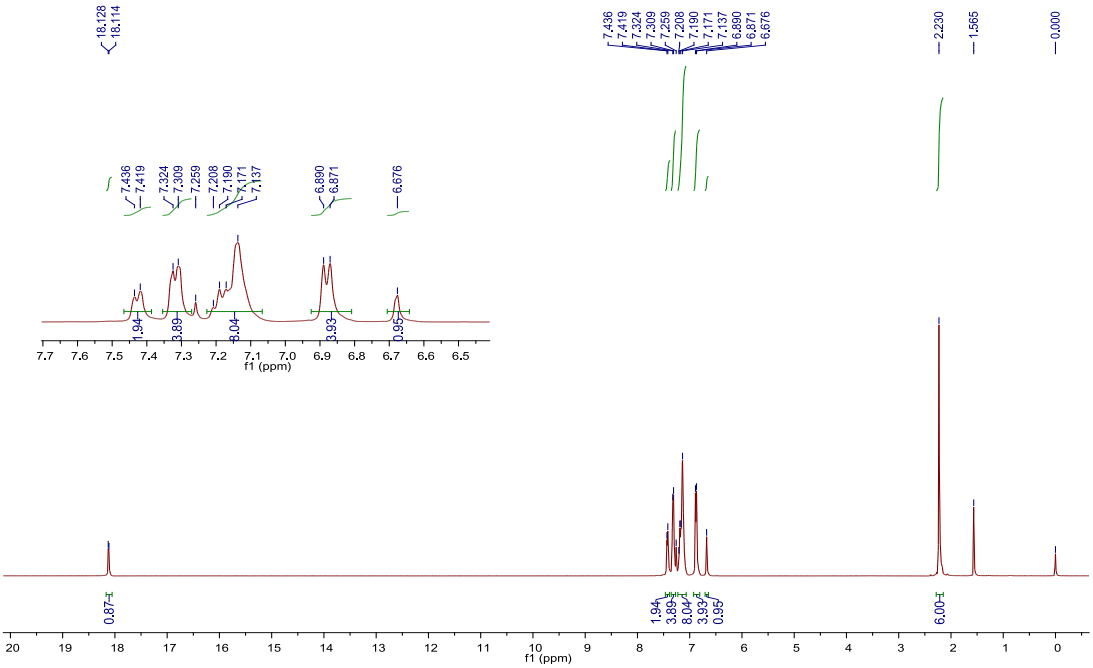
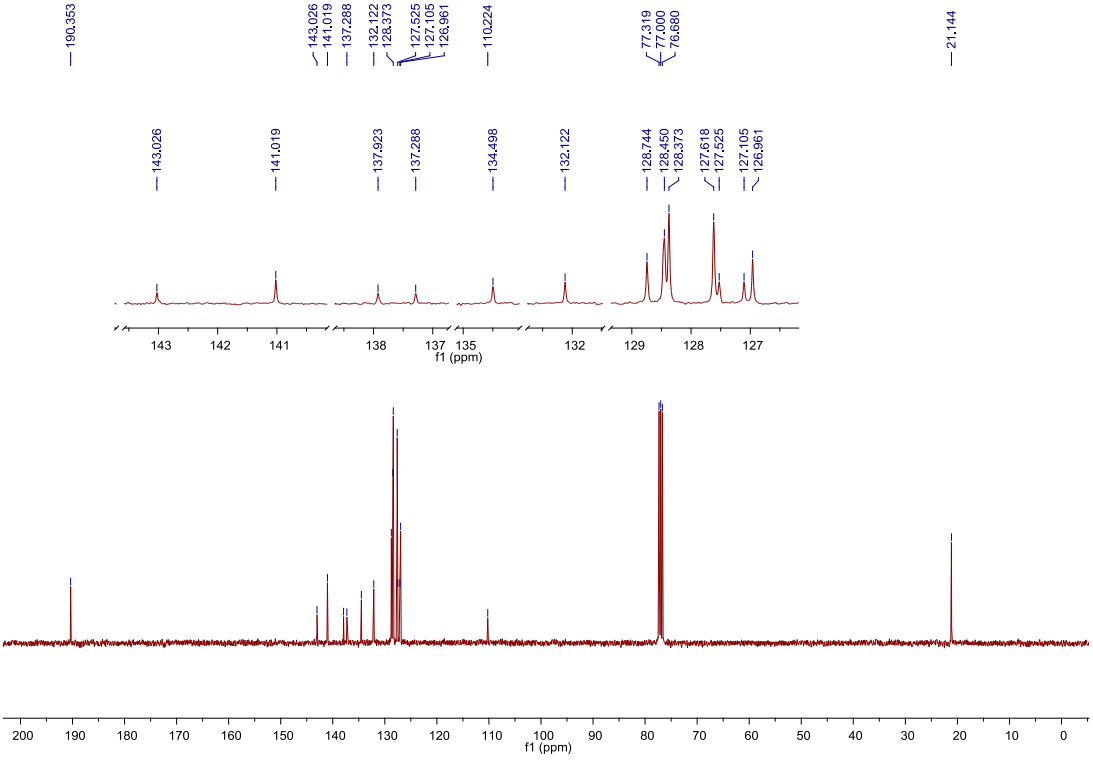
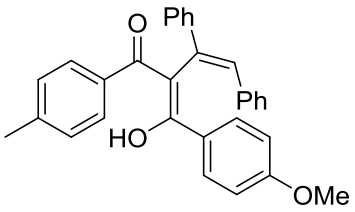
1.598
0.000
6.00
1.98
11.06
0.83
0.91
f1 (ppm)
190.674
141.496
128.726
128.688
128.607
128.054
127.810
127.416
127.372
110.214
77.319
77.000
76.680
137.528
137.026
135.919
133.323
132.676
130.834
f1 (ppm)


O
Ph
Ph
HO
Me

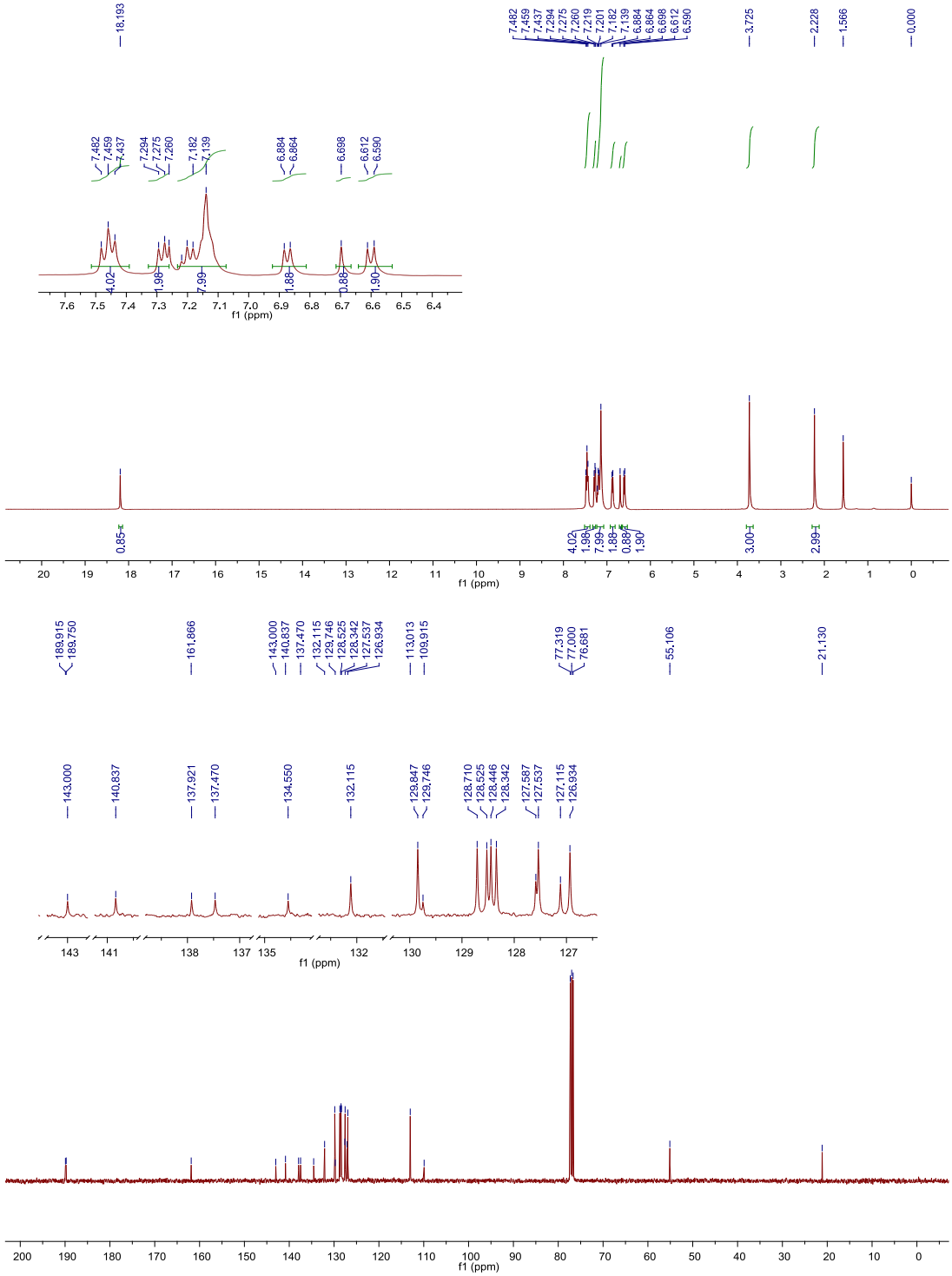
3g

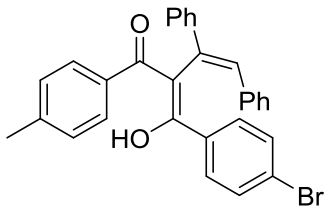

18.128
18.114
7.436
7.419
7.324
7.309
7.259
7.208
7.190
7.171
7.137
6.890
6.871
6.676
2.230
1.565
0.000
1.94
3.89
8.04
3.93
0.95
6.00
f1 (ppm)


190.353
143.026
141.019
137.288
132.122
128.373
127.525
127.105
126.961
110.224
77.319
77.000
76.680
21.144
137.923
134.498
128.744
128.450
127.618
f1 (ppm)

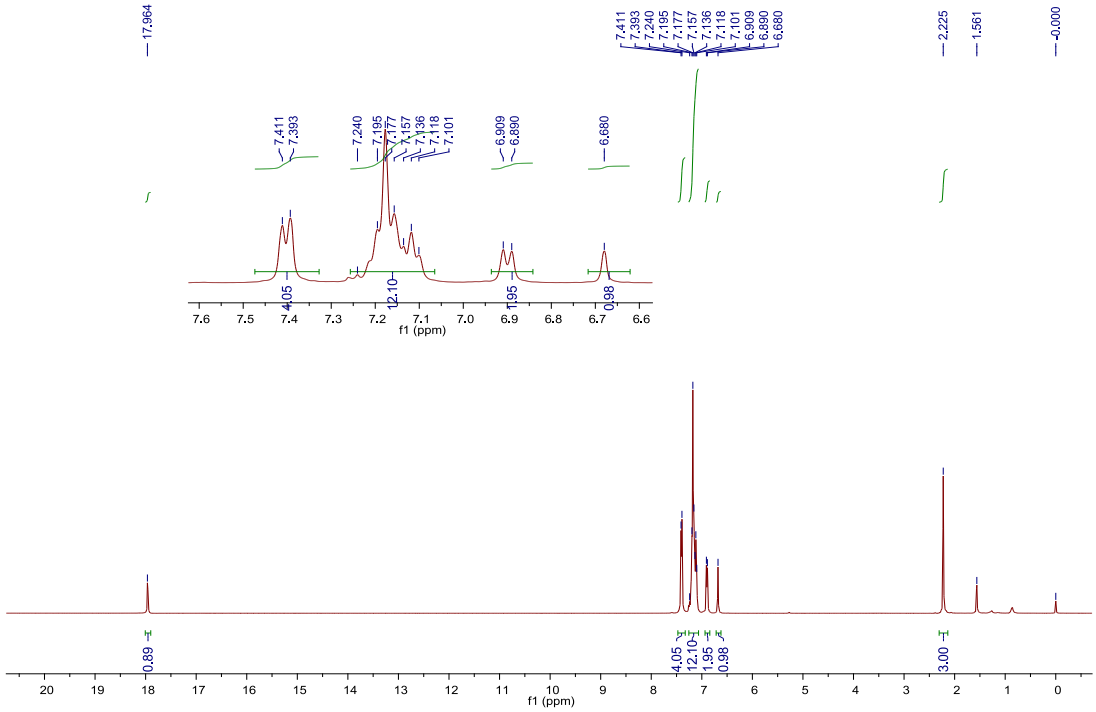


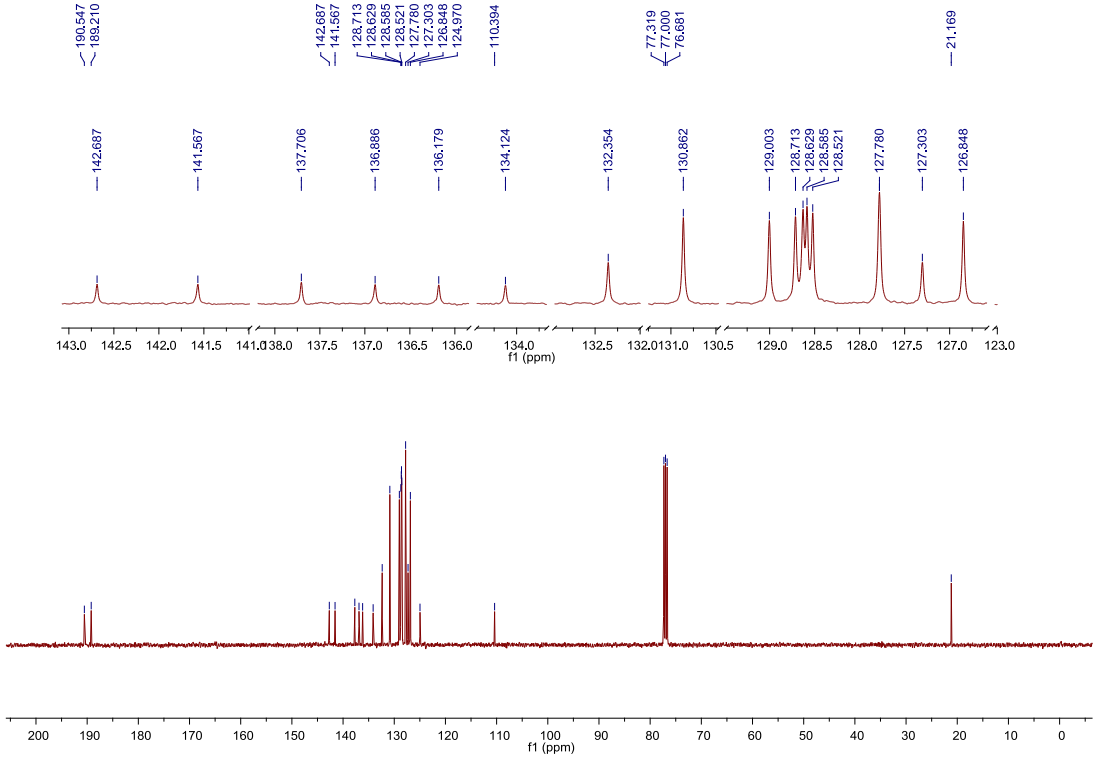
3h

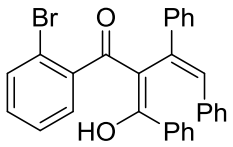



O
Ph
Ph
HO
Br

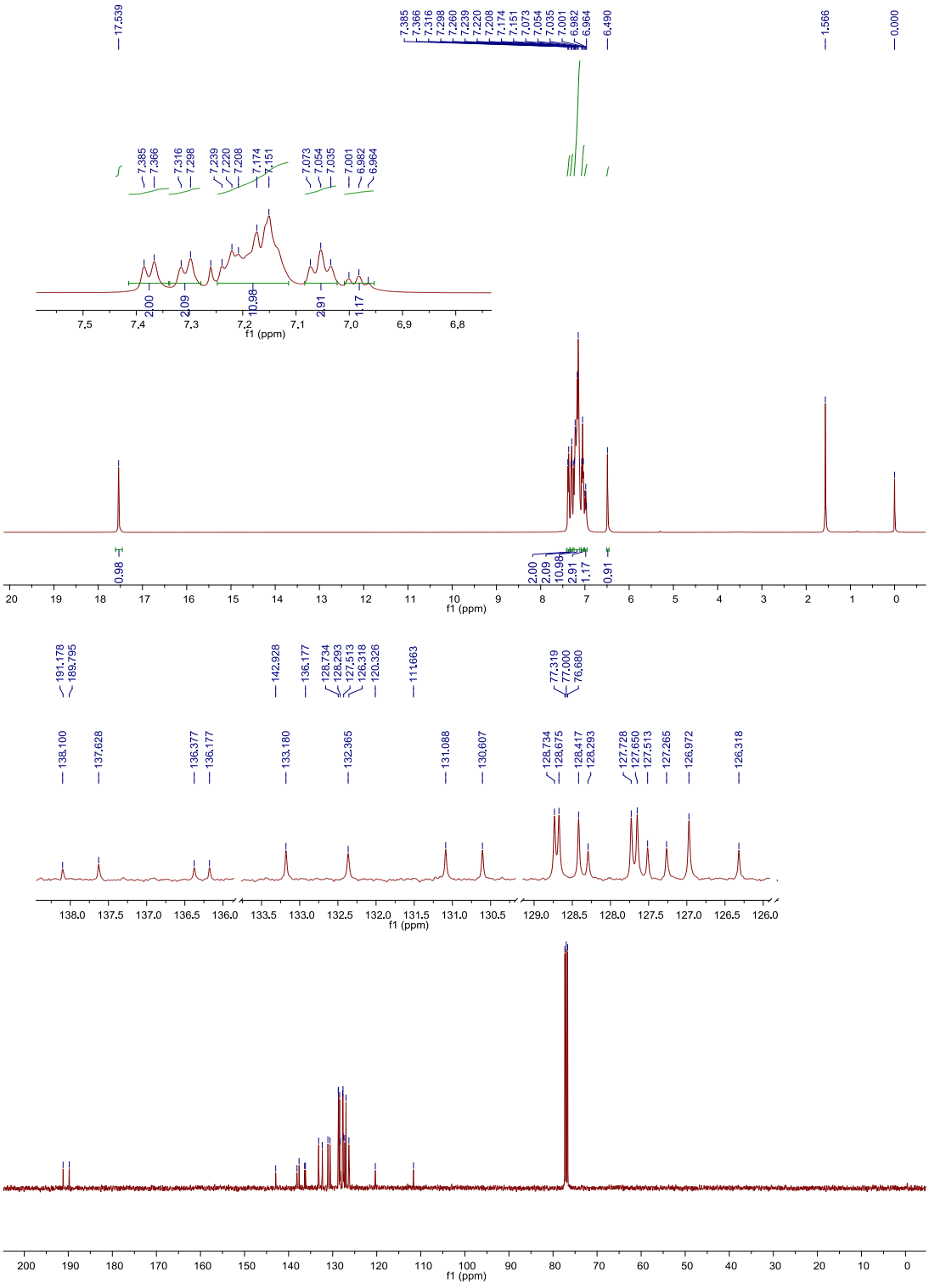
3i

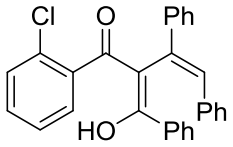

17.964
7.411
7.393
7.240
7.195
7.177
7.157
7.136
7.118
7.101
6.909
6.890
6.680
2.225
1.561
0.000
4.05
12.10
1.95
0.98
3.00
f1 (ppm)


190.547
189.210
142.687
141.567
128.713
128.629
128.585
128.521
127.780
127.303
126.848
124.970
110.394
77.319
77.000
76.681
21.169
137.706
136.886
136.179
134.124
132.354
130.862
129.003
f1 (ppm)

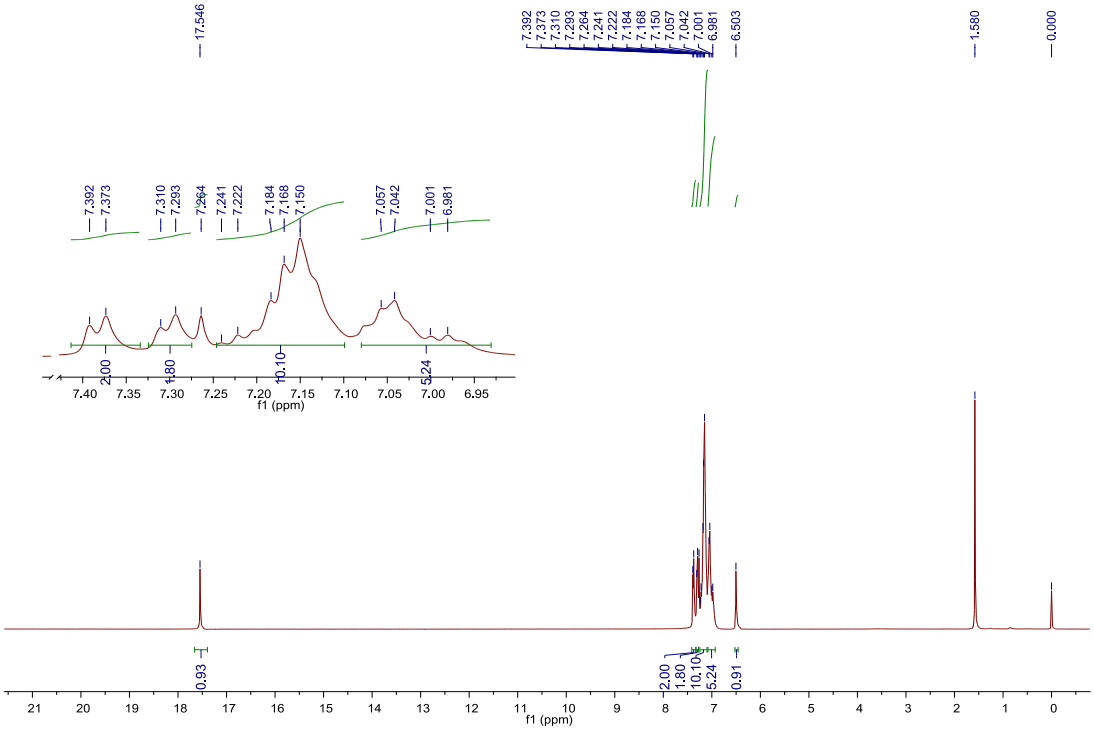

Br
O
Ph
Ph
HO
Ph

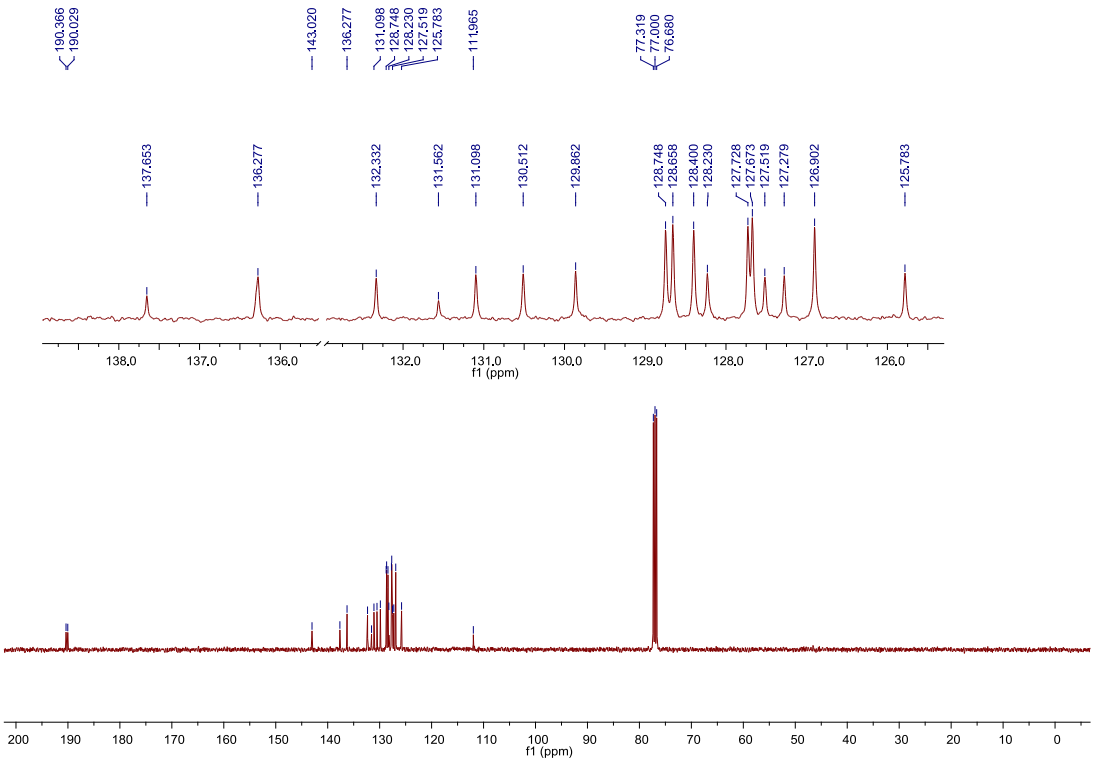
3j

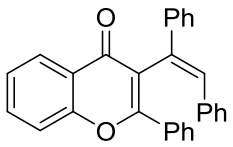

17.539
7.385
7.366
7.316
7.298
7.260
7.239
7.220
7.208
7.174
7.151
7.073
7.054
7.035
7.001
6.982
6.964
6.490
1.566
0.000
f1 (ppm)
191.178
189.795
142.928
136.177
128.734
128.293
127.513
126.318
120.326
111.663
77.319
77.000
76.680
138.100
137.628
136.377
136.177
133.180
132.365
131.088
130.607
128.734
128.675
128.417
128.293
127.728
127.650
127.513
127.265
126.972
126.318
f1 (ppm)
f1 (ppm)


Cl
O
Ph
Ph
HO
Ph

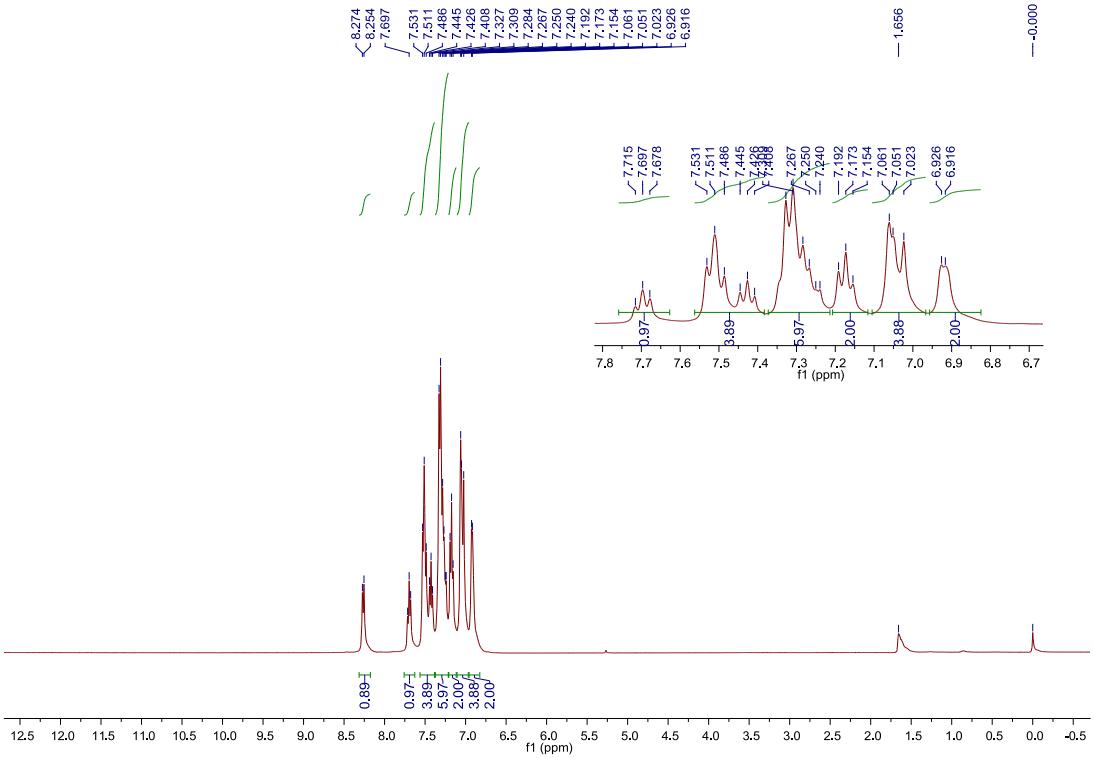
3k

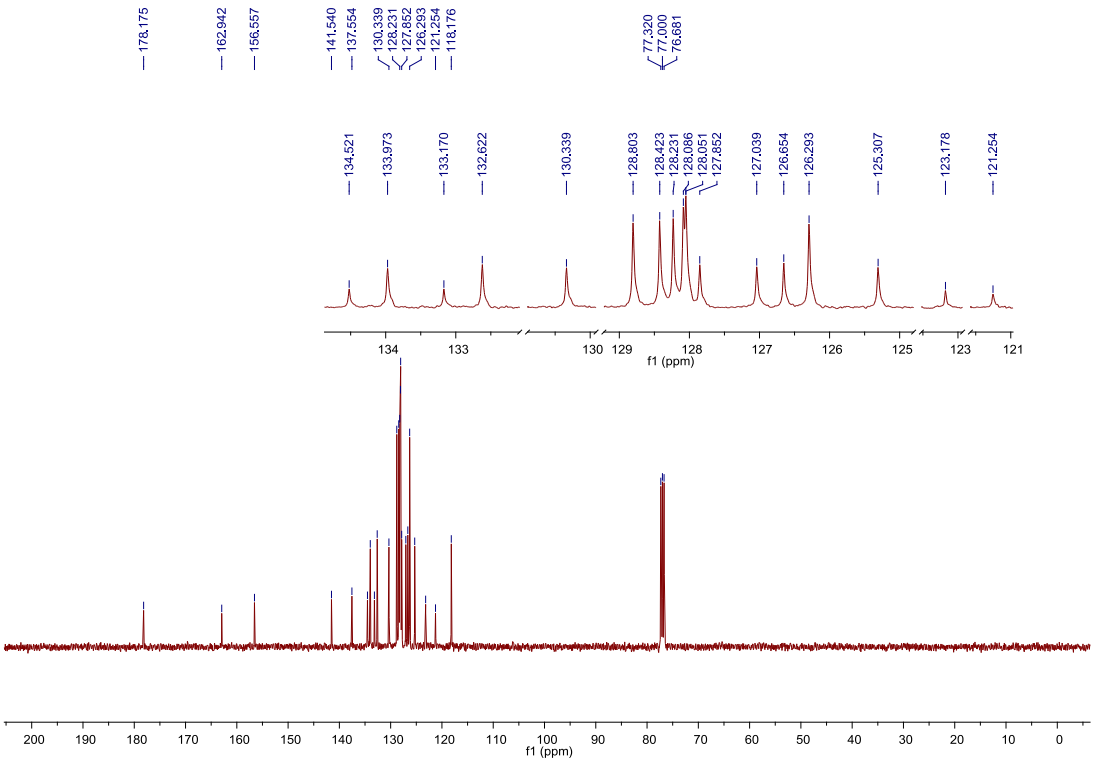

17.546
7.392
7.373
7.310
7.293
7.264
7.241
7.222
7.184
7.168
7.150
7.057
7.042
7.001
6.981
6.503
1.580
0.000
2.00
1.80
10.10
5.24
0.93
0.91
f1 (ppm)

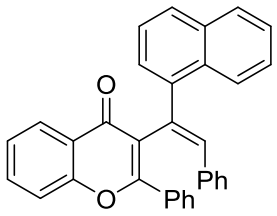

190.366
190.029
143.020
136.277
131.098
128.748
128.230
127.519
125.783
111.965
77.319
77.000
76.680
137.653
136.277
132.332
131.562
131.098
130.512
129.862
128.748
128.658
128.400
128.230
127.728
127.673
127.519
127.279
126.902
125.783
f1 (ppm)


O
Ph
Ph
O
Ph

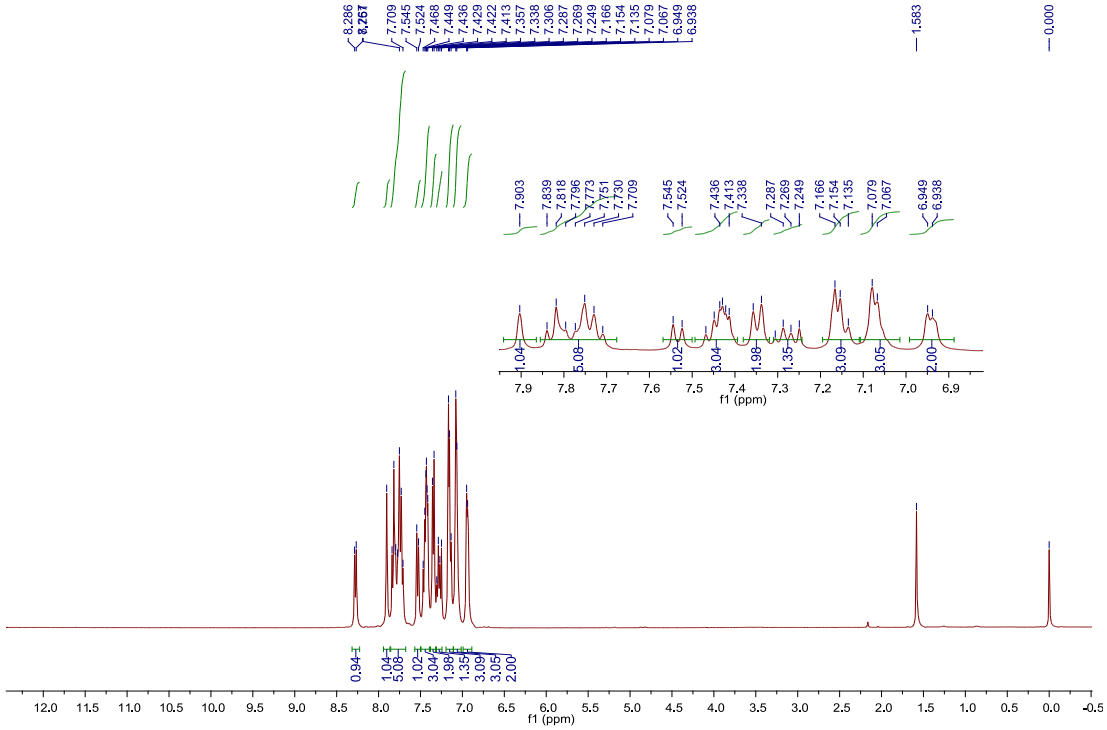
5a

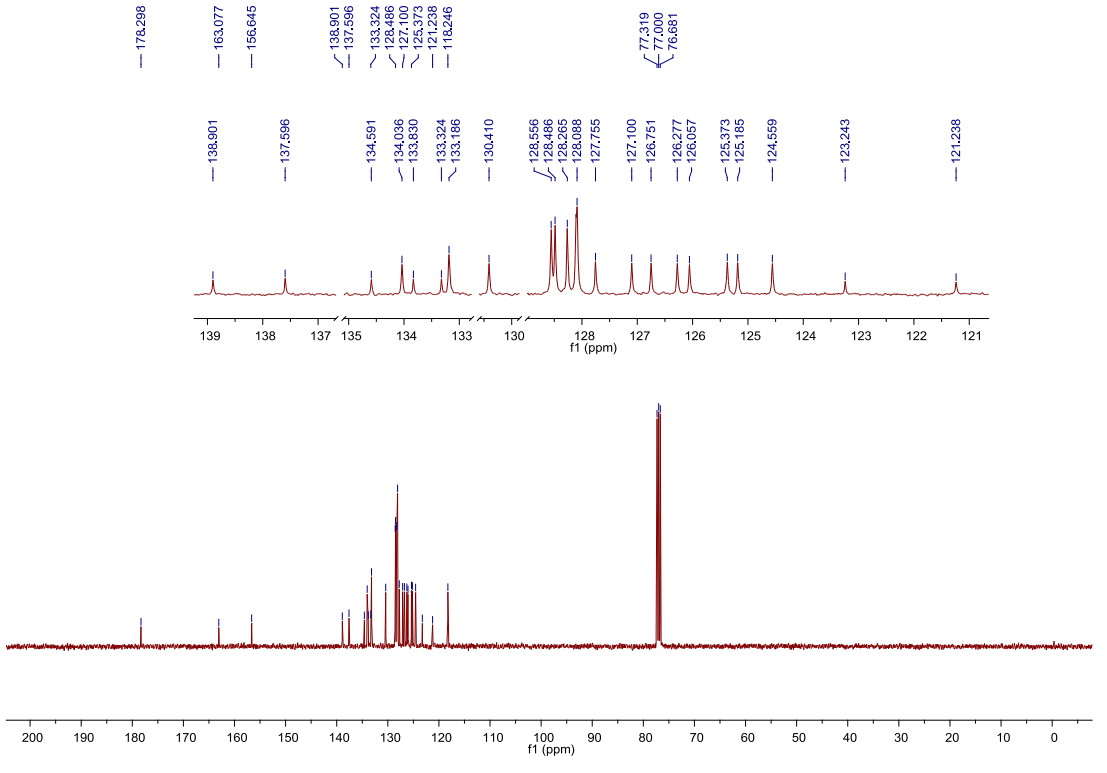

8.274
8.254
7.697
7.531
7.511
7.486
7.445
7.426
7.408
7.327
7.309
7.284
7.267
7.250
7.240
7.192
7.173
7.154
7.061
7.051
7.023
6.926
6.916
1.656
0.000
f1 (ppm)

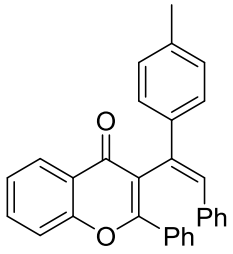

178.175
162.942
156.557
141.540
137.554
130.339
128.231
127.852
126.293
121.254
118.176
77.320
77.000
76.681
134.521
133.973
133.170
132.622
130.339
128.803
128.423
128.231
128.086
128.051
127.852
127.039
126.654
126.293
125.307
123.178
121.254
f1 (ppm)


O
O
Ph
Ph

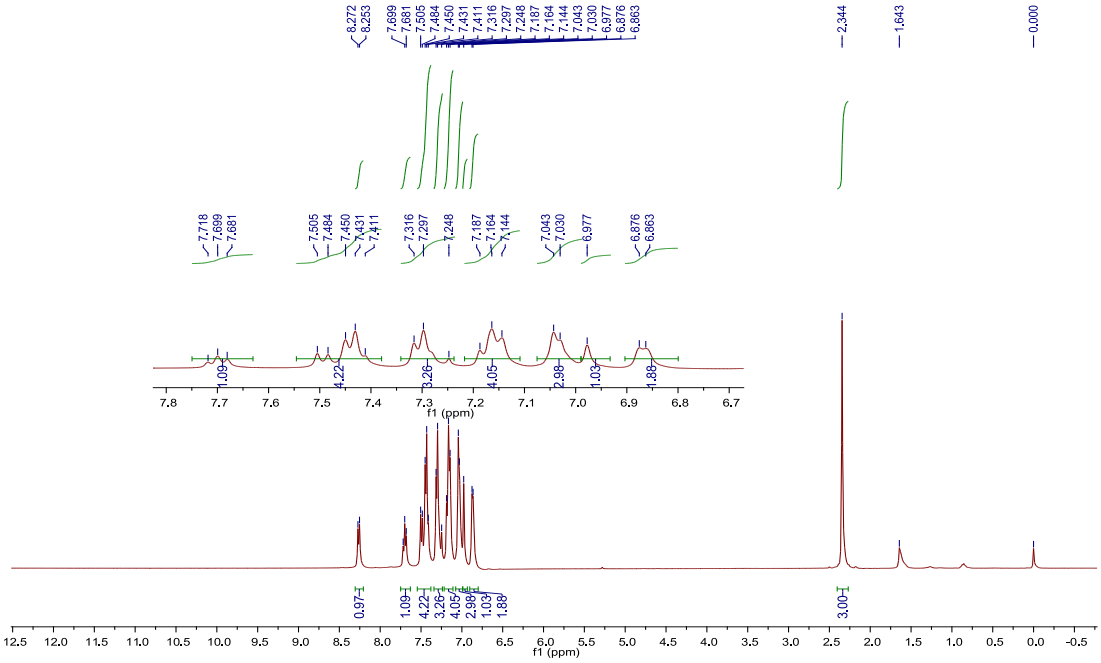
5b

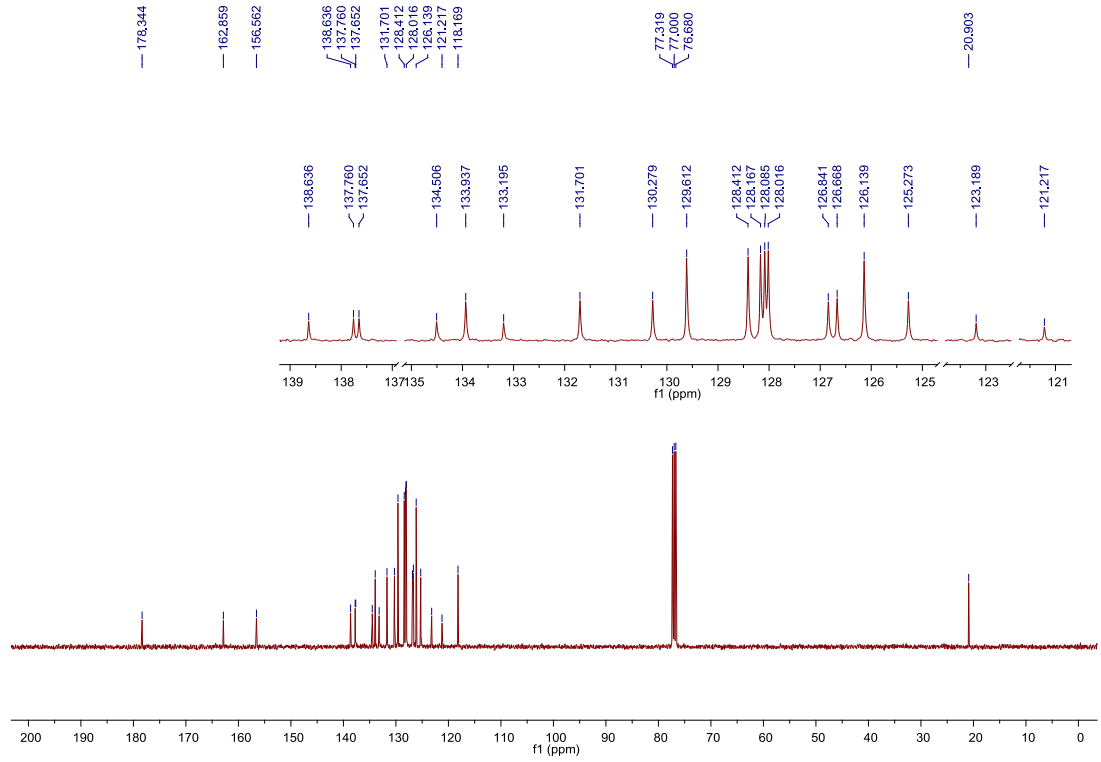

8.286
8.261
7.709
7.545
7.524
7.468
7.449
7.436
7.429
7.422
7.413
7.357
7.338
7.306
7.287
7.269
7.249
7.166
7.154
7.135
7.079
7.067
6.949
6.938
1.583
0.000
f1 (ppm)

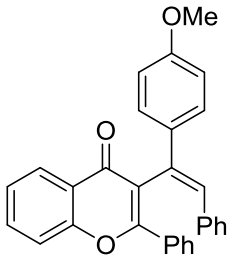

178.298
163.077
156.645
138.901
137.596
133.324
128.486
127.100
125.373
121.238
118.246
77.319
77.000
76.681
134.591
134.036
133.830
133.324
133.186
130.410
128.556
128.486
128.265
128.088
127.755
127.100
126.751
126.277
126.057
125.373
125.185
124.559
123.243
f1 (ppm)


O
O
Ph
Ph

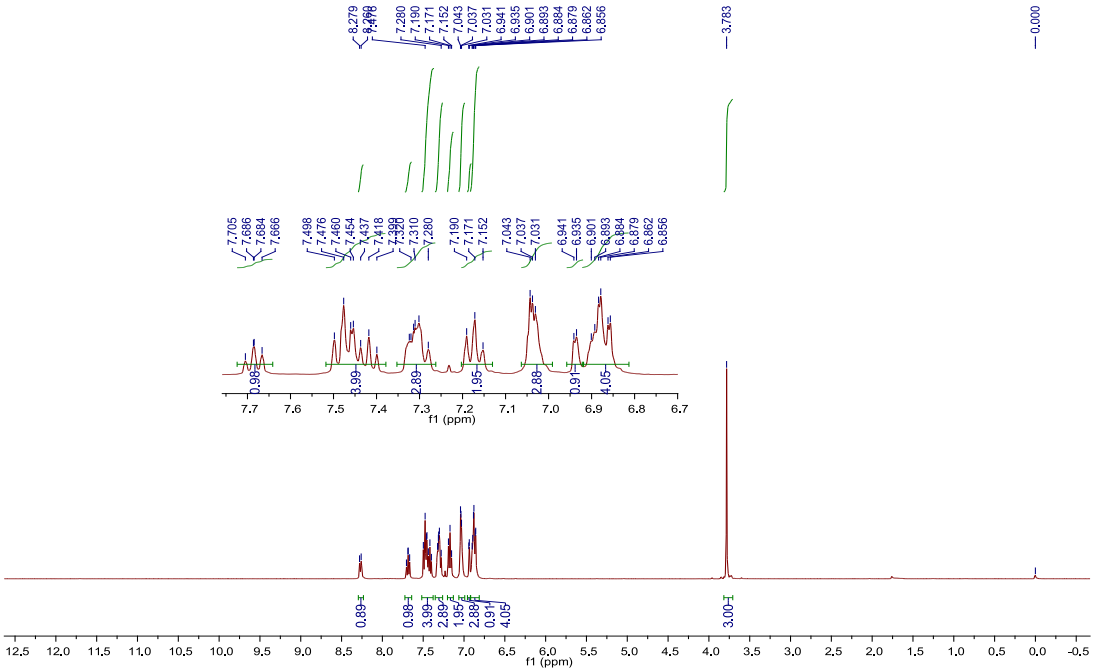
5c

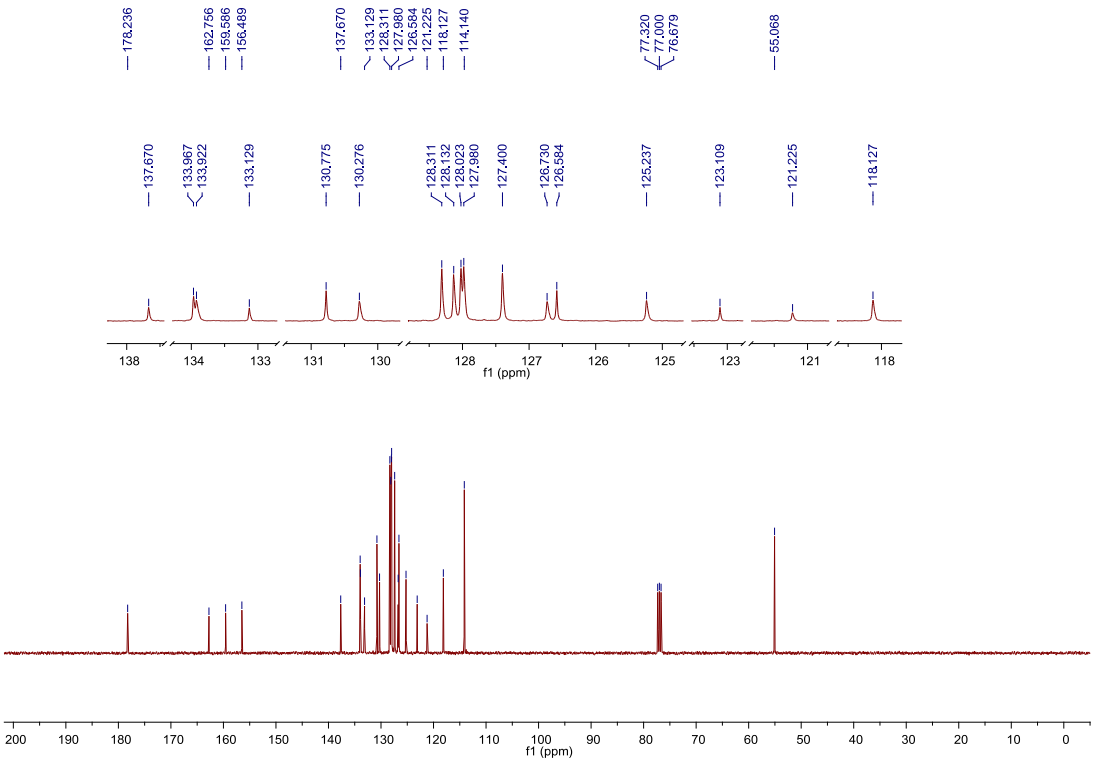

8.272
8.253
7.699
7.681
7.505
7.484
7.450
7.431
7.411
7.316
7.297
7.248
7.187
7.164
7.144
7.043
7.030
6.977
6.876
6.863
2.344
1.643
0.000
0.97
1.09
4.22
3.26
4.05
2.98
1.03
1.88
3.00
f1 (ppm)

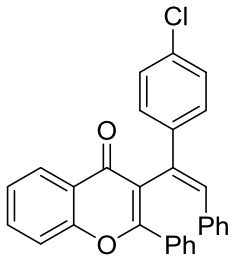

178.344
162.859
156.562
138.636
137.760
137.652
131.701
128.412
128.016
126.139
121.217
118.169
77.319
77.000
76.680
20.903
f1 (ppm)


OMe
O
O
Ph
Ph

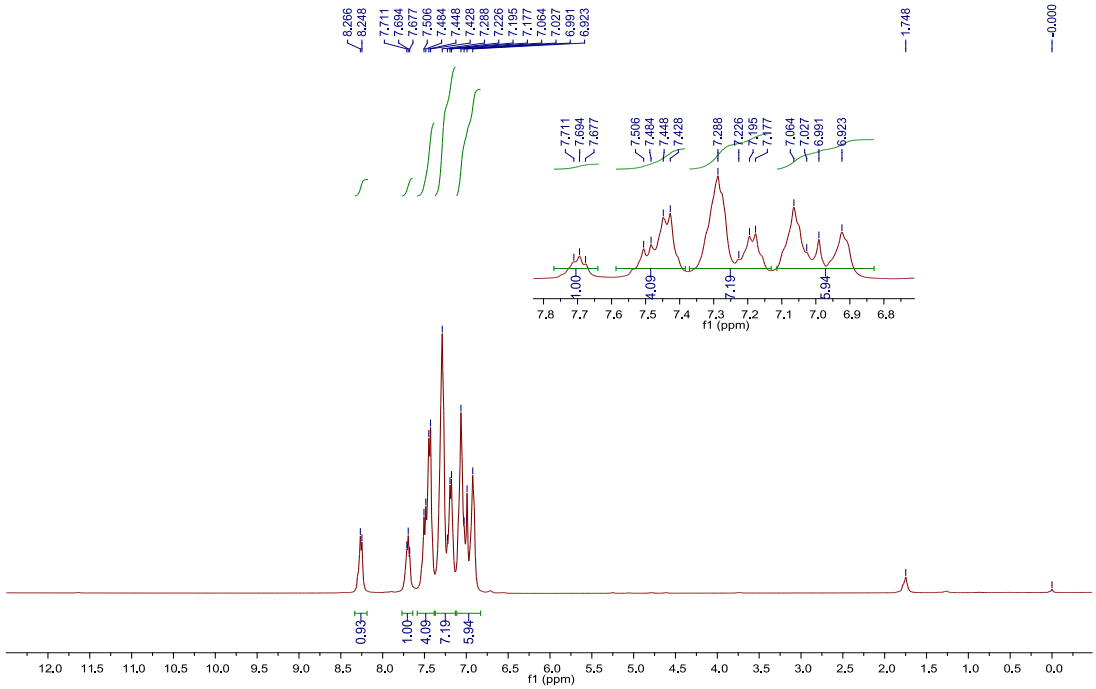
5d

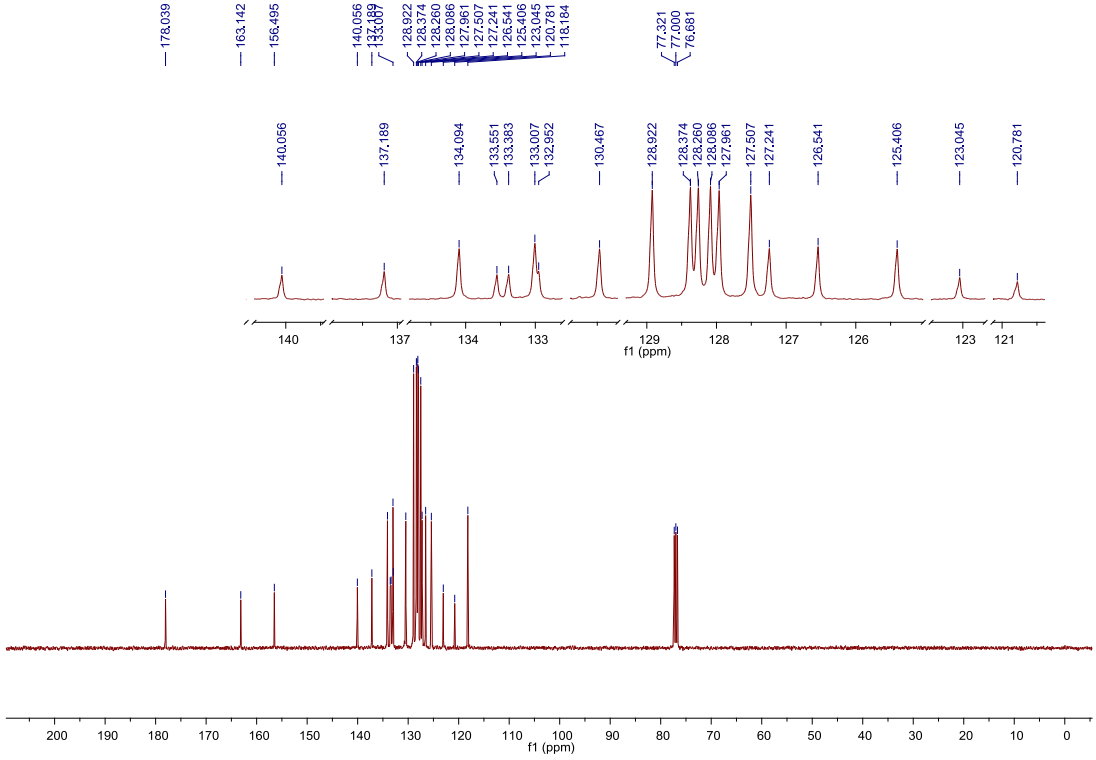

8.279
7.280
7.190
7.171
7.152
7.043
7.037
7.031
6.941
6.935
6.901
6.893
6.884
6.879
6.862
6.856
3.783
0.000
f1 (ppm)

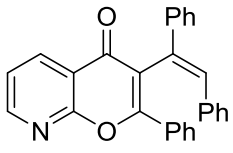

178.236
162.756
159.586
156.489
137.670
133.129
128.311
127.980
126.584
121.225
118.127
114.140
77.320
77.000
76.679
55.068
f1 (ppm)


Cl
O
O
Ph
Ph

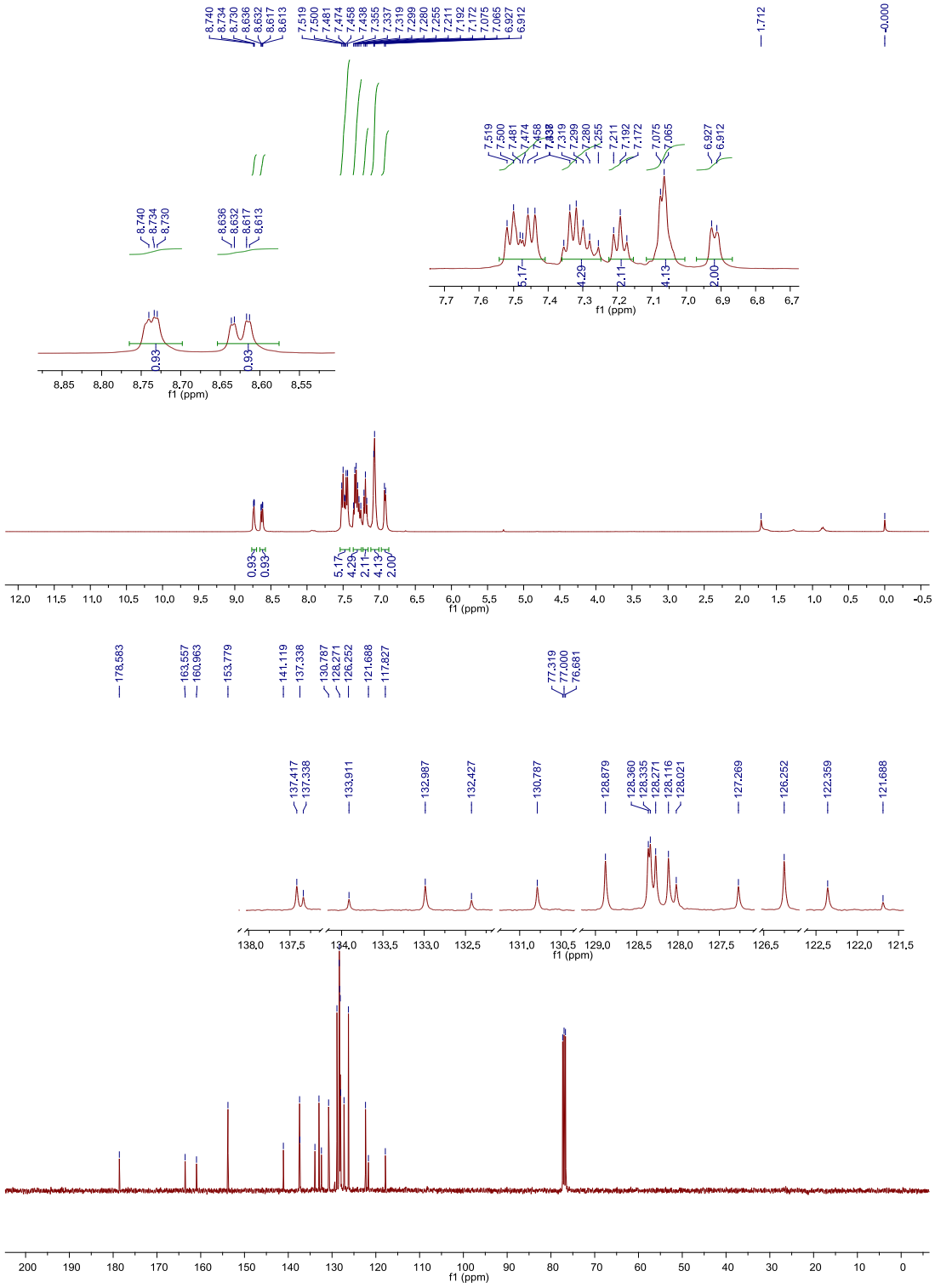
5e

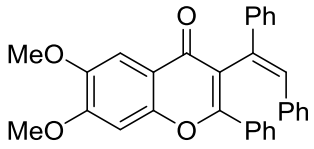

8.266
8.248
7.711
7.694
7.677
7.506
7.484
7.448
7.428
7.288
7.226
7.195
7.177
7.064
7.027
6.991
6.923
1.748
0.000
0.93
1.00
4.09
7.19
5.94
f1 (ppm)


178.039
163.142
156.495
140.056
137.189
134.094
133.551
133.383
133.007
132.952
130.467
128.922
128.374
128.260
128.086
127.961
127.507
127.241
126.541
125.406
123.045
120.781
118.184
77.321
77.000
76.681
f1 (ppm)

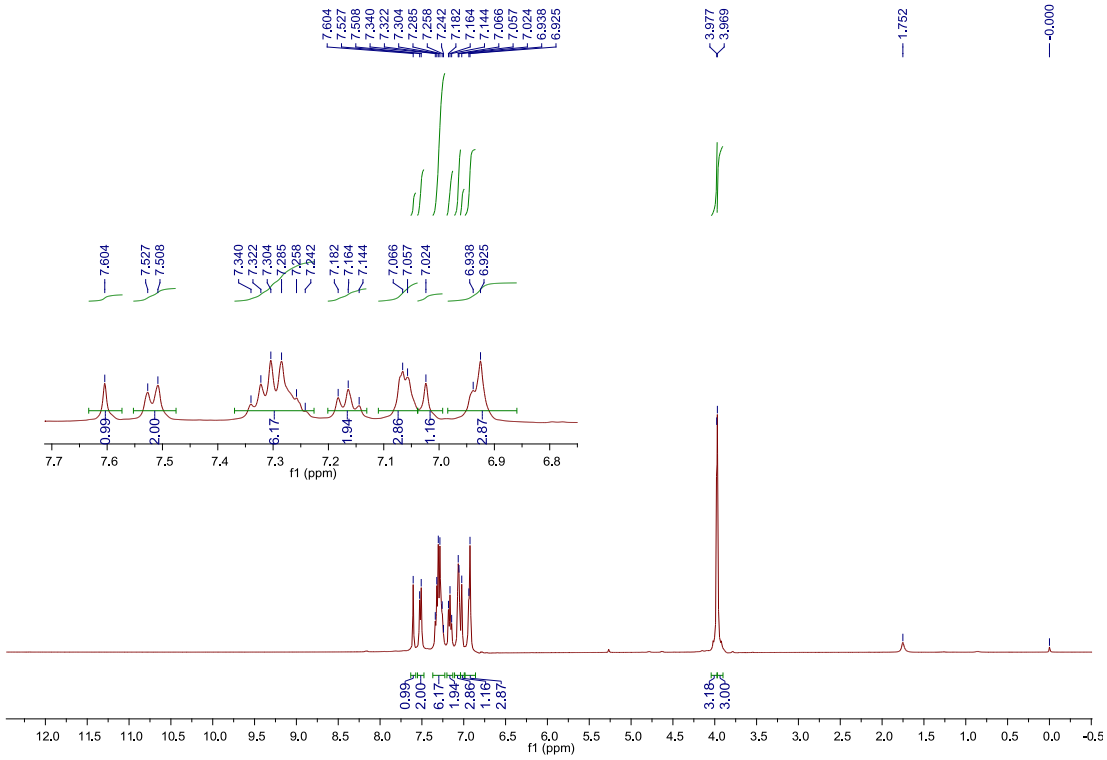

O
Ph
Ph
N
O
Ph

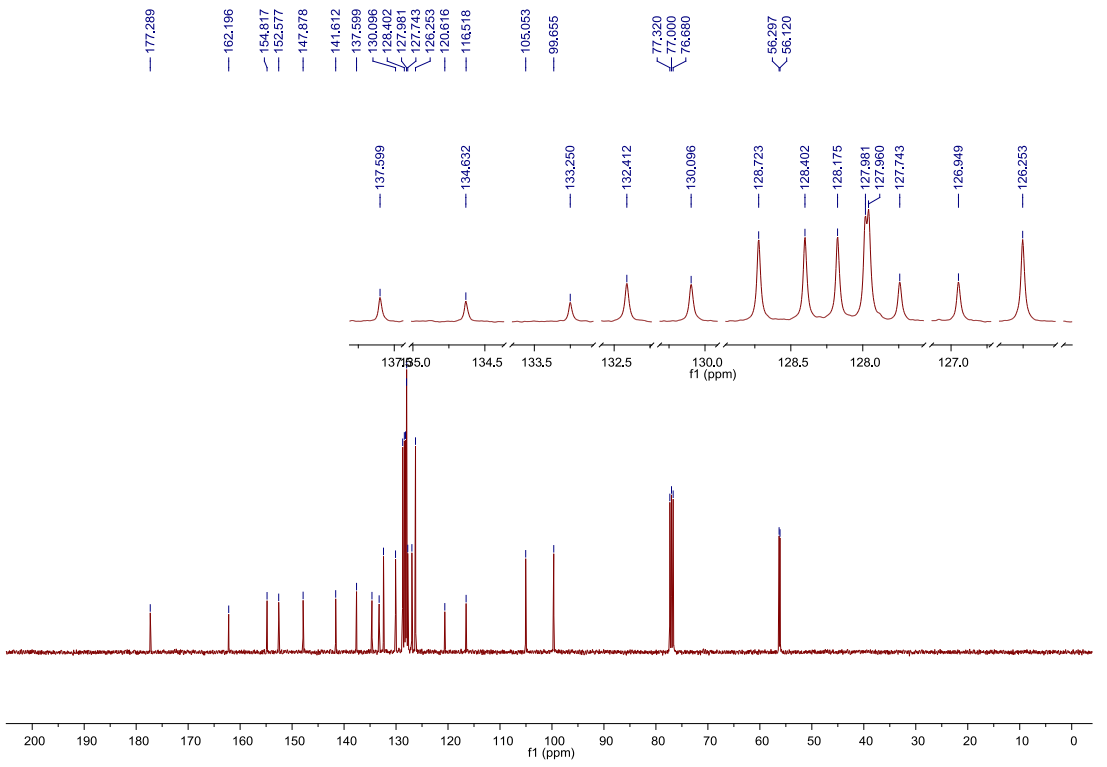
5f

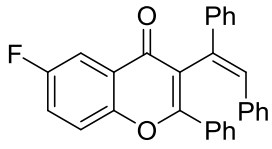

8.740
8.734
8.730
8.636
8.632
8.617
8.613
7.519
7.500
7.481
7.474
7.458
7.438
7.355
7.337
7.319
7.299
7.289
7.280
7.255
7.211
7.192
7.172
7.075
7.065
6.927
6.912
1.712
0.000
0.93
0.93
5.17
4.29
2.11
4.13
2.00
f1 (ppm)
178.583
163.557
160.963
153.779
141.119
137.338
130.787
128.271
126.252
121.688
117.827
77.319
77.000
76.681
137.417
137.338
133.911
132.987
132.427
130.787
128.879
128.360
128.335
128.271
128.116
128.021
127.269
126.252
122.359
121.688


O
Ph
MeO
MeO
O
Ph
Ph

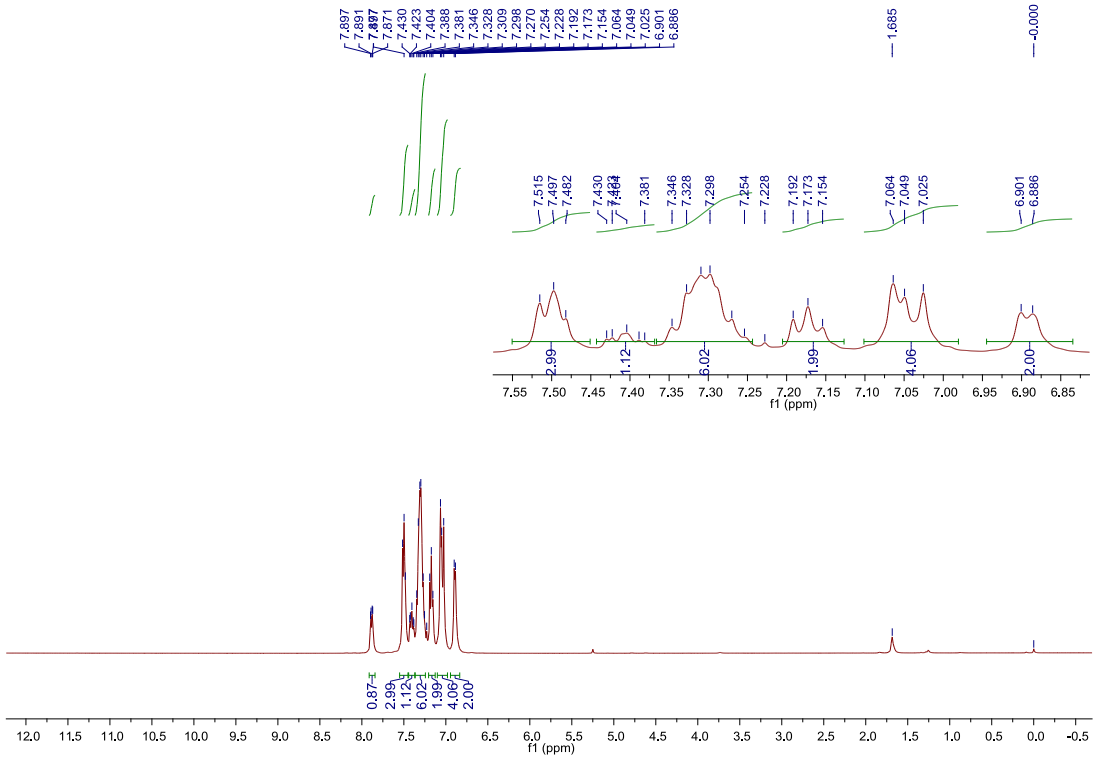
5g


7.604
7.527
7.508
7.340
7.322
7.304
7.285
7.258
7.242
7.182
7.164
7.144
7.066
7.057
7.024
6.938
6.925
3.977
3.969
1.752
0.000
0.99
2.00
6.17
1.94
2.86
1.16
2.87
3.18
3.00
f1 (ppm)

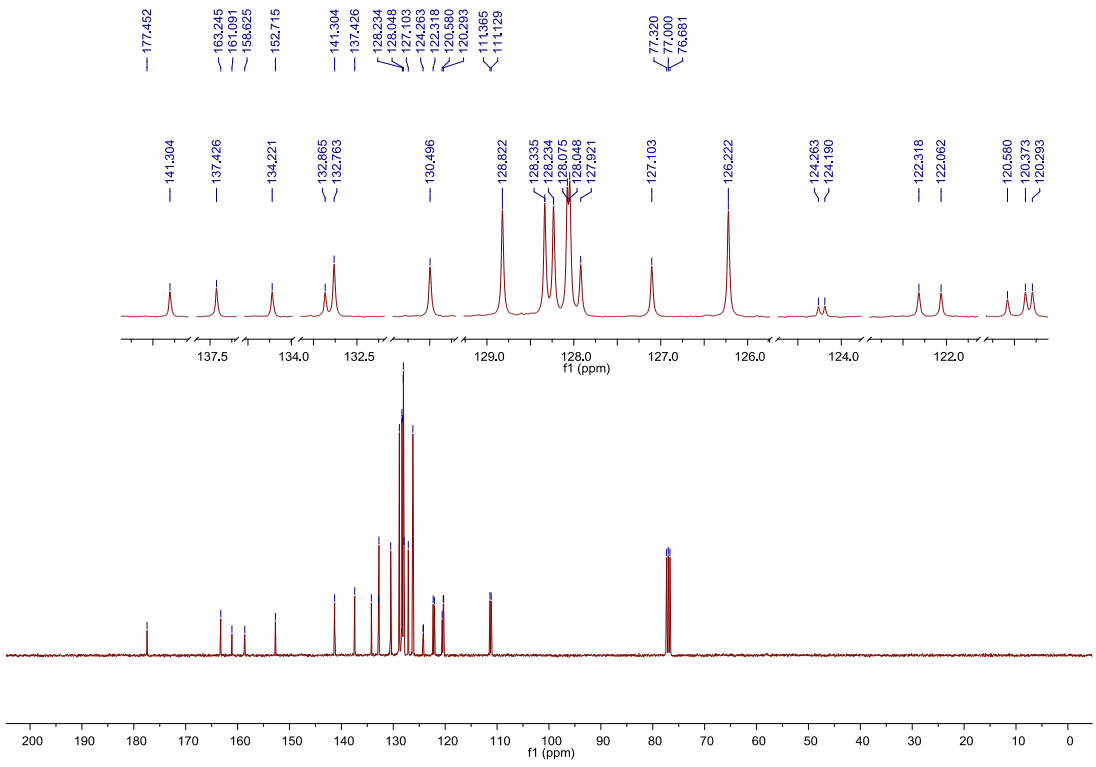

177.289
162.196
154.817
152.577
147.878
141.612
137.599
130.096
128.402
127.981
127.743
126.253
120.616
116.518
105.053
99.655
77.320
77.000
76.680
56.297
56.120
137.599
134.632
133.250
132.412
130.096
128.723
128.402
128.175
127.981
127.960
127.743
126.949
126.253
f1 (ppm)

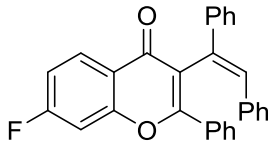

O
Ph
F
Ph
O
Ph

5h

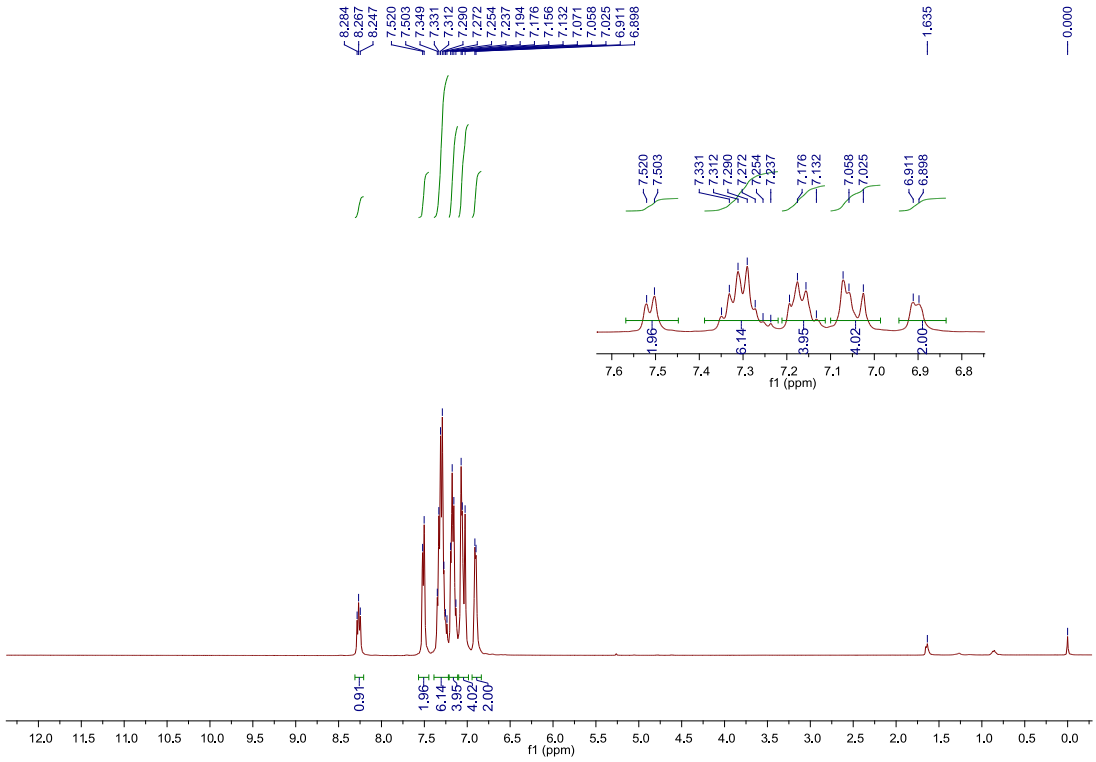

7.897
7.691
7.430
7.423
7.404
7.388
7.381
7.346
7.328
7.309
7.298
7.270
7.254
7.228
7.192
7.173
7.154
7.064
7.049
7.025
6.901
6.886
1.685
-0.000
2.99
1.12
6.02
1.99
4.06
2.00
f1 (ppm)

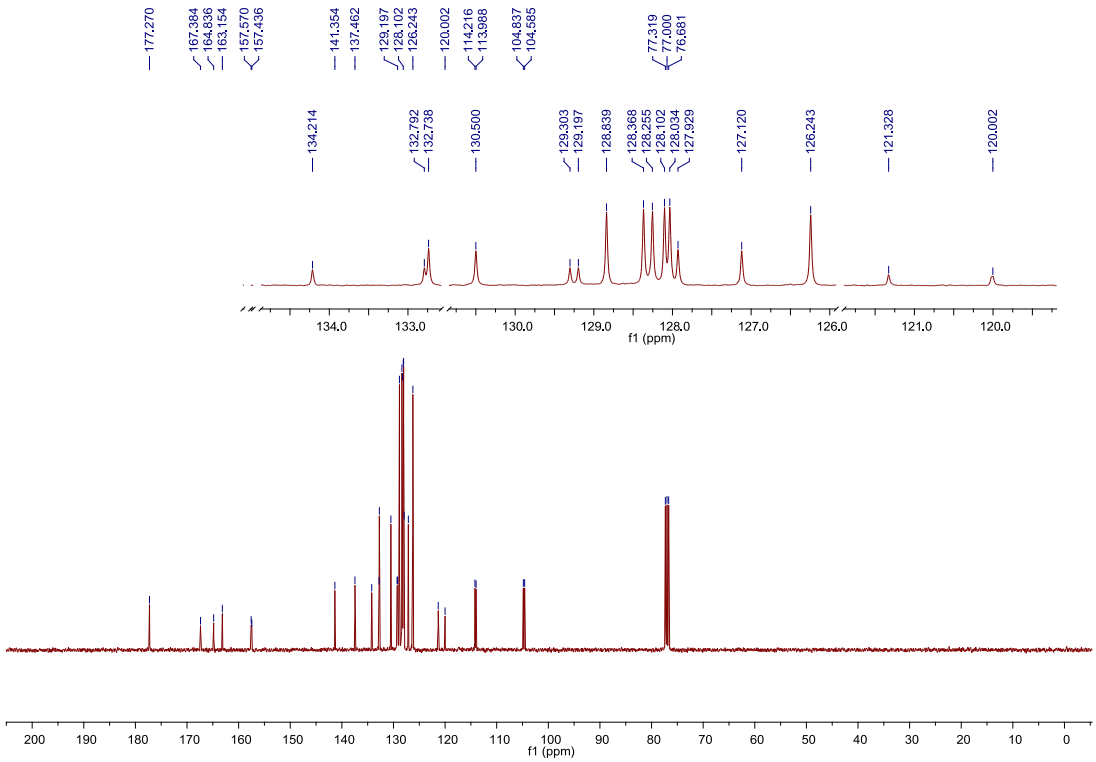
0.87
2.99
1.12
6.02
1.99
4.06
2.00
f1 (ppm)

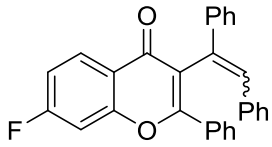

177.452
163.245
161.091
158.625
152.715
141.304
137.426
128.234
128.048
127.103
124.263
122.318
120.580
120.293
111.365
111.129
77.320
77.000
76.681
f1 (ppm)


O
Ph
F
O
Ph
Ph

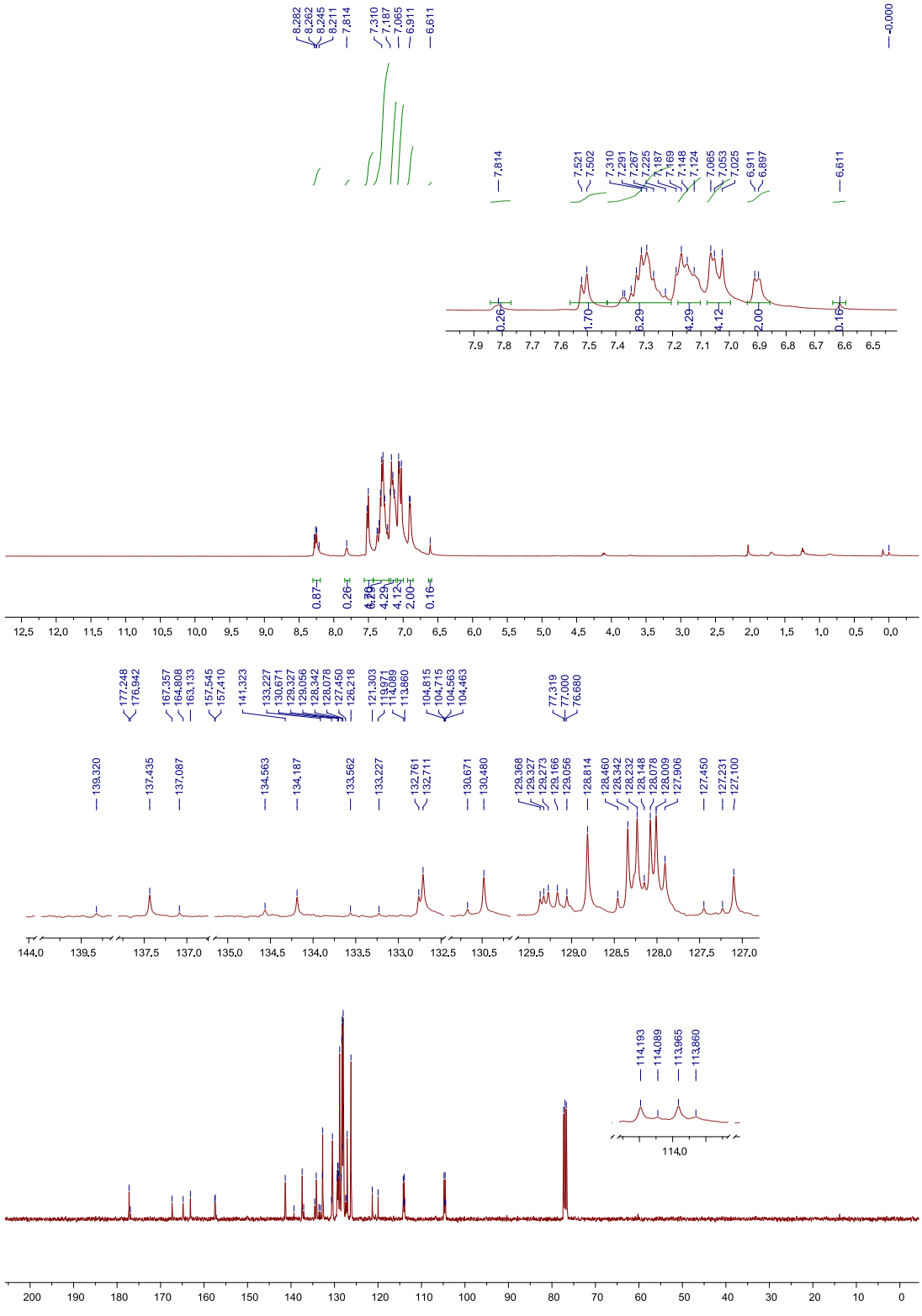
5i

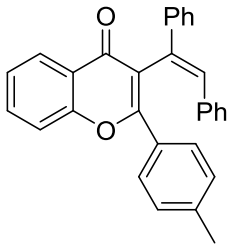

8.284
8.267
8.247
7.520
7.503
7.349
7.331
7.312
7.290
7.272
7.254
7.237
7.194
7.176
7.156
7.132
7.071
7.058
7.025
6.911
6.898
1.635
0.000
f1 (ppm)


177.270
167.384
164.836
163.154
157.570
157.436
141.354
137.462
129.197
128.102
126.243
120.002
114.216
113.988
104.837
104.585
77.319
77.000
76.681
134.214
132.792
132.738
130.500
129.303
129.197
128.839
128.368
128.255
128.102
128.034
127.929
127.120
126.243
121.328
120.002
f1 (ppm)

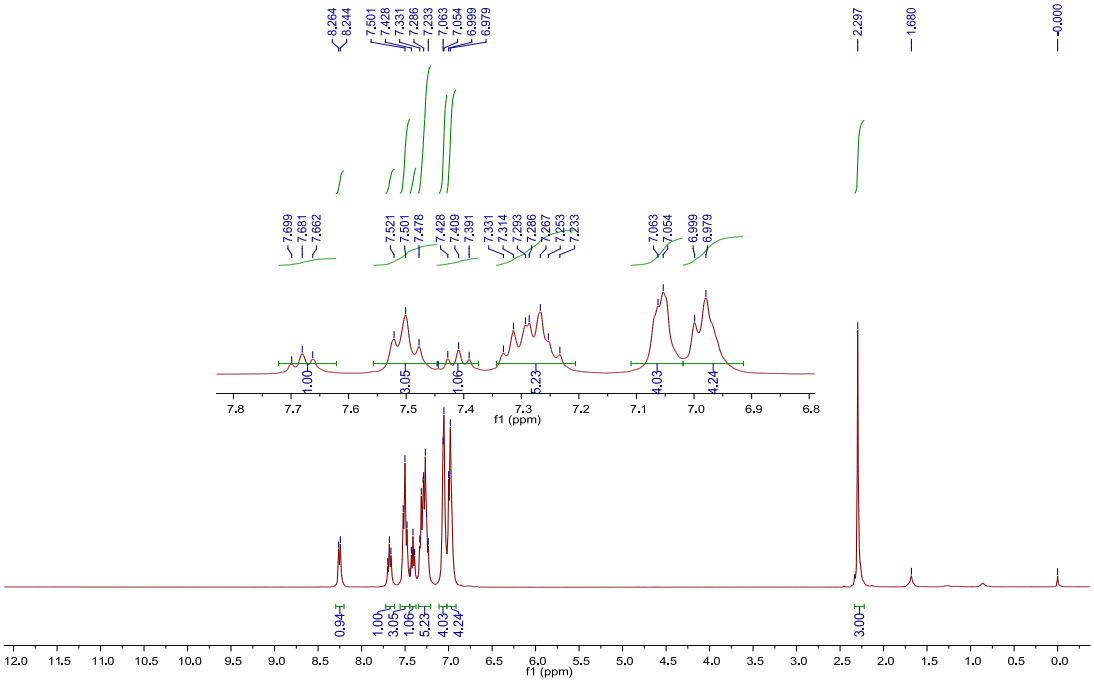


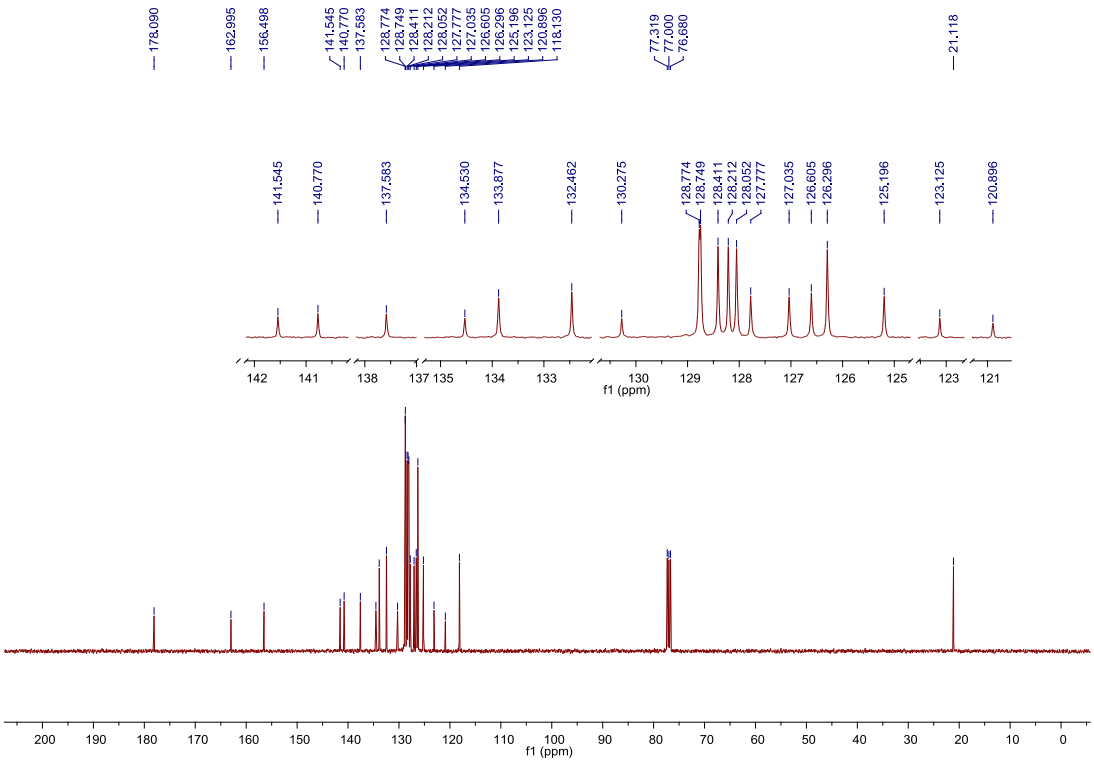
5i

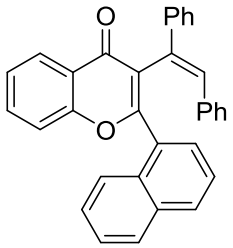



O
Ph
Ph
O

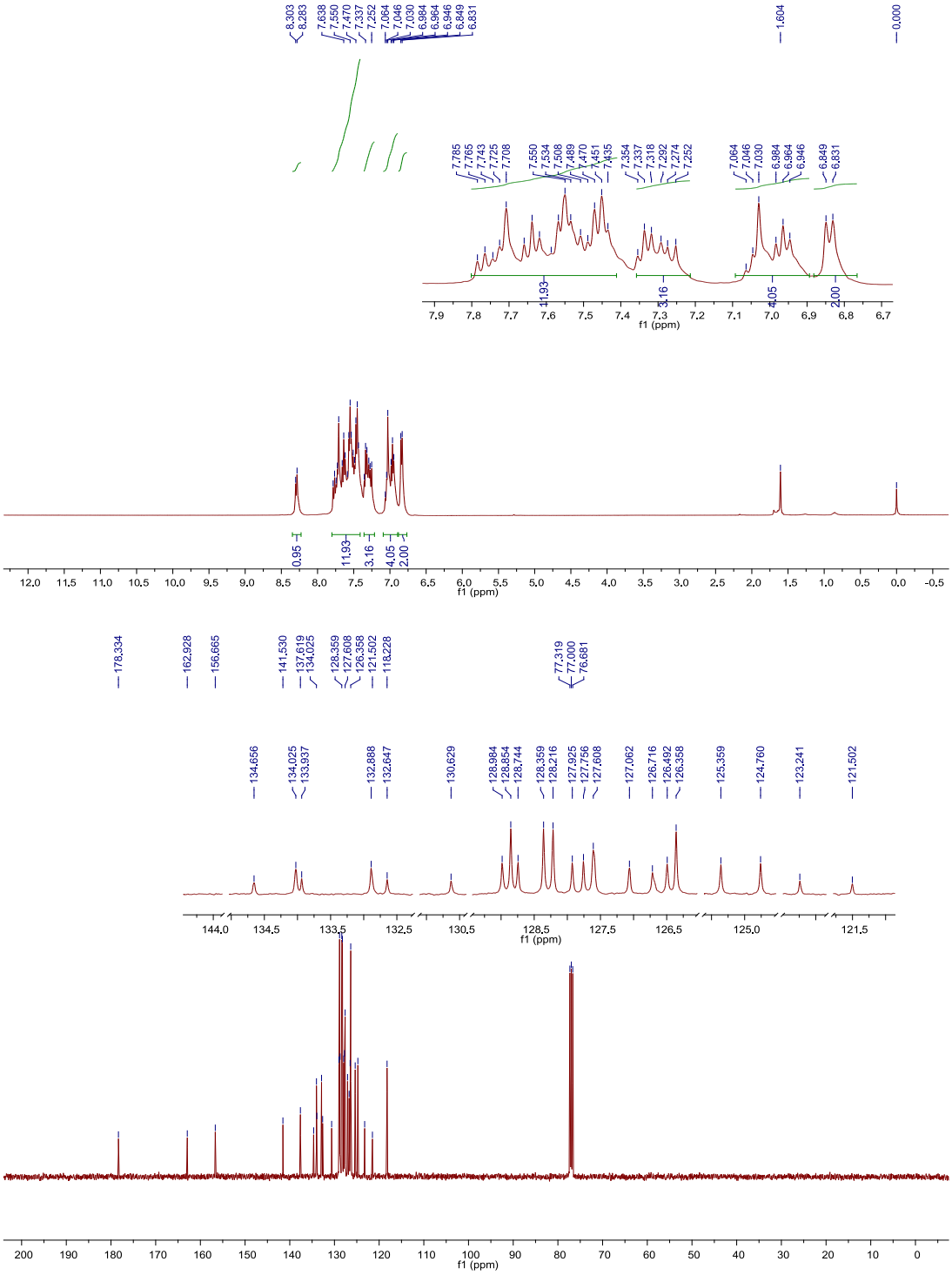
5j

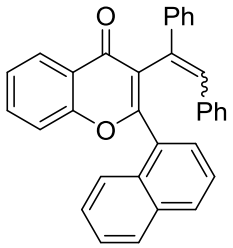

8.264
8.244
7.501
7.428
7.331
7.286
7.233
7.063
7.054
6.999
6.979
2.297
1.680
0.000
f1 (ppm)


178.090
162.995
156.498
141.545
140.770
137.583
128.774
128.749
128.411
128.212
128.052
127.777
127.035
126.605
126.296
125.196
123.125
120.896
118.130
77.319
77.000
76.680
21.118
f1 (ppm)

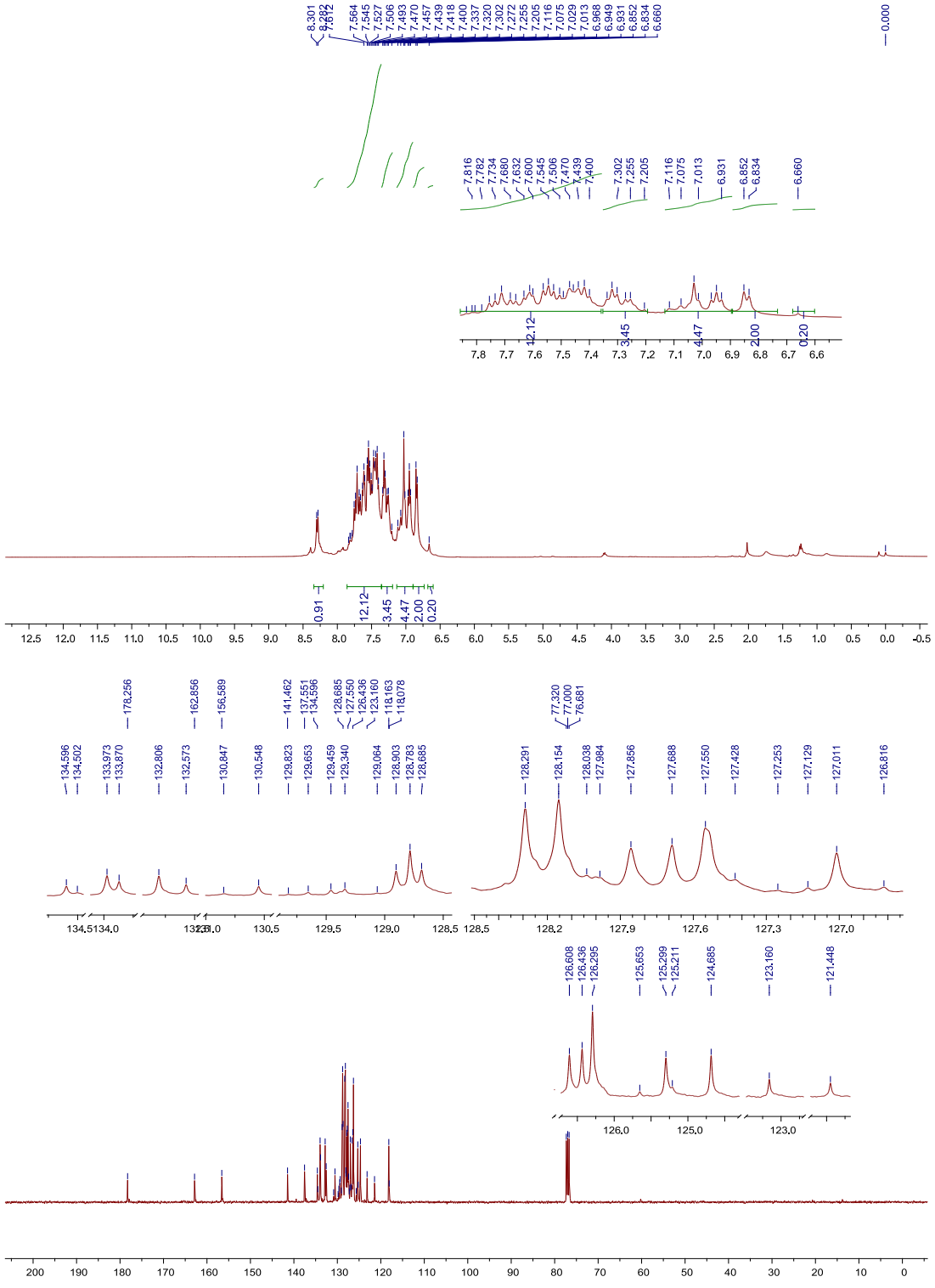

O
Ph
Ph
O

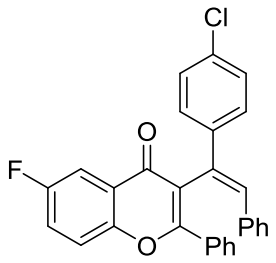
5k


8.303
8.283
7.638
7.550
7.470
7.337
7.252
7.064
7.046
7.030
6.984
6.964
6.946
6.849
6.831
1.604
0.000
f1 (ppm)
0.95
11.93
3.16
4.05
2.00
178.334
162.928
156.665
141.530
137.619
134.025
128.359
127.608
126.388
121.502
118.228
77.319
77.000
76.681
134.656
134.025
133.937
132.888
132.647
130.629
128.984
128.854
128.744
128.359
128.216
127.925
127.756
127.608
127.062
126.716
126.492
126.358
125.359
124.760
123.241
121.502

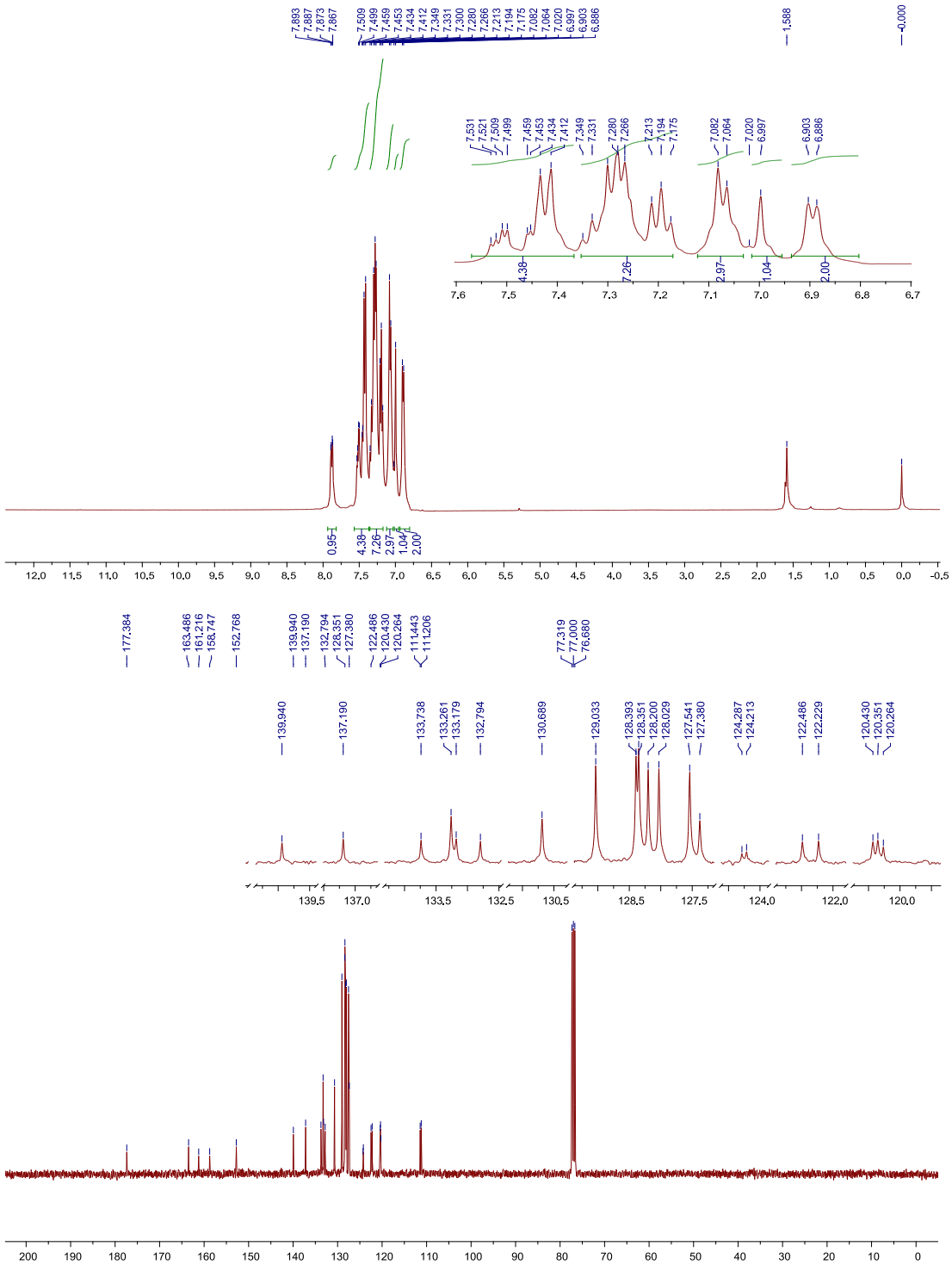

O
Ph
Ph
O

5k


8.301
8.282
7.812
7.564
7.545
7.527
7.506
7.493
7.470
7.457
7.439
7.418
7.400
7.337
7.320
7.302
7.272
7.255
7.205
7.116
7.075
7.029
7.013
6.968
6.949
6.931
6.852
6.834
6.660
0.000
12.12
3.45
4.47
2.00
0.20
0.91
178.256
162.856
156.589
141.462
137.551
134.596
128.685
127.550
126.436
123.160
118.163
118.078
77.320
77.000
76.681
134.596
134.502
133.973
133.870
132.806
132.573
130.847
130.548
129.823
129.653
129.459
129.340
129.064
128.903
128.783
128.685
128.291
128.154
128.038
127.984
127.856
127.688
127.550
127.428
127.253
127.129
127.011
126.816
126.608
126.436
126.295
125.653
125.299
125.211
124.685
123.160
121.448


Cl
O
F
O
Ph
Ph

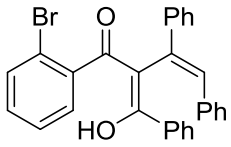
5l


7.893
7.887
7.873
7.867
7.509
7.499
7.459
7.453
7.434
7.412
7.349
7.331
7.300
7.280
7.266
7.213
7.194
7.175
7.082
7.064
7.020
6.997
6.903
6.886
1.588
4.000
0.95
4.38
7.26
2.97
1.04
2.00
177.384
163.486
161.216
158.747
152.768
139.940
137.190
132.794
128.351
127.380
122.486
120.430
120.264
111.443
111.206
77.319
77.000
76.680
133.738
133.261
133.179
130.689
129.033
128.393
128.351
128.200
128.029
127.541
127.380
124.287
124.213
122.486
122.229
120.430
120.351
120.264

8 X-ray Crystallography of Compounds 3j and 5a

(2Z,3Z)-1-(2-bromophenyl)-2-(hydroxy(phenyl)methylene)-3,4-diphenylbut-3-en-1-one（3j, CCDC 1521120）

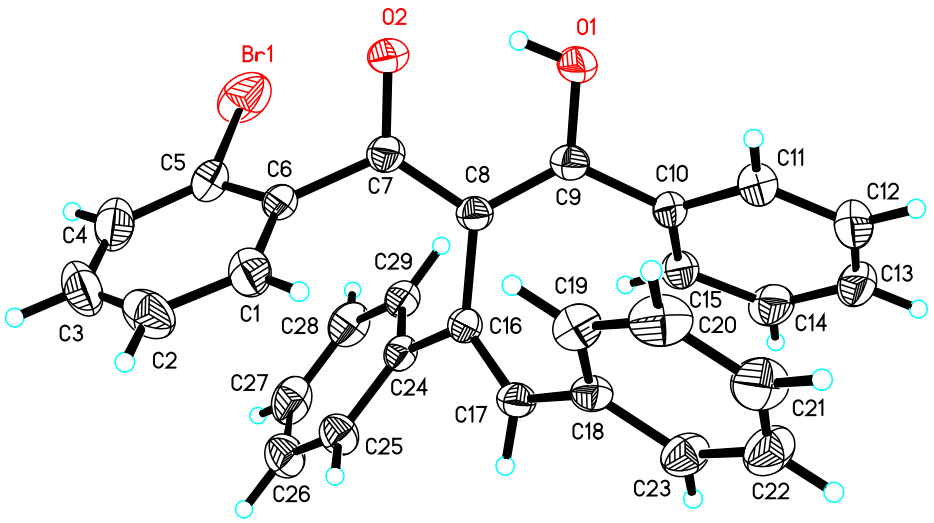
(Ortep ellipsoids are depicted at the 50% level)

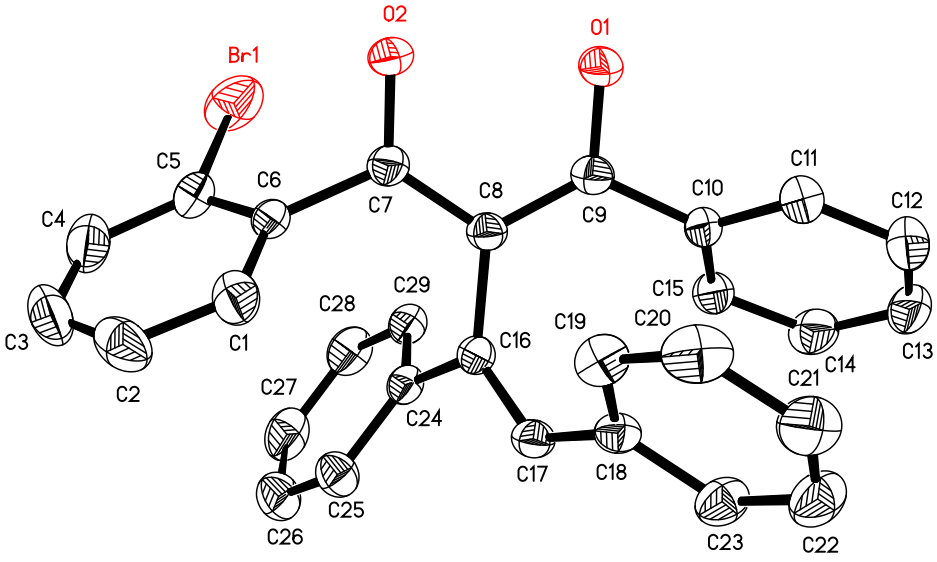


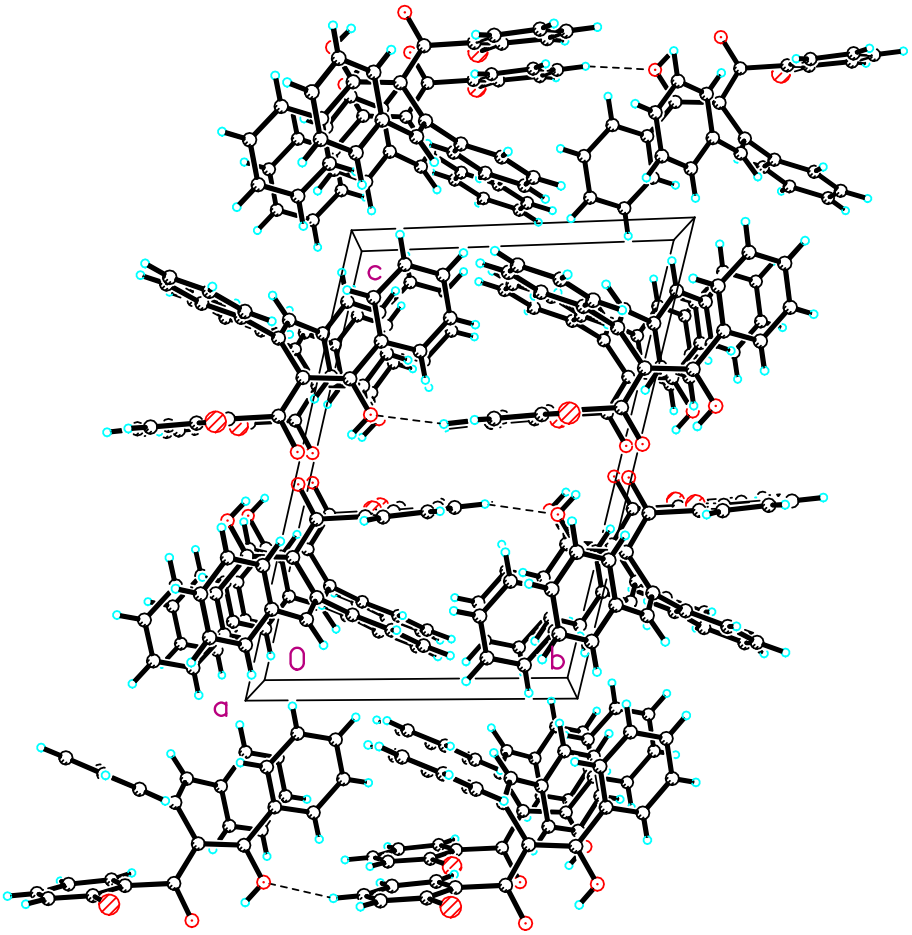
3j

Table 1. Crystal data and structure refinement for **3j**

Identification code	**3j**
Empirical formula	$C_{29}H_{21}BrO_2$
Formula weight	481.37
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 8.1053(11) Å a= 74.381(3) ° b = 10.2013(13) Å b=81.572(3) ° c = 14.6738(19) Å g = 79.622(3) °.
Volume	1143.2(3) $Å^3$
Z, Calculated density	2, 1.398 Mg/m^3
Absorption coefficient	1.821 mm^{-1}
F(000)	492
Crystal size	0.200 x 0.160 x 0.130 mm^3
Theta range for data collection	1.449 to 25.494 °.
Limiting indices	-8<=h<=9, -11<=k<=12, -17<=l<=17
Reflections collected / unique	6653/4253 [R(int) = 0.0219]
Completeness to theta = 25.99	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6453
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4253 / 1 / 290
Goodness-of-fit on F^2	1.025
Final R indices [I>2sigma(I)]	R1 = 0.0517, wR2 = 0.1353
R indices (all data)	R1 = 0.0812, wR2 = 0.1500
Largest diff. peak and hole	0.902 and -0.300 e.$Å^{-3}$

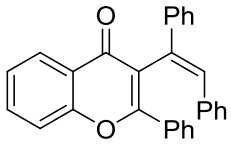

O2
O1
Br1
C5
C6
C7
C8
C9
C10
C11
C12
C4
C13
C29
C19
C15
C1
C28
C16
C20
C14
C3
C2
C27
C24
C17
C18
C21
C25
C23
C22
C26


O2
O1
Br1
C5
C6
C7
C8
C9
C10
C11
C12
C4
C15
C29
C28
C19
C20
C13
C1
C16
C14
C3
C21
C2
C27
C24
C17
C18
C25
C23
C22
C26


c
0
b
a

(Z)-3-(1,2-diphenylvinyl)-2-phenyl-4H-chromen-4-one (5a, CCDC 1521121)

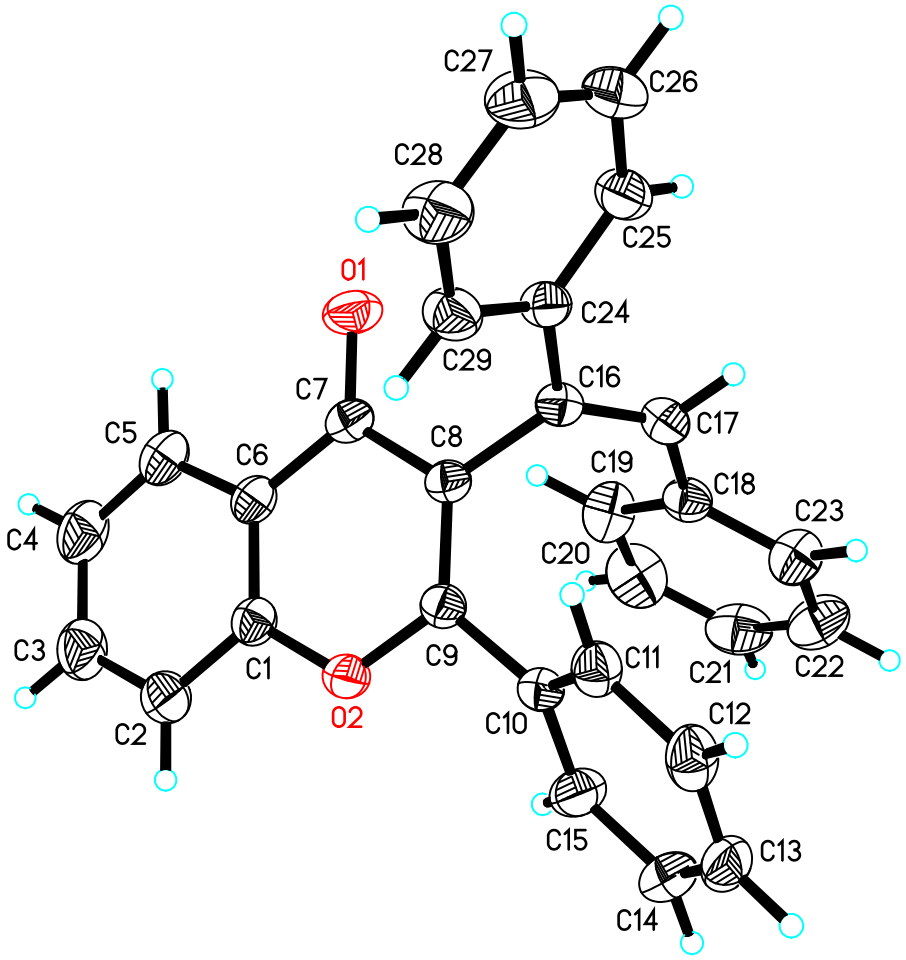
(Ortep ellipsoids are depicted at the 50% level)

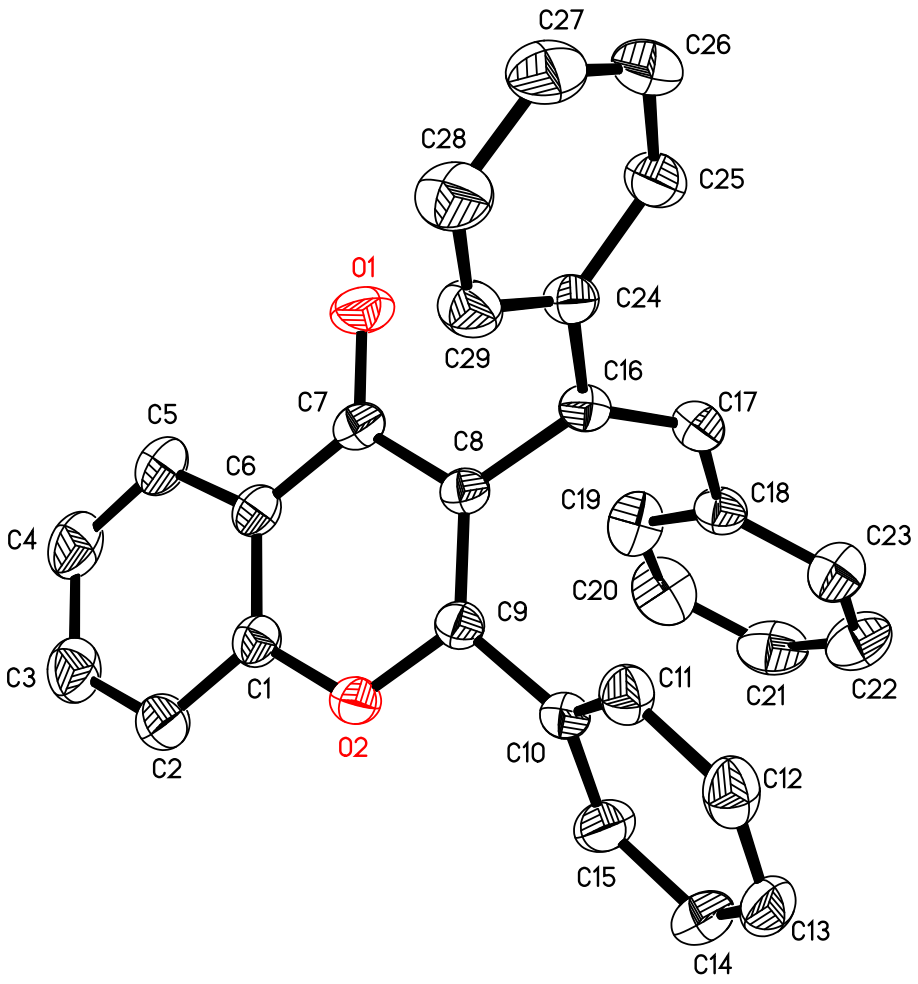


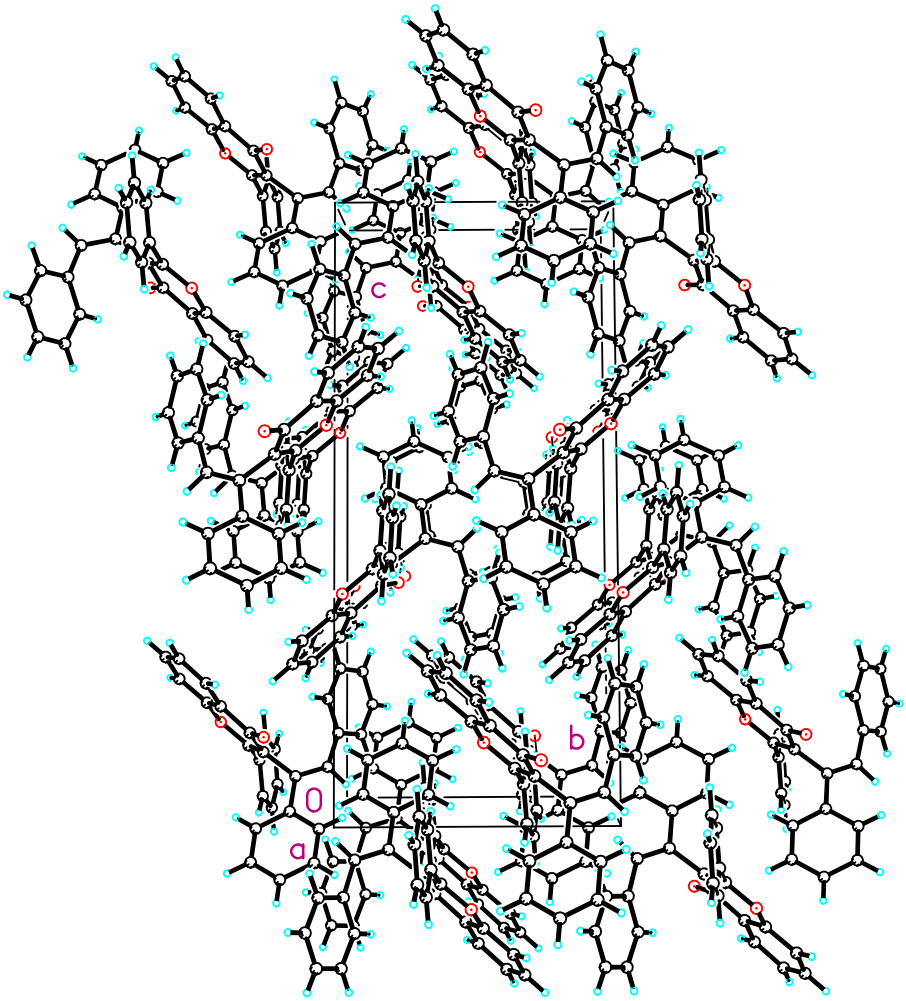
5a

Table 2. Crystal data and structure refinement for **5a**

Identification code	**5a**
Empirical formula	$C_{29}H_{20}O_2$
Formula weight	400.45
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic P 21/c
Unit cell dimensions	a = 10.1572(14) a= 90 °. b = 9.7577(14) b= 98.391(3) °. c = 21.796(3) Å g = 90 °.
Volume	2137.1(5) $Å^3$
Z, Calculated density	4, 1.245 Mg/m^3
Absorption coefficient	0.077 mm^{-1}
F(000)	840
Crystal size	0.200 x 0.170 x 0.130 mm^3
Theta range for data collection	1.889 to 25.999 °.
Limiting indices	-12<=h<=12, -12<=k<=11, -26<=l<=20
Reflections collected / unique	12450/4198 [R(int) = 0.0409]
Completeness to theta = 25.242 °	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6504
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4198 / 0 / 280
Goodness-of-fit on F^2	1.033
Final R indices [I>2sigma(I)]	R1 = 0.0437, wR2 = 0.1035
R indices (all data)	R1 = 0.0713, wR2 = 0.1149
Largest diff. peak and hole	0.175 and -0.138 e.$Å^{-3}$


C27
C26
C28
C25
O1
C24
C29
C16
C7
C17
C5
C6
C8
C19
C18
C23
C4
C20
C3
C1
C9
C11
C21
C22
O2
C10
C12
C15
C13
C14


C27
C26
C28
C25
O1
C24
C29
C16
C7
C17
C5
C8
C6
C18
C19
C23
C4
C20
C9
C3
C1
C11
C21
C22
O2
C10
C2
C12
C15
C13
C14


c
b
0
a