Supporting Information

Cationic Iridium-Catalyzed Enantioselective Decarboxylative Aryl Addition of Aromatic Carboxylic Acids to Bicyclic Alkenes

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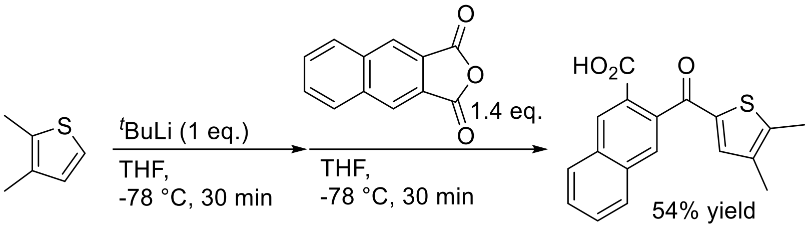
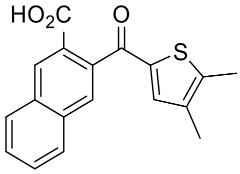
I. General consideration

^1H NMR spectra were recorded on a JEOL ECX-400II or JEOL ECP-400 spectrometer (400 MHz for ^1H). Chemical shifts are reported in part per million (ppm) relative to TMS internal standard (for ^1H, δ 0.00). ^1H-NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet,), coupling constants (Hz), and integration. ^{13}C NMR spectra were recorded on a JEOL ECX-400II (100 MHz) or JEOL ECP-400 spectrometer in $CDCl_3$ (relative to residual $CHCl_3$ δ = 77.0) or DMSO-d_6 (relative to residual DMSO δ = 39.5). Flash column chromatography for Ir-catalyzed reaction was performed with Kanto Chemical silica gel 60N (spherical, neutral, particle size 40–50 μm). Analytical thin layer chromatography (TLC) was performed on FUJIFILM Wako TLC plates (silica gel 70 F_{254}). HPLC analysis was directly performed with chiral stationary phase column, CHIRALPAK and CHIRALCEL purchased from DAICEL Co., Ltd. High resolution mass spectra (HRMS) were recorded on a JEOL JMS-700 spectrometer. Optical rotations were measured on a JASCO P-2200 polarimeter. Unless otherwise noted, materials were purchased from Kanto Chemical Co., LTD., FUJIFILM Wako Pure Chemical Industries, Ltd., Tokyo Chemical Industry Co., LTD., Aldrich Inc. and other commercial suppliers and were used without purification. Dehydrated solvents were purchased from Kanto Chemical Co., Inc. and used under nitrogen atmosphere. $IrCl_3$ xH_2O was purchased from Tokyo Chemical Industry Co., LTD. $[Ir(cod)_2](BAr^F{}_4)$[1] and S-Me-BIPAM[2] were prepared by the literature procedure.

II. Synthetic procedures for starting materials

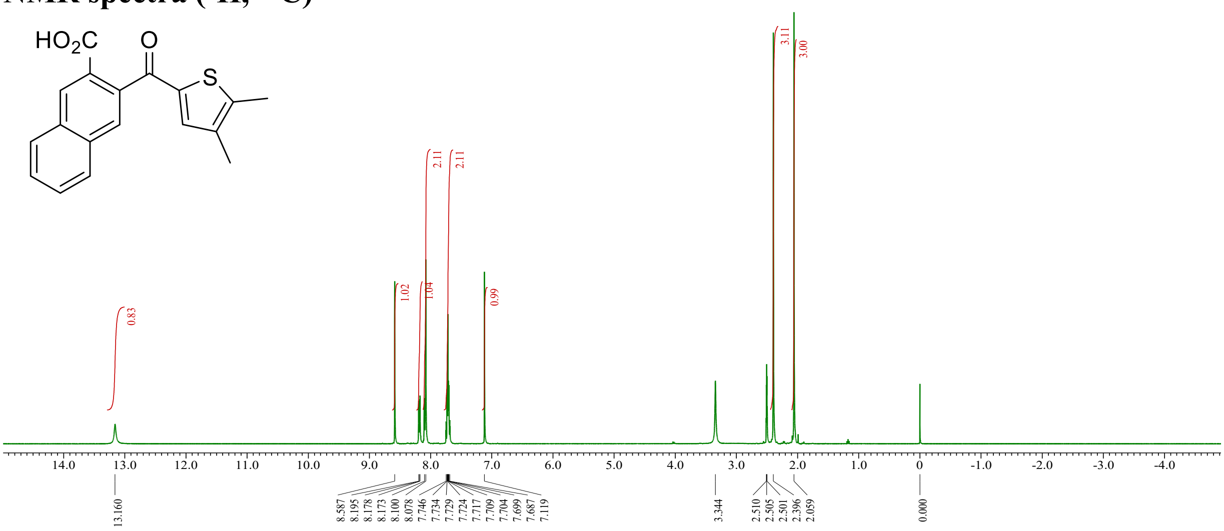


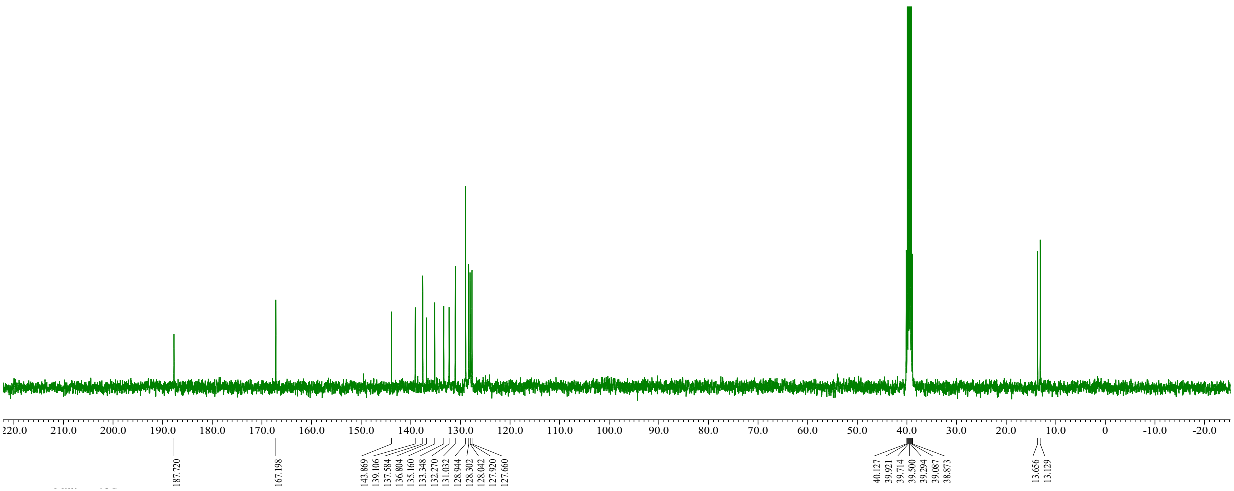


1n

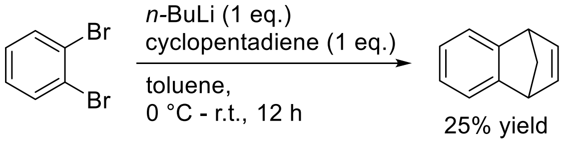
^{1}H NMR (400 MHz, DMSO-d_6): δ = 13.2 (br s, 1H), 8.59 (s, 1H), 8.17–8.20 (m, 1H), 8.07–8.11 (m, 2H), 7.68–7.75 (m, 2H), 7.12 (s, 1H), 2.40 (s, 3H), 2.06 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 187.7, 167.2, 143.9, 139.1, 137.6, 136.8, 135.2, 133.3, 132.3, 131.0, 128.9, 128.3, 128.0, 127.9, 127.7, 13.7, 13.1; HRMS (ESI) *m/z* calcd. for $C_{18}H_{14}NaO_3S$ $(M+Na)^+$: 333.0556, found: 333.0552.

NMR spectra (^{1}H, ^{13}C)





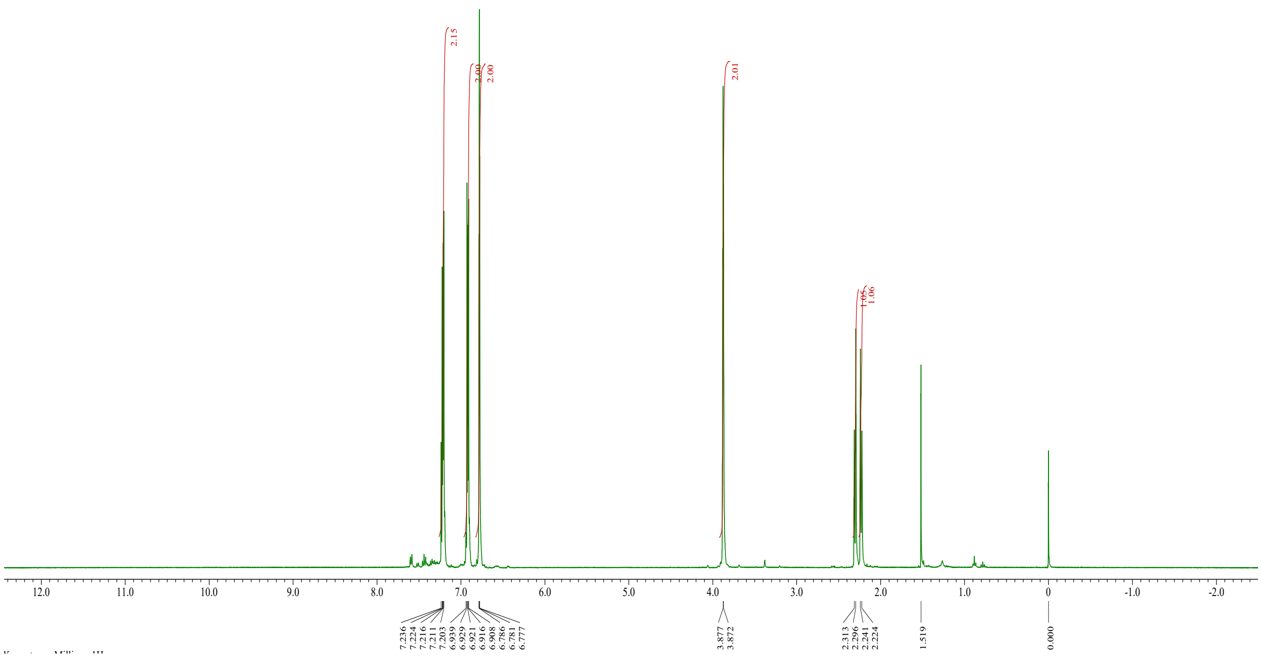
Benzonorbornadiene



1,2-dibromobenzene (10 mmol) and fresh cyclopendadiene (1 equiv) were stirred in dry toluene (20 ml) at 0 °C under N_2 atmosphere. Then, *n*-BuLi (1 equiv) was added dropwise. The mixture was allowed to warm to room temperature and stirred overnight. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (hexane only) to give the product as a colorless liquid.

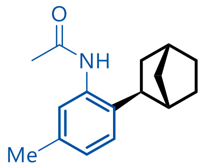
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.19–7.23 (m, 2H), 6.88–6.94 (m, 2H), 6.78 (t, J = 2.2 Hz, 2H), 3.85–3.89 (m, 2H), 2.30 (dt, J = 7.0, 1.8 Hz, 1H), 2.21–2.25 (m 1H); NMR signals are in accordance with the data reported in literature.[3]

^{1}H NMR spectrum



III. General procedure for the catalytic decarboxylative asymmetric aryl addition to bicyclic alkenes

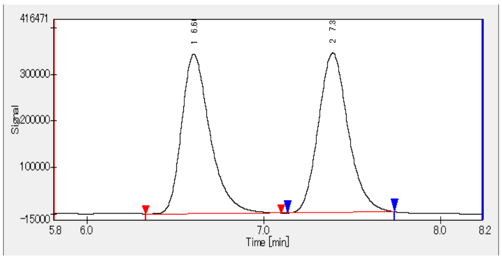
A typical procedure: To a dried sealed tube, $[Ir(cod)_2](BAr^F{}_4)$ (9.5 mg, 3 mol%), (*R,R*)-S-Me-BIPAM (6.4 mg, 3.3 mol%) and dry tetrahydrofuran (1.0 mL) were added under N_2 atmosphere. The solution was stirred at ambient temperature for 30 min. Thereafter, aromatic carboxylic acid **1** (0.25 mmol) and bicyclic alkene (3.5 equiv) were added. The reaction mixture was further heated to 120 °C and stirred for 20 h. Then, the mixture was purified using silica gel column chromatography (eluent: Hexane/AcOEt) to afford a pure product **2**. The products **2a**–**2i** were known compounds.[4]

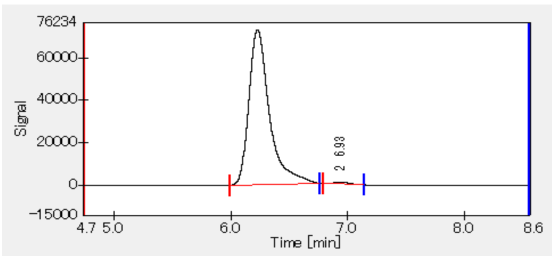


2a

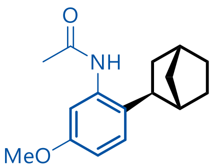
^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.13 (br s, 1H), 7.12 (d, J = 7.8 Hz, 1H), 7.07 (s, 1H), 6.94 (d, J = 7.8 Hz, 1H), 2.87 (dd, J = 8.7, 6.0 Hz, 1H), 2.29-2.24 (m, 2H), 2.23 (s, 3H), 2.02 (s, 3H), 1.70-1.12 (m, 8H); NMR signals are in accordance with the data reported in literature.[4]

HPLC conditions: Daicel Chiralpak AD-H, hexane/2-propanol = 9/1, flow = 1.0 mL/min, wavelength = 230 nm, t_R = 6.2 min (major) and 6.9 min (minor), 98% ee





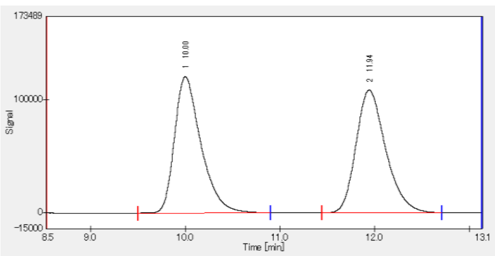
No	Rt (min)	area (%)
1	6.23	98.9986
2	6.93	1.0014

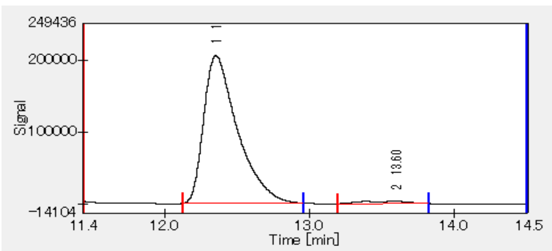


2b

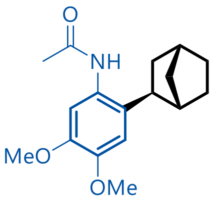
^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.13 (br s, J = 7.3 Hz, 1H), 7.12 (d, J = 8.7 Hz, 1H), 6.89 (d, J = 2.3 Hz, 1H), 6.70 (dd, J = 8.7, 2.3 Hz, 1H), 3.69, (s, 3H), 2.84 (dd, J = 8.2, 4.4 Hz, 1H), 2.28–2.22 (m, 2H), 2.02 (s, 3H), 1.71–1.09 (m, 8H); NMR signals are in accordance with the data reported in literature.[4]

HPLC conditions: Daicel Chiralpak AD-H, hexane/2-propanol = 9/1, flow = 1.0 mL/min, wavelength = 230 nm, t_R = 12.4 min (major) and 13.6 min (minor), 96% ee





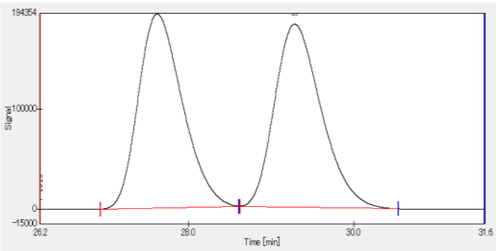
No	Rt (min)	area (%)
1	12.35	97.7363
2	13.6	2.2637

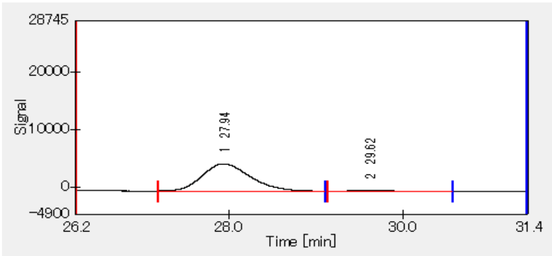


2c

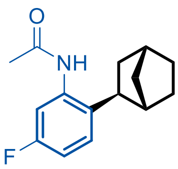
^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.11 (br s, 1H), 6.81 (s, 1H), 6.74 (s, 1H), 3.75 (s, 3H), 3.68 (s, 3H), 2.82 (dd, J = 8.4, 5.9 Hz, 1H), 2.31–2.22 (m, 2H), 2.00 (s, 3H), 1.71–1.09 (m, 8H); NMR signals are in accordance with the data reported in literature.[4]

HPLC conditions: Daicel Chiralpak AD-H×2, hexane/2-propanol = 9/1, flow = 1.0 mL/min, wavelength = 230 nm, t_R = 27.9 min (major) and 29.6 min (minor), 96% ee





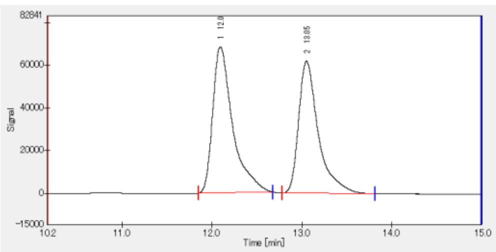
No	Rt (min)	area (%)
1	27.94	97.8837
2	29.62	2.1163

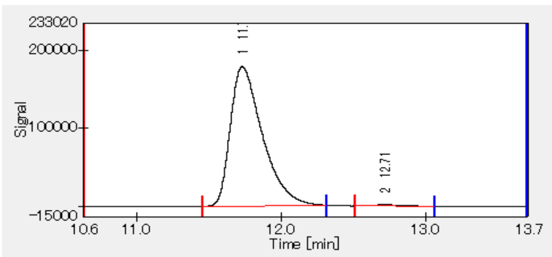


2d

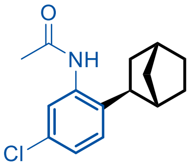
^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.23 (br s, 1H) 7.27–7.21 (m, 2H), 6.93 (td, J = 8.7, 2.8 Hz, 1H), 2.91 (dd, J = 8.7, 6.0 Hz, 1H), 2.31-2.25 (m, 2H), 2.05 (s, 3H), 1.79–1.13 (m, 8H); NMR signals are in accordance with the data reported in literature.[4]

HPLC conditions: Daicel Chiralpak AD-H×2, hexane/2-propanol = 9/1, flow = 1.0 mL/min, wavelength = 230 nm, t_R = 11.7 min (major) and 12.7 min (minor), 98% ee





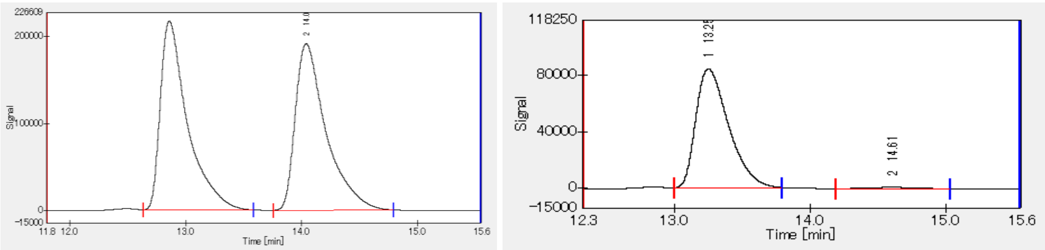
No	Rt (min)	area (%)
1	11.73	99.1634
2	12.71	0.8366



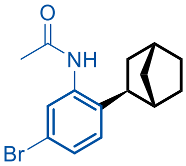
2e

^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.27 (br s, 1H), 7.41 (d, J = 2.3 Hz, 1H), 7.25 (d, J = 8.7 Hz, 1H), 7.16, (dd, J = 8.7, 2.3 Hz, 1H), 2.91 (dd, J = 8.7, 5.5 Hz, 1H), 2.31-2.25 (m, 2H), 2.05 (s, 3H), 1.80–1.12 (m, 8H); NMR signals are in accordance with the data reported in literature.[4]

HPLC conditions: Daicel Chiralpak AD-H×2, hexane/2-propanol = 9/1, flow = 1.0 mL/min, wavelength = 230 nm, t_R = 13.3 min (major) and 14.6 min (minor), 98% ee



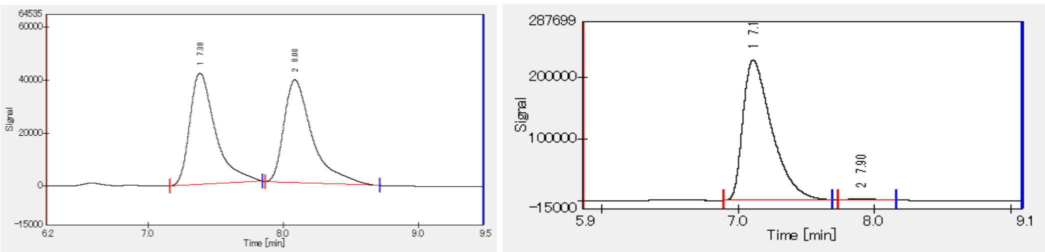
No	Rt (min)	area (%)
1	13.3	98.7587
2	14.6	1.2413



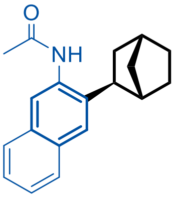
2f

^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.24 (br s, 1H), 7.50 (d, J = 1.8 Hz, 1H), 7.26 (dd, J = 8.7, 1.8 Hz, 1H), 7.16 (d, J = 8.7 Hz, 1H), 2.87 (dd, J = 8.2, 5.5 Hz, 1H), 2.27–2.22 (m, 2H), 2.01 (s, 3H), 1.75–1.10 (m, 8H); NMR signals are in accordance with the data reported in literature.[4]

HPLC conditions: Daicel Chiralpak AD-H, hexane/2-propanol = 9/1, flow = 1.0 mL/min, wavelength = 230 nm, t_R = 7.11 min (major) and 7.90 min (minor), 99% ee



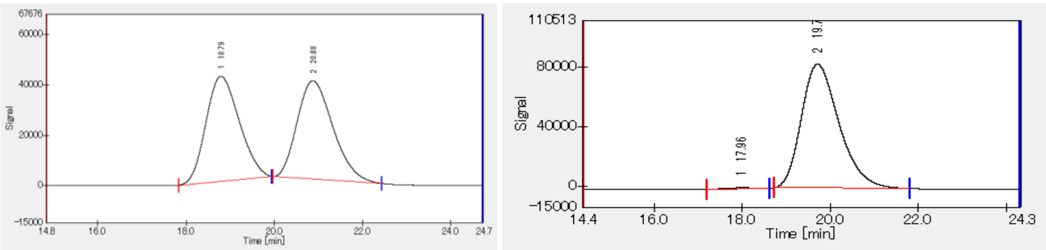
No	Rt (min)	area (%)
1	7.11	99.2607
2	7.9	0.7393



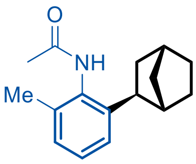
2g

^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.35 (br s, 1H), 7.89–7.85 (m, 1H), 7.84 (s, 1H), 7.80–7.75 (m, 1H), 7.72 (s, 1H), 7.44–7.39 (m, 2H), 3.07 (dd, J = 8.7, 4.4 Hz, 1H), 2.45–2.30 (m, 2H), 2.09 (s, 3H), 1.81–1.15 (m, 8H); NMR signals are in accordance with the data reported in literature.[4]

HPLC conditions: Daicel Chiralcel OD-H, hexane/2-propanol = 9/1, flow = 1.0 mL/min, wavelength = 230 nm, t_R = 18.0 min (minor) and 19.7 min (major), 99% ee



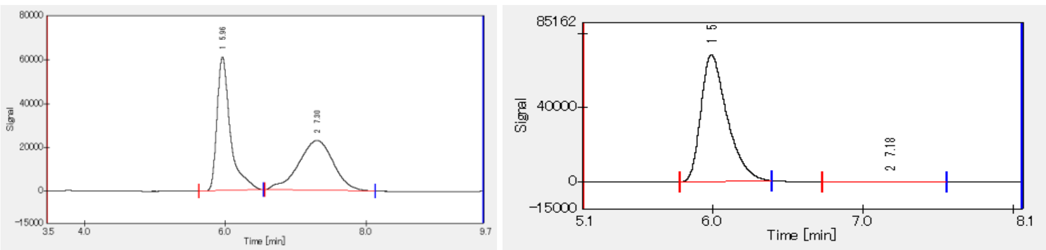
No	Rt (min)	area (%)
1	17.96	0.5383
2	19.71	99.4617



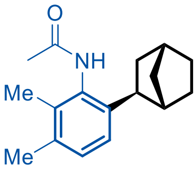
2h

^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.16 (br s, 1H), 7.01–7.14 (m, 3H), 2.86–2.80 (m, 1H), 2.27 (br s, 1H), 2.09 (s, 3H), 2.02 (s, 3H), 1.66–1.06 (m, 9H); NMR signals are in accordance with the data reported in literature.[4]

HPLC conditions: Daicel Chiralpak AD-H, hexane/2-propanol = 9/1, flow = 1.0 mL/min, wavelength = 230 nm, t_R = 5.99 min (major) and 7.18 min (minor), 99% ee



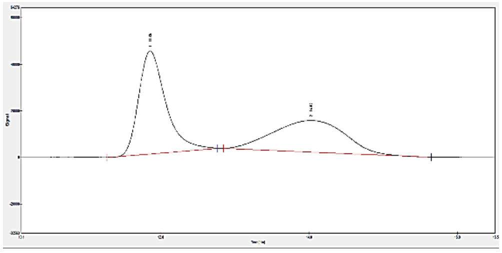
No	Rt (min)	area (%)
1	5.99	99.7931
2	7.18	0.2069

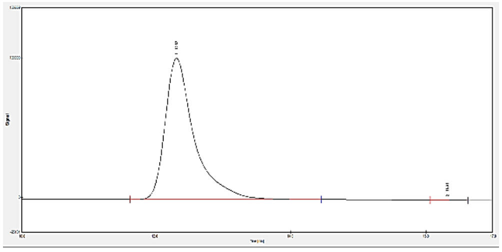


2i

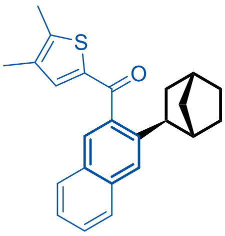
[1]**H NMR** (400 MHz, DMSO-d_6): δ = 9.14 (br s, 1H), 7.00 (d, J = 7.9 Hz, 1H), 6.95 (d, J = 7.9 Hz, 1H), 2.78 (t, J = 7.0 Hz, 1H), 2.36–2.21 (m, 2H), 2.19 (s, 3H), 2.02 (s, 3H), 1.98 (s, 3H),1.64–1.00 (m, 8H); NMR signals are in accordance with the data reported in literature.[4]

HPLC conditions: Daicel Chiralpak AD-H, hexane/2-propanol = 9/1, flow = 0.5 mL/min, wavelength = 230 nm, t_R = 12.3 min (major) and 16.3 min (minor), 99% ee





No	Rt (min)	area (%)
1	12.32	99.9098
2	16.31	0.0902



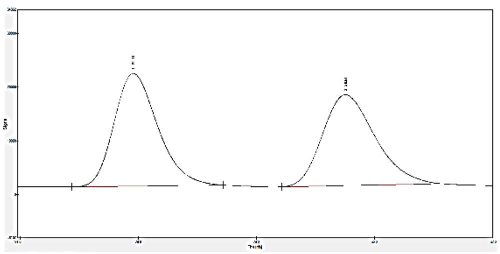
2n

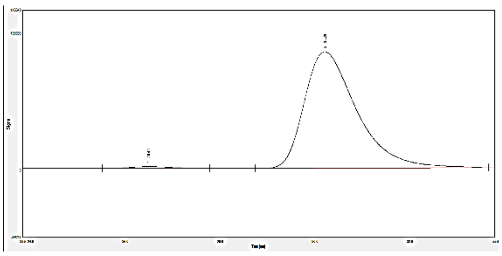
[1]**H NMR** (400 MHz, DMSO-d_6): δ = 7.99–7.90 (m, 2H), 7.94 (s, 1H), 7.87 (s, 1H), 7.57 (dd, J = 8.1, 7.0 Hz, 1H), 7.50 (dd, J = 8.1, 7.0 Hz, 1H), 7.23 (s, 1H), 3.07 (dd, J = 7.3, 7.0 Hz, 1H), 2.44–2.40 (m, 1H), 2.40 (s, 3H), 2.30–2.25 (m, 1H), 2.06 (s, 3H), 1.64–1.42 (m, 5H), 1.22–1.10 (m, 3H)

[13]**C NMR** (100 MHz, DMSO-d_6): δ = 189.3, 145.3, 141.8, 139.3, 138.8, 137.0, 135.6, 133.4, 129.9, 127.9, 127.6, 127.5, 127.3, 126.1, 124.0, 43.0, 41.8, 38.8, 36.5, 35.7, 29.8, 28.3, 13.8, 13.1

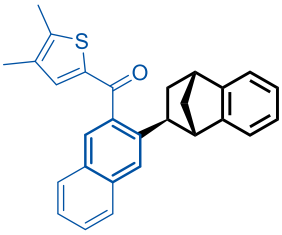
HRMS (ESI) *m/z* calcd. for $C_{24}H_{25}OS$ $(M+H)^+$: 361.1621, found: 361.1617.

HPLC conditions: Daicel Chiralpak AD-H×2, hexane/2-propanol = 99/1, flow = 1.0 mL/min, wavelength = 230 nm, t_R = 26.5 min (minor) and 30.2 min (major), 98% ee; $[\alpha]_D^{20}$ = + 101.704 (*c* 0.28, $CHCl_3$)





No	Rt (min)	area (%)
1	26.49	1.046
2	30.2	98.954



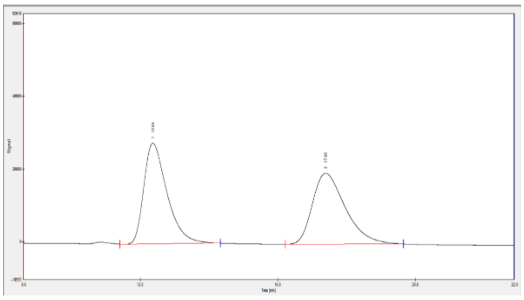
2o

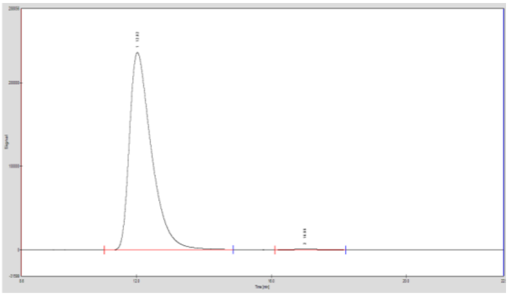
^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.08 (s, 1H), 8.02 (d, J = 8.1 Hz, 1H), 7.98 (s, 1H), 7.96 (d, J = 8.4 Hz, 1H), 7.62–7.50 (m, 2H), 7.26 (s, 1H), 7.17–6.99 (m, 4H), 3.54 (s, 1H), 3.40 (d, J = 3.3 Hz, 1H), 3.06 (dd, J = 8.8, 5.1 Hz, 1H), 2.37 (s, 3H), 2.04 (s, 3H), 2.01-1.90 (m, 2H), 1.69 (d, J = 9.2 Hz, 1H), 1.52–1.44 (m, 1H)

^{13}C NMR (100 MHz, DMSO-d_6): δ = 189.3, 148.3, 148.0, 145.7, 140.3, 139.3, 139.0, 137.3, 135.7, 133.5, 130.1, 128.0, 127.7, 127.4, 127.4, 126.3, 125.7, 125.6, 124.5, 120.7, 120.4, 48.6, 46.1, 43.8, 41.8, 35.9, 13.8, 13.1

HRMS (ESI) *m/z* calcd. for $C_{28}H_{24}ONaS$ $(M+Na)^+$: 431.1440, found: 431.1435.

HPLC conditions: Daicel Chiralcel OD-H, hexane/2-propanol = 99/1, flow = 1.0 mL/min, wavelength = 230 nm, t_R = 12.0 min (major) and 17.0 min (minor), 99% ee; $[\alpha]_D^{20}$ = + 101.706 (c 0.40, $CHCl_3$)

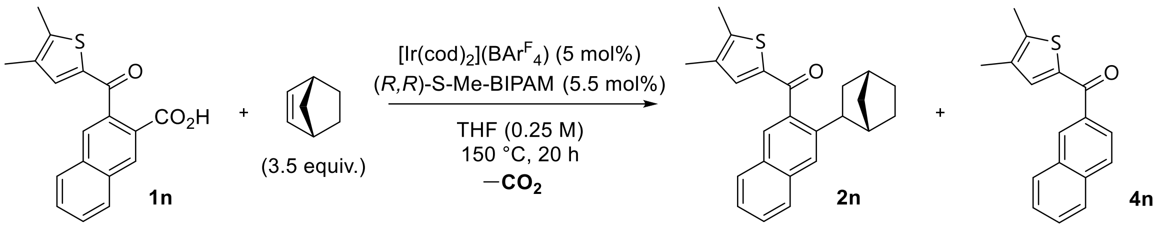


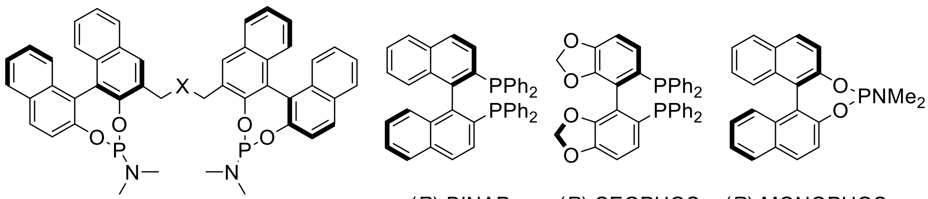


No	Rt (min)	area (%)
1	12.02	99.5984
2	16.99	0.4016

IV. Optimization of reaction conditions of aromatic carboxylic acids bearing ketone moieties

Table S1 Optimization of reaction conditions

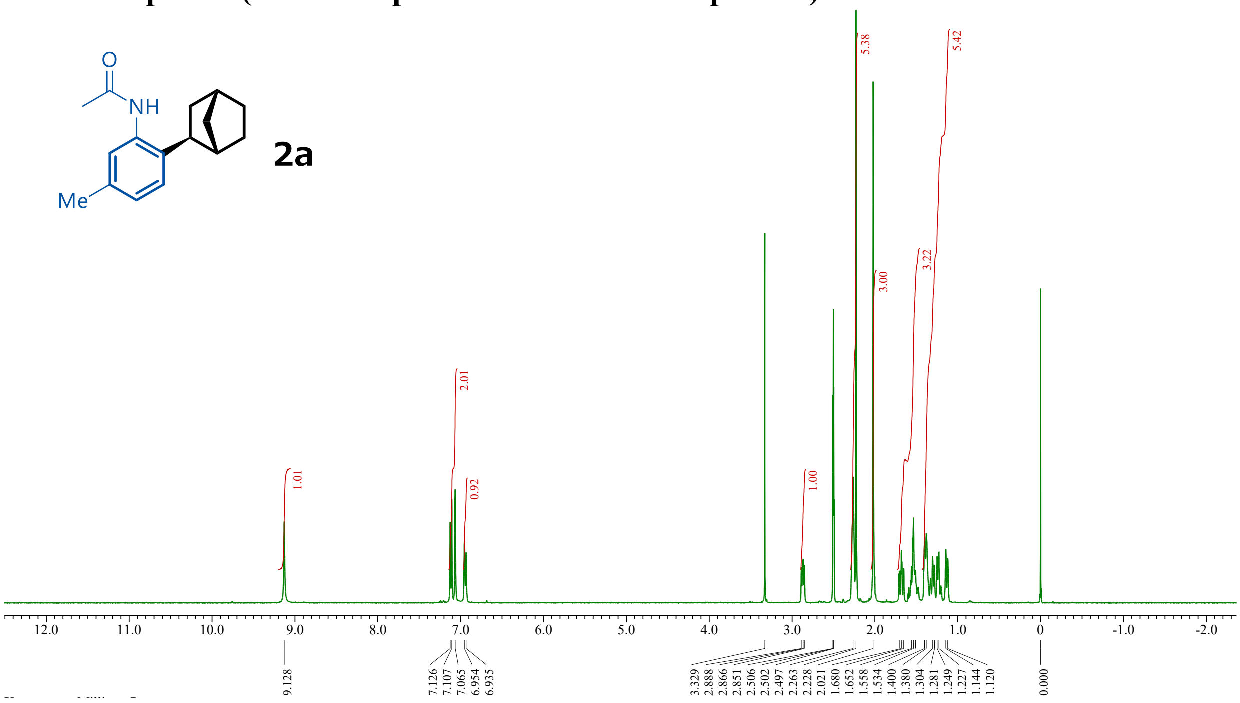




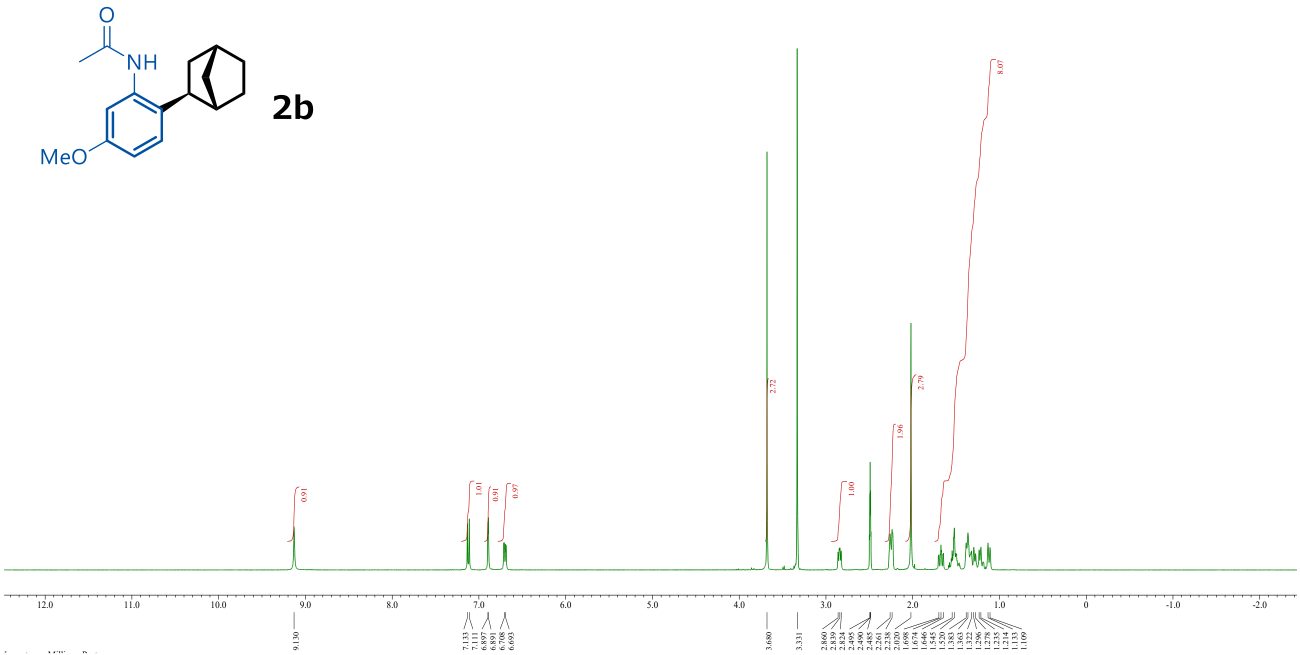
Entry	deviation from above	2n yield (%)	2n %ee	4n yield (%)
1	none	18	90	35
2	$[Ir(cod)Cl]_2$	trace	-	trace
3	$Ir(cod)_2(OTf)$	0	-	trace
4	(*R*)-BINAP	3	77	8
5	(*R,R*)-Me-BIPAM	trace	-	14
6	(*R*)-MONOPHOS	0	-	trace
7	Toluene	0	-	trace
8	DME	0	-	0
9	0.5 M	15	89	24
10	Ir/ligand (10 mol%)	36	98	29

[a] The reaction was carried out on a 0.25 mmol scale. [b] Isolated yield.
[c] Enantiomeric excesses were determined by chiral HPLC analysis.

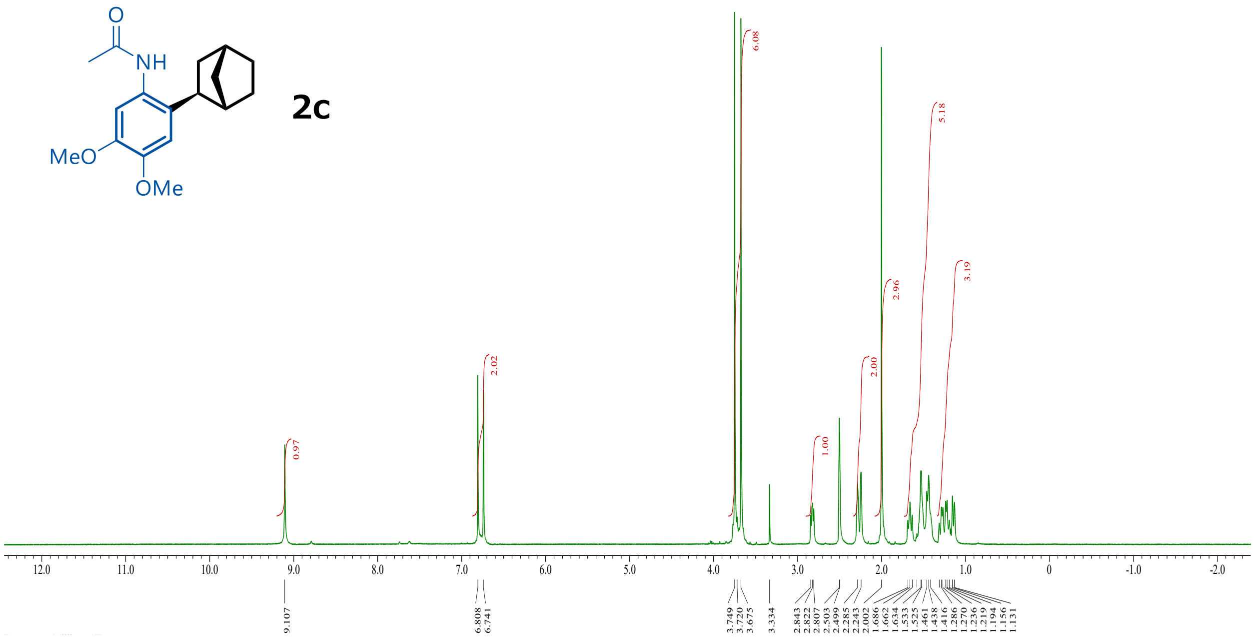
V. NMR Spectra ([1]H NMR spectra for Known Compounds)



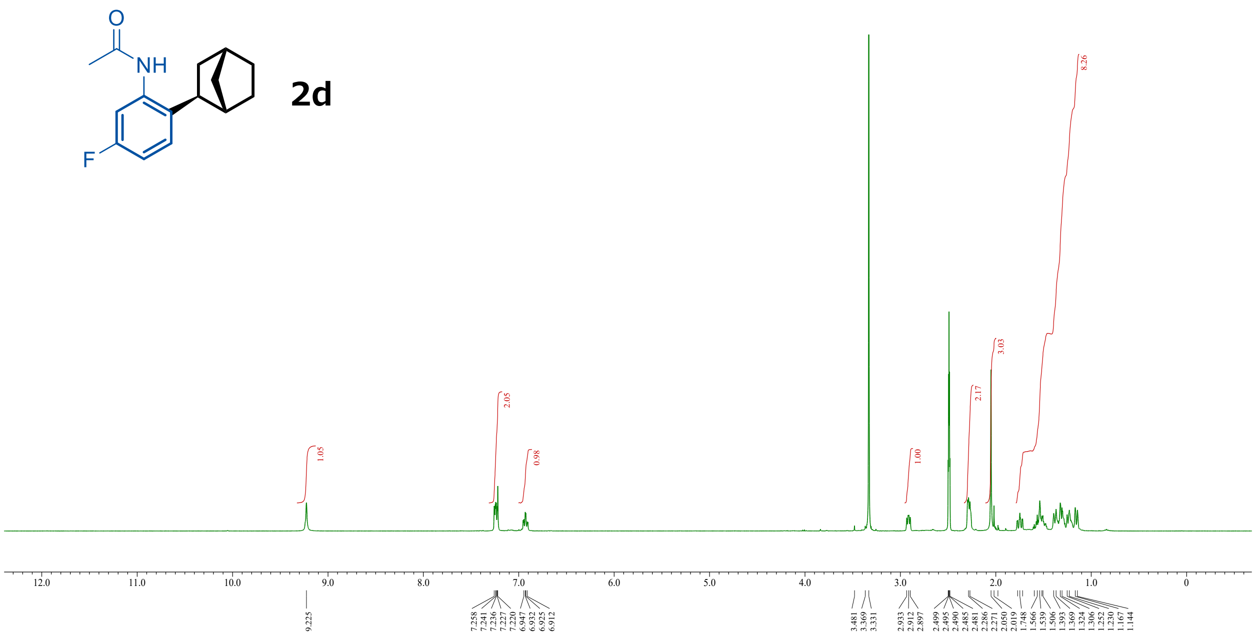
2a



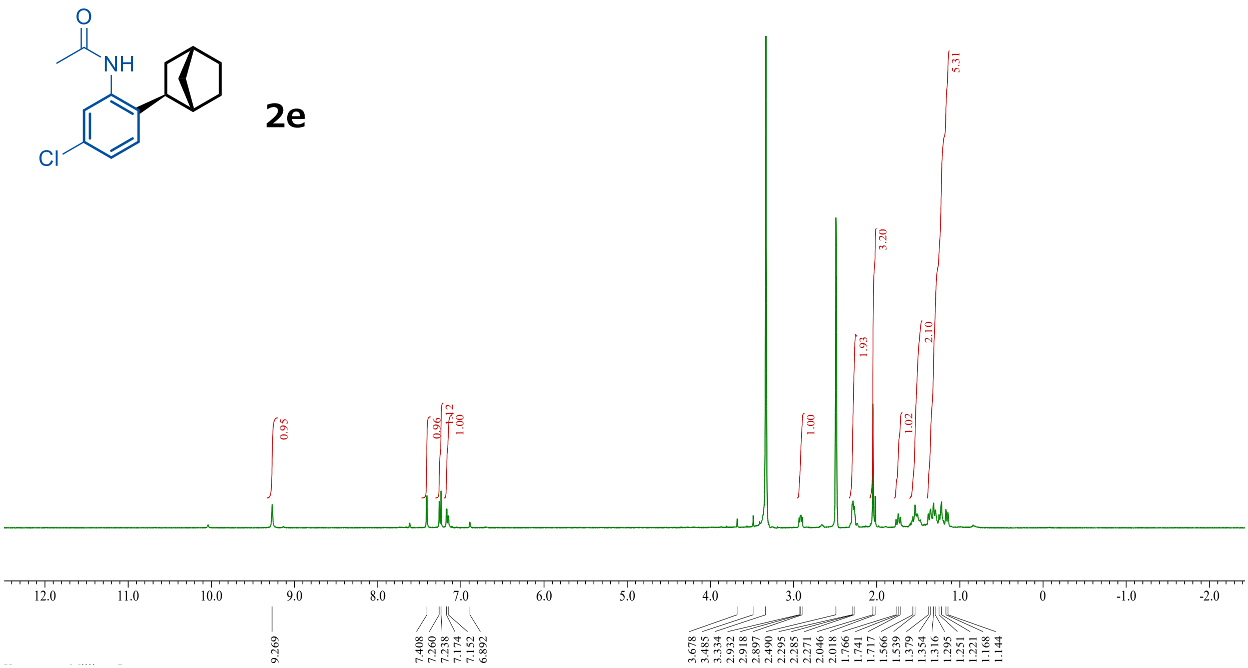
2b



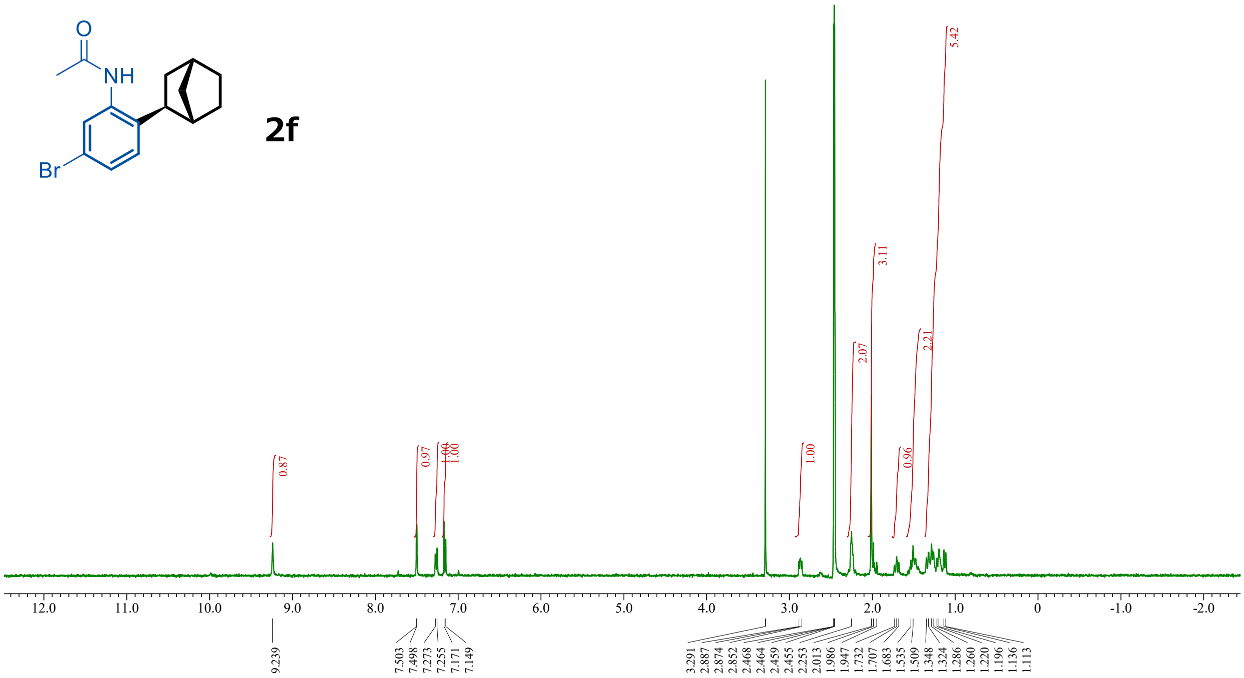
2c



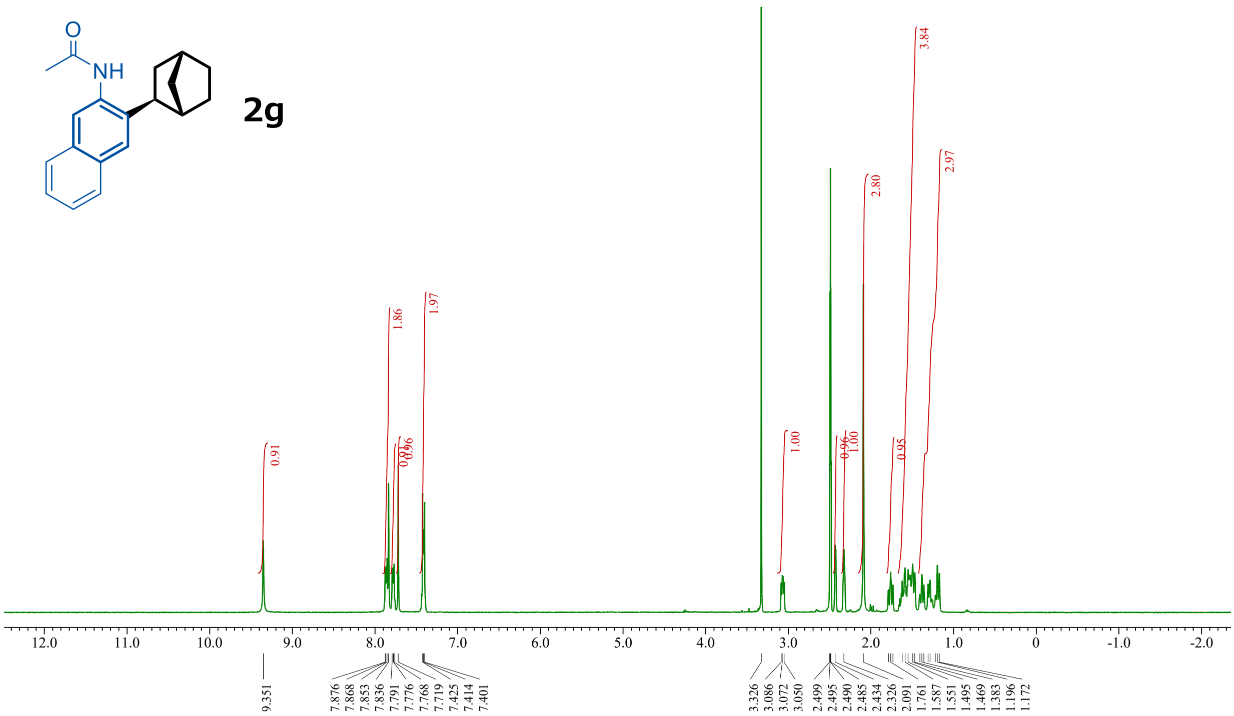
2d



2e

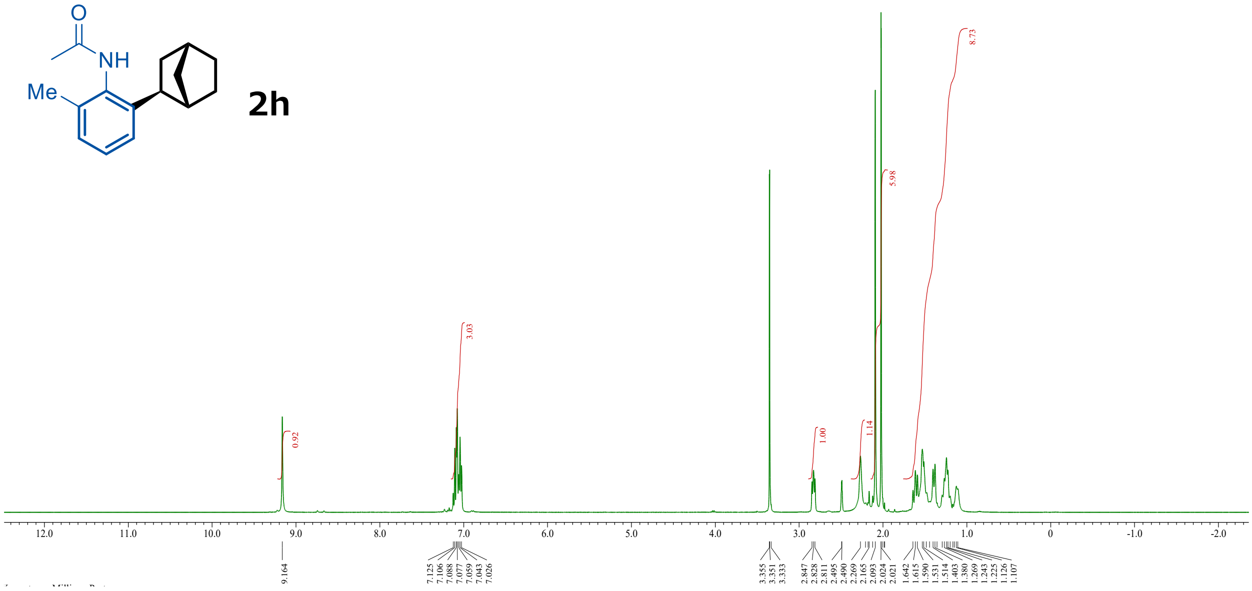


2f



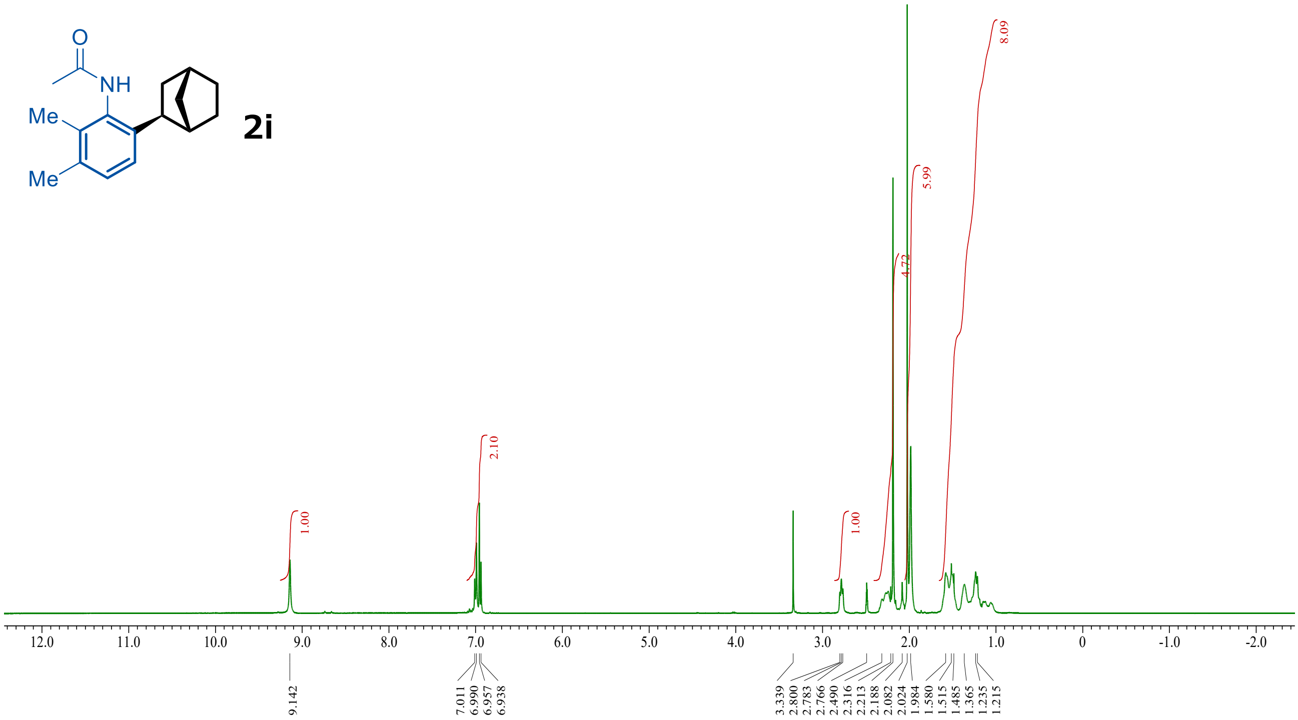
O
NH
0.91
1.86
0.91
0.96
1.97
1.00
0.96
1.00
2.80
0.95
3.84
2.97
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
9.351
7.876
7.868
7.853
7.836
7.791
7.776
7.768
7.719
7.425
7.414
7.401
3.326
3.086
3.072
3.050
2.499
2.495
2.490
2.485
2.434
2.326
2.091
1.761
1.587
1.551
1.495
1.469
1.383
1.196
1.172

2g



O
NH
Me
0.92
3.03
1.00
1.14
5.98
8.73
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
9.164
7.125
7.106
7.088
7.077
7.059
7.043
7.026
3.355
3.351
3.333
2.847
2.828
2.811
2.495
2.490
2.269
2.165
2.093
2.024
2.021
1.642
1.615
1.590
1.531
1.514
1.403
1.380
1.269
1.243
1.225
1.126
1.107

2h



Me
Me
NH
O
2i
1.00
2.10
1.00
4.72
5.99
8.09
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
9.142
7.011
6.990
6.957
6.938
3.339
2.800
2.783
2.766
2.490
2.316
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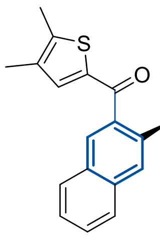
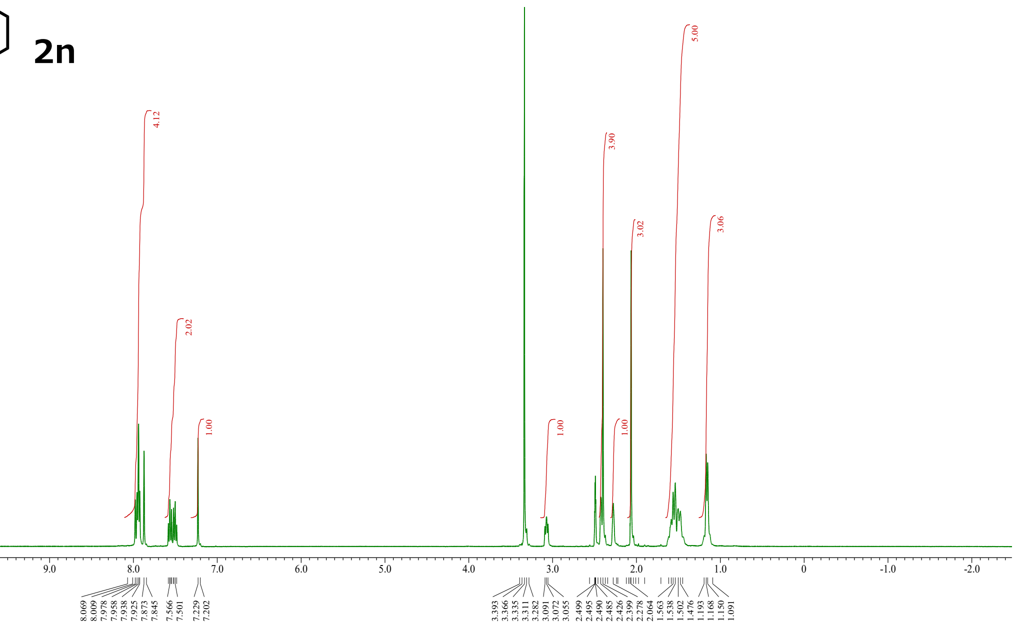
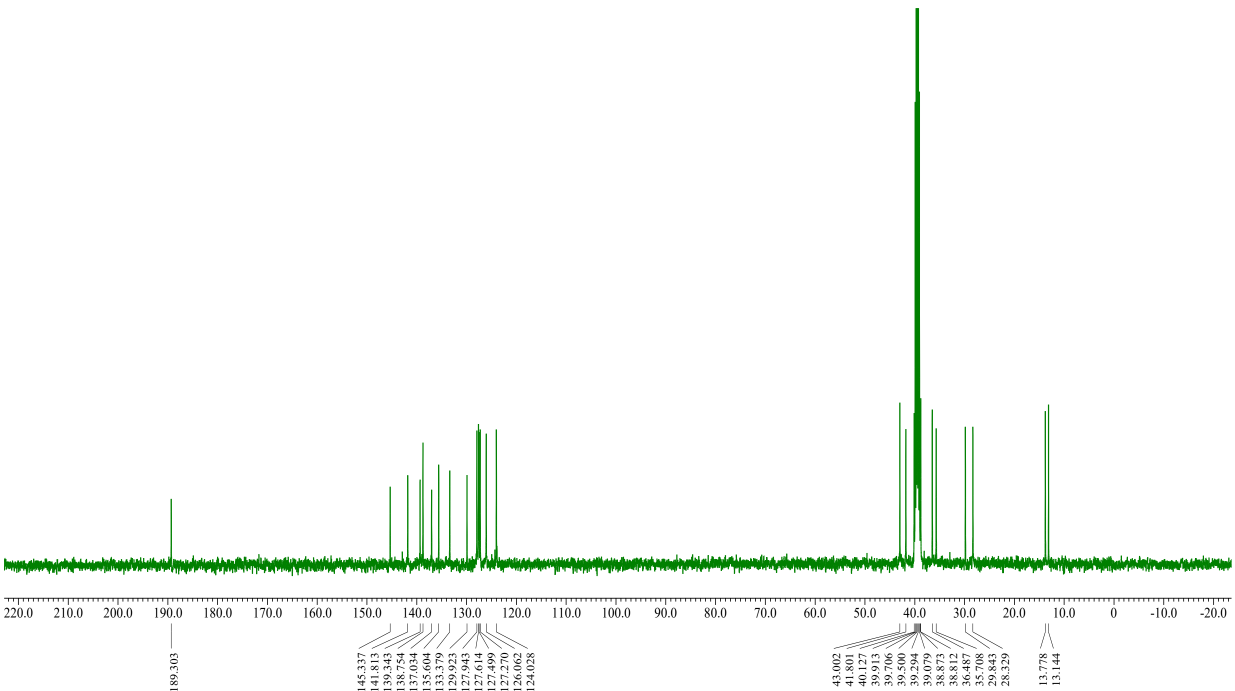
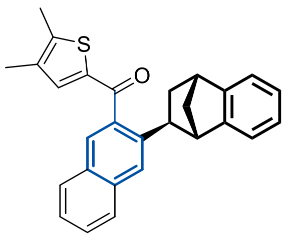
1.515
1.485
1.365
1.235
1.215



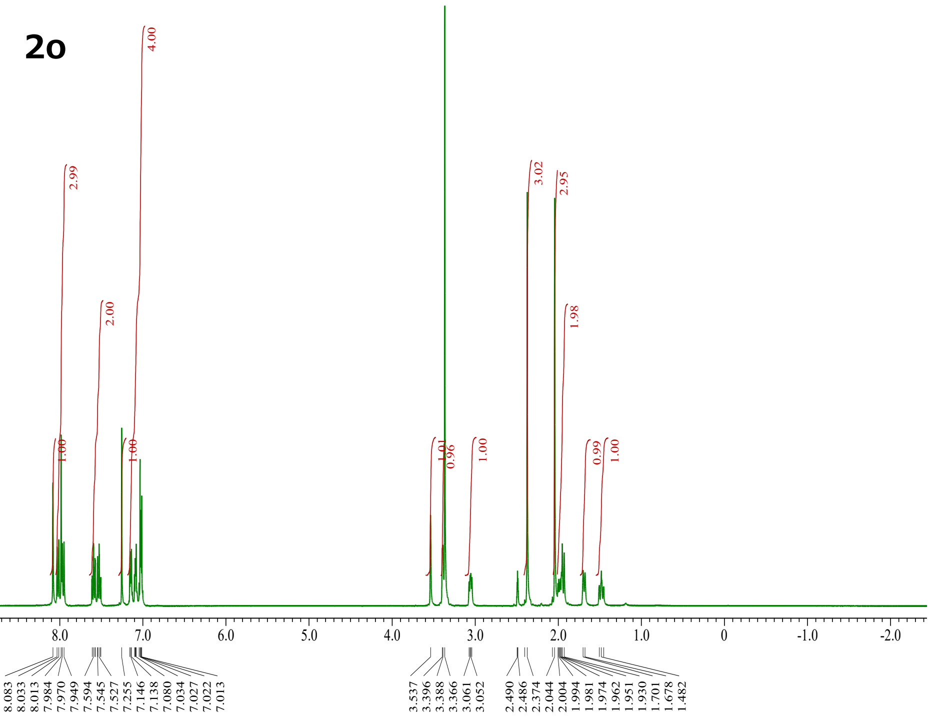
2n

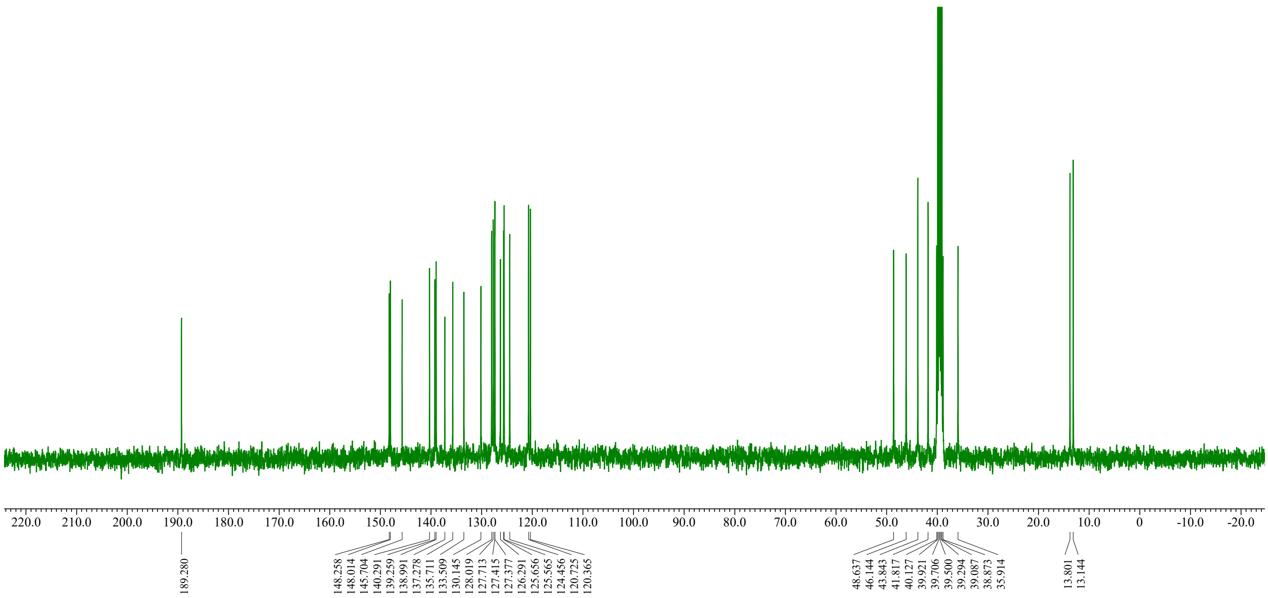






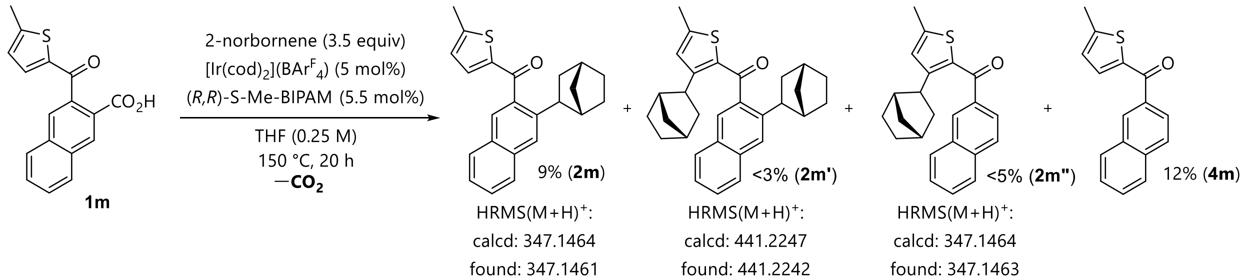
2o

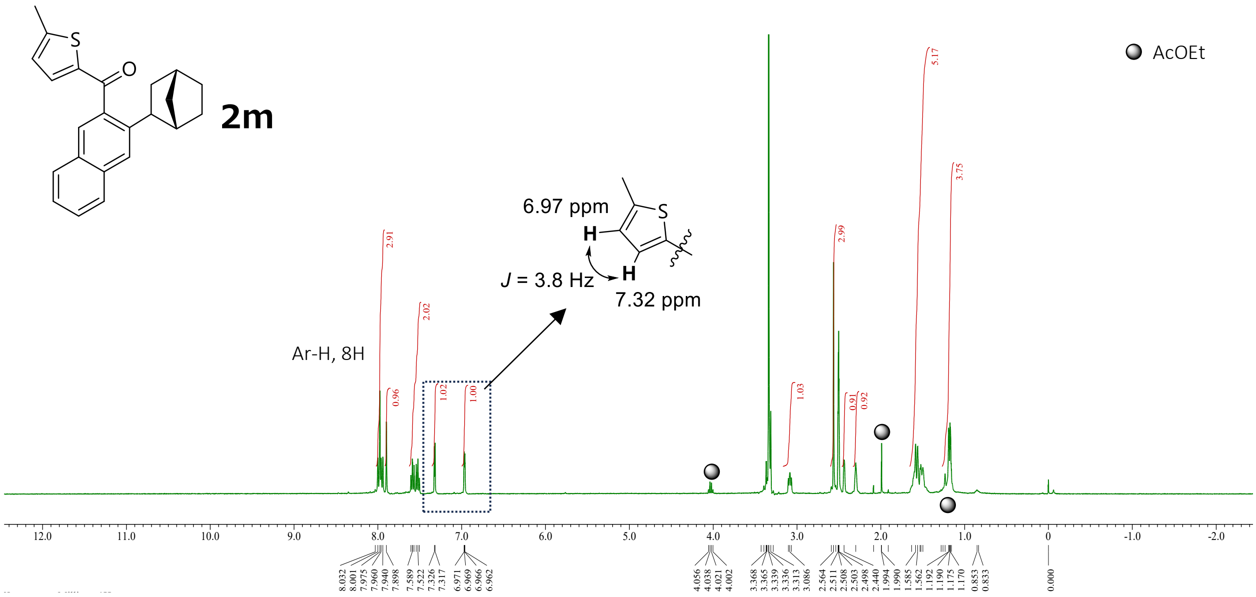

2.99
2.00
4.00
1.00
1.00
1.01
0.96
1.00
3.02
2.95
1.98
0.99
1.00
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0 -2.0
8.083
8.033
8.013
7.984
7.970
7.949
7.594
7.545
7.527
7.255
7.146
7.138
7.080
7.034
7.027
7.022
7.013
3.537
3.396
3.388
3.366
3.061
3.052
2.490
2.486
2.374
2.044
2.004
1.994
1.981
1.974
1.962
1.951
1.930
1.701
1.678
1.482

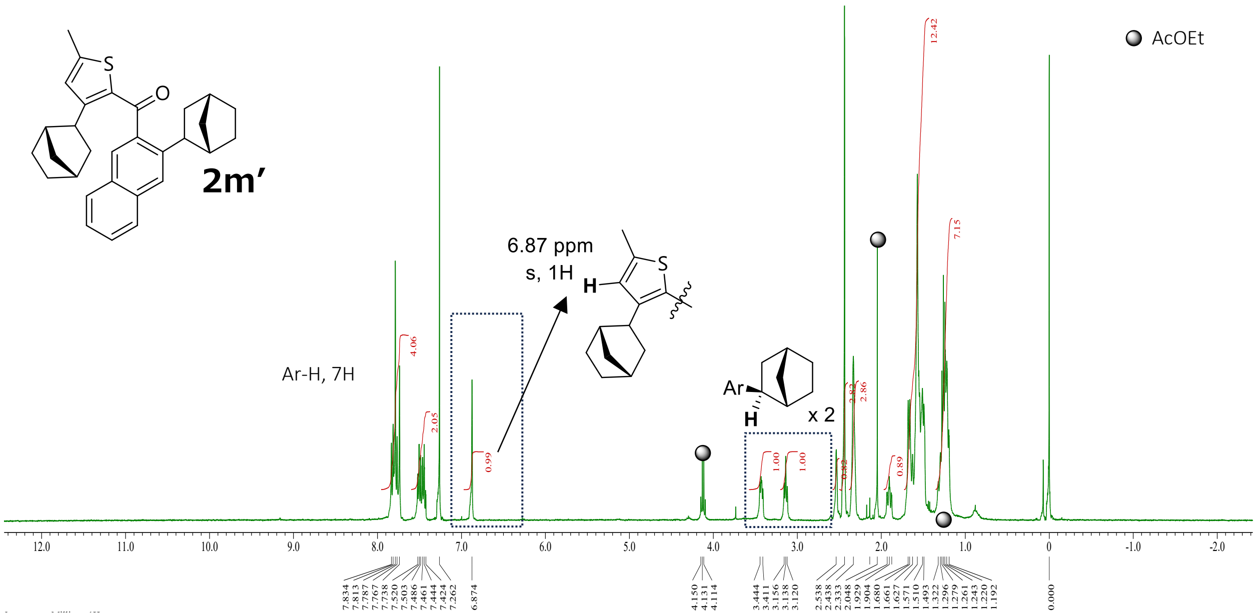

220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
189.280
148.258
148.014
145.704
140.291
139.259
138.991
137.278
135.711
133.509
130.145
128.019
127.713
127.415
127.377
126.291
125.656
125.565
124.456
120.725
120.365
48.637
46.144
43.843
41.817
40.127
39.921
39.706
39.500
39.294
39.087
38.873
35.914
13.801
13.144

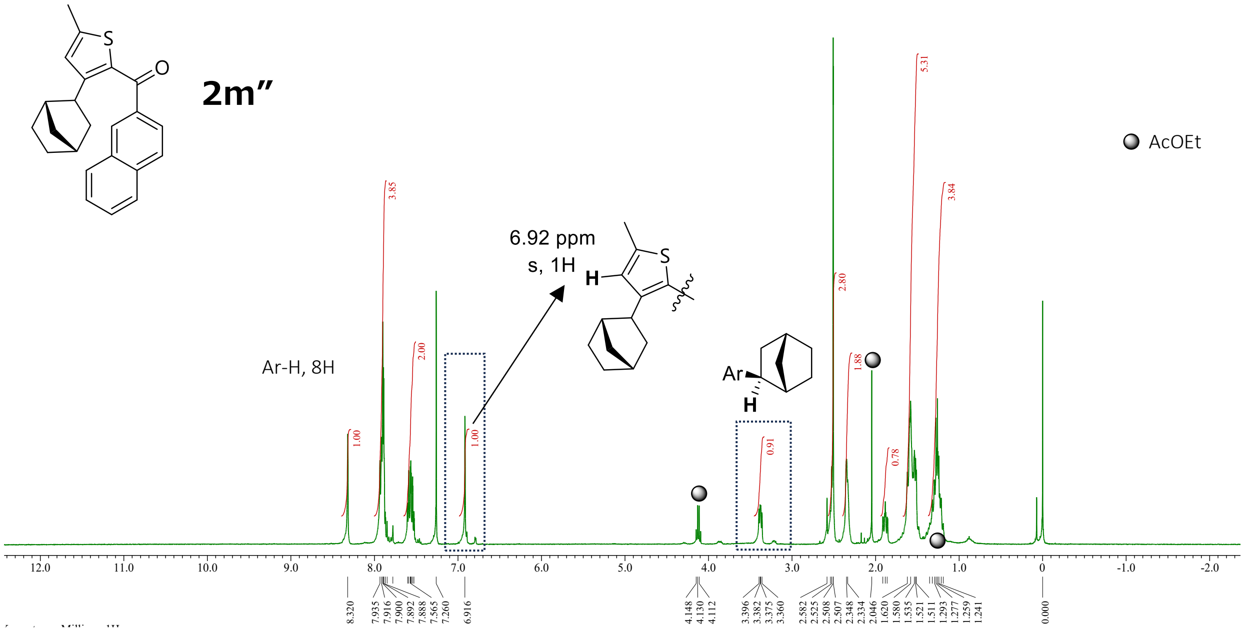
[1]H NMR spectra and HRMS data of regioisomeric side products for the reaction of **1m**

NMR spectra

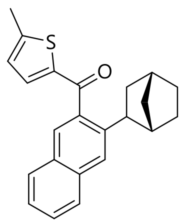




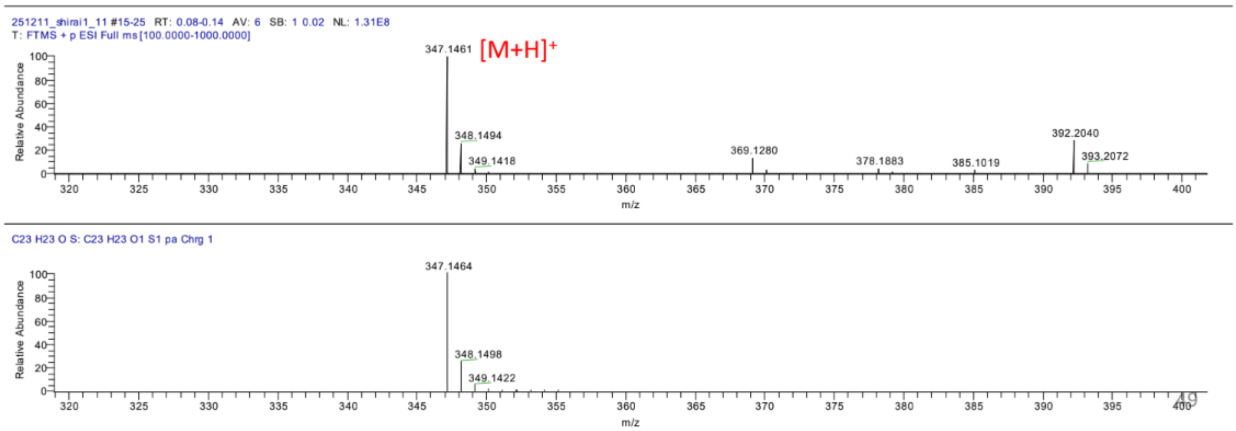


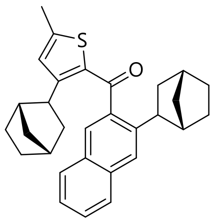

2m”
AcOEt
Ar-H, 8H
6.92 ppm
s, 1H
H
Ar
S
O

HRMS data

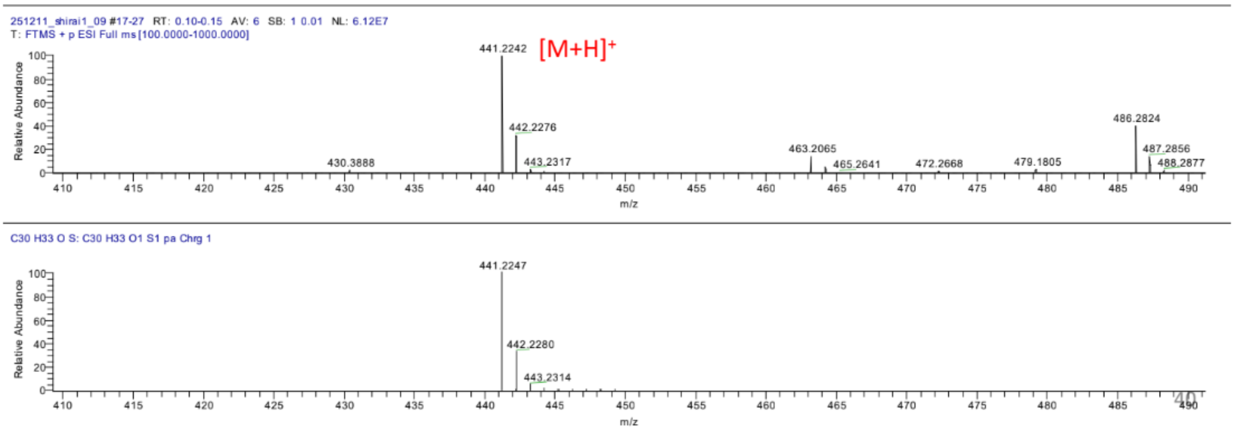


2m

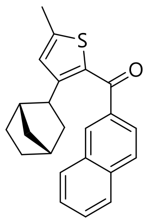

251211_shirai1_11 #15-25 RT: 0.08-0.14 AV: 6 SB: 1 0.02 NL: 1.31E8
T: FTMS + p ESI Full ms [100.0000-1000.0000]
347.1461 [M+H]+
348.1494
349.1418
369.1280
378.1883
385.1019
392.2040
393.2072
Relative Abundance
m/z
C23 H23 O S: C23 H23 O1 S1 pa Chrg 1
347.1464
348.1498
349.1422



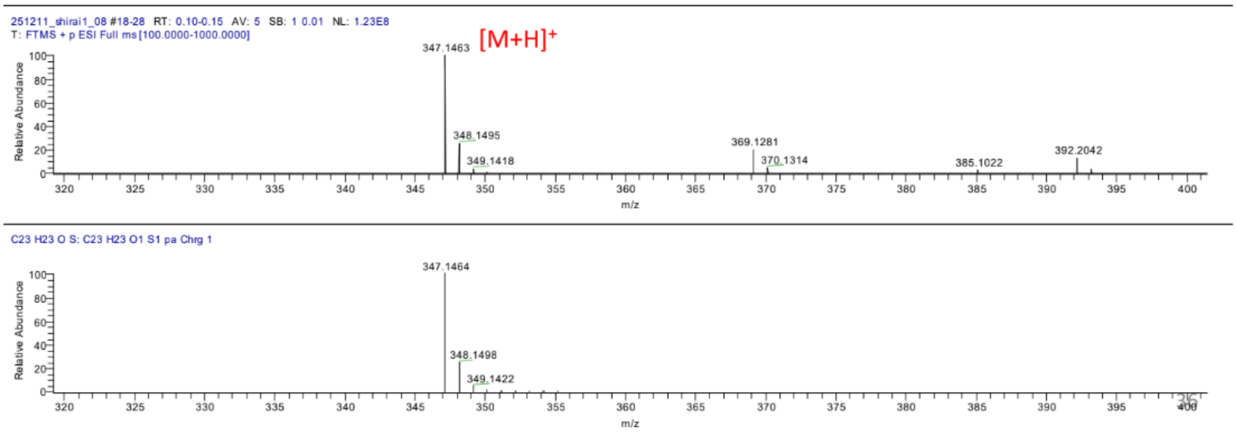
2m'



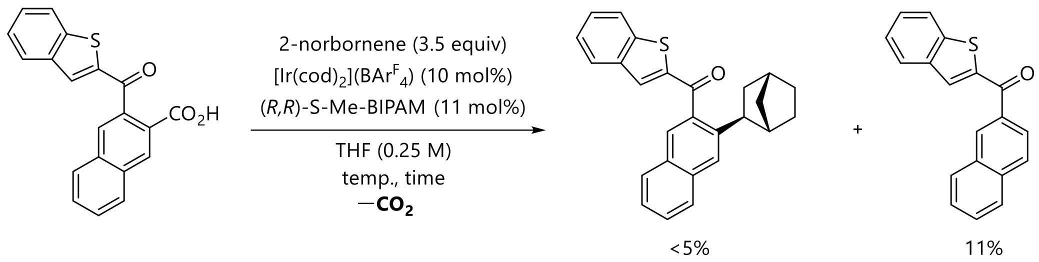
251211_shirai1_09 #17-27 RT: 0.10-0.15 AV: 6 SB: 1 0.01 NL: 6.12E7
T: FTMS + p ESI Full ms [100.0000-1000.0000]
[M+H]+
441.2242
442.2276
443.2317
430.3888
463.2065
465.2641
472.2668
479.1805
486.2824
487.2856
488.2877
Relative Abundance
m/z
C30 H33 O S: C30 H33 O1 S1 pa Chrg 1
441.2247
442.2280
443.2314



2m''



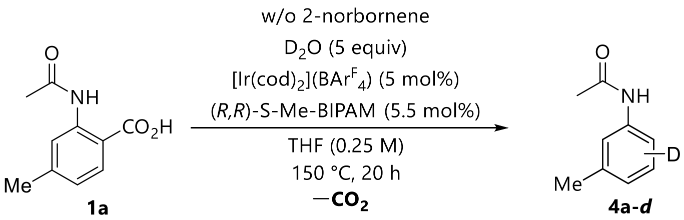
251211_shirai1_08 #18-28 RT: 0.10-0.15 AV: 5 SB: 1 0.01 NL: 1.23E8
T: FTMS + p ESI Full ms [100.0000-1000.0000]
[M+H]+
347.1463
348.1495
349.1418
369.1281
370.1314
385.1022
392.2042
Relative Abundance
m/z
C23 H23 O S: C23 H23 O1 S1 pa Chrg 1
347.1464
348.1498
349.1422

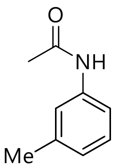


The reaction of 3-(benzo[*b*]thiophene-2-carbonyl)-2-naphthoic acid gave a low yield of the desired product, but regioisomeric products were not formed, other than a simple decarboxylation product.

VI. General Procedure for D_2O Experiments

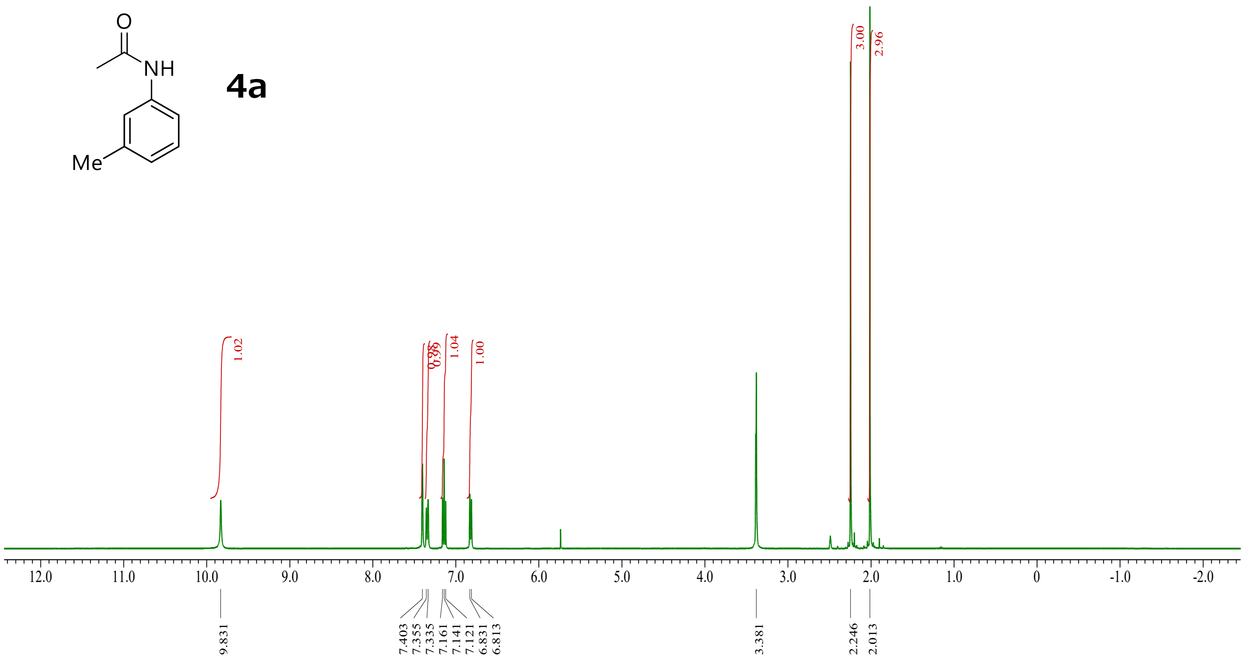
To a dried 20 mL sealed tube, $[Ir(cod)_2](BAr^F{}_4)$ (15.9 mg, 5 mol%), (*R,R*)-S-Me-BIPAM (10.7 mg, 5.5 mol%) and dry tetrahydrofuran (1.0 mL) were added under N_2 atmosphere. The solution was stirred at ambient temperature for 30 min. Thereafter, aromatic carboxylic acid (0.25 mmol) and D_2O (5 equiv.) were added. The reaction mixture was further heated to 150 °C and stirred for 20 h. Then, the mixture was purified using silica gel column chromatography (eluent: Hexane/AcOEt).

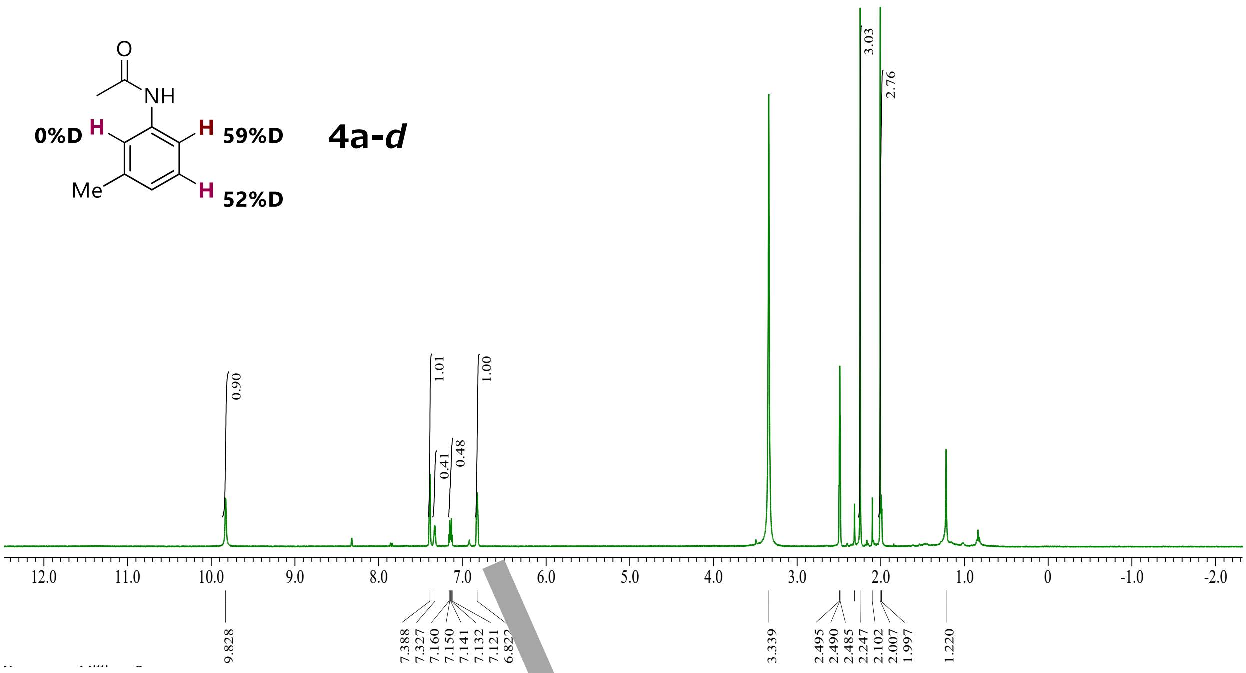


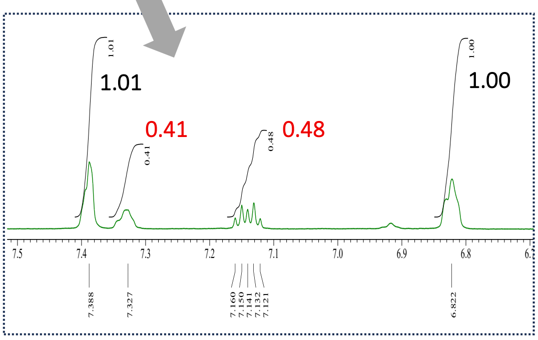


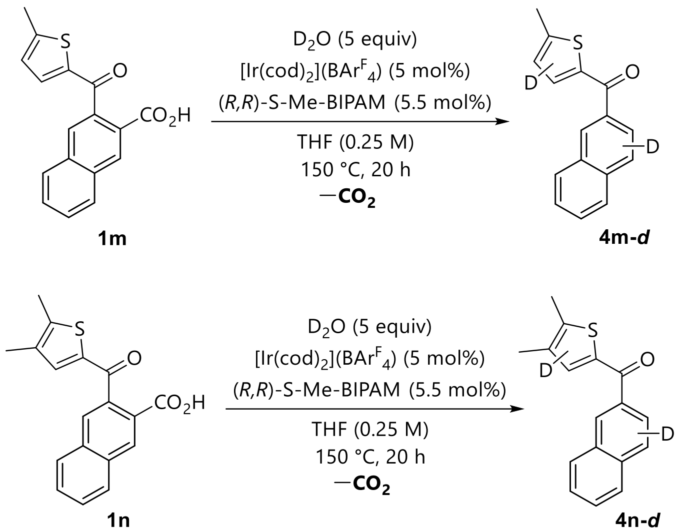
4a

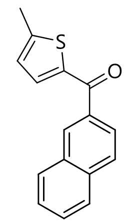
^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.83 (s, 1H), 7.40 (s, 1H), 7.35 (d, J = 8.1 Hz, 1H), 7.14 (dd, J = 8.1, 7.7 Hz, 1H), 6.82 (d, J = 7.7 Hz, 1H), 2.25 (s, 3H), 2.01 (s, 3H)


4a
Me
NH
O


4a-*d*
0%D
59%D
52%D
Me
NH
O

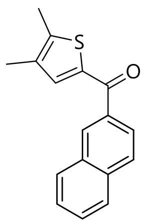

1.01
0.41
0.48
1.00





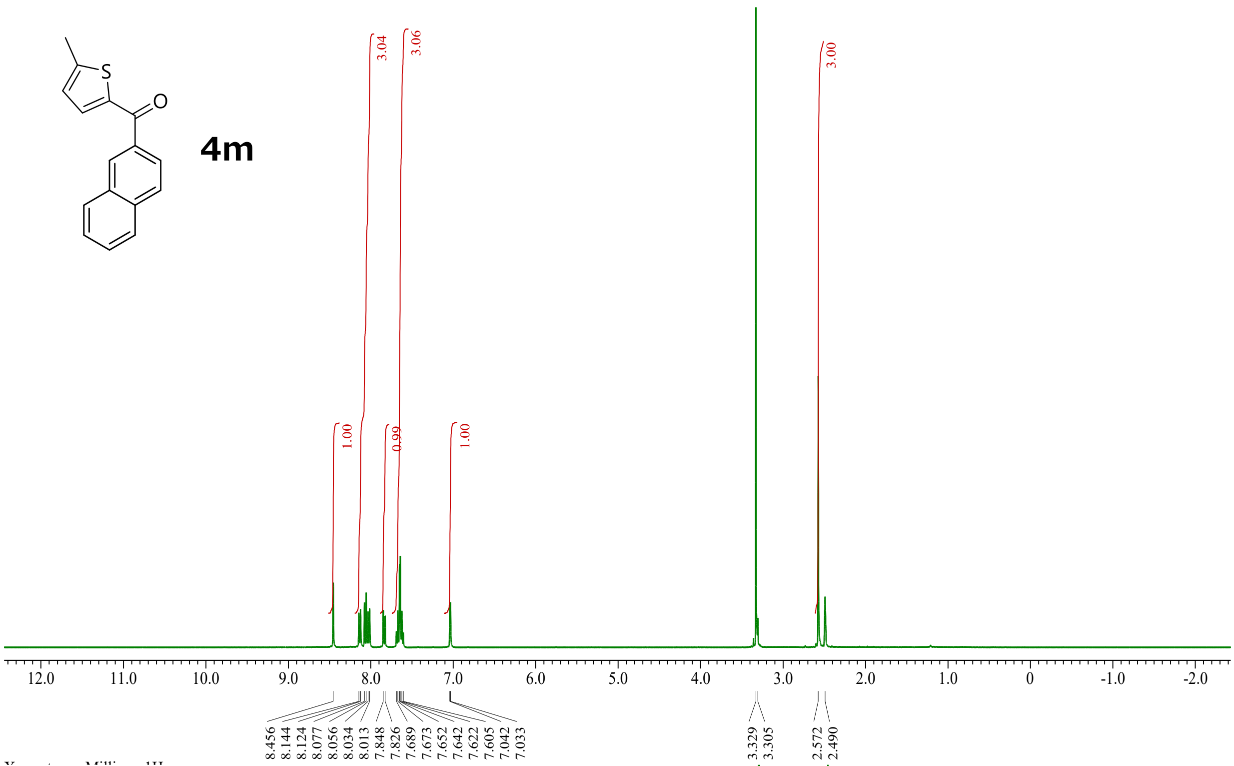
4m

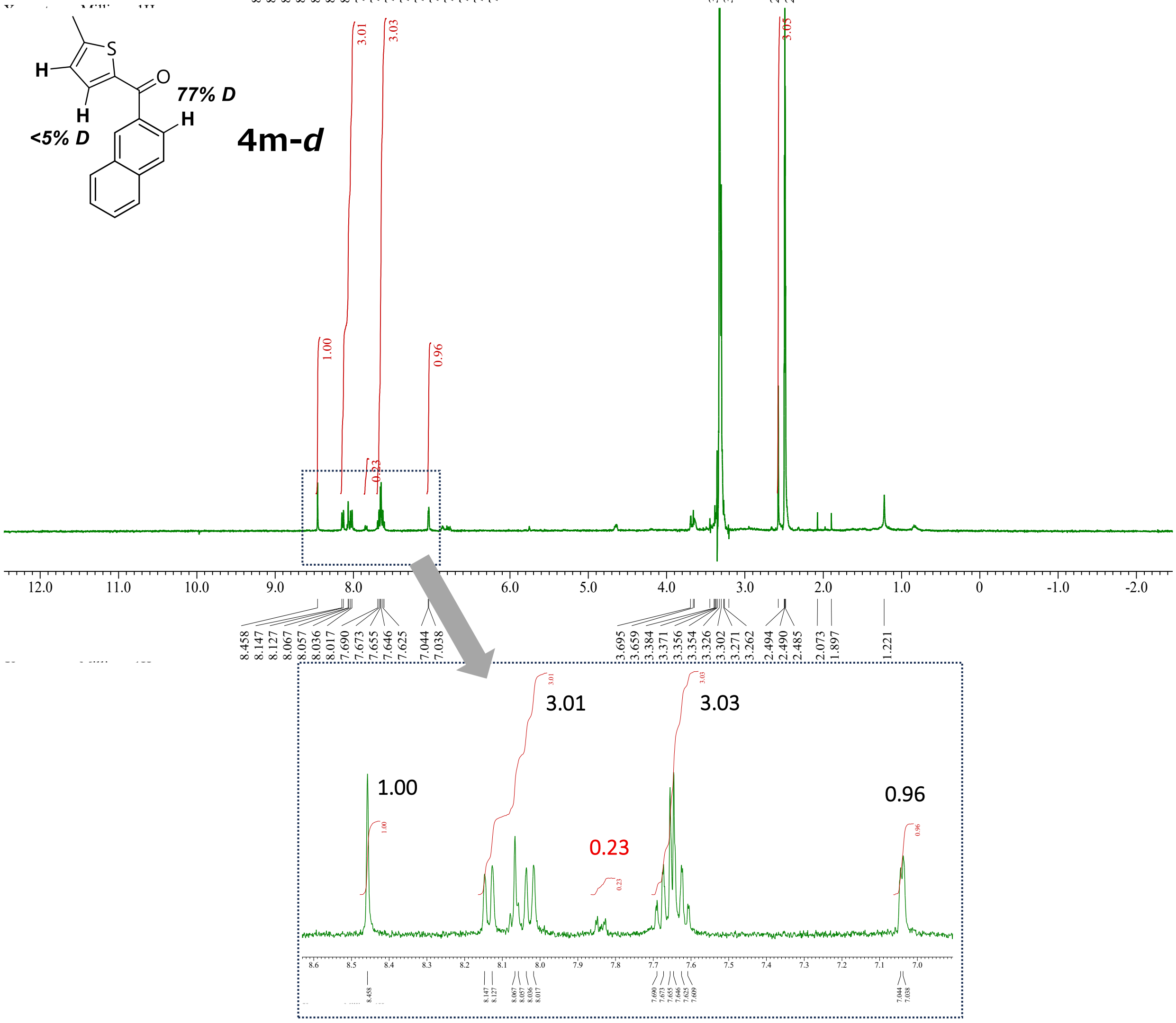
^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.46 (s, 1H), 8.13 (d, J = 8.1 Hz, 1H), 8.07 (d, J = 8.4 Hz, 1H), 8.02 (d, J = 8.1 Hz, 1H), 7.84 (dd, J = 8.4, 1.1 Hz, 1H), 7.70–7.60 (m, 3H), 7.04 (d, J = 3.5 Hz, 1H), 2.57 (s, 3H)

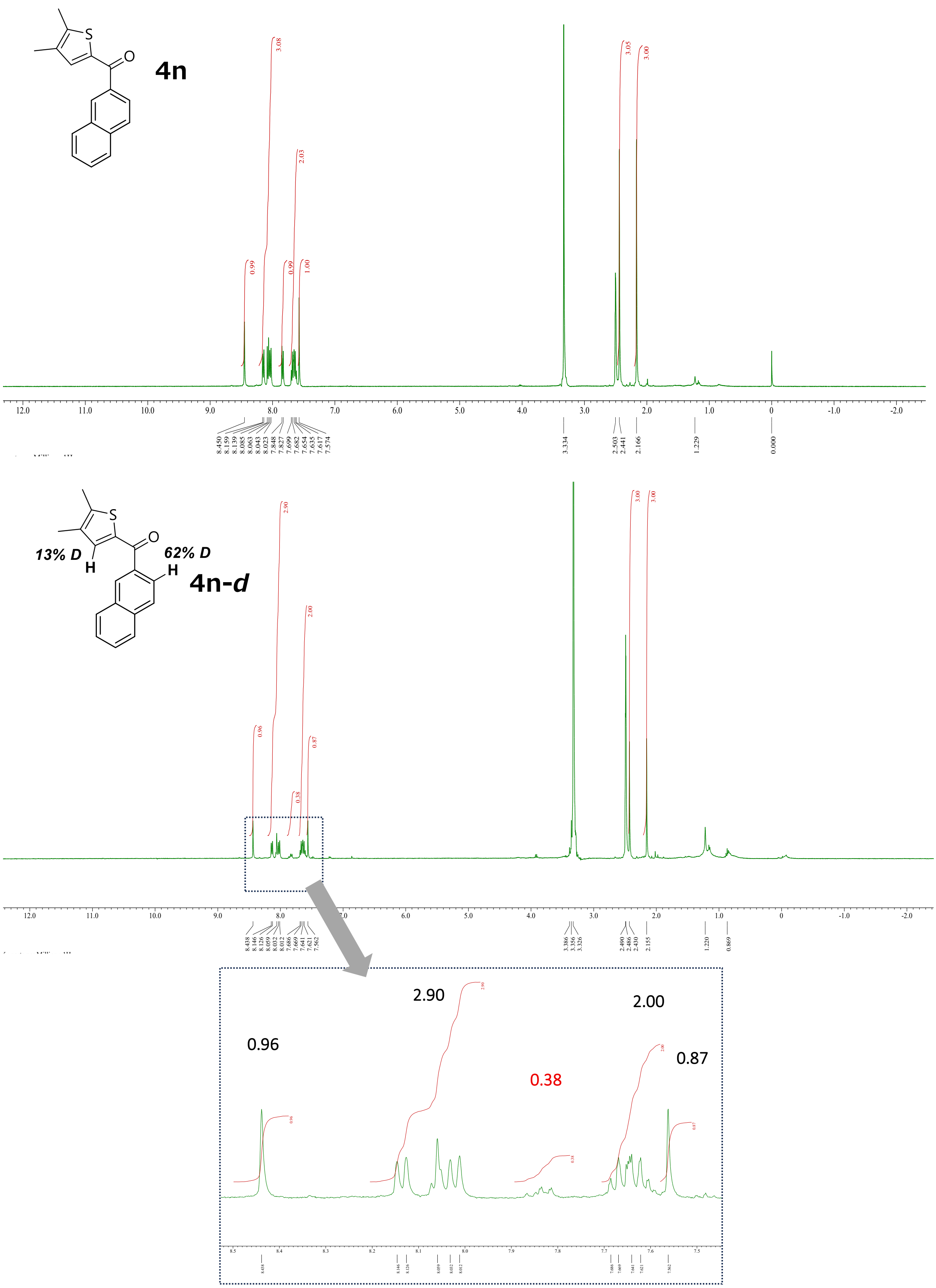


4n

^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.44 (s, 1H), 8.14 (d, J = 8.1 Hz, 1H), 8.06 (d, J = 8.8 Hz, 1H), 8.02 (d, J = 8.1 Hz, 1H), 7.82 (dd, J = 8.4, 1.1 Hz, 1H), 7.69–7.59 (m, 2H), 7.56 (s, 1H), 2.43 (s, 3H), 2.15 (s, 3H)


4m


77% D
<5% D
4m-d
1.00
3.01
0.23
3.03
0.96


4n
13% D
62% D
4n-d
0.96
2.90
0.38
2.00
0.87

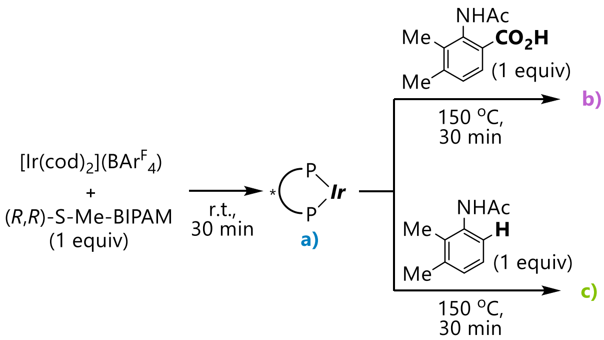
VII. Reaction time profile

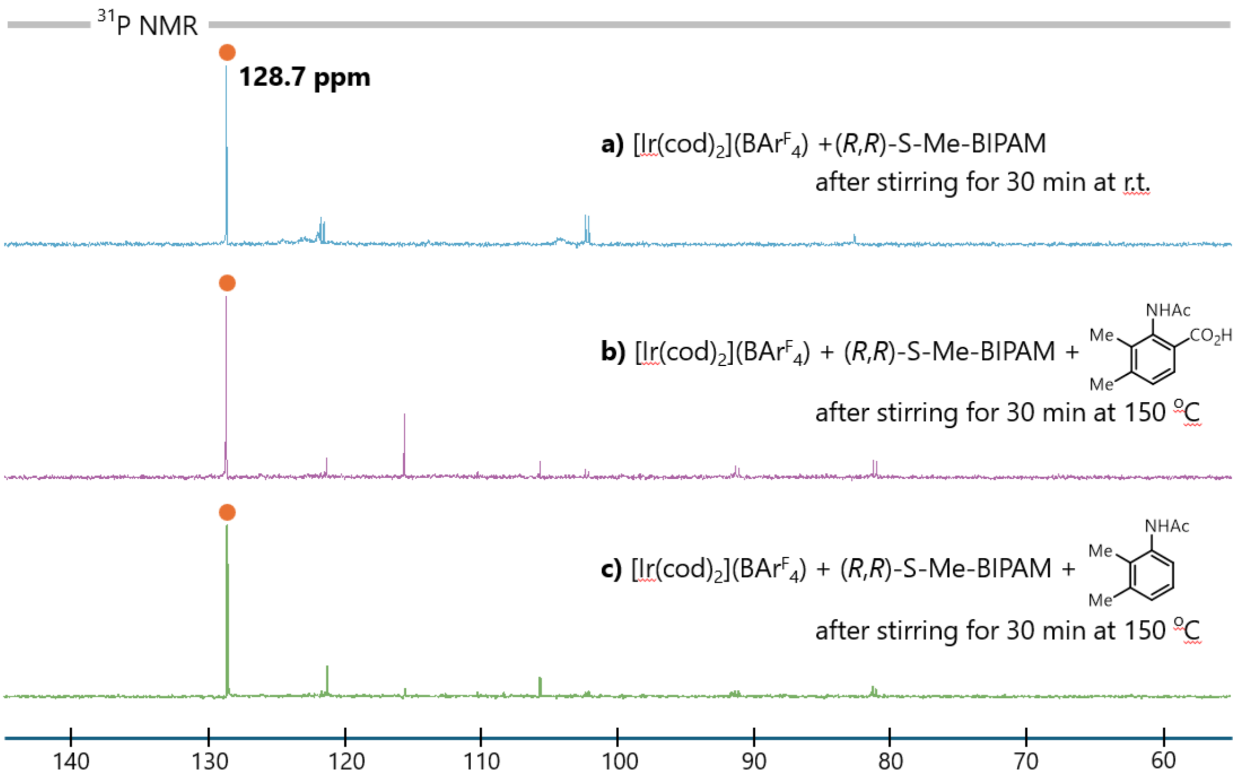
A typical procedurer for decarboxylation: To a dried sealed tube, $[Ir(cod)_2](BAr^F{}_4)$ (31.8 mg, 10 mol%), (*R,R*)-S-Me-BIPAM (21.4 mg, 11 mol%) and dry tetrahydrofuran (1.0 mL) were added under N_2 atmosphere. The solution was stirred at ambient temperature for 30 min. Thereafter, aromatic carboxylic acid **1** (0.25 mmol) was added. The reaction mixture was further heated to 150 °C and stirred. Then, yield of arene product was determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard.

A typical procedurer for hydroarylation via C–H activation: To a dried sealed tube, $[Ir(cod)_2](BAr^F{}_4)$ (31.8 mg, 10 mol%), (*R,R*)-S-Me-BIPAM (21.4 mg, 11 mol%) and dry tetrahydrofuran (1.0 mL) were added under N_2 atmosphere. The solution was stirred at ambient temperature for 30 min. Thereafter, acetanilide (0.25 mmol) and 2-norbornene (3.5 equiv) were added. The reaction mixture was further heated to 150 °C and stirred. Then, yield of addition product was determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard.

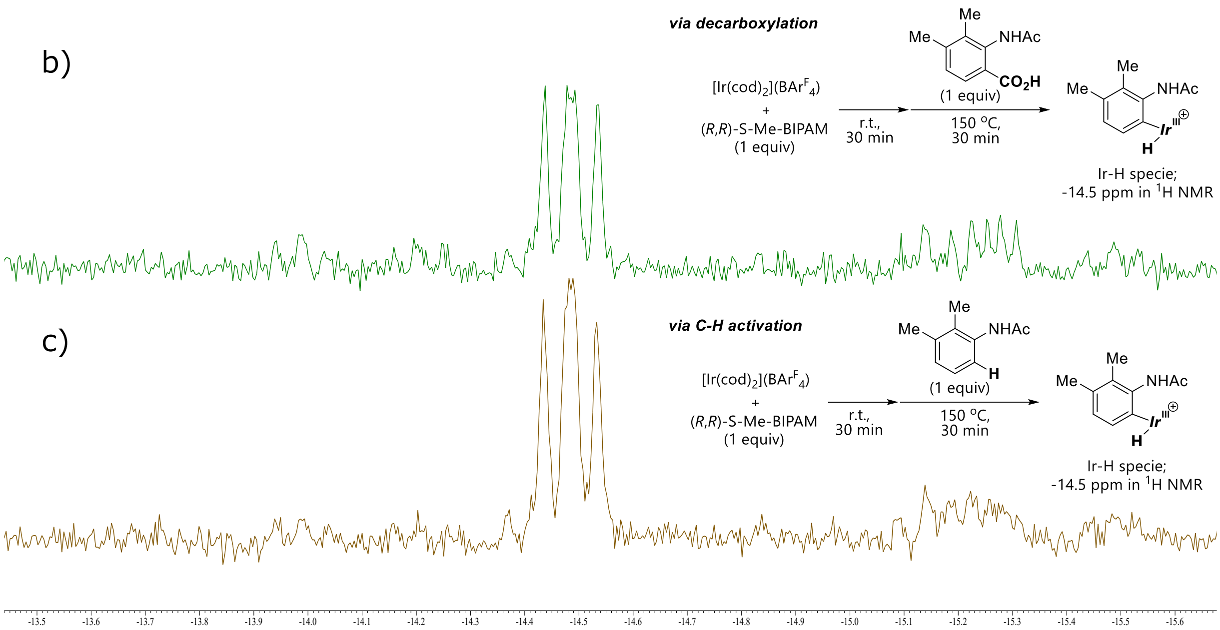
VIII. ^{31}P NMR study

To a dried sealed tube, [Ir(cod)$_2$](BAr$^F_4$) (0.0375 mmol), (*R,R*)-S-Me-BIPAM (1.0 equiv) and dry tetrahydrofuran-*d*$_8$ (1.0 mL) were added under N_2 atmosphere. The solution was stirred at ambient temperature for 30 min. Thereafter, aromatic carboxylic acid or anilide (1.0 equiv) was added. The reaction mixture was further heated to 150 °C and stirred for 30 min. Then, ^{31}P NMR spectra were recorded for each sample.





^{1}H NMR spectra of aryl-iridium hydride species



IX. X-ray crystal structure of compound 2i

The absolute configuration of **2i** was determined by X-ray crystallographic analysis. The details were summarized in **Figure S1** and **Table S2–S8**. Single crystal X-ray structural analyses were carried out on a Rigaku XtaLAB Synergy-R/Si system with 1.2 kW PhotonJet-S microfocus rotating anode using graphite monochromated Cu-Kα radiation and HyPix-6000HE detector. The intensity images were integrated using the CrysAlisPro program package (Rigaku Oxford Diffraction) and the empirical absorption correction was applied for the data. The structures were solved by dual-space methods with (SHELXT)[6] and refined by full-matrix least-squares techniques against F^2 (SHELXL-2018/3)[7] by using Olex2 software package.[8] The intensities were corrected for Lorentz and polarization effects. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using AFIX instructions.

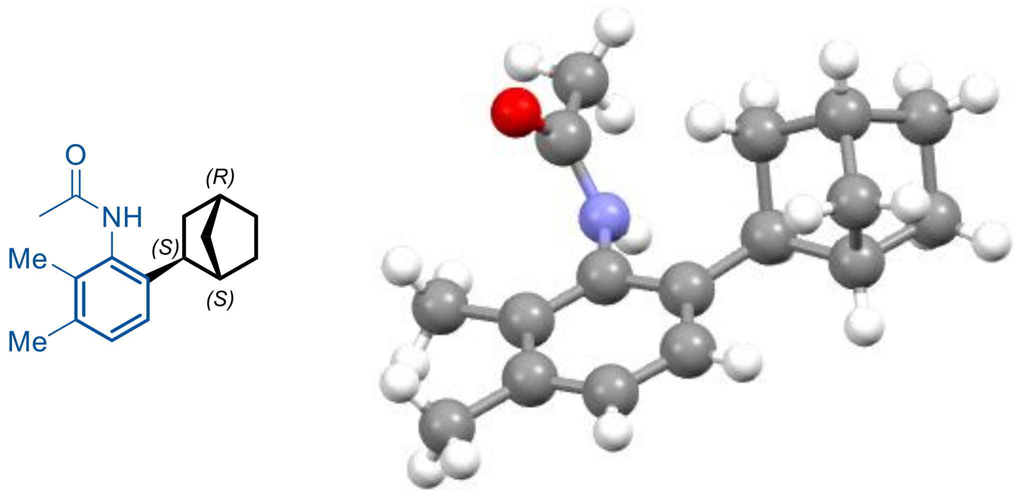
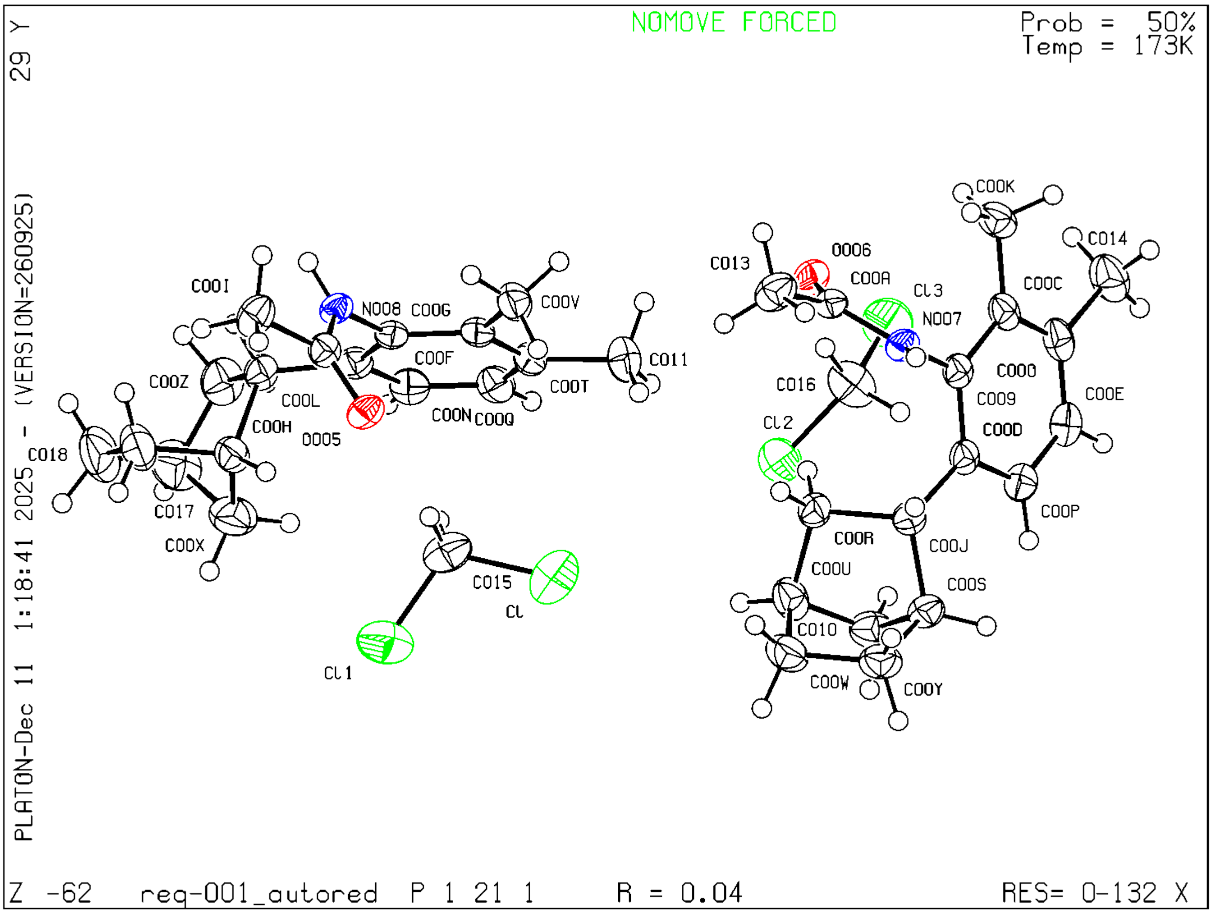


Figure S1. X-ray structure of **2i**

Table S2. Summary of X-ray crystallographic data of **2i**.

CCDC Name	2515012
Empirical Formula	$C_{18}H_{25}Cl_2NO$
Formula Weight	342.29
Temperature / K	173.01(10)
Crystal System	monoclinic
Space Group	$P2_1$
a / Å	13.1647(3)
b / Å	9.6045(2)
c / Å	15.8224(4)
α / °	90
β / °	113.961(3)
γ / °	90
Volume / Å^3	1828.18(8)
Z	4
ρ_{calc} g cm^{-3}	1.244
μ/mm^{-1}	3.193
F(000)	728.0
Crystal Size / mm^3	0.4 × 0.2 × 0.05
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.112 to 136.404
Index ranges	$-15 \leq h \leq 15$, $-11 \leq k \leq 9$, $-18 \leq l \leq 18$
Reflections collected	18745
Independent reflections	5954 [R_{int} = 0.0758, R_{sigma} = 0.0230]
Data/restraints/parameters	5954/1/403
Goodness-of-fit on F^2	1.051
Final R indexes [I >=2σ (I)]	R_1 = 0.0436, wR_2 = 0.1098
Final R indexes [all data]	R_1 = 0.0504, wR_2 = 0.1151
Largest diff. peak/hole / e Å^{-3}	0.24/-0.21
Flack parameter	0.013(11)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C00I
N008
C00G
C00V
C00Z
C00F
C00T
C011
C00L
C00N
C00Q
C018
C00H
O005
C017
C00X
C015
CL
CL1
C013
O006
C00A
CL3
N007
C00K
C014
C00C
C016
C00O
C009
C00E
CL2
C00D
C00P
C00R
C00J
C00U
C00S
C010
C00W
C00Y

Table S3. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **2i**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	*U*(eq)
Cl2	7033.1(8)	4048.9(13)	6321.2(8)	56.2(3)
Cl3	9154.6(10)	2833.1(14)	7532.5(8)	63.3(3)
Cl	4533.6(12)	6301.8(14)	2763.4(8)	68.8(4)
Cl1	2327.0(11)	5620.8(16)	1384.5(10)	76.9(4)
O005	4630.4(19)	4544(3)	174.1(16)	32.5(5)
O006	9568.8(19)	4632(3)	5113.2(17)	34.2(6)
N007	10026(2)	6900(3)	5421.5(18)	28.3(6)
N008	5055(2)	2267(3)	447.6(18)	28.0(6)
C009	10129(2)	6867(4)	6358(2)	27.9(7)
C00A	9705(2)	5799(4)	4851(2)	29.8(8)
C00B	4761(2)	3396(4)	-105(2)	29.1(8)
C00C	10982(2)	6101(4)	7027(2)	31.7(7)
C00D	9361(2)	7659(4)	6564(2)	28.3(7)
C00E	10314(3)	6899(4)	8147(2)	37.7(8)
C00F	6013(3)	2972(4)	2065(2)	31.0(7)
C00G	5151(2)	2244(4)	1379(2)	27.4(7)
C00H	2472(3)	1950(4)	267(2)	36.6(8)
C00I	4582(3)	3125(4)	-1094(2)	41.1(9)
C00J	8416(3)	8413(4)	5799(2)	29.5(7)
C00K	11805(3)	5291(4)	6786(3)	39.6(9)
C00L	3380(3)	833(4)	763(2)	32.0(8)
C00M	4355(3)	1471(4)	1561(2)	30.9(7)
C00N	4474(3)	1429(4)	2476(2)	35.9(8)
C00O	11061(3)	6112(4)	7939(2)	37.8(8)
C00P	9488(3)	7677(4)	7480(2)	34.7(8)
C00Q	5327(3)	2157(4)	3166(2)	38.9(9)
C00R	7541(3)	7375(4)	5113(2)	34.1(8)
C00S	7679(3)	9342(4)	6107(2)	35.1(8)
C00T	6080(3)	2933(4)	2976(2)	35.8(8)
C00U	6436(3)	7850(5)	5124(3)	43.2(9)
C00V	6851(3)	3788(4)	1848(3)	39.9(9)
C00W	6123(3)	9252(5)	4602(3)	48.0(10)

C00X	1726(3)	1823(5)	789(3)	56.6(12)
C00Y	6979(3)	10271(4)	5286(3)	43.1(9)
C00Z	2693(3)	-309(5)	1002(3)	50.6(10)
C010	6797(3)	8317(4)	6126(3)	42.7(9)
C011	6978(3)	3728(5)	3743(3)	51.3(11)
C012	1714(3)	1372(5)	-682(3)	55.3(11)
C013	9500(3)	6086(5)	3860(2)	43.0(9)
C014	11959(3)	5288(5)	8687(3)	51.9(11)
C015	3737(4)	5154(5)	1871(3)	52.2(11)
C016	8484(3)	4113(5)	6709(3)	53.1(11)
C017	1510(4)	288(5)	607(4)	63.6(13)
C018	1053(4)	229(6)	-446(4)	71.3(15)

Table S4. Anisotropic Displacement Parameters (Å^2×10^3) for **2i**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	*U*11	*U*22	*U*33	*U*23	*U*13	*U*12
Cl2	42.9(4)	60.3(7)	65.3(6)	-9.9(5)	21.8(4)	-5.8(5)
Cl3	73.2(7)	53.4(7)	57.3(6)	13.0(5)	20.5(5)	10.3(6)
Cl	91.7(8)	56.6(8)	61.1(6)	-9.9(6)	34.0(6)	-6.8(7)
Cl1	67.5(7)	73.2(9)	86.0(9)	3.1(7)	27.0(6)	24.0(7)
O005	42.5(12)	19.0(14)	36.7(12)	1.4(11)	16.7(10)	2.1(10)
O006	40.4(12)	21.8(14)	40.4(12)	-2.0(11)	16.1(10)	-2.1(10)
N007	33.9(13)	19.0(16)	31.9(14)	1.4(12)	13.3(11)	0.8(12)
N008	32.9(12)	19.3(16)	31.7(13)	-1.3(11)	13.1(11)	1.7(11)
C009	27.7(13)	20.8(18)	32.0(15)	-0.4(14)	8.9(12)	-5.4(13)
C00A	27.6(14)	25(2)	35.2(17)	-2.9(15)	11.1(13)	3.2(13)
C00B	28.6(15)	26(2)	32.1(16)	0.9(15)	11.3(13)	-2.6(13)
C00C	25.6(13)	25.4(19)	38.5(16)	1.1(15)	7.2(12)	-6.9(13)
C00D	28.7(13)	21.3(18)	31.1(15)	-1.5(15)	8.1(12)	-4.9(13)
C00E	42.3(17)	38(2)	28.1(16)	-2.2(16)	9.7(14)	-8.7(16)
C00F	28.5(14)	24.1(19)	34.5(15)	1.6(14)	6.7(12)	8.2(13)
C00G	28.4(14)	21.6(18)	29.5(15)	2.0(13)	9.1(12)	6.7(13)
C00H	30.9(15)	28(2)	44.5(19)	-0.9(16)	8.6(14)	-1.2(15)
C00I	56(2)	37(2)	31.8(17)	-1.8(16)	19.4(16)	-2.3(17)
C00J	31.3(15)	24.4(18)	31.5(16)	1.4(15)	11.4(12)	0.0(14)
C00K	30.9(15)	31(2)	51(2)	4.9(17)	10.5(14)	2.4(15)
C00L	35.4(15)	21.7(19)	36.9(17)	-0.2(15)	12.5(13)	-3.4(14)
C00M	32.3(15)	22.5(19)	36.1(16)	3.3(15)	11.8(13)	4.3(14)
C00N	40.4(16)	30(2)	36.7(16)	8.3(16)	15.3(14)	4.6(16)
C00O	31.4(15)	35(2)	36.6(17)	2.3(17)	3.4(13)	-9.4(15)
C00P	36.0(15)	35(2)	33.1(15)	-4.2(17)	13.8(13)	-4.8(16)
C00Q	40.8(18)	41(2)	29.0(16)	7.4(16)	8.1(14)	11.0(17)
C00R	35.2(16)	26(2)	35.2(16)	-2.6(15)	8.7(13)	0.6(14)
C00S	37.6(16)	28(2)	40.3(18)	-2.8(16)	16.1(14)	2.0(15)
C00T	33.5(16)	33(2)	31.6(16)	-1.4(16)	3.2(13)	8.4(15)
C00U	33.0(16)	41(2)	49(2)	-0.4(19)	9.9(14)	-8.0(17)
C00V	31.1(15)	36(2)	45.2(19)	-3.0(17)	7.3(13)	-2.2(15)
C00W	35.3(17)	44(3)	56(2)	4(2)	9.8(15)	9.1(17)

C00X	41.6(19)	58(3)	75(3)	-4(2)	29(2)	2(2)
C00Y	42.8(18)	34(2)	52(2)	3.5(18)	18.4(16)	9.2(16)
C00Z	54(2)	36(2)	59(2)	2(2)	20.9(19)	-11.1(19)
C010	40.4(18)	38(2)	56(2)	2.6(19)	26.0(16)	1.4(16)
C011	43.3(18)	59(3)	37.0(19)	-8.7(19)	1.0(15)	-0.3(19)
C012	39.0(18)	57(3)	52(2)	-5(2)	0.4(17)	-3(2)
C013	58(2)	34(2)	37.0(18)	1.7(17)	19.3(16)	7.4(18)
C014	45(2)	53(3)	42(2)	11(2)	1.4(16)	3(2)
C015	67(2)	39(3)	56(2)	1(2)	31(2)	8(2)
C016	45(2)	50(3)	62(3)	15(2)	20.2(18)	-1(2)
C017	49(2)	58(3)	89(4)	3(3)	34(2)	-17(2)
C018	46(2)	57(3)	86(3)	-6(3)	1(2)	-17(2)

Table S5 Bond Lengths for **2i**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl2	C016	1.754(4)	C00G	C00M	1.407(5)
Cl3	C016	1.747(5)	C00H	C00L	1.560(5)
Cl	C015	1.762(5)	C00H	C00X	1.524(6)
Cl1	C015	1.755(5)	C00H	C012	1.529(5)
O005	C00B	1.226(5)	C00J	C00R	1.576(5)
O006	C00A	1.234(4)	C00J	C00S	1.537(5)
N007	C009	1.433(4)	C00L	C00M	1.516(4)
N007	C00A	1.342(5)	C00L	C00Z	1.562(5)
N008	C00B	1.347(5)	C00M	C00N	1.393(5)
N008	C00G	1.427(4)	C00N	C00Q	1.395(5)
C009	C00C	1.399(5)	C00O	C014	1.512(5)
C009	C00D	1.405(5)	C00Q	C00T	1.368(6)
C00A	C013	1.504(5)	C00R	C00U	1.530(5)
C00B	C00I	1.507(5)	C00S	C00Y	1.537(5)
C00C	C00K	1.504(5)	C00S	C010	1.532(5)
C00C	C00O	1.404(5)	C00T	C011	1.512(5)
C00D	C00J	1.521(4)	C00U	C00W	1.545(6)
C00D	C00P	1.391(5)	C00U	C010	1.526(5)
C00E	C00O	1.382(6)	C00W	C00Y	1.551(6)
C00E	C00P	1.386(5)	C00X	C017	1.507(7)
C00F	C00G	1.398(5)	C00Z	C017	1.535(7)
C00F	C00T	1.410(5)	C012	C018	1.538(7)
C00F	C00V	1.502(5)	C017	C018	1.527(8)

Table S6 Bond Angles for **2i**.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C00A	N007	C009	123.4(3)	C00M	C00L	C00Z	117.4(3)
C00B	N008	C00G	124.3(3)	C00G	C00M	C00L	119.5(3)
C00C	C009	N007	120.3(3)	C00N	C00M	C00G	116.7(3)
C00C	C009	C00D	122.8(3)	C00N	C00M	C00L	123.6(3)
C00D	C009	N007	116.9(3)	C00M	C00N	C00Q	121.0(3)
O006	C00A	N007	122.6(3)	C00C	C00O	C014	120.6(4)
O006	C00A	C013	121.9(3)	C00E	C00O	C00C	119.1(3)
N007	C00A	C013	115.5(3)	C00E	C00O	C014	120.4(3)
O005	C00B	N008	122.4(3)	C00E	C00P	C00D	120.7(3)
O005	C00B	C00I	122.9(3)	C00T	C00Q	C00N	121.8(3)
N008	C00B	C00I	114.6(3)	C00U	C00R	C00J	103.7(3)
C009	C00C	C00K	121.3(3)	C00Y	C00S	C00J	107.9(3)
C009	C00C	C00O	118.4(3)	C010	C00S	C00J	102.4(3)
C00O	C00C	C00K	120.3(3)	C010	C00S	C00Y	101.0(3)
C009	C00D	C00J	120.4(3)	C00F	C00T	C011	120.8(4)
C00P	C00D	C009	117.1(3)	C00Q	C00T	C00F	119.3(3)
C00P	C00D	C00J	122.5(3)	C00Q	C00T	C011	119.9(3)
C00O	C00E	C00P	121.9(3)	C00R	C00U	C00W	107.6(3)
C00G	C00F	C00T	118.3(3)	C010	C00U	C00R	101.7(3)
C00G	C00F	C00V	121.6(3)	C010	C00U	C00W	101.7(3)
C00T	C00F	C00V	120.1(3)	C00U	C00W	C00Y	102.5(3)
C00F	C00G	N008	119.8(3)	C017	C00X	C00H	95.0(4)
C00F	C00G	C00M	122.9(3)	C00S	C00Y	C00W	103.9(3)
C00M	C00G	N008	117.3(3)	C017	C00Z	C00L	103.4(4)
C00X	C00H	C00L	101.7(3)	C00U	C010	C00S	95.0(3)
C00X	C00H	C012	101.3(3)	C00H	C012	C018	103.3(4)
C012	C00H	C00L	107.8(3)	Cl1	C015	Cl	111.8(3)
C00D	C00J	C00R	112.3(3)	Cl3	C016	Cl2	112.6(2)
C00D	C00J	C00S	116.2(3)	C00X	C017	C00Z	101.9(4)
C00S	C00J	C00R	101.9(3)	C00X	C017	C018	101.8(4)
C00H	C00L	C00Z	101.8(3)	C018	C017	C00Z	108.3(4)
C00M	C00L	C00H	110.9(3)	C017	C018	C012	103.1(3)

Table S7 Torsion Angles for **2i**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
N007	C009	C00C	C00K	-0.4(5)	C00K	C00C	C00O	C00E	178.1(3)
N007	C009	C00C	C00O	179.2(3)	C00K	C00C	C00O	C014	-1.2(5)
N007	C009	C00D	C00J	4.7(5)	C00L	C00H	C00X	C017	-55.8(4)
N007	C009	C00D	C00P	-177.3(3)	C00L	C00H	C012	C018	71.8(4)
N008	C00G	C00M	C00L	-6.2(5)	C00L	C00M	C00N	C00Q	-173.3(3)
N008	C00G	C00M	C00N	178.4(3)	C00L	C00Z	C017	C00X	-35.9(5)
C009	N007	C00A	O006	-6.7(5)	C00L	C00Z	C017	C018	71.0(4)
C009	N007	C00A	C013	172.2(3)	C00M	C00L	C00Z	C017	121.9(4)
C009	C00C	C00O	C00E	-1.5(5)	C00M	C00N	C00Q	C00T	-0.3(6)
C009	C00C	C00O	C014	179.2(3)	C00N	C00Q	C00T	C00F	-1.7(5)
C009	C00D	C00J	C00R	67.9(4)	C00N	C00Q	C00T	C011	178.8(4)
C009	C00D	C00J	C00S	-175.3(3)	C00O	C00E	C00P	C00D	2.0(6)
C009	C00D	C00P	C00E	-2.4(5)	C00P	C00D	C00J	C00R	-109.9(4)
C00A	N007	C009	C00C	70.1(4)	C00P	C00D	C00J	C00S	6.8(5)
C00A	N007	C009	C00D	-111.6(4)	C00P	C00E	C00O	C00C	0.1(5)
C00B	N008	C00G	C00F	-69.6(4)	C00P	C00E	C00O	C014	179.3(4)
C00B	N008	C00G	C00M	110.4(4)	C00R	C00J	C00S	C00Y	-71.3(3)
C00C	C009	C00D	C00J	-177.0(3)	C00R	C00J	C00S	C010	34.7(3)
C00C	C009	C00D	C00P	1.0(5)	C00R	C00U	C00W	C00Y	-71.6(4)
C00D	C009	C00C	C00K	-178.6(3)	C00R	C00U	C010	C00S	55.2(3)
C00D	C009	C00C	C00O	1.0(5)	C00S	C00J	C00R	C00U	0.0(3)
C00D	C00J	C00R	C00U	125.1(3)	C00T	C00F	C00G	N008	179.7(3)
C00D	C00J	C00S	C00Y	166.2(3)	C00T	C00F	C00G	C00M	-0.3(5)
C00D	C00J	C00S	C010	-87.7(3)	C00U	C00W	C00Y	C00S	0.3(4)
C00F	C00G	C00M	C00L	173.8(3)	C00V	C00F	C00G	N008	0.0(5)
C00F	C00G	C00M	C00N	-1.5(5)	C00V	C00F	C00G	C00M	180.0(3)
C00G	N008	C00B	O005	5.8(5)	C00V	C00F	C00T	C00Q	-178.4(3)
C00G	N008	C00B	C00I	-173.0(3)	C00V	C00F	C00T	C011	1.1(5)
C00G	C00F	C00T	C00Q	2.0(5)	C00W	C00U	C010	C00S	-55.8(3)
C00G	C00F	C00T	C011	-178.5(3)	C00X	C00H	C00L	C00M	-91.4(4)
C00G	C00M	C00N	C00Q	1.8(5)	C00X	C00H	C00L	C00Z	34.2(4)
C00H	C00L	C00M	C00G	-78.7(4)	C00X	C00H	C012	C018	-34.6(5)
C00H	C00L	C00M	C00N	96.3(4)	C00X	C017	C018	C012	35.0(5)

C00H	C00L	C00Z	C017	0.7(4)	C00Y	C00S	C010	C00U	55.7(3)
C00H	C00X	C017	C00Z	56.4(4)	C00Z	C00L	C00M	C00G	164.9(3)
C00H	C00X	C017	C018	-55.4(4)	C00Z	C00L	C00M	C00N	-20.0(5)
C00H	C012	C018	C017	0.1(5)	C00Z	C017	C018	C012	-71.9(5)
C00J	C00D	C00P	C00E	175.5(3)	C010	C00S	C00Y	C00W	-35.2(4)
C00J	C00R	C00U	C00W	71.6(3)	C010	C00U	C00W	C00Y	34.8(4)
C00J	C00R	C00U	C010	-34.8(4)	C012	C00H	C00L	C00M	162.5(3)
C00J	C00S	C00Y	C00W	71.8(3)	C012	C00H	C00L	C00Z	-71.8(4)
C00J	C00S	C010	C00U	-55.7(3)	C012	C00H	C00X	C017	55.2(4)

Table S8 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **2i**.

Atom	*x*	*y*	*z*	*U*(eq)
H007	10180.93	7682.08	5209.37	34
H008	5198.43	1492.7	219.14	34
H00M	10367.63	6906.51	8763.95	45
H00H	2764.68	2907.57	256.23	44
H00A	3895.14	2591.01	-1403.79	62
H00B	5211.32	2593.51	-1105.84	62
H00C	4522.65	4013.54	-1414.76	62
H00O	8735.03	8992.87	5441.04	35
H00P	11616.21	4298.99	6741.39	59
H00R	12554.09	5429.13	7267.77	59
H00S	11781.47	5616.93	6191.28	59
H00L	3652.88	440.25	307.94	38
H00N	3967.39	896.71	2633.21	43
H00T	9002.91	8228.52	7651.53	42
H00Q	5386.53	2111.84	3784.35	47
H00U	7525	7447.23	4483.93	41
H00V	7710.51	6401.85	5331.13	41
H00W	8084.76	9853.11	6700.25	42
H00X	5834.21	7132.35	4913.5	52
H00D	6783.34	3551.97	1224.84	60
H00E	7601.55	3558.67	2298.78	60
H00F	6716.03	4786.27	1879.6	60
H00Y	5352.44	9525.36	4484.07	58
H	6203.12	9207.36	4007	58
H00G	2120.18	2040.73	1455.77	68
H00I	1041.63	2390.62	511.86	68
H00Z	7447.19	10703.69	5001.33	52
HA	6600.65	11013.82	5482.1	52
H00J	2721.26	-1206.64	705.04	61
H00K	2971.93	-448.17	1678.7	61
H01H	7117.5	7549.52	6573.73	51
H01I	6192.27	8780.21	6239.59	51

H01A	7707.18	3347.51	3839.71	77
H01B	6862.17	3639.15	4315.02	77
H01C	6945.06	4713.09	3572.28	77
H01D	2154.03	979.49	-1005.18	66
H01E	1213.87	2103.53	-1073.38	66
H01J	9938.83	5439.17	3664.53	64
H01K	9719.39	7044.89	3802.79	64
H01L	8708.65	5961.63	3466.95	64
H01M	11922.09	4312.69	8495.14	78
H01N	11847.27	5344.86	9261.82	78
H01O	12688.45	5673.47	8788.31	78
H01R	4026.28	5157.99	1383.16	63
H01S	3813.01	4196.35	2121.7	63
H01P	8684.14	3993.6	6174.3	64
H01Q	8750.3	5040.92	6981.47	64
H017	1009.17	-126.24	875.75	76
H01F	246.32	429.04	-729.2	86
H01G	1187.24	-694.77	-659.9	86

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