# **Supporting Information**

# Copper-Catalyzed *anti*-Stereoselective 1,2-Silylamination of Alkynes

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### **1. Experimental Section:**

General Considerations. All products were prepared under argon atmosphere using standard Schlenk technique. <sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F data were recorded with Bruker Advance III (500 MHz) spectrometers with tetramethylsilane as an internal standard. All chemical shifts ( $\delta$ ) are reported in ppm and coupling constants (J) in Hz. All chemical shifts are reported relative to tetramethylsilane and d-solvent peaks, respectively. Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), triplet (t), quartet (q), and multiplet (m). Column chromatography was performed on silica gel 200-300 mesh. Analytical thin-layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254 nm). High-resolution mass spectrometry (HRMS) were done on an electrospray ionization (ESI) Fourier transform mass spectrometer (FTMS, Thermo QExactive Focus). Gas chromatograms were completed on a gas chromatograph (Shimazu: Nexis GC-2030). X-ray diffraction (XRD) patterns were recorded on a Rigaku smartlab system at 45 kV and 200 mA with Cu-Ka radiation. 2-Picolinamidederivatives were prepared following a literature procedure.<sup>1</sup> Unless otherwise noted below, all other compounds have been reported in the literature or are commercially available from Aldrich, Acros, Alfa Aesar, and Energy Chemical Company and used as received without any further purification.

	PA O N N 1a	DOEt + Ph 2a	+ Ph <sub>3</sub> SiH Catalyst Oxidant Solvent <b>3a</b> Temp.	(15 mol%) (3 equiv) (1 mL) , 20 h <b>PA</b> Ph Ph <b>4a</b>	<sup>∼</sup> COOEt Ì SiPh <sub>3</sub>
Entry	Catalyst	Oxidant	Solvent	T (°C)	Yield (%) <sup>[b]</sup>
1	CuF <sub>2</sub>	DTBP	Toluene	100	63
2	Cu(OAc) <sub>2</sub>	DTBP	Toluene	100	47
3	Cu(OTf) <sub>2</sub>	DTBP	Toluene	100	0
4	$Cu(acac)_2$	DTBP	Toluene	100	45
5	CuSO <sub>4</sub>	DTBP	Toluene	100	60
6	CuCl <sub>2</sub>	DTBP	Toluene	100	52
7	CuBr <sub>2</sub>	DTBP	Toluene	100	30

# 2. Table S1. Optimization of the Reaction Conditions<sup>a</sup>

8	Cu <sub>2</sub> O	DTBP	Toluene	100	58
9	CuCl	DTBP	Toluene	100	53
10	CuBr	DTBP	Toluene	100	40
11	CuI	DTBP	Toluene	100	35
12	ZnCl <sub>2</sub>	DTBP	Toluene	100	17
13	MnCl <sub>2</sub>	DTBP	Toluene	100	15
14	FeCl <sub>2</sub>	DTBP	Toluene	100	24
15	FeCl <sub>3</sub>	DTBP	Toluene	100	27
16	NiCl <sub>2</sub>	DTBP	Toluene	100	39
17	-	DTBP	Toluene	100	0
18	CuF <sub>2</sub>	TBHP	Toluene	100	37
19	CuF <sub>2</sub>	TBPB	Toluene	100	55
20	CuF <sub>2</sub>	DCP	Toluene	100	48
21	CuF <sub>2</sub>	BPO	Toluene	100	41
22	CuF <sub>2</sub>	$K_2S_2O_8$	Toluene	100	0
23	CuF <sub>2</sub>	-	Toluene	100	0
24	CuF <sub>2</sub>	DTBP	o-xylene	100	54
25	CuF <sub>2</sub>	DTBP	<i>m</i> -xylene	100	61
26	CuF <sub>2</sub>	DTBP	<i>p</i> -xylene	100	55
27	CuF <sub>2</sub>	DTBP	mesitylene	100	50
28	CuF <sub>2</sub>	DTBP	4-chlorotoluene	100	48
29	CuF <sub>2</sub>	DTBP	PhCF <sub>3</sub>	100	74
30	CuF <sub>2</sub>	DTBP	DCE	100	16
31	CuF <sub>2</sub>	DTBP	DMF	100	11
32	CuF <sub>2</sub>	DTBP	PhCF <sub>3</sub>	110	79
33	CuF <sub>2</sub>	DTBP	PhCF <sub>3</sub>	120	82
34	CuF <sub>2</sub>	DTBP	PhCF <sub>3</sub>	130	81
35 <sup>[c]</sup>	CuF <sub>2</sub>	DTBP	PhCF <sub>3</sub>	120	54

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), **3a** (0.6 mmol), catalyst (15 mol%), oxidant (3 equiv) and in the solvent (1 mL) for 20 h under nitrogen atmosphere. DTBP = di-*tert*-butyl peroxide. TBHP = *tert*-Butyl hydroperoxide. TBPB = *tert*-Butyl peroxybenzoate. DCP = Dicumyl peroxide. BPO = Benzoyl Peroxide. PA = 2-Pyridylacyl. [b] Isolated yields. [c] Under air.

# **3. Synthetic Procedures**

# (a) General Procedure for the Copper-Catalyzed Preparation of 4, 5, 6 and 7



A mixture of substituted amides (1) (0.2 mmol, 1.0 equiv), alkynes (2) (0.3 mmol, 1.5 equiv), silanes (3) (0.6 mmol, 3.0 equiv),  $CuF_2$  (0.03 mmol, 15 mol%), and DTBP (0.6 mmol, 3 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry PhCF<sub>3</sub> (1 mL) was added and the mixture was stirred at 120 °C in a pre-heated oil bath for 20 h under N<sub>2</sub> atmosphere. Then, the mixture was cooled to room temperature and concentrated in vacuo and the resulting residue was purified by column chromatography on silica gel with EtOAc/petroleum ether.

#### (b) Gram-Scale Preparation of 4a



A mixture of ethyl picolinoylglycinate (1a) (3 mmol, 1.0 equiv), phenylacetylene (2a) (4.5 mmol, 1.5 equiv), triphenylsilane (3a) (9 mmol, 3.0 equiv), CuF<sub>2</sub> (15 mol%), and DTBP (3 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry PhCF<sub>3</sub> (15 mL) was added and the mixture was stirred at 120 °C in a pre-heated oil bath for 20 h under N<sub>2</sub> atmosphere. Then, the mixture was cooled to room temperature and concentrated in vacuo and the resulting residue was purified by flash column chromatography on silica gel with EtOAc/petroleum ether, the product 4a was affored as a yellow solid in 72% yield (1.229 g, 2.16 mmol).

#### (c) Derivatization Reaction of 4a for the Preparation of 8<sup>2</sup>



A mixture of ethyl (E)-N-(1-phenyl-2-(triphenylsilyl)vinyl)-N-picolinoylglycinate (4a)

(0.2 mmol, 1.0 equiv), and AgF (1.5 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry MeOH (2 mL) was added and the mixture was stirred at 90 °C in a pre-heated oil bath for 24 h. Then, the mixture was cooled to room temperature and concentrated in vacuo and the resulting residue was purified by flash column chromatography on silica gel with EtOAc/petroleum ether, the product **8** was affored as a yellow solid in 78% yield (48.5 mg, 0.156 mmol).

#### (d) Derivatization Reaction of 4a for the Preparation of 9<sup>3</sup>



A mixture of ethyl (*E*)-*N*-(1-phenyl-2-(triphenylsilyl)vinyl)-*N*-picolinoylglycinate (**4a**) (0.2 mmol, 1.0 equiv), and NIS (5 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry CH<sub>3</sub>CN (2 mL) was added and the mixture was stirred at 70 °C in a pre-heated oil bath for 36 h. Then, the mixture was cooled to room temperature and concentrated in vacuo and the resulting residue was purified by flash column chromatography on silica gel with EtOAc/petroleum ether, the product **9** was affored as a yellow solid in 85% yield (95.5 mg, 0.170 mmol).

#### (e) Derivatization Reaction of 4a for the Preparation of 11<sup>4</sup>



A mixture of ethyl (*E*)-*N*-(1-phenyl-2-(triphenylsilyl)vinyl)-*N*-picolinoylglycinate (**4a**) (0.2 mmol, 1.0 equiv), 1-iodo-4-methoxybenzene (**10**),  $Pd(PPh_3)_2Cl_2$  (5 mol%), AgF (2 equiv), and K<sub>2</sub>CO<sub>3</sub> (2 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry CH<sub>3</sub>CN (2 mL) was added and the mixture was stirred at 80 °C in a pre-heated oil bath for 12 h under N<sub>2</sub> atmosphere. Then, the mixture was cooled to room temperature and concentrated in vacuo

and the resulting residue was purified by flash column chromatography on silica gel with EtOAc/petroleum ether, the product **11** was affored as a yellow solid in 71% yield (59.1 mg, 0.142 mmol).

# 4. X-ray Crystallography of 4a

### Crystal preparation of compound 4a.

Compound 4a (25 mg) was dissolved in 5 mL of dichloromethane/*n*-hexane (v1/v2 = 1:1), and it was crystallized to give crystal as colorless prisms after the solvent was slowly volatilized in 4 days at room temperature (~ 25 °C).

CCDC-2348897 (4a), contain the supplementary crystallographic data. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre (http://www.ccdc.cam.ac.uk/). Thermal ellipsoids are shown at the 30% level. Hydrogen atoms have been omitted for clarity. X-ray crystallographic data is available as Figure S1.



Figure S1. The molecular structure of 4a

### Table S2. Crystal Data and Summary of X-ray Data Collection for 4a

Empirical formula	C <sub>36</sub> H <sub>32</sub> N <sub>2</sub> O <sub>3</sub> Si	
Formula weight	568.72	
Temperature	273.15 K	
Wavelength	0.71073 A	
Crystal system, space group	triclinic, P-1	

Unit cell dimensions	a = 9.4969(10) A alpha = 78.497(3) deg.
	b = 10.0179(11) A beta = 81.332(3) deg.
	c = 19.138(2) A gamma = 77.856(3) deg.
Volume	1733.0(3) A^3
Z, Calculated density	2, 1.09 g/cm^3
Absorption coefficient	0.102 mm^-1
F(000)	600
Crystal size	0.1 x 0.05 x 0.05 mm
Radiation	MoKa ( $\lambda = 0.71073$ )
Theta range for data collection	4.222 to 50.698 deg.
Limiting indices	-11<=h<=11, -12<=k<=12, -23<=l<=23
Reflections collected / unique	19028 / 6328 [Rint = 0.0783, Rsigma = 0.1201]
Completeness to theta $= 25.24$	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.6402
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6328/49/380
Goodness-of-fit on F <sup>2</sup>	0.976
Final R indices [I>2sigma(I)]	R1 = 0.0761, wR2 = 0.1870
R indices (all data)	R1 = 0.1700, wR2 = 0.2328
Largest diff. peak and hole	0.43 and -0.40 e.A^-3

# 5. Mechanism Research

# (a) The Effect of N-Protecting Groups



A mixture of substituted amides (1) (0.2 mmol, 1.0 equiv), phenylacetylene (2a) (0.3 mmol,

1.5 equiv), triphenylsilane (**3a**) (0.6 mmol, 3.0 equiv),  $CuF_2$  (15 mol%), and DTBP (3 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry PhCF<sub>3</sub> (1 mL) was added and the mixture was stirred at 120 °C in a pre-heated oil bath for 20 h under N<sub>2</sub> atmosphere. Then, the mixture was cooled to room temperature and concentrated in vacuo and the resulting residue was purified by column chromatography on silica gel with EtOAc/petroleum ether.

#### (b) Intermolecular Competition Experiments



A mixture of *N*-phenylpicolinamide (39.6 mg, 0.2 mmol, 2.0 equiv), ethyl picolinoylglycinate (41.6 mg, 0.2 mmol, 2.0 equiv), phenylacetylene (**2a**) (10.2 mg, 0.1 mmol, 1.0 equiv), triphenylsilane (**3a**) (52.0 mg, 0.2 mmol, 2.0 equiv), CuF<sub>2</sub> (1.5 mg, 0.015 mmol, 15 mol%), and DTBP (52 uL, 0.3 mmol, 3 equiv) were weighted in a Schlenk sealed tube equipped with a stir bar. Dry PhCF<sub>3</sub> (1.5 mL) was added and the mixture was stirred at 120 °C

in a pre-heated oil bath for 20 h under  $N_2$  atmosphere. Then, the mixture was cooled to room temperature and concentrated in vacuo and the resulting residue was purified by flash column chromatography on silica gel with EtOAc/petroleum ether to give a mixture of products **5a** and **4a** at a ratio of 2.2:1.



A mixture of ethyl picolinoylglycinate (41.6 mg, 0.2 mmol, 2.0 equiv), *N*-methylpicolinamide (27.2 mg, 0.2 mmol, 2.0 equiv), phenylacetylene (**2a**) (10.2 mg, 0.1 mmol, 1.0 equiv), triphenylsilane (**3a**) (52.0 mg, 0.2 mmol, 2.0 equiv), CuF<sub>2</sub> (1.5 mg, 0.015 mmol, 15 mol%), and DTBP (52 uL, 0.3 mmol, 3 equiv) were weighted in a Schlenk sealed tube equipped with a stir bar. Dry PhCF<sub>3</sub> (1.5 mL) was added and the mixture was stirred at 120 °C in a pre-heated oil bath for 20 h under N<sub>2</sub> atmosphere. Then, the mixture was cooled to room temperature and concentrated in vacuo and the resulting residue was purified by flash

column chromatography on silica gel with EtOAc/petroleum ether to give a mixture of products **4a** and **5n** at a ratio of 4.0:1.



A mixture of *N*- methylpicolinamide (27.2 mg, 0.2 mmol, 2.0 equiv), *N*benzylpicolinamide (42.4 mg, 0.2 mmol, 2.0 equiv), phenylacetylene (**2a**) (10.2 mg, 0.1 mmol, 1.0 equiv), triphenylsilane (**3a**) (52.0 mg, 0.2 mmol, 2.0 equiv), CuF<sub>2</sub> (1.5 mg, 0.015 mmol, 15 mol%), and DTBP (52 uL, 0.3 mmol, 3 equiv) were weighted in a Schlenk sealed tube equipped with a stir bar. Dry PhCF<sub>3</sub> (1.5 mL) was added and the mixture was stirred at 120 °C in a pre-heated oil bath for 20 h under N<sub>2</sub> atmosphere. Then, the mixture was cooled to room temperature and concentrated in vacuo and the resulting residue was purified by flash column chromatography on silica gel with EtOAc/petroleum ether to give a mixture of products **5n** and **5i** at a ratio of 1.5:1.

Computational details: All calculations were performed at the DFT level using the Gaussian

09 (Rev D.01) suite of programs. The structure of minima was fully optimized using the hybrid functional M06-2X'. C, H, O and N were described using the triple- $\zeta$  Pople-type basis sets (6-311+G(dp)). Bulk solvent effects were represented using the SMD implicit solvent model as implemented in Gaussian. The default cavity parameters, static, and optical dielectric constants for Benzene were used. The nature of optimized stationary points was checked by analytical frequency calculations. Harmonic frequencies were computed to estimate Gibbs energies at 298 K under 1atm pressure using the usual harmonic approximation.

Gibbs free energies account for the change in standard states on going from the gas-phase 1 atm state to the more relevant 1 mol L<sup>-1</sup> solution state:  $\Box_r G_{1atm} \rightarrow \Box_r G_{1M} = 1.89$  kcal mol<sup>-1</sup> for an associative pathway ( $\Delta_r n = -1$ )..Gas-phase calculations were performed using the CBS-QB3 method, with no additional basis set specified.

**Theoretical calculation of**  $pK_a$ : Continuum solvent  $pK_a$  calculations using the direct method employ a thermodynamic cycle (Fig. S2).

$$HA (aq. 1M) \xrightarrow{\bigtriangleup G^{*}_{aq}} H^{\dagger}(aq. 1M) + A^{-}(aq. 1M)$$

$$\downarrow -\bigtriangleup G^{*}_{solv}(HA) \qquad \uparrow \bigtriangleup G^{*}_{solv}(H^{+}) \qquad \uparrow \bigtriangleup G^{*}_{solv}(A^{-})$$

$$HA (g. 1M) \xrightarrow{\bigtriangleup G^{*}_{gas}} H^{\dagger}(g. 1M) + A^{-}(aq. 1M)$$

**Figure S2**. Thermodynamic Cycle Used in  $pK_a$  Calculations with Direct Method. The dissociation of an acid can be represented as follows

 $HA(aq) \longrightarrow H^{+}(aq) + H^{+}(aq)$  (1)

The directly calculated pK<sub>a</sub> is obtained using the equation:  $pK_a = \frac{\Delta G_{aq}^*}{2.303RT}$  (1) (the unit of  $\Delta G_{aq}^*$  is J mol<sup>-</sup>), where  $\Delta G_{aq}^*$  represents the difference in free energies in solution between the acid (HA), its conjugate base (A<sup>-</sup>), and the free proton (H<sup>+</sup>). For computational efficiency,  $\Delta G_{aq}^*$  can using the thermodynamic cycle shown in Fig. S3, following Eqs. (2)–(5).  $\Delta G_{aq}^* = \Delta G_{gas}^* + \delta \Delta G_{solv}^*$ (2) where  $\Delta G_{gas}^{*}$  and  $\delta \Delta G_{solv}^{*}$  are  $\Delta G_{gas}^{*} = \Delta G_{gas}^{*}(H^{+}) + \Delta G_{gas}^{*}(HA)_{(3)}$  $\delta \Delta G_{solv}^{*} = \Delta G_{solv}^{*}(H^{+}) + \Delta G_{solv}^{*}(A^{-}) + \Delta G_{solv}^{*}(HA)_{(4)}$ 

In this work, the gas-phase Gibbs free energies and solvation energies of HA and its anion A<sup>-</sup> were calculated. The most recent experimental-theoretical values were used for the gas-phase Gibbs free energy of H<sup>+</sup> ( $G_{gas}^{*}(H^{+}) = 6.28 \ kcal \ mol^{-}$ ) and the solvation energy of H<sup>+</sup> in water ( $G_{gas}^{*}(H^{+}) = 265.9 \ kcal \ mol^{-}$ ) Gas-phase energy calculations were performed for a standard state of 1 atm, while solvation energies were referenced to 1 mol/L. To account for this difference, a correction factor of 1.89 kcal mol<sup>-</sup> (RT<sup>ln 24.46</sup>) was added to the gas-phase energies.

Therefore,  $\Delta G_{aq}^*$  is obtained as:

$$\Delta G_{aq}^{*} = \Delta G_{gas}^{*}(A^{-}) + \Delta G_{gas}^{*}(HA) + \Delta G_{solv}^{*}(A^{-}) - \Delta G_{solv}^{*}(HA) - 270 \ kcal \ mol^{-1} \ (5)$$

Table S2 presents the gas-phase energies of A, B, C, and D, along with their corresponding anions, calculated at different levels of theory. Using these energy values, the theoretically derived **pKa** values are computed and shown in Figure S3.



Figure S3. Theoretically Derived  $pK_a$  Values.

**Table S3.** Gas-phase and Solvation Energies of A, B, C, D and Its Anion Calculated atDifferent Levels of Theory.

Geometry	$G_{gas}^{*}$	$E_{gasb}$	E <sub>solv</sub> c	$\Delta G_{solv^{\mathrm{d}}}^{*}$
Α	-646.981271	-639.884102	-639.897197	-0.013095
<b>A</b> -anion	-646.423282	-639.184449	-639.239031	-0.054582
В	-722.384729	-714.161957	-714.174223	-0.012265

<b>B</b> -anion	-721.816134	-713.441661	-713.493412	-0.051752
С	-455.581328	-450.479504	-450.487637	-0.00813
C-anion	-454.994512	-449.740482	-449.794922	-0.05444
D	-686.208528	-678.068795	-678.082827	-0.014031
<b>D</b> -anion	-685.630554	-677.987684	-678.043076	-0.055392

<sup>a</sup>The free energy calculated by CBS-QB3. <sup>b</sup>The electronic energy calculated by M06-2X in gas phase. <sup>c</sup>The electronic energy calculated by M06-2X in benzene phase. <sup>d</sup>  $\Delta G_{solv}^{*} = E_{solv} - E_{gas}$ , unit is a.u.

# Geometries for all the optimized compounds

A, gas phase, C	BS-QB3		
С	2.44432100	1.61425000	-2.10929300
С	2.03401800	3.86892300	-2.06236700
С	0.65362700	3.67447400	-2.07706800
С	0.17234200	2.37082000	-2.10959700
С	1.08281200	1.31761500	-2.12609300
Н	3.18499700	0.82032500	-2.12133400
Н	0.00353900	4.53894800	-2.06280500
Н	-0.89440500	2.17840200	-2.12189400
Н	0.75107100	0.28676000	-2.15143400
С	2.57338400	5.28378800	-2.02700100
Ν	3.93626500	5.32620600	-2.01606800
Н	4.36464300	4.40652200	-2.03329500
Ο	1.81952800	6.24450100	-2.01124400
Ν	2.91605600	2.86146000	-2.07809700
С	4.79190500	6.44071700	-1.98541900
С	6.17264600	6.19347400	-1.98138000
С	4.32889100	7.76345500	-1.95923700
С	7.07634000	7.24763200	-1.95177000
Н	6.53256100	5.16955000	-2.00162800
С	5.24874900	8.80836900	-1.92971100
Н	3.26660200	7.95270900	-1.96236800
С	6.61986600	8.56446000	-1.92569300
Н	8.14011900	7.03803400	-1.94909600
Н	4.88118600	9.82839400	-1.90960300
Н	7.32412600	9.38778000	-1.90258200
<b>A</b> -anion, gas ph	ase, CBS-QB3		
С	1.28552000	2.44027200	-3.52886100

С	2.28032200	3.68921800	-1.87845100
С	1.61896900	2.93813000	-0.89101600
С	0.76772000	1.90865300	-1.26374000
С	0.58954800	1.64465600	-2.62106500
Η	1.17394800	2.26672600	-4.59925300
Η	1.80943600	3.20473400	0.14002400
Η	0.24967900	1.31933200	-0.51202100
Η	-0.06453000	0.85141300	-2.96874300
С	3.20842700	4.81439500	-1.39893600
Ν	3.79984600	5.47832000	-2.38513300
0	3.27933700	4.94974500	-0.15145900
Ν	2.10726200	3.43319400	-3.18559300
С	4.66699700	6.52104800	-2.14424400
С	5.06924000	7.05324900	-0.88704000
С	5.22736800	7.13987400	-3.29339900
С	5.96177600	8.11940700	-0.81334600
Η	4.65900200	6.60220600	0.00422800
С	6.11547600	8.20125800	-3.20619200
Η	4.92384500	6.73783700	-4.25429500
С	6.49713000	8.70852000	-1.95965000
Η	6.24586000	8.49916700	0.16612300
Η	6.51674100	8.64069100	-4.11669700
Η	7.19238200	9.53965600	-1.88627400
A, s	olvent phase, M06-2X, 6-311+G(d	dp)	
С	2.45170500	1.62751600	-2.13744700
С	1.99200100	3.89448100	-2.05517800
С	0.61037500	3.66393800	-2.05783000
С	0.14806300	2.34611100	-2.10186900
С	1.08625500	1.31035100	-2.14321200
Η	3.20271200	0.82631200	-2.16884100
Η	-0.07146500	4.51954600	-2.02492400
Η	-0.92490100	2.12855500	-2.10474300
Η	0.77029200	0.26409100	-2.17916400
С	2.53502800	5.34093900	-2.00527700
Ν	3.95053400	5.30479600	-2.00863600
Η	4.31839600	4.32959700	-2.04286800
0	1.81360000	6.35380300	-1.96900900
Ν	2.94626000	2.90408100	-2.09342500
С	4.83858100	6.41436600	-1.98148600
С	6.23047400	6.18867500	-1.98821500
С	4.34510800	7.73427000	-1.94916500
С	7.10766600	7.27120500	-1.96269500
Η	6.60627500	5.16269100	-2.01328800
C	5 23826200	8 80457800	-1 92423600

Н	3.26096600	7.87341600	-1.94456000
С	6.61920400	8.58207200	-1.93093100
Н	8.18624400	7.08935500	-1.96794500
Н	4.85037700	9.82715800	-1.89973500
Н	7.31317500	9.42566700	-1.91139800
A, gas ph	ase, M06-2X, 6-311+G(dp)		
С	2.44246700	1.61781300	-2.12832600
С	2.00056600	3.88750300	-2.05707400
С	0.61690900	3.66738400	-2.06256000
С	0.14351200	2.35366600	-2.10316500
С	1.07472200	1.31076300	-2.13665300
Н	3.18684100	0.81058300	-2.15435000
Н	-0.05353200	4.53202600	-2.03513300
Н	-0.93076400	2.14431700	-2.10882400
Н	0.75095600	0.26713900	-2.16921300
С	2.54559800	5.33414600	-2.01311300
Ν	3.96085000	5.29824300	-2.01793100
Н	4.33013700	4.32422400	-2.04864500
0	1.82043100	6.34460200	-1.97953600
Ν	2.94936900	2.89091900	-2.08909400
С	4.84546900	6.41231000	-1.98652600
С	6.23801800	6.19369600	-1.99684000
С	4.34322200	7.72855400	-1.94536500
С	7.10964000	7.28116400	-1.96624700
Н	6.62014600	5.17050300	-2.02876600
С	5.23077100	8.80361600	-1.91520100
Н	3.25793900	7.85940200	-1.93857600
С	6.61333300	8.58888900	-1.92537300
Н	8.18904100	7.10584500	-1.97442400
Н	4.83759200	9.82375200	-1.88345800
Н	7.30195400	9.43651300	-1.90168400
A-anion,	solvent phase, M06-2X, 6-311	+G(dp)	
С	2.25499600	1.43794200	-2.05174000
С	2.18709400	3.75639900	-2.04771300
С	0.78153300	3.72027500	-2.13376500
С	0.10560500	2.50541400	-2.17830600
С	0.86349000	1.33043400	-2.13688700
Н	2.86395000	0.52405200	-2.01727000
Н	0.27510400	4.69033100	-2.16041100
Н	-0.98598000	2.46466600	-2.24392600
Н	0.38733200	0.34772100	-2.16836500
С	2.84917300	5.18287900	-1.99819900
Ν	4.24167700	5.09026900	-1.95598400
0	2.04308400	6.16221700	-2.00666400

Ν	2.96303400	2.61481200	-2.00366600
С	4.91014400	6.32757300	-1.91522000
С	6.34426700	6.28503800	-1.87186200
С	4.33027400	7.63743100	-1.91265800
С	7.11402000	7.43730700	-1.83309100
Н	6.82288000	5.30307600	-1.87249700
С	5.11658900	8.78249100	-1.87316700
Н	3.23784400	7.66422500	-1.94501700
С	6.51311000	8.70487700	-1.83270000
Н	8.20483300	7.35748400	-1.80204000
Н	4.63478000	9.76561300	-1.87281700
Н	7.12246800	9.60917800	-1.80106400
A-anion, gas ph	ase, M06-2X,6-311+G(0	dp)	
С	2.24169200	1.42633600	-2.07379500
С	2.20455200	3.74441800	-2.05414300
С	0.79568100	3.72309100	-2.11496300
С	0.10314700	2.51869800	-2.15584900
С	0.84777800	1.33408900	-2.13474500
Н	2.83913800	0.50464000	-2.05636900
Н	0.31219600	4.70562900	-2.12654400
Н	-0.98943300	2.49090500	-2.20300900
Н	0.36011300	0.35752600	-2.16464200
С	2.86643200	5.17359100	-2.01242800
Ν	4.25657500	5.07993200	-1.95673000
0	2.05021200	6.14643100	-2.03594700
Ν	2.96947400	2.59289600	-2.03163800
С	4.91937900	6.32249300	-1.91695700
С	6.35347400	6.29116700	-1.85881800
С	4.32901700	7.62846100	-1.92787600
С	7.11320500	7.45049400	-1.81597800
Н	6.83875300	5.31262100	-1.84910800
С	5.10554400	8.77979100	-1.88436800
Н	3.23631500	7.64325000	-1.97252700
С	6.50285700	8.71377000	-1.82794100
Н	8.20408400	7.37978400	-1.77231400
Н	4.61618100	9.75893900	-1.89437100
Н	7.10493600	9.62275100	-1.79396900
<b>B</b> , gas phase, C	BS-QB3		
C	2.09440100	1.83292500	-1.66054700
С	1.67159100	4.06493200	-1.96693400
С	0.45532600	3.79301100	-2.60163200
С	0.06770100	2.46941100	-2.75807400
С	0.90321900	1.46351900	-2.27814800
Н	2.77290600	1.07799200	-1.27323700

Η	-0.14322700	4.62342400	-2.94996000
Η	-0.86920300	2.22461200	-3.24557100
Η	0.64166400	0.41686700	-2.37814800
С	2.05701200	5.52211600	-1.81733200
Ν	3.22574300	5.86235900	-1.20544500
Η	3.37741000	6.86422100	-1.16315600
0	1.30662400	6.38641800	-2.25241000
Ν	2.47746500	3.10289500	-1.50429800
С	4.28297200	5.07361000	-0.60587400
Η	4.75460500	4.39111600	-1.31639600
Η	3.92847800	4.44993400	0.21780100
С	5.34213500	6.02258500	-0.07184600
0	5.29401100	7.22590800	-0.14509800
0	6.34323000	5.33487900	0.49503100
С	7.43217000	6.11906200	1.05132800
Η	7.86090900	6.73117000	0.25490800
Η	7.02339700	6.79259400	1.80765800
С	8.43807200	5.14793000	1.63229400
Η	8.82547600	4.47963900	0.86038100
Η	9.27761200	5.69928000	2.06336000
Η	7.98471700	4.54124200	2.41902100
<b>B</b> -ar	nion, gas phase, CBS-QB3		
С	2.30604400	1.89640300	-1.96998200
С	2.20509700	4.18743400	-2.21810700
С	1.01462700	4.22408400	-1.46593400
С	0.49459900	3.05568900	-0.94155200
С	1.14973500	1.84694300	-1.20573200
Η	2.84455100	0.97921600	-2.20690600
Η	0.52740000	5.18152100	-1.33942200
Η	-0.41302800	3.07256500	-0.34429800
Η	0.77375100	0.90034600	-0.83120000
С	2.67602200	5.50373200	-2.86747000
Ν	3.90781800	5.95922700	-2.78752400
Ο	1.72354000	6.06904200	-3.46143300
Ν	2.84122700	3.02662900	-2.45446600
С	4.89349100	5.24082400	-2.03259300
Η	5.89744600	5.46669600	-2.41673900
Η	4.80895900	4.14040100	-2.06208400
С	4.93763600	5.57296700	-0.54783200
Ο	4.04561800	5.97938000	0.15124500
0	6.19036000	5.30940800	-0.02555200
С	6.32700400	5.50459300	1.38543100
Η	6.07461200	6.53891400	1.63917800
Η	5.61616800	4.86263600	1.91601500

С	7.76166100	5.17252500	1.75598700
Η	8.45804500	5.82358000	1.22138500
Η	7.91983700	5.30392600	2.83127200
Н	7.99733900	4.13767800	1.49506400
<b>B</b> , so	olvent phase, M06-2X, 6-311+G(dp)		
С	2.18875000	1.82673700	-2.31536900
С	1.73670900	4.07839800	-2.06107900
С	0.35407600	3.83401400	-2.02132500
С	-0.11099000	2.52310300	-2.12835800
С	0.82795100	1.49784900	-2.27708900
Н	2.93860600	1.03316000	-2.43654200
Н	-0.32317200	4.68677800	-1.91233500
Н	-1.18264800	2.30240800	-2.09870000
Н	0.51510100	0.45377100	-2.36506400
С	2.19296400	5.55038200	-1.96717400
Ν	3.60120700	5.76322500	-1.83962700
Н	3.84400900	6.75810200	-1.60477400
0	1.38951000	6.49421700	-2.08614800
Ν	2.69126000	3.09947000	-2.21204100
С	4.47802500	4.88483200	-1.02897700
Н	5.07193200	4.19596000	-1.65482100
Н	3.91722600	4.27920300	-0.29675200
С	5.43194600	5.86593000	-0.27510500
0	5.33438600	7.09905700	-0.36303500
0	6.37859300	5.18017200	0.48637500
С	7.25953900	6.12774800	1.18123900
Η	7.77795600	6.77280600	0.44665200
Η	6.66397100	6.78366200	1.84420200
С	8.27497900	5.30395700	1.99774900
Η	8.86894800	4.66465300	1.33513000
Η	8.94961100	5.98167300	2.53323700
Η	7.75597200	4.67238500	2.72740600
<b>B</b> , ga	as phase, M06-2X, 6-311+G(dp)		
С	2.17451700	1.80684100	-2.23642600
С	1.72766000	4.06517200	-2.04643700
С	0.34311700	3.83295900	-2.10804600
С	-0.12623100	2.52576400	-2.23419500
С	0.81178000	1.49027900	-2.29882800
Η	2.92364700	1.00548200	-2.29006600
Н	-0.32683000	4.69725500	-2.06209500
Η	-1.19882900	2.31503800	-2.28400400
Н	0.49630400	0.44841500	-2.39861100
С	2.17412800	5.54038400	-1.94085900
Ν	3.57410500	5.76862800	-1.77352000

Н	3.80621000	6.76545700	-1.54132700
0	1.36362300	6.47549000	-2.08160700
Ν	2.68237400	3.07675000	-2.11081500
С	4.45565800	4.89062500	-0.97063100
Н	5.03522700	4.19261500	-1.59937800
Н	3.90165700	4.29107200	-0.22790100
С	5.42439700	5.87114500	-0.23493700
0	5.32564600	7.10464000	-0.31149900
0	6.39323400	5.18345000	0.50185100
С	7.28538700	6.13453700	1.17561700
Н	7.77351500	6.79040500	0.43021600
Н	6.70396400	6.78160600	1.85934000
С	8.33345500	5.31337200	1.95516600
Н	8.90770900	4.68223400	1.26839100
Н	9.02063700	5.99099100	2.47379700
Н	7.84035700	4.67304700	2.69448100
<b>B</b> -anion, solvent pl	nase, M06-2X, 6-311	+G(dp)	
С	1.33314400	1.91666500	-0.91690000
С	1.98517000	3.89097600	-1.95919800
С	1.18434200	3.55125100	-3.06983600
С	0.45272700	2.37446500	-3.10394800
С	0.53059300	1.52740700	-1.98888500
Н	1.40268100	1.26664500	-0.03365200
Н	1.22347500	4.32622100	-3.84984600
Н	-0.16853100	2.10667700	-3.96439300
Н	-0.02134200	0.58549700	-1.95175500
С	2.72622900	5.31804300	-2.17782300
Ν	3.62286500	5.86833000	-1.30152900
0	2.37777700	5.86688400	-3.27350500
Ν	2.07573300	3.07550300	-0.85004900
С	3.87583900	5.02755500	-0.08303400
Н	4.27896600	4.01759700	-0.28980700
Н	2.99245700	4.88400000	0.56879900
С	4.94399800	5.77098400	0.77704200
0	4.76741700	6.59788600	1.68167700
0	6.25187000	5.38611300	0.37236200
С	7.25286000	6.13331800	1.13046000
Н	7.14407900	7.22137300	0.95875800
Н	7.13186100	5.96185600	2.21758600
С	8.64666300	5.65728600	0.66628700
Н	8.77308800	5.84001300	-0.40655000
Н	9.42893600	6.19924200	1.21024300
Н	8.76666300	4.58457100	0.85424300

**B**-anion, gas phase, M06-2X, 6-311+G(dp)

С	1.84738900	2.02561400	-2.36509300
С	2.32274500	4.29651300	-2.10575900
С	1.27821700	4.39003000	-1.15557900
С	0.53245600	3.27282500	-0.79652400
С	0.82412300	2.05216000	-1.41665200
Н	2.08356900	1.08086700	-2.87398200
Н	1.07023600	5.37217100	-0.72258300
Н	-0.26680700	3.34186100	-0.05279400
Н	0.26743900	1.14478700	-1.17452200
С	3.02012400	5.68359700	-2.55631700
Ν	4.38468000	5.84504000	-2.60882700
0	2.16330100	6.57882100	-2.83214400
Ν	2.61868500	3.10050900	-2.74025300
С	5.12903900	4.61580200	-2.17476800
Н	6.17556000	4.69823200	-2.51546300
Н	4.71274800	3.66162400	-2.54332700
С	5.17722200	4.52295900	-0.61614500
0	4.34319000	4.04527700	0.16616700
0	6.33428200	5.20358000	-0.11820200
С	6.28921400	5.25458800	1.33896000
Н	5.36026000	5.74347800	1.68968800
Н	6.29971600	4.23627200	1.77454100
С	7.52564700	6.05055700	1.81767800
Н	7.50640700	7.06224200	1.39850200
Н	7.53392700	6.12060400	2.91133300
Н	8.44619300	5.55634400	1.48881500
C, gas phase	e, CBS-QB3		
С	2.05715800	1.80464100	-3.07195000
С	2.14711600	3.76604300	-1.89113400
С	0.95762900	3.48151100	-1.22226900
С	0.30537600	2.28906800	-1.51336600
С	0.86387600	1.43098000	-2.45695400
Н	2.52277500	1.16129400	-3.81286000
Н	0.58254200	4.19547600	-0.50121400
Н	-0.62203600	2.03228900	-1.01402400
Н	0.38975200	0.49160200	-2.71466300
С	2.86787500	5.06233900	-1.58309300
Ν	4.00912300	5.23168400	-2.29018500
Н	4.24388400	4.48586300	-2.93104700
С	4.85628500	6.39930800	-2.15429900
0	2.42348200	5.85456400	-0.76324500
Н	4.40224600	7.05573300	-1.41331700
Н	5.85979100	6.12184100	-1.81747200
Ν	2.69137200	2.94658800	-2.79997100

Н	4.94136300	6.93784000	-3.10309800
C-anion, ga	as phase, CBS-QB3		
С	2.33951200	2.07821900	-2.86662700
С	2.04063300	4.23604700	-2.11117600
С	0.94577800	3.81567200	-1.32910800
С	0.58412200	2.48100800	-1.30481700
С	1.29360200	1.57695100	-2.10422600
Н	2.90890600	1.41187700	-3.51498200
Н	0.39865300	4.57649400	-0.78768700
Н	-0.24488500	2.14139800	-0.68908800
Н	1.03945500	0.52216800	-2.13758700
С	2.33779000	5.74955800	-2.16576600
Ν	3.54644800	6.24407100	-2.07771000
С	4.69084700	5.37984700	-1.89781300
0	1.26566300	6.40871700	-2.28496700
Н	5.47336000	5.93570500	-1.35660700
Н	4.51387600	4.45154000	-1.32396600
Ν	2.72782100	3.36076900	-2.86689400
Н	5.14720500	5.05582700	-2.85058200
C, solvent	phase, M06-2X, 6-311+G(dp	)	
С	2.08034200	1.82855800	-3.07632800
С	2.13464700	3.77587900	-1.82735200
С	0.91658500	3.46526000	-1.20796300
С	0.26821300	2.27584500	-1.54801900
С	0.86311800	1.44204000	-2.49961500
Н	2.55891800	1.18599400	-3.82795500
Н	0.50397900	4.16366100	-0.47345900
Н	-0.68355800	2.00262700	-1.08134200
Н	0.39261300	0.50118900	-2.79780300
С	2.86271500	5.09490700	-1.47725200
Ν	4.15292100	5.11313600	-2.05548000
Н	4.26434200	4.38228200	-2.78936400
С	4.87576000	6.38703100	-2.20061300
0	2.38380700	5.98446700	-0.75206100
Н	4.52041100	7.06145600	-1.40813300
Н	5.95925400	6.23198500	-2.08109000
Ν	2.74957700	2.98543600	-2.77193700
Н	4.69596600	6.86691100	-3.17839400
C, gas phas	se, M06-2X, 6-311+G(dp)		
С	2.06862400	1.82368100	-3.08343700
С	2.13605900	3.77286900	-1.84006400
С	0.92496900	3.46343400	-1.20581300
С	0.27290700	2.27342900	-1.53582700
С	0.85798700	1.43780600	-2.49241300

Н	2.53881000	1.18002100	-3.83905200
Н	0.52459800	4.16627200	-0.46863700
Н	-0.67318400	2.00020000	-1.05839800
Н	0.38464700	0.49645800	-2.78332900
С	2.86350700	5.09288100	-1.49302600
Ν	4.13999200	5.12529900	-2.09544900
Н	4.26563200	4.38963000	-2.82006000
С	4.87857200	6.39327600	-2.19215900
0	2.39144400	5.97491800	-0.75421600
Н	4.46163500	7.06592300	-1.42846400
Н	5.95061500	6.24079400	-1.99221900
Ν	2.74260900	2.98172600	-2.79014000
Н	4.77018800	6.87004800	-3.18145700
C-anion, solvent pha	ase, M06-2X, 6-311	+G(dp)	
С	2.26560500	2.14167900	-3.16568600
С	2.04558300	4.29314900	-2.28655700
С	1.15744500	3.79063200	-1.30983900
С	0.83722800	2.43626000	-1.26332200
С	1.40597800	1.58510800	-2.21559700
Н	2.71761500	1.49009300	-3.92666400
Н	0.72334600	4.48632300	-0.58661900
Н	0.15682600	2.04381300	-0.50128600
Н	1.18692500	0.51530700	-2.22398300
С	2.31673300	5.88248700	-2.37692300
Ν	3.53014400	6.38465100	-1.99646400
С	4.46827000	5.30646100	-1.54656200
0	1.31632200	6.54621600	-2.79137600
Н	5.39964800	5.77902000	-1.19106200
Н	4.09928400	4.68532500	-0.70646100
Ν	2.61690500	3.46725300	-3.24283200
Н	4.76493100	4.59209200	-2.33837000
C-anion, gas phase,	M06-2X, 6-311+G	(dp)	
С	2.21132100	2.10694600	-3.17110600
С	2.09767800	4.28062300	-2.32211400
С	1.18825600	3.82723700	-1.33657600
С	0.80445700	2.49139600	-1.27043800
С	1.32887900	1.60139900	-2.21366500
Н	2.63006000	1.42475600	-3.92422700
Н	0.78973900	4.55347300	-0.62310600
Н	0.10936500	2.14066400	-0.50173900
Н	1.05976600	0.54352700	-2.20829500
С	2.40058700	5.87098600	-2.44653800
Ν	3.58724700	6.37347200	-1.99726300
С	4.48289400	5.28851300	-1.47540900

0	1.42585900	6.51276700	-2.94774400
Н	5.40274400	5.75299400	-1.08225200
Н	4.05766700	4.69208500	-0.64366900
Ν	2.62822500	3.41284000	-3.26845400
Н	4.80404300	4.55219000	-2.23700600
<b>D</b> , gas phase, C	CBS-QB3		
С	2.34904500	2.20926500	-3.40817600
С	2.13715400	3.78242700	-1.75666000
С	0.74509600	3.73634800	-1.81462400
С	0.15113400	2.87232900	-2.72734300
С	0.96682800	2.09182400	-3.54210500
Н	3.01735100	1.61670300	-4.02604300
Н	0.17431800	4.37161400	-1.15052100
Н	-0.92844100	2.80783100	-2.80266700
Н	0.54685000	1.40497500	-4.26700700
С	2.79770200	4.71909100	-0.76677100
Ν	4.15206000	4.68454300	-0.80068700
Н	4.56555800	4.04191100	-1.46404900
С	4.99025100	5.48975500	0.07100100
Ο	2.13300700	5.42867300	-0.02432800
Н	4.31194400	6.15686200	0.60912200
Н	5.47746400	4.85329800	0.81825500
С	6.04399200	6.28197100	-0.67889300
С	5.70409600	7.04974600	-1.79809500
С	7.37133800	6.27940700	-0.24530200
С	6.66952500	7.79940100	-2.46282700
Н	4.67787000	7.05528700	-2.14853600
С	8.34035200	7.03210700	-0.90730600
Н	7.65012800	5.68301900	0.61788600
С	7.99168300	7.79406700	-2.01870800
Н	6.39039000	8.39082300	-3.32789200
Н	9.36659200	7.01755500	-0.55729500
Н	8.74347400	8.37792100	-2.53772400
Ν	2.92927000	3.03497800	-2.53566200
<b>D</b> , gas phase, C	CBS-QB3		
С	2.11356400	2.06630100	-1.15373700
С	2.31466500	3.93791800	-2.48324600
С	0.91523600	4.09478900	-2.49024600
С	0.11999400	3.21791400	-1.77372000
С	0.73016200	2.16268100	-1.08802900
Н	2.62912300	1.25188800	-0.64561300
Н	0.50852600	4.89616400	-3.09261900
Н	-0.95987400	3.33782800	-1.75465000
Н	0.15144300	1.43736600	-0.52528700

С	3.13901200	4.90604800	-3.35865300
Ν	4.31478100	5.36518200	-2.99470500
С	4.92001400	5.02700300	-1.73808500
0	2.53626200	5.19832000	-4.42414600
Н	4.21872100	4.98752800	-0.88322700
Н	5.39163000	4.02801200	-1.74443200
С	6.01069900	6.02342700	-1.35592400
С	6.73385600	5.86973500	-0.16624800
С	6.31990500	7.10694100	-2.18158300
С	7.73260600	6.77132300	0.19371000
Н	6.50619700	5.02961000	0.48608000
С	7.31995100	8.01205600	-1.82596000
Н	5.74555300	7.19166100	-3.09708400
С	8.03178800	7.85184400	-0.63809400
Η	8.27866200	6.63316100	1.12293500
Н	7.54557000	8.84890500	-2.48152900
Н	8.80998900	8.55733100	-0.36177900
Ν	2.89717500	2.93000000	-1.81253500
D, s	solvent phase, M06-2X,6-311+G(dp)		
С	2.43084100	2.20414500	-3.32722500
С	2.09918400	3.85548600	-1.72154300
С	0.70420200	3.82319000	-1.91087300
С	0.16695900	2.93425400	-2.85560800
С	1.04742500	2.10967100	-3.57649400
Η	3.13723700	1.56065300	-3.88743200
Η	0.06999500	4.49785700	-1.31159700
Η	-0.92118800	2.88318900	-3.02927100
Η	0.67059100	1.39711200	-4.32752800
С	2.73059100	4.82940000	-0.67684900
Ν	4.12485000	4.63547800	-0.68810500
Η	4.42894500	3.91594500	-1.38661000
С	5.05633200	5.39173100	0.16292900
0	2.09116900	5.62792700	0.03867800
Η	4.41231100	6.05633900	0.78408300
Η	5.61390700	4.71458800	0.84942100
С	6.07046300	6.23579600	-0.64128000
С	5.64612600	6.99264100	-1.75321900
С	7.42863600	6.26628500	-0.26825100
С	6.56457000	7.76879600	-2.47693900
Η	4.58462500	6.96336500	-2.04931900
С	8.34845600	7.04466700	-0.99087600
Η	7.76576100	5.67274700	0.59747500
С	7.91804100	7.79731700	-2.09605300
Н	6.22412100	8.35724900	-3.34444500

Н	9.40889700	7.06118400	-0.69106700
Н	8.63925300	8.40623600	-2.66462400
Ν	3.00373200	3.06048400	-2.41033500
<b>D</b> -anion, gas	phase, M06-2X, 6-311+G(	dp)	
С	2.51109800	2.18558100	-3.27171600
С	2.15949800	3.88027600	-1.71779900
С	0.77887300	3.91061600	-1.99514900
С	0.25890300	3.02930700	-2.95636300
С	1.14271900	2.15025900	-3.60601600
Н	3.21944400	1.50013600	-3.77662100
Н	0.14529400	4.62817000	-1.44727300
Н	-0.81725100	3.02545900	-3.19757200
Н	0.77988400	1.44167800	-4.36729800
С	2.76699400	4.85560000	-0.66076100
Ν	4.13790600	4.55545200	-0.52295300
Н	4.46284100	3.83519400	-1.21128400
С	5.05464800	5.38725200	0.27602400
0	2.12815100	5.73273000	-0.04353900
Н	4.39220000	6.06680000	0.85979000
Н	5.63539400	4.76318100	0.99137700
С	6.03210500	6.21486200	-0.58817700
С	5.53695000	7.00723500	-1.64512600
С	7.41792900	6.18949100	-0.33909800
С	6.41371300	7.76361300	-2.43773600
Н	4.45194500	7.02185700	-1.84009100
С	8.29725200	6.94847500	-1.13086600
Н	7.80984800	5.56951400	0.48390800
С	7.79678900	7.73584400	-2.18104800
Н	6.01842100	8.38049600	-3.26087800
Н	9.38007600	6.92269800	-0.92807200
Н	8.48566400	8.32931600	-2.80319200
Ν	3.06874600	3.03263900	-2.33542800
<b>D</b> -anion, solv	ent phase, M06-2X, 6-311-	+G(dp)	
С	2.16247800	1.93208400	-1.31877700
С	2.40997000	3.89119900	-2.56076600
С	1.06406900	4.22180500	-2.28835200
С	0.27146600	3.39572800	-1.49658000
С	0.83402200	2.21726700	-0.99570400
Н	2.61873100	1.00492400	-0.94470700
Н	0.65834100	5.14028300	-2.72110500
Н	-0.76741100	3.65632400	-1.27220400
Н	0.25537200	1.53136400	-0.37327800
С	3.22999400	4.82240600	-3.58946100
Ν	4.43741100	5.36212900	-3.24575300

С	4.88090100	4.99320000	-1.87136200
0	2.62357500	4.99030000	-4.69280000
Н	4.07969900	4.98781200	-1.10337500
Н	5.34017500	3.98324600	-1.80688400
С	5.95572700	5.99823700	-1.38171600
С	6.58189400	5.87601600	-0.13042800
С	6.31622300	7.06801400	-2.21064700
С	7.54332500	6.80411300	0.27784700
Н	6.31241600	5.04554900	0.52879800
С	7.27653900	7.99898200	-1.80791900
Н	5.79310500	7.10289500	-3.17441100
С	7.89319900	7.86837000	-0.55936600
Н	8.02436900	6.69918100	1.25435200
Н	7.54921300	8.83000800	-2.46492600
Н	8.64579800	8.59315100	-0.23829100
Ν	2.98460900	2.72634900	-2.08059000
<b>D</b> -anion, gas phase,	M06-2X, 6-311+G	(dp)	
С	2.15836400	1.92870800	-1.32533000
С	2.40357700	3.90525200	-2.54155700
С	1.04221600	4.20444500	-2.30045600
С	0.24524000	3.35787800	-1.53663700
С	0.81722600	2.18461100	-1.03218400
Н	2.62194000	1.00595000	-0.94967100
Н	0.63265300	5.11716800	-2.74163500
Н	-0.80356500	3.59607000	-1.33641600
Н	0.23629800	1.48250600	-0.43102700
С	3.21498500	4.87067700	-3.55573200
Ν	4.41116300	5.42346800	-3.19666000
С	4.84604900	5.03551400	-1.82403300
0	2.59775500	5.04259100	-4.65189700
Н	4.04819100	5.05888900	-1.05217700
Н	5.27284500	4.01196800	-1.75953900
С	5.95387900	6.01107000	-1.34853000
С	6.58903100	5.90121800	-0.10134700
С	6.33552200	7.04881400	-2.20951000
С	7.58152800	6.81271400	0.27290100
Н	6.30370300	5.09592400	0.58177600
С	7.32591400	7.96127600	-1.84127000
Н	5.78585300	7.05258200	-3.16158400
С	7.95235500	7.84439100	-0.59492200
Н	8.06991200	6.71981300	1.24666200
Н	7.61616100	8.76758500	-2.52080300
Н	8.72834300	8.55498400	-0.29984100
Ν	2.98807300	2.74487000	-2.05698400



A mixture of ethyl picolinoylglycinate (1a) (20.8 mg, 0.1 mmol, 1.0 equiv), phenylacetylene (2a) (20.4 mg, 0.2 mmol, 2.0 equiv), triphenylsilane (52.0 mg, 0.2 mmol, 2.0 equiv), methyldiphenylsilane (39.6 mg, 0.2 mmol, 2.0 equiv), CuF<sub>2</sub> (1.5 mg, 0.015 mmol, 15 mol%), and DTBP (52 uL, 0.3 mmol, 3 equiv) were weighted in a Schlenk sealed tube equipped with a stir bar. Dry PhCF<sub>3</sub> (1.5 mL) was added and the mixture was stirred at 120 °C in a pre-heated oil bath for 20 h under N<sub>2</sub> atmosphere. Then, the mixture was cooled to room temperature and concentrated in vacuo and the resulting residue was purified by flash column chromatography on silica gel with EtOAc/petroleum ether to give a mixture of products 4a and 6j at a ratio of 1.9:1.







A mixture of ethyl picolinoylglycinate (1a) (20.8 mg, 0.1 mmol, 1.0 equiv), phenylacetylene (2a) (20.4 mg, 0.2 mmol, 2.0 equiv), methyldiphenylsilane (39.6 mg, 0.2 mmol, 2.0 equiv), dimethyl(phenyl)silane (27.2 mg, 0.2 mmol, 2.0 equiv), CuF<sub>2</sub> (1.5 mg, 0.015 mmol, 15 mol%), and DTBP (52 uL, 0.3 mmol, 3 equiv) were weighted in a Schlenk sealed tube equipped with a stir bar. Dry PhCF<sub>3</sub> (1.5 mL) was added and the mixture was stirred at 120 °C in a pre-heated oil bath for 20 h under N<sub>2</sub> atmosphere. Then, the mixture was cooled to room temperature and concentrated in vacuo and the resulting residue was purified by flash column chromatography on silica gel with EtOAc/petroleum ether to give a mixture of products **6j** and **6l** at a ratio of 1.8:1.





A mixture of ethyl picolinoylglycinate (1a) (20.8 mg, 0.1 mmol, 1.0 equiv), phenylacetylene (2a) (20.4 mg, 0.2 mmol, 2.0 equiv), dimethyl(phenyl)silane (27.2 mg, 0.2 mmol, 2.0 equiv), triethylsilane (23.2 mg, 0.2 mmol, 2.0 equiv), CuF<sub>2</sub> (1.5 mg, 0.015 mmol, 15 mol%), and DTBP (52 uL, 0.3 mmol, 3 equiv) were weighted in a Schlenk sealed tube equipped with a stir bar. Dry PhCF<sub>3</sub> (1.5 mL) was added and the mixture was stirred at 120 °C in a pre-heated oil bath for 20 h under N<sub>2</sub> atmosphere. Then, the mixture was cooled to room temperature and concentrated in vacuo and the resulting residue was purified by flash column chromatography on silica gel with EtOAc/petroleum ether to give a mixture of products **61** and **6m** at a ratio of 1.3:1.

-5.5135





#### (c) Deuterium-Labeling Experiments

A mixture of ethyl picolinoylglycinate (1a) (0.2 mmol, 1.0 equiv), (ethynyl-d)benzene (2ad) (0.3 mmol, 1.5 equiv), triphenylsilane (3a) (0.6 mmol, 3.0 equiv),  $CuF_2$  (15 mol%), and DTBP (3 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry PhCF<sub>3</sub> (1.5 mL) was added and the mixture was stirred at 120 °C in a pre-heated oil bath for 20 h under N<sub>2</sub> atmosphere. Then, the mixture was cooled to room temperature and concentrated in vacuo and the resulting residue was purified by flash column chromatography on silica gel with EtOAc/petroleum ether to give products **4a**-*d* and **4a**. The ratio of **4a**-*d* and **4a** was 62:38 according to the <sup>1</sup>H NMR.



A mixture of ethyl picolinoylglycinate (1a) (0.2 mmol, 1.0 equiv), phenylacetylene (2a) (0.3 mmol, 1.5 equiv), triphenylsilane (3a) (0.6 mmol, 3.0 equiv),  $CuF_2$  (15 mol%), DTBP (3 equiv), and  $D_2O$  (0.2 mL) were weighted in a Schlenk tube equipped with a stir bar. Dry PhCF<sub>3</sub> (1.5 mL) was added and the mixture was stirred at 120 °C in a pre-heated oil bath for 20 h under N<sub>2</sub> atmosphere. Then, the mixture was cooled to room temperature and concentrated in vacuo and the resulting residue was purified by flash column chromatography

on silica gel with EtOAc/petroleum ether to give products **4a**-*d* and **4a**. The ratio of **4a**-*d* and **4a** was 75:25 according to the <sup>1</sup>H NMR.



#### (d) Radical Scavenger Experiments

A mixture of ethyl picolinoylglycinate (1a) (0.2 mmol, 1.0 equiv), phenylacetylene (2a) (0.3 mmol, 1.5 equiv), triphenylsilane (3a) (0.6 mmol, 3.0 equiv),  $CuF_2$  (15 mol%), DTBP (3 equiv), and additive (0.4 mmol, 2.0 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry PhCF<sub>3</sub> (1.5 mL) was added and the mixture was stirred at 120 °C in a pre-heated oil bath for 20 h under N<sub>2</sub> atmosphere. Then, the mixture was cooled to room temperature and quenched with brine, the aqueous phase was extracted with EtOAc. The crude mixture was firstly analyzed by HRMS (High Resolution Mass Spectrometry). Then the solvent was concentrated in vacuo and the resulting residue was purified by flash column chromatography on silica gel with EtOAc/petroleum ether to give product 4a.



S33







(e) Competition Experiments for the Hammett Study



A mixture of ethyl picolinoylglycinate (1a) (0.2 mmol, 1.0 equiv), alkyne (2) (0.3 mmol, 1.5 equiv), triethylsilane (0.6 mmol, 3.0 equiv), CuF<sub>2</sub> (15 mol%), and DTBP (3 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry PhCF<sub>3</sub> (1 mL) was added and the mixture was stirred at 120 °C in a pre-heated oil bath under N<sub>2</sub> atmosphere. Then, the small potion solution (50  $\mu$ l) was taken with a syringe every 10 minutes and diluted immediately by brine to quench reaction, and the aqueous phase was extracted with EtOAc. The yields of products **4** were obtained by further gas chromatography analysis.


Figure S2. The kinetic data of *para*-substituted aryl alkynes for the silylamination reaction



**Figure S3.** Hammett plots for the silylamination reaction of *para*-substituted aryl alkynes using  $\sigma$  values from the literature (log(*kX/kH*) vs  $\sigma$ )

### (f) Reaction Progress Kinetic Analysis



A mixture of ethyl picolinoylglycinate (1a) (0.2 mmol, 1.0 equiv), phenylacetylene (2a) (0.3 mmol, 1.5 equiv), triethylsilane (0.6 mmol, 3.0 equiv), CuF<sub>2</sub> (15 mol%), and DTBP (3 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry PhCF<sub>3</sub> (1 mL) was added and the mixture was stirred at 120 °C in a pre-heated oil bath under N<sub>2</sub> atmosphere. Then, the small potion solution (50  $\mu$ l) was taken with a syringe every 5 minutes and diluted immediately by brine to quench reaction, and the aqueous phase was extracted with EtOAc. The yields of product **6m** were obtained by further gas chromatography analysis.



Figure S4. Monitor of the reaction profile.

### The rate on the concentration of ethyl picolinoylglycinate 1a





Figure S5. The rate on the concentration of ethyl picolinoylglycinate 1a from the reaction of 2a (0.1 mmol), Et<sub>3</sub>SiH (3 equiv), CuF<sub>2</sub> (15 mol%), DTBP (3 equiv) with (1.0/1.25/1.5/1.75/2.0 equiv) of 1a in PhCF<sub>3</sub> (1 mL).

### The rate on the concentration of phenylacetylene 2a





Figure S6. The rate on the concentration of phenylacetylene 2a from the reaction of 1a (0.1 mmol), Et<sub>3</sub>SiH (3 equiv), CuF<sub>2</sub> (15 mol%), DTBP (3 equiv) with (1.0/1.5/2.0/2.5/3.0 equiv) of 2a in PhCF<sub>3</sub> (1 mL).

### The rate on the concentration of Et<sub>3</sub>SiH





Figure S7. The rate on the concentration of  $Et_3SiH$  from the reaction of 1a (0.1 mmol), 2a (1.5 equiv),  $CuF_2$  (15 mol%), DTBP (3 equiv) with (2.5/3.0/3.5/4.0/4.5 equiv) of  $Et_3SiH$  in PhCF<sub>3</sub> (1 mL).

### The rate on the concentration of CuF<sub>2</sub>





Figure S8. The rate on the concentration of  $CuF_2$  from the reaction of 1a (0.1 mmol), 2a (1.5 equiv), Et<sub>3</sub>SiH (3 equiv), DTBP (3 equiv) with (15/20/25/30/35 mol%) of CuF<sub>2</sub> in PhCF<sub>3</sub> (1 mL).

### The rate on the concentration of DTBP





Figure S9. The rate on the concentration of DTBP from the reaction of 1a (0.1 mmol), 2a (1.5 equiv), Et<sub>3</sub>SiH (3 equiv), CuF<sub>2</sub> (15 mol%), with (2.5/3.0/3.5/4.0/4.5 equiv) of DTBP in PhCF<sub>3</sub> (1 mL).

### 6. Characterization of Products 4, 5, 6, 7, 8, 9 and 11



J = 7.3 Hz, 2H), 7.25 – 7.22 (m, 3H), 7.19 – 7.12 (m, 12H), 6.98 (t, J = 6.8 Hz, 2H), 6.85 (t, J = 7.7 Hz, 2H), 5.84 (s, 1H), 4.24 – 4.17 (m, 4H), 1.27 (t, J = 5.4 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  170.0, 168.7, 155.4, 153.6, 148.0, 136.2, 136.0, 135.5, 134.3, 129.8, 129.1, 127.5, 127.5, 124.3, 123.9, 122.1, 61.1, 48.9, 14.1. HRMS (ESI): Calcd for C<sub>36</sub>H<sub>32</sub>N<sub>2</sub>NaO<sub>3</sub>Si [M+Na]<sup>+</sup> 591.2074, found: 591.2078.

# ethyl (E)-N-picolinoyl-N-(1-(p-tolyl)-2 (triphenylsilyl)vinyl)glycinate (4b) Et The title compound was isolated by column chromatography (eluent:



The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 84% yield (97.8 mg, 0.168 mmol). Mp: 127 – 128 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):

δ 8.33 (d, J = 4.4 Hz, 1H), 7.63 (d, J = 7.8 Hz, 1H), 7.46 (t, J = 7.7 Hz, 1H), 7.26 – 7.22 (m, 5H), 7.17 – 7.11 (m, 12H), 6.98 – 6.93 (m, 1H), 6.63 (d, J = 7.9 Hz, 2H), 5.77 (s, 1H), 4.24 – 4.17 (m, 4H), 2.11 (s, 3H), 1.25 (t, J = 7.1 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ 170.0, 168.7, 155.4, 153.6, 148.0, 139.1, 136.2, 135.6, 134.4, 133.1, 129.7, 128.9, 128.2, 127.4, 124.3, 123.8, 121.5, 61.1, 48.8, 21.1, 14.1. HRMS (ESI): Calcd for C<sub>37</sub>H<sub>34</sub>N<sub>2</sub>NaO<sub>3</sub>Si [M+Na]<sup>+</sup> 605.2231, found: 605.2232.

# $\begin{array}{c} & \text{ethyl} \\ & \text{picolin} \\ & O & N & CO_2Et \\ & & & \text{The tit} \\ & & & & \text{EtOAc} \end{array}$

# ethyl (*E*)-*N*-(1-(4-ethylphenyl)-2-(triphenylsilyl)vinyl)-*N*picolinoylglycinate (4c)

Et The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 88% yield (104.9 mg, 0.176 mmol). Mp: 151 – 152 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):

δ 8.34 (d, J = 4.6 Hz, 1H), 7.63 (d, J = 7.8 Hz, 1H), 7.45 (t, J = 7.7 Hz, 1H), 7.29 (d, J = 8.0 Hz, 2H), 7.25 – 7.23 (m, 3H), 7.18 – 7.12 (m, 12H), 6.98 – 6.95 (m, 1H), 6.67 (d, J = 8.0 Hz, 2H), 5.78 (s, 1H), 4.24 – 4.20 (m, 4H), 2.41 (q, J = 7.6 Hz, 2H), 1.26 (t, J = 7.1 Hz, 3H), 1.07 (t, J = 7.6 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ 170.0, 168.7, 155.4, 153.7, 148.0, 145.4, 136.2, 135.6, 134.4, 133.3, 129.8, 129.0, 127.4, 127.0, 124.3, 123.8, 121.5, 61.1, 48.9, 28.5, 15.4, 14.1. HRMS (ESI): Calcd for C<sub>38</sub>H<sub>36</sub>N<sub>2</sub>NaO<sub>3</sub>Si [M+Na]<sup>+</sup> 619.2387, found: 619.2385.

# *n*-Pr

# ethyl (*E*)-*N*-picolinoyl-*N*-(1-(4-propylphenyl)-2-(triphenylsilyl)vinyl)glycinate (4d)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 83% yield (101.3 mg, 0.166 mmol). Mp: 134 – 135 °C. <sup>1</sup>H NMR

(CDCl<sub>3</sub>, **500** MHz):  $\delta$  8.34 (d, J = 4.5 Hz, 1H), 7.62 (d, J = 7.8 Hz, 1H), 7.45 (t, J = 7.7 Hz, 1H), 7.29 (d, J = 8.0 Hz, 2H), 7.25 – 7.22 (m, 3H), 7.19 – 7.12 (m, 12H), 6.99 – 6.95 (m, 1H), 6.66 (d, J = 8.0 Hz, 2H), 5.79 (s, 1H), 4.24 – 4.20 (m, 4H), 2.35 (t, J = 7.7 Hz, 2H), 1.49 – 1.42 (m, 2H), 1.26 (t, J = 7.1 Hz, 3H), 0.85 (t, J = 7.3 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  170.0, 168.7, 155.5, 153.7, 148.0, 143.8, 136.2, 135.6, 134.4, 133.4, 129.7, 129.0, 127.6, 127.4, 124.2, 123.8, 121.4, 61.1, 48.9, 37.7, 24.2, 14.1, 13.8. HRMS (ESI): Calcd for C<sub>39</sub>H<sub>38</sub>N<sub>2</sub>NaO<sub>3</sub>Si [M+Na]<sup>+</sup> 633.2544, found: 633.2548.



# ethyl (*E*)-*N*-(1-(4-isopropylphenyl)-2-(triphenylsilyl)vinyl)-*N*picolinoylglycinate (4e)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 78% yield (95.2 mg, 0.156 mmol). Mp: 146 – 147 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>,

**500** MHz):  $\delta 8.35$  (d, J = 4.5 Hz, 1H), 7.62 (d, J = 7.8 Hz, 1H), 7.44 (t, J = 7.2 Hz, 1H), 7.31 (d, J = 8.1 Hz, 2H), 7.26 – 7.23 (m, 3H), 7.19 – 7.13 (m, 12H), 6.98 – 6.94 (m, 1H), 6.70 (d, J = 8.1 Hz, 2H), 5.78 (s, 1H), 4.25 – 4.21 (m, 4H), 2.67 (dq, J = 13.8, 6.9 Hz, 1H), 1.27 (t, J = 7.2 Hz, 3H), 1.08 (d, J = 6.9 Hz, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  170.1, 168.7, 155.4, 153.7, 150.0, 148.0, 136.1, 135.6, 134.3, 133.4, 129.7, 129.0, 127.4, 125.5, 124.2, 123.7, 121.4, 61.1, 48.9, 33.7, 23.7, 14.1. HRMS (ESI): Calcd for C<sub>39</sub>H<sub>38</sub>N<sub>2</sub>NaO<sub>3</sub>Si [M+Na]<sup>+</sup> 633.2544, found: 633.2540.



# ethyl (*E*)-*N*-(1-(4-butylphenyl)-2-(triphenylsilyl)vinyl)-*N*picolinoylglycinate (4f)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 81%

yield (101.1 mg, 0.162 mmol). Mp: 152 – 153 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.34 (d, J = 4.5 Hz, 1H), 7.62 (d, J = 7.8 Hz, 1H), 7.45 (t, J = 7.2 Hz, 1H), 7.29 (d, J = 8.0 Hz, 2H), 7.24 – 7.23 (m, 3H), 7.19 – 7.13 (m, 12H), 6.99 – 6.96 (m, 1H), 6.66 (d, J = 7.9 Hz, 2H), 5.78 (s, 1H), 4.23 – 4.19 (m, 4H), 2.37 (t, J = 7.6 Hz, 2H), 1.43 – 1.38 (m, 2H), 1.27 – 1.22 (m, 5H), 0.90 (t, J = 7.3 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  170.1, 168.7, 155.5, 153.7, 148.1, 144.1, 136.2, 135.6, 134.4, 133.4, 129.7, 129.0, 127.6, 127.4, 124.3, 123.8, 121.4, 61.1, 48.9, 35.3, 33.4, 22.2, 14.2, 13.9. HRMS (ESI): Calcd for C<sub>40</sub>H<sub>40</sub>N<sub>2</sub>NaO<sub>3</sub>Si [M+Na]<sup>+</sup> 647.2700, found: 647.2704.



# ethyl (*E*)-*N*-(1-(4-(tert-butyl)phenyl)-2-(triphenylsilyl)vinyl)-*N*picolinoylglycinate (4g)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 77% yield (96.1 mg, 0.154 mmol). Mp: 159 – 160 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>,

**500** MHz):  $\delta 8.38$  (d, J = 4.4 Hz, 1H), 7.64 (d, J = 7.8 Hz, 1H), 7.46 (t, J = 7.6 Hz, 1H), 7.33 (d, J = 8.2 Hz, 2H), 7.29 – 7.26 (m, 3H), 7.22 – 7.15 (m, 12H), 7.00 – 6.96 (m, 1H), 6.88 (d, J = 8.3 Hz, 2H), 5.80 (s, 1H), 4.28 – 4.24 (m, 4H), 1.30 (t, J = 7.1 Hz, 3H), 1.17 (s, 9H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  170.1, 168.8, 155.3, 153.7, 152.2, 148.0, 136.1, 135.6, 134.3, 132.9, 129.4, 129.0, 127.4, 124.4, 124.2, 123.7, 121.4, 61.1, 48.9, 34.4, 31.1, 14.2. HRMS (ESI): Calcd for C<sub>41</sub>H<sub>43</sub>N<sub>2</sub>NaO<sub>3</sub>Si [M+Na]<sup>+</sup> 647.2700, found: 647.2698.



# ethyl (*E*)-*N*-(1-(4-methoxyphenyl)-2-(triphenylsilyl)vinyl)-*N*picolinoylglycinate (4h)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 74% yield (88.5 mg, 0.148 mmol). Mp:  $155 - 156 \,^{\circ}$ C. <sup>1</sup>H NMR (CDCl<sub>3</sub>,

**500 MHz):**  $\delta$  8.33 (d, J = 4.6 Hz, 1H), 7.61 (d, J = 7.8 Hz, 1H), 7.44 (t, J = 7.7 Hz, 1H), 7.29 (d, J = 8.6 Hz, 2H), 7.25 – 7.23 (m, 3H), 7.17 – 7.13 (m, 12H), 6.97 – 6.94 (m, 1H), 6.35 (d, J = 8.6 Hz, 2H), 5.72 (s, 1H), 4.23 – 4.18 (m, 4H), 3.61 (s, 3H), 1.25 (t, J = 7.1 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  170.1, 168.7, 160.3, 155.2, 153.8, 148.0, 136.2, 135.6, 134.5,

131.2, 129.0, 128.6, 127.5, 124.3, 123.8, 120.6, 112.9, 61.1, 55.1, 49.0, 14.2. **HRMS (ESI):** Calcd for C<sub>37</sub>H<sub>34</sub>N<sub>2</sub>NaO<sub>4</sub>Si [M+Na]<sup>+</sup> 621.2180, found: 621.2183.



# ethyl (*E*)-*N*-(1-([1,1'-biphenyl]-4-yl)-2-(triphenylsilyl)vinyl)-*N*picolinoylglycinate (4i)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 71% yield (91.5 mg, 0.142 mmol). Mp: 161 – 162 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):

δ 8.30 (d, J = 3.5 Hz, 1H), 7.58 (d, J = 7.7 Hz, 1H), 7.41 – 7.28 (m, 7H), 7.26 – 7.23 (m, 1H), 7.19 – 7.12 (m, 9H), 7.09 – 7.06 (m, 6H), 6.96 (d, J = 8.1 Hz, 2H), 6.92 – 6.88 (m, 1H), 5.79 (s, 1H), 4.22 (s, 2H), 4.16 (q, J = 7.1 Hz, 2H), 1.20 (t, J = 7.2 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ 170.1, 168.7, 155.1, 153.6, 148.0, 141.8, 140.7, 136.3, 135.6, 135.0, 134.2, 130.2, 129.1, 128.6, 127.5, 127.3, 127.0, 126.2, 124.4, 123.9, 122.1, 61.2, 49.0, 14.2. HRMS (ESI): Calcd for C<sub>42</sub>H<sub>36</sub>N<sub>2</sub>NaO<sub>3</sub>Si [M+Na]<sup>+</sup> 667.2387, found: 667.2390.



# ethyl (*E*)-*N*-(1-(4-fluorophenyl)-2-(triphenylsilyl)vinyl)-*N*picolinoylglycinate (4j)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 70% yield (82.1 mg, 0.140 mmol). Mp: 116 – 117 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$ 

8.37 (d, J = 2.5 Hz, 1H), 7.65 (d, J = 7.4 Hz, 1H), 7.50 (t, J = 7.6 Hz, 1H), 7.40 – 7.38 (m, 2H), 7.31 – 7.27 (m, 3H), 7.22 – 7.15 (m, 12H), 7.04 – 7.00 (m, 1H), 6.52 (t, J = 8.7 Hz, 2H), 5.85 (s, 1H), 4.25 – 4.21 (m, 4H), 1.28 – 1.26 (m, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  169.9, 168.6, 163.1 (d, J = 249.2 Hz), 154.4, 153.5, 147.9, 136.4, 135.5, 134.0, 132.3, 131.7 (d, J = 8.5 Hz), 129.2, 127.6, 124.5, 124.0, 122.0, 114.3 (d, J = 21.7 Hz), 61.2, 48.9, 14.1. <sup>19</sup>F NMR (CDCl<sub>3</sub>, 471 MHz):  $\delta$  -112.0. HRMS (ESI): Calcd for C<sub>36</sub>H<sub>31</sub>FN<sub>2</sub>NaO<sub>3</sub>Si [M+Na]<sup>+</sup> 609.1980, found: 609.1982.



The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 73% yield (87.9 mg, 0.146 mmol). Mp: 158 – 159 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.37 (d, J = 4.0 Hz, 1H), 7.71 – 7.60 (m, 1H), 7.54 – 7.51 (m, 1H), 7.33 – 7.28 (m, 5H), 7.18 – 7.17 (d, J = 4.5 Hz, 12H), 7.02 (d, J = 4.6 Hz, 1H), 6.79 (d, J = 8.4 Hz, 2H), 5.88 (s, 1H), 4.23 (m, 4H), 1.28 (t, J = 7.4 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  169.8, 168.5, 154.3, 153.3, 147.8, 136.3, 135.5, 134.9, 134.6, 133.8, 131.1, 129.1, 127.6, 127.5, 124.5, 124.0, 122.6, 61.1, 48.8, 14.1. HRMS (ESI): Calcd for C<sub>36</sub>H<sub>31</sub>ClN<sub>2</sub>NaO<sub>3</sub>Si [M+Na]<sup>+</sup> 625.1685, found: 625.1687.

# eth N pic O N CO<sub>2</sub>Et Th Br SiPh<sub>3</sub> Etc

# ethyl (*E*)-*N*-(1-(4-bromophenyl)-2-(triphenylsilyl)vinyl)-*N*picolinoylglycinate (4l)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 71% yield (91.8 mg, 0.142 mmol). Mp: 125 - 126 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):

δ 8.37 (d, J = 4.7 Hz, 1H), 7.66 (d, J = 7.8 Hz, 1H), 7.51 (t, J = 7.7 Hz, 1H), 7.31 (dt, J = 8.8, 4.3 Hz, 3H), 7.27 (d, J = 8.0 Hz, 2H), 7.22 – 7.15 (m, 12H), 7.03 – 7.00 (m, 1H), 6.95 (d, J = 8.4 Hz, 2H), 5.89 (s, 1H), 4.23 (q, J = 7.2 Hz, 4H), 1.28 (t, J = 7.1 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ 169.8, 168.5, 154.3, 153.3, 147.9, 136.4, 135.5, 135.1, 133.9, 131.4, 130.5, 129.2, 127.6, 124.5, 124.0, 123.4, 122.8, 61.2, 48.8, 14.1. HRMS (ESI): Calcd for C<sub>36</sub>H<sub>31</sub>BrN<sub>2</sub>NaO<sub>3</sub>Si [M+Na]<sup>+</sup> 669.1180 and 671.1159, found: 669.1180 and 671.1158.



# ethyl (*E*)-*N*-picolinoyl-*N*-(1-(4-(trifluoromethyl)phenyl)-2-(triphenylsilyl)vinyl)glycinate (4m)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 69% yield (87.8 mg, 0.138 mmol). Mp: 143 – 144 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>,

**500 MHz**): δ 8.38 (d, *J* = 4.5 Hz, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.51 (t, *J* = 8.8 Hz, 3H), 7.30 – 7.27 (m, 3H), 7.21 – 7.14 (m, 12H), 7.07 (d, *J* = 8.2 Hz, 2H), 7.02 (dd, *J* = 7.0, 5.1 Hz, 1H), 5.98 (s, 1H), 4.29 – 4.18 (m, 4H), 1.28 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ 169.8, 168.5, 154.0, 153.2, 147.8, 139.6, 136.5, 135.5, 133.6, 130.7 (q, *J* = 32.3 Hz), 130.1,

129.4, 127.7, 124.7, 124.3 (q, J = 3.8 Hz), 124.2, 123.9, 123.7 (q, J = 272.3 Hz), 61.3, 48.8, 14.1. <sup>19</sup>F NMR (CDCl<sub>3</sub>, 471 MHz):  $\delta$  -63.0. HRMS (ESI): Calcd for C<sub>37</sub>H<sub>31</sub>F<sub>3</sub>N<sub>2</sub>NaO<sub>3</sub>Si [M+Na]<sup>+</sup> 659.1948, found: 659.1948.



# methyl (*E*)-4-(1-(*N*-(2-ethoxy-2-oxoethyl)picolinamido)-2-(triphenylsilyl)vinyl)benzoate (4n)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 71% yield 88.9 mg, 0.142 mmol). Mp: 106 - 107 °C. <sup>1</sup>H NMR

(CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.49 (d, J = 15.5 Hz, 1H), 7.75 (d, J = 7.9 Hz, 1H), 7.62 (d, J = 8.3 Hz, 2H), 7.58 (d, J = 8.3 Hz, 2H), 7.40 – 7.36 (m, 4H), 7.31– 7.27 (m, 11H), 7.15 (d, J = 20.0 Hz, 2H), 6.09 (s, 1H), 4.36 – 4.32 (m, 4H), 3.97 (s, 3H), 1.39 (t, J = 8.2 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  169.8, 168.5, 166.5, 154.4, 153.2, 147.9, 140.7, 136.4, 135.5, 133.8, 130.2, 129.8, 129.2, 128.7, 127.6, 124.6, 124.1, 123.8, 61.2, 52.0, 48.9, 14.1. HRMS (ESI): Calcd for C<sub>38</sub>H<sub>34</sub>N<sub>2</sub>NaO<sub>5</sub>Si [M+Na]<sup>+</sup> 649.2129, found: 649.2136.

# ethyl (*E*)-*N*-(1-(4-cyanophenyl)-2-(triphenylsilyl)vinyl)-*N*picolinoylglycinate (40)



The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 72% yield (85.4 mg, 0.144 mmol). Mp: 174 - 175 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):

δ 8.38 (d, J = 4.4 Hz, 1H), 7.65 (d, J = 7.7 Hz, 1H), 7.51 (d, J = 8.1 Hz, 3H), 7.33 – 7.28 (m, 3H), 7.23 – 7.14 (m, 12H), 7.08 (d, J = 8.1 Hz, 2H), 7.05 – 7.02 (m, 1H), 6.03 (s, 1H), 4.27 – 4.21 (m, 4H), 1.29 – 1.26 (t, J = 7.1 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ 169.7, 168.5, 153.0, 147.8, 140.8, 136.6, 135.5, 133.4, 131.1, 130.4, 129.5, 127.8, 124.8, 124.3, 118.5, 112.3, 61.4, 49.0, 14.1. HRMS (ESI): Calcd for C<sub>37</sub>H<sub>31</sub>N<sub>3</sub>NaO<sub>3</sub>Si [M+Na]<sup>+</sup> 616.2027, found: 616.2029.



The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 75% yield (87.3 mg, 0.150 mmol). Mp: 121 – 122 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.44 (d, *J* = 4.5 Hz, 1H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.67 (t, *J* = 7.7 Hz, 1H), 7.32 – 7.27 (m, 4H), 7.23 – 7.17 (m, 12H), 7.12 (dd, *J* = 6.7, 5.1 Hz, 1H), 6.90 (t, *J* = 7.1 Hz, 1H), 6.69 (t, *J* = 6.2 Hz, 2H), 6.06 (s, 1H), 4.30 – 4.26 (m, 4H), 2.15 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  169.7, 169.0, 154.6, 153.9, 148.0, 136.9, 136.4, 135.8, 135.5, 134.3, 131.6, 130.0, 128.9, 128.7, 127.4, 125.1, 124.4, 124.1, 120.2, 61.2, 49.0, 19.9, 14.2. HRMS (ESI): Calcd for C<sub>37</sub>H<sub>35</sub>N<sub>2</sub>O<sub>3</sub>Si [M+H]<sup>+</sup> 583.2411, found: 583.2414.

# ethyl (*E*)-*N*-(1-(2-methoxyphenyl)-2-(triphenylsilyl)vinyl)-*N*picolinoylglycinate (4q)



The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 72% yield (86.1 mg, 0.144 mmol). Mp: 108 – 109 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.43

(d, J = 4.6 Hz, 1H), 7.64 (d, J = 7.8 Hz, 1H), 7.52 (d, J = 7.5 Hz, 1H), 7.48 (t, J = 7.6 Hz, 1H), 7.26 – 7.12 (m, 15H), 6.99 (dd, J = 6.9, 5.3 Hz, 1H), 6.88 (t, J = 7.8 Hz, 1H), 6.57 (t, J = 7.5 Hz, 1H), 6.11 (d, J = 8.3 Hz, 1H), 6.07 (s, 1H), 4.33 – 4.22 (m, 4H), 3.22 (s, 3H), 1.30 (t, J = 7.1 Hz, 3H). <sup>13</sup>**C** NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  169.5, 168.9, 156.9, 154.0, 150.2, 148.1, 136.0, 135.5, 134.2, 131.4, 130.0, 128.8, 127.2, 124.9, 124.0, 123.5, 123.2, 119.7, 109.4, 61.0, 54.0, 49.0, 14.2. HRMS (ESI): Calcd for C<sub>37</sub>H<sub>35</sub>N<sub>2</sub>O<sub>4</sub>Si [M+H]<sup>+</sup> 599.2361, found: 599.2363.



# ethyl (*E*)-*N*-(1-(2-chlorophenyl)-2-(triphenylsilyl)vinyl)-*N*picolinoylglycinate (4r)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 66% yield (79.5 mg, 0.132 mmol). Mp: 131 - 132 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.43 (d,

J = 4.4 Hz, 1H), 7.67 (d, J = 7.7 Hz, 1H), 7.59 (t, J = 7.5 Hz, 1H), 7.54 (d, J = 7.5 Hz, 1H), 7.27 – 7.19 (m, 9H), 7.16 – 7.13 (m, 6H), 7.10 – 7.07 (m, 1H), 6.79 (t, J = 6.9 Hz, 1H), 6.73 – 6.70 (m, 2H), 6.26 (s, 1H), 4.38 (s, 2H), 4.25 (q, J = 7.1 Hz, 2H), 1.29 (t, J = 7.1 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  169.0, 153.8, 148.0, 136.4, 135.6, 135.4, 133.9, 133.5, 132.7,

129.6, 129.1, 128.9, 127.5, 125.9, 124.5, 124.0, 123.2, 61.2, 49.7, 14.2. **HRMS (ESI):** Calcd for C<sub>36</sub>H<sub>31</sub>ClN<sub>2</sub>NaO<sub>3</sub>Si [M+Na]<sup>+</sup> 625.1685, found: 625.1683.

# ethyl (*E*)-*N*-picolinoyl-*N*-(1-(m-tolyl)-2-(triphenylsilyl)vinyl)glycinate (4s) <sup>CO<sub>2</sub>Et The title compound was isolated by column chromatography (eluent:</sup>

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 80% yield (93.2 mg, 0.160 mmol). Mp: 109 – 110 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.32 (d, J = 4.5 Hz, 1H), 7.64 (d, J = 7.8 Hz, 1H), 7.47 (t, J = 7.7 Hz, 1H), 7.34

(d, J = 7.6 Hz, 1H), 7.26 – 7.23 (m, 3H), 7.16 – 7.13 (m, 12H), 7.04 (s, 1H), 6.97 (dd, J = 7.1, 5.1 Hz, 1H), 6.86 (t, J = 7.6 Hz, 1H), 6.79 (d, J = 7.5 Hz, 1H), 5.81 (s, 1H), 4.22 – 4.19 (m, 4H), 1.89 (s, 3H), 1.25 (t, J = 7.1 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  169.9, 168.6, 155.6, 153.6, 148.0, 137.0, 136.1, 136.0, 135.5, 134.4, 130.9, 129.8, 129.0, 127.6, 127.4, 126.5, 124.2, 123.8, 121.7, 61.0, 48.8, 20.9, 14.1. HRMS (ESI): Calcd for C<sub>37</sub>H<sub>34</sub>N<sub>2</sub>NaO<sub>3</sub>Si [M+Na]<sup>+</sup> 605.2231, found: 605.2228.

# ethyl (*E*)-*N*-(1-(3-methoxyphenyl)-2-(triphenylsilyl)vinyl)-*N*picolinoylglycinate (4t)



SiPh<sub>3</sub>

Me

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 74% yield (88.5 mg, 0.148 mmol). Mp: 106 – 107 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.35 (d, J = 4.7 Hz, 1H), 7.62 (d, J = 7.8 Hz, 1H), 7.49 (t, J = 7.0 Hz, 1H), 7.24 –

7.23 (m, 3H), 7.19 – 7.11 (m, 12H), 7.03 – 7.00 (m, 2H), 6.94 – 6.91 (m, 1H), 6.80 (t, J = 7.9 Hz, 1H), 6.52 (dd, J = 8.2, 2.5 Hz, 1H), 5.82 (s, 1H), 4.23 – 4.19 (m, 4H), 3.35 (s, 3H), 1.26 (t, J = 7.1 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  170.0, 168.7, 158.7, 155.5, 153.7, 148.1, 137.8, 136.3, 135.5, 134.4, 129.1, 128.8, 127.5, 124.4, 123.9, 122.1, 121.9, 115.8, 114.6, 61.1, 54.8, 48.9, 14.2. HRMS (ESI): Calcd for C<sub>37</sub>H<sub>34</sub>N<sub>2</sub>NaO<sub>4</sub>Si [M+Na]<sup>+</sup> 621.2180, found: 621.2179.



The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 71% yield (85.5 mg, 0.142 mmol). Mp: 134 – 135 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.36 (d, *J* = 4.5 Hz, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.35 – 7.30 (m, 2H), 7.26 – 7.21 (m, 3H), 7.19 – 7.12 (m, 12H), 7.00 (dd, *J* = 7.0, 5.1 Hz, 1H), 6.91 (d, *J* = 8.1 Hz, 1H), 6.77 (t, *J* = 7.8 Hz, 1H), 5.89 (s, 1H), 4.24 – 4.14 (m, 4H), 1.24 (t, *J* = 5.4 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  169.8, 168.5, 154.0, 153.3, 148.0, 138.1, 136.4, 135.5, 133.9, 133.4, 130.0, 129.2, 129.0, 128.8, 127.9, 127.6, 124.5, 124.1, 123.2, 61.2, 48.8, 14.1. HRMS (ESI): Calcd for C<sub>36</sub>H<sub>31</sub>ClN<sub>2</sub>NaO<sub>3</sub>Si [M+Na]<sup>+</sup> 625.1685, found: 625.1683.



# ethyl (*E*)-*N*-(1-(3,5-dimethoxyphenyl)-2-(triphenylsilyl)vinyl)-*N*-picolinoylglycinate (4v)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 70% yield (88.0 mg, 0.140 mmol). Mp: 114 - 115 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.36 (d, J = 4.5 Hz, 1H), 7.64 (d, J = 7.8 Hz, 1H),

7.52 (t, J = 7.5 Hz, 1H), 7.26 – 7.22 (m, 3H), 7.18 – 7.14 (m, 12H), 7.04 (dd, J = 7.0, 5.2 Hz, 1H), 6.61 (d, J = 2.1 Hz, 2H), 6.07 (t, J = 2.1 Hz, 1H), 5.81 (s, 1H), 4.25 – 4.20 (m, 4H), 3.37 (s, 6H), 1.26 (t, J = 7.1 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  169.9, 168.7, 160.0, 155.5, 153.7, 148.1, 138.6, 136.3, 135.4, 134.5, 129.0, 127.4, 124.4, 123.9, 121.7, 107.7, 102.3, 61.1, 55.0, 48.8, 14.2. HRMS (ESI): Calcd for C<sub>38</sub>H<sub>36</sub>N<sub>2</sub>NaO<sub>5</sub>Si [M+Na]<sup>+</sup> 651.2286, found: 651.2283.

# ethyl (*E*)-*N*-picolinoyl-*N*-(1-(thiophen-3-yl)-2-(triphenylsilyl)vinyl)glycinate (4w)



The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 82% yield (94.2 mg, 0.164 mmol). Mp: 74 – 75 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.33 (d, J

= 4.6 Hz, 1H), 7.54 (d, J = 7.8 Hz, 1H), 7.46 (t, J = 7.7 Hz, 1H), 7.26 – 7.22 (m, 3H), 7.20 – 7.14 (m, 12H), 7.09 (d, J = 1.9 Hz, 1H), 7.05 (d, J = 5.0 Hz, 1H), 7.00 (dd, J = 6.7, 5.0 Hz, 1H), 6.78 (dd, J = 4.9, 3.0 Hz, 1H), 5.78 (s, 1H), 4.28 (s, 2H), 4.18 (q, J = 7.1 Hz, 2H), 1.23 (t, J = 7.2 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  169.8, 168.7, 153.7, 150.6, 148.1, 138.6,

136.3, 135.5, 134.3, 129.2, 128.5, 128.0, 127.6, 125.0, 124.4, 123.8, 121.2, 61.2, 49.2, 14.2. **HRMS (ESI):** Calcd for C<sub>34</sub>H<sub>30</sub>N<sub>2</sub>NaO<sub>3</sub>SSi [M+Na]<sup>+</sup> 597.1639, found: 597.1638.

# ethyl (*E*)-*N*-(1-(cyclohex-1-en-1-yl)-2-(triphenylsilyl)vinyl)-*N*picolinoylglycinate (4x)



The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 55% yield (62.9 mg, 0.110 mmol). Mp: 101 – 102 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.39

(d, J = 4.6 Hz, 1H), 7.55 (d, J = 3.8 Hz, 1H), 7.47 (t, J = 7.8 Hz, 1H), 7.32 – 7.28 (m, 1H), 7.25 – 7.16 (m, 14H), 6.98 (dd, J = 6.7, 5.4 Hz, 1H), 5.60 – 5.60 (m, 1H), 5.41 (s, 1H), 4.26 – 4.12 (m, 4H), 1.95 – 1.95 (m, 2H), 1.33 (t, J = 11.8 Hz, 2H), 1.22 (t, J = 7.2 Hz, 3H), 1.10 (m, 2H), 0.91 (m, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  170.0, 168.7, 157.9, 153.9, 148.0, 136.1, 135.4, 135.1, 134.7, 134.3, 129.0, 127.5, 124.1, 123.9, 119.8, 61.0, 48.3, 26.2, 24.9, 21.6, 20.8, 14.1. HRMS (ESI): Calcd for C<sub>36</sub>H<sub>36</sub>N<sub>2</sub>NaO<sub>3</sub>Si [M+Na]<sup>+</sup> 595.2387, found: 595.2383.

# ethyl (*E*)-*N*-(1-phenyl-2-(triphenylsilyl)prop-1-en-1-yl)-*N*picolinoylglycinate (4y)



The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 46% yield (53.6 mg, 0.092 mmol). Mp: 159 – 160 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.80 (d,

J = 4.3 Hz, 1H), 7.89 (d, J = 7.8 Hz, 1H), 7.81 (t, J = 8.3 Hz, 1H), 7.63 (d, J = 7.3 Hz, 2H), 7.50 – 7.47 (m, 1H), 7.39 – 7.30 (m, 11H), 7.26 – 7.23 (m, 4H), 6.96 (t, J = 7.3 Hz, 1H), 6.88 (t, J = 7.5 Hz, 2H), 4.47 (d, J = 16.8 Hz, 1H), 4.29 (q, J = 7.1 Hz, 2H), 3.96 (d, J = 16.8 Hz, 1H), 1.78 (s, 3H), 1.35 (t, J = 7.1 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  169.5, 168.8, 154.4, 150.9, 147.3, 137.3, 136.5, 136.1, 135.8, 134.1, 130.9, 128.8, 128.7, 127.4, 126.5, 124.9, 124.3, 61.0, 49.5, 21.6, 14.1. HRMS (ESI): Calcd for C<sub>37</sub>H<sub>34</sub>N<sub>2</sub>NaO<sub>3</sub>Si [M+Na]<sup>+</sup> 605.2231, found: 605.2233.



The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 37% yield (47.7 mg, 0.074 mmol). Mp: 189 – 190 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.78 (d, J = 4.3 Hz, 1H), 7.53 (d, J = 7.4 Hz, 2H), 7.44 (t, J = 7.7 Hz, 2H), 7.40 – 7.39 (m 5H), 7.26 – 7.23 (m, 4H), 7.17 – 7.13 (m, 7H), 7.01 (t, J = 7.2 Hz, 1H), 6.95 (t, J = 7.5 Hz, 2H), 6.73 – 6.71 (m, 3H), 6.61 (t, J = 7.7 Hz, 2H), 4.11 – 3.99 (m, 3H), 3.88 (d, J = 16.6 Hz, 1H), 1.18 (t, J = 7.1 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  168.7, 168.2, 153.7, 153.4, 146.9, 140.2, 138.4, 136.3, 136.2, 134.6, 131.3, 130.8, 130.6, 128.8, 128.4, 127.5, 127.2, 126.8, 126.0, 124.8, 124.8, 60.8, 52.9, 14.0. HRMS (ESI): Calcd for C<sub>42</sub>H<sub>36</sub>N<sub>2</sub>NaO<sub>3</sub>Si [M+Na]<sup>+</sup> 667.2387, found: 667.2386.

### (E)-N-phenyl-N-(1-phenyl-2-(triphenylsilyl)vinyl)picolinamide (5a)



The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 84% yield (93.8 mg, 0.168 mmol). Mp: 130 – 131 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.43 (s, 1H), 7.41

-7.11 (m, 25H), 6.87 (t, J = 7.3 Hz, 1H), 6.76 (t, J = 7.2 Hz, 2H), 5.96 (s, 1H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ 170.0, 156.5, 154.5, 148.0, 141.1, 136.7, 136.2, 135.5, 134.3, 129.6, 129.1, 128.8, 128.4, 127.5, 127.1, 126.8, 126.3, 124.4, 124.0, 122.6. HRMS (ESI): Calcd for C<sub>38</sub>H<sub>30</sub>N<sub>2</sub>NaOSi [M+Na]<sup>+</sup> 581.2020, found: 581.2023.



(*E*)-*N*-(1-phenyl-2-(triphenylsilyl)vinyl)-*N*-(*p*-tolyl)picolinamide (5b) The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 85% yield (97.3 mg, 0.170 mmol). Mp: 167 – 168 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.36 (d, *J* = 4.4 Hz, 1H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.43 (t, *J* = 7.1 Hz, 1H),

7.36 (d, J = 7.4 Hz, 2H), 7.26 – 7.13 (m, 17H), 7.05 (d, J = 8.1 Hz, 2H), 6.98 (dd, J = 7.4, 4.9 Hz, 1H), 6.83 (t, J = 7.4 Hz, 1H), 6.72 (t, J = 7.6 Hz, 2H), 5.90 (s, 1H), 2.21 (s, 3H). <sup>13</sup>C **NMR (CDCl<sub>3</sub>, 125 MHz):**  $\delta$  170.0, 156.6, 154.7, 148.0, 136.8, 136.2, 136.1, 135.5, 134.4, 129.7, 129.5, 129.1, 128.4, 127.5, 127.1, 126.6, 124.3, 124.0, 122.4, 21.0. **HRMS (ESI):** Calcd for C<sub>39</sub>H<sub>32</sub>N<sub>2</sub>NaOSi [M+Na]<sup>+</sup> 595.2176, found: 595.2174.



# (E)-N-(4-chlorophenyl)-N-(1-phenyl-2-

### (triphenylsilyl)vinyl)picolinamide (5c)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 80% yield (94.7 mg, 0.160 mmol). Mp: 173 - 174 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.35 (d,

J = 4.6 Hz, 1H), 7.62 (d, J = 7.8 Hz, 1H), 7.44 (t, J = 7.7 Hz, 1H), 7.34 (d, J = 7.8 Hz, 2H), 7.26 – 7.12 (m, 19H), 6.99 (dd, J = 7.1, 5.2 Hz, 1H), 6.85 (t, J = 7.4 Hz, 1H), 6.73 (t, J = 7.7Hz, 2H), 5.89 (s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  170.0, 156.0, 154.2, 148.1, 139.6, 136.4, 136.4, 135.5, 134.2, 131.8, 129.8, 129.2, 129.0, 128.7, 128.0, 127.6, 127.2, 124.6, 124.1, 123.3. HRMS (ESI): Calcd for C<sub>38</sub>H<sub>29</sub>ClN<sub>2</sub>NaOSi [M+Na]<sup>+</sup> 615.1630, found: 615.1628.



## (*E*)-*N*-(4-bromophenyl)-*N*-(1-phenyl-2-(triphenylsilyl)vinyl)picolinamide (5d)

# The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 77% yield (98.0 mg,

0.154 mmol). Mp: 175 – 176 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.35 (d, J = 4.4 Hz, 1H), 7.62 (d, J = 7.8 Hz, 1H), 7.44 (t, J = 7.4 Hz, 1H), 7.37 – 7.34 (m, 4H), 7.25 – 7.23 (m, 3H), 7.20 – 7.13 (m, 14H), 6.99 (dd, J = 7.1, 5.0 Hz, 1H), 6.85 (t, J = 7.4 Hz, 1H), 6.73 (t, J = 7.6 Hz, 2H), 5.89 (s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  169.9, 155.9, 154.1, 148.1, 140.1, 136.4, 135.5, 134.1, 132.0, 129.7, 129.2, 128.7, 128.3, 127.6, 127.2, 124.6, 124.1, 123.4, 119.8. HRMS (ESI): Calcd for C<sub>38</sub>H<sub>29</sub>BrN<sub>2</sub>NaOSi [M+Na]<sup>+</sup> 659.1125 and 661.1104, found: 659.1123 and 661.1104.



# (*E*)-*N*-(1-phenyl-2-(triphenylsilyl)vinyl)-*N*-(4-(trifluoromethyl)phenyl)picolinamide (5e)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 72% yield (90.2 mg, 0.144 mmol). Mp: 187 – 188 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.42

(d, *J* = 2.9 Hz, 1H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.57 (d, *J* = 8.3 Hz, 2H), 7.52 – 7.48 (m, 3H), 7.42 (d, *J* = 7.5 Hz, 2H), 7.33 – 7.30 (m, 3H), 7.24 – 7.20 (m, 12H), 7.09 – 7.06 (m, 1H), 6.91

(t, J = 7.4 Hz, 1H), 6.79 (t, J = 7.6 Hz, 2H), 5.98 (s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$ 170.1, 155.8, 153.9, 148.1, 144.3, 136.4, 136.3, 135.5, 134.1, 129.8, 129.2, 128.9, 127.9 (q, J = 32.9 Hz), 127.6, 127.3, 126.7, 126.0 (q, J = 3.6 Hz), 124.8, 124.2, 123.9 (q, J = 272.2 Hz). <sup>19</sup>F NMR (CDCl<sub>3</sub>, 471 MHz):  $\delta$  -62.3. HRMS (ESI): Calcd for C<sub>39</sub>H<sub>29</sub>F<sub>3</sub>N<sub>2</sub>NaOSi [M+Na]<sup>+</sup> 649.1893, found: 649.1892.

### (*E*)-4-(*N*-(1-phenyl-2-



methyl

### (triphenylsilyl)vinyl)picolinamido)benzoate (5f)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 75% yield (92.4 mg, 0.150 mmol). Mp: 156 – 157 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):

δ 8.38 (d, J = 4.5 Hz, 1H), 7.95 (d, J = 8.4 Hz, 2H), 7.65 (d, J = 7.8 Hz, 1H), 7.47 (t, J = 7.6 Hz, 1H), 7.41 – 7.37 (m, 4H), 7.29 – 7.26 (m, 3H), 7.23 – 7.16 (m, 12H), 7.03 (dd, J = 7.4, 4.9 Hz, 1H), 6.85 (t, J = 7.4 Hz, 1H), 6.75 (t, J = 7.6 Hz, 2H), 5.96 (s, 1H), 3.83 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ 170.0, 166.4, 155.8, 154.0, 148.1, 145.3, 136.4, 136.3, 135.5, 134.1, 130.2, 129.7, 129.2, 128.7, 127.6, 127.5, 127.2, 126.3, 124.7, 124.1, 123.9, 52.0. HRMS (ESI): Calcd for C<sub>40</sub>H<sub>32</sub>N<sub>2</sub>NaO<sub>3</sub>Si [M+Na]<sup>+</sup> 639.2074, found: 639.2072.

# Ph SiPh<sub>3</sub>

# (*E*)-*N*-(2-chlorophenyl)-*N*-(1-phenyl-2-(triphenylsilyl)vinyl)picolinamide (5g)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 75% yield (88.8 mg, 0.150 mmol). Mp: 162 – 163 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.39 (d, J = 0.5

Hz, 1H), 7.76 (d, J = 7.8 Hz, 1H), 7.53 (t, J = 7.5 Hz, 1H), 7.40 (d, J = 7.5 Hz, 2H), 7.33 – 7.31 (m, 2H), 7.25 – 7.23 (m, 3H), 7.19 – 7.03 (m, 15H), 6.85 (t, J = 7.3 Hz, 1H), 6.74 (t, J = 7.5 Hz, 2H), 5.84 (s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  169.4, 156.1, 153.7, 148.3, 136.3, 135.6, 135.0, 134.5, 132.4, 130.5, 129.6, 129.1, 128.7, 128.3, 127.9, 127.5, 127.4, 127.2, 124.7, 124.3. HRMS (ESI): Calcd for C<sub>38</sub>H<sub>29</sub>ClN<sub>2</sub>NaOSi [M+Na]<sup>+</sup> 615.1630, found: 615.1632.



### (E)-N-(3,4-dichlorophenyl)-N-(1-phenyl-2-

### (triphenylsilyl)vinyl)picolinamide (5h)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 80% yield (100.2 mg, 0.160 mmol). Mp: 187 – 188 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 8.42 (d,

J = 4.6 Hz, 1H), 7.69 (d, J = 7.8 Hz, 1H), 7.54 – 7.49 (m, 2H), 7.41 (d, J = 7.3 Hz, 2H), 7.36 (d, J = 8.6 Hz, 1H), 7.34 - 7.30 (m, 3H), 7.24 - 7.20 (m, 13H), 7.08 (dd, J = 7.1, 5.0 Hz, 1H),6.93 (t, J = 7.4 Hz, 1H), 6.81 (t, J = 7.7 Hz, 2H), 5.95 (s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ 169.9, 155.6, 153.7, 148.1, 140.5, 136.4, 136.1, 135.5, 134.0, 132.6, 130.4, 130.1, 129.7, 129.2, 128.9, 128.6, 127.6, 127.3, 126.0, 124.8, 124.1, 124.0. HRMS (ESI): Calcd for C<sub>38</sub>H<sub>28</sub>Cl<sub>2</sub>N<sub>2</sub>NaOSi [M+Na]<sup>+</sup> 649.1240, found: 649.1244.

(E)-N-benzyl-N-(1-phenyl-2-(triphenylsilyl)vinyl)picolinamide (5i)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 71% yield (81.3 mg, 0.142) Ph mmol). Mp: 127 – 128 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 8.44 – 8.44 (m, . SiPh₃ 1H), 7.71 (d, J = 7.0 Hz, 1H), 7.54 (d, J = 7.3 Hz, 1H), 7.41 – 7.27 (m, 8H), 7.19 - 6.86 (m, 18H), 5.42 (s, 1H), 4.81 (s, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  169.6, 154.8, 154.6, 148.0, 137.2, 136.2, 136.0, 135.5, 134.1, 129.8, 129.4, 129.0, 128.9, 128.4,

127.4, 127.4, 127.3, 124.2, 124.1, 123.7, 49.4. HRMS (ESI): Calcd for C<sub>39</sub>H<sub>33</sub>N<sub>2</sub>OSi [M+H]<sup>+</sup> 573.2357, found: 573.2360.



Pł

# (E)-N-(4-methoxybenzyl)-N-(1-phenyl-2-(triphenylsilyl)vinyl)picolinamide (5j)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 64% yield (77.1 mg, 0.128 mmol). Mp: 157 – 158 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):

δ 8.40 (d, J = 4.6 Hz, 1H), 7.66 (d, J = 7.8 Hz, 1H), 7.50 (t, J = 7.7 Hz, 1H), 7.33 (d, J = 7.4 Hz, 2H), 7.26 – 7.21 (m, 5H), 7.13 – 7.10 (m, 6H), 7.04 – 7.00 (m, 8H), 6.92 – 6.86 (m, 4H), 5.36 (s, 1H), 4.72 (s, 2H), 3.86 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ 169.5, 159.0, 154.8, 154.6, 148.0, 136.1, 136.0, 135.5, 134.2, 130.8, 129.8, 129.3, 129.0, 128.8, 127.4, 127.4, 124.2, 124.1, 123.7, 113.7, 55.2, 48.7. **HRMS (ESI):** Calcd for C<sub>40</sub>H<sub>34</sub>N<sub>2</sub>NaO<sub>2</sub>Si [M+Na]<sup>+</sup> 625.2282, found: 625.2286.



## (*E*)-*N*-(4-bromobenzyl)-*N*-(1-phenyl-2-(triphenylsilyl)vinyl)picolinamide (5k)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 62% yield (80.6 mg, 0.124 mmol). Mp: 165 – 166 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.39

(d, J = 4.4 Hz, 1H), 7.67 (d, J = 7.8 Hz, 1H), 7.56 – 7.44 (m, 3H), 7.31 (d, J = 7.1 Hz, 2H), 7.27 – 7.21 (m, 5H), 7.17 – 7.08 (m, 7H), 7.05 – 7.00 (m, 2H), 6.98 – 6.97 (m, 5H), 6.88 (t, J = 7.7 Hz, 2H), 5.33 (s, 1H), 4.70 (s, 2H). <sup>13</sup>**C** NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  169.6, 154.6, 154.2, 148.1, 136.2, 135.8, 135.4, 134.0, 131.5, 131.2, 129.8, 129.1, 129.0, 127.6, 127.5, 127.4, 124.5, 124.3, 123.8, 121.4, 48.7. HRMS (ESI): Calcd for C<sub>39</sub>H<sub>31</sub>BrN<sub>2</sub>NaOSi [M+Na]<sup>+</sup> 673.1281 and 675.1261, found: 673.1285 and 675.1265.



## (*E*)-*N*-(4-cyanobenzyl)-*N*-(1-phenyl-2-(triphenylsilyl)vinyl)picolinamide (5l)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 70% yield (83.6 mg, 0.140 mmol). Mp: 181 – 182 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$ 

8.42 (d, J = 4.6 Hz, 1H), 7.71 (d, J = 7.8 Hz, 1H), 7.66 (d, J = 8.1 Hz, 2H), 7.57 (t, J = 7.7 Hz, 1H), 7.42 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 7.5 Hz, 2H), 7.29 – 7.26 (m, 3H), 7.16 – 7.13 (m, 6H), 7.09 – 7.05 (m, 2H), 7.00 – 6.99 (m, 6H), 6.92 (t, J = 7.6 Hz, 2H), 5.38 (s, 1H), 4.81 (s, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  169.8, 154.7, 153.8, 148.1, 142.7, 136.3, 135.6, 135.3, 133.9, 132.2, 130.0, 129.7, 129.2, 127.7, 127.5, 124.5, 124.4, 123.9, 118.8, 111.2, 49.2. HRMS (ESI): Calcd for C<sub>40</sub>H<sub>31</sub>N<sub>3</sub>NaOSi [M+Na]<sup>+</sup> 620.2129, found: 620.2125.



The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 57% yield (74.1 mg, 0.114 mmol). Mp: 115 – 116 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.38 (d, *J* = 4.6 Hz, 1H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 1H), 7.29 (t, *J* = 8.2 Hz, 2H), 7.24 – 7.17 (m, 6H), 7.11 – 7.08 (m, 6H), 7.01 – 6.94 (m, 8H), 6.80 (t, *J* = 7.6 Hz, 2H), 5.63 (s, 1H), 4.97 (s, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  169.6, 154.9, 154.6, 148.1, 136.2, 136.0, 135.7, 135.5, 134.1, 132.8, 130.9, 129.7, 129.0, 128.9, 128.7, 127.4, 127.4, 127.3, 124.0, 123.9, 123.5, 123.4, 49.7. HRMS (ESI): Calcd for C<sub>39</sub>H<sub>31</sub>BrN<sub>2</sub>NaOSi [M+Na]<sup>+</sup> 673.1281 and 675.1261, found: 673.1284 and 675.1265.

### (*E*)-*N*-methyl-*N*-(1-phenyl-2-(triphenylsilyl)vinyl)picolinamide (5n)



The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 74% yield (73.4 mg, 0.148 mmol). Mp: 94 – 95 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.35 – 8.35 (m, 1H),

7.55 (d, J = 5.9 Hz, 1H), 7.45 (t, J = 7.6 Hz, 1H), 7.33 (d, J = 7.6 Hz, 2H),

7.30 – 7.26 (m, 3H), 7.21 – 7.15 (m, 12H), 7.03 – 6.96 (m, 2H), 6.87 (t, J = 7.6 Hz, 2H), 5.72 (s, 1H), 3.20 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  169.9, 157.4, 154.5, 148.0, 136.7, 136.2, 135.6, 134.3, 129.4, 129.1, 128.9, 127.5, 127.5, 124.0, 123.5, 120.3, 35.6. HRMS (ESI): Calcd for C<sub>33</sub>H<sub>29</sub>N<sub>2</sub>OSi [M+H]<sup>+</sup> 497.2044, found: 497.2046.

### (E)-N-ethyl-N-(1-phenyl-2-(triphenylsilyl)vinyl)picolinamide (50)



The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 70% yield (71.4 mg, 0.140 mmol). Mp: 96 – 97 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.35 – 8.35 (m, 1H),

7.60 – 7.60 (m, 1H), 7.47 – 7.47 (m, 1H), 7.41 (d, J = 7.4 Hz, 2H), 7.28 – 7.28 (s, 3H), 7.18 – 7.17 (m, 12H), 7.01 (dd, J = 15.7, 8.2 Hz, 2H), 6.90 (t, J = 7.2 Hz, 2H), 5.67 (s, 1H), 3.63 – 3.62 (m, 2H), 1.26 (t, J = 6.8 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  155.6, 136.4, 135.7, 135.5, 134.9, 134.3, 129.9, 129.6, 129.0, 128.9, 128.0, 127.8, 127.5, 127.4, 122.4, 41.4, 12.7. HRMS (ESI): Calcd for C<sub>34</sub>H<sub>30</sub>N<sub>2</sub>NaOSi [M+Na]<sup>+</sup> 533.2020, found: 533.2018.



### (E)-N-(1-phenyl-2-(triphenylsilyl)vinyl)-N-propylpicolinamide (5p)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 73% yield (76.5 mg, 0.146 mmol). Mp: 107 – 108 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): 8.32 (d, J = 4.7 Hz, 1H), 7.59 (d, J = 7.8 Hz, 1H), 7.46 (t, J = 7.7 Hz, 1H), 7.40 (d, J = 7.3 Hz, 2H), 7.29 – 7.26 (m, 3H), 7.19 – 7.13 (m, 12H), 7.02 (t, J = 7.4 Hz, 1H), 6.97 (dd, J = 7.5, 4.9 Hz, 1H), 6.89 (t, J = 7.7 Hz, 2H), 5.66 (s, 1H), 3.57 - 3.42 (m, 2H), 1.75 - 1.67 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  169.6, 156.0, 154.8, 148.0, 136.4, 136.1, 135.5, 134.4, 129.7, 129.1, 128.9, 127.5, 127.5, 123.9, 123.5, 122.3, 47.9, 21.0, 11.4. HRMS (ESI): Calcd for C<sub>35</sub>H<sub>32</sub>N<sub>2</sub>NaOSi [M+Na]<sup>+</sup> 547.2176, found: 547.2174.

(E)-N-butyl-N-(1-phenyl-2-(triphenylsilyl)vinyl)picolinamide (5q)



The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 67% yield (72.1 mg, 0.134 mmol). Mp: 87 – 88 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.33 (d, J = 4.2 Hz, 1H), 7.59 (d, J = 7.8 Hz, 1H), 7.47 (t, J = 7.7 Hz, 1H), 7.40 (d, J = 7.1 Hz,

2H), 7.29 – 7.26 (m, 3H), 7.19 – 7.14 (m, 12H), 7.02 (t, J = 7.4 Hz, 1H), 6.97 (dd, J = 7.0, 5.4 Hz, 1H), 6.89 (t, J = 7.7 Hz, 2H), 5.65 (s, 1H), 3.54 – 3.54 (m, 2H), 1.70 – 1.63 (m, 2H), 1.41 -1.33 (m, 2H), 0.92 (t, J = 7.4 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  169.6, 156.0, 154.9, 148.0, 136.4, 136.1, 135.5, 134.4, 129.7, 129.1, 128.9, 127.5, 127.5, 123.9, 123.5, 122.3, 46.0, 29.9, 20.1, 13.9. HRMS (ESI): Calcd for C<sub>36</sub>H<sub>34</sub>N<sub>2</sub>NaOSi [M+Na]<sup>+</sup> 561.2333, found: 561.2330.

### (E)-N-hexyl-N-(1-phenyl-2-(triphenylsilyl)vinyl)picolinamide (5r)



The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 60% yield (68.0 mg, 0.120 mmol). Mp: 111 – 112 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 8.33 (d, J = 4.6 Hz, 1H), 7.59 (d, J = 7.8 Hz, 1H), 7.47 (t, J = 7.7 Hz, 1H), 7.39 (d, J

= 7.2 Hz, 2H), 7.29 - 7.26 (m, 3H), 7.19 - 7.14 (m, 12H), 7.02 (t, J = 7.4 Hz, 1H), 6.97 (dd, J= 7.0, 5.3 Hz, 1H), 6.89 (t, J = 7.7 Hz, 2H), 5.65 (s, 1H), 3.53 - 3.52 (m, 2H), 1.71 - 1.65 (m, 2H), 1.35 – 1.27 (m, 6H), 0.88 (t, *J* = 6.9 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ 169.5, 156.0, 154.9, 148.0, 136.4, 136.1, 135.6, 134.4, 129.7, 129.1, 128.9, 127.5, 127.5, 123.9, 123.5, 122.3, 46.3, 31.6, 27.7, 26.6, 22.5, 14.1. HRMS (ESI): Calcd for C<sub>38</sub>H<sub>38</sub>N<sub>2</sub>NaOSi [M+Na]<sup>+</sup> 589.2646, found: 589.2643.

(E)-N-octyl-N-(1-phenyl-2-(triphenylsilyl)vinyl)picolinamide (5s) The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 56% yield (66.6 mg, 0.112 mmol). Mp: 101 – 102 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.33 (d, J = 4.5 Hz, 1H), 7.59 (d, J = 7.8 Hz, 1H), 7.46 (t, J = 7.7 Hz, 1H), 7.39 (d, J

= 7.5 Hz, 2H), 7.30 – 7.26 (m, 3H), 7.20 – 7.12 (m, 12H), 7.01 (t, J = 7.4 Hz, 1H), 6.97 (dd, J = 6.9, 5.4 Hz, 1H), 6.89 (t, J = 7.6 Hz, 2H), 5.65 (s, 1H), 3.53 – 3.53 (m, 2H), 1.73 – 1.65 (m, 2H), 1.34 – 1.27 (m, 10H), 0.88 (t, J = 6.8 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  169.5, 156.0, 154.9, 148.0, 136.4, 136.1, 135.5, 134.4, 129.7, 129.1, 128.9, 127.5, 127.5, 123.9, 123.5, 122.3, 46.3, 31.8, 29.4, 29.1, 27.7, 26.9, 22.6, 14.1. HRMS (ESI): Calcd for C<sub>40</sub>H<sub>42</sub>N<sub>2</sub>NaOSi [M+Na]<sup>+</sup> 617.2959, found: 617.2954.

### (E)-N-(3,3-diphenylpropyl)-N-(1-phenyl-2-

(triphenylsilyl)vinyl)picolinamide (5t)



The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 70% yield (94.7 mg,

0.140 mmol). Mp: 125 – 126 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.33 (d, J = 4.5 Hz, 1H), 7.60 (d, J = 7.8 Hz, 1H), 7.49 (t, J = 7.7 Hz, 1H), 7.34 (d, J = 7.2 Hz, 2H), 7.30 – 7.26 (m, 3H), 7.22 – 7.11 (m, 22H), 7.03 – 6.98 (m, 2H), 6.87 (t, J = 7.7 Hz, 2H), 5.61 (s, 1H), 3.92 (t, J = 7.8 Hz, 1H), 3.59 – 3.42 (m, 2H), 2.49 (q, J = 7.9 Hz, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  169.4, 156.1, 154.6, 148.0, 144.2, 136.4, 136.1, 135.6, 134.3, 129.7, 129.1, 128.9, 128.4, 127.7, 127.5, 127.5, 126.2, 124.0, 123.6, 122.3, 48.9, 45.7, 33.1. HRMS (ESI): Calcd for C<sub>47</sub>H<sub>40</sub>N<sub>2</sub>NaOSi [M+Na]<sup>+</sup> 699.2802, found: 699.2802.

# methyl (*E*)-*N*-(1-phenyl-2-(triphenylsilyl)vinyl)-*N*-picolinoylglycinate (5u)

CO<sub>2</sub>Me The title compound was isolated by column chromatography (eluent: Ph SiPh<sub>3</sub> EtOAc/petroleum ether = 1/5) as a yellow solid in 86% yield (95.3 mg, 0.172 mmol). Mp: 94 – 95 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.37 (d, J = 3.8 Hz, 1H), 7.66 (t, J = 11.3 Hz, 1H), 7.50 (t, J = 7.5 Hz, 1H), 7.42 (d, J = 7.6 Hz, 2H), 7.29 – 7.24 (m, 3H), 7.20 – 7.15 (m, 12H), 7.03 – 6.99 (m, 2H), 6.88 (t, J = 7.5 Hz, 2H), 5.87 (s, 1H), 4.25 (s, 2H), 3.77 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  170.0, 169.1, 155.3, 153.5, 148.0, 136.3, 135.9, 135.5, 134.2, 129.8, 129.1, 129.1, 127.5, 127.5, 124.4, 123.9, 122.2, 52.0, 48.7. HRMS (ESI): Calcd for C<sub>35</sub>H<sub>30</sub>N<sub>2</sub>NaO<sub>3</sub>Si [M+Na]<sup>+</sup> 577.1918, found: 577.1915.



methyl

# (triphenylsilyl)vinyl)picolinamido)propanoate (5v)

(E)-3-(N-(1-phenyl-2-

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 80% yield (90.9 mg, 0.160 mmol). Mp: 105 – 106 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.32

(d, J = 4.6 Hz, 1H), 7.62 (d, J = 7.8 Hz, 1H), 7.48 (t, J = 7.7 Hz, 1H), 7.44 (d, J = 7.5 Hz, 2H), 7.29 – 7.26 (m, 3H), 7.20 – 7.13 (m, 12H), 7.04 (t, J = 7.4 Hz, 1H), 6.98 (dd, J = 7.5, 4.8 Hz, 1H), 6.92 (t, J = 7.7 Hz, 2H), 5.64 (s, 1H), 3.83 (t, J = 7.1 Hz, 2H), 3.64 (s, 3H), 2.76 (t, J = 7.3 Hz, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  171.9, 169.7, 155.5, 154.1, 148.1, 136.2, 136.0, 135.5, 134.2, 129.7, 129.2, 129.1, 127.6, 127.5, 124.1, 123.6, 122.8, 51.7, 42.6, 32.3. HRMS (ESI): Calcd for C<sub>36</sub>H<sub>32</sub>N<sub>2</sub>NaO<sub>3</sub>Si [M+Na]<sup>+</sup> 591.2074, found: 591.2069.



# methyl (*E*)-4-(*N*-(1-phenyl-2-(triphenylsilyl)vinyl)picolinamido)butanoate (5w)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 75% yield (87.3 mg, 0.150 mmol). Mp: 121 - 122 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):

δ 8.33 (d, *J* = 4.6 Hz, 1H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.48 (t, *J* = 8.4 Hz, 1H), 7.41 (d, *J* = 7.7 Hz, 2H), 7.29 – 7.26 (m, 3H), 7.19 – 7.13 (m, 12H), 7.03 (t, *J* = 7.4 Hz, 1H), 6.98 (dd, *J* = 7.4,

4.9 Hz, 1H), 6.90 (t, J = 7.6 Hz, 2H), 5.65 (s, 1H), 3.63 (s, 3H), 3.60 – 3.54 (m, 2H), 2.42 (t, J = 7.6 Hz, 2H), 2.05 – 1.98 (m, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  173.3, 169.7, 155.8, 154.5, 148.0, 136.2, 136.1, 135.6, 134.2, 129.7, 129.1, 129.0, 127.5, 124.0, 123.6, 122.7, 51.5, 45.4, 31.5, 23.2. HRMS (ESI): Calcd for C<sub>37</sub>H<sub>34</sub>N<sub>2</sub>NaO<sub>3</sub>Si [M+Na]<sup>+</sup> 605.2231, found: 605.2225.

methyl



# (triphenylsilyl)vinyl)picolinamido)hexanoate (5x)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 54% yield (65.9 mg, 0.108 mmol). Mp: 130 - 131 °C. <sup>1</sup>H NMR

(CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.32 (d, J = 4.6 Hz, 1H), 7.60 (d, J = 7.8 Hz, 1H), 7.47 (t, J = 7.7 Hz, 1H), 7.39 (d, J = 7.2 Hz, 2H), 7.29 – 7.26 (m, 3H), 7.20 – 7.11 (m, 12H), 7.02 (t, J = 7.4 Hz, 1H), 6.97 (dd, J = 7.0, 5.1 Hz, 1H), 6.90 (t, J = 7.7 Hz, 2H), 5.64 (s, 1H), 3.64 (s, 3H), 3.54 (t, J = 5.8 Hz, 2H), 2.30 (t, J = 7.5 Hz, 2H), 1.71 – 1.62 (m, 4H), 1.40 – 1.34 (m, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  174.0, 169.6, 155.9, 154.7, 148.0, 136.3, 136.1, 135.5, 134.3, 129.7, 129.1, 129.0, 127.5, 123.9, 123.5, 122.4, 51.4, 46.0, 33.9, 27.4, 26.4, 24.7. HRMS (ESI): Calcd for C<sub>39</sub>H<sub>38</sub>N<sub>2</sub>NaO<sub>3</sub>Si [M+Na]<sup>+</sup> 633.2544, found: 633.2540.

### (*E*)-4-((*N*-(1-phenyl-2-

(E)-6-(N-(1-phenyl-2-



(triphenylsilyl)vinyl)picolinamido)methyl)cyclohexane-1-

### carboxylate (5y)

methyl

 $CO_2Me$  The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 42%

yield (53.4 mg, 0.084 mmol). Mp: 181 – 182 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta^{1}$ H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.32 (d, J = 4.7 Hz, 1H), 7.62 (d, J = 7.8 Hz, 1H), 7.49 (t, J = 7.7 Hz, 1H), 7.39 (d, J = 7.2 Hz, 2H), 7.29 – 7.26 (m, 3H), 7.20 – 7.09 (m, 12H), 7.03 (t, J = 7.4 Hz, 1H), 6.97 (dd, J = 7.5, 4.8 Hz, 1H), 6.90 (t, J = 7.7 Hz, 2H), 5.64 (s, 1H), 3.68 (s, 3H), 3.39 (s, 2H), 2.29 – 2.22 (m, 1H), 2.02 – 2.00 (m, 2H), 1.88 – 1.86 (m, 2H), 1.77 – 1.72 (m, 1H), 1.47 – 1.38 (m, 2H), 1.11 – 1.02 (m, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  176.4, 169.9, 156.1, 154.8, 148.1, 136.2, 136.0, 135.5, 134.3, 129.7, 129.1, 129.0, 127.6, 127.6, 123.9, 123.5,

122.9, 51.5, 51.3, 43.2, 36.6, 29.8, 28.7. **HRMS (ESI):** Calcd for C<sub>41</sub>H<sub>40</sub>N<sub>2</sub>NaO<sub>3</sub>Si [M+Na]<sup>+</sup> 659.2700, found: 659.2705.



8.37 (d, J = 4.3 Hz, 1H), 7.69 (d, J = 7.8 Hz, 1H), 7.53 (d, J = 7.4 Hz, 2H), 7.30 – 7.24 (m, 4H), 7.19 – 7.12 (m, 12H), 7.04 (t, J = 6.9 Hz, 2H), 6.91 (t, J = 7.1 Hz, 2H), 5.74 (s, 1H), 4.20 (t, J = 6.2 Hz, 1H), 3.72 (s, 3H), 3.56 (s, 3H), 2.62 – 2.56 (m, 1H), 2.55 – 2.47 (m, 2H), 2.43 – 2.38 (m, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  173.1, 170.4, 169.7, 156.2, 153.7, 148.2, 136.3, 135.8, 135.5, 134.2, 130.4, 129.3, 129.1, 127.5, 127.5, 124.4, 123.8, 123.5, 59.1, 52.2, 51.5, 30.9, 24.7. HRMS (ESI): Calcd for C<sub>39</sub>H<sub>36</sub>N<sub>2</sub>NaO<sub>5</sub>Si [M+Na]<sup>+</sup> 663.2286, found: 663.2292.

#### tert-butyl

#### (E)-(4-(N-(1-phenyl-2-



(triphenylsilyl)vinyl)picolinamido)butyl)carbamate (5aa) The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 47% yield (61.4 mg, 0.094 mmol). Mp: 135 – 136 °C. <sup>1</sup>H NMR

(CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.33 (d, J = 4.7 Hz, 1H), 7.61 (d, J = 7.8 Hz, 1H), 7.48 (t, J = 7.7 Hz, 1H), 7.40 (d, J = 7.4 Hz, 2H), 7.29 – 7.26 (m, 3H), 7.20 – 7.11 (m, 12H), 7.03 (t, J = 7.4 Hz, 1H), 6.98 (dd, J = 7.0, 5.0 Hz, 1H), 6.90 (t, J = 7.7 Hz, 2H), 5.63 (s, 1H), 4.60 (s, 1H), 3.53 – 3.52 (m, 2H), 3.13 – 3.12 (m, 2H), 1.73 – 1.67 (m, 2H), 1.56 – 1.50 (m, 2H), 1.44 (s, 9H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  169.6, 155.9, 154.6, 148.1, 136.2, 136.2, 135.5, 134.3, 129.7, 129.1, 129.0, 127.5, 124.0, 123.5, 122.5, 79.0, 45.9, 40.3, 28.4, 27.3, 25.1. HRMS (ESI): Calcd for C<sub>41</sub>H<sub>43</sub>N<sub>3</sub>NaO<sub>3</sub>Si [M+Na]<sup>+</sup> 676.2966, found: 676.2969.



The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 51% yield (60.8 mg, 0.102 mmol). Mp: 92 – 93 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.33 (d, J = 4.7 Hz, 1H), 7.60 (d, J = 7.8 Hz, 1H), 7.47 (t, J = 8.3 Hz, 1H), 7.40 (d, J = 7.8 Hz, 2H), 7.30 – 7.26 (m, 3H), 7.19 – 7.13 (m, 12H), 7.02 (t, J = 7.4 Hz, 1H), 6.98 (dd, J = 7.5, 4.8 Hz, 1H), 6.89 (t, J = 7.6 Hz, 2H), 5.67 (s, 1H), 3.63 (t, J = 6.9 Hz, 2H), 3.50 (t, J = 6.5 Hz, 2H), 3.36 (t, J = 6.6 Hz, 2H), 2.03 – 1.95 (m, 2H), 1.52 – 1.44 (m, 2H), 1.33 – 1.26 (m, 2H), 0.88 (t, J = 7.4 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  169.6, 156.1, 154.7, 148.1, 136.4, 136.1, 135.5, 134.4, 129.7, 129.1, 128.9, 127.5, 127.5, 123.9, 123.5, 122.3, 70.5, 68.4, 44.0, 31.8, 28.0, 19.3, 13.9. HRMS (ESI): Calcd for C<sub>39</sub>H<sub>40</sub>N<sub>2</sub>NaO<sub>2</sub>Si [M+Na]<sup>+</sup> 619.2751, found: 619.2749.

# ethyl (*E*)-*N*-(2-(diphenyl(*p*-tolyl)silyl)-1-phenylvinyl)-*N*picolinoylglycinate (6a)



The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 91% yield (106.0 mg, 0.182 mmol). Mp: 60 - 61 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ
<sup>e</sup> 8.39 (d, J = 4.4 Hz, 1H), 7.68 (d, J = 7.8 Hz, 1H), 7.52 (t, J = 7.3 Hz, 1H)

1H), 7.43 (d, J = 7.3 Hz, 2H), 7.29 – 7.26 (m, 2H), 7.22 – 7.12 (m, 10H), 7.04 – 7.01 (m, 4H), 6.90 (t, J = 7.7 Hz, 2H), 5.89 (s, 1H), 4.33 – 4.18 (m, 4H), 2.34 (s, 3H), 1.30 (t, J = 7.1 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  170.0, 168.6, 155.2, 153.6, 148.0, 139.0, 136.2, 136.0, 135.6, 135.5, 134.5, 130.5, 129.8, 128.9, 128.4, 127.5, 127.4, 124.3, 123.8, 122.4, 61.1, 48.9, 21.4, 14.1. HRMS (ESI): Calcd for C<sub>37</sub>H<sub>34</sub>N<sub>2</sub>NaO<sub>3</sub>Si [M+Na]<sup>+</sup> 605.2231, found: 605.2233.



# ethyl (*E*)-*N*-(2-((4-methoxyphenyl)diphenylsilyl)-1-phenylvinyl)-*N*-picolinoylglycinate (6b)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 83% yield (99.3 mg, 0.166 mmol). Mp: 146 – 147 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.38 (d, J = 4.5 Hz, 1H), 7.67 (d, J = 7.8 Hz, 1H), 7.52 (t, J = 7.7

Hz, 1H), 7.43 (d, J = 7.6 Hz, 2H), 7.29 – 7.26 (m, 2H), 7.22 – 7.11 (m, 10H), 7.03 (t, J = 6.6

Hz, 2H), 6.90 (t, J = 7.7 Hz, 2H), 6.75 (d, J = 8.5 Hz, 2H), 5.87 (s, 1H), 4.27 – 4.23 (m, 4H), 3.80 (s, 3H), 1.30 (t, J = 7.2 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  170.0, 168.7, 160.5, 155.2, 153.7, 148.0, 137.1, 136.2, 136.1, 135.5, 134.7, 129.8, 129.0, 129.0, 127.5, 127.5, 124.9, 124.3, 123.9, 122.5, 113.4, 61.1, 55.0, 48.9, 14.2. HRMS (ESI): Calcd for C<sub>37</sub>H<sub>34</sub>N<sub>2</sub>NaO<sub>4</sub>Si [M+Na]<sup>+</sup> 621.2180, found: 621.2178.

#### ethyl (E)-N-(2-((4-fluorophenyl)diphenylsilyl)-1-phenylvinyl)-Npicolinoylglycinate (6c)



The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 76% yield (89.1 mg, 0.152 mmol). Mp: 132 – 133 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 8.36 (d, J = 4.6 Hz, 1H), 7.67 (d, J = 7.8 Hz, 1H), 7.51 (t, J = 7.7 Hz, 1H),7.40 (d, J = 7.8 Hz, 2H), 7.30 – 7.27 (m, 2H), 7.19 – 7.18 (m, 8H), 7.14 – 7.10 (m, 2H), 7.04 -7.00 (m, 2H), 6.89 (t, J = 7.7 Hz, 2H), 6.84 (t, J = 8.9 Hz, 2H), 5.83 (s, 1H), 4.25 - 4.21 (m, 4H), 1.27 (t, J = 7.1 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  169.9, 168.6, 163.6 (d, J =248.9 Hz), 155.6, 153.6, 148.0, 137.5 (d, *J* = 7.7 Hz), 136.3, 136.0, 135.5, 134.2, 129.8, 129.6 (d, J = 3.6 Hz), 129.2, 129.2, 127.6, 127.6, 124.4, 124.0, 121.7, 114.6 (d, J = 19.9 Hz), 61.1,

48.8, 14.1. <sup>19</sup>F NMR (CDCl<sub>3</sub>, 471 MHz): δ -111.5. HRMS (ESI): Calcd for C<sub>36</sub>H<sub>31</sub>FN<sub>2</sub>NaO<sub>3</sub>Si [M+Na]<sup>+</sup> 609.1980, found: 609.1979.



### ethyl (E)-N-(2-((4-chlorophenyl)diphenylsilyl)-1-phenylvinyl)-Npicolinoylglycinate (6d)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 75% yield (90.3 mg, 0.150 mmol). Mp: 115 – 116 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 8.35 (d, J = 4.6 Hz, 1H), 7.67 (d, J = 7.8 Hz, 1H), 7.51 (t, J = 7.7 Hz, 1H),

7.39 (d, J = 7.1 Hz, 2H), 7.30 – 7.27 (m, 2H), 7.20 – 7.17 (m, 8H), 7.11 (d, J = 8.2 Hz, 2H), 7.06 (d, J = 8.3 Hz, 2H), 7.04 – 7.00 (m, 2H), 6.89 (t, J = 7.7 Hz, 2H), 5.81 (s, 1H), 4.27 – 4.18 (m, 4H), 1.27 (t, J = 7.1 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  169.9, 168.6, 155.8, 153.6, 148.0, 136.8, 136.3, 136.0, 135.5, 133.9, 132.7, 129.8, 129.3, 129.2, 127.7, 127.6, 127.6, 124.4, 124.0, 121.4, 61.1, 48.8, 14.1. **HRMS (ESI):** Calcd for C<sub>36</sub>H<sub>31</sub>ClN<sub>2</sub>NaO<sub>3</sub>Si [M+Na]<sup>+</sup> 625.1685, found: 625.1682.

# ethyl (*E*)-*N*-(2-(diphenyl(o-tolyl)silyl)-1-phenylvinyl)-*N*picolinoylglycinate (6e)



The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 80% yield (93.2 mg, 0.160 mmol). Mp: 77 – 78 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.27 (d, J

= 4.2 Hz, 1H), 7.66 (d, J = 7.7 Hz, 1H), 7.50 (t, J = 7.6 Hz, 1H), 7.37 (d, J

= 7.6 Hz, 2H), 7.31 – 7.26 (m, 3H), 7.22 (t, J = 7.5 Hz, 1H), 7.19 – 7.12 (m, 8H), 7.07 (t, J = 7.4 Hz, 1H), 7.01 – 6.94 (m, 3H), 6.84 (t, J = 7.7 Hz, 2H), 5.97 (s, 1H), 4.26 – 4.21 (m, 4H), 1.89 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  170.0, 168.7, 154.9, 153.6, 148.1, 144.5, 137.1, 136.2, 135.7, 135.4, 134.5, 133.0, 129.8, 129.7, 129.0, 127.6, 127.3, 124.8, 124.3, 123.8, 122.4, 61.1, 49.0, 23.4, 14.1. HRMS (ESI): Calcd for C<sub>37</sub>H<sub>34</sub>N<sub>2</sub>NaO<sub>3</sub>Si [M+Na]<sup>+</sup> 605.2231, found: 605.2228.

# ethyl (*E*)-*N*-(2-(diphenyl(m-tolyl)silyl)-1-phenylvinyl)-*N*picolinoylglycinate (6f)



The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 82% yield (95.5 mg, 0.164 mmol). Mp: 65 – 66 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.36 (d, J = 4.6 Hz, 1H), 7.66 (d, J = 7.7 Hz, 1H), 7.49 (t, J = 7.6 Hz, 1H),

7.42 (d, J = 7.7 Hz, 2H), 7.29 – 7.26 (m, 2H), 7.20 – 7.15 (m, 8H), 7.08 (d, J = 4.8 Hz, 2H), 7.03 – 6.98 (m, 4H), 6.88 (t, J = 7.6 Hz, 2H), 5.86 (s, 1H), 4.26 – 4.22 (m, 4H), 2.22 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  170.0, 168.7, 155.3, 153.6, 148.0, 136.6, 136.2, 136.2, 136.1, 135.6, 134.5, 133.8, 132.7, 129.9, 129.8, 129.0, 127.5, 127.4, 124.3, 123.9, 122.4, 61.1, 48.9, 21.4, 14.2. HRMS (ESI): Calcd for C<sub>37</sub>H<sub>34</sub>N<sub>2</sub>NaO<sub>3</sub>Si [M+Na]<sup>+</sup> 605.2231, found: 605.2229.

### ethyl (E)-N-(2-(naphthalen-1-yldiphenylsilyl)-1-phenylvinyl)-Npicolinoylglycinate (6g)



The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 77% yield (95.2 mg, 0.154 mmol). Mp: 147 – 148 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 8.30 (d, J = 1.3 Hz, 1H), 7.75 (d, J = 8.2 Hz, 1H), 7.67 (d, J = 8.1 Hz, 1H),7.55 – 7.44 (m, 3H), 7.35 – 7.27 (m, 3H), 7.23 – 7.20 (m, 3H), 7.17 – 7.08 (m, 10H), 6.89 (d, J = 1.3 Hz, 1H), 6.72 (t, J = 7.4 Hz, 1H), 6.55 (t, J = 7.7 Hz, 2H), 5.98 (s, 1H), 4.20 - 4.15 (m, 4H), 1.22 (t, J = 7.1 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  170.1, 168.7, 155.1, 153.7,

147.9, 136.9, 136.6, 136.1, 135.7, 135.6, 134.5, 133.3, 132.4, 130.6, 129.4, 129.2, 129.1, 128.7, 128.4, 127.6, 126.8, 125.4, 125.3, 125.0, 124.2, 123.7, 122.2, 61.1, 49.0, 14.1. HRMS (ESI): Calcd for  $C_{40}H_{34}N_2NaO_3Si [M+Na]^+ 641.2231$ , found: 641.2233.



### ethyl (E)-N-(2-(naphthalen-2-yldiphenylsilyl)-1-phenylvinyl)-Npicolinoylglycinate (6h)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 82% yield (101.4) mg, 0.164 mmol). Mp: 133 – 134 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.35 (d, J = 4.6 Hz, 1H), 7.80 – 7.74 (m, 2H), 7.70 – 7.66 (m, 2H),

7.63 (d, J = 8.2 Hz, 1H), 7.50 – 7.44 (m, 4H), 7.40 (t, J = 7.2 Hz, 1H), 7.29 (t, J = 7.2 Hz, 2H), 7.25 - 7.23 (m, 5H), 7.20 - 7.17 (m, 4H), 6.94 - 6.88 (m, 2H), 6.83 (t, J = 7.6 Hz, 2H), 5.94(s, 1H), 4.35 - 4.16 (m, 4H), 1.29 (t, J = 7.1 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  170.0, 168.7, 155.5, 153.6, 148.0, 136.9, 136.2, 136.1, 135.6, 134.3, 133.6, 132.7, 131.8, 131.3, 129.8, 129.1, 129.1, 128.1, 127.6, 127.5, 126.6, 126.5, 125.7, 124.3, 123.9, 122.1, 61.1, 48.8, 14.1. HRMS (ESI): Calcd for C<sub>40</sub>H<sub>34</sub>N<sub>2</sub>NaO<sub>3</sub>Si [M+Na]<sup>+</sup> 641.2231, found: 641.2230.

### (E)-N-(2-(benzo[b]thiophen-2-yldiphenylsilyl)-1ethyl phenylvinyl)-N-picolinoylglycinate (6i)



The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 73% yield (91.1 mg, 0.146 mmol). Mp: 143 – 144 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.33 (d, J = 4.5 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.53 (d, J = 7.7 Hz, 1H), 7.37 – 7.26 (m, 8H), 7.24 – 7.22 (m, 4H), 7.19 – 7.16 (m, 4H), 7.10 (t, J = 7.2 Hz, 1H), 6.95 (dd, J = 7.0, 5.1 Hz, 1H), 6.88 (t, J = 7.4 Hz, 1H), 6.76 (t, J = 7.7 Hz, 2H), 5.94 (s, 1H), 4.26 – 4.18 (m, 4H), 1.27 (t, J = 7.1 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  170.1, 168.7, 155.6, 153.6, 147.9, 142.8, 141.4, 138.2, 136.0, 135.6, 135.4, 133.8, 131.5, 129.5, 129.3, 129.0, 127.7, 127.1, 125.3, 124.2, 123.9, 123.8, 123.7, 122.1, 121.1, 61.1, 48.8, 14.2. HRMS (ESI): Calcd for C<sub>38</sub>H<sub>32</sub>N<sub>2</sub>NaO<sub>3</sub>SSi [M+Na]<sup>+</sup> 647.1795, found: 647.1799.

# ethyl (*E*)-*N*-(2-(methyldiphenylsilyl)-1-phenylvinyl)-*N*picolinoylglycinate (6j)

ONCO2Et Ph SiMePh2

Et The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 77% yield (78.0 mg, 0.154 mmol). Mp: 45 – 46 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 8.48 (d, J

= 4.7 Hz, 1H), 7.68 (d, J = 7.7 Hz, 1H), 7.62 (t, J = 7.7 Hz, 1H), 7.52 (d, J = 7.8 Hz, 2H), 7.28 (t, J = 7.4 Hz, 2H), 7.23 – 7.16 (m, 6H), 7.15 – 7.11 (m, 6H), 5.71 (s, 1H), 4.23 – 4.19 (q, J = 7.1 Hz, 4H), 1.28 – 1.25 (m, 3H), 0.01 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  169.8, 168.6, 154.8, 153.8, 148.1, 137.0, 137.0, 136.4, 134.3, 130.0, 129.3, 128.9, 127.9, 127.6, 124.5, 124.1, 123.8, 61.1, 48.7, 14.1, -4.0. HRMS (ESI): Calcd for C<sub>31</sub>H<sub>30</sub>N<sub>2</sub>NaO<sub>3</sub>Si [M+Na]<sup>+</sup> 529.1918, found: 529.1920.

N ON CO<sub>2</sub>Et Ph SiHPh<sub>2</sub> ethyl (*E*)-*N*-(2-(diphenylsilyl)-1-phenylvinyl)-*N*-picolinoylglycinate (6k) The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 64% yield (63.0 mg, 0.128 mmol). Mp: 53 – 54 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.36 (d, *J* = 4.5 Hz, 1H), 7.62 – 7.59 (m, 3H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.33 – 7.27

(m, 3H), 7.26 - 7.18 (m, 10H), 7.06 (dd, J = 6.6, 5.4 Hz, 1H), 5.69 (d, J = 5.4 Hz, 1H), 4.75 (d, J = 5.5 Hz, 1H), 4.26 (s, 2H), 4.21 (q, J = 7.1 Hz, 2H), 1.26 (t, J = 7.0 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  168.6, 156.0, 153.6, 148.2, 136.8, 136.3, 135.0, 134.0, 129.8, 129.4,

129.4, 128.0, 127.8, 124.4, 123.8, 120.0, 61.2, 49.1, 14.1. HRMS (ESI): Calcd for  $C_{30}H_{28}N_2NaO_3Si [M+Na]^+ 515.1761$ , found: 515.1765.

# ethyl (*E*)-*N*-(2-(dimethyl(phenyl)silyl)-1-phenylvinyl)-*N*picolinoylglycinate (6l)

 $\begin{array}{l} \begin{array}{c} O & \mathsf{N} & \mathsf{CO}_2\mathsf{Et} \\ \mathsf{Ph} & \mathsf{SiMe}_2\mathsf{Ph} \end{array} \\ \begin{array}{c} \mathsf{EtOAc/petroleum\ ether\ =\ 1/5)\ as\ a\ yellow\ solid\ in\ 68\%\ yield\ (60.4\ mg, \\ 0.136\ mmol).\ Mp:\ 41\ -\ 42\ ^\circ\mathsf{C}.\ ^1\mathsf{H}\ \mathbf{NMR}\ (\mathbf{CDCl}_3,\ \mathbf{500\ MHz}):\ \delta\ 8.54\ (d,\ J \\ \end{array} \\ \begin{array}{c} =\ 4.7\ \mathrm{Hz},\ 1\mathrm{H}),\ 7.72\ (d,\ J\ =\ 4.3\ \mathrm{Hz},\ 2\mathrm{H}),\ 7.61\ (d,\ J\ =\ 7.3\ \mathrm{Hz},\ 2\mathrm{H}),\ 7.38\ -\ 7.27\ (m,\ 7\mathrm{H}),\ 7.21\ (d, \\ J\ =\ 6.9\ \mathrm{Hz},\ 2\mathrm{H}),\ 5.52\ (s,\ 1\mathrm{H}),\ 4.28\ -\ 4.23\ (m,\ 4\mathrm{H}),\ 1.32\ (t,\ J\ =\ 2.1\ \mathrm{Hz},\ 3\mathrm{H}),\ -0.12\ (s,\ 6\mathrm{H}).\ ^{13}\mathsf{C} \\ \mathbf{NMR}\ (\mathbf{CDCl}_3,\ \mathbf{125\ MHz}):\ \delta\ 169.9,\ 168.6,\ 154.1,\ 153.6,\ 148.1,\ 138.8,\ 137.3,\ 136.4,\ 133.5,\ 130.0,\ 129.3,\ 128.7,\ 128.0,\ 127.6,\ 125.9,\ 124.4,\ 123.9,\ 61.1,\ 48.5,\ 14.1,\ -1.9.\ \mathbf{HRMS}\ (\mathbf{ESI}):\ \mathbf{Calcd}\ \mathbf{for}\ \mathbf{C}_{26}\mathbf{H}_{28}\mathbf{N}_2\mathbf{NaO}_3\mathbf{Si}\ [\mathsf{M+Na}]^+\ 467.1761,\ found:\ 467.1760. \end{array}$ 

Nethyl (E)-N-(1-phenyl-2-(triethylsilyl)vinyl)-N-picolinoylglycinate (6m)The title compound was isolated by column chromatography (eluent:ONCO2EtEtOAc/petroleum ether = 1/5) as a yellow solid in 65% yield (55.1 mg,0.130 mmol). Mp: 55 - 56 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.47 (d, J= 4.6 Hz, 1H), 7.71 - 7.65 (m, 2H), 7.62 (d, J = 6.6 Hz, 2H), 7.35 - 7.29(m, 3H), 7.23 (t, J = 5.7 Hz, 1H), 5.30 (s, 1H), 4.21 - 4.16 (m, 4H), 1.27 - 1.24 (m, 3H), 0.60(t, J = 7.9 Hz, 9H), 0.14 (q, J = 7.9 Hz, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  169.9, 168.7,

154.3, 152.8, 148.3, 137.8, 136.4, 129.8, 129.1, 127.9, 125.1, 124.3, 123.8, 61.0, 48.6, 14.1, 7.2, 4.3. **HRMS (ESI):** Calcd for C<sub>24</sub>H<sub>32</sub>N<sub>2</sub>NaO<sub>3</sub>Si [M+Na]<sup>+</sup> 447.2074, found: 447.2072.

# ethyl (*E*)-*N*-(1-phenyl-2-(triisopropylsilyl)vinyl)-*N*-picolinoylglycinate (6n)

 $CO_2Et$ The title compound was isolated by column chromatography (eluent: $isi/Pr_3$ EtOAc/petroleum ether = 1/5) as a yellow solid in 67% yield (62.5 mg,0.134 mmol). Mp: 86 - 87 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.47 (d, J

= 4.6 Hz, 1H), 7.72 - 7.66 (m, 4H), 7.33 - 7.27 (m, 3H), 7.23 - 7.20 (m, 1H), 5.41 (s, 1H),

4.20 - 4.16 (m, 4H), 1.26 - 1.24 (m, 3H), 0.78 - 0.68 (m, 21H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125) MHz): δ 168.7, 154.0, 153.0, 148.3, 138.3, 136.5, 129.8, 129.0, 127.8, 124.5, 124.2, 123.6, 61.0, 48.9, 18.8, 14.1, 12.3. HRMS (ESI): Calcd for C<sub>27</sub>H<sub>38</sub>N<sub>2</sub>NaO<sub>3</sub>Si [M+Na]<sup>+</sup> 489.2544, found: 489.2542.



The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a vellow solid in 58% yield (68.7 mg, 0.116 mmol). Mp: 61 – 62 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 8.45 (d, J = 4.7 Hz, 1H), 7.66 (d, J = 3.9 Hz, 2H), 7.61 (d, J = 7.7 Hz, 2H), 7.35 – 7.28 (m, 3H), 7.24 – 7.21 (m, 1H), 5.27 (s, 1H), 4.21 – 4.08 (m, 4H), 1.26 – 1.19 (m, 10H), 1.14 - 1.08 (m, 6H), 1.07 - 1.00 (m, 6H), 0.91 - 0.83 (m, 15H), 0.12 - 0.07 (m, 5H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ 169.8, 168.5, 154.3, 152.2, 148.2, 137.7, 136.3, 129.8, 129.1, 127.9, 126.0, 124.1, 123.8, 60.9, 48.5, 33.3, 31.4, 23.5, 22.5, 14.1, 13.3. HRMS (ESI): Calcd

ethyl (*E*)-*N*-(1-phenyl-2-(trihexylsilyl)vinyl)-*N*-picolinoylglycinate (60)

for C<sub>36</sub>H<sub>56</sub>N<sub>2</sub>NaO<sub>3</sub>Si [M+Na]<sup>+</sup> 615.3952, found: 615.3958. ethyl (E)-N-(1-phenyl-2-(tribenzylsilyl)vinyl)-N-picolinoylglycinate (6p)



The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 53% yield (64.7 mg, 0.106 mmol). Mp: 60 – 61 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 8.44 (d, J = 4.7 Hz, 1H), 7.64 (d, J = 3.8 Hz, 2H), 7.23 - 7.20 (m, 2H), 7.18 - 7.15

(m, 6H), 7.12 - 7.05 (m, 8H), 6.72 - 6.70 (d, J = 7.6 Hz, 5H), 5.30 (s, 1H), 4.23 (q, J = 7.1 Hz, 2H), 4.14 (s, 2H), 1.71 (s, 6H), 1.28 (t, J = 5.8 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$ 168.6, 154.7, 153.8, 147.9, 138.7, 137.9, 136.5, 129.9, 129.3, 128.7, 128.3, 128.0, 124.5, 124.4, 124.2, 120.2, 61.1, 49.4, 22.3, 14.2. HRMS (ESI): Calcd for C<sub>39</sub>H<sub>38</sub>N<sub>2</sub>NaO<sub>3</sub>Si [M+Na]<sup>+</sup> 633.2544, found: 633.2542.



The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 62% yield (52.6 mg, 0.124 mmol). Mp: 48 – 49 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.50 (d, J = 4.7 Hz, 1H), 7.74 – 7.63 (m, 4H), 7.34 – 7.29 (m, 3H), 7.24 – 7.21 (m, 1H), 5.40 (s, 1H), 4.21 – 4.17 (m, 4H), 1.27 – 1.24 (m, 3H), 0.59 (s, 9H), - 0.45 (s, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  168.7, 154.0, 153.6, 148.1, 137.8, 136.6, 130.3, 129.0, 127.8, 124.7, 124.5, 124.2, 61.0, 48.5, 26.2, 16.4, 14.2, -5.0. HRMS (ESI): Calcd for C<sub>24</sub>H<sub>32</sub>N<sub>2</sub>NaO<sub>3</sub>Si [M+Na]<sup>+</sup> 447.2074, found: 447.2073.

## ethyl (*E*)-*N*-(2-(benzyldimethylsilyl)-1-phenylvinyl)-*N*picolinovlglvcinate (6r)



The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 60% yield (55.0 mg,

0.120 mmol). Mp: 54 – 55 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.42 (d, J = 4.6 Hz, 1H), 7.63 – 7.56 (m, 2H), 7.42 (d, J = 7.0 Hz, 2H), 7.24 – 7.17 (m, 4H), 7.08 (t, J = 7.6 Hz, 2H), 6.97 (t, J = 7.4 Hz, 1H), 6.73 (d, J = 7.4 Hz, 2H), 5.20 (s, 1H), 4.18 – 4.07 (m, 4H), 1.65 (s, 2H), 1.21 – 1.18 (m, 3H), -0.53 (s, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  169.8, 168.6, 154.3, 153.3, 148.0, 139.5, 137.6, 136.4, 129.9, 129.3, 128.1, 128.0, 125.7, 124.3, 124.1, 123.9, 61.1, 48.6, 26.2, 14.1, -2.6. HRMS (ESI): Calcd for C<sub>27</sub>H<sub>30</sub>N<sub>2</sub>NaO<sub>3</sub>Si [M+Na]<sup>+</sup> 481.1918, found: 481.1917.



# ethyl (*E*)-*N*-(1-(3-dodecanamidophenyl)-2-(triphenylsilyl)vinyl)-*N*-picolinoylglycinate (7a) The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether =

1/3) as a yellow solid in 75% yield (114.8 mg, 0.150

mmol). Mp: 98 – 99 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 8.27 (d, *J* = 3.9 Hz, 1H), 7.71 (d, *J* = 9.0 Hz, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 1H), 7.31 – 7.28 (m, 3H), 7.26 – 7.24 (m, 1H), 7.22 – 7.10 (m, 12H), 7.01 – 6.97 (m, 1H), 6.95 (t, *J* = 7.9 Hz, 1H), 6.91 (s, 1H), 6.48 (s, 1H), 5.85 (s, 1H), 4.23 – 4.18 (m, 4H), 2.21 (t, *J* = 7.5 Hz, 2H), 1.67 – 1.62 (m, 3H), 1.33 – 1.24 (m, 18H), 0.88 (t, *J* = 6.9 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ 171.0, 169.9,
168.6, 155.1, 153.4, 148.1, 137.3, 136.8, 136.3, 135.6, 134.5, 129.2, 128.7, 127.6, 125.4, 124.4, 123.9, 122.5, 121.2, 121.0, 61.2, 48.8, 37.7, 31.9, 29.6, 29.6, 29.5, 29.4, 29.3, 29.3, 25.5, 22.7, 14.1, 14.1. **HRMS (ESI):** Calcd for C<sub>48</sub>H<sub>55</sub>N<sub>3</sub>NaO<sub>4</sub>Si [M+Na]<sup>+</sup> 788.3854, found: 788.3857.



ethyl (*E*)-*N*-picolinoyl-*N*-(1-(3stearamidophenyl)-2-

#### (triphenylsilyl)vinyl)glycinate (7b)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/3) as a yellow solid in 71% yield

(120.6 mg, 0.142 mmol). Mp: 105 – 106 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.27 (d, J = 4.3 Hz, 1H), 7.71 (d, J = 7.9 Hz, 1H), 7.67 (d, J = 7.8 Hz, 1H), 7.52 (t, J = 7.1 Hz, 1H), 7.31 – 7.24 (m, 3H), 7.26 – 7.24 (m, 1H), 7.20 – 7.12 (m, 12H), 6.99 (dd, J = 6.8, 5.4 Hz, 1H), 6.95 (t, J = 7.9 Hz, 1H), 6.91 (s, 1H), 6.47 (s, 1H), 5.85 (s, 1H), 4.23 – 4.19 (m, 4H), 2.21 (t, J = 7.5 Hz, 2H), 1.69 – 1.62 (m, 3H), 1.29 – 1.25 (m, 30H), 0.87 (t, J = 7.0 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  170.9, 169.9, 168.6, 155.1, 153.4, 148.1, 137.3, 136.8, 136.3, 135.6, 134.5, 129.2, 128.7, 127.6, 125.4, 124.4, 123.9, 122.5, 121.2, 121.0, 61.1, 48.8, 37.7, 31.9, 29.7, 29.6, 29.6, 29.5, 29.4, 29.3, 29.3, 25.5, 22.7, 14.1, 14.1. HRMS (ESI): Calcd for C<sub>54</sub>H<sub>67</sub>N<sub>3</sub>NaO<sub>4</sub>Si [M+Na]<sup>+</sup> 872.4793, found: 872.4799.



ethyl *N*-((*E*)-1-(3-oleamidophenyl)-2-(triphenylsilyl)vinyl)-*N*-picolinoylglycinate (7c)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/3) as a yellow solid in 54% yield

(91.5 mg, 0.108 mmol). Mp: 78 – 79 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 8.36 (d, *J* = 4.3 Hz, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.29 – 7.26 (m, 3H), 7.20 – 7.16 (m, 11H), 7.06 – 7.00 (m, 3H), 6.97 (s, 1H), 5.82 (s, 1H), 5.38 – 5.36 (m,

2H), 4.30 - 4.19 (m, 4H), 2.31 (t, J = 7.4 Hz, 2H), 2.05 - 2.01 (m, 4H), 1.75 - 1.68 (m, 2H), 1.36 - 1.26 (m, 23H), 0.90 (t, J = 6.9 Hz, 3H). <sup>13</sup>**C** NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  170.0, 168.6, 154.9, 153.6, 148.1, 138.7, 136.3, 135.6, 134.3, 130.7, 130.0, 129.7, 129.0, 127.5, 124.4, 123.9, 121.8, 118.3, 61.1, 48.9, 37.8, 31.9, 29.8, 29.7, 29.5, 29.3, 29.2, 29.1, 27.2, 27.2, 25.5, 22.7, 14.2, 14.1. HRMS (ESI): Calcd for C<sub>54</sub>H<sub>65</sub>N<sub>3</sub>NaO<sub>4</sub>Si [M+Na]<sup>+</sup> 870.4637, found: 870.4642.





The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/1)

as a yellow solid in 45% yield (74.7 mg, 0.090 mmol). Mp: 186 – 187 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.26 (d, J = 4.4 Hz, 1H), 7.62 (d, J = 7.8 Hz, 1H), 7.46 (t, J = 7.3 Hz, 1H), 7.36 (d, J = 7.7 Hz, 1H), 7.25 – 7.16 (m, 9H), 7.12 – 7.08 (m, 11H), 7.04 (s, 1H), 6.97 – 6.92 (m, 2H), 6.84 (t, J = 7.9 Hz, 1H), 5.81 (s, 1H), 5.25 (s, 1H), 4.97 (s, 1H), 4.31 (s, 1H), 4.21 – 4.13 (m, 4H), 3.05 (d, J = 6.6 Hz, 2H), 1.38 (s, 9H), 1.23 – 1.21 (m, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  169.9, 169.0, 168.6, 154.7, 153.4, 148.0, 136.8, 136.4, 136.3, 135.5, 134.2, 129.3, 129.2, 128.8, 128.4, 127.6, 127.1, 126.1, 124.4, 123.9, 122.7, 121.6, 121.1, 61.2, 53.4, 48.7, 38.4, 29.7, 28.2, 14.2. HRMS (ESI): Calcd for C<sub>50</sub>H<sub>50</sub>N<sub>4</sub>NaO<sub>6</sub>Si [M+Na]<sup>+</sup> 853.3392, found: 853.3398.



ethyl (*E*)-*N*-(1-(3-(2-(4isobutylphenyl)propanamido)phenyl)-2-(triphenylsilyl)vinyl)-*N*-picolinoylglycinate (7e)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/3) as a yellow solid in 60% yield (92.6 mg, 0.120 mmol). Mp: 90 – 91 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.24 (d, J = 4.1 Hz, 1H), 7.60 (d, J = 7.6 Hz, 1H), 7.49 – 7.42 (m, 2H), 7.25 – 7.20 (m, 4H), 7.15 (d, J = 8.0 Hz, 2H), 7.12 – 7.05 (m, 14H), 6.91 (t, J = 8.0 Hz, 2H), 6.78 (s, 1H), 6.40 (s, 1H), 5.79 (s, 1H), 4.23 – 4.08 (m, 4H), 3.49 (q, J = 7.1 Hz, 1H), 2.44 (d, J = 7.1 Hz, 2H), 1.83 (dt, J = 13.4, 6.7 Hz, 1H), 1.49 (d, J = 7.1 Hz, 3H), 1.23 (t, J = 7.1 Hz, 3H), 0.88 (d, J = 6.6 Hz, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  171.9, 169.9, 168.6, 154.9, 153.5, 148.0, 141.0, 138.1, 136.9, 136.5, 136.3, 135.5, 134.2, 129.7, 129.1, 128.5, 127.5, 127.3, 125.3, 124.3, 123.9, 122.4, 121.7, 121.1, 61.1, 48.8, 47.6, 45.0, 30.1, 22.4, 18.6, 14.1. HRMS (ESI): Calcd for C<sub>49</sub>H<sub>49</sub>N<sub>3</sub>NaO<sub>4</sub>Si [M+Na]<sup>+</sup> 794.3385, found: 794.3388.



ethyl (*E*)-*N*-(1-(4-(2-(4isobutylphenyl)propanamido)phenyl)-2-(triphenylsilyl)vinyl)-*N*-picolinoylglycinate (7f)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum

ether = 1/3) as a yellow solid in 64% yield (98.7 mg, 0.128 mmol). Mp: 92 – 93 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.33 (d, J = 4.5 Hz, 1H), 7.64 (d, J = 7.8 Hz, 1H), 7.48 (t, J = 7.7 Hz, 1H), 7.31 (d, J = 8.5 Hz, 2H), 7.25 – 7.11 (m, 19H), 7.04 (s, 1H), 6.99 (dd, J = 7.1, 5.1 Hz, 1H), 6.94 (d, J = 8.4 Hz, 2H), 5.79 (s, 1H), 4.22 – 4.18 (m, 4H), 3.64 (q, J = 7.0 Hz, 1H), 2.49 (d, J = 7.2 Hz, 2H), 1.88 (dt, J = 13.5, 6.7 Hz, 1H), 1.55 (d, J = 7.1 Hz, 3H), 1.25 (t, J = 7.2 Hz, 3H), 0.92 (d, J = 6.6 Hz, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  172.3, 170.0, 168.6, 154.9, 153.5, 148.0, 141.0, 138.8, 138.1, 136.2, 135.5, 134.2, 131.7, 130.5, 129.7, 128.9, 127.5, 127.2, 124.4, 123.8, 121.8, 118.2, 61.1, 48.8, 47.6, 44.9, 30.1, 22.3, 18.4, 14.1. HRMS (ESI): Calcd for C<sub>49</sub>H<sub>49</sub>N<sub>3</sub>NaO<sub>4</sub>Si [M+Na]<sup>+</sup> 794.3385, found: 794.3389.



ethyl (*S*,*E*)-*N*-(1-(4-(2-((((9*H*-fluoren-9yl)methoxy)carbonyl)amino)-4-oxo-4-(tritylamino)butanamido)phenyl)-2-(triphenylsilyl)vinyl)-*N*-picolinoylglycinate (7g)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether =

1/1) as a yellow solid in 33% yield (76.7 mg, 0.066 mmol). Mp: 122 – 123 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.66 (s, 1H), 8.37 (d, J = 4.6 Hz, 1H), 7.77 (d, J = 7.5 Hz, 2H), 7.69 (d, J = 7.8 Hz, 1H), 7.59 (d, J = 5.1 Hz, 2H), 7.53 (t, J = 7.7 Hz, 1H), 7.41 – 7.37 (m, 4H), 7.31 – 7.16 (m, 33H), 7.05 – 7.02 (m, 1H), 6.92 (d, J = 8.4 Hz, 2H), 6.46 (d, J = 5.1 Hz, 1H), 5.85 (s, 1H), 4.62 – 4.62 (m, 1H), 4.46 – 4.42 (m, 2H), 4.26 – 4.20 (m, 5H), 3.15 (d, J = 15.4 Hz, 1H), 2.67 – 2.62 (m, 1H), 1.28 (t, J = 7.1 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  170.0, 168.6, 156.3, 155.0, 153.6, 148.1, 144.0, 143.6, 143.6, 141.3, 138.1, 136.3, 135.6, 134.4, 132.4, 130.6, 129.1, 128.6, 128.1, 127.8, 127.6, 127.2, 127.1, 125.0, 124.4, 124.0, 120.1, 118.9, 71.1, 67.3, 61.2, 48.9, 47.1, 38.8, 14.2. HRMS (ESI): Calcd for C<sub>74</sub>H<sub>63</sub>N<sub>5</sub>NaO<sub>7</sub>Si [M+Na]<sup>+</sup> 1184.4389, found: 1184.4393.



ethyl (E)-N-(1-(4-(N,Ndipropylsulfamoyl)benzamido)phenyl)-2-(triphenylsilyl)vinyl)-Npicolinoylglycinate (7h)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum

ether = 1/3) as a yellow solid in 63% yield (107.1 mg, 0.126 mmol). Mp:  $151 - 152 \circ C. {}^{1}H$  **NMR (CDCl<sub>3</sub>, 500 MHz):**  $\delta$  8.37 (d, J = 4.4 Hz, 1H), 8.01 (s, 1H), 7.92 (d, J = 8.3 Hz, 2H), 7.83 (d, J = 8.3 Hz, 2H), 7.66 (d, J = 7.8 Hz, 1H), 7.51 (t, J = 7.7 Hz, 1H), 7.43 (d, J = 8.5 Hz, 2H), 7.30 - 7.26 (m, 3H), 7.24 - 7.15 (m, 14H), 7.02 (dd, J = 7.0, 5.2 Hz, 1H), 5.86 (s, 1H), 4.25 - 4.21 (m 4H), 3.12 - 3.07 (m, 4H), 1.60 - 1.52 (m, 4H), 1.28 (t, J = 7.1 Hz, 3H), 0.88 (t, J = 7.4 Hz, 6H).  ${}^{13}C$  NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  170.0, 168.6, 164.1, 154.8, 153.5, 148.1, 143.0, 138.4, 136.3, 135.6, 134.2, 132.6, 130.8, 129.1, 127.9, 127.6, 127.3, 124.5, 123.9, 122.2, 119.0, 61.2, 50.0, 48.9, 21.9, 14.2, 11.1. HRMS (ESI): Calcd for C<sub>19</sub>H<sub>50</sub>N<sub>4</sub>NaO<sub>6</sub>SSi [M+Na]<sup>+</sup> 873.3113, found: 873.3118.



The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/3) as a yellow solid in 55% yield (94.4 mg, 0.110 mmol). Mp: 81 – 82 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.34 – 8.33 (m, 2H), 7.66 – 7.61 (m, 3H), 7.59 – 7.57 (m, 2H), 7.48 (t, J = 8.4 Hz, 1H), 7.39 – 7.30 (m, 9H), 7.25 – 7.21 (m, 3H), 7.18 – 7.11 (m, 11H), 7.04 – 6.96 (m, 3H), 5.80 (s, 1H), 4.32 – 4.10 (m, 4H), 3.25 (t, J = 6.8 Hz, 2H), 2.90 (t, J = 6.6 Hz, 2H), 1.25 (t, J = 7.1 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  170.0, 169.5, 168.6, 162.4, 154.9, 153.6, 148.1, 145.7, 138.8, 136.3, 135.6, 135.0, 134.8, 134.3, 132.2, 131.8, 130.6, 129.0, 128.7, 128.7, 128.6, 128.3, 127.8, 127.5, 126.5, 124.4, 123.9, 121.8, 118.4, 61.1, 48.9, 34.1, 24.0, 14.1. HRMS (ESI): Calcd for C<sub>54</sub>H<sub>46</sub>N<sub>4</sub>NaO<sub>5</sub>Si [M+Na]<sup>+</sup> 881.3130, found: 881.3133.



## ethyl (*E*)-*N*-(1-(3-(2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanamido)phenyl)-2-

(triphenylsilyl)vinyl)-*N*-picolinoylglycinate (7j) The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/3) as a yellow solid in 56% yield (90.6 mg,

0.112 mmol). Mp: 94 – 95 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.28 (d, J = 4.4 Hz, 1H), 7.64 (d, J = 7.8 Hz, 1H), 7.58 – 7.53 (m, 3H), 7.49 – 7.44 (m, 3H), 7.41 – 7.37 (m, 2H), 7.30 (d, J = 7.6 Hz, 1H), 7.25 – 7.23 (m, 3H), 7.14 – 7.11 (m, 14H), 6.97 – 6.94 (m, 2H), 6.89 (s, 1H), 6.54 (s, 1H), 5.82 (s, 1H), 4.22 – 4.18 (m, 4H), 3.57 (q, J = 7.0 Hz, 1H), 1.56 (d, J = 7.1 Hz, 3H), 1.25 (t, J = 7.2 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  171.0, 170.0, 168.6, 159.8 (d, J = 248.9 Hz), 154.8, 153.4, 148.0, 142.3, 142.2, 136.8, 136.7, 136.3, 135.5, 135.2, 134.2, 131.2 (d, J = 4.0 Hz), 129.2, 128.9 (d, J = 2.6 Hz), 128.6, 128.5, 127.8, 127.5, 125.5, 124.4, 123.9, 123.5 (d, J = 3.2 Hz), 122.6, 121.7, 121.1, 115.3 (d, J = 23.6 Hz), 61.2, 48.8, 47.5, 18.6, 14.1. <sup>19</sup>F NMR (CDCl<sub>3</sub>, 471 MHz):  $\delta$  -116.7. HRMS (ESI): Calcd for C<sub>51</sub>H<sub>44</sub>FN<sub>3</sub>NaO<sub>4</sub>Si [M+Na]<sup>+</sup> 832.2977, found: 832.2980.

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ethyl (*E*)-*N*-(1-(4-(2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanamido)phenyl)-2-

(triphenylsilyl)vinyl)-N-picolinoylglycinate (7k)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/3) as a yellow solid in 54% yield (87.4 mg, 0.108 mmol). Mp: 97 – 98 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.33 (d, J = 4.4 Hz, 1H), 7.65 (d, J = 7.8 Hz, 1H), 7.55 (d, J = 8.2 Hz, 2H), 7.50 – 7.43 (m, 4H), 7.39 – 7.33 (m, 3H), 7.23 – 7.10 (m, 17H), 7.03 – 6.97 (m, 4H), 5.80 (s, 1H), 4.22 – 4.18 (m, 4H), 3.67 (q, J = 7.0 Hz, 1H), 1.58 (d, J = 7.1 Hz, 3H), 1.25 (t, J = 6.1 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  171.2, 170.0, 168.6, 159.9 (d, J = 249.1 Hz), 154.8, 153.5, 148.1, 142.3, 142.3, 138.6, 136.3, 135.6, 135.2, 134.3, 132.1, 131.2 (d, J = 3.4 Hz), 130.6, 129.0, 128.9 (d, J = 2.7 Hz), 128.5, 127.8, 127.5, 124.4, 123.9, 123.5 (d, J = 3.3 Hz), 122.0, 118.4, 115.2 (d, J = 23.5 Hz), 61.1, 48.9, 47.6, 18.6, 14.1. <sup>19</sup>F NMR (CDCl<sub>3</sub>, 471 MHz):  $\delta$  -116.7. HRMS (ESI): Calcd for C<sub>51</sub>H<sub>44</sub>FN<sub>3</sub>NaO<sub>4</sub>Si [M+Na]<sup>+</sup> 832.2977, found: 832.2983.



ethyl (*E*)-*N*-(1-(4-(2-(1-(4-chlorobenzoyl)-5methoxy-2-methyl-1H-indol-3vl)acetamido)phenyl)-2-

(triphenylsilyl)vinyl)-*N*-picolinoylglycinate (7l)

The title compound was isolated by column

chromatography (eluent: EtOAc/petroleum ether = 1/1) as a yellow solid in 41% yield (75.6 mg, 0.082 mmol). Mp: 112 – 113 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.32 (d, *J* = 4.4 Hz, 1H), 7.69 (d, *J* = 8.5 Hz, 2H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.51 – 7.48 (m, 3H), 7.32 (d, *J* = 8.5 Hz, 2H), 7.23 – 7.18 (m, 3H), 7.16 – 7.10 (m, 11H), 7.06 (s, 1H), 7.00 (dd, *J* = 6.9, 5.0 Hz, 1H), 6.94 – 6.86 (m, 4H), 6.73 (dd, *J* = 9.1, 2.5 Hz, 1H), 5.79 (s, 1H), 4.25 – 4.13 (m, 4H), 3.83 (s, 3H), 3.75 (s, 2H), 2.45 (s, 3H), 1.27 – 1.25 (m, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  168.6, 168.3, 156.4, 154.8, 153.6, 148.0, 139.7, 138.1, 137.3, 136.6, 136.3, 135.6, 134.3, 133.5, 132.3, 131.2, 131.0, 130.6, 130.1, 129.3, 129.0, 127.5, 126.4, 124.4, 123.9, 118.6, 115.2, 112.3, 112.2, 101.0, 100.0, 61.1, 55.8, 48.8, 33.4, 14.2, 13.3. HRMS (ESI): Calcd for C<sub>55</sub>H<sub>47</sub>ClN<sub>4</sub>NaO<sub>6</sub>Si [M+Na]<sup>+</sup> 945.2846, found: 945.2850.



ethyl N-((*E*)-1-(4-((*R*)-4-((5*S*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-3,7,12trioxohexadecahydro-1*H*cyclopenta[*a*]phenanthren-17yl)pentanamido)phenyl)-2-

#### (triphenylsilyl)vinyl)-N-picolinoylglycinate (7m)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/1) as a yellow solid in 26% yield (50.3 mg, 0.052 mmol). Mp: 133 – 134 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.27 (d, *J* = 4.3 Hz, 1H), 7.69 – 7.66 (m, 2H), 7.51 (t, *J* = 7.7 Hz, 1H), 7.31 – 7.27 (m, 3H), 7.23 (d, *J* = 7.7 Hz, 1H), 7.20 – 7.17 (m, 6H), 7.14 – 7.13 (m, 6H), 6.99 (dd, *J* = 6.9, 5.1 Hz, 1H), 6.95 – 6.92 (m, 2H), 6.57 (s, 1H), 5.84 (s, 1H), 4.24 – 4.16 (m, 4H), 2.93 – 2.82 (m, 3H), 2.38 – 2.12 (m, 12H), 2.08 – 1.80 (m, 8H), 1.65 – 1.58 (m, 1H), 1.39 (s, 3H), 1.27 – 1.24 (m, 3H), 1.08 (s, 3H), 0.89 (d, *J* = 6.4 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  212.0, 208.9, 208.7, 171.0, 169.9, 168.6, 155.1, 153.4, 148.1, 137.3, 136.3, 135.6, 134.5, 129.2, 128.7, 127.6, 125.4, 124.4, 123.9, 121.2, 121.0, 61.1, 56.9, 51.8, 49.0, 46.8, 45.6, 45.5, 45.0, 42.8, 38.6, 36.4, 36.0, 35.4, 35.3, 34.4, 30.8, 27.6, 25.1, 21.9, 18.8, 14.1, 11.9. HRMS (ESI): Calcd for C<sub>60</sub>H<sub>65</sub>N<sub>3</sub>NaO<sub>7</sub>Si [M+Na]<sup>+</sup>990.4484, found: 990.4489.



ethyl (*E*)-*N*-(1-(4-(2-(4-(2-(4chlorobenzamido)ethyl)phenoxy) Et -2-methylpropanamido)phenyl)-2-(triphenylsilyl)vinyl)-*N*picolinoylglycinate (7n)

The title compound was isolated

by column chromatography (eluent: EtOAc/petroleum ether = 1/1) as a yellow solid in 37% yield (68.5 mg, 0.074 mmol). Mp: 92 – 93 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.35 – 8.34 (m, 2H), 7.67 (d, J = 7.8 Hz, 1H), 7.63 – 7.62 (m, J = 8.5 Hz, 3H), 7.51 (t, J = 7.7 Hz, 1H), 7.39 – 7.36 (m, 4H), 7.24 – 7.21 (m, 3H), 7.20 – 7.13 (m, 13H), 7.08 (d, J = 8.5 Hz, 2H), 7.01 (dd, J = 7.1, 4.9 Hz, 1H), 6.92 (d, J = 8.4 Hz, 2H), 6.12 – 6.07 (m, 1H), 5.81 (s, 1H), 4.31 – 4.14 (m,

4H), 3.71 - 3.67 (m, 2H), 2.92 (t, J = 7.0 Hz, 2H), 1.55 (s, 6H), 1.27 (t, J = 7.2 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  172.6, 170.0, 168.6, 166.4, 154.8, 153.5, 152.6, 148.1, 138.2, 137.7, 136.3, 135.6, 134.3, 132.9, 132.2, 130.7, 129.7, 129.0, 128.8, 128.2, 127.5, 124.4, 123.9, 122.1, 121.8, 118.5, 81.9, 61.1, 48.9, 41.3, 34.9, 24.9, 14.1. HRMS (ESI): Calcd for C<sub>55</sub>H<sub>51</sub>ClN<sub>4</sub>NaO<sub>6</sub>Si [M+Na]<sup>+</sup> 949.3159, found: 949.3163.



ethyl

ethyl (E)-N-(1-(4-(4-(4methoxynaphthalen-1-yl)-4oxobutanamido)phenyl)-2-(triphenylsilyl)vinyl)-N-picolinoylglycinate (70)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/1) as a yellow solid in 61% yield (100.4 mg, 0.122 mmol). Mp: 85 – 86 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.95 (d, *J* = 8.7 Hz, 1H), 8.35 – 8.30 (m, 2H), 8.12 (d, *J* = 8.2 Hz, 1H), 7.67 – 7.61 (m, 3H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 1H), 7.34 (d, *J* = 8.3 Hz, 2H), 7.25 – 7.21 (m, 3H), 7.19 – 7.11 (m, 12H), 7.04 (d, *J* = 8.1 Hz, 2H), 6.99 (dd, *J* = 7.0, 5.0 Hz, 1H), 6.82 (d, *J* = 8.3 Hz, 1H), 5.80 (s, 1H), 4.23 – 4.19 (m, 4H), 4.07 (s, 3H), 3.50 (t, *J* = 6.2 Hz, 2H), 2.81 (t, *J* = 5.9 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  200.9, 170.0, 168.6, 159.5, 155.0, 153.6, 148.1, 136.2, 135.6, 135.0, 134.3, 132.0, 131.4, 130.6, 129.0, 128.8, 127.9, 127.5, 126.7, 125.9, 125.9, 125.8, 124.4, 123.9, 122.2, 121.7, 118.4, 102.2, 61.1, 55.8, 48.9, 36.2, 32.1, 14.1. HRMS (ESI): Calcd for C<sub>51</sub>H<sub>45</sub>N<sub>3</sub>NaO<sub>6</sub>Si [M+Na]<sup>+</sup> 846.2970, found: 846.2972.



# (triphenylsilyl)vinyl)picolinamido)benzoate (7p)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 77% yield (97.1 mg, 0.154 mmol). Mp: 117 – 118 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):

(E)-4-(N-(1-phenyl-2-

δ 8.41 (d, *J* = 4.4 Hz, 1H), 7.98 (d, *J* = 8.6 Hz, 2H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.50 (t, *J* = 7.1 Hz, 1H), 7.41 (t, *J* = 8.6 Hz, 4H), 7.32 – 7.28 (m, 3H), 7.25 – 7.17 (m, 13H), 7.06 (dd, *J* = 7.0,

5.1 Hz, 1H), 6.88 (t, J = 7.4 Hz, 1H), 6.77 (t, J = 7.7 Hz, 2H), 5.98 (s, 1H), 4.33 (q, J = 7.1 Hz, 2H), 1.35 (t, J = 7.1 Hz, 3H). <sup>13</sup>**C** NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  170.0, 165.9, 155.8, 154.0, 148.1, 136.4, 136.3, 135.5, 134.1, 130.2, 129.8, 129.2, 128.7, 127.9, 127.6, 127.2, 126.3, 124.7, 124.2, 123.9, 60.9, 14.2. HRMS (ESI): Calcd for C<sub>41</sub>H<sub>34</sub>N<sub>2</sub>NaO<sub>3</sub>Si [M+Na]<sup>+</sup> 653.2231, found: 653.2233.



## *N*-((*Z*)-octadec-9-en-1-yl)-*N*-((*E*)-1-phenyl-2-(triphenylsilyl)vinyl)picolinamide (7q)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/3) as a yellow solid in 42% yield (61.5 mg, 0.084 mmol). Mp:

94 – 95 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.40 (d, *J* = 4.5 Hz, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 1H), 7.47 (d, *J* = 7.9 Hz, 2H), 7.36 – 7.34 (m, 4H), 7.24 – 7.23 (m, 11H), 7.09 (t, *J* = 7.3 Hz, 1H), 7.05 (dd, *J* = 7.2, 5.1 Hz, 1H), 6.97 (t, *J* = 7.6 Hz, 2H), 5.72 (s, 1H), 5.44 – 5.42 (m, 2H), 3.61 – 3.61 (m, 2H), 2.09 – 2.04 (m, 4H), 1.79 – 1.73 (m, 2H), 1.41 – 1.33 (m, 22H), 0.96 (t, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  169.5, 156.1, 154.9, 148.0, 136.5, 136.1, 135.6, 134.4, 129.9, 129.8, 129.7, 129.1, 128.9, 127.5, 127.5, 123.9, 123.5, 122.3, 46.4, 32.6, 31.9, 29.8, 29.7, 29.7, 29.5, 29.4, 29.4, 29.3, 27.7, 27.2, 27.2, 26.9, 22.7, 14.1. HRMS (ESI): Calcd for C<sub>50</sub>H<sub>60</sub>N<sub>2</sub>NaOSi [M+Na]<sup>+</sup> 755.4367, found: 755.4369.



#### ethyl N-(1-phenylvinyl)-N-picolinoylglycinate (8)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 78% yield (48.4 mg, 0.156 mmol). Mp: 42 – 43 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.40 (s,

1H), 7.68 – 7.54 (m, 4H), 7.33 – 7.30 (m, 3H), 7.20 (s, 1H), 5.23 (s, 1H), 4.99 (s, 1H), 4.29 (s, 2H), 4.23 (q, J = 6.9 Hz, 2H), 1.28 (t, J = 7.0 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  168.6, 148.2, 136.3, 136.2, 128.8, 128.4, 127.3, 124.5, 123.6, 112.4, 61.2, 49.4, 14.1. HRMS (ESI): Calcd for C<sub>18</sub>H<sub>18</sub>N<sub>2</sub>NaO<sub>3</sub> [M+Na]<sup>+</sup> 333.1210, found: 333.1206.

ethyl N-(2,2-diiodo-1-phenylvinyl)-N-picolinoylglycinate (9)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 85% yield (95.5 mg, 0.170 mmol). Mp: 67 – 68 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.54 (d, J = 4.5 Hz, 1H), 8.13 (d, J = 7.9 Hz, 1H), 7.99 (dd, J = 7.5, 2.0 Hz, 2H), 7.83 (t, J = 7.7 Hz, 1H), 7.43 – 7.38 (m, 4H), 4.23 (d, J = 16.8 Hz, 1H), 4.11 – 4.06 (m, 2H), 3.93 (d, J = 16.8 Hz, 1H), 1.19 (t, J = 7.1 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  167.7, 167.5, 153.3, 152.4, 147.0, 136.5, 136.5, 131.7, 129.7, 128.2, 125.6, 125.5, 61.2, 48.8, 14.1. HRMS (ESI): Calcd for C<sub>18</sub>H<sub>16</sub>I<sub>2</sub>N<sub>2</sub>NaO<sub>3</sub> [M+Na]<sup>+</sup> 584.9142, found: 584.9152.

## ethyl (*E*)-*N*-(2-(4-methoxyphenyl)-1-phenylvinyl)-*N*-<sup>D</sup><sub>2</sub>Et picolinovlglycinate (11)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 71% yield (59.1 mg, 0.142 mmol). Mp: 55 – 56 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.48 (d, J = 4.2 Hz, 1H), 7.79 (d, J = 7.8 Hz, 1H), 7.66 – 7.59 (m, 3H), 7.31

- 7.26 (m, 3H), 7.16 - 7.12 (m, 1H), 6.83 (d, J = 8.6 Hz, 2H), 6.58 (d, J = 8.7 Hz, 2H), 6.28 (s, 1H), 4.23 (q, J = 7.1 Hz, 2H), 4.14 (s, 2H), 3.69 (s, 3H), 1.29 (t, J = 7.1 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  169.7, 168.7, 158.6, 153.7, 148.0, 139.4, 136.4, 134.9, 130.8, 130.2, 128.6, 128.4, 128.3, 128.0, 124.4, 124.0, 113.4, 61.1, 55.0, 48.1, 14.2. HRMS (ESI): Calcd for C<sub>25</sub>H<sub>24</sub>N<sub>2</sub>NaO<sub>4</sub> [M+Na]<sup>+</sup> 439.1628, found: 439.1626.

ÓMe

SiPha

## ethyl (*E*)-*N*-(1-phenyl-2-(triphenylsilyl)vinyl)-*N*-(pyrimidine-2carbonyl)glycinate (4a-1)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 65% yield (74.0 mg,

0.130 mmol). Mp: 131 – 132 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.38 (d, J = 4.8 Hz, 2H), 7.38 (d, J = 7.3 Hz, 2H), 7.29 – 7.27 (m, 3H), 7.20 – 7.12 (m, 12H), 7.01 (t, J= 7.4 Hz, 1H), 6.88 (t, J = 7.7 Hz, 2H), 6.74 (t, J = 4.8 Hz, 1H), 5.95 (s, 1H), 4.25 – 4.21 (m, 4H), 1.28 (t, J = 7.2 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  168.2, 167.5, 162.2, 156.4, 154.2, 135.6, 135.0, 133.9, 129.8, 129.4, 129.2, 127.7, 127.6, 123.2, 120.4, 61.3, 47.9, 14.2. HRMS (ESI): Calcd for C<sub>35</sub>H<sub>31</sub>N<sub>3</sub>NaO<sub>3</sub>Si [M+Na]<sup>+</sup> 592.2027, found: 592.2031.

#### ethyl (E)-N-(1-phenyl-2-(triphenylsilyl)vinyl)-N-(quinoline-2carbonyl)glycinate (4a-2)



The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 43% yield (53.2 mg, 0.086 mmol). Mp: 126 – 127 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 8.38 (d, J = 7.8 Hz, 1H), 8.31 (d, J = 5.6 Hz, 1H), 7.66 – 7.61 (m, 3H), 7.40 –

7.38 (m, 3H), 7.22 - 7.19 (m, 3H), 7.06 - 7.03 (m, 6H), 6.96 - 6.92 (m, 7H), 6.83 (t, J = 7.6Hz, 2H), 5.99 (s, 1H), 4.37 (s, 2H), 4.32 (q, J = 7.1 Hz, 2H), 1.35 (t, J = 7.1 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ 169.1, 168.7, 154.9, 154.9, 141.0, 136.1, 136.0, 135.3, 134.0, 130.3, 129.7, 129.0, 128.9, 128.0, 127.5, 127.4, 127.1, 126.6, 126.4, 121.4, 121.4, 61.3, 48.4, 14.2. **HRMS (ESI):** Calcd for  $C_{40}H_{35}N_2O_3Si [M+H]^+ 619.2411$ , found: 619.2406.

### ethyl (E)-N-(isoquinoline-1-carbonyl)-N-(1-phenyl-2-(triphenylsilyl)vinyl)glycinate (4a-3)

The title compound was isolated by column chromatography (eluent: CO<sub>2</sub>Et EtOAc/petroleum ether = 1/5) as a yellow solid in 51% yield (63.1 mg, 0.102 mmol). Mp: 118 – 119 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 8.05 (d,

J = 8.5 Hz, 1H), 7.89 (d, J = 8.4 Hz, 1H), 7.74 – 7.66 (m, 2H), 7.64 (d, J = 8.4 Hz, 1H), 7.55 – 7.50 (m, 3H), 7.23 - 7.20 (m, 3H), 7.10 - 6.97 (m, 13H), 6.88 (t, J = 7.6 Hz, 2H), 5.90 (s, 1H), 4.33 (s, 2H), 4.27 (q, J = 7.1 Hz, 2H), 1.31 (t, J = 7.1 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ 170.4, 168.7, 155.3, 153.6, 146.6, 136.5, 135.9, 135.4, 133.9, 129.8, 129.8, 129.6, 129.1, 128.9, 128.1, 127.7, 127.4, 127.4, 127.2, 122.8, 120.6, 61.1, 48.7, 14.2. HRMS (ESI): Calcd for C<sub>40</sub>H<sub>34</sub>N<sub>2</sub>NaO<sub>3</sub>Si [M+Na]<sup>+</sup> 641.2231, found: 641.2228.

### 7. References:

N

0́

Ph

ŠiPh<sub>3</sub>

(1) (a) Li, K.; Tan, G.; Huang, J.; Song, F.; You, J. Angew. Chem., Int. Ed. 2013, 52, 12942-12945. (b) Tan, M.; Li, K.; Yin, J.; You, J. Chem. Commun. 2018, 54, 1221-1224.

(2) Zheng, N.; Song, W.; Zhang, T.; Li, M.; Zheng, Y.; Chen, L. J. Org. Chem. 2018, 83, 6210-6216.

(3) Chang, X.-H.; Wang, Z.-L.; Zhao, M.; Yang, C.; Li, J.-J.; Ma, W.-W.; Xu, Y.-H. Org. Lett. 2020, 22, 1326-1330.

(4) Song, L.-J.; Ding, S.; Wang, Y.; Zhang, X.; Wu, Y.-D.; Sun, J. J. Org. Chem. 2016, 81, 6157–6164.

# 8. NMR Spectra













100 90 f1 (ppm) 



100 90 f1 (ppm) 



100 90 f1 (ppm) 







100 90 f1 (ppm) Ó 

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100 90 f1 (ppm) 









20 10 0 -60 -70 f1 (ppm) -15( -10 -20 -30 -40 -50 -<mark>8</mark>0 -90 -100 -110 -120 -130 -140



100 90 f1 (ppm) 





#### 



100 90 f1 (ppm) 



100 90 f1 (ppm) 









100 90 f1 (ppm) 

#### --3.3748 42462 42269 42126 41983





100 90 f1 (ppm) Ó




-1.7770 -1.3663 -1.3522



100 90 f1 (ppm) 



100 90 f1 (ppm) 



100 90 f1 (ppm) 



100 90 f1 (ppm) 



<sup>100 90</sup> f1 (ppm) 

## 8.3554 8.3554 8.3457 7.6133 7.71357 7.71737 7.71737 7.71737 7.71737 7.71737 7.71737 7.71737 7.71737 7.71737 7.717480



100 90 f1 (ppm) 

## 



100 90 f1 (ppm) 













7.5 7.0 5.0 4.5 f1 (ppm) 0.0 9.5 9.0 8.5 8.0 6.5 6.0 5.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5











































-100 -110 f1 (ppm) -10 -20 -30 -40 -50 -60 -70 -80 -90 -120 -130 -140 -180 -190 -200 -210 -150 -160 -170



100 90 f1 (ppm)














100 90 f1 (ppm) 





![](_page_149_Figure_1.jpeg)

![](_page_150_Figure_0.jpeg)

S151

![](_page_151_Figure_0.jpeg)

![](_page_151_Figure_1.jpeg)

![](_page_152_Figure_0.jpeg)

![](_page_153_Figure_0.jpeg)

100 90 f1 (ppm) 

![](_page_154_Figure_0.jpeg)

<sup>100 90</sup> f1 (ppm) 

![](_page_155_Figure_0.jpeg)

<sup>100 90</sup> f1 (ppm) 

![](_page_156_Figure_0.jpeg)

<sup>100 90</sup> f1 (ppm) -10 

![](_page_157_Figure_0.jpeg)

# ▲ 8.2721 ▲ 8.2643 ▲ 8.2643 ▲ 8.2643 ▲ 1.1572 ▲ 1.1572 ▲ 1.1532 ▲ 1.1532 ▲ 1.1532 ▲ 1.1532 ▲ 1.1532 ▲ 1.1532 ▲ 1.1532 ▲ 1.1532 ▲ 1.1533 ▲ 1.1534

![](_page_158_Figure_1.jpeg)

# 42.724 42.7245 42.245 42.245 42.283 42.284

![](_page_159_Figure_1.jpeg)

100 90 f1 (ppm) 

![](_page_160_Figure_0.jpeg)

### ~ 8 2633 8 2644 7 7 1652 7 7 2128 7 7 2138 7 7 2138 7 7 2138 7 7 186 7 7 186 7 7 186 7 7 186 6 9510 6 9510 6 9510 6 9510 6 9510 6 9510 6 9510 6 9510 6 9510 7 1203 2 11272 2 1212 2

![](_page_161_Figure_1.jpeg)

# California (Construction) California (Construction)

![](_page_162_Figure_1.jpeg)

100 90 f1 (ppm) 

![](_page_163_Figure_0.jpeg)

, (bbu)

# 

![](_page_164_Figure_1.jpeg)

![](_page_165_Figure_0.jpeg)

![](_page_166_Figure_0.jpeg)

100 90 f1 (ppm) 

# ~ 8 2801 ~ 7 7 5220 8 2713 6 2713 7 7 2522 7 7 2522 7 7 2522 7 7 2522 6 2 242 7 7 1552 6 5 2 49 6 5 5 2 49 6 5 5 2 49 7 1 5 63 7 4 1 2037 7 1 5 63 6 5 5 2 49 7 1 5 63 6 5 5 2 49 7 1 5 63 6 5 5 2 49 7 1 5 63 7 1 5 6

![](_page_167_Figure_1.jpeg)

![](_page_168_Figure_0.jpeg)

![](_page_169_Figure_0.jpeg)

<sup>-90 -100</sup> f1 (ppm) -10 -20 -30 -40 -50 -60 -70 -80 -110 -120 -130 -170 -180 -190 -140 -150 -160

![](_page_170_Figure_0.jpeg)

![](_page_170_Figure_1.jpeg)

![](_page_171_Figure_0.jpeg)

110 100 f1 (ppm) Ó 

![](_page_172_Figure_0.jpeg)

![](_page_172_Figure_1.jpeg)

![](_page_173_Figure_0.jpeg)

<sup>110 100</sup> f1 (ppm) Ó 

![](_page_174_Figure_0.jpeg)

![](_page_174_Figure_1.jpeg)

## A 8 4086 A 8 33966 A 8 33967 A 1057 A 10577 A 10577 A 10577 A 10577 A 1

![](_page_175_Figure_1.jpeg)

190 0 180 170 110 100 90 f1 (ppm) 80 70 60 40 30 20 10 160 150 140 130 120 50

![](_page_176_Figure_0.jpeg)

 $\underbrace{ \{ \begin{array}{c} 1 & 2926 \\ 1 & 2786 \\ 1 & 2646 \\ \end{array} }_{1 & 2646 \\ \end{array} }$ 

![](_page_176_Figure_1.jpeg)

100 90 f1 (ppm) 

## 8 5314 8 5315 8 5314

€1,1908 €1,1908

![](_page_177_Figure_1.jpeg)

<ul> <li>48 488 4848</li> <li>48 4763</li> <li>48 4763</li> <li>48 4763</li> <li>48 4763</li> <li>47 5342</li> <li>47 5342</li> <li>47 5342</li> <li>48 5363</li> <li>48 5363</li> <li>48 2533</li> <li>48 2533</li></ul>	€1.3060 1.2917
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![](_page_178_Figure_1.jpeg)

![](_page_179_Figure_0.jpeg)

100 90 f1 (ppm)


100 90 f1 (ppm) 



100 90 f1 (ppm)