Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information

Electrooxidative Palladium- and Enantioselective Rhodium-Catalyzed [3+2] Spiroannulations

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Table of Contents

General Remarks

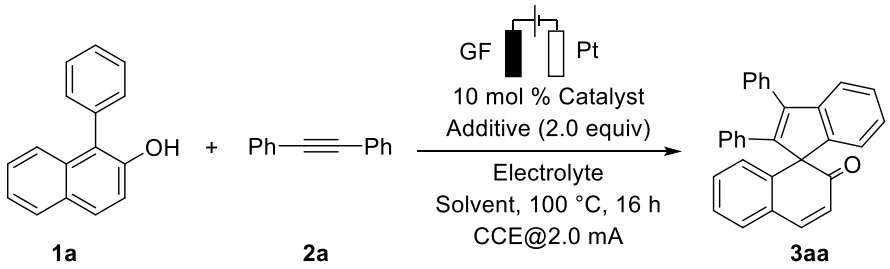
Catalytic reactions were carried out in undivided electrochemical cells (10 mL) using pre-dried glassware, unless otherwise stated.

1-aryl-naphthalenol were synthesized according to previously described methods.[1] Other chemicals were obtained from commercial sources and used without further purification. Platinum electrodes (10 mm × 15 mm × 0.25 mm, 99.9%; obtained from ChemPur® Karlsruhe, Germany) and graphite felt (GF) electrodes (10 mm × 15 mm × 6 mm, SIGRACELL® GFA 6 EA, obtained from SGL Carbon, Wiesbaden, Germany) were connected using stainless steel adapters. Electrocatalysis was conducted using an AXIOMET AX-3003P potentiostat in constant current mode.

Yields refer to isolated compounds, estimated to be >98% pure as determined by ^{1}H NMR. Flash chromatography: Merck silica gel 60 (40–63 μm). NMR: Spectra were recorded on Varian Mercury Vx 300, Varian VNMRS 300, Varian Inova 500, Varian Inova 600, Bruker Avance III 400, Bruker Avance III HD 400 and Bruker Avance III HD 500 instruments in the solvent indicated; chemical shifts (δ) are provided in ppm. IR spectra were recorded on a Bruker FT-IR alpha-P device. EI-MS was recorded on Joel AccuTof at 70 eV. ESI-MS was recorded on Bruker Daltonic micrOTOF. High resolution mass spectrometry (HR-MS) was recorded on micrOTOF, Bruker Daltonic. Melting points (m.p.) were measured on Stuart® melting point apparatus SMP3, Barloworld Scientific, values are uncorrected.

Optimization of the Reaction Conditions

Table S1. Optimization of the electrocatalytic dearomative spiroannulation.[a]

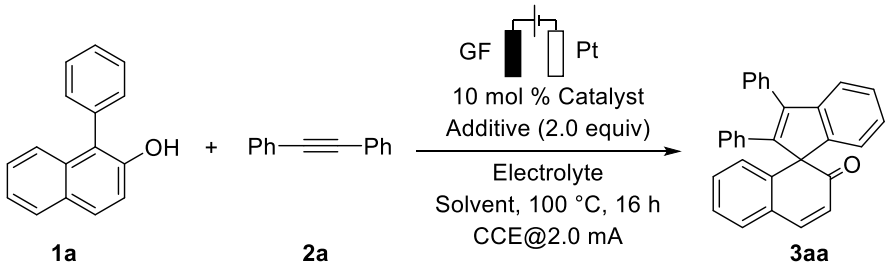


1a **2a** **3aa**

Entry	Catalyst	Electrolyte	Additive	Solvent	Current (mA)	Yield (%)
1	$[RuCl_2(p\text{-cymene})]_2$	---	---	DMA	2.0	Trace
2	$[RuCl_2(p\text{-cymene})]_2$	*n*-Bu_4NOAc	K_2CO_3	DMA	2.0	Trace
3	$[RuCl_2(p\text{-cymene})]_2$	*n*-Bu_4NOAc	K_2CO_3	DMF	4.0	Trace
4	$[RuCl_2(p\text{-cymene})]_2$	---	KPF_6	DMF	4.0	Trace
5	$[RuCl_2(p\text{-cymene})]_2$	---	$(1Ad)CO_2H$	*t*-AmOH/H_2O	4.0	Trace
6	$[RuCl_2(p\text{-cymene})]_2$	---	KOAc	*t*-AmOH/H_2O	4.0	Trace
7	$[RuCl_2(p\text{-cymene})]_2$	---	K_2HPO_4	*m*-Xylene	4.0	Trace
8	$[RuCl_2(p\text{-cymene})]_2$	*n*-Bu_4NOAc	K_2CO_3	dioxane/H_2O	2.0	Trace
9	$[Ru(OAc)_2(p\text{-cymene})]$	*n*-Bu_4NOAc	---	DMF	2.0	Trace
10	$[Ru(OAc)_2(p\text{-cymene})]$	*n*-Bu_4NOAc	Piv-Val-OH	DMF	2.0	Trace
11	$[Ru(OAc)_2(p\text{-cymene})]$	*n*-Bu_4NOAc	---	*t*-AmOH	2.0	Trace
12	$[Ru(OAc)_2(p\text{-cymene})]$	*n*-Bu_4NOAc	K_2CO_3	dioxane	4.0	Trace
13	$RuCl_3{\cdot}3H_2O$	*n*-Bu_4NOAc	K_2CO_3	DMF	2.0	Trace

[a] Reaction conditions: **1a** (88.0 mg, 0.40 mmol), **2a** (70.0 mg, 0.40 mmol), catalyst (10 mol %),electrolyte (1.0 equiv), additive (2.0 equiv), solvent (4.0 mL) at 100 °C, 16 h, under air, yield of isolated product.

Table S2. Optimization of the electrocatalytic dearomative spiroannulation.[a]

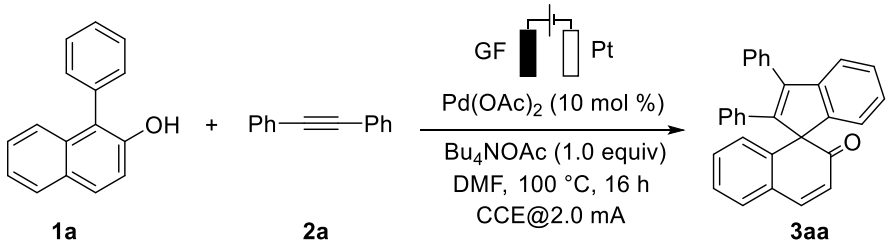


1a **2a** **3aa**

Entry	Catalyst	Electrolyte	Additive	Solvent	Current (mA)	Yield (%)
1	$[RhCp^*Cl_2]_2$	---	KOAc	DMF	4.0	Trace
2	$[RhCp^*Cl_2]_2$	*n*-Bu_4NOAc	K_2CO_3	*t*-AmOH/H_2O	4.0	Trace
3	$CoBr_2$	*n*-Bu_4NOAc	K_2CO_3	DMF	2.0	Trace
4	$Co(OAc)_2$	*n*-Bu_4NOAc	K_2CO_3	DMF	2.0	Trace
5	$Cp^*Co(CO)I_2$	*n*-Bu_4NOAc	K_2CO_3	DMF	2.0	Trace
6	$[Cp^*Co(MeCN)_3](SbF_6)_2$	*n*-Bu_4NOAc	K_2CO_3	DMF	2.0	Trace
7	$Pd(OAc)_2$	*n*-Bu_4NOAc	K_2CO_3	DMF	2.0	25[b,c]
8	$Pd(OAc)_2$	*n*-Bu_4NOAc	K_2CO_3	DMF	4.0	64[b,d]
9	**$Pd(OAc)_2$**	***n*-Bu_4NOAc**	K_2CO_3	**DMF**	**2.0**	**79[b]**
10	$Pd(OAc)_2$	*n*-Bu_4NOAc	---	DMF	---	15[b,e]

[a] Reaction conditions: **1a** (88.0 mg, 0.40 mmol), **2a** (70 .0mg, 0.40 mmol), catalyst (10 mol %),electrolyte (1.0 equiv), additive (2.0 equiv), solvent (4.0 mL) at 100 °C, 16 h, under air, yield of isolated product. [b] **1a** (0.80 mmol), **2a** (0.40 mmol), [c] $Pd(OAc)_2$ (5 mol %).[d] 8 h. [e] without current.

Table S3. Optimization of electrochemically enabled palladium-catalyzed dearomative spiroannulation.[a]



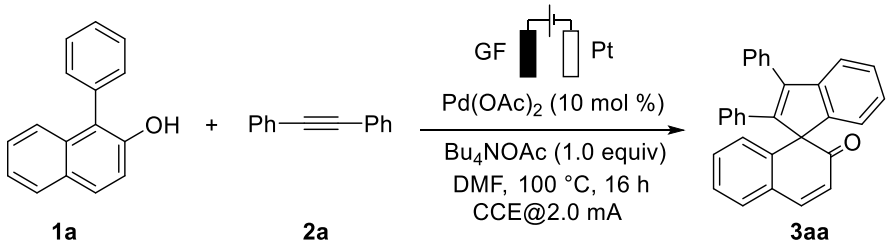
1a **2a** **3aa**

Entry	Catalyst	Electrolyte	Solvent	Current (mA)	Yield (%)
1	$Pd(OAc)_2$	---	DMF	2.0	13[b]
2	$Pd(OAc)_2$	---	*t*-AmOH/H_2O (3:1)	4.0	NR
3	$Pd(OAc)_2$	---	dioxane/H_2O (3:1)	4.0	Trace
4	$Pd(OAc)_2$	---	DMF/H_2O (3:1)	2.0	Trace
5	$Pd(OAc)_2$	---	MeOH/H_2O (3:1)	2.0	Trace[b]
6	$Pd(OAc)_2$	---	DMSO/H_2O (3:1)	2.0	Trace
7	$Pd(OAc)_2$	*n*-$BuNPF_6$	DMF	2.0	37
8	$Pd(OAc)_2$	*n*-$BuNBF_4$	DMF	2.0	45
9	$Pd(OAc)_2$	NMe_4Cl	DMF	2.0	46
10	$Pd(OAc)_2$	KCl	DMF	2.0	25
11	$Pd(OAc)_2$	*n*-Bu_4NI	DMF	2.0	33
12	$Pd(OAc)_2$	Et_4NClO_4	DMF	2.0	44
13	$Pd(OAc)_2$	*n*-Bu_4NClO_4	DMF	2.0	39
14	$Pd(OAc)_2$	*n*-Bu_4NOAc	DMF	2.0	50
15	$Pd(OAc)_2$	NMe_4Cl	DMF	2.0	71%[c]
16	$Pd(OAc)_2$	*n*-Bu_4NOAc	DMF	2.0	87%[c]

[a] Reaction conditions: **1a** (88.0 mg, 0.40 mmol), **2a** (70.0 mg, 0.40 mmol), catalyst (10 mol %), electrolyte (1.0 equiv), solvent (4.0 mL) at 100 °C, 16 h, under air, yield of isolated product. [b] at 60 °C. [c] **1a** (176.0 mg, 0.8 mmol), **2a** (70.0 mg, 0.40 mmol).

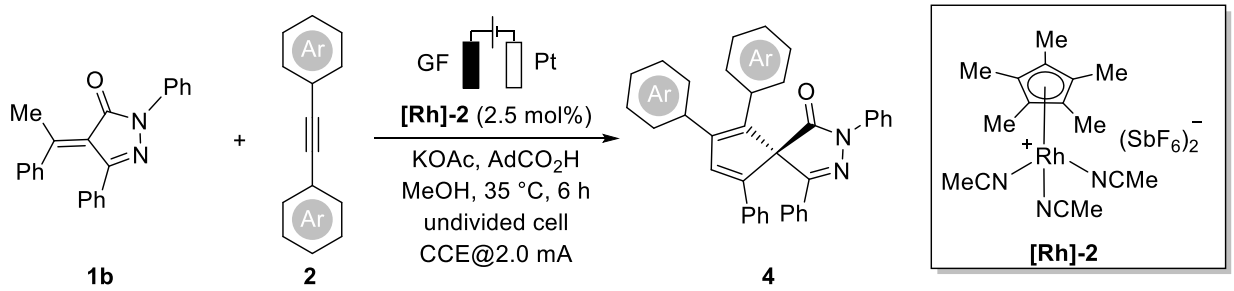
General procedures

General procedure A : Electrooxidative Palladium-Catalyzed [3+2] Dearomative Spiroannulation.



The electrocatalysis was carried out in an undivided cell under air with a graphite felt (GF) anode (10 mm × 15 mm × 6 mm) and a platinum cathode (10 mm × 15 mm × 0.25 mm). 1-Phenylnaphthalen-2-ol (**1a**) (176 mg, 0.80 mmol), 1,2-diphenylethyne (**2a**) (71.0 mg, 0.40 mmol), and *n*-Bu_4NOAc (0.40 mmol, 1.0 equiv) were dissolved in DMF (4.0 mL). Electrocatalysis was performed at 100 °C with a constant current of 2.0 mA maintained for 16 h. The GF anode was washed with CH_2Cl_2 (3×10 mL). Evaporation of the solvent and subsequent purification by column chromatography on silica gel with Ethyl acetate/*n*-hexane (1/5) afforded the corresponding products **3aa**.

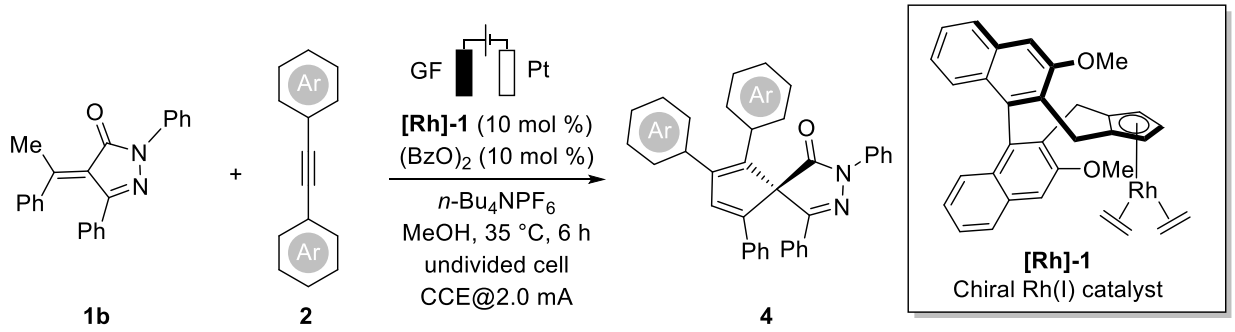
General procedure B : Electrooxidative Rhodium-Catalyzed [3+2] Dearomative Spiroannulation.



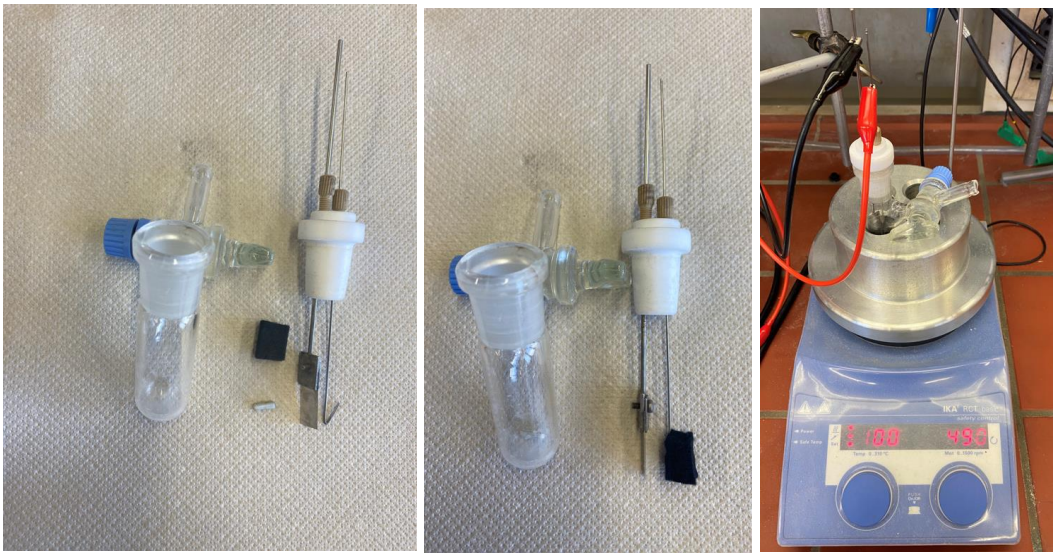
The electrocatalysis was carried out in an undivided cell under air with a graphite felt (GF) anode (10 mm × 15 mm × 6 mm) and a platinum cathode (10 mm × 15 mm × 0.25 mm). 2,5-diphenyl-4-(1-phenylethylidene)-2,4-dihydro-3H-pyrazol-3-one (**1b**) (51 mg, 0.15 mmol), 1,2-diphenylethyne (**2a**) (18.0 mg, 0.10 mmol), **[Rh]-2** (0.0025 mmol, 2.5 mol%), KOAc (0.20 mmol, 2.0 equiv) and AdCOOH (0.01 mmol, 10 mol%) were dissolved in MeOH (4.0 mL). Electrocatalysis was

performed at 35 °C with a constant current of 2.0 mA maintained for 6 h. The GF anode was washed with CH_2Cl_2 (3×10 mL). Evaporation of the solvent and subsequent purification by column chromatography on silica gel with Ethyl acetate/*n*-hexane (1/10) afforded the corresponding products **4**.

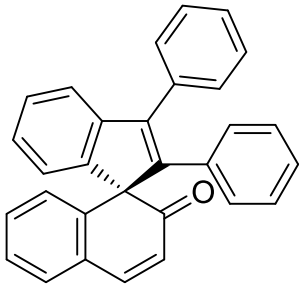
General procedure C : Electrooxidative Rhodium-Catalyzed [3+2] Dearomative Spiroannulation.



The electrocatalysis was carried out in an undivided cell under air with a graphite felt (GF) anode (10 mm × 15 mm × 6 mm) and a platinum cathode (10 mm × 15 mm × 0.25 mm). **[Rh]-1** (0.01 mmol, 10 mol%), $(BzO)_2$ (10 mol%) were dissolved in MeOH (4.0 mL) and the miaxture were stirred at 35 °C for half an hour. 2,5-diphenyl-4-(1-phenylethylidene)-2,4-dihydro-3H-pyrazol-3-one (**1b**) (51 mg, 0.15 mmol), 1,2-diphenylethyne (**2a**) (18.0 mg, 0.10 mmol), *n*-Bu_4NPF6 (0.30 mmol, 3.0 equiv) were dissolved in the solvent. Electrocatalysis was performed at 35 °C with a constant current of 2.0 mA maintained for 6 h. The GF anode was washed with CH_2Cl_2 (3×10 mL). Evaporation of the solvent and subsequent purification by column chromatography on silica gel with Ethyl acetate/*n*-hexane (1/10) afforded the corresponding products **4**.



Characterization Data of Products



2,3-Diphenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (3aa)

The general procedure **A** was followed using 1-phenylnaphthalen-2-ol (**1a**) (176 mg, 0.80 mmol) and 1,2-diphenylethyne (**2a**) (71.0 mg, 0.40 mmol). Purification by column chromatography (*n*-hexane/EtOAc = 10:1) yielded **3aa** (138 mg, 87%), as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 (d, J = 9.9 Hz, 1H), 7.58 (d, J = 7.5 Hz, 2H), 7.50 – 7.40 (m, 4H), 7.33 (d, J = 7.7 Hz, 1H), 7.27 (q, J = 7.3 Hz, 2H), 7.18 (t, J = 7.6 Hz, 1H), 7.09 (t, J = 7.3 Hz, 1H), 7.06 – 6.98 (m, 5H), 6.94 – 6.87 (m, 2H), 6.43 (d, J = 9.9 Hz, 1H).

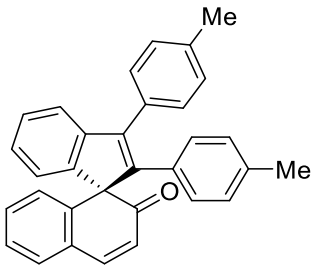
^{13}C NMR (101 MHz, $CDCl_3$): δ = 196.6 (C_q), 147.6 (C_q), 146.1 (CH), 145.4 (C_q), 145.0 (C_q), 144.6 (C_q), 141.0 (C_q), 135.1 (C_q), 134.3 (C_q), 130.6 (CH), 129.9 (CH), 129.6 (C_q), 129.4 (CH), 129.0 (CH), 128.8 (CH), 127.9 (CH), 127.8 (CH), 127.7 (CH), 127.5 (CH), 127.0 (CH), 126.8 (CH), 126.5 (CH), 126.3 (CH), 121.8 (CH), 121.6 (CH), 71.7 (C_q).

IR (ATR): $\tilde{\nu}$ = 3050, 1711, 1664, 1441, 1360, 1219, 1029, 759, 742, 702 cm^{-1}.

MS (ESI) m/z (relative intensity): 397 (100) $[M+H]^+$, 419 (60) $[M+Na]^+$.

HR-MS (ESI): m/z calcd for $C_{30}H_{21}O^+$ $[M+H]^+$: 397.1592, found: 397.1587.

The analytical data are in accordance with those reported in the literature.[2]



2,3-Di-*p*-tolyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (3ab)

The general procedure **A** was followed using 1-phenylnaphthalen-2-ol (**1a**) (176 mg, 0.80 mmol)

and 1,2-di-*p*-tolylethyne (82.0 mg, 0.40 mmol). Purification by column chromatography (*n*-hexane/EtOAc =10:1) yielded **3ab** (144 mg, 85%), as a as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68 (d, *J* = 9.9 Hz, 1H), 7.44 (dd, *J* = 7.7, 5.9 Hz, 3H), 7.27 (dd, *J* = 7.2, 3.1 Hz, 4H), 7.25 – 7.22 (m, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.05 – 6.95 (m, 3H), 6.85 – 6.74 (m, 4H), 6.41 (d, *J* = 9.9 Hz, 1H), 2.44 (s, 3H), 2.16 (s, 3H).

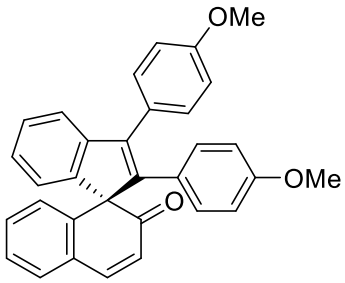
^{13}C NMR (101 MHz, $CDCl_3$): δ = 196.8 (C_q), 147.5 (C_q), 146.0 (CH), 145.7 (C_q), 144.6 (C_q), 144.0 (C_q), 141.4 (C_q), 137.4 (C_q), 136.6 (C_q), 132.3 (C_q), 131.5 (C_q), 130.6 (CH), 129.8 (CH), 129.6 (C_q), 129.5 (CH), 129.3 (CH), 128.9 (CH), 128.7 (CH), 127.6 (CH), 127.4 (CH), 126.8 (CH), 126.6 (CH), 126.0 (CH), 121.7 (CH), 121.5 (CH), 71.6 (C_q), 21.4 (CH_3), 21.1 (CH_3).

IR (ATR): $\tilde{\nu}$ = 3003, 1711, 1665, 1360, 1219, 1197, 1020, 815, 761, 745 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 425 (100) $[M+H]^+$, 447 (33) $[M+Na]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{32}H_{25}O^+$ $[M+H]^+$: 425.1905, found: 425.1900.

The analytical data are in accordance with those reported in the literature.[2]



2,3-Bis(4-methoxyphenyl)-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (3ac)

The general procedure **A** was followed using 1-phenylnaphthalen-2-ol (**1a**) (176.0 mg, 0.80 mmol) and 1,2-bis(4-methoxyphenyl)ethyne (95.0 mg, 0.40 mmol). Purification by column chromatography (*n*-hexane/EtOAc = 10:1) yielded **3ac** (151 mg, 83%), as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 10.0 Hz, 1H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 7.5 Hz, 1H), 7.30 (d, *J* = 7.9 Hz, 2H), 7.28 – 7.21 (m, 1H), 7.16 (td, *J* = 7.6, 1.4 Hz, 1H), 7.07 – 6.95 (m, 5H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.56 (d, *J* = 8.8 Hz, 2H), 6.42 (d, *J* = 9.9 Hz, 1H), 3.88 (s, 3H), 3.65 (s, 3H).

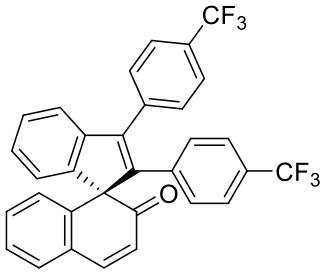
^{13}C NMR (101 MHz, $CDCl_3$): δ = 196.9 (C_q), 159.1 (C_q), 158.2 (C_q), 147.3 (C_q), 146.1 (CH), 145.7 (C_q), 144.1 (C_q), 142.8 (C_q), 141.4 (C_q), 130.7 (CH), 130.6 (CH), 130.2 (CH), 129.8 (CH), 129.5 (C_q), 127.6 (CH), 127.5 (C_q), 127.4 (CH), 127.0 (C_q), 126.8 (CH), 126.5 (CH), 125.8 (CH), 121.5 (CH), 121.4 (CH), 114.2 (CH), 113.4 (CH), 71.5 (C_q), 55.2 (CH_3), 54.9 (CH_3).

IR (ATR): $\tilde{\nu}$ = 2836, 1711, 1664, 1502, 1289, 1245, 1173, 1027, 819, 762 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 457 (100) $[M+H]^+$, 479 (30) $[M+Na]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{32}H_{25}O_3^+$ $[M+H]^+$: 457.1804, found: 457.1798.

The analytical data are in accordance with those reported in the literature.[2]



2,3-Bis[4-(trifluoromethyl)phenyl]-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (3ad)

The general procedure **A** was followed using 1-phenylnaphthalen-2-ol (**1a**) (176 mg, 0.8 mmol) and 1,2-bis[4-(trifluoromethyl)phenyl]ethyne (126 mg, 0.4 mmol). Purification by column chromatography (*n*-hexane/EtOAc = 10:1) yielded **3ad** (151 mg, 71%), as a as a yellow solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.78 – 7.69 (m, 3H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.35 – 7.24 (m, 5H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.14 (dt, *J* = 7.4, 3.9 Hz, 1H), 7.06 (d, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 8.0 Hz, 3H), 6.42 (d, *J* = 10.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 195.9 (C_q), 147.7 (C_q), 146.5 (CH), 145.2 (C_q), 144.6 (C_q), 144.2 (C_q), 140.0 (C_q), 138.4 (C_q), 137.5 (C_q), 130.9 (CH), 130.3 (CH), 130.1 (d, $^2J_{C-F}$ = 32.5 Hz, C_q), 129.8 (2 CH), 129.7 (C_q), 129.2 (CH), 128.1 (CH), 128.0 (CH), 127.2 (CH), 126.8 (CH), 126.4 (CH), 126.0 (q, $^3J_{C-F}$ = 23.1 Hz, CH), 125.1 (q, $^3J_{C-F}$ = 3.8 Hz, CH) 122.6 (d, $^2J_{C-F}$ = 19.0 Hz, C_q), 121.9 (d, $^4J_{C-F}$ = 1.9 Hz, CH), 71.9 (C_q).

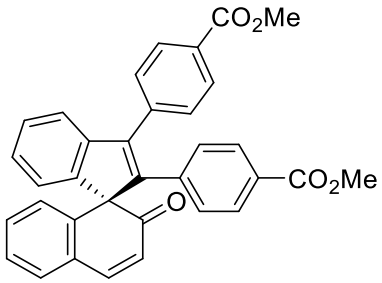
^{19}F NMR (282 MHz, $CDCl_3$): δ = -62.64 (d, *J* = 75.8 Hz).

IR (ATR): $\tilde{\nu}$ = 3060, 1664, 1615, 1317, 1161, 1106, 1065, 1017, 763, 747 cm^{-1}.

MS (ESI) m/z (relative intensity): 533 (100) $[M+H]^+$, 555 (20) $[M+Na]^+$.

HR-MS (ESI): m/z calcd for $C_{32}H_{19}F_6O^+$ $[M+H]^+$: 533.1340, found: 533.1335.

The analytical data are in accordance with those reported in the literature.[2]



Dimethyl 4,4'-{2'-oxo-2'*H*-spiro[indene-1,1'-naphthalene]-2,3-diyl}dibenzoate (3ae)

The general procedure **A** was followed using 1-phenylnaphthalen-2-ol (**1a**) (176 mg, 0.80 mmol) and dimethyl 4,4'-(ethyne-1,2-diyl)dibenzoate (118.0 mg, 0.40 mmol). Purification by column chromatography (*n*-hexane/EtOAc = 10:1) yielded **3ae** (125 mg, 61%), as a yellow solid.

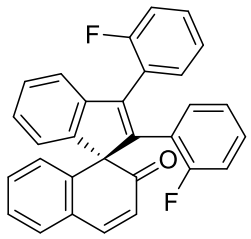
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (d, J = 8.2 Hz, 2H), 7.72 – 7.64 (m, 3H), 7.60 (d, J = 8.3 Hz, 2H), 7.44 (dd, J = 7.6, 1.4 Hz, 1H), 7.32 – 7.25 (m, 3H), 7.17 (td, J = 7.6, 1.4 Hz, 1H), 7.14 – 7.08 (m, 1H), 7.03 (d, J = 7.5 Hz, 1H), 6.89 (tt, J = 8.6, 1.6 Hz, 3H), 6.40 (d, J = 9.9 Hz, 1H), 3.96 (s, 3H), 3.79 (s, J = 1.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 196.0 (C_q), 166.7 (C_q), 166.5 (C_q), 147.7 (C_q), 146.4 (CH), 145.5 (C_q), 145.1 (C_q), 144.3 (C_q), 140.1 (C_q), 139.5 (C_q), 138.6 (C_q), 130.8 (CH), 130.2 (CH), 130.1 (CH), 129.8 (C_q), 129.6 (C_q), 129.5 (CH), 129.3 (CH), 128.9 (CH), 128.6 (C_q), 128.0 (CH), 127.9 (CH), 127.0 (CH), 126.8 (CH), 126.3 (CH), 122.0 (CH), 121.9 (CH), 71.8 (C_q), 52.2 (CH_3), 51.9 (CH_3).

IR (ATR): $\tilde{\nu}$ = 2950, 1709, 1664, 1605, 1434, 1271, 1113, 1018, 747, 709 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 513 (100) $[M+H]^+$, 535 (40) $[M+Na]^+$.

HR-MS (ESI): m/z calcd for $C_{34}H_{25}O_5^+$ $[M+H]^+$: 513.1702, found: 513.1697



2,3-Bis(2-fluorophenyl)-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (3af)

The general procedure **A** was followed using 1-phenylnaphthalen-2-ol (**1a**) (176.0 mg, 0.80 mmol) and 1,2-bis(2-fluorophenyl)ethyne (86.0 mg, 0.40 mmol). Purification by column chromatography (*n*-hexane/EtOAc = 10:1) yielded **3af** (140 mg, 81%), as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56 (d, J = 9.9 Hz, 1H), 7.42 – 7.27 (m, 5H), 7.23 (d, J = 7.5 Hz, 1H), 7.21 – 7.09 (m, 4H), 7.08 – 6.92 (m, 4H), 6.84 (t, J = 7.6 Hz, 1H), 6.75 (dd, J = 10.4, 8.3 Hz, 1H), 6.38 (d, J = 9.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 196.4 (C_q), 161.3 (C_q), 160.7 (C_q), 158.8 (C_q), 158.2 (C_q), 147.8 (C_q), 146.1 (CH), 141.5 (C_q), 144.1 (C_q), 139.5 (C_q), 130.4 (CH), 130.2 (CH), 130.2 (CH), 129.9 (CH), 129.8 (CH), 129.6 (CH), 129.4 (CH), 129.3 (CH), 127.8 (CH), 127.6 (CH), 127.5 (d, $^4J_{C-F}$ =

1.6 Hz, CH), 126.6 (CH), 126.5 (CH), 124.1(CH), 123.5 (d, $^{3}J_{C-F}$ = 3.6 Hz, CH), 122.4 (d, $^{2}J_{C-F}$ = 15.7 Hz, C_q), 121.9 (CH), 115.6 (d, $^{2}J_{C-F}$ = 23.1 Hz, CH), 72.7 (C_q).

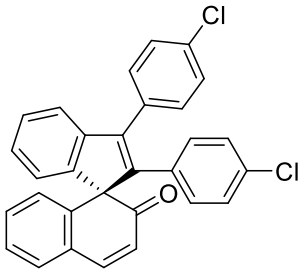
^{19}F NMR (376 MHz, $CDCl_3$): δ = -111.41 (d, J = 335.4 Hz).

IR (ATR): $\tilde{\nu}$ = 3051, 1711, 1657, 1482, 1452, 1361, 1220, 1102, 755, 744 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 433 (100) $[M+H]^+$, 455 (90) $[M+Na]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{30}H_{19}F_2O^+$ $[M+H]^+$: 433.1404, found: 433.1399.

The analytical data are in accordance with those reported in the literature.[3]



2,3-Bis(4-chlorophenyl)-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (3ag)

The general procedure **A** was followed using 1-phenylnaphthalen-2-ol (**1a**) (176.0 mg, 0.80 mmol) and 1,2-bis(4-chlorophenyl)ethyne (98.0 mg, 0.40 mmol). Purification by column chromatography (*n*-hexane/EtOAc = 10:1) yielded **3ag** (148 mg, 80%), as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 (d, J = 9.9 Hz, 1H), 7.53 – 7.40 (m, 5H), 7.34 – 7.25 (m, 3H), 7.18 (td, J = 7.6, 1.3 Hz, 1H), 7.09 (ddd, J = 8.3, 6.1, 2.4 Hz, 1H), 7.06 – 6.96 (m, 3H), 6.91 (d, J = 7.8 Hz, 1H), 6.78 (d, J = 8.5 Hz, 2H), 6.40 (d, J = 10.0 Hz, 1H).

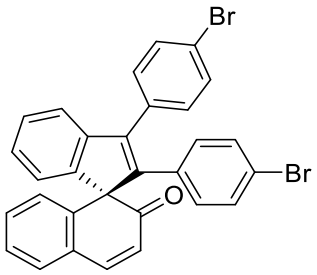
^{13}C NMR (101 MHz, $CDCl_3$): δ = 196.3 (C_q), 147.5 (C_q), 146.3 (CH), 144.6 (C_q), 144.4 (C_q), 144.0 (C_q), 140.3 (C_q), 134.0 (C_q), 133.1 (C_q), 133.1 (C_q), 132.6 (C_q), 130.8 (CH), 130.7 (CH), 130.2 (CH), 130.1 (CH), 129.6 (C_q), 129.2 (CH), 128.3 (CH), 127.9 (CH), 127.8 (CH), 126.8 (CH), 126.7 (CH), 126.4 (CH), 121.8 (CH), 121.7 (CH), 71.7 (C_q).

IR (ATR): $\tilde{\nu}$ = 3054, 1712, 1664, 1484, 1394, 1220, 1088, 1014, 818, 746 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 465 (100) $[M+H]^+$, 487 (10) $[M+Na]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{30}H_{19}Cl_2O^+$ $[M+H]^+$: 465.0813, found: 465.0807.

The analytical data are in accordance with those reported in the literature.[2]



2,3-Bis(4-bromophenyl)-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (3ah)

The general procedure **A** was followed using 1-phenylnaphthalen-2-ol (**1a**) (176.0 mg, 0.80 mmol) and 1,2-bis(4-bromophenyl)ethyne (134.0 mg, 0.40 mmol). Purification by column chromatography (*n*-hexane/EtOAc = 10:1) yielded **3ah** (115 mg, 52%), as a yellow solid.

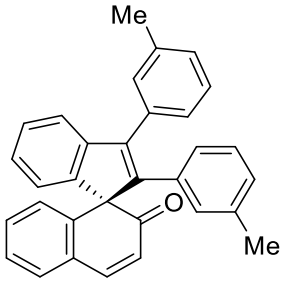
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68 (d, *J* = 9.9 Hz, 1H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 7.6 Hz, 1H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.33 – 7.23 (m, 3H), 7.21 – 7.12 (m, 3H), 7.12 – 7.05 (m, 1H), 7.01 (d, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 6.69 (d, *J* = 8.4 Hz, 2H), 6.38 (d, *J* = 9.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 196.2 (C_q), 147.6 (C_q), 146.3 (CH), 144.5 (C_q), 144.4 (C_q), 144.1 (C_q), 140.3 (C_q), 133.6 (C_q), 133.1 (C_q), 132.2 (CH), 131.3 (CH), 131.1 (CH), 130.8 (CH), 130.5 (CH), 130.1 (CH), 129.7 (C_q), 127.9 (CH), 127.9 (CH), 126.8 (CH), 126.8 (CH), 126.4 (CH), 122.2 (C_q), 121.8 (CH), 121.7 (CH), 121.4 (C_q), 71.7 (C_q).

IR (ATR): $\tilde{\nu}$ = 3053, 1665, 1481, 1393, 1071, 1010, 816, 762, 746, 734 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 552 (100) $[M+H]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{30}H_{19}Br_2O^+$ $[M+H]^+$: 552.9803, found: 552.9797.



2,3-Di-*m*-tolyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (3ai)

The general procedure **A** was followed using 1-phenylnaphthalen-2-ol (**1a**) (176.0 mg, 0.80 mmol) and 1,2-di-*m*-tolylethyne (82.0 mg, 0.40 mmol). Purification by column chromatography (*n*-hexane/EtOAc = 10:1) yielded **3ai** (153 mg, 91%), as a white solid.

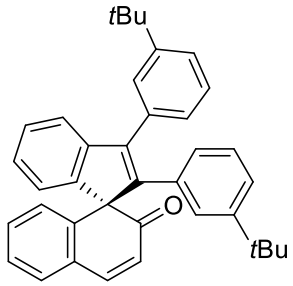
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 (d, *J* = 9.9 Hz, 1H), 7.48 – 7.34 (m, 4H), 7.33 – 7.22 (m, 4H), 7.18 (td, *J* = 7.5, 1.4 Hz, 1H), 7.10 – 6.97 (m, 4H), 6.95 – 6.82 (m, 2H), 6.74 – 6.63 (m, 2H), 6.44 (d, *J* = 9.9 Hz, 1H), 2.42 (s, 3H), 2.05 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 196.7 (C_q), 147.5 (C_q), 146.0 (CH), 145.6 (C_q), 144.8 (C_q), 144.6 (C_q), 141.3 (C_q), 138.3 (C_q), 137.1 (C_q), 135.2 (C_q), 134.1 (C_q), 130.6 (CH), 129.9 (CH), 129.8 (CH), 129.7 (CH), 129.6 (C_q), 128.6 (CH), 128.5 (CH), 127.7 (CH), 127.7 (CH), 127.6 (CH), 127.4 (CH), 126.8 (CH), 126.5 (CH), 126.5 (CH), 126.2 (CH), 126.1 (CH), 121.8 (CH), 121.5 (CH), 71.6 (C_q), 21.4 (CH_3), 21.3 (CH_3).

IR (ATR): $\tilde{\nu}$ = 2952, 1712, 1664, 1562, 1462, 1360, 1220, 762, 746, 699 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 425 (100) $[M+H]^+$, 447 (50) $[M+Na]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{32}H_{25}O^+$ $[M+H]^+$: 425.1905, found: 425.1902.



2,3-Di-*m*-tolyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (3aj)

The general procedure **A** was followed using 1-phenylnaphthalen-2-ol (**1a**) (176.0 mg, 0.80 mmol) and 1,2-bis[3-(*tert*-butyl)phenyl]ethyne (116.0 mg, 0.40 mmol). Purification by column chromatography (*n*-hexane/EtOAc = 10:1) yielded **3aj** (183 mg, 91%), as a white solid.

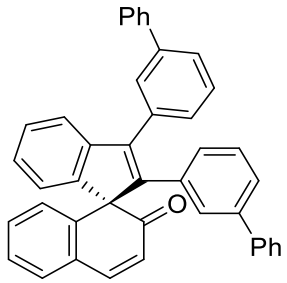
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (d, *J* = 9.9 Hz, 1H), 7.56 (d, *J* = 1.5 Hz, 1H), 7.51 – 7.36 (m, 4H), 7.36 – 7.26 (m, 3H), 7.25 – 7.15 (m, 1H), 7.08 (t, *J* = 7.3 Hz, 1H), 7.05 – 7.00 (m, 3H), 6.97 – 6.87 (m, 2H), 6.64 (dd, *J* = 7.8, 1.7 Hz, 1H), 6.45 (dd, *J* = 9.9, 1.3 Hz, 1H), 1.34 (s, 9H), 0.99 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 196.7 (C_q), 151.7 (C_q), 150.2 (C_q), 147.7 (C_q), 146.0 (CH), 145.9 (C_q), 145.5 (C_q), 144.8 (C_q), 141.6 (C_q), 135.2 (C_q), 133.6 (C_q), 130.7 (CH), 129.8 (CH), 129.6 (C_q), 128.5 (CH), 127.7 (CH), 127.5 (CH), 127.4 (CH), 126.9 (CH), 126.9 (CH), 126.6 (CH), 126.6 (CH), 126.4 (CH), 126.1 (CH), 125.7 (CH), 124.6 (CH), 123.8 (CH), 121.8 (CH), 121.6 (CH), 71.3 (C_q), 31.4 (CH_3), 30.9 (CH_3).

IR (ATR): $\tilde{\nu}$ = 2963, 1667, 1596, 1461, 1393, 1364, 1234, 1198, 745, 699 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 509 (100) $[M+H]^+$, 531 (40) $[M+Na]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{38}H_{37}O^+$ $[M+H]^+$: 509.2944, found: 509.2876.



2,3-Di{[1,1'-biphenyl]-3-yl}-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (3ak)

The general procedure **A** was followed using 1-phenylnaphthalen-2-ol (**1a**) (176.0 mg, 0.80 mmol) and 1,2-di([1,1'-biphenyl]-3-yl)ethyne (132.0 mg, 0.40 mmol). Purification by column chromatography (*n*-hexane/EtOAc = 10:1) yielded **3ak** (153 mg, 70%), as a yellow solid.

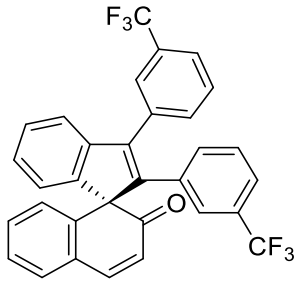
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.87 (s, 1H), 7.72 (d, J = 9.9 Hz, 2H), 7.61 (d, 4H), 7.50 – 7.35 (m, 5H), 7.33 – 7.27 (m, 7H), 7.20 (t, J = 7.6 Hz, 1H), 7.18 – 7.14 (m, 2H), 7.14 – 7.02 (m, 4H), 6.87 (d, J = 7.8 Hz, 1H), 6.47 (d, J = 9.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 196.5 (C_q), 147.7 (C_q), 146.2 (CH), 145.3 (C_q), 144.9 (C_q), 142.0 (C_q), 141.0 (C_q), 140.8 (C_q), 140.6 (C_q), 140.3 (C_q), 135.8 (C_q), 134.5 (C_q), 130.8 (CH), 129.9 (CH), 129.7 (C_q), 129.5 (CH), 128.7 (CH), 128.5 (CH), 128.5 (CH), 128.4 (CH), 128.3 (CH), 127.8 (CH), 127.6 (CH), 127.6 (CH), 127.4 (CH), 127.2 (CH), 127.1 (CH), 127.0 (CH), 126.7 (CH), 126.6 (CH), 126.5 (CH), 126.5 (CH), 125.7 (CH), 121.9 (CH), 121.7 (CH), 71.6 (C_q). One C_q is missing due to the overlap.

IR (ATR): $\tilde{\nu}$ = 2989, 1711, 1657, 1595, 1561, 1450, 1360, 1219, 757, 698 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 549 (100) $[M+H]^+$, 571 (30) $[M+Na]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{42}H_{29}O^+$ $[M+H]^+$: 549.2218, found: 549.2213.



2,3-Bis[3-(trifluoromethyl)phenyl]-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (3al)

The general procedure **A** was followed using 1-phenylnaphthalen-2-ol (**1a**) (176.0 mg, 0.80 mmol) and 1,2-bis[3-(trifluoromethyl)phenyl]ethyne (126.0 mg, 0.40 mmol). Purification by column chromatography (*n*-hexane/EtOAc = 10:1) yielded **3al** (111 mg, 52%), as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 (s, 1H), 7.73 – 7.67 (m, 3H), 7.59 (t, *J* = 7.7 Hz, 1H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.35 – 7.28 (m, 4H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.18 – 7.10 (m, 2H), 7.08 – 7.03 (m, 2H), 6.94 (t, *J* = 8.7 Hz, 2H), 6.41 (d, *J* = 10.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 196.0 (C_q), 147.7 (C_q), 146.4 (CH), 144.8 (C_q), 144.6 (C_q), 144.2 (C_q), 139.9 (C_q), 135.3 (C_q), 134.5 (C_q), 132.8 (d, $^4J_{C-F}$ = 1.4 Hz, CH), 132.0 (d, $^4J_{C-F}$ = 1.5 Hz, CH), 131.5 (d, $^2J_{C-F}$ = 32.4 Hz, C_q),130.9 (CH), 130.6 (C_q), 130.2 (CH), 130.2 (CH), 129.6 (CH), 128.7 (CH), 128.1 (CH), 128.1 (CH), 127.2 (CH), 126.9 (CH), 126.4 (CH), 126.1 (q, $^3J_{C-F}$ = 3.8 Hz, CH), 125.6 (q, $^3J_{C-F}$ = 4.0 Hz, CH), 125.0 (q, $^3J_{C-F}$ = 3.7 Hz, CH), 124.0 (q, $^3J_{C-F}$ = 3.7 Hz, CH), 122.4 (d, $^2J_{C-F}$ = 30.3 Hz, C_q), 121.9 (q, $^2J_{C-F}$ = 27.9 Hz, CH), 71.7 (C_q).

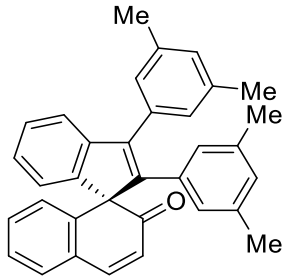
^{19}F NMR (376 MHz, $CDCl_3$): δ = -63.1 (d, *J* = 225.0 Hz).

IR (ATR): $\tilde{\nu}$ = 3063, 1665, 1325, 1301, 1166, 1119, 1073, 908, 762, 706 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 533 (100) $[M+H]^+$, 555 (80) $[M+Na]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{32}H_{19}F_6O^+$ $[M+H]^+$: 533.1340, found: 533.1335.

The analytical data are in accordance with those reported in the literature.[2]



2,3-Bis(3,5-dimethylphenyl)-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (3am)

The general procedure **A** was followed using 1-phenylnaphthalen-2-ol (**1a**) (176.0 mg, 0.80 mmol) and 1,2-bis(3,5-dimethylphenyl)ethyne (94.0 mg, 0.40 mmol). Purification by column chromatography (*n*-hexane/EtOAc = 10:1) yielded **3am** (121 mg, 67%), as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 10.0 Hz, 1H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.25 – 7.13 (m, 5H), 7.08 – 7.00 (m, 2H), 7.00 – 6.90 (m, 2H), 6.64 (s, 1H), 6.47 (s, 2H), 6.42 (d, *J* = 9.9 Hz, 1H), 2.35 (s, 6H), 1.98 (s, 6H).

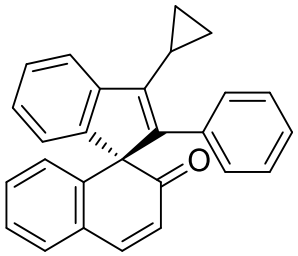
^{13}C NMR (101 MHz, CDCl3): δ = 196.8 (C_q), 147.4 (C_q), 146.0 (CH), 145.9 (C_q), 144.7 (C_q), 144.6 (C_q), 141.6 (C_q), 138.2 (C_q), 136.9 (C_q), 135.3 (C_q), 133.9 (C_q), 130.7 (CH), 129.7 (CH), 129.5 (C_q), 129.3 (CH), 128.7 (CH), 127.6 (CH), 127.4 (CH), 127.0 (CH), 126.9 (CH), 126.7 (CH), 126.6 (CH), 126.0 (CH), 121.9 (CH), 121.4 (CH), 71.5 (C_q), 21.3 (CH_3), 21.2 (CH_3).

IR (ATR): $\tilde{\nu}$ = 2915, 1713, 1665, 1598, 1562, 1462, 1196, 841, 761, 746 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 453 (100) $[M+H]^+$, 475 (33) $[M+Na]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{34}H_{29}O^+$ $[M+H]^+$: 453.2218, found: 453.2213.

The analytical data are in accordance with those reported in the literature.[2]



3-Cyclopropyl-2-phenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (3an)

The general procedure **A** was followed using 1-phenylnaphthalen-2-ol (**1a**) (176.0 mg, 0.80 mmol) and (cyclopropylethynyl)benzene (57.0 mg, 0.40 mmol). Purification by column chromatography (*n*-hexane/EtOAc = 10:1) yielded **3an** (108 mg, 75%), as a yellow solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.58 (dd, *J* = 9.0, 3.6 Hz, 2H), 7.37 (d, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 7.5 Hz, 1H), 7.17 – 7.09 (m, 6H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 7.5 Hz, 1H), 6.76 (d, *J* = 7.8 Hz, 1H), 6.30 (d, *J* = 9.9 Hz, 1H), 2.06 – 1.96 (m, 1H), 1.01 – 0.93 (m, 2H), 0.69 – 0.63 (m, 2H).

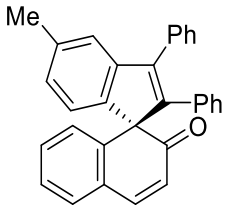
^{13}C NMR (101 MHz, $CDCl_3$): δ = 197.2 (C_q), 147.8 (C_q), 146.1 (C_q), 146.0 (CH), 145.7 (C_q), 144.6 (C_q), 141.2 (C_q), 134.8 (C_q), 130.4 (CH), 129.8 (C_q), 129.7 (CH), 129.0 (CH), 127.8 (CH), 127.6 (CH), 127.4 (CH), 127.0 (CH), 127.0 (CH), 126.6 (CH), 126.0 (CH), 121.5 (CH), 121.4 (CH), 71.5 (C_q), 9.0 (CH), 7.4 (CH_2), 7.4 (CH_2).

IR (ATR): $\tilde{\nu}$ = 2951, 1711, 1657, 1561, 1360, 1220, 1028, 822, 744, 693 cm^{-1}.

MS (ESI) m/z (relative intensity): 361 (100) $[M+H]^+$, 383 (40) $[M+Na]^+$.

HR-MS (ESI): m/z calcd for $C_{27}H_{21}O^+$ $[M+H]^+$: 361.1592, found: 361.1587.

The analytical data are in accordance with those reported in the literature.[2]



5-Methyl-2,3-diphenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (3ba)

The general procedure **A** was followed using 1-(p-tolyl)naphthalen-2-ol (187.0 mg, 0.80 mmol) and 1,2-diphenylethyne (**2a**) (71.0 mg, 0.40 mmol). Purification by column chromatography (*n*-hexane/EtOAc = 10:1) yielded **3ba** (135 mg, 82%), as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67 (d, *J* = 9.9 Hz, 1H), 7.60 – 7.53 (m, 2H), 7.51 – 7.45 (m, 2H), 7.45 – 7.38 (m, 2H), 7.33 – 7.24 (m, 1H), 7.17 (t, *J* = 7.6, 1.4 Hz, 1H), 7.11 (s, 1H), 7.04 – 6.96 (m, 4H), 6.94 – 6.82 (m, 4H), 6.41 (d, *J* = 9.9 Hz, 1H), 2.32 (s, 3H).

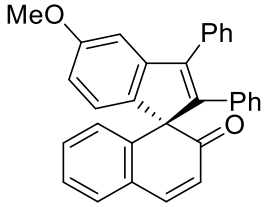
^{13}C NMR (101 MHz, $CDCl_3$): δ = 196.8 (C_q), 146.0 (CH), 145.5 (C_q), 145.2 (C_q), 144.9 (C_q), 144.6 (C_q), 141.3 (C_q), 137.6 (C_q), 135.3 (C_q), 134.3 (C_q), 130.6 (CH), 129.8 (CH), 129.6 (C_q), 129.5 (CH), 129.0 (CH), 128.8 (CH), 127.9 (CH), 127.8 (CH), 127.4 (CH), 127.1 (CH), 126.9 (CH), 126.8 (CH), 126.5 (CH), 122.5 (CH), 121.3 (CH), 71.3 (C_q), 21.5 (CH_3).

IR (ATR): $\tilde{\nu}$ = 3053, 1712, 1664, 1561, 1442, 1361, 1220, 870, 746, 702 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 411 (100) $[M+H]^+$, 433 (10) $[M+Na]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{31}H_{23}O^+$ $[M+H]^+$: 411.1749, found: 411.1741.

The analytical data are in accordance with those reported in the literature.[3]



5-Methoxy-2,3-diphenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (3bb)

The general procedure **A** was followed using 1-(4-methoxyphenyl)naphthalen-2-ol (200.0 mg, 0.80 mmol) and 1,2-diphenylethyne (**2a**) (71.0 mg, 0.40 mmol). Purification by column chromatography (*n*-hexane/EtOAc = 10:1) yielded **3bb** (138 mg, 81%), as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65 (d, *J* = 9.9 Hz, 1H), 7.59 – 7.51 (m, 2H), 7.50 – 7.38 (m, 4H), 7.30 – 7.24 (m, 1H), 7.17 (td, *J* = 7.6, 1.5 Hz, 1H), 7.04 – 6.96 (m, 4H), 6.92 (d, *J* = 8.3 Hz, 1H), 6.87 – 6.81 (m, 3H), 6.62 (dd, *J* = 8.3, 2.5 Hz, 1H), 6.39 (d, *J* = 9.9 Hz, 1H), 3.74 (s, 3H).

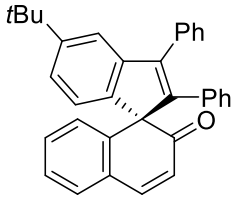
^{13}C NMR (101 MHz, $CDCl_3$): δ = 196.8 (C_q), 159.8 (C_q), 147.0 (C_q), 146.2 (C_q), 146.0 (CH), 144.5 (C_q), 141.4 (C_q), 139.9 (C_q), 135.0 (C_q), 134.3 (C_q), 130.6 (CH), 129.8 (CH), 129.6 (C_q), 129.4 (CH), 129.0 (CH), 128.8 (CH), 127.8 (CH), 127.8 (CH), 127.4 (CH), 127.0 (CH), 126.9 (CH), 126.4 (CH), 122.2 (CH), 111.8 (CH), 107.7 (CH), 71.0 (C_q), 55.4 (CH_3).

IR (ATR): $\tilde{\nu}$ = 2900, 1711, 1657, 1593, 1468, 1218, 1149, 1028, 745, 692 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 427 (100) $[M+H]^+$, 449 (50) $[M+Na]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{31}H_{23}O_2^+$ $[M+H]^+$: 427.1698, found: 427.1693.

The analytical data are in accordance with those reported in the literature.[2]



5-(*Tert*-butyl)-2,3-diphenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (3bc)

The general procedure **A** was followed using 1-(4-(*tert*-butyl)phenyl)naphthalen-2-ol (221.0 mg, 0.80 mmol) and 1,2-diphenylethyne (**2a**) (71.0 mg, 0.40 mmol). Purification by column chromatography (*n*-hexane/EtOAc = 10:1) yielded **3bc** (165 mg, 91%), as a yellow solid.

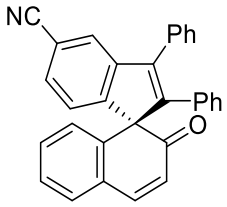
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67 (d, *J* = 9.9 Hz, 1H), 7.56 (d, *J* = 6.9 Hz, 2H), 7.52 – 7.37 (m, 4H), 7.32 (d, *J* = 1.7 Hz, 1H), 7.28 – 7.22 (m, 1H), 7.17 (td, *J* = 7.6, 1.4 Hz, 1H), 7.10 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.08 – 6.89 (m, 5H), 6.90 – 6.81 (m, 2H), 6.40 (d, *J* = 9.9 Hz, 1H), 1.27 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 196.9 (C_q), 150.8 (C_q), 146.1 (CH), 145.0 (C_q), 145.0 (C_q), 144.9 (C_q), 144.7 (C_q), 141.4 (C_q), 135.3 (C_q), 134.5 (C_q), 130.5 (CH), 129.8 (CH), 129.6 (C_q), 129.5 (CH), 129.1 (CH), 128.8 (CH), 127.9 (CH), 127.7 (CH), 127.4 (CH), 127.0 (CH), 126.8 (CH), 126.5 (CH), 123.5 (CH), 121.0 (CH), 118.9 (CH), 71.4 (C_q), 34.8 (C_q), 31.5 (CH_3).

IR (ATR): $\tilde{\nu}$ = 3053, 1663, 1562, 1394, 1264, 1234, 1124, 870, 730, 700 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 453 (100) $[M+H]^+$, 475 (60) $[M+Na]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{34}H_{29}O^+$ $[M+H]^+$: 453.2218, found: 453.2213.



2'-Oxo-2,3-diphenyl-2'*H*-spiro[indene-1,1'-naphthalene]-5-carbonitrile (3bd)

The general procedure **A** was followed using 4-(2-hydroxynaphthalen-1-yl)benzonitrile (196.0 mg, 0.80 mmol) and 1,2-diphenylethyne (**2a**) (71.0 mg, 0.40 mmol). Purification by column chromatography (*n*-hexane/EtOAc = 10:1) yielded **3bd** (140 mg, 83%), as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 (d, *J* = 9.9 Hz, 1H), 7.56 (s, 1H), 7.51 – 7.42 (m, 6H), 7.39 – 7.30 (m, 2H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.10 – 6.97 (m, 4H), 6.92 (d, *J* = 7.8 Hz, 1H), 6.85 (d, *J* = 7.3 Hz, 2H), 6.41 (d, *J* = 9.9 Hz, 1H).

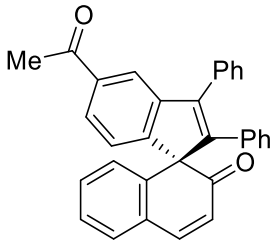
^{13}C NMR (101 MHz, $CDCl_3$): δ = 195.1 (C_q), 151.9 (C_q), 147.4 (C_q), 146.6 (C_q), 146.6 (CH), 143.1 (C_q), 139.1 (C_q), 133.8 (C_q), 133.3 (C_q), 130.9 (CH), 130.3 (CH), 130.2 (CH), 129.6 (C_q), 129.2

(CH), 129.1 (CH), 129.0 (CH), 128.4 (CH), 128.2 (CH), 128.1 (CH), 127.7 (CH), 126.8 (CH), 126.3 (CH), 124.9 (CH), 122.4 (CH), 118.9 (C_q), 111.7 (C_q), 71.8 (C_q).

IR (ATR): $\tilde{\nu}$ = 3003, 1712, 1439, 1418, 1356, 1219, 1092, 901, 786, 528 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 422 (100) $[M+H]^+$, 444 (20) $[M+Na]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{31}H_{20}NO^+$ $[M+H]^+$: 422.1545, found: 422.1539.



5-Acetyl-2,3-diphenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (3be)

The general procedure **A** was followed using 1-(4-(2-hydroxynaphthalen-1-yl)phenyl)ethan-1-one (210.0 mg, 0.80 mmol) and 1,2-diphenylethyne (**2a**) (71.0 mg, 0.40 mmol). Purification by column chromatography (*n*-hexane/EtOAc = 10:1) yielded **3be** (161 mg, 92%), as a yellow solid.

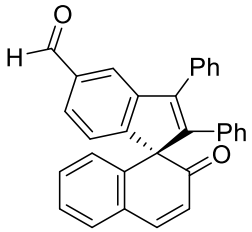
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 1.5 Hz, 1H), 7.74 – 7.64 (m, 2H), 7.54 (d, *J* = 6.7 Hz, 2H), 7.51 – 7.39 (m, 4H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.09 (d, *J* = 7.8 Hz, 1H), 7.04 – 6.93 (m, 4H), 6.85 (dd, *J* = 7.6, 1.7 Hz, 2H), 6.41 (d, *J* = 9.9 Hz, 1H), 2.53 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 197.7 (C_q), 195.7 (C_q), 152.4 (C_q), 146.4 (C_q), 146.1 (CH), 143.9 (C_q), 139.9 (C_q), 137.0 (C_q), 134.4 (C_q), 133.8 (C_q), 130.8 (CH), 130.1 (CH), 129.6 (C_q), 129.3 (CH), 129.0 (CH), 129.0 (CH), 128.1 (CH), 128.0 (CH), 127.9 (CH), 127.3 (CH), 127.0 (CH), 126.8 (CH), 126.3 (CH), 121.7 (CH), 121.3 (CH), 71.6 (C_q), 26.7 (CH_3).

IR (ATR): $\tilde{\nu}$ = 2951, 1711, 1681, 1662, 1424, 1360, 1232, 746, 693, 600 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 439 (100) $[M+H]^+$, 461 (5) $[M+Na]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{32}H_{23}O_2^+$ $[M+H]^+$: 439.1698, found: 439.1694.



2'-Oxo-2,3-diphenyl-2'*H*-spiro[indene-1,1'-naphthalene]-5-carbaldehyde (3bf)

The general procedure **A** was followed using 4-(2-hydroxynaphthalen-1-yl)benzaldehyde (198.0

mg, 0.80 mmol) and 1,2-diphenylethyne (**2a**) (71.0 mg, 0.40 mmol). Purification by column chromatography (*n*-hexane/EtOAc = 10:1) yielded **3bf** (132 mg, 78%), as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.95 (s, 1H), 7.80 (s, 1H), 7.71 (d, *J* = 10.0 Hz, 1H), 7.61 (d, *J* = 7.8, 1.4 Hz, 1H), 7.54 (d, *J* = 6.8 Hz, 2H), 7.51 – 7.40 (m, 4H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.23 – 7.13 (m, 2H), 7.07 – 6.98 (m, 3H), 6.95 (d, *J* = 7.8 Hz, 1H), 6.89 – 6.82 (m, 2H), 6.42 (d, *J* = 9.9 Hz, 1H).

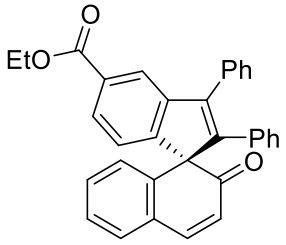
^{13}C NMR (101 MHz, $CDCl_3$): δ = 195.5 (C_q), 191.9 (CHO), 153.8 (C_q), 146.7 (C_q), 146.6 (C_q), 146.5 (CH), 143.7 (C_q), 139.7 (C_q), 136.3 (C_q), 134.3 (C_q), 133.7 (C_q), 130.9 (CH), 130.2 (CH), 129.6 (C_q), 129.3 (CH), 129.0 (CH), 129.0 (CH), 128.9 (CH), 128.2 (CH), 128.1 (CH), 128.0 (CH), 127.5 (CH), 126.8 (CH), 126.4 (CH), 122.2 (CH), 122.2 (CH), 71.7 (C_q).

IR (ATR): $\tilde{\nu}$ = 3050, 1695, 1657, 1593, 1561, 1394, 1196, 813, 733, 701 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 425 (100) $[M+H]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{31}H_{21}O_2^+$ $[M+H]^+$: 425.1542, found: 425.1536.

The analytical data are in accordance with those reported in the literature.[2]



Ethyl 2'-oxo-2,3-diphenyl-2'*H*-spiro[indene-1,1'-naphthalene]-5-carboxylate (3bg)

The general procedure **A** was followed using ethyl 4-(2-hydroxynaphthalen-1-yl)benzoate (234.0 mg, 0.80 mmol) and 1,2-diphenylethyne (**2a**) (71.0 mg, 0.40 mmol). Purification by column chromatography (*n*-hexane/EtOAc = 10:1) yielded **3bg** (157 mg, 84%), as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (s, 1H), 7.81 (d, *J* = 8.3 Hz, 1H), 7.69 (d, *J* = 9.9 Hz, 1H), 7.54 (d, *J* = 7.1 Hz, 2H), 7.52 – 7.39 (m, 4H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.10 – 6.91 (m, 5H), 6.89 – 6.81 (m, 2H), 6.41 (d, *J* = 9.9 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H).

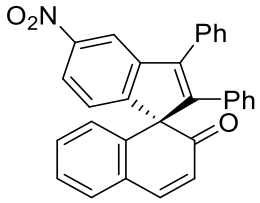
^{13}C NMR (101 MHz, $CDCl_3$): δ = 195.8 (C_q), 166.4 (C_q), 152.2 (C_q), 146.3 (CH), 146.2 (C_q), 145.8 (C_q), 144.0 (C_q), 140.1 (C_q), 134.5 (C_q), 133.9 (C_q), 130.8 (CH), 130.3 (C_q), 130.1 (CH), 129.6 (C_q), 129.4 (CH), 129.0 (CH), 128.9 (CH), 128.0 (CH), 128.0 (CH), 128.0 (CH), 127.9 (CH), 127.3 (CH), 126.8 (CH), 126.4 (CH), 122.7 (CH), 121.6 (CH), 71.6 (C_q), 60.9 (CH_2), 14.3 (CH_3).

IR (ATR): $\tilde{\nu}$ = 3545, 1714, 1665, 1285, 1247, 1231, 1089, 745, 702 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 469 (100) $[M+H]^+$, 491 (30) $[M+Na]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{33}H_{25}O_3^+$ $[M+H]^+$: 469.1804, found: 469.1798.

The analytical data are in accordance with those reported in the literature.[2]



5-Nitro-2,3-diphenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (3bh)

The general procedure **A** was followed using 1-(4-nitrophenyl)naphthalen-2-ol (212.0 mg, 0.80 mmol) and 1,2-diphenylethyne (**2a**) (71.0 mg, 0.40 mmol). Purification by column chromatography (*n*-hexane/EtOAc = 10:1) yielded **3bh** (166 mg, 94%), as a yellow solid.

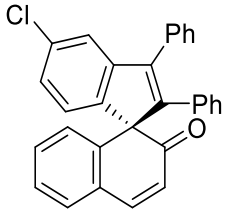
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 (d, *J* = 2.1 Hz, 1H), 7.98 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.72 (d, *J* = 9.9 Hz, 1H), 7.64 – 7.40 (m, 6H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.12 (d, *J* = 8.4 Hz, 1H), 7.09 – 6.97 (m, 3H), 6.93 (d, *J* = 7.6 Hz, 1H), 6.85 (d, *J* = 7.5 Hz, 2H), 6.42 (d, *J* = 9.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 194.9 (C_q), 153.7 (C_q), 148.3 (C_q), 148.1 (C_q), 147.3 (C_q), 146.7 (CH), 143.1 (C_q), 139.0 (C_q), 133.7 (C_q), 133.3 (C_q), 131.0 (CH), 130.4 (CH), 129.6 (C_q), 129.2 (CH), 129.2 (CH), 129.0 (CH), 128.5 (CH), 128.3 (CH), 128.1 (CH), 127.8 (CH), 126.8 (CH), 126.2 (CH), 122.2 (CH), 121.8 (CH), 116.5 (CH), 71.5 (C_q).

IR (ATR): $\tilde{\nu}$ = 3050, 1712, 1665, 1562, 1520, 1343, 1220, 831, 740, 703 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 442 (100) $[M+H]^+$, 464 (60) $[M+Na]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{30}H_{20}NO_3^+$ $[M+H]^+$: 442.1443, found: 442.1441.



5-Chloro-2,3-diphenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (3bi)

The general procedure **A** was followed using 1-(4-chlorophenyl)naphthalen-2-ol (203.0 mg, 0.80 mmol) and 1,2-diphenylethyne (**2a**) (71.0 mg, 0.40 mmol). Purification by column chromatography (*n*-hexane/EtOAc = 5:1) yielded **3bi** (161 mg, 93%), as a yellow solid.

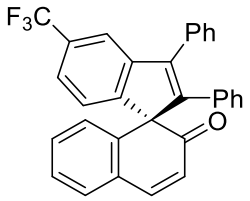
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67 (d, *J* = 9.9 Hz, 1H), 7.52 (d, *J* = 6.7 Hz, 2H), 7.50 – 7.39 (m, 4H), 7.35 – 7.27 (m, 2H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.08 – 6.90 (m, 6H), 6.85 (d, *J* = 7.1 Hz, 2H), 6.40 (d, *J* = 9.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 196.0 (C_q), 147.3 (C_q), 146.8 (C_q), 146.3 (CH), 145.9 (C_q), 143.7 (C_q), 140.3 (C_q), 134.4 (C_q), 133.9 (C_q), 133.8 (C_q), 130.7 (CH), 130.0 (CH), 129.6 (C_q), 129.3 (CH), 129.0 (CH), 129.0 (CH), 128.1 (CH), 128.0 (CH), 127.8 (CH), 127.3 (CH), 126.8 (CH), 126.3 (CH), 126.2 (CH), 122.7 (CH), 121.9 (CH), 71.1(C_q) .

IR (ATR): $\tilde{\nu}$ = 3050, 1711, 1657, 1455, 1360, 1219, 1071, 864, 743, 703 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 431 (100) $[M+H]^+$, 453 (50) $[M+Na]^+$.

HR-MS (ESI): m/z calcd for $C_{30}H_{20}ClO^+$ $[M+H]^+$: 431.1203, found: 431.1201.



2,3-Diphenyl-5-(trifluoromethyl)-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (3bj)

The general procedure **A** was followed using 1-[4-(trifluoromethyl)phenyl]naphthalen-2-ol (230 mg, 0.8 mmol) and 1,2-diphenylethyne (**2a**) (71 mg, 0.4 mmol). Purification by column chromatography (*n*-hexane/EtOAc = 5:1) yielded **3bj** (150 mg, 81%), as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 (d, *J* = 9.9 Hz, 1H), 7.56 – 7.41 (m, 7H), 7.37 – 7.28 (m, 2H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 7.9 Hz, 1H), 7.06 – 6.97 (m, 3H), 6.94 (d, *J* = 7.9 Hz, 1H), 6.85 (d, *J* = 7.8 Hz, 2H), 6.42 (d, *J* = 9.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 195.7 (C_q), 151.0 (C_q), 151.0 (C_q), 147.0 (C_q), 146.5 (CH), 146.3 (C_q), 143.7 (C_q), 139.8 (C_q), 134.2 (C_q), 133.7 (C_q), 130.9 (CH), 130.2 (CH), 129.7 (C_q), 129.4 (CH), 129.1 (CH), 128.2 (CH), 128.0 (CH), 127.5 (CH), 126.9 (CH), 126.4 (CH), 123.3 (q, $^3J_{C-F}$ = 3.9 Hz, CH), 122.0 (CH), 118.5 (q, $^3J_{C-F}$ = 3.7 Hz, CH), 71.6 (C_q).

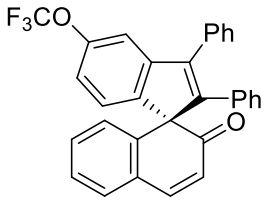
^{19}F NMR (282 MHz, $CDCl_3$): δ = -62.1 (s).

IR (ATR): $\tilde{\nu}$ = 3050, 1668, 1350, 1315, 1263, 1170, 1121, 1060, 746, 700 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 465 (100) $[M+H]^+$, 487 (80) $[M+Na]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{31}H_{20}F_3O^+$ $[M+H]^+$: 465.1466, found: 465.1461.

The analytical data are in accordance with those reported in the literature.[2]



2,3-Diphenyl-5-(trifluoromethoxy)-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (3bk)

The general procedure **A** was followed using 1-(4-(trifluoromethoxy)phenyl)naphthalen-2-ol (243.0 mg, 0.80 mmol) and 1,2-diphenylethyne (**2a**) (71.0 mg, 0.40 mmol). Purification by column chromatography (*n*-hexane/EtOAc = 10:1) yielded **3bk** (169 mg, 88%), as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68 (d, J = 9.9 Hz, 1H), 7.56 – 7.40 (m, 6H), 7.30 (t, J = 7.4 Hz, 1H), 7.21 (t, J = 7.5 Hz, 1H), 7.13 (s, 1H), 7.06 – 6.90 (m, 6H), 6.87 – 6.81 (m, 2H), 6.40 (d, J = 9.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 196.0 (C_q), 149.2 (q, $^{4}J_{C-F}$ = 1,9 Hz, CH), 149.2, 149.2, 149.2, 147.5 (C_q), 147.2 (C_q), 146.3 (CH), 145.9 (C_q), 143.7 (C_q), 140.2 (C_q), 134.3 (C_q), 133.8 (C_q), 130.80 (CH), 130.08 (CH), 129.60 (C_q), 129.31 (CH), 129.06 (CH), 129.00 (CH), 128.18 (CH), 128.0 (CH), 127.9 (CH), 127.4 (CH), 126.9 (CH), 126.4 (CH), 122.6 (CH), 118.7 (CH), 114.7 (CH), 71.2 (C_q).

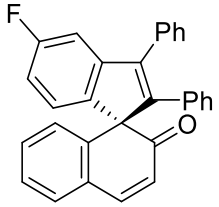
^{19}F NMR (282 MHz, $CDCl_3$): δ = -57.7 (s).

IR (ATR): $\tilde{\nu}$ = 3050, 1664, 1594, 1466, 1253, 1195, 1118, 865, 745, 701 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 481 (100) $[M+H]^+$, 503 (20) $[M+Na]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{31}H_{20}F_3O_2^+$ $[M+H]^+$: 481.1415, found: 481.1410.

The analytical data are in accordance with those reported in the literature.[2]



5-Fluoro-2,3-diphenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (3bl)

The general procedure **A** was followed using 1-(4-fluorophenyl)naphthalen-2-ol (190.0 mg, 0.80 mmol) and 1,2-diphenylethyne (**2a**) (71.0 mg, 0.40 mmol). Purification by column chromatography (*n*-hexane/EtOAc = 5:1) yielded **3bl** (139 mg, 84%), as a yellow solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.67 (d, J = 9.9 Hz, 1H), 7.55 – 7.38 (m, 6H), 7.28 (dd, J = 13.3, 5.6 Hz, 1H), 7.19 (t, J = 7.6 Hz, 1H), 7.06 – 6.90 (m, 6H), 6.84 (d, J = 7.1 Hz, 2H), 6.75 (td, J = 8.7, 2.4 Hz, 1H), 6.39 (d, J = 9.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 196.3 (C_q), 163.0 (d, $^1J_{C-F}$ = 244.8 Hz, C_q), 147.7 (d, $^3J_{C-F}$ = 8.8 Hz, C_q), 147.1 (C_q), 146.2 (CH), 143.8 (d, $^4J_{C-F}$ = 3.2 Hz, C_q), 143.1 (d, $^4J_{C-F}$ = 2.6 Hz, C_q), 140.6 (C_q), 134.5 (C_q), 133.9 (C_q), 130.7 (CH), 130.0 (CH), 129.6 (C_q), 129.3 (CH), 129.0 (CH), 128.9 (CH), 128.1 (CH), 128.0 (CH), 127.7 (CH), 127.3 (CH), 126.8 (CH), 126.4 (CH), 122.7 (d, $^3J_{C-F}$ = 9.2 Hz, CH), 112.9 (d, $^2J_{C-F}$ = 23.5 Hz, CH), 109.1 (d, $^2J_{C-F}$ = 24.3 Hz, CH), 71.0 (C_q).

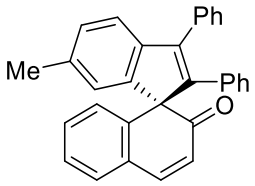
^{19}F NMR (376 MHz, $CDCl_3$): δ = -114.3 (td, J = 9.1, 5.0 Hz).

IR (ATR): $\tilde{\nu}$ = 3060, 1712, 1665, 1593, 1466, 1200, 1140, 872, 745, 702 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 415 (100) $[M+H]^+$, 437 (70) $[M+Na]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{30}H_{20}FO^+$ $[M+H]^+$: 415.1498, found: 415.1493.

The analytical data are in accordance with those reported in the literature.[2]



6-Methyl-2,3-diphenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (3bm)

The general procedure **A** was followed using 1-(m-tolyl)naphthalen-2-ol (187 mg, 0.2 mmol) and 1,2-diphenylethyne (**2a**) (71 mg, 0.4 mmol). Purification by column chromatography (*n*-hexane/EtOAc = 10:1) yielded **3bm** (131 mg, 80%), as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 (d, J = 9.9 Hz, 1H), 7.56 (d, 2H), 7.51 – 7.39 (m, 4H), 7.35 – 7.16 (m, 3H), 7.08 (d, J = 7.9 Hz, 1H), 7.05 – 6.95 (m, 4H), 6.95 – 6.82 (m, 3H), 6.43 (d, J = 9.9 Hz, 1H), 2.26 (s, 3H).

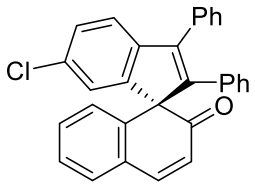
^{13}C NMR (101 MHz, CDCl3): δ = 196.8 (Cq), 147.9 (Cq), 146.1 (CH), 144.5 (Cq), 144.1 (Cq), 142.7 (Cq), 141.3 (Cq), 136.2 (Cq), 135.3 (Cq), 134.4 (Cq), 130.6 (CH), 129.8 (CH), 129.6 (Cq), 129.4 (CH), 129.0 (CH), 128.7 (CH), 128.5 (CH), 127.8 (CH), 127.7 (CH), 127.4 (CH), 126.9 (CH), 126.8 (CH), 126.5 (CH), 122.4 (CH), 121.5 (CH), 71.4 (Cq), 21.4 (CH_3).

IR (ATR): $\tilde{\nu}$ = 3020, 1711, 1657, 1360, 1219, 1029, 845, 743, 700, 530 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 411 (100) $[M+H]^+$, 433 (70) $[M+Na]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{31}H_{23}O^+$ $[M+H]^+$: 411.1749, found: 411.1743.

The analytical data are in accordance with those reported in the literature.[2]



6-Chloro-2,3-diphenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (3bn)

The general procedure **A** was followed using 1-(3-chlorophenyl)naphthalen-2-ol (203 mg, 0.8 mmol) and 1,2-diphenylethyne (**2a**) (71 mg, 0.4 mmol). Purification by column chromatography (*n*-hexane/EtOAc = 10:1) yielded **3bn** (141 mg, 82%), as a yellow solid

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 9.9 Hz, 1H), 7.57 – 7.39 (m, 6H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.21 (d, *J* = 5.6 Hz, 3H), 7.06 – 6.93 (m, 5H), 6.83 (dd, *J* = 7.6, 1.6 Hz, 2H), 6.41 (d, *J* = 9.9 Hz, 1H).

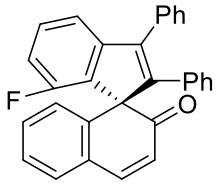
^{13}C NMR (101 MHz, $CDCl_3$): δ = 195.9 (C_q), 149.0 (C_q), 146.4 (CH), 145.5 (C_q), 144.0 (C_q), 143.8 (C_q), 140.1 (C_q), 134.7 (C_q), 133.9 (C_q), 131.9 (C_q), 130.8 (CH), 130.1 (CH), 129.6 (C_q), 129.4 (CH), 129.0 (CH), 128.9 (CH), 128.0 (CH), 128.0 (CH), 128.0 (CH), 127.9 (CH), 127.2 (CH), 126.9 (CH), 126.4 (CH), 122.6 (CH), 122.2 (CH), 71.3 (C_q).

IR (ATR): $\tilde{\nu}$ = 3053, 1657, 1561, 1441, 1233, 1197, 822, 777, 729, 689 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 431 (100) $[M+H]^+$, 453 (60) $[M+Na]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{30}H_{20}ClO^+$ $[M+H]^+$: 431.1203, found: 431.1197.

The analytical data are in accordance with those reported in the literature.[4]



7-Fluoro-2,3-diphenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (3bo)

The general procedure **A** was followed using 1-(2-fluorophenyl)naphthalen-2-ol(190.0 mg, 0.80 mmol) and 1,2-diphenylethyne (**2a**) (71.0 mg, 0.40 mmol). Purification by column chromatography (*n*-hexane/EtOAc = 5:1) yielded **3bo** (90 mg, 54%), as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 9.9 Hz, 1H), 7.45 (d, *J* = 6.9 Hz, 2H), 7.42 – 7.25 (m, 7H), 7.16 (d, *J* = 7.6 Hz, 1H), 7.06 – 6.94 (m, 4H), 6.81 (t, *J* = 8.7 Hz, 1H), 6.76 – 6.69 (m, 2H), 6.37 (d, *J* = 9.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 195.7 (C_q), 158.3 (C_q), 155.8 (C_q), 149.1 (d, $^3J_{C-F}$ = 5.3 Hz, C_q), 148.3 (d, $^4J_{C-F}$ = 1.5 Hz, C_q), 146.1 (CH), 143.3 (d, $^4J_{C-F}$ = 2.5 Hz, C_q), 138.4 (C_q), 135.0 (d, $^2J_{C-F}$ = 15.9 Hz, C_q), 134.1 (d, $^1J_{C-F}$ = 40.2 Hz, C_q), 130.4 (C_q), 130.35 (CH), 130.0 (d, $^3J_{C-F}$ = 7.3 Hz, CH), 129.7 (CH), 129.5 (CH), 128.9 (CH), 128.6 (CH), 127.9 (CH), 127.8 (CH), 127.4 (CH), 126.8 (CH), 126.8 (CH), 117.4 (d, $^4J_{C-F}$ = 3.0 Hz, CH), 113.8 (d, $^2J_{C-F}$ = 20.1 Hz, CH), 69.0 (d, $^3J_{C-F}$ = 2.0 Hz, C_q).

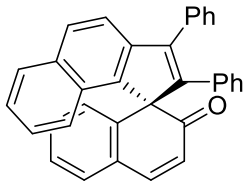
^{19}F NMR (376 MHz, $CDCl_3$): δ = -119.6 (dd, J = 9.2, 5.0 Hz).

IR (ATR): $\tilde{\nu}$ = 3050, 1663, 1616, 1487, 1469, 1240, 1201, 769, 734, 700 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 415 (100) $[M+H]^+$, 437 (10) $[M+Na]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{30}H_{20}FO^+$ $[M+H]^+$: 415.1498, found: 415.1493.

The analytical data are in accordance with those reported in the literature.[2]



2,3-Diphenyl-2'*H*-spiro[cyclopenta[a]naphthalene-1,1'-naphthalen]-2'-one (3bp)

The general procedure **A** was followed using [1,2'-binaphthalen]-2-ol (216.0 mg, 0.80 mmol) and 1,2-diphenylethyne (**2a**) (71.0 mg, 0.40 mmol) .Purification by column chromatography (*n*-hexane/EtOAc = 10:1) yielded **3bp** (162 mg, 91%), as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93 – 7.84 (m, 2H), 7.66 (d, J = 8.5 Hz, 1H), 7.60 (d, J = 9.9 Hz, 1H), 7.47 (d, J = 7.5 Hz, 2H), 7.43 – 7.25 (m, 7H), 7.18 – 7.11 (m, 2H), 7.11 – 7.05 (m, 1H), 7.00 (t, J = 7.5 Hz, 2H), 6.81 (d, J = 7.8 Hz, 1H), 6.71 (d, J = 7.6 Hz, 2H), 6.41 (d, J = 9.9 Hz, 1H).

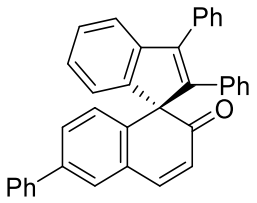
^{13}C NMR (101 MHz, $CDCl_3$): δ = 196.7 (C_q), 150.1 (C_q), 145.9 (CH), 145.8 (C_q),144.6 (C_q), 143.4 (C_q), 140.0 (C_q), 134.4 (C_q), 134.3 (C_q), 133.1 (C_q), 130.6 (CH), 130.3 (C_q), 129.7 (CH), 129.6 (CH), 129.1 (CH), 129.0 (CH), 128.9 (CH), 128.4 (CH), 128.1 (C_q), 127.7 (CH), 127.7 (CH), 127.6 (CH), 127.3 (CH), 127.3 (CH), 127.3 (CH), 127.0 (CH), 124.9 (CH), 123.3 (CH), 119.8 (CH), 71.4 (C_q).

IR (ATR): $\tilde{\nu}$ = 3053, 1656, 1560, 1485, 1263, 1235, 1200, 820, 735, 701 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 447 (100) $[M+H]^+$, 469 (50) $[M+Na]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{34}H_{23}O^+$ $[M+H]^+$: 447.1749, found: 447.1744.

The analytical data are in accordance with those reported in the literature.[2]



2,3,6'-Triphenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (3bq)

The general procedure **A** was followed using 1,6-diphenylnaphthalen-2-ol (237.0 mg, 0.20 mmol) and 1,2-diphenylethyne (**2a**) (71.0 mg, 0.40 mmol). Purification by column chromatography (*n*-hexane/EtOAc=10:1) yielded **3bq** (177 mg, 94%), as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 (d, *J* = 9.9 Hz, 1H), 7.66 (d, *J* = 1.9 Hz, 1H), 7.57 (dd, *J* = 7.5, 2.6 Hz, 4H), 7.50 – 7.30 (m, 9H), 7.13 – 6.98 (m, 6H), 6.94 – 6.89 (m, 2H), 6.46 (d, *J* = 9.9 Hz, 1H).

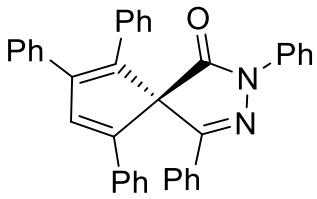
^{13}C NMR (101 MHz, $CDCl_3$): δ = 196.6 (C_q), 147.6 (C_q), 146.1 (CH), 145.4 (C_q), 144.9 (C_q), 144.7 (C_q), 140.5 (C_q), 139.9 (C_q), 139.7 (C_q), 135.1 (C_q), 134.3 (C_q), 130.0 (C_q), 129.5 (CH), 129.3 (CH), 129.1 (CH), 128.9 (CH), 128.8 (CH), 128.4 (CH), 128.0 (CH), 127.8 (CH), 127.8 (CH), 127.7 (CH), 127.3 (CH), 127.0 (CH), 126.9 (CH), 126.8 (CH), 126.3 (CH), 121.9 (CH), 121.7 (CH), 71.5 (C_q).

IR (ATR): $\tilde{\nu}$ = 3050, 1664, 1483, 1264, 1218, 1188, 1029, 895, 729, 690 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 473 (100) $[M+H]^+$, 495 (80) $[M+Na]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{36}H_{25}O^+$ $[M+H]^+$: 473.1905, found: 473.1900.

The analytical data are in accordance with those reported in the literature.[4]



2,4,6,7,9-Pentaphenyl-2,3-diazaspiro[4.4]nona-3,6,8-trien-1-one (*rac*-4a)

The general procedure **B** was followed using 2,5-diphenyl-4-(1-phenylethylidene)-2,4-dihydro-3H-pyrazol-3-one (**1b**) (51.0 mg, 0.15 mmol) and 1,2-diphenylethyne (**2a**) (18.0 mg, 0.10 mmol). Purification by column chromatography (*n*-hexane/EtOAc=10:1) yielded ***rac*-4a** (34 mg, 67%), as a yellow solid.

(*S*)-2,4,6,7,9-pentaphenyl-2,3-diazaspiro[4.4]nona-3,6,8-trien-1-one (4a')

The general procedure **C** was followed using 2,5-diphenyl-4-(1-phenylethylidene)-2,4-dihydro-

3H-pyrazol-3-one (**1b**) (51.0 mg, 0.15 mmol) and 1,2-diphenylethyne (**2a**) (18.0 mg, 0.10 mmol). Purification by column chromatography (*n*-hexane/EtOAc=10:1) yielded **4a'** (30 mg, 57%), as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 – 7.84 (m, 2H), 7.83 – 7.77 (m, 2H), 7.60 (s, 1H), 7.47 – 7.40 (m, 4H), 7.39 – 7.27 (m, 10H), 7.25 – 7.08 (m, 5H), 7.04 – 6.97 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.3 (C_q), 156.2 (C_q), 145.5 (C_q), 145.3 (C_q), 140.3 (C_q), 137.9 (C_q), 135.3 (CH), 134.4 (C_q), 133.5 (C_q), 133.2 (C_q), 131.1 (C_q), 130.8 (CH), 129.0 (CH), 128.9 (CH), 128.8 (CH), 128.5 (CH), 128.4 (CH), 128.4 (CH), 128.1 (CH), 128.0 (CH), 128.0 (CH), 125.8 (CH), 125.7 (CH), 125.2 (CH), 119.8 (CH), 76.6 (C_q).

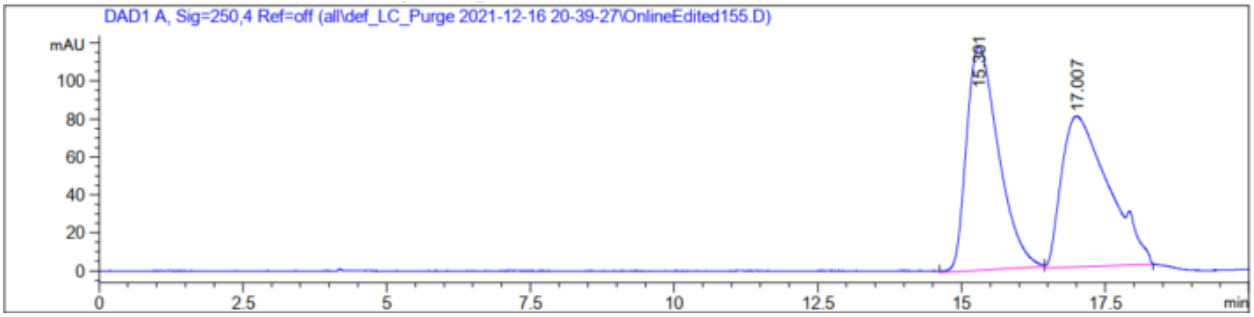
IR (ATR): $\tilde{\nu}$ = 3062, 1712, 1595, 1492, 1445, 1300, 1135, 754, 732, 687 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 515 (40) $[M+H]^+$, 537 (60) $[M+Na]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{37}H_{27}N_2O^+$ $[M+H]^+$: 515.2118, found: 515.2118.

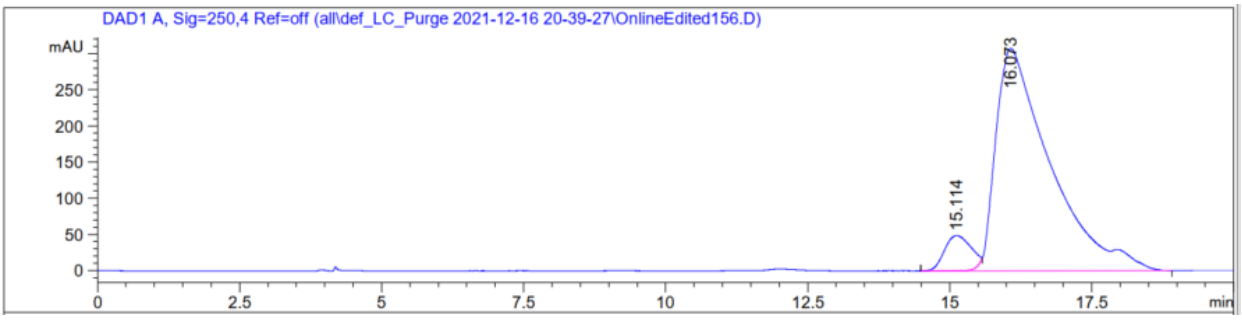
HPLC separation (Chiralpak® IC-3, *n*-hexane/*i*-PrOH 99:1, 1.0 mL/min, detection at 250 nm): tr (major) = 16.1 min, tr (minor) = 15.1 min, 93 : 7 er.

$[\alpha]_D^{20}$: -205.0 (c = 0.1, $CHCl_3$).



Signal 1: DAD1 A, Sig=250,4 Ref=off

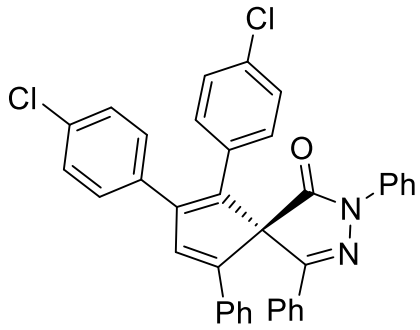
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.301	MM R	0.6444	4552.94629	117.75687	50.2104
2	17.007	MM R	0.9486	4514.78711	79.32169	49.7896



Signal 1: DAD1 A, Sig=250,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.114	BV E	0.3927	1561.50330	48.61350	7.0911
2	16.073	VV R	0.8875	2.04591e4	307.62772	92.9089

The analytical data are in accordance with those reported in the literature.[5]



6,7-Bis(4-chlorophenyl)-2,4,9-triphenyl-2,3-diazaspiro[4.4]nona-3,6,8-trien-1-one (*rac*-4b)

The general procedure **B** was followed using 2,5-diphenyl-4-(1-phenylethylidene)-2,4-dihydro-3H-pyrazol-3-one (**1b**) (51.0 mg, 0.15 mmol) and 1,2-bis(4-chlorophenyl)ethyne (25.0 mg, 0.10 mmol). Purification by column chromatography (*n*-hexane/EtOAc=10:1) yielded ***rac*-4b** (41 mg, 71%), as a yellow solid.

(S)-6,7-bis(4-chlorophenyl)-2,4,9-triphenyl-2,3-diazaspiro[4.4]nona-3,6,8-trien-1-one (4b')

The general procedure **C** was followed using 2,5-diphenyl-4-(1-phenylethylidene)-2,4-dihydro-3H-pyrazol-3-one (**1b**) (51.0 mg, 0.15 mmol) and 1,2-bis(4-chlorophenyl)ethyne (18.0 mg, 0.10 mmol). Purification by column chromatography (*n*-hexane/EtOAc=10:1) yielded **4b'** (40 mg, 68%), as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 – 7.82 (m, 2H), 7.75 – 7.69 (m, 2H), 7.49 (s, 1H), 7.46 – 7.34 (m, 3H), 7.34 – 7.27 (m, 8H), 7.26 – 7.16 (m, 4H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.9 (C_q), 155.9 (C_q), 146.1 (C_q), 145.1 (C_q), 139.2 (C_q), 137.7 (C_q), 134.6 (CH), 134.3 (C_q), 134.2 (C_q), 132.9 (C_q), 132.5 (C_q), 131.7 (C_q), 131.0 (CH), 130.8 (C_q), 130.1 (CH), 129.7 (CH), 129.1 (CH), 129.0 (CH), 129.0 (CH), 128.9 (CH), 128.8 (CH), 128.4 (CH), 126.0 (CH), 125.7 (CH), 125.2 (CH), 119.6 (CH), 76.5 (C_q).

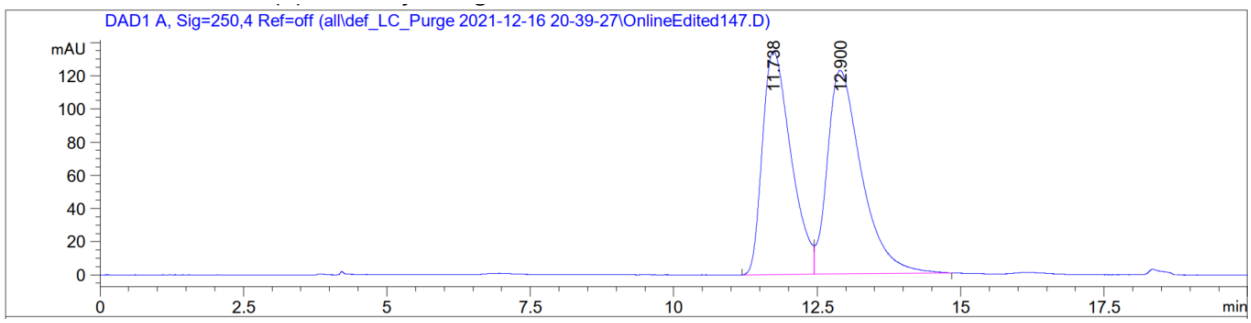
IR (ATR): $\tilde{\nu}$ = 1714, 1595, 1494, 1316, 1299, 1137, 832, 755, 688 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 583 (30) $[M+H]^+$, 605 (100) $[M+Na]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{37}H_{25}Cl_2N_2O^+$ $[M+H]^+$: 583.1338, found: 583.1332.

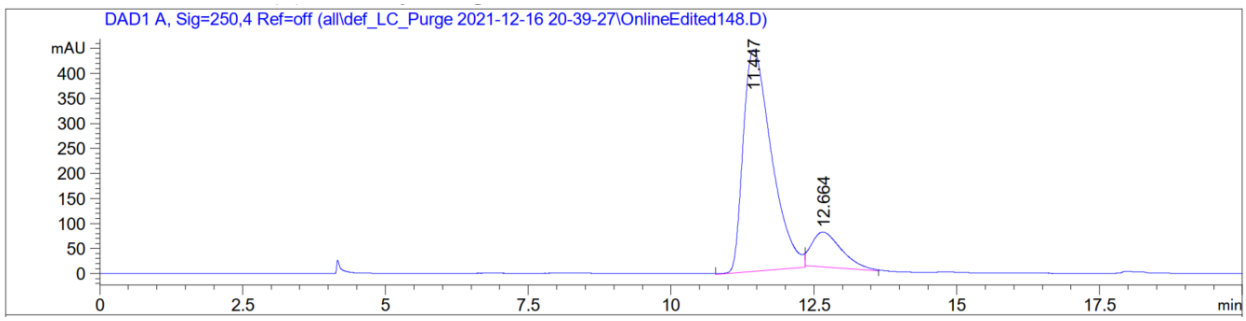
HPLC separation (Chiralpak® IC-3, *n*-hexane/*i*-PrOH 99:1, 1.0 mL/min, detection at 250 nm): tr (major) = 11.4 min, tr (minor) = 12.7 min, 86 : 14 er.

$[\alpha]_D^{20}$: +14.0 (c = 0.1, $CHCl_3$).



Signal 1: DAD1 A, Sig=250,4 Ref=off

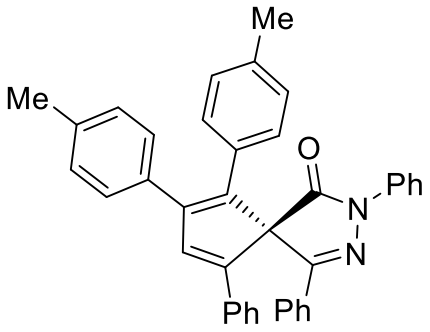
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.738	BV	0.5014	4669.72900	134.71169	47.8135
2	12.900	VB	0.5644	5096.81396	122.74881	52.1865



Signal 1: DAD1 A, Sig=250,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.447	MM R	0.5759	1.53153e4	443.23203	85.7030
2	12.664	MM R	0.6123	2554.90430	69.54311	14.2970

The analytical data are in accordance with those reported in the literature.[5]



2,4,9-Triphenyl-6,7-di-p-tolyl-2,3-diazaspiro[4.4]nona-3,6,8-trien-1-one (*rac*-4c)

The general procedure **B** was followed using 2,5-diphenyl-4-(1-phenylethylidene)-2,4-dihydro-3H-pyrazol-3-one (**1b**) (51.0 mg, 0.15 mmol) and 1,2-di-p-tolylethyne(21.0 mg, 0.10 mmol). Purification by column chromatography (*n*-hexane/EtOAc=10:1) yielded ***rac*-4c** (38 mg, 69%), as a yellow solid.

(*S*)-2,4,9-triphenyl-6,7-di-p-tolyl-2,3-diazaspiro[4.4]nona-3,6,8-trien-1-one (4c')

The general procedure **C** was followed using 2,5-diphenyl-4-(1-phenylethylidene)-2,4-dihydro-3H-pyrazol-3-one (**1b**) (51.0 mg, 0.15 mmol) and 1,2-di-p-tolylethyne (21.0 mg, 0.10 mmol). Purification by column chromatography (*n*-hexane/EtOAc=10:1) yielded **rac-4c'** (30 mg, 54%), as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 – 7.83 (m, 2H), 7.81 – 7.73 (m, 2H), 7.54 (s, 1H), 7.47 – 7.38 (m, 2H), 7.35 – 7.27 (m, 7H), 7.26 – 7.19 (m, 3H), 7.19 – 7.13 (m, 1H), 7.11 – 7.06 (m, 2H), 6.92 – 6.83 (m, 4H), 2.33 (s, 3H), 2.21 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.5 (C_q), 156.5 (C_q), 145.0 (C_q), 144.9 (C_q), 139.8 (C_q), 138.0 (C_q), 137.8 (C_q), 137.7 (C_q), 135.6 (CH), 133.4 (C_q), 131.6 (C_q), 131.1 (C_q), 130.7 (CH), 130.7 (C_q), 129.2 (CH), 129.1 (CH), 129.0 (CH), 128.9 (CH), 128.8 (CH), 128.6 (CH), 128.3 (CH), 127.9 (CH), 125.9 (CH), 125.6 (CH), 125.1 (CH), 119.7 (CH), 76.6 (C_q), 21.3 (CH_3), 21.2 (CH_3).

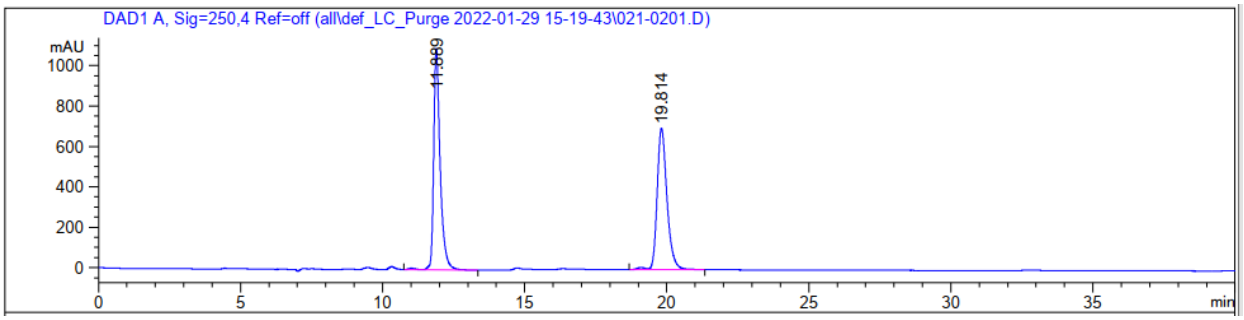
IR (ATR): $\tilde{\nu}$ = 1716, 1595, 1498, 1317, 1300, 1137, 820, 756, 689 cm^{-1}.

MS (ESI) *m/z* (relative intensity): 543 (100) $[M+H]^+$, 565 (60) $[M+Na]^+$.

HR-MS (ESI): *m/z* calcd for $C_{39}H_{31}N_2O^+$ $[M+H]^+$: 543.2436, found: 543.2431.

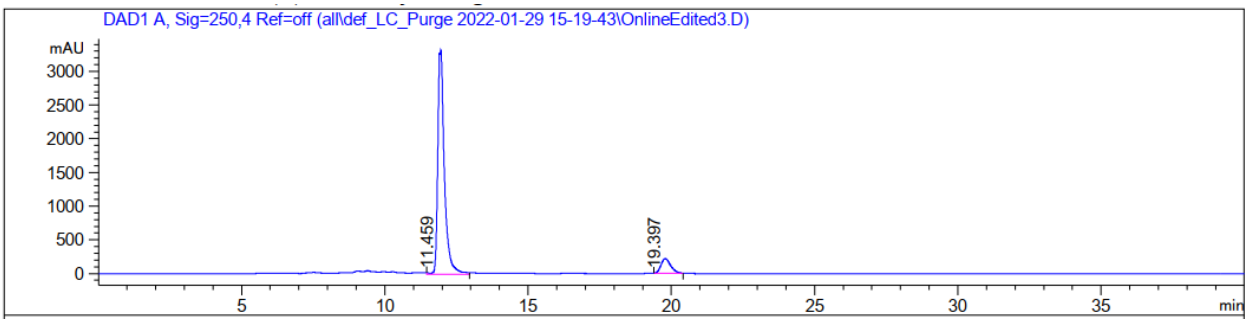
HPLC separation (Chiralpak® IE-3, MeOH/*i*-PrOH 90:10, 0.5 mL/min, detection at 250 nm): tr (major) = 11.5 min, tr (minor) = 19.4 min, 91 : 9 er.

$[\alpha]_D^{20}$:-282.0 (c = 0.1, $CHCl_3$)



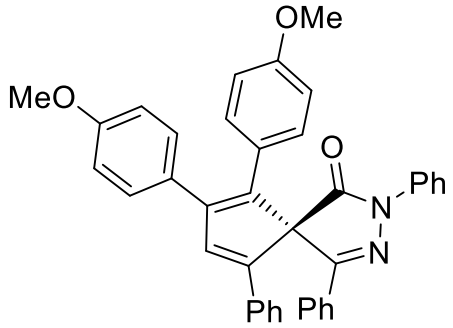
Signal 1: DAD1 A, Sig=250,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.889	VV R	0.2321	1.74361e4	1095.55750	50.7165
2	19.814	VV R	0.3569	1.69434e4	699.79358	49.2835



Signal 1: DAD1 A, Sig=250,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.459	MM R	0.2670	5.33499e4	16.81886	91.2849
2	19.397	MM R	0.3894	5093.37500	1.11502	8.7151



6,7-Bis(4-methoxyphenyl)-2,4,9-triphenyl-2,3-diazaspiro[4.4]nona-3,6,8-trien-1-one (*rac*-4d)
The general procedure **B** was followed using 2,5-diphenyl-4-(1-phenylethylidene)-2,4-dihydro-3H-pyrazol-3-one (**1b**) (51.0 mg, 0.15 mmol) and 1,2-bis(4-methoxyphenyl)ethyne (24.0 mg, 0.10 mmol). Purification by column chromatography (*n*-hexane/EtOAc=10:1) yielded ***rac*-4d** (38 mg, 66%), as a yellow solid.

(*S*)-6,7-bis(4-methoxyphenyl)-2,4,9-triphenyl-2,3-diazaspiro[4.4]nona-3,6,8-trien-1-one (4d')
The general procedure **C** was followed using 2,5-diphenyl-4-(1-phenylethylidene)-2,4-dihydro-3H-pyrazol-3-one (**1b**) (51.0 mg, 0.15 mmol) and 1,2-bis(4-methoxyphenyl)ethyne (24.0 mg, 0.10 mmol). Purification by column chromatography (*n*-hexane/EtOAc=10:1) yielded **4d'** (28 mg, 48%), as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92 – 7.84 (m, 2H), 7.81 – 7.71 (m, 2H), 7.55 (s, 1H), 7.46 – 7.38 (m, 2H), 7.36 – 7.28 (m, 7H), 7.25 – 7.13 (m, 4H), 6.96 – 6.90 (m, 2H), 6.86 – 6.78 (m, 2H), 6.68 – 6.61 (m, 2H), 3.80 (s, 3H), 3.69 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.7 (C_q), 159.2 (C_q), 159.1 (C_q), 156.5 (C_q), 144.7 (C_q), 144.4 (C_q), 138.6 (C_q), 138.0 (C_q), 135.5 (CH), 133.4 (C_q), 131.1 (C_q), 130.7 (CH), 130.0 (CH), 129.7 (CH), 129.0 (CH), 128.9 (CH), 128.8 (CH), 127.9 (CH), 127.0 (C_q), 126.1 (C_q), 125.8 (CH), 125.6 (CH), 125.1 (CH), 119.7 (CH), 114.0 (CH), 113.8 (CH), 76.5 (C_q), 55.2 (CH_3), 55.0 (CH_3).

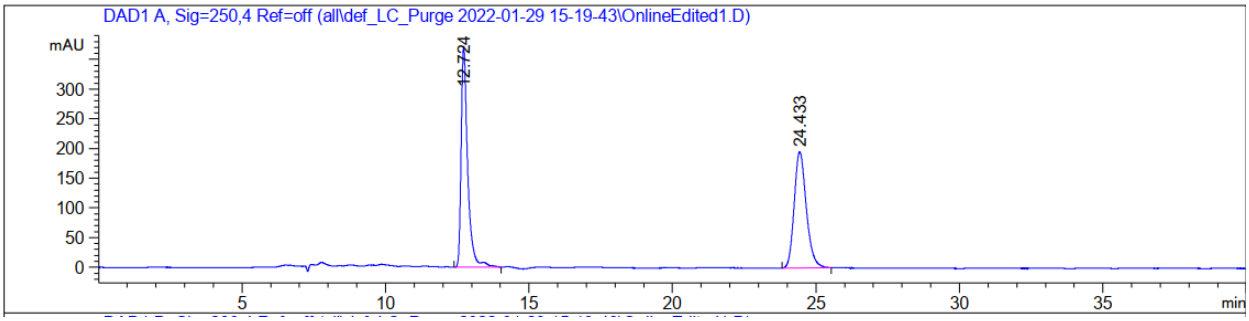
IR (ATR): $\tilde{\nu}$ = 1712, 1595, 1499, 1245, 1176, 1026, 833, 731, 688 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 575 (60) $[M+H]^+$, 597 (100) $[M+Na]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{39}H_{31}N_2O_3^+$ $[M+H]^+$: 575.2335, found: 575.2329.

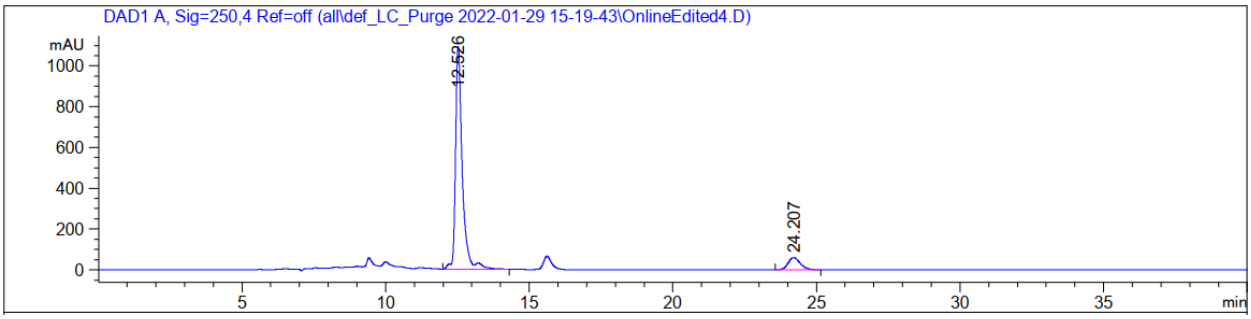
HPLC separation (Chiralpak® IE-3, MeOH/*i*-PrOH 90:10, 0.5 mL/min, detection at 250 nm): tr (major) = 12.5 min, tr (minor) = 24.2 min, 91 : 9 er.

$[\alpha]_D^{20}$:-32.0 (c = 0.1, $CHCl_3$)



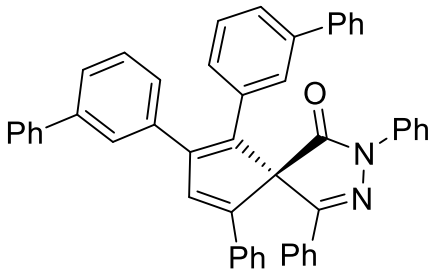
Signal 1: DAD1 A, Sig=250,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.724	BV R	0.2296	5849.47314	371.37332	50.4886
2	24.433	BV R	0.4417	5736.25977	195.83238	49.5114



Signal 1: DAD1 A, Sig=250,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.526	VV R	0.2323	1.78537e4	1090.65503	90.9879
2	24.207	BV R	0.3808	1768.36438	60.01177	9.0121



6,7-Di([1,1'-biphenyl]-3-yl)-2,4,9-triphenyl-2,3-diazaspiro[4.4]nona-3,6,8-trien-1-one (*rac*-4e)

The general procedure **B** was followed using 2,5-diphenyl-4-(1-phenylethylidene)-2,4-dihydro-3H-pyrazol-3-one (**1b**) (51.0 mg, 0.15 mmol) and 1,2-di([1,1'-biphenyl]-3-yl)ethyne (33.0 mg, 0.10 mmol). Purification by column chromatography (*n*-hexane/EtOAc=10:1) yielded ***rac*-4e** (30 mg, 44%), as a yellow solid.

(*S*)-6,7-di([1,1'-biphenyl]-3-yl)-2,4,9-triphenyl-2,3-diazaspiro[4.4]nona-3,6,8-trien-1-one (4e')

The general procedure **C** was followed using 2,5-diphenyl-4-(1-phenylethylidene)-2,4-dihydro-3H-pyrazol-3-one (**1b**) (51.0 mg, 0.15 mmol) and 1,2-di([1,1'-biphenyl]-3-yl)ethyne (33.0 mg, 0.10 mmol). Purification by column chromatography (*n*-hexane/EtOAc=10:1) yielded **4e'** (34 mg, 51%), as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 8.2 Hz, 2H), 7.90 – 7.80 (m, 2H), 7.70 – 7.65 (m, 2H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.49 – 7.28 (m, 19H), 7.30 – 7.16 (m, 7H), 7.03 (d, *J* = 7.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ =169.2 (C_q), 156.3 (C_q), 145.6 (C_q), 145.5 (C_q), 141.4 (C_q), 141.3 (C_q), 140.6 (C_q), 140.4 (C_q), 137.9 (C_q), 135.1 (CH), 134.7 (C_q), 134.1 (C_q), 133.2 (C_q), 131.1 (CH), 130.8 (CH), 129.1 (CH), 129.1 (CH), 128.9 (CH), 128.9 (CH), 128.7 (CH), 128.5 (CH), 128.2 (CH), 127.8 (CH), 127.6 (CH), 127.4 (CH), 127.4 (CH), 127.2 (CH), 127.0 (CH), 126.9 (CH), 126.8 (CH), 125.8 (CH), 125.7 (CH), 125.2 (CH), 119.6 (CH), 76.6 (C_q).

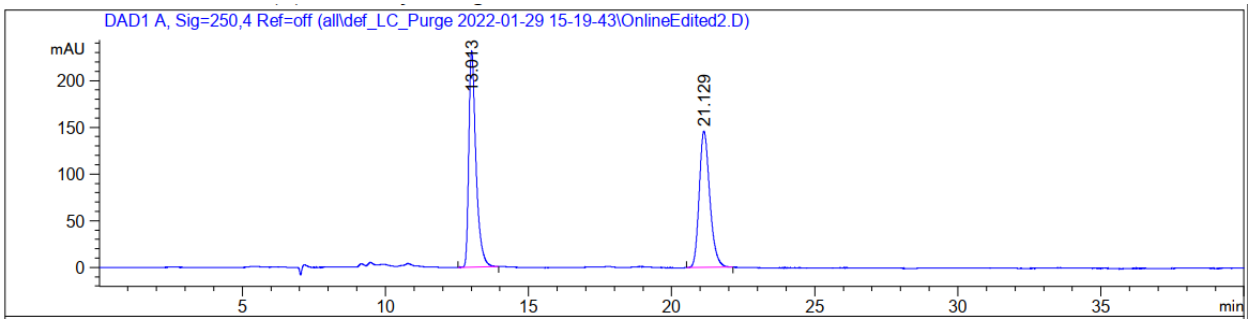
IR (ATR): $\tilde{\nu}$ = 1713, 1595, 1492, 1300, 1136, 756, 734, 687 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 667 (40) $[M+H]^+$, 689 (100) $[M+Na]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{49}H_{35}N_2O^+$ $[M+H]^+$: 667.2749, found: 667.2744.

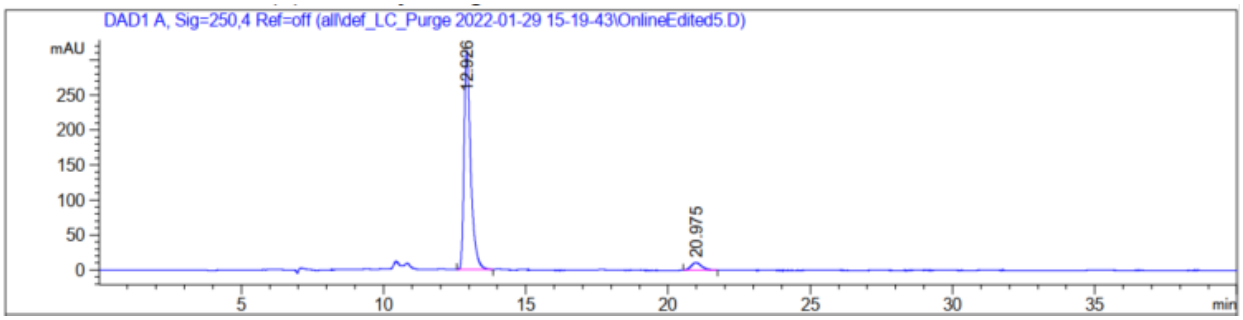
HPLC separation (Chiralpak® IE-3, MeOH/*i*-PrOH 90:10, 0.5 mL/min, detection at 250 nm): tr (major) = 12.9 min, tr (minor) = 20.9 min, 95 : 5 er.

$[\alpha]_D^{20}$:-20.0 (c = 0.1, $CHCl_3$)



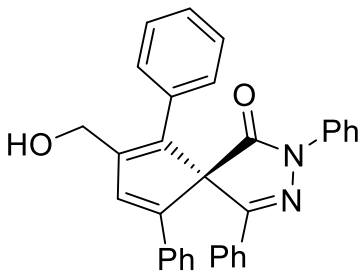
Signal 1: DAD1 A, Sig=250,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.013	VV R	0.2619	4027.20850	231.54088	51.7281
2	21.129	BV R	0.3829	3758.13354	146.21333	48.2719



Signal 1: DAD1 A, Sig=250,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.926	BB	0.2395	5026.89600	312.76038	94.7369
2	20.975	BV R	0.3087	279.26837	10.69275	5.2631



7-(Hydroxymethyl)-2,4,6,9-tetraphenyl-2,3-diazaspiro[4.4]nona-3,6,8-trien-1-one (*rac*-4f)

The general procedure **B** was followed using 2,5-diphenyl-4-(1-phenylethylidene)-2,4-dihydro-3H-pyrazol-3-one (**1b**) (51.0 mg, 0.15 mmol) and 3-phenylprop-2-yn-1-ol (13.0 mg, 0.10 mmol). Purification by column chromatography (*n*-hexane/EtOAc=10:1) yielded ***rac*-4f** (41 mg, 90%), as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 8.2 Hz, 2H), 7.70 (d, *J* = 7.3 Hz, 2H), 7.50 (s, 1H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.33 – 7.09 (m, 12H), 7.03 (dd, *J* = 7.3, 1.9 Hz, 2H), 4.55 (q, *J* = 13.1 Hz, 2H), 3.17 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.8 (C_q), 156.8 (C_q), 146.7 (C_q), 145.5 (C_q), 142.0 (C_q), 137.8 (C_q), 134.4 (CH), 133.1 (C_q), 132.2 (C_q), 130.8 (CH), 130.7 (C_q), 129.0 (CH), 128.9 (CH), 128.8 (CH), 128.5 (CH), 128.3 (CH), 128.3 (CH), 128.0 (CH), 125.9 (CH), 125.8 (CH), 125.0 (CH), 119.7 (CH), 75.7 (C_q), 58.2 (CH2).

IR (ATR): $\tilde{\nu}$ = 3053, 1715, 1688, 1493, 1444, 1318, 1301, 1137, 755, 688 cm^{-1}.

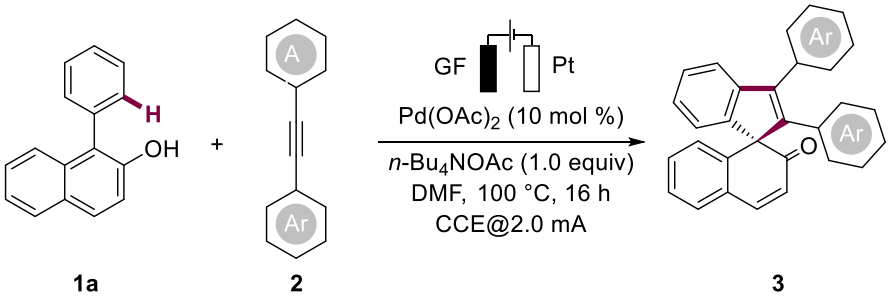
MS (ESI) *m*/*z* (relative intensity): 469 (100) $[M+H]^+$.

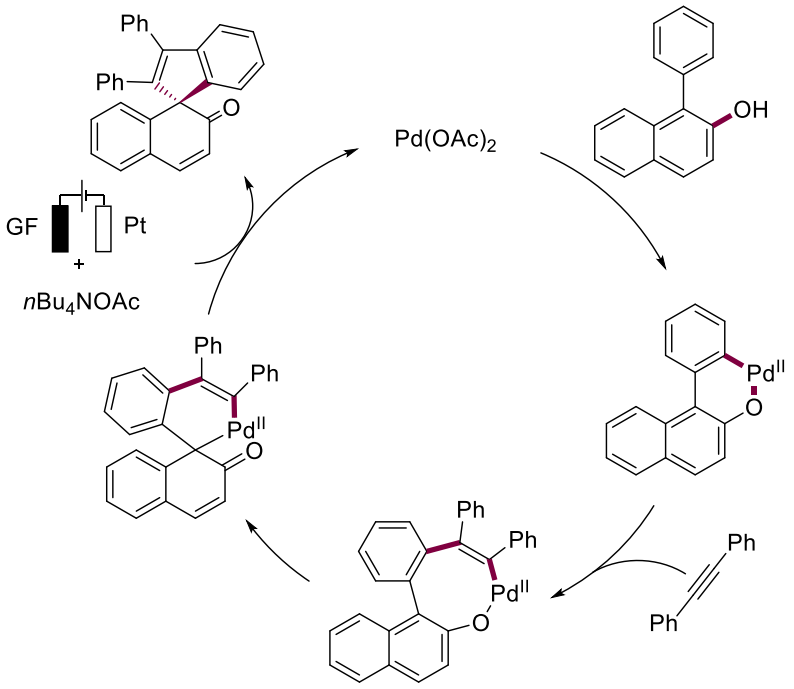
HR-MS (ESI): *m*/*z* calcd for $C_{32}H_{25}N_2O_2^+$ $[M+H]^+$: 4669.1619, found: 469.1619.

The analytical data are in accordance with those reported in the literature.[6]

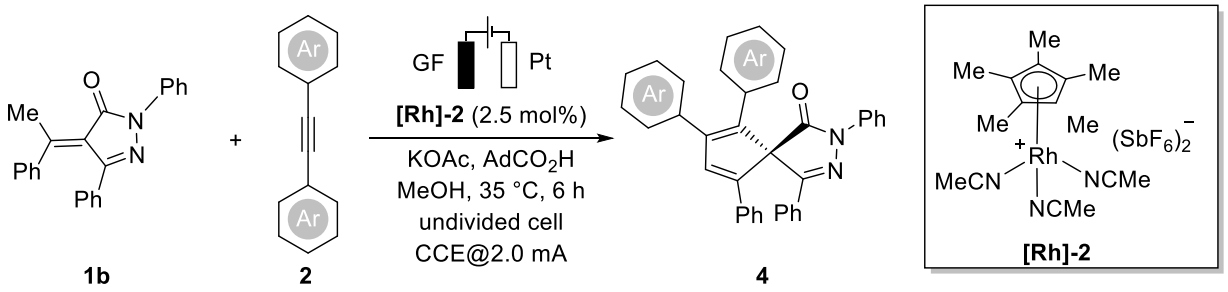
Mechanistic Investigations

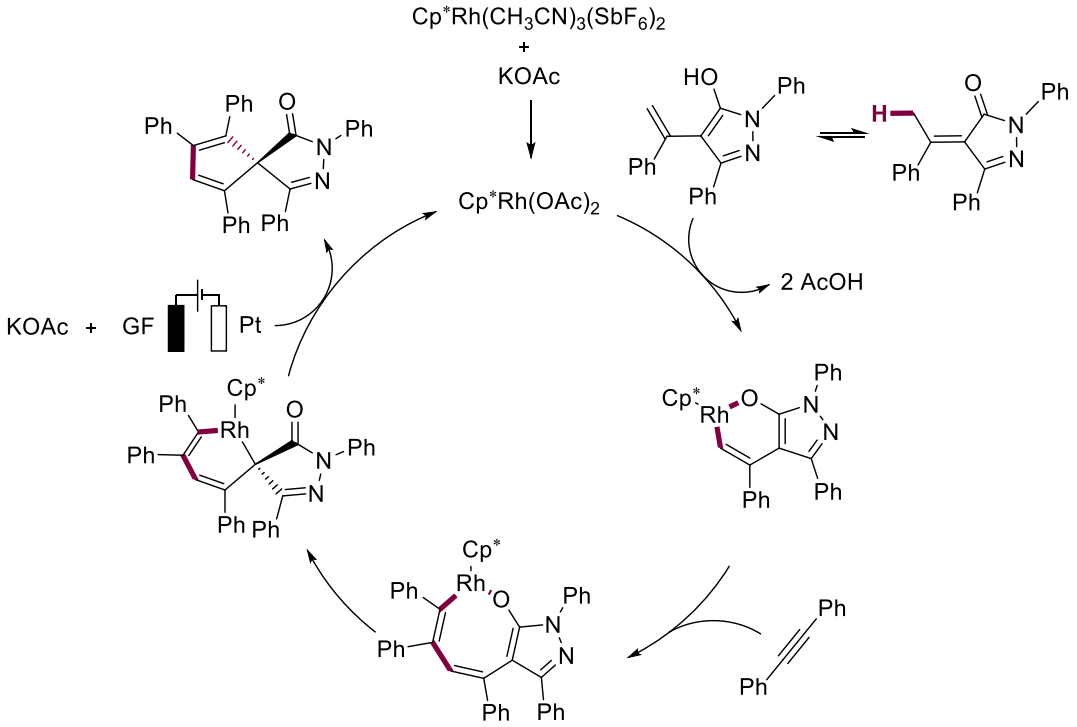
Catalytic cycle for palladaelectro-catalyzed spiroannulation



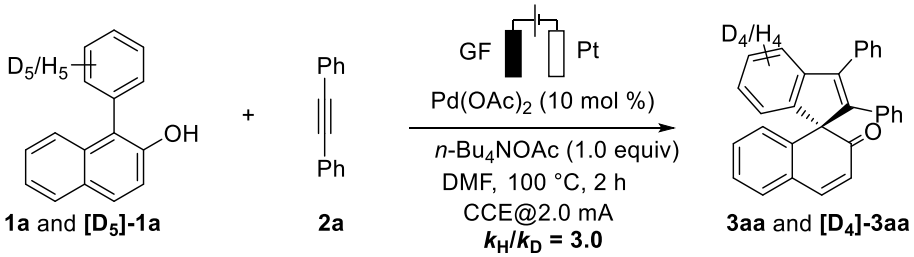


Catalytic cycle for rhodaelectro-catalyzed spiroannulation



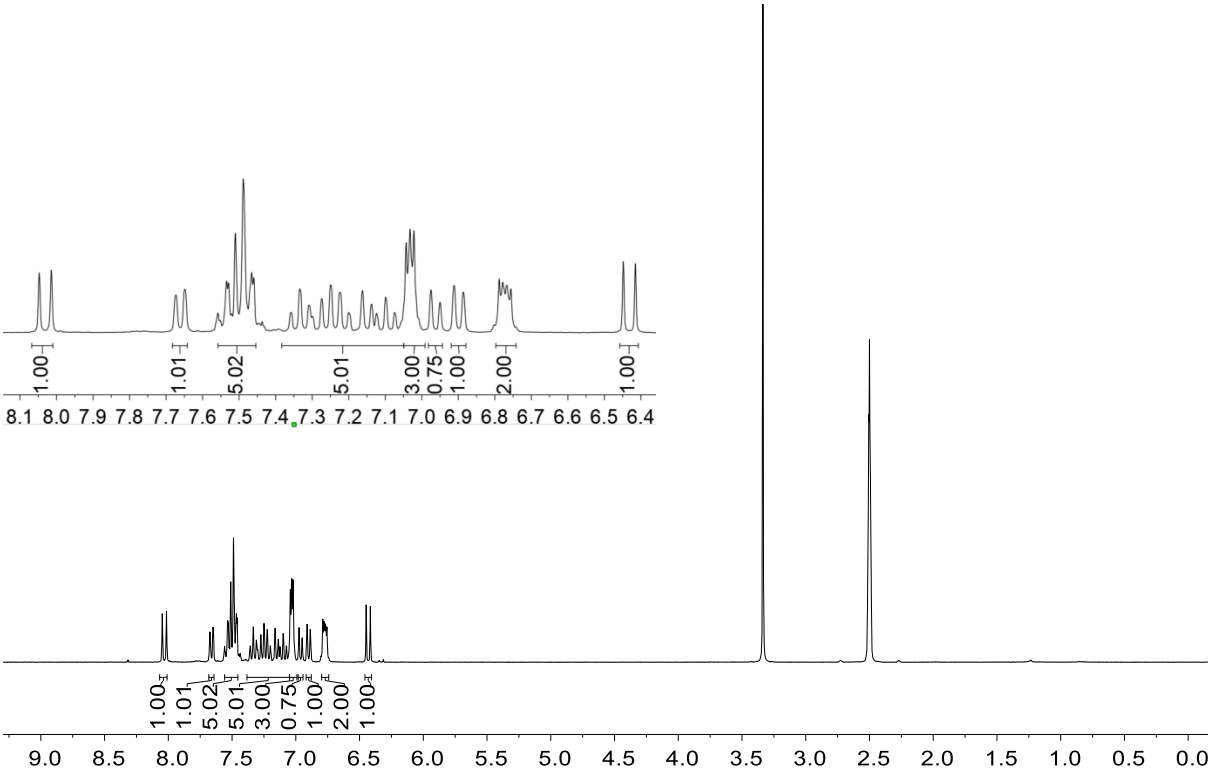


KIE Experiment

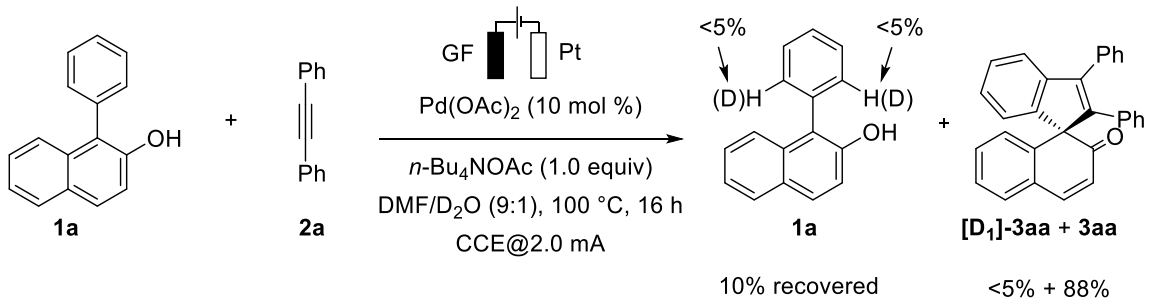


1a and **[D_5]-1a** **2a** **3aa** and **[D_4]-3aa**

The electrocatalysis was carried out in an undivided cell under air with a graphite felt (GF) anode (10 mm × 15 mm × 6 mm) and a platinum cathode (10 mm × 15 mm × 0.25 mm). 1-phenylnaphthalen-2-ol (**1a**) (88.0 mg, 0.40 mmol), [D_5]-**1a** (88.0 mg, 0.40 mmol), 1,2-diphenylethyne (**2a**) (71.0 mg, 0.40 mmol), and *n*-Bu_4NOAc (0.40 mmol, `1.0 equiv) were dissolved in DMF (4.0 mL) . Electrocatalysis was performed at 100 °C with a constant current of 2.0 mA maintained for 2 h. The GF anode was washed with CH_2Cl_2 (3×10 mL). Evaporation of the solvent and subsequent purification by column chromatography on silica gel with EtOAc/*n*-hexane (5/1) afforded the corresponding products **3aa** and [D_4]-**3aa** in 31% yield (49.0 mg). The H/D incorporation in **3aa/**[D_4]**-3aa** was determined by ^{1}H NMR spectroscopy. The kinetic isotopic effect of this reaction was determined to be k_H/k_D = 3.0.

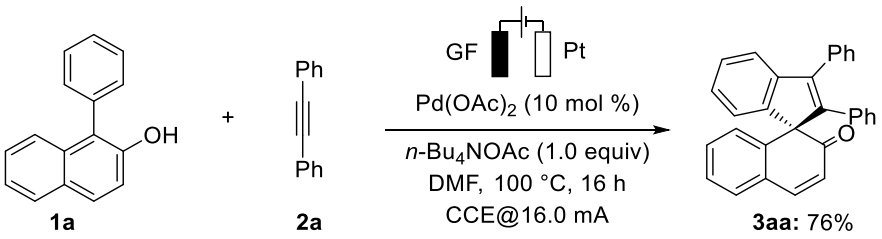

1.00
1.01
5.02
5.01
3.00
0.75
1.00
2.00
1.00
8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4
1.00
1.01
5.02
5.01
3.00
0.75
1.00
2.00
1.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

H/D Exchange experiment



The electrocatalysis was carried out in an undivided cell under air, with a graphite felt (GF) anode (10 mm × 15 mm × 6 mm) and a platinum cathode (10 mm × 15 mm × 0.25 mm). 1-Phenylnaphthalen-2-ol (**1a**) (176.0 mg, 0.80 mmol), 1,2-diphenylethyne (**2a**) (70.0 mg, 0.40 mmol), and *n*-Bu_4NOAc (0.40 mmol, 1.0 equiv) were dissolved in DMF (3.6 mL) and H_2O (0.4 mL). Electrocatalysis was performed at 100 °C with a constant current of 2.0 mA maintained for 16 h. The GF anode was washed with CH_2Cl_2 (3×30 mL). Evaporation of the solvent and subsequent purification by column chromatography on silica gel with EtOAc/*n*-hexane (5/1) afforded the corresponding products **3aa** in 88% yield and ^1H NMR spectroscope showed that no detectable deuterium was observed.

Gram-scale preparation of 3aa



The electrocatalysis was carried out in an undivided cell under air with a graphite felt (GF) anode (25 mm × 50 mm × 6 mm) and a platinum cathode (25 mm × 50 mm × 0.25 mm). 1-Phenylnaphthalen-2-ol (**1a**) (1.50 g, 6.4 mmol), 1,2-diphenylethyne (**2a**) (570 mg, 3.2 mmol), and *n*-Bu_4NOAc (3.2 mmol, 1.0 equiv) were dissolved in DMF (32.0 mL) . Electrocatalysis was performed at 100 °C with a constant current of 16.0 mA maintained for 16 h. The GF anode was washed with CH_2Cl_2 (3×30 mL). Evaporation of the solvent and subsequent purification by column chromatography on silica gel with EtOAc/*n*-hexane (5/1) afforded the corresponding product **3aa** in 76% yield (960 mg).

Cyclic Voltammetry Studies

CV measurements were conducted with a Metrohm Autolab PGSTAT204 potentiostat and Nova 2.1 software. A glassy carbon working electrode (disk, diameter: 3mm), a coiled platinum wire counter electrode and a non-aqueous Ag-wire/ferrocene reference electrode were employed. The voltammograms were recorded at room temperature in DMF at a substrate concentration of 5.0 mmol/L and with 100 mmol/L TBAOAc as supporting electrolyte. All solutions were degassed with N_2 prior to the measurement and an overpressure of protective gas was maintained throughout the experiment. The scan rate is 100 mV/s. Deviations from the general experimental conditions are indicated in the respective figures and descriptions.

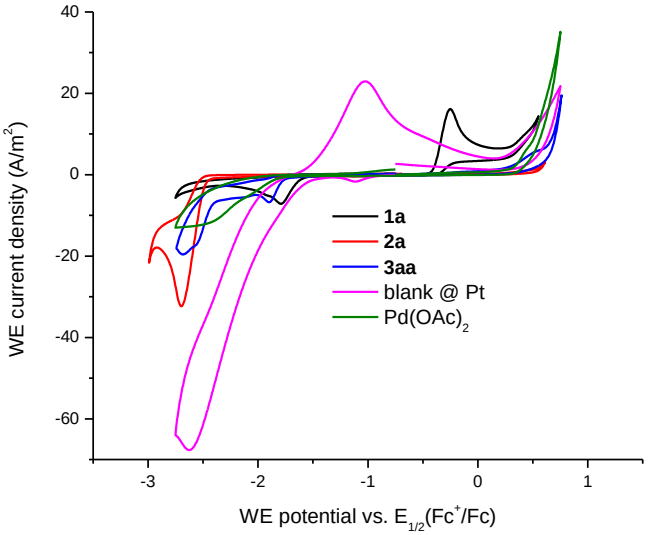


Figure S1. Cyclic voltammetry of the reactants and product **3aa** in DMF.

References

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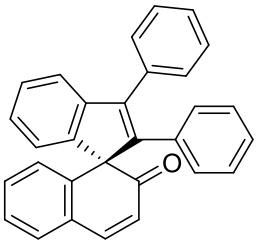
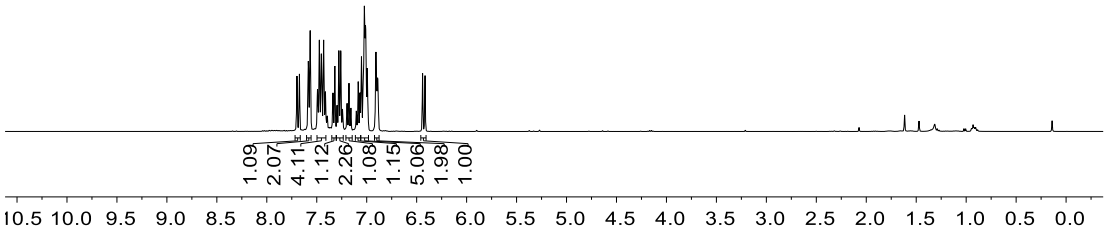
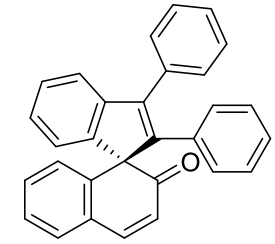
^{1}H, ^{13}C and ^{19}F NMR Spectra



3aa
($CDCl_3$, 300 MHz)





3aa
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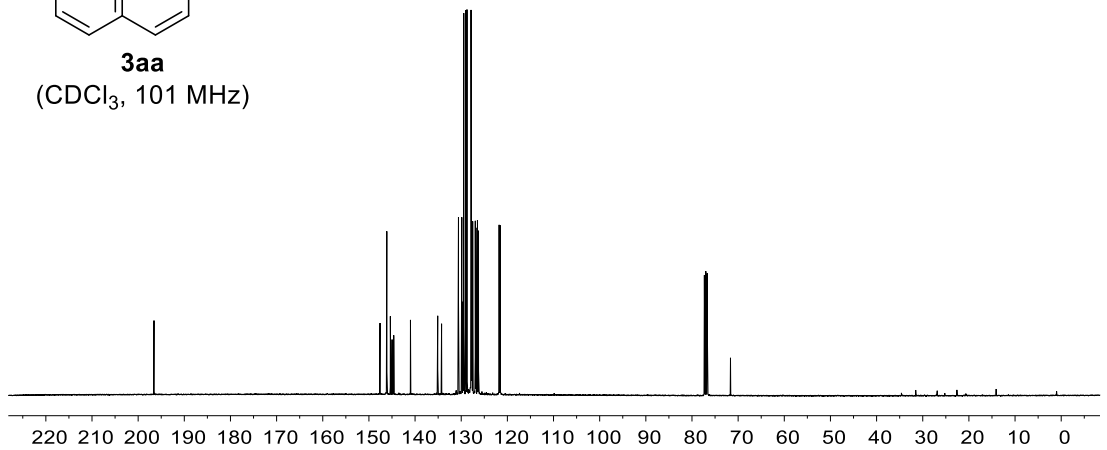

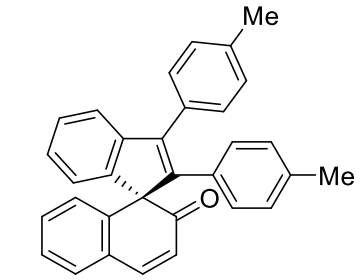

3ab
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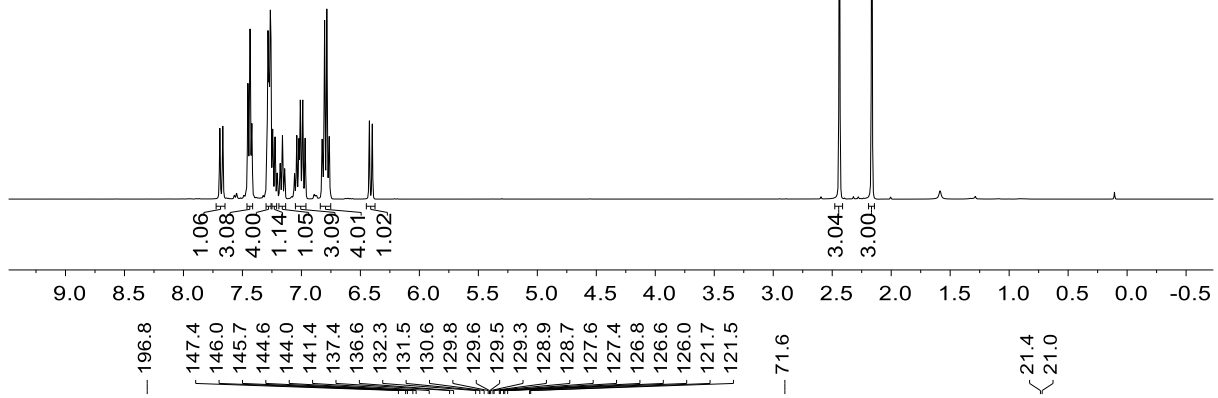

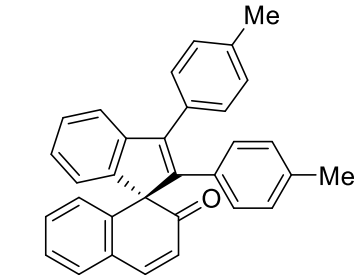

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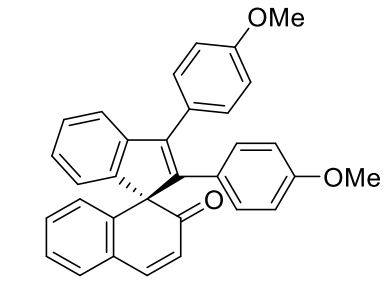

3ac
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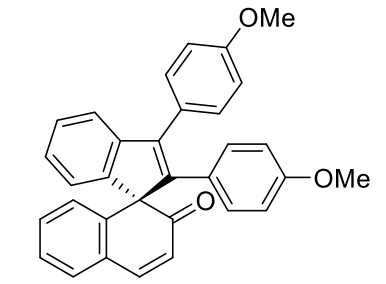

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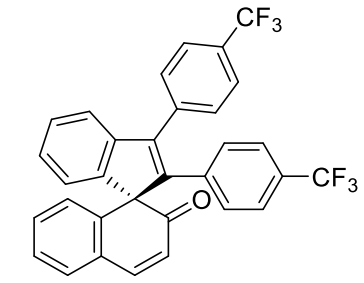

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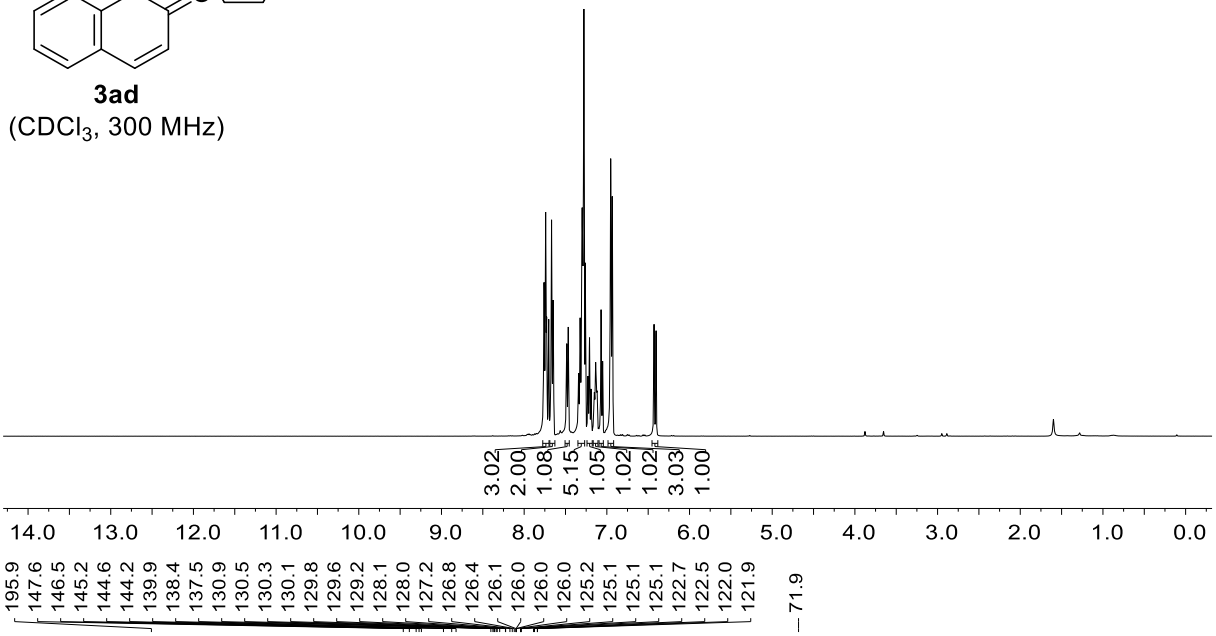

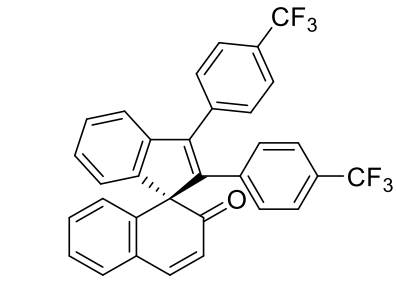

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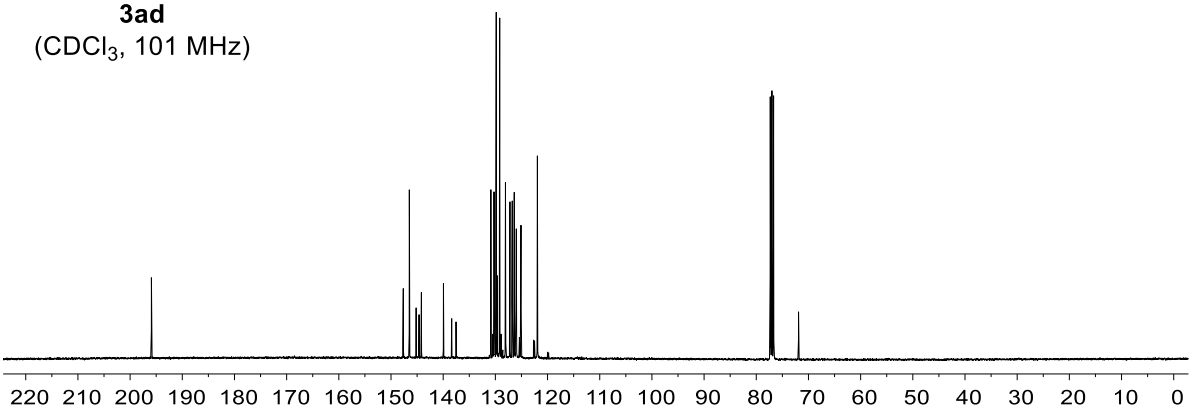

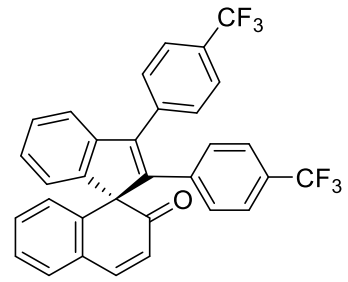

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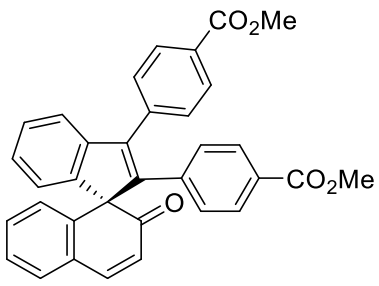
($CDCl_3$, 282 MHz)



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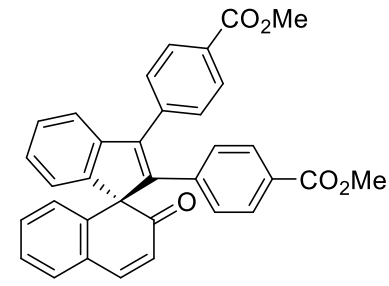

3ae

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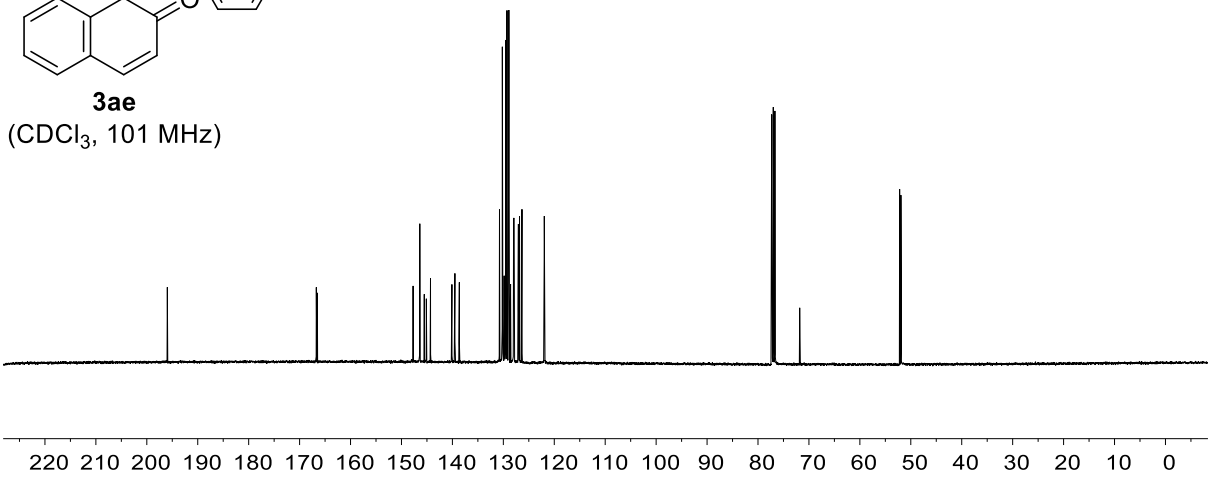

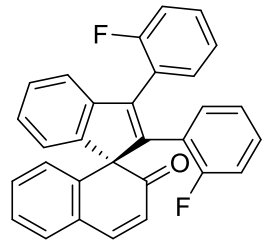

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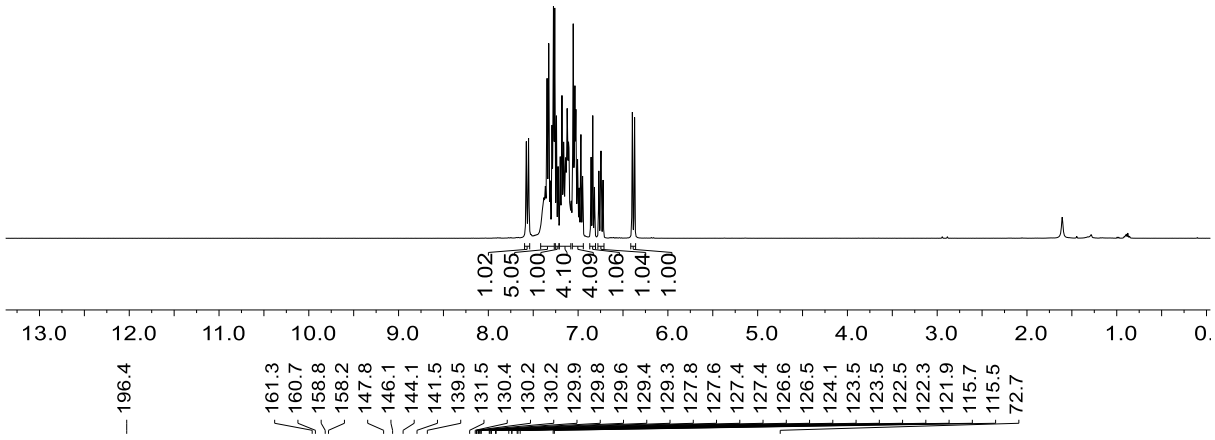

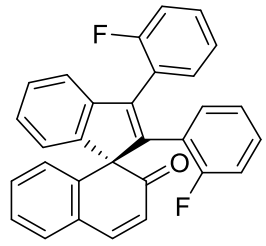

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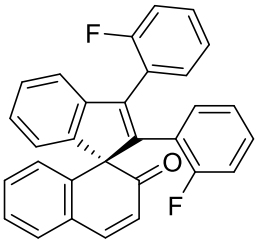

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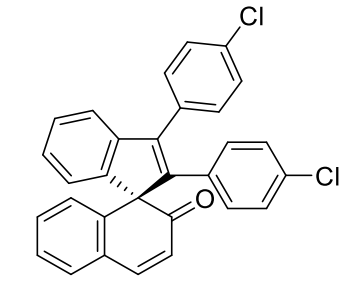
($CDCl_3$, 377 MHz)



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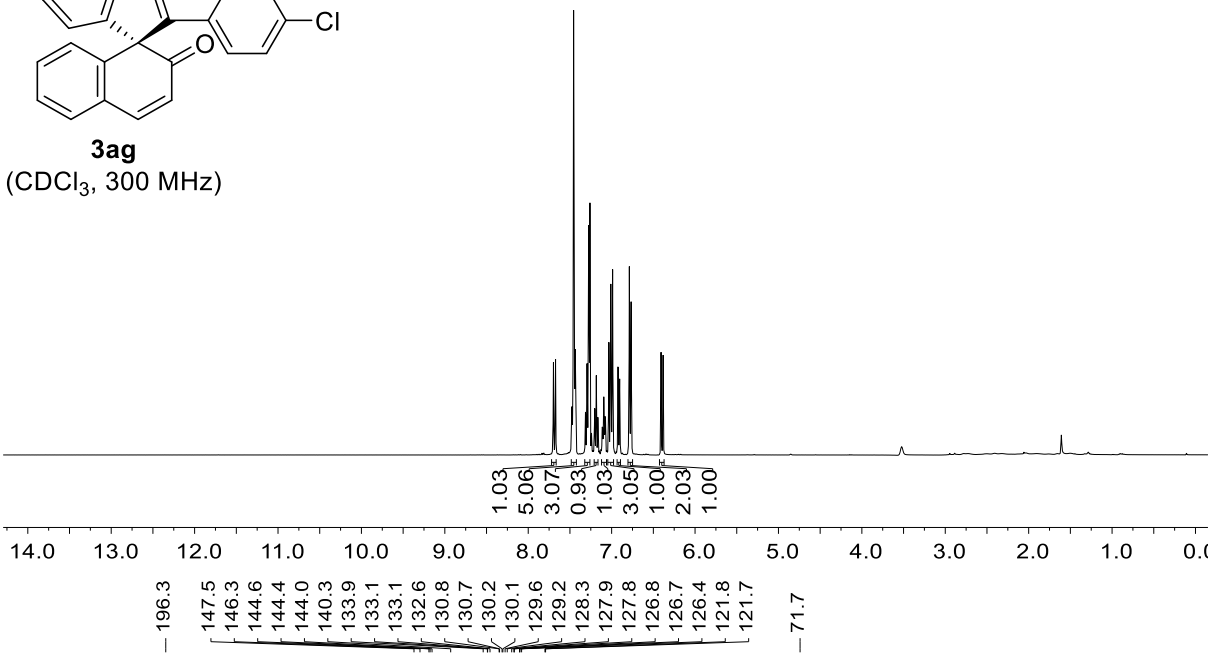

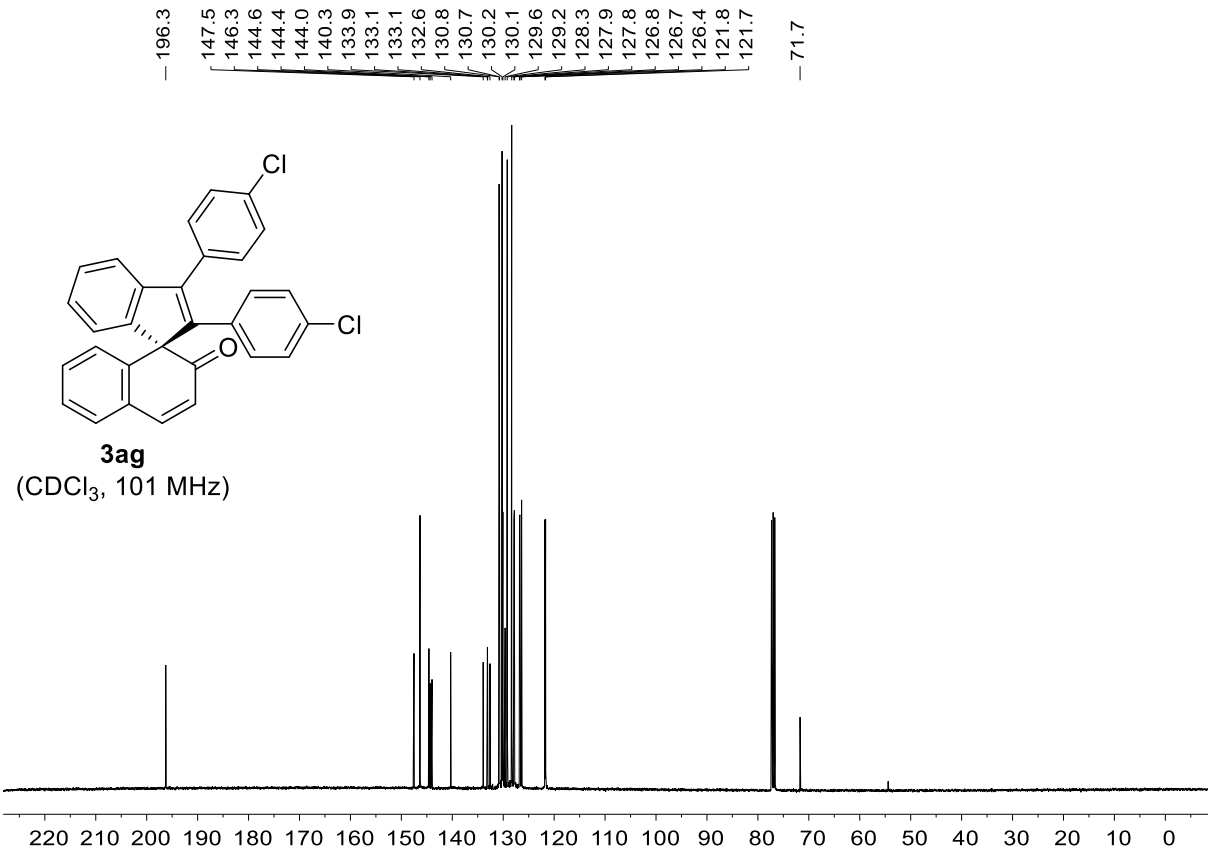

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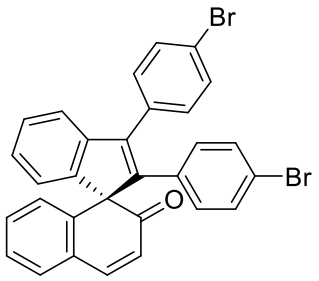

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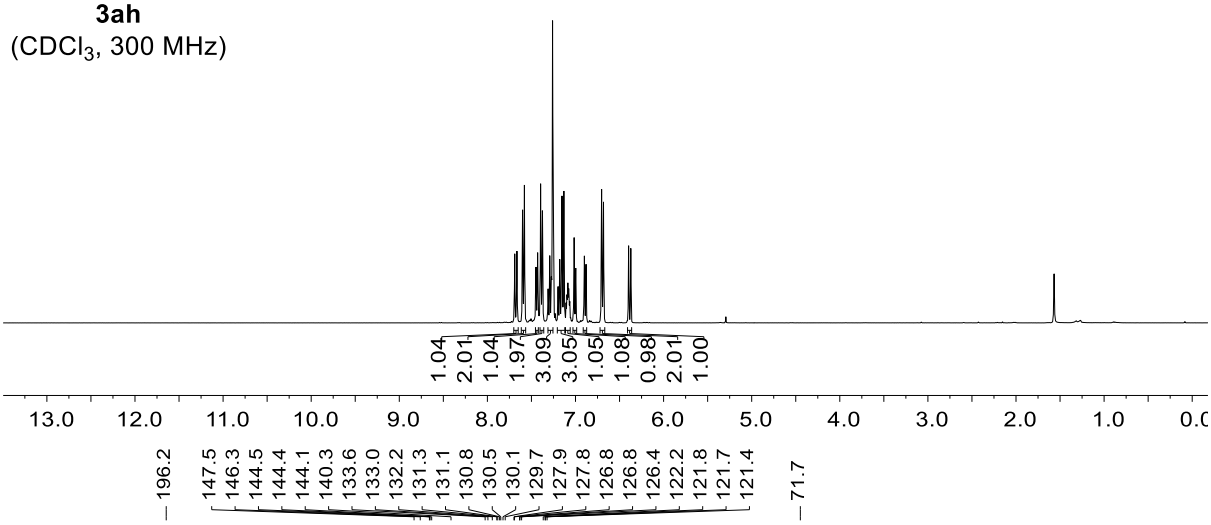

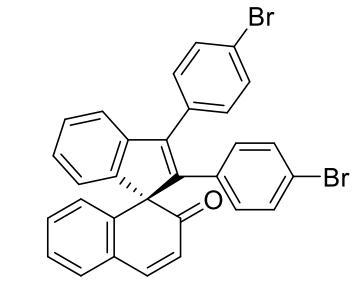

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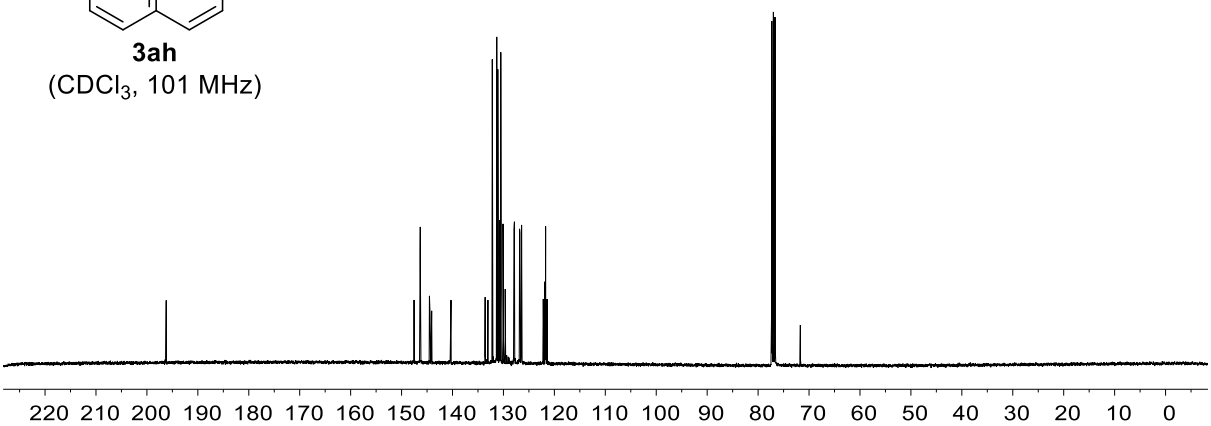

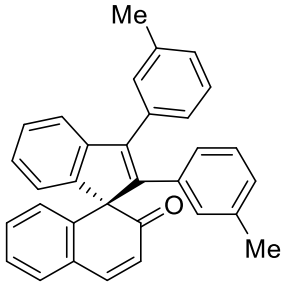

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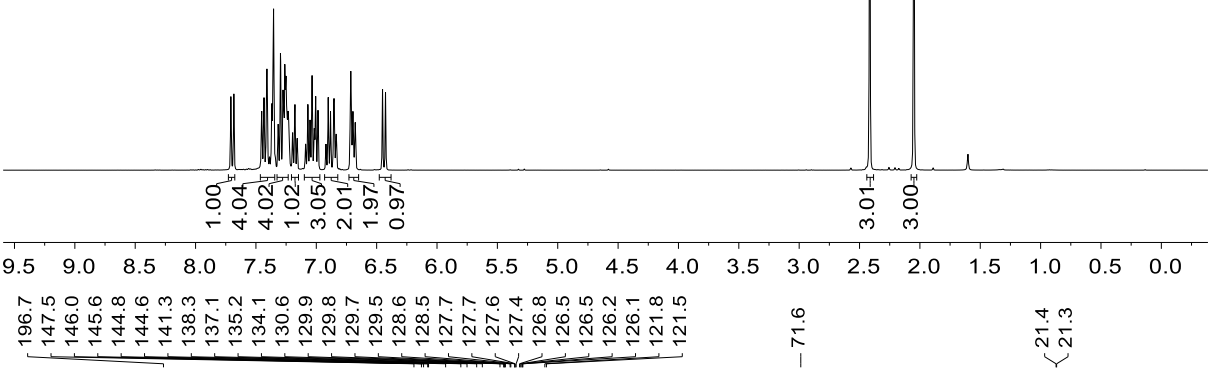

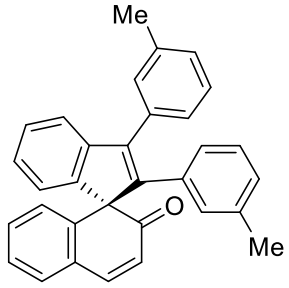

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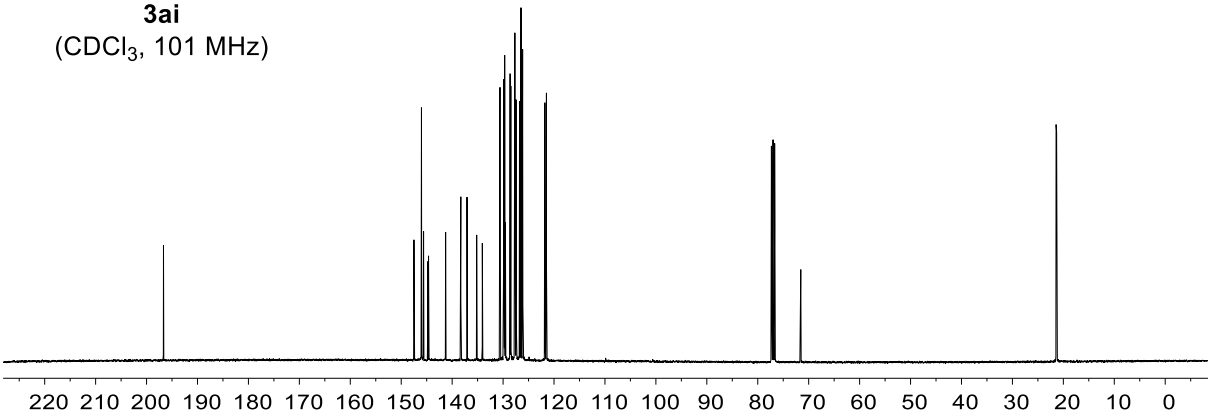

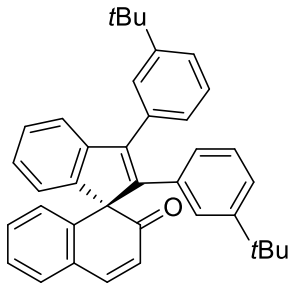

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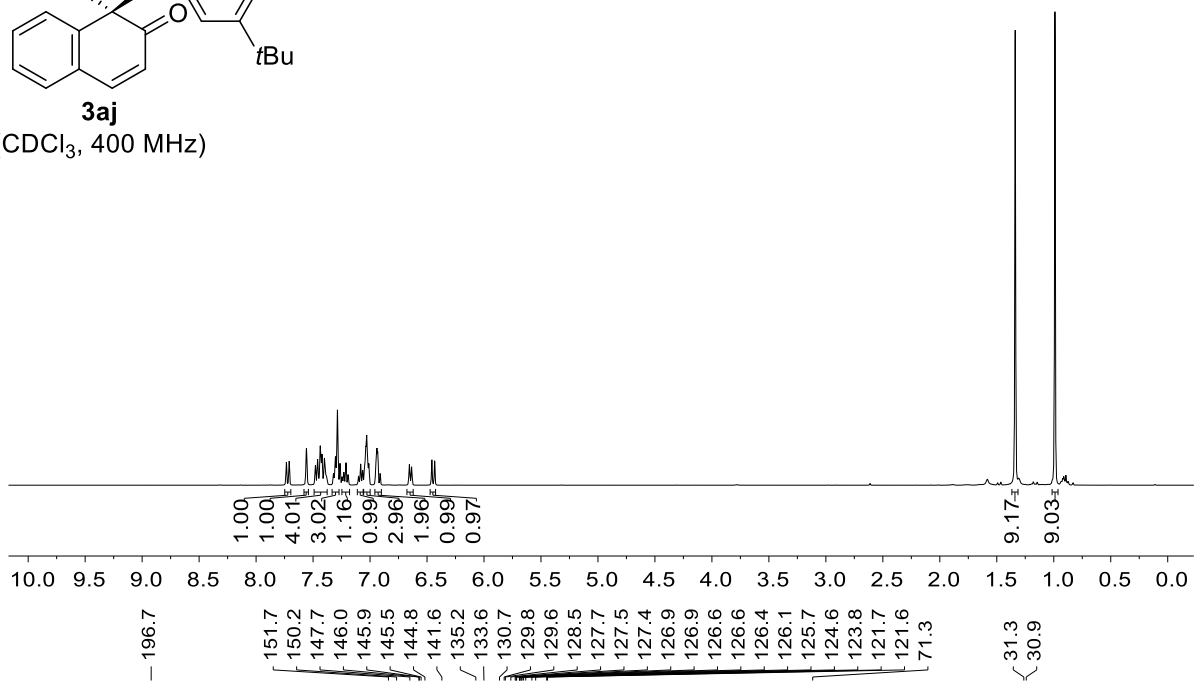

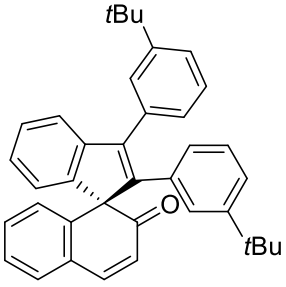

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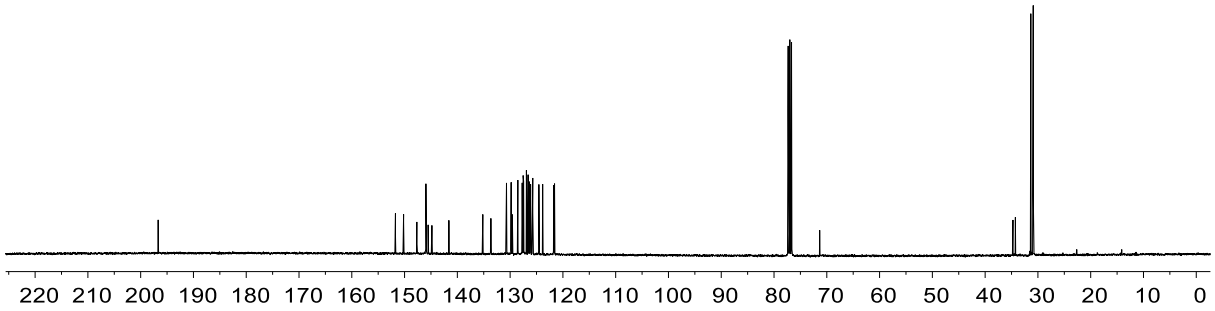

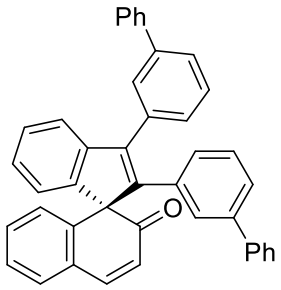

3ak

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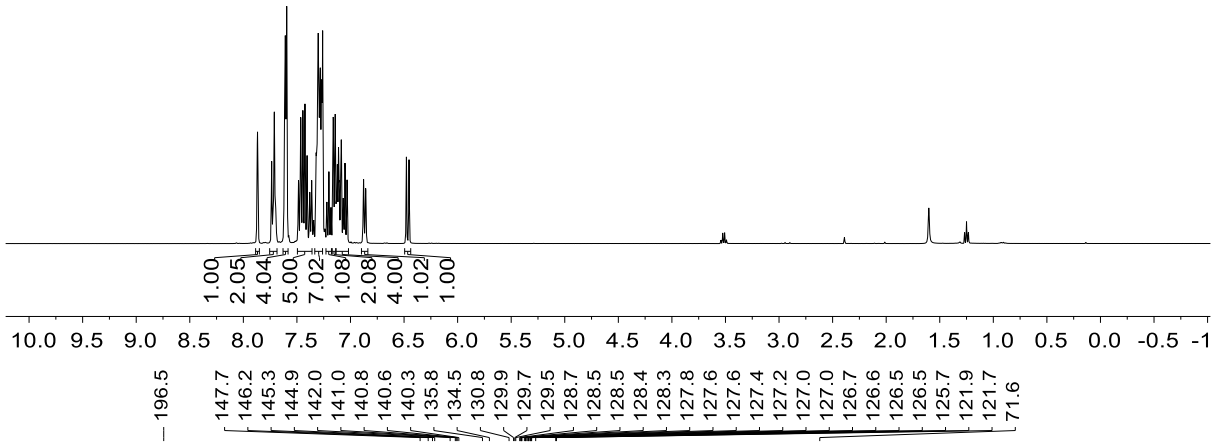

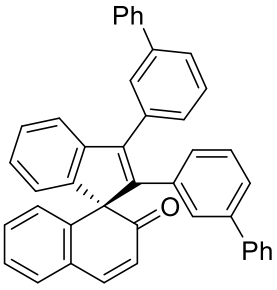

3ak

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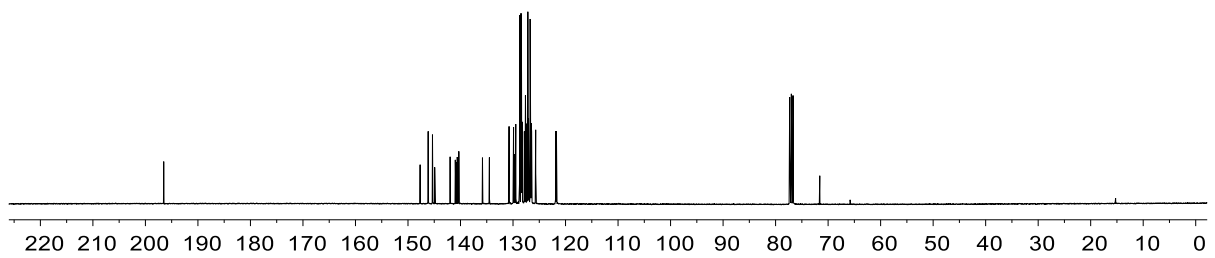

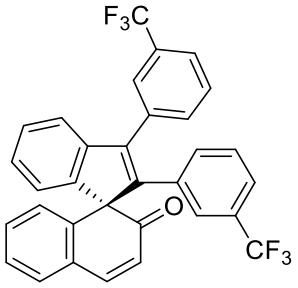

3al
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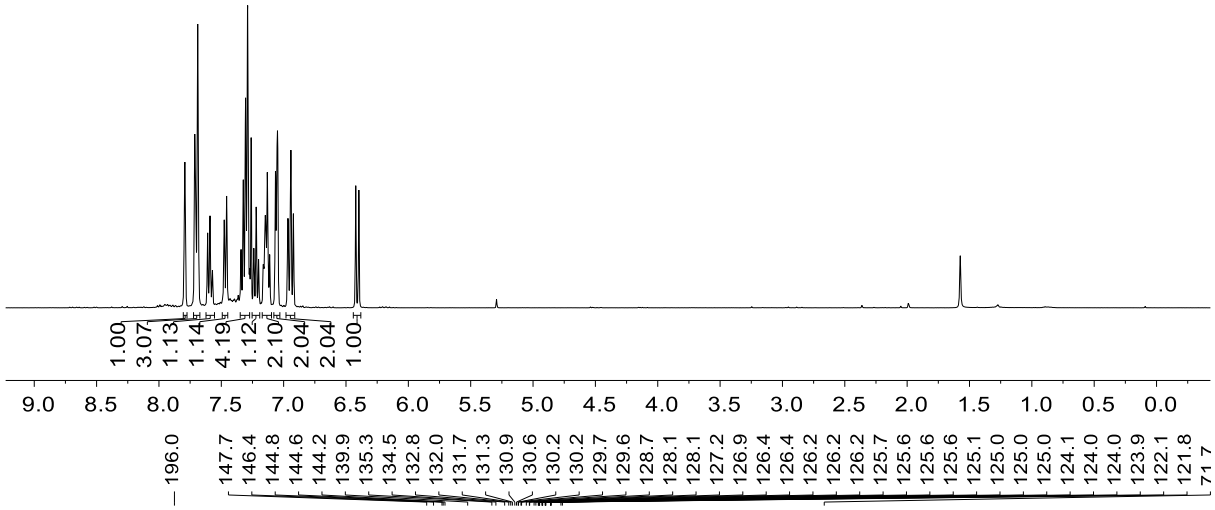

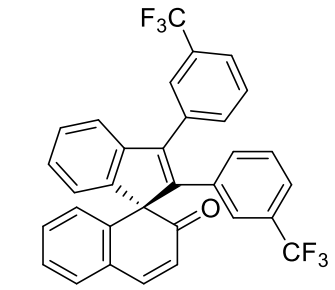

3al
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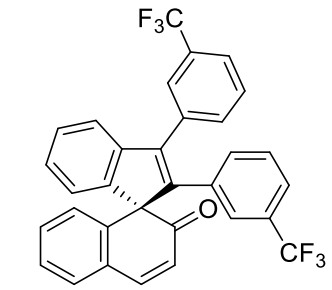

3al

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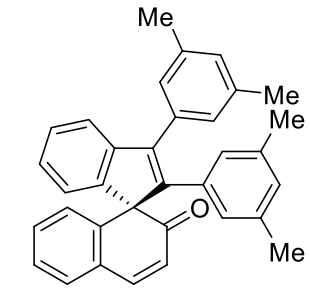

3am
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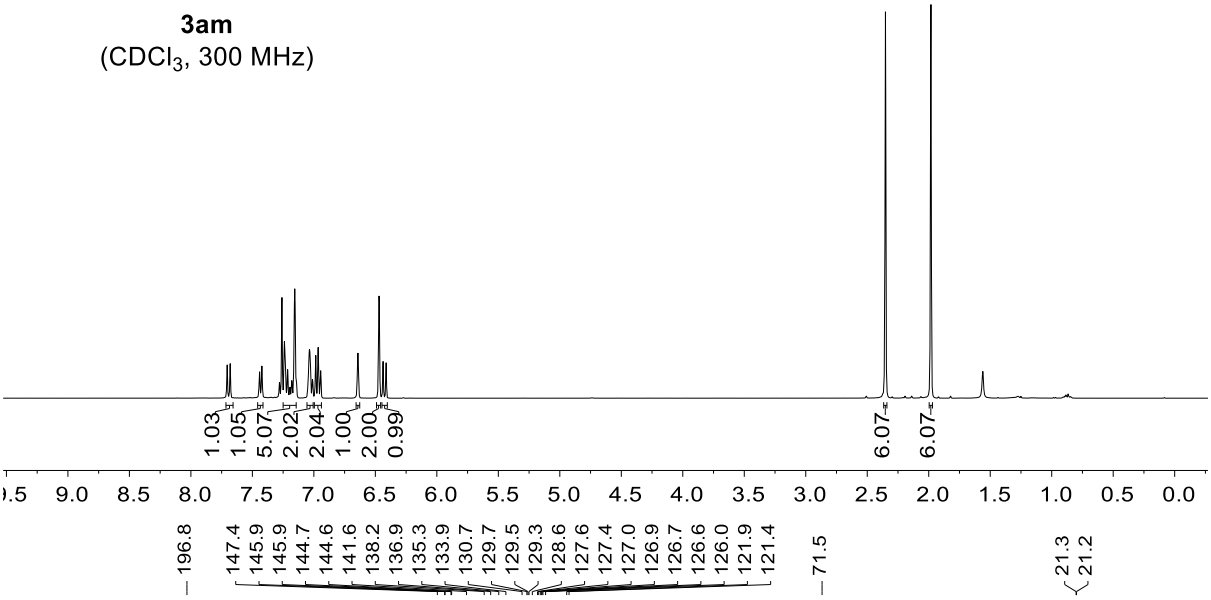

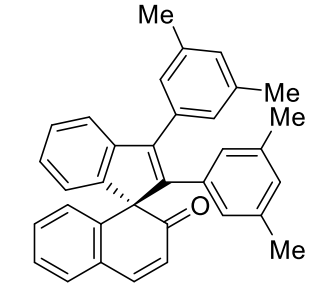

3am
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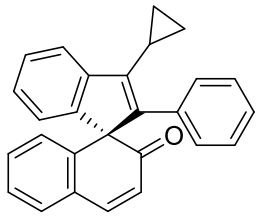
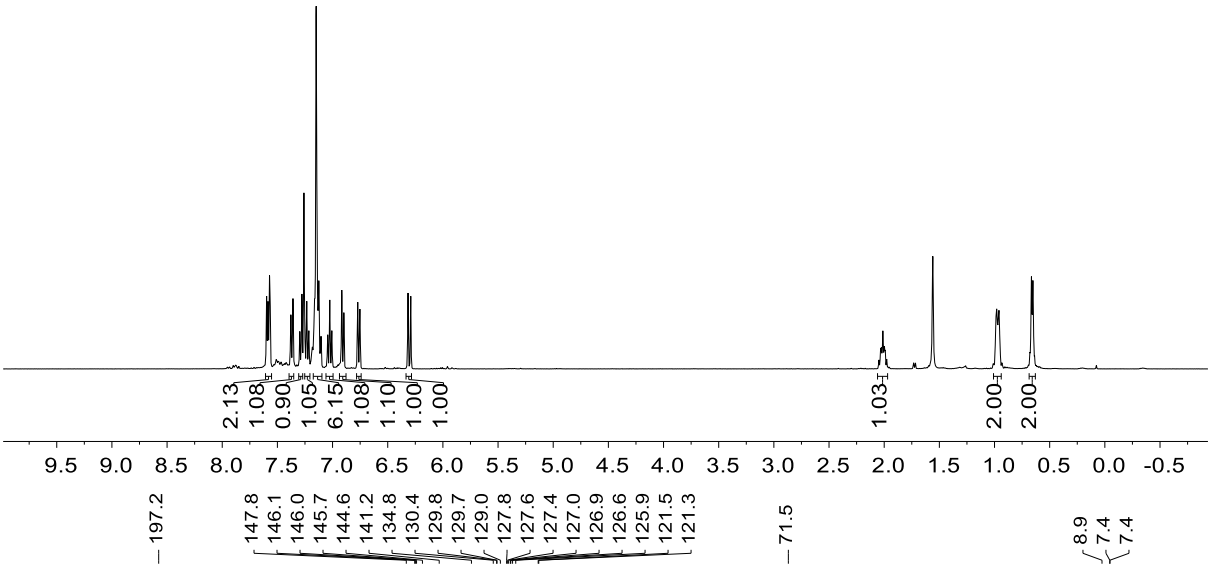
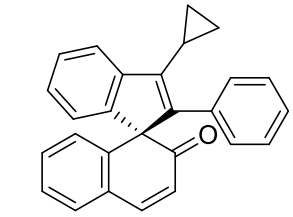
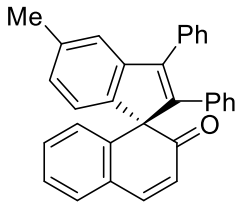


3an
($CDCl_3$, 300 MHz)

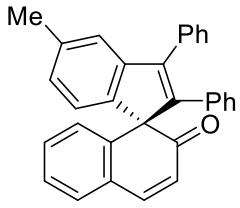




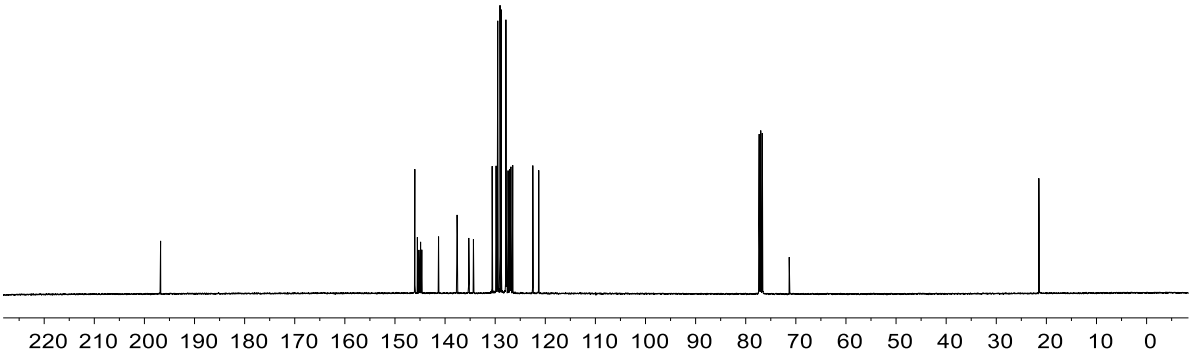
3an
($CDCl_3$, 101 MHz)

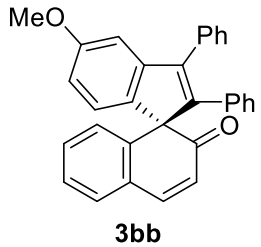


3ba
($CDCl_3$, 300 MHz)



3ba
($CDCl_3$, 101 MHz)





3bb
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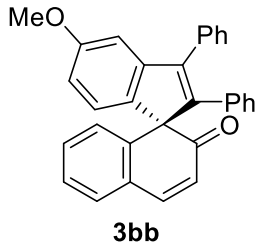
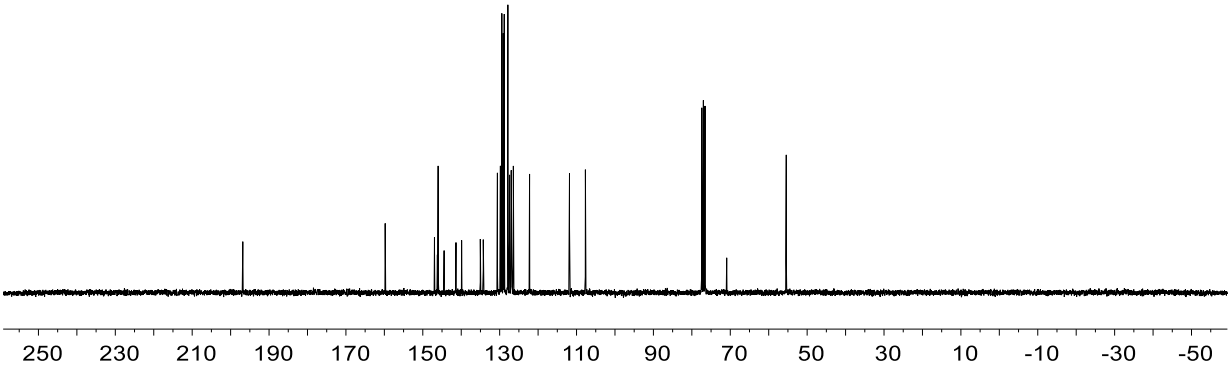
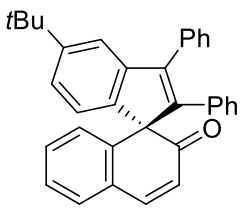
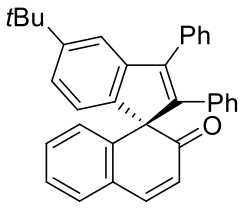


3bb
($CDCl_3$, 101 MHz)

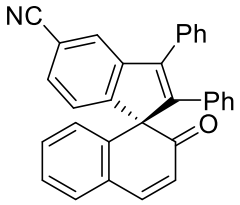




3bc
($CDCl_3$, 300 MHz)

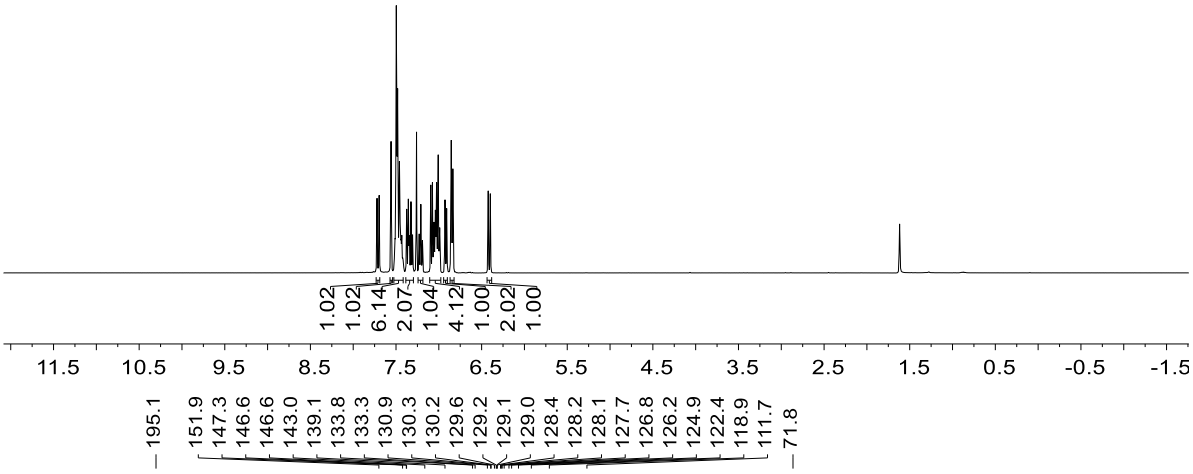


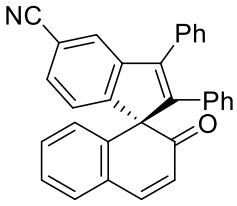
3bc
($CDCl_3$, 101 MHz)



3bd

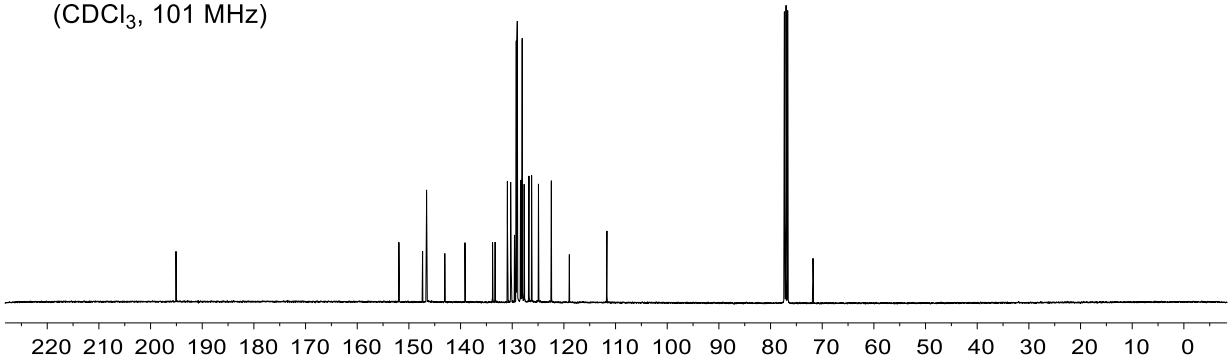
($CDCl_3$, 300 MHz)

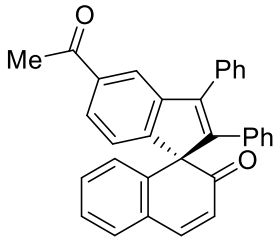




3bd

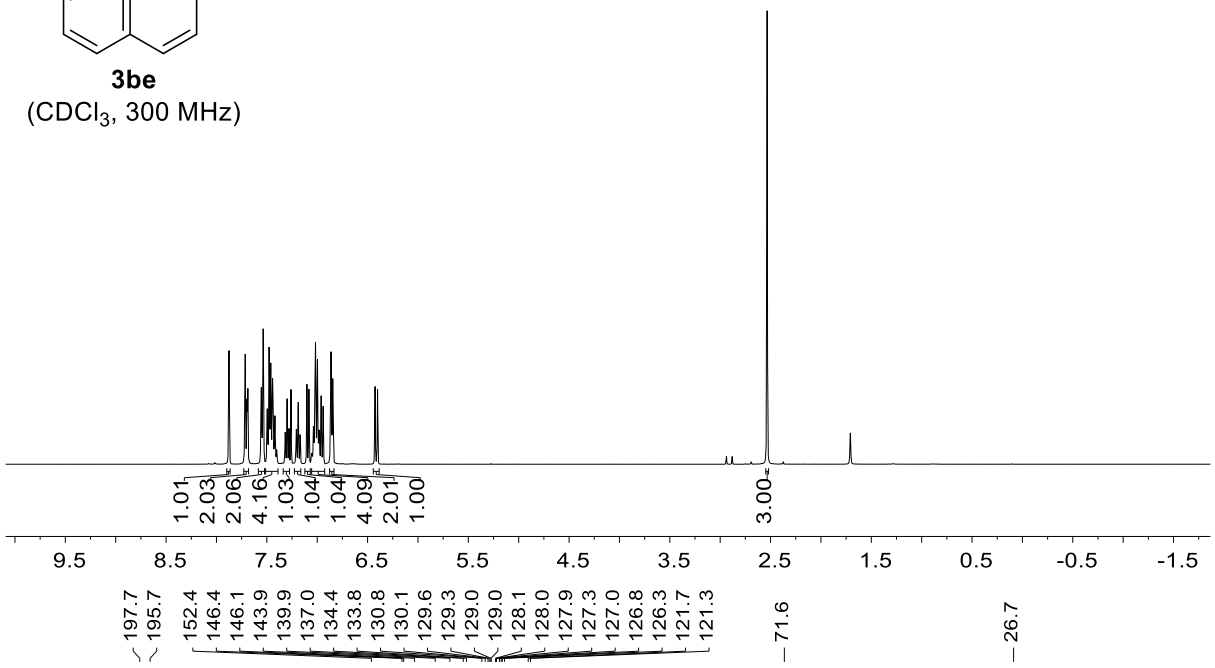
($CDCl_3$, 101 MHz)

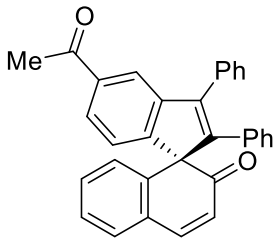




3be

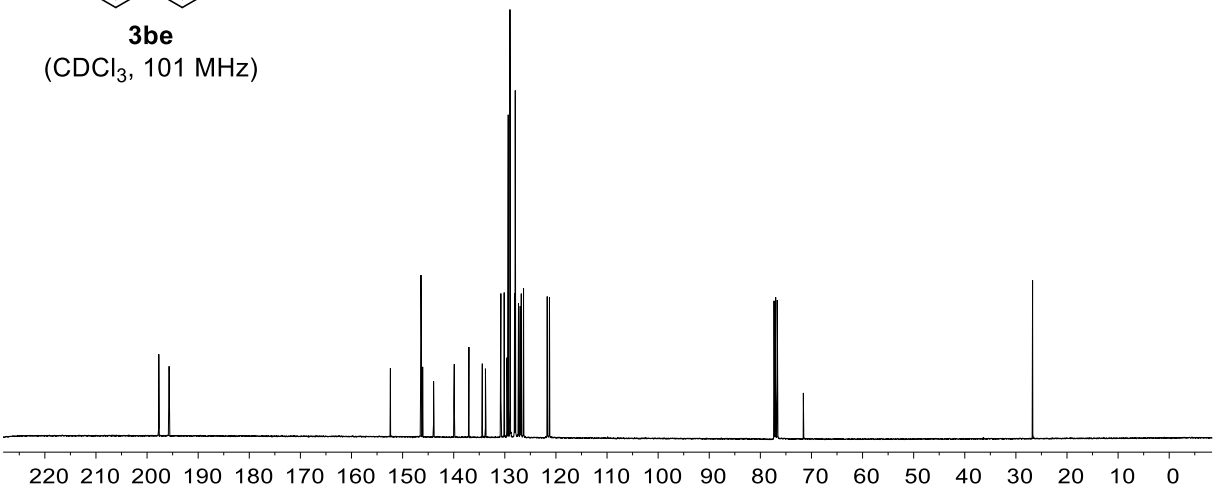
($CDCl_3$, 300 MHz)

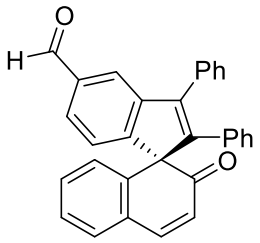




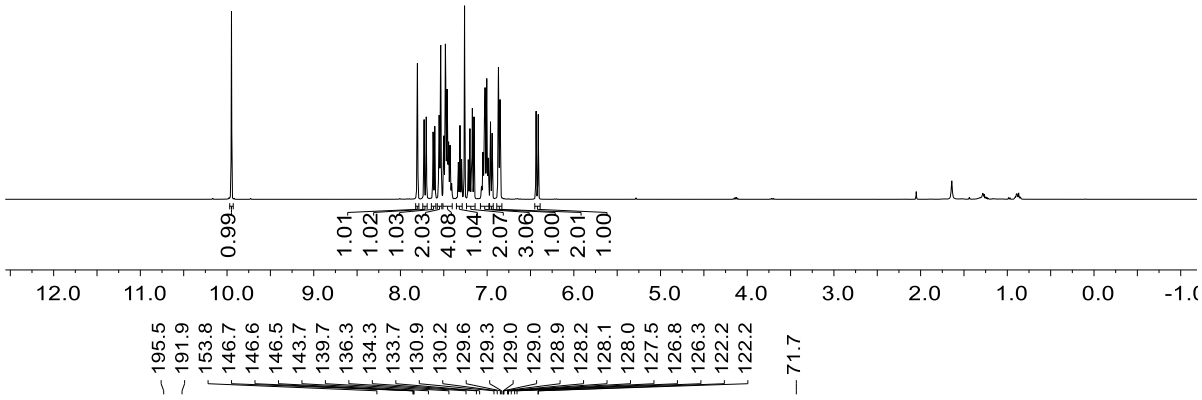
3be

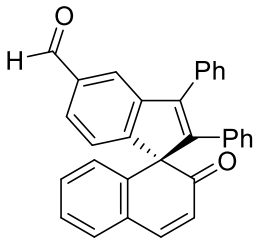
($CDCl_3$, 101 MHz)



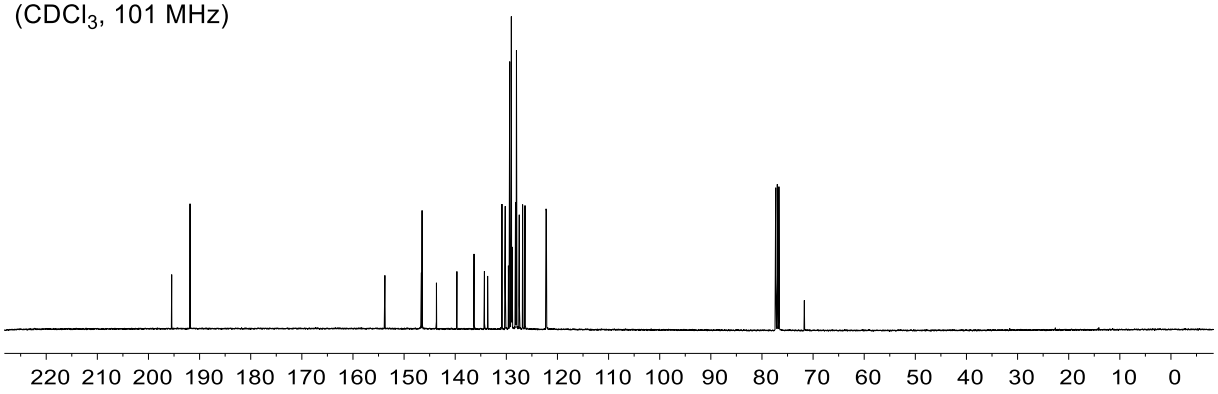


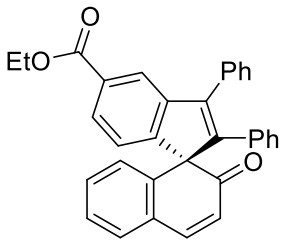
3bf
($CDCl_3$, 300 MHz)





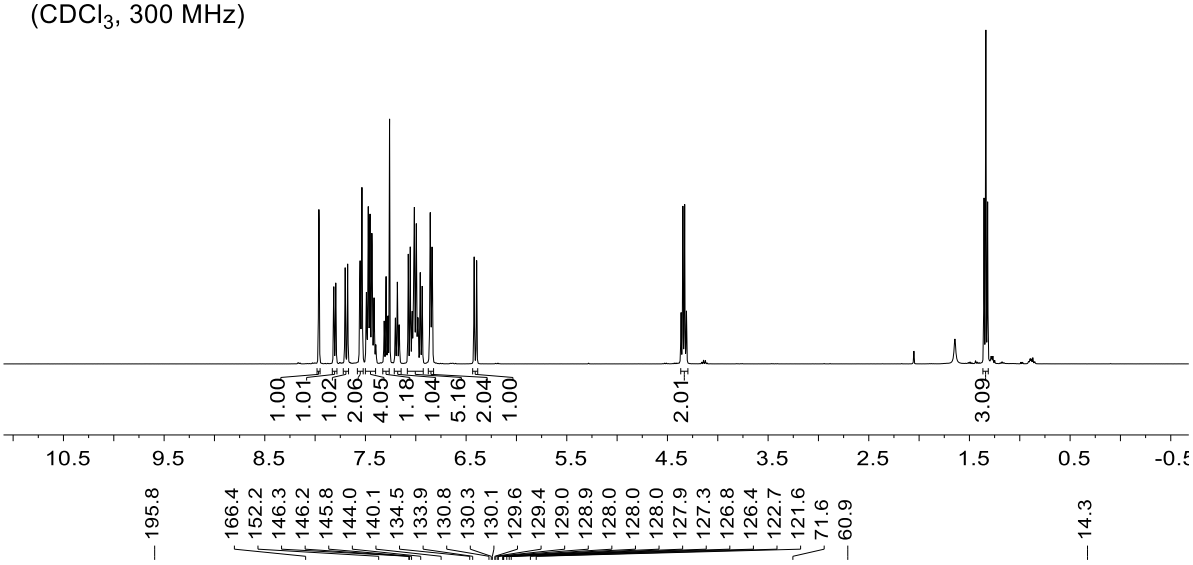
3bf
($CDCl_3$, 101 MHz)

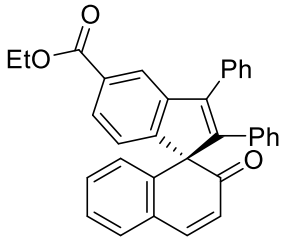




3bg

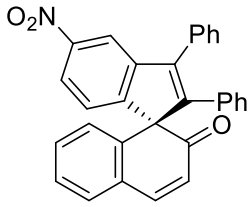
($CDCl_3$, 300 MHz)



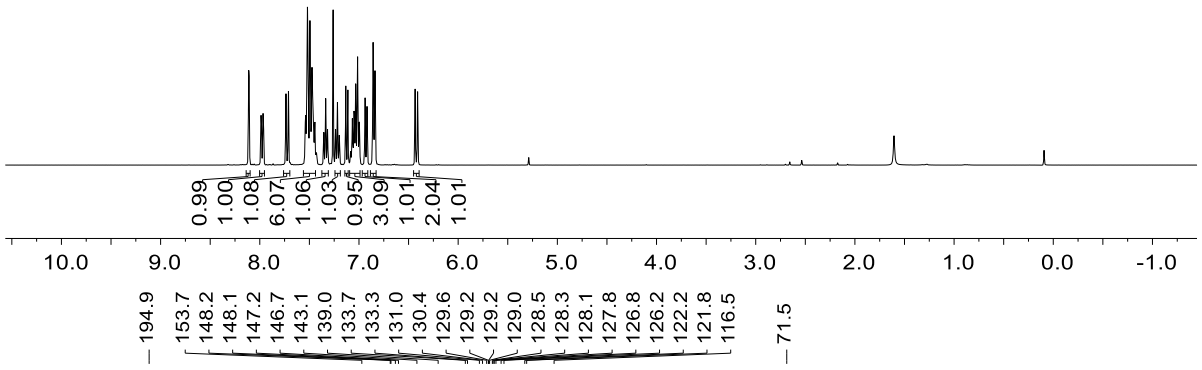


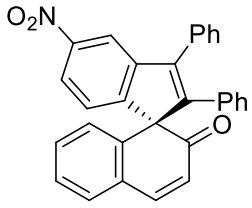
3bg

($CDCl_3$, 101 MHz)

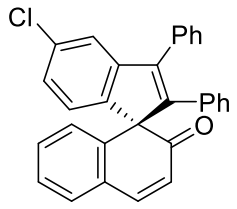


3bh
($CDCl_3$, 300 MHz)

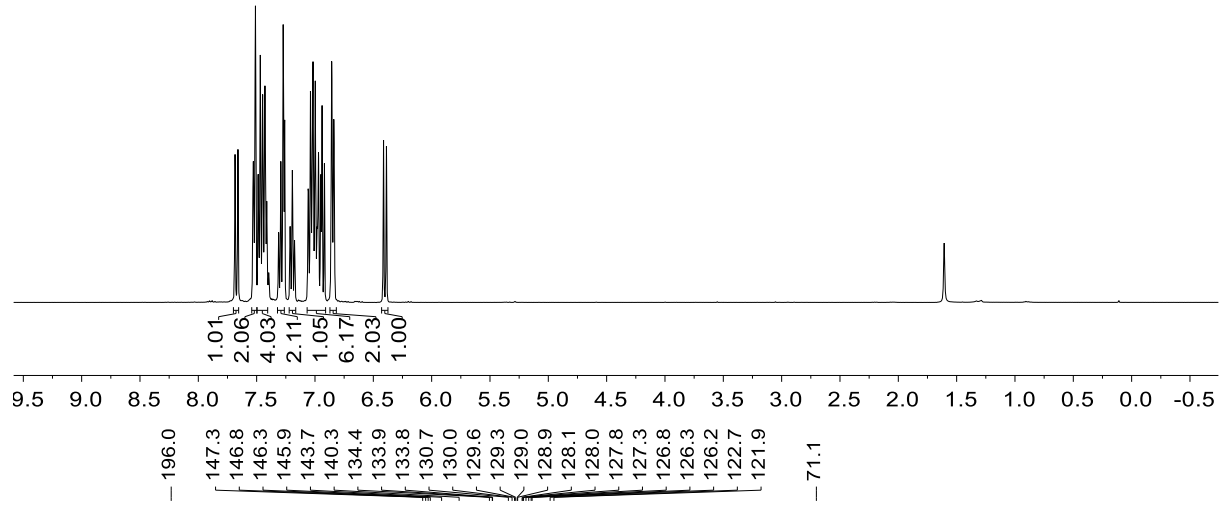


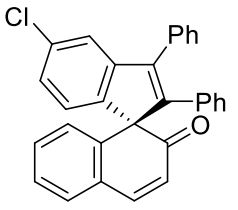


3bh
($CDCl_3$, 101 MHz)

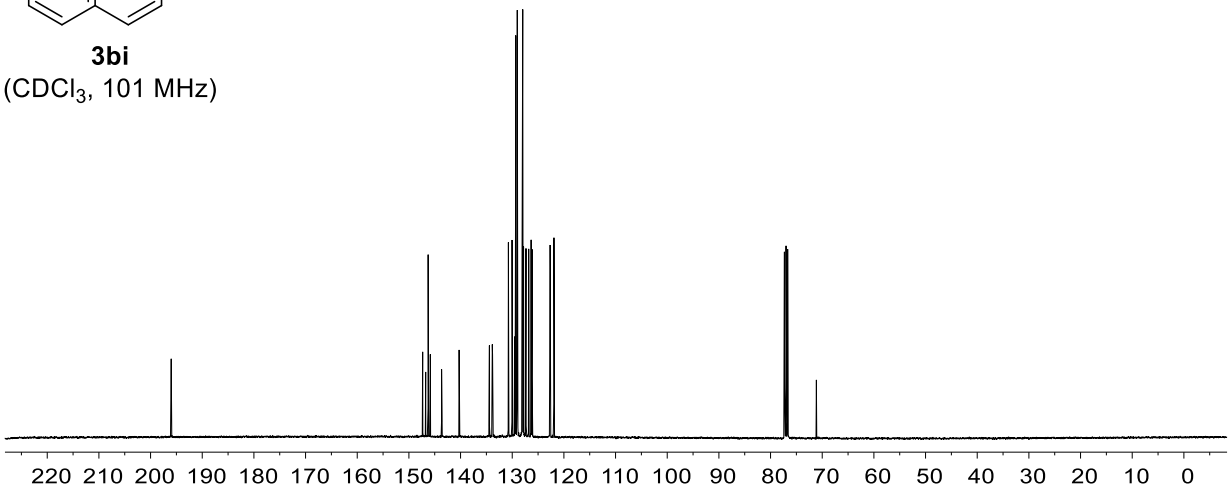


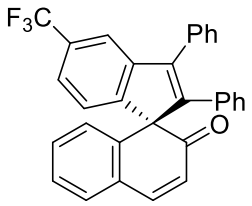
3bi
($CDCl_3$, 300 MHz)



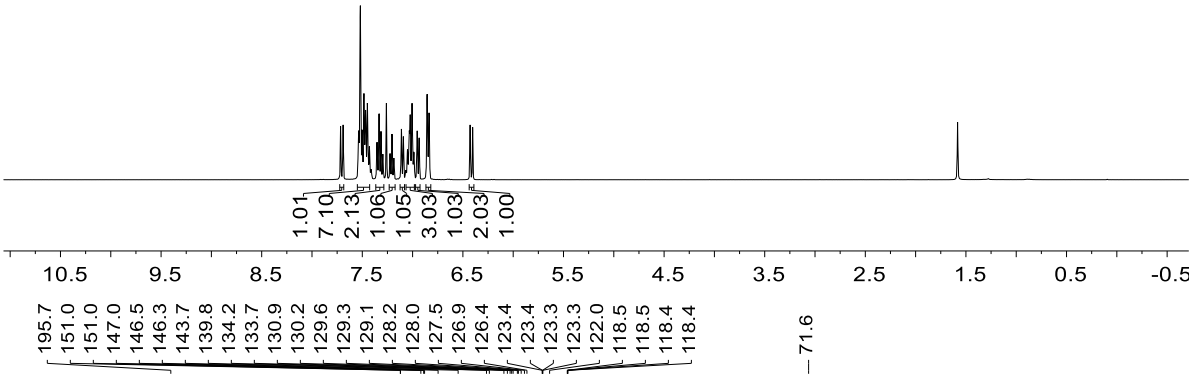


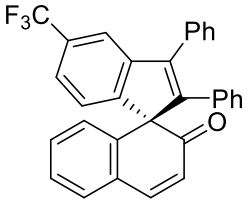
3bi
($CDCl_3$, 101 MHz)



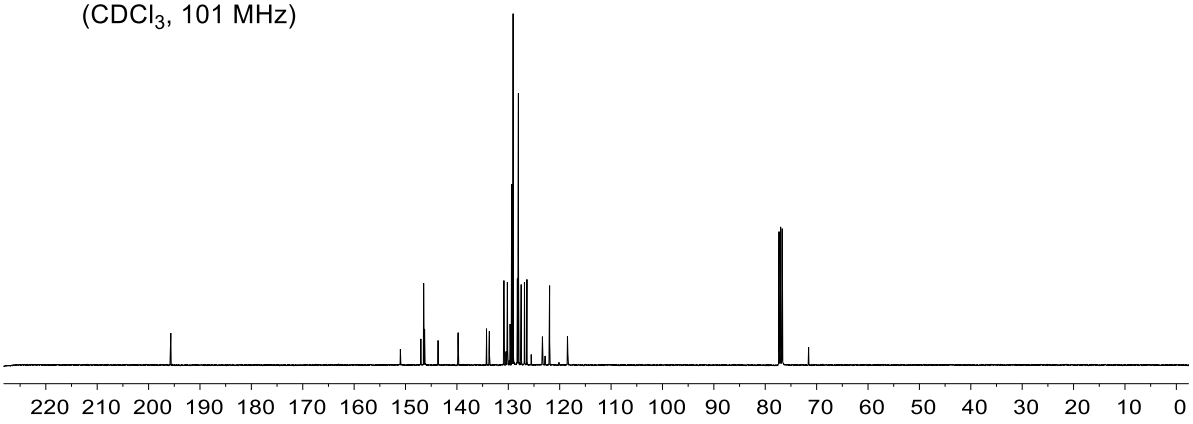


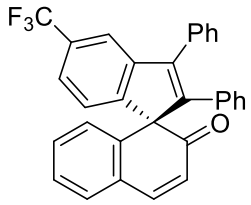
3bj
($CDCl_3$, 300 MHz)



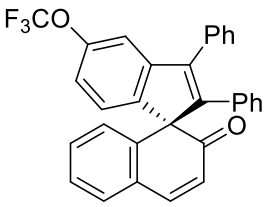


3bj
($CDCl_3$, 101 MHz)

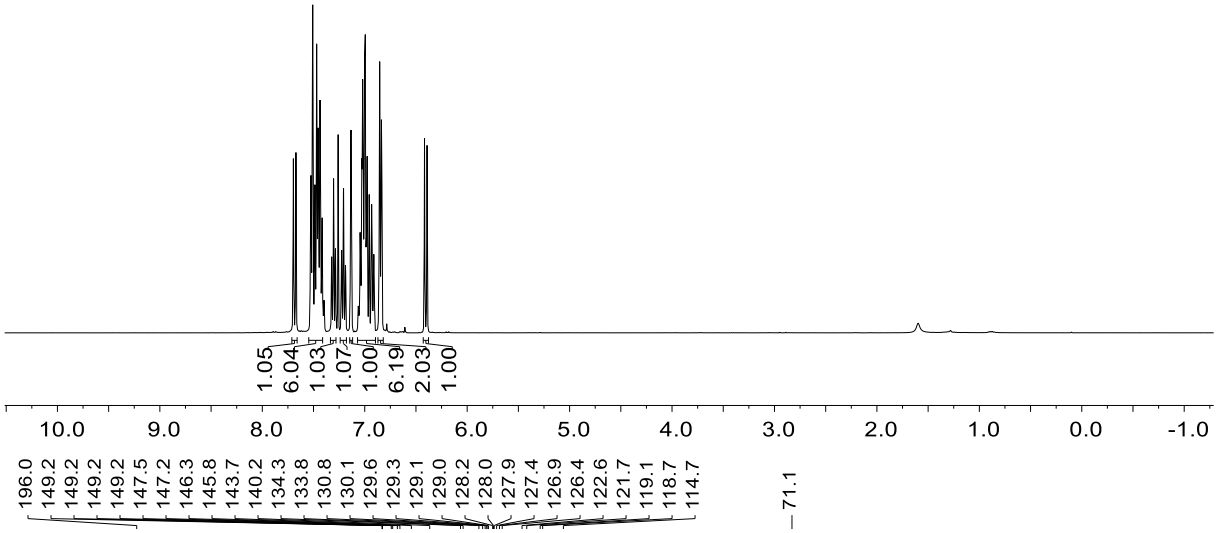


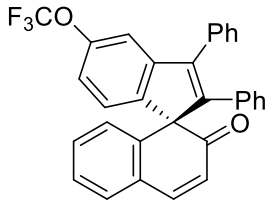


3bj
($CDCl_3$, 282 MHz)

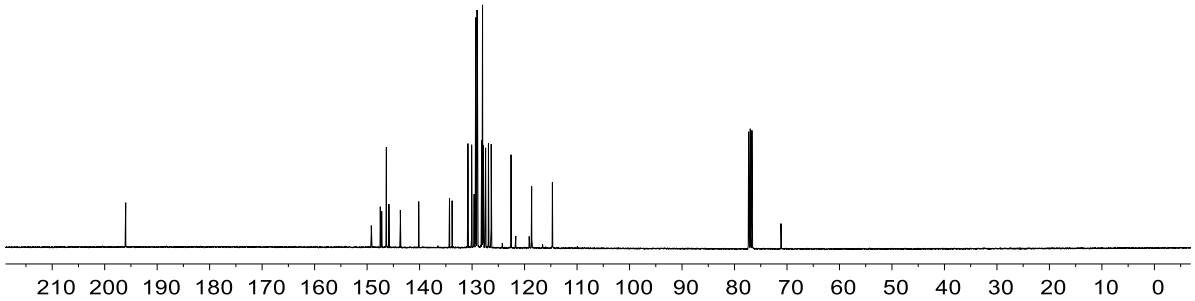


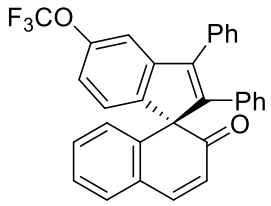
3bk
($CDCl_3$, 300 MHz)





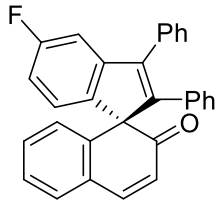
3bk
($CDCl_3$, 101 MHz)



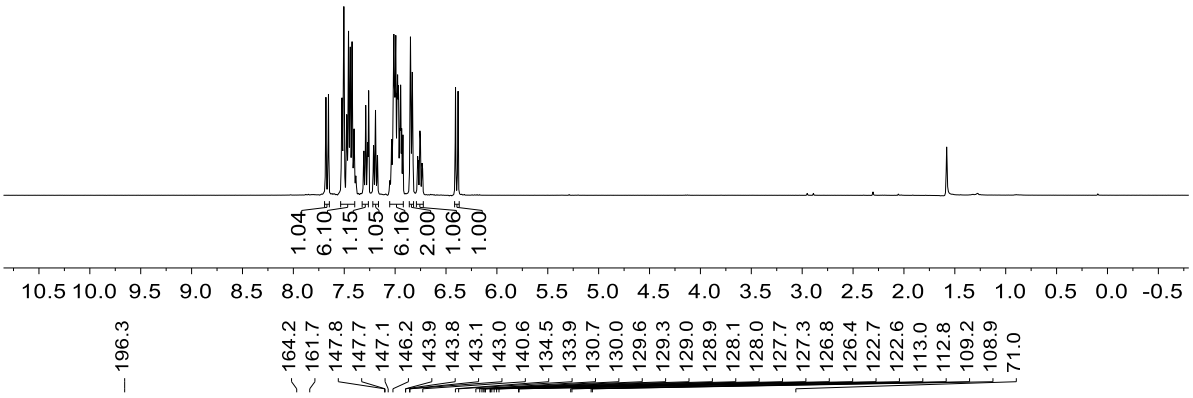


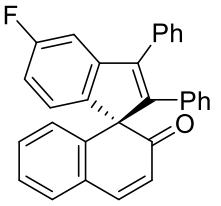
3bk

($CDCl_3$, 282 MHz)

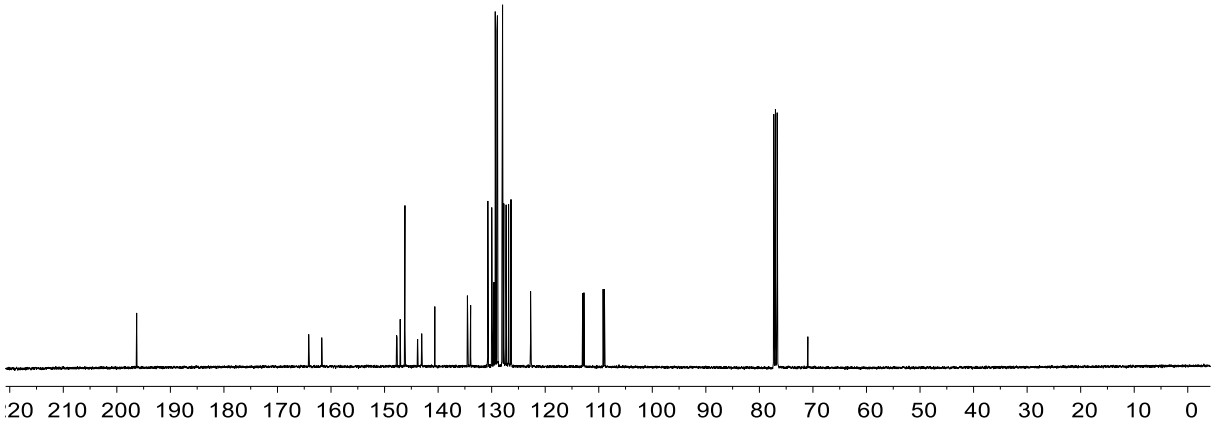


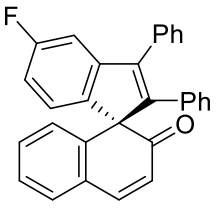
3bl
($CDCl_3$, 300 MHz)





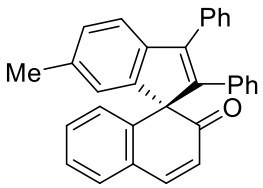
3bl
($CDCl_3$, 101 MHz)



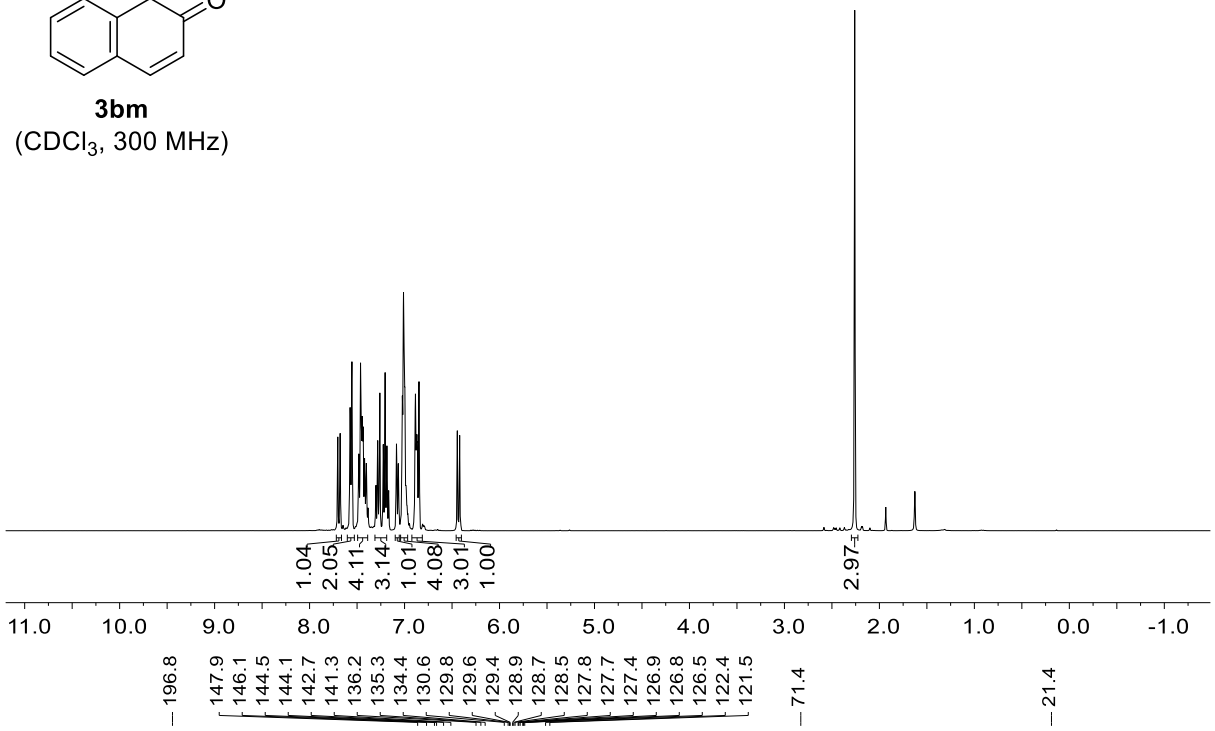


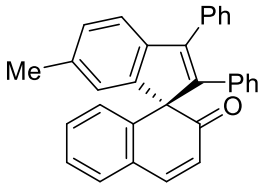
3bl

($CDCl_3$, 377 MHz)

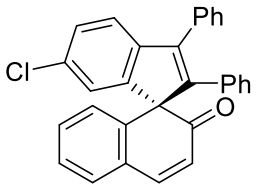


3bm
($CDCl_3$, 300 MHz)

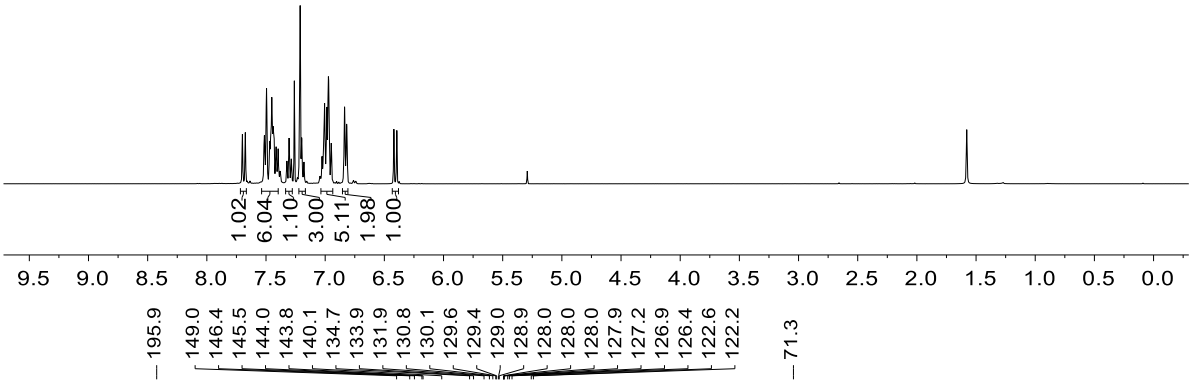


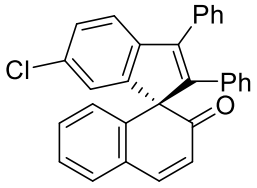


3bm
($CDCl_3$, 101 MHz)

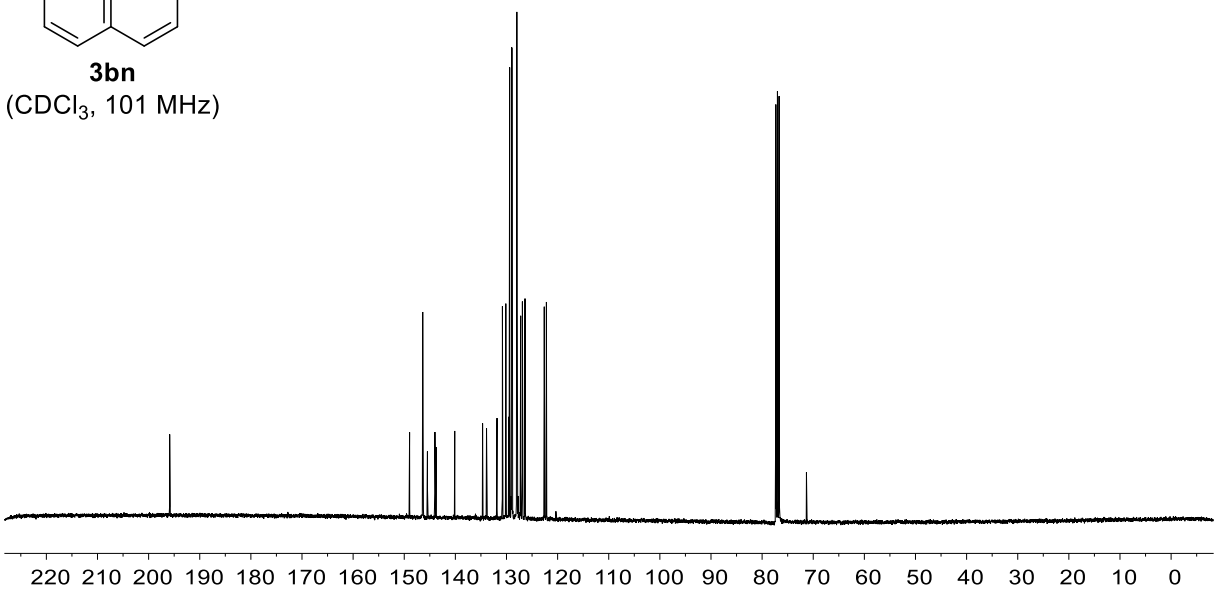


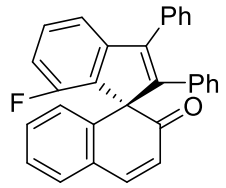
3bn
($CDCl_3$, 300 MHz)



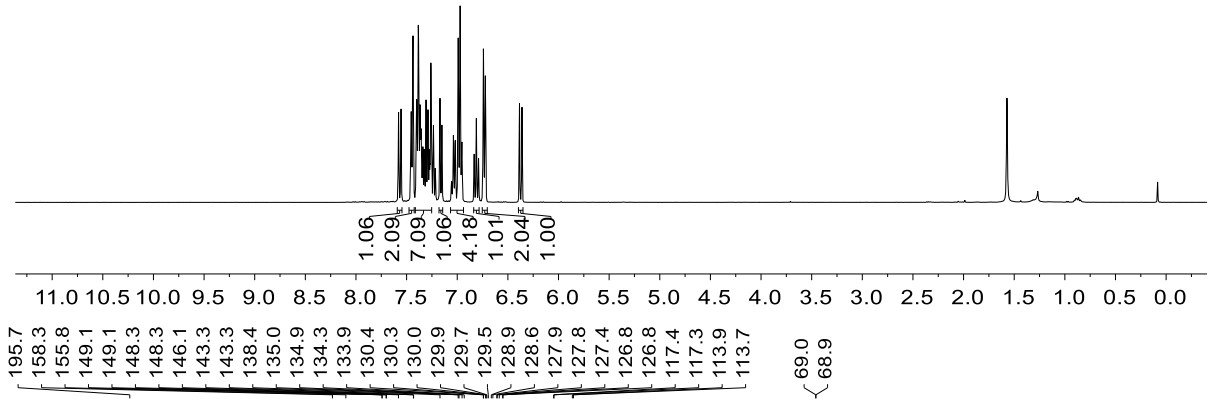


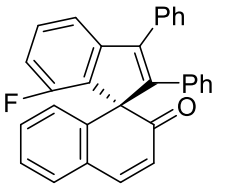
3bn
($CDCl_3$, 101 MHz)



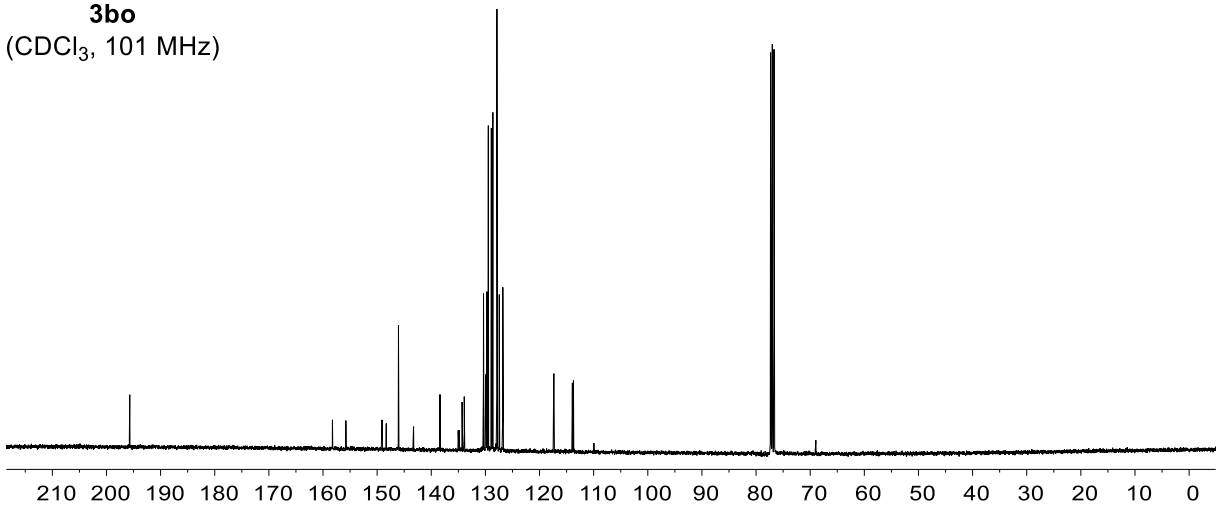


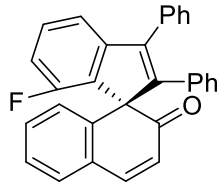
3bo
($CDCl_3$, 300 MHz)



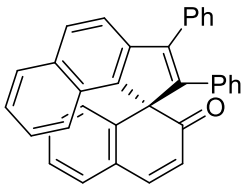


3bo
($CDCl_3$, 101 MHz)

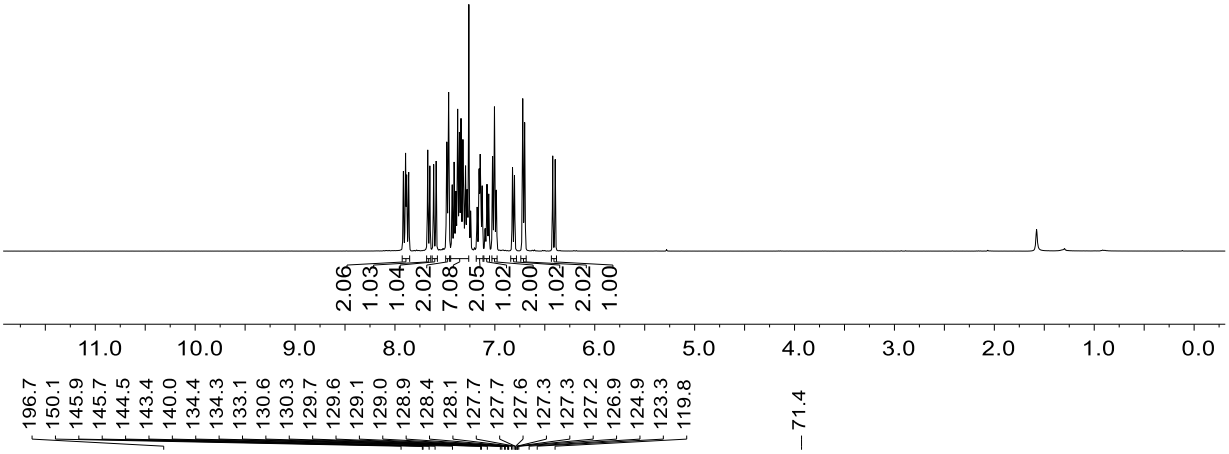


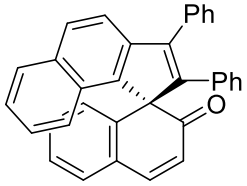


3bo
($CDCl_3$, 377 MHz)

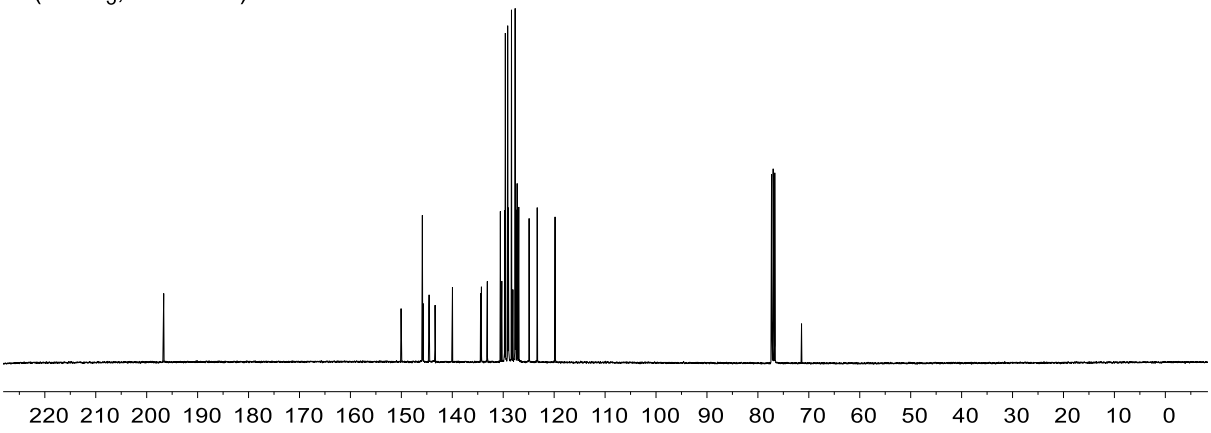


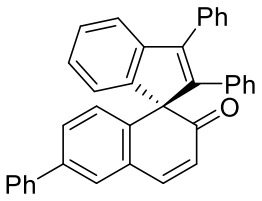
3bp
($CDCl_3$, 300 MHz)



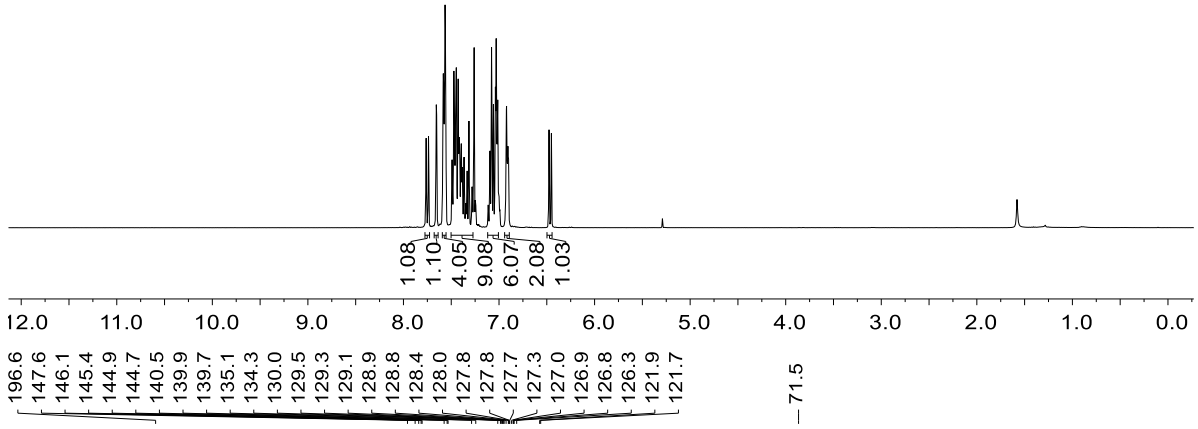


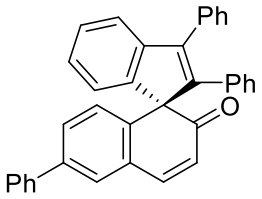
3bp
($CDCl_3$, 101 MHz)



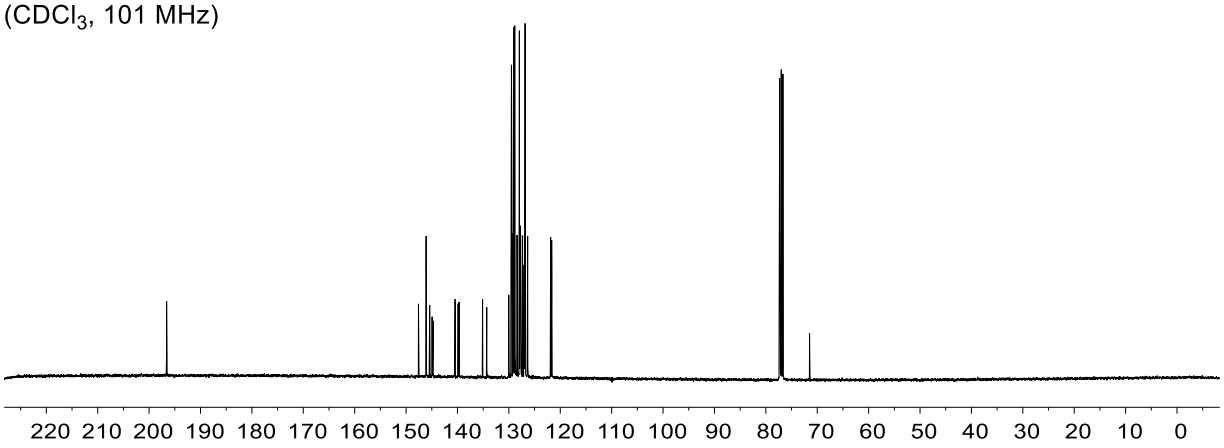


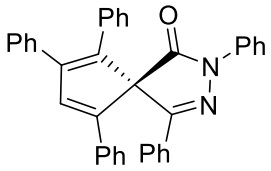
3bq
($CDCl_3$, 300 MHz)



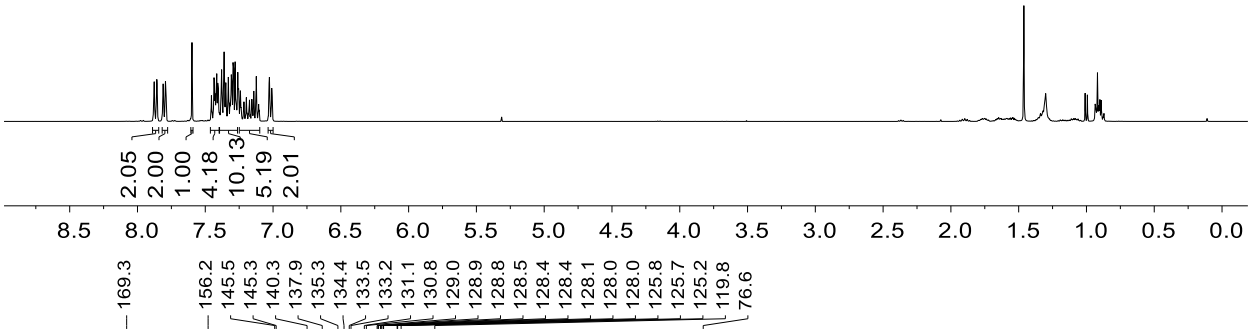


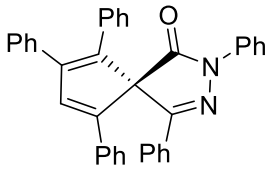
3bq
($CDCl_3$, 101 MHz)



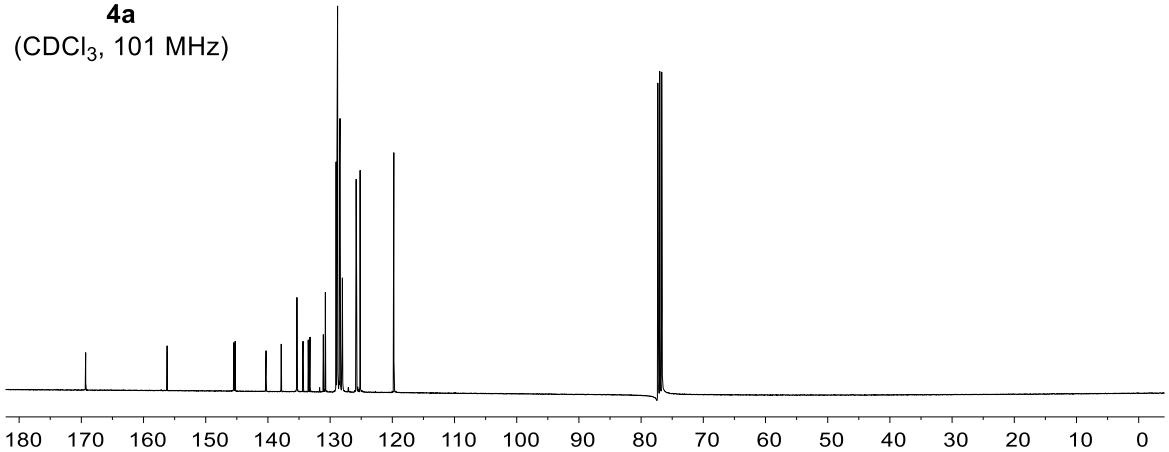


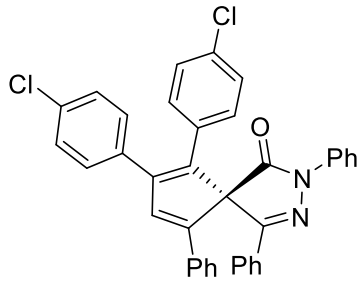
4a
($CDCl_3$, 300 MHz)



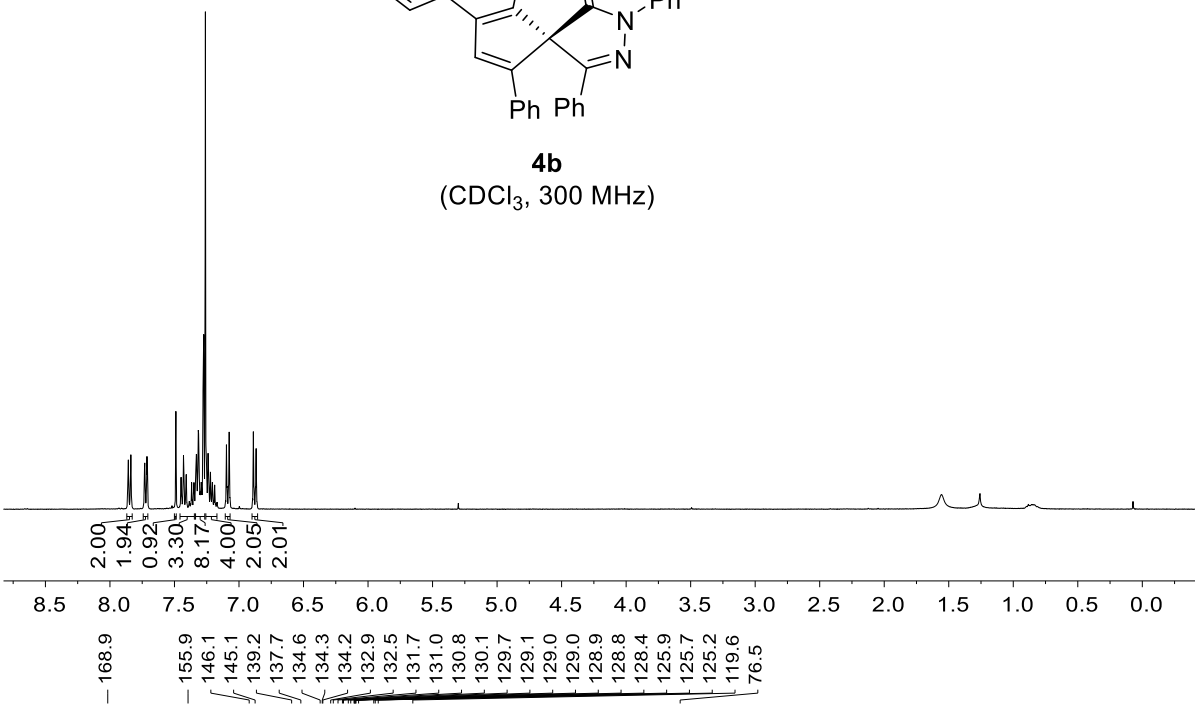


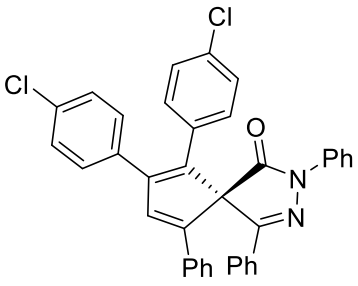
4a
($CDCl_3$, 101 MHz)



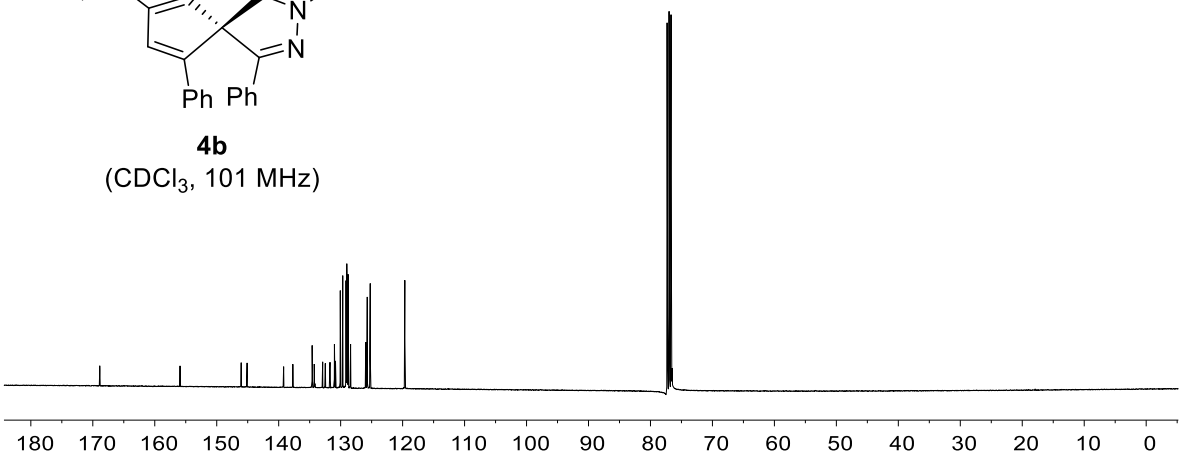


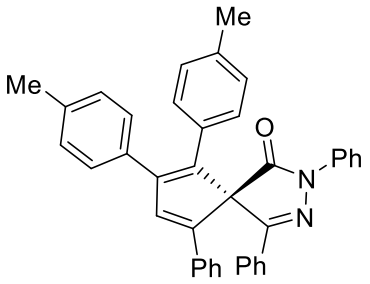
4b
($CDCl_3$, 300 MHz)





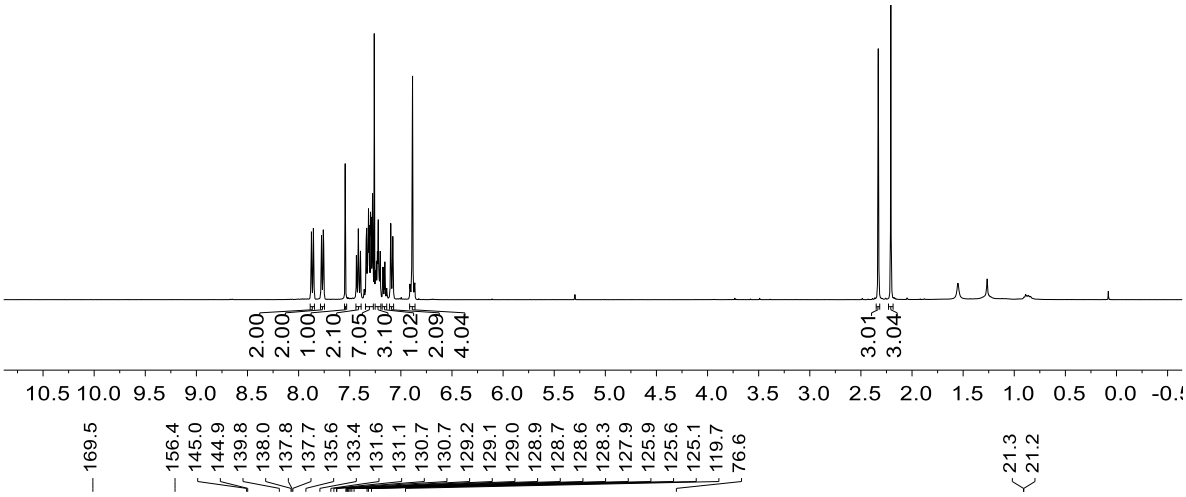
4b
($CDCl_3$, 101 MHz)

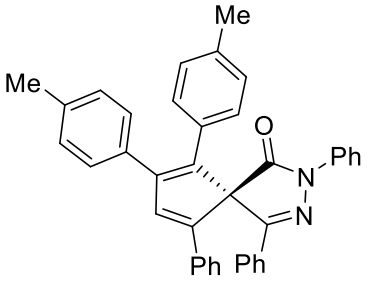




4c

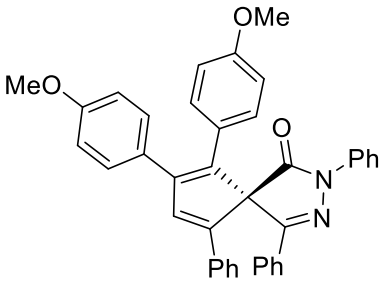
($CDCl_3$, 300 MHz)



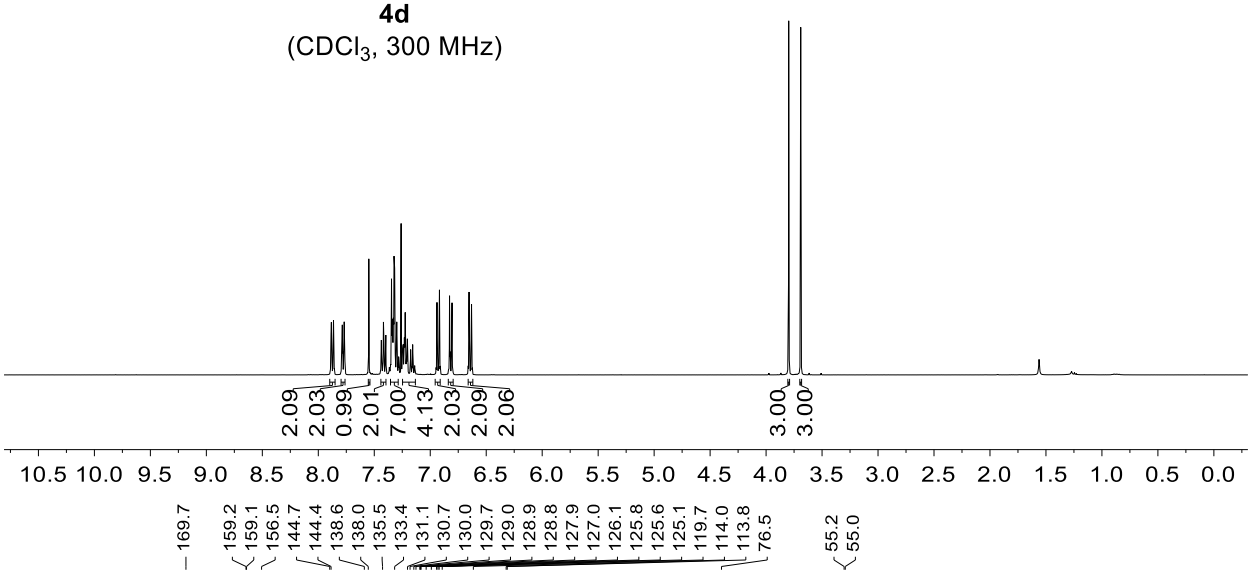


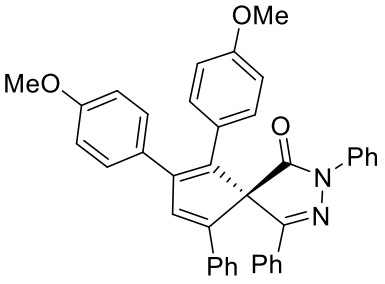
4c

($CDCl_3$, 101 MHz)

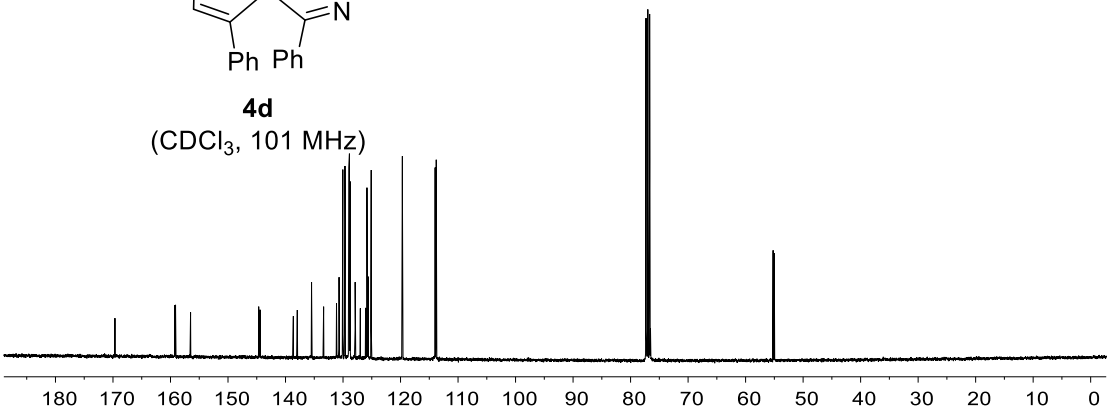


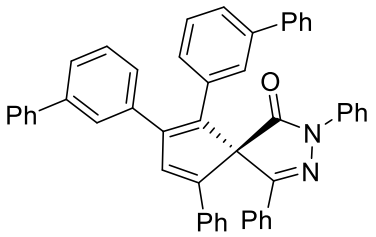
4d
($CDCl_3$, 300 MHz)



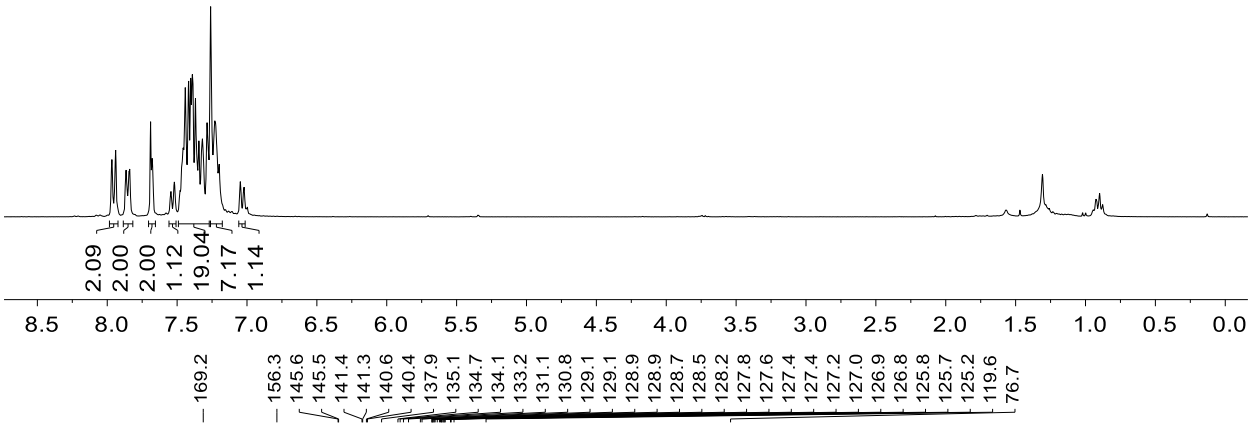


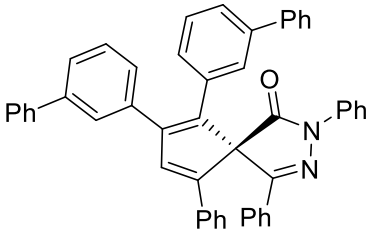
4d
($CDCl_3$, 101 MHz)



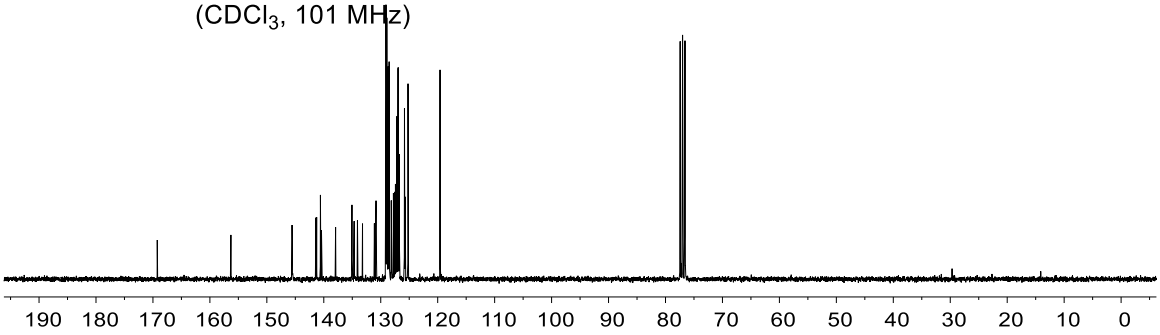


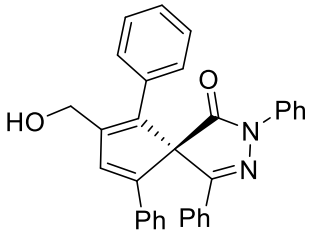
4e
($CDCl_3$, 300 MHz)





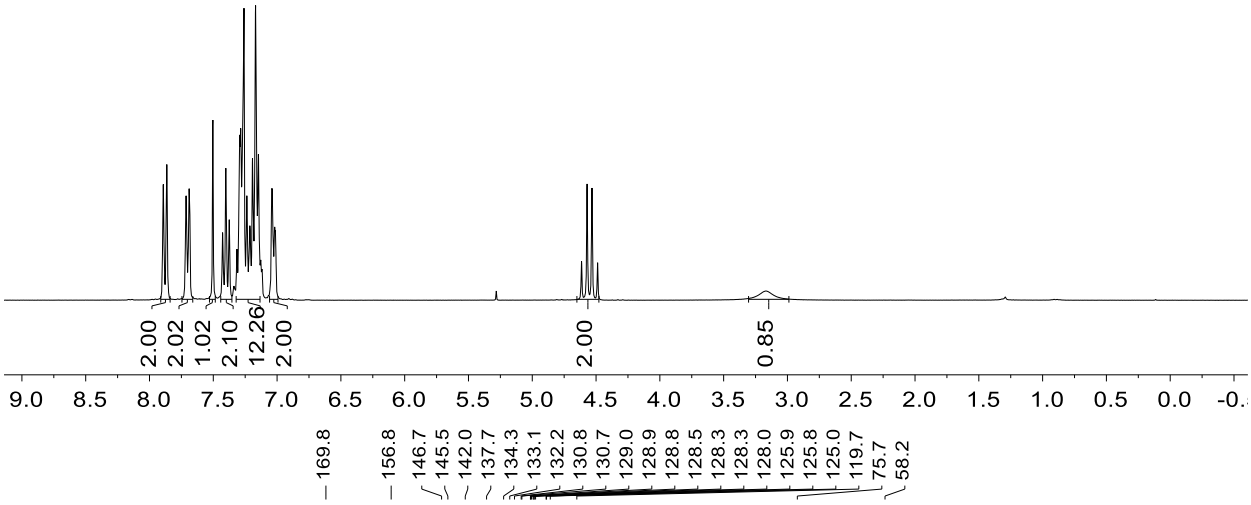
4e
($CDCl_3$, 101 MHz)

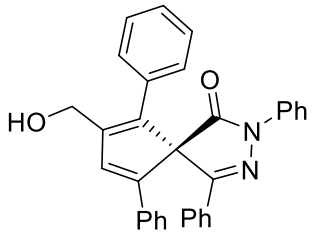




4f

($CDCl_3$, 300 MHz)





4f

($CDCl_3$, 101 MHz)