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Supporting Information

Homogeneous Catalytic Hydrogenation of Amides to Amines

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■ **CONTENTS**

■ SECTION S-1: SUPPORTING FIGURES REFERRED TO IN THE MAIN TEXT

Figures S1-S3 given below should be viewed in conjunction with the main text as. For a more detailed explanation of what each figures represents, please refer back to the main text.

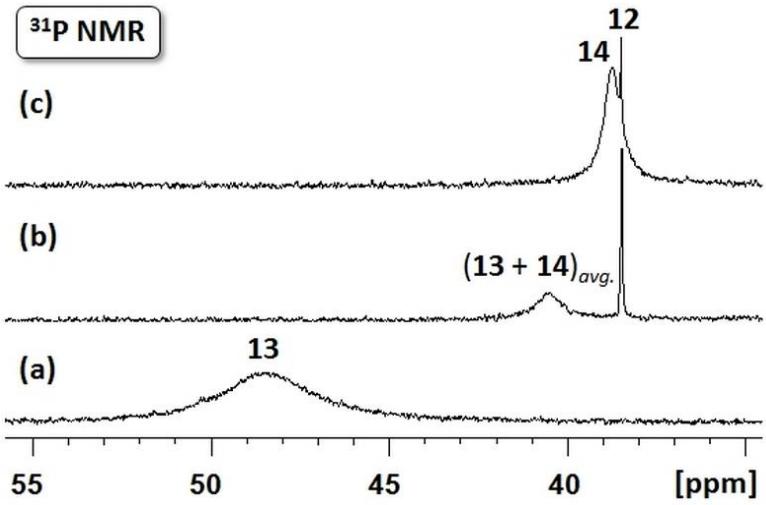


Figure S1. $^{31}P\{^{1}H\}$ NMR spectra for (a) **13** [obtained in the presence of a large excess (> 3 eq) of MSA]; (b) **12** together **13** and **14** (observed as an average); (c) the same sample as in (b) the mixture after equilibration overnight at R.T to give mainly **14**.

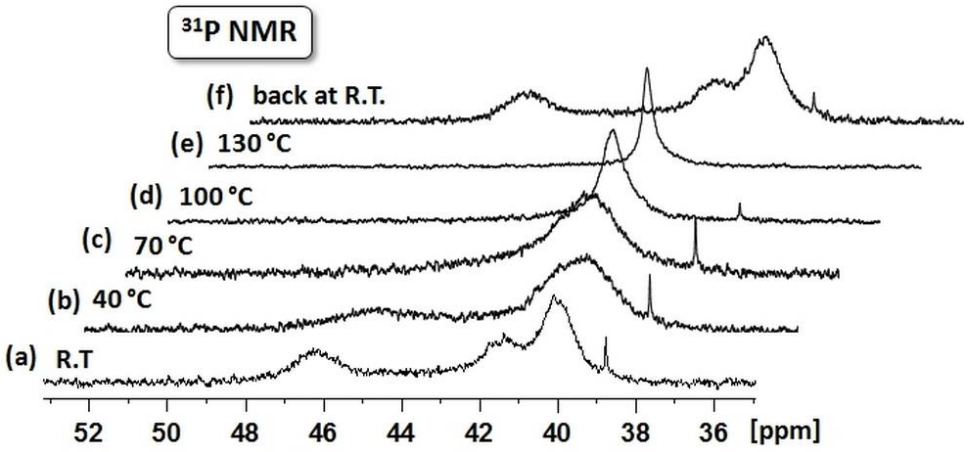


Figure S2. NMR spectra recorded during a VT HP-NMR study on the in solution behaviour of **9** at (a) R.T., (b) 40 °C, (c) 70 °C, (d) 100 °C, (e) 130 °C and (f) back at R.T. Conditions: *N*-phenylacetamide (0.75 mmol), thf-d_8 (3 ml), **9** (10 mol %), MSA (15 mol %) and H_2 (10 bar).

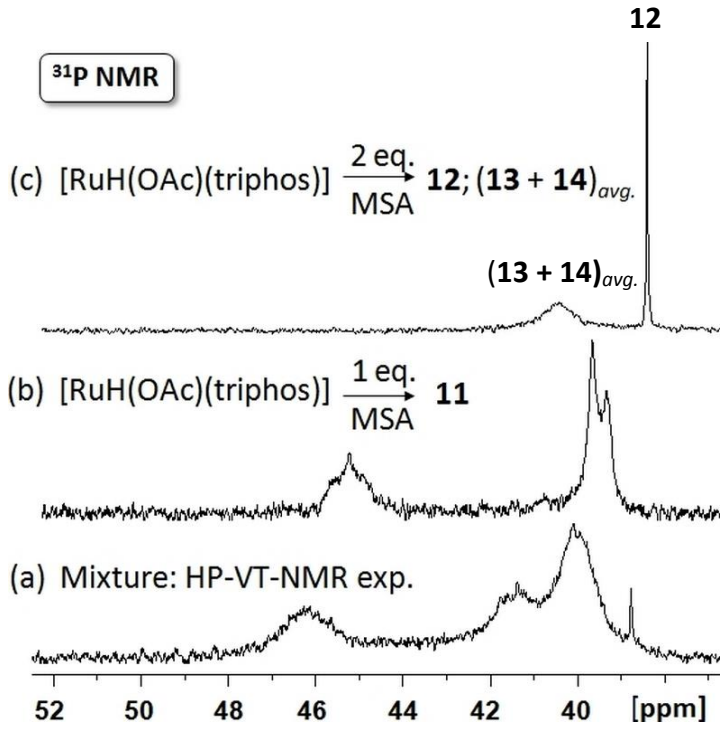


Figure S3. A comparison between the $^{31}P\{^{1}H\}$ NMR spectra of (a) a mixture of *N*-phenylacetamide, **9** and MSA in thf-d_8 under H_2 (10 bar) at R.T (b) **11** and (c) a mixture of **12**, **13** and **14**.

■ SECTION S-2: CRYSTALLOGRAPHIC DISCUSSION

The crystal and molecular structures of complexes **11**, **12** and two water coordinated analogues of **14** and **15**, [Ru(CH_3SO_3-κ^1O)$_2$(H_2O)(triphos)] (**19**) and [Ru(OAc-κ^1O)$_2$(H_2O)(triphos)] (**20**), were determined by single crystal X-ray-diffraction and are depicted in Figures S4–S7 (see main text for the compound numbering scheme). In all of the determined structures, the geometry about the Ru(II) centers are best described as distorted octahedral with the triphos ligands adopting the expected *facial* configuration. Complex **11** crystallises together with two molecules of dichloromethane as yellow prisms in the monoclinic spacegroup $P2_1/c$ (Figure S4). For **11** the Ru(1)–O(1), Ru(1)–O(2) and Ru–P bond lengths are comparable to those reported for the related complex, [RuCl(OAc)(triphos)] [(Ru–O)$_{avg.}$ 2.224 Å and (Ru–P)$_{avg}$ 2.278 Å].[1] Similarly the Ru(1)–O(3) distance of 2.203(4) Å compares well that between the oxygen coordinated dimethylsulfoxide (DMSO) ligands and the metal centre in, *fac*-[Ru(triphos)(DMSO-κ^1O)$_2$(H_2O)]CF_3SO_3 [2.215(4)Å and 2.190(4) Å].[2] The small chelate angle of the acetato ligand [59.80(15)°] forces a distorted octahedral geometry, resulting in widening of the O(1)–Ru(1)–P(2) [105.73(11)°] and O(2)–Ru(1)–P(3) [109.63(11)°] angles. Furthermore, in order to minimise steric congestion the methanesulfonato ligand is bent away from the triphos phenyl rings to give an O(3)–Ru(1)–P(1) angle [171.97(10)°] which deviates significantly from the ideal linearity.

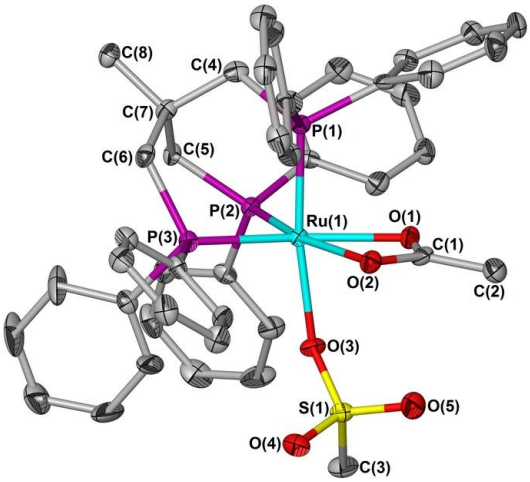


Figure S4 Molecular structure of **11** with thermal ellipsoids set at 50 % probability. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles(°): Ru(1)–O(1) 2.173(4), Ru(1)–O(2) 2.210(4), Ru(1)–O(3) 2.203(4), Ru(1)–P(1) 2.2519(15), Ru(1)–P(2) 2.2731(15), Ru(1)–P(3) 2.2551(13), O(1)–Ru(1)–O(3) 80.83(14), O(1)–Ru(1)–O(2) 59.80(15), O(3)–Ru(1)–O(2) 84.23(14), O(1)–Ru(1)–P(1) 91.50(11), O(3)–Ru(1)–P(1) 171.97(10), O(2)–Ru(1)–P(1) 89.85(11), O(1)–Ru(1)–P(3) 169.42(11), O(3)–Ru(1)–P(3) 99.20(11), O(2)–Ru(1)–P(3) 109.63(11), P(1)–Ru(1)–P(3) 87.89(5), O(1)–Ru(1)–P(2) 105.73(11), O(3)–Ru(1)–P(2) 95.00(11), O(2)–Ru(1)–P(2) 165.48(11), P(1)–Ru(1)–P(2) 89.37(6), P(3)–Ru(1)–P(2) 84.83(5).

The methanesulfonato bridged dimer, **12**, crystallises from dichloromethane, together with three dichloromethane molecules, as yellow prisms in the triclinic space group *P*$\bar{1}$. In the molecular structure of **12**, the coordination sphere around each Ru(II) centre adopts a slightly distorted octahedral geometry. When viewed along the Ru···Ru vector, the two triphos ligands approach an eclipsed conformation while the bridging sulfonato ligands are staggered with respect to the P-atoms (Figure S5). The average Ru–O bonding distance (2.187) of the bridging ligands is comparable to that of the monodentate methanesulfonato ligand to Ru in **11** [Ru(1)–O(3) 2.203(4)]. Similarly, no noteworthy differences exist between the Ru–P bond lengths of compound **11** and **12**.

During an attempt to separate **14** from a mixture of **12**, **13** and **14** by recrystallisation, the water coordinated analogue [Ru(CH_3SO_3-κ^1O)$_2$(H_2O)(triphos)] (**19**) crystallised from solution as yellow prisms in the monoclinic space group *P*2/*n*. Although the asymmetric unit contains two unique molecules of **19** co-crystallised with five solvent molecules, only one of them will be discussed here as no significant difference between their corresponding bond lengths and angles (Figure S6) exist. The methanesulfonato ligands are bent away from the triphos ligand towards the coordinated water molecule not only to minimise steric interactions but also to facilitate the formation of two six membered rings through hydrogen bonding, which aids in stabilising the structure. As for complex **11**, the Ru(1)–O(1) [2.209(5) Å], Ru(1)-O(3) [2.207(5) Å] and the average Ru-P (2.273 Å) bonding distances sit within the range of those reported for *fac*-[Ru(triphos)(DMSO-κ^1O)$_2$(H_2O)]CF_3SO_3 in the literature.[2]

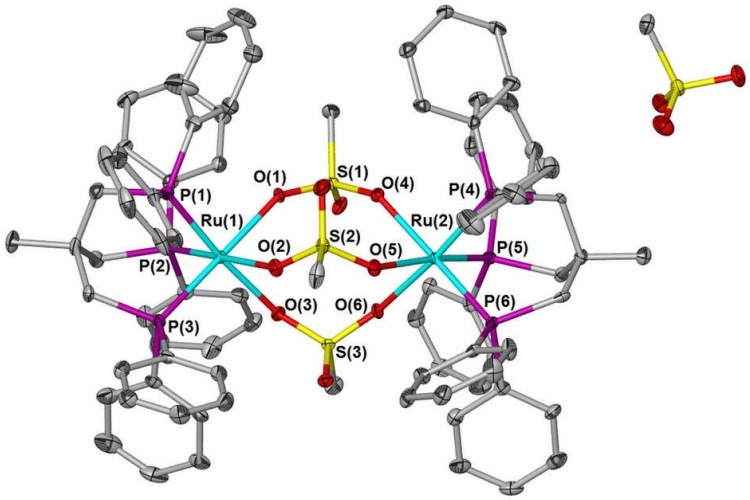


Figure S5 Molecular structure of **12** with thermal ellipsoids set at 50 % probability. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles(°): Ru(1)–O(1) 2.167(6) Ru(1)–O(2) 2.195(6), Ru(1)–O(3) 2.190(6), Ru(2)–O(4) 2.181(7), Ru(2)–O(5) 2.193(6), Ru(2)–O(6) 2.193(5), Ru(1)–P(1) 2.251(3), Ru(1)–P(2) 2.283(3), Ru(1)–P(3) 2.263(3), Ru(2)–P(4) 2.279(2), Ru(2)–P(5) 2.252(3), Ru(2)–P(6) 2.280(3), O(1)–Ru(1)–O(2) 83.5(3), O(1)–Ru(1)–O(3) 84.0(3), O(3)–Ru(1)–O(2) 81.9(3), O(1)–Ru(1)–P(1) 90.71(17), O(3)–Ru(1)–P(1) 174.48(17), O(2)–Ru(1)–P(1) 95.88(17), O(1)–Ru(1)–P(3) 178.94(15), O(3)–Ru(1)–P(3) 96.62(18), O(2)–Ru(1)–P(3) 95.79(19), P(1)–Ru(1)–P(3) 88.62(9), O(1)–Ru(1)–P(2) 94.10(18), O(3)–Ru(1)–P(2) 93.59(17), O(2)–Ru(1)–P(2) 175.05(16), P(1)–Ru(1)–P(2) 88.44(9), P(3)–Ru(1)–P(2) 86.70(9), O(1)–S(1)–O(4) 112.5(4), O(2)–S(2)–O(5) 112.0(4), O(3)–S(3)–O(6) 113.4(4).

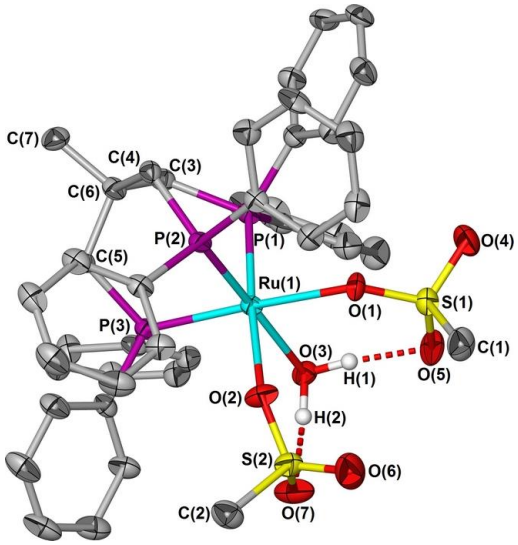


Figure S6 Molecular structure of **19** with thermal ellipsoids set at 50% probability. Included solvent molecules and hydrogen atoms (with the exception of those associated with water) are omitted for clarity. Selected bond lengths (Å) and angles(°): Ru(1)–O(3) 2.207(5), Ru(1)–O(1) 2.209(5), Ru(1)–O(2) 2.223(5), Ru(1)–P(3) 2.2615(19), Ru(1)–P(1) 2.2668(19), Ru(1)–P(2) 2.2914(18), S(1)–O(1) 1.472(5), S(1)–O(1) 1.472(5), P(1)–C(3) 1.841(8), P(2)–C(4) 1.837(7), P(3)–C(5) 1.833(7), O(3)–Ru(1)–O(1) 82.43(19), O(1)–Ru(1)–O(2) 81.8(2), O(3)–Ru(1)–O(2) 81.7(2), O(3)–Ru(1)–P(3) 95.71(15), O(1)–Ru(1)–P(3) 177.77(15), O(2)–Ru(1)–P(3) 96.77(17), O(3)–Ru(1)–P(1) 96.77(15), O(1)–Ru(1)–P(1) 94.92(15), O(2)–Ru(1)–P(1) 176.50(17), P(3)–Ru(1)–P(1) 86.50(7), O(3)–Ru(1)–P(2) 174.13(15), O(1)–Ru(1)–P(2) 94.93(14), O(2)–Ru(1)–P(2) 92.76(15), P(3)–Ru(1)–P(2) 86.81(7), P(1)–Ru(1)–P(2) 88.66(7).

Compound **20**, crystallised from a dichloromethane solution of **15** in the monoclinic space group $P2_1/n$. The structure of **20** is analogous to that of **11** in that the two acetato ligands are again bent towards the coordinated water molecule to allow for stabilisation through hydrogen bonding (Figure S7). Not surprisingly, the Ru(1)–O(1) and Ru(1)–O(3) bond lengths [2.1614(15) Å and 2.1510(15) Å] are slightly shorter than those of the bidentate acetato ligand in **11** [2.167(4) (4) Å and 2.209(4) Å], where slight bond elongation is brought about by ring strain. Similar to complexes **11**, **12** and **19**, the constraints of the tridentate triphos ligand together with steric congestion around the Ru(II) centre causes all angles to deviate significantly from ideality with the largest divergence observed for the angle O(3)–Ru(1)–O(1) [80.86(6) °].

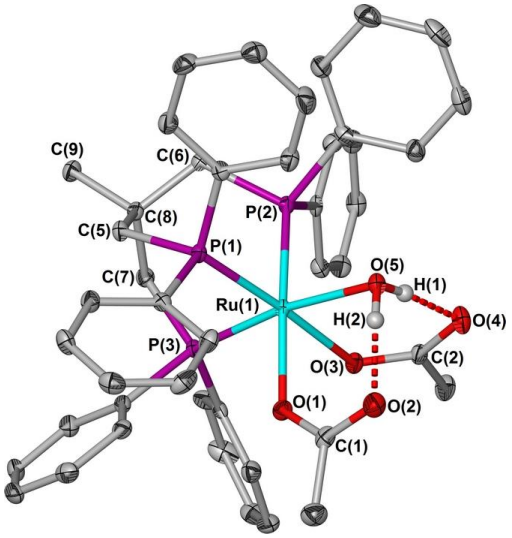


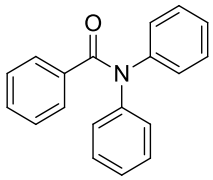
Figure S7 Molecular structure of **20** with thermal ellipsoids set at 50% probability. Hydrogen atoms (with the exception of those associated with water) are omitted for clarity. Selected bond lengths (Å) and angles(°): Ru(1)–O(1) 2.1614(15), Ru(1)–O(3) 2.1510(15), Ru(1)–O(5) 2.1988(15), Ru(1)–P(1) 2.2844(6), Ru(1)–P(2) 2.2776(7), Ru(1)–P(3) 2.2647(6), O(3)–Ru(1)–O(1) 80.86(6), O(3)–Ru(1)–O(5) 85.00(6), O(1)–Ru(1)–O(5) 86.63(6), O(3)–Ru(1)–P(3) 87.82(4), O(1)– Ru(1)–P(3) 87.58(4), O(5)–Ru(1)–P(3) 171.42(4), O(3)–Ru(1) –P(2) 95.07(4), O(1)–Ru(1)–P(2) 175.80(4), O(5)–Ru(1)–P(2) 94.11(5), P(3)–Ru(1)–P(2) 91.21(2), O(3)–Ru(1)–P(1) 175.35(4), O(1)–Ru(1)–P(1) 98.90(4), O(5)–Ru(1)–P(1) 99.62(5), P(3)–Ru(1)–P(1) 87.53(2), P(2)–Ru(1)–P(1) 85.07(2).

■ SECTION S-3: ANALYTICAL DATA FOR AMIDE SUBSTRATES PREPARED IN HOUSE

General procedure for the synthesis of amides

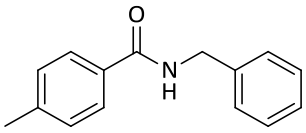
A solution of the corresponding amine (22 mmol) and triethylamine (22 mmol) in dichloromethane (50 ml) was cooled to 0 °C with an ice bath. The appropriate acid chloride (22 mmol) was added dropwise to the mixture over a period of 10 min at 0 °C. The solution was then allowed to warm to room temperature and stirred overnight. The mixture was then washed with a 2 M solution of HCl (3 × 50 ml) and a saturate $NaHCO_3$ solution (3 × 50 ml). The organic phase was subsequently dried over anhydrous $MgSO_3$ and the solvent removed *in vacuo* to give the crude product. Amides were further purified by recrystallisation, typically from hot toluene.[3]

***N*,*N*-diphenylbenzamide[4]**



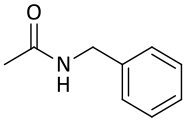
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.38 (2H, m, CH), 7.22 (5H, m, CH), 7.07-7.15 (8H, m, CH); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 170.6 (C=O), 143.9 (C-N), 136.1 (*C*-C=O), 130.1 (CH), 129.2 (CH), 129.1 (CH), 127.9 (CH), 127.5 (CH), 126.3 (CH); GCMS: 273, 180, 167, 105, 77, 51; Elemental analysis: Found: C, 83.27; N, 5.33; H, 5.30. Calc. for $C_{19}H_{15}NO$: C, 83.49; N, 5.12; H, 5.53%.

***N*-benzyl-4-methylbenzamide[3]**



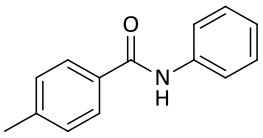
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.71 (2H, d, $^3J_{HH}$ = 8.1 Hz, CH), 7.37 (4H, d, J_{HH} = 4.4 Hz, CH), 7.32 (1H, m, CH), 7.24 (2H, d, $^3J_{HH}$ = 7.9 Hz, CH), 6.47 (1H, s, NH), 4.65 (2H, d, J_{HH} = 5.6 Hz, CH_2), 2.42 (3H, s, CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ = 167.4 (C=O), 142.0 (CMe), 138.4 (*C*CH_2), 131.5 (*C*C=O), 129.3 (CH), 128.8 (CH), 127.9 (CH), 127.6 (CH), 127.0 (CH), 44.1 (CH_2), 21.5 (CH_3); GCMS: 225, 119, 106, 91; Elemental analysis: Found: C, 79.65; N, 6.33; H, 6.62. Calc. for $C_{15}H_{15}NO$: C, 79.97; N, 6.22; H, 6.71%.

_N_-benzylacetamide[3]



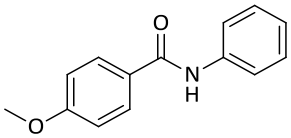
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.33 (2H, m, CH), 7.27 (3H, m, CH), 5.88 (1H, s, NH), 4.42 (2H, d, $^2J_{HH}$ = 5.7 Hz, CH_2), 2.01 (3H, s, CH_3); ^{1}H NMR ($(CD_3)_2SO$, 400 MHz): δ = 8.34 (1H, s, NH), 7.30 (2H, m, CH), 7.22 (3H, m, CH), 4.24 (2H, d, $^2J_{HH}$ = 6.0 Hz, CH_2), 1.86 (3H, s, CH_3); $^{13}C\{^1H\}$ NMR ($(CD_3)_2SO$, 100 MHz): δ = 169.1 (C=O), 139.5 (*C*CH_2)), 128.2 (CH), 127.2 (CH), 126.7 (CH), 42.0 (CH_2), 22.5 (CH_3); Elemental analysis: Found: C, 72.88; N, 9.63; H 7.06,. Calc. for $C_9H_{11}NO$: C, 72.46; N, 9.39; H, 7.43%.

4-Methylbenzanilide[3]



^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.81 (1H, s, NH), 7.77 (2H, d, $^3J_{HH}$ = 8.2 Hz, CH), 7.64 (2H, dd, $^3J_{HH}$ = 8.5, $^4J_{HH}$ = 1.0 Hz, CH), 7.37 (2H, t, J_{HH} = 8.0 Hz, CH), 7.28 (2H, d, $^3J_{HH}$ = 7.9 Hz), 7.14 (1H, tt, $^3J_{HH}$ = 7.4, $^4J_{HH}$ = 1.1 Hz, CH), 2.43 (3H, s, CH_3); ^{1}H NMR ($(CD_3)_2SO$, 400 MHz): δ = 10.14 (1H, s, NH), 7.86 (2H, d, $^3J_{HH}$ = 8.2 Hz, CH), 7.76 (2H, d, $^3J_{HH}$ = 7.6 Hz, CH), 7.33 (4H, m, CH), 7.08 (1H, tt, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.1 Hz, CH), 2.37 (3H, s, CH_3); $^{13}C\{^1H\}$ NMR ($(CD_3)_2SO$, 100 MHz): δ = 165.3 (C=O), 141.5 (CMe), 139.2 (C-NH), 132.0 (*C*-C=O), 128.8 (CH), 128.5 (CH), 127.6 (CH), 123.5 (CH), 120.3 (CH), 21.0 (CH_3).

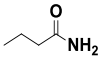
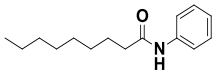
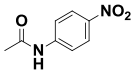
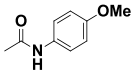
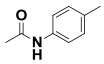
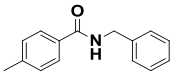
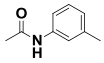
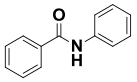
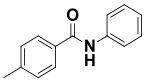
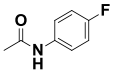
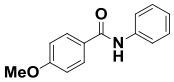
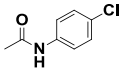
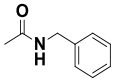
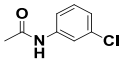
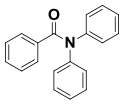
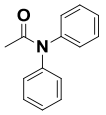
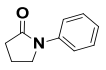
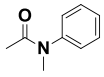
4-Methoxybenzanilide[3]



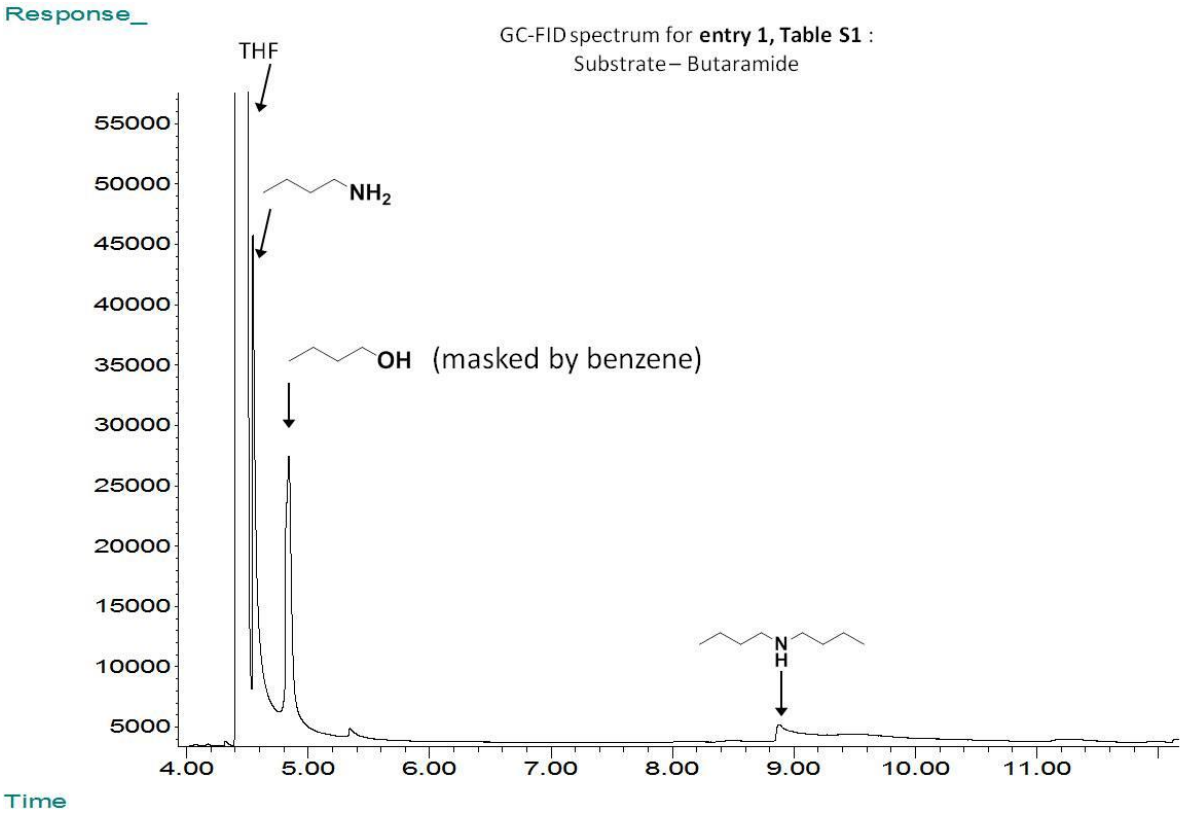
^{1}H NMR ($(CD_3)_2CO$, 300 MHz): δ = 10.09 (1H, s, NH), 7.97 (2H, dt, $^3J_{HH}$ = 9.8 Hz, $^4J_{HH}$ = 2.5 Hz, CH), 7.78 (2H, d, $^3J_{HH}$ = 7.5 Hz, CH), 7.34 (2H, t, $^3J_{HH}$ = 7.9 Hz, CH), 7.08 (3H, m, CH), 3.84 (3H, s, CH_3); $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$, 100 MHz): δ = 220.8 (C=O), 161.8 (C-OMe), 139.3 (C-N), 129.5 (CH), 128.5 (CH), 126.9 (*C*-C=O), 123.4 (CH), 120.3 (CH), 113.5 (CH), 55.4 (CH_3); Elemental analysis: Found: C, 74.24; N, 6.52; H, 6.05. Calc. for $C_9H_{11}NO$: C, 73.99; N, 6.16; H, 5.77%.

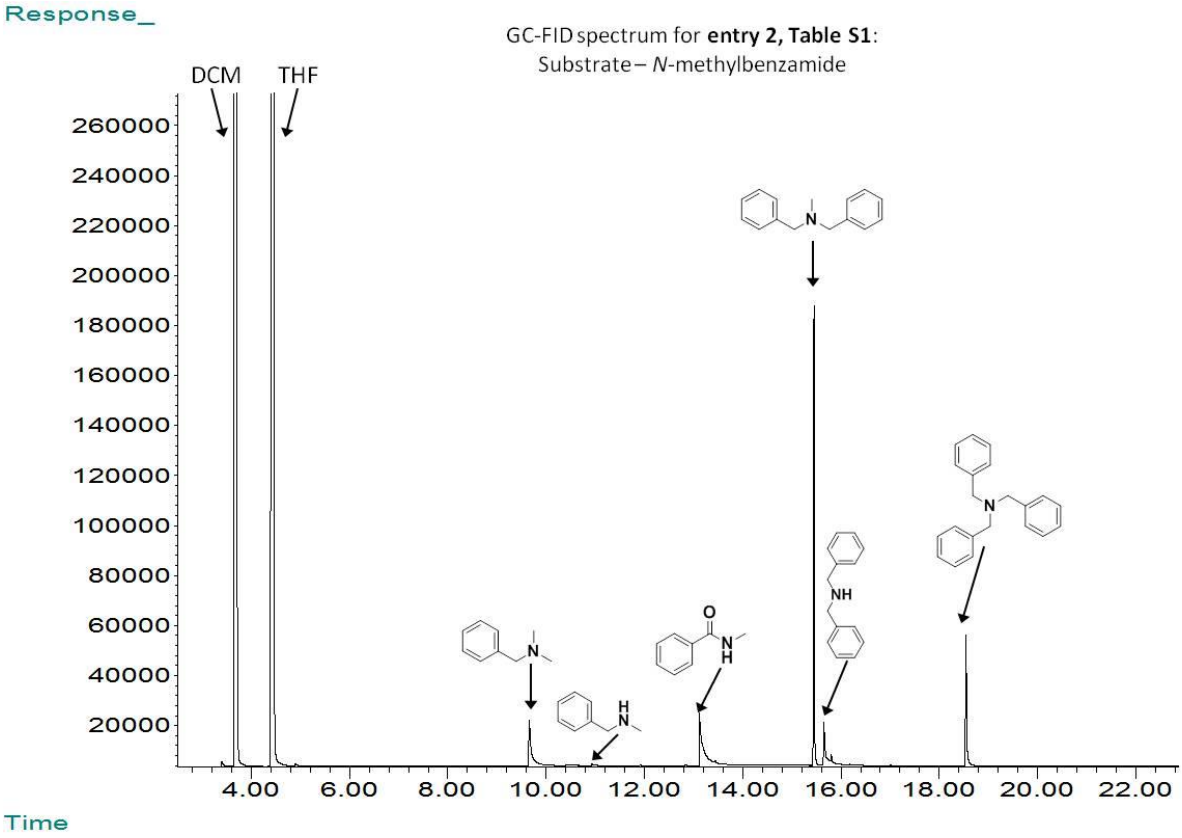
■ SECTION S-4: GC-FID SPECTRA FOR THE POST RUN PRODUCT MIXTURES OBTAINED WITH SELECTED SUBSTRATES (LISTED IN TABLE S1).

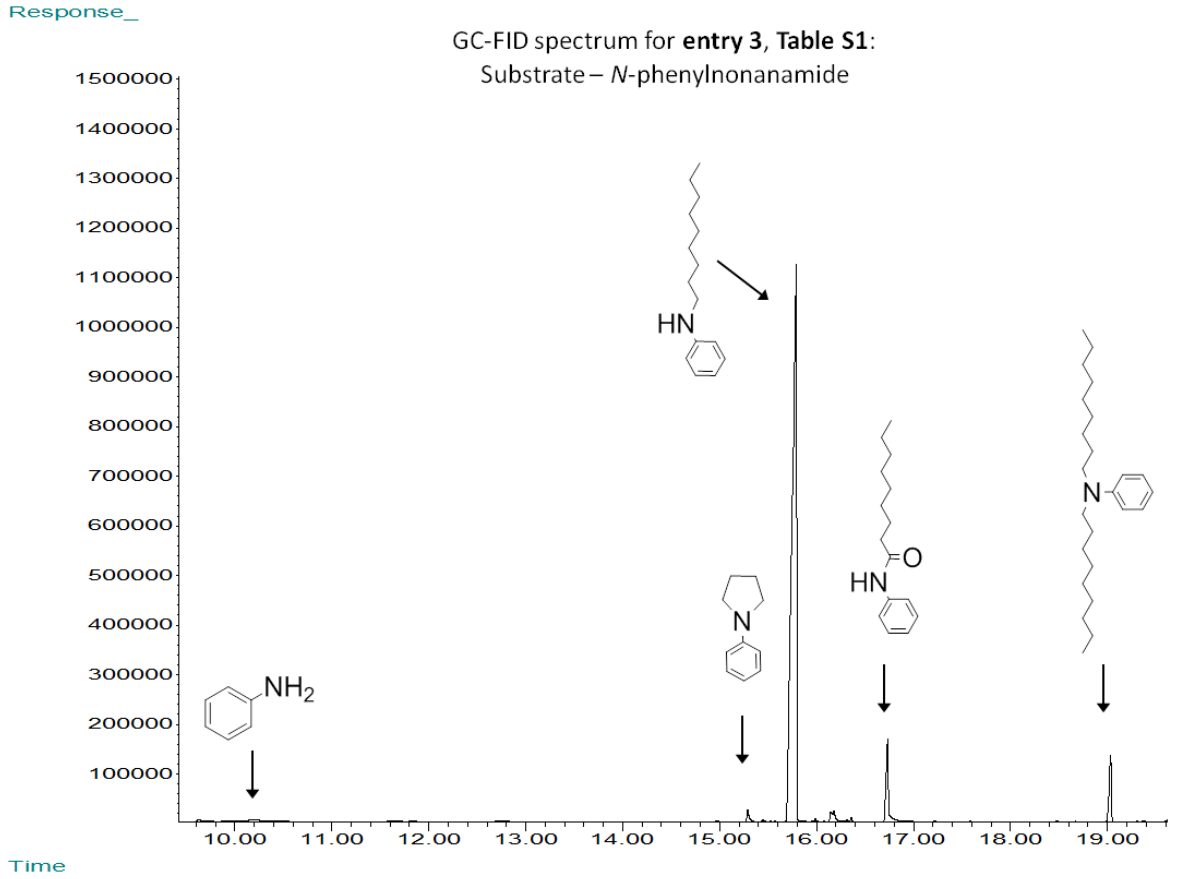
Table S1. Substrate scope for [Ru(acac)$_3$] / triphos catalysed amide hydrogenations.

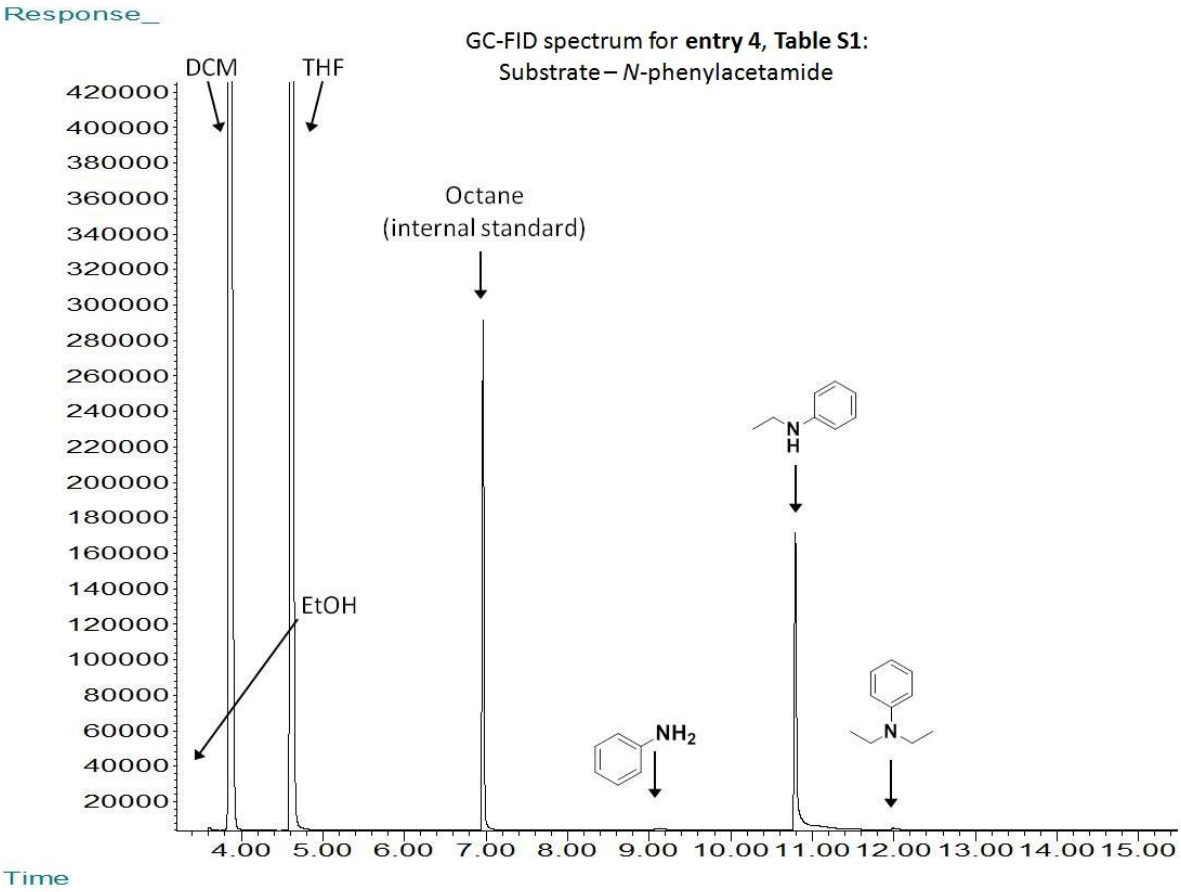
Entry	Substrate	MSA (mol %)	Temp (° C)	P_{H_2} (bar)	Conv. (%)	Sel. (%)	Entry	Substrate	MSA (mol %)	Temp (° C)	P_{H_2} (bar)	Conv. (%)	Sel. (%)
Primary amide [b]													
1		1.5	200	10	100	61							
Secondary amides													
2		1.5	200	10	82 [c]	<5 [c]	**11**		1.5	200	10	45	0
3		1.5	200	10	92 [d]	92 [d]	**12**		1.5	200	10	100	0
4		1.5	200	10	100 [e]	92 [e]	**13**		1.0	220	10	97	78
5		1.0	220	10	98	78	**14**		1.5	200	10	15 [f]	<5 [f]
6		1.5	200	10	100	79	**15**		1.0	220	10	100	92
7		1.5	200	10	100	90	**16**		1.5	200	10	100	94
8		1.0	220	10	99	77	**17**		1.5	200	10	92 [c]	61 [c]
9		1.5	200	10	64	28	**18**		1.5	220	10	100	<5
10		1.5	200	10	75	75							
Tertiary amides													
19		1.5	220	10	92	73	**22**		1.0	220	40	83	42
20		1.5	220	10	33 [c]	7 [c]	**23**		1.5	200	10	19	100
21		1.5	200	10	19	63	**24**		1.5	200	10	0	0

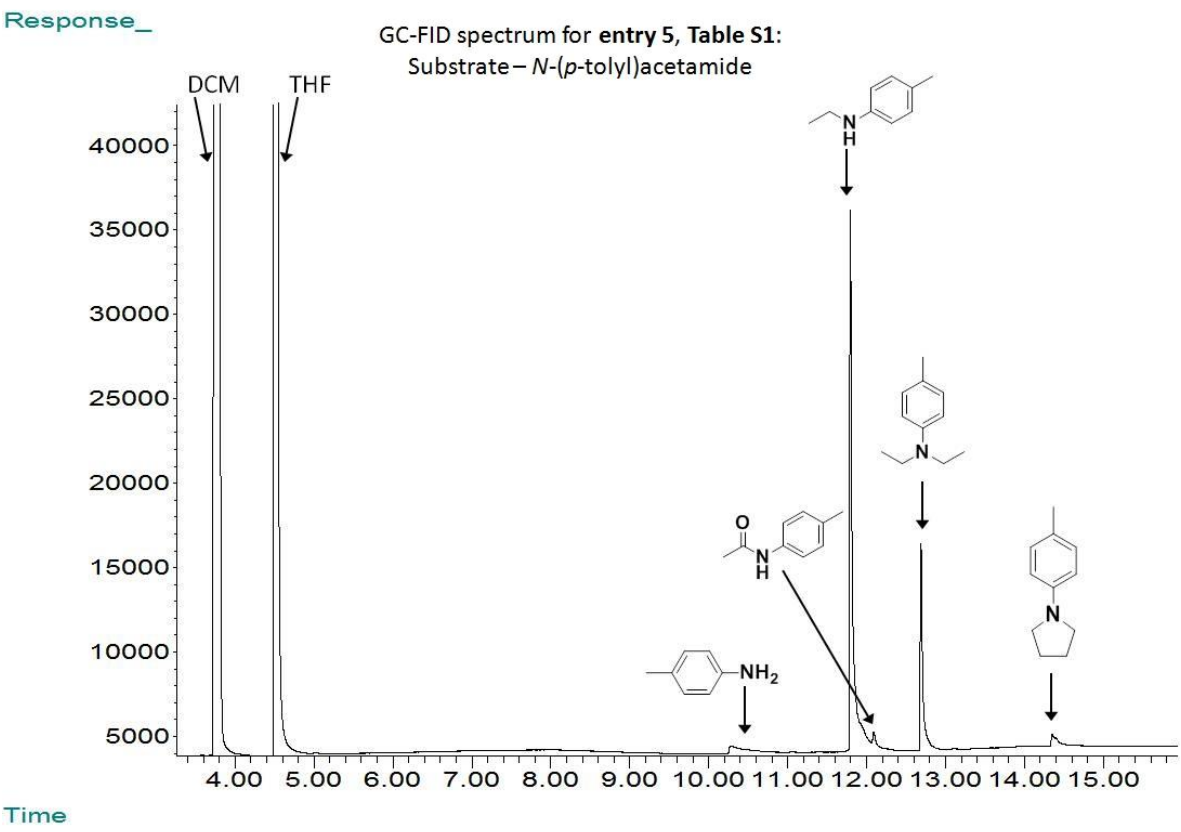
[a] Conditions: Substrate (5 mmol), [Ru(acac)$_3$] (1 mol %), triphos (2 mol %), thf (10 ml), 16 h. Conv. and Sel. calculated using NMR integration. [b] Reaction performed in the presence of NH_3(aq) (10 ml). [c] Based on uncalibrated GC–FID integration. [d] Conv. 86%, Sel. 78% in Lit.[5] [e] The Sel. for different reactions with *N*-phenylacetamide under identical conditions varies between 86-92 %. In the presence of added mercury, 100% Conv. with 84 % Sel. was obtained. [f] Small amounts of mixed tertiary amines formed.

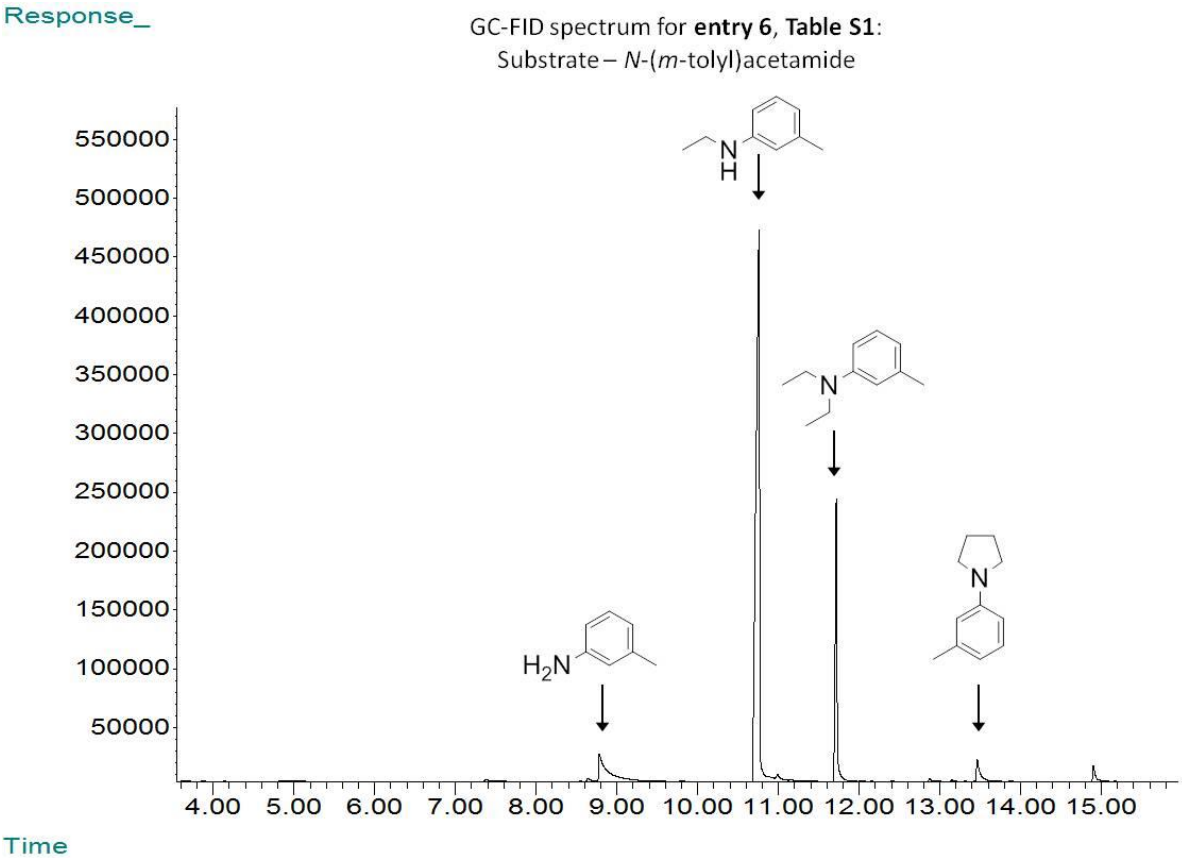

Response_
GC-FID spectrum for **entry 1, Table S1** :
Substrate – Butaramide
THF
NH_2
OH (masked by benzene)
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
4.00
5.00
6.00
7.00
8.00
9.00
10.00
11.00
Time

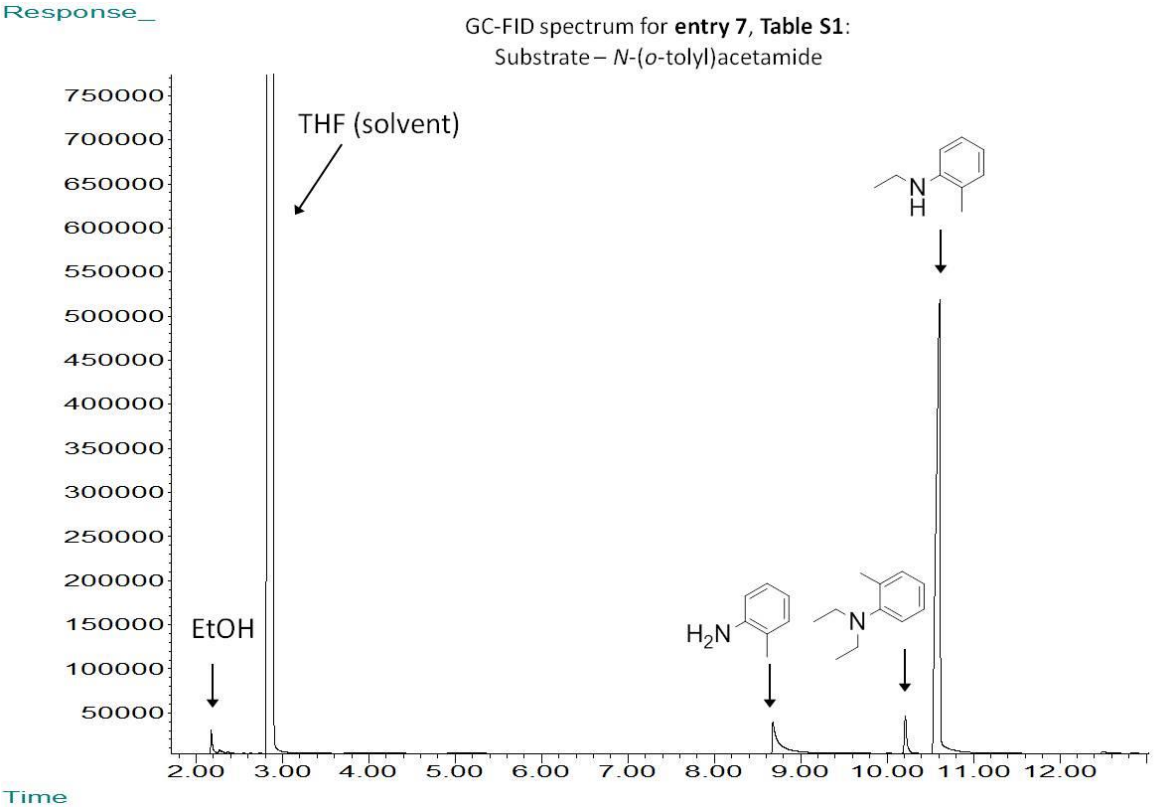

Response_
GC-FID spectrum for **entry 2, Table S1**:
Substrate – *N*-methylbenzamide
DCM
THF
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
4.00
6.00
8.00
10.00
12.00
14.00
16.00
18.00
20.00
22.00
Time

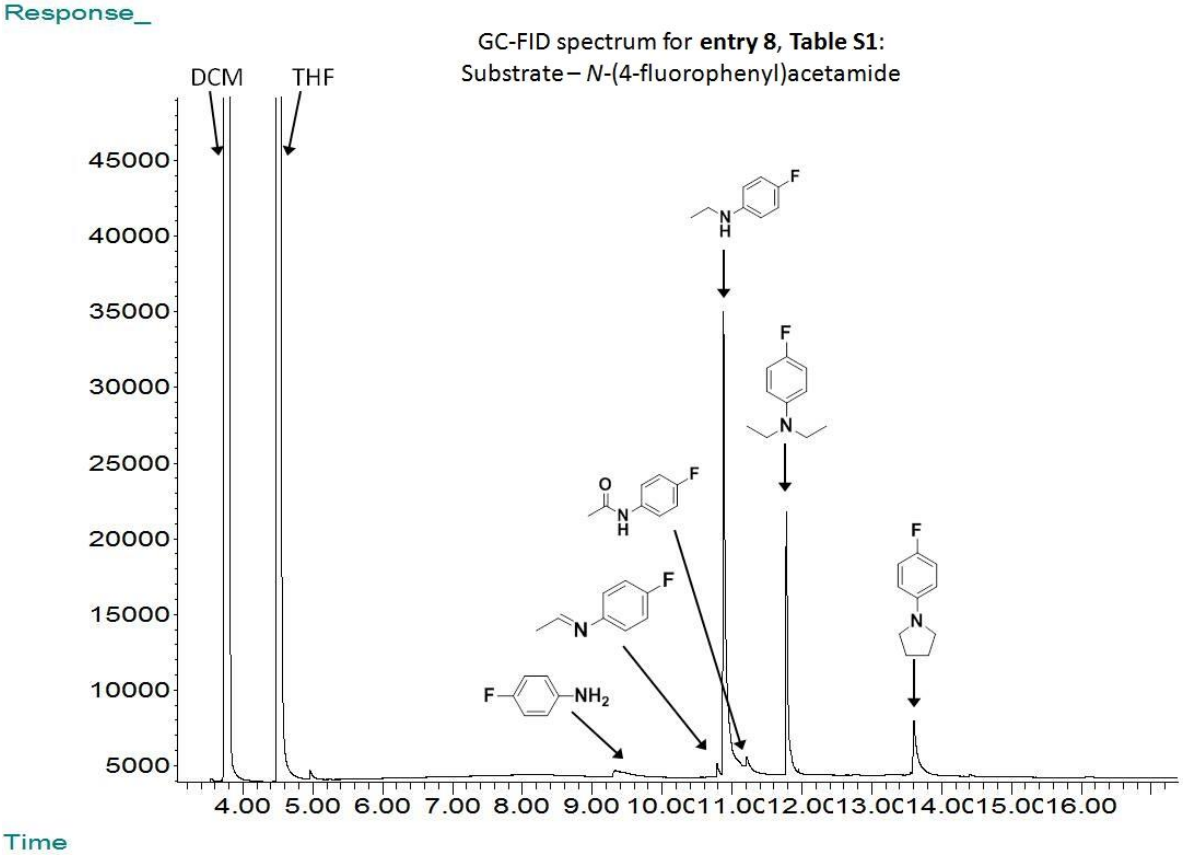

Response_
GC-FID spectrum for **entry 3**, **Table S1**:
Substrate – *N*-phenylnonanamide
1500000
1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
HN
N
HN
O
N
NH2
10.00
11.00
12.00
13.00
14.00
15.00
16.00
17.00
18.00
19.00
Time

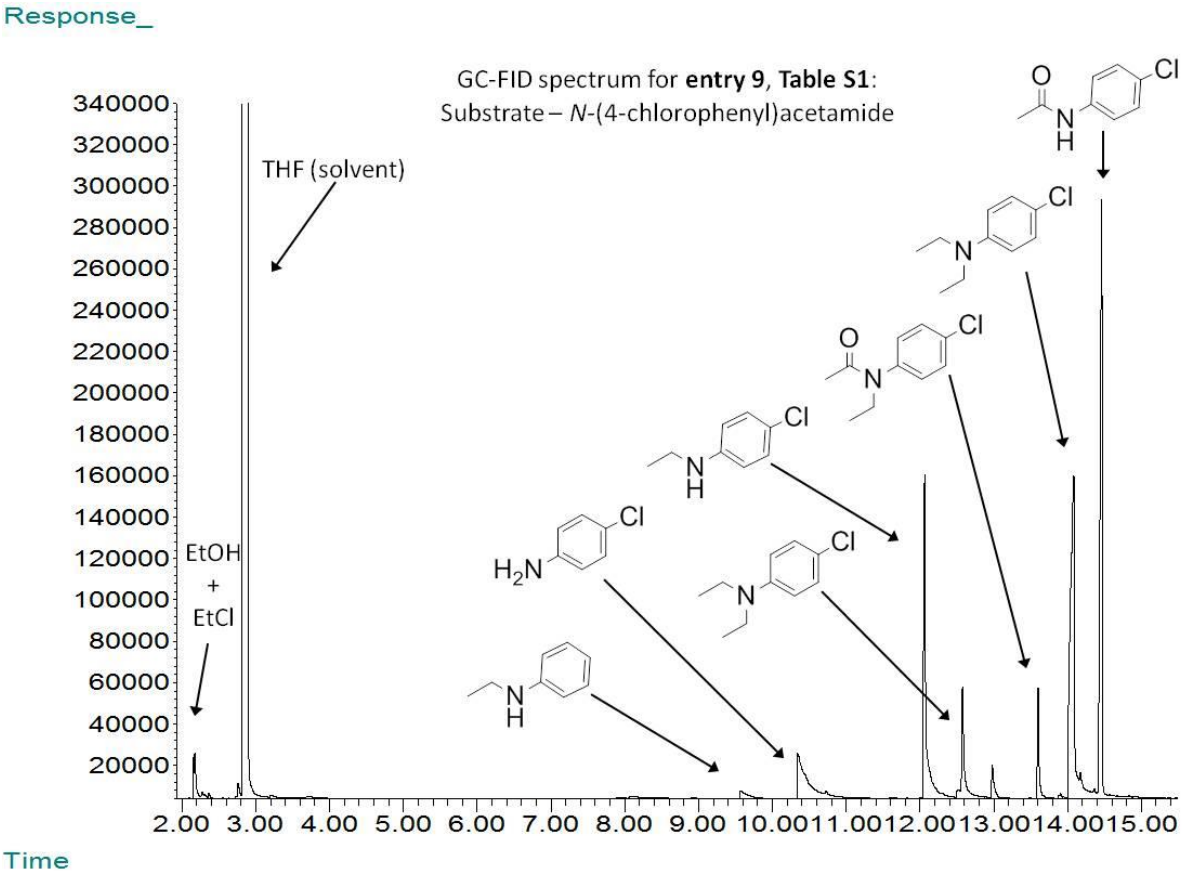

Response_
GC-FID spectrum for **entry 4**, **Table S1**:
Substrate – *N*-phenylacetamide
DCM
THF
Octane
(internal standard)
EtOH
420000
400000
380000
360000
340000
320000
300000
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
N
H
NH2
N
4.00
5.00
6.00
7.00
8.00
9.00
10.00
11.00
12.00
13.00
14.00
15.00
Time

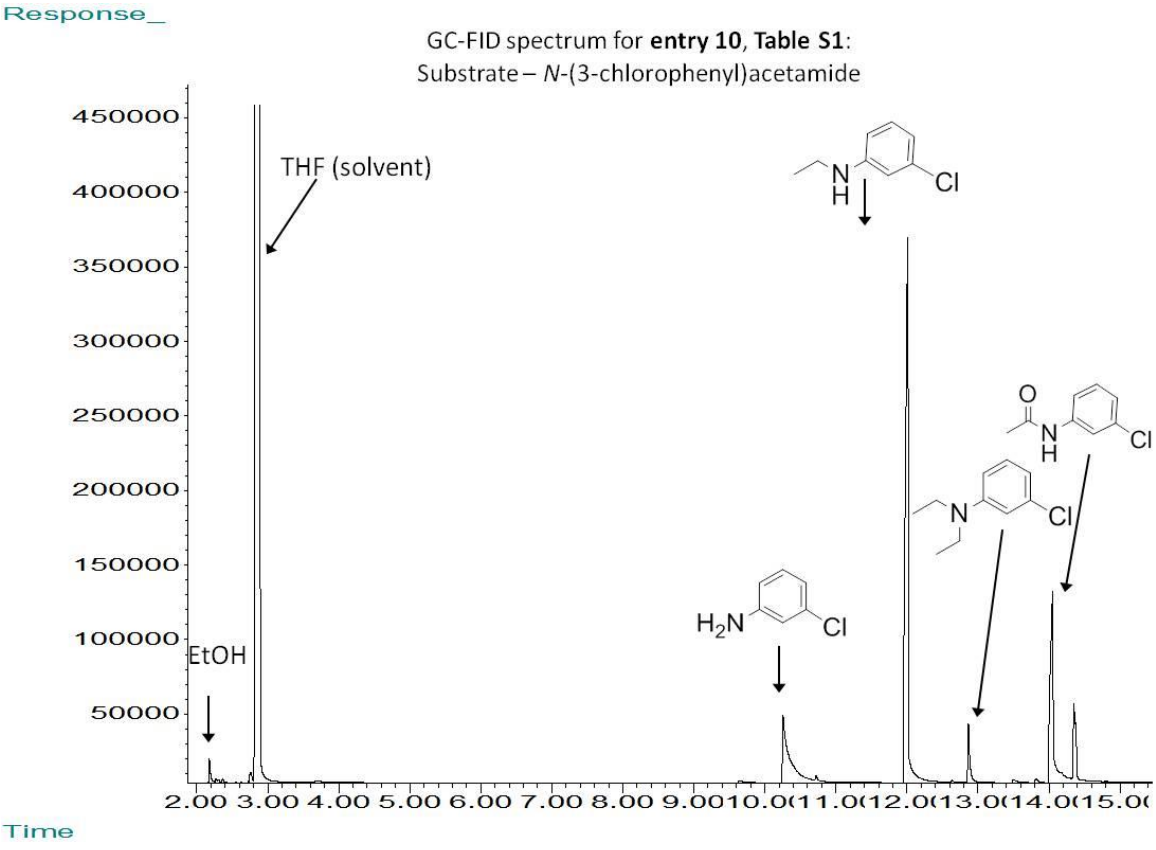

Response_
GC-FID spectrum for **entry 5**, **Table S1**:
Substrate – *N*-(*p*-tolyl)acetamide
DCM
THF
40000
35000
30000
25000
20000
15000
10000
5000
4.00 5.00 6.00 7.00 8.00 9.00 10.00 11.00 12.00 13.00 14.00 15.00
Time

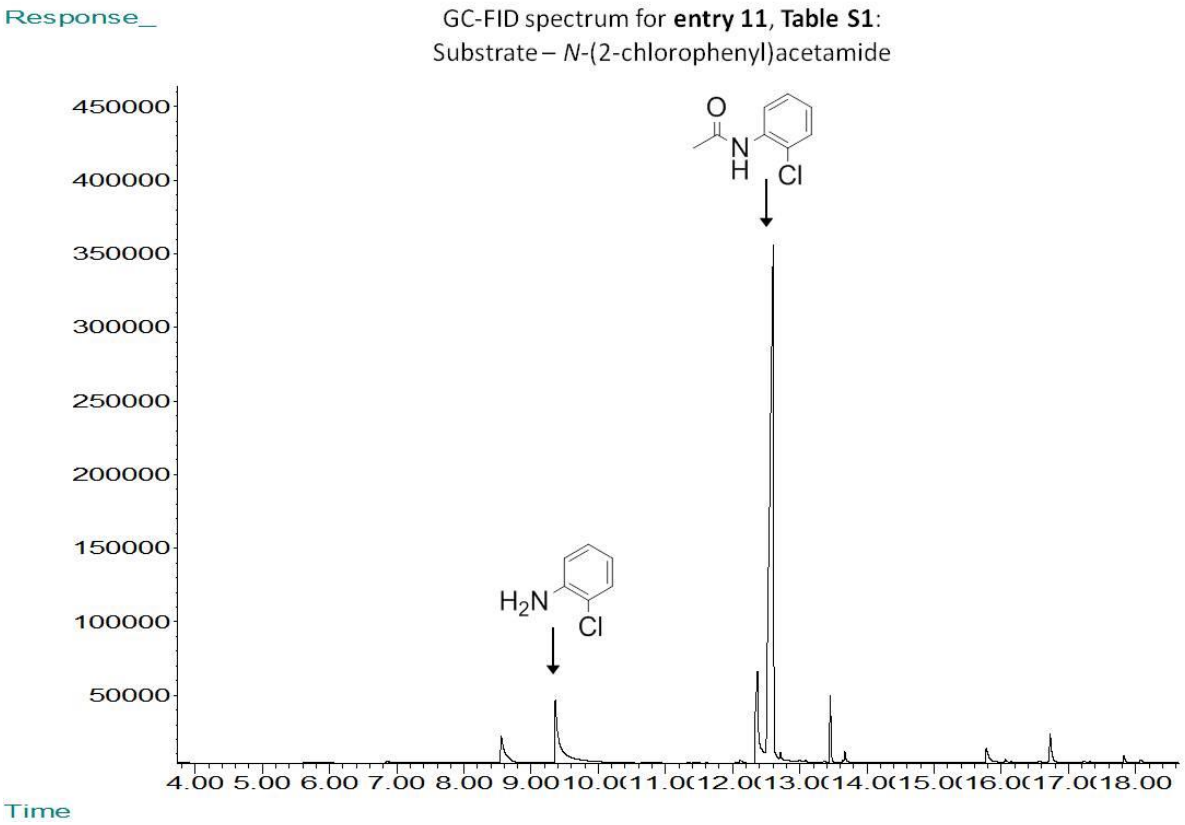

Response_
GC-FID spectrum for **entry 6**, **Table S1**:
Substrate – *N*-(*m*-tolyl)acetamide
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
4.00 5.00 6.00 7.00 8.00 9.00 10.00 11.00 12.00 13.00 14.00 15.00
Time

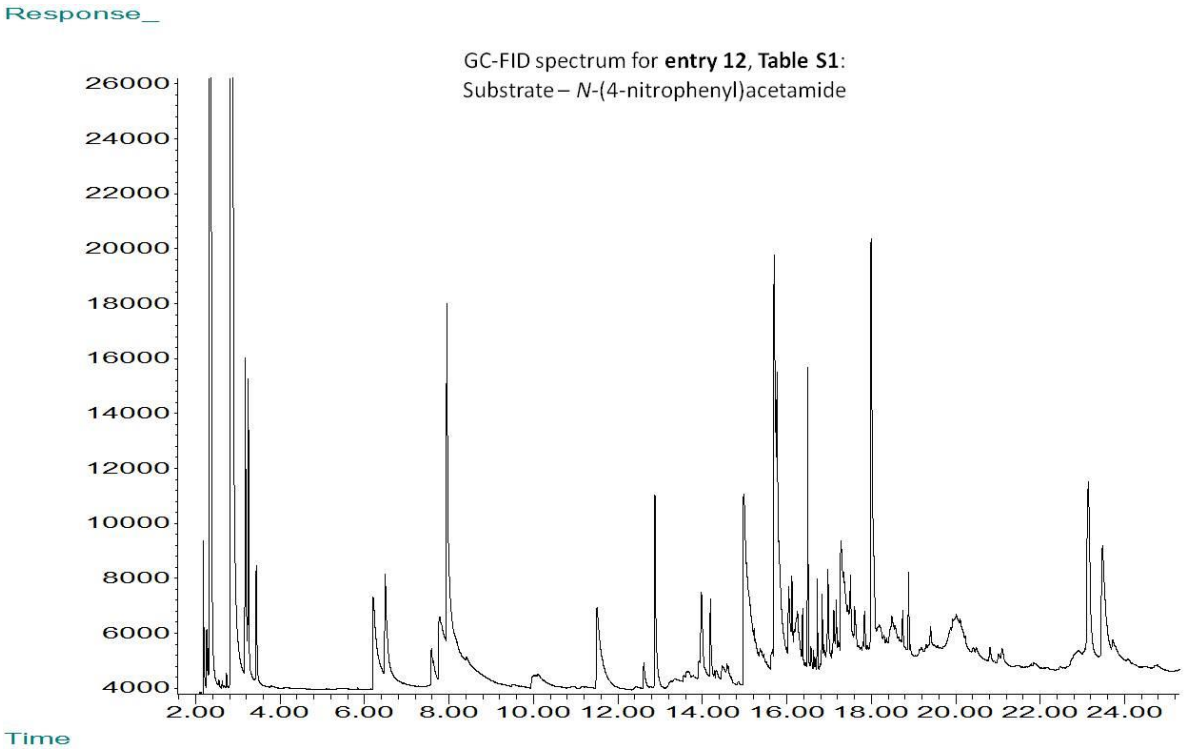

Response_
GC-FID spectrum for **entry 7**, **Table S1**:
Substrate – *N*-(*o*-tolyl)acetamide
THF (solvent)
EtOH
Time

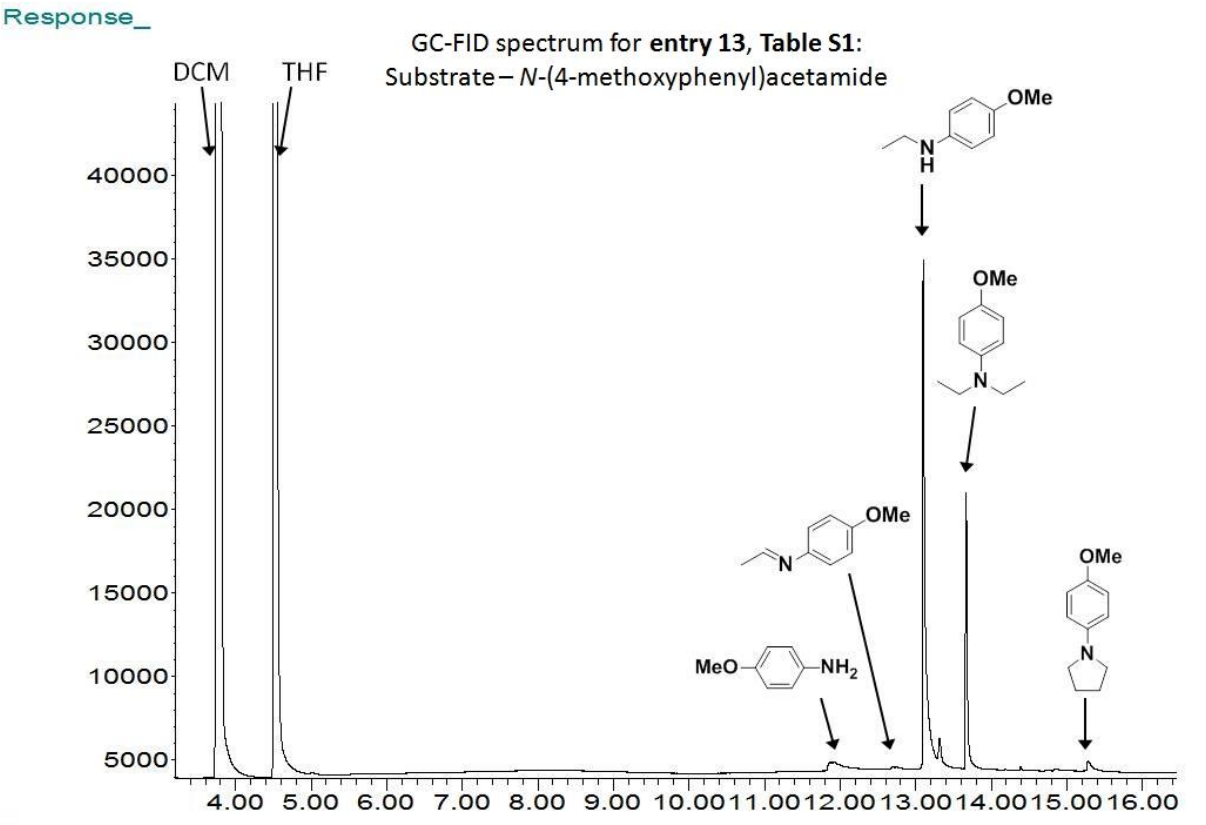

Response_
GC-FID spectrum for **entry 8**, **Table S1**:
Substrate – *N*-(4-fluorophenyl)acetamide
DCM
THF
Time

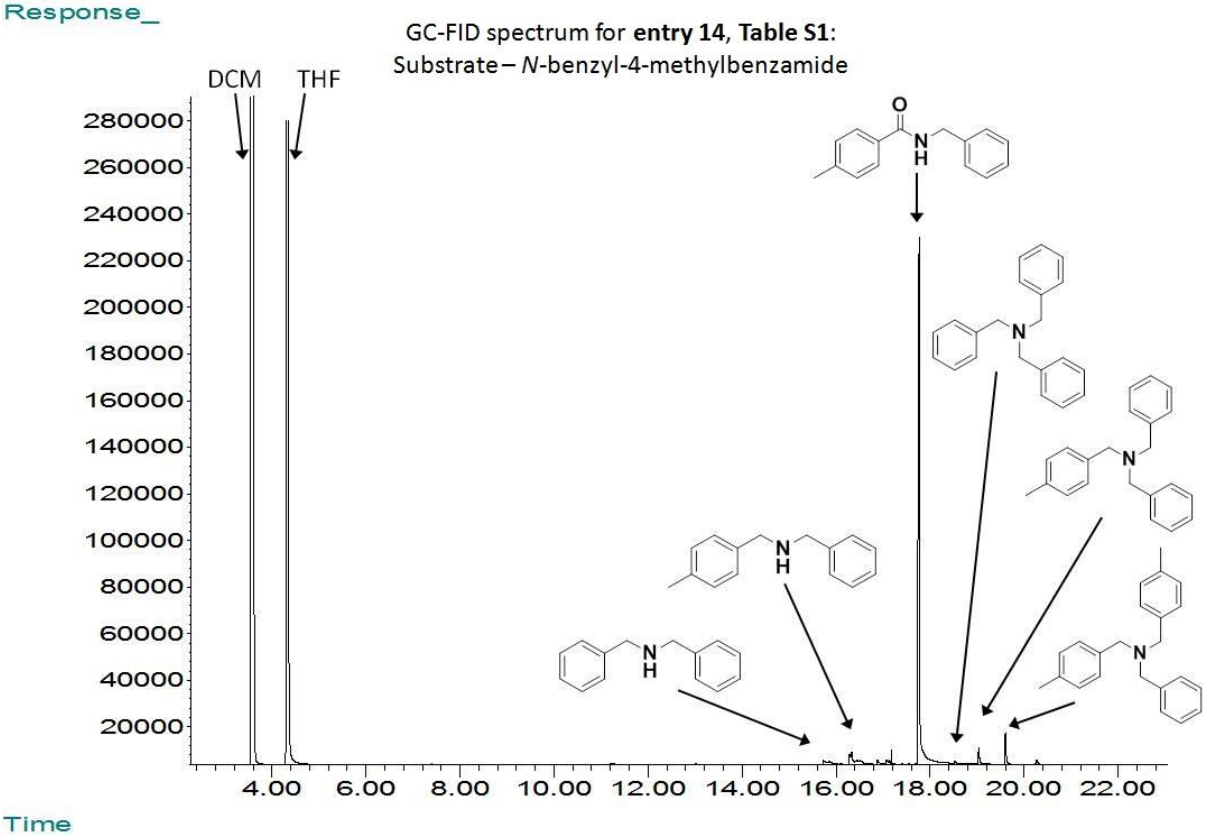

Response_
GC-FID spectrum for **entry 9**, **Table S1**:
Substrate – *N*-(4-chlorophenyl)acetamide
THF (solvent)
EtOH
+
EtCl
Time

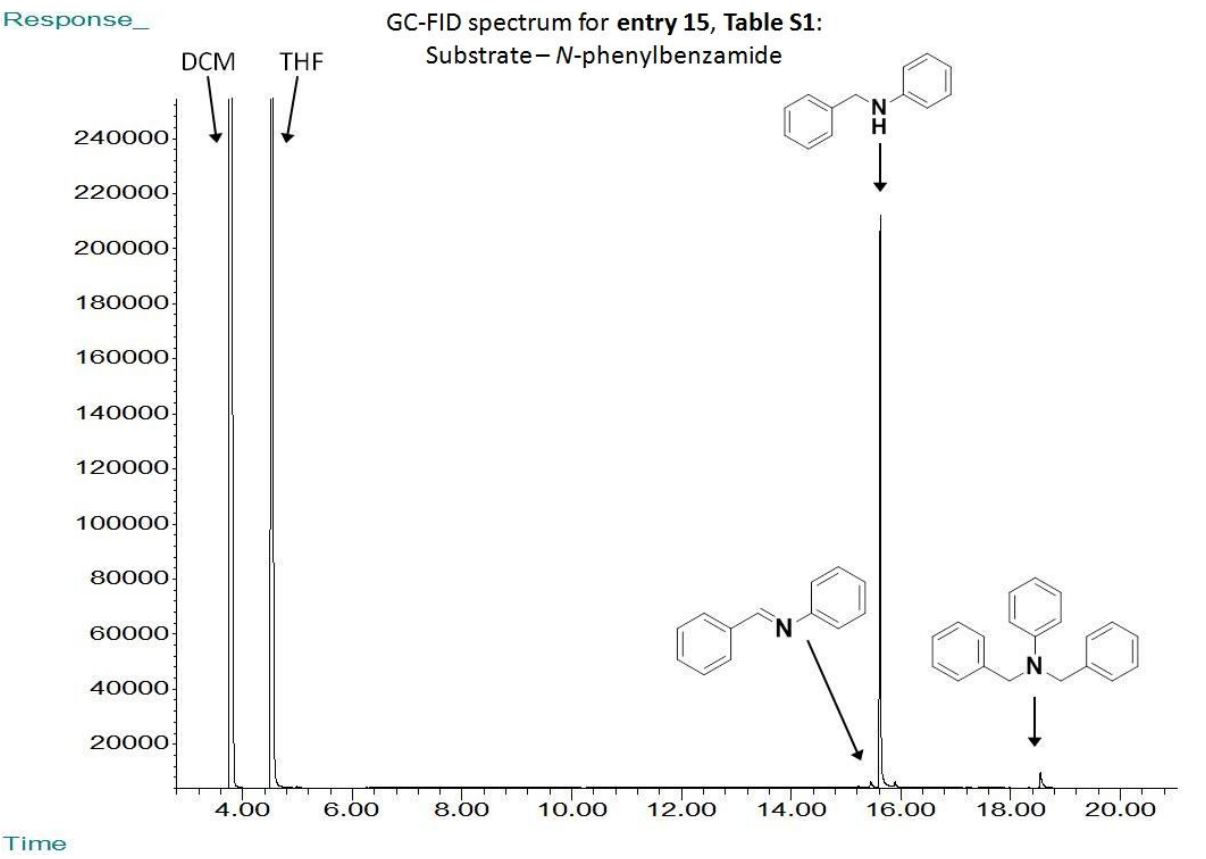

Response_
GC-FID spectrum for **entry 10**, **Table S1**:
Substrate – *N*-(3-chlorophenyl)acetamide
THF (solvent)
EtOH
Time

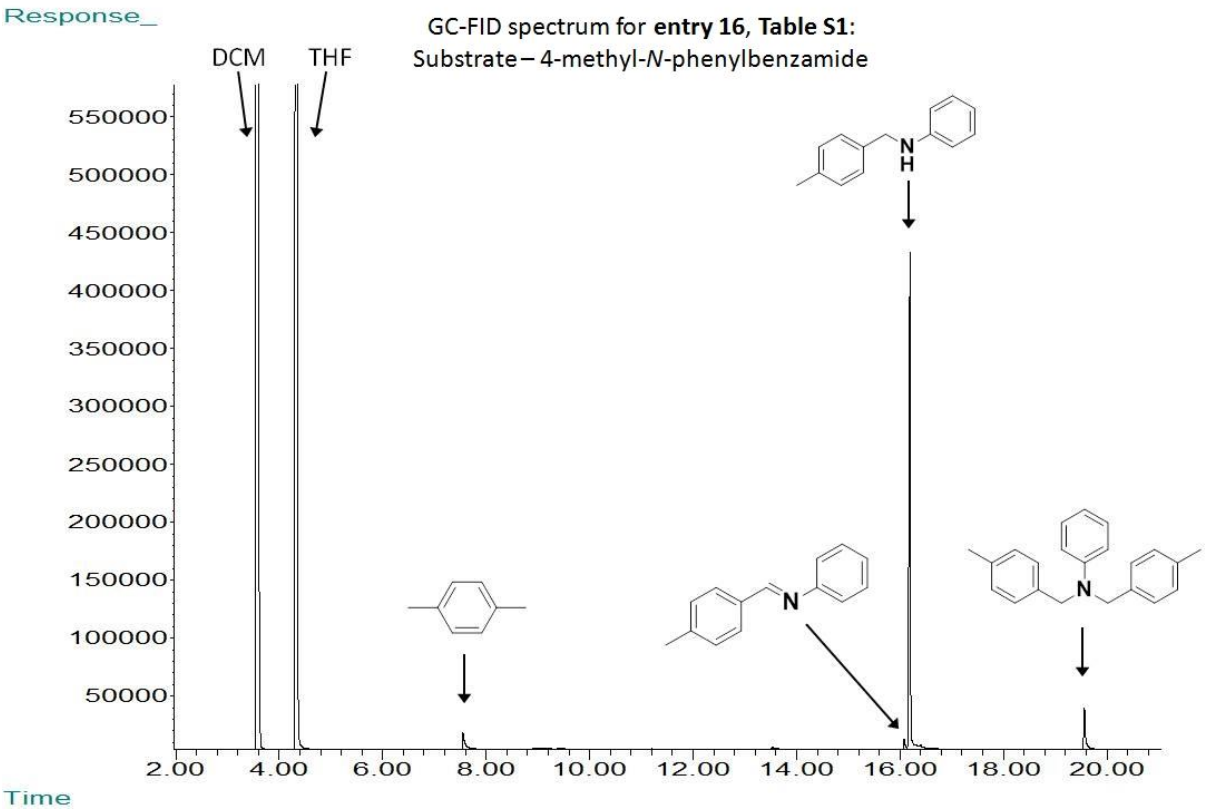

Response_
GC-FID spectrum for entry 11, Table S1:
Substrate – N-(2-chlorophenyl)acetamide
450000
400000
350000
300000
250000
200000
150000
100000
50000
O
N
H
Cl
H2N
Cl
4.00 5.00 6.00 7.00 8.00 9.00 10.0 11.0 12.0 13.0 14.0 15.0 16.0 17.0 18.00
Time

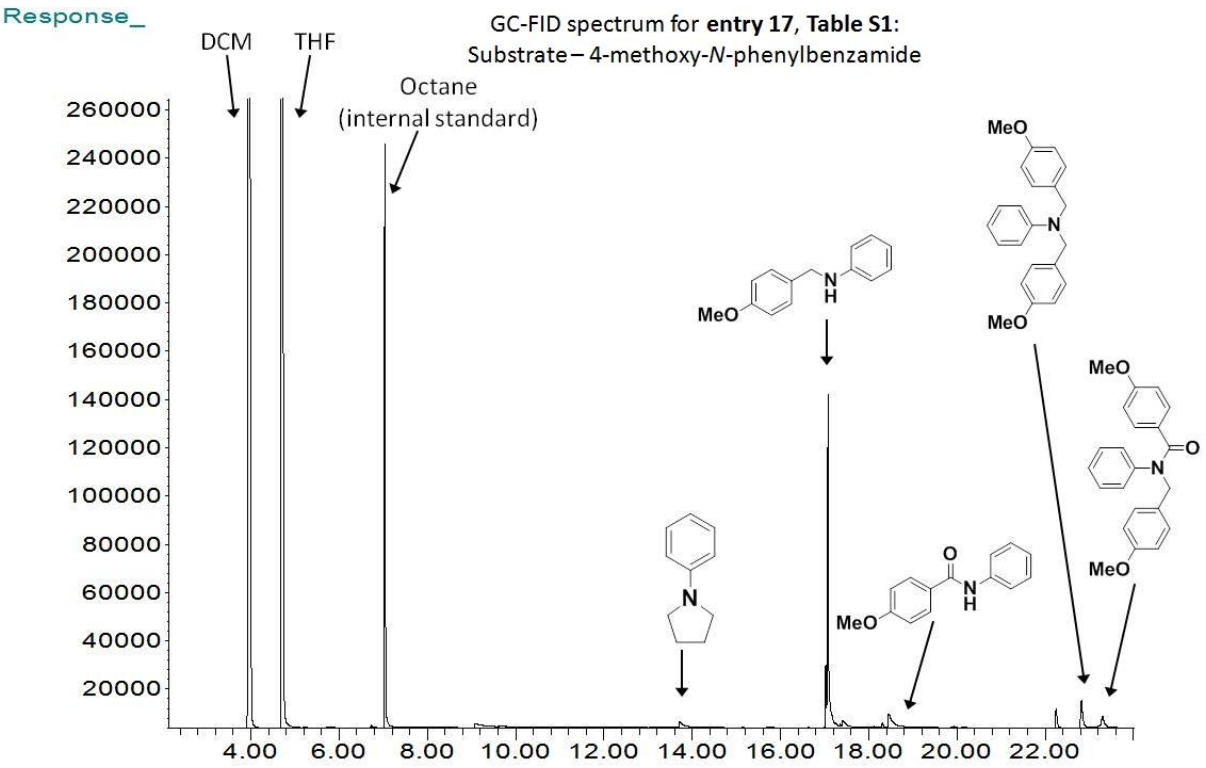

Response_
GC-FID spectrum for entry 12, Table S1:
Substrate – N-(4-nitrophenyl)acetamide
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2.00 4.00 6.00 8.00 10.00 12.00 14.00 16.00 18.00 20.00 22.00 24.00
Time

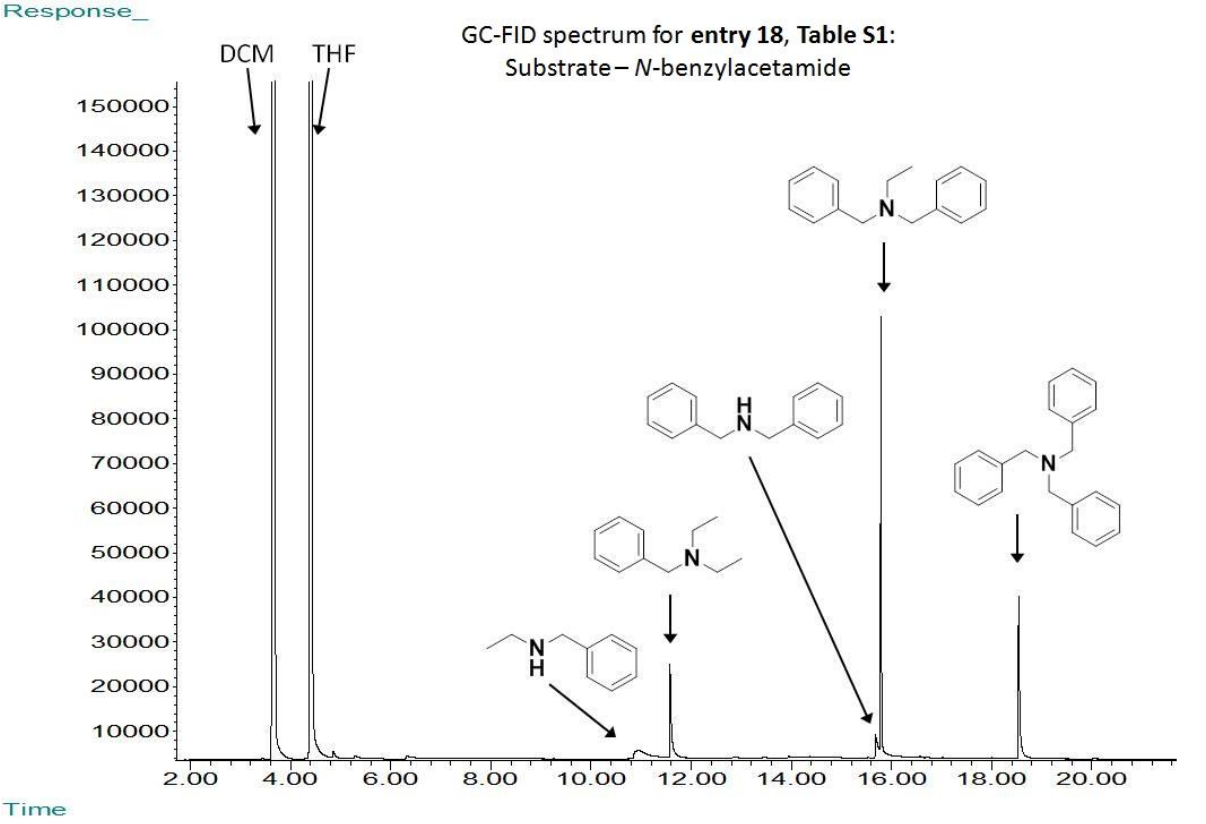

Response_
GC-FID spectrum for **entry 13**, **Table S1**:
Substrate – *N*-(4-methoxyphenyl)acetamide
DCM
THF
OMe
OMe
OMe
OMe
MeO
NH2
40000
35000
30000
25000
20000
15000
10000
5000
4.00 5.00 6.00 7.00 8.00 9.00 10.00 11.00 12.00 13.00 14.00 15.00 16.00
Time

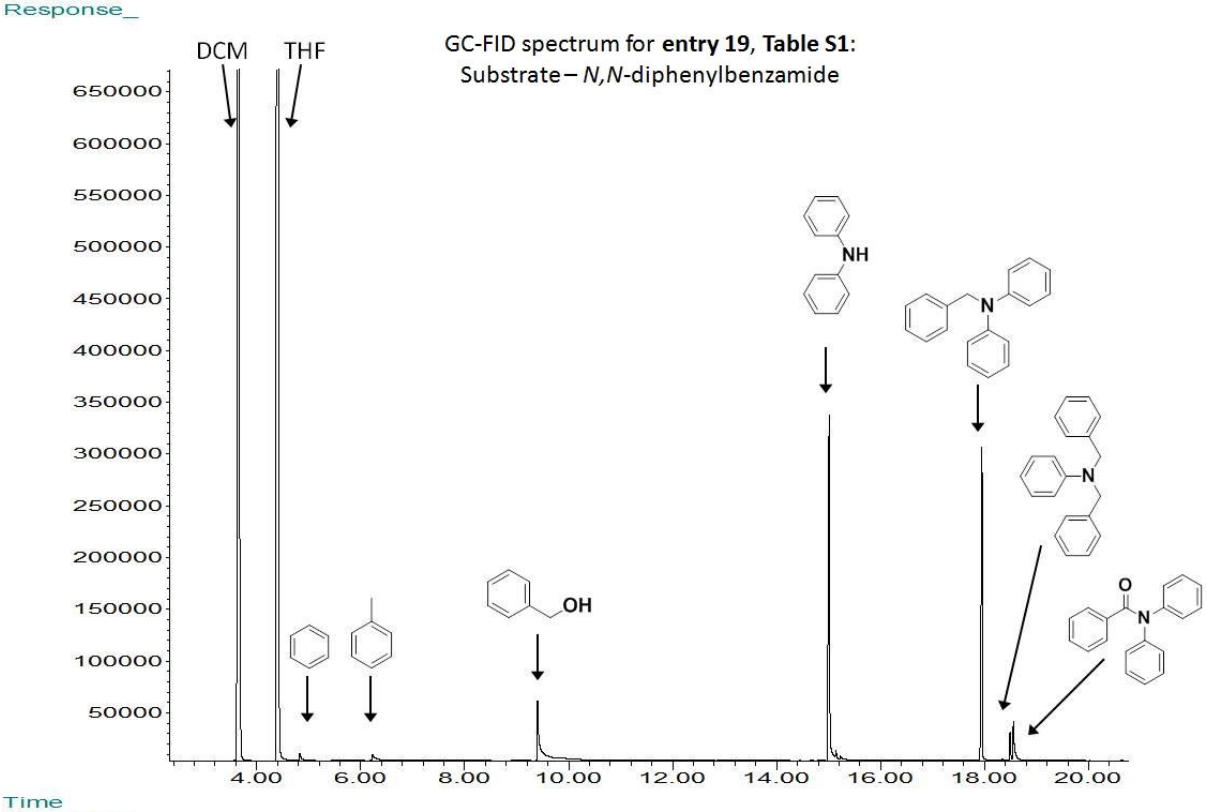

Response_
GC-FID spectrum for **entry 14**, **Table S1**:
Substrate – *N*-benzyl-4-methylbenzamide
DCM
THF
O
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
4.00 6.00 8.00 10.00 12.00 14.00 16.00 18.00 20.00 22.00
Time

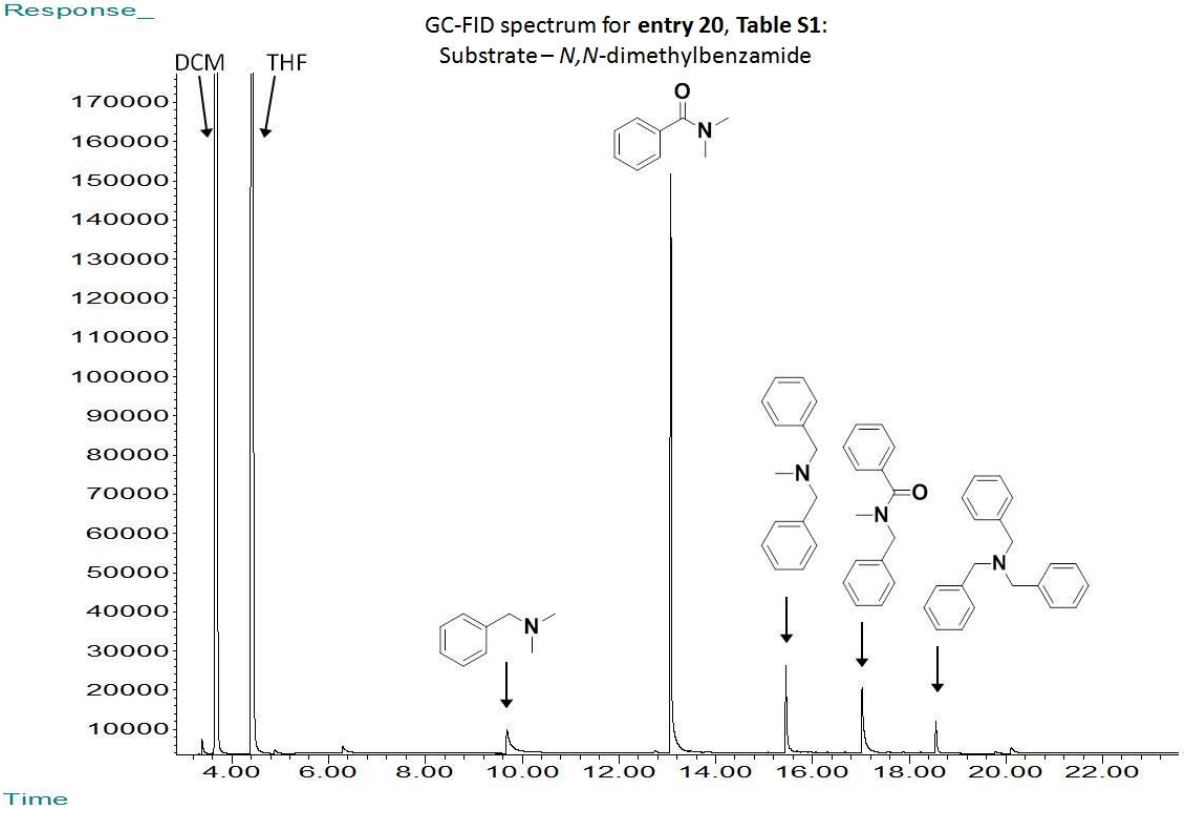

Response_
GC-FID spectrum for **entry 15, Table S1**:
Substrate – *N*-phenylbenzamide
DCM
THF
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
4.00
6.00
8.00
10.00
12.00
14.00
16.00
18.00
20.00
Time

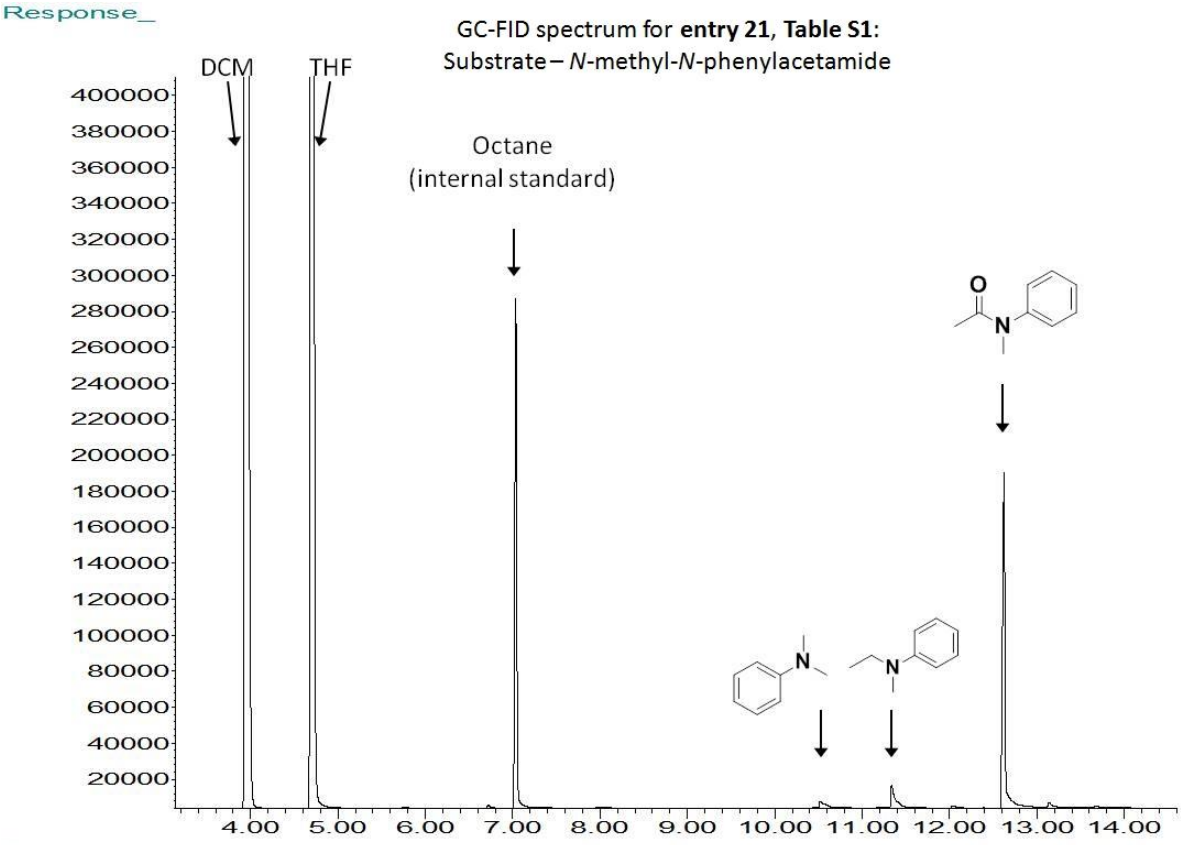

Response_
GC-FID spectrum for **entry 16, Table S1**:
Substrate – 4-methyl-*N*-phenylbenzamide
DCM
THF
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
2.00
4.00
6.00
8.00
10.00
12.00
14.00
16.00
18.00
20.00
Time

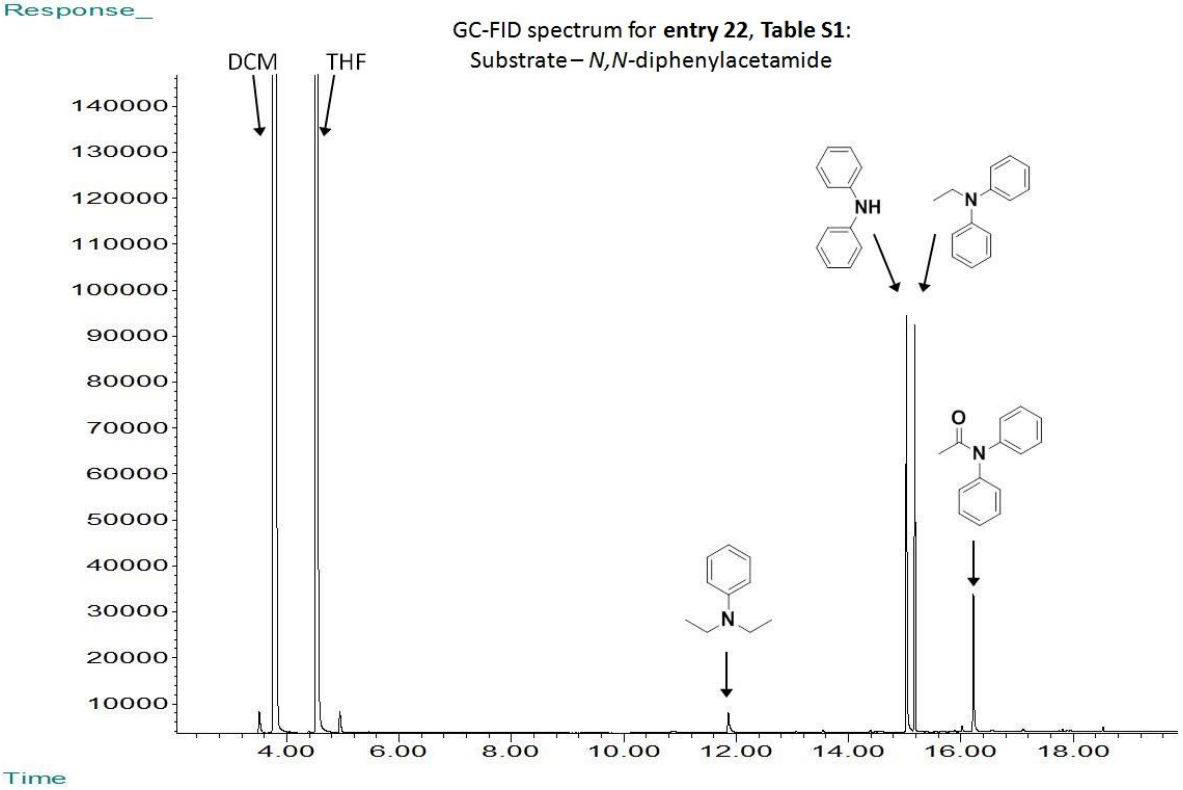

Response_
GC-FID spectrum for **entry 17**, **Table S1**:
Substrate – 4-methoxy-*N*-phenylbenzamide
DCM
THF
Octane
(internal standard)
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
4.00
6.00
8.00
10.00
12.00
14.00
16.00
18.00
20.00
22.00
Time
MeO
N
H
O

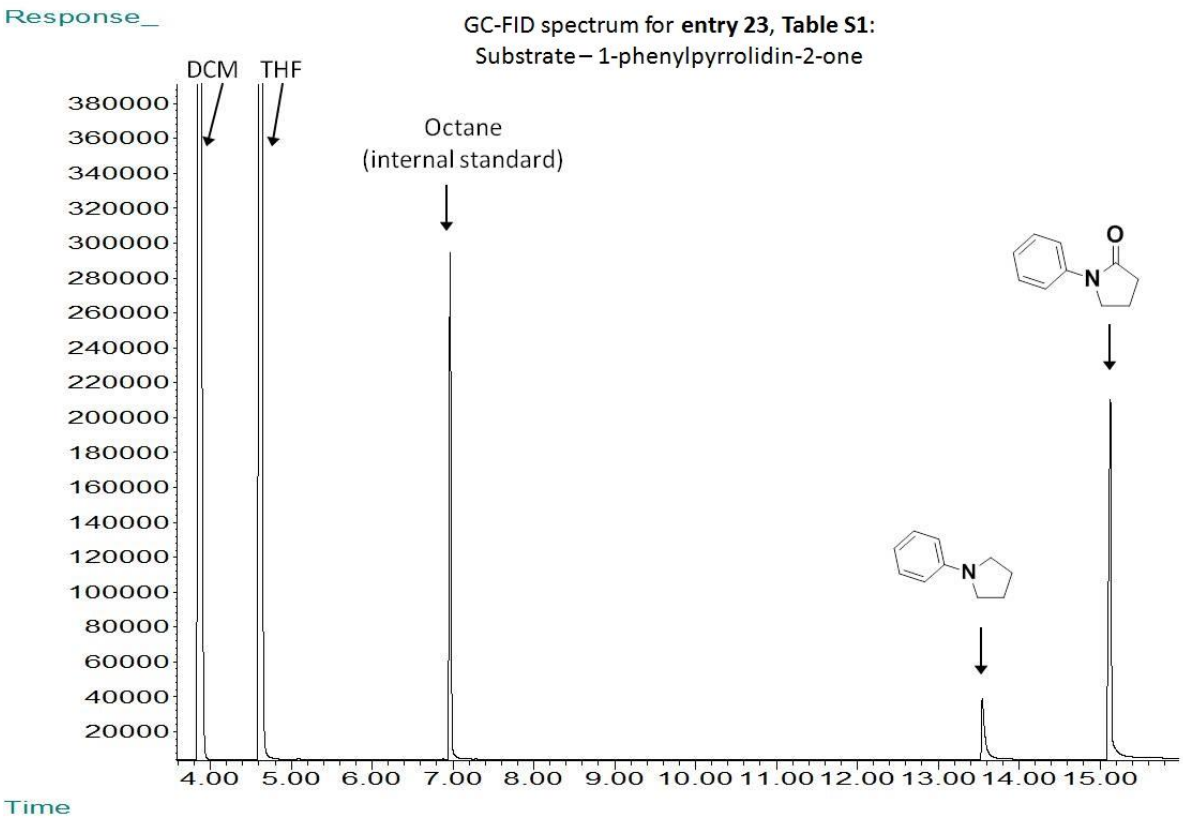

Response_
GC-FID spectrum for **entry 18**, **Table S1**:
Substrate – *N*-benzylacetamide
DCM
THF
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
2.00
4.00
6.00
8.00
10.00
12.00
14.00
16.00
18.00
20.00
Time
N
H


Response_
GC-FID spectrum for **entry 19**, **Table S1**:
Substrate – *N,N*-diphenylbenzamide
DCM
THF
650000
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
NH
N
N
OH
O
N
4.00
6.00
8.00
10.00
12.00
14.00
16.00
18.00
20.00
Time


Response_
GC-FID spectrum for **entry 20**, **Table S1**:
Substrate – *N,N*-dimethylbenzamide
DCM
THF
170000
160000
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
O
N
N
N
O
N
N
4.00
6.00
8.00
10.00
12.00
14.00
16.00
18.00
20.00
22.00
Time

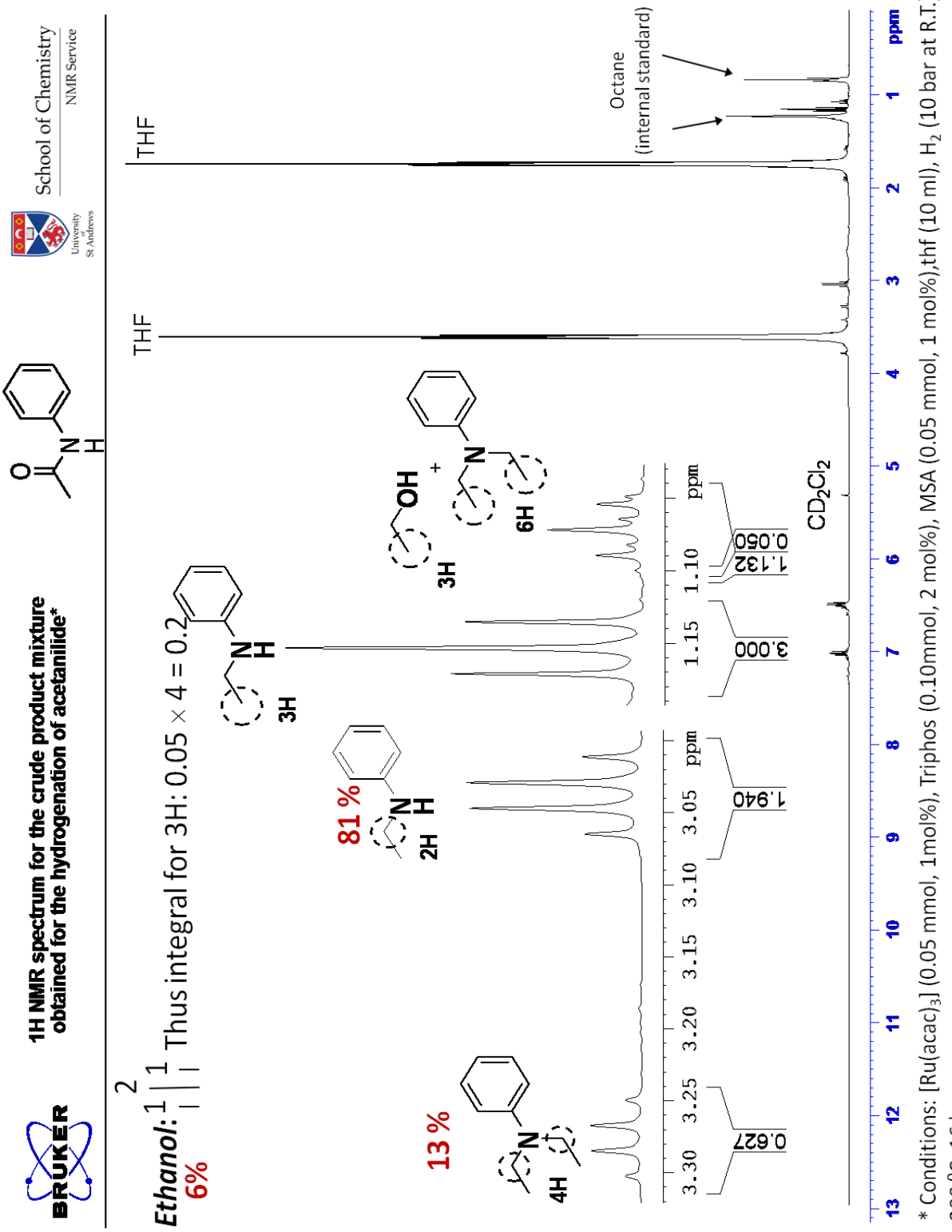

Response_
GC-FID spectrum for **entry 21**, **Table S1**:
Substrate – *N*-methyl-*N*-phenylacetamide
DCM
THF
Octane
(internal standard)
400000
380000
360000
340000
320000
300000
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
4.00
5.00
6.00
7.00
8.00
9.00
10.00
11.00
12.00
13.00
14.00
Time


Response_
GC-FID spectrum for **entry 22**, **Table S1**:
Substrate – *N*,*N*-diphenylacetamide
DCM
THF
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
4.00
6.00
8.00
10.00
12.00
14.00
16.00
18.00
Time


Response_
GC-FID spectrum for entry 23, Table S1:
Substrate – 1-phenylpyrrolidin-2-one
DCM
THF
Octane
(internal standard)
380000
360000
340000
320000
300000
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
4.00
5.00
6.00
7.00
8.00
9.00
10.00
11.00
12.00
13.00
14.00
15.00
O
N
N
Time

■ SECTION S-5: EXAMPLE OF QUANTIFICATION BASED ON ^{1}H NMR INTEGRATION

[example substrate – *N*-phenylacetamide (trivial name - acetanilide)]



■ SECTION S-6: CRYSTALLOGRAPHIC DATA TABLES

Table S2. Crystallographic data for compounds 11 and 12.

Parameter	Compound 11	Compound 12
Chemical formula	$C_{45}H_{45}O_4P_3Ru$	$C_{86}H_{90}O_{12}P_6Ru_2S_4$
Formula weight (g/mol)	843.83	1831.87
Temp. (K)	93(2)	93(2)
Wavelength (Å)	0.71075	0.71075
Crystal system	Monoclinic	Triclinic
Crystal dimensions (mm^3)	$0.20 \times 0.20 \times 0.20$	$0.03 \times 0.03 \times 0.03$
Crystal shape and colour	Prism, yellow	Prism, yellow
Space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
a (Å)	10.057(2)	12.5217(5)
b (Å)	15.075(3)	12.6970(5)
c (Å)	29.442(6)	31.500(3)
α (°)	90.0000	78.307(5)
β (°)	96.663(5)	81.575(6)
γ (°)	90.0000	68.302(5)
Unit cell volume ($Å^3$)	4433.7(15)	4542.6(5)
No. of formula units per unit cell, Z	4	2
d_{calcd} (g/cm^3)	1.573	1.525
Radiation type	MoKα	MoKα
Absorption coefficient, μ (mm^{-1})	0.797	0.766
F(000)	2152	2140
θ-range for data collection (°)	2.04 to 25.35	3.06 to 25.41
Index range	$-11 \le h \le 12$, $-18 \le k \le 14$, $-33 \le l \le 35$	$-10 \le h \le 10$, $-15 \le k \le 15$, $-37 \le l \le 37$
No. of reflections measured	26754	46062
No. of unique reflections	8051	16487
Refinement parameters / restraints	562 / 0	1078 / 18
R_{int}	0.0943	0.0678
Final R_1 values ($I > 2\sigma(I)$)	0.0729	0.0864
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.2099	0.2241
Final R_1 values (all data)	0.0914	0.1126
Final $wR(F^2)$ values (all data)	0.2393	0.2427
Goodness of fit on F^2	1.078	1.037
Largest diff. peak and hole ($e.A^{-3}$)	1.500 and -2.250	7.640 and -2.560
Weighing scheme †	a = 0.1406 b = 8.3130	a = 0.1063 b = 70.0913

* The full Crystallographic Information Framework (CIF) files are also available as electronic supporting information.
† $wR2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2)+(aP)^2+bP+d+\sin\theta]$; $P = [f(\text{Max}(0 \text{ or } F_o^2)] + (1-f)\ F_c^2$

Table S3. Crystallographic data for compounds 19 and 20.

Parameter	Compound 19	Compound 20
Chemical formula	$C_{43}H_{47}O_7P_3Ru$	$C_{45}H_{47}O_5P_3Ru$
Formula weight (g/mol)	869.82	861.84
Temp. (K)	93(2)	93(2)
Wavelength (Å)	0.71075	0.71075
Crystal system	Monoclinic	Monoclinic
Crystal dimensions (mm^3)	0.12 × 0.10 × 0.03	0.03 × 0.03 × 0.03
Crystal shape and colour	Prism, yellow	Prism, yellow
Space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
a (Å)	12.702(2)	11.969(2)
b (Å)	31.997(6)	20.106(4)
c (Å)	24.329(5)	16.576(3)
α (°)	90.00	90.00
β (°)	100.330(2)	102.415(3)
γ (°)	90.00	90.00
Unit cell volume ($Å^3$)	9727(3)	3895.6(12)
No. of formula units per unit cell, Z	8	4
d_{calcd} (g/cm^3)	1.612	1.469
Radiation type	MoKα	MoKα
Absorption coefficient, μ (mm^{-1})	0.887	0.573
F(000)	4824	1784
θ-range for data collection (°)	1.70 to 25.42	1.62 to 25.35
Index range	-15 ≤ h ≤ 15, -38 ≤ k ≤ 38, -29 ≤ l ≤ 29	-14 ≤ h ≤ 14, -23 ≤ k ≤ 24, -19 ≤ l ≤ 19
No. of reflections measured	97095	38423
No. of unique reflections	17854	7119
Refinement parameters / restraints	1159 / 4	498 / 0
R_{int}	0.0621	0.0346
Final R_1 values ($I > 2\sigma(I)$)	0.0951	0.0299
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.2385	0.0622
Final R_1 values (all data)	0.0989	0.0315
Final $wR(F^2)$ values (all data)	0.2413	0.0630
Goodness of fit on F^2	1.150	1.078
Largest diff. peak and hole ($e.A^{-3}$)	1.511 and -2.440	0.330 and -0.464
Weighing scheme †	a = 0.0973 b = 93.0135	a = 0.0193 b = 4.8610

* The full Crystallographic Information Framework (CIF) files are also available as electronic supporting information.
† $wR2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2)+(aP)^2+bP+d+\text{esin}\theta]$; $P = [f(\text{Max}(0 \text{ or } F_o^2)] + (1\text{-f}) F_c^2$

■ SECTION S-7: REFERENCES

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(2) Iengo, E.; Zangrando, E.; Baiutti, E.; Munini, F.; Alessio, E. *Eur. J. Inorg. Chem.* **2005**, 1019.
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(5) Stein, M.; Breit, B. *Angew. Chem. Int. Ed.* **2012**, DOI: 10.1002/anie.201207803.