

Electronic Supplementary Information (ESI)

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Reference

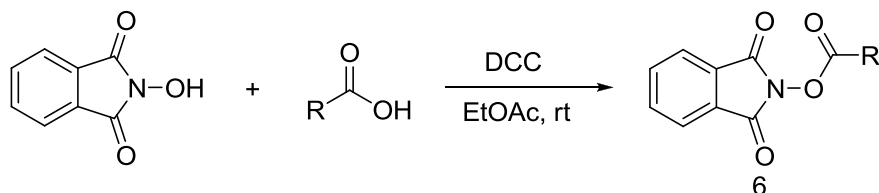
NMR Spectra

General Remarks

All commercially available compounds were purchased from J&K[®], Energy and Macklin, and used without any further purification. Anhydrous MeCN, Dichloromethane, and DMF were purified prior to use via a solvent column system. All other solvents were of reagent grade quality. Flash column chromatography was performed using either Silicycle silica gel (230-400 mesh) or Biotage[®] Isolera flash purification system on SNAP HP-SIL columns. Analytical thin-layer chromatography (TLC) was performed on 0.2 mm coated silica gel plates (EMD 60-F254) and visualized using a UV lamp (254 nm) and KMnO₄ stain. Reactions were performed in a schlenk tube under standard conditions (specific reaction conditions are described below). Analysis of crude reaction mixture was done on an Agilent 7890 GC System with an Agilent 5975 Mass Selective Detector. ¹H-NMR spectra and ¹³C-NMR spectra were recorded on a Bruker AVIII-400 spectrometers and JEOL-600 spectrometers. Chemical shifts are reported in δ , parts per million (ppm) relative to the residual solvent peak. Coupling constants are reported as Hertz (Hz), signal shapes and splitting patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. High resolution mass spectra were obtained with a Bruker APEXIV Fourier transform ion cyclotron resonance mass spectrometer using electrospray ionisation (ESI). The 25W fluorescent light bulbs were directly got from the supermarket.

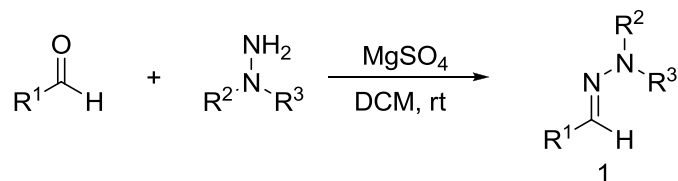
Experimental Procedure

1. Typical procedures for synthesis of substituted N-acyloxyphthalimides **6**¹



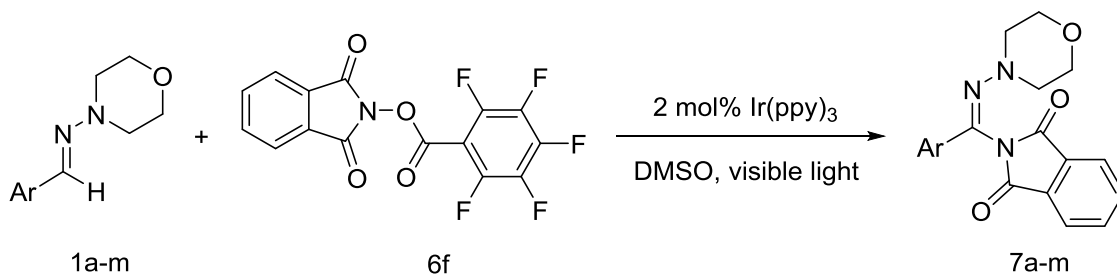
In a 250 mL round bottom flask equipped with magnetic stir bar was added N-hydroxyphthalimide (4.29 mmol, 700 mg, 1.0 equiv) and dicyclohexylcarbodiimide (4.29 mmol, 885 mg, 1.0 equiv). Ethyl acetate (125 mL) was then added followed by the appropriate carboxylic acid (4.29 mmol, 1.0 equiv) and the reaction was stirred at room temperature, open to air for 3 h, during which time the reaction mixture became cloudy and a white solid precipitated from the solution. The white solid was removed via vacuum filtration and the filtrate was dried with MgSO_4 and further dried *in vacuo* to give the crude product. Recrystallization of the crude solid from hot ethanol provided the pure substituted N-acyloxyphthalimide.

2. Typical procedures for the synthesis of starting aldehyde hydrazones **1**²



A mixture of hydrazine (2.4 mmol), aldehyde (2.0 mmol) and anhydrous MgSO_4 (0.5 g) in DCM (10 mL) was stirred overnight at room temperature. After filtration of MgSO_4 , DCM was removed under reduced pressure and the residue was subjected to column chromatography to give the desired product **1** with almost quantitative yields.

3. General Procedure for amination of Aldehyde Hydrazone

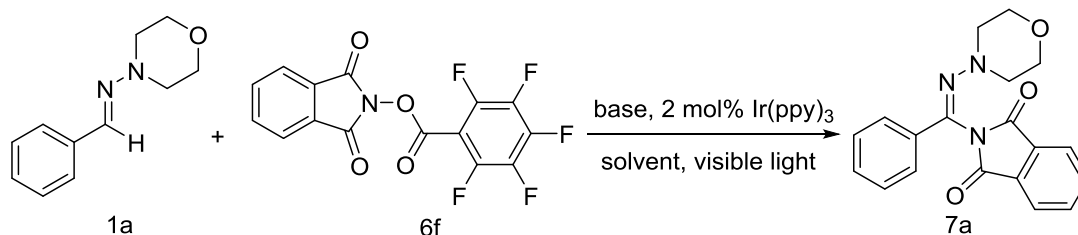


An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar, **1** (0.1 mmol), *fac*- $\text{Ir}(\text{ppy})_3$ (0.02 equiv, 0.002 mmol, 1.3 mg), **6f** (3 equiv, 0.3 mmol). The flask was evacuated and backfilled with N_2 for 3 times. 1.0 ml DMSO was added with syringe under N_2 . The tube was placed at a distance (app. 2.5 cm) from fluorescent light bulb, and the resulting solution was stirred at ambient temperature under visible-light irradiation and monitored by TLC. After the reaction was finished, the mixture was washed with water

and extracted with EtOAc (3 x 1.5 mL). The combined organic layers were washed with brine (2 mL), dried (Na₂SO₄) and concentrated *in vacuo*. And the residue was purified by chromatography on silica gel to afford the **7**.

Optimization of the reaction conditions

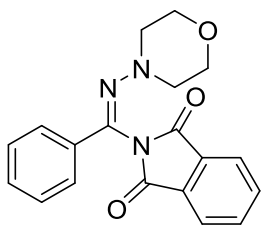
Table S1 Optimization studies



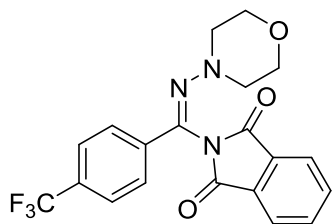
Entry	Base	Solvent	Yield ^b (%)
1	-	DCE	<5
2	-	MeCN:DMF(1:1)	7
3	-	MeCN:DMSO(1:1)	44
4	CsF	DMSO	< 5
5	Cs ₂ CO ₃	DMSO	< 5

^a Reaction condition: **1a** (0.1 mmol), **2a** (0.3 mmol, 3 equiv), base (0.15 mmol, 1.5 equiv), Ir(ppy)₃ (0.002 mmol, 2 mol%), solvent (1.0 mL), at room temperature, fluorescent light bulb, 24h. ^b Yields determined by GC-Mass, decahydronaphthalene used as internal standard.

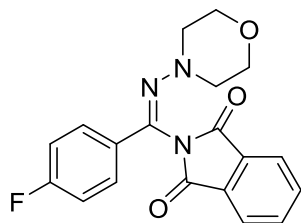
Characterization of new compounds



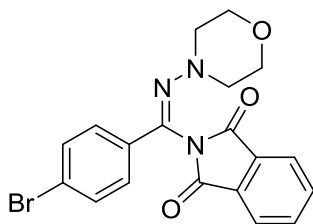
Following general procedure, the crude product was purified by flash column chromatography (8:2 petroleum ether: ethyl acetate) to afford (45% yield) as waxy solid. Reaction time: 24 h. ^1H NMR (400 MHz, CDCl_3) δ 7.96 (dd, $J = 5.5, 3.1$ Hz, 2H), 7.84 (dd, $J = 5.5, 3.1$ Hz, 2H), 7.79 – 7.72 (m, 2H), 7.49 – 7.34 (m, 3H), 3.68 – 3.61 (m, 4H), 2.96 – 2.89 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.1, 145.2, 134.7, 133.0, 131.8, 131.1, 128.6, 127.0, 124.1, 66.1, 55.1. HRMS (ESI) $[\text{M}+\text{H}]^+$ calcd. For $\text{C}_{19}\text{H}_{18}\text{N}_3\text{O}_3$ 336.1342, found 336.1345.



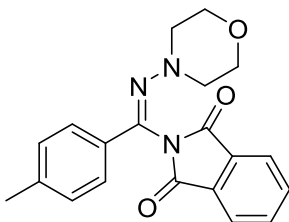
Following general procedure, the crude product was purified by flash column chromatography (8:2 petroleum ether: ethyl acetate) to afford (52% yield) as waxy solid. Reaction time: 24 h. ^1H NMR (400 MHz, CDCl_3) δ 7.98 (dd, $J = 5.5, 3.1$ Hz, 2H), 7.91 – 7.83 (m, 2H), 7.83 – 7.76 (m, 2H), 7.61 (d, $J = 8.3$ Hz, 2H), 3.74 – 3.65 (m, 4H), 3.10 – 3.03 (m, 4H). ^{13}C NMR (150 MHz, CDCl_3) δ 166.1, 138.0, 137.1, 135.1, 132.1 ($^2J_{\text{CF}} = 31.5$ Hz), 131.8, 125.7, 124.0 ($^1J_{\text{CF}} = 270.8$ Hz), 124.0, 124.4, 66.23, 55.14. HRMS (ESI) $[\text{M}+\text{H}]^+$ calcd. For $\text{C}_{20}\text{H}_{17}\text{F}_3\text{N}_3\text{O}_3$ 404.1216, found 404.1219.



Following general procedure, the crude product was purified by flash column chromatography (8:2 petroleum ether: ethyl acetate) to afford (50% yield) as waxy solid. Reaction time: 24 h. ^1H NMR (400 MHz, CDCl_3) δ 7.96 (dd, $J = 5.5, 3.1$ Hz, 2H), 7.85 (dd, $J = 5.5, 3.1$ Hz, 2H), 7.83 – 7.72 (m, 2H), 7.07 (t, $J = 8.6$ Hz, 2H), 3.67 – 3.59 (m, 4H), 2.93 – 2.86 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.1, 164.7 ($^1J_{\text{CF}} = 250.5$ Hz), 144.6, 134.8, 131.8, 129.2 ($^3J_{\text{CF}} = 8.6$ Hz), 124.1, 115.8 ($^2J_{\text{CF}} = 21.9$ Hz), 66.14, 55.08. HRMS (ESI) $[\text{M}+\text{H}]^+$ calcd. For $\text{C}_{19}\text{H}_{17}\text{FN}_3\text{O}_3$ 354.1248, found 354.1248.

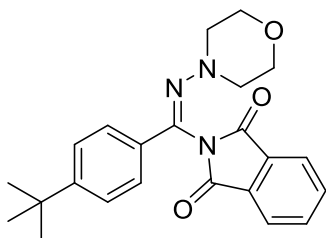


Following general procedure, the crude product was purified by flash column chromatography (8:2 petroleum ether: ethyl acetate) to afford (46% yield) as waxy solid. Reaction time: 24 h. ^1H NMR (400 MHz, CDCl_3) δ 7.96 (dd, $J = 5.5, 3.1$ Hz, 2H), 7.92 – 7.80 (m, 2H), 7.63 – 7.53 (m, 2H), 7.53 – 7.47 (m, 2H), 3.68 – 3.60 (m, 4H), 2.98 – 2.91 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ 165.9, 142.5, 134.8, 132.2, 131.8, 131.7, 128.3, 125.4, 124.2, 66.1, 54.9. HRMS (ESI) $[\text{M}+\text{H}]^+$ calcd. For $\text{C}_{19}\text{H}_{17}\text{BrN}_3\text{O}_3$ 414.0447, found 414.0448.

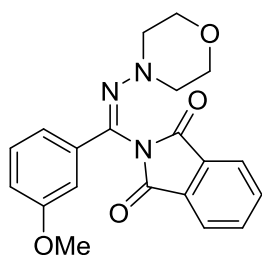


Following general procedure, the crude product was purified by flash column chromatography (8:2 petroleum ether: ethyl acetate)

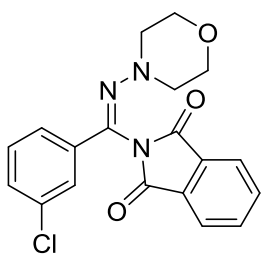
to afford (34% yield) as waxy solid. Reaction time: 24 h. ^1H NMR (600 MHz, CDCl_3) δ 7.95 (dd, $J = 5.4, 3.1$ Hz, 2H), 7.82 (dd, $J = 5.5, 3.2$ Hz, 2H), 7.64 (d, $J = 8.3$ Hz, 2H), 7.18 (d, $J = 8.1$ Hz, 2H), 3.61 (m, 4H), 3.02 – 2.73 (m, 4H), 2.36 (s, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 166.2, 146.7, 141.8, 134.7, 131.9, 130.2, 129.5, 127.2, 124.1, 66.2, 55.2, 21.5. HRMS (ESI) $[\text{M}+\text{H}]^+$ calcd. For $\text{C}_{20}\text{H}_{20}\text{N}_3\text{O}_3$ 350.1499, found 350.1501.



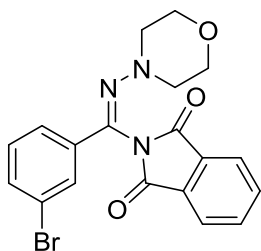
Following general procedure, the crude product was purified by flash column chromatography (8:2 petroleum ether: ethyl acetate) to afford (39% yield) as waxy solid. Reaction time: 24 h. ^1H NMR (400 MHz, CDCl_3) δ 7.96 (dd, $J = 5.5, 3.1$ Hz, 2H), 7.83 (dd, $J = 5.5, 3.1$ Hz, 2H), 7.73 – 7.64 (m, 2H), 7.44 – 7.37 (m, 2H), 3.66 – 3.59 (m, 4H), 2.92 – 2.85 (m, 4H), 1.31 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.1, 154.7, 146.4, 134.6, 131.9, 130.0, 126.9, 125.6, 124.0, 66.1, 55.1, 34.8, 31.1. HRMS (ESI) $[\text{M}+\text{H}]^+$ calcd. For $\text{C}_{23}\text{H}_{26}\text{N}_3\text{O}_3$ 392.1968, found: 392.1968.



Following general procedure, the crude product was purified by flash column chromatography (6:4 petroleum ether: ethyl acetate) to afford (35% yield) as waxy solid. Reaction time: 24 h. ^1H NMR (400 MHz, CDCl_3) δ 7.96 (dd, $J = 5.5, 3.1$ Hz, 2H), 7.89 – 7.79 (m, 2H), 7.40 – 7.34 (m, 1H), 7.32 – 7.20 (m, 2H), 6.99 (ddd, $J = 7.8, 2.6, 1.5$ Hz, 1H), 3.83 (s, 3H), 3.68 – 3.60 (m, 4H), 2.97 – 2.89 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.1, 159.8, 134.7, 134.5, 131.8, 129.6, 124.1, 119.6, 117.1, 112.1, 77.2, 66.2, 55.4, 55.1. HRMS (ESI) $[\text{M}+\text{H}]^+$ calcd. For $\text{C}_{20}\text{H}_{20}\text{N}_3\text{O}_4$ 366.1448, found 366.1449.

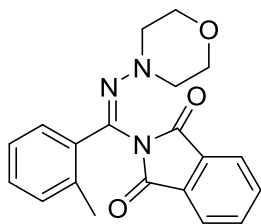


Following general procedure, the crude product was purified by flash column chromatography (6:4 petroleum ether: ethyl acetate) to afford (42% yield) as waxy solid. Reaction time: 24 h. ^1H NMR (400 MHz, CDCl_3) δ 7.97 (dd, $J = 5.5, 3.1$ Hz, 2H), 7.85 (dd, $J = 5.4, 3.1$ Hz, 2H), 7.74 (t, $J = 1.9$ Hz, 1H), 7.54 (dt, $J = 7.8, 1.4$ Hz, 1H), 7.39 (dt, $J = 8.2, 1.3$ Hz, 1H), 7.29 (t, $J = 7.9$ Hz, 1H), 3.69 – 3.62 (m, 4H), 3.01 – 2.95 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ 165.9, 140.8, 135.3, 134.9, 134.8, 134.3, 132.7, 131.7, 130.7, 129.8, 126.8, 124.8, 124.3, 123.5, 66.1, 54.9. HRMS (ESI) $[\text{M}+\text{H}]^+$ calcd. For $\text{C}_{19}\text{H}_{17}\text{ClN}_3\text{O}_3$ 370.0952, found 370.0953.



Following general procedure, the crude product was purified by flash column chromatography (6:4 petroleum ether: ethyl acetate) to afford (40% yield) as waxy solid. Reaction time: 24 h. ^1H NMR (400 MHz, CDCl_3) δ 7.96 (dd, $J = 7.1, 3.6$ Hz, 2H), 7.91 (t, $J = 1.9$

Hz, 1H), 7.84 (dd, $J = 5.5, 3.1$ Hz, 2H), 7.62 – 7.49 (m, 2H), 7.23 (t, $J = 7.9$ Hz, 1H), 3.70 – 3.57 (m, 4H), 3.06 – 2.94 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ 165.95, 140.7, 135.5, 134.9, 133.6, 131.7, 130.1, 129.7, 125.3, 124.3, 122.9, 66.1, 54.9. HRMS (ESI) $[\text{M}+\text{H}]^+$ calcd. For $\text{C}_{19}\text{H}_{17}\text{BrN}_3\text{O}_3$ 414.0447, found 414.0446.



Following general procedure, the crude product was purified by flash column chromatography (7:3 petroleum ether: ethyl acetate) to afford (39% yield) as waxy solid. Reaction time: 24 h. ^1H NMR (400 MHz, CDCl_3) δ 7.90 – 7.79 (m, 2H), 7.73 (dd, $J = 5.5, 3.1$ Hz, 2H), 7.32 (dd, $J = 7.7, 1.4$ Hz, 1H), 7.29 – 7.20 (m, 2H), 7.15 (td, $J = 7.4, 1.6$ Hz, 1H), 3.70 – 3.62 (m, 4H), 3.00 – 2.92 (m, 4H), 2.51 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.8, 137.6, 134.3, 134.1, 131.9, 130.3, 129.7, 127.6, 125.8, 123.7, 66.1, 54.6, 20.1. HRMS (ESI) $[\text{M}+\text{H}]^+$ calcd. For $\text{C}_{20}\text{H}_{20}\text{N}_3\text{O}_3$ 350.1499, found 350.1500.

Details of the X-ray Crystal Structure

Table S2 Crystal data and structure refinements for compounds 7b.

Identification code	A
Empirical formula	$\text{C}_{20}\text{H}_{16}\text{N}_3\text{O}_3\text{F}_3$
Formula weight	403.36
Temperature/K	153.15
Crystal system	orthorhombic
Space group	Pbcn
$a/\text{\AA}$	19.520(4)
$b/\text{\AA}$	13.946(3)
$c/\text{\AA}$	13.312(3)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
Volume/ \AA^3	3623.8(13)
Z	8
$\rho_{\text{calc}}/\text{g/cm}^3$	1.479
μ/mm^{-1}	0.122
F(000)	1664.0
Crystal size/ mm^3	$0.27 \times 0.25 \times 0.23$

Radiation	MoK α ($\lambda = 0.71073$)
2 Θ range for data collection/ $^\circ$	5.842 to 54.956
Index ranges	$-24 \leq h \leq 25$, $-16 \leq k \leq 18$, $-12 \leq l \leq 17$
Reflections collected	20719
Independent reflections	4113 [$R_{\text{int}} = 0.0501$, $R_{\text{sigma}} = 0.0339$]
Data/restraints/parameters	4113/0/262
Goodness-of-fit on F^2	1.251
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0669$, $wR_2 = 0.1318$
Final R indexes [all data]	$R_1 = 0.0719$, $wR_2 = 0.1341$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.22/-0.23

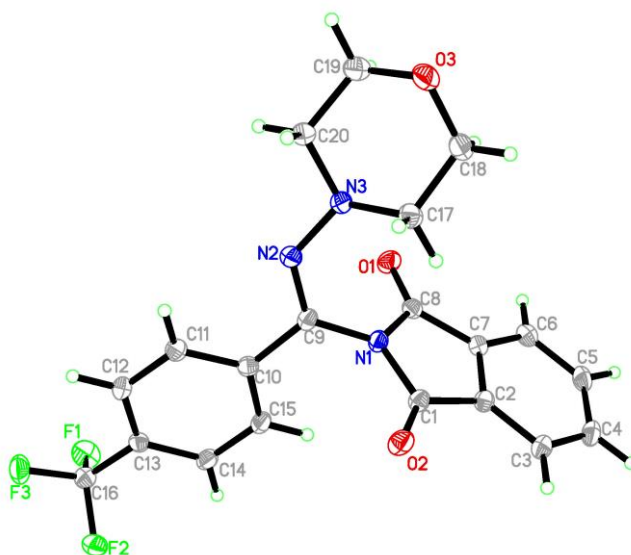
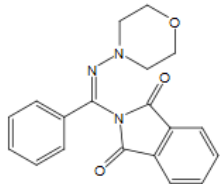
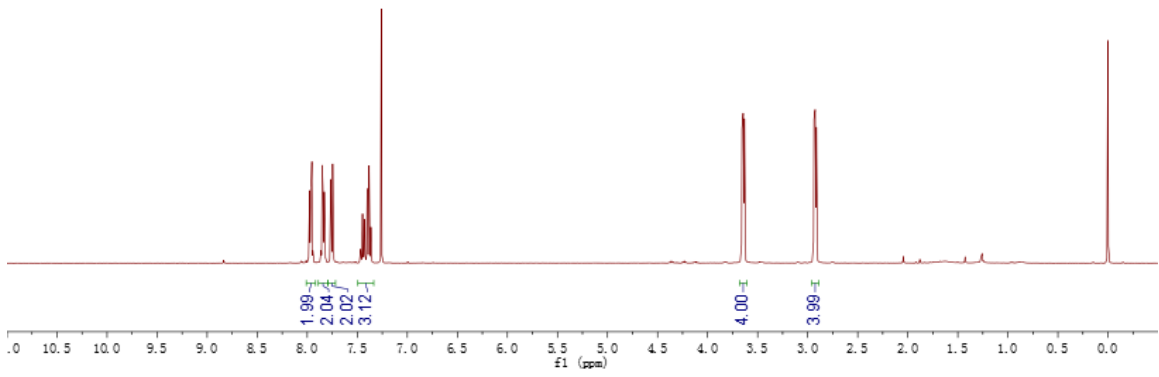
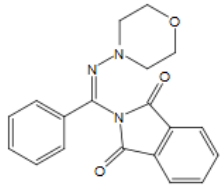


Fig. S1. Crystal structure of compound 7b.

Reference

- 1 P. Xu, G. Wang, Y. Zhu, W. Li, Y. Cheng, S. Li and C. Zhu, *Angew. Chem. Int. Ed.*, 2016, **55**, 2939-2943.
- 2 L. J. Allen, P. J. Cabrera, M. Lee and M. S. Sanford, *J. Am. Chem. Soc.*, 2014, **136**, 5607-5610.

Copies of ^1H NMR, ^{13}C NMR spectra



166.11
145.27
134.71
133.01
131.86
131.12
128.84
127.03
124.13
66.18
55.10

