Supporting Information

Table S1. Effects of variations in additive and solvent for **1**-catalysed hydroamination of phenylacetylene with aniline.

Table S2. Details for hydroamination reaction: Amounts of reagents used, and product formed; nominal and hi-resolution MS data for products.

Table S3. ^{1}H and $^{13}C\{^{1}H\}$ NMR data for **4**.

Table S4. Details for hydroamination reaction followed by reduction: Amounts of reagents used, and product formed; nominal and hi-resolution MS data for products.

Table S5. ^{1}H and $^{13}C\{^{1}H\}$ NMR data for **5**.

Experimental details for single crystal X-ray crystallographic study of **6**.

Table S6. Crystal data and structure refinement for **6**.

Figure S1. ORTEP plot (50% probability thermal ellipsoids) for **6**.

Figure S2. Computationally optimised geometry for intermediates **A-D**.

Figure S3. ^{1}H NMR and MS spectra of the reaction crude between 4-methoxyaniline and phenylacetylene-d.

Figure S4. ^{1}H NMR and MS spectra of the reaction crude between aniline-d_7 and 4-methoxypheneylacetylene.

Table S1.

S/No	Solvent	**1** (mol%)	Additive (mol%)	T (^{o}C)	Yield (%)
1	Toluene	1.0	NH_4PF_6 (2.0)	80	69
2	Toluene	1.0	NH_4PF_6 (3.0)	80	89
3	Toluene	1.0	NH_4PF_6 (5.0)	80	85
4	Toluene	1.0	$AgPF_6$ (3.0)	80	60
5	Toluene	1.0	$LiPF_6$ (3.0)	80	63
6	Toluene	1.0	$NaPF_6$ (3.0)	80	61
7	Toluene	1.0	Bu_4NPF_6(3.0)	80	-
8	Toluene	1.0	AgOTf (3.0)	80	81
9	Toluene	1.0	$AgSbF_6$ (3.0)	80	83
10	DCE	1.0	NH_4PF_6 (3.0)	80	84
11	THF	1.0	NH_4PF_6 (3.0)	80	-
12	IPA	1.0	NH_4PF_6 (3.0)	80	-
13	CH_3OH	1.0	NH_4PF_6 (3.0)	80	-
14	Toluene	1.5	NH_4PF_6 (4.5)	80	90
15	Toluene	1.0	NH_4PF_6 (3.0)	30	-
16	Toluene	1.0	NH_4PF_6 (3.0)	110	83
17	Toluene	0.5	NH_4PF_6 (1.5)	80	87
18	Toluene	0.2	NH_4PF_6 (0.6)	80	53
19	Toluene	-	NH_4PF_6 (3.0)	80	-

Table S2.

Aniline	**Alkyne**	**Product (mg, %)**	**GC/MS (m/z)**	**HRMS**
$C_6H_5NH_2$ (228 µL, 2.5 mmol)	C_6H_5CCH (302 µL, 2.75 mmol)	$C_{14}H_{14}N$, **4a** (434, 89)	195 $[M]^+$, 180 $[M\text{-}CH_3]^+$	Found: 196.1128 Calc $[M+H]^+$: 196.1126
$C_6H_5NH_2$ (228 µL, 2.5 mmol)	*4*-CH_3-C_6H_4CCH (348 µL, 2.75 mmol)	$C_{15}H_{16}N$, **4b** (470, 90)	209 $[M]^+$, 194 $[M\text{-}CH_3]^+$	Found: 210.1281 Calc $[M+H]^+$: 210.1283
$C_6H_5NH_2$ (228 µL, 2.5 mmol)	*4*-CH_3O-C_6H_4CCH (356 µL, 2.75 mmol)	$C_{15}H_{16}NO$, **4c** (517, 92)	225 $[M]^+$, 210 $[M\text{-}CH_3]^+$	Found: 226.1233 Calc $[M+H]^+$: 226.1232
$C_6H_5NH_2$ (228 µL, 2.5 mmol)	*4*-Cl-C_6H_4CCH (375 mg, 2.75 mmol)	$C_{14}H_{13}NCl$, **4d** (481, 84)	229 $[M]^+$, 214 $[M\text{-}CH_3]^+$	Found: 230.0736 Calc $[M+H]^+$: 230.0737
4-$CH_3C_6H_4NH_2$ (268 mg, 2.5 mmol)	C_6H_5CCH (302 µL, 2.75 mmol)	$C_{15}H_{16}N$, **4e** (475, 91)	209 $[M]^+$, 194 $[M\text{-}CH_3]^+$	Found: 210.1282 Calc $[M+H]^+$: 210.1283
4-$CH_3OC_6H_4NH_2$ (308 mg, 2.5 mmol)	C_6H_5CCH (302 µL, 2.75 mmol)	$C_{15}H_{16}NO$, **4f** (523 , 93)	225 $[M]^+$, 210 $[M\text{-}CH_3]^+$	Found: 226.1233 Calc $[M+H]^+$: 226.1232
4-$CH_3OC_6H_4NH_2$ (308 mg, 2.5 mmol)	*3*-CH_3-C_6H_4CCH (355 µL, 2.75 mmol)	$C_{16}H_{18}NO$, **4g** (532, 89)	239 $[M]^+$, 224 $[M\text{-}CH_3]^+$	Found: 240.1387 Calc $[M+H]^+$: 240.1388
4-$CH_3OC_6H_4NH_2$ (308 mg, 2.5 mmol)	*4*-CH_3-C_6H_4CCH (348 µL, 2.75 mmol)	$C_{16}H_{18}NO$, **4h** (544, 91)	239 $[M]^+$, 224 $[M\text{-}CH_3]^+$	Found: 240.1387 Calc $[M+H]^+$: 240.1388
4-$CH_3OC_6H_4NH_2$ (308 mg, 2.5 mmol)	*4*-Cl-C_6H_4CCH (375 mg, 2.75mmol)	$C_{15}H_{15}NOCl$, **4i** (595, 92)	259 $[M]^+$, 244 $[M\text{-}CH_3]^+$	Found: 260.0841 Calc $[M+H]^+$: 260.0842
4-$CH_3OC_6H_4NH_2$ (308 mg, 2.5 mmol)	*4*-CH_3O-C_6H_4CCH (348 µL, 2.75 mmol)	$C_{16}H_{18}NO_2$, **4j** (593, 93)	255 $[M]^+$, 240 $[M\text{-}CH_3]^+$	Found: 256.1336 Calc $[M+H]^+$: 256.1338

Table S3.

	^{1}H NMR data	**^{13}C{^{1}H} NMR data**
4a[1,2,6,7]	2.22 (s, 3H, CH_3), 6.79 (d, J=, 8.46, 2H, aromatic), 7.07 (t, J=7.56, 1H, aromatic), 7.32-7.36 (t, J=8.00, 2H, aromatic), 7.43-7.46 (m, 3H, aromatic), 7.97 (dd, J=2.3, 7.78, 2H, aromatic).	17.59 (CH_3), 119.56, 123.40, 127.35, 128.56 and 129.14 (aromatic, CH), 130.66, 139.65 and 151.87 (aromatic, C), 165.70 (C=N).
4b[1,2,3]	2.20 (s, 3H, CH_3), 2.40 (s, 3H, $ArCH_3$), 6.78 (d, J=7.32, 2H, aromatic), 7.07 (t, J=7.56, 1H, aromatic), 7.24 (d, J=7.32, 3H, aromatic), 7.33 (t, J=7.78, 2H, aromatic), 7.86 (d, J=8.24, 2H, aromatic).	17.53 (CH_3), 21.59 (Ar-CH_3), 119.68, 123.29, 127.36, 129.13 and 129.27 (aromatic, CH), 136.93, 140.92 and 152.05 (aromatic, C), 165.48 (C=N).
4c[1,5,7]	2.20 (s, 3H, CH_3), 3.86 (s, 3H, OCH_3), 6.78 (d, J=8.46, 2H, aromatic), 6.95 (d, J=9.16, 2H, aromatic), 7.07 (t, J=7.32, 1H, aromatic), 7.34 (m, t, J=7.32, 2H, aromatic), 7.94 (d, J=8.68, 2H, aromatic).	17.35 (CH_3), 55.56 (OCH_3), 113.76, 119.77, 123.18, 129.00 and 129.08 (aromatic, CH), 132.36, 152.06 and 161.69 (aromatic, C), 164.71 (C=N).
4d[1,3]	2.20 (s, 3H, CH_3), 6.77 (d, J=7.32, 2H, aromatic), 7.08 (t, J=8.02, 1H, aromatic), 7.34 (t, J=7.54, 2H, aromatic), 7.40 (d, J=8.68, 2H, aromatic), 7.91 (d, J=8.68, 2H, aromatic).	17.48 (CH_3), 119.52, 123.63, 128.76 and 129.21 (aromatic, CH), 136.76, 138.08and 151.46 (aromatic, C), 164.54(C=N).
4e[1,6]	2.22 (s, 3H, CH_3), 2.33 (s, 3H, $ArCH_3$), 6.69 (d, J=8.24, 2H, aromatic), 7.14 (d, J= 8.24, 2H, aromatic), 7.42-7.44 (m, 3H, aromatic), 7.95 (dd, J=2.30, 7.78, 2H, aromatic).	17.51 (CH_3), 21.06 ($ArCH_3$), 119.58, 127.32, 128.53, 129.69 and 130.55 (aromatic, CH), 132.79, 139.82 and 149.21 (aromatic, C), 165.73 (C=N).
4f[1,2,7]	2.23 (s, 3H, CH_3), 3.80 (s, 3H, OCH_3), 6.74 (d, J=7.80, 2H, aromatic), 6.89 (d, J=8.02, 2H, aromatic), 7.42-7.43 (m, 3H, aromatic), 7.94 (d, J=5.26, 2H, aromatic).	17.54 (CH_3), 55.68 (OCH_3), 114.42, 120.96, 127.30, 128.54 and 130.53 (aromatic, CH), 139.94, 144.99 and 156.12 (aromatic, C), 165.97 (C=N).
4g	2.22 (s, 3H, CH_3), 2.39 (s, 3H, $ArCH_3$), 3.80 (s, 3H, OCH_3), 6.73 (d, J=9.16, 2H, aromatic), 6.88 (d, J=8.24, 2H, aromatic),7.25 (d, J= 8.68, 1H, aromatic), 7.31 (t, J=7.54, 1H, aromatic), 7.69 (d, J=7.80, 1H, aromatic), 7.79 (s, 1H, aromatic).	17.63 (CH_3), 21.67 ($ArCH_3$), 55.68 (OCH_3), 114.42, 120.94, 124.53, 127.84, 128.43 and 131.31 (aromatic, CH), 138.26, 139.86, 144.97 and 156.09 (aromatic, C), 166.31 (C=N).
4h[2]	2.22 (s, 3H, CH_3), 2.39 (s, 3H, $ArCH_3$), 3.80 (s, 3H, OCH_3), 6.74 (d, J=6.66, 2H, aromatic), 6.89 (d, J=6.66, 2H, aromatic), 7.23 (d, J=9.38, 2H, aromatic), 7.85 (d, J=8.24, 2H, aromatic).	17.44 (CH_3), 21.57 (CH_3), 55.67 (OCH_3), 114.39, 120.99, 127.27 and 129.22 (aromatic, CH), 137.22, 140.73, 145.10 and 156.01 (aromatic, C), 165.81 (C=N).
4i[5]	2.21 (s, 3H, CH_3), 3.80 (s, 3H, OCH_3), 6.72 (d, J=8.72, 2H, aromatic), 6.89 (d, J=9.16, 2H, aromatic), 7.38 (d, J=8.68, 2H, aromatic), 7.88 (d, J=8.72, 3H, aromatic).	17.42 (CH_3), 55.67 (OCH_3), 114.45, 120.99 and 128.68 (aromatic, CH), 136.42, 138.26, 144.49 and 156.29 (aromatic, C), 164.80 (C=N).
4j[7]	2.20 (s, 3H, CH_3), 3.80 (s, 3H, OCH3), 3.84 (s, 3H, OCH3), 6.72 (d, J=8.24, 2H, aromatic), 6.88 (d, J=7.76, 2H, aromatic), 6.93 (d, J=8.26, 2H, aromatic), 7.91 (d, J=8.24, 2H, aromatic).	17.34 (CH_3), 55.59 and 55.67 (OCH_3), 113.78, 114.40, 121.14 and 128.97 (aromatic, CH), 132.50, 144.94, 156.03 and 161.63 (aromatic, C), 165.24 (C=N).

Table S4.

Aniline	**Alkyne**	**Product (mg, %)**	**GC/MS (m/z)**	**HRMS**
$C_6H_5NH_2$ (228 µL, 2.5 mmol)	*2*-CH_3-C_6H_4CCH (346 µL, 2.75 mmol)	$C_{15}H_{17}N$, **5a** (347, 66)	211 $[M]^+$, 196 $[M\text{-}CH_3]^+$	Found: 212.1440 Calc $[M+H]^+$: 212.1439
$C_6H_5NH_2$ (228 µL, 2.5 mmol)	*2*-CH_3O-C_6H_4CCH (355 µL, 2.75 mmol)	$C_{15}H_{18}NO$, **5b** (436, 77)	227 $[M]^+$, 212 $[M\text{-}CH_3]^+$	Found: 228.1389 Calc $[M+H]^+$: 228.1388
$C_6H_5NH_2$ (228 µL, 2.5 mmol)	*3*-CH_3-C_6H_4CCH (355 µL, 2.75 mmol)	$C_{15}H_{18}N$, **5c** (406, 77)	211 $[M]^+$, 196 $[M\text{-}CH_3]^+$	Found: 212.1441 Calc $[M+H]^+$: 212.1439
$C_6H_5NH_2$ (228 µL, 2.5 mmol)	*3*-CH_3O-C_6H_4CCH (350 µL, 2.75 mmol)	$C_{15}H_{18}NO$, **5d** (346, 61)	227 $[M]^+$, 212 $[M\text{-}CH_3]^+$	Found: 228.1395 Calc $[M+H]^+$: 228.1388
$C_6H_5NH_2$ (228 µL, 2.5 mmol)	*3*-Cl-C_6H_4CCH (338 µL, 2.75 mmol)	$C_{14}H_{14}ClN$, **5e** (375, 65)	231 $[M]^+$, 216 $[M\text{-}CH_3]^+$	Found: 232.0892 Calc $[M+H]^+$: 232.0893
$C_6H_5NH_2$ (228 µL, 2.5 mmol)	*3*-F-C_6H_4CCH (318 µL, 2.75 mmol)	$C_{14}H_{14}FN$, **5f** (381, 71)	215 $[M]^+$, 200 $[M\text{-}CH_3]^+$	Found: 216.1186 Calc $[M+H]^+$: 216.1189
$C_6H_5NH_2$ (228 µL, 2.5 mmol)	*4*-Br-C_6H_4CCH (498 mg, 2.75 mmol)	$C_{14}H_{15}BrN$, **5g** (556, 81)	275 $[M]^+$, 260 $[M\text{-}CH_3]^+$	Found: 276.0384 Calc $[M+H]^+$: 276.0388
$C_6H_5NH_2$ (228 µL, 2.5 mmol)	*4*-F-C_6H_4CCH (315 µL, 2.75 mmol)	$C_{14}H_{14}FN$, **5h** (408, 76)	215 $[M]^+$, 200 $[M\text{-}CH_3]^+$	Found: 216.1191 Calc $[M+H]^+$: 216.1189
$C_6H_5NH_2$ (228 µL, 2.5 mmol)	*4*-$HOCH_2$-C_6H_4CCH (363 mg, 2.75 mmol)	$C_{15}H_{18}NO$, **5i** (312, 55)	227 $[M]^+$, 212 $[M\text{-}CH_3]^+$	Found: 228.1385 Calc $[M+H]^+$: 228.1388
$C_6H_5NH_2$ (228 µL, 2.5 mmol)	*4*-^{t}Bu-C_6H_4CCH (490 µL, 2.75 mmol)	$C_{18}H_{23}N$, **5j** (500, 79)	253 (M^+), 238 $[M\text{-}CH_3]^+$	Found: 254.1906 Calc $[M+H]^+$: 254.1909
$C_6H_5NH_2$ (228 µL, 2.5 mmol)	*2*-CH_3-*4*-OCH_3-C_6H_3CCH (402 mg, 2.75 mmol)	$C_{16}H_{19}NO$, **5k** (470, 78)	241 $[M]^+$, 226 $[M\text{-}CH_3]^+$	Found: 242.1540 Calc $[M+H]^+$: 242.1545
$C_6H_5NH_2$ (228 µL, 2.5 mmol)	$C_{10}H_7CCH$ (391 µL, 2.75 mmol)	$C_{18}H_{17}N$, **5l** (451, 73)	247 (M^+), 232 $[M\text{-}CH_3]^+$	Found: 248.1430 Calc $[M+H]^+$: 248.1439
$C_6H_5NH_2$ (228 µL, 2.5 mmol)	*6*-OCH_3-$C_{10}H_6CCH$ (501 mg, 2.75 mmol)	$C_{19}H_{19}NO$, **5m** (561, 81)	277 $[M]^+$, 262 $[M\text{-}CH_3]^+$	Found: 278.1544 Calc $[M+H]^+$: 278.1545
4-$CH_3OC_6H_4NH_2$ (308 mg, 2.5 mmol)	*2*-CH_3O-C_6H_4CCH (355 µL, 2.75 mmol)	$C_{16}H_{20}NO_2$, **5n** (488, 76)	257 $[M]^+$, 242 $[M\text{-}CH_3]^+$	Found: 258.1494 Calc $[M+H]^+$: 258.1494
4-$CH_3OC_6H_4NH_2$ (308 mg, 2.5 mmol)	*3*-CH_3O-C_6H_4CCH (350 µL, 2.75 mmol)	$C_{16}H_{20}NO_2$, **5o** (475, 74)	257 $[M]^+$, 242 $[M\text{-}CH_3]^+$	Found: 258.1494 Calc $[M+H]^+$: 258.1494
3-$CH_3OC_6H_4NH_2$	C_6H_5CCH	$C_{15}H_{18}NO$, **5p** (454, 80)	227 $[M]^+$, 212 $[M\text{-}CH_3]^+$	Found: 228.1396

(281 µL, 2.5 mmol)	(302 uL, 2.75 mmol)			Calc $[M+H]^+$: 228.1388
3,5-$CH_3OC_6H_4NH_2$ (382 mg, 2.5 mmol)	C_6H_5CCH (302 uL, 2.75 mmol	$C_{16}H19NO_2$, **5q** (430, 67)	257 $[M]^+$, 242 $[M\text{-}CH_3]^+$	Found: 258.1495 Calc $[M+H]^+$: 258.1494
4-$CH_3OC_6H_4NH_2$ (308 mg, 2.5 mmol)	C_6H_5CCH (302 uL, 2.75 mmol)	$C_{15}H_{18}NO$, **5r** (471, 83)	227 $[M]^+$, 212 $[M\text{-}CH_3]^+$	Found: 228.1387 Calc $[M+H]^+$: 228.1388
4-$BrC_6H_4NH_2$ (430 mg, 2.5 mmol)	C_6H_5CCH (302 uL, 2.75 mmol)	$C_{14}H_{15}NBr$, **5s** (536, 78)	275 $[M]^+$, 260 $[M\text{-}CH_3]^+$	Found: 276.0393 Calc $[M+H]^+$: 276.0388
4-$ClC_6H_4NH_2$ (319 mg, 2.5 mmol)	C_6H_5CCH (302 uL, 2.75 mmol)	$C_{14}H_{15}ClN$, **5t** (475 , 82)	231 $[M]^+$, 216 $[M\text{-}CH_3]^+$	Found: 232.0895 Calc $[M+H]^+$: 232.0893

Table S5.

	^{1}H NMR data	^{13}C{^{1}H} NMR data
5a[5]	1.48 (d, J=6.88, 3H, CH_3), 2.45 (s, 3H, $ArCH_3$), 4.01 (bs, 1H, NH), 4.68 (q, J=6.88, 1H, CH), 6.45 (d, J=7.80, 2H, aromatic), 6.64 (t, J=7.32, 1H, aromatic), 7.09 (t, J=7.36, 2H, aromatic), 7.14-7.19 (m, 3H, aromatic), 7.43 (d, J=7.34, 1H, aromatic).	19.17 ($ArCH_3$), 23.17 (CH_3), 49.96 (CH), 113.19, 117.33, 124.83, 126.77, 126.87, 129.33 and 130.79 (aromatic, CH), 134.76, 142.94 and 147.44 (aromatic, C).
5b	1.52 (d, J=6.88, 3H, CH_3), 3.92 (s, 3H, OCH_3), 4.17 (bs, 1H, NH), 4.89 (q, J=6.88, 1H, CH), 6.55 (d, J=8.68, 2H, aromatic), 6.64-6.69 (m, 1H, aromatic), 6.91-6.93 (m, 2H, aromatic), 7.12 (t, J=8.70, 2H, aromatic), 7.23 (t, J=4.34, 1H, aromatic), 7.35 (d, J=8.72, 1H, aromatic).	23.00 (CH_3), 48.24 (CH), 55.47 (OCH_3), 110.62, 113.41, 117.15, 120.96, 126.49, 127.84 and 129.22 (aromatic, CH), 132.86, 147.51 and 156.85 (aromatic, C).
5c	1.53 (d, J=7.32, 3H, CH_3), 2.36 (s, 3H, CH_3), 4.03 (bs, 1H, NH), 4.47 (q, J=6.88, 1H, CH), 6.55 (d, J=8.72, 2H, aromatic), 6.67 (t, J=7.56, 1H, aromatic), 7.06-7.25 (m, 6H, aromatic).	21.73 ($ArCH_3$), 25.22 (CH_3), 53.65 (CH), 113.43, 117.33, 123.04, 126.72, 127.85, 128.70 and 129.28 (aromatic, CH), 138.38, 145.43 and 147.56 (aromatic, C)
5d	1.52 (d, J=2.72, 3H, CH_3), 3.80 (s, 3H, OCH_3), 4.04 (bs, 1H, NH), 4.48 (q, J=6.88, 1H, CH), 6.54 (d, J=8.24, 2H, aromatic), 6.67 (t, J=6.40, 1H, aromatic), 6.78-6.80 (m, 1H, aromatic), 6.96-7.00 (m, 2H, aromatic), 7.10-7.14 (m, 2H, aromatic), 7.27 (t, J=7.56, 1H, aromatic).	25.18 (CH_3), 53.66 (CH), 55.32 (OCH_3), 111.83, 112.10, 113.43, 117.40, 118.36, 129.25 and 129.83 (aromatic, CH), 147.34, 147.44 and 160.07 (aromatic, C).
5e[1,3]	1.50 (d, J=6.88, 3H, CH_3), 4.01 (bs, 1H, NH), 4.45 (q, J=6.88, 1H, CH), 6.49 (d, J=7.80, 2H, aromatic), 6.67 (t, J=7.34, 1H, aromatic), 7.11(t, J=8.59, 2H, aromatic), 7.19-7.27 (m, 3H, aromatic), 7.37 (s, 1H, aromatic).	25.27 (CH_3), 53.43 (CH), 113.47, 117.74, 124.22, 126.21, 127.28, 129.35 and 130.17 (aromatic, CH), 134.71, 147.12 and 147.82 (aromatic, C).
5f	1.51 (d, J=6.84, 3H, CH_3), 4.02 (bs, 1H, NH), 4.47 (q, J=6.86, 1H, CH), 6.50 (d, J=7.80, 2H, aromatic), 6.67 (t, J=7.34, 1H, aromatic), 6.89-6.94(m, 1H, aromatic), 7.08-7.16 (m, 4H, aromatic), 7.25-7.31 (m, 1H, aromatic).	25.23 (CH_3), 53.40 (CH), 112.88 (d, J_{C-F}=22.03), 113.47, 113.95 (d, J_{C-F}=21.07), 117.17, 121.64, 129.34, 130.35(d, J_{C-F}=8.63), 147.17, 148.51 and 163.45 (d, J_{C-F}=247.17) (aromatic, C & CH).
5g[1]	1.46 (d, J=6.44, 3H, CH_3), 3.98 (bs, 1H, NH), 4.41 (q, J=6.80, 1H, CH), 6.45 (d, J=8.68, 2H, aromatic), 6.65 (t, J=7.34, 1H, aromatic), 7.08 (t, J=7.78, 2H, aromatic), 7.23 (d, J=8.68, 2H, aromatic), 7.41 (d, J=8.24, 2H, aromatic).	25.26 (CH_3), 53.20 (CH), 113.47, 117.69, 127.81, 129.33 and 131.90 (aromatic, CH), 120.64, 144.54 and 147.12 (aromatic, C).
5h[1,7]	1.50 (d, J=6.88, 3H, CH_3), 4.00 (bs, 1H, NH), 4.47 (q, J=6.88, 1H, CH), 6.49 (d, J=8.70, 2H, aromatic), 6.65 (t, J=6.40, 1H, aromatic), 7.00 (t, J=6.88, 2H, aromatic), 7.09 (dd, J=7.32, 8.68, 2H, aromatic), 7.31-7.34 (m, 2H, aromatic).	25.41 (CH_3), 53.10 (CH), 113.51, 115.63 (d, J_{C-F}=21.07), 117.63, 127.51 (d, J_{C-F}=8.63), 129.33, 141.09 (d, J_{C-F}=2.87), 147.27 and 161.93 (d, J_{C-F}=245.26) (aromatic, C & CH).
5i	1.52 (d, J=6.84, 3H, CH_3), 1.95 (bs, 1H, OH), 4.06 (bs, 1H, NH), 4.50 (q, J=6.88, 1H, CH), 4.63 (s, 2H, CH_2), 6.52 (d, J=8.92, 2H, aromatic), 6.66 (t,	25.24 (CH_3), 53.37 (CH), 65.24 (CH_2), 113.46, 117.44, 126.19, 127.61 and 129.26 (aromatic, CH), 139.59,

	J=7.10, 1H, aromatic), 7.08-7.12 (m, 2H, aromatic), 7.30-7.38 (m, 4H, aromatic).	144.94, and 147.35 (aromatic, C).
5j	1.37 (s, 9H, 3×CH_3), 1.56 (d, J=6.84, 3H, CH_3), 4.04 (bs, 1H, NH), 4.54 (q, J=6.86, 1H, CH), 6.59 (d, J=8.26, 2H, aromatic), 6.71 (t, J=7.34, 1H, aromatic), 7.16 (t, J=7.32, 1H, aromatic), 7.16 (t, J=7.10, 2H, aromatic), 7.34-7.41 (m, 4H, aromatic).	24.90 (CH_3), 31.59 (3×CH_3), 34.60 ($C(CH_3)_3$) 53.12 (CH), 113.41, 117.28, 125.66, 125.71 and 129.28 (aromatic, CH), 142.22, 147.60 and 149.78 (aromatic, C).
5k	1.49 (d, J=6.40, 3H, CH_3), 2.45 (s, 3H, $ArCH_3$), 3.80 (s, 3H, OCH_3), 4.00 (bs, 1H, NH), 4.66 (q, J=6.88, 1H, CH), 6.50 (d, J=8.22, 2H, aromatic), 6.68 (t, J=7.34, 1H, aromatic), 6.72-6.78 (m, 2H, aromatic), 7.14 (t, J=6.86, 2H, aromatic), 7.37 (d, J=8.72, 1H, aromatic).	19.31 ($ArCH_3$), 23.21 (CH_3), 49.46 (CH), 55.25 (OCH_3), 111.59, 113.17, 116.42, 127.21, 126.02 and 129.29 (aromatic, CH), 135.06, 136.20, 147.48 and 158.30 (aromatic, C).
5l[4]	1.67 (d, J=6.40, 3H, CH_3), 4.15 (bs, 1H, NH), 5.30 (q, J=6.88, 1H, CH), 6.49 (d, J=7.80, 2H, aromatic), 6.65 (t, J=7.34, 1H, aromatic), 7.07 (t, J=7.78, 2H, aromatic), 7.41 (t, J=7.80, 1H, aromatic),7.50-7.59 (m, 2H, aromatic), 7.66 (d, J=6.84, 1H, aromatic), 7.75 (d, J=8.24, 1H, aromatic), 7.91 (d, J=7.80, 1H, aromatic), 8.17 (d, J=8.24, 1H, aromatic).	23.79 (CH_3), 49.65 (CH), 113.36, 117.42, 122.48, 122.80, 125.62, 126.07, 126.25, 127.64 and 129.34 (aromatic, CH), 130.89, 134.30, 140.12 and 147.28 (aromatic, C).
5m[8]	1.61 (d, J=6.88, 3H, CH_3), 3.92 (s, 3H, OCH_3), 4.13 (bs, 1H, NH), 4.65 (q, J=6.88, 1H, CH), 6.60 (d, J=8.02, 2H, aromatic), 6.69 (t, J=7.32, 1H, aromatic), 7.10-7.19 (m, 4H, aromatic), 7.50 (d, J=8.70, 1H, aromatic), 7.74 (t, J=8.46, 2H, aromatic), 7.78 (s, 1H, aromatic).	25.15 (CH_3), 53.71 (CH), 55.44 (OCH_3), 105.87, 113.53, 117.40, 118.95, 124.28, 125.10, 127.46, 129.27 and 129.46 (aromatic, CH), 129.19, 133.93, 140.61, 147.55 and 157.60 (aromatic, C).
5n[11]	1.51 (d, J=6.88, 3H, CH_3), 3.72 (s, 3H, OCH_3), 3.91 (s, 3H, OCH_3), 3.95 (bs, 1H, NH), 4.81 (q, J=6.88, 1H, CH), 6.50-6.55 (m, 2H, aromatic), 6.72-6.76 (m, 2H, aromatic), 6.91-6.95 (m, 2H, aromatic), 7.23 (dt, J=1.84, 8.02, 1H, aromatic), 7.36 (dd, J=2.28, 8.24, 1H, aromatic).	22.98 (CH_3), 49.02 (CH), 55.40 and 55.79 (OCH_3), 110.57, 114.65, 114.82, 120.90, 126.54 and 127.74 (aromatic, CH), 133.01, 141.79, 151.85 and 156.85 (aromatic, C).
5o[11]	1.46 (d, J=6.88, 3H, CH_3), 3.66 (s, 3H, OCH_3), 3.75 (s, 3H, OCH_3), 3.76 (bs, 1H, NH), 4.35 (q, J=6.88, 1H, CH), 6.43-6.47 (m, 2H, aromatic), 6.65-6.68 (m, 1H, aromatic), 6.72-6.75 (m, 1H, aromatic), 6.91-6.94 (m, 2H, aromatic), 7.21 (t, J=8.02, 1H, aromatic).	25.23 (CH_3), 54.40 (CH), 55.26 & 55.82 (OCH_3), 111.81, 112.04, 114.64, 114.85, 118.37 and 129.75 (aromatic, CH), 141.72, 147.58, 151.99 and 160.02 (aromatic, C).
5p[9]	1.52 (d, J=6.88, 3H, CH_3), 3.69 (s, 3H, OCH_3), 4.08 (bs, 1H, NH), 4.49 (q, J=6.56, 1H, CH), 6.08 (t, J=2.30, 1H, aromatic), 6.16 (dd, J=1.80, 8.48, 1H, aromatic), 6.23 (dd, J=2.28, 8.24, 1H, aromatic), 7.01 (t, J=8.24, 1H, aromatic), 7.23-7.33 (m, 5H, aromatic)	25.13 (CH_3), 53.65 (CH), 55.13 (OCH_3), 99.48, 102.55, 106.60, 125.98, 127.06, 128.82 and 129.99 (aromatic, CH), 145.35, 148.84 and 160.79 (aromatic, C).
5q[9]	1.50 (d, J=6.88, 3H, CH_3), 3.67 (s, 6H, 2×OCH_3), 4.05 (bs, 1H, NH), 4.47 (q, J=6.88, 1H, CH), 5.71 (d, J=1.84, 2H, aromatic), 5.82 (t, J=1.84, 1H, aromatic), 7.22 (t, J=7.32, 1H, aromatic), 7.29-7.36 (m, 4H, aromatic).	25.07 (CH_3), 53.75 (CH), 55.26 (OCH_3), 89.89, 92.42, 125.99, 127.11, and 128.87 (aromatic, CH), 145.36, 149.39 and 161.74 (aromatic, C).

5r[9]	1.46 (d, J=6.88, 3H, CH_3), 3.65 (s, 3H, OCH_3), 3.76 (bs, 1H, NH), 4.38 (q, J=6.70, 1H, CH), 6.42-6.46 (m, 2H, aromatic), 6.65-6.69 (m, 2H, aromatic), 7.16-2.21 (m, 1H, aromatic), 7.26-7.34 (m, 4H, aromatic).	25.27 (CH_3), 54.34 (CH), 55.81 (OCH_3), 114.65, 114.87, 126.02, 126.94 and 128.74 (aromatic, CH), 141.70, 145.64 and 151.97 (aromatic, C).
5s[3,9,11]	1.52 (d, J=6.88, 3H, CH_3), 4.08 (bs, 1H, NH), 4.44 (q, J=6.40, 1H, CH), 6.36-6.40 (m, 2H, aromatic), 7.15-7.18 (m, 2H, aromatic), 7.24-7.26 (m, 1H, aromatic), 7.33-7.34 (m, 4H, aromatic)	25.16 (CH_3), 53.64 (CH), 115.05, 125.92, 127.22, 128.91 and 131.94 (aromatic, CH), 109.00, 144.78 and 146.34 (aromatic, C).
5t[3,7,9]	1.51 (d, J=6.88, 3H, CH_3), 4.06 (bs, 1H, NH), 4.44 (q, J=6.42, 1H, CH), 6.40-6.44 (m, 2H, aromatic), 7.01-7.05 (m, 2H, aromatic), 7.22-7.34 (m, 5H, aromatic).	25.18 (CH_3), 53.73 (CH), 114.54, 125.93, 127.21, 128.90 and 129.08 (aromatic, CH), 121.94, 144.87 and 145.94 (aromatic, C)

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Experimental details for single crystal X-ray crystallographic study of **6**.

A crystal of **6**, grown by slow evaporation from a DCM solution, was mounted on a quartz fibre. X-ray data were collected on a Bruker X8 APEX system, using Mo Kα radiation, with the SMART suite of programs.[1] Data were processed and corrected for Lorentz and polarization effects with SAINT,[2] and for absorption effects with SADABS.[3] Structural solution and refinement were carried out with the SHELXTL suite of programs.[4] The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the remaining atoms. Hydrogen atoms were placed in calculated positions, and refined with a riding model. All non-hydrogen atoms were given anisotropic displacement parameters in the final model.

[1] SMART version 5.628, Bruker AXS Inc., Madison, Wisconsin, USA **2001**.

[2] SAINT+ version 6.22a, Bruker AXS Inc., Madison, Wisconsin, USA, **2001**.

[3] Sheldrick, G. M., SADABS **1996**.

[4] SHELXTL version 5.1, Bruker AXS Inc., Madison, Wisconsin, USA **1997**.

Table S5. Crystal data and structure refinement for **6**.

Identification code	lwk19	
Empirical formula	C16 H22 Cl2 N Rh	
Formula weight	402.16	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 7.4450(3) Å	α= 96.332(2)°.
	b = 9.3608(3) Å	β= 93.353(2)°.
	c = 13.0557(4) Å	γ = 112.717(2)°.
Volume	829.08(5) $Å^3$	
Z	2	
Density (calculated)	1.611 Mg/m^3	
Absorption coefficient	1.342 mm^{-1}	
F(000)	408	
Crystal size	0.30 x 0.20 x 0.10 mm^3	
Theta range for data collection	2.98 to 31.16°.	
Index ranges	-9<=h<=10, -13<=k<=13, -18<=l<=18	
Reflections collected	17191	
Independent reflections	5304 [R(int) = 0.0326]	
Completeness to theta = 31.16°	99.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8775 and 0.6889	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5304 / 0 / 186	
Goodness-of-fit on F^2	1.041	
Final R indices [I>2sigma(I)]	R1 = 0.0238, wR2 = 0.0538	
R indices (all data)	R1 = 0.0267, wR2 = 0.0550	
Largest diff. peak and hole	0.585 and -0.583 $e.Å^{-3}$	

Figure S1.

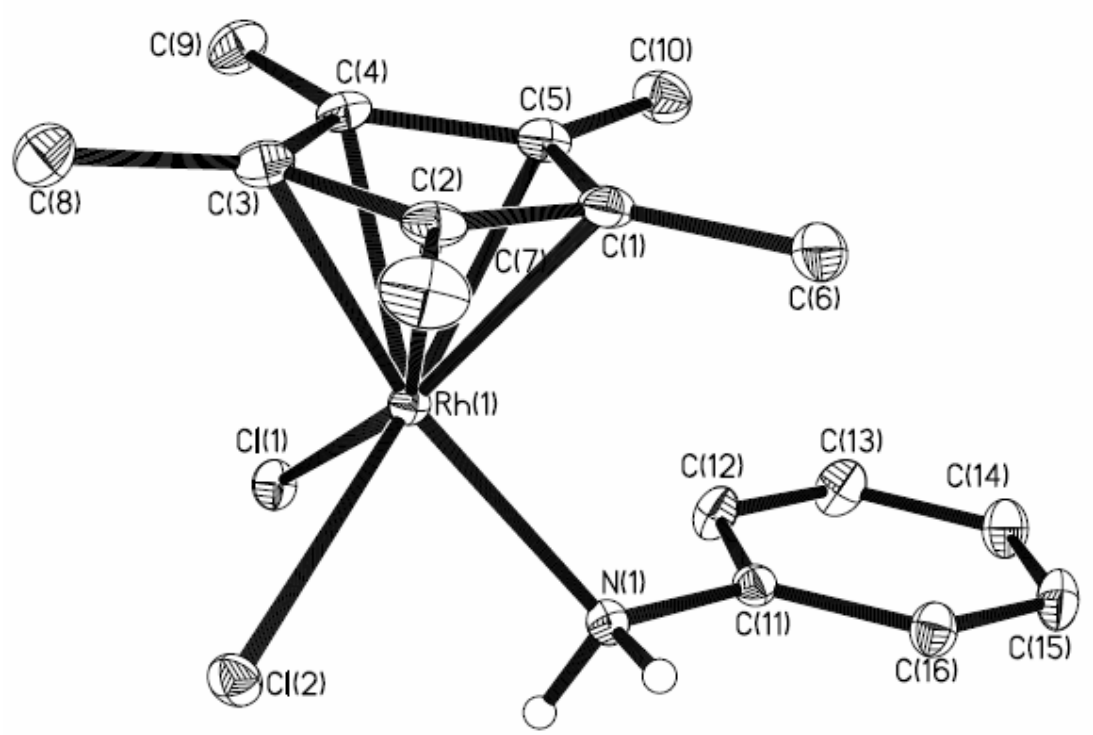
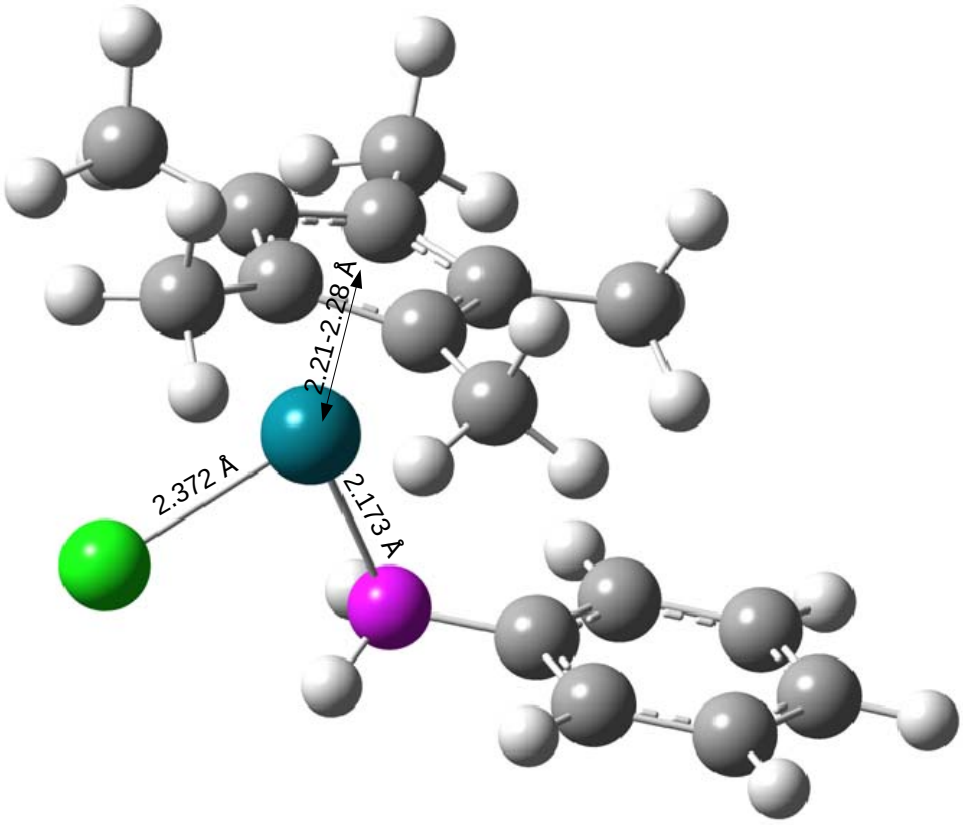
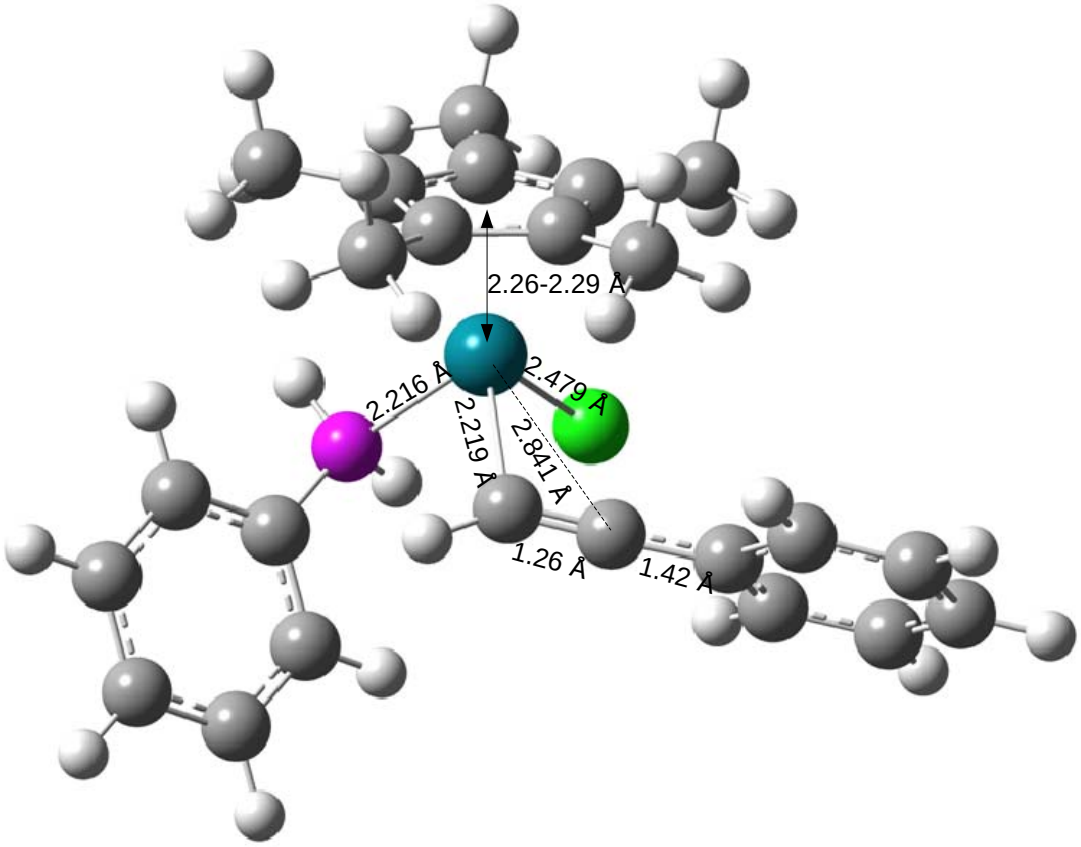

C(9)
C(4)
C(10)
C(5)
C(8)
C(3)
C(2)
C(7)
C(1)
C(6)
Rh(1)
Cl(1)
C(12)
C(13)
C(14)
N(1)
C(11)
C(15)
C(16)
Cl(2)

Figure S2.

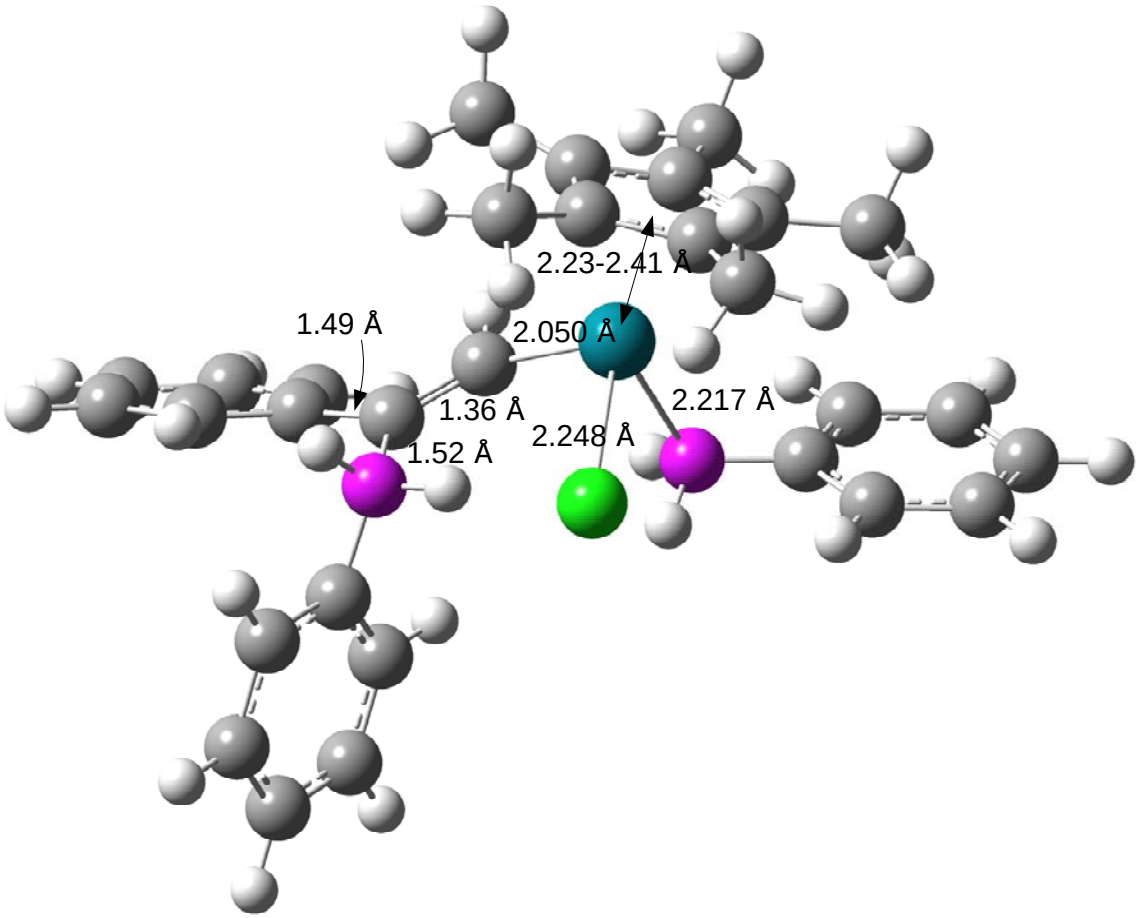
Intermediate A



Intermediate B

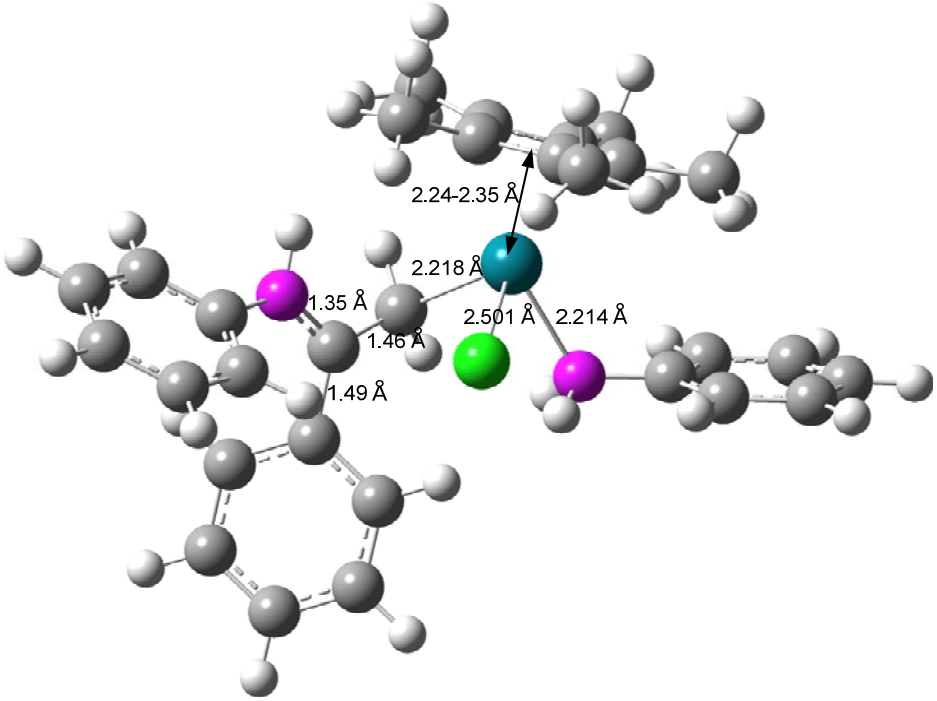


Intermediate C



Intermediate D

cis isomer



trans isomer

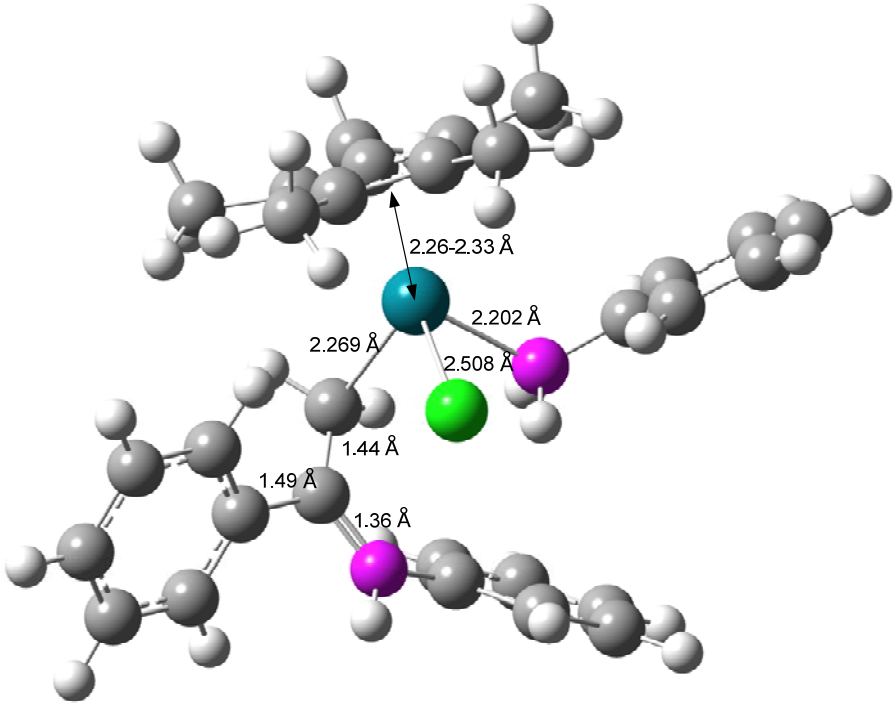
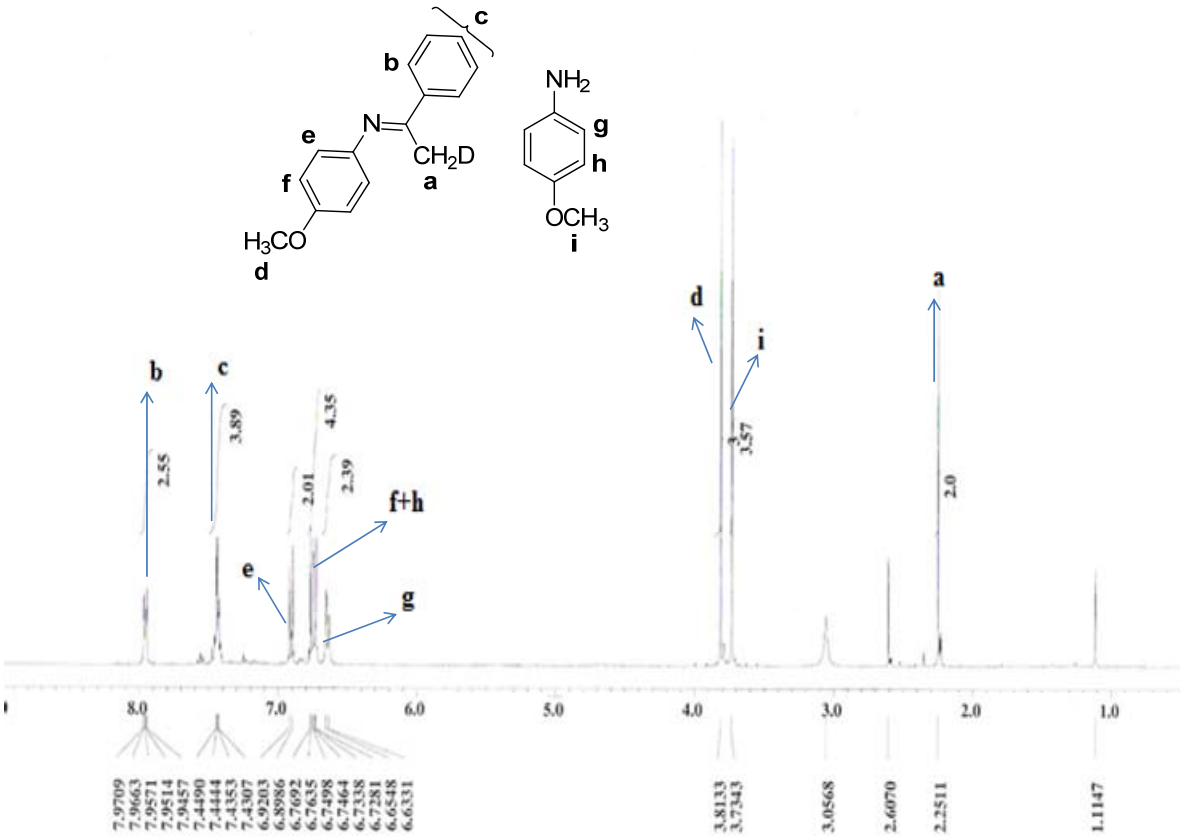


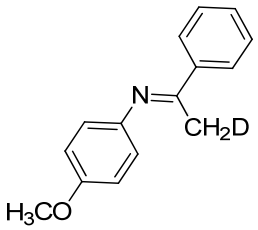
Figure S3.

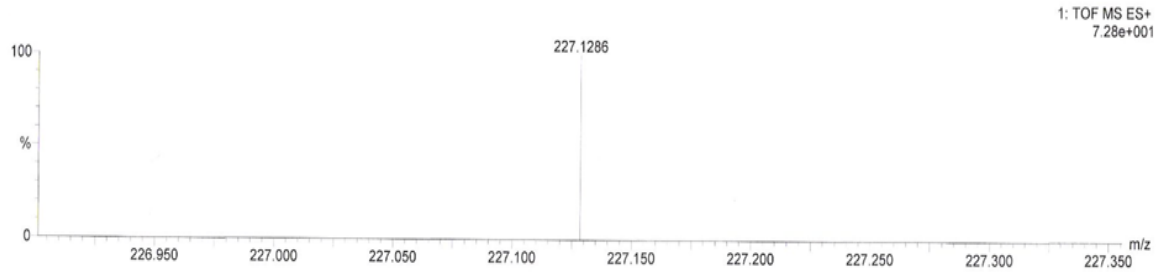


Elemental Composition Report

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

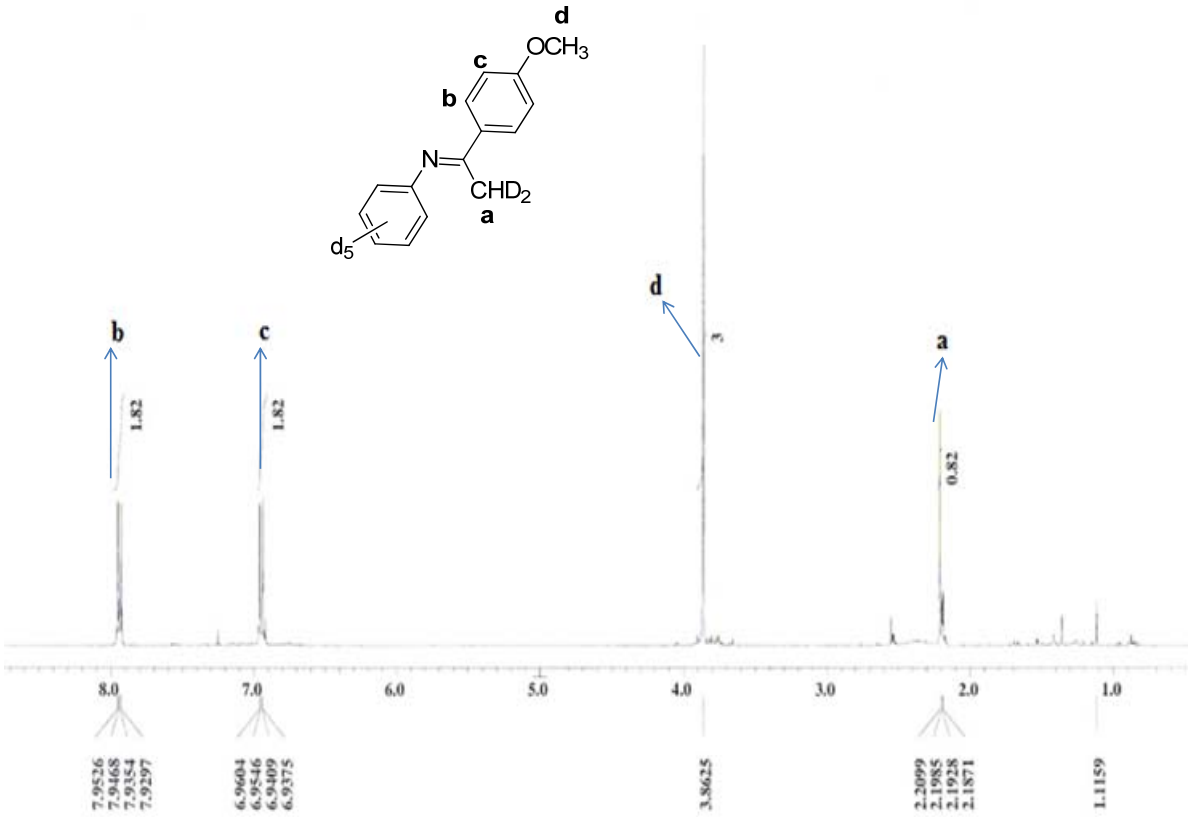
Monoisotopic Mass, Even Electron Ions
34 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-15 1H: 0-15 2H: 1-7 N: 0-1 O: 0-1
C15H14DNO





Minimum:				-1.5			
Maximum:		5.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
227.1286	227.1295	-0.9	-4.0	8.5	16.9	0.0	C15 1H15 2H N O

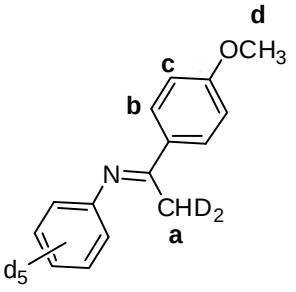
Figure S4.



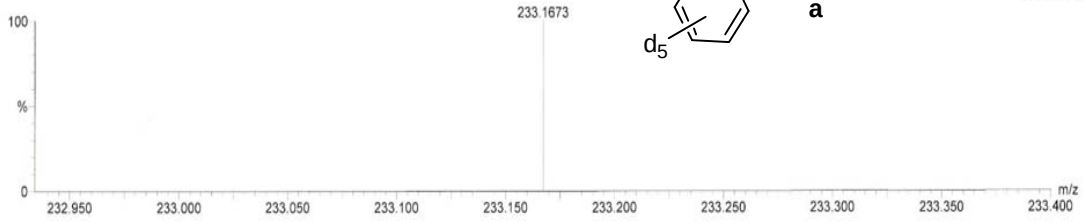
Elemental Composition Report

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
54 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-15 1H: 0-10 2H: 1-7 N: 0-1 O: 0-1
C15H8D7NO



1: TOF MS ES+
1.14e+002



Minimum:				-1.5			
Maximum:		5.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
233.1673	233.1671	0.2	0.9	8.5	17.8	0.0	C15 1H9 2H7 N O