Supporting Information

Ruthenaelectro-Catalyzed C–H Acyloxylation for Late-Stage Tyrosine and Oligopeptide Diversification

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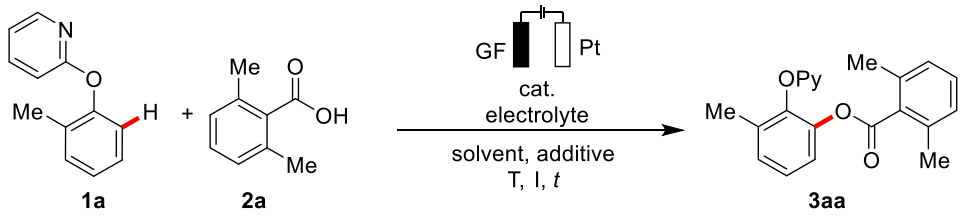
General Remarks

Catalytic reactions were carried out under air using Schlenk techniques. The following substrates **1**[1] and **4**[2] were synthesized according to previously described methods. Other chemicals and solvents were obtained from commercial sources, and were used without further purification. Platinum electrodes (10 mm × 15 mm × 0.25 mm, 99.9%, obtained from ChemPur) and graphite felt (GF) electrodes (10 mm × 15 mm × 6 mm, SIGRACELL®GFA 6EA, obtained from SGL Carbon) were connected using stainless steel adapters. Electrocatalysis was conducted using an AXIOMET AX-3003P potentiostat in constant current mode (CCE). Cyclic Voltammetry studies were performed using a Metrohm Autolab PGSTAT204 workstation and Nova 2.1 software. Yields refer to isolated compounds, estimated to be >95% pure as determined by ^{1}H-NMR and GC analysis. TLC: Macherey-Nagel, TLC plates Alugram® Sil G/UV254, detection under UV light at 254 nm. Chromatography: Separations were carried out on Merck Silica 60 (0.040–0.063 mm, 70–230 mesh ASTM). NMR: Spectra were recorded on a Varian Mercury 300, Varian Inova 500 or Bruker Avance III 300, Bruker Avance III HD 400 and Bruker Avance III HD 500 in the solvent indicated; chemical shifts (δ) are given in ppm relative to the residual solvent peak. IR: All spectra were recorded on a Bruker FT-IR Alpha device. MS: EI-MS-was recorded on Jeol AccuTOF at 70 eV and ESI-MS was recorded on Bruker micrOTOF and maXis. M. p.: Stuart melting point apparatus SMP3, Barloworld Scientific, values are uncorrected. Recycling preparative HPLC system from Japan Analytical Industries (LC-92XX II Series, UV and RI Detector) connected to JAIGEL 2HH series column with HPLC grade chloroform. HPLC chromatograms were recorded on an Agilent 1290 Infinity using CHIRALPAK® IA-3 column (3.0 µm particle size; Ø: 4.6 mm and 250 mm length).

Optimization of Reaction Conditions

Table S1: Optimization of the ruthenium-catalyzed acyloxylation.[a]



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

Entry	solvent	Cat.	electrolyte	additive	I (mA)	T (°C)	*t* (h)	Yield (%)
1	TFE	$[RuCl_2(p\text{-cymene})]_2$	*n*-Bu_4NBF_4	-	5.0	80	8	12[b]
2	TFE	$[RuCl_2(p\text{-cymene})]_2$	*n*-Bu_4NBF_4	-	3.0	80	15	28[b]
3	TFE	$[Ru(OAc)_2(p\text{-cymene})]$	*n*-Bu_4NBF_4	-	3.0	80	15	36
4	TFE	$[RuCl_2(p\text{-cymene})]_2$	*n*-Bu_4NBF_4	-	3.0	100	15	40[b]
5	TFE	$[Ru(OAc)_2(p\text{-cymene})]$	*n*-Bu_4NBF_4	-	3.0	100	15	65
6	EtOH	$[Ru(OAc)_2(p\text{-cymene})]$	*n*-Bu_4NBF_4	-	3.0	100	15	-
7	*t*-AmOH/H_2O (3/1)	$[Ru(OAc)_2(p\text{-cymene})]$	*n*-Bu_4NBF_4	-	3.0	100	15	-
8	DCE	$[Ru(OAc)_2(p\text{-cymene})]$	*n*-Bu_4NBF_4	-	3.0	100	15	87
9	DCE	$[Ru(OAc)_2(p\text{-cymene})]$	*n*-Bu_4NBF_4	PhI	3.0	100	15	87
10	DCE	$[Ru(OAc)_2(p\text{-cymene})]$	*n*-Bu_4NPF_6	-	3.0	100	15	86
11	DCE	$[Ru(OAc)_2(p\text{-cymene})]$	$LiClO_4$	-	3.0	100	15	-
12	DCE	$[Ru(OAc)_2(p\text{-cymene})]$	*n*-Bu_4OAc	-	3.0	100	15	-
13	DCE	$[RuCl_2(p\text{-cymene})]_2$	*n*-Bu_4NBF_4	-	3.0	100	15	78[b]
14	DCE	$[Ru_2(OAc)_4Cl]$	*n*-Bu_4NBF_4	-	3.0	100	15	86[b]
15	DCE	$[RuCl_3{\cdot}3H_2O]$	*n*-Bu_4NBF_4	-	3.0	100	15	66
16	DCE	$[RhCl_3{\cdot}3H_2O]$	*n*-Bu_4NBF_4	-	3.0	100	15	-
17	DCE	$[Cp^*RhCl_2]_2$	*n*-Bu_4NBF_4	-	3.0	100	15	15%[b]
18	DCE	$[Cp^*IrCl_2]_2$	*n*-Bu_4NBF_4	-	3.0	100	15	<5%[b]
19	DCE	$[Cp^*CoI_2(CO)]$	*n*-Bu_4NBF_4	-	3.0	100	15	-
20	DCE	-	*n*-Bu_4NBF_4	-	3.0	100	15	-
21	DCE	$[Ru(OAc)_2(p\text{-cymene})]$	*n*-Bu_4NBF_4	-	3.0	100	15	-[c]

[a] **1a** (0.25 mmol), **2a** (0.40 mmol), [Cat.] (10 mol %), electrolyte (82.3 mg, 0.25 mmol), additive (10 mol %), solvent (4.0 mL), GF (10 x 15 x 6 mm^3), Pt (10 x15 x 0.25 mm^3), air, reaction in a 25 mL Schlenk tube. [b] [Cat.] (5 mol %). [c] no electricity. OPy = 2-pyridyloxy, TFE = 2,2,2-trifluoroethanol, DCE = 1,2-dichloroethane.

General Procedures

General procedure A:

To a 25 mL schlenk tube equipped with a magnetic stirring bar were added phenol derivatives **1** (0.25 mmol), acids **2** (0.40 mmol), [Ru(OAc)$_2$(*p*-cymene)] (8.8 mg, 10 mol %) and *n*-Bu$_4$NBF$_4$ (82.3 mg, 0.25 mmol). The tube was sealed with a septum equipped with a platinum plate electrode (10 mm × 15 mm × 0.25 mm) and graphite felt electrode (10 mm × 15 mm × 6 mm). Then DCE (4.0 mL) were successively added. An oil bulb was attached to the system using a needle. The tube was placed in an oil bath and stirred at 100 °C. After 15 h at 3.0 mA, the tube was cooled to ambient temperature and the solvent was removed under vaccum. Products **3** was obtained by column chromatography on silica gel (*n*-hexane/EtOAc).

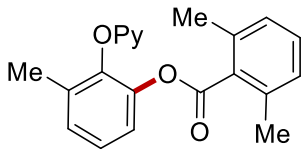
General procedure B:

To a 25 mL schlenk tube equipped with a magnetic stirring bar were added phenol derivative **1** (0.25 mmol), acid **2** (0.40 mmol), RuCl$_3$·3H$_2$O (6.5 mg, 10 mol %) and *n*-Bu$_4$NBF$_4$ (82.3 mg, 0.25 mmol). The tube was sealed with a septum equipped with a platinum plate electrode (10 mm × 15 mm × 0.25 mm) and graphite felt electrode (10 mm × 15 mm × 6 mm). Then DCE (4.0 mL) were successively added. An oil bulb was attached to the system using a needle. The tube was placed in an oil bath and stirred at 100 °C. After 15 h at 3.0 mA, the tube was cooled to ambient temperature and the solvent was removed under vaccum. Products **3** was obtained by column chromatography on silica gel (*n*-hexane/EtOAc).

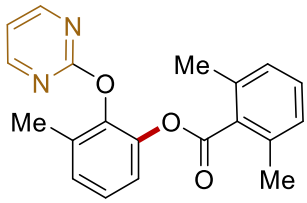
General procedure C:

To a 25 mL schlenk tube equipped with a magnetic stirring bar were added peptides **4** (0.25 mmol), acid **2** (0.75 mmol), [Ru(OAc)$_2$(*p*-cymene)] (8.8 mg, 10 mol %) and *n*-Bu$_4$NBF$_4$ (82.3 mg, 0.25 mmol). The tube was sealed with a septum equipped with a platinum plate electrode (10 mm × 15 mm × 0.25 mm) and graphite felt electrode (10 mm × 15 mm × 6 mm). Then DCE (4.0 mL) were successively added. An oil bulb was attached to the system using a needle. The tube was placed in an oil bath and stirred at 100 °C. After 15 h at 3.0 mA, the tube was cooled to ambient temperature and the solvent was removed under vaccum. Products **5** was obtained by column chromatography on silica gel (*n*-hexane/EtOAc).

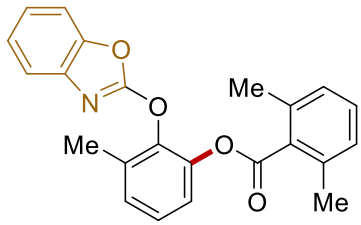
Characterization Data for Products



3-methyl-2-(pyridin-2-yloxy)phenyl 2,6-dimethylbenzoate (3aa): The general procedure **A** was followed using **1a** (46.3 mg, 0.25 mmol) and **2a** (60.1 mg, 0.40 mmol). Isolation by column chromatography on silica gel (*n*-hexane/EtOAc: 10:1→5:1) yielded **3aa** (72.5 mg, 87%) as a white solid. **M. p.** = 95–97 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.13 (ddd, J = 5.0, 2.0, 0.8 Hz, 1H), 7.64 (ddd, J = 8.3, 7.2, 2.0 Hz, 1H), 7.28 – 7.16 (m, 4H), 7.04 – 6.98 (m, 2H), 6.95 – 6.89 (m, 2H), 2.34 (s, 6H), 2.18 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 167.9 (C_q), 162.8 (C_q), 147.8 (CH), 143.7 (C_q), 143.6 (C_q), 139.4 (CH), 135.5 (C_q), 133.7 (C_q), 132.9 (C_q), 129.7 (CH), 128.9 (CH), 127.7 (CH), 125.9 (CH), 121.1 (CH), 118.2 (CH), 110.2 (CH), 19.8 (CH_3), 16.7 (CH_3). **IR** (ATR): 2966, 2924, 2868, 1742, 1595, 1426, 1231, 1055, 883, 774 cm^{-1}**.** **MS** (ESI) *m/z* (relative intensity): 334 (90) $[M+H]^+$, 356 (100) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{21}H_{20}NO_3^+$ $[M+H]^+$ 334.1438, found 334.1438.

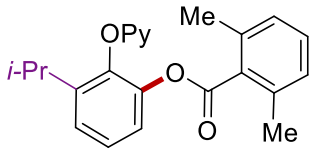


3-methyl-2-(pyrimidin-2-yloxy)phenyl 2,6-dimethylbenzoate (3ba): The general procedure **A** was followed using **1b** (46.6 mg, 0.25 mmol) and **2a** (60.1 mg, 0.40 mmol). Isolation by column chromatography on silica gel (*n*-hexane/EtOAc: 10:1→5:1) yielded **3ba** (75.1 mg, 90%) as a white solid. **M. p.** = 113–115 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.49 (d, J = 4.8 Hz, 2H), 7.28 – 7.18 (m, 3H), 7.15 (t, J = 7.6 Hz, 1H), 7.01 – 6.93 (m, 3H), 2.34 (s, 6H), 2.20 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 167.8 (C_q), 164.5 (C_q), 159.9 (CH), 143.2 (C_q), 143.1 (C_q), 135.6 (C_q), 133.3 (C_q), 132.8 (C_q), 129.8 (CH), 128.9 (CH), 127.7 (CH), 126.2 (CH), 121.2 (CH), 116.3 (CH), 19.9 (CH_3), 16.5 (CH_3). **IR** (ATR): 1752, 1569, 1470, 1397, 1299, 1236, 1049, 900, 764 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 357 (100) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{20}H_{18}N_2O_3Na^+$ $[M+Na]^+$ 357.1210, found 357.1209.

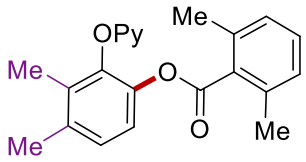


2-(benzo[d]oxazol-2-yloxy)-3-methylphenyl 2,6-dimethylbenzoate (3ca): The general procedure **A** was followed using **1c** (56.3 mg, 0.25 mmol) and **2a** (60.1 mg, 0.40 mmol). Isolation by column chromatography on silica gel (*n*-hexane/EtOAc: 20:1→10:1) yielded **3ca** (65.0 mg, 70%) as a colourless oil. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.48 – 7.44 (m, 1H), 7.40 – 7.36 (m, 1H), 7.35 – 7.31 (m, 1H), 7.27 – 7.25 (m, 1H), 7.25 – 7.23 (m, 1H), 7.23 – 7.19 (m, 2H), 7.18 – 7.14 (m, 1H), 7.02 – 6.98 (m, 2H), 2.38 (s, 6H), 2.34 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 167.6 (C_q), 161.5 (C_q), 148.9 (C_q), 143.0 (C_q), 142.5 (C_q), 140.9 (C_q), 135.6 (C_q), 132.6 (C_q), 132.4 (C_q), 130.0 (CH), 129.3 (CH), 127.8 (CH), 127.5 (CH), 124.7 (CH),

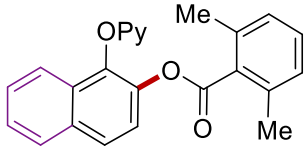
123.5 (CH), 121.6 (CH), 119.0 (CH), 110.0 (CH), 19.8 (CH_3), 16.2 (CH_3). **IR** (ATR): 2925, 1753, 1626, 1569, 1465, 1317, 1231, 1173, 1044, 749 cm^{-1}**. MS** (ESI) *m/z* (relative intensity): 374 (10) $[M+H]^+$, 396 (100) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{23}H_{20}NO_4^+$ $[M+H]^+$ 374,1387, found 374.1372.



3-isopropyl-2-(pyridin-2-yloxy)phenyl 2,6-dimethylbenzoate (3da): The general procedure **A** was followed using **1d** (53.3 mg, 0.25 mmol) and **2a** (60.1 mg, 0.40 mmol). Isolation by column chromatography on silica gel (*n*-hexane/EtOAc: 10:1→5:1) yielded **3da** (83.1 mg, 92%) as a white solid. **M. p.** = 122–124 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.12 (ddd, *J* = 5.0, 2.0, 0.8 Hz, 1H), 7.62 (ddd, *J* = 8.3, 7.2, 2.0 Hz, 1H), 7.36 – 7.31 (m, 2H), 7.23 (dd, *J* = 7.2, 2.5 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 7.6, 2H), 6.94 – 6.88 (m, 2H), 3.10 (hept, *J* = 6.9 Hz, 1H), 2.30 (s, 6H), 1.19 (d, *J* = 6.9 Hz, 6H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 167.9 (C_q), 163.4 (C_q), 147.8 (CH), 143.8 (C_q), 143.6 (C_q), 142.4 (C_q), 139.3 (CH), 135.5 (C_q), 132.9 (C_q), 129.7 (CH), 127.6 (CH), 126.2 (CH), 124.5 (CH), 120.8 (CH), 118.2 (CH), 110.1 (CH), 27.4 (CH), 23.2 (CH_3), 19.8 (CH_3). **IR** (ATR): 2966, 2924, 1739, 1595, 1461, 1428, 1230, 1048, 884, 780 cm^{-1}**. MS** (ESI) *m/z* (relative intensity): 362 (100) $[M+H]^+$, 384 (65) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{23}H_{24}NO_3^+$ $[M+H]^+$ 362.1751, found 362.1753.

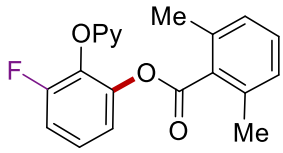


3,4-dimethyl-2-(pyridin-2-yloxy)phenyl 2,6-dimethylbenzoate (3ea): The general procedure **A** was followed using **1e** (50.0 mg, 0.25 mmol) and **2a** (60.1 mg, 0.40 mmol). Isolation by column chromatography on silica gel (*n*-hexane/EtOAc: 10:1→5:1) yielded **3ea** (71.2 mg, 82%) as a white solid. **M. p.** = 116–118 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.13 (ddd, *J* = 5.0, 2.0, 0.9 Hz, 1H), 7.64 (ddd, *J* = 8.3, 7.2, 2.0 Hz, 1H), 7.20 – 7.15 (m, 2H), 7.12 (d, *J* = 8.2 Hz, 1H), 7.01 (d, *J* = 7.6 Hz, 2H), 6.93 – 6.90 (m, 2H), 2.36 – 2.33 (m, 9H), 2.09 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 168.1 (C_q), 163.0 (C_q), 147.8 (CH), 143.3 (C_q), 141.5 (C_q), 139.3 (CH), 136.2 (C_q), 135.4 (C_q), 133.0 (C_q), 132.0 (C_q), 129.6 (CH), 127.6 (CH), 127.2 (CH), 120.1 (CH), 118.1 (CH), 110.2 (CH), 20.0 (CH_3), 19.7 (CH_3), 13.2 (CH_3). **IR** (ATR): 2921, 1745, 1573, 1467, 1426, 1271, 1231, 1055, 838, 779 cm^{-1}**. MS** (ESI) *m/z* (relative intensity): 348 (100) $[M+H]^+$, 370 (85) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{22}H_{22}NO_3^+$ $[M+H]^+$ 348.1594, found 348.1597.

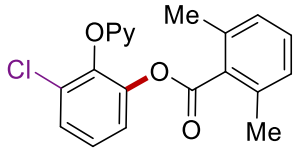


1-(pyridin-2-yloxy)naphthalen-2-yl 2,6-dimethylbenzoate (3fa): The general procedure **A** was followed using **1f** (55.3 mg, 0.25 mmol) and **2a** (60.1 mg, 0.40 mmol). Isolation by column chromatography on silica gel (*n*-hexane/EtOAc: 10:1→5:1) yielded **3fa** (74.8 mg, 81%) as a white solid. **M. p.** = 165–167 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.10 (ddd, *J* = 5.0, 2.0, 0.8 Hz, 1H), 7.96 – 7.85 (m, 3H), 7.66 (ddd, *J* = 8.4, 7.2, 2.0 Hz, 1H), 7.55 – 7.44 (m, 3H), 7.22 (dd, *J* = 8.0, 7.3 Hz, 1H), 7.07 – 6.98 (m, 3H), 6.94 (ddd, *J* = 7.2, 5.0, 0.9 Hz, 1H), 2.40 (s, 6H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 168.0 (C_q), 163.6 (C_q), 147.9 (CH), 140.2 (C_q), 139.9 (C_q), 139.5 (CH), 135.5 (C_q), 133.0 (C_q), 132.7 (C_q), 129.8 (CH), 128.8 (C_q), 128.2 (CH), 127.7 (CH),

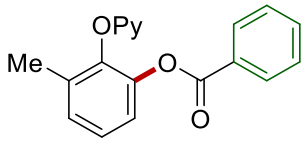
126.8 (CH), 126.5 (CH), 126.3 (CH), 122.3 (CH), 122.0 (CH), 118.5 (CH), 110.1 (CH), 19.8 (CH_3). **IR** (ATR): 2923, 2853, 1753, 1589, 1464, 1426, 1374, 1240, 1050, 774 cm^{-1}**. MS** (ESI) *m/z* (relative intensity): 370 (100) $[M+H]^+$, 392 (50) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{24}H_{20}NO_3^+$ $[M+H]^+$ 370.1438, found 370.1437.



3-fluoro-2-(pyridin-2-yloxy)phenyl 2,6-dimethylbenzoate (3ga): The general procedure **A** was followed using **1g** (47.3 mg, 0.25 mmol) and **2a** (60.1 mg, 0.40 mmol). Isolation by column chromatography on silica gel (*n*-hexane/EtOAc: 10:1→5:1) yielded **3ga** (75.9 mg, 90%) as a white solid. **M. p.** = 113–115 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.13 (ddd, *J* = 4.9, 2.0, 0.8 Hz, 1H), 7.68 (ddd, *J* = 8.3, 7.2, 2.0 Hz, 1H), 7.33 – 7.25 (m, 1H), 7.25 – 7.14 (m, 3H), 7.07 – 6.96 (m, 4H), 2.39 (s, 6H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 167.4 (C_q), 162.1 (C_q), 156.2 (d, $^1J_{C\text{-}F}$ = 250.6 Hz, C_q), 147.5 (CH), 144.7 (d, $^3J_{C\text{-}F}$ = 3.8 Hz, C_q), 139.5 (CH), 135.6 (C_q), 134.1 (d, $^2J_{C\text{-}F}$ = 14.6 Hz, C_q), 132.4 (C_q), 130.0 (CH), 127.8 (CH), 125.6 (d, $^3J_{C\text{-}F}$ = 8.8 Hz, CH), 119.0 (d, $^4J_{C\text{-}F}$ = 2.8 Hz, CH), 119.0 (CH), 114.5 (d, $^2J_{C\text{-}F}$ = 18.8 Hz, CH), 110.5 (CH), 19.9 (CH_3). **^{19}F NMR** (376 MHz, $CDCl_3$) δ= (-124.16) – (-124.22) (m). **IR** (ATR): 2924, 1754, 1592, 1475, 1429, 1279, 1229, 1099, 1040, 772 cm^{-1}**. MS** (ESI) *m/z* (relative intensity): 338 (100) $[M+H]^+$, 360 (90) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{20}H_{17}FNO_3^+$ $[M+H]^+$ 338.1187, found 338.1189.

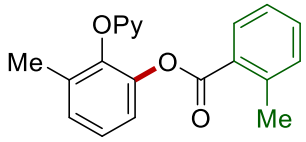


3-chloro-2-(pyridin-2-yloxy)phenyl 2,6-dimethylbenzoate (3ha): The general procedure **A** was followed using **1h** (51.3 mg, 0.25 mmol) and **2a** (60.1 mg, 0.40 mmol). Isolation by column chromatography on silica gel (*n*-hexane/EtOAc: 10:1→5:1) yielded **3ha** (58.4 mg, 66%) as a white solid. **M. p.** = 121–123 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.11 (ddd, *J* = 5.0, 2.0, 0.8 Hz, 1H), 7.68 (ddd, *J* = 8.3, 7.2, 2.0 Hz, 1H), 7.43 (dd, *J* = 6.2, 3.4 Hz, 1H), 7.32 – 7.26 (m, 2H), 7.23 – 7.17 (m, 1H), 7.04 – 6.95 (m, 4H), 2.34 (s, 6H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 167.5 (C_q), 162.2 (C_q), 147.6 (CH), 145.0 (C_q), 142.4 (C_q), 139.6 (CH), 135.6 (C_q), 132.4 (C_q), 130.0 (CH), 129.7 (C_q), 128.1 (CH), 127.8 (CH), 126.2 (CH), 122.3 (CH), 118.8 (CH), 110.6 (CH), 19.8 (CH_3). **IR** (ATR): 2923, 1749, 1575, 1464, 1427, 1228, 1172, 1043, 880, 771 cm^{-1}**. MS** (ESI) *m/z* (relative intensity): 354 (100) $[M+H]^+$, 376 (90) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{20}H_{17}ClNO_3^+$ $[M+H]^+$ 354.0891, found 354.0894.

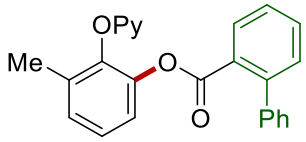


3-methyl-2-(pyridin-2-yloxy)phenyl benzoate (3ab): The general procedure **A/B** was followed using **1a** (46.3 mg, 0.25 mmol) and **2b** (48.8 mg, 0.40 mmol). Isolation by column chromatography on silica gel (*n*-hexane/EtOAc: 10:1→5:1) yielded **3ab** (51.9 mg, 68%, procedure **A**) (45.7 mg, 60%, procedure **B**) as a white solid. **M. p.** = 82–88 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.12 (ddd, *J* = 5.0, 2.0, 0.8 Hz, 1H), 7.86 – 7.79 (m, 2H), 7.57 – 7.49 (m, 2H), 7.38 – 7.31 (m, 2H), 7.24 – 7.18 (m, 3H), 6.89 (ddd, *J* = 7.2, 5.0, 0.9 Hz, 1H), 6.82 (dt, *J* = 8.3, 0.9 Hz, 1H), 2.27 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 164.4 (C_q), 163.0 (C_q), 147.7 (CH), 143.7 (C_q), 143.4 (C_q), 139.3 (CH), 133.5 (CH), 133.2 (C_q), 130.1 (CH), 129.2 (C_q), 128.6 (CH), 128.4

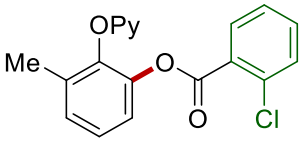
(CH), 125.5 (CH), 121.2 (CH), 118.2 (CH), 110.4 (CH), 16.5 (CH_3). **IR** (ATR): 3031, 2924, 1731, 1597, 1464, 1427, 1264, 1237, 1063, 774 cm^{-1}**. MS** (ESI) *m/z* (relative intensity): 306 (100) $[M+H]^+$, 328 (65) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{19}H_{16}NO_3^+$ $[M+H]^+$ 306.1125, found 306.1122.



3-methyl-2-(pyridin-2-yloxy)phenyl 2-methylbenzoate (3ac): The general procedure **A** was followed using **1a** (46.3 mg, 0.25 mmol) and **2c** (54.4 mg, 0.40 mmol). Isolation by column chromatography on silica gel (*n*-hexane/EtOAc: 10:1→5:1) yielded **3ac** (48.7 mg, 61%) as a white solid. **M. p.** = 90–92 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.13 (ddd, *J* = 5.0, 2.0, 0.8 Hz, 1H), 7.62 – 7.53 (m, 2H), 7.37 (ddd, *J* = 7.5, 7.5, 1.5 Hz, 1H), 7.24 – 7.19 (m, 3H), 7.17 (dd, *J* = 6.9, 2.9 Hz, 1H), 7.09 (dddd, *J* = 8.0, 7.4, 1.4, 0.7 Hz, 1H), 6.91 (ddd, *J* = 7.2, 5.0, 1.0 Hz, 1H), 6.83 (dt, *J* = 8.3, 0.9 Hz, 1H), 2.53 (s, 3H), 2.25 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 165.0 (C_q), 163.0 (C_q), 147.8 (CH), 143.8 (C_q), 143.5 (C_q), 141.4 (C_q), 139.4 (CH), 133.4 (C_q), 132.6 (CH), 131.8 (CH), 131.1 (CH), 128.6 (CH), 128.2 (C_q), 125.7 (CH), 125.6 (CH), 121.3 (CH), 118.3 (CH), 110.4 (CH), 21.8 (CH_3), 16.6 (CH_3). **MS** (ESI) *m/z* (relative intensity): 320 (100) $[M+H]^+$, 342 (40) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{20}H_{18}NO_3^+$ $[M+H]^+$ 320.1281, found 320.1285.

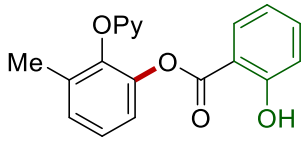


3-methyl-2-(pyridin-2-yloxy)phenyl [1,1'-biphenyl]-2-carboxylate (3ad): The general procedure **B** was followed using **1a** (46.3 mg, 0.25 mmol) and **2d** (79.3 mg, 0.40 mmol). Isolation by column chromatography on silica gel (*n*-hexane/EtOAc: 10:1→5:1) yielded **3ad** (53.4 mg, 56%) as a white solid. **M. p.** = 176–178 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.14 (ddd, *J* = 5.0, 2.0, 0.8 Hz, 1H), 7.64 – 7.54 (m, 2H), 7.50 (ddd, *J* = 7.6, 7.6, 1.4 Hz, 1H), 7.39 – 7.27 (m, 7H), 7.15 – 7.08 (m, 2H), 6.94 (ddd, *J* = 7.2, 5.0, 0.9 Hz, 1H), 6.91 – 6.86 (m, 1H), 6.84 (dt, *J* = 8.3, 0.9 Hz, 1H), 2.18 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 165.7 (C_q), 163.0 (C_q), 147.8 (CH), 143.6 (C_q), 143.4 (C_q), 143.4 (C_q), 141.0 (C_q), 139.4 (CH), 133.2 (C_q), 131.7 (CH), 131.0 (CH), 139.1 (CH), 129.6 (C_q), 128.7 (CH), 128.5 (CH), 128.1 (CH), 127.4 (CH), 127.1 (CH), 125.5 (CH), 120.8 (CH), 118.2 (CH), 110.2 (CH), 16.5 (CH_3). **IR** (ATR): 3059, 2922, 1740, 1570, 1464, 1427, 1232, 1187, 1042, 752 cm^{-1}**. MS** (ESI) *m/z* (relative intensity): 382 (100) $[M+H]^+$, 404 (30) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{25}H_{20}NO_3^+$ $[M+H]^+$ 382.1438, found 382.1440.

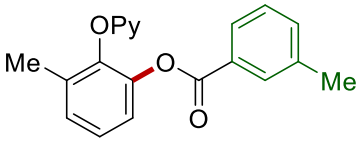


3-methyl-2-(pyridin-2-yloxy)phenyl 2-chlorobenzoate (3ae): The general procedure **A** was followed using **1a** (46.3 mg, 0.25 mmol) and **2e** (62.4 mg, 0.40 mmol). Isolation by column chromatography on silica gel (*n*-hexane/EtOAc: 10:1→5:1) yielded **3ae** (46.7 mg, 55%) as a white solid. **M. p.** = 100–102 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.12 (ddd, *J* = 5.0, 2.0, 0.8 Hz, 1H), 7.59 (ddd, *J* = 8.3, 7.2, 2.0 Hz, 1H), 7.55 – 7.50 (m, 1H), 7.44 – 7.34 (m, 2H), 7.24 – 7.20 (m, 3H), 7.17 (ddd, *J* = 7.8, 6.8, 1.7 Hz, 1H), 6.92 (ddd, *J* = 7.2, 5.0, 0.9 Hz, 1H), 6.88 (dt, *J* = 8.3, 0.9 Hz, 1H), 2.24 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 163.0

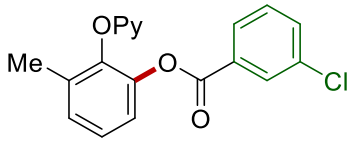
(C_q), 162.9 (C_q), 147.8 (CH), 143.5 (C_q), 143.3 (C_q), 139.4 (CH), 134.6 (C_q), 133.4 (C_q), 133.1 (CH), 131.8 (CH), 131.3 (CH), 128.8 (CH), 128.8 (C_q), 126.5 (CH), 125.6 (CH), 121.1 (CH), 118.3 (CH), 110.3 (CH), 16.5 (CH_3). **IR** (ATR): 2927, 2853, 1718, 1591, 1467, 1425, 1273, 1233, 1109, 774 cm^{-1}**. MS** (ESI) *m/z* (relative intensity): 340 (100) $[M+H]^+$, 362 (30) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{19}H_{15}{}^{35}ClNO_3^+$ $[M+H]^+$ 340.0735, found 340.0742.



3-methyl-2-(pyridin-2-yloxy)phenyl 2-hydroxybenzoate (3af): The general procedure **A** was followed using **1a** (46.3 mg, 0.25 mmol) and **2f** (55.2 mg, 0.40 mmol). Isolation by column chromatography on silica gel (*n*-hexane/EtOAc: 10:1→5:1) yielded **3af** (57.0 mg, 71%) as a white solid. **M. p.** = 111–113 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 10.37 (s, 1H), 8.11 (ddd, *J* = 5.0, 2.0, 0.8 Hz, 1H), 7.55 (ddd, *J* = 8.3, 7.2, 2.0 Hz, 1H), 7.49 – 7.40 (m, 2H), 7.26 – 7.16 (m, 3H), 6.96 (ddd, *J* = 8.4, 1.2, 0.5 Hz, 1H), 6.90 (ddd, *J* = 7.2, 5.0, 0.9 Hz, 1H), 6.84 (dt, *J* = 8.3, 0.9 Hz, 1H), 6.73 (ddd, *J* = 8.0, 7.2, 1.1 Hz, 1H), 2.28 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 168.2 (C_q), 162.8 (C_q), 162.0 (C_q), 147.6 (CH), 143.6 (C_q), 142.6 (C_q), 139.5 (CH), 136.4 (CH), 133.5 (C_q), 130.2 (CH), 129.0 (CH), 125.5 (CH), 121.0 (CH), 119.3 (CH), 118.4 (CH), 117.6 (CH), 111.6 (C_q), 110.4 (CH), 16.5 (CH_3). **IR** (ATR): 3271, 2920, 1686, 1573, 1461, 1425, 1230, 1154, 1064, 778 cm^{-1}**. MS** (ESI) *m/z* (relative intensity): 322 (100) $[M+H]^+$, 344 (90) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{19}H_{16}NO_4^+$ $[M+H]^+$ 322.1074, found 322.1074.

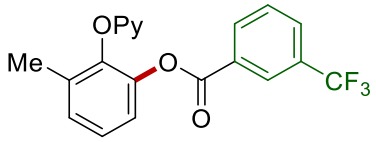


3-methyl-2-(pyridin-2-yloxy)phenyl 3-methylbenzoate (3ag): The general procedure **A/B** was followed using **1a** (46.3 mg, 0.25 mmol) and **2g** (54.4 mg, 0.40 mmol). Isolation by column chromatography on silica gel (*n*-hexane/EtOAc: 10:1→5:1) yielded **3ag** (52.7 mg, 66%, procedure **A**) (45.6 mg, 57%, procedure **B**) as a white solid. **M. p.** = 70–73 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.14 (ddd, *J* = 5.0, 2.0, 0.8 Hz, 1H), 7.63 (dt, *J* = 7.8, 1.6 Hz, 1H), 7.60 – 7.52 (m, 2H), 7.33 (ddt, *J* = 7.8, 1.8, 1.0 Hz, 1H), 7.27 – 7.17 (m, 4H), 6.91 (ddd, *J* = 7.1, 5.0, 0.9 Hz, 1H), 6.83 (dt, *J* = 8.4, 0.9 Hz, 1H), 2.31 (s, 3H), 2.27 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 164.6 (C_q), 163.0 (C_q), 147.7 (CH), 143.7 (C_q), 143.4 (C_q), 139.3 (CH), 138.1 (C_q), 134.2 (CH), 133.2 (C_q), 130.6 (CH), 129.1 (C_q), 128.5 (CH), 128.3 (CH), 127.2 (CH), 125.5 (CH), 121.2 (CH), 118.2 (CH), 110.4 (CH), 21.3 (CH_3), 16.5 (CH_3). **IR** (ATR): 2922, 1732, 1590, 1463, 1426, 1268, 1183, 1066, 883, 737 cm^{-1}**. MS** (ESI) *m/z* (relative intensity): 320 (100) $[M+H]^+$, 342 (50) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{20}H_{18}NO_3^+$ $[M+H]^+$ 320.1281, found 320.1282.

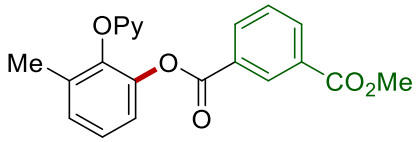


3-methyl-2-(pyridin-2-yloxy)phenyl 3-chlorobenzoate (3ah): The general procedure **A** was followed using **1a** (46.3 mg, 0.25 mmol) and **2h** (62.4 mg, 0.40 mmol). Isolation by column chromatography on silica gel (*n*-hexane/EtOAc: 10:1→5:1) yielded **3ah** (62.9 mg, 74%) as a white solid. **M. p.** = 75–77 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.13 (ddd, *J* = 4.9, 2.0, 0.8 Hz, 1H), 7.75 – 7.67 (m, 2H), 7.57 (ddd, *J* = 8.3, 7.2,

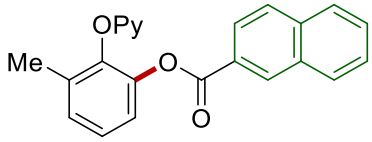
2.0 Hz, 1H), 7.49 (ddd, *J* = 7.9, 2.2, 1.1 Hz, 1H), 7.29 (dd, *J* = 7.9, 7.9 Hz, 1H), 7.24 – 7.17 (m, 3H), 6.92 (ddd, *J* = 7.2, 5.0, 0.9 Hz, 1H), 6.83 (dt, *J* = 8.4, 0.9 Hz, 1H), 2.27 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 163.2 (C_q), 162.9 (C_q), 147.7 (CH), 143.5 (C_q), 143.1 (C_q), 139.5 (CH), 134.5 (C_q), 133.5 (CH), 133.3 (C_q), 131.0 (C_q), 130.0 (CH), 129.7 (CH), 128.8 (CH), 128.2 (CH), 125.5 (CH), 121.0 (CH), 118.4 (CH), 110.4 (CH), 16.5 (CH_3). **IR** (ATR): 3017, 2924, 1744, 1572, 1464, 1425, 1231, 1188, 1059, 833 cm^{-1}**. MS** (ESI) *m/z* (relative intensity): 340 (100) $[M+H]^+$, 362 (50) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{19}H_{15}{}^{35}ClNO_3^+$ $[M+H]^+$ 340.0735, found 340.0739.



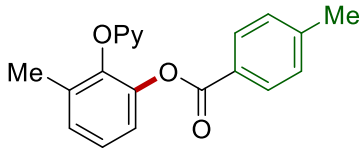
3-methyl-2-(pyridin-2-yloxy)phenyl 3-(trifluoromethyl)benzoate (3ai): The general procedure **A/B** was followed using **1a** (46.3 mg, 0.25 mmol) and **2i** (76.0 mg, 0.40 mmol). Isolation by column chromatography on silica gel (*n*-hexane/EtOAc: 10:1→5:1) yielded **3ai** (75.6 mg, 81%) as a yellow oil. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.11 (ddd, *J* = 5.0, 2.0, 0.8 Hz, 1H), 8.05 (dddd, J = 7.9, 1.8, 1.2, 0.6 Hz, 1H), 7.99 – 7.96 (m, 1H), 7.80 – 7.76 (m, 1H), 7.57 – 7.48 (m, 2H), 7.25 – 7.21 (m, 3H), 6.90 (ddd, *J* = 7.2, 5.0, 0.9 Hz, 1H), 6.82 (dt, *J* = 8.3, 0.9 Hz, 1H), 2.29 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 163.1 (C_q), 162.9 (C_q), 147.7 (CH), 143.5 (C_q), 143.1 (C_q), 139.5 (CH), 133.4 (C_q), 133.3 (CH), 131.1 (q, $^2J_{C\text{-}F}$ = 33.0 Hz, C_q), 130.2 (C_q), 130.0 (q, $^3J_{C\text{-}F}$ = 3.6 Hz, CH), 129.1 (CH), 128.9 (CH), 126.8 (q, $^3J_{C\text{-}F}$ = 3.9 Hz, CH), 125.5 (CH), 123.6 (d, $^1J_{C\text{-}F}$ = 272.8 Hz, C_q), 121.0 (CH), 118.5 (CH), 110.3 (CH), 16.4 (CH_3). **^{19}F NMR** (376 MHz, $CDCl_3$) δ= -62.81 (s). **IR** (ATR): 3076, 2925, 1747, 1595, 1465, 1428, 1335, 1230, 1129, 748 cm^{-1}**. MS** (ESI) *m/z* (relative intensity): 374 (100) $[M+H]^+$, 396 (50) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{20}H_{15}F_3NO_3^+$ $[M+H]^+$ 374.0999, found 374.1004. The spectral data were in accordance with those reported in the literature.[3]



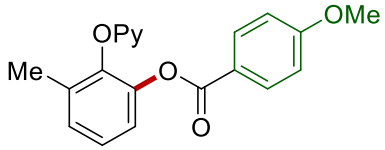
methyl (3-methyl-2-(pyridin-2-yloxy)phenyl) isophthalate (3aj): The general procedure **B** was followed using **1a** (46.3 mg, 0.25 mmol) and **2j** (72.1 mg, 0.40 mmol). Isolation by column chromatography on silica gel (*n*-hexane/EtOAc: 10:1→5:1) yielded **3aj** (52.7 mg, 58%) as a yellow oil. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.47 (ddd, *J* = 1.8, 1.8, 0.6 Hz, 1H), 8.19 (ddd, *J* = 7.8, 1.5, 1.5 Hz, 1H), 8.10 (ddd, *J* = 5.0, 2.1, 0.8 Hz, 1H), 8.03 – 7.96 (m, 1H), 7.52 (ddd, *J* = 8.3, 7.2, 2.0 Hz, 1H), 7.44 (td, *J* = 7.8, 0.6 Hz, 1H), 7.25 – 7.17 (m, 3H), 6.87 (ddd, *J* = 7.2, 5.0, 0.9 Hz, 1H), 6.81 (ddd, *J* = 8.2, 0.9, 0.9 Hz, 1H), 3.92 (s, 3H), 2.26 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 166.1 (C_q), 163.6 (C_q), 162.9 (C_q), 147.7 (CH), 143.6 (C_q), 143.3 (C_q), 139.4 (CH), 134.4 (CH), 134.2 (CH), 133.4 (C_q), 131.2 (CH), 130.7 (C_q), 129.7 (C_q), 128.8 (CH), 128.7 (CH), 125.5 (CH), 121.1 (CH), 118.3 (CH), 110.3 (CH), 52.4 (CH_3), 16.5 (CH_3). **IR** (ATR): 3076, 2952, 1723, 1589, 1464, 1427, 1223, 1187, 1065, 774 cm^{-1}**. MS** (ESI) *m/z* (relative intensity): 364 (100) $[M+H]^+$, 386 (20) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{21}H_{18}NO_5^+$ $[M+H]^+$ 364.1179, found 364.1179.



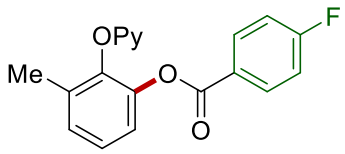
3-methyl-2-(pyridin-2-yloxy)phenyl 2-naphthoate (3ak): The general procedure **A** was followed using **1a** (46.3 mg, 0.25 mmol) and **2k** (68.8 mg, 0.40 mmol). Isolation by column chromatography on silica gel (*n*-hexane/EtOAc: 10:1→5:1) yielded **3ak** (48.8 mg, 55%) as a white solid. **M. p.** = 140–142 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.30 (s, 1H), 8.17 (ddd, *J* = 5.0, 2.0, 0.8 Hz, 1H), 7.90 – 7.83 (m, 2H), 7.82 – 7.77 (m, 2H), 7.59 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1H), 7.56 – 7.48 (m, 2H), 7.29 – 7.21 (m, 3H), 6.91 (ddd, *J* = 7.1, 5.0, 1.0 Hz, 1H), 6.82 (dt, *J* = 8.4, 0.9 Hz, 1H), 2.30 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 164.6 (C_q), 163.1 (C_q), 147.7 (CH), 143.7 (C_q), 143.5 (C_q), 139.4 (CH), 135.8 (C_q), 133.3 (C_q), 132.4 (C_q), 131.8 (CH), 129.5 (CH), 128.6 (CH), 128.6 (CH), 128.2 (CH), 127.9 (CH), 126.8 (CH), 126.4 (C_q), 125.5 (CH), 125.4 (CH), 121.2 (CH), 118.3 (CH), 110.5 (CH), 16.5 (CH_3). **IR** (ATR): 3052, 2921, 1726, 1571, 1463, 1424, 1227, 1183, 1073, 762 cm^{-1}**. MS** (ESI) *m/z* (relative intensity): 356 (100) $[M+H]^+$, 378 (60) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{23}H_{18}NO_3^+$ $[M+H]^+$ 356.1281, found 356.1282.



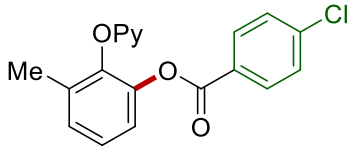
3-methyl-2-(pyridin-2-yloxy)phenyl 4-methylbenzoate (3al): The general procedure **A** was followed using **1a** (46.3 mg, 0.25 mmol) and **2l** (54.4 mg, 0.40 mmol). Isolation by column chromatography on silica gel (*n*-hexane/EtOAc: 10:1→5:1) yielded **3al** (50.3 mg, 63%) as a white solid. **M. p.** = 107–109 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.13 (ddd, *J* = 5.0, 2.0, 0.8 Hz, 1H), 7.74 – 7.68 (m, 2H), 7.54 (ddd, *J* = 8.3, 7.2, 2.0 Hz, 1H), 7.23 – 7.17 (m, 3H), 7.16 – 7.12 (m, 2H), 6.90 (ddd, *J* = 7.2, 4.9, 0.9 Hz, 1H), 6.81 (dt, *J* = 8.3, 0.9 Hz, 1H), 2.38 (s, 3H), 2.27 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 164.5 (C_q), 163.0 (C_q), 147.7 (CH), 144.3 (C_q), 143.7 (C_q), 143.5 (C_q), 139.3 (CH), 133.2 (C_q), 130.1 (CH), 129.1 (CH), 128.5 (CH), 126.4 (C_q), 125.5 (CH), 121.2 (CH), 118.2 (CH), 110.4 (CH), 21.8 (CH_3), 16.5 (CH_3). **IR** (ATR): 2922, 2853, 1732, 1573, 1426, 1233, 1176, 1072, 881, 745 cm^{-1}**. MS** (ESI) *m/z* (relative intensity): 320 (100) $[M+H]^+$, 342 (60) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{20}H_{18}NO_3^+$ $[M+H]^+$ 320.1281, found 320.1283. The spectral data were in accordance with those reported in the literature.[3]



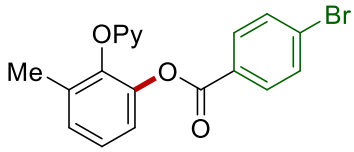
3-methyl-2-(pyridin-2-yloxy)phenyl 4-methoxybenzoate (3am): The general procedure **A** was followed using **1a** (46.3 mg, 0.25 mmol) and **2m** (60.9 mg, 0.40 mmol). Isolation by column chromatography on silica gel (*n*-hexane/EtOAc: 10:1→5:1) yielded **3am** (48.6 mg, 58%) as a white solid. **M. p.** = 120–122 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.12 (ddd, *J* = 5.0, 2.0, 0.8 Hz, 1H), 7.80 – 7.74 (m, 2H), 7.54 (ddd, *J* = 8.3, 7.2, 2.0 Hz, 1H), 7.23 – 7.15 (m, 3H), 6.89 (ddd, *J* = 7.2, 5.0, 0.9 Hz, 1H), 6.84 – 6.78 (m, 3H), 3.83 (s, 3H), 2.26 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 164.1 (C_q), 163.8 (C_q), 163.0 (C_q), 147.7 (CH), 143.8 (C_q), 143.5 (C_q), 139.3 (CH), 133.1 (C_q), 132.2 (CH), 128.4 (CH), 125.4 (CH), 121.5 (C_q), 121.3 (CH), 118.2 (CH), 113.6 (CH), 110.4 (CH), 55.5 (CH_3), 16.5 (CH_3). **IR** (ATR): 2923, 2853, 1722, 1604, 1463, 1426, 1234, 1160, 1073, 760 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 336 (100) $[M+H]^+$, 358 (90) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{20}H_{18}NO_4^+$ $[M+H]^+$ 336.1230, found 336.1232. The spectral data were in accordance with those reported in the literature.[3]



3-methyl-2-(pyridin-2-yloxy)phenyl 4-fluorobenzoate (3an): The general procedure **A** was followed using **1a** (46.3 mg, 0.25 mmol) and **2n** (56.0 mg, 0.40 mmol). Isolation by column chromatography on silica gel (*n*-hexane/EtOAc: 10:1→5:1) yielded **3an** (55.0 mg, 68%) as a white solid. **M. p.** = 110–112 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.12 (ddd, *J* = 5.0, 2.0, 0.8 Hz, 1H), 7.86 – 7.80 (m, 2H), 7.55 (ddd, *J* = 8.3, 7.2, 2.0 Hz, 1H), 7.23 – 7.16 (m, 3H), 7.04 – 6.98 (m, 2H), 6.90 (ddd, *J* = 7.2, 5.0, 0.9 Hz, 1H), 6.81 (dt, *J* = 8.3, 0.9 Hz, 1H), 2.26 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 166.1 (d, $^1J_{C\text{-}F}$ = 254.8 Hz, C_q), 163.4 (C_q), 162.9 (C_q), 147.7 (CH), 143.6 (C_q), 143.3 (C_q), 139.4 (CH), 133.3 (C_q), 132.7 (d, $^3J_{C\text{-}F}$ = 9.5 Hz, CH), 128.7 (CH), 125.5 (CH), 125.4 (d, $^4J_{C\text{-}F}$ = 3.0 Hz, C_q), 121.1 (CH), 118.3 (CH), 115.6 (d, $^2J_{C\text{-}F}$ = 22.1 Hz, CH), 110.3 (CH), 16.5 (CH_3). **^{19}F NMR** (376 MHz, $CDCl_3$) δ= (-104.59) – (-104.67) (m). **IR** (ATR): 3065, 2926, 1732, 1572, 1427, 1235, 1187, 1072, 855, 756 cm^{-1}**. MS** (ESI) *m/z* (relative intensity): 324 (100) $[M+H]^+$, 346 (60) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{19}H_{15}FNO_3^+$ $[M+H]^+$ 324.1030, found 324.1034. The spectral data were in accordance with those reported in the literature.[3]

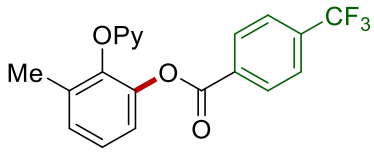


3-methyl-2-(pyridin-2-yloxy)phenyl 4-chlorobenzoate (3ao): The general procedure **A** was followed using **1a** (46.3 mg, 0.25 mmol) and **2o** (62.6 mg, 0.40 mmol). Isolation by column chromatography on silica gel (*n*-hexane/EtOAc: 10:1→5:1) yielded **3ao** (50.9 mg, 60%) as a white solid. **M. p.** = 125–127 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.11 (ddd, *J* = 5.0, 2.0, 0.8 Hz, 1H), 7.77 – 7.71 (m, 2H), 7.56 (ddd, *J* = 8.3, 7.2, 2.0 Hz, 1H), 7.34 – 7.28 (m, 2H), 7.24 – 7.15 (m, 3H), 6.91 (ddd, *J* = 7.2, 5.0, 0.9 Hz, 1H), 6.81 (dt, *J* = 8.3, 0.9 Hz, 1H), 2.26 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 163.6 (C_q), 162.9 (C_q), 147.7 (CH), 143.6 (C_q), 143.2 (C_q), 140.0 (C_q), 139.4 (CH), 133.3 (C_q), 131.4 (CH), 128.8 (CH), 128.7 (CH), 127.7 (C_q), 125.5 (CH), 121.1 (CH), 118.3 (CH), 110.3 (CH), 16.5 (CH_3). **IR** (ATR): 2923, 2852, 1733, 1590, 1465,1428, 1266, 1067, 1011, 752 cm^{-1}**. MS** (ESI) *m/z* (relative intensity): 340 (100) $[M+H]^+$, 362 (65) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{19}H_{15}{}^{35}ClNO_3^+$ $[M+H]^+$ 340.0735, found 340.0737.

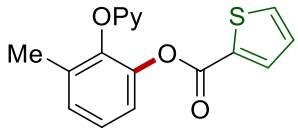


3-methyl-2-(pyridin-2-yloxy)phenyl 4-bromobenzoate (3ap): The general procedure **A** was followed using **1a** (46.3 mg, 0.25 mmol) and **2p** (80.4 mg, 0.40 mmol). Isolation by column chromatography on silica gel (*n*-hexane/EtOAc: 10:1→5:1) yielded **3ap** (68.2 mg, 71%) as a white solid. **M. p.** = 120–122 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.11 (ddd, *J* = 5.0, 2.0, 0.8 Hz, 1H), 7.69 – 7.64 (m, 2H), 7.56 (ddd, *J* = 8.3, 7.2, 2.0 Hz, 1H), 7.51 – 7.45 (m, 2H), 7.24 – 7.16 (m, 3H), 6.91 (ddd, *J* = 7.2, 5.0, 0.9 Hz, 1H), 6.81 (dt, *J* = 8.3, 0.9 Hz, 1H), 2.26 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 163.7 (C_q), 162.9 (C_q), 147.7 (CH), 143.5 (C_q), 143.2 (C_q), 139.4 (CH), 133.3 (C_q), 131.8 (CH), 131.5 (CH), 128.7 (CH), 128.7 (C_q), 128.1 (C_q), 125.5 (CH), 121.0 (CH), 118.3 (CH), 110.3 (CH), 16.5 (CH_3). **IR** (ATR): 3200, 2957, 1648, 1511,1247, 1178, 1035, 804

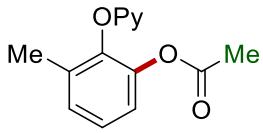
cm^{-1}**. MS** (ESI) *m/z* (relative intensity): 384 (100) $[M+H]^+$, 406 (80) $[M+Na]^+$, 791 (30) $[2M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{19}H_{15}{}^{79}BrNO_3^+$ $[M+H]^+$ 384.0230, found 384.0227.



3-methyl-2-(pyridin-2-yloxy)phenyl 4-(trifluoromethyl)benzoate (3aq): The general procedure **A** was followed using **1a** (46.3 mg, 0.25 mmol) and **2q** (76.0 mg, 0.40 mmol). Isolation by column chromatography on silica gel (*n*-hexane/EtOAc: 10:1→5:1) yielded **3aq** (71.9 mg, 77%) as a white solid. **M. p.** = 90–92 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.12 (ddd, *J* = 5.0, 2.0, 0.8 Hz, 1H), 7.96 – 7.91 (m, 2H), 7.64 – 7.59 (m, 2H), 7.56 (ddd, *J* = 8.3, 7.2, 2.0 Hz, 1H), 7.25 – 7.19 (m, 3H), 6.91 (ddd, *J* = 7.2, 5.0, 1.0 Hz, 1H), 6.82 (dt, *J* = 8.3, 0.9 Hz, 1H), 2.27 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 163.3 (C_q), 162.9 (C_q), 147.8 (CH), 143.5 (C_q), 143.2 (C_q), 139.5 (CH), 134.9 (q, $^2J_{C-F}$ = 32.7 Hz, C_q), 133.4 (C_q), 132.5 (C_q), 130.4 (CH), 128.9 (CH), 125.6 (CH), 125.5 (q, $^3J_{C-F}$ = 3.7 Hz, CH), 123.6 (d, $^1J_{C-F}$ = 272.6 Hz, C_q), 121.0 (CH), 118.4 (CH), 110.3 (CH), 16.5 (CH_3). **^{19}F NMR** (376 MHz, $CDCl_3$) δ= -63.19 (s). **IR** (ATR): 2925, 2853, 1752, 1573, 1426, 1234, 1074, 1014, 857, 763 cm^{-1}**. MS** (ESI) *m/z* (relative intensity): 374 (100) $[M+H]^+$, 396 (75) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{20}H_{15}F_3NO_3^+$ $[M+H]^+$ 374.0999, found 374.0998.

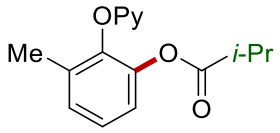


3-methyl-2-(pyridin-2-yloxy)phenyl thiophene-2-carboxylate (3ar): The general procedure **A** was followed using **1a** (46.3 mg, 0.25 mmol) and **2r** (51.3 mg, 0.40 mmol). Isolation by column chromatography on silica gel (*n*-hexane/EtOAc: 10:1→5:1) yielded **3ar** (45.5 mg, 59%) as a brown solid. **M. p.** = 57–63 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.11 (ddd, *J* = 5.0, 2.0, 0.8 Hz, 1H), 7.63 (dd, *J* = 3.8, 1.3 Hz, 1H), 7.56 (ddd, *J* = 8.3, 7.2, 2.0 Hz, 1H), 7.52 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.23 – 7.18 (m, 3H), 7.02 (dd, *J* = 5.0, 3.8 Hz, 1H), 6.90 (ddd, *J* = 7.2, 5.0, 0.9 Hz, 1H), 6.84 (dt, *J* = 8.3, 0.9 Hz, 1H), 2.26 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 162.9 (C_q), 159.8 (C_q), 147.7 (CH), 143.6 (C_q), 143.0 (C_q), 139.3 (CH), 134.5 (CH), 133.5 (CH), 133.3 (C_q), 132.5 (C_q), 128.7 (CH), 127.8 (CH), 125.4 (CH), 121.1 (CH), 118.3 (CH), 110.4 (CH), 16.5 (CH_3). **IR** (ATR): 3082, 2924, 1724, 1593, 1465, 1424, 1231, 1186, 1056, 729 cm^{-1}**. MS** (ESI) *m/z* (relative intensity): 312 (100) $[M+H]^+$, 334 (20) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{17}H_{14}NO_3S^+$ $[M+H]^+$ 312.0689, found 312.0692.

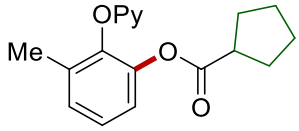


3-methyl-2-(pyridin-2-yloxy)phenyl acetate (3as): The general procedure **A** was followed using **1a** (46.3 mg, 0.25 mmol) and **2s** (24.0 mg, 0.40 mmol). Isolation by column chromatography on silica gel (*n*-hexane/EtOAc: 10:1→5:1) yielded **3as** (51.7 mg, 85%) as a white solid. **M. p.** = 95–97 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.14 (ddd, *J* = 5.0, 2.0, 0.8 Hz, 1H), 7.67 (ddd, *J* = 8.3, 7.2, 2.0 Hz, 1H), 7.19 – 7.13 (m, 2H), 7.07 – 7.01 (m, 1H), 6.96 (ddd, *J* = 7.2, 5.0, 0.9 Hz, 1H), 6.91 (dt, *J* = 8.3, 0.9 Hz, 1H), 2.21 (s, 3H), 2.02 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 168.7 (C_q), 162.9 (C_q), 147.8 (CH), 143.6 (C_q), 143.2 (C_q),

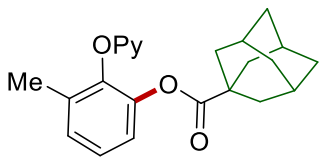
139.5 (CH), 133.2 (C_q), 128.6 (CH), 125.5 (CH), 121.1 (CH), 118.3 (CH), 110.1 (CH), 20.6 (CH_3), 16.5 (CH_3). **IR** (ATR): 2926, 1769, 1588, 1465, 1427, 1272, 1182, 1030, 883, 777 cm^{-1}**. MS** (ESI) *m/z* (relative intensity): 244 (100) $[M+H]^+$, 266 (65) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{14}H_{14}NO_3^+$ $[M+H]^+$ 244.0968, found 244.0986. The spectral data were in accordance with those reported in the literature.[3]



3-methyl-2-(pyridin-2-yloxy)phenyl *iso*butyrate (3at): The general procedure **A** was followed using **1a** (46.3 mg, 0.25 mmol) and **2t** (35.2 mg, 0.40 mmol). Isolation by column chromatography on silica gel (*n*-hexane/EtOAc: 10:1→5:1) yielded **3at** (35.9 mg, 53%) as a white solid. **M. p.** = 60–65 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.13 (ddd, *J* = 5.0, 2.0, 0.8 Hz, 1H), 7.65 (ddd, *J* = 8.3, 7.1, 2.0 Hz, 1H), 7.19 – 7.12 (m, 2H), 7.07 – 7.00 (m, 1H), 6.95 (ddd, *J* = 7.2, 5.0, 0.9 Hz, 1H), 6.88 (dt, *J* = 8.3, 0.9 Hz, 1H), 2.54 (hept, *J* = 7.0 Hz, 1H), 2.20 (s, 3H), 1.05 (d, J = 7.0 Hz, 6H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 174.7 (C_q), 163.0 (C_q), 147.8 (CH), 143.6 (C_q), 143.4 (C_q), 139.4 (CH), 133.2 (C_q), 128.4 (CH), 125.6 (CH), 121.1 (CH), 118.2 (CH), 110.1 (CH), 34.1 (CH), 18.8 (CH_3), 16.5 (CH_3). **IR** (ATR): 2987, 1754, 1594, 1463, 1424, 1272, 1234, 1089, 882, 788 cm^{-1}**. MS** (ESI) *m/z* (relative intensity): 272 (100) $[2M+Na]^+$, 294 (20) $[M+Na]^+$, 285 (90) $[M+H]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{16}H_{18}NO_3^+$ $[M+H]^+$ 272.1281, found 272.1275.

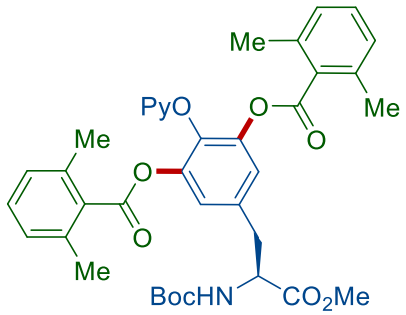


3-methyl-2-(pyridin-2-yloxy)phenyl cyclopentanecarboxylate (3au): The general procedure **A** was followed using **1a** (46.3 mg, 0.25 mmol) and **2u** (45.7 mg, 0.40 mmol). Isolation by column chromatography on silica gel (*n*-hexane/EtOAc: 10:1→5:1) yielded **3au** (44.6 mg, 60%) as a colorless oil. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.14 (ddd, *J* = 5.0, 2.0, 0.8 Hz, 1H), 7.66 (ddd, *J* = 8.3, 7.2, 2.0 Hz, 1H), 7.19 – 7.12 (m, 2H), 7.07 – 7.01 (m, 1H), 6.95 (ddd, *J* = 7.2, 5.0, 1.0 Hz, 1H), 6.87 (dt, *J* = 8.4, 0.9 Hz, 1H), 2.73 (tt, *J* = 8.5, 7.1 Hz, 1H), 2.19 (s, 3H), 1.82 – 1.42 (m, 8H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 174.4 (C_q), 162.9 (C_q), 147.8 (CH), 143.6 (C_q), 143.4 (C_q), 139.4 (CH), 133.2 (C_q), 128.4 (CH), 125.6 (CH), 121.2 (CH), 118.2 (CH), 110.0 (CH), 43.7 (CH), 29.9 (CH_2), 25.8 (CH_2), 16.4 (CH_3). **IR** (ATR): 2955, 2870, 1757, 1589, 1465, 1428, 1273, 1240, 1125, 777 cm^{-1}**. MS** (ESI) *m/z* (relative intensity): 298 (100) $[M+H]^+$, 320 (80) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{18}H_{20}NO_3^+$ $[M+H]^+$ 298.1438, found 298.1453. The spectral data were in accordance with those reported in the literature.[3]

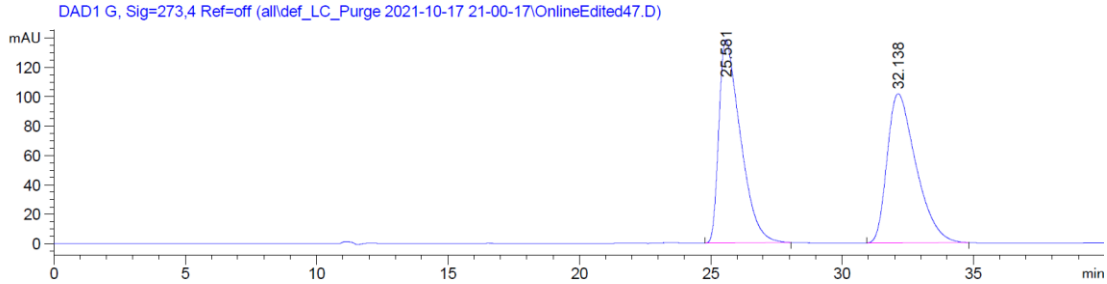


3-methyl-2-(pyridin-2-yloxy)phenyl adamantane-1-carboxylate (3av): The general procedure **A** was followed using **1a** (46.3 mg, 0.25 mmol) and **2v** (72.1 mg, 0.40 mmol). Isolation by column chromatography on silica gel (*n*-hexane/EtOAc: 10:1→5:1) yielded **3av** (68.7 mg, 76%) as a white solid. **M. p.** = 96–98 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.14 (dd, *J* = 5.0, 1.9 Hz, 1H), 7.65 (ddd, *J* = 8.4, 7.2, 2.0 Hz, 1H), 7.18 – 7.10 (m, 2H), 7.05 – 7.00 (m, 1H), 6.95 (ddd, *J* = 7.2, 5.0, 0.9 Hz, 1H), 6.87 (dd, *J* = 8.4, 0.9 Hz, 1H), 2.20 (s, 3H), 1.94 – 1.90 (m, 3H), 1.76 – 1.73 (m, 6H), 1.70–1.57 (m, 6H). **^{13}C-NMR** (101 MHz,

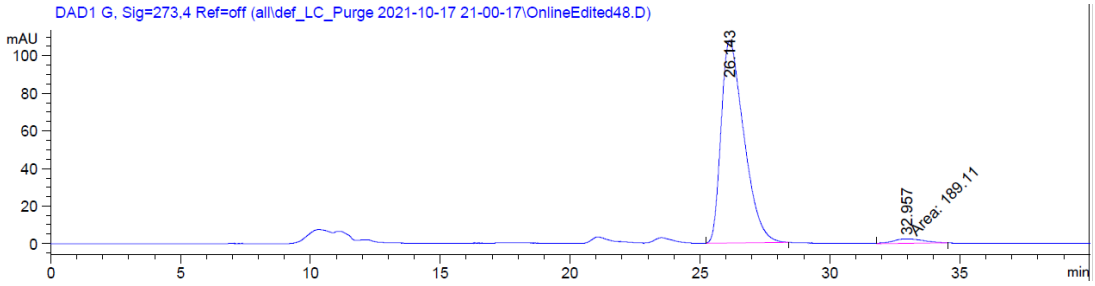
$CDCl_3$) δ = 175.2 (C_q), 162.9 (C_q), 147.8 (CH), 143.7 (C_q), 143.3 (C_q), 139.3 (CH), 133.1 (C_q), 128.2 (CH), 125.5 (CH), 121.1 (CH), 118.1 (CH), 110.1 (CH), 41.0 (C_q), 38.5 (CH_2), 36.4 (CH_2), 27.9 (CH), 16.4 (CH_3). **IR** (ATR): 2906, 2853, 1741, 1590, 1463, 1422, 1269, 1213, 1049, 781 cm^{-1}**. MS** (ESI) *m/z* (relative intensity): 364 (100) $[M+H]^+$, 386 (20) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{23}H_{26}NO_3^+$ $[M+H]^+$ 364.1907, found 364.1905.



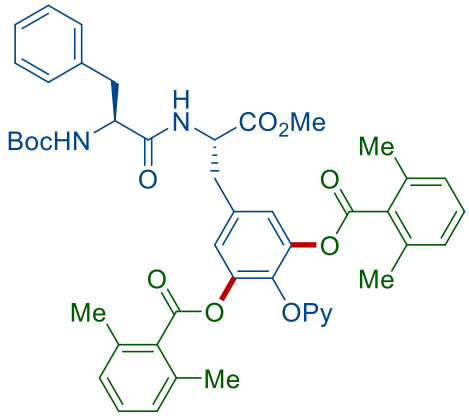
(*S*)-5-{2-[(*tert*-butoxycarbonyl)amino]-3-methoxy-3-oxopropyl}-2-(pyridin-2-yloxy)-1,3-phenylene bis(2,6-dimethylbenzoate) (5aa): The general procedure **C** was followed using **4a** (93.1 mg, 0.25 mmol) and **2a** (112.5 mg, 0.75 mmol). Isolation by column chromatography on silica gel (*n*-hexane/EtOAc: 3:1→1:1) yielded **5aa** (121.9 mg, 73%) as a white solid. **M. p.** = 60–68 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.07 (d, *J* = 4.9 Hz, 1H), 7.58 (td, *J* = 7.7, 6.9, 1.5 Hz, 1H), 7.20 – 7.11 (m, 4H), 7.01 – 6.97 (m, 4H), 6.92 – 6.83 (m, 2H), 5.26 (brs, 1H), 4.70 (ddd, *J* = 7.6, 6.6, 6.6 Hz, 1H), 3.77 (s, 3H), 3.30 – 3.17 (m, 2H), 2.27 (s, 12H), 1.45 (s, 9H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 172.0 (C_q), 167.2 (C_q), 162.4 (C_q), 155.2 (C_q), 147.7 (CH), 144.7 (C_q), 139.4 (CH), 136.7 (C_q), 135.6 (C_q), 134.3 (C_q), 132.4 (C_q), 130.0 (CH), 127.78 (CH), 122.1 (CH), 118.8 (CH), 110.3 (CH), 80.2 (C_q), 54.3 (CH), 52.6 (CH_3), 37.9 (CH_2), 28.4 (CH_3), 19.9 (CH_3). **IR** (ATR): 3318, 2970, 1740, 1592, 1489, 1420, 1222, 1167, 1040, 773 cm^{-1}**. MS** (ESI) *m/z* (relative intensity): 669 (100) $[M+H]^+$, 691 (65) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{38}H_{41}N_2O_9^+$ $[M+H]^+$ 669.2807, found 669.2807. **HPLC** separation (Chiralpak® IA-3, *n*-hexane/ *i*-PrOH 75:25, 1.0 mL/min, detection at 273 nm): t_r (major) = 26.1 min, t_r (minor) = 33.0 min, 98% ee.



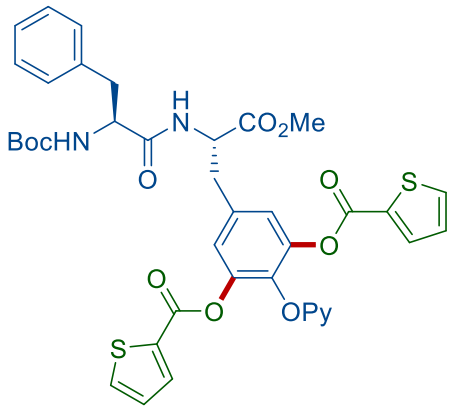
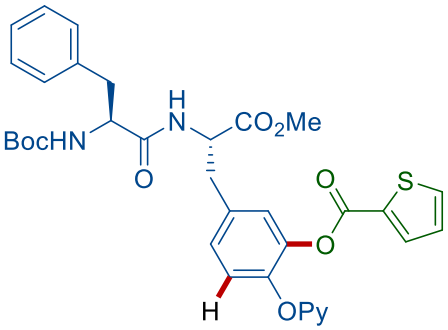
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.581	BB	0.7729	7880.91016	138.49452	50.3793
2	32.138	BB	0.9252	7762.22803	101.61554	49.6207



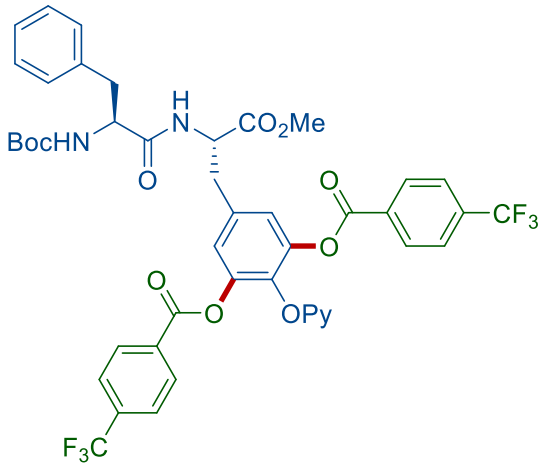
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.143	BB	0.8051	6578.95313	107.78815	99.0214
2	33.031	MM	0.7057	65.01891	1.53551	0.9786



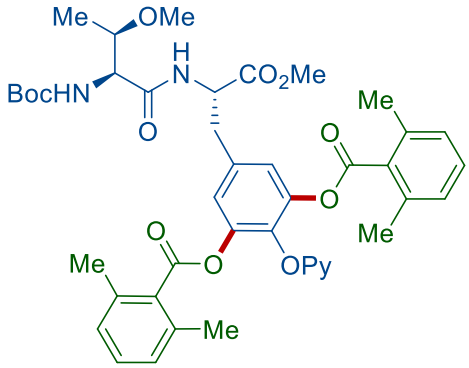
5-({*S*}-2-{[*S*]-2-[(*tert*-Butoxycarbonyl)amino]-3-phenylpropanamido}-3-methoxy-3-oxopropyl)-2-(pyridin-2-yloxy)-1,3-phenylene bis(2,6-dimethylbenzoate) (5ba): The general procedure **C** was followed using **4b** (129.8 mg, 0.25 mmol) and **2a** (112.6 mg, 0.75 mmol). Isolation by column chromatography on silica gel (*n*-hexane/EtOAc: 7:3→5:5) yielded **5ba** (152.5 mg, 75%) as a white solid. **M. p.** = 82–83 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.03 (d, *J* = 4.9 Hz, 1H), 7.68 – 7.53 (m, 1H), 7.25 – 7.14 (m, 7H), 7.10 (s, 2H), 7.02 (d, *J* = 7.6 Hz, 4H), 6.96 – 6.83 (m, 3H), 5.36 (d, *J* = 8.3 Hz, 1H), 5.08 – 4.99 (m, 1H), 4.64 – 4.32 (m, 1H), 3.79 (s, 3H), 3.36 – 3.20 (m, 3H), 2.90 (dd, *J* = 11.6, 4.3 Hz, 1H), 2.30 (s, 12H), 1.32 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 171.5 (C_q), 171.2 (C_q), 167.4 (C_q), 162.5 (C_q), 155.8 (C_q), 147.6 (CH), 144.5 (C_q), 139.4 (CH), 137.1 (C_q), 136.5 (C_q), 135.9 (C_q), 133.8 (C_q), 132.1 (C_q), 130.1 (CH), 129.4 (CH), 128.6 (CH), 127.9 (CH), 126.8 (CH), 122.1 (CH), 118.8 (CH), 110.4 (CH), 80.1 (C_q), 56.2 (CH), 53.0 (CH), 52.7 (CH_3), 38.3 (CH_2), 37.5 (CH_2), 28.2 (CH_3), 20.0 (CH_3). **IR** (ATR): 2964, 2926, 1755, 1716, 1674, 1499, 1429, 1225, 1101, 1060, 773 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 816 (40) $[M+H]^+$,838 (100) $[M+Na]^+$. **HR-MS** (ESI): *m/z* calcd for $C_{47}H_{50}N_3O_{10}^+$ $[M+H]^+$ 816.3491, found 816.3492.

5-({*S*}-2-{[*S*]-2-[(*tert*-Butoxycarbonyl)amino]-3-phenylpropanamido}-3-methoxy-3-oxopropyl)-2-(pyridin-2-yloxy)-1,3-phenylene bis(thiophene-2-carboxylate) (5br) and **5-({*S*}-2-{[*S*]-2-[(*tert*-butoxycarbonyl)amino]-3-phenylpropanamido}-3-methoxy-3-oxopropyl)-2-(pyridin-2-yloxy)phenyl thiophene-2-carboxylate (5br'):** The general procedure **C** was followed using **4b** (129.8 mg, 0.25 mmol) and **2r** (96.1 mg, 0.75 mmol). Isolation by column chromatography on silica gel (*n*-hexane/EtOAc: 7:3→5:5) and recycling preparative HPLC yielded **5br** (73.1 mg, 38%) as a white solid and **5br'** (43.6 mg, 27%) as a white solid. **5br M. p.** = 75–77 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.04 (d, J = 4.9 Hz, 1H), 7.72 (s, 2H), 7.66 – 7.49 (m, 3H), 7.34 – 7.12 (m, 5H), 7.12 – 7.06 (m, 2H), 7.00 – 6.83 (m, 5H), 5.64 – 5.40 (m, 1H), 5.12 – 4.91 (m, 1H), 4.76 – 4.37 (m, 1H), 3.77 (s, 3H), 3.34 – 2.90 (m, 4H), 1.37 (s, 9H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 171.1 (C_q), 170.9 (C_q), 162.2 (C_q), 159.3 (C_q), 155.8 (C_q), 147.3 (CH), 143.5 (C_q), 139.3 (CH), 137.0 (C_q), 136.4 (C_q), 134.9 (CH), 133.9 (CH), 132.8 (C_q), 132.0 (C_q), 129.6 (CH), 128.5 (CH), 127.9 (CH), 126.8 (CH), 122.2 (CH), 118.7 (CH), 110.5 (CH), 79.9 (C_q), 55.8 (CH), 52.9 (CH), 52.7 (CH_3), 37.9 (CH_2), 37.4 (CH_2), 28.2 (CH_3). **IR** (ATR): 2955, 2925, 1736, 1666, 1498, 1429, 1412, 1246, 1218, 1072, 736 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 772 (50) $[M+H]^+$, 794 (100) $[M+Na]^+$. **HR-MS** (ESI): *m/z* calcd for $C_{39}H_{38}N_3O_{10}S_2^+$ $[M+H]^+$ 772.1993, found 772.1999. **5br' M. p.** = 62–64 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.10 (d, J = 4.9 Hz, 1H), 7.77 – 7.46 (m, 3H), 7.29 – 7.17 (m, 6H), 7.07 (t, J = 4.3 Hz, 1H), 7.03 – 6.84 (m, 4H), 6.74 (d, J = 7.8 Hz, 1H), 5.50 – 5.20 (m, 1H), 5.10 – 4.78 (m, 1H), 4.64 – 4.30 (m, 1H), 3.75 (s, 3H), 3.35 – 2.84 (m, 4H), 1.38 (s, 9H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 171.2 (C_q), 171.1 (C_q), 171.1 (C_q), 159.6 (C_q), 155.7 (C_q), 147.5 (CH), 144.1 (C_q), 142.0 (C_q), 139.4 (CH), 136.9 (C_q), 134.7 (CH), 133.8 (CH), 133.2 (C_q), 132.3 (C_q), 129.5 (CH), 128.6 (CH), 128.5 (CH), 127.9 (CH), 127.7 (CH), 125.2 (CH), 123.3 (CH), 118.6 (CH), 110.9 (CH), 80.0 (C_q), 55.7 (CH), 53.0 (CH), 52.5 (CH_3), 38.0 (CH_2), 37.3 (CH_2), 28.2 (CH_3). **IR** (ATR): 2979, 2925, 1737, 1710, 1656, 1504, 1273, 1250, 1233, 1166, 737 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 646 (65) $[M+H]^+$, 668 (100) $[M+Na]^+$. **HR-MS** (ESI): *m/z* calcd for $C_{34}H_{36}N_3O_8S^+$ $[M+H]^+$ 646.2218, found 646.2218.

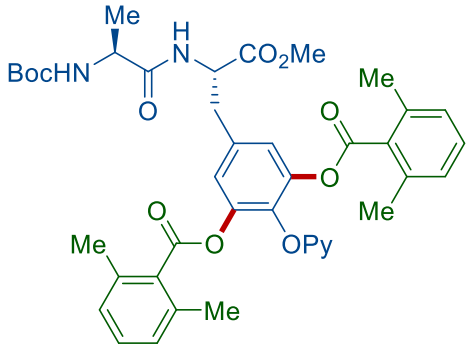


5-({*S*}-2-{[*S*]-2-[(*tert*-Butoxycarbonyl)amino]-3-phenylpropanamido}-3-methoxy-3-oxopropyl)-2-(pyridin-2-yloxy)-1,3-phenylene bis[4-(trifluoromethyl)benzoate] (5bq): The general procedure **C** was followed using **4b** (129.8 mg, 0.25 mmol) and **2q** (142.5 mg, 0.75 mmol). Isolation by column chromatography on silica gel (*n*-hexane/EtOAc: 7:3→5:5) yielded **5bq** (129.9 mg, 58%) as a white solid. **M. p.** = 156–158 °C. **^{1}H-NMR** (600 MHz, $CDCl_3$) δ = 8.08 – 8.04 (m, 1H), 8.02 (d, J = 8.1 Hz, 4H), 7.68 (d, J = 8.1 Hz, 4H), 7.55 (ddd, J = 8.3, 7.2, 2.0 Hz, 1H), 7.25 – 7.20 (m, 2H), 7.20 – 7.10 (m, 3H), 6.98 (s, 2H), 6.90 (dd, J = 7.2, 5.0 Hz, 1H), 6.88 – 6.78 (m, 2H), 5.43 (d, J = 8.8 Hz, 1H), 5.07 – 4.92 (m, 1H), 4.66 – 4.43 (m, 1H), 3.77 (s, 3H), 3.42 – 2.91 (m, 4H), 1.37 (s, 9H). **^{13}C-NMR** (151 MHz, $CDCl_3$) δ = 171.0 (C_q), 170.7 (C_q), 162.7 (C_q), 162.1 (C_q), 155.6 (C_q), 147.4 (CH), 143.6 (C_q), 139.5 (CH), 136.8 (C_q), 136.2 (C_q), 135.1 (q, $^2J_{C\text{-}F}$ = 32.8 Hz, C_q), 133.1 (C_q), 132.0 (C_q), 130.4 (CH), 129.5 (CH), 128.5 (CH), 126.8 (CH), 125.5 (q, $^3J_{C\text{-}F}$ = 3.7 Hz, CH), 123.4 (q, $^1J_{C\text{-}F}$ = 272.9 Hz, C_q), 122.3 (CH), 118.9 (CH), 110.3 (CH), 80.0 (C_q), 55.7 (CH), 52.9 (CH), 52.6 (CH_3), 37.9 (CH_2), 37.5 (CH_2), 28.2 (CH_3). **^{19}F NMR** (565 MHz, $CDCl_3$) δ = -63.2 (s). **IR** (ATR): 3343, 2926, 1747, 1726, 1501, 1429, 1323, 1256, 1089, 767, 697 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 896 (50) $[M+H]^+$, 918 (100) $[M+Na]^+$. **HR-MS** (ESI): *m/z* calcd for $C_{45}H_{40}F_6N_3O_{10}^+$ $[M+H]^+$ 896.2612, found 896.2613.

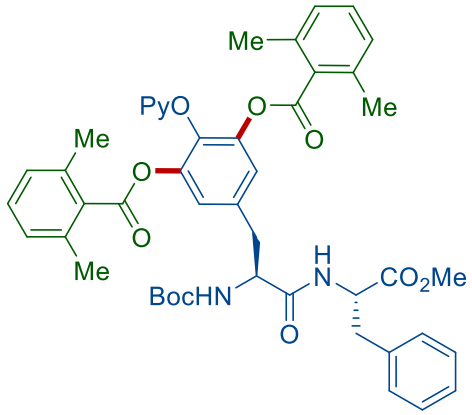


5-({*S*}-2-{[2*S*,3*R*]-2-[(*tert*-Butoxycarbonyl)amino]-3-methoxybutanamido}-3-methoxy-3-oxopropyl)-2-(pyridin-2-yloxy)-1,3-phenylene bis(2,6-dimethylbenzoate) (5ca): The general procedure **C** was followed using **4c** (121.9 mg, 0.25 mmol) and **2a** (112.6 mg, 0.75 mmol). Isolation by column chromatography on silica gel (*n*-hexane/EtOAc: 7:3→5:5) yielded **5ca** (131.1 mg, 67%) as a white solid. **M. p.**: 75–77 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.04 (dd, J = 5.1, 2.0 Hz, 1H), 7.63 – 7.45 (m, 1H), 7.32 (d, J = 7.7 Hz, 1H), 7.23 – 7.11 (m, 4H), 6.99 (d, J = 7.6 Hz, 4H), 6.93 – 6.81 (m, 2H), 5.64 (d, J = 7.5 Hz, 1H), 5.11 – 4.92 (m, 1H), 4.27 (d, J = 6.6 Hz, 1H), 4.07 – 3.91 (m, 1H), 3.77 (s, 3H), 3.33 (s, 3H), 3.28

(dd, *J* = 14.1, 5.5 Hz, 1H), 3.22 (dd, *J* = 14.1, 5.5 Hz, 1H), 2.28 (s, 12H), 1.43 (s, 9H), 1.13 (d, *J* = 6.3 Hz, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 171.1 (C_q), 170.2 (C_q), 167.1 (C_q), 162.4 (C_q), 156.0 (C_q), 147.6 (CH), 144.6 (C_q), 139.3 (CH), 136.6 (C_q), 135.7 (C_q), 133.9 (C_q), 132.3 (C_q), 130.0 (CH), 127.8 (CH), 122.1 (CH), 118.7 (CH), 110.3 (CH), 80.1 (C_q), 76.4 (CH), 58.0 (CH), 57.0 (CH_3), 53.0 (CH), 52.6 (CH_3), 37.6 (CH_2), 28.3 (CH_3), 19.9 (CH_3), 14.5 (CH_3). **IR** (ATR): 2979, 2924, 1748, 1679, 1467, 1428, 1223, 1162, 1048, 772cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 784 (65) $[M+H]^+$, 806 (100) $[M+Na]^+$. **HR-MS** (ESI): *m/z* calcd for $C_{43}H_{50}N_3O_{11}^+$ $[M+H]^+$ 784.3440, found 784.3443.

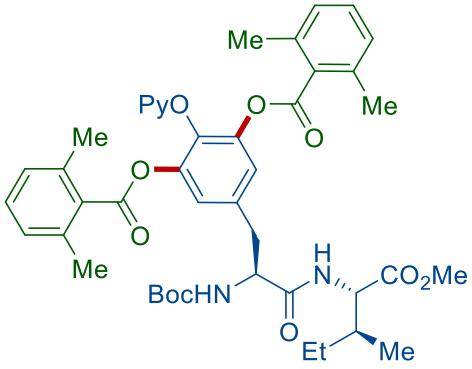


5-({*S*}-2-{[*S*]-2-[(*tert*-Butoxycarbonyl)amino]propanamido}-3-methoxy-3-oxopropyl)-2-(pyridin-2-yloxy)-1,3-phenylene bis(2,6-dimethylbenzoate) (5da): The general procedure C was followed using **4d** (110.9 mg, 0.25 mmol) and **2a** (112.6 mg, 0.75 mmol). Isolation by column chromatography on silica gel (*n*-hexane/EtOAc: 7:3→5:5) yielded **5da** (99.6 mg, 54%) as a white solid. **M. p.** = 83–87 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.06 (d, *J* = 5.0 Hz, 1H), 7.60 (dd, *J* = 7.7, 7.7 Hz, 1H), 7.30 – 7.16 (m, 2H), 7.12 (s, 2H), 7.07 – 6.84 (m, 7H), 5.37 (brs, 1H), 5.15 – 4.89 (m, 1H), 4.41 – 4.05 (m, 1H), 3.82 (s, 3H), 3.35 (dd, *J* = 13.9, 5.9 Hz, 1H), 3.31 (dd, *J* = 13.9, 6.2 Hz, 1H), 2.30 (s, 12H), 1.43 (s, 9H), 1.39 (d, *J* = 7.3 Hz, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 172.8 (C_q), 171.4 (C_q), 167.4 (C_q), 162.4 (C_q), 155.7 (C_q), 147.6 (CH), 144.5 (C_q), 139.4 (CH), 136.5 (C_q), 135.7 (C_q), 133.9 (C_q), 132.3 (C_q), 130.1 (CH), 127.8 (CH), 122.2 (CH), 118.8 (CH), 110.4 (CH), 80.1 (C_q), 52.9 (CH), 52.7 (CH_3), 50.5 (CH), 37.4 (CH_2), 28.3 (CH_3), 19.9 (CH_3), 18.2 (CH_3). **IR** (ATR): 2978, 2929, 1756, 1714, 1501, 1467, 1429, 1259, 1224, 1060, 773 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 740 (85) $[M+H]^+$, 762 (100) $[M+Na]^+$. **HR-MS** (ESI): *m/z* calcd for $C_{41}H_{46}N_3O_{10}^+$ $[M+H]^+$ 740.3178, found 740.3186.

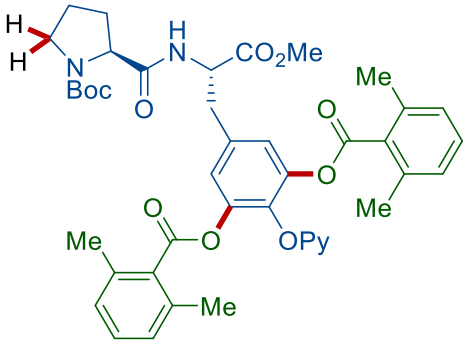


5-{(*S*)-2-[(*tert*-butoxycarbonyl)amino]-3-{[(*S*)-1-methoxy-1-oxo-3-phenylpropan-2-yl]amino}-3-oxopropyl}-2-(pyridin-2-yloxy)-1,3-phenylene bis(2,6-dimethylbenzoate) (5ea): The general procedure **C** was followed using **4e** (129.9 mg, 0.25 mmol) and **2a** (112.5 mg, 0.75 mmol). Isolation by column chromatography on silica gel (*n*-hexane/EtOAc: 3:1→1:1) yielded **5ea** (132.6 mg, 65%) as a white

solid. **M. p.** = 80–83 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.01 (ddd, *J* = 4.9, 2.0, 0.9 Hz, 1H), 7.57 (ddd, *J* = 8.3, 7.2, 2.0 Hz, 1H), 7.29 – 7.21 (m, 5H), 7.20 – 7.15 (m, 2H), 7.10 – 7.04 (m, 2H), 6.99 (d, *J* = 7.6 Hz, 4H), 6.90 – 6.84 (m, 2H), 6.44 (d, *J* = 7.5 Hz, 1H), 5.20 (brs, 1H), 4.79 (ddd, *J* = 7.6, 6.1, 6.1 Hz, 1H), 4.52 – 4.34 (m, 1H), 3.65 (s, 3H), 3.33 – 3.17 (m, 1H), 3.17 – 3.03 (m, 3H), 2.27 (s, 12H), 1.44 (s, 9H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 171.3 (C_q), 170.3 (C_q), 167.1 (C_q), 162.3 (C_q), 155.3 (C_q), 147.5 (CH), 144.6 (C_q), 139.2 (CH), 136.6 (C_q), 135.8 (C_q), 135.6 (C_q), 134.7 (C_q), 132.2 (C_q), 129.9 (CH), 129.3 (CH), 128.7 (CH), 128.6 (CH), 127.7 (CH), 127.1 (CH), 122.2 (CH), 118.6 (CH), 110.2 (CH), 80.3 (C_q), 55.3 (CH), 53.5 (CH), 52.3 (CH_3), 37.7 (CH_2), 37.7 (CH_2), 28.3 (CH_3), 19.8 (CH_3). **IR** (ATR): 3320, 2977, 1739, 1592, 1498, 1428, 1223, 1165, 1046, 772 cm^{-1}**. MS** (ESI) *m/z* (relative intensity): 816 (100) $[M+H]^+$, 838 (5) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{47}H_{50}N_3O_{10}^+$ $[M+H]^+$ 816.3491, found 816.3488.

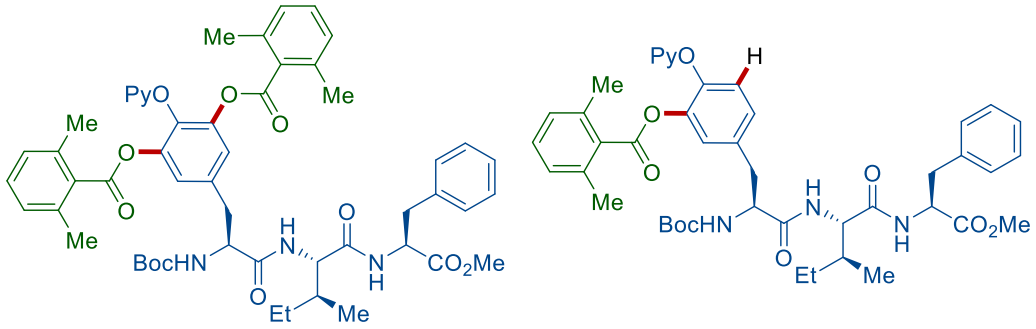


5-{(*S*)-2-[(*tert*-butoxycarbonyl)amino]-3-{[(2*S*,3*S*)-1-methoxy-3-methyl-1-oxopentan-2-yl]amino}-3-oxopropyl}-2-(pyridin-2-yloxy)-1,3-phenylene bis(2,6-dimethylbenzoate) (5fa): The general procedure **C** was followed using **4f** (121.4 mg, 0.25 mmol) and **2a** (112.5 mg, 0.75 mmol). Isolation by column chromatography on silica gel (*n*-hexane/EtOAc: 3:1→1:1) yielded **5fa** (148.6 mg, 76%) as a white solid. **M. p.** = 66–69 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.06 (ddd, *J* = 5.0, 2.0, 0.8 Hz, 1H), 7.57 (ddd, *J* = 8.3, 7.2, 2.0 Hz, 1H), 7.21 (s, 2H), 7.17 (t, *J* = 7.6 Hz, 2H), 7.00 – 6.97 (m, 4H), 6.89 (ddd, *J* = 7.2, 5.0, 0.9 Hz, 1H), 6.86 (dt, *J* = 8.4, 0.9 Hz, 1H), 6.67 (d, *J* = 7.1 Hz, 1H), 5.26 (brs, 1H), 4.55 (dd, *J* = 8.3, 4.9 Hz, 1H), 4.46 (d, *J* = 7.7 Hz, 1H), 3.67 (s, 3H), 3.29 – 3.16 (m, 2H), 2.27 (s, 12H), 1.94 – 1.87 (m, 1H), 1.47 – 1.38 (m, 10H), 1.20 – 1.11 (m, 1H), 0.90 – 0.86 (m, 6H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 171.7 (C_q), 170.5 (C_q), 167.0 (C_q), 162.3 (C_q), 155.5 (C_q), 147.5 (CH), 144.6 (C_q), 139.2 (CH), 136.5 (C_q), 135.6 (C_q), 134.9 (C_q), 132.2 (C_q), 129.8 (CH), 127.6 (CH), 122.0 (CH), 118.6 (CH), 110.2 (CH), 80.4 (C_q), 56.7 (CH), 55.3 (CH), 52.0 (CH_3), 37.8 (CH), 37.0 (CH_2), 28.2 (CH_3), 25.1 (CH_2), 19.8 (CH_3), 15.3 (CH_3), 11.5 (CH_3). **IR** (ATR): 3345, 2967, 1740, 1681, 1592, 1466, 1428, 1223, 1046, 772 cm^{-1}**. MS** (ESI) *m/z* (relative intensity): 782 (100) $[M+H]^+$, 804 (90) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{44}H_{52}N_3O_{10}^+$ $[M+H]^+$ 782.3647, found 782.3631.



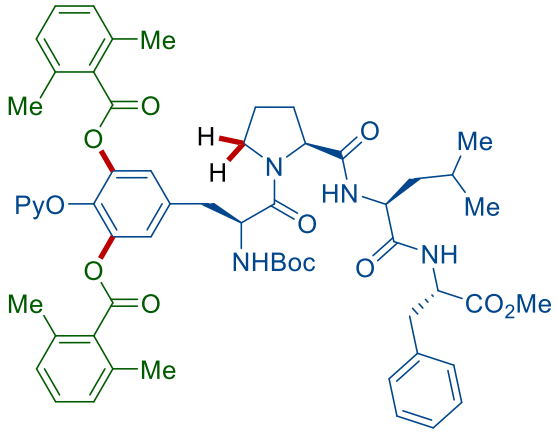
5-({*S*}-2-{[*S*]-1-[*tert*-Butoxycarbonyl]pyrrolidine-2-carboxamido}-3-methoxy-3-oxopropyl)-2-

(pyridin-2-yloxy)-1,3-phenylene bis(2,6-dimethylbenzoate) (5ga): The general procedure **C** was followed using **4g** (117.4 mg, 0.25 mmol) and **2a** (112.6 mg, 0.75 mmol). Isolation by column chromatography on silica gel (*n*-hexane/EtOAc: 5:5) yielded **5ga** (137.5 mg, 72%) as a white solid. **M. p.** = 61–65 °C. **^{1}H-NMR** (600 MHz, DMSO-d_6, 80 °C) δ = 8.06 – 7.97 (m, 2H), 7.74 (ddd, *J* = 8.3, 7.2, 2.0 Hz, 1H), 7.34 (s, 2H), 7.25 (t, *J* = 7.6 Hz, 2H), 7.08 (d, *J* = 7.6 Hz, 4H), 7.02 (ddd, *J* = 7.2, 4.9, 0.9 Hz, 1H), 6.92 (dt, *J* = 8.3, 0.9 Hz, 1H), 4.75 (ddd, *J* = 9.0, 8.5, 5.6 Hz, 1H), 4.19 – 4.07 (m, 1H), 3.69 (s, 3H), 3.39 (ddd, *J* = 10.3, 7.5, 5.0 Hz, 1H), 3.33 – 3.24 (m, 2H), 3.19 (dd, *J* = 14.2, 9.0 Hz, 1H), 2.24 (s, 12H), 2.12 – 2.01 (m, 1H), 1.83–1.65 (m, 3H), 1.34 (s, 9H). **^{13}C-NMR** (101 MHz, DMSO-d_6) δ = 172.8 (C_q), 171.9 (C_q), 166.5 (C_q), 161.7 (C_q), 153.4 (C_q), 147.1 (CH), 143.7 (C_q), 140.1 (CH), 136.1 (C_q), 135.8 (C_q), 134.7 (C_q), 132.0 (C_q), 130.1 (CH), 127.6 (CH), 122.2 (CH), 119.2 (CH), 110.0 (CH), 78.5 (C_q), 59.9 (CH), 52.7 (CH), 51.9 (CH_3), 46.4 (CH_2), 35.4 (CH_2), 30.9 (CH_2), 27.8 (CH_3), 23.0 (CH_2), 19.1 (CH_3). **IR** (ATR): 2979, 2929, 1756, 1748, 1696, 1428, 1224, 1101, 1061, 1050, 772 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 766 (60) $[M+H]^+$, 788 (100) $[M+Na]^+$. **HR-MS** (ESI): *m/z* calcd for $C_{44}H_{48}N_3O_{10}^+$ $[M+H]^+$ 766.3334, found 766.3337.



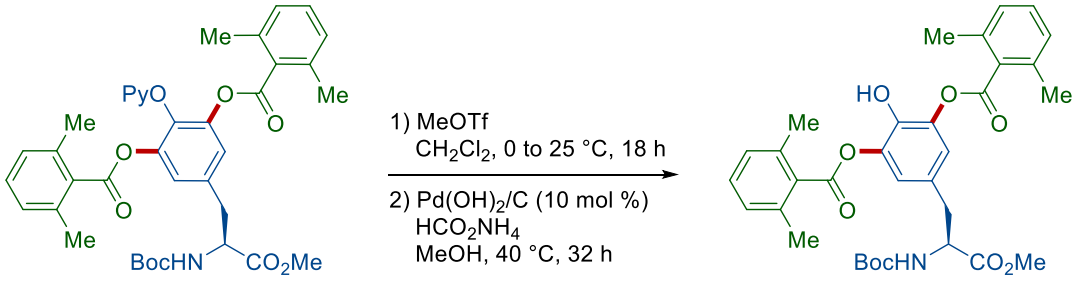
5-([*S*]-2-[(*tert*-Butoxycarbonyl)amino]-3-[({2*S*,3*S*}-1-{[(*S*)-1-methoxy-1-oxo-3-phenylpropan-2-yl]amino}-3-methyl-1-oxopentan-2-yl)amino]-3-oxopropyl}-2-(pyridin-2-yloxy)-1,3-phenylene bis(2,6-dimethylbenzoate) (5ha) and **methyl (6*S*,9*S*,12*S*)-12-benzyl-9-[(*S*)-*sec*-butyl]-6-{3-[(2,6-dimethylbenzoyl)oxy]-4-[pyridin-2-yloxy]benzyl}-2,2-dimethyl-4,7,10-trioxo-3-oxa-5,8,11-triazatridecan-13-oate (5ha'):** The general procedure **C** was followed using **4h** (158.2 mg, 0.25 mmol) and **2a** (112.6 mg, 0.75 mmol). Isolation by column chromatography on silica gel (*n*-hexane/EtOAc: 1:1) and recycling preparative HPLC yielded **5ha** (104.5 mg, 45%) as a white solid and **5ha'** (50.7 mg, 26%) as a white solid. **5ha M. p.** = 104–105 °C. **^{1}H-NMR** (600 MHz, $CDCl_3$) δ = 8.02 (dd, *J* = 5.0, 2.0 Hz, 1H), 7.54 (ddd, *J* = 8.4, 7.2, 2.0 Hz, 1H), 7.25 – 7.22 (m, 2H), 7.21 – 7.17 (m, 3H), 7.15 (t, *J* = 7.6 Hz, 2H), 7.09 – 7.03 (m, 2H), 6.97 (d, *J* = 7.6 Hz, 4H), 6.86 (dd, *J* = 7.2, 4.9 Hz, 1H), 6.83 (d, *J* = 8.4 Hz, 1H), 6.78 (d, *J* = 8.2 Hz, 1H), 6.39 (d, *J* = 7.8 Hz, 1H), 5.21 (d, *J* = 7.8 Hz, 1H), 4.81 (ddd, *J* = 7.8, 6.2, 6.2 Hz, 1H), 4.45 – 4.38 (m, 1H), 4.26 (dd, *J* = 8.3, 6.4 Hz, 1H), 3.65 (s, 3H), 3.25 – 3.17 (m, 2H), 3.06 (dd, *J* = 14.0, 6.2, 1H), 3.02 (dd, *J* = 14.0, 6.4 Hz, 1H), 2.25 (s, 12H), 1.91 – 1.82 (m, 1H), 1.42 (s, 9H), 1.39 – 1.34 (m, 1H), 1.05 (ddd, *J* = 13.5, 9.6, 7.2 Hz, 1H), 0.84 (d, *J* = 6.8 Hz, 3H), 0.81 (t, *J* = 7.4 Hz, 3H). **^{13}C-NMR** (151 MHz, $CDCl_3$) δ = 171.6 (C_q), 170.8 (C_q), 170.2 (C_q), 167.0 (C_q), 162.2 (C_q), 155.6 (C_q), 147.4 (CH), 144.6 (C_q), 139.2 (CH), 136.4 (C_q), 135.7 (C_q), 135.5 (C_q), 134.9 (C_q), 132.1 (C_q), 129.8 (CH), 129.2 (CH), 128.5 (CH), 127.6 (CH), 127.1 (CH), 121.9 (CH), 118.6 (CH), 110.2 (CH), 80.5 (C_q), 57.9 (CH), 55.2 (CH), 53.1 (CH), 52.2 (CH_3), 37.7 (CH_2), 37.0 (CH_2), 36.5 (CH_2), 28.2 (CH_3), 24.7 (CH), 19.8 (CH_3), 15.2 (CH_3), 11.3 (CH_3). **IR** (ATR): 3063, 2963, 1757, 1746, 1641, 1520, 1428, 1265, 1222, 1048, 772, cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 929 (50) $[M+H]^+$, 951 (100) $[M+Na]^+$. **HR-MS** (ESI): *m/z* calcd for $C_{53}H_{61}N_4O_{11}^+$ $[M+H]^+$ 929.4331, found 929.4326. **5ha' M. p.** = 100–102 °C. **^{1}H-NMR** (600 MHz, $CDCl_3$) δ = 8.11 (dd, *J* = 5.0, 2.0 Hz, 1H), 7.62 (ddd, *J* = 8.3, 7.2, 2.0

Hz, 1H), 7.25 – 7.21 (m, 2H), 7.21 – 7.13 (m, 4H), 7.13 – 7.05 (m, 3H), 6.99 (d, *J* = 7.7 Hz, 2H), 6.94 (ddd, *J* = 7.2, 5.0, 1.0 Hz, 1H), 6.88 (ddd, *J* = 8.3, 1.0, 1.0 Hz, 1H), 6.71 (d, *J* = 8.4 Hz, 1H), 6.44 (d, *J* = 8.0 Hz, 1H), 5.13 (d, *J* = 7.9 Hz, 1H), 4.80 (ddd, *J* = 7.9, 6.2, 6.2 Hz, 1H), 4.41 – 4.32 (m, 1H), 4.25 (dd, *J* = 8.4, 6.4 Hz, 1H), 3.66 (s, 3H), 3.16 – 2.98 (m, 4H), 2.34 (s, 6H), 1.87 – 1.76 (m, 1H), 1.40 (s, 9H), 1.37 – 1.30 (m, 1H), 1.09 – 0.99 (m, 1H), 0.88 – 0.76 (m, 6H). **^{13}C-NMR** (151 MHz, $CDCl_3$) δ = 171.6 (C_q), 171.0 (C_q), 170.3 (C_q), 167.4 (C_q), 162.9 (C_q), 155.5 (C_q), 147.6 (CH), 144.5 (C_q), 142.5 (C_q), 139.4 (CH), 135.7 (C_q), 135.5 (C_q), 134.4 (C_q), 132.5 (C_q), 129.7 (CH), 129.2 (CH), 128.6 (CH), 127.8 (CH), 127.6 (CH), 127.1 (CH), 124.4 (CH), 123.5 (CH), 118.7 (CH), 111.2 (CH), 80.4 (C_q), 57.8 (CH), 55.5 (CH), 53.1 (CH), 52.2 (CH_3), 37.7 (CH_2), 37.0 (CH_2), 36.7 (CH_2), 28.2 (CH_3), 24.6 (CH), 19.8 (CH_3), 15.2(CH_3), 11.3 (CH_3). **IR** (ATR): 3272, 2962, 2932, 1746, 1687, 1641, 1467, 1428, 1228, 1049, 771 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 781 (60) $[M+H]^+$, 803 (100) $[M+Na]^+$. **HR-MS** (ESI): *m/z* calcd for $C_{44}H_{53}N_4O_9^+$ $[M+H]^+$ 781.3807, found 781.3809.



5-({*S*}-2-{[*tert*-Butoxycarbonyl]amino}-3-{[*S*]-2-[({*S*}-1-{[(*S*)-1-methoxy-1-oxo-3-phenylpropan-2-yl]amino}-4-methyl-1-oxopentan-2-yl)carbamoyl]pyrrolidin-1-yl}-3-oxopropyl)-2-(pyridin-2-yloxy)-1,3-phenylene bis(2,6-dimethylbenzoate) (5ia): The general procedure **C** was followed using **4i** (182.5 mg, 0.25 mmol) and **2a** (112.6 mg, 0.75 mmol). Isolation by column chromatography on silica gel (CH_2Cl_2/EtOAc: 4:1→2:1) yielded **5ia** (133.3 mg, 52%) as a white solid. **M. p.** = 75–79 °C. **^{1}H-NMR** (600 MHz, DMSO-*d*$_6$, 100 °C) δ = 8.06 – 7.98 (m, 1H), 7.78 – 7.67 (m, 2H), 7.59 (brs, 1H), 7.39 (s, 2H), 7.29 – 7.16 (m, 8H), 7.07 (d, *J* = 7.6 Hz, 4H), 7.01 (dd, *J* = 7.2, 4.9 Hz, 1H), 6.90 (d, *J* = 8.3 Hz, 1H), 4.63 – 4.51 (m, 2H), 4.48 – 4.37 (m, 1H), 4.30 (ddd, *J* = 8.4, 8.4, 5.8 Hz, 1H), 3.77 – 3.61 (m, 2H), 3.60 (s, 3H), 3.20 – 2.97 (m, 4H), 2.25 (s, 12H), 2.10 – 1.81 (m, 4H), 1.72 – 1.58 (m, 1H), 1.59 – 1.45 (m, 2H), 1.36 (s, 9H), 0.89 (d, *J* = 6.6 Hz, 3H), 0.85 (d, *J* = 6.6 Hz, 3H). **^{13}C-NMR** (151 MHz, DMSO-*d*$_6$, 100 °C) δ = 171.2 (C_q), 170.9 (C_q), 170.5 (C_q), 169.8 (C_q), 165.8 (C_q), 161.4 (C_q), 154.5 (C_q), 146.6 (CH), 143.4 (C_q), 139.1 (CH), 136.6 (C_q), 135.9 (C_q), 135.4 (C_q), 134.4 (C_q), 131.6 (C_q), 129.3 (CH), 128.4 (CH), 127.6 (CH), 127.1 (CH), 125.8 (CH), 121.4 (CH), 118.4 (CH), 109.3 (CH), 77.9 (C_q), 59.3 (CH), 52.8 (CH), 51.0 (CH_3), 50.9 (CH), 46.3 (CH_2), 40.2 (CH_2), 36.5 (CH_2), 35.8 (CH_2), 28.1 (CH_2), 27.7 (CH_3), 24.0 (CH_2), 23.7 (CH), 22.2 (CH_3), 21.3 (CH_3), 18.5 (CH_3) One aliphatic CH is missing due to overlap, the overlap was verified by HSQC analysis showing that the peak at 52.8 ppm corresponds to two carbons. **IR** (ATR): 2953, 2869, 1749, 1671, 1650, 1537, 1467, 1224, 1051, 774 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 1026 (40) $[M+H]^+$,1049 (100) $[M+Na]^+$. **HR-MS** (ESI): *m/z* calcd for $C_{58}H_{68}N_5O_{12}^+$ $[M+H]^+$ 1026.4859, found 1026.4864.

Removal of Pyridyl Group

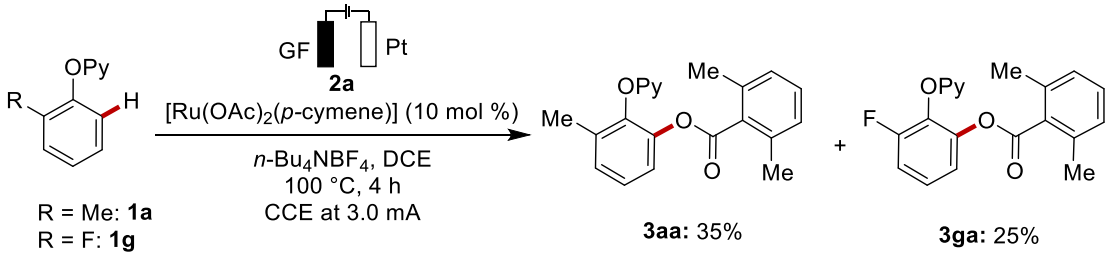


5aa **$5aa_{[OH]}$: 44%**

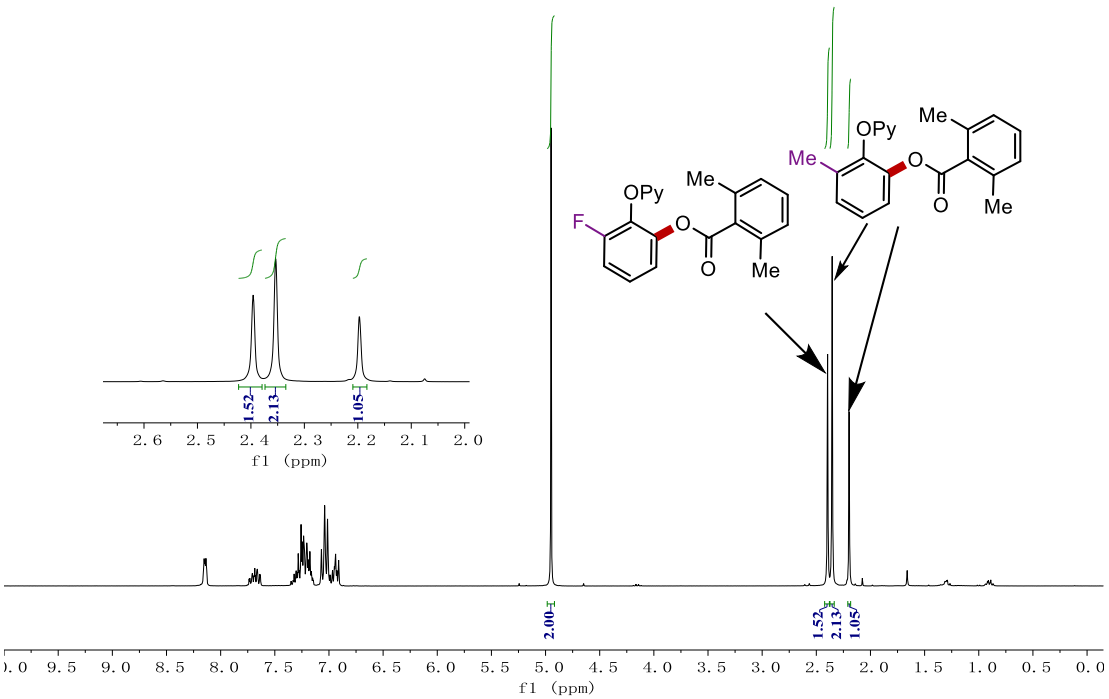
To a stirred solution of **5aa** (100.3 mg, 0.15 mmol) in CH_2Cl_2 (1.0 mL) methyl trifluoromethanesulfonate (73.8 mg, 0.45 mmol) was added at 0 °C. After 30 min, the mixture was allowed to warm up to 25 °C and stirred for 18 h. The crude mixture was concentrated under reduced pressure to afford an white solid. In a sealed-tube, the crude product, $Pd(OH)_2/C$ (20 wt%, containing 50% water) (9.2 mg, 5.0 mol %), and ammonium formate (141.9 mg, 15.0 equiv) were dissolved in methanol (2.0 mL), and stirred at 40 ˚C for 32 hours. The mixture was filtered through a short plug of celite, concentrated under reduced pressure and purified by column chromatography on silica gel (Hexane/EtOAc: 8/2 → 7/3), yielding **$5aa_{[OH]}$** (39.1 mg, 44%) as a white solid.

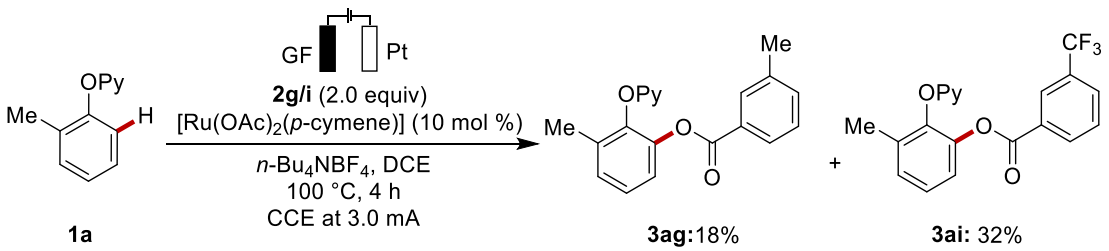
(*S*)-5-{2-[(tert-butoxycarbonyl)amino]-3-methoxy-3-oxopropyl}-2-hydroxy-1,3-phenylene bis(2,6-dimethylbenzoate) (**$5aa_{[OH]}$**): **M. p.** = 63–70 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.26 (t, J = 7.6 Hz, 2H), 7.06 (d, J = 7.7 Hz, 4H), 6.89 – 6.79 (m, 2H), 6.47 (brs, 1H), 5.20 (brs, 1H), 4.66 (ddd, J = 7.7, 6.8, 6.8 Hz, 1H), 3.79 (s, 3H), 3.11 – 3.17 (m, 2H), 2.30 (d, J = 12.4 Hz, 12H), 1.49 (s, 9H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 172.1 (C_q), 167.0 (C_q), 155.3 (C_q), 143.1 (C_q), 136.4 (C_q), 135.8 (C_q), 135.2 (C_q), 132.2 (C_q), 131.7 (CH), 127.8 (CH), 116.2 (CH), 80.4 (C_q), 54.3 (CH), 52.5 (CH_3), 38.0 (CH_2), 28.3 (CH_3), 19.8 (CH_3). **IR** (ATR): 3352, 2928, 1683, 1618, 1440, 1367, 1238, 1160, 1050, 772 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 614 (100) $[M+Na]^+$. **HR-MS** (ESI): *m/z* calcd for $C_{33}H_{37}N_1O_9Na^+$ $[M+Na]^+$ 614.2361, found 614.2353.

Competition Experiments

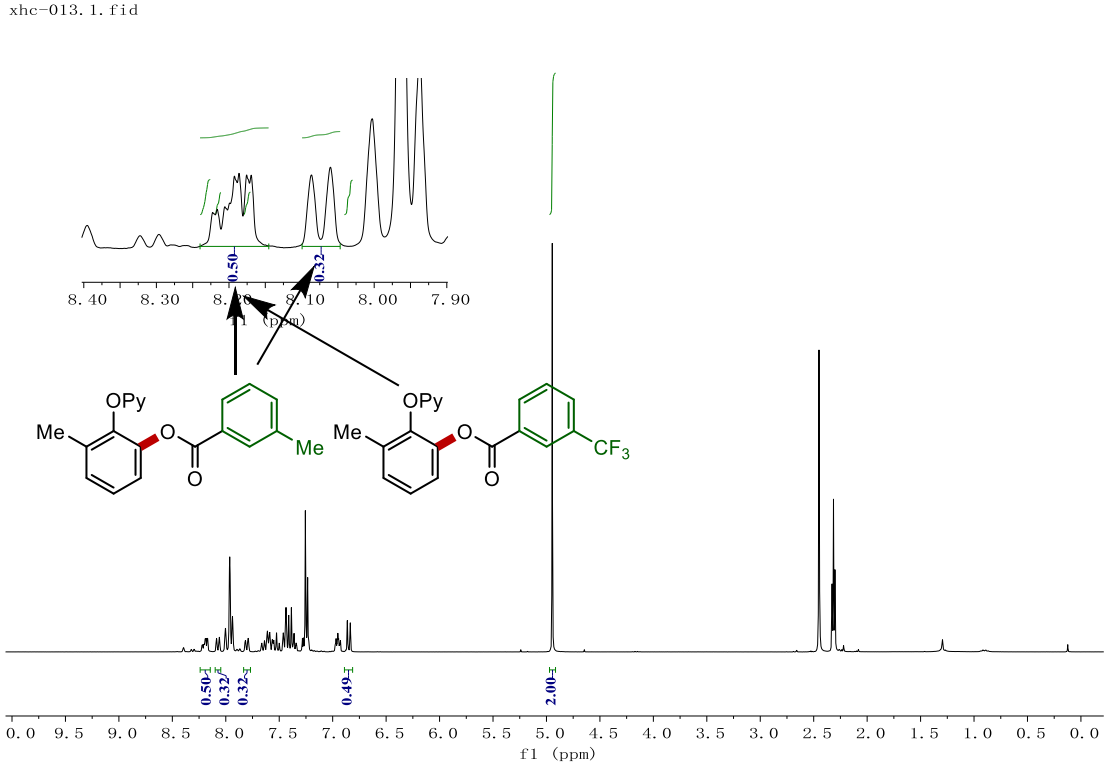


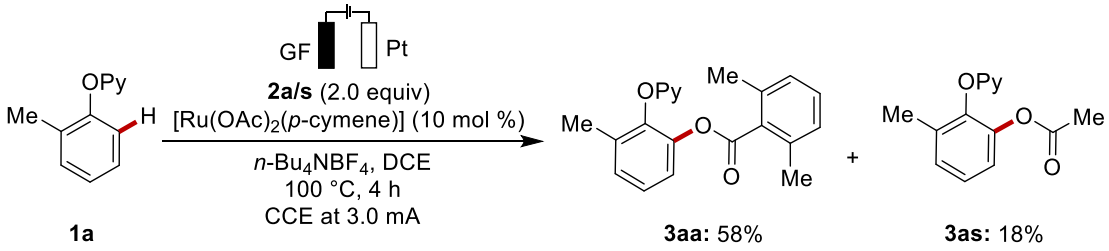
A solution of **1a** (46.3 mg, 0.25 mmol), **1g** (47.3 mg, 0.25 mmol), **2a** (37.5 mg, 0.25 mmol), [Ru(OAc)$_2$(*p*-cymene)] (8.8 mg, 10 mol %) and *n*-Bu$_4$NBF$_4$ (82.3 mg, 0.25 mmol) in DCE (4.0 mL) was place in a 25 mL Schlenk tube. The tube was sealed with a septum equipped with a platinum electrode (10 mm × 15 mm × 0.25 mm) and a graphite felt electrode (10 mm × 15 mm × 6 mm). An oil bulb was attached to the system by using a needle. The tube was placed in an oil bath and stirred at 100 °C. After 4 h at 3.0 mA, the mixture was cooled to ambient temperature and the solvent was removed under vaccum. The residue was purified by column chromatography on silica gel (n-hexane/EtOAc: 20:1→10:1). The products **3aa** (35%) and **3ga** (25%) were obtained as a mixture and the conversion was determined by ^{1}H NMR spectroscopy with CH_2Br_2 (43.5 mg, 0.25 mmol) as internal standard.





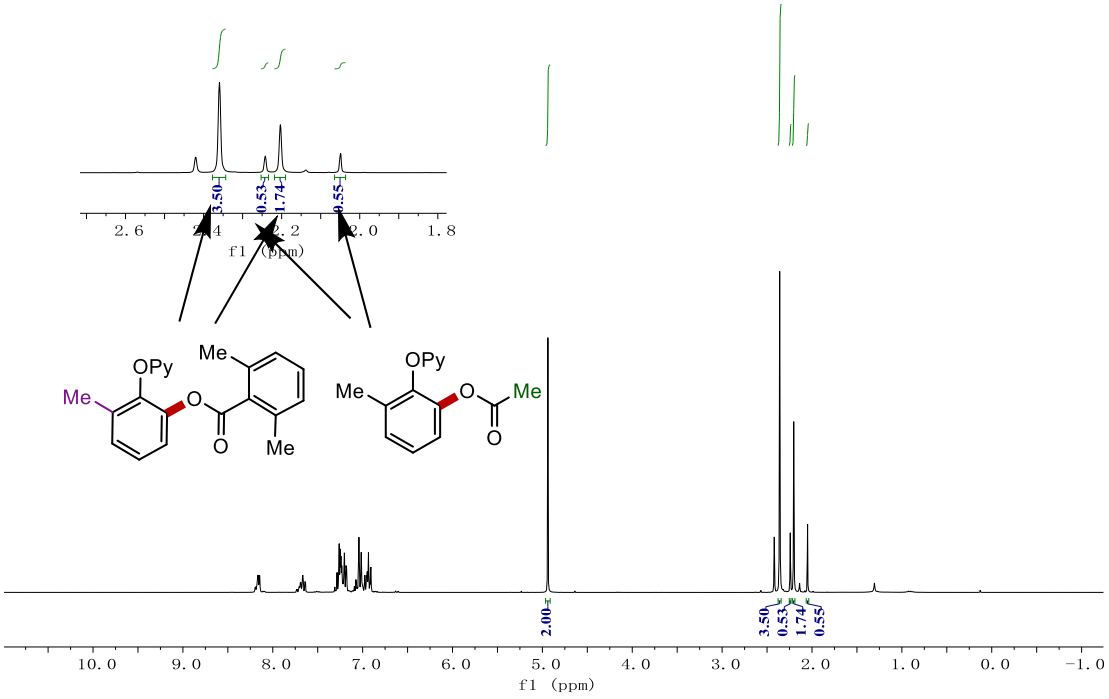
A solution of **1a** (46.3 mg, 0.25 mmol), **2g** (34.0 mg, 0.25 mmol), **2i** (47.5 mg, 0.25 mmol), [Ru(OAc)$_2$(*p*-cymene)] (8.8 mg, 10 mol %) and *n*-Bu$_4$NBF$_4$ (82.3 mg, 0.25 mmol) in DCE (4.0 mL) was place in a 25 mL Schlenk tube. The tube was sealed with a septum equipped with a platinum electrode (10 mm × 15 mm × 0.25 mm) and a graphite felt electrode (10 mm × 15 mm × 6 mm). An oil bulb was attached to the system by using a needle. The tube was placed in an oil bath and stirred at 100 °C. After 4 h at 3.0 mA, the mixture was cooled to ambient temperature and the solvent was removed under vaccum. The residue was purified by column chromatography on silica gel (n-hexane/EtOAc: 20:1→10:1). The products **3ag** (18%) and **3ai** (32%) were obtained as a mixture and the conversion was determined by ^{1}H NMR spectroscopy with CH_2Br_2 (43.5 mg, 0.25 mmol) as internal standard.



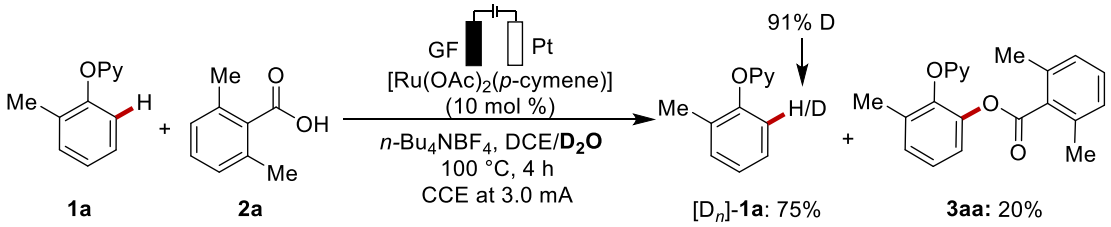


A solution of **1a** (46.3 mg, 0.25 mmol), **2a** (37.5 mg, 0.25 mmol), **2s** (15.0 mg, 0.25 mmol), [Ru(OAc)$_2$(*p*-cymene)] (8.8 mg, 10 mol %) and *n*-Bu$_4$NBF$_4$ (82.3 mg, 0.25 mmol) in DCE (4.0 mL) was place in a 25 mL Schlenk tube. The tube was sealed with a septum equipped with a platinum electrode (10 mm × 15 mm × 0.25 mm) and a graphite felt electrode (10 mm × 15 mm × 6 mm). An oil bulb was attached to the system by using a needle. The tube was placed in an oil bath and stirred at 100 °C. After 4 h at 3.0 mA, the mixture was cooled to ambient temperature and the solvent was removed under vaccum. The

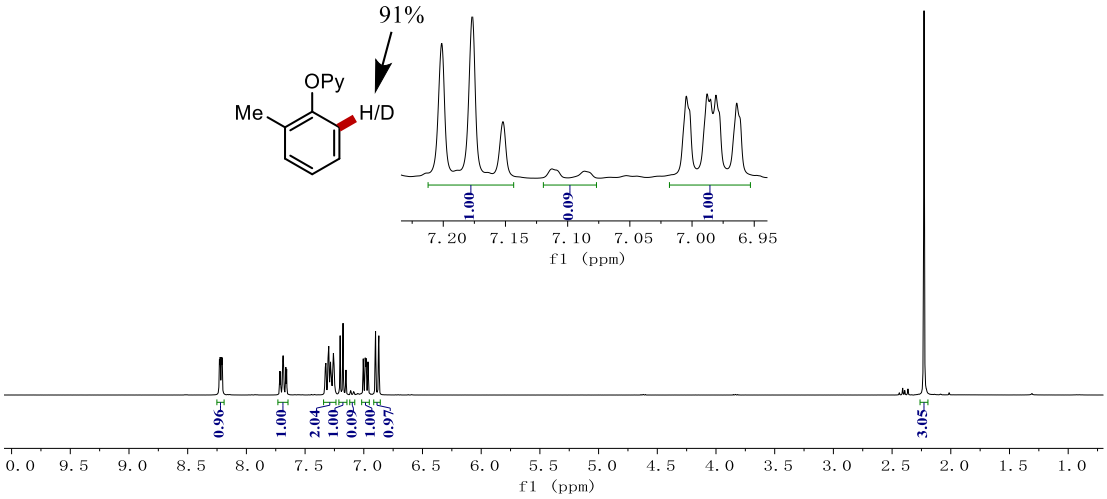
residue was purified by column chromatography on silica gel (n-hexane/EtOAc: 20:1→10:1). The products **3aa** (58%) and **3ar** (18%) were obtained as a mixture and the conversion was determined by ^{1}H NMR spectroscopy with CH_2Br_2 (43.5 mg, 0.25 mmol) as internal standard.



H/D Exchange Experiments

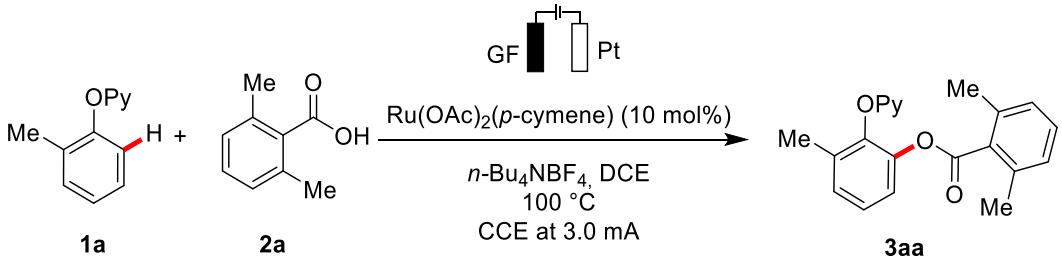


To a 25 mL Schlenk tube equipped with a magnetic stirring bar were added **1a** (46.3 mg, 0.25 mmol), **2a** (60.0 mg, 0.40 mmol), [Ru(OAc)$_2$(*p*-cymene)] (8.8 mg, 10 mol %) and *n*-Bu$_4$NBF$_4$ (82.3 mg, 0.25 mmol) in DCE (3.8 mL) and D$_2$O (0.2 mL). The tube was sealed with a septum equipped with a platinum electrode (10 mm × 15 mm × 0.25 mm) and a graphite felt electrode (10 mm × 15 mm × 6 mm). An oil bulb was attached to the system by using a needle. The tube was placed in an oil bath and stirred at 100 °C. After 4 h at 3.0 mA, the mixture was cooled to ambient temperature and the solvent was removed under vaccum. The residue was purified by column chromatography on silica gel (n-hexane/EtOAc: 20:1→10:1 affording **3aa** (16.6 mg, 20%) and unreacted [D$_n$]-**1a** (34.7 mg, 75%). The deuterium-incorporation was estimated by ^{1}H NMR spectroscopy.



On/off Electricity Experiment

On/off electricity reaction was carried out in a 25 mL Schlenk tube, with a GF anode (10 mm × 15 mm × 6 mm) and a platinum cathode (10 mm × 15 mm × 0.25 mm). **1a** (55.5 mg, 0.30 mmol), **2a** (60.0 mg, 0.40 mmol), [$Ru(OAc)_2$(*p*-cymene)] (10.6 mg, 10 mol %) and *n*-Bu_4NBF_4 (99.0 mg, 0.30 mmol) were placed in the tube and dissolved in DCE (5.0 mL). Electrocatalysis was performed at 100 °C with a constant current of 3.0 mA. Aliquots of 0.20 mL were removed from the cell every 1.0 h, and separately mixed with an aliquot (0.2 mL) of a solution of 1,3,5-trimethoxybenzene (0.30 mmol in 5.0 mL of DCE). The mixture was extracted with EtOAc (3.0 mL). After evaporation of solvent, the crude mixture was analyzed by ^{1}H-NMR spectroscopy.



Time [h]	0	1.0	2.0	3.0	4.0
Yield of **3aa** [%]	0	7	8	16	16

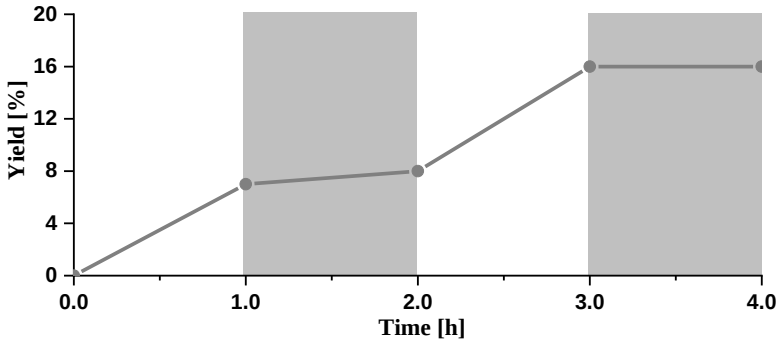
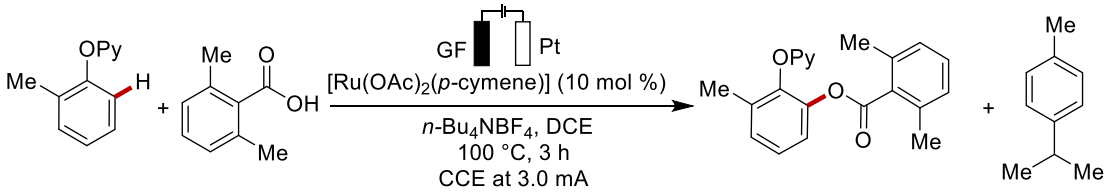


Fig. S1 On/off electricity experiment.

Detection of Free *p*-Cymene



1a **2a** **3aa** **6**

A 25 mL Schlenk-tube was charged with **1a** (46.3 mg, 0.25 mmol), **2a** (60.0 mg, 0.40 mmol), [Ru(OAc)$_2$(*p*-cymene)] (8.8 mg, 10 mol %) and *n*-Bu$_4$NBF$_4$ (82.3 mg, 0.25 mmol). *n*-Dodecane (10 µL) and DCE (4.0 mL) were added and the mixture was stirred at 100 °C with a constant current of 3.0 mA. During the course of the reaction, aliquots of 100 µL were removed via syringe after 0 h, 0.5 h, 1 h, 2 h and 3 h, respectively. The sample was diluted with EtOAc, filtered through a short plug of silica gel and analyzed by gas chromatography.

Time [h]	0	0.5	1.0	2.0	3.0
6 [%]	21.3	43.3	46.5	61.1	68.8
3aa [%]	0	5.3	15.5	29.4	43.7

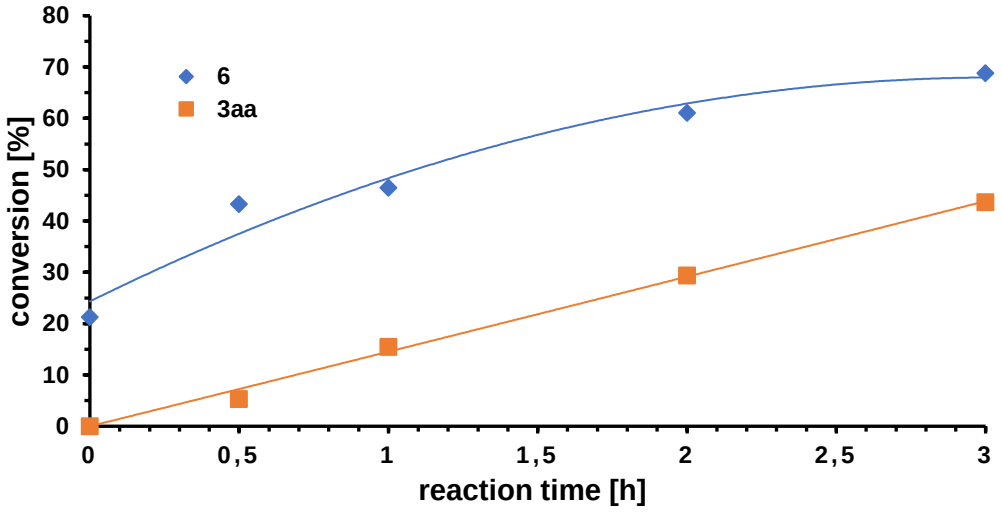
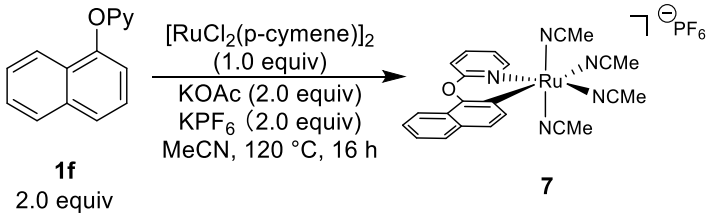


Fig. S2 Release of *p*-cymene (**6**) in the reaction of **1a** and **2a**.

Synthesis of Cyclometalated Ruthenium Complexes



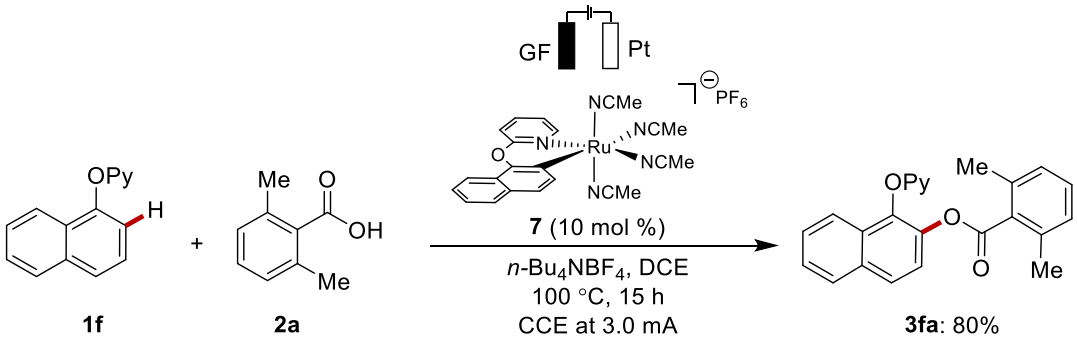
1f
2.0 equiv

7

An oven-dried pressure tube was charged with 2-(naphthalen-1-yloxy)pyridine (**1f**, 221 mg, 1.00 mmol), $[RuCl_2(p\text{-cymene})]_2$ (306 mg, 0.50 mmol), KOAc (196 mg, 2.00 mmol) and KPF_6 (368 mg, 2.00 mmol). After evacuation and refilling with N_2 for three times, MeCN (6.5 mL) was added and the tube was sealed. The reaction mixture was stirred at 120 °C. After 16 h, the reaction was cooled down to the ambient temperature. The crude mixture was loaded on an aluminium oxide (Al_2O_3, neutral, conditioned with CH_2Cl_2) column and eluted with MeCN/CH_2Cl_2 (2:1) using N_2 instead of air. The yellow band was collected and the solvent was removed under reduced pressure. The complex was dissolved in MeCN (4 mL) and precipitated with Et_2O, affording the desired complex **7** (378 mg, 60%) as a yellow solid. The complex **7** was transferred to the glovebox subsequently.

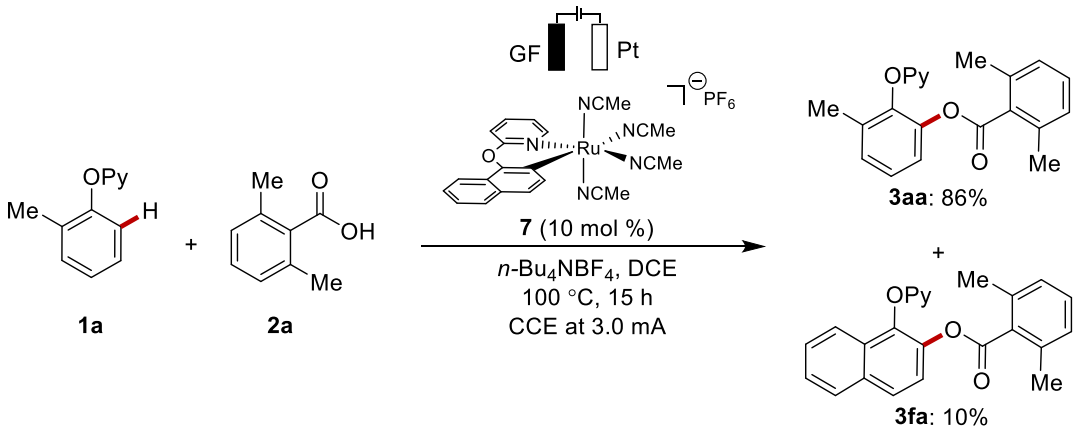
M. p. = >170 °C (decomp.). **^{1}H NMR** (400 MHz, MeCN-*d*$_3$) δ = 8.66 (ddd, *J* = 5.9, 1.9, 0.6 Hz, 1H), 8.26 (dq, *J* = 8.5, 0.9 Hz, 1H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.87 – 7.78 (m, 2H), 7.50 – 7.43 (m, 2H), 7.40 (ddd, *J* = 8.2, 1.4, 0.6 Hz, 1H), 7.30 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H), 7.11 (ddd, *J* = 7.2, 5.9, 1.4 Hz, 1H), 2.49 (s, 3H), 2.18 (s, 6H), 1.96 (s, 3H). **^{13}C NMR** (101 MHz, MeCN-*d*$_3$) δ = 165.4 (C_q), 154.9 (CH), 152.7 (C_q), 152.5 (C_q), 140.9 (CH), 140.4 (CH), 132.8 (C_q), 128.4 (CH), 126.1 (CH), 124.9 (C_q), 124.5 (C_q), 123.9 (CH), 123.5 (C_q), 122.4 (CH), 120.2 (CH), 119.7 (CH), 115.6 (CH), 4.4 (CH_3), 4.0 (CH_3). **^{19}F NMR** (377 MHz, MeCN-*d*$_3$) δ = -72.8 (d, *J* = 706 Hz). **^{31}P NMR** (162 MHz, MeCN-*d*$_3$) δ = -144.58 (hept, *J* = 706 Hz). **IR** (ATR): 2270, 1568, 1472, 1390, 1258, 1155, 1039, 833, 772, 556 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 445 (100) [M–MeCN–PF_6]$^+$. **HR-MS** (ESI) *m/z* calcd for $C_{21}H_{19}N_4ORu^+$ [M–MeCN–PF_6]$^+$ 445.0602, found 445.0596.

Reactions with Cyclometalated Complexes



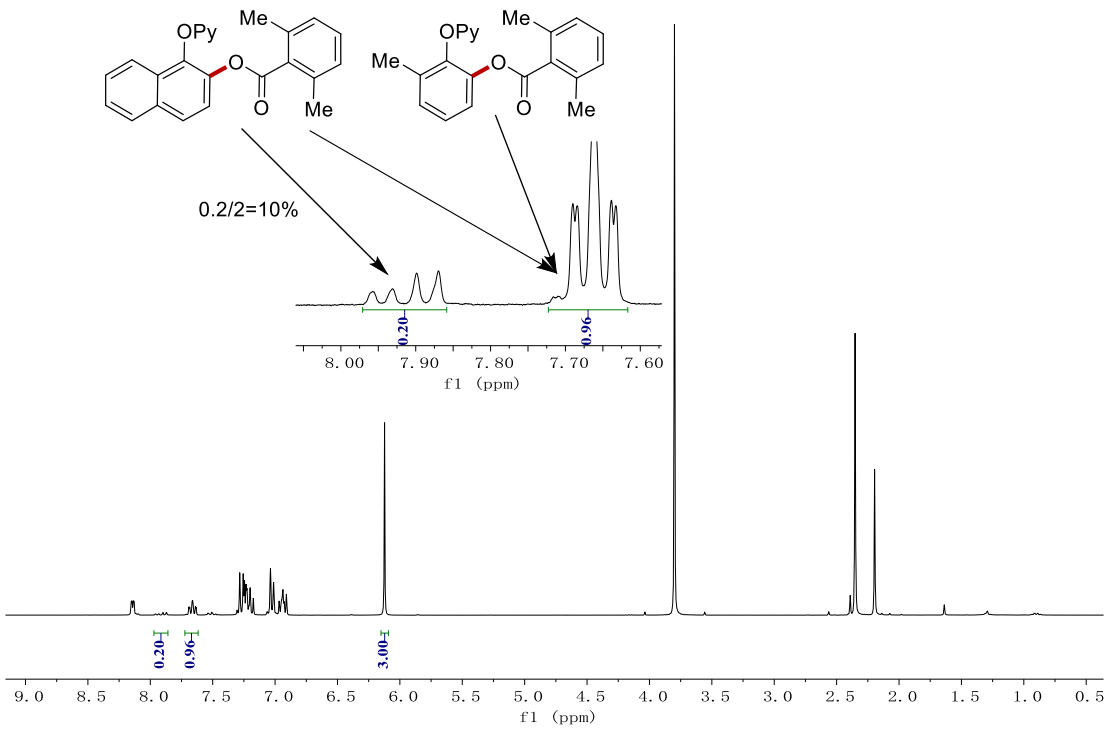
1f **2a** **3fa**: 80%

To a 25 mL Schlenk tube equipped with a magnetic stirring bar, **1f** (55.3 mg, 0.25 mmol), **2a** (60.0 mg, 0.40 mmol), **7** (15.8 mg, 10 mol %) and *n*-Bu_4NBF_4 (82.3 mg, 0.25 mmol) were added. The tube was sealed with a septum equipped with a platinum plate electrode (10 mm × 15 mm × 0.25 mm) and a graphite felt electrode (10 mm × 15 mm × 6 mm). Then the DCE (4.0 mL) were successively added. An oil bulb was attached to the system by using a needle. The tube was placed in an oil bath and stirred at 100 °C. After 15 h at 3.0 mA, the tube was cooled to ambient temperature and the solvent was removed under vaccum. Purification of the residue by column chromatography on silica gel (*n*-hexane/EtOAc: 10:1→5:1) yielded product **3fa** (73.9 mg, 80%) as a white solid.



1a **2a**

To a 25 mL Schlenk tube equipped, **1a** (46.3 mg, 0.25 mmol), **2a** (60.0 mg, 0.40 mmol), **7** (15.8 mg, 10 mol %) and *n*-Bu_4NBF_4 (82.3 mg, 0.25 mmol) were added. The tube was sealed with a septum equipped with a platinum plate electrode (10 mm × 15 mm × 0.25 mm) and a graphite felt electrode (10 mm × 15 mm × 6 mm). Then the DCE (4.0 mL) were successively added. An oil bulb was attached to the system by using a needle. The tube was placed in an oil bath and stirred at 100 °C. After 15 h at 3.0 mA, the tube was cooled to ambient temperature and the solvent was removed under vaccum. The residue was purified by column chromatography on silica gel (n-hexane/EtOAc: 10:1→5:1).The products **3aa** (86%) and **3da** (10%) were obtained as a mixture and the conversion was determined by ^1H NMR spectroscopy with 1,3,5-trimethoxybenzene (42.0 mg, 0.25 mmol) as internal standard.


OPy
Me
O
O
Me
OPy
Me
Me
O
O
Me
0.2/2=10%
0.20
0.96
8.00
7.90
7.80
7.70
7.60
f1 (ppm)
0.20
0.96
3.00
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
f1 (ppm)

Reaction Rate Comparison of Complex 7 and $Ru(OAc)_2$(*p*-cymene)

a) A 25 mL Schlenk-tube was charged with **1f** (66.3 mg, 0.30 mmol), **2a** (60.0 mg, 0.40 mmol), [$Ru(OAc)_2$(*p*-cymene)] (10.6 mg, 10 mol %) and *n*-Bu_4NBF_4 (99.0 mg, 0.30 mmol) were placed in the tube and dissolved in DCE (5.0 mL). Electrocatalysis was performed at 100 °C with a constant current of 3.0 mA. Aliquots of 0.20 mL were removed from the cell every 1.0 h, and separately mixed with an aliquot (0.2 mL) of a solution of 1,3,5-trimethoxybenzene (0.30 mmol in 5.0 mL of DCE). The mixture was extracted with EtOAc (3.0 mL). After evaporation of solvent, the crude mixture was analyzed by ^{1}H-NMR spectroscopy.

b) A 25 mL Schlenk-tube was charged with **1f** (64.1 mg, 0.29 mmol), **2a** (60.0 mg, 0.40 mmol), complex **7** (19.0 mg, 10 mol %) and *n*-Bu_4NBF_4 (99.0 mg, 0.30 mmol) were placed in the tube and dissolved in DCE (5.0 mL). Electrocatalysis was performed at 100 °C with a constant current of 3.0 mA. Aliquots of 0.20 mL were removed from the cell every 1.0 h, and separately mixed with an aliquot (0.2 mL) of a solution of 1,3,5-trimethoxybenzene (0.30 mmol in 5.0 mL of DCE). The mixture was extracted with EtOAc (3.0 mL). After evaporation of solvent, the crude mixture was analyzed by ^{1}H-NMR spectroscopy.

Time [h]	0	0.5	1.0	1.5	2.0	2.5
Yield with complex **7** [%]	0	4	10	14	20	25
Yield with $Ru(OAc)_2$(*p*-cymene) [%]	0	4	9	13	18	24

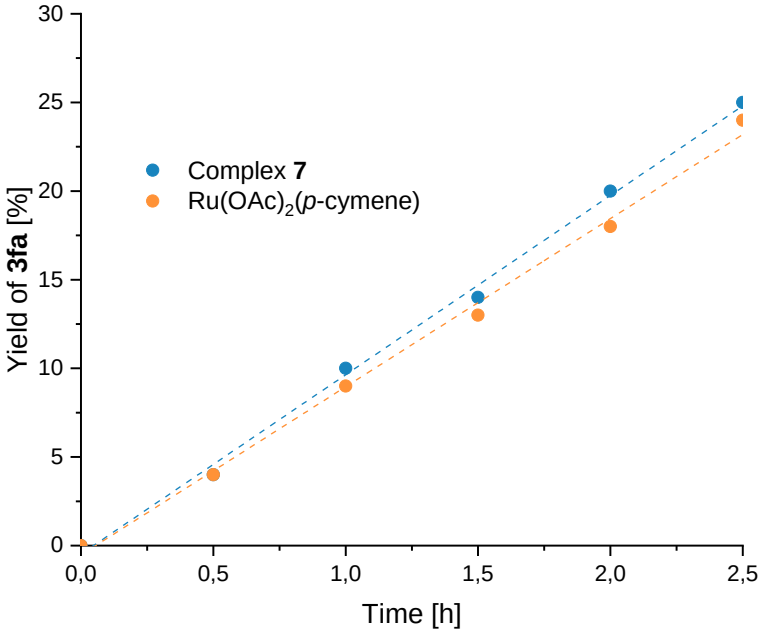


Fig. S3 Rate Comparison of Complex 7 and $Ru(OAc)_2$(*p*-cymene)

Cyclic Voltammetry

The cyclic voltammetry was carried out with a Metrohm Autolab PGSTAT204 workstation and the following analysis was performed with Nova 2.1 software. A glassy-carbon electrode (3 mm diameter, disc-electrode) was used as the working electrode, a platinum wire was employed as the counter electrode and a saturated calomel reference electrode (SCE) electrode was used as a reference electrode. The voltammograms were recorded at room temperature in DCE at a substrate concentration of 5 mmol/L and with 100 mmol/L *n*-Bu_4NPF_6 as supporting electrolyte. The scan rate is 100 mV/s. Deviations from the general experimental conditions are indicated in the respective figures and descriptions.

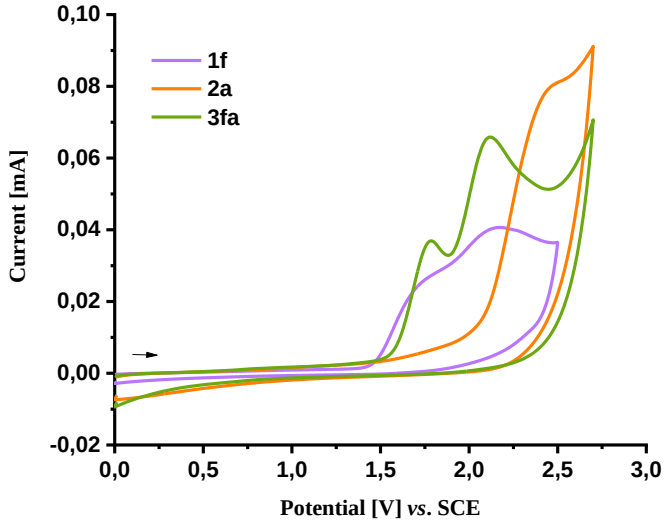


Fig. S4 Cyclic voltammogram of **1f**, **2a** and **3fa** in DCE with *n*-Bu_4NPF_6 (100 mmol/L) at 100 mV/s.

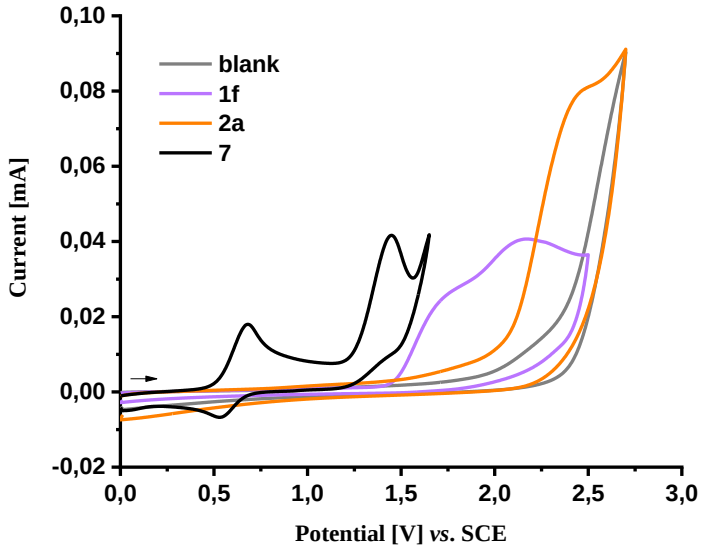


Fig. S5 Cyclic voltammogram of **1f**, **2a** and **7** in DCE with *n*-Bu_4NPF_6 (100 mmol/L) at 100 mV/s.

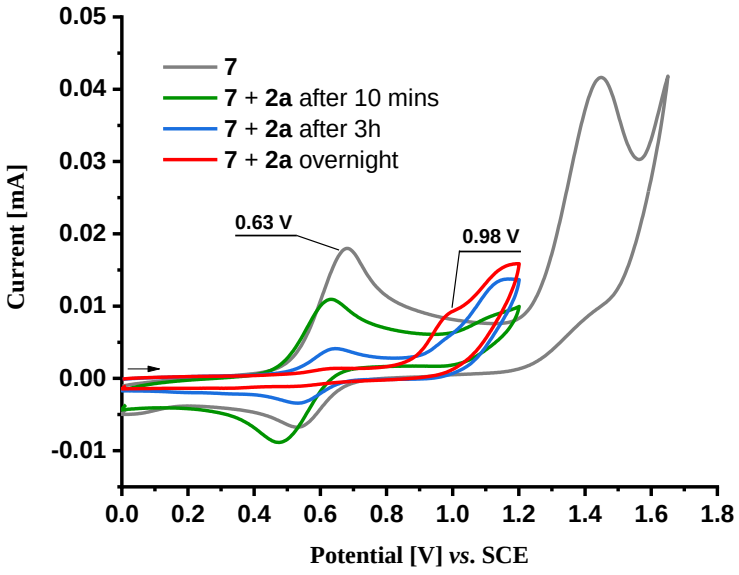


Fig. S6 Cyclic voltammogram of complex **7** with **2a** as additive in DCE with *n*-Bu_4NPF_6 (100 mmol/L) at 100 mV/s.

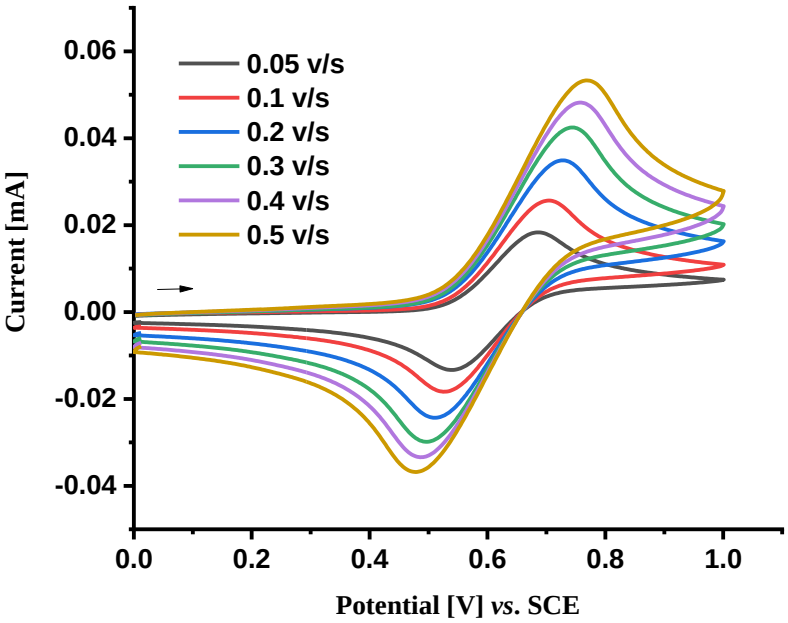
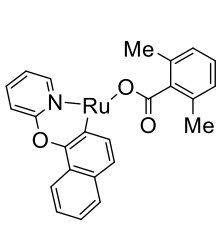


Fig. S7 Cyclic voltammogram of complex **7** in DCE with *n*-Bu_4NPF_6 (100 mmol/L) at diferent scan rates.

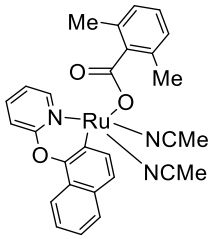
ESI–HRMS Analysis of Complex 7 with 2a

The mixture solution of complex **7** (9.5 mg, 0.015mmol), **2a** (22.5 mg, 0.15 mmol) and *n*-Bu_4NPF_6 (116.2 mg, 0.3 mmol) in DCE (3 mL) was tested by ESI–HRMS after stirring overnight under room temperature.



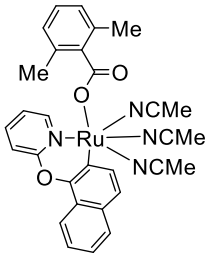
A

Chemical Formula: $C_{24}H_{19}NO_3Ru$
Exact Mass: 471.0408



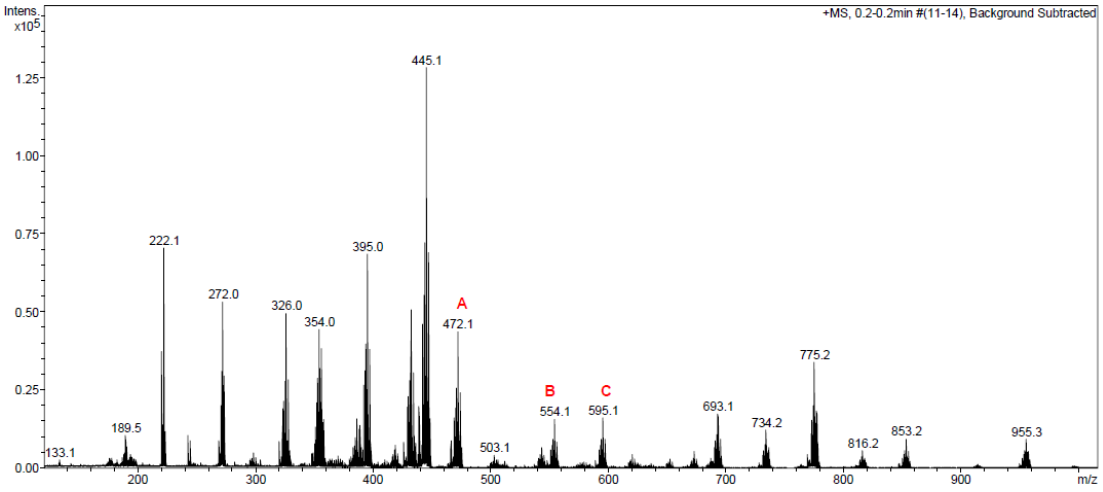
B

Chemical Formula: $C_{28}H_{25}N_3O_3Ru$
Exact Mass: 553.0939

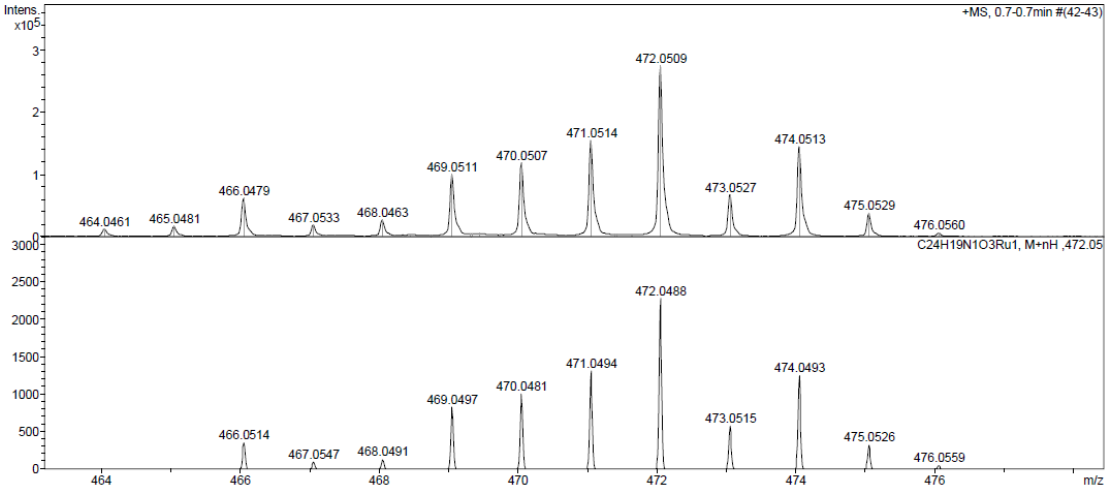


C

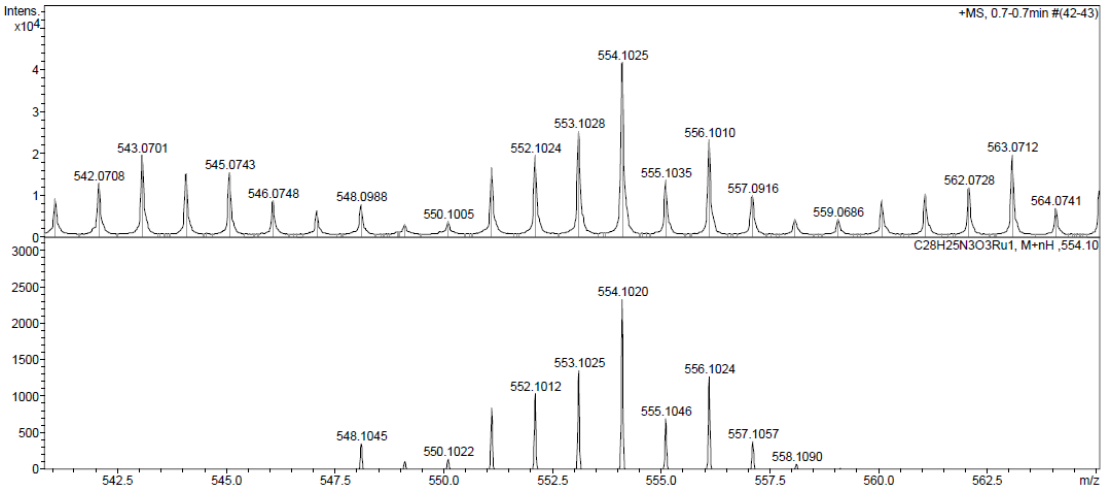
Chemical Formula: $C_{30}H_{28}N_4O_3Ru$
Exact Mass: 594.1205



ESI–HRMS analysis- A:



ESI–HRMS analysis- B:



ESI–HRMS analysis- C:

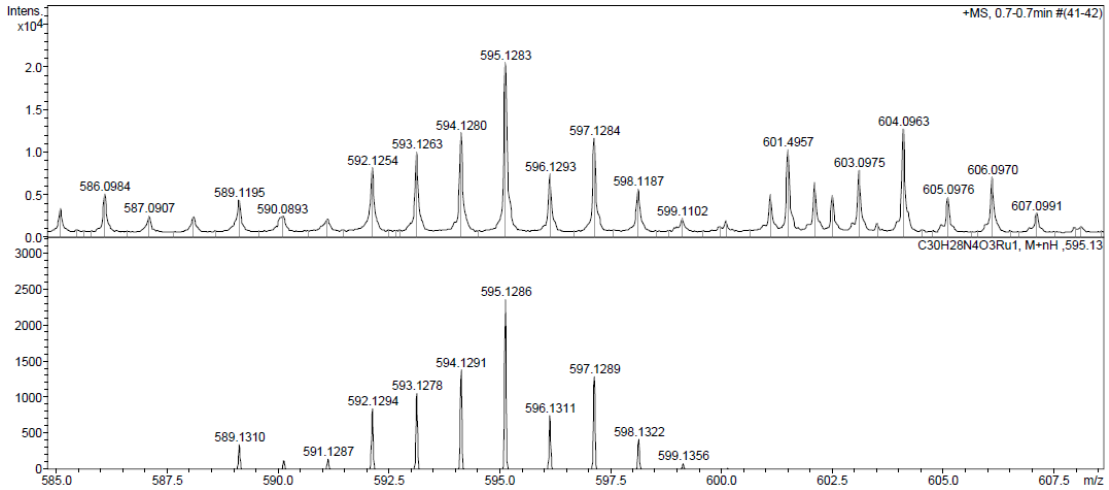


Fig. S8 Monitoring of the mixture solution of **7**and **2a** in DCE after CV studies using high resolution ESI-HRMS.

Computational Studies

All DFT calculations were performed with Gaussian 16, Revision A.03 package.[4] All structures were optimized at the PBE0[5] level of theory in combination with D3 dispersion corrections with a Becke-Johnson damping scheme (D3BJ)[6] in the gas phase. Analytical frequency calculations were carried out at the same level of theory to identify all stationary points as minima (zero imaginary frequencies) or as transition states (one imaginary frequency) and to provide thermal and non-thermal corrections to the Gibbs free energy at 373.15 K and 1 atm. All atoms were described with a def2-SVP basis set,[7] while ruthenium was described also with a SDD pseudopotential.[8] The electronic energy was then further refined by PW6B95[9] single-point calculations in combination with a standalone version of Grimme's D4 dispersion corrections,[10] with a def2-TZVP basis set in combination with a SDD pseudopotential for ruthenium.[8] Solvent effects were taken into account by the use of the implicit solvation model SMD[11] with a dielectric constant of ε = 8.93, which corresponds to dichloromethane, the solvent used in the experiments. All reported energies are based on gas-phase Gibbs free energies with def2-SVP basis set for which the electronic energies were corrected by PW6B95-D4 with a def2-TZVP basis set and solvent effects.

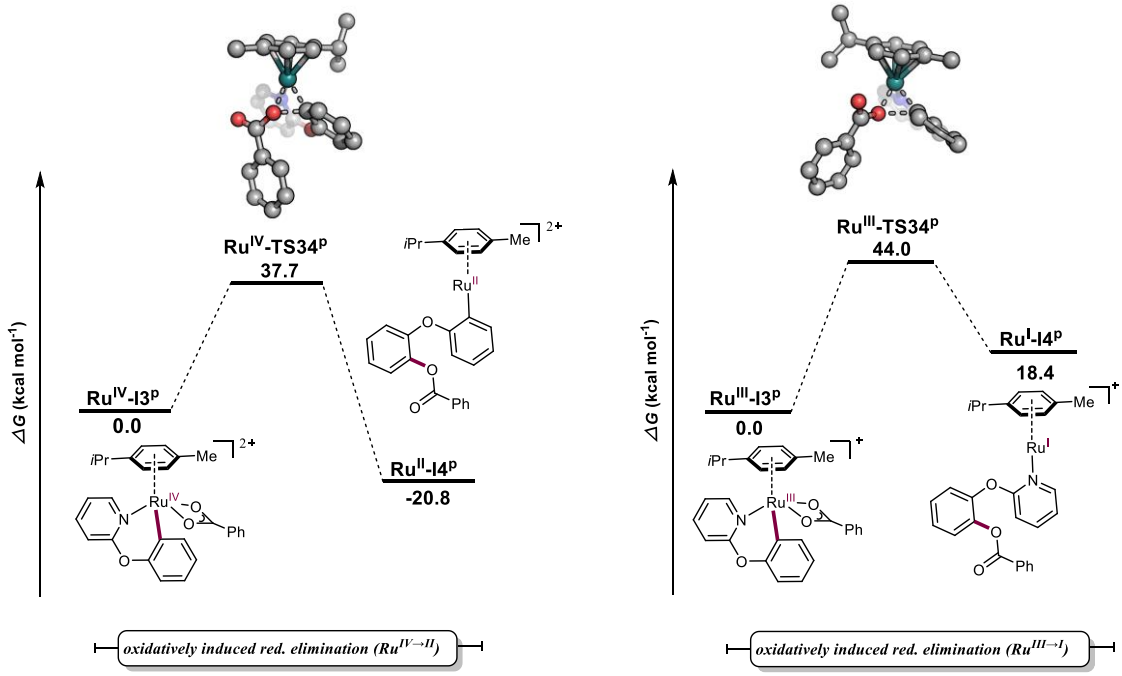


Fig. S9 Computed relative Gibbs free energy profile ($\Delta G_{373.15}$) in kcal mol^{-1} for two different oxidatively induced reductive elimination pathways for the *p*-cymene involved pathway at the PW6B95-D4/def2-TZVP+SMD(DCE)//PBE0-D3BJ/def2-SVP level of theory. Non-participating hydrogen atoms were omitted for clarity.

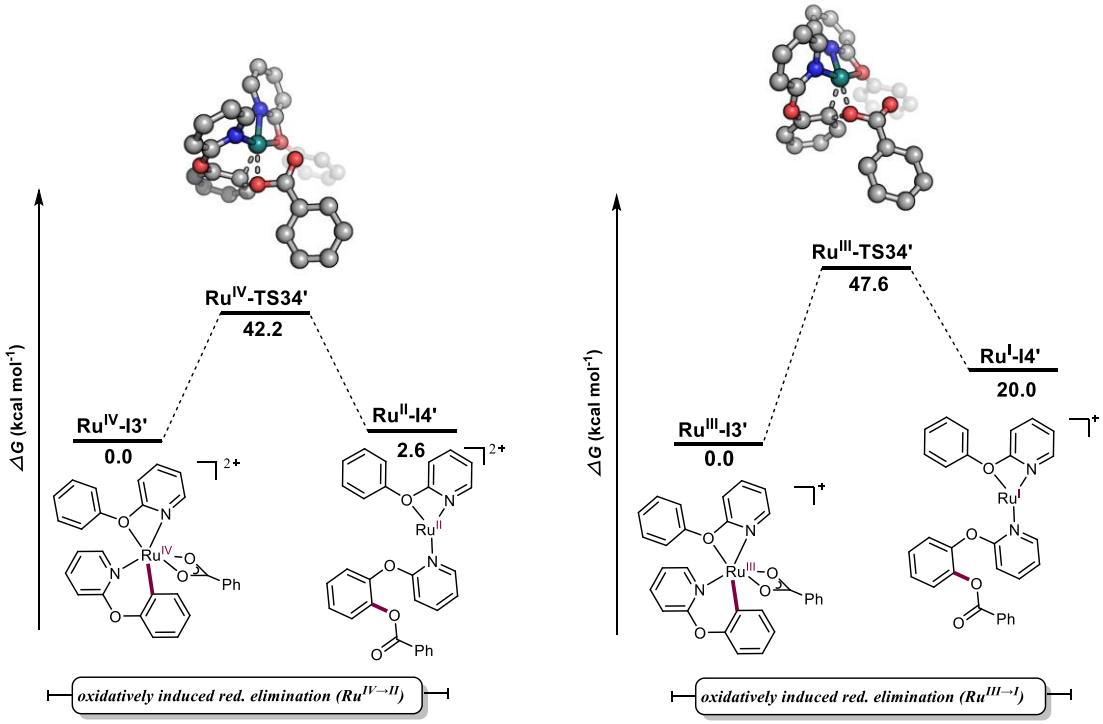


Fig. S10 Computed relative Gibbs free energy profile ($\Delta G_{373.15}$) in kcal mol^{-1} for two different oxidatively induced reductive elimination pathways for a monocyclommetalated ruthenium complex at the PW6B95-D4/def2-TZVP+SMD(DCE)//PBE0-D3BJ/def2-SVP level of theory. Non-participating hydrogen atoms were omitted for clarity.

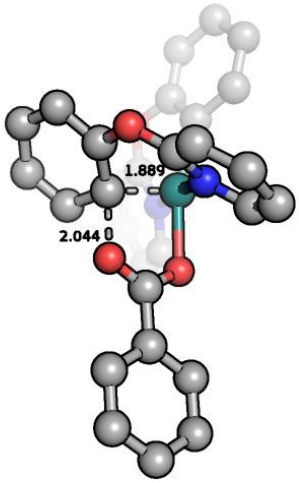


Fig. S11 Computed transition state structure for the reductive elimination step for the bis-cyclometalated pathway, Ru^{IV}-TS34. Nonrelevant hydrogens were omitted for clarity. Bond lengths in the transition stated are given in Å.

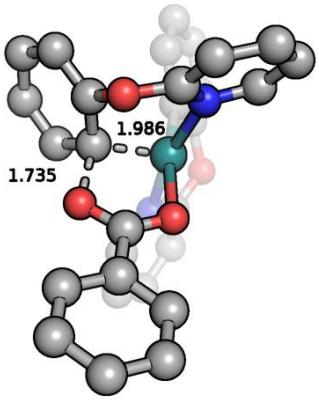


Fig. S12 Computed transition state structure for the reductive elimination step for the bis-cyclometalated pathway, Ru^{III}-TS34. Nonrelevant hydrogens were omitted for clarity. Bond lengths in the transition stated are given in Å.

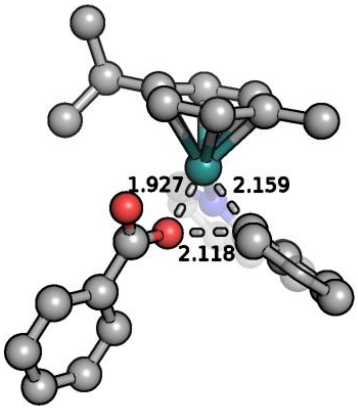


Fig. S13 Computed transition state structure for the reductive elimination step for the *p*-cymene involved pathway, Ru^{IV}-TS34^{p}. Nonrelevant hydrogens were omitted for clarity. Bond lengths in the transition stated are given in Å.

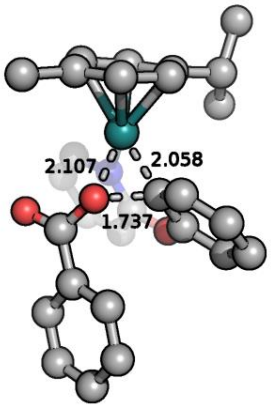


Fig. S14 Computed transition state structure for the reductive elimination step for the *p*-cymene involved pathway, Ru^{III}-TS34^{p}. Nonrelevant hydrogens were omitted for clarity. Bond lengths in the transition stated are given in Å.

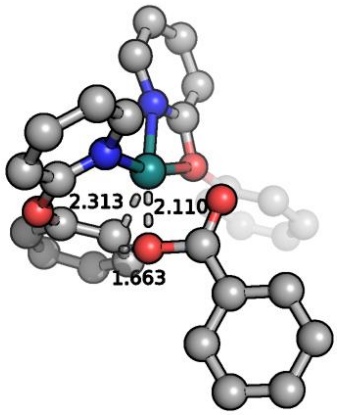


Fig. S15 Computed transition state structure for the reductive elimination step for the mono-cyclommetalated pathway, Ru^{IV}-TS34'. Nonrelevant hydrogens were omitted for clarity. Bond lengths in the transition stated are given in Å.

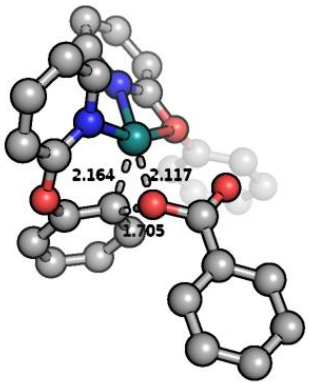


Fig. S16 Computed transition state structure for the reductive elimination step for the mono-cyclommetalated pathway, Ru^{III}-TS34'. Nonrelevant hydrogens were omitted for clarity. Bond lengths in the transition stated are given in Å.

Table S2 Calculated electronic energies at the PW6B95-D4/def2-TZVP+SMD(DCE) level of theory and Gibbs free energies with dispersion corrections for all structures in the present work (all in Hartree).

Structure	Electronic Energy	Total Gibbs Free Energy
Ru^{IV}-I3	-1625.608688	-1625.254712
Ru^{IV}-TS34	-1625.573717	-1625.219466
Ru^{II}-I4	-1625.620747	-1625.261452
Ru^{III}-I3	-1625.792708	-1625.443065
Ru^{III}-TS34	-1625.723547	-1625.372454
Ru^{I}-I4	-1625.725558	-1625.374966
Ru^{IV}-I3-1	-1460.658413	-1460.257026
Ru^{IV}-TS34-1	-1460.597642	-1460.196962
Ru^{II}-I4-1	-1460.695721	-1460.290099
Ru^{III}-I3-1	-1460.886366	-1460.487334
Ru^{III}-TS34-1	-1460.816509	-1460.417282
Ru^{I}-I4-1	-1460.857167	-1460.457940
Ru^{IV}-I3-2	-1626.004923	-1625.642628
Ru^{IV}-TS34-2	-1625.949147	-1625.589249
Ru^{II}-I4-2	-1626.001073	-1625.638510
Ru^{III}-I3-2	-1626.226669	-1625.867251
Ru^{III}-TS34-2	-1626.149374	-1625.791466
Ru^{I}-I4-2	-1626.198415	-1625.835451

Cartesian coordinates of the optimized structure

Ru^{IV}-I3

Lowest frequency = 17.9973 cm^{-1}

Charge = 1, Multiplicity = 1

57

O	-1.172423	0.678205	-0.902916
C	-2.033284	0.443094	0.031382
O	-1.586806	-0.055143	1.084374
C	-3.449225	0.764638	-0.191596
C	-4.371349	0.503405	0.829667
C	-3.873716	1.320455	-1.405403
C	-5.715738	0.798422	0.634512
H	-4.015430	0.069306	1.766105
C	-5.219763	1.613313	-1.593605
H	-3.141073	1.518388	-2.190160
C	-6.138408	1.352455	-0.575204
H	-6.439940	0.597176	1.426660
H	-5.557775	2.047540	-2.536819
H	-7.195465	1.583918	-0.726051
C	2.063754	-0.073157	-1.251377
C	2.602000	-1.304322	-1.711806
C	3.712052	-1.357261	-2.535833
H	2.142441	-2.236484	-1.382869
C	3.817912	1.060061	-2.537638
C	4.310529	-0.165154	-2.963365
H	4.114465	-2.320610	-2.854660
H	4.275169	2.000550	-2.849307
H	5.176128	-0.193411	-3.629095
C	0.186397	2.423302	1.477022
C	1.626483	2.770000	-0.290997
C	0.186460	3.761219	1.810089
H	-0.403675	1.692464	2.032489
C	1.676133	4.145081	-0.024463
H	-0.405312	4.105178	2.658747
H	2.295595	4.772570	-0.665326
N	0.896539	1.923778	0.435475
C	0.948091	4.644797	1.036798
H	0.972264	5.712175	1.266161

C	2.723960	1.103848	-1.671239
O	2.359785	2.369017	-1.331678
Ru	0.510696	-0.048877	-0.080697
C	2.030045	-0.041394	2.433655
C	0.652279	-1.999138	2.117194
C	2.535371	-0.578587	3.608004
H	2.394939	0.928007	2.096527
C	1.130799	-2.524159	3.318198
C	2.068800	-1.817280	4.058433
H	3.286022	-0.029678	4.179835
H	0.757028	-3.495790	3.645495
H	2.442700	-2.238002	4.994425
O	-0.265823	-2.793854	1.503745
C	-0.575907	-2.849783	0.210524
C	-1.331911	-3.964483	-0.178478
C	-0.544921	-2.052594	-1.956365
C	-1.686047	-4.099808	-1.505781
H	-1.610615	-4.690449	0.585292
C	-1.278294	-3.122319	-2.421965
H	-0.217807	-1.253431	-2.623401
H	-2.273583	-4.960483	-1.832192
H	-1.533240	-3.185520	-3.480020
N	-0.193673	-1.910448	-0.655846
C	1.092267	-0.746644	1.646843

Ru^{IV}-TS34

Lowest frequency = -175.9808 cm^{-1}

Charge = 1, Multiplicity = 1

57

O	-1.924045	-0.079810	1.318869
C	-2.321611	0.364858	0.217493
O	-1.543227	0.602911	-0.774280
C	-3.767672	0.641533	0.031087
C	-4.252303	1.048381	-1.218046
C	-4.647997	0.488928	1.109202
C	-5.609616	1.300988	-1.385599
H	-3.554084	1.160659	-2.049106
C	-6.003920	0.746067	0.937362
H	-4.251598	0.170121	2.074675
C	-6.484606	1.151099	-0.308540

H	-5.989983	1.617563	-2.359199
H	-6.691533	0.630530	1.777892
H	-7.550274	1.351770	-0.441668
C	0.113532	0.079476	1.329974
C	0.276553	1.341394	2.005785
C	1.121800	1.456924	3.071752
H	-0.261017	2.207159	1.615086
C	1.596927	-0.936123	3.004612
C	1.804953	0.308613	3.554860
H	1.280070	2.424838	3.550563
H	2.089047	-1.829798	3.391191
H	2.494218	0.409613	4.396489
C	-1.159152	-2.306870	-1.544890
C	-0.308524	-2.729615	0.549697
C	-1.779871	-3.540442	-1.590648
H	-1.246328	-1.591117	-2.365886
C	-0.897645	-3.991759	0.596335
H	-2.364293	-3.820519	-2.467481
H	-0.764351	-4.606660	1.486482
N	-0.413242	-1.910019	-0.493004
C	-1.642117	-4.401870	-0.497115
H	-2.122307	-5.382453	-0.497126
C	0.691648	-1.083393	1.937943
O	0.440791	-2.354323	1.599243
Ru	0.431526	-0.041025	-0.528033
C	2.604416	-1.933938	-1.385676
C	3.407603	0.105053	-0.437889
C	3.912156	-2.392501	-1.515637
H	1.788591	-2.578879	-1.722482
C	4.722821	-0.344627	-0.531199
C	4.973403	-1.600289	-1.073569
H	4.105564	-3.374575	-1.952610
H	5.531330	0.304536	-0.189785
H	6.002001	-1.956272	-1.162128
O	3.266635	1.365808	0.113145
C	2.382100	2.262576	-0.317559
C	2.785360	3.604052	-0.284948
C	0.310673	2.857914	-1.161233
C	1.906629	4.579361	-0.715836
H	3.792778	3.829790	0.064977
C	0.641739	4.196864	-1.178268
H	-0.674840	2.503041	-1.468608
H	2.204093	5.630231	-0.707819

H	-0.081827	4.928680	-1.538658
N	1.158609	1.898044	-0.721473
C	2.312520	-0.675331	-0.825419

Ru^{IV}-I4

Lowest frequency = 20.5451 cm^{-1}

Charge = 1, Multiplicity = 1

57

O	1.710330	-0.540061	1.202579
C	2.230947	-0.769364	0.004049
O	1.499933	-0.830150	-0.987702
C	3.684110	-0.906797	-0.035671
C	4.307189	-1.070005	-1.282223
C	4.447500	-0.875570	1.141364
C	5.687780	-1.201573	-1.348530
H	3.694543	-1.092278	-2.185297
C	5.828575	-1.007359	1.064983
H	3.951693	-0.749858	2.105047
C	6.446548	-1.170062	-0.176281
H	6.178717	-1.330273	-2.315185
H	6.428960	-0.985428	1.976578
H	7.532695	-1.274575	-0.230999
C	0.296279	-0.620806	1.283065
C	-0.188126	-1.865982	1.824346
C	-1.385778	-1.908541	2.470398
H	0.439268	-2.753454	1.719920
C	-1.681969	0.496263	2.285315
C	-2.141222	-0.713514	2.700819
H	-1.753771	-2.857427	2.866098
H	-2.191809	1.427991	2.535406
H	-3.075343	-0.773240	3.262155
C	1.391986	2.279373	-1.514951
C	0.883833	2.344666	0.743228
C	2.217569	3.381948	-1.404747
H	1.236429	1.765563	-2.466843
C	1.700461	3.457550	0.948516
H	2.733414	3.766735	-2.284636
H	1.790251	3.875896	1.950955
N	0.725928	1.776986	-0.458001
C	2.368229	3.979951	-0.147370

H	3.014103	4.852168	-0.025329
C	-0.458598	0.597340	1.518373
O	0.212504	1.806054	1.751425
Ru	-0.479395	0.111656	-0.515452
C	-2.239794	2.509214	-0.669098
C	-3.455707	0.495899	-0.297071
C	-3.431714	3.223126	-0.748270
H	-1.305220	3.059714	-0.786474
C	-4.661185	1.195464	-0.348409
C	-4.649804	2.565098	-0.577226
H	-3.408898	4.299422	-0.932228
H	-5.593527	0.644465	-0.212287
H	-5.590905	3.116869	-0.623497
O	-3.617178	-0.846717	-0.033523
C	-2.837047	-1.835075	-0.440489
C	-3.433571	-3.107877	-0.447273
C	-0.860605	-2.716479	-1.245045
C	-2.701455	-4.191296	-0.882724
H	-4.471342	-3.187098	-0.123225
C	-1.381618	-3.989189	-1.309583
H	0.170715	-2.511972	-1.535940
H	-3.150954	-5.186392	-0.905812
H	-0.765576	-4.809645	-1.678306
N	-1.564017	-1.643833	-0.802189
C	-2.207502	1.114411	-0.454678

Ru^{III}-I3

Lowest frequency = 16.2939 cm^{-1}

Charge = 0, Multiplicity = 2

57

O	-1.543372	-0.378901	1.024856
C	-2.178234	0.000011	-0.000008
O	-1.543298	0.378897	-1.024845
C	-3.665312	0.000056	-0.000052
C	-4.364630	0.424428	-1.134235
C	-4.364718	-0.424268	1.134095
C	-5.756472	0.423995	-1.133020
H	-3.793962	0.751425	-2.005675
C	-5.756560	-0.423745	1.132806
H	-3.794116	-0.751295	2.005566

C	-6.452729	0.000147	-0.000126
H	-6.303834	0.755850	-2.018592
H	-6.303990	-0.755562	2.018350
H	-7.545713	0.000183	-0.000155
C	1.736356	-0.504767	1.387556
C	2.660380	0.394104	1.961096
C	3.512651	0.027666	2.997270
H	2.711548	1.412024	1.567612
C	2.575074	-2.190930	2.964872
C	3.460594	-1.269642	3.512085
H	4.217438	0.754231	3.409037
H	2.515961	-3.217425	3.332221
H	4.116034	-1.568258	4.333534
C	-0.144347	-2.204006	-1.863267
C	0.483667	-2.987644	0.217794
C	-0.441418	-3.474276	-2.317101
H	-0.279043	-1.320372	-2.488742
C	0.196247	-4.306507	-0.162961
H	-0.805245	-3.613921	-3.335342
H	0.361961	-5.098859	0.566924
N	0.302293	-1.956957	-0.612865
C	-0.273105	-4.550355	-1.439984
H	-0.500367	-5.570864	-1.756156
C	1.746623	-1.806000	1.909922
O	0.920511	-2.822586	1.463891
Ru	0.405931	-0.000042	-0.000050
C	2.660600	-0.394113	-1.960882
C	1.746906	1.805996	-1.909817
C	3.513039	-0.027694	-2.996938
H	2.711689	-1.412041	-1.567404
C	2.575508	2.190915	-2.964646
C	3.461087	1.269611	-3.511752
H	4.217863	-0.754277	-3.408607
H	2.516467	3.217415	-3.331994
H	4.116644	1.568219	-4.333110
O	0.920755	2.822590	-1.463882
C	0.483814	2.987625	-0.217842
C	0.196407	4.306484	0.162937
C	-0.144447	2.203941	1.863135
C	-0.273072	4.550306	1.439922
H	0.362231	5.098855	-0.566902
C	-0.441523	3.474207	2.316984
H	-0.279266	1.320296	2.488567

H	-0.500324	5.570815	1.756103
H	-0.805463	3.613823	3.335188
C	1.736523	0.504763	-1.387483
N	0.302324	1.956918	0.612790

Ru^{III}-TS34

Lowest frequency = -301.7347 cm^{-1}

Charge = 0, Multiplicity = 2

57

O	-1.537777	0.278051	-0.876764
C	-2.278987	0.331066	0.125787
O	-1.837990	0.289695	1.325428
C	-3.747085	0.476593	-0.043664
C	-4.595506	0.463929	1.068885
C	-4.279287	0.625961	-1.328957
C	-5.969348	0.600797	0.893891
H	-4.158028	0.343244	2.061383
C	-5.652979	0.763882	-1.499163
H	-3.595964	0.629247	-2.180120
C	-6.498278	0.751432	-0.388469
H	-6.632936	0.588870	1.761645
H	-6.069516	0.881032	-2.502334
H	-7.577397	0.859119	-0.523694
C	2.541877	-0.145419	-0.170294
C	3.195347	-1.258946	0.395737
C	4.583650	-1.367689	0.435892
H	2.586063	-2.058895	0.826404
C	4.776824	0.767017	-0.657824
C	5.382054	-0.356324	-0.101874
H	5.048207	-2.248374	0.887546
H	5.363372	1.586654	-1.078732
H	6.471499	-0.435597	-0.081696
C	-0.209713	2.904499	0.216169
C	1.857447	2.712087	-0.788119
C	-0.202424	4.281754	0.108489
H	-1.037019	2.385870	0.700110
C	1.936224	4.103681	-0.943210
H	-1.044006	4.856656	0.496375
H	2.835145	4.512955	-1.404467
N	0.785754	2.112545	-0.242752

C	0.895127	4.897637	-0.499342
H	0.942515	5.983382	-0.608124
C	3.385866	0.850506	-0.668426
O	2.886934	2.013984	-1.263285
Ru	0.552702	0.050043	-0.371167
C	0.497936	0.511676	2.439226
C	-0.289245	-1.663882	1.722028
C	1.139807	-0.097005	3.504489
H	0.557715	1.593424	2.321082
C	0.339863	-2.262603	2.791226
C	1.072969	-1.481911	3.696271
H	1.713500	0.520001	4.200168
H	0.263529	-3.346600	2.902226
H	1.581574	-1.953041	4.539101
O	-1.039392	-2.461367	0.872221
C	-0.551495	-2.762718	-0.336538
C	-0.981196	-3.949332	-0.938971
C	0.878227	-2.313582	-2.085974
C	-0.437022	-4.307181	-2.160715
H	-1.713351	-4.563108	-0.413764
C	0.532646	-3.481596	-2.739774
H	1.624408	-1.626434	-2.492845
H	-0.746885	-5.232941	-2.650404
H	1.011971	-3.736489	-3.685413
C	-0.195094	-0.256933	1.443138
N	0.316141	-1.930850	-0.920588

Ru^{III}-I4

Lowest frequency = 16.7311 cm^{-1}

Charge = 0, Multiplicity = 2

57

O	-1.592789	0.244338	-0.900097
C	-2.311420	0.283922	0.097865
O	-1.824263	0.250371	1.313986
C	-3.777896	0.416987	0.016615
C	-4.572641	0.393720	1.169351
C	-4.369819	0.566757	-1.243519
C	-5.953389	0.522246	1.057332
H	-4.094631	0.271264	2.142392
C	-5.750012	0.694724	-1.348470

H	-3.727573	0.578927	-2.126139
C	-6.541781	0.673012	-0.198824
H	-6.575889	0.502787	1.954635
H	-6.213692	0.811860	-2.330482
H	-7.626662	0.773333	-0.283079
C	2.512807	-0.176311	-0.140231
C	3.125394	-1.344714	0.364433
C	4.507115	-1.495860	0.464784
H	2.486031	-2.168356	0.688984
C	4.798407	0.703516	-0.451888
C	5.354750	-0.467896	0.052392
H	4.925032	-2.423711	0.865068
H	5.420633	1.535818	-0.788348
H	6.439936	-0.572911	0.122719
C	-0.269608	2.926835	-0.065330
C	1.903422	2.712787	-0.787503
C	-0.264438	4.296588	-0.232103
H	-1.153200	2.429023	0.329927
C	1.987294	4.100600	-0.996701
H	-1.153623	4.874410	0.022389
H	2.935072	4.498392	-1.359883
N	0.776746	2.119366	-0.358217
C	0.896520	4.901682	-0.725225
H	0.950016	5.981928	-0.876626
C	3.411607	0.823778	-0.530051
O	3.001674	2.034234	-1.086701
Ru	0.536345	0.048961	-0.395044
C	0.327429	0.716539	2.372783
C	-0.239228	-1.542185	1.697082
C	1.255551	0.193559	3.256661
H	0.151930	1.792276	2.330040
C	0.670319	-2.055678	2.596608
C	1.441991	-1.187998	3.379801
H	1.845696	0.877437	3.870684
H	0.784864	-3.139955	2.662636
H	2.172901	-1.589288	4.083373
O	-1.025350	-2.402622	0.945586
C	-0.549146	-2.774200	-0.255119
C	-0.962241	-3.999793	-0.780701
C	0.836634	-2.384170	-2.051047
C	-0.433616	-4.410008	-1.994711
H	-1.668164	-4.601990	-0.208167
C	0.502922	-3.593291	-2.635368

H	1.559138	-1.704742	-2.508785
H	-0.730796	-5.367092	-2.428823
H	0.968461	-3.886265	-3.576986
C	-0.410985	-0.129748	1.475620
N	0.291184	-1.952280	-0.895070

Ru^{IV}-I3-1

Lowest frequency = 20.1058 cm^{-1}

Charge = 2, Multiplicity = 1

60

Ru	0.549563	-0.420503	-0.109100
C	0.899131	-1.892272	-1.903011
C	2.192064	-1.743224	-1.309325
C	2.281448	-1.904148	0.087512
C	1.156451	-2.343953	0.836648
C	-0.075795	-2.671627	0.218720
C	-0.200604	-2.353218	-1.165609
C	3.376055	-1.388562	-2.132704
C	-1.211302	-3.256472	1.007209
C	-2.556537	-2.572192	0.787676
O	-1.097379	0.483977	0.042290
C	-2.058431	0.371590	-0.925596
C	-1.264990	-4.753338	0.647002
O	-1.812735	-0.189651	-1.969045
H	3.114032	-0.730942	-2.972004
H	3.772830	-2.325411	-2.562718
H	4.175487	-0.931303	-1.536063
H	3.221934	-1.700283	0.603389
H	1.255833	-2.454190	1.919836
H	-1.160527	-2.458800	-1.671472
H	0.762105	-1.663585	-2.962093
H	-0.942924	-3.175029	2.073232
H	-2.026150	-5.242955	1.271827
H	-0.304683	-5.258223	0.824564
H	-1.548225	-4.900379	-0.406528
H	-2.534523	-1.514573	1.088023
H	-3.322725	-3.072563	1.395682
H	-2.891571	-2.627748	-0.258931
C	-3.327840	1.007444	-0.563938
C	-4.385851	0.925506	-1.485547

C	-3.504437	1.686345	0.656288
C	-5.610627	1.500382	-1.180164
H	-4.226867	0.404306	-2.431412
C	-4.732812	2.261229	0.953254
H	-2.670968	1.775360	1.353713
C	-5.784242	2.167082	0.038303
H	-6.438021	1.434821	-1.889524
H	-4.875904	2.794089	1.895255
H	-6.748995	2.623107	0.272881
C	1.660606	0.895702	-1.047734
C	1.283038	1.271094	-2.350739
C	1.909735	2.352709	-2.952820
H	0.463827	0.754153	-2.859261
C	3.375795	2.610249	-1.024253
C	2.971444	2.999055	-2.301596
H	1.587988	2.686049	-3.941675
H	4.188333	3.117870	-0.500543
H	3.491757	3.820666	-2.799787
C	0.091186	0.603489	2.621192
C	2.215059	1.124928	1.854072
C	0.393739	1.050488	3.891517
H	-0.895587	0.215486	2.367091
C	2.602656	1.579718	3.113519
H	-0.368306	1.016022	4.671290
H	3.610963	1.976908	3.237475
N	1.000032	0.616602	1.619022
C	1.681041	1.534780	4.147038
H	1.954759	1.892547	5.142344
C	2.712500	1.562734	-0.399319
O	3.115645	1.202848	0.856390

Ru^{IV}-TS34-1

Lowest frequency = -270.8608 cm^{-1}

Charge = 2, Multiplicity = 1

60

Ru	-0.957056	0.132118	-0.160032
C	-1.621188	0.644884	-2.221874
C	-2.494263	-0.383075	-1.741898
C	-3.143591	-0.166683	-0.504837
C	-2.934076	1.030172	0.215560

C	-2.124535	2.089640	-0.294308
C	-1.440013	1.848939	-1.519582
C	-2.717046	-1.636571	-2.514077
C	-1.938471	3.368376	0.467057
C	-0.469699	3.747522	0.654918
O	0.962473	0.129803	0.009515
C	1.807445	0.899767	-0.767521
C	-2.726537	4.468614	-0.263379
O	1.390349	1.467699	-1.745403
H	-1.861677	-1.887085	-3.152694
H	-3.590973	-1.476564	-3.168651
H	-2.944040	-2.486714	-1.857751
H	-3.760472	-0.957679	-0.072353
H	-3.404066	1.144915	1.195641
H	-0.728622	2.578439	-1.906878
H	-1.059761	0.483448	-3.142958
H	-2.398340	3.227572	1.459569
H	-2.671912	5.398432	0.321201
H	-3.787166	4.206040	-0.384313
H	-2.301137	4.670502	-1.258313
H	0.097258	2.961328	1.177968
H	-0.402982	4.664207	1.257330
H	0.032610	3.951234	-0.302318
C	3.167295	0.937835	-0.233166
C	4.074776	1.835926	-0.824120
C	3.575646	0.111613	0.832946
C	5.378368	1.898470	-0.357751
H	3.739694	2.465790	-1.650327
C	4.883658	0.180535	1.291054
H	2.866748	-0.583457	1.283288
C	5.781972	1.072616	0.699685
H	6.091677	2.586065	-0.816510
H	5.212471	-0.461490	2.110388
H	6.810876	1.125613	1.063629
C	0.122511	-1.568529	-0.936369
C	0.682166	-1.541278	-2.216134
C	1.025214	-2.730755	-2.842321
H	0.848901	-0.587992	-2.720818
C	0.389622	-3.953535	-0.855664
C	0.870404	-3.942650	-2.155964
H	1.433190	-2.710485	-3.854842
H	0.266066	-4.883234	-0.295068
H	1.160038	-4.883151	-2.629704

C	-1.076944	0.128962	2.748447
C	-0.589659	-2.008616	2.014048
C	-1.083567	-0.265208	4.066992
H	-1.229866	1.175080	2.478775
C	-0.592529	-2.491759	3.330289
H	-1.262102	0.471635	4.851190
H	-0.388172	-3.551129	3.490505
N	-0.849774	-0.731465	1.721065
C	-0.844039	-1.614485	4.364827
H	-0.844893	-1.966932	5.398791
C	0.069397	-2.757495	-0.199997
O	-0.360122	-2.920841	1.073139

Ru^{IV}-I4-1

Lowest frequency = 18.5551 cm^{-1}

Charge = 2, Multiplicity = 1

60

Ru	-1.100080	0.263540	0.241148
C	-2.356255	1.412669	-1.182804
C	-3.201342	0.872236	-0.174564
C	-2.839660	1.101961	1.182893
C	-1.736148	1.934257	1.504770
C	-0.878267	2.459569	0.511265
C	-1.202036	2.145093	-0.849224
C	-4.419177	0.089794	-0.516003
C	0.306466	3.322659	0.865558
C	1.609963	2.852933	0.229658
O	0.625512	-0.754441	-0.838861
C	1.512362	0.014044	-1.712204
C	-0.027085	4.772022	0.494537
O	1.024798	0.712126	-2.542071
H	-4.344372	-0.388112	-1.499990
H	-5.266665	0.795924	-0.554437
H	-4.651681	-0.666297	0.244677
H	-3.422390	0.640405	1.982876
H	-1.487719	2.086245	2.558041
H	-0.517672	2.436429	-1.649202
H	-2.549703	1.169511	-2.229124
H	0.419156	3.276978	1.962354
H	0.785698	5.436222	0.821338

H	-0.956172	5.115164	0.972132
H	-0.136363	4.889586	-0.594991
H	1.860561	1.820790	0.519871
H	2.437121	3.497988	0.557536
H	1.578054	2.907980	-0.869069
C	2.899061	-0.191497	-1.346312
C	3.857338	0.548525	-2.065236
C	3.301810	-1.081513	-0.333267
C	5.203575	0.401662	-1.766176
H	3.528791	1.226794	-2.855323
C	4.651645	-1.219233	-0.043332
H	2.561772	-1.668036	0.211341
C	5.599491	-0.479817	-0.756526
H	5.951694	0.969602	-2.322563
H	4.975327	-1.912654	0.735166
H	6.661185	-0.596969	-0.526468
C	-0.529858	-1.344628	-1.279471
C	-1.025971	-1.317277	-2.600292
C	-2.210960	-1.966253	-2.877425
H	-0.472348	-0.793043	-3.377891
C	-2.447176	-2.700546	-0.587509
C	-2.943108	-2.629393	-1.867366
H	-2.583576	-1.971505	-3.904595
H	-2.926338	-3.309349	0.182230
H	-3.875396	-3.139530	-2.118694
C	0.564833	0.025521	2.779340
C	0.073043	-1.983666	1.748625
C	1.346435	-0.600962	3.724661
H	0.454684	1.108250	2.774758
C	0.846879	-2.698976	2.664846
H	1.843957	-0.008541	4.493403
H	0.917550	-3.782615	2.562609
N	-0.082427	-0.654608	1.800445
C	1.484819	-1.994741	3.669496
H	2.093040	-2.522530	4.407799
C	-1.219608	-2.072251	-0.253695
O	-0.553324	-2.665853	0.795576

Ru^{III}-I3-1

Lowest frequency = 22.3104 cm^{-1}

Charge = 1, Multiplicity = 2

60

Ru	0.270046	0.222501	-0.466109
C	1.080039	0.271506	-2.579289
C	0.038251	1.216410	-2.666132
C	-0.036416	2.134675	-1.582251
C	1.037640	2.302579	-0.670865
C	2.229035	1.530669	-0.790820
C	2.169505	0.427871	-1.668920
C	-1.008758	1.160027	-3.721268
C	3.438951	1.862232	0.043638
C	4.552252	0.828231	-0.034389
O	-1.384252	0.472894	0.738133
C	-2.374771	0.288888	-0.050945
C	3.946767	3.248557	-0.375540
O	-2.149871	-0.004301	-1.247275
H	-2.003867	1.330838	-3.291942
H	-1.010970	0.190210	-4.234841
H	-0.809341	1.943794	-4.470710
H	-0.920950	2.766745	-1.475732
H	0.966095	3.070926	0.101042
H	2.990046	-0.287953	-1.702310
H	1.096488	-0.575803	-3.268809
H	3.089712	1.927840	1.088312
H	4.803941	3.532265	0.251570
H	3.179334	4.028216	-0.263796
H	4.282457	3.247548	-1.424031
H	4.210936	-0.177391	0.245728
H	5.361115	1.105060	0.655845
H	4.988487	0.781898	-1.044962
C	-3.743421	0.427559	0.484962
C	-4.836238	0.264325	-0.375016
C	-3.950229	0.718470	1.839295
C	-6.129921	0.395309	0.117835
H	-4.652910	0.034346	-1.426370
C	-5.246122	0.846857	2.327218
H	-3.086666	0.836070	2.496277
C	-6.334084	0.686544	1.467534
H	-6.984819	0.269602	-0.549988
H	-5.412334	1.071684	3.382894
H	-7.351098	0.788236	1.853573
C	1.167067	0.052375	1.331629

C	0.922721	0.977647	2.353294
C	1.600726	0.890283	3.566145
H	0.182710	1.765647	2.198935
C	2.764171	-1.074812	2.784907
C	2.533504	-0.128579	3.777360
H	1.399458	1.620052	4.353369
H	3.469870	-1.895905	2.924092
H	3.072228	-0.194636	4.724776
C	-0.766497	-2.554605	-0.965103
C	1.321275	-2.565936	0.028812
C	-0.726300	-3.921292	-1.167670
H	-1.615911	-1.946097	-1.279508
C	1.441871	-3.944561	-0.155602
H	-1.575519	-4.416186	-1.639856
H	2.345255	-4.435049	0.207221
N	0.251659	-1.875549	-0.388921
C	0.406801	-4.631356	-0.766163
H	0.473659	-5.711430	-0.913698
C	2.069094	-0.974204	1.581747
O	2.342559	-1.936813	0.625108

Ru^{III}-TS34-1

Lowest frequency = -292.2507 cm^{-1}

Charge = 1, Multiplicity = 2

60

Ru	-1.153009	-0.071432	0.556402
C	-2.786349	-1.406987	1.366474
C	-2.362613	-0.496802	2.360359
C	-2.397664	0.902374	2.049114
C	-2.774207	1.351473	0.767169
C	-3.100549	0.439441	-0.280550
C	-3.082679	-0.940291	0.057538
C	-1.881164	-0.961691	3.695581
C	-3.460999	0.934031	-1.661949
C	-2.750569	0.176675	-2.777937
O	0.767265	0.286866	1.346699
C	1.755267	-0.653813	1.358261
C	-4.981173	0.909464	-1.830207
O	1.499607	-1.772592	1.719373
H	-1.512206	-1.994241	3.650652

H	-2.706287	-0.916252	4.424512
H	-1.068610	-0.320939	4.063456
H	-2.065020	1.622064	2.799649
H	-2.713083	2.417976	0.536394
H	-3.254592	-1.675785	-0.731896
H	-2.777326	-2.477589	1.578692
H	-3.127063	1.984300	-1.708776
H	-5.269172	1.345949	-2.797783
H	-5.486713	1.480016	-1.037121
H	-5.364961	-0.122704	-1.799774
H	-1.658188	0.236484	-2.666365
H	-3.016833	0.606145	-3.754365
H	-3.037059	-0.886319	-2.806467
C	3.086560	-0.193158	0.910815
C	4.033514	-1.175268	0.587948
C	3.422089	1.162988	0.808019
C	5.295489	-0.803026	0.141317
H	3.756185	-2.225907	0.695129
C	4.691253	1.529707	0.371519
H	2.698182	1.929297	1.089031
C	5.623954	0.549727	0.031889
H	6.031531	-1.567658	-0.115963
H	4.956904	2.586534	0.300885
H	6.618553	0.841849	-0.313143
C	0.261859	1.338530	0.059902
C	0.195155	2.636125	0.677703
C	0.633178	3.770894	0.042045
H	-0.209387	2.689668	1.689539
C	1.353527	2.436987	-1.846684
C	1.218726	3.678769	-1.238697
H	0.542991	4.740831	0.535227
H	1.791728	2.333495	-2.840983
H	1.578895	4.574483	-1.747657
C	-0.357170	-2.740922	-0.488489
C	0.781796	-1.110825	-1.636692
C	0.238338	-3.750953	-1.210412
H	-1.045428	-2.967300	0.321916
C	1.435327	-2.074450	-2.419569
H	-0.001062	-4.789669	-0.982000
H	2.153179	-1.728029	-3.162845
N	-0.118173	-1.423587	-0.701896
C	1.158194	-3.408193	-2.208148
H	1.659578	-4.177501	-2.799030

C	0.922159	1.279208	-1.204681
O	1.115301	0.146830	-1.925971

Ru^{III}-I4-1

Lowest frequency = 14.9643 cm^{-1}

Charge = 1, Multiplicity = 2

60

Ru	-1.122024	-0.420671	0.627034
C	-2.955215	-1.431916	1.246767
C	-2.193455	-1.239049	2.426122
C	-1.717254	0.082586	2.654578
C	-2.063179	1.173655	1.809706
C	-2.835971	0.992495	0.638325
C	-3.237946	-0.349537	0.360486
C	-1.853935	-2.364411	3.348936
C	-3.190872	2.145667	-0.269181
C	-2.832079	1.879275	-1.727718
O	0.945306	0.392955	0.908249
C	1.901559	-0.641884	1.025761
C	-4.666386	2.510258	-0.100057
O	1.455645	-1.729243	1.232813
H	-1.876850	-3.330156	2.826450
H	-2.578381	-2.408984	4.178412
H	-0.853179	-2.232321	3.782304
H	-1.034522	0.260100	3.488736
H	-1.650531	2.161660	2.026266
H	-3.775978	-0.558322	-0.567626
H	-3.289785	-2.440350	0.989470
H	-2.585379	3.003310	0.069880
H	-4.918260	3.396826	-0.700873
H	-4.910550	2.729676	0.949696
H	-5.317737	1.685762	-0.431364
H	-1.762428	1.645464	-1.833628
H	-3.054500	2.762916	-2.343747
H	-3.410162	1.040024	-2.145999
C	3.315203	-0.262732	0.926271
C	4.220536	-1.284049	0.602457
C	3.781078	1.033562	1.185310
C	5.577297	-1.002522	0.512521
H	3.840373	-2.291250	0.422260

C	5.142731	1.304104	1.107694
H	3.089434	1.826057	1.470165
C	6.038020	0.291187	0.763702
H	6.282147	-1.794481	0.251605
H	5.509098	2.310196	1.320875
H	7.106224	0.510313	0.697995
C	1.022693	1.378097	-0.064760
C	0.841863	2.717009	0.254172
C	0.801690	3.651156	-0.779348
H	0.724791	3.010861	1.298735
C	1.137679	1.899072	-2.417025
C	0.946678	3.245185	-2.106896
H	0.660116	4.707806	-0.544419
H	1.267496	1.562984	-3.447402
H	0.920035	3.984497	-2.909493
C	-1.570620	-2.266799	-1.713982
C	0.444852	-1.220845	-2.000777
C	-1.384092	-3.056635	-2.832692
H	-2.474970	-2.369615	-1.118736
C	0.720629	-1.977883	-3.139165
H	-2.153411	-3.775289	-3.117339
H	1.663385	-1.801842	-3.657572
N	-0.671921	-1.357708	-1.272475
C	-0.204678	-2.916218	-3.564238
H	-0.014504	-3.522835	-4.452020
C	1.168025	0.967815	-1.387431
O	1.416729	-0.363636	-1.608817

Ru^{IV}-I3-2

Lowest frequency = 16.3406 cm^{-1}

Charge = 2, Multiplicity = 1

58

O	1.375502	-0.770918	0.813215
C	1.130980	-1.638523	-0.079839
O	0.330278	-1.187638	-0.990983
C	1.661197	-2.982668	-0.096085
C	1.350922	-3.847137	-1.160615
C	2.486627	-3.409308	0.958499
C	1.867639	-5.134994	-1.164683
H	0.713114	-3.499253	-1.975937

C	2.995869	-4.700185	0.944110
H	2.714098	-2.724676	1.777861
C	2.686952	-5.558854	-0.114452
H	1.636321	-5.815586	-1.986290
H	3.635565	-5.044964	1.758756
H	3.090751	-6.574090	-0.121260
C	0.108136	1.378163	1.568709
C	-1.058543	1.335564	2.374102
C	-1.079249	1.957892	3.602382
H	-1.943929	0.811382	2.015184
C	1.257052	2.592226	3.352051
C	0.085363	2.588069	4.089317
H	-1.988595	1.950781	4.206337
H	2.168448	3.064815	3.723020
H	0.070400	3.068004	5.070857
C	2.317304	1.285925	-1.987936
C	2.821893	1.805215	0.226164
C	3.597943	1.574721	-2.396959
H	1.558485	0.925899	-2.686764
C	4.147447	2.100510	-0.118200
H	3.865607	1.469745	-3.449224
H	4.825528	2.424031	0.672623
N	1.929972	1.394890	-0.688332
C	4.537174	1.983520	-1.436460
H	5.564886	2.212425	-1.727112
C	1.289665	1.958902	2.106123
O	2.491612	1.994612	1.497894
Ru	0.168435	0.658064	-0.193341
N	-1.125822	1.659896	-1.386855
C	-1.047995	2.657162	-2.289183
C	-2.287147	1.012903	-1.186879
C	-2.157622	3.011906	-3.032671
H	-0.082896	3.157403	-2.393605
C	-3.443077	1.287977	-1.898337
C	-3.357086	2.312422	-2.838516
H	-2.090182	3.822749	-3.759206
H	-4.361034	0.726143	-1.722001
H	-4.239473	2.573222	-3.428286
O	-2.089247	0.103706	-0.215147
C	-3.060880	-0.858500	0.140315
C	-4.159790	-0.454321	0.888540
C	-2.842468	-2.173727	-0.242535
C	-5.091062	-1.424230	1.258398

H	-4.293292	0.592385	1.172521
C	-3.781954	-3.128817	0.143684
H	-1.956649	-2.435295	-0.823126
C	-4.901153	-2.755692	0.888327
H	-5.967074	-1.135481	1.842760
H	-3.637650	-4.172591	-0.142460
H	-5.632614	-3.510195	1.184574

Ru^{IV}-TS34-2

Lowest frequency = -353.4631 cm^{-1}

Charge = 2, Multiplicity = 1

58

O	-1.291542	0.946212	0.520186
C	-0.913408	1.679668	-0.581453
O	-0.373451	1.014752	-1.477730
C	-1.232248	3.078666	-0.602227
C	-0.949402	3.824074	-1.765304
C	-1.813236	3.695491	0.523719
C	-1.244795	5.177348	-1.792849
H	-0.505288	3.328348	-2.630651
C	-2.099246	5.051423	0.482988
H	-2.037324	3.106732	1.414929
C	-1.816819	5.788154	-0.671477
H	-1.033407	5.765771	-2.687687
H	-2.548457	5.542017	1.348454
H	-2.048350	6.855743	-0.699027
C	-0.510545	0.002288	1.590770
C	0.579389	0.578142	2.288471
C	0.917084	0.060083	3.516375
H	1.143795	1.393405	1.831119
C	-0.948294	-1.493570	3.450178
C	0.163543	-0.990670	4.091214
H	1.771335	0.474874	4.055950
H	-1.580165	-2.258135	3.907102
H	0.444861	-1.385065	5.069514
C	-2.603088	-1.662487	-1.747944
C	-3.012897	-1.517928	0.536860
C	-3.906022	-2.027447	-2.003891
H	-1.869556	-1.538932	-2.548932
C	-4.354232	-1.863816	0.354562

H	-4.223619	-2.219900	-3.029449
H	-5.002610	-1.922960	1.229675
N	-2.157182	-1.419157	-0.490199
C	-4.800796	-2.123261	-0.927842
H	-5.844174	-2.398239	-1.097786
C	-1.341447	-0.983247	2.196518
O	-2.592063	-1.327574	1.787179
Ru	-0.302928	-0.766171	-0.216114
N	0.885683	-2.282821	-0.854752
C	0.730154	-3.531075	-1.323928
C	2.109299	-1.745997	-0.760897
C	1.833496	-4.265822	-1.727988
H	-0.288238	-3.922587	-1.367850
C	3.267498	-2.395751	-1.145153
C	3.105259	-3.689311	-1.641427
H	1.699898	-5.279315	-2.108482
H	4.242193	-1.913562	-1.061905
H	3.983226	-4.254935	-1.962354
O	1.959476	-0.505319	-0.236910
C	3.026466	0.405189	-0.119996
C	3.913665	0.263228	0.939805
C	3.117067	1.428031	-1.053798
C	4.948548	1.190441	1.055979
H	3.797645	-0.554515	1.654329
C	4.154607	2.349932	-0.916202
H	2.392495	1.495485	-1.867612
C	5.066642	2.230063	0.132501
H	5.665640	1.099604	1.874521
H	4.253441	3.163152	-1.638123
H	5.879175	2.952789	0.230763

Ru^{IV}-I4-2

Lowest frequency = 13.9682 cm^{-1}

Charge = 2, Multiplicity = 1

58

O	1.646146	0.385155	0.039559
C	2.251184	-0.653027	-0.817688
O	1.545859	-1.067208	-1.681787
C	3.616900	-0.955677	-0.460445
C	4.280174	-1.933278	-1.228308

C	4.277038	-0.316376	0.605990
C	5.589878	-2.269398	-0.922598
H	3.754907	-2.412652	-2.056738
C	5.587167	-0.663343	0.902201
H	3.769814	0.454155	1.188438
C	6.240461	-1.636502	0.140763
H	6.112229	-3.024578	-1.512998
H	6.109365	-0.172319	1.725438
H	7.273364	-1.902912	0.377454
C	0.777967	0.002856	1.023988
C	0.665629	-1.326336	1.515072
C	-0.263469	-1.578305	2.487651
H	1.308063	-2.114882	1.119314
C	-0.943426	0.751855	2.621831
C	-1.092064	-0.542449	3.022311
H	-0.362032	-2.593263	2.878412
H	-1.478949	1.569385	3.109808
H	-1.804068	-0.786661	3.813282
C	0.166670	3.408393	-1.610485
C	0.619409	3.159969	0.660557
C	0.677588	4.690242	-1.608406
H	-0.226248	2.941842	-2.518688
C	1.159741	4.440748	0.744757
H	0.688729	5.271678	-2.531041
H	1.542408	4.798209	1.701445
N	0.132392	2.662211	-0.485146
C	1.182284	5.210246	-0.408375
H	1.597214	6.220411	-0.378775
C	-0.004692	1.102089	1.581096
O	0.552356	2.372282	1.731587
Ru	-0.499377	0.774125	-0.422321
N	-2.500774	0.956427	-0.361699
C	-3.391960	1.955674	-0.271267
C	-2.913987	-0.310554	-0.514592
C	-4.749929	1.687056	-0.348088
H	-2.993984	2.964292	-0.143356
C	-4.244175	-0.673736	-0.614301
C	-5.171680	0.365933	-0.526699
H	-5.469752	2.503376	-0.275293
H	-4.541220	-1.712652	-0.760646
H	-6.237932	0.139283	-0.602095
O	-1.799008	-1.082272	-0.583617
C	-1.809754	-2.483474	-0.446569

C	-2.491870	-3.073240	0.611609
C	-1.069688	-3.210188	-1.366450
C	-2.441901	-4.461572	0.732671
H	-3.052645	-2.468388	1.327381
C	-1.021891	-4.596482	-1.220567
H	-0.538640	-2.700576	-2.171926
C	-1.708063	-5.220924	-0.178962
H	-2.978885	-4.950785	1.548151
H	-0.450971	-5.192295	-1.935691
H	-1.673556	-6.307478	-0.077920

Ru^{III}-I3-2

Lowest frequency = 15.0740 cm^{-1}

Charge = 1, Multiplicity = 2

58

O	-0.682808	-1.304057	0.842866
C	-1.587427	-1.229378	-0.053589
O	-1.322858	-0.532408	-1.081519
C	-2.877642	-1.911479	0.118307
C	-3.835533	-1.848874	-0.901540
C	-3.144605	-2.619226	1.297054
C	-5.057201	-2.492800	-0.740528
H	-3.603698	-1.296200	-1.814100
C	-4.368772	-3.259989	1.452518
H	-2.384454	-2.654078	2.079708
C	-5.322955	-3.196642	0.435510
H	-5.807250	-2.449579	-1.533141
H	-4.583638	-3.811695	2.370109
H	-6.283791	-3.701551	0.560504
C	1.961896	0.125631	1.261104
C	2.232544	1.359378	1.895968
C	3.047222	1.444164	3.014247
H	1.772809	2.269737	1.506865
C	3.401981	-0.945704	2.935913
C	3.628415	0.283520	3.540571
H	3.232156	2.410735	3.487566
H	3.851188	-1.864204	3.317401
H	4.267470	0.340583	4.424253
C	1.199178	-2.180463	-2.032901
C	2.118126	-2.612381	0.057581

C	1.529551	-3.432045	-2.500149
H	0.659926	-1.458984	-2.650273
C	2.472033	-3.909341	-0.346917
H	1.275713	-3.712646	-3.522581
H	2.982503	-4.546696	0.375280
N	1.479394	-1.773663	-0.769385
C	2.175078	-4.321287	-1.628949
H	2.447342	-5.325705	-1.959592
C	2.587146	-1.009844	1.805979
O	2.449230	-2.276492	1.294335
Ru	0.643398	-0.072343	-0.170756
N	1.411163	1.389324	-1.388458
C	2.311641	1.516152	-2.371225
C	0.625651	2.425074	-1.068175
C	2.424575	2.703444	-3.079812
H	2.936108	0.644424	-2.577425
C	0.649329	3.643645	-1.724952
C	1.579869	3.768585	-2.755272
H	3.162722	2.792750	-3.877439
H	-0.026016	4.449587	-1.436563
H	1.649103	4.709135	-3.306212
O	-0.146233	2.063402	-0.016716
C	-1.319100	2.765065	0.307769
C	-1.241975	3.777124	1.254575
C	-2.507448	2.390263	-0.304370
C	-2.413550	4.453840	1.591024
H	-0.287060	4.021521	1.723530
C	-3.668713	3.076017	0.047649
H	-2.512049	1.561609	-1.015359
C	-3.621919	4.105173	0.988147
H	-2.380401	5.252931	2.334360
H	-4.618373	2.796684	-0.413251
H	-4.536741	4.635826	1.259609

Ru^{III}-TS34-2

Lowest frequency = -411.1954 cm^{-1}

Charge = 1, Multiplicity = 2

58

O	1.549116	0.495288	-0.272326
C	1.943570	-0.605817	-0.968504

O	1.125938	-1.211196	-1.625981
C	3.364572	-0.943622	-0.828168
C	3.867020	-2.033194	-1.553780
C	4.206033	-0.213830	0.023181
C	5.203466	-2.389019	-1.427212
H	3.191778	-2.585892	-2.209744
C	5.541913	-0.578497	0.148378
H	3.804136	0.634498	0.579139
C	6.039425	-1.662506	-0.576107
H	5.599887	-3.235465	-1.991793
H	6.201320	-0.015058	0.811692
H	7.090384	-1.944395	-0.477481
C	0.639427	0.278752	1.095682
C	0.556142	-1.029653	1.632178
C	0.484804	-1.206587	3.002741
H	0.525298	-1.884254	0.953182
C	0.704124	1.174065	3.356825
C	0.550527	-0.107969	3.872028
H	0.382186	-2.217732	3.402567
H	0.785382	2.047001	4.007528
H	0.499662	-0.255675	4.951813
C	-0.592578	3.461864	-1.469208
C	0.635705	3.290537	0.486793
C	-0.272078	4.791674	-1.624886
H	-1.216517	2.938497	-2.197749
C	1.019173	4.636752	0.387955
H	-0.655809	5.345191	-2.482312
H	1.662150	5.043566	1.168780
N	-0.143659	2.706478	-0.434308
C	0.565193	5.391631	-0.673436
H	0.853034	6.440780	-0.765201
C	0.780323	1.374445	1.980770
O	1.077137	2.644116	1.563018
Ru	-0.546021	0.745039	-0.442894
N	-2.589207	0.751023	-0.422581
C	-3.550763	1.682013	-0.327295
C	-2.929799	-0.544198	-0.504414
C	-4.891579	1.330632	-0.315537
H	-3.217120	2.719156	-0.253303
C	-4.242322	-0.992244	-0.505185
C	-5.235712	-0.020531	-0.409744
H	-5.655986	2.103988	-0.234292
H	-4.469096	-2.055980	-0.579864

H	-6.285574	-0.321404	-0.410897
O	-1.807202	-1.282625	-0.608922
C	-1.771384	-2.644369	-0.308675
C	-2.248959	-3.103271	0.914956
C	-1.172745	-3.483198	-1.238025
C	-2.144349	-4.463359	1.198569
H	-2.680729	-2.407443	1.637519
C	-1.067902	-4.839448	-0.932894
H	-0.778901	-3.065559	-2.165018
C	-1.556527	-5.330612	0.277201
H	-2.516063	-4.844324	2.152140
H	-0.599273	-5.516430	-1.650131
H	-1.473428	-6.394605	0.507544

Ru^{III}-I4-2

Lowest frequency = 9.2344 cm^{-1}

Charge = 1, Multiplicity = 2

58

O	1.572183	-1.307696	0.858756
C	1.673528	-1.189810	-0.473804
O	0.800239	-0.661080	-1.141990
C	2.933406	-1.718294	-1.015373
C	3.167238	-1.590473	-2.391357
C	3.888089	-2.329219	-0.190398
C	4.350747	-2.070013	-2.938357
H	2.407808	-1.113756	-3.013888
C	5.070278	-2.806695	-0.745064
H	3.694856	-2.426253	0.878788
C	5.301236	-2.677458	-2.115386
H	4.536195	-1.973872	-4.010147
H	5.816444	-3.284981	-0.107268
H	6.230890	-3.055757	-2.547025
C	0.361746	-0.897386	1.439585
C	-0.632628	-1.913599	1.622536
C	-1.629878	-1.746616	2.544791
H	-0.564225	-2.819070	1.016253
C	-0.642454	0.320704	3.354185
C	-1.642097	-0.614985	3.409930
H	-2.401840	-2.511426	2.649002
H	-0.573586	1.135751	4.077519

H	-2.425619	-0.523182	4.164529
C	2.055918	2.334736	-0.490132
C	2.179012	1.529838	1.678545
C	3.339065	2.842776	-0.419845
H	1.458613	2.401019	-1.400470
C	3.477016	2.015163	1.834143
H	3.771017	3.345961	-1.285172
H	3.994292	1.842229	2.777888
N	1.469519	1.703773	0.547784
C	4.058219	2.685363	0.769793
H	5.074791	3.073935	0.858862
C	0.373090	0.237288	2.344420
O	1.590432	0.861654	2.661255
Ru	-0.356524	0.855127	0.492631
N	-1.451442	1.988844	-0.998663
C	-1.320002	3.040310	-1.816297
C	-2.564863	1.255959	-1.066587
C	-2.295596	3.363385	-2.748830
H	-0.407672	3.631549	-1.711963
C	-3.589684	1.475813	-1.974868
C	-3.436423	2.562047	-2.832452
H	-2.162599	4.226826	-3.401527
H	-4.466595	0.828272	-1.996348
H	-4.216453	2.788971	-3.562530
O	-2.545242	0.296252	-0.103101
C	-3.260064	-0.892228	-0.278034
C	-4.403815	-1.090251	0.480470
C	-2.766695	-1.848191	-1.157434
C	-5.086462	-2.299366	0.344827
H	-4.739829	-0.313009	1.168966
C	-3.461416	-3.049023	-1.283742
H	-1.843525	-1.655660	-1.709284
C	-4.617509	-3.274690	-0.534384
H	-5.989276	-2.478623	0.932464
H	-3.092744	-3.816857	-1.967231
H	-5.155352	-4.219513	-0.635682

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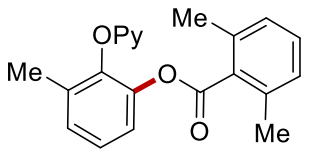
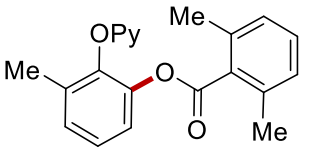
NMR Spectra



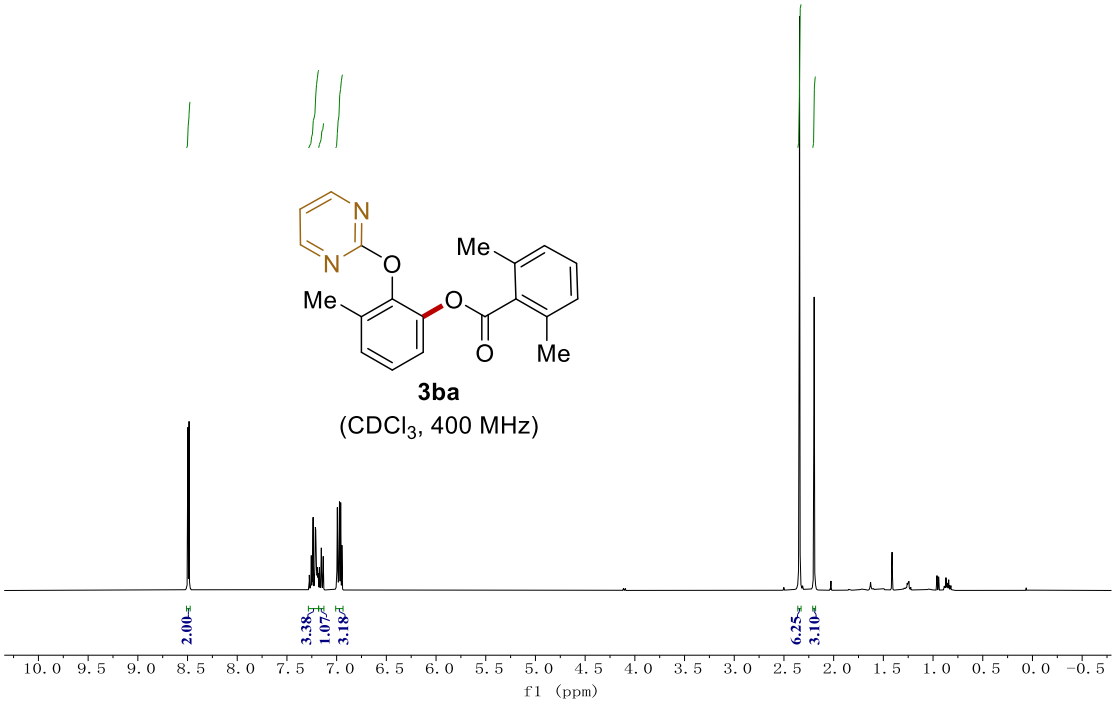
3aa

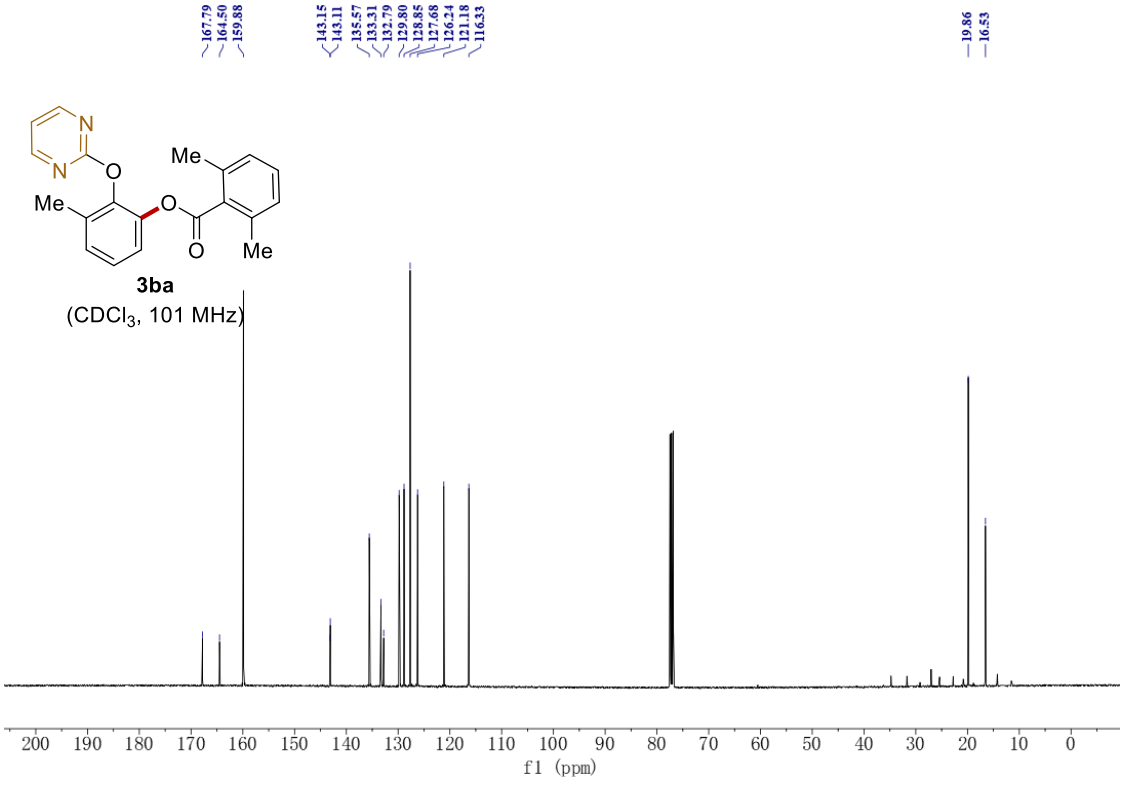
($CDCl_3$, 400 MHz)

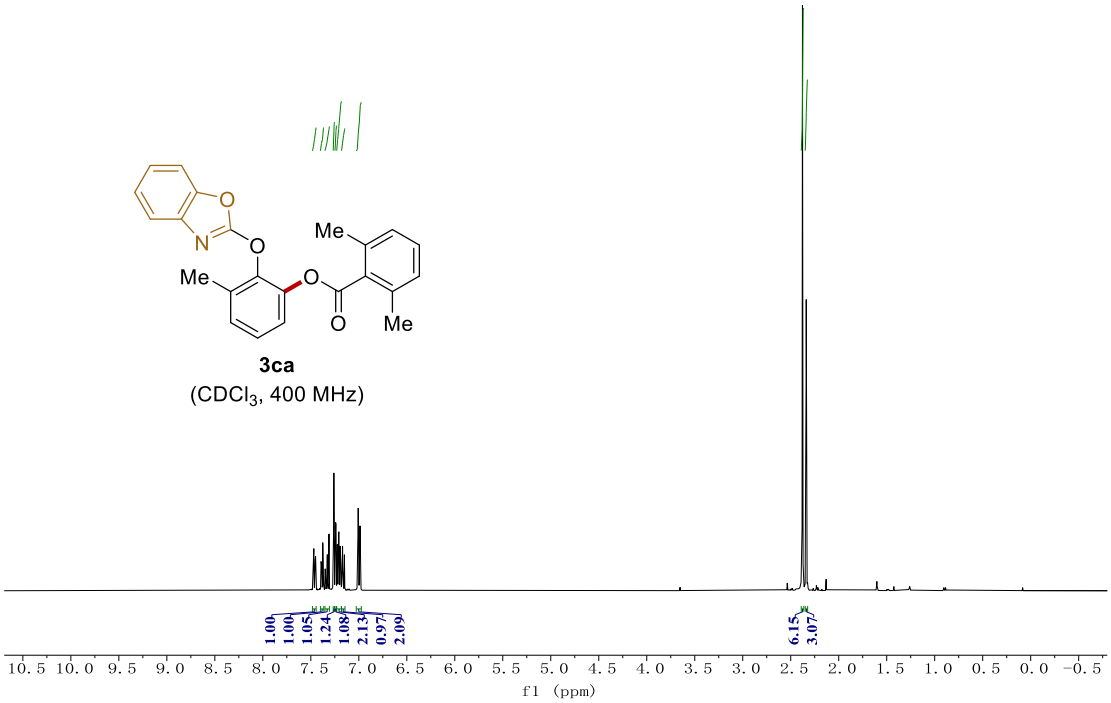


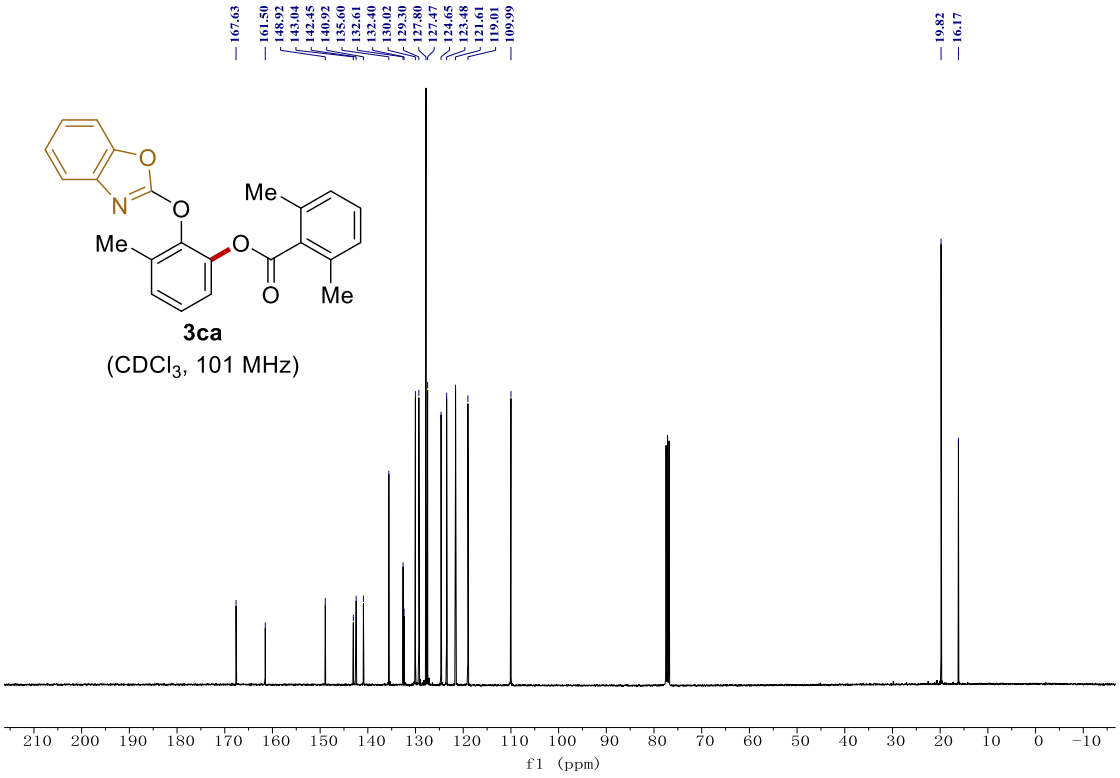
3aa

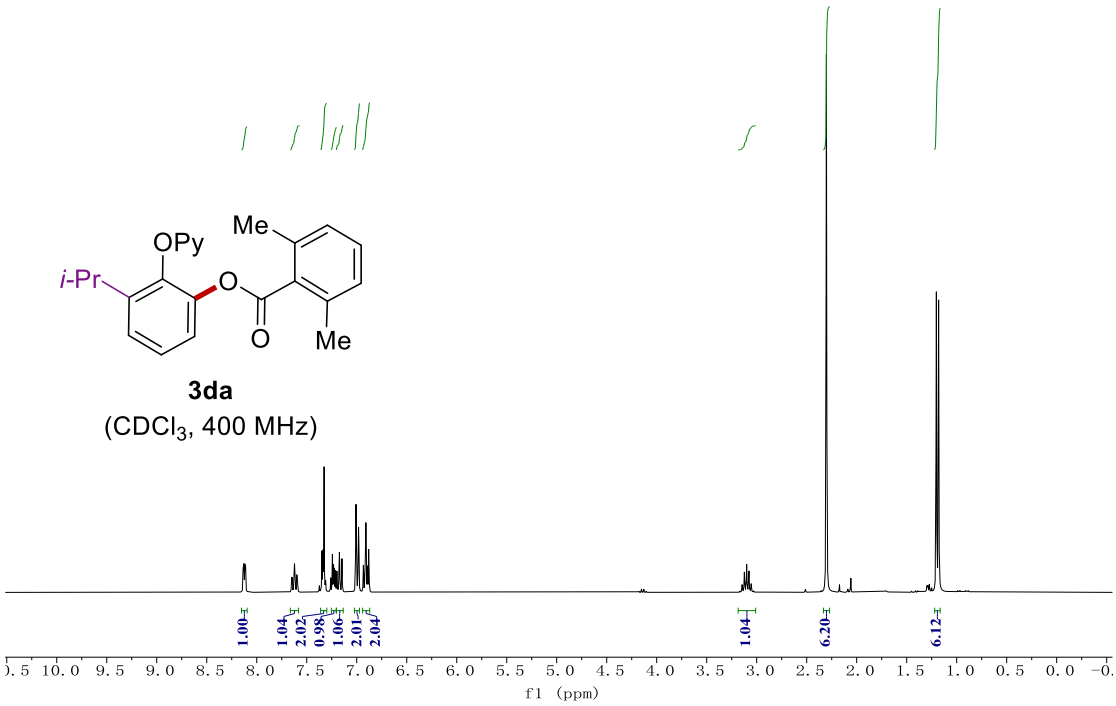
($CDCl_3$, 101 MHz)


N
N
O
Me
Me
O
O
Me
3ba
(CDCl3, 400 MHz)
2.00
3.38
1.07
3.18
6.25
3.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)


167.79
164.50
159.88
143.15
143.11
135.57
133.31
132.79
129.80
128.85
127.68
126.24
121.18
116.33
19.86
16.53
N
N
O
Me
Me
O
O
Me
3ba
(CDCl3, 101 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

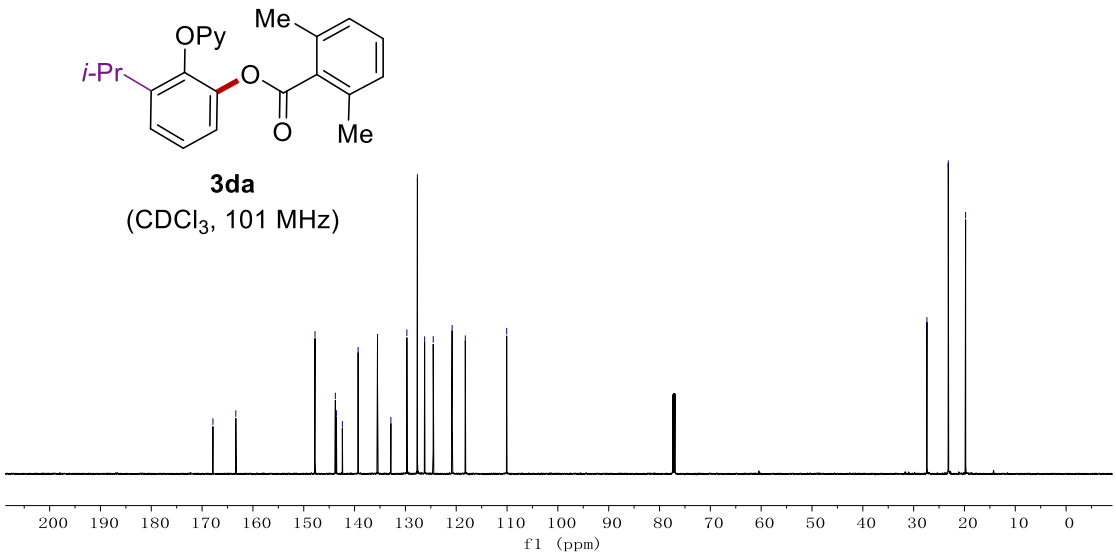

Me
Me
O
O
O
N
O
Me
3ca
(CDCl3, 400 MHz)
1.00
1.00
1.05
1.24
1.08
2.13
0.97
2.09
6.15
3.07
f1 (ppm)


167.63
161.50
148.92
143.04
142.45
140.92
135.60
132.61
132.40
130.02
129.30
127.80
127.47
124.65
123.48
121.61
119.01
109.99
19.82
16.17
Me
Me
O
O
O
N
O
Me
3ca
(CDCl3, 101 MHz)
f1 (ppm)



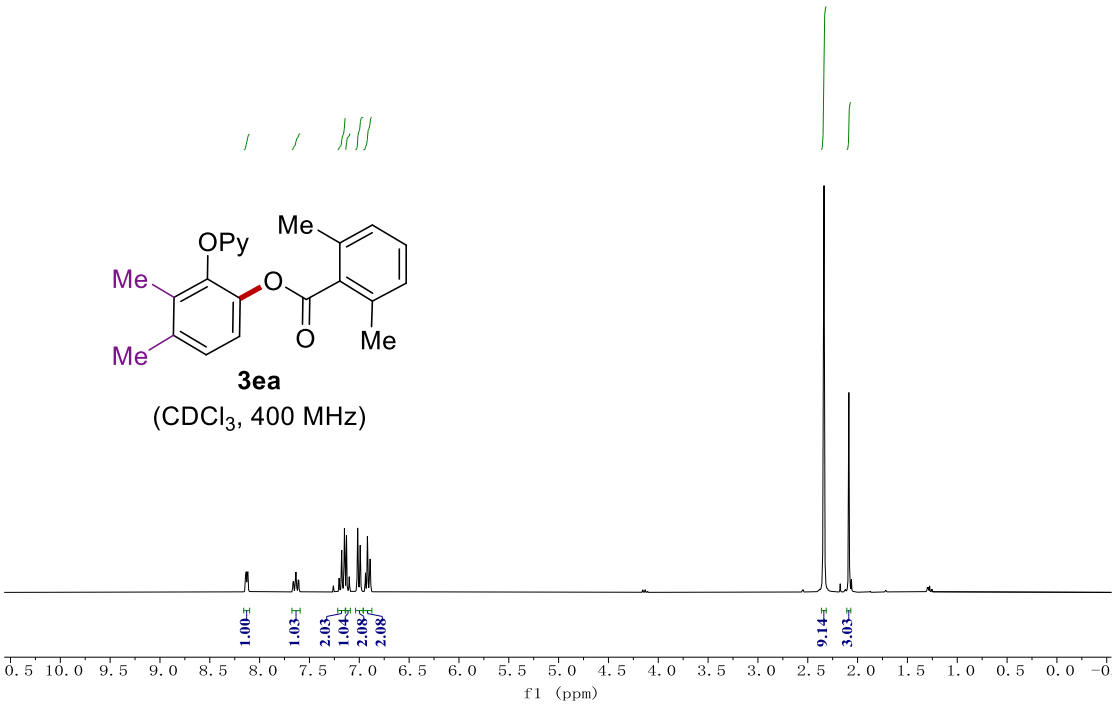
3da

($CDCl_3$, 400 MHz)



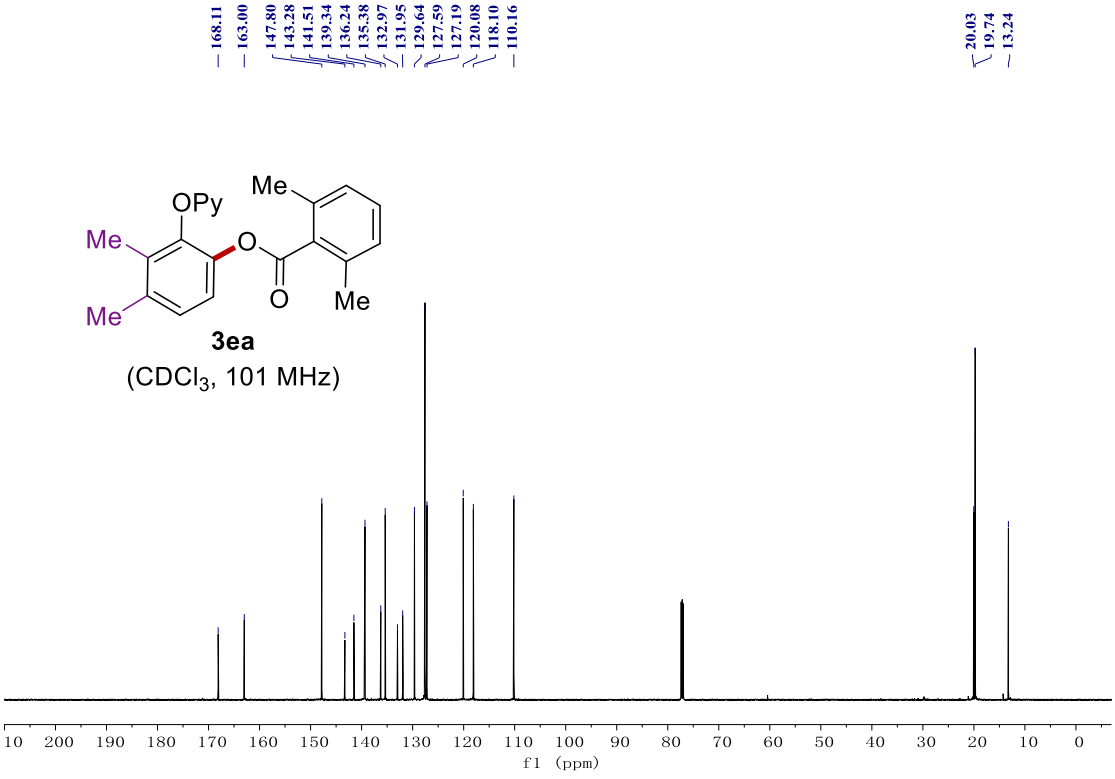
3da

($CDCl_3$, 101 MHz)



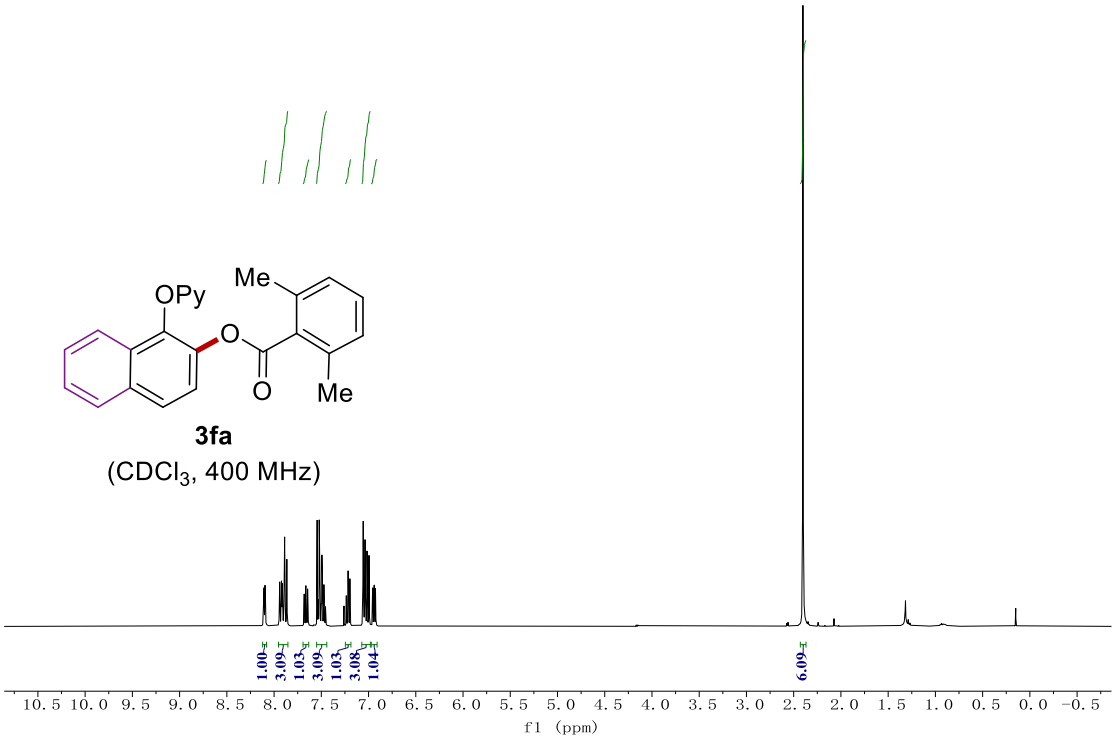
3ea

($CDCl_3$, 400 MHz)



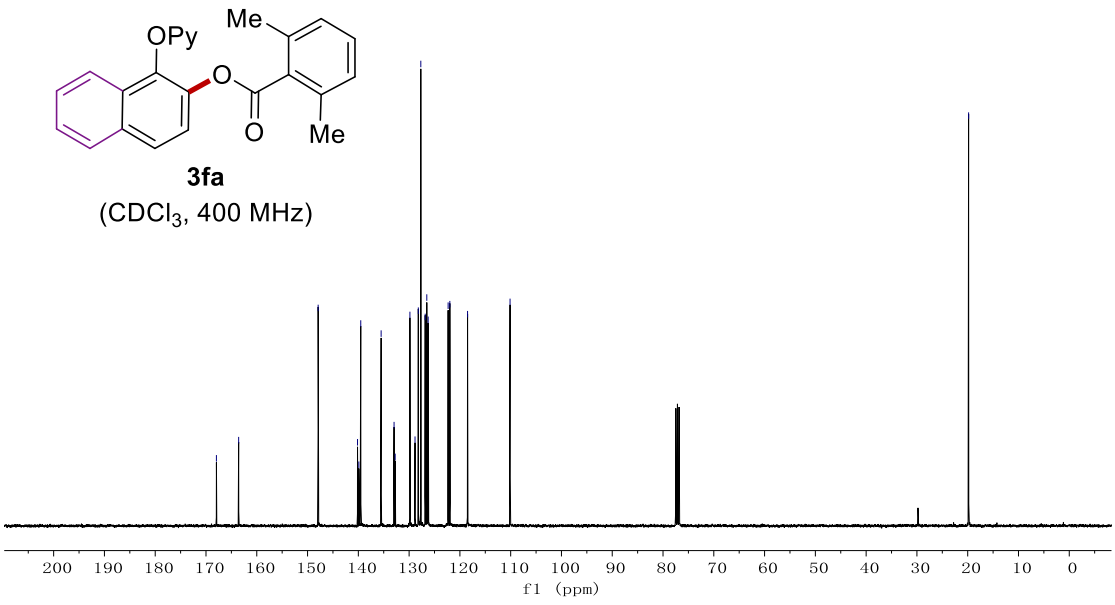
3ea

($CDCl_3$, 101 MHz)



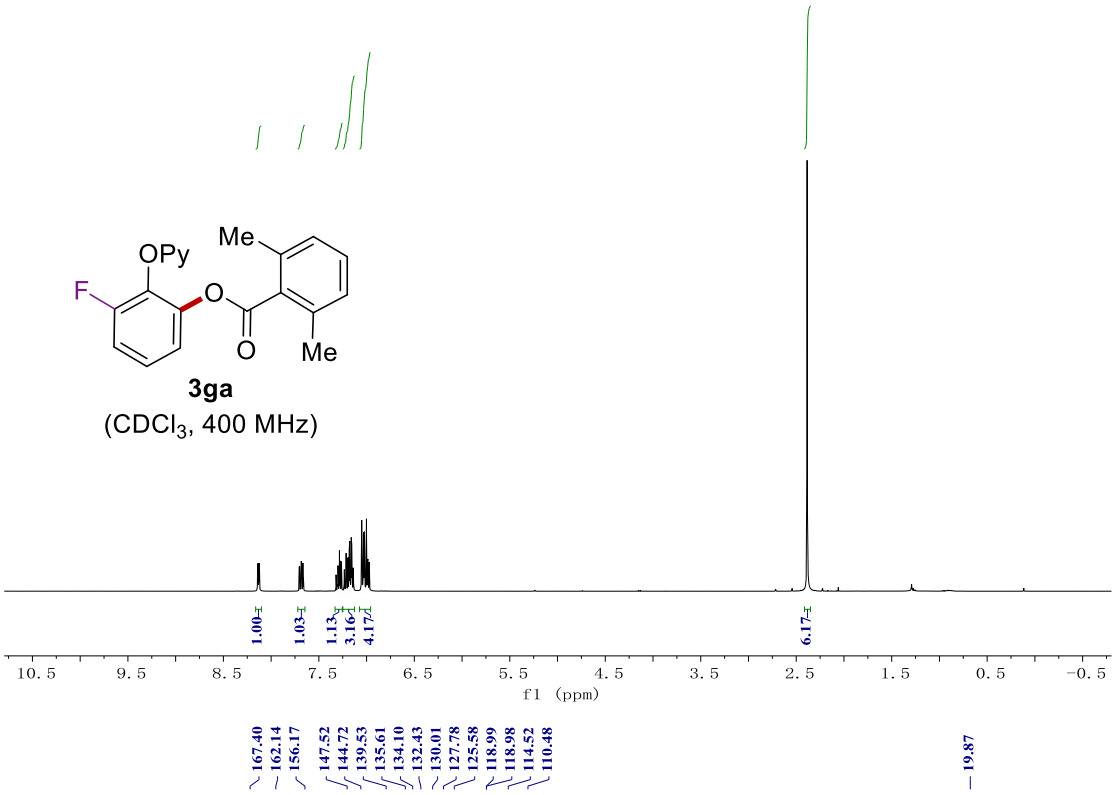
3fa

($CDCl_3$, 400 MHz)



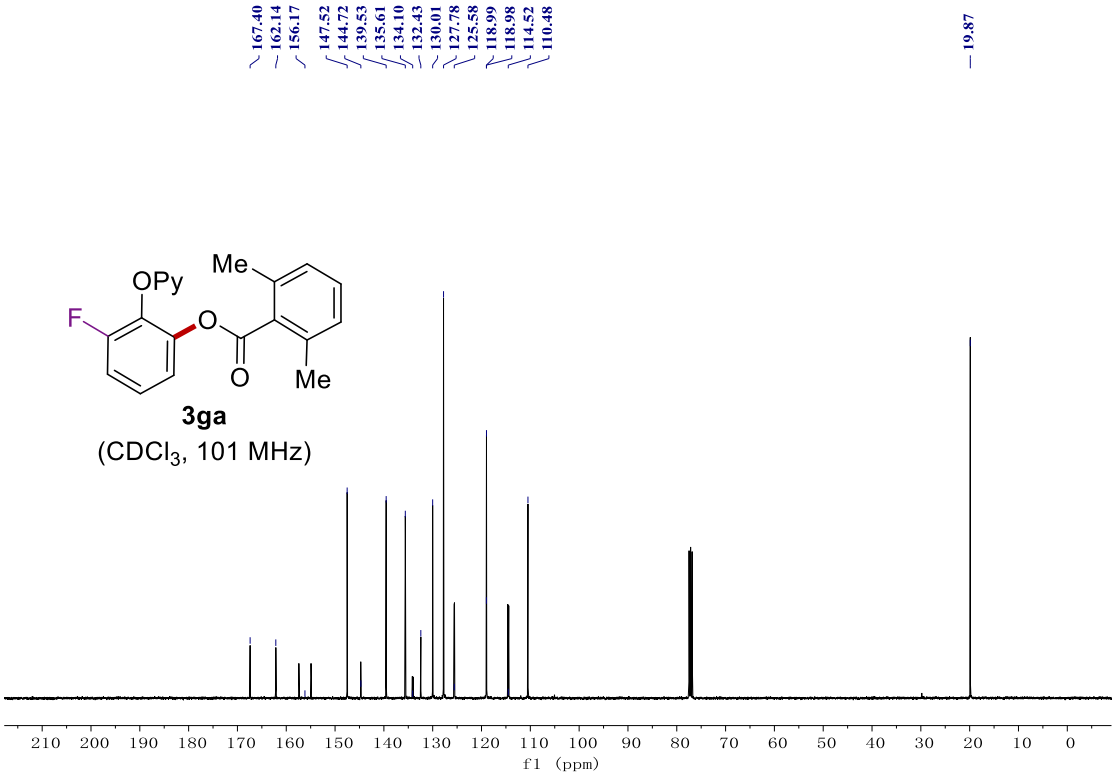
3fa

($CDCl_3$, 400 MHz)



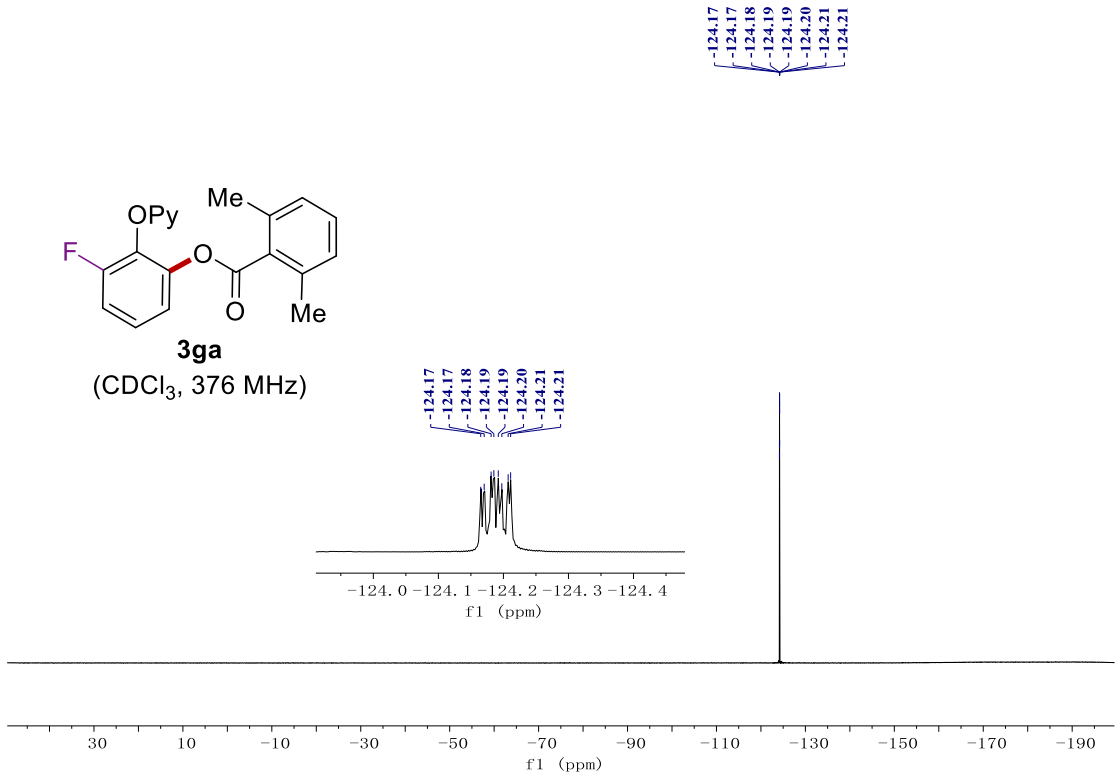
3ga

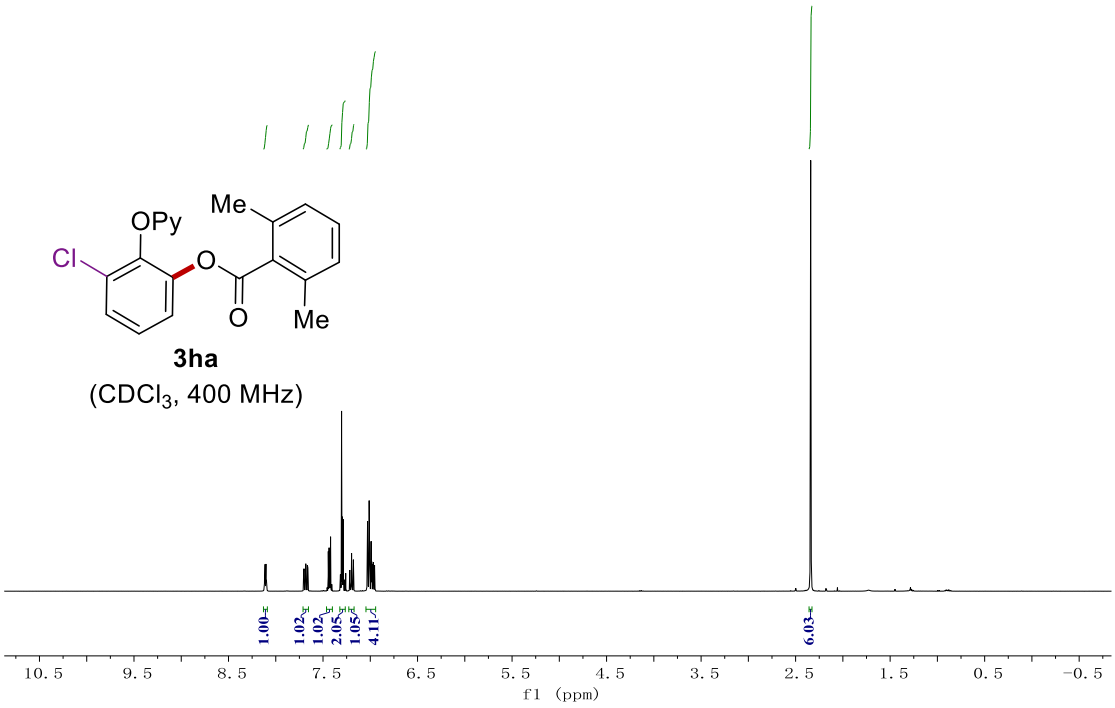
($CDCl_3$, 400 MHz)

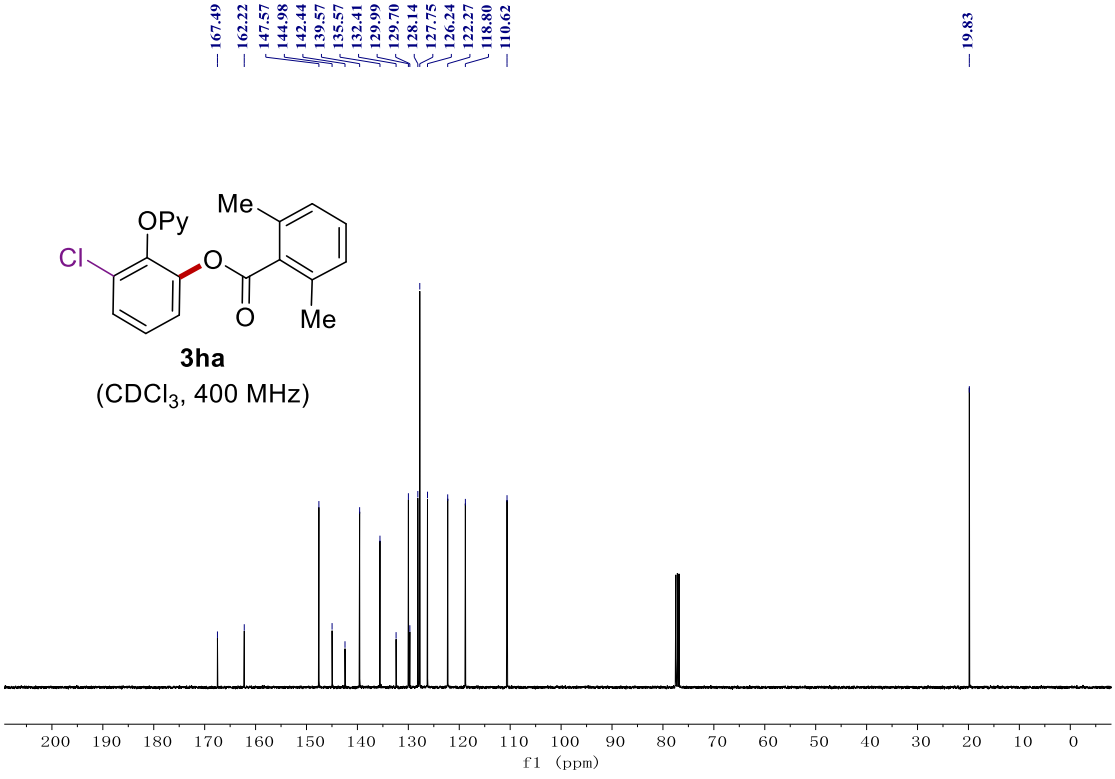


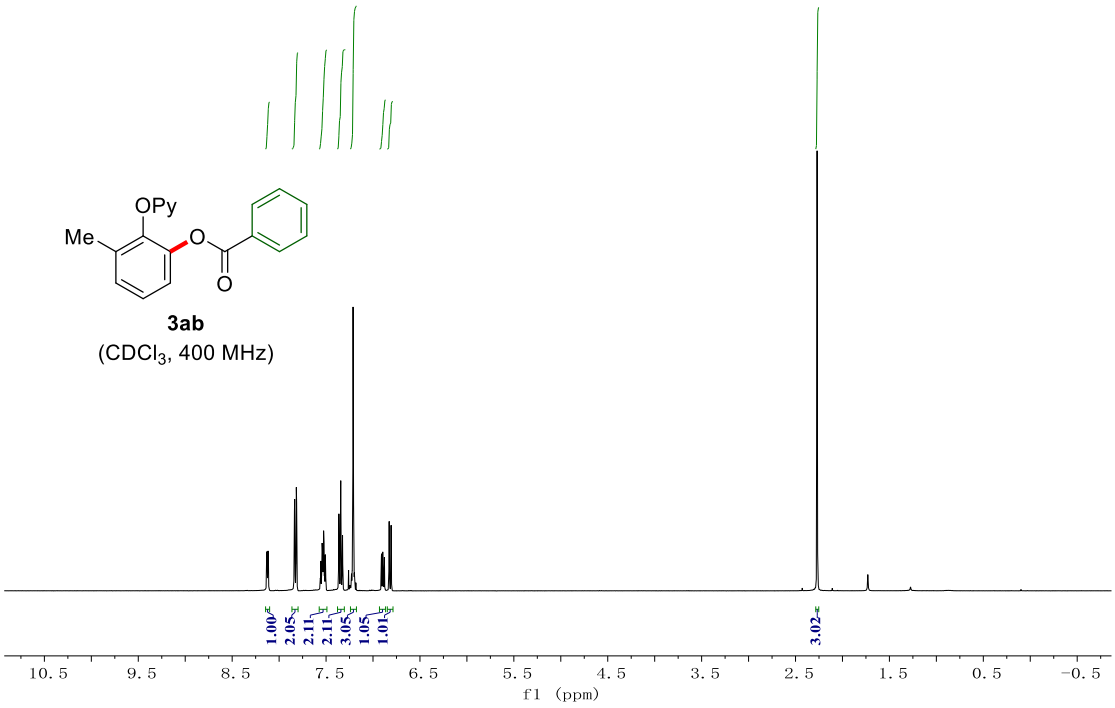
3ga

($CDCl_3$, 101 MHz)


-124.17
-124.17
-124.18
-124.19
-124.19
-124.20
-124.21
-124.21
OPy
Me
F
O
O
Me
3ga
(CDCl3, 376 MHz)
-124.17
-124.17
-124.18
-124.19
-124.19
-124.20
-124.21
-124.21
-124.0 -124.1 -124.2 -124.3 -124.4
f1 (ppm)
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
f1 (ppm)

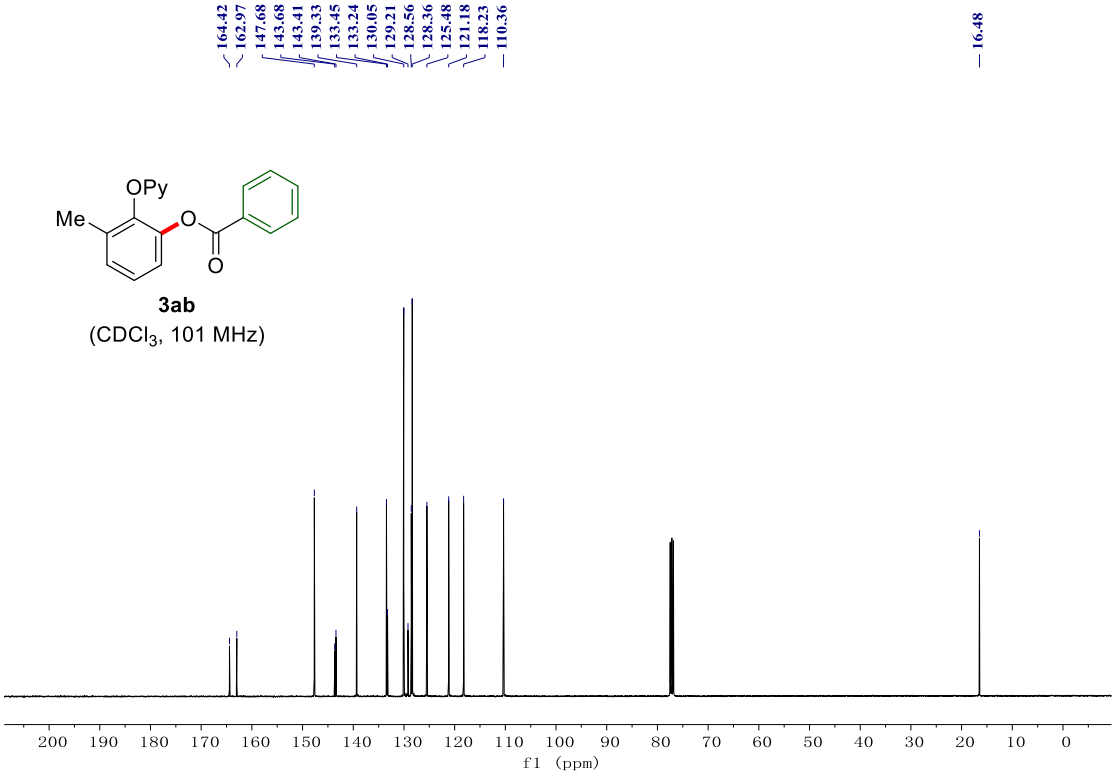

OPy
Me
Cl
O
O
Me
3ha
(CDCl3, 400 MHz)
1.00
1.02
1.02
2.05
1.05
4.11
6.03
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
−0.5
f1 (ppm)


167.49
162.22
147.57
144.98
142.44
139.57
135.57
132.41
129.99
129.70
128.14
127.75
126.24
122.27
118.80
110.62
19.83
OPy
Me
Cl
O
O
Me
3ha
(CDCl3, 400 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



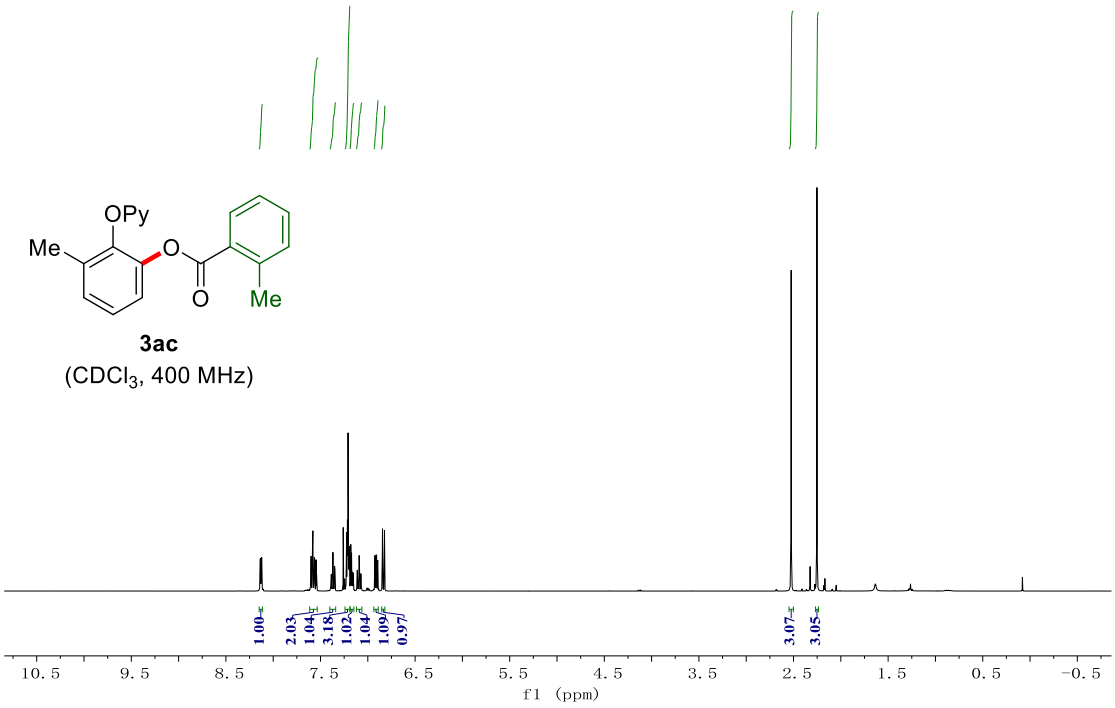
3ab

($CDCl_3$, 400 MHz)



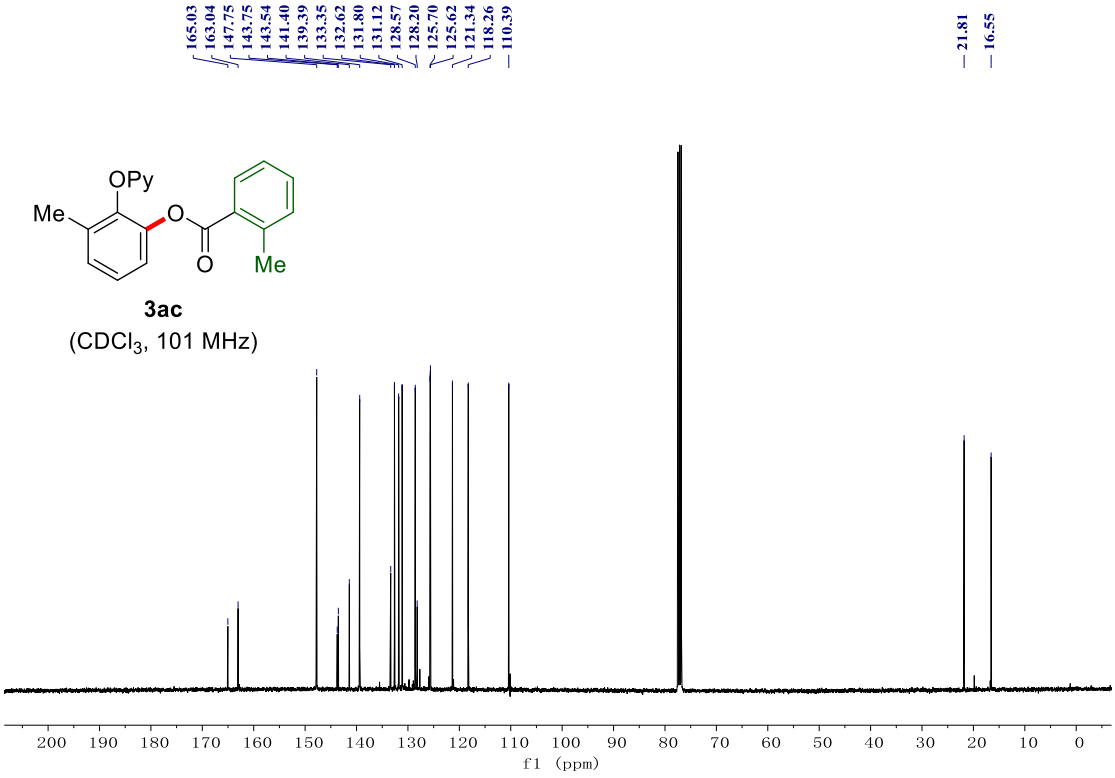
3ab

($CDCl_3$, 101 MHz)



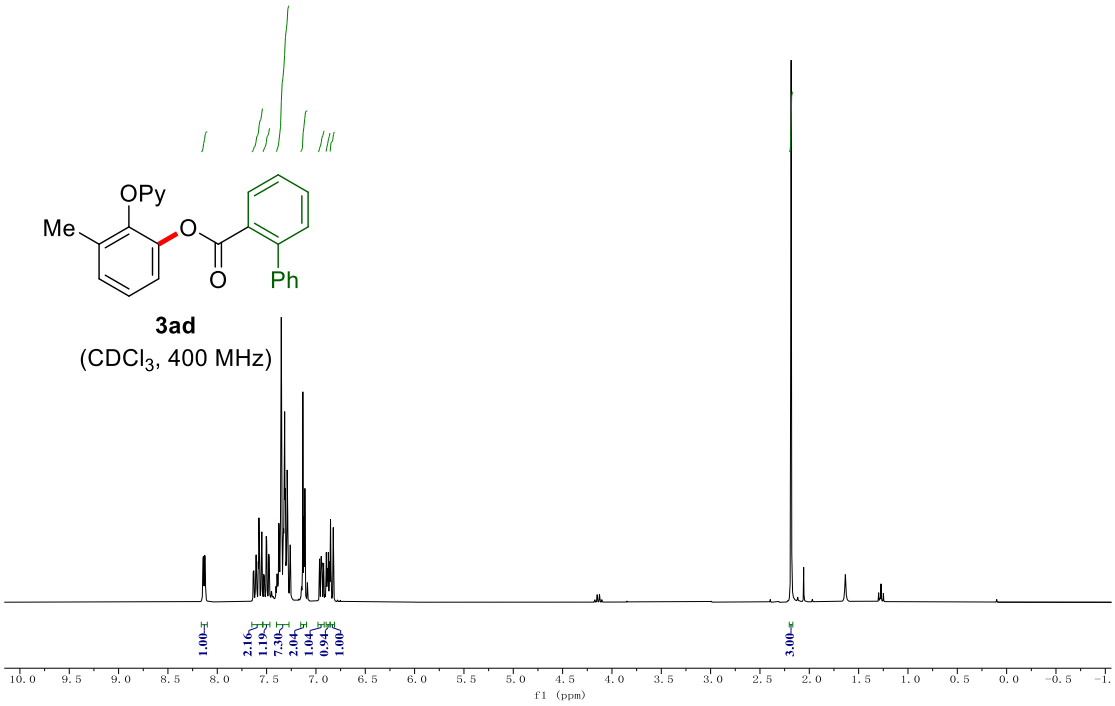
3ac

($CDCl_3$, 400 MHz)

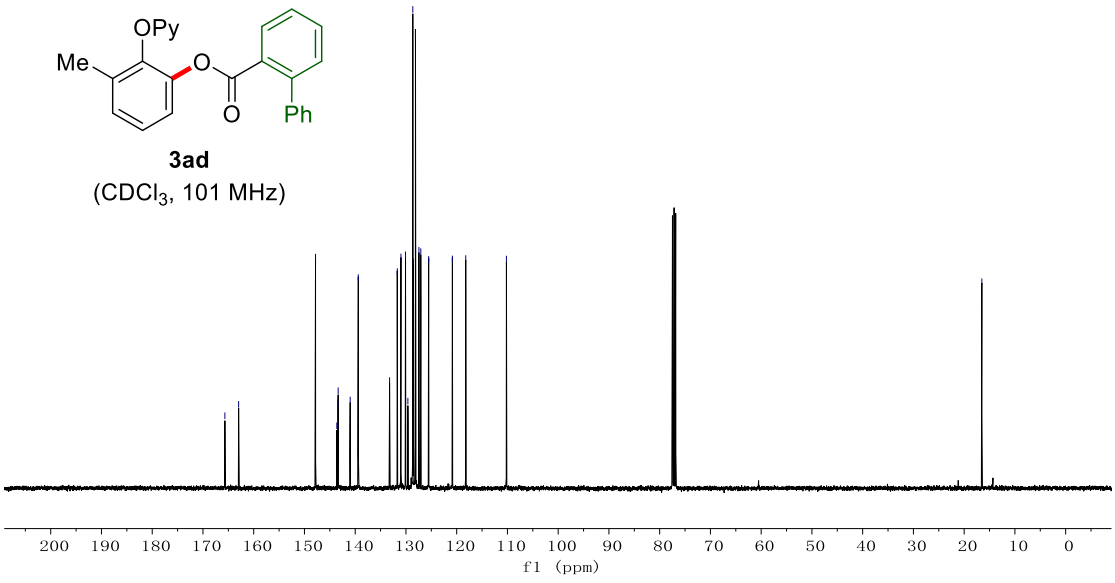


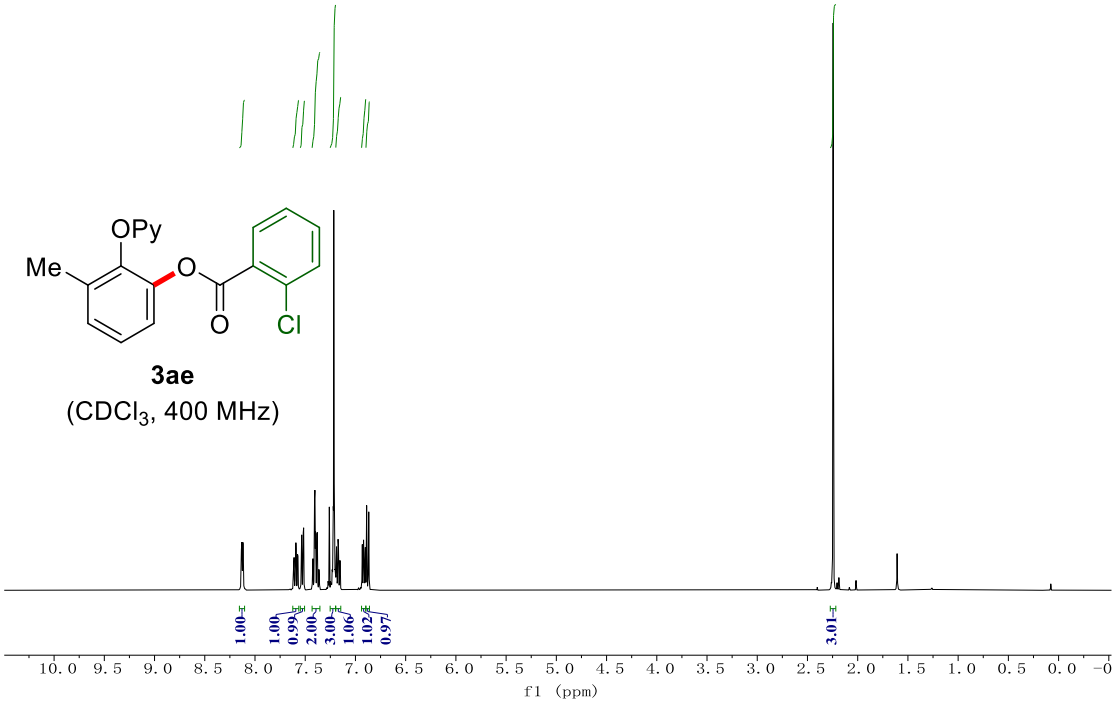
3ac

($CDCl_3$, 101 MHz)


OPy
Me
O
O
Ph
3ad
(CDCl3, 400 MHz)
1.00
2.16
1.19
7.30
2.04
1.04
0.94
1.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.
f1 (ppm)

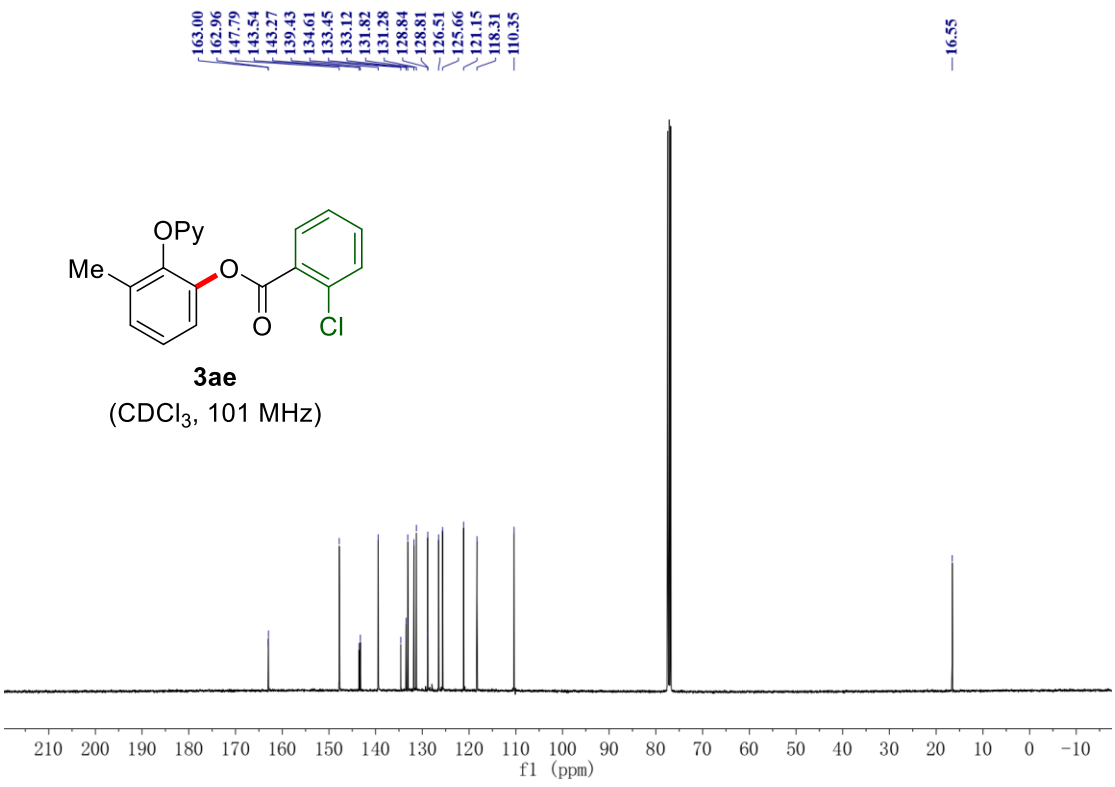

165.68
162.97
147.82
143.62
143.40
143.36
140.99
139.39
133.23
131.71
130.99
130.09
129.62
128.65
128.52
128.13
127.44
127.08
125.52
120.84
118.22
110.20
16.51


OPy
Me
O
O
Ph
3ad
(CDCl3, 101 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



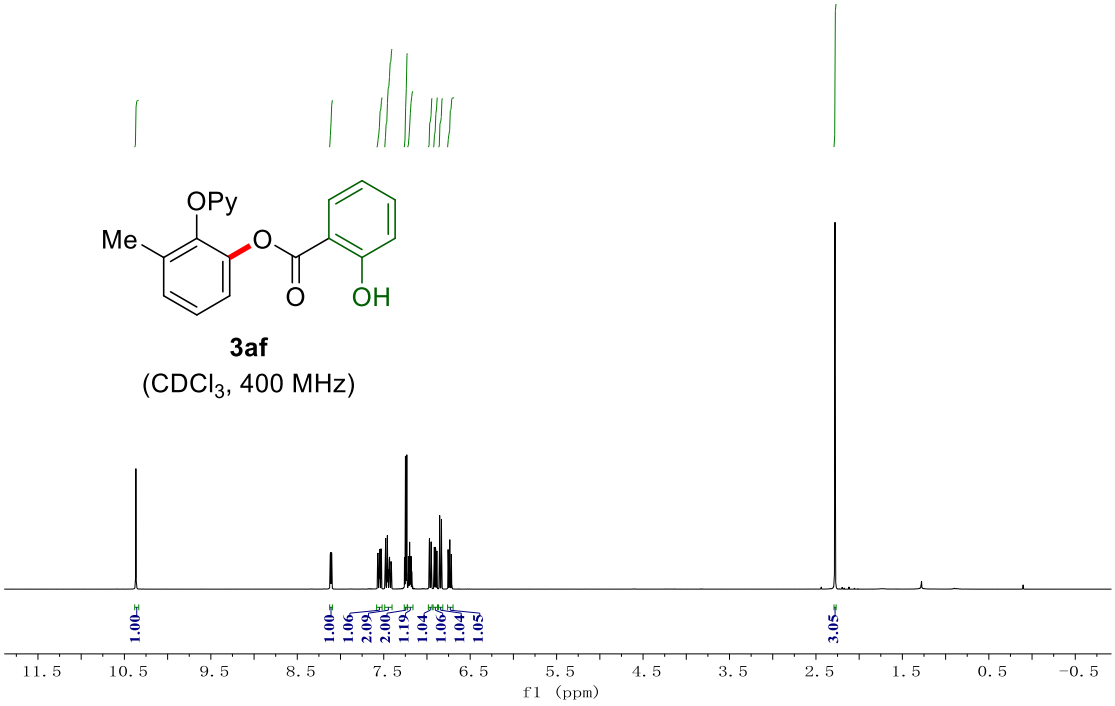
3ae

($CDCl_3$, 400 MHz)



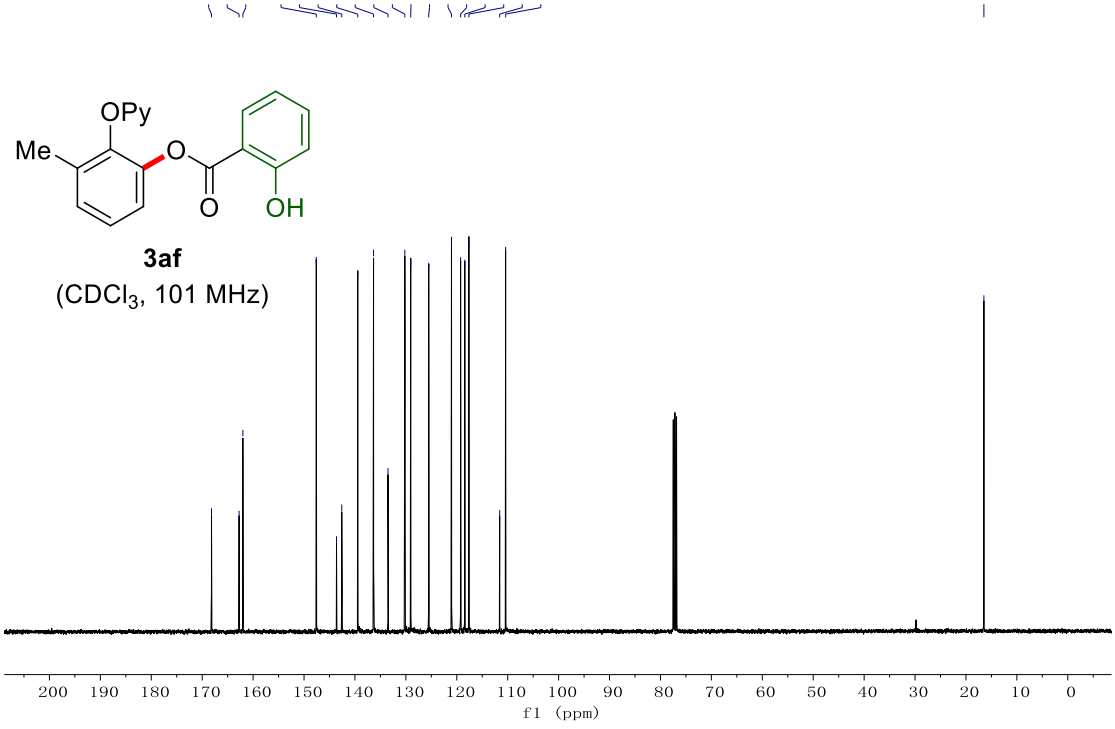
3ae

($CDCl_3$, 101 MHz)



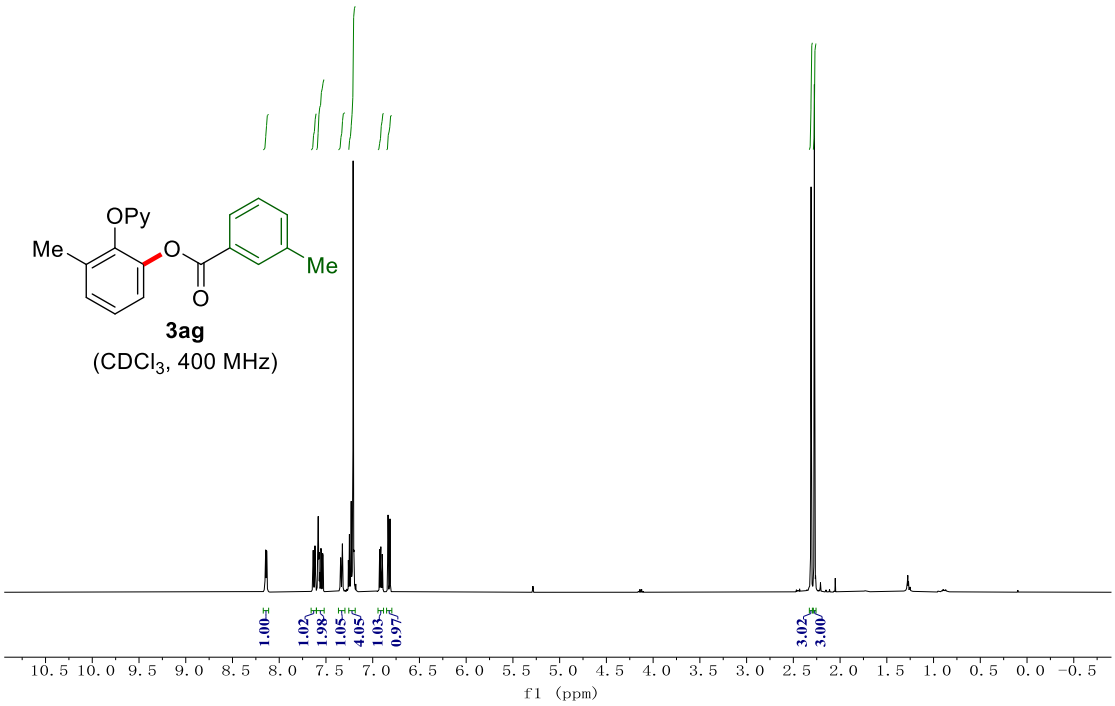
3af

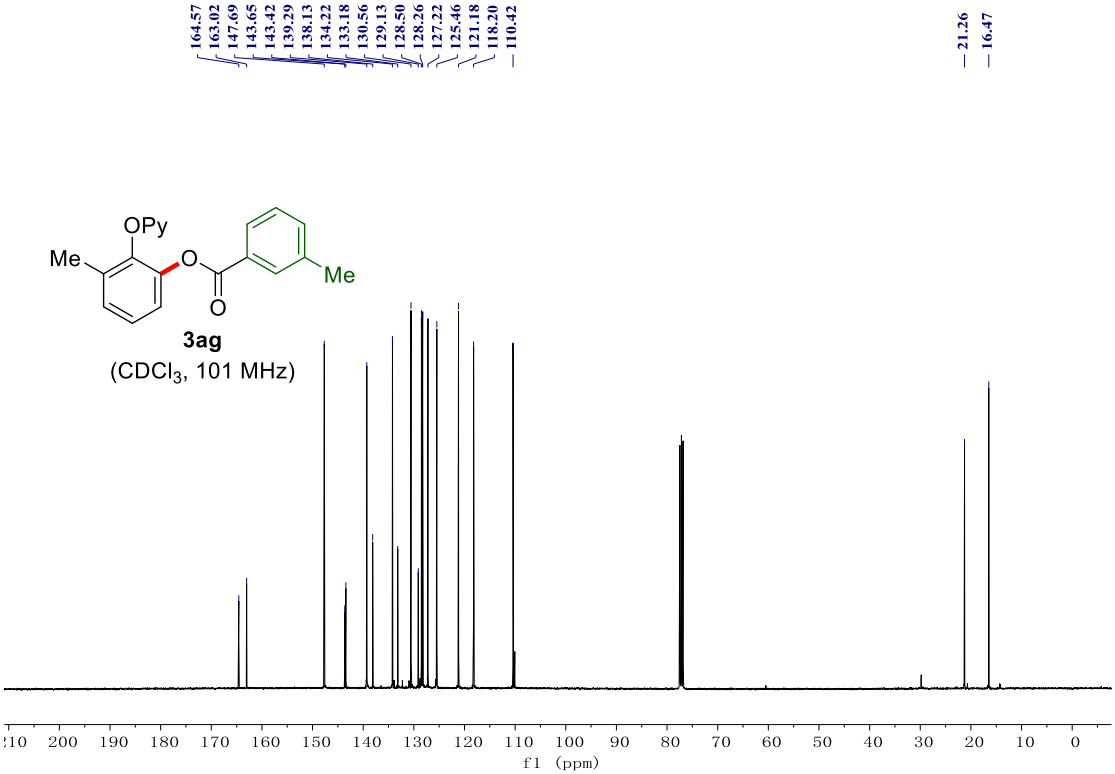
($CDCl_3$, 400 MHz)

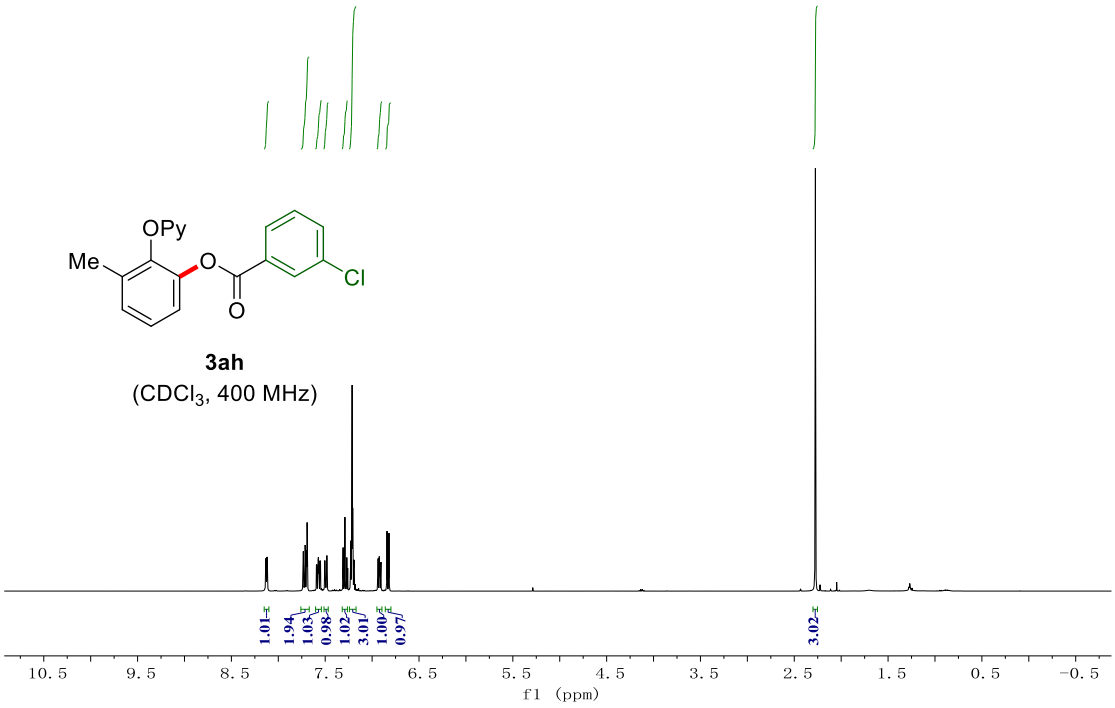


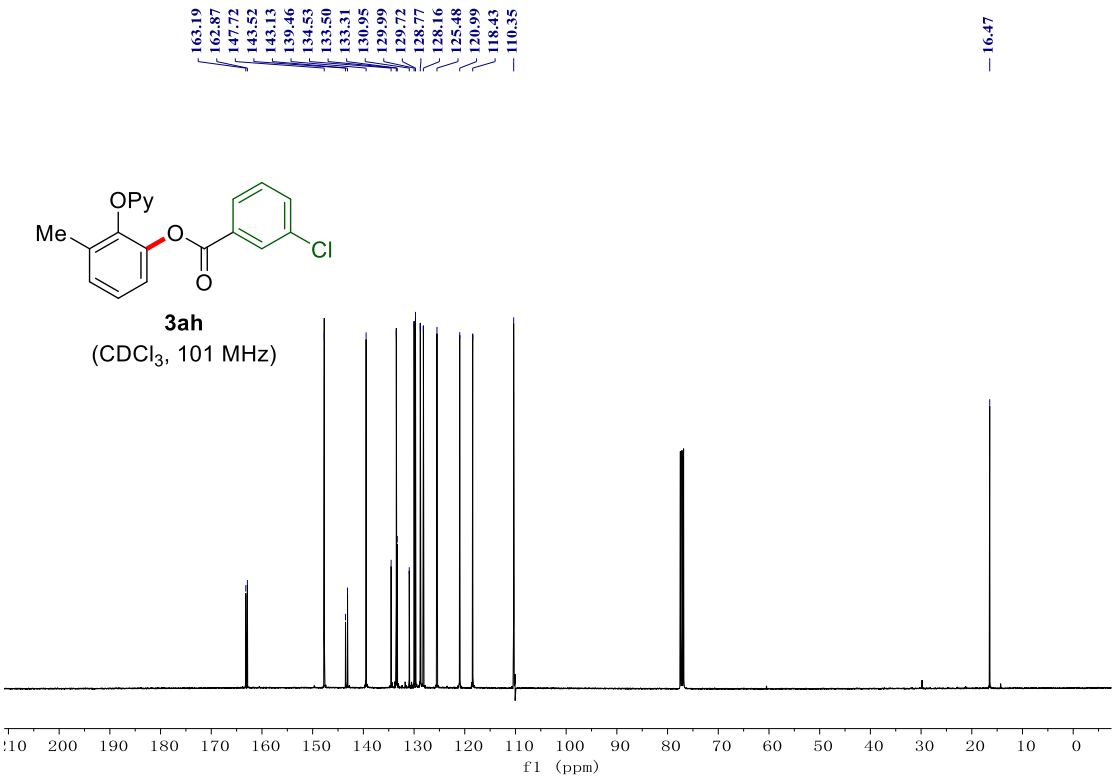
3af

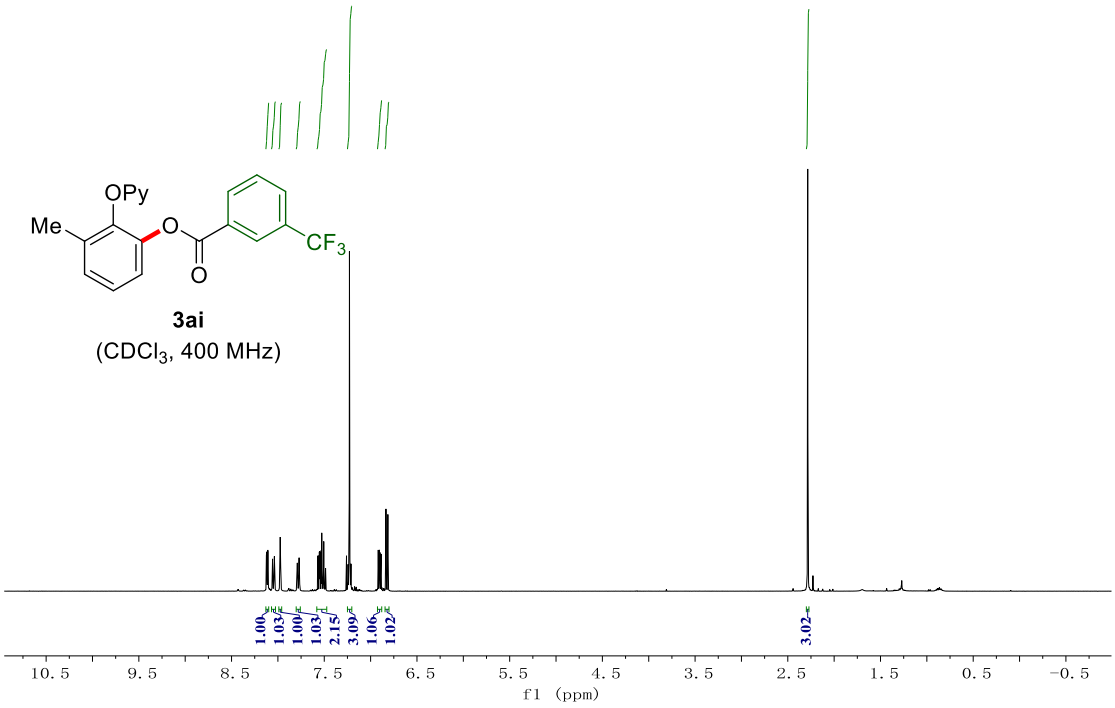
($CDCl_3$, 101 MHz)

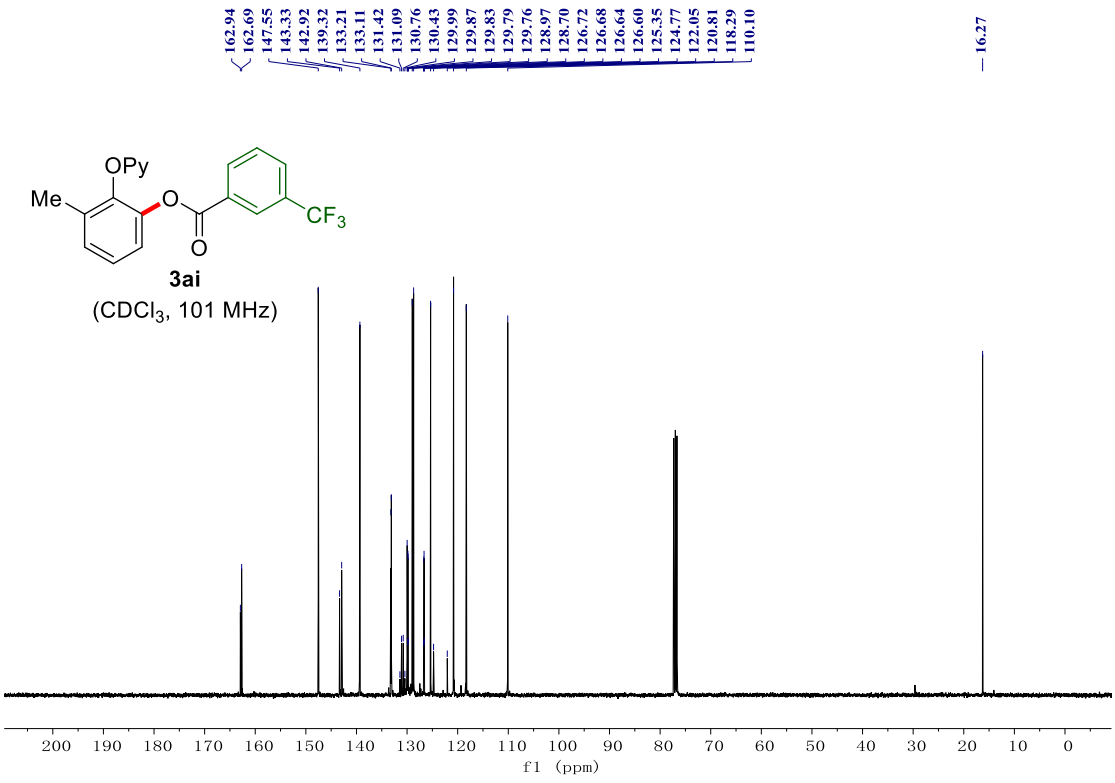

OPy
Me
O
Me
O
3ag
(CDCl3, 400 MHz)
1.00
1.02
1.98
1.05
4.05
1.03
0.97
3.02
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)


164.57
163.02
147.69
143.65
143.42
139.29
138.13
134.22
133.18
130.56
129.13
128.50
128.26
127.22
125.46
121.18
118.20
110.42
21.26
16.47
OPy
Me
O
Me
O
3ag
(CDCl3, 101 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

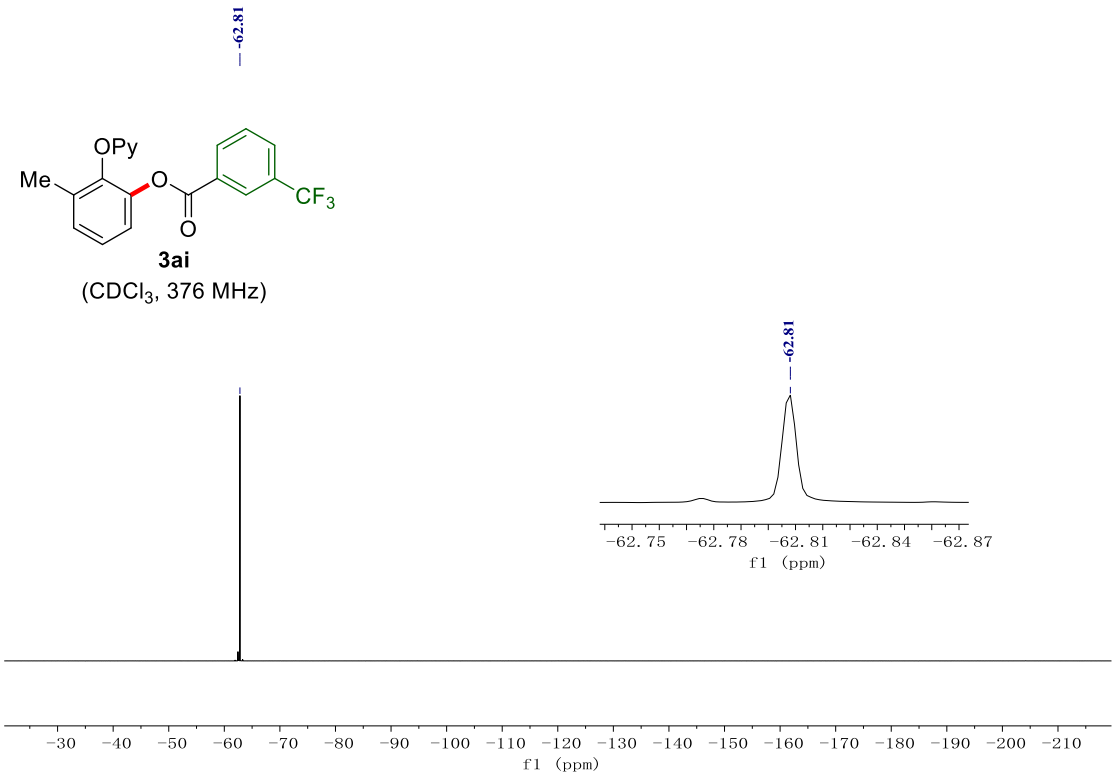

OPy
Me
O
O
Cl
3ah
(CDCl3, 400 MHz)
1.01
1.94
1.03
0.98
1.02
3.01
1.00
0.97
3.02
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
−0.5
f1 (ppm)

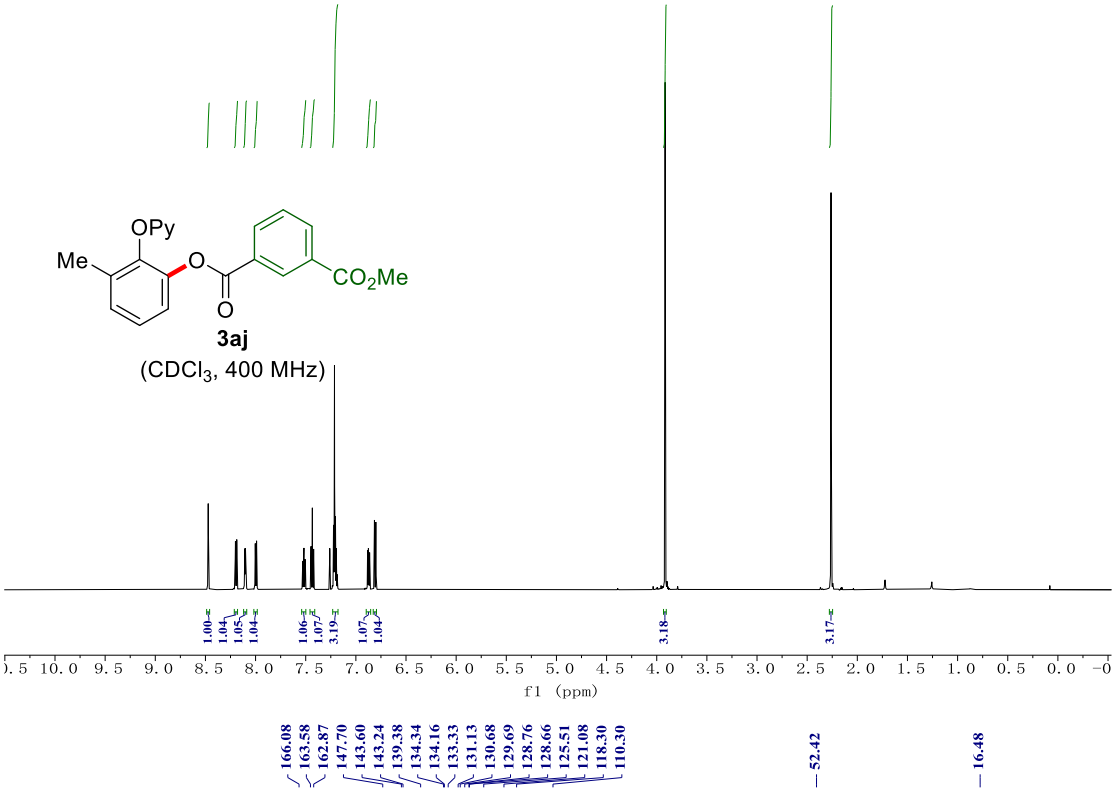

163.19
162.87
147.72
143.52
143.13
139.46
134.53
133.50
133.31
130.95
129.99
129.72
128.77
128.16
125.48
120.99
118.43
110.35
16.47
OPy
Me
O
O
Cl
3ah
(CDCl3, 101 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

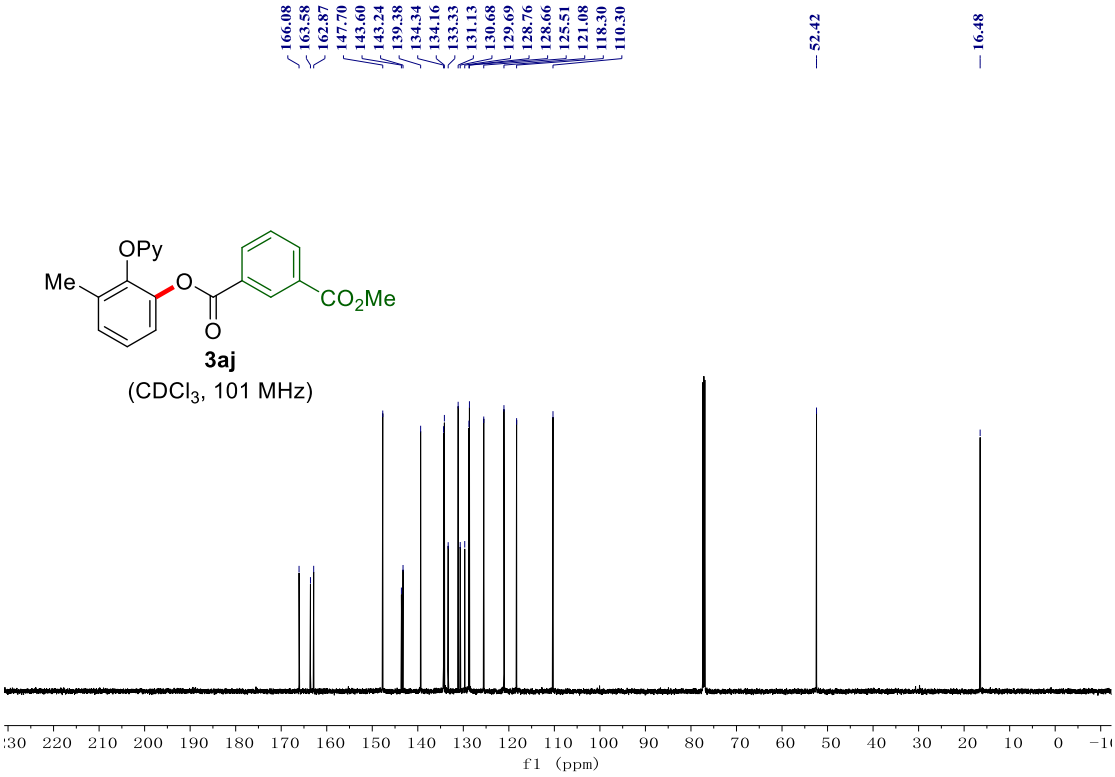


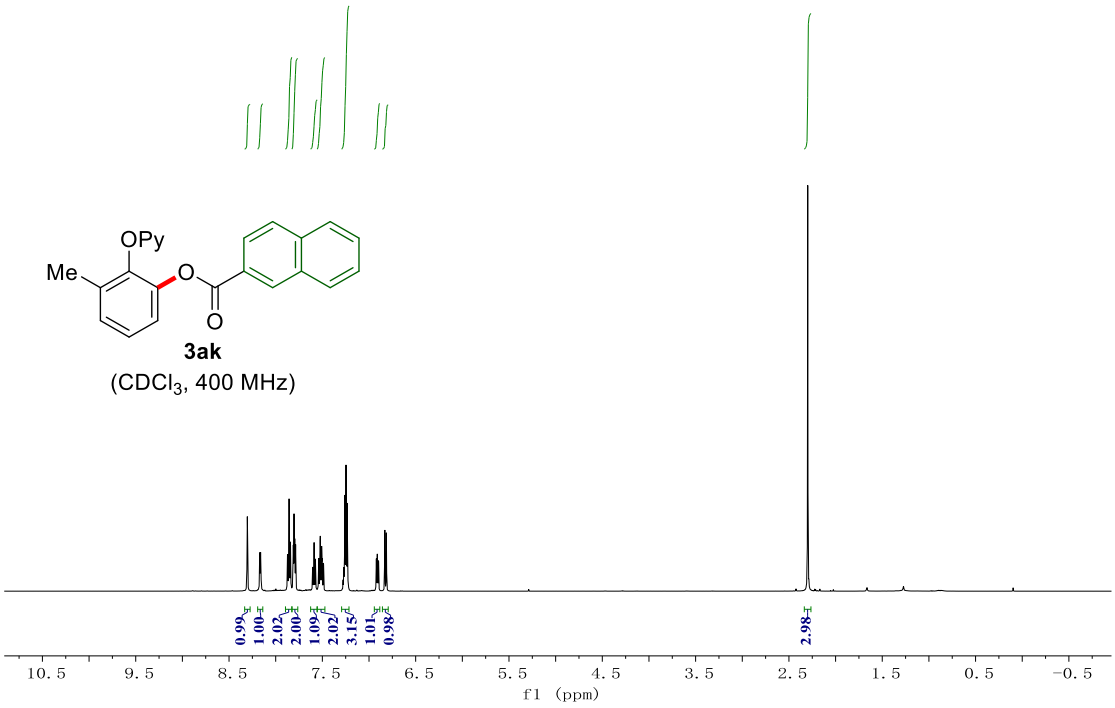


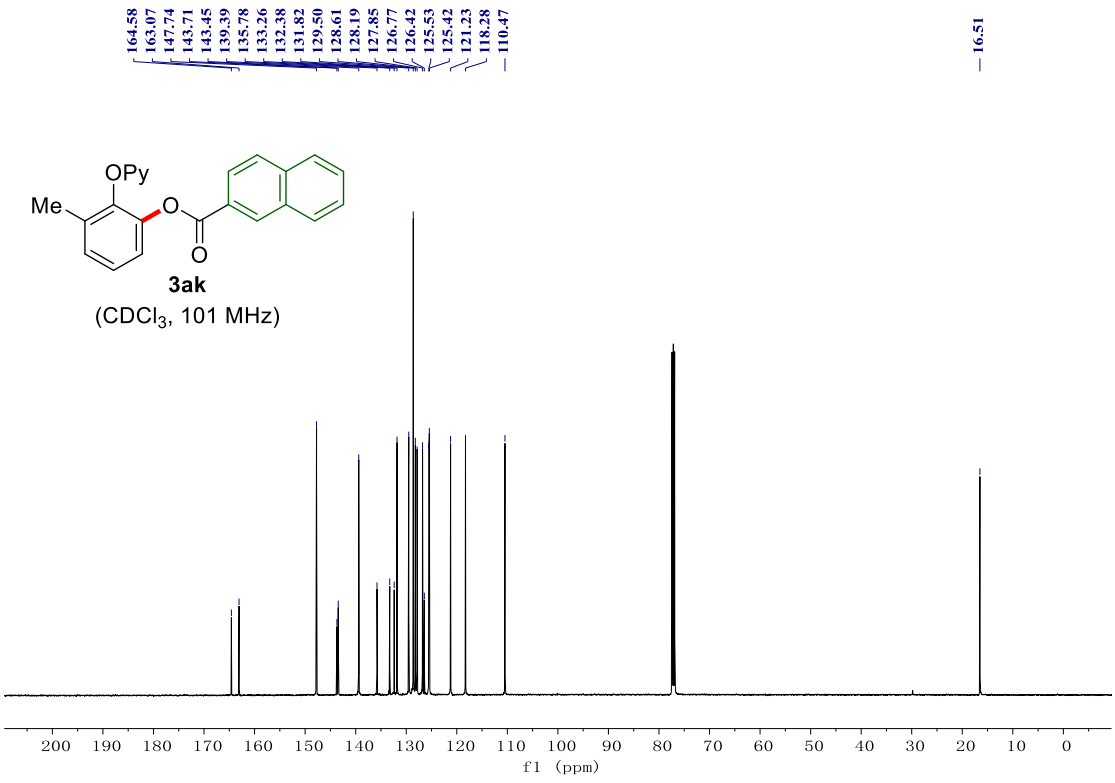
162.94
162.69
147.55
143.33
142.92
139.32
133.21
133.11
131.42
131.09
130.76
130.43
129.99
129.87
129.83
129.79
129.76
128.97
128.70
126.72
126.68
126.64
126.60
125.35
124.77
122.05
120.81
118.29
110.10
16.27

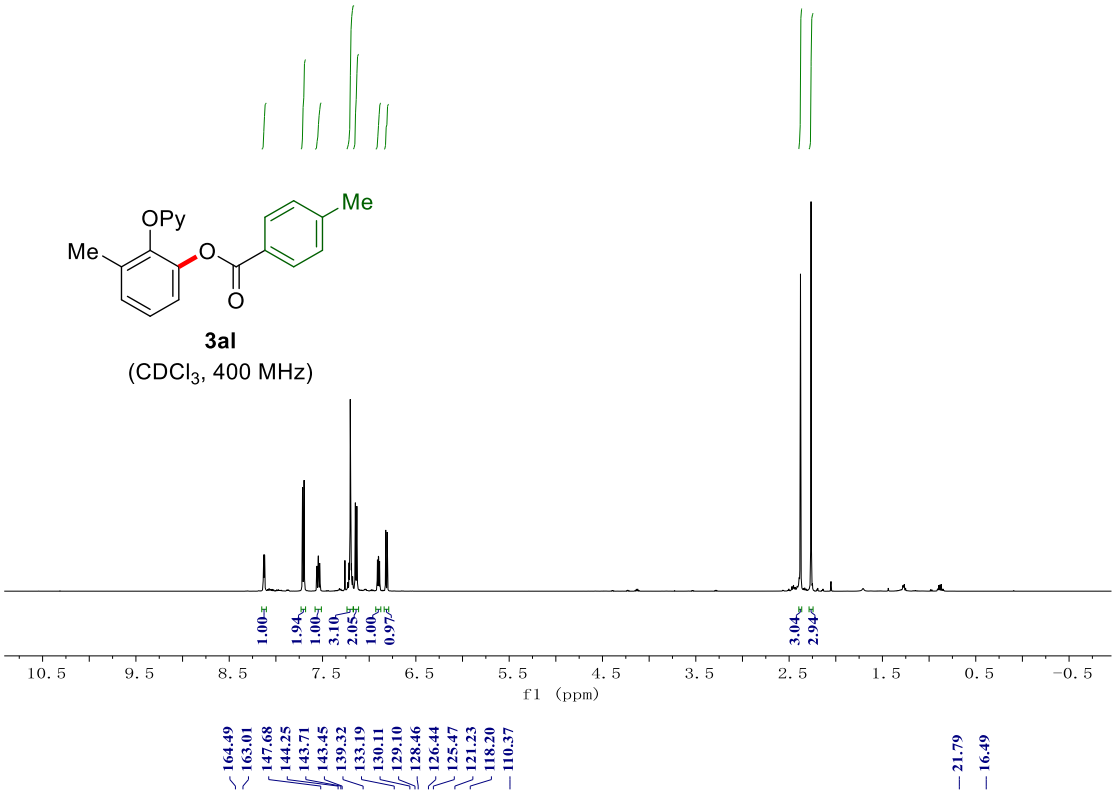

-62.81
OPy
Me
O
O
CF3
3ai
(CDCl3, 376 MHz)
-62.81
-62.75
-62.78
-62.81
-62.84
-62.87
f1 (ppm)
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


OPy
Me
O
O
CO2Me
3aj
(CDCl3, 400 MHz)
1.00
1.04
1.05
1.04
1.06
1.07
3.19
1.07
1.04
3.18
3.17
f1 (ppm)

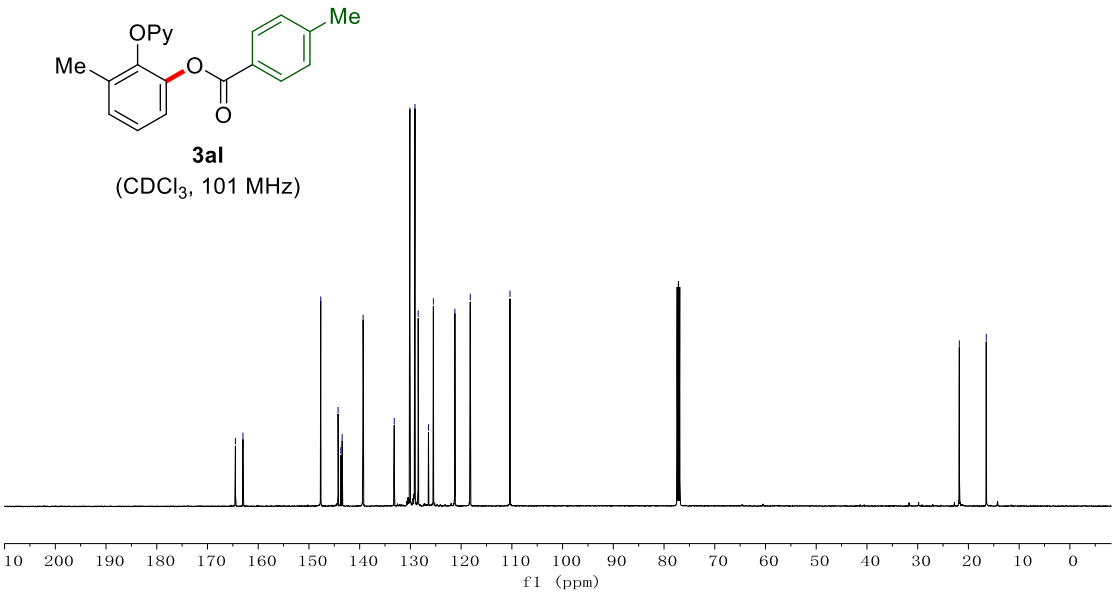

OPy
Me
O
O
CO2Me
3aj
(CDCl3, 101 MHz)
166.08
163.58
162.87
147.70
143.60
143.24
139.38
134.34
134.16
133.33
131.13
130.68
129.69
128.76
128.66
125.51
121.08
118.30
110.30
52.42
16.48
f1 (ppm)

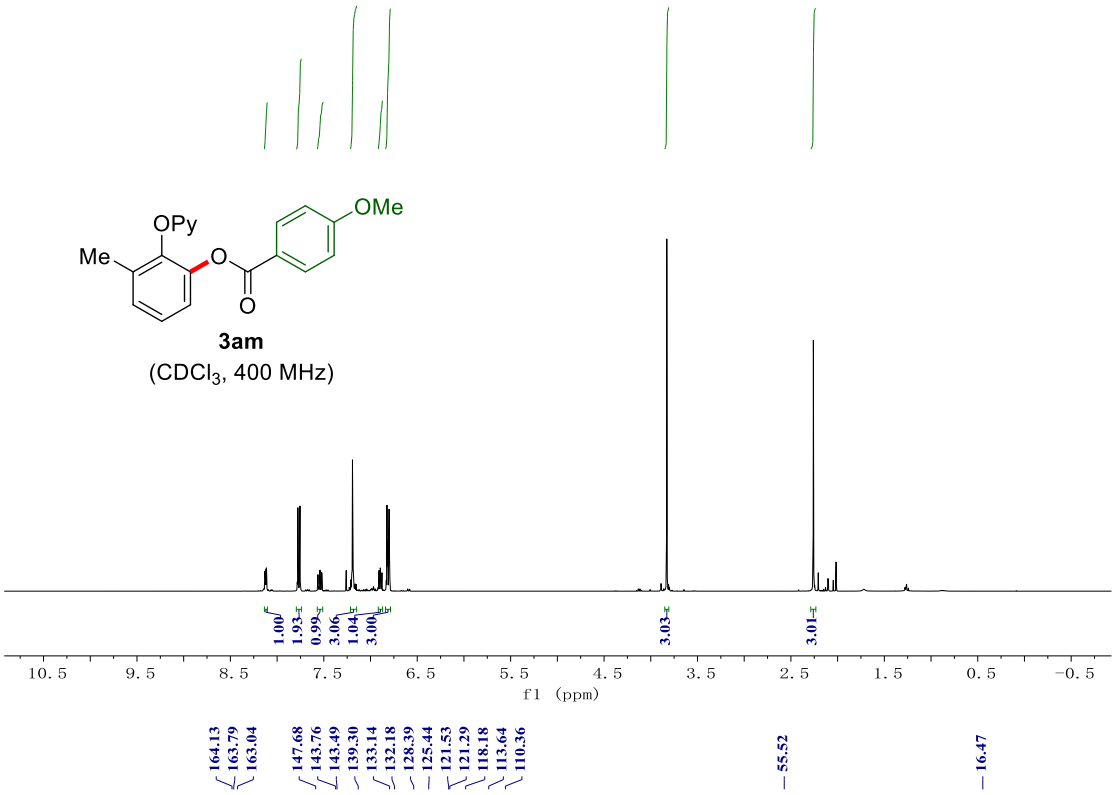

OPy
Me
O
O
3ak
(CDCl3, 400 MHz)
0.99
1.00
2.02
2.00
1.09
2.02
3.15
1.01
0.98
2.98
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
−0.5
f1 (ppm)

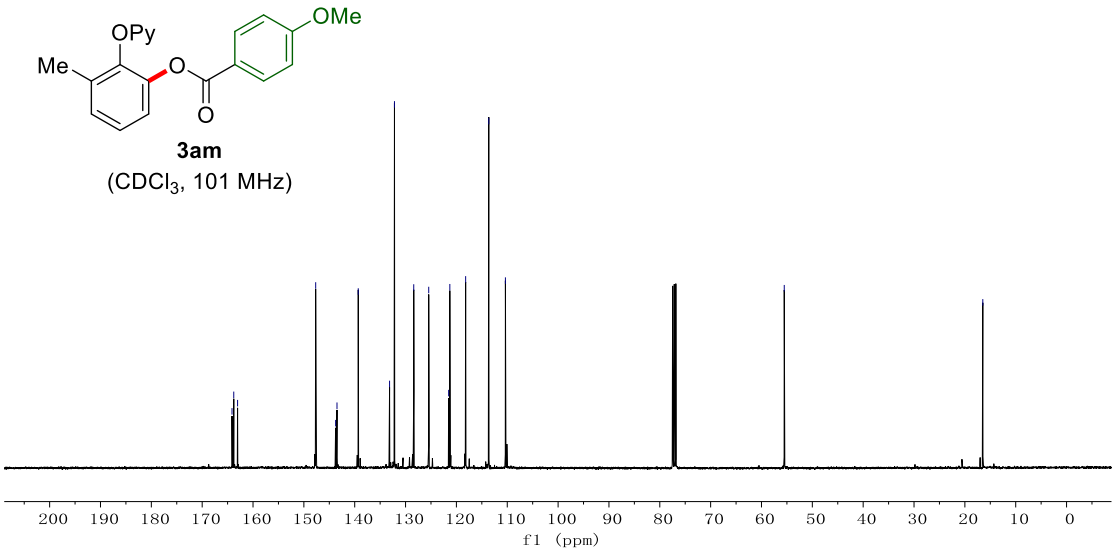

164.58
163.07
147.74
143.71
143.45
139.39
135.78
133.26
132.38
131.82
129.50
128.61
128.19
127.85
126.77
126.42
125.53
125.42
121.23
118.28
110.47
16.51
OPy
Me
O
O
3ak
(CDCl3, 101 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

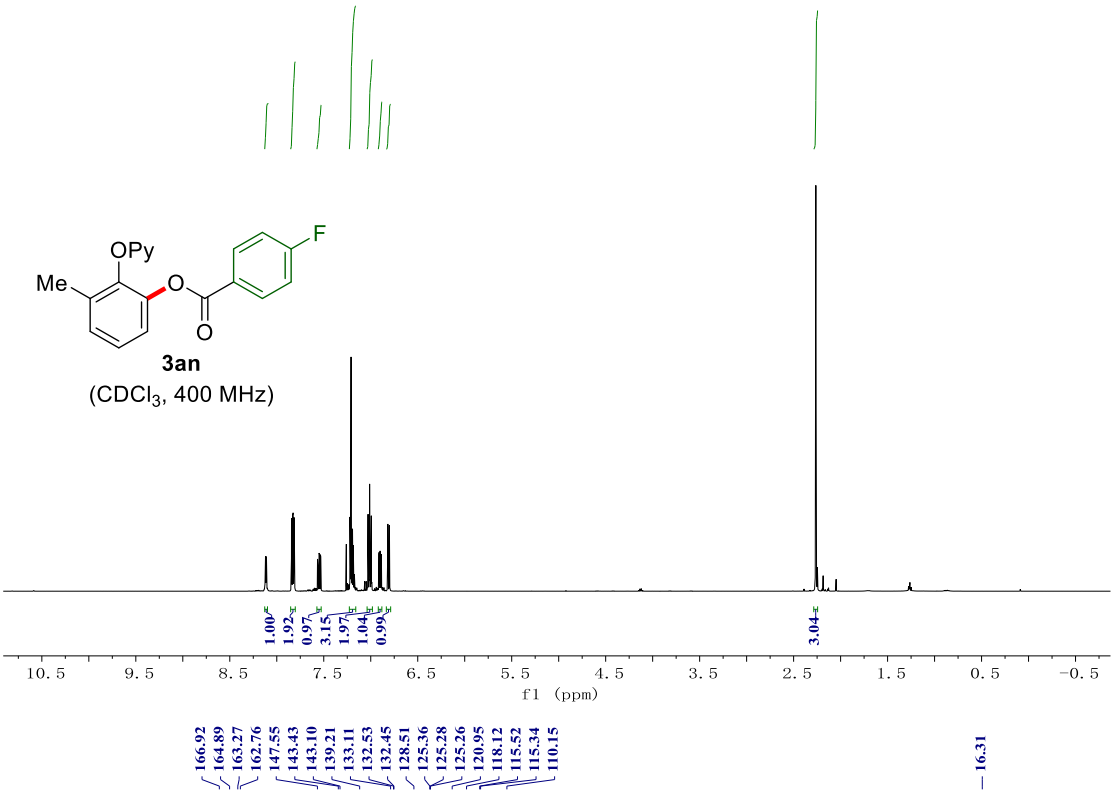

OPy
Me
O
O
Me
3al
(CDCl3, 400 MHz)
1.00
1.94
1.00
3.10
2.05
1.00
0.97
3.04
2.94
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
−0.5
f1 (ppm)

164.49
163.01
147.68
144.25
143.71
143.45
139.32
133.19
130.11
129.10
128.46
126.44
125.47
121.23
118.20
110.37
21.79
16.49

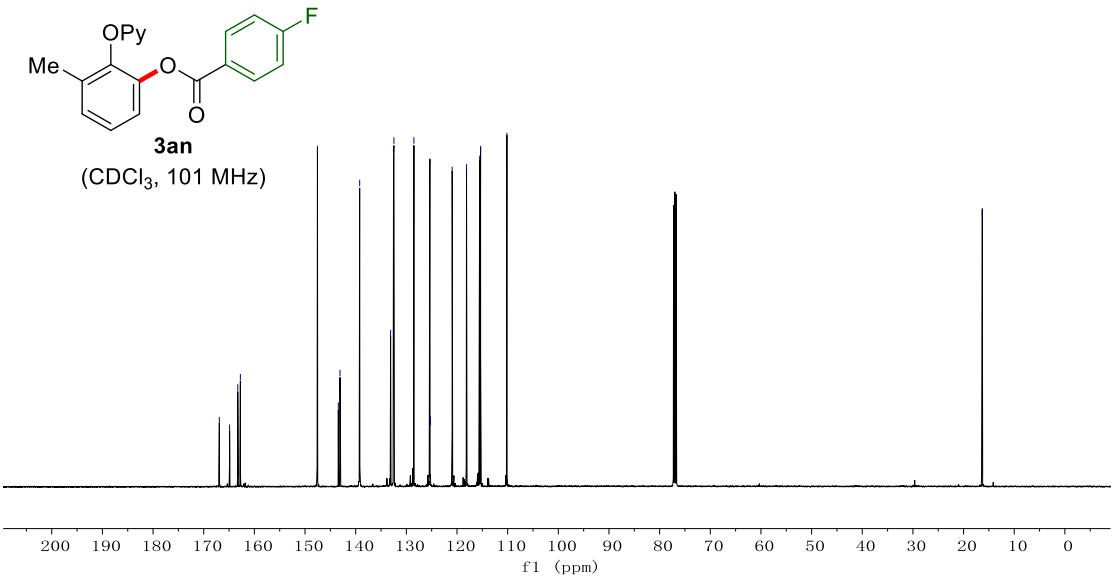

OPy
Me
O
O
Me
3al
(CDCl3, 101 MHz)
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

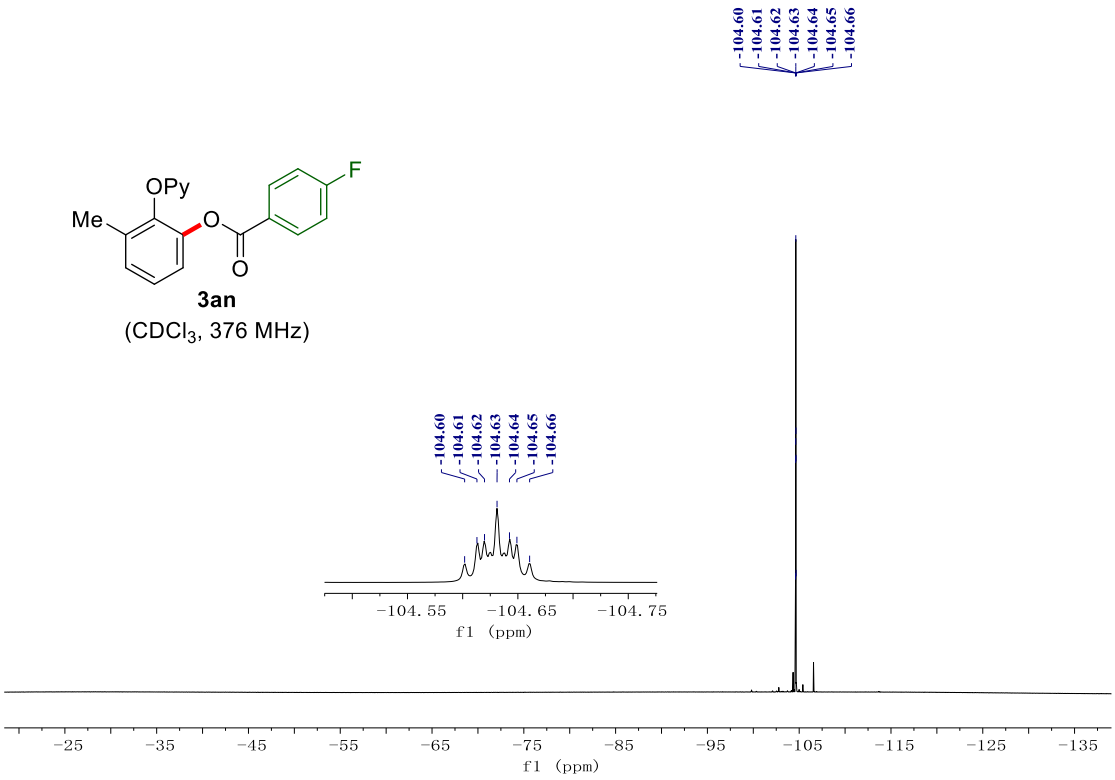

OPy
Me
O
O
OMe
3am
(CDCl3, 400 MHz)
1.00
1.93
0.99
3.06
1.04
3.00
3.03
3.01
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
−0.5
f1 (ppm)
164.13
163.79
163.04
147.68
143.76
143.49
139.30
133.14
132.18
128.39
125.44
121.53
121.29
118.18
113.64
110.36
55.52
16.47

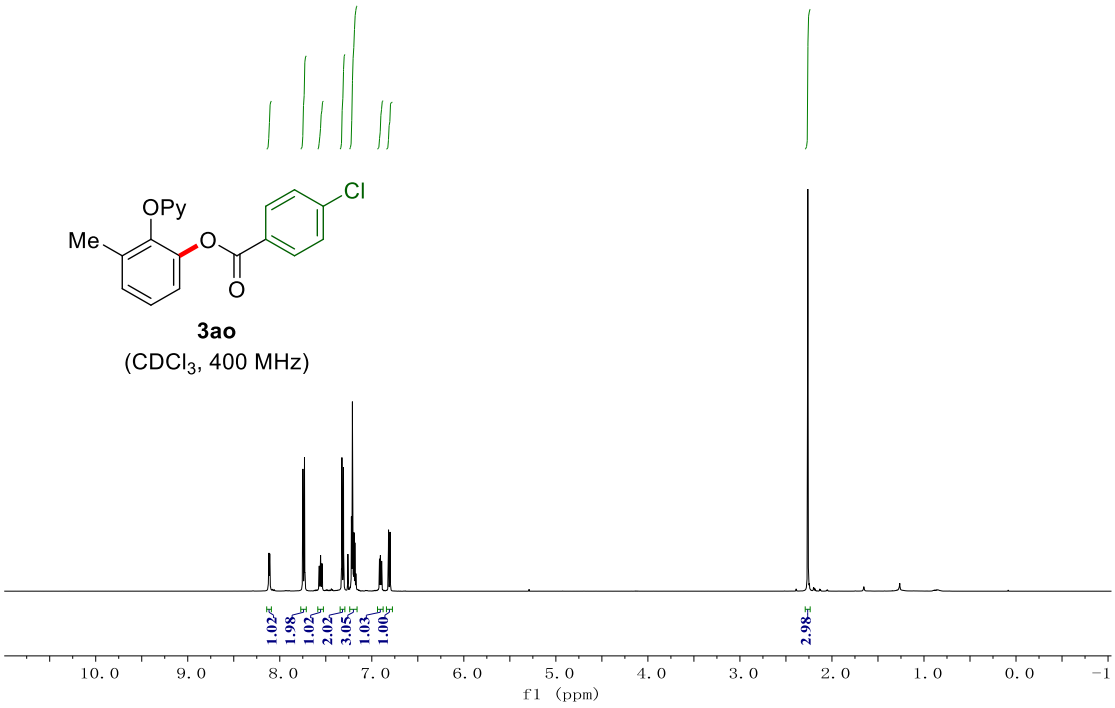

OPy
Me
O
O
OMe
3am
(CDCl3, 101 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

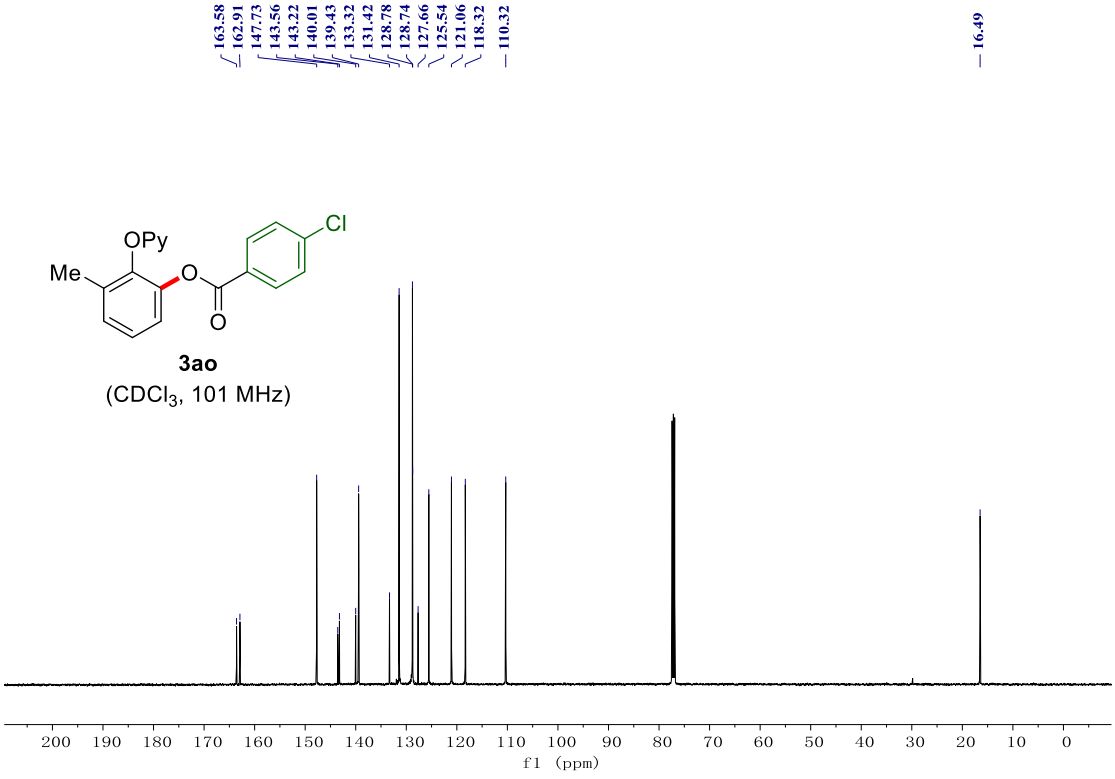

OPy
Me
O
O
F
3an
(CDCl3, 400 MHz)
1.00
1.92
0.97
3.15
1.97
1.04
0.99
3.04
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
−0.5
f1 (ppm)

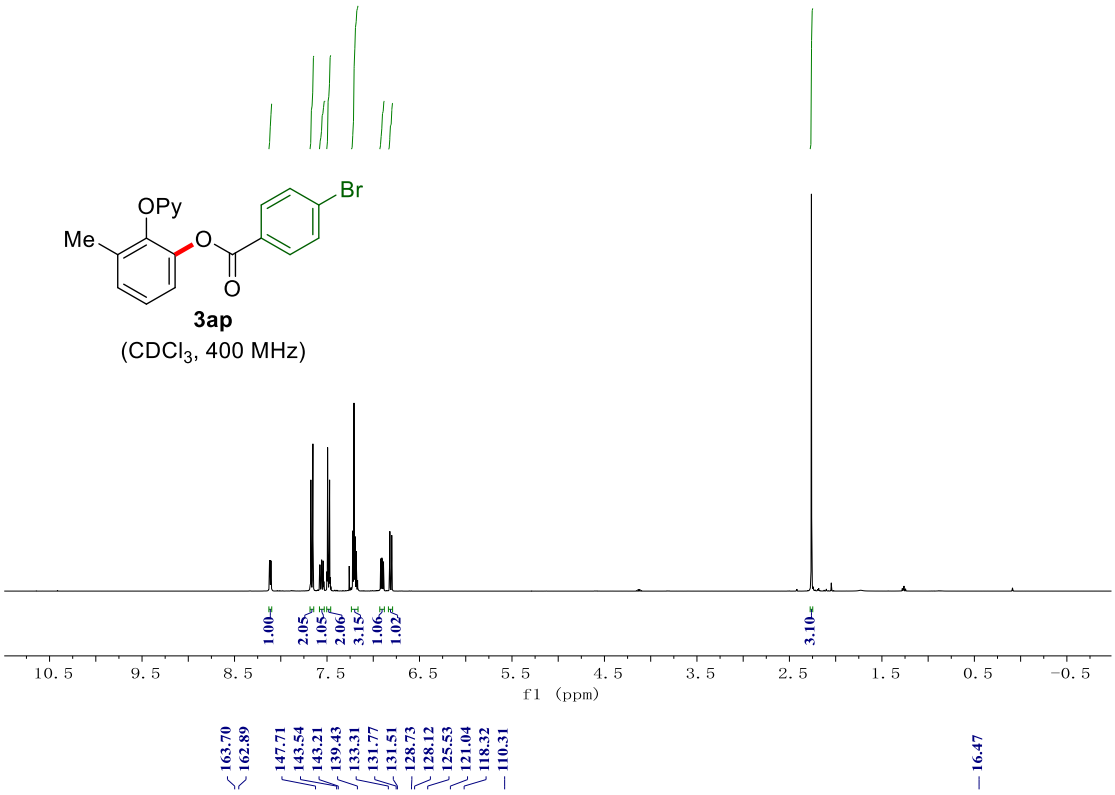
166.92
164.89
163.27
162.76
147.55
143.43
143.10
139.21
133.11
132.53
132.45
128.51
125.36
125.28
125.26
120.95
118.12
115.52
115.34
110.15
16.31

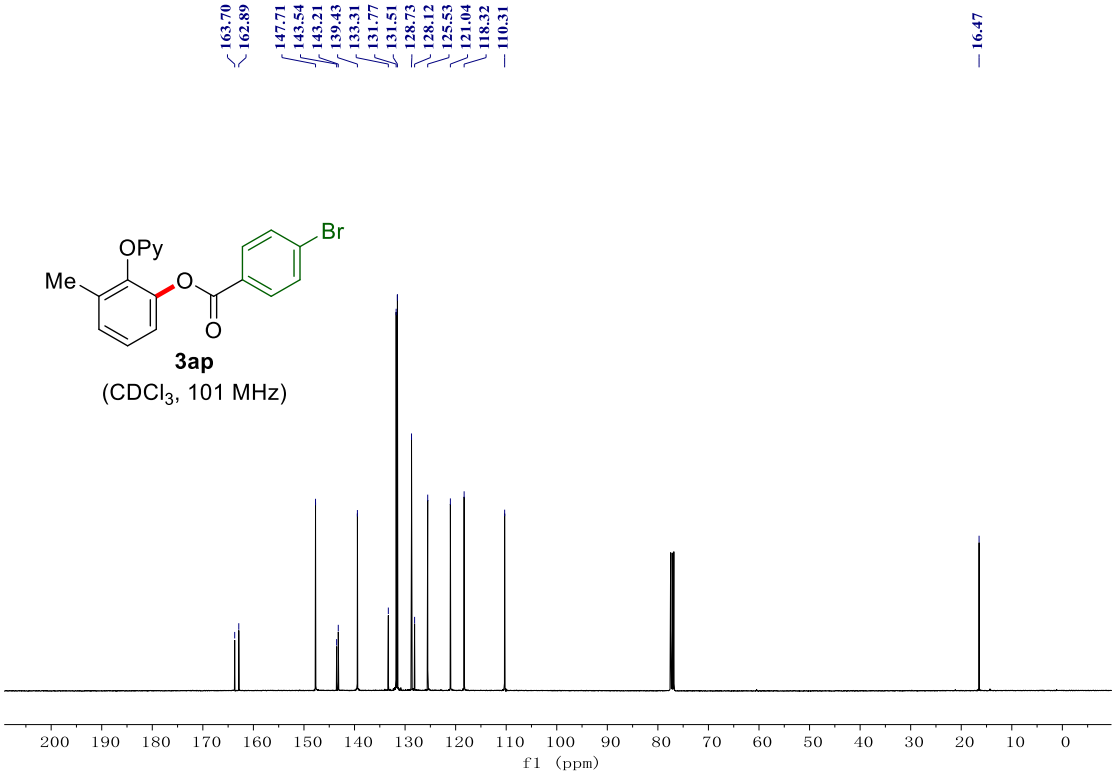

OPy
Me
O
O
F
3an
(CDCl3, 101 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

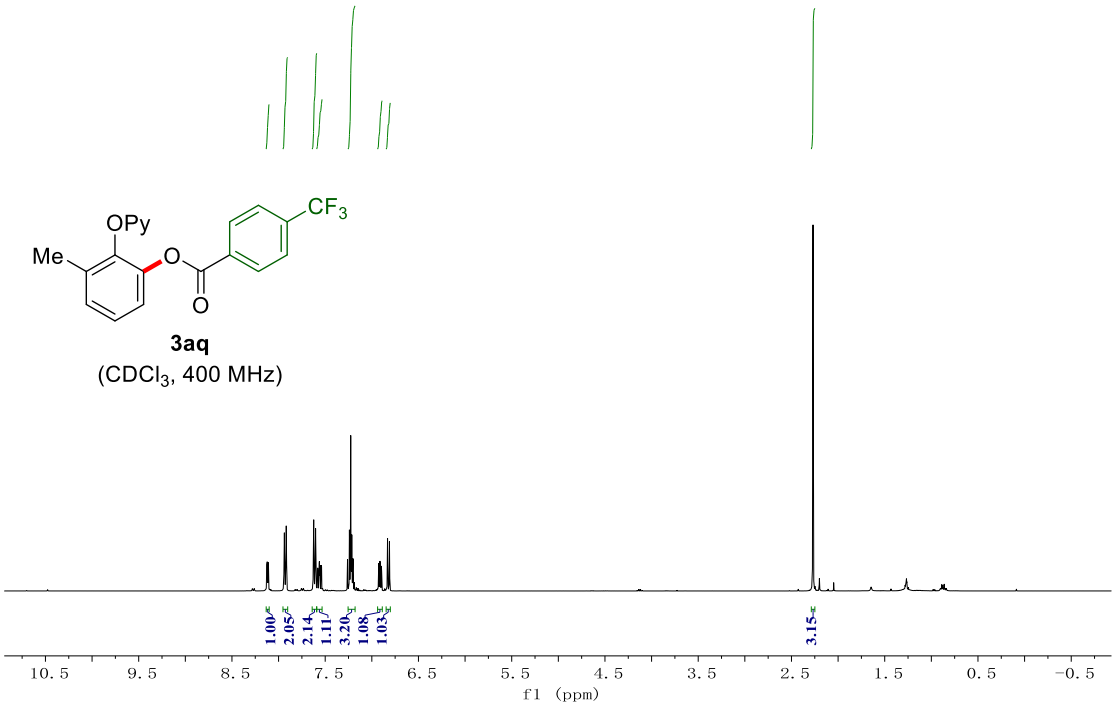

-104.60
-104.61
-104.62
-104.63
-104.64
-104.65
-104.66
OPy
Me
O
O
F
3an
(CDCl3, 376 MHz)
-104.55
-104.65
-104.75
f1 (ppm)
-25
-35
-45
-55
-65
-75
-85
-95
-105
-115
-125
-135
f1 (ppm)

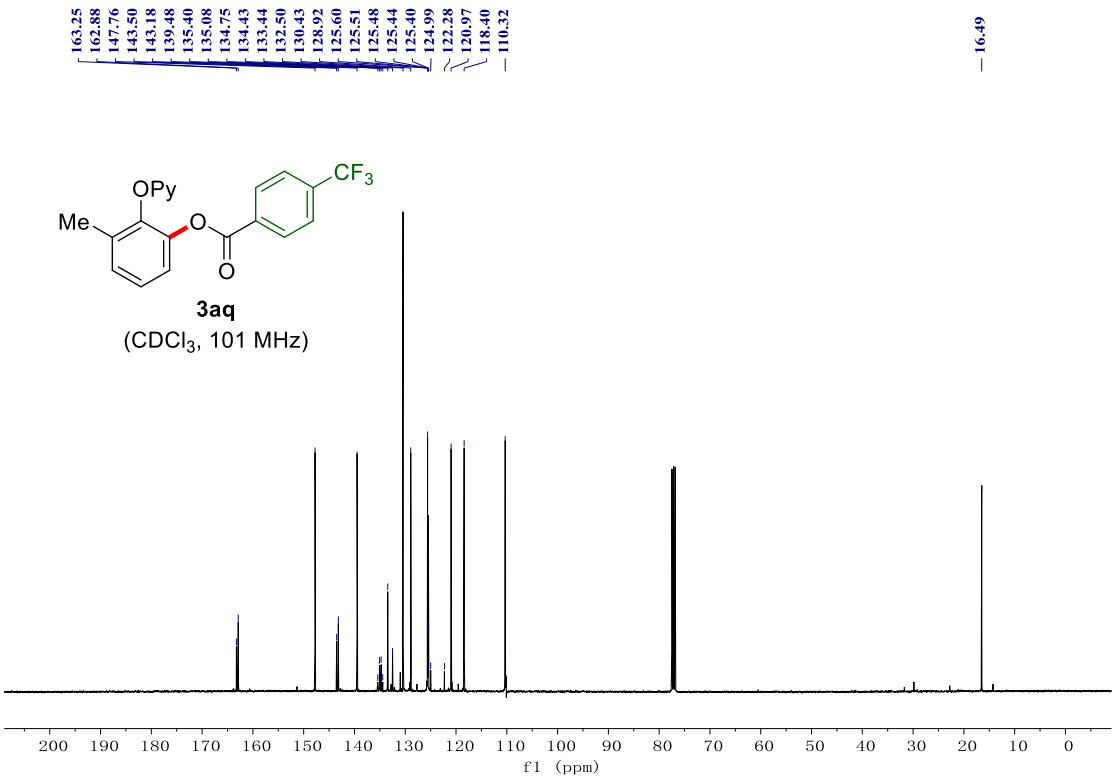

OPy
Me
O
O
Cl
3ao
(CDCl3, 400 MHz)
1.02
1.98
1.02
2.02
3.05
1.03
1.00
2.98
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
−1
f1 (ppm)

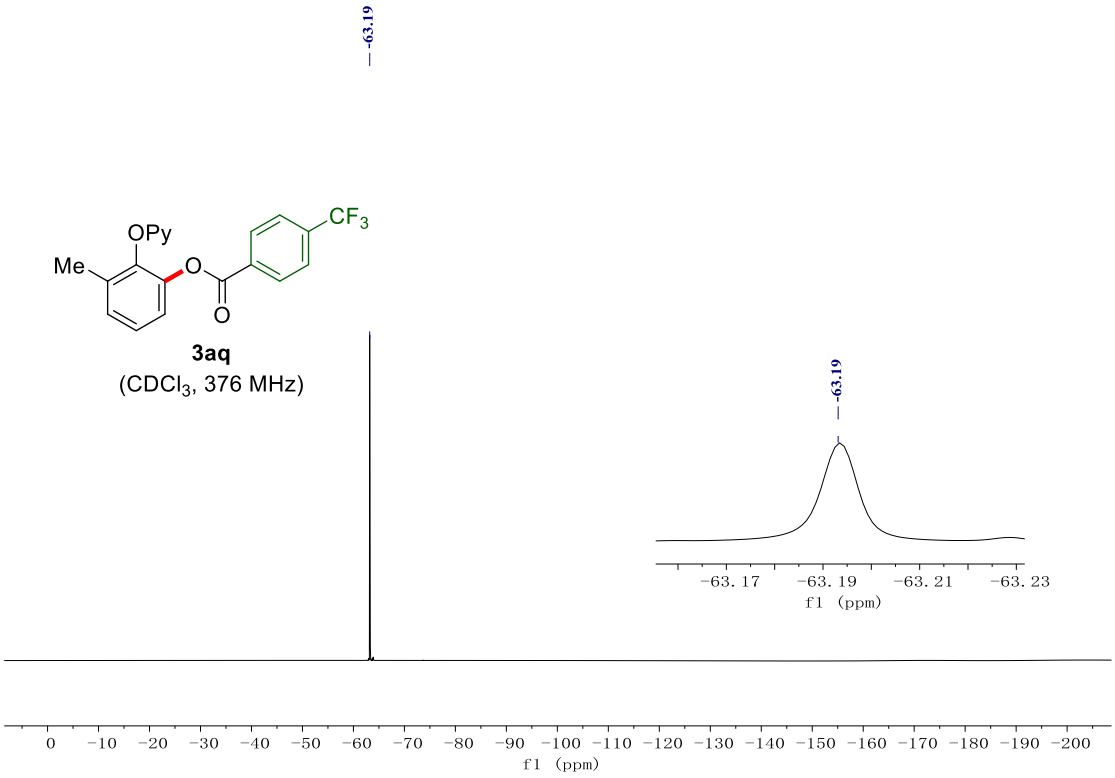

163.58
162.91
147.73
143.56
143.22
140.01
139.43
133.32
131.42
128.78
128.74
127.66
125.54
121.06
118.32
110.32
16.49
OPy
Me
O
O
Cl
3ao
(CDCl3, 101 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

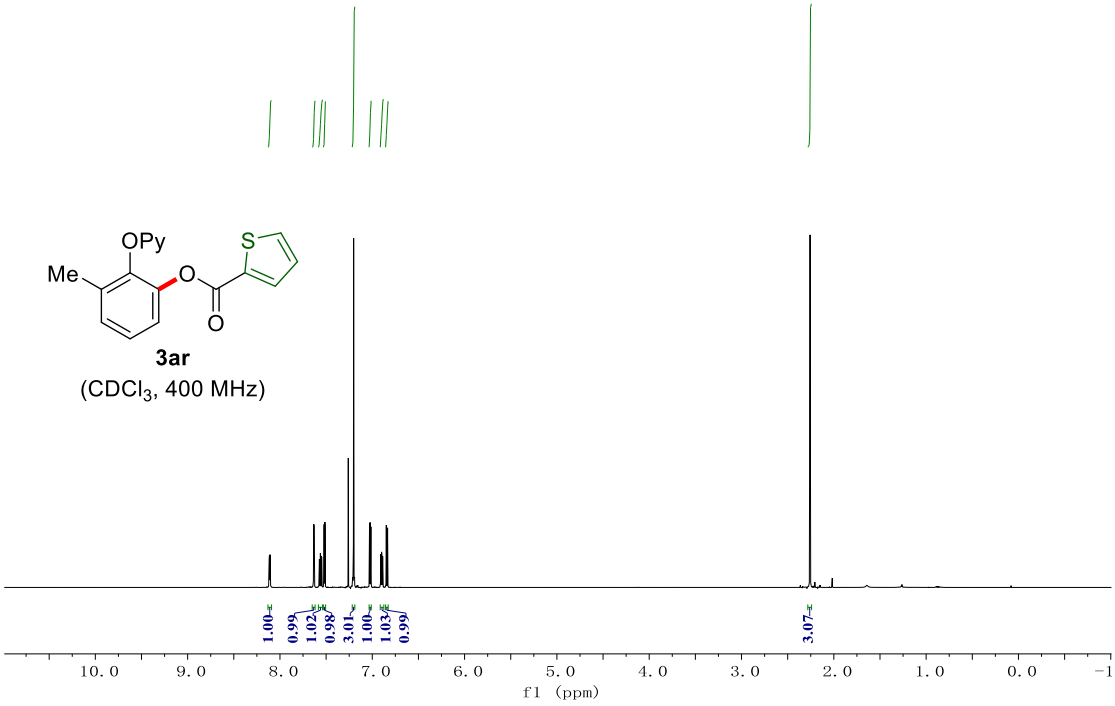

OPy
Me
O
O
Br
3ap
(CDCl3, 400 MHz)
1.00
2.05
1.05
2.06
3.15
1.06
1.02
3.10
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
−0.5
f1 (ppm)


OPy
Me
O
O
Br
3ap
(CDCl3, 101 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

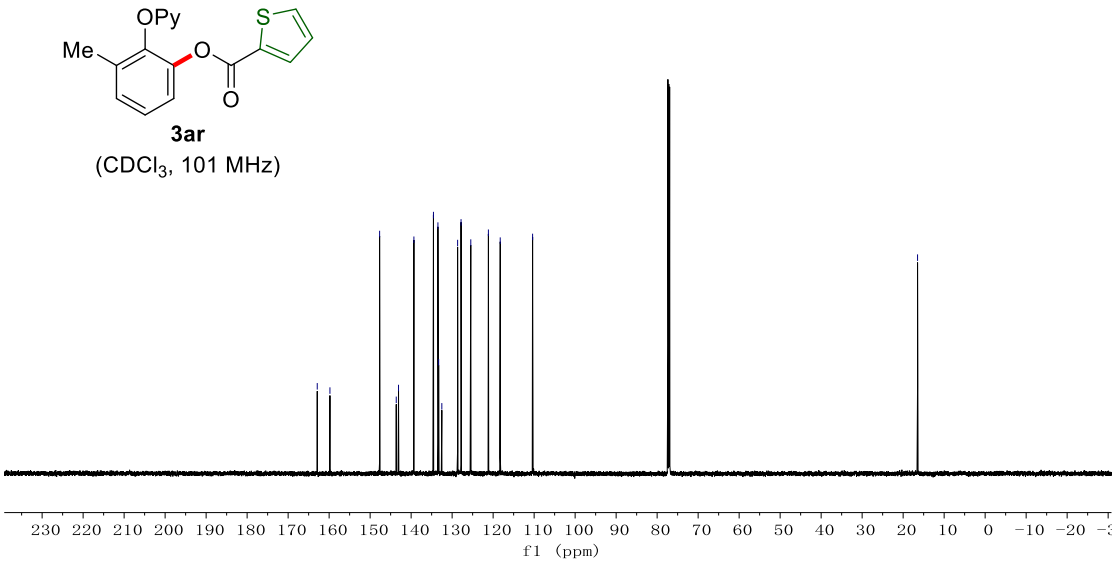

OPy
Me
O
O
CF3
3aq
(CDCl3, 400 MHz)
1.00
2.05
2.14
1.11
3.20
1.08
1.03
3.15
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
−0.5
f1 (ppm)

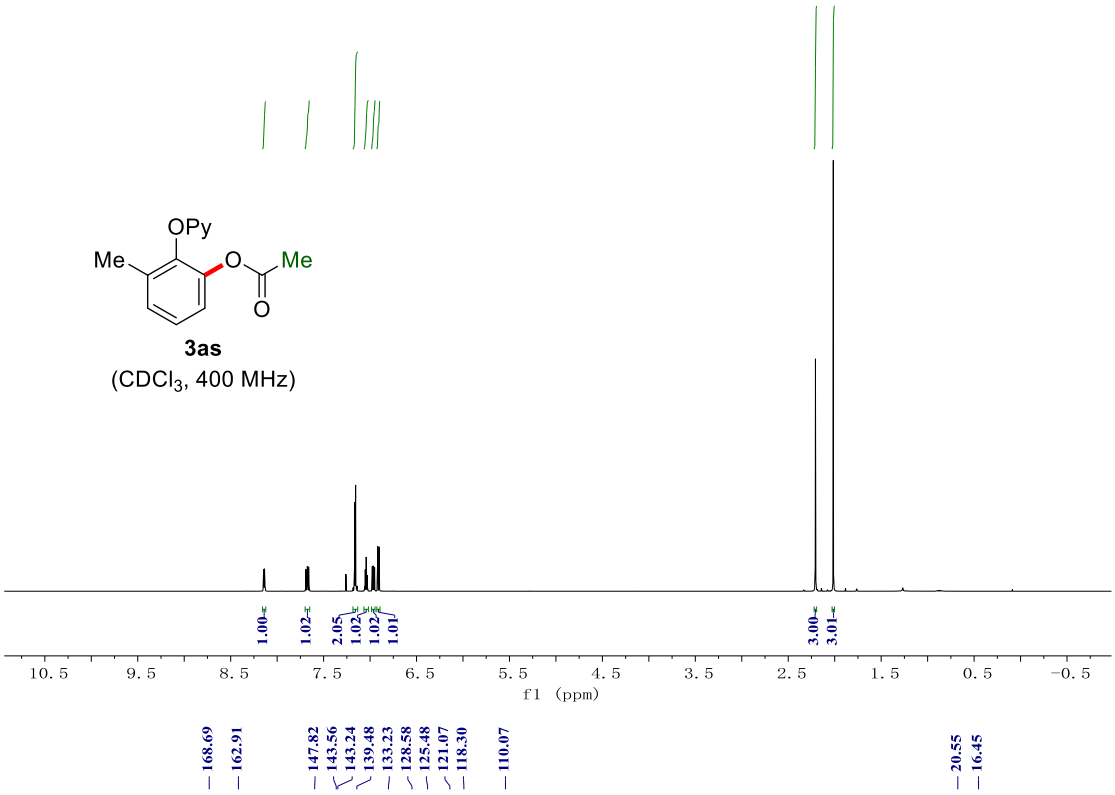

163.25
162.88
147.76
143.50
143.18
139.48
135.40
135.08
134.75
134.43
133.44
132.50
130.43
128.92
125.60
125.51
125.48
125.44
125.40
124.99
122.28
120.97
118.40
110.32
16.49
OPy
Me
O
O
CF3
3aq
(CDCl3, 101 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

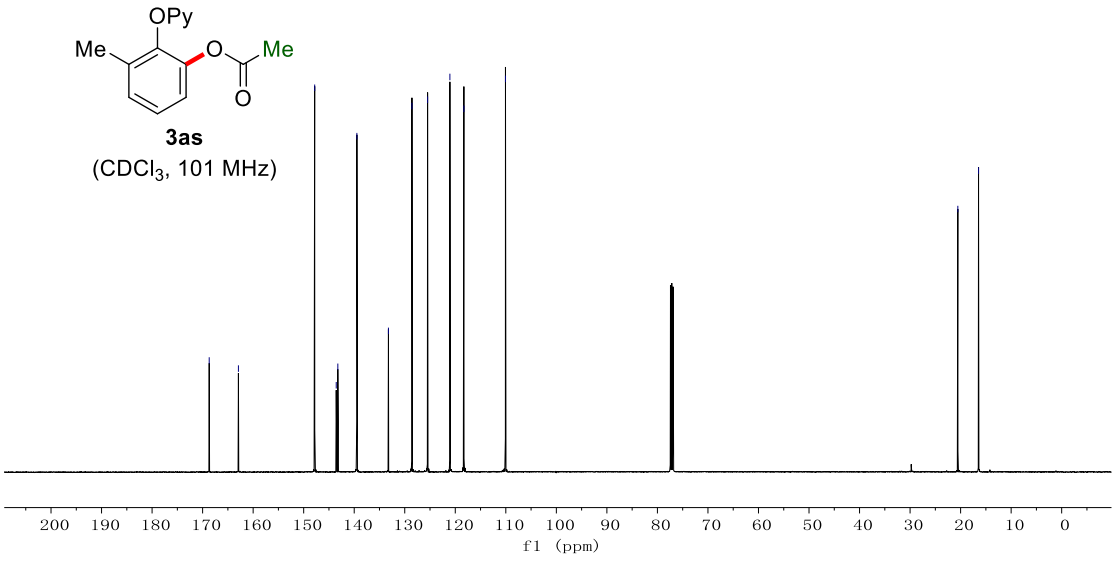

-63.19
OPy
Me
O
O
CF3
3aq
(CDCl3, 376 MHz)
-63.19
-63.17
-63.19
-63.21
-63.23
f1 (ppm)
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

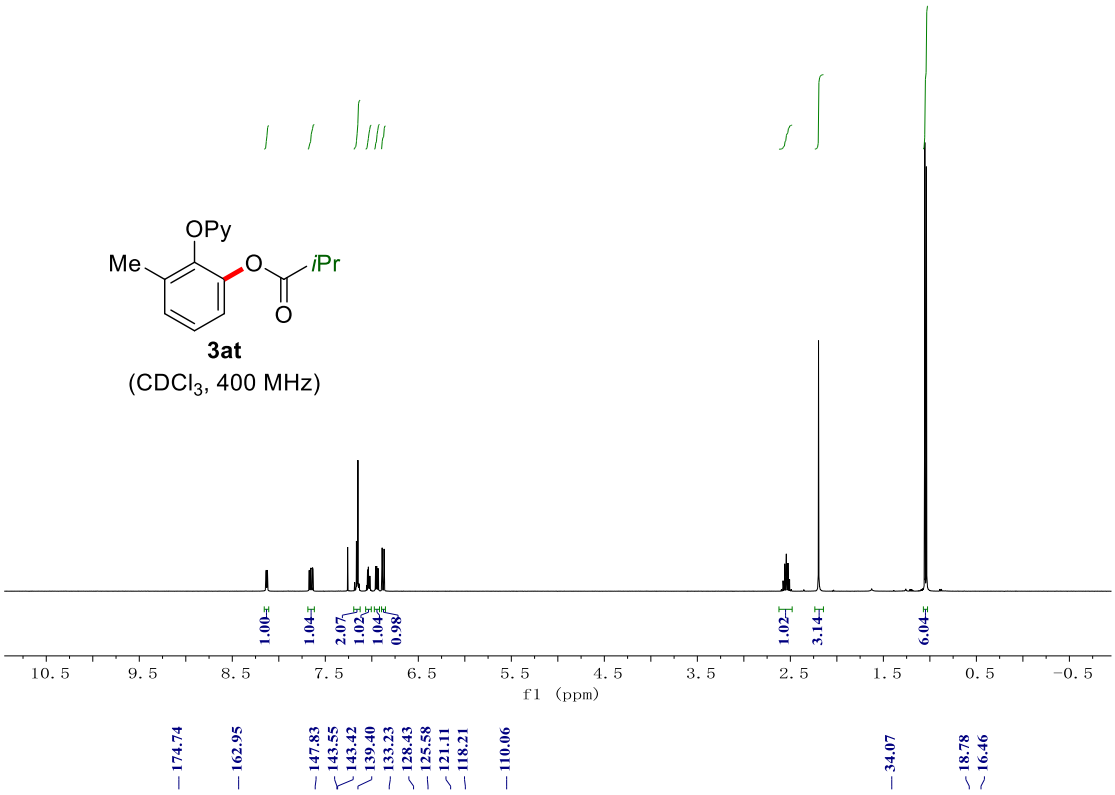

OPy
Me
O
S
O
3ar
(CDCl3, 400 MHz)
1.00
0.99
1.02
0.98
3.01
1.00
1.03
0.99
3.07
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

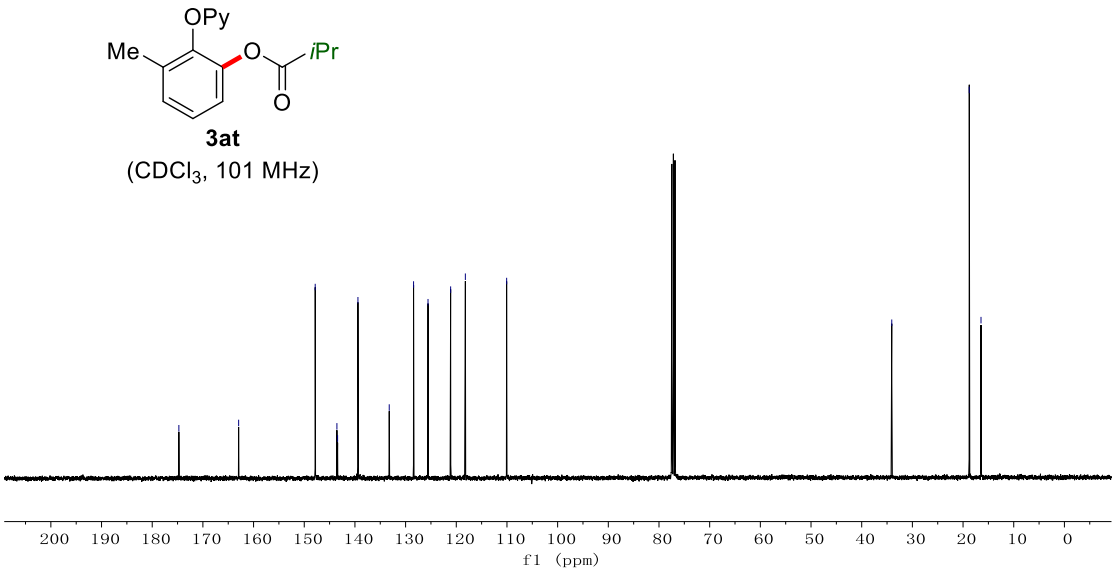

162.90
159.80
147.69
143.63
143.08
139.32
134.56
133.47
133.28
132.51
128.67
127.83
125.45
121.15
118.27
110.38
16.48

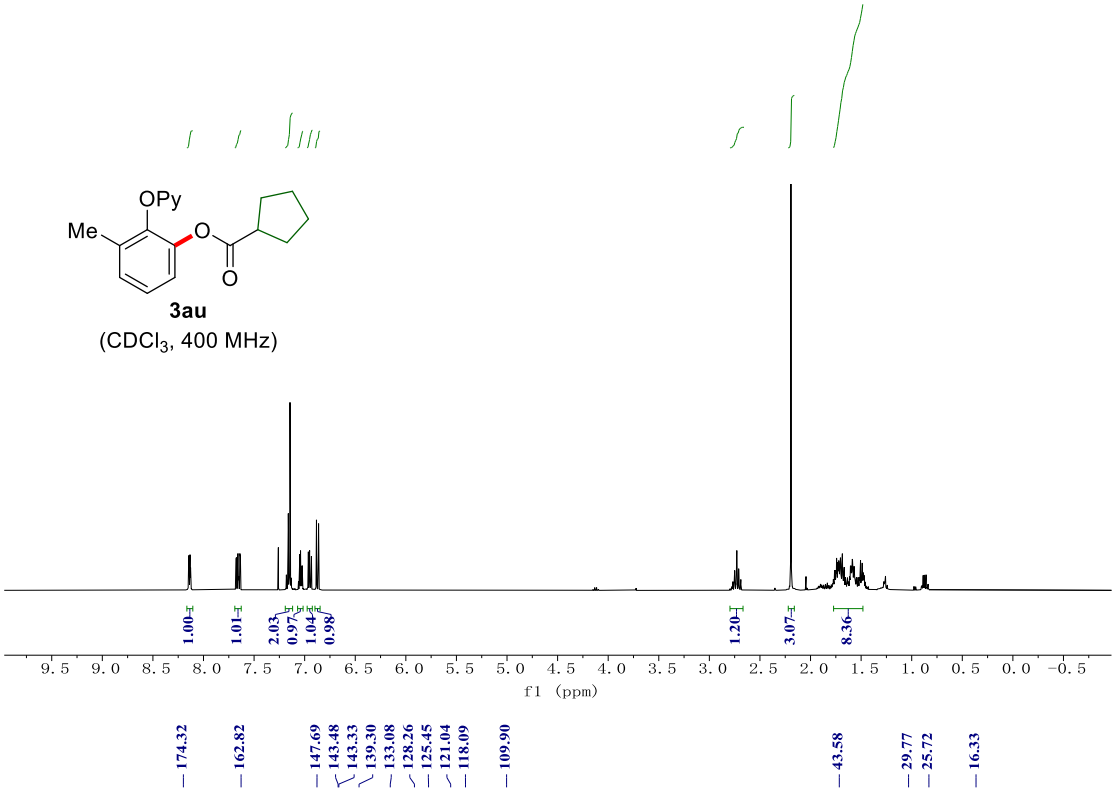

OPy
Me
O
S
O
3ar
(CDCl3, 101 MHz)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)

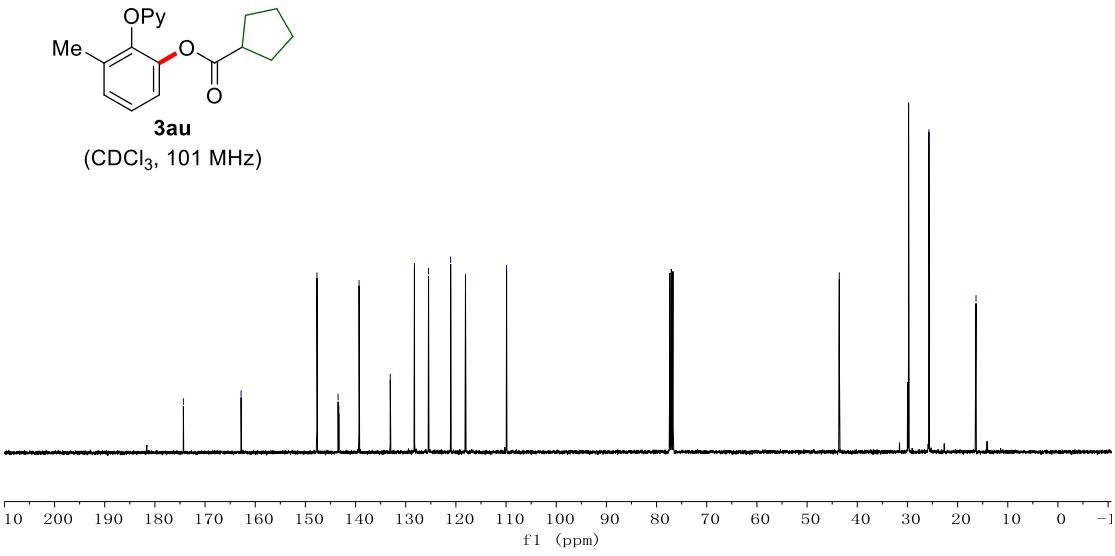

OPy
Me
O
Me
O
3as
(CDCl3, 400 MHz)
1.00
1.02
2.05
1.02
1.02
1.01
3.00
3.01
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
−0.5
f1 (ppm)
168.69
162.91
147.82
143.56
143.24
139.48
133.23
128.58
125.48
121.07
118.30
110.07
20.55
16.45

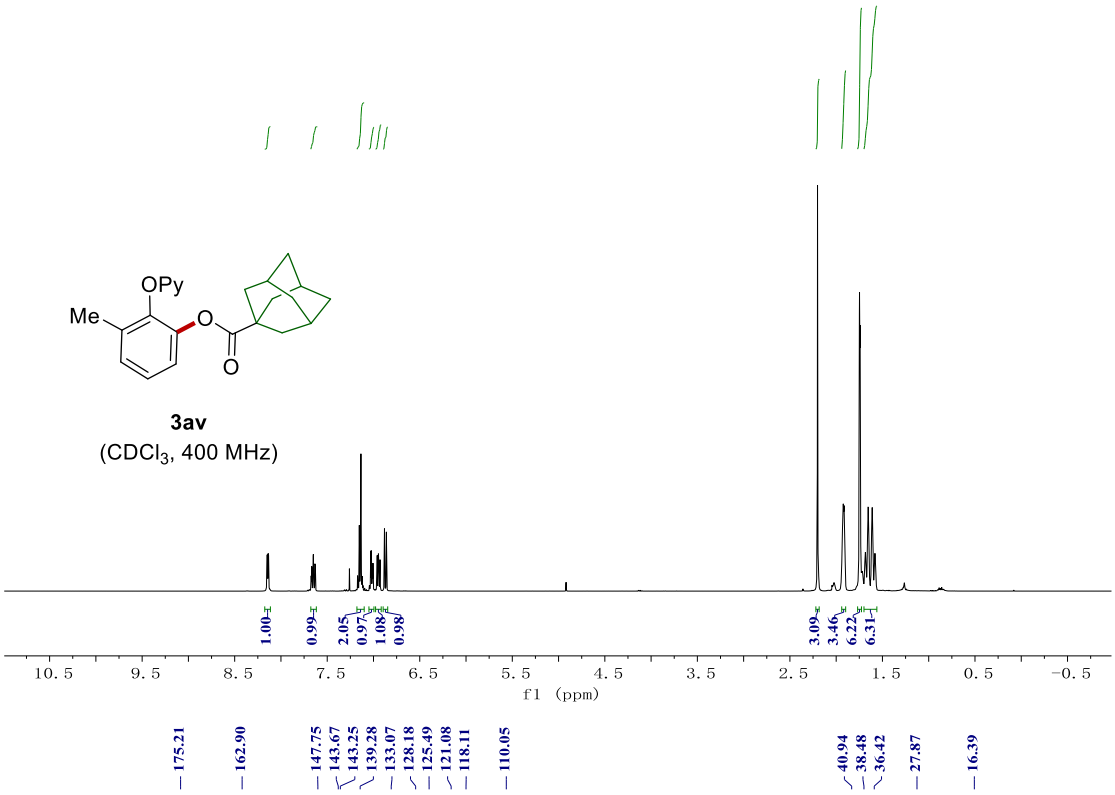

OPy
Me
O
Me
O
3as
(CDCl3, 101 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

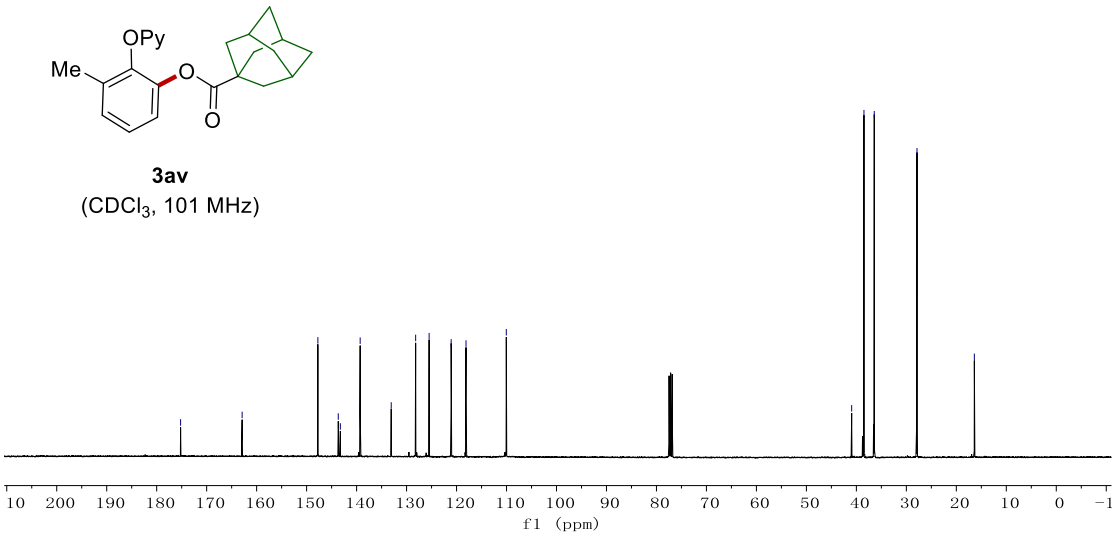

OPy
Me
O
iPr
O
3at
(CDCl3, 400 MHz)
1.00
1.04
2.07
1.02
1.04
0.98
1.02
3.14
6.04
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
−0.5
f1 (ppm)
174.74
162.95
147.83
143.55
143.42
139.40
133.23
128.43
125.58
121.11
118.21
110.06
34.07
18.78
16.46

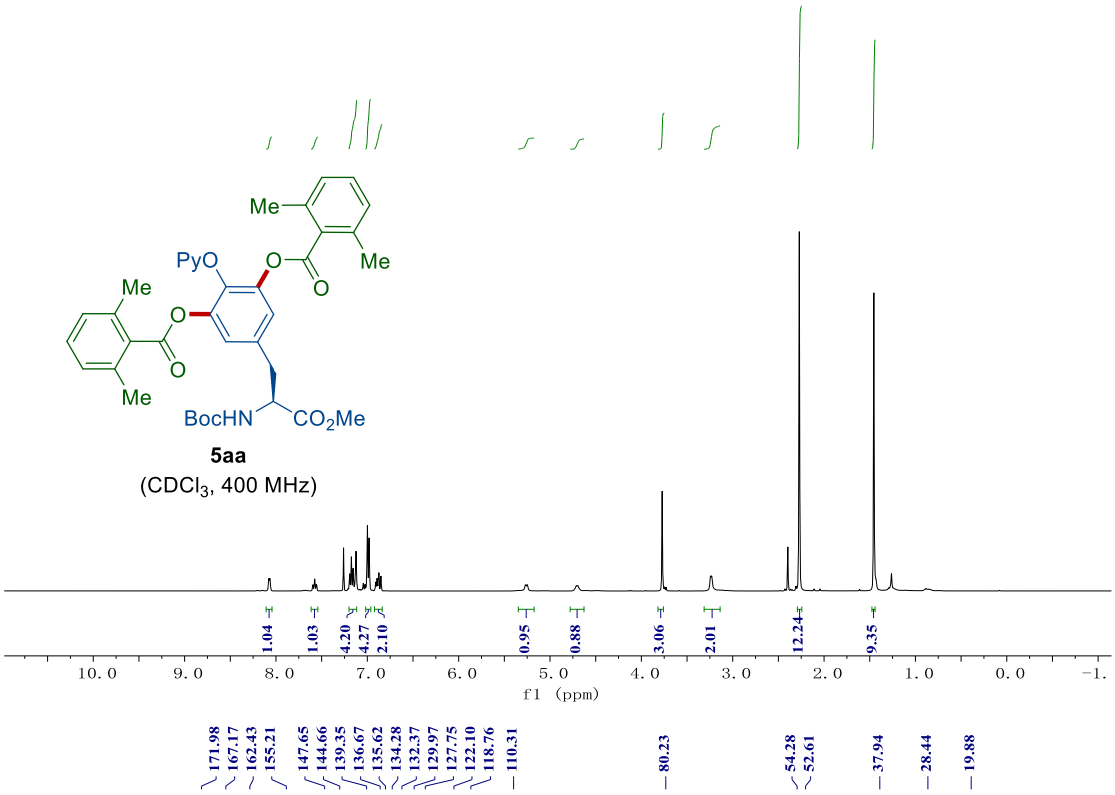

OPy
Me
O
iPr
O
3at
(CDCl3, 101 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OPy
Me
O
O
3au
(CDCl3, 400 MHz)
1.00
1.01
2.03
0.97
1.04
0.98
1.20
3.07
8.36
f1 (ppm)
174.32
162.82
147.69
143.48
143.33
139.30
133.08
128.26
125.45
121.04
118.09
109.90
43.58
29.77
25.72
16.33


OPy
Me
O
O
3au
(CDCl3, 101 MHz)
f1 (ppm)

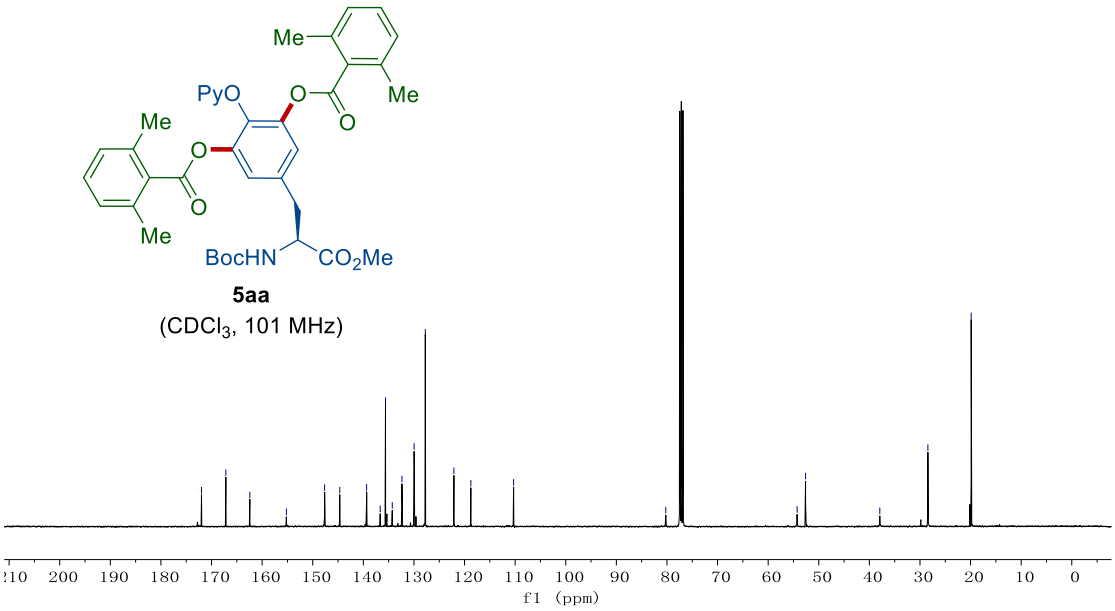

OPy
Me
O
O
3av
(CDCl3, 400 MHz)
1.00
0.99
2.05
0.97
1.08
0.98
3.09
3.46
6.22
6.31
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
−0.5
f1 (ppm)
175.21
162.90
147.75
143.67
143.25
139.28
133.07
128.18
125.49
121.08
118.11
110.05
40.94
38.48
36.42
27.87
16.39


OPy
Me
O
O
3av
(CDCl3, 101 MHz)
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−1
f1 (ppm)



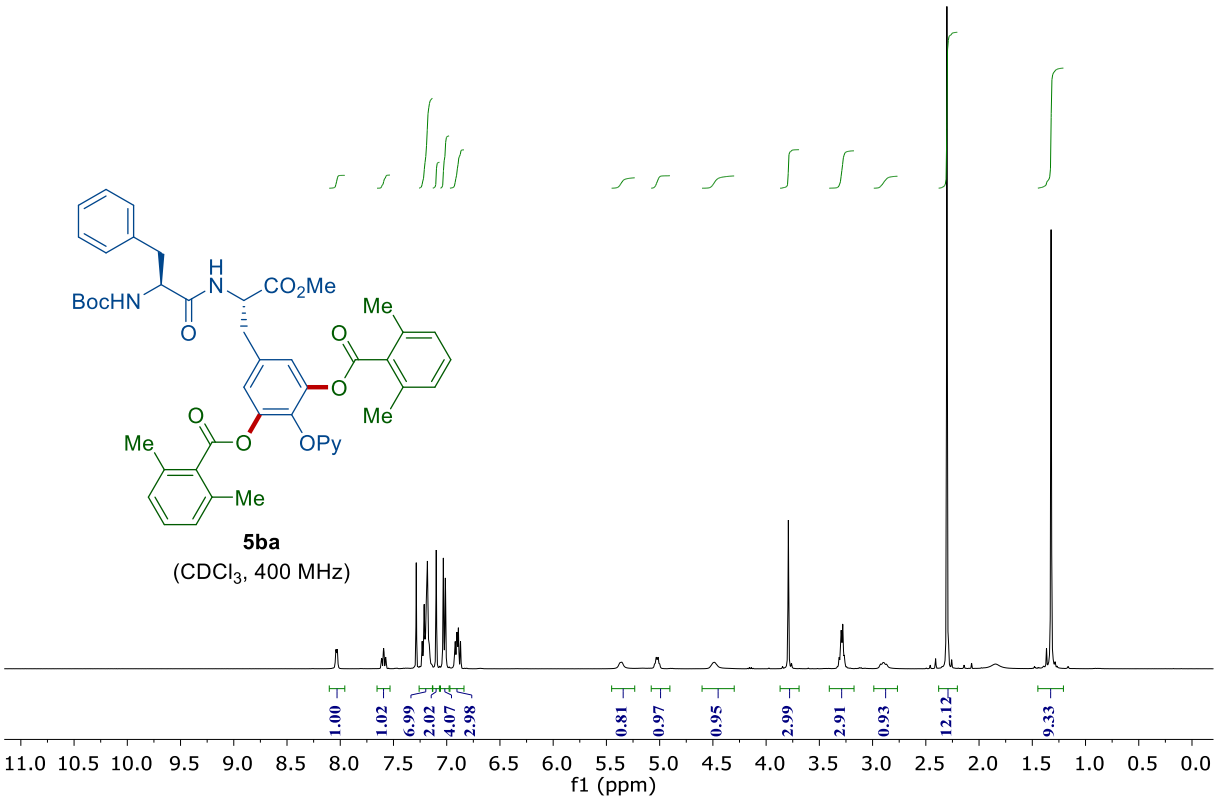
5aa

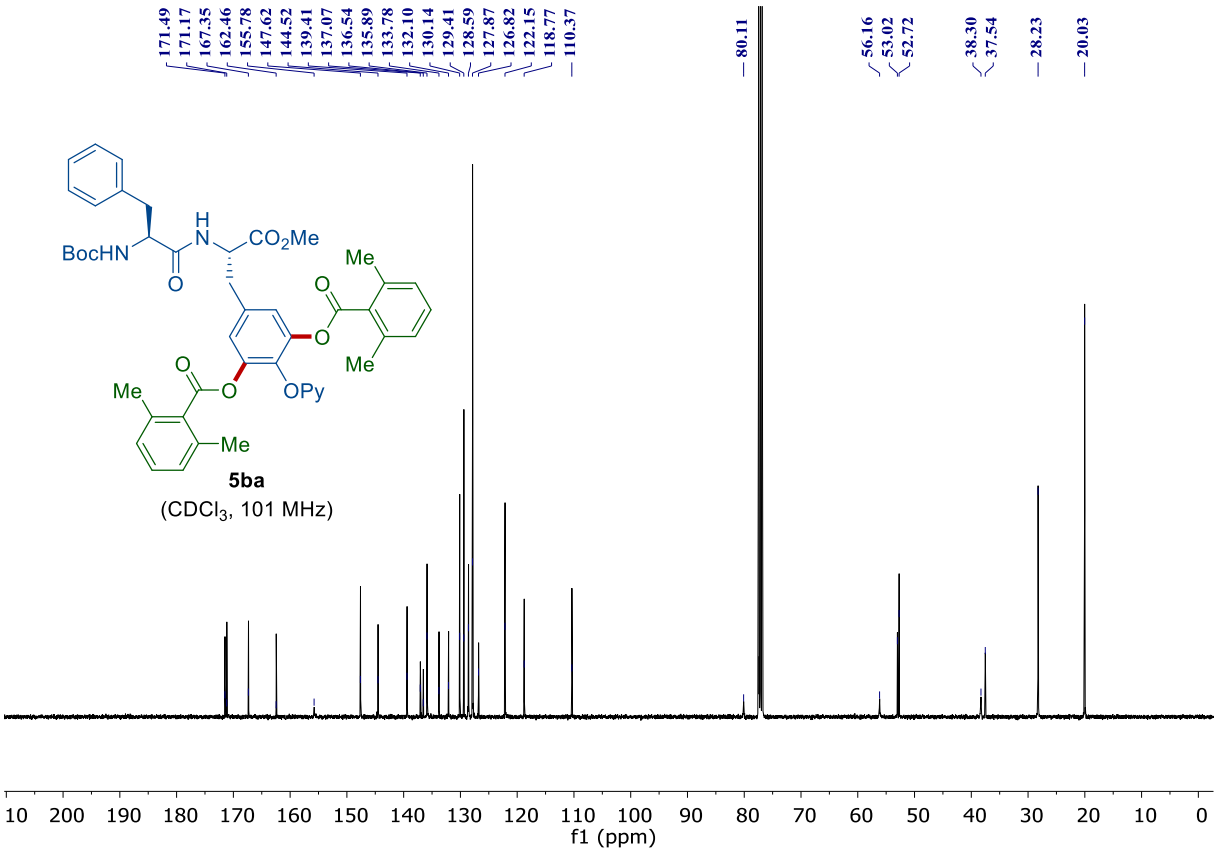
($CDCl_3$, 400 MHz)

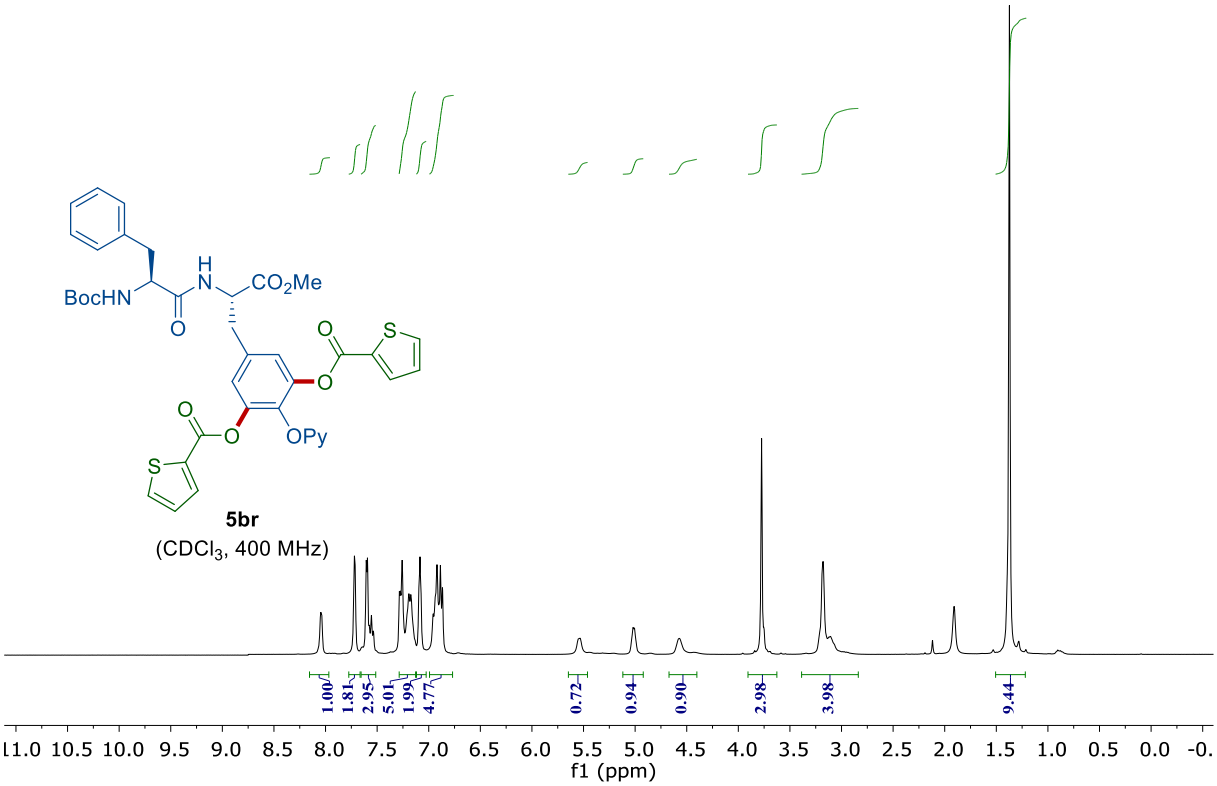


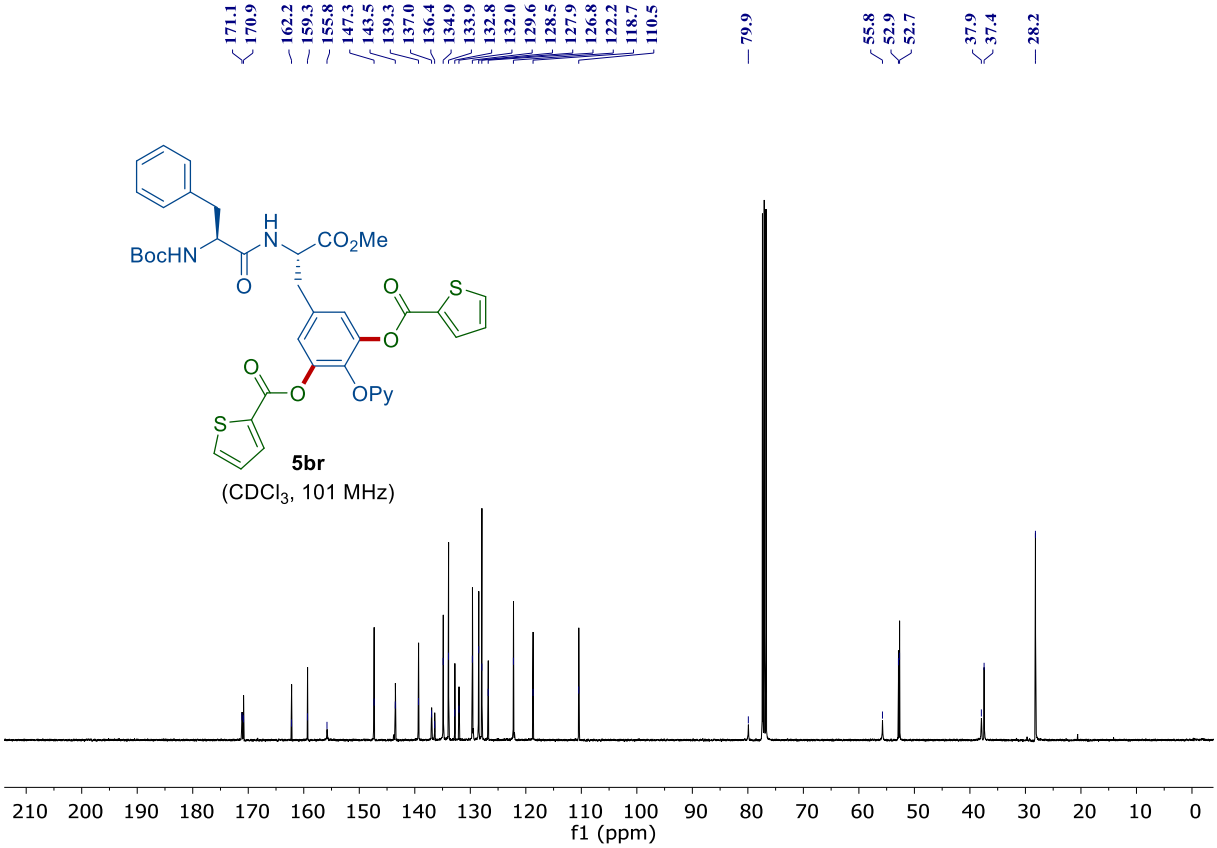
5aa

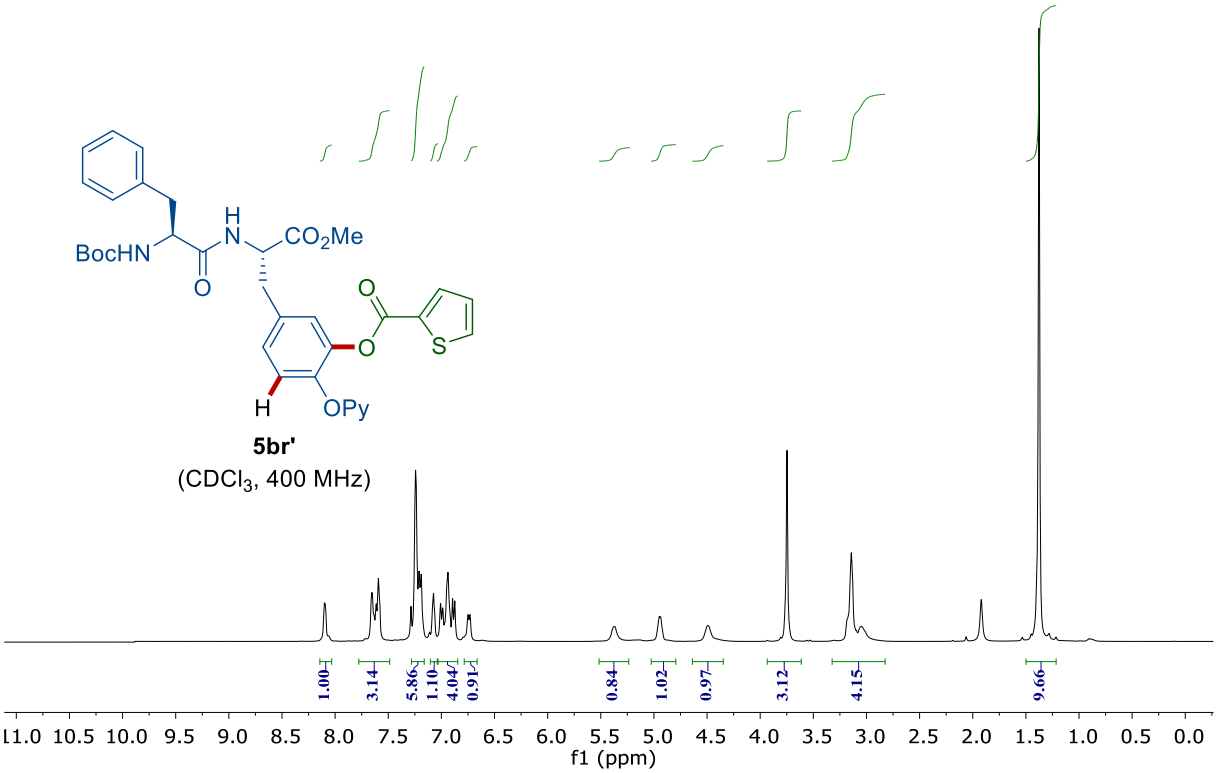
($CDCl_3$, 101 MHz)


BocHN
H
N
CO2Me
O
Me
O
O
Me
O
O
Me
OPy
Me
5ba
(CDCl3, 400 MHz)
1.00
1.02
6.99
2.02
4.07
2.98
0.81
0.97
0.95
2.99
2.91
0.93
12.12
9.33
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


171.49
171.17
167.35
162.46
155.78
147.62
144.52
139.41
137.07
136.54
135.89
133.78
132.10
130.14
129.41
128.59
127.87
126.82
122.15
118.77
110.37
80.11
56.16
53.02
52.72
38.30
37.54
28.23
20.03
BocHN
H
N
CO2Me
O
Me
O
O
Me
O
O
Me
OPy
Me
5ba
(CDCl3, 101 MHz)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

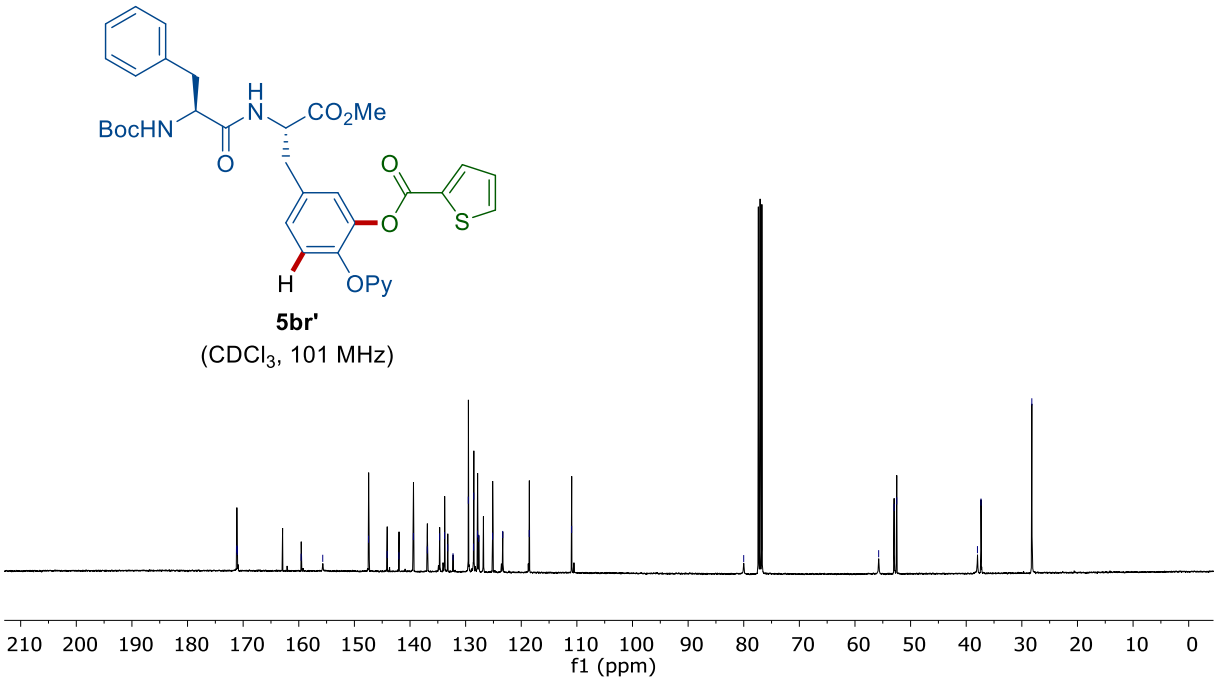

BocHN
H
N
CO2Me
O
O
O
S
O
O
OPy
S
5br
(CDCl3, 400 MHz)
1.00
1.81
2.95
5.01
1.99
4.77
0.72
0.94
0.90
2.98
3.98
9.44
f1 (ppm)


171.1
170.9
162.2
159.3
155.8
147.3
143.5
139.3
137.0
136.4
134.9
133.9
132.8
132.0
129.6
128.5
127.9
126.8
122.2
118.7
110.5
79.9
55.8
52.9
52.7
37.9
37.4
28.2
BocHN
H
N
CO2Me
O
O
O
S
O
O
OPy
S
5br
(CDCl3, 101 MHz)
f1 (ppm)



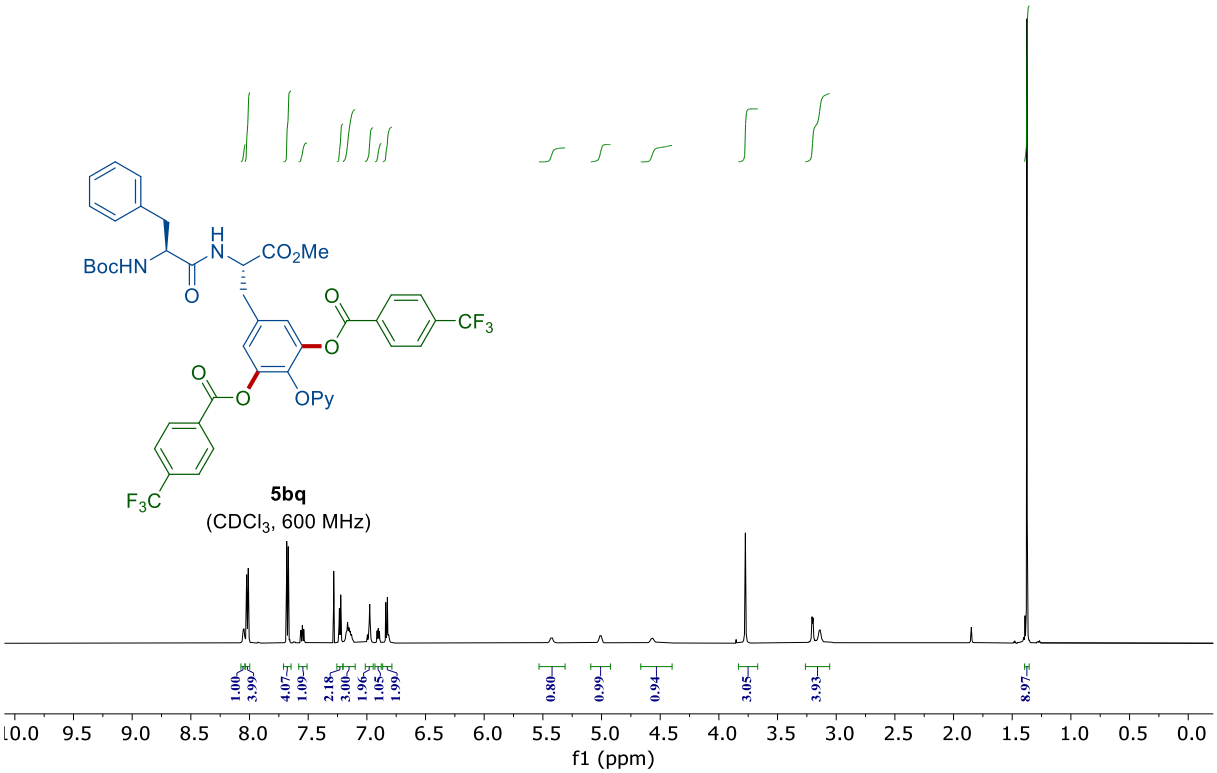
5br'

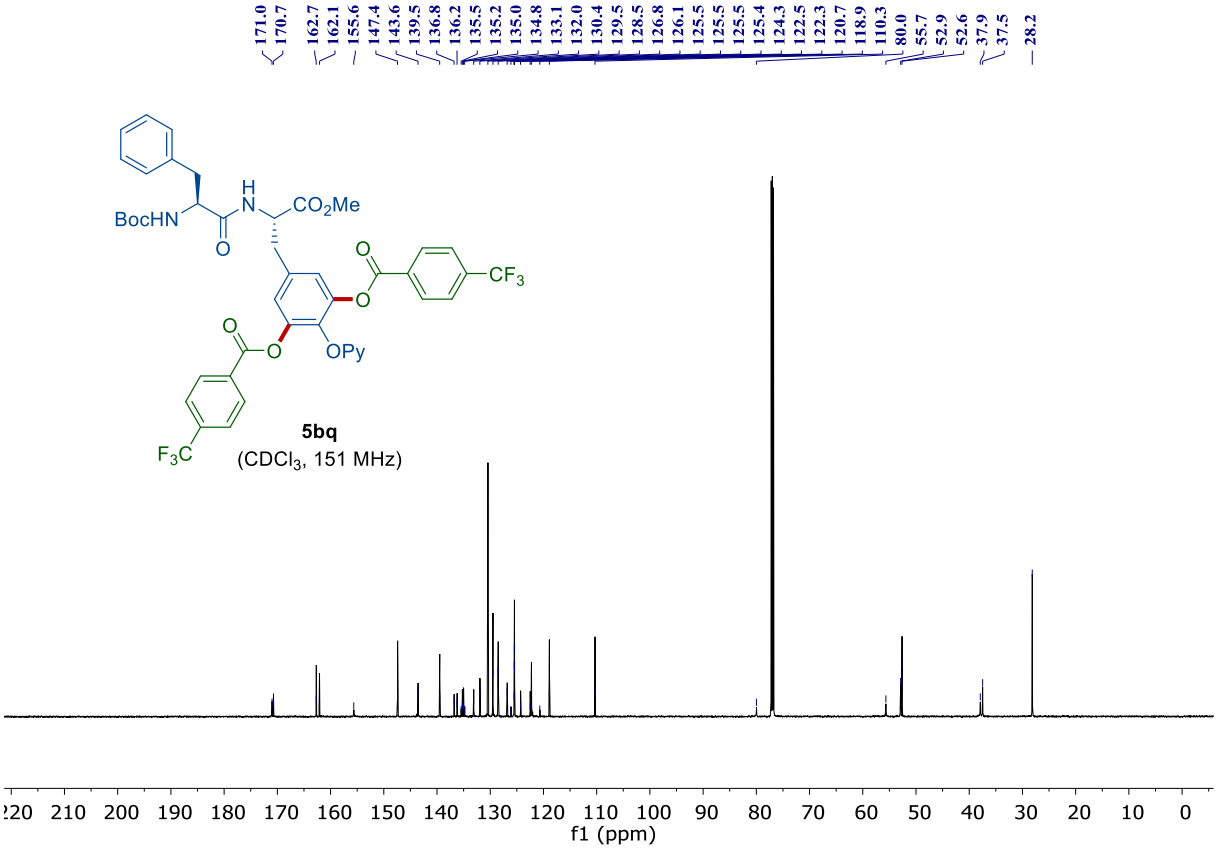
($CDCl_3$, 400 MHz)

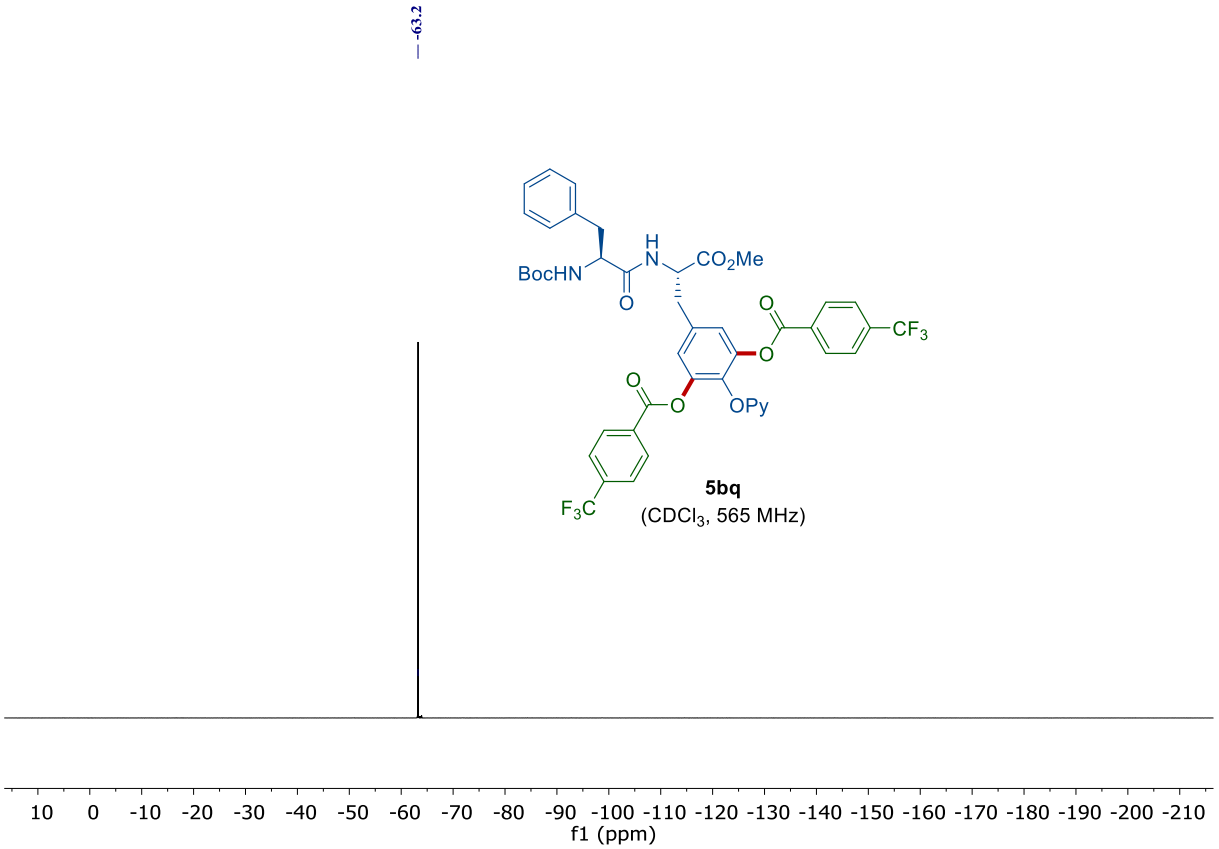


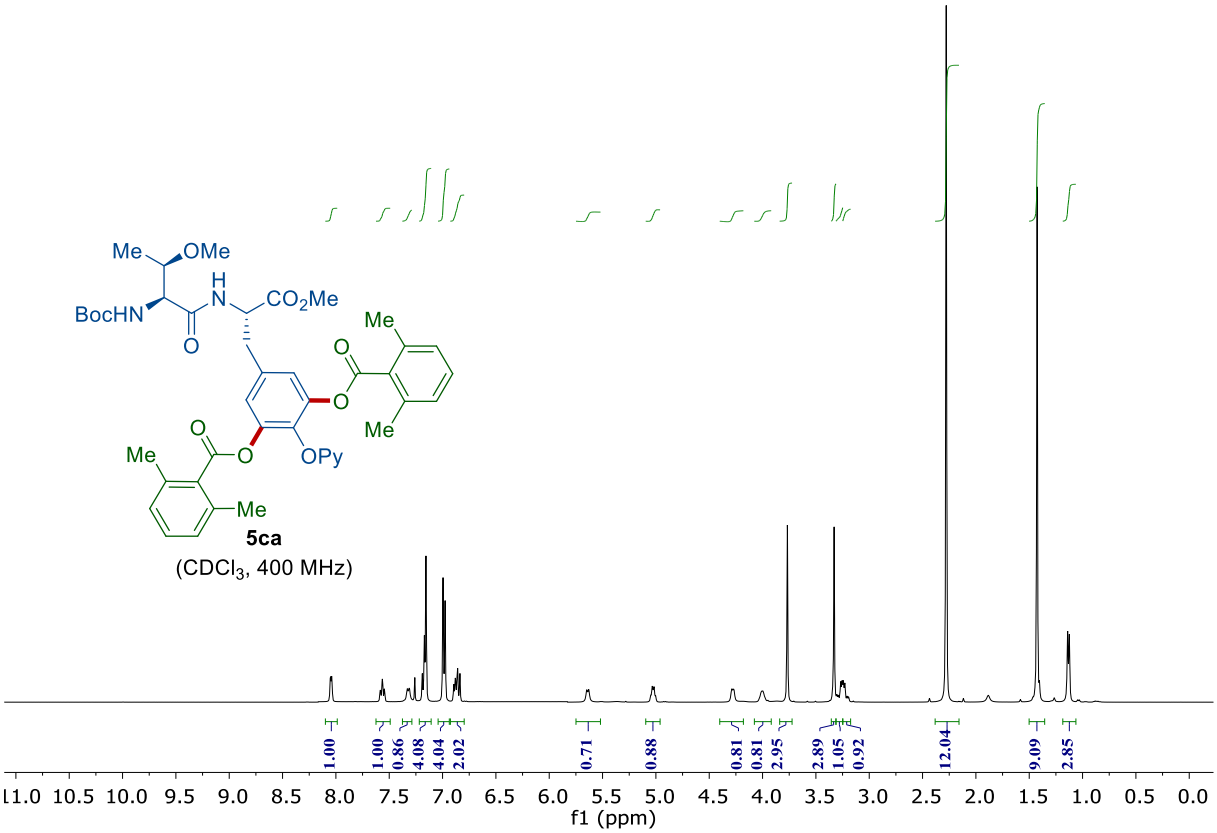
5br'

($CDCl_3$, 101 MHz)


BocHN
H
N
CO2Me
O
O
CF3
O
O
OPy
O
O
F3C
5bq
(CDCl3, 600 MHz)
1.00
3.99
4.07
1.09
2.18
3.00
1.96
1.05
1.99
0.80
0.99
0.94
3.05
3.93
8.97
f1 (ppm)

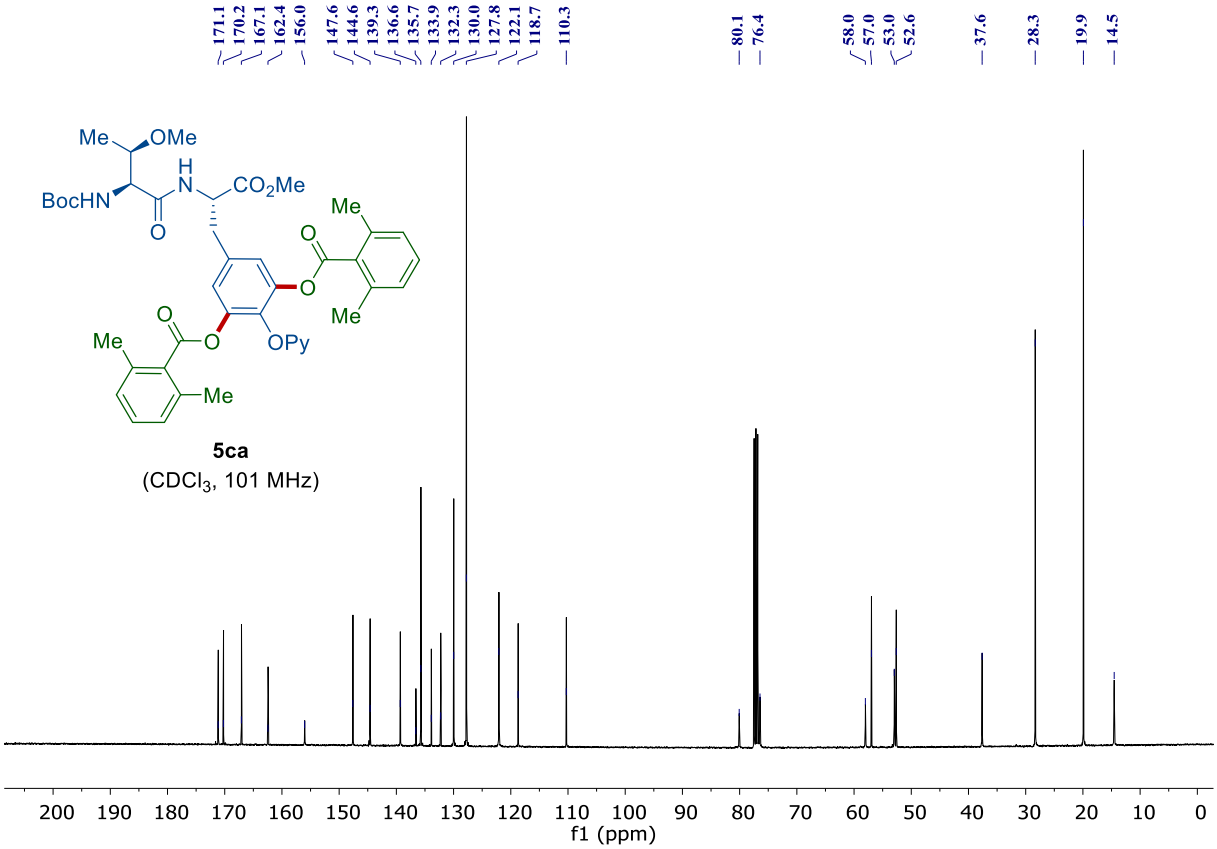

171.0
170.7
162.7
162.1
155.6
147.4
143.6
139.5
136.8
136.2
135.5
135.2
135.0
134.8
133.1
132.0
130.4
129.5
128.5
126.8
126.1
125.5
125.5
125.5
125.4
124.3
122.5
122.3
120.7
118.9
110.3
80.0
55.7
52.9
52.6
37.9
37.5
28.2
BocHN
H
N
CO2Me
O
O
CF3
O
O
OPy
O
O
F3C
5bq
(CDCl3, 151 MHz)
f1 (ppm)


-63.2
BocHN
H
N
O
CO2Me
O
O
CF3
O
O
OPy
F3C
5bq
(CDCl3, 565 MHz)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)



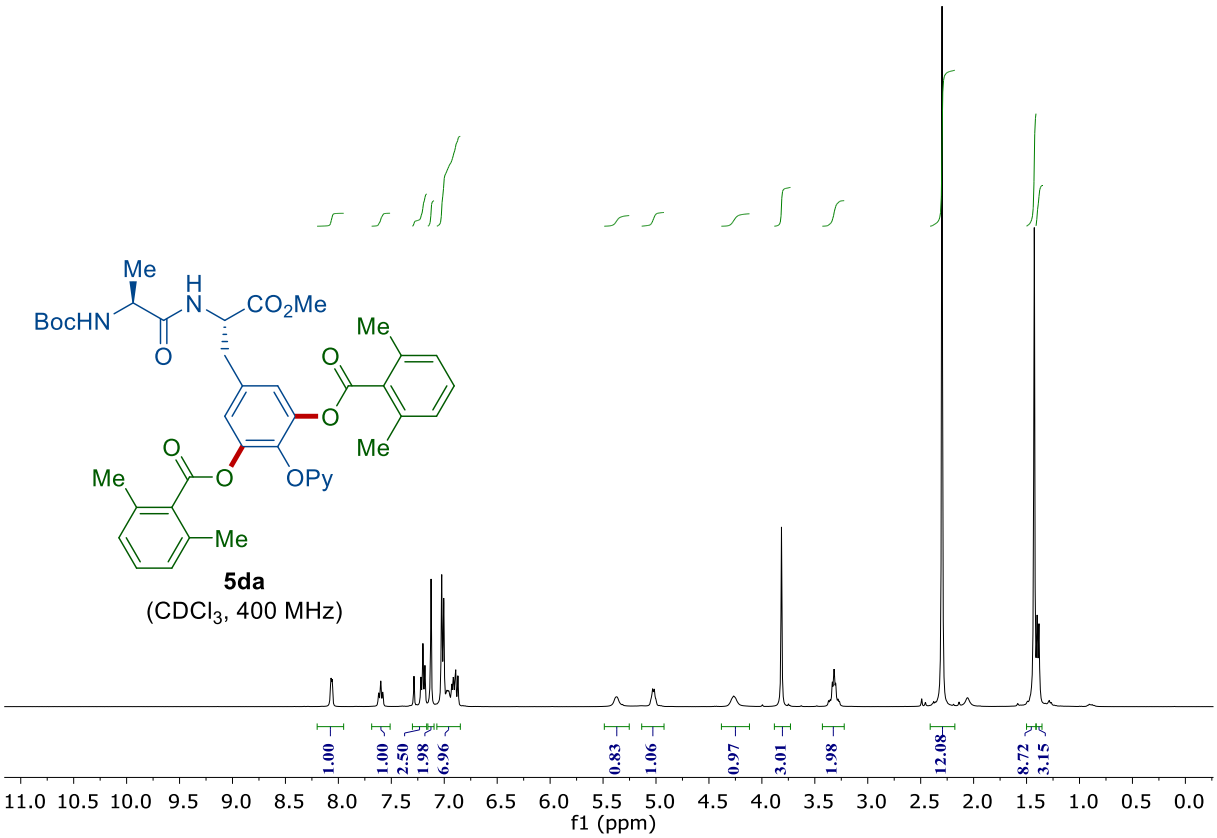
5ca

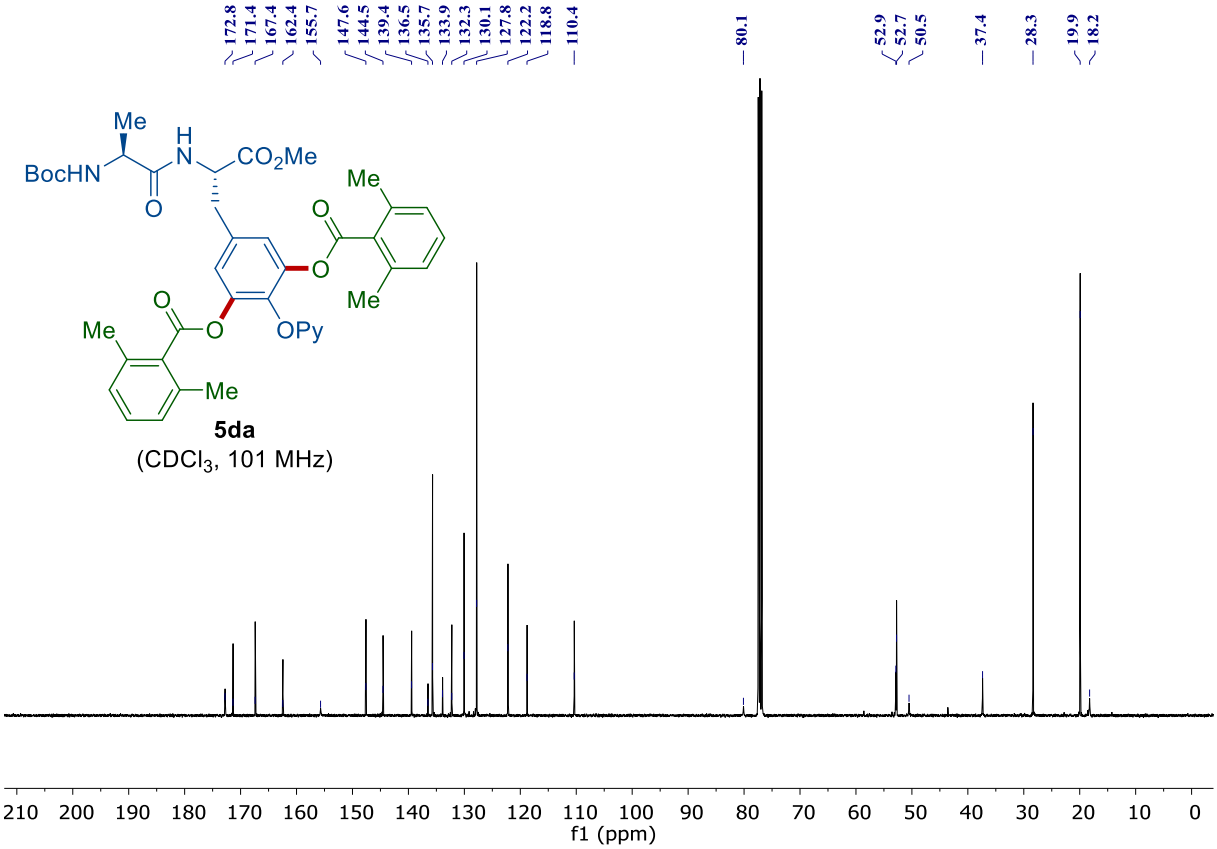
($CDCl_3$, 400 MHz)

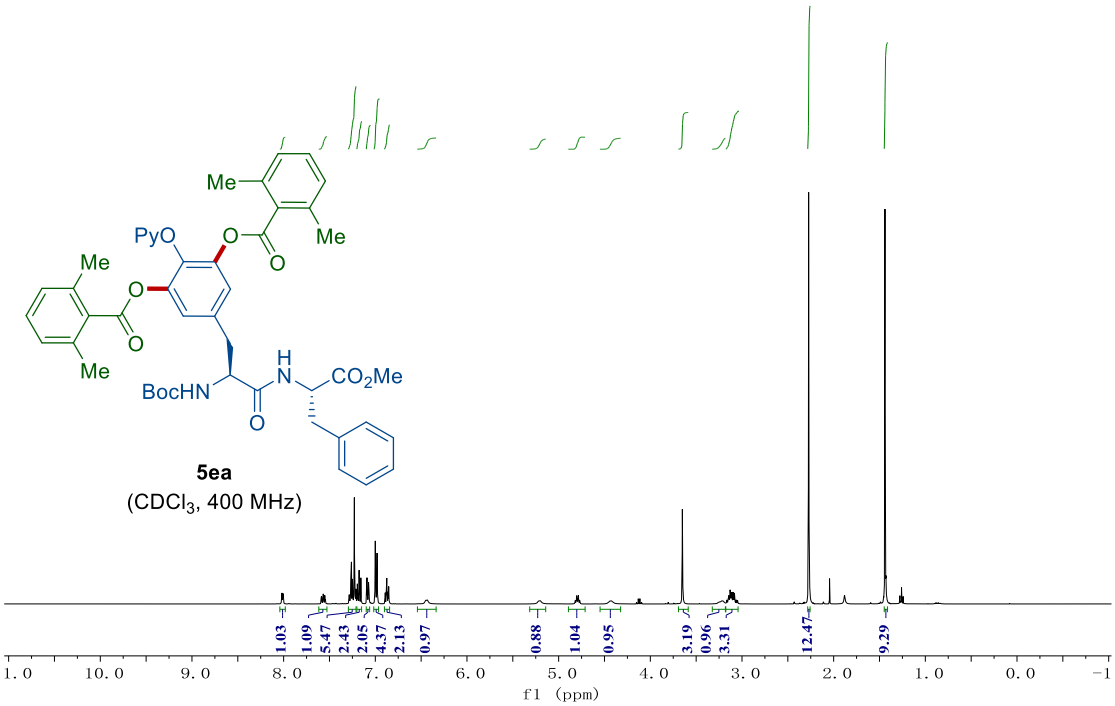


5ca

($CDCl_3$, 101 MHz)

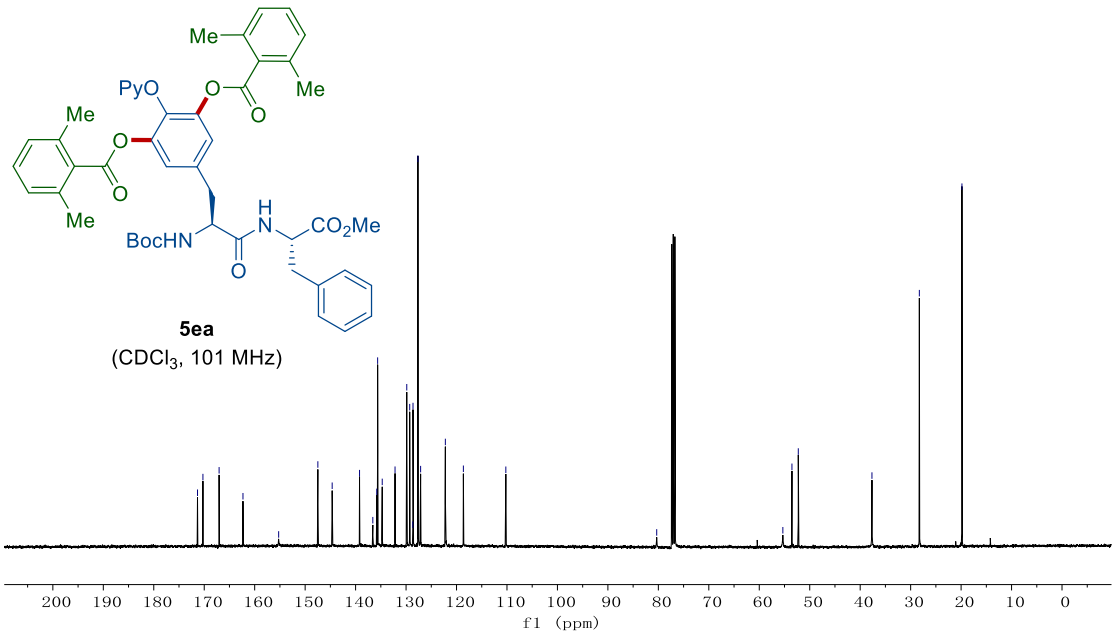

Me
BocHN
H
N
CO2Me
O
Me
O
O
Me
O
O
OPy
Me
Me
5da
(CDCl3, 400 MHz)
1.00
1.00
2.50
1.98
6.96
0.83
1.06
0.97
3.01
1.98
12.08
8.72
3.15
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


172.8
171.4
167.4
162.4
155.7
147.6
144.5
139.4
136.5
135.7
133.9
132.3
130.1
127.8
122.2
118.8
110.4
80.1
52.9
52.7
50.5
37.4
28.3
19.9
18.2
Me
BocHN
H
N
CO2Me
O
Me
O
O
Me
O
O
OPy
Me
Me
5da
(CDCl3, 101 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



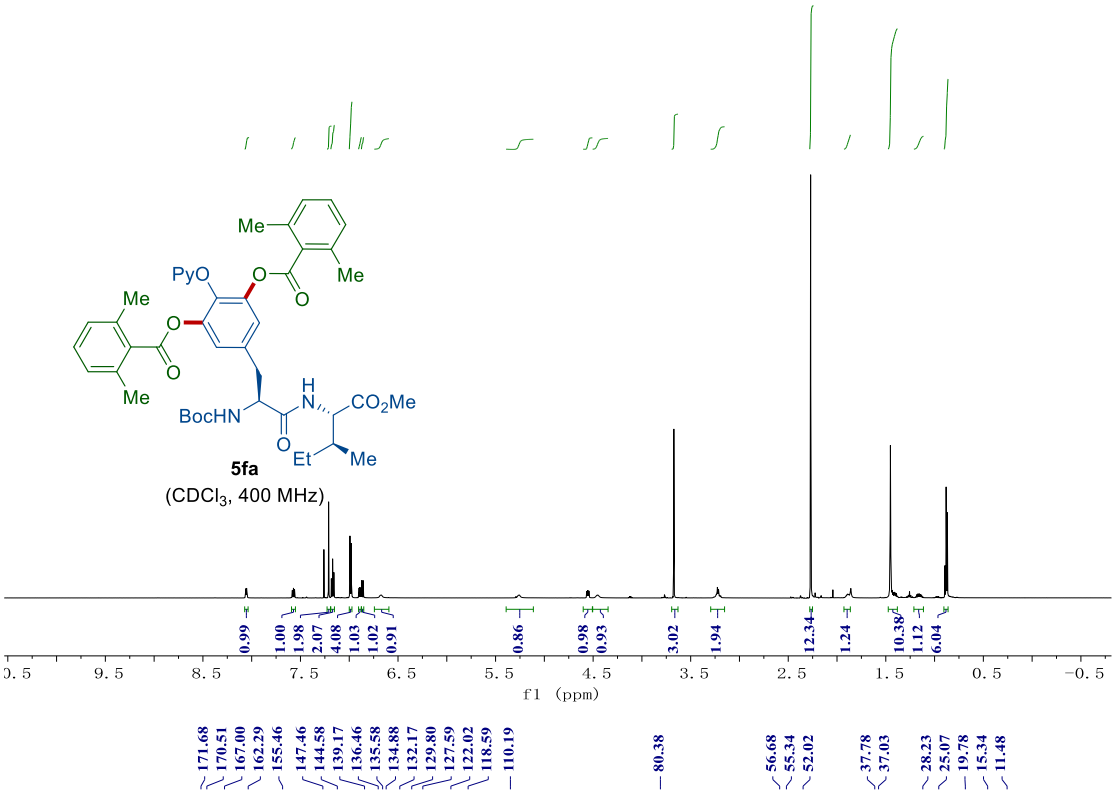
5ea

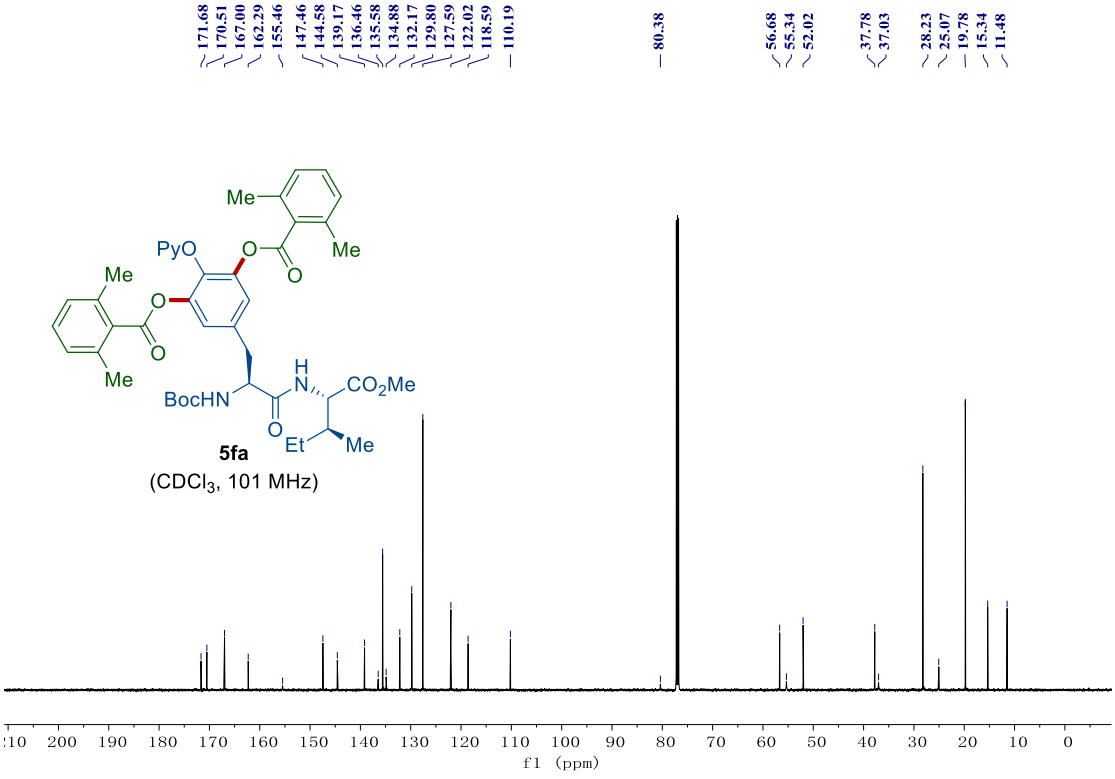
($CDCl_3$, 400 MHz)

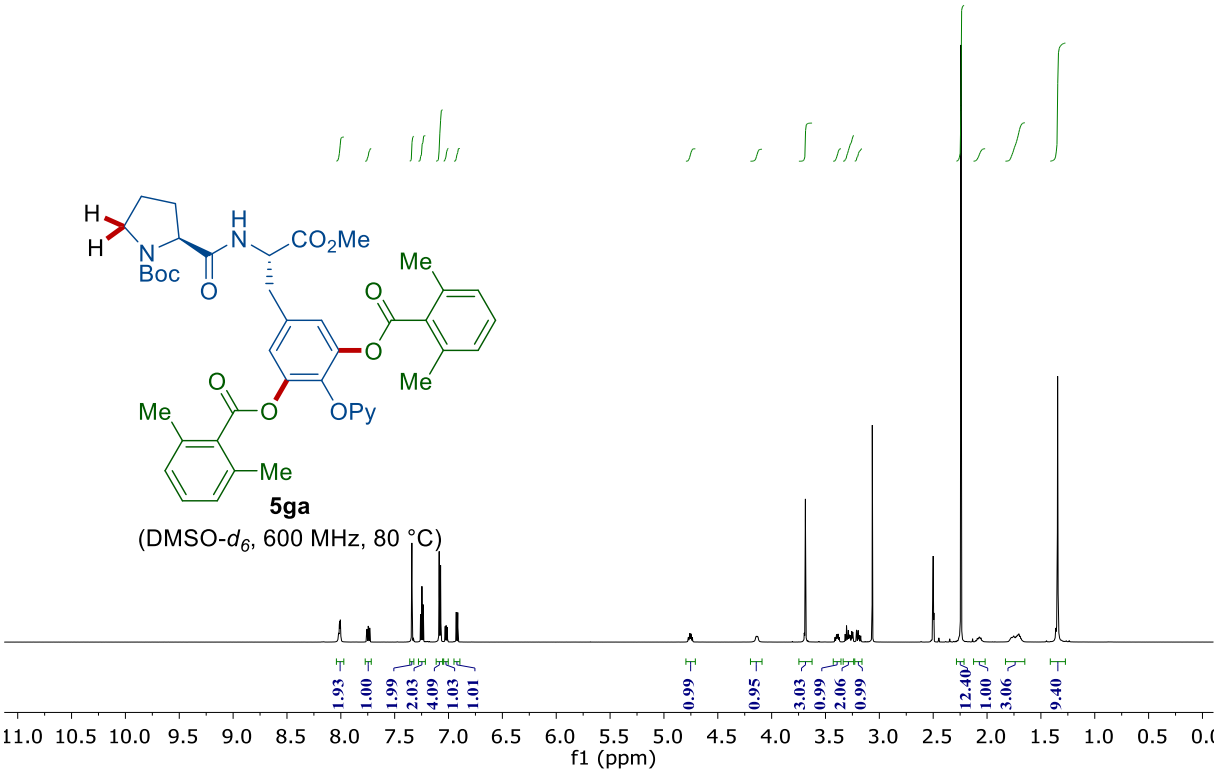


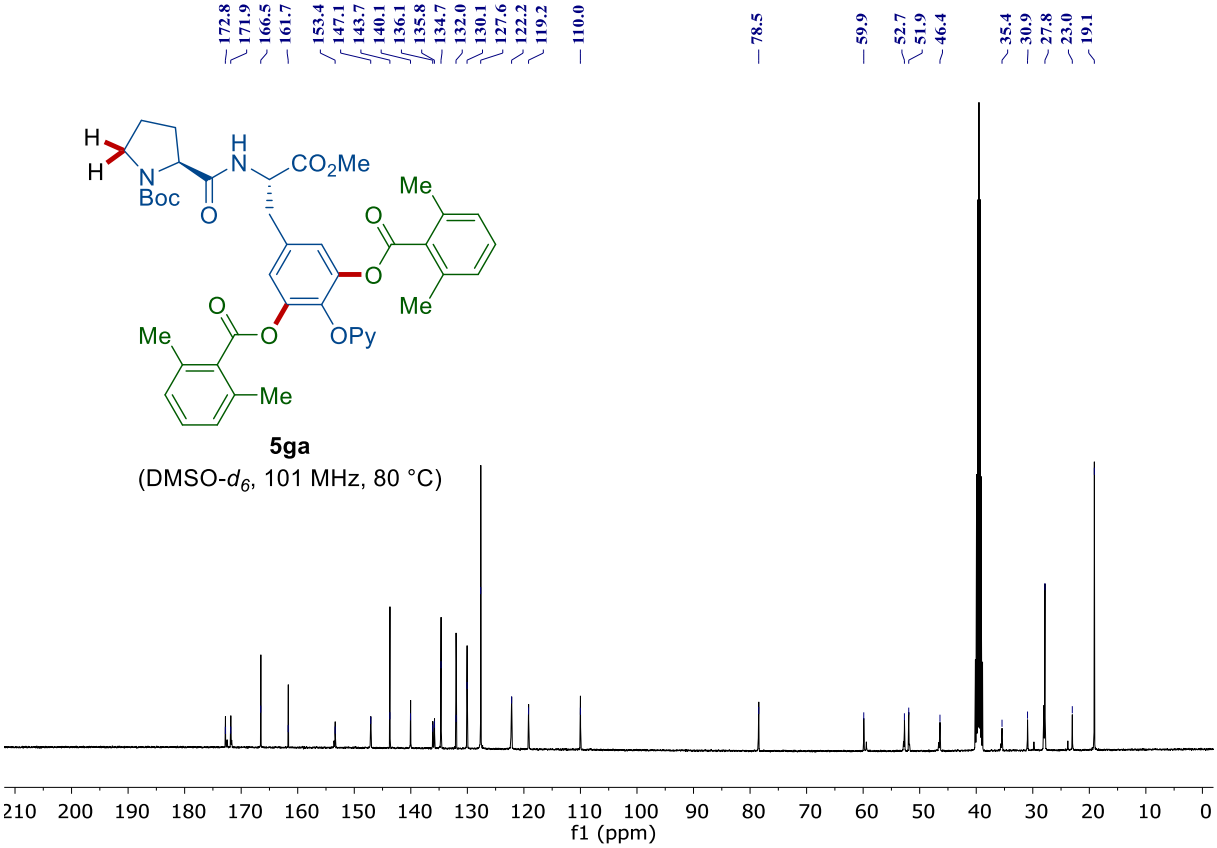
5ea

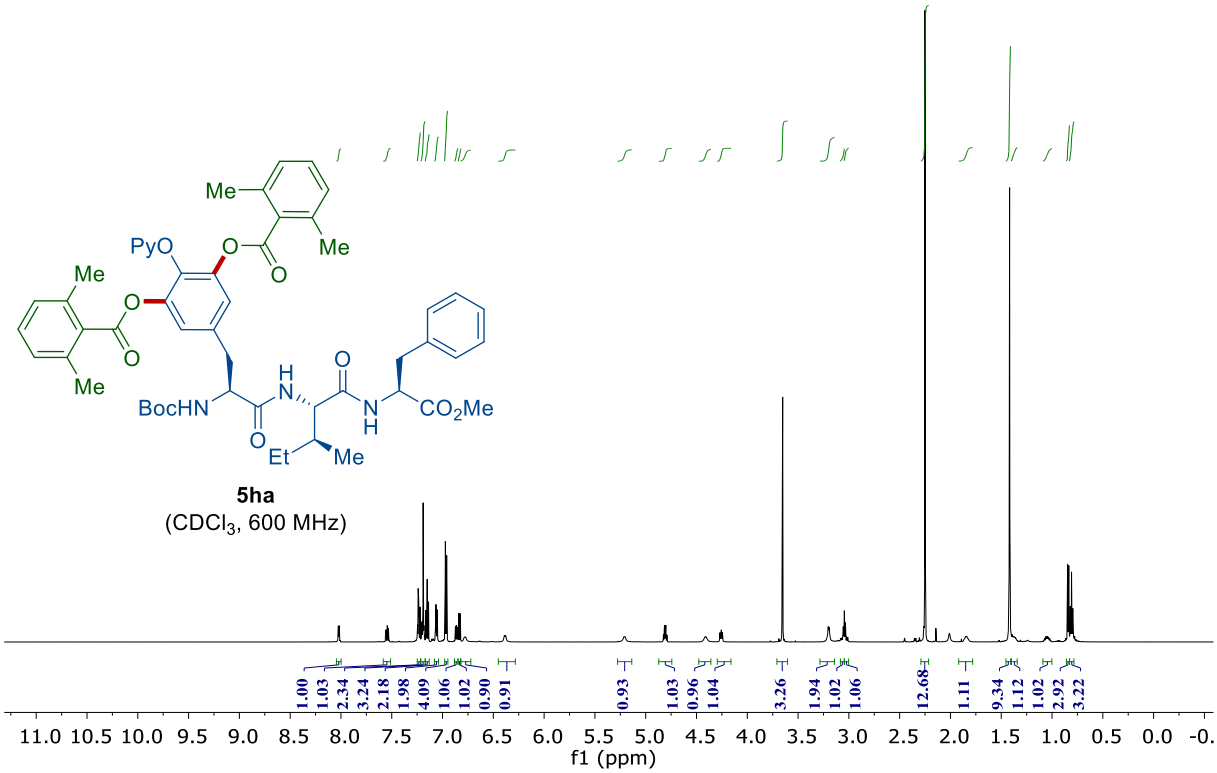
($CDCl_3$, 101 MHz)


Me
PyO
O
Me
O
Me
O
Me
BocHN
H
N
CO2Me
O
Et
Me
5fa
(CDCl3, 400 MHz)
0.99
1.00
1.98
2.07
4.08
1.03
1.02
0.91
0.86
0.98
0.93
3.02
1.94
12.34
1.24
10.38
1.12
6.04
f1 (ppm)

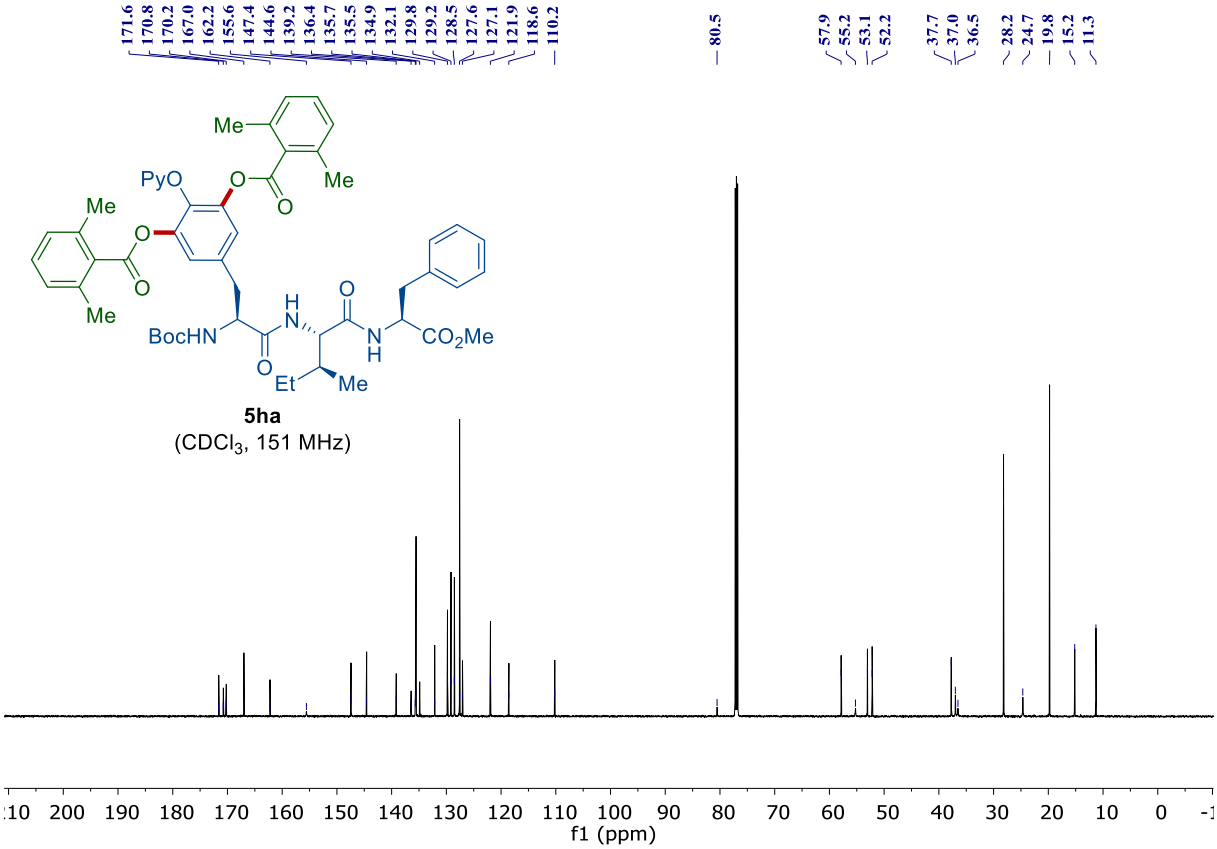

171.68
170.51
167.00
162.29
155.46
147.46
144.58
139.17
136.46
135.58
134.88
132.17
129.80
127.59
122.02
118.59
110.19
80.38
56.68
55.34
52.02
37.78
37.03
28.23
25.07
19.78
15.34
11.48
Me
PyO
O
Me
O
Me
O
Me
BocHN
H
N
CO2Me
O
Et
Me
5fa
(CDCl3, 101 MHz)
f1 (ppm)


5ga
(DMSO-d_6, 600 MHz, 80 °C)
1.93
1.00
1.99
2.03
4.09
1.03
1.01
0.99
0.95
3.03
0.99
2.06
0.99
12.40
1.00
3.06
9.40
f1 (ppm)

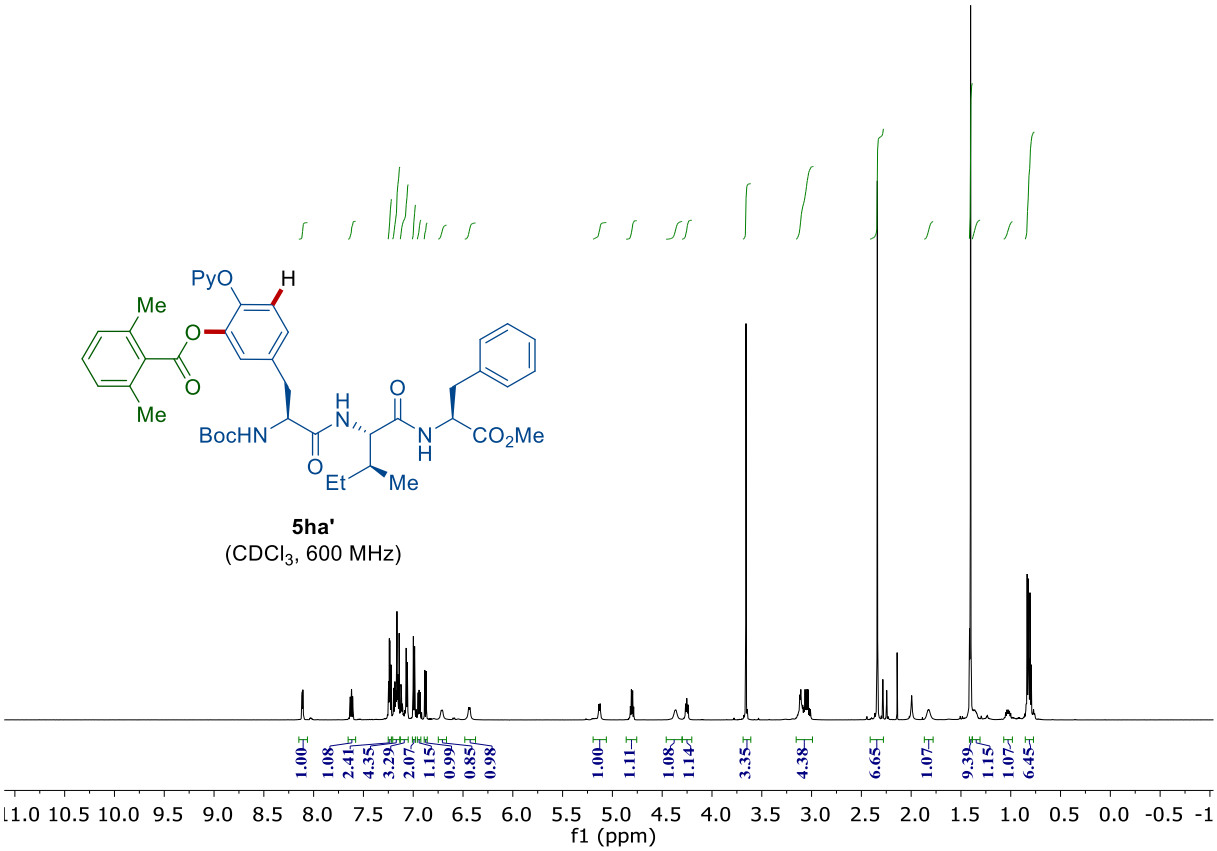

172.8
171.9
166.5
161.7
153.4
147.1
143.7
140.1
136.1
135.8
134.7
132.0
130.1
127.6
122.2
119.2
110.0
78.5
59.9
52.7
51.9
46.4
35.4
30.9
27.8
23.0
19.1
5ga
(DMSO-d_6, 101 MHz, 80 °C)
f1 (ppm)



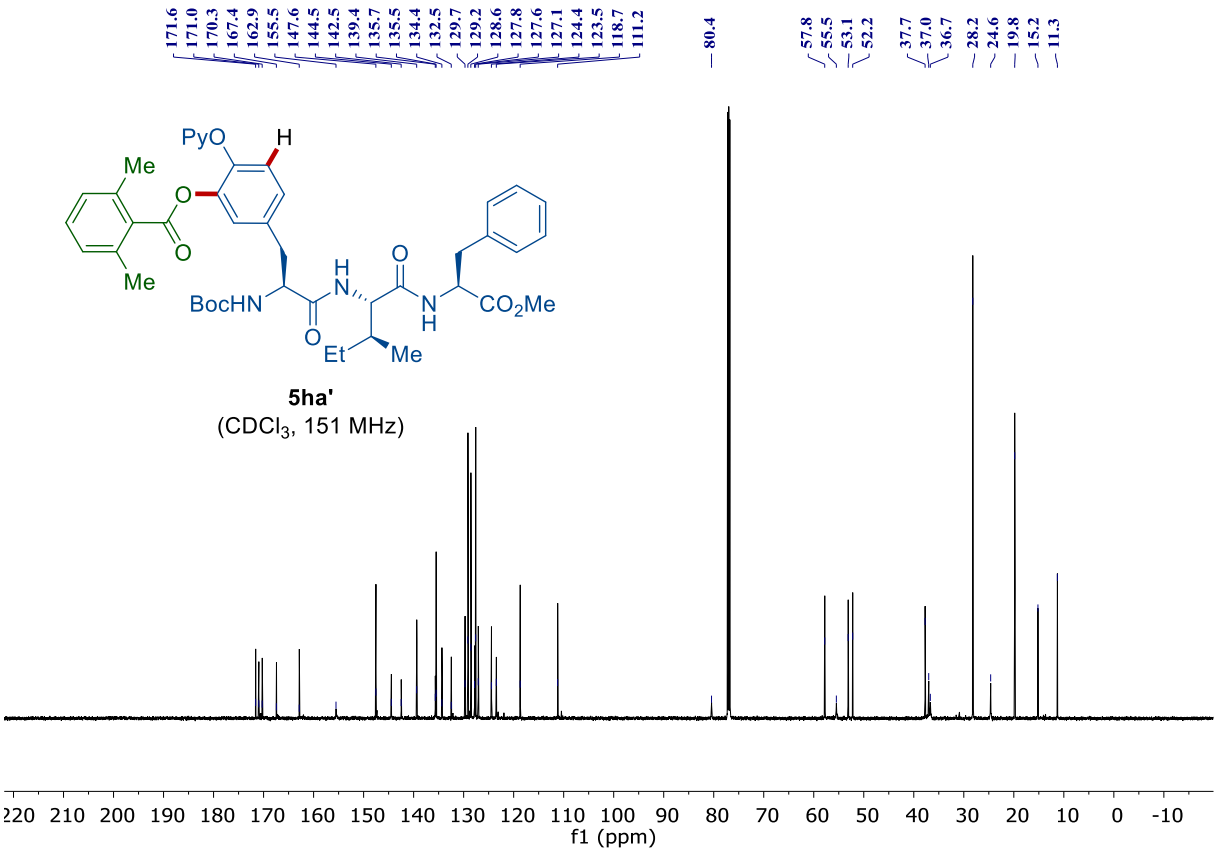
5ha
($CDCl_3$, 600 MHz)



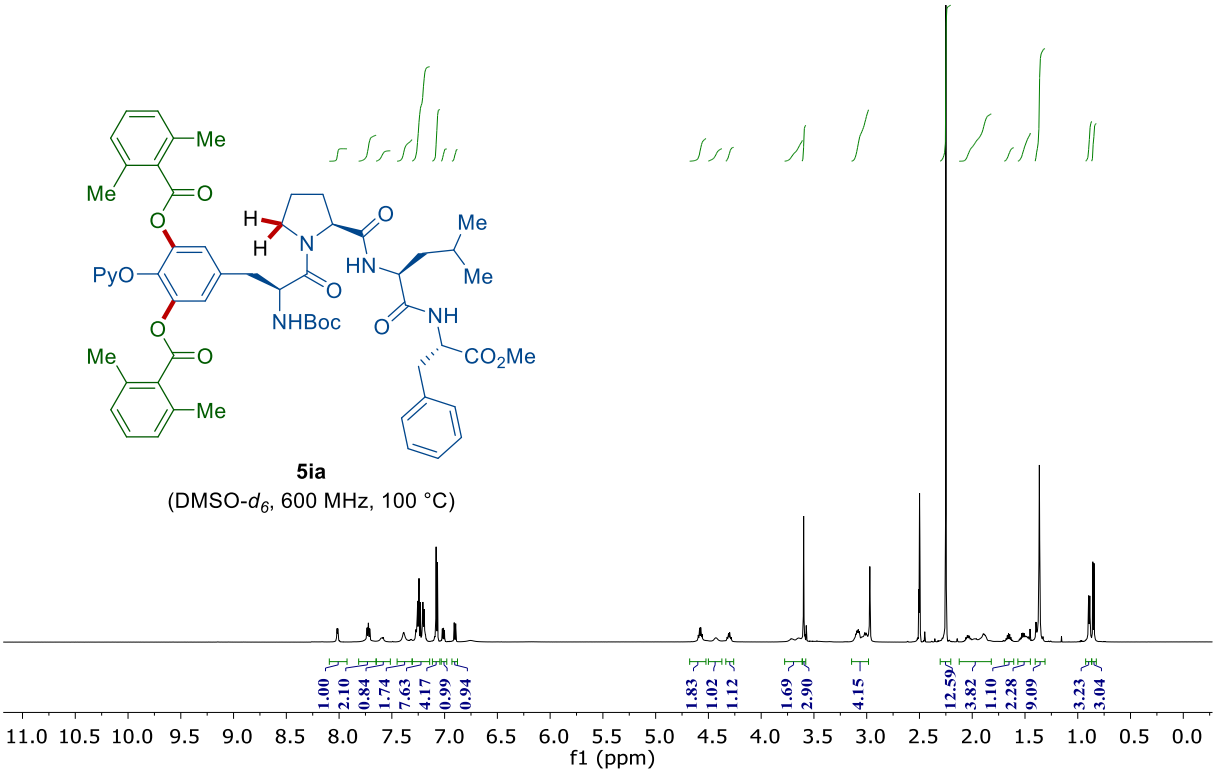
5ha
($CDCl_3$, 151 MHz)



5ha'
($CDCl_3$, 600 MHz)

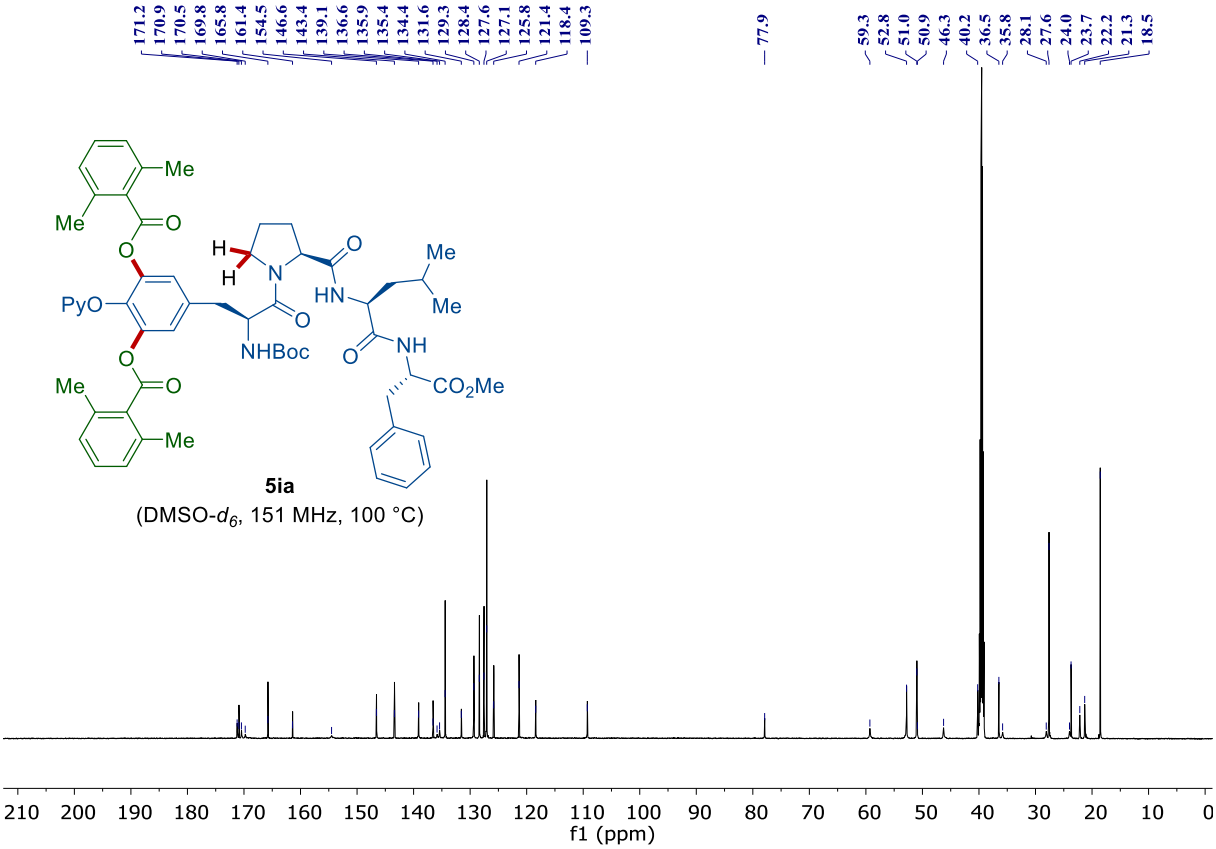


5ha'
($CDCl_3$, 151 MHz)



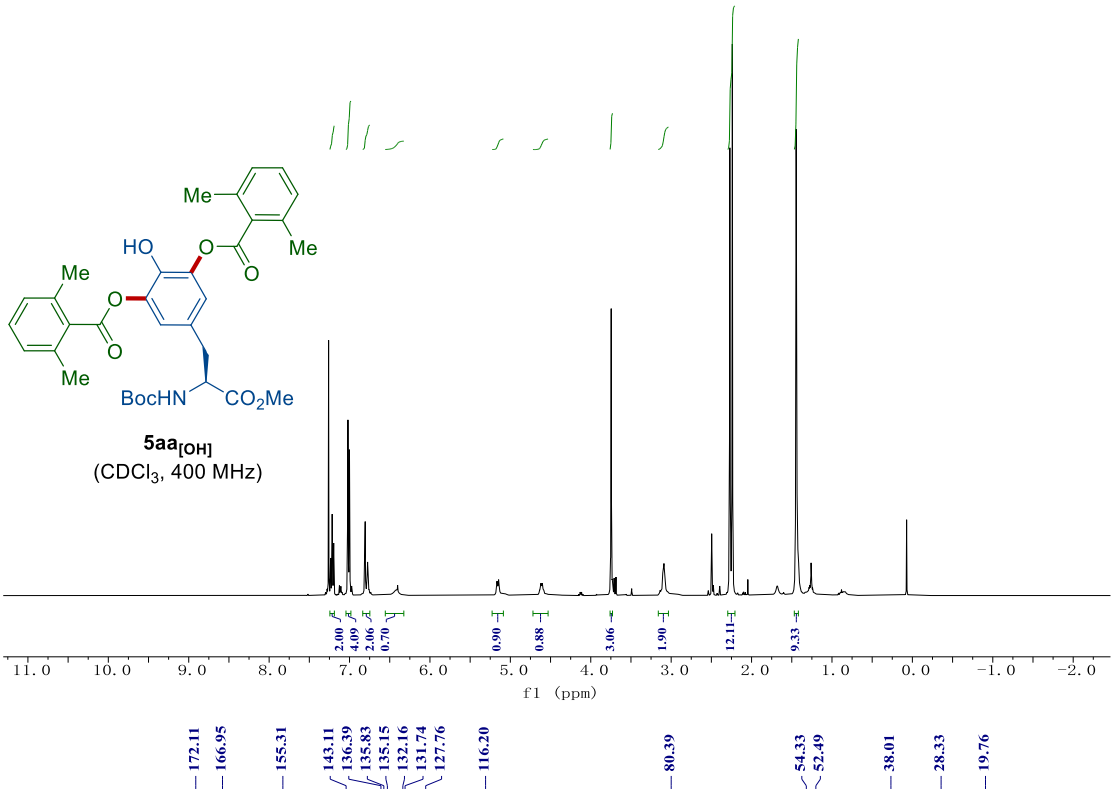
5ia

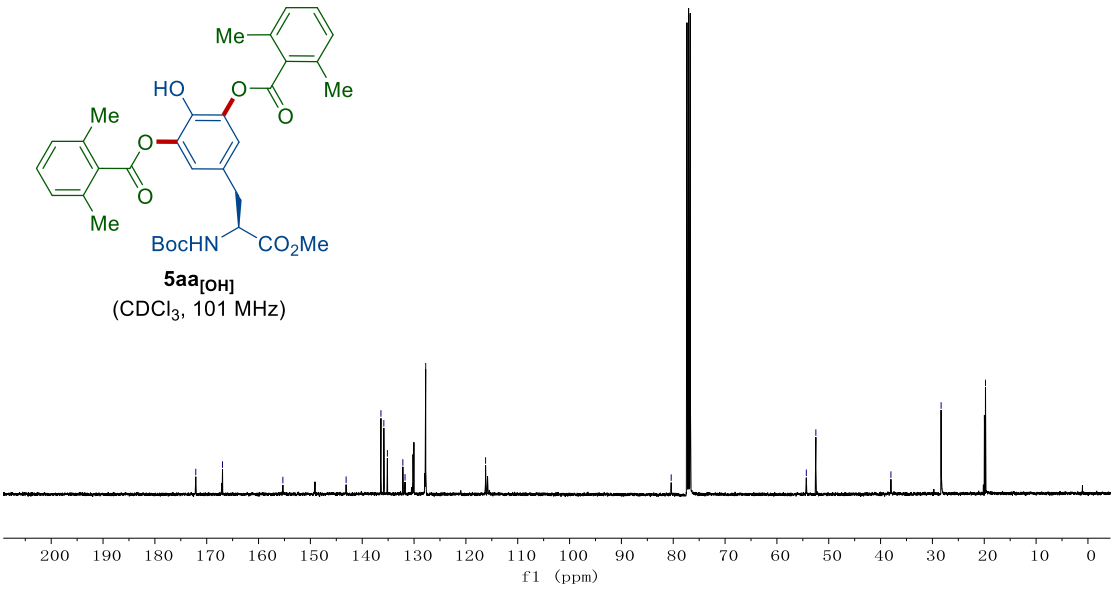
(DMSO-d_6, 600 MHz, 100 °C)

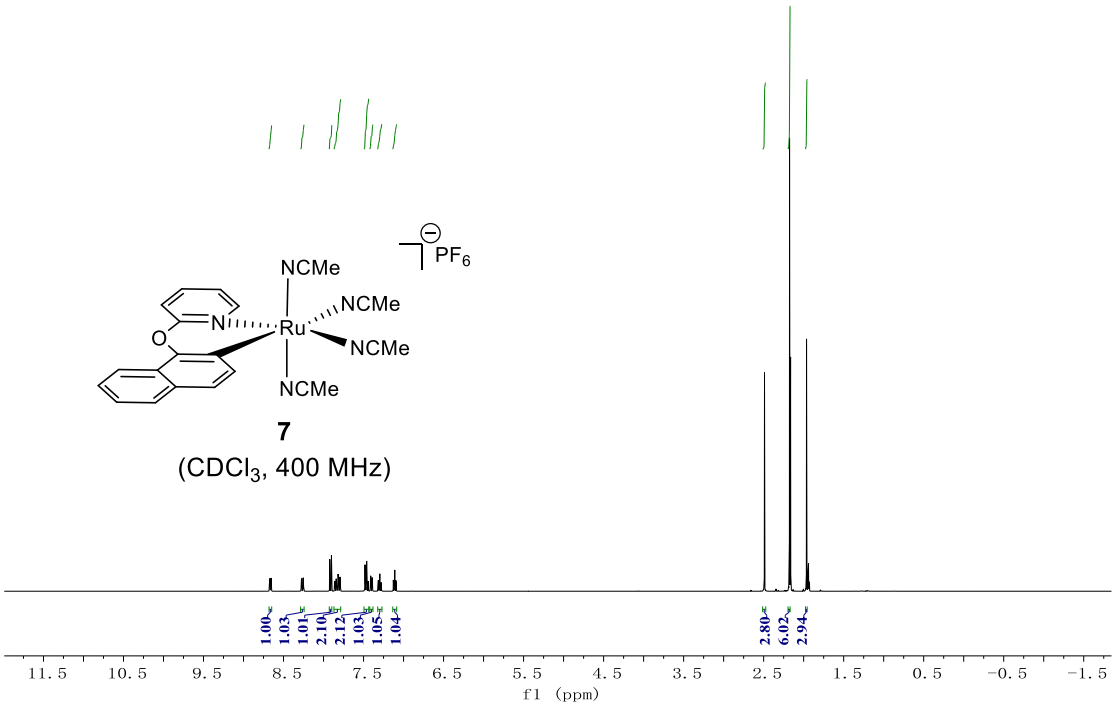


5ia

(DMSO-d_6, 151 MHz, 100 °C)

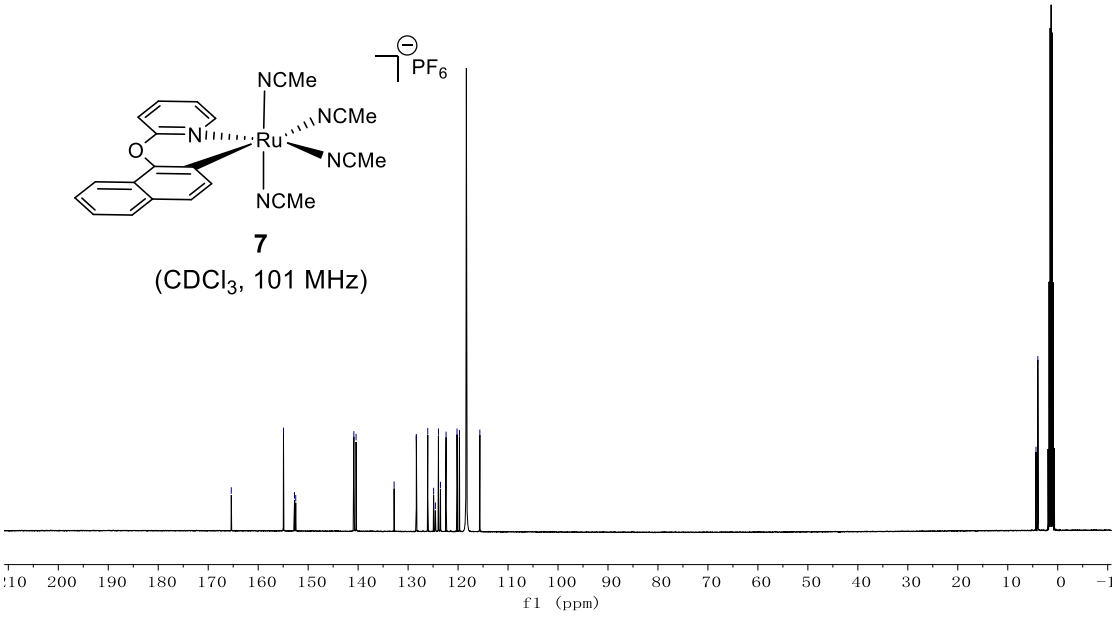

Me
HO
O
O
Me
Me
O
O
Me
BocHN
CO2Me
5aa[OH]
(CDCl3, 400 MHz)
2.00
4.09
2.06
0.70
0.90
0.88
3.06
1.90
12.11
9.33
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
−1.0
−2.0
f1 (ppm)


172.11
166.95
155.31
143.11
136.39
135.83
135.15
132.16
131.74
127.76
116.20
80.39
54.33
52.49
38.01
28.33
19.76
Me
HO
O
O
Me
Me
O
O
Me
BocHN
CO2Me
5aa[OH]
(CDCl3, 101 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



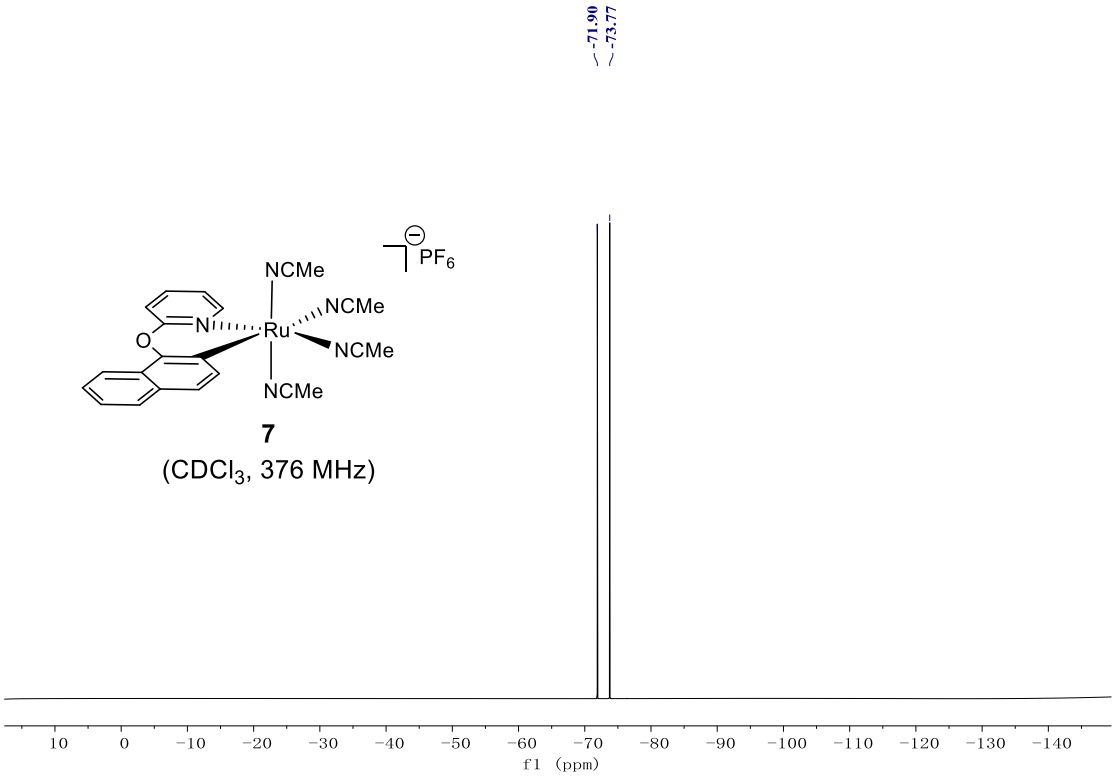
7

($CDCl_3$, 400 MHz)



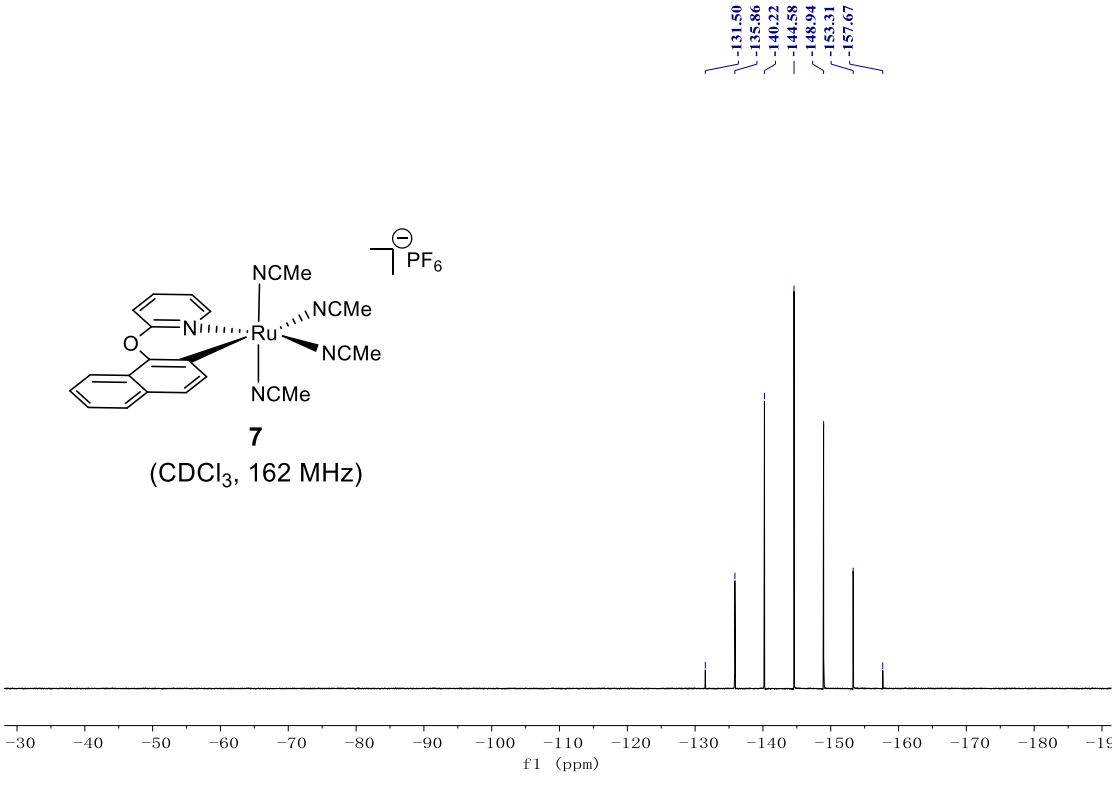
7

($CDCl_3$, 101 MHz)



7

($CDCl_3$, 376 MHz)



7

($CDCl_3$, 162 MHz)