Supporting Information

C(sp^3)−H oxygenation *via* alkoxypalladium(II) species: an update for the mechanism

Shuaizhong Zhang,‡ Jinquan Zhang ‡ and Hongbin Zou*

College of Pharmaceutical Sciences, Zhejiang University, Hangzhou, 310058, P. R. China

* Corresponding Author. Email: zouhb@zju.edu.cn

Table of Contents

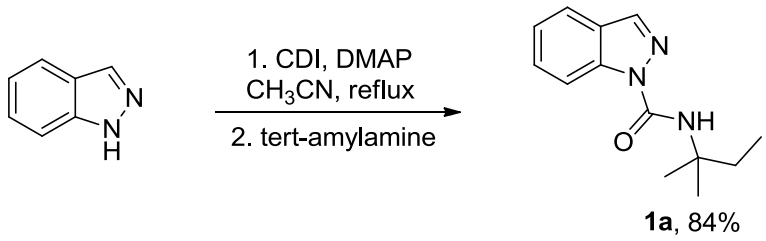
1. General Information

Catalytic reactions were carried out in Schlenk tubes using pre-dried glassware. *N*-(tert-pentyl)-1*H*-indazole-1-carboxamide **(1a)** was synthesized according to previously described procedures[1]. Commercially available reagents were purchased from Energy Chemical, Bidepharm, Sigma Aldrich, Alfa Aesar, Acros or TCI, and used without purification unless otherwise noted. Column chromatography purification was performed using 200–300 mesh silica gel. NMR spectra were mostly recorded for ^{1}H NMR at 500 MHz and for ^{13}C NMR at 125 MHz. $CDCl_3$ was used as solvent. Chemical shifts were referenced relative to residual solvent signal ($CDCl_3$: ^{1}H NMR: δ 7.26 ppm, ^{13}C NMR: δ 77.16 ppm). The following abbreviations are used to describe peak patterns where appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants (*J*) are reported in Hertz (Hz). HRMS was performed on Agilent Technologies 6224 TOF LC/MS apparatus (ESI).

2. Experimental Section

2.1 Substrates Preparation

2.1.1 Preparation of *N*-(tert-pentyl)-1*H*-indazole-1-carboxamide (1a)[1]

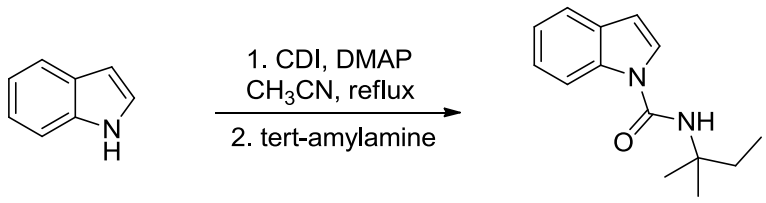


1a, 84%

A reaction tube (100 mL) with magnetic stir bar was charged with 1*H*-indazole (1.18 g, 10.0 mmol), 1,1'-carbonyldiimidazole (CDI, 2.43 g, 15.0 mmol) and 4-dimethylaminepyridine (DMAP, 61 mg, 0.5 mmol). Then 20 mL anhydrous acetonitrile was added to the reaction tube. The system was stirred at 85 ^{o}C for 10 h. After cooling to room temperature, tert-amylamine (1.74 g, 20.0 mmol) was added and then the reaction was stirred at 85 ^{o}C for another 6 hours until most of 1*H*-indazole was consumed by TLC detection. Then the reaction was cooled to room temperature and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (PET: EtOAc = 15:1) to afford **1a** as colorless oil (1.94 g) in 84% yield.

***N*-(tert-pentyl)-1*H*-indazole-1-carboxamide (1a):** ^{1}H NMR (500 MHz, $CDCl_3$): 8.39 (dd, *J* = 8.5, 0.5 Hz, 1H), 8.00 (d, *J* = 0.5 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.51−7.48 (m, 1H), 7.27−7.24 (m, 1H), 7.07 (s, 1H), 1.86 (q, *J* = 7.5 Hz, 2H), 1.47 (s, 6H), 0.96 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): *δ* 150.5, 139.2, 136.8, 128.9, 125.7, 123.1, 120.9, 114.9, 54.2, 33.4, 26.7 (2C), 8.6; HRMS (ESI) *m/z* calcd. for $C_{13}H_{18}N_3O$ $[M+H]^+$ 232.1444, found 232.1449.

2.1.2 Preparation of *N*-(tert-pentyl)-1*H*-indole-1-carboxamide (1b) [1]

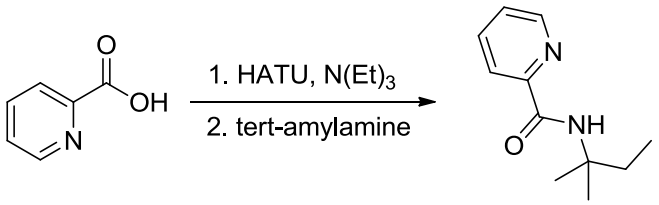


1b, 37%

A reaction tube (100 mL) with magnetic stir bar was charged with indole (1.17 g, 10.0 mmol), 1,1'-carbonyldiimidazole (CDI, 2.43 g, 15.0 mmol) and 4-dimethylaminepyridine (DMAP, 61 mg, 0.5 mmol). Then 20 mL anhydrous acetonitrile was added to reaction tube. The system was stirred at 85 ^{o}C for 10 h. After cooling to room temperature, tert-amylamine (1.74 g, 20.0 mmol) was added and then the reaction was stirred at 85 ^{o}C for another 6 hours until most of indole was consumed by TLC detection. Then the reaction was cooled to room temperature and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (PET: EtOAc = 10:1) to afford **1b** as colorless oil (0.85 g) in 37% yield.

***N*-(tert-pentyl)-1*H*-indole-1-carboxamide (1b):** ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.95 (d, J = 7.5 Hz, 1H), 7.61 (dt, J = 8.0, 1.0 Hz, 1H), 7.47 (d, J = 3.5 Hz, 1H), 7.33−7.29 (m, 1H), 7.23−7.20 (m, 1H), 6.60 (dd, J = 3.5, 1.0 Hz, 1H), 5.35 (s, 1H), 1.87 (q, J = 7.5 Hz, 2H), 1.47 (s, 6H), 0.96 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.7, 134.9, 130.5, 124.8, 124.1, 122.1, 121.5, 113.5, 106.4, 54.9, 33.3, 26.8 (2C), 8.7; HRMS (ESI) *m/z* calcd. for $C_{14}H_{19}N_2O$ $[M+H]^+$ 231.1492, found 231.1496.

2.1.1 Preparation of *N*-(tert-pentyl)picolinamide (1c)[1]



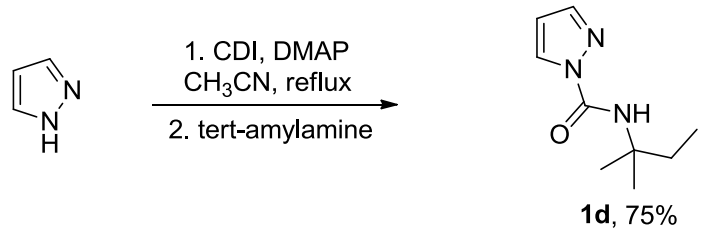
1c, 76%

A reaction tube (100 mL) with magnetic stir bar was charged with picolinic acid (1.23 g, 10.0 mmol),2-(7-Azabenzotriazol-1-yl)-N,N,N',N'-tetramethyluronium hexafluorophosphate (HATU, 4.6 g, 12.0 mmol) and $N(Et)_3$ (1.20 g, 12 mmol). Then 20 mL anhydrous THF was added to the reaction tube. The system was stirred at 25 ^{o}C for 6 h. Tert-amylamine (1.74 g, 20.0 mmol) was added and then the reaction was stirred at 25 ^{o}C for another 2 hours until most of picolinic acid was consumed by TLC detection. Then the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (PET: EtOAc = 10:1) to afford **1c** as colorless oil (1.45 g) in 76% yield.

***N*-(tert-pentyl)picolinamide (1c):** ^{1}H NMR (500 MHz, $CDCl_3$): 8.52−8.50 (m, 1H), 8.16 (dt, J = 8.0, 1.0 Hz, 1H), 7.95 (s, 1H), 7.84−7.80 (m, 1H), 7.40−7.37 (m, 1H), 7.07 (s, 1H), 1.86 (q, J =

7.5 Hz, 2H), 1.44 (s, 6H), 0.91 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.4, 150.9, 147.9, 137.5, 125.9, 121.8, 8.2, 53.8, 33.1, 26.5 (2C), 8.6; HRMS (ESI) *m/z* calcd. for $C_{11}H_{17}N_2O$ $[M+H]^+$ 193.1335, found 193.1337.

2.1.1 Preparation of *N*-(tert-pentyl)-1*H*-pyrazole-1-carboxamide (1d)[1]

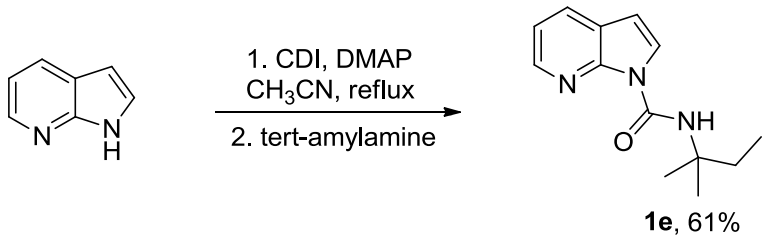


1d, 75%

A reaction tube (100 mL) with magnetic stir bar was charged with 1*H*-pyrazole (680 mg, 10.0 mmol), 1,1'-carbonyldiimidazole (CDI, 2.43 g, 15.0 mmol) and 4-dimethylaminepyridine (DMAP, 61 mg, 0.5 mmol). Then 20 mL anhydrous acetonitrile was added to the reaction tube. The system was stirred at 85 ^{o}C for 10 h. After cooling to room temperature, tert-amylamine (1.74 g, 20.0 mmol) was added and then the reaction was stirred at 85 ^{o}C for another 6 hours until most of 1*H*-pyrazole was consumed by TLC detection. Then the reaction was cooled to room temperature and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (PET: EtOAc = 10:1) to afford **1d** as colorless oil (1.36 g) in 75% yield.

***N*-(tert-pentyl)-1*H*-pyrazole-1-carboxamide (1d):** ^{1}H NMR (500 MHz, $CDCl_3$): 8.19 (dd, *J* = 2.5, 0.5 Hz, 1H), 7.56 (dd, *J* = 1.5, 0.5 Hz, 1H), 7.06 (s, 1H), 6.36−6.35 (m, 1H), 1.82 (q, *J* = 7.5 Hz, 2H), 1.42 (s, 6H), 0.92 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.2, 141.7, 128.3, 108.2, 54.3, 33.3, 26.5 (2C), 8.5.; HRMS (ESI) *m/z* calcd. for $C_8H_{13}N_3O$ $[M+H]^+$ 182.1288, found 182.1284.

2.1.1 Preparation of *N*-(tert-pentyl)-1H-pyrrolo[2,3-b] pyridine-1-carboxamide (1e)[1]



1e, 61%

A reaction tube (100 mL) with magnetic stir bar was charged with 1H-pyrrolo[2,3-b]pyridine (1.18 g, 10.0 mmol), 1,1'-carbonyldiimidazole (CDI, 2.43 g, 15.0 mmol) and 4-dimethylaminepyridine (DMAP, 61 mg, 0.5 mmol). Then 20 mL anhydrous acetonitrile was added to the reaction tube. The system was stirred at 85 ^{o}C for 10 h. After cooling to room temperature, tert-amylamine (1.74 g, 20.0 mmol) was added and then the reaction was stirred at 85 ^{o}C for another 6 hours until most of 1*H*-indazole was consumed by TLC detection. Then the reaction was cooled to room temperature and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (PET: EtOAc = 15:1) to afford **1e** as colorless oil (1.40 g) in 61% yield.

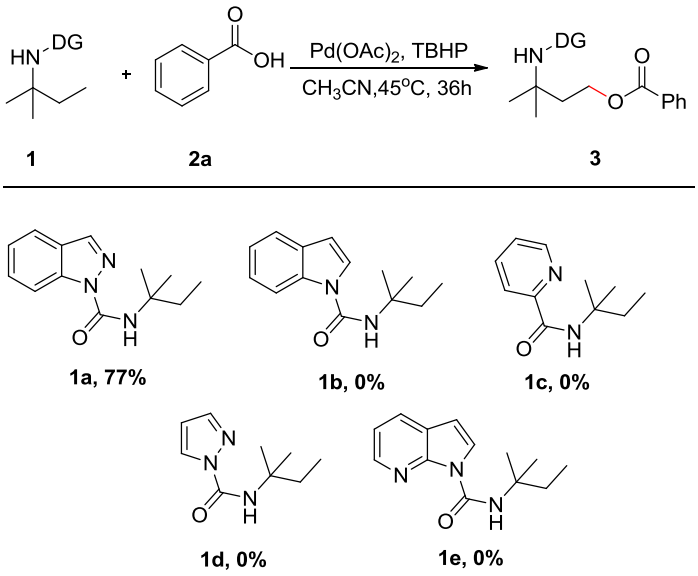
***N*-(tert-pentyl)-1H-pyrrolo[2,3-b] pyridine-1-carboxamide (1e):** ^{1}H NMR (500 MHz, $CDCl_3$): 9.70 (s, 1H), 8.27 (dd, *J* = 5.0, 1.5 Hz, 1H), 7.99 (d, *J* = 4.0 Hz, 1H), 7.90 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.16−7.13 (m, 1H), 6.49 (d, *J* = 4.0 Hz, 1H), 1.86 (q, *J* = 7.5 Hz, 2H), 1.49 (s, 6H), 0.99 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.0, 146.7, 142.2, 129.8, 126.2, 123.6, 117.7, 102.3, 54.2, 33.7, 26.7 (2C), 8.6; HRMS (ESI) *m/z* calcd. for $C_{13}H_{18}N_3O$ $[M+H]^+$ 232.1444, found 232.1445.

2.2 Preliminary Optimization of Reaction Conditions

2.2.1 The Screen of Directing Group

We have synthesized the *N*-(tert-pentyl)-1*H*-indazole-1-carboxamide **(1a),** *N*-(tert-pentyl)-1*H*-indole -1-carboxamide (**1b**),*N*-(tert-pentyl)picolinamide (**1c**), *N*-(tert-pentyl)-1H-pyrazole-1-carboxamide (**1d**) and *N*-(tert-pentyl)-1H-pyrrolo[2,3-b] pyridine-1-carboxamide (**1e**) as follows (Scheme 1). They were subjected to this reaction under the otherwise same reaction conditions, while no reaction was detected except **1a** (77%).

Scheme S1. Screen of directing group

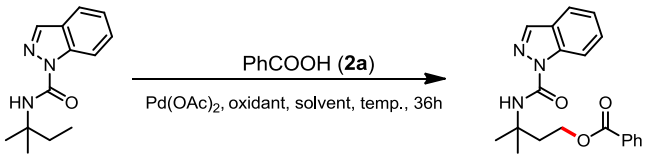


2.2.2 Optimization of Reaction Conditions

Our study was initiated by testing γ-C(sp^3)−H acyloxylation of *N*-(*tert*-pentyl)-1*H*-indazole-1-carboxamide (**1a**) under a wide range of reaction parameters, including oxidants, solvents and temperature (Table S1). Treating **1a** with 3.0 equiv. of bezoic acid (**2a**), 10 mol% of $Pd(OAc)_2$, and 3.0 equiv. of *N*-flouro-2,4,6-trimethylpyridinium tetraflouroborate ($[F^+]BF_4^-$) in HFIP at 45 ^oC for 36 h gave the desired C(sp^3)–H acyloxylation product **3a** in 18% yield (entry 1). Changing the oxidant to TBHP (5 M in decane) increased the isolated yield of **3a** to 55% (entry 2), while TBHP (70% in water) further increased the yield to 68% (entry 3). Other oxidants such as cumene hydroperoxide (CHP), $MeCOOO^tBu$ and H_2O_2 could also drive this reaction with lower transformation rates (entries 4-6). $K_2S_2O_8$ and $PhI(OAc)_2$ was

also tested but no reaction (entries 7, 8) and TBHP (70% in water) was found to be the appropriate oxidant among them (entry 3). Further solvents screening showed that toluene was acceptable to trigger this reaction (entry 9) and CH_3CN was the most favorable solvent for this transformation (entry 10). Hence, entry 7 was found to be the optimal reaction conditions for γ-C(sp3)−H acyloxylation of **1a**.

Table S1. Optimization of Acyloxylation Reaction Conditions



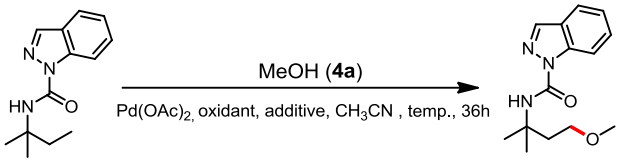
1a **3a**

entry	oxidant	solvent	temp (℃)	yield (%)[b]
1	$[F^+]BF_4^-$	HFIP	45	18
2	TBHP (5 M in decane)	HFIP	45	55
3	TBHP(70% in water)	HFIP	45	68
4	CHP	HFIP	45	23
5	$MeCOOO^tBu$	HFIP	45	26
6	H_2O_2	HFIP	45	15
7	$K_2S_2O_8$	HFIP	45	<5
8	$PhI(OAc)_2$	HFIP	45	<5
9	TBHP(70% in water)	Toluene	45	20
10	TBHP(70% in water)	CH_3CN	45	77

[a]For entries 1-10: Reaction was conducted with **1a** (0.2 mmol), **2a** (0.6 mmol), $Pd(OAc)_2$ (0.02 mmol), oxidant (0.6 mmol) and solvent (1 mL).

Interestingly, replacement of benzoic acid with methanol (**4a**) exclusively resulted in the alkoxylation product **5a** in 24% yield under otherwise same reaction conditions (entry 1, Table S2). Acid additives screening showed that 0.5% acetic acid (AcOH) increased the yield to 39% (entry 2) while 0.5% CF_3COOH (TFA) further improved the yield to 48% (entry 3). Meanwhile, the reaction temperature was also tested and the results (entries 3–5) indicated that 60 ℃ was the most preferred one for **5a** formation with a yield of 71%. Further additive amount of TFA was also tested as entry 16, with a decreased outcome of **5a** (60%, entry 6). Hence, entry 4 was the best choice for γ-C(sp^3)−H alkoxylation of **1a**.

Table S2. Optimization of Alkoxylation Reaction Conditions



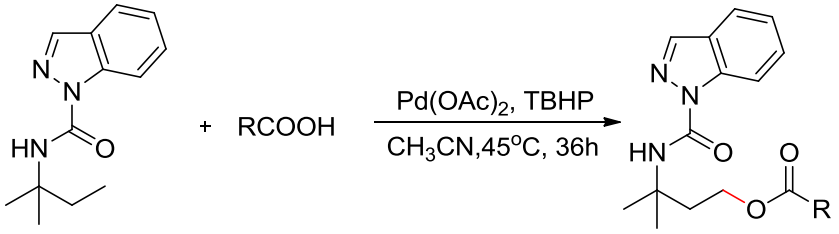
1a 5a

entry	solvent	additive	temp (℃)	yield (%)[b]
1	CH_3CN	-	45	24
2	CH_3CN	AcOH	45	39
3	CH_3CN	TFA	45	48
4	CH_3CN	TFA	60	71
5	CH_3CN	TFA	80	42
6[c]	CH_3CN	TFA	45	60

For entries 2-5: Reaction was conducted with **1a** (0.2 mmol), **4a** (1.0 mmol), $Pd(OAc)_2$ (0.02 mol), oxidant (0.6 mmol), additive (5 μL) and CH_3CN (1mL). [b]Isolated yield.[c]TFA (10 μL).

2.3 General Procedures for C(sp^3)−H Acyloxylation and Alkoxylation

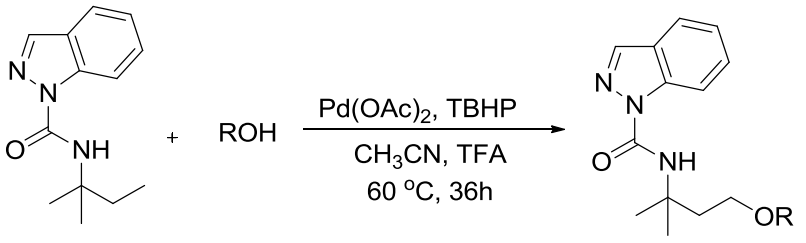
2.3.1 Preparation of Acyloxylation Products (Method A)



1a 2 3

A reaction tube (10 mL) with magnetic stir bar was charged with *N*-(tert-pentyl)-1*H*-indazole-1-carboxamide **1a** (46 mg, 0.20 mmol), acid **2** (0.60 mmol), $Pd(OAc)_2$ (5 mg, 0.020 mmol), TBHP(70% in water) (77mg, 0.60 mmol) and CH_3CN (1.0 mL). The reaction was allowed to stir at 45 ℃ for 36 hours. After cooling to room temperature, the reaction mixture was evaporated to remove the solvent and directly loaded onto silica gel for flash column chromatography (PET/EtOAc) to afford the desired product **3**.

2.3.2 Preparation of Alkoxylation Products (Method B)



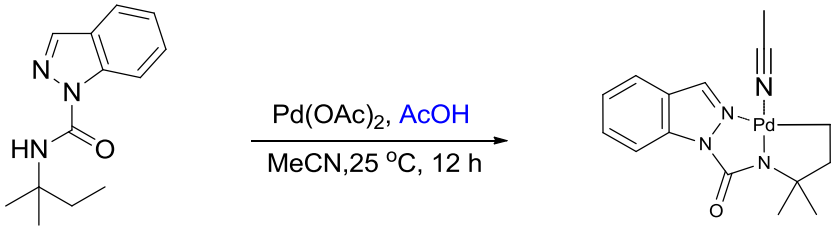
1a **4** **5**

A reaction tube (10 mL) with magnetic stir bar was charged with *N*-(tert-pentyl)-1*H*-indazole-1-carboxamide **1a** (46 mg, 0.20 mmol), **4** (1.00 mmol), $Pd(OAc)_2$ (5 mg, 0.020 mmol), TBHP(70% in water) (77mg, 0.06 mmol), TFA (5 μL) and CH_3CN (1.0 mL). The reaction was allowed to stir at 60 ℃ for 36 hours. After cooling to room temperature, the reaction mixture was evaporated to remove the solvent and directly loaded onto silica gel for flash column chromatography (PET/EtOAc) to afford the desired product **5**.

3. Mechanism Study

3.1 Preparation of Intermediates

3.1.1 Preparation of IN6



1a **IN6, 90%**

A reaction tube (50 mL) with magnetic stir bar was charged with *N*-(tert-pentyl)-1*H*-indazole-1-carboxamide **1a** (55 mg, 0.48 mmol), $Pd(OAc)_2$ (44 mg, 0.20 mmol), AcOH (50 μL) and MeCN (15 mL). The reaction was allowed to stir at room temperature for 12 hours. Upon completion, the reaction mixture was evaporated to remove the solvent and the solid obtained was washed with ether to remove excess **1a** and TBHP. Analytically pure intermediate **IN6** was obtained as solid (68 mg) in 90% yield by recrystallization using dichloromethane and ethyl acetate (DCM / EtOAc = 1:1) at room temperature. **IN6** was then used to perform NMR.

^{1}H NMR (500 MHz, $CDCl_3$): 8.41−8.38 (m, 1H), 7.82 (d, *J* = 1.0 Hz, 1H), 7.63 (dt, *J* = 8.5, 1.0 Hz, 1H), 7.58−7.56 (m, 1H), 7.40−7.37 (m, 1H), 7.14−7.10 (m, 1H), 2.23 (s, 3H), 2.13 (t, *J* = 6.5 Hz, 2H), 1.48 (t, *J* = 6.5 Hz, 2H), 1.48 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): *δ* 153.0, 139.4, 133.0, 129.0, 123.3, 122.7, 120.7, 118.8, 114.3, 65.2, 52.8, 25.3, 23.4 (2C), 3.5.

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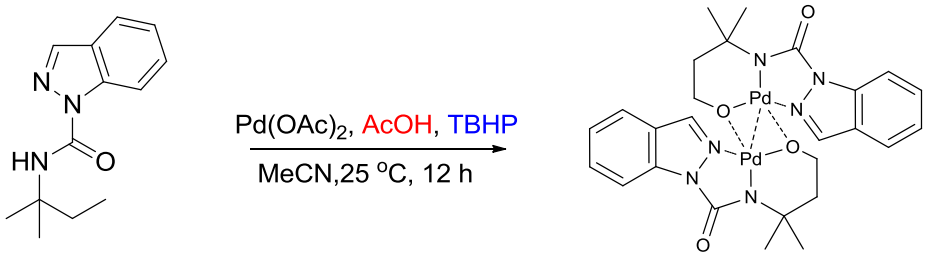
3.1.2 Preparation of IN14

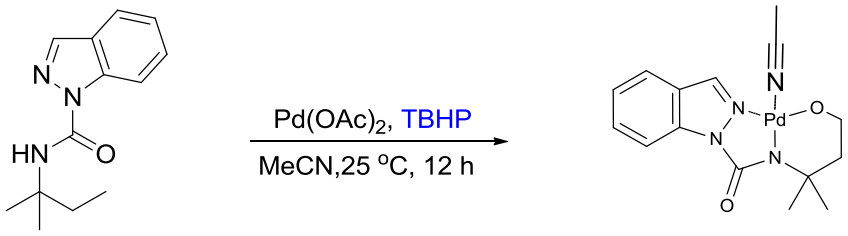


1a **IN14**, 82%

A reaction tube (50 mL) with magnetic stir bar was charged with *N*-(tert-pentyl)-1*H*-indazole-1-carboxamide **1a** (55 mg, 0.24 mmol), $Pd(OAc)_2$ (44 mg, 0.20 mmol), AcOH (50 μL)， TBHP(70% in water) (77mg, 0.6 mmol) and MeCN (15 mL). The reaction was allowed to stir at room temperature for 12 hours. Upon completion, the reaction mixture was evaporated to remove the solvent and the solid obtained was washed with ether to remove excess **1a** and TBHP. Analytically pure intermediate **IN14** was obtained as crystal (57 mg) in 82% yield by recrystallization using dichloromethane and ethyl acetate (DCM / EtOAc = 1:1) at room temperature. The crystal **IN14** was then used to perform NMR and X-ray analysis.

^{1}H NMR (500 MHz, $CDCl_3$): 8.39 (dd, *J* = 8.5, 0.5 Hz, 2H), 7.82 (s, 2H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.56−7.53 (m, 2H), 7.32−7.26 (m, 2H), 3.27 (t, *J* = 5.0 Hz, 4H), 1.72 (t, *J* = 5.0 Hz, 4H), 1.54 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$): *δ* 154.9 (2C), 138.9 (2C), 135.0 (2C), 130.4 (2C), 124.2 (2C), 122.3 (2C), 120.6 (2C), 113.2 (2C), 65.2 (2C), 51.6 (2C), 50.5 (2C), 26.5 (4C); HRMS (ESI) *m/z* calcd for $C_{13}H_{16}N_3O_2Pd$ $[M+H]^+$ 352.0272, found 352.0280 (0.5 **IN14**).

3.1.3 Preparation of IN17



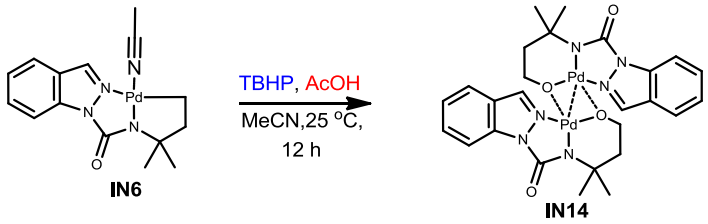
1a **IN17**, 68%

A reaction tube (50 mL) with magnetic stir bar was charged with *N*-(tert-pentyl)-1*H*-indazole-1-carboxamide **1a** (55 mg, 0.24 mmol), $Pd(OAc)_2$ (44 mg, 0.20 mmol), TBHP(70% in water) (77mg, 0.6 mmol) and MeCN (15 mL). The reaction was allowed to stir at room temperature for 12 hours. Upon completion, the reaction mixture was evaporated to remove the solvent and the solid obtained was washed with ether to remove excess **1a** and TBHP. Analytically pure intermediate **IN17** was obtained as solid (53 mg) in 68% yield by recrystallization using dichloromethane and ethyl acetate (DCM / EtOAc = 1:1) at room temperature. **IN17** was then used to perform NMR.

^{1}H NMR (500 MHz, $CDCl_3$): 8.15 (d, *J* = 1.0 Hz, 1H), 7.82−7.70 (m, 2H), 7.67−7.63 (m, 1H),

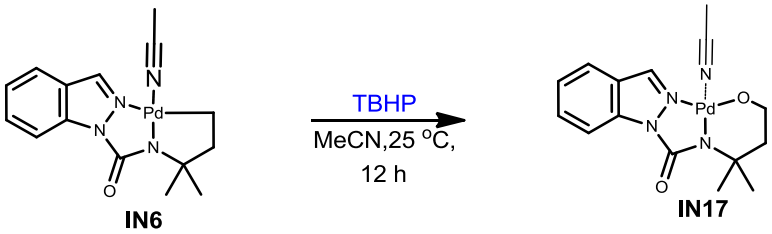
7.44−7.40 (m, 1H), 4.71 (t, J = 5.5 Hz, 2H), 2.11 (t, J = 5.5 Hz, 2H), 2.02 (s, 3H), 1.48 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 178.7, 151.4, 143.1, 137.8, 132.2, 126.0, 123.4, 122.7, 112.3, 66.7, 55.0, 36.4, 28.4, 23.5, 23.0; HRMS (ESI) *m/z* calcd for $C_{15}H_{18}N_4O_2Pd$ $[M+H]^+$ 393.0537, found 393.0529.

3.1.4 The Reaction of IN6 to IN14



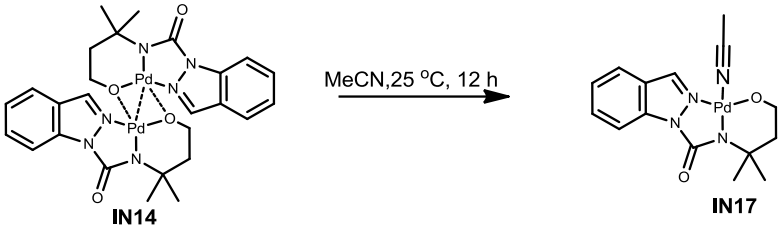
A reaction tube (25 mL) with magnetic stir bar was charged with **IN6** (38 mg, 0.10 mmol), AcOH (25 μL), TBHP(70% in water) (39 mg, 0.3 mmol) and MeCN (8 mL). The reaction was allowed to stir at room temperature for 12 hours. Upon completion, the reaction mixture was evaporated to remove the solvent and the solid obtained was washed with ether to remove excess **1a** and TBHP. Analytically pure intermediate **IN14** was obtained as solid (27 mg) in 76% yield by recrystallization using dichloromethane and ethyl acetate (DCM / EtOAc = 1:1) at room temperature.

3.1.5 The Reaction of IN6 to IN17



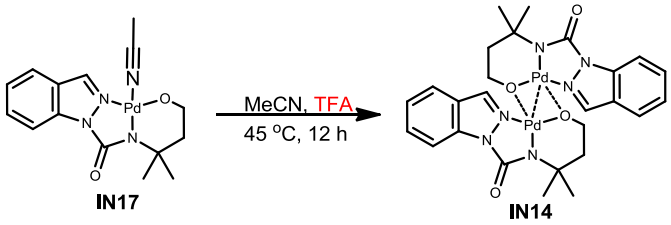
A reaction tube (25 mL) with magnetic stir bar was charged with **IN6** (38 mg, 0.10 mmol), TBHP(70% in water) (39 mg, 0.3 mmol) and MeCN (8 mL). The reaction was allowed to stir at room temperature for 12 hours. Upon completion, the reaction mixture was evaporated to remove the solvent and the solid obtained was washed with ether to remove excess **1a** and TBHP. Analytically pure intermediate **IN17** was obtained as solid (20 mg) in 71% yield by recrystallization using dichloromethane and ethyl acetate (DCM / EtOAc = 1:1) at room temperature.

3.1.6 The Reaction of IN14 to IN17



A reaction tube (25 mL) with magnetic stir bar was charged with **IN14** (35 mg, 0.05 mmol), and MeCN (8 mL). The reaction was allowed to stir at room temperature for 12 hours. Upon completion, the reaction mixture was evaporated to remove the solvent and the solid obtained was washed with ether. Analytically pure intermediate **IN17** was obtained as solid (29 mg) in 75% yield by recrystallization using dichloromethane and ethyl acetate (DCM / EtOAc = 1:1) at room temperature.

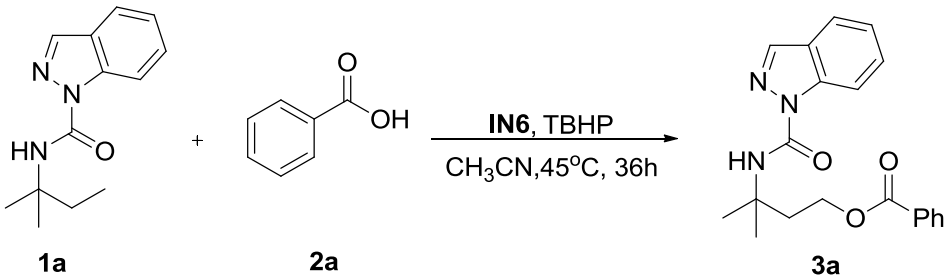
3.1.6 The Reaction of IN17 to IN14



A reaction tube (25 mL) with magnetic stir bar was charged with **IN17** (39 mg, 0.10 mmol), TFA (10 μL)and MeCN (8 mL). The reaction was allowed to stir at 45 ℃ for 12 hours. Upon completion, the reaction mixture was evaporated to remove the solvent and the solid obtained was washed with ether. Analytically pure intermediate **IN14** was obtained as solid (15 mg) in 42% yield by recrystallization using dichloromethane and ethyl acetate (DCM / EtOAc = 1:1) at room temperature.

3.2 1a Leading to Products 3a and 5a Using IN6, IN14 and IN17

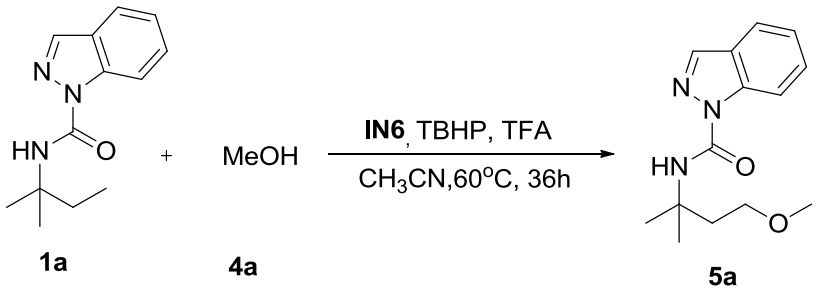
3.2.1 1a Leading to Products 3a Using IN6



A reaction tube (10 mL) with magnetic stir bar was charged with *N*-(*tert*-pentyl)-1*H*-indazole-1-carboxamide **1a** (46 mg, 0.2 mmol), **2a** (73 mg, 0.60 mmol), **IN6** (8 mg, 0.02 mmol), TBHP (70% in water) (77 mg, 0.60 mmol) and CH_3CN (1 mL). The reaction was allowed to stir at 45 ℃ in an oil bath for 36 hours. After cooling to room temperature, the reaction

mixture was evaporated to remove the solvent and directly loaded onto silica gel for flash column chromatography (PET: EtOAc = 12:1) to afford the desired product **3a** in 80% yield.

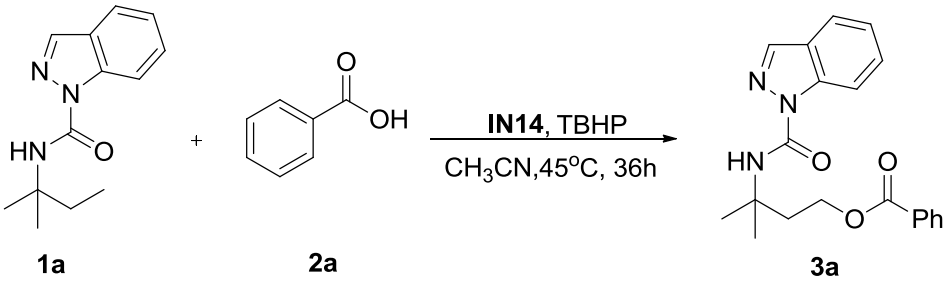
3.2.2 1a Leading to Products 5a Using IN6



1a **4a** **5a**

A reaction tube (10 mL) with magnetic stir bar was charged with *N*-(*tert*-pentyl)-1*H*-indazole-1-carboxamide **1a** (46 mg, 0.2 mmol), **4a** (32 mg, 1.0 mmol), **IN6** (8 mg, 0.01 mmol), TBHP (70% in water) (77 mg, 0.60 mmol), TFA (5 μL) and CH_3CN (1 mL). The reaction was allowed to stir at 60 ℃ in an oil bath for 36 hours. After cooling to room temperature, the reaction mixture was evaporated to remove the solvent and directly loaded onto silica gel for flash column chromatography (PET: EtOAc = 15:1) to afford the desired product **5a** in 72% yield.

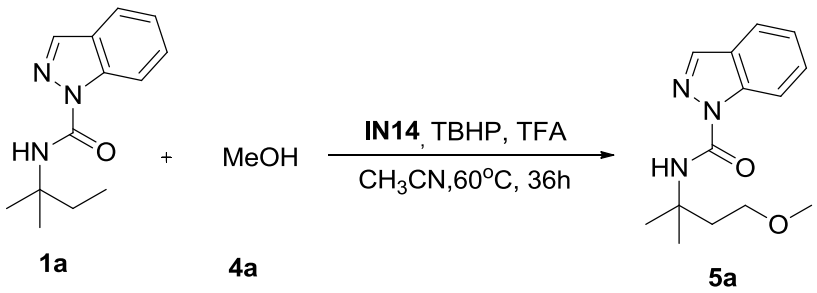
3.2.3 1a Leading to Products 3a Using IN14



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

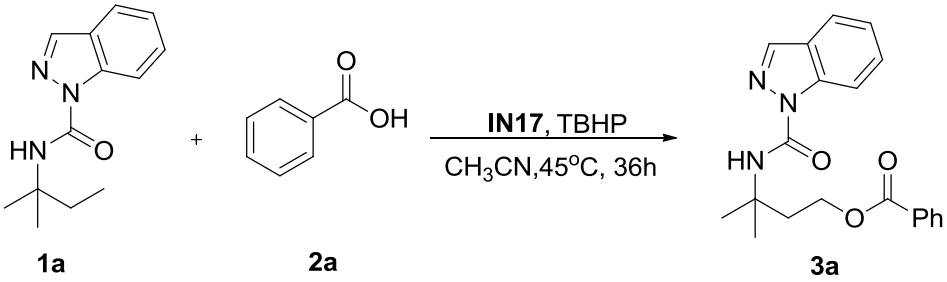
A reaction tube (10 mL) with magnetic stir bar was charged with *N*-(*tert*-pentyl)-1*H*-indazole-1-carboxamide **1a** (46 mg, 0.2 mmol), **2a** (73 mg, 0.60 mmol), **IN14** (8 mg, 0.02 mmol), TBHP (70% in water) (77 mg, 0.60 mmol) and CH_3CN (1 mL). The reaction was allowed to stir at 45 ℃ in an oil bath for 36 hours. After cooling to room temperature, the reaction mixture was evaporated to remove the solvent and directly loaded onto silica gel for flash column chromatography (PET: EtOAc = 12:1) to afford the desired product **3a** in 84% yield.

3.2.4 1a Leading to Products 5a Using IN14



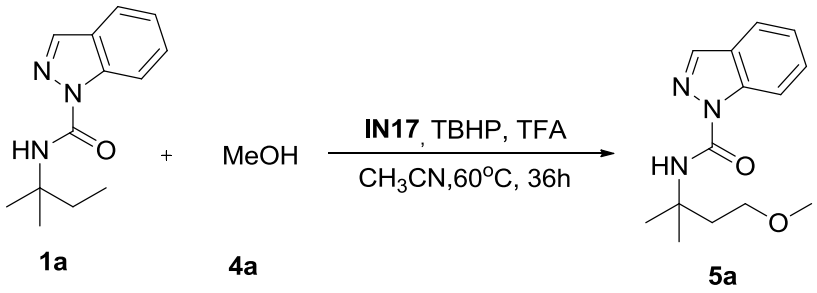
A reaction tube (10 mL) with magnetic stir bar was charged with *N*-(*tert*-pentyl)-1*H*-indazole-1-carboxamide **1a** (46 mg, 0.2 mmol), **4a** (32 mg, 1.0 mmol), **IN14** (8 mg, 0.01 mmol), TBHP (70% in water) (77 mg, 0.60 mmol), TFA (5 μL) and CH_3CN (1 mL). The reaction was allowed to stir at 60 ℃ in an oil bath for 36 hours. After cooling to room temperature, the reaction mixture was evaporated to remove the solvent and directly loaded onto silica gel for flash column chromatography (PET: EtOAc = 15:1) to afford the desired product **5a** in 74% yield.

3.2.5 1a Leading to Products 3a Using IN17



A reaction tube (10 mL) with magnetic stir bar was charged with *N*-(*tert*-pentyl)-1*H*-indazole-1-carboxamide **1a** (46 mg, 0.2 mmol), **2a** (73 mg, 0.60 mmol), **IN17** (8 mg, 0.02 mmol), TBHP (70% in water) (77 mg, 0.60 mmol) and CH_3CN (1 mL). The reaction was allowed to stir at 45 ℃ in an oil bath for 36 hours. After cooling to room temperature, the reaction mixture was evaporated to remove the solvent and directly loaded onto silica gel for flash column chromatography (PET: EtOAc = 12:1) to afford the desired product **3a** in 85% yield.

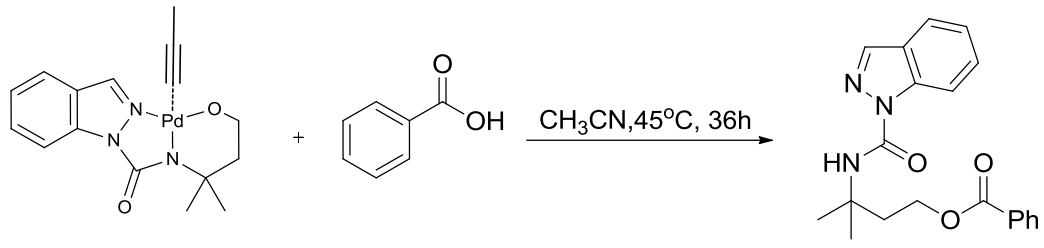
3.2.6 1a Leading to Products 5a Using IN17



A reaction tube (10 mL) with magnetic stir bar was charged with

N-(*tert*-pentyl)-1*H*-indazole-1-carboxamide **1a** (46 mg, 0.2 mmol), **4a** (32 mg, 1.0 mmol), **IN17** (8 mg, 0.01 mmol), TBHP (70% in water) (77 mg, 0.60 mmol), TFA (5 μL) and CH_3CN (1 mL). The reaction was allowed to stir at 60 ℃ in an oil bath for 36 hours. After cooling to room temperature, the reaction mixture was evaporated to remove the solvent and directly loaded onto silica gel for flash column chromatography (PET: EtOAc = 15:1) to afford the desired product **5a** in 73% yield.

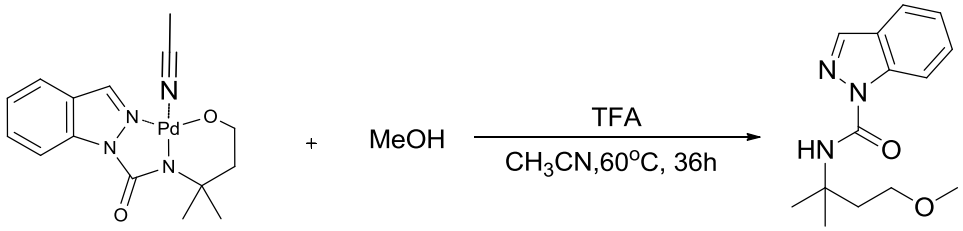
3.2.7 IN17 Leading to Products 3a



IN17 **2a** **3a**

A reaction tube (10 mL) with magnetic stir bar was charged with **IN17** (77 mg, 0.1 mmol), **2a** (73 mg, 0.60 mmol) and CH_3CN (1 mL). The reaction was allowed to stir at 45 ℃ in an oil bath for 36 hours. After cooling to room temperature, the reaction mixture was evaporated to remove the solvent and directly loaded onto silica gel for flash column chromatography (PET: EtOAc = 12:1) to afford the desired product **3a** (61 mg) in 88% yield.

3.2.8 IN17 Leading to Products 5a

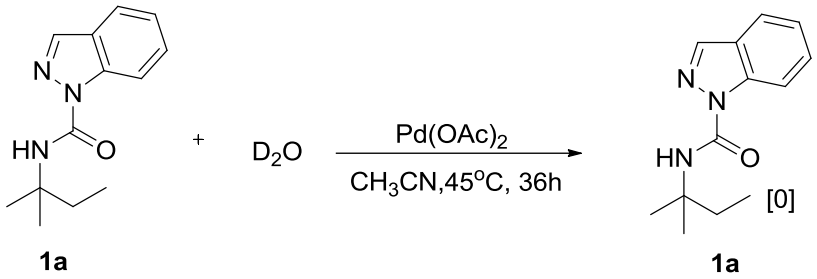


IN17 **4a** **5a**

A reaction tube (10 mL) with magnetic stir bar was charged with *N*-(*tert*-pentyl)-1*H*-indazole-1-carboxamide **IN17** (78 mg, 0.1 mmol), **4a** (32 mg, 1.0 mmol), TFA (5 μL) and CH_3CN (1 mL). The reaction was allowed to stir at 60 ℃ in an oil bath for 36 hours. After cooling to room temperature, the reaction mixture was evaporated to remove the solvent and directly loaded onto silica gel for flash column chromatography (PET: EtOAc = 15:1) to afford the desired product **5a** (40 mg) in 77% yield.

3.3 Deuterium Labeling Experiment

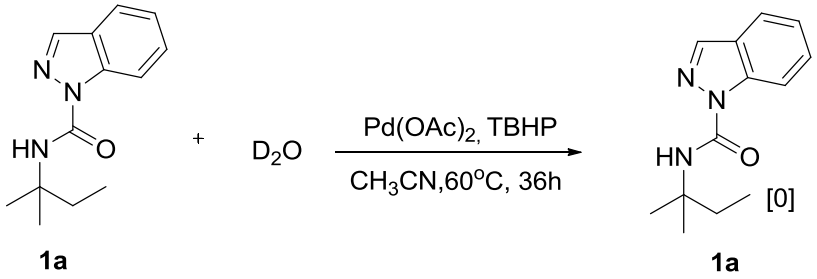
3.3.1 Deuterium Labeling Experiment without TBHP



1a **1a**

A reaction tube (10 mL) with magnetic stir bar was charged with *N*-(*tert*-pentyl)-1*H*-indazole-1-carboxamide **1a** (46 mg, 0.2 mmol), D_2O (0.3 mL), $Pd(OAc)_2$ (5 mg, 0.020 mmol), and CH_3CN (1 mL). The reaction was allowed to stir at 45 ℃ in an oil bath for 36 hours. After cooling to room temperature, the reaction mixture was evaporated to remove the solvent and directly loaded onto silica gel for flash column chromatography (PET: EtOAc = 15:1) to afford the desired product **1a** while no deuterium-labeled **1a** was observed.

3.3.2 Deuterium Labeling Experiment with TBHP



1a **1a**

A reaction tube (10 mL) with magnetic stir bar was charged with *N*-(*tert*-pentyl)-1*H*-indazole-1-carboxamide **1a** (46 mg, 0.2 mmol), D_2O (0.3 mL), $Pd(OAc)_2$ (5 mg, 0.020 mmol), TBHP (5M in decane) (0.12 mL, 0.60 mmol) and CH_3CN (1 mL). The reaction was allowed to stir at 60 ℃ in an oil bath for 36 hours. After cooling to room temperature, the reaction mixture was evaporated to remove the solvent and directly loaded onto silica gel for flash column chromatography (PET: EtOAc = 15:1) to afford the desired product **1a** while no deuterium-labeled **1a** was observed.

4. X-ray Crystallographic Data of IN14

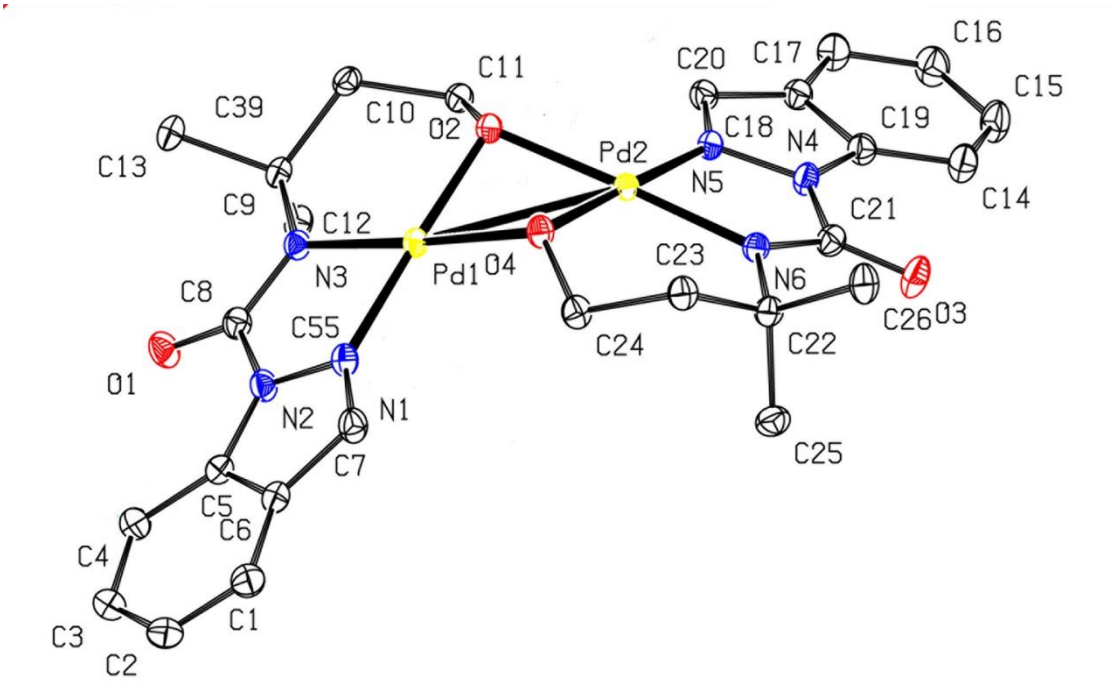


Table S3. Crystal Data and Structure Refinement for IN14

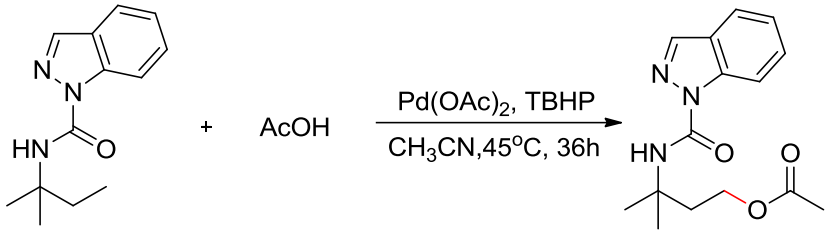
Empirical formula	$C_{54.5}H_{65}Cl_5N_{12}O_8Pd_4$
Formula weight	1619.03
Temperature/K	170(2)
Crystal system	monoclinic
Space group	*C*2/*c*
a/Å	39.352(5)
b/Å	14.1869(16)
c/Å	22.175(2)
α/°	90
β/°	96.411(6)
γ/°	90
Volume/Å^3	12302(2)
Z	8
Wavelength/Å	0.71073
F(000)	6472
Crystal size/mm^3	0.23×0.26×0.38
Radiation	MoK
$_{min}$/°	2.018
$_{max}$/°	27.064
Index ranges	-50 ≤ h ≤ 49, -18 ≤ k ≤ 17, -28 ≤ l ≤ 28
Reflections collected	100301
Independent reflections	13447 [R_{int} = 0.0330]
Data/restraints/parameters	13447/0/789
Goodness-of-fit on F^2	1.031
Final R indexes [I>=2σ (I)]	R_1 = 0.0242, wR_2 = 0.0574
Final R indexes [all data]	R_1 = 0.0290, wR_2 = 0.0596
Largest diff. peak/hole / e Å^{-3}	1.092/-0.989

5. Computational Section

These structures of reactants, products and reaction intermediates were optimized under the framework of density of functional theory (DFT) with PBE0 functional[2] and def2SVP[3] and SDD effective core potential basis set[4]. Here, the SDD effective core potential was used to describe the wavefunction of heavy atom of Pd. The transition states of all possible reaction routes were also searched using the same functional and basis set. The vibrational frequency analysis was carried out for the optimized structure with the same calculation method to obtain the zero-point energy and free energy corrections. In order to obtain the electron energy with higher accuracy which has the major impact on the accuracy of Gibbs free energy, a single point calculation for the optimized structure with m062x functional[5] and def2TZVP basis set was performed. Finally, the single point energy is added to the free energy correction calculated before to obtain the Gibbs free energy. All these DFT calculations were performed using Gaussian 16 program suite[6].

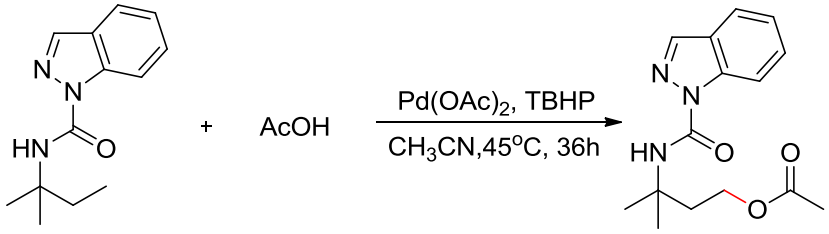
6. Reaction Progress Kinetic Analysis of C(sp^3)–H Acyloxylation

6.1 Reaction Progress Kinetic Analysis



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

A reaction tube (10 mL) with magnetic stir bar was charged with *N*-(tert-pentyl)-1*H*-indazole-1-carboxamide **1a** (46 mg, 0.20 mmol), acetic acid **2aa** (36 mg, 0.60 mmol), TBHP (70% in water) (77mg, 0.60 mmol) and stock solution containing the corresponding concentrations of $Pd(OAc)_2$. The stock solution for the "Standard Conditions" was prepared as follows: $Pd(OAc)_2$ (32.8 mg, 0.14 mmol) was added to a 20 mL volumetric flask and dissolved in MeCN (7 mL) to prepare a 7 mL stock solution. The tube was carefully capped and covered with safety shield. The mixture was then stirred at room temperature for 10 mins before heating to 45 ℃. Base on the above procedure, 7 parallel reactions were set up. Each reaction was heated to 45 ℃ for 1h, 2h, 4h, 6h, 8h, 10h, 12h separately. Upon completion, the reaction mixture was cooled to room temperature. Get the aliquots from each reaction then diluted with solvent and analyzed by HPLC. Analytical high performance liquid chromatography (HPLC) was performed on Agilent 1200 compact chromatograph equipped with Eclipse Plus C18 column (Agilent, 5 μm, 4.6 ×150 mm).



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

Table S4. Determine the Dependance

entry	[1a]	[$Pd(OAc)_2$]	[Oxidant]	[AcOH]
Standard Conditions	[0.20 mmol]	[0.02 mmol]	[0.60 mmol]	[0.60 mmol]
Different [Oxidant]	[0.20 mmol]	[0.02 mmol]	[0.30 mmol]	[0.60 mmol]
Different [1a]	[0.40 mmol]	[0.02 mmol]	[0.60 mmol]	[0.60 mmol]
Different [Pd]	[0.20 mmol]	[0.04 mmol]	[0.60 mmol]	[0.60 mmol]
Different [AcOH]	[0.20 mmol]	[0.02 mmol]	[0.60 mmol]	[0.30 mmol]

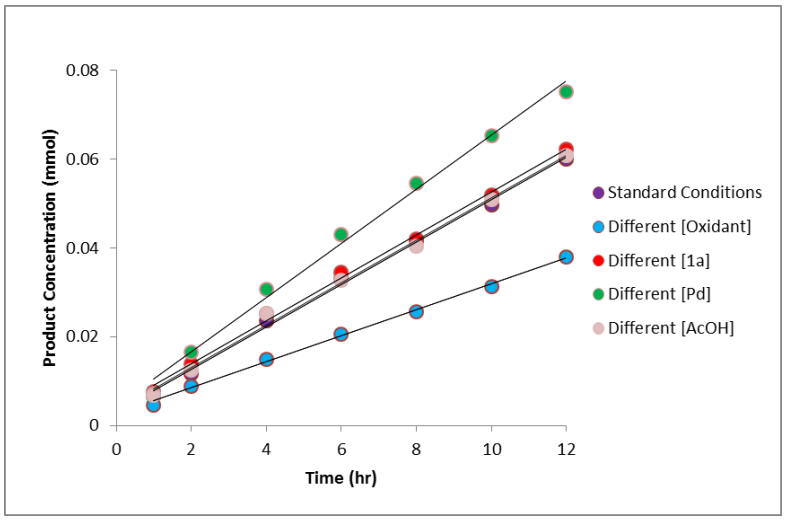


Figure S1. Reaction progress kinetic analysis of [**1a**], [**Oxidant**], [**AcOH**] and [**Pd**].

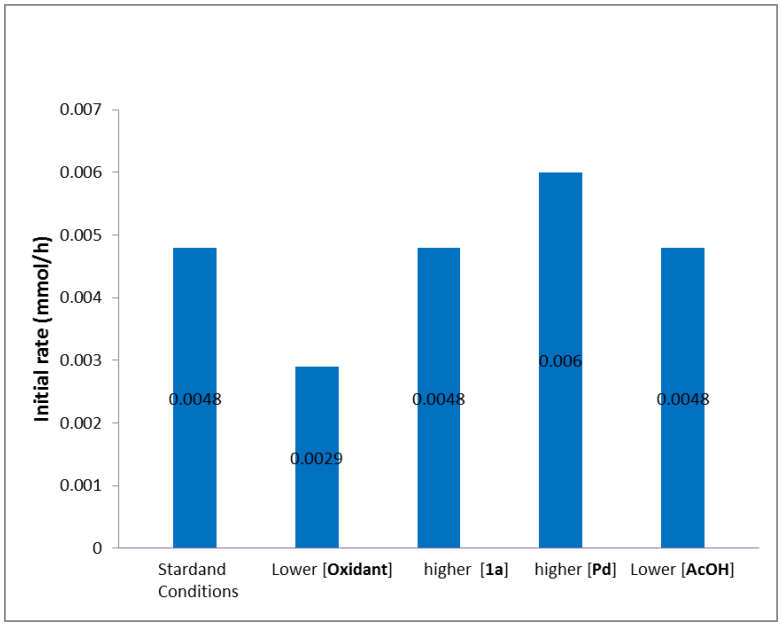


Figure S2. Kinetic studies with different concentrations of [**1a**], [**Oxidant**], [**AcOH**] and [**Pd**]. Reaction conditions unless otherwise stated: **1a** (variable), **2aa** (variable), **Oxidant** (variable), **$Pd(OAc)_2$** (variable), MeCN (1 mL), 45 °C , 0–12 h. The product was quantified *via* HPLC.

The aforementioned computational calculation results indicated that the oxidative addition progress is likely the turnover-limiting step. Reaction Progress Kinetic Analysis using **1a** and **2aa** was thus investigated (Figure 2). The reaction rate comparison between the standard initial condition and higher [**1a**] and lower [**AcOH**] shows zero-order dependence in [**1a**] and [**AcOH**], which shows that **1a** and [**AcOH**] are irrelevant to the rate-determining step of this catalytic cycle. However, lower concentration of [**Oxidant**] or higher concentration of [**Pd**] led to a lower or higher reaction rate, respectively, compared to that of the standard conditions, suggesting a positive-order dependence on [**Oxidant**] and [**Pd**] (see Supporting Information section 6). These results indicate that the [**Oxidant**] and [**Pd**] are involved in the turnover-limiting step and the

oxidation step may be partially rate-limiting.

6.2 Order in [TBHP]

The order in [TBHP] was determined by obtaining the initial rates of the C–H oxygenation at differing concentrations of TBHP with AcOH. A reaction tube (10 mL) with magnetic stir bar was charged with *N*-(tert-pentyl)-1*H*-indazole-1-carboxamide **1a** (46 mg, 0.20 mmol), acetic acid **2aa** (36 mg, 0.60 mmol), $Pd(OAc)_2$ (5 mg, 0.020 mmol). Different amount of TBHP was then added to the Schlenk tube in, followed by CH_3CN (1.0mL). The tube was carefully capped and covered with safety shield. The mixture was then stirred at room temperature for 10 mins before heating to 45 ℃. Base on the above procedure, 6 parallel reactions were set up. Each reaction was heated to 45 ℃ for 1 h, 2 h, 4 h, 6 h, 8 h, 10 h, separately. Upon completion, the reaction mixture was cooled to room temperature. Get the aliquots from each reaction then diluted with solvent and analyzed by HPLC. Analytical high performance liquid chromatography (HPLC) was performed on Agilent 1200 compact chromatograph equipped with Eclipse Plus C18 column (Agilent, 5 μm, 4.6 × 150 mm).

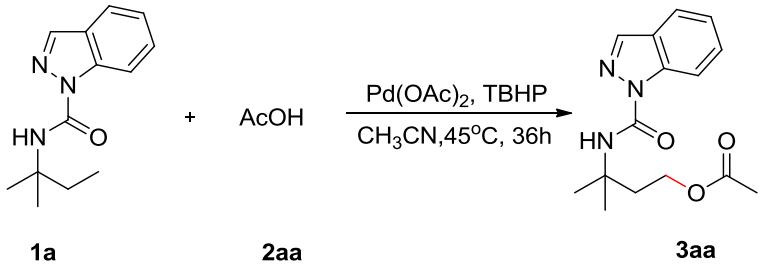


Table S5. Results to Determine the Order of TBHP

entry	Amount of **TBHP**			Rate (mM/h)
	mg	mmol	mM	
1	18.0	0.20	200	0.0033
2	27.0	0.30	300	0.0042
3	36.0	0.40	400	0.0056
4	45.0	0.50	500	0.0061
5	54.0	0.60	600	0.0072

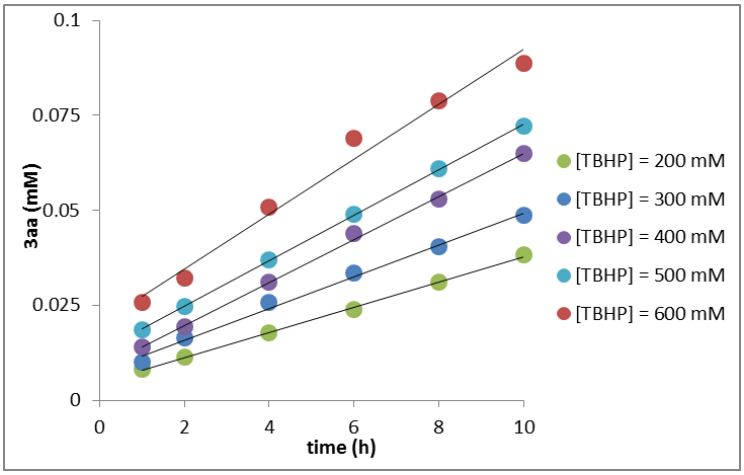


Figure S3. Plot of initial rates of the C–H acyloxylation with different concentration of TBHP

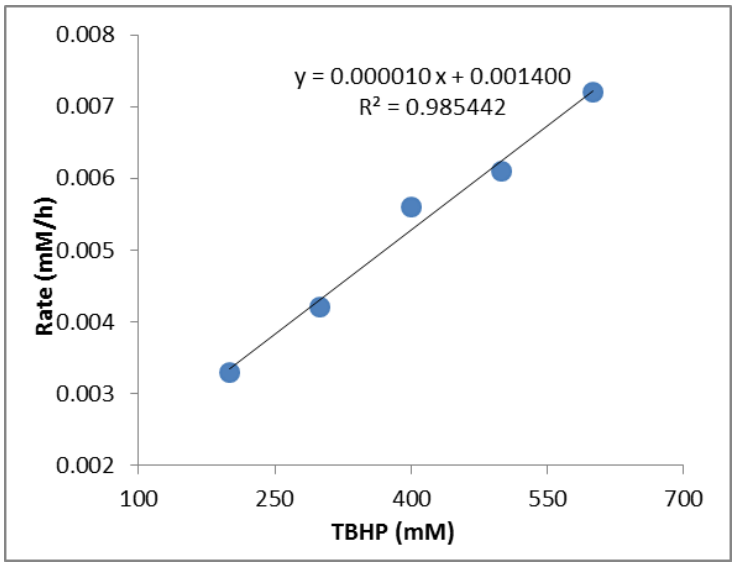


Figure S4. Plot of initial rates with different concentration of TBHP

6.3 Order in [Pd] at Low Concentrations

The order in [Pd] was determined by obtaining the initial rates of the C–H oxygenation at low concentration of $Pd(OAc)_2$ with AcOH. A reaction tube (10 mL) with magnetic stir bar was charged with *N*-(tert-pentyl)-1*H*-indazole-1-carboxamide **1a** (46 mg, 0.20 mmol), acetic acid **2aa** (36 mg, 0.60 mmol), TBHP(70% in water) (77mg, 0.60 mmol). Different amount of $Pd(OAc)_2$ (stock solution in CH_3CN) was then added to the Schlenk tube in, followed by CH_3CN (1.0mL). The tube was carefully capped and covered with safety shield. The mixture was then stirred at room temperature for 10 mins before heating to 45 ℃. Base on the above procedure, 8 parallel reactions were set up. Each reaction was heated to 45 ℃ for 1.5 h, 3 h, 6 h, 9 h, 12 h, 18 h, 24 h, 32h, separately. Upon completion, the reaction mixture was cooled to room temperature. Get the aliquots from each reaction then diluted with solvent and analyzed by HPLC. Analytical high performance liquid chromatography (HPLC) was performed on Agilent 1200 compact

chromatograph equipped with Eclipse Plus C18 column (Agilent, 5 μm, 4.6 × 150 mm).

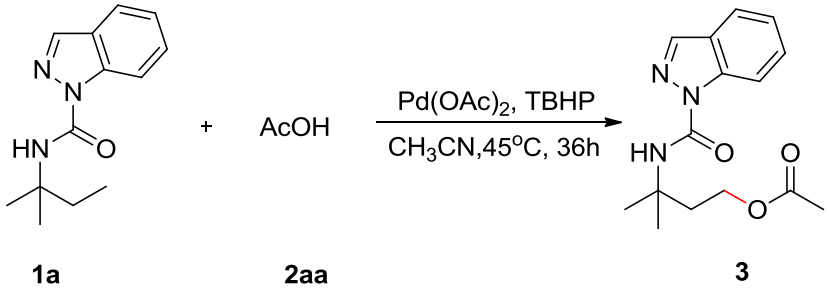


Table S6. Results to Determine the Order of $Pd(OAc)_2$ at Low Concentrations

entry	Amount of **$Pd(OAc)_2$**			Rate (mM/h)
	mg	mmol	mM	
1	0.50	0.002232	2.232	0.000139
2	0.75	0.003348	3.348	0.000307
3	1.00	0.004464	4.464	0.000578
4	1.25	0.05580	5.580	0.000913
5	1.50	0.006696	6.696	0.001437

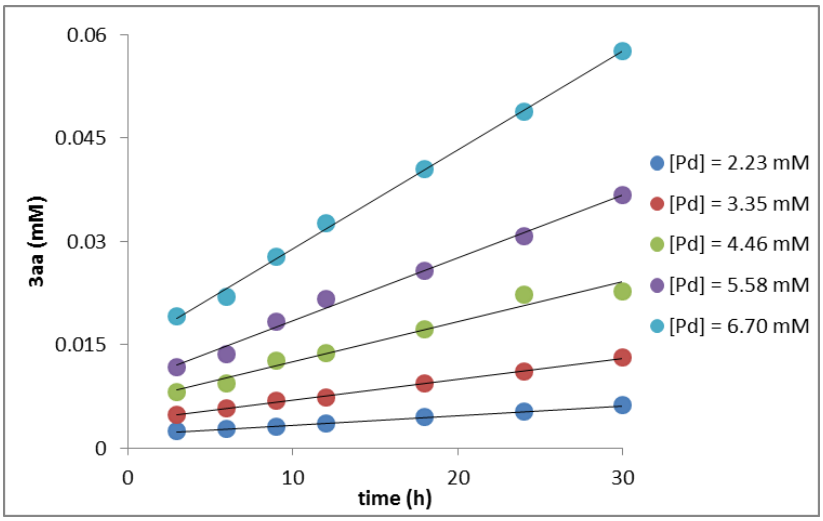


Figure S5. Plot of initial rates of the C–H **acyloxylation** with different concentration of $Pd(OAc)_2$ at low concentrations

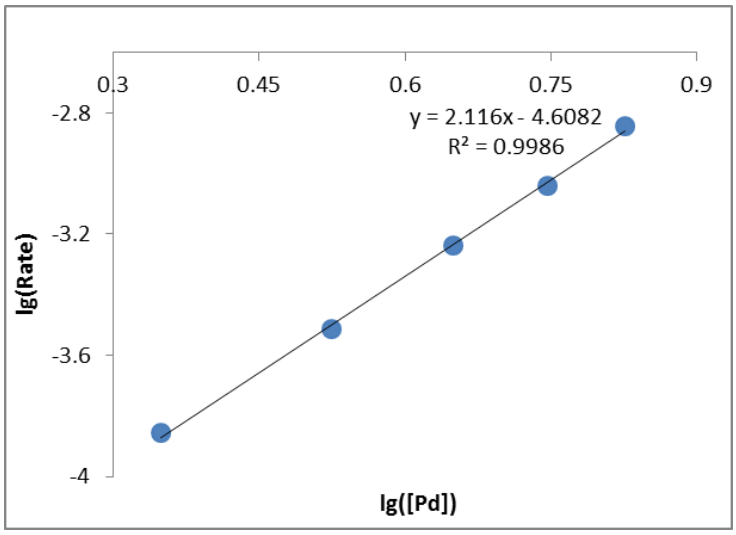
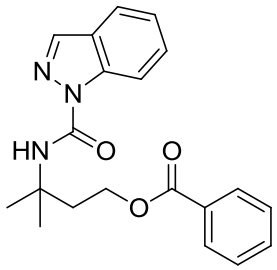
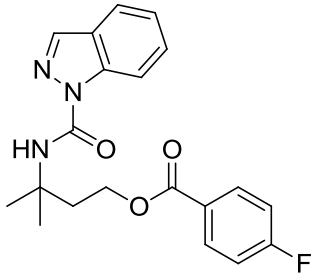


Figure S6. Plot of initial rates with different concentration of $Pd(OAc)_2$

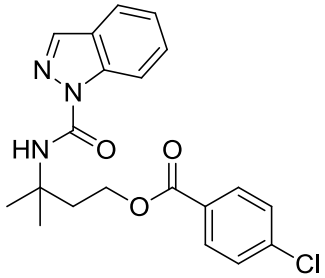
7. Characterization Data



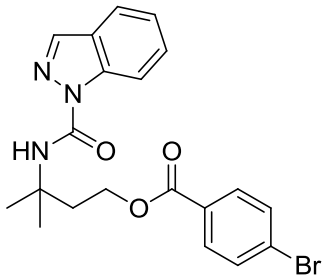
3-(1*H*-indazole-1-carboxamido)-3-methylbutyl benzoate (3a): The title compound was obtained by column chromatography (PET: EtOAc = 12:1) as a colorless oil (54 mg) in 77% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): 8.37 (dd, *J* = 7.5, 0.5 Hz, 1H), 7.94 (dd, *J* = 7.0, 1.5 Hz, 2H), 7.87 (d, *J* = 1.0 Hz, 1H), 7.66 (dt, *J* = 8.0, 0.5 Hz, 1H), 7.50−7.47 (m, 1H), 7.44−7.40 (m, 1H), 7.27−7.22 (m, 4H), 4.51 (t, *J* = 6.0 Hz, 2H), 2.41 (t, *J* = 6.0 Hz, 2H), 1.59 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.7, 150.6, 139.1, 136.9, 132.8, 130.1, 129.6, 128.9 (2C), 128.2 (2C), 125.7, 123.1, 120.9, 114.8, 61.8, 52.9, 38.4, 27.8 (2C); HRMS (ESI) *m/z* calcd. for $C_{20}H_{22}N_3O_3$ $[M+H]^+$ 352.1656, found 352.1651.



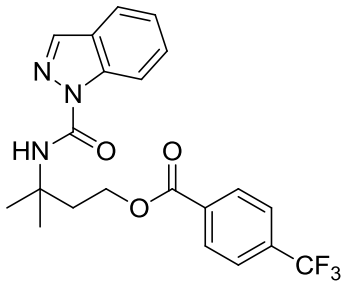
3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 4-fluorobenzoate (3b): The title compound was obtained by column chromatography (PET: EtOAc = 12:1) as a colorless oil (67 mg) in 91% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): 8.34 (dd, *J* = 8.0, 0.5 Hz, 1H), 7.92−7.89 (m, 2H), 7.87 (d, *J* = 1.0 Hz, 1H), 7.67 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.52−7.47 (m, 1H), 7.28−7.25 (m, 1H), 7.23 (s, 1H), 6.84−6.82 (m, 2H) , 4.50 (t, *J* = 6.5 Hz, 2H), 2.40 (t, *J* = 6.5 Hz, 2H), 1.58 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.8, 165.7 (d, *J* = 252.1 Hz), 150.6, 139.0, 136.9, 132.1 (d, *J* = 9.3 Hz, 2C), 129.0, 126.3 (d, *J* = 2.5 Hz), 125.6, 123.2, 120.9, 115.3 (d, *J* = 21.9 Hz, 2C), 114.8, 62.0, 52.9, 38.2, 27.9 (2C); HRMS (ESI) *m/z* calcd. for $C_{20}H_{21}FN_3O_3$ $[M+H]^+$ 370.1561, found 370.1556.



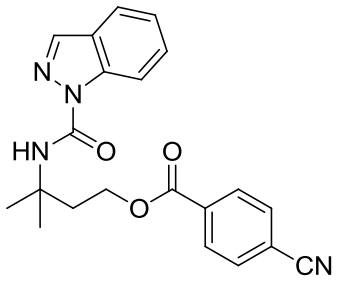
3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 4-chlorobenzoate (3c): The title compound was obtained by column chromatography (PET: EtOAc = 12:1) as a colorless oil (66 mg) in 86% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): 8.32 (dd, *J* = 8.0, 0.5 Hz, 1H), 7.87 (d, *J* = 1.0 Hz, 1H), 7.82−7.80 (m, 2H), 7.67 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.51−7.47 (m, 1H), 7.29−7.25 (m, 1H), 7.20 (s, 1H), 7.13−7.11 (m, 2H) , 4.51 (t, *J* = 6.0 Hz, 2H), 2.41 (t, *J* = 6.0 Hz, 2H), 1.59 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.9, 150.6, 139.2, 139.1, 136.9, 130.9 (2C), 129.0, 128.5 (2C), 125.7, 123.3, 121.0, 114.8, 62.1, 52.9, 38.1, 27.9 (2C); HRMS (ESI) *m/z* calcd. for $C_{20}H_{21}ClN_3O_3$ $[M+H]^+$ 386.1266, found 386.1269.



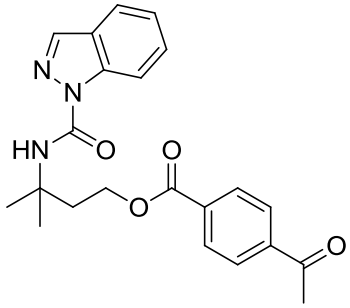
3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 4-bromobenzoate (3d): The title compound was obtained by column chromatography (PET: EtOAc = 12:1) as a colorless oil (73 mg) in 85% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): 8.32 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.86 (d, *J* = 1.0 Hz, 1H), 7.74−7.71 (m, 2H), 7.67 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.51−7.47 (m, 1H), 7.28−7.26 (m, 3H), 7.20 (s, 1H), 4.51 (t, *J* = 6.0 Hz, 2H), 2.41 (t, *J* = 6.0 Hz, 2H), 1.58 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.0, 150.6, 139.1, 136.9, 131.5 (2C), 131.0 (2C), 129.0, 128.9, 127.9, 125.7, 123.3, 121.0, 114.8, 62.1, 52.9, 38.0, 27.9 (2C); HRMS (ESI) *m/z* calcd. for $C_{20}H_{21}{}^{79}BrN_3O_3$ $[M+H]^+$ 430.0761, found 430.0768.



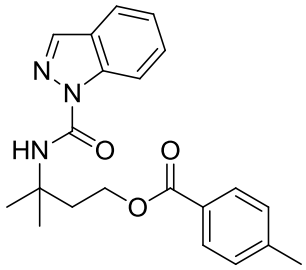
3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 4-(trifluoromethyl)benzoate (3e): The title compound was obtained by column chromatography (PET: EtOAc = 12:1) as a colorless oil (68 mg) in 82% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): 8.30 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 2H), 7.83 (d, *J* = 0.5 Hz, 1H), 7.64 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.49−7.46 (m, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.27−7.25 (m, 1H), 7.17 (s, 1H), 4.55 (t, *J* = 6.0 Hz, 2H), 2.45 (t, *J* = 6.0 Hz, 2H), 1.59 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.5, 150.6, 139.0, 136.9, 134.2 (q, *J* = 32.6 Hz), 133.2, 129.8 (2C), 129.0, 125.7, 125.1 (q, *J* = 3.6 Hz, 2C), 124.7, 123.3 (q, *J* = 291.8 Hz), 122.6, 114.8, 62.3, 52.8, 37.9, 28.0 (2C); HRMS (ESI) *m/z* calcd. for $C_{21}H_{21}F_3N_3O_4$ $[M+H]^+$ 420.1530, found 420. 1535.



3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 4-cyanobenzoate (3f): The title compound was obtained by column chromatography (PET: EtOAc = 12:1) as a colorless oil (69 mg) in 92% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): 8.25 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.88−7.86 (m, 2H), 7.81 (d, *J* = 1.0 Hz, 1H), 7.63 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.48−7.44 (m, 1H), 7.33−7.31 (m, 2H), 7.28−7.25 (m, 1H), 7.14 (s, 1H), 4.54 (t, *J* = 6.0 Hz, 2H), 2.42 (t, *J* = 6.0 Hz, 2H), 1.57 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.9, 150.4, 138.8, 136.8, 133.6, 131.8 (2C), 129.7 (2C), 129.0, 125.6, 123.3, 120.9, 117.9, 115.9, 114.7, 62.4, 52.6, 37.6, 27.9 (2C); HRMS (ESI) *m/z* calcd. for $C_{21}H_{21}N_4O_3$ $[M+H]^+$ 377.1608, found 377.1602.

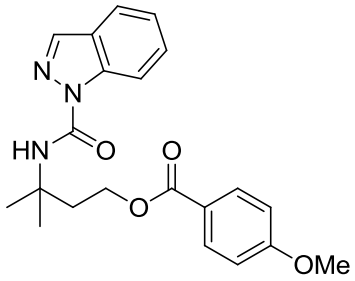


3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 4-acetylbenzoate (3g): The title compound was obtained by column chromatography (PET: EtOAc = 12:1) as a colorless oil (41 mg) in 57% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): 8.30 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.93−7.91 (m, 2H), 7.84 (d, *J* = 1.0 Hz, 1H), 7.67−7.65 (m, 2H), 7.61 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.48−7.45 (m, 1H), 7.24−7.21 (m, 1H), 7.19 (s, 1H), 4.54 (t, *J* = 6.0 Hz, 2H), 2.52 (s, 3H), 2.44 (t, *J* = 6.0 Hz, 2H), 1.58 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.5, 165.8, 150.5, 139.9, 139.00, 136.9, 133.7, 129.6 (2C), 128.9, 127.9 (2C), 125.7, 123.2, 120.9, 114.9, 62.2, 52.8, 37.9, 27.9 (2C), 26.9; HRMS (ESI) *m/z* calcd. for $C_{22}H_{24}N_3O_4$ $[M+H]^+$ 394.1761, found 394.1763.

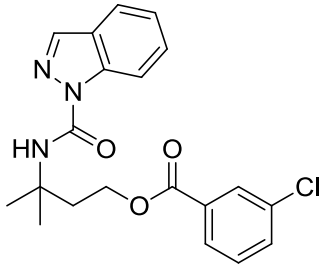


3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 4-methylbenzoate (3h): The title compound was obtained by column chromatography (PET: EtOAc = 12:1) as a colorless oil (53 mg) in 72% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): 8.35 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.88 (d, *J* = 0.5 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.66 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.50−7.47 (m,

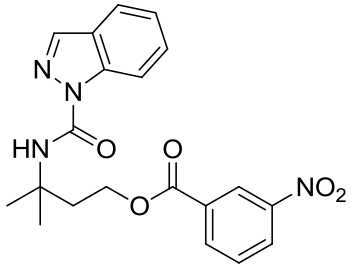
1H), 7.27−7.24 (m, 2H), 7.01 (d, *J* = 8.0 Hz, 2H) , 4.49 (t, *J* = 6.5 Hz, 2H), 2.40 (t, *J* = 6.5 Hz, 2H), 2.31 (s, 3H), 1.58 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.8, 150.6, 143.5, 139.1, 136.9, 129.6, 128.9 (2C), 128.9 (2C), 127.4, 125.7, 123.1, 120.9, 114.9, 61.6, 53.0, 38.4, 27.8 (2C), 21.7; HRMS (ESI) *m/z* calcd. for $C_{21}H_{24}N_3O_3$ $[M+H]^+$ 366.1812, found 366.1815.



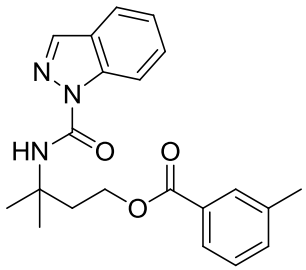
3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 4-methoxybenzoate (3i): The title compound was obtained by column chromatography (PET: EtOAc = 12:1) as a colorless oil (53 mg) in 69% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): 8.35 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.88 (d, *J* = 0.5 Hz, 1H), 7.86 (dt, *J* = 8.5, 2.5 Hz, 2H), 7.67 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.51−7.47 (m, 1H), 7.27−7.24 (m, 2H), 7.01 (dt, *J* = 9.0, 2.5 Hz, 2H) , 4.48 (t, *J* = 6.5 Hz, 2H), 3.78 (s, 3H), 2.39 (t, *J* = 6.5 Hz, 2H), 1.58 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.5, 163.2, 150.6, 139.1, 136.9, 131.6 (2C), 128.9, 125.7, 123.1, 122.5, 120.9, 114.9, 113.4 (2C), 61.5, 55.4, 53.0, 38.4, 27.8 (2C); HRMS (ESI) *m/z* calcd. for $C_{21}H_{24}N_3O_4$ $[M+H]^+$ 382.1761, found 382.1765.



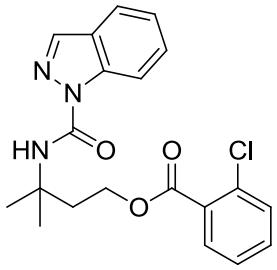
3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 3-chlorobenzoate (3j): The title compound was obtained by column chromatography (PET: EtOAc = 12:1) as a colorless oil (64 mg) in 83% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): 8.31 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.91 (t, *J* = 1.5 Hz, 1H), 7.89 (d, *J* = 1.0 Hz, 1H), 7.77 (dt, *J* = 8.5, 1.0 Hz, 1H), 7.64 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.47−7.44 (m, 1H), 7.35−7.32 (m, 1H), 7.25−7.21 (m, 2H), 7.09 (t, *J* = 8.0 Hz, 1H), 4.52 (t, *J* = 6.0 Hz, 2H), 2.40 (t, *J* = 6.0 Hz, 2H), 1.58 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.4, 150.5, 139.0, 136.9, 134.3, 132.7, 131.7, 129.6, 129.4, 128.9, 127.6, 125.6, 123.1, 120.8, 114.7, 62.3, 52.8, 38.2, 27.8 (2C); HRMS (ESI) *m/z* calcd. for $C_{20}H_{21}ClN_3O_3$ $[M+H]^+$ 386.1266, found 386.1269.



3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 3-nitrobenzoate (3k): The title compound was obtained by column chromatography (PET: EtOAc = 12:1) as a colorless oil (62 mg) in 78% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): 8.61 (t, *J* = 2.0 Hz, 1H), 8.18 (dd, *J* = 8.5, 1.0 Hz, 1H), 8.12 (t, *J* = 7.5, 1.0 Hz, 1H), 8.10−8.08 (m, 1H), 7.82 (d, *J* = 1.0 Hz, 1H), 7.58 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.40−7.36 (m, 1H), 7.27−7.24 (m, 1H), 7.21−7.17 (m, 1H), 7.15 (s, 1H), 4.58 (t, *J* = 6.0 Hz, 2H), 2.45 (t, *J* = 6.0 Hz, 2H), 1.57 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.4, 150.4, 147.9, 138.8, 136.9, 134.9, 131.6, 129.2, 128.8, 126.9, 125.5, 124.2, 123.1, 120.8, 114.6, 62.5, 52.7, 37.7, 27.9 (2C); HRMS (ESI) *m/z* calcd. for $C_{20}H_{21}N_4O_5$ $[M+H]^+$ 397.1506, found 397.1501.

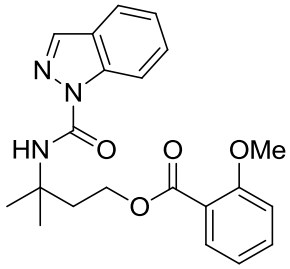


3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 3-methylbenzoate (3l): The title compound was obtained by column chromatography (PET: EtOAc = 12:1) as a colorless oil (54 mg) in 74% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): 8.35 (dd, *J* = 8.5, 0.5 Hz, 1H), 7.87 (d, *J* = 1.0 Hz, 1H), 7.76 (s, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.49−7.45 (m, 1H), 7.27−7.24 (m, 2H), 7.26−7.22 (m, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 4.51 (t, *J* = 6.5 Hz, 2H), 2.41 (t, *J* = 6.5 Hz, 2H), 2.27 (s, 3H), 1.59 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.9, 150.5, 139., 138.0, 136.8, 133.6, 130.1, 130.0, 128.9, 128.1, 126.7, 125.7, 123.1, 120.8, 114.8, 61.7, 52.9, 38.4, 27.8 (2C), 21.2; HRMS (ESI) *m/z* calcd. for $C_{21}H_{24}N_3O_3$ $[M+H]^+$ 366.1812, found 366.1807.

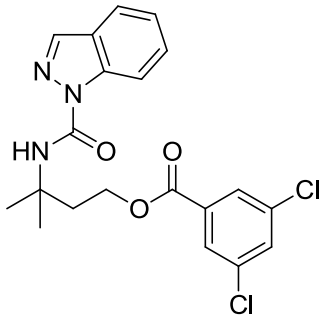


3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 2-chlorobenzoate (3m): The title compound was obtained by column chromatography (PET: EtOAc = 12:1) as a colorless oil (60 mg) in 79% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): 8.35 (dd, *J* = 8.5, 0.5 Hz, 1H), 7.86 (d, *J* = 0.5 Hz, 1H), 7.71 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.65 (d, *J* = 7.5, 2.0 Hz, 1H), 7.49−7.46

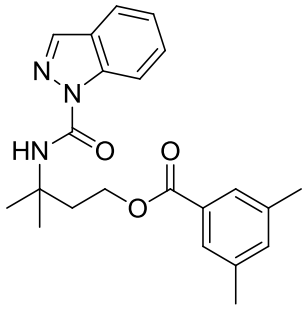
(m, 1H), 7.33 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.29−7.23 (m, 3H), 7.05 (td, *J* = 8.0 Hz, 1H), 4.52 (t, *J* = 6.0 Hz, 2H), 2.40 (t, *J* = 6.0 Hz, 2H), 1.58 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.6, 150.5, 139.0, 136.8, 133.8, 132.4, 131.3, 131.0, 129.8, 128.9, 126.4, 125.6, 123.1, 120.9, 114.8, 62.3, 52.8, 38.2, 27.7 (2C); HRMS (ESI) *m/z* calcd. for $C_{20}H_{21}ClN_3O_3$ $[M+H]^+$ 386.1266, found 386.1263.



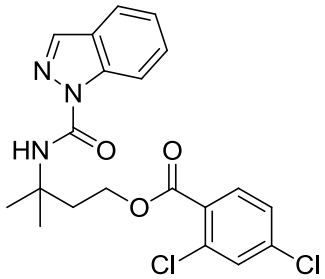
3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 2-methoxybenzoate (3n): The title compound was obtained by column chromatography (PET: EtOAc = 12:1) as a colorless oil (50 mg) in 65% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): 8.36 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.85 (d, *J* = 0.5 Hz, 1H), 7.73 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.67 (dt, *J* = 8.0 Hz, 1H), 7.50−7.47 (m, 1H), 7.40−7.37 (m, 1H), 7.30 (s, 1H), 7.27−7.24 (m, 1H), 6.89 (d, *J* = 8.0 Hz, 1H), 6.78 (td, *J* = 7.5, 1.0 Hz, 1H), 4.48 (t, *J* = 6.5 Hz, 2H), 3.84 (s, 3H), 2.38 (t, *J* = 6.5 Hz, 2H), 1.59 (s, 6H);^{13}C NMR (125 MHz, $CDCl_3$): δ 166.2, 159.3, 150.6, 139.2, 136.8, 133.5, 131.7, 128.9, 125.7, 123.1, 120.9, 120.0, 120.0, 114.9, 111.9, 61.7, 56.0, 53.1, 38.6, 27.7 (2C); HRMS (ESI) *m/z* calcd. for $C_{21}H_{24}N_3O_4$ $[M+H]^+$ 382.1761, found 382.1766.



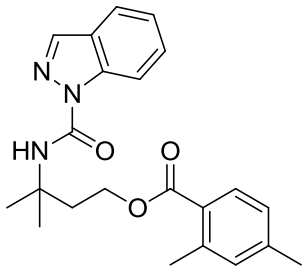
3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 3,5-dichlorobenzoate (3o): The title compound was obtained by column chromatography (PET: EtOAc = 12:1) as a colorless oil (71 mg) in 85% yield according to the **Method A**.^{1}H NMR (500 MHz, $CDCl_3$): 8.23 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.90 (d, *J* = 0.5 Hz, 1H), 7.71 (d, *J* = 2.0 Hz, 2H), 7.62 (dt, *J* = 7.5, 1.0 Hz, 1H), 7.45−7.41 (m, 1H), 7.24 (t, *J* = 7.0 Hz, 1H), 7.23−7.19 (m, 1H), 7.17 (s, 1H), 4.53 (t, *J* = 6.5 Hz, 2H), 2.40 (t, *J* = 6.5 Hz, 2H), 1.56 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.2, 150.4, 138.9, 137.0, 134.9, 132.7, 132.4, 128.9 (2C), 127.8 (2C), 125.5, 123.1, 120.8, 114.6, 62.5, 52.7, 38.0, 27.8 (2C); HRMS (ESI) *m/z* calcd. for $C_{20}H_{20}Cl_2N_3O_3$ $[M+H]^+$ 420.0876, found 420.0874.



3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 3,5-dimethylbenzoate (3p): The title compound was obtained by column chromatography (PET: EtOAc = 12:1) as a colorless oil (55 mg) in 73% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): 8.33 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.88 (d, *J* = 1.0 Hz, 1H), 7.66 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.56 (s, 2H), 7.48−7.45 (m, 1H), 7.26−7.23 (m, 2H), 7.04 (s, 1H), 4.50 (t, *J* = 6.5 Hz, 2H), 2.41 (t, *J* = 6.5 Hz, 2H), 2.23 (s, 6H), 1.59 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.1, 150.5, 139.1, 137.9, 136.8, 134.5, 130.0, 128.8 (2C), 127.3 (2C), 125.7, 123.1, 120.8, 114.8, 61.6, 52.9, 38.4, 27.8 (2C), 21.6 (2C); HRMS (ESI) *m/z* calcd. for $C_{22}H_{26}N_3O_3$ $[M+H]^+$ 380.1969, found 380.1965.

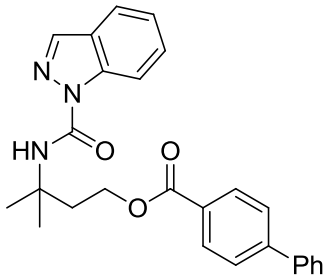


3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 2,4-dichlorobenzoate (3q): The title compound was obtained by column chromatography (PET: EtOAc = 12:1) as a colorless oil (50 mg) in 65% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): 8.30 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.82 (d, *J* = 1.0 Hz, 1H), 7.62 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.58 (d, *J* = 8.5 Hz, 1H), 7.46−7.43 (m, 1H), 7.23−7.20 (m, 2H), 7.16 (s, 1H), 6.87 (dd, *J* = 8.5, 2.5 Hz, 1H), 4.49 (t, *J* = 6.5 Hz, 2H), 2.38(t, *J* = 6.5 Hz, 2H), 1.54 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): 164.4, 150.4, 138.8, 138.0, 73, 134.82, 132.3 130.7, 128.8, 127.8 126.6, 125.5, 123.1, 120.8, 114.6, 62.3, 52.6, 37.7, 27.7 (2C); HRMS (ESI) *m/z* calcd. for $C_{20}H_{20}Cl_2N_3O_3$ $[M+H]^+$ 420.0876, found 420.0881.

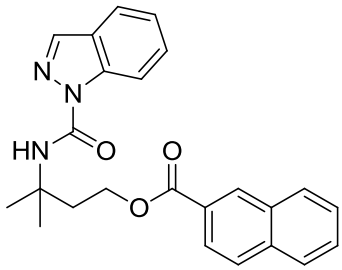


3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 2,4-dimethylbenzoate (3r) The title compound was obtained by column chromatography (PET: EtOAc = 12:1) as a colorless oil (51mg) in 67 yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): 8.34 (dd, *J* = 8.5, 1.0 Hz, 1H),

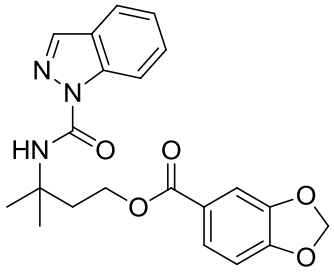
7.86 (d, *J* = 0.5 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.65 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.49−7.46 (m, 1H), 7.26−7.23 (m, 2H), 6.93 (s, 1H), 6.78 (dd, *J* = 8.5, 0.5 Hz, 1H), 4.46 (t, *J* = 6.5 Hz, 2H), 2.53 (s, 3H), 2.38 (t, *J* = 6.5 Hz, 2H), 2.26 (s, 3H), 1.58 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.5 150.6, 142.4 140.5 139.1 136.8 132.4, 130.8 128.8, 126.4, 126.3 125.7, 123.1 120.8, 114.8, 61.3 52.9, 38.4, 27.8(2C), 21.9, 21.4; HRMS (ESI) *m/z* calcd. for $C_{22}H_{26}N_3O_3$ $[M+H]^+$ 380.1969, found 380.1962.



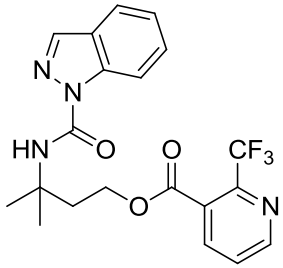
3-(1*H*-indazole-1-carboxamido)-3-methylbutyl [1,1'-biphenyl]-4-carboxylate (3s): The title compound was obtained by column chromatography (PET: EtOAc = 12:1) as a colorless oil (32 mg) in 38% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): 8.37 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.99−7.96 (m, 2H), 7.88 (d, *J* = 1.0 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.54−7.50 (m, 2H), 7.50−7.44 (m, 3H), 7.43−7.37 (m, 3H), 7.25−7.21 (m, 1H), 4.54 (t, *J* = 6.5 Hz, 2H), 2.44 (t, *J* = 6.5 Hz, 2H), 1.60 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.7, 150.6, 145.5, 140.1, 139.1, 136.9, 130.1 (2C), 129.0 (2C), 129.0, 128.8, 128.2, 127.4 (2C), 126.9 (2C), 125.8, 123.2, 120.9, 114.9, 61.9, 53.0, 38.3, 27.9 (2C); HRMS (ESI) *m/z* calcd. for $C_{26}H_{26}N_3O_3$ $[M+H]^+$ 428.1969, found 428.1962.



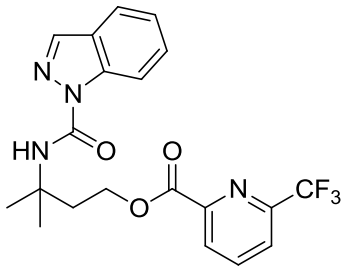
3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 2-naphthoate (3t): The title compound was obtained by column chromatography (PET: EtOAc = 12:1) as a colorless oil (36 mg) in 45% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): 8.49 (s, 1H), 8.32 (dd, *J* = 8.5, 0.5 Hz, 1H), 7.94 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.79 (d, *J* =1.5 Hz, 1H),7.78−7.77 (m, 2H), 7.65 (d, *J* = 8.5 Hz, 1H), 7.57−7.53 (m, 2H), 7.49−7.46 (m, 1H), 7.45−7.42 (m, 1H), 7.28 (s, 1H), 7.20−7.16 (m, 1H), 4.59 (t, *J* = 6.5 Hz, 2H), 2.47 (t, *J* = 6.5 Hz, 2H), 1.61 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.9, 150.6, 139.1, 136.9, 135.5, 132.5, 131.1, 129.4, 128.9, 128.2, 128.0, 127.8, 127.4, 126.6, 125.7, 125.2, 123.1, 120.8, 114.8, 62.0, 53.0, 38.4, 27.9 (2C); HRMS (ESI) *m/z* calcd. for $C_{24}H_{24}N_3O_3$ $[M+H]^+$ 402.1812, found 402.1816.



3-(1*H*-indazole-1-carboxamido)-3-methylbutylbenzo[*d*][1,3]dioxole-5-carboxylate (3u): The title compound was obtained by column chromatography (PET: EtOAc = 12:1) as a colorless oil (42 mg) in 53% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): 8.33 (dd, *J* = 8.5, 0.5 Hz, 1H), 7.94 (d, *J* = 0.5 Hz, 1H), 7.68 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.53 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.50−7.46 (m, 1H), 7.40 (d, *J* = 1.0 Hz, 1H), 7.27−7.24 (m, 2H), 6.60 (d, *J* = 8.0 Hz, 1H), 5.96 (s, 2H), 4.48 (t, *J* = 6.5 Hz, 2H), 2.37 (t, *J* = 6.5 Hz, 2H), 1.58 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.1, 151.5, 150.6, 147.6, 139.2, 136.9, 128.9, 125.7, 125.4, 124.1, 123.1, 120.9, 114.9, 109.5, 107.8, 101.8, 61.7, 53.0, 38.5, 27.8 (2C); HRMS (ESI) *m/z* calcd. for $C_{21}H_{22}N_3O_5$ $[M+H]^+$ 396.1554, found 396.1549.

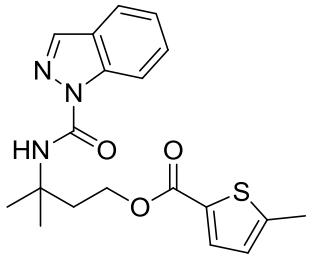


3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 2-(trifluoromethyl)nicotinate (3v): The title compound was obtained by column chromatography (PET: EtOAc = 10:1) as a colorless oil (53 mg) in 63% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): 8.63 (dd, *J* = 5.0, 1.5 Hz, 1H), 8.30 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.94 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.84 (d, *J* = 0.5 Hz, 1H), 7.66 (dt, *J* = 0.5 Hz, 1H), 7.50−7.47 (m, 1H), 7.28−7.24 (m, 2H), 7.17 (s, 1H), 4.55 (t, *J* = 6.0 Hz, 2H), 2.41 (t, *J* = 6.0 Hz, 2H), 1.56 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.2, 150.5, 145.6 (q, *J* = 35.1 Hz), 138.9, 138.0, 136.8, 128.9, 127.6, 125.6, 125.5, 123.1, 122.1, 120.9, 114.7, 63.3, 52.6, 37.7, 27.7 (2C); HRMS (ESI) *m/z* calcd. for $C_{20}H_{20}F_3N_3O_4$ $[M+H]^+$ 420.1530, found 420. 1534.

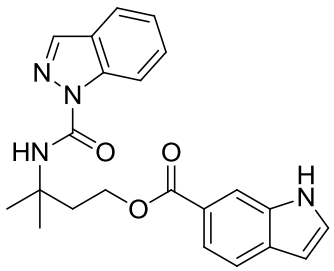


3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 6-(trifluoromethyl)nicotinate (3w): The title compound was obtained by column chromatography (PET: EtOAc = 10:1) as a colorless oil (45 mg) in 54% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): 8.27 (dd, *J* = 8.5,

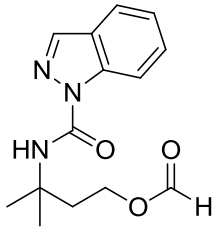
0.5 Hz, 1H), 8.05 (d, *J* = 6.5 Hz, 1H), 7.86 (d, *J* = 0.5 Hz, 1H), 7.67−7.61 (m, 3H), 7.46−7.43 (m, 1H), 7.24−7.21 (m, 1H), 7.16 (s, 1H), 4.60 (t, *J* = 6.0 Hz, 2H), 2.46 (t, *J* = 6.0 Hz, 2H), 1.57 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.9, 150.5, 148.3 (q, *J* = 35.3 Hz), 148.3, 138.9, 138.3, 136.9, 128.9, 127.2, 125.6, 123.1 (q, *J* = 2.6 Hz), 122.2, 120.0 (q, *J* = 273.00 Hz), 120.0, 114.7, 63.0, 52.8, 37.7, 27.9 (2C); HRMS (ESI) *m/z* calcd. for $C_{20}H_{20}F_3N_3O_4$ $[M+H]^+$ 420.1530, found 420. 1532.



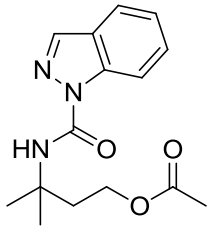
3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 5-methylthiophene-2-carboxylate (3x): The title compound was obtained by column chromatography (PET: EtOAc = 12:1) as a colorless oil (27 mg) in 36% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): 8.36 (dd, *J* = 8.5, 0.5 Hz, 1H), 7.94 (d, *J* = 0.5 Hz, 1H), 7.68 (dt, *J* = 8.0, 0.5 Hz, 1H), 7.51−7.47 (m, 2H), 7.27−7.24 (m, 1H), 7.21 (s, 1H), 6.57 (dd, *J* = 3.5, 1.0 Hz, 1H), 4.45 (t, *J* = 6.0 Hz, 2H), 2.38−2.36 (m, 5H), 1.57 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.4, 150.6, 148.0, 139.2, 136.9, 133.9, 131.0, 128.9, 126.2, 125.7, 123.1, 120.9, 114.9, 77.2, 61.7, 52.9, 38.3, 27.9 (2C), 15.7; HRMS (ESI) *m/z* calcd. for $C_{19}H_{22}N_3O_3S$ $[M+H]^+$ 372.1376, found 372.1371.



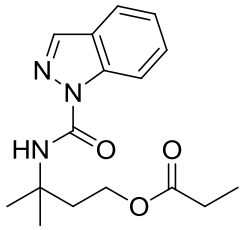
3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 1*H*-indole-6-carboxylate (3y): The title compound was obtained by column chromatography (PET: EtOAc = 12:1) as a colorless oil (46 mg) in 59% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): 8.41 (dd, *J* = 8.5, 1.0 Hz, 1H), 8.04 (s, 1H), 7.95 (s, 1H), 7.81 (d, *J* = 1.0 Hz, 1H), 7.74 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.63 (d, *J* = 8.5 Hz, 1H), 7.52−7.48 (m, 2H), 7.28−7.24 (m, 3H), 6.52−6.51 (m, 1H), 4.53 (t, *J* = 6.5 Hz, 2H), 2.44 (t, *J* = 6.5 Hz, 2H), 1.60 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.8, 150.6, 139.1, 136.8, 135.0, 131.5, 128.9, 127.5, 125.8, 123.7, 123.1, 121.0, 121.0, 120.2, 114.9, 113.3, 103.0, 61.6, 53.0, 38.4, 27.9 (2C); HRMS (ESI) *m/z* calcd. for $C_{22}H_{23}N_4O_3$ $[M+H]^+$ 391.1765, found 391.1760.



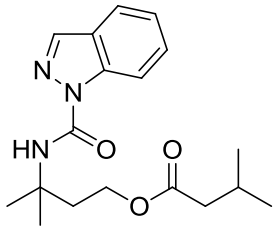
3-(1*H*-indazole-1-carboxamido)-3-methylbutyl formate (3z): The title compound was obtained by column chromatography (PET: EtOAc = 12:1) as a colorless oil (25 mg) in 45% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): 8.37 (dd, *J* = 8.5, 0.5 Hz, 1H), 8.03 (s, 1H), 8.02 (d, *J* = 0.5 Hz, 1H), 7.71 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.53−7.50 (m, 1H), 7.30−7.27 (m, 1H), 7.22(s, 1H), 4.34 (td, *J* = 6.5, 0.5 Hz, 2H), 2.30 (t, *J* = 6.0 Hz, 2H), 1.54 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.1, 150.6, 139.2, 137.1, 129.1, 125.8, 123.3, 121.0, 114.9, 60.9, 52.9, 38.3, 27.8 (2C); HRMS (ESI) *m/z* calcd. for $C_{14}H_{18}N_3O_3$ $[M+H]^+$ 276.01343, found 276.1342.



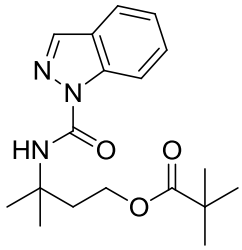
3-(1*H*-indazole-1-carboxamido)-3-methylbutyl acetate (3aa): The title compound was obtained by column chromatography (PET: EtOAc = 12:1) as a colorless oil (47 mg) in 81% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): 8.39 (dd, *J* = 8.5, 0.5 Hz, 1H), 8.00 (d, *J* = 0.5 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.52−7.48 (m, 1H), 7.36(s, 1H), 7.28−7.25 (m, 1H), 4.25 (t, *J* = 6.5, Hz, 2H), 2.21 (t, *J* = 6.5 Hz, 2H), 1.99 (s, 3H), 1.54 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.2, 150.6, 139.1, 136.9, 129.0, 125.7, 123.2, 123.0, 114.8, 61.3, 53.0, 38.7, 27.5 (2C), 21.0; HRMS (ESI) *m/z* calcd. for $C_{15}H_{20}N_3O_3$ $[M+H]^+$ 290.1499, found 290.1492.



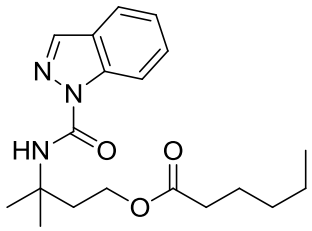
3-(1*H*-indazole-1-carboxamido)-3-methylbutyl propionate (3ab): The title compound was obtained by column chromatography (PET: EtOAc = 12:1) as a colorless oil (46 mg) in 76% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): 8.38 (dd, *J* = 8.5, 1.0 Hz, 1H), 8.00 (d, *J* = 1.0 Hz, 1H), 7.71 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.52−7.49 (m, 1H), 7.33 (s, 1H), 7.29−7.25 (m, 1H), 4.26 (t, *J* = 6.5, Hz, 2H), 2.28 (q, *J* = 7.5 Hz, 2H), 2.22 (t, *J* = 6.5 Hz, 2H), 1.54 (s, 6H), 1.08 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.6, 150.6, 139.2, 136.9, 129.0, 125.7, 123.2, 121.0, 114.9, 61.2, 53.0, 38.8, 27.6 (2C), 27.5, 9.1; HRMS (ESI) *m/z* calcd. for $C_{16}H_{22}N_3O_3$ $[M+H]^+$ 304.1656, found 304.1652.



3-(1H-indazole-1-carboxamido)-3-methylbutyl 3-methylbutanoate (3ac): The title compound was obtained by column chromatography (PET: EtOAc = 12:1) as a colorless oil (52 mg) in 78% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): 8.39 (dd, *J* = 8.5, 1.0 Hz, 1H), 8.00 (d, *J* = 1.0 Hz, 1H), 7.71 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.52−7.49 (m, 1H), 7.33 (s, 1H), 7.29−7.26 (m, 1H), 4.25 (t, *J* = 6.5, Hz, 2H), 2.21 (t, *J* = 6.5 Hz, 2H), 2.12 (d, *J* = 7.0 Hz, 2H), 2.08−1.99 (m, 1H),1.54 (s, 6H), 0.87 (t, *J* = 6.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.2, 150.6, 139.2, 136.9, 129.0, 125.7, 123.2, 123.0, 114.9, 61.1, 53.0, 43.4, 38.8, 27.5 (2C), 25.7, 22.5 (2C); HRMS (ESI) *m/z* calcd. for $C_{18}H_{26}N_3O_3$ $[M+H]^+$ 332.1969, found 332.1963.

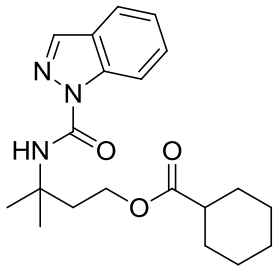


3-(1*H*-indazole-1-carboxamido)-3-methylbutyl pivalate (3ad): The title compound was obtained by column chromatography (PET: EtOAc = 12:1) as a colorless oil (53 mg) in 80% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): 8.38 (dd, *J* = 8.5, 1.0 Hz, 1H), 8.01 (d, *J* = 1.0 Hz, 1H), 7.72 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.53−7.49 (m, 1H), 7.29−7.26 (m, 1H), 7.20 (s, 1H), 4.22 (t, *J* = 6.5, Hz, 2H), 2.26 (t, *J* = 6.5 Hz, 2H), 1.54 (s, 6H), 1.16 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 178.8, 150.5, 139.2, 137.0, 129.0, 125.8, 123.2, 121.0, 114.9, 61.4, 53.0, 38.8, 38.7, 27.7 (2C), 27.3 (3C); HRMS (ESI) *m/z* calcd. for $C_{18}H_{26}N_3O_3$ $[M+H]^+$ 332.1969, found 332.1962.

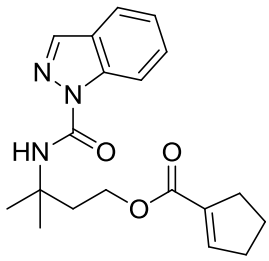


3-(1*H*-indazole-1-carboxamido)-3-methylbutyl hexanoate (3ae): The title compound was obtained by column chromatography (PET: EtOAc = 12:1) as a colorless oil (49 mg) in 71% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): 8.38 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.99 (d, *J* = 1.0 Hz, 1H), 7.71 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.52−7.49 (m, 1H), 7.33 (s, 1H), 7.28−7.25 (m, 1H), 4.25 (t, *J* = 6.5 Hz, 2H), 2.24−2.20 (m, 4H), 1.57−1.51 (m, 8H), 1.25−1.16 (m, 4H), 0.85 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.0, 150.6, 139.2, 136.9, 129.0, 125.7, 123.2,

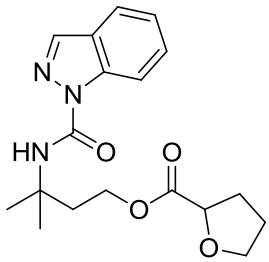
120.9, 114.9, 61.1, 53.0, 38.7, 34.3, 31.4, 27.5 (2C), 24.6, 22.4, 14.0; HRMS (ESI) *m/z* calcd. for $C_{19}H_{28}N_3O_3$ $[M+H]^+$ 346.2125, found 346.2123.



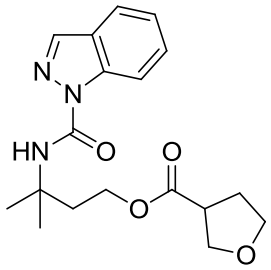
3-(1*H*-indazole-1-carboxamido)-3-methylbutyl hexanoate (3af): The title compound was obtained by column chromatography (PET: EtOAc = 12:1) as a colorless oil (55 mg) in 77% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): 8.38 (dd, *J* = 8.5, 1.0 Hz, 1H), 8.00 (d, *J* = 1.0 Hz, 1H), 7.71 (dt, *J* = 8.5, 1.0 Hz, 1H), 7.51−7.48 (m, 1H), 7.30 (s, 1H), 7.28−7.25 (m, 1H), 4.23 (t, *J* = 6.5 Hz, 2H), 2.22 (t, *J* = 6.5 Hz, 2H), 2.20−2.16 (m, 1H), 1.82−1.80 (m, 2H), 1.67−1.62 (m, 2H), 1.57−1.57 (m, 7H), 1.38−1.30 (m, 2H), 1.13−1.08 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 176.2, 150.5, 139.1, 136.9, 129.0, 125.7, 123.2, 120.9, 114.8, 61.0 (2C), 52.9, 43.2, 38.6, 29.0, 27.6 (2C), 25.7 (2C), 25.5; HRMS (ESI) *m/z* calcd. for $C_{20}H_{28}N_3O_3$ $[M+H]^+$ 358.2125, found 358.2129.



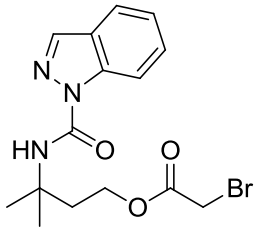
3-(1*H*-indazole-1-carboxamido)-3-methylbutyl cyclopent-1-enecarboxylate (3ag): The title compound was obtained by column chromatography (PET: EtOAc = 12:1) as a colorless oil (43 mg) in 63% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): 8.37 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.98 (d, *J* = 1.0 Hz, 1H), 7.71 (dt, *J* = 8.5, 1.0 Hz, 1H), 7.52−7.48 (m, 1H), 7.28−7.25 (m, 1H), 7.21 (s, 1H), 6.66−6.64 (m, 1H), 4.32 (t, *J* = 6.5 Hz, 2H), 2.47−2.43 (m, 2H), 2.29 (t, *J* = 6.5 Hz, 2H), 2.27−2.24 (m, 2H), 1.82−1.75 (m, 2H), 1.55 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.5, 150.6, 144.0, 139.2, 136.8, 136.3, 129.0, 125.7, 123.2, 120.9, 114.9, 60.9, 53.0, 38.5, 33.35, 31.4, 27.8 (2C), 23.0; HRMS (ESI) *m/z* calcd. for $C_{19}H_{24}N_3O_3$ $[M+H]^+$ 342.1812, found 342.1806.



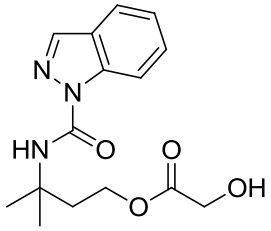
3-(1*H*-indazole-1-carboxamido)-3-methylbutyl tetrahydrofuran-2-carboxylate (3ah): The title compound was obtained by column chromatography (PET: EtOAc = 8:1) as a colorless oil (27 mg) in 39% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): 8.35 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.98 (d, *J* = 1.0 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.49−7.46 (m, 1H), 7.25−7.22 (m, 2H), 4.28−4.33 (m, 1H), 4.32−4.24 (m, 2H), 3.95−3.80 (m, 2H), 2.29−2.20 (m, 2H), 2.13−1.91 (m, 2H), 1.89−1.75 (m, 2H), 1.51 (d, *J* = 3.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.4, 150.4, 139.0, 136.9, 128.9, 125.6, 123.1, 120.9, 114.7, 76.7, 69.3, 61.7, 52.8, 38.4, 30.1, 27.6 (2C), 25.2; HRMS (ESI) *m/z* calcd. for $C_{18}H_{24}N_3O_4$ $[M+H]^+$ 346.1761, found 346.1763.



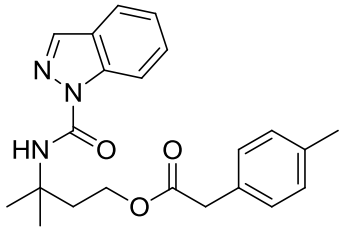
3-(1*H*-indazole-1-carboxamido)-3-methylbutyl tetrahydrofuran-3-carboxylate (3ai): The title compound was obtained by column chromatography (PET: EtOAc = 12:1) as a colorless oil (33 mg) in 48% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): 8.37 (dd, *J* = 8.5, 1.0 Hz, 1H), 8.00 (d, *J* = 1.0 Hz, 1H), 7.70 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.51−7.48 (m, 1H), 7.28−7.25 (m, 2H), 4.32−4.24 (m, 2H), 3.90−3.85 (m, 2H), 3.84−3.70 (m, 2H), 3.04−2.98 (m, 1H), 2.24 (t, *J* = 6.5 Hz, 2H), 2.14−1.97 (m, 2H), 1.53 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.9, 150.5, 139.1, 137.0, 129.0, 125.7, 123.2, 121.0, 114.8, 70.3, 68.3, 61.8, 52.9, 43.8, 38.5, 29.5, 27.6 (2C); HRMS (ESI) *m/z* calcd. for $C_{18}H_{24}N_3O_4$ $[M+H]^+$ 346.1761, found 346.1766.



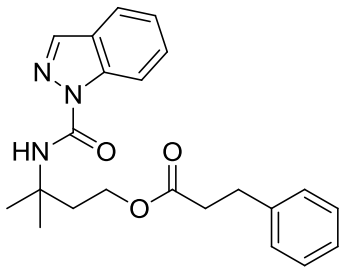
3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 2-bromoacetate (3aj): The title compound was obtained by column chromatography (PET: EtOAc = 12:1) as a colorless oil (54 mg) in 73% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): 8.37 (dd, *J* = 8.5, 0.5 Hz, 1H), 8.02 (d, *J* = 0.5 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.53−7.50 (m, 1H), 7.30−7.27 (m, 2H), 4.36 (t, *J* = 6.5, Hz, 2H), 3.79 (s, 2H), 2.28 (t, *J* = 6.5 Hz, 2H), 1.55 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.3, 150.6, 139.2, 137.1, 129.1, 125.8, 123.3, 121.0, 114.8, 63.3, 52.9, 38.3, 27.7 (2C), 25.9; HRMS (ESI) *m/z* calcd. for $C_{15}H_{19}BrN_3O_3$ $[M+H]^+$ 368.0604, found 368.0601.



3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 2-hydroxyacetate (3ak): The title compound was obtained by column chromatography (PET: EtOAc = 3:1) as a colorless oil (43 mg) in 70% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): 8.36 (dd, *J* = 8.5, 0.5 Hz, 1H), 8.01 (d, *J* = 0.5 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.52−7.49 (m, 1H), 7.33 (s, 1H), 7.28−7.25 (m, 1H), 4.39 (t, *J* = 6.5 Hz, 2H), 4.11 (d, *J* = 6.0 Hz, 2H), 2.82 (t, *J* = 6.0 Hz, 1H), 2.23 (t, *J* = 6.5 Hz, 2H), 1.54 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.1, 150.5, 139.2, 137.2, 129.2, 125.6, 123.3, 121.0, 114.8, 62.4, 60.8, 52.9, 38.7, 27.4 (2C); HRMS (ESI) *m/z* calcd. for $C_{15}H_{20}N_3O_4$ $[M+H]^+$ 306.1448, found 306.1442.

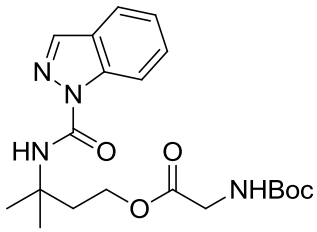


3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 2-(*p*-tolyl)acetate (3al): The title compound was obtained by column chromatography (PET: EtOAc = 12:1) as a colorless oil (55 mg) in 73% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): 8.40 (dd, *J* = 8.5, 1.5 Hz, 1H), 8.01 (d, *J* = 0.5 Hz, 1H), 7.71 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.53−7.50 (m, 1H), 7.35 (s, 1H), 7.29−7.26 (m, 1H), 7.13−7.08 (m, 4H), 4.27 (t, *J* = 6.5 Hz, 2H), 3.55 (s, 2H), 2.32 (s, 3H), 2.22 (t, *J* = 6.5 Hz, 2H), 1.52 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.9, 150.6, 139.2, 137.0, 136.8, 130.9, 129.4, 129.2 (2C), 129.0 (2C), 125.7, 123.2, 121.0, 114.9, 61.8, 53.0, 40.9, 38.7, 27.5 (2C), 21.2; HRMS (ESI) *m/z* calcd. for $C_{22}H_{26}N_3O_3$ $[M+H]^+$ 380.1969, found 380.1964.

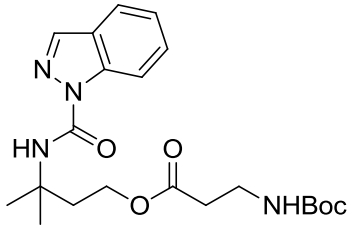


3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 3-phenylpropanoate (3am): The title compound was obtained by column chromatography (PET: EtOAc = 12:1) as a colorless oil (57 mg) in 78% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): 8.39 (dd, *J* = 8.5, 1.5 Hz, 1H), 8.94 (d, *J* = 1.0 Hz, 1H), 7.70 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.52−7.49 (m, 1H), 7.32 (s, 1H), 7.29−7.23 (m, 3H), 7.18 (td, *J* = 7.5, 1.5 Hz, 1H), 7.09 (dd, *J* = 8.5, 1.5 Hz, 2H), 4.26 (t, *J* = 6.5 Hz, 2H), 2.89 (t, *J* = 7.5 Hz, 2H), 2.58 (t, *J* = 7.5 Hz, 2H), 2.20 (t, *J* = 6.5 Hz, 2H), 1.52 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.0, 150.6, 140.6, 139.2, 137.0, 129.0, 128.6 , 128.3 (2C),

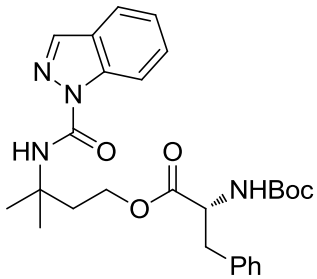
126.4, 125.7, 123.2, 121.0, 114.9, 61.4, 53.0, 38.7, 35.9, 31.0, 27.5 (2C); HRMS (ESI) *m/z* calcd. for $C_{22}H_{26}N_3O_3$ $[M+H]^+$ 380.1969, found 380.1972.



3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 2-((tert-butoxycarbonyl) amino) acetate (3an): The title compound was obtained by column chromatography (PET: EtOAc = 4:1) as a colorless oil (61 mg) in 75% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): 8.37 (dd, *J* = 8.5, 0.5 Hz, 1H), 8.04 (d, *J* = 0.5 Hz, 1H), 7.71 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.52−7.49 (m, 1H), 7.34 (s, 1H), 7.28−7.25 (m, 1H), 5.07 (s, 1H), 4.34 (t, *J* = 6.5, Hz, 2H), 3.91 (d, *J* = 5.5 Hz, 2H), 2.22 (t, *J* = 6.5 Hz, 2H), 1.54 (s, 6H), 1.43 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.4, 155.8, 150.5, 139.2, 137.2, 129.1, 125.7, 123.3, 121.0, 114.8, 80.1, 62.3, 52.9, 42.6, 38.8, 28.4 (2C), 27.5 (3C); HRMS (ESI) *m/z* calcd. for $C_{20}H_{29}N_4O_5$ $[M+H]^+$ 405.2132, found 405.2131.

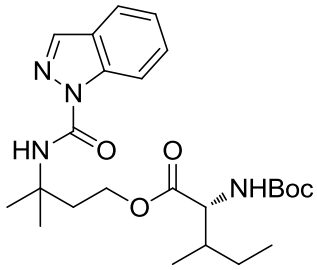


3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 3-((tert-butoxycarbonyl)amino) propanoate (3ao): The title compound was obtained by column chromatography (PET: EtOAc = 4:1) as a colorless oil (54 mg) in 65% yield according to the **Method A**.^{1}H NMR (500 MHz, $CDCl_3$): 8.32 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.96 (d, *J* = 0.5 Hz, 1H), 7.63 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.45−7.42 (m, 1H), 7.30 (s, 1H), 7.22−7.18 (m, 1H), 5.09 (s, 1H), 4.22 (t, *J* = 6.5 Hz, 2H), 3.29 (q, *J* = 6.0 Hz, 2H), 2.44 (t, *J* = 6.0 Hz, 2H), 2.16 (t, *J* = 6.5 Hz, 2H), 1.48 (s, 6H), 1.36 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.3, 155.7, 150.4, 138.9, 136.9, 128.8, 125.5, 123.1, 120.8, 114.6, 79.1, 61.4, 52.7, 38.5, 36.0, 34.5, 28.3 (3C), 27.3 (2C); HRMS (ESI) *m/z* calcd. for $C_{21}H_{31}N_4O_5$ $[M+H]^+$ 419.2289, found 419.2286.

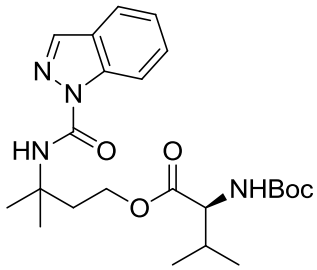


(*R*)-3-(1H-indazole-1-carboxamido)-3-methylbutyl 2-((tert-butoxycarbonyl)amino)-3-phenylpropanoate (3ap): The title compound was obtained by column chromatography (PET: EtOAc = 4:1) as a colorless oil (62 mg) in 63% yield according to the **Method A**. ^{1}H NMR (500

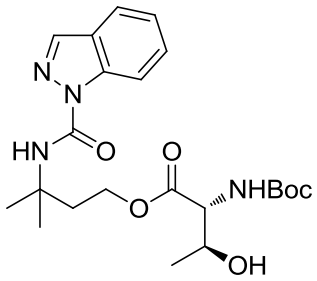
MHz, $CDCl_3$): 8.38 (dd, *J* = 8.5, 0.5 Hz, 1H), 8.05 (s, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.52−7.49 (m, 1H), 7.29−7.26 (m, 2H), 7.21−7.15 (m, 3H), 7.05 (d, *J* = 6.5 Hz, 1H), 5.19 (d, *J* = 8.5 Hz, 1H), 4.68−4.64 (m, 1H), 4.37−4.18 (m, 2H), 3.04 (d, *J* = 6.0 Hz, 2H), 2.18−2.10 (m, 2H), 1.50 (s, 6H), 1.41 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.9, 155.2, 150.4, 139.1, 137.2, 136.0, 129.3 (2C), 129.0, 128.5 (2C), 127.0, 125.7, 123.2, 121.0, 114.8, 79.9, 62.2, 54.6, 52.8, 38.9, 28.4, 27.5 (2C), 27.4, 27.2, 27.1; HRMS (ESI) *m/z* calcd. for $C_{27}H_{35}N_4O_5$ $[M+H]^+$ 495.2602, found 495.2605.



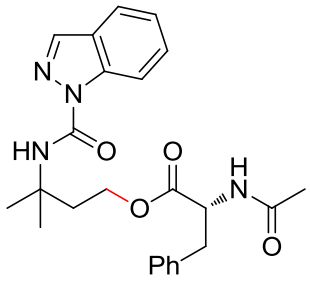
(2*R*)-3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 2-((tert-butoxycarbonyl)amino)-3-methylpentanoate (3aq): The title compound was obtained by column chromatography (PET: EtOAc = 4:1) as a colorless oil (64 mg) in 70% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): 8.37 (dd, *J* = 8.5, 0.5 Hz, 1H), 8.05 (s, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.50−7.47 (m, 1H), 7.32 (s, 1H), 7.27−7.23 (m, 1H), 5.22 (d, *J* = 8.0 Hz, 1H), 4.36−4.23 (m, 3H), 2.26−2.15 (m, 2H), 1.81−1.72 (m, 1H), 1.52 (d, *J* = 7.0 Hz, 6H), 1.40 (s, 9H), 1.37−1.04 (m, 2H), 0.85−0.82 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.3, 155.6, 150.5, 139.1, 137.2, 129.0, 125.7, 123.2, 121.0, 114.8, 79.7, 62.0, 58.1, 52.9, 38.9, 38.0, 28.4 (3C), 27.5, 27.2, 24.9, 15.6, 11.6; HRMS (ESI) *m/z* calcd. for $C_{24}H_{37}N_4O_5$ $[M+H]^+$ 461.2758, found 461.2756.



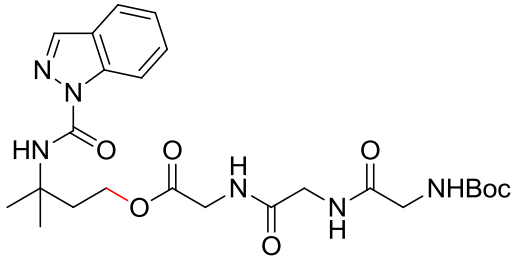
(*S*)-3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 2-((tert-butoxycarbonyl)amino)-3-methylbutanoate (3ar): The title compound was obtained by column chromatography (PET: EtOAc = 4:1) as a colorless oil (64 mg) in 72% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): 8.36 (dd, *J* = 8.5, 0.5 Hz, 1H), 8.06 (s, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.50−7.47 (m, 1H), 7.34 (s, 1H), 7.26−7.23 (m, 1H), 5.21 (d, *J* = 8.5 Hz, 1H), 4.36−4.32 (m, 1H), 4.29−4.24 (m, 2H), 2.25−2.14 (m, 2H), 2.10−2.05 (m, 1H), 1.52 (d, *J* = 6.5 Hz, 6H), 1.40 (s, 9H), 0.88−0.80 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.4, 155.8, 150.5, 139.1, 137.2, 129.0, 125.6, 123.2, 121.0, 114.8, 79.6, 62.0, 58.7, 52.9, 39.0, 31.3, 28.4 (3C), 27.5, 27.2, 19.1, 17.5; HRMS (ESI) *m/z* calcd. for $C_{23}H_{35}N_4O_5$ $[M+H]^+$ 447.2602, found 447.2606.



(2*R*,3*S*)-3-(1H-indazole-1-carboxamido)-3-methylbutyl 2-((tert-butoxycarbonyl)amino)-3-hydroxybutanoate (3as): The title compound was obtained by column chromatography (PET: EtOAc = 2:1) as a colorless oil (55 mg) in 61% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): 8.33 (dd, *J* = 8.5, 0.5 Hz, 1H), 8.04 (s, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.50−7.46 (m, 1H), 7.29 (s, 1H), 7.26−7.23 (m, 1H), 5.59 (d, *J* = 8.5 Hz, 1H), 4.32 (t, *J* = 6.0 Hz, 2H), 4.23 (d, *J* = 8.0 Hz, 2H), 2.83 (s, 1H), 2.28−2.13 (m, 2H), 1.51 (d, *J* = 6.5 Hz, 6H), 1.40 (s, 9H), 1.11 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.3, 155.7, 150.5, 139.1, 137.2, 129.0, 125.7, 123.2, 121.0, 114.8, 79.7, 62.0, 58.2, 52.9, 38.9, 38.0, 28.4, 27.5, 27.2, 24.9, 15.6, 11.6.; HRMS (ESI) *m/z* calcd. for $C_{22}H_{33}N_4O_6$ $[M+H]^+$ 449.2395, found 449.2391.

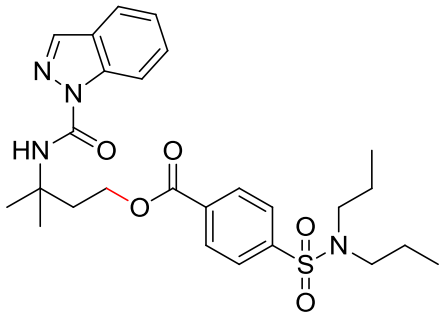


(*R*)-3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 2-acetamido-3-phenylpropanoate (3at): The title compound was obtained by column chromatography (PET: EtOAc = 3:1) as a colorless oil (31 mg) in 36% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): 8.38 (dd, *J* = 8.5, 0.5 Hz, 1H), 8.06 (d, *J* = 0.5 Hz, 1H), 7.72 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.52−7.49 (m, 1H), 7.31 (s, 1H), 7.29−7.26 (m, 1H), 7.23−7.17 (m, 3H), 7.04−7.02 (m, 2H), 6.06 (d, *J* = 8.0 Hz, 1H), 4.98−4.94 (m, 1H), 4.38−4.18 (m, 2H), 3.05 (d, *J* = 6.0 Hz, 2H), 2.21−2.12 (m, 2H), 1.95 (s, 3H), 1.50 (d, *J* = 6.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.7, 169.7, 150.5, 139.2, 137.3, 135.9, 129.3 (2C), 129.1, 128.6 (2C), 127.2, 125.7, 123.3, 121.1, 114.8, 62.4, 53.3, 52.9, 38.7, 38.1, 27.6, 27.2, 23.2; HRMS (ESI) *m/z* calcd. for $C_{24}H_{29}N_4O_4$ $[M+H]^+$ 437.2183, found 437.2186.

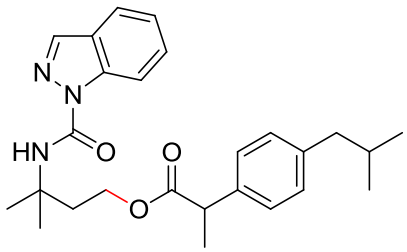


3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 2,2-dimethyl-4,7,10-trioxo-3-oxa-5,8,11-triazatridecan-13-oate (3au): The title compound was obtained by column chromatography (PET: EtOAc = 1:1) as a colorless oil (34 mg) in 33% yield according to the **Method A**. ^{1}H NMR (500

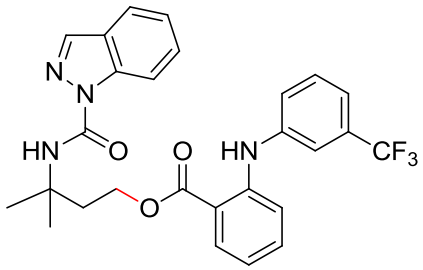
MHz, $CDCl_3$): 8.34 (dd, *J* = 8.5, 0.5 Hz, 1H), 8.03 (s, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.50−7.47 (m, 1H), 7.31 (s, 1H), 7.27−7.24 (m, 1H), 7.20 (s, 1H), 5.55 (s, 1H), 4.30 (t, *J* = 6.5 Hz, 2H), 3.98 (t, *J* = 6.5 Hz, 4H), 3.80 (d, *J* = 5.5 Hz, 2H), 2.20 (t, *J* = 6.5 Hz, 2H), 1.51 (s, 6H), 1.42 (s, 1H), 1.39 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.5, 169.8, 169.5, 156.5, 150.6, 139.1, 137.2, 129.1, 125.7, 123.3, 121.1, 114.7, 80.5, 62.5, 52.9, 44.4, 42.9, 41.3, 38.6, 28.4, 28.1, 27.5 (2C), 26.4; HRMS (ESI) *m/z* calcd. for $C_{24}H_{35}N_6O_7$ $[M+H]^+$ 519.2562, found 519.2568.



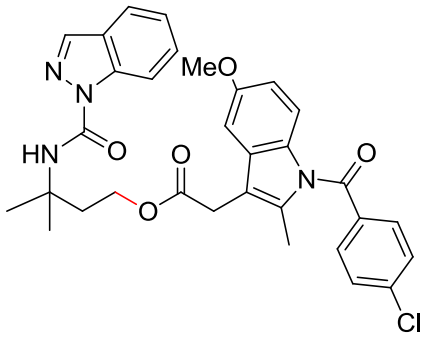
3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 4-(*N*,*N*-dipropylsulfamoyl) benzoate (3av): The title compound was obtained by column chromatography (PET: EtOAc = 3:1) as a colorless oil (49 mg) in 48% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): 8.32 (dd, *J* = 8.0, 0.5 Hz, 1H), 7.90 (dt, *J* = 8.5, 1.5 Hz, 2H), 7.88 (d, *J* = 1.0 Hz, 1H) , 7.68 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.60 (dt, *J* = 8.5, 1.5 Hz, 2H), 7.50−7.47 (m, 1H), 7.29−7.26 (m, 1H), 7.21 (s, 1H), 4.53 (t, *J* = 6.0 Hz, 2H), 3.01 (t, *J* = 7.5 Hz, 4H), 2.43 (t, *J* = 6.0 Hz, 2H), 1.59 (s, 6H), 1.54−1.46 (m, 4H), 0.84 (t, *J* = 8.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.4, 150.6, 144.1, 139.0, 137.0, 133.3, 130.1 (2C), 129.0, 126.8 (2C), 125.7, 123.4, 121.1, 114.7, 62.5, 52.8, 50.0 (2C), 38.0, 27.9 (2C), 22.0 (2C), 11.3 (2C); HRMS (ESI) *m/z* calcd. for $C_{26}H_{35}N_4O_5S$ $[M+H]^+$ 515.2323, found 515.2318.



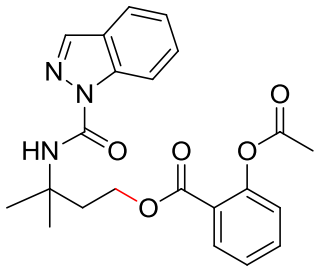
3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 2-(4-isobutylphenyl)propanoate (3aw): The title compound was obtained by column chromatography (PET: EtOAc = 4:1) as a colorless oil (65 mg) in 75% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): 8.39 (dd, *J* = 8.5, 1.5 Hz, 1H), 8.02 (d, *J* = 1.0 Hz, 1H), 7.72 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.53−7.50 (m, 1H), 7.29−7.26 (m, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.5 Hz, 2H), 4.30−4.17 (m, 2H), 3.68 (q, *J* = 7.0 Hz, 1H), 2.43 (d, *J* = 7.0 Hz, 2H), 2.21−2.17 (m, 2H), 1.86−1.81 (m, 1H), 1.46 (s, 6H), 1.45 (d, *J* = 6.0 Hz, 3H), 0.89 (d, *J* = 6.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.8, 150.5, 140.6, 139.2, 137.7, 136.9, 129.4 (2C), 129.0, 127.3 (2C), 125.7, 123.2, 120.9, 114.8, 61.6, 52.9, 45.1, 38.5, 30.3, 27.6 (2C), 27.4, 22.5, 18.5 (2C); HRMS (ESI) *m/z* calcd. for $C_{26}H_{34}N_3O_3$ $[M+H]^+$ 436.2595, found 436.2591.



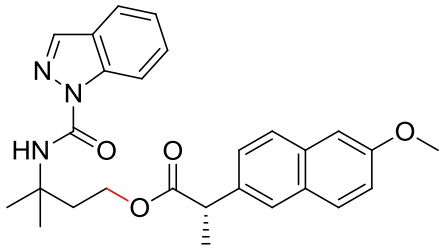
3-(1H-indazole-1-carboxamido)-3-methylbutyl 2-((3-(trifluoromethyl)phenyl)amino) benzoate (3ax): The title compound was obtained by column chromatography (PET: EtOAc = 4:1) as a colorless oil (60 mg) in 59% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): 9.59 (s, 1H), 8.36 (dd, *J* = 8.0, 0.5 Hz, 1H), 7.91 (d, *J* = 0.5 Hz, 1H), 7.88 (dd, *J* = 8.0, 1.5 Hz, 1H) , 7.67 (d, *J* = 8.0 Hz, 1H), 7.50−7.47 (m, 1H), 7.45 (s, 1H), 7.40 (t, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.28−7.25 (m, 2H), 7.24−7.17 (m, 3H), 6.51−6.50 (m, 1H), 4.50 (t, *J* = 6.0 Hz, 2H), 2.43 (t, *J* = 6.0 Hz, 2H), 1.60 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.5, 150.6, 146.7, 141.8, 139.1, 137.0, 134.1, 131.9 (q, *J* = 31.8 Hz), 131.8, 130.0, 129.0, 125.7, 124.6, 124.1 (q, *J* = 270.8 Hz), 123.29, 120.9, 119.6 (q, *J* = 3.15 Hz), 118.2, 118.0 (q, *J* = 3.9 Hz), 114.9, 114.2, 112.9, 61.7, 52.9, 38.3, 27.9 (2C); HRMS (ESI) *m/z* calcd. for $C_{27}H_{26}F_3N_4O_4$ $[M+H]^+$ 511.1952, found 511.1958.



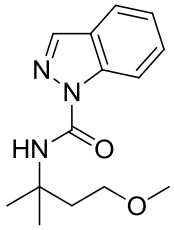
3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl -1*H*-indol-3-yl)acetate (3ay): The title compound was obtained by column chromatography (PET: EtOAc = 4:1) as a colorless oil (64 mg) in 55% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): 8.38 (dd, *J* = 8.5, 1.5 Hz, 1H), 8.01 (d, *J* = 0.5 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.65 (dt, *J* = 8.5, 2.5 Hz, 2H), 7.52−7.49 (m, 1H), 7.45 (dt, *J* = 8.5, 2.5 Hz, 2H), 7.34 (s, 1H), 7.28−7.25 (m, 1H), 6.95 (d, *J* = 2.5 Hz, 1H), 6.85 (d, *J* = 9.0 Hz, 1H), 6.65 (dd, *J* = 9.0, 2.5 Hz, 1H), 4.30 (t, *J* = 6.5 Hz, 2H), 3.79 (s, 3H), 3.64 (s, 2H), 2.34 (s, 3H), 2.25 (t, *J* = 6.5 Hz, 2H), 1.52 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.9, 168.4, 156.2, 150.5, 139.3, 139.1, 137.1, 136.0, 134.0, 131.3 (2C), 130.9, 130.7, 129.2 (2C), 129.1, 125.7, 123.3, 121.0, 115.1, 114.8, 112.6, 111.9, 101.29, 62.0, 55.8, 52.9, 38.7, 30.3, 27.5 (2C), 13.4; HRMS (ESI) *m/z* calcd. for $C_{32}H_{32}ClN_4O_5$ $[M+H]^+$ 587.2056, found 587.2051.



3-(1H-indazole-1-carboxamido)-3-methylbutyl 2-acetoxybenzoate (3az): The title compound was obtained by column chromatography (PET: EtOAc = 4:1) as a colorless oil (37 mg) in 45% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): 8.36 (dd, *J* = 8.0, 0.5 Hz, 1H), 7.91 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.88 (d, *J* = 0.5 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.50−7.47 (m, 1H), 7.44 (td, *J* = 9.0, 1.5 Hz, 1H), 7.27−7.24 (m, 1H), 7.22 (s, 1H), 7.04 (td, *J* = 8.5, 1.5 Hz, 1H), 7.00 (dd, *J* = 8.0, 1.0 Hz, 1H), 4.44 (t, *J* = 6.5 Hz, 2H), 2.39 (t, *J* = 6.5 Hz, 2H), 2.34 (s, 3H), 1.56 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.8, 164.4, 150.8, 150.5, 139.1, 136.9, 133.8, 131.6, 128.9, 125.8, 125.7, 123.7, 123.1, 123.0, 120.9, 114.8, 61.9, 52.8, 38.1, 27.8 (2C), 21.1; HRMS (ESI) *m/z* calcd. for $C_{22}H_{24}N_3O_5$ $[M+H]^+$ 410.1710, found 410.1715.

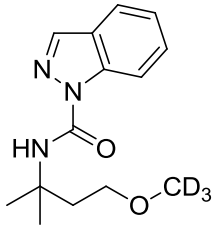


(S)-3-(1H-indazole-1-carboxamido)-3-methylbutyl 2-(6-methoxynaphthalen-2-yl)propanoate (3ba): The title compound was obtained by column chromatography (PET: EtOAc = 4:1) as a colorless oil (73 mg) in 81% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): 8.39 (dd, *J* = 8.5, 1.5 Hz, 1H), 8.01 (d, *J* = 0.5 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.66 (t, *J* = 8.5 Hz, 2H), 7.60 (d, *J* = 1.0 Hz, 1H), 7.53−7.50 (m, 1H), 7.37 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.30−7.26 (m, 2H), 7.13 (dd, *J* = 9.0, 2.5 Hz, 1H), 7.09 (d, *J* = 2.5 Hz, 1H), 4.35−4.18 (m, 2H), 3.90 (s, 3H), 3.84 (q, *J* = 7.5 Hz, 1H), 2.25−2.14 (m, 2H), 1.54 (d, *J* = 7.0 Hz, 3H), 1.46 (d, *J* = 1.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.8, 157.7, 150.5, 139.2, 136.9, 135.6, 133.8, 129.3, 129.0, 127.2, 126.3, 126.0, 125.7, 123.2, 121.0, 119.0, 114.8, 105.6, 61.7, 55.4, 52.9, 45.4, 38.6, 27.6, 27.4 (2C), 18.5; HRMS (ESI) *m/z* calcd. for $C_{27}H_{30}N_3O_4$ $[M+H]^+$ 460.2331, found 460.2335.

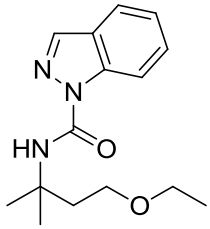


***N*-(4-methoxy-2-methylbutan-2-yl)-1*H*-indazole-1-carboxamide (5a):** The title compound was obtained by column chromatography (PET: EtOAc = 15:1) as a colorless oil (37 mg) in 71% yield according to the **Method B**. ^{1}H NMR (500 MHz, $CDCl_3$): 8.40 (dd, *J* = 8.5, 0.5 Hz, 1H), 8.01 (d, *J*

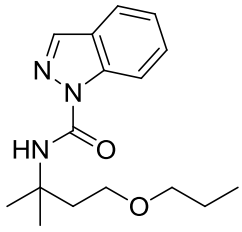
= 0.5 Hz, 1H), 7.99 (s, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.51−7.48 (m, 1H), 7.27−7.24 (m, 1H), 3.61 (t, *J* = 6.0, Hz, 2H), 3.38 (s, 3H), 2.02 (t, *J* = 6.0 Hz, 2H), 1.56 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.9, 139.3, 136.8, 128.8, 125.7, 123.0, 120.9, 114.9, 77.2, 69.5, 58.9, 53.4, 41.1, 27.1 (2C); HRMS (ESI) *m/z* calcd. for $C_{14}H_{20}N_3O_2$ $[M+H]^+$ 262.1550, found 262.1552.



***N*-(2-methyl-4-(trideuteromethoxy)butan-2-yl)-1*H*-indazole-1-carboxamide (5b):** The title compound was obtained by column chromatography (PET: EtOAc = 15:1) as a colorless oil (34 mg) in 65% yield according to the **Method B**. ^{1}H NMR (500 MHz, $CDCl_3$): 8.40 (dd, *J* = 8.5, 0.5 Hz, 1H), 8.01 (d, *J* = 0.5 Hz, 1H), 8.00 (s, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.51−7.48 (m, 1H), 7.28−7.25 (m, 1H), 3.61 (t, *J* = 6.0, Hz, 2H), 2.02 (t, *J* = 6.0 Hz, 2H), 1.56 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.9, 139.3, 136.8, 128.8, 125.7, 123.0, 120.9, 114.9, 77.2, 69.4, 53.4, 41.1, 27.1 (2C); HRMS (ESI) *m/z* calcd. for $C_{14}H_{17}D_3N_3O_2$ $[M+H]^+$ 265.1738, found 265.1742.

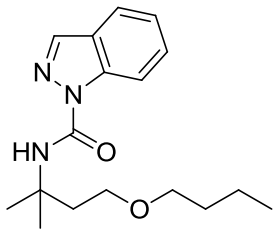


***N*-(4-ethoxy-2-methylbutan-2-yl)-1*H*-indazole-1-carboxamide (5c):** The title compound was obtained by column chromatography (PET: EtOAc = 15:1) as a colorless oil (32 mg) in 59% yield according to the **Method B**. ^{1}H NMR (500 MHz, $CDCl_3$): 8.40 (dd, *J* = 8.5, 0.5 Hz, 1H), 8.22 (s, 1H), 7.99 (d, *J* = 1.0 Hz, 1H), 7.70 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.50−7.47 (m, 1H), 7.27−7.24 (m, 1H), 3.67 (t, *J* = 6.0, Hz, 2H), 3.67 (q, *J* = 7.0, Hz, 2H), 1.98 (t, *J* = 6.0 Hz, 2H), 1.57 (s, 6H), 1.28 (t, *J* = 7.0, Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.0, 139.3, 136.6, 128.7, 125.7, 122.96, 120.8, 114.9, 67.3, 66.8, 53.5, 41.6, 26.9 (2C), 15.2; HRMS (ESI) *m/z* calcd. for $C_{15}H_{22}N_3O_2$ $[M+H]^+$ 276.1707, found 276.1703.

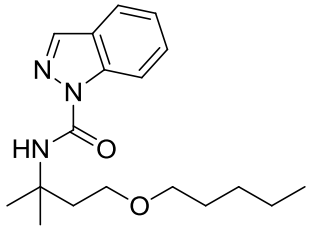


***N*-(2-methyl-4-propoxybutan-2-yl)-1*H*-indazole-1-carboxamide (5d):** The title compound was obtained by column chromatography (PET: EtOAc = 15:1) as a colorless oil (34 mg) in 58%

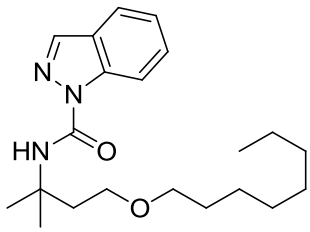
yield according to the **Method B**. ^{1}H NMR (500 MHz, $CDCl_3$): 8.40 (d, *J* = 8.5 Hz, 1H), 8.14 (s, 1H), 7.99 (s, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.27−7.24 (m, 1H), 3.66 (t, *J* = 6.0 Hz, 2H), 3.41 (t, *J* = 6.0 Hz, 2H), 1.99 (t, *J* = 6.0 Hz, 2H), 1.70−1.64 (m, 2H), 1.57 (s, 6H), 0.93 (t, *J* = 8.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.9, 139.3, 136.6, 128.7, 125.7, 123.0, 120.8, 114.9, 73.3, 67.5, 53.5, 41.5, 26.9 (2C), 23.0, 10.8; HRMS (ESI) *m/z* calcd. for $C_{16}H_{24}N_3O_2$ $[M+H]^+$ 290.1863, found 290.1866.



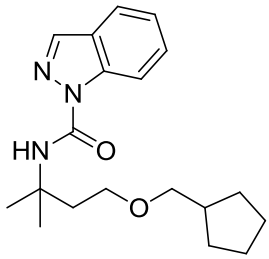
***N*-(4-butoxy-2-methylbutan-2-yl)-1*H*-indazole-1-carboxamide (5e):** The title compound was obtained by column chromatography (PET: EtOAc = 15:1) as a colorless oil (32 mg) in 52% yield according to the **Method B**. ^{1}H NMR (500 MHz, $CDCl_3$): 8.40 (dd, *J* = 8.5, 0.5 Hz, 1H), 8.14 (s, 1H), 7.98 (d, *J* = 0.5 Hz, 1H), 7.70 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.50−7.47 (m, 1H), 7.27−7.24 (m, 1H), 3.65 (t, *J* = 5.5 Hz, 2H), 3.45 (t, *J* = 6.5 Hz, 2H), 1.98 (t, *J* = 6.0 Hz, 2H), 1.66−1.61 (m, 2H), 1.57 (s, 6H), 1.44−1.34 (m, 2H), 0.90 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.0, 139.3, 136.6, 128.7, 125.7, 123.0, 120.8, 114.9, 71.5, 67.6, 53.5, 41.5, 31.9, 26.9 (2C), 19.5, 14.1; HRMS (ESI) *m/z* calcd. for $C_{17}H_{26}N_3O_2$ $[M+H]^+$ 304.2020, found 304.2020.



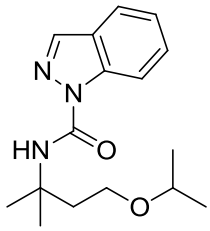
***N*-(2-methyl-4-(pentyloxy)butan-2-yl)-1*H*-indazole-1-carboxamide (5f):** The title compound was obtained by column chromatography (PET: EtOAc = 15:1) as a colorless oil (32 mg) in 50% yield according to the **Method B**. ^{1}H NMR (500 MHz, $CDCl_3$): 8.40 (dd, *J* = 8.5, 0.5 Hz, 1H), 8.12 (s, 1H), 7.98 (d, *J* = 0.5 Hz, 1H), 7.70 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.50−7.47 (m, 1H), 7.27−7.24 (m, 1H), 3.65 (t, *J* = 5.5 Hz, 2H), 3.44 (t, *J* = 6.5 Hz, 2H), 1.99 (t, *J* = 5.5 Hz, 2H), 1.68−1.62 (m, 2H), 1.57 (s, 6H), 1.34−1.31 (m, 4H), 0.87 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.0, 139.3, 136.6, 128.7, 125.7, 123.0, 120.8, 115.0, 71.8, 67.6, 53.5, 41.5, 29.5, 28.5, 27.0 (2C), 22.7, 14.2; HRMS (ESI) *m/z* calcd. for $C_{18}H_{28}N_3O_2$ $[M+H]^+$ 318.2176, found 318.2173.



***N*-(2-methyl-4-(octyloxy)butan-2-yl)-1*H*-indazole-1-carboxamide (5g):** The title compound was obtained by column chromatography (PET: EtOAc = 15:1) as a colorless oil (32 mg) in 45% yield according to the **Method B**. ^{1}H NMR (500 MHz, $CDCl_3$): 8.40 (dd, *J* = 8.5, 0.5 Hz, 1H), 8.13 (s, 1H), 7.98 (d, *J* = 0.5 Hz, 1H), 7.70 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.50−7.47 (m, 1H), 7.27−7.24 (m, 1H), 3.65 (t, *J* = 5.5 Hz, 2H), 3.44 (t, *J* = 6.5 Hz, 2H), 1.98 (t, *J* = 5.5 Hz, 2H), 1.66−1.61 (m, 2H), 1.57 (s, 6H), 1.33−1.23 (m, 12H), 0.87−0.85 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.9, 139.3, 136.6, 128.7, 125.7, 123.0, 120.8, 114.9, 71.8, 67.6, 53.5, 41.5, 32.0, 29.8, 29.7, 29.4, 27.0 (2C), 26.3, 22.8, 14.2; HRMS (ESI) *m/z* calcd. for $C_{21}H_{34}N_3O_2$ $[M+H]^+$ 360.2646, found 360.2641.



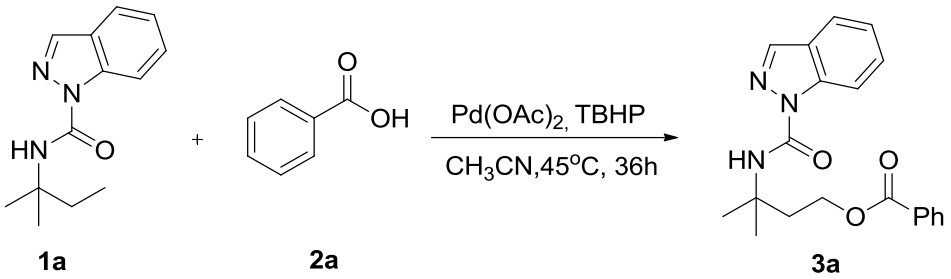
***N*-(4-(cyclopentylmethoxy)-2-methylbutan-2-yl)-1*H*-indazole-1-carboxamide (5h):** The title compound was obtained by column chromatography (PET: EtOAc = 15:1) as a colorless oil (24 mg) in 36% yield according to the **Method B**. ^{1}H NMR (500 MHz, $CDCl_3$): 8.41 (d, *J* = 8.5 Hz, 1H), 8.03 (s, 1H), 7.97 (d, *J* = 1.0 Hz, 1H), 7.70 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.50−7.47 (m, 1H), 7.27−7.24 (m, 1H), 3.65 (t, *J* = 6.0 Hz, 2H), 3.32 (d, *J* = 7.5 Hz, 2H), 2.26−2.20 (m, 1H), 2.00 (t, *J* = 6.0 Hz, 2H), 1.77−1.71 (m, 2H), 1.57 (s, 6H), 1.55−1.50 (m, 2H), 1.28−1.19 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.9, 139.3, 136.6, 128.7, 125.7, 123.0, 120.8, 115.0, 76.3, 67.7, 53.5, 41.4, 39.6, 29.8 (2C), 27.0 (2C), 25.5 (2C); HRMS (ESI) *m/z* calcd. for $C_{19}H_{28}N_3O_2$ $[M+H]^+$ 330.2176, found 330.2179.



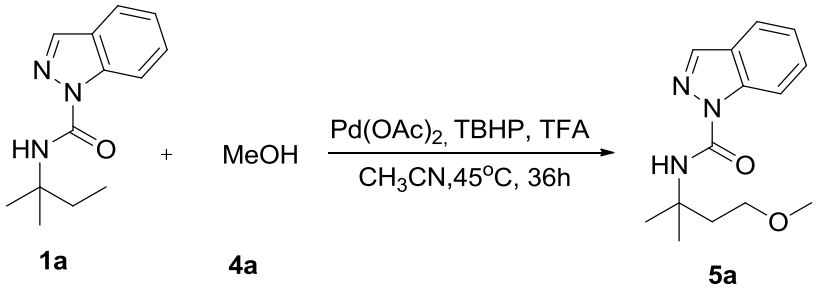
***N*-(4-isopropoxy-2-methylbutan-2-yl)-1*H*-indazole-1-carboxamide (5i):** The title compound was obtained by column chromatography (PET: EtOAc = 15:1) as a colorless oil (28 mg) in 48% yield according to the **Method B**. ^{1}H NMR (500 MHz, $CDCl_3$): 8.40 (d, *J* = 8.5 Hz, 1H), 8.31 (s, 1H), 7.99 (s, 1H), 7.70 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.50−7.47 (m, 1H), 7.27−7.23 (m, 1H), 3.67 (t, *J* = 5.5 Hz, 2H), 3.63−3.56 (m, 1H), 1.95 (t, *J* = 5.5 Hz, 2H), 1.57 (s, 6H), 1.22 (d, *J* = 5.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.0, 139.3, 136.5, 128.6, 125.7, 122.9, 120.8, 114.9, 72.1, 64.5, 53.5, 42.0, 26.8 (2C), 22.1 (2C); HRMS (ESI) *m/z* calcd. for $C_{16}H_{24}N_3O_2$ $[M+H]^+$ 290.1863, found 290.1866.

8. Synthetic Applications

8.1 Lager-Scale Preparation of 3a and 5a

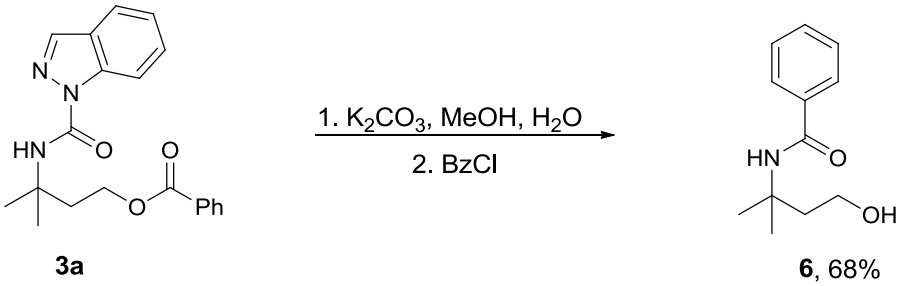


A reaction tube (50 mL) with magnetic stir bar was charged with *N*-(*tert*-pentyl)-1*H*-indazole-1-carboxamide **1a** (462 mg, 2.0 mmol), **2a** (732 mg, 6.0 mmol), $Pd(OAc)_2$ (45 mg, 0.20 mmol), TBHP (70% in water) (770 mg, 6.0 mmol) and CH_3CN (10 mL). The reaction was allowed to stir at 45 ℃ in an oil bath for 36 hours. After cooling to room temperature, the reaction mixture was evaporated to remove the solvent and directly loaded onto silica gel for flash column chromatography (PET: EtOAc = 12:1) to afford the desired product **3a** (379 mg) in 54% yield.



A reaction tube (50 mL) with magnetic stir bar was charged with *N*-(*tert*-pentyl)-1*H*-indazole-1-carboxamide **1a** (462 mg, 2.0 mmol), **4a** (320 mg, 10.0 mmol), $Pd(OAc)_2$ (45 mg, 0.20 mmol), TBHP (70% in water) (770 mg, 6.0 mmol), TFA (50 μL) and CH_3CN (10 mL). The reaction was allowed to stir at 60 ℃ in an oil bath for 36 hours. After cooling to room temperature, the reaction mixture was evaporated to remove the solvent and directly loaded onto silica gel for flash column chromatography (PET: EtOAc = 15:1) to afford the desired product **5a** (250 mg) in 48% yield.

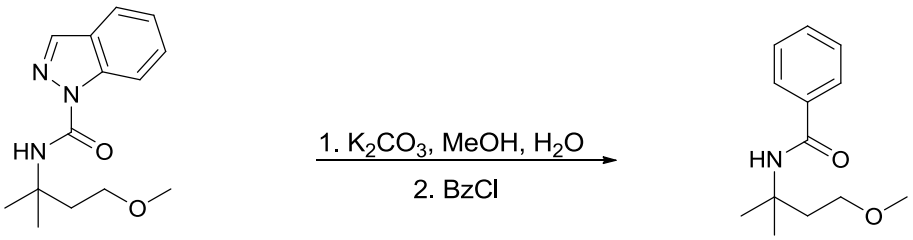
8.2 Directing Group Removal of 3a and 5a



A reaction tube (10 mL) with magnetic stir bar was charged with

3-(1*H*-indazole-1-carboxamido)-3-methylbutyl benzoate **3a** (175 mg, 0.5 mmol), K_2CO_3 (41mg, 0.5 mmol), H_2O (1mL) and MeOH (3 mL). The reaction was allowed to stir at 100 ^oC in an oil bath for 12 hours until most of **3a** was consumed detected by TLC. After cooled to room temperature, the reaction mixture was evaporated to remove the solvent and dissolved in dichloromethane (5 mL), then benzoyl chloride (BzCl, 85mg, 0.6 mmol) was added and then the reaction was stirred at room temperature for another 2 hours. Upon completion, the reaction mixture was evaporated to remove the solvent and the residue was directly purified by flash column chromatography (PET: EtOAc = 2:1) to afford **6** as colorless oil (70 mg) in 68 % yield.

***N*-(4-hydroxy-2-methylbutan-2-yl)benzamide (6):** ^1H NMR (500 MHz, $CDCl_3$): 7.75−7.73 (m, 2H), 7.51 (tt, *J* = 7.0, 1.0 Hz, 1H), 7.43−7.40 (m, 2H), 4.45 (t, *J* = 5.5 Hz, 2H), 2.11 (t, *J* = 5.5 Hz, 2H), 1.62 (s, 6H); ^{13}C NMR (125 MHz, CDCl3): δ 152.9, 136.4, 132.6, 128.6 (2C), 128.4 (2C), 64.3, 58.0, 38.0, 27.6 (2C); HRMS (ESI) *m/z* calcd. for $C_{12}H_{18}NO_2[M+H]^+$ 208.1332, found 208.1338

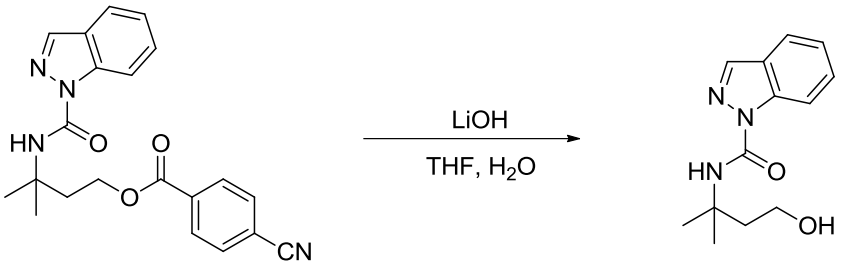


5a **7**, 72%

A reaction tube (10 mL) with magnetic stir bar was charged with 3-(1*H*-indazole-1-carboxamido)-3-methylbutyl benzoate **3a** (131 mg, 0.5 mmol), K_2CO_3 (41mg, 0.5 mmol), H_2O (1mL) and MeOH (3 mL). The reaction was allowed to stir at 100 ^oC in an oil bath for 12 hours until most of **5a** was consumed detected by TLC. After cooled to room temperature, the reaction mixture was evaporated to remove the solvent and dissolved in dichloromethane (5 mL), then benzoyl chloride (BzCl, 106mg, 0.75 mmol) was added and then the reaction was stirred at room temperature for another 2 hours. Upon completion, the reaction mixture was evaporated to remove the solvent and the residue was directly purified by flash column chromatography (PET: EtOAc = 5:1) to afford **6** as colorless oil (80 mg) in 72 % yield.

***N*-(4-methoxy-2-methylbutan-2-yl)benzamide (7):** ^1H NMR (500 MHz, $CDCl_3$): 7.75−7.73 (m, 2H), 7.56 (s, 1H), 7.45 (tt, *J* = 7.0, 1.5 Hz, 1H), 7.42−7.38 (m, 2H), 3.64 (t, *J* = 5.5 Hz, 2H), 3.40 (s, 3H), 1.88 (t, *J* = 5.5 Hz, 2H), 1.54 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.6, 136.0, 131.0, 128.5 (2C), 126.8 (2C), 69.9, 59.1, 53.9, 42.0, 26.4 (2C); HRMS (ESI) *m/z* calcd. for $C_{13}H_{20}NO_2[M+H]^+$ 222.1489, found 222.1487

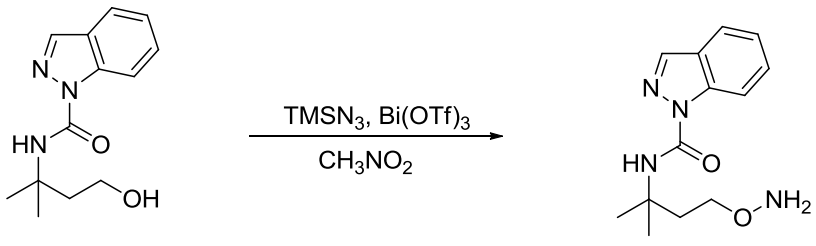
8.3 Further Derivatization of 8



3h **8**, 89%

A reaction tube (10 mL) with magnetic stir bar was charged with 3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 4-cyanobenzoate **3h** (188 mg, 0.5 mmol), LiOH (20mg, 0.5 mmol), H_2O (2mL) and THF (2 mL). The reaction was allowed to stir at room temperature for 1 hours until most of **3h** was consumed detected by TLC. The reaction mixture was evaporated to remove the solvent and diluted with ethyl acetate (5 mL ×3). Afterwards, The organic layer was washed with water (5 mL), brine (5mL), dried with Na_2SO_4. Then, the mixture was evaporated to remove the solvent and the residue was directly purified by flash column chromatography (PET: EtOAc = 3:1) to afford **8** as colorless oil (110 mg) in 89 % yield.

***N*-(4-hydroxy-2-methylbutan-2-yl)-1*H*-indazole-1-carboxamide (8):** ^{1}H NMR (500 MHz, $CDCl_3$): 8.37 (dd, *J* = 8.5, 0.5 Hz, 1H), 7.98 (d, *J* = 0.5 Hz, 1H), 7.75 (s, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.49−7.45 (m, 1H), 7.25−7.22 (m, 1H), 3.87 (t, *J* = 6.5 Hz, 2H), 2.42 (s, 1H), 2.03 (t, *J* = 6.0 Hz, 2H), 1.53 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.0, 139.2, 137.1, 128.9, 125.7, 123.2, 120.9, 114.9, 59.6, 53.4, 43.4, 27.6 (2C); HRMS (ESI) *m/z* calcd. for $C_{13}H_{18}N_3O_2$ $[M+H]^+$ 248.1394, found 248.1389.

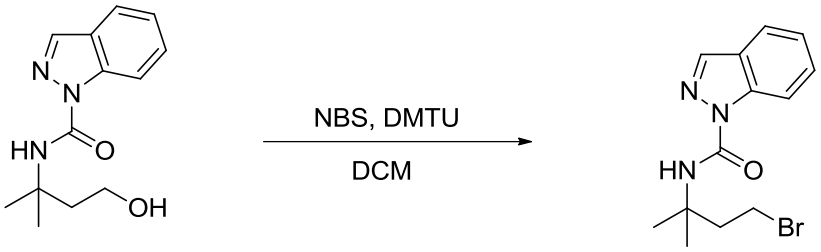


8 **9**, 68%

A reaction tube (10 mL) with magnetic stir bar was charged with *N*-(4-hydroxy-2-methylbutan-2-yl)-1*H*-indazole-1-carboxamide **8** (49 mg, 0.2 mmol), $TMSN_3$ (69mg, 0.6 mmol), $Bi(OTf)_3$ (13mg, 0.02 mmol) and CH_3NO_2 (3 mL). The reaction was allowed to stir at 60 ^{o}C in an oil bath for 12 hours until most of **8** was consumed detected by TLC. Upon completion, the reaction mixture was evaporated to remove the solvent and the residue was directly purified by flash column chromatography (PET: EtOAc = 15:1) to afford **9** as colorless oil (36 mg) in 68 % yield.

***N*-(4-(aminooxy)-2-methylbutan-2-yl)-1*H*-indazole-1-carboxamide (9):** ^{1}H NMR (500 MHz, $CDCl_3$): 8.39 (dd, *J* = 8.5, 0.5 Hz, 1H), 8.01 (d, *J* = 0.5 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.64 (s, 1H), 7.52−7.49 (m, 1H), 7.29−7.25 (m, 1H), 4.68 (s, 2H), 3.83 (t, *J* = 6.0 Hz, 2H), 2.15 (t, *J* = 6.0

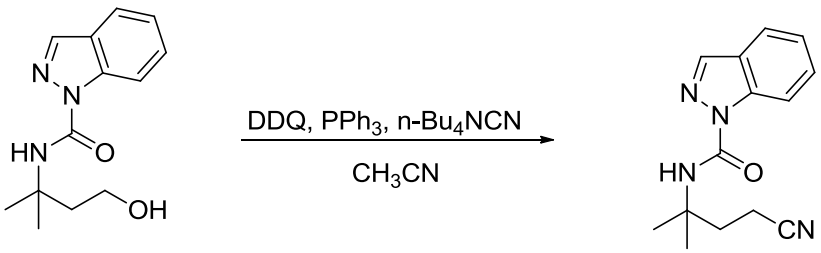
Hz, 2H), 1.56 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.8, 139.2, 137.0, 128.9, 125.7, 123.2, 123.0, 114.9, 83.2, 66.6, 53.2, 40.2, 27.4 (2C); HRMS (ESI) *m/z* calcd. for $C_{13}H_{19}N_4O_2$ $[M+H]^+$ 263.1503, found 263.1506.



8 **10**, 82%

A reaction tube (10 mL) with magnetic stir bar was charged with *N*-(4-hydroxy-2-methylbutan-2-yl)-1*H*-indazole-1-carboxamide **8** (49 mg, 0.2 mmol), dimethylthiourea (DMTU) (10 mg, 0.1 mmol), and CH_2Cl_2 (2 mL). The reaction was allowed to stir at room temperature until the starting materials were completely dissolved. The reaction mixture was vigorously stirred and N-bromosuccinimide (NBS) (53 mg, 0.3 mmol) was added in a single portion. Upon completion, the reaction mixture was evaporated to remove the solvent and the residue was directly purified by flash column chromatography (PET: EtOAc = 12:1) to afford **10** as colorless oil (42 mg) in 82 % yield.

***N*-(4-bromo-2-methylbutan-2-yl)-1*H*-indazole-1-carboxamide (10):** ^{1}H NMR (500 MHz, $CDCl_3$): 8.37 (dd, *J* = 8.5, 0.5 Hz, 1H), 8.02 (d, *J* = 1.0 Hz, 1H), 7.72 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.53−7.50 (m, 1H), 7.30−7.27 (m, 1H), 7.09 (s, 1H), 4.68 (s, 2H), 3.46 (t, *J* = 8.0 Hz, 2H), 2.52 (t, *J* = 8.0 Hz, 2H), 1.51 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.5, 139.2, 137.2, 129.1, 125.8, 123.3, 121.0, 114.9, 54.2, 43.5, 27.9, 27.6 (2C); HRMS (ESI) *m/z* calcd. for $C_{13}H_{17}BrN_3O$ $[M+H]^+$ 310.0550, found 310.0543.



8 **11**, 54%

A reaction tube (10 mL) with magnetic stir bar was charged with 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (91 mg, 0.4 mmol), PPh_3 (105 mg, 0.4 mmol) and n-Bu_4NCN (107 mg, 0.4 mmol) and CH_3CN (2 mL). The reaction was allowed to stir at room temperature until the starting materials were completely dissolved. Then, *N*-(4-hydroxy-2-methylbutan-2-yl)-1*H*-indazole-1-carboxamide **8** (49 mg, 0.2 mmol) was added in a single portion. Upon completion, the reaction mixture was evaporated to remove the solvent and the residue was directly purified by flash column chromatography (PET: EtOAc = 12:1) to afford **11** as colorless oil (28 mg) in 54 % yield.

***N*-(4-cyano-2-methylbutan-2-yl)-1*H*-indazole-1-carboxamide (11):** ^{1}H NMR (500 MHz, $CDCl_3$): 8.37 (dd, *J* = 8.5, 0.5 Hz, 1H), 8.02 (d, *J* = 1.0 Hz, 1H), 7.72 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.53−7.50 (m, 1H), 7.30−7.27 (m, 1H), 7.12 (s, 1H), 7.09 (s, 1H), 3.64 (t, *J* = 8.0 Hz, 2H), 2.42 (t, *J* = 8.0 Hz, 2H), 1.53 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.5, 139.2, 137.2, 129.1, 125.8, 123.3, 121.0, 114.9, 53.5, 42.9, 40.5, 27.7 (2C); HRMS (ESI) *m/z* calcd. for $C_{14}H_{17}BrN_4O$ $[M+H]^+$ 257.1397, found 257.1391.

9. References

(1) (a) Kong, W.; Chen, X.; Wang, M.; Dai, H.; Yu, J. Rapid Syntheses of Heteroaryl-Substituted Imidazo[1,5-a]indole and Pyrrolo[1,2-c]imidazole via Aerobic C2–H Functionalizations. *Org. Lett.* **2018**, *20*, 284–287. (b) Zhang, W.; Wei, J.; Fu, S.; Lin, D.; Jiang, H.; Zeng, W. Highly Stereoselective Ruthenium(II)-Catalyzed Direct C2-syn-Alkenylation of Indoles with Alkynes. *Org. Lett.* **2015**, *17*, 1349–1352.

(2) Adamo, C.; Barone, V. Toward reliable density functional methods without adjustable parameters: The PBE0 model. *J. Chem. Phys.* **1999**, *110*, 6158-6170.

(3) Weigend, F.; Ahlrichs, R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297-3305.

(4) Fuentealba, P.; Preuss, H.; Stoll, H.; Szentpály, L. V. A proper account of core-polarization with pseudopotentials: single valence-electron alkali compounds. *Chem. Phys. Lett.* **1982**, *89*, 418-422.

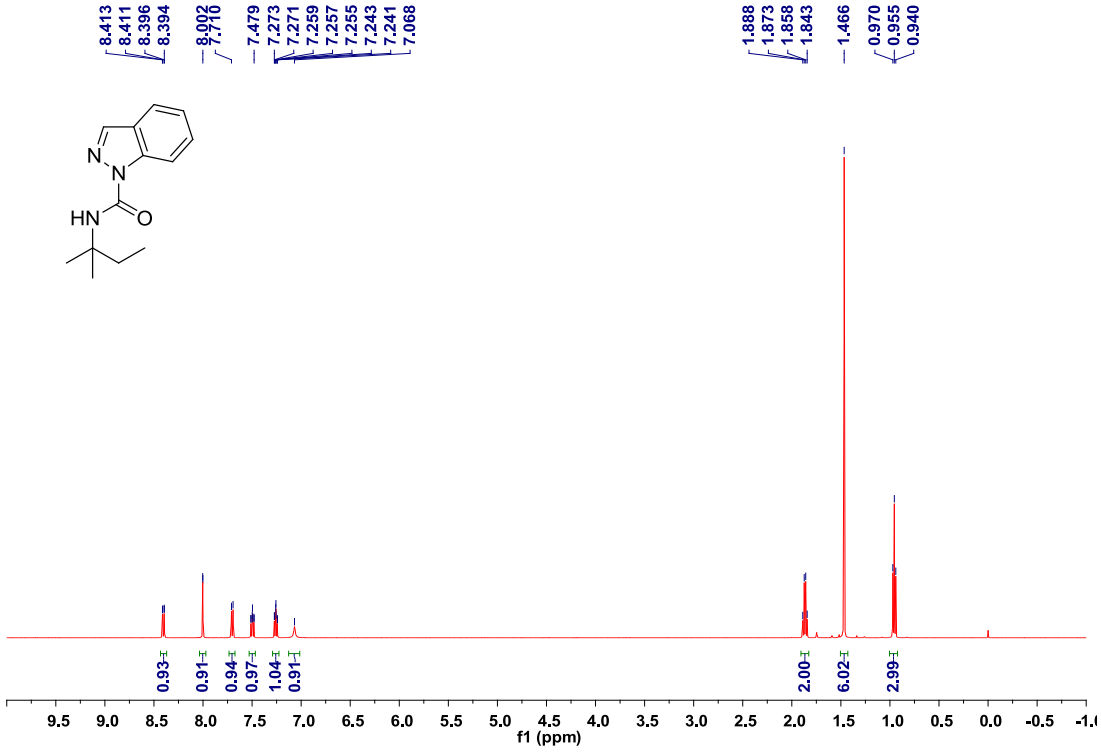
(5) Zhao, Y.; Truhlar, D. G. The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theor. Chem. Acc.* **2008**, *120*, 215-241.

(6) Gaussian, R.; Trucks, G.; Schlegel, H.; Scuseria, G.; Robb, M.; Cheeseman, J.; Scalmani, G.; Barone, V.; Mennuci, B.; Petersson, G.et al. Gaussian, Gaussian, Inc., Wallingford, CT. *Gaussian, Inc., Wallingford CT* **2004**.

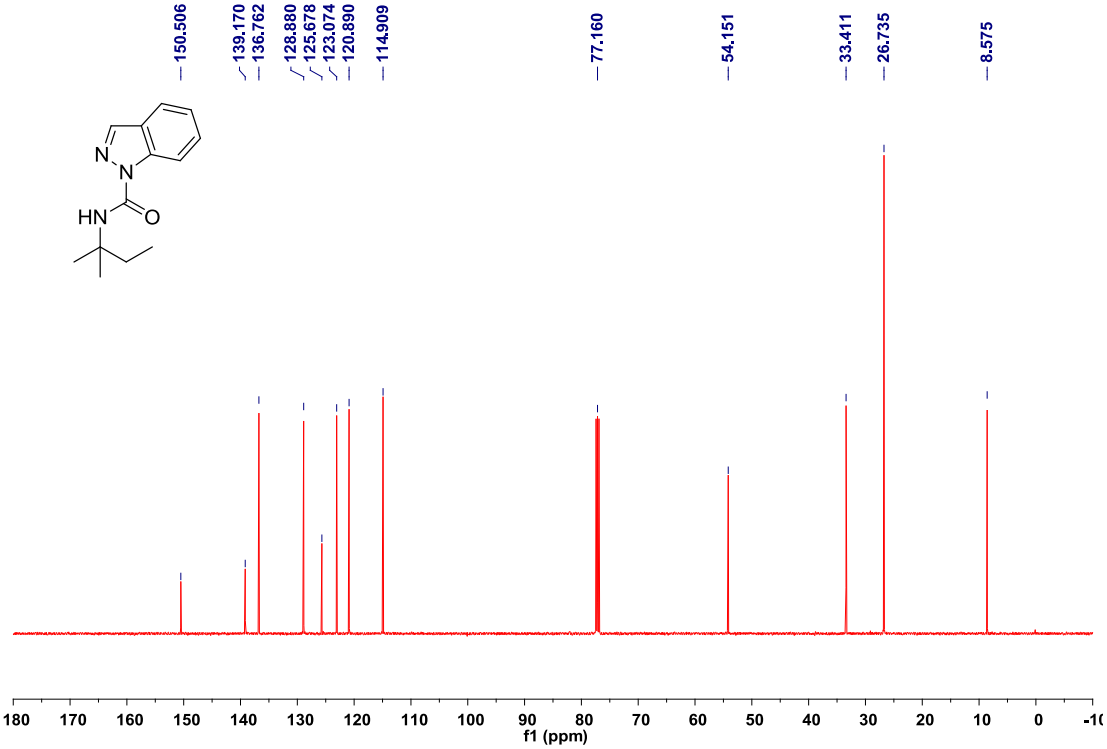
10. NMR Spectra

_N_-(_tert_-pentyl)-1_H_-indazole-1-carboxamide (1a)

^{1}H NMR, 500 MHz, $CDCl_3$

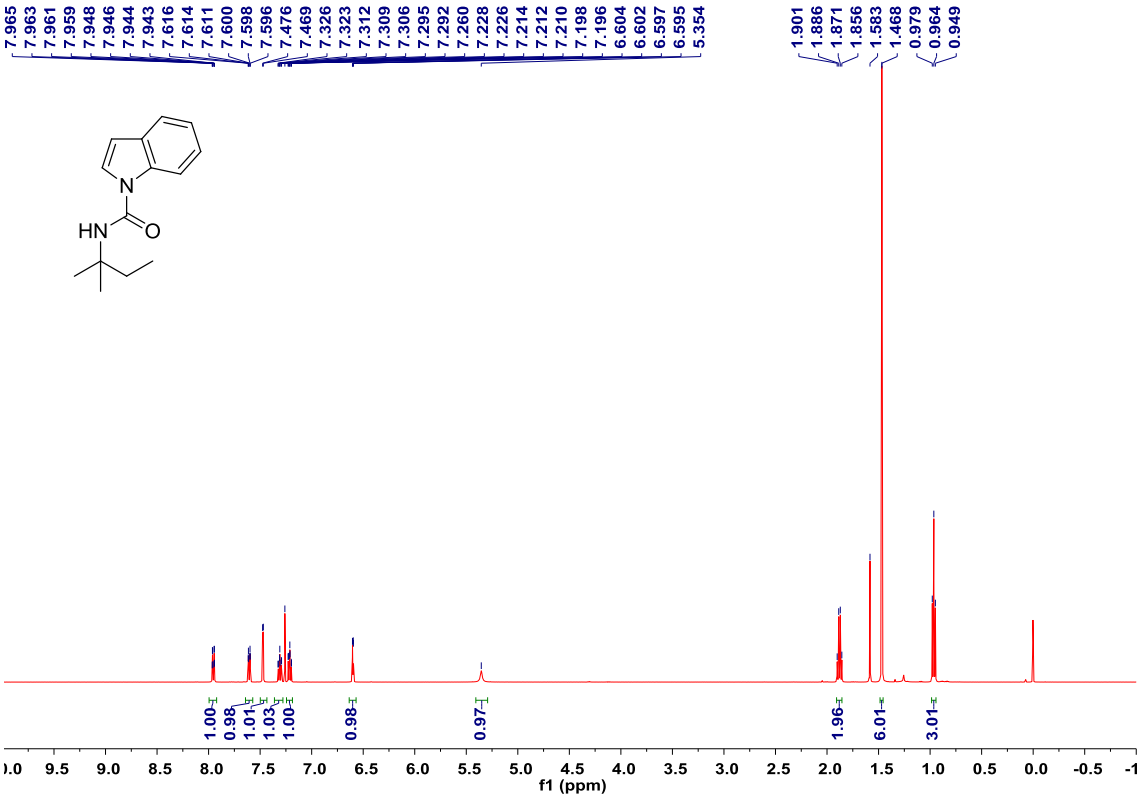


^{13}C NMR, 125 MHz, $CDCl_3$

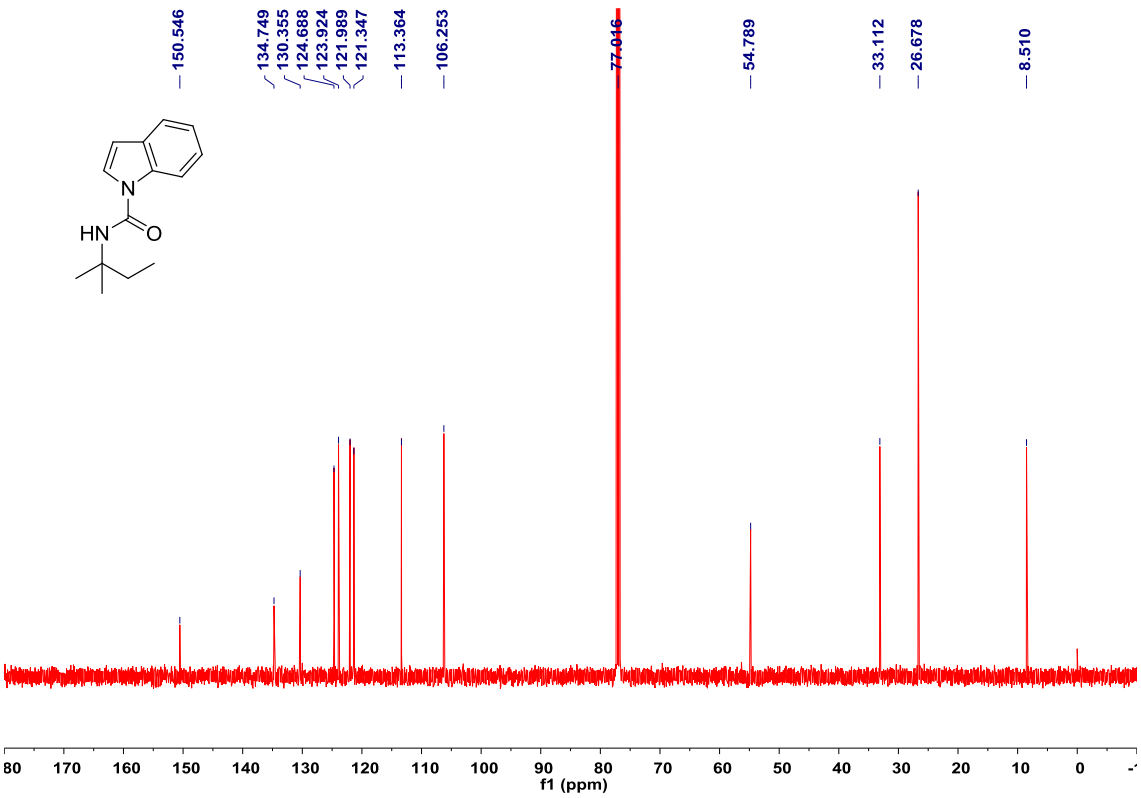


***N*-(tert-pentyl)-1*H*-indole-1-carboxamide (1b)**

^{1}H NMR, 500 MHz, $CDCl_3$

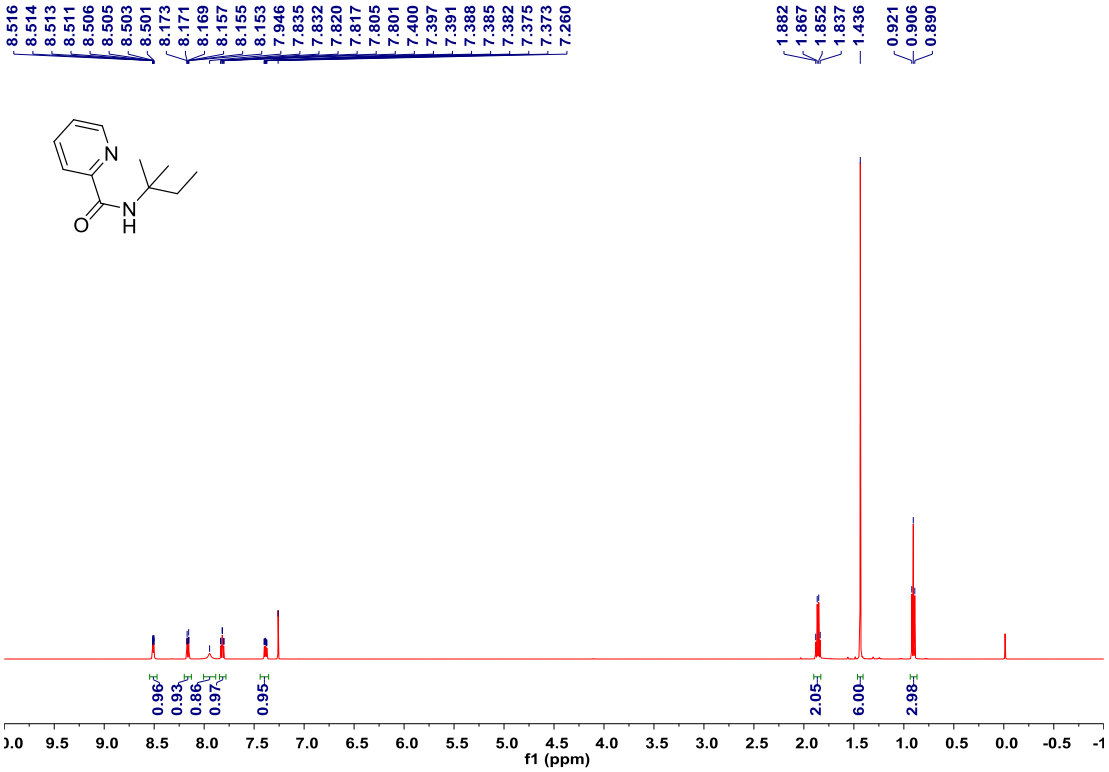


^{13}C NMR, 125 MHz, $CDCl_3$

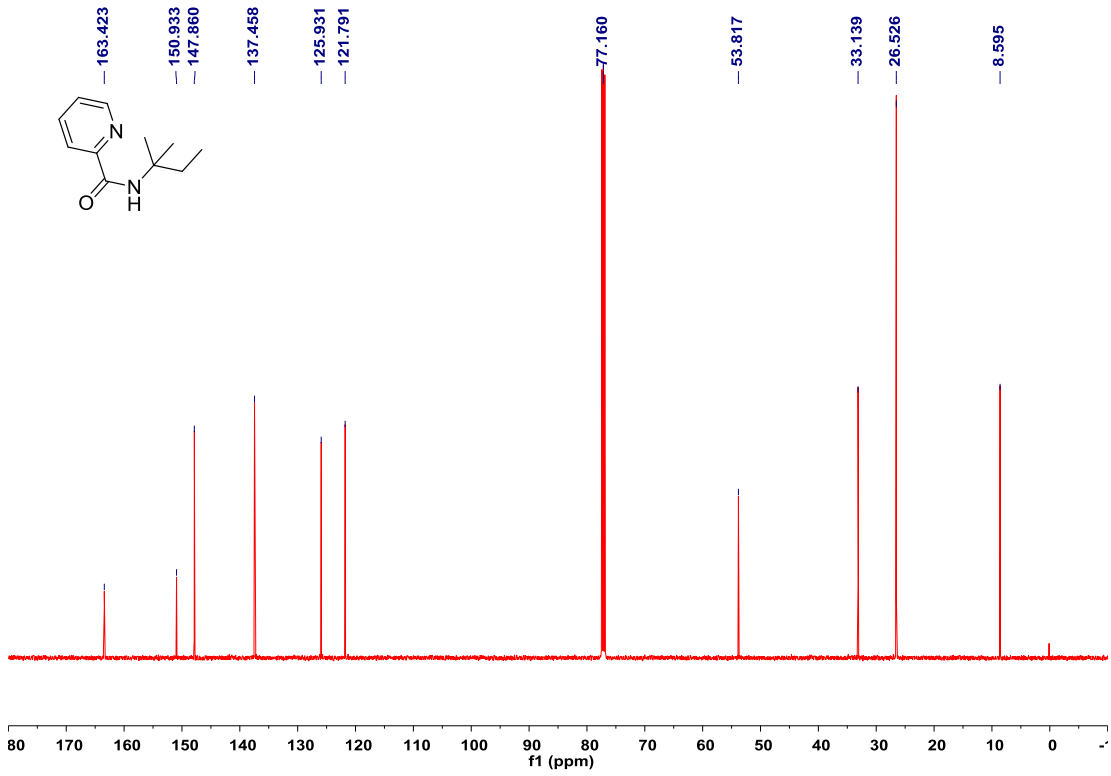


***N*-(tert-pentyl)picolinamide (1c)**

^{1}H NMR, 500 MHz, $CDCl_3$

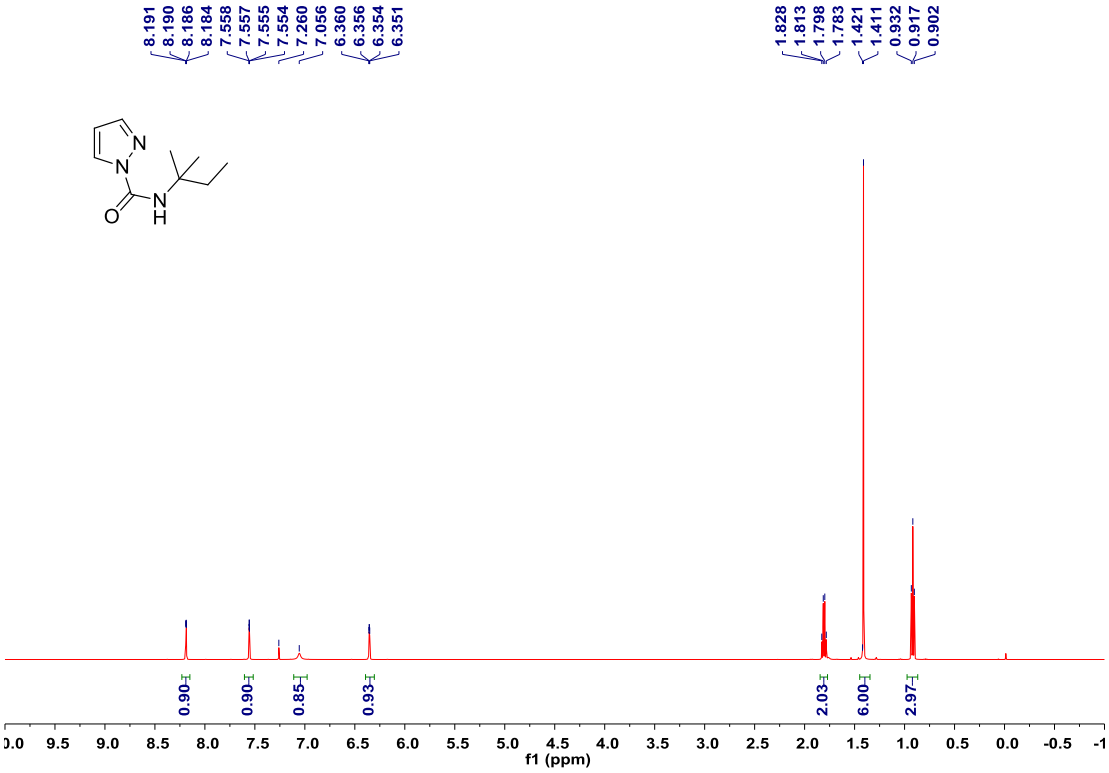


^{13}C NMR, 125 MHz, $CDCl_3$

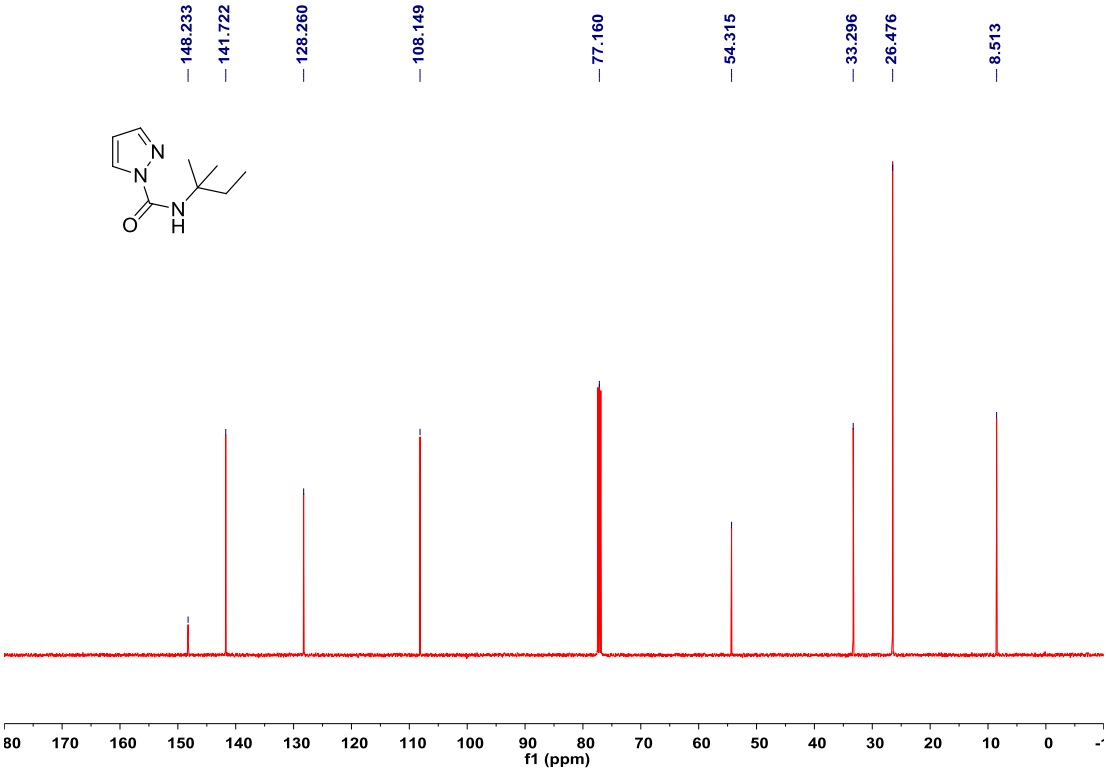


_N_-(tert-pentyl)-1H-pyrazole-1-carboxamide (1d)

^{1}H NMR, 500 MHz, $CDCl_3$

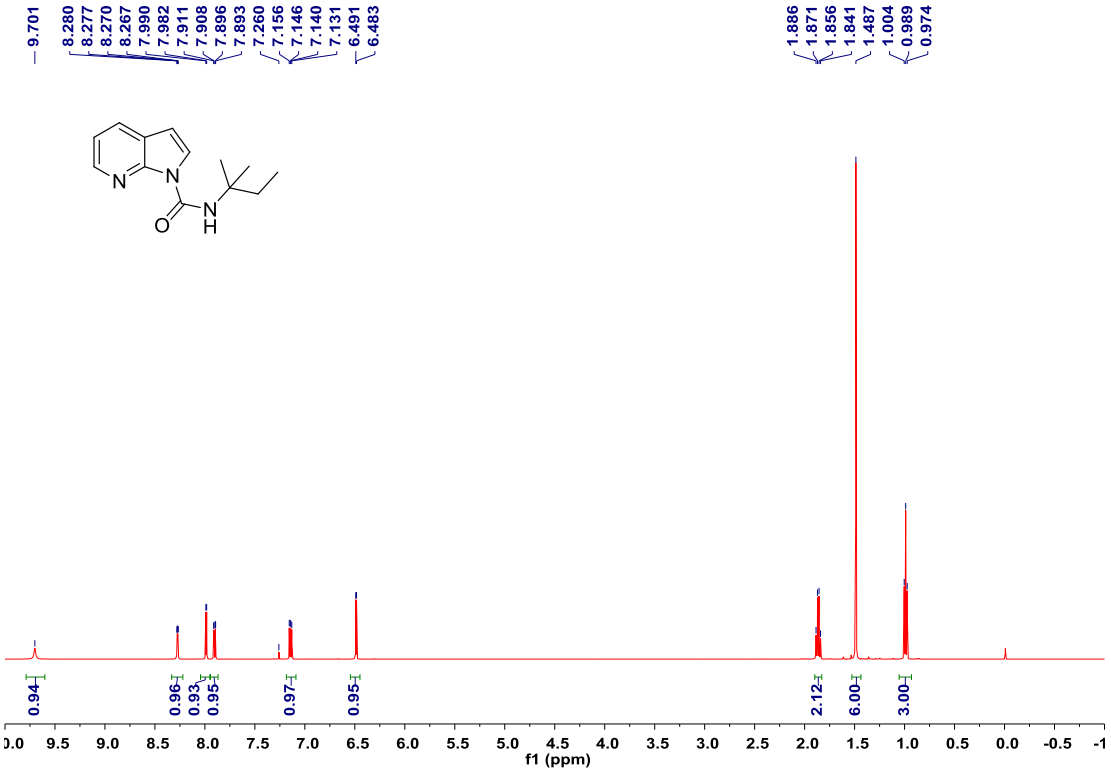


^{13}C NMR, 125 MHz, $CDCl_3$

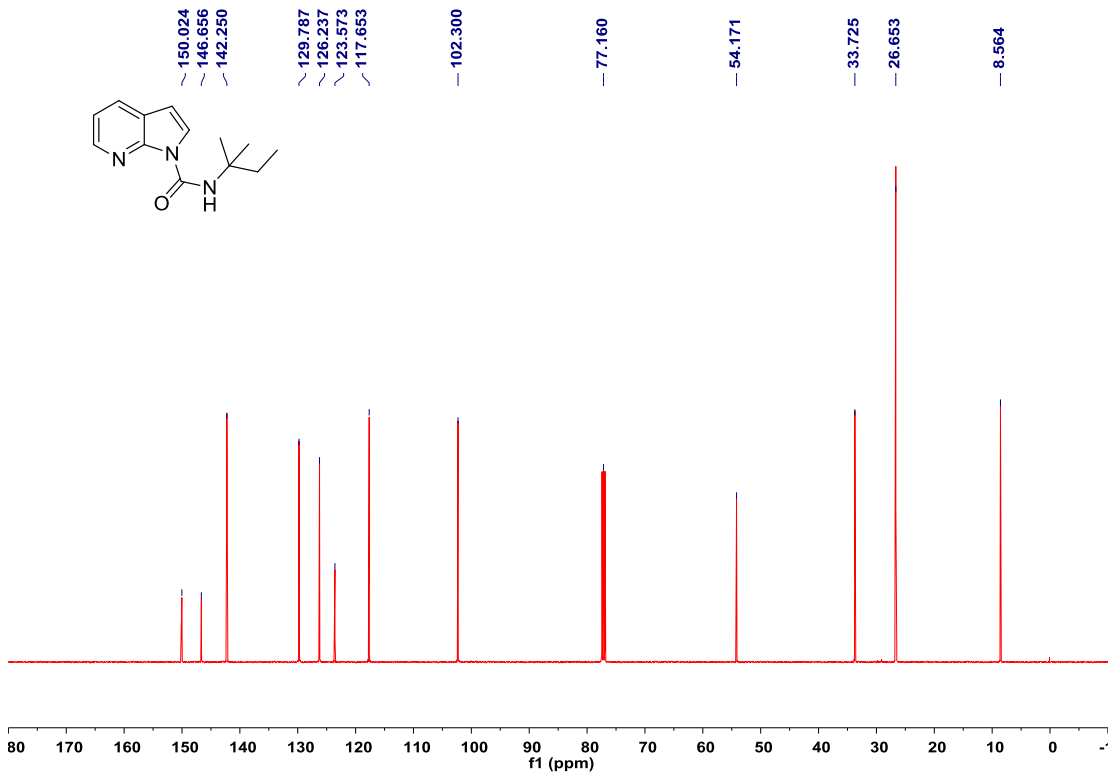


***N*-(tert-pentyl)-1H-pyrrolo[2,3-b] pyridine-1-carboxamide (1e)**

^{1}H NMR, 500 MHz, $CDCl_3$

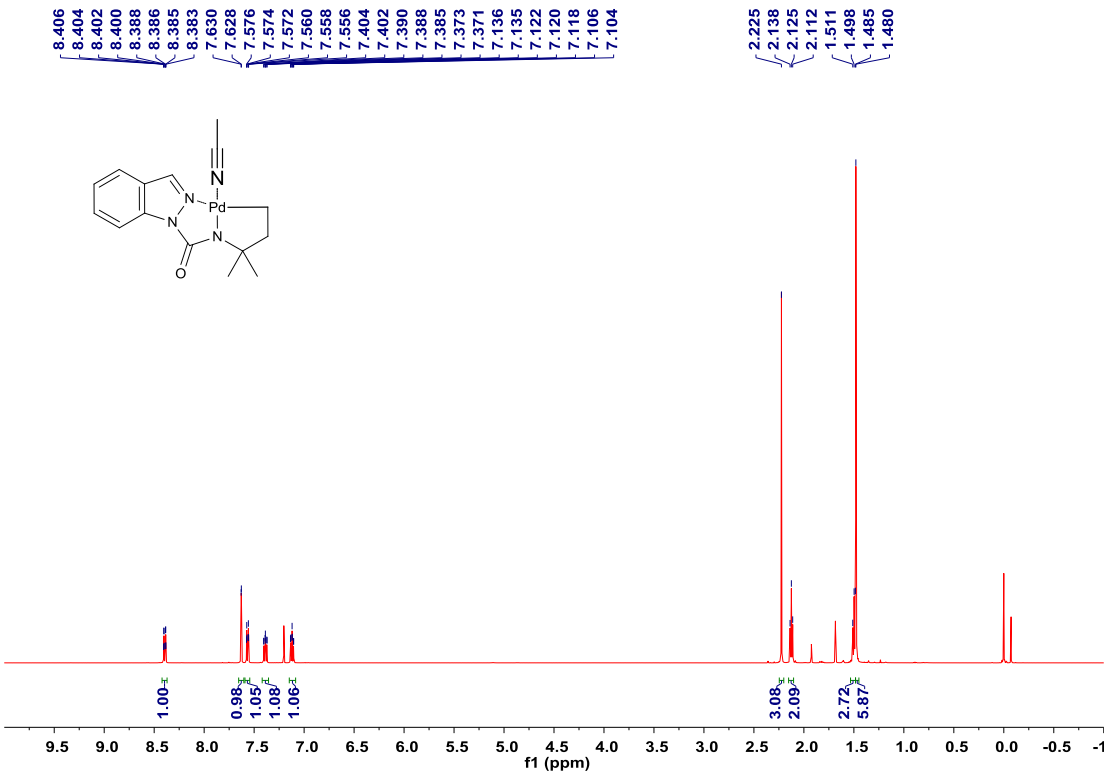


^{13}C NMR, 125 MHz, $CDCl_3$

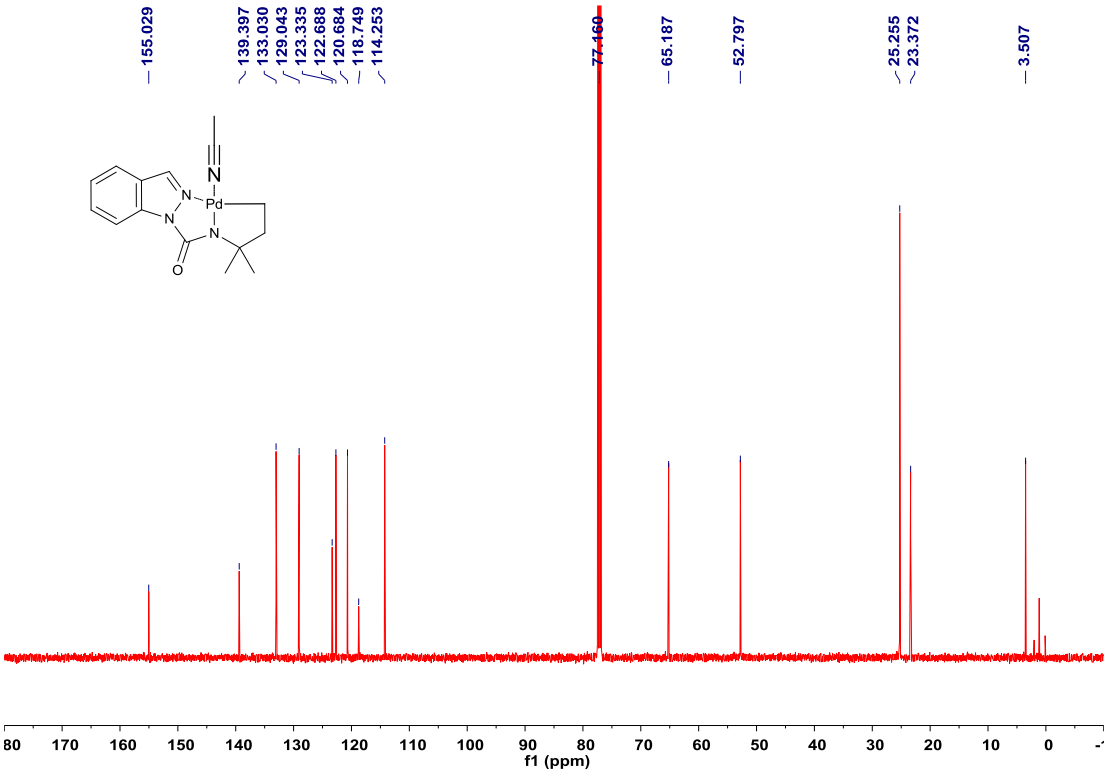


IN6

^{1}H NMR, 500 MHz, $CDCl_3$

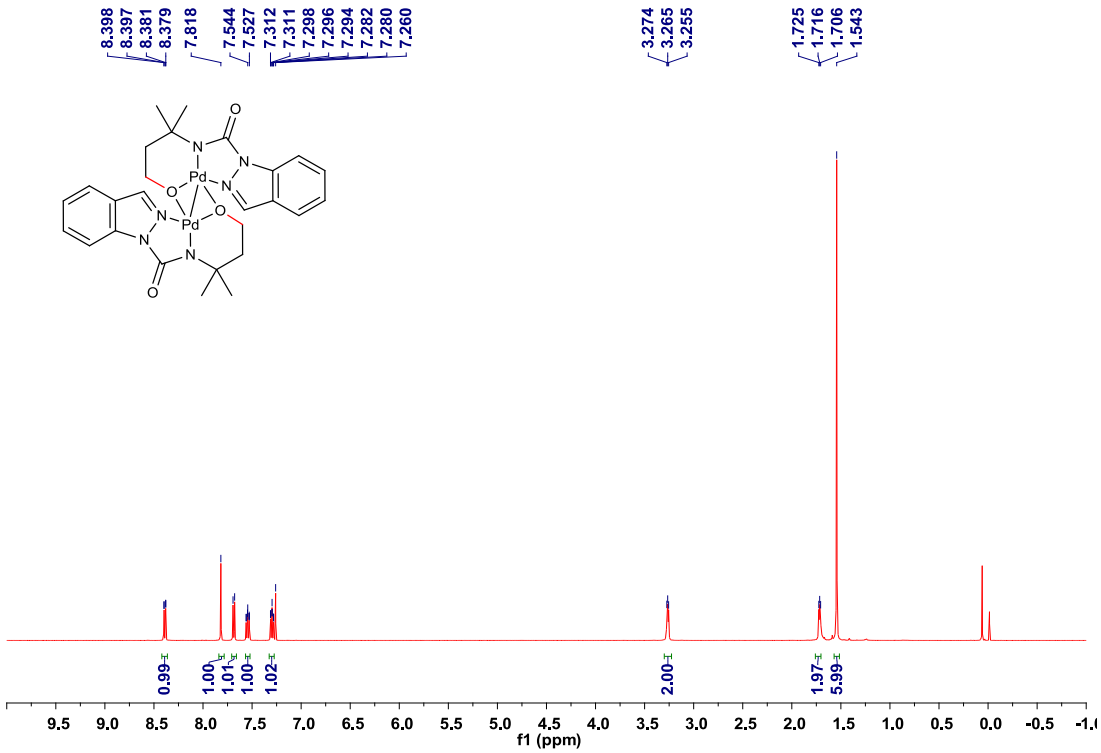


^{13}C NMR, 125 MHz, $CDCl_3$

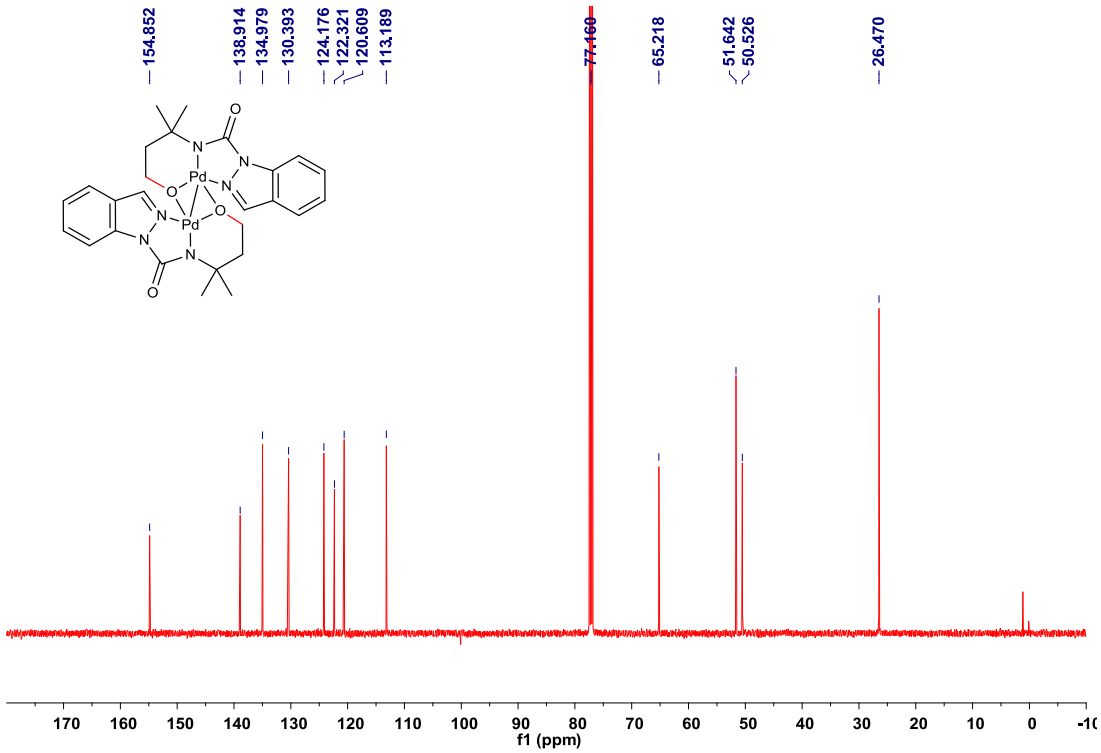


IN14

^{1}H NMR, 500 MHz, $CDCl_3$

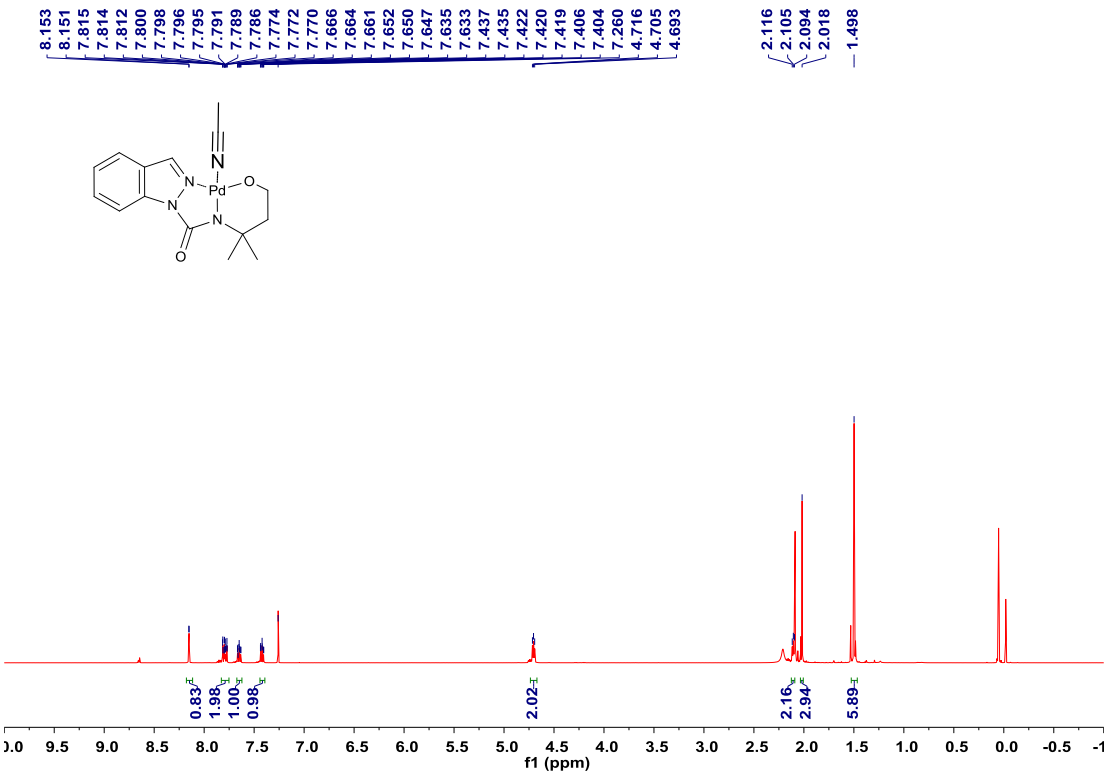


^{13}C NMR, 125 MHz, $CDCl_3$

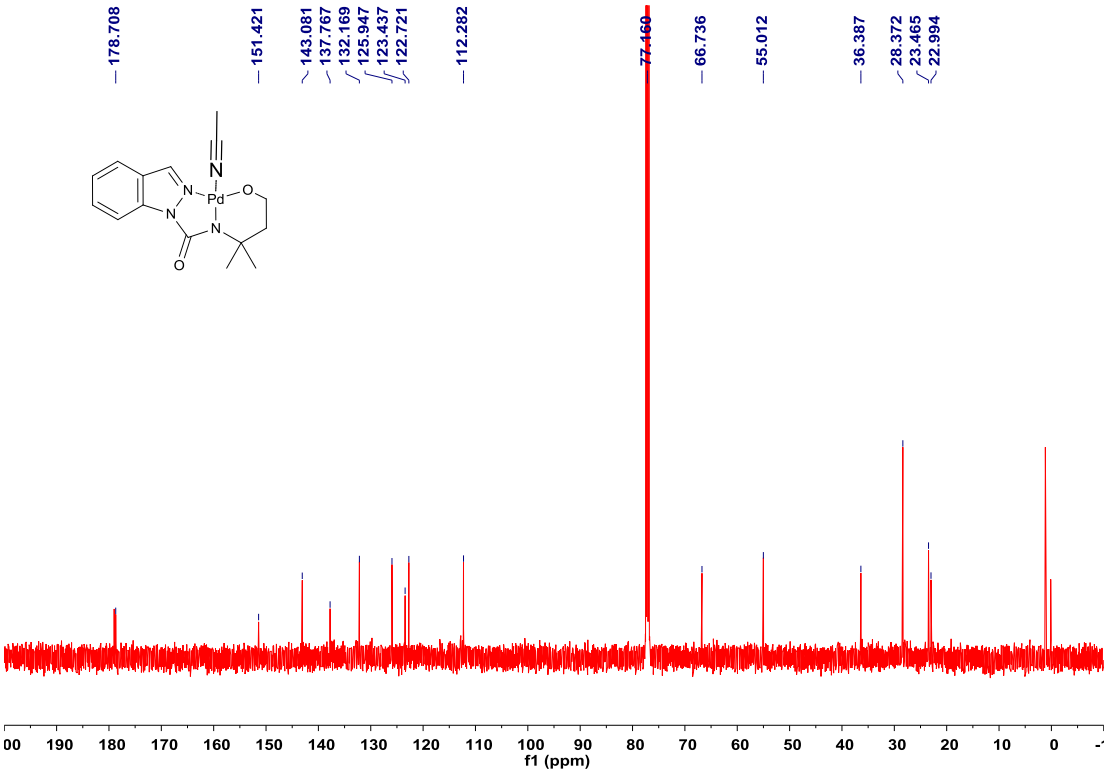


IN17

^{1}H NMR, 500 MHz, $CDCl_3$

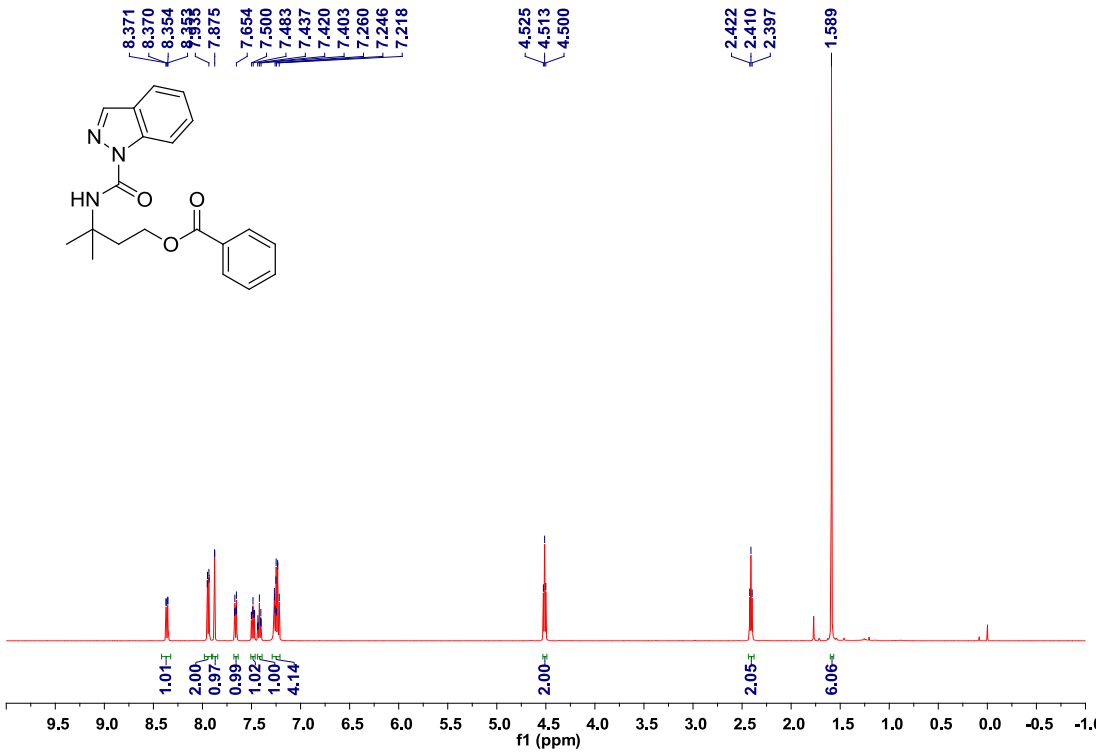


^{13}C NMR, 125 MHz, $CDCl_3$

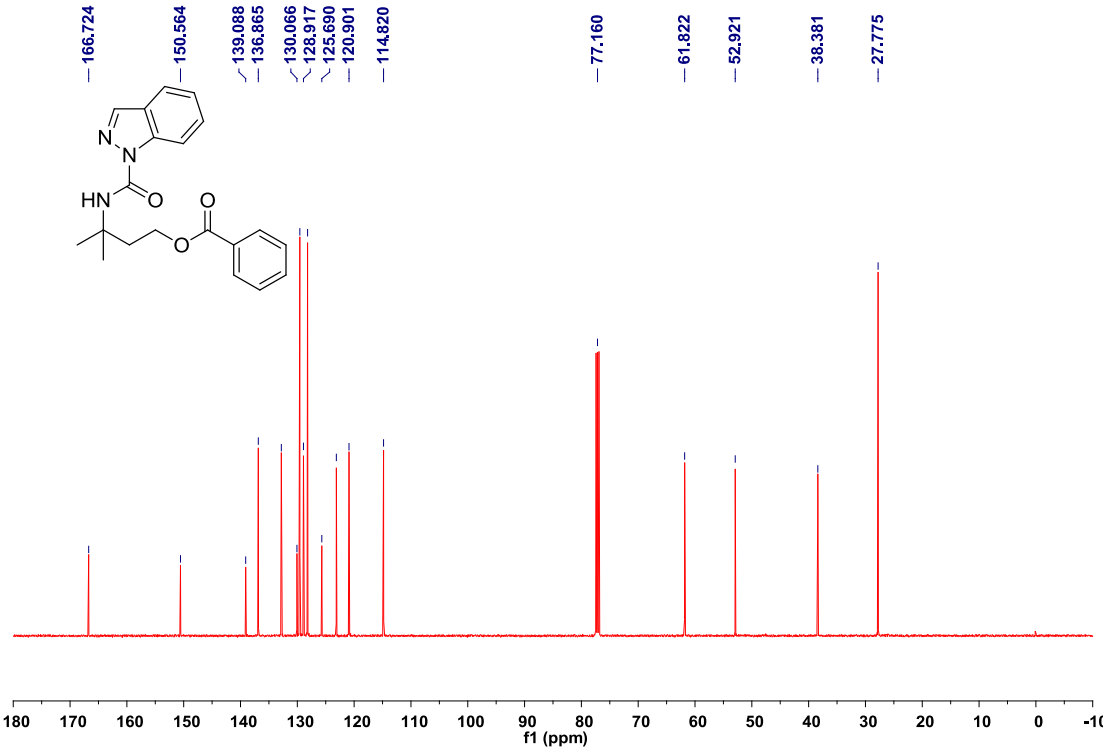


3-(1*H*-indazole-1-carboxamido)-3-methylbutyl benzoate (3a)

^{1}H NMR, 500 MHz, $CDCl_3$

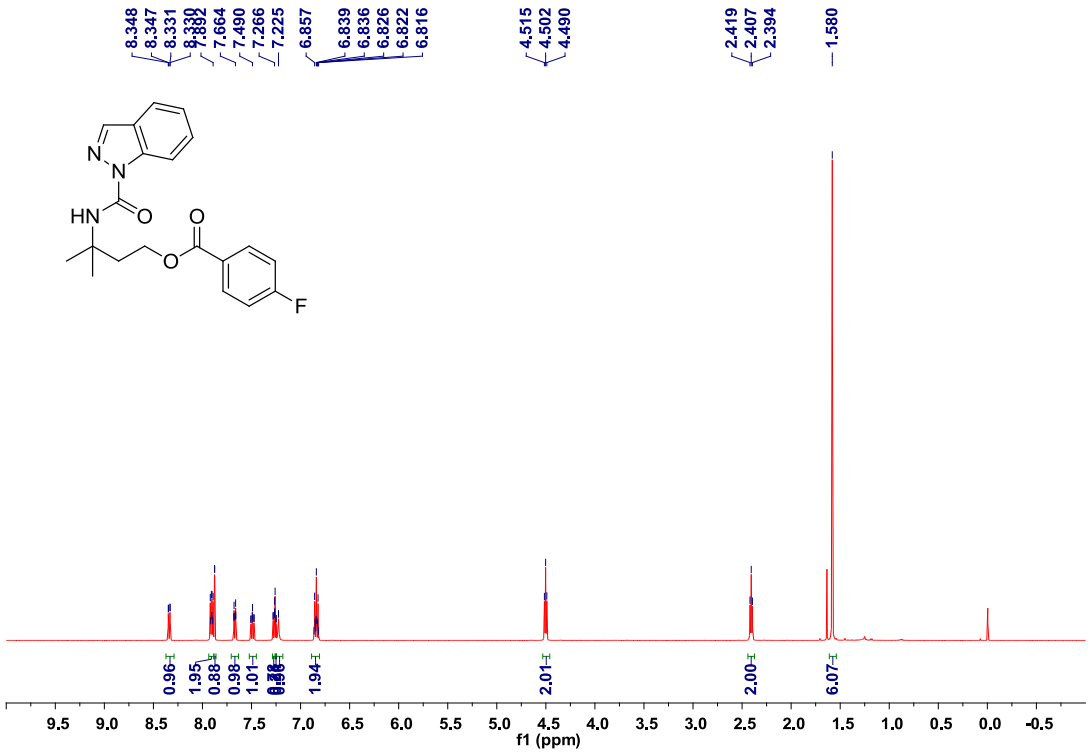


^{13}C NMR, 125 MHz, $CDCl_3$

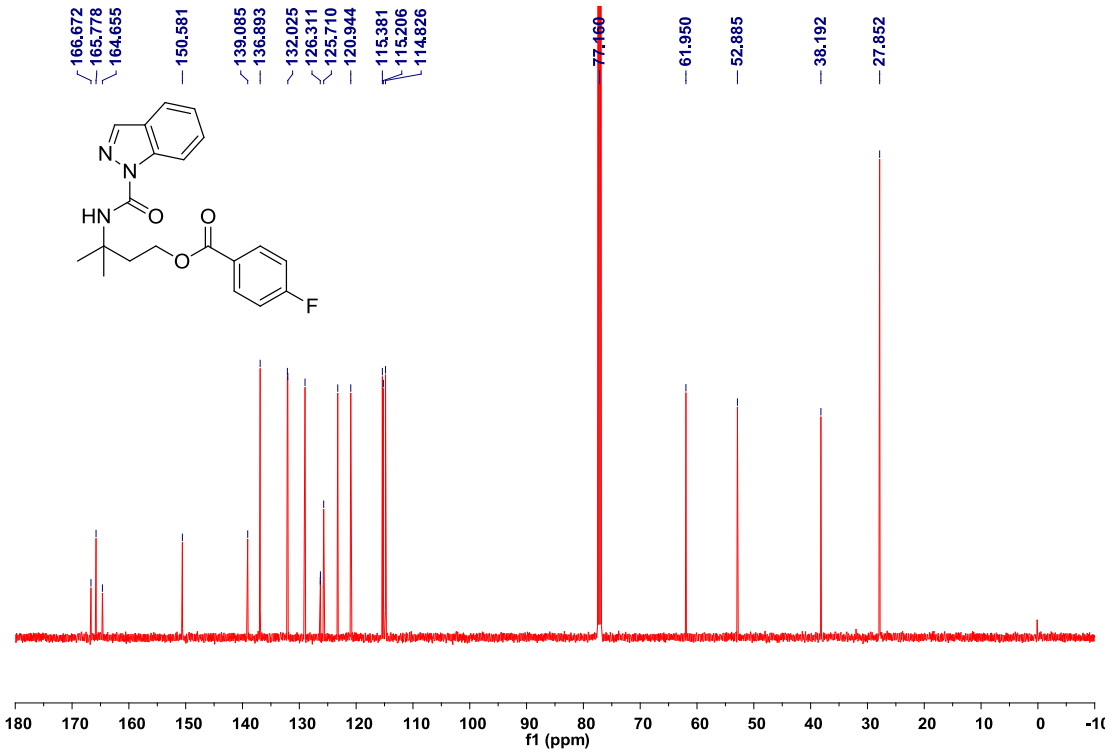


3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 4-fluorobenzoate (3b)

^{1}H NMR, 500 MHz, $CDCl_3$

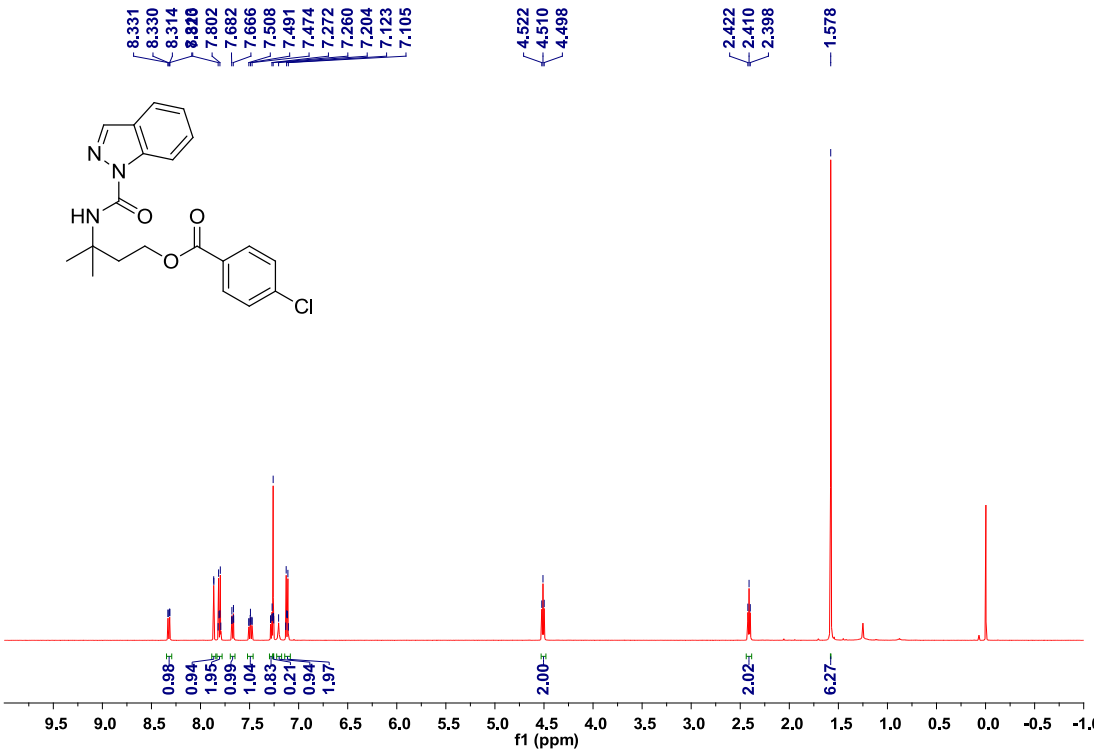


^{13}C NMR, 125 MHz, $CDCl_3$

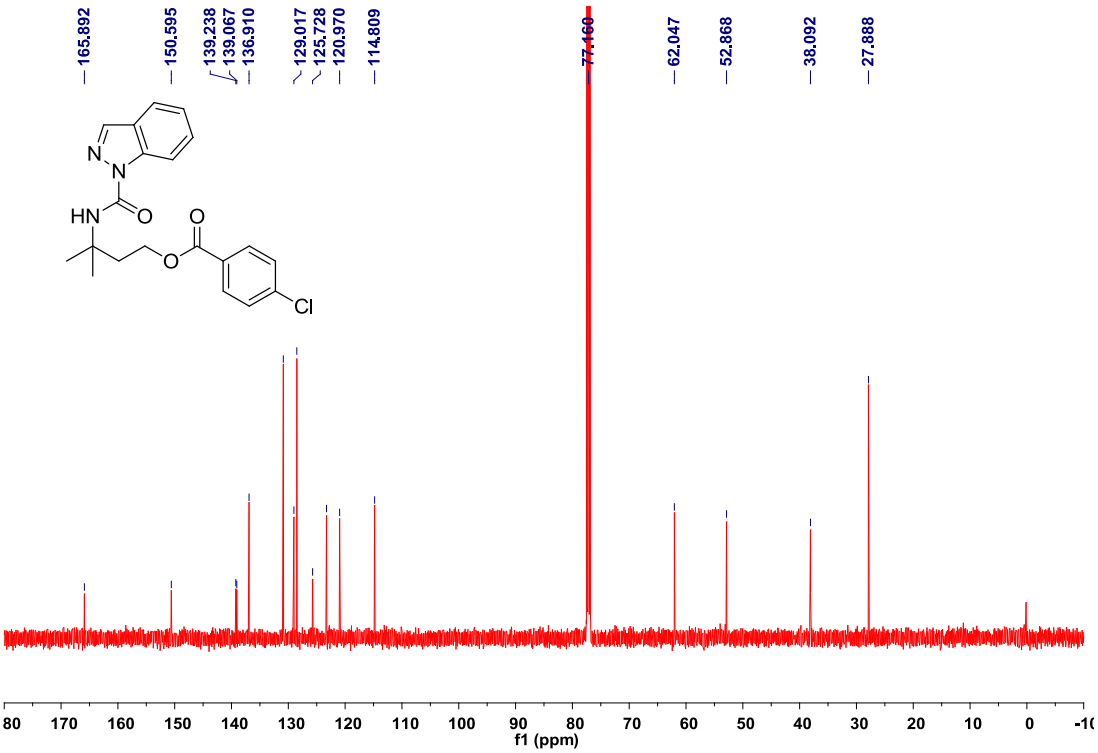


3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 4-chlorobenzoate (3c)

^{1}H NMR, 500 MHz, $CDCl_3$

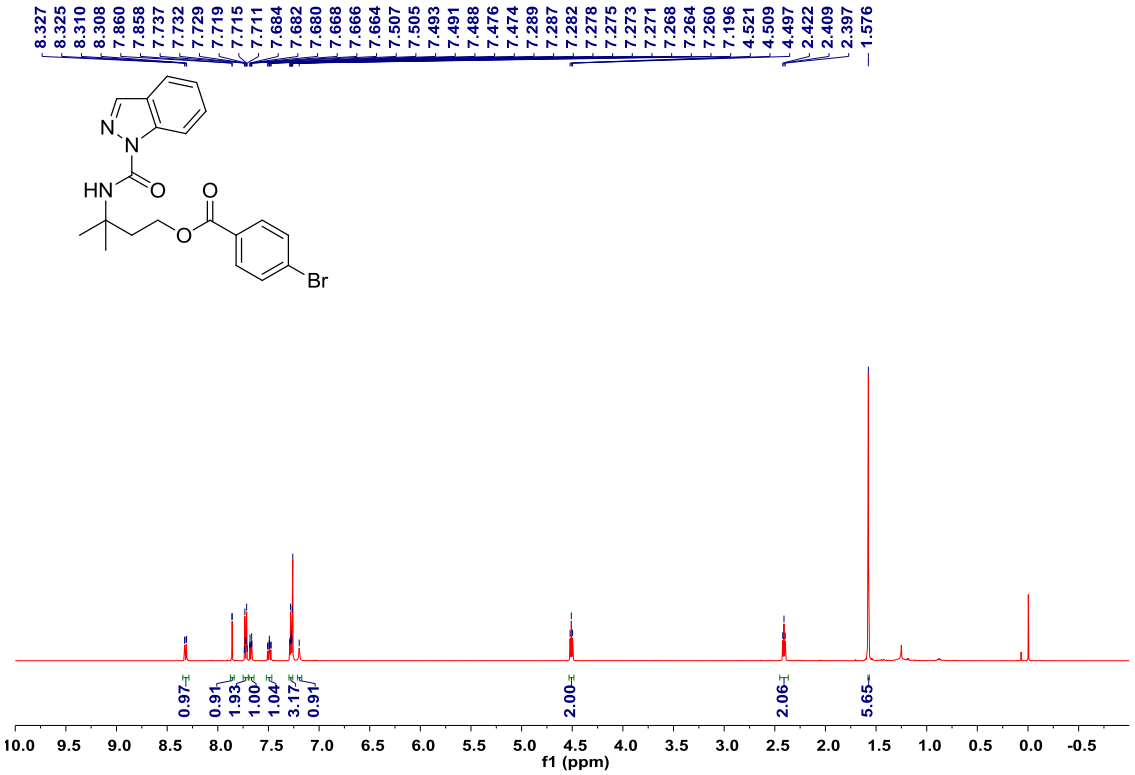


^{13}C NMR, 125 MHz, $CDCl_3$

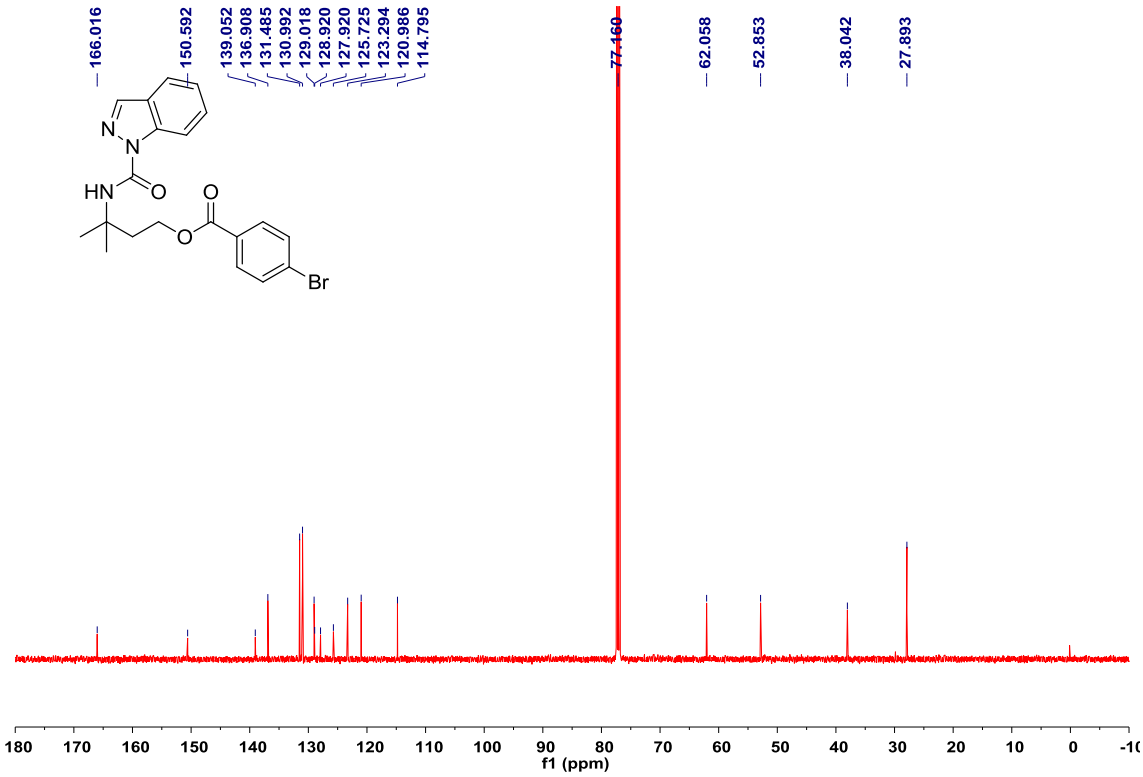


3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 4-bromobenzoate (3d)

^{1}H NMR, 500 MHz, $CDCl_3$

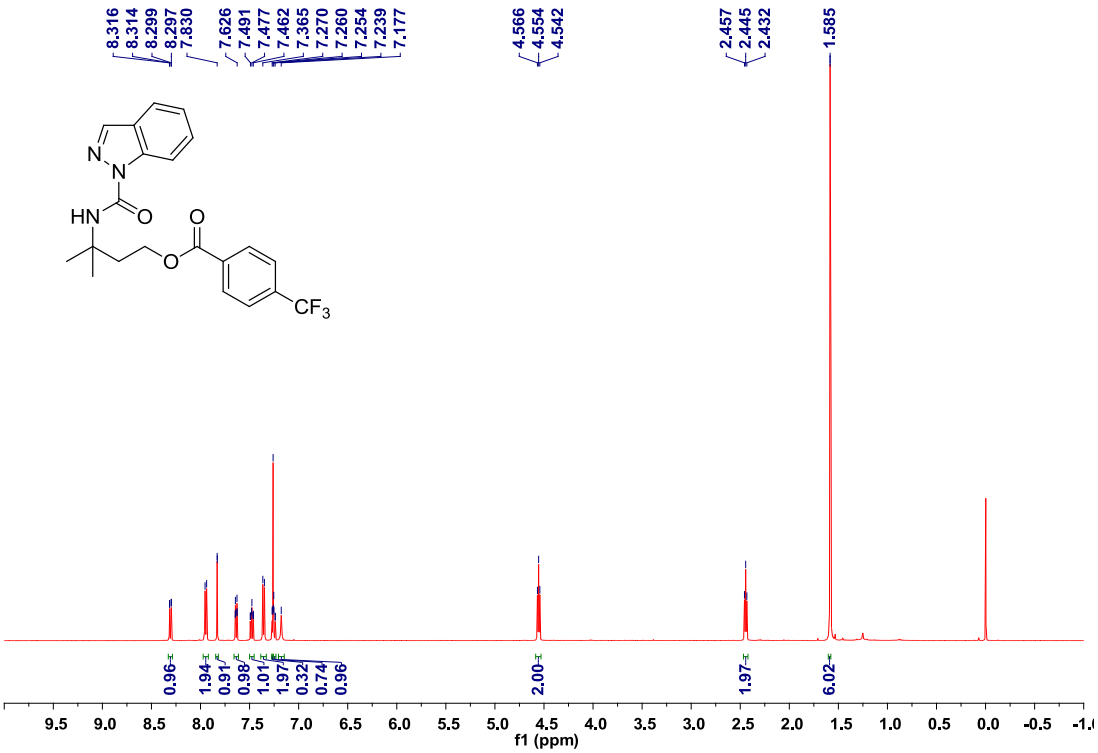


^{13}C NMR, 125 MHz, $CDCl_3$

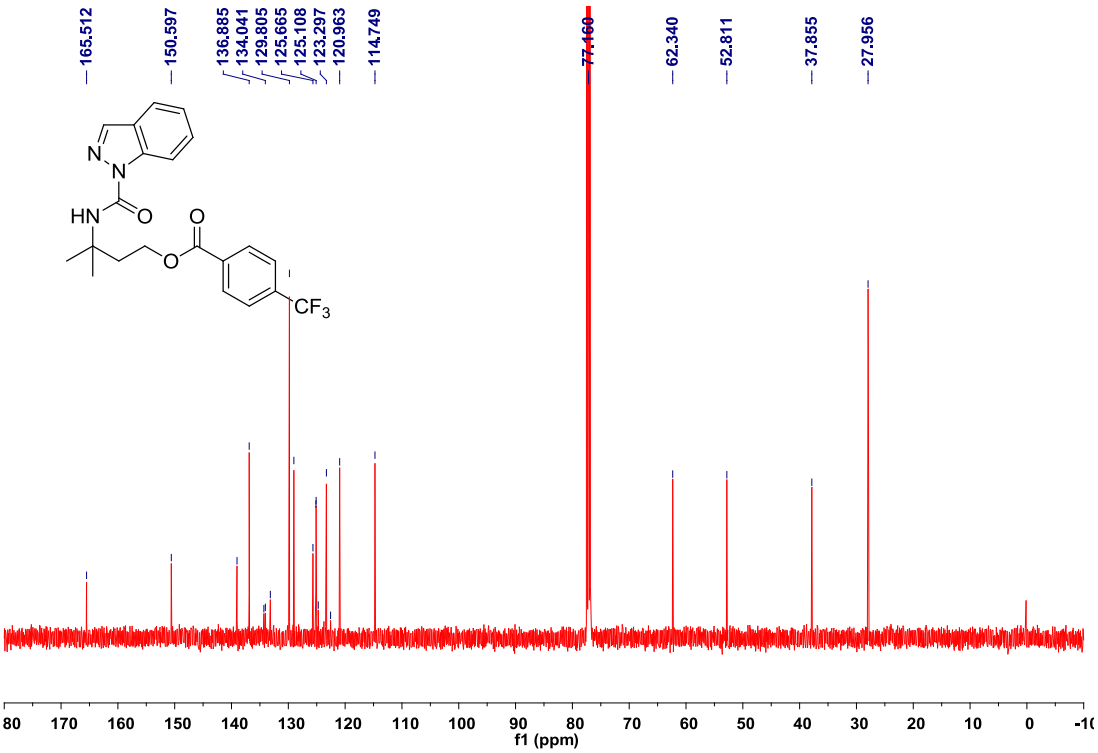


3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 4-(trifluoromethyl)benzoate (3e)

^{1}H NMR, 500 MHz, $CDCl_3$

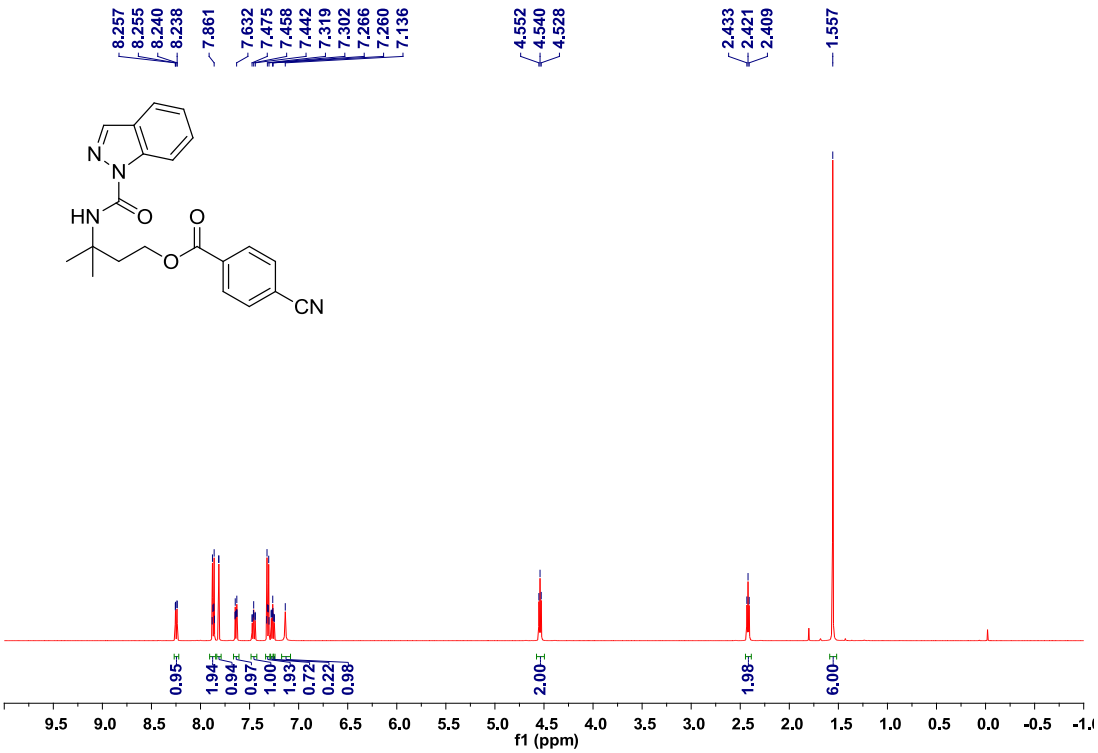


^{13}C NMR, 125 MHz, $CDCl_3$

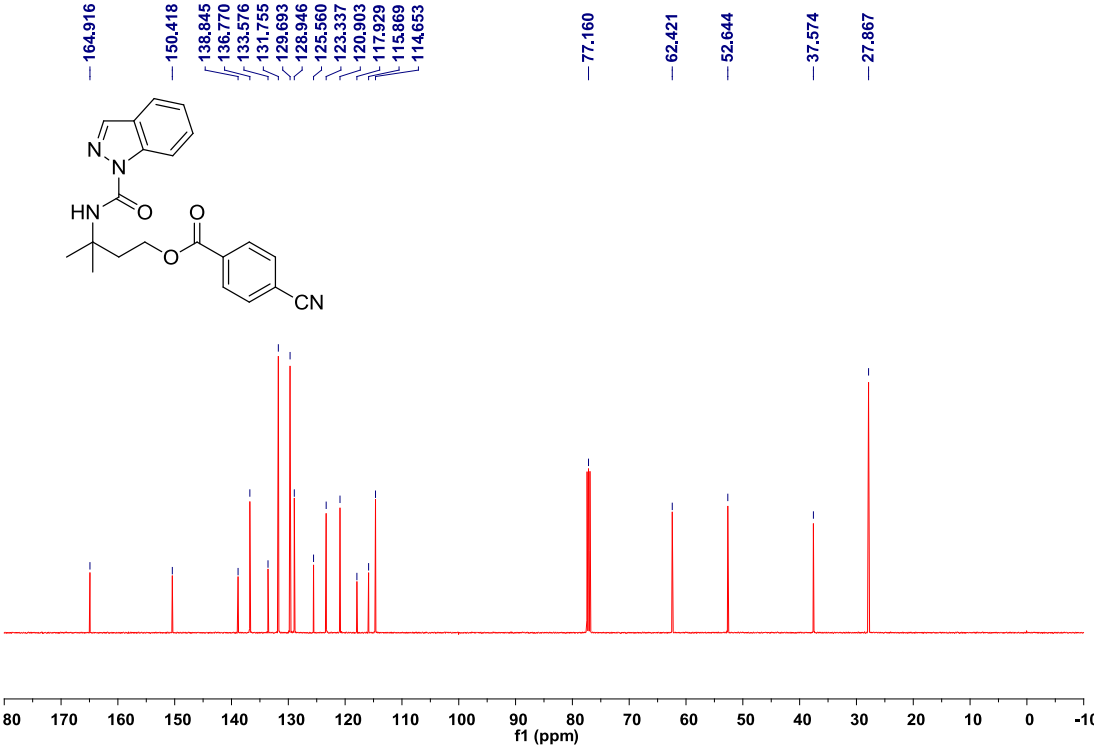


3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 4-cyanobenzoate (3f)

^{1}H NMR, 500 MHz, $CDCl_3$

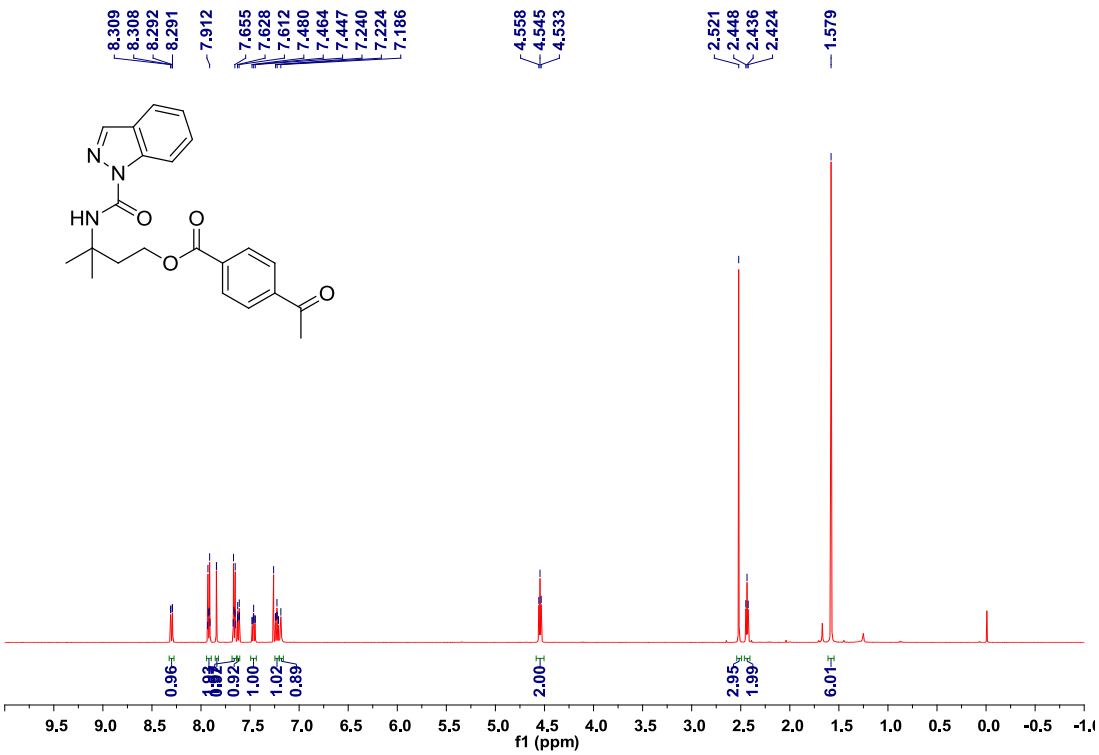


^{13}C NMR, 125 MHz, $CDCl_3$

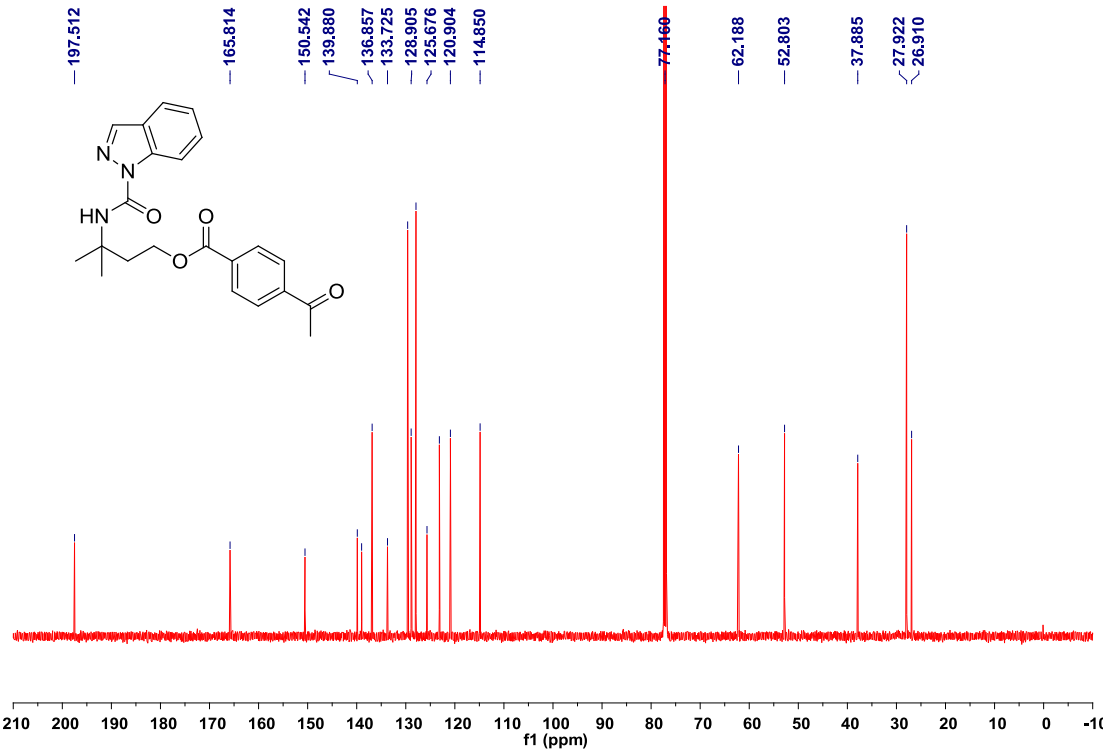


3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 4-acetylbenzoate (3g)

^{1}H NMR, 500 MHz, $CDCl_3$

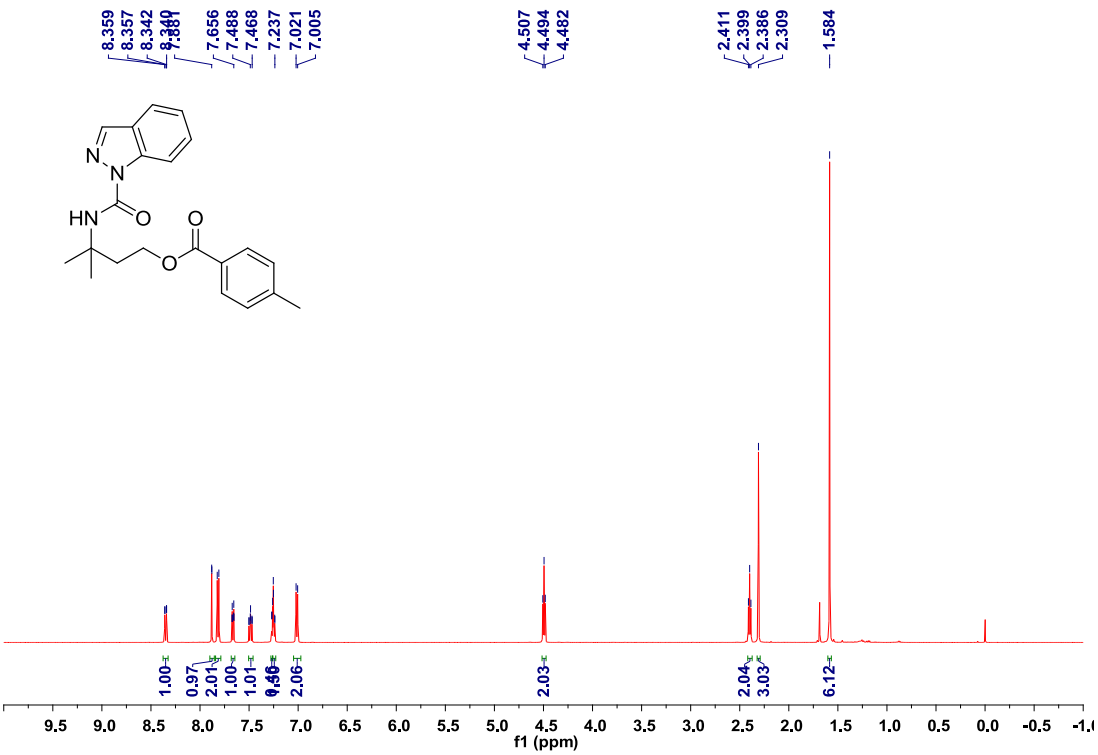


^{13}C NMR, 125 MHz, $CDCl_3$

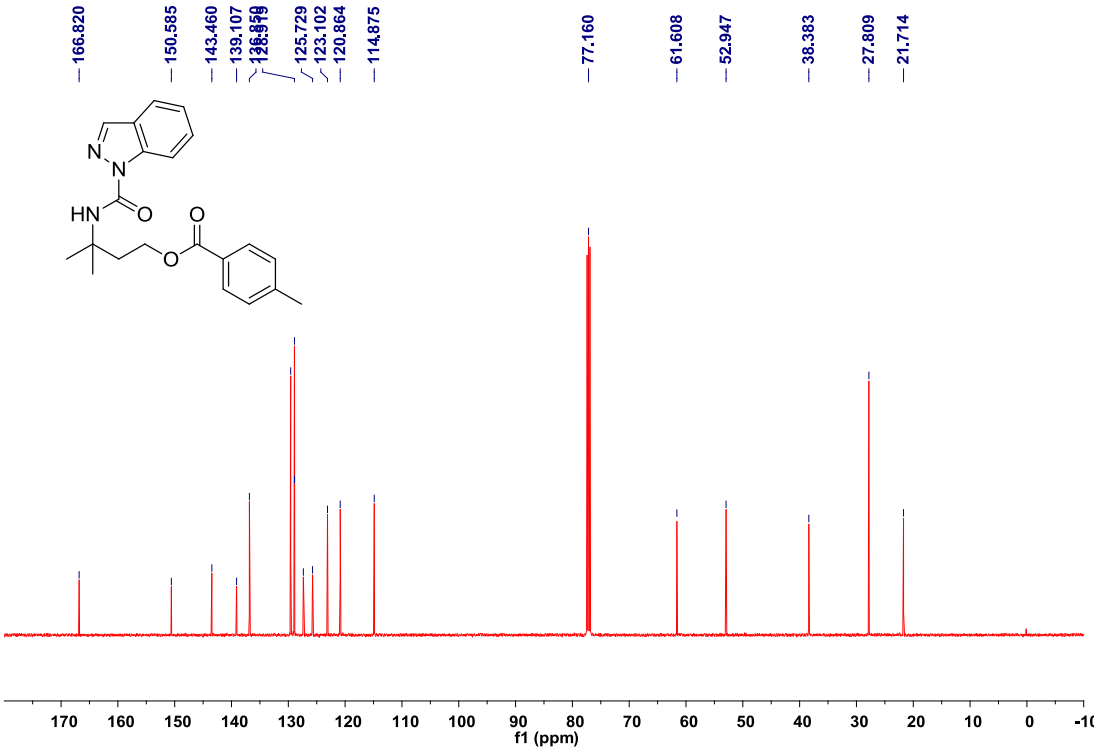


3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 4-methylbenzoate (3h)

^{1}H NMR, 500 MHz, $CDCl_3$

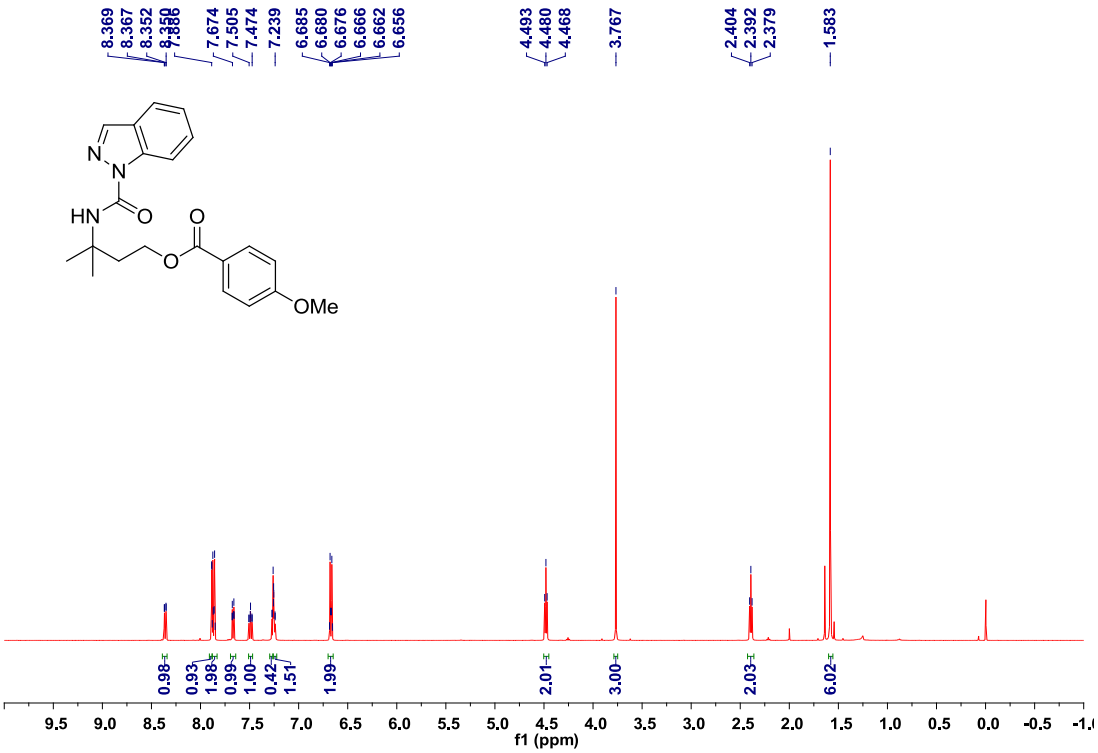


^{13}C NMR, 125 MHz, $CDCl_3$

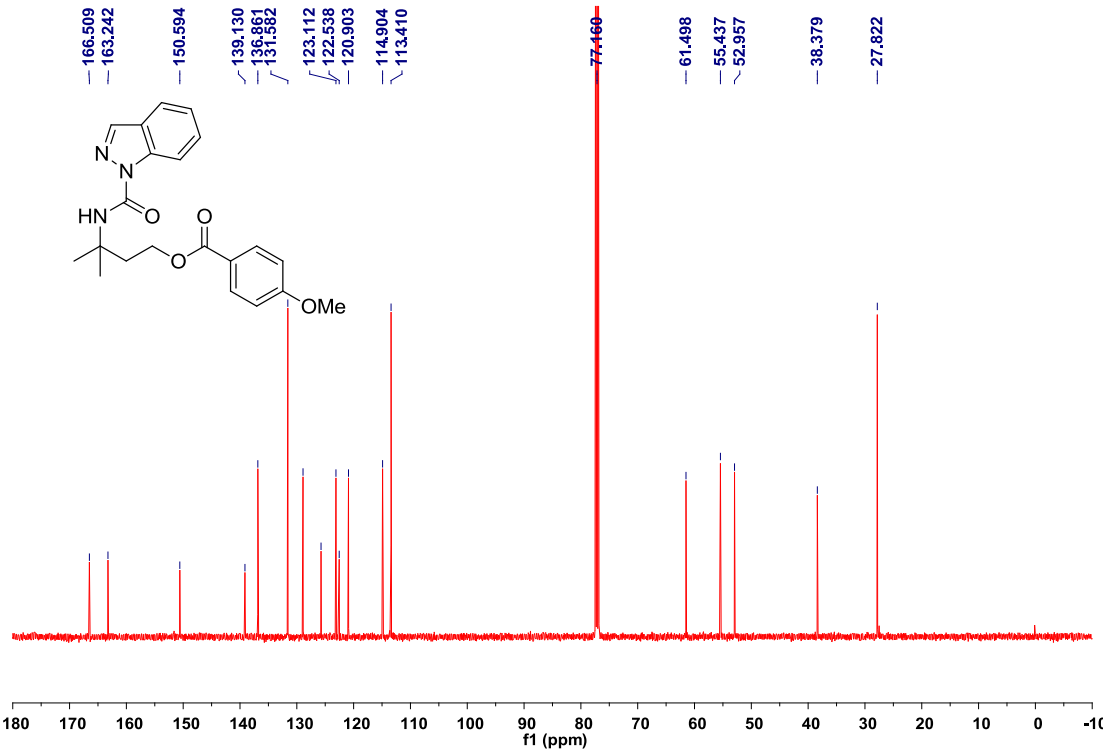


3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 4-methoxybenzoate (3i)

^{1}H NMR, 500 MHz, $CDCl_3$

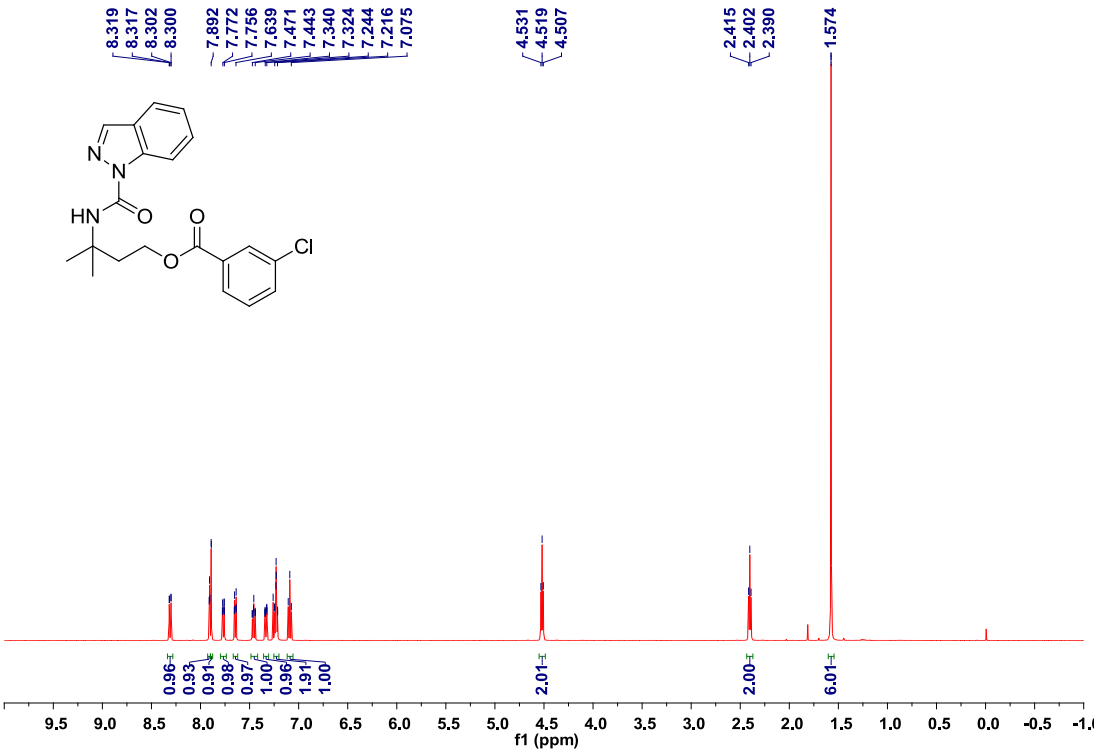


^{13}C NMR, 125 MHz, $CDCl_3$

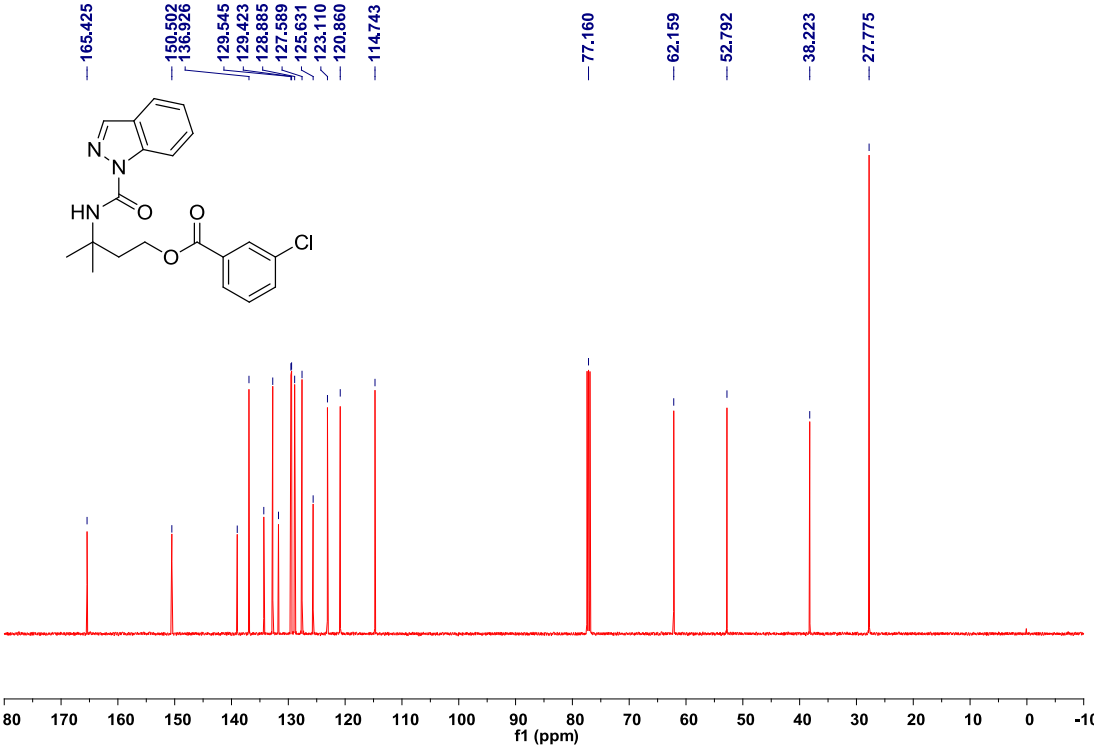


3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 3-chlorobenzoate (3j)

^{1}H NMR, 500 MHz, $CDCl_3$

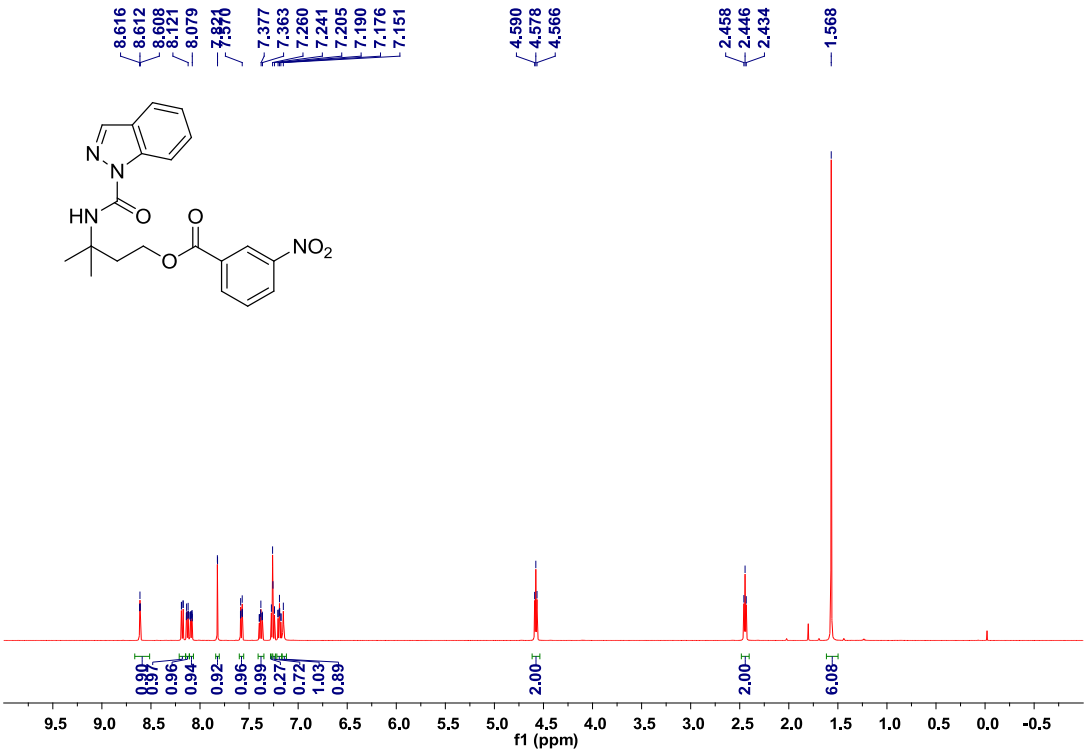


^{13}C NMR, 125 MHz, $CDCl_3$

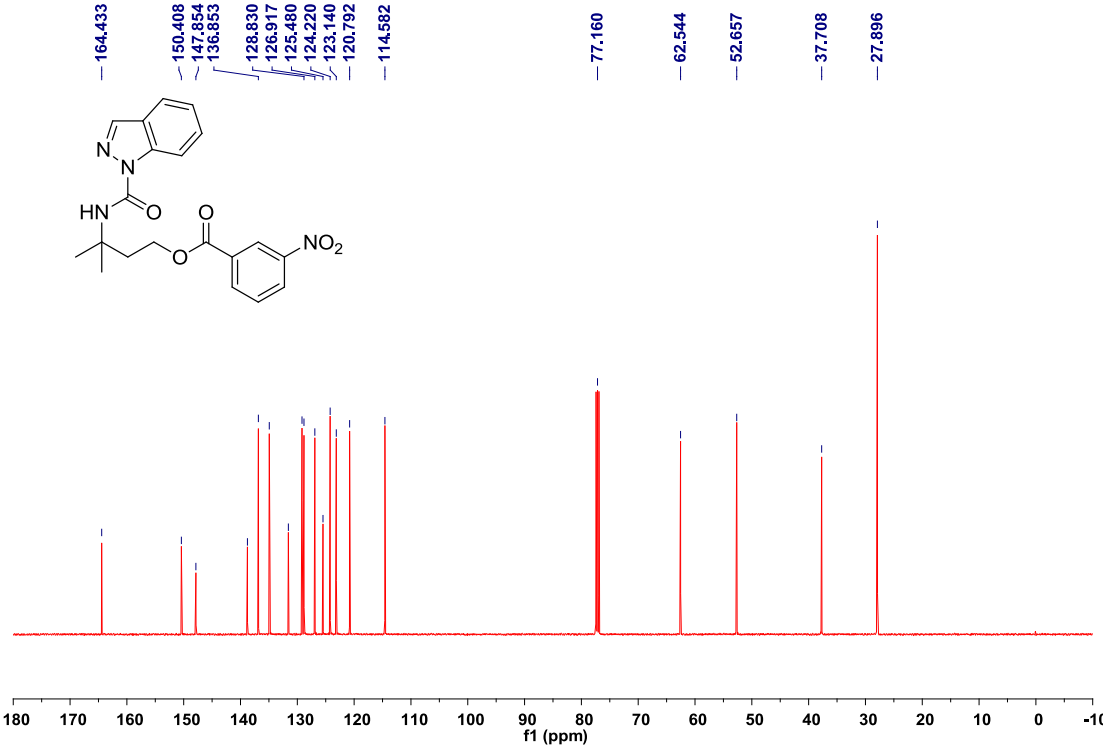


3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 3-nitrobenzoate (3k)

^{1}H NMR, 500 MHz, $CDCl_3$

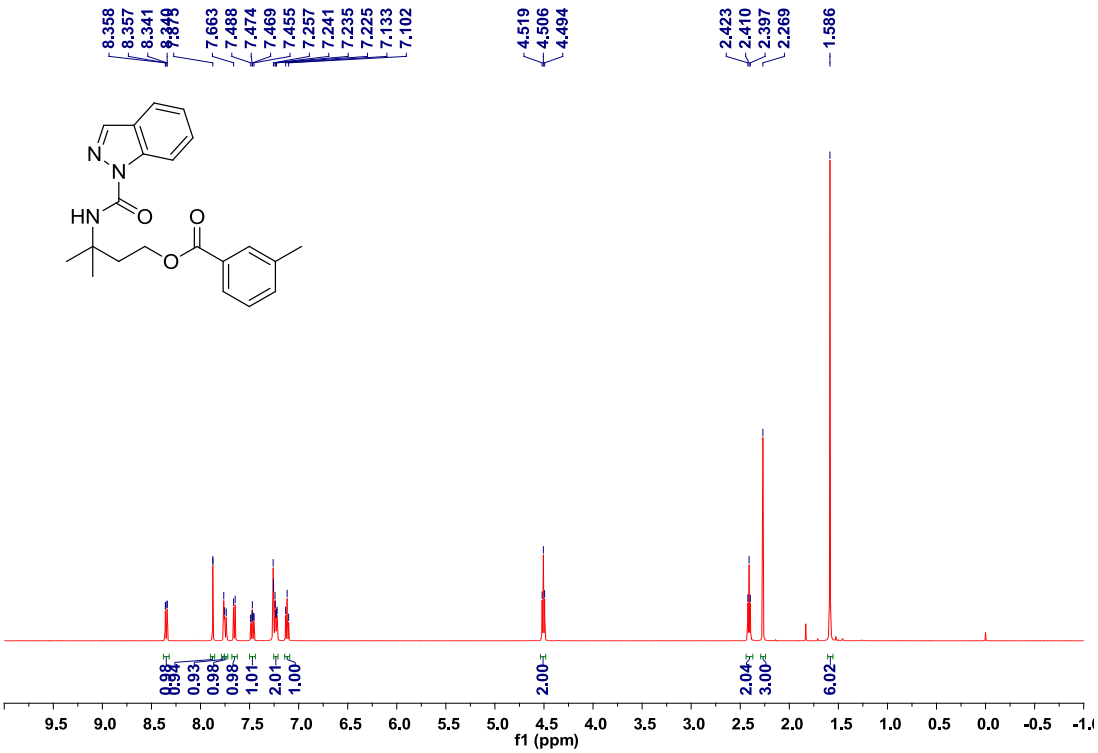


^{13}C NMR, 125 MHz, $CDCl_3$

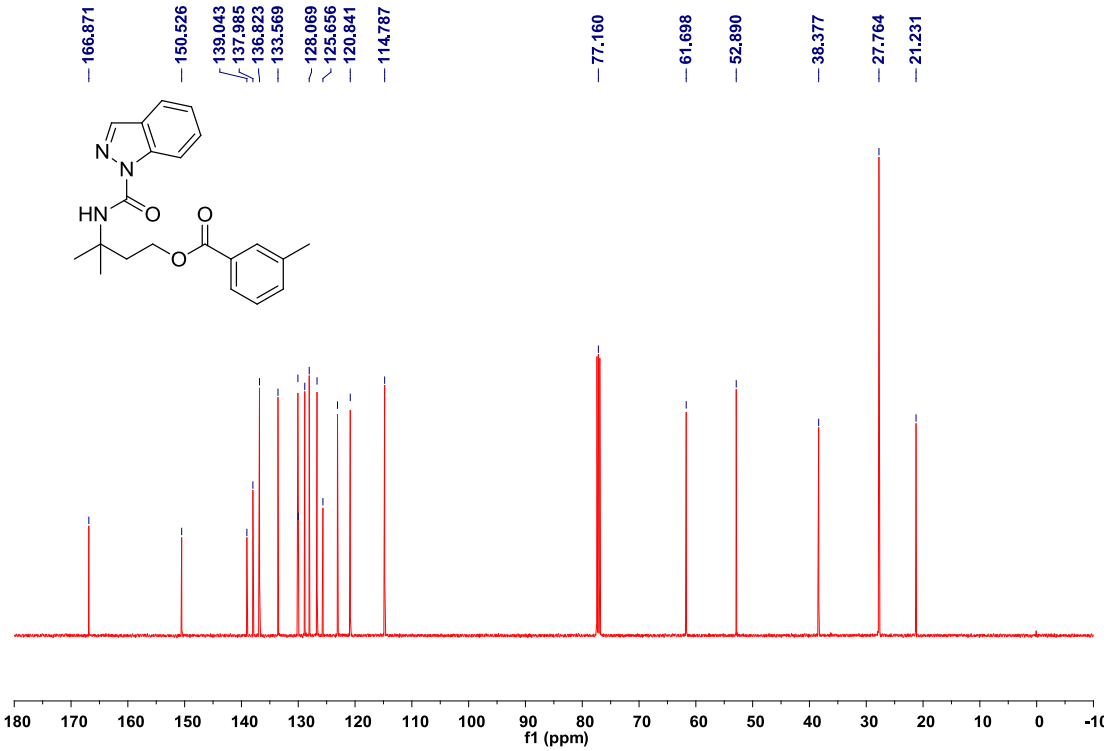


3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 3-methylbenzoate (3l)

^{1}H NMR, 500 MHz, $CDCl_3$

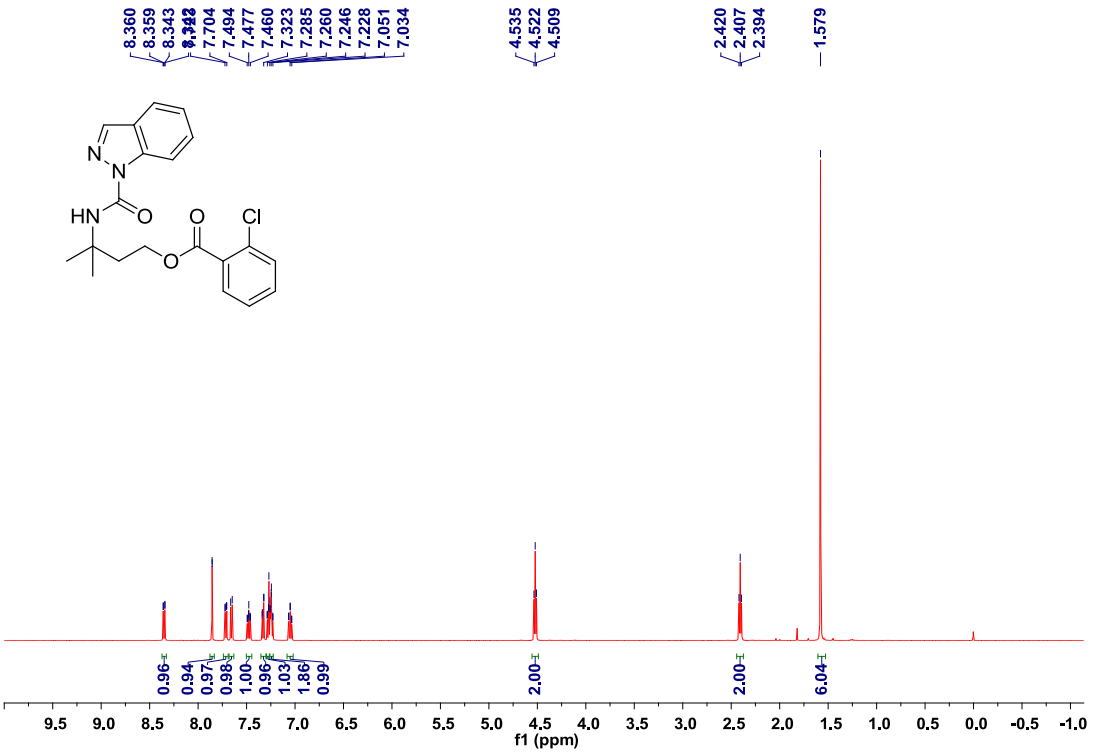


^{13}C NMR, 125 MHz, $CDCl_3$

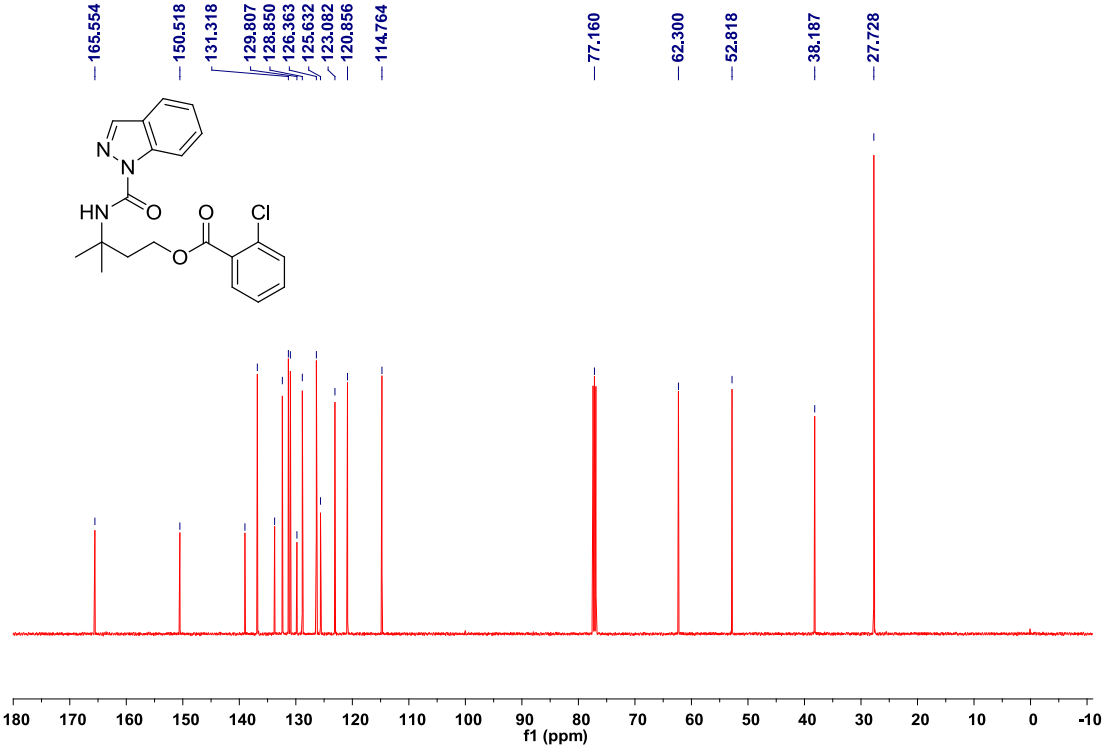


3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 2-chlorobenzoate (3m)

^{1}H NMR, 500 MHz, $CDCl_3$

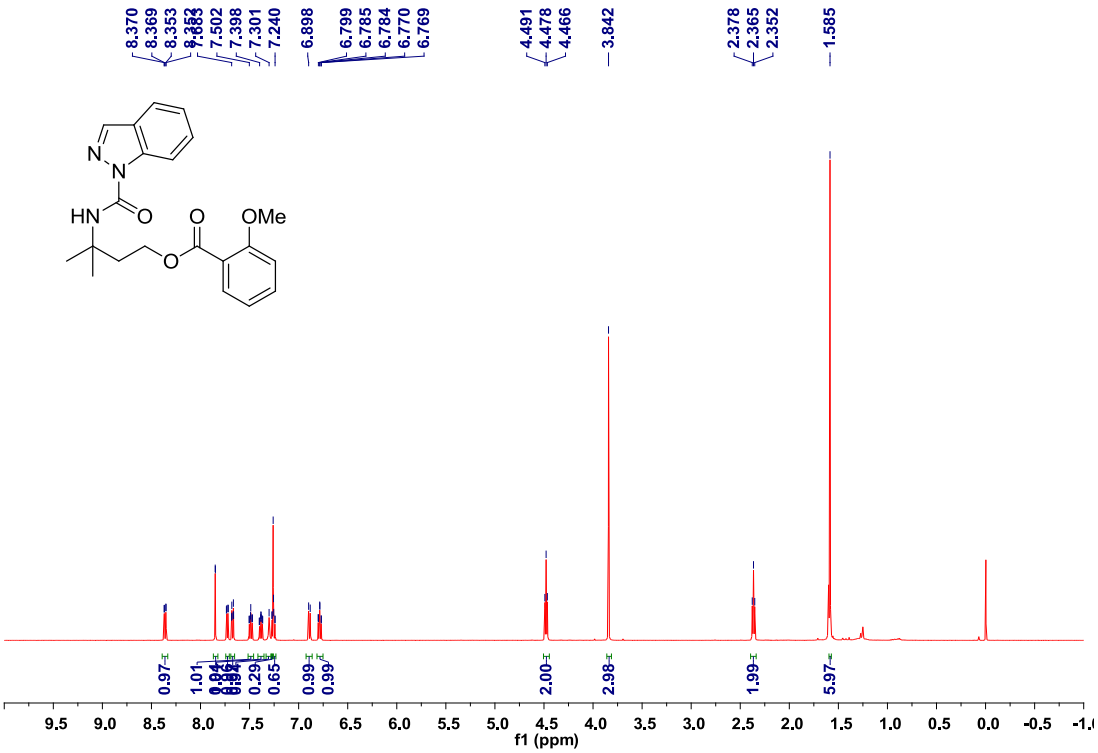


^{13}C NMR, 125 MHz, $CDCl_3$

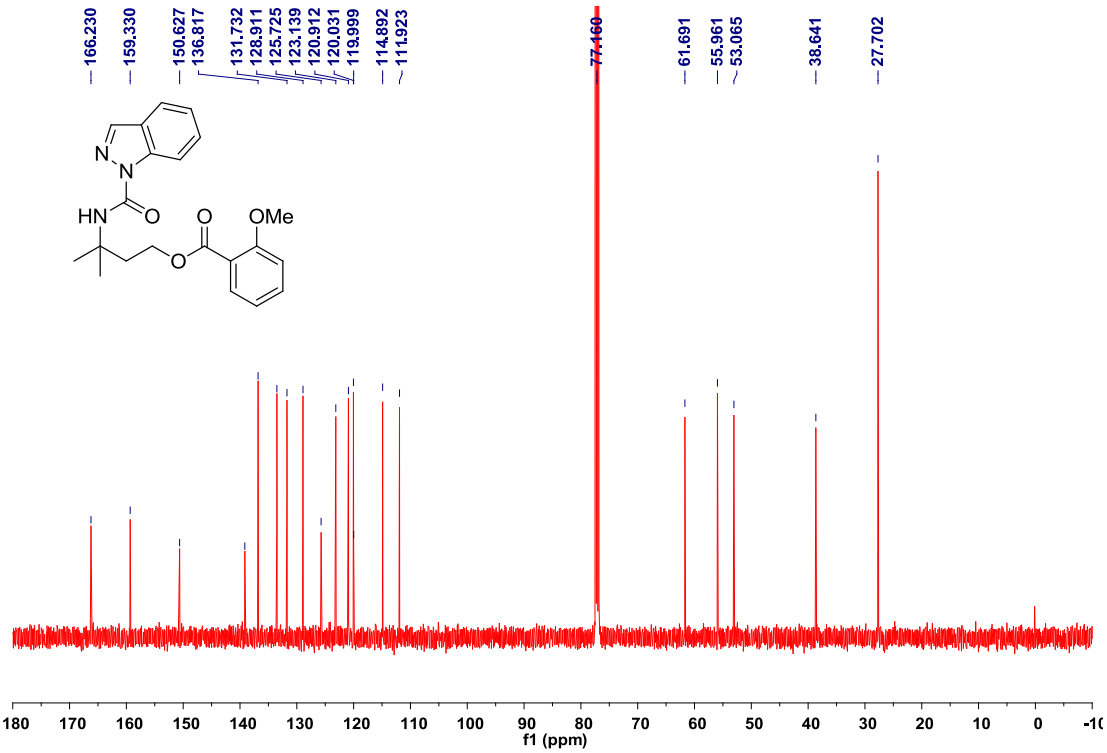


3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 4-methoxybenzoate (3n)

^{1}H NMR, 500 MHz, $CDCl_3$

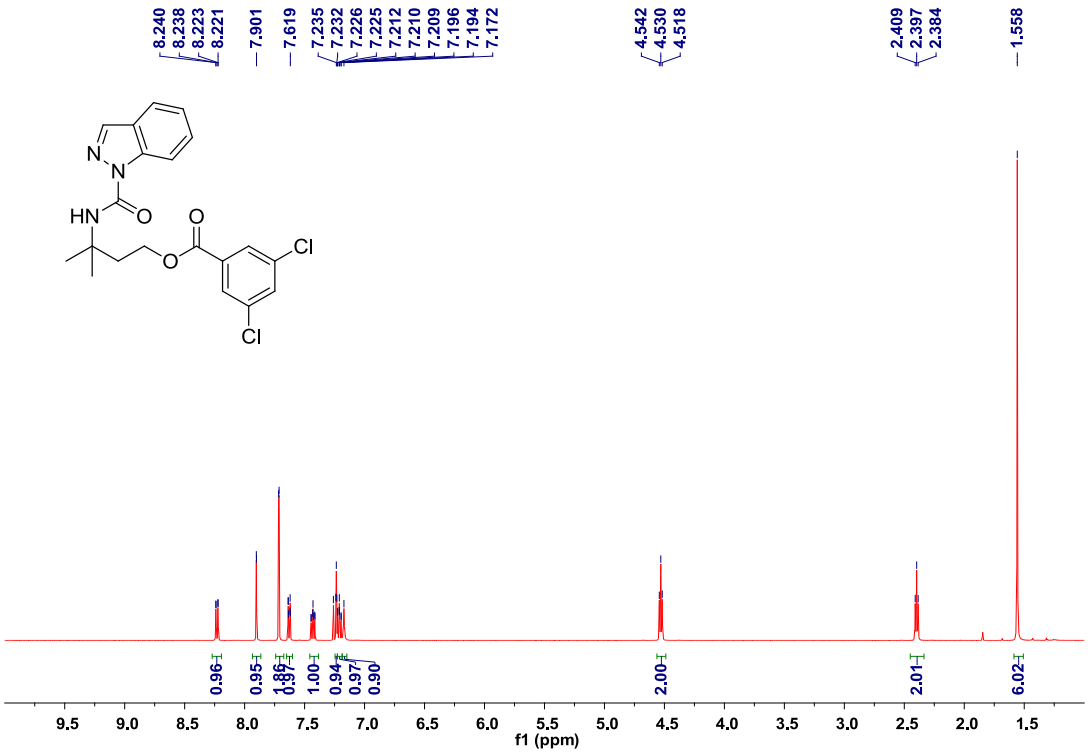


^{13}C NMR, 125 MHz, $CDCl_3$

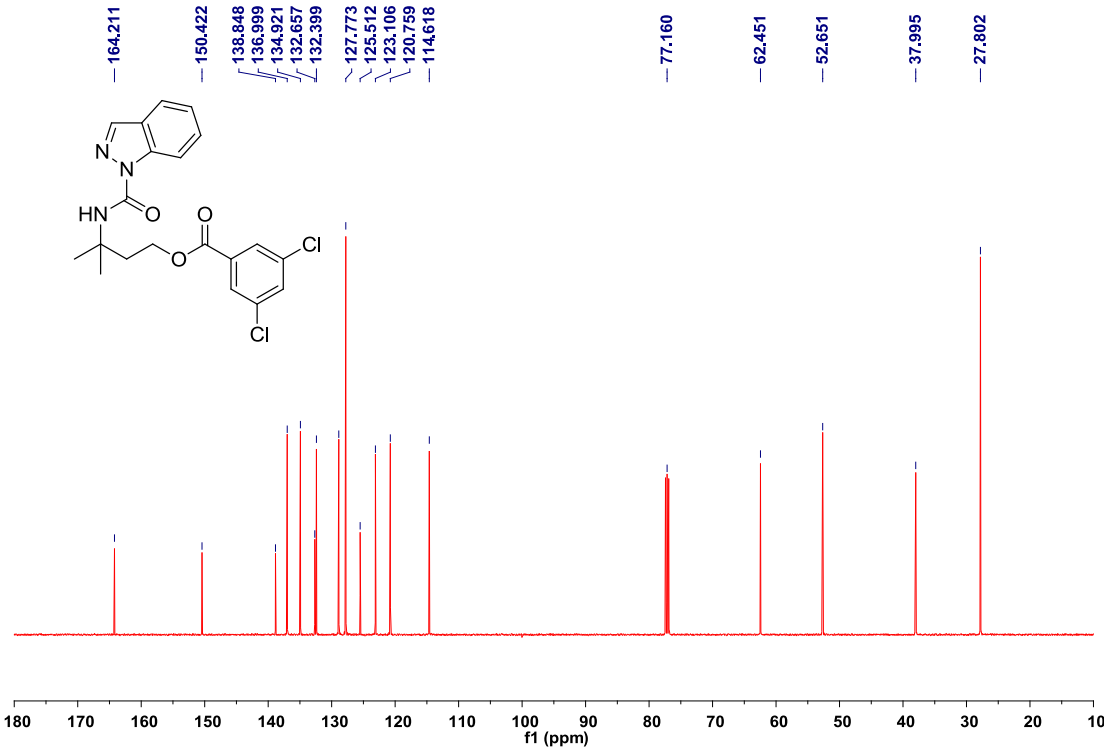


3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 3,5-dichlorobenzoate (3o)

^{1}H NMR, 500 MHz, $CDCl_3$

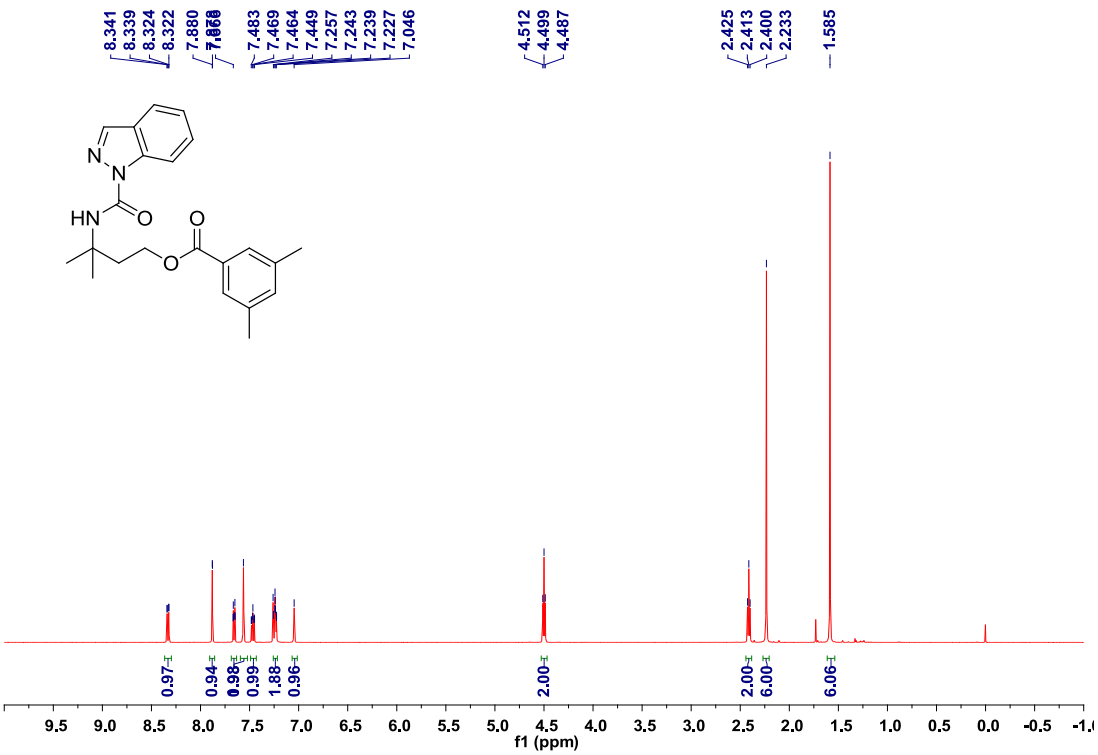


^{13}C NMR, 125 MHz, $CDCl_3$

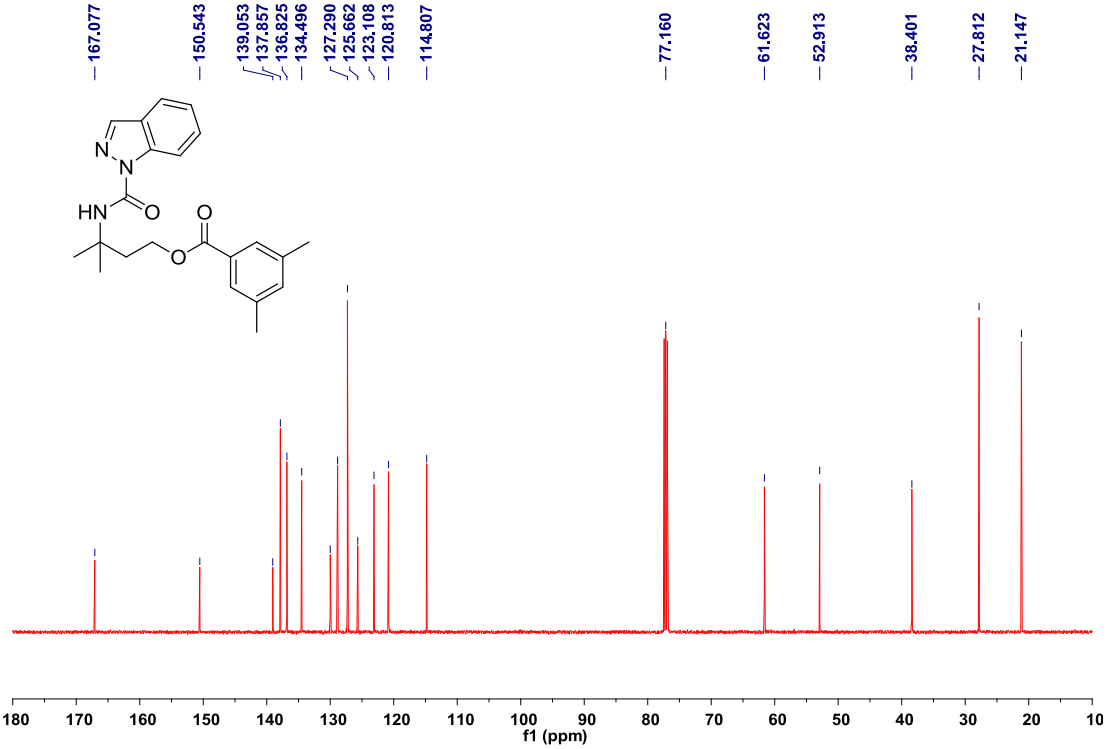


3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 3,5-dimethylbenzoate (3q)

^{1}H NMR, 500 MHz, $CDCl_3$

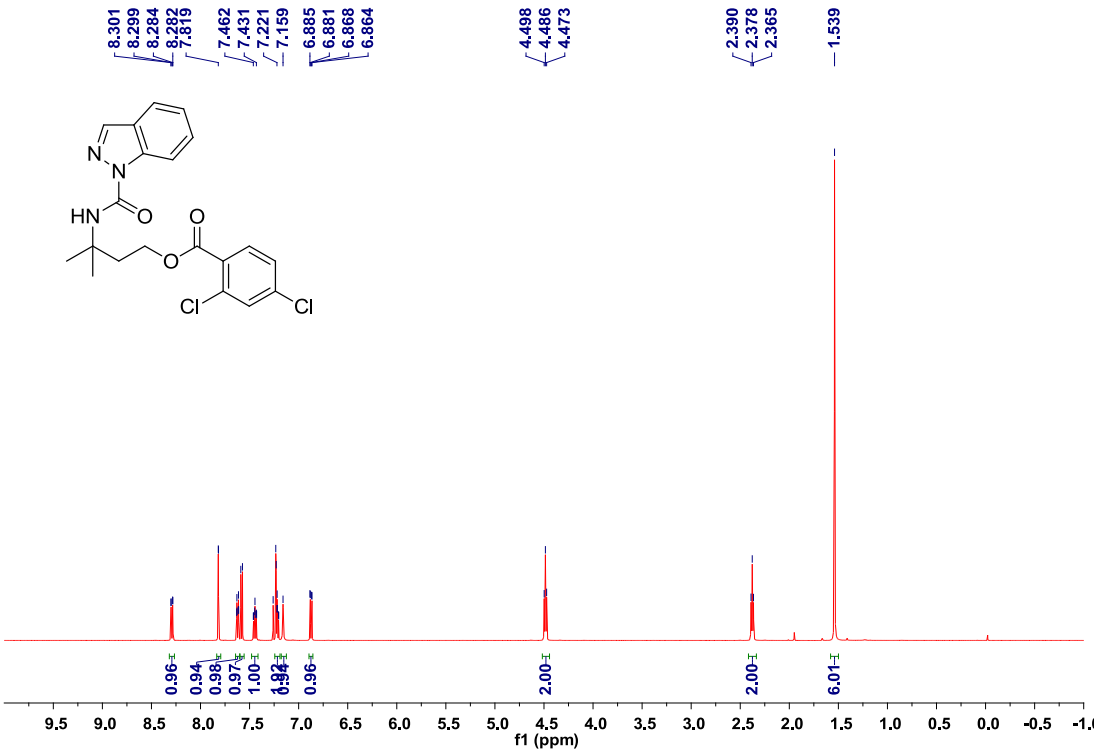


^{13}C NMR, 125 MHz, $CDCl_3$

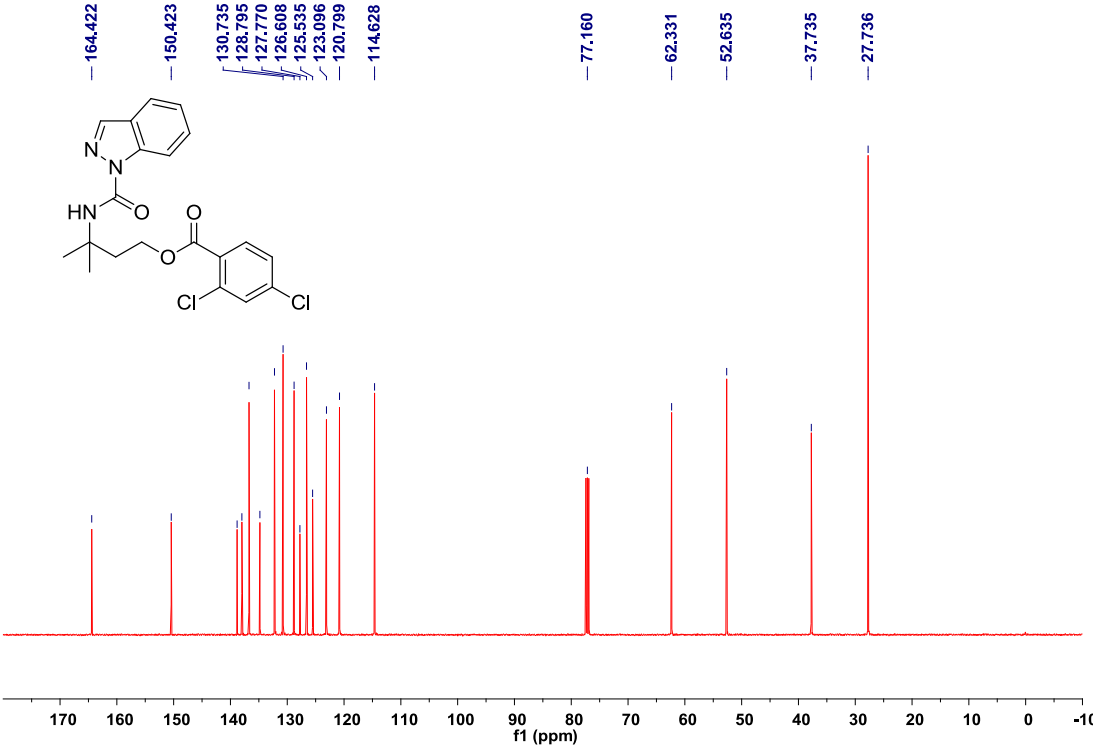


3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 2,4-dichlorobenzoate (3q)

^{1}H NMR, 500 MHz, $CDCl_3$

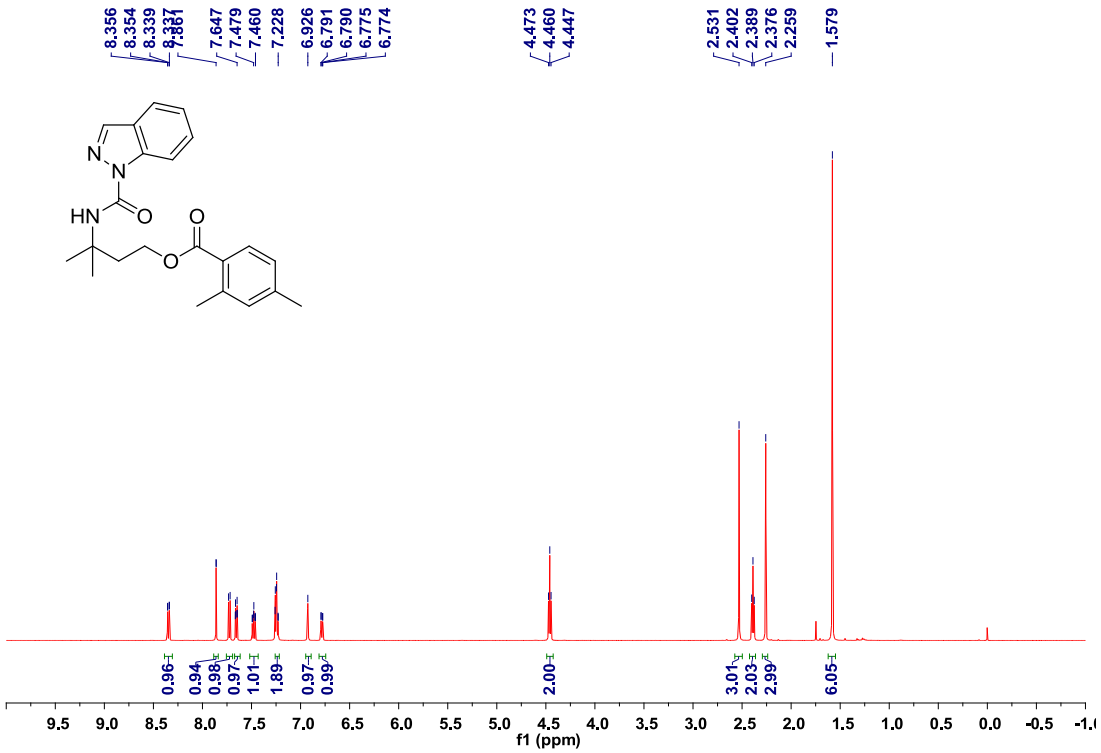


^{13}C NMR, 125 MHz, $CDCl_3$

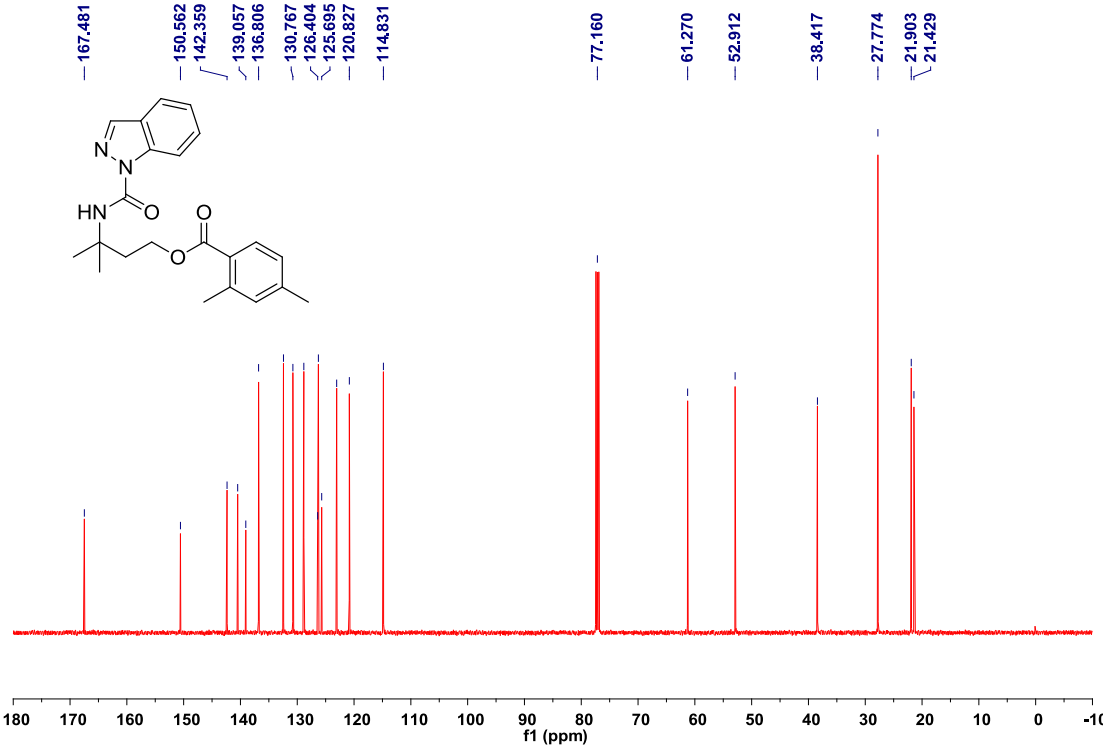


3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 2,4-dimethylbenzoate (3r)

^{1}H NMR, 500 MHz, $CDCl_3$

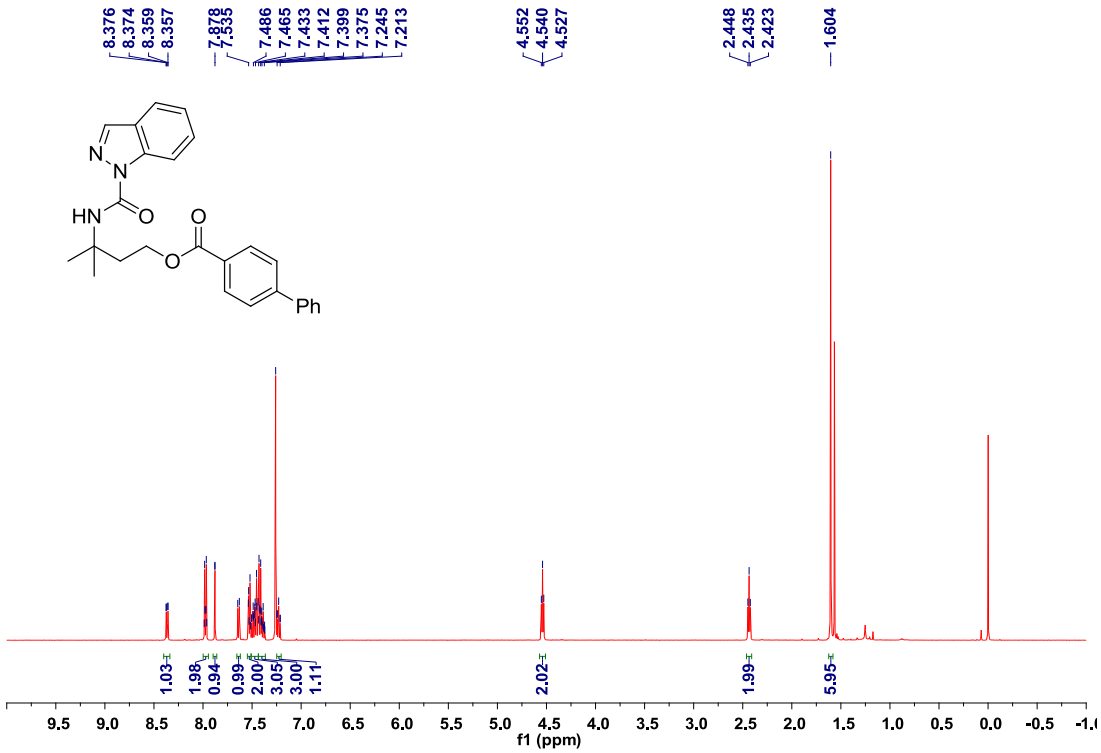


^{13}C NMR, 125 MHz, $CDCl_3$

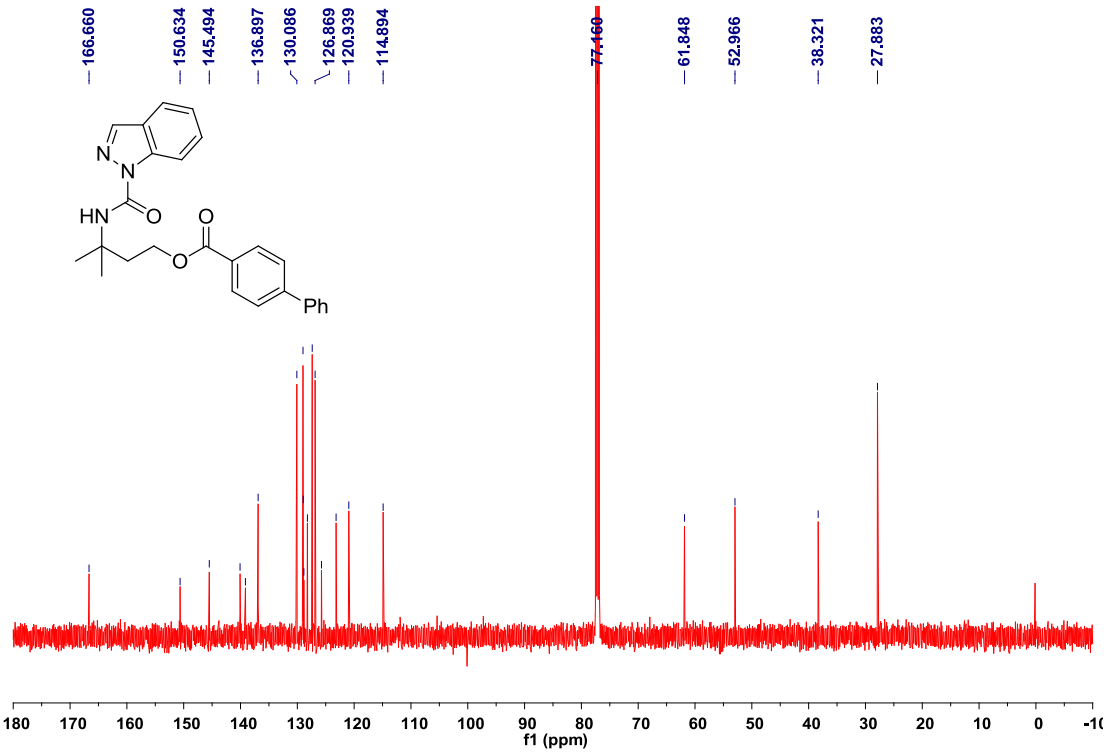


3-(1*H*-indazole-1-carboxamido)-3-methylbutyl [1,1'-biphenyl]-4-carboxylate (3s)

^{1}H NMR, 500 MHz, $CDCl_3$

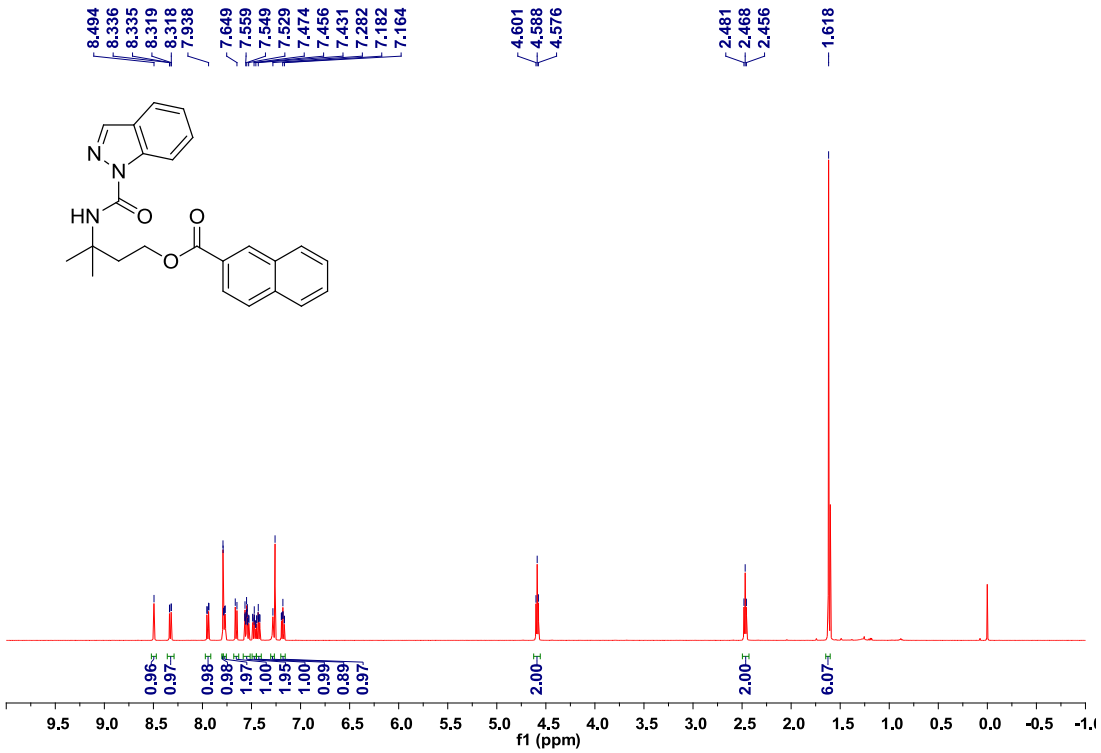


^{13}C NMR, 125 MHz, $CDCl_3$

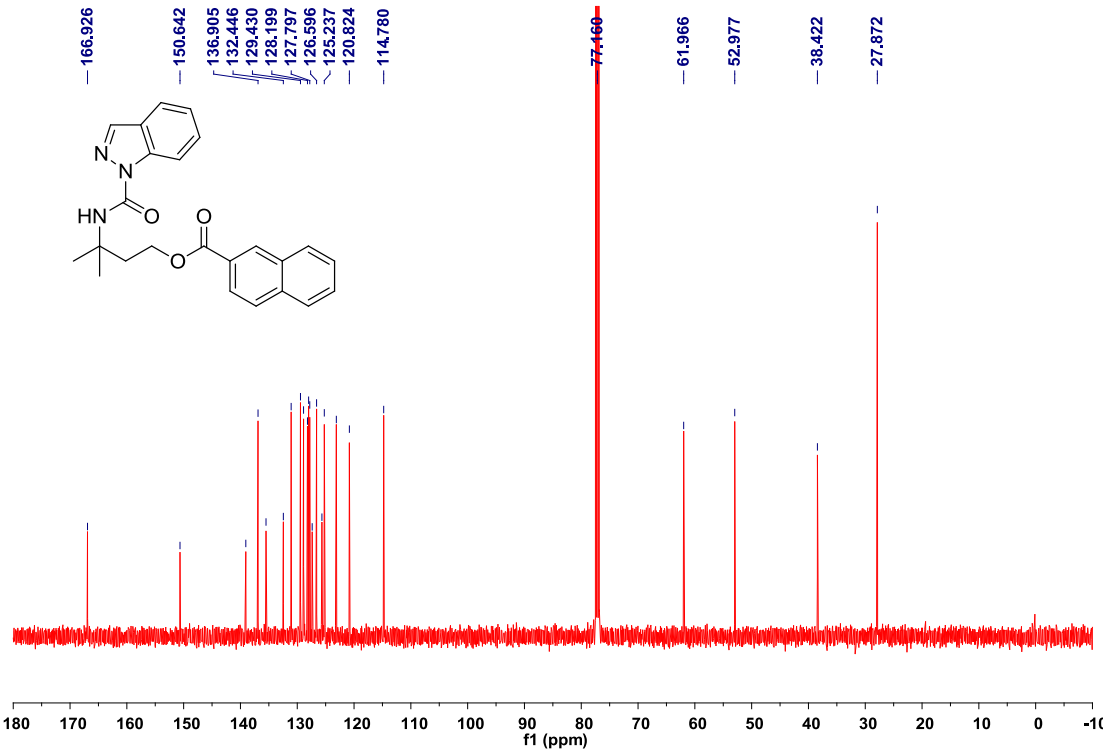


3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 2-naphthoate (3t)

^{1}H NMR, 500 MHz, $CDCl_3$

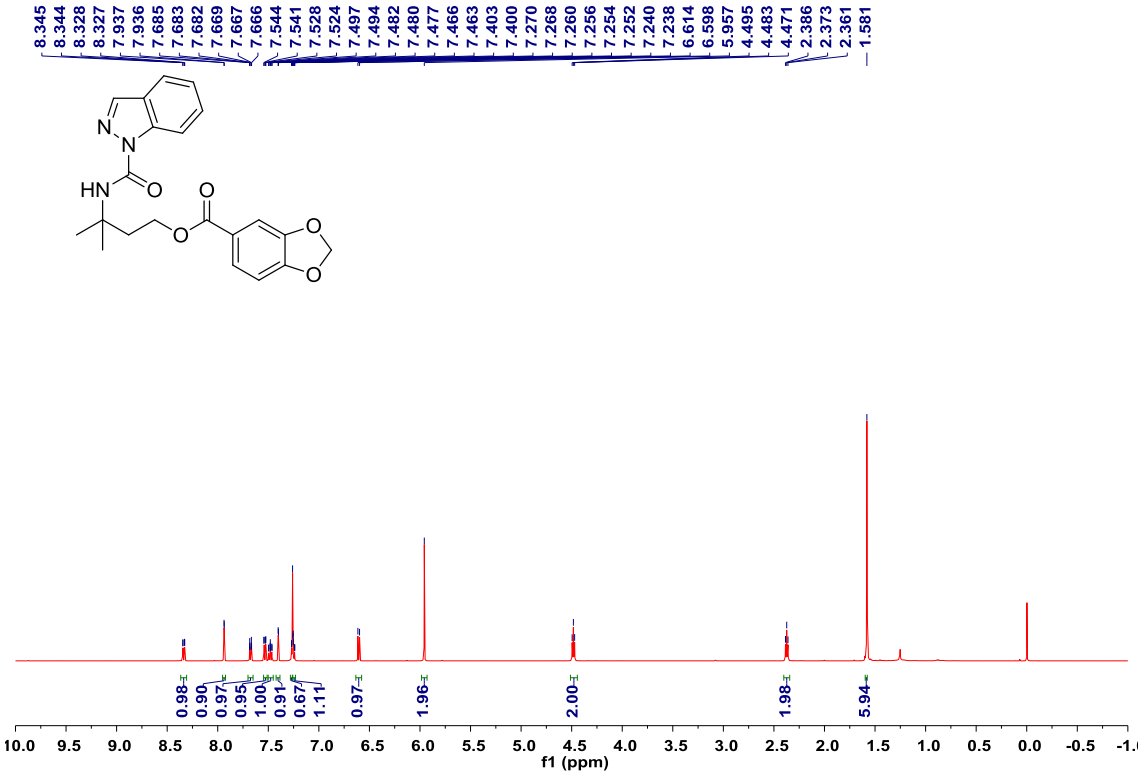


^{13}C NMR, 125 MHz, $CDCl_3$

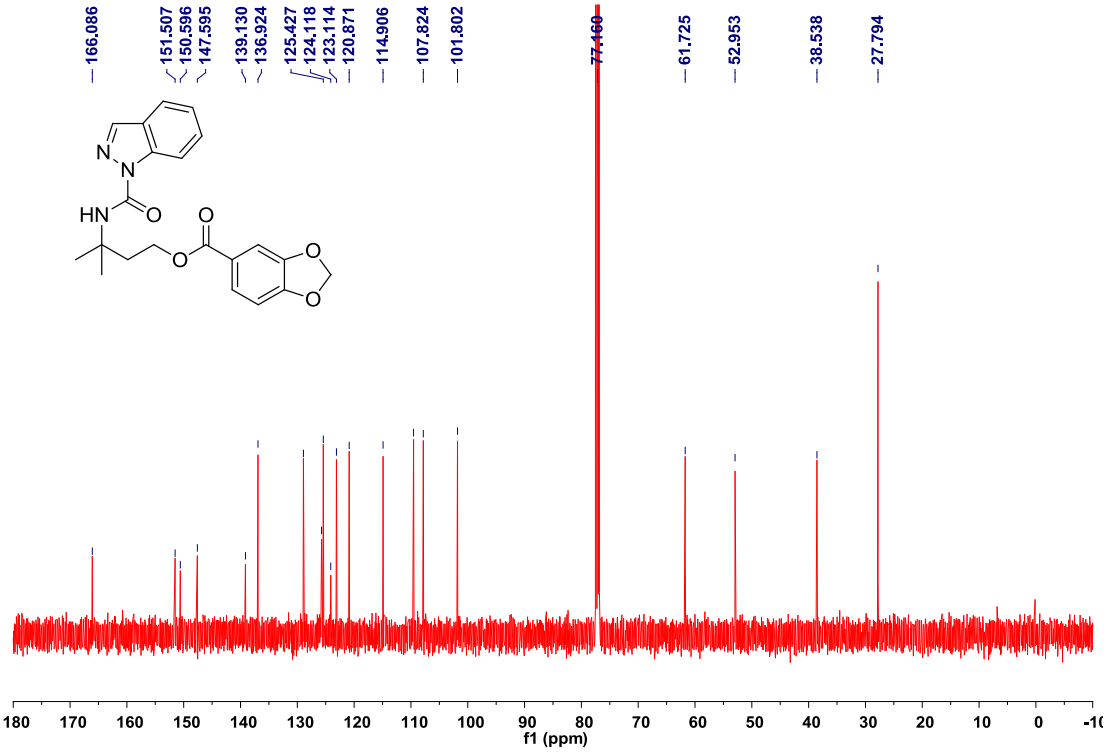


3-(1*H*-indazole-1-carboxamido)-3-methylbutylbenzo[*d*][1,3]dioxole-5-carboxylate (3u)

^{1}H NMR, 500 MHz, $CDCl_3$

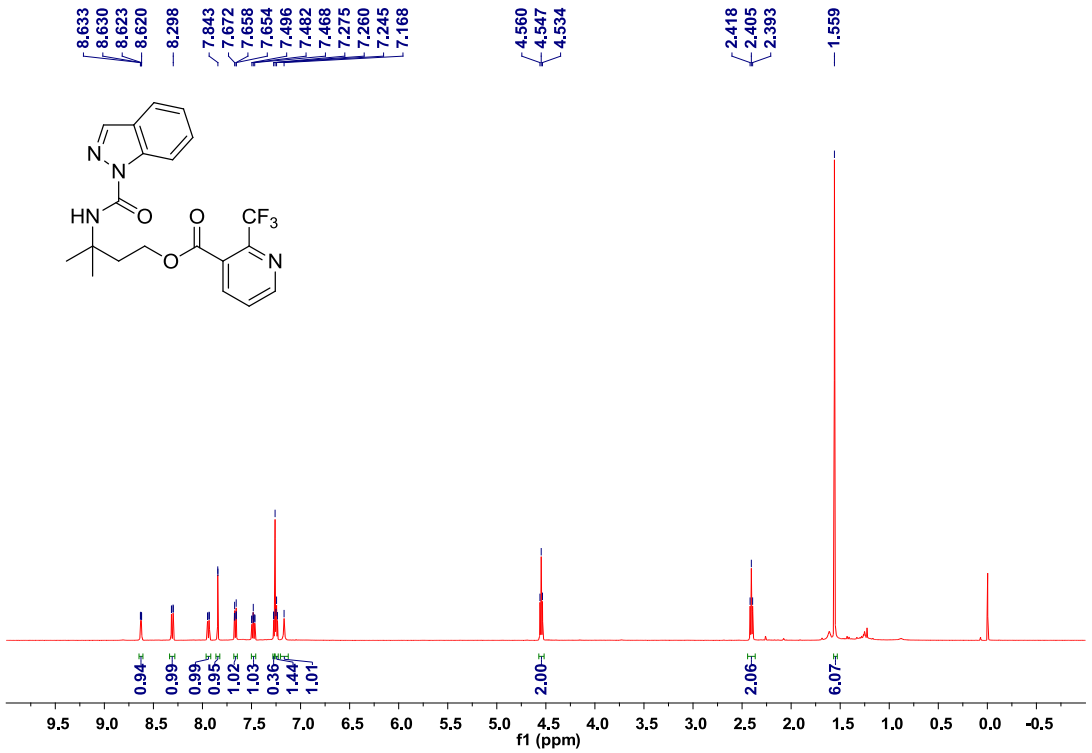


^{13}C NMR, 125 MHz, $CDCl_3$

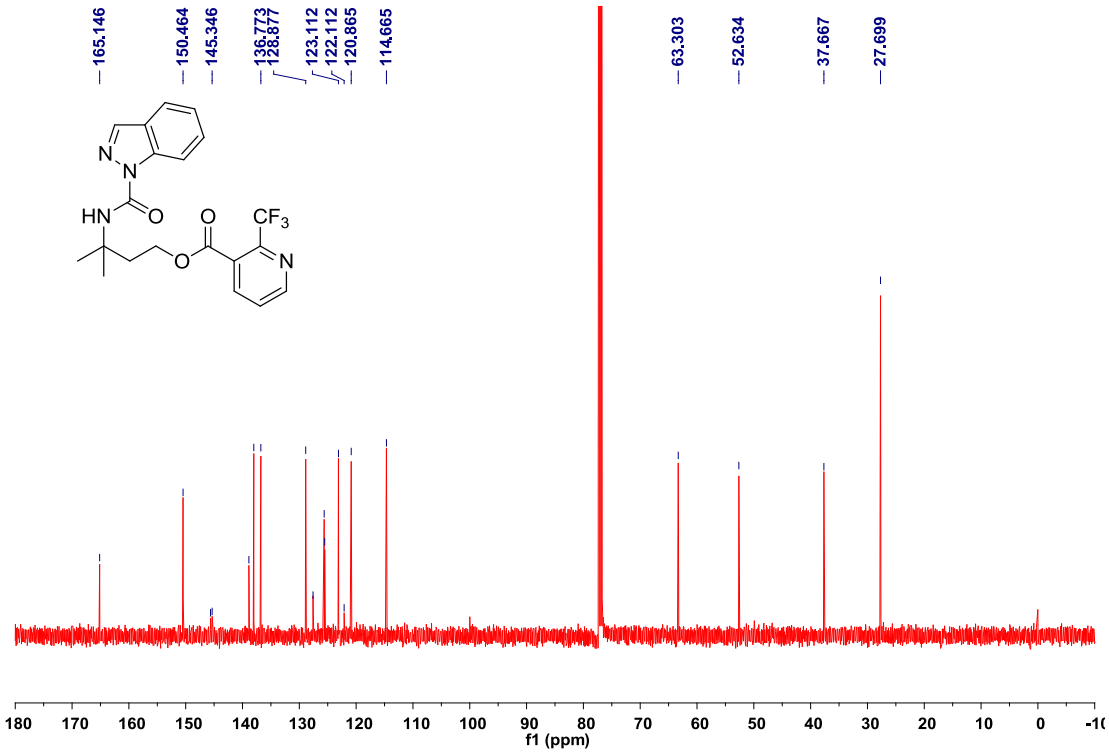


3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 2-(trifluoromethyl)nicotinate (3v)

^{1}H NMR, 500 MHz, $CDCl_3$

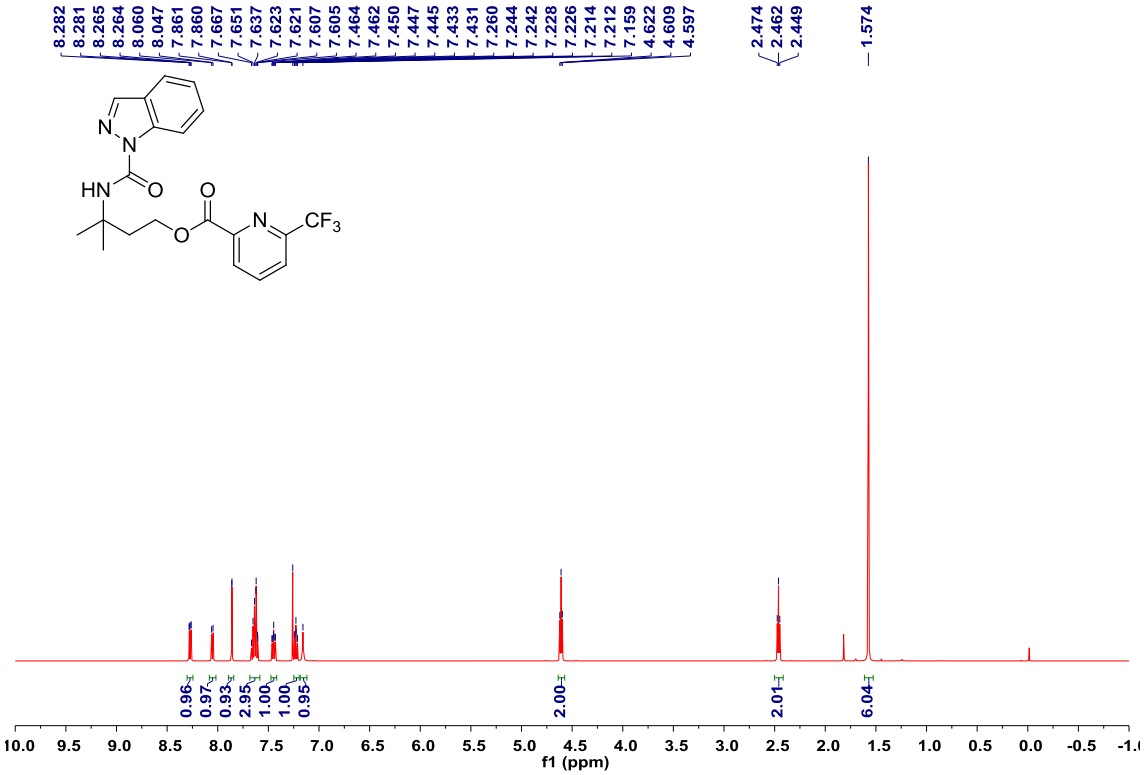


^{13}C NMR, 125 MHz, $CDCl_3$

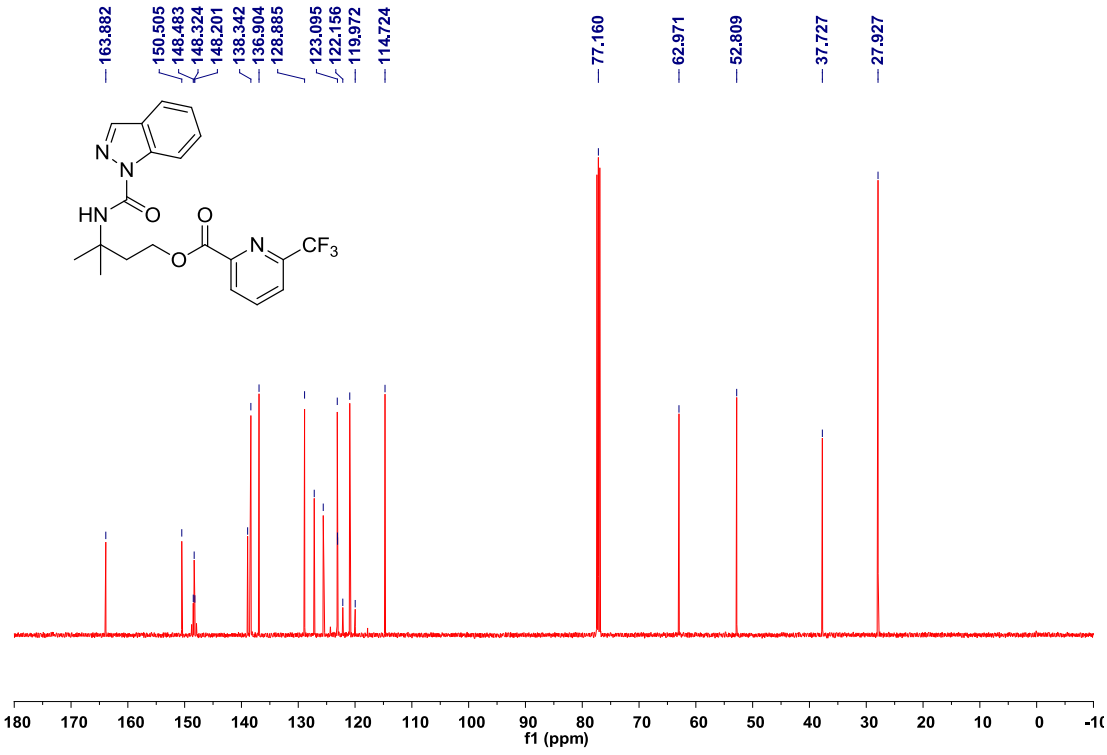


3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 6-(trifluoromethyl)nicotinate (3w)

^{1}H NMR, 500 MHz, $CDCl_3$

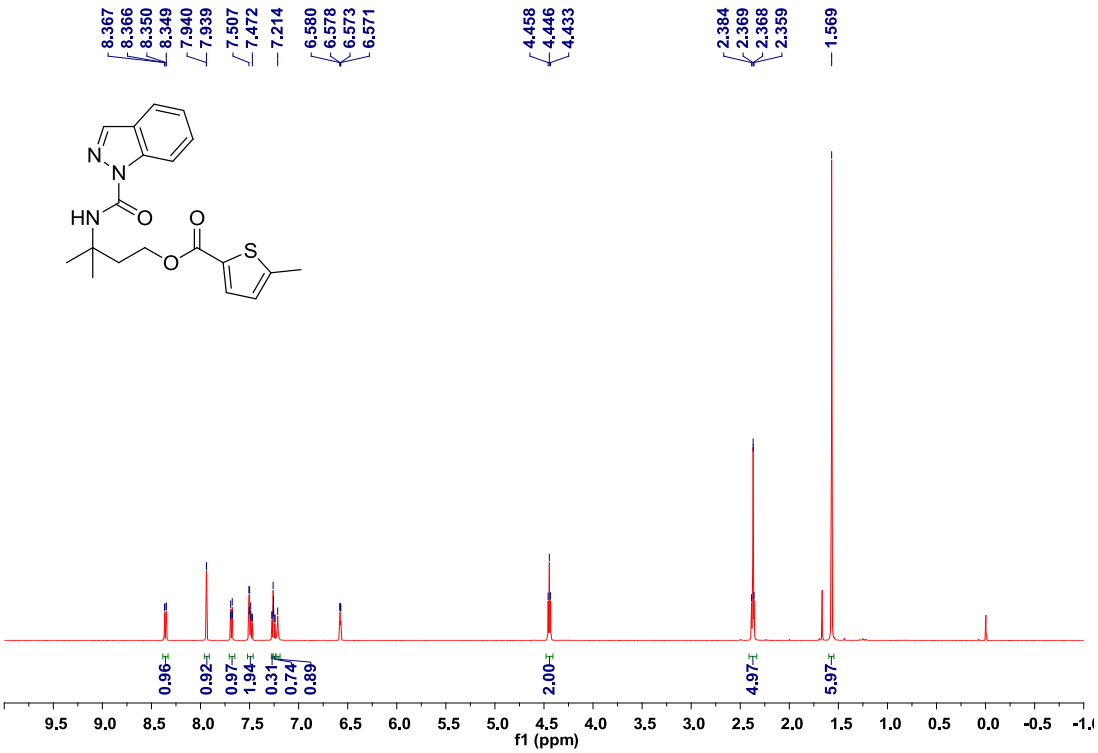


^{13}C NMR, 125 MHz, $CDCl_3$

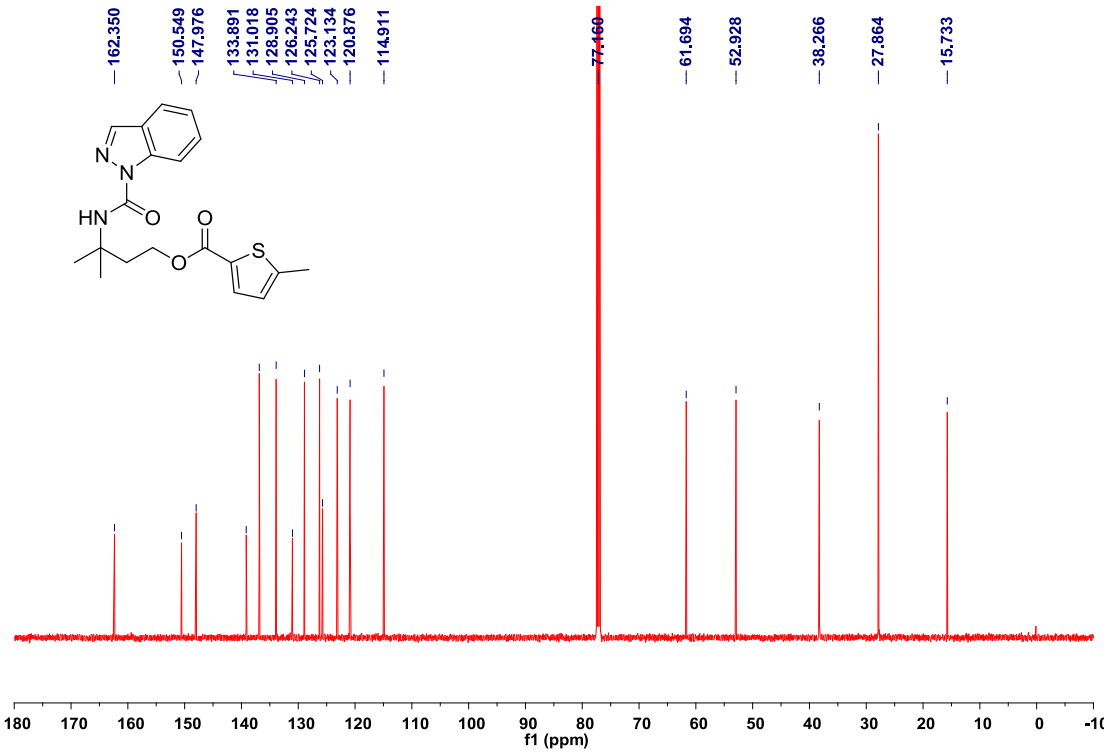


3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 5-methylthiophene-2-carboxylate (3x)

^{1}H NMR, 500 MHz, $CDCl_3$

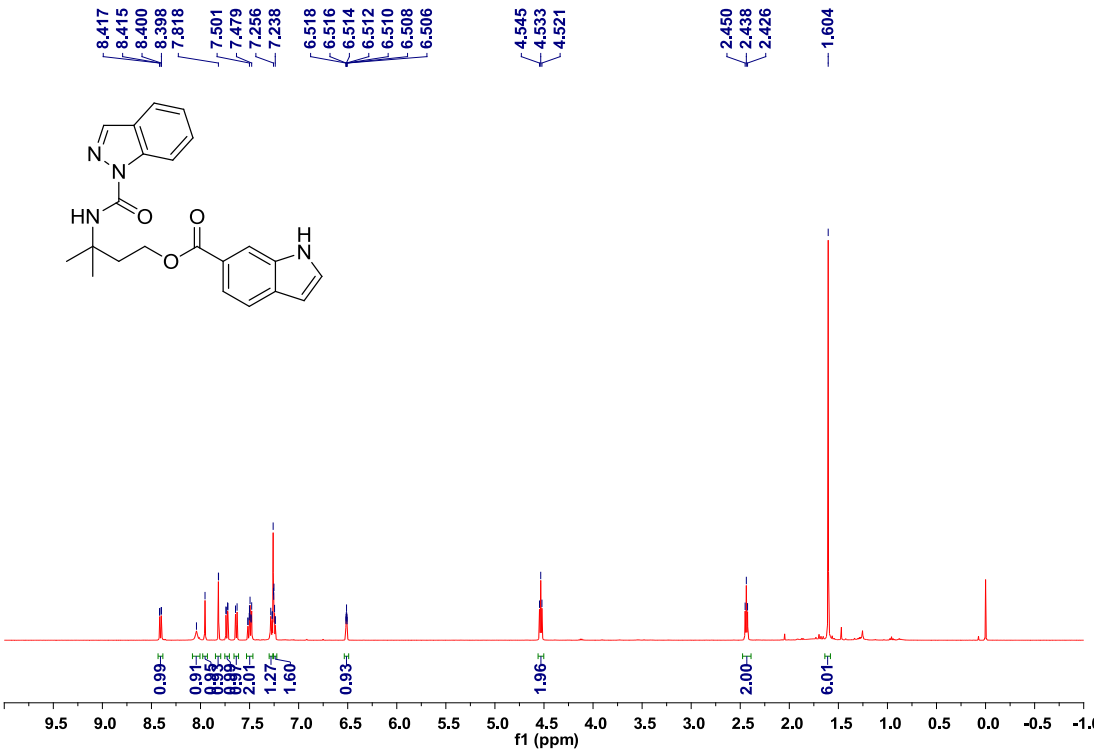


^{13}C NMR, 125 MHz, $CDCl_3$

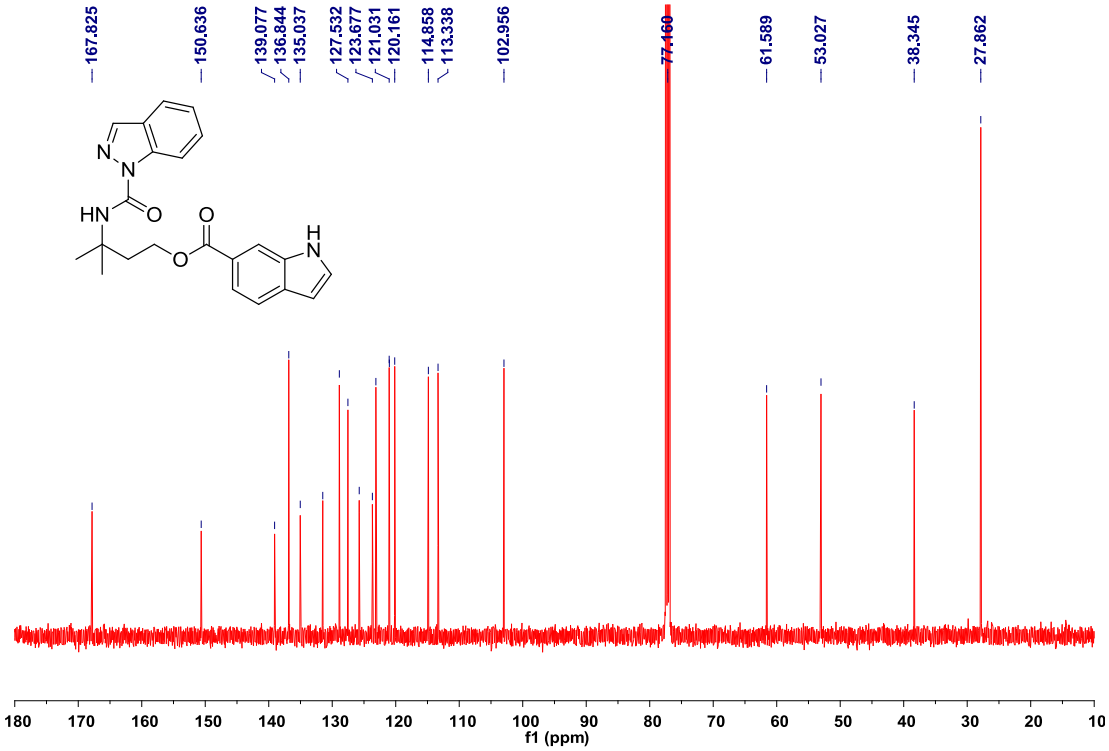


3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 1*H*-indole-6-carboxylate (3y)

^{1}H NMR, 500 MHz, $CDCl_3$

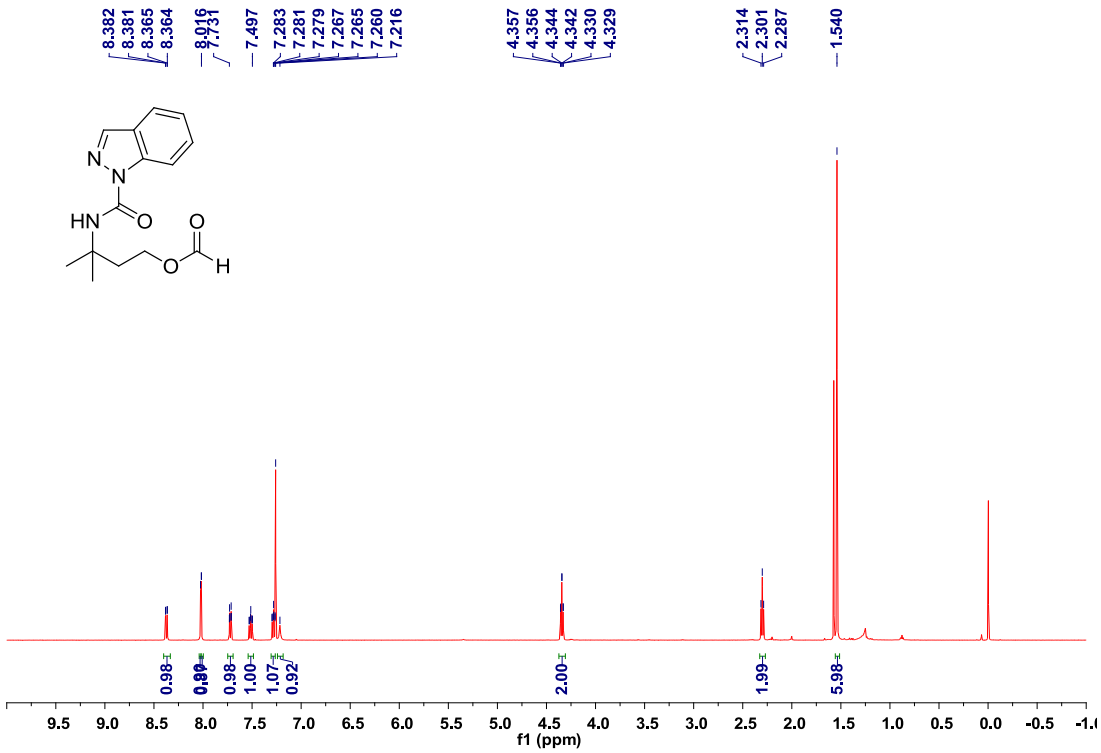


^{13}C NMR, 125 MHz, $CDCl_3$

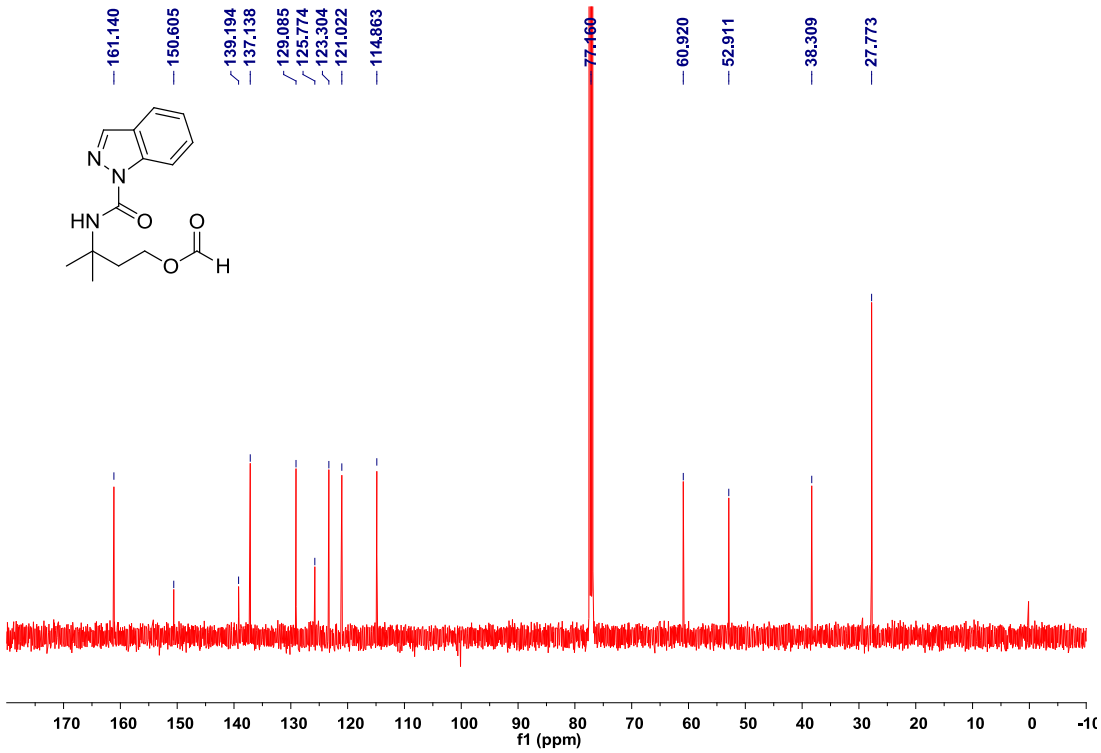


3-(1*H*-indazole-1-carboxamido)-3-methylbutyl formate (3z)

^{1}H NMR, 500 MHz, $CDCl_3$

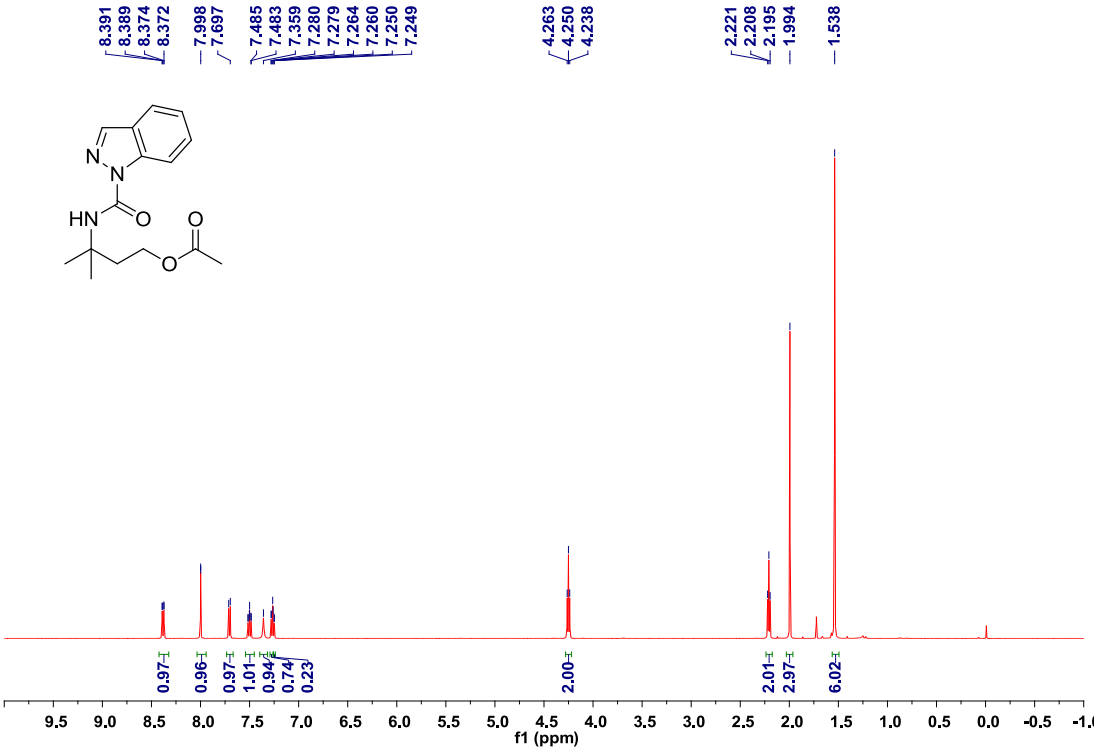


^{13}C NMR, 125 MHz, $CDCl_3$

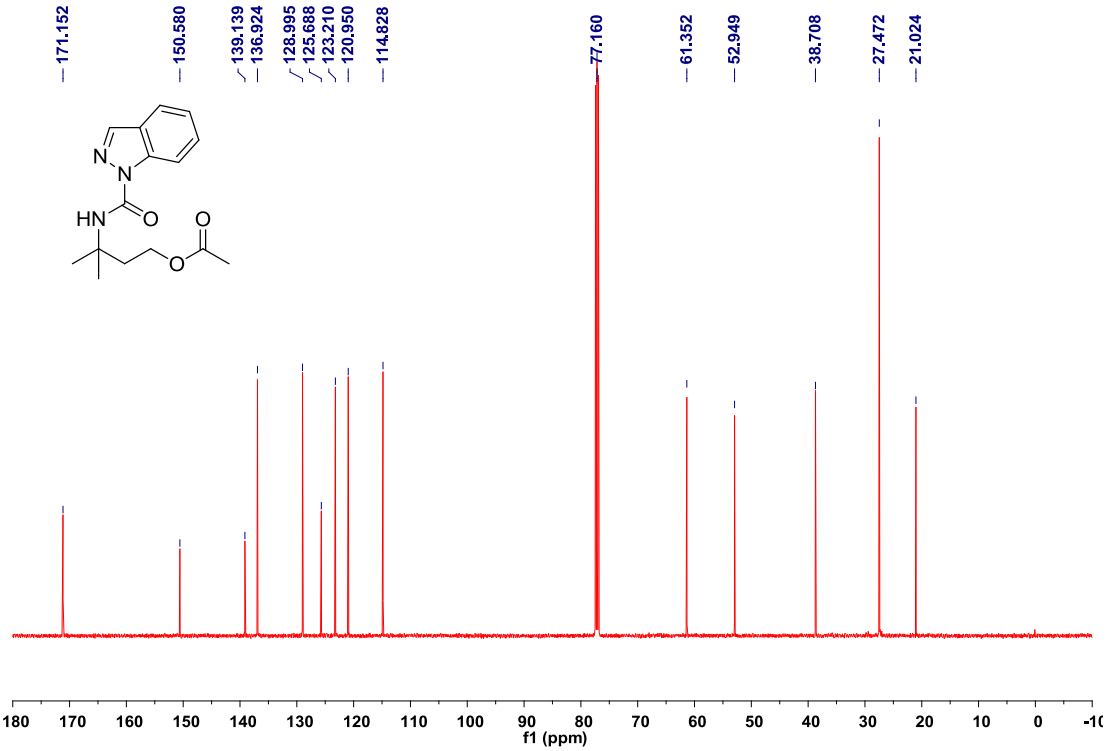


3-(1*H*-indazole-1-carboxamido)-3-methylbutyl acetate (3aa)

^{1}H NMR, 500 MHz, $CDCl_3$

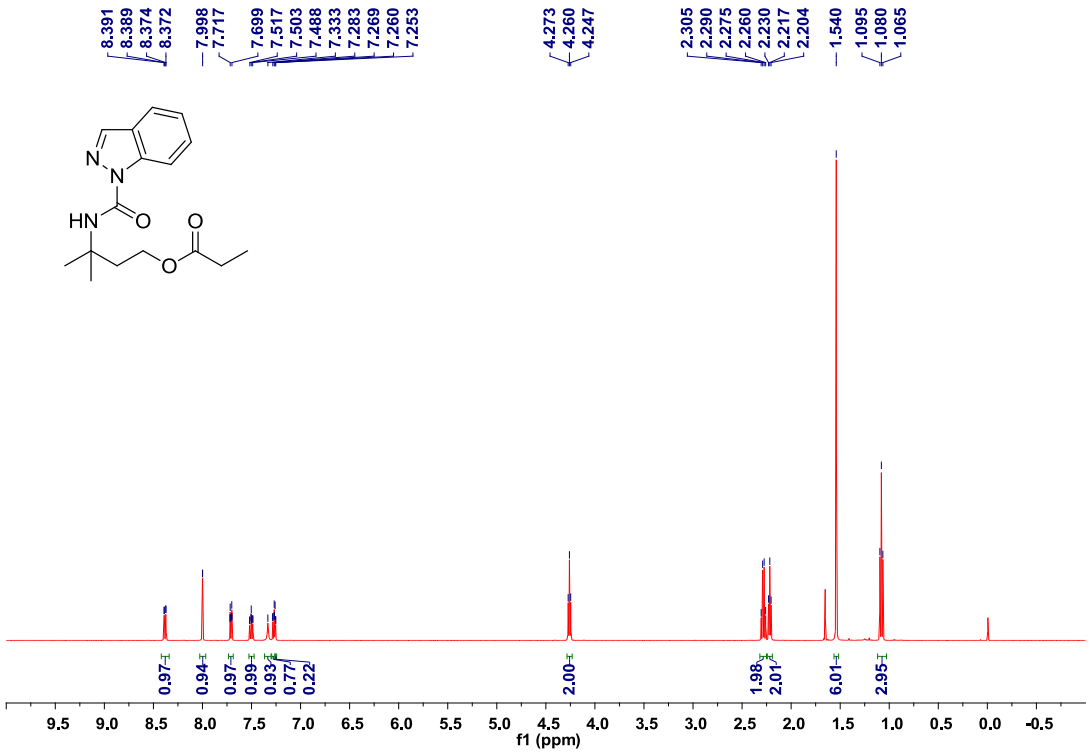


^{13}C NMR, 125 MHz, $CDCl_3$

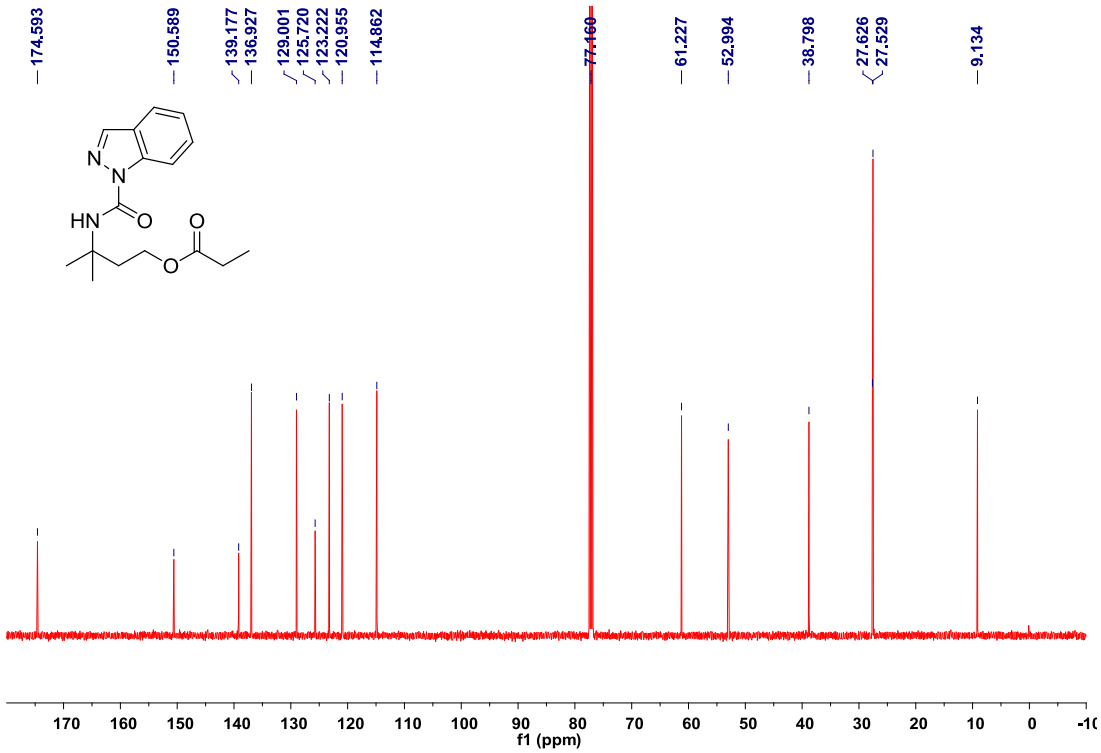


3-(1*H*-indazole-1-carboxamido)-3-methylbutyl propionate (3ab)

^{1}H NMR, 500 MHz, $CDCl_3$

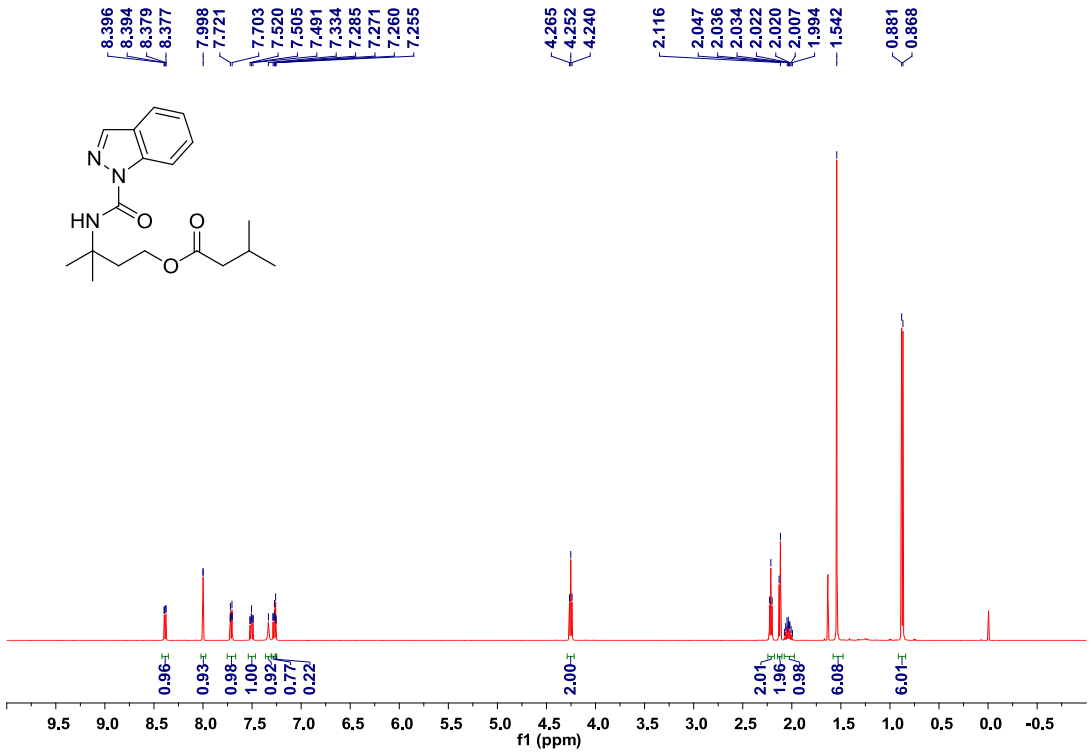


^{13}C NMR, 125 MHz, $CDCl_3$

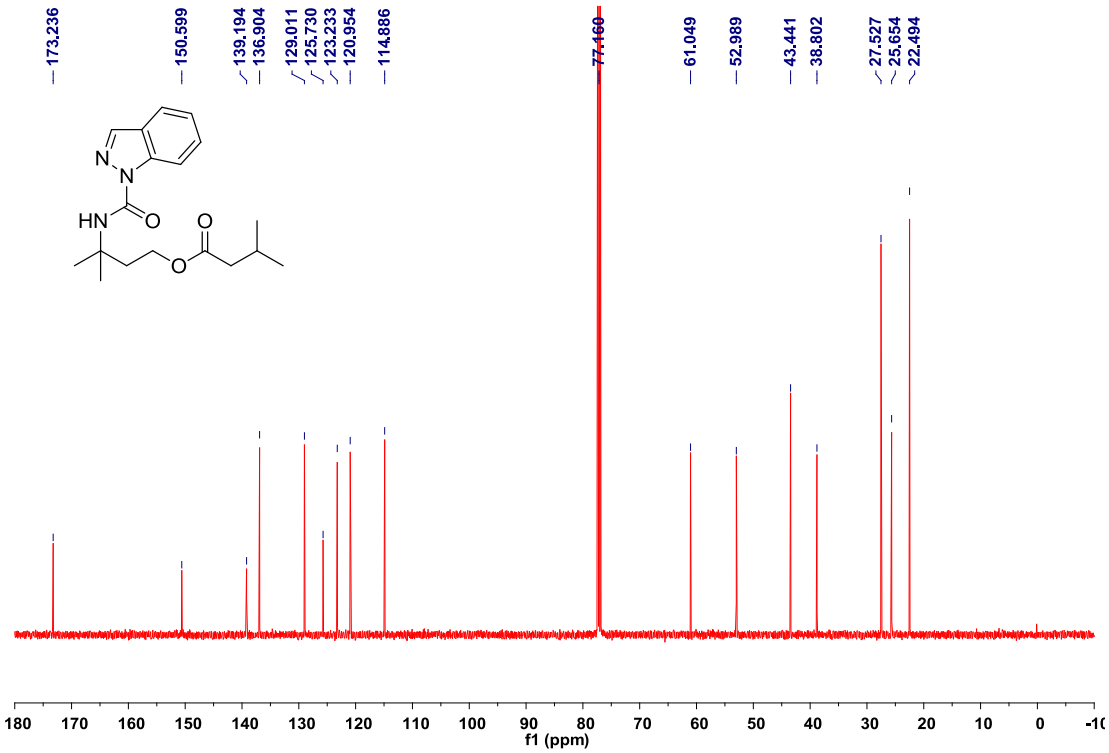


3-(1H-indazole-1-carboxamido)-3-methylbutyl 3-methylbutanoate (3ac)

^{1}H NMR, 500 MHz, $CDCl_3$

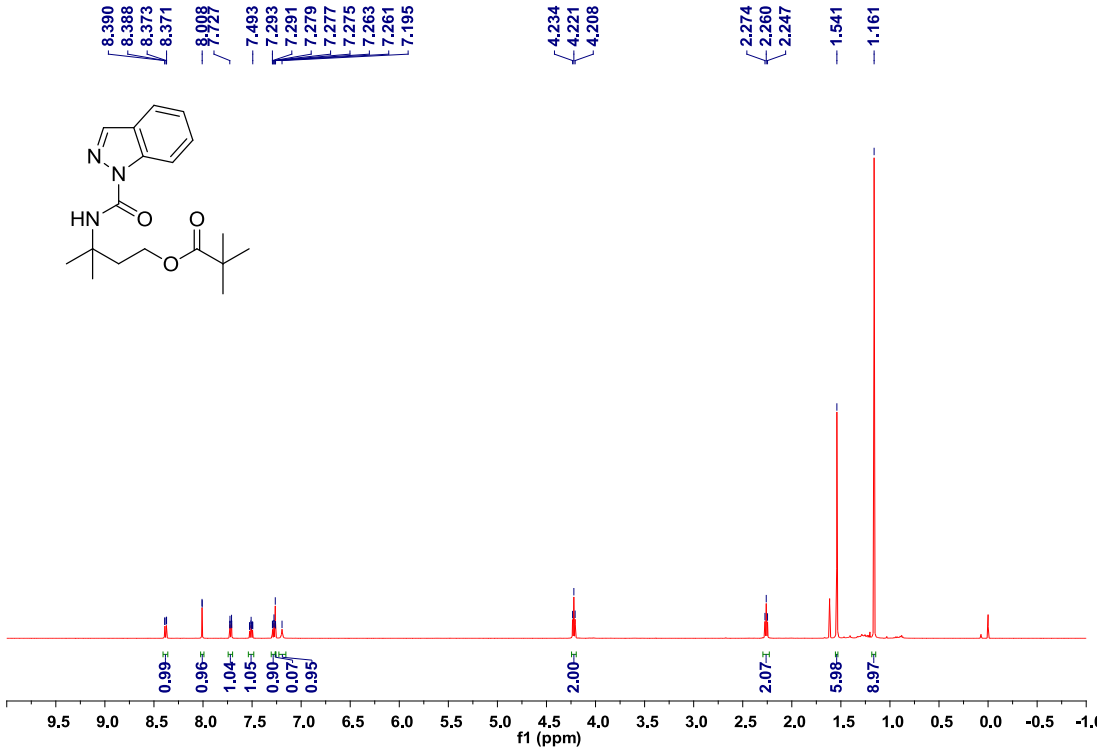


^{13}C NMR, 125 MHz, $CDCl_3$

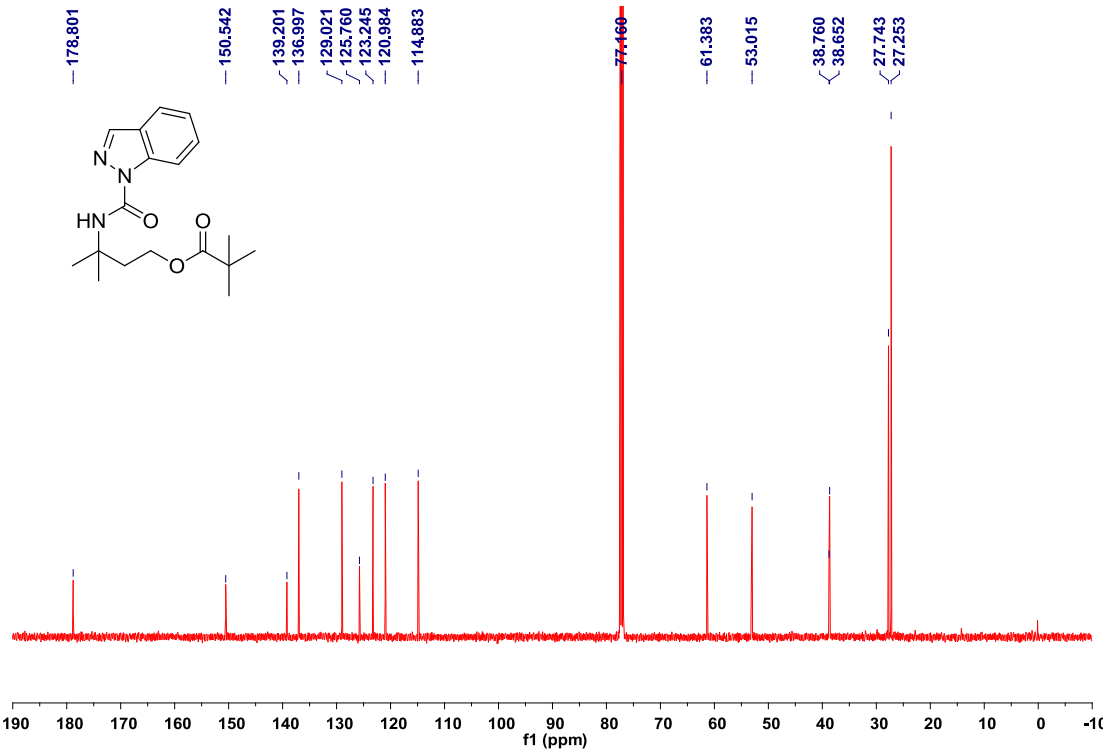


3-(1*H*-indazole-1-carboxamido)-3-methylbutyl pivalate (3ad)

^{1}H NMR, 500 MHz, $CDCl_3$

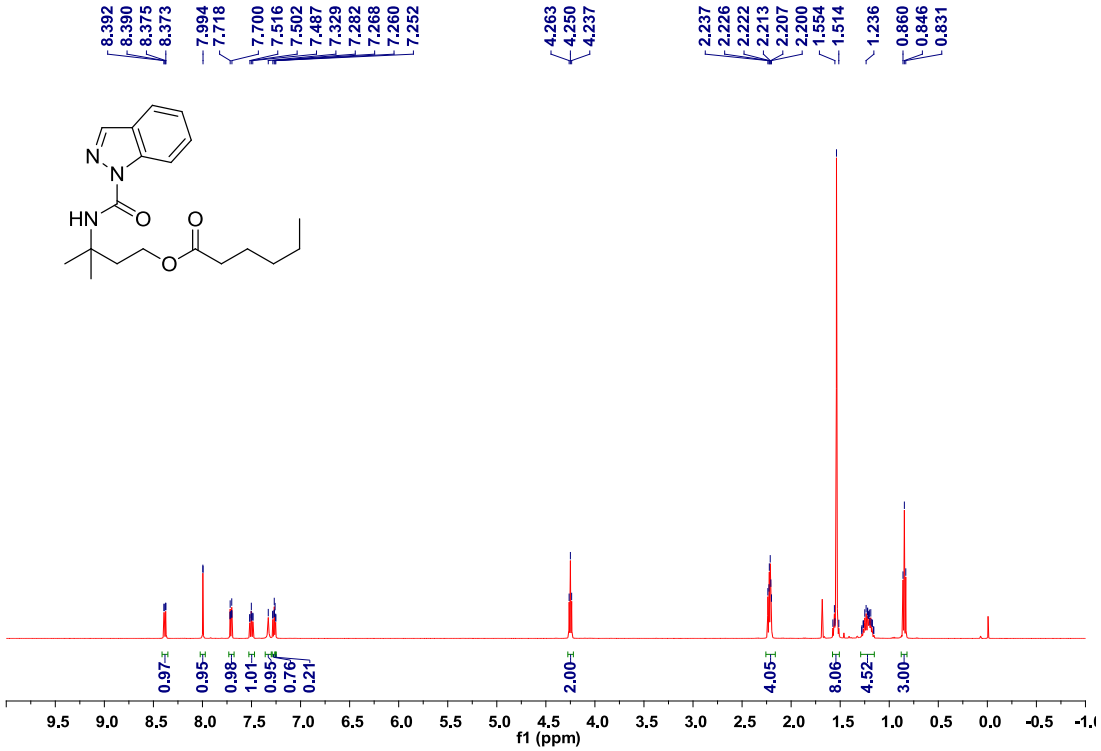


^{13}C NMR, 125 MHz, $CDCl_3$

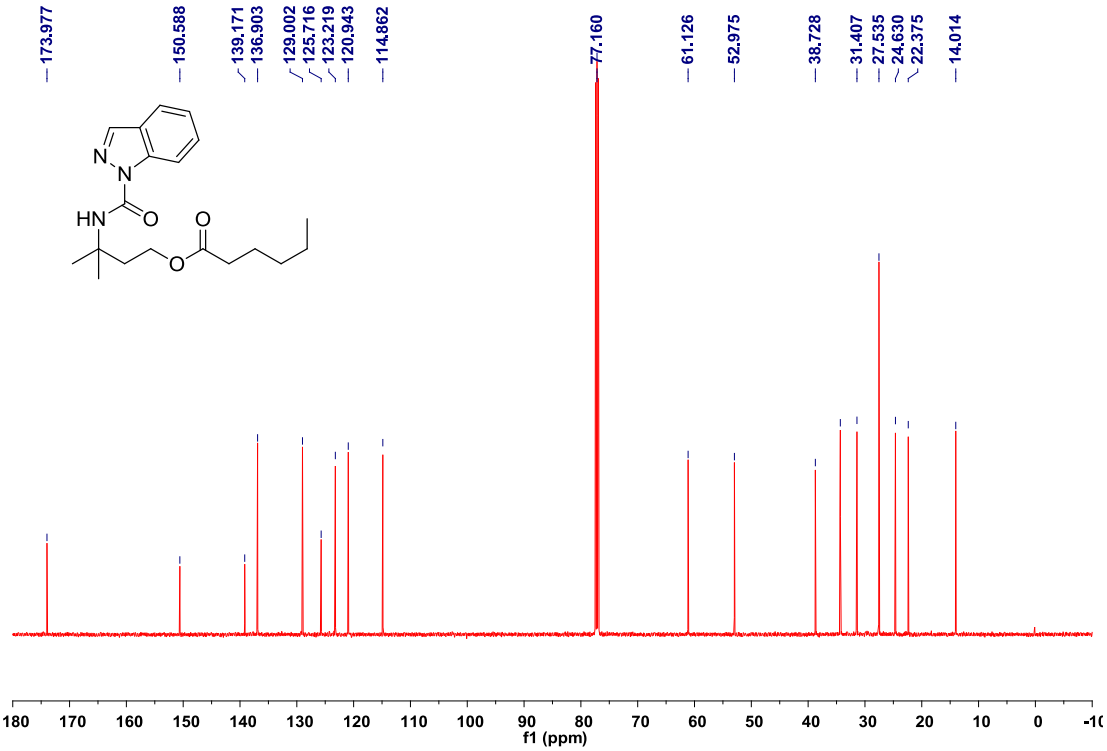


3-(1*H*-indazole-1-carboxamido)-3-methylbutyl hexanoate (3ae)

^{1}H NMR, 500 MHz, $CDCl_3$

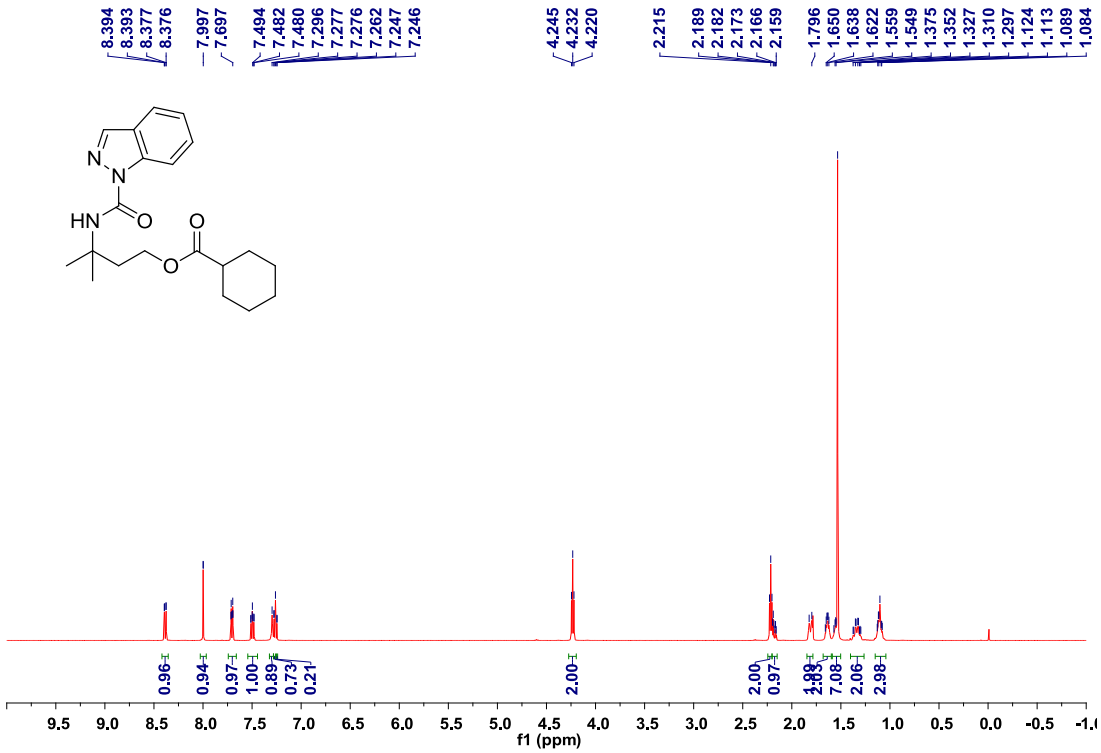


^{13}C NMR, 125 MHz, $CDCl_3$

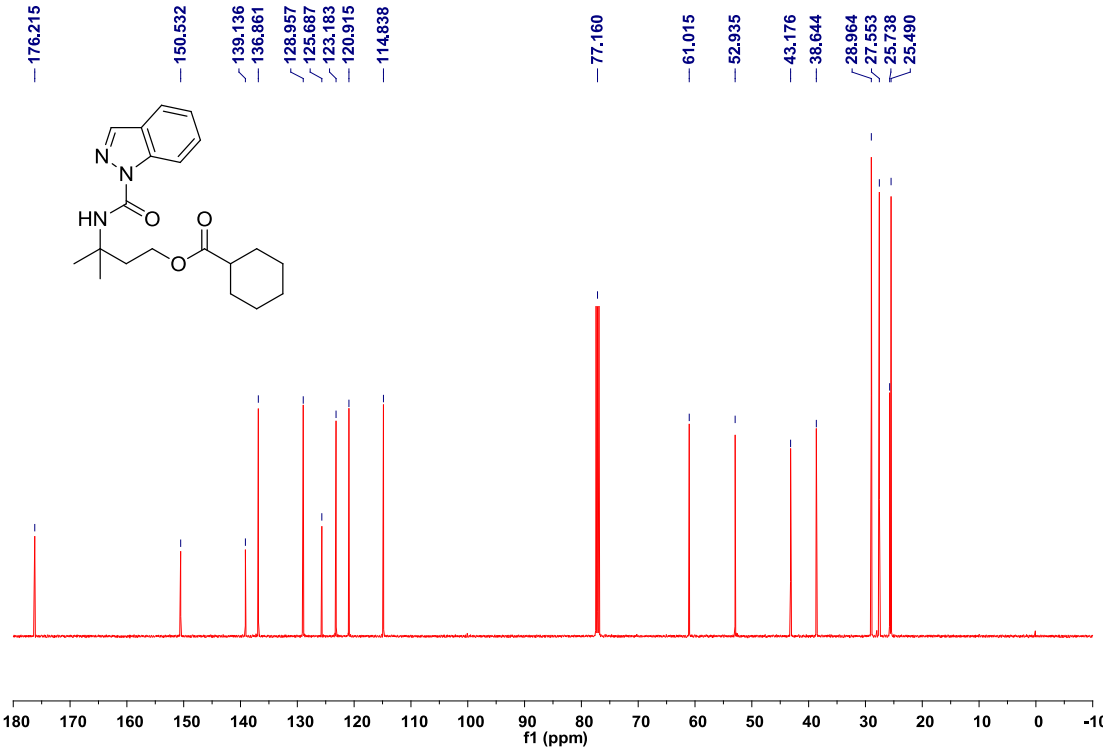


3-(1*H*-indazole-1-carboxamido)-3-methylbutyl hexanoate (3af)

^{1}H NMR, 500 MHz, $CDCl_3$

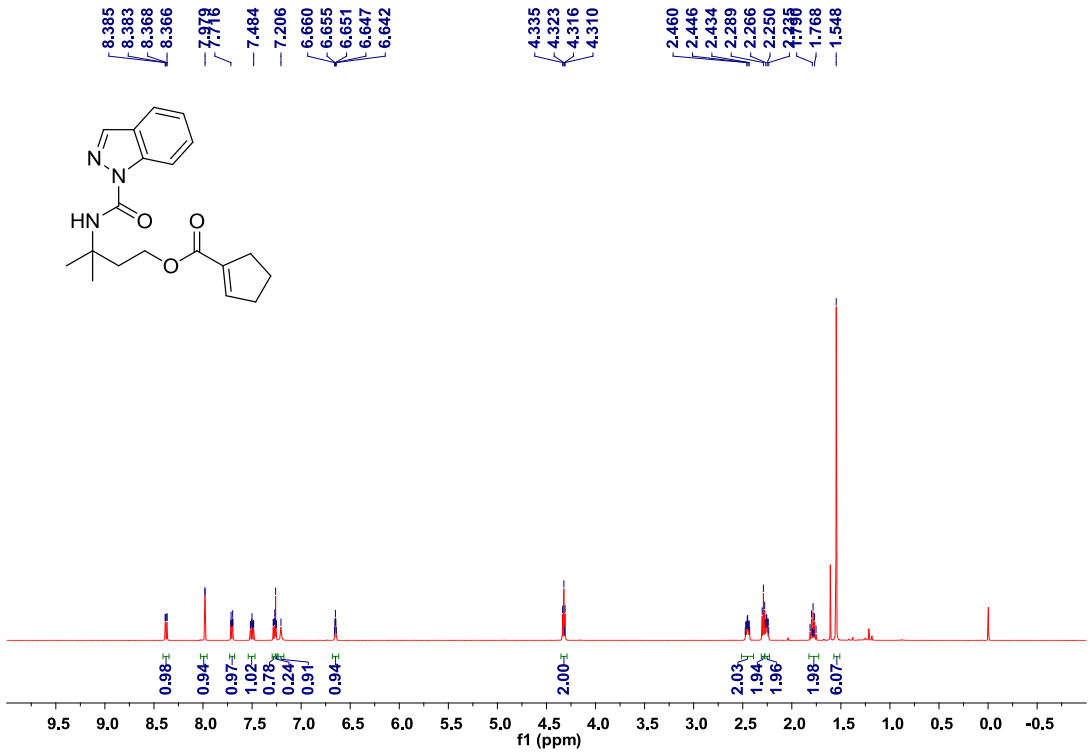


^{13}C NMR, 125 MHz, $CDCl_3$

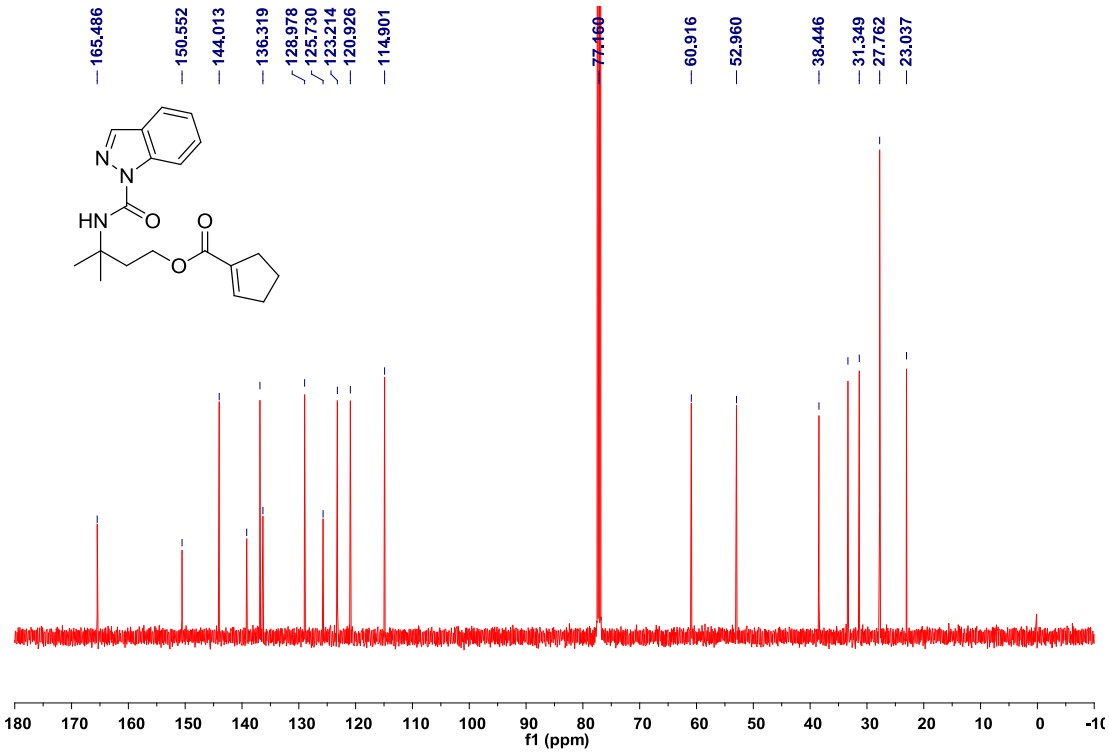


3-(1*H*-indazole-1-carboxamido)-3-methylbutyl cyclopent-1-enecarboxylate (3ag)

^{1}H NMR, 500 MHz, $CDCl_3$

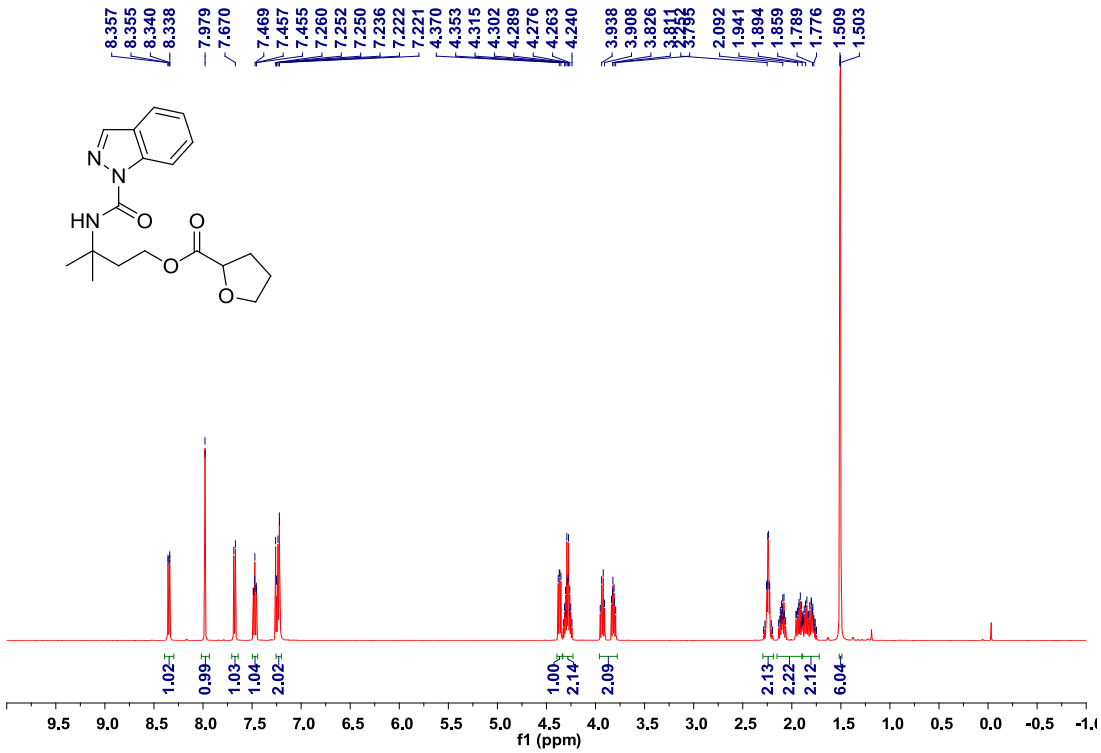


^{13}C NMR, 125 MHz, $CDCl_3$

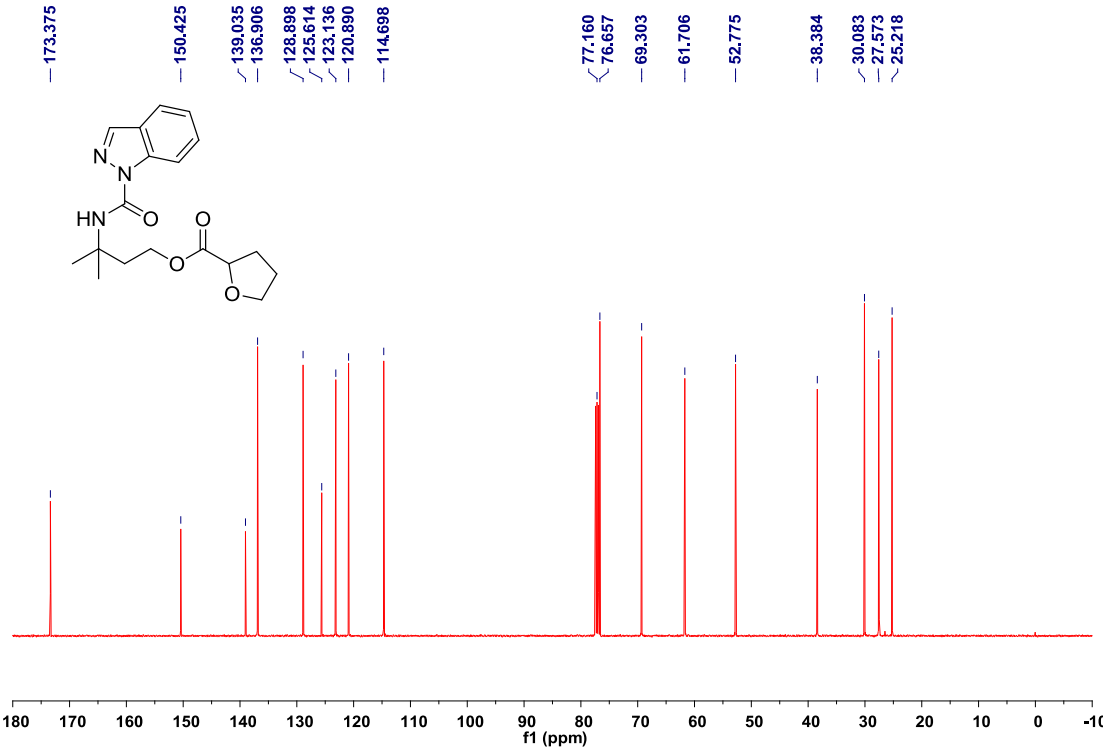


3-(1*H*-indazole-1-carboxamido)-3-methylbutyl tetrahydrofuran-2-carboxylate (3ah)

^{1}H NMR, 500 MHz, $CDCl_3$

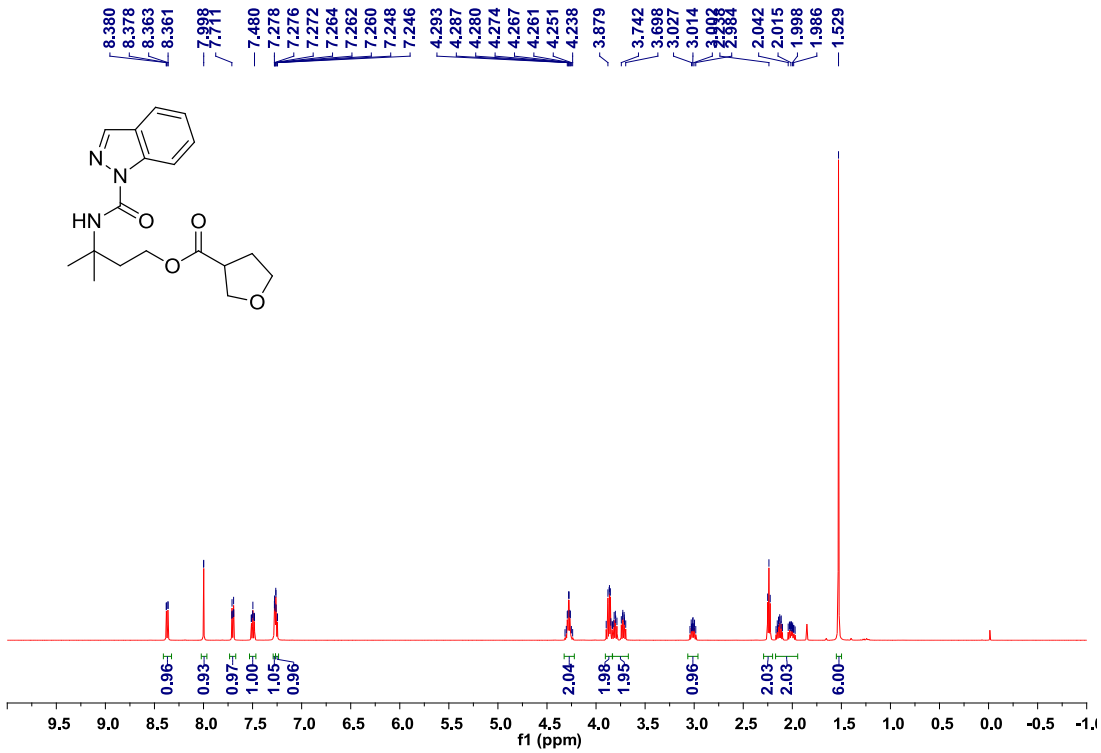


^{13}C NMR, 125 MHz, $CDCl_3$

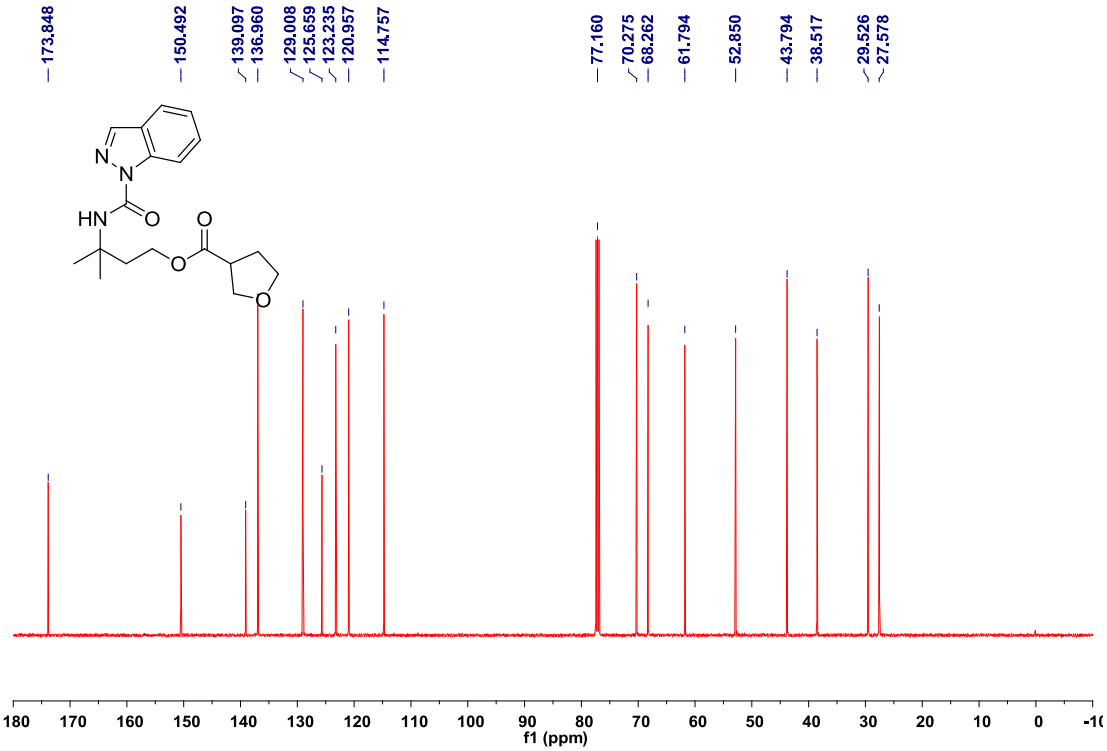


3-(1*H*-indazole-1-carboxamido)-3-methylbutyl tetrahydrofuran-3-carboxylate (3ai)

^{1}H NMR, 500 MHz, $CDCl_3$

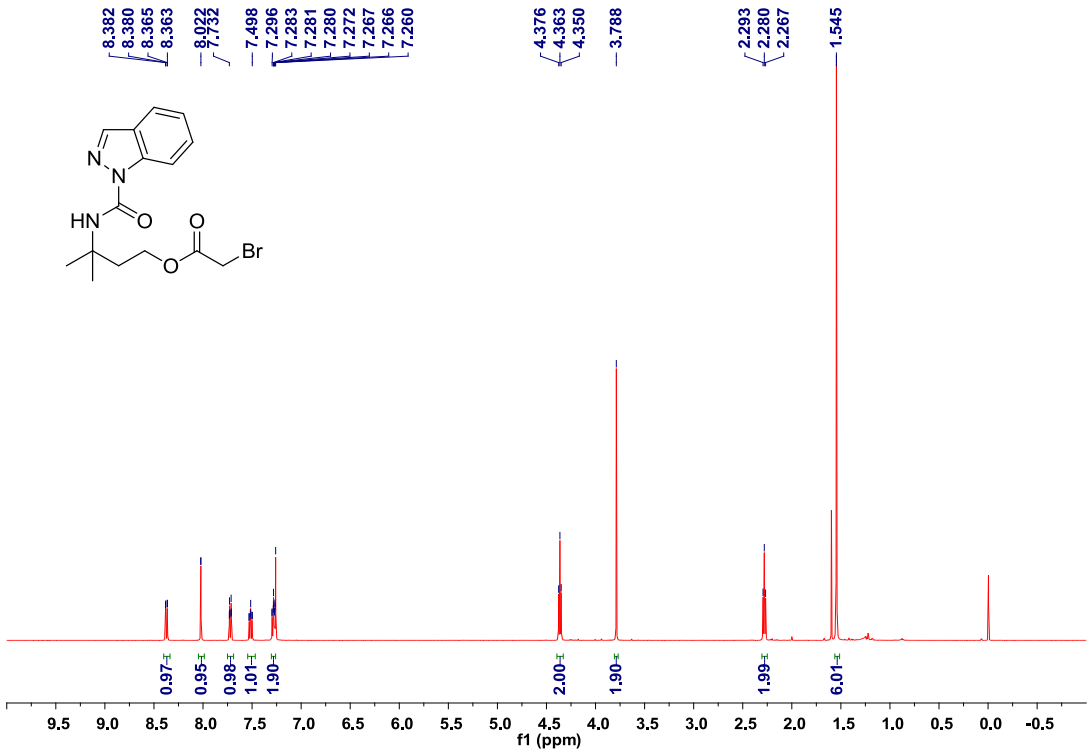


^{13}C NMR, 125 MHz, $CDCl_3$

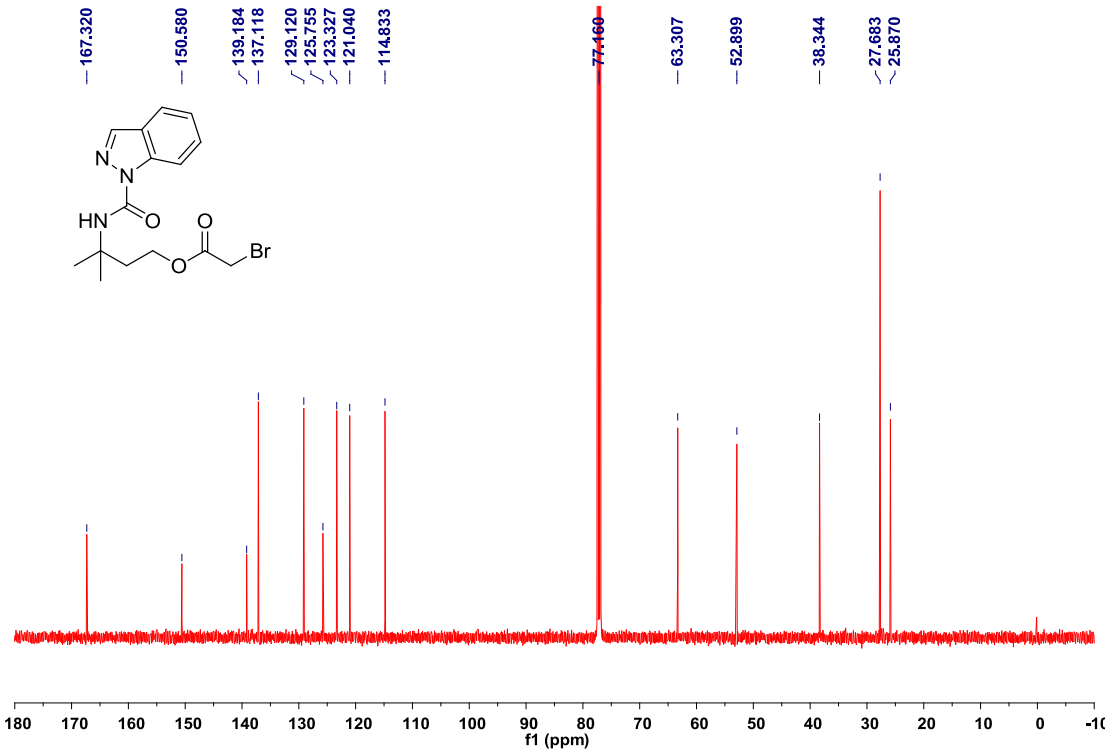


3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 2-bromoacetate (3aj)

^{1}H NMR, 500 MHz, $CDCl_3$

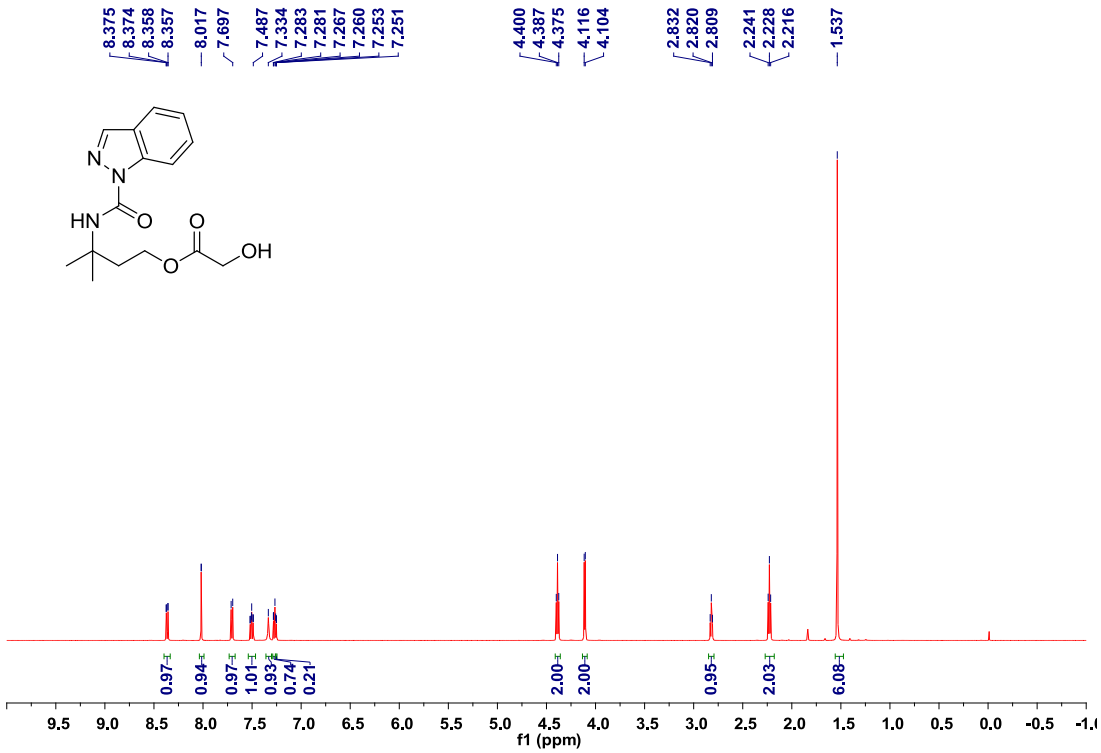


^{13}C NMR, 125 MHz, $CDCl_3$

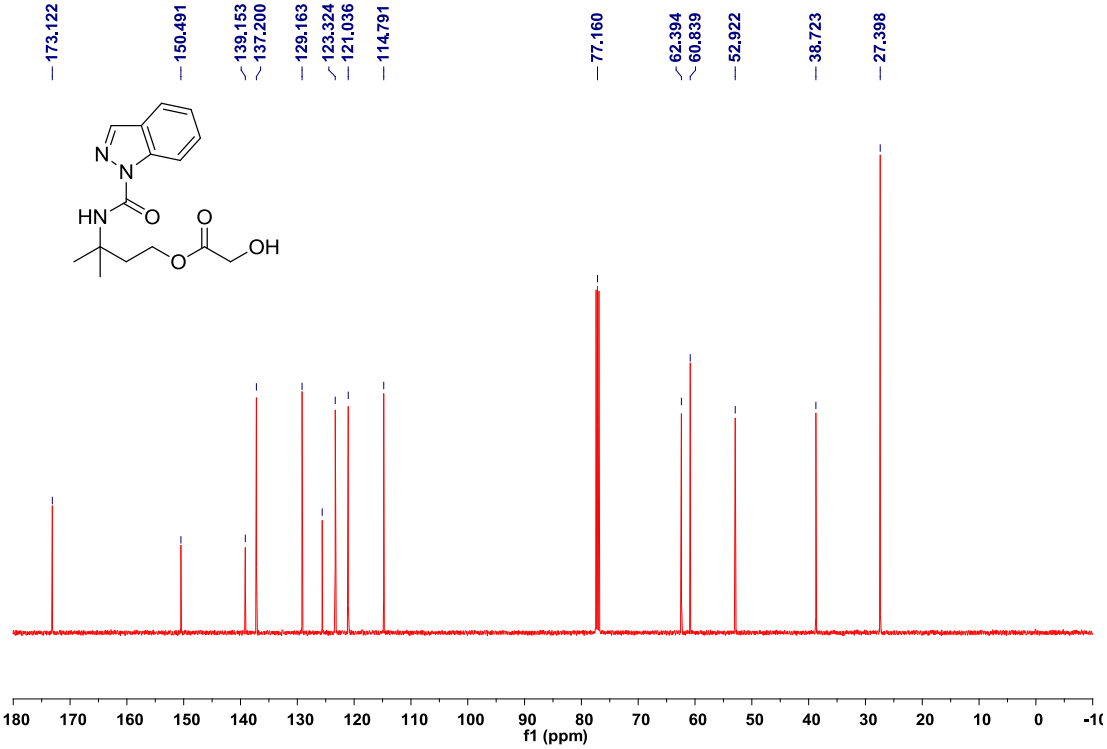


3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 2-hydroxyacetate (3ak)

^{1}H NMR, 500 MHz, $CDCl_3$

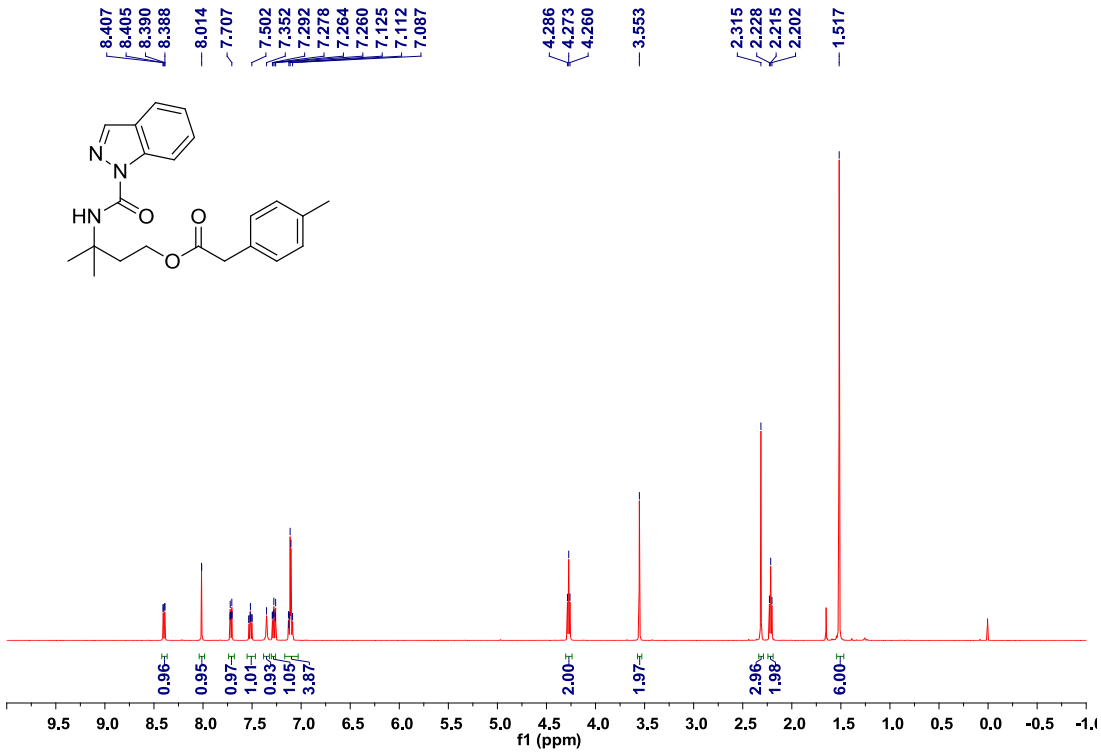


^{13}C NMR, 125 MHz, $CDCl_3$

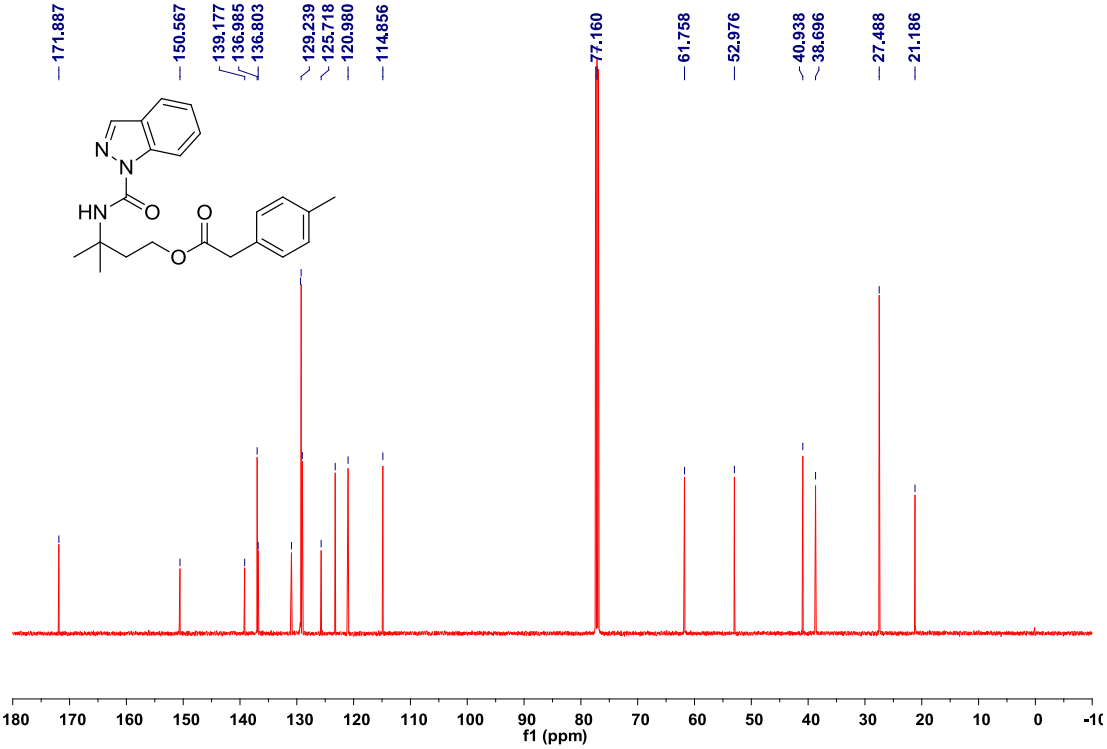


3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 2-(*p*-tolyl)acetate (3al)

^{1}H NMR, 500 MHz, $CDCl_3$

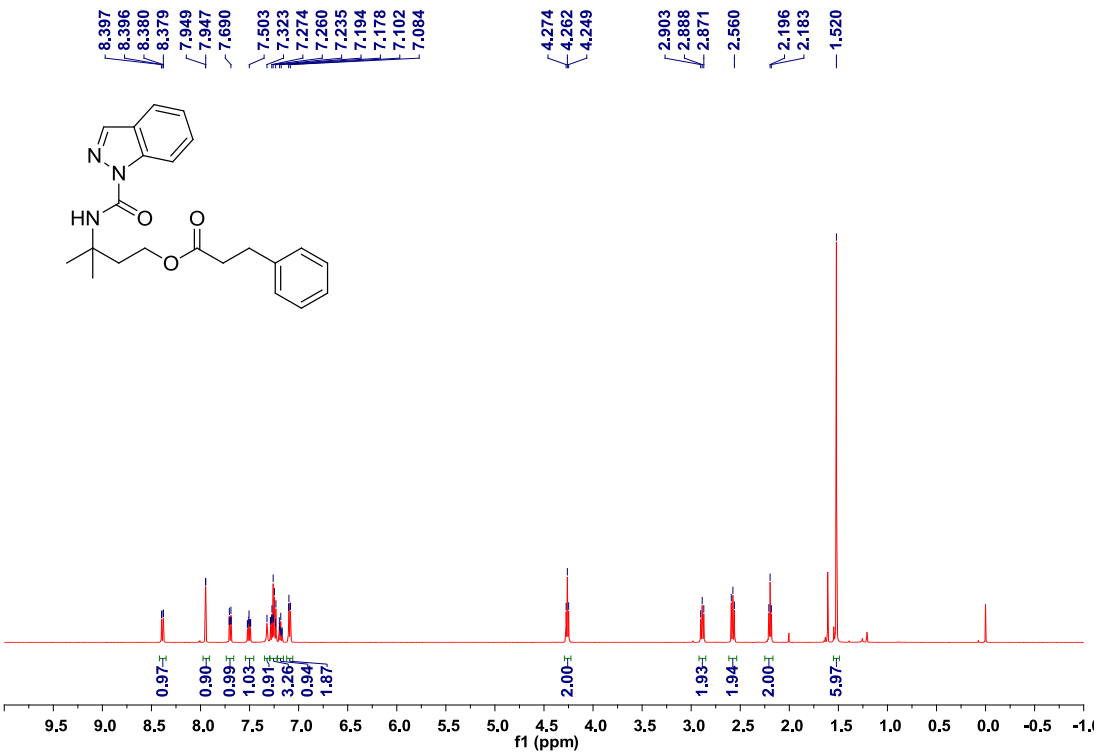


^{13}C NMR, 125 MHz, $CDCl_3$

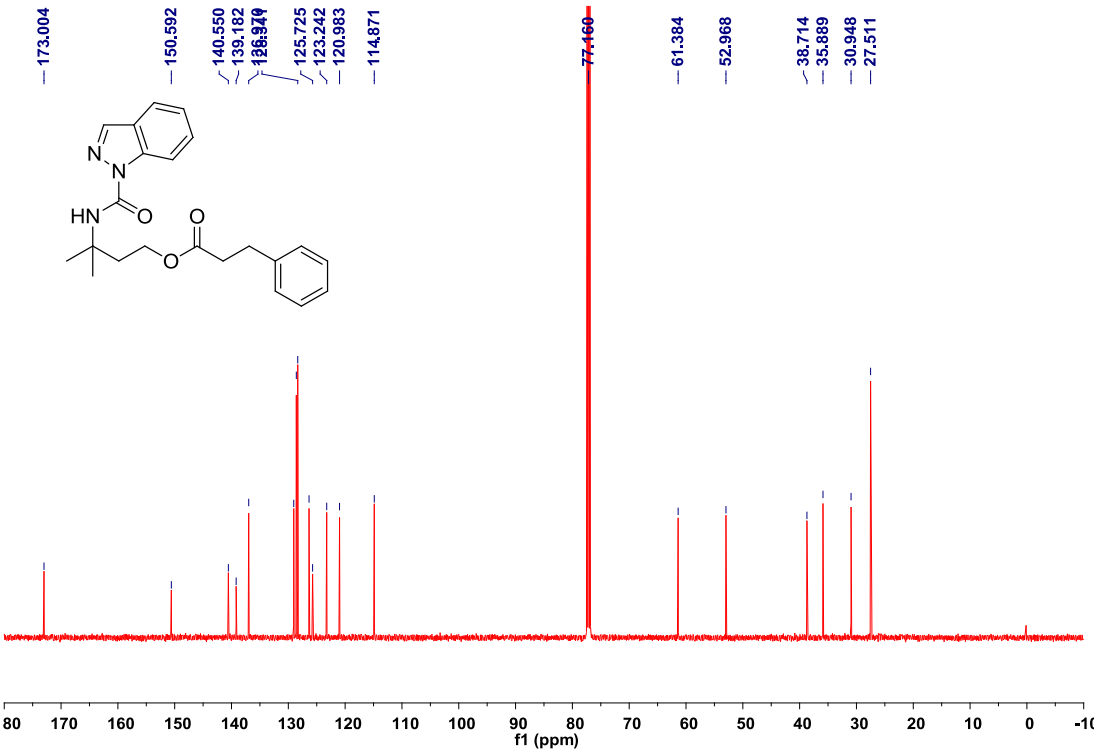


3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 3-phenylpropanoate (3am)

^{1}H NMR, 500 MHz, $CDCl_3$

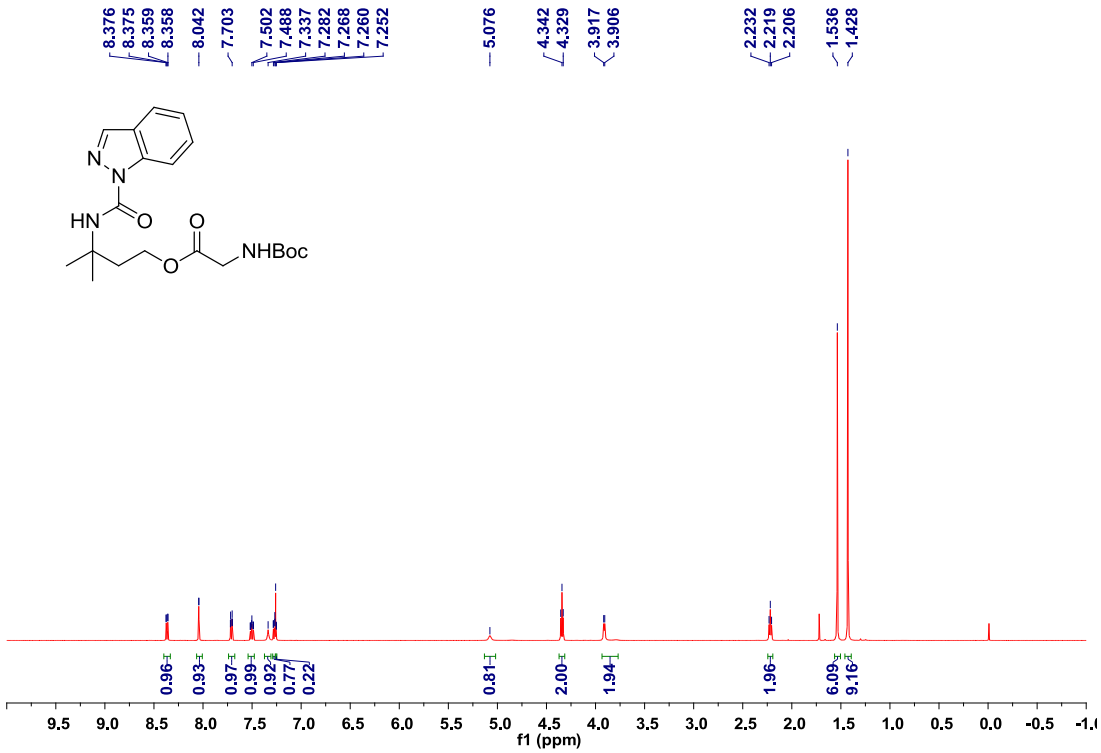


^{13}C NMR, 125 MHz, $CDCl_3$

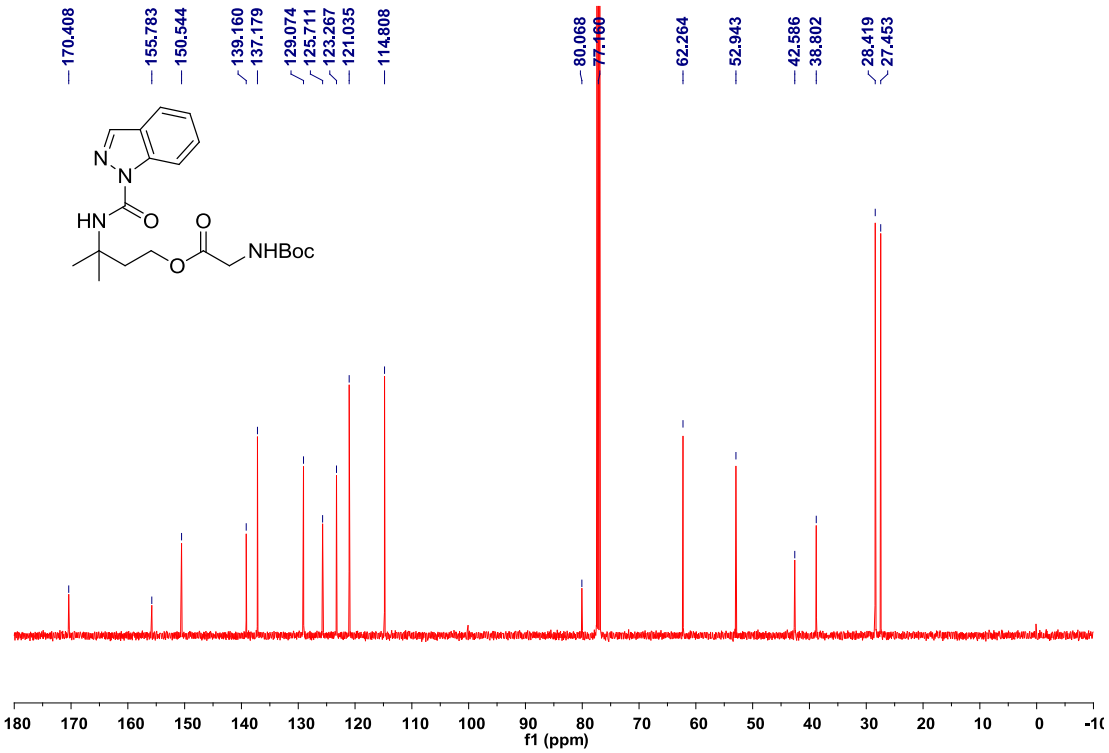


3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 2-((tert-butoxycarbonyl) amino) acetate (3an)

^{1}H NMR, 500 MHz, $CDCl_3$

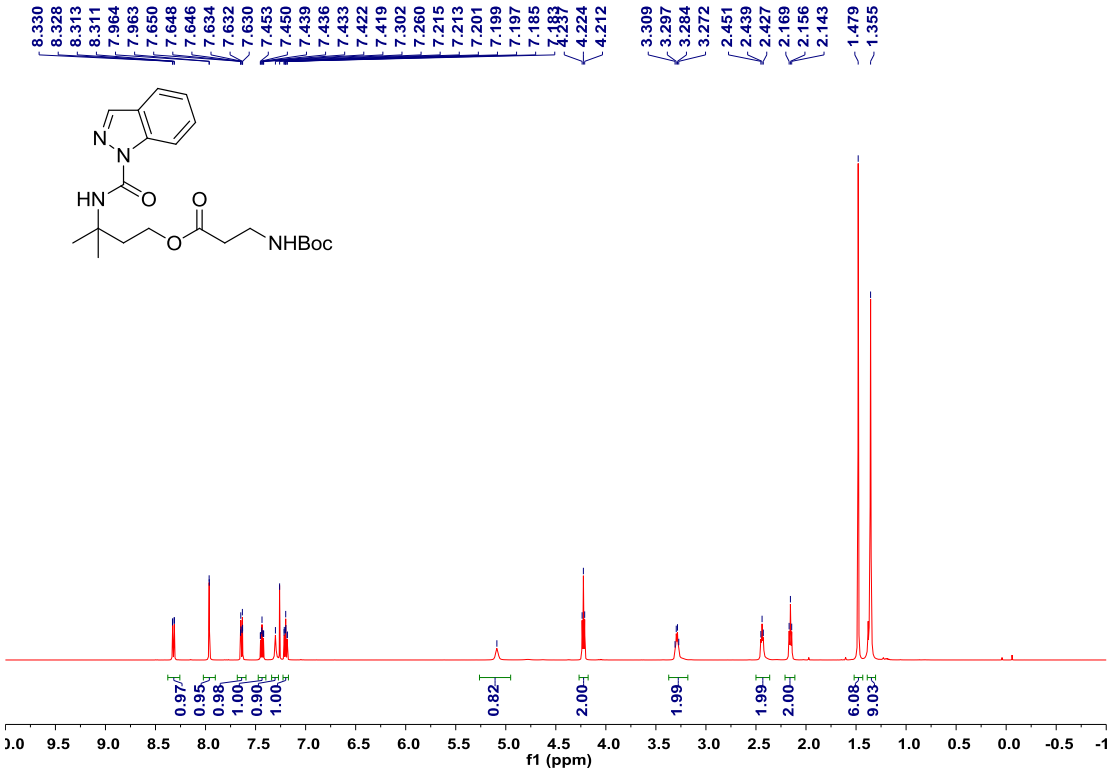


^{13}C NMR, 125 MHz, $CDCl_3$

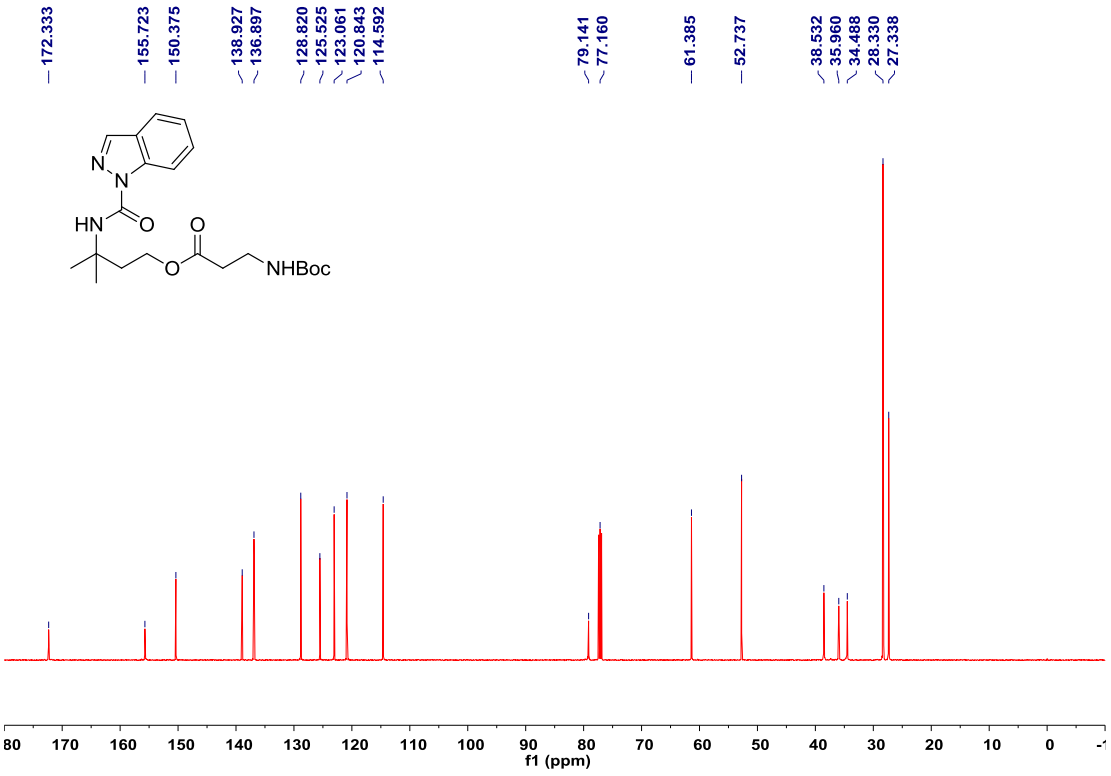


3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 3-((tert-butoxycarbonyl)amino) propanoate (3ao)

^{1}H NMR, 500 MHz, $CDCl_3$

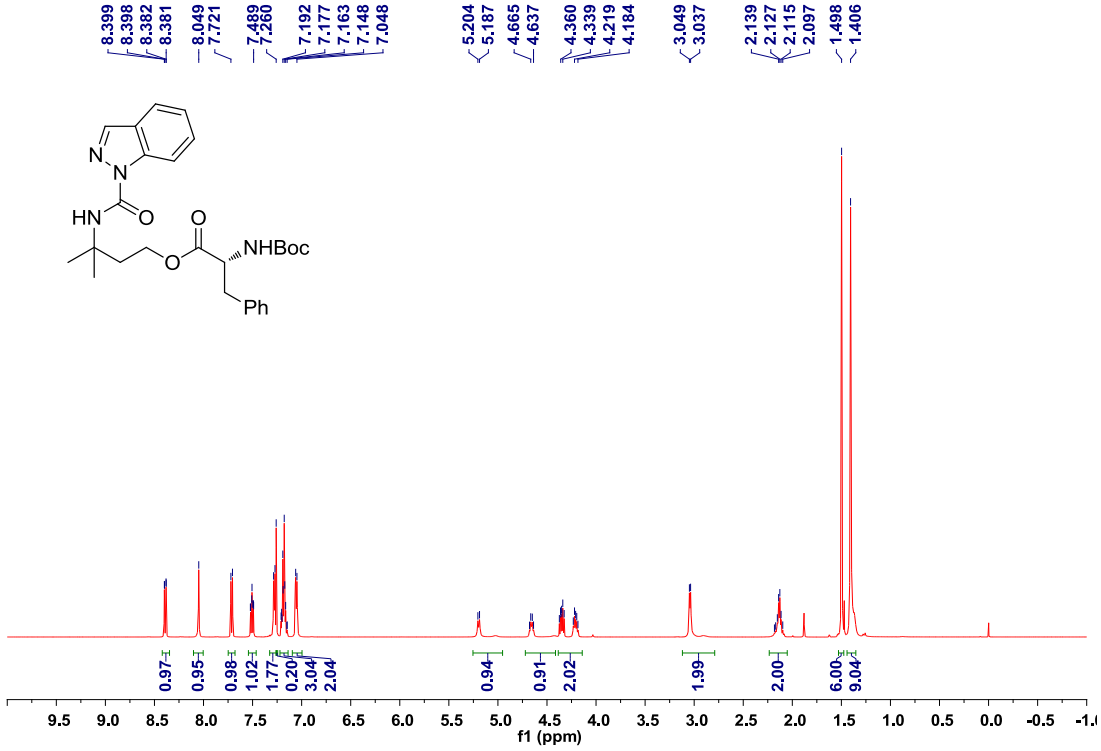


^{13}C NMR, 125 MHz, $CDCl_3$

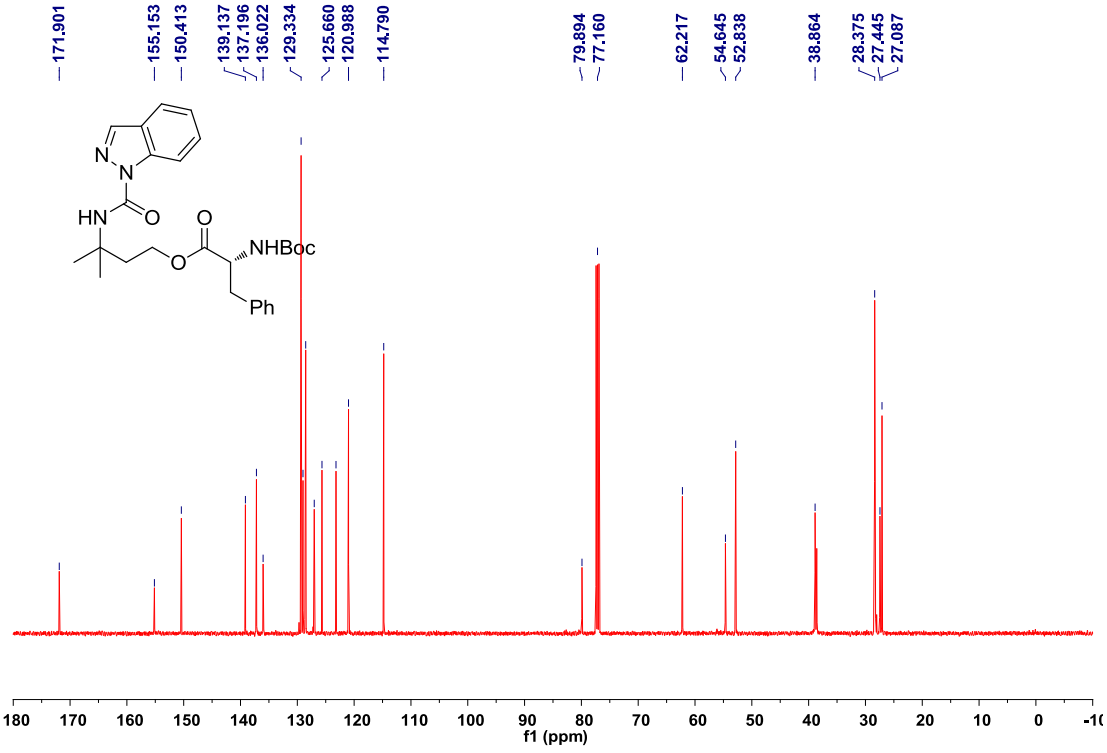


(R)-3-(1H-indazole-1-carboxamido)-3-methylbutyl2-((tert-butoxycarbonyl)amino)-3-phenylpropanoate (3ap)

^{1}H NMR, 500 MHz, $CDCl_3$

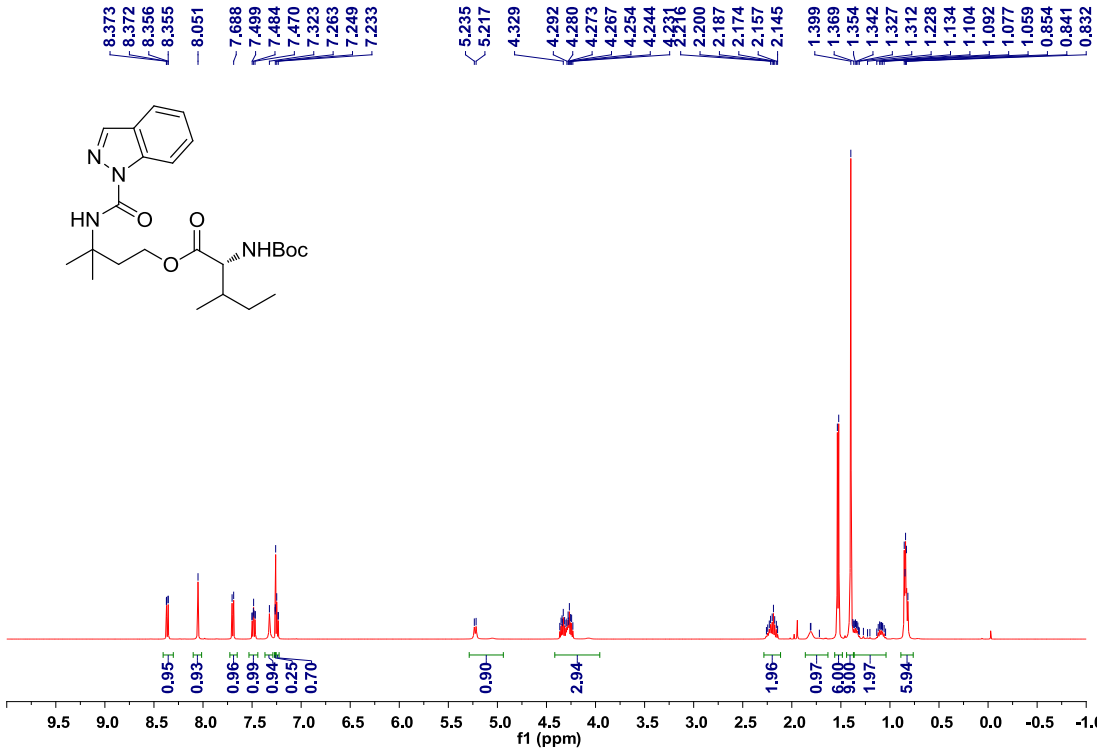


^{13}C NMR, 125 MHz, $CDCl_3$

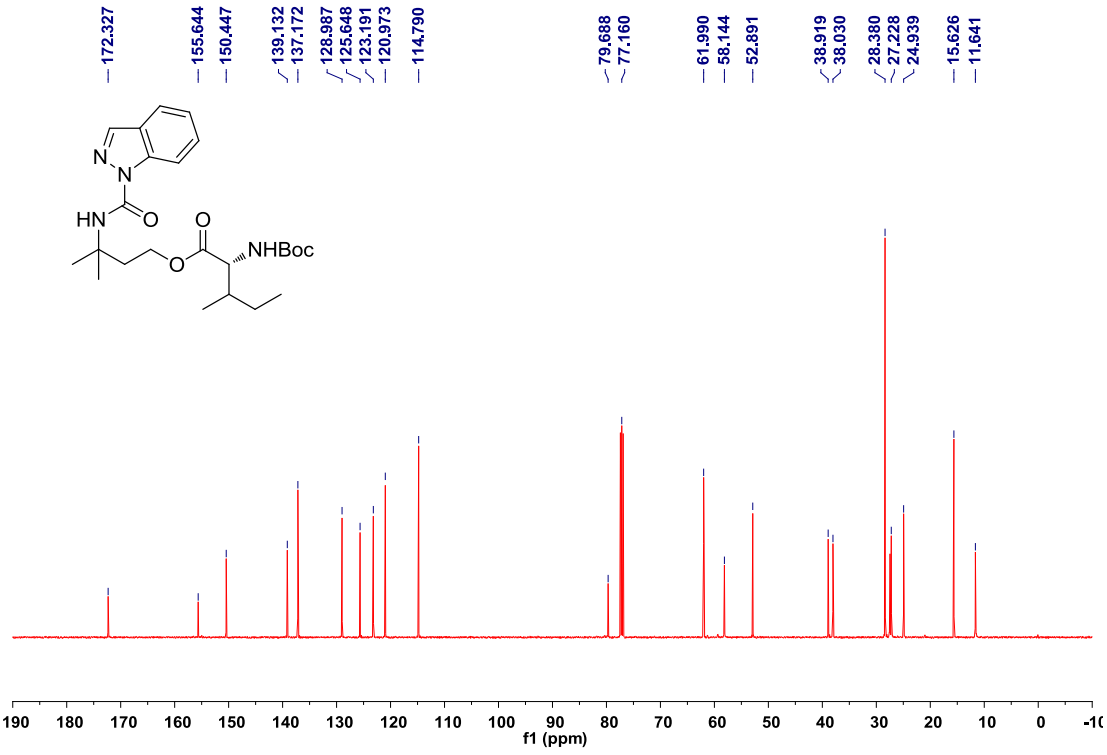


(2*R*)-3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 2-((tert-butoxycarbonyl)amino)-3 -methylpentanoate (3aq)

^{1}H NMR, 500 MHz, $CDCl_3$

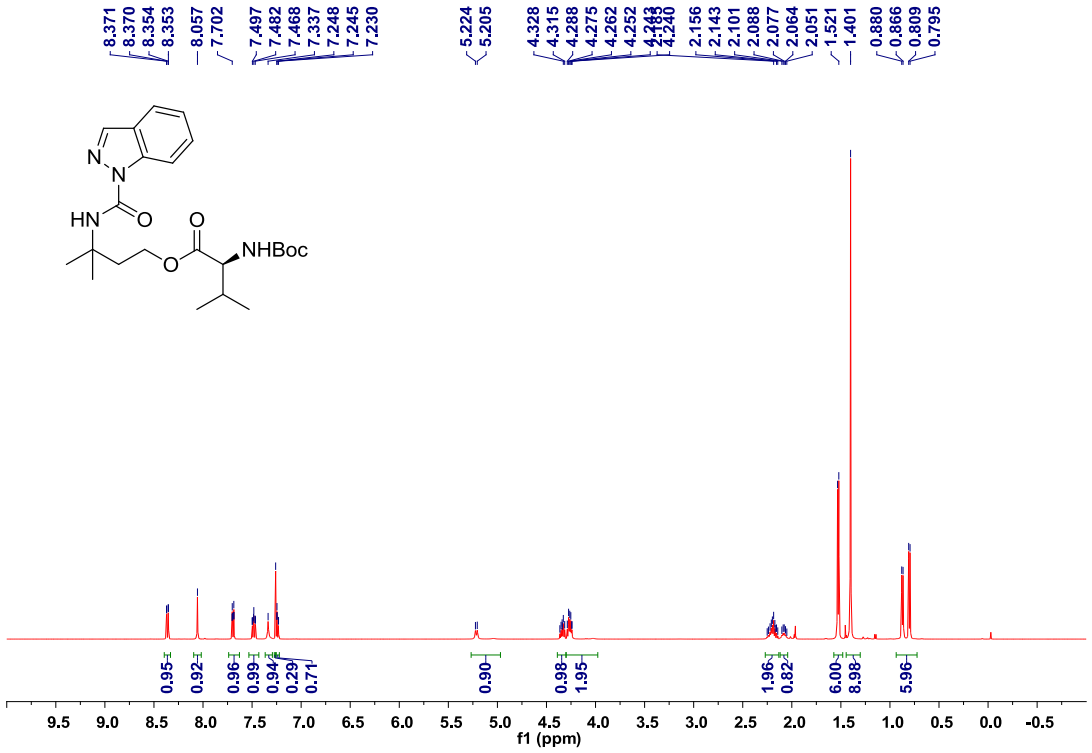


^{13}C NMR, 125 MHz, $CDCl_3$

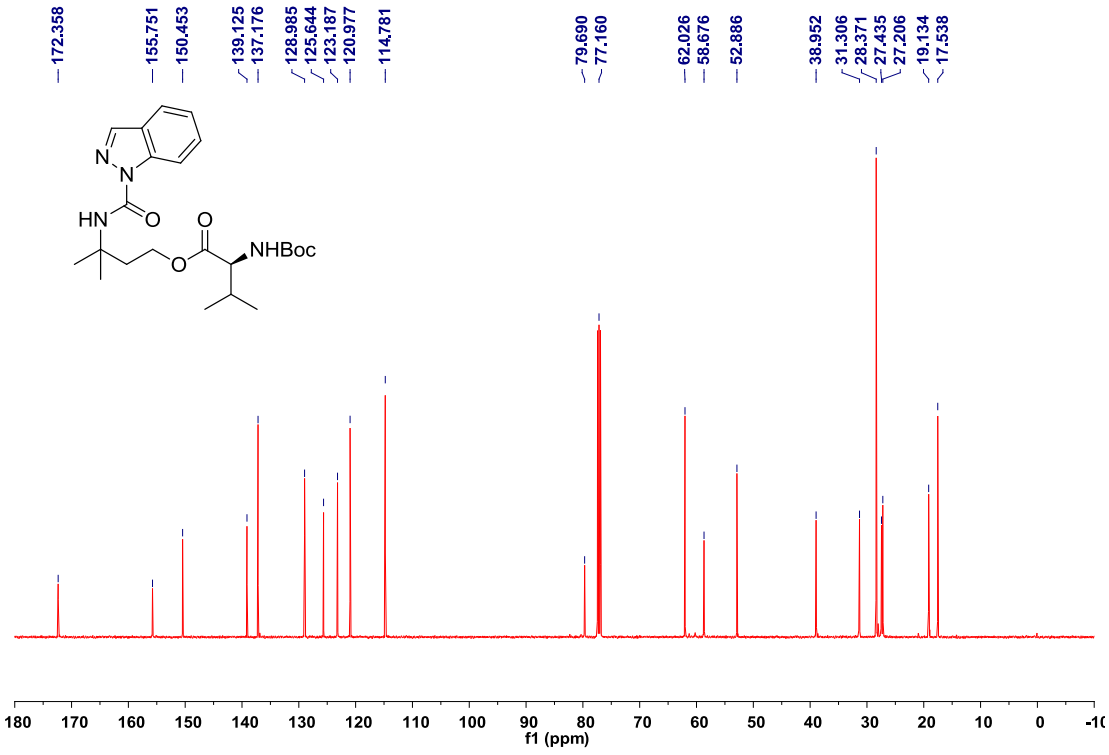


(*S*)-3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 2-((tert-butoxycarbonyl)amino)-3-methylbutanoate (3ar)

^{1}H NMR, 500 MHz, $CDCl_3$

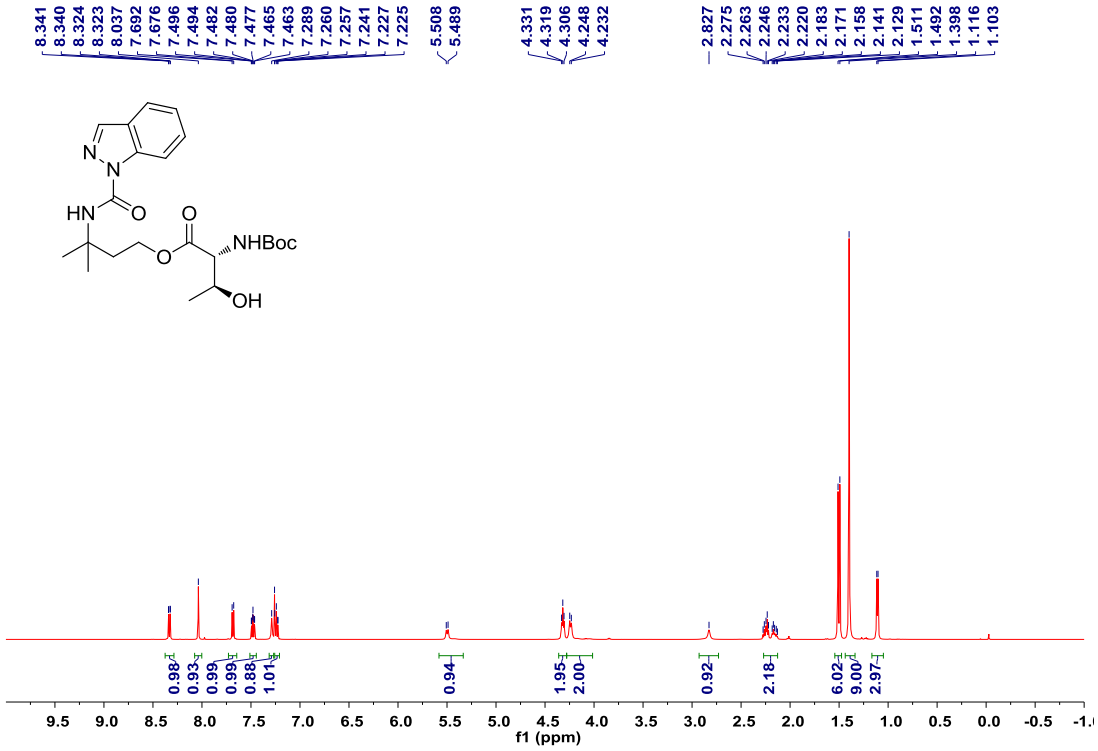


^{13}C NMR, 125 MHz, $CDCl_3$

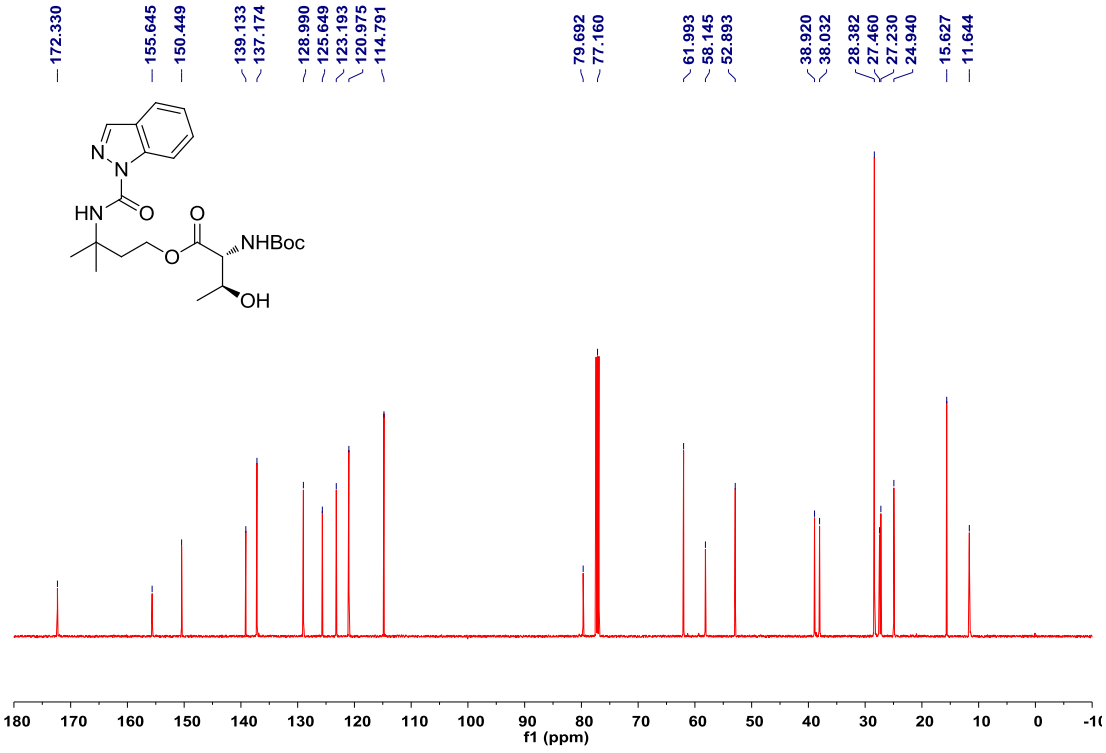


(2*R*,3*S*)-3-(1H-indazole-1-carboxamido)-3-methylbutyl 2-((tert-butoxycarbonyl)amino)-3-hydroxybutanoate (3as)

^{1}H NMR, 500 MHz, $CDCl_3$

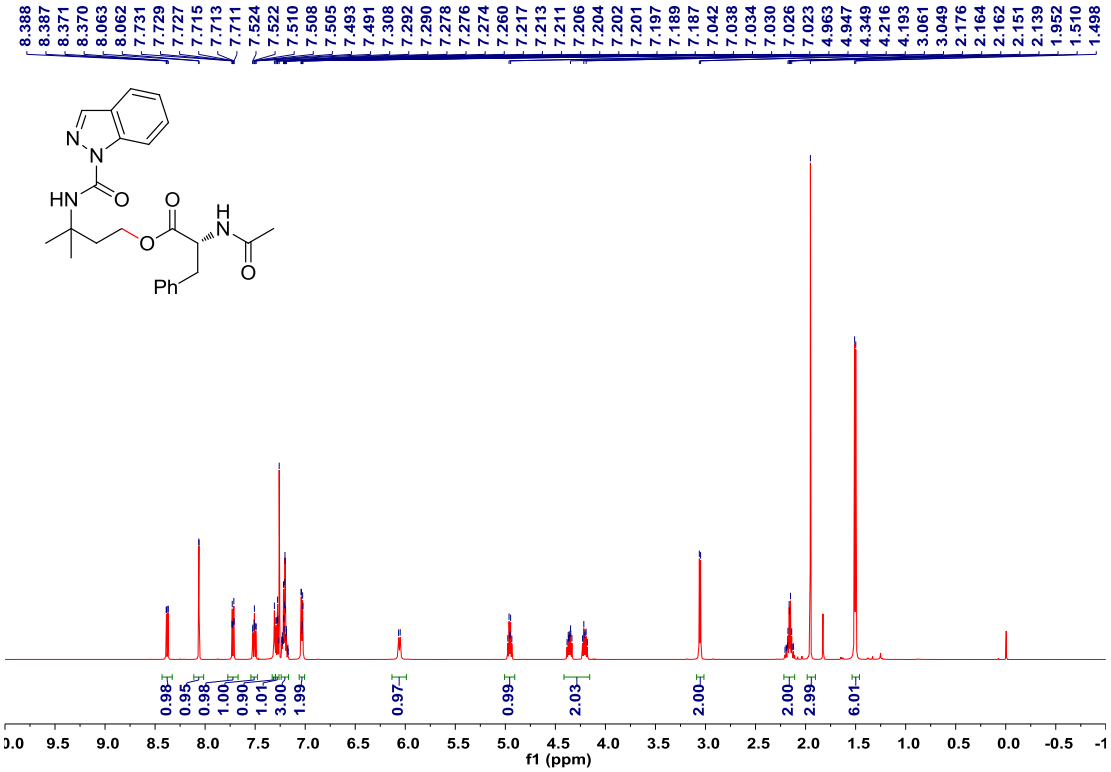


^{13}C NMR, 125 MHz, $CDCl_3$

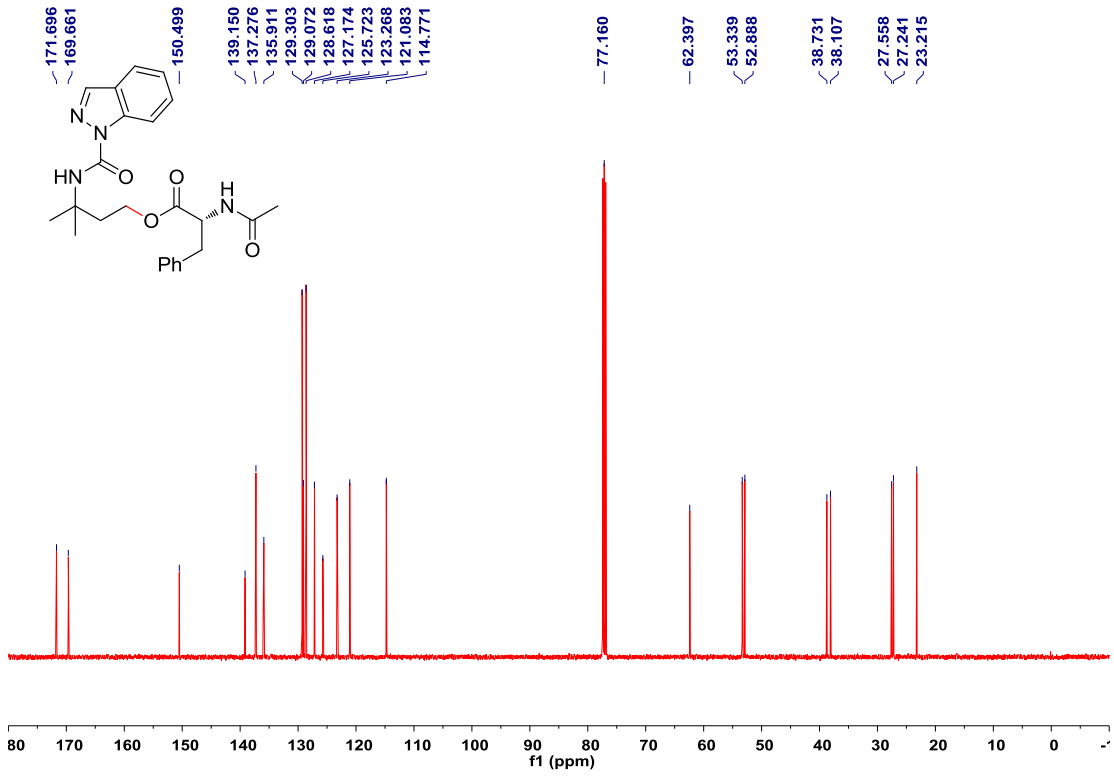


(*R*)-3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 2-acetamido-3-phenylpropanoate (3at)

^{1}H NMR, 500 MHz, $CDCl_3$

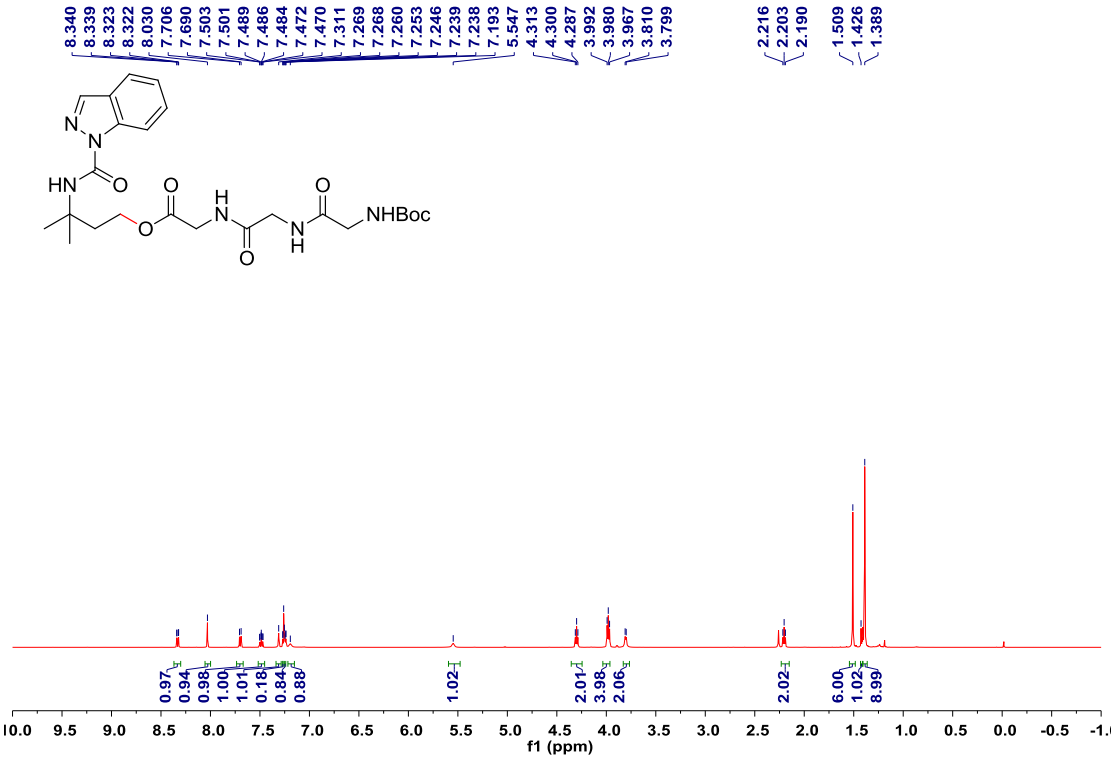


^{13}C NMR, 125 MHz, $CDCl_3$

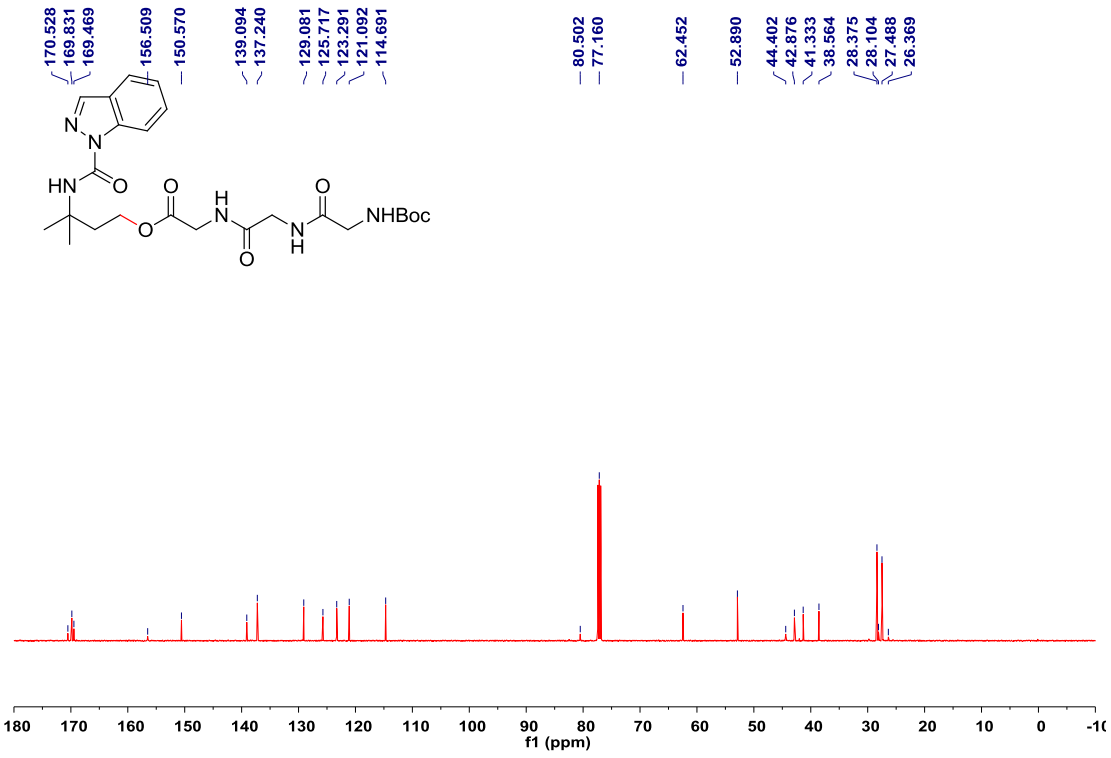


3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 2,2-dimethyl-4,7,10-trioxo-3-oxa-5,8,11-triazatridecan-13-oate (3au)

^{1}H NMR, 500 MHz, $CDCl_3$

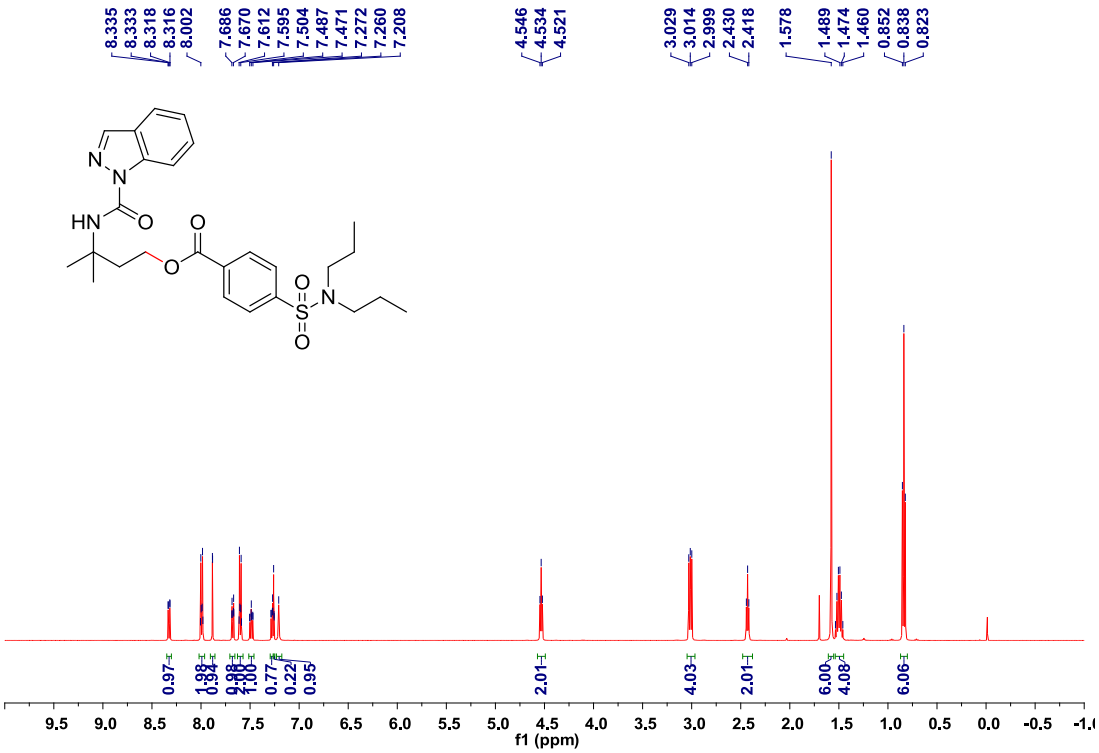


^{13}C NMR, 125 MHz, $CDCl_3$

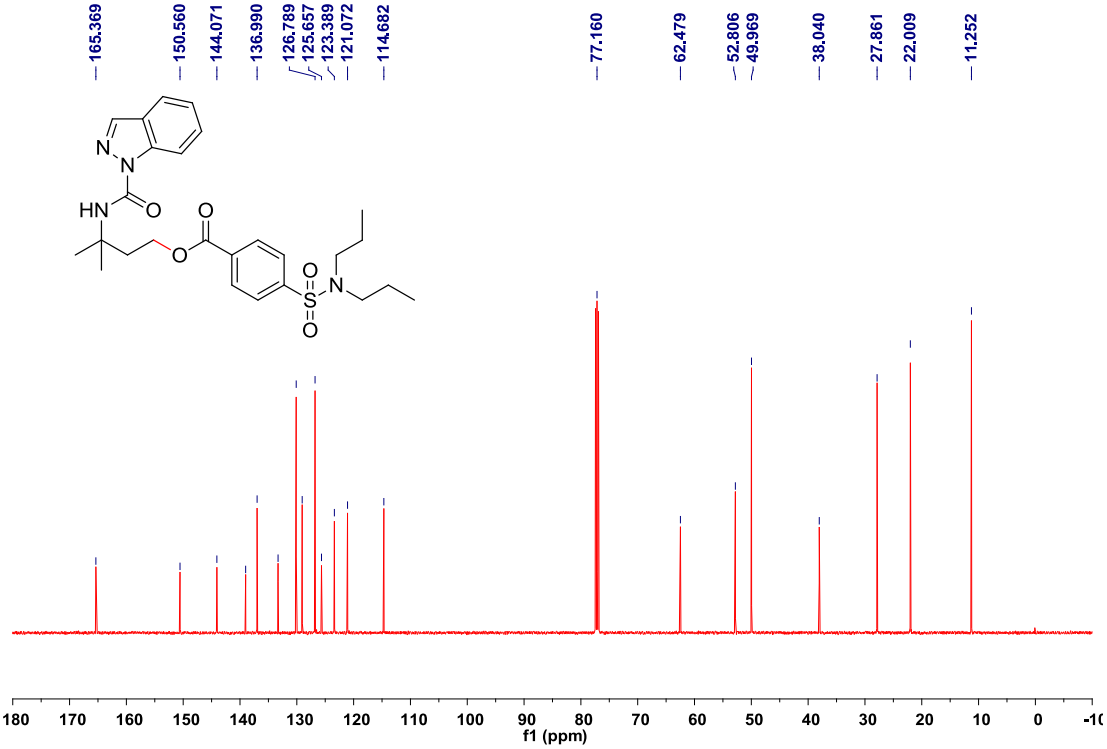


3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 4-(*N*,*N*-dipropylsulfamoyl) benzoate (3av)

^{1}H NMR, 500 MHz, $CDCl_3$

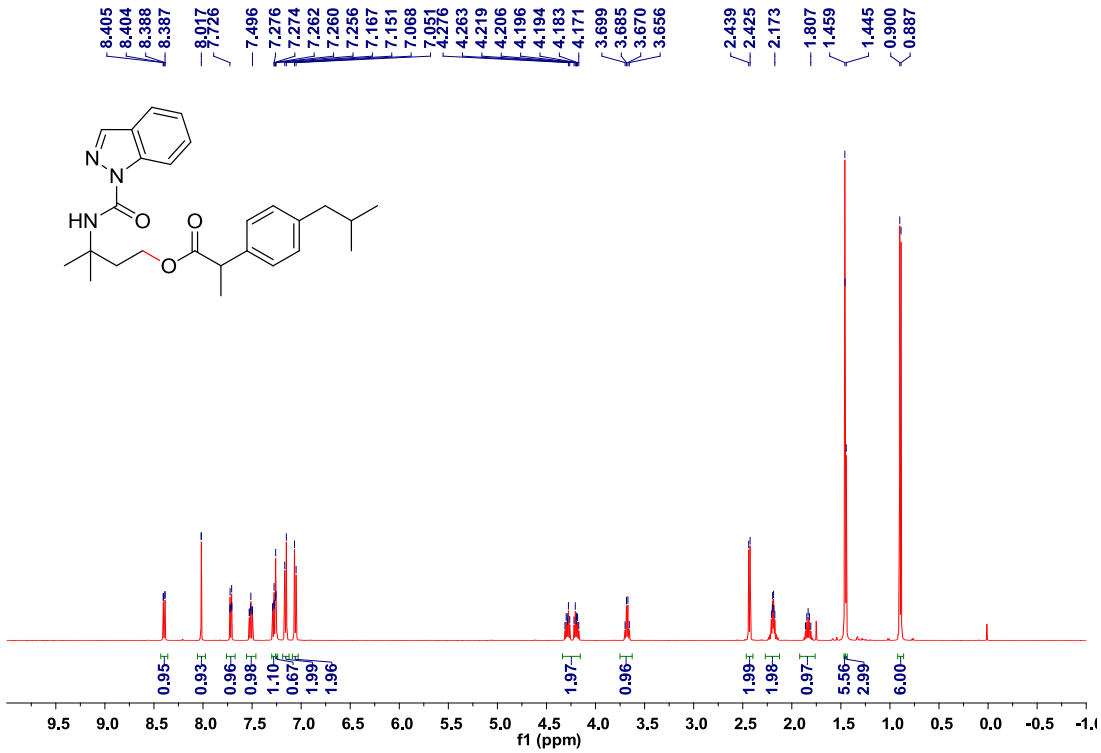


^{13}C NMR, 125 MHz, $CDCl_3$

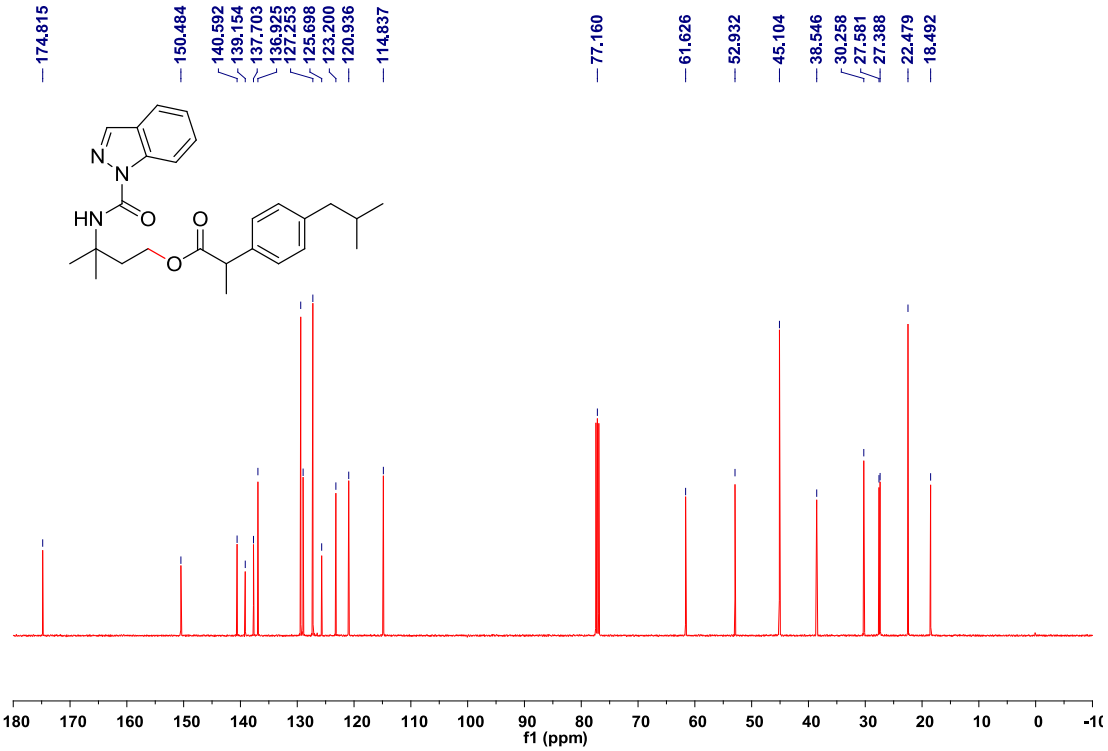


3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 2-(4-isobutylphenyl)propanoate (3aw)

^{1}H NMR, 500 MHz, $CDCl_3$

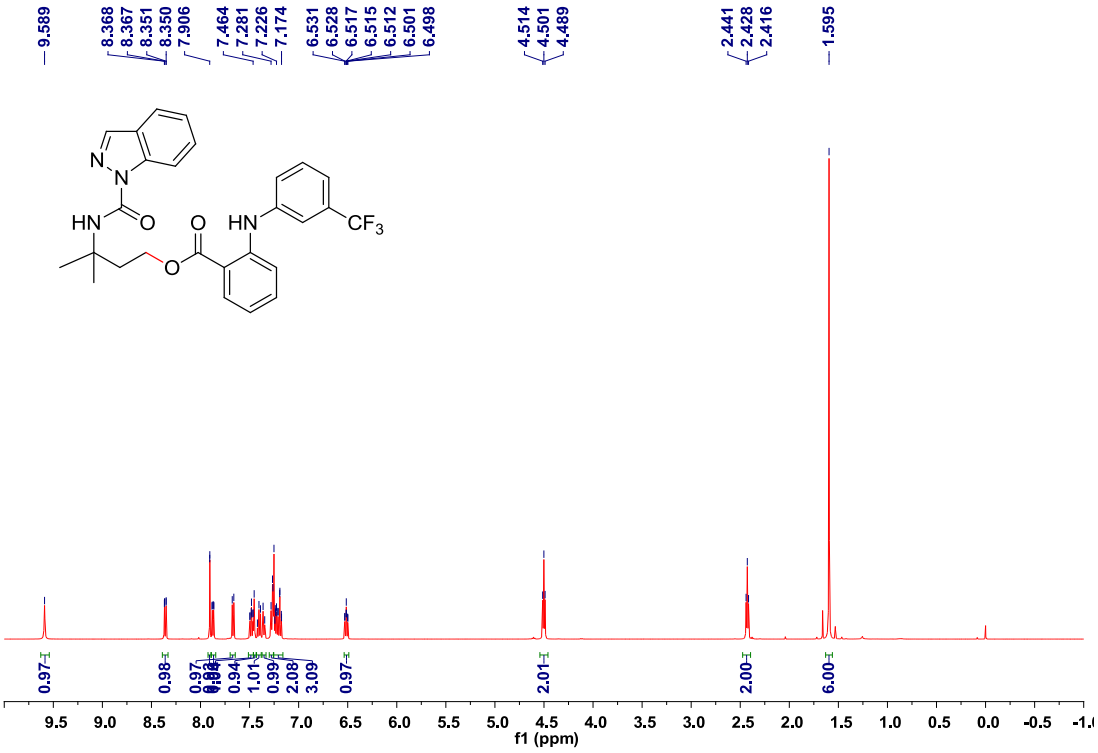


^{13}C NMR, 125 MHz, $CDCl_3$

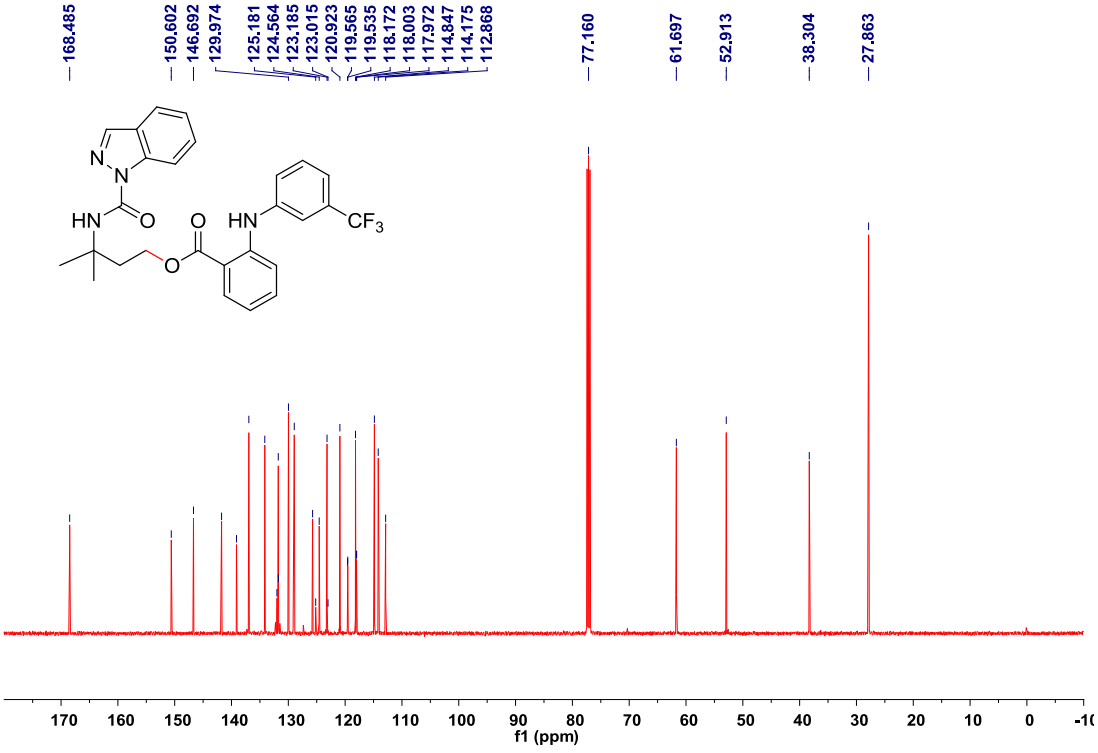


3-(1H-indazole-1-carboxamido)-3-methylbutyl 2-((3-(trifluoromethyl)phenyl)amino) benzoate (3ax)

^{1}H NMR, 500 MHz, $CDCl_3$

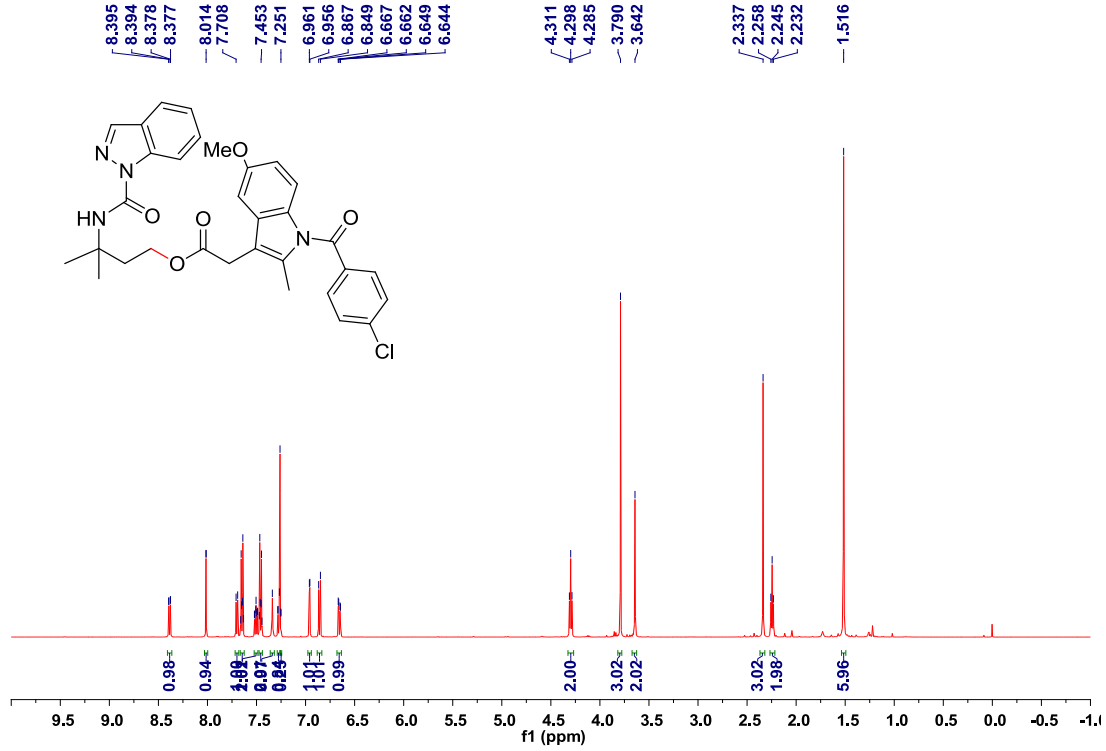


^{13}C NMR, 125 MHz, $CDCl_3$

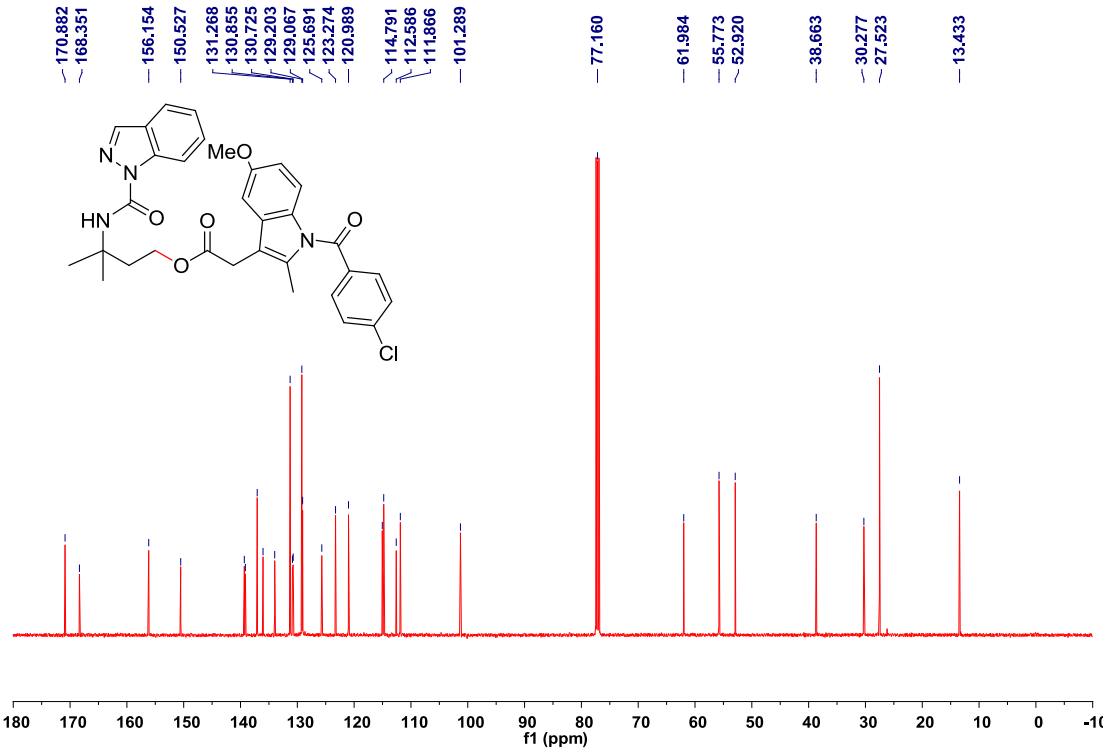


3-(1*H*-indazole-1-carboxamido)-3-methylbutyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate (3ay)

^{1}H NMR, 500 MHz, $CDCl_3$

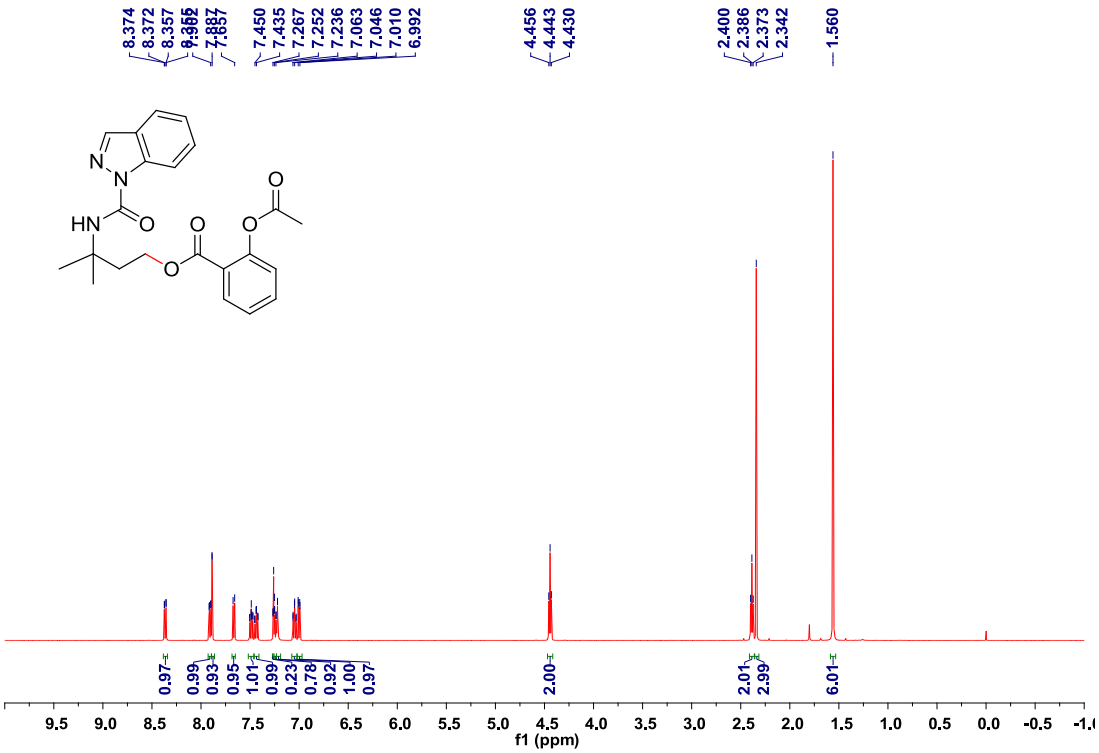


^{13}C NMR, 125 MHz, $CDCl_3$

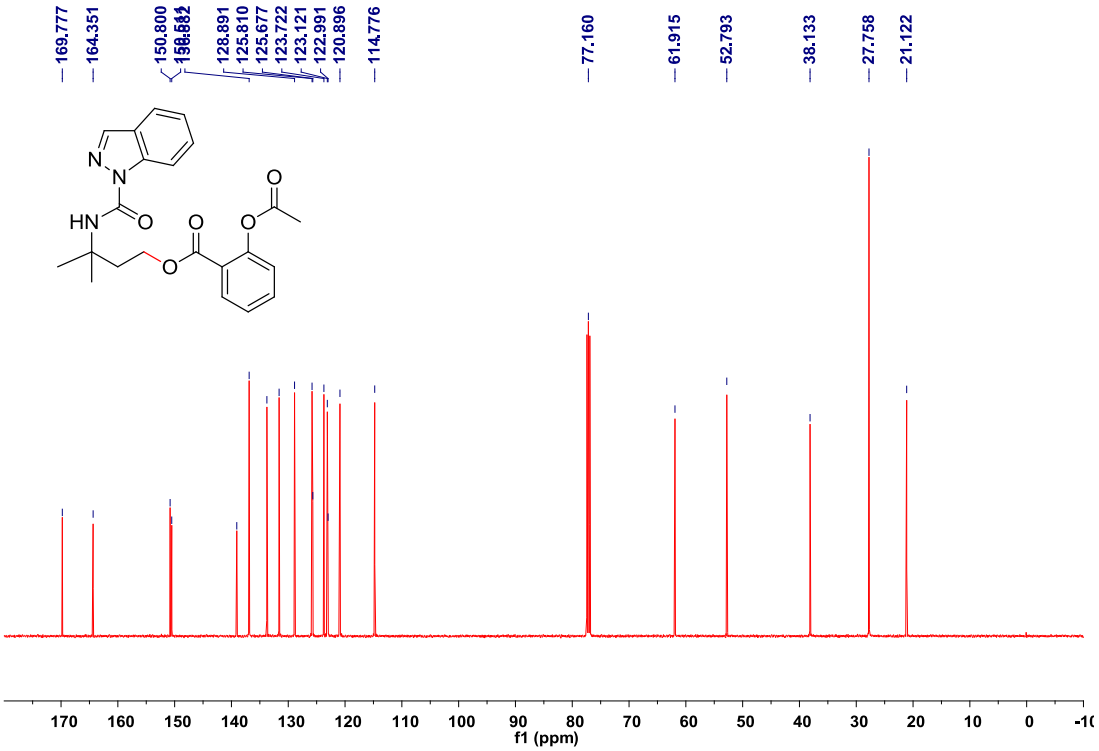


3-(1H-indazole-1-carboxamido)-3-methylbutyl 2-acetoxybenzoate (3az)

^{1}H NMR, 500 MHz, $CDCl_3$

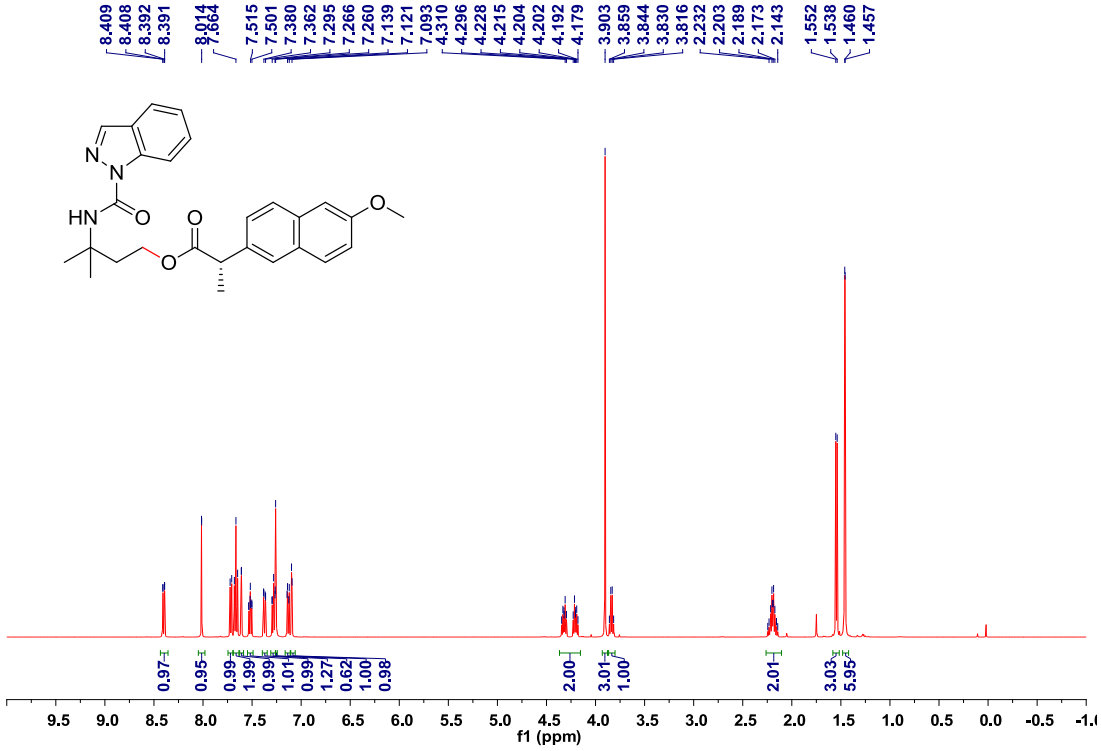


^{13}C NMR, 125 MHz, $CDCl_3$

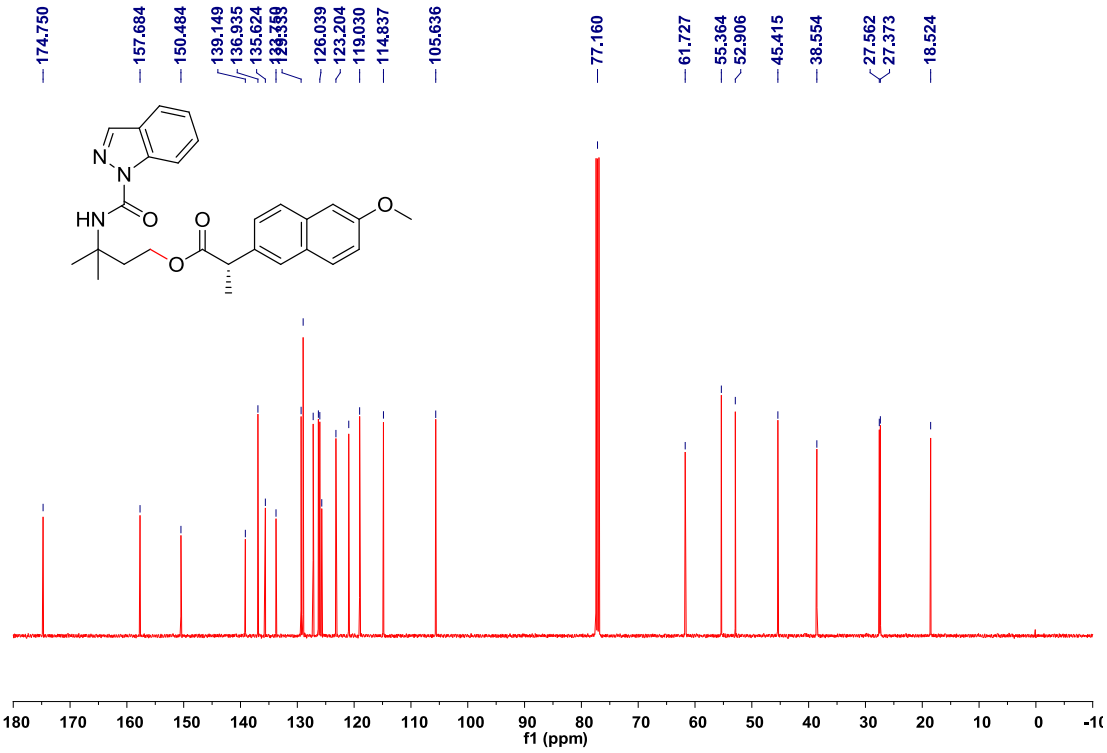


(S)-3-(1H-indazole-1-carboxamido)-3-methylbutyl 2-(6-methoxynaphthalen-2-yl)propanoate (3ba)

^{1}H NMR, 500 MHz, $CDCl_3$

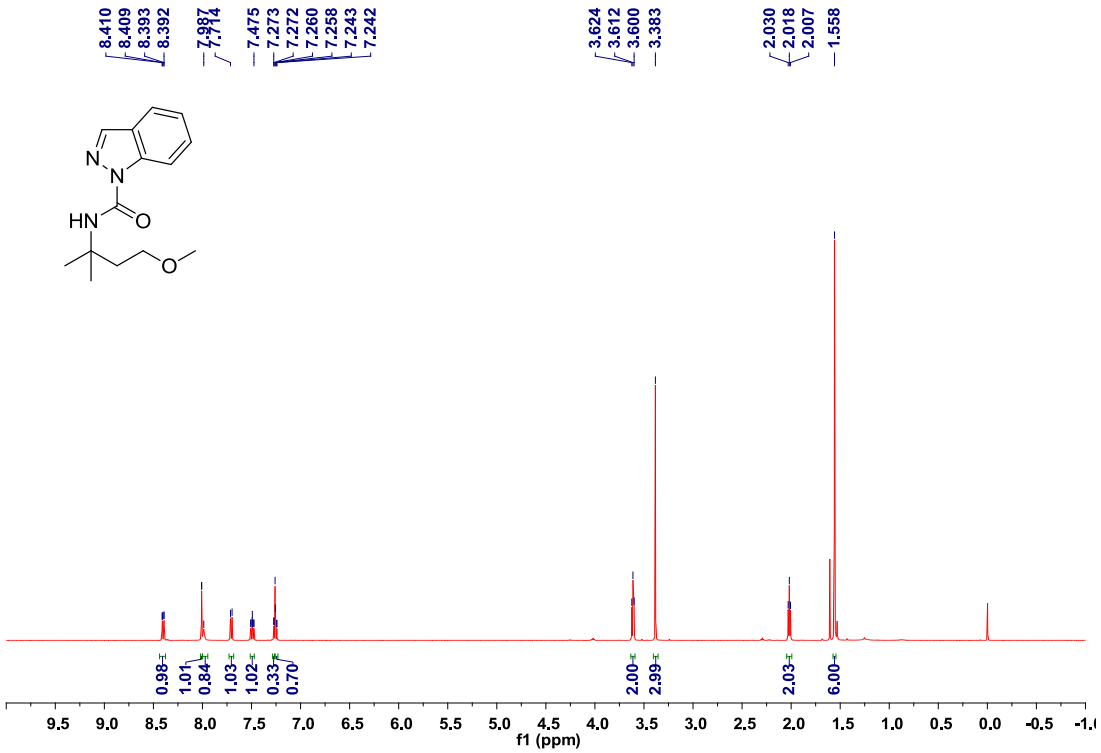


^{13}C NMR, 125 MHz, $CDCl_3$

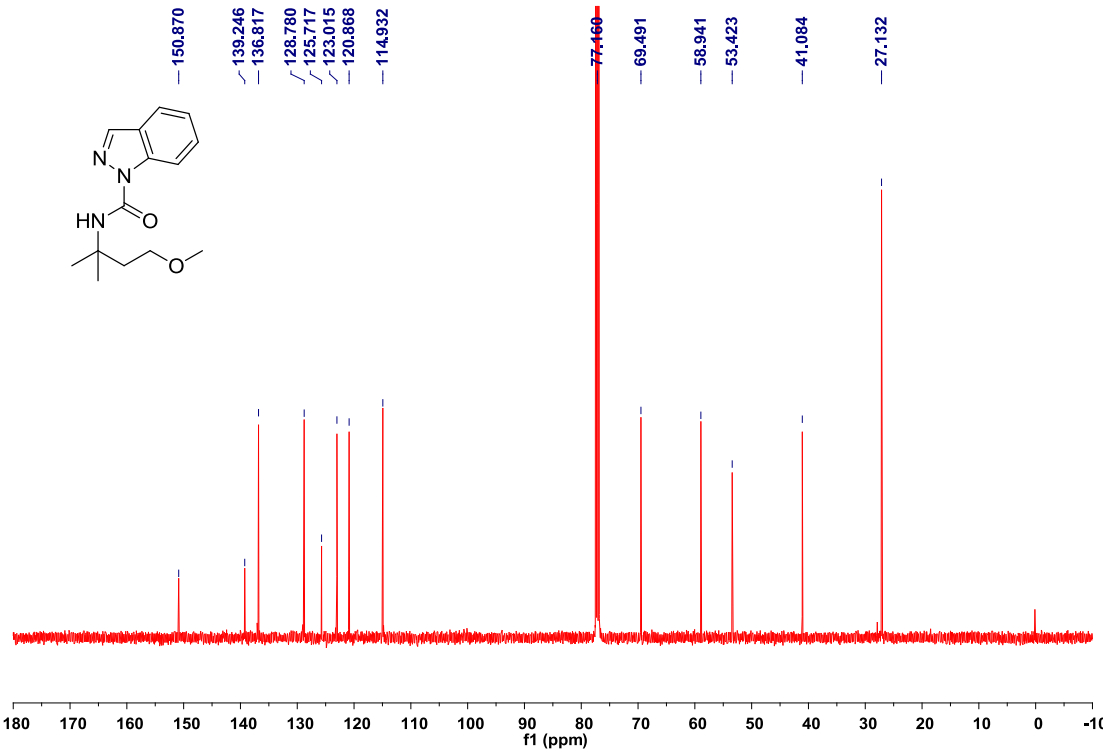


N-(4-methoxy-2-methylbutan-2-yl)-1*H*-indazole-1-carboxamide (5a)

^{1}H NMR, 500 MHz, $CDCl_3$

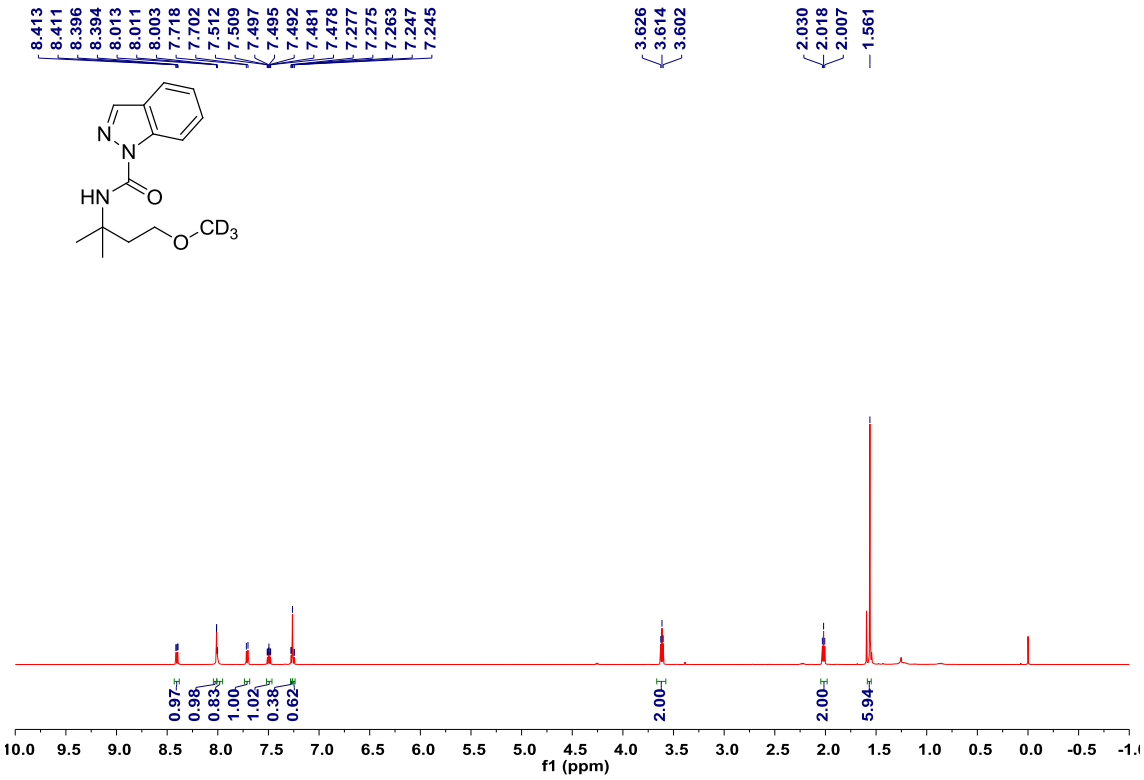


^{13}C NMR, 125 MHz, $CDCl_3$

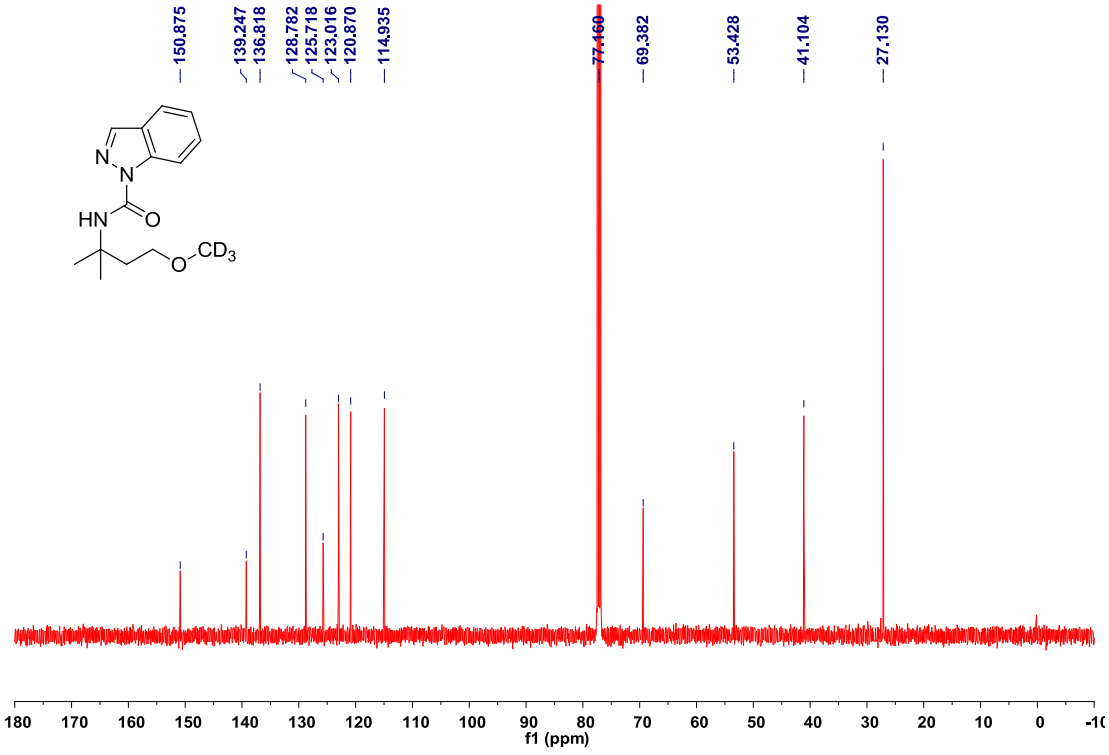


N-(4-methoxy-2-methylbutan-2-yl)-1*H*-indazole-1-carboxamide (5b)

^{1}H NMR, 500 MHz, $CDCl_3$

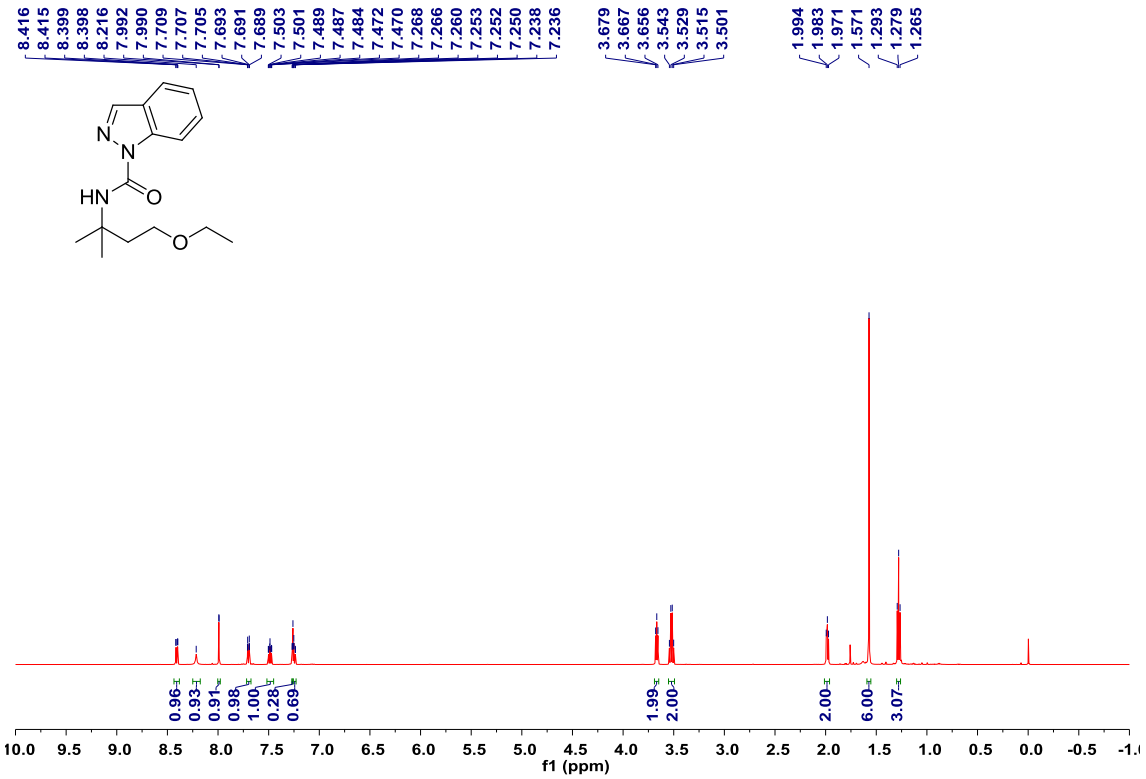


^{13}C NMR, 125 MHz, $CDCl_3$

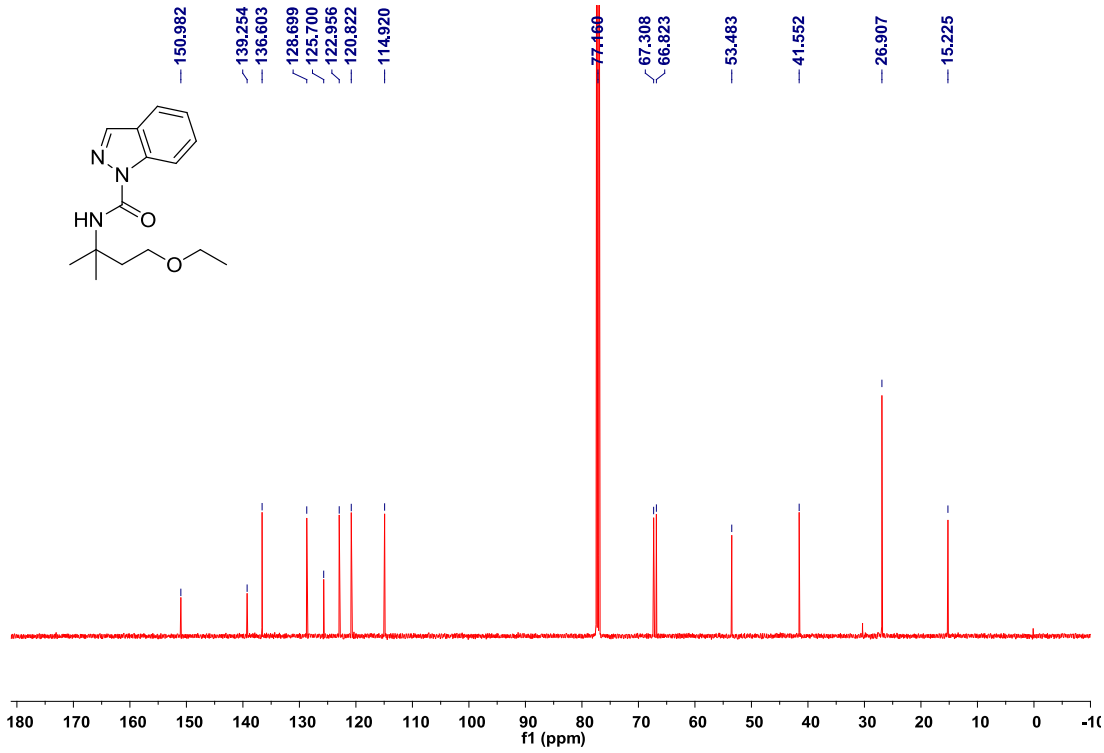


N-(4-ethoxy-2-methylbutan-2-yl)-1*H*-indazole-1-carboxamide (5c)

^{1}H NMR, 500 MHz, $CDCl_3$

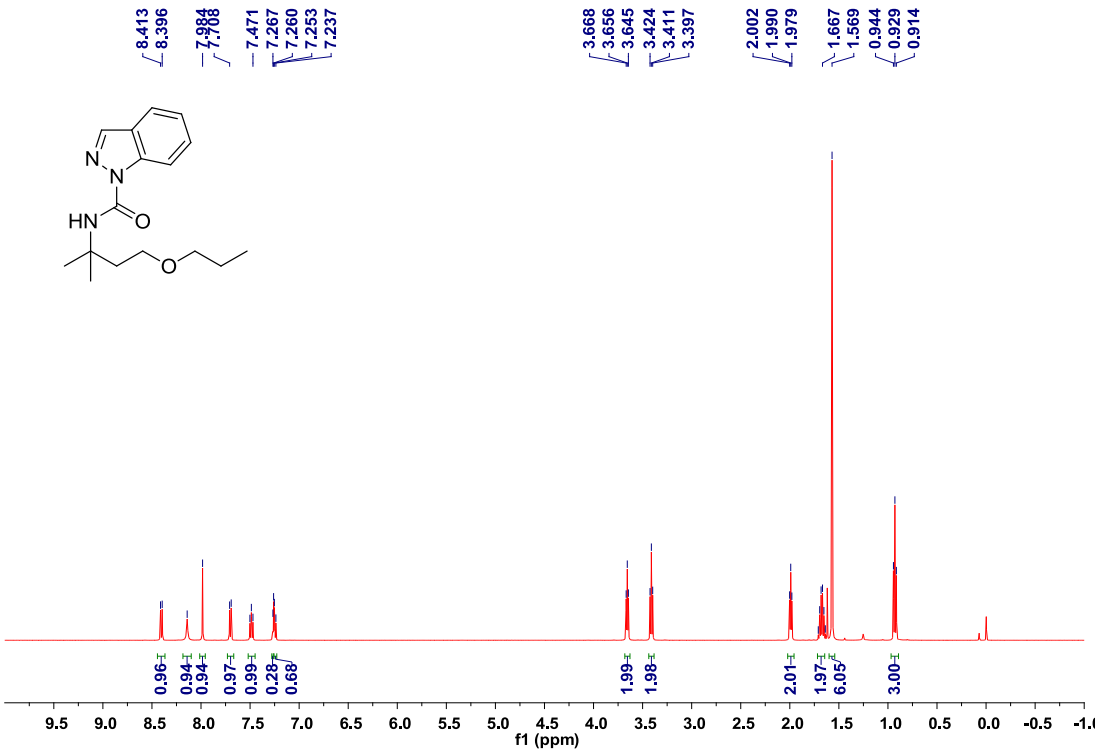


^{13}C NMR, 125 MHz, $CDCl_3$

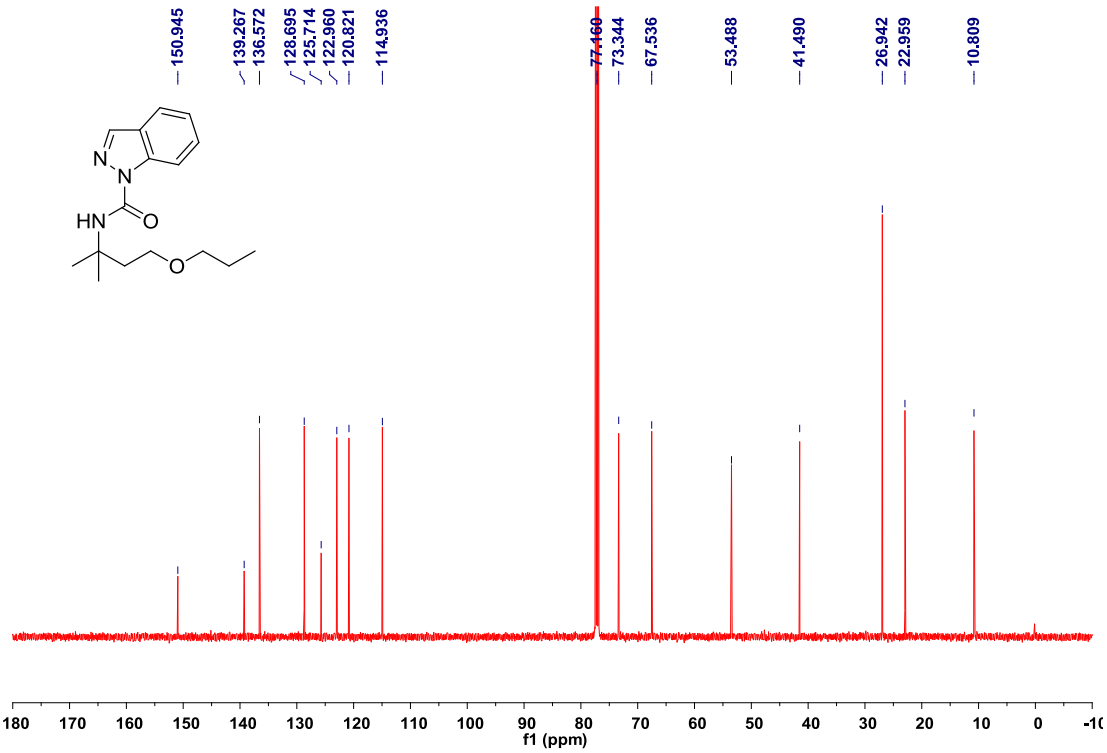


_N_-(2-methyl-4-propoxybutan-2-yl)-1_H_-indazole-1-carboxamide (5d)

^{1}H NMR, 500 MHz, $CDCl_3$

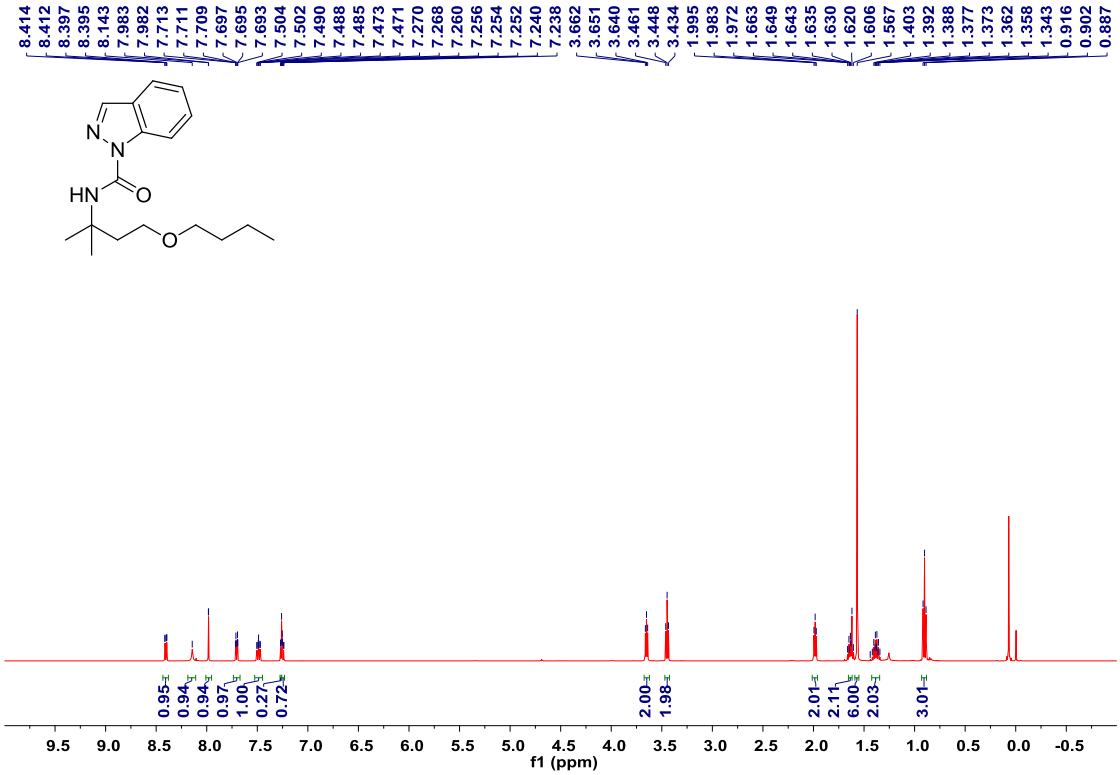


^{13}C NMR, 125 MHz, $CDCl_3$

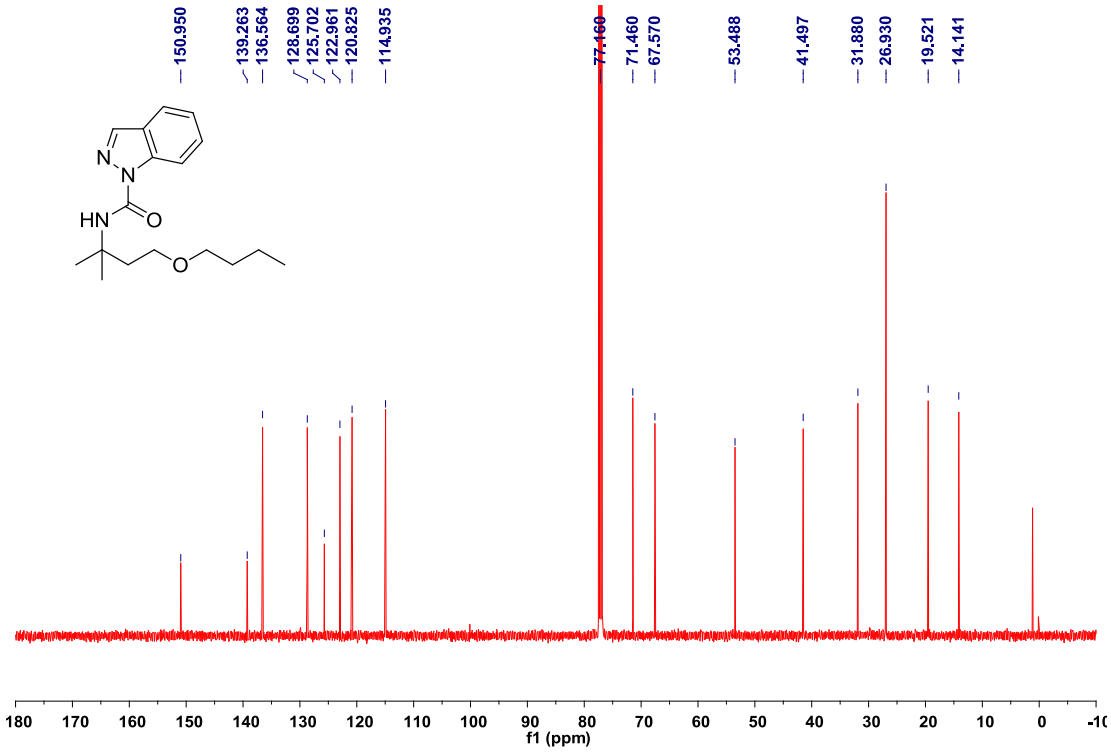


***N*-(4-butoxy-2-methylbutan-2-yl)-1*H*-indazole-1-carboxamide (5e)**

^{1}H NMR, 500 MHz, $CDCl_3$

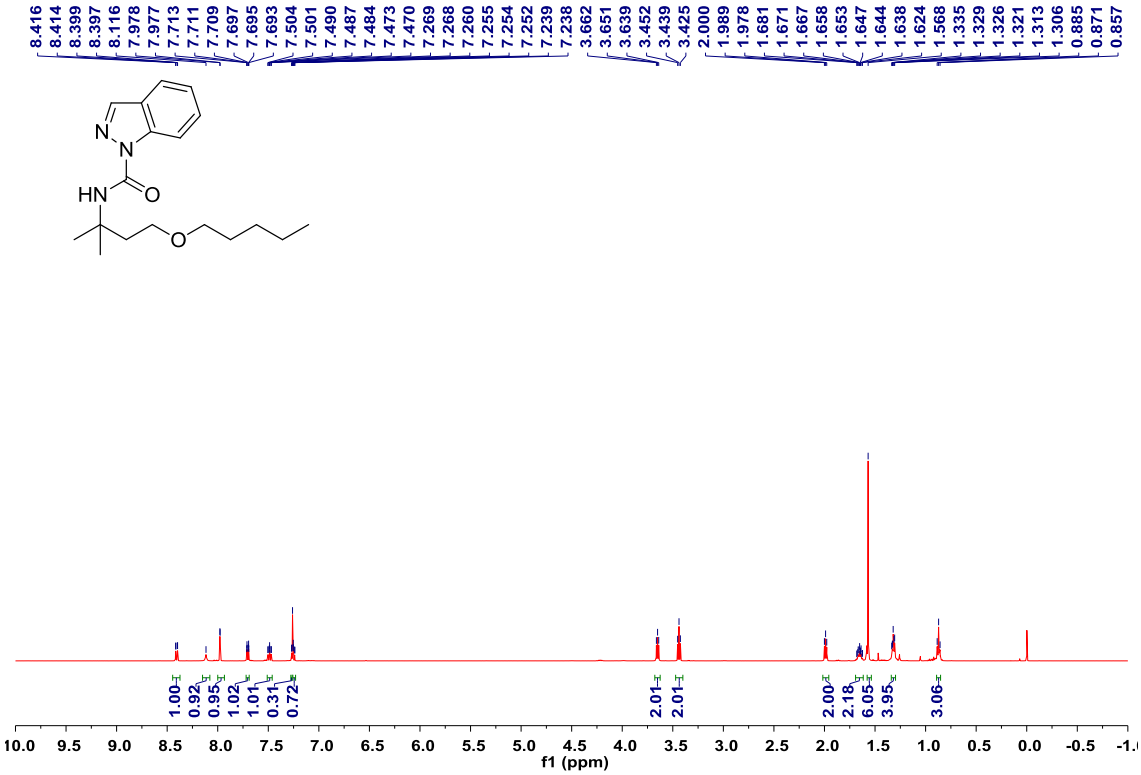


^{13}C NMR, 125 MHz, $CDCl_3$

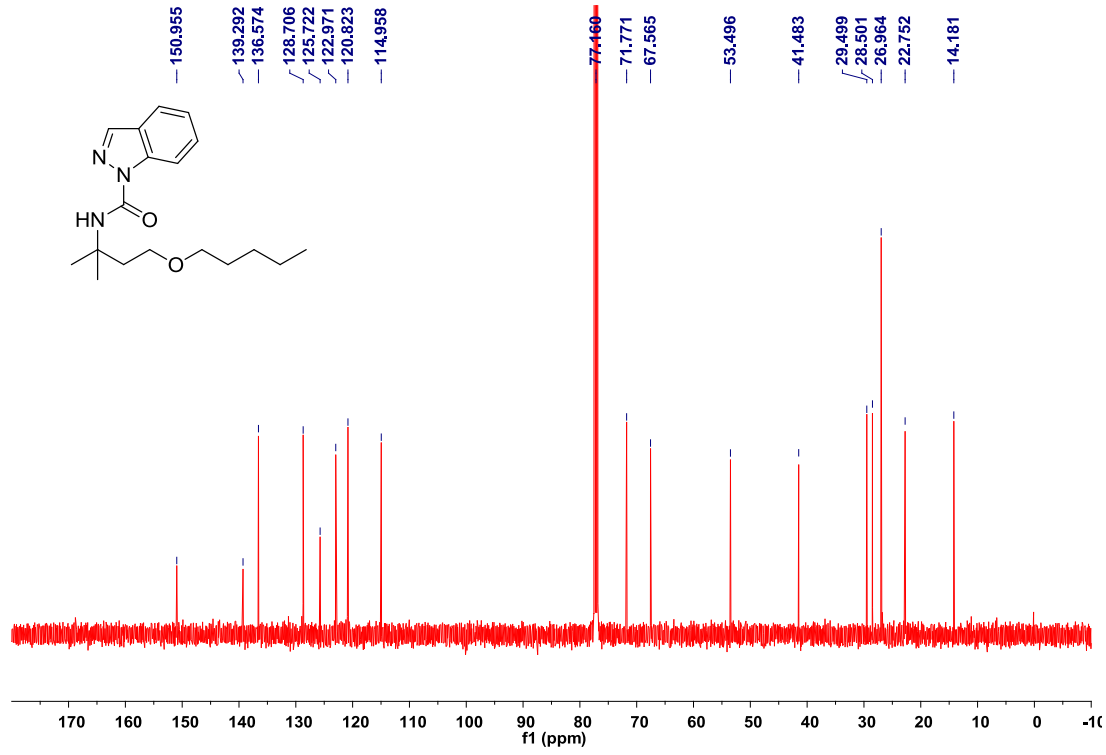


_N_-(2-methyl-4-(pentyloxy)butan-2-yl)-1_H_-indazole-1-carboxamide (5f)

^{1}H NMR, 500 MHz, $CDCl_3$

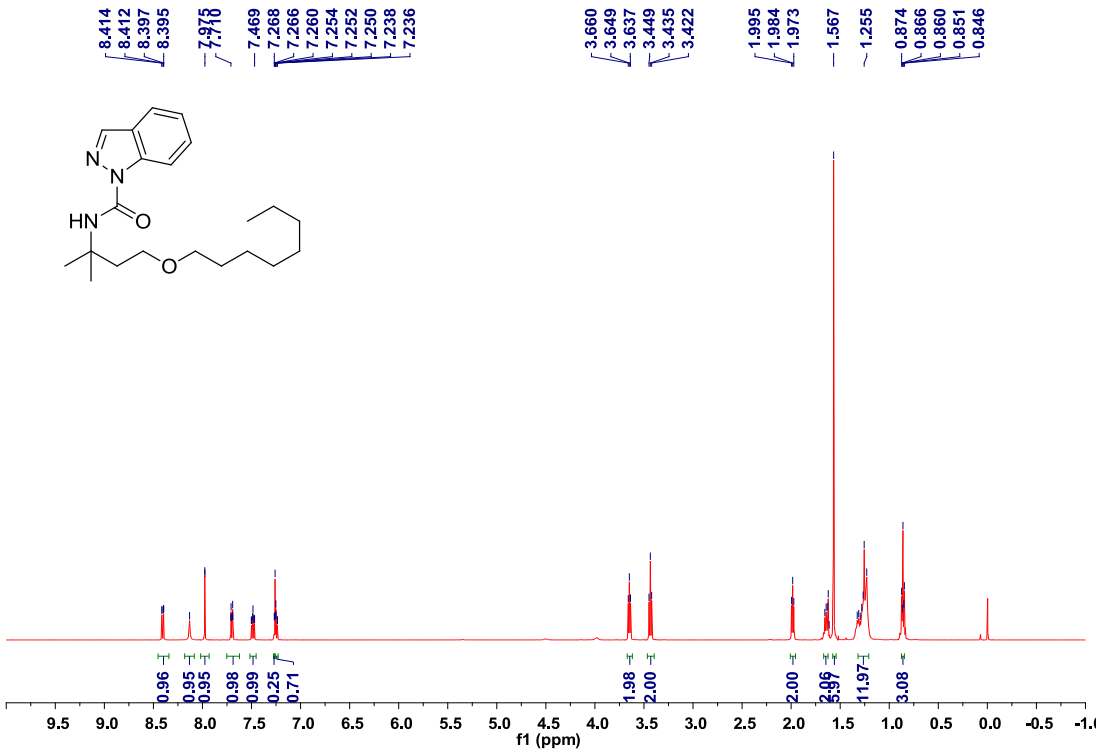


^{13}C NMR, 125 MHz, $CDCl_3$

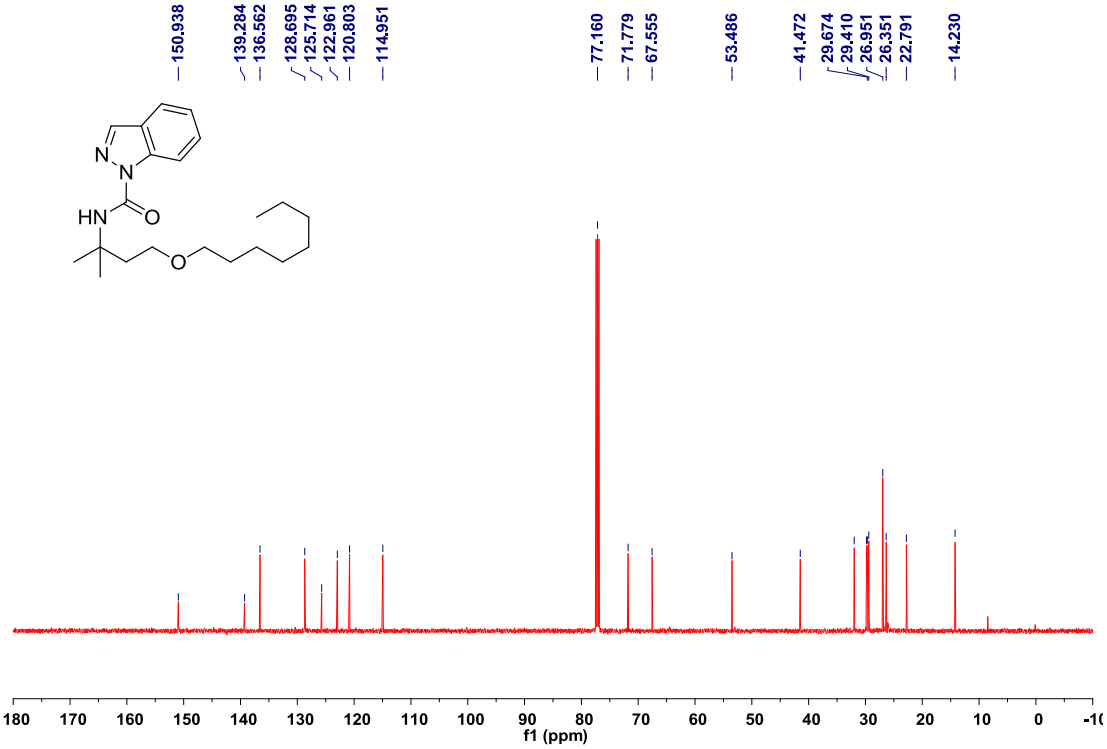


_N_-(2-methyl-4-(octyloxy)butan-2-yl)-1_H_-indazole-1-carboxamide (5g)

^{1}H NMR, 500 MHz, $CDCl_3$

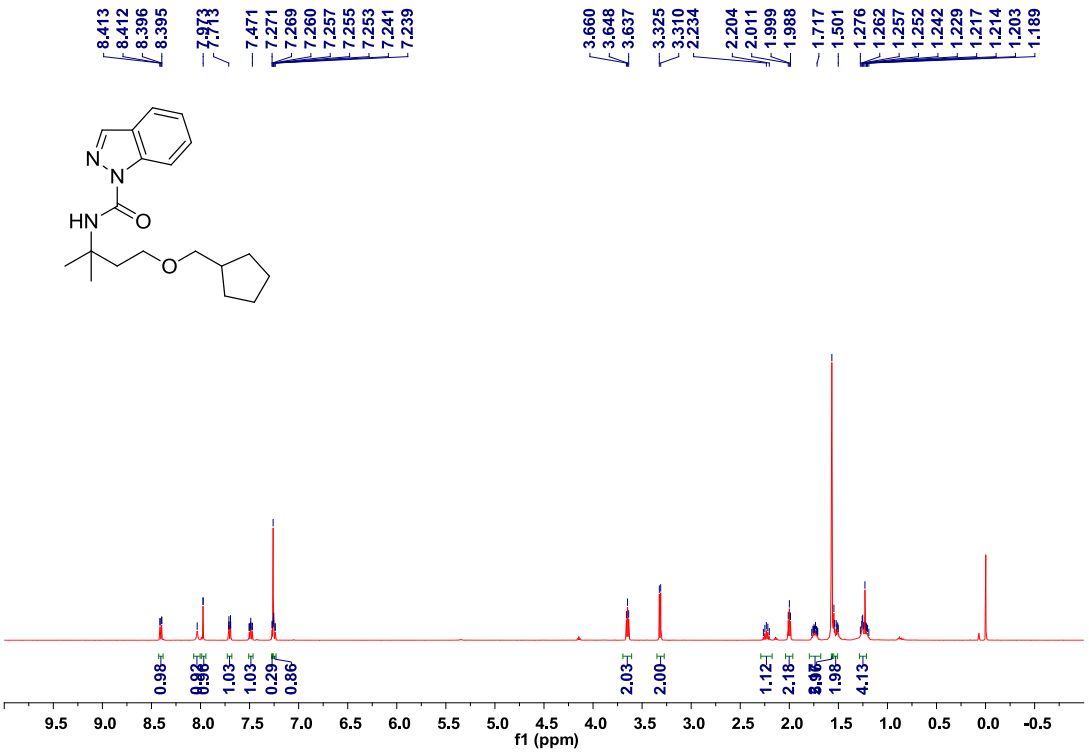


^{13}C NMR, 125 MHz, $CDCl_3$

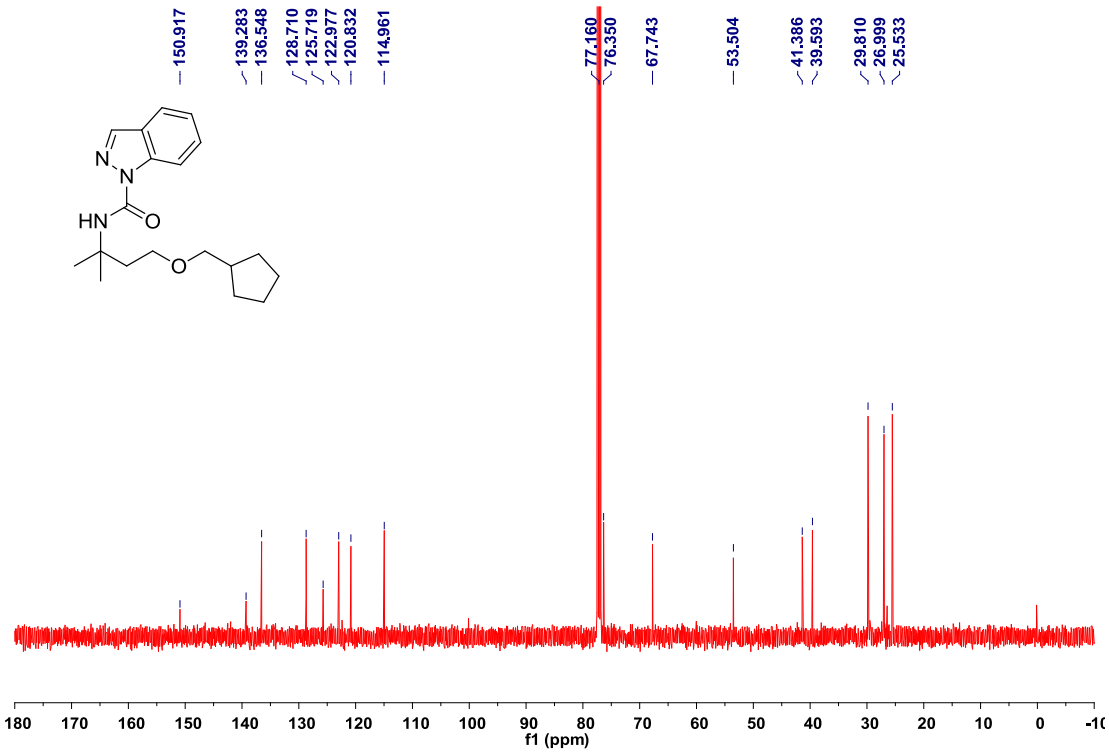


_N_-(4-(cyclopentylmethoxy)-2-methylbutan-2-yl)-1_H_-indazole-1-carboxamide (5h)

^{1}H NMR, 500 MHz, $CDCl_3$

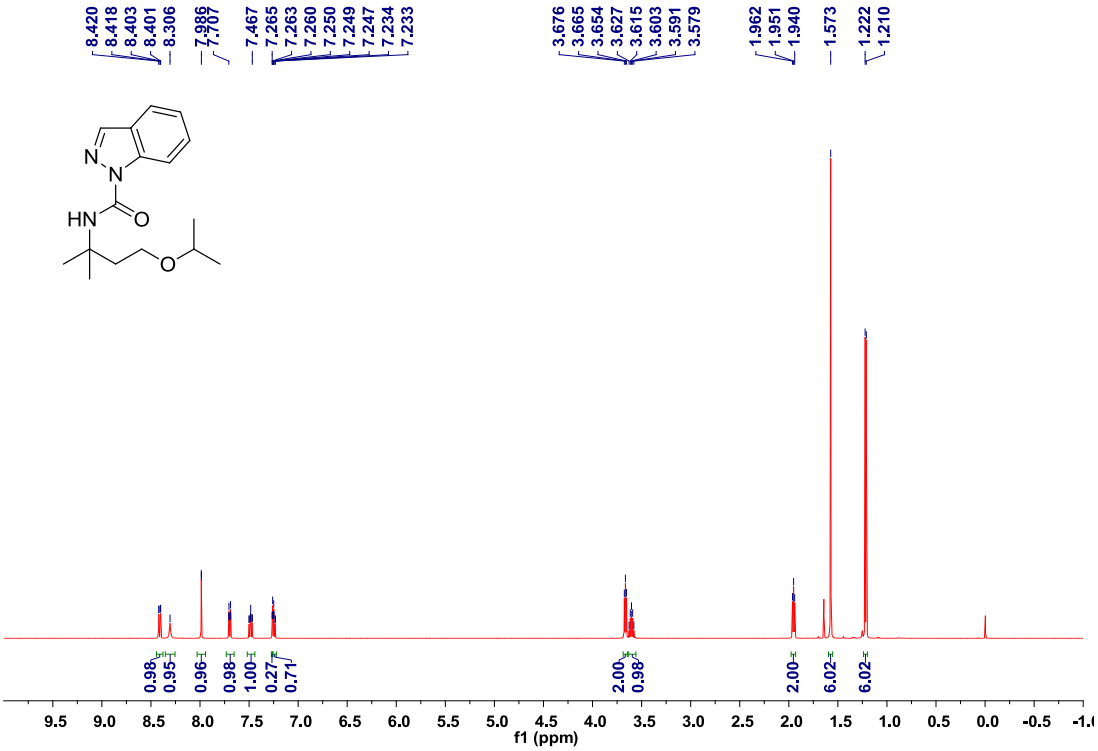


^{13}C NMR, 125 MHz, $CDCl_3$

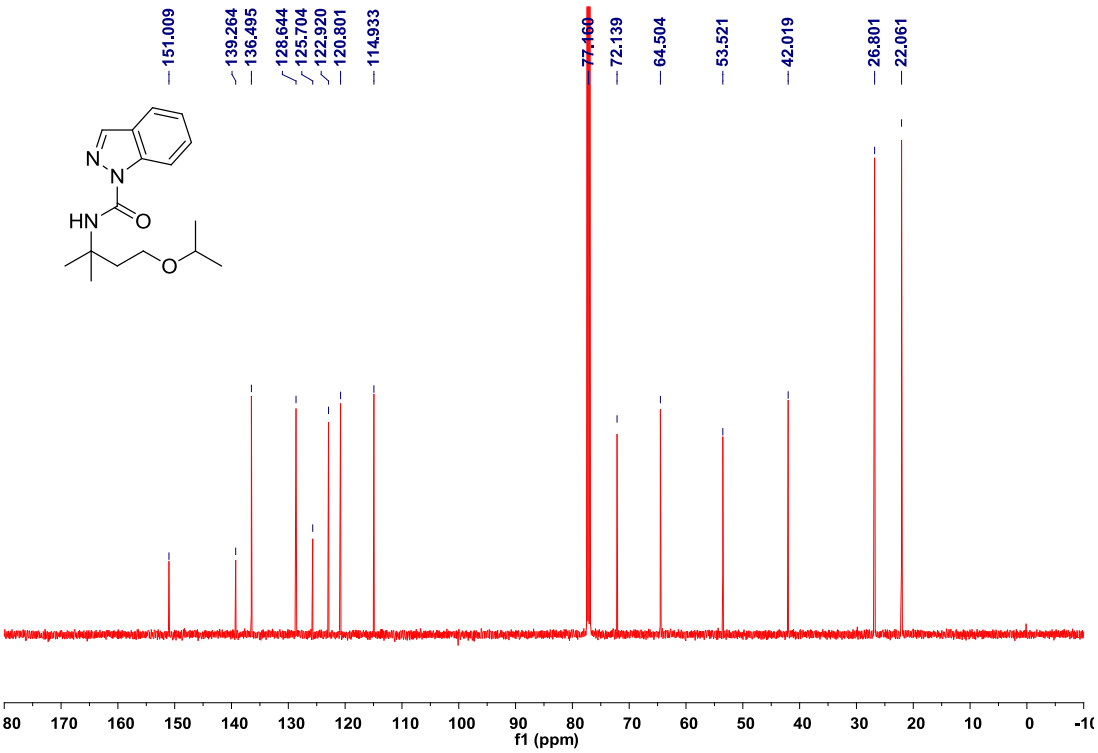


_N_-(4-isopropoxy-2-methylbutan-2-yl)-1_H_-indazole-1-carboxamide (5i)

^{1}H NMR, 500 MHz, $CDCl_3$

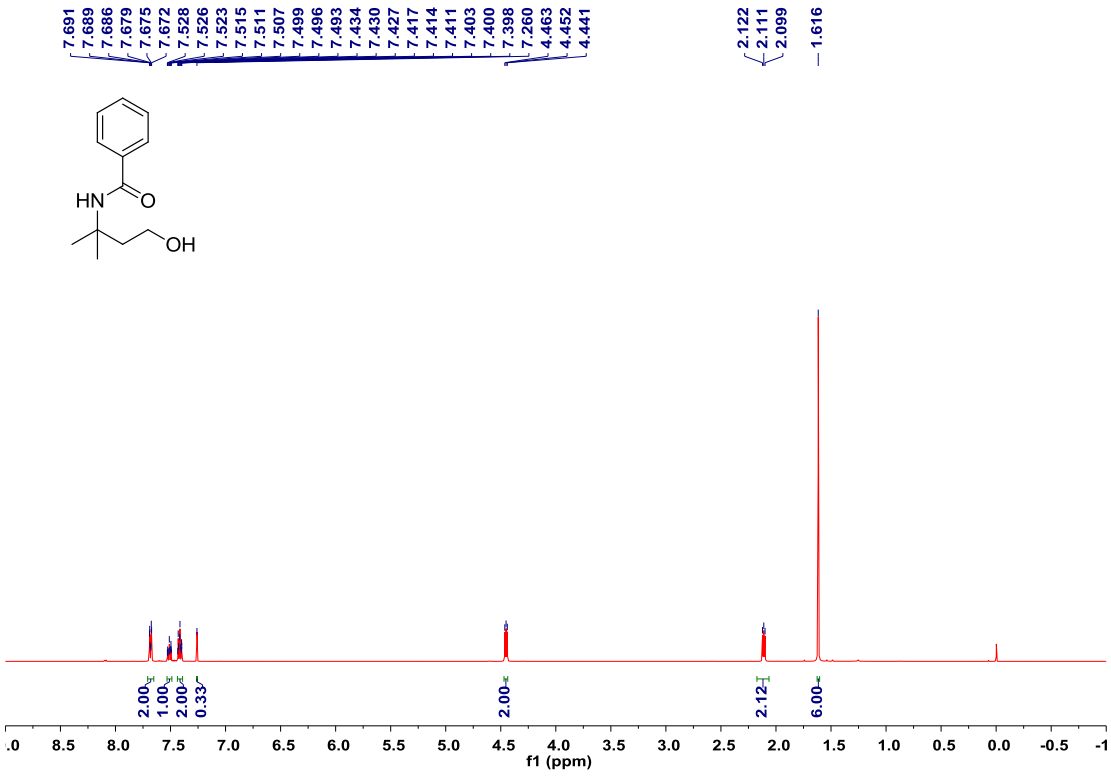


^{13}C NMR, 125 MHz, $CDCl_3$

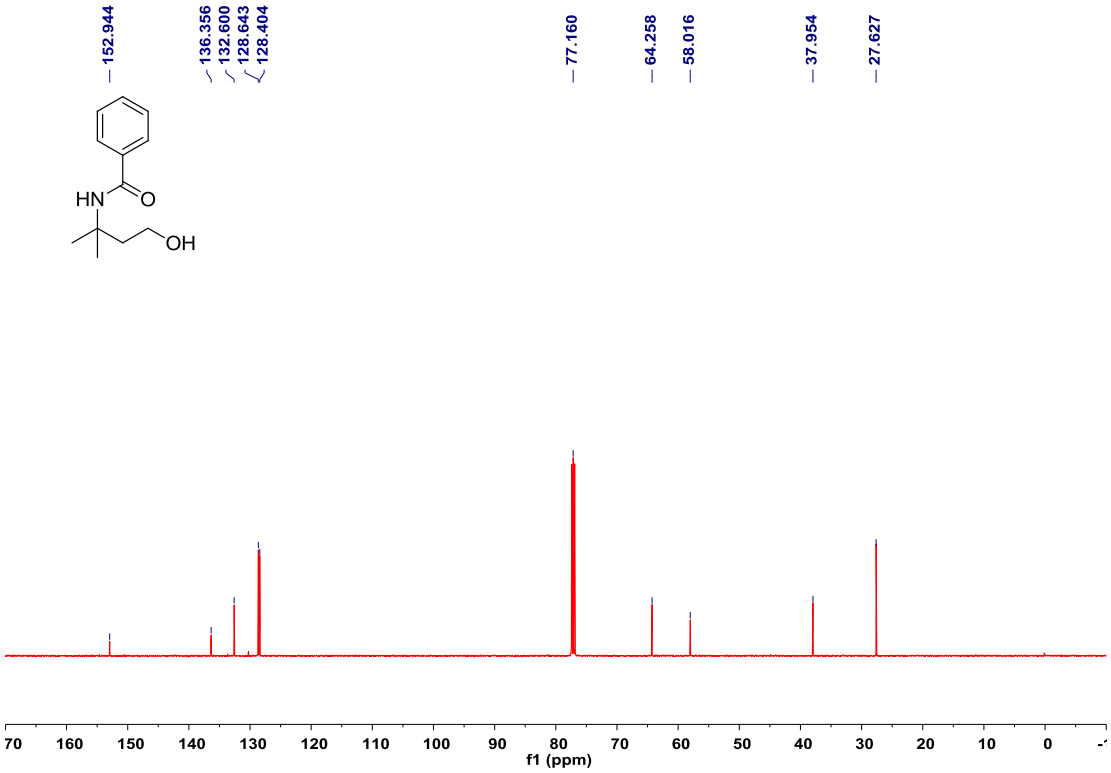


***N*-(4-hydroxy-2-methylbutan-2-yl)benzamide (6)**

^{1}H NMR, 500 MHz, $CDCl_3$

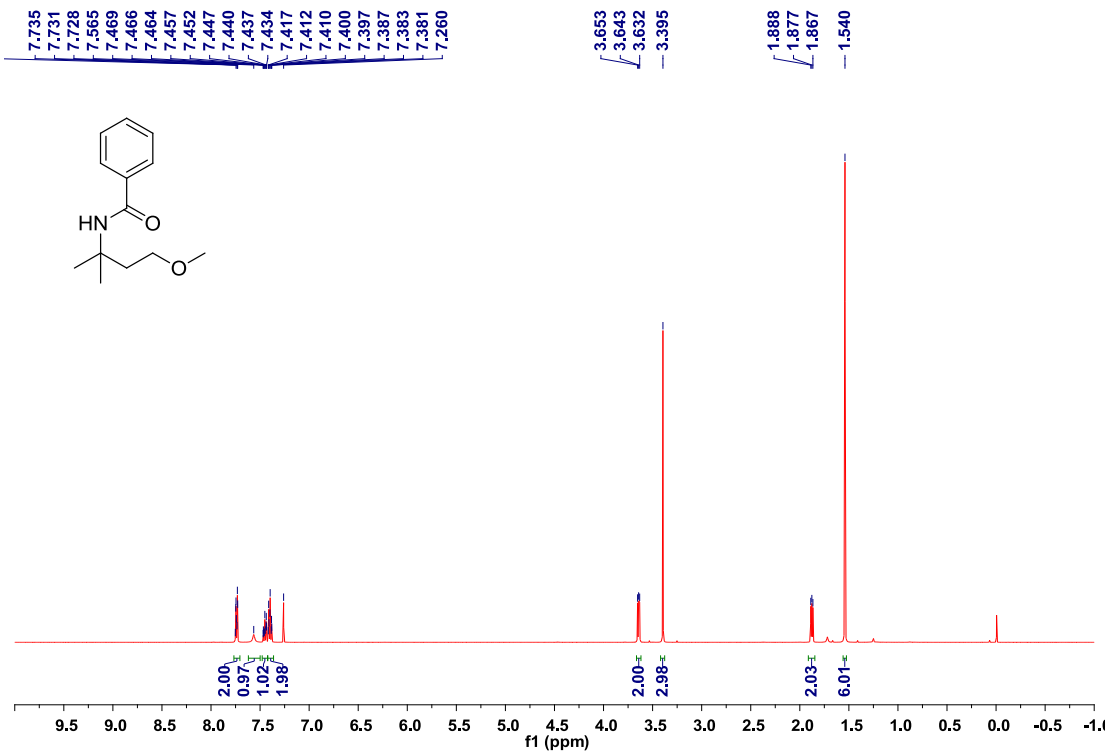


^{13}C NMR, 125 MHz, $CDCl_3$

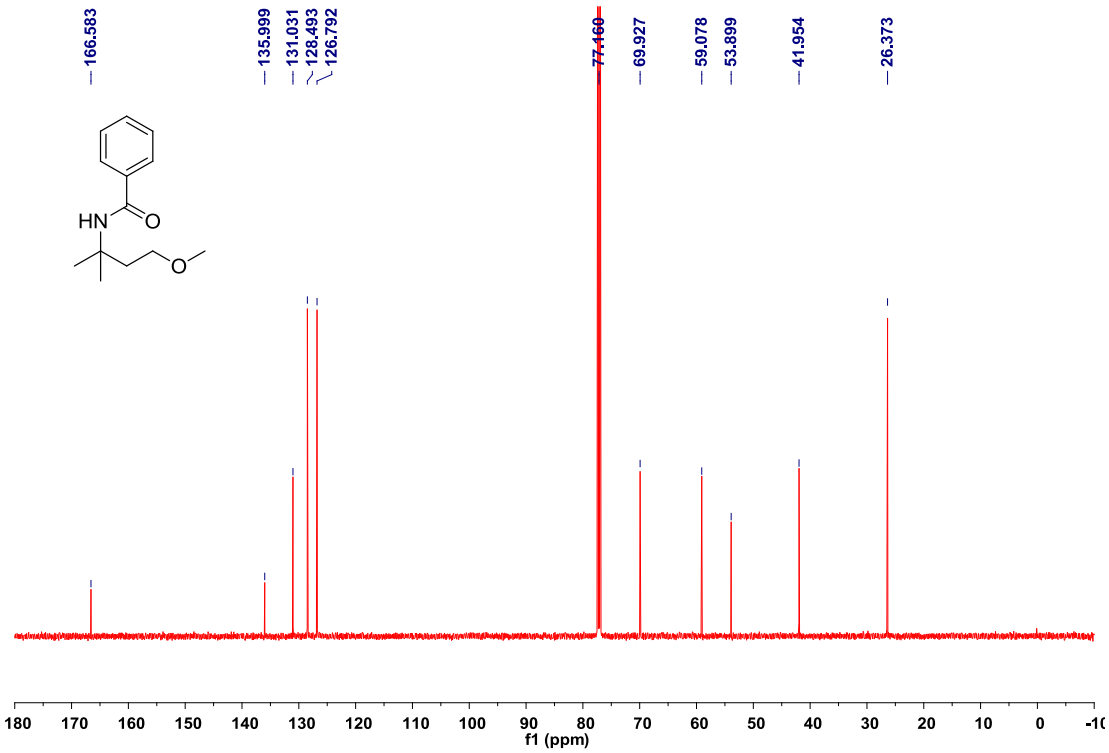


_N_-(4-methoxy-2-methylbutan-2-yl)benzamide (7)

^{1}H NMR, 500 MHz, $CDCl_3$

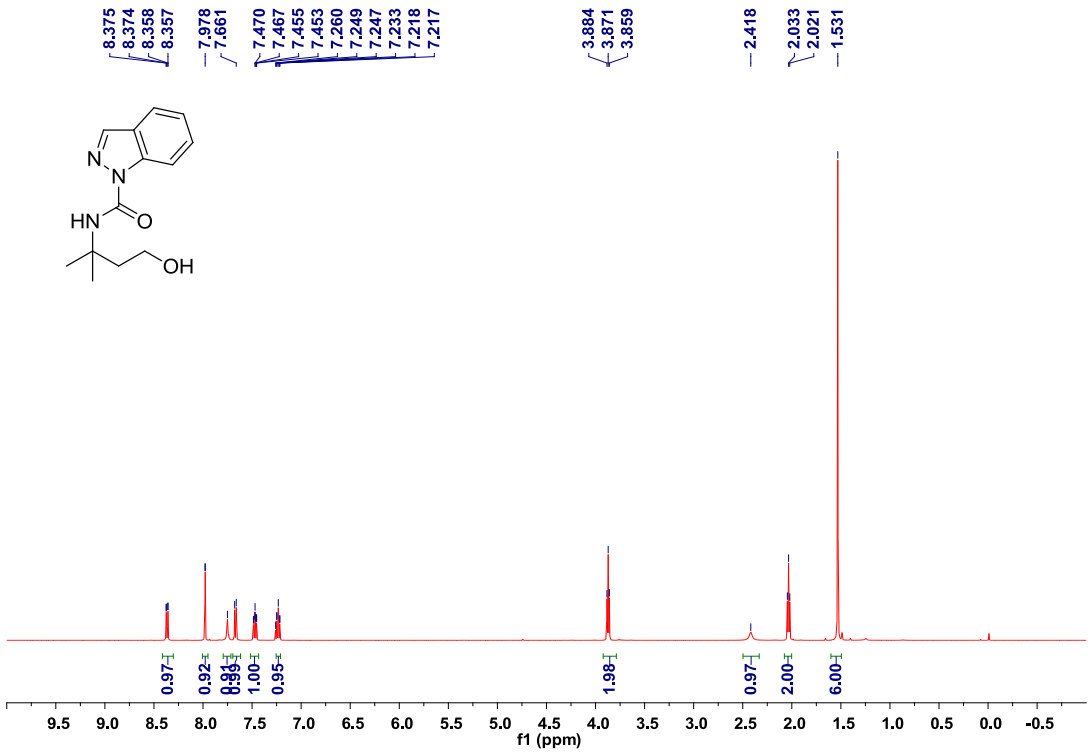


^{13}C NMR, 125 MHz, $CDCl_3$

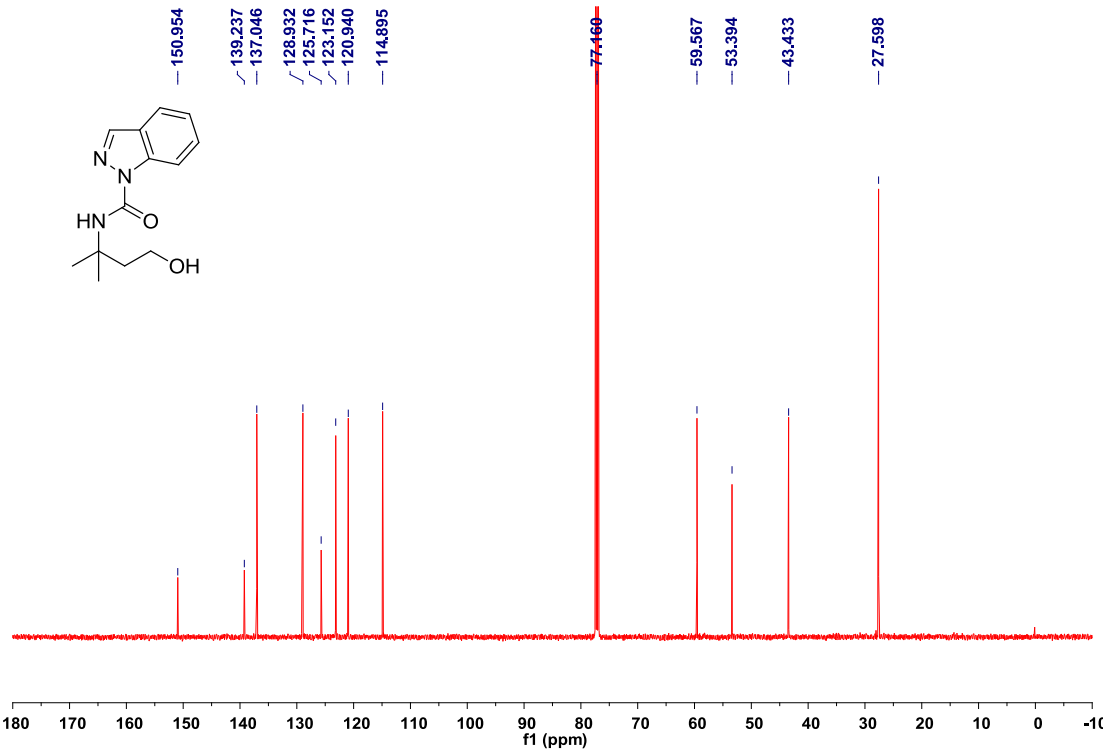


_N_-(4-hydroxy-2-methylbutan-2-yl)-1_H_-indazole-1-carboxamide (8)

^{1}H NMR, 500 MHz, $CDCl_3$

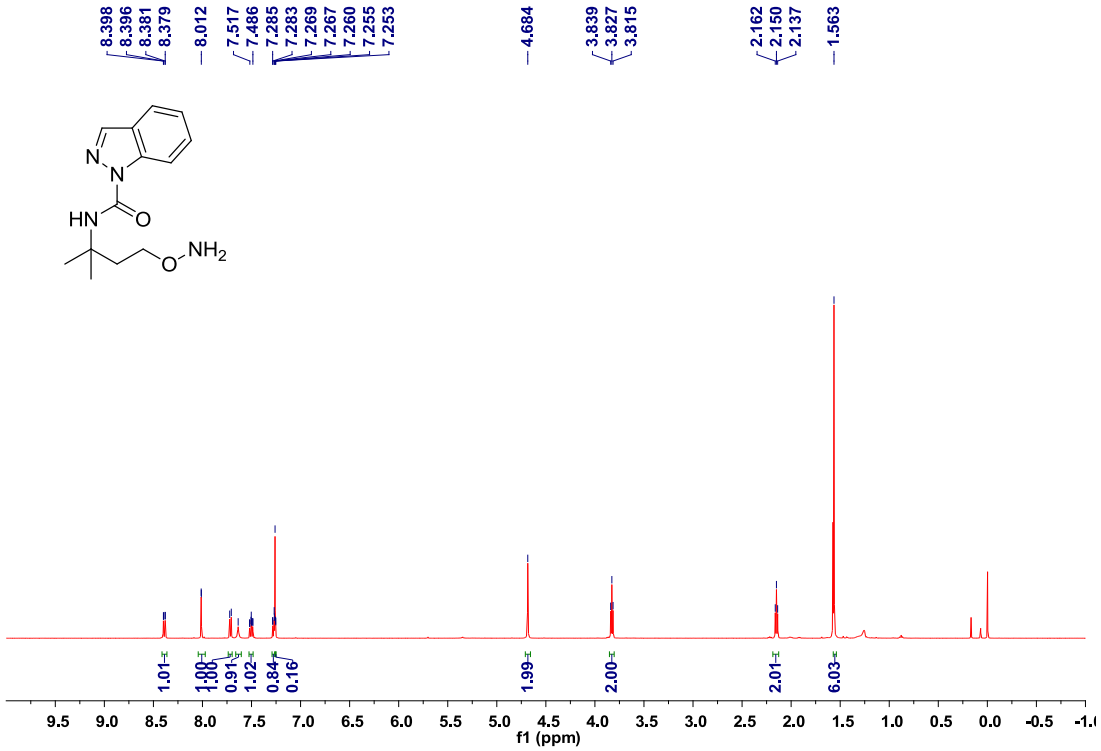


^{13}C NMR, 125 MHz, $CDCl_3$

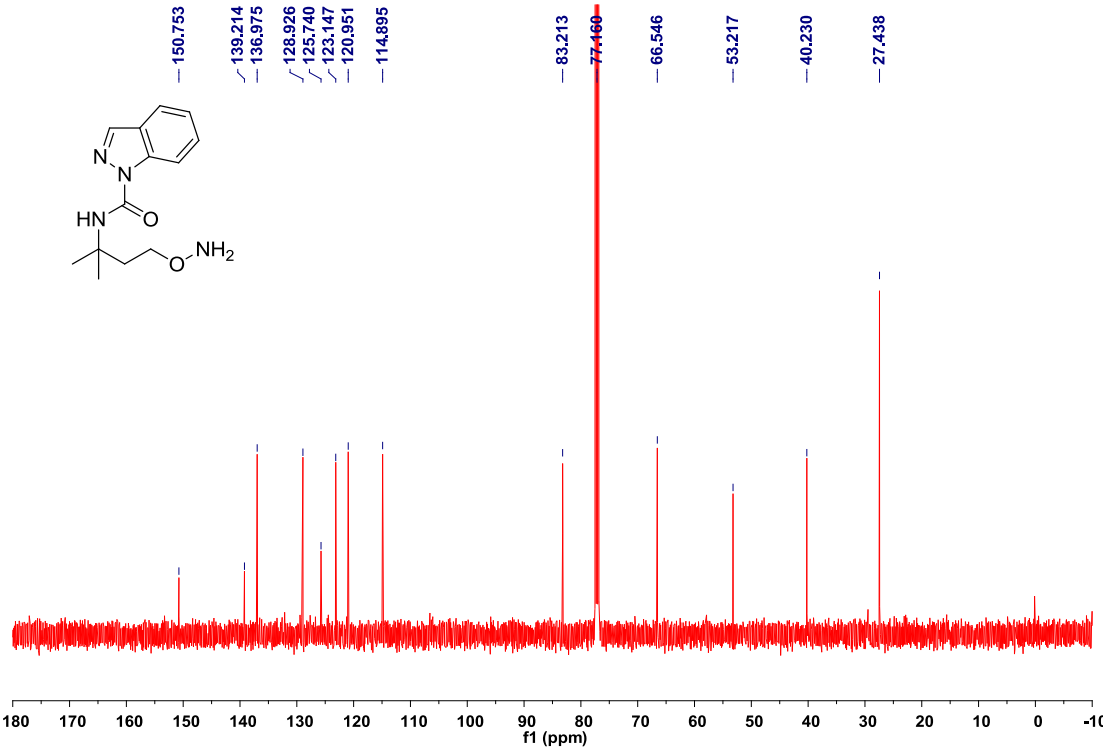


_N_-(4-(aminooxy)-2-methylbutan-2-yl)-1_H_-indazole-1-carboxamide (9)

^{1}H NMR, 500 MHz, $CDCl_3$

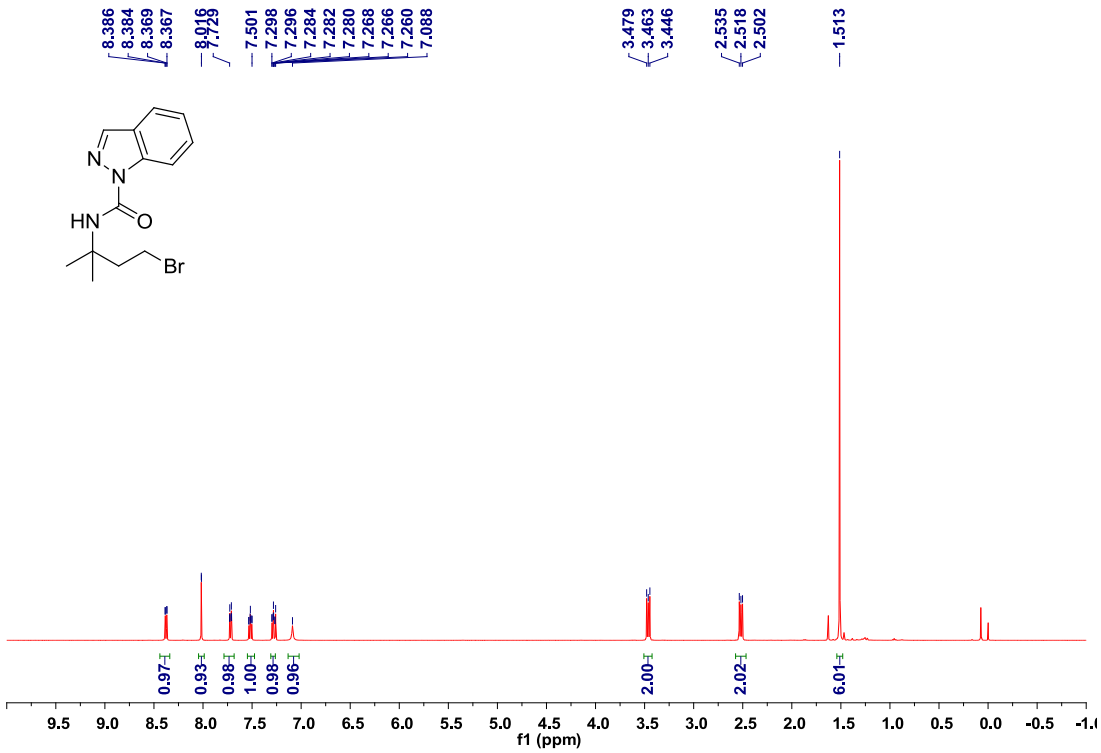


^{13}C NMR, 125 MHz, $CDCl_3$

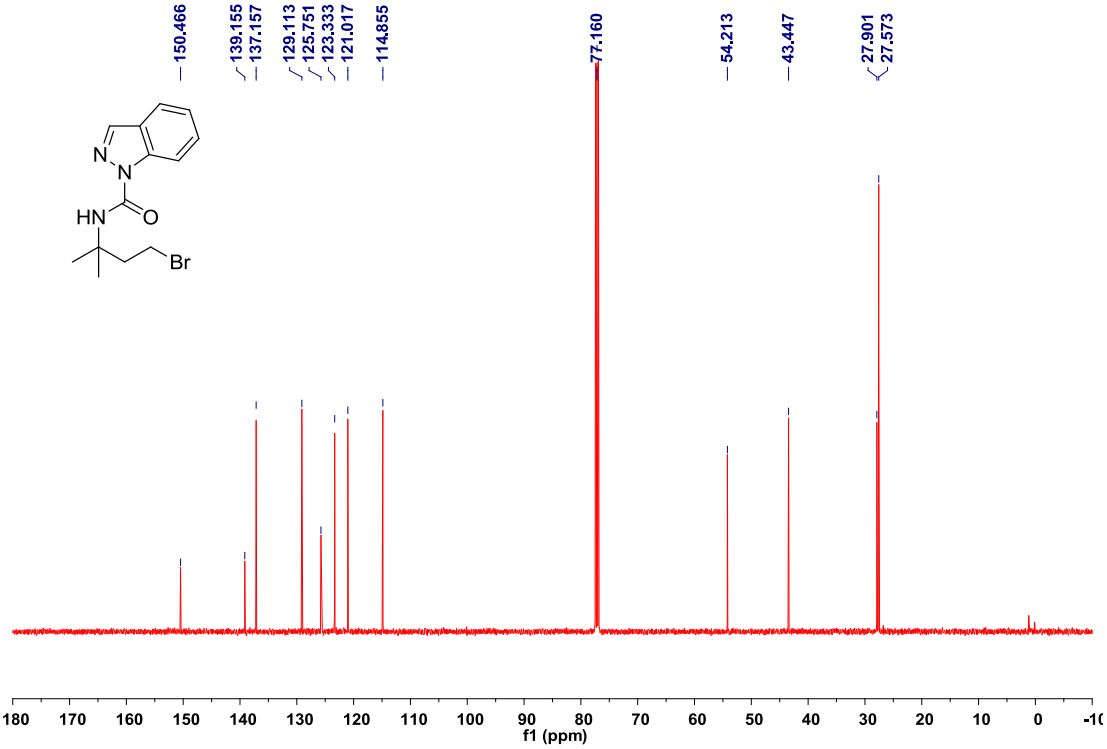


_N_-(4-bromo-2-methylbutan-2-yl)-1_H_-indazole-1-carboxamide (10)

^{1}H NMR, 500 MHz, $CDCl_3$

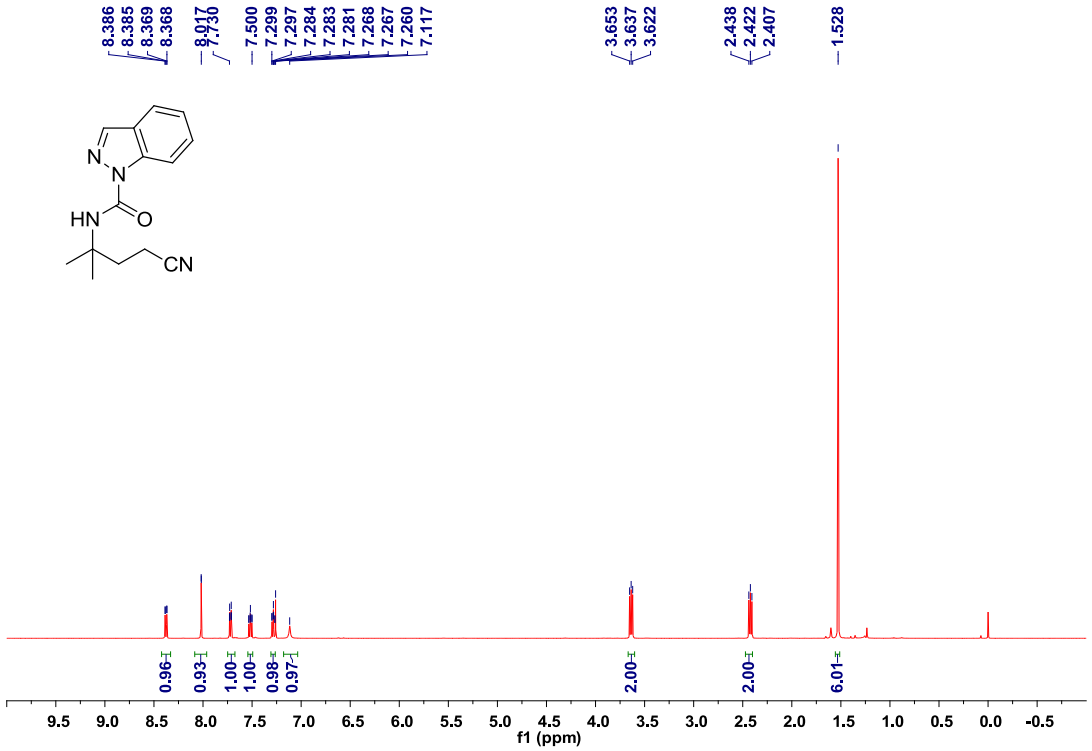


^{13}C NMR, 125 MHz, $CDCl_3$

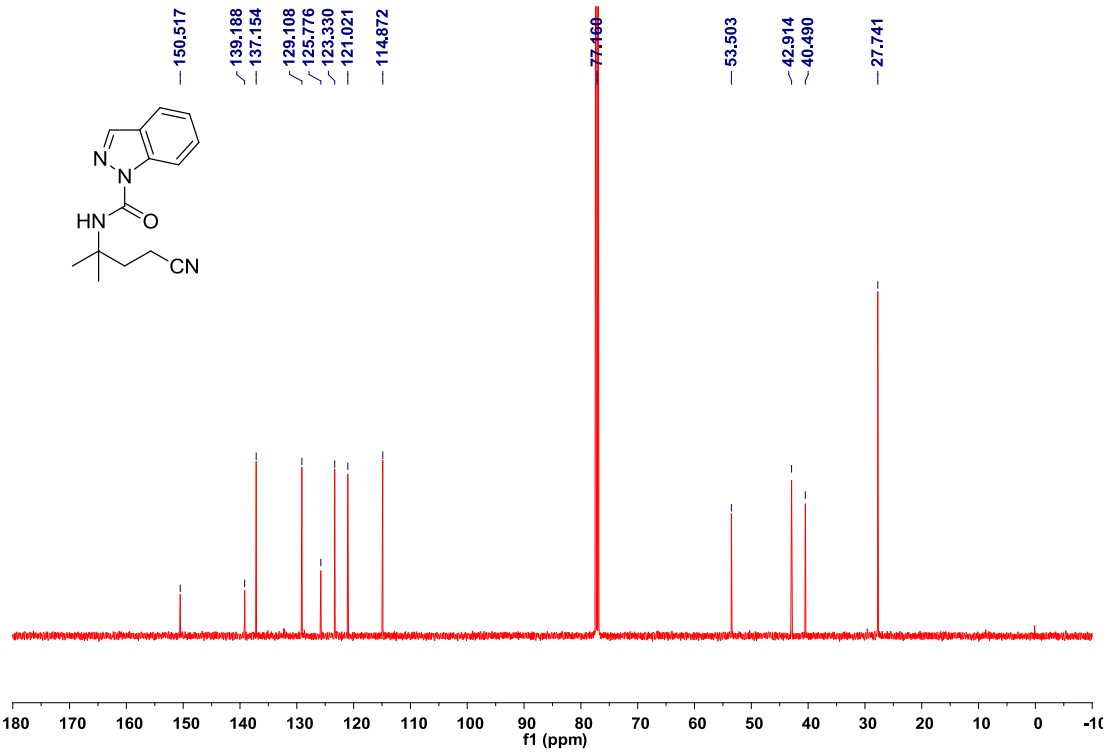


N-(4-cyano-2-methylbutan-2-yl)-1*H*-indazole-1-carboxamide (11)

^{1}H NMR, 500 MHz, $CDCl_3$

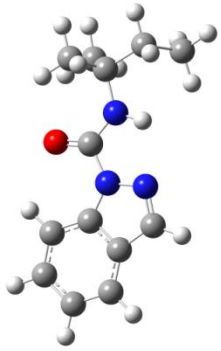


^{13}C NMR, 125 MHz, $CDCl_3$



11. Cartesian coordinates and electronic energies for calculated structures

Table S7. XYZ coordinates of all intermediates and transition states.

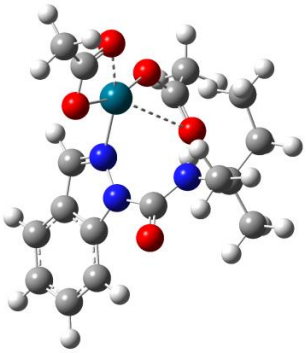


1a

Free Energy = -744.86364 Hartee

C	3.50548200	-0.93089200	-0.12202900
C	3.10795700	-2.21888000	-0.54923800
C	3.93203400	-3.33235000	-0.31302800
C	5.13276800	-3.12520400	0.34536000
C	5.51635200	-1.83276300	0.76601500
C	4.72173100	-0.71736500	0.54491500
H	3.62913600	-4.32979700	-0.64059700
H	5.79663300	-3.96993000	0.54529100
H	6.47131200	-1.70593400	1.28314200
H	5.01694500	0.27916700	0.86874000
C	1.83671700	-2.01194100	-1.17137800
H	1.17952300	-2.74726100	-1.63719500
N	1.49556300	-0.74939500	-1.13047800
N	2.48741900	-0.08137300	-0.50179400
C	2.41468500	1.32524200	-0.29361400
O	3.33621500	1.89658200	0.26065800
N	1.27948300	1.86618100	-0.75620400
C	0.95348400	3.30018300	-0.74815300
C	1.95597000	4.06242200	-1.61868900
C	-0.44783800	3.43751700	-1.36929900
H	2.97855500	3.93987700	-1.23384900
H	1.92620800	3.69561700	-2.65683100
H	1.71625000	5.13674100	-1.62598700
C	-1.59233700	2.77231300	-0.62039700

H	-0.65028400	4.51619100	-1.47082100
H	-0.39822700	3.03890800	-2.39809300
H	-2.53363700	2.89190500	-1.17945400
H	-1.74721700	3.20991500	0.37758100
C	0.97865800	3.84524300	0.68132900
H	0.31400100	3.26848900	1.34175500
H	1.99509600	3.79795200	1.09510700
H	0.64650200	4.89483700	0.68821100
H	0.65084400	1.22721400	-1.23679900
H	-1.43444700	1.68849900	-0.48574100

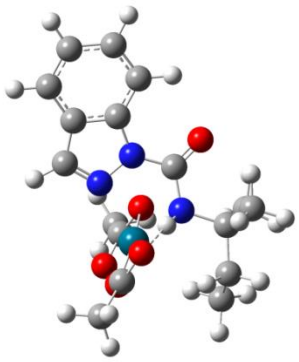


IN1

Free Energy = -1329.6313 Hartee

C	-2.86744400	-0.02675800	-0.43712700
C	-3.06639200	-1.27876900	0.18706500
C	-4.36753700	-1.78747200	0.36624400
C	-5.42524400	-1.02028700	-0.08303400
C	-5.20794800	0.23578900	-0.69923000
C	-3.94002800	0.75737600	-0.88883200
H	-4.52552600	-2.75694400	0.84387400
H	-6.44937900	-1.38211300	0.03387800
H	-6.07151200	0.81171000	-1.04210700
H	-3.77471600	1.71838400	-1.37611600
C	-1.76166000	-1.73750700	0.50435600
H	-1.44535600	-2.67411500	0.96152400
N	-0.87190300	-0.83873100	0.13100600
N	-1.51317700	0.19722200	-0.44928900
C	-0.88401400	1.41922300	-0.88951400
O	-1.35580700	1.96710000	-1.86697100
N	0.12811700	1.82033400	-0.11591000
C	0.85144600	3.08886900	-0.34110600
C	-0.11493600	4.26308800	-0.15720900

C	1.94342100	3.17266300	0.74095000
H	-0.95003300	4.19603800	-0.86932200
H	-0.52465200	4.27444700	0.86525100
H	0.40801500	5.21656500	-0.32795700
C	3.04602300	2.12899700	0.66664300
H	2.38378700	4.18169600	0.68104400
H	1.44532800	3.11499900	1.72359200
H	3.69650900	2.19570100	1.55275100
H	3.68487200	2.26322500	-0.21984600
C	1.46471500	3.12150800	-1.74142000
H	2.07825800	2.22781600	-1.93108900
H	0.68329300	3.16987100	-2.51155200
H	2.10893400	4.00851500	-1.84350400
H	0.21924800	1.38887800	0.82650900
H	2.64034200	1.10520100	0.63003800
Pd	1.09928000	-1.20396600	0.05046500
O	0.19639400	0.75460900	2.44068700
C	0.76486200	-0.27500000	2.81399600
O	1.31874800	-1.14042500	2.03341900
O	2.96033700	-1.85863000	-0.63116200
C	2.45095500	-2.05715600	-1.77866300
O	1.21792200	-1.76281400	-1.91491400
C	0.84055900	-0.62724000	4.27585400
H	0.02121400	-1.32807100	4.50448100
H	1.78751000	-1.12983100	4.51413600
H	0.71615200	0.27131900	4.89384200
C	3.26428000	-2.58934300	-2.89978700
H	3.75117100	-3.52605000	-2.59011800
H	2.64357100	-2.75935200	-3.78814200
H	4.05775200	-1.86383200	-3.13680200

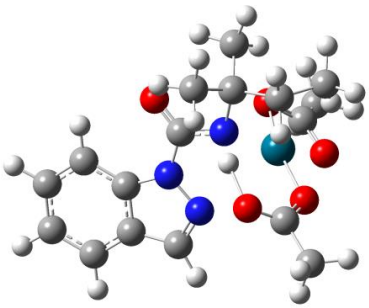


TS1

Free Energy = -1329.604019 Hartee

C	-3.14144000	0.08158800	-0.26421800
C	-3.53629000	-0.73608500	0.81602700
C	-4.89494500	-1.01338400	1.03524900
C	-5.82025000	-0.45321200	0.16811100
C	-5.40813600	0.36703000	-0.90248700
C	-4.06960100	0.64840900	-1.14452800
H	-5.20964900	-1.65235800	1.86315000
H	-6.88595000	-0.64847600	0.31059700
H	-6.16492900	0.79873300	-1.56329600
H	-3.75560600	1.27855400	-1.97471200
C	-2.30672600	-1.10169700	1.45774200
H	-2.15731400	-1.76719700	2.30811400
N	-1.28376500	-0.54991900	0.86210600
N	-1.76075800	0.17901500	-0.17264900
C	-0.92107900	0.92515200	-1.01191900
O	-1.33295300	1.30584900	-2.08103400
N	0.35687400	1.16437300	-0.48594900
C	1.27755600	2.05807500	-1.29167600
C	0.62326500	3.43917100	-1.41623800
C	2.60221000	2.26011400	-0.51186900
H	-0.35332400	3.38915100	-1.91310800
H	0.49338600	3.90340000	-0.42549500
H	1.27768500	4.09498300	-2.00975800
C	3.70597200	1.22558600	-0.66882500
H	3.00002400	3.22897800	-0.85126200
H	2.35619000	2.40380100	0.55085800
H	4.52434100	1.43750600	0.03630100
H	4.13225700	1.23223700	-1.68370200
C	1.54108400	1.45540700	-2.66834800
H	1.88728000	0.41500700	-2.59137000
H	0.63710900	1.47015000	-3.29022500
H	2.31856200	2.04304200	-3.17934500
H	0.28853600	1.51088300	0.52535800
H	3.36388000	0.19815300	-0.46163200
Pd	1.23727700	-0.76045300	0.27722700
O	0.37643700	1.81843000	2.08659400
C	1.17641500	1.04247000	2.62326600
O	1.70796900	0.02163300	2.05047800
O	2.30470200	-2.71634800	0.23095600
C	1.81095600	-2.85270700	-0.92453000
O	1.02446600	-1.92957200	-1.35350600
C	1.61825600	1.24877600	4.04896200
H	1.23185600	0.42423800	4.66830400

H	2.71553300	1.22287500	4.11633500
H	1.23961500	2.20277200	4.43491800
C	2.06944800	-4.04885000	-1.76882200
H	2.80729500	-4.70572900	-1.29233600
H	1.12423700	-4.59494200	-1.91594100
H	2.42264200	-3.73420500	-2.76201800

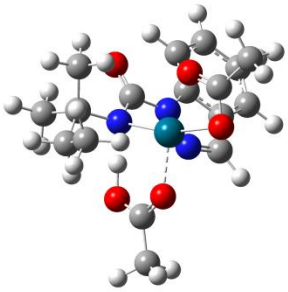


IN2

Free Energy = -1329.615779 Hartee

C	3.14248600	-0.29592800	-0.11557400
C	3.59153700	0.55701400	0.91465200
C	4.95333900	0.86809300	1.03991800
C	5.83426700	0.30637200	0.12764300
C	5.37163700	-0.54844600	-0.89329000
C	4.02674300	-0.86556600	-1.04042600
H	5.30317100	1.52850700	1.83657800
H	6.90253100	0.52529700	0.19706200
H	6.09264000	-0.97518100	-1.59505700
H	3.67767200	-1.52158900	-1.83540600
C	2.40413600	0.90464500	1.63965500
H	2.30697600	1.55801200	2.50663600
N	1.35178900	0.32849000	1.12949100
N	1.76795500	-0.40302500	0.06535500
C	0.88340100	-1.11078400	-0.75646900
O	1.28014300	-1.58015300	-1.79346100
N	-0.44270800	-1.22232700	-0.26636600
C	-1.33328900	-2.24411200	-0.95828600
C	-0.67607000	-3.62151100	-0.80961000
C	-2.69015300	-2.30837300	-0.21527900
H	0.31758500	-3.65898900	-1.27394700
H	-0.58338000	-3.89862600	0.25261800
H	-1.30688300	-4.37723100	-1.30047700
C	-3.76993100	-1.29272900	-0.55846000

H	-3.09370200	-3.30917100	-0.43691700
H	-2.49241200	-2.30809500	0.86744100
H	-4.64825800	-1.46063200	0.08496400
H	-4.10681200	-1.38424600	-1.60175000
C	-1.54861600	-1.89335100	-2.42723000
H	-1.88504600	-0.85316400	-2.54686500
H	-0.63579500	-2.03395100	-3.01729900
H	-2.33011100	-2.55095100	-2.83681100
H	-0.44113200	-1.42751500	0.79055000
H	-3.45040900	-0.24936600	-0.40065600
Pd	-1.23274500	0.72338000	-0.02200900
O	-0.74909200	-1.52365000	2.33961200
C	-1.41590300	-0.53397900	2.67485900
O	-1.79502200	0.40417900	1.88639500
O	-1.86280200	2.70471500	-0.23733600
C	-1.43050700	2.70368500	-1.43182500
O	-0.91060500	1.61772500	-1.85287900
C	-1.83006500	-0.35206900	4.11110200
H	-1.09383100	0.29750300	4.60728200
H	-2.80920700	0.13459100	4.18254000
H	-1.84418400	-1.31865600	4.62818500
C	-1.48839100	3.91817400	-2.28216000
H	-2.34158400	4.54595100	-1.99208100
H	-0.56706200	4.49783800	-2.11211600
H	-1.54107600	3.65517300	-3.34744200

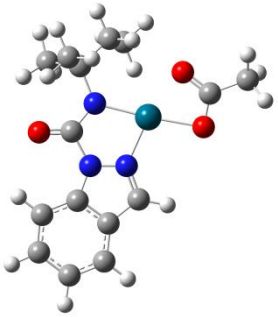


TS2

Free Energy = -1329.606747 Hartee

C	-3.02981200	-0.36189700	0.23504500
C	-3.54776400	0.07731500	-1.00366100
C	-4.91894400	0.33652800	-1.15535300
C	-5.74191600	0.14871900	-0.05647800
C	-5.21298800	-0.29007100	1.17515700
C	-3.86067800	-0.55348700	1.34881600

H	-5.31910200	0.67548900	-2.11385300
H	-6.81444800	0.34091100	-0.13976200
H	-5.88925000	-0.42917500	2.02288100
H	-3.45965700	-0.89523500	2.30061500
C	-2.40709300	0.14342600	-1.86545500
H	-2.36494500	0.43828500	-2.91479900
N	-1.32015600	-0.21333700	-1.23558800
N	-1.66681300	-0.52177800	0.03533100
C	-0.72517200	-0.95016700	1.00488700
O	-1.14806800	-1.24312200	2.10357900
N	0.59042000	-1.01556700	0.57336300
C	1.57096400	-1.64006000	1.53620100
C	1.12750600	-3.08696800	1.80323600
C	2.97154300	-1.73736500	0.87760600
H	0.12544100	-3.13490300	2.24617500
H	1.13240800	-3.67607800	0.87210900
H	1.83271900	-3.56081600	2.50241000
C	3.88249400	-0.51858600	0.86741200
H	3.49640900	-2.53291600	1.43082900
H	2.85528800	-2.13105700	-0.14410000
H	4.82704500	-0.76977100	0.35932200
H	4.13767100	-0.18370500	1.88414400
C	1.66786000	-0.85609800	2.84527800
H	1.87750100	0.20750400	2.65845500
H	0.73768500	-0.92798700	3.42186300
H	2.48853600	-1.26225600	3.45698500
H	0.70518200	-1.66603100	-0.64230600
H	3.44952800	0.34320100	0.33286000
Pd	1.14129100	0.79789800	-0.26803200
O	0.91772400	-2.11998900	-1.65207400
C	1.46649900	-1.24539600	-2.39769500
O	1.73641600	-0.08098000	-2.01726900
O	1.52333400	2.82195800	-0.67919400
C	1.07783500	3.12428400	0.46898800
O	0.69044100	2.15922500	1.20780900
C	1.77900900	-1.63156700	-3.80413900
H	0.87448000	-1.45506300	-4.40944900
H	2.59201000	-1.01552400	-4.20692300
H	2.02791500	-2.69876000	-3.86456100
C	0.97226000	4.53106200	0.92797500
H	1.69225400	5.16541100	0.39522700
H	-0.04531000	4.89231000	0.70669200
H	1.12873400	4.59287200	2.01320400

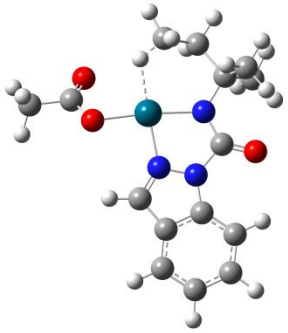


IN3

Free Energy = -1100.574098 Hartee

C	-2.96463200	0.06005600	0.02066000
C	-3.13387400	-1.32965000	-0.20673400
C	-4.42649800	-1.88045800	-0.29693700
C	-5.50356800	-1.02580600	-0.15542200
C	-5.31546700	0.35849600	0.07100400
C	-4.05723700	0.92927200	0.16293100
H	-4.56540900	-2.94938200	-0.47312900
H	-6.52070000	-1.41965500	-0.21908400
H	-6.19464100	0.99954700	0.17646300
H	-3.90747900	1.99386000	0.33643900
C	-1.81657700	-1.85887400	-0.29405700
H	-1.47852600	-2.88171100	-0.45442200
N	-0.95799300	-0.87343900	-0.13903700
N	-1.61504600	0.27961700	0.05229200
C	-0.84922900	1.48476700	0.22414500
O	-1.46566300	2.50905000	0.47392500
N	0.46071600	1.26475100	0.06052000
C	1.38987400	2.41693700	0.15799500
C	1.49766800	2.85334800	1.62278500
C	2.78968400	2.00031100	-0.32845400
H	0.51309400	3.14990100	2.01331600
H	1.88861000	2.03135700	2.24378200
H	2.17996900	3.71201600	1.72460600
C	2.90558300	1.57593000	-1.78427000
H	3.44721400	2.86758600	-0.15022900
H	3.16605200	1.19742500	0.32000200
H	3.92730700	1.22682600	-2.00160400
H	2.68781800	2.40197200	-2.47874200
C	0.91211900	3.59414300	-0.70639700
H	0.68792800	3.27007600	-1.73403800
H	0.00965400	4.05901900	-0.29395400
H	1.71028200	4.35150100	-0.75677000

H	2.21819300	0.74808100	-2.02520800
Pd	0.99683200	-0.69592400	0.03307900
O	1.68963700	-2.65292900	0.05912900
C	2.88362500	-2.25990200	0.25369800
O	3.06833000	-1.00882200	0.34130700
C	4.01106300	-3.22351700	0.33327100
H	4.40157300	-3.38330500	-0.68510400
H	4.82123100	-2.81877600	0.95365600
H	3.66616500	-4.18902900	0.72579100

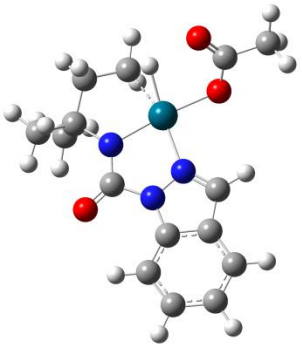


TS3

Free Energy = -1100.559762 Hartee

C	-2.90019100	0.03199800	0.04413000
C	-2.97228100	-1.38187600	-0.04095000
C	-4.22282300	-2.02832800	-0.05395000
C	-5.35704100	-1.24145900	0.01613100
C	-5.26584200	0.16810200	0.10041200
C	-4.05069900	0.83215300	0.11672800
H	-4.28615600	-3.11669800	-0.11925400
H	-6.34403200	-1.70986200	0.00658800
H	-6.18738100	0.75366100	0.15397000
H	-3.97696900	1.91671500	0.18078500
C	-1.62213700	-1.82622100	-0.09804800
H	-1.20896500	-2.83099600	-0.17154000
N	-0.83465300	-0.77475900	-0.04927300
N	-1.56908900	0.34962600	0.03616400
C	-0.89584400	1.62347700	0.07584100
O	-1.58307600	2.63228300	0.08194500
N	0.43193200	1.47018500	0.10453300
C	1.32248600	2.65278900	0.08875400
C	0.97270100	3.61113700	1.23434100
C	2.77388100	2.19529900	0.32234000
H	-0.03046200	4.03607600	1.10738500

H	1.01075100	3.08436800	2.20105300
H	1.70337200	4.43404800	1.26599300
C	3.32207300	1.11911200	-0.59694200
H	3.40717100	3.09170300	0.22584400
H	2.87515700	1.85995500	1.36776400
H	2.98911000	0.06878900	-0.31505300
H	4.40946200	1.00027400	-0.47306600
C	1.19698200	3.37255200	-1.25831300
H	1.45885100	2.70609300	-2.09449500
H	0.16532400	3.72159600	-1.40900200
H	1.86478400	4.24748300	-1.29244700
H	3.11165200	1.28540700	-1.66192600
Pd	1.09875500	-0.39851800	-0.14504500
O	1.57713300	-2.34671200	-0.43531100
C	2.60338900	-2.71910300	0.26153600
O	3.22578800	-1.96001300	1.00174900
C	2.98371700	-4.16685400	0.08539000
H	3.25178200	-4.35478900	-0.96581000
H	3.83235000	-4.42544900	0.73092600
H	2.12515500	-4.81301500	0.32294700

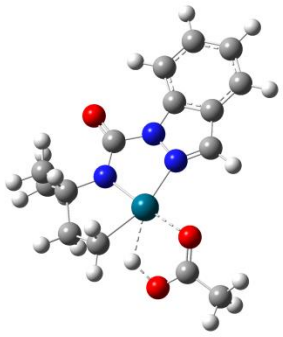


IN4

Free Energy = -1100.560999 Hartee

C	2.90763300	-0.07222200	-0.06892600
C	2.91704200	-1.48258500	0.07434200
C	4.13632200	-2.18573300	0.09011000
C	5.30431100	-1.45687200	-0.03580600
C	5.27621400	-0.04931300	-0.17677900
C	4.09238100	0.66931700	-0.19638800
H	4.15107700	-3.27233600	0.19994200
H	6.26849200	-1.97066500	-0.02668900
H	6.22226000	0.48985200	-0.27359000
H	4.06756900	1.75277800	-0.30353400

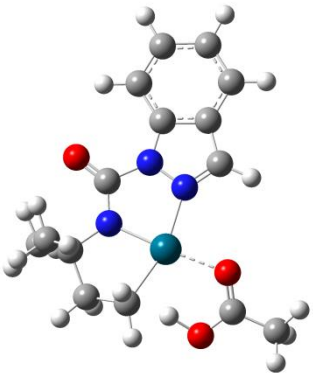
C	1.54786700	-1.85691900	0.17521900
H	1.09434800	-2.83940600	0.29845300
N	0.80272300	-0.77738800	0.09539000
N	1.59231800	0.30612600	-0.05235200
C	0.98788700	1.61343700	-0.11563800
O	1.71855100	2.59094600	-0.13135800
N	-0.34366200	1.52548700	-0.14752000
C	-1.21919700	2.70558300	-0.02524400
C	-0.90588200	3.76316600	-1.08471500
C	-2.64481100	2.17566500	-0.24801800
H	0.08350900	4.20950300	-0.92200700
H	-0.92697900	3.31823800	-2.09210500
H	-1.66389900	4.56133000	-1.04826200
C	-2.86759900	0.78865500	0.35289800
H	-3.36821900	2.89051800	0.17351700
H	-2.84538300	2.12123200	-1.32991500
H	-2.77379500	-0.07985700	-0.43237300
H	-3.95015900	0.56546700	0.40536800
C	-1.08377100	3.30025000	1.38018900
H	-1.37607600	2.56923200	2.15089800
H	-0.04380600	3.60479600	1.56995600
H	-1.72688300	4.18742200	1.48738500
H	-2.58603900	0.70026100	1.42054500
Pd	-1.14996800	-0.27007200	0.13382200
O	-1.79290900	-2.17192200	0.45865200
C	-2.78066100	-2.60400400	-0.25676900
O	-3.39746600	-1.92329400	-1.07399700
C	-3.12300200	-4.05384700	-0.01267800
H	-3.28884200	-4.22971400	1.06052300
H	-4.01657100	-4.34183300	-0.58018500
H	-2.27552600	-4.68638500	-0.31953400



TS4

Free Energy = -1100.541004 Hartee

C	2.95499900	-0.10006200	-0.04769100
C	2.98242300	-1.51513900	0.03325800
C	4.21069400	-2.20254700	0.03179000
C	5.37069700	-1.45450300	-0.04892100
C	5.32532200	-0.04268400	-0.12895400
C	4.13211200	0.66065100	-0.13043800
H	4.23874300	-3.29277700	0.09338800
H	6.34138300	-1.95606600	-0.05166000
H	6.26496900	0.51253500	-0.19176100
H	4.09344600	1.74714900	-0.19178300
C	1.61656800	-1.90941500	0.10060600
H	1.17823700	-2.90376300	0.17396400
N	0.85589500	-0.83820200	0.06119600
N	1.63430800	0.25975400	-0.02741000
C	1.02050700	1.56582100	-0.07234400
O	1.75096900	2.54539000	-0.08790700
N	-0.30879000	1.47415000	-0.09704400
C	-1.18359700	2.66050800	-0.08228200
C	-0.82140000	3.65045600	-1.19186400
C	-2.59970200	2.12189600	-0.33721600
H	0.16392000	4.10279100	-1.02052700
H	-0.80688400	3.14468700	-2.17045600
H	-1.57509000	4.45235200	-1.23464900
C	-2.90317600	0.83888800	0.42996900
H	-3.33054800	2.90925200	-0.08333800
H	-2.71162300	1.93131000	-1.41776700
H	-3.05689100	-0.39758500	-0.21849000
H	-3.98928100	0.63882900	0.37670500
C	-1.09760700	3.34633500	1.28521900
H	-1.40146300	2.66311300	2.09362000
H	-0.06627200	3.67441400	1.48300400
H	-1.75189300	4.23152400	1.31794100
H	-2.72792100	0.93912200	1.51577800
Pd	-1.11226500	-0.32065600	0.16526900
O	-1.81712900	-2.25758900	0.35799800
C	-2.94779800	-2.43792000	-0.17346300
O	-3.63038800	-1.47805900	-0.63154600
C	-3.48300500	-3.82842800	-0.28778800
H	-2.94093600	-4.51766400	0.37036700
H	-4.55749700	-3.83972300	-0.06029400
H	-3.35994000	-4.16032700	-1.33123100

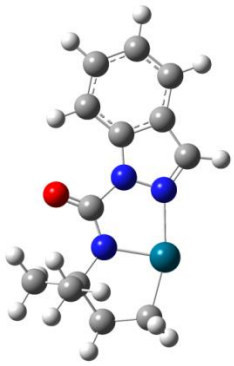


IN5

Free Energy = -1100.565886 Hartee

C	2.96463900	-0.12002600	-0.04342400
C	2.98901900	-1.53561600	0.02530500
C	4.21567500	-2.22576300	0.02131200
C	5.37789300	-1.47997300	-0.04979000
C	5.33589200	-0.06749300	-0.11778800
C	4.14409300	0.63837200	-0.11637100
H	4.24108200	-3.31658500	0.07361900
H	6.34738200	-1.98387900	-0.05422500
H	6.27689000	0.48625000	-0.17329500
H	4.10787200	1.72540000	-0.16856000
C	1.62159500	-1.92625200	0.08554300
H	1.18210900	-2.92079700	0.14972400
N	0.86196100	-0.85409900	0.05318600
N	1.64432900	0.24219000	-0.02331200
C	1.03861000	1.55251300	-0.06367200
O	1.77702400	2.52684300	-0.07363100
N	-0.29041000	1.47174200	-0.09254900
C	-1.15525200	2.66480600	-0.08758000
C	-0.77619200	3.65140600	-1.19443000
C	-2.56938800	2.13036200	-0.35433200
H	0.21076200	4.09708000	-1.01484300
H	-0.75621200	3.14488200	-2.17259000
H	-1.52380500	4.45858900	-1.24495000
C	-2.87514100	0.84536100	0.41355900
H	-3.30226600	2.92022400	-0.11182000
H	-2.66865100	1.93734800	-1.43601200
H	-3.16283400	-0.44705900	-0.21256700
H	-3.96231400	0.65843300	0.33287000
C	-1.07724600	3.35175700	1.27978200
H	-1.39086100	2.67069700	2.08623200

H	-0.04585800	3.67492200	1.48561400
H	-1.72733000	4.24030800	1.30665200
H	-2.74799100	0.97987700	1.50354200
Pd	-1.11671100	-0.31318900	0.16266100
O	-1.85405500	-2.24836600	0.33452100
C	-2.99699000	-2.41421900	-0.15443300
O	-3.69830500	-1.43063000	-0.55884900
C	-3.55686200	-3.78833900	-0.29924400
H	-2.98925600	-4.50862300	0.30116100
H	-4.61813100	-3.79709700	-0.01627900
H	-3.49241000	-4.07627900	-1.36087900

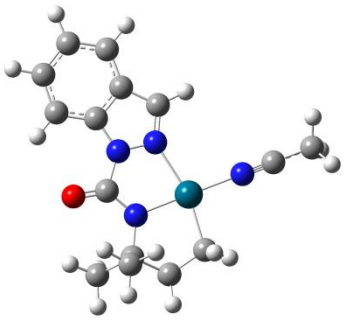


TS5

Free Energy = -871.49473 Hartee

C	2.43447900	0.40396300	-0.00314100
C	3.05099200	-0.87158100	-0.02347300
C	4.45340500	-0.98516600	-0.02123500
C	5.19866100	0.17988300	0.00160000
C	4.56926000	1.44607700	0.02176000
C	3.19088100	1.58738100	0.02016200
H	4.93241800	-1.96690300	-0.03777400
H	6.29013600	0.12755700	0.00371500
H	5.19166600	2.34479000	0.03872000
H	2.70370500	2.56077800	0.03590100
C	1.96956600	-1.79824300	-0.04701000
H	1.99077800	-2.88761600	-0.06596600
N	0.82688600	-1.15059500	-0.04428900
N	1.08147800	0.17686200	-0.01735800
C	0.00410500	1.14080600	0.00421100
O	0.29991700	2.32291900	0.11776500
N	-1.19210400	0.56886400	-0.12121600
Pd	-1.30423300	-1.39371800	0.00695400

C	-2.46452900	1.32868800	-0.04589100
C	-2.47196900	2.53219700	-0.98987100
C	-3.52960800	0.31578500	-0.49190800
H	-1.75104400	3.29758000	-0.67542900
H	-2.22132400	2.22019200	-2.01641100
H	-3.47799500	2.98027600	-1.00823800
C	-3.27429100	-1.06473600	0.10416900
H	-4.53714500	0.69983500	-0.24553600
H	-3.48403400	0.24452300	-1.59212300
H	-3.81850100	-1.86276500	-0.43345600
H	-3.54785600	-1.12113500	1.17463900
C	-2.69969500	1.78613200	1.39615800
H	-2.73315800	0.92771700	2.08505500
H	-1.89099100	2.45775300	1.72199800
H	-3.65265600	2.33206100	1.47975500

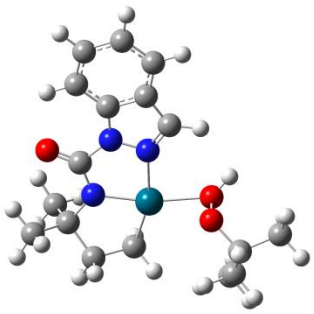


IN6

Free Energy = -1004.245626 Hartee

C	-2.79010100	-0.01883500	0.00729900
C	-2.92950700	1.38968100	-0.06859500
C	-4.20718300	1.97993400	-0.06487200
C	-5.30733000	1.14559700	0.01555500
C	-5.15256000	-0.25853600	0.09097800
C	-3.90788100	-0.86661300	0.08835000
H	-4.31949100	3.06506900	-0.12405900
H	-6.31382000	1.57103800	0.02135300
H	-6.04618500	-0.88558800	0.15249000
H	-3.78495300	-1.94679800	0.14671200
C	-1.59571300	1.88329700	-0.13810400
H	-1.23814300	2.91057200	-0.20318000
N	-0.74822100	0.87949700	-0.11049000
N	-1.44393900	-0.27425200	-0.02456800
C	-0.75688500	-1.54968100	0.03669300

O	-1.44243000	-2.55120800	0.20200300
N	0.55645200	-1.41119700	-0.10955200
C	1.49434400	-2.55229900	-0.02022600
C	1.08662200	-3.71578000	-0.92657500
C	2.83521900	-1.97348500	-0.50138900
H	0.14884500	-4.17696000	-0.59123500
H	0.94995900	-3.36857500	-1.96348800
H	1.87742900	-4.48257400	-0.92794600
C	3.09861400	-0.57642500	0.05672800
H	3.65555600	-2.67488100	-0.25805400
H	2.79443100	-1.91569000	-1.60296800
H	3.90854400	-0.06484900	-0.49048500
C	1.58495200	-3.02645700	1.43354000
H	1.91375100	-2.21121300	2.09694800
H	0.60214400	-3.37802200	1.78284800
H	2.30054300	-3.85840700	1.52985900
H	3.38013000	-0.59516100	1.12543200
Pd	1.34814500	0.41341300	-0.06478900
C	3.22405200	4.60712100	0.16397100
H	3.51262200	4.93562100	-0.84509800
H	4.11539600	4.57591200	0.80710400
H	2.49460900	5.31474000	0.58375800
C	2.63533700	3.29101100	0.09218000
N	2.16449500	2.23841400	0.03476200

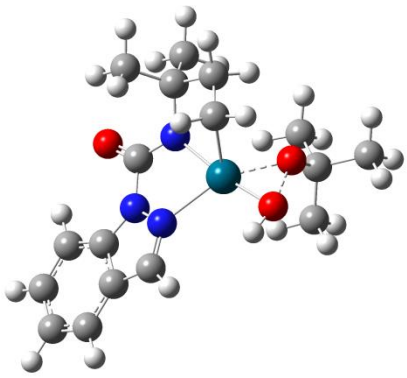


IN7

Free Energy = -1180.189273 Hartee

C	-2.40300800	1.83327300	0.01062200
C	-1.42866000	2.86177100	-0.02124200
C	-1.82075400	4.21306200	-0.04321000
C	-3.17452600	4.49654800	-0.03367000
C	-4.13534100	3.45909700	-0.00213300
C	-3.77822100	2.12072700	0.02038800
H	-1.07332500	5.00961300	-0.06744100

H	-3.51298600	5.53538700	-0.05062500
H	-5.19653200	3.72222200	0.00461900
H	-4.51457300	1.31921800	0.04386200
C	-0.17891000	2.17886700	-0.02309500
H	0.83323700	2.58000900	-0.04889700
N	-0.38055000	0.88105000	0.00864300
N	-1.71153200	0.64957700	0.02904500
C	-2.22862100	-0.70304200	0.03989100
O	-3.44337600	-0.84505500	-0.02678900
N	-1.25757600	-1.60602200	0.13253900
Pd	0.62008800	-1.01286500	-0.06312400
C	-1.51421000	-3.06371400	0.08638400
C	-1.91468000	-3.46696100	-1.33591500
C	-0.17113200	-3.69448200	0.48491700
H	-2.84381900	-2.95659900	-1.63186600
H	-1.12940900	-3.19894900	-2.05994800
H	-2.08543300	-4.55333100	-1.39995600
C	1.01000800	-2.98494500	-0.17168800
H	-0.07420200	-3.61043400	1.58107700
H	-0.18585300	-4.77675500	0.25609300
H	1.10164800	-3.23392700	-1.24568200
H	1.96528500	-3.24858200	0.31649000
C	-2.59518600	-3.49409600	1.07974900
H	-2.34988800	-3.14120100	2.09442600
H	-3.57912400	-3.09355900	0.80391600
H	-2.65611600	-4.59353600	1.10935700
O	2.98394300	0.76580600	-0.65651700
C	4.09695100	1.30166300	0.10604400
O	2.69509000	-0.55968800	-0.22311100
H	3.11416800	-1.11687500	-0.90614500
C	3.73264100	1.37646800	1.58022900
H	4.54754900	1.85652300	2.14205500
H	2.81656900	1.96842700	1.72689400
H	3.57630100	0.37350400	2.00311100
C	5.34294000	0.46250000	-0.13345600
H	5.55735300	0.37967700	-1.21028600
H	6.20911300	0.93437200	0.35345600
H	5.23624800	-0.54809500	0.28841900
C	4.23545700	2.68749500	-0.50645800
H	3.31477500	3.27412600	-0.36853000
H	5.06077800	3.22094200	-0.01301900
H	4.45804800	2.62347800	-1.58205800

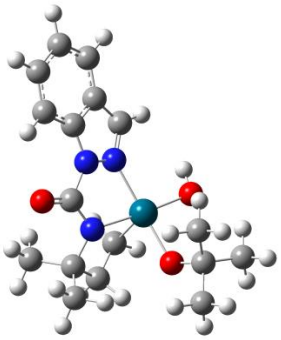


TS6

Free Energy = -1180.054369 Hartee

C	3.14138600	-0.06129900	0.29626600
C	3.36579700	-1.26077700	-0.42562900
C	4.63413300	-1.87208000	-0.41142700
C	5.63529000	-1.26622200	0.32435800
C	5.39460000	-0.06844600	1.03908600
C	4.15881600	0.55625900	1.04168600
H	4.81426600	-2.79551100	-0.96651400
H	6.63174300	-1.71326800	0.35756900
H	6.21424800	0.38048100	1.60638400
H	3.97290100	1.48243700	1.58344600
C	2.11850100	-1.55236000	-1.04587700
H	1.83910100	-2.38281500	-1.69431200
N	1.24492400	-0.62131500	-0.73206900
N	1.83141400	0.27508000	0.08409200
C	1.09271100	1.44710600	0.48394500
O	1.70465900	2.34096300	1.00696100
N	-0.18881600	1.35197800	0.15716500
Pd	-0.90285900	-0.44803300	-0.60017400
C	-0.98539800	2.57529000	-0.10362800
C	-0.20950400	3.55218000	-0.99583600
C	-2.20597400	2.04361400	-0.87152800
H	0.70836200	3.89605100	-0.50015200
H	0.07173100	3.08315800	-1.95193900
H	-0.83337000	4.43171800	-1.21699300
C	-1.80286400	0.93044400	-1.79427000
H	-2.96706200	1.66864500	-0.17072000
H	-2.68804100	2.84692000	-1.45961500
H	-1.01473600	1.17359900	-2.52062700
H	-2.63247800	0.37522600	-2.24858800

C	-1.40164500	3.27604700	1.18835100
H	-1.94833500	2.58887100	1.85079600
H	-0.51560600	3.64605400	1.72464800
H	-2.05670000	4.13397700	0.96811000
O	-2.72034200	-1.06185900	-0.26901400
C	-2.98390700	-1.40536800	1.08416700
O	-1.78533400	-2.01530900	-1.26860000
H	-1.02565900	-2.40800900	-1.81816600
C	-2.04753800	-2.52408700	1.56260500
H	-2.29637700	-2.81612000	2.59439100
H	-2.12253100	-3.40833500	0.91447800
H	-0.99557100	-2.19048600	1.55581300
C	-2.89160100	-0.21840100	2.04349800
H	-3.59151900	0.57819900	1.74822200
H	-3.13591700	-0.52187800	3.07475000
H	-1.87295700	0.20027400	2.04805300
C	-4.42398300	-1.92361100	1.03843700
H	-4.50435300	-2.78426600	0.35768300
H	-4.75046100	-2.24024600	2.04176200
H	-5.10661400	-1.13546300	0.68519500

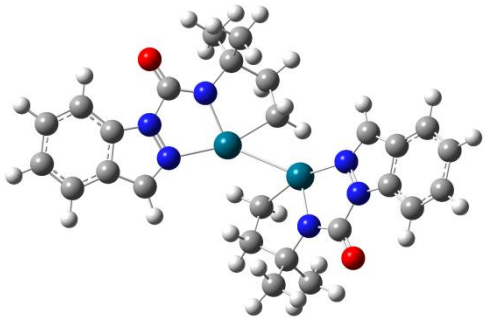


IN8

Free Energy = -1180.189288 Hartee

C	3.10390600	-0.02541300	0.39829400
C	3.37845000	-1.19121700	-0.35930200
C	4.67624100	-1.73682600	-0.38124900
C	5.65633800	-1.09802400	0.35428300
C	5.36602600	0.06767900	1.10270900
C	4.10013800	0.62728100	1.14170000
H	4.89328200	-2.63525900	-0.96320000
H	6.67491300	-1.49311700	0.36095200
H	6.17087800	0.54442500	1.66834600

H	3.87730100	1.52859600	1.71058100
C	2.14207200	-1.53618700	-0.97027400
H	1.90383900	-2.36835900	-1.63215000
N	1.22630400	-0.66003800	-0.61944800
N	1.77555600	0.25020500	0.21564200
C	1.00213900	1.41174800	0.59027800
O	1.57822000	2.32253700	1.15973600
N	-0.26876200	1.30271900	0.19205800
Pd	-0.82828600	-0.52966100	-0.50478900
C	-1.02857000	2.48704700	-0.29012600
C	-0.10822500	3.52985800	-0.93282500
C	-1.95810000	1.90593500	-1.37706800
H	0.61033900	3.94119000	-0.21268700
H	0.45619400	3.09568000	-1.77388200
H	-0.72019100	4.35594000	-1.32526500
C	-1.32382600	0.72101700	-2.04325400
H	-2.90865500	1.58775900	-0.93048600
H	-2.19006300	2.66175800	-2.15012100
H	-0.35600500	0.90257600	-2.53023500
H	-1.99411700	0.11458800	-2.66529300
C	-1.83243700	3.11927000	0.84218400
H	-2.48245400	2.36967200	1.31708200
H	-1.16081500	3.53688500	1.60798300
H	-2.46640100	3.93566600	0.46073400
O	-2.73253500	-0.39230400	-0.01129100
C	-3.18569600	-1.21665900	1.04337600
O	-1.24442000	-2.30871800	-1.23636400
H	-0.47130000	-2.59212600	-1.74304200
C	-2.06186900	-1.57347900	2.02225600
H	-2.45060600	-2.16293900	2.86748000
H	-1.28452000	-2.18357300	1.53053200
H	-1.59051400	-0.66446600	2.42940200
C	-4.24654800	-0.38964400	1.77715900
H	-5.03684800	-0.07710800	1.07647400
H	-4.71595500	-0.97442700	2.58480000
H	-3.79999100	0.51505900	2.21835500
C	-3.82159500	-2.49623700	0.49234400
H	-3.07302000	-3.06520900	-0.07580700
H	-4.22656900	-3.12707300	1.30080300
H	-4.65004600	-2.24094300	-0.18839000

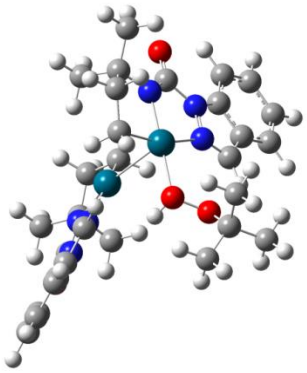


IN9

Free Energy = -1742.988788 Hartee

C	-5.03522600	-0.53194600	1.02796000
C	-4.77859800	-1.92014000	0.90566900
C	-5.69595200	-2.86098800	1.40939600
C	-6.84125500	-2.38621600	2.02213900
C	-7.08316800	-0.99740900	2.13750800
C	-6.19887800	-0.04916100	1.64961400
H	-5.50208800	-3.93216300	1.31696100
H	-7.57385000	-3.08948400	2.42552400
H	-7.99982100	-0.66029200	2.62889300
H	-6.38275800	1.02037300	1.73610200
C	-3.52602700	-2.00172500	0.23377500
H	-2.95423300	-2.88042700	-0.06303400
N	-3.07838100	-0.79275000	-0.02072800
N	-3.97048900	0.10886700	0.44904600
C	-3.73781300	1.52946700	0.29833100
O	-4.58964200	2.29749400	0.72644500
N	-2.58992100	1.77870200	-0.32289300
Pd	-1.36851600	0.26700400	-0.72341100
C	-2.12526700	3.14339800	-0.65831300
C	-1.72116700	3.88365300	0.62002800
C	-0.91412400	2.91725300	-1.58465100
H	-2.58790200	3.98035200	1.29068500
H	-0.92839700	3.34587800	1.16259600
H	-1.35373200	4.89481200	0.38483000
C	-0.05843900	1.76671000	-1.05157800
H	-1.28625700	2.67134200	-2.59240400
H	-0.33133400	3.85151800	-1.67642700
C	-3.19305500	3.94004300	-1.40964100
H	-3.54098500	3.38279500	-2.29399200
H	-4.05946700	4.15099200	-0.76898300
H	-2.77024000	4.89664300	-1.75485800

Pd	1.43848100	-0.07851900	-0.81626600
N	3.11915700	0.76845700	0.12970200
N	2.40759500	-1.72241000	-0.30117900
C	0.18297700	-1.39715600	-1.73385900
C	3.65586100	1.92418200	0.44962100
N	3.97111900	-0.22037400	0.47543400
C	3.63605400	-1.59588900	0.20261800
C	1.86652500	-3.02192900	-0.76148500
C	0.38455000	-2.74279500	-1.04631800
H	-0.91295500	-1.21816100	-1.92014600
H	0.58601600	-1.37177500	-2.76232900
C	4.93290100	1.70997100	1.04231800
H	3.12839700	2.85697200	0.25231100
C	5.10507400	0.30348100	1.04067300
O	4.47166400	-2.45198900	0.45567600
C	1.97933900	-4.10500700	0.31305700
C	2.60023400	-3.45850100	-2.03320600
H	-0.04031400	-3.57133200	-1.64170200
H	-0.15353700	-2.73854900	-0.08433900
C	5.93412300	2.54806500	1.56695600
C	6.26451400	-0.30002000	1.55371400
H	3.02549400	-4.37408100	0.50670000
H	1.52771100	-3.76126800	1.25729300
H	1.43769300	-5.00660600	-0.01369000
H	2.49253600	-2.70847300	-2.83219300
H	3.67305400	-3.59278200	-1.82944300
H	2.19914800	-4.41520900	-2.40278300
C	7.07681300	1.95486500	2.07202900
H	5.80595100	3.63290100	1.57160000
C	7.23366800	0.54931600	2.06251100
H	6.38308800	-1.38224800	1.54448600
H	7.87429400	2.57641200	2.48631400
H	8.15136400	0.11781100	2.47099700
H	0.36843800	2.06024100	-0.07577800
H	0.77458500	1.57688800	-1.79390700



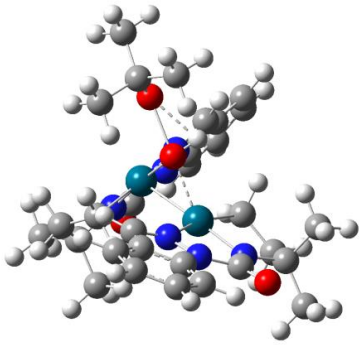
IN10

Free Energy = -2051.689593 Hartee

C	4.76636400	-0.38908600	-0.13986900
C	4.68818300	0.83405600	0.56978500
C	5.84317900	1.60765400	0.79104000
C	7.04414200	1.13409000	0.29634500
C	7.10826800	-0.09092400	-0.40848000
C	5.98786000	-0.87138800	-0.64087100
H	5.78488900	2.55126200	1.33844700
H	7.96077300	1.70875700	0.44980300
H	8.07644000	-0.43372600	-0.78329800
H	6.03482600	-1.81416300	-1.18280500
C	3.31442300	0.96651300	0.91229700
H	2.81894400	1.76195700	1.46744900
N	2.63297200	-0.06451100	0.45514500
N	3.49149400	-0.89308400	-0.18118000
C	3.05118000	-2.16306000	-0.72223600
O	3.86770500	-2.81361600	-1.36395200
N	1.79159200	-2.43713800	-0.40572000
Pd	0.65029600	-0.97991900	0.34983000
C	1.09980400	-3.65159600	-0.89250500
C	1.88702300	-4.92605500	-0.58101000
C	-0.22040400	-3.65773900	-0.11157700
H	2.82292200	-4.97227500	-1.15268300
H	2.13287100	-4.97553600	0.49204000
H	1.27770200	-5.80943300	-0.82942900
C	-0.84139000	-2.26699500	-0.04093800
H	-0.91588900	-4.39665900	-0.55251000
H	-0.00316500	-4.00791600	0.91240100
H	-1.63176400	-2.21729500	0.72539800
H	-1.27984900	-1.95782200	-1.00678500
C	0.85289200	-3.53868400	-2.39976800

H	0.25579800	-2.64478800	-2.63847500
H	1.80872500	-3.46886600	-2.94053900
H	0.31186700	-4.42280600	-2.77249400
C	-4.37684100	-0.49832600	-0.87164000
C	-3.99498600	-0.04736000	-2.15944700
C	-4.78059300	-0.35784900	-3.28478200
C	-5.92415200	-1.11091800	-3.08962400
C	-6.29249300	-1.55358900	-1.79798400
C	-5.53901100	-1.26165600	-0.67238500
H	-4.48963100	-0.01219200	-4.27947000
H	-6.55627700	-1.37111700	-3.94209400
H	-7.20369600	-2.14677700	-1.68322500
H	-5.82144600	-1.60176000	0.32241500
C	-2.78734200	0.67824000	-1.94905200
H	-2.15013100	1.19375700	-2.66608000
N	-2.47868900	0.66587700	-0.67293400
N	-3.41946700	-0.03509400	-0.00489400
C	-3.32562600	-0.22238000	1.42322700
O	-4.17834500	-0.91086700	1.96550800
N	-2.28412400	0.42165700	1.95161500
Pd	-0.95033500	1.21343900	0.74429900
C	-1.94686900	0.36845300	3.39349000
C	-1.33395900	-0.99262200	3.73159700
C	-0.92588700	1.50138900	3.56758800
H	-2.06084900	-1.79821000	3.54756100
H	-0.44129700	-1.18979800	3.11545900
H	-1.03934700	-1.03252400	4.79211900
C	0.09997400	1.51070400	2.44134600
H	-1.47975300	2.45556300	3.56516800
H	-0.44103400	1.42140400	4.55792400
H	0.84331800	0.70238500	2.55015800
H	0.64066900	2.46946300	2.37072500
C	-3.16018500	0.63972900	4.28469000
H	-3.65824700	1.57634000	3.98696200
H	-3.89418700	-0.17404500	4.23261000
H	-2.82896900	0.74966000	5.32928400
O	0.01435300	2.52275200	-1.75454600
C	0.40050700	3.88965100	-2.05429700
O	0.52468200	2.14764800	-0.47754300
H	1.21792500	1.49219400	-0.70013600
C	1.91549400	3.99834800	-2.12582800
H	2.20095000	5.00761700	-2.45743700
H	2.37833300	3.82742200	-1.14261000
H	2.32594500	3.27173300	-2.84396700

C	-0.23739900	4.08191200	-3.42240100
H	-1.32980000	3.96229300	-3.36866600
H	-0.01890200	5.09740300	-3.78327900
H	0.16508800	3.36196500	-4.15063400
C	-0.19556100	4.83537900	-1.02363900
H	0.23010300	4.65758900	-0.02530500
H	0.02290900	5.87673800	-1.30256600
H	-1.28816300	4.71365700	-0.96976400



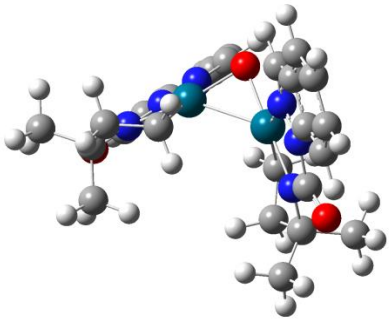
TS7

Free Energy = -2051.621747 Hartee

C	5.10923200	0.12128300	-0.33551500
C	4.89014700	-1.26267400	-0.53272100
C	5.97670100	-2.14482700	-0.67271900
C	7.25310500	-1.61519300	-0.60998700
C	7.45653900	-0.23026400	-0.41246800
C	6.40409200	0.66077000	-0.27251900
H	5.81032600	-3.21358500	-0.82617000
H	8.12042700	-2.27156600	-0.71409500
H	8.47985500	0.15205800	-0.36860200
H	6.56098500	1.72710300	-0.12047400
C	3.47310200	-1.40949600	-0.54026200
H	2.87848800	-2.31268700	-0.66524000
N	2.89711600	-0.24257200	-0.36935600
N	3.86382100	0.69464000	-0.24276200
C	3.53574600	2.07337800	-0.01731700
O	4.45350200	2.85974200	0.15870000
N	2.21538500	2.30518700	-0.04662800
Pd	0.95803400	0.76208800	-0.02467400
C	1.65737700	3.64280900	0.26729900
C	2.28024700	4.74195400	-0.59641900
C	0.17264800	3.50147400	-0.08077000
H	3.33216600	4.91531400	-0.33738000

H	2.22265500	4.47458000	-1.66361200
H	1.72210000	5.68030600	-0.45191000
C	-0.40227800	2.18524000	0.41604700
H	-0.39776400	4.36005900	0.31889100
H	0.07608000	3.54434900	-1.17893900
H	-1.37176300	1.95536500	-0.04938500
H	-0.52351400	2.15648100	1.51319900
C	1.85636900	3.95482200	1.75285100
H	1.37988600	3.19128400	2.38716300
H	2.92784000	3.98820700	1.99942300
H	1.41657200	4.93290200	2.00271700
C	-4.93377000	0.75552600	0.12686400
C	-4.70751300	0.94520500	1.51259500
C	-5.68188900	1.56728300	2.31464500
C	-6.85346600	1.98158800	1.70736900
C	-7.06554600	1.78343100	0.32338300
C	-6.12426300	1.17323200	-0.49001800
H	-5.51144500	1.71555200	3.38350200
H	-7.63078000	2.46928000	2.30056400
H	-8.00501500	2.12333600	-0.12063800
H	-6.28695100	1.01866400	-1.55527700
C	-3.41581400	0.39335900	1.75038900
H	-2.84871600	0.33048100	2.67861700
N	-2.91975700	-0.07510300	0.62936600
N	-3.81331100	0.13139000	-0.36176600
C	-3.55034800	-0.34051300	-1.70006200
O	-4.37670300	-0.09213500	-2.56550600
N	-2.40556600	-1.02409400	-1.77891500
Pd	-1.14601600	-0.95343400	-0.25817400
C	-1.90559500	-1.60589600	-3.04451000
C	-1.36886700	-0.49207700	-3.94739500
C	-0.78638600	-2.54588100	-2.57957600
H	-2.17781700	0.20240800	-4.22024200
H	-0.57866800	0.08381900	-3.44082000
H	-0.94957300	-0.91128600	-4.87550100
C	0.11105200	-1.88821700	-1.53995500
H	-1.26049500	-3.44042400	-2.14118000
H	-0.19687000	-2.89441700	-3.44774100
H	0.79861200	-1.15489900	-1.99070500
H	0.70202800	-2.62358600	-0.97320300
C	-2.97518000	-2.41600800	-3.77849200
H	-3.42606900	-3.16249900	-3.10520500
H	-3.77488700	-1.77423400	-4.16887000
H	-2.51238700	-2.95487200	-4.62016000

O	-0.78858400	-2.10538900	2.38419500
C	0.12955800	-2.92573300	3.00174900
O	0.20958200	-0.76238900	1.27281500
H	-0.17980500	-0.26534000	2.01096600
C	1.08237300	-2.14085700	3.90812500
H	1.73533500	-2.81475100	4.48411300
H	1.72260300	-1.47939100	3.30446500
H	0.51183900	-1.52097000	4.61770300
C	-0.75659300	-3.85316200	3.87124300
H	-1.45559000	-4.42106600	3.23989600
H	-0.11332600	-4.56231400	4.41684200
H	-1.33300200	-3.26434300	4.59985200
C	0.90928000	-3.77149100	1.99356200
H	1.52030200	-3.11485600	1.35621500
H	1.57870400	-4.48475100	2.49905800
H	0.21823800	-4.33695200	1.34947500



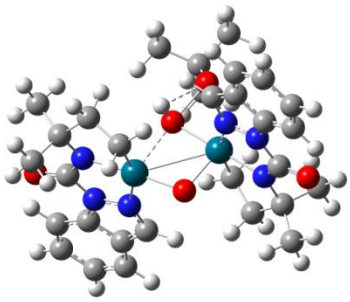
IN11

Free Energy = -1818.128839 Hartee

C	5.14018600	0.20072500	-0.51724800
C	4.90758400	0.95194700	-1.69625200
C	5.96892300	1.61875200	-2.33649700
C	7.22957300	1.51460900	-1.77820300
C	7.44534100	0.76122600	-0.60048100
C	6.42032700	0.09441700	0.05042500
H	5.79424300	2.19877500	-3.24556500
H	8.07628400	2.01972800	-2.24917200
H	8.45689300	0.70263900	-0.18988800
H	6.58460900	-0.48755500	0.95570800
C	3.51285200	0.81712100	-1.94778600
H	2.90636700	1.22990100	-2.75318500
N	2.97090000	0.06773400	-1.01527300
N	3.92450100	-0.31263200	-0.14380900

C	3.59603400	-1.16867000	0.97098900
O	4.51904800	-1.57427000	1.66307000
N	2.28522400	-1.40067900	1.06185600
Pd	1.05882600	-0.69084300	-0.39254600
C	1.74582800	-2.34530400	2.06284600
C	2.19378200	-2.01147100	3.48730200
C	0.22645800	-2.16306600	1.95293300
H	3.27000600	-2.17982900	3.62016900
H	1.97398100	-0.95821000	3.72438600
H	1.64661200	-2.64193000	4.20575300
C	-0.21728400	-2.01061200	0.52095600
H	-0.29683600	-3.01574600	2.42490300
H	-0.06843300	-1.26515300	2.52133700
H	-1.27396000	-1.73191000	0.41911800
H	0.00211000	-2.88244900	-0.11984400
C	2.15618400	-3.77611800	1.70120000
H	1.79725500	-4.05353300	0.69785300
H	3.25181500	-3.87361500	1.71355400
H	1.73969400	-4.49294900	2.42609500
C	-4.99621100	-0.55301300	-0.55824400
C	-4.66288000	-1.36703300	-1.66907300
C	-5.61221900	-2.25125900	-2.21385100
C	-6.86448300	-2.29765900	-1.62872300
C	-7.18128200	-1.47981000	-0.51928600
C	-6.26779600	-0.59815900	0.03565900
H	-5.36050700	-2.87927900	-3.07150100
H	-7.62512000	-2.97451100	-2.02523900
H	-8.18255100	-1.54448700	-0.08511800
H	-6.51112200	0.03412800	0.88790300
C	-3.31187100	-1.03460800	-1.97488400
H	-2.65815800	-1.42350100	-2.75496600
N	-2.88500200	-0.11774600	-1.13874800
N	-3.87482100	0.18508700	-0.27428100
C	-3.67170700	1.18123100	0.74775900
O	-4.60484500	1.43325600	1.49441800
N	-2.44639800	1.71291500	0.68977900
Pd	-1.05652300	0.84490600	-0.47968100
C	-2.03772800	2.82778700	1.56997100
C	-1.85856200	2.32084700	3.00432200
C	-0.70819500	3.28319300	0.95853400
H	-2.81282800	1.93646300	3.39359300
H	-1.11592000	1.50948500	3.05249400
H	-1.52116800	3.13588600	3.66338800
C	0.16508700	2.10681600	0.57654400

H	-0.92856900	3.88533400	0.06118000
H	-0.16535500	3.94640900	1.65775700
H	0.55035500	1.54919800	1.44293700
H	1.00077100	2.38098000	-0.08422100
C	-3.03357000	3.98805100	1.53907500
H	-3.22652500	4.30521000	0.50179000
H	-3.98978100	3.71112700	2.00155600
H	-2.61536800	4.84825100	2.08484200
O	0.04432500	0.05624300	-1.83745800



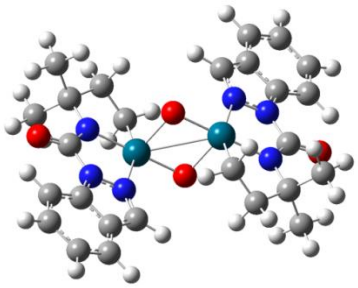
TS8

Free Energy = -2126.766064 Hartee

C	5.17885400	-0.54336300	-0.73034200
C	4.87305900	-1.87848400	-0.37223800
C	5.84730800	-2.88757100	-0.48045100
C	7.10063300	-2.53006000	-0.94293300
C	7.39146200	-1.19215000	-1.29591300
C	6.45097800	-0.17896800	-1.19994500
H	5.61380100	-3.91884600	-0.20615200
H	7.88167500	-3.28801000	-1.03981100
H	8.39373700	-0.94779000	-1.65783400
H	6.67549900	0.85089800	-1.47157000
C	3.51231600	-1.84102800	0.04792700
H	2.87925600	-2.65164700	0.40818800
N	3.04632100	-0.61893600	-0.05187000
N	4.03007700	0.18080300	-0.51716400
C	3.82911400	1.59301400	-0.67240800
O	4.77705100	2.27425200	-1.03014500
N	2.58629600	1.99508000	-0.38157500
Pd	1.28818200	0.70781000	0.33626900
C	2.16801300	3.41842200	-0.45911700
C	2.51935600	4.05227400	-1.80544500
C	0.64030700	3.37685900	-0.30510700
H	3.60420300	4.15600800	-1.93248900

H	2.12534000	3.44403300	-2.63452500
H	2.06027200	5.05119800	-1.86839300
C	0.21687600	2.36510500	0.72687700
H	0.25990700	4.37969400	-0.03945500
H	0.19267600	3.10061800	-1.27160400
H	-0.85127800	2.12167700	0.72440300
H	0.56561000	2.58273700	1.74988600
C	2.81986700	4.19847100	0.68605600
H	2.53190400	3.78636200	1.66560800
H	3.91578300	4.15716900	0.60287100
H	2.51200100	5.25508000	0.65243500
C	-5.14073900	0.79945200	-0.46750500
C	-4.65524300	2.12309400	-0.60400700
C	-5.54374400	3.21422100	-0.59594800
C	-6.89370800	2.95017000	-0.45283700
C	-7.36467000	1.62337200	-0.31869400
C	-6.51242200	0.53101200	-0.32292000
H	-5.17156100	4.23611800	-0.69985800
H	-7.61143800	3.77408400	-0.44230700
H	-8.43899800	1.45324300	-0.20762300
H	-6.87339400	-0.49078600	-0.22153800
C	-3.24374700	1.98037400	-0.72565600
H	-2.48137000	2.74782100	-0.85594700
N	-2.91362100	0.71090100	-0.66189100
N	-4.03974600	-0.01957700	-0.50798300
C	-4.00058000	-1.46592000	-0.50012300
O	-5.07290300	-2.05627200	-0.46513200
N	-2.75962400	-1.94441600	-0.54558300
Pd	-1.22157400	-0.69737000	-0.84876400
C	-2.48791200	-3.39225600	-0.68240900
C	-2.92338600	-3.86548800	-2.07324500
C	-0.96348900	-3.51758200	-0.51696500
H	-4.00420000	-3.71130900	-2.20907300
H	-2.39384000	-3.31226800	-2.86467200
H	-2.71086100	-4.93838300	-2.20264900
C	-0.21237100	-2.39782300	-1.21963300
H	-0.73299300	-3.49623400	0.56284200
H	-0.63099300	-4.50890500	-0.87727200
H	-0.26428500	-2.46683500	-2.32088900
H	0.84745600	-2.34038400	-0.92985900
C	-3.18359700	-4.22178500	0.39850200
H	-2.93068300	-3.84046700	1.40086700
H	-4.27482300	-4.19481600	0.28379400
H	-2.84731400	-5.26904900	0.33957100

O	0.29223500	0.52017000	-1.31039800
O	-0.13002800	-0.58418000	1.18250600
H	0.20647700	-1.49448000	1.11507700
O	0.92263800	-0.43251300	2.70909600
C	0.10397500	-0.43559100	3.83992900
C	1.11237900	-0.33058400	4.99979600
H	1.69949700	0.59663300	4.92180200
H	0.56824500	-0.32095700	5.95761200
H	1.80161500	-1.18808000	4.99652000
C	-0.67263000	-1.74772800	3.94616800
H	-1.22670900	-1.80419900	4.89564700
H	-1.40000900	-1.82952000	3.12350300
H	0.01346200	-2.60758600	3.89376800
C	-0.84423600	0.76058700	3.86502500
H	-0.28169400	1.70569700	3.82689100
H	-1.52504100	0.72356700	3.00116200
H	-1.45293600	0.75878400	4.78227200



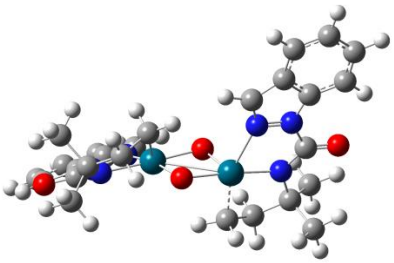
IN12

Free Energy = -1893.276403 Hartee

C	-5.21050800	0.64000000	-0.05914300
C	-4.84195500	1.96726700	0.27024100
C	-5.79906000	2.99861600	0.25748700
C	-7.09863700	2.67211900	-0.08425900
C	-7.45242000	1.34231300	-0.41033100
C	-6.53072600	0.30778400	-0.40559700
H	-5.51682100	4.02327500	0.51021900
H	-7.86760000	3.44820200	-0.10500200
H	-8.49001500	1.12235900	-0.67561000
H	-6.80299300	-0.71605500	-0.65516000
C	-3.44881500	1.89627000	0.55756100
H	-2.76384500	2.68869300	0.85862000
N	-3.02300100	0.66351800	0.41089100
N	-4.06446900	-0.11140800	0.04079800

C	-3.91573500	-1.53477500	-0.13552100
O	-4.92537300	-2.18401600	-0.36811900
N	-2.65641100	-1.95534000	0.00033400
Pd	-1.20682600	-0.69199400	0.55408100
C	-2.29919300	-3.39117500	-0.05672900
C	-2.80455400	-4.06739000	-1.33209300
C	-0.76019800	-3.40526400	-0.05624100
H	-3.90055300	-4.12145700	-1.34853700
H	-2.46867800	-3.51293500	-2.22259700
H	-2.39976600	-5.08968500	-1.39530100
C	-0.17855600	-2.38058600	0.88275700
H	-0.39235400	-4.41407300	0.20592300
H	-0.40073800	-3.18556500	-1.07377800
H	0.89478000	-2.20043500	0.75538800
H	-0.42698700	-2.53185700	1.94864200
C	-2.85340100	-4.10653000	1.17928800
H	-2.45399600	-3.66865500	2.10748700
H	-3.95030100	-4.02986600	1.20611200
H	-2.58389300	-5.17407700	1.15922000
C	5.21039900	-0.64020400	0.05883300
C	4.84163700	-1.96744900	-0.27041200
C	5.79861500	-2.99891800	-0.25771400
C	7.09827800	-2.67255800	0.08383600
C	7.45226900	-1.34277400	0.40977400
C	6.53070300	-0.30813000	0.40509300
H	5.51621400	-4.02355800	-0.51033700
H	7.86714800	-3.44873400	0.10453100
H	8.48992600	-1.12293200	0.67490100
H	6.80313100	0.71569100	0.65455200
C	3.44846800	-1.89630300	-0.55754700
H	2.76336600	-2.68866100	-0.85847100
N	3.02283000	-0.66348400	-0.41092000
N	4.06444300	0.11133900	-0.04100000
C	3.91589600	1.53473800	0.13525700
O	4.92565600	2.18387900	0.36759400
N	2.65657400	1.95541600	-0.00031200
Pd	1.20683900	0.69216300	-0.55384500
C	2.29944000	3.39127100	0.05685800
C	2.85344900	4.10664600	-1.17923600
C	0.76044800	3.40543200	0.05664300
H	3.95034300	4.02997600	-1.20624300
H	2.45388900	3.66879000	-2.10737700
H	2.58394800	5.17419400	-1.15910300
C	0.17857600	2.38081000	-0.88227800

H	0.40115600	3.18572000	1.07423800
H	0.39260000	4.41426700	-0.20542200
H	0.42678000	2.53211600	-1.94821000
H	-0.89474300	2.20071800	-0.75468500
C	2.80504900	4.06743000	1.33215500
H	2.46926500	3.51298400	2.22269900
H	3.90105300	4.12140300	1.34842000
H	2.40036100	5.08975900	1.39544700
O	-0.23870300	-0.54338200	-1.12299300
O	0.23869100	0.54358200	1.12326100



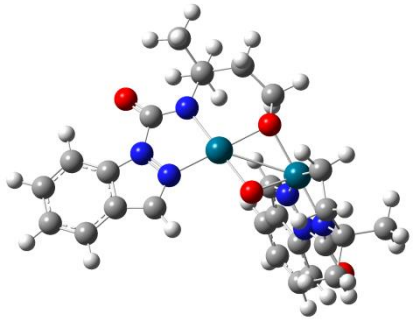
TS9

Free Energy = -1893.272996 Hartee

C	-5.03148300	0.95639900	0.91637800
C	-4.35717500	1.94033800	1.68320500
C	-5.08413800	2.96095400	2.32506400
C	-6.45888200	2.96489900	2.17996400
C	-7.11601900	1.97381900	1.41281900
C	-6.42793300	0.95727200	0.77163300
H	-4.57114200	3.72228300	2.91697600
H	-7.05375800	3.74308600	2.66408000
H	-8.20498800	2.01162200	1.32423400
H	-6.93079400	0.19002200	0.18496400
C	-2.97909900	1.59922700	1.59601200
H	-2.10675700	2.08717900	2.02878300
N	-2.84959800	0.51937600	0.85607500
N	-4.06430000	0.12073200	0.42711800
C	-4.17413700	-1.11004700	-0.31915000
O	-5.29601200	-1.54300100	-0.54206800
N	-2.97440200	-1.60601200	-0.62036200
Pd	-1.35812500	-0.47238500	-0.10293200
C	-2.83365100	-3.04151300	-0.94450300
C	-3.42698900	-3.36342000	-2.31640600
C	-1.32276400	-3.33115000	-0.95450500
H	-4.51367400	-3.19935200	-2.31511700

H	-2.97688600	-2.72268500	-3.09095400
H	-3.23130300	-4.41406900	-2.58372000
C	-0.55839200	-2.56457200	0.06687200
H	-1.14742800	-4.40636600	-0.75972000
H	-0.88903000	-3.12263900	-1.94372000
H	0.51579400	-2.74120200	0.10711900
H	-1.00331800	-2.51346600	1.07394600
C	-3.49900000	-3.90006900	0.13921900
H	-3.03494700	-3.71992500	1.12243700
H	-4.57204500	-3.67861500	0.21598200
H	-3.38278800	-4.96783700	-0.10223700
C	5.10274000	-0.57409600	1.06097400
C	4.71402700	-1.91974100	1.26870500
C	5.57243200	-2.81820100	1.92884000
C	6.79704500	-2.34420600	2.36234400
C	7.17229600	-0.99765700	2.14818000
C	6.34678200	-0.09208100	1.50152100
H	5.27394300	-3.85662600	2.09034800
H	7.48878000	-3.01442700	2.87837400
H	8.14844500	-0.65869600	2.50540800
H	6.63595700	0.94398300	1.33561100
C	3.41612500	-2.01528400	0.69040200
H	2.75515000	-2.87907100	0.62617600
N	3.05837100	-0.85472700	0.19269400
N	4.05751400	0.02898400	0.40417000
C	3.97423000	1.38806900	-0.07029900
O	4.96028100	2.09743000	0.07155100
N	2.79685400	1.68217200	-0.62348600
Pd	1.41330400	0.26250500	-0.91772500
C	2.51626100	3.00922600	-1.21677500
C	3.32629000	3.17612400	-2.50609200
C	1.00683800	2.98472700	-1.51313400
H	4.40359100	3.12246700	-2.29055900
H	3.08113200	2.38934000	-3.23653900
H	3.11670700	4.15286500	-2.96958500
C	0.55014800	1.65848500	-2.06734200
H	0.45846700	3.17629500	-0.57719400
H	0.74571700	3.80046200	-2.21177200
H	0.98513400	1.38927300	-3.04665300
H	-0.53935100	1.52786800	-2.08174800
C	2.81591000	4.15641100	-0.25050700
H	2.29369300	4.00200700	0.70699200
H	3.89159000	4.24090000	-0.05029900
H	2.46137500	5.10585600	-0.68149800

O	0.05375000	-1.12754900	-1.34432900
O	0.15006600	0.67146800	0.47686600

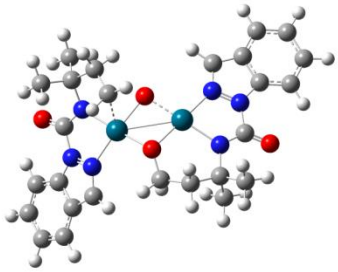


IN13

Free Energy = -1893.386606 Hartee

C	-4.40838200	1.21391700	-1.21031100
C	-3.71878400	1.52678100	-2.40935900
C	-4.31692600	2.35684800	-3.37607500
C	-5.58271800	2.84771800	-3.11419900
C	-6.25662000	2.52628900	-1.91248800
C	-5.69353300	1.71248900	-0.94340300
H	-3.79120800	2.60100600	-4.30196600
H	-6.07586600	3.49484600	-3.84352400
H	-7.25656200	2.93443800	-1.74298400
H	-6.20787700	1.46388400	-0.01648100
C	-2.47271100	0.84750400	-2.30998200
H	-1.63351000	0.81382800	-3.00337200
N	-2.43145900	0.19567800	-1.16828800
N	-3.57772700	0.39749900	-0.49114600
C	-3.75269500	-0.20586200	0.81081400
O	-4.76370900	0.09657300	1.43202400
N	-2.74067300	-1.01728800	1.11713600
Pd	-1.16841800	-0.97433500	-0.16719400
C	-2.69958500	-1.65494200	2.44663200
C	-3.98230000	-2.45812200	2.70568800
C	-1.54175400	-2.67556900	2.52794700
H	-4.86218400	-1.80353500	2.72548300
H	-4.12613100	-3.21498200	1.91795300
H	-3.90881300	-2.98297800	3.67087500
C	-0.11836100	-2.22370600	2.24456700
H	-1.56346200	-3.08060400	3.55259200
H	-1.75838600	-3.52375800	1.85566100
H	0.57626700	-2.97767300	2.65779600
H	0.10875100	-1.26404300	2.74591400

C	-2.52590700	-0.58202900	3.52807900
H	-1.60345400	-0.00218900	3.36738300
H	-3.37556500	0.11551700	3.51308200
H	-2.47268300	-1.04100000	4.52784200
C	3.11913300	2.62034100	0.96582700
C	2.08623600	2.77048800	1.92285300
C	1.96088600	3.96500400	2.65562000
C	2.87345400	4.97454700	2.40943300
C	3.89947200	4.80986200	1.45050800
C	4.04624700	3.64473500	0.71501000
H	1.16464600	4.08420200	3.39398400
H	2.80564700	5.91570400	2.96032500
H	4.60218600	5.63052300	1.28324500
H	4.83676700	3.51744000	-0.02236800
C	1.37089200	1.53893400	1.88371000
H	0.50025900	1.22527100	2.45968100
N	1.91183400	0.73639100	0.99835200
N	2.96393800	1.36409400	0.43067200
C	3.75923800	0.72282400	-0.58140300
O	4.75565300	1.30437000	-0.98132600
N	3.28574100	-0.47110800	-0.95398500
Pd	1.74454000	-1.25813900	-0.00970100
C	3.95799100	-1.32328700	-1.96598400
C	5.23980700	-1.90676200	-1.36511400
C	2.93436400	-2.42804800	-2.27570700
H	5.93270000	-1.10001100	-1.08378500
H	5.02389800	-2.50519100	-0.46641800
H	5.74642600	-2.55475500	-2.09715300
C	2.22541800	-2.91093400	-1.03612100
H	2.18041900	-2.02765900	-2.97103000
H	3.43281000	-3.27131500	-2.78695200
H	2.87234800	-3.41293300	-0.29448300
H	1.31985600	-3.49908400	-1.22808800
C	4.27183500	-0.55999400	-3.25327600
H	3.36636600	-0.06878400	-3.64271500
H	5.04151300	0.20501300	-3.09161600
H	4.63138600	-1.26585000	-4.01819200
O	0.10291100	-2.14977500	0.85684100
O	0.41290400	-0.88148400	-1.36907700

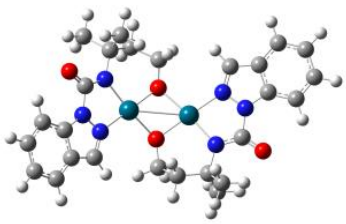


TS10

Free Energy = -1893.382586 Hartee

C	5.12092900	-0.58362500	1.06044900
C	4.74524700	-1.94981500	1.12126000
C	5.62311900	-2.90295700	1.67090700
C	6.84591100	-2.46174700	2.14224400
C	7.20494600	-1.09503600	2.07415900
C	6.36235900	-0.13482600	1.53876000
H	5.34022100	-3.95687000	1.72075000
H	7.55064100	-3.17563900	2.57539400
H	8.18100700	-0.78603700	2.45761500
H	6.63354400	0.91832500	1.48524900
C	3.44265600	-2.00284500	0.55128600
H	2.77490400	-2.84994900	0.40157400
N	3.08539800	-0.79042400	0.18721200
N	4.07227300	0.07767400	0.48034300
C	3.89833900	1.48167600	0.18135200
O	4.78399400	2.24342000	0.54960300
N	2.75851100	1.70554700	-0.47042300
Pd	1.50169600	0.11941400	-0.61106900
C	2.37121900	3.08462800	-0.81563800
C	3.47854700	3.77275800	-1.62698500
C	1.12264100	3.07994800	-1.72638100
H	4.40121000	3.86130900	-1.04031700
H	3.69836800	3.19772000	-2.54084700
H	3.15289600	4.77994600	-1.93017200
C	-0.16117900	2.42890900	-1.23742500
H	0.89499100	4.13693700	-1.94016100
H	1.38407200	2.61742000	-2.69413100
H	-0.99282500	2.79811200	-1.86527800
H	-0.38318900	2.72278600	-0.19449000
C	2.08890000	3.88066700	0.46362800
H	1.29563700	3.40547500	1.06148900
H	2.99550100	3.93774200	1.08310300

H	1.76980100	4.90698500	0.22273700
C	-4.84814000	0.73720700	1.26969800
C	-4.57008800	2.07553800	0.89808400
C	-5.38505400	3.12587900	1.36113800
C	-6.45073600	2.80298300	2.18016600
C	-6.71538000	1.46032000	2.53994800
C	-5.93188500	0.40704000	2.09844200
H	-5.17580100	4.15989200	1.07819300
H	-7.10394300	3.59287300	2.55851600
H	-7.56925000	1.24668200	3.18828200
H	-6.13736900	-0.62736200	2.36927900
C	-3.42317400	1.99788200	0.06087700
H	-2.87787800	2.79465800	-0.44154400
N	-3.05423300	0.74028500	-0.05857300
N	-3.88984300	-0.03427700	0.66856400
C	-3.77172500	-1.46387800	0.58229000
O	-4.65789400	-2.14626400	1.07259300
N	-2.67748600	-1.83460600	-0.09038400
Pd	-1.42327300	-0.37194000	-0.64702000
C	-2.64603600	-3.16022100	-0.76070700
C	-3.90189000	-3.33525800	-1.62427400
C	-1.40738300	-3.17062900	-1.67398500
H	-4.81494400	-3.28333700	-1.01591800
H	-3.95443700	-2.55572900	-2.40131500
H	-3.87762400	-4.31513900	-2.12505400
C	-1.09430300	-1.84291400	-2.26978400
H	-0.52361600	-3.52699300	-1.12852300
H	-1.57430700	-3.87772000	-2.50869700
H	-1.93424200	-1.31915700	-2.75674700
H	-0.17405300	-1.76789400	-2.84980300
C	-2.53622100	-4.29232000	0.26059300
H	-1.65863300	-4.14247900	0.90861800
H	-3.43457000	-4.33478200	0.89162300
H	-2.42198700	-5.25953100	-0.25401600
O	-0.10107100	1.03246400	-1.38080800
O	0.23702100	-1.42557500	-0.66402400

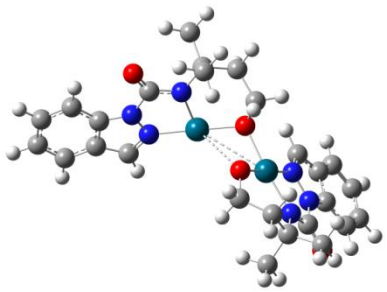


IN14

Free Energy = -1893.49846 Hartee

C	-5.14065300	-0.51158600	0.77780000
C	-4.89875400	-1.86612400	0.44172100
C	-5.85486100	-2.85497300	0.74070800
C	-7.02108300	-2.45694600	1.36728400
C	-7.24689000	-1.09952800	1.69639900
C	-6.32481300	-0.10554400	1.41341100
H	-5.67391900	-3.90094700	0.48327700
H	-7.78494000	-3.19788400	1.61480600
H	-8.18213700	-0.82570200	2.19188500
H	-6.49500300	0.93990200	1.66508900
C	-3.61790200	-1.87251600	-0.17495000
H	-3.05075000	-2.70890200	-0.57850200
N	-3.14492000	-0.64449500	-0.20736200
N	-4.04045900	0.18757000	0.35996800
C	-3.75156700	1.59321200	0.43816000
O	-4.57044900	2.30615200	1.00156000
N	-2.59316800	1.89635400	-0.15279200
Pd	-1.46871100	0.33274700	-0.72725800
C	-2.15323400	3.30499800	-0.18932500
C	-1.84832100	3.79515200	1.23061100
C	-0.90735000	3.45663600	-1.08468700
H	-2.75683800	3.76016200	1.84812600
H	-1.08192000	3.16969500	1.71359700
H	-1.48207100	4.83360700	1.21133800
C	0.33914800	2.66956000	-0.73334100
H	-1.17795100	3.21602100	-2.12758800
H	-0.64468500	4.52651600	-1.06986800
H	0.56710500	2.74910900	0.34630300
H	1.19046100	3.11621200	-1.27959500
C	-3.23540900	4.18724200	-0.82986300
H	-3.47160200	3.82883300	-1.84451900
H	-4.15609000	4.18546100	-0.23391300
H	-2.87068200	5.22266300	-0.91241600
O	0.22667300	1.33335300	-1.14043500
C	5.25721600	0.36083500	0.68860700
C	4.98846200	1.75145700	0.64995300
C	5.99807300	2.67917300	0.96835900
C	7.24284200	2.18664000	1.31388700
C	7.49385300	0.79470500	1.34855500
C	6.51991800	-0.14102500	1.04148200

H	5.79688500	3.75242800	0.94078900
H	8.05005500	2.87852300	1.56581300
H	8.49148000	0.44559300	1.62784600
H	6.70847900	-1.21299000	1.06875600
C	3.62461900	1.85637000	0.26065300
H	3.01286700	2.74280300	0.10672200
N	3.13065700	0.64851400	0.08766600
N	4.09177000	-0.26379300	0.33520600
C	3.77301500	-1.66524100	0.25542200
O	4.67262100	-2.46412900	0.47518000
N	2.48640500	-1.85925000	-0.04129900
Pd	1.45549700	-0.22645600	-0.58168200
C	1.93370300	-3.22680400	-0.05417900
C	2.23809600	-3.93717100	1.27326300
C	0.39446900	-3.17328300	-0.15879400
H	3.31842700	-4.04898200	1.42724900
H	1.81933800	-3.36791300	2.11849600
H	1.77670700	-4.93659400	1.27532100
C	-0.21670600	-2.52349100	-1.38399200
H	0.04466600	-4.21781100	-0.12121900
H	-0.01173800	-2.67489400	0.73959400
H	-1.27402600	-2.82728400	-1.45900800
H	0.27148200	-2.89649100	-2.30383200
C	2.52648500	-4.02262100	-1.22180800
H	2.34145100	-3.52061100	-2.18385500
H	3.61356900	-4.12532400	-1.09458000
H	2.08602900	-5.03096500	-1.26988700
O	-0.14796500	-1.12446500	-1.38339500



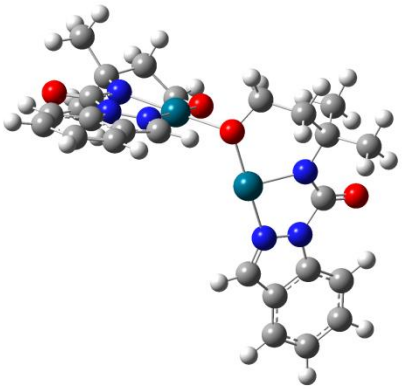
TS11

Free Energy = -1893.458518 Hartee

C	5.27947400	-0.83182400	-0.96924700
C	4.76621400	-1.87000900	-1.78660500
C	5.60289800	-2.52648700	-2.70878300

C	6.92304800	-2.12324100	-2.78417900
C	7.41866800	-1.08530100	-1.96026200
C	6.61985900	-0.42229200	-1.04339800
H	5.21390100	-3.32741800	-3.34141700
H	7.60024600	-2.61062300	-3.48960900
H	8.46922900	-0.79679500	-2.05033700
H	6.99831300	0.37557900	-0.40642400
C	3.39709800	-1.99130400	-1.42075000
H	2.62820600	-2.66168400	-1.80112400
N	3.12899000	-1.11524500	-0.47610000
N	4.23572200	-0.40590000	-0.19284900
C	4.18205800	0.58396400	0.84862200
O	5.20591000	1.20456500	1.09227600
N	2.97189300	0.64542900	1.41566100
Pd	1.53376200	-0.42254100	0.50698100
C	2.78249600	1.48753100	2.61062200
C	2.91020100	2.96986700	2.24398900
C	1.40026500	1.19645500	3.22175900
H	3.92565400	3.18379700	1.88229500
H	2.19959600	3.24945300	1.45181800
H	2.71337700	3.60420800	3.12258200
C	0.18672200	1.44912400	2.35468000
H	1.37143700	0.15015600	3.57462000
H	1.31074900	1.83144300	4.11783100
H	0.26930800	2.42612300	1.84608700
H	-0.70334500	1.49798800	3.01037200
C	3.81107800	1.12467600	3.69191000
H	3.73434800	0.05720800	3.95354300
H	4.83524900	1.33142700	3.35750400
H	3.61434400	1.71170400	4.60216600
O	-0.04435700	0.42626100	1.41617500
C	-4.74357200	-1.51680900	0.44730300
C	-4.05035600	-2.14261100	1.51466500
C	-4.62410000	-3.23862600	2.18558700
C	-5.86919800	-3.67492600	1.76961000
C	-6.54686200	-3.03915400	0.70347500
C	-6.00751400	-1.95798700	0.02509000
H	-4.09716800	-3.72476600	3.00981900
H	-6.34226300	-4.52334400	2.26998500
H	-7.52991300	-3.41288400	0.40482000
H	-6.52532800	-1.46408300	-0.79559300
C	-2.83038200	-1.41866300	1.63994200
H	-1.99612900	-1.55789700	2.32574000
N	-2.80495400	-0.46095900	0.73909800

N	-3.93641900	-0.49845500	0.01329000
C	-4.14307900	0.47993200	-1.02664500
O	-5.16484700	0.37119500	-1.69398500
N	-3.15470800	1.37553000	-1.07992300
Pd	-1.54532400	0.95843600	0.07428100
C	-3.23573400	2.47127700	-2.06347100
C	-4.56179600	3.23410800	-1.92589400
C	-2.12196000	3.50061100	-1.78997100
H	-5.42057100	2.59402300	-2.16242700
H	-4.68035900	3.61445000	-0.89841200
H	-4.56668500	4.09866200	-2.60787600
C	-0.68282300	3.00826400	-1.75818700
H	-2.21469000	4.27539100	-2.56980700
H	-2.32850400	3.99863300	-0.82540800
H	-0.03538300	3.90722400	-1.84347700
H	-0.47714000	2.41237400	-2.67726200
C	-3.10293200	1.90868100	-3.48359700
H	-2.15463200	1.36329500	-3.60790300
H	-3.92912000	1.21534100	-3.69695000
H	-3.13076200	2.71969300	-4.22854800
O	-0.32657600	2.33800200	-0.60501300



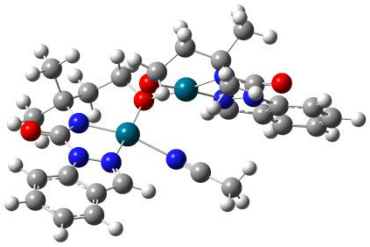
IN15

Free Energy = -1893.465413 Hartee

C	5.27947400	-0.83182400	-0.96924700
C	4.76621400	-1.87000900	-1.78660500
C	5.60289800	-2.52648700	-2.70878300
C	6.92304800	-2.12324100	-2.78417900
C	7.41866800	-1.08530100	-1.96026200
C	6.61985900	-0.42229200	-1.04339800
H	5.21390100	-3.32741800	-3.34141700

H	7.60024600	-2.61062300	-3.48960900
H	8.46922900	-0.79679500	-2.05033700
H	6.99831300	0.37557900	-0.40642400
C	3.39709800	-1.99130400	-1.42075000
H	2.62820600	-2.66168400	-1.80112400
N	3.12899000	-1.11524500	-0.47610000
N	4.23572200	-0.40590000	-0.19284900
C	4.18205800	0.58396400	0.84862200
O	5.20591000	1.20456500	1.09227600
N	2.97189300	0.64542900	1.41566100
Pd	1.53376200	-0.42254100	0.50698100
C	2.78249600	1.48753100	2.61062200
C	2.91020100	2.96986700	2.24398900
C	1.40026500	1.19645500	3.22175900
H	3.92565400	3.18379700	1.88229500
H	2.19959600	3.24945300	1.45181800
H	2.71337700	3.60420800	3.12258200
C	0.18672200	1.44912400	2.35468000
H	1.37143700	0.15015600	3.57462000
H	1.31074900	1.83144300	4.11783100
H	0.26930800	2.42612300	1.84608700
H	-0.70334500	1.49798800	3.01037200
C	3.81107800	1.12467600	3.69191000
H	3.73434800	0.05720800	3.95354300
H	4.83524900	1.33142700	3.35750400
H	3.61434400	1.71170400	4.60216600
O	-0.04435700	0.42626100	1.41617500
C	-4.74357200	-1.51680900	0.44730300
C	-4.05035600	-2.14261100	1.51466500
C	-4.62410000	-3.23862600	2.18558700
C	-5.86919800	-3.67492600	1.76961000
C	-6.54686200	-3.03915400	0.70347500
C	-6.00751400	-1.95798700	0.02509000
H	-4.09716800	-3.72476600	3.00981900
H	-6.34226300	-4.52334400	2.26998500
H	-7.52991300	-3.41288400	0.40482000
H	-6.52532800	-1.46408300	-0.79559300
C	-2.83038200	-1.41866300	1.63994200
H	-1.99612900	-1.55789700	2.32574000
N	-2.80495400	-0.46095900	0.73909800
N	-3.93641900	-0.49845500	0.01329000
C	-4.14307900	0.47993200	-1.02664500
O	-5.16484700	0.37119500	-1.69398500
N	-3.15470800	1.37553000	-1.07992300

Pd	-1.54532400	0.95843600	0.07428100
C	-3.23573400	2.47127700	-2.06347100
C	-4.56179600	3.23410800	-1.92589400
C	-2.12196000	3.50061100	-1.78997100
H	-5.42057100	2.59402300	-2.16242700
H	-4.68035900	3.61445000	-0.89841200
H	-4.56668500	4.09866200	-2.60787600
C	-0.68282300	3.00826400	-1.75818700
H	-2.21469000	4.27539100	-2.56980700
H	-2.32850400	3.99863300	-0.82540800
H	-0.03538300	3.90722400	-1.84347700
H	-0.47714000	2.41237400	-2.67726200
C	-3.10293200	1.90868100	-3.48359700
H	-2.15463200	1.36329500	-3.60790300
H	-3.92912000	1.21534100	-3.69695000
H	-3.13076200	2.71969300	-4.22854800
O	-0.32657600	2.33800200	-0.60501300



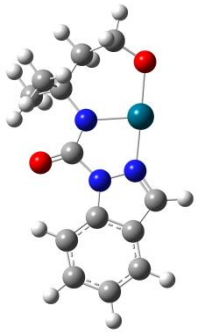
IN16

Free Energy = -2026.216117 Hartee

C	-4.89978700	0.51049300	-1.30558300
C	-4.71077700	1.85844600	-0.91353700
C	-5.64198500	2.84500500	-1.28854000
C	-6.73235700	2.45199600	-2.04264700
C	-6.90725400	1.10111100	-2.42449100
C	-6.00744300	0.10952600	-2.06964300
H	-5.50126900	3.88625800	-0.98978900
H	-7.47431100	3.19217900	-2.35169400
H	-7.78295000	0.83037200	-3.02036500
H	-6.13775300	-0.93133100	-2.36090900
C	-3.50041500	1.86011300	-0.16630600
H	-2.98810500	2.68910800	0.31747200
N	-3.01708800	0.63773700	-0.11838500
N	-3.83899200	-0.18828400	-0.79386500

C	-3.54060200	-1.59397900	-0.86070900
O	-4.30636300	-2.30005000	-1.50591300
N	-2.44234300	-1.90489100	-0.17368400
Pd	-1.40620800	-0.35106300	0.60256900
C	-2.01342700	-3.31428300	-0.10788700
C	-1.62420600	-3.81287900	-1.50483400
C	-0.82106800	-3.46951900	0.85766500
H	-2.49265200	-3.77662800	-2.17695000
H	-0.82689300	-3.19320500	-1.94315100
H	-1.26396900	-4.85260500	-1.45734700
C	0.43688700	-2.66646400	0.58569400
H	-1.15143300	-3.24491000	1.88650700
H	-0.55078700	-4.53764600	0.84421000
H	0.70265300	-2.70662000	-0.48780900
H	1.26887500	-3.13623600	1.14361700
C	-3.13933700	-4.18788200	0.46542300
H	-3.43140600	-3.82964000	1.46550200
H	-4.02296800	-4.17174000	-0.18483800
H	-2.79416600	-5.22869500	0.56486000
O	0.30986300	-1.34747400	1.03860400
C	3.99628418	2.10969878	3.03840348
C	3.64496478	1.12622687	3.99577863
C	4.16872375	1.18606115	5.30092895
C	5.02557981	2.22716034	5.60661300
C	5.36680195	3.20053785	4.63823573
C	4.86784622	3.16634171	3.34655922
H	3.90212993	0.43016559	6.04302472
H	5.44995655	2.30467636	6.61044806
H	6.04868359	4.00755324	4.91917548
H	5.12967026	3.91207539	2.59776322
C	2.76479256	0.24129041	3.31409582
H	2.25885458	-0.65005958	3.67856273
N	2.61000967	0.65463176	2.07378486
N	3.33597557	1.77542227	1.88702453
C	3.36412772	2.39260077	0.58666781
O	4.02573454	3.41390933	0.45999639
N	2.64502252	1.70234362	-0.29988417
Pd	1.50959000	0.22553000	0.44964400
C	2.64762366	2.10578624	-1.71855912
C	4.08828931	2.21794239	-2.23945702
C	1.97346136	1.01438483	-2.57667764
H	4.64686166	2.99568154	-1.70423209
H	4.61646732	1.25871926	-2.11781849
H	4.07841496	2.46609571	-3.31189214

C	0.52211024	0.68095159	-2.29325861
H	2.04541633	1.35259527	-3.62335370
H	2.56531508	0.08414802	-2.50657031
H	0.11087071	0.12532365	-3.15357106
H	-0.07732699	1.60851970	-2.21907433
C	1.92561499	3.44710154	-1.88541437
H	0.89652508	3.39937123	-1.49746035
H	2.46092356	4.23422535	-1.33549991
H	1.87941099	3.73597675	-2.94728809
O	0.32073898	-0.07295849	-1.13293296
C	-0.13479356	3.78305659	2.55538081
H	-0.92165855	4.48673370	2.24687288
H	0.81614412	4.07730301	2.08609754
H	-0.02492896	3.82711232	3.64886021
C	-0.48392451	2.43881433	2.14988039
N	-0.72051738	1.35535594	1.80675149

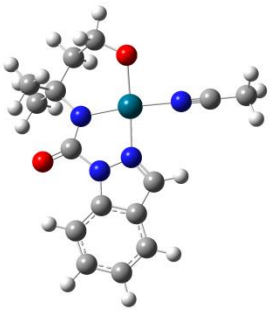


IN12

Free Energy = -946.720791 Hartee

C	-5.14065300	-0.51158600	0.77780000
C	-4.89875400	-1.86612400	0.44172100
C	-5.85486100	-2.85497300	0.74070800
C	-7.02108300	-2.45694600	1.36728400
C	-7.24689000	-1.09952800	1.69639900
C	-6.32481300	-0.10554400	1.41341100
H	-5.67391900	-3.90094700	0.48327700
H	-7.78494000	-3.19788400	1.61480600
H	-8.18213700	-0.82570200	2.19188500
H	-6.49500300	0.93990200	1.66508900
C	-3.61790200	-1.87251600	-0.17495000
H	-3.05075000	-2.70890200	-0.57850200
N	-3.14492000	-0.64449500	-0.20736200
N	-4.04045900	0.18757000	0.35996800

C	-3.75156700	1.59321200	0.43816000
O	-4.57044900	2.30615200	1.00156000
N	-2.59316800	1.89635400	-0.15279200
Pd	-1.46871100	0.33274700	-0.72725800
C	-2.15323400	3.30499800	-0.18932500
C	-1.84832100	3.79515200	1.23061100
C	-0.90735000	3.45663600	-1.08468700
H	-2.75683800	3.76016200	1.84812600
H	-1.08192000	3.16969500	1.71359700
H	-1.48207100	4.83360700	1.21133800
C	0.33914800	2.66956000	-0.73334100
H	-1.17795100	3.21602100	-2.12758800
H	-0.64468500	4.52651600	-1.06986800
H	0.56710500	2.74910900	0.34630300
H	1.19046100	3.11621200	-1.27959500
C	-3.23540900	4.18724200	-0.82986300
H	-3.47160200	3.82883300	-1.84451900
H	-4.15609000	4.18546100	-0.23391300
H	-2.87068200	5.22266300	-0.91241600
O	0.22667300	1.33335300	-1.14043500

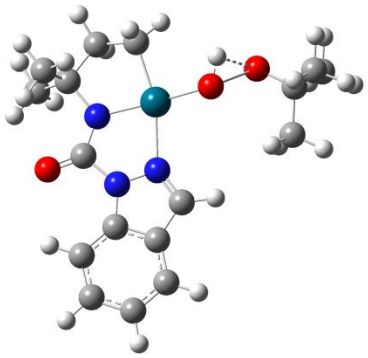


IN17

Free Energy = -1079.469226 Hartee

C	5.30678800	-0.72321400	-0.99313100
C	4.80539100	-1.66319800	-1.92825400
C	5.65622600	-2.21703800	-2.90332100
C	6.97821400	-1.81279400	-2.91201300
C	7.46190100	-0.87393600	-1.97052500
C	6.64905600	-0.31318000	-0.99933300
H	5.27659600	-2.94216100	-3.62657000
H	7.66623800	-2.22211400	-3.65554200
H	8.51434000	-0.58108700	-2.01091700
H	7.01835300	0.40806100	-0.27200900
C	3.43008400	-1.81884700	-1.60059100

H	2.66625900	-2.44055300	-2.06468700
N	3.14766600	-1.05027200	-0.57045300
N	4.25096200	-0.38119100	-0.19202600
C	4.18157500	0.48705400	0.95192800
O	5.20251900	1.07281100	1.27966100
N	2.96234800	0.48877300	1.50279900
Pd	1.53626500	-0.46128900	0.45335300
C	2.75498700	1.19515400	2.77988500
C	2.89211100	2.70835800	2.58041900
C	1.36272100	0.84401500	3.33366800
H	3.91409200	2.95659700	2.26149600
H	2.19574600	3.07590800	1.81183100
H	2.68174500	3.24331800	3.51987300
C	0.16208200	1.19213300	2.48169200
H	1.32681000	-0.23440000	3.56988200
H	1.26045000	1.37768000	4.29227000
H	0.25095400	2.21899100	2.08429900
H	-0.73681700	1.17021400	3.12668700
C	3.76454100	0.71151300	3.83144800
H	3.68166500	-0.37811000	3.97194900
H	4.79452400	0.95038900	3.53906400
H	3.55326000	1.19490600	4.79765400
O	-0.05614300	0.27739300	1.43502700
C	-1.37936200	-3.00783600	-2.07659200
H	-0.91026800	-3.26180900	-3.03838100
H	-2.29619600	-2.42752000	-2.25839200
H	-1.63122600	-3.93174300	-1.53562500
C	-0.46602500	-2.21958900	-1.28851700
N	0.25333300	-1.58010000	-0.65335400



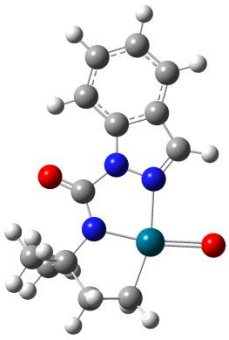
TS13

Free Energy = -1180.104217 Hartee

C	-3.05548400	-1.33672600	-0.03992600

C	-2.39591100	-2.58810500	-0.00236400
C	-3.13606200	-3.78270700	0.02358300
C	-4.51698800	-3.68874900	0.01318000
C	-5.16036600	-2.43172200	-0.02373600
C	-4.45429700	-1.23821700	-0.05129100
H	-2.63084100	-4.75072500	0.05153800
H	-5.12385600	-4.59706900	0.03348900
H	-6.25301500	-2.39746400	-0.03108500
H	-4.95127300	-0.27008000	-0.07991500
C	-1.00521200	-2.27016700	-0.00293000
H	-0.14310400	-2.93655300	0.02190100
N	-0.84376600	-0.97035000	-0.03962600
N	-2.06286300	-0.38368700	-0.06234500
C	-2.19092000	1.03853800	-0.08507800
O	-3.30395200	1.52808800	-0.04459300
N	-0.99202200	1.66630500	-0.17286200
Pd	0.63741700	0.63796000	0.09256700
C	-0.88158100	3.14516400	-0.12291700
C	-1.24025600	3.63923200	1.28168300
C	0.59382600	3.41491400	-0.45383000
H	-2.28059700	3.38296400	1.52997000
H	-0.58122700	3.19060200	2.04096300
H	-1.13396900	4.73357400	1.33561900
C	1.52575500	2.44079100	0.25311200
H	0.71977100	3.30784500	-1.54450800
H	0.84508300	4.46313000	-0.20976700
H	1.62176400	2.64165600	1.33328200
H	2.53304600	2.42025000	-0.19119800
C	-1.77046800	3.81719400	-1.17195800
H	-1.58885600	3.38428000	-2.16831900
H	-2.83589900	3.71105200	-0.93282900
H	-1.52435600	4.88943800	-1.21789300
O	3.98228700	-0.29610700	-0.29677400
C	4.65520600	-1.49125600	-0.14905100
O	2.12926100	-0.30089300	0.80826600
H	3.06539900	0.09439000	0.70368500
C	5.99130700	-1.26035100	-0.90051600
H	6.59932900	-2.17738700	-0.84672700
H	5.80112300	-1.01830700	-1.95622000
H	6.55042800	-0.43269300	-0.44030000
C	4.94016100	-1.81067400	1.31892700
H	3.99481700	-1.96331000	1.86211600
H	5.54646300	-2.72379000	1.41989700
H	5.48286100	-0.97866500	1.79477100

C	3.88937700	-2.63252200	-0.82227000
H	3.69590800	-2.39563400	-1.87978600
H	4.45001000	-3.57841000	-0.77076900
H	2.92108700	-2.76764300	-0.31506100

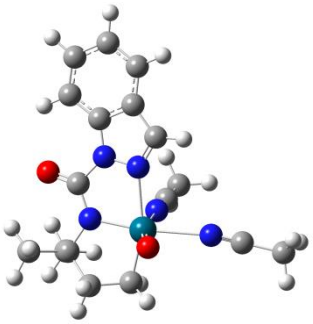


IN18

Free Energy = -946.592591 Hartee

C	2.56328300	0.40210600	-0.00665300
C	3.12256000	-0.89724000	-0.03933200
C	4.51679900	-1.07365800	-0.00635600
C	5.31077800	0.05795800	0.05679200
C	4.73674700	1.34849800	0.08712100
C	3.36510300	1.55081300	0.05637400
H	4.95213500	-2.07519600	-0.02990900
H	6.39847100	-0.04175000	0.08388100
H	5.39632400	2.21894500	0.13591100
H	2.92521700	2.54642400	0.07787200
C	2.00178700	-1.77784800	-0.10404700
H	1.97905000	-2.86682700	-0.14664700
N	0.88928300	-1.08707400	-0.10718500
N	1.19757100	0.22727400	-0.04653200
C	0.17639000	1.21927600	-0.03636400
O	0.49249500	2.39304700	-0.05515800
N	-1.08100700	0.71289500	-0.04127800
Pd	-1.35133600	-1.20424300	-0.17050700
C	-2.29400400	1.56689300	0.09242900
C	-2.56250300	2.23634600	-1.25853900
C	-3.41754700	0.58225000	0.45934800
H	-1.71526600	2.87563300	-1.54718300
H	-2.71777400	1.48782100	-2.05051100
H	-3.46294300	2.86657100	-1.19467000
C	-3.30173600	-0.72645900	-0.29569500
H	-3.35869600	0.37854600	1.54159500

H	-4.39717200	1.06100800	0.28117100
H	-3.48112800	-0.63424900	-1.38067100
H	-3.91879900	-1.53255000	0.12264100
C	-2.16343200	2.61438700	1.19691800
H	-1.85494100	2.14524900	2.14435400
H	-1.43670700	3.39456900	0.93929500
H	-3.14383100	3.08856800	1.35813100
O	-1.66359100	-2.53169200	1.01278600



IN19

Free Energy = -1212.06553 Hartee

C	-2.66604000	0.50789800	-0.02339700
C	-3.22009800	-0.61813400	-0.67819500
C	-4.61338300	-0.80417100	-0.72060600
C	-5.41369400	0.14229700	-0.10545600
C	-4.84650200	1.26193600	0.54427000
C	-3.47720200	1.46979900	0.60034100
H	-5.04442600	-1.67123900	-1.22654900
H	-6.50038600	0.02845700	-0.12014900
H	-5.51005700	1.99037100	1.01805300
H	-3.03935000	2.33316800	1.09789600
C	-2.09393200	-1.33710900	-1.17844200
H	-2.06588800	-2.26734200	-1.74597700
N	-0.98626800	-0.71388500	-0.86442000
N	-1.30158000	0.39720500	-0.16486100
C	-0.29382500	1.30053300	0.31432600
O	-0.65548000	2.27928400	0.95214000
N	0.94911400	0.95557100	-0.02565300
Pd	1.31800000	-0.83888300	-0.79512300
C	2.15033500	1.72776100	0.36820200
C	2.40046100	1.58332900	1.87118500
C	3.29228500	1.10815600	-0.45426800
H	1.54095500	1.96845500	2.43967300

H	2.55976700	0.53240700	2.15516500
H	3.29268400	2.15729300	2.16613600
C	3.25533100	-0.40433900	-0.45784800
H	3.19625300	1.46232900	-1.49331900
H	4.26496800	1.47391800	-0.07806300
H	3.49748100	-0.86939700	0.51004800
H	3.85879400	-0.84925800	-1.25892100
C	2.01171800	3.20407800	-0.00951900
H	1.75129800	3.30614200	-1.07470800
H	1.23757300	3.70117900	0.58831500
H	2.97210000	3.71634000	0.15753000
O	1.64262900	-0.74051600	-2.56363200
C	0.50843600	-2.79623800	3.44638000
H	0.45994400	-3.88573200	3.29978800
H	1.31299100	-2.55908000	4.15838100
H	-0.45158700	-2.43926100	3.84828300
C	0.77582500	-2.15011100	2.18568300
N	0.98493700	-1.64237800	1.17065700
C	2.12125981	-5.66758126	-2.41291901
H	1.53813818	-5.89494303	-3.28077601
H	1.90774745	-6.37951527	-1.64320320
H	3.16129399	-5.71118370	-2.66056340
C	1.77094518	-4.25294277	-1.91524683
N	1.50707934	-3.18737183	-1.54036899