SUPPORTING INFORMATION FOR

On the reactions of (hetero)aryl and vinyl triflates with [Ni(COD)(dppf)]

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Contents

1 Synthetic Chemistry

1.1 General Information

Anhydrous solvents for synthetic work were obtained from an Inert Technology PureSolv apparatus; water content was less than 10 ppm, as judged from regular Karl-Fischer analyses of samples withdrawn from the apparatus. All deuterated solvents were obtained from commercial sources. Those used for kinetic studies were dried overnight on 4 Å molecular sieves before use.

Any manipulations of air-sensitive nickel complexes were carried out under nitrogen or argon using Schlenk techniques or in an argon-filled glovebox (<0.1 ppm oxygen; <0.1 ppm water). Substrates used in kinetic experiments and cross-coupling reactions were obtained from commercial sources and used as supplied, unless stated otherwise. Details of substrates prepared for this work are provided in sections 1.3.1 and 1.3.2. 4-(Trifluoromethyl)phenyl triflate[1] and pyridin-2-yl triflate[2] were prepared as documented in our previous studies. Cross-coupling products (1-phenylcycloalkenes) were prepared according to a literature method.[3] [Ni(COD)(dppf)] was prepared according to a literature procedure.[4]

NMR spectroscopy was performed using Bruker NMR spectrometers, either: (i) an AV3-400 equipped with a liquid nitrogen cryoprobe; (ii) an AV3-400Nano equipped with a BBFO-z-ATMA probe and temperature control; (iii) an AV3-500HD equipped with a smartprobe and temperature control; or (iv) an AVII-600 equipped with a BBO-z-ATMA probe and temperature control. All kinetic experiments were performed using the AV3-400Nano or the AVII-600. ^{1}H NMR chemical shifts are reported relative to residual solvent signals.[5] ^{13}C{^{1}H} NMR chemical shifts are reported relative to deuterated solvent signals.[5] ^{19}F and ^{31}P NMR chemical shifts are reported relative to external standards. Chemical shifts are reported in ppm and scalar couplings are reported in Hertz (Hz).

GC-MS analyses were carried out using an Agilent 7890A gas chromatograph fitted with a RESTEK RXi-5Sil column (30 m × 0.32 mm × 0.25 µm) and an Agilent 6975C MSD running in EI mode. GC-FID analyses were carried out using an Agilent 7890A gas chromatograph fitted with an Agilent HP5 column (30 m × 0.25 mm I.D. × 0.25 µm).

X-band EPR spectra were collected on a Bruker ELEXSYS E500 spectrometer and simulations were performed using Bruker's Xsophe software package.

1.2 Characterisation Data

1.2.1 Alk-1-en-1-yl Triflates

General Procedure A: Synthesis of Alk-1-en-1-yl Triflates. These were prepared following a literature procedure.[6] DTBMP (11 mmol, 1.1 equiv.) was added to a solution of the corresponding ketone (10 mmol, 1 equiv.) in DCM (30 mL) at 0°C. Tf_2O (12 mmol, 1.2 equiv.) was added dropwise, and the solution was warmed to room temperature and stirred overnight. The solvent was removed *in vacuo*, and the crude solid was dissolved in petroleum ether and filtered to remove pyridinium triflate. This solution was washed with cold HCl (1 M) and brine, dried over Na_2SO_4, and concentrated. The product was then purified by distillation at low pressure.

Cyclopent-1-en-1-yl triflate (5a). Synthesised according to General Procedure A from cyclopentanone (0.88 mL, 10 mmol). Isolated as a colourless oil (0.52 g, 24%).
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.63 (p, J_{HH} = 2.3, 1H), 2.60-2.54 (m, 2H), 2.44-2.39 (m, 2H), 2.07-1.99 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 149.7, 118.7 (d, J_{CF} = 321.0, CF_3), 117.9, 31.0, 28.1, 21.0.
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ -73.6 (s, 3F, CF_3).
NMR data are consistent with the literature.[6]

Cyclohex-1-en-1-yl triflate (5b). Synthesised according to General Procedure A from cyclohexanone (1.04 mL, 10 mmol). Isolated as a colourless oil (1.27 g, 54%).
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.75 (tt, J_{HH} = 4.0, 1.5 Hz, 1H), 2.33-2.28 (m, 2H), 2.19-2.14 (m, 2H), 1.80-1.74 (m, 2H), 1.62-1.58 (m, 2H)
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 149.5, 118.7 (d, J_{CF} = 320.2, CF_3), 118.6, 27.7, 24.0, 22.8, 21.1.
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ -74.1 (s, 3F, CF_3).
NMR data are consistent with the literature.[6]

Cyclohept-1-en-1-yl triflate (5c). Synthesised from cycloheptanone (2.40 mL, 20 mmol) following the general procedure. Isolated as a colourless oil (2.83 g, 58%).
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.88 (t, J_{HH} = 6.4 Hz, 1H), 2.53-2.51 (m, 2H), 2.16 (ddt, J_{HH} = 11.3, 6.4, 1.3 Hz, 2H), 1.76-1.60 (m, 6H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 153.2, 123.2, 118.7 (d, J_{CF} = 320.2, CF_3), 33.4, 30.0, 26.5, 24.93, 24.88.
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ -74.0 (s, 3F, CF_3).
NMR data are consistent with the literature.[6]

Cyclooct-1-en-1-yl triflate (5d). Synthesised from cyclooctanone (1.26 g, 10 mmol) following the general procedure. Isolated as a colourless oil (1.48 g, 62%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.69 (t, J_{HH} = 8.7 Hz, 1H), 2.49-2.45 (m, 2H), 2.19-2.14 (m, 2H), 1.75-1.69 (m, 2H), 1.65-1.53 (m, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 151.1, 120.7, 118.7 (d, J_{CF} = 319.8 Hz), 29.7, 29.2, 27.3, 25.9, 25.6, 25.1.

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ -74.2 (s, 3F, CF_3).

NMR data are consistent with the literature.[6]

1.2.2 (Hetero)Aryl Triflates

General Procedure B: Synthesis of (Hetero)Aryl Triflates. These were prepared following a literature procedure.[7] The corresponding phenol or pyridinol (1 equiv.) was added to a biphasic mixture of toluene (40 mL) and aqueous K_3PO_4 (40 mL, 30% *w*/*v*), after which the reaction was cooled to 0 °C. Tf_2O (1.2 equiv.) was added dropwise. The mixture was warmed to room temperature and stirred for 30 minutes, after which the organic layer was separated, washed with water, and concentrated. The crude product was purified by column chromatography.

Phenyl triflate (2c). Synthesised from phenol (2.0 g, 21.3 mmol) following general procedure B. Isolated as a colourless oil (2.89 g, 61%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49-7.44 (m, 2H), 7.42-7.37 (m, 1H), 7.30-7.27 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 149.8, 130.4, 128.5, 121.5, 118.9 (d, J_{CF} = 320.6 Hz).

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ -72.9 (s, 3F, CF_3).

NMR data are consistent with literature data.[8]

3-Pyridinyl triflate (2d). Synthesised from 3-hydroxypyridine (1.0 g, 10.5 mmol) following general procedure B. Isolated as a pale-yellow oil (1.22 g, 50%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.66 (dd, J_{HH} = 4.8, 1.4 Hz, 1H), 8.62 (d, J_{HH} = 2.8 Hz, 1H), 7.65 (ddd, J_{HH} = 8.4, 2.8, 1.4 Hz, 1H), 7.44 (ddd, J_{HH} = 8.4, 4.8, 0.8 Hz, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 149.6, 146.8, 142.9, 129.0, 124.7, 118.7 (q, J_{CF} = 321.2 Hz).

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ -72.5 (s, 3F, CF3).

NMR data are consistent with literature data.[9]

1.2.3 Other Electrophiles

Phenyl tosylate (9). Phenol (0.94 g, 10 mmol) was added to a mixture of dichloromethane (3 mL) and NEt_3 (3 mL), and *p*-toluenesulfonyl chloride (1.91 g, 10 mmol) was added. The mixture was stirred for 16 h, after which it was treated with water (5 mL) and extracted with dichloromethane (3 x 5 mL). The organic extracts were combined, washed with brine, and dried over $MgSO_4$. The crude solution was concentrated and purified by column chromatography to give a white solid (2.03 g, 82%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72-7.69 (m, 2H), 7.32-7.21 (m, 5H), 7.00-6.96 (m, 2H), 2.45 (s, 3H)
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 149.8, 145.4, 132.6, 129.9, 129.7, 128.7, 127.2, 122.5, 21.9
NMR data are consistent with literature data.[10]

1.2.4 Reaction Products

[1,1'-Bi(cyclopentane)]-1,1'-diene. Prepared according to a literature procedure.[11] Phosphorus oxychloride (1.2 mL, 12.9 mmol) was added to a solution of 1,1'-bicyclopentyl-1,1'-diol (1 g, 5.9 mmol) in pyridine (10 mL) in a flask equipped with an internal thermometer. The reaction was heated to 70 °C, and then an ice bath was used to maintain the temperature at 90 °C until the initial exotherm had subsided. The reaction was then heated to 90 °C for 2 h, cooled to room temperature, poured into pentane (20 mL), and stirred. The pentane was decanted and the solid residue was quenched with HCl (50 mL of a 1 mol/L aqueous solution). This solution was then extracted with pentane (2x 20 mL), and the organic fractions were combined and washed with 1 mol/L aqueous HCl (50 mL). The organic fraction was then dried over magnesium sulfate, filtered through a silica plug, and concentrated to give the product as a yellow oil (0.3 g, 38%).
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.61 (s, 2H), 2.53 - 2.43 (m, 8H), 1.94 (app. pent., J_{HH} = 7.7, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 139.9, 126.1, 32.5, 32.4, 22.9.
GC-MS (EI) m/z: 134.2.
NMR data are consistent with the literature.[11]

4-(Trifluoromethyl)-1,1'-biphenyl. A microwave vial was charged with [PdCl$_2$(dppf)]·CH$_2$Cl$_2$ (171 mg, 0.21 mmol), phenylboronic acid (293 mg, 2.4 mmol), and potassium phosphate (1.3 g, 6.3 mmol). The vial was capped and then evacuated and backfilled with nitrogen three times. A degassed 4/1 *v*/*v* THF/water solution was added, followed by 4-bromobenzotrifluoride (0.3 mL, 2.1 mmol). The reaction was stirred at 85 °C for 6 h. After the reaction had cooled to room temperature, the reaction was filtered through a pad of celite and the solvent was removed under reduced pressure. The crude product was purified *via* column chromatography on silica gel to give the product as a white solid (0.3 g, 65%).

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.72 (app. s, 4H), 7.64 - 7.62 (m, 2H), 7.52 - 7.41 (m, 3H).

^{19}F{^{1}H} NMR (376 MHz, CDCl$_3$): δ -62.4.

GC-MS (EI) m/z: 222.2.

NMR data are consistent with the literature.[12]

2 Kinetic Studies

2.1 Methodology

The decrease in the concentration of [Ni(COD)(dppf)] (**1**) over time was monitored by NMR spectroscopy. A stock sample of [Ni(COD)(dppf)] (30 mg, 0.04 mmol) in C_6D_6 (6 mL) was prepared in the glovebox and charged to septum-fitted NMR tubes in 0.5 mL portions.

Using this sample, the spectrometer was matched, tuned, locked, and shimmed, and the receiver gain was set. A spectrum was taken at this time to check the integrity of the sample and represents the integration at this point ($t = 0$). For the kinetic experiment, the substrate being tested was added to the sample *via* syringe, the time was noted, and the sample was placed back into the NMR spectrometer.

To track the progress of the reaction, $^{31}P\{^1H\}$ NMR spectra (16 scans per spectra, 2-second pulse delay) were taken at 100-second intervals until at least three half-lives of the sample were reached (~85% conversion).

All experiments were performed in duplicate. For substrates where ln(A) vs time gave a linear plot, the rate constant could be obtained from the gradient of the line.

2.2 Kinetic Data

Data are provided as integral *vs* time profiles for the integral of the signal corresponding to [Ni(COD)(dppf)] (**1**), scaled to the integral of the signal in the first spectrum, which is set to 1.0.

2.2.1 Phenyl triflate (2b)

Table S1. Kinetic data for the reaction of phenyl triflate (**2b**) (0.14 mol L^{-1}) with [Ni(COD)(dppf)] (**1**) (0.007 mol L^{-1}) at 323 K.

Replicate 1		**Replicate 2**	
Time (s)	**Integral**	**Time (s)**	**Integral**
0	1.000	0	1.000
76	0.931	85	0.899
214	0.917	232	0.906
351	0.916	380	0.850
488	0.844	527	0.846
626	0.801	674	0.811
763	0.765	822	0.770
900	0.753	969	0.752
1037	0.722	1116	0.729
1174	0.686	1264	0.705
1311	0.645	1411	0.679
1448	0.626	1558	0.652
1586	0.592	1705	0.608
1723	0.557	1852	0.624

1860	0.551	2000	0.579
1998	0.511	2147	0.538
2135	0.484	2294	0.532
2272	0.465	2441	0.503
2409	0.465	2589	0.489
2546	0.411	2736	0.477
2684	0.427	2884	0.442
2821	0.400	3031	0.437
2958	0.380	3178	0.431
3095	0.350	3325	0.397
3233	0.348	3473	0.359
3370	0.339	3620	0.353
3507	0.331	3767	0.344
3645	0.306	3914	0.327
3782	0.274	4062	0.335
3919	0.278	4209	0.324
4057	0.281	4356	0.297
4194	0.265	4504	0.272
4332	0.239	4651	0.266
4469	0.252	4798	0.254
4606	0.221	4946	0.272
4744	0.235	5093	0.235
4881	0.200	5240	0.226
5018	0.215	5387	0.229
5156	0.215	5535	0.213
5293	0.198	5682	0.204
5430	0.172	5829	0.214
5567	0.185	5977	0.159
5705	0.179	6124	0.194
5842	0.170	6271	0.176
5980	0.142	6418	0.160
6117	0.150	6566	0.152
6255	0.155	6713	0.133
6392	0.147	6860	0.157
6529	0.132	7008	0.129
6666	0.158	7155	0.124
6803	0.138	7303	0.107
6941	0.129	7450	0.119
7078	0.109	7597	0.100
7216	0.135		

2.2.3 Chlorobenzene (8)

Table S2. Kinetic data for the reaction of chlorobenzene (**8**) (0.14 mol L^{-1}) with [Ni(COD)(dppf)] (**1**) (0.007 mol L^{-1}) at 323 K.

Replicate 1		**Replicate 2**	
Time (s)	**Integral**	**Time (s)**	**Integral**
0	1.000	0	1.000
139	0.947	99	0.938
296	0.947	255	0.936
452	0.928	411	0.933
608	0.915	567	0.924
764	0.899	723	0.904
920	0.878	878	0.890
1075	0.866	1034	0.875
1232	0.829	1189	0.858
1388	0.823	1345	0.852
1544	0.805	1501	0.836
1699	0.777	1657	0.819
1855	0.763	1813	0.788
2011	0.747	1968	0.786
2168	0.740	2124	0.766
2324	0.717	2280	0.748
2481	0.702	2436	0.738
2637	0.684	2591	0.704
2793	0.675	2747	0.698
2948	0.658	2902	0.679
3105	0.643	3058	0.666
3261	0.622	3213	0.648
3417	0.615	3369	0.625
3573	0.604	3525	0.613
3729	0.584	3681	0.591
3884	0.572	3836	0.595
4041	0.563	3992	0.573
4197	0.532	4148	0.559
4353	0.528	4304	0.550
4508	0.512	4459	0.541
4664	0.514	4615	0.521
4821	0.494	4770	0.519
4977	0.480	4926	0.502
5133	0.469	5082	0.487
5289	0.454	5238	0.486
5444	0.444	5393	0.466
5600	0.440	5549	0.461
5757	0.437	5704	0.444
5913	0.421	5860	0.439

6068	0.400	6016	0.440
6224	0.406	6172	0.430
6380	0.393	6327	0.414
6536	0.387	6483	0.415
6693	0.367	6638	0.401
6849	0.366	6794	0.389
7005	0.369	6950	0.383
7161	0.355	7105	0.366
7317	0.342	7261	0.355
7473	0.339	7416	0.361
7629	0.336	7572	0.350
7785	0.333	7728	0.345
7941	0.310	7883	0.339
8097	0.310	8039	0.322
8253	0.290	8195	0.318
8409	0.288	8350	0.309
8565	0.287	8506	0.306
8722	0.289	8662	0.304
8878	0.269	8818	0.290
9033	0.260	8974	0.272
9189	0.271	9129	0.278
9345	0.255	9285	0.262
9502	0.244	9440	0.241
9657	0.226	9596	0.248
9813	0.241	9752	0.239
9969	0.221	9907	0.239
10125	0.227	10063	0.234
10281	0.218	10218	0.225
10437	0.209	10373	0.223
10593	0.207	10529	0.215
10749	0.208	10685	0.208
10905	0.191	10841	0.193
11060	0.179	10996	0.194
11217	0.192	11152	0.175
11373	0.179	11307	0.173
11529	0.170	11463	0.182
11685	0.175	11619	0.173
11841	0.157	11774	0.165
11996	0.161	11930	0.175
12153	0.149		
12309	0.152		

2.2.4 Phenyl tosylate (9)

Table S3. Kinetic data for the reaction of phenyl tosylate (**9**) (0.14 mol L^{-1}) with [Ni(COD)(dppf)] (**1**) (0.007 mol L^{-1}) at 323 K.

Replicate 1		**Replicate 2**	
Time (s)	**Integral**	**Time (s)**	**Integral**
116	1.000	115	1.000
271	0.969	270	1.001
427	0.975	426	0.969
582	0.933	581	0.928
737	0.928	737	0.904
892	0.905	892	0.914
1047	0.863	1048	0.897
1203	0.855	1203	0.863
1358	0.829	1358	0.842
1513	0.812	1514	0.813
1669	0.768	1669	0.793
1824	0.759	1825	0.777
1979	0.743	1980	0.779
2135	0.707	2135	0.772
2290	0.720	2291	0.724
2446	0.666	2446	0.702
2601	0.672	2602	0.678
2756	0.648	2757	0.676
2911	0.647	2912	0.636
3066	0.638	3068	0.627
3222	0.611	3223	0.645
3377	0.607	3379	0.612
3532	0.569	3534	0.590
3688	0.554	3690	0.580
3843	0.550	3845	0.584
3998	0.540	4000	0.575
4153	0.531	4156	0.521
4308	0.522	4311	0.526
4464	0.505	4467	0.521
4619	0.483	4622	0.502
4774	0.482	4778	0.500
4930	0.474	4933	0.480
5086	0.462	5089	0.476
5241	0.446	5244	0.466
5396	0.444	5400	0.442
5551	0.436	5555	0.447
5707	0.435	5710	0.465
5862	0.424	5866	0.433
6017	0.415	6021	0.428

6173	0.419	6177	0.398
6328	0.396	6333	0.421
6483	0.381	6488	0.394
6639	0.341	6644	0.397
6795	0.368	6799	0.386
6950	0.356	6954	0.381
7106	0.352	7110	0.390
7261	0.376	7266	0.372
7416	0.340	7421	0.349
7572	0.343	7576	0.359
7727	0.333	7732	0.351
7882	0.326	7887	0.333
8038	0.318	8043	0.322
8193	0.321	8198	0.343
8348	0.307	8353	0.320
8504	0.302	8509	0.317
8659	0.271	8664	0.316
8815	0.300	8819	0.297
8970	0.296	8975	0.313
9125	0.293	9131	0.283
9280	0.297	9286	0.284
9436	0.270	9442	0.287
9591	0.266	9598	0.293
9747	0.262	9753	0.259
9902	0.258	9909	0.264
10057	0.243	10064	0.286
10213	0.248	10220	0.260
10368	0.245	10375	0.256
10524	0.224	10531	0.241
10679	0.228	10687	0.245
10834	0.236	10842	0.248
10989	0.237	10997	0.231
11145	0.231	11153	0.226
11300	0.222	11308	0.228
11455	0.211	11464	0.227
11611	0.224	11620	0.229
11766	0.204	11775	0.205
11921	0.195	11931	0.220
12077	0.208	12086	0.202
12232	0.200	12241	0.204
		12397	0.209
		12552	0.196
		12708	0.192
		12863	0.186
		13019	0.173
		13174	0.158

		13329	0.167
		13485	0.183
		13641	0.160
		13796	0.155
		13951	0.150
		14107	0.165
		14262	0.161
		14418	0.143
		14574	0.135

2.2.5 2-Pyridinyl triflate (2b)

Table S4. Kinetic data for the reaction of 2-pyridinyl triflate (**2b**) (0.14 mol L^{-1}) with [Ni(COD)(dppf)] (**1**) (0.007 mol L^{-1}) at 293 K.

Replicate 1		**Replicate 2**	
Time (s)	**Integral**	**Time (s)**	**Integral**
0	1.000	0	1.000
81	0.931	84	0.998
218	0.912	221	0.994
355	0.913	358	0.957
493	0.867	495	0.927
630	0.847	633	0.904
767	0.822	770	0.852
904	0.776	907	0.835
1042	0.750	1044	0.802
1179	0.731	1182	0.766
1316	0.694	1319	0.720
1453	0.650	1457	0.689
1590	0.628	1594	0.648
1728	0.600	1731	0.617
1865	0.574	1868	0.574
2002	0.522	2005	0.545
2139	0.499	2143	0.486
2277	0.444	2280	0.433
2414	0.417	2417	0.390
2551	0.378	2554	0.368
2688	0.344	2691	0.325
2825	0.307	2829	0.272
2962	0.280	2966	0.238
3100	0.257	3103	0.202
3237	0.227	3240	0.168
3374	0.190	3378	0.153
3511	0.168	3515	0.126
3648	0.147	3652	0.120
3786	0.121		
3923	0.102		

Table S5. Kinetic data for the reaction of 2-pyridinyl triflate (**2b**) (0.14 mol L^{-1}) with [Ni(COD)(dppf)] (**1**) (0.0035 mol L^{-1}) at 293 K.

Time (s)	**Integral**
0	1.000
87	0.799
224	0.800
361	0.799
499	0.777

636	0.768
773	0.766
910	0.776
1047	0.748
1185	0.729
1322	0.728
1459	0.725
1596	0.699
1734	0.680
1871	0.672
2008	0.660
2145	0.635
2282	0.628
2419	0.596
2556	0.583
2693	0.560
2831	0.559
2968	0.520
3105	0.498
3242	0.475
3379	0.432
3517	0.424
3654	0.390
3791	0.364
3928	0.330
4065	0.314
4203	0.267
4340	0.220
4477	0.220
4615	0.188
4752	0.167
4889	0.169
5026	0.135
5164	0.118
5301	0.079
5438	0.102
5575	0.077

Table S6. Kinetic data for the reaction of 2-pyridinyl triflate (**2b**) (0.07 mol L^{-1}) with [Ni(COD)(dppf)] (**1**) (0.007 mol L^{-1}) at 293 K.

Time (s)	**Integral**
0	1.000
77	0.980
214	0.942
352	0.968
489	0.952

626	0.908
763	0.875
901	0.841
1038	0.823
1175	0.787
1313	0.747
1450	0.744
1587	0.708
1725	0.690
1862	0.648
1999	0.620
2136	0.592
2273	0.549
2411	0.521
2548	0.488
2685	0.445
2823	0.407
2960	0.370
3097	0.349
3235	0.315
3372	0.286
3509	0.247
3647	0.236
3784	0.222
3921	0.178
4059	0.155
4196	0.140
4333	0.135
4471	0.109
4608	0.091

Table S7. Kinetic data for the reaction of 2-pyridinyl triflate (**2b**) (0.035 mol L^{-1}) with [Ni(COD)(dppf)] (**1**) (0.007 mol L^{-1}) at 293 K.

Time (s)	**Integral**
0	1.000
72	0.952
209	0.962
346	0.962
484	0.944
621	0.946
758	0.919
896	0.905
1033	0.889
1171	0.879
1308	0.852
1445	0.834

1583	0.813
1720	0.798
1857	0.780
1995	0.747
2132	0.733
2269	0.703
2406	0.680
2543	0.641
2681	0.644
2818	0.607
2955	0.562
3093	0.554
3230	0.512
3367	0.472
3505	0.456
3642	0.429
3779	0.378
3917	0.366
4054	0.345
4191	0.322
4328	0.296
4465	0.268
4602	0.247
4740	0.236
4877	0.214
5015	0.193
5152	0.178
5289	0.167
5426	0.156
5563	0.150
5700	0.123
5837	0.107
5974	0.101
6111	0.095

2.2.6 3-Pyridinyl triflate (2d)

Table S8. Kinetic data for the reaction of 3-pyridinyl triflate (**2d**) (0.14 mol L^{-1}) with [Ni(COD)(dppf)] (**1**) (0.007 mol L^{-1}) at 293 K.

Replicate 1		**Replicate 2**	
Time (s)	**Integral**	**Time (s)**	**Integral**
0	1.000	0	1.000
121	0.738	73	0.824
175	0.639	133	0.737
228	0.534	186	0.640
282	0.455	239	0.542
335	0.375	292	0.446
389	0.304	345	0.341
443	0.234	398	0.282
496	0.188	451	0.227
550	0.148	503	0.179
603	0.116	557	0.142
657	0.082	609	0.116
		662	0.092

2.2.7 Cyclopent-1-en-1-yl triflate (5a)

Table S9. Kinetic data for the reaction of cyclopent-1-en-1-yl triflate (**5a**) (0.14 mol L^{-1}) with [Ni(COD)(dppf)] (**1**) (0.007 mol L^{-1}) at 323 K.

Replicate 1		**Replicate 2**	
Time (s)	**Integral**	**Time (s)**	**Integral**
0	1.000	0	1.000
103	0.918	54	0.773
250	0.867	201	0.868
381	0.808	348	0.750
497	0.736	496	0.703
629	0.678	643	0.676
745	0.648	790	0.558
876	0.614	937	0.551
992	0.595	1085	0.519
1123	0.553	1232	0.449
1239	0.508	1379	0.428
1371	0.468	1527	0.396
1487	0.435	1674	0.372
1618	0.423	1821	0.342
1734	0.389	1968	0.316
1865	0.353	2115	0.263
1981	0.333	2262	0.247
2112	0.259	2410	0.224
2228	0.231	2557	0.204
2359	0.231	2704	0.163
2475	0.227	2851	0.149
2606	0.183		
2723	0.216		
2854	0.205		
2970	0.168		
3101	0.162		
3217	0.169		
3348	0.134		
3465	0.105		

2.2.8 Cyclohex-1-en-1-yl triflate (5b)

Table S10. Kinetic data for the reaction of cyclohex-1-en-1-yl triflate (**5b**) (0.14 mol L^{-1}) with [Ni(COD)(dppf)] (**1**) (0.007 mol L^{-1}) at 333 K.

Replicate 1		**Replicate 2**	
Time (s)	**Integral**	**Time (s)**	**Integral**
0	1.000	0	1.000
90	0.925	86	0.916
228	0.935	223	0.912
365	0.850	361	0.891
502	0.787	498	0.858
640	0.790	635	0.817
783	0.748	773	0.817
920	0.683	910	0.728
1057	0.636	1048	0.712
1195	0.604	1185	0.664
1332	0.551	1323	0.620
1469	0.522	1460	0.547
1606	0.460	1597	0.510
1743	0.426	1735	0.473
1881	0.357	1872	0.431
2018	0.315	2009	0.404
2155	0.271	2146	0.353
2293	0.237	2283	0.308
2430	0.213	2420	0.261
2568	0.154	2558	0.231
2705	0.134	2695	0.181
		2832	0.155
		2969	0.145
		3107	0.118
		3244	0.100

2.2.9 Cyclohept-1-en-1-yl triflate (5c)

Table S11. Kinetic data for the reaction of cyclohept-1-en-1-yl triflate (**5c**) (0.14 mol L^{-1}) with [Ni(COD)(dppf)] (**1**) (0.007 mol L^{-1}) at 323 K.

Replicate 1		**Replicate 2**	
Time (s)	**Integral**	**Time (s)**	**Integral**
0	1.000	0	1.000
190	0.783	424	0.732
249	0.740	485	0.705
307	0.720	543	0.688
366	0.691	601	0.654
425	0.674	660	0.635
484	0.636	718	0.620
543	0.626	776	0.593
601	0.608	835	0.572
660	0.577	893	0.540
719	0.564	951	0.526
778	0.546	1010	0.509
837	0.532	1068	0.493
895	0.505	1127	0.477
954	0.484	1185	0.446
1013	0.466	1243	0.445
1072	0.449	1302	0.421
1131	0.445	1360	0.405
1189	0.417	1419	0.373
1248	0.403	1477	0.370
1306	0.392	1535	0.348
1365	0.361	1594	0.349
1424	0.360	1652	0.315
1483	0.350	1710	0.305
1542	0.338	1769	0.287
1601	0.321	1827	0.283
1659	0.293	1885	0.269
1718	0.291	1944	0.255
1777	0.272	2002	0.245
1836	0.269	2061	0.216
1894	0.253	2119	0.225
1953	0.247	2177	0.195
2012	0.231	2236	0.187
2071	0.208	2294	0.182
2130	0.206	2352	0.165
2188	0.194	2410	0.159
2247	0.177	2469	0.131
2306	0.172	2527	0.140
2365	0.157	2586	0.115

2424	0.144	2644	0.109
2482	0.134		
2541	0.127		
2600	0.115		
2658	0.105		

2.2.10 Cyclooct-1-en-1-yl triflate (5d)

Table S12. Kinetic data for the reaction of cyclooct-1-en-1-yl triflate (**5d**) (0.14 mol L^{-1}) with [Ni(COD)(dppf)] (**1**) (0.007 mol L^{-1}) at 323 K.

Replicate 1		**Replicate 2**	
Time (s)	**Integral**	**Time (s)**	**Integral**
0	1.000	0	1.000
90	0.887	131	0.804
227	0.759	268	0.715
365	0.723	405	0.718
502	0.667	542	0.668
639	0.638	680	0.606
776	0.587	817	0.600
913	0.554	954	0.555
1050	0.584	1091	0.557
1188	0.499	1228	0.480
1325	0.517	1366	0.481
1462	0.445	1503	0.404
1599	0.422	1640	0.400
1736	0.381	1777	0.366
1874	0.339	1915	0.277
2011	0.307	2052	0.296
2148	0.304	2189	0.292
2285	0.306	2326	0.250
2422	0.247	2464	0.221
2559	0.223	2601	0.180
2972	0.154	2738	0.206

2.3 VTNA Treatment

Methodology. It was assumed that the weighing of [Ni(COD)(dppf)] (**1**) and 2-pyridinyl triflate (**2b**) were accurate, and that an integral of 1.000 corresponds to the initial charge of **1**, as determined by mass. This was then used to convert the integral corresponding to **1** into [**1**] in mol L^{-1}. It was assumed that 1 equiv. of **1** reacts with 1 equiv. of substrate to produce 1 equiv. [Ni(OTf)(dppf)] **6** plus 0.5 equiv. 2,2'-bipyridine, and therefore that for every mole of **1** consumed, one mole of **2b** was consumed. This allows profiles of [**1**] and [**2b**] *versus* time to be constructed. The timescales for these profiles were then adjusted using VTNA methodology, so that for each time point t, a new timepoint tT was calculated, according to equation S1.

$$tT_n = tT_{n-1} + (\Delta[\mathbf{1}]/2)^a \times (\Delta[\mathbf{2b}]/2)^b \times (t_n - t_{n-1}) \qquad \text{(S1)}$$

where Δ[**1**] and Δ[**2b**] are the changes in concentration of **1** and **2b** (respectively) during the time period between t_n and t_{n-1}, a is the order in **1**, and b is the order in **2b**.

This leads to a new profile, which qualitatively overlaps for each of the four experiments used for the VNTA treatment. In each case the concentration of **6** – assuming that one molecule of **1** forms one molecule of **6** – is plotted to allow ready comparison between experiments.

Table S13. Data for the VTNA treatment of the reaction of **1** (0.007 mol L^{-1}) with **2b** (0.14 mol L^{-1}) with an order of 0.9 in **1** and 0.3 in **2b**.

Time (s)	Integral for 1	[1] (mol L^{-1})	[2b] (mol L^{-1})	tT	[6] (mol L^{-1})
0	1	0.00694	0.13884	0	0
81	0.93149	0.00646	0.13836	0.49501	0.000475
218	0.91227	0.00633	0.13823	1.29742	0.000609
355	0.9126	0.00633	0.13823	2.09231	0.000607
493	0.86699	0.00602	0.13792	2.87484	0.000923
630	0.84749	0.00588	0.13778	3.62569	0.00106
767	0.82237	0.00571	0.13761	4.35869	0.00123
904	0.77582	0.00538	0.13728	5.06293	0.00156
1042	0.75018	0.00521	0.13711	5.74304	0.00173
1179	0.73094	0.00507	0.13697	6.40009	0.00187
1316	0.69418	0.00482	0.13672	7.03447	0.00212
1453	0.64955	0.00451	0.13641	7.63578	0.00243
1590	0.62802	0.00436	0.13626	8.21009	0.00258
1728	0.59963	0.00416	0.13606	8.76799	0.00278
1865	0.57374	0.00398	0.13588	9.29954	0.00296
2002	0.52186	0.00362	0.13552	9.79898	0.00332
2139	0.49929	0.00347	0.13537	10.2675	0.00347
2277	0.44364	0.00308	0.13498	10.70651	0.00386
2414	0.41677	0.00289	0.13479	11.1076	0.00405
2551	0.3785	0.00263	0.13453	11.48107	0.00431
2688	0.34387	0.00239	0.13429	11.82339	0.00455

2825	0.30693	0.00213	0.13403	12.13485	0.00481
2962	0.27967	0.00194	0.13384	12.41837	0.005
3100	0.25707	0.00178	0.13368	12.68192	0.00516
3237	0.22679	0.00157	0.13347	12.92014	0.00537
3374	0.19005	0.00132	0.13322	13.12835	0.00562
3511	0.16837	0.00117	0.13307	13.31001	0.00577
3648	0.14744	0.00102	0.13292	13.47206	0.00592
3786	0.12147	0.000843	0.13274	13.61326	0.0061
3923	0.10167	0.000706	0.13261	13.73172	0.00623

Table S14. Data for the VTNA treatment of the reaction of **1** (0.0035 mol L^{-1}) with **2b** (0.14 mol L^{-1}) with an order of 0.9 in **1** and 0.3 in **2b**.

Time (s)	Integral for 1	[1] (mol L^{-1})	[2b] (mol L^{-1})	tT	[6] (mol L^{-1})
0	1	0.00347	0.13884	0	0
87	0.79937	0.00277	0.13814	0.26725	0.000696
224	0.80048	0.00278	0.13815	0.64558	0.000692
361	0.79864	0.00277	0.13814	1.02375	0.000699
499	0.77691	0.0027	0.13807	1.39958	0.000774
636	0.76828	0.00267	0.13804	1.76618	0.000804
773	0.76599	0.00266	0.13803	2.13042	0.000812
910	0.77637	0.00269	0.13806	2.49641	0.000776
1047	0.74752	0.00259	0.13796	2.85842	0.000876
1185	0.72856	0.00253	0.1379	3.2127	0.000942
1322	0.72781	0.00253	0.1379	3.56016	0.000944
1459	0.72482	0.00252	0.13789	3.90681	0.000955
1596	0.69892	0.00243	0.1378	4.24721	0.00104
1734	0.67983	0.00236	0.13773	4.58027	0.00111
1871	0.67226	0.00233	0.1377	4.90512	0.00114
2008	0.66019	0.00229	0.13766	5.22571	0.00118
2145	0.6346	0.0022	0.13757	5.53808	0.00127
2282	0.62761	0.00218	0.13755	5.84332	0.00129
2419	0.59572	0.00207	0.13744	6.14005	0.0014
2556	0.58337	0.00202	0.13739	6.42706	0.00145
2693	0.56008	0.00194	0.13731	6.70621	0.00153
2831	0.55879	0.00194	0.13731	6.98193	0.00153
2968	0.52044	0.00181	0.13718	7.24686	0.00166
3105	0.49763	0.00173	0.1371	7.49819	0.00174
3242	0.4754	0.00165	0.13702	7.73944	0.00182
3379	0.43163	0.0015	0.13687	7.96586	0.00197
3517	0.42359	0.00147	0.13684	8.18213	0.002
3654	0.38966	0.00135	0.13672	8.3873	0.00212
3791	0.36365	0.00126	0.13663	8.57876	0.00221
3928	0.33036	0.00115	0.13652	8.75656	0.00232
4065	0.3135	0.00109	0.13646	8.92272	0.00238
4203	0.26664	0.000925	0.1363	9.07507	0.00254
4340	0.21979	0.000763	0.13613	9.20409	0.00271

4477	0.22035	0.000765	0.13613	9.32199	0.00271
4615	0.18828	0.000653	0.13602	9.43306	0.00282
4752	0.16744	0.000581	0.13595	9.53036	0.00289
4889	0.16852	0.000585	0.13595	9.62278	0.00289
5026	0.13523	0.000469	0.13584	9.70718	0.003
5164	0.11779	0.000409	0.13578	9.77928	0.00306
5301	0.07932	0.000275	0.13565	9.83645	0.00319
5438	0.10177	0.000353	0.13572	9.88941	0.00312
5575	0.07688	0.000267	0.13564	9.94173	0.0032

Table S15. Data for the VTNA treatment of the reaction of **1** (0.007 mol L^{-1}) with **2b** (0.07 mol L^{-1}) with an order of 0.9 in **1** and 0.3 in **2b**.

Time (s)	**Integral for 1**	**[1] (mol L^{-1})**	**[2b] (mol L^{-1})**	**tT**	**[6] (mol L^{-1})**
0	1	0.00694	0.0694	0	0
77	0.98025	0.0068	0.06926	0.39094	0.000137
214	0.94219	0.00654	0.069	1.06763	0.000401
352	0.96823	0.00672	0.06918	1.7453	0.000220
489	0.95158	0.0066	0.06906	2.42112	0.000336
626	0.90779	0.0063	0.06876	3.07717	0.000640
763	0.87466	0.00607	0.06853	3.708	0.000870
901	0.84082	0.00584	0.0683	4.32129	0.0011
1038	0.8231	0.00571	0.06817	4.91317	0.00123
1175	0.78683	0.00546	0.06792	5.48727	0.00148
1313	0.74744	0.00519	0.06765	6.0404	0.00175
1450	0.74366	0.00516	0.06762	6.57524	0.00178
1587	0.70789	0.00491	0.06737	7.09698	0.00203
1725	0.69009	0.00479	0.06725	7.60461	0.00215
1862	0.64826	0.0045	0.06696	8.08873	0.00244
1999	0.61969	0.0043	0.06676	8.54937	0.00264
2136	0.59202	0.00411	0.06657	8.99119	0.00283
2273	0.54877	0.00381	0.06627	9.4092	0.00313
2411	0.52067	0.00361	0.06607	9.80604	0.00333
2548	0.48841	0.00339	0.06585	10.17958	0.00355
2685	0.44454	0.00309	0.06555	10.52724	0.00385
2823	0.40747	0.00283	0.06529	10.84956	0.00411
2960	0.36951	0.00256	0.06502	11.14371	0.00438
3097	0.34861	0.00242	0.06488	11.41747	0.00452
3235	0.31505	0.00219	0.06465	11.67411	0.00475
3372	0.28554	0.00198	0.06444	11.90675	0.00496
3509	0.24719	0.00172	0.06418	12.11537	0.00522
3647	0.2356	0.00164	0.0641	12.30755	0.0053
3784	0.22212	0.00154	0.064	12.48931	0.0054
3921	0.17812	0.00124	0.0637	12.65025	0.0057
4059	0.15483	0.00107	0.06353	12.78746	0.00587
4196	0.13989	0.000971	0.06343	12.90943	0.00597

4333	0.13463	0.000934	0.06339	13.02382	0.00601
4471	0.10918	0.000758	0.06322	13.12733	0.00618
4608	0.09101	0.000632	0.06309	13.21331	0.00631

Table S16. Data for the VTNA treatment of the reaction of **1** (0.007 mol L^{-1}) with **2b** (0.035 mol L^{-1}) with an order of 0.9 in **1** and 0.3 in **2b**.

Time (s)	**Integral for 1**	**[1] (mol L^{-1})**	**[2b] (mol L^{-1})**	**tT**	**[6] (mol L^{-1})**
0	1	0.00694	0.0347	0	0
72	0.95244	0.00661	0.03437	0.29284	0.000330
209	0.96248	0.00668	0.03444	0.83978	0.000260
346	0.9624	0.00668	0.03444	1.38944	0.000261
484	0.94385	0.00655	0.03431	1.93798	0.000390
621	0.94581	0.00656	0.03432	2.47801	0.000376
758	0.91911	0.00638	0.03414	3.01127	0.000561
896	0.90469	0.00628	0.03404	3.53709	0.000661
1033	0.88914	0.00617	0.03393	4.0509	0.000769
1171	0.87922	0.0061	0.03386	4.56145	0.000838
1308	0.85192	0.00591	0.03367	5.05811	0.00103
1445	0.8342	0.00579	0.03355	5.54246	0.00115
1583	0.81284	0.00564	0.0334	6.01958	0.0013
1720	0.79779	0.00554	0.0333	6.48328	0.0014
1857	0.78042	0.00542	0.03318	6.93811	0.00152
1995	0.7472	0.00519	0.03295	7.38232	0.00175
2132	0.73289	0.00509	0.03285	7.8103	0.00185
2269	0.70321	0.00488	0.03264	8.22623	0.00206
2406	0.68046	0.00472	0.03248	8.62779	0.00222
2543	0.64107	0.00445	0.03221	9.01232	0.00249
2681	0.64431	0.00447	0.03223	9.38967	0.00247
2818	0.60748	0.00422	0.03198	9.75506	0.00272
2955	0.56198	0.0039	0.03166	10.09784	0.00304
3093	0.55435	0.00385	0.03161	10.42838	0.00309
3230	0.51188	0.00355	0.03131	10.74273	0.00339
3367	0.47221	0.00328	0.03104	11.0344	0.00366
3505	0.45603	0.00316	0.03092	11.31263	0.00378
3642	0.42883	0.00298	0.03074	11.5768	0.00396
3779	0.37764	0.00262	0.03038	11.81918	0.00432
3917	0.36565	0.00254	0.0303	12.04555	0.0044
4054	0.34451	0.00239	0.03015	12.26099	0.00455
4191	0.32199	0.00223	0.02999	12.46418	0.00471
4328	0.29582	0.00205	0.02981	12.65363	0.00489
4465	0.26793	0.00186	0.02962	12.82777	0.00508
4602	0.2465	0.00171	0.02947	12.98785	0.00523
4740	0.23554	0.00163	0.02939	13.13977	0.00531
4877	0.21437	0.00149	0.02925	13.28135	0.00545
5015	0.19328	0.00134	0.0291	13.41164	0.0056

5152	0.17772	0.00123	0.02899	13.53033	0.00571
5289	0.16668	0.00116	0.02892	13.64122	0.00578
5426	0.15633	0.00108	0.02884	13.74581	0.00586
5563	0.15039	0.00104	0.0288	13.84558	0.0059
5700	0.12301	0.000854	0.02861	13.93543	0.00609
5837	0.10725	0.000744	0.0285	14.0123	0.0062
5974	0.1009	0.000700	0.02846	14.08243	0.00624
6111	0.09493	0.000659	0.02842	14.14879	0.00628

3 Measurement of Equilibrium Constants

3.1 Methodology

Equilibrium constants were measured by ^{31}P NMR spectroscopic analysis of a mixture of [Ni(COD)(dppf)] and the alkene of interest in benzene-d_6, in the presence of $OPPh_3$ as an internal standard. The integral of the internal standard was set to 1 and all other integrals were measured relative to this.

The equilibrium constant K_{eq} can be defined as per eq. S1.

$$K_{eq} = \frac{[Ni(alkene)(dppf)]\cdot[COD]}{[Ni(COD)(dppf)]\cdot[alkene]} \tag{S1}$$

The concentration of COD cannot be measured by ^{31}P NMR spectroscopy but will be equal to the concentration of [Ni(alkene)(dppf)]. Likewise, the concentration of alkene will be equal to the initial concentration of alkene minus the concentration of [Ni(alkene)(dppf)]. Therefore, we can derive eq. S2.

$$K_{eq} = \frac{[Ni(alkene)(dppf)]^2}{[Ni(COD)(dppf)]\cdot([alkene]_0 - [Ni(alkene)(dppf)])} \tag{S2}$$

This allows the equilibrium constant to be measured provided that the concentrations of [Ni(alkene)(dppf)] and [Ni(COD)(dppf)] are known – although in theory the latter might be calculated from the former – provided the initial concentration of alkene is known.

3.2 Equilibrium Constants

Alkene	**[$OPPh_3$]** mol L^{-1}	**[Ni(COD)(dppf)]** Integral	**[Ni(alkene)(dppf)]** Integral	**[Alkene]$_0$** mol L^{-1}	**[Ni(COD)(dppf)]** mol L^{-1}	**[Ni(alkene)(dppf)]** mol L^{-1}	**K_{eq}**
Cyclopentene	0.022	2.734	0.338	0.022	0.030	0.0037	2.5×10^{-2}
Cyclohexene		2.517	0		0.028	0	0
Cycloheptene		2.490	0.163		0.027	0.0018	5.8×10^{-3}
Cis-Cyclooctene		2.458	0.217		0.027	0.0024	1.1×10^{-2}

In the case of cyclohexene, if the limit of detection is assumed to be an integral of 0.05 (i.e. 5% of the integral for the internal standard), then the maximum K_{eq} can be estimated at 5.1×10^{-4}.

4 Cross-Coupling Reactions

4.1 General Procedure

In an argon-filled glovebox, [Ni(COD)(dppf)] (**1**) was added to a microwave vial equipped with a stir bar. The vial was sealed with a septum-fitted crimp cap and removed from the glovebox. On the Schlenk line, anhydrous THF (1 mL) was added via syringe, followed by phenylmagnesium chloride (0.28 mL, 1.1 equiv.). The vial was heated, with stirring, to 85 °C, and the organotriflate substrate was added *via* microsyringe. The reaction was stirred at 85 °C for 24 h, before being allowed to cool to room temperature. The vial was vented using a needle and then opened. A known mass of *n*-tetradecane was added. The solution was allowed to stir briefly and then a sample was withdrawn for GC-FID analysis. All reactions were performed in duplicate and so average conversions are reported in the manuscript text. The GCFID apparatus was calibrated using authentic samples of each product, which were prepared as described previously in this document.

4.2 Cross-Coupling Reaction Outcomes

Table S17: Outcomes of single-substrate cross-coupling reactions (n.d. = not detected).

Entry	Substrate	Substrate	Product
1a	4-(Trifluoromethyl)phenyl triflate (**2b**)	8%	80%
1b		11%	78%
2a	Cyclopent-1-en-1-yl triflate (**5a**)	5%	48%
2b		5%	51%
3a	Cyclohex-1-en-1-yl triflate (**5b**)	n.d.	84%
3b		n.d.	86%
4a	Cyclohept-1-en-1-yl triflate (**5c**)	n.d.	91%
4b		n.d.	82%
5a	Cyclooct-1-en-1-yl triflate (**5d**)	n.d.	96%
5b		n.d.	96%

Table S18: Outcome of competition cross-coupling reaction with 1 equiv. of each of cyclooct-1-en-1-yl triflate (**5d**) and 4-(trifluoromethyl)phenyl triflate (**2a**), plus 1.1 equiv. PhMgCl.

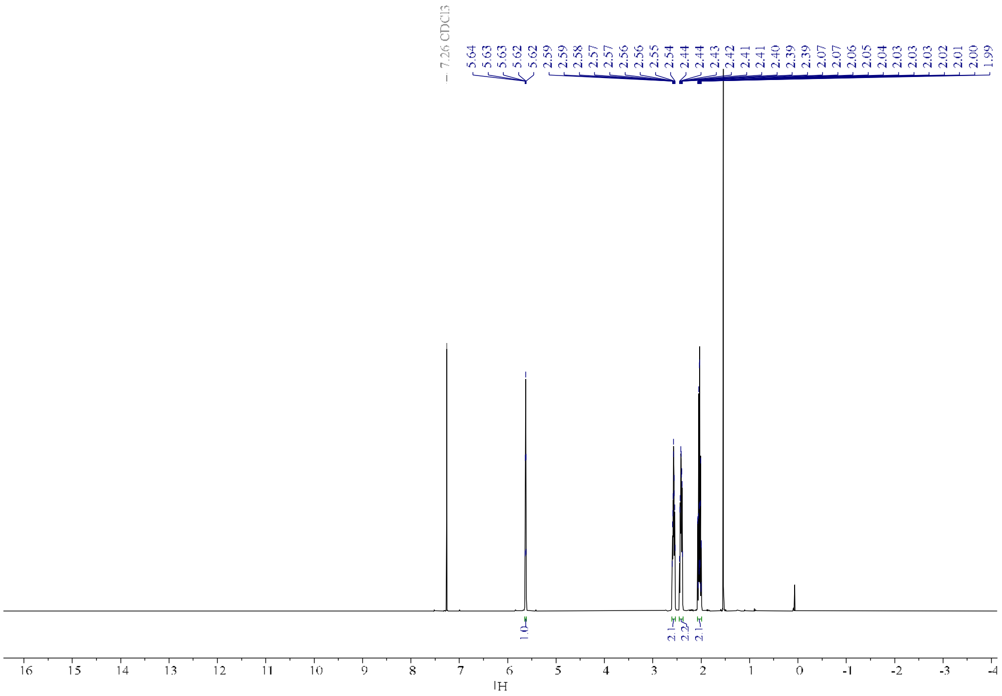
Replicate	1-Phenylcyclooct-1-ene	4-Phenyl-1-(Trifluoromethylphenyl)benzene
1	49%	51%
2	54%	46%

5 NMR Spectra

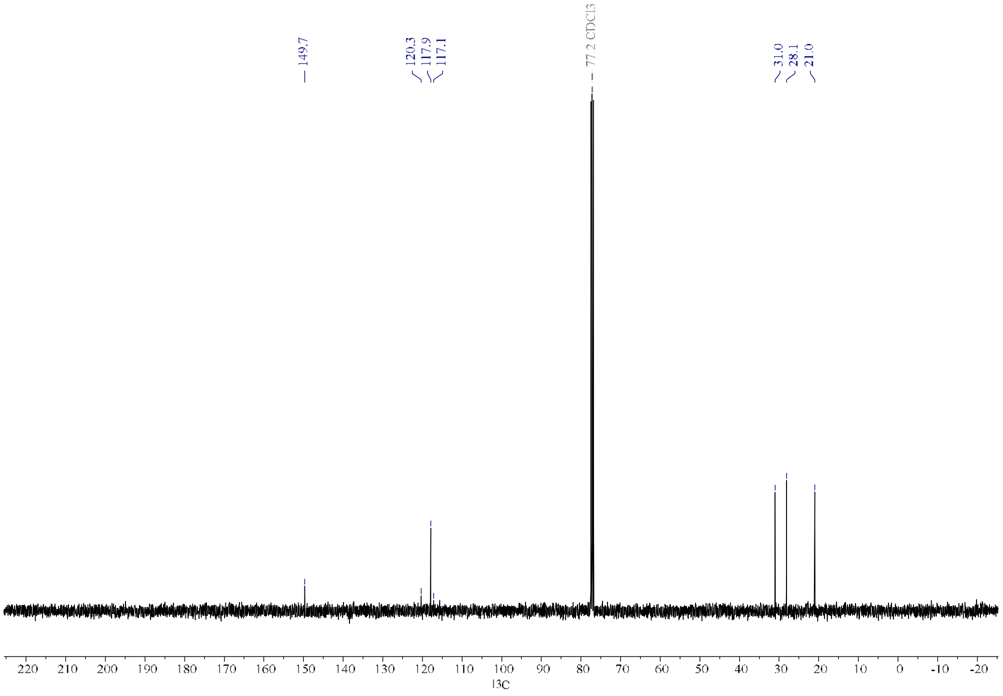
5.1 Alk-1-en-1-yl Triflates

Cyclopent-1-en-1-yl triflate (5a)

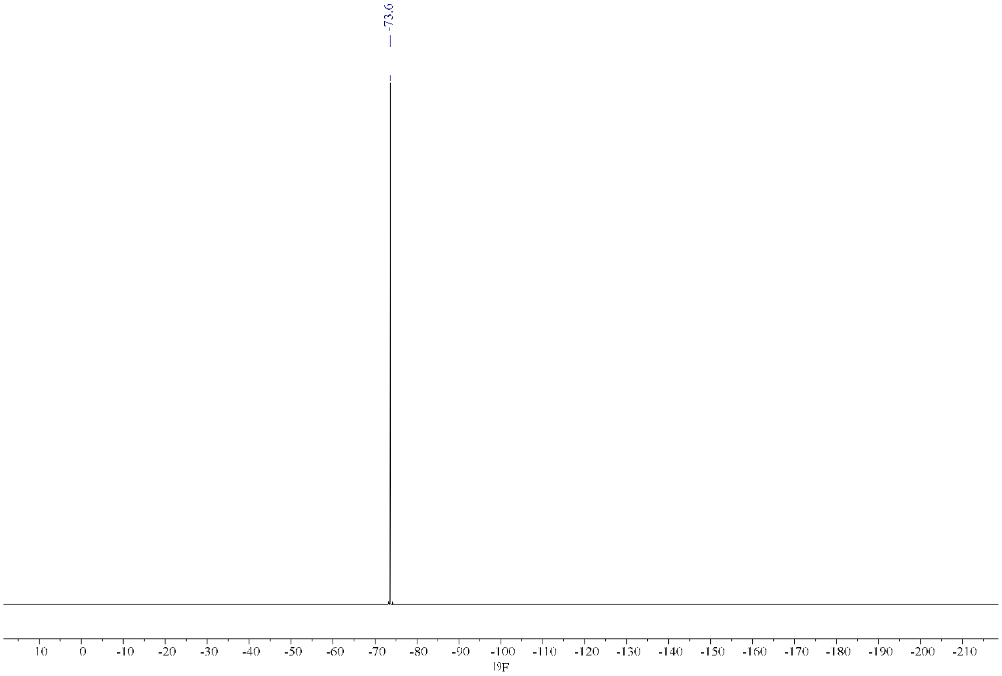
^{1}H NMR Spectrum



^{13}C{^{1}H} NMR Spectrum

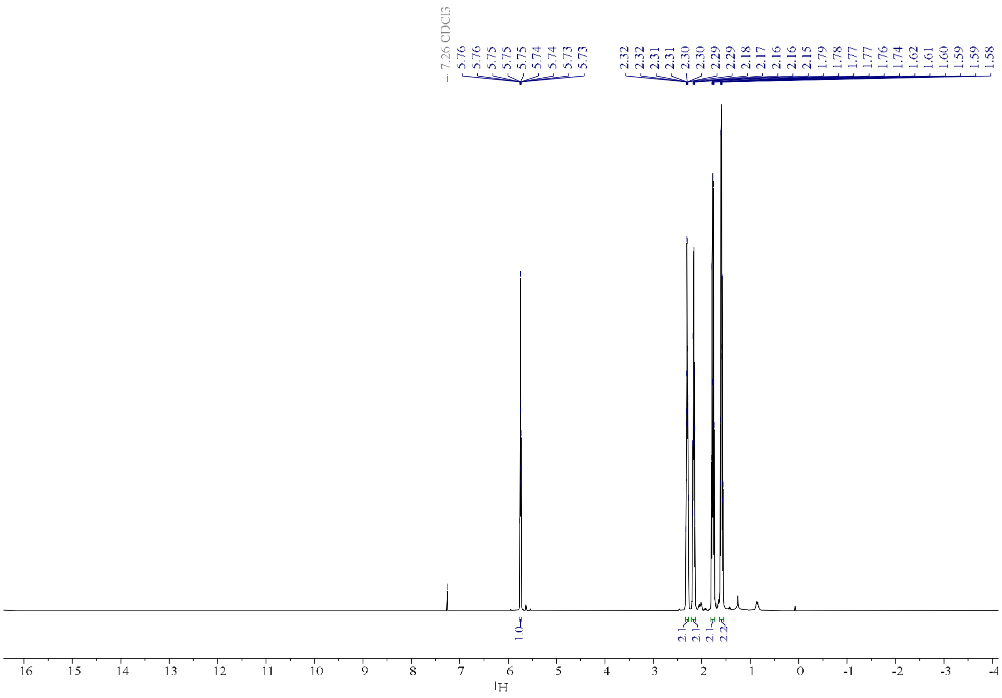


$^{19}F\{^1H\}$ NMR Spectrum

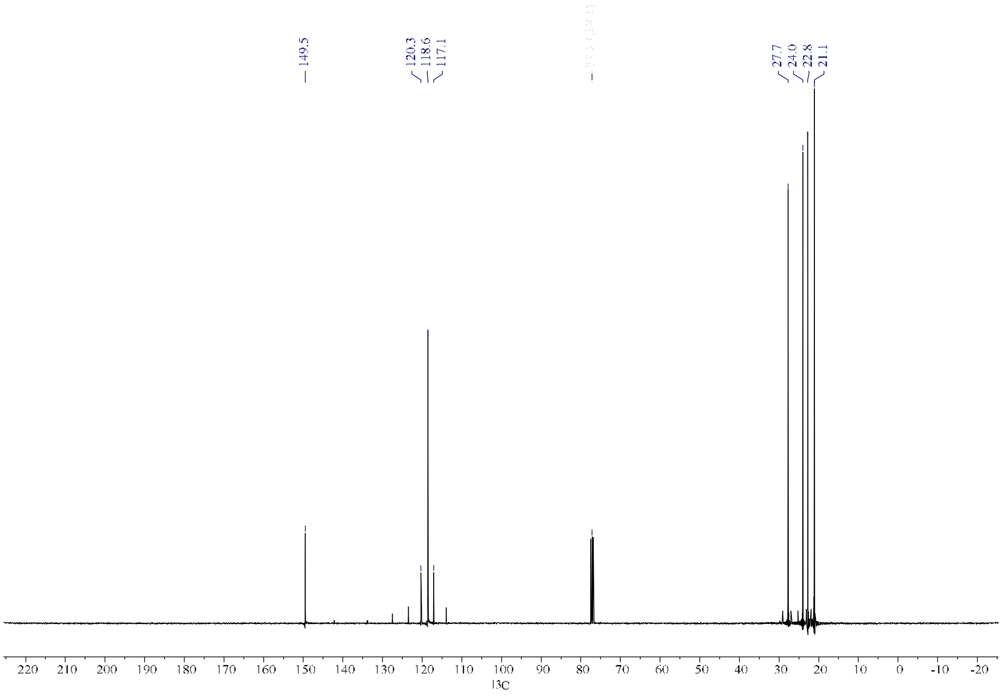


Cyclohex-1-en-1-yl triflate (5b)

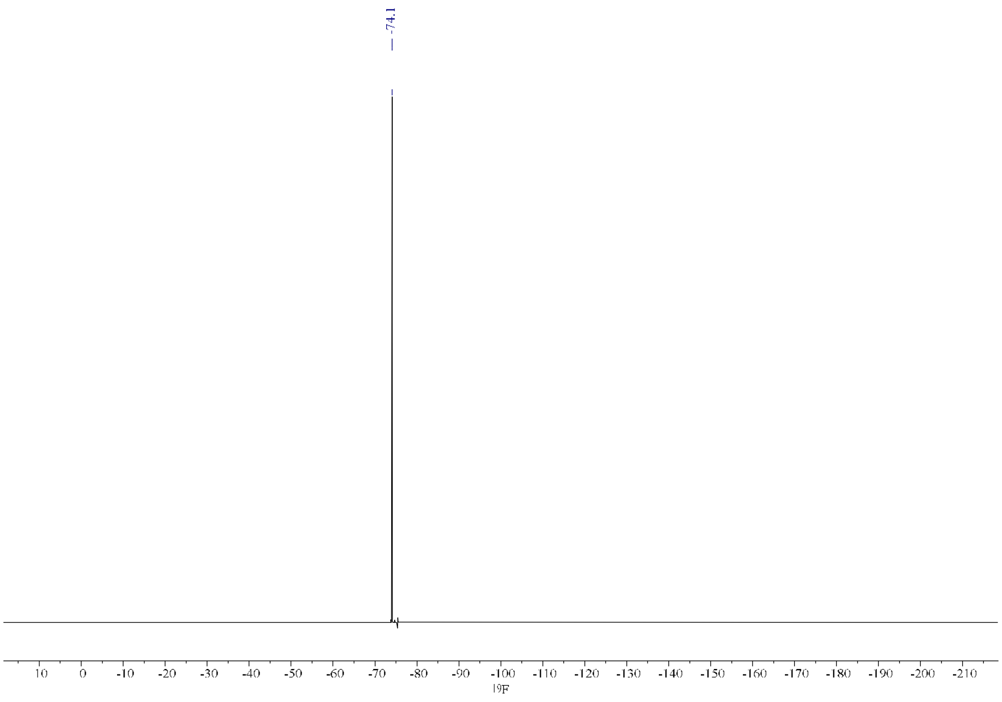
^1H NMR Spectrum



$^{13}C\{^{1}H\}$ NMR Spectrum

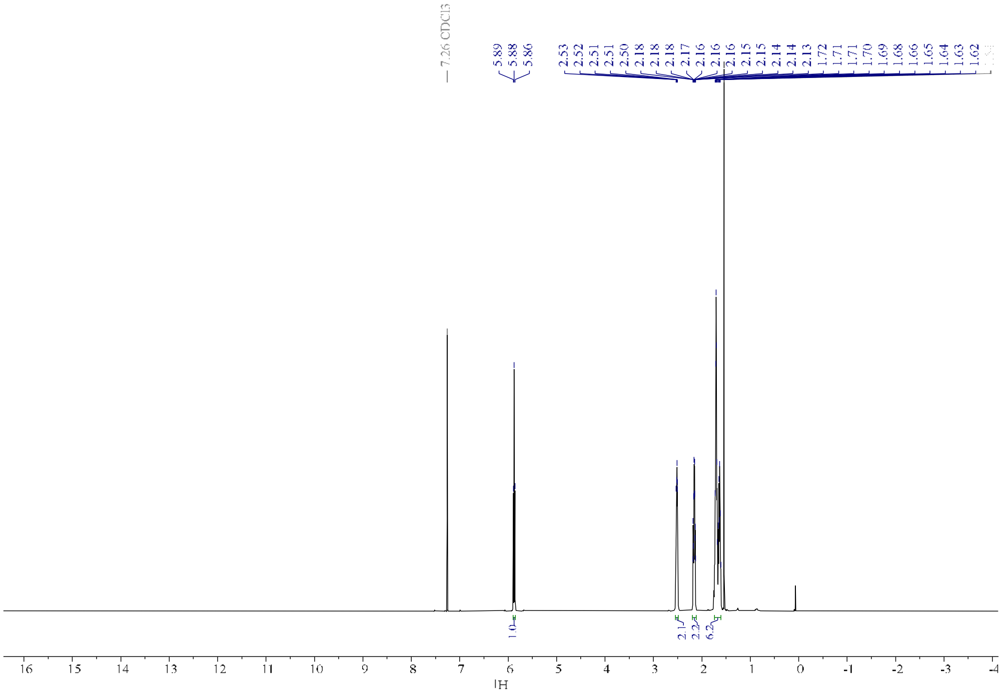


$^{19}F\{^{1}H\}$ NMR Spectrum

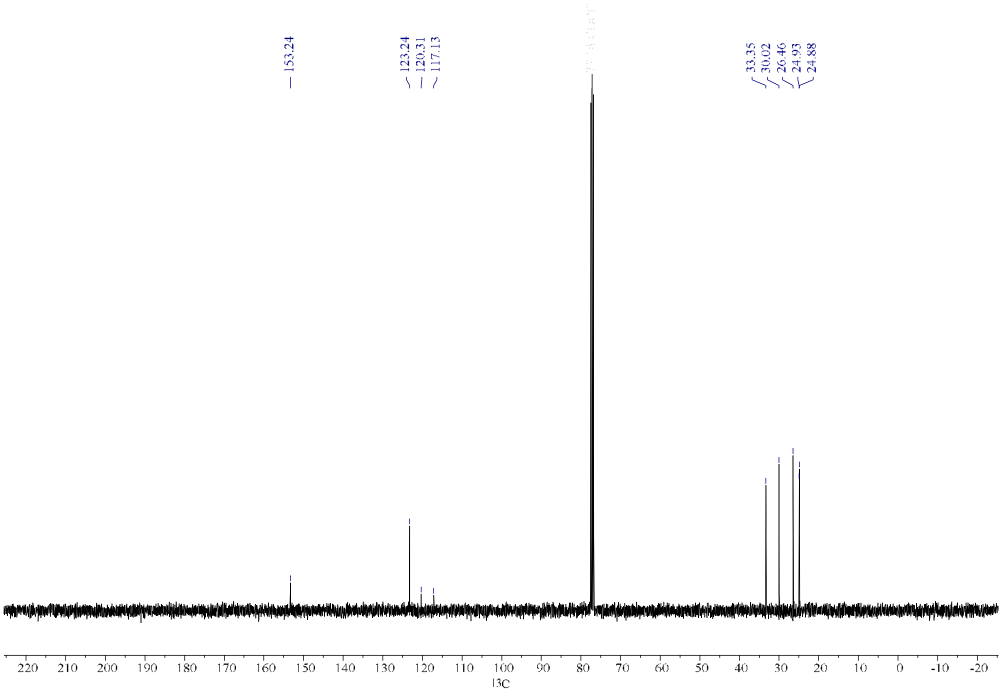


Cyclohept-1-en-1-yl triflate (5c)

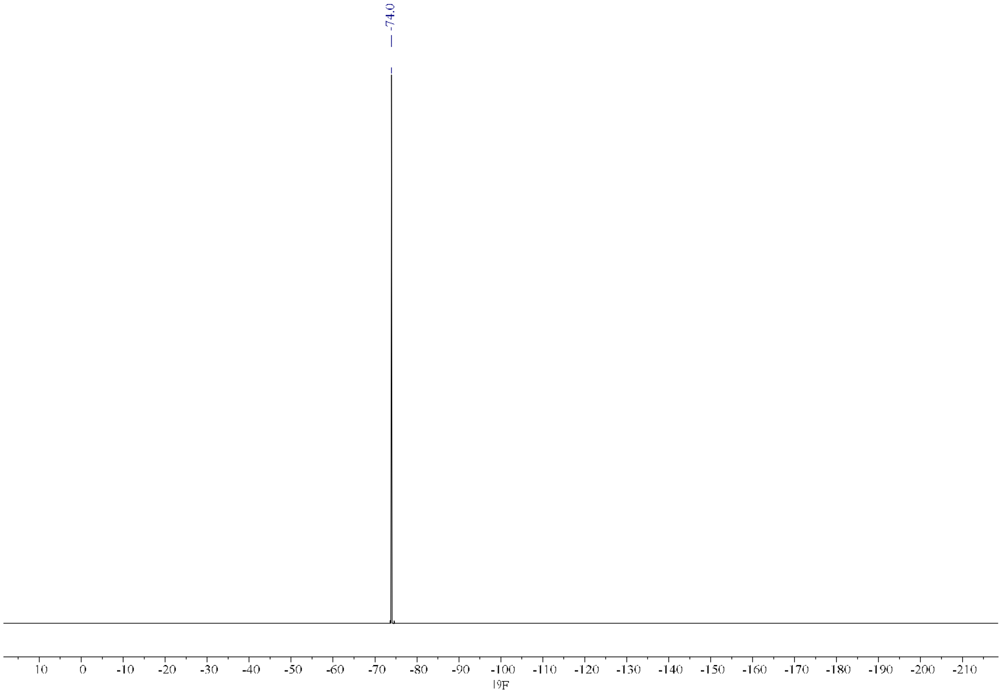
¹H NMR Spectrum



¹³C{¹H} NMR Spectrum

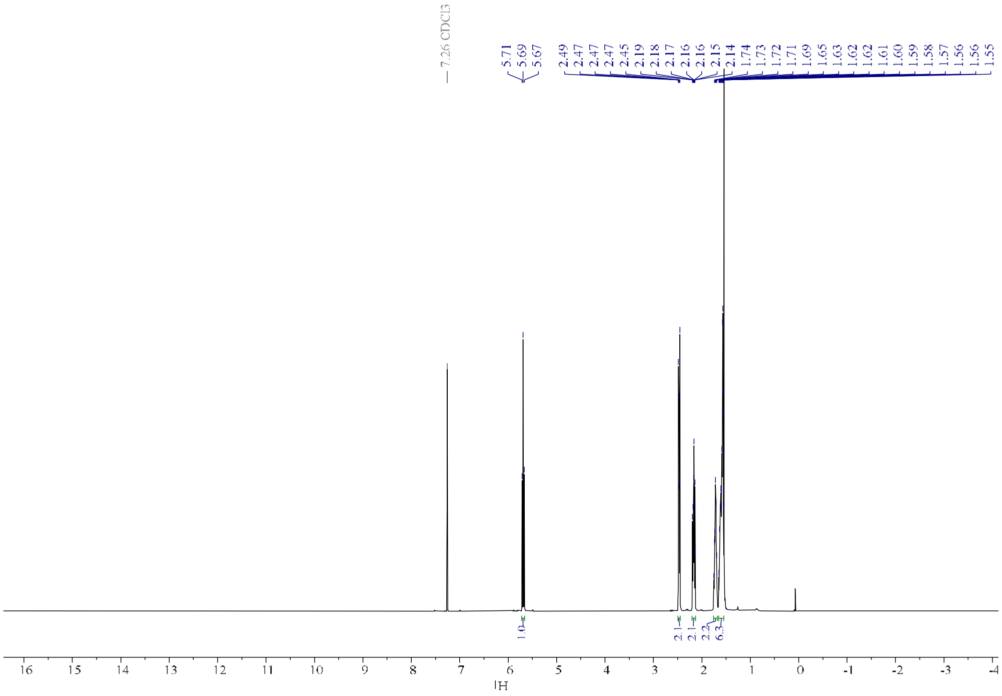


$^{19}F\{^1H\}$ NMR Spectrum

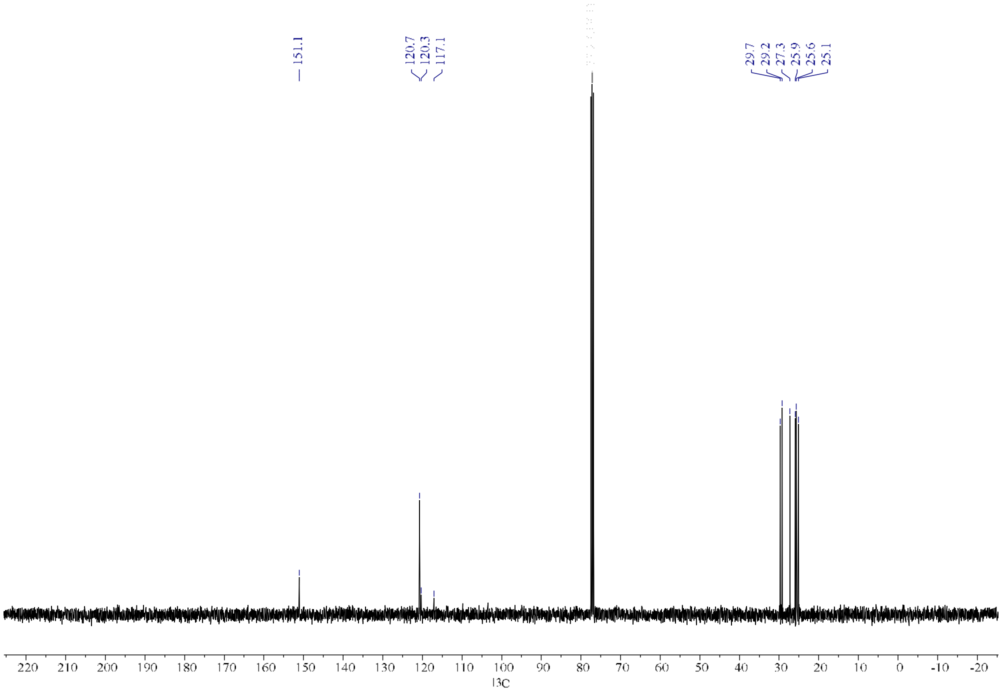


Cyclooct-1-en-1-yl triflate (5d)

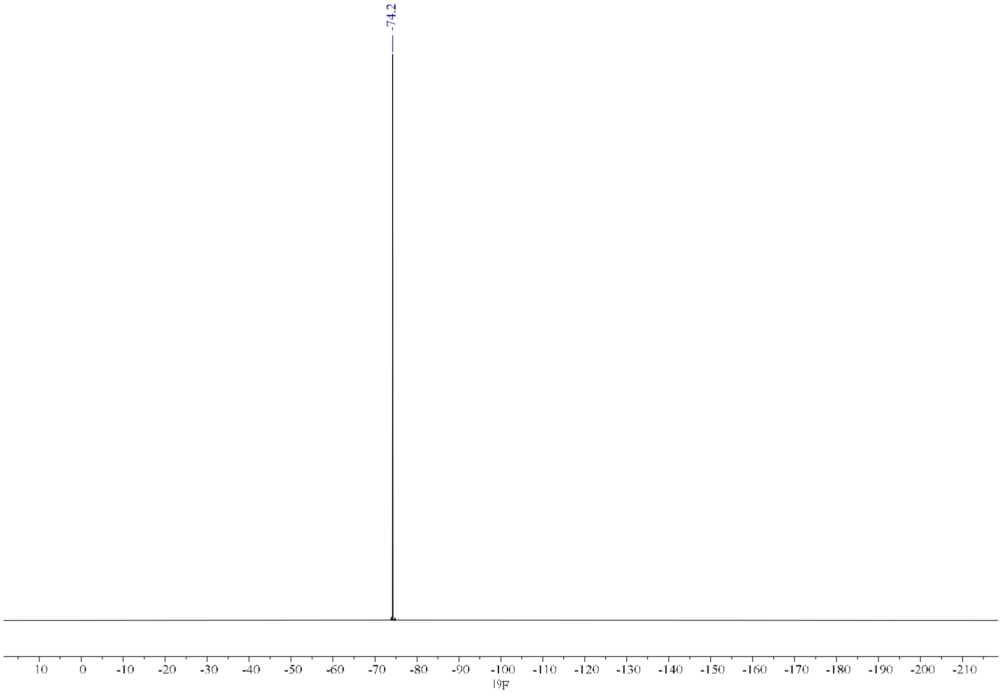
^1H NMR Spectrum



$^{13}C\{^1H\}$ NMR Spectrum



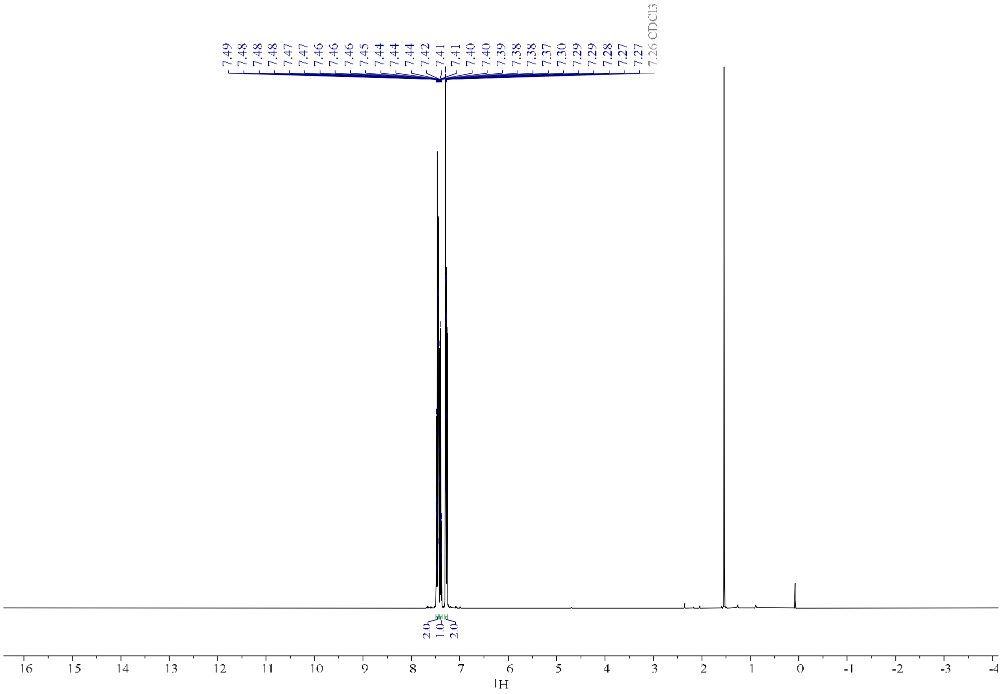
$^{19}F\{^1H\}$ NMR Spectrum



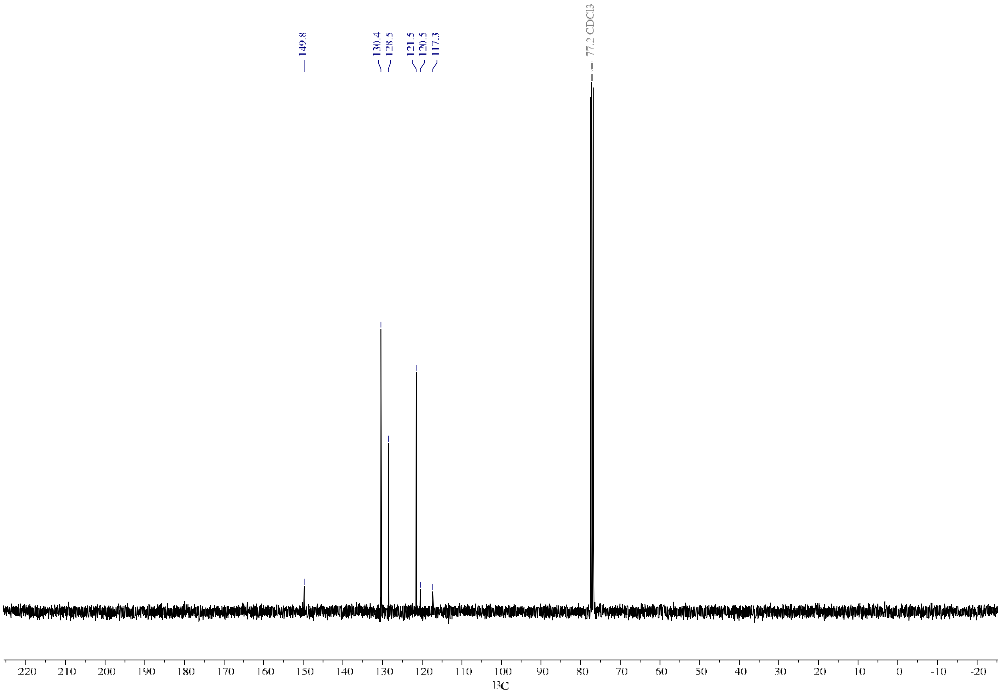
5.2 (Hetero)Aryl Triflates

Phenyl triflate (2c)

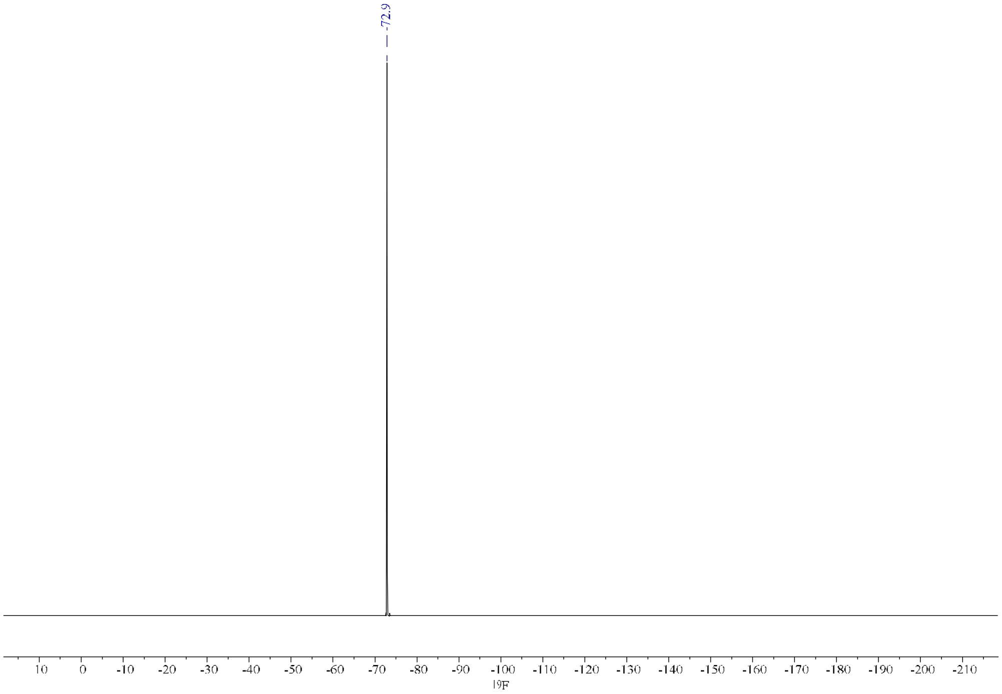
¹H NMR Spectrum



¹³C{¹H} NMR Spectrum

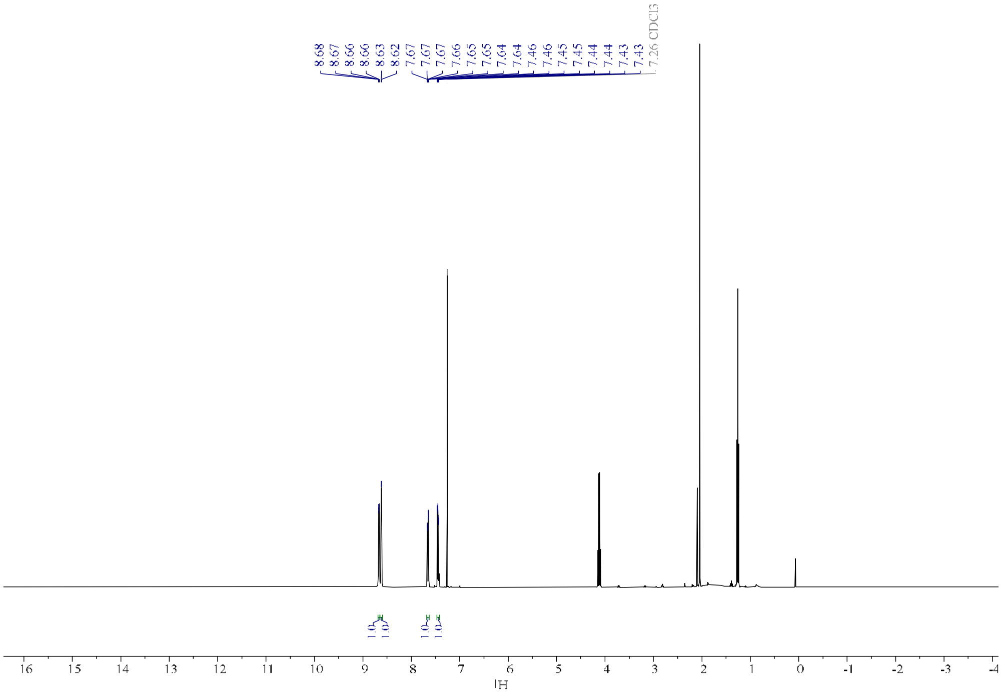


¹⁹F{¹H} NMR Spectrum

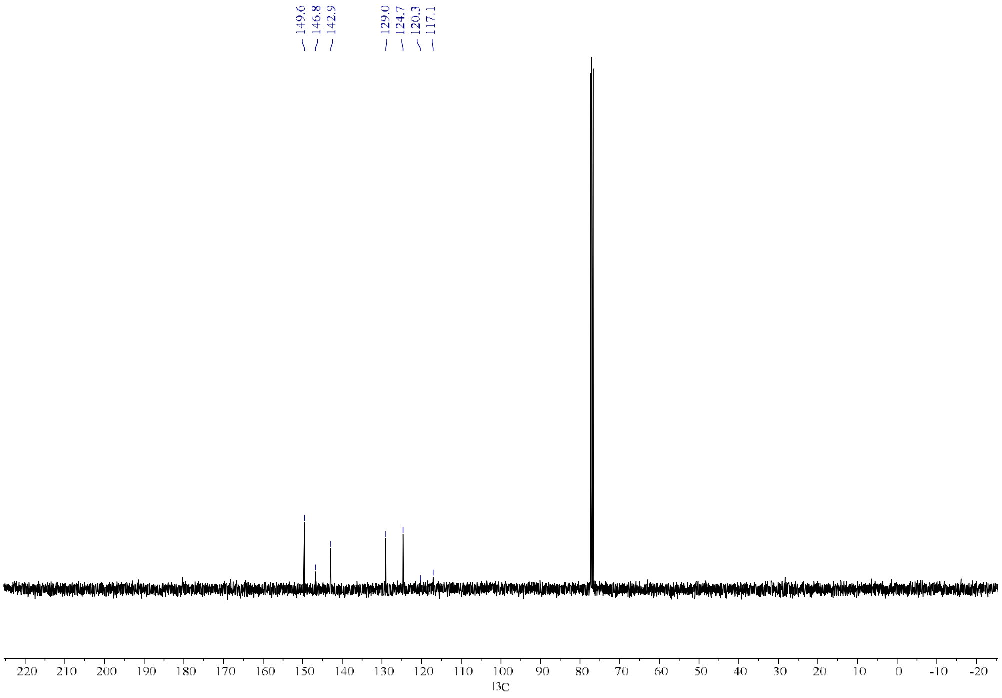


3-Pyridinyl triflate (2d)

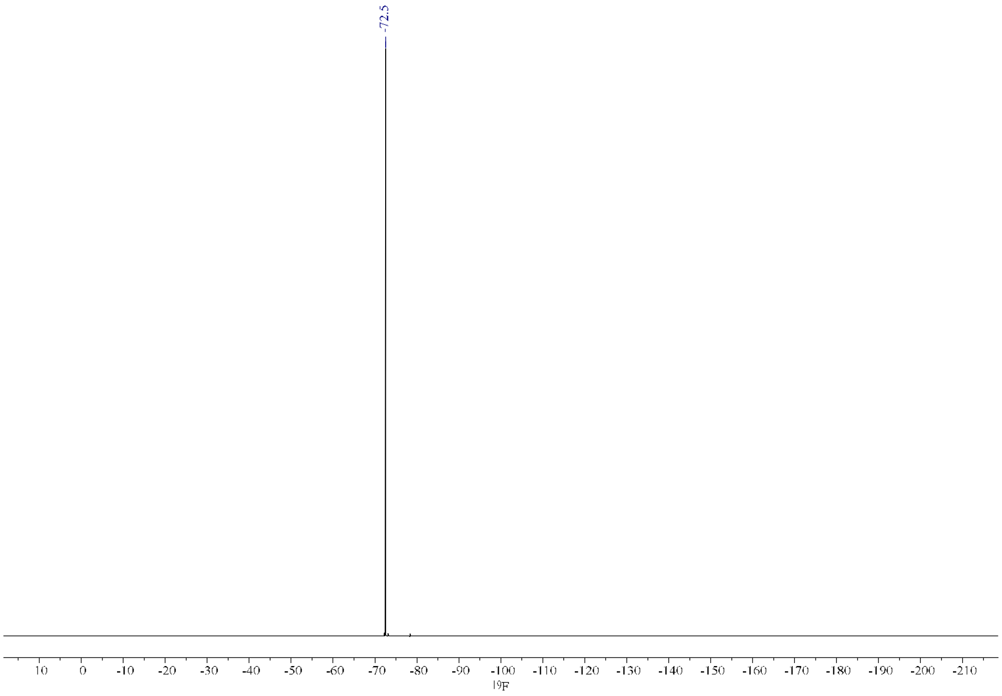
¹H NMR Spectrum



$^{13}C\{^1H\}$ NMR Spectrum



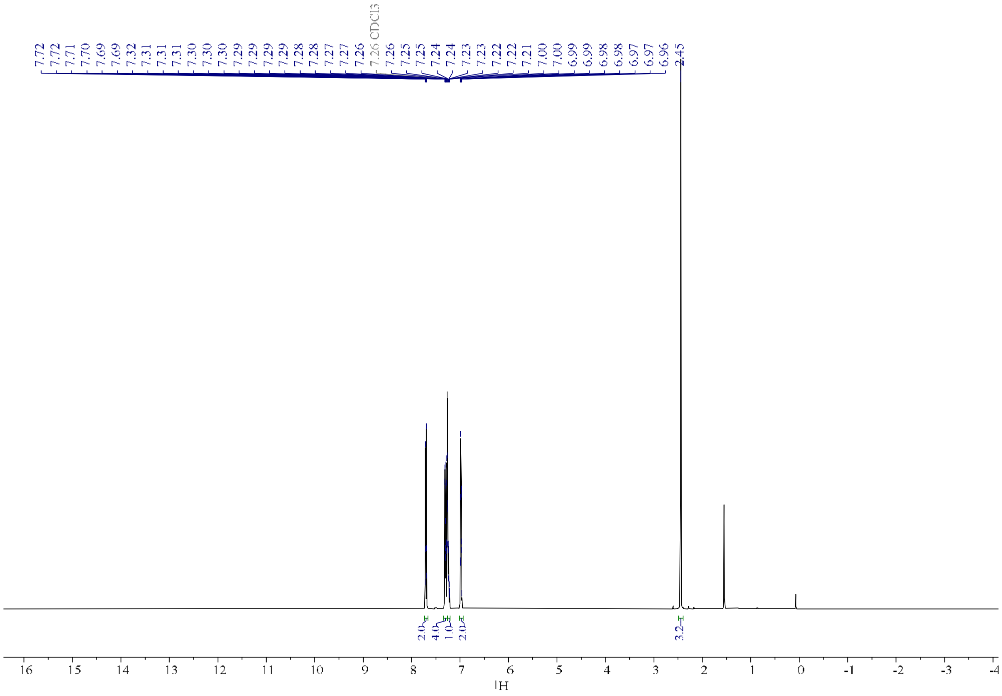
$^{19}F\{^1H\}$ NMR Spectrum



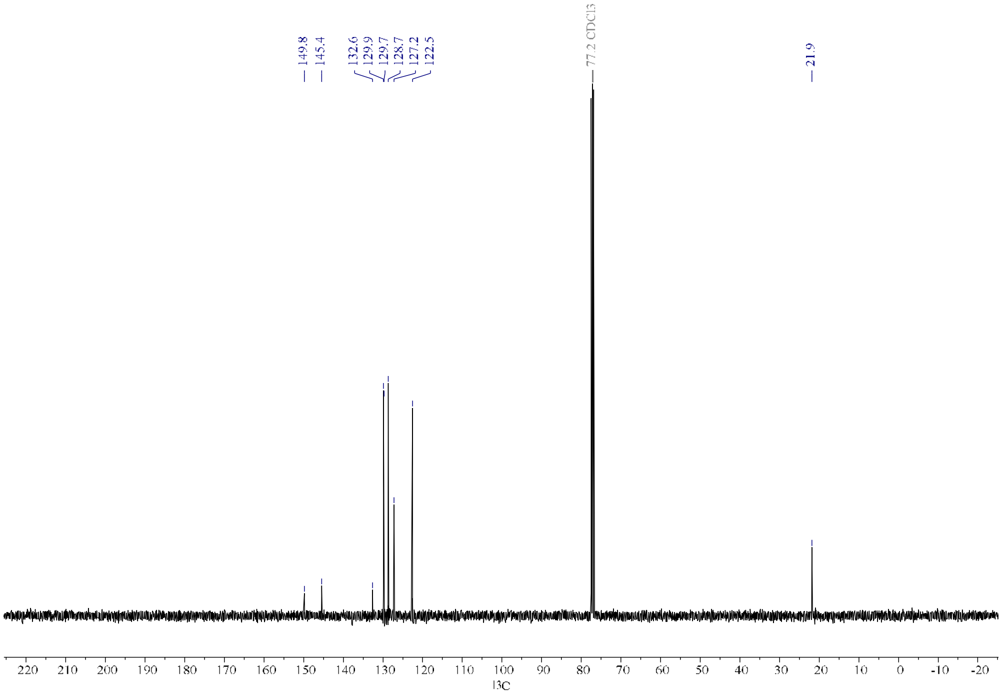
5.3 Other Electrophiles

Phenyl tosylate (9)

¹H NMR Spectrum



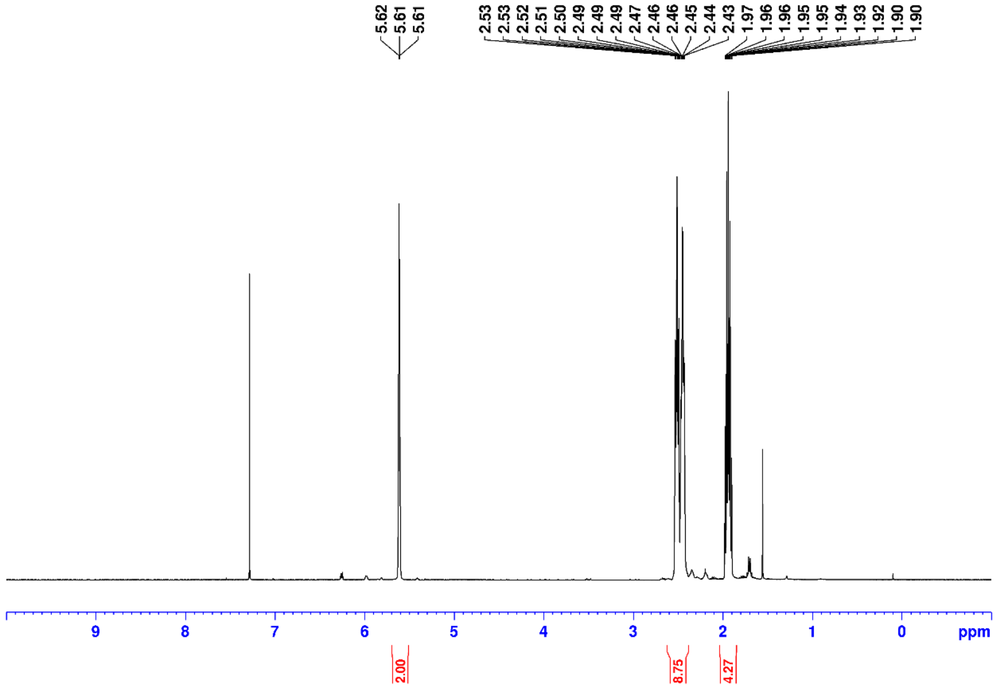
¹³C{¹H} NMR Spectrum



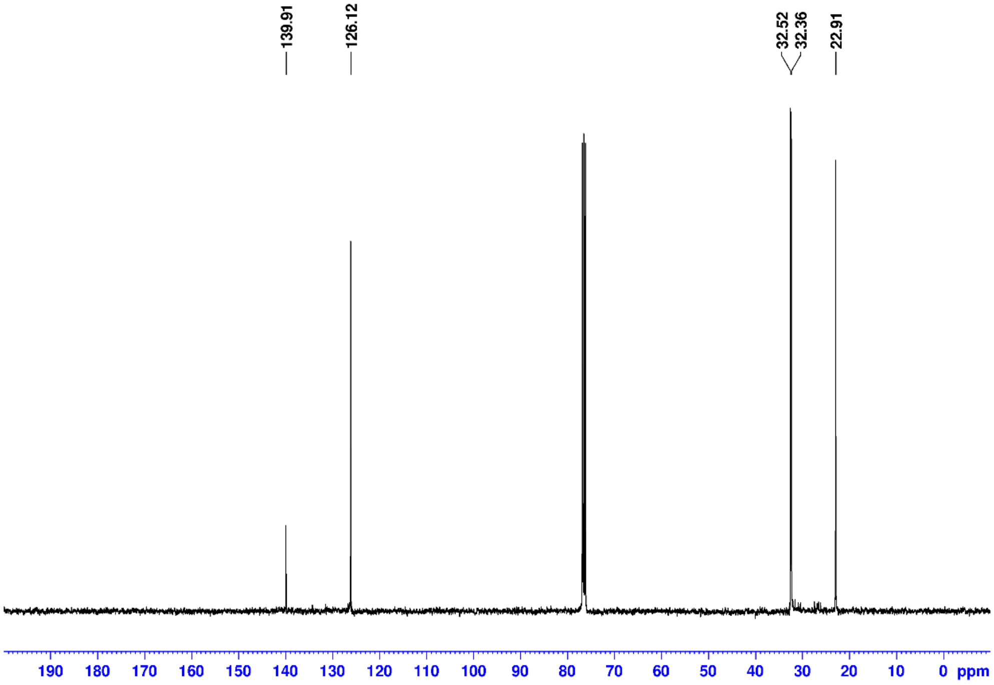
5.4 Reaction Products

[1,1’-Bi(cyclopentane)]-1,1’-diene

^{1}H NMR Spectrum

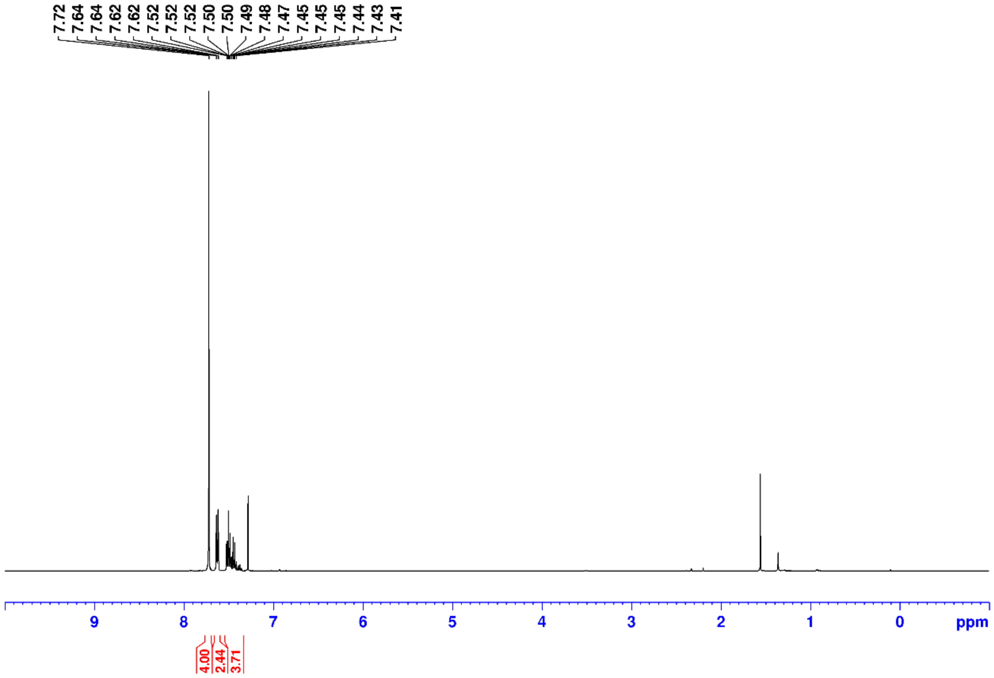


^{13}C{^{1}H} NMR Spectrum

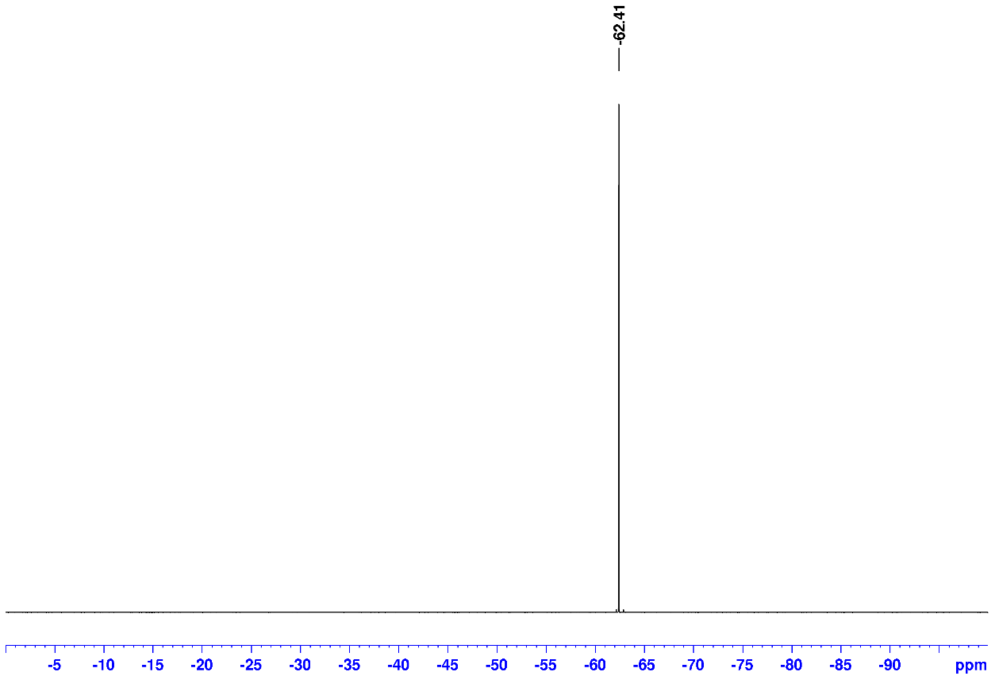


4-(Trifluoromethyl)biphenyl

^{1}H NMR Spectrum



^{19}F{^{1}H} NMR Spectrum



6 EPR Spectra

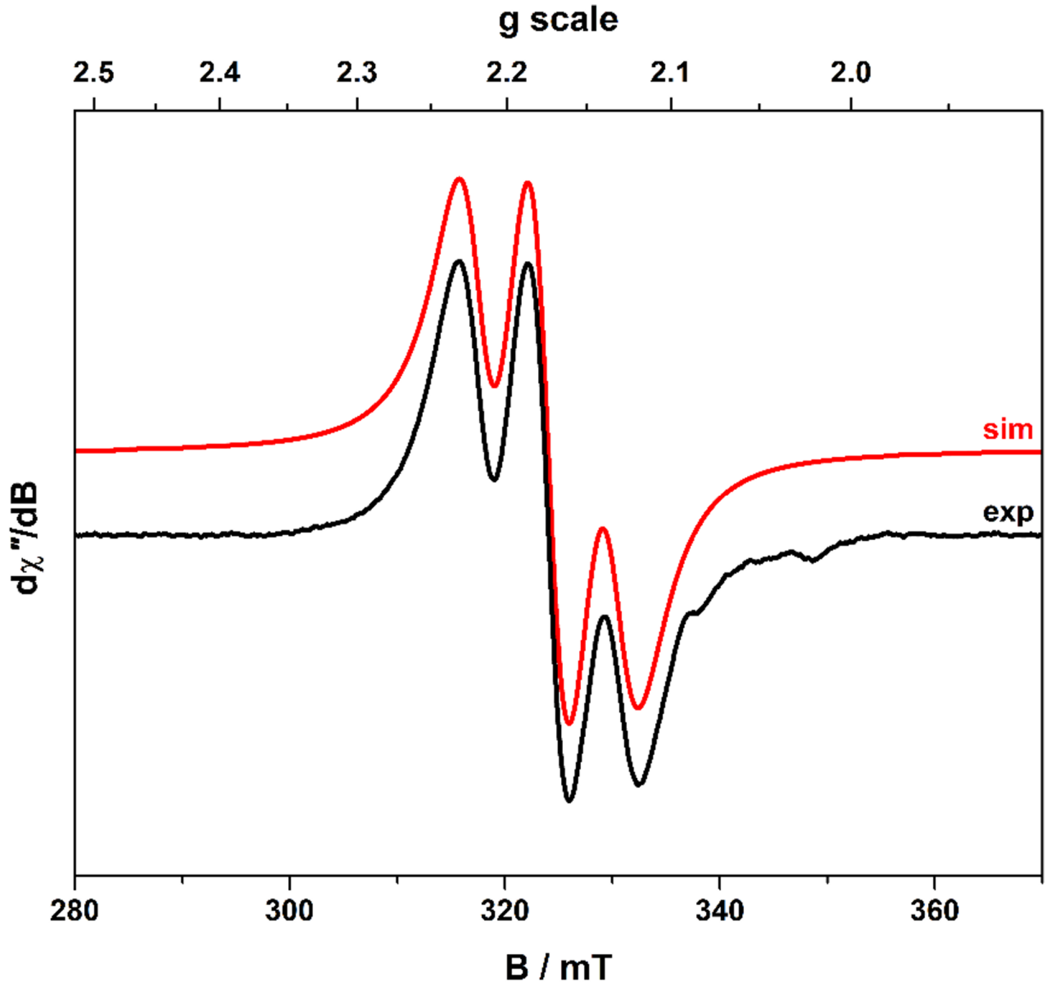


Figure S1. X-band EPR spectrum of [Ni(OTf)(dppf)] recorded in THF solution at 293 K (experimental conditions: frequency, 9.8593 GHz; power, 6.3 mW; modulation, 0.6 mT). Experimental spectrum is shown as the black line, simulation as the red trace: $g_{iso} = 2.1733$; $A_{iso} = 65 \times 10^{-4}$ cm^{-1}.

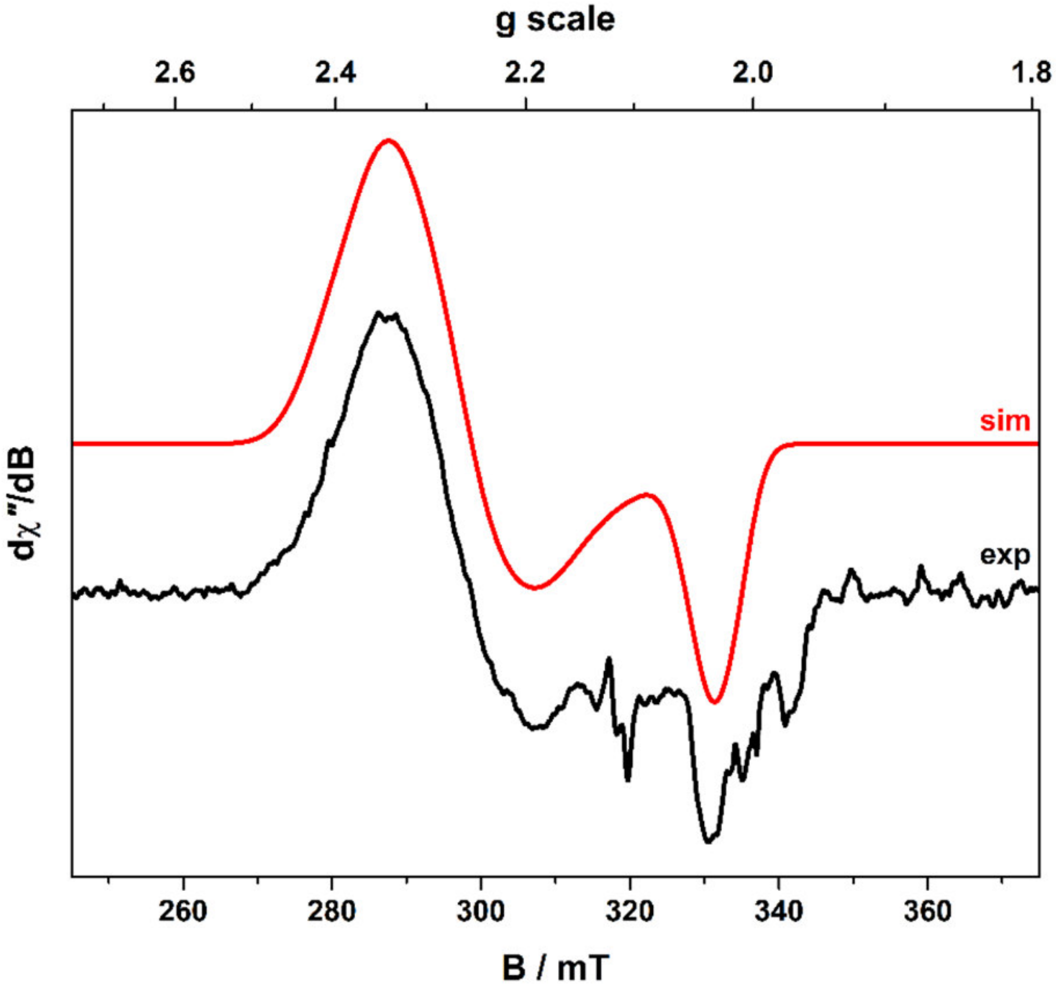


Figure S2. X-band EPR spectrum of [Ni(OTf)(dppf)] recorded in THF solution at 77 K (experimental conditions: frequency, 9.4215 GHz; power, 2.0 mW; modulation, 0.7 mT). Experimental spectrum is shown as the black line, simulation as the red trace: $g = 2.340, 2.265, 2.035$; $A = (80, 80, 30) \times 10^{-4}$ cm^{-1}.

7 Computational Studies

7.1 Methodology

(Note that the level of theory was selected as a result of a brief benchmarking study, which is described in sections 7.2.1 and 7.2.2, below.)

7.1.1 Conformational Searches

The lowest energy conformer for each structure was identified using CREST[13] to generate ensembles of conformers, which were then evaluated using single point calculations, with the lowest energy species used as input for geometry optimisations. In addition, relevant literature on the known conformations of these species – such as the cycloalkenes – was consulted.

7.1.2 DFT Calculations

Geometry optimisations were carried out using standard convergence criteria and the r^2SCAN-3c composite functional,[14] implemented in ORCA v6.[15] A frequency calculation was carried out in each case, with all reported stationary points having either zero imaginary frequencies (for minima) or a single imaginary frequency (for transition states).

For transition state structures, the relevant imaginary frequency was animated using Chemcraft to ensure that this corresponded to the process of interest. Following this, IRC calculations were carried out to identify which minima were linked by the transition state. In some cases these were the expected structures, and in others further intermediates were identified; these are discussed in the manuscript text where appropriate.

Free energies were refined using single point calculations at the ωB97M-V/ma-Def2-QZVP/SMD(benzene) level of theory;[16–18] ωB97M-V includes the VV10 non-local functional for the treatment of van der Waals interactions. Free energies quoted in the manuscript text are therefore the sum of the electronic energy at ωB97M-V/ma-Def2-QZVP/SMD(benzene) (E_{sp}) and the correction to free energy calculated at r^2SCAN-3c (G_{corr}).

7.2 Computational Results

7.2.1 Benchmarking: Geometry Optimisations

A brief benchmarking study was carried out to compare geometry optimisation at r^2SCAN-3c with geometry optimisation at ωB97M-V/ma-Def2-SVP. This showed minimal differences in geometry and energy. Table S19 notes the outcomes of this benchmarking.

Table S19: Outcomes of geometry benchmarking calculations.

	ωB97M-V/ma-Def2-SVP		**ωB97M-V/ma-Def2-QZVP/SMD(benzene)**	
Structure	**E (Ha)**	**G_{corr} (Ha)**	**E (Ha)**	**G_{rel} (kcal/mol)**
COD	-311.4981302	0.149094	-312.0139843	
[Ni(COD)(dppf)]	-5076.223256	0.640419	-5079.387008	0
PhOTf	-1192.046815	0.081285	-1193.286274	
[Ni(η^2-PhOTf)(dppf)]	-5956.750929	0.572627	-5960.642627	10.5
[Ni(OTf)(Ph)(dppf)]	-5956.795305	0.573726	-5960.694070	-21.1

7.2.2 Benchmarking: Single Point Calculations

A series of different functionals were evaluated for the single point calculations. The ma-Def2-QZVP basis set was deemed sufficient in each case. The free energy change for the displacement of COD from [Ni(COD)(dppf)] (**1**) by cyclopentene was used as a model reaction, noting that the experimental K_{eq} of 7.6×10^{-4} at 300 K corresponds to $\Delta G°$ (300 K) = 2.2 kcal mol^{-1} (Table S20).

While ωr^2SCAN-D4 achieves the closest match to experiment, we note that this a relatively new functional, relies on empirical dispersion corrections, and has not been widely used, while ωB97M-V is acknowledged as a high quality, robust functional that uses the VV10 nonlocal correlation method to treat dispersion effects. We therefore selected the latter for this study.

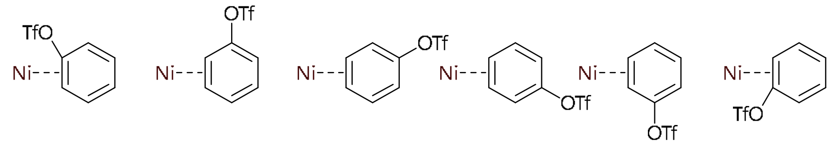
Table S20: Outcomes of single point benchmarking calculations.

Methodology	**ΔG° (kcal mol^{-1})**	**ΔΔG° *vs* exp't (kcal mol^{-1})**
Experiment	2.2	
r^2SCAN-3c/no solvent model	6.8	+4.6
r^2SCAN0-D4/ma-Def2-QZVP	0.6	-1.6
ωr^2SCAN-D4/ma-Def2-QZVP	2.3	+0.1
PBE0-D4/ma-Def2-QZVP	1.1	-1.1
ωB97X-D4(rev)/ma-Def2-QZVP	-2.4	-4.6
ωB97X-V/ma-Def2-QZVP	-0.1	-2.3
ωB97M-V/ma-Def2-QZVP	2.6	+0.4

7.2.3 Alternative Pathways

Note: in some cases, below, it will appear that structures should be related by symmetry (e.g. **e2-PhOTf** *vs* **e2-PhOTf(6)**). However, in these cases, there are differences in the conformations of the diphenylphosphino groups of the dppf ligand.

Phenyl triflate (2c). Alternative [Ni(η^2-PhOTf)(dppf)] isomers were considered, where nickel coordinates to different positions on the phenyl triflate substrate (**e2-PhOTf(2)** – **e2-PhOTf(6)**); however, all of these are higher in energy than the productive η^2-complex **e2-PhOTf**.



e2-PhOTf	**e2-PhOTf(2)**	**e2-PhOTf(3)**	**e2-PhOTf(4)**	**e2-PhOTf(5)**	**e2-PhOTf(6)**
11.3	15.1	12.5	13.6	12.2	12.1

Figure S3. Isomers of [Ni(η^2-PhOTf)(dppf)] and their Gibbs free energies.

2-Pyridinyl triflate (2b). A total of twelve isomers of [Ni(η^2-2PyOTf)(dppf)] were examined, of which four can lead to productive oxidative addition. The preferred pathway proceeds *via* the second-lowest energy η^2-complex. The other three productive isomers of [Ni(η^2-2PyOTf)(dppf)] present higher barriers. Figure S4 outlines all of the possible structures that were characterised computationally.

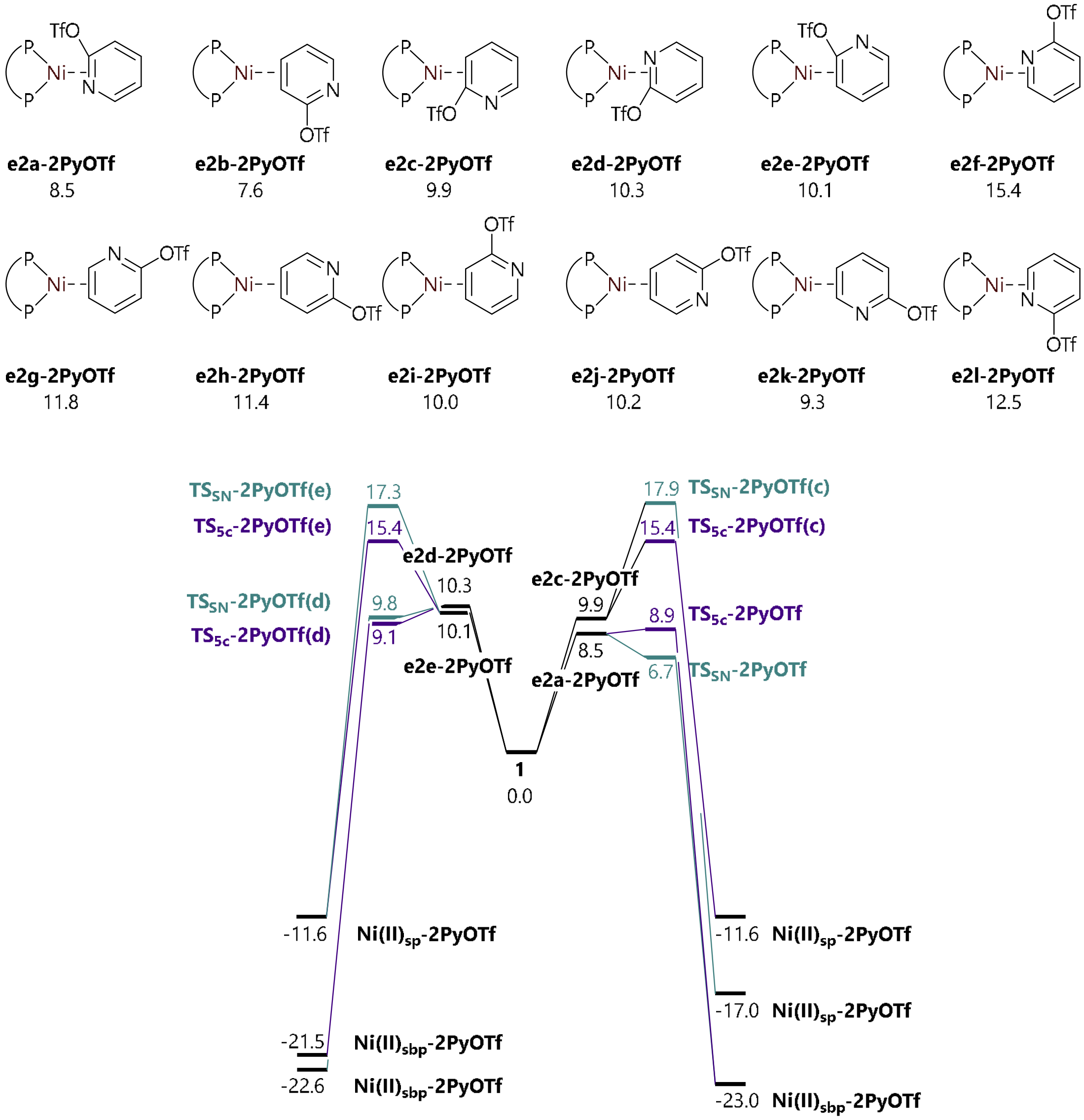


Figure S4. All pathways considered for the reaction of 2-pyridinyl triflate (**2b**) with [Ni(COD)(dppf)] (**1**). Energies are Gibbs free energies in kcal mol^{-1}.

3-Pyridinyl triflate (2d). Similarly to the 2-pyridinyl triflate substrate, atotal of twelve isomers of [Ni(η^2-3PyOTf)(dppf)] were examined, of which four can lead to productive oxidative addition. The preferred pathways proceeds *via* the lowest and second-lowest energy η^2-complexes. The other three productive isomers of [Ni(η^2-2PyOTf)(dppf)] present higher barriers. Figure S5 outlines all of the possible structures that were characterised computationally.

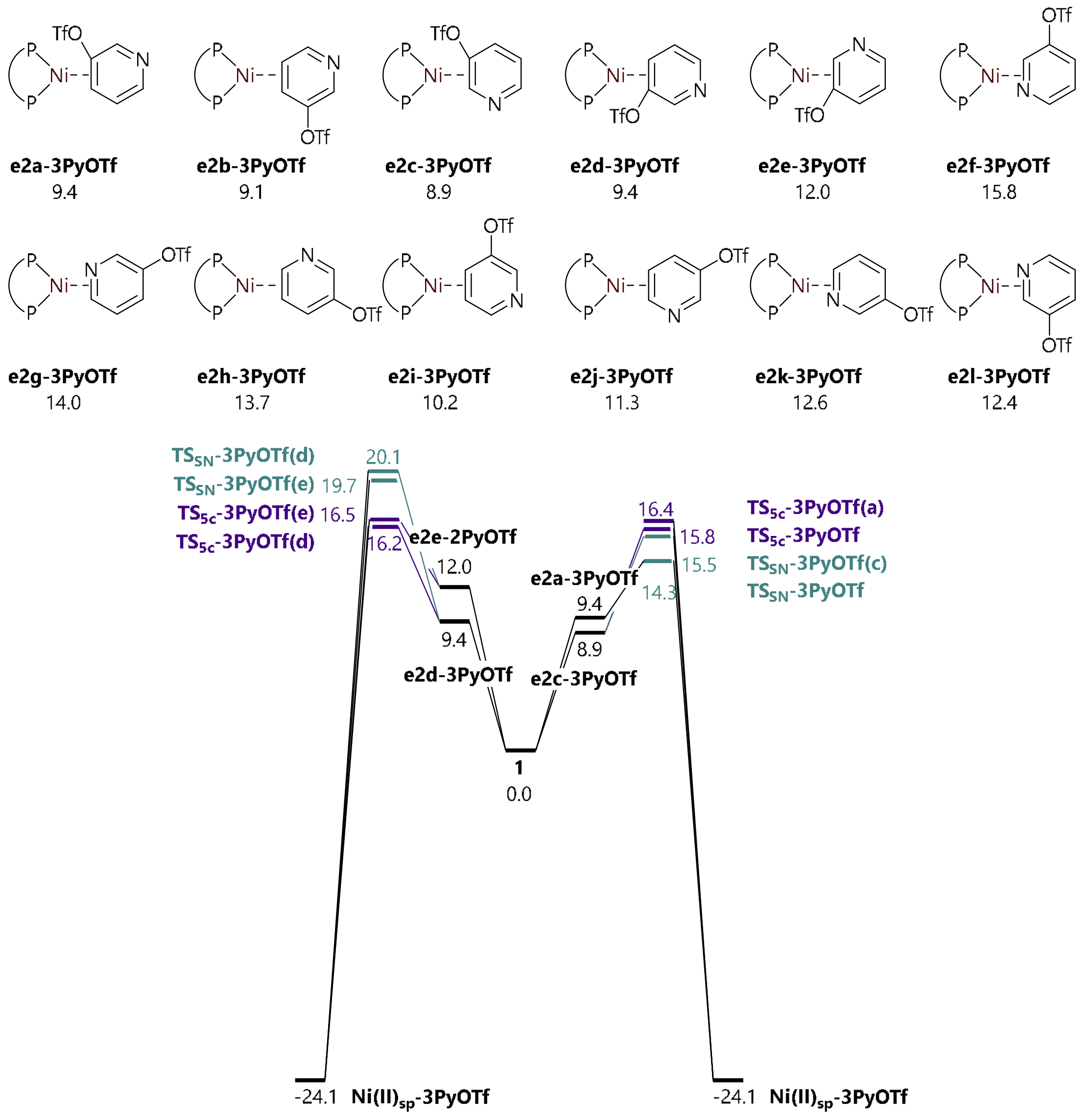


Figure S5. All pathways considered for the reaction of 3-pyridinyl triflate (**2d**) with [Ni(COD)(dppf)] (**1**). Energies are Gibbs free energies in kcal mol^{-1}.

Cyclohex-1-en-1-yl triflate (5b). The alternative pathway involving boat conformations presents higher barriers for both the S_N-type and five-centred oxidative addition pathways (Figure S6). Both pathways *via* boat intermediates and transition states lead initially to a distorted square-based pyramidal complex.

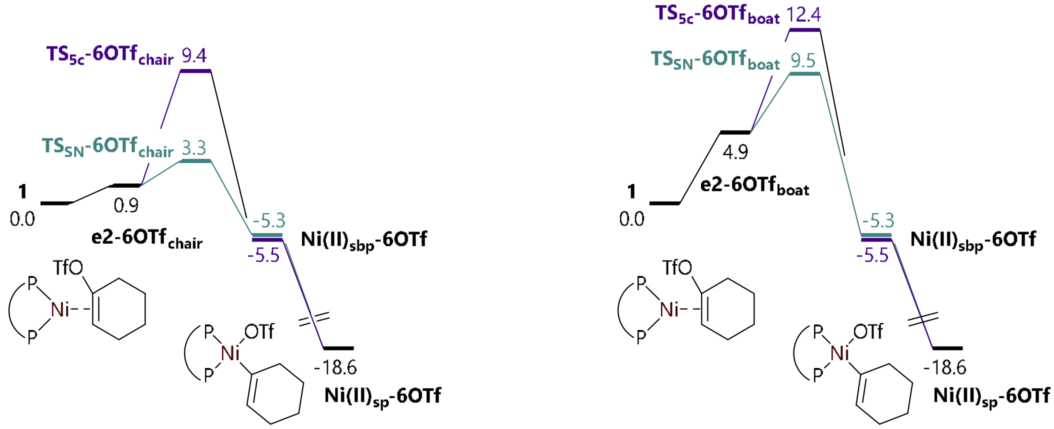


Figure S6. All considered pathways for the oxidative addition of cyclohex-1-en-1-yl triflate (**5b**) to [Ni(COD)(dppf)] (**1**). Energies are Gibbs free energies in kcal mol^{-1}.

Cyclohept-1-en-1-yl triflate (5c). The alternative pathway involving boat conformations presents higher barriers for both the S_N-type and five-centred oxidative addition pathways (Figure S7). These pathways *via* boat intermediates and transition states also lead initially to a distorted square-based pyramidal complex.

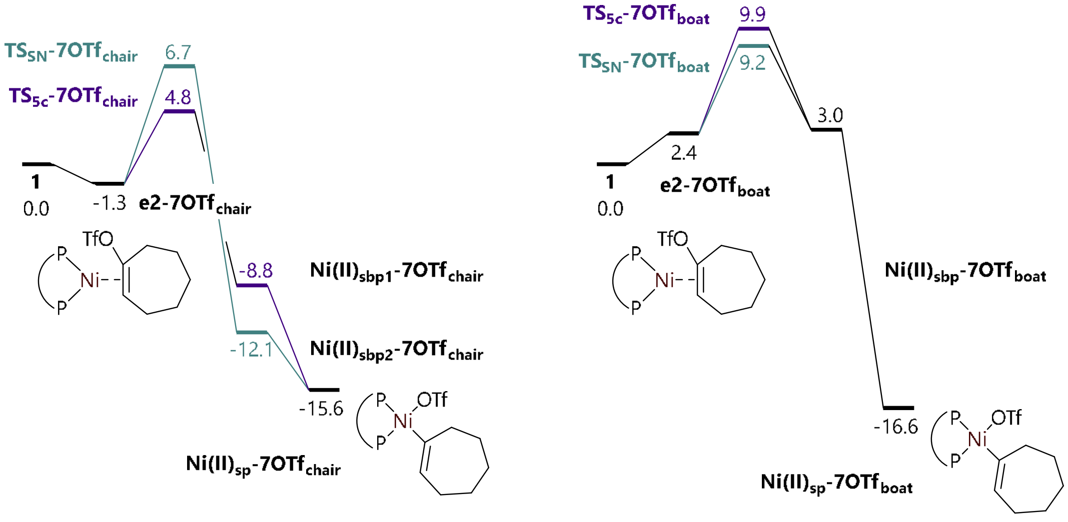


Figure S7. All considered pathways for the oxidative addition of cyclohept-1-en-1-yl triflate (**5c**) to [Ni(COD)(dppf)] (**1**). Energies are Gibbs free energies in kcal mol^{-1}.

Cyclooct-1-en-1-yl triflate (5d). These reactions can proceed through four different conformations, which we label A-D in the same way as Neuenschwander and Hermans[19] (Figure S8). While conformation D gives the lowest energy η^2-complex, the most productive pathway is *via* conformation A. The relative energies of each conformation of **5d** are recorded in Table S21 for comparison.

Table S21. Relative energies of the conformations of cyclooct-1-en-1-yl triflate (**5d**).

Conformation	A	B	C	D
G_{rel} (kcal mol^{-1})	0.0	0.7	4.8	2.2

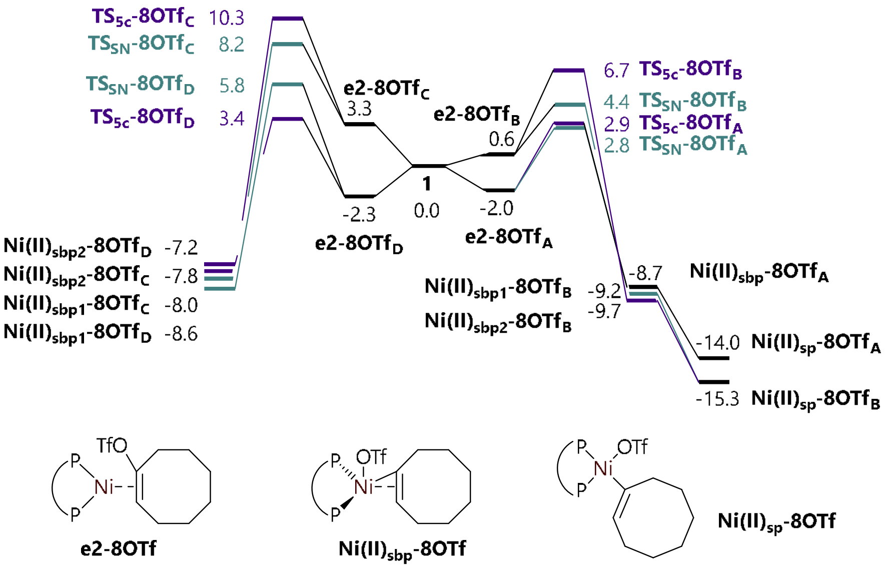


Figure S8. All considered pathways for the oxidative addition of cyclooct-1-en-1-yl triflate (**5d**) to [Ni(COD)(dppf)] (**1**). Energies are Gibbs free energies in kcal mol^{-1}.

7.2.4 Table of Energies

Table S22: Energies of all structures characterised as part of this work.

	r2SCAN-3c		ωB97M-V/ma-Def2-QZVP/SMD(benzene)	
Structure	**G (Ha)**	**G_{corr} (Ha)**	**E (Ha)**	**G_{rel} (kcal/mol)**
COD	-311.785955	0.148113	-312.014786	
[Ni(COD)(dppf)]	-5078.365247	0.632949	-5079.389560	
cpent-OTf (**5a**)	-1155.974778	0.096193	-1156.354682	
e2-5OTf	-5922.550877	0.578840	-5923.731976	-3.0
TS(SN)-5OTf	-5922.525750	0.576960	-5923.715287	6.3
Ni(II)(os)-5OTf	-5922.530693	0.575684	-5923.727842	-2.3
TS(5c)-5OTf	-5922.528079	0.577870	-5923.713851	7.8
Ni(II)(sp)-5OTf	-5922.561458	0.578757	-5923.759180	-20.1
[Ni(dppf)(cpent-OTf)$_2$]	-7078.477399	0.707898	-7080.056931	36.3
chex-OTf (**5b**)	-1195.258149	0.124314	-1195.674231	
e2-6OTf(chair)	-5961.828573	0.607336	-5963.045740	0.9
TS(SN)-6OTf(chair)	-5961.810392	0.602417	-5963.036936	3.3
Ni(II)(sbp)-6OTf(chair)	-5961.826201	0.604605	-5963.052959	-5.3
TS(5c)-6OTf(chair)	-5961.814117	0.605795	-5963.030686	9.4
Ni(II)(sbp)-6OTf(chair)	-5961.828434	0.604419	-5963.052995	-5.5
e2-6OTf(boat)	-5961.822794	0.605924	-5963.038044	4.9
TS(SN)-6OTf(boat)	-5961.801561	0.604420	-5963.029181	9.5
Ni(II)(sbp)-6OTf(boat)	-5961.828167	0.604682	-5963.052938	-5.3
TS(5c)-6OTf(boat)	-5961.808332	0.605284	-5963.025317	12.4
Ni(II)(sbp)-6OTf(boat)	-5961.828448	0.604408	-5963.053057	-5.5
Ni(II)(sp)-6OTf	-5961.845055	0.606953	-5963.076415	-18.6
chept-OTf (**5c**) (chair)	-1234.524906	0.151967	-1234.976534	
e2-7OTf(chair)	-6001.098833	0.634900	-6002.351431	-1.3
TS(SN)-7OTf(chair)	-6001.079572	0.630701	-6002.334452	6.7
Ni(II)(sbp)-7OTf(chair)	-6001.103019	0.632752	-6002.366473	-12.1
TS(5c)-7OTf(chair)	-6001.087436	0.633558	-6002.340338	4.8
Ni(II)(sbp)-7OTf(chair)	-6001.094800	0.634462	-6002.363019	-8.8
Ni(II)(sp)-7OTf(chair)	-6001.107825	0.633827	-6002.373252	-15.6
chept-OTf (**5c**) (boat)	-1234.519819	0.151896	-1234.971989	
e2-7OTf(boat)	-6001.092925	0.634675	-6002.345295	2.4
TS(SN)-7OTf(boat)	-6001.076387	0.631674	-6002.331565	9.2
Ni(II)(sbp)-7OTf(boat)	-6001.089538	0.632616	-6002.342294	3.0
TS(5c)-7OTf(boat)	-6001.081613	0.634142	-6002.332794	9.9
Ni(II)(sbp)-7OTf(boat)	-6001.091152	0.632442	-6002.342148	3.0
Ni(II)(sp)-7OTf(boat)	-6001.107681	0.634694	-6002.375598	-16.6
coct-OTf (**5d**) (A)	-1273.793867	0.179739	-1274.280584	
e2-8OTf(A)	-6040.368099	0.661935	-6041.655838	-2.0
TS(SN)-8OTf(A)	-6040.355116	0.660169	-6041.646539	2.8
Ni(II)(sbp)-8OTf(A)	-6040.367783	0.659918	-6041.664506	-8.7
TS(5c)-8OTf(A)	-6040.357682	0.661068	-6041.647264	2.9
Ni(II)(sbp)-8OTf(A)	-6040.367960	0.659682	-6041.664277	-8.7
Ni(II)(sp)-8OTf(A)	-6040.370700	0.663139	-6041.676173	-14.0

coct-OTf (**5d**) (B)	-1273.791738	0.180493	-1274.280260	
e2-8OTf(B)	-6040.364822	0.663039	-6041.652932	0.6
TS(SN)-8OTf(B)	-6040.353269	0.659282	-6041.642975	4.4
Ni(II)(sbp)-8OTf(B)	-6040.364674	0.662369	-6041.667779	-9.2
TS(5c)-8OTf(B)	-6040.352219	0.662016	-6041.642108	6.7
Ni(II)(sbp)-8OTf(B)	-6040.365185	0.661663	-6041.667872	-9.7
Ni(II)(sp)-8OTf(B)	-6040.373837	0.662669	-6041.677894	-15.3
coct-OTf (**5d**) (C)	-1273.784831	0.179502	-1274.272742	
e2-8OTf(C)	-6040.360585	0.662874	-6041.648329	3.3
TS(SN)-8OTf(C)	-6040.348705	0.660169	-6041.637940	8.2
Ni(II)(sbp)-8OTf(C)	-6040.362603	0.662453	-6041.665974	-8.0
TS(5c)-8OTf(C)	-6040.346548	0.662200	-6041.636622	10.3
Ni(II)(sbp)-8OTf(C)	-6040.362550	0.662284	-6041.665492	-7.8
Ni(II)(sp)-8OTf(C)	-6040.371046	0.662211	-6041.673259	-12.7
coct-OTf (**5d**) (D)	-1273.788835	0.179496	-1274.276773	
e2-8OTf(D)	-6040.367518	0.663000	-6041.657469	-2.3
TS(SN)-8OTf(D)	-6040.349214	0.659632	-6041.641181	5.8
Ni(II)(sbp)-8OTf(D)	-6040.364406	0.661556	-6041.666064	-8.6
TS(5c)-8OTf(D)	-6040.358989	0.660730	-6041.646172	3.4
Ni(II)(sbp)-8OTf(D)	-6040.368464	0.659854	-6041.662060	-7.2
Ni(II)(sp)-8OTf(D)	-6040.371902	0.662157	-6041.674536	-13.6
PhOTf (**2c**)	-1192.907800	0.078911	-1193.286274	
e2-PhOTf	-5959.464762	0.560359	-5960.639579	11.3
TS(SN)-PhOTf	-5959.445830	0.557900	-5960.632263	14.4
TS(5c)-PhOTf	-5959.452830	0.560181	-5960.632665	15.6
Ni(II)(sp)-PhOTf	-5959.494556	0.561715	-5960.693038	-21.3
e2-PhOTf(2)	-5959.459181	0.560736	-5960.633979	15.1
e2-PhOTf(3)	-5959.462064	0.560034	-5960.637405	12.5
e2-PhOTf(4)	-5959.460930	0.560335	-5960.636009	13.6
e2-PhOTf(5)	-5959.464031	0.560829	-5960.638716	12.2
e2-PhOTf(6)	-5959.462831	0.560028	-5960.637989	12.1
2-PyOTf (**2b**)	-1208.961880	0.067800	-1209.342590	
e2a-2PyOTf	-5975.523354	0.548712	-5976.699835	8.5
TS(SN)-2PyOTf	-5975.519311	0.548062	-5976.702137	6.7
Ni(II)(sbp)-2PyOTf	-5975.554572	0.548979	-5976.750328	-23.0
TS(5c)-2PyOTf	-5975.519117	0.549987	-5976.700480	8.9
e2f-2PyOTf	-5975.513985	0.550368	-5976.690524	15.4
e2g-2PyOTf	-5975.516938	0.549254	-5976.695211	11.8
e2h-2PyOTf	-5975.518134	0.548988	-5976.695507	11.4
e2b-2PyOTf	-5975.525380	0.549962	-5976.702644	7.6
e2c-2PyOTf	-5975.521177	0.548644	-5976.697559	9.9
TS(SN)-2PyOTf(c)	-5975.499394	0.547098	-5976.683271	17.9
Ni(II)(sp)-2PyOTf	-5975.546745	0.549926	-5976.741705	-17.0
TS(5c)-2PyOTf(c)	-5975.510329	0.547787	-5976.687965	15.4
Ni(II)(sp)-2PyOTf	-5975.541622	0.550031	-5976.733191	-11.6
e2d-2PyOTf	-5975.519320	0.550514	-5976.698833	10.3
TS(SN)-2PyOTf(d)	-5975.513875	0.548460	-5976.697562	9.8
Ni(II)(sp)-2PyOTf	-5975.553492	0.549317	-5976.750047	-22.6

TS(5c)-2PyOTf(d)	-5975.519019	0.550074	-5976.700253	9.1
Ni(II)(sp)-2PyOTf	-5975.552085	0.549806	-5976.748795	-21.5
e2e-2PyOTf	-5975.519768	0.547442	-5976.696064	10.1
TS(SN)-2PyOTf(e)	-5975.513875	0.548460	-5976.685609	17.3
TS(5c)-2PyOTf(e)	-5975.510295	0.547821	-5976.687955	15.4
Ni(II)(sp)-2PyOTf	-5975.541624	0.550027	-5976.733193	-11.6
e2i-2PyOTf	-5975.520962	0.551009	-5976.699746	10.0
e2j-2PyOTf	-5975.519789	0.549067	-5976.697607	10.2
e2k-2PyOTf	-5975.522316	0.550805	-5976.700766	9.3
e2l-2PyOTf	-5975.519384	0.549659	-5976.694520	12.5
[Ni(dppf)(κ-N-2-PyOTf)]	-5975.512475	0.549117	-5976.681764	20.1
[Ni(dppf)(κ-N-2-PyOTf)$_2$]	-7184.467297	0.645245		
3-PyOTf (**2d**)	-1208.954059	0.067579	-1209.333231	
e2c-3PyOTf	-5975.515764	0.549503	-5976.690956	8.9
TS(SN)-3PyOTf(c)	-5975.492612	0.547524	-5976.678490	15.5
TS(5c)-3PyOTf	-5975.500620	0.547495	-5976.677969	15.8
e2f-3PyOTf	-5975.506552	0.549988	-5976.680374	15.8
e2g-3PyOTf	-5975.509569	0.548474	-5976.681682	14.0
e2h-3PyOTf	-5975.507697	0.548276	-5976.681981	13.7
e2b-3PyOTf	-5975.513478	0.549408	-5976.690469	9.1
e2d-3PyOTf	-5975.514549	0.548479	-5976.689129	9.4
TS(SN)-3PyOTf(d)	-5975.490725	0.547654	-5976.671167	20.1
TS(5c)-3PyOTf(d)	-5975.499872	0.548431	-5976.678253	16.2
e2e-3PyOTf	-5975.511737	0.549310	-5976.685830	12.0
TS(SN)-3PyOTf(e)	-5975.492208	0.547483	-5976.671697	19.7
TS(5c)-3PyOTf(e)	-5975.499578	0.548432	-5976.677790	16.5
e2a-3PyOTf	-5975.513683	0.548948	-5976.689519	9.4
TS(SN)-3PyOTf	-5975.491593	0.546035	-5976.678799	14.3
TS(5c)-3PyOTf(a)	-5975.499947	0.548453	-5976.677901	16.4
e2i-3PyOTf	-5975.511949	0.549528	-5976.688794	10.2
e2j-3PyOTf	-5975.511726	0.549556	-5976.687192	11.3
e2k-3PyOTf	-5975.512008	0.548607	-5976.684117	12.6
e2l-3PyOTf	-5975.511390	0.549309	-5976.685160	12.4
Ni(II)-3PyOTf	-5975.545077	0.55015308	-5976.744105	-24.1
[Ni(dppf)(κ-N-3-PyOTf)$_2$]	-7184.465816	0.64311232	-7186.028678	22.4
Cyclopentene	-195.174789	0.088916	-195.313046	
[Ni(e2-cyclopentene)(dppf)]	-4961.743184	0.569455	-4962.679436	2.6
Cyclohexene	-234.455186	0.116954	-234.628763	
[Ni(e2-cyclohexene)(dppf)] boat	-5001.012257	0.59668438	-5001.983944	9.1
[Ni(e2-cyclohexene)(dppf)] chair	-5001.017877	0.59752506	-5001.989659	6.0
Cycloheptene (boat)	-273.717168	0.144235	-273.926474	
Cycloheptene (chair)	-273.721962	0.143979	-273.930825	
[Ni(e2-cycloheptene)(dppf)] boat	-5040.282205	0.625424	-5041.290186	7.5
[Ni(e2-cycloheptene)(dppf)] chair	-5040.289371	0.625085	-5041.296892	3.1
Cyclooctene (A1)	-312.9917146	0.17189991	-313.236148	
Cyclooctene (B1)	-312.9883894	0.17193093	-313.233018	
Cyclooctene (C1)	-312.9822868	0.17137233	-313.226504	
Cyclooctene (D2)	-312.9861446	0.17157079	-313.230664	

[Ni(e2-cyclooctene)(dppf)] (A1)	-5079.561008	0.65294043	-5080.604106	1.9
[Ni(e2-cyclooctene)(dppf)] (B1)	-5079.554153	0.65299099	-5080.597372	6.2
[Ni(e2-cyclooctene)(dppf)] (C1)	-5079.547157	0.65344441	-5080.590848	10.5
[Ni(e2-cyclooctene)(dppf)] (D2)	-5079.548134	0.65256633	-5080.591145	9.8

7.2.5 Cartesian Coordinates

Cartesian coordinates are supplied as a separate XYZ file as part of the Supporting Information associated with this publication. These can be obtained from the publisher's website.
In addition, the computational data associated with this publication, including cartesian coordinates, can be obtained from the BD[20] repository hosted by the Barcelona Supercomputing Centre at the DOI noted within the manuscript.

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